March 2017
Vol. 1 - n. 1

Substantia

An International Journal of the History of Chemistry

FIRENZE UNIVERSITY PRESS

Substantia

An International Journal of the History of Chemistry

Vol. 1, n. 1 - March 2017

Firenze University Press

*Substantia***. An International Journal of the History of Chemistry**

Published by
Firenze University Press – University of Florence, Italy
Via Cittadella, 7 - 50144 Florence - Italy
http://www.fupress.com/substantia

Direttore Responsabile: **Romeo Perrotta**, University of Florence, Italy

Cover image: **Crystals of ethylene carbonate under polarized light, magnification 10 X.**

Substantia is honoured to declare the patronage of:

Museo Galileo - Institute and Museum of the History of Science
Piazza dei Giudici, 1 - 50122 Florence, Italy
http://www.museogalileo.it

Fondazione Prof. Enzo Ferroni - Onlus
Via della Lastruccia, 3 – 50019 Sesto Fiorentino, Italy
http://www.fondazioneferroni.it

Substantia
An International Journal of the History of Chemistry

No walls. Just bridges

Substantia is an open access, peer-reviewed, academic international journal dedicated to traditional perspectives as well as innovative and synergistic implications of history and philosophy of Chemistry.
It is meant to be a crucible for discussions on science, on making science and its outcomes.
Substantia hosts discussions on the connections between chemistry and other horizons of human activities, and on the historical aspects of chemistry.
Substantia is published *open access* two times per year and offers top quality original full papers, essays, experimental works, reviews, biographies and dissemination manuscripts.
All contributions are in English.

Substantia
An International Journal of the History of Chemistry

Firenze University Press
www.fupress.com/substantia

Substantia in Latin means substance, matter, material, that is the realm of chemistry. Indeed, chemistry has always studied – since its ancestor alchemy – matter around us and its transformations. An international journal with this title opens its own perspective to every theme associated to this fantastic discipline: history of the chemical thought, relationship between chemistry evolution and mankind, position of science and scientists in the society, role of creativity in the progress of the field of science mostly connected to the daily life, and many other intriguing aspects. Chemistry has always wanted to challenge what Primo Levi used to call the *Mater materia* (Mother matter), trying to solve the infinite mysteries of such ineffable Sphynx, and during this long lasting struggle chemists and matter have been at the same time friends and enemies.

This journal aims at investigating some topics of history of chemistry, but has also the ambitious scope of ensuring that scientists continuously ponder and worry about a different way of working with respect to that our society, infected by the terrible profit-syndrome, day by day suggests and dictates.

In 1933 Maria Skłodowska Curie, speaking about the decision not to patent the procedure for isolating radium, that sounded outrageous to some people, pointed out: "Humanity needs practical men … But humanity also needs dreamers, for whom the disinterested pursuit of an end is so captivating that it becomes impossible for them to think of their own material profit." Another great Polish scientist, Albert Sabin, pursued the same path in the 1960s for the anti-polio vaccine. He decided not to patent his discovery, thus permitting very low production costs, and earning not even a penny out of it. The justification for his stance looks almost naïve in a world that was already irremediably infected by the disease of capitalistic profit at all costs: "lots of people insisted that I should patent the vaccine, but I didn't want to: it is my present to all the children in the world."

The aim of this journal is to inspire those who are working in the world of chemistry about the harmful effect of the market on research, the importance of disclosing the scientific results, the necessity of recovering the unity of knowledge and culture in the frame of a multi-disciplinary approach.

We want to create bridges between disciplines, but also between different perspectives and languages: as an example the appreciation of the "far and diverse", both in space and time, and the choice of adopting open access.

Today we terribly need bridges against walls and it is not by chance that we launch this new journal, with these distinctive features, from Florence, the cradle of the Renaissance: we take the baton of the cultural Florentine renaissance from the Camerata dei Bardi, progenitor of the modern opera, and from the Accademia del Cimento, mother of the contemporary scientific Societies.

Luigi Dei

Substantia. An International Journal of the History of Chemistry 1(1): 5, 2017
DOI: 10.13128/Substantia-4

Substantia
An International Journal of the History of Chemistry

Firenze University Press
www.fupress.com/substantia

OPEN ACCESS

Citation: B.W. Ninham (2017) The Biological/Physical Sciences Divide, and the Age of Unreason. *Substantia* 1(1): 7-24. doi: 10.13128/Substantia-6

Data Availability Statement: All relevant data are within the paper and its Supporting Information files.

Competing Interests: The author declares no competing interests.

Feature Article

The Biological/Physical Sciences Divide, and the Age of Unreason

Barry W. Ninham

Department of Applied Mathematics, Research School of Physical Sciences and Engineering, Australian National University, Canberra ACT 2600, Australia
E-mail: barry.ninham@anu.edu.au

Abstract. D'Arcy Thompson in *On Growth and Form* tells us that the early founders of the cell theory of biology, and the physiologists believed that progress in their sciences depended critically on our knowledge of molecular forces. The hubris of a new science that followed the application of X-rays and other techniques to the structure of proteins, the focus on DNA, transport in neurophysiology and ion pumps is understandable. In that progress, the environment, molecular forces and lipids played no role.
Structure and Form took a giant, unifying step forward in the recognition of a key role for hyperbolic (non Euclidean, bicontinuous) geometries, from the self assembly of lipids, surfactants and proteins; to nanostructure in inorganic and solid state chemistry generally.
But the complementary concepts of Function and Growth that depend on molecular forces remained poor cousins. The reasons are becoming clear. Changes in the foundations of colloid and physical science took place over the last 70 years since the theory of Deryaguin, Landau, Verwey and Overbeek took center stage.
A number of related advances occurred.
The first is in the conceptualisation and quantification, and understanding of recognition built into Lifshitz theory, its many body, temperature and frequecy dependencies.
The second lay in the quantification of Hofmeister (specific ion) effects. These, due to dispersion and related hydration forces, had been inaccessible to classical theories of electrolytes and molecular forces. This defect rendered theory impotent for prediction.
The third has to do with the startling recognition that dissolved atmospheric gas, at a molecular level has qualitative effects which have been ignored.
Also ion specific, the effects are ubiquitous and range over enzyme activities to protein structure, catalysis and emulsion stability – "Hydrophobic interactions" apparently disappear when gas is removed.
The fourth is a new "non- Hofmeister" universal ion specificity that occurs for bubble bubble interactions. Inhomogeneity in temperature between bubbles and solvent can be used to catalyse high temperature reactions at low temperatures. These so far inexplicable effects open up other new technologies unimagined., in e.g., desalination, water purification and sterilisation and others.
In other words the classical theories of physical chemistry that inform our intuition had become rigid and inhibiting to progress. Application of fundamentally wrong theories of molecular forces based on electrostatic forces to many areas of biology like has produced an unhappy muddle.
An account is given of these complexities that are missing from classical theories of physical chemistry. Essentially although the Greeks told us that the elements were water, earth, fire and air, we forgot the last two.

When we include them, a different intuition and a new vistas emerge.
The paper is complemented by two other relevant manuscripts: one is published in Colloids and Surfaces Science B: Biointerfaces 2017, vol. 152, 326-338. *Two sides of the coin. Part 1. Lipid and surfactant self-assembly revisited.* The second has appeared in Current Opinion in Colloid & Interface Science 2016, vol. 27, 25-32, *Surface forces: Changing concepts and complexity with dissolved gas, bubbles, salt and heat***.**

Keywords. progress of sciences, molecular forces, surface forces, specific ion effects, bubble-bubble interactions, dissolved gas.

---

1. INTRODUCTION

This essay has a precedent in and pays homage to the magnificent book *Mathematics: The Loss of Certainty* by Morris Kline.[1] Kline relates the calamities that have befallen Mathematics. The realisation that the foundations were insecure, and did not as we thought, represent absolute truth led to a widening gap between Mathematics and Science. They are both poorer for it. Mathematics, once the Queen of the Sciences, and Science are hardly on speaking terms.

Our essay mirrors Kline and explores a similar calamity that has befallen Physical Chemistry. That subject is the enabling discipline that underpins subjects as diverse as Chemical Engineering to Soil Science to Molecular Biology and Physiology .

The discipline of chemistry, whose name, from Khemia, the black soil of Egypt that gave it life, is the most venerable of the tribes of the physical sciences. It has failed to contribute to biology as it ought to have done. The reasons lie deep. We will show that the foundations were flawed. And that when they are repaired, a wall of non communication between biological and physical sciences begins to come down.

2. JOHN W. DRAPER AND CELEBRATION OF THE ENLIGHTENMENT

In the heyday of the Age of Reason in the 19th century there was an unlimited confidence in reductionism. Let us hear from the American polymath and Professor of Chemistry at New York University, J.W. Draper in the peroration to his encyclopaedic *History of the Intellectual Development of Europe* published in 1876 by Harper Brothers.[2]

Here is his peroration:

In such things are manifested the essential differences between the Age of Faith and the Age of Reason.
In the former, if life was enjoyed in calmness, it was enjoyed in stagnation, in unproductiveness and in a worthless way. But how different is the latter! Everything is in movement. So many are the changes we witness even in the course of a very brief period, that no one, though of the largest intellect, or in the most favourable position, can predict the future of only a few years hence. We see that ideas which yesterday served us as a guide, die today and will be replaced by others, we know not what, tomorrow.
In this scientfic advancement, among the triumphs of which we are living, all the nations of Europe have been engaged. Some, with a venial pride, claim for themselves the glory of having taken the lead.
But perhaps each of them, if it might designate the country - alas - not yet a nation - that should occupy the succeeding post of honour, would inscribe Italy on its ballot.
It was in Italy that Columbus was born; in Venice, destined one day to be restored to Italy, newspapers were first issued. It was in Italy that the laws of the descent of bodies to the earth and of the equilibrium of fluids were first determined by Galileo. In the Cathedral of Pisa that illustrious philosopher watched the swinging of the chandelier, and observing its vibrations, large and small, were made in equal times, left the house of God, his prayers unsaid, but the pendulum clock invented. To the Venetian senators he first showed the satellites of Jupiter, the crescent form of Venus, and, in the Garden of Cardinal Bandini, the spots upon the sun. It was in Italy that Sanctorio invented the thermometer; that Torricelli constructed the barometer and demonstrated the pressure of air. It was there that Castelli laid the foundations of hydraulics and discovered the laws of the flowing of water. There too, the first Christian astronomical observatory was established, and there Stancari counted the number of vibrations of a string emitting musical notes. There Grimaldi discovered the diffraction of light, and the Florentine academicians showed that dark heat may be reflected by mirrors across space. In our own times Melloni furnished the means of proving that it may be polarised. The first philosophical societies were the Italian; the first botanical garden was established at Pisa; the first classification of plants given by Caesalpinus. The first geological museum was founded at Verona; the first who cultivated the study of fossil remains were Leonardo da Vinci and Fracasta. The growth of chemical discoveries of this century were made by instruments which bear the names of Galvani and Volta.
Why need to speak of science alone? Who will dispute with that illustrious people the palm of music and painting, of statuary and architecture? The dark cloud which for a thousand years has hung over that beautiful peninsular is fringed with irradiations of light. There is no a department if human knowledge from which Italy has not extracted glory, no art she has not adorned.

Draper's book was written first in 1859 before Italy became a nation; when the industrial revolution was coming into its apogee. It was reissued in 1876 America was still young and had recovered its confidence. Hubris abounded in the emerging empires. It was as if, quoth General Smuts, statesman of the British empire: "Mankind has struck its tents and is on the march" .

We can forgive Draper's naivete on an apparently boundless future driven by science and too easy dismissal of the Age of Faith.

If we imagined that the core of what he says still rings true today, we face a rude shock. In the 19th century it was possible for one man to understand all science. The meetings of the British Association for the Advancement of Science of the 19th century were attended and followed with much interest by the Press and "Gentlemen", products of greater Public Schools who knew Latin and Greek. Huxley argued with Bishop Wilberforce in defense of Darwin. They followed Burton and Speke's dispute over priority on the sources of the Nile. They waited on the translation of the Rosetta stone and Layard's and the French and German archeologists in Nineveh, were excited by Adams and Le Verrier's prediction and observation of Neptune in 1846. They were excited by the fossil record. They rejoiced with Queen Victoria when Stanley greeted the lost hero missionary in darkest Africa with: *Dr. Livingston I presume*. They rejoiced with the expansion of the railroads and even more when Kitchener avenged General Gordon with the systematic massacre of the Mahdi's large part of army with the new machine guns in Khartoum.

It has changed now. There is now fragmentation into a multitude of disciplines. Each is surrounded by firewalls, and there is litle intercommunication.

Hubris now attends modern science, biology, and quantum mechanics. Mindless replacement of thought by computers is our century's equivalent of the Age of Faith.

To computers are imputed all wisdom just like the Church in the worst of pre- reformation times. This is a reflection of the tides of fashion or a gestalt, the periodic emergence and dominance of which we are hardly aware.

Just a time when science seems dominant, triumphant even, the new age of Reason has disappeared, again. A new Age of Unreason is upon us.

3. D'ARCY THOMPSON'S PLEA

It is exactly 100 years since D'Arcy Thompson (1860-1948) published his book on *Growth and Form*.[3] He told us that the early founders of the cell theory of biology and the physiologists emphasised that progress in their disciplines had to wait on advances in our understanding of molecular forces and what even then we called colloid science. Immanuel Kant (1724-1804) had much the same to say, reported D'Arcy. He said "of the chemistry of his day and age that it was a science but not a Science – *eine wissenschaft aber nicht Wissenschaft*, - for that the criterion of a true science lay in its relation to on Mathematics".[3] Curiously, an aside, D'Arcy could not bring himself to mention the great German chemists of the preceeding century on the track of what he pleaded for, Fredrik W. Ostwald (1853-1932) who mentored the first four Nobel prizes in chemistry men like Wöhler who synthesised urea to break down the myth of a special life force for biomolecules and Friedrich August Kekulé von Stradonitz (1829-1896). Perhaps this was because Britain was at war with Germany. The same recurs. Witness the furious prejudice attached to "polywater" in Felix Franks' book *Polywater* and the Russians during the cold war.[4]

Lest our thesis be misinterpreted as an unfair attack on orthodoxy, let us remark that the claim that "the science is settled" raises a red alert. It is unique to the science of Climate Change only.

There is no other science for which that claim is made by its acolytes.

Indeed if it were, the "science" would be dead and uninteresting.

Let us go through some of them.

Astronomy: At an international meeting in Kyoto in 2016 the astronomers/cosmologists agreed that they have no idea of how to find dark matter or what it is, after 30 years of looking. (They are missing 98% of the mass of the universe necessary to explain the too rapid motion of spiral arms of galaxies). This is a bit of a problem to practitioners who can nontheless tell us the age of the universe with great precison.

Solar Physics: We have no idea of the source of solar magnetic field nor of the origin and genesis of sunspots.[5] These dark spots on the sun's surface are gigantic magnetic storms.

They cause a solar wind of ionised particles that hit the poles of the Earth and ionise the upper atmosphere. Hence ozone. But the sunspots flucuate and have disappeared in the last few years as they have in the past, coinciding with major weather fluctuations. For that matter the standard solar model lacks conviction.

Quantum Mechanics: Considered possibly the greatest achievement of physics. It is still in a mess.

Particle Physics: It seems in a worse mess. The story of the many species of neutrinos and the Higgs giant boson CERN is as credible to those of us not adepts as the Book of Genesis, but less useful.

Geology. Remember how Samuel W. Carey in Tasmania who pushed the theory of continental drift was excoriated? The theory was only accepted in the 1960s. Revolutionary theories of the formation of granite and oregenesis are in the wind with the new book of John Elliston.[6]

Biology of all kinds. These new sciences still very much in the process of big changes. The sex of crocodiles depends on the temperature. Kangaroo sex depends on concerted work between 17 different chromosomes. Hence epigenetics, a word that means imputing all wisdom to DNA is too simplistic. The physico-chemical environment of DNA is important too. As for the source of the energy that drives ubiquitous enzymatic action, most are content with the statement that energy flows downhill.

Agriculture: The practice of planting without ploughing, a previously unheard of idiocy for millenia, is now often de rigueur – we forgot about the soil microbes.

Mathematics: As already remarked, it never recovered from Gödel's theorem that showed 100 years ago too that there was no such thing as absolute proof. In a stunning example of delusions of claims of rationality, the mathematicians not only rejected divergent series, but also rejected the delta function and periodic delta functions and their other generalised function cousins until 1950.

The rejection is of major significance and still uncomprehended. The fact that a periodic delta function is a sum of cosines is both intuitive and profound. It is equivalent to the two forms of Euler's product, to Jacobi's theta function transformations, and the Riemann relation. The latter is also intuitive and its equivalence to the periodic delta function means geometry and arithmetic, shape and that we count, are two sides of the same coin. A finite version of the calculus can be derived from these which also gives analytic continuation automatically. The usual infinitesimal calculus is a special case. The Schrödinger equation of quantum mechanics and the diffusion equation are satisfied by the Jacobi theta functions, which give out the classical, Fermi Dirac and Bose Einstein statistics of statistical mechanics. The uncertainty principle is not necessary in the more physical finite calculus.[7]

Archaeology. A bit closer to the bone: The Old Kingdom in Egypt ground to a big full stop after Pharoah Pepi I about 4500 years ago. This was discovered only thirty years ago. It turned out that the Blue Nile stopped flooding for thirty years. Egypt was completely destroyed. The Middle Kingdom remerged in bastardised form several hundred years later. And of course they found the same happened to the Euphrates and Tigris rivers in Mesopotamia. We had no idea.

And the climate scientists forget what Herodotus (484-425 BC) and Strabo (65 BC-23 AD) reminded us about the rapid changes that took place in central Asia. A much larger Oxus river used to flow into the Caspian Sea and spill over to the Black Sea before it changed course again to the Aral Sea - so explaining how Alexander went so far so fast.

And so it goes in all these sciences, the Science is definitely not settled. And all are deficient. This is not bad. It means that the challenges make life more interesting.

We can be comfortable, not threatened if physical chemistry has some problems.

To these we now turn.

4. GROWTH AND FORM, STRUCTURE AND FUNCTION, LOCK AND KEY

Structure, form, lock imply visual images, geometry and shape of living things.

Growth, function, key imply forces, dynamics, more than visualisable streaming matter in hydrodynamic movement like the gel interior of an amoeba in chemotactic motion. Forces also implies the aether, the fifth element of the Greeks, mysterious, that cause molecules to signal and recognise each other and come together as a result.

Forces will be our central preoccupation. They depend on all 5 of the elements of the Greeks: earth, water, fire, air, aether (or quintessence). We will take fire to mean temperature.

The secrets of Greek fire which kept the Turks at bay and the Roman Empire alive for 1000 years has been revealed by Marcus Graecus:

Recipe for Greek Fire: (due to Marcus Graecus, 10th century, quoted by John Julius Norwich) "Take pure sulphur, tartar, sarcocolla (Persian gum), pitch, dissolved nitre, petroleum, (obtainable from surface deposits in Mesopotamia and the Caucasus) and pure resin; boil these together, then saturate tow with the result and set fire to it. The conflagration will spread, and can be extinguished only by wine, vinegar or sand."[8]

Further illumination on Greek fire we leave to the to the erudition of Professor Partington.[9]

But first consider.

4.1 Structure

It is self evidently a matter of physics. From bone to DNA, with the discovery of X-rays by Wilhelm Conrad Röntgen (1845-1923) and their deployment in X-ray spectroscopy by the Braggs, father and son around 1912, structure took off, culminating in the structure of haemoglobin by M. Perutz to 2 Å resolution. Although always plagued by the inverse scattering problem, of which more later, biology and physics came together in a productive synthesis. (After papering over a few problems! The fact that revisiting the original X-ray data of Rosalind Franklin showed 4 stranded not two stranded DNA as interpreted by Watson and Crick was dismissed by Wilkins. He shared their Nobel prize. When confronted with this annoyance he said: "Why reject a good theory because of an experiment!" (told to the author by Sir Ernest Titterton who knew him)).

And then post the 1960s it all went pear shaped. For soft matter like self assembled lipids and microemulsions and colloidal suspensions. Light scattering, sophisticated low angle x-ray scattering, neutron scattering, became possible because of accessibility of more and bigger machines for rent in search of problems and off-the-shelf computer programs. The results have been catastrophic. The non uniqueness of the inverse scattering problem means that the interpretation of an experiment depends on a theory. For example, with light scattering the inference of the zeta potential of a colloidal particle assumes that the theory applies to all particles and for all electrolytes. The theory is wrong and the results meaningless. With lipid-water self assembled structures, for thirty years distinguished physicists like Luzzatti insisted on interpreting data in terms of models involving alternating stacks of rods. This was opposed by Larsson and colleagues who interpreted the data in terms of *bicontinuous* cubic phases (see Figure 1 for an example). The geometries are non Euclidean. Invented 200 years ago by Gauss, Lobatchevsky, Bolyai and Riemann, they were first thought to be mathematical anomalies. Not so. The realisation that such geometries are the rule rather than the exception in biological structures was revolutionary.[10-13]

Here then is a classical illustration of Stephen Jay Gould's (1941-2002) maxim: "I have long believed that conceptual locks are far more important barrier to progress in science than factual lacks".[14]

Ironically, Gould's main academic research devoted to the geometry of snail shells, committed the same error. He analysed them in terms of Euclidean geometries when they were in fact non Euclidean shapes.[15]

For microemulsions, self assembled soft matter from water or brine, oils and surfactant, the story is much the same. Powerful and expensive scattering data interpreted microstructure in terms of spheres, cyinders and bilayers because that was all the the computer algorithms allowed. Or more often than not, they are random bicontinuous structures as that revealed by cryo-scanning electron microscopy in microemulsion system containing iso-octane, water and DDAB (didodecyl dimethylammonium bromide).[16] A structure – depicted in Figure 2 - that was easily determinable by use of a conductivity meter.[17] Or by taking account of constraints on packing by geometric packing, and volume constraints.[18]

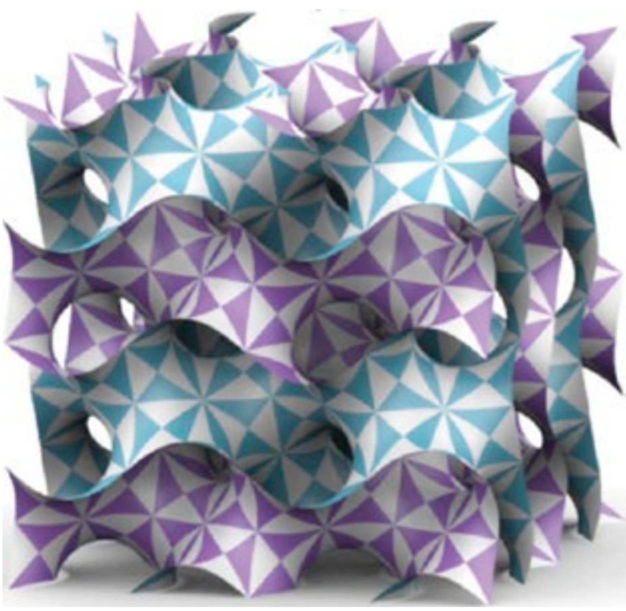

Figure 1. Bicontinuous cubic phases of phospholipids. The average or sum of normal curvatures is everywhere zero, the Gaussian curvatures varies continuously. Reproduced from Ref. 12 with permission of the International Union of Crystallography. http://journals.iucr.org/

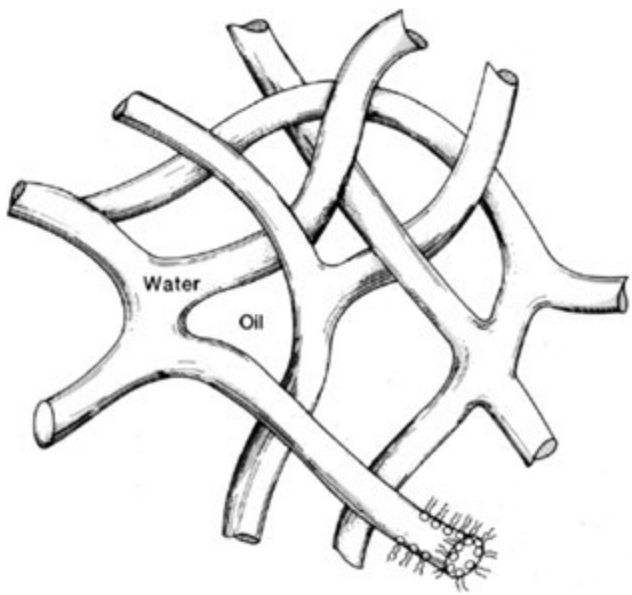

Figure 2. The bicontinuous structure inferred by a conductivity meter 30 years before the cryo-SEM micrographs. The conductivity meter is cheaper than an electron microscope. Such structures were often interpreted as spheres or cylinders from techniques like neutron scattering. Reprinted with permission from Ref. 17. Copyright 1986 American Chemical Society.

4.2 Structure and Simulation

At a Nobel symposium in 1986 devoted principally to simulation in biology the first speaker, a Swiss German working in the pharmaceutical industry began with a slide that said "NMR". What, said he, does this mean? Not Nuclear Magnetic Resonance. No, quoth this enthusiast. It means: "*NO MORE RESEARCH*". He proceeded to explain. With modern computer power and with 30,000 molecular potentials for each possible group – CH_3, –OH, -NH_2 –Cl, etc. (but note, no water molecules) he could simulate the structure of any required drug and enzyme. Game, set and match.

When asked how he would deal with the fact that his model (human) enzyme denatured at 37 degrees centigrade this genius replied. "NO PROBLEMS. WE CHANGE THE PARAMETERS!"

And more, we still can not explain or simulate why ice floats on water.

For more than 40 years this evident insanity has persisted, and does to this day. Much larger programs are bought on NIH grants to "predict" the "structure" of proteins for extravagant amounts of money, by biologists mainly, and cancer research grants. The molecular parameters used have no relation to real molecular interactions, and the key ingredient, water, is missing. When asked if they would please turn off all parameters except that for neon-neon interactions, to test if their program would decide if the ground state energy of solid neon was a face centered or body centered crystal at zero temperature - there is no simpler problem for simulation - they resolutely refuse.

The acceptance by hapless biologist and chemists of such evident charlatism is difficult to comprehend, and arose from frustration and ignorance.

4.3 Structure: The Rise of Computers and Simulation

The story of this deviant science due to misuse of and unquestioning reliance on computers has lessons for the future progression of the Age of Unreason.

One side of this we have already discussed. The easy interpretation of scattering data for structure in self organised soft matter through automated computer programs was clearly a massive and helpful development. But the programs depended on the assigment of structure via Euclidean geometry, restricted to spheres, cylinders and planes. Fitting of data was always possible by allowing an arbitary parameter that covered "interactions". The fact that these were impossibly unphysical was ignored.

This can be forgiven. No one was aware that the real geometries of nature were non Euclidean, an example of Stephen J. Gould's *conceptual locks* as a barrier to progress in science.[14]

This was not a fault of the physical sciences. It was a consequence of ignorance on the art of the life scientists and of chemists.

The more serious issue is how such massive assignment of resources could be devoted to mindless simulation of matter.[19] By simulation we mean for example taking a collection of spherical atoms like argon that interact via hard core repulsion and a two body van der Waals interaction. Program a collection of these in a theoretical box and let them go buzzing around like a bunch of bees until they reach a state of equilibrium. Do this all at different "temperatures" and so construct the whole phase diagram for argon and its thermodynamic properties. The ultimate aim is described by practitioners as the "vision thing". This is a state of nirvana where all proteins, all states of assembly, micelles, vesicles, membranes can be simulated by big enough computers, and as the German said: NMR.

4.4 Life from Outer Space

In his elegant account on the debate between Galileo and Lodovico Delle Colombe on the question of why ice floats on water, remarked that "Galileo, I will argue, had a scientific style marked by overconfidence. He tended to downplay the importance of obvious contradictory evidence that undermined his claims, and he did this by producing auxiliary hypotheses that sometimes verged on the extravagant. If we focus on this somewhat neglected aspect of his style, some interesting new questions emerge: To what extent did Galileo depend on such auxiliary hypotheses?".[20]

Very much so it turns out, and so for all of us in ways we do well to recognise.

His thesis on reliance on "auxiliary hypotheses" is, in our parlance, tampering with the truth in support of one's own prejudice.

Here is a true story that is relevant to our thesis: A professor from California came to my research Department on sabbatical leave with a piece of a chondoraceous meteorite. These are meteorites containing organic material. The particular meteorite was called the Murchison meteorite after a small rural town in the state of Victoria, Australia where it arrived on a farm. The farmer sold it, illegally, to NASA. NASA divided it up amongst scientists interested in such objects. Their question was since the meteorites contain organic material, could it be that the material contained life-forming molecules. Life might then be considered to have arrived on Earth from outer space. Our expertise was in colloid and surface chemistry, relevant to the investigation. A very beautiful honours student was assigned this as a research project.

She extracted the organic material and tested it out on a Langmuir trough, a simple apparatus used for examining surface active molecules like proteins, polymers and other molecules. Indeed the pressure-area curves showed all the signatures of biological molecules. This caused great excitement, celebrated by the appearance on a world wide science TV show by the student. The American professor went home happy. The success of his next grant application was guaranteed. Alas, after he left the student and her professor finally got hold of a surface infrared spectrometer from another lab and tested these life forming molecules.

They had all the signature of a protein called bovine serum albumin. The conclusion was obvious: either there are cows flying around in space or the Murchison meteorite arrived at the farm on a piece of cow dung. It was clearly genuinely bullshit.

When I told this story to the NASA chief scientist after his invited lecture to a Gordon conference, he laughed and said – "of course". But the American Congress like this kind of stuff. It was good for funding.

4.5 Berthollet and Water Structure

Claude Louis Berthollet (1748-1822) was a famous French chemist who went down to Egypt with Napoleon's 1795 expedition.[21,22]

He observed on dried salt beds of the retreating Nile flood lakes shiny deposits of soda lime, sodium carbonate. (This key observation marks the beginning of physical chemistry). How could it be? Everyone knows that with a solution of sodium carbonate and calcium chloride as the water evaporates calcium carbonate, limestone, is precipitated first with the sodium and chloride ions remaining in solution. The missing factor is temperature. With the midday sun above 60° C the water structure is different, and the reverse happens. In many dried up rivers in Egypt natron sodium carbonate essential for the economy in mummy preservation is the dominate precipitate. Whatever water "structure" means it depends on temperature. Water, H_2O, above 80-90° C, is not hydrogen bonded, at all whatever that means. Above such a temperature it behaves exactly like hydrazine, N_2H_4. The thermodynamics are identical for both water and hydrazine except that hydrazine is explosive.

In solutions of calcium carbonate aragonite is the preferred precipitate above 100° C, calcite that at lower temperatures.

Water structure changes not just with temperature, but also with background solutes.

This can be seen in precipitating nanoparticles. With magnesium or calcium hydroxide particles the size can be varied from microns to zero at will by adding sugars or indifferent salts to change the ambient water structure.

The role of atmospheric dissolved gas is another overlooked and ignored factor that determines these matters. It depends on temperature and background solutes. It is generally considered irrelevant because it is so low. This is absolutely not so, as we shall see below.

4.6 Microfossils and Siderite

Recent debates on the age of life forms and astrobiology occurred with the observation of "microfossils" in very ancient rocks. The microfosills are much smaller than the familiar fossils, too small to represent traces of early life. That conclusion received support from the extraordinary observations in crystallography of Juanma Garcia, Stephen T. Hyde and other collaborators on "microfossils".[13] They can be made in the lab with simple experiments. Such inorganic structures probably result from precipitation under double diffusion gradients, and mimic precisely real fossils in form. I leave this challenging new old world to the reader to explore.

Relevant to these matters is the work of McCollom on the formation of meteorite hydrocarbons from thermal decomposition of siderite, $FeCO_3$.[23]

Thermal decomposition of siderite had been proposed as a source of magnetite in martian meteorites. Laboratory experiments were conducted to evaluate the possibility that this process might also result in abiotic synthesis of organic compounds. Siderite decomposition in the presence of water vapor at 300° C generated a variety of organic products dominated by alkylated and hydroxylated aromatic compounds. The results suggest that formation of magnetite by thermal decomposition of siderite on the precursor rock of the martian meteorite ALH84001 would have been accompanied by formation of organic compounds and may represent a source of extraterrestrial organic matter in the meteorite and on Mars. The results also suggest that thermal decomposition of siderite during metamorphism could account for some of the reduced carbon observed in metasedimentary rocks from the early Earth.[23]

The important point hardly noticed is that the addition of water to the inorganic iron carbonate rock produced a huge range of complex organic products that occur in oil reservoirs. It had been thought that such "life" product molecules in oil reservoirs had to be the consequence of bacterial activity or forests. It had been postulated by T. Gold in 1990's and other model experiments done in 2004 confirmed that such processes can indeed be the source of semi infinite as yet untapped sources of natural gas and oil.[24]

The matter is completely open and of extreme interest. It is connected also to the present interest in "climate change".

4.7 The Business of Water Structure

The several examples above have been chosen to illustrate something we will continue to emphasise. In the absence of solutes or interfaces we think of water and model it as a Greek element in its own right. Hydrogen bonding is a concept widely used. It derives from a calculation of interactions between two water molecules only. It is elusive and even as an effective quantity a la Pople changes with temperature. Attempts to model water structure cooperatively, imitating a kind of dynamic zeolite that go back to Bernal seem to capture some of it.[25]

But dissolved atmospheric gas is missing. And that really matters. The tensile strength of water against cavitation is 200 times larger than for gas free water, a matter of profound economic importance for the shipping industry. Even if we were to make a molecular model of pure water correctly, the reality is this business of gas, temperature and salts and other solutes, and of their interdependence.

And of chirality. Is water chiralic?[26] And of magnetic and electric fields. And of jellyfish, last studied seriously by Gortner[27-29] in 1933. Jellyfish exist with as little as 2% nonaqueous material. There are some very long range forces that might explain their existence.[30] But nobody knows. And And And ...

So much then for Structure and Form.

Let us see how we are placed with Forces and Function.

5. SURFACE FORCES

We have reviewed the state of surface and molecular forces in a number of recent papers, in particular ref. 31.

The situation is evolving. By and large it has been mired in dogma and catastrophic. The entire foundations of the 150 year old venerable field of physical chemistry are flawed. The edifice built on those foundations, has necessarily been built on sand and continually patched up and papered over with more and more effective parameters. The intuition drawn from the theories was wrong and all predictability was lost. Where theory failed, reconciliation was sought by invoking undefined and unquantifed words like hydration, hydrophobic, hydrophilic, hydrogen bonds. After a long time, there is at last a clearer path through the morass. At risk of repetition, but it is so complex that to put our thesis into context, and how to go forward we do so partially and briefly again.

Several missing factors influence real surface forces remarkably. So much that the classical theory is often useless to the real world. Among these factors, we count dissolved atmospheric gas or other sparsely soluble solutes, bubble–bubble interactions. Moreover, inhomogeneity in temperature between bubbles and solvent can be exploited to catalyse endothermic reactions at low temperatures.

Further, the additivity of electrostatic and dispersion forces assumed in the classical theory of forces is wrong. It also ignores ion specificity (Hofmeister effects) due to dispersion forces acting on ions.

We will explain below the complications that we are missing from classical theories of surface forces. Some are explained, most not. Once revealed however, fortunately these phenomena can be exploited for a range of novel technologies as we shall see.

5.1 The Classical Picture of Molecular and Surface Forces: Limitations and Insights

The van der Waals interaction potential between two atoms behaves as $V(r) \sim 1/r^6$, where r is the distance between the centre of the atoms. This was known to Newton. The potential of interaction between two planar surfaces at separation L follows by pairwise addition. It varies as $1/L^2$. Newton tried to quantify this force, but gave up, with the comment (Art. 31 of the Principia): *surface combinations were owing.*

Unlike gravity, surface forces vanish rapidly over very short distances and depend critically on the material properties. And, as for contamination, it will always be with us.

For the opposing electrical double layer forces between two charged surfaces in a continuum electrolyte, the repulsive forces decrease exponentially with distance; asymptotically, $V(L) \sim exp(-\kappa L)$ where κ^{-1} is the electrolyte Debye length. The pre-factor depends on assumed boundary conditions, constant potential or constant charge. These conditions were relaxed with the extension to allow charge regulation.[32] This was a great conceptual advance. The degree of ionisation of surface charges – and therefore surfaces forces – recognises, and changes in its response to the proximity of, and signalling from, another body.

These few short lines underlie the DLVO (Deryaguin, Landau, Verwey, Overbeek) theory of colloidal particle interactions. The theory has been a core belief to physical chemists for 50 years. It still is so in spite the fact the theory has severe limitations, already acknowledged by both Deryaguin and Overbeek. These have to do with the assumption that a liquid between interacting bodies keeps its bulk properties up to a molecular distance from an idealised surface. Further, apart from the contamination problem, most surfaces are not molecularly smooth or chemically homogeneous and pure. In addition solvent molecules may interact directly with the surface, for example through hydrophilic or hydrophobic effects in the case of water. Specific ion effects are also ignored. And more, the theory has other amplified problems when the background electrolyte concentration increases, where only very short range surface forces emerge and these other factors can dominate. Especially in the real world.

The DLVO ansatz supposes that van der Waals and electrostatic forces are additive. Sadly they are not.[33,34] Note that this key ansatz is wrong even for a continuum solvent approximation, and wrong for free energies of transfer (Born energies), interfacial tension, activities of electrolytes and particle interactions. It is deficient in two crucial respects even within the constraints of its own assumptions. The additivity of forces ansatz is wrong. Which implies that the theory can not handle specific ion effects crucial in biology. It is wrong for any problem involving interpretation of experiments on electrolytes at interfaces, zeta potentials, electrochemistry, pH, buffers, ion binding to proteins or lipids, conduction of the nervous impulse and ion transport. The statement is heretical but remains true. Even the IUPAC Committee on pH warns us about the problems of pH and its meaning. And as for buffers, every biologist knows one does not mess with any protocol that accidentally works!

5.2 First Steps Beyond DLVO Theory: Complexities with Double Layer and Oscillatory Forces

A not insignificant aside is that the standard equation to calculate the Debye length for symmetric electrolytes is not valid for asymmetric electrolytes. It has a much more complex form. Direct force measurements for 12:1, 8:1 electrolytes (cytochrome C) and insulin 5:1 and 3:1 give precise agreement with theory.[35,36]

At small distances, i.e. several molecular sizes, the electrostatic forces are dominated by oscillations. These are sometimes called depletion forces. They act to stabilise emulsions and other systems where e.g. proteins or micelles form part of a fluid that separates two interacting objects.[37]

This "molecular granularity" emerges in all liquids, from van der Waals hard core fluids[38-40] to micellar suspensions.[37] The oscillations decay with separation and merge into the continuum theories after about 6 oscillations.

5.3 Hydration: Surface Induced Liquid Structure

The assumption that a liquid adjoining a surface has its own bulk properties up to contact (at molecular distance) breaks down for reasons other than molecular granularity. The profiles of surface induced liquid order can overlap and originate either repulsive or attractive "hydration" forces. (The terms surface dipole or hydrogen bond ordering are often used and cause much damage. The effects are cooperative not individual molecular properties)

These forces dominate at small separation. For surfaces that are rough at the molecular level, e.g. phospholipid head groups in a bilayer, the oscillations are smoothed out and decay with an exponential form with a range of about a molecular diameter (0.3 nm). They dictate van der Waals interactions up to say 3 nm separations. Correlated fluctuations in the surface dipoles of the head groups can produce other forces. They can appear in force measurements as a hidden contribution that changes effective hydration decay lengths. Thus, for example in the smaller ethanolamine polar head group such contribution is larger than in the bulkier phosphatidylcholine residue. The apparent hydration range is smaller for the former.[41]

Maxwell was the first to calculate correctly hydration forces,[42] followed by Marcelja 100 years later.[43,44]

5.4 Complexity in van der Waals Forces. Lifshitz Theory: Emerging Concepts of Recognition

Lebedev, the discoverer of light radiation pressure, renovated D'Arcy Thompson's criticism and wrote:[45]

> *... of special interest and difficulty is the process which takes place in a physical body when many molecules interact simultaneously, the oscillations of the latter being interdependent owing to their proximity. If the solution of this problem ever becomes possible we shall be able to calculate in advance the values of the intermolecuar forces due to molecular inter-radiation, deduce the laws of their temperature dependence, solve the fundamental problem of molecular physics whether all the so-called 'molecular forces' are confined to the already known mechanical interaction of light radiation, to electromagnetic forces, or whether forces of hitherto unknown origin are involved.*

Lifshitz with theory in 1955, and Abrikossova and Deryaguin with experiments in 1956, confirmed Lebedev's vision on molecular forces. The work was continued also by Dzyaloshinski and Pitaevski who developed – with Lifshitz - a theory of interactions between two planar dielectric surfaces separated by a liquid. Again, the hydration was neglected, as the liquid in contact with the two surfaces was assumed to retain its bulk properties.[45-47]

Under these premises, the theory was developed in the framework quantum field theory and was expected to provide the full solution of the problem. It comprised the temperature dependence of the intermolecular interactions, all many body interactions, and contributions from the entire electromagnetic spectrum. The major step was the acknowledgment that the measured dielectric susceptibilities of interacting bodies – that depend on the frequency – include implicitly all many body interactions.[46,47]

This topic is still an active field of basic research. However, the theory was difficult to test, until the work of Ninham and Parsegian on lipid-water systems.[48,49] The theory was then extended to include different shapes, layered, conducting and magnetic bodies, and electrolytes.[50]

Again, the crucial point for us here is the fact that the potential is given by all the contributions that derive from the electromagnetic spectrum. Some of these terms are positive, some repulsive, depending on the specific interacting materials, i.e. depending on their dielectric properties. For a planar geometry, the frequency term F(ω) decreases exponentially as:

$$F(\omega,L) \sim -\frac{A(\omega)}{L^2} exp\left[-\frac{2\omega L}{c\varepsilon(i\omega)}\right] \tag{1}$$

where ω, L, c, and ε(iω) are the frequency, the distance between the two bodies, the velocity of light and the imaginary dielectric susceptibility of the medium at frequency ω, respectively. For simplicity I omit the expression of the pre-factor.

The most important result of this model is that two bodies feel and recognise temperature dependent zero frequencies first. As they come closer and closer, then frequencies contribute in order of increasing energy: first the lower energy infrared components (with wavelenghts λ between 2 and 5 micron), followed by optical (λ ~ 400 nm), far ultraviolet (λ ~ 100 nm), until the two ojects come into atomic contact or hydration. This is precisely where chemistry takes over.

Alternatively, two objects sense each other's "specific vibrations", and respond appropriately. In some cases this specific interaction is very strong and extended in space. It is interesting to calculate the interaction potential for two thin parallel rods of a conducting material at a distance L, which is the case of DNA strands:

$$V(L) \sim 1/L \qquad \text{for } r \ll \kappa^{-1} \tag{2}$$

$$V(L) \sim \left[L \bullet ln\left(\frac{L}{r}\right)^2\right]^{-1} \qquad \text{for } r \gg \kappa^{-1} \tag{3}$$

where r is the radius of the rod and κ^{-1} is the Debye length.

The force is strictly non additive and basically infinitely long ranged. Instead, two planar conducting surfaces interact with a short ranged potential.[51]

The problem becomes more intricate, as the temperature dependent contributions decrease with another factor that is related to the reciprocal of the Debye length, i.e. as $exp(-\kappa L)$.

The concept of recognition, that depends on the physico-chemical features of the materials and of the surrounding medium, was captivating. But the claims for generality went too far. In fact at the end the theory turned out to comprise an integration trick. The mystique of quantum field theory (QFT) was exposed and the entire building collapsed to a semi-classical theory: it was shown to be nothing more than Maxwell's equations for the electromagnetic field with boundary conditions plus the Planck hypothesis for quantisation of light.[31,51]

The equivalence of QFT with a semi-classical theory brought about a deep extension of the theory. But the theory on molecular interactions is constructed at zero temperature, for example the Casimir-Polder and Casimir interactions for "retarded" van der Waals interactions. "Retardation" refers to a reduction in the interactions because of the finite speed of light. The problem is that all this is quite wrong![52,53]

In a similar way the discussion of resonance or retarded Forster interactions involving excited state-ground state interactions - that are the basis for disputed quantum computing procedures - are even more incorrect and with no physical correspondence.[54] Nonetheless the visions, as in the case of the DLVO theory, endure and cheer the Boetians.

Furthermore, another overlooked development emerges if we try to relate Casimir–Lifshitz forces at finite temperature in a vacuum and particle physics. Weak interactions (mesons) seem to merge naturally and quantitatively.[55,56]

We have mentioned these matters because however arcane that may appear, it is reassuring that the same errors underlie both physical chemistry and physics.

6. HOFMEISTER PHENOMENA AND THE INADEQUACY OF DLVO THEORY

Hundred and fifty years have passed, since the pioneering work of Franz Hofmeister in Prague at the end of the 19th century, and physical chemistry is still unable to comprehend and predict specific ion effects. Unless one introduces arbitrary parameters like postulated ion size. As in the Debye-Hückel theory, the size is adjustable and different for every solvent and temperature.[57] The issue propagates and affects Born energies, interfacial tensions, activities, pH, pK_as, buffers, ion binding, viscosities and all other bulk or interfacial experimental parameters.[58]

Hofmeister investigated the relative effectiveness of different salts in precipitating albumin in water and established the so-called "Hofmeister series":[58]

anions at fixed cation:
citrate^{3-} > CH_3COO^- > SO_4^{2-} > F^- > Cl^- > Br^- > I^-
cations at fixed anion:
$N(CH_3)_4^+$ > NH_4^+ > Cs^+ > Rb^+ > K^+ > Na^+ > Li^+ > Ca^{2+} > Mg^{2+}

Such series occur in chemistry, biology, biochemistry, geochemistry, practically everywhere. It is not universal but depends on substrate and probably dissolved gas.[58] Hofmeister's original work is translated and re-published in Ref. 59.

Two examples are illustrative of the problem.

6.1 Measuring the pH

If one measures the pH of 1:1 strong sodium electrolytes in buffered solutions with a glass electrode, the "pH" change in a phosphate buffer follows a Hofmeister sequence. But if sodium is replaced by potassium salts the sequence reverses! And using a cacodylate buffer at the same stated pH as phosphate the sequence reverses from the phosphate case also.[34,60] This and several other common measurements are inexplicable with classical theory, because it does not have room for specific ion effects.

None of the measurements make any sense in classical theory. According to common knowledge and understanding the two buffers must give the same results, and these must not - according to textbook theory - depend on the nature of background electrolyte (Hofmeister effects). Though the measurements are performed in terms of that erroneous theory. If we ask what a pH measurement in the ocean means, it makes sense only if interpreted as Alice in Wonderland says: *When I use a word, Humpty Dumpty said, in rather a scornful tone, it means just what I choose it to mean—neither more nor less.*[61] The same problem emerges in a plethora of different phenomena and measurements, like ion binding to proteins.

6.2 Indirect Forces and the Activity of Enzymes

Another stark example of the failure and inadequacy of theory is any explanation of the energy that drives enzyme action. The cutting by a restriction enzyme of linear DNA[44,62] is an essential tool of molecular biology. Like the problem of pH, cutting efficiency makes no sense in terms of DNA-enzyme forces predicted by DLVO. The energy required to cut segments on the DNA chain seems to be indirect and subtle. It seems to be given by hydrophobic cavitation that originates free radicals.

Figure 3 shows the efficiency of enzyme (expressed as percentage of linear DNA) as a function of the electrolyte concentrations for a set of sodium salts. Similar results exist for cation sequences.[44,62a] As for our pH problem the phenomenon is remarkably ion specific. It depends on the buffer used to set the nominal pH value of 7.5. Strikingly, the trend reverses when the phosphate buffer is replaced by cacodylate.[44] The standard theories of forces cannot explain the experiments. Nor does it provide any hint at the source of the energy to carry out the enzymatic activity. Specific ions, both cations and anions, and buffer anions compete to set hydration and inter-substrate and enzyme water structure that determine association. The enzyme dimerises, diffuses up and down the linear DNA chain to find the right palandromic sequence (Figure 4).[62b] There follows hydrophobic cavitation, a cooperative harnessing of all the weak van de Waals forces that creates free radicals. These then cut the DNA at precise palandromic sequence. Whether the cavitation phenomenon depends on dissolved gas is unknown. That this mechanism is likely can be seen if a free radial scavenger is added to the mix. It stops the enzyme dead. The gap between physical theories and real molecular biology is evident. But, importantly this example shows there is a way through what seems to be a bewilderingly inexplicable mess.

6.3 More on Hofmeister Effects: Unpleasant Facts and Pleasant Consequences

As I mentioned, specific ion effects emerge dramatically in a myriad of other phenomena, e.g., in the formation of self-assembled micelles, vesicles and microemulsions from surfactants. Interestingly here we observed that forces with different coions and counterions and forces between interfaces can change very remarkably.[34,58,63,64]

The DLVO theory unsuccessfully tries to explain such variability by importing extra non predictive parameters like ion size. These are often absurd. The ansatz of

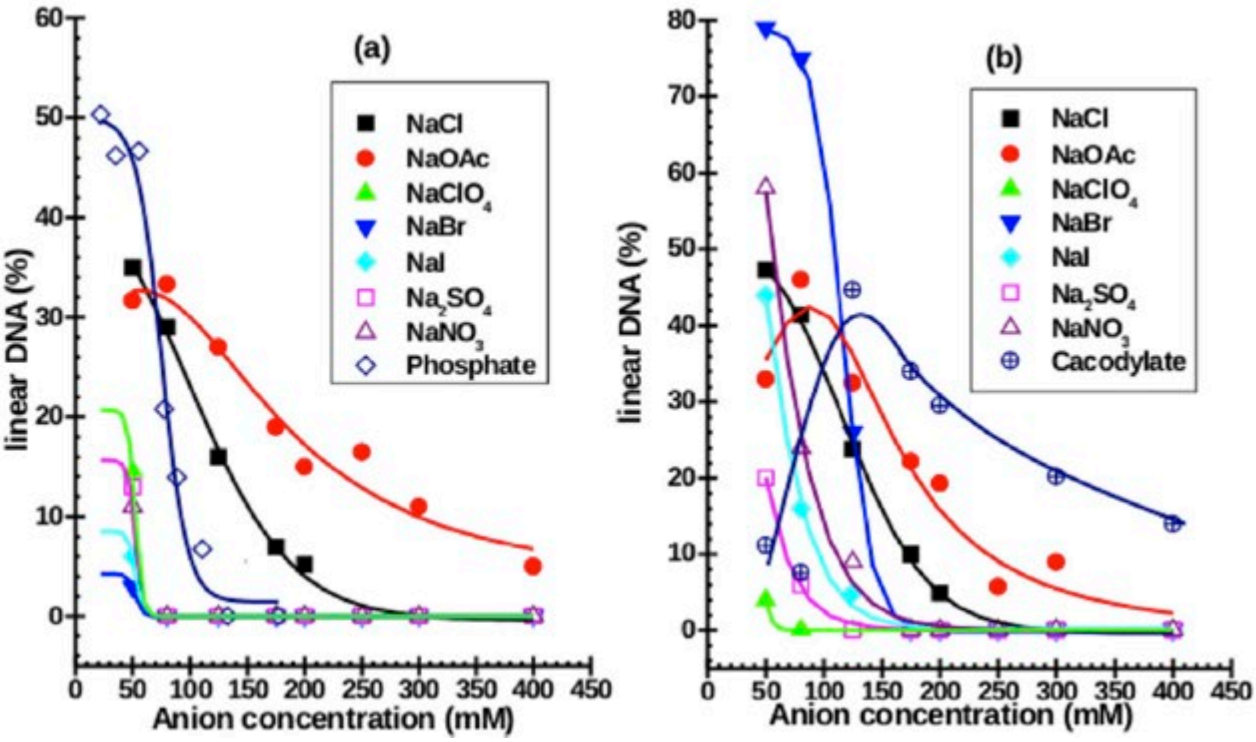

Figure 3. Enzyme cutting efficiency versus the concentration of the electrolyte at pH 7.5, for a set of different 1:1 sodium salts. The buffer used was phosphate (a) or cacodylate (b). Reprinted from Ref. 44, Copyright 2016, with permission from Elsevier.

DLVO theory that supports the entire fabric of the discipline is flawed. In fact physics does not allow to add electrostatic forces, treated in non-linear theory, to van der Waals forces treated in a linear theory. The problem is not simply a matter of approximation, the entire theory has to be rewritten. The bad consequences are that most measurements like pH and ion binding - that are based on the classical theory - are of unsure meaning. On one hand this is unpleasant and disappointing and is therefore almost universally ignored. On the other hand, a great effect is that the few who do not try to hide or neglect the problems are in a good position to use forces due to specific ion effects. Deryaguin and Overbeek both were well aware of the limitations of their theory of interactions of colloids, of specific ion effects and that it failed above a concentration of 50 mM.

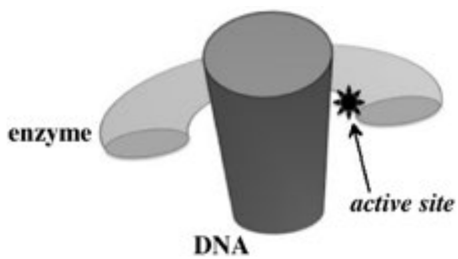

Figure 4. Cartoon of the problem of restriction enzymes. The enzyme cuts a DNA strand at a specific sequence of nucleotides. The star represents the enzyme active site. Adapted from Ref. 62b with permission of Springer.

The best advice of the IUPAC Committee on pH is to avoid electrolyte concentrations above at most 100 mM. And anything more complicated: Forget it. For a detailed account of the present state of affairs and opinion on Hofmeister effects see a recent Current Opinion in Colloid & Interface Science special issue[63] and a recent paper of Leontidis.[64] The physical chemistry of electrolytes, and electrochemistry, got stuck in a frustrating swamp, a parameter-rich hiatus for a century.

More recently the recognition that we lack the quantification and inclusion by *ab initio* quantum mechanics of ion size, hydration and dispersion forces was understood and at least partially accepted. Some promising advances on Born self energies, interfacial tensions, ion activities and the vexed problem of the air-water interface potential. Average ionic activities of twenty one monovalent electrolytes can be actually predicted with just three universal parameters. Whether these advances can be extended to asymmetric, and mixed electrolytes and include temperature is still an open question.[65-69]

7. HYDROPHOBIC FORCES AND DISSOLVED GAS

However, the challenge generated by the flaws in the foundations of the theory and the disregard of Hofmeister effects is a minor concern.[44]

Long ranged hydrophobic forces between interfaces have been measured and reported in several papers. But the mystery that surrounds this kind of forces remains: when the dissolved atmospheric gas is removed from the sample these forces disappear. Although tricky, this fact offers a possible hint to clarify thr mechanism: Surface-induced water structure can extend only a six molecular diameters or so. The perturbation lowers the density of a thin film compared with bulk water. This causes a density lowering in the gap between the interfaces and generates the force due to the difference between the pressure inside the gap and outside. The range should be about 3 nm, i.e. 6 water molecules. Dissolved gas molecules play the same role that defects do in a solid. They disturb the tensile strength of a thin film of water between the two surfaces. The fluctuations or defects that result in the lowering of the liquid film density are carried from the surfaces from one gas molecule to another and percolate across the gap. Ions can either oppose or promote these complex fluctuations in the interfacial liquid density.

Further discussion on the mechanisms of hydrophobic forces can be found in the literature.[70-73] Yaminski pioneered studies on hydrophobic forces along with — and independently of Pashley and Kitchener. He actually had read and understood Gibbs' work, famous for its obscurity.

"Hydrophobic" forces exist, extend across long distances and depend on interacting surfaces and dissolved gas, no matter which microscopic mechanisms control them. Unfortunately they cannot be easily simulated. They are not explained or predicted by classical theory, but must be part in any picture of self-assembly and interactions in biologically relevant systems.

An outstanding, surprising and graphic demonstration of surface forces arises when a mixture of a hydrocarbon and water is almost completely de-gassed.[74] Some years ago it was reported that cavitation occurs when two hydrophobic surfaces immersed in water were pulled apart. This means that the removal of dissolved gases may facilitate 'oil mixing with water' because dissolved gases promote cavitation. This idea has now been well established. The degassed oil-water dispersion remains stable for several hours, whereas a regular mixture (with dissolved gas in) phase separates very rapidly.

If dissolved gases significantly affect hydrophobic interactions then direct surface force measurements should be able to detect and quantify such effects. These have been reported, although the topic is fraught with contraddictory results. In the future it will be interesting to check the effect of dissolved gases on coalescing a single oil droplet, an experiment that has not yet been performed.

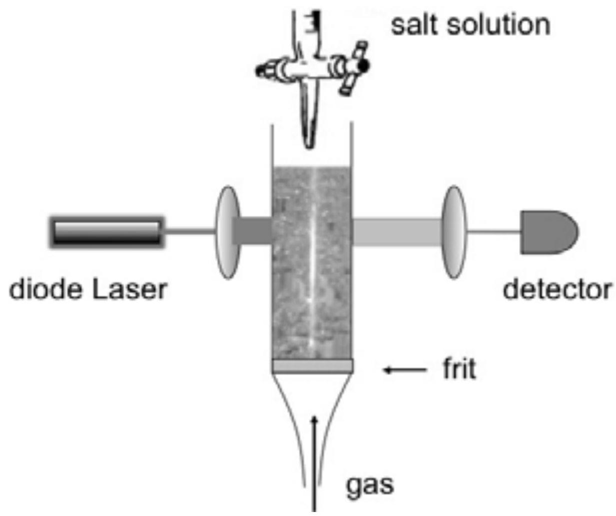

Figure 5. Scheme of the apparatus for producing bubbles and measuring their optical density. The gas is admitted from the bottom, passes through the frit and bubbles through the liquid contained in the chromatographic column. From the top more solvent or a salt solution can be added. Courtesy of Vincent S. J. Craig.

Dissolved gas and other poorly soluble solutes must propagate the attractive force between two hydrophobic surfaces to a much longer distance than should be predicted from merely a solvent molecular ordering perturbation, which in water can extend a few nanometers. By comparison, hydrophobic attractions have been reported out to about 90 nm.

The gas problem poses more than just a dilemna.

The solubility of a gas in water depends also on salt nature and concentration. So far this evidence has been simply ignored. As Descartes might have said "I breathe, therefore I am". Fish philosophers would have a similar view. And they are certainly correct.

8. BUBBLE-BUBBLE INTERACTIONS: A CASE OF NON HOFMEISTER ION SPECIFICITY

An even more perplexing problem is the phenomenon of bubble-bubble coalescence in electrolytes. It is hard to think of a simpler and relaxing experiment – contemplate the ocean. In fresh water bubbles coalesce (look at a water fall). Instead the ocean is foamy, and this is not a consequence of pollution or of the presence of organic matter. The effects of salts on inhibiting bubble-

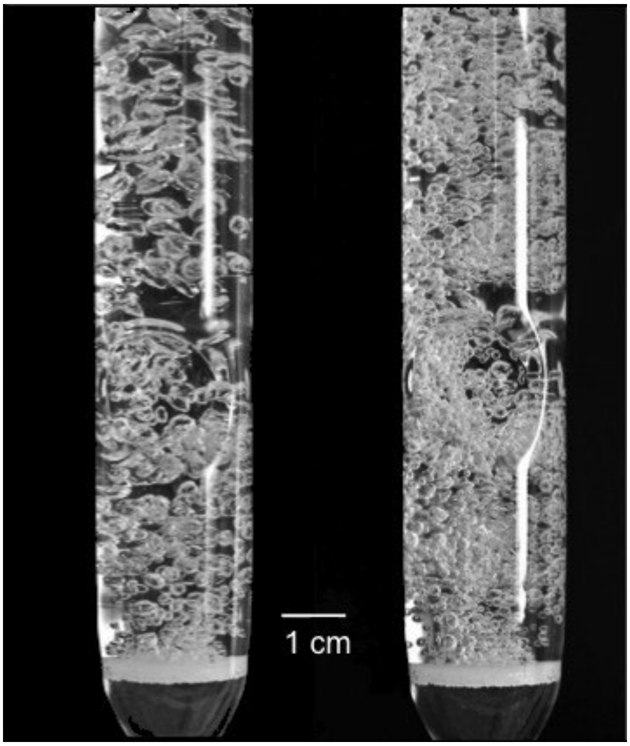

Figure 6. The gas bubbles diffuse through water (left) and through a 0.3 M NaCl solution. In the salt solution the bubbles coalescence is remarkably reduced. Courtesy of Vincent S. J. Craig.

bubble coalescence has been well studied for more than 30 years.[75-79] But there is still no explanation at all. The background (and more references) is described in Ref. 44. This is the experiment: air or another gas are passed through a frit to a column filled with salt solutions. Figure 5 illustrates the very simple apparatus. The bubbles collide as they rise in the column and fuse. The column remains clear. As the salt concentration increases, in a sharply defined range the bubbles no longer fuse and the column becomes opaque. It is filled with a mass of fine bubbles. The effect is the same for a whole range of all salts (see Figure 6) and scales with the Debye length of the electrolyte 1:1, 2:1, 1:2, 3:1, etc. The phenomenon occurs for one class of ion pairs. For another class no effect occurs the bubbles continue to fuse at all concentrations!

This is inexplicable within the framework of a classical physical chemistry theory of forces between bubbles (DLVO). In fact DLVO predicts a bubble coalescence enhancement with added salt because (i) it should screen out any electrical double layer repulsion between negatively charged bubbles and (ii) should increase the surface tension — favouring bubble coalescence. The situation is further, and greatly complicated, by the fact that some salts inhibit coalescence and some do not. And similar effects occur in polar non-aqueous organic solvents too, like methanol, propylene carbonate, formamide and dimethylsulfoxide.

"Explanations" of Hofmeister effects re-appear every decade, but they are specious and wrong.[44] They reflect the religious fervour in which the DLVO theory is clung to. These results are as profound as they are simple and inexplicable. Temperature, gas type, adsorbed ion hydration and film viscosity and other candidates have all been ruled out of contention and appear not to influence the observations and their ion pair dependence.

The same kind of specifc bubble-bubble interaction inhibition occurs for different isomers of sugars or mixtures of sugars.

A related puzzle is that of the *sign* of the air-water interface. Is H_3O^+ or OH^- the more favoured species? Bubbles are negatively charged. It is a simple question. See Ref. 44 for the latest state of play.

8.1. Contingency in Evolution

An interesting speculation is suggested by the bubble bubble salt inhibition phenomenon. In the Ediacaran extinction, 570 million years BP, multicelled animals all died. In the Burgess Shales extinctions, 530 million years BP there were considered to be at least 24 highly successful phyla. That figure may have been reduced by now due to better classification. But only 4 phyla surface to become us. Only 4 survived including us. In the Permian extinction, 230 million years BP 95% of all species disappeared.

These extinctions coincide with known CO_2 cycles and consequent ice ages. There followed precipitation and removal of salt from isolated oceanic regions.

After the ice ages and melting of the ice, there would follow a reduction of salinity below 0.175 M, as for example in the Baltic ocean. The present ocean is about 0.4 M, while all animals including us have Permian ocean salt concentration 0.175 M.

Massive extinction of phytoplankton would follow the end of the ice age. It is possible the extinctions occurred as every species would have died of the bends, due to bubble-bubble fusion!

9. WISHING REASON OF THE OCEAN

Jan Morris in the third of her exquisite volumes on the British empire, *Farewell the Trumpets* began with the fin de siècle celebration of Queen Victoria's Diamond Jubilee of 1897. She said:[80]

If to the Queen herself all the myriad peoples of the Empire really did seem one, to the outsider their unity seemed less than apparent. Part of the purpose of the Jubilee jamboree was to give the empire a new sense of cohesion. But it was like wishing reason upon the ocean, so enormous was the span of that association, and so unimaginable its contrasts and contradictions.

Physical Chemistry is a bit like that. Like the Empire it made a muddled progress during the same period. And like the Empire it was like wishing reason upon the ocean. Literally!

As Morris said of the Empire that had reached its nadir. Suddenly it was time to go, like the whisking away of an opera set on a revolving stage. And maybe too for our venerable discipline of Physical Chemistry. It ought to be supporting the rambunctious new tribes of the biologists still confident in the first flush of success in a new science, but is not. In our essay, we have seen that what we considered dependable, and the ritual experiments we practiced and their paraphenalia to give us reassurance were false gods.

Think of non Euclidean and random bicontinuous geometries that are taking center stage, of erroneous force laws, of Hofmeister specific effects, of the astonishing pervasive role of dissolved gas and hydrophobic interactions, and of the equally astonishing phenomenon of bubble-bubble interactions. So, is nothing sacred? Probably not. At least now though we can recognise the value of Stephen J. Gould's aphorism on conceptual locks[14] and practice the first steps towards a Damascene insight and conversion. There are difficulties that can be identified. A major one is that the biologists have been seduced into paying lip service to false gods which are now deeply imbedded into their dogmas. Perhaps that can be overcome as the rewards for service have been few.

We began with Morris Kline. In his peroration on the plight of mathematics he said:[1]

It behooves us therefore to learn why, despite its uncertain foundations and despite the conflicting theories of mathematics, mathematics has proved to be so incredibly successful.

For the physical sciences in biology and medicine the question is reversed. Why is it that we have been so incredibly unsuccessful? The reasons seem clear enough.

Time to rebuild the temple. Heresy, but necessary.

From that vantage point we return to John W. Draper and his enthusiastic boundless confidenee in the Age of Reason.[2] It parallels the confidence of the Mathematicians at the World Congress in Paris in 1900. Hilbert the acknowedged best of the brightest announced 21 propositions that remained to be proved before the edifice of mathenatics was consistent. The edifice fell to the ground almost immediately after.

Is Draper's confidence justified? Not in the Age of Reason which led us via Kantian certainty to a sterile cul de sac. When the physicists have a theory that allows neutrinos en masse to penetrate 100 light years of solid lead before a few are detected, reason has to go.

10. THE OCEAN FIGHTS BACK

Curiously, we can hope that Draper's confidence will be justfied in the new age of unreason. And here is why.

We have identified substantial deficiencies in theory, and in consequence, in measurements that depend on those theories. Suppose those difficulties are resolved — the matter is more complex still. Dissolved gas, cavitation and bubbles, specific ion effects, and temperature, are all components of the ancient Greek view of the elements: earth, air, water and fire. We have been missing air and fire and light, which we have hardly touched on.

We have described some of the astonishing phenomena that attend admitting gas as one of our elements. We have no theory. If we now do include temperature by allowing hot bubbles through a sinter to our electrolyte bubble column marvellous things happen that we never dreamed of. Some are described in Refs. 44 and 81.

Technologies have emerged that allow high temperature aqueous solution reactions to be done at low temperature. The hot bubble surfaces are amazingly reactive. Desalination can be done without membranes very much more cheaply than the best conventional methods. Viruses and drug molecules are killed so that the use of recycled water becomes possible. Removal of heavy metals like arsenic, lead and mercury becomes easy. Carbon dioxide gas bubbles are extraordinarily reactive even at room temperature. And more that experiment reveals, that we can use, and we have not the faintest idea of why they work. These new breakthroughs are pioneered by R.M. Pashley. Watch this space.

Finally in homage to Morris Kline we repeat his translation of some aphorisms of Xenophanes (6th century BC) that seem to be apposite:

The Gods have not revealed all things from the beginning. But men seek and so find out better in time. Let us suppose these things are like the truth. But surely no man knows or will ever know the truth about the gods and all I speak of. For even if he happens to tell the perfect truth, he does not know it, but appearance is fashioned over everything.

There are rapid strides being made to improve and remedy present theories. And what is encouraging is that when the chemistry is done correctly, when the conceptual locks are removed, more often than not the emerging theories do actually work, predictively.

ACKNOWLEDGMENTS

I have worked on the topics of this paper since 1968 when I began an exciting collaboration with V. Adrian Parsegian. Since then I have had the luxury and privilege of working with very many colleagues and students. I am indebted to them all.

I owe a special debt to Pierandrea Lo Nostro, Stephen Hyde, Adrian Parsegian, and Richard Pashley.

REFERENCES

1. M. Kline, Mathematics: *The Loss of Certainty*, Oxford University Press, **1960**.
2. J.W. Draper, *History of the Intellectual Development of Europe*, Harper Brothers, New York, **1864**.
3. D'Arcy W. Thompson, *On Growth and Form*, Cambridge University Press, 1917, 1942, **1969**.
4. F. Franks, *Polywater*, The MIT Press, **1981**.
5. O.K. Manuel, B.W. Ninham, S.E. Friberg, *J. Fusion Energ.* **2003**, *21*, 193.
6. J. Elliston, *The Origin of Rocks and Mineral Deposits*, Connor Court Publ., Ballarat, **2017**.
7. B. Hughes, B W Ninham, *Physica A* **2016**, *443*, 495. See the book of James Lighthill and the papers of M.J. Berry cited therein.
8. J.J. Norwich, *Byzantium: The Early Centuries*, Penguin, London, **1990**.
9. J.R. Partington, *A History of Greek Fire and Gunpowder*, W. Heffer & So., Cambridge, **1980**.
10. S.T. Hyde, S. Andersson, K. Larsson, S. Lidin, T. Landh, Z. Blum, B.W. Ninham, *The Language of Shape. The Role of Curvature in Condensed Matter: Physics, Chemistry and Biology*, Elsevier, Science B.V., Amsterdam, **1997**.
11. http://people.physics.anu.edu.au/~sth110/sth_papers.html, last accessed on Jan 12, 2017.
12. M.E. Evans, V. Robins, S.T. Hyde, *Acta Cryst.* **2013**, *A69*, 241.
13. J.M. García-Ruiz, E. Melero-Garcia, S.T. Hyde, *Science* **2009**, *323*, 362.
14. S.J. Gould, Eight little piggies. Reflections in Natural History, W.W. Norton & Co., New York, **1993**.
15. S.T. Hyde, *Forma* **1998**, *13*, 145.
16. I. Ben-Barak, Y. Talmon, *Z. Phys. Chem.* **2012**, *226*, 665.
17. S.J. Chen, D.F. Evans, B.W. Ninham, D.J. Mitchell, F.D. Blum, S. Pickup, *J. Phys. Chem.* **1986**, *90*, 842.
18. B.W. Ninham, K. Larsson, P. Lo Nostro, *Colloids Surf. B Biointerfaces* **2017**, *152*, 326-338.
19. This is how it came about. The late 1950's saw the apogee of attempts to derive quantum statistical mechanical theories of liquids, plasmas, electrons in metals, and nuclear matter, or in ab initio quantum mechanics.

    For liquid matter and random media there was and still is no theory in the sense that there is for solids and gases. For solids, an underlying framework on which to build a perturbation theory exists in periodic lattices. For gases it is a completely random distribution function, diagrammatic expansions of partition functions generalised similar expansions in quantum electrodynamics, their resummation was associated with names of Joe Mayer — who predated QED, Montroll and Ward, Bloch and De Dominics. It all became too hard.

    Partial resummation gave approximate integral equations that could be solved with certain assumptions connecting direct and indirect distribution functions. These took on names like Hartree-Fock, exchange, hypernetted chain with added bridge diagrams became de rigueur approximations. Random matrices were another trick. The mess was ripe for computers. Monte Carlo and direct simulation of atoms and their interaction became appealing.

    Thus a pioneer, John Barker an Australian theoretician working in liquids became frustrated with analytic approaches. He went to IBM in California to access computer power. With colleagues Henderson and Watts they published a landmark paper that computed by simulation the entire phase diagram of argon. When the author pointed out to Watts the fact that their van der Waals interaction was wrong by factor of two, he said, as usual, "no problem we can change the parameters!". This achievement laid the foundations for an entire new industry, computer simulation and the "Vision Thing" in biological simulation. (Overlooked was the fact that even for this simplest possible case, argon, the ground state structure (FCC) and the interfacial tension of the liquid can not be predicted without inclusion of three body forces. These are impossible to include. It is evident that simulation of a liquid like water then is not possible).

    IBM seized the opportunity and went on the front foot selling main frame computers and simulation as the way ahead for biology. In this enterprise they were very successful (Clementi - pioneer of Monte Carlo simulation and Heller were two of the scien-

tists who did such marketing very well, citing Barker, Henderson and Watts). The belief of such adepts is unquestioned. The author and V.A. Parsegian were approached at NIH in 1969 to set an example and support the purchase of such a computer, while working in the Division of Computer Research and Technology. Having seen the wreck of Nixon's data driven war on cancer we did not support such silliness).

It was about that time and for ten years later major companies like IBM and Bell Labs moved from an enlightened policy of allowing their scientists to do untrammeled research – the author finished his Ph.D thesis working on white dwarf stars! — to directed market direct profit oriented research.

The same catastrophe took over in models of evolution, economics and other areas.

Here endeth the lesson.

20. L. Caruana in *Aqua Incognita. Why Ice floats on Water and Galileo 400 years on*, (Eds. P. Lo Nostro and B.W. Ninham), Connor Court Publ. Ltd, Ballarat, **2014**, pp. 1-17. And this issue.
21. C.C. Gillispie . *Proc. Am. Phil. Soc.* **1989**, *133*, 447.
22. A. Lucas, *J. Egyptian Arch.* **1932**, *18*, 62.
23. T.M. McCollom, *Geochim. Cosmochim. Acta* **2003**, *67*, 311.
24. F. Dyson in *Excerpts Many Colored Glass: Reflections on the Place of Life in the Universe* (Page Barbour Lectures), University of Virgina Press, **2007**.
25. S.T. Hyde in *Aqua Incognita. Why Ice floats on Water and Galileo 400 years on*, (Eds. P. Lo Nostro and B.W. Ninham), Connor Court Publ. Ltd, Ballarat, **2014**, pp. 142-171.
26. Y. Scolnik in *Aqua Incognita. Why Ice floats on Water and Galileo 400 years on*, (Eds. P. Lo Nostro and B.W. Ninham), Connor Court Publ. Ltd, Ballarat, **2014**, pp. 179-192.
27. R.A. Gortner, *Trans. Faraday Soc.* **193**0, *26*, 678.
28. M. Henry in *Aqua Incognita. Why Ice floats on Water and Galileo 400 years on*, (Eds. P. Lo Nostro and B.W. Ninham), Connor Court Publ. Ltd, Ballarat, **2014**, pp. 34-99.
29. S. Deguchi, K. Kinoshita, T. Kubota in *Aqua Incognita. Why Ice floats on Water and Galileo 400 years on*, (Eds. P. Lo Nostro and B.W. Ninham), Connor Court Publ. Ltd, Ballarat, **2014**, pp. 231-246.
30. B. Davies, B.W. Ninham, P. Richmond, *J. Chem. Phys.* **1973**, *58*, 744.
31. B.W. Ninham, V.A. Parsegian, G.H. Weiss, *J. Stat. Phys.* **1970**, *2*, 323.
32. B.W. Ninham, V.A. Parsegian, *J. Theor. Biol.* **1971**, *31*, 405.
33. B.W. Ninham, V.V. Yaminsky, *Langmuir* **1997**, *13*, 2097.
34. B.W. Ninham, P. Lo Nostro, *Molecular Forces in Colloid and Nanosciences and Biology*, Cambridge University Press, **2010**.
35. P. Kékicheff, B.W. Ninham, *Europhys. Lett.* **1990**, *12*, 471.
36. T. Nylander, P. Kékicheff, B.W. Ninham, *J. Coll. Interface Sci.* **1994**, *164*, 136.
37. R.M. Pashley, B.W. Ninham, *J. Phys. Chem.* **1987**, *91*, 2902.
38. D.J. Mitchell, B.W. Ninham, B.A. Pailthorpe, *J. Chem. Soc. Faraday Trans. II* **1978**, *74*, 1116.
39. R.G. Horn, J.N. Israelachvili, *J. Chem. Phys.* **1981**, *75*, 1400.
40. R.G. Horn, B.W. Ninham, in *Micellar solutions and microemulsions*, (Eds.: S.H. Chen, A. Rajagopalan), Springer-Verlag Publ., Berlin, **1990**, pp. 81–99.
41. P. Attard, D.J. Mitchell, B.W. Ninham, *Biophys. J.* **1988**, *53*, 457.
42. J.C. Maxwell in *Encyclopeadia Britannica*, 11th ed., **1911**.
43. S. Marcelja, N. Radic, *Chem. Phys. Lett.* **1976**, *42*, 129.
44. B.W. Ninham, R.M Pashley, P. Lo Nostro, *Curr. Opin. Colloid Interface Sci.* **2016**, *27*, 25.
45. B.V. Deryaguin, I.I. Abrikossova, E.M. Lifshitz, *Quart. Rev. Chem. Soc.* **1956**, *10*, 195.
46. B.V. Deryaguin, I.I. Abrikossova, *J. Exp. Theor. Phys.* **1956**, *30*, 993.
47. I.E. Dzyaloshinski, E.M. Lifshitz, I.P. Pitaevski, *Adv. Phys.* **1961**, *10*, 165.
48. B.W. Ninham, V.A. Parsegian, *J. Chem. Phys.* **1970**, *52*, 4578.
49. B.W. Ninham, V.A. Parsegian, *Biophys. J.* **1970**, *10*, 646.
50. V.A. Parsegian, *Van der Waals forces. A handbook for chemists, biologists, engineers*, Cambridge University Press, **2005**.
51. B. Davies, B.W. Ninham, P. Richmond, *J. Chem. Phys.* **1973**, *58*, 744.
52. B.W. Ninham, J. Daicic, *Phys. Rev. A* **1998**, *57*, 1870.
53. H. Wennerström, J. Daicic, B.W. Ninham, *Phys. Rev. A* **1998**, *60*, 2581.
54. M. Boström, J.J. Longdell, D.J. Mitchell, B.W. Ninham, *Eur. Phys. J. D* **2003**, *22*, 47.
55. B.W. Ninham, M. Boström, *Phys. Rev. A* **2003**, *67*, 030701.
56. B.W. Ninham, M. Boström, C. Persson, I. Brevik, S.Y. Buhmann, B.E. Sernelius, *Eur. Phys. J. D* **2003**, *68*, 1.
57. R.A. Robinson, R.H. Stokes, *Electrolyte Solutions*, Butterworths, London, **1959**.
58. P. Lo Nostro, B.W. Ninham, Chem. Rev. 2012, 112, 2286 and references therein.
59. W. Kunz, J. Henle, B.W. Ninham, *Curr. Opin. Colloid Interface Sci.* **2004**, *9*, 19.

60. A. Salis, M.C. Pinna, D. Bilaničová, P. Lo Nostro, B.W. Ninham, *J. Phys. Chem. B* **2006**, *110*, 2949.
61. L. Carroll, *Alice's Adventures in Wonderland*, Macmillan Publ., London, **1865**.
62. a: H.-K. Kim, E. Tuite, B. Nordén, B.W. Ninham, *Eur. Phys. J.* **2001**, *4*, 411. b: B.W. Ninham, *Progr. Coll. Polymer Sci.* **2006**, *133*, 65.
63. P. Lo Nostro, B. W. Ninham Eds., *Curr. Opin. Colloid Interface Sci.* **2016**, *23*, A1-A6, 1-126.
64. E. Leontidis, *Langmuir* **2017**, in press.
65. T. Duignan, D.F. Parsons, B.W. Ninham, *J. Phys. Chem. B* **2014**, *118*, 3122.
66. T. Duignan, D.F. Parsons, B.W. Ninham, *Chem. Phys. Lett.* **2014**, *608*, 55.
67. T. Duignan, D.F. Parsons, B.W. Ninham, *J. Phys. Chem. B* **2014**, *118*, 8700.
68. T. Duignan, D.F. Parsons, B.W. Ninham, *Phys. Chem. Chem. Phys.* **2014**, *16*, 22014.
69. T. Duignan, D.F. Parsons, B.W. Ninham, *Chem. Phys. Lett.* **2015**, *635*, 1.
70. V.V. Yaminsky, B.W. Ninham, *Langmuir* **1996**, *12*, 4969.
71. V.V. Yaminsky, B.W. Ninham, *Langmuir* **1993**, *9*, 3618.
72. V.V. Yaminsky, B.W. Ninham , *Adv. Coll. Interface Sci.* **1999**, *83*, 227.
73. V.V. Yaminsky, S. Ohnishi, B.W. Ninham, in *Handbook of Surfaces and Interfaces of Materials*, vol. 4., Chapter 3, pp. 131-227. Academic Press, Cambridge, **2001**.
74. R.M. Pashley, *J. Phys. Chem. B* **2003**, *107*, 1714.
75. B.W. Ninham, *Adv. Coll. Interface Sci.* **1982**, *16*, 3.
76. V.S.J. Craig, B.W. Ninham, R.M. Pashley, *Nature* **1993**, *364*, 317.
77. V.S.J. Craig, B.W. Ninham, R.M. Pashley, *J. Phys. Chem.* **1993**, *97*, 10192.
78. C.L. Henry, V.S.J. Craig, *Langmuir* **2008**, *24*, 7979.
79. G. Liu, Y. Hou, G. Zhang, V.S.J. Craig, *Langmuir* **2009**, *25*, 10495.
80. J. Morris, *Farewell the Trumpets*, vol. 111 of the Pax Britannica Trilogy, Penguin, London, **1979**.
81. A. Garrido, R.M. Pashley, B.W. Ninham, *Colloids Surf. B Biointerfaces* **2016**, *151*, 1.

Substantia
An International Journal of the History of Chemistry

Firenze University Press
www.fupress.com/substantia

OPEN ACCESS

Citation: C.L. Khetrapal, K.V. Ramanathan (2017) Title. *Substantia* 1(1): 25-36. doi: 10.13128/Substantia-11

Data Availability Statement: All relevant data are within the paper and its Supporting Information files.

Competing Interests: The authors declare no competing interests.

Feature Article

Developments of NMR - From Molecules to Human Behaviour and Beyond

C.L. Khetrapal[1]* and K.V. Ramanathan[2]

[1]*Centre for Biomedical Research, Sanjay Gandhi Post Graduate Institute of Medical Sciences Campus, Raebareli Road, Lucknow 226 014, India*
[2]*NMR Research Centre, Indian Institute of Science, Bangalore 560012, India*
Corresponding author. E-mail: clkhetrapal@hotmail.com

Abstract. NMR has made rapid progress in the last more than seven decades after its discovery. This article reviews the development of this field over the years with emphasis on some of the recent developments with interesting consequences for the study of mental health and human behaviour.

Keywords. NMR, MRI, fMRI, Molecular structure, Brain imaging

INTRODUCTION

Nuclear Magnetic Resonance (NMR) is perhaps the only field which has produced seven Nobel Laureates till date in all the disciplines of science in which the prize is given, in a short span of about seventy years from the discovery of the phenomenon. Over this period, it has thus established itself as a full-fledged interdisciplinary science rather than being just an analytical technique. Its utility has been fully exploited by physicists, chemists, biologists, clinicians, agriculturists, industrialists, computer scientists, psychologists and social scientists. The developments of the field up to 1996 are described in the eight-volume Encyclopaedia of NMR[1] published in the year 1996 to commemorate 50 years of the discovery of the phenomenon. The growth of the field has been so voluminous that a supplementary 9th volume of the encyclopaedia had to be published within 5 years of the initial publication.[2] This presentation gives a brief description of the field over these years from the perspective of the authors. The articles published by the authors earlier have been liberally used. Developments of the field 'at a glance' are presented in Fig.1.

NMR IN BULK MATERIAL

Purcell in MIT/Harvard and Bloch in Stanford became interested in experiments leading to accurate measurements of magnetic fields/magnetic

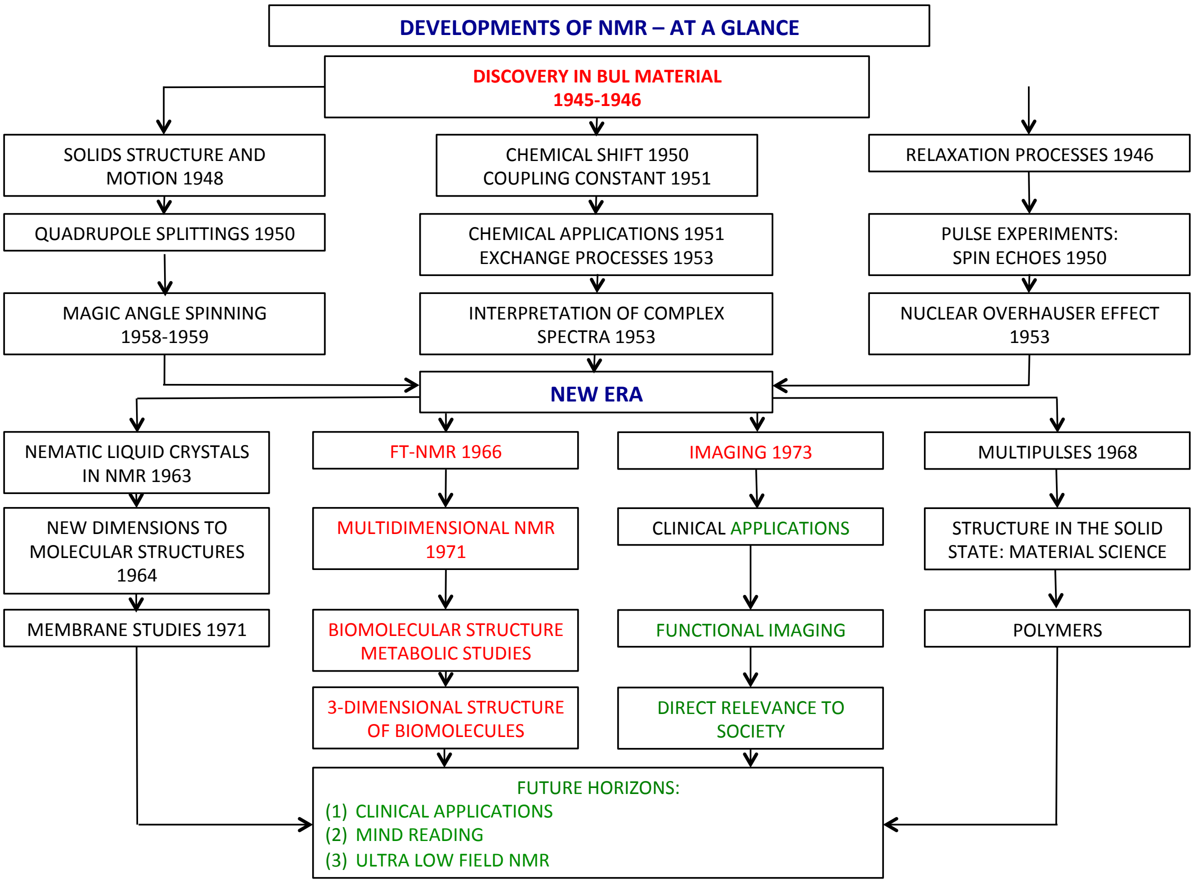

Figure 1. Developments of NMR at a glance.

moments. Both the groups succeeded and NMR in Bulk materials was born in 1945 and the results published in the same issue of the Physical Review.[3,4] Both the scientists got the Nobel Prize in Physics in 1952. NMR in India started in 1951 with the first report of NMR experiments carried out in flowing liquids by Suryan[5] who demonstrated that the arrival of fresh polarized sample at the RF coil decreases saturation and results in a more intense NMR signal. He was able to estimate Spin – lattice relaxation time (T_1) from the flow rate and the geometrical parameters of the system.

NMR IN CHEMISTRY

Proton Chemical Shifts: Dramatic observation[6] of separate lines for non-equivalent protons in the same molecule, by Arnold, Dharmatti and Packard in 1951 set the stage for most of the applications of NMR in various branches of sciences dealing with structural studies. The first molecule to be studied was acetic acid and then ethyl alcohol (Fig. 2). This led to the discovery of 'Chemical Shifts' in protons and it formed the basis of most of the applications of NMR.

Indirect Spin-Spin Couplings: This is another parameter which is of great significance in structural studies.

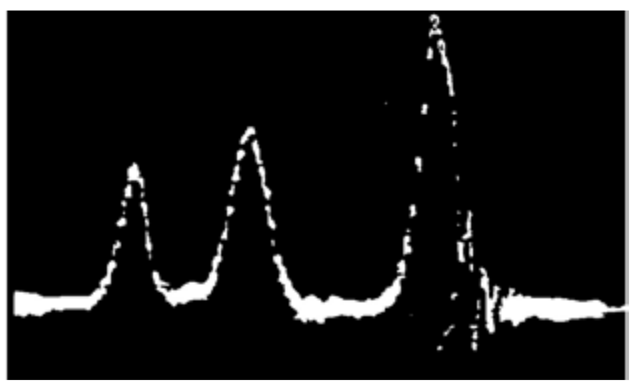

Figure 2. First reported proton NMR spectrum 1 spectrum of ethyl alcohol. Reprinted from Ref. 6, with the permission of AIP Publishing.

Unlike Chemical Shifts, it is field-independent. It is difficult to establish unequivocally the real discoverer of Spin-spin Couplings; at least the following three groups can be considered independently responsible for its observation.

1. Arnold, Dharmatti and Packard did get the indication of some fine structure as line-distortion particularly in the methyl peak in their original spectrum of ethyl alcohol (Fig. 2) but this distortion went unnoticed.
2. Gutowsky and Hoffman observed 2 lines of comparable intensity in the ^{19}F spectrum of PF_3.[7]
3. Hahn and Maxwell observed the same effect in entirely different manner – as 'slow-beats' in the spin-echo envelope for non-equivalent protons[8].

In structural studies, the spin-spin couplings have been extensively employed to estimate the dihedral angles using Karplus equations.[9] The couplings for protons on adjacent saturated carbons ($J_{Vicinal}$) can be employed to estimate the dihedral angles within a precision of a few degrees using the following empirical equations:

$(J_{Vicinal})$ = 8.5 cos2 j-0.28 Hz (for 0°<j<90°)
$(J_{Vicinal})$ = 9.5 cos2 j-0.28 Hz (for 90°<j<180°)

NEW ERA IN NMR

The following discoveries changed the destiny of NMR and the field entered a new era.

1. Fourier Transform NMR (1965-66)
2. Two-dimensional NMR (1971-72)
3. Magnetic Resonance Imaging (1973-74)

Fourier Transform NMR: The development of Fourier transform methods[10] represents a turning point in the history of NMR. In an NMR experiment at a particular magnetic field strength (B_o), the angular frequency of precession (ω_o) of the nuclei is given by the Larmor equation $\omega_o = \gamma B_o$ where the proportionality constant γ is the magnetogyric ratio (ratio of the magnetic moment to the angular momentum). In a conventional continuous wave NMR experiment, the resonance condition is arrived at either by keeping the frequency of irradiation fixed while varying the magnetic field fixed or vice versa. Such slow scan experiments were of limited utility especially for studies of solutions with low concentrations of the nuclei of interest, nuclei with low natural abundance, larger molecules, fast dynamic processes and so on. Even as efforts to improve the sensitivity of the NMR experiment were in progress, to speed up the experiment Ernst and Anderson[10] suggested the use of the Fourier transform method. Herein, a short burst of radiofrequency (r.f.) excitation, called a pulse of r.f., excites nuclear spin resonances over a broad band of frequencies. The precession of nuclear spins having resonance frequencies falling in this band-width generates the NMR signal in the time domain. Subsequent Fourier transform of the signal provides the frequency domain NMR spectrum. This innovation changed NMR signal acquisition from frequency-domain to time-domain and thus on the one-hand made the NMR experiment faster by several-folds. On the other-hand, it opened up the flood-gates for innovation in NMR and the possibility of carrying out a whole lot of new experiments. Thus a new era of research and applications of NMR was born. Though difficult to publish the results at the time, the experiment formed the basis of the 1991 Nobel Prize in Chemistry to Richard Ernst.

Two –dimensional NMR: The concept of two-dimensional (2D) Fourier transform NMR was given by the Belgian Physicist J. Jeener who presented his results at Ampere International Summer School, in 1971.[11] He proposed a simple sequence of two 90° pulses separated by a time period $t_1$which is incremented between the experiments. This is followed by double Fourier transformation of the signal acquired after the second pulse. A spectrum is thus obtained which has spread in two frequency dimensions and for homonuclear experiments has diagonal as well as cross peaks. The cross peaks carry important information as they result due to magnetization transferred from one nuclear spin species to another that has an indirect spin-spin coupling to it. The results were never published formally. The school was attended by Thomas Bauman of Richard Ernst's group. When briefed by Baumann, Ernst was very excited but still did not pursue the idea for quite some time since firstly he considered it as "Jeener's Property" and secondly he did not have a computer adequate to handle the two-dimensional data storage and processing. Eventually, he applied the concept to a different area namely magnetic resonance imaging (vide below) initially and later on published a series of papers that formed the foundation of two-dimensional NMR as a methodology.[12]

Magnetic Resonance Imaging (MRI): Paul Lauterbur conceived the idea of using magnetic field gradients to obtain 2 and 3 dimensional spatial information about the distribution of magnetic nuclei in a sample placed inside NMR coil. He thus created the picture of the object by NMR and called the technique as Zeugmatography. He published the work in Nature[13] in 1973 and also submitted it as a poster presentation at the triennial conference of the International Society of Magnetic Resonance held in Bombay in 1974. The presentation was however, converted into an invited plenary talk by the organizers.

MRI is based on the principles of NMR but instead of revealing structures of molecules, MRI reveals the structure of an object, by mapping the distribution of a molecule (usually water) in the object. MRI's most successful and well known application is in the field of medicine where it is used to image organs of a human body in microscopic details. In human MRI, a person lies inside a large hollow magnet. With a combination of magnetic field gradients and radio waves, signals are produced. A computer converts these signals into a series of 2-D images. The images can then be combined to create high-resolution 3-D pictures of the subject. Advancements in the area such as Fourier imaging (by Kumar et al.[14]) and Echo Planar Imaging (EPI) introduced by Mansfield[15] contributed to a rapid expansion of the use of the technique in a number of contexts.

Nuclear Magnetic Resonance and Magnetic Resonance Imaging and Spectroscopy have developed into valuable diagnostic tools during the past three decades. The Radiologists and the Clinicians have literally captured the technique during this period like what the chemists did about a half a century back. Reasons for such a widespread growth are built into the origin of the phenomenon, which involves the use of low energy electromagnetic radiation. The effects produced are, however, large and easily detectable with the present day technology, leading to details of molecular structures obtained at the atomic level.

APPLICATIONS OF NMR AND MRI

NMR is being used in a variety of areas. The range of application of NMR is illustrated in Fig.3. Leaving out

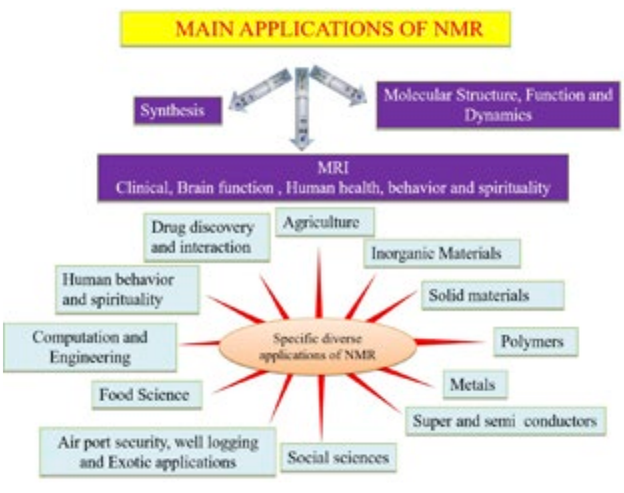

Figure 3. Major applications of NMR in different areas.

some of the well known applications of NMR in Chemistry, in Bio-molecular structure determination and in Material Science, we highlight here applications in some of the other areas.

NMR APPLICATION IN AGRICULTURE

Hydration in food stuffs: It is based on the fact that water molecules in many such products are more mobile than the protons in the host matrix. The proton spectra thus consist of sharp signals superimposed on broad background.[16]

The state of absorbed water: It has been investigated in meat, seeds, dairy products, and vegetables.[17]

The effect of storage: Significant differences in the free and bound water on storage have been reported on potatoes, garlic and apples.[18]

Rapid distinction between oil and water in agricultural products: NMR has been employed in rapid distinction of oil and water and dedicated instruments manufactured for such purposes. The instrument manufacturers with publicity such as "…. Accurate moisture contents in SECONDS…. Not in hours" became multi-billionaires.[19]

Oil build-up as a function of time after flowering of the seeds: NMR has been used to examine the quality of the oil as a function of maturity of the seeds as well as the determination of percentages of individual saturated and unsaturated fatty acids in intact seeds .[20]

Total oil content in individual seeds: NMR has found extensive utility for selecting the best seeds for plant breeding. Such a fast and non-destructive method provides a means to increase the average oil content of corn 2.25 times when compared with traditional selection methods resulting in gains over five generations that would have otherwise taken 20-30 generations.[21]

Spatial distribution of water and oil in intact seeds: The spatial distribution of oil and water in intact groundnut and sunflower seeds have been obtained.[22] In the immature commercial groundnut seeds complementary oil and water distributions have been observed (Fig.4). The two images exhibit distinctly different features indicative of different intracellular environments in the two cotyledons – oils is present predominantly in one the cotyledons and water in the other. In this immature groundnut seed, it has been interpreted as the incomplete oil-build up with the result that the oil and water within the seed are preferentially localized in complementary manner. The water soluble sugars yet to be converted to storage lipids are confined in one of the cotyledons. A physiological disorder may be responsible for this differential micro environment in the two cotyledons.

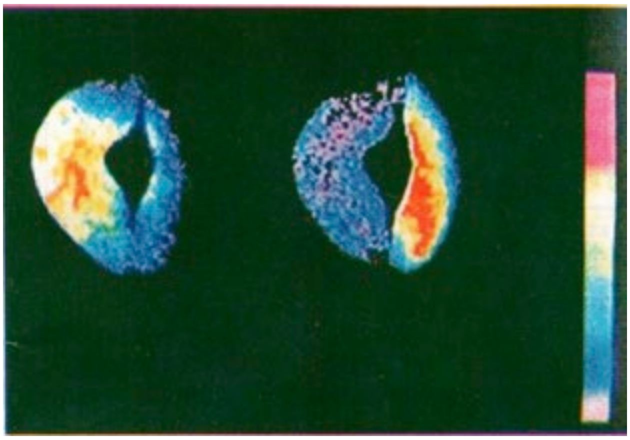

Figure 4. [1]H NMR images of transverse section of a commercial variety of ground nut seed. Left: Water image and right: Oil image. The extreme right shows the scale with the concentration increasing from top to bottom. PERMISSION IN ATTESA

SOME CLINICAL PROBLEMS INVESTIGATED USING NMR

The objective has been to identify specific markers for the quick and non-invasive diagnosis of the diseases and to monitor the treatment. Several problems related to human bile, liver graft dysfunction, Fulminant Hepatic Failure, bacterial urinary tract infection, mal-absorption syndrome, obstructive jaundice, breast disorders, congenital heart disorders, benign and malignant gallbladders, alkaptonuria, and mitochondrial diseases have been reported.[23-33] Results on three typical studies are briefly mentioned below. For details, one may refer to the cited literature.

Human Bile: Human bile being a complex mixture of numerous metabolites provides highly overlapping and complex spectra requiring the need for the highest field NMR especially for quantification of the individual components. A typical 800 MHz is reproduced in Fig.5. The

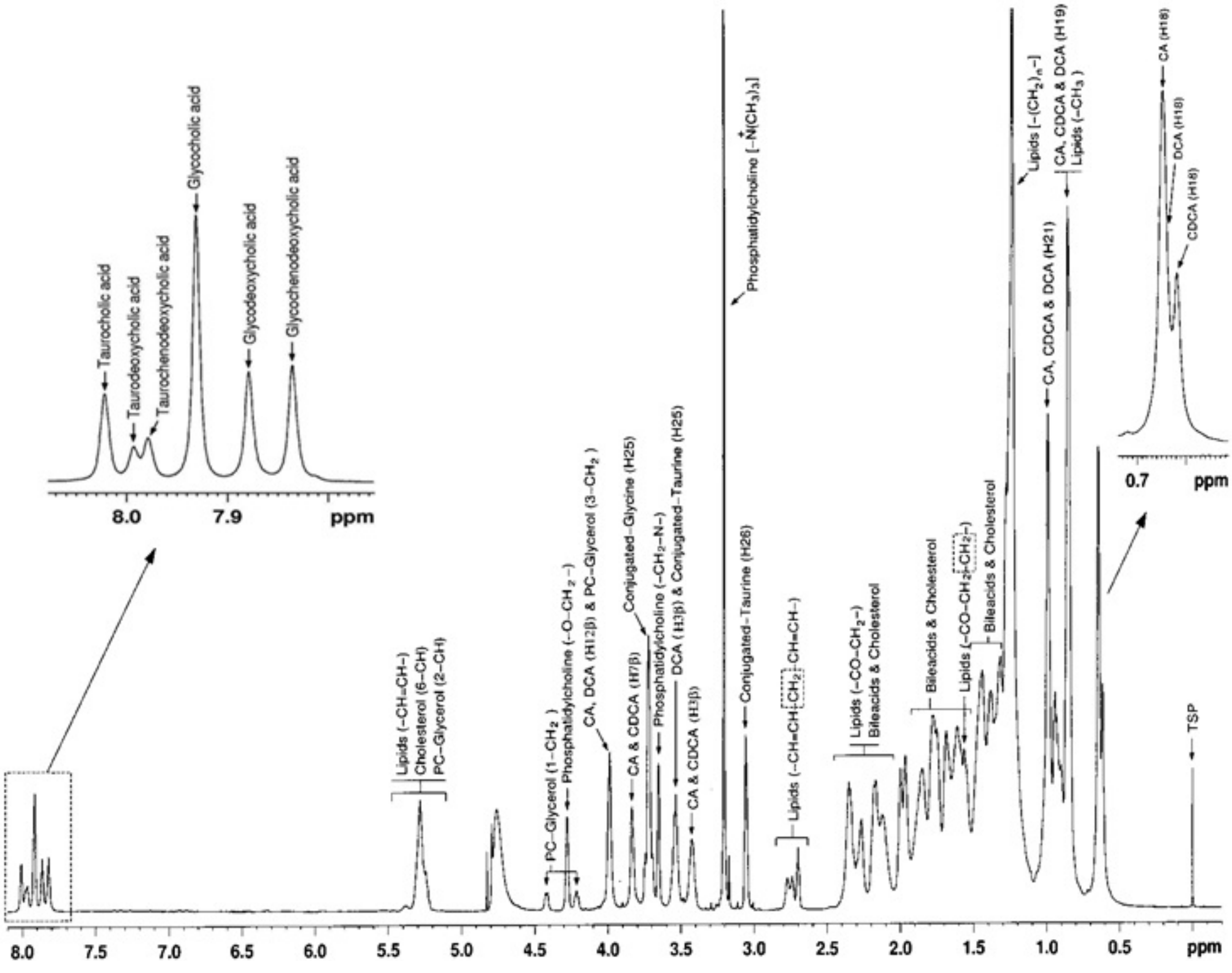

Figure 5. [1]H NMR spectrum of human bile at 800 MHz. Reproduced from Ref. 26 with permission of Springer.

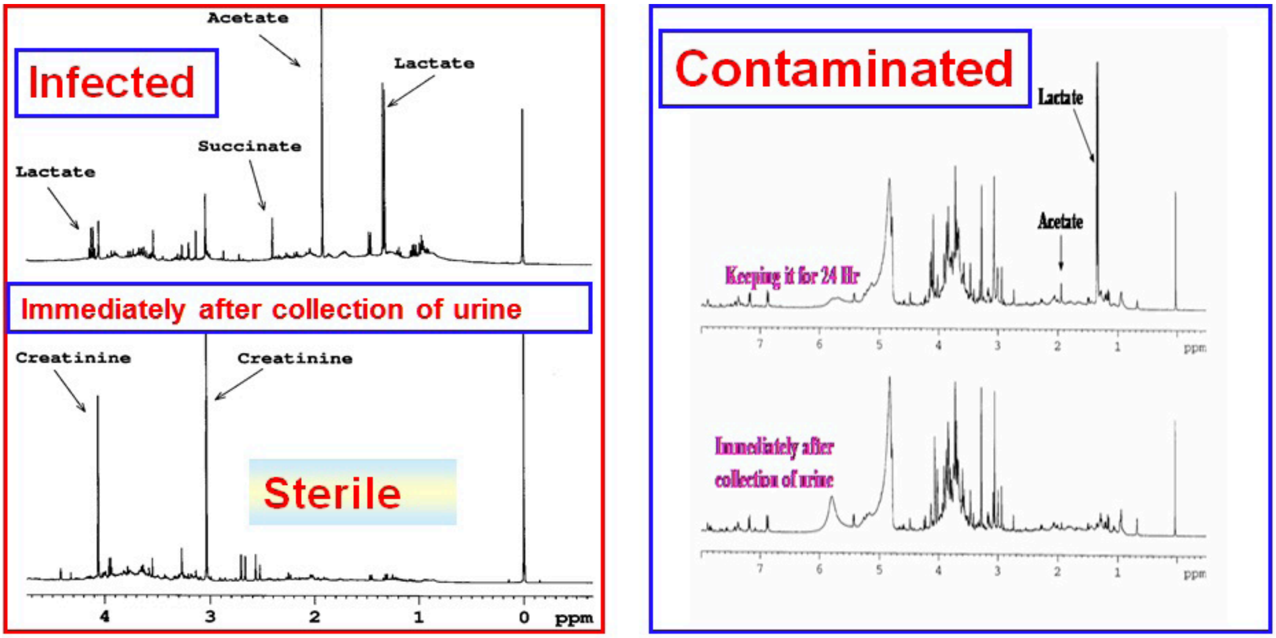

Figure 6. Distinction between real bacterial infection and contamination. Reproduced from Ref. 31 with permission from John Wiley & Sons, Inc.

assignments of the resonances due to various metabolites are shown in the Figure. NMR in fact, provides a novel, unique single step method to identify and quantify such a large number of metabolites present in a mixture. Once this was achieved several problems related to Human Bile have been investigated.[23-27]

Assessment of liver graft dysfunction: A study of patients who underwent liver transplant was carried out. It was noted that some of the patients died before they were discharged from the hospital though surgically all operations appeared satisfactory. In this study, the use of NMR has been made to find out the reason for the death. Studies on serum and urine samples of patients before liver transplantation and every 24 hours after the liver transplantation, till the time they were discharged/alive, were taken. High levels of glutamine in both serum and urine and concomitant reduced urea levels in urine were found to be evidence of impairment in urea cycles and compatible with abnormal graft function. Increased glutamine levels lead to brain death, if untreated. This is medically useful information since it gives prior information on what is going to happen and one may take corrective measures in advance.[28]

Prediction of therapeutic outcome in patients with Fulminant Hepatic Failure: Fulminant Hepatic Failures (FHF) are associated with severe liver injuries leading to impairment of hepatic function followed by hepatic encephalopathy within eight weeks of the onset of the illness. The mortality rate is as high as 80%. Liver transplant for FHF patient appears to be the only effective answer to this. Since the survival rates are low, rapid diagnosis is necessary to identify patients for transplantation. Until today, there is no means to predict the spontaneous recovery or non-recovery for such patients. ^{1}H NMR to quickly identify molecular markers such as glutamine in serum and urine and urea in urine promise a potential in quickly deciding on liver transplantation. NMR spectroscopy has been used to determine the molecular markers in serum and urine to distinguish between those recovered patients and those who did not. Glutamine in serum and urine glutamine/Creatinine ratios were higher in non-surviving patients compared with surviving patients. On the other hand, no significant differences were found in conventionally employed clinical parameters such as serum alanyl-amino transferase, aspartyl-aminotransferase and bilirubin.[29]

Bacterial urinary tract infection: Qualitative and quantitative estimations of metabolites produced as a result of bacterial infection in the urinary tract have been reported. Absolute concentrations of the metabolites provide the severity of the infection and, are likely to be very valuable in patients on antibiotic therapy with negative urine cultures.Major bacteria in UTI are E.coli, K. penumoniae, P. aeruginods and P. mirabilis. They uniquely metabolize lactose to lactate, glycerol to 1, 3- propanediol, nicotinic acid to 6 hydroxy nicotinic and methionine to 4-methyl-oxobutyric acid, respectively.[30-33] These properties have been exploited to identify and quantify specific bacteria responsible for the infections. The NMR technique has also been employed to distinguish between the real infection and contamination as shown in Fig.6. This is in fact one of the major problems in the precise diagnosis of UTI and NMR provides a solution.

EXAMPLES OF APPLICATIONS OF MRI

MRI is especially valuable for detailed imaging of the brain and the spinal cord. Nearly all brain disorders lead to alterations in water content, which is reflected in the MRI picture. A difference in water content of less than a percent is enough to detect a pathological change. In multiple sclerosis, examination with MRI is superior for diagnosis and follow-up of the disease.[34] The symptoms associated with multiple sclerosis are caused by local inflammation in the brain and the spinal cord. With MRI, it is possible to see the of the inflammation in the nervous system and how intense it is, and also how it is influenced by treatment. MRI is an important preoperative, improved diagnostic and reduced suffering tool for patients.

MRI has been used to reveal the effects of YOGA on brain. The results show that concentration of Gamma Amino Butyric Acid (GABA), increases by performing certain YOGA exercises.[35] It implies that YOGA, and perhaps some other forms of exercise should be utilized as a complementary treatment for depression and anxiety disorders. The results have clear public health utility. Yoga should be compared with other forms of exercise to determine whether or not it is the nature of YOGA postures that results in raised GABA levels, or it is an effect of any exercise.

FUNCTIONAL MRI (fMRI)

Functional MRI is based on the fact that oxyhemoglobin is diamagnetic but when oxygen is consumed in metabolism, the haemoglobin becomes paramagnetic. This permits visualization of the regions of the brain in which metabolic activity occurs in response to an external stimulus.[36] It can characterize functions while brain processes thoughts, sensations, memories, and motor commands. Functional MRI makes it possible for neurologists to detect early signs of Alzheimer's disease and other disorders, to evaluate drug treatments, and pinpoint tissue housing critical abilities like speech before venturing into a patient's brain with a scalpel. Such results provide a basis for designing new intervention techniques.

ILLUSTRATIVE APPLICATIONS OF fMRI

Considering the importance of the subject and its direct societal relevance, numerous interdisciplinary groups and institutions in this field have been established all over the world during the past few years. Basic and social scientists, psychologists and medical doctors are now joining hands to exploit the interdisciplinary nature of the field in order to diagnose and understand not only the molecular structure and the diseases in human beings but also to understand the metabolic and structural changes in them. Some illustrative applications are briefly described below:

The dyslexics and non-dyslexics: Numerous groups all over the world are involved in investigating biological bases of learning and learning disorders essentially because of great societal need. It has been reported that the deficiencies in functional brain organization underlying dyslexia can be reversed after sufficiently intense intervention lasting as little as 2 months. The reading difficulties in many children represent a variation of normal development that can be altered by intensive intervention.[37] Such investigations are of great importance.Immediate creation of an interdisciplinary school on child psychiatry, social science and fMRI is the need of the hour in societal interest.

Alcoholism in young adult, female alcoholics: Specific areas of the brain impaired by years of heavy drinking have been identified in young adult women. Previously, investigators have relied on thinking and memory tests to gauge brain dysfunction in alcoholics, but no one had identified the actual brain sites where impairment occurs in young adults. Even young and physically healthy individuals risk damaging their brains through chronic, heavy use of alcohol.[38]

Pretty female faces: They trigger activity in men's brains. A beautiful woman's face is like chocolate, cash or cocaine to a young man's brain.[39] When men in the study were shown pictures of various faces, only the female faces deemed beautiful triggered activity in brain regions previously associated with food, drugs and money.

Sex differences in mental rotation and spatial working memory: Behavioural and neural sex differences in sex-specific spatial abilities have been investigated.[40] Males typically surpass females on tasks dealing with mental rotation and spatial navigation, while females tend to excel males on tasks dealing with object location, relational object location memory or spatial working memory.

Crime and lie detection: During the past few years, the data on crime detection by NMR has become voluminous. Several hundred thousand entries are found in 'Google search' under this category. Pathological liars have been found to have brain abnormalities. Brain deformities have been observed in people who habitually lie, cheat and manipulate. The brain area just behind the forehead exhibits structural difference among pathological liars[41] and their white matter content is more. The finding could be used in making clinical diagnosis and may find applications in daily life, criminal justice system and the business world. The fMRI is bound to transform the societal values system, the security and the judicial processes. By mapping the neural circuit behind deception, fMRI will provide a new kind of 'lie detector' that is more probing and accurate than the polygraph – the standard lie-detection tool being employed for nearly a century. fMRI may change the entire judicial system. It will be useful in high-profile crimes like terrorism. It may appear that fMRI is expensive, bulky, noisy and time consuming for such routine applications. However, if one thinks of the cost of judicial process taking years to discover the truth or the price of missing a terrorist, nations can certainly afford it as far as the present costs are concerned. With more advances in technology, many of the limitations may be overcome as discussed in the subsequent sections.

Enhancement of trust among humans: Intranasal administration of oxytocin, a neuropeptide causes a substantial increase in trust among humans.[42] Oxytocin specifically affects an individual's willingness to accept social risks arising through interpersonal interactions. An fMRI study may throw light on Biological basis and provide scientific evidence on the role of oxytocin or human behaviour.Most charitable people show enhanced activity in the top and back of the brain – an area normally linked to processing incoming information, sorting out social relationships and controlling movements! Understanding the function of this region may give clues on the origin of social behavior.[43]

*Science behind health benefits of YOGA and meditation***:** Though it is well known that YOGA and MEDITATION can reduce stress and cure many diseases, recent times have seen the emergence of scientific evidence to demonstrate these beneficial effects using modern scientific technologies such as fMRI. These results are drawing worldwide attention. Neuro-imaging and genomics technology have been employed to measure physiological changes in greater detail. Some typical studies are outlined below:

fMRI study of neuro-cognitive effect of sound "OM" on human Brain: The sound "OM" is of paramount importance and is supposed to relax human beings physically, mentally and emotionally. The fMRI results delineate the exact brain area involved in response to OM sound and reveal that listening OM recruits areas of both left and right hemispheres including left prefrontal cortex. This corresponds to "OM" as a pleasant melodic sound which increases attention and emotional quotient and creates intuitive feeling towards spirituality (Fig. 7). Such studies provide a unique idea to employ modern scientific technologies to demonstrate whether YOGA pertains to a

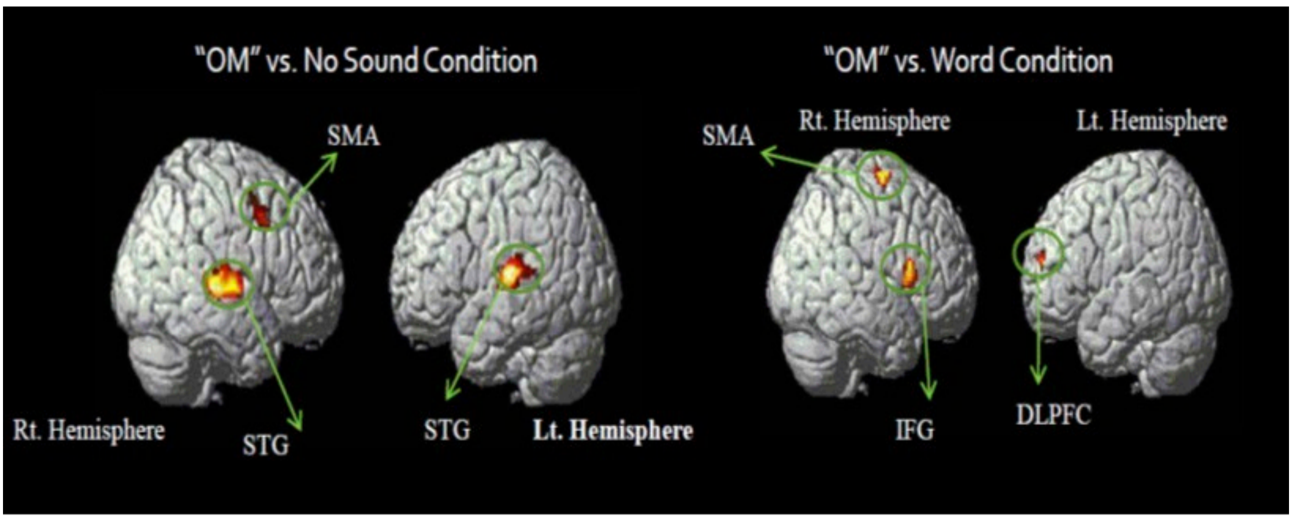

Figure 7. Neuro-cognitive effect of "OM" sound. (Supplementary Motor Area (SMA):Involved in MotorcoordinationSuperior temporal gyrus (STG): Auditory perceptionInferior frontal gyrus (IFG): Perception of pleasant soundDorso-lateral pre-frontal cortex (DLPC): involved in monitoring of attention process.)

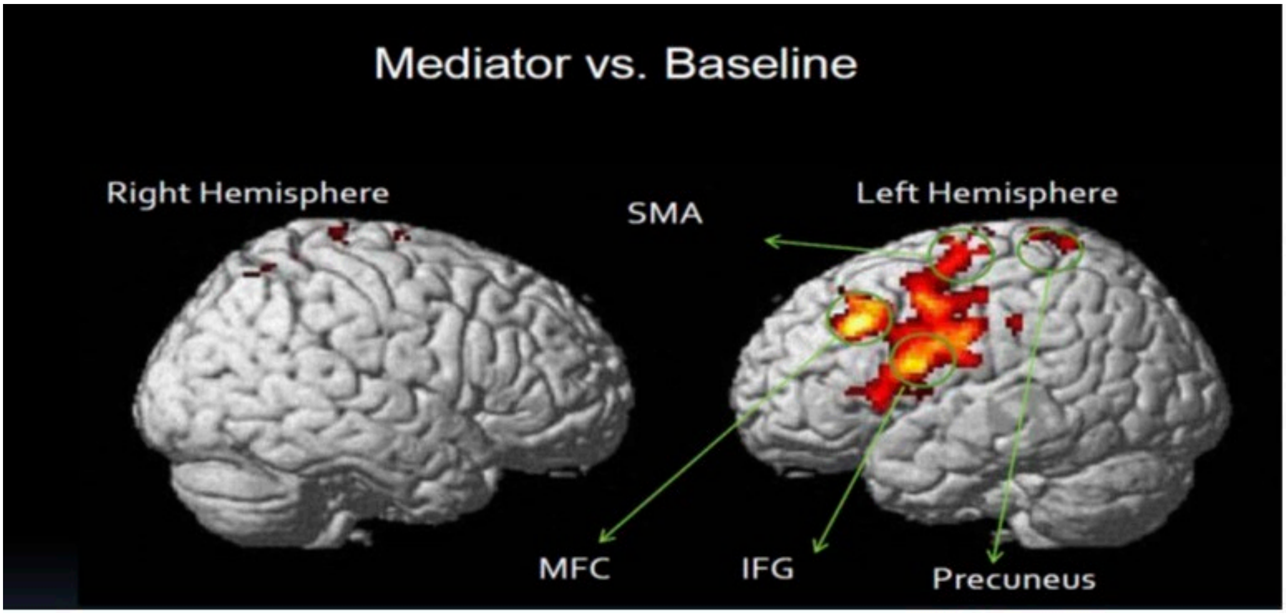

Figure 8. Effect of SOHAM Meditation on the brain. Middle frontal cortex (MFC): This implies regulation of attention, which in the case of meditation is directed at the subjects own mental and bodily state.Left Inferior frontal gyrus (IFG): involved in the cognitive aspects of emotional processing , such as paying attention to emotion or the identification of emotion.Precuneus: involved in the execution or preparation of spatially guided behaviors. Reprinted from Ref. 45, Copyright 2013, with permission from Elsevier.

particular faith or religion or it is universal. It may go a long way to establish religious harmony and world peace if such an idea is pursued. The observation of the international YOGA day has generated hot debates particularly in India on whether YOGA pertains to a particular religion or faith. The use of modern scientific technologies such as functional MRI and other technologies can throw light on the issue in an unbiased manner and will go a long way to establish world peace and happiness and religious harmony. The functional MRI studies reported above delineate the exact brain areas involved in response to OM sound and reveal that listening to OM sound recruits areas in the brain involved in increasing attention and emotional quotient and creates intuitive feelings of happiness.[44-47] A question arises whether such studies can result in providing a scientific approach to achieve religious harmony and world peace? It would be interesting to see whether 'OM' is faith specific or it affects similarly to all irrespective of the religion or faith. One could even study the effects of "Mantras" preached by different religions. If all have similar effects, it will establish scientifically for the first time that all religions preach the same thing and if the effects are specific only to OM, then it will establish that this sound is universal and is independent of the religion. If studies of the Mantras preached by different religions demonstrate changes in different areas of the brain but they too have positive health benefits it will throw a challenge to scientists to discover a "universal Mantra" which takes into accounts positive aspects of all faiths. The results will establish a correlation between spirituality and science.

"SOHAM" Meditation: The parts of the brain that show activity during meditation in general in fMRI is illustrated in Fig. 8. In "SOHAM" meditation one merely observes the breathing process even as one repeats the word "SOHAM" in mind, synchronising it with breath. Therefore the process is when one inhales, one mentally repeats the sound "SO" and while exhaling the sound "HAM" is repeated. As one breathes in and out the sound "SOHAM" is repeated. Grey Matter in the brain fills about 40 percent of the whole brain in humans and consumes 94 percent of oxygen. The senses of the body (speech, hearing, feelings, seeing and memory) and control of the muscles, are part of the grey matter's functions.

Differences in Grey Matter are observed between "SOHAM" meditators and non-meditators (Fig. 9). Three distinct regions show higher grey matter concentration in meditators .

*Positive attitude insures happiness***:** The power of positive attitude or perception, meditation, reciting and listening *mantras* etc in coping up of the various stresses and strains in human daily life is well known and is widely practiced. However, it may have better impact on common man's daily life if one can demonstrate this by a sci-

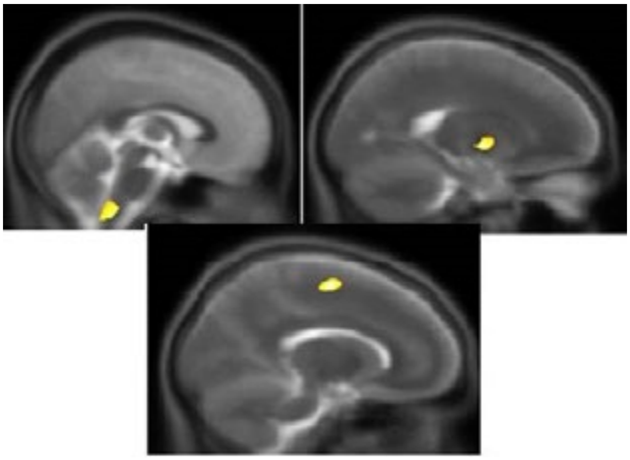

Figure 9. Grey Matter differences in "SOHAM" meditators and non-meditators: Three distinct regions show higher grey matter concentration in meditators. Left Image: Brain stem - Regulates breathing and anxiety level. Right Image:Ventral palladium- Regulates positive mood and motivation. Bottom Bottom:Motor area - Regulates motor aspects.

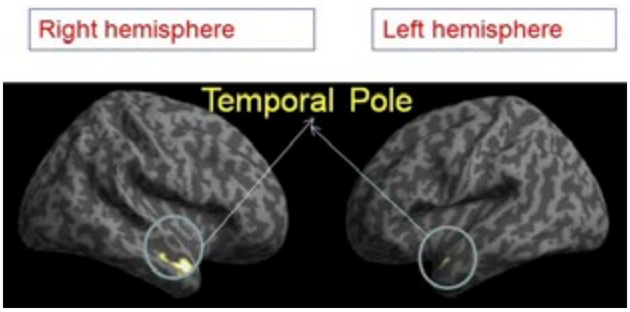

Figure 10. Influence of negation on Human Brain. Distinct neural regions for negative sentences: Temporal Pole: This region is associated with anxiety and depression.

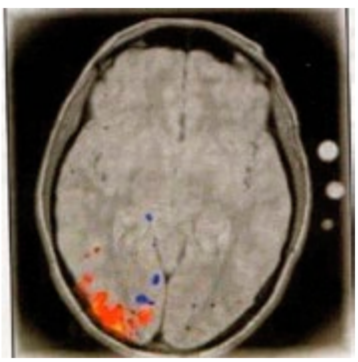

Figure 11. Brain activation (bright color) characterizing the functioning of anxious and depressed persons as they Process emotional information and respond to various types of positive and negative stimuli. Reproduced with permission of the Stanford Mood and Anxiety Disorder Laboratory.

entific evidence. A preliminary fMRI study *(Brain imaging and behavior, August 2012)* demonstrates that negativity is perceived by different brain regions compared to positive perception. The experiments decode specific regions in human brain involved in positive and negative perceptions. A crucial finding was the activation of the bilateral temporal pole for negative sentences (indicating sadness, anxiety and stress). No such effects were observed in affirmative sentences (Fig. 10). A study[48] on mentally depressed and anxious individuals also shows activation pattern similar to that in subjects with negative thoughts (Fig. 11).

RECENT ADVANCES IN NMR, MRI AND FMRI TECHNOLOGY

Nano particles and fMRI: The new generation of nanoscale calcium contrast agents being developed will have applications in understanding learning, memory, and behaviour and will allow functional fMRI to make transition from imaging gross properties of brain to a fine-tunes analysis based on information flow involving cells and circuits .[49]

A new low-cost, portable MRI technology: A novel laser-based MRI technique is being developed by the Alex Pines and his colleagues in Berkeley. It provides a viable alternative for MRI detection with substantially enhanced sensitivity and time resolution. It will result in the development of a low cost, compact, portable and battery-powered portable MRI technology and an on-line analytical instrument for monitoring chemical reactions and biological processes.[50]

NMR: *From K gm to Pico gm*: The quantity of the paraffin sample initially used by Purcell when he discovered NMR in bulk material was 1 K gm in weight and with developments or organic molecules possessing electronic properties analogous to those of Gallium Arsenide, it seems likely that NMR spectra of Pico gm quantities of Proteins and Nucleic acids could be recorded.[51]

NMR nanometer-scale device: NMR has received considerable attention in the context of quantum computation and information processing which require controlled coherent qubit operations. Towards achieving this goal, a self-contained NMR semiconductor device has been implemented that can control nuclear spins in a nanometre-scale region. High sensitivity at the microscopic level has been demonstrated for probing materials whose nuclei contain multiple spin levels and thus form the basis of a versatile multiple qubit device.[52]

NMR on a chip: If a Nanoscale gallium Arsenide structure is excited with an oscillating Magnetic Field, superposition of nuclear spin states can be created and detected electrically. Quantum computing could be the beneficiary.[51]

CONCLUSIONS

To the question "Is there an end in sight for the new exciting developments in NMR?", the answer is a simple "NO". If one just looks at the advances in technology and the possible applications outlined above, one may predict that the best is yet to come. If a young man wants to remain "young", here is an opportunity to enter the "young" field and get assured enjoyment and excitement for the rest of the life.

ACKNOWLEDGEMENT

K V Ramanathan would like to thank the Council of Scientific and Industrial Research, India for the grant of an Emeritus Scientist position to him. The authors would like to thank Prof. Anil Kumar for a careful reading of the manuscript and for his comments.

REFERENCES

1. E.D. Becker, C.L. Fisk, C.L. Khetrapal in *Encyclopaedia of Nuclear Magnetic Resonance*, Vol. 11, (Eds.-in-Chief: D.M. Grant, R.K. Harris), J. Wiley & Sons Publ., **1996**, chapter 11, pp. 168.
2. *Encyclopaedia of Nuclear Magnetic Resonance, Advances in NMR*, (Ed.s-in-Chief: D.M. Grant, R.K. Harris), Vol. 9, J. Wiley & Sons Publ., **2002**.
3. E.M. Purcell, H.C. Torrey, R.V. Pound, *Phys. Rev.* **1946**, *69*, 37.
4. F. Bloch, W.W. Hansen, M. Packard, *Phys. Rev.* **1946**, *69*, 127.
5. G. Suryan, *Proc. Ind. Acad. Sci.* **1951**, *A33*, 107.
6. J.T. Arnold, S.S. Dharmatti, M. Packard, *J. Chem. Phys.* **1951**, *19*, 507.
7. H.S. Gutowsky, C.J. Hoffman, *Phys. Rev.* **1950**, *80*, 110.
8. E.L. Hahn, D.E. Maxwell, *Phys. Rev.* **1950**, *85*, 143.
9. M. Karplus, *J. Chem. Phys.* **1959**, *30*, 11.
10. R.R. Ernst, W. A. Anderson, *Rev. Sci. Instrum.* **1966**, *37*, 93.
11. J. Jeener, in *NMR and More*, (Eds.: M. Goldman, M. Porneuf), Les Editions de Physique, Les Ulis, France, **1994**, p. 265 and J. Jeener, G. Alewaeters, *Prog. Nucl. Magn. Reson. Spectrosc.* **2016**, *94-95*, 75.
12. R.R. Ernst, G. Bodenhausen, A. Wokaun, *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*, Clarendon Press, **1990**.
13. P.C. Lauterbur, *Nature* **1973**, *242*, 190.
14. A. Kumar, D. Welti, R.R. Ernst, *J. Magn. Reson.* **1975**, *18*, 69.
15. P. Mansfield, *J. Phys. C Solid State Phys.* **1977**, *10*, L55.
16. T.M. Shaw, R.H. Elsken, *J. Chem. Phys.* **1950**, *18*, 1113.
17. W.L. Rollwitz, *Proc. Natl. Electron. Conf.* **1956**, *12*, 113.
18. B.S. Miller, M.S. Lee, J.W. Hughes, Y. Pomeranz, *Cereal Chem.* **1980**, *57*, 126.
19. W.L. Rollwitz, *A Nuclear Magnetic Resonance Moisture Meter*, Rep. Southwest Research Inst., San Antonio, TX, **1956**.
20. M.R. Lakshminarayana, A. Seetharam, K.V. Ramanathan, C. L. Khetrapal, *Curr. Sci.* **1980**, *49*, 308.
21. L.F. Bauman, T.F. Conway, S.A. Watson, *Science* **1963**, *139*, 498.
22. M.R. Lakshminarayana, S.S. Joshi, G.A. Nagana Gowda, C.L. Khetrapal, *J. Biosci.* **1992**, *17*, 87.
23. M. Srivatsava, J. Madhulika, Y. Jadegoud, Y.G.A. Nagana Gowda, A. Sharma, V.K. Kapoor, C.L. Khetrapal, *Anal. Lett.* **2005**, *38*, 2135.
24. O.B. Ijare, B.S. Somashekar, G.A. Nagana Gowda, A. Sharma, V.K. Kapoor, C.L. Khetrapal, *Magn. Reson. Med.* **2005**, *53*, 1441.
25. O.B. Ijare, B.S. Somashekar, Y. Jadegoud, G.A. Nagana Gowda, *Lipids* **2005**, *40*, 1031.
26. G.A. Nagana Gowda, B.S. Somashekar, O.B. Ijare, A. Sharma, V.K. Kapoor, C.L. Khetrapal, *Lipids* **2006**, *41*, 577.
27. G.A. Nagana Gowda, O.B. Ijare, B.S. Somashekar, A.Sharma, V.K. Kapoor, C.L. Khetrapal, *Lipids* **2006**, *41*, 591.
28. H.K. Singh, S.K. Yachha, R. Rajan, A. Gupta, G.A. Nagana Gowda, M. Bhandari, C. L. Khetrapal, *NMR Biomed.* **2003**, *16*, 185.
29. V.G. Saxena, A. Gupta, G.A.G. Nagana Gowda, R. Saxena, S. K. Yaccha, C.L. Khetrapal, *NMR Biomed.* **2006**, *19*, 521.
30. A. Gupta, M. Dwivedi, G.A. Nagana Gowda, A. Ayyagari, A. A. Mahdi, , M. Bhandari, C.L. Khetrapal, *NMR Biomed.* **2005**, *18*, 293.
31. A. Gupta, M. Dwivedi, G.A. Nagana Gowda, A.A. Mahdi, A. Jain, A. Ayyagari, R. Roy, M. Bhandari, C. L. Khetrapal, *NMR Biomed.* **2006**, *19*, 1055.
32. A. Gupta, M. Dwivedi, G.A. Nagana Gowda, A.A. Mahdi, A. Jain, A. Ayyagari, R. Roy, M. Bhandari, C.L. Khetrapal, *Proc. Intl. Soc. Mag. Reson. Med.* **2006**, 14^{th} meeting.

33. A. Gupta, M. Dwivedi, A. A. Mahdi, A. Jain, A. Ayyagari, R. Roy, C. L. Khetrapal, *Proc. Intl. Soc. Magn. Reson. Med.Sci. Meet.* **2007**, 15th meeting.
34. Y. Ge, *Am. J. Neuroradiol.* **2006**, *27*, 1165.
35. C. C. Streeter, T. H. Whitfield, L. Owen, T. Rein, S. K. Karri, A. Yakhkind, R. Perlmutter, A. Prescot, P. F. Renshaw, D. A. Ciraulo, J. E. Jensen, *J. Altern. Complement. Med.* **2010**, *16*, 1145.
36. S. Ogawa, T. M. Lee, A. R. Kay, D. W. Tank, *Proc. Natl. Acad. Sci. USA* **1990**, *87*, 9868.
37. P. G. Simos, J. M. Fletcher, E. Bergman, J. I. Breier, B. R. Foorman, E. M. Castillo, R. N. Davis, M. Fitzgerald, A. C. Papanicolaou, *Neurology* **2002**, *58*, 1203.
38. S. F. Tapert, G. G. Brown, S. S. Kindermann, E. H. Cheung, L. R. Frank, S. A. Brown, *Alcohol. Clin. Exp. Res.* **2001**, *2*, 236.
39. I. Aharon, N. Etcoff, D. Ariely, C. F. Chabris, E. O'Connor, H. C. Breiter, *Neuron* **2001**, *32*, 537.
40. S. L. Levin, F. B. Mohamed, S. M. Platek, *Evol. Psychol.* **2005**, *3*, 227.
41. Y. Yang, A. Raine, T. Lencz, S. Bihrle, L. LaCasse, P. Colletti, *Br. J. Psychiatry* **2005**, *187*, 320.
42. M. Kosfeld, M. Heinrichs, P. J. Zak, U. Fischbacher, E. Fehr, *Nature* **2005**, *435*, 673.
43. D. Tankersley, C. J. Stowe, S. A Huettel, *Nature Neuroscience* **2007**, *10*, 150.
44. http://www.outlookindia.com/article/an-omnipotent-quest/294134.
45. A. Guleria, U. Kumar, S. S. Kunal Kishan, C.L. Khetrapal, *Psychiat. Res.- Neuroimaging*, **2013**, *214*, 462.
46. U. Kumar, A. Guleria, C. L. Khetrapal, *Cogn. Emot.* **2014**, *29*, 432.
47. https://www.youtube.com/watch?v=GjvjsayoTrg, last accessed on Jan 14, 2017.
48. T. Canli, H. Sivers, M. E. Thomason, S. Whitfield-Gabrieli, J. D. Gabrieli, I. H. Gotlib, *Neuroreport* **2004**, *15*, 2585.
49. T. Atanasijevic, M. Shusteff, P. Fam, A. Jasanoff, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 14707.
50. S. Xu, V. V. Yashchuk, M. H. Donaldson, S. M. Rochester, D. Budker, A. Pines, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 12668.
51. R. Tycko, *Nature* **2005**, *434*, 966.
52. Y. Go, M. Koji, T. Kei, H. Katsushi, H. Yoshiro, *Nature* **2005**, *434*, 1001.

Substantia
An International Journal of the History of Chemistry

Firenze University Press
www.fupress.com/substantia

OPEN ACCESS

Citation: P.-G. De Gennes (2017) The tribulations of the inventor. *Substantia* 1(1): 37-41. doi: 10.13128/Substantia-9

Data Availability Statement: All relevant data are within the paper and its Supporting Information files.

Competing Interests: The author declares no competing interests.

Feature Article

The Tribulations of the Inventor

Pierre-Gilles De Gennes*

Keywords. Progress of science, innovation, inventor.

This is the translated transcription of a speech given in May 2005 in Florence.

My topic is innovation. The starting remark is that we are sick and tired of the innovation in the form of speeches, colloquia, prizes, etc. A great deal of people speak about it and, as usual, it does not result in anything concrete. However, we need innovation. If we look at the world as it is, we can say that we need innovation at two levels. There is, I would say, a selfish perspective, the perspective of a Western country's citizen who says: "we live in an incredible luxury in comparison to the Third World. If we want to keep this situation of comfort, we have to be constantly in lead, we must have more patents to sell, and industries to create that are not those of today because these will be much better ruled for example in Southeast Asia. We must do something else". There is this reducing point of view and then there is a more generous point of view which consists in saying: "Actually, we are in front of this Third World. If we want that this Earth remains in the long term, we have to discover its own way of evolution, and this implies a considerable technical innovation." Thus one way or the other, we cannot escape it.

But it is not so simple to do. I have to admit, contrary to what you just heard, that I am not at all an inventor. All that I can say is that I have been the advisor of a number of inventors at the industrial and academic level. And also I see some of the pupils of the École de Physique et Chimie coming up, at least we must try not to suffocate their enthusiasm, I would say. It is more or less the level of what we know to do. I should also tell you that there are heaps of Epinal prints on invention and innovation that are completely off the track. The first maybe is Bernard Palissy, a little bit crazy inventor who burns his last chair to cook its ceramics, to make something extraordinary. This picture is very dangerous. It often goes with the idea that this inventor is also misunderstood. This situation is dangerous. Being misunderstood does not mean to be a real creator.

I could quote the most famous newspaper in France, dedicated for a considerable time to people who made only stupid things, but that became heroes by their condition of being misunderstood. Thus, as for Bernard Palissy, this is distrust. There is another aspect that we still find in novels or things like that, which is the lightning revelation of the gentleman which suddenly has an idea that is going to submerge an entire domain.

It certainly occurs in some cases. There is a funny case, it is the story, that takes place more or less in 1900, of a young Hungarian who was walking in a park in Budapest and who suddenly decided with his friend that he knew the way to build an electric engine that could work.

At that time electric engines worked horribly badly. He drew with his cane (at that time, they still had sticks) in the sand of the park what will be the synchronous engine, the future engine, that will turn direct electricity used by Edison into the alternating electricity in which we live. It is an illumination, it is true. There is a very small number of cases of this kind. A lightning revelation is not at all what we expect from a pioneer.

And then, there is a third feature which concerns you more, a sort of creed of the current companies: in order to innovate, it is necessary and sufficient to follow the market, to know what your customers demand and to come out with the substantial answer to their request. This is absolutely insufficient. I can try to make two or three examples.

A first example is the story of the liquid crystals watches, the liquid crystal display in general, but in particular for the watches.

As this appeared, the industry of the watch was a Swiss factory that worked magnificently, used to listen very well to its market, and developed market oriented quartz watches. However at the time the company did not see the upheaval that this type of display and the associate microprocessors represented. Because of this error the Swiss industry knew 10 or 15 years of dramatic slump. It came out finally with a nice restoring as in the case of Swatch or things like that, but in any case it was a considerable strategic fault.

Thus, the market piloting in that case was completely dangerous. Another example that fortunately affects you at a minor extent, is the one of a sir named Hounsfield who worked in a disks company. The disks company used to make good bargains and had a certain investment policy in all-out research.

He was persuaded that X-rays pictures could be taken to look at objects. He did that with what was at hand, that is a target, a rotating arm which was pulled by the engine of a vacuum cleaner and an X-ray tube. Instead of taking one picture as we usually do to get an X-ray radiography as we say in medicine, he took hundred pictures by turning the arm.

Later, through a smart reconstruction, he got something that was much more informative. Then he went to the doctors. For a decade the customers and the market kept answering: "no interest". And then finally the device became a breakthrough and this object, that before was mounted on a vacuum cleaner, became what we call now a scanner, an object on which we are all dependent regrettably at one point or another during our life.

We gladly crow on the invention of the laser, a little bit dangerous pride because if we look at the old reports, we notice that the laser would have been invented much earlier, probably 20 years earlier. There were the practical and theoretical tools to make it. So probably, it was made unknowingly. In certain arc discharges or things like that, there are strange phenomena that people did not look deeper into, but probably they were producing lasers without knowing it.

If you like, the laser, but it is not the case for making a trumpet blow, is a discovery guided by the theory. Good! That's very good. But in many other cases, it is not at all the theory that created the economic activity and finally did a service. An example that I came across this morning is the glass. You know how the glass came out: some Phoenician traders were transporting natron, that is sodium carbonate, and they arrived to a river in Palestine, they made a stop by the river and set a fire to cook their chow. It was necessary to build a sort of oven to make the fire and the only thing handy they had - there was no stone - was blocks of natron. They made it on a beach in flint, on a sandy beach.

And then suddenly they saw - while cooking - that something like a river of fire - this is what Pliny reports - spread and that later, this cooled river became a transparent extraordinary material. This is how the glass appeared, but the glass developed through a sequence of fabulous technological inventions. The melting pots to avoid dirt inside, the ovens to blow - it was necessary to let air in - and also the blowing in another sense, i.e. the idea to have a pipe and inflate in a glass pocket to make a bowl, all this dates from Syria-Phoenicia-Carthage, well before the Christian era. It was a fabulous technological innovation and after that there have been other remarkable developments. There has been something like that at the time of a technology transfer to the West, towards Cumae, at the end of the Roman Empire, and then towards Murano and Altare, in the middle of the Middle Ages. This technological transfer was not made without troubles because there was no more natron.

The natron is found in the Dead Sea or places like that, but not in the West. We had no sodium carbonate, it was necessary to find something else. People eventually noticed that the ash of ferns, was a good starting point. It is not the same carbonate, it is potassium carbonate. This allowed to restore the industry in the West. It was not made without difficulties because the practical properties, the melting points, all the miscibility properties of potassium are not the same as those of sodium salts. But people of the year 1000 AD more or less knew how to make it because they were pushed by the invasions - the invasions that cut the West from the East.

Then, here we are, the glass. Yet, this glass that nowadays is an extraordinary technological tool: in the 19^{th} century was used for lenses and optical instruments, in the 20^{th} century for what we call the ice flow (the glass made on a molten metal that allows to make it very smooth) and recently the glass of the optical fibers which allow to communicate stupidities at a large scale, it is still the technology of the glass. This magnificent technology - here is where I return to my original subject - is made up of a material that we do not understand. We do not have a serious description of what we call the glassy state.

Franklin, you know Franklin, great man, ambassador of the young republic of the United States in France, but also one of those who understood the electricity, he was curious about everything. Franklin had what we regrettably have no more: a robust Greek culture. He had read by the Greeks that if we put some oil which is a kind of cleaner on the sea, the waves are calmed down. But this observation had remained at the level where Greece was, that is, I would say in a pretty provocative way, at the level of the philosophers. We have a fact like that, but we do not learn anything real. Franklin had the idea to learn something out of that. At that time he used to live in London, and he went to Clapham Common, near London. There was a puddle - which some of you maybe saw if you are interested in cricket or things like that, there are still activities of this kind - and he chose one pretty windy day, with small ripples at the surface of the puddle, very easy to see. He brought a small bottle of a cleaner of his time, probably an oleate or something like that, a by-product of oil. He poured on the puddle a teaspoon of this cleaner and it calmed the waves on a surface probably a little bigger than this room.

There, he got a number. It was not simply a qualitative idea, he had a number. In fact, this number was extraordinarily precious as it represented one of the biggest stages, we can say, of the knowledge of matter. If he knew the volume - it was one teaspoon - and if he knew the surface over which this volume spread out - let's say the surface of this room -, dividing the volume by the surface he could find the height. In fact, he found the height of the molecules of surfactant, he found the size of molecules. Exactly, it was an immense progress compared to the Greek miracle. The Greeks had conceived an idea of atoms and molecules for a difficulty in reasoning, because they did not know how to go to the infinitely small, they badly knew how to manipulate atoms and molecules. But because of a lack of mathematical ease, they figured out: "it has to stop". By the way, small size objects, atoms, microlites and some others, but it is purely philosophical.

Since the experiment of Franklin, his finding becomes a scientific fact because we do not say that there must be something, but we say that there is something and that it has this size. From this moment, slowly things *are*. But you will notice the simplicity of the methods - one teaspoon, a small jar of oil and a puddle - and one of the biggest discoveries of the conceptual history of the matter follows.

There is a second example on the same line, due to a lady (I might be wrong, but maybe she was the first woman scientist in the Western world). Maybe I am wrong, but it is the first that I know personally, she was called Agnes Pockels. She lived in Germany in the middle of the 19^{th} century, fascinated by sciences, wanting to go to the university, but it was impossible for a woman. Her brother went to the university and did nothing. But she tackled a problem that fascinated people at that time, which is what we call the surface tension of water. Water does not like to lay bare, there is an energy associated with the surface. This energy by square centimeter is what we call the surface tension that we measure by pulling a drop of water by very fine devices and by seeing which strength is necessary to engage in order to convince the water to undress.

But the measures that were made at that time gave totally conflicting results. Sir X in Naples and Sir Y in Göttingen, etc., found absolutely different results. Of course the good scientists used to say: "you did not clean your water, it must be dirty". They said: "we did everything that current chemistry allows us to do, that is we distill, we crystallize the water and then we melt it again, etc.". We eliminate the maximum of impurities, but no go, nothing. Agnes understood that it was not the usual impurities that are in the water such as the common salt or things like that that made the tragedy, but that they were some very rare molecules of these cleaners that I just mentioned. How to get rid of these cleaners? Certainly not by the classic methods because they are so few that those methods are useless, there is a much simpler method. She took her water, shook it strongly – this produces foam where there was a cleaner, an impurity - and she skimmed this foam with a paddle about twenty times.

Once she made it in her kitchen, she obtained a perfectly reproducible water.

She was the first to measure the surface tension of the water. Very happily, it came out. Lord Rayleigh who was the big guru at that time in this field of science gave her a considerable publicity and she came out well. I will show this story to you. Do not expect someone line Marilyn Monroe, she was an austere lady of the 19^{th} century, but she was someone infinitely respectable in her working.

There is another aspect, it is the tenacity. Innovation is not exactly a job where you find something close by. The Concours Lépine that started in France in the 19^{th} century is very dangerous, is not at all like that. Innovation requires a long time, it is a long investment. It is important to underline this point because it is also an opinion that often escapes to the big companies' shareholders. I am going to make an example which is a little bit older.

We go back to 1891. At that time, ladies carried corsets and ankle boots. A very difficult problem is to manage how to tie all the sequential units of the corset or even more in certain hot occasions to untie the same stuff.

Judson in the United States is convinced that it would be necessary to find something better. His attitude at the beginning is to try to find a sort of key which opens all the locks at the same time. There was an absolutely horrible mechanical device with stalks in brass meant to open the corset along the lady's back. Obviously, this device did not work, but Judson worked hard. In 1905 - look at the timescale -, he found a partner called Sundback. In two, it works better. Finally, they came very gradually with this idea to have, instead of a stalk, a flexible join and they created, just before the Great War, what we call nowadays the zipper, which is a very beautiful discovery.

Look at the timescale from 1891 till 1910 that was necessary for this thing. Thus, the tenacity of these people is something extraordinarily respectable and we still need it. I often say that if an extraterrestrial came with the idea to observe a little what is going on on this small planet, he will note maybe with interest that we found as I said the transistor, the laser, etc., but I believe that he will also note that we found the zipper and maybe that we did not find a number of things which are under our nose. Let us be humble.

This experiment that requires a rather complex material that I am going to collect here, is about what we call the dewetting. I take here some water, H_2O, that I am going to place on a sheet of polyethylene. Polyethylene hates water. First I put a small drop, you will not see it very well, I try to add two or three. When it is quite small, it tries to minimize its surface to be exposed. The shape that has the smallest surface for a given volume is the sphere. Thus, it is a spherical cap, it is a portion of sphere. If I force a little the nature, I put some more there, I face a difficulty which is due to the slope of my system. You see, what is made here is an object that is an interesting compromise. It is an object in which the capillarity and the surface forces want to retract this drop, to make it expose less surface, but there is its weight that goes the other way and that forces the drop to flatten. There is a compromise weight-capillarity analyzed by Laplace in 1805 which leads to a thickness very well defined of the order of the millimeter. The object which is there, and that we usually call a puddle, is a very precise object of interface science.

It is all good, but it is not enough to look at the nature in this way.

We try to tease it a little more, that is we force the sheet of plastic to be wetter than what it likes. I will make it by means of this experimental device.

I have some troubles with this story of the slope, but in any case you can see that the sheet gets by quite well. It retracts, there are dry regions which grow either from a small hole inside, or from edges or from defects. If you have a good eye and some faith, you will see that as long as it moves forward, it does it at a constant rate. This process, it is what we call dewetting. It is something that we meet in our everyday life, but that is also important in many industrial applications. These things were made at the Institut Curie by Françoise Brochard's team. They sensed that it was going to be important, they did not very well figure out how, but they established the fundamental laws.

Obviously, it is not as simple as in the air. To prepare clean surfaces with no defect that may hamper the movement, etc., we need the chemical synthesis on surfaces, it means three years of work, or something like that.

Then, there is some hydrodynamics. It is very interdisciplinary, it is necessary to understand how it moves, etc. But finally, everything has been clarified and they had the very clear impression that it was going to serve, but they did not know so much where. It turned out to serve in several domains that have an interesting industrial impact. Since it is late, I am only going to quote one that is described by what I call the British experiment.

In the British experiment, these British wanted the rain. On the road there is more or less 1 mm - maybe less, some micrometers - of water. Under the water there is the asphalt and there comes a car that drives at a British speed of the order of 50 km/h. If this car was really on a film of water like that, you would immediately lose control. It is absolutely necessary to recover a contact between the rubber of the tire and the asphalt. The rubber of the tire turns like this. It keeps the contact with the asphalt during the short moment that corresponds to the flattened part of the tire of your car, which is not very large. At this speed, it means that the tire remains only some milliseconds in contact with the asphalt.

During these few milliseconds, the film of water has to strip out.

This problem is not so that far from what I showed you in my superb experiment. In my magnificent experiment, there was some polyethylene, there was some plastic, some water and air. In this experiment, there is some asphalt that behaves precisely as the plastic, which hates the water, some water and the rubber. It is not the same problem, as rubber is very different from air, but it is a cousin of this problem. These people at the Institut Curie dedicated three generations of theses to understand these phenomena.

Now, we can say that they are relatively well understood and that we have an idea of what a car aquaplaning is. The industrial impact is not so much on the industry of the tire because many of the countermeasures that you can think of to facilitate this process would consist in carving the surface of the tire, like a lace on the surface of the tire. Unfortunately, as you know, a tire wears out very fast and this lace would be very quickly removed. Thus, many of the countermeasures designed for the tire are not good.

On the other hand, the countermeasures about the road, some effective dewetting initiators on the road, are the most interesting for the future.

Thus in that respect, there are interesting hopes. I mention this to show you that this kind of very simple experiment remains valid even in the 21st century and that it is not of the past that I am talking about. If I come on the big perspectives - it is necessary a little bit in a way - I would say that what strikes me, is the fact that the inventors had several following cycles. There was an extraordinary time in the 19th century with people working alone such as Edison, who really changed our world. And then, there was also another extraordinary time, that of the heavy industries. In the domains that I know - it is very restrictive -, it is for example General Eletric. General Electric had a big pilot, Langmuir, who was, let us say, the author of the flashlight as we know it today. The Edison' flashlight was made with a roasted fern had no mechanical stability and did not resist in time. Whom shall I quote still? Dupont. And Carothers for the nylon, or Bell Labs and Schockley for the transistor.

Thus, there was this superb time of the heavy industries that was an admirable superposition. But you should be aware that this time is about to go and that these heavy industries do not play anymore the same piloting role in the future as they did in the 20th century for a simple reason that your professors will explain to you better than I, what is the grip of the power by the shareholders of the big companies. At present, the shareholders have the power and these shareholders are not you and me, they are rather the pension funds of California or things like that, they are very demanding on the profitability in the short term, that is in three years. In other words, they accept to support all the projects of innovation that are very fast, within three years. They do not support anymore whatever is in a 10-year frame. A big part of what was made in all these examples that I mentioned there was exactly a research that lasted at least 10 years. Thus under this point of view, the heavy industries are in a very difficult situation. You see in France the bosses of companies who are in troubles and try to defend a long-term corporate development plan, but who do not always succeed. Some are kicked out, others are threatened, let us say. Thus, there is a hole there.

Thank you for your attention.

* Pierre-Gilles De Gennes (1932 - 2007) was awarded the Nobel Prize for Physics in 1991.

Translation by Pierandrea Lo Nostro

Substantia
An International Journal of the History of Chemistry

Firenze University Press
www.fupress.com/substantia

Research Article

Modelling Polymers as Compressible Elastic Spheres in Couette Flow

OPEN ACCESS

Citation: D. Xie, D.E. Dunstan (2017) Modelling polymers as compressible elastic spheres in Couette flow. *Substantia* 1(1): 43-48. doi: 10.13128/Substantia-10

Data Availability Statement: All relevant data are within the paper and its Supporting Information files.

Competing Interests: The authors declare no competing interests.

Donglin Xie and Dave E. Dunstan*

Department of Chemical and Biomolecular Engineering, University of Melbourne, VIC 3010, Australia.
E-mail: davided@unimelb.edu.au

Abstract. A model of polymer chains as compressible elastic spheres in flow is presented. The spherical polymer blobs are assumed to compress in simple Couette flow in accord with recent rheo-optic measurements on semi-dilute solutions. The experimentally determined decrease in radius with increasing shear rate is predicted by the model. Furthermore, the model predicts power law exponents for the viscosity-shear rate within the range of measured values for polymer chains.

Keywords. Semi-dilute Polymer solutions, Couette Flow, compression, modelling, power law.

INTRODUCTION

The rheology of polymers is of both fundamental interest and considerable practical importance.[1-4] Predicting the flow behaviour of polymeric solutions from the fundamental physics of the individual chains has long been the quest of soft condensed matter.[5,6] The combination of statistical mechanics and fluid mechanics has been used to predict polymer rheology.[7,8] Kuhn was the first to develop a model of chains in flow.[9] He modelled the chains as beads on a spring in which the beads account for the hydrodynamic forces and the spring embodies the elastic nature of the chain. He also developed the first statistical mechanical model that enabled the calculation of the effective spring constant from the chain properties.[9] Kuhn's 1933 *Kolloid Z.* paper also showed that the chains experience both extensional and compressive hydrodynamic forces as they tumble in flow in so called Jeffery Orbits.[10] Interestingly, since Kuhn's original paper, the compressive forces have been ignored and only extension is assumed to occur. The dumbbell model presented by Kuhn enables the hydrodynamic forces to be evaluated and the steady state condition of the forces to be equated as a function of the angle around the vorticity axis. Since Kuhn's pioneering work, an essential assumption of polymer dynamics is that the single molecule response to applied stress may be used to interpret the observed macroscopic material behaviour.[2,4,6] The elegant models of single polymer chains which assume that the chain can be described as a random walk on a periodic lattice have been successful in predicting a number of the key properties of polymers.[5,6] Furthermore, the inclusion of excluded volume to the ideal chain has enabled prediction of the solution size of polymers.[3,11,12] The entropy of the chain is derived in terms of the end-to-end vector of the random chains.[2] This model forms the basis of rubber elasticity and is used to incorporate elasticity in models of flow where chain deformation results in entropy reduction and elasticity.[13] The *theory of rubber elasticity* (based on the same physical assumptions) predicts the elastic behaviour of rubbers over a wide strain range.[13] Importantly, the *"Rubber Theory"* predicts both the compressive and extensional behaviour of rubbers. This agreement between the theory and experiment, albeit at effectively "*infinite*" molecular weight and high polymer concentration with excluded volume interactions neglected, gives confidence that the fundamental tenets of the theory are correct. However, due to their complexity there exist very few simulations of polymer solutions and melts in the semi-dilute and concentrated regimes.[8,14-16]

A general assumption used in models of polymers in flow is that the chains extend in response to the hydrodynamic forces.[14-16] Recent experimental evidence shows that synthetic polymer chains compress in Couette flow at semi-dilute concentrations.[17-19] Recent studies on semi-dilute DNA solutions shows that extension and tumbling occurs.[20,21] It appears that the general assumption of chain extension in flow may not be valid for concentrations above critical overlap in Couette flow.[18,19,22,23] Furthermore, recent Brownian dynamics simulations for dilute solutions predict chain compression by neglecting excluded volume effects and including hydrodynamic interactions.[24,25] While these simulations have been done for dilute chains, the neglect of excluded volume effects is consistent with concentrated solution behaviour. The inclusion of hydrodynamic interactions in concentrated solution where they are screened is not however consistent with the physics of concentrated solutions. Many of the models and experiments presented in the literature are for purely extensional flows.[2,26] Recent simulations on the blood borne protein von Willebrand Factor (vWF) show that in Couette flow the vWF chain tumbles when exposed to high shear rates to extend and then refold. When exposed to relatively low extensional shear rates, the vWF unfolds and extends.[27-29]

In light of recent experimental evidence showing chain compression in Couette flow, a new model is presented where the chains compress in response to the hydrodynamic forces. We also note that coil compression is an elastic event which leads to reduced friction in the system and is therefore consistent with the shear thinning and visco-elasticity observed for polymer solutions in simple flow. Purely extensional flow results in an increasing extensional viscosity with shear rate.[30]

RESULTS

The shear rate dependence of the end-to-end distance, r, has been measured for polymethyl methacrylate (PMMA) using fluorescence resonance energy transfer (FRET) tagged chains in laminar Couette flow.[22] The conformation of poly-4-butoxy-carbonyl-methylurethane (4-BCMU) in flow has been measured using absorption spectroscopy where the change in segment length with shear is used to determine the change in polymer size.[18] The results of the previous studies are re-plotted on a log-log scale in Figure 1 below. Both polymers show a decrease in the end-to-end distance with increasing shear rate. Reversibility was observed upon cessation of shear for all shear rates measured.[18,22]

The results presented in Figure 1 are from two different rheo-optical experiments for two different polymeric systems. The data for PMMA was collected using time resolved FRET measurements on end tagged PMMA as a molecular tracer in a matrix of untagged PMMA

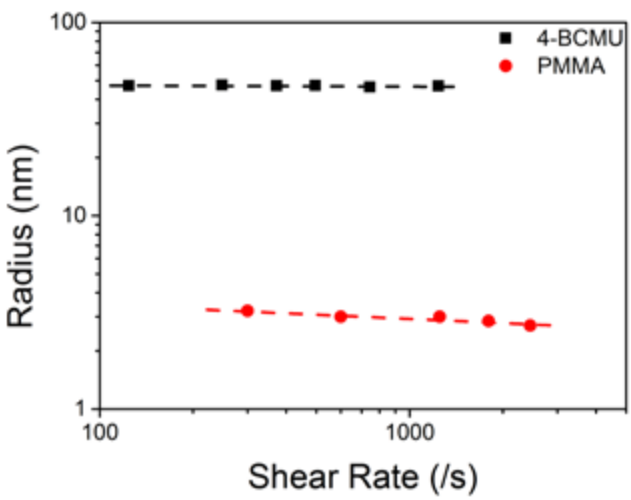

Figure 1. Measured end-to-end distance plotted as log r versus log shear rate. ata for 800kD 4-BCMU.[18] has the fitted equation: $log(r) = -0.0046 log(\dot{\gamma}) + 1.7$ with the coefficient of determination: $R^2 = 0.23$. Data for 49kD FRET tagged PMMA in Couette flow[22] shows the fitted equation: $log(r) = -0.0072 log(\dot{\gamma}) + 0.69$ with $R^2 = 0.88$. The lines of best fit yield an inverse 0.07±0.02 power of the radius with shear rate for the PMMA and 0.0042±0.002 for the 4-BCMU. The error bars are approximately the size of the symbols. The error associated with each point is: ~5% in the shear rate due to the radius/gap ratio of the Couette cell. For the 4-BCMU the un-sheared size of the chain is 49±1nm and for PMMA the size is 4±0.1nm.

at ~2C*. The data for 4-BCMU is taken from reference 1 where the segment lengths of the 4-BCMU are measured to decrease with increasing shear rate at a polymer concentration of ~1.6C*.[18] Calculation of the average segment length and conversion to an end-to end distance using the equation r = a$N^{1/2}$ yields the results presented in Figure 1 for 4-BCMU. Here N is the number of segments and a the segment length as taken from literature values.[18] Both data sets show a decreasing radius with shear rate with a power law behaviour.

THEORY

The polymers are modelled as space filling, spherical elastic objects at semi-dilute concentration. The spheres are compressible and may change their volume through deformation. The flow is defined as simple Couette flow where the spherical blobs are exposed to a uniform velocity gradient at low Reynolds number, $R_e = vr/\eta$ for neutral buoyancy spheres. In view of recent experimental evidence showing that polymer chains compress in Couette flow (see Figure 1), we assume that the translational hydrodynamic forces on the sphere act to compress the chain in accord with the experimental evidence.[17,22,31] The semi-dilute concentration is such that the spherical blobs are in contact with each other and compress in flow. We postulate that the reason compression rather than extension dominates the flow response of these polymers is due to the crowding of the single chain by the neighbouring chains in semi-dilute solution. The tumbling motion of the chains results in a time average compressive hydrodynamic force on the sphere in semi-dilute solutions.

For the semi-dilute solutions, the blobs experience both rotational and compressive forces in flow. The rotational force (torque) acts to make the compressive hydrodynamic forces on the sphere uniform. As such the hydrodynamic translational force acts isotropically inward on the blob and is opposed by the elastic force. The force acting on each half space in the Couette flow acts in the opposite direction and is simply one half of the Stokes' drag on the sphere. Goldman, Cox and Brenner[32,33] determined the hydrodynamic force on a sphere in Couette flow at low Reynolds number as:

$$F_y^{s*} = F_y^s / 6\pi\eta rU \quad (1)$$

Here F is the force with the subscript y defining the direction of the translational motion in the unperturbed shear rate s, r is the sphere radius, U the fluid velocity and h the solvent viscosity.

Equation 1 defines the force on the sphere at distances from the walls greater than the radius as:

$$f_{hyd} = 6\pi\eta rU \quad (2)$$

The torque on the sphere, Faxen's Law, was also determined as:[33]

$$T_x^{s*} = T_x^s / 8\pi\eta r^3\Omega \quad (3)$$

where T is the torque on the sphere, with the superscript s defining the undisturbed shear rate, the subscript x is the vorticity axis and Ω is the rotational velocity.

The local forces may then be equated under steady state flow. The elastic and hydrodynamic forces on sphere then act to change the radius in flow. The forces are used in the following treatment as at each point in the system the hydrodynamic and elastic forces oppose each other. In order for the system to reach steady state, the

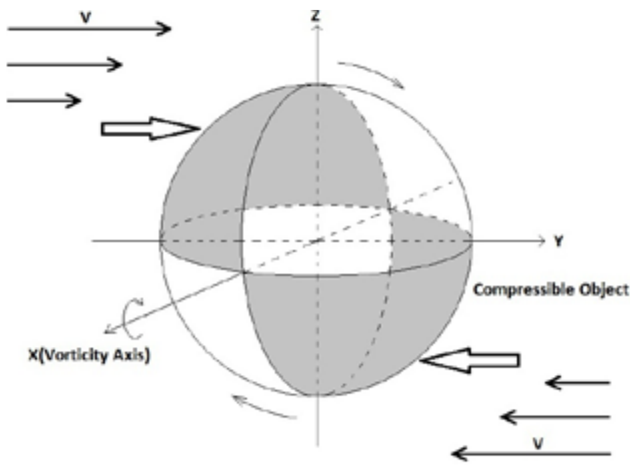

Figure 2. Schematic showing the polymer represented as a sphere in Couette flow. At semi-dilute concentrations each sphere is in "contact with the surrounding spheres. The shaded area shows the region which experiences a compressive force from the flow. The upper half experiences a compressive force from left to right while the bottom right hand part of the image experiences a similar compressive force from the flow from right to left. Each surface experiences a compressive force equal to one half the Stokes' drag on a sphere. The total compressive force is then equal to $f_{compressive} = f_{hyd} = 6\pi\eta rU$ where η is the solution viscosity, r the sphere radius and U the velocity difference across the sphere in the direction shown. The sphere also experiences a torque around the vorticity axis. This rotational motion causes a tumbling which yields an averaged symmetric compression on the blobs in flow. At each point across the surface the hydrodynamic force is equal to the elastic force under steady shear. Local fluctuations will occur with the system reaching an average reduced size of the coil with increasing shear rate and commensurate hydrodynamic force. The arrows pointing inward on the blob represent the local hydrodynamic compressive force.

completely isotropic forces throughout the solution are equivalent. Obviously, the forces will fluctuate around the steady state average as the blobs rotate around the vorticity axis in the shear field. In steady state flow the hydrodynamic and elastic forces are then equated:

$$f_{el} = f_{hyd} \tag{4}$$

Where the magnitude of the elastic force for the blob is taken from the theory of rubber elasticity and has a similar form as that reported previously:[13,34]

$$f_{el} = E \times Area = \frac{3nk_BT}{r} \tag{5}$$

Where E is the Young's modulus of the blob, k_B is Boltzmann's constant, T the absolute temperature and r the sphere radius. The elastic force so described embodies the entropic nature of the chain. Here we define n as the number of chain interactions (usually assumed to be entanglements) where n may be assumed to be constant for finite deformation. The *theory of rubber elasticity defines* n as the number of cross links in the gel.[13] Note that the theory of rubber elasticity introduces an r_0 term into equation 5 to allow for compression and the finite size of the chain in the quiescent state.[13] Neumann has previously suggested that the inability to account for r_0 in the Hookean force law used in models of polymers in flow arbitrarily restricts the chain to extension.[35,36] Indeed the neglect of the r_0 term results in a Hookean response of the chains that is not physically correct in that the radius is zero at zero force and infinite at infinite extension. The formalism introduced by Neumann has the correct limiting behaviour for the force law in both extension and compression. Compression of the chains to point size would require an infinite force as would large stretching.

At each localised point, we assume that the elastic force acting normal to the surface of the blob as shown in Figure 2 opposes the hydrodynamic force.

The hydrodynamic force on the spherical blob is developed from equation 2 above using the assumption that the velocity in Couette flow U defines the shear rate as:

$$\dot{\gamma} = U / 2r \tag{6}$$

Then

$$f_{hyd} = 6\pi\eta\dot{\gamma}r^2 \tag{7}$$

Here the viscosity of the polymer solution is η, $\dot{\gamma}$ the shear rate experienced by the chain and r the average end-to-end vector of the chain as defined above. It is assumed that the end-to-end distance is equivalent to the radius of the sphere that experiences the hydrodynamic force. The hydrodynamic force varies as r^2 in accord with the original derivation of the hydrodynamic drag on a dumbbell derived by Kuhn.[9]

To first order the viscosity of the solution, is approximated by a modified version of Einstein's equation:

$$\eta \sim \eta_0\phi \tag{8}$$

Where the η_0 is the effective solvent viscosity and ϕ the volume fraction of the chains. We assume that the effective solvent viscosity composed of solvent and the surrounding polymers. The polymer chains in flow act as compressible objects where the (incompressible solvent) may exchange freely throughout the system. The solution viscosity will depend on the polymer volume fraction and the shear rate. We assume that η_0 is also proportional to the volume fraction ϕ so that:

$$\eta \sim \phi^m \tag{9}$$

De Gennes and later Rubinstein and Colby have derived the volume fraction dependence for the viscosity of semi-dilute solutions using scaling arguments and determined that m = 2. Furthermore, experimental data confirms the scaling arguments for polyethylene oxide in the semi-dilute concentration range.[2,37] By assuming $\phi \sim r^3$ by substitution into equation 5 we obtain the following:

$$\eta \sim r^{3m} \tag{10}$$

Equating the hydrodynamic and elastic forces on the spherical object in flow;

$$\frac{3nk_BT}{r} = 6\pi r^{3m}\dot{\gamma}r^2 \tag{11}$$

Yields:

$$nk_BT \sim \dot{\gamma}r^{3(m+1)} \tag{12}$$

so that

$$r \sim nk_BT\dot{\gamma}^{-1/3(m+1)} \tag{13}$$

The generally accepted power law model is of the form:

$$\eta \sim \dot{\gamma}^n \tag{14}$$

Values of n reported for polymeric systems range between p ~ -0.2 to -1.0.[38-40] Interpretation of the data presented by Stratton indicates that for monodisperse polystyrene, p = -0.82.[40] The value of p = -2/3 predicted by the model is well within the range of accepted values for shear thinning polymers.[38]

The viscosity-shear rate in model developed has the power law form:

$$\eta \sim \dot{\gamma}^{-m/(m+1)} \tag{15}$$

The dependence of the radius with shear rate for m = 2 is then:

$$r \sim k_B T \dot{\gamma}^{-1/9} \tag{16}$$

and

$$\eta \sim \dot{\gamma}^{-2/3} \tag{17}$$

Thus the model predicts values for the power law model in accord with those determined experimentally for polymer solutions and hard sphere suspensions.[39,40]

DISCUSSION

The measured dependence of the decrease in the radius with increasing shear rate (power law of -0.09±0.02) is in close agreement with the model prediction of -1/9 (-0.11) (Equation 16) when m = 2 is used for the volume fraction power law of the viscosity for the PMMA data.

Furthermore, the model predicts a power law for the shear thinning viscosity of -2/3 (-0.67) that is within the range observed for polymer solutions which have been found to lie within the range of -1.0 to -0.2.[38-40] Using the approximation that the viscosity follows a volume fraction squared behavior allows the model to fit both the power law behavior of the radius and viscosity with shear rate for PMMA. Expansion of the Einstein Equation involves the addition of higher order terms in the volume fraction as attributed to Batchelor.[33] Any correction to the viscosity-volume fraction dependence would presumably require higher order terms (m > 2) that would yield lower values of the predicted power law at higher concentrations. Indeed, scaling arguments predict that the viscosity follows a 14/3 power of the volume fraction at concentrations above the entanglement concentration.[37] The measured viscosity-molecular weight behavior for a range of polymers is consistent with the volume fraction dependence used in Equation 7.[41] Furthermore, de Gennes and later Rubinstein and Colby have modeled the viscosity-polymer volume fraction dependence described in Equation 9 using scaling arguments to show that m = 2 in the semi-dilute concentration range.[2,37] This relationship between the volume fraction of the polymer and the effective solvent viscosity enables the macroscopic viscosity-shear rate power law to be predicted (Equation 15). The predicted and measured decrease in radius with shear rate for the PMMA are in excellent agreement when the second order dependence of the viscosity on volume fraction (m = 2) is used. Fitting the BCMU data requires that m is approximately 1 (m = 1.0015). This suggests a power law for the viscosity of ~-1/2. Equation 7 yields an unbounded radius (and viscosity) as the shear rate tends to zero so that a modified form of the above equations must be used at low shear rates. The form of the equations at low shear rates will be similar to the Cross equation for shear thinning.[39] The recently measured shear induced phase separation observed in semi-dilute polymer solutions may be explained by chain compression in flow where the solutions appear to be more heterogeneous as reflected in the scattering measurements. The observed compression in flow lays the foundation for an explanation of the observed shear induced phase changes observed for polymer solutions.[42,43]

Furthermore, it is noted that the model predicts a value of p = -1/2 and a radius dependence of the shear rate with a power of -1/6 for dilute solutions where it is assumed that the viscosity is proportional to the volume fraction. A review of the literature on the power law behavior observed for polymer solutions of differing volume fraction would be appropriate in validating the current model. The power law of the viscosity with volume fraction is used as an adjustable parameter in the model and suggests possible reasons for the different power law behavior reported in the literature for the same polymer systems.

CONCLUSIONS

The model for polymers in flow is presented where the chains behave as elastically deformable spheres that compress in simple shear flow at semi-dilute concentrations. Equating the elastic and hydrodynamic forces on the blob enables the power law observed for shear thinning and the reduction in end-to-end distance with shear rate to be predicted over the range of shear thinning. Physically the model is consistent with the observed rheology of polymer solutions in Couette flow which is attributed here to compression of the chains in flow rather than the previously assumed extension. Development of the model using the assumption that the chains compress enables a simple analytical prediction of polymer visco-elastic behavior including the power law for shear thinning.

AUTHORS' CONTRIBUTIONS

DX undertook data analysis and contributed to writing the paper. DD contributed to writing the paper and developed the model.

ACKNOWLEDGEMENTS

We would like to thank Elisabeth Hill, Yalin Wei, Ming Chen and Nikko Chan for their experimental work in undertaking the rheo-optical measurements.

REFERENCES

1. L.H. Sperling, *Introduction to Physical Polymer Science*, Wiley Interscience, New Jersey, **1992**.
2. P.G. de Gennes, *Scaling Concepts in Polymer Physics*, Cornell University Press, Ithaca, **1979**.
3. W.W. Graessley, *Polymeric Liquids & Networks: Structure and Properties*. New York, Garland Science, **2004**.
4. M. Doi, S.F. Edwards, *The Theory of Polymer Dynamics*, Clarendon Press, Oxford, **1986**.
5. P.J. Flory, *Principles of Polymer Chemistry*. Ithaca, Cornell University Press, **1953**.
6. P. Flory, *Statistical Mechanics of Chain Molecules*, Hanser Publications, New York, **1988**.
7. J.D. Ferry, *Viscoelastic Properties of Polymers*. New York, John Wiley, **1980**.
8. R.B. Bird; C.F. Curtiss; R.C. Armstrong, O. Hassager, *Dynamics of Polymeric Liquids, Volume II, Kinetic Theory*, Wiley-Interscience, New York, **1987**.
9. W. Kuhn, *Kolloid Z.* **1933**, *62*, 269.
10. G.B. Jeffery, *Proc. Roy. Soc. London Series A* **1922**, *102*, 161.
11. G. Cheng, W.W. Graessley, Y.B. Melnichenko, *Phys. Rev. Lett.* **2009**, *102*, 157801.
12. M. Daoud, J.P. Cotton, B. Farnoux, G. Jannink, G. Sarma, H. Benoit, R. Duplessix, C. Picot, P.G. de Gennes, *Macromolecules* **1975**, *8*, 804.
13. L.R.G. Treloar, *The Physics of Rubber Elasticity*, Oxford University Press, Oxford, **1975**.
14. G. Marrucci, J.J. Hermans, *Macromolecules* **1980**, *13*, 380.
15. G. Marrucci, N. Grizzuti, *J. Nonnewton Fluid Mech.* **1986**, *21*, 319.
16. R.B. Bird, J.R. Deaguiar, *J. Nonnewton Fluid Mech.* **1983**, *13*, 149.
17. S. Gason, D.E. Dunstan, T.A. Smith, D.Y.C. Chan, L. R. White, D. V. Boger, *J. Phys. Chem. B.* **1997**, *101*, 7732.
18. D.E. Dunstan, E.K. Hill, Y. Wei, *Macromolecules,* **2004**, *37*, 1663.
19. N. Y. Chan, M. Chen, D.E. Dunstan, *Eur. Phys. J. E,* **2009**, *30*, 37.
20. P. LeDuc, C. Haber, G. Bao, D. Wirtz, *Nature* **1999**, *399*, 564.
21. R.E. Teixeira, H. . Babcock, E.S.G. Shaqfeh, S. Chu, *Macromolecules* **2004**, *38*, 581.
22. N.Y. Chan, M. Chen, X.-T. Hao, T.A. Smith, D.E. Dunstan, *J. Phys. Chem. Lett.* **2010**, *1*, 1912.
23. D.E. Dunstan, *Eur. J. Phys.* **2008**, *29*, 977.
24. D. Petera, M. Muthukumar, *J. Chem. Phys.* **1999**, *111*, 7614.
25. C. Sendner, R.R. Netz, *Eur. Phys. J. E,* **2009**, *30*, 75.
26. E.C. Lee, S.J. Muller, *Macromolecules* **1999**, *32*, 3295.
27. C.E. Sing, A. Alexander-Katz, *Biophys. J.* **2010**, *98*, L35.
28. T.A. Springer, *Blood* **2014**, *124*, 1412.
29. X. Zhang, K. Halvorsen, C.-Z. Zhang, W.P. Wong, T.A. Springer, *Science* **2009**, *324*, 1330.
30. C.W. Macosko, *Rheology, Principles, Measurement and Applications*. New York, VCH Publishers, **1994**.
31. D.E. Dunstan, Y. Wei. *Eur. Phys. J. Appl. Phys.* **2007**, *38*, 93.
32. A.J. Goldman, R.G. Cox, H. Brenner, *Chem. Eng. Sci.* **1967**, *22*, 653.
33. J. Happel, H. Brenner, *Low Reynolds Number Hydrodynamics*, Kluwer, Boston, **1983**.
34. T.G. Mason, D. A. Weitz. *Phys. Rev. Lett.* **1995**, *75*, 2770.
35. R.M. Neumann, *J. Chem. Phys.* **1999**, *110*, 7513.
36. R.M. Neumann, *Phys. Rev. A.* **1986**, *34*, 3486.
37. M. Rubinstein, R. H. Colby, *Polymer Physics*, Oxford University Press, **2003**.
38. D. Song, R.K. Gupta, R.P. Chhabra, *Ind. Eng. Chem. Res.* **2011**, *50*, 13105.
39. H.A. Barnes, J.F. Hutton, K. Walters, *An Introduction to Rheology*, Elsevier, Amsterdam, **1989**.
40. R.A. Stratton, *J. Coll. Interface Sci.* **1966**, *22*, 517.
41. R.A. L. Jones, *Soft Condensed Matter*, New York, Oxford University Press, **2002**.
42. M. Minale, K.F. Wissbrun, D.F. Massouda, *J. Rheol.* **2003**, *47*, 1.
43. B. Hammouda, A.I. Nakatani, D.A. Waldow, C.C. Han, *Macromolecules* **1992**, *25*, 2903.

Substantia
An International Journal of the History of Chemistry

Firenze University Press
www.fupress.com/substantia

Research Article

From Water to the Stars: A Reinterpretation of Galileo's Style*

Louis Caruana SJ

Faculty of Philosophy, Pontificia Università Gregoriana, 00187 Rome, Italy
E-mail: caruana@unigre.it

OPEN ACCESS

Citation: L. Caruana SJ (2017) From Water to the Stars: A Reinterpretation of Galileo's Style. *Substantia* 1(1): 49-53. doi: 10.13128/Substantia-7

Data Availability Statement: All relevant data are within the paper and its Supporting Information files.

Competing Interests: The author declares no competing interests.

Abstract. Galileo Galilei's contribution during the early stages of the scientific revolution and his clash with the Catholic Church have been discussed, studied, and written about for many decades. There are indications however that recent work in this area has tended to underestimate the fact that Galileo had a particular style. By style here I mean a particular combination of behavioural features that are specific to a person or a historical period. Style of course can be related to behaviour in general, but what is relevant in this paper is the combination of dispositions that determine a particular way of engaging in science, as discussed by scholars like A.C. Crombie.[1] Galileo, I will argue, had a scientific style marked by overconfidence. He tended to downplay the importance of obvious contradictory evidence that undermined his claims, and he did this by producing auxiliary hypotheses that sometimes verged on the extravagant. If we focus on this somewhat neglected aspect of his style, some interesting new questions emerge: To what extent did Galileo depend on such auxiliary hypotheses? How insecure did they render his position? And how *ad hoc* were they? In this paper, I explore these questions by comparing two important debates: one about the nature of water and buoyancy, the other about cosmology. Since the main features of the cosmology debate, the one involving Galileo's defence of heliocentrism, are well known, I will dedicate more time to the water debate, before proceeding to highlight the elements of style that are common to both debates, and to evaluate the relevance of these elements for current understanding of scientific practice.

Keywords. Galileo, auxiliary hypotheses, ice, buoyancy

1. THE BUOYANCY DEBATE

First, a word about Galileo's social and cultural situation. The way empirical inquiry used to be motivated and propagated at that time, when what we now call the scientific revolution was at its infancy, differed considerably from the way it is today. In that context, the driving force used to originate mainly not from scientific questioning as such but from what the major patrons of individual scholars regarded as marvels and curiosities, from what these patrons

* Republished from "Aqua Incognita. Why ice floats on water and Galileo 400 years on". P. Lo Nostro and B.W. Ninham, Eds., Connor Court Publishing Pty Ltd., Ballarat (Australia), 2014. ISBN: 978-19-2513-821-4.

considered worthy of exciting debates and controversy. The question "Why does ice float on water?" was one clear example of an exciting question because we all know that ice is in fact nothing more than water. The overall social, political, and cultural context in the seventeenth century was such that science was dependent to a very large extent on what patrons wanted, and this meant that natural philosophers, or anyone we would now recognize as a scientist, could never be fully in control of their research. Patron-dependence was crucial: through financial support, it made the scientist's work possible. But it produced a number of difficulties as well, mainly because the general habitat for science, where science happened, was not the isolated laboratory but pubic disputation, and this mode of scientific practice usually drew attention not to careful and technical understanding but to quick, publicly accessible answers. Moreover, during the period when Galileo flourished, mathematics was still considered a discipline that was less important than Aristotelian philosophy within the overall hierarchy of knowledge. Galileo had to struggle hard against this mindset. The only way he could gain a hearing was to make himself philosophically versatile enough to engage with the Aristotelians on the same level.[2]

With this background in mind, we can now appreciate better the various forces at work during the debate that concerns us here, the one concerning water and buoyancy. This was launched in the summer of 1611, a session that took three days. It started with a dispute about the nature of cold as a quality, but then shifted into one about buoyancy. The major contention arose when the Aristotelians among those present were shocked to learn that, for Galileo, ice was not condensed water, as they had always assumed. They had to admit that the issue was not completely clear in the classic texts. Although Aristotle had indeed indicated that ice was condensed water, his reflections on this point were rather sketchy. For instance, in his *Metaphysics* he discussed the different senses in which the word "is" can be used, and the examples he offers include ice. He writes: "[the word] 'is' has [a] number of senses; for a thing 'is' a threshold because it is situated in a particular way, and 'to be a threshold' means to be situated in this particular way, and 'to be ice' means to be condensed in this particular way. Some things have their being defined in all these ways: by being partly mixed, partly blended, partly bound, partly condensed."[7,8] Aristotle here takes the idea that ice is condensed water as obvious. Why? We find no clear answer in Aristotle's own works, but his followers filled up the reasoning behind this in the following way. He must have started not from the fact that ice floats on water but from the fact that it is colder than water. Since ice is colder than water, it must be water minus something, minus some amount of heat, and this lack leads to a condensation. It is water with a deficiency, as it were, not with something extra. And as regards the question why ice floats, Aristotelians considered this fact as just one example of buoyancy in general. For them, buoyancy is a matter of shape only. It had nothing to do with density. On this issue, they were certainly following their master who had explained this point quite carefully. In his book *De Caelo*, he argued that shape matters because the determining factor in buoyancy is the difference that the various materials we consider show as regards penetrability. For instance, air is more penetrable than water, and water is more penetrable than earth. He adds: "the reason why broad things keep their place [e.g. a plank of wood afloat on water] is because they cover so wide a surface, and the greater quantity [i.e. the water] is less easily disrupted. Bodies of the opposite shape sink down because they occupy so little of the surface, which is therefore easily parted."[9] It is good for us to recall here that, in Galileo's times, Aristotelians used to feel obliged to defend Aristotle, be it on buoyancy or geocentrism, or any other issue, not only because his positions were justified, as indeed they thought they were, but also because they considered these various positions important individual bricks that held an entire worldview in place. For them, removing one brick could have devastating consequences that would destabilize the entire conceptual scheme.

What was Galileo's reaction to this? For him, Aristotelians were seeing the entire issue the wrong way round. They had started from the observation that ice is colder than water and had sidelined the fact that ice floats on water. What they should have done was to start from the fact that ice floats on water. For Galileo, since ice floats on water, it must be rarified water, not condensed water. And as regards buoyancy, Galileo resorted to another ancient source: Archimedes. While Aristotle had developed a shape-theory of buoyancy, Archimedes had developed a density-theory, according to which a thing in water experiences a buoyant force equal to the weight of water displaced. Galileo did not deny that shape matters. He conceded that the shape of a body affected the speed with which it sinks or rises, but was convinced that shape does not affect *whether* it sinks or rises.

Up to this point, the debate seemed well balanced. Both sides presented interesting insights, and both had a heavyweight from Ancient Greece as support. The decisive factor came when Galileo's main opponent, Lodovico delle Colombe, devised a simple but spectacular and decisive experiment. He did not want to resort to Aristotelian deductive reasoning or anything like that. He appealed instead to direct evidence, just like Galileo. He made all the participants gather round the demonstrating table and he showed them how a sphere of ebony, whose density is higher than that of water, sinks when placed on water, while a thin piece of the same material remains afloat even with some weights on it. So the determining factor was shape, not density – full stop.

Galileo must have been quite astounded by this, but he did not give up. He tried to come up with some way of explaining this experiment in his own terms. This was not easy at all, because according to his worldview there should not be any special effect at the surface of a liquid which does not arise elsewhere within liquid. In other words, his view of liquids ruled out what we now call surface tension. He took therefore another line of argument and tried to bring in the relevance of wetness, but this lead to no convincing conclusion. Since the dispute itself became noisy and inconclusive, the meeting was brought to a close, and the main protagonists left with the intention of producing a full written version of their position. Galileo, encouraged to proceed with this by his patron, Duke Cosimo II, took his task seriously, and produced his written text within a year. For him, maintaining the duke's favour was obviously important. We notice once again how science was dependent on patronage to an extent that is hard for us to accept today.

Galileo's written version, entitled *Discourse on Bodies in Water* and published in 1612, was based on Archimedes's classic work *On Floating Bodies*, which had emphasized hydrostatics. Archimedes had offered an account of buoyancy that had been intended to explain the situation once equilibrium is reached. In other words, he had described the state of affairs when a body is stationary and floating, or when it has sunk and lies at the bottom. He had said nothing about the *process* of rising to the surface or of sinking; his view had been limited to *statics* as opposed to *dynamics*. Galileo therefore saw a way of breaking new ground by delving into hydrodynamics. This was a risky business, because in claiming the right to give an account of motion, he was encroaching into the philosophers' domain – yet again. Resorting to the model of the lever, he wanted to explain the downward motion of a sinking body and the corresponding upward rise of the water surface, two motions with different speeds. And he did this by resorting to the model of a lever with different arm-lengths, a lever that makes a short swing on the short side and a quick swing on the long side. He adopts therefore a mechanical view of the world – and this was seriously at odds with the Aristotelian worldview, at least in two senses.

First of all, Aristotelians had always believed that each of the four elements had its own specific motion: for instance earthly bodies move down because they have heaviness, while fiery ones move up, because they have lightness. Heaviness and lightness were for them real attributes belonging to things according to their nature. Each object or material will therefore have its share of overall heaviness or lightness in proportion to its constitution from the elements. From these fundamental, elemental motions, therefore Aristotelians offered the explanation of all motion. As regards the specific case we are dealing with here, the case of sinking or floating, the shape of the body, they used to say, was not the determining factor but only a *causa per accidens*, an explanation of secondary importance. The floating object needs to be understood in terms of its own inherent constitution in terms of the elements, the proportion of which determines the object's intrinsic quantity of heaviness and of lightness. Galileo was dissociating himself entirely from this kind of explanation. He was proposing a worldview in which buoyancy was the result neither of an innate upward trend (lightness as an attribute) nor of an effect of shape. For him, it was the result of the body's downward motion being counterbalanced by a counterforce. The implication here was that bodies, be they predominantly earthy or predominantly fiery, have only one type of motion: downwards. The Aristotelians were not amused.

Secondly, the fact that water shows a kind of skin at its surface was perfectly in line with the Aristotelians' broad view of liquids in general. For them, water, being a continuum, has a tendency to preserve its cohesion and integrity, as their master had expressed quite clearly in his work *De Caelo*: "Since there are two factors, the force responsible for the downward motion of the heavy body and the disruption-resisting force of the continuous surface, there must be some ratio between the two. For in proportion as the force applied by the heavy thing towards disruption and division exceeds that which resides in the continuum, the quicker will it force its way down; only if the force of the heavy thing is the weaker, will it ride upon the surface."[10] On this issue, Galileo had a problem. For him, water was made up of corpuscles with no intrinsic difference between them. It did not matter whether these corpuscles were at the surface or within the interior of the liquid. This view therefore, as mentioned above, ruled out any idea of surface-tension. How could Galileo then account for the impressive demonstration of his opponent Delle Colombe? To account for the intriguing floating chip of ebony, he had no choice but to resort to an explanation that was considerably extravagant. He proposed that, as the chip is lowered onto the surface, the observable slight depression of the water surface as it floats makes the chip associate itself with a layer of air above it. In this way, the composite object, layer of air and layer of ebony, will have a specific weight less than that of water. Was he introducing, through the back door, some occult forces here, some "magnetic virtue of air" as his opponents were quick to remark? These are his words:

> *But if it [the ebony chip as it presses down onto the water surface] has already penetrated and is, by its nature, denser than water, then why does it not proceed to sink but stops and remains suspended within that small cavity that had been produced by its weight? I would say: because, as it moves down until its [upper] surface arrives at the water level, it loses a part of its own weight, and it then proceeds to lose the rest of its weight as well by descending deeper even below the water surface, which produces a ridge and a bank around it. It loses weight as it descends in such a way that it drags down to itself the air above it, by adherent contact. This air proceeds to fill up the cavity produced by the little water ridges, in such a way that, in this case, what really descends and is located in water is not just the ebony chip, or the iron chip, but the composite of ebony and air, from which there results a solid [solido]which does not exceed water in density as does ebony on its own, or gold on its own.*[11,12]

This is the best Galileo could come up with as he tried to reason things out from within his system. I think it is fair to say that, as an explanation, it looks farfetched and *ad hoc*. What it shows is a strong determination on his part to save his overall worldview at all costs. He was ready to go even that far.

So, all in all, we can say that debate on water and buoyancy that had started *viva voce* in 1611 and then dragged on in writing for more than four years had no clear winner.[13] As historians now recognize, one important thing we see in this debate is the emergence of a growing gap between two very different professional identities: on the one side, we have professional philosophers, the Aristotelians, whose principles are derived from acknowledged philosophers; on the other side, we have a specimen of a new species of intellectual, a mathematician-philosopher, who seemed to violate the disciplinary boundaries that had been well established and respected for hundreds of years.

2. COMPARING WITH THE ASTRONOMY DEBATE

Let us draw a quick comparison now between this debate and the one on the solar system. As is well known, the main story of the solar-system debate, in short, was this. With the use of the telescope, Galileo discovered new evidence in favour of the heliocentric view that had been promoted mathematically by Nicholas Copernicus about fifty years beforehand. Galileo therefore started to defend the idea that Copernicus's view was not a mere mathematical shortcut to obtain quick predictions of planetary positions, but was a true description of how things are. In the ensuing debate, which involved Aristotelians yet again, Galileo was challenged to explain some pretty glaring instances of counterevidence to his proposals. And this is the crucial point where this solar-system debate shows some remarkable similarity with the buoyancy debate. In both cases, Galileo had to deal with counterevidence that seemed obvious and convincing. In both cases, he made proposals that were unconventional and therefore somewhat suspicious.

Instead of going into all the intricate detail of the solar-system debate, let us consider the crucial points only. One obvious element of counterevidence for the proposal that the Earth is in motion is direct experience. We simply have no sensation of movement. In line with this, as common sense suggests, if the Earth were in motion, there should be some detectable displacement during the falling of an object, because, by the time the object hits the ground, the Earth would have moved a little. But nothing of the kind is observed. Here we have, therefore, a serious challenge to anyone who wants to argue that the Earth moves. For Galileo, however, this kind of argument was not the most worrying. He rose to this challenge in a spectacular way by establishing the basic principles of relativity. He proved that, for two reference frames in uniform motion, no such displacement should be expected.[14]

The real worrying element of counterevidence was the lack of stellar parallax. If the Earth were really in motion through space, then the nearby stars should show some displacement with respect to the distant stars. Our view of the night sky would be somewhat like what we see from a moving train: nearby trees shifting across the distant background. But no such effect is evident in the night sky. So again, Galileo had a problem. He tried to use his telescope, but it was all in vain.[15] The only way he could respond to this problem was to adopt what had already been suggested by some commentators before him, namely that the absence of stellar parallax was due to the fact that all stars were infinitely far out in space.[16,17] This suggestion, of course, did solve the problem. It was however *ad hoc* and embarrassing – embarrassing because it went against Galileo's own idea that Aristotle had made a mistake in assuming that there is an essential difference between the sub-lunar universe and the rest. For Galileo, the entire universe should be homogenous with a uniform distribution of stars throughout.

So here we see a clear common feature with the previous debate, a common stylistic feature involving the way science was engaged in. In both cases, Galileo faces an insurmountable problem but sticks to his guns; he does not shy away from defending himself by walking on stilts, as it were: by producing auxiliary hypotheses that, because of their *ad hoc* nature, apparently drain his position of its convincing power.

3. CONCLUSION

What conclusion can be drawn? There is of course much more that can be said about all the major points highlighted above. The little that has been mentioned however is enough to justify the following three points. First, we need to accept that the practice of science rarely involves clear-cut crucial experiments that decide an issue at one go. What has been highlighted in both debates confirms the idea, proposed by philosopher Imre Lakatos, that science does not develop according to naïve falsificationism but according to a more complex process involving auxiliary hypotheses.[18] These auxiliary hypotheses can have various degrees of plausibility or acceptability, depending on how they fit in with background beliefs that are shared by both the proponent and the opponent of the theory. The early stages of the new scientific paradigm inaugurated by Galileo were vulnerable. There was no knock-down argument on either side. It is true that, in both debates, Galileo's view did eventually turn out to be correct. At that time, however, his case had some obvious weaknesses, even on his own terms. Secondly, a few words about the Church. Although the way the Church handled Galileo during the solar-system debate remains an embarrassment, especially because of its official declaration that heliocentrism was heretical, which it certainly is not since it is not even theological, the arguments mentioned above can nevertheless help us understand why the case was so intriguing, and why some Aristotelians and theologians were not immediately won over by Galileo's arguments.[19,20] And finally, a word about Galileo's genius: as we know, time proved Galileo right in both debates. This shows that he was a man of genius: he had a way of seeing ahead, a way of seeing beyond what can be expressed by reasoned argument and experiment. We see him sometimes groping in the dark, especially in formulating auxiliary hypotheses, but in fact he was groping in the right direction.

REFERENCES

1. A.C. Crombie, *Styles of Scientific Thinking in the European Tradition: The History of Argument and Explanation Especially in the Mathematical and Biomedical Sciences and Arts*, Gerald Duckworth & Company, London, **1995**.
2. This is discussed in Ref. 3, chapter 3; the following paragraphs owe a lot to Biagioli's excellent study. Other useful sources are Refs. 4-6.
3. M. Biagioli, *Galileo Courtier*, University of Chicago Press, **1993**.
4. S. Drake, *Cause, Experiment and Science: A Galilean Dialogue Incorporating a New English Translation of Galileo's "Bodies That Stay atop Water, or Move in It"*, University of Chicago Press, **1981**.
5. P. Palmieri, *Arch. Hist. Exact Sci.* **2005**, *59*, 189.
6. S. Straulino, C.M.C. Gambi, A. Righini, *Am. J. Phys.* **2011**, *79*, 32.
7. Metaphysics 1042b 25-28 (my translation). The crucial Greek word here is πεπυκνῶσθαι; this is derived from πυκνόω, which means to make close, to condense. Some translators, like W.D. Ross (see Ref. 8), miss the important nuances by translating πεπυκνῶσθαι as 'solidified' instead of 'condensed'.
8. *The Basic Works of Aristotle*, (Ed.: R. McKeon), Random House, New York, **1941**.
9. Aristotle, *De Caelo*, 313b 14-16, see Ref. 8.
10. Aristotle, *De Caelo* 313b 16-22, see Ref. 8.
11. G. Galilei **1612**, p. 98 (my translation), see Ref. 12.
12. G. Galilei, *Discorso intorno alle cose che stanno in su l'acqua o che in quella si muovono* (1612), http://www.ousia.it/SitoOusia/SitoOusia/TestiDiFilosofia/TestiPDF/ Galilei/DiscorsoInSuL'acqua.pdf, last accessed on Jan 03, 2017.
13. The other main texts directly related to this debate include the following. On the side of the Aristotelians: Lodovico delle Colombe, Discorso apologetico d'intorno al Discorso di Galileo Galilei (1612); and Vincenzo di Grazia, Considerazioni sopra 'l Discorso di Galileo Galilei (1613); on the side of Galileo: Benedetto Castelli, Risposta alle opposizioni del S. Lodovico delle Colombe e del S. Vincenzo di Grazia contro al Trattato del Sig. Galileo delle cose che stanno in su l'acqua (1615). This latter author was a friend of Galileo's, but we have now clear indications that this book had been written by Galileo himself.
14. He shows this in "Day Two" of his Dialogue Concerning the Two Chief World Systems.
15. C.M. Graney, *Phys. Persp.* **2008**, *10/3*, 258.
16. This had been proposed by Thomas Digges (c. 1546-1595) in his translation of Copernicus's book *De revolutionibus*; see Ref. 17, p. 207.
17. J.R. Ravetz in *A Companion to the History of Modern Science*, (Eds.: R.C. Olby, G.N. Cantor, J.R.R. Christie, M.J.S. Hodge), Routledge, **1996**, pp. 201.
18. I. Lakatos in *Criticism and the Growth of Knowledge*, (Eds.: I. Lakatos, A. Musgrave), Cambridge University Press, **1970**, pp. 91.
19. For more on how Galileo's ideas where incorporated slowly within the school curriculum during the century following his death, see Ref. 20.
20. L. Caruana in *The Cambridge Companion to the Jesuits*, (Ed.: T. Worcester SJ), Cambridge University Press, **2008**, pp. 243-260.

Substantia
An International Journal of the History of Chemistry

Firenze University Press
www.fupress.com/substantia

OPEN ACCESS

Citation: L. Dei (2017) *I felt reborn* (Primo Levi): from the Nobel dynamite factory to a remembrance place. *Substantia* 1(1): 55-59. doi: 10.13128/Substantia-8

Data Availability Statement: All relevant data are within the paper and its Supporting Information files.

Competing Interests: The author declares no competing interests.

Historical Article

I Felt Reborn (Primo Levi): From the Nobel Dynamite Factory to a Remembrance Place

Luigi Dei

Università degli Studi di Firenze, Piazza San Marco 4, Firenze, Italy
E-mail: luigi.dei@unifi.it

Keywords. Primo Levi, Holocaust, dynamite, literature.

The Periodic Table[1] by Primo Levi has been designed by the Royal Institution of Great Britain "the best science book ever written".[2] Indeed, in this book there is a perfect mixture of science, allegory, chemistry, life, memory, history and human experience. The book is built as a collection of chapters or stories each entitled with an element of the very periodic table by Mendeleev: in total 21 elements each recalling a life experience of the author, the chemist and writer Primo Levi, an author famous in the world as one of the most important witnesses of the Shoah. Primo Levi was born in Turin on July 31st, 1919 to two Jewish families of Provence (France) and Spanish origins. Immediately we discover in his childhood, adolescence, and youth a first paradox of the fate: he could not attend with constancy the primary school due to the very precarious conditions of his health, the same health that in the future will reveal fundamental for his survival in the lager. From 1934 Primo attended the High School Liceo Classico "Massimo D'Azeglio" in Turin where got his baccalaureate in 1937: second paradox of the fate, he didn't succeed in passing the exam of Italian literature – he had to pass a supplementary exam – the subject that made him famous in all the world. In the same years he started to attend the Chemistry Faculty at the University of Turin. In 1938 the Italian government under the Fascist tyranny of Mussolini promulgated the "racial laws" imitating the German anti-Semitism actions. These laws prohibited the University studies to young people of "Jewish race", but allowed them to conclude their studies if they already attended University courses at the coming into force of them. Therefore, Primo Levi succeeded in graduating in Chemistry in 1941 discussing a thesis on the Walden inversion with the grade 100/100 cum laude.[3] In the following two years he worked as chemist in an asbestos quarry close to Turin to extract nickel from the waste of asbestos production and then he moved to Milan to work in a Swiss drug factory. During this period he wrote two little tales – *Nickel* and *Chromium* – that successfully will go to constitute two chapters of the book *The Periodic Table*. In 1943 he joined a Resistance fighting brigade against the Nazi-fascists in Valle D'Aosta, but in December 1943 the fascist militia arrested him and he was imprisoned in a transit concentration camp at Fossoli close to Modena. On February 22nd, 1944 Levi, together with other 650 Jewish prisoners, was crowded in a supply train and taken to Auschwitz lager (Buna-Monowitz) where he remained until January 27th, 1945 when he was liberated by the Russian Army together with only 20 of the 650 calamity companions. At Auschwitz he was registered with the number 174517 which is now carved on the gravestone that remembers him at the Jewish camp of the Monumental Cemetery in Turin. Since he was a chemist and knew reasonably well German, due to his chemical studies at the University, towards the end of 1944 he was recruited to work as a chemist in a factory close to the camp, called Buna, which produced synthetic rubber. During this last period, together with a friend working with him, Alberto Dalla Volta, succeeded in earning a living selling flints for cigarette-lighters, that they succeeded in preparing in the chemical laboratory from some cerium-iron little rods used to ignite the flame of the oxyacetylene torches. This real story originated the chapter C*erium* of the same book *The Periodic Table*. Some days before the liberation of the camp by the Russians he fell ill by scarlet fever and therefore he was abandoned in the sickroom called Ka-be (from the German *Krankenbau*, camp sickroom) by the Germans in fight. His friend Alberto had already contracted this disease and due to the immunity memory didn't fall ill and was compelled to follow the Germans in fight: "Alberto didn't return and no trace remains of him." The homeward journey was long and turbulent and ended after nine months in October 1945: it will be narrated in the book *The Truce* published in Italian in 1963.[4,5] The experience of the concentration camp profoundly shocked him physically and psychologically. After recovering the health he started to work in a paint company – and this paint company named Duco will be at the centre of this contribution since it had been in the past a Nobel dynamite factory– and during this period he met Lucia Morpurgo who then became his wife. During this period he devoted feverishly himself to the writing of a book that was witnessing of his experience at Auschwitz and that will be entitled *If this is a man*.[6] An important role in reinforcing the idea to write his memories of the terrible experience in the lager is attributable to the date with his future wife as he declared some years later stating that she succeeded in allowing him to pass from the painful perspective of a convalescent to that described by himself in *The Periodic Table*: "a work by a chemist who weighs and divides, measures and judges on the basis of firm evidences, and strives to answer the whys and wherefores".

Figure 1. Primo Levi writing an article. By courtesy of Lisa and Renzo Levi.

In 1947 he published this book with the little publisher De Silva – the great publishing house Einaudi refused the book – without any success: of the 2,500 copies only 1,500 were sold and mostly in Turin. At the beginning of 1950s he was engaged by the Siva company which produced paints: after some years he became Director and remained there until retirement in 1975. For more than ten years Levi did not write any book and dedicated himself completely to chemistry.

In 1956 Levi participated in Turin to an important exhibition on the lager deportation where he had great success as witness and he started to attend many meetings in the schools where he received sincere sympathy from the audience. Einaudi decided to print *If this is a man* and this time the success was amazing: immediately the book was translated in English and German under the supervision of the author. Encouraged by the success of *If this is a man*, in 1962 Levi started to write *The Truce*, where he narrated his turbulent return to Turin after the liberation of the camp. The book was published in 1963 and soon gained an important prize, the *Premio Campiello*. In the following literary production he was inspired by his experiences as a chemist, by the observation of nature, and by the impact of science and technology on the daily life. The most representative book of this inspiration was *The Periodic Table*, translated in many languages and defined by the Royal Institution of Great Britain the greatest book for the popularisation of science in the world. On April 11th, 1987 he died falling down from his home stairwell. This episode gave rise to the suspect he took his own life.

Apart from the very famous books above mentioned, *If this is a man* and *The Truce*, two of the most impressive witnesses of the Shoah, the rest of the literary work by Primo Levi is strictly linked to his way of reading the reality as a chemist. In *The Periodic Table*, as stated at the beginning, autobiographic episodes and fiction tales are associated to single chemical elements, each constituting a chapter of this book. Saul Bellow declared: "the book it is necessary to read next. After a few pages I immersed myself gladly and gratefully. There is nothing superfluous here, everything this book contains is essential. It is wonderfully pure, and beautifully translated … I was deeply impressed". Maybe the story of the paint factory called Duco where Primo Levi had the first employ after the Second World War and his terrible experience in the lager is not well known to many people and this is the reason why I decided to write this contribution remembering Alfred Nobel work and life. Using an expression coined by Levi – "stealing others' trade" – I, chemist as Levi, would like to narrate the story of the Nobel dynamite factory in Avigliana close to Turin that became a remembrance place, retracing a chapter of *The Periodic Table*, *Chromium*, seemingly so distant from Nobel and really strictly connected and married into.

In 1872, when the law on the abolition of the government monopoly on the explosives fabrication was promulgated, the *Nobel Dinamite Anonymous Society* in Hamburg decided to found close to Avigliana near Turin a dynamite factory that was called in Italian the *Dinamitificio Nobel* and therefore the dynamite industry was born in that place in that time. The site was selected for security and safety reasons that were necessary for the type of manufacture. Now in the Avigliana territory, in the lower part of the Susa Valley, we can find the monumental remains of the most important explosives factory ever created in the 20th century.[7]

The complex, that represents one of the most significant and interesting examples of architectural industry at the beginning of the 20th century, hosted for more than ninety years (from 1872 until 1965) the most important explosives factory in Europe. It was built by the initiative of a group of five bankers from Paris and of the Alfred Nobel Society in Hamburg. This Society chose this site probably due to two reasons: the important location on the communication axis with northern Europe and the proximity to the railway lines and, maybe mainly, because of the alternation in the territory of flat regions and hill zones that allowed protection of the built-up area from the deflagrations that could be caused by the activity of such industry. In 1908 the Nobel Society purchased other grounds in the surroundings from the Carvotto family to produce new types of explosive powders. In 1925

Figure 2. Verso and recto of a photo portrait of a worker engaged in the test of the gunpowder. By courtesy of Ermis Gamba.[8]

from the small department of the first-born plant called Valloya, thanks to a patent of the American Dupont, the little factory of paints Duco got underway; this complex then merged into the big national Group Montecatini constituted in the frame of the great Italian chemical research lead by the future 1963 Nobel Prize winner, Giulio Natta. During the World War II the area was subjected to bombing and war actions by the Resistance fighters. The successive crisis of the military orders and the changing of the urban planning requirements caused the progressive decay of the industrial complex until the stoppage in 1965: now the remains host a Museum.

A part of the Nobel dynamite factory was destined to host, since 1925, a factory of paint,

« … a large factory on the shores of a lake, the same on which I had learned the rudiments of the varnish-making trade during the years 1946-1947. »

In this factory Primo Levi had his first employ as chemist after the end of the darkness of our continent. In January 1946 all Europe was trying to rebuild new life in peace with strong difficulty: meat and coal rationed, no cars in the streets, but hope and freedom warmed up the people. The period was very difficult even for the chemist Primo Levi: indeed, he felt something different from the others when he started to work close the factory that had produced so many weapons, the Nobel dynamite factory in Avigliana. These were his feelings:

« The things I had seen and suffered were burning inside me; I felt closer to the dead than the living, and felt guilty at a being a man, because men had built Auschwitz and Auschwitz had gulped down millions of human beings, and many of my friends, and a woman who was dear to my heart. It seemed to me that I would be purified if I told its story, and I felt like Coleridge's Ancient Mariner, who waylays on the street the wedding guests going to the feast, inflicting on them the story of his misfortune . »

The Nobel factory was the place where the survival Primo tried to build his new life: indeed he would never succeed in building a new life. His life ever remained sharply splitted in two: before Auschwitz and after Auschwitz. Nevertheless, in that paints factory day by day he started to live again, to reborn. But at the same time this rebirth was accompanied by the reconstruction of the memory, the remembrance of what he had seen and for which he started to build his role of witness. This rebirth is extraordinarily expressed and condensed in his literary art in the tale *Chromium*:

« I, unoccupied as a chemist and in a state of utter alienation (but then it wasn't called that), was writing in a haphazard fashion page after page of the memories which were poisoning me, and my colleagues watched me stealthily as a harmless nut. The book grew under my hands, almost spontaneously, without plan or system, as intricate and crowded as an anthill. »

The book that Levi was talking about is the very famous *If this is a man*. Therefore, the Duco paints factory just in the same environment of the Nobel dynamite factory is the place where Primo Levi wrote, in a wonderful manner as described above, one of the most marvellous book of the world literature. Primo Levi started to work as a chemist and in the meantime to become one of the most famous writer in the world. The Nobel factory witnessed the metamorphosis of a man who had become not-a-man, and that gradually was becoming again a man. Now we know that this second man was no longer like the first one and maybe after many years matured in his mind the thought to draw a close to his days as man / not-a-man / man / no-longer-a-man by returning to nothingness. However, the destiny had decided that this reconstruction of a man from a prisoner had to occur there and that love had to have a beautiful role …

« Now it happened that the next day the destiny reserved for me a different and unique gift: the encounter with a woman, young and made of flesh and blood, warm against my side through our overcoats, gay in the humid mist of the avenues, patient, wise, and sure as we were walking down streets still bordered with ruins. In a few hours we knew that we belonged to each other, not for one meeting but for life, as in fact has been the case. In a few hours ***I felt reborn*** *and replete with new powers, washed clean and cured of a long sickness, finally ready to enter life with joy and vigour; equally cured was suddenly the world around me, and exorcized the name and the face of the woman who had gone down into the lower depths with me and had not returned. My very writing became a different adventure, no longer the dolorous itinerary of a convalescent, no longer a begging for compassion and friendly faces, but a lucid building, which now was not longer solitary; the work of a chemist who weighs and divides, measures and judges on the basis of assured proofs, and strives to answer questions . »*

The absolute original style of writing was germinating in that place: literature that draws ideas, reasoning, and narrating "contraptions" from chemistry and that has made this character of the world literature a kind of *unicum*. The way of remembering the dreadful experience of the Holocaust with an aseptic method that vivisects the events like the scientist analyses the matter and its transformation. This metamorphosis is perfectly explained by the very author in the same tale:

« Alongside the liberating relief of the veteran who tells his story, I now felt in the writing a complex, intense, and new

pleasure, similar to that I felt as a student when penetrating the solemn order of differential calculus. It was exalting to search and find, or create, the right word, that is, commensurate, concise, and strong; to dredge up events from my memory and describe them with the greatest rigor and the least clutter. Paradoxically, my baggage of atrocious memories became a wealth, a seed; it seemed to me that, by writing, I was growing like a plant. »

I believe that now is clear why I decided to entitle this contribution "*I felt reborn* (Primo Levi): from the Nobel dynamite factory to a remembrance place". In a certain sense dynamite, chromium, chemistry, the job of the chemist are all strictly connected with matter, but the way to treat chemistry treats matter can be exactly the same people deal with human events: this is the strong Primo Levi's lesson. The quintessence of this concept is well articulated in the last quotation I would like to add from the tale *Chromium* by *The Periodic Table*:

« *It is the spirit that dominates matter, is that no so? Was it not this that they hammered into my head in the Fascist and Gentile Liceo? I threw myself into the work with the same intensity that, at not so distant a period, we had attacked a rock wall; and the adversary was still the same, the not-I, the Button Molder – a character in Ibsen's Peer Gynt – the Hyle: stupid matter, slothfully hostile as human stupidity is hostile, and like it strong because of its obtuse passivity. Our trade is to conduct and win this interminable battle; a livered paint is much more rebellious, more refractory to your will than a lion in its mad pounce; but let's admit it, it's also less dangerous.* »

We can say that the properties of the elements often reflect the properties of life itself: volatile, inert, lustrous, precious, poisonous, brittle, explosive … I believe Alfred Nobel would have appreciated so much the work by Primo Levi.

In conclusion, the story I tried to narrate thanks to the beautiful help of Levi's writing can be considered the third and last paradox of Primo Levi's life: the Nobel dynamite factory, emblem and symbol in some way of the atrocity of the war due to the product of its activity (the explosives) hosted the "saved" – opposed to the "drowned" – Primo Levi and made him to feel the sensation he condensed in the sentence "I felt reborn".

ACKNOWLEDGMENTS

The author would like to express sincere and deep gratitude to Primo Levi's daughter and son, Lisa and Renzo, for the kind gift of the photo of their father.

The quotations from *The Periodic Table* are drawn from the translation by Raymond Rosenthal first published in the USA by Shocken Books Inc., 1984, first published in Great Britain by Michael Joseph 1985, and finally by Penguin Books 2000.

REFERENCES

1. P. Levi, *The Periodic Table*, Penguin Books Ltd., London, **2000**.
2. http://www.rigb.org/, last accessed on Jan 04, 2017.
3. http://www.chemistry.unito.it/do/home.pl/ViewMobile?doc=history.html, last accessed on Jan 04, 2017.
4. P. Levi, *The Truce*, The Bodley Head, London, **1965**.
5. http://www.wollheim-memorial.de/en/der_roman_la_tregua_von_primo_levi_1963#_edn1, last accessed on Jan 04, 2017.
6. P. Levi, *If This is a man*, Orion Press, **1959**.
7. http://www.provincia.torino.gov.it/culturamateriale/english/tempo_industria/Dinamitificio_Nobel_Avigliana_en.pdf, last accessed on Jan 04, 2017.
8. https://acomearchivista.com/2015/09/09/al-lavoro-nel-dinamitificio-nobel-di-avigliana/#more-229, last accessed on Jan 24, 2017.

Substantia
An International Journal of the History of Chemistry

Firenze University Press
www.fupress.com/substantia

OPEN ACCESS

Citation: S. Gottardo (2017) New Astronomical Observations: Joseph Weber's Contribution to Gravitational Waves and Neutrinos Detection. *Substantia* 1(1): 61-67. doi: 10.13128/Substantia-13

Data Availability Statement: All relevant data are within the paper and its Supporting Information files.

Competing Interests: The author declares no competing interests.

Historical Article

New Astronomical Observations: Joseph Weber's Contribution to Gravitational Waves and Neutrinos Detection

Stefano Gottardo

European Laboratory for Nonlinear Spectroscopy (LENS), 50019 Sesto Fiorentino (Florence), Italy
E-mail: gottardo.stefano@gmail.com

Abstract. Joseph Weber, form Maryland University, was a pioneer in the experimental research of gravitational waves and neutrinos. Today these two techniques are very promising for astronomical observation, since will allow to observe astrophysical phenomena under a new light. We review here almost 30 years of Weber's career spent on gravity waves and neutrinos; Weber's experimental results were strongly criticized by the international community, but his research, despite critics, boosted the brand new (in mid-sixties of last century) research field of gravity waves to become one of the most important in XXI century. On neutrino side, he found an unorthodox way to reduce the size of detectors typically huge and he claimed to observe neutrinos flux with a small pure crystal of sapphire.

Keywords. Gravitational wave, Neutrino, Joseph Weber, Bar detector, Torsion balance.

INTRODUCTION

The astronomic observations will grow rich, in the next few years, two new methods of investigation. Today the sky is observed and measured almost exclusively by electromagnetic radiation. Until 1950 the available radiation was only the visible or near-infrared. Then in the second half of the last century, thanks to enormous technological advances, we added X-ray radiation, microwaves, radio-waves that almost complete the electromagnetic spectrum. These frequencies allowed to discover objects like pulsars, quasars, neutron stars and cosmic background radiation. Many things are still hidden to electromagnetic radiation. An example is the photons (the quanta of electromagnetic field) that come from the sun. The earth is illuminated by a "old" radiation, about 100,000 years old. The photons are created in the center of the sun, but employ about 100,000 years to arrive on Earth surface. The reason is the very high temperature inside our star. Matter is not what we know at such temperature. The core of the sun has a density 150 times larger than water and a temperature of $1{,}5 \times 10^7$ °C. The core is formed by a plasma of ions and electrons, which traps the light. Photons cannot escape from the core, except after a long time, this is because the plasma of ions and electrons is opaque to electromagnetic radiation (the scattering cross section of photons with plasma is much higher with respects to the ordinary matter, where nuclei and electrons form atoms). One type of particles, however, manages to escape quickly from the solar core and to get on the Earth after only 8 minutes, with a velocity very close to the speed of light. These particles are neutrinos. Hypothesized by Austrian physicist Wolfgang Pauli and structured theoretically by Enrico Fermi in the 1920s, neutrinos are elusive particles that do not interact electromagnetically, but only through the weak interaction. They are produced during the nuclear fusion process that occurs in the sun and tell us the types of nuclear reaction that is occurring inside our star. The typical decay that involves neutrino is the so called β-decay, where a free neutron *n* decays into a proton *p*, an electron e^- and an electronic antineutrino $\overline{\nu_e}$.[1]

$$n \rightarrow p + e^- + \overline{\nu_e}$$

Neutrinos can also reveal hidden features in supernovae explosions. The huge flow of neutrinos will invest the Earth when a supernova explodes. The neutrino detectors on the Earth will alert telescopes and radio telescopes on supernova position. In fact, the neutrinos emitted by the explosion will travel undisturbed towards us, while the electromagnetic radiation will need a bit of time, as it will encounter in its path the hot plasma of ions and electrons. There is a worldwide alert on neutrinos called SNEWS (supernova Early Warning System), active since 2005 with the participation of seven detectors around the world including the two Italian LVD and BOREXINO. Neutrino detection can give very precious information on neutron stars' structure and on the merger process between two neutron stars in a binary system.

The very new second method of astronomical investigation is the detection of gravitational waves. According to the present theories, such types of waves are emitted by nearly all astrophysical objects and the most violent ones give off gravity radiations in copious amounts. Supernova explosion observed via gravitational waves can reveal how the star collapse is going on, what happens to star core and how the final explosion takes place. The internal part of supernova will be accessible only to gravitational waves or neutrinos. Another violent astrophysical event is the black holes merging. Two black holes, orbiting one on each other (binary system), release gravitational waves when they become more and more close and at the end an enormous amount of gravity radiation will be emitted when they will merge into a more massive black hole. Black holes are the only massive astrophysical object that cannot be observed directly with electromagnetic waves detectors or neutrinos. Nothing can escape from black hole, neither light. But an exception are gravitational waves that can be observed during the merging of black holes binary systems.

Gravitational waves were predicted in 1916 by Einstein, by finding that they are the carrier of the energy of the gravitational field, as electromagnetic waves transport the energy of electromagnetic field. In 1915 Einstein developed, after seven years, the theory of general relativity[2] that fixed a lot of paradoxes present in the old Newtonian gravitational theory (see Ref. 3 for an introduction to general relativity). The gravity force in general relativity is due to the curvature of the spacetime that is generated by masses (as in Newtonian theory) but also by any form of energy and momentum. Einstein field equation in tensorial notation has a simple form of:

$$G_{\mu\nu} = \frac{8\pi G}{c^4} T_{\mu\nu} \tag{1}$$

where *G* is the gravitational constant, c the speed of light in vacuum. A part from the constants, the equation tells that $G_{\mu\nu}$ called the Einstein tensor that contains the spacetime curvature, is equal to stress-energy tensor $T_{\mu\nu}$. In other words, the stress-energy tensor modifies the spacetime form flat ($T_{\mu\nu} = 0$) to curved ($T_{\mu\nu} \neq 0$). The indexes $\mu,\nu = 0,1,2,3$ (the spacetime has 4 dimensions, 3 space type, 1 time type and the index 0 is usually the time component), so the eq. 1 are in practice 16 equations. It is interesting to see how gravitational waves emerge from Einstein field equation (1), to estimate the order of magnitude of such space time ripples that can be detected on the Earth. The Einstein tensor depends in a complicated way by the spacetime metric $g_{\mu\nu}$ If the space is flat, called the Euclidian space, the spacetime metric is identified by the tensor $\eta_{\mu\nu}$ that is:

$$\eta_{\mu\nu} = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \tag{2}$$

We can suppose for the moment that extreme astrophysical events, like binary black holes merging, happen very distant form our observation point, and that we are in a place where the stress-energy tensor $T_{\mu\nu} = 0$ (no gravity at all). The flat space will become nearly flat when spacetime ripples, caused by some event, will hit our detector. In this weak field hypothesis, the metric tensor $g_{\mu\nu}$ becomes $g_{\mu\nu} = \eta_{\mu\nu} + h_{\mu\nu}$, where $h_{\mu\nu}$ is the correction to flat space and we can consider $|h_{\mu\nu}| << 1$. With the latter two hypothesis Einstein field equation eq. (1) becomes:

$$\frac{\partial^2 h_{\mu\nu}}{\partial^2 x_\mu} = -\frac{16\pi G}{c^4} T_{\mu\nu} = 0 \tag{3}$$

Eq. (3) are now 4 equations since only the index ν survived the index contraction. Eq (3) can be expressed in a more familiar way:

$$\left(-\frac{\partial^2}{\partial^2 t}+\nabla^2\right)h_{\mu\nu}=0 \quad (4)$$

that is the standard wave equation. The solution of Eq. (4) is:

$$A_{\mu\nu}\exp\left(i\omega t+ik_1x+ik_2y+ik_3z\right) \quad (5)$$

where k is the three-dimensional wave vector and ω is the frequency of the wave; so, the spacetime oscillates with an amplitude $A_{\mu\nu}$, after some distant astrophysical event. Eq. (5) is the gravitational wave. The first step to detect gravitational waves is to estimate their strength for a detector on Earth. The order of magnitude of the wave amplitude depends on the phenomena, for example one of the most violent one could be a supernova explosion and a formation of a black hole of 10 solar masses $(10M_\odot)$. Genearally the upper limit for $A \le M/r$ where r is the distance from the event and M is the mass of the object; if it happens in Andromeda galaxy, that is the closest galaxy to our Milky Way, distant from Earth roughly 2,5 million of light-years, $A \le 10^{-17}$. The probability to observe such close and violent event is very rare and the wave amplitude typical for events that can happen two-three times per year is 10^{-21}. So, the target for detector sensitivity should be 10^{-22}. The first who claimed to observe gravitational waves in 1969 was Joseph Weber.[4] He worked in his carrier on both gravitational waves and neutrino, mainly giving an enormous and unique boost to the first one.

RESULTS AND DISCUSSION

In the history of gravitational waves a prominent place belongs to Joseph Weber, American physicist of Maryland University. Early in his career he has proposed a mechanism that explained the proper operation of the laser,[5] but without funds to experimentally prove his idea, has been overtaken by others who have demonstrated the laser mechanism and got Nobel prizes and glory. Forced to change the research field, he went to Princeton University under the supervision of John Archibald Wheeler. Wheeler in the decades 1950-1970 was considered the main expert of general relativity.[6] Weber learned of the existence of gravitational waves and chose them as a research field. He was an experimental physicist, so he decided to design a detector for gravitational waves. After years of study to understand the best way to measure gravitational waves, he decided to use a bar detector, a resonant mass detector that responds to incident gravitational waves by vibrating.[7] The detector was a simple aluminum cylinder, 2 m long and with diameter of 96 cm. Gravitational waves, ripples of spacetime, would compress and then tend the bar. Weber chose the size of the bar to reveal the gravitational wave frequency of about 1600 Hz. He based the choice on very rough estimate. In the early 1960s a clear picture of which astronomical events could emit gravitational waves around 1 kHz was not clear. This frequency is typical of black holes and neutron stars binary systems that with a spiral motion merge and release a large part of their mass via gravitational waves. To measure the deformation of the bar detector, he adopted piezoelectric crystals, which property is that under mechanical deformation respond with an electric voltage, see Figure 1. In measuring this voltage, Weber could understand how his bar has been deformed from a gravitational wave. In the early sixties of last century, Weber was the only experimental physicist who developed a detector and tried to observe gravitational waves, while today there are four operating gravity waves observatories and other under construction or design. In the late sixties,[4,8] Weber began to publish data on the possible extent of gravitational waves. At that point, several research groups started gravitational waves search and adopted bar detectors to try to reveal the ripples of spacetime. No group in the early 1970s, however, was neither able to replicate Weber result's, nor confirm his results.[9] Weber continued to publish results of gravitational waves detection[10] and in the meanwhile he added a new bar detector placed about 1000 km away from the previous one. This method based on the coincidence

Figure 1. Weber's bar detector. Joseph Weber with his bar detector. The small metallic squares on the aluminum cylinder (the bar) are the piezoelectric crystals that were used to quantify the bar deformation. Image credit: University of Maryland Libraries Special Collections and University Archives.

between the two detectors, allowed to identify more easily spurious signals that come from any source but gravitational waves. Since Weber was the only one to detect gravitational, while all other experiments around the world failed, the physics community discredited Weber and his measurements were decreed not reproducible. For many physicists Weber made mistakes or manipulated data in identifying the threshold for gravity waves event detection. As a general rule an experiment must be repeated by anyone under the same conditions in different places and at different times, otherwise it is labeled not reproducible and it means that the original experiment is suffering from some weird error that alters the results.

We will not enter here into the dispute between Weber and the physics community, but a very interesting problem that plagues bar detectors is the uncertainty principle. Quantum mechanics, the theory in physics that very precisely describes the behavior of the infinitely small as atoms and elementary particles, includes the uncertainty principle. If we take an electron and, for instance, we want to measure at a given instant of time its position and its velocity very precisely, we would be disappointed. If we measure its position very precisely its speed will be almost completely indeterminate, and vice versa. So, nature does it on microscopic scales, but what does it happen in the macroscopic world to bar detectors that are two meters long? In 1978 the Russian physicist Braginsky showed that resonant bar detectors were affected by the uncertainty principle.[11] More accurately was the measurement of the position of one end of the bar, more unpredictable was the force that caused the vibration. By making calculations of the intensity of spacetime deformation due to the passage of gravitational waves, one get that powerful gravity waves were about 10 times weaker than the quantum limit of Braginsky for bar type detectors, meaning that the quantum fluctuations were much larger than gravitational wave signal; in other words, the wave amplitude limit of Weber's bar was 10^{-16}, accordingly to uncertainty principle. This could be the main reason for which none, except Weber, detected gravitational wave with bar detectors. The quantum limit will be always present any system, but different detectors have different quantum noise threshold.

Instead of bar detectors, one possible way to measure the deformation of space is to send light back and forth and measure how light travelling time changes. To do this, one can use a Michelson-type interferometer. The light from a laser crosses a beam splitter, which send half to one arm and half to the other interferometer arm (perpendicular to the first). The phase difference of photons in the two arms of the interferometer is correlated. When light comes back from the two arms an interference pattern is visible in the detector. This pattern will change if a gravitational wave will cross the interferometer and stretches and squeezes the spacetime. Interferometers have two main advantage with respect to bar detector, one is that they operate in range of frequency of about 1000 Hz and their sensitivity can reach very large value.

LIGO (Laser Interferometer Gravitational wave Observatory) is formed by 2 interferometers with 4 km long arms. Proposed in 1976 by Kip Thorne,[6] 40 years later in 2016 LIGO observed for the first time directly the ripples of spacetime.[12] To date there are two direct observations of gravitational waves by LIGO that occurred in 2016.[13] The first observation was caused by two black holes orbiting one around each other, with masses respectively 36 and 29 solar masses.[14] After the merge, a black hole of 62 solar masses has been created, while 3 solar masses instead have been converted into gravi-

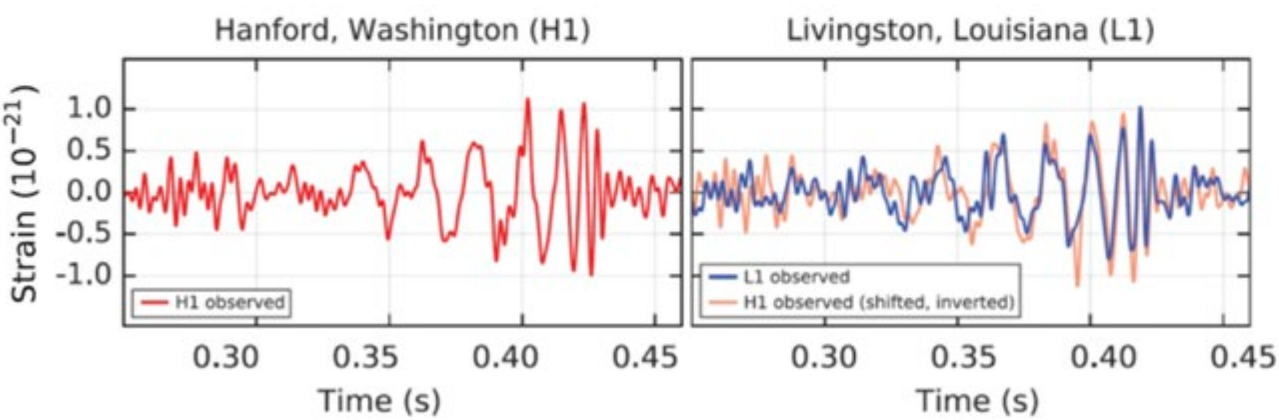

Figure 2. First gravity wave measured. The gravitational-wave event GW150914 observed by the LIGO Hanford (H1, left column panels) and Livingston (L1, right column panels) detectors. Image credit: LIGO, picture taken from Ref. 13.

tational waves that were measured by LIGO detectors. The event was distant from Earth 1,3 billion light-years and generated a wave amplitude (called also strain) of 2 10^{-21}. In Figure 2 the measurements from the two LIGO interferometers were depicted, around 0.4 s the two black holes were merged (courtesy of LIGO, Ref. 13).

There are other detectors similar to LIGO, the more similar is VIRGO, located in Italy, an interferometer of 3 km long arms (see Figure 3). VIRGO was upgraded during LIGO observation and will be in operation early in 2017. The Japanese observatory called KAGRA is under construction in Kamioka observatory, near the neutrino detector Super-Kamiokande, and it should be ready to run in 2018. The interferometric detectors work on frequency range from 10 Hz to 2000 Hz roughly. As for electromagnetic waves, gravitational waves exist in a very broad frequency window. Very challenging for European Space Agency is the project eLISA (Evolved Laser Interferometer Space Antenna), where 3 satellites (distant 1 million km one from each other) will form a giant Michelson interferometer. eLISA will work in a frequency range form few Hz to 10^{-5} Hz (complementary to observatories on Earth) allowing to observe gravitational signals from many astrophysical interesting sources such as binary stars within our galaxy and binary supermassive black holes in other galaxies. eLISA proposed launch date is 2034.

Joseph Weber's work inspired and boosted the research in gravitational waves detection. Kip Thorne, one of the founder of LIGO project, was inspired by Weber's research in mid-sixties of the last century and after a conference, where Weber showed his preliminary experimental work, he decided to investigated theoretically the gravitational waves.[6] Perhaps, without Weber pioneering work, we wouldn't have had any detection of gravity waves in 2016. He used very simple and cheap detector; nowadays we have very expensive observatories and the others planned will be more and more expensive, e.g. eLISA estimated cost is 2,4 billion of USD. On the other side, some research is still running on "alternative" detectors, based on resonant mass detectors. The bar type detector is replaced by spherical mass detector, that use the same working principle of the bar but with the advantage of having a larger frequency range. Two experiments are quite active, Mario Schenberg Brazialian graviton project[14] and MiniGRAIL of Leiden University in the Netherlands.[15] At the current time, no direct gravitational waves observation was reported from these two experiments, due to their quantum limit around $\approx 4x10^{-21}$, higher than LIGO measured signal in the first direct observation (see Figure 2).

Figure 3. EGO observatory. View of EGO (European Gravitational Observatory) that guest the experiment VIRGO. EGO is a French-Italian consortium and the observatory is located near Pisa (Italy). Image credit: VIRGO Collaboration.

The interest of Weber for gravitational waves weakened after the debate with physics community and his discredit on this research field. He continued to receive founding on gravitational wave detection, but he published most of his research on not peer review journals.[16] His interest moved towards another fundamental research line, the neutrino detection. In 1984 Weber proposed a new mechanism to detect neutrinos with a very simple apparatus.[17] Weber theoretical claim involved scattering of low energy neutrinos on an infinite stiff crystal. The weak interaction theory of Lee and Yang predicts a scattering cross section for low energy neutrinos by a quark, that depends on N, where N is the number of nuclei of the medium.[18] Weber coherent scattering theory applied to infinite stiff crystal predicts a scattering cross section that depended on N^2.[19] The major experiments around the world that detect neutrinos from various sources, as for instance ICE CUBE,[20] SUPERKAMIOKANDE,[21] BOREXINO,[22] have detectors formed by enormous amount of liquid-solid material (south pole ice, ultra-pure water, peculiar scintillator respectively). Neutrinos cross section is proportional to the number of molecules N of the detectors, for this reason to increase the probability of detection many experiments use very large amount of matter. The proposal of Weber for low energy neutrinos, applicable for example to radioactive source or to solar neutrinos could enhance instruments sensitivity by a factor of 10^{23} !

The theoretical work of Weber of 1985 was criticized by two papers of 1986 and 1987. The conclusion of both papers is,[23,24] as reported by Butler in Ref. 25: "Weber's derivation of large total cross section is wrong on the basis of elementary physical arguments and that is a result of an incorrect mathematical derivation". Weber in 1988 published a detailed paper where he showed experimentally how "coherent scattering of neutrinos can give measurable force due to coherent momentum transfer to crystal of cm of dimensions".[26] Weber used a torsion balance equipped with single crystal sapphire target. He had three different torsion balances for three different experiments. The low defect sapphire crystal used mimicked the infinite stiff crystal for low energy neutrinos predicted by Weber's theory.[19] In the first experiment, where neutrino energy was 12 keV, the balance was equipped with two identical mass bars. One made of lead, and the second made of titanium tritide, acting as antineutrino source, with an activity of roughly 3000 Ci). The β-decay from tritium created electrons and electronic antineutrinos. Such neutrinos flux is enough to move the balance of a measurable quantity. The measured force per antineutrino was $(1,05\pm0,12)\text{x}10^{-23}$ N cm^{-2} s^{-1}. In the second experiment Weber used the balance to measure the antineutrino flux from a nuclear reactor. In the third experiment Weber measured the solar antineutrino flux (neutrino energy from 0 keV to 430 keV). The scheme of the torsion balance used for solar antineutrinos is shown in Figure 4.

As reported by Weber in Ref. 25: "A diurnal effect is predicted as the position of the Sun changes, relative to the balance. We have been observing the diurnal effect during the past two years, with a peak, when the Sun is in the direction of the line normal to the line joining the two masses". In all three experiments the torsion balance

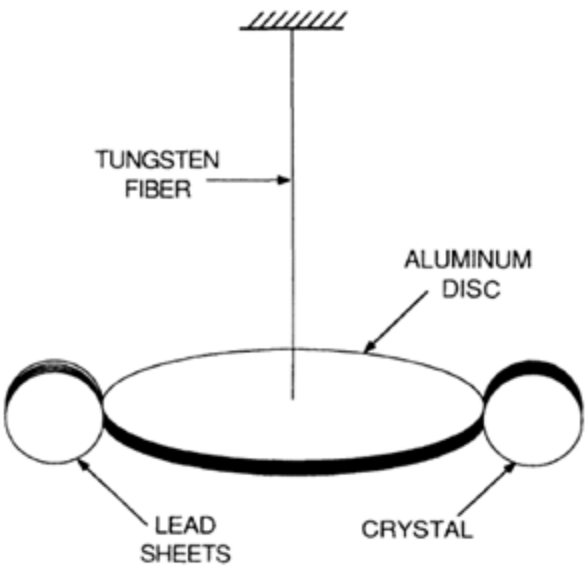

Figure 4. Solar antineutrino detector. Schematic view of torsion balance used by Weber in solar antineutrino experiment, where neutrino coherent scattering from sapphire crystal produced a measurable torque. Picture taken form Ref. 24. Image credit: American Physical Society.

of Weber succeeded to measure the antineutrino flux.

Weber experimental paper, even though the theory of neutrino coherent scattering was considered wrong, were taken seriously by other research groups. The giant effect on solar antineutrinos observed by Weber inspired James Franson and Bryan Jacobs to replicate in a more precise and sophisticated way Weber's observations.[26] They used two torsion balances suspended in a vacuum chamber. The expected different angle between the two balances was measured trough a Mach-Zender interferometer. Weber in his paper in 1988 obtained a value of 0,86 for the efficiency of momentum transfer from antineutrinos to sapphire crystal. The very precise experiment of Franson and Jacobs gave an efficiency of 0,0033. In practice this value represented the lower limit of their apparatus; they measured nothing but apparatus noise. They concluded that their experiment was in strongly disagreement with Weber's one. After that, other three experiments with similar torsion balance were conducted by other teams. All of them concluded that Weber's observation of momentum transfer form solar antineutrinos to torsion balance was incorrect. No team measured any torque from neutrino scattering.[27-29] But in 2011 a team succeed to confirm Weber's experiment on solar antineutrinos.[30] They used a torsion balance under vacuum, with one target of low defect sapphire and the other made of lead. They observed the diurnal effect, with intensity similar to Weber's one. But except from the latter paper, where only preliminary results were reported, no detail study has been published yet. Weber unorthodox theory and experimental proof on neutrino scattering was considered not correct by scientific community, as happened for gravitational waves detection.

CONCLUSION

We reviewed here Joseph Weber's scientific career in gravitational waves and neutrinos detection. These two research fields are today considered the future of astrophysical observation. This demonstrated the intuition of Joseph Weber in working in fields of physics with great prospects. Weber was mainly a solitary researcher; in the majority of his papers he was the only contributing author. This fact was also confirmed by Kip Thorne in Ref. 6, where he reported the affinity between him and Weber in working in loneliness and in unexplored research fields. In the 1970s and 1980s the debate between Weber and scientific community was very harsh. The experimental results of Weber were almost considered not valid. This does not diminish the impulse that Weber's work has given and will give to both research fields. Today neutrino and gravity waves researches are what is called Big Science fields, in the sense of large projects involving large research groups for decades. The challenge is that neutrino and gravitational waves should become Small science, in the sense to have more compact and cheaper detectors. Weber with his experimental intuition performed experiments on both fields with a reasonable amount of money, but unfortunately, at the current time, the physics itself requires larger and expensive experiments to succeed.

REFERENCES

1. B.R. Martin, G. Shaw, *Particle Physics* (3rd edition), Wiley, **2008**, pp. 28-38.
2. A. Einstein, *Preussische Akademie der Wissenschaften, Sitzungsberichte*, **1915**, 844.
3. B. Shutz, *A first course in general relativity*, Cambridge University press, **2009**.
4. J. Weber, *Phys. Rev. Lett*., **1969**, *22*, 1320.
5. J. Weber, *Trans. IEEE, PG electron device*, **1953**, *3*, 1.
6. K. S. Thorne, *Black hole and time warps. Einstein's outrageous legacy*, Commonwealth Fund Book Program, **1994.**
7. J. Weber, *Phys. Rev*., **1960**, *117*, 306.
8. J. Weber, *Phys. Rev. Lett*., **1970**, *25*, 1.
9. R.W.P. Drever, J. Hough, R. Bland, G.W. Lessnoff, *Nature*, **1973**, *246,* 340.
10. M. Lee, D. Gretz, S. Steppel, J. Weber, *Phys. Rev. D*, **1976**, *14*, 893.
11. V.B. Braginsky, Y.I. Voronstov, F.Y. Khalili, *JTEP Lett.* **1978**, *27*, 276.
12. LIGO-VIRGO collaboration, *Phys. Rev. Lett*., **2016**, *116*, 061102.
13. LIGO-VIRGO collaboration, *Phys. Rev. Lett*., **2016**, *116*, 241103.
14. V. Aguiar et al., *Class. Quantum Grav*., **2008**, *25*, S209.
15. A. De Waard et al., *Class. Quantum Grav*., **2005**, *22*, S215.
16. A. Frenklin, *Prospective on science*, **2010**, *18*, 119.
17. J. Weber, *Found. of Phys*., **1984**, *14*, 1185.
18. T.D. Lee, C.N. Yang, *Phys. Rev. Lett*., **1960**, *4*, 307.
19. J. Weber, *Phys. Rev. C*, **1985**, *31*, 1468.
20. R. Abbasi et al., *Nucl. Instrum. Meth. A*, **2009**, *601*, 294.
21. S. Fukuda et al., *Nucl. Instrum. Meth.A*, **2003**, *501*, 418.
22. G. Alimonti et al, *Nucl. Instrum. Meth.A*, **2009**, *600*, 568.
23. G.F. Bertsch, S.M. Austin, *Phys. Rev. C*, **1986**, *34*, 361.
24. M.N. Butler , *Phys. Rev. C*, **1987**, *35*, 1164.
25. J. Weber, *Phys. Rev. D*, **1988**, *38*, 32.
26. J.D. Franson, B.C. Jacobs, *Phys. Rev. A*, **1992**, *46*, 2235.
27. Y. Su, B.R. Heckel, E.G. Adelberger, J.H. Gundlach, M. Harris, G.L. Smith, H.E. Swanson, *Phys. Rev. D*, **1994**, *50*, 3614.
28. J. Luo et al., *Chin. Phys. Lett.,* **1995**, *12*, 36.
29. G. Feng et al., *Chin. Phys. Lett.,* **2006**, *23*, 2052.
30. M. Crucero et al., *Inter. Jour. Mod. Phys. A*, **2011**, *16*, 2773.

Substantia
An International Journal of the History of Chemistry

Firenze University Press
www.fupress.com/substantia

OPEN ACCESS

Citation: V. Schettino (2017) Isaac Newton and Alchemy. *Substantia* 1(1): 69-76. doi: 10.13128/Substantia-12

Data Availability Statement: All relevant data are within the paper and its Supporting Information files.

Competing Interests: The author declares no competing interests.

Historical Article

Isaac Newton and Alchemy

Vincenzo Schettino

University of Florence
E-mail: vincenzo.schettino@unifi.it

Abstract. Isaac Newton dedicated a good part of his activity to alchemical experiments. This article tries to discuss the motivations that drove Newton to spend so much of his time in the laboratory: the search for a unitary vision of the forces acting in the macrocosm and in the microcosm, the belief on a hidden *prisca sapientia* in the occult philosophy to be rediscovered with a scientific approach and the dispute with materialistic philosophy.

Keywords. Newton, Alchemy, transmutation, cosmology, physics.

1. THE SPIRITUAL SIDE OF ALCHEMY

In the popular imagination the idea of alchemy is mostly bound to current definitions that can be found in dictionaries or encyclopedias. For instance, the *Webster's New World Dictionary of American Language* reports that alchemy is:

> *The chemistry of Middle Ages, the chief aims of which were to change the baser metals into gold and to discover the elixir of perpetual youth or Seemingly miraculous change of one thing into another.*

Alternatively, one can find that metaphorically alchemy can be intended as synonymous with subtle artifice or deception. If the story were as simple as this, alchemy would be reduced to a kind of philosophy or pseudo-science definitely passed away, albeit still of interest for a historical reappraisal.

However, in that case it would be quite hard to explain how alchemy could have lasted for more than two millenia.[1] In like manner it is quite surprising that the novel *The Alchemist*, written in the 1980s by Paulo Coelho, had such an extraordinary success to sell more that 100 million copies, with translations in 65 different languages.[2] Yet, the novel is about an entirely alchemical journey. The story is about Santiago, an Andalusian shepherd boy. After a recurring prophetic dream Santiago meets Melchizedek, the misterious king of Salem, who reveals that a treasure is waiting for him at the feet of the pyramids in Egypt and gives him two magical stones, Urim and Tummim, that will show him the path to reach the treasure. [At the beginning of the story we find one of the key features of alchemy, the revelation]. Santiago sells the flock and leaves to Africa, but is soon victim of a robbery and plunges into the deepest misery, remaining with only the two magic stones; it is the black phase of the opus alchemicum. But Santiago succeeds in recovering a good economic condition by hard working for a crystal merchant until he gets in the condition to resume his journey through the desert. Santiago makes three important meetings, the first with Fatima, an Arab girl with whom he falls in love. But he must leave Fatima to continue his journey in search for the treasure. The second meeting is with an Englishman who has studied alchemy and is travelling to meet a famous Alchemist, 200 hundred years old. Santiago learns some alchemy from the Englishman and finally meets the Alchemist who becomes his guide for part of the remaining travel. Finally, and after many adventures, Santiago gets to the Pyramids and finds the treasure, but this is not the philosopher's stone that transmutes metals into gold. What Santiago will discover is the World Language which is in all things and, understanding the nature, with this language he will realize his personal legend. The alchemical journey is thus the attainment of knowledge and a journey of purification and self-fulfillment:

Also the Alchemist, indeed, though understanding the World Language, though knowing how to transform lead in gold, lived in the desert. Without a need to demonstrate to anybody his science and his art. While continuing on the way toward his Personal Legend, the boy had learned all needed to know and had experienced every thing he might have dreamed of.

To better investigate this point let us try to read a brief passage from a treatise on alchemy:[3]

It is possible to create the medicine with different compounds, however it is a single matter and does not require any other extraneous thing, apart from some white and red ferment. Pure and natural, the Opus has no other manifestation; at right times different colours will appear.
The first days it will be necessary to get up early and see if the vineyard is in flower; the following days it is necessary to see if it has changed into raven's head. Later it will change in different colours and among them one must look for the intense white because this is what we expect without error: our king, the elixir or the simple powder, soft to the touch, which has as many names as the things of the world ...

If, apart from the hermetic language typical of alchemy,[4] we simply dwell on the surface of such a description of alchemical procedures, it is apparent that alchemy is an antiquated, faded practice. However, when we consider that this excerpt is taken from the *Tractatus in arte Alchemiae* (Treatise in Alchemical art) attributed to Saint Thomas Aquinas, one of the Saints of the Church and a leading philosopher of the Middle Ages, a reflection is in order. In fact, in Thomas' conception: *Laboratorium est Oratorium* (The Laboratory is an Oratory), which means that the exploration of natural elements that can be looked after in the crucible of the alchemical laboratory is only a pathway to a more substantial knowledge of the truth that is guaranteed by religion. For Thomas alchemy was a moral and religious activity rather than simply a practical or scientific activity and this has been also the attitude of many other philosophers of the Middle Ages and of the Renaissance. Outside this context it would be quite impossible to figure out that a description of the search for the Philosopher Stone, usually taken as a foolish attempt of charlatans and visionaries, can be found in another treatise, *De Lapide Philosophico* (On the Philosopher Stone),[3] attributed again to Thomas:

I also attempted to transform in gold our red Sulphur, after boiling it in aqua fortis on low flame; when this water became red, I distilled it in the alembic and at the bottom of the retort a pure rubedo of the Sulphur remained which I freezed with the aforesaid white stone to make it red. Then I threw part of it over much copper and I obtained very pure gold. However, about this procedure I can only speak quite generally and in obscure word, neither I will reveal it here, in order that anybody wishing to operate will do it not before a full comprehension of the methods of sublimation, distillation, freezing, and of the shapes of the containers and quantity and quality of the flames.

For Thomas Aquinas (1225-1274) alchemy was not a prosaic search for the philosopher stone but a quest of a divine spirit that, in a unified vision, permeates all nature in its material and spiritual manifestations.

2. ISAAC NEWTON, THE ALCHEMIST

A similar attitude toward alchemy has continued a long time after the Middle Ages and is expressed in the following way by Isaac Newton in a letter of his *Correspondences*:

For alchemy does not trade with metals as ignorant vulgars think, which error has made them distress that noble science; but she has also material veins of whose nature God created handmaidens to conceive and bring forth its creatures... This philosophy is not of that kind which tends to vanity and deceit but rather to profit and to edification inducing first the knowledge of God and secondly the way to find out true medicines in the creatures ... the scope is to glorify God in his wonderful works, to teach a man how to live well ... This philosophy both speculative and active is not only to be found in the volume of nature but also in the sacred scrip-

tures, as in Genesis, Job, Psalms, Isaiah and others. In the knowledge of this philosophy God made Solomon the greatest philosopher in the world.

Isaac Newton has been the founder of modern science and an advocate of the scientific rigour who expressed his working method by the motto *hypotheses non fingo*. Newton was very meticulous in his researches and rarely completely satisfied with the obtained results. Speaking of himself he said:

I do not know what I may appear to the world, but to myself I seem to have been only like a boy playing on the seashore, and diverting myself in now and then finding a smoother pebble or a prettier shell than ordinary, whilst the great ocean of truth lay all undiscovered before me.

Yet, Newton dedicated his time almost exclusively to alchemy for some 25 years, in the same period when he completed his *Philosophiae Naturalis Principia Mathematica*.[5-8] Initially, and for several years, he studied with great accuracy all had been published on alchemy, and unpublished works as well, making annotations and résumés and transcribing several texts (see Figure 1). Then he established and equipped his own alchemical laboratory and started to carry experiments. When Newton died, in his library, among others, 169 books were found, 138 on alchemy and 31 on chemistry. Actually, he always tried to consider separately experiments on chemistry and on alchemy. But many other books on alchemy may have been lost when Newton moved from Cambridge to London and, possibly, others were lost during a fire that occurred in his laboratory. Newton never published anything on alchemy but he left notes and writings on alchemy for almost one million of words, a patrimony that has remained unexplored for a long time.

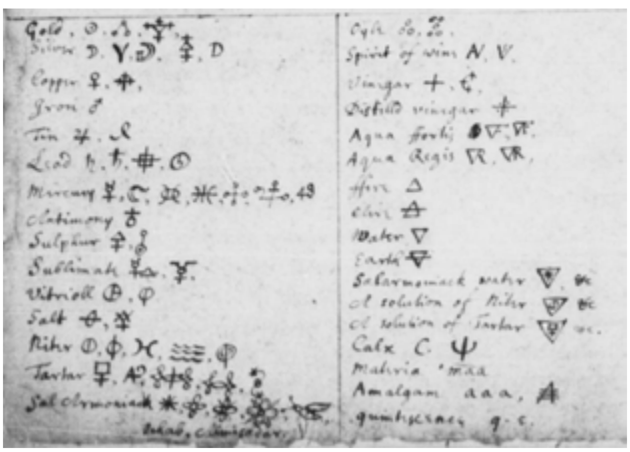

Figure 1. An autograph note by Newton with the alchemical symbols in the *Liber Mercuriorum Corporum*. Partly taken from "The Chymistry of Isaac Newton". Reproduced by permission of the Provost and Scholars of King's College.

The absolute commitment of Newton to alchemical experiments has been described by his assistant Humphrey Newton:[9]

He very rarely went to Bed, till 2 or 3 of the clock, sometimes not till 5 or 6, lying about 4 or 5 hours, especially at spring & ffall of the Leaf, at which Times he us'd to employ about 6 weeks in his Elaboratory, the ffire scarcely going out either Night or Day, he siting up one Night, as I did another till he had finished his Chymical Experiments, in the Performances of which he was the most accurate, strict, exact: What his Aim might be, I was not able to penetrate into but his Paine, his Diligence at those sett times, made me think, he aim'd at something beyond the Reach of humane Art & Industry.

...

About 6 weeks at Spring & 6 at the ffall the fire in the Elaboratory scarcely went out, which was well furnished with chymical Materials, as Bodyes, Receivers, ffends, Crucibles &c, which was made very little use of, the Crucibles excepted, in which he {fused} his Metals: He would sometimes, thô very seldom, look into an old mouldy Book, which lay in his Elaboratory, I think it was titled, – Agricola de Metallis, The transmuting of Metals, being his Chief Design, for which Purpose Antimony was a great Ingredient. Near his Elaboratory was his Garden, which was kept in Order by a Gardiner I scarcely ever saw him do any thing (as pruning &c) at it himself. When he has sometimes taken a Turn or two, has made a sudden stand, turn'd himself about, run up the stairs, like another Archimedes, with an Ε'ύρηκα, fall to write on his Desk standing, without giving himself the Leasure to draw a Chair to sit down in.

By the end of the 1670s and again around 1690s, Newton got into a deep crisis from nervous breakdown and depression touching the madness as it is evident from several letters that he wrote in those periods. The causes of these crisis are not really clear. Certainly Newton was a brilliant man but his family and affective events were rather poor and may have been at the origin of these crisis.

For the purpose of the present discussion it is of interest that a lock of Newton's hair has been analyzed and a high concentration of mercury, in particular, and lead has been found.[10,11] From this result it has been hypothesized the Newton's illness was caused by mercury poisoning. But this inference does not seem certain since the reported symptoms do not seem to correspond to mercury poisoning. The high level of metals in the hair, however, once again demonstrates that Newton spent a considerable time in the alchemical laboratory. To such an extent that John Maynard Keynes, the famous economist which at an auction bought a good part of the alchemical writings by Newton stated that:

Newton was not the first of the age of reason. He was the last of the magicians, the last of the Babylonians and Sumerians, the last great mind which looked out on the visible and intellectual world with the same eyes of those who began to build our intellectual inheritance rather less than 10,000 years ago.

3. THE ALCHEMY MEETS THE MECHANICS

Newton applied to all his alchemical experiments with the same rigour as in his scientific experiments in mathematics, mechanics and optics and, as already noted above, his writings and notes in alchemy are quite consistent. David Brewster, one of the first biographers of Newton, accurately examined all his alchemical writings and, to his disappointment, had to observe that these investigations looked at variance with the idealized picture of Newton as a great scientist:[9]

In so far as Newton inquiries were limited to the transmutation and multiplication of metals, and even to the discovery of the universal tincture, we may find some apology for his researches; but we cannot understand how a mind of such power, and so nobly occupied with abstractions of geometry, and the study of the material world, could stoop to be even the copyist of the most contemptible alchemical poetry, and the annotator of a work, the obvious production of a fool and a knave.

Although Brewster was still convinced that the purpose of Newton, and of his other great contemporaries interested in alchemy, was to rescue alchemy from the condition of a *process commencing in fraud and terminating in mysticism*:

The alchemy of Boyle, Newton and Locke cannot be thus characterized. The ambition neither of wealth nor of praise prompted their study, and we may safely say that a love of truth alone, a desire to make new discoveries in chemistry, and a wish to test the extraordinary pretensions of their predecessors and their contemporaries were the only motives by which they were actuated,

in practice, the alchemical writings were finally considered not fit for publication and were not included in Newton's *Opera Omnia,* as obscuring his fame as a scientist, to remain neglected until the twentieth century.

The reasons why Newton never published anything on his researches on alchemy may be various. In a letter to John Conduit he states that:

They who search after the Philosopher's Stone by their own rules [are] obliged to a strict and religious life,

which complies with the common attitude of alchemists that the secrets of the Great Work should not be revealed to non adepts. In a letter to the President of the Royal Academy, Henry Oldenburg, Newton likewise recommends that Boyle should not make the results of his alchemical researches available to the vulgar because:

It may be an inlet to something more noble, not to be communicated without immense damage to the world if there should be any verity in the hermetic writers, therefore I question not but the great wisdom of the noble author will sway him to high silence till he shall be resolved of what consequences the thing may be either by his own experience, or the judgment of some other ... that is of a true hermetic philosopher ... there being other things beside the transmutation of metals (if those great pretenders brag not which none but they understand).

Apart from this general belief in secrecy, it is more likely that Newton had been unable to sort from his alchemical experiments the answers he was actually looking for and probably wanted to include in the *Principia*. So, the real question is about the actual motivations that made Newton so deeply interested in Alchemy. A hint to the problem can be found in the same Newtons's writings. In the preface to one of the editions of the *Principia* Newton writes:

I wish that we could derive the rest of the phenomena of Nature by the same kind of reasoning from mechanical principle ... For if Nature be simple and pretty comfortable to herself, causes will operate in the same kind of way in all phenomena, so that the motion of smaller bodies depend upon certain smaller forces just as the motion of larger bodies are ruled by the greater force of gravity. It remains therefore that we inquire by means of fitting experiments whether there are forces of this kind in nature, then what are their properties, quantities and effects.

After discovering the laws of gravitation governing the motion of the celestial bodies and of the planets, Newton conceived the idea that the principles active in the macrocosm could have an equivalent in the microcosm:

So far I have explained the system of this visible world, as regards the larger movements that we can easily observe. But any reasoning is valid for larger motions must be valid also for the smaller ones. The first rely on larger forces of attraction of larger bodies, and I think that the latter are dependent on smaller forces, for now not observed, between microscopic particles.

Newton's attempt was to discover this equivalent in the crucible of the alchemist. In essence, Newton was interested in a synthesis of all knowledge, a unified theory of the principles governing the universe. On the one hand this interest derived from the profound religious beliefs of Newton, as described by Yates:[12]

> *As a deeply religious man, ... Newton was profoundly occupied by the search for One, for the One God, and for the divine Unity in nature. Newton's marvellous physical and mathematical exploration of nature had not entirely satisfied him. Perhaps he entertained, or half-entertained, a hope that the "Rosicrucian" alchemical way through nature might led him even higher.*

In his search for a unified theory of the universe Newton may have been attracted by the central concept of alchemy of a *prima materia*, a concept originally attributed to the Greek philosophers and to Aristotle,in particular, of a starting material at the origin of all the materials of the world (a kind of *anima mundi*). A pictorial representation of a kind of alchemical cosmogony in the frame of the four elements (earth, water, air, fire) or alternatively of the *tria prima* (salt, mercury, sulphur) is shown in Figure 2. According to a definition attributed to Arnaldo de Villanova, there is in nature a certain pure matter that art (*i.e.* Alchemy) can discover and bring to perfection such that it can convert to itself all the imperfect bodies of nature by contact. In the Emblem XXXVI of his *Atalanta Fugiens* (see Figure 3) Michael Maier represents the first matter as cubes that pervade all the world as explained in an attached epigram:

The Stone that is Mercury, is cast upon the Earth, exalted on Mountains, resides in the Air, and is nourished in the Waters.

Maier also explains how to find the *materia prima*:

All persons that have once heard of the name or power of the Stone, unless they are altogether incredulous, ask presently where it may be found, that so they may run directly to it. The Philosophers answer is twofold: First Adam brought it with him out of Paradise, that is, in you and in me, and in every man that, birds flying, bring it with them out of far countries. Secondly, it may be found in the Earth, Mountain, Air and Rivers. Which path therefore must be taken? I say, both, but in a different respect, although the last pleases us best, and seems most safe.

But Newton's research for a unified theory through alchemy was unsuccessful and this is likely the reason why his alchemical results were neither included in the *Principia*, nor published in any form. However, concerning Newton's interest in alchemy there are two more points deserving a discussion.

A famous sentence by Newton concerning his major scientific achievements reads:

> *If I have seen further it is by standing on the shoulders of Giants.*

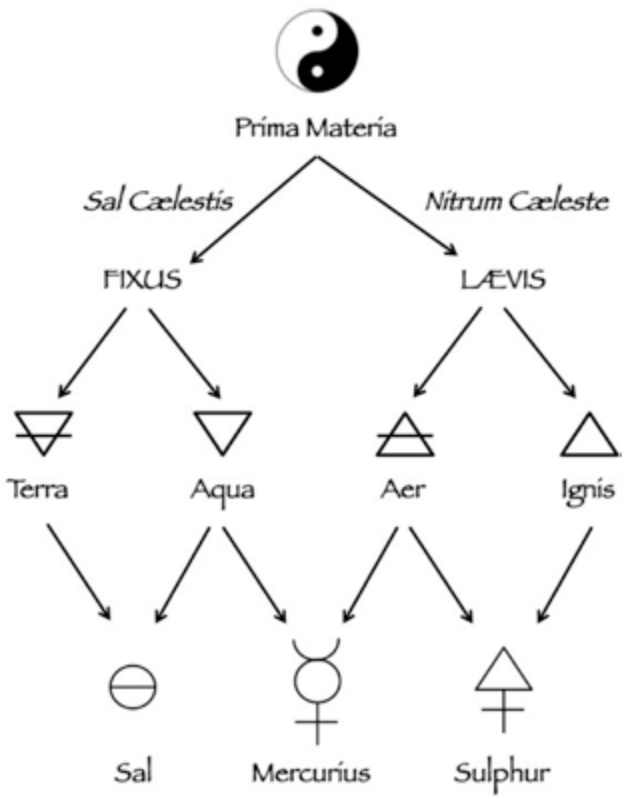

Figure 2. A picture of the unitary alchemical cosmology.

Figure 3. Michael Maier, *Atalanta Fugiens* – Emblem XXXVI. See Ref. 13.

a metaphor, first used in a more elaborate form by Bernard de Chartres:

Dicebat Bernardus Carnotensis nos esse quasi nanos, gigantium humeris insidentes, ut possimus plura eis et remotiora videre, non utique proprii visus acumine, aut eminentia corporis, sed quia in altum subvenimur et extollimur magnitudine gigantea[14]

This same metaphor has later been used by several great scientists to signify that the scientific progress is not simply the achievement of a single leading scientist but is rather a collective enterprise with contributions by a series of researchers from the same and from previous times. The underlying idea in Newton's understanding was that of a *prisca sapientia*. Newton believed that in the earliest times the truth about the natural world was revealed and was in the possession of mankind and that, dissipated in the arcane philosophy, was to be sought in the wisdom of the ancients by a correct interpretation of the occult language of alchemy and the accurate interpretation of the sacred scriptures, as we have already quoted:

This philosophy, both speculative and active, is not only to be found in the volume of nature, but also in the sacred scriptures, as in Genesis, Job, Psalms, Isaiah and others. In the knowledge of this philosophy, God made Solomon the greatest philosopher in the world.

The concept of a primeval revelation of the truth is a characteristic feature of the alchemical philosophy that we already find in the *Corpus Hermeticum* of Hermes Trismegistus, the supposed founder of alchemy:

Hermes saw the totality of things, and, seeing it, he understood; and with the understanding gained the strength to testify and reveal. He wrote down his thoughts and hid most of his writings, sometimes wisely keeping silent, sometimes talking, so that in the future the world would continue to look for these things.

To unravel the secrets of the ancient wisdom and of alchemy Newton proceeded with the same rigour as in the study of mechanics and optics.

A second point worth to be remarked is that the idea of a unitary universe is in harmony with the transmutation of the elements, and of the metals in particular, a transmutation in which Newton definitely believed as we can argue from this statement in *Opticks* (Query 31):

The changing of Bodies into Light, and Light into Bodies, is very conformable to the Course of Nature, which seems delighted with Transmutations.

The unitary concept, in fact, implied the transformation and convergence of opposites like, for instance, it can be seen from Figure 2 for fixed and volatile. Indeed, in Newton's transcription from Hermes Trismegistus we find:

That which is Above is like that which is Below and that which is Below is like that which is Above, to accomplish the miracles of only one thing.

This was an essential point in Newton's ideas about gravitation. In fact, he realized that, although the laws of attraction between the heavenly bodies had been laid down,

Thus far I have explained the phenomena of the heavens and of our sea by the force of gravity, but I have not yet assigned a cause to gravity. Indeed, this force arises from some cause that penetrates as far as the centers of the sun and planets without any diminution of its power to act, and that acts not in proportion to the quantity of the surfaces of the particles on which it acts (as mechanical causes are want to do) but in proportion to the quantity of solid matter, and whose action is extended everywhere to immense distances, always decreasing as the squares of the distances,

the causes that maintained the planets in motion were not clarified:

It is inconceivable, that inanimate brute matter should, without the mediation of something else, which is not material, operate upon and affect other matter without mutual contact … That gravity should be innate, inherent, and essential to matter, so that one body may act upon another at a distance, through a vacuum, without the mediation of anything else, by and through which their action and force may be conveyed from one to another, is to me so great an absurdity, that I believe no man who has in philosophical matters a competent faculty of thinking, can ever fall into it. Gravity must be caused by an agent, acting constantly according to certain laws; but whether this agent be material or immaterial, I have left to the consideration of my readers.

The existence of attraction forces between inanimate bodies at a distance, and not in contact through something intermediate, was not conceivable in the XVII century. The prevailing ideas were rather tied to the mechanist philosophy of Descartes which denied the possibility of any occult force and assumed that the action only depends on contact. The universe is packed with tiny material particles in continuous motion and colliding to form vortices that transmit the interaction. On the contrary, Newton refused this purely materialistic view thinking that the attraction occurred through something immaterial and that the motion of the planets was set by a divine willing. Therefore, in Newton's view, the universe relied on the convergence of opposites, material and immaterial. The dispute about the two conceptions was harsh. From one side, the exaltation of Newton's figure could lead to things like the following drinking song:

The atoms of Cartes Sir Isaac destroyed;
Leibniz pilfer'd our countryman's fluxions;
Newton found out attraction, and proved nature's void
Spite of prejudic'd Plenum's constructions.
Gravitation can boast,
In the form of my toast,
More power than all of them knew, Sir

and on the other side we can find expressions of distrust of Newton's ideas of interaction through the vacuum:

Nor does great Newton's famous system stands,
On one compact foundation, simply plann'd . . .
Reflect how vainly is that Art employed,
Which founds a stately fabrik on a Void;
Can less the fair result of sober thought,
WHO BUILDS ON VACUUM, MERELY BUILD ON NOUGHT

The discussion on the alchemy of Newton has been restricted to what we have called the spiritual side. But Newton heavily worked on the practical aspects of alchemy in a more properly chemical approach with the usual rigour of his method. One aspect of practical alchemy has been the pretention of fools and imposters to obtain miraculous medicines and elixirs, to transform lead in gold and other wonders. As already noted, it has been for these aspects of alchemy that the Newton's work on alchemy has been neglected for a long time. However, the role of imagination and of at first sight improbable ideas for the progress of science should not be minimized. Indeed, Newton writes that:

No great discovery was ever made without a bold guess.

Claude Bernard (1813-1878), the french physiologist founder of the experimental medicine, referring in particular to chemistry, writes that:

Even mistaken hypotheses and theories are of use in leading to discoveries. This remark is true in all the sciences. The alchemists founded chemistry by pursuing chimerical problems and theories which are false. In physical science, which is more advanced than biology, we might still cite men of science who make great discoveries by relying on false theories. It seems, indeed, a necessary weakness of our mind to be able to reach truth only across a multitude of errors and obstacles.

Along the same lines, August Kekulé turned into a legend his discovery of the cyclic structure of benzene

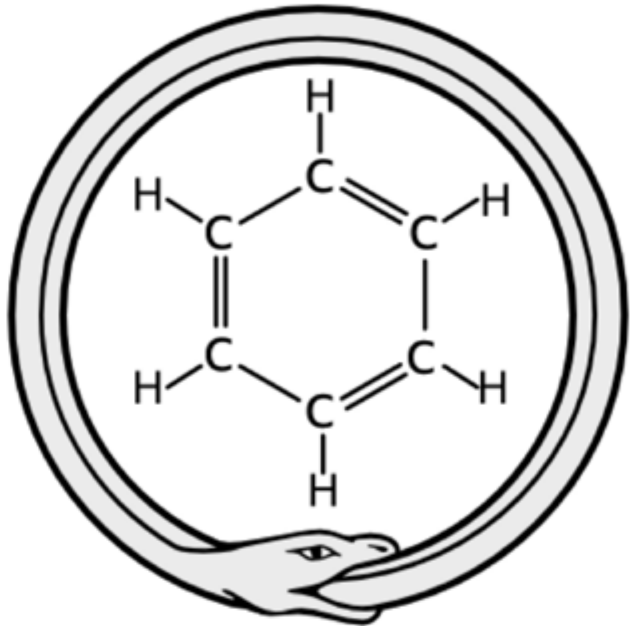

Figure 4. The cyclic molecular structure of benzene and the ouroboros eating its own tail. Image credit: Haltopub / CC BY-SA.

(see Figure 4) ascribing the discovery to a dream were a serpent, the ouroboros, appeared eating its own tail, again an image of opposites that meet. In a famous conference Kekulé, after recalling the metaphor of sitting on the shoulders of giants, concluded exalting the dream and the imagination for the progress of science:

Let's learn to dream, gentlemen, then perhaps we shall find the truth
And to those who don't think
The truth will be given
They'll have it without effort
But let us beware of publishing our dreams till they have been tested by the waking understanding.

Finally, the old dream of the alchemists to transmute one element into another has been realized in modern science, albeit not in the form they really looked for. The realization of today's chemistry closer the to dream of the alchemists to transform a base into a precious, valuable material has been the obtainment at high pressure of diamond, the most precious stone, from graphite or carbon, the most worthless material.

REFERENCES

1. S. Califano, *Storia dell'alchimia. Misticismo ed esoterismo all'origine della chimica moderna*, Firenze University Press, Firenze, **2015**.

2. P. Coelho, *The alchemist*, HarperTorch, New York, **1988**.
3. Tommaso d'Aquino, *L'alchimia ovvero Trattato della pietra filosofale*, Newton Compton Editori, Roma, **2006**.
4. For example, the vineyard in flower stands for green, one phase of the colours of the *Opus Alchemicum* (the Great Work of Alchemy), symbolizing the life force in the leaves of the plants, and the raven's head stands for blackening, another important phase of the great work.
5. M. White, *Isaac Newton. The last sorcerer*, Perseus Books Group, New York, **1997**.
6. B.J.T. Dobbs, *The foundation of Newton's alchemy*, Cambridge University Press, **1994**.
7. B.J.T. Dobbs, *The Janus face of a genius: The Role of Alchemy in Newton's Thought*, Cambridge University Press **1991**.
8. P. Fara, *Newton. The making of a Genius*, Columbia University Press, New York, **2002**.
9. D. Brewster, *Memoirs of the life, writings and discoveries of Sir Isaac Newton*, Th. Constable & Co., Edinburgh, **1855**.
10. L.W. Johnson, M.L. Wolbarsht, *Notes Rec. R. Soc. Lond.* **1979**, *34*, 1.
11. P.E. Spargo, C.A. Pounds, *Notes Rec. R. Soc. Lond.* **1979**, *34*, 116.
12. F. A. Yates, *The Rosicrucian enlightenment*, Routledge, London, **1972**.
13. M. Maier, *Atalanta fugiens*, Johann Theodor de Bry, Oppenheim, **1617**.
14. Bernard the Chartres said that we are like dwarfs, sitting on the shoulders of giants, such that we can see more things and farther away not quite by our own better insight or ability, but because we are brought to a higher position by the gigantic greatness.

Substantia
An International Journal of the History of Chemistry

Firenze University Press
www.fupress.com/substantia

Citation: M. Fontani, M.V. Orna, M. Costa, S. Vater (2017) Science is not a Totally Transparent Structure: Ştefania Mărăcineanu and the Presumed Discovery of Artificial Radioactivity. *Substantia* 1(1): 77-96. doi: 10.13128/Substantia-14

Data Availability Statement: All relevant data are within the paper and its Supporting Information files.

Competing Interests: The authors declare no competing interests.

Historical Article

Science is Not a Totally Transparent Structure: Ştefania Mărăcineanu and the Presumed Discovery of Artificial Radioactivity

Marco Fontani[1]*, Mary Virginia Orna[2], Mariagrazia Costa[1] and Sabine Vater[1,3]

[1] *Dipartimento di Chimica "Ugo Schiff", Università degli Studi di Firenze, via della Lastruccia 13, Sesto Fiorentino (FI) Italy.* E-mail: marco.fontani@unifi.it
[2] *The College of New Rochelle, New York, USA.* E-mail: maryvirginiaorna@gmail.com
[3] *Freiberg University of Mining and Technology, Faculty of Chemistry and Physics, Leipziger Straße 29, Freiberg, Germany.* E-mail: sabinevater1993@googlemail.com

Abstract. A not very recent, but widely documented, event whose echo still resounds, the discovery of artificial radioactivity, might still cause some historians to lose a little sleep. The topic of this article recounts a noble attempt by historians of science to make known to the general public a woman who managed - in a backward country like România Mare[1] - to ascend the ranks of the university hierarchy and enter the hallowed halls of Academe. We could talk about a Romanian Madame Curie, similar to Lise Meitner (1878-1968), who embodied the same figure for the German world; but Romanian historians add other ideas.

Stephanie (Ştefania) Mărăcineanu (1882-1944) - the correct spelling of her name is in brackets - according to some would be nothing less than the discoverer of artificial radioactivity as well as the chemical transmutation of lead into gold and mercury, and of artificial rain. The discovery of induced or artificial radioactivity is universally attributed to the daughter and the son-in-law of Marie (1867-1934) and Pierre Curie (1859-1906). Furthermore, Irène Joliot-Curie (1897-1956) and her husband, Frédéric Joliot (1900-1958) were awarded the Nobel Prize in chemistry 1935 for this work. This study is divided into both an historic framing of the real and presumptive discoveries and in an analysis of the original data in light of our current knowledge of physics. An initial historic study, albeit partial, and with the aim of shedding light on the female personalities in the field of radioactivity, has already been done.[2] Other scholars have examined Ştefania Mărăcineanu's work focusing on its social, political, cultural and ideological aspects.[3] But no matter how much scientists try to be objective, they must always struggle between their beliefs and their human prejudices, including all of their habits of thought more or less imposed, and often inadvertently, by the society and the country in which they are formed.[4] It will therefore be our task to take account of the difficulties hitherto reported, and for that it will be absolutely necessary to exercise judicial restraint.

Keywords. Mărăcineanu, Artificial Radioactivity, History of Chemistry,

SCIENCE WHISPERED ABOUT IN THE HALLWAYS

At the beginning of the 1920s, when the phenomenon of radioactivity had finally been clarified as spontaneous nuclear fragmentation, a series of controversial publications - initially given to the press with the full support of respected professors - appeared in minor journals, as well as in prestigious ones such as *Comptes Rendus* of the French Academy of Sciences.

One example is the controversial case of Marie Curie's not-so-young student, Ştefania Mărăcineanu, who obtained a Ph.D. at the *Institut du Radium* at the age of 42, and within five years, she published some articles containing her scientific results. With a nonchalance at the limit of scientific orthodoxy, she announced four different (false or incomplete) findings: artificial radioactivity induced by alpha bombardment, the transmutation of lead into mercury and gold, the discovery of artificial rain, and an alleged link between earthquakes and radioactivity.[5] Only one of these discoveries, if true, could assure a Nobel Prize; they were of such magnitude that three of them would have placed her in the pantheon of scientists in all of history. On the contrary, if one, or more, of these presumed breakthroughs, so hastily announced, should prove a huge blunder, it would have severely compromised her career.We will set aside for the epilogue of this story a duplicate turn of events: two of the four announcements were immediately branded as examples of "pathological science,"[6] but at the same time Ştefania Mărăcineanu could be found in her home country with a university professorship and membership in the Romanian Academy of Sciences.[7] After her first article on artificial radioactivity, there was no talk of this except as a springboard for her subsequent discovery. Critics attacked her on this second far trickier topic: the transmutation of the elements.

On the one hand, Mărăcineanu did not seem to be aware of the possible scope of her first discovery, and would persist in dwelling on a subject much more intriguing as the transmutation of lead, but this was not acceptable to the scientific community.

Despite the fact that her work on chemical transmutation induced by solar radiation was immediately refuted, on the contrary, decades after her death, in her native Romania, a historiographic approach to her work on artificial radioactivity smacking of a lively, colorful, even aggressive, revisionism had reached a crescendo. Unfortunately many of these enthusiastic interpretations are not supported by the same scientific rigor and the data reported counting on a posthumous rehabilitation are either very weak or ontologically unacceptable because the authors seem to rewrite history for their own convenience. Furthermore, none of the authors were able to produce any new documentation[8] or got themselves lost in a useless speculative extrapolation of phrases taken out of context, passing over the most controversial and fallacious aspects.[9]

In a post-ideological period such as the first decade of the 21st century, freed from certain cultural constraints, greater objectivity is not only possible but required. This is a new task laid upon the shoulders of those who "do" history of science: to be vigilant and never regard certain discoveries as unassailable, and to uncritically accept a new revisionism that might be vaguely nationalistic.[10]

Regarding scientific knowledge: we do not know whether it can and whether it should be considered a cumulative cognitive process and, above all, axiomatic and immutable, but the events related to this episode have in themselves some aspects so conflicting, embedded in an aura of alchemy and xenophobia as to create doubts that "Science" can be advanced as a symbol of progress and civilization.

ARTIFICIAL RADIOACTIVITY

Ştefania Mărăcineanu had begun to work in Marie Curie's laboratory in the early 1920s when she was about 40 years old. In 1923, her Paris address was rue Cassette, 11. It is known that Nicolae Iorga[11] (1871-1940) had founded the „Şcoala Română din Paris"[12] in 1920 and probably Ştefania Mărăcineanu was one of the first scholarship recipients to go to the French capital. At that time, she was busy working on her PhD that she received two years later. In this case we can speak of scientific "maturity," in which a scientist, over the years, has probed and tilled different (scientific) fields and has come to full consciousness of himself/herself and has already given signs of his or her genius.

We have to start by saying that we are basically opposed to using the birth certificate as a yardstick, but it is undeniable that in scientific disciplines such as physics or physical chemistry - unlike love or literature - age is not simply a bourgeois convention, but an objective fact.

Her PhD research was supposed to focus on a more accurate measurement of polonium's decay constant. This element, highly radioactive but with a relatively short half life,[13] was concentrated as much as possible and electrolytically purified. It was the 10th anniversary of the outbreak of World War I: Marie Curie commissioned the no longer young Romanian PhD student to determine this element's decay constant with a level of precision and accuracy unimaginable in 1914, before Europe was falling to pieces.

Table 1. The Naturally Occurring Isotopes of Polonium.

Isotope	*Old Name*	*Z*	*N*	*Isotopic Mass (u)*	*Half Life*	*Type of Decay*	*Daughter Isotope*
^{210}Po	Radium F	84	126	209.9828737(13)	138.376(2) d	α	^{206}Pb
^{211}Po	Actinium C'	84	127	210.9866532(14)	0.516(3) s	α	^{207}Pb
^{212}Po	Thorium C'	84	128	211.9888680(13)	299(2) ns	α	^{208}Pb
^{214}Po	Radium C'	84	130	213.9952014(16)	164.3(20) ms	α	^{210}Pb
^{215}Po	Actinium A	84	131	214.9994200(27)	1.781(4) ms	α (99.99%) β^- (2.3×10^{-4}%)	^{211}Pb ^{215}At

As is now well known, radioactivity may either be natural or induced (artificial), depending on whether nuclear decay is spontaneous or is caused by means of some other nuclear reaction.

In 1924, only natural radioactivity, discovered by Henri Becquerel (1852-1908) in 1896, was known. Marie Curie, the greatest expert in the world in the field of radioactivity, had discovered two naturally occurring radioactive elements (calling them radium and polonium). Certainly she could not have imagined that within a decade of these discoveries, the courage she had exhibited and the intellectual satisfaction she had derived from her life's work would bestow on her a gift with a two-edged sword. Contaminated by her radioactive substances and prematurely robbed of her health, Marie Curie would be brought to her grave in July 1934; in January of that same year, although worn out and suffering from a chronic fever, she witnessed the greatest discovery that ever took place at the *Institut Curie* through the work of her daughter and son-in-law: artificial radioactivity.

As mentioned previously, in 1922, Ştefania Mărăcineanu was trying to record the average half life of polonium in that same period. Polonium (Po) has 33 isotopes, all of them radioactive, the number of nucleons ranging between 186 and 227. The isotope ^{210}Po is a pure alpha-emitter and has a half life of 138.376 days, the longest of its five naturally occurring isotopes (Table 1).[14]

The subject of Mărăcineanu's doctoral research was to accurately and precisely determine the decay constant of element 84. This was, for Marie Curie, a fundamental topic and at the same time a great worry: in fact, the value of the half life varied from 135 to 143 days depending on the source from which the polonium was extracted: for many radiochemists, such a wide range was uncomfortable, and even unacceptable.[15]

At the French Academy's session of June 23, 1923, the newly appointed Academician, Georges Urbain (1872-1938), read Mărăcineanu's PhD thesis to the assembly. The polonium used came from ampules of *emanation* [*i.e.*, radium] which had been previously used for medical purposes. The electrolytic process for the obtaining of the polonium-free radium-D impurities [*e.g.*, Pb; see Table 2, below] had been developed in the chemistry laboratory of the *Institut du Radium.*

A drop of polonium chloride, $PoCl_2$, solution was deposited on a metallic or glass plate and left to evaporate. The plate was subsequently rinsed with distilled water to remove traces of acid. An ionization camera, complete with a piezoelectric quartz electrometer (as a current compensator), to detect alpha particles allowed for the determination of the activity of the radioelement - in the form of an electric current - over the course of time. Mărăcineanu was able to derive polonium's decay constant by measuring the logarithm of the current against time.

Ştefania Mărăcineanu conducted numerous experiments divided into two series: the first series of 38 measurements was carried out between March and May of 1922. She re-covered the polonium with slips of aluminum foil of varying thicknesses between 3/1000 and 7/1000 of a millimeter. In the second set of measurements, which began in May, she offset the aluminum sheet by 1 mm from the plate on which she had deposited the polonium.

Table 2. The Products of the Decay of Radium-226.

The products of 226Ra decay were initially called radium-A, radium-B, radium-C, etc. Later they were understood to be other chemical elements	Chemical Symbol of the Isotope
Emanation of radium (Em)	^{222}Rn
Radium A	^{218}Po
Radium B	^{214}Pb
Radium C	^{214}Bi
Radium C_1	^{214}Po
Radium C_2	^{210}Tl
Radium D	^{210}Pb
Radium E	^{210}Bi
Radium F	^{210}Po

Ştefania Mărăcineanu derived a half life equal to 139-140 days in all cases except when the measurements were recorded on a lead plate. In this case, the value was shorter: 135 days. Concerned with this unexplained variation of what was supposed to be a constant, she began to conduct a series of additional experiments to determine the reason for this anomaly. Thanks to previous work done by Marie Curie in 1920, she could exclude the presence of ^{210}Pb, radium-D, from the sample. She also examined the aluminum sheets and observed that they were not radioactive. A likely source of error could have been the effect of saturation for measurements conducted over a long period of time (greater than 136 days), but in this case as well, Ştefania Mărăcineanu had taken drastic precautions. The result left no doubt that no error had been committed, so much so that the Director of the *Institut* in person, Marie Curie, felt compelled to give an interpretation to the phenomenon observed: she said she witnessed a "penetration of polonium into the substance used to support it."

Marie Curie asked her to conduct a third set of measurements in support of this hypothesis, and this was completed in December, 1923. The diffusion phenomenon increased when the support was heated; the phenomenon was observed over a range of metal supports. If the support were glass, no penetration (diffusion) effect of polonium into the support was observed. However, the problem was not resolved: at first it was assumed that the disintegration of the polonium helped it to penetrate lead's crystal lattice. This conclusion was rather hard to accept. Later she resorted to the hypothesis of microcracks (or faults) in the metal support. This allowed her to shelve the problem for a short time. A practical arrangement made it possible to calculate the decay constant: diluted solutions were used,[16] no heat was applied, and glass was substituted for lead as the solid support.

INDUCED RADIOACTIVITY BY SOLAR RADIATION

Having finished her PhD with Marie Curie, Ştefania Mărăcineanu continued her research first in Romania (for a short time) and later at the Institute of Optics at the Meudon Observatory, near Paris, under the supervision of Henri Deslandres (1853-1948).

Mărăcineanu noticed that the decay constant of polonium, far from remaining immutable, varied depending on which metal was used as a support for the sample. She also noticed that the atoms of the substrate were "transformed" into radioactive isotopes. In all this, her superiors suspected nothing, but not for the reasons that the supporters of Ştefania Mărăcineanu eventually gave. If what she timidly asserted had really happened, this experiment would have shed light on the phenomenon of artificial radioactivity ten years in advance. It was not so, and, as we shall see, could not have been otherwise.

Continuing her doctoral work, in an article of November 25, 1925,[1] Ştefania Mărăcineanu suggested that sunlight could have an action on the radioactive decay of uranium and polonium.

After extended periods of exposing sheets of non-radioactive lead to direct sunlight, they would later be shown to be radioactive. Likewise, uranium oxide, if exposed to sunlight, began to show a change in the decay process, a variation that Mărăcineanu called "curious periodic variations." She tried many other things, but only Pb and Sb exhibited such behavior. After exposure to the sun these elements were able to:

- Expose photographic plates
- If placed in front of a zinc sulfide screen (detector), many scintillations were observed
- Lead or a Pb/Sb alloy exhibited a weak ionization current, detectable with an electroscope.

Over the years Marie Curie had also observed a change in the decay constant of uranium, with an order of magnitude of about 3%. Ştefania Mărăcineanu stated that by the action of sunlight, this change was amplified up to 50%.

On August 2 of the following year, Ştefania Mărăcineanu published a further note in which she pointed out the progress of her discoveries,[18] with reference to the observed solar effects on polonium. She placed a drop of a solution of highly purified polonium chloride on a somewhat thin lead sheet (1/10 mm). The polonium-210 she used was a pure alpha emitter. At the atomic level, 0.10 mm of lead is extremely thick and easily stops the alpha particles emitted by polonium, but inexplicably, she discovered an ionization current on the opposite side of the metal plate which was not exposed to the alpha source. She could think of only two reasons for this effect: induced radioactivity OR the following hypothesis.

Polonium is a very strong alpha emitter, but Ştefania Mărăcineanu dismissed this fact. As a side effect (which, for Ştefania Mărăcineanu, was the primary effect), she observed that if the lead sheet on which the polonium solution had been deposited were exposed to the sun or kept in the shade, the ionization current varied widely. At the conclusion of her work, Mărăcineanu reported: "One might have thought of a penetration of polonium from one side to the other of lead, but if this were the case, one would have had to have a loss of polonium inside the lead, which has not been observed".[19]

This sentence could have been the starting point to see if, indeed, the scientist had observed the phenomenon of artificial radioactivity, but how often does it happen that ideas ahead of their time are overlooked or dismissed? And she herself, first of all, put forward a very different explanation for the observed phenomenon.

By further work on polonium decay curves in bismuth, curves obtained from experimental observations after deposition of the polonium and before irradiation, Ştefania Mărăcineanu speculated that the facts "... seem to show that solar radiation can cause the reintegration of Radium-E [Bi] from Radium-F [Po], and thus can cause a reversal in the radiation series".[20]

This unorthodox hypothesis, based on an actual observation but certainly misunderstood, should have been immediately rejected, both by Marie Curie, her former director, as well as by Henri Deslandres. Things did not go well. Curie - maybe - was busy with wedding preparations for her daughter Irène, who was to marry the young and promising engineer, Frédéric Joliot (who would be assured a more flexible career by marrying the daughter of his employer). Henri Deslandres, on the other hand, was an astro-physicist who had done all of his scientific work before the mere mention of "radioactivity" was whispered by Marie Curie to her husband, Pierre, in the late 19th century. At the time, he was 73 years old, much older than Pierre Curie, and perhaps too sidelined at this point to contribute to the debate by siding in favor or not of this hypothesis. But this was not the case. As we will see in three notes, which appeared in the *Comptes Rendus*, he encouraged and praised the work and discoveries of Ştefania Mărăcineanu.

A further communication from Ştefania Mărăcineanu appeared in *Comptes Rendus* reporting on the session held on May 30, 1927.[21]

In this case as well, Marie Curie never said a word.[22] Perhaps she was occupied both within and outside of the laboratory walls with many other affairs: after her daughter's wedding on October 9, 1926, her new son-in-law was promoted, to the great chagrin of Marie Curie's long-standing collaborators, to the rank of "Prince Consort".[23] Irène, meanwhile, was "in a family way",[24] and Marie was "experimenting" with the idea of becoming a grandmother.

Following the advice of her colleague Lebel, Ştefania Mărăcineanu began to study the radioactivity of the lead sheets used as covering for French public buildings and therefore exposed to the sun's rays from time immemorial. It happened that the Paris Observatory's roof was covered with lead sheets. Ştefania Mărăcineanu, as she herself confessed a year later, climbed up to the top of the cupola and at high risk began to scrape off some of this roof covering in order to subject it to analysis. Since she found that the samples' radioactivity was so high as to be off the scale, she assumed that the lead - radioactive by solar induction - had an extremely rapid decay rate. As a matter of fact, Mărăcineanu carried out her measurements three times a day, after breakfast, lunch, and dinner. But not only that, said she: "at noon, when the sun hits the instrument, the lead appears to become twice as active...".[25]

To compare these results with ordinary lead, she also prepared daily a solution of "white" lead by treating commercial galena (PbS) with acid,[26] and observed: "Commercial lead, prepared every day with galena, is not, as is known, radioactive…".[27]

Henri Deslandres, her advisor and director of the observatory at Meudon, was so favorably impressed with Ştefania Mărăcineanu's research that he published a brief note[28] in the margin of the previous article where, in the euphoria of discovery, sent out an enthusiastic appeal to readers: "The people here have lead (that has lain) for a long time in the sun, and who do not have the necessary apparatus to do research on radioactivity, are asked to send a sample to the Observatory of Paris".[29]

The research was begun in earnest. Twenty days after the last communication a new work appeared[30] by Ştefania Mărăcineanu in *Comptes Rendus*. Following the advice of her director, she extended her research to other metals besides lead and polonium, such as copper and zinc. These last two elements were, like lead, used for the protection of the limestone ledges of the observatory. Ştefania Mărăcineanu collected specimens of them and observed that the surfaces hidden from the sun's rays exhibited no radioactivity.

She posed the dilemma of whether the radioactivity might be due to atmospheric radioactivity deposited over the years on coatings of copper and zinc, but in a short time disproved this hypothesis because there was no any trace of radioactivity in the blocks of limestone. This article, too, was followed by a laudatory note[31] by her superior - about as long as the article which preceded it:

"Mademoiselle Mărăcineanu's research on the old roofs of the Observatory of Paris is of increasing interest. Lead is not the only metal that acquires, under the influence of the sun's rays, a special radioactivity…".[32]

Dwelling on the more practical aspects of how to continue these experiments, Deslandres pointed out that the radioactivity - that we can define as induced - was not attributable to the diffusion of only radioactive bodies as happened for polonium, but it was an established fact that it was a special action of light on matter and could be said that it clarified the action of ultra-X rays, very penetrating X-rays, whose cosmic origin was demonstrated by Werner Kolhörster (1887- 1946),[33] Robert A. Millikan (1868-1953) and Russell M. Otis.[34]

Deslandres expressed a personal interest in the research of his Romanian assistant because it allowed him to reminisce over events that had occurred more than thirty years before when, in 1896, he had observed the emission of particles and X-rays from the sun, the other planets, and nebulae. These 19th century works were collected in a monograph[35] in precisely the year in which Ştefania Mărăcineanu began her collaboration with him.

Ştefania Mărăcineanu's third article[36] in 1927 appeared on July 11. In this case as well, at the suggestion of Henri Deslandres, she repeated the experiments of depositing polonium solutions on 0.1 mm thick lead plates. But this time, again at Deslandres' suggestion, she subjected the plates to a potential of 120,000 volts. For the occasion, they had to dismantle a large transformer that operated the observatory and dedicate it to this use.

After depositing the polonium solution, the experimental samples were divided into four groups:

1. plates not subjected to any potential
2. plates subjected to high voltage only
3. plates subjected to high voltage and solar radiation simultaneously
4. plates subjected only to solar radiation

In these cases, radioactivity was not observed on the surfaces of the lead plates not exposed to polonium; despite the fact that an extremely high voltage was applied, no nuclear rearrangement could be said to have taken place because there was no substantial difference between samples 1 and 2 . This was certainly a negative result. However, increased radioactivity continued to be observed in the samples exposed to the action of sunlight.

For the first time Ştefania Mărăcineanu reported the following phenomenon: "It has been observed that the ionization current exhibited on the opposite side (of the plate) is proportional to the initial amount of polonium deposited".[37]

But what is even more surprising is Ştefania Mărăcineanu's almost prophetic conclusion. Apparently, following the reasoning that she reported in the article, it seemed evident that Henri Deslandres, the teacher with his "forced suggestion" and counterproductive increase in the complexity of the experiments, derailed the entire project.

However Mărăcineanu remained stubbornly faithful to her earlier ideas; stripping the experiments bare from unnecessary complications derived from sunlight or high voltage, she seemed to really observe the phenomenon that less than ten years later would take the name of artificial radioactivity and so she closed the the article with the words:

If we consider the appearance of the curves, the ionization current, which increases daily by itself, passes through a maximum, then decreases according to an exponential law, as happens when a radioactive substance is formed, develops, and then decays. I think that a new radioactive substance is being formed in the body of the lead.[38]

Again Henri Deslandres wanted to comment with a note on the work of his student.[39] Outside of congratulating her and highlighting the enormous importance of the subject in the scientific landscape and recognizing its extreme complexity, he added almost nothing new.

Meanwhile the alleged discovery of radioactivity induced by solar radiation gave Ştefania Mărăcineanu an unexpected fame on a global level:[40] within a short time she became the most famous Romanian scientist in the world. The field of radioactivity lent itself to this sort of thing: it was a relatively new field of research; it was a kingdom ruled by a tiny little woman that she, Marie Curie, had created herself and the "world of little nations" wanted to have at home a "little Curie," to pamper and show off to exalt their own homegrown glories to their citizens. In a late positivist spirit, radium was viewed as an instrument of human progress, the weapon to fight cancer, which, in the years of industrialization, was defined by the late-19th century Pharmacopoeia as the most widespread and insidious disease, which nothing could oppose. All this, like a fairy tale, fascinated the public and newspapers competed to bring - often with sensationalist reportage - the most diverse and contrary reports, both scientific and pseudo-scientific, to the attention of the public. Among these they found wide-ranging opportunities in Ştefania Mărăcineanu. Already in 1925, during his official visit to Paris, King Ferdinand I of Romania (1865-1927) and his wife, Queen Marie of Edinburgh (1875-1938), invited Ştefania Mărăcineanu to demonstrate her scientific achievements to them. The queen, impressed by the work of her compatriot, took her personal prerogative to subsidize her research on chemical transmutation. In 1929, in Iasi, Ştefania Mărăcineanu received the award in memory of the recently-deceased King Ferdinand given by the Foundation of the same name.[41]

THE ANNOUNCEMENT OF THE DISCOVERY OF CHEMICAL TRANSMUTATION

1928 marked a year of more radical change. In March of that year, in fact, Ştefania Mărăcineanu published together with her director, Deslandres, a further development on the research on this phenomenon.[42]

From January 20 to February 17, Ştefania Mărăcineanu exposed to sunlight not only lead, but also old copper, aluminum, iron and zinc plates. She repeated, in parallel, experiments with other samples of the same elements, but obtained from commercial venues. Only lead showed radioactivity. With a complex reasoning resulting from a series of measurements, she excluded the idea that the specific activation of lead derived from a radioactive emanation from the atmosphere (external contamination). A careful study of the results led Ştefania Mărăcineanu to a suddenly change the ideas that she had espoused in the previous summer and she asserted instead: "In my experiments on lead, I have always found (decay) periods of this order of magnitude and at one point I thought of a reintegration of lead into polonium by solar energy".[43]

In other words, after an understandable hesitancy, Ştefania Mărăcineanu, announced that she had observed a chemical transmutation process by the action of sunlight. She reported that this phenomenon could be explained if associated with another inexplicable phenomenon, the presence of alpha particles, and the appearance of extremely penetrating rays (γ rays, perhaps, but these are not specifically named).

As a corollary to this controversial hypothesis, Ştefania Mărăcineanu speculated that the change in the decay constant of polonium was due precisely to this phenomenon. This would explain why, four years before, she had obtained such a variation in her data.

A year passed and Ştefania Mărăcineanu left France for her native Romania. We do not know the reason for this more or less voluntary removal from the observatory at Meudon. In her native country she gave to the press an article[44] having as its subject the effects of solar radiation on radioactive phenomena and transmutation. It was work conducted in France, described in summary in some communications in *Comptes Rendu*s, but quoted in full in Romania. If it had been national pride or an ill-concealed desire to reduce the effects of a likely fiasco that drove Ştefania Mărăcineanu to explicitly publish the phenomenon of transmutation of the elements in a Romanian journal is not known. The fact is that, in this work, values were observed in the spectroscope, *i.e.*, the appearance of spectral lines, attributable to elements that would be formed by the transmutation of lead explicitly appear. In confirmation of this hypothesis, the appearance of helium (alpha particles) and mercury lines were observed. In both publications, that of 1928 in the *Comptes Rendus* and that in the *Bulletin de la Section de l'Academie Scientifique Roumaine*, the word transmutation is not to be ascribed to an alchemical concept, but to the idea of radioactive decay (or its unlikely opposite: "radiative accretion"). If we must impute any kind of an error to Mărăcineanu, it would be to have formulated the concept of chemical reversibility in the process of radioactive decay, and to accept the fact that lead was not the end of the line for the thorium and uranium decay series (that includes radium):

$Pb + \alpha \rightarrow Po$
$Pb \rightarrow Hg + \alpha$

The extensive work of Ştefania Mărăcineanu consisted of numerous pages and photographs of samples taken from lead roofs that had been exposed for centuries to solar radiation. She took her time about her means of investigation, employing a few tricks to enhance the observed effect and in the end she added a note in italics that could not go unnoticed:

"The action of solar radiation could possibly cause a transmutation of 0.001% lead in gold".[45]

At the end of the article after the usual sentences relating to the circumstances of the work that scientists always expect, with a little bit discovered and much more to do, you can read in *ad hoc* italics, like a Wagnerian finale, the words:

> *But it is in solar radiation that one must recognize the philosopher's stone and the source of formidable radioactive energy, which will become needed more and more.*[46]

The year 1929 opened auspiciously for Ştefania Mărăcineanu. Her publications appeared both in Romania and in France and her work could be said to be truly cutting edge. Many scholars began to repeat her experiments, seeking to confirm her observations, but also to shed more light on an effect of nature that she had discovered and that she too easily had wished to define using such "hot button" words as "transmutation" and "philosopher's stone."

THE OLYMPIC CALM OF THE EUROPEAN COLLEAGUES COMES TO AN END

By return mail, Professor Nicolae Vasilesco Karpen (1870-1964), who a few days earlier had presented Ştefania Mărăcineanu's work to the Romanian Academy of Sciences, was forced to report a preliminary note under the signatures of Charles Fabry (1867-1945) and E. Dubreuil in which the two French physicists expressed their censure of tests carried out by the Romanian scientist that they repeated in their Paris laboratory: they were the experiments relating to the transmutation of lead into gold, mercury, and helium.[47]

They pointed out:

> *The experiments in question were conducted with results exactly contrary to those reported by Mlle. Mărăcineanu.*[48]

That was the first salvo that began to discredit the Romanian researcher's work. Shortly thereafter, she was the object of a great deal of criticism for her real or alleged discoveries. First the French, and then many other scientists, began to pour down condemnation on her like so many arrows.[49]

On February 22 of that same year, it was the Director of the *Institut du Radium* herself, Marie Curie, who pressed Mlle. Eliane Montel[50] (1898-1992) into service to investigate the embarrassing phenomenon of induced radioactivity discovered in the heart of her own laboratory.

Montel studied the evidence in great detail with the aid of a rigorous photographic analysis; the methodology followed was that of Ştefania Mărăcineanu, but she obtained very different results: as Mărăcineanu observed, a lead sheet on which was placed a solution of polonium hydrochloride exhibited radioactivity after the polonium had been removed. However, the radioactivity observed was not due to its induction by polonium in the lead as Elizabeth Róna (1890-1981) and E.-A. W. Schmidt demonstrated,[51] but to its penetration through microscopic cracks, between the lead crystals, and conveyed by the presence of a weakly acidic environment. This hypothesis was suggested to Eliane Montel by Fernand Holweck (1895-1941) and her laboratory subsequently tested it. Lead sheets were melted and then cooled so as to obtain crystals whose dimensions were visible to the naked eye. Then a solution of polonium hydrochloride was deposited on the sheets and their radioactivity was monitored photographically. What struck Eliane Montel was that on her photographic emulsions she saw the outlines of lead crystals, *i.e.*, the regions where the polonium had penetrated them. Eliane Montel asserted without a doubt that polonium passed through the lead only in the zones which she called "faults." It was a clear proof that damaged the hypothesis advanced by Ştefania Mărăcineanu on induced radioactivity.

A few months later, on May 25, 1929, the Dutch professor A. Smits and his assistant Mlle. Caroline Henriette MacGillavry[52] (1904-93) published an extensive piece of research[53] on another aspect of Mărăcineanu's work: the radioactivity of lead induced by solar radiation. Their work was conducted on sheets of lead from the roofing of the Observatory of Paris as well. The results were encouraging and gave confirmation of the comments previously made by Ştefania Mărăcineanu.[54]

Smits and Mac Gillavry reported the following:

> *... these results were perhaps of great importance because if the lead really is activated and emits α particles, it is likely that there is a transmutation of lead into mercury.*[55]

This was the first, albeit modest, confirmation Ştefania Mărăcineanu's work outside of French and Romanian borders, but it was short-lived. On February 9, 1930 she wrote from Paris, where she resided at 9 Rue Ernest Cresson, to her friend Alexandrina Fălcoianu.[56] It is an excerpt of a letter that foreshadows possible friction between her and her French colleagues:

> *I will fight, dear lady, for me, for justice, the honor of our country, and for women.*[57]

A few months later she will have come back to Romania for good. In fact, a deed of patent on artificial rain, dated June 10, 1930, gives her address as Boulevard Col. Mihai Ghica n. 57, Bucharest.

Six days before she drafted the letter to her friend, February 3, 1930, the French physicists Charles Fabry and E. Dubreuil officially opened hostilities against Ştefania Mărăcineanu and released a statement which seriously criticized her work and her heterodox theories. The two French colleagues also neglected to mention Mărăcineanu's earlier work that had appeared in the very same *Comptes Rendus*, as well as the encouraging articles of the famous astronomer, Deslandres, which had supported Ştefania Mărăcineanu. Even if they were correct, it was a petty attack on a "foreigner" as well as a chauvinistic attempt to make sure that a French institution was not tarnished.

The experimental work was conducted by E. Dubreuil at the *Institut d'Optique*. He had repeated the Romanian researcher's same experiments but ended up getting totally negative results, even in the case of lead.

Her reply was swift: seven days later, Ştefania Mărăcineanu transmitted her reply in the pages of *Comptes Rendus*.[58] It was, however, weak both in tone and in content. She realized she was a foreigner and could not reply to such aggressive criticism in the same tone with which she had been attacked. She hypothesized that her colleagues, Fabry and Dubreuil, had scraped lead from the observatory roof in the precise places where she had taken her samples and by so doing, they would have analyzed the underlying layer, which had not been exposed to sunlight for the centuries to which her own samples had been subjected. In addition, Ştefania Mărăcineanu openly reprimanded Dubreuil, saying that when she was at the Institute of Optics, he had provided the spectra and had offered to interpret them.

The Romanian researcher acknowledged the negative assessment of her work and tried to scientifically counter the accusations brought against her. If the cause of the radioactivity of the lead could be debated and could even change her hypothesis, she was firmly convinced that her observations were correct so much so that they were confirmed by Professor Smits, the Director of the Chemistry Department of the University of Amsterdam. As support, Ştefania Mărăcineanu reported some excerpts of a personal communication sent to her by Smits which confirmed the results that she had arrived at: in the arc spectra of lead, the spectral lines of mercury were readily apparent. This evidence could only lead to one conclusion: the transmutation of lead into mercury by the action of solar radiation. In support of her statement, Mărăcineanu emphasized that traces of mercury are always in lead and that scientists have always defined this fact as a "permanent impurity" without specifying any others. Now she, Ştefania Mărăcineanu, could explain this presence as the slow transformation of lead into mercury (with α particle emission) brought about by the prolonged action of solar radiation.

Ştefania Mărăcineanu cited the data of Professor Smits before their publication: the amount of observed alpha particles was equal to impingement of 1.6 α-particles per second on a surface area of with a diameter of 16 cm^2. At the conclusion of her article, Mărăcineanu summarized her convictions as a challenging hypothesis:

> *Wouldn't this be the result of a transmutation that has moved beyond lead in the periodic series of elements? And is radioactivity not a general property of matter?*[59]

But the attack had not been able to direct the French colleagues to the pages of a French newspaper that appeared with calculated coolness:

> *I can't understand how Messrs. M. Fabry and Dureuil haven't found [traces of gold, helium or mercury].*[60]

Ştefania Mărăcineanu had also given some samples of lead sheets used for the Meudon Observatory roof lining to some French colleagues: Augustine Boutaric[61] (1885-1949) and Mlle. Madeleine Roy[62] (1900-40) who conducted in turn their own personal investigation.[63] In addition to the samples supplied by the Romanian researcher, the two Dijon chemists analyzed lead sheets from old and recent roof coverings: the palace of Versailles, the tiles donated by the alchemist Mme Mary Dina-Shillito[64] (1876-1938), owner of the Avenières Castle (1050 meters above sea level) and even Vallot Observatory on Mont Blanc (4362 meters high).

In addition to the lead study they analyzed cladding sheets of zinc and copper which, exposed to sunlight, would be expected to become radioactive. The Boutaric and Roy results refuted the hypothesis advanced by Ştefania Mărăcineanu, according to which lead would not be the terminus of the atomic disintegration of all radioactive decay processes, but simply the next-to-last stop before its slow transmutation into Hg.

Boutaric and Roy put forth three hypotheses:

1. all the metals studied were undergoing a process of spontaneous disintegration (presumably emission of alpha particles, although these were not expressly mentioned in the article)
2. radioactive impurities were present in all their samples
3. radioactive products could accumulate over time in the atmosphere (water vapor, fog, rain, snow and ice)

The fact that only the face exposed to the elements exhibited radioactivity automatically excluded both the first and the second hypothesis. To confirm the third hypothesis, the chemists analyzed the stones in the walls of the buildings from which the lead was taken and did not observe any radioactivity, which they ascribed to the slow but continuous disintegration of the lithic material through weathering.

Although Ştefania Mărăcineanu's relationship with Smits and MacGillavry was most cordial and collaborative, in her latest work she quoted incorrectly and without permission some data extracted from a personal letter sent by them to her superior, the former Director of the Meudon Observatory. Smits and MacGillavry were forced to issue a note of reprimand in the *Comptes Rendus*[65] in which they expressed disappointment not only about the violation of communications protocol (citing publicly a work not intended for publication), but also certain doubts about Ştefania Mărăcineanu's conclusions. The two Dutch authors, although they had confirmed the radioactivity in the lead exposed to the sun, were not able to experimentally determine if that property was indeed of extraterrestrial origin or due to a radioactive deposit by atmospheric agents. Deslandres, the man to whom Smits had sent the letter containing the confidential data, the former director of the Observatory, and Ştefania Mărăcineanu's patron, replied by return mail in the pages of *Comptes Rendus*.[66]

Far from offering the slightest form of apology, she continued to cite Smits's work as a support for her hypothesis, or rather she kept on saying that although the action of the sun's rays were not yet regarded as established as the cause of the radioactivity of lead, to her way of thinking, it was indisputably the most likely. At this point, what we are witnessing in these more recent articles, is a fact both objective and sad at the same time: the experimental data had been supplanted by a flood of words and personal opinions.

To make the situation more problematic, Deslandres improperly cited the work of Reboul[67] and Pokrovsky[68] regarding the capacity of solar radiation to modify the radioactivity of uranium.

As befits any article which does not conclude with the certainty of solid experimental results, this intervention ended with a terse: "It is necessary to wait for further study of these facts".[69]

Ştefania Mărăcineanu also provided samples of lead to other French colleagues, Lepape Adolphe (1886-1977) and Marcel Geslin (1894-1962) who immediately carried out similar experiments.[70] Their investigation was extended to other coatings: not only to metals such as lead, copper and zinc, but to stone such as slate, as well as the deposits left from rainwater in gutters. Their conclusions were positive; Lepape and Geslin observed in all materials the emission of penetrating radiation. But the next step threw more light on the phenomenon: the dust in the air could have been the vehicle of radioactivity, with the help of rainwater.

Ştefania Mărăcineanu, as many often do when finding themselves in unpleasant situations, tried to get out of the line of fire by replying jointly to Smits, Boutaric and Lepape, with an article in the *Bulletin de la Section de l'Academie Scientifique Roumaine*.[71] There were only two reasonable ways out: admit error or place the blame on others, and she chose the second way.

She said that from 1895 on, astronomers like Sir Oliver Lodge (1851-1940) in England and Henri Deslandres in France had the intuition that the sun emitted "radioelectric" waves; but Deslandres had gone further and better in that regard: in 1898 he proposed the existence of an unspecified "penetrating corpuscular radiation" emitted by the sun. It was a way to shift many of the shortcomings of her research on her old colleague. But it should also be reasonably said that Ştefania Mărăcineanu firmly believed in her results and could not accept the simple idea that the roof samples she observed had been contaminated by radioactive atmospheric dust. Her article was a meticulously drawn up objection to her colleagues' data, though not always backed up by thorough research and reliable data. In fact, she cited in her favor the research of some of her colleagues: Nodon in Bordeaux, Fauvot of Courmelle, and Risler and Werner Kolhöster, without supplying any bibliographic references.

On June 11 of that year, Augustine Boutaric and Mlle. Madeleine Roy published an article[72] in which they confirmed the results of Lepape and Geslin: radioactivity accumulated on ancient rooftops was due to rainwater. It was a simple and effective work. An analysis of the sand and charcoal used for making rainwater potable was collected in a closed tank of an old building. They observed radioactivity of about the same amount and type found in samples exposed to sunlight.

It was the "coup de grace" to the complex theory put forth by Mărăcineanu and abundantly supported by old Deslandres.

For Ştefania Mărăcineanu it was the beginning of the end. After having departed France for good, she completely abandoned her research on the phenomenon of induced radioactivity for a very long period of time.

Eleven years later, smack dab in the middle of World War II, José Baltá Elías[73] (1893-1973) decided it was time to dust off the phenomenon of radioactivity induced by solar radiation. He began his research in 1935 but the worsening of the Spanish political situation, ensuing in civil war, had delayed the publication of his findings for six years, by which time international interest in this subject had waned considerably. The results however, deserve to be reported because they contradict both Ştefania Mărăcineanu, but also Augustine Boutaric and Mlle. Madeleine Roy. In his view, and supported by the highest precision instruments, the phenomenon of radioactivity induced by solar radiation was not observed for the simple reason that it did not exist.[74]

Heedless of the criticisms that rained down from all sides, Ştefania Mărăcineanu published her last work concerning radioactivity and the transmutation of lead. In this work, containing repetitive material and lacking even a minimal bibliography, she sought to take stock of all her previous work on balance:

- As the Joliot-Curie team had discovered artificial radioactivity for the light elements, so she had done for heavy elements (lead) and Otto Hahn (1879-1968) for uranium, although this finding is reported without any specific notation. She also speculated about how it would take place. To do this, she proposed a new mechanism, "chemical transmutation for integration." Alpha particles (positive) expelled by polonium would be able to overcome lead's Coulomb barrier since, before the impact with the nucleus, it would be subjected to great acceleration due to the attractive force of the outer electron cloud of the atom.
- And finally, Mărăcineanu suggested a second phenomenon independent of the induced radioactivity in the lead, but still a property of the same element: the lead, in itself, would encounter a very slow process of radioactive decay with the formation of mercury. She estimated a very long half life for the lead, of the order of 10^{27} years.

Current observations suggest that the age of the universe is about 13,799,000,000 years (1.3799×10^{10} years),[75] with an uncertainty of about 21 million years. The figures provided by Mărăcineanu are not accompanied by any supporting experimental data. Her estimate is totally unreliable and can only serve to put the researcher in an even worse light. Since this estimated time period was too large to cause the spontaneous transmutation mercury, even the author of the article, Ştefania Mărăcineanu had to come to the conclusion that lead would be a metastable element and external agents such as sunlight could accelerate the spontaneous process by a factor of 10^{29}. In point of fact, the decay period would change from 10^{27} years to only 200 days.

BIOGRAPHY

Ştefania was born June 17, 1882 in Bucharest and her birth was added to the official registry the next day by her 20-year-old father, Sebastian Mărăcineanu.

Very few details of her childhood have been found. What we do know is that they were not happy years; Ştefania did not like to talk about them. In 1907, she enrolled at the *Facultatea de ştiinţe a Universităţii din Bucureşti* where, three years later, she received a doctorate in the chemical and physical sciences.[76] She followed courses in pedagogy for a short period and, in 1914, she passed the qualifying examination that permitted her to teach in secondary schools. She was present in Bucharest, teaching at the "Şcoala Centrală" during the Austro-German invasion of 1916. After the conclusion of World War I, she obtained a scholarship and went to the *Institut du Radium* in Paris, where she worked on and off until 1925.[77] Meanwhile, she had enrolled at the Sorbonne for a research PhD, which she obtained in 1924. Returning to Romania in 1925, the Faculty of Science at the University of Bucharest gave her a post as assistant instructor. However, in that same year, she returned to Paris for four years, working at the Astronomical Observatory of Meudon.

In 1929 we find Ştefania Mărăcineanu back once again in Romania. In that year, she had the opportunity to hold a conference on the constitution of matter at the "Şcoala Centrală de fete" that she subsequently repeated at the "Universitară Carol I."[78] It was printed[79] and it served as the nucleus of a manual on radioactivity that Ştefania Mărăcineanu would write some years later.[80]

When in 1929 she returned to Romania for good, perhaps in response to criticism leveled at her for her improbable discoveries, Ştefania Mărăcineanu installed, manned and directed the first laboratory for the study of radioactive substances in Romania.

Meanwhile, on January 15, 1934, Irène and Frédérick Joliot-Curie announced the results of their experiments and shocked the world with their discovery: artificial radioactivity. With uncommon haste, the Nobel Committee awarded them the Nobel Prize in chemistry the following year.

In early June of 1934, Irène Joliot-Curie, after having brought her terminally ill mother to the sanatorium of Sancellemoz in the Haute Savoy, traveled to Vienna to hold a conference hosted by the famous physicist Stefan Meyer (1872-1949).

On June 5, 1934 in the *Neues Wiener Journal*, an article appeared that reported excerpts of that conference, including anecdotes, bits of the animated discussions with colleagues, the opera galas, and interviews with journalists. Among the latter, the name of Ştefania Mărăcineanu was mentioned, and the enlightening contribution to understanding this new physical phenomenon of this relatively unknown researcher was emphasized.[81]

> *It was a Romanian, Miss Mărăcineanu, who a few years ago was probably the first one to observe that non-radioactive elements could be made radioactive under certain conditions, meaning they emit radiation similar to the type which, until now, has been only observed for the few radioactive elements.*

It was the only recognition, albeit marginal, that Marie Curie's daughter was willing to give to the Romanian researcher. On November 29, 1935, eleven days before Irène Joliot-Curie and her husband received the Nobel Prize from the hands of the king of Sweden, in Romania, Nicolae Vasilescu-Karpen[82] (1870-1964) gave a lecture at the Academy of Romanian Science entitled: *Radioactivitatea artificială şi lucrări româneşti în acest domeniu*[83] with clear allusions to the work of Ştefania Mărăcineanu's unique research done years earlier.

On June 24, 1936, Ştefania Mărăcineanu officially asked the Academy of Sciences of Romania to support her officially and to recognize the priority of her work. Her request was granted and in 1937 she was elected a corresponding member of the Academy of Sciences of Romania, and two years later *Sefa de lucrări*, *i.e.*, Director of Research.

In a letter preserved at the Academy of Sciences, Mărăcineanu, wrote a strongly critical version of the events that took place in Paris in the early twenties, while Marie Curie was still living:

> *Nu contest premiul Nobel soţilor Curie Joliot pentru perfecţionarea ce au adus în această descoperire ca metode de investigaţie, punere în evidenţă a fenomenului şi chiar pentru aporturi noui. Cer însă să mi se recunoască rolul ce am avut în această descoperire. Am fost prima care am îndrăsnit să anunţ acest fenomen în 1924,când părea o nebunie.*
> *Aceiaş metodă a întrebuinţat şi D-na Joliot Curie la începutul cercetărilor D-sale. ... Singura deosebire consista în faptul că D-sa aşeza foiţa metalică peste poloniu iar eu depuneam polonium pe foiţa metalică.*

D-na Pierre Curie nu mi-a permis a da această explicație în teza de doctorat și mia spus: vom continua lucrarea și va figura și numele d-tale. Am făcut totuși rezerve în teza de doctorat. [...] Imediat după obținerea gradului de Doctor am publicat pe propria mea răspundere la Academia Română...[84]

By 1941 Ștefania Mărăcineanu was 59 years old and was nearing the end of her life and just in time to be appointed Associate Professor. It would be her last personal "victory," as documented in several passages taken from letters addressed to colleagues. She spent much of her time in the laboratory, in a workplace which she had personally built at the cost of great sacrifice:

... Laboratorul acesta este viața mea,de care nu m'aș putea despărți de cât când n'aș mai fi.[85]

From personal sources, it can be clearly seen that the final days of the scientific collaboration between Ștefania Mărăcineanu and Marie Curie was not painless:

A fost o persecuție și o opoziție care m'a urmărit pas cu pas, de când am rupt cu Institutul de Radium pe chestia dreptului meu.[86]

For as long as she lived, the (Romanian) Academy denied her the highest recognition by not creating a professorship of radiochemistry.

This could have been due to the concurrent political situation. The follies and the horrors of the despotic regime of King Carol II (1893-1953) of Romania led him to accede to, in 1940, the triple dismemberment of his kingdom.[87] When, in June of 1941, General Ion Antonescu (1882-1946) threw Romania into the war against the Soviet Union, many Romanians were happy about it. What attracted them was not only the possibility of regaining the lost province of Bessarabia, but the prospect that the uncomfortably neighboring and powerful Russian State, a constant threat to national integrity for over twenty years, would be destroyed. That thousands of persons would be sent to their slaughter on the battlefields of Odessa, Sebastopol, Stalingrad, and the Caucasus, although appalling, ultimately did not seem to matter very much.

For Ștefania Mărăcineanu the news that arrived on June 20, 1942 was the prelude to the end of her career; the Ministry of Culture announced its decision to relieve her of her position by reason of age, effective October 1, 1942.

Her retirement would be neither a long nor happy one. She undertook volunteer work at a hospital, at Câmpulug Muscel, in the Muntenia region, but at the same time she continued to devote herself to various scientific issues that were dear to her heart.

On February 5, 1943, Ștefania Mărăcineanu sent a communication to the Academy of Sciences of Romania, entitled "Artifical Rain During the Drought Year of 1942." It would be her last work; she took care to assure her academic colleagues that her data were officially recorded. However, with the country at war and all that followed from that, the work was never published.

Simultaneously with the worsening of the war against the Soviet Union, Ștefania Mărăcineanu's health continued to deteriorate. She had been certifiably ill from cancer for quite some time, undoubtedly caused by long and unprotected exposure to nuclear radiation. She died on August 15, 1944 in Bucharest, two weeks before the Soviets invaded the city which was devastated by U.S. air strikes and direct fire from Russian artillery in the front line. As a result, the documents concerning Mărăcineanu's death were destroyed. Her last resting place, along with many other Romanian personages, is the Bellu Cemetery in Bucharest.[88]

Although some historians record her date of death as March 18, 1947, and the place of burial Bellu cemetery, in fact, neither this nor the previous data were confirmed by the "Consiliul General Municipuli Bucuresti." The only burial documents on file in the monumental cemetery is related to a certain Ștefan Mărăcineanu, who died March 18, 1944. Ironically, the authenticity of Ștefania Mărăcineanu's discoveries as well as the circumstances surrounding her end, are still a topic of discussion.

CONCLUSION: COULD THE ALPHA RADIATION EMITTED BY POLONIUM ACTIVATE LEAD?

Leaving aside any quantum interaction, "tunneling," or short-range effects, but maintaining a purely deterministic perspective, it may be assumed that:

The minimum kinetic energy required for an alpha particle to diminish the distance between itself and the lead nucleus, equal to or less than the sum of their nuclear radii, is obtained as a simple interaction between two charged particles which are acted on only by the Coulombic force.

Cross sections (σ) for inelastic scattering of α particles on lead are not reported in the literature, but the energies of α particles emitted by polonium are known to be about 5 MeV.[89]

In the case of bombardment of a lead target (Pb) with alpha particles (He), the barrier (determinable in MeV) is given by the approximate formula:

$$\frac{0.9 \cdot Z_1 \cdot Z_2}{\sqrt[3]{A_1}\sqrt[3]{A_2}} \tag{1}$$

where Z_1 and Z_2 are the atomic numbers of the two elements and A_1 and A_2 are the atomic masses of the interacting nuclei.

The value obtained is about 20 MeV, or about four times the energy of alpha particles emitted by isotopes of Po, and therefore a simple calculation excludes alpha particle activation of lead by that source. In fact, recent work shows that lead activation can occur with alpha particles with energies of about 40 MeV,[90] or even 30 MeV.[91]

However, relying purely on classical physics, the theoretical results can have different values from those observed in the laboratory by a factor of ten. Having recourse to quantum mechanics can help the investigator explain how some phenomena can happen when a deterministic calculation predicts that they are forbidden. In fact, a not so simple quantum calculation permits, for a sufficiently short period of time, that an alpha particle can have a much greater kinetic energy than normal because of the tunneling effect, provided that Heisenberg's uncertainty principle

$$\Delta E \Delta t \geq \frac{\hbar}{2} \qquad (2)$$

is not violated. Therefore, it would be theoretically possible that an alpha particle with an energy of about 5 MeV could overcome the Coulomb barrier between itself and a lead nucleus, thus giving rise to the latter's activation as allegedly observed by Ştefania Mărăcineanu.

However, it should be mentioned that Enrico Fermi (1901-54), in his work on slow neutron bombardment of a large number of known elements, did not observe the activation phenomenon for lead.[92]

In the end, in the case of the "official" discovery of artificial radioactivity by Irène and Frédéric Joliot-Curie at the beginning of 1934, an aluminum foil was bombarded with alpha particles from a radium source with energies of about 4.6 MeV.[93] In this case, Eq. 1 would give an approximate result as 4.8 MeV.

In light of our current knowledge of the physics of cosmic rays and on the basis of the work appearing in the literature,[94] cosmic rays would have been able to induce radioactivity in the lead nuclei. But since all the substances present in the lead were exposed to the cosmic rays as well, then they all should have become radioactive, which we know is not the case. Cosmic rays, or rather cosmic radiation, is a shower of high-energy particles arriving from outer space. It is very different from the alpha and beta radiation emitted by radioactive nuclei. When the primary radiation coming from space interacts with the atoms and molecules of the atmosphere, it produces swarms (a sort of decay) of secondary particles, some of which may reach Earth. The primary cosmic rays have much higher energies than those in play in the decay of the radioactive substances, while secondary swarms have much lower energy, but higher than those required for activation of the lead and through which Ştefania Mărăcineanu may have observed this phenomenon. But it must be said that the flow of secondary particles that reach sea level is very low; only one particle per cm^2 per minute. This heterogeneous mix of modern data and those reported in the 1920s and 1930s shows that it is impossible to treat them strictly quantitatively. Therefore, it is not possible to give a clear assessment of the reliability of the investigations conducted by Mărăcineanu. It is not possible to make clear-cut, definitive judgment, although Ştefania Mărăcineanu's hypothesis was possibly derived from erroneous experimental data or certainly by poor interpretation of them.

On the other hand, it is possible to point to an objective piece of data, about which Romanian historians are very insistent: how Ştefania Mărăcineanu was removed from Marie Curie's entourage and how some members of the *Institut du Radium* openly condemned and refuted her work.

But not only that. These historians claim that the results were stolen from Mărăcineanu, at night, when, for a reason not specified, she was not at home. Romanian sources make mention also of a great scandal and a subsequent lawsuit that involved her and the Curie family. If we follow these allegations to their appropriate conclusion, the chair at the University of Bucharest that would be given to Ştefania Mărăcineanu would be at the price of her silence. But all these statements, with no supporting documentation, are nothing but speculations, incipient libel. If they actually existed, they would deserve to be studied thoroughly and objectively.

To date, the only evidence proving the hostile resentment of the "clan Curie" against Ştefania Mărăcineanu is in a document produced by the latter; in a letter addressed by the Romanian researcher to Lise Meitner on March 12, 1936 and found in the Meitner Files of Churchill College Archives (Cambridge), she wrote:[95]

> *Madame,*
> *J'ai présenté au mois de février mes travaux sur la Radioactivité artificielle à l'appréciation de la Science allemande. Vous éte une autorité dans la spécialité et votre opinion la dessus comptera beaucoup. J'espère que les travaux vous ont été déjà présentées par qui de droit.*
> *Madame, je ne demande pas une faveur, mais seulement*[96] *la justice et je fais chaleureusement*
> *appel à vôtre*[97] *esprit de "équité" et a vôtre amour pour la science.*
> *Je ne demande pas à tenir les lauriers de M.me Joliot-Curie; mais je demande seulement que l'on reconnaisse la part que j'ai joué au début de cette découverte et que l'on contrôle aus-*

si la question de la pluie artificielle. J'ai vu qu'en France on commence à parler aussi de cette question sans mentionner mes expériences dans cette direction.
Madame, vous avez été connue moi dans l'élève de M.me Curie, je ne sais pas de quelle manière M.me regarderez cette question; dans tous les cas, je vous prie beaucoup de ne pas en parler au M.me J. Curie. Ne pas lui écrire que je me suis adressée aussi à vous. Elle ne m'aime pas et elle s'appuye[98] *sur une group organisation très puissante judéo-massonique.*[99] *Elle est communiste.*[100] *M[']en parle ici, je la croyons,*[101] *car j'ai eu l'occasion de sentir sa puissance. Seulement en Allemagne on pourrait me rendre raison.*
Je vous prie d'agréer, Madame, l'expression de mes salutations très distinguées,
Dr. Stéphanie Mărăcineanu[102]

It was known that at the *Institut du Radium*, there was competition among the scientists, not only present, but downright encouraged. It was compounded by the alleged disparities in the treatment of some of its members at the expense of others. Not surprisingly, people grumbled about the special treatment that Mme. Curie had reserved for her daughter.[103]

Ştefania Mărăcineanu did not belong to the Curie family circle and, moreover, she was a foreigner. The same adjective with which Mme. Curie had been labeled at the beginning of the century, before marrying a Frenchman (and university professor), then, widowed, and then trying to steal a married woman's husband. Yet, the insidious poison of xenophobia with which she was greeted in France by the most reactionary fringe of the country turned into a paternalistic scientific nepotism towards her daughter, who was assured - according to some – a too rapid career at the Institute which she directed. Regarding the more personal, Marie became extremely jealous: the most prestigious discoveries in the field of radioactivity could not but be due - as if it were by right of blood – to any other than a member of her family. And so it seemed regarding the discovery of artificial radioactivity in 1934: a milestone in the study and understanding of atomic nuclei.

When a great discovery reaches its fiftieth or hundredth anniversary, it is usually remembered with great celebration in the country that boasts of being the birthplace of the discoverer and recognizes him/her first as their own child and then as a their teacher. If the country is really great, it organizes a conference where scholars discuss the discovery, and commissions documentaries on the life of this man or woman of science. This is exactly what happened in 1984 for the celebration of the fiftieth anniversary of the discovery of artificial radioactivity.[104]

When the discovery involves a minor character, maybe embarrassing or in a marginal country, often we limit ourselves to a biographical retrospective, perhaps out of a condescending gallantry, not wanting to point out the inadequacy of the small country or the mediocre scientist compared to such a great discovery: in fact, because of ingrained prejudice, the discovery is assumed to be less influential.

In our study, however, elements of judgment are mixed up with the most insidious and agonizing doubts: did Ştefania Mărăcineanu actually discover induced radioactivity? To this question we can answer with certainty: no.

But it might be better to reformulate a more complex question thus: when Ştefania Mărăcineanu announced her discovery was it reasonable to consider her correct?

Although it may seem counterintuitive, with what was written a moment ago, the answer is: yes.

Therefore, we could sense a certain "stink of persecution" in her regard and so feel first hand "the ostracism assigned to her by Mme Curie." The same aloofness that Marie experienced as a student would then be ascribed to her students when she became a professor, and Romanian historians perhaps too often tend to emphasize this.

An objective fact, already well documented, is the decline of French science (chemistry[105] and physics) between the two world wars. It can be said that most of French science was addressed by leading ideas coming from Paris and in Paris there were the so-called Tetrarchs: Marie Curie, for Radioactivity; Paul Langevin for Theoretical Physics; Jean Perrin (1870-1942) for Physical Chemistry; Georges Urbain (1872-1938) for General Chemistry and Mineralogy. All these famous people, as well as being linked by having maintained relationships with their own subordinates or colleagues,[106] had strongly authoritarian, if not downright despotic, personalities.[107]

Let's not dwell too much on the details of events that could simply be traced to adulterous characters in the public eye, but this point of view is also very important, not merely voyeuristic, because it solidifies with uncommon clarity a bond, sometimes ideological, sometimes loaded with political and social tensions, that allows us to appreciate yet more the strength and power of these "masters of French science."[108]

After the death of Marie Curie, direction of the *Institut du Radium* passed to André Debierne (1874-1949), who had, in common with many of his colleagues, the dubious repute of observing physical or chemical phenomena that do not exist, for example, the frigdaréction a supposed nuclear reaction that would take place at temperatures of the order of -200 °C.

As another example, Georges Urbain posited a unifying theory of organic chemistry with mineral or inorganic chemistry[109] (Homéomérie) on a basis so qualitative and so simplistic as to be already obsolete at the time of its publication, so much so that no one ever considered it.

His many colleagues and disciples were careful to mention it only at the time of drawing up his numerous obituaries.[110]

Finally Jean Perrin, a sacred cow of French science: Ministre de la Troisième République, founder of CNRS (*Centre national de la recherche scientifique*), the father of the atom, Nobel Laureate in Physics in 1926, between the end of World War I and the early 1920s put forth - with stolid determination - the fallacious radiative theory, according to which every chemical reaction would be caused by luminous radiation and its kinetic energy would be determined by the intensity of said radiation.[111] Perrin, in addition to being the author of erroneous assumptions, was the mentor of two famous physicists, Yvette Cauchois (1908-1999) and Horia Hulubei (1896-1972) who, in turn, announced the discovery of three nonexistent chemical elements: *sequanium*, *dor*, and *moldavium*.[112]

When, in the early 1920s, Ştefania Mărăcineanu arrived in Paris, we are no longer in the Belle Epoque, where the capital was one of the driving forces of an enthusiastic confidence in the future, nurtured by continuous discoveries and inventions, regularly augmented by recurring expositions. We could advance the hypothesis that the environment of the chemists and physcists in France in those years[113] could have stimulated students and researchers over a healthy competition in the search for new physical phenomena and that this research has turned into obsession of wanting to discover something new at any cost, thus committing inevitable blunders. If an Urbain was driven to do this to refresh his fame in a futile attempt to bring down upon himself the attention of the Nobel Foundation, for Ştefania Mărăcineanu, we could talk about self-deception.[114]

The illusion of finding oneself before a vast unexplored ocean that represented the ultimate structure of matter and to be able to scrape together a few more great experimental discoveries escaped the scrutiny of the great scientists of the previous generation. But Ştefania Mărăcineanu's flaw, like many researchers formed at the *Institut du Radium*, was that although they belonged to the generation following that of Marie Curie, continued to remain mentally contemporary, unable to grasp many of those discoveries that would have been the preserve of scientists more cosmopolitan: in the U.S., Britain, and Germany. Because ultimately Ştefania Mărăcineanu, coming from a peripheral and marginal country in terms of the international scientific scene, had acquired French know-how when it was at its lowest point at the international level. For example, Jean Perrin, the undisputed head of French physical chemistry between the two world wars, forbade publication of any article on quantum mechanics in the journals he directly or indirectly controlled.[115]

On the one hand we have the characters (Curie and Perrin to name only two) so famous that they have become monuments of our cultural history that the very idea of attacking them frightens us. Yet we have to pull together the threads of this story.

For a long time a misunderstanding has surrounded the figure of Ştefania Mărăcineanu as if the glow of the flames burning Bucharest in her long siege, had clouded her virtues as a scientist and the city collapsing into ruin deleted along with her true and presumed discoveries its anti-Semitism and adherence to an authoritarian fascist regime, which it was replacing bloodily with a long communist dictatorship. It is difficult in this climate to move important details out of the shadows, like the fact that in her narrow view of the physical world, Ştefania Mărăcineanu, saw too many phenomena being derived from or, ultimately, due to radioactivity. Certainly to Ştefania Mărăcineanu it was not an easy life, but it should be added that when, in 1929, she returned to Romania, she did not stop to making an "incendiary tour" wherever she went, thundering against her old mentor and, after her death, against her daughter.

Her improbable discoveries of the 1920s were side by side, a decade later, with others: she wanted to see a correlation between exposure of radioactive substances to air and the formation of storm clouds or earthquakes. It was almost a leap of faith, made with an old nationalistic spirit of science in spite of the continued declining times; World War II was unveiling its monstruous dimensions and its obscene ideology leading to the extermination of men, women, old people, and children, using in all this the only too willing and zealous men of science. It is a situation in which Mărăcineanu took part, against her will, at the end of her life: a military conflict, the political and cultural identity, which has destroyed the conscience of a generation of her scientific peers.

At a time when all the characters seem to "shout and no one listens to the other's voice," we can only conclude that stories like these are - in our opinion – an incomparable antidote to the temptation of writing scientific hagiographies.[116]

ACKNOWLEDGMENTS

The authors wish to thank Mr. Adrian Tudoroiu, Doctors Alessandro Ciandella, Dina Scarpi, Roberto di Camillo and Stefano Fedeli, Professors Roberto Livi, Andrea Stefanini and Massimo Chiari for their help in the preparation of the present work.

A simple thank you cannot express the immeasurable help from the personnel of the *Biblioteca del Polo Scientifico di Sesto Fiorentino* in the persons of Laura Guarnieri, Serena Terzani, Sabina Cavicchi, Marzia Fiorini, Sabrina Albanese and Angela Landolfi, as well as the Archives Assistants Julia Schmidt and Heidi Egginton of the Churchill College Archives Centre (Cambridge, UK).

BIBLIOGRAPHY

1. Greater Romania, which assumed the name of Romania between 1918 and 1940. In 1918, Romania was defeated by the Austro-Germans but actually won the war. It participated with the winners in the partition of the territories of both its Austro-Hungarian enemy as well as of its Russian ally. The only country that had its territory doubled by the terms of the Peace of Versailles, Romania basically had designs on establishing its hegemony over the entire area of the Lower Danube. But it made the error of overestimating its own strength, leading to the failure of its more ambitious ideas and to a foreign policy that struggled mightily to forge its own path in a post-World War I Europe, skirting both integration and a less-welcome annexation, thus paralyzing its internal politics for twenty years.
2. M. Popescu, M.F. Rayner-Canham, G.W. Rayner-Canham, "Stefania Mărăcineanu: Ignored Romanian Scientist" in "A Devotion to their Science: Pioneer Women in Radioactivity" by Marelene F. Rayner-Canham, Geoffrey W. Rayner-Canham Editors, **1997**, Chemical Heritage Foundation, Philadelphia & McGill-Queen's University Press, Montreal; pp. 87-91.
3. I.N. Iacovachi, *Noesis*, No. 10, **1984**; M. Rogai, *Evenimentul Zilei*, 13 septembrie (2009); G. Marcu, *Ziarul Financiar - Ziarul de Duminică*, 26 noiembrie **2009**; Professor Ing. Dănuţ Şerban's website: http://www.stefania-maracineanu.ro/; last access 06/12/2016.
4. M. Rogai, *Formula AS*, nr. 928, **2010**.
5. M. Popescu, M.F. Rayner-Canham, G.W. Rayner-Canham, "Stefania Mărăcineanu: Ignored Romanian Scientist" in "A Devotion to their Science: Pioneer Women in Radioactivity" by Marelene F. Rayner-Canham, Geoffrey W. Rayner-Canham Editors, **1997**, Chemical Heritage Foundation, Philadelphia & McGill-Queen's University Press, Montreal; p. 90.
6. I. Langmuir, "Colloquium on Pathological Science", held at the Knolls Research Laboratory, Niskayuna, New York on 18 December 1953. A recording of the actual talk was made, but apparently lost, but a recorded transcript was produced by Langmuir a few months later. See also: I. Langmuir, *Physics Today*, **1989**, *42*, Issue 10, October, pp.36–48.
7. The alleged discoveries relating to artificial rain induced by radioactive substances and the link between radioactivity and earthquakes, as we shall see, were not refuted presumably for two reasons: the announcements were made in minor scientific journals, in the middle of World War II; in addition, Mărăcineanu died shortly after the publication of these works.
8. J.-P. Adloff, G. B. Kauffman, *Chem. Educator*, **2008**, *13*, 318-325.
9. www.segretidipulcinella.it/sdp24/temp_02.htm, last accessed 18/10/2016: Stefania Mărăcineanu (1882-1944), in *Segreti di Pulcinella, Rivista di Letteratura e Cultura Varia*, numero 24.
10. G. Steinhauser, G. Loeffler, R. Adunka, *J. Radioanal. Nucl. Chem.*, **2013**, *296*, 157-163; Arhivele Naţionale ale României – Direcţia Municipiului Bucureşti, Stefania Mărăcineanu; Ion N. Iacovachi, *Noesis*, **1984**, No. *10*.
11. Romanian historian, politician, and man of letters. President of the Council between 1931-32, he was also adviser to King Carol II (1893-1953). For reasons of cultural affinity, he was fascinated by Italy, although not an admirer of Benito Mussolini (1883-1945) and fascism. He was rather suspicious of Soviet and German hegemonic designs on his country and because of his firm opposition to the Romanian government's pro-Nazi policy, he was assassinated by elements of the radically fascist "Iron Guard" in 1940.
12. Professor Ing. Dănuţ Şerban's website: http://www.stefania-maracineanu.ro/; last access 06/12/2016.
13. The half life, $T_{1/2}$, and the decay constant, λ, are often used interchangeably; they are related by $T_{1/2} = 0.693/\lambda$.
14. M.E. Wieser (2006). *IUPAC Technical Report, Pure and Applied Chemistry*, **2005**, *78*(11), 2051–2066; G. Audi, A. H. Wapstra, C. Thibault, J. Blachot, O. Bersillon, *Nuclear Physics A.*, **2004**, *729*, 3–128; N. E. Holden. "Table of the Isotopes." In D. R. Lide. *CRC Handbook of Chemistry and Physics* (85th ed.), **2004**, CRC Press. p. 11-50.
15. M. Curie, *C.R.*, **1906**, *142*, 273; Rutherford, E., *Phil. Mag.* **1905**, *10*, 290; Marckwald W., *Jahr. d. Rad.*, **1905**, 136; Meyer, von Sweidler, *Wien Ber.*, **1906**, *115*, 63; Regener, *Ber. der D. Physik Ges.*, **1911**, *13*, 1027.
16. This precaution was considered necessary because of the extreme difficulty in the treatment of polonium. One milligram of the isotope ^{210}Po (the only one manageable because the other four isotopes' half lives were too short), emits the same number of alpha

particles as five grams of radium. In the process of decay, polonium-210 also releases a large amount of energy.

17. Ş. Mărăcineanu, *C.R.*, **1925**, 774.
18. Ş. Mărăcineanu, *C.R.*, **1926**, 345.
19. “On aurait pu croire à une pénétration du polonium d’une face a l’autre du plomb; mais dans ce cas on aurait dù avoir une forte perte de polonium à l’intérieur du blomb, ce qui n’a pas été constaté…”
20. “…semblent inique que le rayonnement solaire peut provoquer la réintégration du Radium-E [Bi] a partir du Radium-F [Po], et donc una reversibilité dans la série radiactive”
21. Ş. Mărăcineanu, *C.R.*, **1927**, 1322.
22. Madame Curie was a combative woman and so sure of herself that she never gave way in debate, even when fraught with a possible acrimonious aftermath. She savagely attacked both Willy Marckwald and Sir William Ramsay when they committed egregious errors in the field of radioactivity. The two colleagues harbored bitter memories of this incredible woman’s stubborn tenacity. It seems very strange that Marie Curie did not openly take a position on this matter, which was nurtured under her own roof. See M. Fontani, M. Costa, M. V. Orna, “The Lost Elements: the Periodic Table’s Shadow Side”, Oxford University Press (2015), p. 471-475.
23. The Institute of Radium, according to Bertrand Goldschmidt (1912-2002), one of the last students to have known her personally, was ruled despotically and with certain inclinations toward nepotism by Marie Curie. After her death, André Debierne (1874-1949), the new director, had repeatedly clashed with her daughter, Irène Joliot-Curie (1897-1956). The following anecdote is worth quoting as an explanatory example: “During one disagreement, when Irène objected to the appointment of Bertrand Goldschmidt to a position she believed belonged to someone else, Debierne retorted ‘Goldschmidt possesses a quality that ALL the others do not have - he did not work with your mother. Now get out of here!’ “ Goldschmidt, B. Atomic rivals. Rutgers University Press, New Brunswick & London; 1990, page 19.
24. Marie Curie’s granddaughter, Hélène Joliot, was born on September 17, 1927 and at 21 years of age, she married Michel Langevin, the grandson of her grandmother’s lover, Paul Langevin (1872-1946).
25. “a midi, quand le Soleil darde sur l’appareil, le plomb semble devenir deux fois plus active…”
26. It is not clear what lead compounds might have been formed; their identities would certainly depend upon the acid used. It is also not clear if the lead compound thus formed were reduced by experiment to elemental lead prior to testing.
27. “Le plomb du commerce, préparé toujours avec la galéne, n’est pas, comme on sait, radioactif…”
28. H. Deslandres, *C.R.*, **1927**, 1324.
29. “Les persone qui ont du plomb longtemps insolé, et qui n’ont pas appareils nécessaires à la recherche de la radioactivité, sont priées d’en envoyer un échantillon à l’Observatorie de Paris”.
30. Ş. Mărăcineanu, *C.R.*, **1927**, 1547.
31. H. Deslandres, *C.R.*, **1927**, 1549.
32. “Les recherches de Mlle Mărăcineanu sur le toitures anciennes de l’Observatorie de Paris offrent un intérêt de plus en plus grand. Le plomb n’est pas le seul métal qui acquiere, sous l’influence des rayons solaires, une radioactivité spéciale…”.
33. W. Kolhorster, *Physikalische Zeitschrift*, **1914**, *14*, 1153; W. Kolhorster, *Naturwissenschaften*, **1926**, *14*, 290.
34. R.A. Millikan, R. M. Otis, *Physical Review*, **1926**, *27*, 645.
35. H. Deslandres, *C.R.*, **1922**, 622.
36. Ş. Mărăcineanu, *C.R.*, **1927**(*II*), 122.
37. “On a vu que le courant d’ionisation donné par la côte opposé est proportionel à la valeur initiale du polonium déposé”.
38. “Si l’on considère l’allure des cuorbes, ce courant d’ionisation qui augmente chaque jour de lui-même passe par un maximum, descend ensuite d’après une loi explonetielle, ainsi qu’il se passe, quand une substance radioactive prend naissance, se développe et se detruit, je pense qu’il y a formation d’une substance radioactive nouvelle dans la masse du plomb”.
39. H. Deslandres, *C.R.*, **1927**(*II*), 124.
40. The Argus, **1927** August 6, Saturday, No. 25269, p. 10, Australia, Melbourne; Kalgoorlie Miner, **1927** August 15, Monday, Vol. 33, no. 8680, p. 1, Australia, Kalgoorlie; The Canberra Times Week-End Edition, **1927** August 19, Friday, Vol. I, no. 67, p. 12, Australia, Canberra; The Border Watch, **1927** August 20, Saturday, Vol. LXV, no. 6661, p. 2, Australia, Mount Gambier; The Western Argus, **1927** August 23, Tuesday, Vol. 34, no. **1937**, p. 2, Australia, Kalgoorlie; The Daily News, **1927** August 30, Tuesday, Vol. XLVI, no. 16.329, p. 9, Australia, Perth; The Evening Post, **1927** September 10, Saturday, Vol. CIV, no. 62, p. 13, New Zealand, Wellington; The Geraldton Guardian, **1927** September 17, Saturday, Vol. XXI, no. 4743, p. 1, Australia, Geraldton. Professor Ing. Dănuţ Şerban’s website: http://www.stefania-maracineanu.ro/; last access 06/12/2016.
41. Professor Ing. Dănuţ Şerban’s website: http://www.

stefania-maracineanu.ro/; last access 06/12/2016.
42. Ş. Mărăcineanu, *C.R.*, **1928**(*II*), 746.
43. "Si l'on considère l'allure des cuorbes, ce courant d'ionisation qui augmente chaque jour de lui-même passe par un maximum, descend ensuite d'après une loi explonetielle, ainsi qu'il se passe, quand une substance radioactive prend naissance, se développe et se detruit, je pense qu'il y a formation d'une substance radioactive nouvelle dans la masse du plomb".
44. Ş. Mărăcineanu, *Bullettin de la Section Scientifique de l'Academie Roumaine*, **1929**, *12*, 5.
45. "L'action du raynonnament solaire porrai peu-être provoquer une transmutation del 0,001% plomb en or".
46. "Mais c'est dans les radioations solaires qu'on doit voire la pierre philosophale et la source de la formidabile énergie radioactive, don't la necéssité s'impose et s'imposera de plus en plus".
47. N. Vasilesco Karpen, *Bullettin de la Section Scientifique de l'Academie Roumaine*, **1929**, *12*, 60.
48. "Les expériences en question ont conduit à des résultats exactement contraires à ceux indiqués par M-lle Mărăcineanu".
49. It is not inconceivable that the French physicists were particularly "sensitive" to a similar subject, whose only result could only lead to the accusation pathological science. The unfortunate incident relating to Nancy rays or "N" rays was a blow to the pride of French science, whose ghost had to be still very present in their minds. Regarding this see: Nye, M. J., *Historical studies in the physical sciences*, **1980**, *11*(*1*), 125.
50. She was a French chemist and physicist. On the recommendation of the physicist, Paul Langevin in 1926 she arrived at the Curie *Institut du Radium* laboratory as an "aide-bénévole" (a volunteer) and then the following year became a "travailleur libre" (independent collaborator). She became Paul Langevin's lover twenty years after he had had a turbulent affair with Marie Curie, and she remained faithful to him, especially in the period of his exile in Troyes during the war. From their relationship, Paul Gilbert Langevin (1933-86) was born.
51. E. Róna, E.-A.W. Schmidt, *Wien. Ber.*, **1927**, *136*, 65.
52. She was a Dutch chemist and crystallographer. After completing her studies in 1932 she became assistant to the chemist A. Smits at the General and Inorganic Chemistry Laboratory of the University of Amsterdam. She is mainly known for her work in X-ray crystallography.
53. Smits, A., MacGillavry, C.H., *Proceedings of the Koninklijke Nederlandse Akademie van Wetenschappen*, **1929**, *32*, 610.
54. Ş. Mărăcineanu, *C.R.*, **1925**, 774.
55. "…ces résultats étaient peut-être de grande importance parce que si vraiment le plomb s'active et émet des particules α, il estvraisemblable qu'il y a une transmutation de plomb en mercure".
56. Dănuţ Şerban - *Drumurile mele toate ..., Ştefania Mărăcineanu,* Memoriae Ingenii, Revista Muzeului Naţional Tehnic *Prof. ing. Dimitrie Leonida*, octombrie **2013**, page 6.
57. Voi lupta, dragă Doamnă, şi pentru mine şi pentru dreptate şi pentru onoarea ţării şi a femeilor.
58. Ş. Mărăcineanu, *C.R.*, **1930**, *190*, 373.
59. "Ne serait-ce pas là le resultat d'une transmutation poussée au delà du plomb dans la serie periodique des éléments? et la radioactivité ne serait-elle pas une propriété générale de la matiére?"
60. "je ne peux pas comprendre comment M. M. Fabry et Dureuil n'en ont pas trouvé [trace d'or, d'helium ou de mercure]".
61. He was a French physicist and chemist. He was appointed Associate Professor of Physical Sciences in 1908. He then became Professor at the Faculty of Sciences at Dijon, where he spent all of his career. He was also a member of the Academy of Sciences, Arts and Letters of Dijon. Wounded in World War I, he was decorated with the Legion of Honor in 1929.
62. A. Boutaric, *Bulletin de l'asociation des Diplomes de Microbiologie de la Faculté de Pharmacie de Nancy*, **1941**, *19/23*, 5.
63. A. Boutaric, Mlle. Madeleine Roy, *C.R.*, **1930**, *190*, 483.
64. Mme Mary Wallace Shillito was the widow of a wealthy Mauritian businessman, Assan Farid Dina (1871-1928). Both were allegedlly occultists and alchemists. She died at the age of 62 of a heart attack brought on by an accident, and is buried in Geneva.
65. A. Smits, Mlle. MacGillavry, *C.R.*, **1930**, *190*, 635.
66. H. Deslandres, *C.R.*, **1930**, *190*, 637.
67. G. Reboul, *C.R.*, **1929**, *189*, 1256; G. Reboul, *C.R.*, **1930**, *190*, 374.
68. Pokrovsky, *Zeitschrift fuer Physik*, **1930**, *59*, 127.
69. "il faut attendre que l'étude des faits ait été pousée plus loin".
70. A. Lepape, M. Geslin, *C.R.*, **1930**, *190*, 676.
71. Ş. Mărăcineanu, *Bullettin de la Section Scientifique de l'Academie Roumaine*, **1930**, *13*, 55.
72. A. Boutaric, Mlle. M. Roy, *C.R.*, **1930**, *190*, 1410.
73. Catalan physicist, whose name is often written as Josep Baltà i Elies.
74. J. Baltá Elías, *Anales de Física y Química*, **1941**, 180.
75. C.R. Lawrence, JPL, for the Planck Collaboration,

Astrophysics Subcommittee, NASA HQ (18 March 2015) "Planck 2015 Results" (See page 29 of pdf).
76. Faculty of Science of the University of Bucharest.
77. Professor Ing. Dănuţ Şerban's website: http://www.stefania-maracineanu.ro/; last access 06/12/2016.
78. Middle school for girls.
79. S. Mărăcineanu, *Radioactivitatea şi constituţia materiei*. (*Efectul razelor solare in fenomenele radioactive*), Editura Casei coalelor, Bucuresti, **1929**, pp. 37.
80. S. Mărăcineanu, *Radioactivitatea*, Tipografia C. Lazarescu, Bucuresti, **1936**, pp. 218.
81. I. Joliot-Curie,"Gespraech mit Irene Curie. Die Tochter derr Radiumentdeckerin in Wien" "Conversation with Irene Curie. The daughter of radium's discoverer at Vienna", Neues Wiener Journal, 5 giugno **1934**, pag 6.
82. "Romanian engineer and physicist, and also known for some of his achievements in mechanical engineering and electrochemistry. He created a controversial contrivance that goes by the name of the Karpen Pile: a battery capable of self-perpetuating recharge which provided power for over 60 years. A fraud according to scientists; an example of perpetual motion according to some newspapers". Sandru, Ovidiu. "Karpen's Pile: A Battery That Produces Energy Continuously Since 1950 Exists in Romanian Museum". Retrieved 20 July 2012. http://www.greenoptimistic.com/karpen-pile/; last access 06/12/2016.
83. "Artificial radioactivity, a discovery of Romanian [scientists] in this area". Professor Ing. Dănuţ Şerban's website: http://www.stefania-maracineanu.ro/; last access 06/12/2016.
84. I do not dispute the award of the Nobel Prize to Mme. Joliot-Curie for the advancements that she made to this discovery, such as investigative methods, highlighting the phenomenon that I consider to have discovered. But I ask you to recognize the role I played in this discovery. I was the first to announce this phenomenon in 1924 when it seemed utter foolishness. Mme. Joliot-Curie used the same method that I used at the beginning of her research. ... The only difference is that she placed a metal sheet over polonium, while I deposited a polonium solution on the metal foil.
Pierre Curie's widow [in this second stage of the letter, the Romanian researcher refers to Marie Curie in 1923] did not allow me to give this explanation in my thesis and assured me that if I listened to her, the work would be continued and that when my PhD was finished, an article in my name would appear. In that case, I held back. […] Immediately after obtaining the PhD, I published my results on my own at the Romanian Academy". English translation from http://www.mnt-leonida.ro/09Noutati/090043Noutati2013.10.17/StMaracineanu2013AR.pdf; last access 06/12/2016.
85. "... This laboratory is my life, from which I could never be separated." English translation from http://www.mnt-leonida.ro/09Noutati/090043Noutati2013.10.17/StMaracineanu2013AR.pdf; last access 06/12/2016.
86. It was persecution and personal opposition that has followed me step by step, since I broke off with the *Institut du Radium* ... English translation from from: http://www.mnt-leonida.ro/09Noutati/090043Noutati2013.10.17/StMaracineanu2013AR.pdf; last access 06/12/2016.
87. France was the only ally and guarantor of Romanian borders. Her collapse under German tanks in May 1940 threw the Romanian government into complete panic. King Carol decided to make a last-minute proposal to Hitler to curry favor with the Axis, but a few days afterward, Russia commanded Romania to cede the province of Bessarabia, while the Axis didn't bat an eyelash. During July and August 1940, the Hungarians and Bulgarians prepared (with German support) to further amputate Romania (the Kingdom of Transylvania and Southern Dobruja). The day after signing the *Diktat of Vienna* (August 30, 1940) King Carol named General Antonescu governor, and abdicated in favor of his son, Michael (b. 1921) who ten years earlier had been deposed with a *coup d'état*.
88. Information supplied by Gheorghe Bezviconi (1910-1966) in his book "Necropoli Capitale", published posthumously by the Institute of History "Nicolae Iorga," 1972.
89. D.G. Karraker, A. Ghiorso, and D.H. Templeton, *Phys. Rev.*, **1951**, *83*, July, 390.
90. Woolum, S. Dorothy, D.S. Burnett, L.S. August, *Nuclear Instruments & Methods*, **1976**, *138*(*4*), 655.
91. J.J. Howland, D.H. Templeton, I. Perlman, *Physical Review*, **1947**, *71*, 552; D. H. Templeton, J.J. Howland, I. Perlman, *Physical Review*, **1947**, *72*, 766.
92. E. Amaldi, O. D'Agostino, E. Fermi, B. Pontecorvo, F. Rasetti, E. Segrè, *Proceedings of the Royal Society*, **1935**, *149A*, 522; O. D'Agostino, E. Fermi, B. Pontecorvo, F. Rasetti, E. Segrè, *Ricerca Scientifica*, **1934**, *1*, 380.
93. W.Y. Chang, *Phys. Rev.*, **1946**, *70* November 1, 632.
94. J. Clay, K.H.J. Jonker, *Physica* (*The Hague*), **1938**, *5*, 171.
95. CCA, Doc. Reference MTNR 5/12; letter from Ştefania Mărăcineanu to Lise Meitner, 12/03/1936.

96. Word written between the lines.
97. Grammatically, it should be "vos".
98. In the original letter, the "y" is written "i".
99. It should be: "maçonnique".
100. Words added between the lines.
101. In the original letter, the "y" is written "i".
102. Madam,
In February I presented my work - on artificial radioactivity - to the attention of German Science. You are an authority in this field and your opinion on it will be highly esteemed. I hope that the work has already been presented to you by those people who may be concerned. Madam, I do not ask for a favor, but only justice and I warmly do appeal to your spirit of "equity" and your love for science. I do not ask for the laurels of Madame Joliot-Curie; but I only ask that the part I played at the beginning of this discovery is recognized as well as my pioneering work on artificial rain. I have seen that in France they are beginning to talk about this subject without mentioning my experiments in that area. Madame, you have known me as Mme. Curie's pupil, I do not know how she would have looked at this question; In any case, I beg you very much not to speak of me to Mme. J. Curie. Do not write to her that I have also addressed you [by this letter]. She hates me and she belongs to a very powerful Judeo-Masonic organization. | She is a Communist |. I speak of it knowledgeably, believe me, because I have had occasion to feel her power. Only in Germany can I be vindicated. Please accept, Madam, the expression of my most distinguished greetings,
Dr. Stéphanie Mărăcineanu
103. E. Tina Crossfield, "Irène Joliot-Curie: following in her Mother's Footsteps", in "A Devotion to their Science: Pioneer Women in Radioactivity" by Marelene F. Rayner-Canham, Geoffrey W. Rayner-Canham Editors, **1997**, Chemical Heritage Foundation Philadelphia & McGill-Queen's University Press, Montreal pp. 97-124.
104. E. Amaldi, "La radioactivité artificielle a 50 ans, 1934-1984", Éditions du Physique, **1984**, pp. 164.
105. J.C. Gomes, "Georges Urbain (1872-1938), chimie e philosophie", Doctoral dissertation, **2003**, Université de Paris X, Nanterre, 235-242.
106. M. Charpentier-Morize, "Perrin, Savant et homme politique", **1997**, Ed. Belin, 217-226; B. Bensaude-Vincent, *Langevin (1872-1946) science et vigilance*, Paris, Ed. Belin, **1987**, 271.
107. J.C. Gomes, Ibid., 40-44.
108. A colleague, Fortunée Schecroun (1896-1978), known as Nine Choucroun, officially became the *compagne* of Jean Perrin after the death of Heniette Perrin (1869-1938); Eliane Montel (1898-1992) had a lengthy relationship with Paul Langevin after he left his first lover, Marie Curie, and their bed-sit that they had rented in rue de Banquier, not far from the Sorbonne. Finally, Georges Urbain (1872-1938), left a widower in 1936, married his "personal nurse," Jacqueline Nancy Ullern (1910-78), nearly forty years his junior.
109. G. Urbain, *Scientia* (*Milan*), **1934**, *56*, 71; G. Urbain, *Bulletin de la Société Chimique de France*: *Memoires*, **1937**, *4*, 1612.
110. Between 1938 and 1940, about a half-dozen obituaries were published to remember him. Also, two biographies came out on the occasion of the centenary of his birth (1972). In one of them, there is an outline of his *homéomérie* theory.
111. J. Perrin, *Annales de Physique*, **1919**, *11*, 5.
112. M. Fontani , M. Costa, M.V. Orna, "The Lost Elements: the Periodic Table's Shadow Side", Oxford University Press, **2015**, p. 331-334.
113. D. Pestre, *Physique et physiciens en France 1918-1949*, Edition des Archives Contemporaines, **1984**; M.J. Nye, *From Chemical Philosophy to Theoretical Chemistry 1800-1950*, University of California Press, **1993**.
114. R. Trivers, *Annals of the New York Academy of Science*, **2000**, *907*, 114.
115. M. Charpentier-Morize, "Perrin, Savant et homme politique", **1997**, Ed. Belin, 107-109.
116. R. Hoffmann, in M. Fontani, M. Costa, M.V. Orna, "The Lost Elements: the Periodic Table's Shadow Side", Oxford University Press, **2015**, p. xvi.

Substantia
An International Journal of the
History of Chemistry

Firenze University Press
www.fupress.com/substantia

Manifesto of the journal

PREAMBLE

In the current historical period, marked by tragic conflicts and dramatic tensions in various areas, it is absolutely appropriate to ponder and recoup the fundamental aspects of culture, e.g. the relationship with the past, people's common history, and the universal values on which our coexistence and civilization are based upon.

In such a context it seems important to deepen the relationship with the past history, and not only the ancient history or that of a few centuries ago, but also the more recent history, of the Short Century that has just gone. For us, researchers and university teachers of disciplines related to Chemistry, it seems crucial to deepen the bonds with those forerunners who preceded us in research and in education, in order to mature a more convinced and deep awareness of the world and of the civilization from which we come and to pass the baton to the future generations, in total liberty, as stated by the art. 33 of the Constitution of the Italian Republic, that reads "The Republic guarantees the freedom of the arts and sciences, which may be freely taught."[1]

PRESENTATION

Substantia is an international electronic peer-reviewed journal. It is published in English by the University of Florence, at the initiative of the Department of Chemistry "Ugo Schiff". The journal aims at offering an original cultural contribution in Europe to the History of Chemistry and a scientific tool of communication, debate and close examination of all topics related to Chemical Sciences and similar disciplines.

Substantia is born in Florence, one of the cradles for Science, and particularly for Chemistry. As a matter of fact it was during the Florentine Renaissance that the studies and the practices pertaining to Chemistry received a new impetus: the Camerata de' Bardi was born in the 16th century and promoted a new way to look at sciences, arts and literature (the first records date back to 1573 AD). During the following decades the Accademia dei Lincei (1603), the Accademia del Cimento (1657), the Royal Society in London (1662), the Académie Royale des Sciences in Paris (1666), the Kurfürstlich Akademie der Wissenschaften in Berlin (1700), the Russian Academy of Sciences in St. Petersburg (Российская академия наук, *Rossíiskaya akadémiya naúk*, 1724), the Kungliga Vetenskapsakademien in Stockholm (1739), and the American Academy of Arts and Sciences of the Massachusetts (1780) were progressively born. These academies became the places of aggregation, dispute and divulgation of the rising Chemistry.

Substantia is addressed to teachers, researchers and university students, and to all those interested in deepening the scientific themes related to Chemistry. The journal publishes original articles that comply with the criteria of scientific rigour, originality and depth and it is freely distributed over the Internet with no restriction in open access, in compliance with the principles of the "Berlin Declaration on Open Access": open access to knowledge, largest dissemination and visibility on the Web for scientific research, and public distribution of the results of the studies. The journal may host monographic issues focusing onto specific themes of interest.

The aims of *Substantia*, in the attempt to conjugate scientific rigour and an interdisciplinary outlook, include:

1) the promotion of research activities in History of Chemistry through the publication of papers devoted to classical or contemporary Chemistry issues, and in particular of studies that leap over the fences of the rigid academic organization and promote the combination and intersection of knowledges, techniques, methodologies and diversified languages
2) the recovery and republication of unpublished or unlikely available works, that represent milestones in the development of Chemistry and related disciplines, and whose validity and scientific relevance remain untouched also after decades
3) the recovery or the revival of past literature sources, in the attempt to limit the "loss of knowledge" that

Substantia. An International Journal of the History of Chemistry 1(1): 97-98, 2017
DOI: 10.13128/Substantia-5

relentlessly strikes the human culture, and that is inadvertently favored by the extreme fragmentation and specialization of science

4) the promotion of a critical outlook towards current and past theoretical models, in order to encourage and develop the job of young researchers.

A SPACE ALSO FOR SIMILAR DISCIPLINES

Substantia will always welcome scientific contributions focusing on topics related to all Chemical Sciences, Physics, Mathematics, Life and Earth Sciences, History and Philosophy of the Sciences, Engineering, Medicine, Economics, Social Sciences and Arts.

1. "L'arte e la scienza sono libere e libero ne è l'insegnamento." https://www.senato.it/documenti/repository/istituzione/costituzione_inglese.pdf, last accessed on Jan 02, 2017.

Substantia
An International Journal of the History of Chemistry

Firenze University Press
www.fupress.com/substantia

Acknowledgments

Our first thanks is for you, who are reading this page and this first issue of *Substantia*. We do rely on you, on your interest and on your patience, on your approval and also on your sincere criticism.

Substantia is the product of a great effort, of a great pleasure and of a renewed hope in the human capability to wonder about the beauty and complexity of reality and matter, and to inspect their features with the strength of reason..

Without this hope - or better without this certainty - any attempt to uncover and understand the world would be nosense and we would be pulled back to darkness.

We sincerely thank the authors of this first issue: they granted us the strength of their knowledge and wisdom, and gladly accepted the challenge of a new journal.

Thank you to the members of the international Scientific Board, who offered their prestige and reliability for the benefit of the scientific level of the journal and to our colleagues in the Department of Chemistry, who welcomed the birth of *Substantia*.

Finally I want to express my deepest loyal gratitude to Moira Ambrosi, Antonella Capperucci, Laura Colli, Marco Fontani, Romeo Perrotta and Alessandro Pierno for sharing with me this challenging and tantalizing adventure. Their enthusiastic and tireless commitment was the first nourishment for our journal.

We tried to do our best, it has been and will be a great struggle. And for sure we could have done it better.

We apologize for any mistake and we thank you - the reader of these articles - for your invaluable support and for all the suggestions that you may want to share with us in the future.

Firenze, 25 January 2017

Pierandrea Lo Nostro
Editor-in-Chief

Substantia. An International Journal of the History of Chemistry 1(1): 99, 2017
DOI: 10.13128/Substantia-15

Substantia
An International Journal of the
History of Chemistry

Author Guidelines for Substantia

as of March 2017

Substantia is an open access, peer-reviewed, academic international journal dedicated to traditional perspectives as well as innovative and synergistic implications of history and philosophy of Chemistry.

It is meant to be a crucible for discussions on science, on making science and its outcomes.

Substantia hosts discussions on the connections between chemistry and other horizons of human activities, and on the historical aspects of chemistry.

Substantia is published *open access* two times per year and offers top quality original full papers, essays, experimental works, reviews, biographies and dissemination manuscripts.

All contributions are in English.

We are interested in:

- fundamentals and gnosiological implications of chemical theories and related sciences

the progress of single discoveries, the life of scientists, the historical advancement of technology, in other words the stories of the people behind breakthroughs and innovations

- the historical overview and critical reviews of chemical theories and their interweaving with the cultural and social environment
- the critical discussion of past concepts and experimental works, in the light of the present chemical knowledge
- contributions on contemporary science reporting and scientific dissemination
- discussions on making science and on the role and efforts of basic research in a world where the practical and financial outcomes seem to be the main driving forces

REQUIREMENTS FOR PUBLICATION

The criteria for a publishable manuscript include novelty, education, suitability, and presentation. To be considered for publication by *Substantia*, a manuscript must:

- Demonstrate scientific and scholarly rigor, supported by up-to-date citations to relevant literature and guided by a rationale for how the work fits into existing knowledge
- Exhibit novelty through original scholarship or a creative or innovative practice
- Present well-developed ideas in a comprehensive, organized discussion written in clear, concise English and making effective use of display elements (figures, schemes, tables, etc.)
- Adhere to the requirements and *Substantia* protocols outlined in this document for the different types of manuscript and be submitted according to Firenze University Press publishing policies
- Be submitted electronically to our Editorial System www.fupress.com/substantia or to substantia@unifi.it

Audience: Scholars in Chemistry, History and Philosophy of Science, Physics, Mathematics, Life Sciences, Earth and Atmosphere Sciences, Medicine, and related disciplines.

FIRST STEPS

Before the submission of your manuscript to the Editorial Support for peer review, you are kindly requested to:

- read the "Focus and Scope";
- read the "Licence and copyright agreement for *Substantia*";
- read the manuscript preparation for this journal;
- agree and comply with the "General obligations for authors";

We recommend that any data set used in your manuscript is submitted to a reliable data repository and linked from your manuscript through a DOI.

SUBMISSION CHECKLIST

Cover Letter. A cover letter is mandatory and should give the justification of the submission, highlights of the article, and a general impact statement.

Articles. Full-length research manuscripts, consistent with the objectives of *Substantia*, are the main focus of the Journal. Regular articles should have a maximum total length of 50,000 characters including spaces. Exceptions to this rule should be motivated and justified in the cover letter. In general, a combined maximum of 8 normal-sized figures and/or tables is allowed (for instance 3 tables and 5 figures). For multiple-panel figures each set of two panels equates to one figure. Manuscripts can be submitted as a single Word or PDF file to be used in the refereeing process. Only when the paper is at the revision stage, the contributing author will you be requested to fit the paper into a "correct format" for acceptance and provide the items required for the publication of the article.

You can use this list to carry out a final check of your submission before you send it to the Journal for review. Please make sure that the following items are present:

Contact details of the corresponding author:

- Affilitation(s)
- E-mail address, Telephone Number, Website URL
- Full postal address

Manuscript:

- Include up to 5 keywords immediately after the Abstract
- All figures (including figure captions)
- All tables (including titles, description and footnotes)
- Make sure all figures and table citations in the text match the files provided
- Graphical Abstracts / Highlights files (where applicable)
- Supplementary Information files (where applicable)

Further considerations:

- Manuscript should be "spell checked" and "grammar checked"
- All references mentioned in the Reference List must be cited in the text, and vice versa
- Permission to reproduce must be obtained for use of copyrighted material from other sources (<u>including the Internet</u>)
- Relevant declarations of interest are made
- Journal policies detailed in this guide were reviewed

Referees. In the cover letter, please provide the names, affiliation and email addresses of up to five potential Referees. Appropriate Referees should be knowledgeable about the subject but have no close connection with any of the authors. In addition, Referees should be from institutions other than (and possibly countries other than) those of any of the Authors. The editors of the Journal may or may not contact the suggested Referees.

References and Footnotes. References to the literature or to footnotes are typed as superscripts <u>*after*</u> punctuation. These are numbered consecutively and listed (but not as superscripts) at the end of the manuscript. Footnotes should not contain comprehensive experimental details (which should be included in the Supplementary Information instead) or long explanatory text. In the list of references, the names of <u>all</u> authors should be given in upper- and lowercase, starting with the initials of first names followed by the surname). Please double-check your references, for example by using CrossRef, to ensure correct (online) links.

Journal citations. Only a comma is required between the name of the last author and the title of the journal. Journal titles should be italicized and abbreviated according to the "Chemical Abstracts Service Source Index" (CASSI; no commas appear in the journal names). The journal title should be followed (no comma) by the year of publication (in boldface), comma, volume number (in italics), comma, first page. Alternatively, the DOI code can be indicated after the journal name (and a comma), instead of year, volume and first page. If the correct abbreviation is not known, the title of the journal should be given in full.

Examples:

1) J. P. Kraft, D. H. Johnson, *Chem. Commun.* **1996**, *77*, 2851.
2) M. Krebs, H. U. Hürter, *Acta Crystallogr. Sect. A* **1981**, *37*, and references therein.
3) D. Bruss, *Appl. Phys. B*, DOI 10.1007/s003409900185.

Book citations. Books without editor: E. Wingender, *Gene Regulation in Eukaryotes*, VCH, Weinheim, **1993**, p. 215. Books with editor: T. D. Tullius in *Comprehensive Supramolecular Chemistry*, Vol. 5 (Eds.: J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle, K. S. Suslick), Pergamon, Oxford, **1996**, pp. 317–343.

Miscellaneous citations. Patents: C. R. A. Botta (Bayer AG), DE-B 2235093, **1973** (in cases where the patent is not available online at the respective patent office the corresponding reference to *Chemical Abstracts* should be added). PhD or Master thesis: A. Student's last name, title of the thesis, University of (city), country, year (in boldface). Website: http://www.wesleyan.edu/chem/faculty/

novick/vdw.html, last accessed on dd/mm/yyyy.
Note that missing data will be highlighted at proof stage for the author to correct.

Formatting requirements. There are no strict formatting requirements but all manuscripts must contain the essential elements, for example Abstract, Keywords, Introduction, Materials and Methods, Results and Discussion, Conclusions, Acknowledgments, References, Artwork and Tables with Captions. If your article includes any Videos and/or other Supplementary material, this should be included in your initial submission for peer review purposes. Divide the article into clearly defined sections.

Figures and tables embedded in text. Please ensure the figures and the tables included in the single file are placed next to the relevant text in the manuscript, rather than at the bottom or the top of the file.

Use of word processing software. Regardless of the file format of the original submission, at revision you must provide us with an editable file of the entire article. Keep the layout of the text as simple as possible. Most formatting codes will be removed and replaced on processing the article. The electronic text should be prepared in a way very similar to that of conventional manuscripts. To avoid unnecessary errors you are strongly advised to use the "spell-check" and "grammar-check" functions of your word processor.

Subdivision - unnumbered sections. Divide your article into clearly defined sections. Each subsection is given a brief heading. Each heading should appear on its own separate line. Subsections should be used as much as possible when crossreferencing text: refer to the subsection by heading as opposed to simply 'the text'.

STRUCTURE OF THE MANUSCRIPT

Abstract (no more than 1,500 characters including spaces). A concise and factual abstract is required. The abstract should state briefly the purpose of the research, the principal results and major conclusions. An abstract is often presented separately from the article, so it must be able to stand alone. For this reason, References should be avoided, but if essential, then cite the author(s) and year(s). Also, non-standard or uncommon abbreviations should be avoided, but if essential they must be defined at their first mention in the abstract itself.

Keywords (immediately after the abstract please provide up to five words using American spelling and avoiding general and plural terms and multiple concepts. Be sparing with abbreviations: only abbreviations firmly established in the field may be eligible). These keywords will be used for indexing purposes.

Graphical abstract (a Graphical abstract is not mandatory but recommended. It should summarize the contents of the article in a concise, pictorial form designed to capture the attention of a wide readership online. Authors must provide images that clearly represent the work described in the article. Graphical abstracts should be submitted as a separate file in the online submission system. Image size: please provide an image with a minimum of 531 × 1328 pixels (height × width) or proportionally more. The image should be readable at a size of 5 × 13 cm using a regular screen resolution of 96 dpi. Preferred file types are TIFF, EPS, PDF or MS Office files.

Introduction (state the objectives of the work and provide a strong and adequate background, avoiding a summary of the results).

Materials and methods (if applicable, provide sufficient detail to allow the work to be reproduced. Methods already published should be indicated by a reference: only relevant modifications should be described).

Results and Discussion (if applicable, should be clear and concise, and explore the significance of the results of the work).

Conclusions

Appendices (if necessary).

Ackowledgments (collate acknowledgements in a separate section at the end of the article before the references. List here those individuals who provided help during the research, e.g., providing language help, writing assistance or proof reading the article, etc.).

ESSENTIAL TITLE PAGE INFORMATION

Title. Concise and informative. Titles are often used in information-retrieval systems. Avoid abbreviations and formulae where possible.

Author names and affiliations. Please clearly indicate the given name(s) and family name(s) of each author and check that all names are accurately spelled. Present the authors' affiliation addresses (where the actual work was done) below the

names. Indicate all affiliations with a lowercase superscript letter immediately after the author's name and in front of the appropriate address.
Provide the full postal address of each affiliation, including the country name and the
e-mail address of each author.

Corresponding author. Clearly indicate who will handle correspondence at all stages of refereeing and publication, also post-publication. Ensure that the e-mail address is given and that contact details are kept up to date by the corresponding author.

Present/permanent address. If an author has moved since the work described in the article was done, or was visiting at the time, a 'Present address' (or 'Permanent address') may be indicated as a footnote to that author's name. The address at which the author actually did the work must be retained as the main, affiliation address. Superscript Arabic numerals are used for such footnotes.

Nomenclature and Units. The use of nomenclature and symbols adopted by IUPAC is recommended (Quantities, Units and Symbols in Physical Chemistry, Blackwell Scientific, Oxford, 1988).

Mathematics formulae. Please submit math equations as editable text and *not as images*. Present simple formulae in line with normal text where possible and use the solidus (/) instead of a horizontal line for small fractional terms, e.g., $q = (4\text{psin}q)/l$. In principle, variables are to be presented in italics. Powers of e are often more conveniently denoted by exp. Number consecutively any equations that have to be displayed separately from the text (if referred to explicitly in the text).

General points:

- Make sure you use uniform lettering and sizing of your original artwork.
- Embed the used fonts if the application provides that option.
- Aim to use the following fonts in your illustrations: Arial, Courier, Times New Roman, Symbol, or use fonts that look similar.
- Number the illustrations according to their sequence in the text.
- Use a logical naming convention for your artwork files.
- Provide captions to illustrations separately.
- Size the illustrations close to the desired dimensions of the published version.
- Submit each illustration as a separate file.

Formats. If your electronic artwork is created in a Microsoft Office application (Word, PowerPoint, Excel) then please supply 'as is' in the native document format. Regardless of the application used other than Microsoft Office, when your electronic artwork is finalized, please 'Save as' or convert the images to one of the following formats (note the resolution requirements for line drawings, halftones, and line/halftone combinations given below): EPS (or PDF): Vector drawings, embed all used fonts. TIFF (or JPEG): Color or grayscale photographs (halftones), keep to a minimum of 300 dpi. TIFF (or JPEG): Bitmapped (pure black & white pixels) line drawings, keep to a minimum of 1000 dpi. TIFF (or JPEG): Combinations bitmapped line/half-tone (color or grayscale), keep to a minimum of 500 dpi.

Please do not:

- Supply files that are optimized for screen use (e.g., GIF, BMP, PICT, WPG); these typically have a low number of pixels and limited set of colors;
- Supply files that are too low in resolution;
- Submit graphics that are disproportionately large for the content.

Figure captions. Ensure that each illustration is followed by a caption. A caption should comprise a brief title (not on the figure itself) and a description of the illustration. Keep text in the illustrations themselves to a minimum but explain all symbols and abbreviations used.

Tables. Please submit tables as editable text and not as images. Tables are placed next to the relevant text in the article. Number tables consecutively in accordance with their appearance in the text and place any table notes below the table body. Be sparing in the use of tables and ensure that the data presented in them do not duplicate results described elsewhere in the article. Please avoid using vertical rules.

Citation in text. Please ensure that every reference cited in the text is also present in the reference list (and vice versa). Any references cited in the abstract must be given in full. Unpublished results and personal_communications are not listed in the reference list, but may be mentioned in the text. Citation of a reference as 'in press' implies that the item has been accepted for publication.

AFTER ACCEPTANCE

Corresponding authors will receive an e-mail requesting the correction of proofs.
We will do everything possible to get your article pub-

lished quickly and accurately. Please use this proof only for checking the typesetting, editing, completeness and correctness of the text, tables and figures. Significant changes to the article as accepted for publication will only be considered at this stage with permission from the Editor. It is important to ensure that all corrections are sent back to us in one communication. Please check carefully before replying, as inclusion of any subsequent corrections cannot be guaranteed.
Proofreading is solely your responsibility.

GENERAL OBLIGATIONS FOR AUTHORS

- An author's primary obligation is to present a concise, accurate account of the research performed, as well as an objective discussion of its significance.
- A paper should contain sufficient detail and references to public sources of information to permit the author's peers to replicate the work.
- A paper should be as concise as possible but not at the expense of scientific accuracy and completeness. To promote scientific conciseness and completeness at the same time, the inclusion of a comprehensive abstract is encouraged.
- Papers have to be written in English, and authors should pay attention to correct spelling and grammar.
- An author should cite those publications that have been influential in determining the nature of the reported work and that will quickly guide the reader to the initial work essential for understanding the present investigation. Information obtained privately, as in conversation, correspondence, or discussion with third parties, should not be used or reported in the author's work without explicit permission from the investigator with whom the information originated. Information obtained in the course of confidential services, such as refereeing manuscripts or grant applications, should be treated similarly.
- Fragmentation of research papers should be avoided. A scientist who has done extensive work on a system or group of related systems should organize publication so that each paper gives a complete account of a particular aspect of the general study.
- It is inappropriate for an author to submit manuscripts describing essentially the same research to more than one journal of primary publication.
- A criticism of a published paper may sometimes be justified; however, in no case is personal criticism considered to be appropriate.
- To protect the integrity of authorship, only persons who have significantly contributed to the research and paper preparation should be listed as authors. The corresponding author attests to the fact that any others named as authors have seen the final version of the paper and have agreed to its submission for publication. Deceased persons who meet the criterion for co-authorship should be included, with a footnote reporting date of death. No fictitious names should be listed as authors or co-authors. The author who submits a manuscript for publication accepts the responsibility of having included as co-authors all persons that are appropriate and none that are inappropriate.
- An author should declare any potential conflicts of interest in a special section prior to the acknowledgements.

LICENCE AND COPYRIGHT AGREEMENT

The following licence and copyright agreement is valid for any article published by *Substantia*.

Author's certification
By submitting the manuscript, the authors certify the following:

- They are authorized by their co-authors to enter into these arrangements.
- The work described has not been published before (except in the form of an abstract or proceedings-type publication – including discussion papers – or as part of a published lecture or thesis); it is not under consideration for publication elsewhere; and its publication has been approved by all the author(s) and by the responsible authorities – tacitly or explicitly – of the institutes where the work was carried out.
- They have secured the right to reproduce any material that has already been published or copyrighted elsewhere.
- They agree to the following licence and copyright agreement:

Copyright

- The copyright of any article is retained by the author(s). More information on the transfer of copyright can be found below.
- Authors grant *Substantia* a licence to publish the article and identify itself as the original publisher.
- Authors grant any third party the right to use the article freely under the stipulation that the original authors are given credit and the appropriate citation details are mentioned.
- The article is distributed under the Creative Commons Attribution 4.0 License. Unless otherwise stated, associated published material is distributed under the same licence.

Creative Commons Attribution 4.0 License
Anyone is free to share — to copy, distribute, and transmit the work to remix — to adapt the work under the following conditions:

- Attribution — The original authors must be given credit.
- For any reuse or distribution, it must be made clear to others what the licence terms of this work are.
- Any of these conditions can be waived if the copyright holders give permission.
- Nothing in this licence impairs or restricts the author's moral rights.

The full legal code of this licence.

Copyright transfers
Many authors have strict regulations in their employment contract regarding their publications. A transfer of copyright to the institution or company is common as well as the reservation of specific usage rights. In open-access publications in combination with the Creative Commons License, a transfer of the copyright to the institution is possible as it belongs to the author anyway.
Any usage rights are regulated through the Creative Commons License. As *Substantia* uses the Creative Commons Attribution 4.0 License, anyone (the author, his/her institution/company, the publisher, as well as the public) is free to copy, distribute, transmit, and adapt the work as long as the original author is given credit (see above). Therefore, specific usage rights cannot be reserved by the author or his/her institution/company, and the publisher cannot include the statement "all rights reserved" in any published paper.
A copyright transfer from the author to his/her institution/company can be expressed in a special "copyright statement" at the end of the publication. Authors are asked to include the following sentence: "The author's copyright for this publication has been transferred to institution/company".

Reproduction requests
All articles published by *Substantia* are licensed under the Creative Commons Attribution 4.0 License (see details above) together with an author copyright. Therefore, there is no need from the publisher's side to give permission for the reproduction of articles. We suggest contacting the author to inform him/her about the further usage of the material. However, as the author decided to publish the scientific results under the CC-BY licence, he/she consented to share the work under the condition that the original authors be given credit.

PUBLICATION ETHICS AND PUBLICATION MALPRACTICE STATEMENT

Substantia's Publication Ethics and Publication Malpractice Statement is based, in large part, on the guidelines and standards developed by the Committee on Publication Ethics (COPE). The relevant duties and expectations of authors, reviewers, and editors of the journal are set out below.

Responsibilities of authors
By submitting a manuscript to *Substantia*, the author(s) warrant that the manuscript is their own, original work and that it has neither been published previously nor is currently being considered for publication elsewhere. They also warrant that the sources of any ideas and/or words in the manuscript that are not their own have been properly attributed through appropriate citations and/or quotes.

An author should not normally publish manuscripts describing essentially the same research in multiple journals or publication venues. Such redundant publication is generally considered to constitute unethical publishing behavior, and if discovered may result in a manuscript under consideration being rejected, or a published article being retracted.

Authors of manuscripts reporting on original research should present an accurate account of the work performed, accompanied by an objective discussion of its significance. Underlying data should be represented accurately in the manuscript. The manuscript should contain sufficient detail and references to permit others to replicate the work. The fabrication of results and the making of fraudulent or knowingly inaccurate statements constitute unethical behavior and may be cause for rejection or retraction of a manuscript or published article.

Where the manuscript reports on commercial software, hardware, or other products, authors must include a declaration at the beginning of the manuscript in which they must either state that no conflict of interest exists or describe the nature of any potential conflict. All sources of financial support for the research should also be disclosed in the manuscript.

The author(s) of a manuscript agree that if the manuscript is accepted for publication in *Substantia*, the published article will be copyrighted using a Creative Commons "Attribution 4.0 International". This license allows the author(s) to retain the copyright and allows anyone to download, reuse, re-print, modify, distribute and/or copy the final version of the papers. The works must be properly attributed to its author(s). It is not necessary to ask further permissions both to author(s) or journal board, although you are kindly requested to inform the Journal Board for every reuse of the papers.

Authors are responsible for obtaining written permission to include any images or artwork for which they do not hold copyright in their articles, or to adapt any such images or artwork for inclusion in their articles. The copyright holder must be made explicitly aware that the image(s) or artwork will be made freely available online as part of the article under a Creative Commons "Attribution 4.0 International" license.

The authors' names should be listed on the article in order of their contribution to the article, and all authors take responsibility for their own contributions. Only those individuals who have made a substantive contribution should be listed as authors; those whose contributions are indirect or marginal (e.g., colleagues or supervisors who have reviewed drafts of the work or provided proofreading assistance, and heads of research institutes/centers/labs) should be named in an "Acknowledgments" section at the end of the article, immediately preceding the Reference List. The corresponding author must ensure that all appropriate co-authors and no inappropriate co-authors are included on the article, and that all listed co-authors have seen and approved the final version of the article and agreed to its publication.

Where an author discovers a significant error or inaccuracy in an article of his/hers that has been published in *Substantia*, he/she has an obligation to promptly notify the editors and cooperate with them to correct the article or retract it as appropriate.

Responsibilities of reviewers

Substantia's reviewers perform work for the journal on a volunteer basis. Given that most of these individuals are in full-time employment, their reviewing activities for *Substantia* must, by necessity, not be their top priority. Reviewers are free to decline invitations to review particular manuscripts at their discretion, for example, if their current employment workload and/or other commitments make it prohibitive for them to complete a review in a timely fashion and to do justice to the task in the available timeframe. They should also not accept manuscript review assignments for which they feel unqualified.

Reviewers who have accepted manuscript assignments are normally expected to submit their reviews within three weeks. They should recuse themselves from the assignment if it becomes apparent to them at any stage that they do not possess the required expertise to perform the review, or that they may have a potential conflict of interest in performing the review (e.g., one resulting from competitive, collaborative, or other relationships or connections with any of the authors, institutions, or companies associated with the manuscript).

Privileged information or ideas obtained by reviewers through the peer review process must be kept confidential and not used for personal advantage. Any manuscripts received for review must be treated as confidential documents, and must not be shown to or discussed with others except as authorized by the *Substantia* Editor.

When conducting their reviews, reviewers are asked to do so as objectively as possible, refraining from engaging in personal criticism of the author(s). They are encouraged to express their views clearly, explaining and justifying all recommendations made. They should always attempt to provide detailed and constructive feedback to assist the author(s) in improving their work, even if the manuscript is, in their opinion, not publishable.

Reviewers should identify in their reviews relevant published work that has not been cited by the author(s), together with any instances in which proper attribution of sources has not been provided. They should call to the responsible editor's attention any major resemblances between a manuscript under consideration and other published articles or papers of which they are aware, as well as any concerns they might have in relation to the ethical acceptability of the research reported in the manuscript.

Responsibilities of editors

The *Substantia* Editor has ultimate responsibility for deciding if a manuscript submitted to *Substantia* should be published, and in doing so is guided by the Journal's policies as determined by the *Substantia* editorial board and constrained by such legal requirements as shall then be in force regarding libel, copyright infringement, and plagiarism. The Editor may consult with the Associate Editor and other members of the editorial team, as well as with reviewers, in making publication decisions.

The editors will evaluate manuscripts for their intellectual content without regard to the race, color, gender, sexual orientation, religious beliefs, ethnic origin, citizenship, or political philosophy of the author(s). They will not disclose any information about a manuscript under consideration to anyone other than the author(s), reviewers and potential reviewers, and in some instances the *Substantia* editorial board members, as appropriate. Additionally, the editors will make every effort to ensure the integrity of the blind review process by not revealing the identity of the author(s) of a manuscript to the reviewers of that manuscript, and vice versa.

When evaluating a manuscript for publication, in addition to considering standard criteria pertaining to the rigor of the manuscript, the quality of its presentation, and its contribution to humanity's stock of knowledge, the editors will also seek evidence that ethical harms have been minimized in the conduct of the reported research. They will question whether the benefits outweigh the harms in the particular study's case. Since *Substantia* welcomes the submission of manuscripts from any country, it is necessary to recognize that laws and regulations regarding research ethics and ethical approval vary worldwide. As such, the editors may need to seek clarification in this regard with the author(s) and request that they supply a letter from the relevant institutional ethics committee or board that approved the research.

The editors will be guided by CORE's Guidelines for Retracting Articles when considering retracting, issuing an expressions of concern about, and issuing corrections pertaining to articles that have been published in *Substantia*. They are committed to working closely with research organizations and institutions in line with CORE's advice on Cooperation between Research Institutions and Journals on Research Integrity Cases.

Finito di stampare da
Logo s.r.l. – Borgoricco (PD) – Italia

March 2017 No walls. Just bridges

Substantia

An International Journal of the History of Chemistry

Vol. 1 – n. 1

Table of contents