ONE AND A HALF CENTURY OF DIFFUSION : FICK, EINSTEIN, BEFORE AND BEYOND

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ABSTRACT – Year 2005 gave us , through two anniversaries (1855, Fick and 1905 Einstein), the wish to go back to these authors seminal papers, whose aftermaths had been (and still are) prodigious. This essay describes the contents of these articles : the macroscopic approach with Fick equations and the microscopic one with Einstein-Smoluchowski random walk (Brownian motion) equation, while considering them in their historical context. Some further developments are briefly discussed.

I-INTRODUCTION

It always comes as a surprise, when one looks back at the genesis of concepts and models we are now so familiar with, to discover how prone we are to consider them as quite obvious. Reading old publications, we realise how these "evidences" required decades – perhaps centuries – of approximations, errors, intuitions, advances and recessions… We also realise how dangerous and counterproductive are certain dogmas (and scholars !) : the quarrel of energetists and atomists gives a perfect illustration of the danger of dogmatism. Diffusion was at the heart of these quarrels.

Another surprise is worth to be underlined : understanding the elementary processes, i.e. the microscopic world, is not compulsory for the derivation of reliable macroscopic laws. What did Fourier know about a the nature of heat, Ohm about electricity, Fick about salt solutions, Darcy about structure of water in pores ? The beauty of mathematics allowed them to derive predictive laws, with at the key the possibility of quantitative experiments and engineering applications.

In the case of diffusion, the bridge between microscopic and macroscopic world was thrown by A. Einstein : his fundamental result expresses a macroscopic quantity – the coefficient of diffusion – in terms of microscopic data (elementary jumps of atoms or molecules). As an offspring of the kinetic theory of gases, Brownian motion was the key to decipher the microscopic world, first in gases and liquids, and later on – surely more difficult to admit – in crystalline solids. We are faced here with an incredible convergence : Brownian motion was actually modelled for the first time by a mathematician, Louis Bachelier, who didn't considered physical events, but Stock-market quotations ! We are here facing again the beauty – and power – of mathematics : Brownian motion is a mathematical object, treated in many text-books as well as a physical one allowing us to rationalize natural facts as varied as the flight of birds or mosquitoes, the propagation of diseases, the dissemination of pollutants, the properties of biological membranes, the brain imaging by NMR…

With the benefit of hindsight, it seems rather surprising that scholars of the Enlightenment Century apparently didn't question the mechanisms of many technical processes, which are, as we know, controlled by diffusion phenomena. Let us just mention a few ones: "cementation", first used for Gold or Silver refining — a process attested since several centuries B.C. — , Carbon diffusion to produce steel from Iron — a process already known in medieval times and perhaps earlier —, diffusion soldering of gold artefacts, the colours of stained glasses or earthenware and chinas (have a look at the diffusion of Copper (green colour) in the glaze of some earthenware artefacts).

II - THOMAS GRAHAM

The first systematic study of diffusion was due to a Scottish chemist, Thomas Graham (1805-1869). He was born in Glasgow and considered as the "leading chemist of his generation". Let us just mention that Graham was the inventor of dialysis, that he defined as a method of separation, by diffusion through a membrane (1854). His research work on diffusion in gases was performed from 1828 to 1833 and he presented his results to the Royal Society of Edinburgh in 1831. These were later published in the Philosophical Magazine in 1833 [1]. Let us quote the first lines of his first paper [2]:

"Fruitful as the miscibility of the gases has been in interesting speculations, the experimental information we possess on the subject amounts to little more than the well established fact, that gases of different nature, when brought into contact, do not arrange themselves according to their density, the heaviest undermost, and the lighter uppermost, *but they spontaneously diffuse, mutually and equally, through each other*, and so remain in the intimate state of mixture for any length of time." The Graham's law claims that the volume of gas exchanges are inversely proportional to the square root of their masses. Combined with Avogadro's number, this law allows the determination of the molar masses (in modern language). For this reason, an experimental set-up identical to Graham's was later used by J. Loschmidt in 1863 for his classical measurements on diffusion in a handful of gas couples.

Graham did not only perform the first *quantitative* experiment of diffusion, but moreover the first reliable measurement allowing the determination of a coefficient of diffusion. The notion of coefficient of diffusion was not yet established at this time, not until 26 years later thanks to Fick. But time flowed until 1867, when Maxwell calculated the coefficients of diffusion in gases from the numerical results of Graham ! His coefficient of diffusion of CO_2 in air is accurate to ± 5%. Isn't it extraordinary ?

Later on, Graham performed a series of diffusion experiments in liquids and noticed that diffusion in liquids is by three orders of magnitude smaller than in gases and that the diffusion rate slowed down with increasing time. But application of his law to solutions of a series of salts appears as a wrong assumption – because of his wrong ideas about the nature of solutions (for a discussion of Graham's ideas, see ref [1b]).

Graham also studied the uptake of Hydrogen by Palladium.

III – ADOLF FICK

Adolf Fick (1829-1901) was born in Kassel (Germany) and very early he intended to study mathematics and physics, so he enrolled at the university of Marburg, but after two years he changed his mind towards medicine. After graduating in medicine, in accepted in 1852 a position as an assistant of Carl Ludwig, a professor of anatomy and physiology in Zurich, where he remained for 16 years. Later he got a chair of physiology in Würzburg, which he occupied for 31 years.

His contributions to physics are limited to a few years around 1855, – he was then 26 years old – when he published his famous papers on diffusion, establishing the now classical Fick's equation of diffusion. His major field of research was later devoted to the physiology of muscular contraction, but he is also famous for his formula which allows the calculation of the cardiac output. Fick was the author of the first treatise of "Medical Physics"[1], the first book of this kind, where he discussed biophysical problems, such as the mixing of air in the lungs, the work of the heart, the heat economy of the human body, the mechanics of muscular contraction,

[1] *Die medizinische Physik*, Braunschweig, 1856.

the hydrodynamics of blood circulation, etc…Fick's name remains well known in the history of cardiology. He was also the author of three philosophical essays (cited in [5]).

In the first half of the nineteenth century, the concept of diffusion in liquids was not clear, opinions were rather confused about the dissolution phenomena of salts. The distinction between physical mixture of phases, solutions and compounds came out progressively. In other respects, physiologists became interested in membranes through which osmotic and diffusive processes take place. In 1752 "abbé" Nollet (1700-1770) described an astonishing experiment [3] : a tube full of "wine spirit" (ethanol) closed with a membrane made of pork bladder, was immersed in a vessel of pure water. With increasing time, Nollet observed a bulging of the membrane, water permeating through the membrane, as we understand, to lower the alcohol concentration. Was this property specific of living organisms ? – a subject of many discussions (the quarrel of vitalism). The problem of hydrodiffusion through membranes was , according to Fick's German paper, at the origin of his studies on diffusion in solutions — a simple problem to begin with : Let us quote the first sentence of his paper [6a]: "Hydrodiffusion through membranes should captivate the attention of physicists much more than it has been so far, because it is not only one of the basic factors of organic life, but also a process of the highest interest as such". At the same time (1856), quite independently, a French engineer, Henry Darcy (1803-1858), established on a series of experiments the law of water flow through sand beds, i.e. porous media, as proportional to the pressure difference [4].

Let us come back to diffusion by quoting the first lines of Fick's paper published in the Philosophical Magazine (a paper "translated" from the original one in Poggendorff's Annalen)[2] [6b] : " A few years ago, Graham published an extensive investigation on the diffusion of salts in water, in which he more especially compared the "diffusibility" of different salts. It appears to me a matter of regret, however, that in such an exceedingly valuable and extensive investigation, *the development of a fundamental law*, for the operation of diffusion in a single element of space, was neglected, and *I have therefore endeavoured to supply this omission*."

Let us be reminded that a year earlier, Fick published an article on the thermal dilatation of bodies [7], an interesting paper to understand the intellectual substrate of Fick's understanding of the atomistic structure of matter (for a thorough discussion, see ref [5]). The seminal German paper of 1855 reveals some interesting ideas which don't appear in the English one. Fick made allusion to the atomic theory, as accepted by most of the physicists as an help to get "an insight, a description and a discovery", allowing a mechanical account of the observed phenomena. But we are to be cautious, these ideas about atoms and molecules are very far from our modern concepts. Nevertheless, they were important to understand that dissolution and diffusion processes in water result from the movement of separate entities of salt and water. But Fick was unable on this basis to deduce a quantitative law. It took another fifty years for this ambitious purpose to be realised by A. Einstein. Fick had the idea of proceeding by analogy with heat diffusion – which is nevertheless a marvellous intuition !

Thinking about Graham results, Fick perceived the deep analogy between diffusion and conduction of heat or electricity, a premonitory intuition [6] :"It was quite natural to suppose that this law for diffusion of a salt in its solvent must be identical with that according to which the diffusion of heat in a conducting body takes place; upon this law Fourier founded his celebrated theory of heat, and it is the same that Ohm applied… to the conduction of electricity [3]… according to this law, the transfer of salt and water occurring in a unit of time between two elements of space filled with two different solutions of the same salt, must be, *ceteris partibus*, directly proportional to the difference of concentrations, and inversely proportional to the distance of the elements from one another".

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[2] Not exactly a direct translation. Introductions for instance are different in the two papers.

[3] Joseph Fourier , Théorie analytique de la Chaleur 1822 ; Georg Simon Ohm, Die Galvanische Kette mathematisch bearbeitet, 1827.

Going along this analogy, he assumed that the flux of matter is proportional to its concentration gradient with a proportionality factor *k*, which he called "a constant dependent upon the nature of the substances".

Following Graham set-up, Fick considers in a vertical vessel — translating this model in terms of differentials — a layer of concentration y defined by two horizontal planes x and x+dx and he writes the quantity of solvent diffusing during dt in the adjacent layer (x+dx, x+2dx) in which the concentration is y + (dy/dx)dx as :

– Q *k*.(dy/dx)dt ,

where Q is the area through which diffusion occurs. According to Fick, "*k* is a constant dependent upon the nature of the substances". Surprisingly, Fick was describing a flux – a new concept created by Fourier as the basis of his theory of heat diffusion — without using this word.

The fundamental law of diffusion is then given by the differential equation (the so called second Fick equation) which he derived "according to the model of Fourier's mathematical development" [8] :

$$\frac{\delta y}{\delta t} = k\left(\frac{\delta^2 y}{\delta x^2} + \frac{1}{Q}\frac{dQ}{dx}.\frac{\delta y}{\delta x}\right)$$

with the section Q as a function of the height x. In the case of a constant section, the equation simplifies :

$$\frac{\delta y}{\delta t} = k\frac{\delta^2 y}{\delta x^2}$$

following Fick's notation[4].

Fick had a lot of difficulties to verify the validity of his equation. Let us point out how his approach is different from Graham's. Instead of performing experiments on a series of different salts, he only used salt (kitchen salt) solutions, but he varied the geometrical conditions. The second derivative of a concentration versus distance is not an easy quantity to measure with the required accuracy. However, he was successful in performing a series of experiments under a stationary regime in two series of experiments. Fick considered only *stationary states.* With dy/dt=0, the fundamental equation simplifies. Fick gave the solution in two cases corresponding to his experiments. First for a cylinder (Q constant):

$$\frac{d^2 y}{dx^2} = 0$$

whose solution is linear : y = ax+b. In the case of a cone (in his experiment Fick used a funnel) whose section is proportional to x^2 the fundamental equation becomes :

$$\frac{d^2 y}{dx^2} + \frac{2}{x}\frac{dy}{dx} = 0$$

whose solution is easily found : y+a = -(c/x).

In Fick experiments the bottom of his tubes was in both cases in closed contact with the salt in order to maintain at this level a saturated solution, while the top was in contact with a large reservoir of pure water. The concentration versus depth was measured thanks to a small bulb immerged in the solution and hanging to the arm of a balance, which allows the measurement of the "specific gravity" (i.e. the density).

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[4] . Actually a minus sign is present on the right hand side in the German original paper as well as in the further English one. Such a sign will give unstable solutions, as it is well known by metallurgists for the spinodal decomposition. This obvious "error" was not a source of difficulty for Fick : because of the available experimental conditions, he made his measurements and the subsequent analysis only in the case of stationary states .

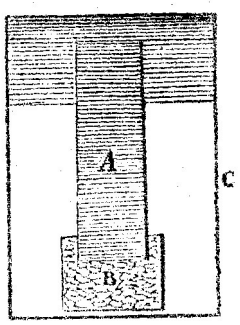

Fig.1 Experimental set-up, after Fick [9]. At the bottom, B is a reservoir of saturated salt solution, C a big vessel full of pure water, and the salt gradient is created in the cylindrical tube A.

It is sometimes difficult to understand all the details, because the author did not provide any drawing, nor any graph, just one table of results for both cases. However, there are more details about the experimental set-up in the third paper[5] [9] (fig.1)

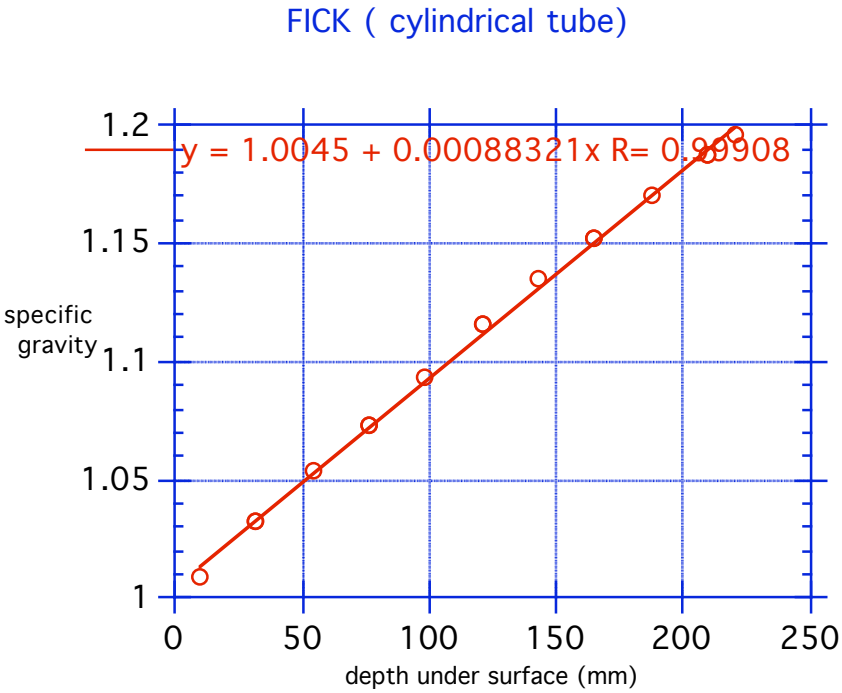

Figure 2 – From Fick's tables (cylindrical tube) [6]

I could easily plot the results of the cylindrical tube, which gives a nice straight line (fig. 2) as predicted from his equation. For the funnel, it is not so easy, as Fick gave the distance as depths from the top, while the distance x in the solution was measured from the apex of the cone ! I assumed the funnel set with the larger area at the top, but I had to guess the virtual position of the apex. Assuming the cone apex lying 250 mm below the upper surface (which Fick chose as the origin of distances), I obtained a nice verification of the expected relation (fig. 3) in spite of the fact the saturation was not attained, so that the stationary state remains doubtful in this case[6].

[5] [5] Fick published three papers on diffusion in 1855 [6,9] and, according to [5], a fourth one two years later [10]

[6] A very careful analysis of Fick's experiments has been carried out by T.W. Patzak [11]

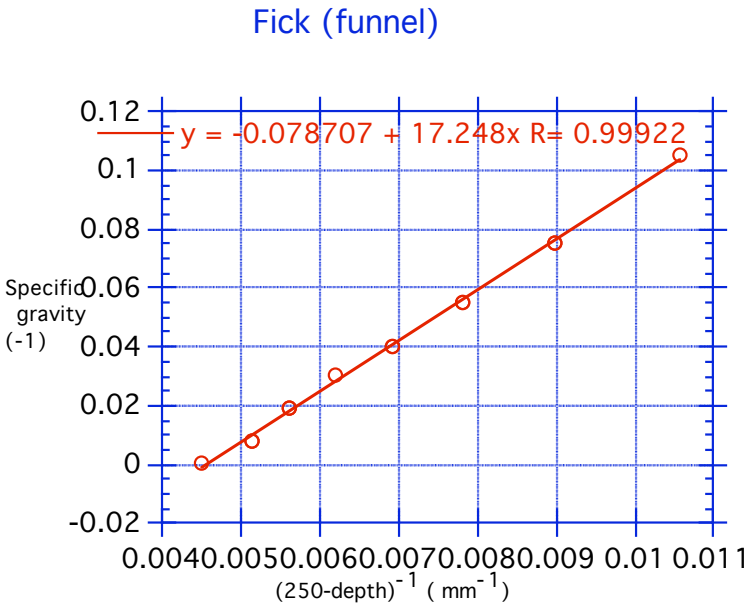

Figure 3 – from Fick's table [6], assuming thc apex of the funnel was 250 mm below the upper surface

The results of these experiments (apparently a rather small number according to the few data given in the article, for a unique system (salt dissolved at saturation in water) made Fick confident in the validity of his equation for any combination of bodies. So he decided to determine the "diffusibility"[7] *k* of salt in water. He proceeded with three cylindrical tubes of different lengths, and measured, when the stationary state was realised, the amounts of salt which in a given time diffused out of the upper section of the tube and diffused during the same time through any section of the tube according to the assumption of a stationary state. This quantity M is inversely proportional to the length, so that by multiplying this quantity by the time and dividing it by the tube lengths, the same value must be obtained for the three tubes, from which *k* (our D) is determined.

$$ML/t = JL = k\, C_S$$

I suppose Fick assumed the concentration of salt was zero at the top and equal to the saturation value C_S at the bottom of the tubes.

In a unique table, Fick gave a series of results at different temperatures between 15 and 22°C. The agreement between the three tubes was fine (better than 10%). The values are of the order of 11 mm^2 per day, i.e. $1.2.10^{-6}$ cm^2/s. Fick points out that *k* increases with increasing temperature, as already expected from Graham's experiments. But according to his comments, "this dependence upon temperature is not a simple one".

Actually Fick theory did not lie on very strong basis, neither theoretical nor experimental. This weakness explains the criticisms it received. According to the chemist Fr. Beilstein (cited by [5]) the flux of diffusion could as well be proportional to the square root of the difference of concentration between two adjacent layers. In a last paper [10] Fick argued that in such a case a stationary state should not be possible. Actually this state lies at the basis of Fourier model : assuming a "permanent "regime of heat flow, Fourier shows that the temperature does vary linearly with distance in a rod and that the expression of the flux is a quantity equal in any section of the rod, which *ipso facto* is proportional to the gradient of temperature [12].

[7] This word was probably coined by analogy with "conductibility" created by Fourier.

Another criticism was relative to the implicit assumption that k is independent of the concentration and of its gradient. This remains an actual problem, and we now know a number of cases where these two assumptions are not valid. However, one usually prefers to keep the diffusion equation in its primitive form with a variable D, this dependence being understood in the frame of theoretical models.

At that time, diffusion measurements by Graham and Fick were confined to fluids, because such measurements were possible at temperatures around room temperature. Apparently diffusion in solids was not a subject of concern to scientists, because such a process was not credible, as, for instance, acknowledged by such famous scholars as Lavoisier or Gay-Lussac. This belief was founded on a common opinion among chemists, according to the well known old adage :"*corpora non agunt nisi soluta*". According to common sense, if diffusion in fluids appears as a quite "natural" process, in solids on the contrary it could seem exceptional, if not impossible. However, solid state diffusion was active in many technical processes which should have been well known from scientists of that time[8]. Not only technical processes, but also some experiments could have been seen as a signature of diffusion. But most of the reported experiments in these old papers are rather obscure for a modern reader. Perhaps Robert Boyle (1627-1691) was, according to ref [13], the author of the first experimental demonstration of solid state diffusion in a series of experiments on "the Porosity of Bodies". He observed the penetration of a "solid and heavy body" (probably Zinc) in a farthing (a small Copper coin), so that this side took a golden colour, while the other side kept its original one. Boyle was a wise experimentalist : he explained in his essay : "To convince the scrupulous, that the pigment really did sink… and did not merely colour the superficies, … By filing off a wide gap from the edge of the coin towards, it plainly appeared that the golden colour had penetrated a pretty way beneath the surface of the farthing" (quotation from ref [13]). Boyle successfully synthesized Brass by the means of interdiffusion !

Other experiments were quite demonstrative, for instance "diffusion welding" between two pieces of two metals pressed again each other (Walthère Spring, a Belgian chemist, 1894) [13b]. Carbon diffusion in iron was measured in 1881 by Albert Colson [13c] who claims : " at a given temperature, corresponds a constant coefficient of diffusion of Carbon in Iron". Colson underlined the deep analogy of solid/solid diffusion with the liquid/liquid one. He also prepared platinum silicides by solid interdiffusion.

IV - W.C. ROBERTS-AUSTEN

In the second part of the nineteenth century, metallurgical studies on steels opened the way to the study of diffusion in metals. But quantitative measurements were not performed before the very last years of the nineteenth century, thanks to William Chandler Roberts-Austen (1843-1905), a well known British metallurgist celebrated for his study of the equilibrium diagram Fe-C (one of the main steel component has been named 'austenite'). The excellent micrographs of specimens of carburised iron, due to his French friend Floris Osmond (1849-1912), clearly showed the penetration of Carbon inside the bulk of Iron.

The interest of Roberts-Austen for diffusion is not a surprise, as he began as an assistant of Thomas Graham and later on succeeded him as Master of the Mint in London. When he was 'chemist and essayer" in this institution, he had at his disposal good analytical tools, useful to investigate systems based on precious metals. The limitations were essentially the range of temperatures he could manage, but he was lucky since the Pt/RhPt thermocouple was just invented at that time by the French physico-chemist Henry LeChatelier (1850-1936).

[8] A review of processes and experiments involving solid state diffusion is given by Roberts-Austen in the introduction of his paper [14, part II].

Stationary states are not the most common, except for the permeation of gases. The large majority of experiments correspond to time dependent processes, such as the interdiffusion between two bodies, liquids or solids. This was the case in the remarkable series of experiments Roberts-Austen carried out in liquid (and solid) metals. As underlined by this author [14] "the difficulty was obvious" (specially in the case of liquids because of convection movements), "but my long connection with Graham's research made it almost a duty to attempt to extend his work on liquid diffusion to metals" – in spite of Ostwald's warning : "To make accurate experiments on diffusion is one of the most difficult problem in Physics". Roberts-Austen analysis of his measurements is based on Fick's law : "It appears probable that the law of diffusion of salts, framed by Fick, would also applied to the diffusion of one metal with another". The diffusion equation (the now so-called second Fick's equation) is expressed by Roberts-Austen according to Lord Kelvin's : "The rate of augmentation of the "quality" per unit of time, is equal to the diffusivity multiplied by the rate of augmentation per unit of space of the rate of augmentation per unit of space of the "quality". Here, "quality" means the concentration of the matter which had diffused. And Roberts-Austen writes this long sentence[9] in a shorter formula :

$$\frac{dv}{dt} = k\frac{d^2v}{dx^2}$$

for one dimensional diffusion. It follows that the diffusion constant k may be expressed in square centimetres per day (or per second). Roberts–Austen performed experiments on the diffusion of precious metals (Au, Pt, Rh) in liquid Lead, of Au and Ag in liquid Tin, and Au in liquid Bismuth.[14]. The specimens were cut in thin sections which were analysed by weight measurements (with a balance of maximum load 0.5 g and a sensitivity of 2 μg). Finally he made a tentative of solid interdiffusion, Gold into Lead. [14] On the basis of 6 or 7 sections of the lead substrate, he analysed the diffusion profiles after heat treatments at 4 different temperatures

To determine k from the diffusion profiles (concentration versus distance) , Roberts-Austen used the tables calculated by J. Stefan[10] for the diffusion of salts, formerly studied by Graham. Stefan (1835-1893) [15] gave the solution of the diffusion equation in two forms : either as a trigonometric series or as the complementary error function erfc $(h/2\sqrt{kt})$. In the case of specimens of finite length, Stefan recommended to apply the principle of reflection plus superposition[11]. Thanks to these analytical solutions, he calculated a set of numerical tables giving the concentration profiles for tubes, with $h/2(kt)^{1/2}$ as a parameter, where h is the thickness of the successive layers defined for chemical analysis through the diffusion zone. Roberts-Austen used these tables to analyse his results [14].

Roberts-Austen's results on solid systems are quite comparable to modern tracer measurements, with a right value of the activation energy, if the lower temperature coefficient is discarded. Roberts-Austen was specially lucky in choosing for his investigations the system Au/Pb, since it is now known that gold is a "fast" diffuser in lead - an imperative condition for measurements with the space resolution he could manage in his experiments.

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[9] The way to tell in words the second derivative was rather heavy…

[10] Josef Stefan (1815-1893), an Austrian theoretician physicist is well known for his expression of the emission power of a black body as proportional to the fourth power of temperature (Stefan-Boltzmann law). His contributions to transport phenomena in fluids were of great importance in the context illustrated by Maxwell, Nernst, etc [16]. In his celebrated 1867 paper " On the Dynamical Theory of Gases" , Maxwell gave a theoretical derivation of the diffusion equation , written in terms of gas pressure [17].

[11] The concentration profile is first calculated for a semi-infinite medium, and that part of the curve which lies beyond the surface is reflected through this interface and added to the inside part of the curve.

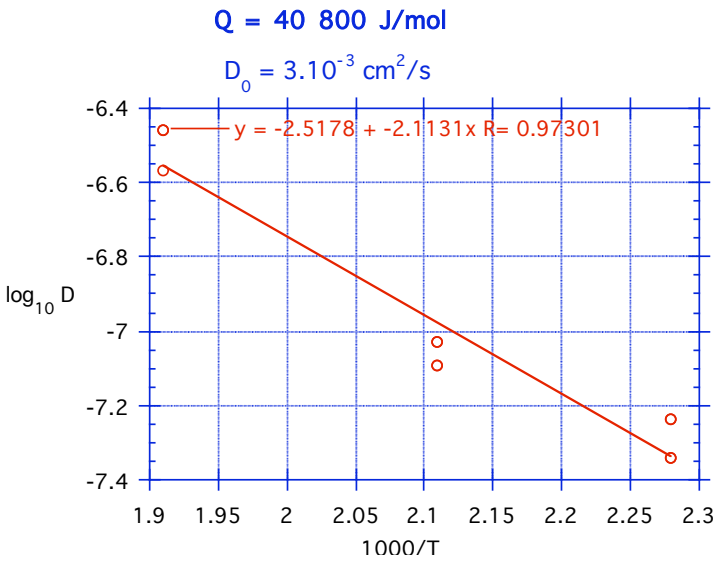


Fig4 – Roberts-Austin data Au/Pb [14]

The Arrhenius graph (figure 4) is not Roberts-Austen's, it is mine. Apparently, he didn't discuss the temperature dependence of the coefficient of diffusion in his "Bakerian Lecture" on the *Diffusion in Metals* published in 1896 [14]. The Arrhenius graph, so familiar to everybody with its pervasive use – and abuses – is based on Arrhenius equation, that Svante Arrhenius (1859-1927) proposed in his 1889 paper [18],— in the course of his investigations on the reaction rate of cane sugar (i.e. saccharose) inversion by means of polarised light rotation — to describe quantitatively his experimental results as well as a collection of published temperature dependences of several chemical reaction rates. This proposal was completed by a theoretical assumption on the "active" state of the concerned substances, an assumption which allowed him to derive theoretically the temperature dependence of the reaction rates. It came as a surprise to me, when I found that the exp(-Q/T) variation with temperature of the coefficient of diffusion was only invoked 30 years later (1922-1923) by Saul Dushman and Irving Langmuir (1881-1957) [19] and independently by H. Braune (1924) [20] and that Langmuir considered this T-dependence as an empirical relation, without mentioning Arrhenius name !

It is worth to mention here another important contribution from Josef Stefan in the case of multiphase diffusion, when the interface between two contiguous phases is moving with time (as the square root of time as derived by Stefan). Stefan actually was working on the formation of ice under a thermal gradient [21] : as the heat and diffusion equations are identical, Stefan conditions at the interface are now classical : the latent heat (or the solute difference) is respectively balanced by the gradient of heat (or of solute concentration).

Let me conclude this paragraph with a quotation from Roberts-Austen [14] : "The evidence gathered by the metallurgist of active atomic movement in fluid and solid metals may sustain the hope of the physiologist that he will ultimately be able to measure the atomic movements upon which vitality and thought depend". This audacious sentence should take us back to Adolph Fick, a physiologist. Is life and consciousness purely a matter of chemistry ? I leave it to the reader to choose!

V - Albert Einstein

If you decide to teach basic diffusion, there are two ways to begin with either a phenomenological approach starting with Fick's laws and their mathematical solutions, or a physical and atomistic one, by considering the "random walk" of the diffusing particles. While this last approach was rather straightforward in gases thanks to Maxwell's kinetic theory of

gases, the first one follows the historical development of diffusion studies in solid materials under a gradient of chemical potential as in Roberts-Austen experiments. People began to be concerned with an atomic scale approach first of all with the electrical conductivity of ionic crystals, and later with the Kirkendall effect which was observed in several interdiffusion systems. As diffusion processes depend on atom (ions) jumps whose occurrence is dictated by atomic defects (vacancies or interstitials), a description based on atom movements became compulsory[12].

The never-ending movement of particles in suspension in a fluid was discovered by a Scottish botanist, Robert Brown (1773-1858), who was observing with his microscope the "swarming" motion in the fluid of small particles extracted from living pollen grains[13]. He noticed that this motion was quite general in fresh pollen grains, as well as in dried ones. Brown's experiments with organic and inorganic substances, reduced to a fine powder and suspended in water, revealed such motion to be a general property of matter in this state. He published these results in a paper " A brief Account of Microscopic Observations" in 1828 [22]. The name *"Brownian motion"* has been coined in honour of Brown to qualify the *random walk* of microscopic particles in suspension in a fluid. This was probably one of the origins of Maxwell's kinetic theory of gases. It is pleasant to describe it in popular books (e.g. George Gamow renown books [23]) as the wanderings of a "drunk sailor" (fig. 5) !

A careful investigation of Brownian motion was performed by Georges Gouy (1854-1926) [24] in a series of experiments with different kinds of particles in different kinds of fluids. He could demonstrate that this motion is independent of external forces (such as vibrations, light, magnetism, temperature gradient) and is more intense in less viscous fluids. Let us quote his conclusion : "Brownian motion, unique among physical processes, makes visible the constant state of internal restlessness of bodies, in the absence of any external cause…. It is a weakened and remote testimony of thermal molecular motions".

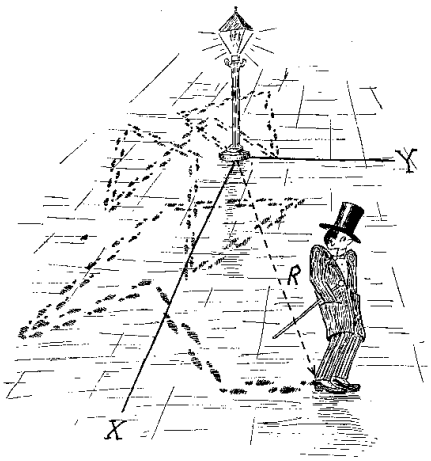


Figure 5- Random walk according to Gamow [23])

The mathematical form of Brownian motion was derived almost a little bit later (in 1905) by Albert Einstein (1879-1955) [14] [25]. He was the first to understand, contrarily to many scientists

[12] For a history of the Kirkendall effect, see ref [41].

[13] Brown was interested in the fecundation process of plants.

[14] According to the title of his paper "On the movement of small particles suspended in a stationary liquid…" Einstein was not aware of the details of the "Brownian motion" He explains : "It is probable that the movements to be discussed here are identical to the so-called "Brownian molecular motion". However the information available to me regarding the latter is so lacking in precision, that I can form no judgment in the matter". .After the publication of his paper, several scientists, specially Georges Gouy, informed him of their experimental observations of the

of his time, that the basic quantity was not the average velocity of the particles, but their mean square displacement in a given time $<R^2(t)>$.Trajectories are such (see fig.3) that velocity is meaningless.
Investigations on the Brownian movement was the subject of five papers by Einstein (1905-1908)[15]. Einstein – at that time employed as an engineer at the Patent Office in Bern — got interested in the motion of small particles suspended in a liquid, as a "visible" testimony of the molecular kinetic theory of heat. At that time "atomic theory "was still an object of controversies: in 1895 the famous physico-chemist Wilhelm Ostwald (1853-1932) published an article[16] : "La déroute de l'atomisme contemporain". Several other papers due to famous scientists of this time were discussing these topics (e.g. is Brownian motion violating Carnot principle?). These discussions will deserve a special paper.
Einstein was studying the fluctuations of a thermodynamical system, which on the basis of the Boltzmann's relation for entropy, could allow the experimental determination of the Boltzmann constant k and therefore of the Avogadro number. Some discussion of the black body radiation convinced Einstein of this possibility and, with his doctor thesis, he became interested in suspensions of particles in a fluid, which should give a "zoom" image of molecular movements.. The "magic" idea was to apply the laws of solute molecules to bigger particles in suspension in a liquid. Einstein's derivation is probably not a model of rigor : as a main assumption he balances the osmotic pressure due to solutes by the drag force due to the solvent viscosity. Whence for the steady state the relation for the diffusivity of solute molecules and, by extension, of suspended particles :

$$D = \frac{RT}{N}\frac{1}{6\pi\eta\rho} \qquad (1)$$

Where R and N are respectively the ideal gas constant and the Avogadro number, η and ρ the solvent viscosity and the particle radius..

In a second step Einstein describes the successive positions of a particle at time intervals τ, assuming that its movement is independent of the movement of all other articles and that τ is sufficiently small, but such that the movements of a single particle in two consecutive intervals of time τcan be considered as mutually independent. We here identify the two basic assumptions of the "Brownian motion". Assuming the displacements Δ of particles in a given time along a given direction obeys a symmetrical distribution function $f(\Delta)$ (actually a Gaussian, for sufficiently long times, as it is easily derived without new assumptions), Einstein derives an equation for the space distribution of the particles that is just the second Fick's law ; with the diffusivity defined on a microscopic basis

$$D = \frac{1}{2\tau}\int_{-\infty}^{+\infty}\Delta^2 f(\Delta)d\Delta = \frac{1}{2\tau} < \Delta^2 >. \qquad (2)$$

The mean displacement $<R(t)>$ of a large number of particles is nil in the case of a truly random walk, in the absence of external "forces", so it is the mean square which is the meaningful quantity. The fundamental relation above links a macroscopic quantity, i.e. the coefficient of diffusion, and a microscopic one, the mean square displacement. We can re-write it in 3-d as :

$$D = <R^2>/6t. \qquad (3)$$

Brownian motion, as he explains in the introduction of his second paper "On the theory of Brownian motion" published the next year.

[15] The 1905 paper is the most cited in the literature among the famous papers Einstein published in 1905.

[16] Ostwald's speech "Die Überwindung (triomphe) des wissenschaftlichen Materialismus" was delivered in Lübeck , published in 1895, and shortly after translated in French (Revue générale des sciences pures et appliquées (15 Nov. 1895) pp.952-958 (O. Hardouin Duparc, private communication).

Eliminating the coefficient of diffusion between equations (2) and (3), Einstein obtains a relation for the "mean displacement" in a time t : $L = \sqrt{(2Dt)}$ which should allow the experimental determination of Avogadro's number. A simple numerical calculation convinced Einstein that the order of magnitude should make the experimental verification quite possible.

Relation (3) is frequently quoted as Einstein- Smoluchowski relation, as this last author published independently a year later a theory of the Brownian motion, based on a kinetic approach of the interactions and collisions between particles – quite different from the thermodynamic approach of Einstein [26][17]. M. Smoluchowski (1872-1917) claims his "method allows a better understanding of the intimate mechanism of the phenomenon" — actually a true assertion ! Nevertheless, Einstein was finally obliged to look at the details of the kinetics in order to derive the dependence of the viscosity with the volume fraction of particles

This first paper was followed a few months later by a more theoretical one, where Einstein studied not only the translational movement of suspended particles, but also the rotational one of spherical particles. Let us just quote the first lines of this paper : " Soon after the appearance of my paper on the movement of particles suspended in liquids, demanded by the theory of heat, Siedentopf … informed me that he and other physicists – in the first instance Prof. Gouy (from Lyon) – had been convinced by direct observations that the so-called *brownian motion* is caused by the irregular thermal movements of the molecules of the liquid [25].

Later on (1908) Einstein published "a simple theory of this phenomenon" (Brownian motion), which "would be welcomed by … chemists" ! In this paper, Einstein proposed, thank to "simplified assumptions", a straightforward derivation of his equation, the one which was later given in most elementary text-books[18].

I shall mention the very elegant approach due to Paul Langevin. (1872-1946) [32], which as he claimed is more direct than Einstein's and simpler than Smoluchowski's. He describes the motion of free (i.e. in the absence of external force) particles of mass m in the x direction, on the basis of the law of dynamics, with two force terms : a viscous resistance according to Stokes formula plus a fluctuating force F(t) independent of the velocity , which results from the molecular impacts on the Brownian particles, such that its time average $\langle F(t)\rangle = 0$:

$$m\,(dv/dt) = -\,6\,\pi\eta\rho\, v + F(t).$$

By integration and taking the time average [with $(1/2)\, m\langle v^2\rangle = (1/2)kT$], he ends up with :

$$\langle X^2(t)\rangle = (RT/N)\,(1/3\pi\eta\rho)\,t, \qquad (4)$$

i.e. exactly Einstein's formula for the steady state regime, which is realized after a very short time $M/6\pi\eta\rho$. For shorter times, i.e. between two impacts, the motion would become ballistic with $\langle X^2\rangle \approx t^2$. Actually this time can be longer because of a kind of memory effect in the exchange of momentum between the molecules and the impacted particle.

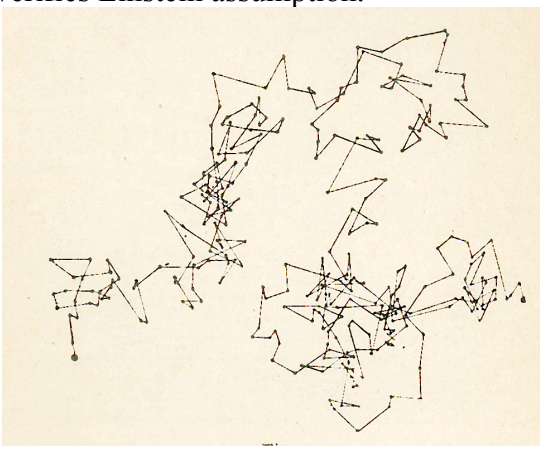
It was the privilege of Jean Perrin (1870-1942) to fully exploit Einstein's theory, probably — I guess —following a suggestion of Langevin, definitively establishing the reality of atoms and molecules, a work for which he was granted the Nobel Prize in 1926 [19]. In a series of clever experiments, Jean Perrin and his students Chaudesaigues, Dabrowski, Bjerrum, Costantin [29] could verify Einstein's relations, beautifully described in two chapters of his book "Les

[17] Smoluchowski arrived at the same formula as Einstein's (eq. 1 and 4), with a numerical factor larger by $\sqrt{(64/27)}$. Following Smoluchowski approach, Langevin [32] arrived at the Einstein formula without this factor. Moreover experimental results didn't confirm this factor.

[18] The five Einstein papers on Brownian movement have been published in an English translation with several notes and comments in a book [25].

[19] A biography of jean Perrin is available in English : Marie Jo Nye : "*Molecular Reality : a Perspective on the scientific Work of Jean Perrin*" (Mc Donald, London, 1972)

Atomes" [29], published in 1913, a book whose reading can still be warmly recommended. Perrin experiments just require a microscope, and a suspension in a liquid of small spherical particles (a few tenths of micron in diameter). From the observation of the distribution of particles in a vertical tube, J. Perrin concluded " an emulsion is an atmosphere in miniature" which verifies Einstein assumption.



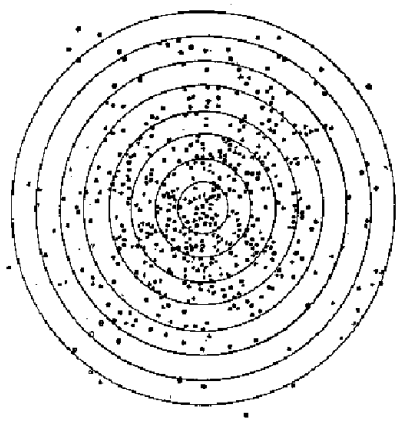


Fig 6- Brownian motion, after Jean Perrin [29] : (above) an example of a trajectory and (below) statistical distribution of displacements (the circles correspond to fractions and multiples of the square root of the mean square displacement $<R^2(t)>$.

To check Einstein- Smoluchowski formula, you just have to observe under the microscope the motion of a given particle and to point its positions at regular time intervals. Jean Perrin describes enthusiastically " *le prodigieux enchevêtrement de la trajectoire réelle*" (fig.6), "the prodigious entanglement of the real trajectory". If we could plot the particle positions at time intervals hundred times smaller, every linear segment of the trajectory would take a polygonal shape as complicated as the whole trajectory, and so forth… We can see how in such a case the notion of a tangent to a trajectory vanishes". What a premonitory description of a fractal line, fifty years before Benoît Mandelbrot's work [30] !

Jean Perrin checked that the particle displacements did exactly follow random laws. In two dimensions, i.e. in the plane of the observations under the microscope, the values of R(t) are distributed according to a Gaussian law. With a well defined standard deviation around the square root of $<R^2(t)>$ (fig. 6). According to J. Perrin again, " the randomness of the particle motion is definitely established".

In the same series of experiments, easy to reproduce with a simple experimental set-up, Jean Perrin succeeded in a quite remarkable result : the measurement of Avogadro's number

according to another relation given in Einstein's first paper (eq.4). The result, with ***N*** of the order of a few unites time 10^{23}, is quite remarkable as it is an *absolute* determination, thanks to so simple an experimental tool – so far from our modern and sophisticated investigation machines ! These simple experiments bore the definite proof of the existence of atoms against ambient scepticism. Let us quote Einstein:

"The agreement of these considerations with experience together with Planck's determination of the true molecular size from the law of radiation (for high temperatures) convinced the sceptics, who were quite numerous at that time (W.Ostwald, E.Mach, …) of the reality of atoms. The antipathy of these scholars towards atomic theory can indubitably be traced back to their positivistic philosophical attitude. This is an interesting example of the fact that even scholars of audacious spirit and fine instinct can be obstructed in the interpretation of facts by philosophical prejudices." [31].

Let us come back to Einstein's papers. Unknowingly, Einstein was answering a question expressed the same year (1905) by the genetician-statistitian Karl Pearson (1857-1936) in a letter published in *Nature*, entitled "The problem of the Random Walk"– a question arising perhaps from the contagion due to mosquitoes [27]:

"Can any of your readers refer me to a work wherein I should find a solution of the following problem, or failing the knowledge of any existing solution, provide me with an original one? …A man starts from the point O and walks *z* yards in a straight line, he then turns to any angle whatever and walks another *x* yards in a second straight line. He repeats this process n times. Inquire the probability that after n stretches he is at a distance between r and $r + \delta r$ from his starting point O." The Pearson thought trajectory is perfectly illustrated by Jean Perrin's ones (fig. 6). The expression "random walk" was probably coined at that time , from the exact words Pearson used.

Quite remarkably, the answer had been given five years before, by a young French mathematician Louis Bachelier (1970-1946) in his doctor dissertation [28]. But concerns of Bachelier were very far from Pearson's; In his thesis entitled " Théorie de la Spéculation", he was studying the fluctuations of stock-market prices as they vary up and/or down. Let us just translate the daily quotations in particle positions at equal time intervals, we are faced with a series of random numbers. Applying the central limit theorem, Bachelier describes these values through a Gaussian dispersion law. Calculating the probability *P* that the price be equal or larger than a given value on a given day, he showed *P* obeys Fourier equation. He describes the elementary process as a law of *diffusion of probability.* As a fine mathematician, the second part of his derivation relates to the limit case where the variable is a continuous one and still obeys the same equation[20]. Later on this first model received considerable developments, as random walk is just the sum of random variables. A famous theorem on random walks on an integer lattice was derived in 1921 by G. Pólya (1887-1985) [21]— a renown mathematician who coined the name of the "central limit theorem" — giving a strong basis to the classical model.

But let us remember that the movement of material particles in suspension in a liquid were the starting point of our speculations. It is interesting at this stage to mention some later developments of the theory of the random walk. Starting with the *stricto sensu* Brownian motion of a particle in suspension in a fluid, people got interested in the random walk of … anything. For mathematicians he expression "Brownian motion" is rather devoted to a mathematical object defined by extrapolation at the zero limit of the space and time increments : the trajectory become a "monster curve" with two paradoxical properties : continuous

[20] To get a doctor degree, it was compulsory to write a small dissertation on another topics proposed by the examination board. Quite remarkably, this "second dissertation" discussed the small translational movements of a solid sphere immerged in a fluid, — a premonitory view…[40]

[21] In 1 and 2-D lattices, the probability the particle will *never* reach any given point is nil. In a 3-D lattice, according to Polya, this is no more true (this probability has a finite value).

everywhere *and* nowhere derivable in a n-D space.. Let us quote specially the mathematical theory of Norbert Wiener (1926) and the discussion of dispersion functions more realistic than the Gaussian one (Black, Scholes, Merton, 1973) [33].

Physicists, busy in another world, whish to understand the basis of diffusion in solids, i.e. the movement of an atom (ion, molecule) on a lattice or in a disordered network). Just assuming a symmetrical probability distribution function (pdf) $f(X,\tau)$ of distances X that a particle walked in a given time τ, it easy to derive, as Einstein actually did in his last paper, the relation between the diffusivity D and $<X^2(\tau)>$ or $<R^2(\tau)>$, (see eq.3). Statistical basis of this assumption lies in the central limit theorem, which predicts this pdf is a gaussian with a standard deviation equal to $2<X^2>$ as we underlined above. In crystals the situation is rather simple, since the jump lengths are fixed, randomness is due to jump directions.
Further important developments of random walk models was due to physicists, statisticians and mathematicians. Let us mention the CTRW model (Continuous Time Random Walk) [33b], [34] : in this model the time intervals between two jumps are no more fixed ; they instead obey a probability distribution function (pdf). A complete model assumes two pdf's, one for time intervals (or "waiting" times between two consecutive jumps), another one for jump lengths. When these pdf's are Gaussian, Einstein's formula remains valid : the square root of time law is obeyed. Further developments rely on other kinds of pdf's. : a power law distributions for time intervals leads to "subdiffusion", i.e $<X^2> \approx t^n$, with $n<1$. Inversely a power law for lengths can lead to "superdiffusion" (the so called "Lévy flights", fig.7) with $n>1$ [34] ; in this case on can define a mean length but not an average, as the pdf doesn't have a upper limit.

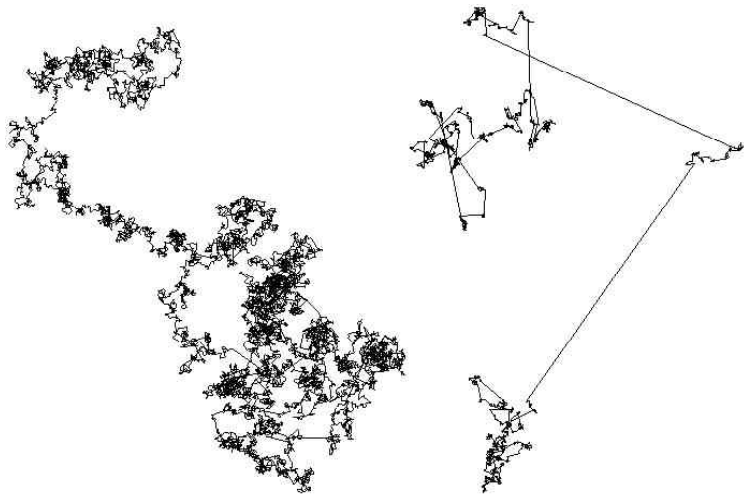


Fig.7 – One thousand steps: random (left) and Levy flights (right)

VI - … AND LATER ON…

With these strong bases, Fick's and Einstein's equations, the way was open to new experiments in order to determine diffusion coefficients in solids and identify the atomic mechanisms in the frame of theoretical developments, specially in connection with models of random walks and departures from purely random movements (cf. the so-called "correlation factors"). Their study was specially suited for numerical simulations by the Monte-Carlo methods. But this history could be the subject of another paper.

On the other hand there was still the need for better experimental techniques. I would just select two of them, for the sake of limiting the length of this paper : radioactive tracers for self (and hetero-) diffusion, and electron microprobe for interdiffusion.

A critical stage in diffusion measurements was accomplished by György von Hevesy, a Hungarian born and European personage (1885-1966) who worked in several famous places with celebrated scientists such as A. Rutherford, Henry Moseley or Niels Bohr. He was probably the first one to understand the usefulness of radioactive tracers as a tool in physics and chemistry. In 1912, when he was working in Vienna at the Radium Institute, he used radioactive Lead as a "radioindicator" – "radiotracer" in modern language— (^{210}Pb, also called radium D, ^{212}Pb or Thorium B) in several studies, including Pb self-diffusion. Later on, in Vienna, Budapest or Copenhagen, he was using these radiotracers to study diffusion in salts, in liquid and solid Lead, and even in vegetables. After the discoveries in 1934 of artificial radioactivity by Irene and Frederic Joliot-Curie and neutron activation by E. Fermi, he prepared several artificial radio-elements to study the assimilation of Phosphorus by plants or the metabolism of this element in rats. These studies are a little far away from our field, but because of this large range of applications, the Nobel Prize in Chemistry was awarded to Hevesy in 1943. An account of these studies was the object of a book " Radioactive Indicators" he published in 1946 [35][22]. Radiotracers were largely used after World War in many various ways developed by a lot of scientists in several countries, because this technique allowed very accurate measurements of diffusion coefficients in most of solids. Their importance is even underlined by their absence or rarity (and high price !) in a few important cases: Aluminium, Silicon and Oxygen, to cite the more important. There was no good remedy to this lack until the mass spectroscopy analysis of stable isotopes (specially Oxygen thanks to ^{18}O) became available.

Finally, I would like to mention another important tool which appear in 1950-51, the Electron probe Microanalyser, build by the French physicist R. Castaing (1921-1998), an instrument in which a very fine beam of electrons excites characteristic X-Rays. Chemical analysis on a micron scale was made possible by X-ray emission spectroscopy and showed its powerful applications with the diffusion profile through the multiphase couple Cu/Zn. [36]. A new way of investigating interdiffusion processes became rapidly available to a large number of laboratories thanks to the commercial production of the instrument.

Later on other analytical tools were available allowing new diffusivity measurements [37], [38], [39], specially secondary ion emission coupled with mass spectrometry and nuclear methods (NMR, Mössbauer spectroscopy, Rutherford back scattering, …), but the history of their development lies out of the scope of the present paper.

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[22] Hevesy's works are not limited to radiotracer applications. He was the initiator of chemical analysis by X-ray fluorescence(the subject of a book published in 1932), and with Coster in 1923 he discovered the element hafnium.

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NOTES

1-– Fick's publications have been collected in four volumes : *Gesammelte Schriften* (Würzburg, Stahel'sche VerlagAnstalt, (1903-1904) with an introduction by F. Schenk, an assistant of Fick: *Zum Andenken an A. Fick* [after10].
A detailed biography of Fick, written by K.E. Rothschuh, was published in the *Dictionary of Scientific Biography*, Dir. Charles C. Gillispie, Scribners, New-York, 1970-1980,.

2 – Ref [23] gives English translations of five papers

- 1- Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen
- On the movement of small particles suspended in a stationary liquid demanded by the kinetic molecular theory of heat.
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- On the theory of Brownian Movement
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