Heroes and Highlights in the History of Diffusion

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Abstract

The science of diffusion had its beginnings in the nineteenth century, although the blacksmiths and metal artisans of antiquity already used diffusion phenomena to make such objects as hardened iron swords and gilded bronze wares. Diffusion as a scientific discipline is based on several cornerstones. The most important ones are: (i) The continuum theory of diffusion originating from the work of the German physiologist *Adolf Fick*, who was inspired by elegant experiments on diffusion in gases and of salt in water performed by the Scotsman *Thomas Graham*. (ii) The Brownian motion, observed for the first time by the Scotish botanist *Robert Brown*, was interpreted decades later by the famous German-Jewish physicist *Albert Einstein* and almost at the same time by the Polish physicist *Marian von Smoluchowski*. Their theory related the mean square displacement of atoms to the diffusion coefficient. This provided the statistical cornerstone of diffusion and bridged the gap between mechanics and thermodynamics. The Einstein-Smoluchowski relation was verified in tedious experiments by the French Nobel laureate *Jean Baptiste Perrin* and his coworkers. (iii) Solid-state diffusion was first studied systematically on the example of gold in lead by the British metallurgist *Roberts-Austen* in 1896. Using a natural radioisotope of lead the Austro-Hungarian *Georg von Hevesy* and his coworkers performed for the first time studies of self-diffusion in liquid and solid lead around 1920. (iv) The atomistics of diffusion in materials had to wait for the birthday of solid-state physics, heralded by the experiments of the German Nobel laureate *Max von* Laue. Equally important was the perception of the Russian and German scientists *Jakov Frenkel* and *Walter Schottky,* reinforced by the experiments of the American metallurgist *Ernest Kirkendall*, that point defects play an important role for the properties of crystalline substances, most notably for those controlling diffusion and the many properties that stem from it. (v) The American physicist and twofold Nobel laureate *John Bardeen* was the first who pointed out the role of correlation in defect-mediated diffusion in solids, an aspect, which was treated in great detail by the American physicist *John Manning*. (vi) The first systematic studies of grain-boundary diffusion, a transport phenomenon of fundamental as well as technological importance, were initiated by the American materials scientist *David Turnbull*.

This paper is devoted to some major landmarks and eminent pioneers of diffusion from the nineteenth and twentieth century. The heroes of the nineteenth century were Graham, Brown, Fick, Roberts-Austen, and Boltzmann. In the twentieth century diffusion science was driven by significant contributions of several Nobel laureates, such as Einstein, Arrhenius, Perrin, von Hevesy, and Bardeen.

Keywords: Diffusion Pioneers, Landmarks, Discoveries, Concepts, Achievements

1. Introduction

The Latin word '*diffundere*' means 'to spread out'. Depositing a droplet of ink in a basin of water without stirring gives a simple demonstration of diffusion. After a few hours the colour will have spread a few millimetres and after several days the solution will be uniformly coloured. Diffusion is caused by the Brownian motion of atoms or molecules that leads to complete mixing. The water molecules even in pure water are in continuous random motion; their migration through the liquid constitutes an example of *self-diffusion*. This atomic-scale motion is fairly rapid in gases – gas diffusion progresses at a rate of centimetres per second. In liquids it is slower but still easy to visualize – its rate is typically fractions of millimetres per second. It is more difficult to observe diffusion in the solid state. Nonetheless, diffusion in solids occurs. It is a fairly slow process and the rate of diffusion decreases strongly with decreasing temperature. Near the melting temperature of a metal a typical rate is about one micrometer per second; near half of the melting temperature it is only on the order of nanometres per second.

Until the end of the nineteenth century the paradigm that diffusion occurs only in gases and liquids was widely accepted by the scientific community. It was mainly due the pioneering work of William Roberts-Austen and Georg von Hevesy that this paradigm had to be abandoned. Having in mind the crystal structures of solids, one can appreciate that diffusion of atoms or ions through those generally 'dense' structures is difficult. The energies necessary to 'squeeze' atoms or molecules through *perfect* lattice structures are so high that diffusion may become virtually impossible. A deeper knowledge about diffusion requires information on the position of atoms and how they move in solids. It has been found that imperfections on the atomic scale play a paramount role. Specifically in crystalline solids, the atomic mechanisms of diffusion are closely connected with lattice defects. Point defects like vacancies or interstitials are the simplest defects and often mediate diffusion in crystals. Dislocations, grain-boundaries, phase boundaries, and free surfaces are other types of defects. They can act as high-diffusivity paths (diffusion short circuits), because the mobility of atoms along such extended defects is usually much higher than in the lattice.

Solid-state diffusion is a process that is fundamental in the art and science of materials and thus forms an important topic of solid-state physics, physical metallurgy, and materials science. Diffusion processes are relevant for the kinetics of many microstructural changes that occur during preparation, processing, and heat treatment of materials. Typical examples are nucleation of new phases, diffusive phase transformations, precipitation and dissolution of a second phase, homogenisation of

alloys, recrystallisation, high-temperature creep, and thermal oxidation. Diffusion and electric conduction in ion conductors are closely related phenomena. Direct applications of diffusion concern a multitude of important technological processes such as doping during fabrication of microelectronic devices, the operation of solid electrolytes for batteries and fuel cells, surface hardening of steel through carburisation or nitridation, diffusion bonding, and sintering.

2. Pioneers and Cornerstones of Diffusion

2.1 Thomas Graham – diffusion in gases

The first systematic studies of diffusion in gases were probably performed by the Scottish chemist *Thomas Graham* (1805 – 1869). He is considered as one of the leading chemists of his generation. Graham was born in Glasgow. His father was a successful textile manufacturer. He wished his son to enter the Church of Scotland. Defying his father's wishes, Graham studied natural sciences, developed a strong interest in chemistry and became professor of chemistry in 1830 at the Andersonian Institute (now Strathclyde University) in Glasgow. Later he became professor of chemistry at several colleges including the Royal College of Science and Technology and the University of London in 1837. Graham also founded the Chemical Society of London and became its first president. In 1855 Graham succeeded Sir John Herschel as '*Master of the Mint'* in London following the tradition – established by Sir Isaac Newton – of distinguished scientists occupying the post. Graham is one of the founders of physical chemistry and he discovered the medical method of 'dialysis'.
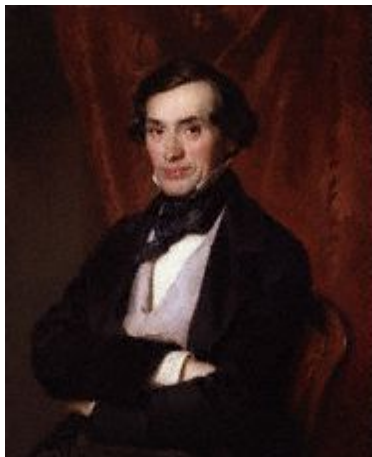
The Scottish chemist Thomas Graham (1805 – 1869)

Graham initiated the quantitative study of diffusion in gases, largely conducted over the years 1828 to 1833 [1, 2]. He recognized that gases of different nature, when brought into contact, do not arrange themselves according to their density with the heaviest undermost. Instead they diffuse through each other and finally achieve an intimate state of mixture. In one of his articles he explicitly stated what we now call Graham's law: *'The diffusion or spontaneous intermixture of two gasses is effected by an interchange in position of indefinitely minute volumes of the gases, which volumes are not of equal magnitude, being, in the case of each gas, inversely proportional to the square root of the density of that gas.'* In modern language:

$$\frac{v_A}{v_B} = \sqrt{M_B / M_A} \; , \tag{1}$$

where v_A and v_B denote mean atom velocities and M_A and M_B the molar masses of A and B molecules. The crucial point about Graham's work on diffusion in gases was that it could be understood by the kinetic theory of gases developed by *Maxwell* and *Clausius* shortly after the middle of the 19th century. Graham's law can be attributed to the equipartition of kinetic energies between molecules with different molecular masses:

$$M_A v_A^2 / 2 = M_B v_B^2 / 2 = 3 k_B T / 2 \, . \tag{2}$$

Here k_B denotes the Boltzmann constant and T is absolute temperature. In this way diffusion was connected with the more or less random motion of atoms or molecules, and the idea of the mean free path entered science. The notion of the diffusion coefficient was not yet established when Graham performed his experiments. It was introduced about three decades later by Fick. However, when Maxwell calculated the diffusion coefficient of CO_2 in air from Graham's data, he obtained a value which was accurate to 5% with modern studies.

Later on Graham also extended his studies to diffusion of salts in liquids [3] and to the uptake of hydrogen in metals. He noticed that diffusion in liquids was at least several thousand times slower than in gases. Combined with the number of Avogadro, Graham's law permits the determination of molecular masses. Later on, the Tschech-Austrian physico-chemist *Johann Joseph Loschmidt* (1821 – 1895) used an experimental device similar to that of Graham for his classical measurements of diffusion in several gas pairs.

2.2 Adolf Fick – phenomenological laws of diffusion

A major advance in the field of diffusion came from the work of the German physiologist *Adolf Eugen Fick* (1829–1901). He was born in Kassel, Germany, as the youngest of nine children. His father, a civil engineer, was a superintendent of buildings. During his secondary schooling, Adolf Fick was delighted by mathematics, especially by the work of the French scientists *Poisson* and *Fourier*. He entered the University of Marburg with the intention to specialise in mathematics, but switched to medicine on the advice of an elder brother, who became later a professor of law. Fick received his doctorate with a thesis on *'Visual Errors due to Astigmatism'*. He spent the years from 1852 to 1868 at the University of Zürich, Switzerland, as an assistant of *Carl Ludwig*, a professor of anatomy and physiology. After sixteen years in Zürich, Fick was appointed to a chair in physiology in Würzburg, Germany.

Fick's papers on diffusion are signed as *'Demonstrator of Anatomy, Zürich'* and they were published in high-ranking journals. His approach was a phenomenological one and it uses a continuum description. Nowadays, we would call his theory a 'linear response' approach. Fick is even better known in medicine. He published a well-rounded monography on *'Medical Physics'* [6] and a textbook on *'The Anatomy of Sense Organs'*. He became an outstanding person in the small group of nineteenth century physiologists who applied concepts and methods of physics to the study of living organisms, and thereby laid the foundations of modern physiology.

The German physiologist Adolf
Eugen Fick (1821 – 1901)

Graham's work on the diffusion of salt in water stimulated Fick to develop a mathematical framework for diffusion phenomena [4, 5] using the analogy between Fourier's law of thermal conduction (or Ohm's law of electric conduction) and diffusion [7, 8]. He postulated that the flux of salt occurring in a unit of time between two infinitesimal test volumes of space filled with solutions of the same salt but with different salt concentration must be directly proportional to the concentration difference and inversely proportional to the distance between the test volumes. In modern notation Fick postulated that the flux of matter j in x direction is proportional to the pertaining gradient of concentration C:

$$j = -D\frac{\partial C}{\partial x} \ .$$
(3)

This is what we nowadays call *Fick's first law*. *D* is denoted as diffusion coefficient or diffusivity. In his paper, Fick uses the symbol *k* instead of *D*, which he rightly called '*a constant dependent upon the nature of the substance*'. Using the conservation of matter in analogy to Fourier's treatment, where the conservation of heat energy is important, Fick derived the second fundamental law of diffusion

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \ ,$$
(4)

which we nowadays call *Fick's second law* or *diffusion equation*. Mathematically, the diffusion equation is a linear partial differential equation of second order.

In his own experiments Fick used Graham's experimental set-up for diffusion of salt in water, which consisted either of a vertical cylinder or a funnel. For a cylinder the cross section q is constant, whereas for a funnel it is a function $q(x)$. In this case, instead of equation (4), Fick had to use the modified equation

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2} + \frac{1}{q}\frac{dq}{dx}\frac{\partial C}{\partial x}\right).$$
(4a)

In his experimental set-up the bottom of the tube (cylinder or funnel) was placed in a reservoir of saturated salt solution and both, tube and reservoir, were immersed into a

large vessel of pure water. In this way, a concentration gradient of salt in water was created in the tube. The salt concentration versus depth was measured gravimetrically via the density of the solution, using a small bulb hanging on the arm of a balance. In the analysis of his experiments Fick considered only stationary states. For a cylinder the stationary solution is linear: $C = a + bx$. For a funnel, whose cross section is proportional to x^2, the solution is $C = a' - b'/x$. Recently, *Jean Philibert* plotted Fick's data according to these stationary solutions and found very good agreement (see Figs. 2 and 3 in [9]). Fick also measured the diffusion coefficient using three cylinders of different length. When the stationary state was reached, he determined the flux of salt that diffused out of the upper end of the cylinder. He obtained a diffusion coefficient of about 1.2×10^{-6} cm^{2}s^{-1} at temperatures between 15 and 22 °C. Fick's vital contributions to the field of diffusion were to introduce the fundamental equations, to define the diffusion coefficient and to measure the diffusion coefficients of salt in water.

Mathematical solutions of Fick's equations began with the nineteenth century luminaries *Josef Stefan* (1835 – 1893) [10] and *Franz Neumann* (1798 – 1895), who were among the first to recognise the significance of boundary conditions for solutions of the diffusion equation. Stefan gave solutions of Fick's second law either as a trigonometric series or as the complementary error function. For specimens of finite length Stefan recommended to use the principle of reflection plus superposition, which is based on the linearity of equation (4). He also considered diffusion from a slab source of width 2Δ having a uniform initial concentration C_0 joined by two half-spaces. In modern language the concentration $C(x,t)$ at position x and time t is

$$C(x,t) = \frac{C_0}{2} [\text{erf}(\frac{x+\Delta}{2\sqrt{Dt}}) + \text{erf}(\frac{x-\Delta}{2\sqrt{Dt}})] \ , \tag{5}$$

where erf denotes the error function. Stefan calculated numerical tables of concentration-depth profiles with $h/2\sqrt{Dt}$ as a parameter, where h is the thickness of successive layers used for chemical analysis. Later on Roberts-Austen used Stefan's tables to evaluate his data. Another important solution of Fick's second law is the *thin-film solution* or Gaussian solution. It applies when a thin layer of M diffusing atoms per unit area is deposited initially at $x = 0$:

$$C(x,t) = \frac{M}{\sqrt{\pi Dt}} \exp(-\frac{x^2}{4Dt}) \ . \tag{6}$$

This solution is frequently used for the analysis of radiotracer experiments (see below and Fig. 6).

2.3 Sir William Chandler Roberts-Austen – solid-state diffusion:

Already in ancient times reactions in the solid state such as surface hardening of steels were in use, which according to our present knowledge involves the diffusion of carbon atoms in the crystal lattice of iron. Nevertheless, until the end of the nineteenth century the paradigm *'Corpora non agunt nisi fluida'* was widely accepted by the scientific community. According to *Barr* [11], perhaps *Robert Boyle* (1627 – 1691) reported the first clear experimental evidence for solid-state diffusion in a study called *'The Porosity of Bodies'*. He observed the penetration of a '*solid and heavy body*', probably zinc in a small coin of copper. The side of the coin exposed to zinc took a golden colour, while the other side kept its original colour. He also observed that '*the golden colour had penetrated a pretty way beneath the surface of the coin*'. It appears that Boyle has observed the formation of brass by solid-state diffusion between zinc and copper.

*Sir William Chandler Roberts-Austen (*1843 – 1902) records his devotion to diffusion researches as follows [12]*: '... My long connection with Graham's researches made it almost a duty to attempt to extend his work on liquid diffusion to metals.'* Roberts-Austen graduated from the Royal school of Mines, London, in 1861 and became personal assistant to Graham at the Mint. After Graham's death in 1869 Roberts-Austen became first *'Chemist and Assayer of the Mint'*, a position he occupied until his death. He was appointed professor of metallurgy at the Royal School of Mines in 1882 and was knighted by Queen Victoria in 1899. He was a man of wide interests with charm and an understanding of people, which made him very popular. He conducted studies on the effects of impurities on the physical properties of pure metals and alloys and became a world authority on the technical aspects of minting coins. His work had many practical and industrial applications. Austenite – a non-magnetic solution of carbon in iron – is named after Sir Roberts-Austen. His studies of the iron-carbon phase diagram together with the micrographs of carburized iron, taken by his French friend *Floris Osmond* (1849 – 1912), clearly showed the penetration of carbon inside the bulk of iron.

Roberts-Austen perfected the technique for measuring high temperatures adopting platinum-based thermocouples, which were just invented at that time by the French physico-chemist *Henry LeChatelier* (1850 – 1936). As the leading scientist at the Mint, Roberts-Austen had at his disposal very good assessment tools to study systems based on noble metals. In spite of Ostwald's warning '*... accurate measurements on diffusion is one of the most difficult problems in physics*', Roberts-Austen conducted a series of remarkable diffusion experiments. He studied the diffusion of gold, platinum, and rhodium in liquid lead; of gold, silver, and lead in liquid tin and of gold in bismuth. These solvents were selected because of their relatively low melting temperatures. The solidified samples were sectioned and the concentration of the diffused species determined in each section using the high precision assaying techniques (precision balance) available at the Mint.

In the experiments on Au and Pt in *liquid lead,* typically 12 to 14 sections were taken and diffusion coefficients were determined by comparison with Stefan's solution of Fick's second law [12]. However, in the printed version of the Bakerian Lecture the

experimental data and their analysis are only presented in tabular form [12]. Figure 1 shows a graphical representation of a Au profile that was obtained from the data compiled in Roberts-Austen´s Table A and that originated from diffusion at 492 °C for 6.96 days. The data points in Fig. 1 reproduce the weight fractions of Au in cylindrical sections of 1.054 cm height, which were cut from a vertically arranged lead column inside a tube with a total height of about 15 cm. Initially, all gold was homogeneously distributed over twice the section height (2.108 cm) in the low end of the lead cylinder. As usual, each concentration value in Fig. 1 is assigned to the middle of the pertaining section. Using modern computer facilities, we have fitted the data with the aid of Eq. (5) by setting $\Delta = 2.108$ cm and by ignoring the last section of the lead column. In Fig. 1, the almost perfect match between the fitted solid line and the experimental data demonstrates the high quality of Roberts-Austen´s work. Moreover, our fitting procedure results in a Au diffusivity at 492 °C of 3.4×10^{-5} cm^2s^{-1} (2.97 cm^2d^{-1}), which is very close to the value given in the original article (3.00 cm^2d^{-1}) [12].
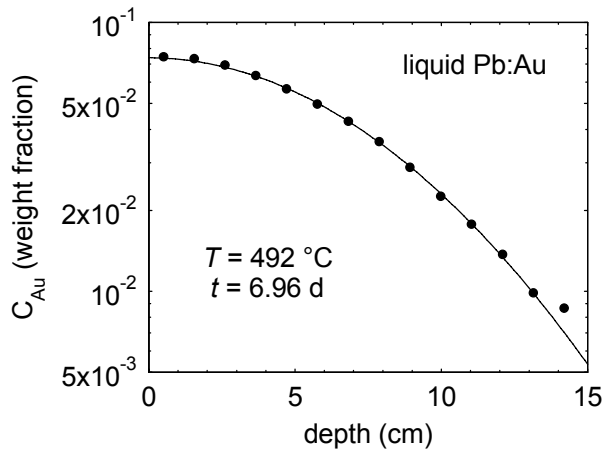

Fig. 1: Diffusion profile of Au in molten lead as reconstructed from the data tabulated in the original work of Roberts-Austen [12]. The solid line is a least-squares fit based on Eq. (5).

Even more important is that Roberts-Austen applied his experimental techniques to the study of gold diffusion in *solid lead*. To this aim, `*thin plates of gold were fused on to the end of cylindrical rods´* which varied in diameter and length depending on temperature and the specific experiment. Compared to the measurements in molten lead the challenge was much greater not only because of the smaller penetration depths but in particular due to the extremely low solubility of Au in solid Pb. Figure 2 displays two of the better diffusion profiles that were reconstructed from the data compiled in the original paper [12] and then fitted by the complementary error function. In this procedure, the high data point near the front end was omitted, which agrees with Roberts-Austen´s treatment stated as follows: `*The first section in each case, which of course contained pieces of partially alloyed gold, was neglected´*. Our analysis yields $D_{Au} = 5.1 \times 10^{-7}$ cm^2s^{-1} (0.044 cm^2d^{-1}) at 251 °C, which is about 50% higher than the initially reported value (0.03 cm^2d^{-1}, Experiment II [12]). For the 200 °C profile we obtain $D_{Au} = 1.0 \times 10^{-7}$ cm^2s^{-1}

(0.0087 cm^{2}d^{-1}) which compares well the original result of (0.008 cm^{2}d^{-1}, Experiment II). At yet lower temperatures (165 °C and 100 °C) only three or two sections could be measured, so that the reported data should be considered as rough estimates only.
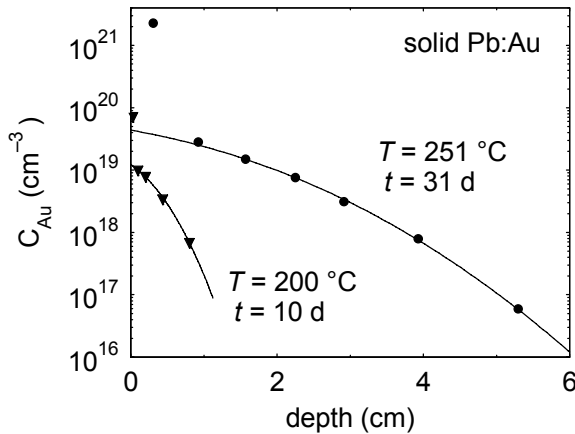

Fig. 2: Diffusion profiles of Au in solid lead as reconstructed from the data tabulated in the original work of Roberts-Austen (Experiment II for both temperatures) [12]. The solid lines are least-squares fits of the complementary error function.

It is interesting to note that the diffusion coefficients of gold in lead reported by Roberts-Austen are close to those determined by modern techniques using radioactive isotopes. This is seen in Fig. 3 where most of his data points are only about a factor of 2 below the straight line representing the radiotracer results of *Weyland et al.* (1971) collected in Ref. 13. Taking our evaluation of his data, the agreement tends to be even somewhat better. A similar conclusion can be drawn for the solubility of Au in solid Pb, which may be taken in Fig.2 from the extrapolation of the fitted curves to zero penetration depth. This approach complies with Roberts-Austen´s statement that `*the initial concentration of the solid lead-gold alloy from which diffusion starts was deduced from the general trend of the concentration curves ...´*.
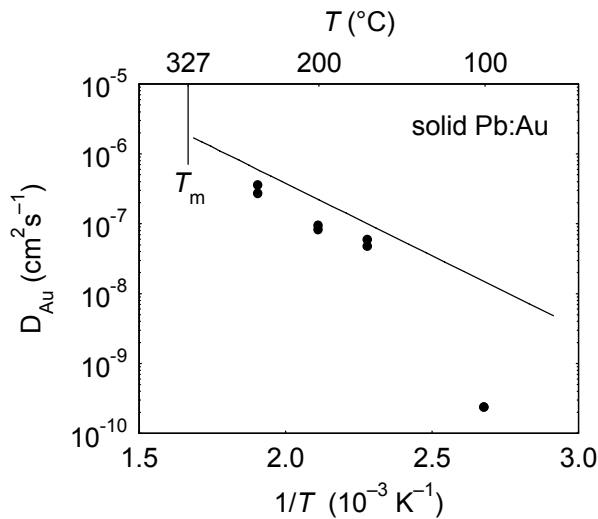
Fig. 3: Comparison of the Au diffusivity in solid lead reported for the first time by Roberts-Austen (closed circles [12]) with that obtained by modern radiotracer techniques (solid line [13])

With hindsight it can be said that the choice of the system gold in lead was really fortunate. Nowadays, we know that the diffusion of noble metals in lead is exceptionally fast in comparison to most other diffusion processes in solids (see, e.g. [13]).

The British metallurgist Sir William Chandler Roberts-Austen (1843 – 1905)

2.4 Svante Arrhenius – temperature dependence of diffusion:

The most surprising omission in Roberts-Austen's work is any discussion of the temperature dependence of the diffusion coefficient. Actually, Roberts-Austen observed a temperature dependence of Au diffusion in lead (see Fig. 3). However, he did not discuss this in his 'Bakerian Lecture' of 1896 [12]. Historically, the temperature dependence of reaction rates and diffusivities, now generally referred to as 'Arrhenius law', is named after the Swedish scientist *Svante Arrhenius* (1859 – 1927). He proposed this relation in his paper of 1889 [14] to describe reactions rate of cane sugar as well as reaction rates of several published chemical reactions. Arrhenius received a doctor degree in chemistry in Uppsala, Sweden, in 1894. He was awarded a travel fellowship which enabled him to work with *Ostwald* in Riga, Latvia, and with *Kohlrausch* in Würzburg, Germany. He also cooperated with *Boltzmann* in Graz, Austria, and with *van 't Hoff* in Amsterdam, The Netherlands. Arrhenius was awarded the Nobel prize in chemistry in 1903. It appears that the

Arrhenius law for chemical reactions was also proposed by the Dutch scientist *Jacobus Hendrik van 't Hoff* (1852 – 1921), the first Nobel laureate in chemistry (1901).

The suggestion that the temperature dependence of the diffusivity in solids obeys what we now call the Arrhenius law,

$$D = D^0 \exp(-Q/k_B T),\qquad\qquad(7)$$

was made about thirty years later by *Saul Dushman and Irving Langmuir* in 1922 [15], and independently by *Braune* in 1924 [16]. Langmuir considered this relation as an empirical one, without mentioning Arrhenius. Nowadays, Q is called the activation enthalpy of diffusion and D^0 the pre-exponential factor.

2.5 Brownian motion – Albert Einstein, Marian Smoluchowski and Jean Baptist Perrin

So far we have focused on the phenomenological approach of diffusion condensed in Fick's laws, their mathematical solutions, and on experiments that utilize solutions of the diffusion equations. In this section we highlight the cornerstones of a physical, more atomistic approach of diffusion.

The phenomenon of a never ending, irregular motion of small particles suspended in a liquid had been long known. It was discovered by the Scottish botanist *Robert Brown* (1773 – 1858). Brown was the son of an Episcopalian priest. He studied medicine in Edinburgh but did not finish his degree. At the age of twenty-one he enlisted in a newly raised Scottish regiment. At that time he already knew that his true interests did not lie in medicine and he had already acquired some reputation as botanist. On a visit to London in 1798, to recruit for his regiment, he met the botanist Sir Joseph Banks, president of the Royal Society, who recommended Brown to the Admiralty for the post of a naturalist aboard of a ship. The ship was to embark on a surveying voyage at the coasts of Australia. Brown made extensive plant collections in Australia and it took him about five years to classify approximately 3900 species he had gathered, almost all of which were new for science. Later, Charles Darwin referred to him as *'... princeps botanicorum'*. In addition to collecting and classifying, Brown made several important discoveries. Perhaps the most celebrated by biologists is his discovery that plant cells have a nucleus.

Robert Brown is well-known in science for his observation of the random movement of small particles in liquid suspension first described in 1827 in a paper entitled *'A brief account of microscopical observations in the months June, July and August 1827 on the particles contained in pollen...'*, which was originally intended for private circulation, but was reprinted in the archival literature shortly after its appearance [17]. Brown investigated the way in which pollen acted during impregnation. One of the plants he studied under the microscope was *Clarkia pulchella*, a wildflower found in the Pacific Northwest of the United States. The pollen of this plant contains granules varying from about five to six micrometers in linear dimension. It is these granules, not the whole

pollen grains, upon which Brown made his observation in his microscope. He wrote ' ... *While examining the form of these particles immersed in water, I observed many of them very evidently in motion ... . These motions were such as to satisfy me, after frequently repeated observation, that they arose neither from currents in the fluid, nor from its gradual evaporation, but belonged to the particle itself'*. This inherent, incessant motion of small particles is nowadays called Brownian motion.
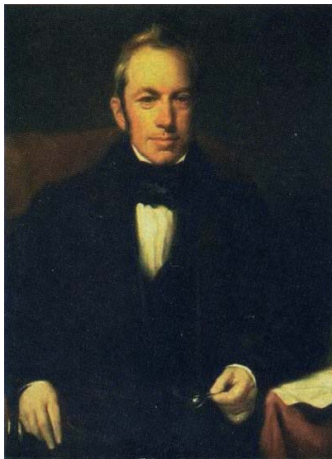
The Scottish botanist Robert Brown (1773 – 1858)

Brownian motion was carefully re-investigated by the French scientist *Georges Gouy* (1854 – 1926) [18]. He studied different kinds of particles in various fluids. He showed that the motion is independent of external forces and less intense in more viscous fluids. He concluded: *'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.'* However, until about 1900 not much progress was made in the theoretical understanding of Brownian motion although developments in the theory of heat and kinetic theory stimulated new experiments and conjectures. It is striking, however, that the founders and developers of kinetic theory, *Maxwell, Boltzmann* and *Clausius*, never published anything on Brownian motion. The reason for the lack in progress was that the major studies of that period focused on the particle velocities. Measurements of the particle velocities gave puzzling results. The reason is that the path of a small particle, on the length scales available from observations in a microscope, is an extremely erratic curve. In modern language we would say that it is a fractal, a concept developed many decades later by *Mandelbrot* [19]. Such curves are almost nowhere differentiable. Consequently, the particles whose trajectories they represent, have no velocity, as usually defined. Not until the work of *Einstein* and *Smoluchowski* appeared it was understood that the velocity is not a useful concept in this context.

Albert Einstein (1879 – 1955), born in Ulm, Germany, is certainly the best known physicist of the twentieth century, perhaps even of all time. In the year 1905 he published four papers that at once raised him to the rank of a physicist of highest calibre: the photon hypothesis to explain the photo effect (for which he received the Nobel prize in physics in 1922 for the year 1921), his first paper on Brownian motion, and his two first papers on relativity theory. At that time Einstein was employed at the *'Eidgenössisches Amt für Geistiges Eigentum'* in Bern, Switzerland. He did not receive the doctoral degree until the following year 1906. Interestingly, his thesis was on none of the above problems, but concerned the determination of the dimensions of molecules. His first paper on Brownian motion was entitled: *'Die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen'* [20]. A second paper

was entitled *'Zur Theorie der Brownschen Bewegung'* [21]. Einstein published two additional short papers on this topics [22, 23], but these were of relatively minor interest. Einstein was the first to understand, contrary to many scientists of his time, that the basic quantity is not the velocity but the mean-square displacement of particles. It is perhaps interesting to note that both seminal papers on diffusion were printed in Leipzig, Germany, in famous journals – Einstein's paper in the 'Annalen der Physik' in 1905 and Fick's paper in the 'Annalen der Physik and Chemie' in 1855.

The German-Jewish physicist Albert Einstein (1879 – 1955)

Einstein derived in a first step a relation between the diffusivity of particles suspended in a liquid and the solvent viscosity η. By extending the *Stokes* friction force, $6\pi\eta r$, to solute molecules of radius r he obtained

$$D = \frac{R_g T}{N_A} \frac{1}{6\pi\eta r}. \tag{8}$$

R_g denotes the gas constant and N_A the Avogadro number. This relation is nowadays denoted as *Stokes-Einstein relation*. In a second step Einstein considered the positions of a particle at small time intervals. The total displacement R of each particle during time t consists of many individual displacements r_i:

$$R = \sum r_i \tag{9}$$

Considering an ensemble of particles and assuming that their displacements obey a symmetrical distribution function (no drift), Einstein derived an equation for the distribution of particles that has just the form of Fick's second law, with the diffusivity defined on a microscopic basis. In this way he related the mean-square displacement $\langle R^2 \rangle$ to the diffusion coefficient and time. In three dimensions we can write

$$\langle R^2 \rangle = 6Dt. \tag{10}$$

Equation (10) is denoted as *Einstein relation* or as *Einstein-Smoluchowski relation*. Smoluchowski published shortly after Einstein a theory of Brownian motion based on a kinetic approach of collisions between particles – quite different from Einstein's thermodynamic approach.

The Polish physicist Marian von Smoluchowski (1872 – 1917)

The Polish physicist and mountaineer *Marian von Smoluchowski* (1872 – 1917) was born in Vienna, Austria. During his lifetime, Poland was not an independent country; it was partitioned between Russia, Prussia, and Austria. Smoluchowski's father was a lawyer in Cracow, in the Austrian part of Poland. Marian von Smoluchowski entered the University of Vienna and studied physics under *Josef Stefan* and *Franz Exner*. He also attended lectures of *Ludwig Boltzmann*. In his later life he was called *'der geistige Nachfolger Boltzmanns'* (the intellectual successor of Boltzmann). He received his PhD and his 'venia legendi' in Vienna and was appointed as full professor at Lvov (now Ukraine) in 1903 and at the Jagellonian University in Cracow in 1913. Smoluchowski also served as president of the Polish Tatra Society and was awarded as a distinguished alpinist (*'Silbernes Edelweiss'*) by the German and Austrian Alpine Society

Smoluchowski's interest for molecular statistics led him already around 1900 to consider Brownian motion. He did publish his results not before 1906 [24, 25] under the impetus of Einstein's first paper. Smoluchowski later studied Brownian motion for particles under the influence of an external force [26, 27]. Einstein's and Smoluchowski's scientific paths crossed again, when both considered the theory of the scattering of light near the critical state of a fluid, the critical opalescence. Smoluchowski died as a result of a diphtheria epidemic, aggravated by wartime conditions in 1917. At that time he was rector of the University. Einstein wrote a sympathetic obituary for him with special reference to Smoluchowski's interest in fluctuations [28].

The idea that matter was made up of atoms was already postulated by *Demokrit of Abdeira*, an ancient Greek philosopher, who lived about four hundred years before Christ. However, an experimental prove had to wait for more than two millennia. The concept of atoms and molecules took strong hold of the scientific community since the time of the British chemist and teacher *John Dalton* (1766 – 1844). It was also shown that the ideas of Dalton and of the Italian physico-chemist *Amadeo Avogadro* (1776 – 1856) could be used to construct a rational table of atomic weights, a central idea of chemistry and physics. Most scientists were willing to accept atoms as real, since the facts of chemistry and the kinetic theory of gases provided strong indirect evidence. Yet there were famous sceptics. Perhaps the most prominent ones were the German physical chemist and Nobel laureate *Wilhelm Ostwald* (1853 – 1932) and the Austrian physicist *Ernst Mach* (1938 – 1916). They agreed that atomic theory was a useful way of summarising experience. However, the lack of direct experimental verification led them to maintain their sceptics against atomic theory with great vigour.

The Einstein-Smoluchowski theory of Brownian motion provided ammunition for the atomists. This theory explains the incessant motion of small particles by fluctuations,

which seems to violate the second law of thermodynamics. The question remained, what fluctuates? Clearly, fluctuations can be explained on the basis of atoms that collide with a Brownian particle and push it around. The key question was then, what is the experimental evidence that the Einstein-Smoluchowski theory is quantitatively correct?

The answer came from the experiments of the French physicist *Jean Baptiste Perrin* (1870 – 1942), a convinced atomist. In order to study the dependence of the mean-square displacement on the particle radius, it was necessary to prepare monodisperse suspensions. For the check of the Einstein-Smoluchowski relation he and his students observed the motion of particles under the microscope and marked their positions at given time intervals. If one would plot the particle positions at shorter time intervals, each linear segment of the trajectory takes a polygonal shape similar to the whole trajectory. This is a description of a fractal line, decades before *Mandelbrot's* work [19]. The experiments of Perrin showed excellent agreement with the Einstein-Smoluchowski theory [29, 30]. He and his students continued refining the work and Perrin published a long paper in 1909 on his own and his students' researches [31]. He became an energetic advocate for the reality of atoms and received the Nobel prize in physics 1926 *'... for his work on the discontinuous structure of matter ...'*.

2.6 Interdiffusion – Boltzmann and Matano
An early criticism of Fick's laws was related to the inherent assumption that the diffusivity was considered to be independent of concentration and its gradient. Nowadays, numerous situations are known, where these assumptions are not valid. Nevertheless, one usually prefers to keep Fick's laws in its original form and instead admit for a variable diffusivity $D(C)$. Then the diffusion equation (4) has to be replaced by

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}[D(C)\frac{\partial C}{\partial x}] =$$
$$D(C)\frac{\partial^2 C}{\partial x^2} + \frac{\mathrm{d}D(C)}{\mathrm{d}C}(\frac{\partial C}{\partial x})^2 \tag{11}$$

The French physicist Jean Baptiste Perrin (1870 – 1942)

Mathematically, equation (11) is a partial differential equation of second order but nonlinear. The second term on the right-hand side can be considered as an 'internal driving force'. For an arbitrary concentration dependence of $D(C)$ it is usually not possible to give an analytical solution of equation (11).

Ludwig Boltzmann (1844 – 1906) made a significant contribution to the mathematics of diffusion in the case of compostion-dependent diffusion coefficients. This contribution is documented in his paper of 1894 with the title *'Zur Integration der Diffusionsgleichung mit variablem Diffusionskoeffizienten'* [32]. Boltzmann is a well-known hero of classical

physics with important contributions to statistical thermodynamics. He was a convinced atomist and developed the statistical interpretation of the entropy. Expressions such as Boltzmann constant, Boltzmann factor, and Boltzmann contribution remind us to his great merits in statistical physics. However, Boltzmann had further widespread interests, which included fluid dynamics, evolution theory, biophysics and diffusion.

Boltzmann suggested what we nowadays call the Boltzmann transformation of equation (11) by introducing a new variable

$$\eta = \frac{x}{2\sqrt{t}}. \tag{12a}$$

Applying this transformation, Fick's second law becomes an ordinary, nonlinear differential equation of second order:

$$-2\eta \frac{dC}{d\eta} = \frac{d}{d\eta}[D(C)\frac{dC}{d\eta}]. \tag{12b}$$

Together with the initial condition for a diffusion couple ($C = C_L$ for $x < 0$, $t = 0$ and $C = C_R$ for $x > 0$, $t = 0$), suggested by the Japanese physicist *Matano* [33], the transformed diffusion equation provides a convenient way to deduce the diffusion coefficient for each composition $C*$ in the diffusion zone of a composition-depth profile. The as-deduced diffusivity is called the interdiffusion coefficient and is obtained from

$$D(C*) = -\frac{1}{2t} \frac{\int_{C_L}^{C*}(x - x_M)dC}{(dC/dx)_{C*}} \tag{13}$$

x_M denotes the position of so-called Matano plane. It can be determined for a given diffusion profile from the following balancing condition of two integrals

$$\int_{C_L}^{C_M} xdC = \int_{C_R}^{C_M} xdC. \tag{14}$$

C_M denotes the concentration at the Matano plane. The Boltzmann-Matano method based on equations (13) and (14) permits the determination of a composition-dependent diffusion coefficient $D(C*)$ from an experimentally determined interdiffusion profile.

The Austrian physicist Ludwig Boltzmann (1844 – 1906)

The Japanese physicist Chujiro Matano (1905 – 1947)

Boltzmann was born in Linz, Austria, and studied physics and mathematics at the universities of Vienna, Austria, Heidelberg and Berlin in Germany. He received his PhD in 1866 in Vienna and was for two years assistant to his highly esteemed teacher Josef Stefan. At the age of 25 he became professor of mathematical physics at the University of Graz, Austria. In the following years he occupied positions in Vienna and Munich and returned to Graz again, where he spent his scientifically most fruitful time. From 1894 until his death he was successor of *Josef Stefan* at the University of Vienna.

Chujiro Matano (1905 – 1947) graduated 1929 in physics from Kyoto University, Japan, and worked afterwards until 1935 as research associate at Osaka University. From 1935 to 1944 he was a member of the Muto Research Institute of Kanekabuchi Boseki Co. Ltd., a big Japanese cotton spinning company. He wrote a textbook on topics of cotton spinning with the title 'Physics of Fibers'. From 1944 until his death in 1947 he was a professor at the Kyushu University, Japan.

A modern experimental tool for the study of interdiffusion profiles – electron-probe microanalysis – was developed by the French physicist *R. Castaing* (1921 – 1998). A fine focused beam of electrons excites characteristic X-rays and permits a chemical analysis on a micrometer scale. Castaing demonstrated the power of this technique by investigating diffusion profiles deduced from linear scans of the electron beam through the diffusion zone of the multiphase diffusion couple of Cu and Zn [34].

2.7 Georg Karl von Hevesy – first measurements of self-diffusion using radioisotopes

A very important step in experimental diffusion studies was the measurement of self-diffusion – the most basic diffusion process. The idea of self-diffusion was already introduced by *Maxwell*, when treating the rate of diffusion of gases. The first attempts to measure self-diffusion in condensed matter were those of the physico-chemist *Georg Karl von Hevesy* (1885 – 1966), who studied self-diffusion in liquid [35] and in solid lead [36] by using a natural radioactive isotope (^{210}Pb also called Radium D, ^{212}Pb also called Thorium B) of lead.

Von Hevesy had a fascinating scientific career. He was born in Budapest, Hungary (at that time part of the Austro-Hungarian monarchy), and studied at the universities of Budapest, Berlin and Freiburg. He did research work in physical chemistry at the ETH in Zürich, with *Fritz Haber* in Karlsruhe, with *Ernest Rutherford* in Manchester, and with *Fritz Paneth* in Vienna. He became professor in Budapest in 1919 and from 1920 to 1926 he worked with *Niels Bohr* in Copenhagen, Denmark. Together with the Dutch physicist *Dirk Coster* he discovered the new element 'hafnium'. He was professor in Freiburg, Germany, from 1926 to 1934. During his eight years in Freiburg he initiated work with radiotracers in solids and in animal tissues. Fleeing from the Nazis in Germany he moved to the Niels Bohr institute in Copenhagen in 1934 and from there to Stockholm. In 1944 the Swedish Royal Academy of Sciences awarded him the Nobel prize in Chemistry of the year 1943 for '*... his work on the use of isotopes as tracers in the study of chemical processes.'* He became a Swedish citizen and was appointed professor of organic chemistry in Stockholm in 1959. Von Hevesy, who married Pia Riis, daughter of a Danish ship owner, had four children. He died in Freiburg in 1966.

The Austro-Hungarian chemist Georg Karl von Hevesy (1885 – 1966)

After the discovery of artificial radioisotopes by *Irene and Pierre Joliot-Curie* in 1934, the development of accelerators, and the advancement of neutron activation in nuclear reactors due to *Enrico Fermi* (1901 – 1954), radioisotopes for many elements became available. The period shortly before and during World War II saw first measurements of self-diffusion on metallic elements other than Pb.

2.8 Atomic Defects in solids – Frenkel, Schottky and Kirkendall

Solid-state physics was born when *Max von Laue* (1879 – 1960) detected diffraction of X-rays on crystals. His experiments demonstrated that solid matter usually occurs in three-dimensional periodic arrangements of atoms. His discovery was awarded with the Nobel prize of physics in 1914. However, the ideal crystal of Max von Laue is a *'dead'* crystal. Solid-state diffusion and many other properties require deviations from ideality. In

the thirties and fourties of the twentieth century people began to be concerned with an atomic scale approach of ion conductivity in ionic crystals and solid-state diffusion in general. This led to the concept of atomic defects in solids.

The Russian physicist *Jakov Ilich Frenkel* (1894 – 1952) introduced the concept of disorder in the field of solid-state physics. He suggested that thermal agitation causes transitions of atoms from their regular lattice sites into an interstitial position leaving behind lattice vacancies [37]. This kind of disorder is now called *Frenkel disorder* and consists of pairs of vacant lattice sites (vacancies) and lattice atoms on interstitial sites of the host crystal (self-interstitials). Only a few years later *Wagner* and *Schottky* [38] generalised the concept of disorder by treating binary compounds and introducing point-defect thermodynamics. They considered the occurrence of vacancies, interstititals and antisite defects on both sublattices. Nowadays, it is common wisdom that atomic defects are necessary to mediate diffusion in crystals.

The German physicist *Walter Schottky* (1886 -1976) taught at the universities of Rostock and Würzburg, Germany, and worked in the research laboratories of the Siemens company. He had also a major influence on the development of telecommunication. Among Schottky's many achievements a major one was the development of a theory which explained the rectifying behaviour of metal-semiconductor contacts and revolutionised semiconductor technology. Since 1973 the German Physical Society decorates outstanding achievements of young German scientists in solid-state physics by the *'Walter-Schottky award'*.

The basis of diffusion in solids is the movement of atoms, ions or molecules on a lattice. The link between the diffusivity and the mean square displacement, the Einstein – Smoluchowski relation, is valid for crystals as well. In crystals the situation is in a sense even simpler than in gases and liquids, since the crystal lattice restricts the positions and the migration paths of atoms. The individual displacements are jumps with a fixed jump length, often nearest-neighbour jumps (see Fig. 4). A certain degree of randomness is due to the jump directions. This contrasts with diffusion in a gas, where random displacements in length and direction occur.
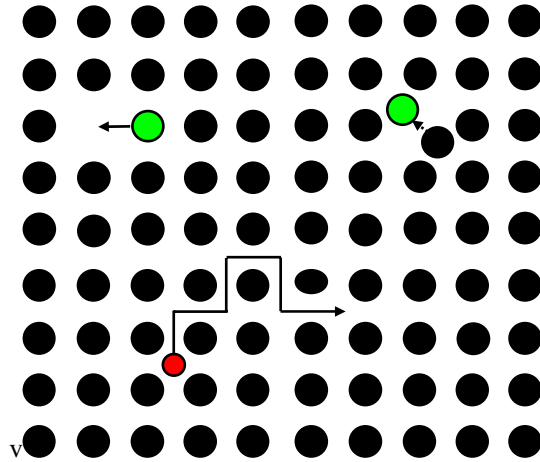
Fig. 4: Atomic defects and their jumps in a crystal: vacancy (top left), self-interstitial (top right), foreign interstitial (lower part).

A further cornerstone of solid-state diffusion comes from the work of the American metallurgist *Ernest Kirkendall* (1914 – 2005). In the 1940s, it was still a widespread belief that atomic diffusion in metals takes place via direct exchange or ring mechanisms. This would indicate that the diffusion of components in binary alloys occurs at the same rate.

The American metallurgist Ernest Kirkendall (1914 – 2005)

Kirkendall's experiment is illustrated in Fig. 5. Diffusion couples composed of pure Cu and brass – a Cu-Zn alloy – were studied. The interface, where the couple was initially joined, was marked by thin Mo wires as inert markers. The shift of the markers during the diffusion anneal is denoted as *Kirkendall effect*. This shift is indicated in Fig. 5 and shows that Zn atoms diffused faster outwards than Cu atoms inward. In such studies Kirkendall and his coworkers demonstrated the inequality of copper and zinc diffusion during interdiffusion between brass and copper [39, 40, 41]. The Kirkendall effect has been observed in the meantime on many other alloys. Kirkendall's discovery, which took the scientific world about 10 years to be accepted, is taken as evidence for a vacancy mechanism of diffusion in metals and alloys. Kirkendall left research in 1947 and served for almost thirty years as secretary of the American Institute of Mining, Metallurgical and Petroleum Engineers.
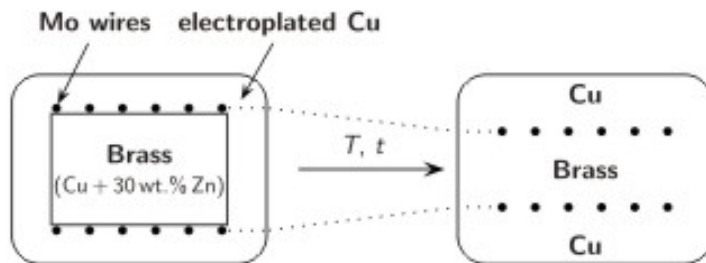
Fig. 5: Schematic illustration of the Kirkendall effect for a copper – brass diffusion couple.

2.9 Correlation in solid-state diffusion – John Bardeen, John Manning

Defects are usually the vehicles of diffusion in a crystalline solid. If diffusion would occur by a pure random walk on a lattice, the jump probabilities of atoms would not depend on the direction of the preceding jump. It was not until 1951 that *Bardeen and Herring* drew attention to the fact that for the vacancy mechanism, correlation exists between the jump directions of consecutive jumps of tagged atoms [42]. The American physicist *John Bardeen* (1908 – 1091) was one of the few scientists, who received the Nobel prize in physics twice. Together with *Shockley* and *Brattain,* he was awarded for the development of the transistor in 1956. *Bardeen, Cooper and Schrieffer* received the 1972 prize for the BCS theory of superconductivity.

The American physicist John Bardeen (1908 – 1991)

Bardeen and Herring pointed out that correlation is important: after the site exchange of a tagged atom (tracer) with a neighbouring vacant lattice site (see Fig. 4) the vacancy appears on the position left by the tagged atom. After this site exchange the tracer-vacancy configuration is no longer random but depends on the direction of the first exchange. This non-randomness can be accounted for by introducing a correlation factor. We remind the reader to the Einstein-Smoluchowski relation, which connects the mean square displacement of a serie of n individual jumps to the diffusion coefficient:

$$\langle R^2 \rangle = \langle (r_1 + r_2 + ... + r_n)(r_1 + r_2 + ... + r_n) \rangle$$

$$= \sum_{i=1}^{n} r_i^2 \left(1 + 2\frac{\sum_{i=1}^{n-1}\sum_{j=i+1}^{n} \langle r_i r_j \rangle}{\sum_{i=1}^{n} r_i^2}\right) = 6Dt \qquad (15)$$

The single sum in front of the brackets corresponds to the mean square displacement for a completely random series of individual jumps. The term in brackets with the double sum includes correlations. With the abbreviations

$$\langle R_{random}^2 \rangle = \sum_{i=1}^{n} r_i^2 \quad \text{and} \quad f = 1 + 2\frac{\sum_{i=1}^{n-1}\sum_{j=i+1}^{n} \langle r_i r_j \rangle}{\sum_{i=1}^{n} r_i^2} , \qquad (16)$$

the mean square displacement can be written as

$$\langle R^2 \rangle = \langle R_{random}^2 \rangle f \quad \text{or} \quad \langle R^2 \rangle = nd^2 f . \qquad (17)$$

The second equation (17) holds for a coordination lattice with nearest neighbour distance d. f is the correlation factor introduced by Bardeen and Herring. For a true random walk the double sum vanishes and the correlation factor is unity. Correlation arises from the double sum, which reduces the correlation factor to a value $f < 1$.

Correlation effects are important in solid-state diffusion, whenever diffusion is mediated by defects that act as diffusion vehicles. Examples for diffusion vehicles are vacancies, divacancies, self-interstitials, etc. An equivalent statement is to say, there must at least three identifiable 'species' be involved in the elementary jump process. For example, tracer diffusion via vacancies involves vacancies, host atoms and tracer atoms. Interstitial diffusion in a dilute interstitial alloy is uncorrelated, because only host atoms and interstitial solutes but no diffusion vehicle is involved.

Self-diffusion is the most basic diffusion process in a solid. In metals it is mediated by vacancies, which jump to nearest-neighbour sites in the lattice (distance d). Self-diffusion is studied conveniently by tracer techniques, which were used for the first time by von Hevesy and coworkers. The tracer diffusion coefficient contains a correlation factor. For a cubic Bravais lattice the tracer self-diffusion coefficient can be written as

$$D = \frac{1}{6} f d^2 Z \frac{n}{t} \quad \text{or} \quad D = \frac{1}{6} f d^2 Z \omega \, C_V^{eq} . \tag{18}$$

Z denotes the coordination number and n/t is the atomic jump rate, which for a vacancy mechanism can be expressed in terms of vacancy site fractions and exchange rate between tracer atom and vacancy. The second equation contains explicitly the exchange rate ω and the site fraction of vacancies in thermal equilibrium C_V^{eq}. Both quantities are thermally activated:

$$C_V^{eq} = \exp(-G^F / k_B T) \quad \text{and} \quad \omega = \upsilon_0 \exp(-G^M / k_B T) . \tag{19}$$

Here $G^F = H^F - TS^F$ denotes the Gibbs energy of vacancy formation, which is composed of an enthalpy and entropy term. ν_0 is the attempt frequency of the atom–vacancy jump. This frequency is of the order of the Debye frequency of the lattice. $G^M = H^M - TS^M$ denotes the Gibbs energy of vacancy migration, which again contains an enthalpy and entropy term. Taken together, the self-diffusion coefficient can be written as

$$\begin{aligned} D = \frac{1}{6} f d^2 Z \nu_0 \exp[(S^F + S^M) / k_B] \exp[-(H^F + H^M) / k_B T] \\ = D^0 \exp(-Q_{self} / k_B T) \end{aligned} \tag{20}$$

Self-diffusion is Arrhenius activated with an activation enthalpy $Q_{self} = H^F + H^M$, which is composed of the formation and migration enthalpy of the vacancy. D^0 is a pre-exponential factor, which contains geometrical quantities, entropy terms, the attempt frequency and the correlation factor. In an Arrhenius diagram the diffusion coefficient is plotted on a logarithmic scale versus the reciprocal temperature. Usually, the Arrhenius diagram is a straight line, whose slope is determined by the activation enthalpy. Small deviations, which are sometimes observed, occur for microstructural and/or intrinsic reasons (for details see, e.g., [43, 44]). They are beyond the scope of the present paper

For self-diffusion the correlation factor is often just a number. Its value depends on the type of the lattice and on the diffusion mechanism (for examples, see the table below and Refs. [43, 44]). The correlation factor lowers the tracer self-diffusivity with respect to a (hypothetical) 'random walk value'. In the case of self-diffusion the correlation factors take often values between 0.5 and unity. Nevertheless, for a complete description of the atomic diffusion it is necessary to include correlation.

	Face-centered cubic	Body-centered cubic	Diamond structure
Vacancy mechanism	0.7815	0.7272	0.5
Divacancy mechanism	0.4579	0.337 to 0.469	

There are additional good reasons why correlation effects are of interest. The correlation factor is quite sensitive to the diffusion mechanism. For example, the correlation factor for divacancies is smaller than that for monovacancies in the same lattice (see table). Thus an experimental determination of correlation factors can throw considerable light on the mechanism(s) of diffusion. The knowledge of the diffusion mechanism is certainly of prime importance for the basic understanding of diffusion. Measurements of the so-called isotope-effect of diffusion and in some cases measurements of the Haven ratio in ionic crystals proved to be very useful in this context. Details are beyond the scope of the present paper and can be found, e.g., in textbooks of Philibert [43] and one of the present authors [44]

Impurity diffusion (diffusion of substitutional solutes in very dilute solutions) like self-diffusion is vacancy-mediated. The impurity diffusion coefficient can be written as follows:

$$D_{imp} = \frac{1}{6}d^2 f_{imp} \omega_{imp} C_V^{eq} \exp(G^B/k_B T). \tag{21}$$

Here f_{imp} denotes the impurity correlation factor and ω_{imp} is the impurity-vacancy exchange jump rate. $G^B = H^B - TS^B$ indicates the Gibbs energy of binding between impurity and vacancy, which can be decomposed into an enthalpy and entropy of binding. For $G^B > 0$ the impurity-vacancy interaction is attractive and for $G^B < 0$ it is repulsive.

For the face-centred cubic lattice within the framework of *Alan Lidiard´s* 'five frequency model´ [45] the correlation factor takes the following form:

$$f_{imp} = \frac{\omega_1 + 3.5\omega_3 F_3}{\omega_{imp} + \omega_1 + 3.5\omega_3 F_3}. \tag{22}$$

ω_1 is the vacancy jump rate for vacancy exchange with atoms that are nearest neighbours of the impurity; ω_3 is the dissociation jump rate of the vacancy, which removes the vacancy from its nearest-neighbour position to the impurity towards one of the seven lattice sites that are not nearest neighbours of the impurity. F_3 is the so-called escape

probability, which is a function of the ratio of the vacancy jump rate ω in the pure solvent and of the association jump rate ω_4. The pertaining jump brings the vacancy towards a nearest-neighbour site of the impurity (association jump). For self-diffusion all jump rates are equal and the correlation factor obtained from equation (22) is just the number 0.7815 given in the table. If the vacancy-impurity exchange is much slower than the vacancy - solvent atom exchanges, i.e. $\omega_{imp} << \omega_3$, ω_1, the correlation factor tends to unity. If the opposite is true the correlation factor tends to zero. Association and dissociation jump rates of the vacancy are related via the detailed balancing condition

$$\frac{\omega_4}{\omega_3} = \exp(\frac{G^B}{k_B T}) ,$$ (23)

which includes the Gibbs energy of binding for the impurity – vacancy complex.

In contrast to self-diffusion, the correlation factor of impurity diffusion is no longer just a number. It is a function of several jump rates with different barrier heights. Therefore, the correlation factor is a quantity that depends on temperature. The temperature dependence of the impurity correlation factor can be attributed to an activation enthalpy, which is defined via

$$C_{corr} = -k_B \frac{\partial \ln f_{imp}}{\partial (1/T)} .$$ (24)

From equation (21) for the impurity diffusion coefficient, it is evident that the activation enthalpy for diffusion of substitutional impurities, Q_{imp}, can be written as

$$Q_{imp} = C_{corr} + H_{imp}^M + H^F - H^B .$$ (25)

H_{imp}^M denotes the activation barrier for impurity-vacancy exchange and $H^F - H^B$ can be interpreted as the enthalpy of vacancy formation at a nearest-neighbour site of the impurity. Clearly, correlation contributes via C_{corr} to the temperature dependence of impurity diffusion.

Impurity correlation factors for various cubic structures have been calculated in detail by the American physicist *John Manning* (1933 – 2005). Manning had strong interests in the '*Diffusion kinetics of atoms in crystals*' as evidenced by the same title of his book [46]. He received his PhD from the University of Illinois, Urbana, US. Then he joined the metals physics group at the National Bureau of Standards (NBS/NIST) in Washington. Later he was the chief of the group until his retirement. He also led the `Diffusion in

Metals Data Center´ together with *Dan Butrymowics* and *Michael Read*. The obituary published by NIST has the following very rightful statement: '*His papers have explained the significance of the correlation factor and brought about an appreciation of its importance in a variety of diffusion phenomena*'. The authors of this paper met John Manning at several conferences. Manning was a great listener and a strong advocate, fair, honest, friendly, courteous, kind and above all a gentleman.

The American physicist John Randolf Manning (1933 – 2005)

2.10 Grain-Boundary Diffusion

By 1950, the fact that *grain-boundary diffusion* exists had been well documented by autoradiographic images [47], from which the ratio of grain-boundary to lattice diffusion coefficients in metals was estimated to be several orders of magnitude [48]. *Fisher* published his now classic paper presenting the first theoretical model of grain-boundary diffusion based on Fick's laws in 1951 [49]. In Fisher's model the grain boundary is represented as a slab with high diffusivity embedded into two crystal grains with lower diffusivity.

At about the same time the metallurgy group at the General Electric Research Laboratories investigated under the guidance of the American materials scientist *David Turnbull (*1915 – 2007) self-diffusion of radioactive silver in poly- and monocrystals of silver [50]. That pioneering paper together with Fisher's theoretical approach initiated the field of quantitative studies of grain-boundary diffusion in solids.

The American metallurgist David Turnbull (1915 – 2007)

Nowadays, grain-boundary diffusion is well recognized to be a transport phenomenon of great fundamental interest and of technical importance in polycrystals and particularly in nanocrystalline materials. Diffusion along grain boundaries often controls the evolution of the microstructure and the properties of materials at elevated temperatures. In Coble creep, sintering, diffusion-induced grain-boundary motion, discontinuous precipitation, recrystallisation and grain growth, diffusion along grain boundaries plays a prominent role. Grain-boundary diffusion is important in thin-film interconnects and in various kinds of thin-film multilayer devices. For a broad overview of fundamental aspects and more recent developments the reader may consult a textbook on grain-boundary diffusion by *Kaur, Mishin and Gust* [51].

3. Concluding Remarks

The equations of Fick, the statistical interpretation of the diffusion coefficient by *Einstein* and *Smoluchowski* and the *Boltzmann-Matano* method for concentration-dependent diffusion coefficients provided a theoretical framework for diffusion studies and also opened the way for new experimental techniques. The first period of solid-state diffusion experiments under the influence of the seminal papers of *Roberts-Austen* and *von Hevesy* was followed by a period which started when 'artificial' radioactive isotopes, produced in accelerators, became available. After World War II nuclear reactors provided additional sources for radioisotopes. This period saw first measurements of self-diffusion on elements other than lead. Examples are self-diffusion of gold [52, 53], copper [54], silver [55], zinc [56], and iron [57]. In all these experiments the temperature dependence of diffusion was adequately described by the Arrhenius law, which by about 1950, had become an accepted 'law of nature'.
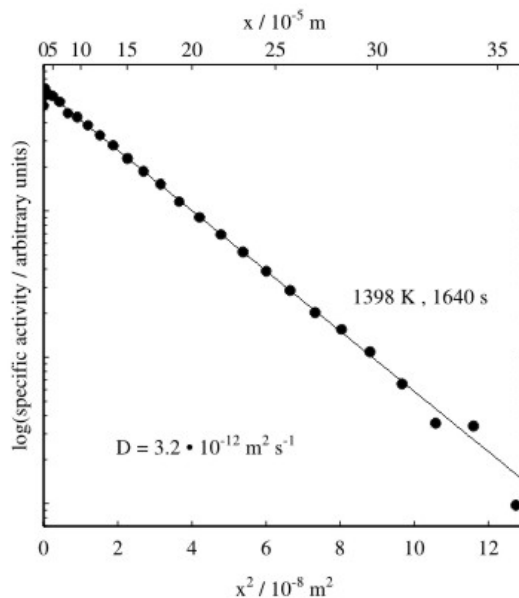

Fig. 6: Example of a concentration-depth profile of ^{59}Fe in Fe$_3$Si according to [58, 44]. Diffusion annealing was performed at 1198 K for 1640 s. The solid line represents a fit of the thin-film solution of Fick's second law to the data.

Many of the precise diffusion studies in recent decades were performed by the radiotracer technique [13]. We illustrate the power of this method just by one example. Due to the high sensitivity of nuclear counting facilities, radiotracer studies are often superior to other techniques. A very important advantage is that self-diffusion – the most basic diffusion process in a solid – can be studied by using a radioisotope of an element which is a constituent of that solid. As an example, Fig. 6 shows the concentration-depth profile of the radioisotope ^{59}Fe in a sample of the intermetallic alloy Fe$_3$Si. The reader may note that the experimental data follow the thin-film solution of Fick's second law (Eq. (6)) over almost five orders of magnitude. From experimental data of this quality, diffusion coefficients can be determined with an accuracy of a few percent.
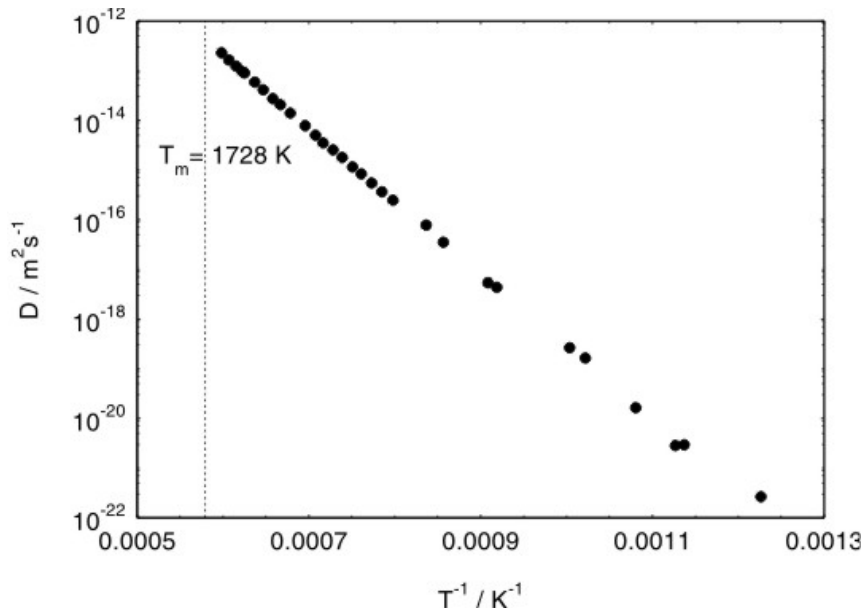
Fig. 7: Diffusion of the radioisotope [63]Ni in monocrystals of nickel according to [44].

Self-diffusion in many elements has been studied over wide temperature ranges using radiotracer methods. As an example Fig. 7 shows an Arrhenius diagram of self-diffusion in monocrystalline nickel studied with the radioisotope [63]Ni. For depth profiling both mechanical and sputter techniques were applied (see [44] for details). The reader may note that the data cover more than nine orders of magnitude in the diffusion coefficient.

A review of the more recent development of diffusion science is beyond the scope of this paper, since the field has grown explosively. This period is characterised by the extensive use of *radioisotopes*, the study of the dependence of diffusion on the tracer mass (isotope effect) and of diffusion under hydrostatic pressure. Great improvements in the precision of diffusion measurements and in the accessible temperature ranges were achieved by using refined profiling techniques such as *sputter sectioning* [59, 60], *secondary ion mass spectroscopy* (SIMS), *Rutherford back-scattering* (RBS), and *nuclear reaction analysis* (NRA) (see [44] for details). Methods not directly based on Fick's law to study atomic motion such as the *anelastic or magnetic after-effect*, *internal friction*, and *impedance spectroscopy* for ion-conducting materials were developed and widely applied. Completely new approaches making use of nuclear methods such as *nuclear magnetic relaxation* (NMR) applied first by *Bloembergen, Purcell and Pound* [61], *Mössbauer spectroscopy* (MBS) detected by the German Nobel laureate *Mössbauer* [62], *a*nd *quasi-elastic neutron scattering* (QENS) were successfully applied to diffusion problems.

Up-to-date reviews for the application of nuclear methods to diffusion studies have been given, e.g., by *Heitjans, Schirmer and Indris* for NMR [63], by *Mullen* and by *Vogl and Sepiol* for MBS [64, 65], by *Zabel* and by *Springer and Lechner* for QENS [66, 67]. The main virtue of MBS and QENS is that these methods are sensitive to the elementary diffusion steps on a microscopic scale. A direct determination of length and direction of the diffusion jump is possible, when single crystals are used. In addition, the diffusion coefficient can be deduced and compared with tracer data. Both techniques are limited to relatively high diffusion coefficients, i.e to temperatures near the melting temperature: Only systems with a suitable Mössbauer isotope or a large enough incoherent cross section for neutrons can be studied by MBS or QENS (see [44] for details).

The past decades have also seen a tremendous increase in the application of *computer modelling and simulation methods* to diffusion processes in materials. Along with continuum modelling aimed at describing complex diffusion problems by differential equations, atomic-level modelling by a variety of methods, such as *ab-initio* calculations, molecular dynamics studies, and Monte Carlo simulations, plays an increasingly important role as means of gaining fundamental insights into diffusion processes. Among a group of pioneers, *Graeme Murch* from the University of Newcastle in Australia is an outstanding person in this area that is now known as computational materials science. He initiated the use of Monte Carlo methods for calculating diffusion kinetics of solids, especially tracer correlation effects. He developed together with *Irina Belova* a number of Monte Carlo-based simulation techniques to address an extremely wide range of complex diffusion kinetic problems documented in a large number of papers. It is beyond the scope of our paper to list these all. We just mention a recent review provided by these authors [76].

It may be also interesting to note that diffusion has a fairly long tradition at the authors' University of Münster. *Wolfgang Seith* (1900 – 1955), who collaborated with *von Hevesy* in Freiburg, was appointed in 1937 as professor of physical chemistry. Seith established diffusion as scientific topic in Münster and authored a first book on *'Diffusion in Metallen'* in 1939 [68]. The second edition of this book appeared in 1956 and was co-authored by *Theodor Heumann* (1914 – 2002) [18], who was then associated with Seith. Later Theodor Heumann occupied a chair in physics in Münster. He introduced together with his associate *Christian Herzig* the radiotracer technique in the Münster diffusion laboratory, which had not been possible during Seith's time due to aggravated war and post-war conditions. Heumann published a new book on *'Diffusion in Metallen'* in 1992 [19]. One of the present authors (H.M.) succeeded Heumann on the chair in 1984 and retired 2005. During H.M.'s period diffusion was one of the major research topics of the group. Diffusion has been studied in many kinds of solids including metals, intermetallics, metallic glasses, elemental and compound semiconductors, ion-conducting oxide glasses and polymers. Lattice as well as grain-boundary diffusion has been studied using radiotracer techniques. Interdiffusion and multiphase diffusion was investigated by electron microprobe analysis using the Boltzmann-Matano analysis. Monte Carlo techniques were applied to diffusion problems and diffusion-related phenomena were considered as well. One of the authors (H.M.) has edited a collection of diffusion data

'Diffusion in Solid Metals and Alloys' [13] and published a new textbook with the title 'Diffusion in Solids – Fundamentals, Methods, Materials, Diffusion-controlled Processes', which appeared in 2007 [44].

We end this paper by drawing the readers´ attention to some additional literature on the history of diffusion. An essay on the early history of diffusion with the title 'The origin of quantitative diffusion measurements in solids. A centenary view' was given by *L.W. Barr* [11]. At a conference on the occasion of the 150th anniversary of Fick's publications and the 100th anniversary of Einstein's paper on Brownian motion, *Jean Philibert* presented a very informative article on 'One and a Half Century of Diffusion: Fick, Einstein, before and beyond' [9]. Readers interested in the history of diffusion mechanisms in the solid-state will benefit from *C. Tuijn's* article on the 'History of models for solid-state diffusion' [71]. Remarks about the more recent history can be found in papers of *Steven Rothman* [72], *M. Koiwa* [73], *Alfred Seeger* [74], and one of the present authors [44, 75]

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