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# Chemical kinetics and diffusion approach: the history of the Klein–Kramers equation

Stefano Zambelli

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**Abstract** In this essay, the first statistical and stochastic treatments of chemical dynamics are analyzed and discussed, in particular the diffusive description of chemical reactions. The first part of the paper introduces the historical and methodological basis of the theories about stochastic processes and diffusion as well as their lesser-known applications in chemical kinetics, which were advanced by Jens Anton Christiansen (1888–1969). In the second, part we will focus our attention on the early works of Oskar Benjamin Klein (1894–1977) and Hendrik Anton Kramers (1894–1952) on electrolytes and the latter’s more mature work, which completes and gives a firm theoretical background to Christiansen’s description.

**Keywords** Christiansen · Kramers · Diffusion · Reaction · Kramers-Klein · Stochastic

## 1 Introduction

The main development of the history of chemical kinetics, as it is usually known, seems to be nearly linear. This may be largely true but there are several notable exceptions, including Perrin’s radiation hypothesis and the diffusion approach to chemical dynamics. Introduced in 1915 and developed until 1928, the radiation hypothesis turned out to be unsuccessful, but in spite of its failure that hypothesis was fiercely debated

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during its brief lifetime (King and Laidler 1984). The diffusion description, however, elaborated by Christiansen around 1935 (Christiansen 1936) and fully systematised in 1940 by Kramers (1940), was an interesting and successful method complementary to transition state theory (TST). It received, however, little or no attention in chemistry circles for a long time. The mechanical approach to molecular interactions and reaction dynamics, in combination with the newly developed quantum theory (Polanyi and Eyring 1931a), provided a strong foundation for the historical achievement of transition state theory by Henry Eyring (1901–1981) and Michael Polanyi (1891–1976) in 1935 (Eyring 1935; Evans and Polanyi 1935). This represented the first self-consistent theory on chemical kinetics not flawed by phenomenological data or approximations. At about the same time, Christiansen introduced the diffusive-stochastic approach to reaction dynamics. In this approach chemical reactions are interpreted as diffusive processes. This description derived from the tradition of studies about Brownian motion and colloid dynamics started by Albert Einstein (1879–1955) and Marion von Smoluchowski (1853–1932) (Einstein 1905; Smoluchowski 1906, 1916) and culminated in a significant paper by Kramers in 1940.

Didactical explanations follow the history of kinetics from 1800 to the development of TST, see, e.g., Laidler and King (1983). As it had happened during the thirties, diffusion-controlled reactions and the Christiansen–Kramers approach are again being ignored. This approach is treated only in rather advanced and specific courses of physical chemistry. A similar situation exists regarding the researches in this field. Few scholars are today directly concerned with chemical kinetics, although there are many of them indirectly involved. The stochastic-diffusion description of chemical dynamics, in particular, involves only a handful of researchers in theoretical and computational chemistry. Owing to its intrinsic difficulties and the great chemical success of TST, due probably to its “pseudo-molecular dynamics” vision, the diffusion description has been completely forgotten for nearly thirty years. It was only rediscovered, with some notable prior exceptions (Delbrück 1940; McQuarrie 1967), at the end of the seventies (Skinner and Wolynes 1978), with the birth of computational chemistry. The Christiansen–Kramers vision has some advantages over TST because, being equally independent from phenomenologies and approximations, it considers intrinsically the interactions with a solvent, even though results are more difficult to apply to real systems that are not extremely simple. It describes better the case of diffusion-controlled reactions, which, however, are relatively rare. A description of the origins and the developments of the Christiansen–Kramers approach is useful to comprehend the reasons why it was underestimated and its chequered history. In the last two sections, the main part of this essay, I will carefully examine one of the first papers written by Klein (1922) and the work of Kramers himself, which was exposed in the today famous paper of 1940: “*Brownian motion in a field of force and the diffusion model of chemical reactions*”. The paper of Klein resulted from an early collaboration with Kramers, and in it we will discover the origins of the well-known Klein–Kramers equation.

## 2 Einstein’s theory of Brownian motion

As a background for the later development, we will briefly review here Einstein’s work on Brownian motion and its historical relevance. These remarks are not intended as a

thorough discussion of Einstein's and Smoluchowski's work, but rather to place these works into a historical perspective relevant for the diffusion approach to chemical kinetics. Around the turn of the twentieth century the debate about the compatibility of the kinetic theory of gases, more generally the new statistical mechanics, and classical thermodynamics was at a critical point (Brush 1976), particularly concerning the explanation of Brownian motion. From a purely abstract point of view the question had already been resolved by Ludwig Eduard Boltzmann (1844–1906), relative to the maximal entropy tendency of systems, but his work was fully recognized only after the first decade of the twentieth century. It was therefore necessary to gain an alternative vision to conjugate the kinetic and thermodynamic models.

Albert Einstein found such a solution in 1905 (Renn 2005). He began research on the mechanical nature of heat in 1903 (Einstein 1903) with a first paper in this field, *Eine Theorie der Grundlagen der Thermodynamik*, then in 1904 (Einstein 1904) followed it with a second one, *Zur allgemeinen molekularen Theorie der Wärme*. The second work laid the basis for two of the papers of 1905, the *annus mirabilis*. One of these two papers is particularly important in our context: *Ueber die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen* (Einstein 1905). This work is of extraordinary significance and, although it is less esteemed than other papers of the *annus mirabilis*, it established the starting-point for all disciplinary ambits. In his paper, Einstein emphasized that he had no experimental data for his theory on Brownian motion, the existing data lacking precision or sense. Direct experimental observations suggested the absurd conclusion that the velocity of Brownian particles grew larger when times of observation were smaller. The velocity would be infinite in the limit of infinitesimally small observation time. As we know today, from a statistical point of view, it is impossible to define the distance covered by a single Brownian particle, so it is impossible to obtain the classical velocity of that particle. Einstein assumed another fundamental discordance with macroscopical behaviour: classical thermodynamics was inapplicable for microscopically small systems. On the other hand, if the assumptions relative to Brownian motion are inconsistent the kinetic-molecular description of heat would be false. How did Einstein resolve this conflict? He introduced, indirectly, the modern concept of fluctuations. There is a first exception to thermodynamics if we find an osmotic pressure for particles suspended in a solution (colloids). Then the free energy of the system does not change, because it is independent of the position of these particles or of a half-permeable barrier. So, according to thermodynamics, there will be no particular forces against the barrier. On the other hand, according to kinetic theory, the irregular motion of the suspended particles may very well generate forces against the barrier. Einstein assumed that suspended particles are not different from solute molecules or ions and obtained the expression for osmotic pressure from Newton's equations of the particles in phase space and from thermodynamical expressions for the entropy and free energy. After these considerations on osmosis it is natural to consider the diffusion of suspended particles. Assuming dynamical equilibrium, Einstein noted that the free energy does not change for an arbitrary motion of a suspended substance. He obtained the free energy as a function of internal energy and entropy using Boltzmann's  $H$  theorem. The equilibrium is between osmotic pressure and irregular forces due to thermal agitation. Assuming spherical particles and applying Stoke's law Einstein

found a relation between the diffusion coefficient and the viscosity (Kirchhoff 1897, p. 26, Vorlesung 4). This is the simplest and earliest form of what we today call the fluctuation-dissipation theorem. In particular, Einstein ignored the apparent incompatibility of these two coefficients, the first obtained from thermodynamics, the second from micro-mechanics. There is no explicit demonstration of the consistency between these different conceptual frameworks, but Einstein's carelessness in this respect, which was probably intended, opened the way for that demonstration, which would later be given explicitly by Smoluchowski, and for the development of the concept of fluctuations. Einstein put down two fundamental premises relative to the motion of the particles:

- (1) Their motion is mutually independent (in the limit of low concentration). Similarly, the motion of a single particle is independent of its previous movements.
- (2) Time intervals must be short in relation to observation times but long enough to validate the first premise.

These conditions are similar to those of the Markov processes, the simplest cases of stochastic dynamics. Although Norbert Wiener (1894–1964) in 1923 and Andrej Nikolaevič Kolmogorov (1903–1987) in 1930 were the first scientists who treated the Markov processes with rigour and provided the foundation of a general theory for them, the pioneering use of their assumptions by Einstein is very interesting. Andrej Andreevič Markov (1856–1922) did his research on this subject around 1900 (Markov 1906) and it would be interesting to know whether or not Einstein knew the Russian's work. In any case, the use of statistics in the Einstein paper is relatively basic. He introduced the distribution function for particle displacements and compared it with the solution's concentration, finding, from a purely statistical consideration, the second law of Fick (which says:  $\frac{dC}{dt} = D \frac{d^2C}{dx^2}$ ). The displacement probability follows a Gaussian distribution, the same as for random errors. The same result turns out to be valid for variations of concentration in a given volume in time:

$$C(x, t) = \frac{n}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right). \quad (2.1)$$

Here  $C(x, t)$  is the concentration at the position  $x$  at the instant of time  $t$ ,  $n$  denotes the number of particles and  $D$  the diffusion coefficient. With a Gaussian distribution we can consider the standard deviation of the displacement rather than the displacement itself for the study of the motion of Brownian particles. The same conclusion is valid for concentration variations. This was the reason for the lack of significance of previous measurements of Brownian motion, as they were based on the direct observation of displacements rather than on their standard deviation. Einstein found his well-known formula,  $\delta_x = \sqrt{x^2} = \sqrt{2Dt}$ , where he put into relation the standard deviation of the displacements  $\delta_x$  with the diffusion coefficient  $D$  and time  $t$ . So the resulting movement is statistically proportional to the square root of time, not directly to time as in a classical description. In the last and most famous part of the paper, Einstein used these relations to obtain the Avogadro number  $N_a$  as:

$$N_a = \frac{t}{x^2} \frac{RT}{3\pi\xi R}. \quad (2.2)$$

With water at 17°C, its viscosity coefficient  $\xi$ , a radius of Brownian particles of  $R = 1\ \mu$ , and a mean square displacement  $\overline{x^2}$  of  $6\ \mu$  after a time  $t$  of 1 min, the resulting value for  $N_a = 6 \times 10^{23}$  was in good agreement with other estimates, and so Einstein's methodology was confirmed. This was the first theoretical self-consistent proof of the validity of an atomistic theory and hence of the existence of atoms as well. The issue was so important that Einstein reconsidered it a year later in 1906. But he remained on theoretical grounds and left the experimental proof to Perrin.

Jean Baptiste Perrin (1870–1942) was awarded the Nobel prize in physics in 1926 for his work on the discontinuous structure of matter and for his discovery of sedimentation equilibrium. Using Zeiss cells he did microscopic observations and counting of colloid particles of constant and known size.

Apart from the extraordinary importance of the first direct demonstration of atomic theory there is another fundamental point to consider in the work of Einstein and Perrin. On a theoretical level their work gave the basis for the mechanics of stochastic processes, a necessary basis for their application to physical and chemical systems. Furthermore, Einstein introduced the first material examples of Boltzmann's statistical description, thus reconciling the apparent incompatibility between thermodynamics and gas kinetics. On a practical level, the work of Perrin allowed important developments in the observation of colloids and diffusion.

Smoluchowski would continue to develop this work. He found laws for the dynamics of suspended particle solutions and for diffusion processes in general. From these researches the first applications to chemical systems and reactions would be developed.

### 3 Smoluchowski's applications to colloids and chemistry

The study of diffusion is fundamental for the understanding of the nature of fluids and of their dynamics. It is therefore useful not only in the investigation of specific chemical phenomena, like electrolysis, but also for the investigation of all condensed-phase chemical processes.

The theoretical basis of diffusive processes in chemistry was established by the Polish physicist Marion von Smoluchowski, who studied mainly diffusion and related topics (Teske 1977). He arrived at almost the same conclusions as Einstein about Brownian motion but he published his results a year later in 1906 (Smoluchowski 1906). Interesting to us are his work around 1915 and two papers that appeared in 1916 (Smoluchowski 1916) and 1917 (Smoluchowski 1917). Those publications, together with the works of Paul Langevin (1872–1946), bear directly on the Christiansen–Kramers view of chemical reactions as diffusive processes.

Smoluchowski examined the diffusion and coagulation dynamics of colloidal solutions. It is curious that the same Smoluchowski denounced the scientific community's lack of attention to this argument in the introduction of the 1916 paper, because the debate about atomic theory, confirmed by Einstein's theory and Perrin's experiments (Perrin 1913), nearly monopolized the scientific debate in that period. What exactly did Smoluchowski intend?

He referred (Smoluchowski 1916) to the part of Einstein's paper that in his opinion was less well-reputed: the first successful attempt to reconcile thermodynamics with

statistical mechanics for a general system that is relevant in practice: a fluid where Brownian motion is observable. As mentioned above, Boltzmann's reconciliation with a statistical system, which is well-known today, was too abstract and theoretical. As we will see, Smoluchowski built a more representative example with a specific real system.

Smoluchowski associated Einstein's probability distribution of displacements with the mean free path in the kinetic theory of gases. Then he introduced the simplest model of Brownian motion: a one-dimensional random walker.

Subramaniam Chandrashekar (1910–1995) was to take up this simple model again in his 1943 review of Kramers's problem and its first applications (Chandrashekar 1943). It consists of an object that moves indifferently, by discrete, random steps, to the right or left along a straight line. The probability that the object reach a definite position after a certain number of steps, if the distance of the final position is small compared with the total number of steps times the step width, is a result that is equivalent to Einstein's distribution of the displacements of a Brownian particle.

There is a nice practical realization of that model: a marble that rolls down an inclined plane bouncing on a lattice of nails. If we let several marbles start from the same point we will observe a Gaussian distribution at the bottom of the plane. Using this simple apparatus, the Galton Box, Smoluchowski evaluated what would happen when the system possessed a definite initial configuration. He imagined the marbles rolling free from different initial positions, as in the case of real diffusion. Smoluchowski found that the real cause of diffusion and of osmotic pressure is the Brownian motion of the suspended particles and the temporal evolution of their distribution. There are, however, some discrepancies between the expressions obtained via Brownian motion and those deduced from the diffusion equation. The diffusion equation gives a mean value of the position of single particles, while the Brownian motion of a single particle is described by deviations from that mean value. Smoluchowski argued that a theory about fluctuations (“Schwankungen”) of concentration would be necessary for the investigations of these statistical deviations. Such a theory would be based on the observation of a fixed microscopic volume inside a solution while diffusion occurred. Studying the amplitude and frequency of these fluctuations Smoluchowski obtained a microscopic theory of equilibrium, and this theory produced interesting results for their similarities with actual theories of non-equilibrium processes, in particular for the definition of the boundary conditions imposed on the intensive variables of a sample in a non-equilibrium state and the definition of the so called thermodynamics forces. Although such theoretical efforts had not been made in that period some interesting approaches by the Swedish chemist Theodore Svedberg (1884–1971) in this direction were made. Svedberg confronted the results of the theory of probabilities with the observed counting of gold colloidal particles in a microscopic sample volume of a homogeneous suspension in a given time (Svedberg 1912). He found that the fluctuations of the number of particles depend only on their average number, but not on the physical nature of the system. We now know that, according to statistical mechanics, this independence is a general property of fluctuations, and the resulting distribution law results independent of the considered mechanical system. This independence is the theoretical justification for the phenomenological similarities mentioned above.

Smoluchowski also investigated another essential aspect of diffusion processes: while the distribution law and the entity of fluctuations do not depend on the particular system this is not strictly true for the frequencies of the fluctuations. Svedberg had observed this fact experimentally, and Smoluchowski examined it from a quantitative point of view, considering one of the simplest physical variables of the system, the volume.

Smoluchowski calculated the fluctuation of the number of particles inside a given volume given the displacement distribution for the particles in solution. In other words, he found the variation of the concentration in a given volume of the sample. He found an important discrepancy in Einstein's formula for the mean square displacement because in Einstein's theory it was assumed that a displacement is statistically independent of previous movements of the particle. In Smoluchowski's case the number of particles that occupies a given volume in a given time will not vary drastically. The actual number of molecules partially determines the subsequent number and the microscopic events and therefore the number of particles at one point is not statistically independent of its prehistory. Smoluchowski developed a theoretical description for this case and discussed practical examples of that description. This consideration determines a limit between macroscopic samples, which obey thermodynamic irreversibility, and microscopic samples, described by mechanical and dynamically reversible models. Smoluchowski posed the question in terms of times of recurrence, taking up an earlier debate by Ernst Friedrich Ferdinand Zermelo (1871–1973), Jules Henri Poincaré (1854–1912), and Boltzmann. He considered the time that would elapse between recurrences of a certain configuration, the number of particles in a given volume in this case, for larger and larger systems. If the size of the volume of the system, and so the number of its constituents, increases the reoccurrence of a determinate configuration is more and more improbable, or alternatively longer and longer times elapse between the occurrence of the same state of affairs.

Smoluchowski (1967) took up Boltzmann's justification of the apparent irreversibility of macroscopic systems, but he considered a specific physical example. Considering different samples of air (in cubes of side length  $l$ ) he calculated the recurrence time  $\tau$  of the following event: the variation, caused only by fluctuations of air density, of exceeding the mean oxygen density in one half of the container by 1%. The results found by Smoluchowski are represented in the following table:

$l$ (cm)	$\tau$ (s)
1	$10^{10^{14}}$
$5 \times 10^{-5}$	$10^{68}$
$3 \times 10^{-5}$	$10^6$
$2.5 \times 10^{-5}$	1
$10^{-5}$	$10^{-11}$

From these results we can see that for microscopic samples (around  $0,1 \mu$ ) the recurrence is extremely fast, so the dynamics of the system is completely reversible in accordance with statistical mechanics. At this level, the Brownian motion begins to be observable, too.

Smoluchowski generalized the role of fluctuations also in other fields. For example he assumed that the diffusion of heat depends on energy fluctuations. Smoluchowski



also paid particular attention to the experimental works on colloids, conducted by important researchers like Perrin, Louis Marcel Brillouin (1854–1948), Svedberg and others. He was particularly interested in those systems because he wanted to generalize diffusion theory for the case where forces, like gravitation or inter-molecular interactions, are present. From the papers of 1916 and 1917 the famous expression for generalized diffusion that bears his name was deduced (the case presented is for a single particle):

$$\frac{\partial P(x, x_0, t)}{\partial t} = D \frac{\partial^2 P(x, x_0, t)}{\partial^2 x^2} - \frac{\partial}{\partial x} \left[ \frac{F(x)}{\xi} P(x, x_0, t) \right], \quad (3.1)$$

where  $P$  is the probability density function,  $t$  the time,  $D$  the diffusion constant,  $x$  the position, with  $x_0$  the initial configuration,  $F(x)$  a generic force, and  $\xi$  the viscosity coefficient. If we consider only the first term on the right side of the equation it corresponds to the common diffusion equation. The second term represents the case in which a field of force  $F(x)$  is present. This expression is strictly valid only in the case of large viscosity  $\xi$  and differs from the Fokker-Planck equation by being independent from velocity which is supposed to follow from a Maxwell distribution. It is important to mention briefly another important formula that Smoluchowski introduced in 1916 (Smoluchowski 1916), an integrodifferential equation describing the coagulation dynamics of colloid solutions:

$$\frac{dn_k}{dt} = \frac{1}{2} \sum_{i+j=k} \beta_{ij} n_i n_j - \sum_{i=1}^c \beta_{ik} n_i. \quad (3.2)$$

This relation expresses the concentration dynamics of coagulated particles  $k$  by means of the balancing between the formation (first term on right) and disappearance (second term on right) of these particles.  $\beta_{ij}$  represents the probability of collision between the  $i$ th and  $j$ th particles.

Smoluchowski's conclusions in this case are very interesting for chemistry because they describe also the dynamics of diffusion-controlled reactions. In those reactions, the diffusion of approaching reactants is the long stage with respect to the reactive interaction itself. We can extend an analogy between coagulation and diffusion controlled reaction phenomenologies, for example.

#### 4 The Christiansen–Kramers collaboration

From the main biography of Kramers (Dresden 1987), we know that Kramers arrived in Copenhagen during the middle of the First World War, in August 1916. Soon after his arrival, he became a close collaborator of Niels Bohr (1885–1962), some years before the official foundation of the Institute of Theoretical Physics, today Bohr Institute, in March 1921. In the subsequent years, Kramers often acted as a spokesman for Bohr's ideas: he gave lectures around Europe to present and explain Bohr's ideas and he also introduced these concepts to new students and assistants of Bohr's. It is

possible that Kramers encountered Christiansen thanks to this mediating role in the Copenhagen institute. Christiansen visited the Bohr Institute around 1922 after his PhD graduation for a period of nearly 1 year (Bak 1974). It is possible that he already came to Copenhagen with the hope of finding some mathematical-physical assistance for his studies of chemical reactions.

Christiansen's PhD thesis treated the dynamics of specific chemical reactions: in this work he introduced for the first time the term *chain reactions* (*ketten reaction* in Danish). Christiansen tried to apply the description and the model of chain reactions to different mechanisms of chemical reaction. He was particularly interested in the problem of activation, as can be seen in a paper of August 1922 (Christiansen 1922). In this work he confronted the two mechanisms of activation by radiation and by collisions, in particular for uni-molecular reactions. He anticipated Kramers interest; this will happen again 15 years later for the diffusive approach to chemical kinetics. Today we know that pure uni-molecular reactions, where a stable isolated molecule transforms itself spontaneously, do not exist: there is always a contribution due to thermal collisions. Kinetic expressions of reaction rates of some chemical processes, mainly dissociations, induced chemical physicists between 1920 and 1930 to elaborate the so-called radiative hypothesis (King and Laidler 1984), in which energy activations and relaxations of molecules are entirely or mainly due to radiations exchange. Perrin was the main promoter of this school (Perrin 1922). In the work of 1922 Christiansen examined the works of Dusham and Trautz (Dusham 1921; Trautz 1920) in the light of Einstein's coefficients of emission and absorption. He showed a mild scepticism about radiation mechanisms. In a supplement to the paper Christiansen thanked Bohr for his help on the interpretation of Einstein's radiative coefficients from a molecular point of view and for the observations Bohr made relative to the underestimation of collisions factors.

A year later Christiansen wrote another paper on this subject, this time together with Kramers. Bohr may also have contributed to the ideas of this publication because the authors again thanked him at the end of the paper (Christiansen and Kramers 1923). Probably Bohr assigned Kramers the task to help Christiansen due to Kramers extensive interest in atomic and molecular spectroscopy, as we can see from the number of papers and works in this field that he published in that period (Mehra and Rechenberg 1982, p. 490).

In their joint paper, "*Über die Geschwindigkeit chemischer Reactionen*" (Christiansen and Kramers 1923), the dynamics of a general uni-molecular gaseous reaction is treated first purely on the basis of a collision activation mechanism and the results are then confronted again with an analysis of a mechanism of activation by radiation, as in Perrin's hypothesis. Christiansen and Kramers estimated the exponential factor obtained in the radiative and collision mechanisms and compared that estimate with experimental data. Kramers and Christiansen considered the gaseous dissociation represented by the following reaction:  $n \longrightarrow n' + n''$ , where  $n$  is the original gas molecule and  $n'$ ,  $n''$  the dissociated species. Christiansen took again the viewpoint of Svante August Arrhenius (1859–1927) where dissociation happens when activated molecules, which are in thermal equilibrium with reactants, spontaneously turn to products. The ratio between the concentration of activated molecules  $C_a$  and the

concentration of reacting molecules  $C_n$  is given by the expression:

$$\frac{C_a}{C_n} = \frac{p_a}{p_n} e^{-\frac{\varepsilon_a - \varepsilon_n}{RT}}, \quad (4.1)$$

where  $\varepsilon$  and  $p$  are the energy and the statistical weight of the considered species,  $R$  the gas constant and  $T$  the absolute temperature. If  $A$  is the probability of change per second, the rate of reaction is then obtained by the following expression:

$$k = -\frac{1}{C_n} \frac{dC_n}{dt} = A \frac{p_a}{p_n} e^{-\frac{\varepsilon_a - \varepsilon_n}{RT}}. \quad (4.2)$$

This expression, a kinetic rate in the Arrhenius form with the pre-exponential factor calculated as a function of the radiation-matter interactions is typical in the ambit of radiation hypothesis as discussed in the first part of this paragraph. The frequency of change per volume and per second according to Einstein's equations results in:  $N_{\text{rad}} = C_n B_n^a \rho_\nu$ , where  $B_n^a \rho_\nu$  is the probability per second of a stimulated transition  $n \rightarrow a$  promoted by blackbody radiation of energy density  $\rho_\nu$  (Einstein 1917).

It is important to note that in the original Einstein paper, *Zur Quantentheorie der Strahlung*, published in 1917, there is only an allusion to molecular transition or in general to chemistry. Einstein's work of 1917 mainly concerns the nature of radiation. The use of the transition coefficients, basic for spectroscopy, in chemical kinetics, was introduced later by Perrin in the context of his radiation hypothesis (Perrin 1919), a theory that Einstein considered with mild scepticism as we can see from a letter between the two scientists around 1920 (Einstein 1972). Considering Einstein's coefficients Kramers and Christiansen found in the radiative case a pre-exponential factor for the rate constant:  $k_{\text{RAD}} \approx 10^8 e^{-\frac{Q}{RT}}$ , where  $Q = \varepsilon_a - \varepsilon_n$  represents the heat of activation. The calculations in the collision case give a greater constant:  $k_{\text{COLL}} \approx 10^{10} e^{-\frac{Q}{RT}}$ , supposing the collisions happen between reactive molecules. So Kramers and Christiansen demonstrated that a simple activation by radiation (without considering more complex mechanisms like the contributions of multiple photons or different frequencies of activation and so on), has negligible results in comparison to a pure collision activation. The problem is also that a simple mechanism by collision is not sufficient to justify the much greater experimental value for uni-molecular gaseous reactions:  $k_{\text{EXP}} \approx 10^{14} e^{-\frac{Q}{RT}}$ . Christiansen and Kramers, excluding the mechanism by radiation, had to consider other possible collisions inside the system. In particular, they supposed that rich energy products, called  $a'$ , collide with the molecules of reactants  $n$ , promoting them to the activated state  $a$ . In stationary conditions the concentrations of energized products and activated complexes do not change:  $dC_a/dt = dC_{a'}/dt = 0$ . Taking into account all the processes that increase or decrease the concentrations of the considered species the authors introduced the following expression:

$$\frac{dC_a}{dt} = C_n^2 Z_n^n \xi + \alpha C_n C_{a'} Z_n^{a'} - A C_a - C_n C_a Z_n^a \quad (4.3)$$

and, assuming stationarity for  $a'$ , the following rate constant is obtained:

$$k = -\frac{1}{C_n} \frac{dC_n}{dt} = A \frac{C_n Z_n^n \xi}{C_n Z_a^n + A(1 - \alpha)}, \quad (4.4)$$

where  $Z_n^n$ ,  $Z_n^{a'}$ ,  $Z_a^n$  are the numbers of collisions per second between, respectively, two  $n$  molecules,  $n$  and  $a'$  molecules,  $a$  and  $n$  molecules,  $\xi$  and  $\alpha$  are coefficients that determine the probability for the collisions to be activating,  $C$  is as usual the concentration and finally  $A$  is the probability per second of the spontaneous transformation:  $a \rightarrow a'$ . Kramers and Christiansen assumed equilibrium between reactants and the activated complex obtaining:  $C_n^2 Z_n^n \xi = C_n C_a Z_a^n$ . Combining this equation with the (4.4), and assuming that  $\alpha = 1$ , they obtained again:

$$k = A \frac{p_a}{p_n} e^{-\frac{\varepsilon_a - \varepsilon_n}{RT}} \quad (4.5)$$

in accordance with Arrhenius' equation. So the lifetime of the activated state is related to  $A$  and is found to be of the order  $10^{-14}$  s, but this lifetime is shorter than the estimated time between two successive collisions,  $10^{-13}$  s. This fact brought Christiansen and Kramers to suppose that the reaction arises solely from collisions among reactant molecules and energized products, and that these collision processes have to be seen as elementary. They supposed moreover a deactivation mechanism, introducing a description that would later be found useful in the analysis of chain reactions. The assumption of a deactivation mechanism is very important because it excludes the necessity of a stable activated state, an improbable fact according to its too brief lifetime. Moreover this hypothesis would play a role in future works of the authors approximately 10 years later, where they did not need to consider a definite and discrete activated state, looking at a chemical reaction as a continuous series of stages of an interatomic diffusion process. Kramers and Christiansen, in any case, considered the possible existence of the activated state but thought that its exact description would be very complex because the briefness of its lifetime requires not only simple time-independent quantum mechanics but time-dependent quantum dynamics. The authors removed the problem of the discrepancy between the lifetime of the activated complex and the interval between consecutive collisions by the argument that the activation process itself needs a certain time to happen. With these considerations, Christiansen and Kramers reached the following conclusion about the  $\alpha$  factor that appears in the previous expression for the rate constant. They argued that for uni-molecular mechanisms this factor must be near one, but in most cases it is found almost zero. This, they reasoned, means that the majority of reactions follow a bi-molecular mechanism. In the case of chain reactions  $\alpha$  would be greater than unity.

The last part of the 1923 paper would be revisited by Cyril Norman Hinshelwood (1897–1987) and Nikolaj Nikolaevič Semenov (1896–1986) around 20 years later in their works about uni-molecular and chain reactions clearly explained in the lectures the two scientists held on occasion of receiving the Nobel Prize in 1956 ([http://nobelprize.org/nobel\\_prizes/chemistry/laureates/1956/hinshelwood-lecture.pdf](http://nobelprize.org/nobel_prizes/chemistry/laureates/1956/hinshelwood-lecture.pdf); [http://nobelprize.org/nobel\\_prizes/chemistry/laureates/1956/semenov-lecture.pdf](http://nobelprize.org/nobel_prizes/chemistry/laureates/1956/semenov-lecture.pdf)).

But in spite of the fact that the radiation hypothesis was intensely debated in the theory of chemical kinetics during that period, their work did not receive much attention.

The interesting idea that highly energized products may activate the reactants in a chain mechanism has, however, a major flaw. As a reaction advances, the molecules produced are more and more numerous and there is no reason why they cannot exchange energy among themselves. The assumption that they must exchange energy exclusively with reactants is arbitrary. In Kramers's and Christiansen's paper there are also some interesting remarks about reactions in solution and the role of collisions with solvent molecules. The treatment of reactions in condensed phase would become the main thrust of the work of Christiansen around 1935 and the basis for the famous paper of Kramers in 1940 that will be treated in the following section of this article.

## 5 Christiansen's approach

Christiansen developed the model of a chemical reaction as an intra-molecular diffusion process during the first half of the thirties. He published two papers in 1935 (Christiansen 1935) and 1936 (Christiansen 1936) on this research. The paper of 1936 is particularly significant, while the earlier one simply established the basic thermodynamic treatment necessary for the subsequent work. Christiansen confronted Arrhenius's theory of activated states (Arrhenius 1889) with a little known theory (Nernst 1893b) of Walther Hermann Nernst (1864–1941). In Nernst's theory, the reaction velocity is obtained, by analogy with Ohm's law, as the ratio between a chemical potential and a chemical resistance. Christiansen took the chemical force or potential (both Nernst and Christiansen present some ambiguity on this point) as the difference of the chemical activities of the beginning and the final states and the chemical resistance is represented by a particular integral depending on temperature and diffusion constant. The purpose of Christiansen was to demonstrate, extending Arrhenius's conception, that the methods of Nernst and Arrhenius are analogous. The generalization of Arrhenius's theory is obtained by supposing an open, possibly infinite, sequence of many consecutive steps, thus gaining an expression consistent with that of Nernst. Christiansen discretized a chemical reaction of the kind  $A_1 \Rightarrow B_n$ , considering not only one activated state, as in Arrhenius's model, but a series of consecutive  $n$  stages which result in reciprocal virtual equilibrium:  $A_1 \Rightarrow X_1 \Rightarrow X_2 \Rightarrow \dots \Rightarrow X_{n-1} \Rightarrow B_n$ . He also assumed that the elementary steps of this sequence were composed of uni-molecular reactions and obtained the following expression for the reciprocal rate of reaction:

$$\frac{1}{v} = \frac{1}{a_1 w_1} + \frac{1}{x_1^0 w_2} + \frac{1}{x_2^0 w_3} + \dots + \frac{1}{x_{n-1}^0 w_n}, \quad (5.1)$$

where  $a_1$  is the reactant concentration,  $x_i$  the equilibrium concentration of activated complexes and  $w_{\pm i}$  is the probability per unit time that reactants, products or intermediates transform into each other by the uni-molecular reactions  $\pm i$ .

The terms of the previous equation are of a purely thermodynamic nature, in the sense that they can be imagined as being derived from virtual equilibrium expressions

between species with a lifetime too brief to get real equilibria. The equilibria between reactants, products and intermediates are supposed to be valid because Christiansen considered the quantity of intermediates constant during the slow stages of reaction, so the process is stationary or quasi-stationary. These are a group of assumptions similar to those made in the theory of diffusion. In fact, according to Christiansen's hypothesis, the equilibrium quantity of the activated complexes may be put in relationship to the concentrations of a diffusing substance along the sections of a column. From this diffusive description, he obtained an expression for the reciprocal reaction rate which was consistent with the previous one, obtained on a thermodynamic basis. He introduced the activity coefficients  $\varphi_i$  relating them to single stage transition rates  $w_i$  to justify also the deviations from equilibrium or from a uniform distribution. Christiansen considered a column in which a potential field is present, so that the diffusing molecules are influenced by forces. The concentrations of the diffusing substance at the ends of the column  $x = 0$ ,  $x = l$  are constant and equal to  $c_0$  and  $c_n$ . A stationary gradient of concentration will be achieved after a certain time, and Christiansen's task was to find the quantities of substance diffusing per unit time assuming stationarity. He divided the column in  $n + 1$  cells separated by  $n$  slices, with the thickness of the  $i$ th cell equal to  $\Delta_i$ . The probability per unit time that a molecule in the  $i - 1$ th cell passes into the  $i$ th cell is denoted by  $w_i$ , and  $w_{-i}$  indicates the reverse process, as before for activated complexes, reactants and products. Christiansen assumed that the products of the activity coefficients  $\varphi_i$  and equilibrium concentrations  $c_i^0$  are equal at different positions of the column and from this deduced:

$$c_i^0 = c_0 \frac{\varphi_0}{\varphi_i} \quad \text{and} \quad c_i^0 = c_n \frac{\varphi_n}{\varphi_i} \quad (5.2)$$

for positive and negative reactions. From the expression (5.1) for reciprocal velocity he found:

$$\frac{c_0 \varphi_0}{v_+} = \sum_0^{n-1} \frac{\varphi_i}{\Delta_i w_{i+1}} \quad \text{and} \quad \frac{c_n \varphi_n}{v_-} = \sum_1^n \frac{\varphi_i}{\Delta_i w_{-i}} \quad (5.3)$$

for direct and inverse processes. Taking the velocity of the net process to be  $v = v_+ - v_-$  Christiansen obtained:

$$v \sum_0^{n-1} \frac{\varphi_i}{\Delta_i w_{i+1}} = c_0 \varphi_0 - c_n \varphi_n. \quad (5.4)$$

Since this expression, similar to an equivalent diffusion process, results independent from the size of the column cells, so it must be for their sum:  $J = \sum_0^{n-1} \frac{\varphi_i}{\Delta_i w_{i+1}}$ , and, in the limit, this sum can be represented by the integral:

$$J = \lim_{n \rightarrow \infty} \sum_0^{n-1} \frac{\varphi_i}{\Delta^2 w_{i+1}} \Delta = \int_0^l \frac{\varphi}{D} dx \quad (5.5)$$

with  $D = \Delta^2 w$  and  $\varphi$  as a continuous function of the position  $x$ .

Christiansen thus obtained the rate of diffusion as:  $v = (c_0\varphi_0 - c_n\varphi_n)/J$ . The expression for  $J$  is yet dependent on the length  $l$  of the column, so Christiansen considered the passage only through a column section (in stationary conditions  $v$  must be constant in all the sections of the column):

$$v = -\Delta c\varphi \frac{1}{\int_x^{x+\Delta x} \frac{\varphi}{D} dx}, \quad (5.6)$$

which in differential form turns into a diffusion law:

$$v = -\frac{D}{\varphi} \frac{\partial c\varphi}{\partial x}. \quad (5.7)$$

This expression implies that the transport of molecules is produced by the concentration gradient and possibly also by forces acting on the molecules (their contribution is represented by the activities  $\varphi$ ). Separating the activity contribution, Christiansen obtained the following expression:

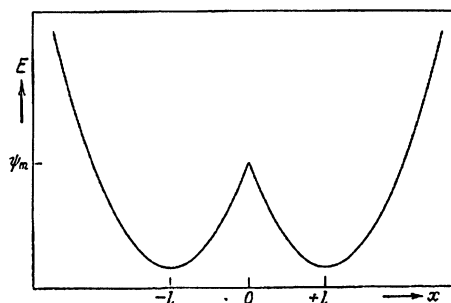
$$v = -D \frac{\partial c}{\partial x} - Dc \frac{\partial \ln \varphi}{\partial x}, \quad (5.8)$$

in which the first term on the right represents an ordinary diffusion without a field. The second term, if we call  $\psi$  the potential energy in a given position and  $K$  the force, is equal to  $\frac{D}{RT} cK$ , considering that  $K = -\frac{\partial \psi}{\partial x}$ , and  $RT \ln \varphi = \psi$  from Boltzmann's principle. Equation 5.8 then becomes:

$$v = -D \frac{\partial c}{\partial x} + \frac{D}{RT} cK, \quad (5.9)$$

which is analogous to that obtained by Smoluchowski and Einstein, but Christiansen was the first scholar who applied it to reaction kinetics, thus showing the close analogy that exists between the rate of reaction and the rate of diffusion. He investigated also the possibility of dividing a chemical process into a continuous number of stages, citing the famous paper written in 1931 by Eyring and Polanyi, where, for the first time, a continuous description of chemical potential energy along reaction coordinates was found (Polanyi and Eyring 1931b). In particular Christiansen's work will be scarcely cited later in the mainstream researches on chemical kinetics and only about his contributions to catalysis as can be seen examining the most important publications of the sector, from the introductory one (Eyring and Eyring 1963; Laidler 1997) to the more complex (Eyring 1975). The publication of 1963 (Eyring and Eyring 1963) is emblematic: there is only an hint about Christiansen's method in the transport mechanism chapter, but Christiansen's work is not cited explicitly and used only for specific systems, not generalized for all chemical reactions; the work of Kramers was completely ignored.

**Fig. 1** Bi-stable potential barrier, the figure is taken from Christiansen's 1936 paper (Christiansen 1936)



The generalization of the Arrhenius conception brings us naturally to consider the transformation of a molecule during a reaction as an intra-molecular diffusion. To demonstrate this generalization Christiansen made some fundamental assumptions. He considered the case of a simple potential barrier, a symmetrical bi-stable one as shown in Fig. 1.

This case will be used again by Kramers in his work of 1940. There are other assertions, as we will see, that are similar in Christiansen's and Kramers's papers: Christiansen considered various events that occur in the function of the energy of the system. If the diffusing particle has an energy lower than  $\psi_m$ , without considering tunnelling quantum effects, the rate of reaction will be zero. The particle simply cannot overcome the potential barrier. In the opposite case, when the particle has an energy greater than  $\psi_m$ , it will oscillate between the two potential minima indefinitely. So it is impossible to observe a definite transformation, because of the large frequency of oscillation. Half of the time, the molecule will have one form, the other half a different form. To observe a definite transformation Christiansen affirmed that it is senseless to assume a definite energy for the chemical system, and even that it is impossible to realize a similar case because the reacting molecules will always exchange energy directly with the medium or by radiation. Therefore only the case of definite temperature and fluctuating energy is realistic because of the external disturbances. If these disturbances are rare the rate will be defined mainly by the reacting molecules' interactions, and the reaction can be seen as a bi-molecular one. On the other hand, if the experiment shows a uni-molecular behaviour, the disturbances are frequent and influential.

With the expression  $v = (c_0\varphi_0 - c_n\varphi_n)/J$ , Christiansen quantified Nernst's qualitative description. He obtained this expression by increasing the intermediate states of the Arrhenius conception in which only one intermediate or activated state is considered. In this sense the Arrhenius conception is connected to that of Nernst. There are other interesting conclusions drawn by Christiansen that will be fundamental for future works in this field. The first conclusion is about the constant of inter-molecular diffusion  $D$ . If this constant varies during the reaction the resulting equations are extremely difficult to solve. So we have to assume  $D$  to be a characteristic constant of the reaction. The related problem of viscosity change was re-examined by Kramers and remains an essential, unresolved issue today. The second conclusion is that the main problem is to find solutions of a second order partial differential equation for the



determination of chemical activity as a function of space and time. The rate of reaction thus results as an intensity of current inside the molecule. Christiansen emphasized the fact that finding special solutions of this differential equation for a given potential is not so difficult: the difficulty is the search for a reasonable physical solution. We can clearly demonstrate the pioneering intuition of Christiansen by citing the last sentence of the 1936 paper (Christiansen 1936):

This task is similar to that of quantum theory, and it would seem premature if at the present moment I could get some conclusion.

The link between the mathematical structure of a diffusive stochastic description and a quantum mechanical description of a system has interesting and profound relations that we will briefly examine in the following sections of this paper.

## 6 Klein's visit to Copenhagen

The main biographers of Kramers, in particular Dirk ter Haar, claim that his interest in chemical kinetics is a simple mathematical exercise of style (ter Haar 1998, Chap. 6). I am convinced that this is only partly true, and, in particular, I claim that Kramers's work would be impossible without Christiansen's previous contribution. We will argue for this claim more fully in Sects. 7 and 8 of this paper, where we will examine the early work of Kramers and Klein, Kramers' paper of 1940 (Kramers 1940) and the quantitative applications of stochastic processes to chemical kinetics. Although Kramers is most known for his works in quantum mechanics and spectroscopy, he was a wide-ranging thinker and the range of his interests was impressive. The paper of 1940 was a generalization and an application to chemical dynamics of some not very well known and appreciated works done by Kramers and Klein soon after Kramers arrival in Copenhagen. To clarify Klein's role in this phase we have to consider some biographical hints of this period. During the years from 1917 to 1921 Klein travelled many times back and forth between Copenhagen and Stockholm. He became a student of Svante Arrhenius at the Nobel Institute and later he was on his way to Jean Baptiste Perrin in France when First World War broke out and he was drafted into the military. His initial studies were on solubility. At the end of his military service in 1917 Klein received a fellowship to study abroad and arrived in Copenhagen for a longer stay in 1918. Klein did work for both Arrhenius and Bohr in this period, spending the summer of 1919 with Kramers, and finally returned to Stockholm. In the same year Bohr travelled to Stockholm to visit Klein and convinced him to return to Copenhagen and work with him at the institute for theoretical physics. Klein continued his studies on solutions turning his attention from solubility to ionic diffusion. This research led him to his PhD thesis in which he examined the forces between ions in strong electrolyte solutions using the statistical mechanics of Josiah Willard Gibbs (1839–1903). The result was a generalized description of liquid dynamics and the formulation of what we call today the Klein–Kramers equation in a paper of 1922 (Klein 1922).

We will discuss in some detail Klein's paper: "*Zur statistischen Theorie der Suspensionen und Lösungen*" (Klein 1922), a statistical theory about suspensions and solutions. This work was written in 1921, toward the end of Klein's doctorate, and

represents a sum of the collaboration with Kramers during the two preceding years. This collaboration was very fruitful because this work gave the fundamental theoretical basis for a complete and general statistical–mechanical description of solutions. It introduced for the first time the Klein–Kramers equation. It is interesting to note that many experts in stochastic methods also today do not know the origins of this fundamental equation which they use. Its origins are hidden in one of the first works of a young graduate student and they are published in a minor journal with little international circulation outside of Scandinavia.

Let us now focus on Klein's paper in its details to observe the discovery of the famous equation, but also its links with the work of Einstein and Smoluchowski described in the previous parts of this paper.

## 7 The discovery of the Klein–Kramers equation

In the work of 1921, Klein considered a statistical mechanical treatment of a suspension of tiny particles in a viscous fluid. He considered dilute solutions and strong electrolytes and assumed the presence of both external fields and internal forces. The important question for Klein was the interaction of the solvent medium with the solute or suspended particles. In need of a mechanical model for the fluid he looked for analogies with the problem of the mean free path in the gaseous phase. This was a purely theoretical assumption, a real fluid is much more complex, as Klein very well knew, but approaching the problem by means of statistical methods and on the basis of experimental data on viscosity a theory based on a rough model that included the interactions inside liquids was possible.

The action of the solvent on a solute or suspended particle depends on the velocity of the particle or ion and varies quickly and randomly according to the equipartition principle at the temperature of the fluid under consideration. The same assumption is valid for the angular momentum. In fact, these hypotheses are really valid only for suspensions because of the great dimension of the particles, as Einstein and Smoluchowski had demonstrated. Klein wanted to correlate a theoretical mechanical–statistical description of the system to other phenomenological characteristics of the solutions or suspensions, such as the electric conductivity of electrolytes. Using Gibbs's description Klein's goal was to solve the differential equation that describes the system. But it was necessary to impose boundary conditions relating to the mechanical state of the fluid. Klein's innovative approach consists in making no preliminary assumptions at the outset, introducing further assumptions only in a second step, for the solution of cumbersome calculations. He used the conclusions of Hendrik Antoon Lorentz (1853–1928) about energy equipartition to assume the conservation of the mean square displacements of the particles due to Brownian interactions and linked them to the macroscopic properties of the fluid: viscosity and temperature. Thanks to Einstein's work this can be done with nearly any hypothesis on the nature of the system. The irregular thermal impulses determine a velocity distribution of the suspended particles, which generates a diffusion current that adds to that due to external forces. Klein introduced a phase space description for the treatment of this current and obtained a Gibbs equation that takes into account irregular impulses from the fluid.

Klein obtained a general equation for the probability distribution of the suspension and studied its dynamics, generalizing and correcting Einstein and Smoluchowski works. For this goal Klein introduced some approximations to solve the difficult equations obtained and applied them to the problem of electrolytic conductivity. Klein's major contribution consists in finding a general integral that solves Gibbs equations for this system and takes into account the influences of external and internal forces.

After Arrhenius had opened the way to the study of solutions with the theory of electrolytic dissociation, Klein wanted to comprehend and justify the deviations for strong electrolytes, taking into account the reciprocal action between ions due to their electrical charge and the physical characteristics of the solvent such as its viscosity. Klein, following some works (Hevesy 1914, 1916) of George Charles de Hevesy (1885–1966) about the ionic mobility, wanted to correlate the influence of the ionic charge to the characteristics of the solution. For this purpose, it is necessary to introduce some approximation from the beginning: the interaction of the medium with an ion is independent from the presence of other ions. The electrostatic interactions between strong electrolytes determine some deviation from the behaviour of an ideal solution: the properties that depend on the number of ions take on values that derive from a smaller number of ions than are actually present in the solution, such as for a weak electrolyte only partially dissociated. This deviation also affects the Arrhenius mass action law. Also Nernst (1893a), Joseph John Thomson (1856–1940) (Thomson 1893) had studied, for example, the influence of the apparent low dissociation on the dielectric constant of the solution. But in the consideration of these deviations, it is not sufficient to introduce only a correction to the concentrations, it is necessary to introduce more than one correcting term that also depends on the respective deviation. Klein followed Bjerrum's work and introduced a coefficient for osmotic pressure  $f_0$  and another one for conductivity  $f_u$  that corresponds to the ratio of the real and ideal quantities for solutions with the same number of particles. He obtained an activity coefficient  $f_a$  from the osmotic pressure  $f_0$  that characterizes the deviation from the ideal free energy. Klein generalized Bjerrum's empirical formula for the osmotic coefficient with the following expression:

$$f_0 = 1 - \varphi \left( \frac{g^2 \sqrt{c}}{\varepsilon T} \right), \quad (7.1)$$

where  $g$  is the valence of the ion,  $T$  the temperature,  $c$  the concentration,  $\varepsilon$  the dielectric constant.  $\varphi$  cannot be a linear function of the argument, as Bjerrum thought, because then the potential energy would diverge for high temperatures. Klein found a similar result for electrolytic conductivity, generalizing Walden's results. He wanted to consider also the osmotic pressure with a similar description as Milner had done. In a very interesting note, in which he criticized some errors in Milner's expressions that would violate the virial theorem (Milner 1912), he cited the name of Kramers and promised a future paper written jointly with him. Such a work, however, would never be written, a work by Kramers and also Klein in this case, and we have here therefore another *near missed discovery*, as we will see at the end of this section. Klein also wanted to consider dipolar solutes, not only ions, but the extreme difficulties that he encountered in finding the basis for a generalization of Peter Debye's (1884–1966)

theories (Debye 1912) led him to make only some qualitative considerations. At the end of the introduction Klein thanked Professor Arrhenius and Professor Bohr, who hosted him in Copenhagen in that period, Klein's best period in his own words (Klein 1922).

To achieve those goals, Klein considered a dilute solution of  $n$  suspended particles. In this case deviations from an ideal solution are proportional to various powers of concentration and derive from the interactions of the particles with the glass wall and between themselves. The system is considered nearly adiabatic, and the particles are assumed spherical and homogeneous. The translational and rotational degrees of freedom of the particles are independent, but Klein considered only translational motion. The positions of the particles are characterized by Cartesian coordinates of their mass centres in the fluid system of reference. The velocities of the particles are the simple time derivatives of the coordinates. The masses of the suspended particles mass are much greater than the mass of the molecules of the medium, so one can consider a time interval in which their motion is negligible compared to the motion of the solvent. There are three kinds of forces that act on particles: external forces, fluid-particle interactions or solvent forces, and interactions between particles, or reciprocal forces. Solvent forces consist in a succession of rapid irregular impulses that derive from configuration relaxations of the liquid. Particle motions determine configuration changes in the solvent. These facts are in accordance with the dependence of the shear stress on the velocity of a body inside a fluid. Solvent interactions thus depend on the temperature of the system and on the velocity of suspended particles but we have to consider also the influence of external and internal fields of force. For example, if a tiny particle carries a strong charge it exerts a strong action on the solvent and so the frictional force is altered significantly. To describe the influences of the last two contribution we write the equation of motion of the particles with the resultants of the velocities along the Cartesian axis of internal and external fields:

$$\begin{aligned} m_i \frac{du_i}{dt} &= X_i + K_{x_i}, u_i = \frac{dx_i}{dt} \\ m_i \frac{dv_i}{dt} &= Y_i + K_{y_i}, v_i = \frac{dy_i}{dt} \\ m_i \frac{dw_i}{dt} &= Z_i + K_{z_i}, w_i = \frac{dz_i}{dt} \end{aligned} \quad (7.2)$$

where  $m_i$  is the mass of the  $i$ th particle,  $X_i, Y_i, Z_i$  the components of the forces due to thermal collisions and  $K_{x_i}, K_{y_i}, K_{z_i}$  the terms introduced for external and internal fields.  $X_i, Y_i$  and  $Z_i$  vary so quickly and irregularly around their mean values that we can consider a time  $\tau$  in which the velocities and field forces change negligibly. With these classical assumptions Klein discussed directly a Gibbsian statistical mechanics of the system. He considered a number of system copies in thermal equilibrium at temperature  $T$  that differs not so much for positions and velocities of the particles but mainly for the forces acting on them. As usual he introduced a  $6-n$  dimensional phase space and a system density that depends on the considered volume, its position and time. Initially, a current moves the particles, and

$X_i, Y_i, Z_i$  are discontinuous quantities. The integrals of these forces over time  $\tau$ , which are the linear momenta, turn out to be independent of each other and discontinuous:

$$\begin{aligned} m_i \xi_i(\tau) &= \int_t^{t+\tau} X_i dt \\ m_i \eta_i(\tau) &= \int_t^{t+\tau} Y_i dt \\ m_i \varsigma_i(\tau) &= \int_t^{t+\tau} Z_i dt \end{aligned} \quad (7.3)$$

$\xi_i, \eta_i$  and  $\varsigma_i$  have a Gaussian distribution for specific forms of the forces  $X_i, Y_i, Z_i$ . Their mean values are local functions of the phase space:

$$\begin{aligned} \overline{\xi_i}(\tau) &= -\frac{B_i}{m_i} u_i \tau - \frac{\alpha_i}{m_i} K_{x_i} \tau \\ \overline{\eta_i}(\tau) &= -\frac{B_i}{m_i} v_i \tau - \frac{\alpha_i}{m_i} K_{y_i} \tau \\ \overline{\varsigma_i}(\tau) &= -\frac{B_i}{m_i} w_i \tau - \frac{\alpha_i}{m_i} K_{z_i} \tau \end{aligned} \quad (7.4)$$

The quantities  $u_i, v_i, w_i, K_{x_i}, K_{y_i}, K_{z_i}$  refer to the initial time  $t$ ,  $B_i$  is the friction coefficient of the  $i$ -particle and  $\alpha_i$  a constant that depends on the nature of the solvent and of the particles. We obtain also that the mean square values of the impulses result proportional to  $\tau$ :

$$\begin{aligned} \overline{\xi_i^2}(\tau) &= 2\chi_i \tau \\ \overline{\eta_i^2}(\tau) &= 2\lambda_i \tau \\ \overline{\varsigma_i^2}(\tau) &= 2\mu_i \tau \end{aligned} \quad (7.5)$$

The quantities  $\chi_i, \lambda_i, \mu_i$  had been calculated by Lorentz considering thermal equilibrium between particles and solvent and turn out to be independent from the particles' velocity (Lorentz 1916). Klein then defined the probability that the values of  $\xi_i(\tau), \eta_i(\tau), \varsigma_i(\tau)$  would be found between  $\xi_i$  and  $\xi_i + d\xi_i, \eta_i$  and  $\eta_i + d\eta_i, \varsigma_i$  and  $\varsigma_i + d\varsigma_i$ , for all  $i$ , and obtained the probability that a point in the phase space with initial position and velocity  $x_1^0, \dots, w_n^0$  after time  $\tau$  would have velocity components between the limits  $u_1$  and  $u_1 + du_1, \dots, w_n$  and  $w_n + dw_n$  as:

$$W(\xi_1, \dots, \varsigma_n, u_1^0, \dots, w_1^0) du_1 \dots dw_n. \quad (7.6)$$

The number of phase space points with initial position between  $x_1^0$  and  $x_1^0 + dx_1, \dots, z_1^0$  and  $z_1^0 + dz_1$  and velocity between  $u_1^0$  and  $u_1^0 + d\xi_1, \dots, w_1^0$  and  $w_1^0 + d\varsigma_1$  is given by:

$$\nu f(x_1^0, \dots, z_n^0, u_1^0, \dots, w_n^0, t) dx_1 \dots dz_n d\xi_1 \dots d\varsigma_n, \quad (7.7)$$

where  $\nu$  represents a number of system copies sufficient to fill the entire space of the recipient walls and the volume of the particles themselves, the element  $d\xi_1 \dots d\varsigma_n$  is small compared with  $du_1 \dots dw_n$ . If we consider a volume element of the phase space  $d\omega = dx_1 \dots dz_n du_1 \dots dw_n$ , where  $x_1 = x_1^0 + u_1 \tau$ ,  $z_n = z_n^0 + w_1 \tau$ , so small that all points have passed through it from the initial volume after a time  $\tau$ , the number of these points will be:

$$\nu f(x_1, \dots, w_n, t + \tau) d\omega. \quad (7.8)$$

$f$  is obtained by integration over all possible velocities, considering  $u_1^0, \dots, w_1^0$  as functions of  $\xi_1 \dots \varsigma_n$ :

$$f(x_1, \dots, w_n, t + \tau) = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} f(x_1^0, \dots, z_n^0, u_1^0, \dots, w_n^0, t) \times W(\xi_1, \dots, \varsigma_n, u_1^0, \dots, w_1^0) d\xi_1 \dots d\varsigma_n \quad (7.9)$$

$$\xi_i = u_i - u_i^0 - \frac{K_{x_i}}{m_i} \tau \quad (7.10)$$

$$\eta_i = v_i - v_i^0 - \frac{K_{y_i}}{m_i} \tau$$

$$\varsigma_i = w_i - w_i^0 - \frac{K_{z_i}}{m_i} \tau$$

Klein expanded the integral (7.9) into a power series to first order:

$$\begin{aligned} & \frac{1}{\tau} \left[ f(x_1, \dots, w_n, t + \tau) - f(x_1^0, \dots, w_n^0, t) \right] \\ &= \sum_{i=1}^n \left[ \left( \frac{\partial^2(\chi_i f)}{\partial u_i^2} + \frac{\partial^2(\lambda_i f)}{\partial v_i^2} + \frac{\partial^2(\eta_i f)}{\partial w_i^2} \right) \right. \\ & \quad \left. - \left( \frac{\partial(\bar{\xi}_i f)}{\partial u_i} + \frac{\partial(\bar{\eta}_i f)}{\partial v_i} + \frac{\partial(\bar{\varsigma}_i f)}{\partial w_i} \right) - \left( u_i \frac{\partial f}{\partial x_i} + v_i \frac{\partial f}{\partial y_i} + w_i \frac{\partial f}{\partial z_i} \right) \right] \quad (7.11) \end{aligned}$$

The solution of this equation determines the number of points that migrate from a volume in time  $\tau$ , and this represents a diffusion equation. Introducing the mean values of  $\xi_i(\tau)$ ,  $\eta_i(\tau)$  and  $\varsigma_i(\tau)$  previously obtained in (7.4), the Eq. 7.11 turns into the differential form:

$$\frac{\partial f}{\partial t} = \sum_{i=1}^n \left[ \left( \frac{\partial^2(\chi_i f)}{\partial u_i^2} + \frac{\partial^2(\lambda_i f)}{\partial v_i^2} + \frac{\partial^2(\mu_i f)}{\partial w_i^2} \right) + \frac{B_i}{m_i} \left( \frac{\partial(u_i f)}{\partial u_i} + \frac{\partial(v_i f)}{\partial v_i} + \frac{\partial(w_i f)}{\partial w_i} \right) \right] + \frac{\alpha_i - 1}{m_i} \left( K_{x_i} \frac{\partial f}{\partial u_i} + K_{y_i} \frac{\partial f}{\partial v_i} + K_{z_i} \frac{\partial f}{\partial w_i} \right) - \left( u_i \frac{\partial f}{\partial x_i} + v_i \frac{\partial f}{\partial y_i} + w_i \frac{\partial f}{\partial z_i} \right). \quad (7.12)$$

This new equation determines the distribution function and represents the first form of the Klein–Kramers equation. Its validity is limited to times of the order of  $\tau$ , for arbitrary times we have to consider the general Gibbs equation but we would have to know also the exact mechanical properties of the liquid. Klein, by integration of the preceding equation, obtained the quantities  $\chi_i, \dots, \mu_n$  in the absence of active forces and with the assumption of a Maxwell distribution for the velocities:

$$\chi_i = \frac{kT B_i}{m_i} e^{-\frac{m_i}{2kT} u_i^2} (a_1 u_1 + b_1), \quad (7.13)$$

where  $a_1$  and  $b_1$  are constants independent from the velocity  $u_1$ . However, the mean values of  $\chi_i, \dots, \mu_n$  are:  $\chi_i = \lambda_i = \mu_i \frac{kT B_i}{m_i}$ , so  $a_1$  and  $b_1$  must be zero. The presence of forces  $K_{x_1}, \dots, K_{z_n}$  cannot change these values provided that they have no influence on  $B_i$ . Klein then considered the presence of forces due to potential fields independent of time:  $(\alpha_i - 1)K_{x_i, y_i, z_i} = \frac{\partial V}{\partial x_i, y_i, z_i}$ , but dependent on the nature of the fluid and the temperature by virtue of the constant  $\alpha_i$ . The Klein–Kramers equation finally assumes the well-known form:

$$\frac{\partial f}{\partial t} = \sum_{i=1}^n \left[ \frac{kT B_i}{m_i} \left( \frac{\partial^2 f}{\partial u_i^2} + \frac{\partial^2 f}{\partial v_i^2} + \frac{\partial^2 f}{\partial w_i^2} \right) + \frac{B_i}{m_i} \left( \frac{\partial(u_i f)}{\partial u_i} + \frac{\partial(v_i f)}{\partial v_i} + \frac{\partial(w_i f)}{\partial w_i} \right) \right] + \frac{1}{m_i} \left( \frac{\partial V}{\partial x_i} \frac{\partial f}{\partial u_i} + \frac{\partial V}{\partial y_i} \frac{\partial f}{\partial v_i} + \frac{\partial V}{\partial z_i} \frac{\partial f}{\partial w_i} \right) - \left( u_i \frac{\partial f}{\partial x_i} + v_i \frac{\partial f}{\partial y_i} + w_i \frac{\partial f}{\partial z_i} \right). \quad (7.14)$$

Klein wanted to apply the Klein–Kramers equation to different cases, once its general form had been obtained. He noted that Einstein and Smoluchowski had treated extensively the case without external forces. In those works, nevertheless, only the positions of the particles are considered, not their velocities. The simple assumption on the time allows him to obtain the Maxwell distribution for velocities. In any case, Klein's approach is very different from that of Einstein's (1905) and Smoluchowski's (1916). He tried to apply the dynamical equation of the distribution function for any time even if this has no practical meaning. Maxwell's distribution is valid also in presence of external forces, as Smoluchowski had demonstrated. Klein, however, asserted that Smoluchowski in person had showed him that his theory was not valid for very short times. There are some problems also for longer times. To gain a description for all times, not only for  $\tau$ , Klein limited his treatment to one system of  $\nu$  particles with only one copy:  $n = 1$ . This limitation makes the phase space simply correspond to two three-dimensional spaces, one for positions and the other for velocities. The coordinate space corresponds to the volume occupied by

the solution. In order to simplify the system Klein introduced the classical example of a thin, infinitely long cylinder. External forces act only along the cylinder axis, and the cylinder walls play no role in the considered example. The motion along the cylinder is free with any possible distribution of particles whereas the motion perpendicular to axis direction is negligible or considered in an equilibrium state. So we are considering a one-dimensional system. For this case, Klein begins by applying the Klein–Kramers equation to the following distribution function:

$$f = e^{-\frac{1}{kT}\left(\frac{mu^2}{2} + V\right)} \varphi(x, u, t), \quad (7.15)$$

where  $\varphi$  represents a measure of the deviations from equilibrium distribution. The Klein–Kramers equation for  $\varphi$  then becomes:

$$\frac{\partial \varphi}{\partial t} = kT\beta \frac{\partial^2 \varphi}{\partial u^2} - \beta u \frac{\partial \varphi}{\partial u} + \frac{1}{m} \frac{\partial V}{\partial x} \frac{\partial \varphi}{\partial u} - u \frac{\partial \varphi}{\partial x}, \quad \beta = \frac{B}{m}. \quad (7.16)$$

Klein emphasized the great difficulties in the integration of this equation in the presence of external forces. He took up Smoluchowski's treatment of an harmonic potential:  $V = \frac{a}{2}x^2$ ,  $a = m\beta\gamma$ , where  $\gamma$  is a positive constant much smaller than  $\beta$ , a quantity related to the viscosity. Smoluchowski had used this treatment for a statistical proof of the second theorem of thermodynamics, as we have seen in the third section of this paper. Klein, beginning as usually from the particles' equation of motion, found the analytical solution of Eq. 7.16. It has the cumbersome form:

$$\varphi = \frac{m}{2\pi kT e^{-\frac{m}{2kT}(u^2 + \beta\gamma x^2)}} \sqrt{\frac{r_1 r_2}{1 - \left(\frac{r_1 + r_2}{r_1 - r_2}\right) e^{-2r_1 t}}} \times e^{\left[ -\frac{m}{2kT}(u^2 + r_1 r_2 x^2) - \frac{m r_1 r_2}{2kT} \left(\frac{r_2}{r_1 + r_2}\right) \left( \frac{p - b \frac{r_1 - r_2}{r_1 + r_2} e^{r_1 t}}{\left(\frac{r_1 - r_2}{r_1 + r_2}\right)^2 e^{2r_1 t} - 1} \right)^2 + \frac{m r_1 r_2}{2kT} \left(\frac{r_2}{r_1 + r_2}\right) b^2 \right]}, \quad (7.17)$$

where  $r_1$  and  $r_2$  are the solutions of the equation  $r^2 - \beta r + \beta\gamma = 0$ ,  $p = x - \frac{u}{r_2}$  and  $b = x_0 - \frac{u_0}{r_2}$ . This formula represents a valid solution of all statistical problems about solutions or suspensions if we consider times of a magnitude much greater than  $1/\beta$ . Starting from an initial distribution  $f(x_0, u_0, t)$  the current distribution results:

$$f(x, u, t + \tau) = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} f(x_0, u_0, t) e^{-\frac{m}{2kT}(u^2 + \beta\gamma x^2)} \varphi dx_0 du_0. \quad (7.18)$$



If  $r_1 = 0$  we are considering a system without external forces. For  $t \rightarrow \infty$  we find the equilibrium distribution as expected to be:

$$f(x, u, \infty) = \frac{m\sqrt{\beta\gamma}}{2\pi kT} e^{-\frac{m}{2kT}(u^2 + \beta\gamma x^2)}. \quad (7.19)$$

Klein then compared his results with that of Smoluchowski (3.1). Smoluchowski had studied only overdamped dynamics imposing an instantaneous equilibrium for the velocities. The interesting thing is that Klein not only confirmed Smoluchowski's equations and solutions but obtained general results that are applicable to different cases. Klein found that Smoluchowski's expressions were correct only by virtue of imposing a particular distribution for initial velocities:  $u_0/\beta \approx 0$ , the ratio between initial velocity and friction must be nearly zero, but Smoluchowski had not imposed this assumption explicitly in his treatment. Klein found the solutions for the three-dimensional case from the simple one-dimensional cylinder system and again confronted his results with that of Smoluchowski. The expressions of the Polish scientist turn out to be valid in general if the variation of the acting forces on a suspended particle is small over a displacement of  $\bar{u}/\beta$ . Klein's theoretical and more methodical approach to this kind of systems was necessary for the description of ionic solutions and processes like electrolysis, the precedent works being only valid for colloidal suspensions. Finding exact solutions for this kind of systems however presents, also today, insurmountable difficulties in most of the cases. So Klein introduced, qualitatively and quantitatively, the first necessary approximation needed to obtain some useful results: he considered only a single ion and the mean value of reciprocal actions of other ions by setting it constant. The mean action of other ions was in such a way considered together with the solvent's action. For ionic solutions, the description of Einstein and Smoluchowski is too simple because in this case the viscosity and its dependence on temperature are influenced also by Coulomb interactions. Klein considered ionic friction as a product of the macroscopic viscosity coefficient of the solvent multiplied by quantities dependent on the nature of the considered ion but independent from temperature. Temperature dependence remains included in the viscosity coefficient. In a similar way he rescaled the positions, time, and the concentration, and he demonstrated the validity of his expressions for solutions with different temperatures and concentrations. At the end of the paper, Klein found again the expression for the conductivity coefficient. The new expression is consistent with Bjerrum's. Bjerrum's formula was shown to be a special case of Klein's general expression. Thanks to Klein's work the study of bipolar solutions gained a formal basis. Klein's and Kramers's purely theoretical approach was necessary for a general description of solution dynamics. It allowed for the theoretical description of solution characteristics, varying the number of the solute particles, the solvent, the interaction between them, as well as external influences. This work established the general basis for the description of complex condensed phase phenomena like the deviation from the behaviour of ideal solutions, diffusion, electrolysis, and the kinetics of chemical reactions.

Solutions and ionic reactions are suitable systems of charged particles to be studied by Boltzmann's statistical methods. Before the publication of Klein's paper of 1922,

Kramers and Klein came also to the important result that the logarithm of the activity coefficient was proportional to the square root of the ionic strength. But they were unsatisfied with their formal derivation, Kramers in particular intended to obtain that result using Gibbs statistical mechanics more rigorously. However, both Klein and Kramers soon became occupied with others problems. Klein began his work on relativity and Kramers returned to atomic physics, his main research subject during his Copenhagen years.

In 1923, in a famous paper (Debye and Hückel 1923), Peter Debye and Erich Armand Arthur Joseph Hückel (1896–1980) obtained exactly the same law considered earlier by Kramers and Klein:

$$\Delta G = -\log \gamma_{\pm} = \frac{z_+ z_- A \sqrt{I}}{1 + Ba \sqrt{I}}. \quad (7.20)$$

Four years later Kramers returned to this topic and published a paper on the statistical mechanics of ionic solutions, always using Gibbsian statistics. His work was more systematic than that of Debye and Hückel. In fact, Kramers introduced corrections to their law (Kramers 1927). But the impact and importance of that result was in any case much smaller than that of the original Debye–Hückel paper.

The joint work of Kramers and Klein on the theory of strong electrolytes is a good example of what Max Dresden, one of the most famous students of Kramers and his major biographer, called the *conundrum of the near misses* (Dresden 1987, p. 446). Many times during his career Kramers was very near to conclusive theoretical conceptions but he abandoned them without publishing his main results, or he published later only minor and misunderstood papers. As Dresden noted, this was due to Kramers personality, he was very timid and consequently cautious about his results. Another reason may be Kramers impressive eclecticism that led him to shift from one subject to another in quick and rapid succession.

## 8 Kramers work in 1940

This was Kramers's first approach to solution dynamics, and, after the brief collaboration with Christiansen, he returned to the study of chemical reactions only around 1940.

The little attention that Kramers paper of 1940 (Kramers 1940) received at the time has led many physicists and historians of science to consider this work as a simple exercise of style, a curious and interesting application of advanced statistical mechanics. Notable in this sense are the words spoken by Nicholas van Kampen, the most famous of Kramers's students, during the after-dinner speech to the *50 years after Kramers* meeting in 1991 (Hanggi and Troe 1991) as reported in the excellent book of D. ter Haar (1998), another famous student and biographer of Kramers. Van Kampen suggested that although the apparent motivation of Kramers's paper was a discussion of chemical dissociation, and, possibly, nuclear fission, the real reason for this research was his fascination with the mathematical intricacies of the problem.

Van Kampen's statement may carry some truth but as we have seen in our reconstruction of the origins of the 1940 paper (Christiansen 1936), reaction kinetics and chemical dynamics were important fields of study that interested Kramers profoundly although he attended to it only irregularly. There are about six papers dedicated directly to chemistry and another 20 related to that field in his whole oeuvre of 148 publications (ter Haar 1998). In the chemistry papers, Kramers shows good knowledge of chemical problems, and the bibliographical references demonstrate that he was aware of the debates and problems inside the physical chemistry community.

The paper of 1940 presents what today we call the "Kramers problem": the dynamics of a particle moving in a bi-stable external field of force, subject to the irregular forces of a surrounding medium in thermal equilibrium. The particle, originally caught in a potential well, may escape by passing over a potential barrier. Constructing a diffusion equation for the density distribution of particles in phase space it is possible to calculate the probability and the escape rate as a function of the temperature and viscosity of the medium.

It is important to note that also today one does not know a model for Kramers's problem which is valid over the whole range of possible values for the viscosity. Approximations have to be made and, as van Kampen said: "it seems as if almost everything that can be done in that direction has been done by Kramers". Van Kampen's comments are precise and well-phrased and it is hard to say anything more significant, so I shall limit myself here to relate some of them.

The 1940 paper is, as van Kampen puts it, "a typical Kramers paper, containing many gems, but as a whole somewhat confusing. It needs a careful perusal and that may well be the reason that it was not well known for many years" (ter Haar 1998, p. 95).

Kramers considered the one dimensional motion of a particle of unit mass starting from a Langevin equation for the system:

$$\frac{dv}{dt} = -\xi v + f(t) - \frac{dV(x)}{dx}, \quad (8.1)$$

where  $V(x)$  is the potential field,  $\xi$  the friction and  $f(t)$  a time dependent stochastic force with the following statistical properties:

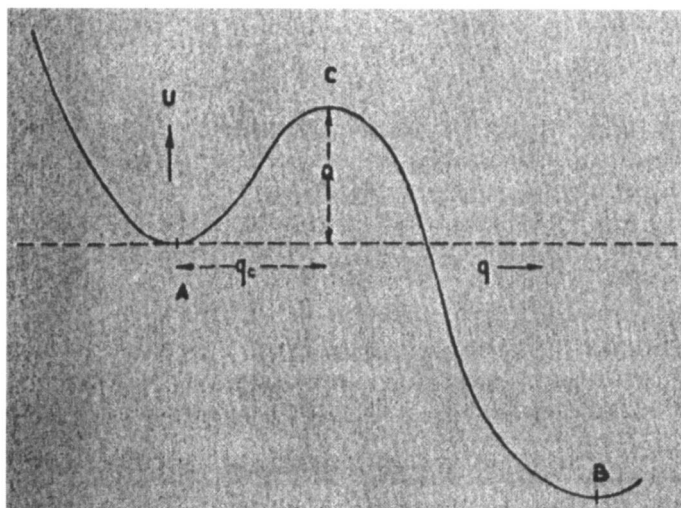
$$\langle f(t) \rangle = 0, \quad \langle f(0)f(t) \rangle = C\delta(t). \quad (8.2)$$

Kramers searched in particular for the distribution law of the particles in phase space on the basis of a given distribution of the random forces. He obtained the diffusion equation for the particle distribution from the statistical moments of the random force:

$$\frac{\partial P(x, x_0, v, v_0, t)}{\partial t} = -\Gamma P(x, x_0, v, v_0, t), \quad (8.3)$$

where the operator  $\Gamma$  is defined as:

$$\Gamma = v \frac{\partial}{\partial x} - \frac{dV(x)}{dx} \frac{\partial}{\partial v} - \xi \frac{\partial}{\partial v} \left( v + k_B T \frac{\partial}{\partial v} \right) \quad (8.4)$$



**Fig. 2** Kramers's asymmetric potential, taken from Kramers's 1940 paper (Kramers 1940)

This expression is generally known as the Kramers equation although it had been derived originally by Klein in 1922 as we have discussed above. Kramers looked for solutions of Eq. 8.4 for the cases of two different potentials, an asymmetric one with a smooth barrier (see Fig. 2) and a symmetric one with a sharp barrier. Taking up van Kampen's words, the *first gem* of the paper is the discovery that it is sufficient to investigate the stationary case, even though one is interested in a decay rate (ter Haar 1998, p. 95). This fundamental assumption, at least for a symmetric potential, was really due to Christiansen (1936), as we have seen, albeit only in a qualitative way Kramers (1940). We remark that the stationarity condition is not strictly an approximation, but rather the simplest case of a non-equilibrium state of a system. However, we can approximate the distribution near A and B, the initial and final potential well, with an equilibrium distribution if the barrier is high compared to  $k_B T$  and the diffusion will be slow.

Kramers did not succeed in finding solutions for the whole range of values of the friction coefficient, but only considered the limiting cases of large and small values of  $\xi$ . He first considered the case of large viscosity, and, in van Kampen's words, this is a *second gem*: "in the limit of large friction the equation reduces to a diffusion equation in coordinate space alone" (ter Haar 1998, p. 96). This requires the elimination of the momentum of the particle, which Kramers achieved by means of an ingenious step. Assuming a Maxwell distribution for the velocities (the fast variables with large friction) we can write directly:

$$P(x, v, t) = \sigma(x, t) e^{-\frac{v^2}{2k_B T}}, \quad (8.5)$$

where  $\sigma(x, t)$  is the distribution over spatial coordinates. The diffusion equation may then be written as:

$$\frac{\partial \sigma(x, t)}{\partial t} = \frac{k_B T}{\xi} \frac{\partial^2 \sigma(x, t)}{\partial x^2} - \frac{\partial}{\partial x} \left[ \frac{F(x)}{\xi} \sigma(x, t) \right], \quad (8.6)$$

where  $F(x)$  is the force of the field and  $D$  the diffusion coefficient. This corresponds to the well-known Smoluchowski Eq. 3.1 and is obtained from the Kramers equation of diffusion by an integration along a straight line  $x + v/\xi = x_1 = \text{const}$ . One can see the similarities with Klein's discussion. The solution for the flux  $w$  in the stationary case is:

$$w = -\frac{k_B T}{\xi} e^{-\frac{V(x)}{k_B T}} \frac{\partial}{\partial x} \left( \sigma(x, t) \cdot e^{\frac{V(x)}{k_B T}} \right). \quad (8.7)$$

One can now ask the question: what is the mean first passage time, or the probability of escape from A to B?

We now have van Kampen's *third gem*: "having obtained the one-dimensional diffusion equation Kramers found the mean first passage time by deriving a formula for it, which is today common knowledge, although it is occasionally rediscovered (ter Haar 1998, p. 97)".

The escape probability  $r$  turns out to be:

$$r = w/n_a,$$

where  $n_a$  is the number of particles near A. This method to obtain the rate  $r$  is today known as the flux over population method. Kramers estimated  $r$  also in another way which van Kampen takes to be the *fourth gem*: "He decomposed the range of the coordinate into one region around the top of the potential region, and another region covering the potential well. This has now become a standard trick of singular perturbation theory. It enables one to apply different expansions in both regions, provided one can fit them smoothly together so as to get an approximation that covers the whole range (ter Haar 1998, p. 97)". Assuming that the potential well near A can be approximated as a harmonic potential:  $V(x_A) = \frac{1}{2}(2\pi\omega)^2 x^2$ , and that the potential near the top of the barrier of height  $Q$  at position C can similarly approximated by a quadratic potential:

$$V(x_C) = Q - \frac{1}{2}(2\pi\omega')^2 (x - x_C)^2. \quad (8.8)$$

Kramers finds, in the case of the asymmetrical potential:

$$r \approx \frac{2\pi\omega\omega'}{\eta} e^{-\frac{Q}{k_B T}}, \quad (8.9)$$

where  $\eta$  is the viscosity. For the symmetric potential, he obtained:

$$r \approx \frac{2\pi\omega^2}{\eta} \sqrt{\frac{\pi Q}{k_B T}} e^{-\frac{Q}{k_B T}}. \quad (8.10)$$

In stationary conditions, by approximating a bi-stable asymmetric potential near the barrier with the preceding expression (8.8) for  $V(x_C)$ , it is possible to solve Kramers diffusion equation exactly near the potential well for all values of viscosity. Van Kampen talks of the *fifth real gem*: “the very ingenious construction of a solution in the barrier region. It is true that this is only a special solution, but it is precisely the one he needs: no incident particles from infinity, and thermal equilibrium on the side of the well. Hence it can be attached smoothly to the equilibrium distribution inside the well (ter Haar 1998, p. 98)”.

In the case of medium–small viscosities ( $\eta \gg \omega'$ ) we get:

$$r \approx \omega \cdot e^{-\frac{Q}{k_B T}} = r_{TR}, \quad (8.11)$$

a result that is independent of viscosity. This is the transition state theory (TST) value of Henry Eyring (1935) and Michael Polanyi (Evans and Polanyi 1935), who did not consider the role of the. It may seem impressive to see that the results of TST, based on quantum mechanics (Polanyi and Eyring 1931a), come out as a particular case of Kramers’ pure classical method. But there are precise limitations to the use of Kramers’s method as we will see in the conclusions.

Then Kramers examined the case of very small viscosity that also gave results different from the TST value. TST assumes a perfect thermodynamic equilibrium between reactants, (particles in A in our case), and products (particles in B). However, van Kampen notes: “Kramers also realised that for very small friction the fluctuations might not be able to maintain the equilibrium in the well; rather the leakage across the barrier would deplete the high energy tail of the distribution. For this case he introduced the *sixth gem*. In the limit of low friction the particle in the well oscillates roughly with a constant energy. It is therefore possible to average out the phase. This leads to a one-dimensional diffusion equation in the energy scale, from which it is easy to compute the average time needed to reach the energy of the top of the barrier”.

Kramers introduced the action  $I(E)$  instead of the energy, which represents the area in phase space within a curve of constant energy:

$$I(E) = \oint v dx. \quad (8.12)$$

He thus found a diffusion equation for the ensemble density:

$$\frac{\partial \varepsilon}{\partial t} = \eta \frac{\partial}{\partial I} \left( I \varepsilon + k_B T I \frac{\partial \varepsilon}{\partial E} \right). \quad (8.13)$$

The motion of the particles in the potential wells will be oscillatory, with a period of oscillation  $\omega$ , which satisfies the equation:

$$\omega = \frac{\partial E}{\partial I}. \quad (8.14)$$

In the stationary state, the solution of the ensemble density diffusion equation is:

$$w = -\eta k_{\text{B}} T l e^{-\frac{E}{k_{\text{B}} T}} \frac{\partial}{\partial E} \left( \varepsilon e^{\frac{E}{k_{\text{B}} T}} \right). \quad (8.15)$$

In the small viscosity case, the escape probability results as:

$$r \approx \eta \frac{Q}{T} e^{-\frac{Q}{k_{\text{B}} T}}. \quad (8.16)$$

Thus Kramers found solutions and the rate of the process for a great part of viscosity range: very small, small, and large. The intermediate region that would join the different regimes was not considered by Kramers because it is difficult to find useful approximation schemes. This problem remains a complex question, and even today no definite solution for the whole viscosity range is known, although the Russian physicists Sergey V. Meshkov and mainly Vladimir Ivanovich Mel'nikov found a description for the intermediate range in 1990 (Melnikov and Meshkov 1986).

## 9 Conclusions

The second section of this paper may appear as yet another discussion of Einstein well-known *annus mirabilis* paper, but it was included here to present again Einstein's work in the context of the application of stochastic methodologies to chemical kinetics, which has not received much consideration by historians of science until now. A similar observation holds for the third section about Smoluchowski's lesser known work, but again one may consider his work as the first quantitative description of diffusion-controlled reactions and therefore as a basis for a different way of seeing chemical processes.

Christiansen's work of the years 1935–36 is largely misunderstood, known only for his research on chain reactions, and also in this field its significance is obscured by the Nobel Laureates Semenov and Hinshelwood. Christiansen left the description of chemical reaction as diffusion processes largely incomplete and only on a qualitative basis. But he made the right conjectures and introduced the necessary conditions for the formal approach that Kramers would develop in 1940.

All of van Kampen's gems make a precious jewel for chemistry: a very basic model for the description of reactions in condensed phase. It is very important because the major deficiency of TST is that it treats the reactive event by considering only the interactions between single molecules of the reactant and not with the medium. The interaction with the medium may be included only via phenomenological factors. To get an exact description of condensed phase reactions by TST one needs a quantum mechanical description of all molecules of the solvent involved in addition to the molecules directly involved in the reaction. This in turn results in an impractical complexity of the quantum mechanical description.

Furthermore TST, imposing an equilibrium condition, treats a dynamical event as a static one. The reaction, from a microscopic point of view, is considered as a "big" molecule that comprises, configuration states, reactants, activated complex and

products. It is not a dynamical description of the process and this is another flaw of TST. In fact, the equilibrium condition, although useful, is the most questionable assumption of TST. Kramers, on the other hand, made a better assumption: the stationarity condition. This is a more reasonable assumption because it is dynamical and it represents the simplest case of a non-equilibrium process, as a chemical reaction is when it takes place. As Max Dresden (1988) pointed out, Kramers was more familiar with non-equilibrium statistical mechanics and its subtleties than most other physicists. In classes, lectures, seminars and discussions, he pointed out the difficulties and also the inconsistencies that were present in many traditional treatments of the subject (Melnikov and Meshkov 1986). A possible link between Kramers and Eyring could have been the theory of plasticity that Eyring elaborated around 1955: Eyring used analogous premises to that of stochastic diffusion methods but did not generalize it, applying instead a modified application of transition state theory (Bak 1974).

But, as we have seen, Christiansen had resumed his studies on kinetics before Kramers, in the first half of the thirties and published two papers in 1935 (Christiansen 1935) and 1936 (Christiansen 1936). The paper of 1936 is of great importance because Christiansen introduced the basis of a purely diffusion treatment of chemical reaction in the condensed phase. Christiansen's description is formally weak and not so rigorous but he without doubt took the right way of the stationary state from a qualitative and intuitive point of view.

The role of Christiansen is largely misunderstood even for scientists working on thermodynamics and stochastic or diffusion processes; so it is not surprising that his work is barely known by the majority of the scientific community. This fact may be observed at various stages, from scientific popularization to scholarly studies. It is not so surprising, on the side of popular science, that these concepts are not known. They treat profound questions that are not simply accessible to people outside the scientific community because of their theoretical and formal complexity. Inside the scientific community those concepts are obviously more known but only few specialized researchers are deeply concerned directly with them. They are revolutionary as much as relativity and quantum mechanics although less spectacular and evident.

The general difficulties about statistical mechanics are, however, not sufficient to comprehend completely the scant and delayed interest in the Christiansen–Kramers approach to activated processes. The problems of TST would lead one to think that the diffusive model is better, also because the TST expression results as a particular case of Kramers's treatment. So why has this approach not been considered for nearly thirty years and why is it even today underestimated? The causes are manifold, for historical and methodological reasons.

Christiansen, timidly, tried to popularize his approach, as we can see from his own words spoken at the 67th general discussion of the Faraday Society in 1938 (Guggenheim and Weiss 1938), titled *Reaction Kinetics*, during the debate of the lecture of Edward Armand Guggenheim (1901–1970) and J. Weiss.

As to whether it is permissible to assume, in the neighbourhood of the critical state, anything like an equilibrium state density of representative points, I have sought to show that it is at least natural to consider a chemical reaction as an intramolecular diffusion process. According to this picture the velocity of reaction must be identified with the intensity of flow of representative points at that part of the reaction path which



correspond to maximum potential energy. If we set out the differential equation for the diffusion process and, as a first approximation, solve it for the case of a stationary flow, we find that the density of points at the place of maximum potential is exactly half of the equilibrium value calculated from the number of systems in the original state, if we assume that, in the final state the reacting molecules are practically not existent (p. 73).

Christiansen received no response. Although he inherited the chair of Johannes Nicolaus Brønsted (1879–1947) of physical chemistry in Copenhagen, he remained a relatively isolated scientific figure and did not write many papers. He gained some influence only in his own country, Denmark (Bak 1974).

Kramers's paper of 1940 (Kramers 1940), on the other hand, seems to have come out of nowhere. He worked directly on chemical kinetics only once before with Christiansen in 1923 (Christiansen and Kramers 1923). We can assume that Kramers kept a particular interest in this theme and stayed in contact with Christiansen but only in private. Kramers's studies on this subject are eclipsed by his more relevant contributions to quantum mechanics.

The great success of TST in a similar way eclipsed Christiansen's approach in the chemical ambit. This approach is purely classic and was born in a period in which the attention of scientific community was catalyzed by the first developments and the formalization of quantum mechanics. During and after the second world war these studies were almost totally forgotten, with the notable exception of Chandrashekhar's review of 1943 (Chandrashekhar 1943). That work is the only one explicitly cited by Eyring and collaborators for example and only for very specific cases of diffusion controlled reactions and processes in the condensed phase (Eyring et al 1980; Eyring and Eyring 1963; Laidler 1997; Eyring 1975).

Methodologically, even if the diffusive stochastic approach has some theoretical advantages, it is more difficult to adapt and apply to the description of chemical reactions than TST. It requires notable mathematical knowledges and physical concepts that are not so familiar in chemistry. TST on the other hand, relying on the powerful means of quantum mechanics, produces more predictive results, although one has to apply phenomenological coefficients in some cases and make some arbitrary assumptions.

Mathematically, the stochastic operators have the same structure as Hamiltonian operators, so one could think of applying the same approximation techniques that have brought about the extraordinary progress of quantum mechanics. Unfortunately, this is not possible because there are no analytical solutions for a complex phenomenology such as the temporal evolution of a distribution of particles interacting with the medium, neither for the simplest cases (excluding the phenomenology with no potential present). On the contrary, in quantum mechanics there is a simple phenomenology described analytically: the motion of an electron around a nucleus or the hydrogen atom. This is mainly the reason why stochastic methods were rediscovered during the sixties in chemistry and in physics. The introduction and the first developments of computer science have allowed one to fill partially the gap of the deficiency of a fundamental analytical solution by means of computational methods. In this way, the Christiansen–Kramers theories have found today a new strength and are applied in various chemical problems, as we can see looking at the titles of the papers of a

congress dedicated to Kramers in 1990 Hanggi and Troe (1991). In particular, today the Christiansen–Kramers approach and the Eyring–Polanyi mainstream theory are treated together Berglung and Gents (2008). This is fortunate because the diffusion approach could also have been forgotten.

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