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BROWNIAN MOTION IN A FIELD OF FORCE AND THE DIFFUSION MODEL OF CHEMICAL REACTIONS

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Summary

A particle which is caught in a potential hole and which, through the shuttling action of Brownian motion, can escape over a potential barrier yields a suitable model for elucidating the applicability of the transition state method for calculating the rate of chemical reactions.

§ 1. *Introduction.* In order to elucidate some points in the theory of the velocity of chemical reactions, the following problem is studied. A particle moves in an external field of force, but — in addition to this — is subject to the irregular forces of a surrounding medium in temperature equilibrium (Brownian motion). The conditions are such, that the particle is originally caught in a potential hole but may escape in the course of time by passing over a potential barrier. We want to calculate the probability of escape in its dependency on temperature and viscosity of the medium and to compare the values found with the results of the so-called „transition-state-method" for determining reaction-velocities. The calculation rests on the construction and discussion of the equation of diffusion obeyed by a density-distribution of particles in phase space.

For the sake of simplicity only a one-dimensional model is studied. Definite results could be obtained in the limiting cases of small and large viscosity; in both cases there exists a close analogy with Christiansen's treatment of chemical reactions as a diffusion problem. In the fairly general case where the potential barrier corresponds to a smooth maximum a reliable solution for any value of the viscosity is obtained. In that case the probability for escape is, for a large range of the value of the viscosity, practically equal to that computed by the transition method.

Our problem has also a direct bearing on the fission of an electrically charged hot drop of liquid, a question which was recently considered by B o h r and Wh e e l e r in their discussion of the fission of uranium nuclei.

In § 2 the principles of Brownian motion are briefly discussed, and applied in order tot set up an equation of diffusion in phase space.

In § 3 and § 4 the limiting cases of large and small viscosity are studied; they reduce both to a one-dimensional diffusion process.

In § 5 the formulae found are applied to calculate the escape over a potential barrier. The results are compared with the transition method.

§ 6 discusses the relation of our model to actual problems of reaction velocity.

§ 2. *Principles of Brownian motion in phase-space.* The equations of motion of a particle of mass 1 in a one-dimensional extension, where it is acted upon by the external field of force $K(q)$ and the irregular force $X(t)$ due to the medium, can be written as follows:

$$\dot{p} = K(q) + X(t), \qquad \dot{q} = p. \tag{1}$$

A theory of Brownian motion on the E i n s t e i n pattern can be set up if there exists a range of time intervals τ which has the following properties: On the one hand τ must be so short, that the change of velocity suffered in the course of τ may be considered as very small; on the other hand τ must be so large, that the chance for X to take a given value at the time $t + \tau$ is independent of the value which X possessed at the time t. We then consider the probability distribution of the quantity

$$B_\tau = \int_t^{t+\tau} X(t')\, dt' \tag{2}$$

which is assumed to be independent of t. Calling the distribution function $\varphi_\tau(B; p, q)$ — besides on τ and on temperature it may depend on the velocity p and the position q of the particle — it is further assumed that the moments

$$\overline{B_\tau^n} = \int_{-\infty}^{+\infty} B^n\, \varphi\, dB, \qquad (\overline{B_\tau^0} = 1) \tag{3}$$

depend on τ in such a way that, practically, they can be represented by the first non-vanishing term of a development $a\tau + b\tau^2 + \ldots$. The possibility of a term proportional to τ in the expression for $\overline{B_\tau^n}(n > 1)$ is clearly due to the fact that the values which X takes at moments $t_1, t_2 \ldots t_n$ which lie sufficiently close together are no longer independent; in fact $\overline{B_\tau^n}$ is represented by a volume integral $\int \ldots \int X(t_1)\ X(t_2) \ldots X(t_n)\ dt_1 \ldots dt_n$ over an n-dimensional cube; the contribution to this integral due to a narrow cylinder extending along the diagonal $t_1 = t_2 = \ldots = t_n$ may give a term proportional to τ.

Einstein's original theory can be expressed by the assertions

$$\overline{B_\tau} = -\eta\, p\, \tau$$
$$\overline{B_\tau^2} = \nu\, \tau + \ldots \tag{4}$$
$$\overline{B_\tau^n} = 0\,.\,\tau + \ldots \quad (n > 2)$$

where the „viscosity" η and the constant ν may still depend on temperature and position. Between η and ν the relation

$$\nu = 2\eta T \tag{5}$$

must hold, where T is the absolute temperature (defined in such a way that Boltzmann's constant equals 1); this is most easily seen by remarking that the Brownian motion does not disturb the equipartition of kinetic energy (Langevin). Expressing this fact, by

$$\overline{p(t+\tau)^2} = \overline{p(t)^2}$$

we get immediately from

$$p(t+\tau) = p(t) + B,$$
$$\overline{2p(t)B} + \overline{B^2} = 0 \rightarrow -2\overline{p^2}\eta + \nu = 0 \rightarrow -2T\eta + \nu = 0.$$

From this proof we see too, that $\overline{B_\tau}$ never can vanish. We will see presently, however, that (4) represents by no means the only possible dependence of $\overline{B_\tau}/\tau$ and $\overline{B_\tau^2}/\tau$ on p, and also that there is no a priori reason why the higher moments of B_τ should contain no term linear in τ.

Writing generally

$$\overline{B_\tau^n} = \mu_n\, \tau, \tag{6}$$

we will now derive the equation of diffusion for an ensemble of particles with density $\rho(p, q)$ in p, q-space. The density at a point $A(p_1, q_1)$ at time $t + \tau$ may be thought of as being derived from the densities at a previous moment t along the straight line for which $q = q_2 = q_1 - p_1\tau$. Denoting by $p_2 = p_1 - K\tau$ the value which p would have taken at the time t if no Brownian forces had acted, we may write

$$\rho(p_1, q_1, t+\tau) = \rho(p_2 + K\tau, q_2 + p_2\tau, t+\tau) =$$

$$= \int_{-\infty}^{+\infty} \rho(p_2 - B, q_2)\, \varphi(B; p_2 - B, q_2)\, dB.$$

Developing with respect to the first power of τ and to the first and higher powers of B (as far as it appears in $p_2 - B$) we get

$$\rho(p_2, q_2) + \frac{\partial\rho}{\partial t}\tau + \frac{\partial\rho}{\partial p} K\tau + \frac{\partial\rho}{\partial q} p\tau =$$

$$= \int_{-\infty}^{+\infty} \left(\rho\varphi - B\frac{\partial}{\partial p}(\rho\varphi) + \frac{B^2}{2}\frac{\partial^2}{\partial p^2}(\rho\varphi) - \ldots\right) dB.$$

Using (6) we obtain the following equation of the Fokker-Planck type:

$$\frac{\partial\rho}{\partial t} = -K(q)\frac{\partial\rho}{\partial p} - p\frac{\partial\rho}{\partial q} - \frac{\partial}{\partial p}(\mu_1\rho) + \frac{1}{2}\frac{\partial^2}{\partial p^2}(\mu_2\rho) - \ldots \quad (7)$$

This is the well known Gibbs equation completed with terms, due to the Brownian motion. The current density has a q-component equal to $p\rho$ and a p-component equal to

$$K\rho + \mu_1\rho - \frac{1}{2}\frac{\partial}{\partial p}(\mu_2\rho) \ldots$$

The fundamental condition to be imposed on the μ's states that the Boltzmann-distribution

$$\rho_B = e^{-(\frac{1}{2}p^2 + U(q))/T}, \quad K = -\frac{\partial U}{\partial q} \quad (8)$$

should be stationary. This gives

$$\frac{\partial}{\partial p}\left\{-\mu_1 e^{-p^2/2T} + \frac{1}{2}\frac{\partial}{\partial p}(\mu_2 e^{-p^2/2T}) - \frac{1}{6}\frac{\partial^2}{\partial p^2}(\mu_3 e^{-p^2/2T}) \ldots\right\} = 0$$

$$-\mu_1 - \frac{p}{2T}\mu_2 + \frac{1}{2}\frac{\partial\mu_2}{\partial p} - \ldots = F(q, T)\, e^{p^2/2T}.$$

nuclear matter. The transition method in this case is therefore justified if the friction is not very small, nor so large that the drop vibrations are overaperiodically damped to a high degree. Of course, at the present state of our knowledge, a marked error in Bohr and Wheeler's estimate would only be due to the friction being abnormally small or abnormally large. Still it is not uninteresting to consider the question of the coefficient of viscosity of nuclear matter somewhat more closely. Even if a nucleus in its normal state behaved as a perfectly hard, non plastic crystal, there is no reason to exclude the possibility that the excited nucleus possesses a finite coefficient of internal friction. In view of the surprising properties of He II it is even dangerous to assert that this coefficient cannot be extremely small; this assumption would not necessarily contradict Bohr's asssumption that a single neutron impinging on a nucleus is in first instance captured. This assumption is, however, not well reconcilable with the idea that nuclear matter should behave as a perfectly hard crystal, i.e. a certain amount of plasticity is anyhow to be expected.

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REFERENCES

1) G. Uhlenbeck and L. S. Ornstein, Phys. Rev. **36**, 823, 1930.
2) J. A. Christiansen, Z. Phys. Chem. *B* **33**, 145, 1936.
3) H. Pelzer and E. Wigner, Z. Phys. Chem. *B* **15**, 445, 1932.
H. Eyring, J. chem. Phys. **3**, 107, 1935.
M. C. Evans and M. Polanyi, Trans. Far. Soc. **31**, 875, 1935.
4) J. A. Christiansen and H. A. Kramers, Z. Phys. Chem. **104**, 451, 1923.
5) In Trans. Faraday Soc. **34**, 3—81, 1938 a general discussion on reaction kinetics is given, in which the question of the transition state method is frequently touched upon. For quantum-mechanical effects compare J. O. Hirschfelder and E. Wigner, Journ. chem. Phys. **7**, 616, 1939.
6) H. A. Lorentz, Les théories statistiques en thermodynamique, p. 47. Teubner, 1912.
7) Compare L. S. Kassel, The kinetics of homogeneous gas reactions, Ch. V.
8) N. Bohr and J. A. Wheeler, Phys. Rev. **56**, 426, 1939.