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 B r o w n i a n 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 C h r i s t i a n s e n'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 momenta

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

$\overline{B_\tau^n} \, | \, p, q \, |$

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

$$\overline{B_\tau} = -\eta\, p\, \tau$$

$$\overline{B_\tau^2} = \nu\, \tau + \ldots \tag{4}$$

$$\overline{B_\tau^n} = 0 \cdot \tau + \ldots \quad (n > 2)$$

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

$$p(t+\tau) = p(t) + B,$$

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

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

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

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

Using (6) we obtain the following equation of the F o k k e r-P l a n c k type:

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

This is the well known G i b b s equation completed with terms, due to the B r o w n i a n motion. The current density has a q-component equal to $p\rho$ and a p-component equal to

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

The fundamental condition to be imposed on the μ's states that the B o l t z m a n n-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

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

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

From physical considerations we expect that μ_1, μ_3 .... are odd functions of p whereas μ_2, μ_4 .... are even, so that F should be zero. The simplest possibility is E i n s t e i n's case:

$$\mu_1 = -\eta p, \quad \mu_2 = 2\eta T, \quad \mu_3 = \mu_4 = ... = 0.$$

Other laws of friction should also be possible, however; for instance

$$\mu_1 = -\eta p - \zeta p^3, \quad \mu_2 = (2\eta T + 4\zeta T^2) + 2\zeta T p^2, \quad \mu_3 = \mu_4 = ... = 0.$$

An example of a case where μ_3 does not vanish would be

$$\mu_1 = -\eta p - \zeta p^3, \quad \mu_2 = 2\eta T + 6\zeta T^2, \quad \mu_3 = 6\zeta T^2 p, \quad \mu_4 = ... = 0.$$

I do not know if the more complicated cases might have some physical application. In the following we will restrict ourselves to the simple E i n s t e i n case, where the diffusion equation takes the form (η is taken independent of q)

$$\frac{\partial \rho}{\partial t} = -K(q)\frac{\partial \rho}{\partial p} - p\frac{\partial \rho}{\partial q} + \eta\frac{\partial}{\partial p}\left(p\rho + T\frac{\partial \rho}{\partial p}\right). \qquad (9)$$

For previous work on the B r o w n i a n motion, the reader is referred to U h l e n b e c k and O r n s t e i n's article of 1930 [1]), in which also diffusion equations of the F o k k e r-P l a n c k type are discussed (although not in phase space) and in which references to the earlier work are to be found. I have found no discussion of the possibility that μ_3, μ_4 .... should not be negligible.

§ 3. *The case of large viscosity.* Large viscosity means, that the effect of the B r o w n i a n forces on the velocity of the particle is much larger than that of the external force $K(q)$. Assuming that K does not change very much over a distance $\sqrt{T/\eta}$, we expect that, starting from an arbitrary initial ρ distribution, a M a x w e l l velocity distribution will be established very soon (i.e. after a time lapse of the order $1/\eta$) for every value of q:

$$\rho(q, p, t) \leqq \sigma(q, t)\, e^{-p^2/2T}. \qquad (10)$$

From that time on a slow diffusion of the density distribution σ in the q-coordinate will take place, which may be expected to satisfy the S m o l u c h o w s k i diffusion equation

$$\frac{\partial \sigma}{\partial t} = -\frac{\partial}{\partial q}\left(\frac{K}{\eta}\sigma - \frac{T}{\eta}\frac{\partial \sigma}{\partial q}\right) \qquad (11)$$

where T/η represents the diffusion constant. As long as no perfect temperature equilibrium is attained, (10) holds only approximately. This is even the case when the external force is zero. In that case it is true enough that the velocities, which a particle takes in the course of time, are exactly distributed in the M a x w e l l way; the velocity distribution of the particles at a given point q deviates, however, from M a x w e l l , since otherwise there would be no diffusion current $(= \int \rho \, p \, dp)$.

In order to derive (11) from (9), we rewrite (9) in the following form:

$$\frac{\partial \rho}{\partial t} = \eta \left(\frac{\partial}{\partial p} - \frac{1}{\eta} \frac{\partial}{\partial q} \right) \left(p\rho + T \frac{\partial \rho}{\partial p} - \frac{K}{\eta} \rho + \frac{T}{\eta} \frac{\partial \rho}{\partial q} \right) -$$

$$- \frac{\partial}{\partial q} \left(\frac{K}{\eta} \rho - \frac{T}{\eta} \frac{\partial \rho}{\partial q} \right).$$

We now integrate the right and left side of this equation along a straight line $q + p/\eta = \text{const.} = q_0$ from $p = -\infty$ to $+\infty$. Denoting the integral of ρ along this line by $\sigma(q_0)$, we obtain:

$$\frac{\partial \sigma}{\partial t} = - \int_{q+p/\eta=q_0} \frac{\partial}{\partial q} \left(\frac{K}{\eta} \rho - \frac{T}{\eta} \frac{\partial \rho}{\partial q} \right) dp \cong - \frac{\partial}{\partial q_0} \left(\frac{K(q_0)}{\eta} \sigma(q_0) - \frac{T}{\eta} \frac{\partial \sigma(q_0)}{\partial q_0} \right).$$

The approximate validity of this equation is a consequence of the approximate validity of (10), if it is also allowed to assume that in the region of p-values which contributes essentially to the value of the integral, (i.e. for $|p| \gtrsim \sqrt{T}$) the variation of q (which is of the order $\sqrt{T}/\eta$) is small compared to q-distances over which K and σ (and η) undergo marked variations. These are, however, precisely the conditions which a priori have to be imposed in order to ensure the applicability of (11).

A stationary diffusion current obeys the law

$$w = \frac{K}{\eta} \sigma - \frac{T}{\eta} \frac{\partial \sigma}{\partial q} = \text{const.} \tag{12}$$

Since it can also be written in the form

$$w = - \frac{T}{\eta} e^{-U/T} \frac{\partial}{\partial q} \left(\sigma \, e^{U/T} \right)$$

we obtain, on integration between two points A and B on the q-co-

ordinate:

$$w = \frac{T \mid \sigma \, e^{U/T} \mid_B^A}{\int\limits_A^B \eta \, e^{U/T} \, dq} . \tag{13}$$

This result will enable us to derive in § 5 an expression for the escape of a particle from a potential hole over a potential barrier.

§ 4. *The case of small viscosity.* We will restrict ourselves to the case where the particle would perform a motion of oscillatory type if no B r o w n i a n forces were present. By small viscosity is meant that the latter forces cause only a small variation of the energy during the time of an oscillation. The effect of the B r o w n i a n motion will therefore, in its main aspect, consist in the gradual change of the distribution of the ensemble over the different energy-values. Denoting by I the area inside a curve of constant energy:

$$I(E) = \oint p \, dq$$

and denoting by $\bar{\rho} dI$ the fraction of the ensemble lying inside the ring-shaped area dI, we find an equation for $\bar{\rho}(E, t)$ by averaging (9) over such a ring dI. The first two members on the right-hand side of (9) give zero, since in the absence of B r o w n i a n forces the distribution in energy is maintained. As regards the third member, we may write, on account of $\partial E/\partial p = p$,

$$\overline{\frac{\partial}{\partial p} \left(p\rho + T \frac{\partial \rho}{\partial p} \right)} = \overline{\frac{\partial}{\partial p} \left(p\bar{\rho} + T \frac{\partial E}{\partial p} \cdot \frac{\partial \bar{\rho}}{\partial E} \right)}$$

$$= \bar{\rho} + T \frac{\partial \bar{\rho}}{\partial E} + \overline{p^2} \frac{\partial}{\partial E} \left(\bar{\rho} + T \frac{\partial \bar{\rho}}{\partial E} \right).$$

The mean value $\overline{p^2}$ is equal to the action-integral over one period (i.e. I) divided by the period of oscillation. Denoting the frequency by ω:

$$\omega = \frac{dE}{dI} ,$$

we have therefore $\overline{p^2} = I\omega$, and the diffusion equation takes the form:

$$\frac{\partial \bar{\rho}}{\partial t} = \eta \left(1 + \omega I \frac{\partial}{\partial E} \right) \left(\bar{\rho} + T \frac{\partial \bar{\rho}}{\partial E} \right) = \eta \left(1 + I \frac{\partial}{\partial I} \right) \left(\bar{\rho} + T \frac{\partial \bar{\rho}}{\partial E} \right)$$

or, writing ρ for $\bar{\rho}$:

$$\frac{\partial \rho}{\partial t} = \eta \frac{\partial}{\partial I} \left(I\rho + TI \frac{\partial \rho}{\partial E} \right). \tag{14}$$

This corresponds to a diffusion along the I- (or E-)coördinate; the diffusion-term proper is given by

$$\eta \frac{\partial}{\partial I} \left(TI \frac{\partial \rho}{\partial E} \right) = \eta \frac{\partial}{\partial I} \left(T \frac{I}{\omega} \frac{\partial \rho}{\partial I} \right)$$

and corresponds to a diffusion coefficient $\eta T I/\omega$.

A stationary state of diffusion with current density w corresponds to

$$w = - \eta \left(I\rho + TI \frac{\partial \rho}{\partial E} \right) = - \eta T I e^{-E/T} \frac{\partial}{\partial E} (\rho \, e^{E/T}).$$

Integration between two points A and B along the $E(I)$ coördinate gives

$$w = \frac{\eta T \mid \rho \, e^{E/T} \mid_B^A}{\int_A^B \frac{1}{I} e^{E/T} \, dE}. \tag{15}$$
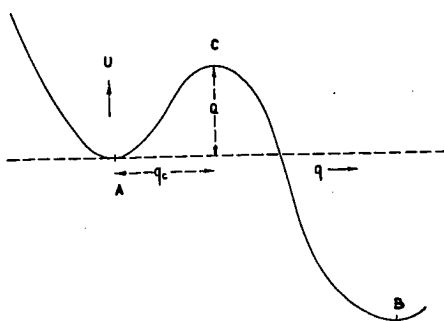

Fig. 1. Potential field with smooth barrier.

§ 5. *Escape over a potential barrier.* Let the potential function U be of the type illustrated in Fig. 1. The particle is originally caught at A. The height Q of the potential-barrier is supposed to be large compared with T. The discussion of the escape from A over C to B follows closely the line of thought in C h r i s t i a n s e n's treatment of chemical reaction as a diffusion problem [2] *). Our ensemble

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in phase-space is thought of as illustrating the phases of a great number of similar particles each in its own field U. Our treatment corresponds obviously to the assumption that quantum-theory effects are negligible.

At A the particle can be in a bound state. In the figure, B corresponds to another state of binding but of lower energy. If our system of particles were in thermodynamical equilibrium, the ensemble-density would be proportional to $e^{-E/T}$ and the net number of particles passing from A to B would vanish. If, however, to start with, the number of particles bound at A is larger than would correspond to thermal equilibrium with the number at B, a diffusion process will be started, tending to establish equilibrium. This process will be slow if, as we have already assumed, the potential barrier Q is large compared with T. We may therefore expect that — at any moment — it can be compared with a stationary diffusion process. Even if, to start with, the particles in the hole A should not yet be B o l t z m a n n-like distributed, a B o l t z m a n n distribution near A (and also near B) will have been established a long time before an appreciable number of particles have escaped; our quasi-stationary diffusion will thus correspond to a flow from a quasi-infinite supply of B o l t z m a n n-distributed particles at A to the region B.

I have not been able to solve exactly the problem of this quasi-stationary diffusion in p, q-space for arbitrary values of the viscosity η. In the limiting cases of large and small η, however, it reduces to a one-dimensional problem.

L a r g e   v i s c o s i t y. Assuming a quasi-stationary state, in which practically no particle has yet arrived at B, whereas near A thermal equilibrium has practically been established, application of (13) gives

$$w = \frac{T}{\eta}\, \sigma_A \left\{ \int_A^B e^{U/T}\, dq \right\}^{-1}, \quad \sigma_A = (\sigma\, e^{U/T})_{near\ A}.$$

The number n_A of particles near A can be calculated, if we assume that U near A can be represented by $\frac{1}{2}(2\pi\omega)^2 q^2$ (harmonic oscillator of frequency ω):

$$n_A = \int_{-\infty}^{+\infty} \sigma_A\, e^{-(2\pi\omega)^2 q^2/2T}\, dq = \frac{\sigma_A}{\omega}\sqrt{\frac{T}{2\pi}}.$$

The reaction velocity $r = w/n_A$ denotes the chance in unit time that a particle which originally was caught at A escapes to B. It is given by

$$r = \frac{w}{n_A} = \frac{\omega}{\eta} \sqrt{2\pi T} \left\{ \int_A^B e^{U/T} dq \right\}^{-1}.$$

The main contribution to the integral is due to a small region near C. Assuming, as would correspond to the drawing of U in Fig. 1, that there is no sudden jump in the curvature, we may write

$$U_{near\ C} = Q - \tfrac{1}{2}(2\pi\omega')^2 (q - q_C)^2 \tag{16}$$

$$\int_A^B e^{U/T} dq \cong e^{Q/T} \int_{-\infty}^{+\infty} e^{-(2\pi\omega')^2(q-q_C)^2/2T} dq = \frac{1}{\omega'} \sqrt{\frac{T}{2\pi}} e^{Q/T}$$

and for the reaction velocity we find:

$$r \cong \frac{2\pi\omega\omega'}{\eta} e^{-Q/T}. \tag{17}$$
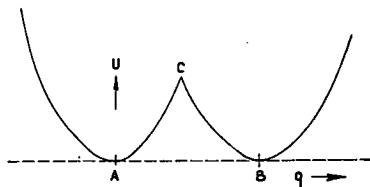

Fig. 2. Potential field with edge shaped barrier.

As an example of an another behaviour of $U(q)$ near C, let us consider the case where U between A and C can be exactly represented by $U = \tfrac{1}{2}(2\pi\omega)^2 q^2$, and that the curve CB is obtained by reflection of AC with respect to C (compare Fig. 2). We now find

$$\int_A^B e^{U/T} dq \cong 2 e^{Q/T} \int_0^\infty e^{-(2\pi\omega)^2 q_C(q-q_C)/T} d(q - q_C) =$$

$$= \frac{2T}{(2\pi\omega)^2 q_C} e^{Q/T} = \frac{2T}{2\pi\omega \sqrt{2Q}} e^{Q/T}$$

$$r \cong \frac{2\pi\omega^2}{\eta} \sqrt{\pi} \sqrt{\frac{Q}{T}} e^{-Q/T}.$$

The fact, that the drop of the value of $\sigma e^{U/T}$ from σ_A to zero occurs in a small q region near C (at C itself $\sigma e^{U/T}$ practically equals $^1/_2$)

means that the resistance against escape is practically localized in
this region. Assuming again the validity of (16) in this region, the
corresponding diffusion process in phase space can even be described
exactly for any value of η. In fact, considering the situation as sta-
tionary, the equation (9) now assume the form

$$0 = - (2\pi\omega')^2 \, q' \, \frac{\partial \rho}{\partial p} - p \, \frac{\partial \rho}{\partial q'} + \eta \, \frac{\partial}{\partial p} \left(p\rho + T \, \frac{\partial \rho}{\partial p} \right)$$

where, for simplicity, we have written q' instead of $q - q_c$. With the
substitution

$$\rho = \zeta \, e^{-(p^2 - (2\pi\omega')^2 q'^2)/2T}$$

we get

$$0 = - (2\pi\omega')^2 \, q' \, \frac{\partial \zeta}{\partial p} - p \, \frac{\partial \zeta}{\partial q'} - \eta p \, \frac{\partial \zeta}{\partial p} + \eta T \, \frac{\partial^2 \zeta}{\partial p^2} . \qquad (18)$$

The solution $\zeta = $ const. corresponds to thermal equilibrium. The
equation (18) admits also a solution where ζ is a function of a
linear combination u of p and q'

$$\zeta = \zeta(u), \qquad u = p - aq' \qquad (19)$$

Inserting (19) in (18) we obtain

$$0 = (ap - (2\pi\omega')^2 \, q' - \eta p) \, \zeta' + \eta \, T \, \zeta''. \qquad (20)$$

This equation can be fulfilled if

$$(a - \eta) \, p - (2\pi\omega')^2 \, q' = (a - \eta) \, (p - aq'),$$

which gives for a the condition

$$(2\pi\omega')^2 = a(a - \eta)$$

$$a = \frac{\eta}{2} \pm \sqrt{\frac{\eta^2}{4} + (2\pi\omega')^2} . \qquad (21)$$

(20) now takes the form

$$0 = (a - \eta) \, u \, \frac{d\zeta}{du} + \eta T \, \frac{d^2\zeta}{du^2}$$

which is solved, apart from $\zeta = $ const., by

$$\zeta = K \int^u e^{-(a-\eta)u^2/2\eta T} \, du. \qquad (22)$$

If in (21) the upper sign is chosen, $a - \eta$ will be positive and (22)

just represents a diffusion of the desired type. It will correspond to a situation where practically no particles are yet to be found in the region to the right of C, if we take $-\infty$ for the lower limit of the integral. In the region well to the left of C we find then

$$\zeta = K \sqrt{\frac{2\pi\eta T}{a - \eta}}$$

and the density in phase-space near A will become equal to

$$\zeta = K \sqrt{\frac{2\pi\eta T}{a - \eta}}\, e^{Q/T}\, e^{-(p^2 + (2\pi\omega)^2 q^2)/2T}. \tag{23}$$

The number w of particles passing in unit time the point C will be obtained by integrating ρp over p from $-\infty$ to $+\infty$ for $q' = 0$

$$w = \int_{-\infty}^{\infty} dp \cdot \rho p = K \int_{-\infty}^{+\infty} dp \cdot p\, e^{-p^2/2T} \int_{-\infty}^{p} e^{-(a-\eta)p^2/2\eta T}\, dp = KT \sqrt{\frac{2\pi\eta T}{a}}.$$

On the other hand, the number of particles caught near A equals

$$n_A = K \sqrt{\frac{2\pi\eta T}{a - \eta}}\, e^{Q/T} \iint_{-\infty}^{+\infty} e^{-(p^2 + (2\pi\omega)^2 q^2)/2T}\, dp\, dq = K \sqrt{\frac{2\pi\eta T}{a - \eta}}\, e^{Q/T} \frac{T}{\omega}. \tag{24}$$

The probability of escape is therefore now given by

$$r = \frac{w}{n_A} = \omega \sqrt{\frac{a - \eta}{a}}\, e^{-Q/T}$$

which by (21) (upper sign) gives

$$r = \frac{\omega}{2\pi\omega'} \left(\sqrt{\frac{\eta^2}{4} + (2\pi\omega')^2} - \frac{\eta}{2} \right) e^{-Q/T}. \tag{25}$$

For $\eta/2 \gg 2\pi\omega'$ this formula reduces to the formula (17) previously found, whereas for small viscosity $\eta/2 \ll 2\pi\omega'$ it reduces to

$$r \simeq \omega\, e^{-Q/T} = r_{tr} \quad \text{(Transition-state-method value)}. \tag{26}$$

The probability of escape represented by this formula corresponds exactly to the value which would be given by the *transition state method* of calculating reaction velocities [3]). In fact, according to this method, one considers the particles near A to be in perfect temperature equilibrium with those near B so that we have thermal equili-

brium also at C, and one calculated the number of particles w which
in unit time pass the transition-point C from the left to the right.
This number is of course equal to that passing C from the right to
the left and is given by

$$w = \int\limits_{\substack{0 \\ (C)}}^{\infty} \rho_0 \, p \, dp = e^{-Q/T} \int\limits_{0}^{\infty} p \, e^{-p^2/2T} \, dp = T \, e^{-Q/T}$$

where

$$\rho_0 = e^{-E/T}$$

represents the B o l t z m a n n-G i b b s distribution in phase
space. The number n_A of particles caught near A is now given by the
value T/ω of the double integral occurring in (24), and for the
reaction velocity r we get exactly the value (26). This result can be
interpreted by stating, that the region near C offers no additional
resistance in the case of small η. It would, however, be wrong to
conclude from this that the transition-method is unconditionally
applicable in this case, since now the shuttling effect of the B r o w-
n i a n motion is so small that the subsequent delivery of particles
with energy Q (or more) near C may be insufficient. The rate of
escape is now determined by a diffusion-process along the energy-
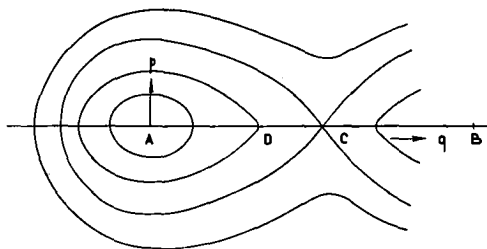coördinate, and can be calculated as follows.

Fig 3. Phase space for smooth potential barrier.

S m a l l   v i s c o s i t y. We consider a quasi-stationary diffusion-
process in phase space of the type investigated in § 4. The density ρ
is practically constant along curves of constant energy over a range
which starts at A (energy zero) and which extends to energy curves
cutting the q-axis not in the transition point C itself but in points D
very near to C (compare Fig. 3). This last restriction has to be made,
if the U function near C has a smooth maximum as in Fig. 1, be-

cause in this case the frequency tends to zero, when the energy tends to Q; for energies near Q the viscosity is therefor e no longer small in the sense used in § 4. If, on the other hand, the U-function behaves near C in the way illustrated by Fig. 2, such a restriction is not necessary and the stationary diffusion in energy extends up to the energy curve passing through C itself. Points in phase space which are shuttled up to an energy larger than Q w ill immediately travel to the region to the right of C. As our calculati on will anyhow be some-what less exact than in the case of large vi scosity, we will moreover make the simplifying assumption that particles leaving the A region near C will practically never return (as for instance would be the case if the escape corresponded to d issociation, and if at the time considered practically no dissoc iated states of the system are yet at hand).

We can now apply formula (15) and write it i n the form:

$$w = \eta T \frac{(\rho \, e^{E/T})_{near \, A} - (\rho \, e^{E/T})_c}{\int\limits_{near \, A}^{C} \frac{1}{I} \, e^{E/T} \, dE}. \tag{27}$$

The subscript „near A" is necessary, because if we integrated strictly from the point A, i.e. from energy zero $(E = I = 0)$, the integral would diverge. We may take it, that „near A" means an energy value of the order T and thus corresponds to points in phase space, where ρ is still of the same or der as in A itself, i.e. to points within the region in which practically all particles of the ensemble are assembled. Furthermore, the assumption that particles leaving at C will practically never reenter the A region means that $(\rho \, e^{E/T})_c$ may be equalled to zero and that t he upper limit in the integral could be taken to correspond to the energy at C. It is easily seen that, in the case of a symmetrical U-function of the type illustrated in Fig. 2, the value for w thus calculated will need a correction in the form of a factor $\frac{1}{2}$, since $(\rho \, e^{E/T})_c$ will then be $\frac{1}{2}$ of $(\rho \, e^{E/T})_{near \, A}$.

Denoting $(\rho \, e^{E/T})_{near \, A}$ by ρ_A, we have therefore:

$$w \cong \eta T \, \rho_A \left\{ \int\limits_T^Q \frac{1}{I} \, e^{E/T} \, dE \right\}^{-1}.$$

Since the main contribution to the integral is due to E-values which differ from Q by a quantity of the order of magnitude T, we

may for I take the value I_C corresponding to the energy curve through C:

$$\int_T^Q \frac{1}{I} e^{E/T} dE \lesssim \frac{1}{I_C} e^{Q/T} \int_0^\infty e^{-(Q-E)/T} d(Q-E) = \frac{T}{I_C} e^{Q/T}.$$

Since I_C will be of the order of magnitude Q/ω, where ω is the proper frequency of particles near A, we get:

$$w \lesssim \frac{\eta \rho_A Q}{\omega} e^{-Q/T}.$$

The probability of escape is again obtained by dividing w by the number of particles assembled near A, i.e. by $n_A = \rho_A T/\omega$. Thus we get

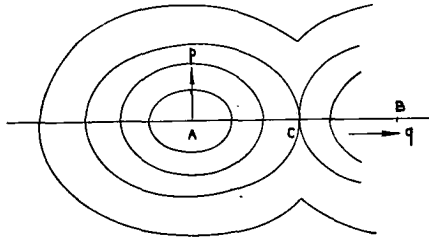$$r = \frac{w}{n_A} \lesssim \eta \frac{Q}{T} e^{-Q/T}. \tag{28}$$

Fig. 4. Phase space for edge shaped potential barrier.

If the U-function to the left of C could be represented exactly by $\frac{1}{2}(2\pi\omega)q^2$, the error in this approximation for r would only be of the relative order of magnitude T/Q. In a case like that corresponding to Fig. 3, it might be wrong by a factor of the order of a few units; not only the estimate for the value of I_C is too low, but also the upper limit of the integral in (27) is too high so that the estimate for r is too small.

The validity of (28) implies that η is small compared with ω, i.e. that the motion of the oscillator is a periodically damped one. Aperiodic damping would mean $\eta = 4\pi\omega$, and one may expect that in this case the subsequent delivery of particles near C is well provided for, so that the rate of escape is now fairly well described by (25). I have not been able to find a trustworthy method for extending (28) to η-values which are not small compared to $4\pi\omega$. One might

hope to find an exact solution in the case where U to the left of C is
exactly equal to $\frac{1}{2}(2\pi\omega)^2 q^2$: it would depend on the solution of the
fundamental diffusion equation with particularly chosen boundary
conditions.

Due to our assumption that Q/T is large (at least of the order of
magnitude, say, 5; without this assumption the problem of the pro-
bability of escape is not well defined anyhow, since the conception of
a B o l t z m a n n distribution near A would no longer be valid), it
is hardly of any importance, however, to try to improve on (28) in
the region of small η. In fact, even for a very small value of η
$(\eta/\omega \lesssim T/Q)$, formula (28) yields a value for r equal to that given by
(25), i.e. practically equal to that given by the transition state
method. Fig. 5 illustrates this in the particular case $Q/T = 10$, $\omega' = \omega$.
We conclude that formula (28) or (25) applies according as η/ω is
smaller or larger than T/Q. *In particular we expect that the transition*
state method gives results which are correct, say, within 10% in a rather
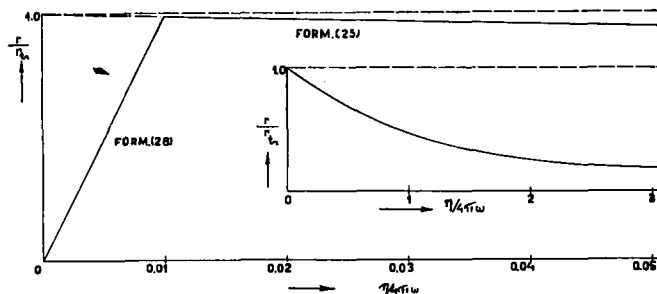*wide range of η-values $(\omega T/Q \lesssim \eta \lesssim 1,2\,\omega')$.*

Fig. 5. Probability of escape as a function of viscosity $(\omega' = \omega, Q/T = 10)$.

In the region of small η-values this is supported by a consideration
of what happens to particles which enter the A-region through C
with a velocity of the order $\sqrt{T}$. If such particles are practically
caught all of them after a time of the order $1/\omega$, it means that the
transition method is very reliable. Now it is clear that such a capture
will take place not only when η is equal to $4\pi\omega$ (aperiodic damping),
but also when η is smaller even by a factor of the order T/Q. In fact,
this means that after a time $1/\omega$ the systematic friction has been
sufficient to lower the energy by an amount of the order T.

§ 6. *Relation of our model to actual reaction processes*. As well
known, the appearance of the A r r h e n i u s-factor $e^{-Q/T}$ in the

expression for a reaction velocity can often be interpreted by assu-
ming that in the chain of elementary reactions which lead from an
initial state A to a final state B there occurs an intermediate product
in such a state C, that a (free) energy Q would be required in order to
reach C from A. In simple cases C may just correspond to an activa-
ted state of a molecule the normal state of which corresponds to
state A. The *activation energy* Q should be the highest energy barrier
through which the system should have to pass, even if it chooses the
energetically most economic way. If the molecules in the *transition
state* C (concentration N_C) were in temperature equilibrium with
those in state A (concentration N_A), the temperature dependence of
their relative concentration N_A/N_C would be given mainly by $e^{-Q/T}$.
They would therefore correspond to the rarest of all intermediate
products occurring in the reaction, and it is plausible that their con-
centration mainly determines the rate of the reaction. The so-called
transition state method calculates the „flow" of reaction products on
their way from A through C to B, which in thermodynamical equi-
librium between A and C would be present at C, and declares this
flow to be a reliable value for the actual reaction velocity r. In some
cases this method is not unambiguous, because it is difficult to
decide what assumptions have to be made about the concentration
of products between state C and the final state B; in many cases it
yields, however, definite results.

When discussing the reliability of this transition method, reactions
of an outspoken autokatalytic character (chain-reactions) must as a
rule be discarded, since here the necessary activation-energy can be
supplied by reaction-products appearing between C and B; the
mechanism of reactions which lead from A to C and which are respon-
sible for the temperature equilibrium between A and C is now no
longer the only one which counts *). But even if autokatalytic
reactions are excluded, there are several reasons why the transition-
method might give wrong results. The very fact that a reaction is
going on means that state C will never be in exact temperature
equilibrium with the state A; there may be a one-sided supply of
molecules in state C from state A: those in state C which pass in the
direction of B may never be compensated by a backward flow
$B \to C \to A$. Thus the problem is raised if the subsequent delivery

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*) Still, chain reactions may, in particular cases, just lead to the transition-method
value for r. Compare Christiansen and Kramers[4]).

(Nachlieferung) $A \to C$ is sufficient in order to maintain the equilibrium-concentration at C. The simplest example where the subsequent delivery gets too small is that of a homogeneous gas reaction, where the pressure is so low that a sufficient number of activated molecules is no longer supplied by the collisions. But even if there is no difficulty as regards the concentration at C, the reaction may be much slower than that given by the transition method, due to the fact that the molecules in C are still practically in temperature equilibrium with stages in the reaction $D, E \ldots$ on the way from C to B, so that the flow at C in the direction B is compensated to a smaller or larger extent by a flow from E, D through C backward in the direction of A [5]).

Our problem of the escape of a particle in a potential hole A over a barrier C clearly supplies a simplified classical model, in which it is possible to judge the reliability of the transition method. The B r o w n i a n forces of the medium illustrate the mechanism which strives to bring about temperature equilibrium. The value of the viscosity coefficient η (which may depend on T even in the manner of an exponential function) is a measure for the intensity with which the molecules in the different states react with the surrounding medium. If η is too small, the subsequent delivery is too small, and the reaction velocity falls beneath the transition-method value; if it is too large, the net flow at the transition point will be much smaller than the flow in the direction $A \to C \to B$ alone: in a fairly large region of η-values, however, the transition-method holds good $(\omega T/Q \gtrsim \eta \gtrsim 1,2 \, \omega')$.

The model illustrates also the ambiguity involved in the conception „transition state". For small η, it should be a state of definite energy Q, and one imagines easily in what manner the model might be generalized, in order to obtain a closer resemblance to actual processes, especially as regards the introduction of discrete quantized energy-states. For larger η the transition state in our model is, however, mainly characterised by the value of the spatial coordinate q_C; in actual problems we may indeed meet cases where the main characteristic of the potential barrier to be overcome corresponds to a definite spatial arrangement of atoms in a molecule, while their velocities can be treated more or less on classical lines. If the latter condition is far from fulfilled, quantummechanical „tunnel-effects" for which there is no room in our model, could also play a part [5]).

In order to get some insight in the virtues and the defects of our model, let us consider three examples of reactions.

Consider first a simple reaction of molecules in a solvent, for instance the slow racemisation of an optically active substance in water. The transition from the left-handed to the right-handed configuration comes mainly about through the existence of states in which some atomic vibrations are so strongly excited that the activated molecule now easily flaps over from the left-handed into the right-handed state, or that even the difference between these two states is obliterated. It is true that the flapping over is also possible in non-activated states (tunnel-effect) but its probability is negligible then. The activation comes about through the interaction with the water molecules and this interaction is symbolized in our model by the B r o w n i a n forces. This symbolization is more or less justified when we compare our model with a sort of pulsating structure in a homogeneous medium, but it may of course be that actually the activation is better described by comparing it with short-timed interactions (,,collisions" with a water molecule) which cause sudden considerable changes in the vibrational state. Anyhow, an estimate, based on the value of the coefficient of viscosity in water, of the effective η to be inserted in our formulae in this case suggests that the subsequent delivery is well provided for and that we are probably justified in applying the transition method.

In homogeneous gas reactions (one might think of the racemization of an evaporated optically active substance) our B r o w n i a n forces would represent the action of the separate collisions between the molecules. Such a representation would only be of quantitative value in the extreme case where the change in the state of motion of a reactive molecule due to a single collision with another gas molecule is — on the average — only very small. This case would be realised if the vibrating atoms in the molecule were heavy compared with the mass of the majority of the molecules in the gas (say, dissociation of diatomic iodine molecules in helium). It reminds us of L o r e n t z' calculation [6]) of the B r o w n i a n motion of a spherical particle in a highly rarified gas, although here, of course, only the effect on the translational (and rotational) motion of a free particle was considered. In general, the collisions may induce sudden jumps of the reactive molecule to states in which the energy is quite

different and the B r o w n i a n motion model has, at its best, no
more than a qualitative significance.

In this connection it might be of interes t to calculate the probabi-
lity of escape of a particle in a potential-hole A over a barrier C
under the assumption that the particle is subject to the collisions
with the molecules of a M a x w e l l-distributed gas. If the mass of
such a molecule is small compared to that of the particle, the
B r o w n i a n motion model holds good; if the ratio of the masses
is not small, the diffusion equation in phase space is no longer .a
differential equation but an integro-differential equation. Still in the
limit of large viscosity the S m o l u c h o w s k i equation (11)
would apply.

Our second example is that of a polyatomic molecule with a great
number of vibrational degrees of freedom, one of which may lead to
reaction (say, dissociation of N_2O_5 [7])). Here the coupling between the
different modes of vibration (due to terms in the potential energy
higher than quadratic) influence the „reactive" vibration in a similar
way as the B r o w n i a n forces influences the motion of the particle
in our model. It may of course be that in the activated state the dis-
tinction of one particular reactive vibration, which is subject to
perturbations from the other vibrations, is no longer sound and that
consequently a one-dimensional model of the transition state is
largely at fault.

As a third example consider the fission of heavy nuclei in the way
in which this phenomenon was treated by B o h r and W h e e-
l e r [8]). They consider the nucleus as a hot drop of homogeneously
charged liquid; such a drop has five modes of vibration which may
lead to fission. B o h r and W h e e l e r justify the assumption
that the problem may be treated as a classical one and they calculate
the probability of fission by the transition method. The temperature
of the nucleus is not introduced explicitely, but the calculation is in
essence not different from a classical application of the transition
method. The occurrence of h in B o h r's and W h e e l e r's for-
mula is only due to the circumstance that the excitation of the
nucleus is described in terms of a density of levels.

As a matter of fact, our model corresponds rather closely to the
B o h r-W h e e l e r model. Our q corresponds to their fission co-
ordinate and our η corresponds to the resistance to which the vibra-
tion of the drop is subject as a consequence of the „viscosity" of the

nuclear matter. The transition method in this case is therefore justi-
fied if the friction is not very small, nor so large that the drop vibra-
tions are overaperiodically damped to a high degree. Of course, at
the present state of our knowledge, a marked error in B o h r and
W h e e l e r'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
B o h r'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.

3 Jan. 1940

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