Frequency Factors in the Thermally Activated Process

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Discussions of the rate $\nu e^{-U/kT}$ for thermally activated processes are usually based on the phase-space distribution function for thermal equilibrium. Kramers has gone beyond this and for the particle in a bistable one-dimensional well has treated the relaxation to equilibrium as a Brownian motion problem in which the one-dimensional motion is coupled to a reservoir through a viscosity. Kramers' arguments are readily extendable to many dimensions. In the overdamped case the reaction rate is reduced below the value derived from thermal equilibrium theory by the factor ω_s/η, where ω_s is the angular frequency associated with the direction of steepest descent at the saddle point and η the viscosity. In the underdamped case equilibrium theory is valid for many-dimensional systems, except for extreme degrees of underdamping.

1. INTRODUCTION

THE probability, per unit time, for the thermally activated jump of a particle over a barrier is generally given by an expression of the form $\nu e^{-U/kT}$, where U is the barrier height. The factor ν is often taken to be an oscillation frequency characterizing the initial state. This sort of expression occurs in many problems, but has received particular attention in connection with chemical reaction rate theory and the closely allied field of solid-state diffusion. Excellent summaries of the two viewpoints generated by these fields will be found, respectively, in a book by Slater[1] and in a paper by Vineyard.[2] Both treatments are devoted to detailed discussions of the frequency factor ν. The thermally activated jump is also of interest in the computing process,[3] where both the intentional switching, as well as the subsequently undesired decay of information, can be thermally activated. In fact, if the system making an activated jump is allowed to have a sufficiently large number of degrees of freedom, then the jump can actually be the description of a phase transition from a metastable state to a state of absolute stability. We shall, however, in most of our considerations exclude systems with such a really large number of degrees of freedom. They are briefly discussed in Sec. 6.

Most of the more sophisticated treatments of the frequency factor ν are equilibrium theories, or closely related thereto. These theories assume that there is a many-dimensional space, illustrated by the two- dimensional diagram of Fig. 1, in which we consider an ensemble of the systems in question under thermal equilibrium. Points A and B are potential minima. Point S is a saddle point. The typical equilibrium theory then asks how many ensemble members, per second, make the passage over the saddle point, in the direction from A towards B. This rate, divided by the total ensemble population of well A, is then taken as the probability, per unit time, that a system initially near A will make the transition to the region near B. In an equilibrium ensemble the net flow across the saddle point is zero; a nonvanishing current is obtained by selecting only half the systems near the saddle point, i.e., those which have a velocity vector pointing toward B rather than A. If the systems, in passing from A to B, and vice versa, passed through the saddle-point region only once, the equilibrium argument would be rigorously correct. Unfortunately, as has been pointed out by Kramers,[4] a system in going from A to B may cross and recross the saddle-point region several times. Therefore, the equilibrium flux across the saddle-point region is larger than the number of really independent crossings and the equilibrium theories overestimate reaction rates.

The equilibrium theory, with some relatively innocuous approximations,[2] which we shall also make, yields a transition rate

$$\Gamma=\Big(\prod_{j=1}^{N-1}\nu_j'\Big)^{-1}\Big(\prod_{j=1}^{N}\nu_j\Big)\,e^{-U/kT}. \tag{1.1}$$

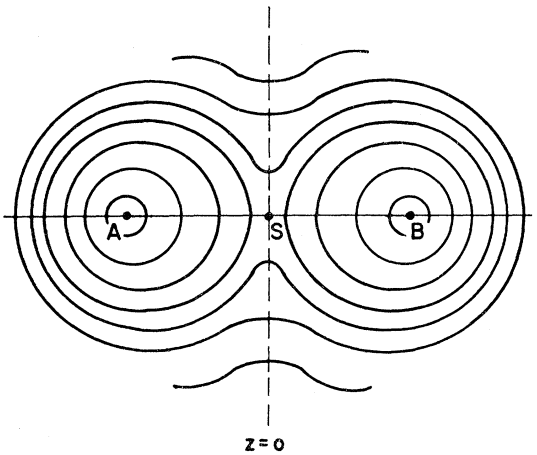

FIG. 1. Equipotential contours in two dimensions, but intended here to suggest the general n-directional situation. A and B are minima. $z=0$ is a symmetry hyperplane and S the saddle point.

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[2] G. H. Vineyard, J. Phys. Chem. Solids **3**, 121 (1957).

[3] J. A. Swanson, IBM J. Research Develop. **4**, 305 (1960).

[4] H. A. Kramers, Physica **7**, 284 (1940); see also W. F. Brown, J. Appl. Phys. **30**, 130S (1959), for an application of Kramers' concepts to fine magnetic particles.

Here the ν_j are the vibrational frequencies in the initial well and the ν_j' are the vibrational frequencies at the saddle point. The saddle point is associated with one less real frequency than the minima, since there is one direction at the saddle point in which the particle is pushed away from the saddle point, rather than restored to it. Kramers[4] has gone beyond the equilibrium theory, for the one-dimensional barrier, and treated the Brownian motion of the particle in the well. He obtains transition rates smaller than those given by Eq. (1.1). It is our purpose to extend Kramers' arguments to the many-dimensional case.

Like Kramers, we shall consider motion in a potential well, supplemented by damping forces. The damping results from an interaction with dynamical coordinates not explicitly represented by the potential well. These are coordinates whose values are not relevant to the assignment of the particle to a well, and are furthermore coordinates which are only loosely coupled to the degrees of freedom which are essential to the discussion of the well jumping. The same interaction which provides damping will also provide fluctuating forces which are responsible for the random Brownian motion. Two separate cases will be considered explicitly: overdamping and underdamping. In the overdamped case the motion is of a highly diffusive sort and Eq. (1.1) overestimates the transition rate because particles stay in the neighborhood of the saddle point, crossing and recrossing it, before finally diffusing away from it. In the underdamped case Eq. (1.1) overestimates the transition rate because particles may bounce back out of a well, once they have crossed into it, without having had a chance to come into equilibrium.

2. GENERAL CONCEPTS

We are treating a relaxation process. It is, therefore, inadequate to invoke the Liouville equation for the many-dimensional motion, but we must supplement it by the effect of damping forces and fluctuating forces. The density, ρ, in the many-dimensional phase space can, in general, be written

$$\rho=\rho_t+\rho_d. \tag{2.1}$$

Here ρ_t is the thermal equilibrium portion of ρ and its normalization is defined by

$$\int \rho d\Gamma=\int \rho_t d\Gamma. \tag{2.2}$$

ρ_d is the deviation from equilibrium, which obeys

$$\int \rho_d d\Gamma=0. \tag{2.3}$$

The deviation ρ_d is therefore of variable sign. The equilibrium portion, ρ_t is time independent whereas ρ_d decays with time and has the form

$$\rho_d=\sum_i \rho_{di}\exp(-t/\tau_i). \tag{2.4}$$

We are interested in the particular τ_i associated with an unbalance between the two wells. The time constants associated with unbalances within a well are presumably much shorter. The unbalance, Δ, between the two wells will be given by

$$\Delta=\int_{\text{near } A}\rho_d d\Gamma-\int_{\text{near } B}\rho_d d\Gamma=2\int_{\text{near } A}\rho_d d\Gamma, \tag{2.5}$$

where we have invoked both the vanishing of the integral of ρ_d over all phase space, as well as the fact that even in the nonequilibrium case most of the ensemble population is concentrated near the minima. If the number of ensemble members crossing the saddle point per unit time is J, then we will have

$$d\Delta/dt=-2J=-\Delta/\tau, \tag{2.6}$$

where τ is the particular time constant of interest. Hence, a simultaneous evaluation of Δ and J will give us τ. The relaxation time defined in this fashion is a more generally applicable quantity than the reaction rate r used by Kramers, which consists of the current J, divided by the total population of *one* of the wells. Our relaxation time τ is independent of the sign or magnitude of the deviation from equilibrium. Furthermore, instead of explicitly evaluating the time dependent relaxation, we will find it simpler to examine a closely related steady state. If the particles are replaced in the bottom of well A as quickly as they leak away, and taken out of well B as quickly as they arrive there, then the well populations can remain time independent, and the current can continue without being reduced from its initial value. The exact points at which we set up sources and sinks do not matter, since the equilibrium near the bottom of each well is rapid, compared to the intervalley motion. In the event that one of the wells is occupied and the other is empty (the case which Kramers explicitly considered) the rate $1/\tau$ given by Eq. (2.6) is just twice the reaction rate r that Kramers discusses.

3. OVERDAMPED CASE

In the overdamped case we follow Kramers'[4] procedure of first finding the Fokker-Planck equation in phase space, and then integrating over the momentum variables. If the motion is sufficiently damped, so that regions where the concentrations differ appreciably cannot exchange ensemble members, then an equation can be found which involves only the ensemble density at a spatial point, but not the momentum distribution. The flow of ensemble members has the form [see Kramers' Eq. (11)]

$$\mathbf{j}=-n\mu\nabla U-D\nabla n. \tag{3.1}$$

Here n is the density of systems and U their potential energy. The diffusion coefficient D and the mobility μ must satisfy the Einstein relation $D=kT\mu$, so that the

Boltman distribution,

$$n=ce^{-U/kT}, \tag{3.2}$$

corresponds to $\mathbf{j}=0$. If, in the nonequilibrium case we set

$$n=\beta e^{-U/kT}, \tag{3.3}$$

then the variation of β indicates the extent of the deviation from equilibrium and Eq. (3.1) becomes

$$\mathbf{j}=-D(\nabla\beta)e^{-U/kT}. \tag{3.4}$$

In Eq. (3.4) D can still be a function of position; and, in fact, for complete generality D must be allowed to be a matrix with positive real eigenvalues (in the absence of a magnetic field). We will assume in the subsequent reasoning that D is sensibly constant in the neighborhood of the saddle point, and that one of its principal directions is parallel to the line connecting the two minima.

To obtain a given magnitude of current from Eq. (3.4), assuming not too much variation in the value of D, requires a relatively large value of $\nabla\beta$ near the saddle point, where $e^{-U/kT}$ is small, and much smaller values of $\nabla\beta$ near the minima, where $e^{U/kT}$ has larger values. We can therefore expect that the serious departures from equilibrium occur only near the saddle point.

Consider now the case where the two potential minima are at the same value of potential and the situation is symmetrical about a plane through the saddle point. The case where a biasing force is present, and one of the minima is favored, will be considered in Sec. 5.

In the symmetrical case n_d, the ensemble density deviation from equilibrium, will be odd about the plane bisecting the line AB, as will $\beta_d=n_d\exp(U/kT)$. Therefore, Eq. (3.4) tells us that at the symmetry plane $\mathbf{j}$ is perpendicular to the symmetry plane. Let us now assume that $\mathbf{j}$ has this same direction throughout the neighborhood of the saddle point, and see whether this leads to a satisfactory solution.

Let z be the coordinate perpendicular to the symmetry plane. If we assume that a principal axis of D lies along the z direction, and that none of the other principal values of D vanish, then Eq. (3.4) tells us that β is only a function of z, in the neighborhood of the saddle point. We can then integrate Eq. (3.4) immediately

$$\beta(z)=-\int_0^z \frac{j_z}{D}e^{U(z')/kT}dz'. \tag{3.5}$$

In the saddle-point neighborhood, U depends quadratically on the spatial coordinates:

$$U=U_s-\tfrac{1}{2}\alpha z^2+\sum_{n=1}^{N-1}\alpha_i x_i^2, \tag{3.6}$$

where the $(N-1)$ coordinates x_i are confined to the symmetry hyperplane. Substituted in Eq. (3.5), this gives

$$\beta(z)=-D^{-1}\int_0^z j_z \times\exp\left[\frac{U_s}{kT}-\frac{\alpha(z')^2}{2kT}+\frac{1}{2kT}\sum\alpha_i x_i^2\right]dz'. \tag{3.7}$$

The factor $j_z\exp[\sum_1^{N-1}\alpha_i x_i^2/2kT]$ is, by Eq. (3.4), only a function of z. The continuity of current, $\operatorname{div} j=0$, requires, however, that j_z be independent of z. Hence, the term $j_z\exp[\sum_1^{N-1}\alpha_i x_i^2/2kT]$ is, in fact, a constant. The only remaining variable in the integrand is $\exp[-\alpha(z')^2/2kT]$. The integrand of (3.7) is then large only at the saddle-point plane $z=0$, and diminishes rapidly, through the factor $\exp[-\alpha(z')^2/2kT]$ as we move away from this plane. Therefore, at a relatively short distance away from the plane $z=0$, $\beta(z)$ approaches constant limiting values, a positive one in well A, and a negative one in well B. These are, however, exactly the desired boundary conditions: approximate thermal equilibrium within each well and appreciable departures from this only near the saddle point. Therefore, Eq. (3.5) describes the desired solution, since it satisfies the equation of continuity: $\operatorname{div}\mathbf{j}=0$; it satisfies the constitutive equation (3.4), and also the boundary conditions. (A variational principle can be devised which establishes that a solution satisfying these conditions is at least locally unique—i.e., that there is not a whole continuous family of solutions.)

To evaluate τ from Eq. (2.6), we must first find the values of both J and Δ. The population difference Δ is equal to twice the population of well A, giving

$$\begin{aligned}\Delta&=2\int_{\text{well }A} dx_1\cdots dx_n\, n_d\\ &=2\int_{\text{well }A} dx_1\cdots dx_n\,\beta(A)\exp(-U/kT)\\ &=2\beta(A)\exp(-U_A/kT)\int_{\text{well }A} dx_1\cdots dx_n \times\exp\left(-\frac{1}{2kT}\sum_1^N\gamma_i x_i^2\right).\end{aligned} \tag{3.8}$$

In the final form of the integral we have used an expansion appropriate to the bottom of well A:

$$U=U_A+\tfrac{1}{2}\sum\gamma_i x_i^2, \tag{3.9}$$

and assumed that almost all of the well population is contained in the range in which the potential is representable by a quadratic form. This yields:

$$\Delta=2\beta(A)\exp(-U_A/kT)\prod_1^N(2\pi kT/\gamma_i)^{\frac{1}{2}}. \tag{3.10}$$

The other quantity needed for an evaluation of τ is the total current J crossing the saddle point. The current density is

$$j_z = -\mu kT(\partial\beta/\partial z)\exp(-U/kT). \tag{3.11}$$

In the symmetry plane containing the saddle point, Eq. (3.11) becomes

$$j_z = -\mu kT\left(\frac{\partial\beta}{\partial z}\right)_{z=0}\exp\left(-\frac{U_s}{kT}-\frac{1}{2kT}\sum\alpha_i x_i^2\right). \tag{3.12}$$

Integrating over the $N-1$ transverse coordinates gives a total current:

$$J = -\mu kT\left(\frac{\partial\beta}{\partial z}\right)_{z=0} e^{-U_s/kT}\int\cdots\int dx_1\cdots dx_{N-1} \times\exp\left(-\frac{1}{2kT}\sum_1^N \alpha_i x_i^2\right)$$

$$= -\mu kT\left(\frac{\partial\beta}{\partial z}\right)_{z=0} e^{-U_s/kT}\prod_1^{N-1}\left(\frac{2\pi kT}{\alpha_i}\right)^{\frac{1}{2}}. \tag{3.13}$$

The ratio $1/\tau = 2J/\Delta$ is then given by dividing Eq. (3.13) by Eq. (3.10):

$$\frac{1}{\tau} = -2\mu kT\frac{(\partial\beta/\partial z)_{z=0}}{\beta(A)}e^{-(U_s-U_A)/kT} \times\prod_1^{N-1}(2\pi kT/\alpha_i)^{\frac{1}{2}}/[2\prod_1^N(2\pi kT/\gamma_i)^{\frac{1}{2}}]. \tag{3.14}$$

To make use of Eq. (3.14) we still have to evaluate $(\partial\beta/\partial z)_{z=0}/\beta(A)$ from Eq. (3.5) which gives

$$\beta(A) = -\int_0^A \frac{j_z}{D}\exp\left(\frac{U_s}{kT}-\frac{\alpha z^2}{2kT}\right)dz, \tag{3.15}$$

where j_z in Eq. (3.15) is the current density at the saddle point itself. This is given by Eq. (3.4) as

$$j_z(S) = -D(\partial\beta/\partial z)_S\exp(-U_s/kT). \tag{3.16}$$

Equation (3.16) substituted in (3.15) gives

$$\beta(A) = \left(\frac{\partial\beta}{\partial z}\right)_S\int_0^A \exp(-\alpha z^2/2kT)dz \cong -\left(\frac{\partial\beta}{\partial z}\right)_S\frac{1}{2}\left(\frac{2\pi kT}{\alpha}\right)^{\frac{1}{2}}, \tag{3.17}$$

or equivalently

$$\frac{(\partial\beta/\partial z)_S}{\beta(A)} = -\frac{2}{(2\pi kT/\alpha)^{\frac{1}{2}}}, \tag{3.18}$$

which if used in Eq. (3.14), puts this into the form

$$\frac{1}{\tau} = 2\mu kT e^{-(U_s-U_A)/kT} \times\prod_1^N(2\pi kT/\alpha_i)^{\frac{1}{2}}/[(2\pi kT/\alpha)^{\frac{1}{2}}\prod_1^N(2\pi kT/\gamma_i)^{\frac{1}{2}}]$$

$$= \frac{\mu}{\tau}[(\alpha)^{\frac{1}{2}}\prod_1^N\gamma_i^{\frac{1}{2}}/\prod_1^N\alpha_i^{\frac{1}{2}}]e^{-(U_s-U_A)/kT}. \tag{3.19}$$

In order to introduce the frequencies of Eq. (1.1), we must use the particle mass m. In case the real physical problem involves a number of different masses it is assumed that a canonical transformation was introduced which makes all masses identical, and that we have been working with the transformed coordinates. Using $(\gamma_i/m)^{\frac{1}{2}} = 2\pi\nu_i$ and $(\alpha_i/m)^{\frac{1}{2}} = 2\pi\nu_i'$, we get

$$\frac{1}{\tau} = 2\mu m\left(\frac{\alpha}{m}\right)^{\frac{1}{2}}[(\prod_1^N\nu_i/\prod_1^{N-1}\nu_i')e^{-(U_s-U_A)/kT}]. \tag{3.20}$$

The quantity in square brackets, on the right-hand side of Eq. (3.20), is just the rate given by equilibrium theory, in Eq. (1). Denoting this by $(1/2\tau)_{\text{eq.}}$, we have

$$(1/\tau) = \mu m(\alpha/m)^{\frac{1}{2}}(1/\tau)_{\text{eq.}}. \tag{3.21}$$

The quantity μm is just the viscosity η, used by Kramers.[4] η gives the rate of momentum relaxation, due to dissipative effects, according to the equation

$$dp/dt = -\eta p. \tag{3.22}$$

The quantity $(\alpha/m)^{\frac{1}{2}}$ is an angular frequency, ω_s, associated with the unstable equilibrium at the saddle point. [Note that our $\omega_s = (\alpha/m)^{\frac{1}{2}}$, whereas Kramers uses the symbol ω' to stand for a frequency which is $(2\pi)^{-1}(\alpha/m)^{\frac{1}{2}}$.] In this new notation, Eq. (3.21) can be written

$$(1/\tau) = (\omega_s/\eta)(1/\tau)_{\text{eq.}}. \tag{3.23}$$

The reduction factor (ω_s/η) is the same as the one Kramers found for the one-dimensional case. The smaller the damping, the more rapid the diffusive motion of the overdamped system becomes. Decreasing values of ω_s represent increasingly flat saddle-point barriers and therefore thicker obstacles for the diffusing system.

4. THE UNDERDAMPED CASE

In the one-dimensional underdamped case, it is pointed out by Kramers that a very considerable degree of underdamping is required to cause appreciable deviation from the equilibrium theory. Kramers points out that a typical particle crosses the energy barrier with about kT of excess kinetic energy. During its motion through the new well it only has to dissipate this excess kinetic energy to become trapped. Since this excess kinetic energy is only a small fraction of the

total energy, a relatively small degree of damping will insure trapping. Instead of giving a detailed treatment of the underdamped case, we will be satisfied in extending the above argument to the many-dimensional case with very rough statistical considerations. This will leave us with an estimate of the degree of underdamping that is required to produce appreciable deviations from Eq. (1.1).

Again there is a balance, in equilibrium, between damping forces and fluctuation forces. For a particle, however, which has already a considerable kinetic energy, such as one which has just crossed the saddle point, and entered into a well, the damping forces (which we will assume proportional to the particle momentum) are predominant compared to the fluctuating forces, and we shall consider only the damping effects.

We first wish to find the mean energy in excess of the saddle-point energy, U_s, with which particles in thermal equilibrium cross the saddle point. Consider the particles with excess energy between ϵ and $\epsilon+d\epsilon$, at a point in the symmetry plane where the potential exceeds U_s by δU. The kinetic energy of the particles is then $\epsilon-\delta U$, and their momentum is proportional to $(\epsilon-\delta U)^{\frac{1}{2}}$. The rate at which they contribute to the current flowing from one well to the other, per unit volume of phase space, is then proportional to the particle velocity, $2^{\frac{1}{2}}m^{-\frac{1}{2}}(\epsilon-\delta U)^{\frac{1}{2}}$. [The fact that these particles have a total momentum $2^{\frac{1}{2}}m^{\frac{1}{2}}(\epsilon-\delta U)^{\frac{1}{2}}$, and that only one component of this momentum gives their rate of flow in the z direction brings in a multiplying factor which depends only on the dimensionality of the system.] In integrating over phase space, consider the integration over momentum first. The range of integration is proportional to $p^{N-1}dp$, where N is the total number of spatial dimensions. The current flow, per unit volume, is therefore proportional to $(\epsilon-\delta U)^{\frac{1}{2}}p^{N-1}dp$, or equivalently to $p^{N-1}d\epsilon$. We must now still consider the integration over the transverse spatial dimensions. Hence, we have an integral of the form

$$\phi(\epsilon)d\epsilon=d\epsilon\int p^{N-1}dx_1\cdots dx_{N-1}$$

$$=d\epsilon\int[2m(\epsilon-\sum_1^{N-1}\alpha_i x_i^2)]^{(N-1)/2}dx_1\cdots dx_{N-1}, \quad (4.1)$$

for the saddle-point flux in the range $d\epsilon$. The range of integration is the region in which the integrand remains positive. A change of variables, $t_i^2=\alpha_i x_i^2$ brings this integral into the more symmetrical form

$$\phi(\epsilon)d\epsilon=cd\epsilon\int[2m(\epsilon-\sum_1^{N-1}t_i^2)]^{(N-1)/2}dt_1\cdots dt_{N-1}, \quad (4.2)$$

where the constant c is independent of ϵ. An additional change of scale $t_i=\epsilon^{\frac{1}{2}}v_i$ takes us into

$$\phi(\epsilon)d\epsilon=c\epsilon^{N-1}d\epsilon\int[2m(1-\sum_1^{N-1}v_i^2)]^{(N-1)/2}\times dv_i\cdots dv_{N-1}. \quad (4.3)$$

The flux per unit energy range, across the saddle point, would therefore be proportional to ϵ^{N-1} if all parts of phase space were given equal probability. In thermal equilibrium, therefore, the flux will be proportional to $\epsilon^{N-1}\exp(-\epsilon/kT)$. The mean excess energy of the flux across the saddle point will be

$$\langle\epsilon\rangle=\int\epsilon^N\exp(-\epsilon/kT)d\epsilon\Big/\int\epsilon^{N-1}\exp(-\epsilon/kT)d\epsilon$$

$$=kT[\Gamma(N+1)/\Gamma(N)]=NkT. \quad (4.4)$$

How much of this excess energy NkT must be dissipated in order that the particle be trapped? In order for it to be trapped with absolute certainty all of the excess energy must be dissipated. For large N, however, the distribution $\epsilon^{N-1}\exp(-\epsilon/kT)$ becomes a very sharply peaked function at $\epsilon\sim NkT$, indicating that particles with ϵ appreciably less than NkT have very little chance of passing through the saddle point opening. Hence, the particle need not really lose all of its NkT excess energy to become effectively trapped.

Let us consider this point slightly more quantitatively. Assume that the particle is subject to a damping force

$$dp/dt=-\eta p, \quad (4.5)$$

or equivalently, for the kinetic energy T

$$dT/dt=-2\eta T. \quad (4.6)$$

Now assume that averaged, over the particle motion in a well, T constitutes a fraction $\frac{1}{2}\delta$ of the total energy, where δ is a coefficient of order unity. The total energy U is then lost according to

$$dU/dt=-\eta\delta U. \quad (4.7)$$

A particle with an initial total energy (ϵ_0+U_s) will therefore lose excess energy according to the law

$$\epsilon(t)=(\epsilon_0+U_s)e^{-\eta\delta t}-U_s. \quad (4.8)$$

In the typical case we have in mind ϵ_0 is smaller than U_s and therefore the energy relaxation is described fairly well by

$$\epsilon(t)=(\epsilon_0+U_s)(1-\eta\delta t)-U_s. \quad (4.9)$$

This equation is particularly accurate in the very initial stages of the damping process, where it will be really necessary to invoke it.

Let $\Gamma_E dE$ be the total amount of phase space in one well, in a range dE above the saddle-point energy U_s. Let us furthermore assume that the saddle-point opening is reached with somewhat similar ease from all parts of this phase space. (See Sec. 6 for an additional dis-

cussion related to this point.) The escape probability from a well per unit time, for a particle with energy greater than U_s, is therefore given by $b\epsilon^{N-1}/\Gamma_E$, where $b\epsilon^{N-1}$ is the flux calculated in Eq. (4.3). We shall, for these qualitative considerations assume Γ_E is independent of E. For very large N this is certainly incorrect, but even there Γ_E will vary relatively slowly compared to ϵ^{N-1}. (Furthermore, our considerations generally are intended to apply to relatively modest values of N. See Sec. 6.)

The particle which loses energy according to Eq. (4.9), therefore has a probability per unit time, dr/dt, of returning to its original well, given by

$$dr/dt=(1-r)b\epsilon^{N-1}/\Gamma_E, \tag{4.10}$$

where the factor $(1-r)$ on the right-hand side accounts for the possibility that the particle has already returned. Equation (4.10) integrates to

$$r(t)=\exp\left[-\int_0^t dt'\, b\epsilon^{N-1}/\Gamma_E\right]. \tag{4.11}$$

We are interested in the maximum value $r(t)$ reaches when the limit of integration t, on the right-hand side extends to the time at which ϵ vanishes. Using Eq. (4.9) to perform the integration indicated in Eq. (4.11) gives

$$r_{\max}=1-\exp\left[-\left(\frac{b\epsilon_0{}^{N-1}}{\Gamma_E}\right)\left(\frac{\epsilon_0/N}{\eta\alpha[\epsilon_0+U_s]}\right)\right]. \tag{4.12}$$

Note that for very small N, Eq. (4.9) is a good approximation if the typical value of $\epsilon_0\sim NkT$ is small compared to U_s. For larger values of N Eq. (4.9) becomes poorer in describing $\epsilon(t)$, in the range where it is positive. For larger values of N, however, the high power of the integrand [in Eq. (4.11)] makes the integrand important only at times where $\epsilon(t)$ is still close to ϵ_0, and hence Eq. (4.11) is still accurate. The factor $b\epsilon_0{}^{N-1}/\Gamma_E$ in the exponential term of Eq. (4.12) is just the rate of leakage out of the initial energy range. The factor multiplying it is the time taken to lose an energy ϵ_0/N, by damping, out of the total initial energy $[\epsilon_0+U_s]$. Hence, if the particle loses appreciably more than $(\epsilon_0/N)\sim kT$ energy within the time taken for escape in the absence of damping, $r_{\max}$ in Eq. (4.12) does not come close to unity, and the particle is effectively trapped.

The energy loss required, kT, is therefore the same as in the one-dimensional case. The time available, however, for this loss of about kT is likely to be much larger in the many-dimensional case, than in the one-dimensional case. In one dimension the escape time in the absence of damping is the oscillation period of the well. In many dimensions a particle must be aimed in a very particular way, in order to bounce right back, and most paths through the saddle-point opening will lead to complicated orbits, returning to the saddle-point opening only after many oscillations.

Thus, for all practical purposes, one can assume the equilibrium expressions valid in the many-dimensional underdamped case, unless the damping is extraordinarily weak.

5. THE UNSYMMETRICAL WELL

Our arguments in Sec. 3 assumed a symmetrical well. In this section we will generalize the results. The basic point is as follows: The deviations from equilibrium, in both the underdamped and the overdamped case, are confined to energies close to, or above the saddle-point energy U_s. At appreciably lower energies very slight deviations from equilibrium suffice to generate the required current flowing up (or down) along the energy scale. Hence, if we are given a solution for the non-equilibrium part of the phase space density, ρ_d, for a symmetrical well, corresponding to a current flow J, we can proceed to deepen one of the two wells, and as long as we have left the potential variation near the saddle point unaffected obtain a solution for the new situation very trivially. We simply have to populate the new (deepened) well in such a fashion that it is in equilibrium with the original well, and then the current flow across the saddle point will remain unaffected. Let us evaluate how such changes affect the relaxation time τ.

For the symmetrical situation we have $1/\tau=2J/\Delta$. The excess population in well A is $\Delta/2$, as is the deficit in well B. If we change the minima away from their original positions at $U=0$, let the new minima be at U_A and U_B, respectively, and let the saddle point remain at $U=U_s$. The original population of well A was of the form

$$N_A=c\int_A d\Gamma\, \exp(-U/kT)=-N_B, \tag{5.1}$$

where the integration is over the phase space of well A. The new populations, which are in equilibrium with the above will be

$$\begin{aligned} N_A'&=c\int_{A'} d\Gamma\, \exp(-U/kT)=N_A e^{-U_A/kT}\frac{Z_A'}{Z_0},\\ N_B'&=-c\int_{B'} d\Gamma\, \exp(-U/kT)=-N_A e^{-U_B/kT}\frac{Z_B'}{Z_0}, \end{aligned} \tag{5.2}$$

where $Z=\int d\Gamma\, \exp(-U/kT)$, with U measured from the bottom of the well concerned. The subscript 0 designates the original symmetrical well. An alternative way of writing Eqs. (5.2) is to define a free energy $F_A=U_A-kT\ln Z_A'$, and similarly for F_B, and also F_0 for the original well. Then Eqs. (5.2) become

$$\begin{aligned} N_A'&=N_A e^{-(F_A-F_0)/kT},\\ N_B'&=-N_A e^{-(F_B-F_0)/kT}. \end{aligned} \tag{5.3}$$

The distinction between (F_A-F_0) and U_A becomes relevant only if the well minimum at A changes its

shape as well as its energy level, when the deviation from symmetry is established. The values N_A' and N_B' given by Eqs. (5.3) are associated with the original current J. The solution to the modified problem does not obey $N_A'=-N_B'$, i.e., it contains a certain amount of equilibrium solution. To obtain Δ' we must subtract out this portion. After subtracting out enough of the equilibrium distribution to give us a total population of zero, we find a remaining population difference:

$$\Delta'=2\Delta/(e^{(Z_B-Z_0)/kT}+e^{(Z_A-Z_0)/kT}). \tag{5.4}$$

For the relaxation rate this gives

$$\begin{aligned}\tau/\tau'&=\Delta/\Delta'\\&=\tfrac{1}{2}(e^{(Z_B-Z_0)/kT}+e^{(Z_A-Z_0)/kT}).\end{aligned} \tag{5.5}$$

In the case where the deviation from symmetry is caused by a uniform applied field, we will have to first order in the field

$$Z_B-Z_0=-(Z_A-Z_0). \tag{5.6}$$

Denoting this difference by ξ, and bearing in mind that ξ will, in general, be largely an energy difference and will reflect changes in vibrational entropy only to a minor extent, we have

$$\tau/\tau'=\cosh(\xi/kT). \tag{5.7}$$

Equation (5.7) describes the speeding up of the relaxation process due to an unbalance, and can also be deduced from more elementary kinetic considerations.

In the solid-state diffusion process this is likely to be a small effect, particularly if we neglect the structural changes resulting from the field and consider only the applied field itself as the source of an unbalance. Fields of the order 10^5 and 10^6 volt/cm would be required to produce a 1% increase in electrolytic mobility, if the structure is symmetric in its initial state. In piezoelectric materials an initial symmetry will not obtain and a first-order change of mobility with field can be expected. Equation (5.7) does have a real application: the theory of computing devices. This will be discussed in a separate publication.

6. SYSTEMS WITH VERY MANY DIMENSIONS

If a system has a very large number of dimensions a number of our approximations will break down. First of all, the concept of two wells, within each of which equilibrium is rapid compared to the exchange between wells, is likely to break down. *Furthermore, the system as a whole is likely to have an energy comparable to, or large compared to the saddle-point energy.* The relevant question then does not concern the damping—that is energy exchange with still further coordinates—but only concerns the energy exchange between the degrees of freedom explicitly specified. That is, for sufficiently large N, most of the populated parts of phase space will be at an energy greater than U_s.

The overdamped case with very many dimensions, all of them equally overdamped, seems to be an unlikely and unrealistic situation. If there were such a situation, however, our analysis of Sec. 3 would still apply, if the specific mathematical approximations involved are still valid. The latter only involve the quadratic potential variations, near the minima and the saddle point.

The high-dimensional underdamped case seems more likely, and can be easily visualized. A solid-state diffusion problem, in which all the crystalline degrees of freedom are explicitly represented, is an example. The high-dimensional underdamped case can be separated into two categories.

1. The case where most of the degrees of freedom are only very loosely coupled to the activated process. This is true for the crystalline example mentioned above. Most of these extra degrees of freedom could have been represented simply through a viscosity, and it is only as a matter of rigor that one would want to include them explicitly as part of the process. If one does, however, our considerations of Sec. 4 break down completely. The system does not have to lose any energy to become "trapped," since it never had to become atypical and gain energy to cross the saddle point in the first place. Furthermore there is an assumption in the use of Eq. (4.10) that all parts of the well (with the correct energy) are about equally on "speaking terms" with the saddle point. The slow energy exchange with the many coordinates explicitly represented in the motion, rules this out.

2. The case where all of the many underdamped degrees of freedom are really intimately connected with the activated process, and must be examined, in order to know which well is occupied. This is again hard to imagine. In this case, however, the particle can be assumed to have thermalized immediately, when it crosses the saddle point—i.e., its motion has a character typical of the well in question. Therefore, equilibrium theory is valid, i.e., the probability of a particle bouncing back is negligible, since it has so much phase space to get "lost" in. The specific expression (1.1), of course, depends also upon the validity of quadratic potential expansions.

SUMMARY

In the overdamped case the reaction rate for the many-dimensional problem is reduced by the factor already found by Kramers in the one-dimensional problem. In the underdamped case very extreme underdamping is required to produce deviations from the equilibrium theory.

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