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Diffusion tensor for atomic migration in crystals

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The diffusion of holes or interstitials in a crystal is treated by several types of asymptotic analyses, of which the starting point is the Fokker-Planck equation. First, we show that the standard Smoluchowski equation holds, for large as well as intermediate or small values of the interatomic potential Φ, as an approximation of the Fokker-Planck equation. Next, we derive from the Smoluchowski equation a "homogenized" Smoluchowski equation, which contains only constant coefficients. Finally, we expand these coefficients for large Φ and obtain explicit formulas for the diffusion coefficients in terms of Φ and other physical quantities.

I. INTRODUCTION

The diffusion of holes or interstitials in a crystal is caused by thermal vibrations of the crystal lattice. A particle (i.e., a hole or interstitial) is bound by the interatomic forces inside a crystaline cell and is located, most of the time, near the bottom of a potential well. It is forced to move from one cell to another by the random (thermal) vibrations of a lattice.[1]

The motion of the particle is described, according to three levels of approximation, by the Langevin equation, the Fokker-Planck equation, or the Smoluchowski equation.[2] The basic purpose of this paper is to derive a fourth and simpler level of approximation, namely, a *homogenized* Smoluchowski equation. This will be a diffusion equation with constant coefficients, which are integrals of various quantities across a cell. However, as the activation energy (the minimum value of the potential on the boundary of a cell) becomes large, we show that these coefficients become explicit functions of the activation energy and other physical quantities. For this case our results can be compared to those of Kramers,[3] Vineyard,[4] and Glyde.[5]

We describe now in greater detail the problem under consideration, and the nature of our results.

The motion of a particle in a crystal is defined by the Langevin equations[2]

$$\frac{d}{dt}\vec{x} = \vec{v}\,, \tag{1.1}$$

$$\frac{d}{dt}\vec{v} = -\beta\vec{v} - \vec{\nabla}_x\Phi(\vec{x}) + \left(\frac{2\beta kT}{m}\right)^{1/2}\vec{\nu}\,. \tag{1.2}$$

Here $\vec{x} = (x_1, x_2, x_3)$ and $\vec{v} = (v_1, v_2, v_3)$ are the displacement and velocity vectors, β is a friction coefficient, assumed to be very large, $\Phi(\vec{x})$ is the potential per unit mass of the interatomic forces in the crystalline lattice, T is the absolute temperature, k is Boltzmann's constant, and $\vec{\nu}$ is white noise. The last term in (1.2) represents the thermal vibrations which exert a random force on the particle.

The transition probability density

$$P(\vec{x}, \vec{v}, \vec{\xi}, \vec{\eta}, t) = P_r(\vec{x}(t) = \vec{x}, \vec{v}(t) = \vec{v} | \vec{x}(0) = \vec{\xi}, \vec{v}(0) = \vec{\eta})$$

of the point $\vec{x}, \vec{v}$ in phase space can be shown, by a derivation from the Langevin equation, to satisfy the Fokker-Planck equation[2]

$$0 = \frac{\partial P}{\partial t} + \vec{v}\cdot\vec{\nabla}_x P - \vec{\nabla}_x\Phi\cdot\vec{\nabla}_v P - \beta\nabla_v\cdot(\vec{v}P) - \frac{\beta kT}{m}\Delta_v P\,, \tag{1.3}$$

$$P(\vec{x}, \vec{v}, \vec{\xi}, \vec{\eta}, 0) = \delta(\vec{x} - \vec{\xi})\delta(\vec{v} - \vec{\eta})\,. \tag{1.4}$$

For large dissipation ($\beta \gg 1$), a Maxwellian distribution of velocities sets in after a short relaxation time of order β^{-1}; then, for $t > \beta^{-1}$;

$$P(\vec{x}, \vec{v}, \vec{\xi}, \vec{\eta}, t) \sim (m/2\pi KT)^{3/2} e^{-mv^2/2kT} p(\vec{x}, \vec{\xi}, t)\,, \tag{1.5}$$

and the displacement p is governed by the Smoluchowski equation[2]:

$$\beta\frac{\partial p}{\partial t} = \frac{kT}{m}\Delta_x p + \vec{\nabla}_x\cdot p\vec{\nabla}_x\Phi\,, \tag{1.6}$$

$$p(\vec{x}, \vec{\xi}, 0) = \delta(\vec{x} - \vec{\xi})\,. \tag{1.7}$$

In (1.2), (1.3), and (1.6), $\Phi(\vec{x})$ is periodic and takes identical values in each crystalline cell.

In this paper, we derive the following three results: first, in Sec. II, we derive (1.6) from (1.3) using an asymptotic method which shows that for

Φ large, of order $\sqrt{\beta}$, (1.5) and (1.6) remain valid, and p can have large spatial derivatives, of order $\sqrt{\beta}$. Then, in Sec. III, we show that for very large t, i.e., $t \gg \beta^{-1}$,

$$p(\vec{x}, \vec{\xi}, t) \approx e^{-(m/kT)\Phi(\vec{x})} u(\vec{x}, \vec{\xi}, t), \tag{1.8}$$

where u is determined by the "homogenized" problem:

$$\beta \frac{\partial u}{\partial t} = \vec{\nabla}_x \cdot \vec{D} \cdot \vec{\nabla}_x u, \tag{1.9}$$

$$u(\vec{x}, \vec{\xi}, 0) = \delta(\vec{x} - \vec{\xi}). \tag{1.10}$$

Here $\vec{D}$ is a *constant* tensor, whose elements involve integrals of $\vec{\nabla}\Phi$ across a cell [see (3.18) and (3.13)]. Finally, in Sec. IV, we take Φ to be large (of order $\sqrt{\beta}$) and derive the leading term of an asymptotic expansion for $\vec{D}$ for large Φ. [See Eq. (4.16).]

To derive the Smoluchowski equation in Sec. II, we make the (standard) assumption $\beta \gg 1$. Specifically, we define the dimensionless parameter ϵ by $\epsilon = (v_0/\beta l)^{1/2}$, where v_0 is a typical particle speed and l is a typical cell diameter. Then l/v_0 is a typical "passage" time for a particle, unaffected by the interatomic forces, to cross a cell, and

$$\epsilon = \left(\frac{\text{relaxation time}}{\text{passage time}}\right)^{1/2}.$$

The requirement $\beta \gg 1$ is then equivalent to $\epsilon \ll 1$. The Smoluchowski equation is derived in Sec. II as an asymptotic solution of the Fokker-Planck equation for $\epsilon \ll 1$, and for $O(1)$ or $O(\epsilon^{-1})$ values of the interatomic potential Φ. It is valid after a time interval of order ϵ^2, i.e., for $t > \beta^{-1}$.

To derive the homogenized Smoluchowski equation [Eqs. (1.8) and (1.9)] in Sec. III, we assume only that $t \gg \beta^{-1}$. Then the displacement varies on a time scale slower than β^{-1}, and spatially is near periodic, with a slow nonperiodic spatial variation. The slow time and space variations are described analytically by means of a small dimensionless parameter δ, but the final results are independent of δ. These results, Eqs. (1.9), (1.10), (3.18), and (3.13), are new and have not been reported elsewhere. The diffusion tensor $\vec{D}$ is analytically complicated, but is explicitly defined. In general it is not proportional to the identity tensor, and so diffusion is anisotropic. This is due to geometrical properties of the lattice. For example, the zinc lattice is hexagonal in a certain plane, but not in the direction perpendicular to this plane.

In Sec. IV, we assume that the height of the potential barrier is large compared to the thermal energy of the particles. This assumption was also made by Kramers,[3] Vineyard,[4] and Glyde.[5] Specifically, we assume that the interatomic potential Φ is $O(\epsilon^{-1})$, which was accounted for in Secs. II and III, and we then compute the leading term of an expansion of the diffusion tensor, derived in Sec. III, for $\epsilon \ll 1$. The result is Eq. (4.16). Here $\vec{D}$ is expressed explicitly in terms of the activation energies at the saddle points of Φ on the cell boundaries, on directional derivatives of Φ at these points, and on directional derivatives of Φ at the bottom of the potential well. We compare our result to those of Vineyard[4] and Glyde[5] in the discussion (Sec. VI), and we note and discuss the differences.

Also in the discussion, we show that our result is identical to that of Matkowsky and Schuss,[6] who derived $\vec{D}$ by using the Smoluchowski equation to asymptotically compute the average time of a single jump across the potential barrier. (In this work, Φ is large, but its size relative to β is not made clear.) The formulas for $\vec{D}$ are then obtained by approximating the random walk of the particle between cells by a diffusion. These authors used solutions of the Smoluchowski equation that contain boundary layers, but they did not verify the validity of the Smoluchowski equation as an approximation to the Fokker-Planck equation in the boundary layers.

In this paper, we show that the boundary layer expansions are justified if $\Phi = O(\sqrt{\beta})$, and moreover, we obtain the same formulas for $\vec{D}$ without resorting to the theory of stochastic differential equations, exit times, and exit probabilities.

In Sec. V, we specialize our results to the simple case of one-dimensional cells, and we show that our results agree with those of Kramers.[2,3]

II. DERIVATION OF THE SMOLUCHOWSKI EQUATION

We begin by introducing the following dimensionless variables

$$\vec{r} = (1/l)\vec{x}, \quad \vec{\omega} = (1/v_0)\vec{v}, \quad \tau = (v_0/l)t. \tag{2.1}$$

Here l is a typical diameter of a cell C and v_0 is a typical particle velocity. [Thus, $\vec{r}$ is a dimensionless position variable, in terms of which a typical cell diameter is $O(1)$, $\vec{\omega}$ is a dimensionless velocity variable in terms of which a typical velocity is $O(1)$, and τ is a dimensionless time variable in terms of which the time required for a typical particle unaffected by Φ to traverse a cell is $O(1)$.] We also define

$$\epsilon = (v_0/\beta l)^{1/2}, \quad \lambda = kT/m v_0^2, \tag{2.2}$$

and

$$\phi(\vec{r},\epsilon)=(1/\epsilon)\phi_0(\vec{r})+\phi_1(\vec{r})=(1/v_0^2)\Phi(\vec{x})\,, \tag{2.3}$$

$$\psi(\vec{r},\vec{\omega},\tau)=(1/l^3v_0^3)P(\vec{x},\vec{v},t)\,. \tag{2.4}$$

In (2.3) we require

$$\min_{\vec{r}\in\partial C}\ \phi_i(\vec{r})=O(1)\,,\quad i=0,1\,,$$

where ∂C is the boundary of C. Also, we allow $\phi_0=0$ or $\phi_1=0$ (or both). Thus, for $\epsilon\ll 1$, our analysis accounts for the possibilities that the activation energy, related to

$$\min_{\vec{x}\in\partial C}\Phi(\vec{x})\,,$$

is large [i.e., $O(\epsilon^{-1})=O(\sqrt{\beta}\,)$], is $O(1)$, or is zero. In (2.4) and the remainder of this paper, we drop the dependence on $\vec{\xi}$ and $\vec{\eta}$.

The starting point of our analysis is the Fokker-Planck equation (1.3). Thus we introduce the above equations into (1.3) and get

$$0=\epsilon^2\left(\frac{\partial\psi}{\partial\tau}+\vec{\omega}\cdot\vec{\nabla}_r\psi-\vec{\nabla}_x\phi_1\cdot\vec{\nabla}_\omega\psi\right)-\epsilon\left(\vec{\nabla}_x\phi_0\cdot\vec{\nabla}_\omega\psi\right)$$

$$-(\vec{\nabla}_\omega\cdot(\vec{\omega}\psi)+\lambda\Delta_\omega\psi)\,. \tag{2.5}$$

We shall study this equation for $\epsilon\ll 1$. By (2.2), this means that the viscosity β must be large compared to the frequency v_0/l by which particles unaffected by ϕ pass through a cell. Equation (2.5) has the equilibrium solution

$$\psi=\left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left[-\frac{1}{\lambda}\left(\frac{1}{\epsilon}\,\phi_0+\phi_1+\tfrac{1}{2}\omega^2\right)\right],$$

$$\omega^2=\vec{\omega}\cdot\vec{\omega}\,.$$

After a finite relaxation time, ψ should have the above form, modulo certain spatial and time variations. Thus, our ansatz for (2.5) is

$$\psi\sim\left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left[-\frac{1}{\lambda}\left(\frac{1}{\epsilon}\,\phi_0+\phi_1+\tfrac{1}{2}\omega^2\right)\right]$$

$$\times\sum_{n=0}^{\infty}\epsilon^n\psi_n(\vec{y};\vec{r},\vec{\omega},\tau;s,\sigma)\,, \tag{2.6}$$

where

$$\vec{y}=(1/\epsilon)\vec{r}\,,$$

$$s=\epsilon\tau\,, \tag{2.7}$$

$$\sigma=\epsilon^2\tau\,.$$

The spatial variable $\vec{y}$ describes boundary layers, if any exist, and s,σ are slow time variables.

Introducing (2.6) and (2.7) into (2.5), and equating the coefficients of different powers of ϵ, we obtain the following system of equations:

$$\vec{\omega}\cdot\vec{\nabla}_\omega\psi_n-\lambda\Delta_\omega\psi_n$$

$$=(\vec{\nabla}_r\phi_0\cdot\vec{\nabla}_\omega\psi_{n-1}-\vec{\omega}\cdot\vec{\nabla}_y\psi_{n-1})$$

$$-\left(\vec{\omega}\cdot\vec{\nabla}_r\psi_{n-2}+\vec{\nabla}_r\phi_1\cdot\vec{\nabla}_\omega\psi_{n-2}+\frac{\partial}{\partial\tau}\,\psi_{n-2}\right)$$

$$-\frac{\partial}{\partial s}\,\psi_{n-3}-\frac{\partial}{\partial\sigma}\,\psi_{n-4}\,. \tag{2.8}$$

We reject exponential growth in ω and require each ψ_n to have at most polynomial growth in ω as $\omega\to\infty$. Then, by (2.6), ψ will essentially decay exponentially as $\omega\to\infty$.

Setting $n=0$ in (2.8) gives

$$\vec{\omega}\cdot\vec{\nabla}_\omega\psi_0-\lambda\Delta_\omega\psi_0=0\,.$$

This equation has the bounded solution

$$\psi_0=A(\vec{y};\vec{r},\tau;s;\sigma)\,, \tag{2.9}$$

where A is (at this point) undetermined.

Next we set $n=1$ in Eq. (2.8) and get

$$\vec{\omega}\cdot\vec{\nabla}_\omega\psi_1-\lambda\Delta_\omega\psi_1=-\vec{\omega}\cdot\vec{\nabla}_y A\,.$$

By (A1) of the Appendix, this equation has the polynomial solution

$$\psi_1=-\vec{\omega}\cdot\vec{\nabla}_y A(\vec{y};\vec{r},\tau;s;\sigma)\,.$$

We could include a solution of the homogeneous equation in ψ_1, but do not since this can be incorporated into A.

Setting $n=2$ in (2.8) and rearranging gives

$$\vec{\omega}\cdot\vec{\nabla}_\omega\psi_2-\lambda\Delta_\omega\psi_2=-\vec{\omega}\cdot\vec{\nabla}_r A+\vec{\nabla}_y\cdot(\vec{\omega}\vec{\omega}-\lambda\vec{I})\cdot\vec{\nabla}_y A$$

$$+\left(\lambda\Delta_y A-\nabla_r\phi_0\cdot\nabla_y A-\frac{\partial A}{\partial\tau}\right). \tag{2.10}$$

By (A1), (A2), and (A6) of the Appendix, ψ_2 is a polynomial in ω only if the terms in parenthesis (2.10) is zero; otherwise, ψ_2 will grow exponentially in ω. Hence, we set this last term equal to zero. This is the "solvability condition" for (2.10):

$$\frac{\partial A}{\partial\tau}=\lambda\Delta_y A-\vec{\nabla}_r\phi_0\cdot\vec{\nabla}_y A\,. \tag{2.11}$$

Then u_2 is given by

$$u_2=-\vec{\omega}\cdot\vec{\nabla}_r A(\vec{y};r,\tau;s;\sigma)$$

$$+\tfrac{1}{2}(\vec{\omega}\cdot\vec{\nabla}_y)^2A(\vec{y};\vec{r},\tau;s;\sigma)\,.$$

As above, we choose not to include a solution of the homogeneous equation in u_2.

We continue the above procedure by solving (2.8) for $n=3$ and 4. Since only the solvability conditions are of interest to us and the calculations follow exactly as above, we shall just state these conditions. For $n=3$, we get

$$\frac{\partial A}{\partial s} = 2\lambda \vec{\nabla}_y \cdot \vec{\nabla}_r A - \vec{\nabla}_r \phi_0 \cdot \vec{\nabla}_r A - \vec{\nabla}_r \phi_1 \cdot \vec{\nabla}_y A , \quad (2.12)$$

and for $n=4$,

$$\frac{\partial A}{\partial \sigma} = \lambda \Delta_r A - \vec{\nabla}_r \phi_1 \cdot \vec{\nabla}_r A . \quad (2.13)$$

Equations (2.11)–(2.13) describe the evolution of A according to the three time variables τ, s, and σ, and the two position variables $\vec{r}$ and $\vec{y}$. We can combine these equations into a single equation for

$$\mathfrak{a}(\vec{r}, \sigma) = A(\vec{y}; \vec{r}, \tau; s; \sigma) , \quad (2.14)$$

where the dependent variables are related by (2.7). By (2.3), (2.7), and (2.11)–(2.13),

$$\begin{aligned} \epsilon^2 \frac{\partial \mathfrak{a}}{\partial \sigma} &= \frac{\partial A}{\partial \tau} + \epsilon \frac{\partial A}{\partial s} + \epsilon^2 \frac{\partial A}{\partial \sigma} \\ &= \epsilon^2 \lambda (\vec{\nabla}_r + (1/\epsilon)\vec{\nabla}_y) \cdot (\vec{\nabla}_r + (1/\epsilon)\vec{\nabla}_y) A \\ &\quad - \epsilon^2 \vec{\nabla}_r ((1/\epsilon)\phi_0 + \phi_1) \cdot (\vec{\nabla}_r + (1/\epsilon)\vec{\nabla}_y) A \\ &= \epsilon^2 \lambda \Delta_r \mathfrak{a} - \epsilon^2 \vec{\nabla}_r \phi \cdot \vec{\nabla}_r \mathfrak{a} . \end{aligned}$$

Therefore, by (2.3), (2.6), (2.9), and (2.14),

$$\psi \sim \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left[-\frac{1}{\lambda}\left(\phi(\vec{r}) + \tfrac{1}{2}\omega^2\right)\right] \mathfrak{a}(\vec{r}, \sigma) , \quad (2.15)$$

where

$$\frac{\partial \mathfrak{a}}{\partial \sigma} = \lambda \Delta_r \mathfrak{a} - \vec{\nabla}_r \phi \cdot \vec{\nabla}_r \mathfrak{a} . \quad (2.16)$$

Equations (2.15) and (2.16) describe the asymptotic solution of the Fokker-Planck equation (2.5) for large times. It is essential to keep in mind that by (2.3), ϕ can be $O(1/\epsilon)$, and by (2.7) and (2.14), $\partial \mathfrak{a}/\partial \sigma$ can be $O(1/\epsilon^2)$, and $\vec{\nabla}_r \mathfrak{a}$ can be $O(1/\epsilon)$. In other words, ϕ can be (suitably) large, and $\mathfrak{a}$ can have (suitable) boundary layers.

Using (2.1)–(2.3), and (2.7), we may write (2.15) as

$$\psi \sim \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{m v^2}{2kT}\right) p(\vec{x}, t) \left(\frac{1}{l^3 v_0^3}\right) , \quad (2.17)$$

where

$$p(\vec{x}, t) = \exp\left[-\frac{m}{kT}\Phi(\vec{x})\right] \ddot{\mathfrak{a}}\left(\frac{1}{l}\vec{x}, \frac{v_0^2}{\beta l^2} t\right) l^3 v_0^3 . \quad (2.18)$$

Then using (2.16) and (2.18), one can show that p satisfies (1.6). Also, Eqs. (2.4) and (2.17) imply (1.5).

To summarize, in this section we have derived the Smoluchowski equation (1.6) from the Fokker-Planch equation (1.3). In so doing, we have shown that the Smoluchowski equation remains valid if the potential and spatial derivatives of the solution are suitably large. We have not derived the initial condition (1.7) from (1.4), but we remark that it can be derived by means of an asymptotic "initial layer" analysis of Eqs. (1.3) and (1.4).[8]

III. HOMOGENIZED SMOLUCHOWSKI EQUATION

In this section, we analyze (2.15) and (2.16), which we have shown are equivalent to (1.5) and (1.6). Equation (2.16) has the equilibrium solution $\mathfrak{a} = \text{const}$. Thus, after a finite relaxation time, we expect $\mathfrak{a}$ to be nearly constant, i.e., $\mathfrak{a}_\sigma$ and $\vec{\nabla}_r \mathfrak{a}$ to be small. We therefore take

$$\mathfrak{a} \sim \sum_{n=0}^{\infty} \delta^n f_n(\vec{r}, \vec{r}', \sigma'') , \quad (3.1)$$

with

$$\begin{aligned} \vec{r}' &= \delta \vec{r} , \\ \sigma'' &= \delta^2 \sigma , \end{aligned} \quad (3.2)$$

and

$$\delta \ll 1 .$$

The variables $\vec{r}'$ and σ'' describe slow changes of $\mathfrak{a}$ in space and time; δ is an artificial small parameter which does not appear in the final results. Since (2.16) contains $\phi(\vec{r})$, which is periodic across a cell, we allow each f_n to depend on $\vec{r}$ periodically.

Introducing (3.1) and (3.2) into (2.16) and equating the coefficients of different powers of δ, we obtain the following sequence of equations:

$$\begin{aligned} 0 &= \lambda \Delta_r f_n - \vec{\nabla}_r \phi \cdot \vec{\nabla}_r f_n \\ &\quad + 2\lambda \vec{\nabla}_{r'} \cdot \vec{\nabla}_r f_{n-1} - \vec{\nabla}_r \phi \cdot \vec{\nabla}_{r'} f_{n-1} \\ &\quad + \lambda \Delta_{r'} f_{n-2} - \frac{\partial}{\partial \sigma''} f_{n-2} . \end{aligned} \quad (3.3)$$

Setting $n=0$ in (3.3) yields

$$0 = L f_0 = \lambda \Delta_r f_0 - \vec{\nabla}_r \phi \cdot \vec{\nabla}_r f_0 , \quad (3.4)$$

which has the "constant" solution

$$f_0 = F(\vec{r}', \sigma'') . \quad (3.5)$$

The operator L acts on a space of functions $f(\vec{r})$, each of which is periodic in $\vec{r}$ across a cell C. To be more precise, we shall assume that ∂C consists of $2n$ planar faces, and we require

$$f(\vec{r}) = f(\vec{r} + \vec{l}_i) , \quad |i| = 1, \ldots, n , \quad (3.6)$$

where $\vec{l}_i$ are vectors which connect a point on the ith face to its related point on the opposite ($-i$th) face and $\vec{l}_i = -\vec{l}_i$ (see Fig. 1).

It can be shown that L^*, the adjoint of L, is

$$L^* f(\vec{r}) = \lambda \Delta_r f + \vec{\nabla}_r \cdot f \vec{\nabla}_r \phi , \quad (3.7)$$

and that

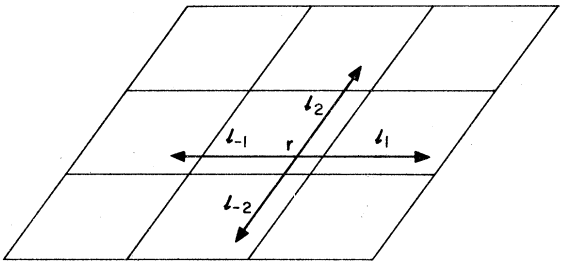

FIG. 1. Representation of a two-dimensional lattice and the vectors $\vec{l}_{i'}$.

$$L^*(e^{-\phi(\vec{r})/\lambda}) = 0 . \tag{3.8}$$

Next we set $n=1$ in (3.3) and get

$$0 = Lf_1 - \vec{\nabla}_r\phi(\vec{r}) \cdot \vec{\nabla}_{r'}F(\vec{r}', \sigma'') . \tag{3.9}$$

For a solution f_1 to exist, a solvability condition must be met.[9] This condition is obtained by multiplying (3.9) by $e^{-\phi/\lambda}$ and integrating over a cell. By (3.8), the resulting condition is

$$0 = -\int_C e^{-\phi/\lambda}\vec{\nabla}_r\phi \cdot \vec{\nabla}_{r'}F\, d^3r$$

$$= \lambda \int_C \vec{\nabla}_{r'}F(\vec{r}', \sigma'') \cdot \vec{\nabla}_r e^{-\phi(\vec{r})/\lambda}\, d^3r$$

$$= \lambda \vec{\nabla}_{r'}F(\vec{r}', \sigma'') \cdot \int_{\partial C} \vec{n}(\vec{r}) e^{-\phi/\lambda}\, d^2r .$$

But the surface integral vanishes, so this solvability condition is automatically satisfied.

Thus (3.9) has the solution

$$f_1 = (L^{-1}\vec{\nabla}_r\phi(\vec{r})) \cdot \vec{\nabla}_{r'}F(\vec{r}', \sigma'') , \tag{3.10}$$

where the scalar operator L^{-1} is the pseudoinverse of L, defined uniquely as follows: for a periodic function $f(\vec{r})$ satisfying

$$0 = \int_C e^{-\phi/\lambda} f\, d^3r ,$$

$L^{-1}f$ is the unique solution of the equation

$$L(L^{-1}f) = f ,$$

which satisfies

$$0 = \int_C e^{-\phi/\lambda} L^{-1}f\, d^3r .$$

Next, we set $n=2$ in (3.3) and apply the solvability condition, obtaining

$$\frac{\partial F}{\partial \sigma''}\left(\int_C e^{-\phi/\lambda}\, d^3r\right)$$

$$= \vec{\nabla}_{r'} \cdot \left(\int_C e^{-\phi/\lambda}[\lambda \vec{\vec{I}} - (\vec{\nabla}_r\phi)L^{-1}(\vec{\nabla}_r\phi)$$

$$+ 2\lambda \vec{\nabla}_r L^{-1}(\vec{\nabla}_r\phi)]\, d^3r \right) \cdot \nabla_{r'}F . \tag{3.11}$$

However, Green's theorem gives

$$\int_C e^{-\phi/\lambda} 2\lambda \vec{\nabla}_r L^{-1}(\vec{\nabla}_r\phi)\, d^3r$$

$$= \int_C e^{-\phi/\lambda} 2(\vec{\nabla}_r\phi)L^{-1}(\vec{\nabla}_r\phi)\, d^3r ,$$

so (3.11) reduces to

$$\frac{\partial F}{\partial \sigma''} = \vec{\nabla}_{r'} \cdot \vec{\vec{M}} \cdot \vec{\nabla}_{r'}F , \tag{3.12}$$

where the constant diffusion tensor $\vec{\vec{M}}$ is defined by

$$\vec{\vec{M}} = \frac{\int_C e^{-\phi/\lambda}[\lambda \vec{\vec{I}} + (\vec{\nabla}_r\phi)L^{-1}(\vec{\nabla}_r\phi)]\, d^3r}{\int_C e^{-\phi/\lambda}\, d^3r} . \tag{3.13}$$

To leading order in δ, (3.1), (3.2), and (3.5) imply

$$\mathcal{A}(\vec{r}, \sigma) = F(\delta\vec{r}, \delta^2\sigma) ,$$

and then (3.12) yields

$$\frac{\partial \mathcal{A}}{\partial \sigma} = \vec{\nabla}_r \cdot \vec{\vec{M}} \cdot \vec{\nabla}_r \mathcal{A} . \tag{3.14}$$

Next, (2.18) can be written as

$$p(\vec{x}, t) = e^{(-m/kT)\Phi(\vec{x})} u(\vec{x}, t) , \tag{3.15}$$

with

$$u(\vec{x}, t) = \mathcal{A}\left(\frac{1}{l}\vec{x}, \frac{v_0^2}{\beta l^2}\, t\right) l^3 v_0^3 , \tag{3.16}$$

and by (3.14), the equation governing u is

$$\beta \frac{\partial u}{\partial t} = \vec{\nabla}_x \cdot \vec{\vec{D}} \cdot \vec{\nabla}_x u , \tag{3.17}$$

where

$$\vec{\vec{D}} = v_0^2 \vec{\vec{M}} . \tag{3.18}$$

Equations (3.15) and (3.17) are identical to (1.8) and (1.9), stated earlier. As a check, we see from (3.13) that for $\Phi = 0$, $\vec{\vec{M}} = \lambda \vec{\vec{I}}$, so $\vec{\vec{D}} = v_0^2 \lambda \vec{\vec{I}} = (kT/m)\vec{\vec{I}}$. Thus, for $\Phi = 0$, the homogenized Smoluchowski equation (3.17) reduces to the original Smoluchowski equation (1.6), as it should. Of course, the dependent variables in these equations, u and p, are also identical by virtue of (1.8).

Finally, we note that we have not derived the initial condition (1.10) from (1.7), but as before, we remark that it can be derived by means of an initial layer analysis of (1.6) and (1.7).

IV. DIFFUSION TENSOR FOR LARGE ACTIVATION ENERGY

In this section, we analyze the results of Sec. III for $\phi = 0(1/\epsilon)$. However, first we must rewrite $\vec{M}$ in a more useful form. From (3.13) and (3.4),

$$\vec{M} = \frac{\int_C e^{-\phi/\lambda}[\lambda \vec{I} + (\vec{\nabla}_r \phi)(\vec{\chi})]\, d^3r}{\int_C e^{-\phi/\lambda}\, d^3r},$$

where

$$\lambda \Delta_r \vec{\chi} - (\vec{\nabla}_r \phi \cdot \vec{\nabla}_r)\vec{\chi} = \vec{\nabla}\phi$$

in C, and $\vec{\chi}$ is periodic across C.

Introducing $\vec{\chi} = -\vec{r} + \vec{\Psi}$, we obtain (after an integration by parts)

$$\vec{M} = \lambda \int_C e^{-\phi/\lambda} \vec{\nabla}\vec{\Psi}\, d^3r \Big/ \int_C e^{-\phi/\lambda}\, d^3r, \tag{4.1}$$

where $\vec{\Psi}$ satisfies the equation

$$\vec{\nabla} \cdot (e^{-\phi/\lambda} \vec{\nabla}\vec{\Psi}) = \vec{0}. \tag{4.2}$$

Equation (4.2) shows that the integrand in the numerator of (4.1) is divergence free. Thus we make use of the summation convention to obtain

$$\begin{aligned}\int_C e^{-\phi/\lambda} \frac{\partial}{\partial r_i} \Psi_j\, d^3r &= \int_C \left(\frac{\partial}{\partial r_k} r_i\right) e^{-\phi/\lambda} \frac{\partial}{\partial r_k} \Psi_j\, d^3r \\ &= \int_C \frac{\partial}{\partial r_k}\left(r_i e^{-\phi/\lambda} \frac{\partial}{\partial r_k} \Psi_j\right) d^3r \\ &= \int_{\partial C} e^{-\phi/\lambda} r_i \left(\nu_k \frac{\partial}{\partial r_k}\right)\Psi_j\, d^2r,\end{aligned}$$

where $\vec{\nu}$ is the outer normal. Therefore,

$$\vec{M} = \lambda \int_{\partial C} e^{-\phi/\lambda} \vec{r} \frac{\partial}{\partial \nu} \vec{\Psi}\, d^2r \int e^{-\phi/\lambda}\, d^3r, \tag{4.3}$$

where $\partial/\partial\nu = \vec{\nu} \cdot \vec{\nabla}_r$ is the outer normal derivative. The problem for $\vec{\Psi}$ can be taken to be

$$\lambda \Delta_r \vec{\Psi} - (\vec{\nabla}\phi \cdot \vec{\nabla})\vec{\Psi} = \vec{0} \quad \text{in } C, \tag{4.4}$$

$$\vec{\Psi} = \vec{r} + \vec{\chi}(\vec{r}) \quad \text{on } \partial C, \tag{4.5}$$

where $\vec{\chi}(\vec{r}) = \vec{\chi}(\vec{r} + \vec{I}_i)$ for $\vec{r}$ a point on the ith face. [See Eq. (3.6).]

Now we assume that ϕ is large. Thus, as in (2.3), we set

$$\phi = (1/\epsilon)\phi_0,$$

and then

$$\vec{M} = \lambda \int_{\partial C} e^{-\phi_0/\epsilon\lambda} \vec{r} \frac{\partial}{\partial \nu} \vec{\Psi}\, d^2r \int_C e^{-\phi_0/\epsilon\lambda}\, d^3r, \tag{4.6}$$

$$\epsilon\lambda \Delta_r \vec{\Psi} - (\vec{\nabla}_r \phi_0 \cdot \vec{\nabla}_r)\vec{\Psi} = \vec{0} \text{ in } C, \tag{4.7}$$

$$\vec{\Psi} = \vec{r} + \vec{\chi}(\vec{r}) \quad \text{on } \partial C. \tag{4.8}$$

If $\vec{r} = \vec{0}$ is taken to be the (single) point in C at which the minimum value of ϕ occurs, then[7]

$$\int_C e^{-\phi_0/\epsilon\lambda}\, d^3r \approx (2\pi\epsilon\lambda)^{3/2} \mathcal{H}^{-1/2}(\phi_0, \vec{0}) e^{-\phi_0(\vec{0})/\epsilon\lambda}, \tag{4.9}$$

$$\mathcal{H}(\phi_0, \vec{0}) = \det \frac{\partial}{\partial r_j} \frac{\partial}{\partial r_k} \phi_0(\vec{0}), \quad j,k = 1,2,3. \tag{4.10}$$

Also if $\vec{r}_i$ denote the points on ∂C at which ϕ takes on (local) minima, then[7]

$$\begin{aligned}\int_{\partial C} e^{-\phi_0/\epsilon\lambda} \vec{r} \frac{\partial}{\partial \nu} \vec{\Psi}\, d^2r &\\ \approx 2\pi\epsilon\lambda \sum_i H^{-1/2}(\phi_0, \vec{r}_i) e^{-\phi_0(\vec{r}_i)/\epsilon\lambda} \vec{r}_i \frac{\partial}{\partial \nu} \vec{\Psi}(\vec{r}_i),&\end{aligned} \tag{4.11}$$

where

$$H(\phi_0, \vec{r}_i) = \det \frac{\partial}{\partial r_j'} \frac{\partial}{\partial r_k'} \phi_0(\vec{r}_i), \quad j,k = 1,2, \tag{4.12}$$

and r_1', r_2' are local tangential coordinates on ∂C near $\vec{r}_i$. Thus to determine $\vec{M}$ it remains to determine $\partial\vec{\Psi}/\partial\nu$ at the points $\vec{r}_i$, which are saddle points for ϕ.

To do this we argue that $\vec{\Psi}$ is a boundary layer which quickly decays to zero away from ∂C. Thus, along the line $\vec{r}_i + s\vec{\nu}$ we take, for $|s|$ small,

$$\begin{aligned}&\vec{\Psi}(\vec{r}_i + s\vec{\nu}) = \vec{F}(\eta), \quad \eta = s/\sqrt{\epsilon}, \\ &\lim_{\eta \to -\infty} \vec{F} = 0, \quad \vec{F}(0) = \vec{r}_i + \vec{\chi}(\vec{r}_i)\end{aligned} \tag{4.13}$$

and

$$\phi_0(\vec{r}_i + s\vec{\nu}) \approx \phi_0(\vec{r}_i) + \tfrac{1}{2} s^2 \left(\frac{\partial}{\partial \nu}\right)^2 \phi_0(\vec{r}_i).$$

To leading order (i.e., ignoring the transverse derivatives), Eq. (4.7) becomes

$$\lambda F''(\eta) - \eta \left(\frac{\partial}{\partial \nu}\right)^2 \phi_0(\vec{r}_i) F'(\eta) = \vec{0}.$$

This equation and (4.13) have the solution

$$\begin{aligned}\vec{\Psi}(\vec{r}_i + s\vec{\nu}) = [\vec{r}_i + \vec{\chi}(\vec{r}_i)] \left(\frac{2}{\lambda\pi}\right)^{1/2} \left| \left(\frac{\partial}{\partial \nu}\right)^2 \phi_0(\vec{r}_i) \right|^{1/2} &\\ \times \int_{-\infty}^{s/\sqrt{\epsilon}} \exp\left[\frac{t^2}{2\lambda} \left(\frac{\partial}{\partial \nu}\right)^2 \phi_0(\vec{r}_i)\right] dt.&\end{aligned}$$

Thus

$$\frac{\partial}{\partial \nu} \vec{\Psi}(\vec{r}_i) = [\vec{r}_i + \vec{\chi}(\vec{r}_i)] \left(\frac{2}{\epsilon\lambda\pi}\right)^{1/2} \left| \left(\frac{\partial}{\partial \nu}\right)^2 \phi_0(\vec{r}_i) \right|^{1/2}. \tag{4.14}$$

Now we combine (4.6), (4.9), (4.11), and (4.14) to get

$$\vec{M} = \frac{1}{\pi\epsilon}\,\mathcal{K}^{1/2}(\phi_0,\vec{0})\sum_i \vec{r}_i\vec{r}_i\left|\left(\frac{\partial}{\partial\nu}\right)^2\phi_0(\vec{r}_i)\right|^{1/2} H^{-1/2}(\phi_0,\vec{r}_i)\exp\left(-\frac{1}{\epsilon\lambda}\left[\phi_0(\vec{r}_i)-\phi_0(\vec{0})\right]\right). \tag{4.15}$$

We note that the terms $\vec{\chi}(\vec{r}_i)$ have cancelled out because $\vec{\chi}(\vec{r}_i)=\vec{\chi}(\vec{r}_{-i})=\vec{\chi}(-\vec{r}_i)$. Therefore all of the quantities in (4.15) are known.

Converting to the (original) dimensional variables and using Eqs. (3.18), (2.3), (2.2), and (2.1) we obtain

$$\vec{D} = \frac{1}{\pi}\,\mathcal{K}^{1/2}(\Phi,\vec{0})\sum_i \vec{x}_i\vec{x}_i|\Phi_{nn}(\vec{x}_i)|^{1/2}H^{-1/2}(\Phi,\vec{x}_i)\exp\left(-\frac{m}{kT}\left[\Phi(\vec{x}_i)-\Phi(\vec{0})\right]\right). \tag{4.16}$$

Here $\mathcal{K}$ and H are defined as in (4.10) and (4.12), except for the derivatives which are taken with respect to $\vec{x}$ instead of $\vec{r}$. Also, $\Phi_{nn}(\vec{x}_i)$ denotes the second normal derivative of Φ at the saddle point $\vec{x}_i$.

V. ONE-DIMENSIONAL PROBLEMS

To illustrate the homogenization method in Sec. III and the method of expansion for a large potential in Sec. IV, we consider a one-dimensional potential well, since for this the calculations are simpler and more explicit. The Smoluchowski equation (2.16) becomes, in one spatial dimension,

$$\frac{\partial\mathcal{A}}{\partial\sigma} = \lambda\frac{\partial^2\mathcal{A}}{\partial r^2} - \phi'(r)\frac{\partial\mathcal{A}}{\partial r}\,. \tag{5.1}$$

Here ϕ is periodic: $\phi(r)=\phi(r+1)$. As in Eq. (3.1), we set

$$\mathcal{A} \sim \sum_{n=0}^{\infty}\delta^n f_n(r,r',\sigma''), \tag{5.2}$$

with

$$r' = \delta r\,,\quad \sigma'' = \delta^2\sigma\,,\quad \delta \ll 1\,, \tag{5.3}$$

and we require each f_n to be periodic in r with period 1.

We introduce (5.2) and (5.3) into (5.1) to obtain the system

$$0 = \left[\lambda\frac{\partial^2}{\partial r^2}f_n - \phi'(r)\frac{\partial}{\partial r}f_n\right] + \left[2\lambda\frac{\partial}{\partial r'}\frac{\partial}{\partial r}f_{n-1} - \phi'(r)\frac{\partial}{\partial r'}f_{n-1}\right] + \left[\lambda\left(\frac{\partial}{\partial r'}\right)^2 f_{n-2} - \frac{\partial}{\partial\sigma''}f_{n-2}\right], \tag{5.4}$$

and as before, the $n=0$ equation gives

$$f_0 = F(r',\sigma''). \tag{5.5}$$

We next set $n=1$ in Eq. (5.4) and get

$$0 = \lambda\frac{\partial^2}{\partial r^2}f_1 - \phi'(r)\frac{\partial}{\partial r}f_1 - \phi'(r)\frac{\partial}{\partial r'}F(r',\sigma''). \tag{5.6}$$

As before, the solvability condition (i.e., multiply by $e^{-\phi/\lambda}$ and integrate over $0\le r\le 1$) is satisfied automatically. But now, Eq. (5.6)—along with the periodicity condition—is an ordinary differential equation which can be solved explicitly, giving:

$$f_1 = \left[-r + \frac{\int_0^r e^{\phi(s)/\lambda}\,ds}{\int_0^1 e^{\phi(s)/\lambda}\,ds}\right]\frac{\partial F}{\partial r'}(r',\sigma''). \tag{5.7}$$

We now set $n=2$ in (5.4), introduce (5.5) and (5.7), and apply the solvability condition. After integrating by parts and rearranging, this solvability condition reduces to

$$\frac{\partial F}{\partial\sigma''} = \frac{\lambda}{\left(\int_0^1 e^{\phi/\lambda}\,ds\right)\left(\int_0^1 e^{-\phi/\lambda}\,ds\right)}\left(\frac{\partial}{\partial r'}\right)^2 F \tag{5.8}$$

which is the one-dimensional version of (3.12). If we return to the original variables using (5.3), (2.7), (2.1), and define

$$u(x,t) = \mathcal{A}\left(\frac{1}{l}x, \frac{v_0^2}{\beta l^2}t\right) l^3v_0^3 \approx F\left(\frac{\delta}{l}x, \frac{\delta^2v_0^2}{\beta l^2}t\right) l^3v_0^3,$$

then by (5.8), the equation governing the dimensional quantity u is

$$\beta\frac{\partial u}{\partial t} = \left[\frac{kT}{m}\,\frac{l^2}{\left(\int_0^l e^{(m/kT)\Phi(s)}\,ds\right)\left(\int_0^l e^{-(m/kT)\Phi(s)}\,ds\right)}\right]\frac{\partial^2 u}{\partial x^2}\,. \tag{5.9}$$

Here l is the dimensional width of a cell: $\Phi(x) = \Phi(x+l)$.

The diffusion coefficients in (5.8), (5.9) can be evaluated asymptotically for large Φ. if

$$\Phi(x) = \Phi(x_0) + \tfrac{1}{2}(x - x_0)^2\Phi''(x_0) + \cdots$$

is the Taylor series expansion for Φ at its minimum value, and $\Phi''(x_0) > 0$, then for large Φ,

$$\int_0^l e^{(-m/kT)\Phi(s)}\,ds \approx \left(\frac{2\pi kT}{m\Phi''(x_0)}\right)^{1/2} e^{(-m/kT)\Phi(x_0)}. \quad (5.10)$$

Also, if

$$\Phi(x) = \Phi(x_1) + \tfrac{1}{2}(x - x_1)^2\Phi''(x_1) + \cdots$$

is the Taylor series expansion for Φ at its maximum values, and $\Phi''(x_1) < 0$, then for large Φ,

$$\int_0^l e^{(m/kT)\Phi(s)}\,ds \approx \left(\frac{2\pi kT}{-m\Phi''(x_1)}\right)^{1/2} e^{(m/kT)\Phi(x_1)}. \quad (5.11)$$

Combining (5.9)–(5.11), we obtain, for large Φ,

$$\beta\frac{\partial u}{\partial t} = \left(\frac{l^2}{2\pi}\right)[\Phi''(x_0)]^{1/2}[-\Phi''(x_1)]^{1/2} \times \exp\left(-\frac{m}{kT}\,[\Phi(x_1) - \Phi(x_0)]\right)\frac{\partial^2 u}{\partial x^2}. \quad (5.12)$$

Formula (5.12) is the one-dimensional version of (4.16). Making notational adjustments, it is equivalent to the results obtained by Kramers for the escape of particles over potential barriers.[3] Also, see Ref. 2, Eq. (476).

VI. DISCUSSION

It is worthwhile to compare the homogenization procedure with the random walk approach of Matkowsky and Schuss[7] and others. Such an approach is based on the average exit time $\bar{\tau}$ of a particle from a cell, and on assuming that ϕ is large. It is shown in Ref. 7 that $\bar{\tau}(\vec{r})$, the average exit time of a particle from a cell, given that the particle was initially at the point $\vec{r}$, satisfies the problem

$$\lambda\Delta_r\bar{\tau} - \vec{\nabla}_r\phi \cdot \vec{\nabla}_r\bar{\tau} = -1 \quad \text{in } C$$
$$\bar{\tau} = 0 \quad \text{on } \partial C.$$

The asymptotic solution (for large ϕ) satisfies

$$\frac{1}{\bar{\tau}} \equiv \frac{1}{\bar{\tau}(\vec{0})} \approx \frac{1}{2\pi}\,\mathcal{K}^{1/2}(\vec{0}) \sum_j |\phi_{vv}(\vec{r}_j)|^{1/2} H^{-1/2}(\vec{r}_j) \exp\{-(1/\lambda)[\phi(\vec{r}_j) - \phi(\vec{0})]\}. \quad (6.1)$$

Next, the probability $p(\vec{r}, \vec{z})$ that a particle initially at $\vec{r}$ in C will leave the cell at $\vec{z}$ in ∂C is shown in Ref. 7 to be the Green's function of the Dirichlet problem

$$\lambda\Delta_r U - \vec{\nabla}_r\phi \cdot \vec{\nabla}_r U = 0 \quad \text{in } C$$
$$u = f \quad \text{on } \partial C.$$

The asymptotic solution (for large ϕ) is computed to be

$$p(\vec{r}, \vec{z}) = \sum_i p_i \delta(\vec{z} - \vec{r}_i),$$

where p_i, the probability of exit from $\vec{r}_i$, is

$$p_i = \frac{|\phi_{vv}(\vec{r}_i)|^{1/2} H^{-1/2}(\vec{r}_i) \exp(-(1/\lambda)[\phi(\vec{r}_i) - \phi(\vec{0})])}{\sum_j |\phi_{vv}(\vec{r}_j)|^{1/2} H^{-1/2}(\vec{r}_j) \exp(-(1/\lambda)[\phi(\vec{r}_j) - \phi(0)])} \quad (6.2)$$

(Note that p is asymptotically independent of $\vec{r}$.)

Now since the structure of a cell is symmetric about its center point ($\vec{r} = \vec{0}$), then there are an even number of boundary points at which ϕ has a minimum ($\vec{r}_{-i} = -\vec{r}_i$, with $i = 1, \ldots, n$, and $p_{-i} = p_i$).

Also if $\vec{r}$ is the center of an arbitrary cell, then $\vec{r} - 2\vec{r}_i$ are the centers of the adjoining cells, and

$$P(\vec{r}, (n+1)\bar{\tau}) = \sum_i p_i P(\vec{r} - 2\vec{r}_i, n\bar{\tau}),$$
$$P(\vec{r}, 0) = \delta(\vec{r}_0), \quad (6.3)$$

where $P(\vec{r}, n\bar{\tau})$ is the probability of arriving at $\vec{r}$ in n jumps $\bar{\tau}$ apart, given that initially the particle was at $\vec{r}_0$.

Expanding (6.3) about $\vec{r}$ and $\sigma = n\tau$ and invoking symmetry, we get

$$\frac{\partial}{\partial\sigma}P = \vec{\nabla}_r \cdot \left(\frac{2}{\tau}\sum_i p_i \vec{r}_i \vec{r}_i\right) \cdot \vec{\nabla}_r P. \quad (6.4)$$

Combining (6.4), (6.2), and (6.1), formulas (3.14) and (4.15) follow.

In Eqs. (3.17) and (4.16), $\mathcal{K}(\Phi, \vec{0})$ is the Hessian of the potential evaluated at the bottom of the cell. It is known from classical mechanics that $\mathcal{K}^{1/2}(\Phi, \vec{0})$ is the product of the principal frequencies of vibration of the particle at the bottom of the cell. Thus the faster it oscillates, the more likely is the particle to jump to the next cell.

The term $H^{1/2}(\Phi, \vec{x}_i)$ is the product of the tangential frequencies at the points $\vec{x}_i$, which are saddle points for Φ. The faster are these oscillations at $\vec{x}_i$ the longer will the particle stay at $\vec{x}_i$, thus lowering the diffusion rate. Both terms $\mathcal{K}^{1/2}$ and $H^{1/2}$

are present in Vineyard's[4] and Glyde's[5] papers. However, the terms $|\Phi_{mn}(x_i)|^{1/2}$ do not appear in Refs. 4 and 5, although they do appear in Refs. 2 and 3. These are related to the curvature at $\vec{x}_i$ in the direction across the saddle point, which is the direction of the path the particle takes upon jumping to the next cell. Thus the flatter the path through the saddle point, the thicker is the potential barrier, and so (thinking quantum mechanically) the longer the particle takes to escape.

Formula (4.16) accounts for anisotropy in the diffusion rates in different directions due to different jump rates in different directions. For example, in the hexagonal zinc lattice the diffusion is isotropic in the hexagonal plane, but this rate is different by an exponential factor from the rate of diffusion from one plane to another.

It is worthwhile to note that our analysis, although three dimensional, can be extended to any number of degrees of freedom, as in Refs. 4 and 5. Also, we emphasize that our analysis (in Sec. III) is more general than in Refs. 4 and 5 because it holds for small, intermediate, and large potentials; only for large potentials can one make approximations to obtain formulas similar to those in Refs. 4 and 5.

APPENDIX

The following identities were used to derive the Smoluchowski equation in Sec. II. In these identities, $\vec{A}$ and $\vec{B}$ are constant vectors, and $\vec{\vec{M}}$ is a constant 3×3 tensor:

$$(\vec{\omega}\circ\vec{\nabla}_\omega-\lambda\Delta_\omega)(\vec{\omega}\cdot\vec{A})=\vec{\omega}\circ\vec{A}, \tag{A1}$$

$$(\vec{\omega}\cdot\vec{\nabla}_\omega-\lambda\Delta_\omega)[\vec{A}\circ(\tfrac{1}{2}\vec{\omega}\vec{\omega})\circ\vec{B}]=A\circ(\vec{\omega}\vec{\omega}-\lambda\vec{\vec{I}})\cdot\vec{B}, \tag{A2}$$

$$(\vec{\omega}\circ\vec{\nabla}_\omega-\lambda\Delta_\omega)[\tfrac{1}{3}(\vec{\omega}\cdot\vec{A})^3+2\lambda(\vec{A}\circ\vec{A})(\vec{\omega}\cdot\vec{A})]=(\vec{\omega}\cdot\vec{A})^3, \tag{A3}$$

$$(\vec{\omega}\circ\vec{\nabla}_\omega-\lambda\Delta_\omega)[\tfrac{1}{4}(\vec{\omega}\cdot\vec{A})^4+\tfrac{3}{2}\lambda(\vec{A}\cdot\vec{A})(\vec{\omega}\circ\vec{A})^2]=(\vec{\omega}\circ\vec{A})^4-3\lambda^2(\vec{A}\circ\vec{A})^2, \tag{A4}$$

$$(\vec{\omega}\circ\vec{\nabla}_\omega-\lambda\Delta_\omega)(\vec{\omega}\circ\vec{\vec{M}}\circ\vec{\omega})=2[\vec{\omega}\circ\vec{\vec{M}}\circ\vec{\omega}-\lambda(M_{11}+M_{22}+M_{33})]. \tag{A5}$$

Also, the equation

$$(\vec{\omega}\cdot\vec{\nabla}_\omega-\lambda\Delta_\omega)f(\vec{\omega})=1$$

has the particular solution

$$f(\vec{\omega})=-\frac{1}{\lambda}\int_{r=0}^{\omega}\frac{e^{r^2/2\lambda}}{r^2}\int_{s=0}^{r}s^2e^{-s^2/2\lambda}ds. \tag{A6}$$

This solution grows exponentially as $\omega\to\infty$.

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