Some aspects of cluster diffusion on surfaces[a)]

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We consider models, based on a master equation, for the motion of bound clusters of adatoms, over a crystalline surface or along one-dimensional channels on such a surface. In particular, we outline efficient methods for determining the diffusion tensor and other quantities that characterize the motion of such clusters for long times.

I. INTRODUCTION

Recent advances in experimental techniques, especially field ion microscopy,[1] have made it possible to perform detailed experiments on the migration of clusters of adatoms on crystal surfaces. These experiments open the possibility of determining the rates for the various single-adatom jumps through which the cluster migration proceeds. Accordingly, a number of theoretical treatments of this problem have appeared. In particular, Reed and Ehrlich[2] and Wrigley, Reed, and Ehrlich[3] have given an exhaustive theoretical treatment of a number of models for the one-dimensional motion of dimers and trimers, based on a master equation description. Landman and Shlesinger[4] presented a general framework for problems of this type, based on the continuous-time random walk formalism,[5] as well as some case studies.

The aim of the present paper is not to formulate an alternative general treatment, but rather to point out some simple ways in which more limited information about cluster diffusion can be extracted from a stochastic model. For example, the diffusion coefficient, or diffusion tensor, can be determined with minimal calculational effort by exploiting the analogy with an equivalent electrical network of capacitors and resistors.[6] Similarly, when the available experimental information concerns only the long-time behavior of certain average moments of the distance traveled by the center of mass of the cluster, the only information needed from the theoretical model is the behavior of the lowest, "acoustical" branch of the spectrum of relaxation times of the master equation describing the system. We hope that by concentrating on the most economical way of obtaining certain partial information, our treatment may be of some assistance in facilitating the analysis of experimental data.

In Sec. II, we formulate the basic underlying master equation that constitutes our theoretical description. We choose a parametrization of the transition rates that brings out clearly the symmetry inherent in the detailed balance requirement. In addition, it separates those parameters that are relevant for determining the effective diffusion coefficient from those that can only be provided by more refined measurements. A similar parametrization proved useful in an earlier study of diffusion in random chains.[7] In the remainder of Sec. II, we reduce the solution of the master equation to that of a wave vector dependent matrix eigenvalue problem.

In Sec. III, we point out the relation between the asymptotic growth rate of certain averaged moments of the distance traveled by the center of mass of the cluster and the secular determinant of the matrix introduced in Sec. II. In Sec. IV, we discuss in particular the diffusion coefficient and several independent ways of measuring and calculating it.

In Secs. V and VI, we present a few case studies of dimer and trimer diffusion. For a symmetric dimer, the diffusion coefficient is equal to the *short-time* rate of increase of the averaged square of the distance traveled by the cluster center of mass. For a three-state symmetric dimer, the asymptotic growth rate of the fourth order cumulant of this distance is also a simple function of the system parameters. The use of the electric network analogy to calculate the diffusion coefficient is demonstrated for models of an asymmetric three-state dimer and a nine-state trimer. The final section contains a few concluding remarks.

II. BASIC EQUATIONS

Consider a cluster of n particles, each of which may occupy points on a regular Bravais lattice in d dimensions. Our interest is in motion over surfaces ($d=2$), but one-dimensional models may be used to describe diffusion on surfaces with highly anisotropic mobility or diffusion of clusters bound to a step discontinuity on the surface. We assume the cluster can exist in S internal configurations, labeled by the index $s=1,2,\ldots,S$, with characteristic energies E_s. (In many situations it will be more appropriate to use configurational *free* energies; in such cases E_s denotes this free energy.) The energies E_s enter our equations via the statistical weights α_s^{-1} defined by

$$\alpha_s^{-1}=\exp(-E_s/k_BT)\sum_{t=1}^{S}\exp(-E_t/k_BT)\,, \tag{2.1}$$

with T the substrate temperature and k_B Boltzmann's constant. The state of the cluster is described completely by its configuration s and the position of its center of mass $\mathbf{r}_s$; the possible values of $\mathbf{r}_s$ are $\mathbf{R}_l+\boldsymbol{\rho}_s$ with $\mathbf{R}_l$ a vector from the substrate lattice and $\boldsymbol{\rho}_s$ a vector inside its unit cell. A jump from configuration s to configuration t causes a shift $\boldsymbol{\rho}_{ts}$ of the center of mass. If

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we assume that only jumps changing the position of one of the cluster particles are allowed, then there is a unique ρ_{ts} for each jump for clusters of three or more particles. Furthermore, we must have $\rho_{st} = -\rho_{ts}$. For dimers, the same configuration change can be caused by two distinct transitions, either by the leading or by the trailing particle. They have, in general, different rates and always different ρ_{st}, differing by a lattice vector. For a symmetric dimer the rates are equal when detailed balance holds and the two ρ_{st} are equal in magnitude and opposite in direction. The difference between dimers and larger clusters indicated above stems from the fact that the "parallel" translation of a cluster of n particles towards a state with the same internal configuration but a different position of the center of mass may be carried out in n jumps, one for each constituent particle. Specific examples will be given in Secs. V and VI.

We shall assume that the probability $P_s(\mathbf{r}_s, \tau)$ of finding the cluster at time τ in configuration s with center of mass at $\mathbf{r}_s$ changes according to the master equation

$$\frac{d}{d\tau} P_s(\mathbf{r}_s, \tau) = \sum_{t \neq s} [\alpha_t \beta_{st} P_t(\mathbf{r}_s - \rho_{st}, \tau) - \alpha_s \beta_{ts} P_s(\mathbf{r}_s, t)] , \tag{2.2}$$

where we write the transition rate from configuration s to configuration t in the form $\alpha_s \beta_{ts}$.

(For dimers there are two terms for each t corresponding to the two different ρ_{st}.) When the microscopic dynamics underlying the mesoscopic description in Eq. (2.2) is invariant under time reversal, then the master Eq. (2.2) fulfills detailed balance, which, for the parametrization of transition rates chosen in Eq. (2.2), is expressed by the relation

$$\beta_{st} = \beta_{ts} . \tag{2.3}$$

In view of the translational invariance of the substrate, the β_{st} do not depend on the center-of-mass position.

We can exploit this translational invariance further by introducing Fourier transforms via

$$P_s(\mathbf{r}_s, \tau) = \exp(-i\mathbf{k} \cdot \mathbf{r}_s) P_{s\mathbf{k}}(\tau) ; \tag{2.4}$$

the $P_{s\mathbf{k}}(\tau)$ then obey the equation

$$\frac{d}{d\tau} P_{s\mathbf{k}}(\tau) = \sum_{t \neq s} [\alpha_t \beta_{st} \exp(i\mathbf{k} \cdot \rho_{st}) P_{t\mathbf{k}}(\tau) - \alpha_s \beta_{ts} P_{s\mathbf{k}}(\tau)] \tag{2.5}$$

for general clusters. For dimers one has two terms for each t. For the special case of symmetric dimers one obtains

$$\frac{d}{d\tau} P_{s\mathbf{k}}(\tau) = \sum_{t \neq s} [2\alpha_t \beta_{st} \cos(\mathbf{k} \cdot \rho_{st}) P_{t\mathbf{k}}(\tau) - 2\alpha_s \beta_{ts} P_{s\mathbf{k}}(\tau)] . \tag{2.6}$$

Any solution of Eq. (2.2) can be obtained by combining solutions of type Eq. (2.4) with $P_{s\mathbf{k}}(\tau)$ obeying Eq. (2.5) and $\mathbf{k}$ taken from the first Brillouin zone of the substrate lattice.

Associated with the evolution problem Eqs. (2.5) or (2.6) one has the eigenvalue problem

$$-\lambda_i(\mathbf{k}) P^i_{s\mathbf{k}} = \sum_{t=1}^{S} M_{st}(\mathbf{k}) P^i_{t\mathbf{k}} , \tag{2.7}$$

where $\lambda_i(\mathbf{k})$ and $P^i_{s\mathbf{k}}$ denote the eigenvalues and the eigenvectors belonging to them, and

$$M_{st}(\mathbf{k}) = \alpha_t \beta_{st} \exp(i\mathbf{k} \cdot \rho_{st}) \quad (t \neq s) ;$$

$$M_{ss}(\mathbf{k}) = -\alpha_s \sum_{t \neq s} \beta_{ts} \tag{2.8}$$

for clusters with $n \geq 3$; for symmetric dimers one has

$$M_{st}(\mathbf{k}) = 2\alpha_t \beta_{st} \cos(\mathbf{k} \cdot \rho_{st}) ;$$

$$M_{ss}(\mathbf{k}) = -2\alpha_s \sum_{t \neq s} \beta_{ts} . \tag{2.9}$$

When the detailed balance condition in Eq. (2.3) is fulfilled, it follows from the general properties of the master equation that all $\lambda_i(\mathbf{k})$ are real and non-negative. The eigenvalue zero occurs at $\mathbf{k} = 0$. The corresponding right and left eigenvectors are $\mathbf{P}^1_{s0} = \alpha_s^{-1}$ and $\tilde{P}^1_{s0} = 1$, respectively, as one sees from the identities

$$\sum_s M_{ts}(\mathbf{0}) \alpha_s^{-1} = 0 ,$$

$$\sum_t M_{st}(\mathbf{0}) = 0 , \tag{2.10}$$

that follow directly from Eqs. (2.8) or (2.9). The matrix $\mathbf{M}(\mathbf{k})$ may be symmetrized by means of a similarity transformation; the matrix $\hat{\mathbf{M}}(\mathbf{k})$ defined by

$$\hat{M}_{st}(\mathbf{k}) = \alpha_s^{1/2} M_{st}(\mathbf{k}) \alpha_t^{-1/2} \tag{2.11}$$

is Hermitian and moreover analytic in $\mathbf{k}$. Hence,[8] its eigenvalues $\lambda_i(\mathbf{k})$, which are just those of $\mathbf{M}(\mathbf{k})$, are also analytic functions of $\mathbf{k}$ (except possibly at points of degeneracy; even there they are analytic functions of each component of $\mathbf{k}$ separately). Since $M_{st}(\mathbf{k}) = M^*_{ts}(-\mathbf{k})$, all $\lambda_i(\mathbf{k})$ must be even functions of $\mathbf{k}$:

$$\lambda_i(\mathbf{k}) = \lambda_i(-\mathbf{k}) . \tag{2.12}$$

The branches $-\lambda_i(\mathbf{k})$ of the spectrum of relaxation times of the master Eq. (2.2) resemble those of the phonon frequency spectrum of an harmonic crystal with S atoms per unit cell. If we assume that the master Eq. (2.2) is irreducible, i.e., any configuration can be reached from any other one via a sequence of possible transitions and cluster migrations is possible, then there is only one acoustical branch $\lambda_1(\mathbf{k})$ with $\lambda_1(0) = 0$, irrespective of dimensionality, and $S-1$ "optical" branches that stay finite at all $\mathbf{k}$. Moreover, any minima in $\lambda_1(\mathbf{k})$ other than that at $\mathbf{k} = 0$ occur at finite λ. We will denote by λ_c the minimum of all $\lambda_i(\mathbf{k})$ with $i \neq 1$ and of all minima in $\lambda_1(\mathbf{k})$ at nonzero $\mathbf{k}$. All $\lambda_i(\mathbf{k}) < \lambda_c$ lie on the acoustical branch $\lambda_1(\mathbf{k})$ near $\mathbf{k} = 0$.

III. ASYMPTOTIC GROWTH OF THE CUMULANTS

Typically, the experimental information about cluster diffusion concerns the asymptotic growth of certain moments of the configuration averaged position of the center of mass of the cluster. From the consideration in Sec. II it is clear that for $\tau \gg \lambda_c^{-1}$ only the components of the general solution corresponding to the branch $\lambda_1(\mathbf{k})$ in the spectrum of relaxation times survive, and, moreover, only those which have in addition a $\mathbf{k}$ near the origin. These correspond to solutions of the Chapman–Enskog type[9]

$$P_s^{\mathrm{CE}}(\mathbf{r}_s, \tau) = n(\mathbf{R}_l, \tau)\alpha_s^{-1} + P_s^{(1)}(\mathbf{r}_s, \tau) \qquad (3.1)$$

that are to leading order the product of α_s^{-1} and a function $n(\mathbf{r}, \tau)$ that varies slowly compared to lattice distances, taken at the center $\mathbf{R}_l$ of the lattice cell containing $\mathbf{r}_s$. The correction term $P^{(1)}$ is a linear combination of eigenvectors of $M_{st}(0)$ other than α_s^{-1}, hence it obeys

$$\sum_{\mathbf{r}_s}{}' P_s^{(1)}(\mathbf{r}_s, \tau) = 0 , \qquad (3.2)$$

where the sum runs over all $\mathbf{r}_s$ in any lattice cell. The Fourier transform $n(\mathbf{k}, \tau)$ of $n(\mathbf{R}, \tau)$ decays, for values of k inside the first Brillouin zone, according to

$$\frac{\partial}{\partial\tau} n(\mathbf{k}, \tau) = -\lambda_1(\mathbf{k}) n(\mathbf{k}, \tau) . \qquad (3.3)$$

Extending this equation of motion to all **k** yields, after an inverse Fourier transform, a continuous function $\tilde{n}(\mathbf{r}, \tau)$ with an integral over the ith cell equal to $n(\mathbf{R}_i, \tau)$ (values of k in higher Brillouin zones affect only the mass distribution inside the cells). The "smoothed density" $\tilde{n}(\mathbf{r}, \tau)$ obeys the differential equation

$$\frac{\partial}{\partial\tau} \tilde{n}(\mathbf{r}, \tau) = -\lambda_1\left(i \frac{\partial}{\partial\mathbf{r}}\right) \tilde{n}(\mathbf{r}, \tau) , \qquad (3.4)$$

with $\lambda_1[i(\partial/\partial\mathbf{r})]$ defined by its power series. Since $\lambda_1(\mathbf{k})$ is analytic, this operator power series is well defined for smooth $\tilde{n}(\mathbf{r}, \tau)$. The expansion coefficients $D_{i_1,\ldots,i_{2n}}^{(n)}$ in

$$\lambda_1(\mathbf{k}) = \sum_{i,j=1}^{d} D_{ij}^{(1)} k_i k_j - \sum_{i,j,k,l=1}^{d} D_{ijkl}^{(2)} k_i k_j k_k k_l + \cdots , \qquad (3.5)$$

where i, j, k, and l denote Cartesian components of vectors and tensors, are simply related to the growth rates of the cumulants of the position vector **r**. For example, one easily derives by partial integration,

$$\frac{d}{d\tau} \langle r_i r_j \rangle = 2D_{ij}^{(1)} , \qquad (3.6a)$$

$$\frac{d}{d\tau} (\langle r_i^4 \rangle - 3\langle r_i^2 \rangle^2) = 4!\, D_{iiii}^{(2)} , \qquad (3.6b)$$

with

$$\langle f(\mathbf{r}) \rangle = \int n(\mathbf{r}) f(\mathbf{r}) d\mathbf{r} . \qquad (3.6c)$$

To determine the coefficients $D_{i_1,\ldots,i_{2n}}^{(n)}$ it is not necessary to solve the full eigenvalue problem (2.7). Instead, it suffices to calculate the secular determinant

$$\Delta(\mathbf{k}, \lambda) = \det[\mathbf{M}(\mathbf{k}) - \lambda \mathbf{I}] ; \qquad (3.7)$$

in the equation

$$\Delta(\mathbf{k}, \lambda) \equiv \sum_{n=0}^{S} C_{17}(\mathbf{k}) \lambda^n = 0 , \qquad (3.8)$$

one substitutes the power series Eq. (3.6) for $\lambda_1(\mathbf{k})$ and equates terms containing the same powers of the Cartesian components of **k**.

The terms encountered in evaluating the determinant Eq. (3.7) correspond to all possible permutations of the indices $(1, 2, \ldots, S)$. Any such permutation can be decomposed[10] into a product of cyclic permutations of subsets of the set $(1, 2, \ldots, S)$. Corresponding to each cyclic permutation one has a factor

$$(s_1, s_2, \ldots, s_l) \to (-1)^{l+1} \sum_{m=1}^{l} \{\alpha_{s_m}^{-1} ,$$

$$\beta_{s_1 s_2} \beta_{s_2 s_3}, \ldots, \beta_{s_l s_1} \exp[i\mathbf{k} \cdot (\boldsymbol{\rho}_{s_1 s_2} + \boldsymbol{\rho}_{s_2 s_3} + \cdots + \boldsymbol{\rho}_{s_l s_1})]\} . \qquad (3.9)$$

The product of cyclic permutation factors has to be multiplied with a diagonal element of $\mathbf{M} - \lambda\mathbf{I}$ for each index left in place by the permutation. The important point in all this is that the vectors $\boldsymbol{\rho}_{st}$ occur only in sums over "closed walks" around the configurations; such sums over $\boldsymbol{\rho}_{st}$ are either zero or equal to a lattice vector $\mathbf{R}_{(s_1,\ldots,s_l)}$. The "mirror image" permutation $(s_l, \ldots, s_1)$ carries with it a factor that is the complex conjugate of Eq. (3.9); the determinant $\Delta(\mathbf{k}, \lambda)$ contains the sum of these terms, hence, it depends on **k** only via factors $\cos \mathbf{k} \cdot \mathbf{R}_l$ in each of its terms, with R_l a small lattice vector. [For $l = 2$, the mirror permutation is equal to the original one, but, except for dimers, permutations with $l = 2$ carry **k**-independent factors in view of $\boldsymbol{\rho}_{st} = -\boldsymbol{\rho}_{ts}$. For dimers the form (3.9) must be modified but the conclusion about the **k** dependence of $\Delta(\mathbf{k}, \lambda)$ remains valid. For further details see Sec. V.]

IV. THE DIFFUSION COEFFICIENT; THE ELECTRICAL NETWORK ANALOGY

The simplest measurement in cluster diffusion concerns the diffusion tensor, defined by

$$\lim_{\tau\to\infty} \frac{\langle r_i(\tau) r_j(\tau) \rangle}{\tau} = 2 D_{ij}^{(1)} , \qquad (4.1)$$

with the $\mathbf{r}_i(\tau)$ the ith component of the center-of-mass position at time τ of a cluster that was near the origin at $\tau = 0$. One may expand the coefficient functions $C_n(\mathbf{k})$ of the secular determinant $\Delta(\mathbf{k}, \lambda)$ in Eq. (3.8) as

$$C_0(\mathbf{k}) = \sum_{ij} C_0^{ij} k_i k_j + \sum_{ijkl} C_0^{ijkl} k_i k_j k_k k_l + \cdots , \qquad (4.2a)$$

$$C_1(\mathbf{k}) = C_1^{(0)} + \sum_{ij} C_1^{ij} k_i k_j + \cdots \qquad (4.2b)$$

(note that $C_0(\mathbf{k})$ has no constant term, since $\Delta(\mathbf{k}, \lambda)$ must vanish for $\mathbf{k} = \mathbf{0}$). Substitution of Eq. (4.2) into Eq. (3.5) and comparison of terms of the same order in k yields

$$D_{ij}^{(1)} = C_0^{ij} / C_1^{(0)} . \qquad (4.3)$$

Another way to measure the diffusion tensor is via the drift velocity in a weak external field that acts on the mass of the particles, hence effectively on their center of mass. The transition rates in an external field must obey the relation

$$\beta_{st}(\mathbf{F}) / \beta_{ts}(\mathbf{F}) = \exp[\hat{\mathbf{F}} \cdot \boldsymbol{\rho}_{st}] \qquad (4.4)$$

with $\hat{\mathbf{F}} = \mathbf{F}/k_B T$ in order to remain consistent with detailed balance. If we assume that $\beta_{st}(\mathbf{F})$ depends analytically on **F**, the linear term in **F** is fixed by Eq. (4.4),

$$\beta_{st}(\mathbf{F}) = \beta_{st}(0)[1 + \tfrac{1}{2} \hat{\mathbf{F}} \cdot \boldsymbol{\rho}_{st} + \mathcal{O}(\mathbf{F}^2)] , \qquad (4.5)$$

but the higher terms are model dependent. For convenience, we will presently choose

$$\beta_{st}(\mathbf{F}) = \beta_{st} \exp[\tfrac{1}{2} \hat{\mathbf{F}} \cdot \boldsymbol{\rho}_{st}] , \qquad (4.6)$$

but the result will only be used to calculate the *linear* response. If Eq. (4.6) is substituted for β_{st} in Eqs. (2.8) and (2.9) the result is that in all off-diagonal terms one makes the substitution

$$\exp[i\mathbf{k}\cdot\rho_{st}] \Rightarrow \exp[(i\mathbf{k}+\tfrac{1}{2}\hat{\mathbf{F}})\cdot\rho_{st}] \tag{4.7a}$$

or

$$\mathbf{k}\to\mathbf{k}-\tfrac{1}{2}i\,\hat{\mathbf{F}}\,. \tag{4.7b}$$

In addition, there are changes in the diagonal terms of no further concern to us. As a result, one has for the coefficients in Eq. (4.2):

$$C_0(\mathbf{k},\mathbf{F}) = -\frac{1}{2}\sum_{ij} C_0^{ij}(k_i\hat{F}_j+\hat{F}_ik_j)+\mathcal{O}(\hat{F}^2,k^2)\,, \tag{4.8a}$$

$$C_1(\mathbf{k},\mathbf{F}) = C_1^{(0)}+\mathcal{O}(\hat{F}^2,k^2)\,; \tag{4.8b}$$

the latter expression follows from the fact that for $\mathbf{k}=0$ the determinant Δ, a scalar, can only depend quadratically on $\mathbf{F}$. From Eq. (4.8) we conclude that

$$\lambda_1(\mathbf{k},\mathbf{F}) = -i\sum_{ij} D_{ij}^{(1)}k_i\hat{F}_j+\mathcal{O}(\hat{F}^2,k^2)\,, \tag{4.9}$$

where we used the symmetry of C_0^{ij}, and hence of $D_{ij}^{(1)}$. This oscillatory time dependence of a plane-wavelike disturbance contained in Eq. (4.9) is readily explained: the disturbance is carried along by a uniform drift in the uniform force $\mathbf{F}$ with drift velocity $\mathbf{v}_D$ given by

$$\mathbf{v}_D = \mathbf{D}^{(1)}\cdot\mathbf{F}(k_BT)^{-1}\,. \tag{4.10}$$

Evidently, drift experiments are simply another way of measuring the diffusion tensor, as one would expect from the fluctuation–dissipation theorem.

Our discussion of this point is motivated by the recent article by Landman and Schlesinger,[4] where it is argued that experiments in an external field may provide new information about the zero-field transition rates for clusters. Closer scrutiny of their argument shows that this is brought about by the assumption that all transition rates depend on $\mathbf{F}$ via a single universal function of $\hat{\mathbf{F}}\cdot\rho_{st}$. In a model where all transition rates β_{st} are treated as arbitrary parameters, to be determined eventually by experiment, it seems reasonable to treat the "saturation terms," i.e., the terms of quadratic and higher order in $\mathbf{F}$ in Eq. (4.6), also as adjustable parameters, to be determined for each transition separately. If we choose our model in such a way, the field dependence of the asymptotic growth of cumulants involves many new, undetermined parameters, and it cannot be exploited to obtain additional information about the zero-field transition rates.

We conclude this section by pointing out an analogy with electrical network theory which may be useful in calculating the diffusion tensor. Equation (2.2) can also be read[6] as the equation for the time evolution of the charge $P_s(\mathbf{r}_s,\tau)$ on a capacitor of capacity α_s^{-1} at $\mathbf{r}_s$ that is connected to other capacitors at $\mathbf{r}_t$ via resistances β_{st}^{-1} [note that $\alpha_sP_s(\mathbf{r}_s,\tau)$ is the potential of the capacitor]. The problem addressed in this paper is therefore equivalent to determining the properties of an infinite periodic array of capacitors and resistances. The eigenvalues $\lambda_i(\mathbf{k})$ are the typical relaxation times of the free network. By a reasoning completely analogous to the one used in this section one sees that the coefficient $D_{ij}^{(1)}$ in $\lambda_1(\mathbf{k})$ can also be determined by calculating the stationary response of this network to an externally imposed potential drop per lattice cell. More specifically, the drift velocity $\mathbf{v}_D$ corresponds to the net flow of current from one cell in this periodic array of capacitors to the next one for a given potential difference $\mathbf{F}\cdot\mathbf{R}_l$ between corresponding capacitors in different cells of the array separated by a lattice vector $\mathbf{R}_l$. Especially in one-dimensional problems this "effective resistance" per unit lattice cell can often be read off immediately from the network diagram, using the simple rules for resistors connnected in parallel or in series. We shall encounter examples of this in the next two sections.

V. SOME EXAMPLES OF DIMER DIFFUSION

The simplest case of cluster diffusion is that of a symmetric dimer. The simplifying feature is that the matrix $\mathbf{M}(\mathbf{k})$ contains no terms linear in $\mathbf{k}$. Expanding Eq. (2.9) one finds

$$\mathbf{M}(\mathbf{k}) = \mathbf{M}^{(0)}+\mathbf{M}^{(2)}(\mathbf{k})+\quad(k^4)\,, \tag{5.1}$$

with

$$M_{st}^{(0)} = 2\alpha_t\beta_{st}\quad(s\neq t)\,, \tag{5.2a}$$

$$M_{ss}^{(0)} = -2\alpha_s\sum_{t\neq s}\beta_{ts}\,, \tag{5.2b}$$

$$M_{st}^{(2)} = -\alpha_t\beta_{st}(\mathbf{k}\cdot\rho_{st})^2\quad(s\neq t)\,, \tag{5.3a}$$

$$M_{ss}^{(2)} = 0\,. \tag{5.3b}$$

Due to the absence of terms linear in $\mathbf{k}$, the quadratic term of $\lambda_1(\mathbf{k})$ can be obtained by ordinary first order perturbation theory, i.e., by determining the expectation value of $\mathbf{M}^{(2)}$ between left and right eigenvectors of $\mathbf{M}^{(0)}$ with $\lambda=0$:

$$\begin{aligned}-\sum_{ij} D_{ij}k_ik_j &= \sum_{s,t} M_{st}^{(2)}(\mathbf{k})\alpha_t^{-1}\\ &= -\sum_{s,t}\beta_{st}(\mathbf{k}\cdot\rho_{st})^2\,,\end{aligned} \tag{5.4}$$

and hence

$$D_{ij}^{(1)} = \sum_{s,t}\beta_{st}\rho_{st}^i\rho_{st}^j\,, \tag{5.5}$$

where the superscripts denote Cartesian components of the jump distance ρ_{st}.

It is worth noting that the diffusion tensor $D_{ij}^{(1)}$, which describes the asymptotic growth of $\langle r_ir_j\rangle$ coincides in this case with the second moment of the transition matrix, that describes the *short-time* evolution of $\langle[r_i(\tau)-r_i(0)][r_j(\tau)-r_j(0)]\rangle$ for any initial condition in which there is "local equilibrium," i.e., when the probability to find the configuration s, summed over all positions of the center of mass, equals the equilibrium probability α_s^{-1}. For intermediate times correlations between $\mathbf{r}(\tau)-\mathbf{r}(0)$ and the internal configuration of the dimer may develop, causing an instantaneous growth rate for $\langle[r_i(\tau)-r_i(0)][r_j(\tau)-r_j(0)]\rangle$ different from $2D_{ij}^{(1)}$, but for long times the correlations disappear and the growth rate $2D_{ij}^{(1)}$ takes over again. The intermediate regime is absent in some simple models, such as the one-dimensional two-state dimer model discussed in Sec. IV A of Ref. 3. Equation (5.5) can also be read off directly from the equivalent electrical network, a method we shall discuss later in this section in our discussion of the asymmetric dimer.

The determination of the diffusion constant did not require the full formalism of Secs. IV and V. We shall now discuss the next coefficient $D^{(2)}_{ijkl}$ in Eq. (3.5) for a simple model of one-dimensional diffusion of a dimer, first discussed by Reed and Ehrlich.[2] The dimer consists of two atoms constrained to move in two adjacent "channels" on the surface. The relative distance in the channel direction may assume the values 0, $+l$, and $-l$; the corresponding configurations are labeled 0, +1, and −1. Configurations +1 and −1 have the same energy, corresponding to a statistical weight α_1^{-1}; the configuration 0 has weight α_0^{-1}. Normalization requires

$$2\alpha_1^{-1}+\alpha_0^{-1}=1 \ . \tag{5.6}$$

Since all four possible transitions are equivalent, there is only a single kinetic coefficient β and the matrix $\mathbf{M}(k)$ assumes the form

$$\mathbf{M}(k)=\begin{pmatrix} -2\alpha_1\beta & 2\alpha_0\beta\cos(\frac{1}{2}kl) & 0 \\ 2\alpha_1\beta\cos(\frac{1}{2}kl) & -4\alpha_0\beta & 2\alpha_1\beta\cos(\frac{1}{2}kl) \\ 0 & 2\alpha_0\beta\cos(\frac{1}{2}kl) & -2\alpha_1\beta \end{pmatrix}, \tag{5.7}$$

where the rows correspond to the configurations −1, 0, and +1, respectively. The eigenvalues of this matrix are easily determined by exploiting the symmetry under exchange of configurations +1 and −1; the three eigenvalues are

$$\begin{aligned} \lambda_{1,2}(k)&=\beta\{(\alpha_1+2\alpha_0) \\ &\quad\mp[(\alpha_1+2\alpha_0)^2-\delta\alpha_1^2\alpha_0^2\sin^2(\tfrac{1}{2}kl)]^{-1/2} \ , \\ \lambda_3(k)&=2\beta\alpha_1 \ . \end{aligned} \tag{5.8}$$

By expansion of $\lambda_1(k)$ or, alternatively, using the method of Sec. III, and application of Eq. (5.6) to simplify the expressions, one finds

$$D^{(1)}=\beta l^2 \ , \tag{5.9}$$

$$D^{(2)}=\beta l^4\left(\frac{1}{12}-\frac{1}{4\alpha_0}+\frac{1}{4\alpha_0^2}\right) \ . \tag{5.10}$$

Equation (5.9) is just a special case of Eq. (5.5) with each of the four possible transitions contributing $\frac{1}{4}\beta l^2$. The coefficient $D^{(2)}$ contains information about the statistical weight α_0^{-1} that does not enter into the expression for $D^{(1)}$. The coefficient of βl^4 varies between the extremes 1/12 for $\alpha_0^{-1}=0$ or $\alpha_0^{-1}=1$ and 1/48 for $\alpha_0^{-1}=\frac{1}{2}$. Solving for α_0^{-1} from $D^{(2)}$ yields two solutions with sum 1. To decide between them one might repeat the experiment at a higher temperature, which would shift α_0^{-1} in the direction of the equipartition value $(\alpha_0^{-1})_\infty=1/3$.

The simple model just discussed can be extended in many ways, either by admitting more configurations or by admitting a direct transition between states +1 and −1 with rate α,γ. From Eq. (5.5) we see that this changes the diffusion coefficient $D^{(1)}$ into

$$D^{(1)}=l^2(\beta+2\gamma) \ . \tag{5.11}$$

For asymmetric dimers additional changes occur. To illustrate some of them we next discuss a modification of the Reed–Ehrlich model with different mobilities for the two particles. The matrix $\mathbf{M}(k)$ becomes

$$\begin{bmatrix} -\alpha_1(\beta_1+\beta_2+\gamma_1+\gamma_2) & \alpha_0(\beta_1\xi^*+\beta_2\xi) & \alpha_1(\gamma_1\xi^{*2}+\gamma_2\xi^2) \\ \alpha_1(\beta_1\xi+\beta_2\xi^*) & -2\alpha_0(\beta_1+\beta_2) & \alpha_1(\beta_1\xi^*+\beta_2\xi) \\ \alpha_1(\gamma_1\xi^2+\gamma_2\xi^{*2}) & \alpha_0(\beta_1\xi+\beta_2\xi^*) & -\alpha_1(\beta_1+\beta_2+\gamma_1+\gamma_2) \end{bmatrix}, \tag{5.12a}$$

with

$$\xi=\exp(\tfrac{1}{2}ikl) \ . \tag{5.12b}$$

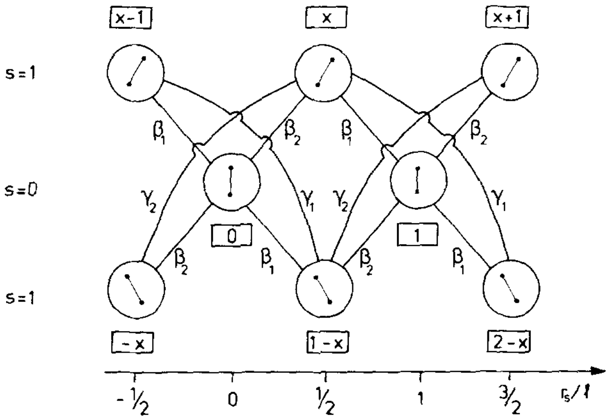

FIG. 1. Two unit cells of the equivalent periodic electrical network for the asymmetric dimer, with model parameters as in Eq. (5.12). The numbers in boxes near each node denote the node potential divided by the lattice parameter l. The numbers near each connector are the inverse of the corresponding resistances, and r_s is the position of the center of mass. The drawings inside the circles representing the nodes depict the corresponding cluster configurations.

Instead of determining the diffusion coefficient $D^{(1)}$ for this case from the determinant of $\mathbf{M}(k)-\lambda\mathbf{I}$, we draw the equivalent electric network, shown in Fig. 1. Each of the cluster states is a node in the network, and each transition with rate β corresponds to a resistance with value β^{-1}. The diffusion coefficient is now equal to the current through the network for a potential drop l per unit cell in the network. Let the nodes with $s=0$, $r=nl$ have potential nl and those with $s=-1$, $r=(n+\frac{1}{2})l$ have potential $(n+x)l$. From the symmetry under 180° rotation it follows that the nodes with $s=+1$, $r=(n+\frac{1}{2})l$ have potential $(n+1-x)l$. The undetermined quantity x now follows from the current balance equation at the node with potential x:

$$x=\frac{\beta_2+2\gamma_2}{\beta_1+2\gamma_1+\beta_2+2\gamma_2} \ . \tag{5.13}$$

For the total current, hence for $D^{(1)}$, we find

$$D^{(1)}=2l^2[(\beta_1+2\gamma_1)^{-1}+(\beta_2+2\gamma_2)^{-1}]^{-1} \ . \tag{5.14}$$

This differs from the short-time rate of growth $D^{(1)}_{st}$ of $\langle[r(\tau)-r(0)]^2\rangle$ in local equilibrium, obtained by adding the second moments of the jump rates $\sum_t\beta_{ts}\rho^2_{ts}$ as discussed after Eq. (5.5),

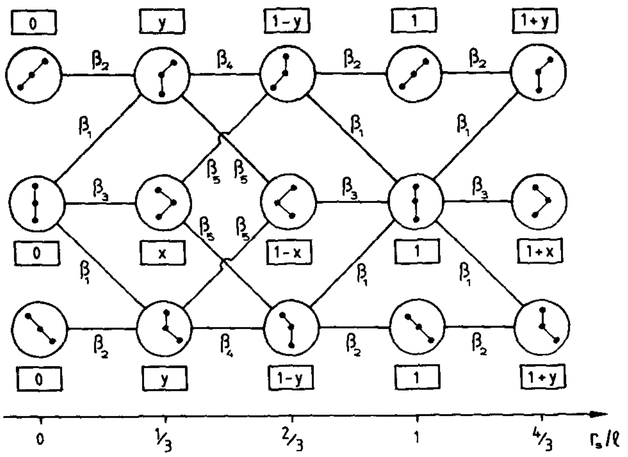

FIG. 2. One and one third cell of the equivalent periodic electrical network for the Reed–Ehrlich trimer, discussed in Sec. VI. Configurations, voltages, and resistances are indicated as in Fig. 1.

$$D_{st}^{(1)} = \tfrac{1}{2} l^2(\beta_1 + 2\gamma_1 + \beta_2 + 2\gamma_2) . \tag{5.15}$$

The way in which the various rates in Eq. (5.14) contribute to the final result is intuitively appealing. The β_i and γ_i rates are combined as resistances in parallel: single and double jumps provide alternative means of locomotion for the cluster. However, rates for the motion of each of the two particles are combined as resistances in series: in order to move the cluster as a whole each one of its components must be moved. For equal mobilities of both component particles, both Eqs. (5.14) and (5.15) reduce to the earlier result (5.12).

VI. A MODEL FOR TRIMER DIFFUSION

As an example of a cluster with $n > 2$ we consider the trimer model introduced by Reed and Ehrlich[2]: three particles moving in three adjacent, parallel channels on a surface, each of which may have a distance 0, $-l$, or $+l$ parallel to the channels with respect to its immediate neighbor. This trimer can thus have nine internal configurations, shown at the nodes of the electrical network diagram in Fig. 2. If the two outer particles are assumed to be identical, one expects four different statistical weights, corresponding to the vertical, the diagonal, and the two bent configurations. If, moreover, only those transitions are allowed in which one of the particles moves a single step, the model is completely specified by giving the five inequivalent kinetic coefficients β_1, β_2, β_3, β_4, and β_5, shown in Fig. 2 at the connecting resistances. Note that our parametrization, as the one employed by Reed and Ehrlich, has nine model parameters; ours, however, separates the five that are relevant for the diffusion coefficient, the β_i, from those that do not enter there, the statistical weights α_s^{-1}.

To determine the diffusion coefficient $D^{(1)}$ for this model, we again determine the resistance per unit length of the equivalent network in Fig. 2. From the symmetry of the network it is clear that the vertical and diagonal configurations will have the same potential, and that only two node voltages denoted by xl and yl have to be determined; all the other then follow by symmetry and translational invariance. The current balance conditions at the two nodes yield two equations for x and y:

$$\beta_3 x = 2\beta_5(1 - y - x) , \tag{6.1a}$$

$$(\beta_1 + \beta_2)y = \beta_4(1 - 2y) + \beta_5(1 - x - y) . \tag{6.1b}$$

The current for a voltage drop l per lattice cell equals

$$I = l^2[\beta_3 x + 2(\beta_1 + \beta_2)y] . \tag{6.1c}$$

Solving this simple set of equations results in

$$Il^{-2} = D^{(1)}\Gamma^{-2} = 2\left(\frac{\beta_1\beta_3\beta_4 + \beta_2\beta_3\beta_4 + 2\beta_1\beta_3\beta_5 + 2\beta_1\beta_4\beta_5 + 2\beta_2\beta_3\beta_5 + 2\beta_2\beta_4\beta_5 + \beta_3\beta_4\beta_5}{\beta_1\beta_3 + \beta_2\beta_3 + \beta_3\beta_5 + 2\beta_1\beta_5 + 2\beta_2\beta_5 + 2\beta_3\beta_4 + 4\beta_4\beta_5}\right) . \tag{6.2}$$

The rather complicated result in Eq. (6.2) simplifies in a few limiting cases. If we eliminate the vertical configuration, as might be appropriate for large adatoms, we obtain

$$(\beta_1 = \beta_3 = 0) \rightarrow D^{(1)} = 2l^2(\beta_4^{-1} + 2\beta_2^{-1})^{-1} , \tag{6.3}$$

as would be appropriate for the simple network then remaining, which has a ladder structure; the rungs of the ladder containing two resistances β_5^{-1} cannot carry any current, since they connect nodes at equal voltages. It is therefore not surprising that the rate β_5 does not occur in Eq. (6.3). If we eliminate the symmetrically bent configurations we obtain

$$(\beta_3 = \beta_5 = 0) \rightarrow D^{(1)} = 2l^2[\beta_4^{-1} + 2(\beta_1 + \beta_2)^{-1}]^{-1} , \tag{6.4}$$

again readily understood in terms of the network that remains after the β_3 and β_5 connections have been removed. Note that in cases where the symmetrically bent configuration is excluded (strong nearest-neighbor bonds) the diagonal configuration should probably be excluded as well; then β_2 must also be put equal to zero in Eq. (6.4).

Finally, we consider the case where the rates β_4 and β_5 are much larger than the other ones. In that case

$$(\beta_4, \beta_5 \rightarrow \infty) \rightarrow D^{(1)} = l^2(\beta_1 + \beta_2 + \beta_{3/2}) , \tag{6.5}$$

again reasonable since the three rate-limiting kinetic coefficients correspond to resistances in parallel.

The results just given agree with those reported in the literature, after the appropriate changes in notation, except for Eq. (6.5), which may be new. We presented them mainly to show the advantages of the equivalent network method: we had to solve two simple linear Eqs. (6.2), instead of nine (or six when symmetry is exploited) coupled equations for the occupation probabilities of the cluster configurations. Of course our method is restricted to the calculation of $D^{(1)}$; if one is interested in the growth rates of higher cumulants, the full complexity of the underlying dynamics must be confronted. Even then the methods presented in Sec. III are more economical than those thus far available in the literature.

VII. CONCLUDING REMARKS

The network analogy not only provides an efficient method for calculating diffusion coefficients or tensors for specific models; it also provides direct proof for two general properties of the diffusion coefficient. First, the resistance is determined by topology of the periodic network, and by the dimensions of its unit cell; it does not depend on the location of each of the nodes inside the unit cell; i.e., on the individual ρ_{st}. This confirms the result derived algebraically at the end of Sec. IV. Secondly, the diffusion constant depends on the "resistances" β_i^{-1}, but not on the "capacitances" α_s^{-1}. This result can also be obtained algebraically from Eq. (4.3), using the fact that the matrix of minors of $\mathbf{M}(0)-\lambda\mathbf{I}$ approaches a constant times the projection $A_{st}=\alpha_t^{-1}$ on the ground state eigenvector for λ approaching zero, and the normalization requirement $\sum_s \alpha_s^{-1}=1$ that follows from Eq. (2.1). The proof using the network analogy is certainly more transparent.

The calculation of the growth rates of higher cumulants is simplified greatly for one-dimensional problems in which there is a unique sequence of steps through which the diffusion must proceed, as for the symmetric three-state dimer of Sec. V or the simplified trimer model of Eq. (6.3) or (6.4) with $\beta_2=0$. The matrix $\mathbf{M}(k)$ then becomes tridiagonal and one may use the methods expounded, e.g., in Ref. 7 to determine the coefficient functions $C_n(k)$ discussed in Sec. III.

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