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Collective diffusion in two-dimensional systems: Exact results to establish limitations of the Reed-Ehrlich factorization

S. H. Payne* and H. J. Kreuzer†

Department of Physics and Atmospheric Science, Dalhousie University, Halifax, NS, Canada B3H 3J5

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Using a gradient expansion, we derive an exact expression for the diffusivity in terms of correlation functions. The latter are calculated by transfer matrix methods generalized to an adsorbate with lateral interactions and subjected to an external field. It is shown that the Reed-Ehrlich factorization, commonly assumed, does not apply for generalized hopping kinetics where initial- and final-state interactions are involved, such as saddlepoint interactions.

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The theoretical study of collective (and tracer) diffusion[1–5] of two-dimensional (2D) adsorbates is usefully described on the basis of the lattice gas model, which allows an examination of the effects of multiple binding sites within cells, lateral interactions, and hops of different lengths. The evolution of the local lattice occupancy can be described by the master equation, with the hopping of particles between sites treated as a Markovian process, i.e., transition rates independent of time. (Memory effects have been introduced with a Mori-type equation[6,7] but, in practice, this is mathematically intractable.) Adsorbate lateral interactions lead to a strong dependence of the diffusivity on the adsorbate coverage, θ, via the kinetics assumed for the hopping process. A common simplification is to consider only the interactions of the hopping particle with its initial neighborhood. However, the hopping kinetics can depend on both initial- and final-state configurations, e.g., saddlepoint interactions. This leads to varied diffusion behavior in one dimension (1D)[1] and should do so in 2D as well.

Another common *a priori* assumption, due to Reed and Ehrlich,[8] is to express the collective diffusion coefficient as a product of thermodynamic and kinetic (or "dynamic") factors,

$$D(\theta,T) = \chi^{-1}\langle W\rangle, \tag{1}$$

where χ is the lattice gas susceptibility and $\langle W\rangle$ is the average transition rate, defined by Eq. (3); the standard jump rate is $\langle W\rangle/\theta$. They argued on the basis of nonequilibrium thermodynamics: the diffusion current in the linear regime is given by $\mathbf{j}=L\nabla(\beta\mu)=L[\partial(\beta\mu)/\partial n]\nabla n$. (Here n and μ are the local particle density and chemical potential. $\beta=1/k_BT$). Identifying the Onsager coefficient L with the average hopping rate then gives Eq. (1), independently of choice of interactions and (microscopic) hopping kinetics. There is no *a priori* reason that this identification is correct. Statistical mechanical justifications of Eq. (1) are based on linear response theory[4,6,7,9,10] in which the density fluctuations are expressed in terms of the local chemical potential as the driving force, with the latter eliminated via the susceptibility. In the absence of memory effects,[6,7] this procedure guarantees Eq. (1) and thus is not a general proof. Moreover, works employing linear response theory have been limited to initial-state kinetics.[6,7,10–12] No formulation has established the factorization (1) beyond initial-state-interaction kinetics; indeed, we will show that it is not always valid, in particular, not for the physically relevant case of saddlepoint interactions. In contrast, calculations of $D(\theta,T)$ within linear response theory do not advance beyond the form of Eq. (1), exclusive of memory effects. (The latter are not crucial to the accuracy of results.[4])

We recently presented an alternate method of calculating the collective diffusivity, $D(\theta,T)$.[13] It involves a gradient expansion of all correlators appearing in the diffusion current in the continuum limit. Formally, it is equivalent to obtaining the diffusion equation by a Kramers-Moyal expansion[14,15] of the lattice gas probability distribution, but it is more direct and transparent. We proved that the factorization (1) is exact (in 1D), without restriction of hopping kinetics or lateral interactions. Importantly, the method bypassed insurmountable difficulties in linear response theory associated with arbitrary kinetics.

Here, we outline the generalization of this method to 2D systems to obtain the diffusivity for all kinetics and lateral interactions on a homogeneous substrate. To evaluate the general expression, we extend the transfer matrix method for the calculation of correlators to adsorbates subject to an external field, namely, a density gradient. We give some results for realistic scenarios of the hopping kinetics and for first neighbor interactions. The factorization (1) is only correct for initial-state *or* final-state interaction kinetics; it fails otherwise, in particular, for the physically important case of saddlepoint interactions.

We label the sites of the lattice gas by a two-component vector $\mathbf{i}=(i_a,i_b)$. An imposed density gradient results in particles hopping from an occupied site $\mathbf{i}$ to a neighboring unoccupied site $\mathbf{i}+\mathbf{a}$; we define the microscopic particle current through the bond $\mathbf{i}\rightarrow\mathbf{i}+\mathbf{a}$,

$$j_i = a[W_i^{>}(\mathbf{n}) - W_{i+a}^{<}(\mathbf{n})], \tag{2}$$

where $\mathbf{n}$ labels the occupational microstate. $W_i^{>}(\mathbf{n})$ is the forward transition rate from site $\mathbf{i}$ and is given for a rectangular lattice, as an example, by

$$\begin{aligned} W_i^{>}(\mathbf{n}) = J_0 n_i(1-n_{i+a})[&1 + A_1 n_{i-a} + A_1'(n_{i+b}+n_{i-b}) \\ &+ A_2 n_{i-a}(n_{i+b}+n_{i-b}) + A_2' n_{i-b}n_{i+b} + A_3 n_{i-a}n_{i-b}n_{i+b} \\ &+ B_1 n_{i+2a} + \cdots] + \cdots . \end{aligned} \tag{3}$$

This expresses the effect on the current due to the anisotropic interactions of the hopping particle with m nearest neighbors, either in its initial state, with coefficients $A_m^{(\prime)}$, or its final state, with coefficients $B_m^{(\prime)}$. There are another 29 cross coefficients to fully specify both initial- and final-state-interaction effects. Detailed balance imposes constraints on about half the coefficients; a simple example is $(1+A_1^{(\prime)})u_{a(b)}=(1+B_1^{(\prime)})$, with $u_a=\exp(-\beta V_{1a})$, V_{1a} the first neighbor interaction along $\mathbf{a}$.

The current enters the time evolution of the site occupancy, obtained from the first moment of the master equation. The diffusion equation ultimately emerges from this in the hydrodynamic limit, for which we can introduce a local density or coverage, $\theta(\mathbf{r},t)=\langle n_i\rangle(t)$, and a local current, $j(\mathbf{r},t)=\langle j_i\rangle(t)$; $\mathbf{r}=(x,y)=i_a\mathbf{a}+i_b\mathbf{b}$. The current contains a number of differences of correlation functions with continuous space and time dependence and we get from Eqs. (2) and (3) the form

$$\begin{aligned} j(\mathbf{r},t) = aJ_0\{&\theta(\mathbf{r},t) - \theta(\mathbf{r}+\mathbf{a},t) + A_1[F_{2a}(\mathbf{r}-\mathbf{a},t) \\ &- F_{2a}(\mathbf{r}+\mathbf{a},t) - (F_{3a}(\mathbf{r},t) - F_{3a}(\mathbf{r}+\mathbf{a},t))] \\ &+ 2A_1'[F_{2b}(\mathbf{r},t) - F_{2b}(\mathbf{r}+\mathbf{a},t) - (F_3^{>}(\mathbf{r}) - F_3^{<}(\mathbf{r}+\mathbf{a}))] \\ &+ \cdots\}. \end{aligned} \tag{4}$$

Here, we display a few of the terms appearing in the complete expression: $F_{2a}(\mathbf{r},t)=\langle n_i n_{i+a}\rangle(t)$ and $F_{3a}(\mathbf{r},t) =\langle n_{i-a}n_i n_{i+a}\rangle(t)$ are neighboring pair and linear trio correlators, respectively, along $\mathbf{a}$; $F_3^{>}(\mathbf{r},t)=\langle n_i n_{i+a} n_{i+b}\rangle(t)$ is a directed triangular trio correlator and $F_3^{<}$ is its reflection about site $\mathbf{i}$, i.e., $n_{i+a}\rightarrow n_{i-a}$. For densities varying slowly on the length scale of the lattice constant, i.e., in the continuum limit, we expand the current to terms linear in the spatial gradient

$$\begin{aligned} j(\mathbf{r},t) \approx - a^2J_0\{&\partial_a[\theta(\mathbf{r},t) + A_1(2F_{2a}(\mathbf{r},t) - F_{3a}(\mathbf{r},t)) \\ &+ 2A_1'(F_{2b}(\mathbf{r},t) - F_3^{<}(\mathbf{r},t)\ ] + \cdots \\ &- a^{-1}[2A_1'(F_3^{<}(\mathbf{r},t) - F_3^{>}(\mathbf{r},t)) + \cdots]\}. \end{aligned} \tag{5}$$

Two classes of terms are indicated: the first involves the gradient of the correlation functions directly, while the second, with four terms in all, involves the difference of left- and right-directed functions at the same position. (The additional right-directed functions that occur are $F_{3h}^{>}=\langle(1-n_i)n_{i+a}n_{i+b}\rangle$, $F_4^{>}(\mathbf{r},t)=\langle n_i n_{i+a} n_{i-b} n_{i+b}\rangle$, $F_{4h}^{>}(\mathbf{r},t) =\langle(1-n_i)n_{i+a}n_{i-b}n_{i+b}\rangle$). For long time and length scales, a system is maintained in local equilibrium by much faster relaxation processes. This implies that the space and time dependence of correlation functions is completely given by that of the local density, i.e., we must have

$$\partial_a F_\alpha(\mathbf{r},t) = \frac{d}{d\theta}F_\alpha(\theta(\mathbf{r},t))\partial_a\theta \tag{6}$$

and from the first class of terms we obtain the form of Fick's first law for the diffusion current, $j(\mathbf{r},t)=-D(\theta)\partial_a\theta$. The second class has this form also because the spatial variation of the density is implicit in such differences.[13] If we define

$$\lim_{a\to 0} a^{-1}[(F_\alpha^{<}(\mathbf{r},t) - F_\alpha^{>}(\mathbf{r},t)) = D_\alpha(\theta)\partial_a\theta\ , \tag{7}$$

we obtain the complete density-dependent diffusion coefficient, exactly, as

$$\begin{aligned} D(\theta,T)/D_0 = 1 + &\frac{d}{d\theta}[\langle\widetilde{W}_A\rangle - \langle\widetilde{W}_B\rangle + A_1\langle\bullet\bullet\rangle] - 2(A_1' + A_2)D_3 \\ &- (A_2' + A_3)D_4 - 2B_1'D_{3h} - B_2'D_{4h}, \end{aligned} \tag{8}$$

in terms of correlators at the local density. Here, $D_0=a^2J_0$ is the diffusion coefficient in the absence of lateral interactions. In diagrammatic form, e.g., $F_{2a}(\theta)=\langle\bullet\bullet\rangle$, the normalized, partial (average) transition rates simplify

$$\begin{aligned} \langle\widetilde{W}_A\rangle = A_1\langle\bullet\bullet\circ\rangle + 2A_1'\left\langle\begin{array}{cc} \bullet & \\ \bullet & \circ \end{array}\right\rangle + 2A_2\left\langle\begin{array}{ccc} & \bullet & \\ \bullet & \bullet & \circ \end{array}\right\rangle \\ + A_2'\left\langle\begin{array}{cc} \bullet & \\ \bullet & \circ \\ \bullet & \end{array}\right\rangle + A_3\left\langle\begin{array}{ccc} & \bullet & \\ \bullet & \bullet & \circ \\ & \bullet & \end{array}\right\rangle \end{aligned} \tag{9}$$

and similarly for $\langle\widetilde{W}_B\rangle$, after exchanging the right-hand particle-hole pair and the coefficients. The total average transition rate corresponding to Eq. (3) is

$$\langle W\rangle = J_o\langle\widetilde{W}\rangle = J_o[\langle\bullet\circ\rangle + \langle\widetilde{W}_A\rangle + \langle\widetilde{W}_B\rangle]. \tag{10}$$

The expressions (8) and (10) reflect the interaction neighborhoods for the hopping process, including anisotropy, via the orientation of the correlators.

Quasianalytic methods are necessary for an accurate evaluation of the functions in Eq. (8). We use the transfer matrix method.[16] For the calculation of anisotropic correlators spanning three rows, the lattice is taken to be an infinite cylinder of axial circumference N sites, and a matrix of Boltzmann factors is constructed, in the grand-canonical representation, within the basis of states of a strip of length (period) N sites and width two rows (i.e., rings)—a four-row transfer matrix. The left and right eigenvectors of its leading eigenvalue determine the coverage $\theta(\mu,T)$; the correlators follow by contraction of appropriate derivatives of the matrix with these vectors.

To calculate D_α, we introduce a constant external field which maintains a population gradient and then evaluate the factors $\partial\theta/\partial x$ and $F_\alpha^{<}-F_\alpha^{>}$ in Eq. (7) as finite differences of averages on a lattice of dimension Ma. As M increases, their ratio will tend to D_α. For the application of the transfer matrix method, we choose a toroidal lattice of size $M\times N$ with periodicity in the planar circumference, M, in addition. The single particle energy, E_0, say, of the homogeneous system, now depends on position through the external potential, ϕ, as $E_0+i\phi$. We choose as a basis the 2^N states of a single ring and denote the position-dependent transfer matrix connecting rings i and $i+1$ by $\mathbf{T}_{i,i+1}$. The average site occupation at the central ring, indexed $l=(M-1)/2$, M odd, is then given by

$$\langle n_l \rangle = \frac{1}{N\Xi}\mathrm{Tr}(\mathbf{T}_{1,2}\mathbf{T}_{2,3}\cdots\mathbf{T}_{l,l-1}\mathbf{P}\mathbf{T}_{l,l+1}\cdots\mathbf{T}_{M,1}). \qquad (11)$$

Here, $\mathbf{P}$ is a particle matrix and Ξ is the grand partition function. The coverage gradient at site l follows by expanding $\langle n_{l\pm 1}\rangle$ about the zero-field values

$$\theta(x=(l\pm 1)a) = \langle n_{l\pm 1}\rangle_0 - \phi Q^{(1)}_{l\pm 1} + O(\phi^2) \qquad (12)$$

and evaluating the limiting three-point difference

$$\frac{\partial\theta}{\partial x} = -\frac{\phi}{2a}\lim_{M\to\infty}(Q^{(1)}_{l+1} - Q^{(1)}_{l-1}) + O(\phi^3). \qquad (13)$$

For this, we expand each matrix in Eq. (11) as $\mathbf{T}_{i,i+1} = \mathbf{T}_0 - \phi\mathbf{U}_i/2$ and retain products linear in ϕ overall. Here, $\mathbf{T}_0$ is the two-row (ring) transfer matrix for the homogeneous system on N sites and $\mathbf{U}_i$ specifies the external potential at ring i; its matrix elements between states of neighboring rings i, $i+1$, are proportional to those of $\mathbf{T}_0$. Finally, Eq. (13) appears as sums of structured products of matrices. The factors $F^<_\alpha - F^>_\alpha$ can be evaluated as differences of pairs of directed correlators which span the same three rings and, with expansions about their zero-field values, one obtains quite similar forms, $F^<_\alpha - F^>_\alpha \sim (Q^{(\alpha)}_{l+1} - Q^{(\alpha)}_{l-1})$. In short, there is a well-defined and repetitive procedure for evaluating the functions D_α in terms of bilinear combinations of elements of the transfer matrix of the homogeneous system. In practice, $M \sim 10^2$ suffices to recover the precision of correlators calculated on the cylinder.

Analytic forms of Eq. (8) only occur in special cases. For a quasi-1D system, with the interaction parallel to the particle gradient negligible, $\beta V_{1a} \approx 0$, the correlators factorize with one-site overlap, e.g., $\langle \bullet\bullet\circ \rangle = \langle \bullet\bullet \rangle\langle \bullet\circ \rangle / \langle \bullet \rangle$, $F^<_3 - F^>_3 \to (\langle \bullet_{i-1}\rangle - \langle \bullet_{i+1}\rangle)\langle {\bullet \atop \bullet} \rangle$, and a simple formula results. Amongst the various choices of hopping kinetics, three cases are of interest: (i) initial-state interactions $[B^{(\prime)}_n = 0;\ A^{(\prime)}_n = (A^{(\prime)}_1)^n]$, the standard choice; (ii) final-state interactions $[A^{(\prime)}_n = 0;\ B^{(\prime)}_n = (B^{(\prime)}_1)^n]$; and (iii) symmetric, initial-, and final-state interactions $[A^{(\prime)}_n = -B^{(\prime)}_n]$. With standard expressions for $\beta\mu$ and $\langle \bullet\bullet \rangle$, it is easy to show that the factored form (1) is valid for cases (i) and (ii) but not for case (iii). In contrast, for a true 1D system, with interactions along the population gradient, Eq. (1) is also correct for case (iii).[13] In the quasichemical approximation (QCA) to the 2D lattice, in which the one-site overlap factorization is enforced, one can also show that Eq. (1) applies for cases (i) and (ii) but not for case (iii). The QCA is known to produce a diffusivity that is qualitatively correct above the ordering temperature of the adsorbate.

The results for the general case, obtained by evaluating Eq. (8) with the transfer matrix method, follow this rule. For cases (i) and (ii), $D(\theta, T)$ is numerically equal to $\chi^{-1}\langle W \rangle$ for all values, N, of the axial circumference of the torus, with M large enough, and for any values of the interactions V_{1a}, V_{1b}. (Note that the correlators in Eqs. (8) and (10), are inherently anisotropic for small N, even for isotropic interactions.) We suspect that an analytic proof of the equality rests on a transformation of the matrix products appearing in Eq. (13) to a representation in which $\mathbf{T}_0$ is diagonal; it is not trivial. For case (iii), $D(\theta, T)$ is never given by the factored form.

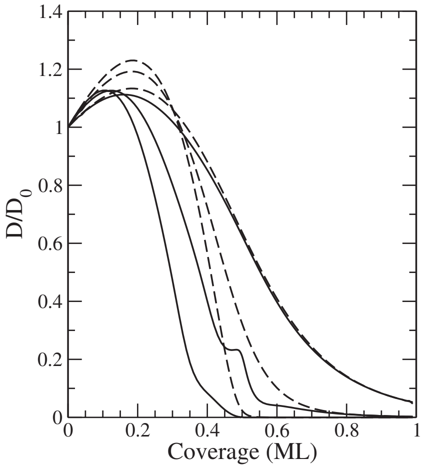

FIG. 1. Normalized diffusivity, Eq. (8), (solid lines) on a square lattice with hopping kinetics of repulsive, first neighbor interactions within the final state, with coefficients $B_n = (e^{-\beta V_1} - 1)^n$ and evaluated in the quasichemical approximation (dashed lines). $\beta V_1 = 1, 2, 5$ (top to bottom at $\theta = 0.4$).

We discuss a few results for the coverage and temperature dependence of D for isotropic interactions (square lattice). For cases (i) and (ii), we have calculated χ and $\langle W \rangle$ almost exactly with a two-row, reduced transfer matrix construction with $N = 18$. Our results for case (i) are similar or superior to the best existing results; we shall present them elsewhere.

In Fig. 1, we show the diffusivity for case (ii) for repulsion only, a scenario which has had little attention. Results

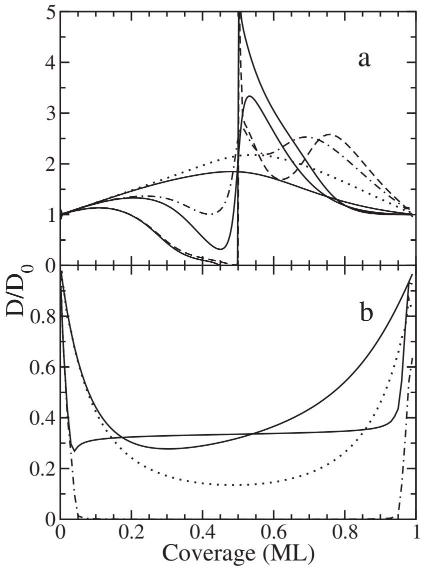

FIG. 2. Normalized diffusivity on a square lattice with the hopping kinetics of first neighbor interactions within both initial and final states, with coefficients $A_1 = C_1$, $A_2 = C_2 - 2A_1$, $A_3 = C_3 - 3A_1 - 2A_2$, $B_n = -A_n$, $C_n = (1 - e^{-n\beta V_1})/(1 + e^{-n\beta V_1})$. Displayed for the gradient expression (8) (solid lines) and the factorization (1) (other). (a) Particle repulsion, $\beta V_1 = 1, 2, 5$ (top to bottom at $\theta = 0.4$); (b) Particle attraction $\beta V_1 = -1, -2$ (top to bottom, $\theta = 0.8$).

for QCA (dashed lines) are included for comparison. In contrast to case (i), the increasing presence of neighbors in the final state results in a decreasing diffusivity for most of the coverage range. For βV_1 large enough site blocking dominates and diffusion is negligible above 1/2 ML. The onset of the $c(2\times 2)$ structure of the final state, around the ordering temperature, is manifested just below 1/2 ML as a shoulder in D. The only existing result is that of Goldstein and Ehrlich[17] for hardcore repulsion, $\beta V_1 \rightarrow \infty$; they assumed Eq. (1) to apply and calculated $D(\theta \lesssim 1/3)$. The behavior of $D(\theta, T)$ for $V_1 < 0$ is not very different from that in 1D[13] after allowance is made for the higher lattice coordination.

In Fig. 2, we compare for case (iii) the diffusivity calculated from Eq. (8), for $N=8$ (solid lines), to that from Eq. (1) (dashed/dotted lines). For V_1 repulsive, the latter form is only acceptable at the lowest coverage. For weak repulsion, the diffusivity is nearly symmetric about 1/2 ML, as expected for this kinetics, in which initial and final neighbors of the hopping particle, respectively, aid and hinder the hop. For strong repulsion, the final-state configuration limits the diffusivity below 1/2 ML so that it resembles case (ii). Above 1/2 ML, D decreases smoothly from a sharp maximum, a behavior not dissimilar to that in 1D for this situation.[13] For V_1 attractive, the factorization (1) is incorrect. In particular, if the attraction is large enough to create a two-phase region for the lattice gas, then χ^{-1} vanishes, although $\langle W \rangle$ is constant. In contrast, the proper D is roughly constant except at the extremes of coverage. The inadequacy of the factorization, for hopping kinetics not controlled by initial- or final-state effects alone, is glaring.

Based on our results for both 1D and 2D diffusion, the effects on the variation of $D(\theta, T)$ due to a particular kinetics choice is as pertinent to the explanation of data as the variation of lateral interactions. An advantage of our gradient expansion is that all choices are easily examined with the relevant correlators at hand. Extensions to other lattice geometries, longer-range interactions, more than one binding site, etc., are straightforward.

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*payne@dal.ca
†h.j.kreuzer@dal.ca

[1] W. Dieterich, P. Fulde, and I. Peschel, Adv. Phys. **29**, 527 (1980).
[2] A. R. Allnatt and A. B. Lidiard, Rep. Prog. Phys. **50**, 373 (1987).
[3] J. W. Haus and K. Kehr, Phys. Rep. **150**, 263 (1987).
[4] T. Ala-Nissila, R. Ferrando, and S. C. Ying, Adv. Phys. **51**, 949 (2002).
[5] G. Antczak and G. Ehrlich, Surf. Sci. Rep. **62**, 39 (2007).
[6] A. Danani, R. Ferrando, E. Scalas, and M. Torri, Int. J. Mod. Phys. B **11**, 2217 (1997).
[7] P. Argyrakis, Y. G. Groda, G. S. Bokun, and V. S. Vikhrenko, Phys. Rev. E **64**, 066108 (2001).
[8] D. A. Reed and G. Ehrlich, Surf. Sci. **102**, 588 (1981).
[9] K. Kawasaki, Phys. Rev. **145**, 224 (1966).
[10] A. A. Tarasenko, L. Jastrabik, and C. Uebing, Phys. Rev. B **57**, 10166 (1998).
[11] A. V. Myshlyavtsev and V. P. Zhdanov, Surf. Sci. **291**, 145 (1993).
[12] S. Lapinskas, E. E. Tornau, V. E. Zubkus, and A. Rosengren, Surf. Sci. **414**, 44 (1998).
[13] S. H. Payne and H. J. Kreuzer, Phys. Rev. B **75**, 115403 (2007).
[14] C. W. Gardiner, *Handbook of Stochastic Methods* (Springer, Berlin, 1985).
[15] Z. Chvoj, J. Phys.: Condens. Matter **12**, 2135 (2000).
[16] H. J. Kreuzer and S. H. Payne, *Computional Methods in Colloid and Interface Science* (Dekker, New York, 1999).
[17] J. T. Goldstein and G. Ehrlich, Surf. Sci. **420**, 1 (1999).