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Many-particle surface diffusion coefficients near first-order phase transitions at low temperatures

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We analyze the chemical and jump surface diffusion coefficients, D_c and D_J, near a first-order phase transition at which two phases coexist and the surface coverage, θ, jumps between single-phase values θ_-^* and θ_+^*. Contrary to other studies, we consider temperatures that are sufficiently subcritical. Using the local equilibrium approximation, we obtain approximate analytical formulas for the dependences of D_c and D_J on the coverage and system size, N, near such a transition. In the two-phase regime, when θ ranges between θ_-^* and θ_+^*, the diffusion coefficients behave as the sums of two hyperbolas, $D_c \approx A_-/N|\theta-\theta_-^*| + A_+/N|\theta-\theta_+^*|$ and $D_J \approx A_-|\theta-\theta_+^*|/\theta + A_+|\theta-\theta_-^*|/\theta$. This behavior rapidly changes as the system goes from the two-phase regime to either of the single-phase regimes (when θ goes below θ_-^* or above θ_+^*). The crossover behavior of $D_c(\theta)$ and $D_J(\theta)$ between the two-phase and single-phase regimes is described by rather complex formulas involving the Lambert function. We consider a lattice-gas model on a triangular lattice to illustrate these general results, applying them to four specific examples of transitions exhibited by the model.

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I. INTRODUCTION

The chemical (or collective) surface diffusion coefficient, D_c, is defined via Fick's first law and describes surface mass-transport processes for a many-particle system. Another relevant many-particle coefficient is the jump surface diffusion coefficient, D_J, that describes the asymptotic behavior of the mean-square displacement of the center of mass of the system (hence, it is also called the center-of-mass diffusion coefficient) [1]. The two diffusion coefficients are related by the Kubo-Green equation [1–3],

$$D_c = \Phi D_J \quad \text{with} \quad \Phi = \frac{\theta}{\chi/\beta}, \tag{1}$$

where $\beta = 1/k_B T$ is the inverse temperature, θ is the surface coverage, and χ is the isothermal susceptibility. The thermodynamic factor Φ is associated with thermodynamic properties of D_c, while D_J is associated with its kinetic properties.

Theoretical studies of the diffusion coefficients D_c and D_J and of the influence of lateral interparticle interactions on these coefficients have often used lattice-gas models to simulate surface diffusion. In these models the migration of adparticles is given by the potential relief of the substrate surface: most of the time the adparticles stay at the positions (sites) where the relief attains its minima, but from time to time they perform random jumps to the adjacent vacant sites. Assuming the jumps to be instant, the states of the system of adparticles are represented by occupation numbers (one number for each site), like in a lattice gas. Although this description is rather oversimplifying, it should possess the key aspects of the diffusion and, moreover, it can be treated by a number of statistical mechanical methods, such as the mean-field, real-space renormalization group, and computer simulation techniques [1,4].

In order to determine the chemical diffusion coefficient D_c in general, one should solve a system of balance equations for a large number of adparticles that strongly interact with each other as well as with the substrate surface. Analytic treatment of such a formidable kinetic problem often results in some kind of approximation. In particular, assuming that the adparticle surface coverage varies only very slowly with time and space (the local equilibrium limit), purely thermodynamic quantities are sufficient to obtain D_c, i.e., the problem reduces to the evaluation of the finite-size specific free energy, f, of the system [2,5–7]. This approximation has been extensively tested for lattice gases, and the results obtained from it by analytical methods have been in good agreement with the numerical results obtained by kinetic simulations [8].

Now, assume that the jumps of adparticles are mutually uncorrelated and restricted to nearest neighbors. In addition, assume that an activated adparticle at a saddle point of the potential barrier interacts only with the adjacent adparticles. Then in the local equilibrium approximation the original problem can be reduced to a diffusion equation, with the corresponding diffusion coefficient given as [5,9,10]

$$D_c \approx D_0\, e^{\beta\mu} \frac{P}{\chi/\beta}, \tag{2}$$

which furthermore yields, due to Eq. (1),

$$D_J \approx D_0\, e^{\beta\mu} \frac{P}{\theta}. \tag{3}$$

Here D_0 is the diffusion coefficient of noninteracting particles and μ is the chemical potential. The correlation factor P can be expressed via derivatives of the free energy f [see Eqs. (4) below] so that it is a thermodynamic quantity, like the coverage θ and susceptibility χ. Consequently, the evaluation of f is sufficient to yield the diffusion coefficients D_c and D_J from the approximative expressions (2) and (3).

The correlation factor P is associated with the interactions of an activated adparticle with other particles. It is given as a sum of the probabilities that certain clusters of adjacent sites are vacant [8,9,11]. The clusters contain the lattice bond on which a particle jump is performed, plus the neighboring sites with which an activated adparticle is considered to

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interact. Usually, only the sites nearest to the saddle point are considered. Then the clusters are quite small (for example, for a triangular lattice they can be bonds, elementary triangles, and parallelograms [9]). Clearly, the probabilities that clusters are vacant may be expressed via derivatives of f with respect to suitable interparticle interaction parameters, u_i. Therefore, quite generally, the factor P has the form given as

$$P = C_0 + \sum_i C_i \xi_i \quad \text{with} \quad \xi_i \equiv \frac{\partial f}{\partial u_i}, \tag{4}$$

where the constants C_i may depend on the interaction parameters of an activated adparticle.

One of the intriguing problems that has attracted particular attention is the presence of phase transitions and their effects on surface diffusion. Since lattice gases can be used to model such transitions, they have provided a convenient framework also in this regard [3,9,10,12–20]. However, below critical temperatures ordered phases may arise due to lateral interactions, and sophisticated arguments should be applied to analyze surface diffusion [9]. In fact, very low temperatures have not been considered in the previous studies.

In this paper we wish to fill in this gap and study the diffusion coefficients D_c and D_J at sufficiently low temperatures. We shall concentrate on their dependences on the chemical potential μ, surface coverage θ, and the number N, of adparticles in the system. Our analysis is based on two key points. First, we assume that the approximative expressions (2) and (3) for D_c and D_J can be applied. This is appropriate only in the local equilibrium limit and under the above-mentioned assumptions on the adparticle jumps. Then D_c and D_J can be obtained just from the finite-size specific free energy $f = -(1/\beta N)\ln Z$ of the system, where Z is the finite-size partition function. Second, we assume that a first-order phase transition between two phases, p_+ and p_-, takes place in the system at a transition point $\mu = \mu_t$. At low temperatures and near the transition point (for $|\mu - \mu_t| \leqslant \text{const}/\beta\sqrt{N}$), we will employ the formula [21,22]

$$Z = (\nu_- e^{-\beta f_- N} + \nu_+ e^{-\beta f_+ N})(1 + r) \tag{5}$$

that is applicable for a large class of lattice-gas models with periodic boundary conditions, such as the models with a finite range m-potential and a finite number of ground states. Here $\nu_\pm$ are the degeneracies of phases $p_\pm$, $f_\pm$ are their single-phase specific free energies, and the error term $r = O[\exp(-\text{const}\beta\sqrt{N})]$. [We use the symbol $O(x)$ to represent a term that can be bounded by const x.]

Combining Eqs. (2)–(5), we will be able to obtain general finite-size formulas for the diffusion coefficients D_c and D_J near a low-temperature phase transition of first-order (see Sec. II). For the sake of illustration, we find it useful to consider a specific lattice-gas model of surface diffusion and show how our general results on D_c and D_J can be applied to this particular model (see Sec. III).

II. GENERAL FORMULAS FOR THE DIFFUSION COEFFICIENTS NEAR A PHASE TRANSITION

Our starting point in the study of the diffusion coefficients D_c and D_J is the general expression (5) for the partition function Z. It enables us to write the finite-size specific free energy f as

$$f = \varphi + r, \tag{6a}$$

where the shorthand

$$\varphi \equiv -\frac{1}{\beta N}\ln(\nu_- e^{-\beta f_- N} + \nu_+ e^{-\beta f_+ N}). \tag{6b}$$

Thus, f coincides with φ up to the error term r. Analogously, derivatives of f coincide with the corresponding derivatives of φ up to the same error term r [22].

Next, we use Eq. (6) to evaluate the coverage θ, susceptibility χ, and correlation factor P. We easily get [23]

$$\begin{aligned} \theta &= -\frac{\partial f}{\partial \mu} = \theta_- \lambda_- + \theta_+ \lambda_+ + r, \\ \xi_i &= \frac{\partial f}{\partial u_i} = \xi_{i-}\lambda_- + \xi_{i+}\lambda_+ + r, \\ \chi &= -\frac{\partial^2 f}{\partial \mu^2} = (\theta_+ - \theta_-)^2 \beta N \lambda_- \lambda_+ + \chi_- \lambda_- + \chi_+ \lambda_+ + r, \end{aligned} \tag{7}$$

where

$$\lambda_\pm \equiv \frac{\nu_\pm e^{-\beta f_\pm N}}{\nu_- e^{-\beta f_- N} + \nu_+ e^{-\beta f_+ N}} \tag{8}$$

may be viewed as weight factors (because $\lambda_\pm > 0$ and $\lambda_- + \lambda_+ = 1$). Equation (7) shows that the coverage θ is, up to the error r, the weighted average of the single-phase coverages $\theta_\pm \equiv \partial f_\pm/\partial \mu$, the weights being $\lambda_\pm$. Similarly, the quantities ξ_i from the factor P are the weighted averages of their single-phase versions $\xi_{i\pm} \equiv \partial f_\pm/\partial u_i$. The susceptibility χ has a more complex structure: it is a sum of a term proportional to the system size N and the weighted average of the single-phase susceptibilities $\chi_\pm \equiv -\partial^2 f_\pm/\partial \mu^2$.

Relations (7) provide the dependences of θ, ξ_i (or P), and χ on the chemical potential μ (via the μ dependences of the single-phase free energies $f_\pm$). Consequently, combining the relations with Eqs. (2)–(4), we immediately get approximative expressions for the μ dependences of the diffusion coefficients D_c and D_J. In order to get the coverage dependences of the diffusion coefficients, one needs to eliminate μ between $D_c(\mu)$ and $D_J(\mu)$ on the one hand and $\theta(\mu)$ on the other one. This can be easily carried out numerically for a given system as soon as $f_\pm(\mu)$ are evaluated.

Nevertheless, explicit finite-size formulas for the coverage dependences of the diffusion coefficients can be also derived. To this end, we shall consider three different regimes in the behavior of D_c and D_J. The regimes are distinguished by the relative importance of phases p_- and p_+ as given by their weights λ_+ and λ_-, respectively. Namely, if neither λ_+ nor λ_- is negligible, both phases are dominant, and we speak of a two-phase regime. On the other hand, if one of the weights is negligible, only one phase is dominant, and we speak of a single-phase regime. In transition between the two regimes yet another regime arises; we call it a crossover regime. Let us now consider the three regimes separately. Without loss of generality, we will assume that phase p_- (p_+) is stable for μ below (above) the transition point μ_t; then the coverage jump at the transition is $\theta_+(\mu_t) - \theta_-(\mu_t)$.

Notation. We shall use Δq to denote the difference, $q_+ - q_-$, of single-phase quantities q_+ and q_-. Moreover, the starred quantity, q^*, will denote the value $q(\mu_t)$ of a quantity q at the transition. For example, the coverage jump at the transition will read $\theta_+^* - \theta_-^* = \Delta\theta^*$.

A. Two-phase regime

The two-phase regime occurs when the leading term in the susceptibility χ is the term proportional to the system size (then both λ_- and λ_+ are of order larger than N^{-1}). This is true only very near the transition point, namely, for μ satisfying [21,23]

$$\beta|\mu - \mu_t| \leqslant \delta \quad \text{with} \quad \delta = \frac{\gamma}{\Delta\theta^*}\frac{\ln N}{N}. \tag{9}$$

The constant γ can range from 1/2 to 1. To be specific, we shall take $\gamma = 3/4$ in the following.

In the two-phase range (9) the single-phase quantities $\theta_\pm$ and $\xi_{i\pm}$ coincide with their values $\theta_\pm^*$ and $\xi_{i\pm}^*$ at the transition, up to errors of order δ. Therefore, the expressions in Eq. (7) may be written as

$$\begin{aligned} \theta &= \theta_-^*\lambda_- + \theta_+^*\lambda_+ + O(\delta), \\ \xi_i &= \xi_{i-}^*\lambda_- + \xi_{i+}^*\lambda_+ + O(\delta), \\ \chi &= (\Delta\theta^*)^2\beta N\lambda_+\lambda_-[1 + O(N^{-1/4})]. \end{aligned} \tag{10}$$

Hence, θ and ξ_i are the weighted averages of the constants $\theta_\pm^*$ and $\xi_{i\pm}^*$, while the susceptibility is proportional to the system size N. Note that, as μ varies within range (9), the coverage varies within the range

$$t_- \leqslant \theta \leqslant t_+, \tag{11}$$

where $t_\pm \equiv \theta(\mu_t \pm \delta/\beta) = \theta_\pm^* \mp \Delta\theta^*(\nu_\mp/\nu_\pm)N^{-3/4} + O(\delta)$ by Eq. (10). Thus, in the two-phase regime the coverage attains almost all values between θ_-^* and θ_+^*.

The μ dependences of θ, ξ_i, and χ in Eq. (10) are primarily given by the weights $\lambda_\pm$. So, the elimination of μ amounts to the elimination of $\lambda_\pm$. From Eq. (10) and the equality $\lambda_+ + \lambda_- = 1$, the coverage dependences $\lambda_\pm = \pm(\theta - \theta_\mp^*)/\Delta\theta^* + O(\delta)$ of the weights follow. They in turn yield the coverage dependences of ξ_i and χ. Substituting the latter into Eqs. (2)–(4), we get the coverage dependence of the diffusion coefficients as

$$\begin{aligned} D_c &\approx \frac{D_0 e^{\beta\mu_t}}{\Delta\theta^* N}\left(\frac{P_-^*}{\theta - \theta_-^*} + \frac{P_+^*}{\theta_+^* - \theta} + \epsilon\right)(1 + \epsilon), \\ D_J &\approx \frac{D_0 e^{\beta\mu_t}}{\Delta\theta^*}\left(P_-^*\frac{\theta_+^* - \theta}{\theta} + P_+^*\frac{\theta - \theta_-^*}{\theta} + \epsilon\right), \end{aligned} \tag{12}$$

where $P_\pm^* = C_0 + \sum_i C_i\xi_{i\pm}^*$ are the single-phase values of the correlation factor P at the transition and the error term $\epsilon = O(N^{3/4}\delta) = O(N^{-1/4}\ln N)$.

The first formula in Eq. (12) shows that the coverage dependence of D_c behaves as the sum of two hyperbolas, $A_\pm/N|\theta - \theta_\pm^*|$, decreasing with the system size as $1/N$. For a given size N, it quite slowly varies if θ is well between t_- and t_+, while it rapidly increases in a hyperbolic way if θ is close to $t_\pm$. The second formula in Eq. (12) shows that the coverage dependence of D_J is essentially independent of the system size N. It also behaves as the sum of two hyperbolas, $A_\pm|\theta - \theta_\mp^*|/\theta$. These results will be illustrated for a specific model in the following section (see Fig. 2).

B. Crossover regimes

The two-phase region is at either end neighbored by a crossover region. The crossover corresponds to a rapid change of the term in χ that is proportional to the system size N—from the leading term it suddenly turns into an error term (the order of either λ_- or λ_+ decreases from above N^{-1} below it). The two crossovers take place within the ranges

$$\delta \leqslant \beta|\mu - \mu_t| \leqslant d \quad \text{with} \quad d = \frac{c}{\Delta\theta^*}\frac{\ln N}{N}. \tag{13}$$

The constant c must exceed 1, and we shall take $c = 5/4$ in the following.

In the crossover ranges (13) we may approximate the single-phase quantities $\theta_\pm$ and $\xi_{i\pm}$ by the linear perturbations $\theta_\pm^* + \chi_\pm^*(\mu - \mu_t)$ and $\xi_{i\pm}^* + \zeta_{i\pm}^*(\mu - \mu_t)$ from their values at the transition, making errors of order d^2. (Here $\zeta_{i\pm}^*$ are the derivatives $\zeta_{i\pm} = \partial\xi_{i\pm}/\partial\mu$ evaluated at μ_t.) The single-phase susceptibilities $\chi_\pm$ coincide with their transition values $\chi_\pm^*$, up to errors of order βd. As for the weights, in the crossover above (below) the transition we have $\lambda_+ = 1 - \mathcal{E}_+$ and $\lambda_- = \mathcal{E}_+$ ($\lambda_+ = \mathcal{E}_-$ and $\lambda_- = 1 - \mathcal{E}_-$) with $\mathcal{E}_\pm = (\nu_\mp/\nu_\pm)\exp(-\Delta\theta^*\beta N|\mu - \mu_t|)$, the errors being of order $N^{-3/2}$. Consequently, Eq. (7) may be written as

$$\begin{aligned} \theta &= \theta_\pm^* \pm \left(\chi_\pm^*|\mu - \mu_t| - \Delta\theta^*\frac{\nu_\mp}{\nu_\pm}e^{-\Delta\theta^*\beta N|\mu - \mu_t|}\right) + \epsilon', \\ \xi_i &= \xi_{i\pm}^* \pm \left(\zeta_{i\pm}^*|\mu - \mu_t| - \Delta\xi_i^*\frac{\nu_\mp}{\nu_\pm}e^{-\Delta\theta^*\beta N|\mu - \mu_t|}\right) + \epsilon', \\ \chi &= \chi_\pm^* + (\Delta\theta^*)^2\beta N\frac{\nu_\mp}{\nu_\pm}e^{-\Delta\theta^*\beta N|\mu - \mu_t|} + \beta N\epsilon', \end{aligned} \tag{14}$$

where the upper/lower signs correspond to the crossover range above/below μ_t and the error term $\epsilon' = O(N^{-3/2})$. Thus, θ and ξ_i differ from their single-phase values $\theta_\pm^*$ and $\xi_{i\pm}^*$ by a small (positive or negative) amount whose value is given by an interplay between two terms, one being linear and one exponential in $|\mu - \mu_t|$. The exponential term also determines the difference between χ and its single-phase value $\chi_\pm^*$. Note that, as μ varies within ranges (13), the coverage varies within the ranges

$$\tau_- \leqslant \theta \leqslant t_-, \quad t_+ \leqslant \theta \leqslant \tau_+ \tag{15}$$

with $\tau_\pm \equiv \theta(\mu_t \pm d/\beta) = \theta_\pm^* \pm (\chi_\pm^*/\beta)d + O(N^{-5/4})$ by Eq. (14). These are very narrow intervals concentrated around $\theta_\pm^*$.

The μ dependences of θ, ξ_i, and χ in Eq. (14) are essentially given via the difference $|\mu - \mu_t|$. Evaluating the difference as a function of θ from the first of these dependences, the coverage dependences of ξ_i and χ can be deduced. Combining them with Eqs. (2)–(4), the coverage dependences of the diffusion coefficients follow. We get

$$\begin{aligned} D_c &\approx D_0 e^{\beta\mu_t}\left(\frac{\omega_\pm + N\epsilon'}{\Delta\theta^*\frac{\nu_\mp}{\nu_\pm}K_\pm}\right)^{\mp\frac{1}{\Delta\theta^* N}}\frac{\mathcal{P}_\pm(1 + N\epsilon')}{\frac{1}{\beta}\chi_\pm^*[1 + \omega_\pm]}, \\ D_J &\approx D_0 e^{\beta\mu_t}\left(\frac{\omega_\pm + N\epsilon'}{\Delta\theta^*\frac{\nu_\mp}{\nu_\pm}K_\pm}\right)^{\mp\frac{1}{\Delta\theta^* N}}\frac{\mathcal{P}_\pm}{\theta}, \end{aligned} \tag{16}$$

where

$$\mathcal{P}_\pm = P^*_\pm + \frac{P'^*_\pm}{\chi^*_\pm}(\theta-\theta^*_\pm) \pm \left(\frac{P'^*_\pm}{\chi^*_\pm} - \frac{\Delta P^*}{\Delta\theta^*}\right)\frac{\omega_\pm}{K_\pm} + \epsilon' \qquad (17)$$

are the coverage dependences of the correlation factor P in the crossover regimes and the shorthand

$$\omega_\pm \equiv W\left(\Delta\theta^* \frac{\nu_\mp}{\nu_\pm} K_\pm e^{\mp K_\pm(\theta-\theta^*_\pm)}\right). \qquad (18)$$

The constant $P'^*_\pm \equiv \sum_i C_i \zeta^*_{i\pm}$ is equal to the derivative $\partial P_\pm/\partial\mu$ of $P_\pm = C_0 + \sum_i C_i \xi_{i\pm}$ evaluated at $\mu = \mu_t$, so it represents the rate of change of P with μ in a given phase at the transition. The constant $K_\pm \equiv \Delta\theta^* \beta N/\chi^*_\pm$, while $W(y)$ is the Lambert function (the inverse to $y = W \exp W$). The upper and lower signs in Eqs. (16)–(18) correspond to the crossover range (15) around the points θ^*_+ and θ^*_-, respectively.

The behavior of the diffusion coefficients in the crossover regime as given by Eq. (16) is quite complex. To describe it, we may consider two extreme cases. First, if θ is close to the two-phase region (close to $t_\pm$), then $\omega_\pm \approx K_\pm|\theta-\theta^*_\pm| \gg 1$, $\mathcal{P}_\pm \approx P^*_\pm \mp (\Delta P^*/\Delta\theta^*)|\theta-\theta^*_\pm|$, and $\chi \approx \Delta\theta^*\beta N|\theta-\theta^*_\pm|$. Hence, for these coverages formula (16) yields the same D_c and D_J as the two-phase regime formula (12) would predict. Second, if θ is close to one of the two single-phase regions (close to $\tau_\pm$), then $\omega_\pm \approx \Delta\theta^*(\nu_\mp/\nu_\pm)K_\pm \exp(-K_\pm|\theta-\theta^*_\pm|) \ll 1$ so that $\mathcal{P}_\pm \approx P^*_\pm + (P'^*_\pm/\chi^*_\pm)(\theta-\theta^*_\pm)$ and $\chi \approx \chi^*_\pm$. Hence, for these coverages the diffusion coefficients are linearly disturbed from their single-phase values evaluated at the transition. The two extremes show that within the crossover regions the diffusion coefficients D_c and D_J suddenly change from their two-phase to their single-phase behavior. We will illustrate these results for a specific model in the following section (see Fig. 3).

C. Single-phase regimes

Finally, far from the transition there is a single dominant phase: p_- for $\mu < \mu_t - d$ (i.e., θ below τ_-) and p_+ for $\mu > \mu_t + d$ (i.e., θ above τ_+). Then θ, ξ_i (or P), and χ reduce to their single-phase values [22,23],

$$\theta \approx -\frac{\partial f_\pm}{\partial\mu}, \quad \xi_i \approx \frac{\partial f_\pm}{\partial u_i}, \quad \chi \approx -\frac{\partial^2 f_\pm}{\partial\mu^2}. \qquad (19)$$

The upper/lower sign corresponds to the μ range where phase p_+/p_- is stable and the errors are of order N^{-1}. In order to obtain the coverage dependences of D_c and D_J in this regime, explicit expressions for $f_\pm$ are needed. Therefore, we will discuss the dependences only for the illustrative model in the following section (see Fig. 3).

III. APPLICATION TO A MODEL

Let us now apply the above general results to a specific lattice model of surface diffusion.

A. The model

The model assumes that particles can be adsorbed on a solid surface only at sites forming a regular triangular lattice. The system contains a rectangular array with a large but finite number N of adsorption sites. Periodic boundary conditions are applied so that the array forms a finite torus. For the mesh size equal to 1, the elementary lattice vectors are taken as (1,0) and $(1/2,\sqrt{3}/2)$. The torus cell is specified by the vectors $(3n,0)$ and $(0,2\sqrt{3}n)$ with $n = 1,2,\ldots$; thus, $N = 3n \times 4n$.

Each lattice site is either vacant or occupied by a particle. The interaction between two particles is limited to nearest-neighbor pairs (bonds) with an interaction energy that depends on the surrounding particles in the simplest possible way—only on the presence of particles at the sites closest to the bond. For the triangular lattice there are two such sites. The bond together with either of the sites forms an elementary triangle. Hence, the varying interaction energy is equivalent to having two constant interaction energies: one, ε_b, for occupied bonds and one, ε_t, for occupied elementary triangles. The corresponding Hamiltonian is given as [9,10]

$$H = \varepsilon_b N_b + \varepsilon_t N_t - \mu N_s, \qquad (20)$$

where N_b, N_t, and N_s is the number of occupied bonds, elementary triangles, and sites, respectively. This model was already used to study surface diffusion at high temperatures in the special cases when $\varepsilon_b = 0$ (for T above $0.21|\varepsilon_t|/k_B$) and $\varepsilon_t = 0$ (for T above $0.1|\varepsilon_b|/k_B$) [10]. Here we consider the general case when both the bond and triangle interactions ε_b and ε_t are present, while temperatures are supposed to be sufficiently low.

As we proved in Ref. [21], model (20) has four ground states [see Fig. 1(a)]: a fully vacant state, σ_0, a fully occupied state, σ_1, and two threefold degenerate states, $\sigma_{1/3}$ and $\sigma_{2/3}$.

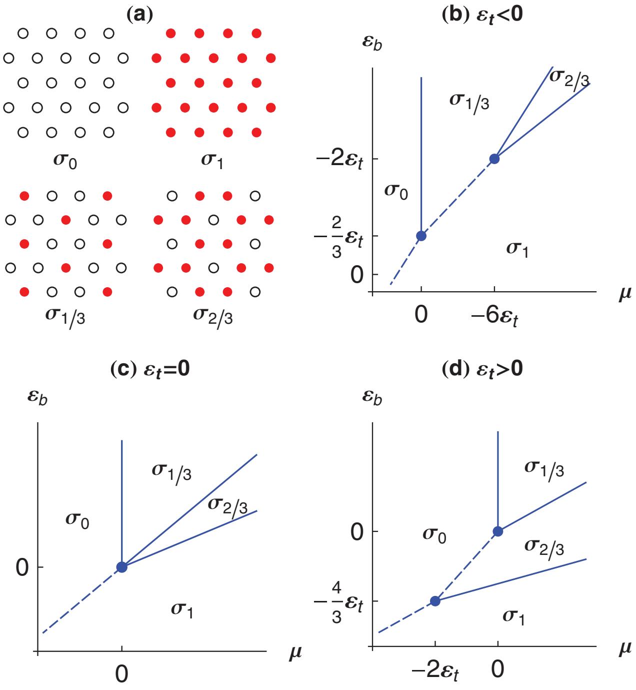


FIG. 1. (Color online) (a) The ground states of the model. Circles (disks) represent vacant (occupied) sites. (b)–(d) The ground-state diagram in dependence on the sign (attractivity or repulsivity) of the triangle interaction ε_t. On the boundaries between two ground-state regions either the two ground states coexist (the dashed lines) or there are infinitely many ground states (the solid lines, including their end points depicted by disks).

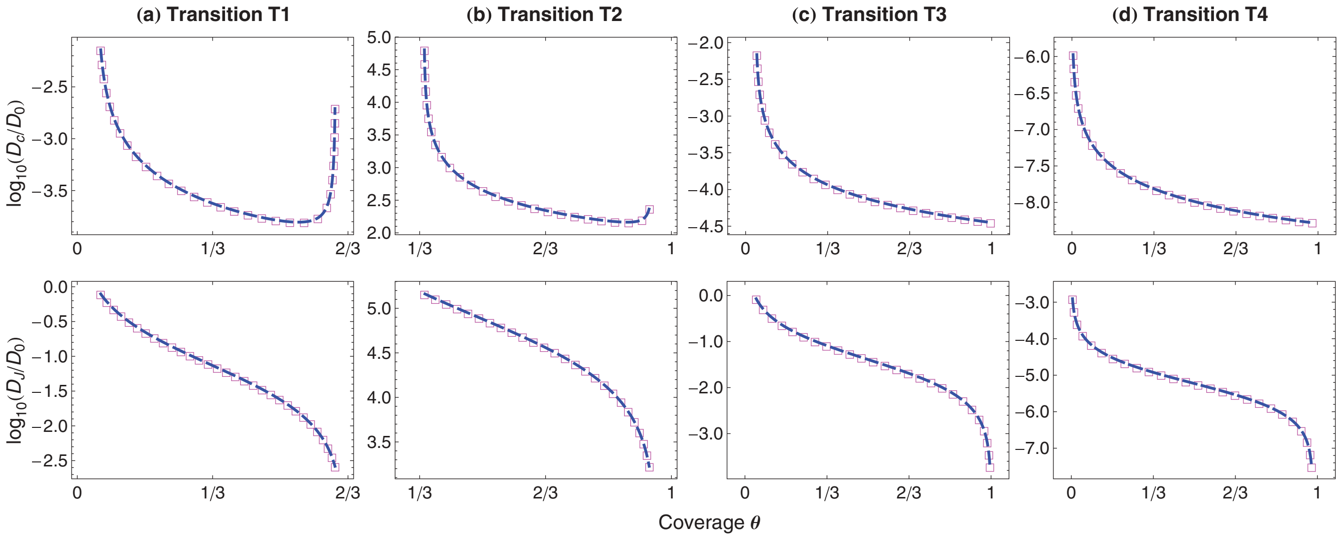


FIG. 2. (Color online) The coverage dependence of the logarithm the diffusion coefficients D_c and D_J (relative to D_0) in the two-phase region (11) for $N = 30 \times 40$. The bond interactions are (a) $\varepsilon_b = -\varepsilon_t/2 < 0$, (b) $\varepsilon_b = -4\varepsilon_t/3 > 0$, (c) $\varepsilon_b = -2\varepsilon_t/5 > 0$, and (d) $\varepsilon_b = -5\varepsilon_t/3 < 0$. The triangle interaction $\beta|\varepsilon_t| = 4$ in all cases. The squares correspond to numerical values, whereas the dashed lines correspond to the analytical formula (12).

The coverage of the two latter states is only partial, namely, 1/3 and 2/3, respectively. The ground-state diagram is shown in Figs. 1(b)–1(d) and can be easily constructed by comparing the four ground-state energies $e_0 = 0$, $e_1 = 3\varepsilon_b + 2\varepsilon_t - \mu$, $e_{1/3} = -\mu/3$, and $e_{2/3} = \varepsilon_b - 2\mu/3$. On the lines separating the regions of ground states σ_0 and σ_1, σ_0 and $\sigma_{2/3}$, and σ_1 and $\sigma_{1/3}$ (the dashed lines in Fig. 1), only these two ground states coexist. However, on the remaining lines (the solid lines in Fig. 1) as well as at the points where three or all four ground-state regions meet, there is an infinite number of ground states, yielding in fact a residual entropy.

Each ground state σ_α, $\alpha = 0,1/3,2/3,1$, gives rise to a unique low-temperature phase, p_α, whose typical configuration looks like a "sea" of the ground state σ_α in which isolated "islands" of non-ground-state configurations are scattered, thus resembling the structure of σ_α [21]. So, phase p_0 (p_1) is fully vacant (fully occupied), while phase $p_{1/3}$ ($p_{2/3}$) has an occupancy of 1/3 (2/3). The existence of these low-temperature phases can be concluded only if the number of ground states is finite, i.e., only within each ground-state region and on the lines between these regions where only two ground states coexist (the dashed lines in Fig. 1). Otherwise, no conclusions concerning low-temperature phases were drawn in Ref. [21]. Consequently, a first-order phase transition takes place between phases p_0 and p_1, p_0 and $p_{2/3}$, and $p_{1/3}$ and p_1, whereas transitions between other phases need not be of first order.

The specific free energy f_α of phase p_α is essentially equal to its ground-state specific energy e_α because the contributions from the thermal perturbations of the ground states σ_α are suppressed exponentially in β (the Peierls condition). Namely, taking into account only one-site perturbations (which represent the leading corrections), one has [21]

$$f_\alpha \approx e_\alpha - \frac{1}{\beta}\ln\left[\left(1+e^{-\beta\,\Delta H_\alpha^\circ}\right)^{\alpha}\left(1+e^{-\beta\,\Delta H_\alpha^\bullet}\right)^{1-\alpha}\right], \tag{21}$$

where

$$\begin{aligned}\Delta H_0^\bullet &= -\Delta H_{1/3}^\circ = -\mu,\\ \Delta H_{1/3}^\bullet &= -\Delta H_{2/3}^\circ = 3\varepsilon_b - \mu,\\ \Delta H_{2/3}^\bullet &= -\Delta H_1^\circ = 6\varepsilon_b + 6\varepsilon_t - \mu\end{aligned} \tag{22}$$

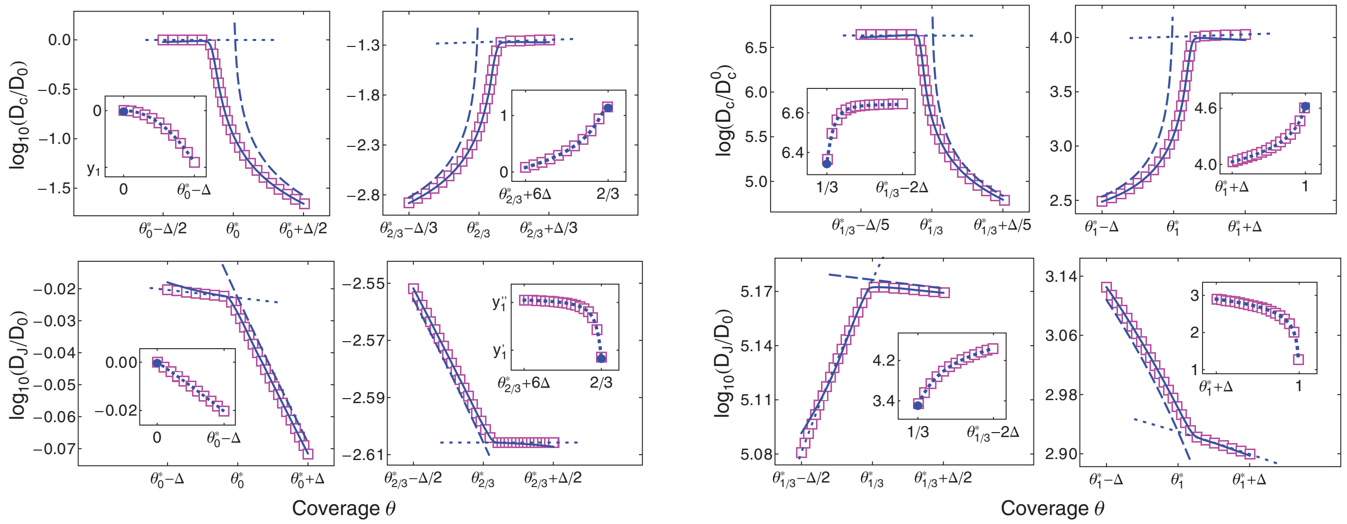
are the energy excesses of one-site perturbations of σ_α over σ_α. The superscript "$\circ$" corresponds to removing one particle from σ_α and "$\bullet$" to adding one particle to σ_α. Since a particle can be only added to σ_0 (only removed from σ_1), in Eq. (21) for $\alpha = 0$ ($\alpha = 1$) the first (second) term in ln is set equal to 1.

B. The diffusion coefficients

We shall apply the general results, Eqs. (12) and (16), to model (20) for the following four representative examples of first-order phase transitions.

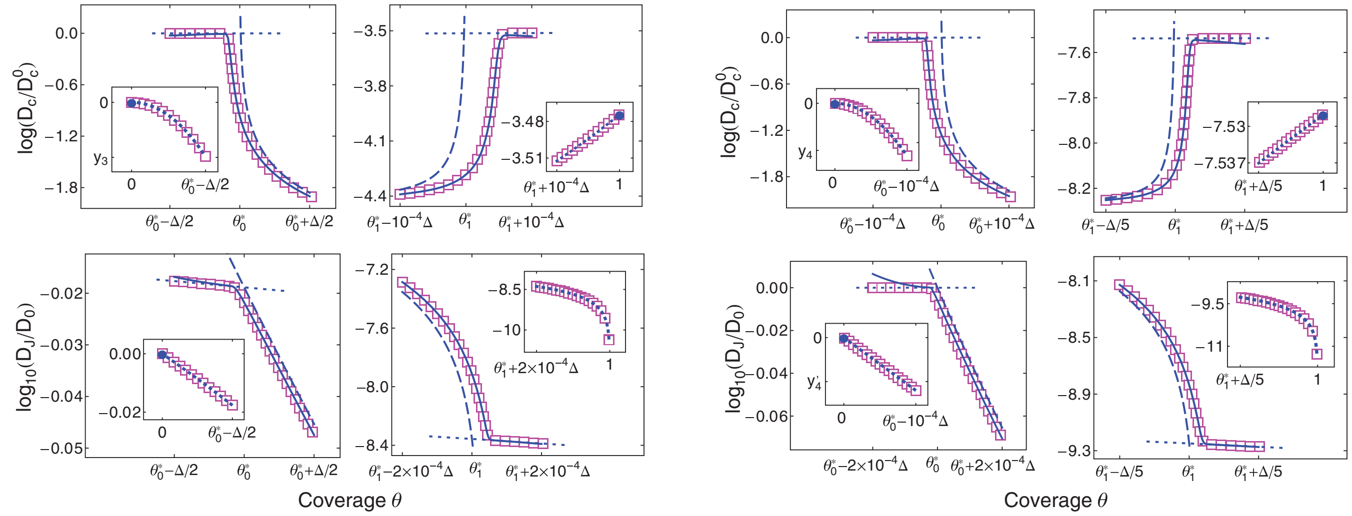
(T1) Transition between phases p_0 and $p_{2/3}$: $\varepsilon_t > 0$ (repulsion), $\varepsilon_b = -\varepsilon_t/2$ (attraction), and $|\mu - \mu_0| \leqslant \varepsilon_t$ with $\mu_0 = 3\varepsilon_b/2$.
(T2) Transition between phases $p_{1/3}$ and p_1: $\varepsilon_t < 0$ (attraction), $\varepsilon_b = -4\varepsilon_t/3$ (repulsion), and $|\mu - \mu_0| \leqslant |\varepsilon_t|$ with $\mu_0 = (9\varepsilon_b + 6\varepsilon_t)/2$.
(T3) Transition between phases p_0 and p_1: $\varepsilon_t < 0$ (attraction), $\varepsilon_b = -\varepsilon_t/3$ (repulsion), and $|\mu - \mu_0| \leqslant |\varepsilon_t|$ with $\mu_0 = 3\varepsilon_b + 2\varepsilon_t$.
(T4) Transition between phases p_0 and p_1: $\varepsilon_t > 0$ (repulsion), $\varepsilon_b = -2\varepsilon_t$ (attraction), and $|\mu - \mu_0| \leqslant \varepsilon_t$ with $\mu_0 = 3\varepsilon_b + 2\varepsilon_t$.

The finite-size specific free energy f of the model near any of these transitions can be readily evaluated from Eqs. (6) and (21). (The degeneracies of phases p_0 and p_1 are equal to 1, while those of phases $p_{1/3}$ and $p_{2/3}$ to 3.) The value μ_t of the point of transition between two phases can be also evaluated—



(a) Transition T1

(b) Transition T2



(c) Transition T3

(d) Transition T4

FIG. 3. (Color online) The coverage dependence of the logarithm of the diffusion coefficients D_c and D_J (relative to D_0) in the crossover and single-phase regions for the same system size and interparticle interactions as in Fig. 2. The squares represent numerical values, whereas the dashed and solid lines correspond to the analytical formula (12) and (16), respectively. The dotted lines represent the analytical dependence obtained in the single-phase regions, and the disks depict their limiting values. The shorthand notations are $\Delta = N^{-3/4}$, $y_1 = -0.001$, $y_1' = -2.6058$, $y_1'' = -2.60577$, $y_3 = -0.0007$, $y_4 = -1.2 \times 10^{-11}$, and $y_4' = -2 \times 10^{-6}$.

it is the chemical potential at which the free energies (21) of the two phases coincide [22].

Moreover, we will work with the widely used form of the correlation factor P that corresponds to the simplest case when an activated adparticle does not interact with any neighbors. Then P is identified with the probability that a lattice bond is vacant so that, for the triangular lattice, one has [9,10]

$$P = 1 - 2\theta + \tfrac{1}{3}\xi, \tag{23}$$

where $\xi \equiv \partial f/\partial \varepsilon_b$ is the statistical average number of occupied bonds. (The coverage θ is, of course, the statistical average number of occupied sites.) Note that factor (23) is a special case of the general form (4) with $C_0 = 1$, $C_1 = -2$, $C_2 = 1/3$, $u_1 = \mu$, and $u_2 = \varepsilon_b$.

We first obtain the coverage dependences of the diffusion coefficients D_c and D_J near transitions T1–T4 numerically, using Eqs. (2), (3), (6), and (7). Then we compare them to the dependences yielded by the analytical formulas (12) and (16) in which the error terms are neglected.

In Fig. 2 we depict the coverage dependences of the diffusion coefficients in the two-phase interval for transitions T1–T4. Obviously, the analytical formulas very accurately reproduce the numerical results. If we neglect thermal effects and the error terms in Eq. (12), for model (20) we can approximately write

$$\frac{D_c}{D_0} \approx \frac{e^{\beta\mu_t}}{N} \times \begin{cases} 3/2\theta & \text{transition } p_0 - p_{2/3}, \\ 3/2(3\theta - 1) & \text{transition } p_{1/3} - p_1, \\ 1/\theta & \text{transition } p_0 - p_1 \end{cases} \tag{24a}$$

and

$$\frac{D_J}{D_0} \approx e^{\beta\mu_t} \times \begin{cases} 1/\theta - 3/2 & \text{transition } p_0 - p_{2/3}, \\ (1/\theta - 1)/2 & \text{transition } p_{1/3} - p_1, \\ 1/\theta - 1 & \text{transition } p_0 - p_1. \end{cases} \tag{24b}$$

In the crossover regions the coverage dependences of the diffusion coefficients for transitions T1–T4 are shown in Fig. 3. Very good agreement between the analytical and numerical results is again obtained.

In the single-phase regions the coverage dependences of D_c and D_J can be derived from Eq. (19), using the explicit expressions (21) and (23) for the single-phase free energies and correlation factor. This is simple to carry out for phases p_0 and p_1, yielding

$$\frac{D_c}{D_0} \approx \frac{1-2\theta}{(1-\theta)^2}, \quad \frac{D_J}{D_0} \approx \frac{1-2\theta}{1-\theta} \quad \text{regime of } p_0, \tag{25}$$

while $D_c \approx 0$ and $D_J \approx 0$ in the regime of phase p_1. However, for phases $p_{1/3}$ and $p_{2/3}$ the obtained formulas are very complex, and thus we will only present their simplified versions. Namely, using the approximation $\ln(1+x) \approx x$ in Eq. (21) [because $x = \exp(-\beta\Delta H_\alpha^\circ)$ and $x = \exp(-\beta\Delta H_\alpha^\bullet)$ are small at low temperatures], we get

$$\frac{D_c}{D_0} \approx \begin{cases} (5-9\theta+a)(3\theta-1+a)/8q_b^3 a & \text{regime of } p_{1/3}, \\ 2/q_b^3\sqrt{8q_b^3 q_t^6 + (2-3\theta)^2} & \text{regime of } p_{2/3} \end{cases} \tag{26a}$$

and

$$\frac{D_J}{D_0} \approx \begin{cases} (5-9\theta+a)(3\theta-1+a)/24q_b^3\theta & \text{regime of } p_{1/3}, \\ 2/3q_b^3\theta & \text{regime of } p_{2/3}, \end{cases} \tag{26b}$$

where $a \equiv [8q_b^3 + (1-3\theta)^2]^{1/2}$, $q_b \equiv \exp(-\beta\varepsilon_b)$, and $q_t \equiv \exp(-\beta\varepsilon_t)$.

The approximation (21) that uses only one-site perturbations is not sufficient to get a nonvanishing diffusion coefficient in the regime of phase p_1. To resolve this drawback, we need to take into account the next dominant contributions arising from two-site perturbations (the removal of two particles in a bond). Then the additional term $(-3/\beta)\ln[1+\exp(-\beta\Delta H_1^{\bullet\bullet})]$ appears in f_1, where $\Delta H_1^{\bullet\bullet} = 2\mu - 11\varepsilon_b - 10\varepsilon_t$ is the energy excess of a two-site perturbation of σ_1 over σ_1 [21]. Applying this refined expression for f_1, we get an analytic formula for nonvanishing coverage dependences of D_c and D_J. Since the formula is complex, we may use again the approximation $\ln(1+x) \approx x$ to obtain its simplified version

$$\frac{D_c}{D_0} \approx \frac{1}{q_b^5 q_t^4 b}, \quad \frac{D_J}{D_0} \approx \frac{b-1}{12q_b^6 q_t^6\theta} \quad \text{regime of } p_1 \tag{26c}$$

with $b \equiv [1 + 24q_b q_t^2(1-\theta)]^{1/2}$.

The coverage dependences of D_c and D_J in the single-phase regions for transitions T1–T4 are detailed in the insets in Fig. 3. To avoid possible inaccuracies in formulas (26), we employed their complete versions to fit numerical results in the figure.

Notice that, as is clearly demonstrated in Fig. 3, the formulas valid in one of the three regions quite smoothly take over from the formulas valid in a neighboring region. The agreement between different formulas increases quite fast as the system size N grows. Since the transitions between phases p_0 and $p_{1/3}$ and phases $p_{2/3}$ and p_1 need not be of first order, we cannot analyze the behavior of the diffusion coefficients at the points $\theta = 1/3$ and $\theta = 2/3$ from both sides.

IV. CONCLUSIONS

We have investigated the dependences of the chemical and jump diffusion coefficients on the chemical potential and surface coverage at low temperatures. It was assumed that a first-order phase transition between two phases takes place in the system and that the local limit approximation is applicable. The key aspect of the approximation was that the diffusion coefficients could be evaluated only from the finite-size specific free energy f of the system. Hence, rather crudely but plausibly, the original kinetic problem was reduced to a thermodynamic one. Our analysis was based on a general formula, Eq. (6), for the free energy f valid near the transition.

We identified three types of regions, each of which was associated with a different behavior of the diffusion coefficients: a two-phase region at and very close to the transition, two single-phase regions farther away from the transition, and two crossover regions in between. We derived finite-size formulas for the diffusion coefficients in the two-phase and crossover regions, Eqs. (12) and (16), and applied them to an illustrative model of surface diffusion on a triangular lattice (see Figs. 2 and 3). In the single-phase regions we were able to obtain only model-dependent formulas.

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