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ПОВЕРХНОСТНАЯ ДИФФУЗИЯ ПРИ СУБКРИТИЧЕСКИХ ТЕМПЕРАТУРАХ

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Аннотация. Представлен статистическо-механический подход к изучению поверхностной диффузии с помощью модели газовой решётки. Обсуждаются общие формулы для функции покрытия химических и скачковых диффузионных коэффициентов при низких температурах и в локальном равновесном пределе. Также обсуждается использование специфической двухмерной модели.

Ключевые слова: зависимость покрытия, низкие температуры, фазовые переходы, коэффициент поверхностной диффузии

SURFACE DIFFUSION AT SUBCRITICAL TEMPERATURES: SELECTED RIGOROUS RESULTS

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Abstract. A statistical mechanical approach to study surface diffusion by lattice-gas models is presented. General formulas for the coverage dependences of chemical and jump diffusion coefficients are discussed at low temperatures and in the local equilibrium limit. An application to a specific two-dimensional model is considered.

Keywords: Coverage dependence, low temperatures, phase transition, surface diffusion coefficient

1. Introduction

Migration of adsorbates on solid surfaces is essential in many physical-chemical processes, for example, adsorption and desorption, crystal and film growth, melting, or roughening. Good understanding of the migration, and surface diffusion in particular, is important if one should be able to control these processes.

A relevant parameter that describes surface mass transport for a many-particle system is the chemical surface diffusion coefficient, D_c . It is defined via the Fick's first law, $\mathbf{J} = -D_c \nabla \theta$, where \mathbf{J} is the surface diffusion flux and θ is the surface coverage. Due to the Kubo-Green equation [1-3],

$$D_c = \Phi D_j, \quad \Phi = \frac{1}{k_B T} \frac{\theta}{\chi}, \quad (1)$$

one may separate thermodynamic and kinetic properties of D_c : the former are represented by the thermodynamic factor Φ , while the latter by the jump surface diffusion coefficient D_j . Here k_B is the Boltzmann constant, T is the temperature, and χ is the isothermal susceptibility.

Lattice-gas models are conveniently used 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 particles are at the positions (sites) where the relief has minima, but occasionally they make random jumps to neighboring vacant sites. If the jumps are considered to be instant, the microstates of a system can be represented by occupation numbers (one number for each site), exactly as in a lattice-gas model. Although this description is rather simplifying, it is expected that it contains the principal features of the diffusion. Moreover, there are several statistical mechanical methods (the mean-field, real-space renormalization group, or computer simulation techniques) that can be applied to study lattice-gas models [3, 4].

To determine the diffusion coefficient D_c , it is necessary to solve a set of balance equations for a system of particles strongly interacting among themselves as well as with the substrate surface. An approximation is usually considered to treat such a complex kinetic problem. One of them is the local equilibrium limit in which the surface coverage θ is supposed to vary very slowly with time and space. Then the coefficient D_c can be expressed via thermodynamic quantities, i.e., via the free energy, f , of the system [1, 5-7]. This approach is rather safe for lattice gases: the obtained analytical results were shown to be in good agreement with the numerical (Monte Carlo) results [8].

An intriguing problem is a sudden deposition of an adsorbate (a sudden change in θ) during surface diffusion, i.e., the presence of a first-order phase transition. Lattice gases can be used to model also such phase changes. Thus, they also provide a suitable framework to investigate the effects of these transitions on surface diffusion [2, 9-19]. In this paper, we briefly outline our recent rigorous results concerning this problem at low (sufficiently subcritical) temperatures. We will illustrate application of our general formulas, using a one-component lattice-gas model of surface diffusion.

2 General results

2.1 Two starting points

Our approach is based on two main points as follows. First, we assume that the local equilibrium approximation is applicable so that the free energy f is sufficient to obtain the diffusion coefficient D_c . Namely, if the jumps of particles are uncorrelated and restricted to the nearest neighbors and if an activated particle interacts only with the adjacent adparticles, then the chemical diffusion coefficient can be approximated as [5, 11, 12]

$$D_c \approx D_0 \frac{e^{\mu/k_B T} P}{k_B T \chi}, \quad (2)$$

where D_0 is the diffusion coefficient of non-interacting particles and μ is the chemical potential. The correlation factor P is a sum of the probabilities that certain clusters of

adjacent sites are vacant [8, 11, 20], which can be expressed via derivatives of f with respect to suitable (fictitious) parameters, u_i , as

$$P = C_0 + \sum_i C_i \frac{\partial f}{\partial u_i}. \quad (3)$$

Note that the factor P is a thermodynamic quantity, as are the coverage θ and susceptibility χ . Thus, the evaluation of f is sufficient to yield D_c from Eq. (2). The same is true for the jump diffusion coefficient because

$$D_J \approx D_0 e^{\mu/k_B T} \frac{P}{\theta} \quad (4)$$

due to Eqs. (1) and (4).

Second, we assume that a first-order phase transition between two phases, denoted as p_1 and p_2 , occurs in the system at a transition point $\mu = \mu_t$. At low temperatures, the finite-size specific free energy f of a system with a large number, N , of adparticles can be evaluated near such a transition from the Borgs-Kotecký theory [21, 22]. The theory is rather general, as it is applicable to a large class of lattice-gas models with periodic boundary conditions, including those with a translation invariant finite range m -potential and a finite number of ground states.

2.2 The Coverage Dependences

Using Eqs. (2) – (4), it is possible to obtain the diffusion coefficients D_c and D_J and the thermodynamic factor Φ near a low-temperature phase transition of first order. Namely, we showed that [23]

$$D_c(\theta) \approx \frac{D_0 e^{\mu_t/k_B T}}{\Delta\theta^* N} \left(\frac{P_1^*}{\theta - \theta_1^*} + \frac{P_2^*}{\theta_2^* - \theta} \right) \quad (5)$$

and

$$D_J(\theta) \approx \frac{D_0 e^{\mu_t/k_B T}}{\Delta\theta^*} \left(P_1^* \frac{\theta_2^* - \theta}{\theta} + P_2^* \frac{\theta - \theta_1^*}{\theta} \right), \quad (6)$$

as well as [24]

$$\Phi(\theta) \approx \frac{\theta}{(\theta_2^* - \theta)(\theta - \theta_1^*)N}. \quad (7)$$

Here θ_k^* are the single-phase coverages evaluated at the transition, $\Delta\theta^* = \theta_2^* - \theta_1^*$ is the coverage jump at the transition, and P_k^* are the single-phase values of the correlation factor P at the transition. It is clear that the coverage dependences of D_c , D_J , and Φ in the two-phase regime behave as hyperbolas. The coefficient D_J is essentially independent of the

system size N , while D_c and Φ are inversely proportional to N . Thus, there is an enormous drop of order $1/N$ in D_c due to a first-order phase transition.

Remark. Formulas (5) – (7) are valid for coverages in the range $\theta_1^* < \theta < \theta_2^*$. Here both phases coexist in the system. However, as soon as only one of the two phases is stable in the system, these formulas are not applicable any more. In this case we were able to obtain only model-dependent formulas [21, 23]. Nevertheless, in two tiny crossover regions (lying between the two single-phase regions and the two-phase region), the coverage dependences of D_c , D_j , and Φ can still be obtained in a general fashion, but the resulting formulas are rather complex [24, 23].

3 Application to a specific model

Let us now illustrate the above general results for a simple lattice-gas model that was used previously to simulate surface diffusion on a triangular lattice [10-12]. In the model each lattice site is either vacant or occupied by a particle, and its Hamiltonian is given as

$$H = \varepsilon N_b - \mu N_s. \quad (8)$$

Here N_b and N_s are the number of occupied pairs of nearest-neighbor sites and sites in a given microstate, respectively, and $\varepsilon < 0$ is an attractive interaction energy between two nearest-neighbor particles. The model is equivalent to the standard Ising model and exhibits a first-order transition at $\mu_t = 3\varepsilon$ between the fully occupied and the fully vacant phases at sufficiently low temperatures (for $k_B T < |\varepsilon| / \ln 3$) [25]. The phase diagram of this model is very simple: the fully vacant phase is stable for $\mu \leq \mu_t$, while the fully occupied phase is stable for $\mu \geq \mu_t$. Both the phases coexist at the point μ_t that is independent of the temperature.

Let the occupied and vacant phase correspond to phase p_1 (p_2). The single-phase free energies of the model from Eq. (8) can be easily calculated near the transition point μ_t . Taking into account only one-site thermal perturbations (they are the dominant contributions at low temperatures), we have [24]

$$f_1 \approx -k_B T \eta e^{(\mu - \mu_t)/k_B T}, \quad f_2 \approx 3\varepsilon - \mu - k_B T \eta e^{-(\mu - \mu_t)/k_B T} \quad (9)$$

with the shorthand $\eta \equiv \exp(\mu_t/k_B T) = \exp(-3|\varepsilon|/k_B T) = 1$. Consequently,

$$\theta_1 = -\frac{\partial f_1}{\partial \mu} \approx \eta e^{(\mu - \mu_t)/k_B T}, \quad \theta_2 = -\frac{\partial f_2}{\partial \mu} \approx 1 - \eta e^{-(\mu - \mu_t)/k_B T}, \quad (10)$$

$$\chi_1 = \frac{\partial \theta_1}{\partial \mu} \approx \frac{1}{k_B T} \eta e^{(\mu - \mu_t)/k_B T}, \quad \chi_2 = \frac{\partial \theta_2}{\partial \mu} \approx \frac{1}{k_B T} \eta e^{-(\mu - \mu_t)/k_B T}. \quad (11)$$

In addition, using the correlation factor P equal to the probability that a lattice bond is vacant (this corresponds to the simplest case when a particle in an activated state interacts

with no adsorbed particles), we have $P = 1 - 2\theta + \xi/3$ for the triangular lattice, where $\xi \equiv \partial f / \partial \varepsilon$ is the statistical average number of occupied bonds. Its single-phase values are

$$P_1 = 1 - 2\theta_1 + \frac{\xi_1}{3} \approx 1 - 2\eta e^{(\mu - \mu_1)/k_B T}, \quad P_2 = 1 - 2\theta_2 + \frac{\xi_2}{3} \approx 0. \quad (12)$$

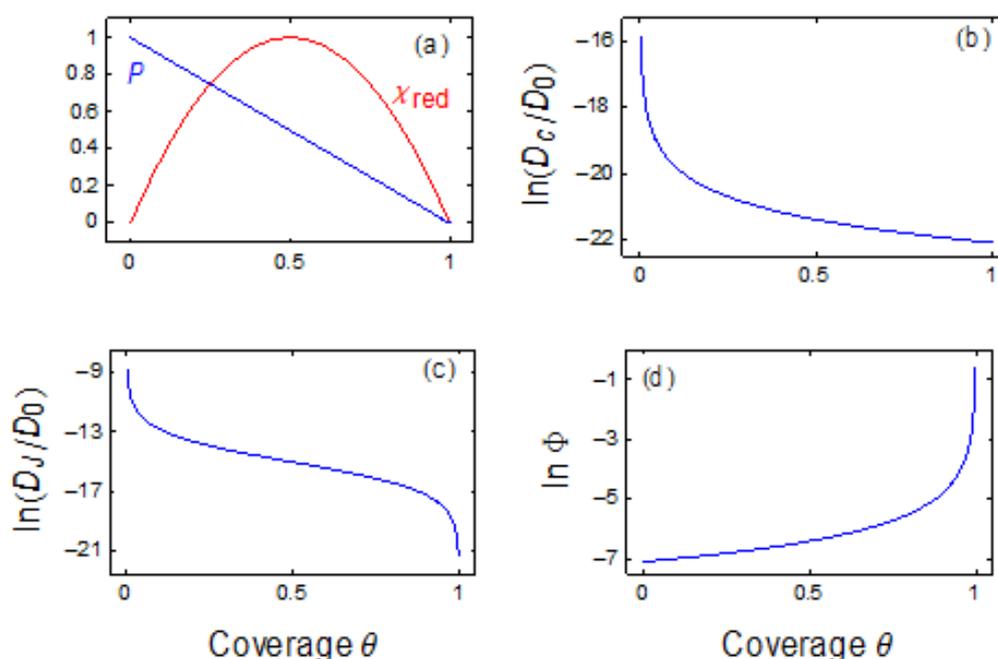


Fig. 1. The coverage dependence of (a) the correlation factor P and reduced susceptibility $\chi_{red} \equiv 4k_B T \chi / N$; (b) the chemical diffusion coefficient; (c) the jump diffusion coefficient; (d) the thermodynamic factor for model (8) as given by Eq. (11). The interaction energy is chosen as $\varepsilon/k_B T = -5$ and the system size $N = 30 \times 40$.

Evaluating the single-phase quantities at the transition point μ_t , we get $\theta_1^* \approx \eta$, $\theta_2^* \approx 1 - \eta$, $\Delta\theta^* \approx 1 - 2\eta$, $P_1^* \approx 1 - 2\eta$, and $P_2^* \approx 0$. Plugging these expressions into Eqs. (5) – (7), we obtain

$$P(\theta) \approx 1 - \theta, \quad \chi(\theta) \approx \frac{1}{k_B T} N(1 - \theta)\theta, \quad \Phi(\theta) \approx \frac{1}{(1 - \theta)N}, \quad (13)$$

$$D_c(\theta) \approx \frac{D_0 e^{-3|\varepsilon|/k_B T}}{N} \frac{1}{\theta}, \quad D_j(\theta) \approx D_0 e^{-3|\varepsilon|/k_B T} \frac{1 - \theta}{\theta}. \quad (14)$$

These coverage dependences are depicted in Fig. 1.

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СКОРОСТЬ ЗВУКА И МОДУЛЬ УПРУГОСТИ ЮНГА СМЕСЕЙ ИЛЛИТА И ЛЕТУЧЕЙ ЗОЛЫ

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