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Surface diffusion and continuous phase transitions in adsorbed overlayers

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Singularities in the coverage dependence of the chemical diffusion coefficient near the critical points corresponding to transitions from one phase to another are studied by employing two different lattice-gas models. (i) For the hard hexagon model, the chemical diffusion coefficient is shown to be exactly equal to zero at the critical coverage and its behavior near this point is in agreement with the predictions of the scaling theory provided that one takes into account the Fisher renormalization of the specific-heat exponent. (ii) For a square lattice with repulsive interactions between nearest-neighbor particles, the detailed transfer-matrix and Monte Carlo data indicate that the chemical diffusion coefficient has a minimum at critical coverages and its value at these points decreases with increasing lattice size (there is even evidence that $D \rightarrow 0$ at $L \rightarrow \infty$).

I. INTRODUCTION

Coefficients of diffusion on single-crystal surfaces are often strongly dependent on coverage due to lateral interactions between diffusing particles.[1-5] Discussing this effect, we need to distinguish two types of such interactions.[5] The first one is attributed to nonactivated particles and referred to below as "the interaction in the ground state." The second one is introduced in order to take into account the interaction of the activated complex with adjacent nonactivated particles and is referred to as "the interaction in the activated state." The former interactions affect thermodynamic properties of the adsorbed overlayer. The latter ones are manifested only in the kinetics of diffusion.

With decreasing temperature, the lateral interactions in the ground state result in the formation of ordered phases in adsorbed overlayers.[5-7] The simplest phase diagram occurs for a square lattice if one takes into account the nearest-neighbor repulsion between adsorbed particles, $\varepsilon_1 > 0$ (Fig. 1). In this case, the system exhibits a continuous phase transition from a disordered state at high temperatures to a doubly degenerated $c(2\times2)$ state at low temperatures $T < T_0$, where T_0 is the critical temperature at $\theta = 0.5$. Let us now assume that one explores diffusion at $T < T_0$. The fundamental question arising in such a study is: "What kind of singularities may be observed in the coverage dependence of the diffusion coefficient near the critical points corresponding to transitions from one phase to another?"

Employing above the words "diffusion coefficient," we bear in mind first of all the chemical diffusion coefficient because it is of interest for describing the mass-transfer processes along the surface. In general, the chemical diffusion coefficient is defined by the well-known Kubo linear-response theory.[8] For an adsorbed overlayer, this theory yields

$$D = \int_0^\infty dt \langle F(t)F(0)\rangle \frac{1}{2N_0 T}\frac{\partial\mu}{\partial\theta} , \qquad (1)$$

where $F(t) = \sum_{i=1}^{N} v_i(t)$ is the total particle flux, v_i is the

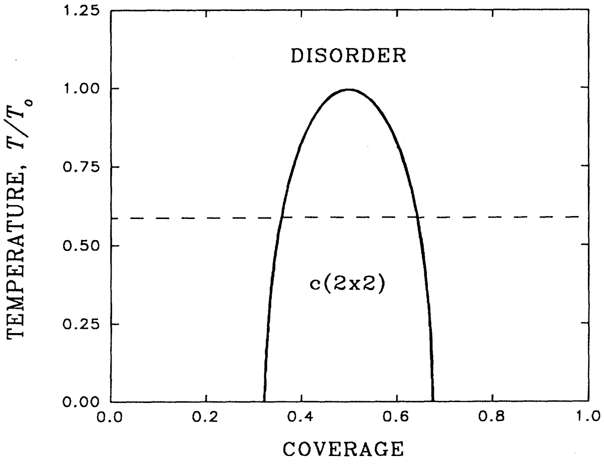

FIG. 1. Phase diagram of an overlayer on a square lattice in the case of repulsion between nearest-neighbor adsorbed particles, $\varepsilon_1 > 0$ (from Refs. 5–7). The critical temperature at $\theta = \frac{1}{2}$ is given by $T_0 = 0.567\varepsilon_1$ (we set $k_B = 1$). At $T < T_0$, the critical coverages are defined as the ones corresponding to crossing the dashed line with the phase-separation-boundary line. The dashed line shown is constructed for $T = \varepsilon_1/3$.

velocity of the particle i at time t, and N and N_0 are the numbers of particles and elementary sites, respectively. Equation (1) may also be rewritten as

$$D = D_J \frac{\theta}{T} \frac{\partial \mu}{\partial \theta} , \tag{2}$$

where D_J is given by

$$D_J = \frac{1}{2\langle N \rangle} \int_0^\infty dt \langle F(t) F(0) \rangle \tag{3}$$

$$\equiv \lim_{t \to \infty} \frac{1}{4Nt} \left\langle \left[\sum_{i=1}^{N} [r_i(t) - r_i(0)] \right]^2 \right\rangle . \tag{4}$$

The latter expression can be explicitly compared with the tracer diffusion coefficient defined by

$$D^* = \lim_{t \to \infty} \frac{1}{4Nt} \left\langle \sum_{i=1}^{N} [r_i(t) - r_i(0)]^2 \right\rangle . \tag{5}$$

Expression (2) for the chemical diffusion coefficient has also been proposed by Reed and Ehrlich[9] but with

$$D_J = (zl^2/4)\Gamma , \tag{6}$$

where l is the jump length, z the number of nearest-neighbor sites ($z=4$ for a square lattice), and Γ the average rate of jumps to one nearest-neighbor site. The original arguments of Reed and Ehrlich[9] were heuristic. Later, it has been shown[5,10] that, assuming a local equilibrium in the adsorbed overlayer, Eqs. (2) and (6) can be obtained directly from the grand canonical distribution. Equation (2) in combination with (6) is now often referred to as the "jump-rate" expression for the chemical diffusion coefficient.

Equation (1) presented above shows that the coverage dependence of the chemical diffusion coefficient is defined by two factors, namely, D_J and $(\theta/T)\partial\mu/\partial\theta$. The first of them is kinetic, and the second one is thermodynamic.

In analogy with such values as free energy or the chemical potential, the coverage dependence of the coefficients D_J, D^*, and Γ is smooth at critical coverages. This statement, important for further discussion, is more or less obvious. It may be illustrated, for example, by considering diffusion with no lateral interaction in the activated state. In this case, the jump rate Γ can be directly expressed via the chemical potential (see Sec. 7.3.1 in Ref. 15 or Ref. 10)

$$\Gamma(\theta)/\Gamma(0) = (\mathcal{P}_{00}/\theta) \exp(\mu/T) ,$$

where $\mathcal{P}_{00}$ is the probability that a pair of nearest-neighbor sites is empty. Taking into account that μ and $\mathcal{P}_{00}$ are smooth functions of coverage, we obtain that the coverage dependence of Γ is smooth as well. Our detailed Monte Carlo simulations also indicate that the coefficients D_J, D^*, and Γ have no visible extremes at critical coverages.

On the other hand, the thermodynamic factor proportional to the derivative $\partial\mu/\partial\theta$ may have anomalies at critical coverages. To emphasize the physical background of these anomalies, we recall that according to statistical physics[11] the thermodynamic factor can be represented as

$$\frac{\theta}{T} \frac{\partial \mu}{\partial \theta} = \frac{\langle N \rangle}{\langle (\delta N)^2 \rangle} , \tag{7}$$

where $\langle (\delta N)^2 \rangle$ is the mean square number fluctuation. At critical coverages, fluctuations are well developed. The latter may result in unusual behavior of the thermodynamic factor.

Our goal is to study in detail the anomalies mentioned above. This problem can be explored by employing various analytical approaches or by Monte Carlo simulations. In both cases, the requirements for calculations are high because an accurate analysis of fluctuations at critical coverages is difficult. This is a reason why at present the available data in this field of theory are rather scarce. The analytical results[12–15] based primarily on the scaling hypothesis are controversial and not quantitative (see Sec. II). The Monte Carlo simulations carried out in the past are devoted to the "global" coverage dependence of the chemical diffusion coefficient connected first of all with the coverage dependence of D_J (see the review in Ref. 5 and also Refs. 16–19). A lot of attention has also been paid to the relationship between the results obtained in the framework of different schemes of simulations corresponding respectively to the Kubo equation, fluctuation method, or Boltzmann-Matano procedure. On the other hand, the anomalies of diffusion at critical coverages were not explored carefully. In fact, this phenomenon was ignored because the lattice size employed in simulations was often too small, the coverage grid was too rare, and the statistics were too poor. (In the 3D case, the effect under consideration has apparently not been studied in detail either.[20,21])

Our paper is organized as follows. Section II contains a brief review of the available analytical results[12–15] based on such ideas as scaling, critical exponents, Fisher renormalization, and renormalization-group theory. The information collected in this section is essential for a deeper understanding of the types of problems we want to discuss and the significance of the results obtained in our work for the hard hexagon model by employing the analytical solution constructed by Baxter[22] (Sec. III) and for the lattice-gas model (a square lattice with nearest-neighbor repulsion) by using the transfer-matrix technique (Sec. IV A) and Monte Carlo simulations (Sec. IV B). Our main conclusions are summarized in Sec. V.

II. REVIEW OF ANALYTICAL RESULTS

The mean-field approximation and phenomenological Landau theory are well known to result in a stepwise coverage dependence of the chemical diffusion coefficient near critical converges (see, e.g., Ref. 23). These approaches are, however, too approximate. More accurate predictions may be obtained by employing the scaling hypothesis, which yields for the singular contribution to the temperature dependence of the free energy at $\theta=$const the following well-known expression:[24]

$$F \propto |T - T_c(\theta)|^{2-\alpha} , \tag{8}$$

where $T_c(\theta)$ is the critical temperature at a given coverage, and α the specific-heat exponent. Using simple arguments, Bolshov and Veshchunov[12] (see also Ref. 13) have shown that Eq. (8) can be converted into the singular contribution to the coverage dependence of the free energy at $T=\text{const}$,

$$F \propto |\theta-\theta_1|^{2-\alpha} , \tag{9}$$

where θ_1 is the critical coverage corresponding to a given temperature [the transition from (8) to (9) is possible at $T<T_0$, where T_0 is the maximum critical temperature]. Considering that $\mu=\partial F/\partial\theta$ and $D \propto \partial\mu/\partial\theta$, one then has[12]

$$D \propto |\theta-\theta_1|^{-\alpha} . \tag{10}$$

Discussing Eq. (10), Bolshov and Veshchunov[12] treated α as a formal parameter and admitted that it may be both positive and negative. If $\alpha>0$, Eq. (10) was assumed to predict an infinite power-law anomaly at $\theta=\theta_1$. For $\alpha<0$, the diffusion coefficient was expected to have a cusplike minimum at coverages near θ_1, with $D(\theta_1)=0$ at $\theta=\theta_1$.

From our point of view, Eq. (10) is correct but its formal application may result in confusion. The problem is that the critical exponents are customarily calculated (and measured) at extreme points such as $\theta_0=0.5$ (Fig. 1). These points correspond to zero external field if we employ the "magnetic" terminology. Critical exponents at other points can be calculated by assuming that the nature of the phase transition is the same along lines with fixed external field (i.e., with a fixed value of the chemical potential for a lattice gas). Using this hypothesis, Fisher[25] has shown that beyond the region near θ_0 the free energy along lines with fixed coverage can be represented as

$$F \propto |T-T_c(\theta)|^{(2-\alpha)/(1-\alpha)} , \tag{11}$$

where α is the specific-heat exponent calculated or measured at $\theta=\theta_0$ [formally, Eq. (11) can be obtained from Eq. (9) by replacing α by $-\alpha/(1-\alpha)$]. Then, we have (see Ref. 13 written by one of the authors of the present paper)

$$D \propto |\theta-\theta_1|^{\alpha/(1-\alpha)} . \tag{12}$$

Equations (11) and (12) hold at $\alpha>0$. On the other hand, if $\alpha<0$, Fisher[25] has shown that the critical exponents should not be renormalized [i.e., we may use Eq. (10)]. Using the Fisher renormalization, it is possible also to show that for $\alpha=0$ (the Ising case) the theory yields[13]

$$D \propto 1/|\ln|\theta-\theta_1|| . \tag{13}$$

In all the cases [Eq. (12) for $\alpha>0$, Eq. (10) for $\alpha<0$, or Eq. (13) for $\alpha=0$], the diffusion coefficient is seen to be a continuous function of coverage, and contrary to the predictions of Bolshov and Veshchunov[12] *any infinite anomalies are absent.* In fact, we have no grounds to expect at $\theta\neq\theta_0$ even finite cusplike maxima caused by the factor $\partial\mu/\partial\theta$. Instead, we should have cusplike minima (the cusplike maxima really occur but at such points as θ_0 where a low-temperature phase is well ordered, fluctuations are suppressed, and the derivative $\partial\mu/\partial\theta$ is very high[5,17]). The value of the diffusion coefficient at $\theta=\theta_1$ was not discussed explicitly in Ref. 13. Implicitly, the author, however, bore in mind that $D>0$ at $\theta=\theta_1$ due to regular terms in the expansion of free energy near θ_1.

From symmetry consideration,[26] the continuous phase transitions in adsorbed overlayers usually belong to one of four universality classes: Ising ($\alpha=0$), *x*-*y* with cubic anisotropy (nonuniversal), three-state Potts ($\alpha=\frac{1}{3}$), and four-state Potts ($\alpha=\frac{2}{3}$). For all these classes, $\alpha\geq 0$. Thus, the Fisher renormalization discussed above is particularly important for real systems.

Responding to the comments in Ref. 13, Veshchunov wrote a paper[14] containing the following three statements. (i) With the Fisher renormalization for $\alpha>0$, the coverage dependence of the chemical diffusion coefficient is described near critical coverages by Eq. (11) and the diffusion coefficient *precisely* equals zero at $\theta=\theta_1$. (ii) In some exceptional case, the Fisher renormalization may occur at $\alpha<0$ and the diffusion coefficient *may* have an infinite anomaly. (iii) In Ref. 12, the sign and values of the critical exponents are confused.

From our point of view, Veshchunov's statements (i) and (ii) support in fact the main conclusion of Ref. 12 where the infinite anomalies were rejected (the exceptional cases mentioned by Veshchunov may take place only under the conditions that do not have any physical sense). Comment (iii) written by Veshchunov is wrong (it has no grounds).

Special features of the coverage dependence of the chemical diffusion coefficient at $T<T_0$ have also been studied by Tarasenko and Chumak[15] employing the site-cell renormalization technique to describe diffusion on triangular and hexagonal lattices. According to their calculations, the diffusion coefficient has shallow cusplike minima at critical converges. Qualitatively, this result is in agreement with the scaling analysis given in Ref. [13]. On the other hand, the quantitative accuracy of the data obtained is not quite clear because they are based on the simplest renormalization procedures.

In summary, the available analytical results seem to indicate that at $T<T_0$ the chemical diffusion coefficient should have cusplike minima at critical coverages. There is even a prediction[14] that the diffusion coefficient should equal zero at these points.

III. THE HARD HEXAGON MODEL

The ideas outlined in Sec. II are based primarily on the scaling hypothesis. It is of interest to verify the predictions obtained in such a way by using the results derived for exactly solved models. At present, the exact solutions are available for a few models.[22] Almost all these solutions correspond unfortunately to the "zero-field" case (i.e., to points such as θ_0) and accordingly cannot be employed for our discussion. Some relevant results seem to occur only for the hard hexagon model. Our goal is to consider these results in the context of surface diffusion.

The hard hexagon model involves a two-dimensional gas of hard (i.e., nonoverlapping) particles on a triangular lattice.[22] If one regards each particle as the center of a hexagon covering the six adjacent faces, then the rule only allows hexagons that do not overlap. This model in fact does not contain temperature but, with increasing coverage, exhibits a continuous phase transition at $\theta=\theta_1=0.276$ with $\alpha=\frac{1}{3}$. Near this point, the Baxter exact solution [see Eqs. (14.7.10) and (14.7.11) in Ref. 22] yields

$$|\theta-\theta_1| \propto |\mu-\mu_1|^{2/3} , \tag{14}$$

or

$$|\mu-\mu_1| \propto |\theta-\theta_1|^{3/2} . \tag{15}$$

Using Eq. (15), we have

$$\left|\frac{\partial\mu}{\partial\theta}\right| \propto |\theta-\theta_1|^{1/2} . \tag{16}$$

This equation indicates that the diffusion coefficient should have a cusplike minimum near θ_1, with $D(\theta_1)=0$. Taking into account that $\alpha=\frac{1}{3}$, we also conclude that the exponent in Eq. (16) is in agreement with that predicted by Eq. (12) [in other words, Eq. (16) is in agreement with the Fisher renormalization].

IV. DIFFUSION ON A SQUARE LATTICE

In this section, we consider diffusion of particles on a square lattice. The nearest-neighbor adsorbate-adsorbate interaction is assumed to be repulsive, $\varepsilon_1>0$. The other interactions are ignored. A phase diagram for the system under consideration is shown in Fig. 1. To study peculiarities of the chemical diffusion coefficient at critical coverages, we use the transfer-matrix technique (Sec. IV A) and Monte Carlo simulations (Sec. IV B). All the numerical results presented below have been obtained for $T=\varepsilon_1/3$ (see the dashed line in Fig. 1).

A. Transfer-matrix technique

In the framework of the transfer-matrix technique (TMT), the lattice is replaced by a strip infinite in one direction and of the finite width L with periodic boundary conditions along the other direction. Then, the grand canonical partition function, free energy, and chemical potential can be obtained exactly by calculating the largest eigenvalue of the transfer matrix, λ_0 (see, e.g., Refs. 27–29). In addition, one can obtain the correlation length given by $\xi=a/\ln(\lambda_0/|\lambda_1|)$, where a is the lattice spacing, and λ_1 the second largest (by its absolute value) eigenvalue. The critical temperature is calculated from the equation given by the scaling hypothesis for the correlation length,

$$\xi(L)/L=\xi(L_1)/L_1 , \tag{17}$$

where $\xi(L)$ and $\xi(L_1)$ are the correlation lengths for strips with the sizes L and L_1. Employing TMT, one can also calculate the probabilities of different arrangements of adsorbed particles.[28,29] The latter makes it possible to use TMT to describe the kinetic processes in adsorbed overlayers.

Studies of surface diffusion by employing TMT are just beginning. The results available at present[28,30] have been obtained at small L, such as $L=4$ or 6. Such L are reasonable if the goal is to obtain a "global" coverage dependence of the diffusion coefficient. The anomalies at critical coverages can, however, be explored only if L is much larger than 6. In the present study, we changed L from 6 up to 16 in order to calculate the coverage dependence of the chemical potential.

In principle, we are interested in the derivative $\partial\mu/\partial\theta$. In practice, however, it is reasonable to calculate $\partial\theta/\partial\mu$ because the latter derivative is proportional to the mean square number fluctuation [cf. Eq. (7)],

$$\frac{T}{\theta}\frac{\partial\theta}{\partial\mu}=\frac{\langle(\delta N)^2\rangle}{\langle N\rangle} , \tag{18}$$

and can be directly compared with the results of Monte Carlo simulations (Sec. IV B).

Using Eq. (17), we have obtained that at $T=\varepsilon_1/3$ the critical coverage is 0.387. Near this coverage, the derivative $\partial\theta/\partial\mu$ has a maximum (Fig. 2). The important point is that this maximum increases with increasing L. The asymptotic behavior of the maximum value of $\partial\theta/\partial\mu$ is expected to be given by

$$\left[\frac{\partial\theta}{\partial\mu}\right]_{\max}=A+BL^{\gamma} . \tag{19}$$

Our calculations indicate that $\gamma\approx0.2$ at $L=16$ (Fig. 3). If representation (19) is correct and the parameter γ is

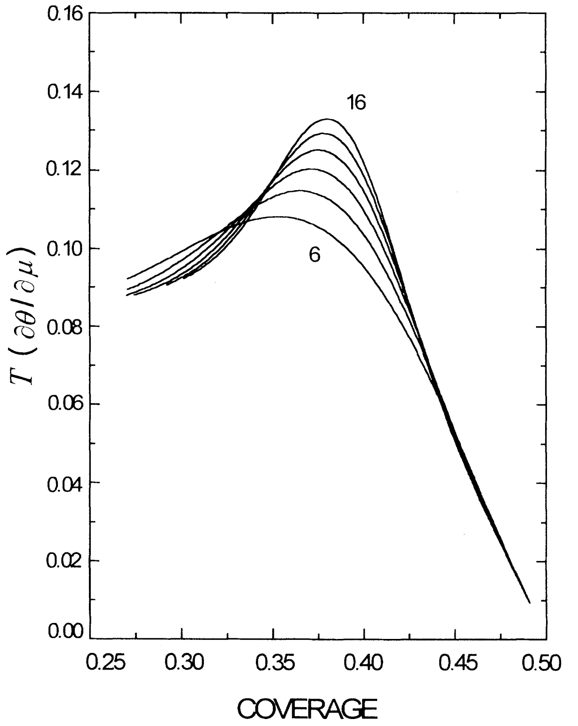

FIG. 2. Derivative $\partial\theta/\partial\mu$ as a function of coverage for $T=\varepsilon_1/3$. The different curves have been obtained by employing the transfer-matrix technique with $L=6$, 8, 10, 12, 14, and 16, respectively.

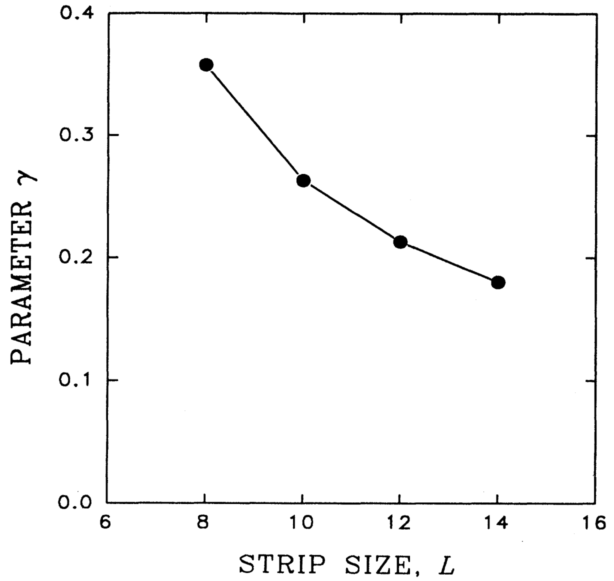

FIG. 3. Parameter γ in Eq. (19) as a function of L. For a given value of L, this parameter (together with the parameters A and B) was derived from the maximum values of the derivative $\partial\theta/\partial\mu$ at $L-2$, L, and $L+2$.

really positive at $L \to \infty$, the derivative $\partial\theta/\partial\mu$ should be infinite at the critical coverage. Accordingly, the derivative $\partial\mu/\partial\theta$ should be equal to zero. In the context of this analysis, it is of interest to note that our TMT calculations for the hard hexagon model yield $\gamma \approx 0.42$ at $L=20$, and in this case the derivative $\partial\mu/\partial\theta$ is really equal to zero at the critical coverage (Sec. III).

In summary, the TMT results indicate that the derivative $\partial\mu/\partial\theta$ has a minimum at critical coverages. Accordingly, the chemical diffusion coefficient should have the same anomalies. The minimum obtained is fairly weak even at $L=16$. On the other hand, the calculations clearly indicate that the effect should be more pronounced upon further increasing L. The latter is unfortunately beyond our capabilities.

B. Monte Carlo simulations

General schemes of Monte Carlo (MC) simulation of surface diffusion are described in detail in Refs. 16,17. In the present study, the results have been obtained by employing the approach based on the Kubo theory [Eq. (2) with expression (4) for D_J]. The kinetic and thermodynamic factors, D_J and $(\theta/T)\partial\mu/\partial\theta$, were calculated separately. The first one, given by Eq. (4), was derived by using the canonical ensemble (CE) and assuming that the lateral interaction in the activated state is absent (i.e., the saddle points for jumps are unaffected by adjacent particles). The second one was calculated by analyzing fluctuations of the number of particles on the whole array of sites in the framework of the grand canonical distribution [see the right-hand part of Eq. (18)]. All the simulations were carried out on square arrays containing $L \times L$ sites with L from 32 up to 256. The numerical algorithm involved parallelized steps in order to take full advantage

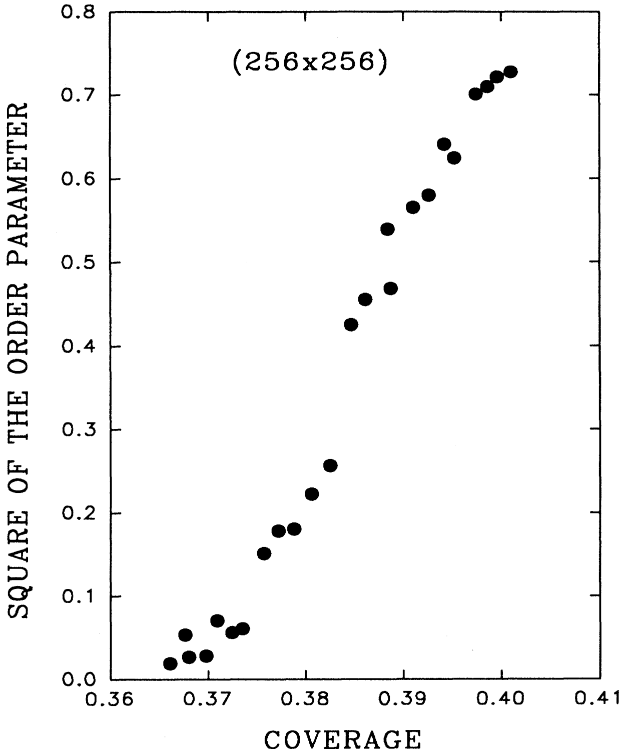

FIG. 4. Square of the order parameter as a function of coverage for the 256×256 lattice at $T=\varepsilon_1/3$. The data presented indicate that the critical coverage, defined as that corresponding to the inflection point, is 0.385.

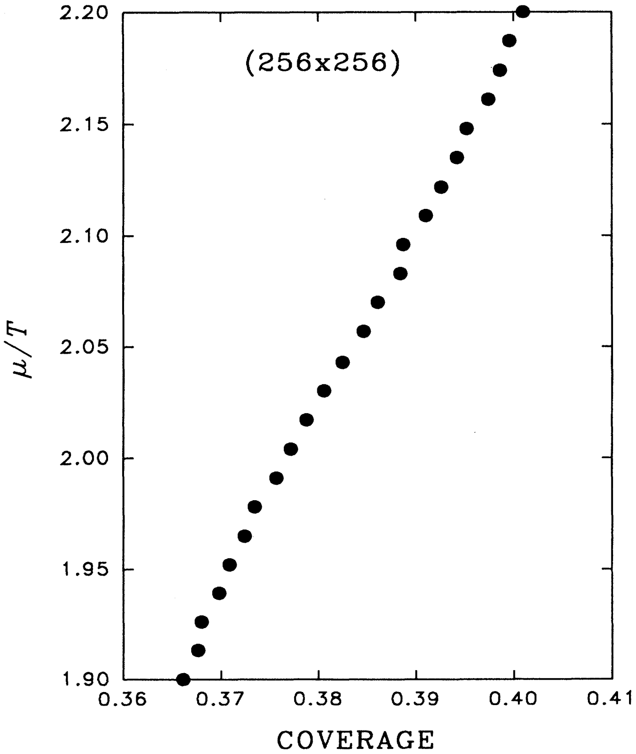

FIG. 5. Chemical potential as a function of coverage for the 256×256 lattice at $T=\varepsilon_1/3$.

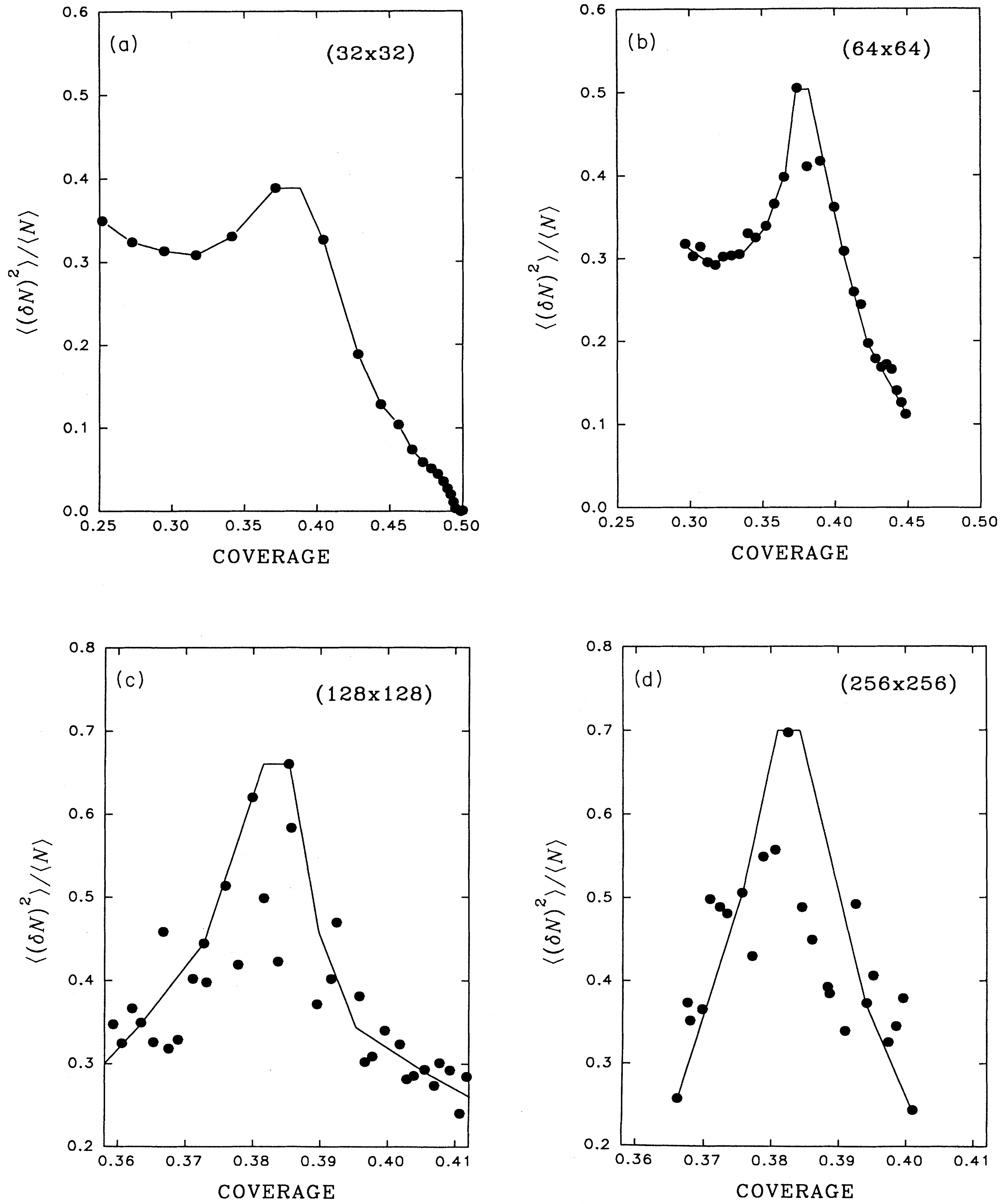

FIG. 6. Mean square number fluctuation as a function of coverage for the lattices with sizes (a) 32×32, (b) 64×64, (c) 128×128, and (d) 256×256 at $T=\varepsilon_1/3$. Filled circles show the data obtained from Monte Carlo simulations. Solid lines were constructed by "hands" in order to emphasize general tendencies observed.

of the computational power of the Paragon XP/S-10 supercomputer at Jülich.

Our preliminary simulations have shown that the number of Monte Carlo steps (MCS) required for equilibration in the grand canonical ensemble (GCE) is well below 1000 for all the lattice sizes studied (both for ordered and disordered initial arrangements). In the final runs, we used 2000 MCS for equilibration and then an additional 5000 MCS for determination of the desired quantities. In this case, the statistics are good for relatively small and medium lattices (e.g., for $L=32$ and 64). With increasing the lattice size (e.g., for $L=128$ and 256), the data contain a considerable noise. Our experience indicates that the noise decreases with increasing the number of MCS but very slowly. To reduce significantly the noise for large lattices, one should increase the number of MCS by at least one order of magnitude (the latter was beyond our capabilities).

Typical results for GCE are presented in Figs. 4–6. In particular, Fig. 4 shows that at $T=\varepsilon_1/3$ the critical coverage is 0.385. Figure 5 indicates that the chemical potential is a smooth function of coverage. Figure 6 demonstrates that the coverage dependence of the mean square number fluctuation has a maximum at critical points and this maximum increases with increasing L. All these predictions are in qualitative agreement with those obtained by employing TMT (Sec. A). One may naturally expect that the agreement should be quantitative if L in MC simulations is slightly higher than that in TMT. Figure 7 shows that the latter does take place.

Figure 8 exhibits the coverage dependence of the Kubo chemical diffusion coefficient. As pointed out above, the thermodynamic factor has been calculated by employing GCE, and the kinetic factor has been gotten by using CE. Simulations with CE including an analysis of correlations in the arrangement of different particles [Eq. (4)] are extremely time consuming [to construct Fig. 8 it was necessary to spend 10 h of the CPU time on 64 (out 140) nodes of the Paragon]. However, the result obtained justifies the expenses because it clearly indicates that the chemical diffusion coefficient does have a minimum at the critical coverage.

V. CONCLUSION

We have studied anomalies in the coverage dependence of the chemical diffusion coefficient at points corresponding to continuous phase transitions. The results obtained are of interest from the differential points of view including methodology of simulations, general theory, and experiment.

Our methodological finding is that the anomalies under consideration are visible only if the lattice size is considerable. Employing TMT, it is desirable to use $L>20$. In

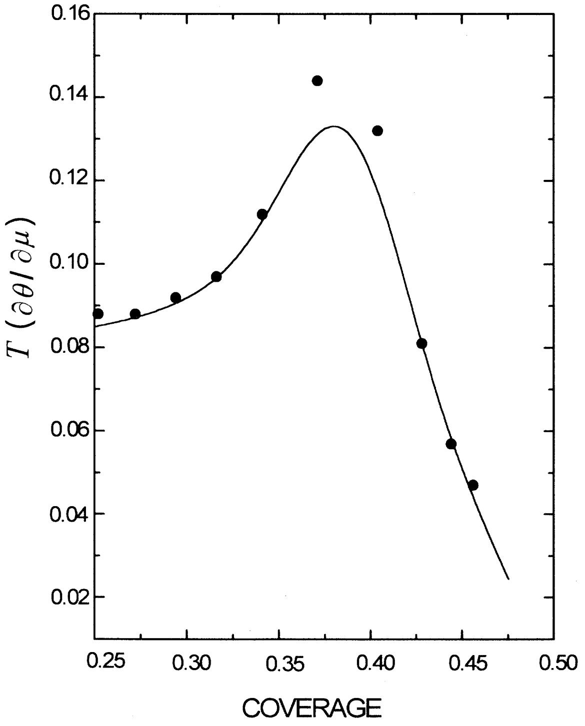

FIG. 7. Derivative $\partial\theta/\partial\mu$ as a function of coverage for $T=\varepsilon_1/3$. The solid line represents the results given by the transfer-matrix technique with $L=16$ (cf. Fig. 2). The filled circles were obtained by substituting into Eq. (18) the Monte Carlo data shown in Fig. 6(a) for the 32×32 lattice.

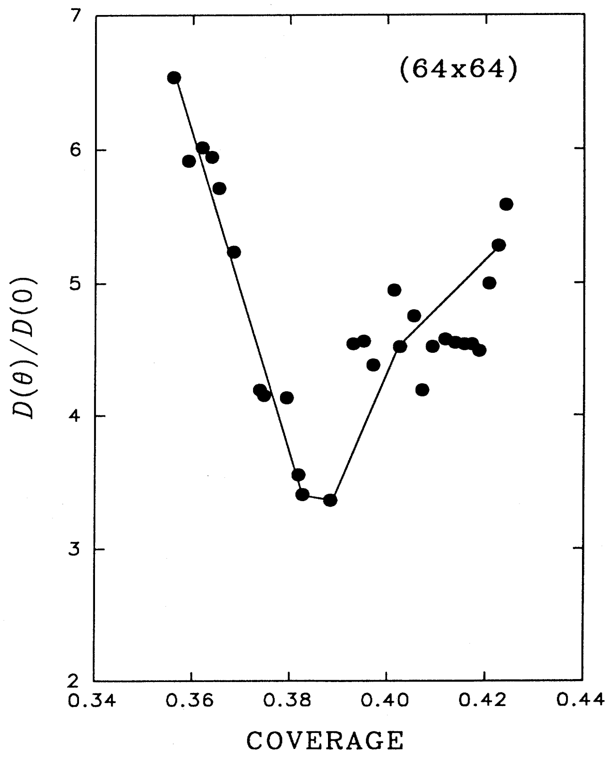

FIG. 8. Chemical diffusion coefficient as a function of coverage for $T=\varepsilon_1/3$. Filled circles show the Monte Carlo data for the 64×64 lattice. The solid line was constructed by "hands" in order to emphasize general tendencies observed.

MC simulations, L should be larger than 50. In our TMT and MC calculations, the maximum L was 16 and 256, respectively. Our main result (Fig. 8) was obtained by MC simulations. We should also note that by employing TMT we can in principle calculate the average jump rate in Eq. (6) (see Refs. 28–30), but we are not able to obtain the coefficient D_J defined by Eq. (4) because the latter coefficient depends in general on long-range correlations in the arrangements of particles. Calculating the thermodynamic properties (e.g., the chemical potential), TMT takes into account correlations with lengths up to L automatically but such correlations cannot be tracked in detail in order to calculate the coefficient D_J given by Eq. (4). Thus, one might conclude that MC simulations are much more powerful compared to TMT. However, this conclusion is not quite right because if the computer resources are the same and we are interested only in the thermodynamic properties, the TMT results may be more accurate compared to MC simulations (note that the computer resources employed to obtain the TMT data presented in Sec. IV A were *much* lower compared to those used to get the MC results shown in Sec. IV B).

Our main contributions to general theory of surface diffusion are as follows. (i) For the hard hexagon model, we have shown that the chemical diffusion coefficient exactly equals zero at the critical coverage and its behavior near this point is in agreement with the predictions of the scaling theory provided that one takes into account the Fisher renormalization of the specific-heat exponent. (ii) For a square lattice with repulsive interactions between nearest-neighbor particles, our detailed TMT and MC data indicate that the chemical diffusion coefficient has a minimum at critical coverages and its value at these points decreases with increasing lattice size (there is even evidence that $D \rightarrow 0$ at $L \rightarrow \infty$).

Our simulations show also that the phase-transition-induced peculiarities in the coverage dependence of the chemical diffusion coefficient are localized in rather narrow regions near critical points. Typically, the width of these regions is lower than or about a few percent of the monolayer. The change in the value of the diffusion coefficient near critical points is, however, considerable. On the other hand, the contribution of the critical points to the "global" coverage dependence of the diffusion coefficient is relatively minor. All these conclusions may be instructive from the point of view of experimental studies of surface diffusion.

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