Diffusion on a honeycomb lattice: Real-space renormalization-group approach

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A two-dimensional lattice-gas model with honeycomb symmetry is investigated by using the real-space renormalization group (RSRG) approach with a number of RSRG transformations based on clusters of different symmetries and sizes (up to 42 sites). The accuracy of calculations is found to be a nonmonotonic function of the size of a cluster, and to depend strongly on its symmetry. The highest obtained accuracy with respect to the determination of the critical value of the pair interaction parameter is 0.38%. The phase diagram of the Ising antiferromagnetic spin model and of the corresponding lattice-gas model is constructed with this accuracy. The ordered phase in the lattice system is shown to appear in the very narrow density interval, $0.447 < n < 0.553$. In addition, the coverage dependence of the chemical diffusion coefficient and mean-square density fluctuations are studied at temperatures below the critical one. Both quantities are demonstrated to exhibit singularities at the critical coverages. The type of singularities (in particular, the critical slowdown of diffusion) is in agreement with the predictions of the scaling theory and also with recent results obtained for a model treating the effect of surface reconstruction on diffusion. [S0163-1829(98)06516-3]

I. INTRODUCTION

The migration of adsorbates on solid surfaces plays an essential role in many physical and chemical processes such as adsorption, desorption, melting, roughening, crystal and film growth, catalysis, and corrosion. Understanding surface diffusion is one of the keys to controlling these processes.

For a quantitative description of diffusion, two important concepts have been developed, each of them with its own ''coefficient of diffusion.'' In the following we will apply these two concepts, which describe the general diffusion problem in three dimensions, to the specific case of surface diffusion.

The conceptually most simplest surface diffusion coefficient is the tracer surface diffusion coefficient D_t, which addresses the random walk of individual tagged particles on a two-dimensional lattice, i.e.,

$$D_t = \lim_{t \to \infty} \frac{1}{4t} \langle |\vec{r}(t) - \vec{r}(0)|^2 \rangle. \qquad (1)$$

Here $\vec{r}(t)$ denotes the total displacement of the tagged adparticle as a function of time t. The tracer surface diffusion coefficient is a single-particle diffusion coefficient. In contrast, the chemical surface diffusion coefficient D_c is a many-particle diffusion coefficient defined by Fick's law $J = -D_c \nabla n$. D_c can be calculated by the well-known Kubo linear-response theory,[1] and refers to the total flux J of N_a particles:

$$J = \sum_{i=1}^{N_a} v_i. \qquad (2)$$

D_c can be expressed in terms of a corresponding correlation function[2]

$$D_c = \frac{1}{2\kappa \langle n \rangle^2} \frac{1}{k_B T A} \int_0^\infty \langle J(t) J(0) \rangle dt, \qquad (3)$$

where κ is the isothermal compressibility and A is the surface area. It is important to note that the chemical surface diffusion coefficient is of interest for describing the mass-transfer processes along the surface. Therefore, when we employ the term ''diffusion coefficient'' in the remaining part of this paper, we have to bear in mind the chemical diffusion coefficient in the first place.

In recent years the effects of lateral interactions on the chemical surface diffusion coefficient of adsorbed particles have been analyzed in Refs. 3–6. It was found that adparticle interactions can strongly influence surface diffusion, especially at low temperatures and in the close vicinity of surface phase transitions.[7] From simple physical considerations, it is intuitively expected that attractive interactions between adsorbed species inhibit the adparticle migration and thus slow down surface diffusion. In contrast, repulsive interactions are expected to accelerate surface diffusion. Despite their simplicity, these rules describe the qualitative behavior of surface diffusion processes for many systems, at least in the limit of high temperatures, quite well.[6] However, more sophisticated arguments are required for the description of surface diffusion in case of ordering, i.e., if strong lateral interactions force the system to order below a critical temperature. It is well known that phase transitions on two-dimensional lattices give rise to a logarithmic divergence of the specific heat. In a similar manner, such phase transitions

are expected to affect the chemical surface diffusion coefficient in the vicinity of such phase transitions. The critical behavior of the diffusion coefficient has been discussed in the literature (see Ref. 7 and references therein).

In general, the determination of the chemical surface diffusion coefficient requires the solution of a kinetic equation for a system of many strongly interacting particles. However, if interactions are restricted to affect only the ground state and not the activated state of the diffusing adparticles, the problem can be reduced to the calculation of purely thermodynamic quantities.[8–12] In this case, the problem of determining the adparticle diffusion coefficient reduces to a calculation of the free energy of the system, and the critical behavior of the diffusion coefficient is fully determined by the divergence of the mean-square adparticle density fluctuation. In recent years this problem was attacked using almost all theoretical methods applicable to critical phenomena: mean-field approximation,[13] Bethe-Peierls approximation,[14] real-space renormalization group,[15,16] transfer-matrix technique, and Monte-Carlo method.[7] Scaling arguments give a weak logarithmic critical slowdown of the diffusion coefficient[17]

$$D_c \propto 1/|\ln|n - n_c||. \qquad (4)$$

The same critical slowdown is found in Ref. 18, where an exact expression for the diffusion coefficient on reconstructive surfaces was obtained. It is probably interesting to note that this expression (Eq. 5 of Ref. 18) is the only exact expression for the critical behavior of the diffusion coefficient of interacting particles in two dimensions (exact expressions have been also obtained for one-dimensional Ising chains[11,19]). A general expression for the diffusion coefficient was analyzed in Ref. 7 for the hard hexagon model, yielding a power-law critical slowdown of D. Classical mean-field-type approximations predict a stepwise decrease of the diffusion coefficient in the ordered phase (see, for example, Refs. 13 and 14), and it is obviously clear that mean-field approximations are too crude even for a qualitative analysis. The real-space renormalization-group (RSRG) approach, suggested by Niemeyer and van Leeuwen[20] and Nauenberg and Nienhuis,[21,22] has been used to investigate the critical behavior of surface diffusion. The RSRG approach yields cusplike minima of the diffusion coefficient in the close vicinity of the critical points,[15,16,23] which resemble the corresponding minima on the exact dependences $D(n)$, shown in Ref. 18. However, even at the critical coverage $n = n_c$, i.e., at the minimum of the cusp, the diffusion coefficient stays finite ($D \neq 0$), which obviously contradicts Eq. (4). The calculations of $D(n)$ in Ref. 15 were, however, based on the simplest possible renormalization procedures, with the smallest possible blocks and clusters of lattice sites. Therefore, the accuracy of the method was not high.

The behavior of the diffusion coefficient near the critical points has also been studied by employing the transfer-matrix technique.[7] The results obtained for a square lattice clearly indicate that the value of the diffusion coefficient at these points becomes lower and lower if the size of the strip used in calculations is increased from 6 up to 16. But the results obtained with these strip sizes were found to be insufficient for understanding the type of singularities in detail.

The Monte Carlo (MC) simulation of surface diffusion is probably the most reliable method which can be used to study adparticle diffusion on different lattices and for various sets of interaction parameters. However, the MC method is very time consuming and requires powerful computers. In a recent work, the MC method was used to study adparticle diffusion on a square lattice, taking pairwise nearest-neighbor repulsive interactions into account.[7] The lattice size has been varied from 32×32 up to 256×256. The diffusion coefficient in the critical region has been found to have a distinct minimum, with $D(n) \neq 0$ for $n \to n_c$. The accuracy of the statistics in MC calculations near the critical points is unfortunately not very high even for large lattices (e.g., for 256×256).

In the present work, we explore phase diagram of the system of adsorbed particles and their diffusion on a honeycomb lattice by the RSRG approach. Using a supermassive parallel computer (Intel Paragon) in conjunction with a fully parallelized algorithm, we have increased the accuracy of the method substantially (compared to our earlier study[15]) simply by increasing the number of sites in the blocks of the cluster considered. The outline of this paper is as follows: the derivation of the diffusion equation and expression for diffusion coefficient are described in Sec. II. The RSRG approach employed is described in Sec. III. The phase diagram obtained for an interacting lattice gas is presented in Sec. IV. The chemical diffusion coefficient dependences are treated in Sec. V, with special emphasis on the behavior in the vicinity of the critical points.

II. DIFFUSION OF ADPARTICLES ON THE HONEYCOMB LATTICE

Let us consider some ideal solid surface. The potential relief minima of the surface form a two-dimensional (2D) honeycomb lattice with side a (as shown in Fig. 1). Foreign particles adsorbed on the surface occupy the sites. If the depth of the minima ε is much greater than the temperature ($\varepsilon \gg k_B T$), the adparticles will be in the minima, jumping from time to time in the empty neighbor sites. In this case the thermodynamical state of the adparticle system is described completely by the set of occupation number of the sites $\{n_i\}$. Index i labels sites of the lattice: $i = 1, 2, \ldots, N$ and

$$n_i = \begin{cases} 1 & \text{if the } i\text{th site is occupied} \\ 0 & \text{if the } i\text{th is empty.} \end{cases} \qquad (5)$$

In thermodynamic equilibrium, the system is described by the statistical operator ρ,

$$\rho = Q^{-1} \exp \beta(\mu N_a - H_a), \qquad (6)$$

where the number of adparticles N_a and system Hamiltonian H_a have the following forms:

$$H_a = -\varepsilon N_a + \frac{1}{2} \sum_{ij} \varphi_{ij} n_i n_j, \quad \text{and} \quad N_a = \sum_{i=1}^{N} n_i, \qquad (7)$$

where μ is the chemical potential, $\varphi_{ij} \equiv \varphi(r_i - r_j)$ is the pair interaction energy of adparticles in the ith and jth sites, $\beta \equiv 1/k_B T$; Q is the great partition function
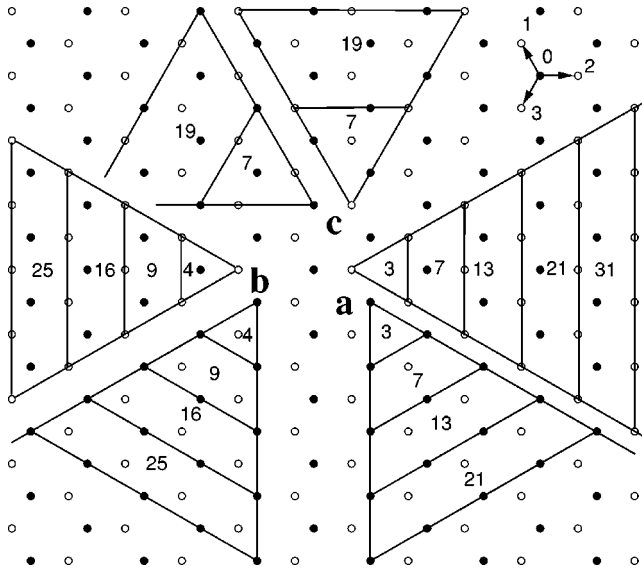
FIG. 1. Antiferromagnetic ordered phase ($n = \frac{1}{2}$) on the honeycomb lattice with three series of RSRG clusters investigated in the course of the present work (a, b, and c). Any pair of blocks, having equal number of sites L from the a, b, or c sequences, form a cluster. Arrows show three possible jumps of an adparticle out of the zeroth site.

$$Q = \sum_{\{n_i\}} \exp \beta(\mu N_a - H_a), \tag{8}$$

and summation is carried out over all 2^N configurations of the occupation numbers.

The occupation numbers are changed with time due to the hops of adparticles. The balance equation for any definite site, say the zeroth in Fig. 1, can be written as

$$n_0(t + \Delta t) - n_0(t) = \sum_i (J_{i0} - J_{0i}), \tag{9}$$

where J_{ij} is the number of hops from the ith site to the jth site during the time interval Δt. For small Δt, one can define the regular and fluctuating parts of the particle flux as follows:

$$J_{ij} = (\nu_{ij} n_i h_j + \delta J_{ij}) \Delta t \quad \text{where} \quad h_j = 1 - n_j.$$

Here ν_{ij} is the frequency of hops from the ith site to the jth site. The multiplier $n_i h_j$ ensures that the hop proceeds from occupied to empty sites only; $\delta J_{ij} \Delta t \equiv J_{ij} - \nu_{ij} n_i h_j \Delta t$ is the fluctuation of the number of adparticles hops from the ith site to the jth site during the small time interval Δt. The balance equation in new notation has the following form:

$$\frac{1}{\Delta t}[n_0(t + \Delta t) - n_0(t)] = \sum_i (\nu_{i0} n_i h_0 - \nu_{0i} n_0 h_i)$$

$$+ \sum_i (\delta J_{i0} - \delta J_{0i}). \tag{10}$$

The last sum on the right-hand side of Eq. (10) plays the role of the Langevin source of fluctuations $J_0^L(t)$. The correlation function of the source was investigated in Ref. 11.

The balance equation describes the kinetic stage of the relaxation with a characteristic frequency of adparticle hops $\langle \nu_{ij} n_i h_j \rangle$ (the angular brackets $\langle \cdots \rangle$ denote averaging with statistical operator ρ) and a space scale a. The fluctuations are large in the general case, and one cannot solve the nonlinear balance equation or linearize it over small adparticle density fluctuations. For many situations the detailed description of the relaxation is unnecessary, because the characteristic length of the surface density inhomogeneities is much greater than the lattice side a, and decaying of the inhomogeneities proceeds as a result of a great number of hops of many adparticles with characteristic frequencies much less than the mean frequency of adparticle hops.

Let us consider the states of the adparticle system averaged over large times interval τ. The time interval τ must satisfy the inequality

$$\langle \nu_{ij} n_i h_j \rangle \tau \gg 1.$$

The averaging smooths out the processes with characteristic frequencies $\omega \gtrsim \tau^{-1}$. We suppose that the averaging over time interval τ is equivalent to the averaging with the statistical operator $\widetilde{\rho}$ having the form of the equilibrium operator ρ, but the chemical potential of adparticles μ_i varies gradually in space and time. The statistical operator $\widetilde{\rho}$ is the local-equilibrium operator of the system. The approximation works well if the system has two scales of the relaxation processes. The first scale is determined by establishing the local equilibrium in different parts of the system. The characteristic frequency of the first stage is equal to $\langle \nu_{ij} n_i h_j \rangle$. During the time $\langle \nu_{ij} n_i h_j \rangle^{-1}$, every site establishes equilibrium with its neighbors. In the second stage of the relaxation, different parts of the system come into equilibrium with each other by diffusion of adparticles. The characteristic space scale of the second stage l and characteristic frequencies ω must satisfy the conditions $l \gg a$ and $\omega \tau \ll 1$. During the time interval τ, many adparticles visit any given site i. The fluctuations of the occupation numbers and other physical quantities averaged over time τ will be small because of averaging over a great number of particles.

One can obtain an explicit form of the local equilibrium operator by developing the exponent into a series of small deviations of the chemical potential $\delta \mu_i = \mu_i - \mu$ ($|\delta \mu_i / \mu| \ll 1$):

$$\widetilde{\rho} = \widetilde{Q}^{-1} \exp\left[\beta\left(\sum_i \mu_i n_i - H_a\right)\right]$$

$$\approx \rho + \delta\rho = \rho\left[1 + \beta \sum_i \delta\mu_i(n_i - n)\right]; \tag{11}$$

here $n \equiv \langle n_i \rangle$ is the mean surface density of adparticles.

The averaging of the balance equation with the local-equilibrium statistical operator gives the following equation for evolution of the fluctuation of the zeroth site occupation number

$$\partial_t \delta n_0(t) = \sum_i [\delta(\nu_{i0} n_i h_0) - \delta(\nu_{0i} n_0 h_i)] + J_0^L(t), \tag{12}$$

where

$$\delta n_0 = \beta \sum_i \delta\mu_i \langle n_0(n_i - n)\rangle,$$

$$\tag{13}$$

$$\delta(\nu_{i0} n_i h_0) = \beta \sum_j \delta\mu_j \langle \nu_{i0} n_i h_0 (n_j - n)\rangle.$$

In order to obtain a closed equation for surface density fluctuations, one must obtain expressions for $\delta\mu_i$ and fluctuation of adparticle fluxes as functions of δn_j. For this purpose one must know the mechanism of an adparticle hop from one lattice site to another one. Here we restrict considerations to nearest-neighbor hops only. An adparticle on the zeroth site can jump to one of its nearest-neighbor sites (labeled 1, 2, and 3 in Fig. 1) if the destination is empty. The diffusing adparticle must surmount the potential barrier from the initial site to the final site. In case of interacting lattice gases the activation energies of hops are affected by the presence of adjacent adparticles. If is assumed that the lateral interactions modify the minima of the periodic potential but not the saddle points, then the hop frequency from the zeroth site to the first site is simply given by

$$\nu_{01} = \nu \exp[\beta\varphi(n_2 + n_3)]. \tag{14}$$

Here ν is the hop frequency of a single adparticle on a clean surface. The terms in brackets account for the variation of the potential minimum due to the lateral interaction between the jumping particle (on site 0) and its nearest neighbors on sites 2 and/or 3 (the energy of interaction between the nearest neighbors is equal to φ). This simple hop model neglects interaction of the jumping adparticle at the saddle point of the potential relief with its neighbors. As already mentioned, this condition permits one to obtain diffusion coefficients by purely thermodynamical calculations. Using the expression for hop frequency [Eq. (14)], one arrives at the simple equation

$$\partial_t \delta n_0(t) = \nu\beta \exp(\beta\mu)\langle h_0 h_1\rangle \sum_{i=1}^{3} (\delta\mu_i - \delta\mu_0) + J_0^L(t)$$

where $\langle h_0 h_1\rangle \equiv \langle (1-n_0)(1-n_1)\rangle$ is the correlation function of two holes on the nearest-neighbor sites.

Developing the fluctuations of the chemical potential in series, one can obtain easily the diffusion equation

$$\partial_t \delta n(\vec{r},t) = (3a^2/4)\nu\beta \exp(\beta\mu)\langle h_0 h_1\rangle \left(\frac{\partial\mu}{\partial n}\right)\vec{\nabla}^2 \delta n(\vec{r},t)$$

$$+ J^L(\vec{r},t).$$

The expression for the diffusion coefficient has the form

$$D = D_0\beta \exp(\beta\mu)[1 - 2n + 2\langle n_0 n_1\rangle]\left(\frac{\partial\mu}{\partial n}\right), \tag{15}$$

where $D_0 = 3\nu a^2/4$ is the diffusion coefficient of the noninteracting adparticles. If one introduces the free energy of the system f as

$$f = k_B T N^{-1} \ln Q,$$

then all quantities in the expression for the diffusion coefficient can be calculated as follows:

$$n = \frac{\partial f}{\partial\mu},$$

$$\langle n_0 n_1\rangle = -\frac{2}{3}\frac{\partial f}{\partial\varphi}, \tag{16}$$

$$\beta\left(\frac{\partial\mu}{\partial n}\right) = \left(k_B T \frac{\partial^2 f}{\partial\mu^2}\right)^{-1} \equiv \langle \delta n_i \delta n_j\rangle^{-1},$$

where $\langle \delta n_i \delta n_j\rangle$ is the mean-square adparticle density fluctuation.

It should be noted that the expression for the diffusion coefficient is valid in the hydrodynamical limit for adparticle density inhomogeneities slowly varying in space and time and when the adparticle hop frequency is determined by Eq. (14).

III. HONEYCOMB LATTICE AND REAL-SPACE RENORMALIZATION GROUP

We obtain an expression for the diffusion coefficient D by using a very simple model for adparticle hops. All we need to calculate the diffusion coefficient is the free energy of the system f. Even for a simple model the problem remains too complex to be solved exactly. The well-known Onsager's solution for a 2D Ising spin model was obtained in zero magnetic field, which is equivalent to $\frac{1}{2}$-ML adparticle density. In order to obtain the explicit dependences of the diffusion coefficient on the adparticle density $D(n)$, the approximate methods must be used to calculate the free energy of the system. In this section we outline briefly the RSRG method used for this purpose.

We consider the Hamiltonian of the adparticle system (7), with account of the nearest-neighbors interaction only:

$$H = -\varepsilon\sum_i^N n_i + \varphi\sum_{\langle ij\rangle} n_i n_j. \tag{17}$$

The summation is performed over all lattice bonds ($\langle ij\rangle$) just once.

It is well known that the lattice-gas model as described above is equivalent to the Ising spin model with an external magnetic field. The equivalent reduced Hamiltonian of the Ising model has the form

$$-\beta H_I = h\sum_i^N s_i + k\sum_{\langle ij\rangle} s_i s_j + Nc, \tag{18}$$

where $h = \beta(\mu + \varepsilon)/2 + 3k$, $k = -\beta\varphi/4$, $c = h + 3k/2$, and $s_i = \pm 1$. Empty sites are equivalent to $s = -1$, and full sites to $s = 1$. Strong lateral interactions k cause ferromagnetic ($k > 0$) or antiferromagnetic ($k < 0$) phase transitions. The exact critical value of the interaction parameter k^* in the absence of an external magnetic field is equal to $\pm 0.5 \ln(2 + \sqrt{3}) \approx \pm 0.658\,478$.[24]

Although the lattice-gas model [Eq. (17)] and Ising spin model [Eq. (18)] are fully equivalent, we prefer to use the spin representation in the following sections because of its symmetry with respect to the magnetic field. However, we will refer to lattice-gas terms where they appear to be necessary.

It the RSRG method of Niemeyer and van Leeuwen[20] and Nauenberg and Nienhuis,[21,22] the whole lattice is divided into blocks of L sites.[25] All blocks together must form a honeycomb lattice with the side $\sqrt{L}a$. In the framework of the RSRG approach, one usually employs periodic boundary conditions. It is assumed that the whole lattice is given by the periodic continuation of a small cluster of blocks. A block spin S_α is assigned to each block. S_α is determined by the so-called ''majority rule''

$$S_\alpha = \mathrm{sgn}\left(\sum_{i=1}^{L} s_i\right) \quad \text{where} \quad \mathrm{sgn}(x) = \begin{cases} +1 & \text{if } x>0 \\ -1 & \text{if } x<0. \end{cases}$$
(19)

Each value of the block spin $S_\alpha = \pm 1$ corresponds to 2^{L-1} site spin configurations. If we carry out the partial summation over all those configurations, which leave block spins unchanged, we are able to do an exact real-space renormalization of the original lattice to the lattice composed of the block spins. The main idea of the RSRG transformation is that the result of the summation would have the same form as the original Hamiltonian [Eq. (18)] plus insignificant terms, which do not affect the critical behavior of the system. For the RSRG transformation, one can write

$$\exp[\psi(\{S_\alpha\})] \equiv \sum_{\{s_i\}} \exp\{H_I\}$$
$$= \exp\left\{ h_1 \sum_\alpha^{N/L} S_\alpha + k_1 \sum_{\langle\alpha\beta\rangle} S_\alpha S_\beta + g(h,k) \right\}.$$
(20)

Here the summation is carried out over all possible configurations $\{s_i\}$ for fixed values of the block spins $\{S_\alpha\}$. h_1 is the renormalized magnetic field, and k_1 is the renormalized interaction energy. g is the ''empty set'' term which plays an important role in the method. As was shown by Nauenberg and Nienhuis,[21,22] the free energy of the system f can be evaluated in the series of sequential RSRG transformations of the Hamiltonian [Eq. (18)]

$$f = k_B T \sum_{m=0}^{\infty} L^{-m} g(h_m, k_m).$$
(21)

Here h_m and k_m are the parameters of the mth RSRG transformation; $h_0 = h$; $k_0 = k$.

In the present work we consider only antiferromagnetic interactions between the spins (in lattice-gas terminology these interactions represent repulsion between adjacent adparticles). In this case the lattice can be subdivided into two sublattices with opposite magnetizations and, therefore, there must be at least two blocks in the cluster. For this choice the system of the renormalization equations has the form

$$h_1 = (\psi_{++} - \psi_{--})/4,$$

$$k_1 = (\psi_{++} + \psi_{--} - 2\psi_{+-})/12,$$
(22)

$$g = (\psi_{++} + \psi_{--} + 2\psi_{+-})/8L,$$

with $\psi_{\pm\pm} \equiv \psi(S_1 = \pm 1, S_2 = \pm 1)$, $\psi_{+-} = \psi_{-+}$, and $\psi_{--}(h,k) = \psi_{++}(-h,k)$.

The RSRG transformation functions $\psi_{\pm\pm}$ depend on the size and symmetry of the block of sites. The most important property of any RSRG transformation is the existence of fixed points of the system of the renormalization equations where the transformation is analytic. The fixed points are determined by conditions $h_1 = h$ and $k_1 = k$. The nontrivial (i.e., not $h=k=0$) unstable fixed points of the system [Eq. (22)] correspond to the critical points of the corresponding Hamiltonian [Eq. (18)]. From the symmetry of the first equation of Eq. (22), it is obvious that all fixed points are located on the k axis ($h_c = 0$). In order to determine the stability of the fixed point (h_c, k_c), one must investigate the properties of the transformation at the point. In the vicinity of the fixed point, we have

$$h_1 - h_c = T_{hh}(h - h_c) + T_{hk}(k - k_c),$$
$$k_1 - k_c = T_{kh}(h - h_c) + T_{kk}(k - k_c),$$
(23)

The matrix $T_{\alpha\beta}$ describes the linear response of the renormalized parameters of the Hamiltonian Eq. (18), h_1 and k_1, on variations of the original values h and k around the fixed points. This matrix has two eigenvalues: λ_h and λ_k. The condition for critical behavior is the existence of eigenvalues $\lambda_{h,k} > 1$ (unstable fixed points). The eigenvalues are related to the critical indices of the 2D Ising model α and δ as follows:[26]

$$\alpha = 2 - \ln L/\ln \lambda_k, \quad \text{and} \quad \delta = \ln \lambda_h/(\ln L - \ln \lambda_h).$$
(24)

For the 2D Ising spin model, the exact values of these critical indices are well known: $\alpha = 0$ and $\delta = 15$. Therefore, the exact RSRG transformation should have two nontrivial fixed points $(0, \pm k^*)$ with $\lambda_k^* = \sqrt{L}$ and $\lambda_h^* = L^{15/16}$ (for the ferromagnetic fixed point). Comparing the computed values of k_c, λ_h, and λ_k with the exact ones gives a valuable measure for the accuracy of the RSRG transformation.

We have investigated 11 $L \times 2$ RSRG transformations (using the notation of Refs. 27,28) with the clusters shown in Figs. 1 and 2. The first series of blocks used in the RSRG transformations are shown in Fig. 1. It should be noted that the computing time grows exponentially with the number of spins in the blocks. Using a fully parallelized algorithm for a supermassive parallel computer (Intel Paragon with 136 nodes), we have been able to handle clusters consisting of up to 42 spins for the honeycomb lattice [as the 21×2 cluster, shown in Fig. 1(a)].

In the present work we have also investigated an alternative method of dividing the lattice into blocks. In this method suggested by Schick, Walker, and Wortis,[29,30] the lattice is divided into sublattices. For each sublattice one choose L sites forming a periodic array. The blocks interpenetrate each other as is seen in Fig. 2. For the honeycomb lattice symmetry requires the hexagonal form of the blocks. The two smallest possible hexagons contain seven or 19 sites, and are shown in Fig. 2. The properties of all transformations used in the present work are summarized in Table I.

IV. PHASE DIAGRAM OF THE HONEYCOMB LATTICE

All RSRG transformations have some general properties. As usual, the transformations have two fixed points; one in
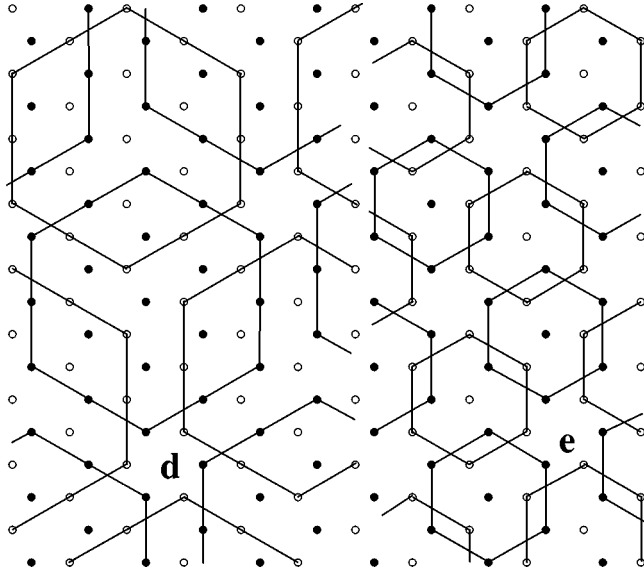
FIG. 2. Sites of the honeycomb lattice grouped into interpenetrating hexagonal blocks: d—$L=19$; e—$L=7$.

FIG. 3. Critical line of the RSRG transformation $13\times 2a$.

the ferromagnetic region ($k_c>0$) and another one in the antiferromagnetic domain ($k_c<0$). In general, the critical values of the interaction parameter approach the exact values if the number of the spin in the block is increased. However, the accuracy of the transformation depends not only on the block size L but also on the symmetry of the block and the relation between the spins from different sublattices (i.e., the relative numbers of intrablock and interblock spin-spin interactions).

The phase diagram of antiferromagnetic spins on the honeycomb lattice shows two critical lines which divide the antiferromagnetic half-plane ($h,k<0$) into antiferromagnetically ordered and disordered spin phases (Fig. 3). These critical lines have asymptotes $k=\pm h/3$ corresponding to the exact relation for the zero-temperature critical field $|h_c|=z|k|$. Here z is the lattice coordination number.

In the present work, the most accurate results are obtained for blocks of the a series (Fig. 1). The best accuracy for determining k_c was not obtained for the largest $21\times 2a$ clus-
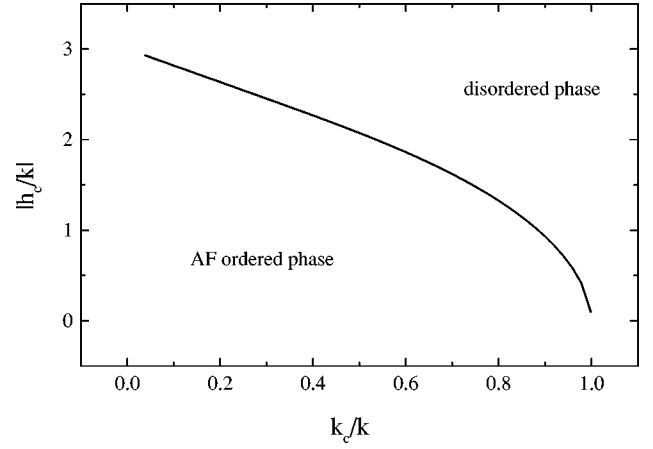
ter, but for the relatively small $13\times 2a$ cluster (Table I). This striking finding obviously indicates that the error in determining the critical value of the interaction energy ϵ does not follow a simple power law in the present case, although such a $\epsilon\propto L^{-1}$ dependence was obtained in Ref. 31 for a square lattice. The accuracy for the $13\times 2a$ cluster, $\epsilon=0.38$, is close to the remarkable result of Niemeyer and van Leeuwen, $\epsilon=0.18$,[20] obtained with a cluster of 21 spins for the ferromagnetic phase transition on the triangular lattice.

The b- and c-type blocks do not appear to be suitable for investigations of the antiferromagnetic phase transition on the honeycomb lattice. For the b-type blocks the accuracy of the RSRG method is not improved upon increasing the block size. As a matter of fact, the 4×2 cluster gives a better accuracy than the 16×2 one. RSRG transformation with the b-type blocks yield an unrealistically narrow stability range for the antiferromagnetically ordered lattice-gas phase. RSRG transformations with the c-type blocks do not show fixed points for $k<0$ at all. The clusters $L\times 2c$ are less symmetrical (blocks have not mirror planes), as compared with the cluster $L\times 2a$. In Table I the critical values are compiled for the different clusters studied in the present work.

In order to calculate the phase diagrams of the antiferromagnetic honeycomb lattice gas, we used the best RSRG transformations with the a-type blocks (see Fig. 4). The phase boundaries between ordered and disordered lattice-gas

TABLE I. Critical values of interaction parameter, indices and adparticle density. F stands for ferro- and AF stands for antiferromagnetic phase transitions.

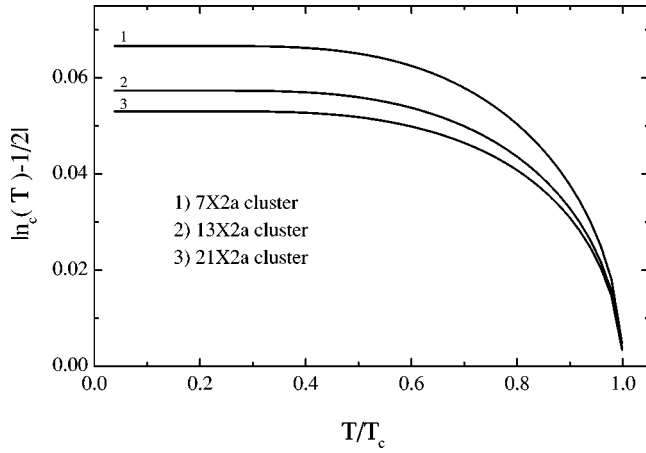| Cluster	k_c (F)	$|k_c|$ (AF)	α	β	$n_c(0)$
$3\times 2a$	0.516 (22%)	0.516 (22%)	-1.24	6.75	0.333
$7\times 2a$	0.6835 (3.8%)	0.6475 (1.7%)	-0.77	20.6	0.433
$13\times 2a$	0.6826 (3.7%)	0.6610 (0.38%)	-0.55	20.9	0.443
$21\times 2a$	0.6768 (2.8%)	0.6635 (0.76%)	-0.55	20.0	0.447
$4\times 2b$	0.85 (29%)	0.85 (29%)	-1.61	67.6	0.408
$9\times 2b$	0.725 (10%)	0.8230 (25%)	-0.63	30.3	0.485
$16\times 2b$	0.6854 (4.1%)	0.8853 (34%)	-0.47	21.7	0.493
$7\times 2c$	0.725 (10%)	—	-0.70	29.7	—
$19\times 2c$	0.6847 (4%)	—	-0.44	21.9	—
$19\times 2d$	0.5761 (13%)	0.5761 (13%)	-1.26	6.22	0.400
$7\times 2e$	0.5694 (14%)	0.5694 (14%)	-1.23	7.63	0.388

FIG. 4. Phase boundaries for the antiferromagnetic honeycomb lattice gas, calculated with different RSRG transformations.
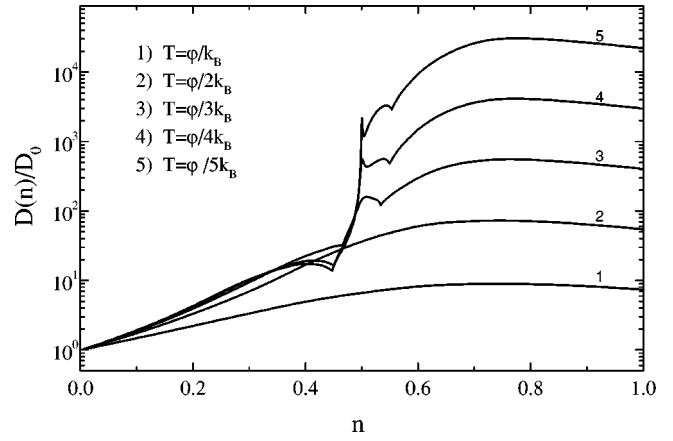
FIG. 5. Coverage dependence of the normalized chemical surface diffusion coefficient D/D_0. The calculations are performed for different temperatures as indicated in the figure.

phases (corresponding to the phase boundaries between antiferromagnetically ordered and disordered spin phases in magnetic terminology) are symmetric about half-coverage, $n = \frac{1}{2}$. For the $21 \times 2a$ transformation the ordered phase is found to exist only in a very narrow region of coverages near $\frac{1}{2}$ ML. The width of the region depends on the temperature monotonically increasing from zero value at $T = T_c$ to $0.447 \lesssim n \lesssim 0.553$ at $T = 0$ (Fig. 4). It is interesting to note that all RSRG transformations exhibit the same asymptotic behavior of the critical lines in spin representation, but yield different zero-temperature critical adparticle densities $n_c(0)$ in the lattice-gas representation (see Table I and Fig. 4).

V. DIFFUSION COEFFICIENT DEPENDENCES

The expression for the diffusion coefficient in spin variables h and k has the form[15]

$$D = D_0 \exp(2h - 6k)]\{1 - 2f_h + 2f_k/3\}/f_{hh}, \quad (25)$$

where f_h and f_k are the first derivatives of the free energy over magnetic field and interaction parameter, respectively, and f_{hh} is the second derivative of the free energy over the magnetic field. The derivatives have simple physical meanings. The first derivative over the magnetic field, f_h, gives the mean magnetization $\langle s_i \rangle$, and is proportional to the mean surface density of adparticles n. The first derivative over the interaction parameter, f_k, is equal to the nearest-neighbor correlation function $\langle s_0 s_1 \rangle$. The second derivative of the free energy over magnetic field is proportional to the mean-square density fluctuations $f_{hh} = 4\langle \delta n_i \delta n_j \rangle$. In the vicinity of the critical points these fluctuations diverge, which results in a critical slowdown of the diffusion coefficient.

In the limits of $n \to 0,1$, a hopping adparticle has none or two nearest neighbors, respectively. Therefore, the limiting values of the diffusion coefficient are equal to

$$\lim_{n \to 0} D = D_0,$$
$$\lim_{n \to 1} D = D_0 \exp(2\beta\varphi). \quad (26)$$

We have calculated the required derivatives of the free energy using the expression for the free energy [Eq. (21)], and

obtained the dependences of the chemical diffusion coefficient D and the mean-square density fluctuations vs adparticle density for different values of the interaction parameter φ. The coverage dependence of the chemical surface diffusion coefficient, $D(n)$, is shown in Figs. 5 and 6. In the disordered phase the diffusion coefficient grows with the average density of adparticles n, as the mean number of nearest neighbors for any hopping particle is also growing. One can see qualitatively the same behavior at a coverage region of nearly a monolayer. The relaxation of the density fluctuations proceeds due to diffusion of holes. It should be noted that the diffusion coefficient for holes is equal to $D_0 \exp(2\beta\varphi)$ for zero density of holes ($h = 0$). Due to the
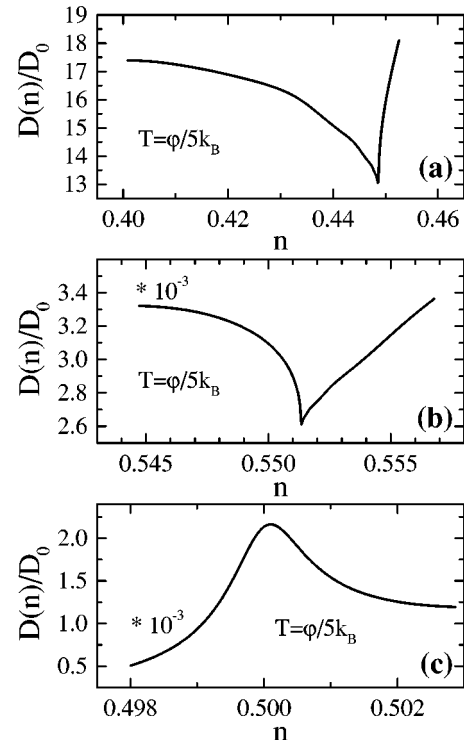
FIG. 6. (a) and (b) Singularities of the coverage dependence of D/D_0 in the critical regions: (a) $n_c < \frac{1}{2}$ and (b) $n_c > \frac{1}{2}$. (c) Maximum of the chemical diffusion coefficient D/D_0 at half coverage, $n = \frac{1}{2}$.
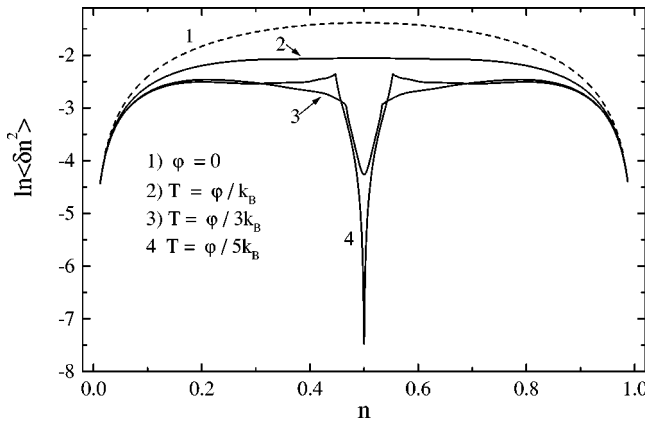
FIG. 7. Coverage dependence of the mean-square density fluctuations, $\langle \delta n_i \delta n_j \rangle$. The calculations are performed for different temperatures, as indicated in the figure.

evident Hamiltonian's symmetry ''particles↔holes,'' the nearest-neighbor interaction parameter for holes is also equal to φ. Increasing the density of adparticles or holes increases the effective hopping frequency of the particles, and D also increases. When approaching the critical density, the density fluctuations grow rapidly, and cause a reduction of the chemical diffusion coefficient. The nonanalytical nature of these minima, caused by a phase transition between the disordered and ordered phase, is clearly seen in Figs. 6(a) (for $n < 0.5$) and 6(b) (for $n > 0.5$). The shapes of both minima are similar to the exact logarithmic slowdown of the diffusion coefficient, obtained in Ref. 18 for a reconstructive surface. The depth of the minima is determined by the critical index α. The exact value $\alpha = 0$ yields a logarithmic divergence of the mean-square density fluctuations and a critical slowdown of D at $n = n_c$. If $-1 < \alpha < 0$, one must expect cusplike maxima for $\langle \delta n_i \delta n_j \rangle$ and corresponding minima for $D(n)$.[17] If $\alpha < -1$, there should be no singularities of the chemical diffusion coefficient and of the mean-square density fluctuations at all.

The diffusion coefficient grows rapidly at a $\frac{1}{2}$-ML density, and exhibits a sharp maximum at low temperatures. The physical origin of this maximum is not related to a corresponding singularity of the derivatives, and thus cannot be attributed to the disorder-order phase transition at n_c [Fig. 6(c) clearly shows that the dependence $D(n)$ at half-coverage remains analytical]. The maximum of the chemical diffusion coefficient can be explained on purely thermodynamic grounds.[9,10] At half-coverage the lattice gas is well ordered, and thus largely incompressible. Density fluctuations are strongly suppressed due to repulsive interactions between the adparticles: Any density disturbance (i.e., the inclusion of additional adparticles into the ideally ordered lattice-gas phase) substantially increases the configurational energy and is thermodynamically unfavorable. Therefore, density disturbances result in a high mobility of adparticles, allowing the density disturbances to heal out. As the density is not equal to $\frac{1}{2}$, there are fluctuations of the nonstoichiometric nature that do not require energy for their existence (see Fig. 7). Therefore, the diffusion coefficient decreases when n deviates from the $\frac{1}{2}$-ML coverage.

It should be mentioned that diffusion coefficient grows rapidly at $\frac{1}{2}$-ML coverage, especially at low temperatures.

This growth is due to the fast increase of the mean number of the nearest neighbors for hopping adparticles at $n = \frac{1}{2}$. For $n < \frac{1}{2}$ the density inhomogeneities may be considered as deletion of adparticles from perfect structure, and for $n > \frac{1}{2}$ they are formed by inserting additional adparticles into the ideally ordered phase. Roughly speaking the system has two values of the diffusion coefficient $D(n < \frac{1}{2})$ and $D(n > \frac{1}{2})$; moreover, $D(n > \frac{1}{2}) \gg D(n < \frac{1}{2})$. This creates additional difficulties for experimental investigations of the weak diffusion coefficient peculiarities, arising due to order-disorder phase transitions. It seems that the most suitable method for measuring the diffusion coefficient fine details will be the fluctuation method, suggested by Gomer (see, for example, Ref. 5). The measurements are carried out at a constant adparticle density, which can be adjusted to any desired value. The methods, using Boltzmann-Matano analysis, give an average over some density interval values of the diffusion coefficient.

The dependences $\langle \delta n_i \delta n_j \rangle$ versus adparticle density are shown in Fig. 7. In the absence of lateral interaction between the adparticles, the intensity of the fluctuations is proportional to $n(1-n)$ [curve (1) is close to this dependence]. Repulsion inhibits any density disturbances as is clearly seen for curves (2) and (3) of Fig. 7. The disorder-order phase transitions cause cusplike peaks at the critical points as already mentioned. The minimum at $n = \frac{1}{2}$ corresponds to the maximum on the coverage dependence of the chemical diffusion coefficient. It does not depend on the symmetry of the lattice, and is caused by the strict ordering of adparticles on the sublattices. Qualitatively the same behavior of $D(n)$ and $\langle \delta n_i \delta n_j \rangle$ at $n = \frac{1}{2}$ was also found using mean-field[13] and Bethe-Peierls approximations.[14]

It should be noted that the classical Bethe-Peierls approximation and RSRG method give similar dependences of the diffusion coefficient $D(n, \varphi)$ in the regions far from critical points of the system both in disordered and ordered phases, but in the vicinities of the critical points the dependences are quite different. The classical approximations give stepwise changes of the diffusion coefficient at the critical densities: $D(n_c - 0) \neq D(n_c + 0)$. The RSRG method gives cusplike minima, which are similar to the exact logarithmic critical slowdown of the diffusion coefficient obtained in Ref. 18 for adatom diffusion on a reconstructive surface. The accuracy of the RSRG method can be increased significantly by increasing the size of the block spins and choosing the most appropriate symmetry of the blocks.

VI. SUMMARY

We have investigated a number of RSRG transformations on the honeycomb lattice with blocks of different sizes and symmetries. It has been shown that the accuracy of the method depends strongly not only on the number of sites in the block but also on the symmetry of the blocks. The accuracy of the method increases in a nonmonotonic fashion with the number of sites L in the block. The most accurate results were obtained for relatively small cluster of 26 sites. Using a fully parallelized algorithm on a supermassive parallel computer (Intel Paragon), we can handle clusters of up to 42 spins.

In the present work we have studied the phase diagram of the lattice gas with nearest-neighbor repulsive interactions

and the fully equivalent antiferromagnetic spin model on a honeycomb lattice. It is shown that the ordered phase in the lattice system appears in the very narrow density interval $0.447 < n < 0.553$.

Using the RSRG method, we have investigated the surface diffusion of adparticles on the honeycomb lattice. The accuracy of the RSRG transformations was sufficiently high, and permits us to obtain all peculiarities of the chemical surface diffusion coefficient. At the order-disorder phase transitions the chemical diffusion coefficient exhibits nonanalytical minima which are due to the rapid growth of the mean-square density fluctuations. At half-coverage and low temperatures, i.e., deeply within the ordered lattice-gas phase, the diffusion coefficient shows a strong maximum which is attributed to the large incompressibility of the well-ordered lattice-gas phase.

The RSRG approach used in the present work reproduces all peculiarities of the chemical diffusion coefficient which have been predicted by theoretical considerations. Thus the RSRG approach is a very powerful method for the investigation of surface diffusion processes on two-dimensional lattices which, in contrast to the Monte Carlo technique, requires only moderate computational resources.

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