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Collective surface diffusion: *n*-fold way kinetic Monte Carlo simulation

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Collective surface diffusion of strongly interacting particles is simulated on the basis of an *n*-fold way kinetic Monte Carlo scheme. The coverage dependence of the jump and tracer diffusion coefficients is calculated for one- and two-dimensional lattice gases at very low (subcritical) temperatures. Results are compared with exact analytical ones and Monte Carlo simulations using the standard Metropolis algorithm. The method proves to be highly reliable to investigate surface diffusion at subcritical temperatures where phase coexistence in the adlayer occurs. [S1063-651X(98)07306-1]

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I. INTRODUCTION

Monte Carlo (MC) simulation is increasingly becoming a generalized set of computational tools for inferring equilibrium and dynamical properties of physical systems. Its applications range all branches of science. MC is continuously renewing its usefulness for dependable prediction of physical properties of a model system hardly tractable by analytical means or experimentally inaccessible [1]. In surface science, the collective diffusion of species bounded to an adsorbent's surface by a highly inhomogeneous potential is, perhaps, one of the most challenging phenomena to be addressed both theoretically and experimentally [2,3].

Monte Carlo simulation appears particulary useful to investigate strongly interacting adsorbates at low temperatures on heterogeneous substrates (i.e., when $w/kT \gg 1$ and $w/\sigma = 1$, where w is the typical energy scale of the adsorbate-adsorbate interaction and σ the variance of the adsorption potential minima). Collective dynamical relaxation at low temperatures is seriously hampered by critical slowing down of density fluctuations. When the system goes through phase boundaries, the computer time budget necessary to drive the system into a stationary regime increases, roughly, exponentially with the ratio w/kT.

The calculation of static (or equilibrium) properties has been long investigated and upgraded in such a way that numerous algorithms are currently available that quickly relax the system from arbitrary initial configurations to equilibrium [4–7]. However, in most cases the local dynamics of the original system is appreciably distorted, such that the kinetic behavior in the non-equilibrium, as well as in the stationary regime, become meaningless (think of a lattice gas where a ''natural'' local dynamics driven by jump of adsorbed molecules to nearest neighbor empty sites is replaced by a nonlocal relaxation algorithm allowing the molecule to jump over any empty site of the lattice regardless of its separation from the starting site).

Although insight into the collective dynamical behavior of strongly chemisorbed atoms is essential to understand elementary surface phenomena such as domain growth, surface aggregation, catalysis, thermal desorption, etc., experimental determination of the surface diffusion coefficient and its dependence on thermodynamical variables, such as the temperature and surface coverage, are difficult to achieve even for adlayers on perfectly homogeneous substrates. Furthermore, surface diffusion represents a very sensitive probe for phase transitions in adlayer of monoatomic and polyatomic adparticles [3,12,14–18]. A comprehensive and conceptually plain review of this topic in surface science was presented by Gomer [3].

Exact analytical calculations are only possible for simple systems such as diffusion of noninteracting monoatomic adparticles in one- or two-dimensional regular lattices. For interacting particles, mean field, quasichemical, or cluster approximations are necessary [8,9]. However, these approximations are expected to be inappropriate to describe surface diffusion of interacting particles either at subcritical temperatures or strongly inhomogeneous external fields.

Standard Monte Carlo simulations (SMC) of collective diffusion have been already performed for monoatomic adparticles [10,11] and dimers [12] on square lattices at slightly subcritical and supercritical temperatures. However, the use of SMC (i.e., Metropolis scheme) [13] far below the critical temperature and high surface coverage may turn the simulation of collective dynamics into an exceedingly time-demanding task.

In the present work we investigate collective surface diffusion in the canonical ensemble by introducing a fast kinetic Monte Carlo scheme on the basis of the *n*-fold way–like algorithm (hereafter we use the acronym nFWMC for *n*-fold way Monte Carlo scheme) [19]. It relies on the exact computation of transition probabilities from each state of the whole set of adparticles and the association of the time evolution to a random variable sampled from the waiting-time distribution for the state of the system. Henceforth, dynamics of strongly interacting particles at very low temperatures can be readily achieved at a computational cost several orders of magnitude less (typically 10^{-3} for $w/kT \approx 5$) than required by the Metropolis algorithm. Although *n*-fold way–like algorithms have been long known, and sometimes used for reproducing equilibrium states [19], they have been almost overlooked in relation to collective dynamics of particles [20]. A more elaborate version of the *n*-fold way scheme has been recently proposed, which can give further improvement on it [21]. However, as claimed by the author, they are really

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advantageous for slow dynamics in models with a limited number of states. Hence, its efficiency in inhomogeneous systems is still unknown.

There is one salient contribution in this work. It is demonstrated that nFWMC allows for the calculation of a collective diffusion coefficient with remarkable exactness and speed at subcritical temperatures. This is shown by a thorough comparison between analytical results [22], SMC in one and two dimensions and nFWMC. In addition, diffusion of interacting lattice gases is studied at temperatures appreciably lower than those reported before. Attractive, as well as repulsive, interaction between nearest neighbor adparticles are considered in this work.

Other kinetic processes such as thermal desorption, adsorption, and reaction kinetics can be identically simulated through nFWMC owing to their isomorphism with collective diffusion.

II. *N*-FOLD WAY KINETIC SCHEME

Hereforth, we assume our model physical system to be a set of N particles adsorbed on M sites of a lattice having either regular geometry or nonuniform connectivity. Since we are ultimately interested in describing surface diffusion at constant coverage, $\theta = N/M$ (canonical ensemble), N will be kept constant. Nevertheless, the following discussion applies in general to any kinetic processes such as thermal desorption or surface reaction for which N varies in time.

The state of the whole system at any given time t is denoted by $(\mathbf{N},t)$ ($\mathbf{N}$ contains the information about all particle's coordinates on the lattice). For the sake of simplicity, let us suppose the particles can jump only to nearest neighbor empty sites of a regular lattice with connectivity c. Since every particle can, in principle, attempt a jump to any of its c neighboring sites, there is at most cN possible events to happen at the time t. Provided the system is at the state $(\mathbf{N},t)$ the probability that the kth event ($k=1,2,\ldots,cN$) occurs within the time interval $(t',t'+dt')$ is $p_k(t'|\mathbf{N},t)dt'$ (t' being the time interval elapsed from t),

$$p_k(t'|\mathbf{N},t)dt' = P(t'|\mathbf{N},t)W_k(\mathbf{N},t)dt', \tag{1}$$

where $P(t'|\mathbf{N},t)$ is the probability that nothing (out of the cN events) occurs in the interval $(t,t+t')$, and $W_k(\mathbf{N},t)$ the transition probability for the kth event per unit of time. From the definition of $P(t'|\mathbf{N},t)$ it arises that

$$\begin{aligned} P(t'+\Delta t'|\mathbf{N},t) &= P(t'|\mathbf{N},t)P(\Delta t'|\mathbf{N},t) \\ &= P(t'|\mathbf{N},t)[1-W(\mathbf{N},t)\Delta t'] + O(\Delta t') \end{aligned} \tag{2}$$

where $W(\mathbf{N},t) = \Sigma_k W_k(\mathbf{N},t)$.

Therefore

$$\begin{aligned} \frac{\partial P(t'|\mathbf{N},t)}{\partial t'} &= \lim_{\Delta t' \to 0} \frac{[P(t'+\Delta t'|\mathbf{N},t) - P(t'|\mathbf{N},t)]}{\Delta t'} \\ &= P(t'|\mathbf{N},t)W(\mathbf{N},t) \end{aligned} \tag{3}$$

whose solution is

$$P(t'|\mathbf{N},t) = \exp[-t'W(\mathbf{N},t)] \tag{4}$$

with the boundary condition $P(t'=0|\mathbf{N},t)=1$, provided that the system is in the state $\mathbf{N}$ at $t'=0$.

This represents a distribution with mean waiting time

$$\tau_N = \frac{1}{W(\mathbf{N},t)}.$$

By replacing Eq. (4) to Eq. (1) one gets

$$p_k(t'|\mathbf{N},t)dt' = W_k(\mathbf{N},t)\exp[-t'W(\mathbf{N},t)]dt'. \tag{5}$$

Equation (5) clearly defines a density function of two stochastic variables k and t'; k has a discrete domain ($k \in \{1,2,3,\ldots,cN\}$ for surface diffusion through jumps between nearest neighbor sites), and t', the time elapsed from t for the kth event to occur, has a continuous one. The associated marginal density functions are straightforward from Eq. (5):

$$g_k(\mathbf{N},t) = \int_0^\infty p_k(t'|\mathbf{N},t)dt' = \frac{W_k(\mathbf{N},t)}{W(\mathbf{N},t)}, \tag{6}$$

where g_k is the probability that the kth event occurs anytime after the time t, and

$$\begin{aligned} h(t'|\mathbf{N},t)dt' &= \sum_k p_k(t'|\mathbf{N},t)dt' \\ &= W(\mathbf{N},t)\exp[-t'W(\mathbf{N},t)]dt', \end{aligned} \tag{7}$$

where $h(t'|\mathbf{N},t)dt'$ accounts for the probability that any event occurs in the time interval $(t',t'+dt')$.

Furthermore, since

$$p_k(t'|\mathbf{N},t)dt' = g_k(\mathbf{N},t)h(t'|\mathbf{N},t)dt', \tag{8}$$

k and t' are independent stochastic variables within the present formulation, as it comes out from Eqs. (5)–(8). Henceforth, they can be separately sampled from their corresponding probability distribution functions $G_k(\mathbf{N},t)$ and $H(t'|\mathbf{N},t)$, defined respectively by

$$G_k(\mathbf{N},t) = \sum_{i=1}^{k} g_i(\mathbf{N},t) = \frac{1}{W(\mathbf{N},t)} \sum_{i=1}^{k} W_i(\mathbf{N},t) \tag{9}$$

and

$$H(t'|\mathbf{N},t) = \int_{t'}^\infty h(t''|\mathbf{N},t)dt'' = P(t'|\mathbf{N},t). \tag{10}$$

Thus, we can effectively represent the dynamical evolution of the system by using two basic functions, G and H. The simulation of collective dynamics turns out to be straightforward and relies on only two steps, which can be stated in a general manner: for any given state $(\mathbf{N},t)$ of the system we have the following:

(i) The transition probabilities W_i, $i=1,2,\ldots,cN$, are evaluated. Then the kth event to happen is chosen when the condition [23]

$$\frac{1}{W}\sum_{i=1}^{k-1} W_i < \xi_1 \leqslant \frac{1}{W}\sum_{i=1}^{k} W_i \tag{11}$$

is performed, where ξ_1 is randomly uniformly distributed in (0,1).

(ii) The time t' elapsed from t in the transition of step (i) is $t' = (-1/W)\ln \xi_2$. Then, the time elapsed from the initial state $(\mathbf{N}_0, t=0)$ is incremented as [24]

$$t = t + t' = t - \frac{1}{W}\ln \xi_2 . \tag{12}$$

The collective dynamics proceeds by successively repeating steps (i) and (ii).

In terms of simulation, every step (i) produces a successful jump to a nearest neighbor site (generally speaking, it is a successful transition). In (ii), the time is treated as being a dependent variable that is updated according to the waiting-time distribution for the given state.

The above formalism is generally valid for any kinetic process for which the rates of the elementary events are known.

The transition probabilities W_k have not been specified yet. An explicit form for diffusion on homogeneous and heterogeneous surfaces will be given in Sec. III. However, it can be already rationalized that, for thermally activated processes, $W \sim \exp(-\Delta E/kT)$ where ΔE is a typical free energy variation. The number of trials for a successful transition to take place in the SMC framework scales as $1/W \sim \exp(\Delta E/kT)$.

For an attractive interacting lattice gas at $T \ll T_c$, $\Delta E/kT \gg 1$ so the efficiency of SMC is extremely low. Contrarily, the efficiency of (i) and (ii) [Eqs. (11) and (12)] is not affected by the ratio $\Delta E/kT$. Simply, every trial turns into a successful one.

III. SURFACE DIFFUSION

A. Basic definitions

Very promising experimental techniques to measure surface diffusion have been recently developed [3]. Among others, the fluctuation method allows for the calculation of coverage and temperature dependence of the diffusion constant D from the time autocorrelation function of local density fluctuations [3]. Since in most cases adsorbed particles interact each other, and the experiments are carried out at low temperatures [10], it is likely that the chosen surface coverage θ and temperature T (that define the thermodynamic state) place the system in a phase-coexistence region. It is expected that further insight and improvement of this technique will turn the analysis of surface diffusion at very low temperatures into a sensitive tool for analyzing phase transitions.

We start defining the collective diffusion coefficient D (usually it is referred to as chemical diffusion coefficient) by the general Kubo-Green formula from the linear response theory [3]

$$D = \frac{\langle [\delta N]^2 \rangle^{-1}}{2} \int_0^\infty C(t)\,dt, \tag{13}$$

where $C(t)$ is the N-particle velocity cross-correlation function

$$C(t) = \left\langle \sum_{i,j}^{N} \vec{v}_i(0)\cdot \vec{v}_j(t) \right\rangle, \tag{14}$$

where the average is taken over all time origins and statistical ensemble; $\langle(\delta N)^2\rangle$ in Eq. (13) is the mean-square fluctuation of the number of particles. D can alternatively be written as [3]

$$D = \left[\frac{\langle(\delta N)^2\rangle}{\langle N\rangle}\right]^{-1} \lim_{t\to\infty}\left[\frac{1}{2dt}\left\langle \frac{1}{N}\left(\sum_{i=1}^{N} \Delta\vec{r}_i(t)\right)^2\right\rangle\right] \tag{15}$$

for a d dimensional system, where $\Delta\vec{r}_i(t)$ denotes the ith particle's displacement at time t. Using shorter notation Eq. (15) reads

$$D = T_h\, D_j , \tag{16}$$

where

$$T_h = \left[\frac{\langle(\delta N)^2\rangle}{\langle N\rangle}\right]^{-1} \tag{17}$$

is named thermodynamic factor, which can also be written in terms of the chemical potential derivative with respect to surface coverage, namely,

$$T_h = \left[\frac{\partial(\mu/kT)}{\partial \ln \theta}\right]_T . \tag{18}$$

Furthermore D_j is the so-called jump diffusion coefficient, and holds for the second factor on the right side of Eq. (15):

$$D_j = \lim_{t\to\infty}\left[\frac{1}{2dt}\left\langle \frac{1}{N}\left(\sum_{i=1}^{N} \Delta\vec{r}_i(t)\right)^2\right\rangle\right] = \lim_{t\to\infty}\left[\frac{1}{2dt}\langle R^2(t)\rangle\right]. \tag{19}$$

In addition, the tracer diffusion coefficient D^* can be drawn by averaging the mean square displacement of tagged particles as

$$D^* = \lim_{t\to\infty}\left[\frac{1}{2dt}\left(\frac{1}{N}\sum_{i=1}^{N} \langle[\Delta\vec{r}_i(t)]^2\rangle\right)\right]. \tag{20}$$

It should be noted that D^* refers to the displacement of single particles while D_j does for the center of mass of the whole set of diffusing particles. T_h can be determined by either evaluating fluctuations of N in the grand canonical ensemble (i.e., μ and T fixed) according to Eq. (17), or by deriving the adsorption isotherm (i.e., θ versus μ/kT) as in Eq. (18). D_j, in turn, can be readily drawn from the slope of the center of mass mean-square displacement $\langle R^2(t)\rangle$ for long times, as its definition [Eq. (19)] states.

B. Elementary jump probabilities

Now we precise the particular form for the transition probabilities $W_k(N)$ in terms of the particle-surface and particle-particle interactions. As stated in Sec. II, we assume the surface to have M adsorption sites regularly arranged with connectivity c; $c=2$ (one dimension) and $c=4$ (square lattice) were used in the present work. We denote the site energies (particle-surface potential energy) by ε_i, $i=1,2,\ldots,M$. For a given configuration of the particles on the lattice sites, the total interaction energy of a single particle on site i, E_i, is

$$E_i=\varepsilon_i+\sum_{j,\mathrm{NN}i} J_{\mathrm{NN}}\, s_j+\sum_{k,\mathrm{NNN}i} J_{\mathrm{NNN}}\, s_k+U_i, \tag{21}$$

where J_{NN} and J_{NNN} are the nearest neighbor (NN) and next nearest neighbor (NNN) coupling constants, s_j ($s_j=0$ or 1) the occupation number of site j, and U_i symbolically represents all other interactions that may be taken into account (interaction between more distant sites, three body interactions, etc.). In the present study only NN interaction has been considered. Jumps are thermally activated processes with transition probability

$$W_{ij}=\kappa\ \exp\left[-\frac{\Delta E_{ij}}{kT}\right](1-s_j), \tag{22}$$

where i and j denote the initial and final sites respectively and $\Delta E_{ij}=\varepsilon_{ij}^b-E_i$ is the activation energy barrier defined in terms of interaction energy of the adparticle at the saddle point between sites i and j, ε_{ij}^b, and the energy E_i at the initial equilibrium site. The factor $(1-s_j)$ accounts for the fact that only single occupancy of sites is allowed. It is worth noticing that the detailed balance principle is fulfilled because

$$P_i W_{ij}=P_j W_{ji}, \tag{23}$$

where $P_i \propto \exp[-E_i/kT]$ denotes the probability to have a particle in site i with energy E_i in the canonical ensemble. This assures that thermodynamic equilibrium is observed during the simulation of collective diffusion according to Eqs. (11), (12), and (22). In SMC simulations the factor κ in Eq. (20) is chosen to be $\kappa=\exp[-\Delta E_m/kT]$, where ΔE_m is the energy difference of the most favorable jump. Thus κ refers to the transition probability of the fastest process in the system. In this way, computational efficiency is improved and transition probabilities larger than unity are circumvented when repulsive interactions apply [10,18].

However, for the kinetic scheme presented in Eqs. (11) and (12) the election of κ is irrelevant to the simulation efficiency, which is already maximun because every step leads to a successful jump [κ cancels out in Eq. (11); it only affects the unit of time in Eq. (12)]. The simulation of collective diffusion through the n-fold way algorithm in the canonical ensemble is then simply carried out by fixing the surface coverage θ and temperature T, evaluating the jump probabilities according to Eq. (22), and following the basic steps (i) and (ii) [Eqs. (11) and (12)] up to reaching the asymptotic regime [typically, when $\langle (1/N)(\Sigma_{i=1}^{N}\Delta\vec{r}_i)^2\rangle \propto t$].

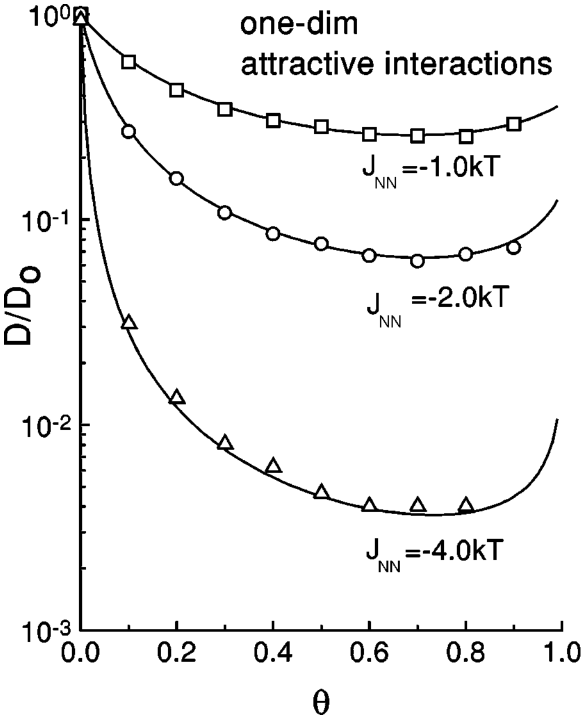

FIG. 1. Collective diffusion coefficient vs coverage for a one-dimensional lattice gas with attractive interaction J_{NN} between NN particles [the dimensionless ratio D/D_0 is represented, where $D_0=\lim_{\theta\to 0} D(\theta)$]. The solid lines represent the exact solutions for D from Ref. [22]. The symbols are results from nFWMC; squares, $J_{\mathrm{NN}}/kT=-1$; circles, $J_{\mathrm{NN}}/kT=-2$; triangles, $J_{\mathrm{NN}}/kT=-4$.

IV. RESULTS AND CONCLUSIONS

In order to check the dependability of nFWMC at very low temperature, comparisons with exact analytical results and previous SMC simulations have been carried out. Futhermore, simulation of diffusion in two dimensions at extremely low subcritical temperatures is performed. The results can be sorted out in three categories.

A. Interacting lattice gas in one dimension

Calculations of D [collective diffusion coefficient in Eq. (16)] were carried out by following the nFWMC outlined in Sec. II. Strongly attractive as well as repulsive NN particles were considered. In Fig. 1 the coverage dependence of D is compared with exact results from Ref. [22] for weakly ($J_{\mathrm{NN}}/kT=-1$) and strongly ($J_{\mathrm{NN}}/kT=-4$) attractive interactions. The agreement is absolute for all coverages. Results for repulsive interactions are shown in Fig. 2. Full agreement between the exact solution and simulation is also found. Much larger ratios J_{NN}/kT ($J_{\mathrm{NN}}/kT=5$ and 8) were used in this case compared with those of Fig. 1. The expected pronounced increase [22] of D with a maximun at $\theta=0.5$, as well as the slow monotonic decrease for $\theta>0.5$ are clearly reproduced. A detailed discussion of the coverage dependence of D was given in Ref. [22]. A common characteristic of the curves in Fig. 1 and 2 is that no qualitative changes are observed in each set as the interaction increases. This is because of the absence of phase transition in a one dimensional lattice gas.

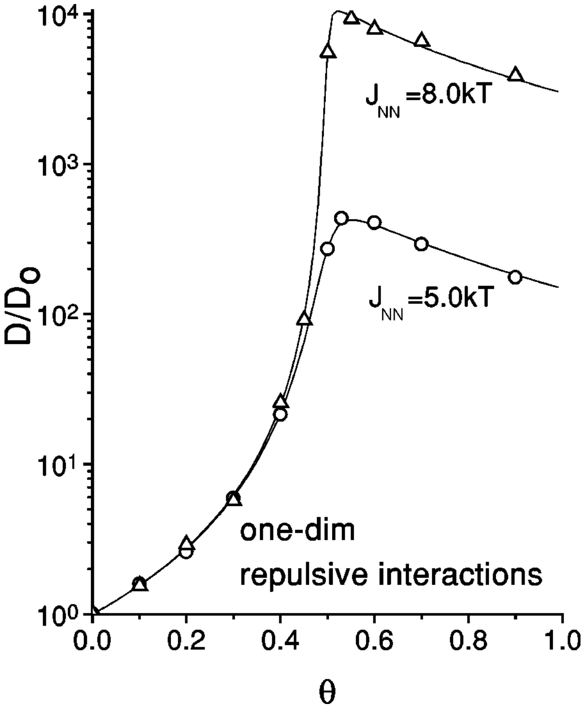

FIG. 2. Same as Fig. 1 for repulsive interaction between NN particles; circles, $J_{\mathrm{NN}}/kT=5$; triangles, $J_{\mathrm{NN}}/kT=8$.

B. Interacting lattice gas in two dimensions

Calculations of D^* by using the nFWMC for a lattice gas on a square lattice were compared with previous simulations applying SMC (Metropolis scheme) done by Uebing *et al.* in Ref. [10]. The cases of both attractive and repulsive NN interactions are thoroughly reproduced for various values of the ratio J_{NN}/kT. In Fig. 3, the variation of D^* on J_{NN}/kT for different surface coverages is shown. All data have been obtained by averaging over 5×10^3 runs. A particularly interesting result is shown in Fig. 4 where D^* versus θ is plotted for repulsive interactions at supercritical and subcritical temperatures ($kT_c/|J_{\mathrm{NN}}|=0.567$ at $\theta=0.5$). The behavior changes from a smooth variation, showing a broad maximum at $\theta\approx0.5$ for temperatures well above T_c, to a completely distinct coverage dependence for temperatures slightly below T_c. The sharp minima at $\theta=0.5$, due to the presence of a $c(2\times2)$ ordered phase, is plainly reproduced by the nFWMC simulation.

C. Interacting lattice gases at extremely subcritical temperatures

One of the main advantages of the nFWMC is to allow for the calculation of dynamical quantities at very low subcritical temperatures. An illustrating example is shown in Fig. 5 where the coverage dependence of D^* in two dimensions has been calculated at $T/T_c=0.3$. Although D^* behaves similarly to the case shown in Fig. 4, it varies over almost ten orders of magnitude. It is worth mentioning that, as will be discussed below, SMC would have taken about e^{22} to e^{24} MC steps to reach the asymptotic diffusion regime at $\theta\approx0.5$ (see, for example, Fig. 6). No SMC simulation has been carried out at such a low temperature. The case displayed in Fig. 5 provides a clarifying example for the reliability of nFWMC at very low temperatures. It should be noticed that the linear regime of diffusion is very well attained for all coverages, as shown in Fig. 6.

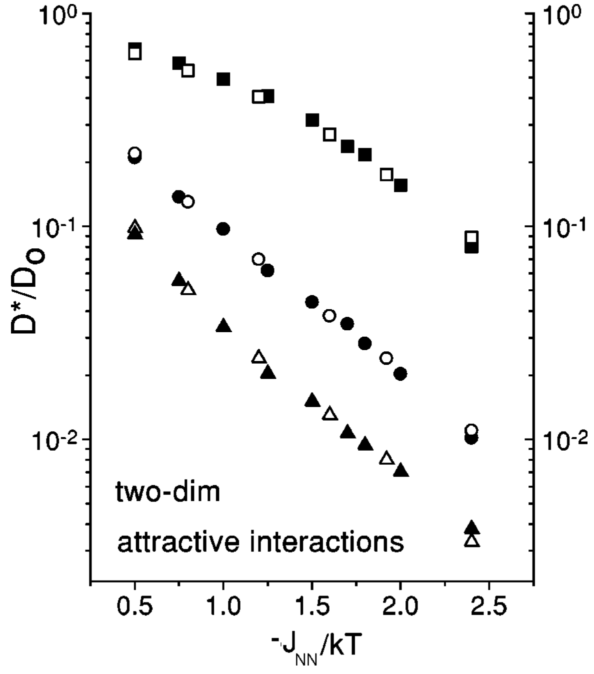

FIG. 3. Tracer diffusion coefficient D^* vs J_{NN}/kT for various surface coverages; squares, $\theta=0.1$; circles, $\theta=0.4$; triangles, $\theta=0.6$. [The dimensional ratio D^*/D_0^* is represented, where $D_0^*=\lim_{\theta\to0}D^*(\theta)$]. All the results correspond to a lattice gas on a square lattice. Full symbols were obtained by simulation using nFWMC; open symbols correspond to SMC from Ref. [10].

D. Method efficiency

Finally we present results concerning the relative efficiency of both methods. Figure 7 shows the temperature de-

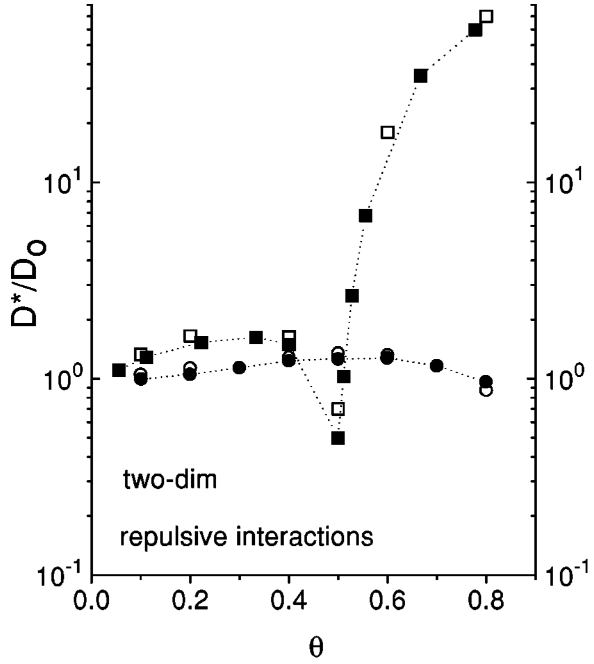

FIG. 4. D^*/D_0^* vs θ for supercritical temperature, $T=2.2T_c$ (squares) and subcritical temperature, $T=0.73T_c$ (circles). Full and open symbols have the same meaning as they do in Fig. 3.

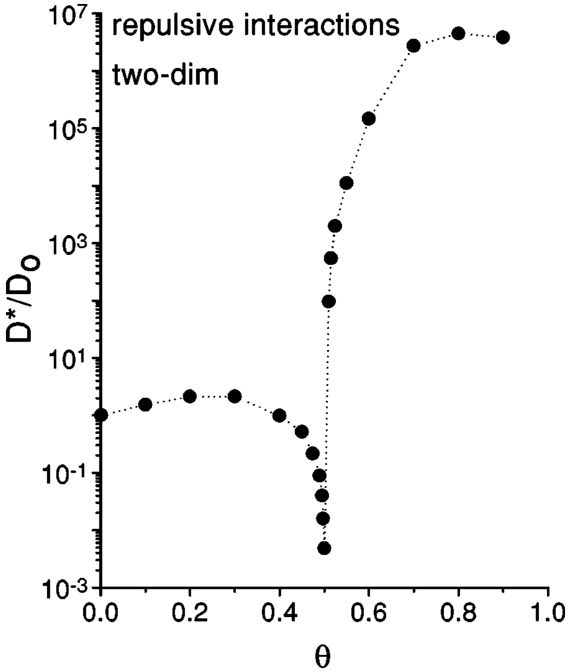

FIG. 5. Same as Fig. 4 for $T=0.3T_c$ Only the result from nFWMC simulation is shown (no SMC have been reported at this temperature).

pendence of the relative time taken by nFWMC and SMC simulation runs. We define the ratio $R_x(T)=t_x(T)/t_x(T_c)$ where $x\equiv$nFW holds for the nFWMC method and $x\equiv$S holds for the standard Metropolis method; $t_x(T)$ denotes the computer time (in seconds for instance) taken by a simulation run to perform a fixed number of successful jumps N_0 (as many as neccesary to reach the asymptotic regime) through the x-labeled method. R_x basically shows how the efficiency of the algorithm x varies with temperature. The data in Fig. 7 apply to the two-dimensional lattice gas discussed in subsections B and C. It is seen that nFWMC's

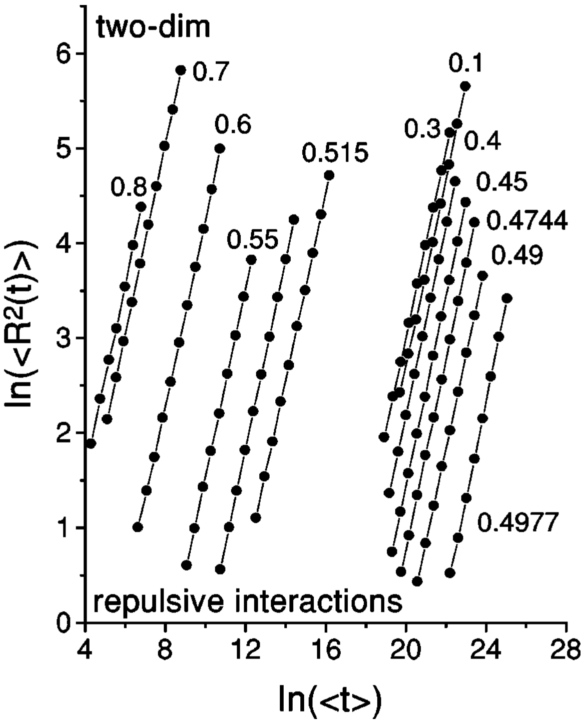

FIG. 6. Log-log plot of the mean square displacement vs time for tracer diffusion at finite coverage on a square lattice. The slope of all curves equals unity. D^* is obtained from the ordinate through the Einstein relation $\ln\langle R^2\rangle = \ln(D^*/2d)+\ln(t)$ with $d=2$. Time t is given in units of MC steps and mean square displacement $\langle R^2\rangle$, in units of the lattice constant.

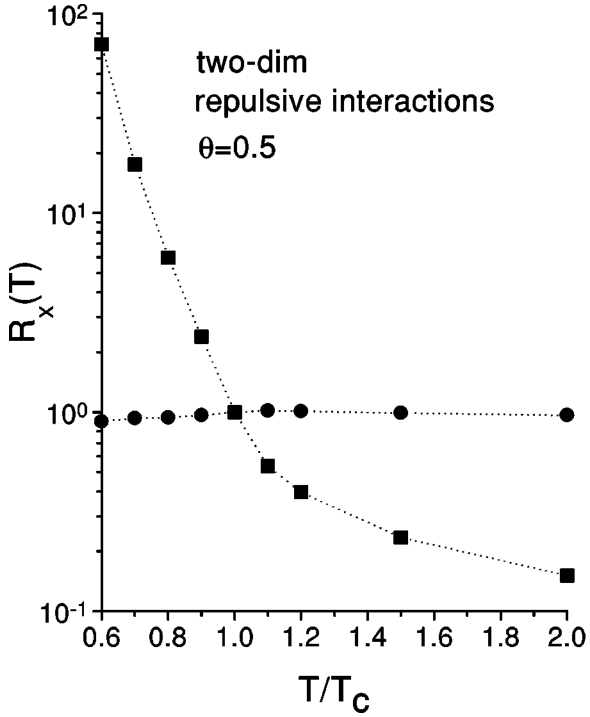

FIG. 7. R_x (as defined in Sec. V) vs the relative temperature T/T_c for a lattice gas on a square lattice with repulsive interactions. Circles represent the nFWMC method; squares do for SMC.

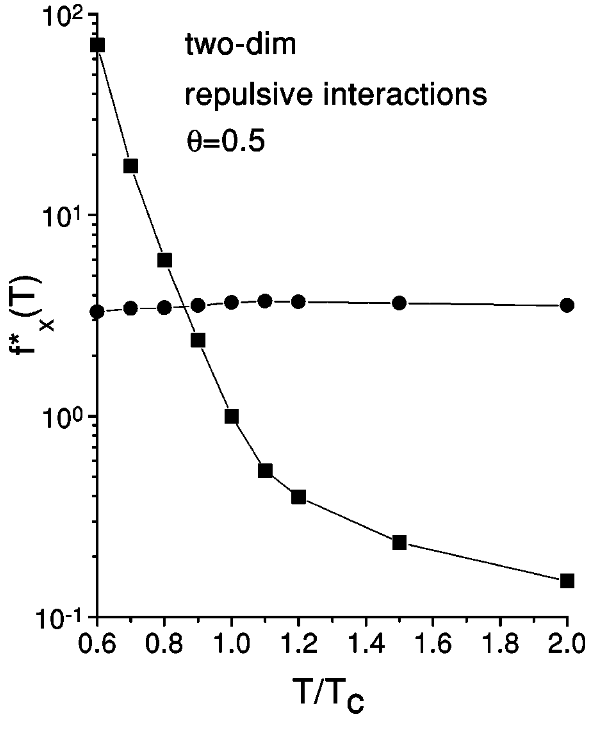

FIG. 8. Same as Fig. 7 for $f_x^*(T)$.

efficiency is approximately temperature independent. Conversely, SMC's efficiency decreases exponentially with temperature as expected.

Since both methods are implemented by means of substantially different codes (for instance, nFWMC requires one to update transition probabilities at every step) $R_x(T)$ is still highly code dependent and does not allow one to compare the efficiency of one scheme with respect to the other. It is worth comparing the computer time taken in either case under identical conditions. Accordingly, we define the mean computer time per successful jump, $f_x = t_x(N)/N$ where $t_x(N)$ is the time elapsed to perform N transitions by using the x-labeled method. Since $t_x(N)$ depends, in general, on the temperature at which diffusion is simulated, it follows that $f_x \equiv f_x(T)$. It is better to express f_x relative to a unit of time. Thus, $f_x^*(T) = t_x(N)/t_s(N)$ is a useful unitless measure of the relative efficiency of nFWMC with respect to SMC. This is shown in Fig. 8.

E. Conclusions

We conclude that the nFWMC presented here makes possible the simulation of kinetics of surface diffusion at very low temperatures in a very dependable manner. All simulations agreed remarkably well with exact analytical results and standard MC results reported before [10]. In addition surface diffusion has been simulated at much lower temperatures and higher coverages than those of previous studies.

It is worth mentioning that all calculations have been carried out in a personal computer (133 MHz Intel-based processor).

In general, this methodology allows one to simulate kinetics processes, involving many particles at subcritical temperatures, with the use of very modest computational resources. In such conditions standard MC algorithms become useless or require expensive computational supply.

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[23] The relationship shown in Eq. (11) comes from the general way of sampling a stochastic variable k from $G_k(\mathbf{N},t)$, namely, $G_k(\mathbf{N},t) = \xi_1$.

[24] Accordingly, $P(t'|N,t) = \xi_2$. Hence $t' = (-1/W)\ln \xi_2$.