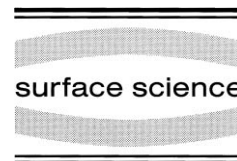




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Non-equilibrium effects in profile evolution measurements of surface diffusion

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Abstract

In this work, we use the Boltzmann–Matano method to determine the collective diffusion coefficient, $D_C(\theta)$, as a function of coverage, θ , from scaled coverage profiles obtained from Monte Carlo simulations using a lattice-gas model of O/W(110). We focus on the temporal behavior of $D_C(\theta)$ as the system approaches equilibrium. We demonstrate that the effective $D_C(\theta)$ obtained in this fashion depends strongly on the time regime chosen for analysis of the density profiles, and thus may differ significantly from results obtained from equilibrium simulations within ordered phases and close to phase boundaries. This is due to the interplay between spreading and phase-ordering kinetics and is reflected in enhanced particle number fluctuations with respect to the equilibrium case. Also, both the effective diffusion barriers of D_C and the location of phase boundaries, as extracted from the data, depend on time. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Computer simulations; Models of non-equilibrium phenomena; Surface diffusion

1. Introduction

The diffusive motion of adatoms and molecules on surfaces governs various important surface phenomena such as epitaxial growth, ordering, and spreading [1]. This has inspired a large number of activities in both theory [1–3] and experiments [1,4–6] to explore and resolve the diffusion properties of many surface systems. As far as experimen-

tal work is concerned, one of the long-standing problems regards a variety of experimental techniques, whose results even for the same surface systems may strongly depend on the technique used [5]. This is relatively easy to understand in extreme cases, when one compares methods that probe the diffusion process strictly in equilibrium with other techniques that operate under conditions far from equilibrium. Various experimental and theoretical studies [5–9] have shown that such non-equilibrium measurements yield results that are often distinctly different from the equilibrium ones.

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An interesting situation arises when there are only *slight* deviations from equilibrium, in the sense that one might expect the assumption of local equilibrium to be satisfied and the linear response theory leading to the diffusion equation to be valid. In such cases, the equilibrium theory is used to analyze the measurements. This is typically the case in profile evolution measurements of surface diffusion [4,10–17]. In situations where there are no ordered phases present, recent careful studies [16–19] have shown that a very good agreement with the equilibrium results can be obtained. However, in the case of strong interactions leading to ordered phases, the experiments clearly indicate [13,15] that the diffusion behavior can be affected by non-equilibrium effects.

In this work, we concentrate on the case of the well-established Boltzmann–Matano (BM) method [5,20], which is commonly used to extract the collective diffusion coefficient, $D_C(\theta)$, as a function of coverage, θ , from scaled coverage profiles. We study a lattice-gas model of O/W(110) [21,22] under conditions where there are several ordered phases present at different coverages. We use Monte Carlo simulations to generate the coverage profiles from which $D_C(\theta)$ is then extracted. We expect this approach to provide an insight into non-equilibrium effects on adatom dynamics in systems, where the lattice-gas approach is valid to a good approximation. We focus on the temporal behavior of $D_C(\theta)$ as the system approaches equilibrium starting from a step function density profile. We demonstrate that the effective $D_C(\theta)$ obtained in this fashion in fact depends strongly on the time regime chosen for analysis of the density profiles, and thus deviates significantly from results obtained from equilibrium simulations [22] within the corresponding ordered phases. This is due to the interplay between spreading and phase-ordering kinetics, whose effect is particularly pronounced in particle number fluctuations. Local properties such as the average transition rate of activated adatom jumps are only weakly affected by the non-equilibrium conditions, however. We furthermore find effective diffusion barriers to vary strongly as the system approaches equilibrium, and notice that the locations of phase boundaries

determined from the BM data are shifted from their equilibrium counterparts. To make contact with experimental work, we finally discuss our results in view of existing experimental measurements and the difficulties associated with interpreting non-equilibrium data.

2. Lattice-gas model and methods

The lattice-gas Hamiltonian employed in this work is a model of the O/W(110) adsorption system. The interaction parameters are chosen [21,22] such that the resulting phase diagram (that can be found in Ref. [22]) is in close agreement with the experimental observations [23–25]. In the present study, we concentrate on the coverage and the temperature dependence of D_C at a temperature region around $T=590$ K, which is characterized by a disordered phase (DO) at low coverages, from which one crosses continuously over to an ordered $p(2 \times 1)$ phase at $\theta \approx 0.35$. At higher coverages, there is another transition of the second order to an ordered $p(2 \times 2)$ phase at $\theta \approx 0.59$, which in turn crosses continuously over to a disordered phase at $\theta \approx 0.78$. The model has been extensively studied, and a complete set of equilibrium data for $D_C(\theta)$ at various temperatures is available for purposes of comparison in Refs. [21,22].

A key point in studies of dynamic processes with the Monte Carlo method is the choice of transition probabilities, $w_{i,f}$, from an initial state, i , with energy, E_i , to a final state, f , with energy, E_f [26]. As explained in Ref. [21], in addition to the usual detailed balance condition, $w_{i,f}$ should facilitate a realistic description of thermally activated jumps via a transition state. Here, we use the so-called transition dynamics algorithm (TDA), in which a single-particle jump proceeds by two successive steps via an intermediate state, I , with energy $E_I = \Delta + (E_i + E_f)/2$ such that $w_{i,f} = w_{i,I} w_{I,f}$. The rates have a Metropolis form, $w_{i,j} = \min\{1, \exp[-(E_j - E_i)/k_B T]\}$, and the quantity $\Delta > 0$ characterizes the effect of the (bare) saddle point of the adiabatic substrate potential. The use of TDA is supported by recent molecular dynamics studies [26,27], where it was found that TDA is

qualitatively consistent with the dynamics seen in a true microscopic model of a system consisting of interacting particles. Further details and additional references can be found in Ref. [21].

In the simulations, we consider the spreading of a coverage profile $\theta(x, t)$ in a semi-infinite system, which ranges from $-\infty$ to $+\infty$ in the x direction, and whose width, L_y , is typically 1000 lattice units in the y direction. For the latter, periodic boundary conditions are employed. The coverage profile is initially an ideal step function at $x=0$ [$\theta(x, 0)=1$ for $x<0$ and $\theta(x, 0)=0$ for $x>0$], which evolves in time, t , as the particles diffuse in the positive x direction. Here, x is the coordinate with respect to the dividing line $x=0$, which accounts for particle number conservation via

$$\int_0^1 x(\theta') d\theta' = 0.$$

To determine the collective diffusion coefficient, $D_c(\theta)$, we use the Boltzmann–Matano method [5,20], which is based on the assumption that, in the long-time limit, the coverage profiles $\theta(x, t)$ collapse to a single scaling function when expressed as $\theta(x/\sqrt{t})$. Under these circumstances, one can use a transformation $\eta=x/\sqrt{t}$ to write the non-linear diffusion equation as an ordinary differential equation [28], whose solution reads as:

$$D_c(\theta) = -\frac{1}{2t} \left(\frac{dx}{d\theta'} \right) \Big|_{\theta} \int_0^{\theta} x(\theta') d\theta'. \quad (1)$$

The Boltzmann–Matano analysis thus enables one to calculate the coverage dependence of the collective diffusion coefficient $D_c(\theta)$ over the whole coverage range even from a single coverage profile. This is a great advantage in experimental work. However, since Eq. (1) can be applied to *any* profile to obtain $D_c(\theta)$, great care must be taken to ensure that non-equilibrium effects do not affect the data.

3. Results and discussion

In Fig. 1, we show the scaled coverage profiles $\theta(x/\sqrt{t})$ at three different time regimes during the

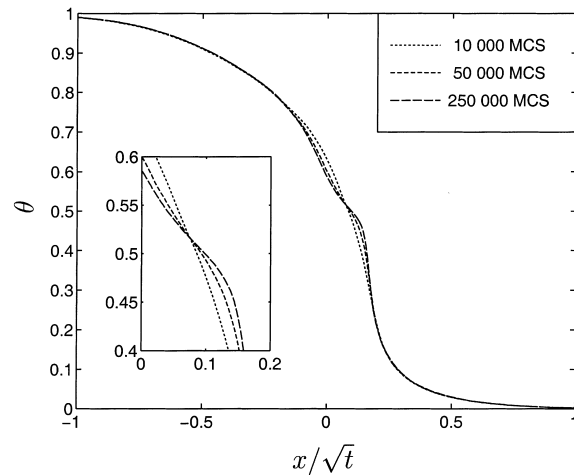


Fig. 1. Scaled coverage profiles $\theta(x/\sqrt{t})$ at three different times during the profile evolution process. The time is defined in terms of one Monte Carlo step (MCS), during which every particle attempts to jump once on the average. In the data, several profiles from the time regimes 10 000–12 000 MCS, 50 000–60 000 MCS, and 250 000–300 000 MCS have been collapsed to obtain the scaled curves. The inset shows details of the profiles within the developing $p(2 \times 1)$ phase.

profile evolution process (10 000–12 000 MCS, 50 000–60 000 MCS, and 250 000–300 000 MCS). Demonstrative snapshots of the profiles are furthermore shown in Fig. 2. The coverage profiles in Fig. 1 clearly evolve in time and tend towards some universal curve at late times. The late-time behavior is particularly interesting since experimentally obtained coverage profiles of similar kind have been used to analyze $D_c(\theta)$ by the BM technique¹. However, as becomes shortly evident in the following discussion, even the longest time scales shown in Fig. 1 do *not* correspond to true equilibrium behavior.

To quantify the deviation from equilibrium during the profile evolution process, we have considered the time evolution of ordering within the

¹ Recent experimental data [13,15] for $\theta(x/\sqrt{t})$ indicate that the asymptotic region, where scale invariance really holds true, is very difficult to achieve. These studies undoubtedly consider the long-time behavior, but based on the slight deviations from scale invariance (see results in Refs. [13,15]), it is not obvious that the profiles analyzed in these works yield a true equilibrium behavior of $D_c(\theta)$.

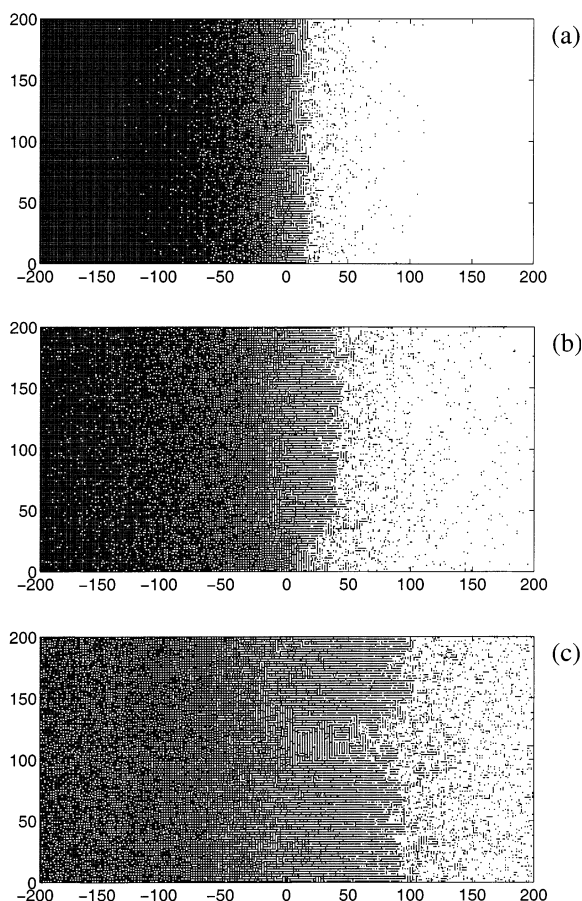


Fig. 2. Snapshots of profile evolution simulations at times (a) 10 000 MCS, (b) 50 000 MCS and (c) 250 000 MCS. Note that only part of the system is shown here. Also note the appearance of the $p(2 \times 2)$ phase right below and the $p(2 \times 1)$ phase right above $x=0$, where the coordinates are given in lattice units. The profiles spread in the $[1\bar{1}1]$ (or $[\bar{1}11]$) direction on the surface.

$p(2 \times 1)$ phase in terms of the quantities

$$\begin{cases} \phi_{2 \times 1}(t) \equiv \frac{2}{L^2} \sum_{i,j=1}^L n_{i,j}(t) (-1)^i \\ \phi_{1 \times 2}(t) \equiv \frac{2}{L^2} \sum_{i,j=1}^L n_{i,j}(t) (-1)^j, \end{cases} \quad (2)$$

which define the order parameters of the degenerate $p(2 \times 1)$ and $p(1 \times 2)$ phases in a square system of size $L \times L$, where $n_{i,j}(t) = 0, 1$ is the occupation variable of the lattice site at (i, j) at time t . Since

the two phases are energetically equivalent in the present system, we define the order parameter $\phi(t) \equiv \sqrt{\phi_{2 \times 1}^2(t) + \phi_{1 \times 2}^2(t)}$ to quantify the approach towards equilibrium².

In the present system, we find that although $\phi(t)$ approaches the equilibrium behavior at long times, it has not converged to this limit within the time scales ($t \lesssim 250\,000$ MCS) shown above (data to be shown elsewhere [29]). This implies that none of the coverage profiles in Fig. 1 is in the linear response regime of local equilibrium. This finding is readily supported by the temporal dependence of $D_C(\theta)$ shown in Fig. 3a, which is in qualitative agreement with recent BM experiments [13]. These results highlight the important role of non-equilibrium effects played in the BM experiments. This is particularly true *within ordered phases* and *close to phase boundaries*, where deviations from equilibrium behavior are most pronounced.

We now discuss the origin of the deviations from equilibrium behavior in $D_C(\theta)$ (see Fig. 3a). In the present work, where we are dealing with a lattice-gas description of surface diffusion, we can study this problem by decomposing D_C as [3,30]

$$D_C(T, \theta) = \frac{a^2}{4} \xi(T, \theta) \Gamma(T, \theta) f_C(T, \theta). \quad (3)$$

The first term on the RHS is just a geometric constant, ξ is the thermodynamic factor, which is inversely proportional to the compressibility of the adlayer, Γ describes the average transition rate of single-particle jumps, and f_C is the correlation factor³, which accounts for dynamical correlations

² In the profile-spreading simulations, the time-dependent order parameter, $\phi(t)$, and the effective jump rate, Γ^{BM} , have been averaged over successive strips of size $2 \times L_y$ to determine their coverage dependence.

³ In equilibrium, one considers the density–density autocorrelation function $S(|r-r', t|) = \langle \delta n(r, t) \delta n(r', 0) \rangle$, in which $\delta n(r, t) = n(r, t) - \langle n(r, t) \rangle$ with an occupation variable $n(r, t) = 0, 1$ at a lattice site, r , at time, t . Then, D_C can be obtained from the pole of the corresponding Laplace–Fourier transform $S(k, z)$ [30], yielding Eq. (3). The correlation factor, f_C , comes from the memory function of $S(k, z)$ and characterizes the extent of correlations between successive displacements in the center of mass of the system. In the absence of dynamical correlations (the memory function) f_C is 1, while correlations lead to $f_C \neq 1$.

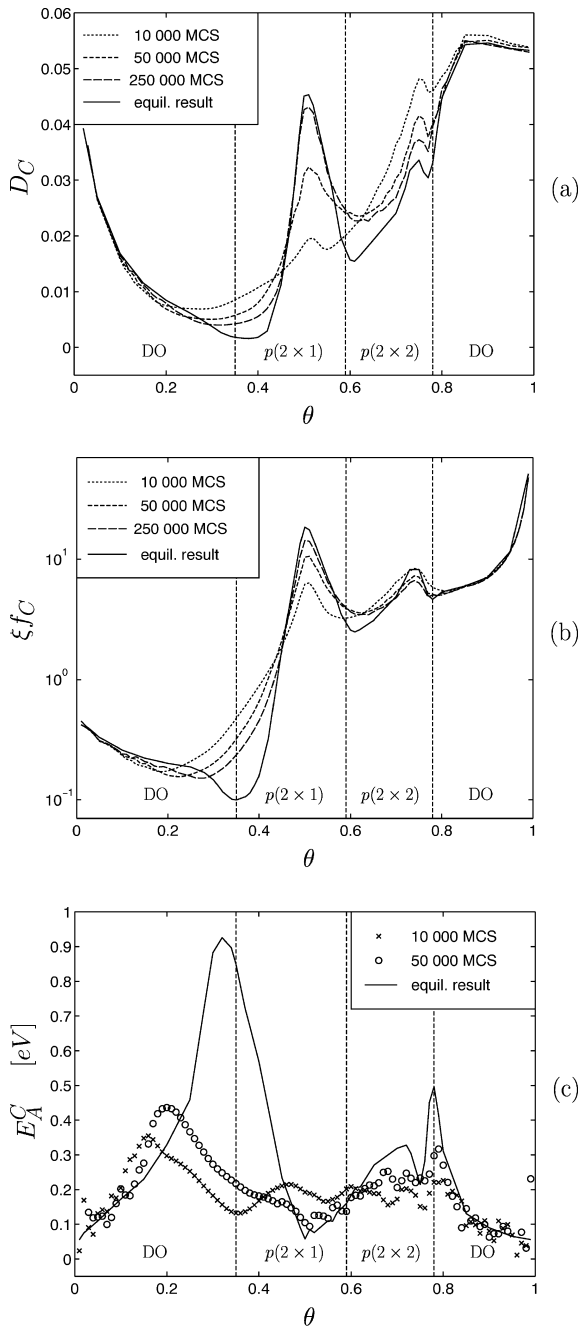


Fig. 3. (a) Coverage dependence of the collective diffusion coefficient $D_C(\theta)$ at three different time scales during the profile evolution process. The results corresponding to a true equilibrium study [22] are also shown for comparison purposes. (b) Quantity ξf_C as obtained using Eqs. (3) and (4). (c) Effective activation barriers, $E_A^C(\theta)$, as they arise from an Arrhenius analysis of $D_C(T, \theta)$. In this case, the error bars for BM simulations are somewhat larger than the size of the symbols. The dashed lines indicate phase boundaries in equilibrium.

in the center-of-mass motion of the system [30]. We stress that Eq. (3) is formally an exact description of D_C within the lattice-gas approach in equilibrium. Here, we will apply Eq. (3) under non-equilibrium conditions also. In this case, we formally write

$$D_C^{\text{BM}}(T, \theta) = \frac{a^2}{4} \xi^{\text{BM}}(T, \theta) \Gamma^{\text{BM}}(T, \theta) f_C^{\text{BM}}(T, \theta), \quad (4)$$

where the superscript BM indicates that the corresponding quantities have been computed during profile spreading, and thus may not correspond to their equilibrium counterparts. We emphasize that Eq. (4) should be regarded as an operational definition only that reduces to the correct limit when the quantities are evaluated in equilibrium.

We first focus on the average transition rate Γ^{BM} , which can readily be calculated from the simulations. As is evident from Fig. 4a, $\Gamma^{\text{BM}}(T, \theta)$ only weakly depends on the non-equilibrium conditions and approaches its equilibrium limit, $\Gamma^{\text{eq}}(T, \theta)$, at long times. The largest deviations occur close to the ideal coverages of the $p(2 \times 1)$ and $p(2 \times 2)$ phases. A similar behavior is observed in the effective barrier, E_A^C , of Γ shown in Fig. 4b (as extracted from the usual Arrhenius description). Within and close to the $p(2 \times 1)$ phase, there seems to be an ‘over-shooting’ effect [31,32] in Γ and in the corresponding effective Arrhenius barrier, which suggests that during the ordering process at intermediate times, the local order within small ordered domains is larger than the average order in a corresponding system in equilibrium. This is due to the competition between kinetics of ordering and approach to equilibrium in the system.

To obtain the combination $\xi^{\text{BM}}(T, \theta) f_C^{\text{BM}}(T, \theta)$, we simply use $D_C^{\text{BM}}(T, \theta)$, as obtained from the BM analysis of the density profiles, and divide it by the factor $(a^2/4) \Gamma^{\text{BM}}(T, \theta)$ using Eq. (4). These results are shown in Fig. 3b. As far as the correlation factor, f_C , is concerned, previous studies [21,22] have shown that dynamical correlations are not very important in collective diffusion under equilibrium conditions. This is evidently true in non-equilibrium, too, and we thus simply

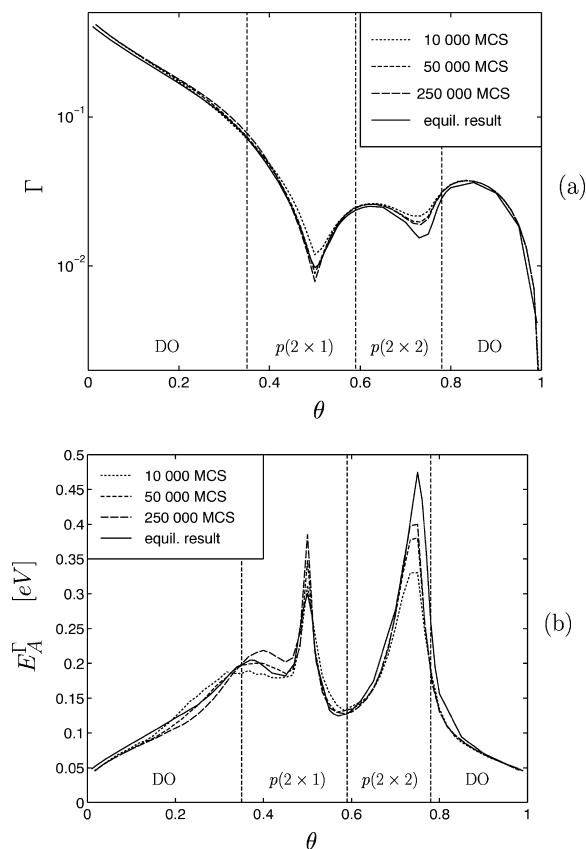


Fig. 4. (a) Average transition rate, $\Gamma^{\text{BM}}(\theta)$, of single-particle jumps at various time scales, as in Fig. 2, including equilibrium results, $\Gamma^{\text{eq}}(\theta)$ from Ref. [22]. (b) Effective activation barriers, $E_A^{\text{eff}}(\theta)$, as they arise from an Arrhenius analysis of $\Gamma(T, \theta)$. The dashed lines indicate phase boundaries in equilibrium.

assume⁴ that $f_C^{\text{BM}} \approx f_C$. Our results therefore suggest that the non-equilibrium nature of diffusion in the BM experiments is most strongly manifested in the particle number fluctuations.

We next discuss two aspects that are of experimental interest in BM studies, namely the effective barrier for collective diffusion, E_A^{C} , and the loca-

⁴ We have carried out additional non-equilibrium studies by quenching the system from a totally disordered state to a low-temperature $p(2 \times 1)$ ordered phase, and followed the time evolution of dynamical correlations during the equilibration process in terms of directional correlations between two jumps by the particle [22]. We have found [29] the dynamical correlation effects to be strongest in equilibrium, while under non-equilibrium conditions, their effect is less pronounced.

tions of phase boundaries determined from the BM data. The barrier, E_A^{C} , has been a subject of many experimental studies [5,10,11,14,15], where it has been observed that the barriers found in BM studies are not fully consistent with barriers extracted from measurements with other techniques [5]. This could be due to defects, whose role in macroscopic BM experiments is more important than in microscopic techniques such as scanning tunneling microscopy. However, as the results in Fig. 3c demonstrate, the temporal evolution of the profile prior to the linear response regime provides another possible explanation for this difference. Namely, we find that the barriers E_A^{C} determined from BM studies can be significantly different from the corresponding equilibrium results. This is, again, mainly due to particle number fluctuations, since the barriers, E_A^{eff} , in Fig. 4b cannot explain the differences in Fig. 3c, and the temperature dependence of f_C accounts typically for only about 10% of the total barrier [22,33]. Another aspect of experimental interest regards the locations of phase boundaries, which are usually determined from the minima⁵ of ξ . Using this approach, the results in Fig. 3a and b reveal that if one analyzes BM data too early, the estimated locations of phase boundaries can deviate significantly from the actual equilibrium values. This conclusion is supported by our further studies of $|\partial\phi(t, T, \theta)/\partial\theta|T$, whose maxima characterize phase transition boundaries [29].

4. Summary and discussion

In summary, we have presented results for the collective diffusion coefficient, $D_C(\theta)$, in Boltzmann–Matano studies for a model adsorption system as the system approaches equilibrium. In agreement with recent BM experiments [13],

⁵ The actual locations of phase boundaries should be interpreted from response functions such as the compressibility of the adlayer, κ_T , which is expected to have a maximum at a (second-order) phase transition boundary. Due to practical difficulties in measuring this quantity directly, however, one usually considers the thermodynamic factor $\xi = 1/(k_B T \theta \kappa_T)$ directly (such as in Gomer’s fluctuation method [5]) or assumes that D_C is dominated by ξ .

we have found that $D_C(\theta)$ obtained in this fashion depends strongly on the time regime analyzed, and may differ significantly from results obtained from equilibrium simulations within ordered phases and close to phase boundaries. Based on our results, this observation can be traced back to particle number fluctuations, which are significantly enhanced due to the prominent role of non-equilibrium mass transport in BM experiments. Consequently, various quantities of experimental interest such as the effective diffusion barrier of D_C also depend strongly on the time regime studied. We note, however, that all quantities studied in this work eventually approach their equilibrium limits at very long times, as expected. The BM method therefore works well and yields the equilibrium behavior of $D_C(\theta)$ if one is only able to achieve the actual linear response regime of local equilibrium, where the coverage profiles obey a true scale invariance. To ensure this, particular care must be taken when profile spreading experiments are being carried out.

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