## Adatom dynamics and diffusion in a model of O/W(110)

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We consider adatom dynamics and diffusion in a lattice-gas model of the O/W(110) system under conditions where the adatom interaction effects are important. In particular, we study the behavior of the tracer and collective diffusion coefficients as a function of temperature when crossing over from the high-temperature disordered phase to a low-temperature symmetry broken phase. To this end, we utilize a combined analytical and numerical approach based on the recently developed dynamical mean field theory (DMF) in addition to conventional Monte Carlo simulations. In the case studied here, the origin of the strong temperature dependence of the effective activation barrier  $E_A^D$  close to an order-disorder transition, i.e., the non-Arrhenius behavior of the diffusion coefficients, can be traced back to that of the average microscopic jump rate  $\Gamma$ appearing within the DMF. This is in contrast to the usual assumption that thermodynamics controls diffusion near phase transitions. The behavior of  $\Gamma$ , in turn, is found to arise predominantly from critical effects in the short-time behavior of the waiting-time distribution of single-particle jumps, W(t), which is an experimentally accessible quantity. The long-time decay of W(t) is then used to define another effective barrier  $E_A^W$ , which shows no anomalous effects near the transition. [S0163-1829(98)07703-0]

# I. INTRODUCTION

The migration of atoms and molecules is one of the most important processes taking place on solid surfaces. It appears in many phenomena such as catalytic reactions and surface growth that are important for practical applications.<sup>1,2</sup> With the advent of the modern high vacuum technology together with the field ion microscope<sup>3</sup> (FIM) and especially the scanning tunneling microscope (STM),<sup>4</sup> a microscopic look at these phenomena has become feasible. At the same time, theoretical understanding of the microscopics of surface dynamics has increased significantly via both realistic totalenergy calculations<sup>5</sup> and statistical mechanical studies.<sup>6-29</sup>

However, there are still several important problems related to surface diffusion that are not very well understood. One of the most challenging problems is the description of surface diffusion at finite coverages in the presence of strong interparticle interactions, which corresponds to a situation in many applications. At finite coverages, there are two different diffusion coefficients. The tracer diffusion coefficient  $D_T$ is related to the motion of a tagged particle as observed in STM and FIM measurements, while the collective diffusion coefficient  $D_C$  describes the macroscopic density fluctuations as measured in field emission and optical grating experiments.<sup>30</sup> Most of the existing theoretical descriptions<sup>6-19</sup> for  $D_T$  and  $D_C$  have been developed for cases where the interparticle interactions do not play an important role. Approximations for strongly interacting systems have been developed in some special cases,<sup>20-27</sup> and especially for  $D_C$  some phenomenological descriptions<sup>21,27,28</sup> have been suggested. One appealing suggestion was given by Reed and Ehrlich<sup>21</sup> already in 1981. They related  $D_C$  to the microscopic adparticle motion, and proposed that  $D_C$  can be expressed as a product of a thermodynamical factor and an effective jump rate of adparticles. Since studies of microscopic jump dynamics have become available from STM experiments,<sup>31</sup> this constitutes an important link between microscopic and macroscopic mass transport, which is not completely understood. The Reed-Erlich description has recently been given a firm theoretical basis,<sup>24,25,32</sup> which shows that it essentially corresponds to neglecting the memory effects in diffusion.<sup>33</sup> The validity of this approximation for strongly interacting systems has been studied only in a few cases, however.3

The observed temperature dependence of the surface diffusion coefficient *D* is usually fitted to an activated Arrhenius form, where *D* is written as a product of an entropic prefactor  $D_0$  and a term  $\exp(-E_A^D/k_BT)$  describing thermally

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activated jumps over an energy barrier  $E_A^D$ . In the limit of single-particle diffusion on an ideal surface, the Arrhenius form can be shown to arise from a microscopic theory in the appropriate limits.<sup>17,19</sup> At low temperatures and in the highfriction Markovian limit in particular, the activation barrier  $E_A^D$  is precisely the difference in the adiabatic potential between the lowest saddle point that the particle has to cross to move from one unit cell to another and its value at a minimum.<sup>17,34</sup> This simple picture may be invalidated by many factors such as the adatom phonon coupling<sup>35,36</sup> and phonon anomalies.<sup>37</sup> In many-particle diffusion in the presence of strong adsorbate interactions the situation is even more complicated due to the fact that the actual local configuration around an adatom fluctuates, thus leading to fluctuating activation barriers for the microscopic jump processes. In this case, there is no theoretical reason a priori why the Arrhenius form should still hold. Even if an approximate Arrhenius form seems reasonable, the effective barrier must involve a complicated average over the distribution of microscopic barriers and offers no simple microscopic interpretation.

The aim of the present work is to consider surface diffusion in a system with adatom-adatom interactions under conditions where the interaction effects are particularly pronounced and broken symmetry phases appear. To this end, we carry out Monte Carlo (MC) simulations<sup>38</sup> for a latticegas model of the O/W(110) system which is described in detail in Sec. II. We concentrate on the behavior of the diffusion coefficients  $D_C$  and  $D_T$  when crossing over from a high-temperature disordered phase down to a lowtemperature  $p(2 \times 1)$  phase in the model. The diffusion coefficients are computed accurately from their corresponding definitions, and the results are compared with the approximate method of Ref. 32. It consists of a combination of an analytic approach and MC simulations, the only approximation being that the memory effects are replaced by the known results for the Langmuir gas model,<sup>28</sup> where the only interaction between the adatoms is the exclusion of the double occupancy of lattice sites. For  $D_C$ , this yields exactly the form proposed by Reed and Ehrlich.<sup>21</sup> In Sec. IV, we find that there is a very good quantitative agreement between the full MC results and the approximate theory for  $D_C$ . For  $D_T$ , however, we find the influence of interactions on the memory effects to be more pronounced. These observations together imply that the often employed Darken's equation,<sup>28</sup> in which one equates  $D_C$  to the product of a thermodynamic factor and  $D_T$ , is not a good approximation for strongly interacting systems. As for the temperature dependence of the diffusion coefficients, we find that an Arrhenius form with a single activation barrier cannot describe the behavior across the order-disorder phase boundary at  $T_c$ ,<sup>39</sup> as expected. Near  $T_c$ , the diffusion coefficients have a rapid temperature variation that arises from the onset of the ordering process as the temperature is decreased below the transition temperature. However, we demonstrate that unlike what is usually assumed, the behavior for this system is not due to thermodynamic effects but arises predominantly from the average microscopic jump rate  $\Gamma$ . The underlying physics is clarified via the study of waiting-time distributions, which offer better insight into how the fluctuating configurations determine the jump rate.<sup>39</sup> The waiting-time distribution is a

quantity that can be directly probed in STM experiments.<sup>31</sup> Finally, we discuss the effect of ordering on transition rates and activation barriers, and comprise a brief summary in Sec. V.

#### II. MODEL FOR THE O/W(110) SYSTEM

#### A. The lattice-gas model

The O/W(110) system is undoubtedly one of the most studied adsorption systems. Its phase diagram has been determined through experimental studies<sup>40–43</sup> using low-energy electron diffraction (LEED) spot profile analysis and STM. Its main features can be summarized as follows. At temperatures  $T \ge 710$  K,<sup>42</sup> the system is in a disordered phase, while at lower temperatures there is a wide variety of ordered phases at different coverages, namely, the  $p(2 \times 1)$ ,  $p(2 \times 2)$ , and  $(1 \times 1)$  phases corresponding to ideal coverages of 1/2, 3/4, and 1, respectively. At intermediate coverages, some coexistence regions also exist.43 The substrate remains unreconstructed at all coverages,<sup>44-46</sup> the oxygen atoms have well-defined adsorption sites on the surface, 43,47,48 and desorption of oxygen occurs only at temperatures as high as 1600 K or above. 45,46 Therefore, this system is suitable for simulation studies using a lattice-gas description over a wide temperature range, the first attempt to our knowledge being that by Ching *et al.*<sup>41</sup>

We shall use the lattice-gas model constructed by Sahu *et al.*<sup>49</sup> to describe the main features of the phase diagram. The Hamiltonian includes pair interactions up to fifth nearest neighbors and certain three-body interactions:<sup>49</sup>

$$\mathcal{H} = \sum_{m=1}^{5} \sum_{\langle ij \rangle} J_m n_i n_j + \sum_{m=1}^{2} \sum_{\langle ijk \rangle} J_{tm} n_i n_j n_k - \mu \sum_i n_i.$$
(1)

Here  $n_i = 0,1$  is the occupation variable of the lattice site *i*,  $\langle ij \rangle$  and  $\langle ijk \rangle$  denote every pair and three-body interaction to occur only once in the sum, and the strengths of these interactions are denoted by  $J_m$  and  $J_{tm}$  (m = 1, 2, ...). Following Ref. 49 we take  $J_2 = J_3 = -0.390J_1$ ,  $J_5 = 0.680J_1$ , and  $J_{t1} = J_{t2} = -0.720J_1$ . In this work we shall focus on the coverage  $\theta = 0.45$ , and set the temperature and energy scales by choosing  $J_1 = -58.3$  meV, which reproduces the experimental value  $T_c \approx 710$  K of a continuous order-disorder phase transition boundary at this coverage.<sup>42,50</sup> All the other J's are set to zero. An illustration of the relevant coupling coefficients is presented in Fig. 1. The principal axes x and yare along the  $[1\overline{10}]$  and [001] directions of the underlying bcc lattice, respectively, and the unit vectors  $\hat{x}$  and  $\hat{y}$  show the directions of nearest-neighbor jumps between lattice sites. All our results for the diffusion coefficients will be presented in units where the lattice coefficient is set to unity.

In canonical simulations with a constant value of  $N = \sum_i n_i$ , the term proportional to  $\mu$  is irrelevant and one may set  $\mu = 0$  in Eq. (1). In the grand canonical case N fluctuates and this term must be included in  $\mathcal{H}$ . For such a purpose, we introduce the field<sup>49</sup>

$$h = \frac{1}{2} \left[ \mu - 2J_1 - J_2 - J_3 - 2J_5 - \frac{3}{2} (J_{t1} + J_{t2}) \right].$$
(2)



FIG. 1. An illustration of the relevant pair and three-body interactions in the O/W(110) system. Substrate atoms and possible adsorption sites are denoted by crosses and open circles, respectively. The principal directions x and y are along the  $[1\overline{10}]$  and [001]directions, respectively. The two independent directions of nearestneighbor jumps are denoted by  $\hat{x}$  and  $\hat{y}$ .

The resulting phase diagrams in the T- $\theta$  and T-h planes are presented in Fig. 2. The asymmetry about  $\theta = 1/2$  is due to the three-body interactions in the Hamiltonian. We further define the particle number density  $\rho = N/N_{\text{max}}$  (where  $N_{\text{max}}$  is the total number of adsorption sites) whose ensemble average  $\langle \rho \rangle$  equals the coverage  $\theta$ .

Having introduced the lattice-gas Hamiltonian, we now want to comment on two underlying simplifications in it.



FIG. 2. Schematic phase diagrams of the O/W(110) system in the (a)  $T-\theta$  and (b) T-h planes (Ref. 49). The energy parameters of the model have been scaled so that the critical temperature of the order-disorder phase transition at  $\theta=0.45$  is  $T_c=710$  K (Ref. 42), and the unit of h in (b) is  $|J_1|/2$ . DO denotes the disordered region, while (2×1) and (2×2) denote the ordered phases. The CX<sub>i</sub>, i =1,2,3, are the coexistence phases. In (b), solid and dashed lines denote continuous and first-order phase transition boundaries, respectively.

First, in our model the oxygen atoms occupy the hollow sites of the underlying surface (see Fig. 1). Recent STM measurements<sup>43</sup> together with some LEED results<sup>47</sup> have revealed that the true adsorption site is the triply coordinated site instead. However, this alone does not induce serious problems, since the lattice-gas picture is still valid and the sequence of the ordered phases does not change. The degeneracy of the ground state of the  $p(2 \times 1)$  increases from the value of four as produced by our Hamiltonian to eight, which modifies the local energetics at domain walls without affecting the qualitative role of interaction effects in diffusion. The second simplification is the absence of interaction between the substrate and the adsorbate in the Hamiltonian. However, since no strong relaxation effects such as reconstruction are taking place in this system, we expect this interaction to be reasonably well approximated by a suitable choice of dynamics in our MC simulations, which we shall discuss next.

#### B. Microscopic dynamics of the model

The lattice-gas Hamiltonian alone as given above does not constitute a complete model for surface diffusion, because it does not specify any microscopic dynamics for how the system evolves in time. In the context of lattice-gas models, stochastic methods such as Monte Carlo (MC) simulations<sup>51</sup> are widely used for modeling of their static and dynamic properties.<sup>52–54</sup> However, they do not describe time in the usual sense but rather the order of events taking place in the system studied.55 This may be particularly problematic when dynamic processes involving several time scales, such as diffusion of complex molecules, are studied. A related ambiguity is associated with the choice of the transition probabilities.<sup>52,53</sup> Namely, the detailed balance condition  $w_{i,f}p_i = w_{f,i}p_f$ , where  $w_{i,f}$  is the transition rate from an initial state *i* to a final state *f*, and  $p_i$  and  $p_f$  are the equilibrium probabilities corresponding to the Hamiltonian, does not specify the transition rates uniquely.<sup>52-54</sup> Nevertheless, recent experience<sup>53,54</sup> with the MC method suggests that it describes many static and time-dependent properties of simple adsorption systems rather well, and thus its use in the present context is justified. However, if true quantitative information is needed, methods based on true microscopic dynamics should be used.

In the context of diffusion, the fundamental problem with the traditional choices of  $w_{i,f}$  such as the standard Metropolis form,<sup>51</sup> the Kawasaki form,<sup>56</sup> and the initial value dynamics<sup>57</sup> is that they do not take into account the effect of the saddle point of the adiabatic surface potential. One possibility to facilitate a more realistic description in this sense is to introduce an intermediate state *I* and write the transition probability of each jump as a product of two probabilities as

$$w_{i,f} = w_{i,I} w_{I,f} \,. \tag{3}$$

Within this *transition dynamics algorithm*<sup>17</sup> (TDA), the transition from the initial state with energy  $E_i$  to the final state with energy  $E_f$  actually proceeds by two successive steps via the intermediate state with energy  $E_I$ . Here  $E_I$  has to be chosen to describe a jump attempt of a particle in the presence of interactions as realistically as possible without violating the detailed balance condition. We have used the form<sup>17</sup>

$$E_I = \frac{(E_i + E_f)}{2} + \Delta, \tag{4}$$

where the quantity  $\Delta$  characterizes the activation barrier in the zero coverage limit due to the substrate-adatom interaction. For the rates  $w_{i,I}$  and  $w_{I,f}$  any suitable form satisfying the condition of detailed balance is applicable, although we have taken them both to be of the Metropolis form  $w_{j,j'}$  $= w_0 \min[1, \exp(-\delta E_{j,j'}/k_B T)]$ , where  $w_0$  is the attempt frequency that is usually set to unity and  $\delta E_{j,j'} = E_{j'} - E_j$  are the appropriate energy differences. The *instantaneous activation barrier*  $E_a$  for a jump attempt from a filled to a vacant site is then

$$E_{a} = \max(E_{I} - E_{i}, E_{f} - E_{i}, 0).$$
(5)

This illustrates the main advantage of the TDA method. Namely, for  $\Delta > 0$  the rates can be of activated form also for jumps with  $E_i \ge E_f$ . Satisfying the detailed balance,<sup>17</sup> the TDA method therefore complements the description of the Hamiltonian given by Eq. (1). Other schemes accounting for the barrier effects in the MC studies have also been used.<sup>29,55</sup>

For the present study, we chose  $\Delta = 0.0437$  eV. This value is believed to be much lower than the true value, which should be closer to the experimentally observed barrier<sup>40,58</sup> of 0.5 to 0.6 eV in the disordered phase and in the limit of zero coverage. Our choice is necessitated by the need to speed up the jump rate in the numerical simulations at low temperatures, but we will show below how the effect of changing  $\Delta$  can be estimated (see Sec. IV B below).

#### **III. THEORETICAL METHODS**

## A. Definitions of collective and tracer diffusion

The *collective* diffusion tensor  $D_C$  can be conveniently defined via the density-fluctuation autocorrelation function<sup>28</sup>

$$S(\vec{r},\vec{r'},t) = \langle \delta\rho(\vec{r},t) \,\delta\rho(\vec{r'},0) \rangle, \tag{6}$$

where  $\vec{r}$  and  $\vec{r'}$  denote position vectors on a lattice, the density fluctuations are given by  $\delta \rho(\vec{r},t) = \rho(\vec{r},t) - \theta$ , and the angular brackets denote an ensemble average. In the hydrodynamic regime, the corresponding Fourier transform decays as  $S(\vec{k},t) = S(\vec{k},0)\exp(-\vec{k}\cdot\mathbf{D}_C\cdot\vec{k}t)$ , allowing us to extract the elements of the collective diffusion tensor  $\mathbf{D}_C$  for small *k*. We shall refer to the use of this definition as the "densityfluctuation method."

An equivalent and a very useful way of describing collective diffusion is to write the diagonal elements of  $D_C$  as<sup>28</sup>

$$D_{C,\alpha\alpha} = \xi \lim_{t \to \infty} \frac{1}{4Nt} \left\langle \left| \sum_{i=1}^{N} \left[ R^{i}_{\alpha}(t) - R^{i}_{\alpha}(0) \right] \right|^{2} \right\rangle = \xi D_{\text{c.m.},\alpha\alpha},$$
(7)

where the two spatial components  $\alpha = x, y$  of the position vector for a particle *i* at time *t* are denoted by  $R^i_{\alpha}(t)$ , and the sum is over the *N* particles in the system. The "thermodynamic factor"<sup>28</sup>

$$\xi = \frac{\langle N \rangle}{\langle (\delta N)^2 \rangle} = \frac{\theta}{S_0} \tag{8}$$

is defined through the particle number fluctuations  $\langle (\delta N)^2 \rangle = \langle N^2 \rangle - \langle N \rangle^2$  in the grand canonical ensemble, or in terms of the static structure factor  $S_0 \equiv \lim_{\vec{k} \to 0} S(\vec{k}, 0)$ , or the compressibility of the adlayer  $\kappa_T = 1/(k_B T \theta \xi)$  (see also Sec. III B). The term  $D_{\text{c.m.},\alpha\alpha}$  in Eq. (7) is proportional to the center-of-mass motion of the adsorbate layer. This approach is sometimes called the "Kubo-Green method."

The diagonal elements of the *tracer* diffusion tensor are defined by  $2^{28}$ 

$$D_{T,\alpha\alpha} = \lim_{t \to \infty} \frac{1}{4Nt} \sum_{i=1}^{N} \langle |R^{i}_{\alpha}(t) - R^{i}_{\alpha}(0)|^{2} \rangle.$$
(9)

The tracer diffusion coefficient  $D_T$  is therefore proportional to the slope of the mean square displacement of a tagged particle in the hydrodynamic limit.

#### B. Microscopic transition rates and waiting times

Recently, an approximate theory of diffusion has been presented and shown to give rather good results for some strongly interacting systems.<sup>32</sup> For collective diffusion, the starting point of the theory is the density-density autocorrelation function  $S(\vec{r},\vec{r'},t)$  introduced in Eq. (6). Using the Mori projection operator formalism,<sup>59</sup> it can be shown that its Laplace-Fourier transform can be written as<sup>25</sup>

$$S(\vec{q},z) = \frac{\chi(\vec{q})}{z - b(\vec{q})\chi(\vec{q})^{-1} + M(\vec{q},z)},$$
 (10)

where  $b(\vec{q})$  contains microscopic jump rate information,  $\chi(\vec{q})$  is the thermodynamical susceptibility, and the memory function  $M(\vec{q},z)$  contains the dynamical correlations. The collective diffusion coefficient can be obtained from the correlation function  $S(\vec{q},z)$  by examining its pole in the limits  $\vec{q} \rightarrow 0$  and  $z \rightarrow 0.^{24,25}$  In the limit  $\vec{q} \rightarrow 0$ ,  $b(\vec{q})$   $\sim N\Sigma_{\alpha}\Gamma_{\alpha}q_{\alpha}^{2}\ell_{\alpha}^{2}$ , where  $\Gamma_{\alpha}$  is the average jump rate and  $\ell_{\alpha}$ is the jump length along the direction  $\alpha$ . Also, the compressibility term  $\chi_{0} = \lim_{q \rightarrow 0} \chi(\vec{q})/N = k_{B}T\theta\kappa_{T}$  is an equivalent expression for the inverse of the thermodynamic factor  $\xi$ . When the memory function  $M(\vec{q},z)$  is left out, this constitutes a dynamical mean field theory (DMF) for  $D_{C}$ .<sup>32</sup>

The *combined approach* proposed originally in Ref. 32 consists of evaluating the average jump rate  $\Gamma_{\alpha}$  and the compressibility  $\chi_0$  not through further analytic approximations as attempted previously<sup>24,25</sup> but rather by MC simulations.  $\Gamma_{\alpha}$  is directly obtained from the success ratio of individual particle jumps in the canonical ensemble, while  $\chi_0$  is more conveniently evaluated within the grand canonical ensemble. This procedure is easily implemented for arbitrary interaction strengths<sup>60</sup> and transition algorithms and is computationally very efficient when compared with brute force simulations in the hydrodynamic limit. Neglecting the memory function  $M(\vec{q},z)$  in Eq. (10) is equivalent to the Langmuir gas approximation,<sup>24,25,32</sup> where for collective diffusion the memory effects cancel out exactly.<sup>28,61</sup> This leads to the form first proposed by Reed and Ehrlich:<sup>21</sup>

$$D_{C,\alpha\alpha}^{\text{appr}} = \frac{\ell_{\alpha}^{2}}{2d} \frac{\Gamma_{\alpha}}{\chi_{0}}.$$
 (11)

For *tracer* diffusion, a similar analysis can be performed for the self-correlation function  $S_s(\vec{r},\vec{r'},t)$ , which differs from  $S(\vec{r},\vec{r'},t)$  defined by Eq. (6) in that it refers to the probability of finding a *tagged* particle at the given sites.<sup>24</sup> In the expression analogous to Eq. (10), the jump rate factor  $b(\vec{q})$  remains the same and  $\chi(\vec{q})$  is replaced by unity. In this case the Langmuir model gives a nontrivial correlation factor  $f(\theta)$ . This quantity has been calculated accurately for the twodimensional (2D) square lattice in Refs. 10–12. The resulting expression for  $D_T$  becomes<sup>24</sup>

$$D_{T,\alpha\alpha}^{\text{appr}} = \frac{\ell_{\alpha}^{2}}{2d} f(\theta) \Gamma_{\alpha}.$$
 (12)

Another useful quantity related to jump rates is the *waiting-time distribution* W(t) defined as follows.<sup>15</sup> Let the particle have performed its last transition at t=0. Then W(t) is the probability density that the particle in question performs its next transition at *t* after it remained still until *t*. The natural definition of time in the MC simulations is the number of jump attempts per particle, denoted by *n*, with the corresponding distribution function W(n). The average jump rate  $\Gamma$  is related to W(t) via

$$\frac{1}{\Gamma} = \langle n \rangle = \sum_{n=1}^{\infty} n W(n), \qquad (13)$$

where  $\langle n \rangle$  is the mean waiting time of the particle.

#### C. Monte Carlo method

The actual Monte Carlo simulations to sample the quantities defined above were carried out in an  $L \times L$  lattice with fully periodic boundary conditions, the linear size L being 30 unless mentioned otherwise. This is large enough for the finite-size effects to be negligible, provided that one is not very close to the critical point. The number of independent runs in our studies varied typically between 1000 and 10 000. We used the RANMAR pseudorandom number generator, which has performed very well in a number of extensive test programs.<sup>62</sup> Some additional test runs were performed using the ZIFF9689 generator,<sup>63</sup> whose diffusion results were found to be consistent with those obtained with RANMAR.

We paid particular attention to ensuring that the proper regimes for evaluating  $D_C$  and  $D_T$  were achieved in the MC simulations. Within the density fluctuation method for  $D_C$ , we need to sample fluctuations in the hydrodynamic regime characterized by small k and long time. We used the two smallest values of k ( $k \propto 2 \pi i/L$ , i=1,2), whose results were found to be consistent with each other. We followed the approach of Mak, Andersen, and George<sup>64</sup> by studying the decay of  $S(\vec{k},t)$  separately for the sine and cosine transforms, and used the deviation between the two resulting values to obtain an error estimate for  $D_C$ . For comparison, we



FIG. 3. Results for  $D_c$  in an Arrhenius plot at  $\theta$ =0.45. The results along the two principal axes (x,y) are based on the density fluctuation method and are given by squares and circles, respectively. The error bars are of the size of the symbols. The corresponding approximations based on Eq. (11) are given by lines. The critical temperature  $T_c$  of the order-disorder phase transition is denoted by a dotted line.

also used the Kubo-Green method to calculate  $D_C$ . Here getting good statistics for the center-of-mass term  $D_{c.m.,\alpha\alpha}$  becomes the major problem.

Of the many possible ways to calculate the thermodynamic factor  $\xi$ , we evaluated  $\langle (\delta N)^2 \rangle$  within the grandcanonical ensemble, in which the particle number density  $\rho$ is not fixed but is fluctuating around its mean value  $\theta$ . At all temperatures considered, the results of the Kubo-Green method were consistent with those given by the density fluctuation method. For  $D_T$  to be well defined, long simulation times were needed to overcome the initial nonlinearity of the mean-square displacement as a function of time due to the memory effects. This is too often taken for granted in the research literature, apparently because of the seemingly good statistics for the mean-square displacement.

Throughout the present work, we make our numerical results for the quantities  $D_T$ ,  $D_C$ , and  $\Gamma$  dimensionless by expressing them in the natural units of  $a^2/t_0$ ,  $a^2/t_0$ , and  $1/t_0$ , respectively, where *a* is the lattice constant and  $t_0$  is one Monte Carlo step per particle.

## **IV. RESULTS**

#### A. The role of dynamical correlations

We first compare the results for  $D_C$  and  $D_T$  given by the approximations of Eqs. (11) and (12) with those obtained from full MC simulations via the definitions in Sec. III A. Since in the former the only approximation is the absence of memory effects beyond those in the Langmuir gas model, a comparison of the two results provides information on the effect of interactions on dynamical correlations. All the results presented here are for the coverage  $\theta = 0.45$  for which the low-temperature ordered phase is  $p(2 \times 1)$ .

In Figs. 3 and 4 the full MC results for  $D_C$  and  $D_T$  are shown by open symbols while the corresponding approximate descriptions are shown by lines. In the case of *collective* diffusion, the agreement between the DMF result and the direct MC data is remarkably good, indicating that the memory effects are not very important. At very high temperatures, this is an expected result. However, DMF turns



FIG. 4. Results for  $D_T$  in an Arrhenius plot at  $\theta = 0.45$ . The results along the two principal axes (x, y) are given by squares and circles, respectively. The error bars are much smaller than the size of the symbols. The corresponding approximations based on Eq. (12) are given by lines. Again, the critical temperature  $T_c$  is denoted by a dotted line.

out to be a good approximation also at low temperatures in the ordered phase and even in the vicinity of a phase transition, the difference being always less than 15%. This means that the memory effects are not very important for collective diffusion, since the *static* quantity  $\Gamma_{\alpha}$  is a good approximation of the *dynamic* center-of-mass term  $D_{c.m.,\alpha\alpha}$ . The same observation has very recently been made in other strongly interacting systems such as a lattice-gas model on a stepped substrate and a model polymer system,<sup>32</sup> thus justifying the use of the Reed-Ehrlich description.<sup>21</sup>

We next consider the behavior of *tracer* diffusion along the same lines. We first note that the general behavior of  $D_T$ is to a great extent similar to  $D_C$ . Yet Eq. (12) seems to be an inadequate description of  $D_T$  under circumstances where the effect of interparticle interactions is significant, i.e., at temperatures below  $T_c$ . Here the difference between the approximation and the direct MC data is entirely due to the memory effects: in Eq. (12) the correlation factor  $f(\theta)$  includes only the backcorrelation effect in the Langmuir gas.<sup>24</sup> Thus, since the other memory effects arising from the direct interparticle interactions are not taken into account, and the approximation  $D_{T,\alpha\alpha}^{\text{appr}}$  is an overestimate of  $D_T$ , we may conclude that the remaining memory effects are also predominantly of the backcorrelation type. In the specific case studied here, the microscopic origin of the additional memory effects can be understood by considering the snapshots of typical lattice configurations shown in Fig. 5. At low tem-



FIG. 5. Representative snapshots of the configurations in the O/W(110) system with  $\theta$ =0.45. The occupied sites are denoted by filled circles. The temperatures corresponding to (a), (b), and (c) are T=0.714 $T_c$ , T=0.952 $T_c$ , and T=2.143 $T_c$ , respectively.



FIG. 6. A comparison of tracer and collective diffusion in terms of the ratio  $r_{\alpha} = D_{\text{c.m.},\alpha\alpha}/D_{T,\alpha\alpha}$ . Results for both directions  $\alpha = x, y$  are shown. The critical temperature is denoted by a dotted line.

peratures, the adatoms are mostly standing still, while only a few mobile atoms at a time are wandering around small vacancy islands and along the channels that separate filled rows of adatoms. Due to the interactions, the jump rate of a mobile tracer particle is much higher than that of the surrounding atoms. Therefore it is moving in a practically "frozen" environment, where the memory of the vacant sites left behind has a long lifetime.<sup>12</sup>

To further compare the diffusion coefficients, one can also consider the Darken equation,<sup>20,28,33,65</sup> which is based on the assumption that the velocities (displacements) of different adatoms are not correlated. If this were true, then the center-of-mass term  $D_{c.m.,\alpha\alpha}$  in Eq. (7) could be replaced with  $D_{T,\alpha\alpha}$  and thus the collective diffusion coefficient could be written as  $D_C = \xi D_T$ . To characterize the validity of this assumption, we considered the ratio  $r_{\alpha} = D_{c.m.,\alpha\alpha}/D_{T,\alpha\alpha}$ . Our results for  $r_{\alpha}$  in Fig. 6 show that the Darken equation holds reasonably well in the disordered phase, while in the ordered phase this is no longer true. As a matter of fact, at all temperatures considered in the present work, the DMF description for  $D_C$  works better than the Darken equation. Therefore, to conclude the discussion on the memory effects, the results of the present model system suggest that dynamical correlations do not seem to play a major role in collective diffusion, whereas for tracer diffusion the conclusion is exactly the opposite.

# B. Non-Arrhenius behavior of the diffusion coefficients around $T_c$

The observed temperature dependence of a diffusion coefficient D is commonly fitted to an activated Arrhenius form,

$$D \approx D_0 e^{-E_A^D/k_B T}.$$
 (14)

Within the transition state theory,<sup>16</sup> the prefactor  $D_0$  arises from the entropic barrier, while the remaining part describes thermally activated jumps over an effective energy barrier  $E_A^D$ . It is evident that the behavior displayed by the diffusion coefficients in Figs. 3 and 4 cannot be reasonably described by a constant effective activation barrier over the whole temperature regime. Further, for this kind of a *non-Arrhenius* 



FIG. 7. Results for the (dimensionless) thermodynamic factor  $\xi$  (squares for L=30 and triangles for L=120) and the average transition rate  $\Gamma$  (circles) in an Arrhenius plot. For  $\xi$ , results with two system sizes L are given to demonstrate the cusplike behavior; the critical regime is further illustrated in the inset. The L dependence (not shown) of  $\Gamma$  is extremely weak (Ref. 68). The error bars are smaller than the sizes of the symbols. The thermodynamic factor has been shifted for clarity's sake. The critical temperature of the order-disorder phase transition is denoted by  $T_c$  and a dotted line.

*temperature dependence*, there is no unique way of defining a temperature-dependent barrier. One way is to use the local slope while another possibility is to choose a constant effective prefactor and leave all the temperature dependence in the effective barrier. These two procedures would lead to very different values for the barrier. We now follow the practice commonly used in analysis of experiments and define an effective diffusion barrier  $E_A^D$  as the local slope of an Arrhenius plot, namely,

$$E_A^D \equiv -\frac{\partial}{\partial (1/k_B T)} \ln D.$$
 (15)

In Figs. 3 and 4, the local slope is approximately constant at low and high temperatures away from  $T_c$ . This implies that the diffusion coefficients obey simple Arrhenius behavior in these limits. Overall, however, the Arrhenius form with a single activation barrier cannot successfully describe their temperature dependence since near  $T_c$  the diffusion coefficients show strong temperature variations.

Since the definition of  $D_C$  contains the inverse compressibility, <sup>28</sup> it is often assumed that the non-Arrhenius behavior is due to nonlocal thermodynamic effects. This assumption is well justified in cases where the thermodynamic factor  $\xi$  has rapid temperature variations close to  $T_c$ , and then the behavior of the collective diffusion coefficient is expected to be dominated by  $\xi$ .<sup>66</sup> In the present case, however, the compressibility shows only a cusplike behavior<sup>67</sup> at  $T_c$  and thus the non-Arrhenius behavior of both  $D_T$  and  $D_C$  is predominantly determined by the average local jump rate  $\Gamma$  of single particles. This can be easily seen from Eqs. (11) and (12). We indeed observe that the temperature dependence of  $\Gamma$ shown by circles in Fig. 7 is very similar to that of  $D_C$  as well as  $D_T$ , with a turning point and sharp temperature variations near  $T_c$ . It is evident that  $\xi$  only slightly steepens the slope of  $D_C$  versus 1/T around  $T_c$ .

We next focus on the effective diffusion barrier  $E_A^D$  as extracted from Eq. (15) for  $D_T$ . As shown by squares in Fig.



FIG. 8. Results for the effective activation barriers  $E_A$ . The squares denote results based on the Arrhenius form, while open circles represent the data based on the tail of the waiting-time distribution. For the former, a typical error bar is shown, while for the latter the errors are smaller than the size of the symbols. Behavior of the prefactor  $D_0$  is illustrated in the inset. The critical temperature is denoted by a dotted line.

8,  $E_A^D$  tends to a constant value of about 0.28 eV at low temperatures and to the value of about 0.12 eV at high temperatures. We will come back to the interpretation of these barriers in Sec. IV D. Here we consider the barrier at temperatures around  $T_c$ , where  $E_A^D$  has a very pronounced peak centered at  $T_c$ , arising from the steeper slope of the  $D_T$ versus T curves around the transition temperature. This peak in  $E_A^D$  is accompanied by a strong increase in the value of the corresponding prefactor  $D_0$  shown in the inset of Fig. 8. This is yet another example of the well-known compensation effect.<sup>28,69</sup> Here the compensation simply results from the fact that when the temperature dependence is non-Arrhenius, there is no unique way of separating the prefactor and the barrier contributions. Since the temperature dependence of the diffusion coefficient itself near  $T_c$  is smooth and nonsingular, any dramatic change in the temperature dependence of the effective barrier  $E_A^D$  must be followed by a corresponding change in the effective prefactor  $D_0$ .

To understand the observed strong temperature variation of  $E_A^D$  near  $T_c$ , we need to consider the energetics of the microscopic jump processes that determine the average jump rate  $\Gamma$ . At finite coverages, there is a very complex distribution  $P(E_a)$  for the instantaneous activation barriers  $E_a$  [see Eq. (5)] that an adatom needs to overcome in a jump attempt from one configuration to another. For our model, the range of values is illustrated in Fig. 9. At high temperatures,  $P(E_a)$ is strongly peaked at small values of  $E_a$ , while at low temperatures the situation is completely the opposite. The change in the distribution takes place around  $T_c$ , thus characterizing the ordering of the adlayer as the temperature is decreased below  $T_c$ . This change in turn results in a strong temperature dependence of the average transition rate  $\Gamma$ around  $T_c$ , as shown in Fig. 7.

We should point out, however, that the instantaneous activation barriers  $E_a$  cannot explain the peak of the effective barrier  $E_A^D$  in Fig. 8, since the largest value of  $E_a$  in our model system is only about 0.4 eV, as is evident from Fig. 9. Thus, the peak does not refer to any microscopic ratelimiting jump process. Instead, it arises from an entropic



FIG. 9. Normalized probability distributions  $P(E_a)$  of the instantaneous activation barriers  $E_a$  [see Eq. (5)] at three different temperatures: (a)  $T=0.714T_c$ , (b)  $T=1.012T_c$ , and (c) T $=2.143T_c$ . The barrier that corresponds to a jump from a fully ordered row in the perfect  $p(2\times1)$  phase to an empty channel nearby, thus forming a vacancy behind [process (4) in Fig. 12], is 0.392 eV. In all three figures, one of the peaks extends beyond the vertical scale: in (a) P(0.392 eV)=0.496, in (b) P(0.392 eV)=0.171, and in (c) P(0.0 eV)=0.120. For these histograms, more than  $10^7$  samples were taken.

contribution<sup>70</sup> to  $\Gamma$  that has a strong temperature dependence in the vicinity of  $T_c$ . We note that these conclusions apply to both tracer and collective diffusion since the qualitative behavior of  $D_T$  and  $D_C$  around  $T_c$  is similar.

#### C. Long-time and short-time behavior of W(t)

To gain more insight into the microscopic dynamical processes and the anomalous temperature dependence near  $T_c$ , we next consider the waiting-time distribution W(t) of single-particle jumps as defined in Sec. III B. At very long times, we expect W(t) to decay as  $W(t) \sim \exp(-t/\tau)$ . Here  $\tau$ corresponds to the longest characteristic time scale among the various jump processes. The expected exponential decay at long times is indeed observed for our model system, as demonstrated in Fig. 10. The main contribution to  $\Gamma$  from the right-hand side of Eq. (13) comes from the short-time regime. This can be demonstrated as follows: we divide the sum in Eq. (13) into two parts, the first of which is the short-time contribution  $\langle n \rangle_S = \sum_{n=1}^{n_{co}} n W(n)$ . This quantity accounts for the contribution up to a crossover time  $n_{co}$ ,<sup>71</sup> which separates the short-time regime from the asymptotic exponential decay. What remains is the long-time contribution  $\langle n \rangle_L = \langle n \rangle - \langle n \rangle_S$ . From Fig. 11 we observe that the short-time regime indeed gives the dominant contribution to  $\Gamma$  and is thus mainly responsible for the anomalous temperature dependence of the diffusion coefficients. The temperature dependencies of  $\langle n \rangle_S$  and  $\langle n \rangle_L$  are qualitatively very similar, however.

## **D.** Effective energy barrier from W(t)

To further illustrate the importance of how one defines an effective energy barrier, we define another barrier  $E_A^W$  via the asymptotic exponential decay of W(t) by considering the jump probability  $p = 1/\tau = p_0 \exp(-E_A^W/k_B T)$ ,<sup>73</sup> where the fac-



FIG. 10. An example of the waiting-time distribution at temperatures of  $0.774T_c$  (circles),  $1.012T_c$  (triangles), and  $2.143T_c$  (dashed line), showing an exponential decay at large times. At temperatures of  $1.012T_c$  and  $2.143T_c$ , the time scales have been multiplied by 5 and 90, respectively. Also, at temperatures of  $0.774T_c$  and  $1.012T_c$ , only some of the data points are shown here to clarify the representation. The full curve is an exponential fit to the tail of W(n) at  $0.774T_c$ . In this case, the approximate crossover time  $n_{co}$  from the early-time regime to the asymptotic long-time regime is indicated by an arrow (Ref. 71).

tor  $p_0 = 1 - (N-1)/(N_{\text{max}} - 1) \approx 1 - \theta$  is kept *constant* with a value corresponding to average blocking of jumps. We emphasize that this effective barrier, defined as

$$E_A^W \equiv -k_B T \ln(p/p_0), \qquad (16)$$

is thus *not* extracted from the local slope of an Arrhenius plot.

Qualitatively, the temperature dependencies of p and  $\Gamma$  are rather similar. At high temperatures, the absolute value of p is close to that of  $\Gamma$ . For decreasing the temperature, p decreases more steeply than  $\Gamma$  or  $D_T$  (cf. Fig. 4) around  $T_c$ . In Fig. 8 the barrier  $E_A^W$  (shown by circles) is compared with the barrier  $E_A^D$  as extracted from the local slope of  $D_T$ . The two barriers agree away from  $T_c$ , while around  $T_c$  their behavior is completely different. This is clearly due to the use of a constant prefactor  $p_0$  in determining  $E_A^W$ , while  $E_A^D$  is determined from the local slope of  $D_T$ .



FIG. 11. Comparison of the early-time contribution  $\langle n \rangle_S$  and the late-time contribution  $\langle n \rangle_L$  to the average waiting time  $\langle n \rangle$ . The slight increase of  $\langle n \rangle_L$  at small *T* is due to  $n_{co}$  whose value is difficult to determine accurately at very low temperatures (Ref. 72). The quantities  $\langle n \rangle_S$ ,  $\langle n \rangle_L$ , and  $\langle n \rangle$  are all expressed in units of one Monte Carlo step per particle.



FIG. 12. Some important jump processes in the  $p(2 \times 1)$  phase in the O/W(110) system. Filled and open circles represent occupied and vacant adsorption sites, respectively.

Concerning the actual values of  $E_A^W$  in various limits, the high-temperature value of about 0.12 eV appears to be a combination of  $\Delta$  and some average barrier arising from the interparticle interactions in the disordered phase. At low temperature,  $E_A^W$  levels off to a value of about 0.28 eV. To understand this value, we first note that within the  $p(2 \times 1)$ phase at  $\theta = 0.45$ , diffusion occurs mainly through the motion of vacancies within occupied, ordered rows, or through the motion of adatoms between them. This corresponds to the processes (1) and (2) shown in Fig. 12. For long range mass transport of a tracer particle, the first process is necessary. Two typical processes that facilitate this are (3) and (4)in Fig. 12. In our case, the instantaneous activation barriers  $E_a$  of these two processes are 0.311 eV and 0.392 eV [see Eq. (5)], respectively. These two barriers correspond to the energy cost of local symmetry breaking and are rather close<sup>74</sup> to the low-temperature value  $E_A^W = 0.28$  eV mentioned above. In this respect, as becomes most evident near  $T_c$ , the interpretation of  $E_A^W$  in terms of microscopic singleparticle jump processes is more transparent than that of  $E_A^D$ . A detailed comparison between  $E_A^D$  and  $E_A^W$  in different ordered phases of O/W(110) will be presented elsewhere.<sup>75</sup>

## E. Influence of $\Delta$ on $E_A^D$

Let us now comment on the influence of the intrinsic barrier  $\Delta$  defined in Sec. II B on  $E_A^D$ . In the results presented so far, we have used a rather small value of  $\Delta = 0.0437$  eV to speed up the MC simulations so that the leading contribution to our results for  $E_A^D$  comes from the adatom-adatom interactions. With large values of  $\Delta$ , on the other hand, one might expect  $E_A^D$  to be dominated by the intrinsic barrier. We studied this issue by calculating  $E_A^D$  for tracer diffusion between  $T = 1.667T_c$  and  $T = 2.143T_c$  as a function of  $\Delta$ . The results for the contribution of  $\Delta$  in  $E_A^D$  are given in Fig. 13. For small values of  $\Delta$  the curve is nonlinear, which means that changing  $\Delta$  cannot be included as a constant prefactor of the transition rate in Eq. (3). For large values of  $\Delta$ , the slope of the curve approaches unity, which means that all further increase in  $\Delta$  goes directly into the effective barrier. The initial shift of approximately 0.05 eV, which can also be considered as a threshold value for  $\Delta$  to dominate, prevails in  $E_A^D$  for all values of  $\Delta$ . This is close to the value of  $\Delta$  chosen in this work, and therefore it is roughly half of the high-temperature value of  $E_A^D$  in Fig. 8. At low temperatures this threshold value is naturally expected to be larger, because there the



FIG. 13. The dependence of the effective diffusion barrier  $E_A^D(\Delta)$  for tracer diffusion on the intrinsic barrier  $\Delta$ . The studies were carried out between  $T=1.667T_c$  and  $T=2.143T_c$ . The line is only a guide to the eye, and the barrier at  $\Delta=0$  is  $E_A^D(0)=0.105$  eV.

interaction effects are stronger. Nevertheless, the contribution of  $\Delta$  to  $E_A^D$  is approximately additive, which can be used when a quantitative comparison between simulation results and experimental data is desired.<sup>76</sup>

#### F. Ordering and diffusion anisotropy

Within the ordered phase around  $\theta \approx 0.5$ , at any time there is only one of the equivalent  $p(2 \times 1)$  and  $p(1 \times 2)$  phases present in the system. One of them corresponds to ordering along the  $\hat{x}$  direction and the other along the  $\hat{y}$  direction (see Fig. 1). At low temperatures, due to the long characteristic time scales involved, a switching from one to the other does not occur during simulations. Thus the ordering results in an anisotropy of transition rates and corresponding activation barriers, which manifests itself as diffusion anisotropy.<sup>77,78</sup>

The anisotropy is characterized by the ratio of the diagonal terms in the diffusion tensor, i.e.,  $D_{C,xx}/D_{C,yy}$  and  $D_{T,xx}/D_{T,yy}$ . In our results shown in Figs. 3 and 4 this ratio is two. The reason for this is that in the  $p(2 \times 1)$  and  $p(1 \times 2)$  phases, the symmetry axes of the Hamiltonian and the principal axes of diffusion are actually the nearest neighbor directions  $\hat{x}$  and  $\hat{y}$ .<sup>17</sup> Thus the anisotropy ratio we observed is simply the geometrical factor describing the anisotropy of the underlying substrate. This is in agreement with experimental observations<sup>79</sup> and previous MC calculations.<sup>77,80</sup> For the same reason, the diffusion barriers  $E_A^D$  are identical for directions x and y. It is therefore obvious that the off-diagonal elements  $D_{C,\alpha\alpha'}$  and  $D_{T,\alpha\alpha'}$  with  $\alpha$  $\neq \alpha'$  measure the degree of ordering in the adlayer. Therefore, to study the influence of ordering, it is necessary to consider diffusion along the directions  $\hat{x}$  and  $\hat{y}$  instead of x and y. To measure this anisotropy we shall use the quantities  $\Gamma_{\max} = \max\{\Gamma_{\hat{x}}, \Gamma_{\hat{y}}\}$  and  $\Gamma_{\min} = \min\{\Gamma_{\hat{x}}, \Gamma_{\hat{y}}\}$ , where  $\Gamma_{\hat{x}}$  ( $\Gamma_{\hat{y}}$ ) is the average transition rate in the  $\hat{x}(\hat{y})$  direction (see Fig. 1). Note that within the framework of DMF, they yield the same anisotropy for  $D_C$  and  $D_T$ . The results are presented in Fig. 14. As expected, above  $T_c$  there is no difference between the two quantities, but in the ordered phase the anisotropy is clearly present. For  $T \leq 0.9T_c$ , the system is not capable of



FIG. 14. The results for the transition rates  $\Gamma_{\max} = \max\{\Gamma_{\hat{x}}, \Gamma_{\hat{y}}\}$  (circles),  $\Gamma_{\min} = \min\{\Gamma_{\hat{x}}, \Gamma_{\hat{y}}\}$  (crosses), and  $\Gamma$  (full line). The error bars are much smaller than the sizes of the symbols. The critical temperature is denoted by a dotted line.

switching from one of the equivalent phases to the other during the simulation. The anisotropy obtained here is consistent with previous findings,<sup>17</sup> and is naturally expected to be most pronounced at  $\theta = 0.5$ .

Within the ordered phase also the activation barriers for diffusion along the  $\hat{x}$  and  $\hat{y}$  directions are rather different. To study this, we considered the waiting-time distributions  $W_{\hat{x}}(n)$  and  $W_{\hat{y}}(n)$  along the directions  $\hat{x}$  and  $\hat{y}$ , respectively. From the tails of these distributions we indeed find the larger of the two barriers to be about 6% larger than the activation barrier we get from W(n), while the lower is considerably smaller than the effective activation barrier. Thus the effective activation barrier  $E_A^W$  we find is indeed dominated by the largest barriers in the system.

We also note here that although in the  $p(2 \times 2)$  phase at higher coverages, for example, there is no anisotropy between the jump directions  $\hat{x}$  and  $\hat{y}$ , diffusion is still considerably influenced by ordering. However, in that case ordering manifests itself only via the high instantaneous activation barriers as discussed in the preceding sections, and has the maximum effect on diffusion at the ideal coverage  $\theta = 0.75$ . The interplay of long-range order and local jump rates in diffusion within the coexistence phases of the model remains an open question. Work in this direction is in progress.<sup>75</sup>

#### V. SUMMARY AND DISCUSSION

In this work, we have considered adatom dynamics and surface diffusion in a lattice gas model of the O/W(110) system at a fixed coverage as a function of temperature. In particular, we have studied a wide temperature range from the high temperature disordered phase down to the  $p(2 \times 1)$  ordered phase, where adatom-adatom interactions play an important role. The expected non-Arrhenius behavior was analyzed using the framework provided by the DMF theory,<sup>24,25,32</sup> which in the case of collective diffusion constitutes the theoretical foundation of the phenomenological Reed-Ehrlich description.<sup>21</sup> For the model considered here, the non-Arrhenius behavior of the collective diffusion coefficient  $D_C$  was found to be predominantly determined by the microscopic average jump rate  $\Gamma$ , while the compressibility factor  $\xi$  due to the nature of the transition only weakly contributes to the observed temperature dependence. Over the whole temperature range,  $D_C$  is very accurately described by the DMF formula  $D_C \propto \xi \Gamma$ .

The temperature dependence of the tracer diffusion coefficient  $D_T$  is qualitatively very similar to that of  $D_C$  and  $\Gamma$ , but at low temperatures memory effects enhanced by adparticle interactions are very prominent in  $D_T$ . We have also shown how the single-atom waiting-time distribution W(t)can be used to assess the role of various microscopic processes with different instantaneous activation barriers in determining the observed macroscopic behavior. The non-Arrhenius behavior was related to critical effects in W(t)already at short times, while the long-time decay of W(t) is closely associated with the slowest microscopic processes.

Based on the success of the DMF description in several strongly interacting model systems,<sup>32</sup> we expect the methods and concepts presented here to be applicable to a wide variety of systems. Experimental studies using the recently developed methods utilizing the STM to extract the waiting times<sup>31</sup> would be very interesting. A particularly interesting further application is diffusion within coexistence phases. Work in this direction is under way.

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- <sup>71</sup> It is obvious that there is no unique choice for the crossover time  $n_{co}$ . In this work, it was chosen to be the value of *n*, at which the relative deviation of  $\ln W(n)$  from its asymptotic form was half a percent. We also used various alternative criteria for the choice of  $n_{co}$ , and the conclusions remained unchanged.
- <sup>72</sup>At low temperatures, W(n) decays very slowly to its asymptotic behavior. Thus for numerical reasons, the value of  $\tau$  as extracted from the data at low *T* may be slightly smaller than its true value. This does not affect the value of  $E_A^W$ , which depends logarithmically on  $\tau$ , but makes an accurate determination of  $n_{co}$ very difficult.

<sup>73</sup>For uncorrelated jumps characterized by a single barrier  $E_A$ , the

problem reduces to Brownian motion on a lattice. For a *single* particle, the waiting-time distribution is given by  $W(n) = p(1 - p)^{n-1} \equiv [p/(1-p)] \exp[n\ln(1-p)]$  with  $p = \exp(-E_A/k_BT)$ . At the same time, we expect  $W(n) \sim \exp(-n/\tau)$  with  $\tau = \exp(E_A^W/k_BT)$ , resulting in the requirement  $\ln(1-p) \approx -1/\tau$ . The two barriers  $E_A$  and  $E_A^W$  are thus consistent with each other if  $p \ll 1$ . For practical purposes a milder condition such as  $E_A > 3k_BT$  turns out to be sufficient. In the case considered in the present work this corresponds to the situation within the ordered phase.

- <sup>74</sup> In a complex many-particle system like the one studied here, the instantaneous activation barrier  $E_a$  may naturally change due to jumps of the neighboring particles while the tagged particle is waiting for a successful jump to occur. Also, right after a jump, the site left behind is more likely to be vacant than other neighboring sites [K. W. Kehr, R. Kutner, and K. Binder, Phys. Rev. B 23, 4931 (1981)].
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