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Comment on "Surface diffusion near the points corresponding to continuous phase transitions" [J. Chem. Phys. 109, 3197 (1998)]

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COMMENTS

Comment on ''Surface diffusion near the points corresponding to continuous phase transitions'' [J. Chem. Phys. 109, 3197 (1998)]

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In a recent article,[1] Uebing and Zhdanov (UZ) reported results of Monte Carlo (MC) simulations for diffusion of oxygen adatoms on the W(110) surface close to a second-order phase transition boundary. It is well known[2] that unlike static equilibrium properties, kinetic quantities in MC are very sensitive to the details of the algorithm used for the microscopic transition rates between different configurations, and one would expect an even larger sensitivity in the critical region. We show in this Comment that this is indeed the case. Our results imply that the particular dynamic algorithm used by UZ (Ref. 1) is inappropriate for studies of critical effects in diffusion. As a consequence, their conclusion on the critical effects of diffusion coefficients is incorrect and the criticism presented by UZ concerning our previous work[3] is unjustified.

We start by assessing the validity of various dynamical algorithms, including the one chosen by UZ, in describing the diffusion process in terms of MC simulations. To this end, we consider a model lattice-gas Hamiltonian for the O/W(110) system.[3,4] Unlike the one used by UZ, it produces a phase diagram in close agreement with the experimental observations for O/W(110),[5] including all known ordered phases and coexistence regions. To introduce the dynamics in MC, we consider the following choices for the transition rate $w_{i,f}$ from an initial state i with energy ϵ_i to a final state f with energy ϵ_f:

(1) The Metropolis form,[2] in which $w_{i,f}=\exp[-(\epsilon_f-\epsilon_i)/k_BT]$, if $\epsilon_f>\epsilon_i$. Otherwise $w_{i,f}=1$.
(2) The Kawasaki form,[2] in which $w_{i,f}=1/(1+\exp[(\epsilon_f-\epsilon_i)/k_BT])$.
(3) The transition dynamics algorithm (TDA),[6] where the transition proceeds by two steps via an intermediate state I with energy $\epsilon_I=\Delta+(\epsilon_i+\epsilon_f)/2$ such that $w_{i,f}=w_{i,I}w_{I,f}$. The rates for the two steps are of the Metropolis form and the quantity $\Delta>0$ characterizes the effect of the saddle point of the adiabatic substrate potential.
(4) The dynamics of UZ,[1] in which $w_{i,f}=(1/\kappa)\exp[-(\epsilon_S-\epsilon_i)/k_BT]$ and κ is a normalization constant. The quantity $\epsilon_S=\epsilon_S^0+\phi_N^*\Sigma_{NN}c_j'$ is chosen to model the saddle point energy, and ϵ_S^0 is the corresponding quantity in the limit of low coverages $\theta\to 0$. The value of ϵ_S^0 used has not been reported,[1,7] but our choice $\epsilon_S^0=0$ does not affect our conclusions. The term $\Sigma_{NN}c_j'$ is a sum of the occupation variables of ''nearest neighbors'' with respect to the transition state, and ϕ_N^* is an interaction parameter.

In Fig. 1(a) we show our simulation results for the average single-particle transition rate $\Gamma\equiv\langle n_i(1-n_f)w_{i,f}\rangle$ at $\theta=0.45$ around the second-order phase transition boundary with the algorithm choices (1)–(4) described above (n_i and n_f are the occupation variables of the initial and final sites, respectively). Clearly, the results of the dynamics (4) used by UZ are distinctly different from those of (1)–(3). The difference is further demonstrated by considering the effective activation barriers $E_A(\theta,T)\equiv-\partial\ln\Gamma(\theta,T)/\partial(1/k_BT)$ shown in Fig. 1(b). The dynamics of (1)–(3) show a prominent peak near T_c, whereas the dynamics of UZ shows a much smaller cusp.[8]

The physical origin of the discrepancy between the results using the UZ algorithm and those from the other three algorithms stems from the choice of saddle point energies in terms of the interaction parameter ϕ_N^*. The choice of ϕ_N^* is completely arbitrary and cannot be judged by experimental data. Further, since it is not related to the true interaction parameters in the Hamiltonian, the influence of the critical fluctuations near T_c to the saddle point configurations and to the diffusion coefficient is largely left out. To demonstrate this, we can consider the special case of the UZ algorithm

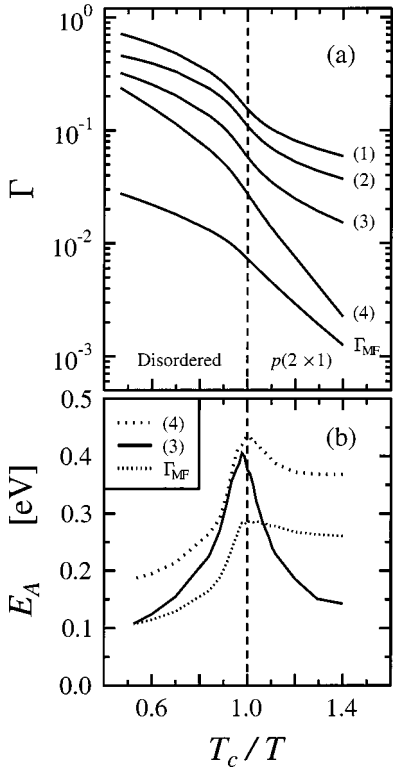

FIG. 1. (a) Γ for various dynamical algorithms in the O/W(110) system (Refs. 4, 3) with Γ_{MF} also shown (some curves have been shifted for clarity). In the dynamics of UZ, we chose ϕ_N^* as the pair interaction between second nearest neighbors (Ref. 1). In TDA, $\Delta=0.044$ eV (larger values give similar results). (b) Effective activation barriers E_A corresponding to the rates shown in (a). Results of items (1) and (2) are not shown, since they are almost identical to those of item (3).

with the choice $\phi_N^*=\epsilon_S^0=0$. In this case, the transition rate is only determined by the initial configuration and can be represented as[1]

$$\Gamma_{MF}=\Gamma_0(\mathcal{P}_{00}/\theta)\exp(\mu/k_BT). \tag{1}$$

Here $\mathcal{P}_{00}$ is the probability that a nearest neighbor pair is vacant, μ is the chemical potential, and $\Gamma_0(T)$ is the bare jump rate (in the limit $\theta\to0$).[1] Aside from the constant $\Gamma_0(T)$, Γ_{MF} contains only static quantities and no dynamical information at all. It is obviously a *mean-field*-type of description for the true transition rate. In Fig. 1(a) we plot Γ_{MF} as computed for the present model. It is qualitatively very similar to the result from using the UZ algorithm with finite ϕ_N^*.[9] They both fail to describe the strong non-Arrhenius behavior of Γ near T_c clearly revealed by the choices (1)–(3).[10]

To further demonstrate the unrealistic choice of the saddle point energy in the UZ algorithm, we have performed molecular dynamics simulations using effective medium theory for some fcc metal systems[11] and mapped the interactions to a lattice-gas description. We calculated the true activation barrier for every configuration change and compared the energetics of the saddle point configuration to the form postulated in the UZ dynamics to estimate ϕ_N^*. It turns out that the values of ϕ_N^* obtained in this fashion vary over a wide range of values, having *both* positive (repulsive interactions) *and* negative (attractive) values. This inconsistency of the UZ dynamics is in contrast with, e.g., the TDA dynamics,[6] which describes the instantaneous jumps via a transition state in a simple but physically sensible manner.

To conclude, the present results demonstrate the sensitivity of activated rates close to T_c to the choice of the dynamical algorithm in MC simulations. This observation is of general concern and necessitates further work to clarify the reasons of why various commonly used algorithms lead to distinctly different behavior of kinetic quantities in MC studies. In the present case, we have shown that the dynamics used by UZ suppress an essential part of the physical problem under study, namely, the effect of the critical fluctuations on the microscopic transition rates Γ close to T_c.[12] A true description of the critical fluctuations around both the equilibrium configurations and the transition states is therefore crucial for a correct MC study of the critical dynamics effect. One realistic approach to accomplish this effect is the TDA dynamics discussed above. Nevertheless, in spite of the long history of MC, it is clear that this issue still requires more attention to clarify the role of dynamical algorithms in general.

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[2] See K. W. Kehr and K. Binder, in *Applications of the Monte Carlo Method in Statistical Physics*, edited by K. Binder (Springer-Verlag, Berlin, 1984), and references therein.
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[7] C. Uebing and R. Gomer, Surf. Sci. **381**, 33 (1997).
[8] Close to a critical point where fluctuations are enhanced, there is a well-known ''compensation effect'' for barriers of activated processes. This is due to the entropic contribution to the rate coefficients. Thus, a peak for E_A at T_c is to be expected.
[9] In Ref. 1, results for the case where $\phi_N^*=0$ and where it is nonzero show similar behavior around T_c.
[10] In fact, in Ref. 1 UZ finds a broad peak in the activation barriers around $1.2T_c$, instead of T_c as expected (Ref. 8).
[11] J. Merikoski, I. Vattulainen, J. Heinonen, and T. Ala-Nissila, Surf. Sci. **387**, 167 (1997).
[12] The criticism in Ref. 1 by UZ concerning finite-size effects in our works is irrelevant, and fully discussed and refuted in our work [I. Vattulainen, J. Merikoski, T. Ala-Nissila, and S. C. Ying, Phys. Rev. Lett. **80**, 5456 (1998)].