Non-Arrhenius Behavior of Surface Diffusion near a Phase Transition Boundary

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We study the non-Arrhenius behavior of surface diffusion near the second-order phase transition boundary of an adsorbate layer. In contrast to expectations based on macroscopic thermodynamic effects, we show that this behavior can be related to the average microscopic jump rate, which in turn is determined by the waiting-time distribution $W(t)$ of single-particle jumps at short times. At long times, $W(t)$ yields a barrier that corresponds to the rate-limiting step in diffusion. The microscopic information in $W(t)$ should be accessible by scanning tunneling microscopy measurements.
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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 [1]. In most experimental and theoretical studies of the surface diffusion constant D, its temperature dependence is analyzed through an assumed 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 activated jumps over an energy barrier E_A^D. Although the Arrhenius form can be derived from microscopic considerations in some special cases [2,3], a rigorous justification for its use in interacting systems at finite coverages is not available. Further, even in the cases where D appears to have an Arrhenius temperature dependence over a finite temperature range, its microscopic interpretation may not always be clear. This is because for an interacting system, there may be many microscopic activation barriers. Thus the value of the measured effective diffusion barrier E_A^D must result from some complex average of all of them, and does not refer to any microscopic process in particular [4].

In fact, the values for D_0 and E_A^D can be strongly temperature dependent indicating a region of non-Arrhenius behavior. This becomes especially pronounced near surface phase transition boundaries, where rapid variations of D have been observed in experiments [4–6] and computer simulations [2,7]. Such rapid changes are often accompanied by the well-known "compensation" effect [8], where an apparent increase in E_A^D is compensated by an increase in the prefactor D_0 [6]. However, in most cases the underlying reasons for non-Arrhenius behavior are not understood. It is the purpose of the present Letter to study these issues near a second-order phase transition in a surface adsorbate layer. We show that in contrast to the common folklore that an anomalous temperature dependence in D near T_c would be predominantly due to nonlocal thermodynamic effects, it can be explained by the microscopic single-particle jump rate Γ. This quantity is determined by the short-time behavior of the waiting-time distribution $W(t)$ for single-particle jumps. Moreover, we show that for long times, $W(t)$ yields an effective activation barrier that corresponds to the rate-limiting step in diffusion. Thus $W(t)$ provides a connection between microscopic and macroscopic aspects of diffusion. Further, it is experimentally available through, e.g., scanning tunneling microscopy (STM) measurements [9].

In this Letter, we have carried out Monte Carlo (MC) simulations for a model of oxygen on the W(110) surface [10,11]. In this system, the substrate remains unreconstructed [12], the oxygen atoms have well-defined adsorption sites [13], and desorption of oxygen occurs only at temperatures 1600 K or above [12]. Therefore, this system is very suitable for simulation studies using a lattice-gas description. We use the lattice-gas model constructed by Sahu *et al.* [11] to describe the main features of the phase diagram. The Hamiltonian includes pair interactions up to fifth nearest neighbors and some three-body interactions [11], the attractive ones being dominant. We concentrate on results for the coverage $\theta = 0.45$ over a wide temperature range. For this coverage at a low temperature, the adlayer is in the ordered $p(2 \times 1)$ phase, while at $T_c \approx 710$ K it undergoes a second-order transition [11] to a disordered phase [14]. For details of the model and MC simulations, see Refs. [10,15].

Our simulation results for the tracer and collective diffusion coefficients D_T and D_C (for definitions, see, e.g., Ref. [4]), respectively, are given in Fig. 1. We first note that their qualitative behavior is similar and that the effective diffusion barrier E_A^D defined as

$$E_A^D \equiv -\frac{\partial(\ln D)}{\partial(1/k_BT)} \tag{1}$$

is approximately constant at low and high temperatures away from T_c. This implies that the diffusion constants

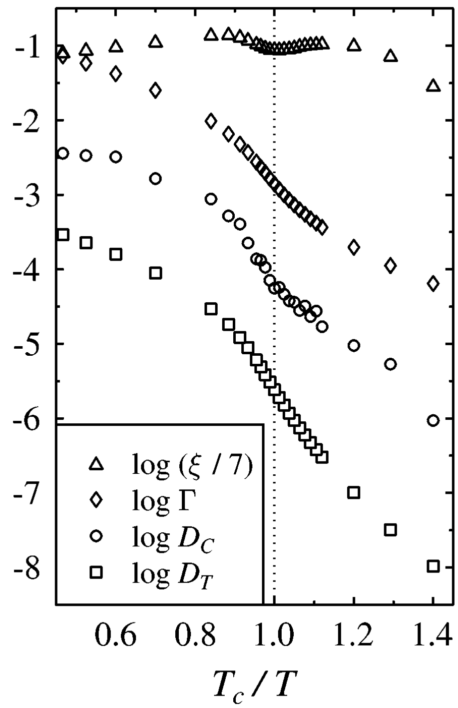

FIG. 1. Results for D_T and D_C as a typical Arrhenius plot in the O/W(110) system at $\theta = 0.45$. We also show the behavior of the average transition rate Γ and the thermodynamic factor ξ. The quantities D_T, D_C, and Γ have been made dimensionless by expressing them in units of a^2/t_0, a^2/t_0, and $1/t_0$, respectively, where a is the lattice constant and t_0 is one Monte Carlo step per particle. The value of ξ, which is a dimensionless quantity, has been scaled by a factor of 7 to make the graphic representation more readable while other quantities are expressed directly in the units given above. The critical temperature of the order-disorder phase transition is denoted by T_c and a dotted line.

obey simple Arrhenius behavior. Near T_c, however, the temperature dependence of the diffusion constants is strongly non-Arrhenius.

In the Green-Kubo formalism [4], the expression for D_C contains a thermodynamic factor ξ inversely proportional to the compressibility, which is governed by the *global* number fluctuations of the adlayer. It is often assumed that a possible non-Arrhenius behavior of D_C near the phase transition boundary is predominantly due to the critical behavior of this factor [7]. We show below that this is not the case here: The non-Arrhenius behavior of both D_T and D_C has a dynamic origin and can be traced back to the temperature dependence of the *local* single-particle jump rate Γ. To demonstrate this, we show in Fig. 1 the temperature dependence of ξ and Γ as well as that of D_T and D_C. It can be seen from Fig. 1 that while the diffusion constants have a turning point and sharp temperature variations close to T_c, the thermodynamic factor ξ has only a relatively weak temperature dependence in this region and cannot account for the non-Arrhenius behavior of the diffusion constants. On the other hand, the single-particle jump rate Γ has exactly the same behavior near T_c as D_T and D_C. These observations can be understood theoretically within the dynamical mean field theory [16], which yields $D_T \propto \Gamma$ and $D_C \propto \xi\Gamma$. We can conclude that the strong temperature dependence of both D_T and D_C near T_c is indeed of the same dynamic origin, coming from the average single-particle transition rate Γ.

We next focus on the effective diffusion barrier E_A^D as extracted from Eq. (1) for D_T. As shown by squares in Fig. 2, E_A^D has a sharp peak near T_c. 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. 2. This is yet another example of the well-known compensation effect [4,8]. 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 constant 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. We note that the same phenomenon occurs for collective diffusion as well.

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 which determine the average jump rate Γ. At finite coverages, there is a very complex distribution $P(E_a)$ for the instantaneous activation barriers E_a [17] which an adatom needs to overcome in a jump attempt from one configuration to another. At high T, $P(E_a)$ is strongly peaked at small values of E_a, while at low temperatures the situation is completely the

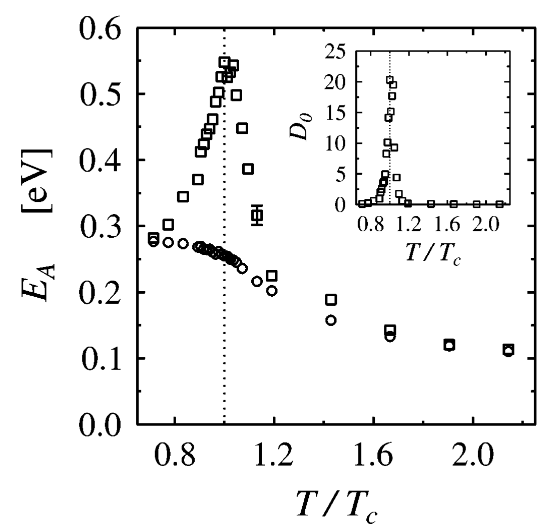

FIG. 2. Results for the effective activation barriers. The squares denote results based on the Arrhenius form [see Eq. (1)] for tracer diffusion, while open circles represent the data based on the tail of $W(n)$. Behavior of the prefactor D_0 is illustrated in the inset. The critical temperature is denoted by a dotted line.

opposite [18]. 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 Γ around T_c, as shown in Fig. 1. We point out that the instantaneous activation barriers E_a cannot explain the peak of the effective barrier E_A^D in Fig. 2, since the largest value of E_a in our model system is only about 0.4 eV [18]. Thus, the peak does not refer to any microscopic rate-limiting process. Instead, it arises from an entropic contribution [19] to Γ which has a strong temperature dependence in the vicinity of T_c.

To gain more insight into the microscopic dynamical processes and the anomalous temperature dependence near T_c, we next introduce the waiting-time distribution $W(t)$ of single-particle jumps [20]. Suppose a single particle (in the presence of other particles) had performed its last transition at time $t = 0$. Then $W(t)$ is the probability density that the particle in question performs its next transition at time t after it remained still until t. Here the most practical definition of "time" in the MC simulations is to consider the time scale as the number of jump attempts of the particle, denoted by n. Then the waiting-time distribution is simply $W(n)$. This provides a direct connection with the dynamic jump rate Γ discussed above via

$$\langle n \rangle \equiv \frac{1}{\Gamma} = \sum_{n=1}^{\infty} nW(n), \tag{2}$$

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

At very long times, we expect $W(t)$ to decay as $W(t) \sim \exp(-t/\tau)$. Here the characteristic time τ describes the longest time scale among the various microscopic processes, which constitutes the rate-limiting factor for mass transport. This expected exponential decay at long times is indeed observed for our model system, as demonstrated in Fig. 3. We can then define an effective activation barrier E_A^W via τ by considering the jump probability $p = 1/\tau = p_0 \exp(-E_A^W/k_B T)$. As shown by circles in Fig. 2, the activation barrier E_A^W extracted from the asymptotic region of $W(t)$ decreases monotonically with increasing temperature, and agrees with the effective diffusion barrier E_A^D extracted from an Arrhenius analysis of D_T far from T_c. Additional studies in our model system [18] indicate that the value of E_A^W is closely related to the instantaneous activation barrier characterizing the dominant microscopic processes. In our model the microscopic barriers have a maximum value of about 0.4 eV and thus the barrier E_A^W does not have the sharp peak displayed by the effective diffusion barrier E_A^D.

It turns out that the temperature dependence of the barrier E_A^D results mainly from the short-time behavior of $W(n)$. This is demonstrated by dividing the sum in Eq. (2) into two parts, the first of which is the short-time contribution $\langle n \rangle_S = \sum_{n=1}^{n_{co}} nW(n)$. This quantity accounts for the contribution up to a crossover time n_{co}, which separates the short-time regime from the asymptotic exponential decay. What remains is the long-time contribution $\langle n \rangle_L = \langle n \rangle - \langle n \rangle_S$. As expected, from Fig. 4 we observe that the short-time regime gives the dominant contribution to Γ. Further, the short-time regime of $W(n)$ is strongly affected by the critical fluctuations, being mainly responsible for the anomalous temperature dependence of the diffusion constants near T_c.

To summarize, within the present model of O/W(110), the non-Arrhenius behavior near T_c was found to have a mainly dynamic origin, reflecting the dependence of the

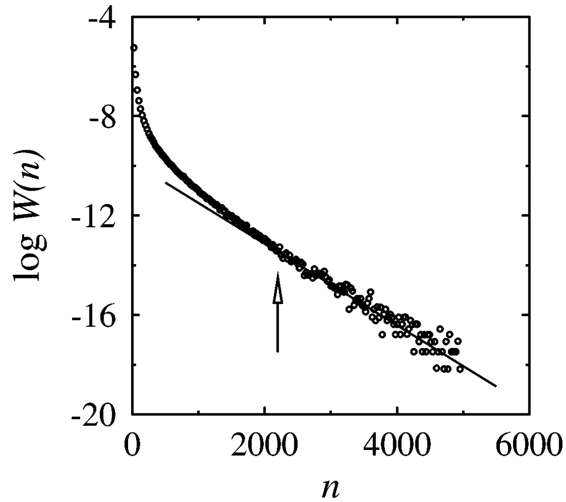

FIG. 3. An example of a waiting-time distribution $W(n)$ at a temperature of 0.774 T_c showing an exponential decay at long times. For clarity, only some of the data points are shown here. The full curve is an exponential fit to the tail of $W(n)$. The approximate crossover time n_{co} for the crossover from the small-time regime to the asymptotic long-time regime [21] is indicated by an arrow.

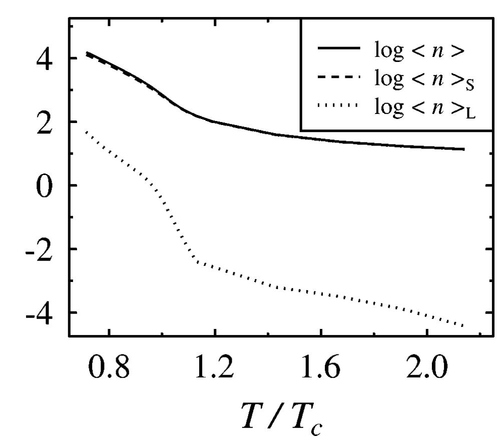

FIG. 4. Comparison of the short-time contribution $\langle n \rangle_S$ and the long-time contribution $\langle n \rangle_L$ to the average waiting time $\langle n \rangle$. The slight increase of $\langle n \rangle_L$ at small T is due to n_{co} whose value is difficult to determine accurately at very low temperatures. 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.

single-particle jump rate Γ on the critical fluctuations close to T_c. Surprisingly, in our studies the thermodynamic factor gives only a minor contribution to the temperature dependence of the collective diffusion constant D_C, and the anomalous temperature dependence for both D_T and D_C results from the dynamic factor Γ. We find that the single-particle waiting-time distribution $W(t)$ gives the most detailed picture of the microscopic processes. It has been recently demonstrated by Swartzentruber [9] that this distribution function in the presence of several different microscopic activation barriers can indeed be measured using the STM. From the long-time tail of $W(t)$ one can obtain information on the energetics of the rate-limiting processes of diffusion in the form of an effective activation barrier E_A^W. On the other hand, the temperature variation of the effective diffusion barrier E_A^D directly reflects that of the microscopic jump rate Γ, and depends not only on the long-time tail of $W(t)$ but also on its short-time behavior. In the short-time regime near T_c, $W(t)$ is strongly affected by the critical fluctuations. The fluctuations there lead to a strong temperature dependence of the transition entropy and an additional contribution to the effective barrier E_A^D.

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