Diffusion Anomaly near Structural Phase Transitions

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We consider the diffusion of a particle coupled to a surface which undergoes a structural phase transition. Using a recently developed microscopic theory of diffusion we show that the diffusion coefficient is anomalously reduced near the transition because of diverging value of the friction near the transition. To demonstrate this anomaly, we evaluate the diffusion coefficient for a model Hamiltonian describing an adatom on the W(100) surface which undergoes a $(1\times1)\rightarrow c(2\times2)$ reconstruction.

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Anomalous behavior of diffusion has often been used to identify phase transitions on surfaces [1], and has implications for a variety of systems, including diffusion-limited chemical reactions [2] and flux-line motion in high-T_c superconductors [3]. In this Letter, we consider an adatom diffusing on a surface which undergoes a structural phase transition at some critical temperature T_c. Near a structural transition, it is well established that the vibrational excitations of the medium display strong anomalies [4,5]. Besides the softening of a phonon branch, there is also a collective "central peak" excitation, which is apparent in the dynamical structure function $S(\mathbf{q},\omega)$, near the critical wave vector $\mathbf{q}_0$. The coupling of these excitations to the adatom leads to anomalous temperature dependence of the friction exerted by the medium on the diffusion particle. In fact, we will show using a recently developed microscopic theory of diffusion that the diffusion coefficient is expected to *vanish anomalously* at T_c, due to the divergence of $S(\mathbf{q}_0,\omega=0)$. To demonstrate this anomaly, we apply our formalism to study the diffusion of adatoms for a model of the W(100) surface, which undergoes a $(1\times1)\rightarrow c(2\times2)$ reconstruction [6,7].

The microscopic theory [8] describes the diffusion of classical particles in a periodic medium, where the background particles execute vibrational motion about their equilibrium positions. The diffusion constant is evaluated at the zero-frequency limit of the velocity autocorrelation function. In the limit of high friction and slow diffusion (as compared to the vibrational time scale), the elements of the diffusion tensor are given as the $\mathbf{G}=0$, $\mathbf{G}'=0$ element of the inverse of an infinite matrix:

$$D_{\mu\nu}=\lim_{\omega\rightarrow0}\{-i\omega\beta m\chi^{-1}(\mathbf{G}-\mathbf{G}')\delta_{\mu\nu}+\Sigma_{\mu\nu}(\mathbf{G}-\mathbf{G}';\omega)-(i/\omega)G_\mu\chi^{-1}(\mathbf{G}-\mathbf{G}')G_\nu\}^{-1}|_{\mathbf{G}=0,\mathbf{G}'=0}. \quad (1)$$

In Eq. (1), ω is the frequency and $\mathbf{G},\mathbf{G}'$ denote reciprocal-lattice vectors. $\chi^{-1}(\mathbf{G}-\mathbf{G}')$ is the Fourier transform of the inverse density

$$n^{-1}(\mathbf{r})\equiv e^{\beta V_A(\mathbf{r})}\int e^{-\beta V_A(\mathbf{r})}d\mathbf{r},$$

where $V_A(\mathbf{r})=\sum_l v(\mathbf{r}-\mathbf{R}_l)$ denotes the adiabatic potential seen by the diffusing particle, and the v's denote interactions between the adatom and background atoms at $\mathbf{R}_l$, averaged over the background vibrational degrees of freedom. The memory function $\Sigma_{\mu\nu}(\mathbf{G}-\mathbf{G}';\omega)$ is given by

$$\Sigma_{\mu\nu}(\mathbf{G}-\mathbf{G}';\omega)=\frac{m}{k_BTV_0^2}\int n^{-1}(\mathbf{r})\eta_{\mu\nu}(\mathbf{r},\omega)\times e^{-i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}}d\mathbf{r}, \quad (2)$$

where the friction tensor is defined as

$$\eta_{\mu\nu}(\mathbf{r},\omega)=\frac{1}{k_BTm}\sum_{ll',\gamma\delta}S_{ll'}^{\gamma\delta}(\omega)v^{\mu\gamma}(\mathbf{r}-\mathbf{R}_l^0)v^{\nu\delta}(\mathbf{r}-\mathbf{R}_{l'}^0). \quad (3)$$

Here $S_{ll'}^{\gamma\delta}(\omega)$ is the Laplace transform of the lattice correlation function, and $v^{\mu\gamma}(\mathbf{r}-\mathbf{R}_l^0)\equiv\partial^2v(\mathbf{r}-\mathbf{R}_l^0)/\partial r_\mu\partial r_\gamma$. The key point to note from Eqs. (1)–(3) is that the friction tensor η depends on the zero-frequency limit of the dynamic structure factor $S(\mathbf{q},\omega=0)$. Near the structural transition, this quantity actually diverges for $q\rightarrow q_0$ which leads to the diffusion anomaly near the structural transition.

We now describe the quantitative evaluation of D near T_c with the specific application of our theory to adatom diffusion on the W(100) surface. The substrate is described by the two-dimensional Hamiltonian

$$H=\sum_i\left(\frac{\mathbf{p}_i^2}{2}+\frac{A}{2}\mathbf{u}_i^2+\frac{B}{4}\mathbf{u}_i^4+8H_4u_{ix}^2u_{iy}^2\right)+C_1\sum_{nn}\mathbf{u}_i\cdot\mathbf{u}_j. \quad (4)$$

This is a prototype Hamiltonian for structural phase transitions, which has been very successful in describing the $(1\times1)\rightarrow c(2\times2)$ reconstruction of the W(100) surface [7]. Here $\mathbf{u}_i$ is the in-plane displacement of a W atom on the ith site, and $\mathbf{R}_i^0=a_0(l,m)$, with integers l and m indicating the equilibrium position of W atoms in units of the lattice constant $a_0=3.16$ Å. C_1 (>0) is the nearest-neighbor interaction strength. For the on-site terms,

$A<0$ and $B>0$, and H_4 (<0) determines the anisotropy of the system. In our model, the Hamiltonian parametrization in a dimensionless unit system is such that $A=-10$, $B=40$, $H_4=-1.85$, and $C_1=3.75$. Length scale L_0 and temperature scale T_0 are chosen such that the transition temperature T_c and ground-state displacement u_0 agree with the experimentally observed values.

The dynamic structure factor $S(\mathbf{q},\omega)$ is evaluated with a recently developed formalism [5] based on Mori projection operator techniques. First, $S(\mathbf{q},\omega)$ is expressed as a continued-fraction expansion:

$$S(\mathbf{q},\omega)=-2\frac{k_BT}{N}\chi(\mathbf{q})\lim_{\delta\to 0}\mathrm{Im}\cfrac{1}{\omega+i\delta+\cfrac{\Delta^{(1)}}{\omega+i\delta+\cfrac{\Delta^{(2)}}{\omega+i\delta+\cdots}}}. \tag{5}$$

The physical quantities $\Delta^{(n)}$ appearing in this expansion are related to the various moments of $S(\mathbf{q},\omega)$. They are evaluated by Monte Carlo simulations for substrates of sizes 20×20, 30×30, and 40×40. The quantity that shows the most pronounced critical and size effect is $\Delta^{(1)}=\chi^{-1}$ [9]. This is extended to arbitrary sizes through the use of finite-size scaling techniques [10,11]. The dynamical structure factor thus obtained is substituted back into Eq. (3) to obtain the friction tensor. For the interaction potential of the adatom with the substrate, we have used simple model potentials of the form $v(\mathbf{q})=we^{-\alpha(q-q_0)^2}-re^{-\alpha'(q-q_0)^2}$, where $q_0=(\pi/a,\pi/a)$. We choose the parameters $\alpha=(a_0/\pi)^2$ and $\alpha'=2(a_0/\pi)^2$. The friction tensor η determines the memory kernel Σ through Eq. (2) which is then substituted into Eq. (1) for the evaluation of the diffusion tensor. For the inversion of the matrix in Eq. (1), the number of $\mathbf{G}$ vectors needed depends on the temperature. At lower temperatures, the density function is more corrugated and a larger number is required. A maximum of 333 $\mathbf{G}$ vectors were used in the matrix inversion of Eq. (1) to assure convergence. In Fig. 1, we show the results for $\ln D$ versus temperature. Compared with the simple Arrhenius form with a constant friction $D=(kT/m\eta)e^{-\Delta/k_BT}$ the actual value of D is reduced by several orders of magnitude near T_c, where $D\approx\epsilon^x$ near T_c. Here $\epsilon\equiv|T-T_c|/T$ and the exponent x is about 0.9–1.8 depending on the choice of the scaling region. Because of numerical uncertainties, the exact exponent cannot be determined with great accuracy. However, the diffusion anomaly itself is very robust. With other choices of the coupling potential the results are very similar to those of Fig. 1, except that the strength of the anomaly depends on the relative weighting of the critical region for different choices of $v(\mathbf{q})$.

It is easy to understand the source of this anomaly. According to our calculations, $S(q,\omega)\propto\chi^2(q)$. Near T_c, $\chi(q)$ obeys the scaling form $\chi(q)=q^{-2+\hat{\eta}}F(\epsilon^\nu/q)$. Substitution of this into Eq. (3) for the friction yields

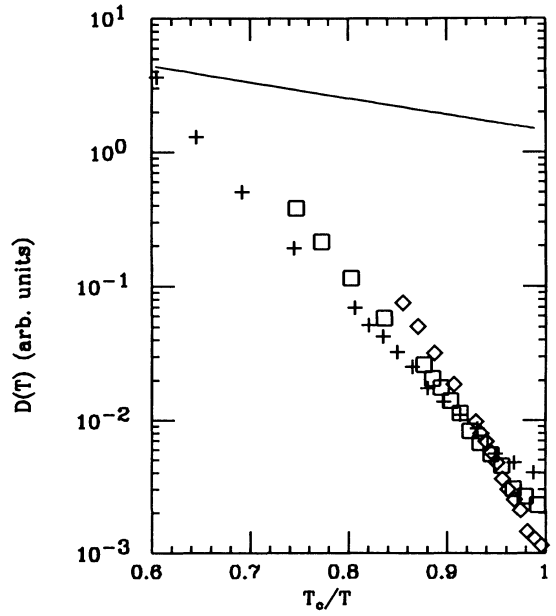

FIG. 1. The diffusion coefficient $D(T)$ shown as a function of the inverse temperature. The crosses are for a 40×40, the squares for a 60×60, and the diamonds for a 100×100 system. The solid line is the expected Arrhenius behavior in the absence of critical fluctuations of the substrate.

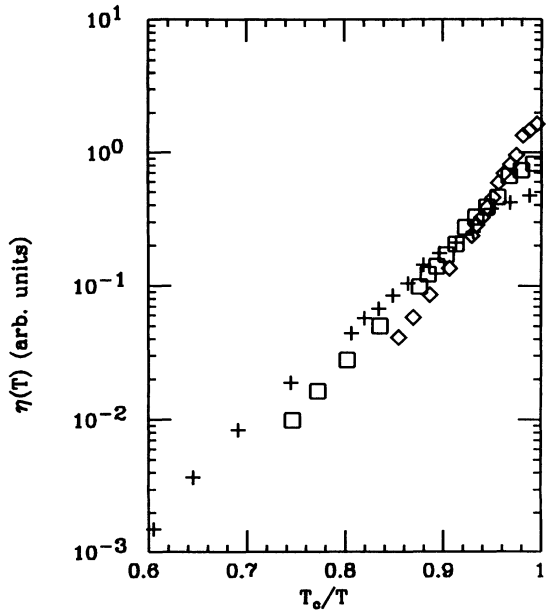

FIG. 2. The saddle-point friction $\eta(T)$ as a function of the inverse temperature. Symbols are as in Fig. 1.

$\eta \sim \epsilon^{\nu(-2+2\hat{\eta})}$ [12]. Our previous studies of diffusion show that the diffusion constant at low temperatures is inversely proportional to the value of the friction at the saddle point [13]. In Fig. 2 we show results for the saddle-point value of the friction for three different system sizes. As expected, on approaching T_c the value of the friction diverges until a finite-size rounding occurs just before T_c. This then leads to the power-law anomaly for the diffusion constant as observed in our numerical work. From our scaling studies of χ we estimate that $\nu(2-2\hat{\eta}) = 1.6 \pm 0.2$. This is consistent with our numerical estimate of the exponent $x = 0.9$–1.8. Note that the divergence of η near T_c is analogous to the behavior of the EPR linewidth near a structural transition [14].

Experimentally, anomalous dips in the temperature dependence of surface diffusion have been observed, and qualitatively interpreted as indicating phase transitions on surfaces [1]. For example, data for H diffusion on the W(110) surface display a distinct downward cusp around $T = 74$–91 K, which was ascribed to a phase transition on the surface [15]. Unfortunately, the true nature of this transition is not known. At present, the $(1\times1) \rightarrow c(2\times2)$ surface reconstruction on W(100) is best studied and understood. Measurements of adatom diffusion and other kinetic processes on this surface in the vicinity of T_c would be the best avenue to study the anomaly described here.

To summarize, we have presented a new prediction of an anomalous behavior of the diffusion coefficient of a particle coupled to a medium which undergoes a structural phase transition. We have shown through an explicit calculation how this behavior arises for adatom diffusion for a model of the W(100) surface near its (1×1) to $c(2\times2)$ transition. Because of the rather universal behavior of the dynamic structure factor near structural transitions, the theory has important implications for physical processes such as diffusion-limited surface reactions, where a slowing down of the reaction may result if the underlying substrate undergoes a transition. Also, in the case of weak randomness the linear part of the resistivity of high-T_c superconductors, which is proportional to the diffusion coefficient of the flux lines, may exhibit an anomalous dip near structural transitions of the Abrikosov flux lattice.

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