VOLUME 65, NUMBER 7 PHYSICAL REVIEW LETTERS 13 AUGUST 1990

Universal Properties of Classical Surface Diffusion

Tapio Ala-Nissila and S. C. Ying
Department of Physics, Brown University, Providence, Rhode Island 02912

(Received 30 October 1989)

We examine the classical diffusion of independent adatoms on periodic substrates using a recently developed microscopic theory. We show how the universal properties of surface diffusion arise from this theory in the high-friction limit at low temperatures. At high temperatures, the theory crosses over correctly to that of a Brownian particle in a viscous medium.

PACS numbers: 68.35.Fx, 05.40.+j, 05.60.+w

In the study of adatom diffusion on a substrate, the temperature dependence and the anisotropy of diffusion are two of the most important issues.[1] The Arrhenius form of activated temperature dependence is almost universally used in the interpretation of experimental data.[2] For the anisotropy of the diffusion tensor, the simple geometric random-walk model is often evoked.[3] To date, most of the theoretical studies of these questions are based on molecular-dynamics simulations.[4-6] A highly successful approach to the numerical study of surface diffusion is through the concept of dynamical corrections to the transition-state theory (TST).[4,7] It has been shown that at low temperatures, the correction to TST is small.[4] The TST picture of diffusion corresponds to a series of independent activated jumps across the saddle-point barrier. Thus, these studies provide a justification for the phenomenological assumptions of temperature dependence and anisotropy of the diffusion constant. As the temperature increases, trajectories not included within TST become important and one expects deviations from the simple random-walk picture.[4] However, how this influences the diffusion anisotropies has not yet been investigated to our knowledge. There is also no simple theory which describes correctly the crossover from the low-temperature activated jump regime to the high-temperature Brownian motion regime.

Recently, an analytic theory to the diffusive motion of an atom interacting with an inhomogenous background has been developed by Ying.[8] In this approach, the time-dependent correlation functions are expressed as a continued-fraction expansion. In particular, the diffusion tensor **D** of an adatom can be obtained as the zero-frequency limit of the velocity autocorrelation function. The result for **D** takes a very transparent form in the high-friction limit. There is no reference to TST trajectories in this approach, and the result is valid *at all temperatures*. It is the purpose of this Letter to show how the universal properties of surface diffusion arise from this theory at low temperatures, and how the behavior crosses over smoothly to a free-particle Brownian motion at high temperatures. We will also show how the diffusion anisotropy depends on the topology of the surface potential.

The existing theory is formulated for extended motion of an adatom in all dimensions. When applied to surface kinetics, the motion of an adatom has to be treated as strictly two dimensional. For a more realistic treatment, we have generalized the theory to the case where the motion of the adatom is extended in the surface plane and bounded in the normal direction.[9] Within the Mori formalism developed in Ref. 8, this involves using the set of plane waves $\{e^{i\mathbf{G}\cdot\mathbf{r}}\}$, with **G** denoting the two-dimensional reciprocal-lattice vectors to describe the position dependence within the surface plane, and the set of normalized harmonic-oscillator eigenfunctions $\{\phi_n(z)\}$ for describing position dependence involving the normal coordinate.

Using this theory, the components of the diffusion tensor **D** in the high-friction limit can be obtained as the inverse of an infinite matrix **Q** given by[9]

$$\begin{aligned}Q_{\mu\nu}(\omega;\mathbf{s},\mathbf{s}') \equiv {} & -i\omega\beta m\chi^{-1}(\mathbf{s},\mathbf{s}')\delta_{\mu\nu} \\ & +\Sigma_{\mu\nu}(\omega;\mathbf{s},\mathbf{s}') - \frac{i}{\omega}G_\mu\chi^{-1}(\mathbf{s},\mathbf{s}')G'_\nu . \quad (1)\end{aligned}$$

Here ω is the frequency, μ and ν refer to Cartesian coordinates, and $\mathbf{s}\equiv(\mathbf{G},n)$ is the combined label for the rows and columns in the matrix. The two fundamental matrices in (1) are

$$\chi(\mathbf{s},\mathbf{s}') = \int e^{-i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}}\phi_n(z)\phi_{n'}(z)n(\mathbf{r},z)\,d\mathbf{r}\,dz ,$$

and

$$\begin{aligned}\Sigma_{\mu\nu}(\omega;\mathbf{s},\mathbf{s}') = \int & e^{-i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}}\phi_n(z)\phi_{n'}(z) \\ & \times n^{-1}(\mathbf{r},z)\eta_{\mu\nu}(\omega;\mathbf{r},z)\,d\mathbf{r}\,dz .\end{aligned}$$

These are generalized transforms involving the density $n(\mathbf{r},z)$ of the adatom and the frequency-dependent friction tensor $\eta_{\mu\nu}(\omega;\mathbf{r},z)$. The density can be expressed in terms of the adiabatic potential $V_A(\mathbf{r},z)$ as $n(\mathbf{r},z) = Z^{-1}e^{-\beta V_A(\mathbf{r},z)}$, with $Z\equiv\int e^{-\beta V_A(\mathbf{r},z)}d\mathbf{r}\,dz$. Detailed forms for $V_A(\mathbf{r},z)$ and $\eta_{\mu\nu}(\omega;\mathbf{r},z)$ are given in Ref. 8. Both of these quantities have a weak temperature dependence arising from the Debye-Waller factor correction to the interaction potential of the adatom with the substrate.[10] In this Letter, we shall neglect this source of temperature dependence for the clarity of discussion.[11]

We now first consider the solution of the diffusion tensor for a square lattice. Under normal conditions in the study of surface diffusion, the motion of the adatom perpendicular to the surface involves only small-amplitude oscillations. Thus, for each position $\mathbf{r}$ on the surface, we can expand the potential $V_A(\mathbf{r},z)$ around the local minimum $z_0(\mathbf{r})$ as $V_A(\mathbf{r},z) \approx V_1(\mathbf{r}) + C[1+V_2(\mathbf{r})] \times [z-z_0(\mathbf{r})]^2$. Here $V_1(\mathbf{r})$ and $V_2(\mathbf{r})$ are periodic functions of $\mathbf{r}$ with the latter defined such that it contains only nonzero Fourier components. Following now the procedures outlined in Ref. 8, we can invert the matrix $\mathbf{Q}$ analytically in the limit $\omega \rightarrow 0$ to obtain the diffusion tensor

$$D_{\mu\nu} \equiv \lim_{\omega \rightarrow 0} \mathbf{Q}_{\mu\nu}^{-1}(\omega;\mathbf{G}=0,\mathbf{G}'=0,n=0,n'=0)\,.$$

The element D_{xx} is given as

$$D_{xx} = \frac{a^2 k_B T}{m} Z^{-1} \int dy \int_{-\infty}^{+\infty} du \frac{e^{-u^2}}{\sqrt{\pi}} \left[\int dx\, e^{\beta V_1(\mathbf{r})} e^{V_2(\mathbf{r}) u^2} \eta(\omega=0;\mathbf{r},u) \right]^{-1}, \tag{2}$$

where a is the linear dimension of the unit cell over which x and y are integrated. For a square lattice, $D_{yy} = D_{xx}$ by the symmetry of the integrand in Eq. (2). The normal coordinate in (2) has been transformed from z to $u \equiv \beta C[z - z_0(\mathbf{r})]$.

This remarkably simple analytic result allows us to examine the temperature dependence of $\mathbf{D}$ without any assumptions about the potentials. First, at low temperatures it is easy to see that the integral in (2) is dominated by a contribution from the saddle-point region of $V_1(\mathbf{r})$, whereas the contribution to Z is mainly from the minimum of $V_1(\mathbf{r})$. Thus, the diffusion coefficient takes the form $D = D_0 e^{-\beta\Delta}$, with Δ being the difference between the saddle point and minimum of $V_1(\mathbf{r})$. The prefactor D_0 has only a weak power-law dependence on temperature. To our knowledge, this is the first time that such an Arrhenius form has been derived analytically starting from a microscopic Hamiltonian.

From (2), we can see that the Arrhenius form only holds in the limit $\beta\Delta \gg 1$. As the temperature becomes comparable with the diffusion barrier, considerable deviations should occur. In the extreme high-temperature limit $\beta\Delta \rightarrow 0$, the barrier plays no role in diffusion and we recover from (2) the correct high-temperature behavior for the diffusion constant

$$D = k_B T / m\eta'\,, \tag{3}$$

where η' is a renormalized friction. This is of the same form as diffusion of a free Brownian particle in a uniform viscous medium. This kind of continuous crossover from the Arrhenius behavior at low temperatures to unactivated diffusion at high temperatures has been observed experimentally[12] as well as in molecular-dynamics simulations.[6] In the high-temperature limit $\beta\Delta \ll 1$, the periodicity of the substrate becomes irrelevant. Thus, motion of the particle becomes Brownian type and very different from that associated with the TST trajectories. This gives rise to the deviations from the activated behavior and the eventual linear temperature dependence of D.

Next, we will focus on the important question of diffusion anisotropy. For this purpose, we have calculated $\mathbf{D}$ for lattices of other symmetries. For simplicity, we shall henceforth set $V_2(\mathbf{r}) = 0$. The vertical motion then becomes decoupled from the diffusive motion within the plane, and need not be taken explicitly into account. This obviously does not influence the qualitative features of diffusion anisotropy.[13] We choose an effective potential as $V_A(\mathbf{r}) = V_0(\cos\mathbf{G}_1\cdot\mathbf{r} + \cos\mathbf{G}_2\cdot\mathbf{r})$, with $\mathbf{G}_1 = (\cos\theta, \sin\theta)G_0$, $\mathbf{G}_2 = (-\cos\theta, \sin\theta)G_0$, and $G_0 = \pi/(a\cos\theta\sin\theta)$. Here a is the separation between nearest-neighbor atoms. A choice of $\theta = \pi/4$ would correspond to a square lattice. Here we choose $\theta = \cot^{-1}\sqrt{2}$, which corresponds to the W(110) surface, with a centered rectangular geometry. The classical saddle points here are located on the short bridge sites between atoms.[3] Our choice of x and y axes corresponds to the principal axes of diffusion so that $D_{xy} = D_{yx} = 0$. The diagonal elements of the friction tensor were chosen to be $\eta_{xx} = \eta_{yy} = 1$, while the off-diagonal elements were set to zero. To evaluate D_{xx} and D_{yy}, we invert the matrix $\mathbf{Q}$ in (1) numerically. The number of $\mathbf{G}$ vectors kept is determined by the convergence of the inversion. A total of 335 $\mathbf{G}$ vectors were needed for the lowest temperatures studied.

In Fig. 1(a) we display our results. The approach towards the Arrhenius form is qualitatively the same as described above for the square-lattice case. The Arrhenius form sets in at about $\beta\Delta \sim 5$ with the activation energy exactly equal to the saddle-point barrier Δ. At higher temperatures a significant deviation occurs because of the crossover to the Brownian behavior, Eq. (3). In addition, at and below temperatures of $\beta\Delta \sim 10$, the anisotropy ratio D_{yy}/D_{xx} tends towards a universal geometric value $\cot^2\theta = 2$ for this surface independent of the details of the potential $V_A(\mathbf{r})$. This is precisely the result obtained assuming single random-walk jumps between unit cells via the saddle points.[3] However, we note that this geometric value is only reached at temperatures well into the activated regime. This is because the anisotropy ratio is sensitive to finite-temperature corrections to *both* the prefactor *and* the barrier.

To verify the universal character of these considerations we have also done calculations for another rhomboidal lattice, with $\theta = \pi/6$. The results are shown in Fig. 1(b). Transitions from the low-temperature activat-

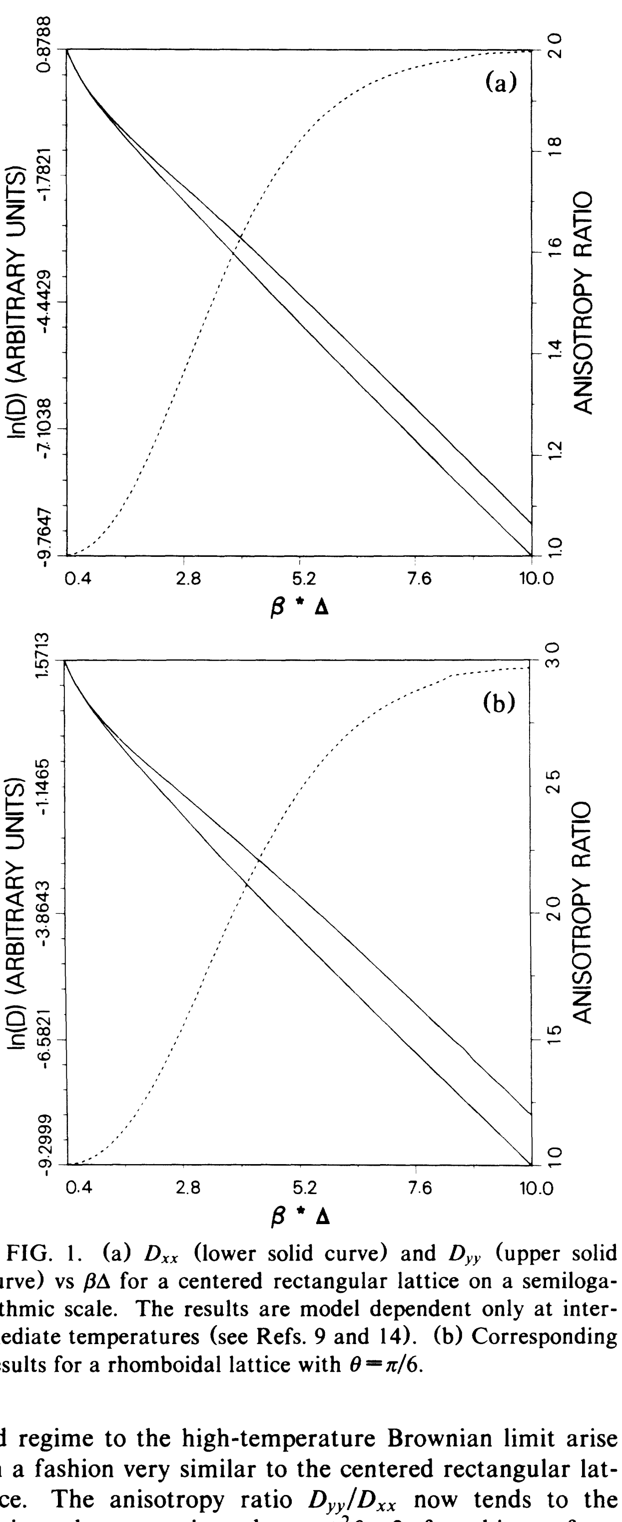

FIG. 1. (a) D_{xx} (lower solid curve) and D_{yy} (upper solid curve) vs $\beta\Delta$ for a centered rectangular lattice on a semilogarithmic scale. The results are model dependent only at intermediate temperatures (see Refs. 9 and 14). (b) Corresponding results for a rhomboidal lattice with $\theta=\pi/6$.

ed regime to the high-temperature Brownian limit arise in a fashion very similar to the centered rectangular lattice. The anisotropy ratio D_{yy}/D_{xx} now tends to the universal geometric value $\cot^2\theta=3$ for this surface. Again, this ratio is only reached well into the activated regime.

Finally, we investigate diffusion on a surface with different saddle points. We choose here a simple rectangular lattice. Using a potential

$$V_A(\mathbf{r})=V_0\cos(2\pi x/a_x)+V_0'\cos(2\pi y/a_y)\,,$$

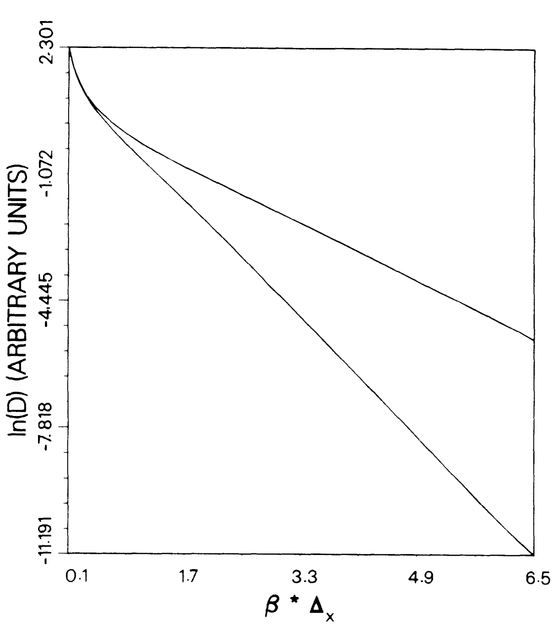

FIG. 2. D_{xx} (upper curve) and D_{yy} (lower curve) for a simple rectangular lattice. Both components cross over to an Arrhenius form corresponding to the barriers Δ_x and $\Delta_y=2\Delta_x$. Again, the high-temperature limit is given by Eq. (3).

with $V_0\neq V_0'$, creates different barriers Δ_x and Δ_y along the x and y directions, respectively. In Fig. 2 we show results of calculations for $\Delta_y=2\Delta_x$. The friction-tensor components were set as above, and 335 **G** vectors were needed for the lowest temperatures studied. Both D_{xx} and D_{yy} again tend to the Arrhenius behavior at low temperatures, but each with a different slope corresponding to the two distinct barriers. Consequently, the ratio D_{yy}/D_{xx} tends to zero exponentially fast, with the lower barrier eventually dominating diffusion at low temperatures.

In summary, we have demonstrated how the universal behavior of surface diffusion, in particular, the Arrhenius form of temperature dependence and the geometric anisotropy ratio, arise from our microscopic theory in the high-friction limit at low temperatures. Because the theory assumes no particular jump trajectories, we can follow deviations from the universal behavior as temperature increases. Eventually, the theory crosses over correctly to the behavior of a free Brownian particle. The details of this crossover depend on the form of the interaction potentials, but for most cases the results should be very similar to what we have presented here.[14] We can go beyond the high-friction limit discussed in this Letter by truncating the continued fraction for the velocity autocorrelation function at a higher level.[8] The inclusion of higher-order terms is expected to influence the details of the crossover behavior in temperature dependence and a renormalization of the friction, but we believe that the important low-temperature properties, such as the Arrhenius form and the geometric anisotropy ratio, should remain intact.

This research was supported in part by an ONR contract.

---

[1] For a general review, see, e.g., *Diffusion in Crystalline Solids,* edited by G. E. Murch and A. S. Norwick (Academic, New York, 1984).

[2] See, e.g., A. A. Deckert, J. L. Brand, M. V. Arena, and S. M. George, Surf. Sci. **208**, 441 (1989); S. C. Wang and G. Erlich, Surf. Sci. **206**, 451 (1988).

[3] M. Tringides and R. Gomer, Surf. Sci. **155**, 254 (1985); **166**, 419 (1986); J. Kjoll, T. Ala-Nissila, and S. C. Ying, Surf. Sci. **218**, L476 (1989).

[4] J. D. Doll and A. F. Voter, Annu. Rev. Phys. Chem. **38**, 413 (1987); A. F. Voter and J. D. Doll, J. Phys. Chem. **82**, 80 (1985); J. M. Cohen and A. F. Voter, J. Chem. Phys. **91**, 5082 (1989).

[5] J. C. Tully, G. H. Gilmer, and M. Schugard, J. Chem. Phys. **71**, 1630 (1979).

[6] S. Paik and S. Das Sarma, Surf. Sci. **208**, L53 (1989); J. D. Doll and H. K. McDowell, J. Chem. Phys. **77**, 479 (1982).

[7] C. P. Flynn and G. Jacucci, Phys. Rev. B **25**, 6225 (1982).

[8] S. C. Ying, Phys. Rev. B **41**, 7068 (1990).

[9] T. Ala-Nissila and S. C. Ying (to be published).

[10] See G. Wahnström, Surf. Sci. **164**, 437 (1985), and references therein.

[11] Neglecting the Debye-Waller factor gives generally the *fastest* approach towards the Arrhenius form. Calculations with realistic Debye-Waller corrections give results very similar to Fig. 1 beyond $\beta \Delta E \gtrsim 5$ (Ref. 9).

[12] V. T. Bihn and P. Melinon, Surf. Sci. **161**, 234 (1985), and references therein.

[13] Calculations with nonzero $V_2(\mathbf{r})$ indicate rather weak corrections to D at intermediate temperatures (Ref. 9).

[14] More complicated, locally distorted surface potentials are examined in detail in a forthcoming publication [T. Ala-Nissila and S. C. Ying (to be published)].