Role of Lattice Vibrations in Adatom Diffusion

Ulrike Kürpick, Abdelkader Kara, and Talat. S. Rahman
Kansas State University, Department of Physics, Cardwell Hall 116, Manhattan, Kansas 66506

(Received 22 April 1996; revised manuscript received 28 October 1996)

We have examined the impact of the vibrational free energy on self-diffusion on Cu(100) and Ag(100) within the framework of transition state theory. The local thermodynamic functions are calculated from vibrational density of states extracted using interaction potentials based on the embedded atom method. We find that, as temperature rises to 600 K, vibrational contributions lead to a decrease of the preexponential factor of about 2 orders of magnitude, a lowering of the barriers by about 10%, and an increase in the activation free energy by about 20%. The net effect on the diffusion constant is significant. [S0031-9007(97)02361-2]

PACS numbers: 68.35.Fx, 65.50.+m, 68.35.Ja, 68.35.Md

Migration of atoms on metal surfaces attracts much interest, both experimentally and theoretically, because of the important role that diffusion plays in the growth of thin films, in the formation of epitaxial layers, and in heterogeneous catalysis. For several decades now field ion microscopy (FIM) has provided very intriguing and detailed information on adatom diffusion on a number of metal surfaces [1]. These and related studies supplemented by a number of theoretical investigations, ranging from detailed computer simulations [2–4] to *ab initio* electronic structure calculations [5,6] have yielded a good deal of insight into the characteristics of diffusion processes and barriers for several materials. With the exception of a few studies in which vibrational entropy effects were found to be significant [7,8], theoretical investigations, while recognizing the role of surface vibrations in adatom diffusion, have ignored any such contribution. Energy barriers have been calculated for static lattices, and diffusion prefactors have been assumed to be devoid of vibrational entropic effects. The choice of the prefactors and the energy barriers derived from Arrhenius plots have thus involved an arbitrariness and the neglect of microscopic details of the system.

The goal of the present work is to examine the influence of vibrational internal energy and entropy on single atom migration on perfect metal surfaces. As prototype systems we have chosen to study the process of self-diffusion via single hops between equivalent equilibrium positions on Cu(100) and Ag(100). This simple hopping mechanism is consistent with direct observations of atomic displacements with the FIM for a number of bcc and fcc adatom-substrate combinations [1]. While on (100) surfaces of Al, Pt, and Ir there is evidence that diffusion occurs via an exchange mechanism [5,9], on Ag(100) and Cu(100) there has been some debate about the relevant mechanism, and no direct experimental data have been reported to our knowledge. Earlier calculations [10] using the effective medium theory had predicted exchange to be the dominant process for the diffusion of Cu on Cu(100). However, a recent molecular dynamics study [2] in agreement with previous studies based on embedded atom method (EAM) potentials [11] and also those based on *ab initio* electronic structure calculation of surface diffusion of Cu adatoms on Cu(100) [12] and of Ag on Ag(100) [13] came to the conclusion that hopping is energetically favorable over the exchange mechanism.

For an isolated atom migrating on a surface, the *intrinsic* diffusion coefficient D may be obtained from the Einstein relation, $D = \langle \Delta r^2 \rangle / 2\alpha t$, for random walk, where $\langle \Delta r^2 \rangle = N l^2$ is the mean-square displacement of the diffusing particle during the time period t, α is the dimensionality of the motion (here: $\alpha = 2$), and l is the jump distance. The number of jumps N is simply the product of the time period and a hopping rate Γ, which for thermally activated diffusion may be expressed according to transition state theory (TST) [14] as

$$\Gamma = \frac{k_B T}{h} \exp\left(\frac{-\Delta F}{k_B T} \right), \tag{1}$$

where ΔF is the difference in the Helmholtz free energy between the maximum (saddle point) and the minimum (equilibrium site) of the potential energy curve. The essential feature in Eq. (1) is the dependence of Γ on the free energy of activation, $F = \Phi + f_{\mathrm{vib}}$, where Φ is the static potential energy of the system, and $f_{\mathrm{vib}} = U_{\mathrm{vib}} - T S_{\mathrm{vib}}$ is the vibrational free energy, with U_{vib} the internal energy due to vibrations and S_{vib}, the vibrational entropy. The diffusion coefficient may now be written as

$$D = D_0(T) \exp\left(\frac{-E_d(T)}{k_B T} \right), \tag{2}$$

with

$$D_0(T) = \frac{k_B T}{h} \frac{n l^2}{2\alpha} \exp\left(\frac{\Delta S_{\mathrm{vib}}}{k_B} \right)$$

and

$$E_d(T) = \Delta\Phi + \Delta U_{\mathrm{vib}},$$

where ΔS_{vib}, ΔU_{vib}, and $\Delta\Phi$ are the differences in the respective quantities between the maximum and minimum of the potential energy curve and n is the number of jump-equivalent directions available to the adatom (here $n = 4$). In most calculations of the diffusion coefficient, ΔS_{vib} and ΔU_{vib} are assumed to be zero. Experimentalists assume the preexponential factor to be independent of temperature. As we shall see, the presence of ΔS_{vib} in the preexponential term makes it indeed almost temperature independent. In the following we will calculate explicitly Δf_{vib}, ΔS_{vib}, and ΔU_{vib} for self-diffusion on Cu(100) and Ag(100). Note that the assumption of negligible recrossing of the barrier in TST affects only the absolute values of the diffusion coefficient and not the thermodynamic functions.

In this initial study we invoke the harmonic approximation of lattice dynamics to calculate the thermodynamic functions needed in the evaluation of Eq. (2). The partition function for harmonic or quasiharmonic vibrations then yields the following equations:

$$U_{\text{vib}} = k_B T \int_0^{\nu_{\max}} N(\nu) \left(\frac{1}{2} x + \frac{x}{e^x - 1} \right) d\nu \,,$$

$$S_{\text{vib}} = k_B \int_0^{\nu_{\max}} N(\nu) \left(-\ln(1 - e^{-x}) + \frac{x}{e^x - 1} \right) d\nu \,, \tag{3}$$

where $x = h\nu / k_B T$ and $N(\nu)$ is the vibrational density of states. The notable quantity here is the vibrational density of states which can be written as $N(\nu) = \sum_i N_i(\nu)$, where $N_i(\nu)$ is the local density of states (LDOS) as projected onto the region i. Depending on the location of the adatom on the surface, it encounters a particular LDOS which, as we shall see, is strikingly different for the bridge and the fourfold positions leading to differences in the local thermodynamic functions in these two regions.

To calculate the LDOS we use the real space Green's function method which has been described in detail earlier [15]. Very briefly, the Green's function corresponding to a force constant matrix H^D can be written as

$$G(\omega^2 - i\epsilon) = [(\omega^2 - i\epsilon)I - H^D]^{-1}, \tag{4}$$

where I is a unit matrix and the LDOS of region i is given by

$$N_i(\omega^2) = -\frac{1}{\pi} \operatorname{Im}_{\epsilon \to 0} \operatorname{Tr} G^{(i)}(\omega^2 - i\epsilon) \,. \tag{5}$$

We use interaction potentials from the embedded atom method [16] to calculate the force constant matrix for adatom positions along the diffusion path (equilibrium and saddle point positions). For the adatom in the fourfold equilibrium site the total energy was minimized using a conjugate gradient technique in the $3N$-dimensional coordinate space, where N is the number of atoms in the cell. To keep the adatom in the bridge position from moving back to its equilibrium position, and to avoid the whole crystal from shifting relative to the adatom position, we fixed the coordinates of the adatom and those of the 8 edge atoms of the cubic cell in the direction of the reaction coordinate (x direction) and allowed minimization of the total energy in the $3N$-9 dimensional coordinate space.

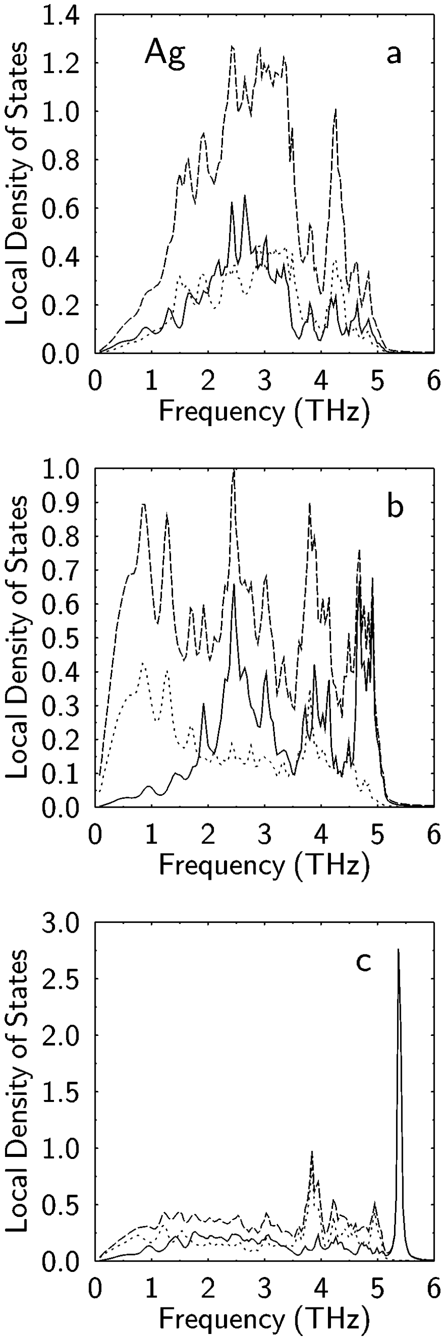

FIG. 1. The LDOS for (a) Ag(100) surface atom, (b) adatom in fourfold site, and (c) adatom in bridge site, calculated with $\epsilon = 0.1$. Dashed line shows the total LDOS, dotted line the x and y components, and solid line the z component.

The LDOS for a surface atom on Ag(100) presented in Fig. 1(a) show that the z component (perpendicular to the surface) has its major weight between 2–3 THz, while the frequency distribution in x and y directions are strictly degenerate and more bulklike [17]. The LDOS for an adatom in the fourfold position shown in Fig. 1(b) differ significantly from the one obtained for an Ag(100) surface atom. The major weight for the z component is now shifted towards higher frequencies and shows three peaks, while the LDOS for the degenerate x and y directions are now shifted towards lower frequencies. Finally, the frequency distribution for an adatom in the bridge position on Ag(100), presented in Fig. 1(c), shows a drastic change. The most striking feature is a narrow peak at high frequencies, which is exclusively contributed by a vibration in the z direction. The LDOS in the x and y directions are no longer degenerate, and the stable mode contribution of the x component is zero, consistent with TST. The LDOS for an adatom on Cu(100) exhibit similar differences between the bridge and the fourfold positions.

Our calculated values of the static activation barriers for adatom self-diffusion on Cu(100) and Ag(100) are 0.51 and 0.48 eV, respectively. These values agree very well with a previous study using two different sets of EAM potentials [11]. For Ag(100) an activation energy of (0.50 ± 0.03) eV was derived from an *ab initio* calculation [18] which is close to that obtained by us. For the hopping mechanism on Cu(100) the activation energy we find is also similar to values derived with two versions of the corrected effective medium potential (0.47 and 0.52 eV) [19], while from the effective medium theory itself this quantity is 0.43 eV [10].

The calculated activation vibrational free energy Δf_{vib}, the corresponding internal energy ΔU_{vib}, and entropy ΔS_{vib} for hopping self-diffusion on Ag(100) and Cu(100) are shown in Fig. 2. The inset in Fig. 2(c) shows the preexponential factor D_0 (including ΔS_{vib}) to be almost constant. For ΔU_{vib} [Fig. 2(b)] the results for Ag and Cu are almost identical and lead to a decrease of the diffusion barrier of about 10% at 600 K. This effect is overcompensated by the negative vibrational entropy contribution, which leads to a drastic decrease of the preexponential factor by about 2 orders of magnitude at 600 K [$\exp(\Delta S/k) \approx 0.03$]. Both effects together lead to a significant increase of the activation vibrational free energy of about 120 meV at 600 K, as can be seen from Fig. 2(a). At least for self-diffusion via hopping on Ag(100) and Cu(100) these results demonstrate clearly that vibrational contributions play an important role.

For self-diffusion on Cu(100) experimental studies using He-atom scattering, report values of $E_d = 0.40$ eV and $D_0 = (1.4 \times 10^{-4})$ cm^2/s [20], while in a subsequent study the extracted values are $E_d = (0.28 \pm 0.06)$ eV and $D_0 = 10^{-5}$ cm^2/s [21]. The temperature interval ranged from 260 to 450 K [20] and from 170 to 250 K [21] in these two experiments. A third study using low-energy ion scattering proposed an activation barrier $E_d = (0.39 \pm 0.06)$ eV [22] and finally from high-resolution low-energy electron diffraction experiments a value of $E_d = (0.36 \pm 0.03)$ eV was suggested for self-diffusion on Cu(100) [23]. For self-diffusion on Ag(100) a recent study reports an activation barrier of (0.40 ± 0.05) eV [24], from the temperature for the onset of diffusion at 160 K. In the temperature range 260 to 450 K our calculated average activation barrier for hopping self-diffusion on Cu(100) is 0.48 eV, and the preexponential factor is (3.2×10^{-4}) cm^2/s. For Ag we find an activation barrier at 160 K of 0.46 eV. The lowering of the activation barrier due to phonons thus leads to a better agreement with experimental values for Cu and Ag. Our preexponential factor for Cu which includes vibrational entropy contribution is also in excellent agreement with that suggested from the experimental data. Note that although usage of the harmonic approximation may be problematic at high temperatures, previous work [25] has shown that anharmonic effects on Cu(100) become significant only beyond 600 K. On recalculating the thermodynamic quantities discussed here in the quasiharmonic approximation [26] we find that at 600 K the calculated values of the preexponential factors for Cu and Ag change by 19% and 13%, respectively, from those obtained in the harmonic approximation. The vibrational contribution to the activation barrier is found to be the same in both approximations, and the overall conclusions reached here about self-diffusion on Ag(100) and Cu(100) remain unaffected in the quasiharmonic approximation.

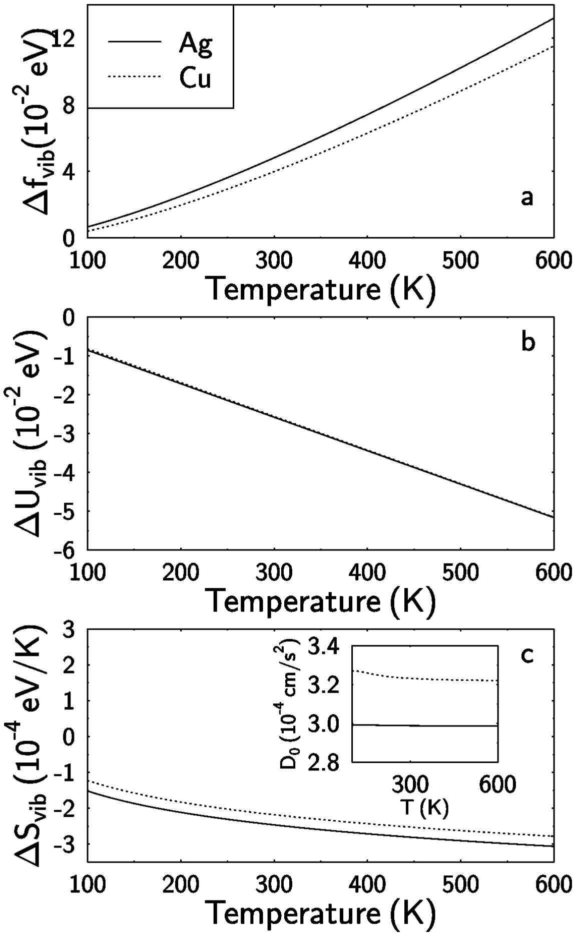

FIG. 2. The temperature dependence of (a) the activation vibrational Helmholtz free energy Δf_{vib}, (b) the activation vibrational internal energy ΔU_{vib}, and (c) the activation vibrational entropy ΔS_{vib}. The inset in (c) shows the preexponential factors including ΔS_{vib}.

In the case of self-diffusion on Ag(100) [3,27] and Cu(100) [2] molecular dynamics simulations have yielded Arrhenius behavior for the temperature dependence of the diffusion coefficients. The advantage of molecular dynamics simulations is that anharmonic vibrations are included automatically. Difficulties arise, however, in obtaining good statistics to extract accurate diffusion coefficients. Also, the temperature variation of the diffusion coefficients cannot be assigned solely to contributions from phonons. Nevertheless, for exchange mechanism on Cu(100) [2] molecular dynamics simulations find the dynamic barrier to be about 18% lower than the static one. For hopping mechanism any lowering of the barrier lies within the statistical error range. Self-diffusion studies on Rh(100) and Ag(100), on the other hand, report [3] very similar values for the static and dynamic activation barriers. However, as the statistical error for the dynamic barrier in these calculations is about 8%, the effect of the vibrational internal energy is difficult to extract from this simulation. Molecular dynamics simulations for self-diffusion on flat fcc(111) surfaces have led to debatable results. While for self-diffusion on Ag(111) and Au(111) [28] no difference was found for the dynamic and static barriers, significantly higher dynamic barriers as compared to the static ones have been reported for Ag(111) and Rh(111) [4]. For the latter case the higher barriers are shown to result from frequent recrossing events on the smooth (111) surface. These studies point to the timeliness of the subject and the need for detailed calculations of the vibrational contributions to self-diffusion in a systematic study as presented in this Letter.

To test the dependence of the results quantitatively on the interaction potential we have repeated our calculations [26] with another type of EAM potentials as fitted by Voter and Chen [29]. We find that while for Cu(100) the results are the same as those presented here, there are small differences in the preexponential factors calculated for Ag(100). We have also made extensive comparisons [30] between our results using the two types of EAM potentials and available first principles results [13] for static energy barriers, for several diffusion mechanisms on flat and stepped surfaces of Ag(100), to conclude that the results presented here are reliable despite the empirical nature of the interaction potentials.

In summary, our investigation of the role of phonons in self-diffusion on (100) surfaces of Cu and Ag establishes that vibrational effects should be included in any complete description of the temperature dependence of the diffusion coefficient. We find that inclusion of vibrational internal energy lowers the activation barrier by about 10% for Ag and Cu, as temperature rises to 600 K, while vibrational entropy produces a decrease of the preexponential factor of about 2 orders of magnitude. At 600 K, there is thus a vibrational free energy contribution of 120 meV, and a diffusion constant that is lowered by about an order of magnitude. The diffusion barriers and preexponential factors arising from these results are in excellent agreement with experimental data. Most importantly, these calculations provide for the first time a reliable method for the calculation of preexponential factors which may then be used in any theoretical and experimental study of growth at crystal surfaces. Results of similar calculations on Ni(100) [26] convince us of the generality of conclusions reached here *vis-à-vis* the (100) surface. It will be interesting to examine the dependence of the vibrational activation free energy on surface orientation.

U. K. thanks the Deutsche Forschungsgemeinschaft for a postdoctoral grant. We thank S. Durukanoglu, P. Staikov, L. Weaver, and P. Kürpick for fruitful discussions. This work was supported in part by the NSF under Grant No. DMR-9120440 and computations were performed on a Convex Exemplar supported in part by Grant No. DMR-9413513.

---

[1] G. Ehrlich, Surf. Sci. **299/300**, 628 (1994).
[2] G. A. Evangelakis *et al.*, Surf. Sci. **347**, 376 (1996).
[3] D. E. Sanders and A. E. DePristo, Surf. Sci. **260**, 116 (1992).
[4] D. E. Sanders *et al.*, Surf. Sci. **264**, L169 (1992).
[5] P. J. Feibelman, Phys. Rev. Lett. **65**, 729 (1990).
[6] R. Stumpf and M. Scheffler, Phys. Rev. Lett. **72**, 254 (1994).
[7] E. Kaxiras and K. C. Pandey, Phys. Rev. B **47**, 1659 (1993).
[8] L. B. Hansen *et al.*, Surf. Sci. **289**, 68 (1993).
[9] G. L. Kellogg *et al.*, Phys. Rev. Lett. **64**, 3143 (1990); C. Chen *et al.*, Phys. Rev. Lett. **64**, 3147 (1990).
[10] L. Hansen *et al.*, Phys. Rev. B **44**, 6523 (1991).
[11] C. L. Liu *et al.*, Surf. Sci. **253**, 334 (1991).
[12] C. Lee *et al.*, Surf. Sci. Lett. **306**, L575 (1994).
[13] B. D. Yu and M. Scheffler, Phys. Rev. Lett. **77**, 1095 (1996).
[14] S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill, New York, 1941); D. A. King, J. Vac. Sci. Technol. **17**, 241 (1980).
[15] S. Y. Wu *et al.*, Phys. Rev. B **49**, 7957 (1994).
[16] S. M. Foiles *et al.*, Phys. Rev. B **33**, 7983 (1986).
[17] G. Tréglia *et al.*, J. Phys. (Paris) **46**, 987 (1985).
[18] G. Boisvert *et al.*, Phys. Rev. B **52**, 9078 (1995).
[19] L. J. Perkins and A. E. DePristo, Surf. Sci. **294**, 67 (1993).
[20] J. J. Miguel *et al.*, Surf. Sci. **189/190**, 1062 (1987).
[21] H.-J. Ernst *et al.*, Phys. Rev. B **46**, 1929 (1992).
[22] M. Breeman *et al.*, Surf. Sci. **269/270**, 224 (1992).
[23] H. Dürr *et al.*, Surf. Sci. **328**, L527 (1995).
[24] M. H. Langelaar *et al.*, Surf. Sci. **352–354**, 597 (1996).
[25] L. Yang *et al.*, Phys. Rev. B **44**, 13 725 (1991).
[26] U. Kürpick and T. S. Rahman (to be published).
[27] G. Boisvert and L. Lewis, Mater. Res. Soc. Symp. Proc. **317**, 71 (1994).
[28] R. Ferrando and G. Tréglia, Surf. Sci. **331–333**, 920 (1995).
[29] A. F. Voter *et al.*, Proc. Mater. Res. Soc. **82**, 175 (1986).
[30] U. Kürpick and T. S. Rahman, in "Surface Diffusion: Atomistic and Collective Processes," NATO-ASI Series (to be published).