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The mechanism of surface heterodiffusion at elevated temperatures

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Abstract

Molecular dynamics simulations employing the Lennard-Jones potential have been performed on Kr/Ar(111) to investigate the nature of high-temperature surface heterodiffusion. These suggest that high activation energies and preexponential factors observed experimentally at temperatures above approximately 0.70 $T_m$ arise from adatom–vacancy pair formation, which sharply increases the number of mobile species. Evidence is also obtained that at intermediate temperatures (0.45 $T_m < T < 0.66 T_m$), Arrhenius curves for mass transfer diffusivity can depend on both coverage and adsorbate interactions. For adsorbates which exhibit islanding, low coverage diffusion is characterized by an activation energy equal to the enthalpy of migration, whereas at moderate coverage the activation energy contains an additional term due to the enthalpy of formation of mobile adatoms from immobile islands.

Keywords: Growth; Molecular dynamics; Single crystal surfaces; Surface diffusion; Surface melting

Surface diffusion plays a key role in a number of technologically important physical processes, including crystal growth and dissolution, sintering, and heterogeneous catalysis. Surface diffusion at low temperature has been intensively studied and is reasonably well understood mechanistically [1,2]. At temperatures where thermal processes dominate, the most common diffusion mechanism is adatom hopping between nearly isoenergetic positions on the potential energy surface. Different systems can be compared by normalizing to the bond strength via the corrugation ratio ($\Omega$), the ratio of the activation energy for surface diffusion to that for desorption. On metal surfaces adatom hopping is characterized by a corrugation ratio ($\Omega$) in the range 0.05–0.2 and a preexponential factor ($D_0$) near $10^{-3}$ cm$^2$/s [2]. Self-diffusion can also occur on both homogeneous [3] and heterogeneous [4] surfaces, particularly fcc (100) surfaces, by sequential exchange between an adatom and a substrate atom. This mechanism is characterized by activation energies and preexponential factors similar to those observed for adatom hopping [2].

The situation at elevated temperatures is not as clear. Self-diffusion on metal surfaces often shows Arrhenius behavior characterized by a discontinuity at approximately 0.70–0.75 $T_m$ [5]. Above this temperature the activation energy increases by approximately 2$\times$ and, more dramatically, the preexponential factor rises by 3–6 orders of magnitude. Although diffusion on semiconductor surfaces has been less well studied, several recent experiments measuring heterodiffusion at high temperatures have also yielded high activation energies and preexponential factors [6–10]. The peak

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pre-exponential factors obtained range from $10^2$–$10^6$ cm$^2$/s for diffusion of several species on Ge(111) and Si(111) [6–10].

The high-temperature measurements on metal and semiconductor surfaces suggest an alternative mechanism for surface diffusion, and several competing theories have been proposed. Bonzel has suggested that at high temperatures surface diffusion occurs primarily by freely rotating dimers and trimers [5]. However, the jump lengths required ($10^4$–$10^5$ atomic diameters) greatly exceed the expected mean free path of such species [11]. In addition, FIM experiments on Ir(111) suggest that surface clusters dissociate far below the melting point [12], as expected from simple thermodynamic arguments. Other investigators have suggested that surface premelting at elevated temperatures allows cooperative diffusive motion as seen in liquids [13,14], where diffusivities are typically $10^{-5}$ cm$^2$/s. However, this explanation is improbable since diffusion in liquids is characterized by extremely low activation energies not observed for the systems in question.

Recent molecular dynamics simulations on Ar(111) and Ge(111) surfaces suggest an alternative, physically reasonable explanation for anomalous high temperature surface self-diffusion [11,15]. These demonstrated that above approximately 0.70 $T_m$, enhanced creation of adatom–vacancy pairs on terraces sharply increased the number of mobile adatoms. Thus, high temperature experiments which measure mass transfer diffusivities have activation energies that include the enthalpy of activation for adatom–vacancy pair formation and preexponential factors that include the entropy of activation. As is the case for bulk vacancy formation [16], surface vacancy formation should be accompanied by significant lattice relaxation. This yields a large entropy of activation, which enters the prefactor as

$$D_0 = \frac{1}{2} v \lambda^2 e^{\Delta S}/R.$$  

Thus the preexponential factor $D_0$ increases exponentially with an increase in the activation entropy. The present work reports the first simulational evidence that high activation energies and preexponential factors can arise for high temperature sur-

face hetero-diffusion through the formation of adatom–vacancy pairs. In addition, the present work also provides evidence that at intermediate temperatures and a surface coverage $\theta = 0.08$, the mass transfer diffusivity is dominated by formation of mobile adatoms from immobile islands. This is similar to a recent suggestion that adatom sources such as kink sites may become activated at intermediate temperatures [2].

The details of the simulation method have been described previously and will be only briefly outlined here [11,15]. Bulk simulations were employed to obtain the zero-pressure lattice constants using the Virial theorem and correcting for the potential cut-off at 3.2$\sigma$. The Ar(111) surface ensemble consists of either one or twenty adatoms placed atop three layers of 256 mobile atoms, which sit atop three layers of 256 fixed atoms. The equations of motion were integrated using Beeman’s third-order predictor-corrector algorithm [17] after initialization with a random normal distribution of velocities. Each simulation was equilibrated for about 54 ps, then between 4 and 20 simulations (54 ps) were performed at each temperature. Some low temperature simulations were extended to 270 ps to allow significant diffusion. The intrinsic diffusivity ($D_1$) was calculated from [2]

$$\langle x^2 \rangle = 4D_1 t,$$

where the ensemble average is conducted only over the mobile Kr(Ar) atoms. Visual inspection of the simulations reveals that only adatoms are mobile. Due to interchange between the adlayer and top substrate layer, the intrinsic diffusivities obtained at high temperatures were unreliable. The mass transfer diffusivity ($D_M$) was obtained from

$$\langle x^2 \rangle = 4D_M t,$$

where the ensemble average is conducted over all Kr(Ar) atoms in the adlayer and the top substrate layer [5].

The intermolecular potential chosen was the Lennard-Jones potential, where $\sigma = 3.405$ Å and $\epsilon = 119.8$ K for Ar [18], and $\sigma = 3.633$ Å and $\epsilon = 167.0$ K for Kr [19]. For the Ar–Kr interaction, the distance parameter was chosen as the arithmetic mean and the energy parameter the geometric
mean of the self-interaction parameters. The simulations were designed to recreate the experimental conditions under which heterodiffusion has been measured on Ge(111) [6,7]. Prior to measurement, the surface was partially covered with adsorbate, then annealed to about 400°C. Above approximately 300°C, Ge(111) undergoes a disordering phase transition similar to surface melting, where atom interchange between the adlayer and top substrate layer is rapid [20]. This suggests the adsorbate is partitioned between the adlayer and the top substrate layer before measurement, so random partitioning of Kr between the adlayer and the top substrate layer was assumed when initializing the simulations.

The results for the mass transfer diffusivity of Kr and Ar at coverages of one adatom (θ=0.004 ML) and twenty adatoms (θ=0.08 ML) are shown in Figs. 1 and 2. A clear discontinuity is seen in all Arrhenius plots at approximately 0.65–0.70 $T_m$. Visual inspection of the simulation results shows clearly that the increased mass transfer at high temperature arises from an increase of mobile adatoms caused by adatom–vacancy pair formation. Fig. 3 shows graphically the movement of an adatom away from a vacancy about 1 ps after creation. It should be noted that adatom–vacancy pair formation has been suggested to cause pre-melting on close-packed surfaces [21,22]. The mechanism described herein does not require pre-melting, as many surfaces roughen at elevated temperatures [23] and might also exhibit increased surface mobility.

Table 1 summarizes the activation energies and preexponentials seen for Kr and Ar at the two surface coverages studied. The results are in agreement with those reported previously [11], although the low-temperature activation energies at θ=0.004 are lower than previous results due to better statistics. An important difference between Figs. 1 and 2 is the higher activation energies and preexponential factors observed for the higher surface coverage (θ=0.08 ML) at low temperature. Visual inspection of the simulations reveals a simple explanation, the intermittent creation of mobile adatoms from the edges of immobile

Table 1

<table>
<thead>
<tr>
<th>Species</th>
<th>$E_{	ext{diff}}$ (cal/mol)</th>
<th>$D_0$ (cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>θ=0.004 (1 adatom)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kr ($T&lt;0.66 \ T_m$)</td>
<td>109</td>
<td>$7.0 \times 10^{-7}$</td>
</tr>
<tr>
<td>Kr ($0.66 \ T_m&lt;T&lt;0.83 \ T_m$)</td>
<td>2575</td>
<td>$6.7 \times 10^{-3}$</td>
</tr>
<tr>
<td>Ar ($T&lt;0.66 \ T_m$)</td>
<td>116</td>
<td>$1.3 \times 10^{-6}$</td>
</tr>
<tr>
<td>Ar ($0.66 \ T_m&lt;T&lt;0.83 \ T_m$)</td>
<td>2337</td>
<td>$1.7 \times 10^{-3}$</td>
</tr>
<tr>
<td>θ=0.08 (20 adatoms)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kr ($T&lt;0.66 \ T_m$)</td>
<td>255</td>
<td>$3.1 \times 10^{-5}$</td>
</tr>
<tr>
<td>Kr ($0.66 \ T_m&lt;T&lt;0.80 \ T_m$)</td>
<td>1101</td>
<td>$7.6 \times 10^{-2}$</td>
</tr>
<tr>
<td>Ar ($T&lt;0.62 \ T_m$)</td>
<td>272</td>
<td>$5.7 \times 10^{-5}$</td>
</tr>
<tr>
<td>Ar ($0.62 \ T_m&lt;T&lt;0.83 \ T_m$)</td>
<td>809</td>
<td>$1.3 \times 10^{-2}$</td>
</tr>
</tbody>
</table>
islands. Thus the activation energy for mass transfer diffusion contains contributions from both the enthalpy of adatom formation and the enthalpy of migration. The present results suggest these are of approximately equal magnitude. A similar prediction has recently been made that at intermediate temperatures, mass transfer diffusivity will be dominated by adatom formation from kinks [2].

As seen previously, the Arrhenius curves in Figs. 1 and 2 clearly flatten above approximately 0.83 $T_m$ [11]. The surface diffusivity plateau of approximately $10^{-5} \text{cm}^2/\text{s}$ coincides with the decline of the two-dimensional structure factors [15], providing strong evidence this is caused by surface melting.

References


Fig. 3. (a), (b) Formation and (b), (c) diffusion of an adatom on an Ar(111) terrace.