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A molecular dynamics simulation of the diffusion of sodium on a Cu(001) surface

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Abstract

A molecular dynamics simulation of the diffusion of sodium adatoms on a Cu(001) surface has been performed. A pairwise Morse potential, fitted to the adatom adsorption geometry, binding energy, vibrational frequencies and activation energy for diffusion is used to model the sodium–copper interaction. Good agreement is obtained with quasielastic helium scattering data for the system, confirming the interpretation that sodium diffuses by jumps from one four-fold hollow site to another with an effective activation energy of 51 meV and a jump attempt frequency of 0.53 THz. The measured jump rate is lower than that predicted by transition state theory. The MD simulation suggests that this discrepancy arises because the rate of energy transfer between the adatom and the substrate is so slow that it controls the attempt rate rather than the vibrational frequencies of the adatom as transition state theory would predict.

1. Introduction

Quasielastic scattering techniques have been shown to be powerful probes of surface diffusion and melting [1–4]. When a particle such as a helium atom or neutron is scattered "elastically" from a moving surface species its energy shows a quasielastic broadening. The magnitude of this broadening varies with the scattering wavevector ($\boldsymbol{k}$) in a way determined by the details of the microscopic motions of the scattering particles. Experimental measurements of the $\boldsymbol{k}$ dependence of the quasielastic broadening can therefore be used to determine a diffusion rate and mechanism. It has been shown that for kinematic scattering, the cross section for scattering from a set of identical scatterers is proportional to the scattering function [5,6]

$$\Gamma(\boldsymbol{k}, \omega) = \int\int \exp[\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{r} - \omega t)] G(\boldsymbol{r}, t)\, \mathrm{d}\boldsymbol{r}\, \mathrm{d}t, \tag{1}$$

where the pair correlation function $G(\boldsymbol{r}, t)$ is defined as the probability that a particle will be found at position $\boldsymbol{r}$ at a time t given that there was a particle at the origin at time $t = 0$. For simple models of the surface motion such as continuous or jump diffusion, $G(\boldsymbol{r}, t)$, and hence $\Gamma(\boldsymbol{k}, \omega)$, can be calculated analytically. For example it has been shown that for a surface jump diffusion mechanism with instantaneous jumps

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with vectors $\{j\}$ and mean jump frequencies $\{\nu_j\}$ the quasielastic peak shape is a Lorentzian with an energy FWHM

$$\Delta E(\Delta K) = 2\hbar \sum_j \nu_j [1 - \cos(\Delta K \cdot j)], \qquad (2)$$

where ΔK is the component of the scattering wavevector parallel to the surface [8]. Such simple models are useful for classifying the motion in question, but have proved insufficient for interpreting the detailed data available from quasielastic helium scattering measurements [1,2]. It is therefore necessary to resort to molecular dynamics simulations in order to obtain a full understanding of the available data. If a MD simulation can be performed that reproduces the experimental data reliably and if enough experimental data is available to rule out fortuitous agreement with the simulation, then the simulation can be used to assess the effect of the various system parameters on the diffusion mechanism.

In this paper we present a MD simulation of the diffusion of isolated sodium atoms on Cu(001). This system was chosen because in addition to our quasielastic scattering measurements, which are reported in detail elsewhere [2], there is a good basis of data that has either been directly measured, or may be estimated from similar systems. This substantial data set can be used to give a solid basis for a MD simulation which can then in turn shed new light upon the diffusion processes involved.

2. Experimental data

By studying the diffuse scattering of helium atoms from the surface we have shown that low coverages of sodium on Cu(001) exist as isolated adatoms held apart by the repulsive dipole–dipole interactions between them [7]. The binding energy (BE) of the sodium adatoms on the surface is estimated to be 2.5 eV on the assumption that it should be similar to that measured for sodium on the Ni(001) surface [9]. From the diffusion jump length consistent with the quasielastic scattering results [2] it may be deduced that sodium adsorbs at a unique site in the unit cell, i.e. either at an on-top site or a four-fold hollow site. The latter is chosen because LEED measurements indicate that this site is occupied in the 1 monolayer structure of sodium on Ni(001) and Al(001) [10,11] and top site adsorption of alkalis on metal surfaces has only been reported for the larger potassium and rubidium atoms on (111) surfaces which are more closely packed than the (001) surface [12]. The height (h) of the sodium above the surface is estimated to be 2.2 Å by taking the Na–Ni separation for sodium adsorbed on Ni(001) determined from LEED measurements [10] and adjusting it according to the difference between the copper and nickel bulk atomic radii. Two vibrational frequencies have been measured for isolated sodium atoms on Cu(001). The frequencies of the mode polarised perpendicular to the surface (ν_z) and the two degenerate modes (ν_x, ν_y) polarised parallel to the surface have been determined with EELS and inelastic helium atom scattering to be 4.5 and 1.23 THz, respectively [2,13].

The quasielastic helium scattering measurements are reported elsewhere [2]. Fig. 1 shows the dependence of the quasielastic energy broadening (ΔE) on ΔK, the component of $\boldsymbol{k}$ parallel to the surface in the [100] direction, for two surface temperatures ($T_s = 300$ K and $T_s = 200$ K). The data are characterised by a broadening that is zero at $\Delta K = 0$, rises to a maximum at around $\Delta K = 1.7$ Å^{-1} and then remains approximately constant for $T_s = 200$ K and for $T_s = 300$ K drops slightly. The jumps are in the $\langle 110 \rangle$ directions and proceed from one four-fold hollow site to another over two-fold bridge sites. (See insert to Fig. 1.) This behaviour contrasts with that expected for continuous diffusion ($\Delta E \propto (\Delta K)^2$) and suggests a jump diffusion mechanism. The solid and dashed lines in Fig. 1 show the $\Delta E(\Delta K)$ predicted by Eq. (2) for single and single plus a fraction x of double jumps, where x is 0.32 for $T_s = 200$ K and 0.16 for $T_s = 300$ K. Although a good fit to the data is obtained in the region $0 < \Delta K < 2.5$ Å the experimental data does not show the zero broadening at $\Delta K = 3.48$ Å^{-1} predicted by the simple analytical model. This zero arises analytically because the model assumes that

the atoms remain stationary on lattice sites between jumps and that the jumps are instantaneous. In this simplified model, therefore, the scatterers always sit on lattice sites. Therefore, at $\Delta K = 3.48$ Å^{-1}, which corresponds to the position of the first-order diffraction peak, all the atoms scatter with the same phase, the scattering helium atom sees no change in the scattering when a jump occurs and so experiences no quasielastic broadening. The non-zero value of the experimental broadening at $\Delta K = 3.48$ Å^{-1} shows, however, that the random motion of the adatoms about their mean adsorption sites, and the finite time taken to perform a jump contribute significantly to the quasielastic broadening. This demonstrates the need for a molecular dynamics model that can simulate realistically the detailed motion of the adatoms.

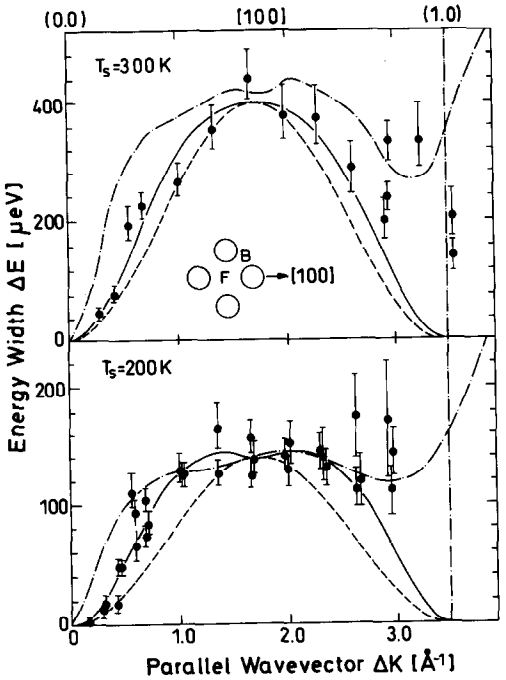

Fig. 1. Wave vector dependence of the quasielastic peak energy broadening in the [100] direction for helium atoms, incident energy 15.15 meV, scattered from a coverage $\theta = 0.1$ of sodium atoms on a Cu(001) surface [2]. Dashed curve: fit for single jumps between four-fold sites. Solid curve: single jumps with an additional fraction of double jumps of 0.16 at 300 K and 0.32 at 200 K. Dash-dotted line: broadening predicted by MD simulation. Insert: location of four-fold (F) adsorption site and two-fold transition state bridge site (B) with respect to the first copper surface layer.

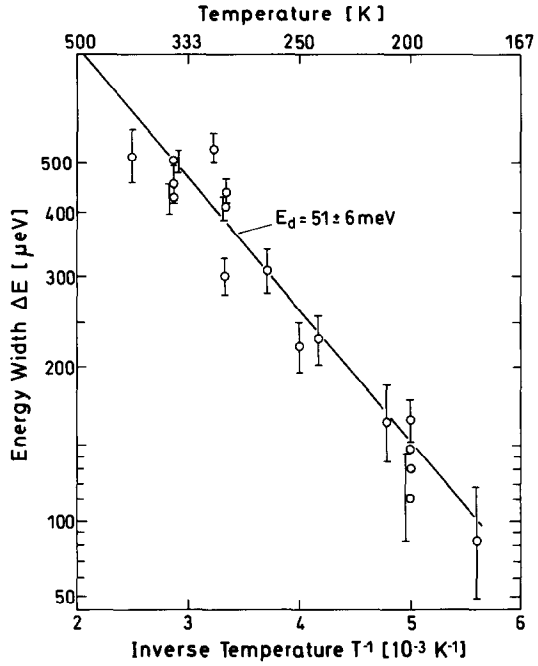

Fig. 2. Arrhenius plot of the measured energy width at $\Delta K = 1.74$ Å^{-1} for the quasielastic peak in the TOF spectra of helium atoms, incident energy 15.15 meV, scattered from sodium adatoms ($\theta = 0.1$) on a Cu(001) surface in the [100] direction.

The activation energy (E_d) and preexponential factor (ν_0) for the jump process, as defined by the equation

$$\nu_j = \nu_0 \exp(-E_d/k_B T_s) \quad (3)$$

were determined by measuring the temperature dependence of $\Delta E(\Delta K)$ at the local maximum at $\Delta K = 1.74$ Å^{-1}. Fig. 2 shows the Arrhenius plot obtained, which yields values of 0.53 ± 0.2 THz and 51 ± 6 meV for ν_0 and E_d, respectively. (ν_j is taken here as the total jump rate in the forward and backward directions in one of the two, symmetry related, ⟨110⟩ directions.)

3. Molecular dynamics simulation

The molecular dynamics simulation was performed for a microcannonical ensemble consist-

ing of a single sodium atom adsorbed on a slab of four layers of 8×8 freely moving copper atoms supported on a fifth layer of fixed copper atoms. Cyclic boundary conditions were imposed in the two coordinate directions parallel to the surface. Only nearest neighbour Cu–Cu interactions were considered, and these were modelled by the single force constant, value 28 N/m, that is necessary to fit the bulk phonon dispersion curves [14]. The sodium–copper interaction was modelled with a pairwise Morse potential of the form

$$V(r) = V_0\{1 - \exp[-\beta(r - r_0)]\}^2, \qquad (4)$$

summed over successive shells of nearest neighbour copper atoms until convergence was achieved at a distance of 4 times the Cu–Cu separation. The values of V_0, β and r_0 were varied to optimise the simulation's fit to the measured or estimated values of the BE, h, ν_x, ν_z and E_d, values (with percentage deviations for the measured or estimated values) of 2.35 eV (−6%), 1.8 Å (−18%), 1.34 THz (9%), 3.8 THz (−16%), and 49 meV (−4%) being obtained for $V_0 = 0.135$ eV, $\beta = 0.875$ Å^{-1}, and $r_0 = 3.30$ Å. In order to determine the simulated values of ν_x and ν_z, the system was first allowed to relax into its minimum energy configuration, the adatom then displaced by a fraction of an ångström in the x or z directions and the frequency obtained from the maximum in the Fourier transform of the atom's subsequent displacement as a function of time. The value of E_d for a particular set of potential parameters was determined dynamically, that is by running the simulation at different temperatures and then analysing an Arrhenius plot of the temperature dependence of the diffusion rate. The static "activation energy", i.e. the difference between the system's energy minima for sodium in the four-fold hollow site and the bridge site transition state (see insert to Fig. 1) was 71 meV, 24% larger than the dynamic value. A similar effect has been reported by Chen and Ying [15,16] in a theoretical analysis of the same data based on the Mori projection operator formalism in which they found a static activation energy of 67 meV was required to fit the dynamical data. They ascribe the difference to the influence of the vibrational motion on the quasielastic broadening at the local maximum that occurs at $\Delta K = 1.74$ Å^{-1}.

The choice of a pairwise Morse potential as a model sodium–copper interaction that could be fitted to the available experimental data was made because of the transparent way in which the three Morse parameters can be related to the potential's depth, breadth and location of its minimum. Ideally, many body effects should be included in the calculation. However, since a reasonable fit to the five items of experimental data is obtained, even though the three parameter Morse potential is over constrained, it seems that a realistic potential has been created and that the effects of many body forces are smaller than the errors in our fit to the data. Further proof of this is given by the remarkably good fit to the experimental ΔK dependence of the quasielastic energy broadening produced by the simulation. It should be emphasized that the magnitude and ΔK dependence of the calculated quasielastic broadening were not fitted to the data, but are the results obtained from the simulation with the potential fitted as described above.

The simulation was started with the atoms in their minimum potential configuration, i.e. with the sodium atom sitting in the four-fold site and the lattice fully relaxed. Each atom was given a random amount of kinetic energy in each coordinate direction taken from a Boltzmann distribution with an average of $k_B T_s$. Within less than 1 ps the energy was distributed evenly between potential and kinetic energy by the vibrations of the atoms. Each simulation was run for 500 ps with the integration of the classical equations of motion performed by the robust fourth-order Runge–Kutta method and a time step of 0.01 ps. The data presented in Fig. 1 represents averages over eight such runs. In order to eliminate any effect caused by the accumulation of integration errors the total kinetic energy of the system of N particles was rescaled to $\frac{3}{2}N k_B T_s$ every 10 ps by multiplying all the individual velocities by an appropriate scalar. Such a model, with only one moving adatom, can only yield $G_s(\boldsymbol{r}, t)$, the self-correlation function of the adatom's position, i.e. the probability that if an atom is found at the

origin at $t = 0$ then the *same* atom will be found at position r at a time t later. Vineyard showed [17] that if the atoms move independently of each other then the Fourier transform $\Gamma_s(k, \omega)$ of $G_s(r, t)$ is related to the Fourier transform $\Gamma(k, \omega)$ of $G(r, t)$ (Eq. (1)) by:

$$\Gamma(k, \omega) = \Gamma_s(k, \omega)[1 + \gamma(k)], \quad (5)$$

where $\gamma(k)$ is the Fourier transform with respect to r of $G(r, t = 0)$. Since $\gamma(k)$ is independent of ω, the shape of the quasielastic peak is entirely determined by $\Gamma(k, \omega)$, which is derived from the motion of a single particle and is identical to that given by $\Gamma_s(k, \omega)$, which is derived from the motion of all the particles. Thus, if inter-adatom interactions are negligible, the shape of the quasielastic peak can be determined from the motion of a single adatom. To assess if this condition is fulfilled for the present system, the inter-adatom potential was modelled with the dipole–dipole interaction proposed by Kohn and Lau [18] which has been shown to be consistent with the low temperature ordering of the adatoms on the surface [7]. A typical configuration of one sodium adatom surrounded by six nearest neighbours was considered. If one of these neighbours is completely removed, the activation energy for jumps towards its position is reduced by only 1.0 meV, which is small in comparison to the total activation energy, and increases the jump probability in that direction by only 4%. Thus at these relatively large adatom separations (mean value 12.3 Å), the coupling of the adatoms motion is indeed weak, the Vineyard approximation should apply, and the quasielastic peak shape is given by $\Gamma_s(k, \omega)$. Γ_s may be calculated directly from the simulated position of the adatom as a function of time ($r_s(t)$) by the following method, provided the model is run for long enough or repeated enough times to give good averaging. Use is made of the relation:

$$\Gamma_s(k, \omega) = |S(k, \omega)|^2, \quad (6)$$

which follows from the convolution theory of Fourier transforms where

$$S(k, \omega) = \int\int \exp[i(k \cdot r - \omega t)] P(r, t)\, dr\, dt, \quad (7)$$

and $P(r, t)$ is the probability of finding a particle at position r at time t. P is given for a single particle MD simulation by:

$$P(r, t) = \delta(r - r_s(t)), \quad (8)$$

where $r_s(t)$ is the particles position as a function of time.

In order to compare the results of the molecular dynamics model with the measured data, experimental spectra are first simulated by smoothing the calculated peak shape with the experimental resolution function (a Gaussian of FWHM 0.42 meV, 0.102 THz) and then, exactly as for the analysis of the experimental data, the width ΔE of the Lorentzian is found, which, when smoothed by the experimental resolution function, gave the best fit to the calculated peak shape. The experimental resolution is too poor to permit any more detail of the peak shape other than its width to be extracted from the data.

In order to understand the mechanism of the adatom's diffusion, it is useful to have a measure of the rate at which energy is transferred between the adatom and the substrate. To do this an energy function $E(t)$ was defined which is given by the sum of the kinetic energy of the adatom and an effective potential energy, modelled by the two-dimensional potential:

$$V(x, y) = A[\cos(2\pi x/a) + \cos(2\pi y/a)]. \quad (9)$$

A has the value $\nu_x^2 m_{Na} a^2$ (m_{Na} is the mass of the sodium atom and a is the separation between four-fold hollow sites on the surface) chosen so as to give the correct vibrational frequency for motion parallel to the surface. Although this is only an approximation to the variation of the total energy of the system as the adatom moves across the surface, as can be seen from the small amplitude oscillations in the autocorrelation function associated with the vibration of the atom parallel to the surface that are found in Fig. 6, it permits a reasonable estimate of the potential energy associated with the position of the sodium adatom. The autocorrelation function is then calculated as

$$A(t) = \langle E(t)E(t - t_0) - \langle E(t)\rangle^2 \rangle \quad (10)$$

for a range of values of t_0. As can be seen from

Fig. 6, $A(t)$ decays approximately exponentially as a function of t_0. The rate of decay can be related to a mean value of the friction, η, by the following formula:

$$\frac{1}{A}\frac{\mathrm{d}A}{\mathrm{d}t} = \frac{1}{v}\frac{\mathrm{d}v}{\mathrm{d}t} = \eta, \tag{11}$$

where v is the velocity of the adatom. This friction parameter is widely used as a measure of the rate of energy transfer between a diffusing adsorbate and a substrate [15,16,20,21].

4. Results and discussion

Fig. 3 shows a typical 50 ps time interval from a simulated trajectory of a sodium adatom on the surface. The trajectories are characterised by large amplitude oscillations (rms value of roughly 0.3 Å) around four-fold hollow adsorption sites, interrupted by jumps over one or more inter-site separations. The jumps proceed in the ⟨110⟩ directions via two-fold bridge sites. The jump rate at 300 K is very rapid, one occurring, on average, every five or six vibrational periods. The Γ_s obtained from the simulation by using Eqs. (6)–(8) is shown as a function of frequency in Fig. 4 and in Fig. 5 the simulated spectra obtained by

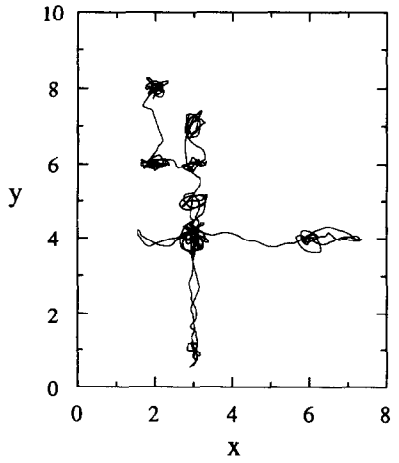

Fig. 3. A 50 ps interval from a simulated trajectory of a single sodium adatom on a Cu(001) surface, $T_s = 300$ K. The x and y distances are given as multiples of the inter-four-fold hollow site separation, 2.55 Å.

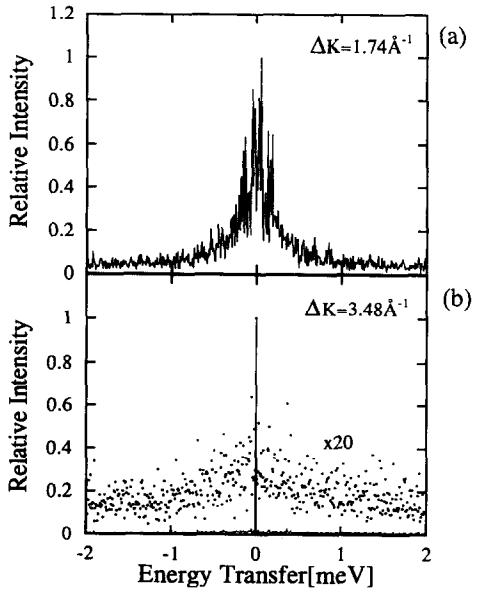

Fig. 4. Γ_s, the theoretical quasielastic peak shape, unbroadened by instrumental factors, plotted as a function of energy transfer from the helium atom for two values of momentum transfer to the surface for $T_s = 300$ K. In (b) the background is shown magnified by 20 to show the broad shoulder around the sharp central peak which acts to broaden the measured peak (Fig. 5b).

smoothing Γ_s with the instrumental resolution function are shown. At $\Delta K = 1.74$ Å^{-1}, where a maximum in the broadening occurs, Γ_s has an approximately Lorentzian profile, whereas at $\Delta K = 3.48$ Å^{-1} Γ_s is characterised by a δ-function like peak with a broad shoulder. This broad shoulder is caused by the large amplitude oscillations and finite jump times exhibited by the adatoms and explains the finite broadening observed at $\Delta K = 3.48$ Å^{-1}.

The calculated quasielastic broadening as a function of ΔK is compared with the experimental data in Fig. 1, where the good agreement both in magnitude and form is to be seen. The only serious deviation occurs at low values of ΔK where the simulation shows a more rapid rise in $\Delta E(\Delta K)$ than the measured data. This is due to a small number of multiple jumps the ratio of whose frequencies to that of single jumps is given in Table 1.

The experimental form of $\Delta E(\Delta K)$ for $0 < \Delta K < 1.74$ Å^{-1} can, however, be fitted by considering only single and double jumps on the basis of Eq. (2). One explanation of the presence of a higher fraction of multiple jumps in the MD simulation is that the adatoms in the real system experience a greater friction than is present in the model. This could either be associated with many body forces, or it could be due to the electron–hole pair interactions between the polarised sodium atom and the conduction electrons as it moves across the surface. As is discussed below, the MD model predicts a friction (η) of 0.8 ps^{-1} at 300 K and 0.63 ps^{-1} at 200 K. In Chen and Ying's [15] theoretical study of this system η was varied to fit the quasielastic scattering data and they quote a best fit value of 1.3 ps^{-1} for both temperatures. In a separate, two-dimensional simulation, in which the substrate was modelled by a sinusoidal potential of the form given in Eq. (9) above and the dynamic coupling by a friction and an appropriate white noise random energy coupling scaled to give the correct surface temperature, we found $\eta = 1.0$ ps^{-1} was necessary to fit the magnitude of the experimental data. These two fits to η indicate that the friction due to electronic coupling should be a multiple somewhere in the range 0.2–1.0 of the phonon friction. As can be seen in Ref. [15] the increased friction does indeed improve the fit to the data at low values of ΔK.

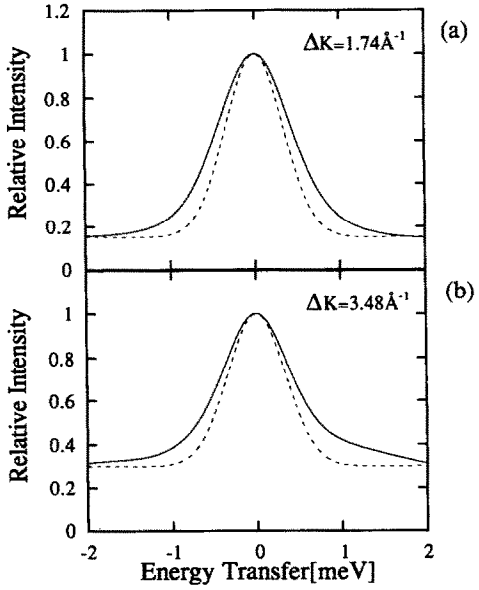

Fig. 5. Simulations of the experimental quasielastic peakshape obtained by convoluting the instrument function (dashed line) with Γ_s (Fig. 4) for $T_s = 300$ K and the indicated values of the momentum transfer.

Table 1
Relative jump frequencies from the MD simulation

Jump length (in units of a)	200 K	300 K
1	1	1
2	0.397	0.381
3	0.187	0.191
4	0.101	0.062
5	0.033	0.046

Table 2
A comparison of calculated and measured jump frequencies (in THz)

Temperature (K)	Simulated jump rate		Measured jump rate
	All jump lengths	Odd jump lengths	Odd jump lengths
200	0.0927	0.0666	0.0459
300	0.239	0.167	0.147

Table 2 compares the measured jump rate, calculated from the size of the experimental broadening at $\Delta K = 1.74$ Å^{-1} for $T_s = 300$ K and $T_s = 200$ K using the Chudley and Elliot formula given in Eq. (2) [8], with that derived from the model. The values given refer to the frequency of jumps over an odd number of adsorption site separations because these are the only length jumps that contribute to the broadening at this point. The reasonable agreement between the calculated and measured values, coupled with the good fit of the $\Delta E(\Delta K)$ curves both confirms the validity of the MD simulation, and also of the basic interpretation of the data in terms of jumps from one four-fold hollow site to another, with an effective activation energy of 51 meV and preexponential factor ν_0 of 0.53 THz [2]. As discussed above, the true activation energy is somewhat higher and if the static value obtained from the MD simulation is taken (71 meV) the preexponential factor must be increased to 1.15 THz in

order to maintain the same jump rate at 300 K. Ferrando et al. [20] have discussed the type of diffusion behaviour expected for such a system for various ranges of values of activation energy and η. Their analysis indicates that an activation energy roughly equal to $2k_BT_s$, as is the case in this instance for $T_s = 300$ K, represents the lower end of a regime in which jump diffusion is a valid description of the processes involved. Lower activation energies would require a continuous diffusion model to describe the motion.

Having now established a rigorous interpretation of the experimental data, we are now in a position to compare the experimentally measured jump rate with that predicted by transition state theory (TST), which is commonly taken as the reference point for discussions of surface rate processes. The theory predicts that the preexponential factor for jumps in a particular direction (taken here as the x direction) is given by:

$$\nu_0^{TST} = \frac{2k_BT_s}{h}\frac{Q_y^*Q_z^*}{Q_x^0Q_y^0Q_z^0}, \tag{12}$$

where Q_y^*, Q_y^0 etc. are the partition functions for motion in particular directions for the ground and transition states, respectively, and may be written as products of partition functions in the three directions [19]. In the harmonic approximation, and for temperatures $T_s \gg h\nu_x/k_B$ the partition functions are given by $Q_x = k_BT_s/h\nu_x$ and Eq. (12) may be rewritten as:

$$\nu_0^{TST} = 2\nu_x\frac{Q_y^*Q_z^*}{Q_y^0Q_z^0}. \tag{13}$$

The attempt rate is therefore given by the frequency with which the adatom approaches confining potential barriers ($2\nu_x$) multiplied by a factor that gives the effective difference in density of states in the transition state and the ground state. In the present case, the molecular dynamics simulation shows that it is reasonable to assume that the frequencies of the vibrational modes in the y (surface parallel, perpendicular to jump) and z directions (surface perpendicular) are closely similar for the ground and transition states, and thus that the partition functions in these two states are approximately equal. The preexponential factor is therefore given by $2\nu_x$ and, based on the inelastic helium scattering data [2], should be 2.46 THz, 4.6 times higher than the value derived from the effective activation energy (51 meV) and 2.1 times the result obtained if the static activation energy (71 meV) predicted by the simulation is used. Deviations from transition state theory were discussed by Kramers as early as 1940 [21] in terms of the rate at which energy is transferred from the substrate to the adatom which is proportional to the friction, η. In the high rate, high friction region, the rate of energy transfer is high enough to turn an atom around directly after crossing the transition state and cause it to recross back to its original site. In addition, the adatom can no longer be considered to travel freely across the unit cell, but diffuse by Brownian motion with a diffusion constant given by k_BT_s/η. Both these effects reduce the effective jump rate as η rises. In the low energy transfer regime, however the rate of energy transfer is too slow to maintain the equilibrium population of the transition state. In terms of the picture of a vibrating atom, this means that unless the atom approaches the barrier each time with a new energy, i.e. the energy exchange process is faster than the vibrational frequency, then the atom may well be trying to jump with the same energy as at the last attempt, and so it is in fact no new attempt at all, simply a repeat of the last one which failed, and the effective jump frequency is reduced. It is anticipated that the TST result will be most closely matched when $\eta \approx 2\pi\nu_x$ [16].

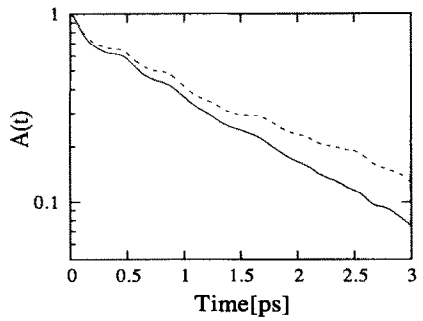

Fig. 6. Plot of the energy autocorrelation function, $A(t)$, for $T_s = 300$ K (solid) and $T_s = 200$ K (dashed).

In order to assess in which energy transfer regime this system lies, the autocorrelation function was evaluated as described above. Fig. 6 shows that semilog plots of the autocorrelation function at $T_s = 300$ K and $T_s = 200$ K are approximately straight lines, indicating that the function decays roughly exponentially with a decay constant $(1/\eta)$ of 1.25 ps at $T_s = 300$ K and 1.58 ps at $T_s = 200$ K. These characteristic times are longer than the vibrational half period (0.41 ps) and suggests that the system is indeed in the low energy exchange rate regime, and that this explains the fact that the experimentally measured preexponential factor is lower than that predicted by transition state theory. The fact that the decay constant is larger at lower temperatures indicates that, as expected, the rate of energy transfer decreases as the surface temperature drops. One consequence of this would be a greater fraction of multiple jumps at lower surface temperatures. This is indeed observed experimentally. The fraction x of double jumps required to fit the form of $\Delta E(\Delta K)$ at low values of ΔK at 200 K is 0.32 but only 0.16 at 300 K.

5. Conclusion

A molecular dynamic simulation has been performed of the motion of isolated sodium adatoms on a Cu(001) surface. The Na–Cu(001) potential was fitted to available data on the binding energy, vibrational frequencies, activation energy for diffusion and the equilibrium height of the adatom above the surface plane. With this potential the MD simulation reproduces well the experimental quasielastic scattering data, confirming the interpretation of the data as indicative of a jump diffusion mechanism, with single and a small number of double jumps with an activation energy of 51 meV (effective) or 71 meV (static) and a preexponential factor in the jump rate equation of 0.53 THz (effective), 1.15 THz (static). The observed finite broadening at the first diffraction position ($\Delta K = 3.48$ Å^{-1}) is explained by the large amplitude oscillations of the adatoms about their mean positions, and the finite time taken to perform the frequent jumps. The model does, however, predict a small probability of jumps over a large number of site separations which is not observed experimentally. We suggest that this arises because the model has not taken into account additional damping of the adatoms motion produced by multi-body or electron–hole pair interactions. The MD simulation has been used to show that the characteristic time for energy exchange between the substrate and adatoms drops as the temperature rises and is longer than the vibrational half period of the adatom, suggesting that the reduction in jump rate from that predicted by transition state theory arises because this energy exchange rate is too slow to maintain an equilibrium population of the transition state. This work demonstrates the power of such simulations in the interpretation of quasielastic helium scattering data. Clearly it would be much more satisfactory if an ab initio adatom–surface potential was available which properly modelled the effects of electronic interactions and many body effects instead of the simple addition on pairwise Morse potential terms used here. The simulation could then be used with confidence to explore the dynamical mechanisms in greater detail.

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