Diffusion and Vibration of Adatoms on a Solid Surface

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A microscopic theory for the diffusive and vibrational motion of absorbed atoms on a solid surface is presented. We evaluate and analyze the dynamical structure factor. The quasielastic scattering peak is found to consist of mixed contributions from both diffusion and vibration. The vibrational peak in the dynamic structure factor indicates both a shift and broadening from anharmonic effects and frictional damping. Applied to Na on Cu(001) surface, the theory agrees quantitatively with recent experimental measurements.

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The diffusive motion of adsorbed atoms and their vibrational motion near the minima of the adsorption potential are usually studied as separate topics because they involve different length and time scales [1–7]. At low temperatures, the adatom spends most of its time vibrating rapidly around an absorption potential minimum and diffusion proceeds by thermally activated rare events of jumping from one absorption site to another in its neighborhood. The information about the diffusive motion can be extracted from the quasielastic spectrum of the dynamic structure factor at small wave vectors, whereas the adatom vibrational motion can be studied at finite frequencies. Indeed both these aspects have been successfully probed via He atom scattering studies [8]. There are, however, situations in which the two modes of motion become coupled and their effects are difficult to separate. The first is at temperatures higher than the diffusion barrier height in which the time spent by the adatom near the minima of the adsorption potential is comparable to the time in the in-between regions. The second situation is at larger wave vectors corresponding to the motion of the adatom at smaller length scales. In the study of the quasielastic spectrum of the dynamic structure factor, the full width at half maximum (FWHM) $\Delta E(\mathbf{q})$ contains the crucial information. It is usually assumed that its wave vector dependence can be modeled by a multisite jumping theory [5,9]. However, such a model neglects the vibrational motion of the adatom altogether and cannot describe $\Delta E(\mathbf{q})$ properly at larger wave vectors. A scrutiny of the He scattering experimental data [8] indicates that this is indeed the situation. This suggests that the diffusive and vibrational motion both contribute to the quasielastic peak and are intimately coupled. This fact is particularly noticeable for wave vectors along nonprincipal axes as demonstrated below.

In this Letter, we present a theoretical study of adatom dynamics in which diffusion and vibration are treated on equal footing. The motion of the adatom is restricted to two dimensions and hence vibrational motion normal to the surface is not included. We start with a model Hamiltonian of the form

$$H = \frac{\mathbf{p}^2}{2m} + V(\mathbf{R}) + \sum_\lambda M(\mathbf{R},\lambda)u_\lambda + H_{\text{ph}}\,. \qquad (1)$$

Here m, $\mathbf{R}$, and $\mathbf{p}$ are, respectively, the mass, displacement vector, and momentum of the adatom, u_λ is the coordinate for the λth eigenmode of the substrate vibrational excitations described by the harmonic Hamiltonian H_{ph}, and $M(\mathbf{R},\lambda)$ describes the coupling of the adatom to the substrate phonons [10]. For the present work, a model potential $V(\mathbf{R}) = V_0[\cos(2\pi x/a) + \cos(2\pi y/a)]$ is employed. The scattering off substrate phonons results in an effective friction which plays a central role in the diffusion process and broadens the vibrational spectrum at very low temperatures. At temperatures of interest, the diffusion is mainly due to thermally activated jumping over barriers and the vibrational mode is broadened and shifted by anharmonicity as well as frictional damping.

In order to characterize the motion of an adatom on a surface, we calculate the dynamic structure factor defined as

$$S(\mathbf{q},\omega) = \int dt\, e^{-i\omega t} \left\langle e^{-i\mathbf{q}\cdot\mathbf{R}(t)} e^{i\mathbf{q}\cdot\mathbf{R}} \right\rangle, \qquad (2)$$

where $\mathbf{q}$ is the wave vector and the brackets stand for thermal statistical average. For our simple separable potential, the dynamical correlation function factors into the product of two correlation functions: one for the x direction and one for the y direction. The dynamic structure factor then has the convolution form

$$S(\mathbf{q},\omega) = \int \frac{d\omega'}{2\pi} S(q_x,\omega-\omega')S(q_y,\omega'). \qquad (3)$$

It is therefore only necessary to calculate the corresponding $S(q_x,\omega)$ or $S(q_y,\omega)$ for the one-dimensional motion.

We have previously developed a formalism for the evaluation of $S(q,\omega)$ based on the Mori projection operator formalism [11]. Here we briefly summarize the main features for the one-dimensional case. In the Hilbert space consisting of all the dynamic variables of the adatom as its vectors, the scalar product of two arbitrary variables A and B is defined as the thermal statistical average of their products, i.e., $\langle A|B\rangle = \langle A^*B\rangle$. The following set of vectors is complete in the subspace of the adatom's dynamics:

$$A_n(K) = h_n(p)e^{i(K+q)x}, \qquad (4)$$

where $h_n(p) = 2^{-n/2}H_n(p/\sqrt{2mkT})$ and H_n are the usual Hermite's polynomials, $n = 0, 1, 2, \ldots$. The K stand for the reciprocal lattice vectors. The norm matrix $\chi = \langle A|A \rangle$,

$$\chi_{n,n'}(K, K') = n! \delta_{nn'} \rho(K - K'), \tag{5}$$

where $\rho(K - K')$ is the Fourier transform of the density. The dynamic structure factor matrix,

$$C_{nn'}(K, K', \omega) = \int dt\, e^{i\omega t} \langle A_n(K, t) | A_{n'}(K') \rangle\,, \tag{6}$$

with $A_n(K, t) = e^{iLt} A_n(K)$ (L being the Liouville operator), is given by the expansion

$$C(\omega) = \chi \left[-i\omega + b + \Sigma(\omega) \right]^{-1}. \tag{7}$$

Equation (7) is written in a matrix form where the indices n and K are implicit. Here $b = \chi^{-1} \langle A|iL|A \rangle$ and the memory function $\Sigma = \chi^{-1} \langle QLA | i(\omega - QLQ)^{-1} | QLA \rangle$, with Q being the projection operator out of the adatom subspace defined as $QB = B - A\chi^{-1} \langle A|B \rangle$. When the motion of the adatom is on a time scale much longer than that for the substrate phonons, one can employ the initial value approximation (IVA) in which the memory function simplifies to

$$\Sigma_{nn'}(K, K'; \omega) = \eta n \delta_{nn'} \delta_{KK'} \times \left(\theta(\omega_D - \omega) - \frac{i}{2\pi} \ln \left| \frac{\omega - \omega_D}{\omega + \omega_D} \right| \right). \tag{8}$$

Here we have employed a three-dimensional Debye model for the substrate phonon, η is the friction coefficient which characterizes the strength of coupling of the adatom to substrate phonons, and ω_D is the Debye frequency. IVA is valid when $\omega_D \gg \omega_0 \equiv 2\pi\sqrt{V_0/ma^2}$.

The dynamical structure factor $S(q_x, \omega)$ is just equal to $C_{00}(K_x = K_x' = 0, \omega)$ and can be obtained from a continued fraction expansion of the right-hand side of Eq. (7). Note that although only the coupling to substrate phonons is explicitly included in our model, the coupling to other substrate excitations such as electron-hole pairs can be included in a similar fashion. Since the electronic motion is on a much faster time scale than typical diffusional or vibrational time, IVA is an excellent approximation for this situation. In fact, the corresponding contribution to the memory function would be similar to that given by Eq. (9) with details only differing in the imaginary part, in addition to the fact that ω_D would be replaced by the frequency scale appropriate for the electron-hole pair excitation, namely, the plasmon frequency. For the remaining discussion in this paper we are concerned with $S(\mathbf{q}, \omega)$ in the region $\omega \ll \omega_D$ and also $\mathrm{Im}\Sigma$ does not play a significant role. Thus we can regard η as an effective friction which contains the effect of coupling of the adatom to all substrate excitations (electronic and vibrational).

Qualitatively, $S(q_x, \omega)$ [or $S(q_y, \omega)$] has a quasielastic peak at $\omega = 0$ due to the diffusive motion of the adatom and a peak near $\omega = \omega_0$ due to the localized adatom vibrational motion near the minima of the adsorption potential. As the wave vector increases, the strength of the vibrational peak increases at the expense of the diffusive peak. When the convolution of the x and y directions is considered for a wave vector having both q_x and q_y components as in Eq. (3), then the full width of the quasielastic peak is given by $\Delta E(\mathbf{q}) = 2D(q_x^2 + q_y^2)$ for $q \sim 0$. However, as q increases, the diffusive and vibrational motion are coupled and the quasielastic peak becomes distinctively non-Lorentzian. It can be written in the following form:

$$S(\mathbf{q}, \omega) = \frac{A(\mathbf{q})}{\omega^2 + [\Delta E_D(\mathbf{q})/2]^2} + \tilde{S}(\mathbf{q}, \omega), \tag{9}$$

where $\tilde{S}(\mathbf{q}, \omega)$ is slowly varying near $\omega = 0$ but peaks at ω near ω_0. In Eq. (9), the pure Lorentzian part represents the contribution of the adatom jumping randomly from one site to another, whereas $\tilde{S}(\mathbf{q}, \omega)$ contains the dynamics of motion in a continuous potential including vibrational motion that is neglected in a lattice gas model.

To illustrate the above discussions, we apply our theory to analyze the Na/Cu(001) system for which He scattering data appeared recently [8]. As argued in Ref. [8], the interaction effects are weak at the experimental Na coverage ($\theta \sim 0.1$) and the adatom motions can be considered as independent. Thus our single adatom theory is appropriate for the analysis. For this system, the adsorption sites are the fourfold hollow sites. The x and y directions correspond to [1,1,0] and [-1,1,0] and $a = 2.56$ Å. The dynamical structure factor was measured for wave vector $\mathbf{q}$ along the [100] direction; thus it can be factored into the convolution form as described in Eq. (3). First, we focus on the width of the quasielastic peak. Experimentally, an effective $\Delta E(\mathbf{q})$ was extracted by assuming that the observed data result from the convolution of a Lorentzian with an instrument resolution function having a width of $0.05\omega_0$. We follow the same procedure to extract an effective $\Delta E(\mathbf{q})$ from the theoretical value of $S(\mathbf{q}, \omega)$. The best fit to the data is obtained by choosing the parameters in the Hamiltonian as $\eta = 0.15\omega_0$ and $\Delta = 2V_0 = 780$ K (67 meV). The choice of V_0 implies a bare adatom vibrational frequency $\nu_0 = \frac{\omega_0}{2\pi} = 1.4$ THz. (This is the frustrated translation mode.) This is considerably less than the Debye frequency $\frac{\omega_D}{2\pi} \simeq 7$ THz and justifies the use of IVA in the evaluation of $S(\mathbf{q}, \omega)$. In Figs. 1 and 2, we plot $\Delta E(\mathbf{q})$ together with the experimental data taken from Ref. [8] for temperature $T = 300$ K and 200 K, respectively. The theoretical fit of the data is very good. Beyond the first Brillouin zone, $\Delta E(\mathbf{q})$ increases rather than decreases to zero toward the center of the second Brillouin zone as predicted by the multisite jumping theory. This clearly indicates the contribution of the vibrational mode to the quasielastic spectrum. The same conclusion about the importance of the vibrational motion contribution to the quasielastic peak has also been reached via molecular dynamics

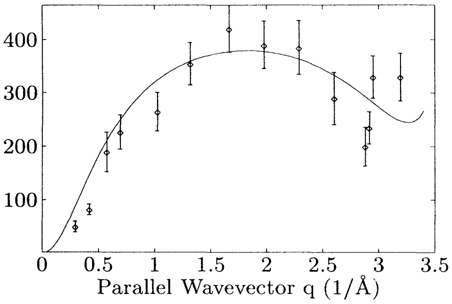

FIG. 1. The FWHM (μeV) of the quasielastic peak vs parallel wave vector $\mathbf{q}$ in the [100] direction at temperature 300 K. $\eta = 0.15\omega_0$, $\omega_D = 5\omega_0$. The solid curve is from theory and the experimental data with error bars taken from Ref. [8].

(MD) simulation studies [8]. We find that along the x or y direction, the behavior of $\Delta E(\mathbf{q})$ is close to the simple predictions of the multijump theory without the mixing of the diffusive and vibrational motion.

To analyze the microscopic picture of the diffusion, we investigate $S(\mathbf{q},\omega)$ in more detail. In Fig. 3, we plot $S(\mathbf{q},\omega)$ for $\mathbf{q} = (1.9\pi/a, 1.9\pi/a)$ and $T = 200$ K. It can clearly be decomposed into a narrow Lorentzian part near $\omega = 0$ plus a more slowly varying part $\tilde{S}(\mathbf{q},\omega)$ as indicated in Eq. (9). We extract $A(\mathbf{q})$ and $\Delta E_D(\mathbf{q})$ of Eq. (9) by a least-squares fitting in the frequency range $0 \leq \omega \leq 0.02\omega_0$. We then compare $\Delta E_D(\mathbf{q})$ to the prediction of the multisite jumping model [5],

$$\Delta E_D(\mathbf{q}) = 2\nu \sum_n P_n[2 - \cos(naq_x) - \cos(naq_y)]. \quad (10)$$

Here ν is the total jumping rate and P_n, the probability for the event of jumping n sites. In Fig. 4, we plot $\{P_n\}$ for the two temperatures 200 K and 300 K. We note that at both temperatures multiple jumps of two and three steps are sizable. Also the jump rate $\nu \simeq 0.17\nu_0 e^{-\Delta/kT}$ is considerably smaller than the value given by the transition state theory $\nu_{\mathrm{TST}} = \nu_0 e^{-\Delta/kT}$. This is consistent with the recent theoretical result [9,12] that the probability of multisite jumps increases while the jump rate decreases as $\eta \rightarrow 0$. The diffusion constant actually increases as $1/\eta$ in this limit [13]. Our result for the fraction of double jumps is approximately the same at $T = 200$ K and 300 K in contrast to that of Ref. [8] which finds a larger fraction of double jumps at $T = 200$ K compared with $T = 300$ K.

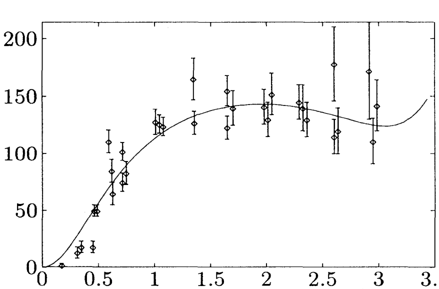

FIG. 2. The same as Fig. 1 except $T = 200$ K.

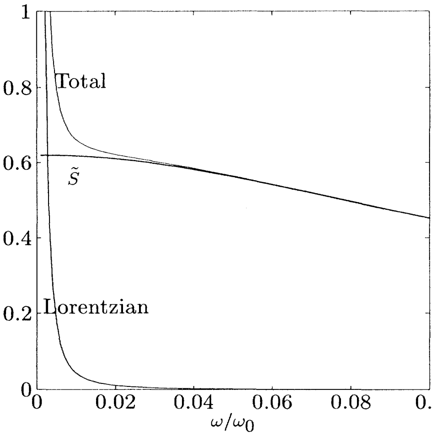

FIG. 3. The dynamic structure factor $S(q_x = q_y = 1.9\pi/a, \omega)$ (scaled with $1/\omega_0$, marked as Total) decomposed into a sharp Lorentzian peak and a slowly varying part $\tilde{S}$ for $T = 200$ K. The frequency ω is scaled by ω_0.

The fact that our theoretical result fits the experimental data better than the MD simulation of Ref. [8] can come from two sources. First of all, as discussed earlier, the friction parameter η chosen here to be $0.15\omega_0$ should be considered as an effective friction originating from coupling to all substrate excitations and not just substrate phonons. In fact if we use the estimate of η from the continum elasticity theory [7], η/ω_0 is found to be only 0.025. Even though this estimate is rather crude, it indicates at least a substantial contribution to the effective friction parameter from coupling to electronic excitations for Na/Cu(001). In the MD simulation, only coupling to substrate phonons is included and this re-

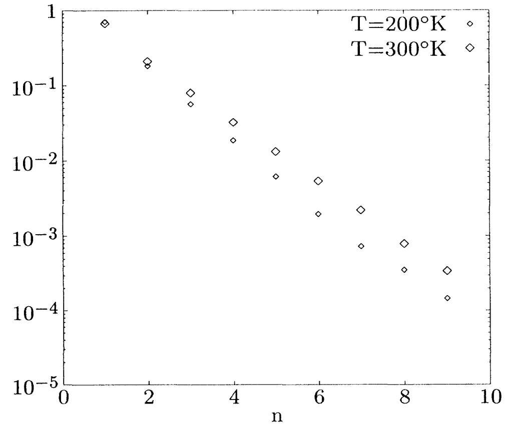

FIG. 4. The jumping probabilities vs jumping distances (in units of lattice constant).

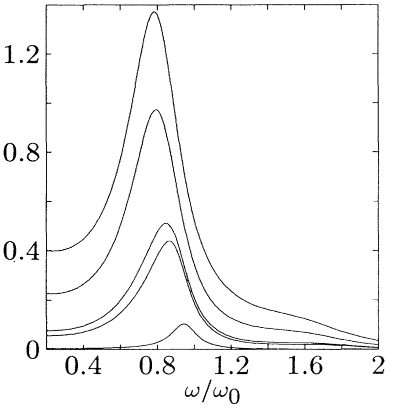

FIG. 5. The vibrational spectra $S_{00}(q_x = q_y = \pi/a, \omega)$ (scaled with $1/\omega_0$) for T=512 K, 300 K, 200 K, 180 K, and 70 K (from top to bottom), the barrier Δ=780 K, η=0.15ω_0, and ω_D=5ω_0.

sults in an underestimate of η. Second, the diffusion constant, or, equivalently, the jumping rate, is thermally activated with the Arrhenius form $Ae^{-\Delta/kT}$ with Δ equal to the diffusion barrier. In our work $\Delta = 2V_0$ is chosen as 780 K (67 meV). In Ref. [8], the effective barrier is extracted from the maximum broadening at the zone boundary which contains both vibrational and diffusive contributions and theoretically does not obey a rigorous Arrhenius form. This leads to their choice of a smaller barrier height Δ=51 meV.

Next we examine the vibrational spectra. In Fig. 5, we plot $S(q_x = \pi/a, q_y = \pi/a, \omega)$ for various temperatures. At higher temperatures, the vibrational peak is located at the low frequency side of ω_0. The peak becomes sharper as temperature decreases, and its position moves gradually toward ω_0. At very low temperatures, the vibrational linewidth is dominated by frictional damping. It is interesting to note that the temperature dependence of the shift of the vibrational peak comes from two different sources. The coupling with substrate excitations tends to shift the peak frequency to the high frequency end, while the anharmonicity effect pulls it toward the low frequency side and is dominant for $\omega_D \gg \omega_0$. Moreover, the anharmonicity induced line shift has much stronger temperature dependence. At lower temperatures, the anharmonicity effect is smaller and thus the peak position is closer to ω_0. Once we have chosen the parameters for the best fit of $\Delta E(\mathbf{q})$ for the quasielastic scattering peak, the vibrational peak is completely determined in our theory with no further adjustable parameters. Our choice of Δ=780 K corresponds to a bare vibrational frequency ν_0 = 1.4 THz. At 70 K, our results indicate a vibrational peak at ν_{70}=1.35 THz while at 180 K, the peak is shifted to ν_{180}=1.22 THz. These theoretical results are in excellent agreement with the measured values of the frequency of the frustrated translation mode ν_0=1.4 THz at 70 K and 1.23 THz at 180 K [8]. It would be desirable to have more detailed line shape analysis of the experimental data for a comparison with our theoretical prediction of the shift and broadening of this vibrational mode.

In summary, we have presented a microscopic theory of diffusion and vibration of an adatom on a surface and compare our theoretical results for the dynamics of Na on Cu(001) surface with recent He scattering studies. The calculated width of the quasielastic spectrum and the temperature dependent shift of the frustrated translation mode are in excellent agreement with the experimental data. The quasielastic scattering spectrum is demonstrated to have contributions from the vibrational as well as from the diffusive modes. The contribution of both the anharmonic potential and frictional damping to the adatom vibrational mode are discussed in detail.

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