

Phonon lineshapes in atom-surface scattering

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Abstract. Phonon lineshapes in atom-surface scattering are obtained from a simple stochastic model based on the so-called Caldeira-Leggett Hamiltonian. In this single-bath model, the excited phonon resulting from a creation or annihilation event is coupled to a thermal bath consisting of an infinite number of harmonic oscillators, namely the bath phonons. The diagonalization of the corresponding Hamiltonian leads to a renormalization of the phonon frequencies in terms of the phonon friction or damping coefficient. Moreover, when there are adsorbates on the surface, this single-bath model can be extended to a two-bath model accounting for the effect induced by the adsorbates on the phonon lineshapes as well as their corresponding lineshapes.

Submitted to: *J. Phys.: Condens. Matter*

1. Introduction

Bulk and surface phonon dynamics is a very active field of research. Usually the information about this dynamics arises from scattering experiments, where the typical observable quantity is the lineshape associated with a surface excitation, i.e. a creation or an annihilation event. At present, the available experimental techniques, such as the surface scattering with He-atom beams [1] or the He spin echo [2], allow to explore higher and higher angular and energy resolutions. Therefore, it is important and necessary to have at our disposal appropriate theoretical formalisms which allow us to extract reliable information from the experiment, such as phonon lifetimes and frequency shifts, phonon-dispersion relations or multiphonon backgrounds, for example. In this regard, a qualitative explanation was formerly provided for multiphonon scattering processes in terms of a semiclassical formula for energy and momentum exchange within the so-called trajectory approximation as a generalization of the Brako-Newns formula [3, 4]. Levi and Bortolani [5] also developed a general multiphonon formalism based on the time-evolution approach. More recently, Gumhalter [6] has made a revision on single and multiphonon atom-surface scattering within the quantum regime. However, as far as we know, little attention has been paid to the theory of phonon lineshapes.

In this work we develop a theory of phonon lineshapes within a stochastic approach based on the so-called Caldeira-Legget Hamiltonian [7], which constitutes the paradigm of stochastic dynamics and system-plus-reservoir approaches. In particular, we focus on an excited phonon in the presence of a phonon field and study its relaxation. To this end, in next Section we shortly review the theory of Manson and Celli, based on the transition matrix formalism [8–10], in order to introduce the notation and their main theoretical findings on single- and multiphonon scattering. In Section 3, the Caldeira-Leggett Hamiltonian is introduced to develop a theory for damping phonons within a single-bath model (phonon bath). This Hamiltonian, which displays a high degree of versatility, has been used by our group to describe surface diffusion of single adsorbates [11–13] and interacting adsorbates within a two-bath model (phonon and adsorbate baths) [14, 15]. This Hamiltonian has been applied, also recently, to classical atom-surface scattering to describe angular distributions [16, 17] and energy loss spectra [18, 19]. Finally, in Section 4, different aspects of this new approach are discussed and applied to He scattering off a Cu(001) surface with a 3% CO coverage at low (surface) temperatures [20].

2. A brief account on the transition matrix formalism

The observable in atom-surface inelastic scattering experiments is usually the so-called differential reflection coefficient, which gives the fraction of probe particles (e.g. He atoms) scattered off into a final solid angle $d\Omega_f$ and an energy interval dE_f . At a theoretical level, this observable is obtained as a transition rate, dividing the incident flux crossing a plane parallel to the surface and then multiplying by the density of

available final states of the probe particle [8–10]. This allows us to express the transition rate as [8, 9]

$$\mathcal{R}(\mathbf{k}_f, \mathbf{k}_i) = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} e^{-i(\epsilon_i - \epsilon_f)t/\hbar} |\tau(\mathbf{k}_f, \mathbf{k}_i)|^2 \sum_{j,l} \langle e^{-i\mathbf{k}\cdot[\mathbf{R}_l + \mathbf{u}_l(0)]} e^{i\mathbf{k}\cdot[\mathbf{R}_j + \mathbf{u}_j(t)]} \rangle dt, \quad (1)$$

where ϵ_i and ϵ_f are, respectively, the initial and final particle energies, $\hbar\omega = \epsilon_f - \epsilon_i$ is the energy exchanged in the scattering process, $\mathbf{k} = \mathbf{k}_f - \mathbf{k}_i$ is the total wave vector exchanged by the scattering particles, and $\tau_{fi} \equiv \tau(\mathbf{k}_f, \mathbf{k}_i)$ is a pairwise transition operator. The (time-independent) equilibrium position of the j th surface unit cell is given by \mathbf{R}_j , with j being a discrete two-dimensional variable for each layer. For simplicity, we will assume that there is only one atom per unit cell and, therefore, \mathbf{u}_j corresponds to the displacement of the j th atom with respect to \mathbf{R}_j due to its vibrational motion. In (1), the sums extend over all \mathbf{R}_j and the average is over all initial lattice states (once the sum over all possible final lattice states has been carried out).

Equation (1) has the general form of the fundamental equation for a large class of scattering treatments involving a many-body target,

$$\mathcal{R}(\mathbf{k}_f, \mathbf{k}_i) = \frac{2\pi}{\hbar} |\tau(\mathbf{k}_f, \mathbf{k}_i)|^2 S(\mathbf{k}, \omega). \quad (2)$$

This equation is the product of a *form factor*, $|\tau(\mathbf{k}_f, \mathbf{k}_i)|^2$, for the scattering centers and a *dynamical structure factor*, $S(\mathbf{k}, \omega)$, which depends on the average over scattering center positions. The latter factor describes, precisely, the lineshapes in the kind of experiments we are interested in here, and can be expressed as

$$S(\mathbf{k}, \omega) = \int I(\mathbf{k}, t) e^{i\omega t} dt, \quad (3)$$

i.e. as a time Fourier transform of the so-called *intermediate scattering function*,

$$I(\mathbf{k}, t) \equiv \sum_{j,l} e^{-i\mathbf{k}\cdot\mathbf{R}_l} e^{i\mathbf{k}\cdot\mathbf{R}_j} \langle e^{-i\mathbf{k}\cdot\mathbf{u}_l(0)} e^{i\mathbf{k}\cdot\mathbf{u}_j(t)} \rangle. \quad (4)$$

If the harmonic approximation is valid for any vibrational lattice mode, then the (vibrational) average in (4) can be easily carried out by standard methods, which yields

$$\langle e^{-i\mathbf{k}\cdot\mathbf{u}_l(0)} e^{i\mathbf{k}\cdot\mathbf{u}_j(t)} \rangle = e^{-\Upsilon_{lj}(\mathbf{k}, t)}, \quad (5)$$

where

$$\Upsilon_{lj}(\mathbf{k}, t) = 2W(\mathbf{k}) - \langle [\mathbf{k}\cdot\mathbf{u}_l(0)][\mathbf{k}\cdot\mathbf{u}_j(t)] \rangle, \quad (6)$$

and

$$W(\mathbf{k}) = \frac{1}{2} \langle [\mathbf{k}\cdot\mathbf{u}_j(t)]^2 \rangle = \frac{1}{2} \langle [\mathbf{k}\cdot\mathbf{u}_j(0)]^2 \rangle. \quad (7)$$

The factor $W(\mathbf{k})$ is the argument of the so-called *Debye-Waller (DW) factor*, $e^{-2W(\mathbf{k})}$, which governs the decay of the scattered intensity as a function of the surface temperature through the canonical ensemble average. This contribution to the thermal attenuation of the scattered intensities arises mainly from the momentum transfer perpendicular to the surface.

The second term in (6) accounts for the energy transfer between the surface and the scattered particles, which is governed by the displacement autocorrelation function

$$U_{jl}(\mathbf{k}, t) \equiv \langle [\mathbf{k} \cdot \mathbf{u}_l(0)] [\mathbf{k} \cdot \mathbf{u}_j(t)] \rangle. \quad (8)$$

Here we are dealing with the problem of inelastic scattering and, therefore, our interest relies on the evaluation of this displacement correlation function. Hence we express the vibrational amplitude of the j th scattering center in terms of surface normal modes as

$$\mathbf{u}_j(t) = \sum_{\mathbf{Q}, \nu} \lambda_{\mathbf{Q}, \nu} \mathbf{e}(\mathbf{Q}, \nu) \left[a_{\mathbf{Q}, \nu}(t) e^{-i\mathbf{Q} \cdot \mathbf{R}_j} + a_{-\mathbf{Q}, \nu}^\dagger(t) e^{i\mathbf{Q} \cdot \mathbf{R}_j} \right], \quad (9)$$

where

$$a_{\mathbf{Q}, \nu}(t) = a_{\mathbf{Q}, \nu}(0) e^{-i\omega_\nu(\mathbf{Q})t}, \quad (10)$$

and

$$\lambda_{\mathbf{Q}, \nu} = \sqrt{\frac{\hbar}{2NM\omega_\nu(\mathbf{Q})}}. \quad (11)$$

In these expressions, \mathbf{Q} is the parallel-phonon momentum, ν represents additional phonon quantum numbers (e.g. the Rayleigh-mode branch or normal momentum of bulk modes), M is the mass of the surface atom in the unit cell, $\mathbf{e}(\mathbf{Q}, \nu)$ is the polarization vector, and $a_{\mathbf{Q}, \nu}(t)$ and $a_{-\mathbf{Q}, \nu}^\dagger(t)$ are the time-dependent phonon annihilation and creation operators, respectively. The polarization vector is related to the frequency distribution function, $\rho_{\alpha\beta}$, as [8, 9]

$$\rho_{\alpha\beta} = \sum_{\mathbf{Q}, \nu} \mathbf{e}_\alpha(\mathbf{Q}, \nu) \cdot \mathbf{e}_\beta(\mathbf{Q}, \nu) \delta(\omega - \omega_\nu(\mathbf{Q})), \quad (12)$$

where α and β are the Cartesian components of the polarization vectors. From (9) and (10), and after performing the corresponding thermal averages, (8) becomes

$$\begin{aligned} U_{jl}(\mathbf{k}, t) = & \sum_{\mathbf{Q}, \nu} \lambda_{\mathbf{Q}, \nu}^2 [\mathbf{k} \cdot \mathbf{e}(\mathbf{Q}, \nu)]^2 \left\{ n_\nu(\mathbf{Q}) e^{i\mathbf{Q} \cdot (\mathbf{R}_l - \mathbf{R}_j)} e^{-i\omega_\nu(\mathbf{Q})t} \right. \\ & \left. + [n_\nu(\mathbf{Q}) + 1] e^{-i\mathbf{Q} \cdot (\mathbf{R}_l - \mathbf{R}_j)} e^{i\omega_\nu(\mathbf{Q})t} \right\}, \end{aligned} \quad (13)$$

where $n_\nu(\mathbf{Q}) = [e^{\hbar\omega_\nu(\mathbf{Q})/k_B T} - 1]^{-1}$ is the *Bose-Einstein factor*. By Taylor expanding the exponential of $U_{lj}(\mathbf{k}, t)$, with Υ_{lj} decomposed as in (6), the multiphonon contributions associated with the total inelastic scattering process can be obtained. The first term of this series expansion (namely the unity) gives the diffraction intensities, i.e. the elastic contribution to the scattering process, after carrying out the integral (3) and then computing the transition rate (2). At this level of approximation, as reported by Manson [9], these diffraction intensities will be given by the product of three factors: the DW factor, the form factor and the structure factor. In particular, the (static) structure factor is the time-independent factor arising from (4) at zero temperature,

$$S(\mathbf{k}) \equiv \sum_{j,l} e^{-i\mathbf{k} \cdot \mathbf{R}_j} e^{i\mathbf{k} \cdot \mathbf{R}_l}, \quad (14)$$

with the diffraction peaks then expressed in term of δ -functions. The next term, the linear one, provides the single-phonon contribution, with its corresponding rate containing an extra factor, namely the Bose-Einstein factor. Also in this case inelastic intensities are given by δ -peaks. Finally, the multiphonon contribution is obtained from the remaining terms of the Taylor expansion or, equivalently, by subtraction of the zero and single-phonon contributions.

Since we are interested in phonon lineshapes, a damping mechanism has to be introduced in a theoretical model in order to replace the δ -peaks by Lorentzian lineshapes. The goal in next Section is to assume a simple model, the so-called Caldeira-Leggett (single-bath) model. The corresponding Hamiltonian [7] has been widely used and applied in the literature to a large variety of physical processes in presence of dissipation [21]. More specifically, this approach has been extensively used in the so-called Kramers' turnover problem [22, 23] describing the escape from a metastable potential, in the vibrational dephasing problem of small molecules in liquids [24], and in diffusion problems [11–15] with no application to lineshapes.

3. A simple model for phonon lineshapes: The Caldeira-Leggett model

Consider the damping of a single phonon (system) excited by some external source and coupled to a thermal bath at a given temperature (heat bath). This dissipation mechanism is not very sensitive to the particular loss process involved and, therefore, the heat bath can be assumed as consisting of an infinite number of independent oscillators (phonon field) in thermal equilibrium at the surface temperature. Thermal fluctuations in the bath or reservoir, which feed with noise the excited phonon, are related to the friction coefficient or damping constant through the well-known fluctuation-dissipation theorem. The system is usually represented by a harmonic oscillator weakly coupled to the reservoir and undergoing an energy flow towards the reservoir. Conversely, the reservoir fluctuations also couple back into the system. The driving force (He atoms) exciting the phonon is assumed to be a linear perturbation and, at zero order, no influence in the subsequent phonon dynamics is expected. From the linear response theory, the dynamical susceptibility will be that of a particle subject to a one-dimensional harmonic potential [14, 15].

Taking into account the comments above, the full Hamiltonian describing the process can be written as [7, 21]

$$H = H_S + H_R + H_{SR}, \quad (15)$$

where H_S describes the Hamiltonian accounting for the system dynamics (i.e. the excited phonon), H_R is the Hamiltonian associated with the thermal bath and H_{SR} represents the coupling between system and bath. The so-called Caldeira-Leggett Hamiltonian has the structure given by (15) and is usually expressed in the form

$$H = \frac{p^2}{2m} + V(q) + \sum_{i=1}^N \left[\frac{p_i^2}{2m_i} + \frac{1}{2} m_i \left(\omega_i x_i - \frac{c_i}{m_i \omega_i} q \right)^2 \right], \quad (16)$$

where (q, p) and m represent the system variables (coordinate and conjugate momentum) and its mass, respectively; $V(q)$ is the external potential acting on the uncoupled system, which here we assume to be harmonic; (x_i, p_i) stand for the variables of the i th bath oscillator, characterized by a mass m_i and a frequency ω_i ; and c_i is the coupling constant between the i th bath oscillator and the system.

Within this single-bath model, tracing over the bath degrees of freedom in the equations of motion (expressed in the Heisenberg picture) makes evident the damped motion undergone by the system coordinate [21]. This tracing gives rise to a quantum generalized Langevin equation,

$$m\ddot{q} + \frac{\partial V(q)}{\partial q} + m \int_0^t \gamma(t-t') \dot{q}(t') dt' = \xi(t), \quad (17)$$

which describes the evolution of the system coordinate (q) under the influence of the external harmonic potential $V(q)$, a friction kernel $\gamma(t)$ and a random force $\xi(t)$ coming from the bath thermal motion. In this model, the friction kernel (phonon friction) is

$$\gamma(t) = \frac{1}{m} \sum_{i=1}^N \frac{c_i^2}{m_i \omega_i^2} \cos \omega_i t, \quad (18)$$

while the spectral density characterizing the bath oscillators is

$$\rho(\omega) = \pi \sum_{i=1}^N \frac{c_i^2}{2m_i \omega_i} \delta(\omega - \omega_i). \quad (19)$$

On the other hand, the random force reads as

$$\xi(t) = \sum_{j=1}^N c_j \left\{ \left[x_j(0) - \frac{c_j}{m_j \omega_j^2} q(0) \right] \cos \omega_j t + \frac{p_j(0)}{m_j \omega_j} \sin \omega_j t \right\}, \quad (20)$$

which satisfies the conditions for a Gaussian white noise provided the friction is Ohmic, i.e. $\gamma(t) = 2\gamma\delta(t)$. In this case, Eq. (17) becomes a standard quantum Langevin equation,

$$m\ddot{q} + \frac{\partial V(q)}{\partial q} + m\gamma \dot{q}(t) = \xi(t). \quad (21)$$

Quantum-mechanically, the Hamiltonian (16) for a harmonic potential $V(q) = m\omega_0^2 q^2/2$ can be expressed in terms of system (a, a^\dagger) and bath (b_j, b_j^\dagger) operators as

$$\begin{aligned} H = & \hbar\omega_0(a^\dagger a + 1/2) + \sum_{j=1}^N \hbar\omega_j(b_j^\dagger b_j + 1/2) + \hbar \sum_{j=1}^N \kappa_j (ab_j^\dagger + a^\dagger b_j + a^\dagger b_j^\dagger + ab_j) \\ & + \frac{\hbar}{4\mu\omega_0} (a^{\dagger 2} + a^2 + 2a^\dagger a + 1) \sum_{j=1}^N \frac{c_j^2}{m_j \omega_j^2}, \end{aligned} \quad (22)$$

with

$$\kappa_j = \frac{c_j}{2\sqrt{\mu m_j \omega_0 \omega_j}} \quad (23)$$

accounting for the strength of the bilinear coupling between the system and the bath oscillators. As is apparent, two quantum transitions in the system are allowed according

to the existing second order terms. The Hamiltonian (22) can be diagonalized via a normal mode transformation with mass weighted coordinates. The corresponding normal-mode Hamiltonian can be then written as a sum of $N+1$ oscillators [22–24],

$$H = \frac{1}{2}P^2 + \frac{1}{2}w_0^2Q^2 + \sum_{j=1}^N \left(\frac{1}{2}P_j^2 + \frac{1}{2}w_j^2Q_j^2 \right), \quad (24)$$

where (w_0, w_j) denote the new system and bath frequencies (eigenvalues) and (Q, P) and (Q_j, P_j) are the new system and bath variables, respectively. For Ohmic friction, the explicit expression of w_0 is

$$w_0 = \pm \sqrt{\omega_0^2 - \gamma_0^2/4} + i\gamma_0/2 = \pm \bar{w}_0 + i\gamma_0/2. \quad (25)$$

Similarly, for w_j ,

$$w_j = \pm \sqrt{\omega_j^2 - \gamma_j^2/4} + i\gamma_j/2 = \pm \bar{w}_j + i\gamma_j/2. \quad (26)$$

The real parts in both cases give renormalized frequencies, \bar{w}_0 and \bar{w}_j , and the imaginary ones the damping constant or phonon friction coefficient. Notice that the new frequencies are no longer a simple linear function of the friction coefficient, as it usually happens when only single quantum transitions are allowed. Furthermore, after diagonalization, we have a set of $N+1$ damping phonons. This procedure is equivalent to write Hamiltonian (24) in terms of real frequencies \bar{w}_k [25,26]. Hence, in terms of operators, the Hamiltonian (24) can be recast as

$$H = \sum_{k=0}^N \hbar \bar{w}_k (\bar{a}_k^\dagger \bar{a}_k + 1/2), \quad (27)$$

where $(\bar{a}^\dagger, \bar{a})$ are related to the new phonon variables (Q_k, P_k) . The time evolution of such operators is given by

$$\bar{a}_k(t) = \bar{a}_k(0) e^{i\bar{w}_k t}, \quad (28)$$

with the minus sign usually chosen for the real part of the frequencies in (25) and (26).

In order to obtain the phonon lineshapes, we proceed as previously shown, although now the vibrational amplitude of the j th scattering center is given in terms of the new normal modes or damping phonons, expressed through $(\bar{a}_k^\dagger, \bar{a}_k)$ as

$$\mathbf{u}_j(t) = \sum_{\mathbf{Q}, \nu} \bar{\lambda}_{\mathbf{Q}, \nu} \mathbf{e}(\mathbf{Q}, \nu) e^{-\gamma_\nu(\mathbf{Q})t/2} \left[\bar{a}_{\mathbf{Q}, \nu}(t) e^{-i\mathbf{Q} \cdot \mathbf{R}_j} + \bar{a}_{-\mathbf{Q}, \nu}^\dagger(t) e^{i\mathbf{Q} \cdot \mathbf{R}_j} \right], \quad (29)$$

where, for simplicity, we keep the same notation (\mathbf{Q}, ν) for quantum numbers, as in (9), and

$$\bar{\lambda}_{\mathbf{Q}, \nu} = \sqrt{\frac{\hbar}{2(N+1)\bar{w}_\nu(\mathbf{Q})}}. \quad (30)$$

Note that now the time-dependent operators are thus given by (28) and the corresponding frequencies by (25) and (26), unlike Eq. (10), where frequencies were real. In this way, (6) acquires formally the same expression,

$$\Upsilon_{lj}(\mathbf{k}, t) = \frac{1}{2} \langle [\mathbf{k} \cdot \mathbf{u}_l(0)]^2 \rangle + \frac{1}{2} \langle [\mathbf{k} \cdot \mathbf{u}_j(t)]^2 \rangle - U_{jl}(\mathbf{k}, t), \quad (31)$$

but with the displacements being given by (29). This fact has important consequences: though the first term in (31) is W , as in (7), the second one is no longer independent of time (it depends on time as $e^{-\gamma_\nu(\mathbf{Q})t}$) and, therefore, will not contribute as a new W term. Regarding the third term, it is also time-dependent, containing the new extra factors $e^{-\gamma_\nu(\mathbf{Q})t/2}$, $e^{i\bar{w}_\nu(\mathbf{Q})t}$ and the complex conjugate of the latter. In particular, this displacement autocorrelation function, given above by (13), can now be expressed taking into account the new normal modes as

$$U_{jl}(\mathbf{k}, t) = \sum_{\mathbf{Q}, \nu} \bar{\lambda}_{\mathbf{Q}, \nu}^2 [\mathbf{k} \cdot \mathbf{e}(\mathbf{Q}, \nu)]^2 \left\{ n_\nu(\mathbf{Q}) e^{i\mathbf{Q} \cdot (\mathbf{R}_l - \mathbf{R}_j)} e^{-i\bar{w}_\nu(\mathbf{Q})t} e^{-\gamma_\nu(\mathbf{Q})t/2} + [n_\nu(\mathbf{Q}) + 1] e^{-i\mathbf{Q} \cdot (\mathbf{R}_l - \mathbf{R}_j)} e^{i\bar{w}_\nu(\mathbf{Q})t} e^{-\gamma_\nu(\mathbf{Q})t/2} \right\}, \quad (32)$$

where $\bar{w}_\nu(\mathbf{Q})$ can be identified by \bar{w}_k . Observe that this equation is similar to (13) except for the presence of damping factors. Therefore, phonon lineshapes will be obtained from the time Fourier transform, as given by (3), but considering the damping normal modes in terms of (\mathbf{Q}, ν) and $w_\nu(\mathbf{Q})$. The interest here relies on the fact that lineshapes can be obtained as a function of the new system and bath frequencies issued from a given diagonalization due to the presence of the heat bath. This approach thus allows us to consider the excited phonon and the phonon bath on *equal footing*.

Specifically, the phonon lineshapes obtained from the time Fourier transform (3) read as

$$S(\mathbf{k}, \omega) = \frac{1}{2\pi\hbar} e^{-W(\mathbf{k})} \sum_{j,l} \prod_{\mathbf{Q}, \nu} \sum_{n,m,p=0}^{\infty} \left(\frac{-1}{2}\right)^p \frac{\bar{\lambda}_{\mathbf{Q}, \nu}^{2(n+m+p)}}{n!m!p!} [\mathbf{k} \cdot \mathbf{e}(\mathbf{Q}, \nu)]^{2(n+m+p)} \\ \times n_\nu(\mathbf{Q})^n [n_\nu(\mathbf{Q}) + 1]^m [2n_\nu(\mathbf{Q}) + 1]^p e^{i\mathbf{Q} \cdot (\mathbf{R}_l - \mathbf{R}_j)n} e^{-i\mathbf{Q} \cdot (\mathbf{R}_l - \mathbf{R}_j)m} \\ \times \frac{(n+m+2p)\gamma_\nu(\mathbf{Q})}{[\omega - (m-n)\bar{w}_\nu(\mathbf{Q})]^2 + [(n+m+2p)\gamma_\nu(\mathbf{Q})/2]^2}. \quad (33)$$

In principle, this expression contains the main ingredients of the phonon relaxation dynamics. For a given phonon, (33) consists of an infinite sum of weighted Lorentzian functions which describes all phonon creation and annihilation events.

4. Discussion and applications

Some consequences of (33) can be discussed at different levels:

(a) *Damping phonons in clean surfaces: positions and lifetimes*

The first point to be stressed from (33) is the frequency position and lifetime of each (creation or annihilation) phonon event. The frequency position is given by (25) and involves the phonon friction. Thus, the nominal value of the phonon frequency ω_0 or ω_j has to be replaced by a renormalized frequency due to the coupling with the phonon bath. The phonon lifetime is directly related to such a friction, $\hbar/\gamma_\nu(\mathbf{Q})$. The different excitations of a certain phonon event are given by the sums running over n and m . Each elementary contribution is expressed by a weighted Lorentzian shape. Obviously, the

most prominent Lorentzian lineshape is related to the most likely phonon event. When $n = m$, we have the diffuse elastic peak. This contribution arises from the creation and annihilation of the same number of phonons and is essentially associated with single-phonon exchanges (the multiphonon contribution is substantially smaller). The product in the quantum numbers (\mathbf{Q}, ν) shows the contributions of different excited phonons. The multiphonon background is given by the different factors appearing in (33). The temperature dependence comes through the Bose-Einstein and DW factors. Regarding the symmetry of the total lineshape, and according to the detailed balance condition, particle energy gains (which requires the system to be in the higher energy state) are less frequent than atom energy losses, in agreement with the Boltzmann population factor.

(b) *Damping phonons and the DW factor*

In (33), the DW factor appears as e^{-W} instead of the standard factor e^{-2W} . This is a consequence of the diagonalization carried out in the Caldeira-Leggett Hamiltonian (16). The normal modes are now damping phonons given by (28) and, therefore, the square thermal averages of the displacements are no longer independent of time. As is well known, this factor is a measure of the effect of thermal motions in reducing the periodicity of the lattice. It is also a measure of the number of phonons involved in a scattering event. In this formalism, it is clearly seen that there is a new contribution to the lifetimes (the sum running over p) independent of the creation or annihilation of phonons. This contribution comes from the whole damping lattice.

(c) *Adsorbates and phonons*

The diffuse elastic intensity of the He atoms scattered at large angles away from the specular direction provides very detailed information on the mobility of adsorbates on surfaces. At low coverages, the interaction among adsorbates can be ignored, thus allowing to work within the so-called *single-adsorbate approximation* describing the quasielastic and low frequency vibrational lineshapes in terms of the *motional narrowing* effect [27]. The relaxation processes of creation or annihilation adsorbate events are due to the coupling of the adsorbate modes (considered as the system) to the phonon substrate (single-bath model). Thus, (33) is also valid for describing the relaxation dynamics of an excited single adsorbate with a renormalized frequency given by (25). Furthermore, it can be considered as a generalization of previous lineshapes obtained in a more phenomenological way [27].

Based on the transition matrix formalism, Manson and Celli [8] proposed a quantum diffuse inelastic theory for small and intermediate coverages of adsorbates on the surface by ignoring multiple scattering effects of He atoms. The dynamical structure factor is then obtained by assuming all the lattice vibrational modes (N_{ph}) and point-like scattering centers (N_{ad}) satisfying the harmonic approximation with a given frequency distribution function. Therefore, following the same type of arguments, we could assume two independent, uncorrelated baths to describe diffusion of interacting adsorbates:

the first bath consists of the surface phonons and the second bath is formed by N_{ad} adsorbates which obviously changes with the surface coverage given by experimental conditions [14, 15, 28]. The same procedure can now be used to obtain lineshapes of adsorbates; in particular, the lowest frequency mode or frustrated translational mode. To this end, we have to generalize the Hamiltonian (16) to two baths, one for phonons and the other for adsorbates. In this two-bath model (at a given coverage), we take one adsorbate as the tagged particle or system, while the remaining ones constitute the second bath described by M harmonic oscillators. Thus, when a given adsorbate is excited the coupling to phonons and adsorbates simultaneously governs to the relaxation dynamics. In this way, the corresponding total Hamiltonian in one dimension will read as [14, 15]

$$\begin{aligned}
H = & \frac{p^2}{2m} + V(q) \\
& + \sum_{i=1}^{N_{ph}} \left[\frac{p_i^2}{2m_i} + \frac{m_i}{2} \left(\omega_i x_i - \frac{c_i}{m_i \omega_i} q \right)^2 \right] \\
& + \sum_{j=1}^{N_{ad}} \left[\frac{\tilde{p}_j^2}{2\tilde{m}_j} + \frac{\tilde{m}_j}{2} \left(\tilde{\omega}_j \tilde{x}_j - \frac{d_j}{\tilde{m}_j \tilde{\omega}_j} q \right)^2 \right], \tag{34}
\end{aligned}$$

where now the tilde magnitudes refer to the second bath of N_{ad} adsorbates, which are also taken as harmonic oscillators. The c_i and d_i coefficients give the coupling strengths between the adsorbate (system) and the substrate phonons or other adsorbates, respectively. The spectral density for the two baths is defined analogously to the single-bath model,

$$J(\omega) = \frac{\pi}{2} \sum_{i=1}^{N_{ph}} \frac{c_i^2}{m_i \omega_i^2} \delta(\omega - \omega_i) + \frac{\pi}{2} \sum_{j=1}^{N_{ad}} \frac{d_j^2}{\tilde{m}_j \tilde{\omega}_j^2} \delta(\omega - \tilde{\omega}_j), \tag{35}$$

but now it is split up into two terms, one spectral density associated with the surface phonons and another one with the adsorbates. In a similar way, the friction functions are defined as in (18), but with the spectral density being (35). The total friction function $\eta(t)$ also splits into two terms, one due to the phonons, $\gamma(t)$, and another due to the collisions with the the adsorbates or *collisional friction*, $\lambda(t)$: $\eta(t) = \gamma(t) + \lambda(t)$ [14, 15]. After diagonalization of Hamiltonian (34) and if Ohmic friction is assumed, the new renormalized frequencies of the set of $N_{ph} + N_{ad}$ oscillators are expressed in a similar way to Eqs. (25) and (26) but now in terms of η instead of γ . A straightforward generalization of lineshapes accounting for both phonon and adsorbate (low-frequency modes) excitations at the same time is then easily obtained. Again, this theoretical procedure is more general than that previously reported based on phenomenological arguments [28].

(d) *The convolution problem. Some simple applications*

As a final remark, we would like to mention that, taking into account all the previous information, one could carry out the calculation of the convolution of phonon and adsorbate lineshapes in order to extract reliable lifetimes and damping coefficients or phonon frictions in a more careful way. Thus, as an illustration, now we will focus on experimental lineshapes obtained from typical time-of-flight measurements from He atom-surface scattering: an isolated frustrated translational (T) mode peak and the masking of a T -mode by a substrate Rayleigh phonon. In particular, we will consider He scattering off a Cu(001) surface with a 3% of CO coverage at low (surface) temperatures [20], displaying the results in terms of the energy transferred (ΔE) in the scattering process. Experimentally, the intrinsic peak width is of the same order of magnitude as the apparatus energy resolution. Therefore, quantitative reliable results can only be extracted by using deconvolution techniques. Thus, in the case of low surface temperatures, one proceeds (numerically) by assigning a single Lorentzian function to the intrinsic lineshape and convoluting it with the apparatus response function, which is usually assumed to be a Gaussian function. Then, by means of standard least squares fitting techniques, the resulting curve is optimized until it fits the experimental one, extracting finally from this procedure the good Lorentzian lineshape. In the applications below, we have used this procedure rather than Eq. (33), since we are within a low temperature regime and only one Lorentzian function is going to contribute. Information about position of the maximum and full width at half maximum is processed in terms of renormalized frequencies according to (25) and (26). As the surface temperature, more and more Lorentzian functions have to be added in order to determine the lineshape, in agreement with (33).

In Fig. 1 we show the result obtained (solid line) from the convolution of a single Lorentzian function with the Gaussian apparatus response function, i.e., a typical Voigt profile, which describes the creation of a T -mode peak at $\Delta E = \hbar\bar{\omega}_0 \approx -4$ meV and a surface temperature $T_s = 60$ K. The dashed line represents the best-fitting Lorentzian function whose position and full width at half maximum (FWHM) are determined, as mentioned above, by convoluting the Lorentzian with the apparatus response function and then finding the best fit to the experimental data (here, they have been extracted from Ref. [20] and are represented with open circles). As can be seen, the agreement between the experimental data [20] and our fitting is fairly good. The FWHM is around 0.38 meV (damping constant) and ω_0 can be calculated from (25). As mentioned above, as the surface temperature increases, the number of Lorentzian terms to be considered in (33) will also increase in order to reproduce a wider and lower convolution profile, which can be later compared with the experimental peak.

In Fig. 2, the results from the convolution (solid line) describe the case where the peaks corresponding to the annihilation of both a substrate Rayleigh phonon (at $\Delta E \approx 3.5$ meV) and the T -mode of the adsorbate (at $\Delta E \approx 4$ meV) are very close. Here, again, the surface temperature is $T_s = 60$ K, which allows us to consider only one

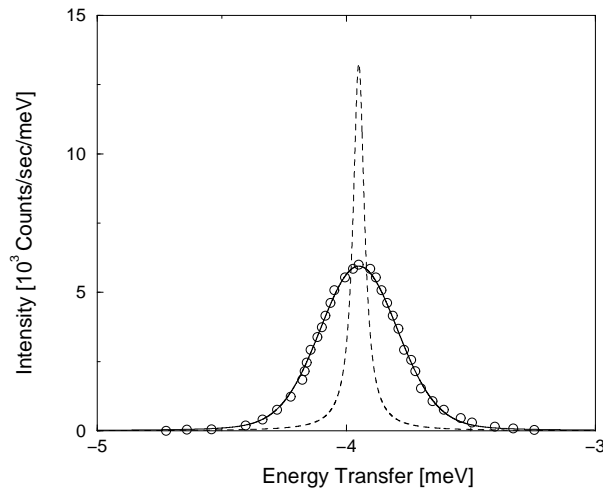


Figure 1. Comparison between experimental data (\circ) [20] and convolution results (solid line) for the creation of the T -mode peak ($\Delta E \approx -4$ meV) at $T_s = 60$ K. The dashed line represents the best-fitting Lorentzian function whose position and FWHM are determined in such a way that, once the Lorentzian is convoluted with the (Gaussian) apparatus response function, it best fits the experimental data.

Lorentzian function (dashed lines) for each event, the excitation of the substrate phonon and the adsorbate T -mode. As can be seen, we find a fairly good agreement between our theoretical results and the experimental data (open circles) [20]. Both peaks are so close that they overlap, which leads the Rayleigh phonon peak, more intense, to mask the peak corresponding to the T -mode. This is in a sharp contrast with the relative height of the corresponding Lorentzians, which is lower for the former. This overlapping of the two Lorentzian functions (dashed lines) thus explains the formation of the shoulder observed at larger ΔE .

Acknowledgments

We would like to thank Profs. V. Celli and J. R. Manson for very interesting and stimulating comments and discussions about this work. This is a very good opportunity to express our deep gratitude to Vittorio and Dick to be always scientific references in the atom-surface scattering field. This work is dedicated to both of them.

This work has been supported in part by the Ministerio de Ciencia e Innovación (Spain) under Project FIS2007-02461. R.M.-C. thanks the Royal Society for a Newton Fellowship. A.S. Sanz thanks the Consejo Superior de Investigaciones Científicas for a JAE-Doc contract.

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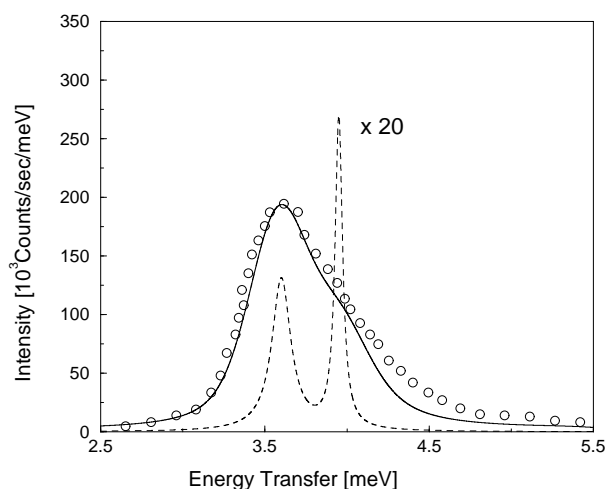


Figure 2. Comparison between experimental data (\circ) [20] and convolution results (solid line) for the overlapping of the peaks corresponding to the annihilation of both a substrate Rayleigh phonon (at $\Delta E \approx 3.5$ meV) and the T -mode of the adsorbate (at $\Delta E \approx 4$ meV) at $T_s = 60$ K [20]. The dashed lines represent the best-fitting Lorentzian functions whose positions and FWHMs are determined in such a way that, once the Lorentzians are convoluted with the (Gaussian) apparatus response function, they best fit the experimental data.

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