

Adsorbate aggregation and relaxation of low-frequency vibrations

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We present a study of resonant vibrational coupling between adsorbates and an elastic substrate at low macroscopic coverages. In the first part of the paper we consider the situation in which adsorbates form aggregates with high local coverage. Based upon our previously published theory, we derive formulas describing the damping rate of adsorbate vibrations for two cases of such aggregation: (i) adsorbates attached to step edges and (ii) adsorbates forming two-dimensional islands. We have shown that damping is governed by local coverage. Particularly, for a wide range of resonant frequencies, the damping rate of adsorbates forming well-separated islands is described by the damping rate formula for a periodic overlayer with the coverage equal to the local coverage in the island. The second part of the paper is devoted to facilitating the evaluation of damping rates for a disordered overlayer. The formula describing the damping rate involves the parameter β , which is related to the local density of phonon states at the substrate surface and does not allow a closed-form representation. For substrates of isotropic and cubic symmetries, we have developed a good analytical approximation to this parameter. For a vast majority of cubic substrates the difference between the analytical approximation and numerical calculation does not exceed 4%.

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I. INTRODUCTION

Molecules or atoms adsorbed on surfaces of materials can oscillate about the adsorption bond. If this motion corresponds, in the absence of the adsorption bond, to free translation relative to the surface, then this mode is called a frustrated translation (FT). It plays an important role in such dynamical processes as reactivity, surface diffusion, and desorption. For many systems, especially with a metallic substrate, the frequency of the FT mode is so low that it readily couples to low-energy excitations in the substrate, which, in the case of metals, include both phonons and electron-hole pair excitations. These bulk excitations provide decay channels for FT modes, which thus acquire a finite lifetime τ and become resonances. Associated with this lifetime is the resonance width, or damping rate, $\gamma=1/\tau$. In many cases the electronic contribution to the damping rate is small compared with the phononic contribution.¹

We recently developed a general theory of phonon-mediated FT relaxation that can be applied to any adsorbate overlayer pattern. Using this theory we derived simple FT damping rate laws for three important classes of adsorbate patterns: an isolated adsorbate, an ordered overlayer, and a randomly disordered overlayer. Although there are no experimental results with which to compare for isolated adsorbates, agreement with experiment for ordered and disordered overlayers is excellent.²

However, these three structural models do not cover all possible experimental conditions. Depending on the interactions of the adsorbates with the substrate and with each other, their distribution on the surface can differ strongly from the periodic or random uncorrelated cases. Under certain conditions the adsorbates may gather into aggregates even at very low coverages. In this paper we consider two possible examples of such adsorbate aggregation: (i) adsorbates accumulating along the edges of surface steps; and (ii) adsorbates forming two-dimensional (2D) islands. We assume that the *average* coverage is low enough that these aggregates are well-separated from each other and can be treated as isolated. For each of these cases we derive a corresponding damping rate formula from our general result.

Another goal of this paper is to facilitate the evaluation of damping rates for a disordered overlayer. The main difficulty here is that one needs to integrate the Green's function for a semi-infinite elastic medium over the in-plane wave vector at a dense array of frequencies. Regrettably, no closed-form expression for this integral exists, and it must be computed numerically. In this paper we present a good analytical approximation of this integral for elastic media of isotropic and cubic symmetries. We have tested our approximation formula for 88 different materials with cubic symmetry, comparing it against well-converged numerical calculations. The difference between the analytical approximation and the reference numerical values never exceeds 6%, and

for a vast majority of the materials is under 4%.

The remainder of this paper is organized as follows. In Sec. II we briefly review our theory of phonon-mediated FT damping. For details of the derivation, the reader is referred to Ref. 2. This theory is then applied in Secs. III and IV to the cases of adsorbates aggregated along step edges and in islands, respectively. In Sec. V we present our approximation formula for the \mathbf{k} -space integral of the substrate Green's function, thus facilitating the evaluation of the damping rate of a disordered overlayer. Finally, in Sec. VI we summarize and draw conclusions.

II. REVIEW OF THEORY

The phonon contribution to the damping of low-frequency adsorbate vibrations was considered earlier by Persson and Ryberg³ (PR) and by Hall, Mills, and Black⁴ (HMB). Persson and Ryberg considered a single, isolated adsorbate coupled to a semi-infinite isotropic elastic substrate. Since direct adsorbate-adsorbate interactions are weak for all but the densest coverages, this case was presumed applicable for most experimental conditions. Their model gives a damping rate law that varies with the vibrational frequency as ω_0^4 . However, when applied to various experimental systems, the PR model predicts damping rates that are much smaller than the measured values. Furthermore, the PR model has no explicit coverage dependence; coverage enters the damping rate law only implicitly through its effect on the resonance frequency. The applicability of the model is limited to extremely low coverage ($<1\%$). Hall, Mills, and Black considered a periodic overlayer of rare-gas molecules physisorbed at an isotropic substrate. The damping rate implied by their result is proportional to the coverage and to the square of the resonant frequency. The periodic distribution of the adsorbates over the surface implied by the HMB model generally occurs at high coverage ($\geq 25\%$). In general, most adsorbate systems have structures that differ from both of these special cases.

In our recent work² we developed a general theory for a completely arbitrary overlayer structure. We considered an array of N noninteracting adsorbates of mass m located at arbitrary positions $\{\mathbf{R}_a\}$ at the surface of an anisotropic, semi-infinite elastic substrate of mass density ρ and elastic modulus tensor C_{ijkl} , occupying the half-space $z < 0$. The adsorbates are coupled to the substrate by harmonic springs of frequency ω_0 and are allowed to oscillate along one of the Cartesian axes α . The adsorbates do not interact with each other directly. We showed that the damping rate for this system is described by

$$\gamma = \frac{m}{\rho} \omega_0^2 \int \frac{d^2k}{(2\pi)^2} [\omega_0 \text{Im} D_{\alpha\alpha}(\mathbf{k}, \omega_0)] S(\mathbf{k}) \equiv \frac{m}{\rho} \omega_0^2 I(\omega_0), \quad (1)$$

where $D_{ij}(\mathbf{k}, \omega)$ is the in-plane Fourier transform of the substrate elastic Green's function evaluated at the surface ($z = z' = 0$), and $S(\mathbf{k})$ is the structure factor defined as

$$S(\mathbf{k}) = \frac{1}{N} \left\langle \sum_{a,b} \exp[-i\mathbf{k} \cdot (\mathbf{R}_a - \mathbf{R}_b)] \right\rangle, \quad (2)$$

where the angle brackets denote the appropriate ensemble average. The integration in Eq. (1) is taken over the bare-surface Brillouin zone. The integral $I(\omega)$ in Eq. (1) is a convolution of two quantities, one of which (inside the square brackets) describes all the substrate properties, while $S(\mathbf{k})$ provides all the information on how the adsorbates are distributed over the surface. Except for a unitless factor of order unity, the quantity in the square brackets is equal to the \mathbf{k} -resolved density of elastic modes at the substrate surface for frequency ω_0 . Any possible explicit dependence of the damping rate upon the coverage or the structural order comes from the structure factor $S(\mathbf{k})$.

We previously applied this general result to three different structure models: an isolated adsorbate, a periodic array of adsorbates (appropriate at high coverages), and a random array of adsorbates (appropriate at low coverages). For each of these models, the structure factor has a simple algebraic form. Their substitution into Eq. (1) leads to

$$\gamma = \frac{m}{\rho} \omega_0^4 \beta \quad (3)$$

for an isolated adsorbate,

$$\gamma = \frac{m}{\rho} \omega_0^2 \frac{\theta}{A_0 c_{\perp}^{(\alpha)}} \quad (4)$$

for a periodic overlayer,^{7,8} and

$$\gamma = (1 - \theta) \frac{m}{\rho} \omega_0^4 \beta + \frac{m}{\rho} \omega_0^2 \frac{\theta}{A_0 c_{\perp}^{(\alpha)}} \quad (5)$$

for a random overlayer,⁹ where θ is the coverage, A_0 is the area per surface site, $c_{\perp}^{(\alpha)}$ is the speed of an α -polarized sound wave propagating perpendicular to the surface, and β is defined according to

$$\beta = \frac{1}{\omega} \int \frac{d^2k}{(2\pi)^2} \text{Im} D_{\alpha\alpha}(\mathbf{k}, \omega). \quad (6)$$

The integral in Eq. (6) is proportional to the density of α -polarized states divided by frequency. For a 3D elastic medium the density of α -polarized states is proportional to ω^2 , and thus β is independent of frequency ω . The evaluation of this parameter is discussed in Sec. V. The damping rates given by Eqs. (3) and (4) are just the anisotropic versions of the PR³ and HMB⁴ results, respectively. No experimental results are available for an isolated adsorbate. However, we compared the other two models with experiments on CO on Cu(001) by applying Eq. (4) to the case of an ordered overlayer at 50% coverage,⁵ and Eq. (5) to the case of a disordered overlayer at 3% coverage.⁶ Both models predict the lifetimes in excellent agreement with the measured values. Equation (5) was independently derived later by Persson *et al.*¹⁰ for the case of an isotropic substrate. They also considered the case of an isolated adsorbate of finite size.

III. ADSORBATES ALIGNED ALONG STEP EDGES

In this section we study the case of adsorbates located at step edges. This geometry is important since steps are always

present at surfaces and they generally attract adsorbates to their edges.¹¹ While the macroscopic coverage is low for this case, the local coverage is high.

In our analysis we ignore the influence of the steps on the substrate Green's function. The only effect of steps that we consider is to set the distribution of adsorbates. We assume that the adsorbates form one-dimensional (1D), locally periodic arrays. Starting from Eq. (1) we derive the damping rate for an infinite, 1D periodic chain of adsorbates, and then we extend the derivation for a finite, locally periodic chain.

A. One-dimensional infinite chain

We assume that the adsorbates are arranged in an infinite, 1D, periodic array along the x axis. The adsorbate positions are given by $\mathbf{R}_a = (X_a, 0)$, and the nearest-neighbor distance is d . The 1D coverage of the step edge can be defined as $\theta_{1D} = a_0/d$, where a_0 is the nearest-neighbor distance between the substrate atoms along the step edge. Then the structure factor $S(\mathbf{k})$ takes the form

$$S(\mathbf{k}) = \frac{2\pi}{d} \sum_n \delta(k_x - G_n), \quad (7)$$

where $\{G_n\}$ is the set of 1D reciprocal vectors defined as $G_n = 2\pi n/d$. Substitution of Eq. (7) into Eq. (1) leads to

$$\gamma = \frac{m}{\rho} \omega_0^3 \frac{1}{d} \int \frac{dk_y}{2\pi} \sum_n [\text{Im} D_{\alpha\alpha}(G_n, k_y; \omega_0)]. \quad (8)$$

Since there are no resonant phonon states available in the substrate for in-plane wave vectors $|G_n| > \omega_0/c_R$, where c_R is the speed of the Rayleigh wave, the imaginary part of the Green's function in Eq. (8) vanishes for these values of G_n , and thus these terms do not contribute to the sum. Similar to the case of a two-dimensional (2D) periodic overlayer discussed in detail in our earlier work,⁸ it turns out that for all 1D coverages presently accessible to experiment ($\theta_{1D} > \theta_{1D}^{(c)} \approx 10\%$), only the term with $G_n = 0$ contributes to the damping rate. Moreover, the integral of this term in Eq. (8) does not depend on frequency ω_0 , and we can define a constant ζ_α according to

$$\zeta_\alpha = \int \frac{dk_y}{2\pi} [\text{Im} D_{\alpha\alpha}(0, k_y; \omega_0)]. \quad (9)$$

It turns out that ζ_x (vibration parallel to the step) differs significantly from ζ_y (vibration perpendicular to the step). However, for substrates with isotropic or cubic symmetry, these values, while different from each other, are independent of the orientation of the step. It is, therefore, appropriate to use the notation ζ_{\parallel} for oscillations along the step and ζ_{\perp} for oscillations perpendicular to the step but still in the plane. We can now write the damping rate formula compactly as

$$\gamma_{\parallel, \perp} = \frac{m}{\rho} \omega_0^3 \frac{\zeta_{\parallel, \perp}}{d}. \quad (10)$$

Thus oscillations along the step are damped at a different rate than oscillations perpendicular to the step. Typically, the damping rate is higher for vibrations along the step.

Experimentally measured damping rates can be related to Eq. (10) in two possible ways. If the frequencies for both

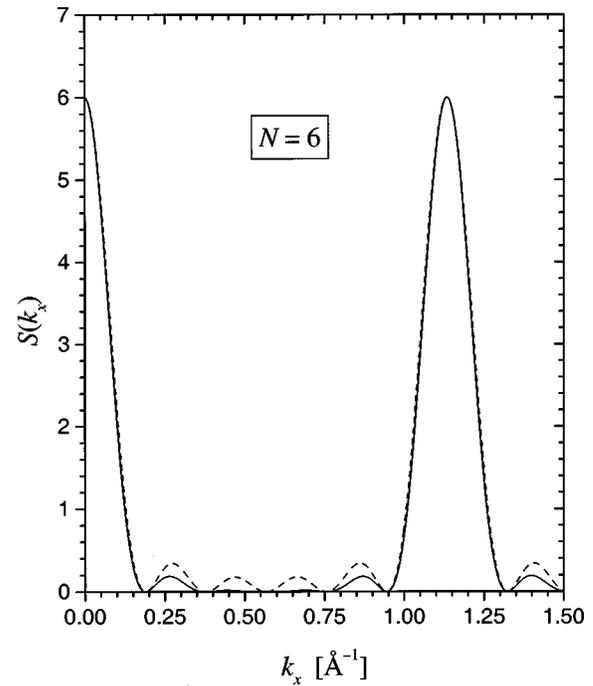


FIG. 1. The structure factor $S(k_x)$ for a chain of six atoms separated by $d = 5.54 \text{ \AA}$. The solid (dashed) curve was computed according to Eq. (11) [Eq. (12)].

vibrational modes are close, then the measured damping rate will correspond to an average of γ_{\parallel} and γ_{\perp} . Otherwise, both modes can be resolved experimentally, each exhibiting its own damping rate.

B. One-dimensional finite chain

Here we consider a finite, locally periodic chain of N adsorbates along one of the step edges. As before, the x axis is along the step, and the nearest-neighbor distance in the chain is d . The total length of the chain is $L = Nd$. The structure factor corresponding to this configuration is given by

$$S(\mathbf{k}) = N \left[\sum_n \frac{\sin[(k_x - G_n)L/2]}{[(k_x - G_n)L/2]} \right]^2. \quad (11)$$

Most of the weight of this function is in the peaks centered at the reciprocal vectors $G_n = 2\pi n/d$. Even at relatively small values of N the cross terms in Eq. (11) may be neglected, and the square of the sum can be approximated by a sum of squares

$$S(\mathbf{k}) = N \sum_n \left[\frac{\sin[(k_x - G_n)L/2]}{[(k_x - G_n)L/2]} \right]^2. \quad (12)$$

Equations (11) and (12) are compared for a chain of $N=6$ adsorbates separated by $d = 5.54 \text{ \AA}$ (twice the nearest-neighbor distance for platinum) in Fig. 1. The solid line corresponds to the structure factor computed according to Eq. (11), while the dashed line represents $S(\mathbf{k})$ given by Eq. (12). As N increases, the main peaks become narrower (the width of the peaks is approximately $2\pi/L$), and the difference between the two formulas decreases. In the limit $N \rightarrow \infty$, both expressions take the form of Eq. (7).

Finally, we show that the damping rate for a finite chain of adsorbates can be computed approximately from Eq. (10) for large enough N (where “large enough” may be as small as 6). First, we assume that all the weight in the structure factor comes from the main peaks. Then, repeating the argument we gave for the infinite chain, we conclude that if $\omega_0/c_R < 2\pi(1-1/N)/d$, only the peak centered at $G=0$ contributes to the integral in Eq. (1), and the damping rate becomes

$$\gamma = \frac{m}{\rho} \omega_0^3 \int \frac{dk_x}{2\pi} N \left[\frac{\sin(k_x L/2)}{(k_x L/2)} \right]^2 \int \frac{dk_y}{2\pi} [\text{Im} D_{\alpha\alpha}(\mathbf{k}, \omega_0)]. \quad (13)$$

If the peak is narrow enough, the imaginary part of the Green's function does not change significantly over its width (the region $k_x < 2\pi/L$). Thus for each value of k_y the Green's function can be replaced by its value at $k_x=0$. The integral over k_x can now be carried out explicitly, and Eq. (10) follows.

IV. ADSORBATES FORMING ISLANDS

In this section we analyze the damping of the FT mode when adsorbates form 2D islands at the substrate surface. As with 1D step-edge aggregation, this case corresponds to low macroscopic coverage, but high local coverage. We assume that each island is a locally periodic array of N adsorbates with local coverage θ_{loc} and area A . We also assume that the distance between islands is large enough that the islands can be treated as isolated.

Unlike in the previous section, there is no need here for considering the case of an infinite island, because an infinite island is the same as a periodic overlayer with $\theta_{\text{loc}} = \theta$, and its FT damping rate is given by Eq. (4). The problem of a finite island appears to be more complicated than that of a finite 1D chain at a step edge. The reason is that, apart from its local coverage and size, the island is also characterized by its shape. It is convenient to represent the shape of the island by a function $f(\mathbf{r})$ defined as

$$f(\mathbf{r}) = \begin{cases} 1 & \text{if } \mathbf{r} \text{ is inside island,} \\ 0 & \text{otherwise.} \end{cases} \quad (14)$$

It is straightforward to show that the structure factor can be expressed in terms of the Fourier transform $f(\mathbf{k})$ of this function as

$$S(\mathbf{k}) = \frac{N}{A^2} \sum_{\mathbf{G}, \mathbf{G}'} f(\mathbf{k} - \mathbf{G}) f(\mathbf{k} - \mathbf{G}'), \quad (15)$$

where summation is over reciprocal vectors defined by the local periodicity of the adsorbate distribution inside the island.

We further assume that the island is a convex set with similar dimensions in all directions (i.e., its width is of the same order of magnitude as its length). If the number of adsorbates in the island is not too small (the meaning of which is discussed below), then the function $f(\mathbf{k})$ will have a strong peak at $\mathbf{k}=0$, with most of the function's weight within the peak. Analytical examples of this function include

$$f_{\text{rect}}(\mathbf{k}) = A \frac{\sin[k_x a/2]}{[k_x a/2]} \frac{\sin[k_y b/2]}{[k_y b/2]}, \quad (16)$$

for a rectangular island with dimensions a along the x axis and b along the y axis, and

$$f_{\text{circ}}(\mathbf{k}) = 2A \frac{J_1(|\mathbf{k}|R)}{|\mathbf{k}|R} \quad (17)$$

for a circular island of radius R , where $J_1(x)$ is the first-order Bessel function.

We now follow the arguments of the 1D case. First, we neglect the cross-terms in Eq. (15) and write it as

$$S(\mathbf{k}) = \frac{N}{A^2} \sum_{\mathbf{G}} [f(\mathbf{k} - \mathbf{G})]^2. \quad (18)$$

Then, we assume that all the weight in the structure factor comes from the main peaks. If the resonant frequency of the FT mode ω_0 is small enough that $\omega_0/c_R < G_1 - \Delta$, where G_1 is the magnitude of the smallest reciprocal vector, and Δ is the maximal width of the main peak in $S(\mathbf{k})$, then only the $\mathbf{G}=0$ term will contribute to the integral in Eq. (1). Thus this equation now takes the form

$$\gamma = \frac{m}{\rho} \omega_0^2 \int \frac{d^2k}{(2\pi)^2} [\omega_0 \text{Im} D_{\alpha\alpha}(\mathbf{k}, \omega_0)] \frac{N}{A^2} [f(\mathbf{k})]^2. \quad (19)$$

If the peak of $[f(\mathbf{k})]^2$ is narrow enough, the imaginary part of the Green's function does not change significantly over its width (i.e., the region $|\mathbf{k}| < \Delta$), and it can be replaced by its value at $\mathbf{k}=0$ given by $\text{Im} D_{\alpha\alpha}(0, \omega_0) = 1/(c_{\perp}^{(\alpha)} \omega_0)$, and taken out of the integral. The remaining integral can be evaluated with the help of Parseval's theorem as

$$\int \frac{d^2k}{(2\pi)^2} \frac{N}{A^2} [f(\mathbf{k})]^2 = \int d^2r \frac{N}{A^2} [f(\mathbf{r})]^2 = \frac{N}{A} = \frac{\theta_{\text{loc}}}{A_0},$$

where, as before, A_0 is the area of the surface unit cell. Substituting this result into Eq. (19) we obtain

$$\gamma = \frac{m}{\rho} \omega_0^2 \frac{\theta_{\text{loc}}}{A_0 c_{\perp}^{(\alpha)}}, \quad (20)$$

which is exactly the damping rate of a periodic overlayer given by Eq. (4) with the total coverage θ being replaced by the local coverage θ_{loc} .

Finally, we need to determine for which values of N the approximation given by Eq. (20) really works. We consider, as an example, an isolated island of hexagonal shape on the Pt(111) surface with local coverage $\theta_{\text{loc}} = 1/4$. This is about the lowest local coverage observed for islands of small molecular adsorbates. If the approximation given by Eq. (20) holds for this coverage, it will also hold for higher coverages. We have computed the integral $I(\omega)$ in Eq. (1) for hexagonal islands of different sizes, and, in Fig. 2, plot $I(\omega)$ vs ω for each island size. The value of the integral for the two limiting cases of an isolated adsorbate and an infinite periodic overlayer are shown by the dashed and solid lines, respectively. The dotted, dashed-dotted, and dashed-double-dotted lines correspond to the cases of one, two, and three hexagonal shells of adsorbates around the center adsor-

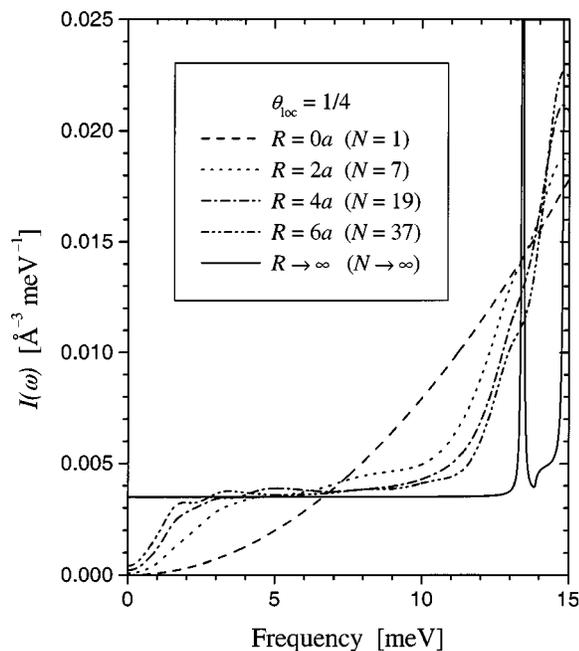


FIG. 2. Function $I(\omega)$ for an isolated adsorbate (dashed line), for an infinite periodic overlayer (solid line) at coverage $\theta = 1/4$, and for one-shell (dotted line), two-shell (dashed-dotted line), and three-shell (dashed-double-dotted line) hexagonal islands at local coverage $\theta_{\text{loc}} = 1/4$. The substrate is Pt(111). In the inset, R is the circumscribing radius of an island, a is the nearest-neighbor distance between the substrate atoms, and N is the number of adsorbates inside an island. The features at 13.3 meV are caused by coupling to Rayleigh waves at G_1 .

bate, respectively. The inset to Fig. 2 characterizes the islands by their circumscribing radius R , and the number of adsorbates, N , within the island.

The behavior of $I(\omega)$ shown in Fig. 2 can be readily explained in terms of resonant phonon wavelengths at frequency ω . For small frequencies the phonon wavelengths are much greater than the island size, and the adsorbates in the island behave like a single isolated adsorbate of mass Nm . Thus for small frequencies we have $I(\omega) = N\beta\omega^2$ in accordance with Eq. (3).¹² Mathematically, this result can be obtained from Eq. (19) by setting $f(\mathbf{k}) = f(0) = A$. Frequencies for which the resonant phonon wavelengths become comparable with the island size correspond to the crossover region where this quadratic behavior changes. When the phonon wavelengths are smaller than the island size, but still significantly greater than the nearest-neighbor distance between the adsorbates, only phonons with in-plane wave vector component, \mathbf{k} , near zero couple strongly to the FT mode due to the $\mathbf{G} = 0$ peak in the structure factor given by Eq. (18). Terms with $\mathbf{G} \neq 0$ have no corresponding resonant phonons at these frequencies. In this frequency region we expect $I(\omega)$ to closely follow its limiting value of a full periodic overlayer. Finally, when ω is large enough that the phonon wavelengths become comparable to the inter-adsorbate nearest-neighbor distance, nonzero \mathbf{G} -vectors in the structure factor become available channels for resonant phonon coupling. However, for realistic local coverages ($\theta_{\text{loc}} \geq 1/4$) these wave vectors lie at the boundary of the bare-surface Brillouin zone, where continuum models are no longer applicable. For the case $\theta_{\text{loc}} = 1$, this second crossover region does not exist, because

all nonzero \mathbf{G} -vectors lie outside the surface Brillouin zone.

From Fig. 2 one can determine the range of resonant FT frequencies for which the approximation given by Eq. (20) holds. Even for the island with only one hexagonal shell ($N=7$), there is such a frequency range: $I(\omega)$ stays close to its limiting value of a periodic overlayer for a range of frequencies between about 3 and 7 meV. For larger islands this range expands to frequencies between 2 and 11 meV.

We can analytically estimate this frequency range for an island of size D . The low-frequency threshold corresponds to a transverse wave with wave vector magnitude equal to the width, Δ , of a peak in the structure factor, which can be estimated as $2\pi/D$. The frequency of such a wave is $\omega_{\text{low}} = 2\pi c_T/D$. The high-frequency threshold corresponds to a transverse wave with wave vector magnitude equal to $G_1 - \Delta$, which is approximately $2(D/d - 1)\pi c_T/D$, where d is the inter-adsorbate nearest-neighbor distance, as before. The frequency of this wave is $\omega_{\text{high}} = (D/d - 1)\omega_{\text{low}}$. For a three-shell hexagonal island ($N=37$) with $\theta_{\text{loc}} = 1/4$ on the Pt(111) surface, we have $d = 5.54 \text{ \AA}$, $D/d = 6$, and $c_T = 11 \text{ \AA meV}$, which leads to the estimates $\omega_{\text{low}} = 2.1 \text{ meV}$ and $\omega_{\text{high}} = 10.5 \text{ meV}$. This frequency range is in excellent agreement with the corresponding plot in Fig. 2. Thus the example of a hexagonal island on the Pt(111) surface demonstrates that, when most of the adsorbates form widely separated islands, the damping rate can be computed from Eq. (20) for FT resonant frequencies within a broad range.

V. APPROXIMATION FORMULA FOR β PARAMETER

The main difficulty researchers may encounter in using Eq. (5) to determine the damping rate for low-coverage systems is the necessity to compute the integral in Eq. (6) numerically. In this section we present an analytical approximation for the parameter β defined by Eq. (6). The approximation is developed for the cases of systems with isotropic or cubic symmetry.

We start from the observation that β must be a function of the substrate parameters of the model, namely, the mass density ρ and the elastic constants c_{ij} . Generally, $i, j = 1, \dots, 6$, but we include only independent constants characteristic of a given symmetry. This function must obey certain global constraints, however. It follows from the equation of motion and the boundary conditions that any quantity depending on the model inputs may depend only on the ratios c_{ij}/ρ , which we denote as k_{ij} . Because β does not depend on the frequency ω , one can show from the equations of motion that β , as a function of density-normalized elastic constants k_{ij} , must satisfy a scaling property given by

$$\beta(vk_{ij}) = v^{-3/2} \beta(k_{ij}), \quad (21)$$

where v is an arbitrary number. This scaling property reduces the number of independent variables in the function $\beta(k_{ij})$ by one. We have found an excellent analytical approximation to this function for the cases of isotropic and cubic substrates.

A. Isotropic substrate

An isotropic medium is characterized by only two density-normalized elastic constants: k_{11} and k_{44} . The trans-

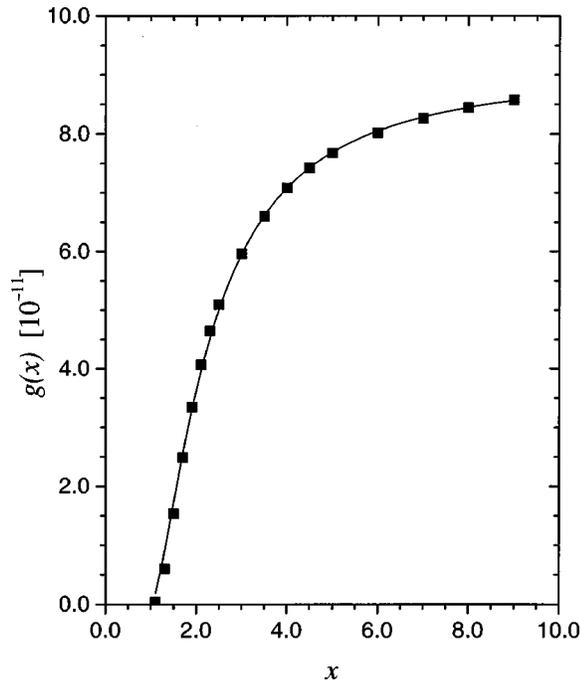


FIG. 3. Fitting function $g(x)$ defined in Eq. (22), computed numerically (squares) and using the analytical approximation given in Eq. (23) (solid line).

verse and the longitudinal speeds of sound are related to these constants by $c_T = \sqrt{k_{44}}$ and $c_L = \sqrt{k_{11}}$, respectively. Taking into account the scaling property given by Eq. (21), we can express β^{-2} as

$$\beta^{-2} = k_{44}^3 g\left(\frac{k_{11}}{k_{44}}\right), \quad (22)$$

where $g(x)$ is an unknown dimensionless function of one variable.

To elucidate the behavior of $g(x)$, we have computed β numerically for a wide range of k_{11}/k_{44} . The result of these calculations is shown by squares in Fig. 3. From Fig. 3 we obtain that (i) $g(x)$ goes to zero at $x=1$ as $(x-1)^\alpha$, where $1 < \alpha < 2$, and (ii) $g(x)$ asymptotically approaches a constant as $x \rightarrow \infty$. We find that the function

$$g(x) = P \frac{(x-1)^{3/2}}{3/2 + (x-1)^{3/2}} \quad (23)$$

almost perfectly approximates the numerical data (solid line in Fig. 3). The parameter P is dimensionless and has an optimal value of $P = 9.14 \times 10^{-11}$.

B. Cubic substrate

The isotropic approximation is not correct for most single-crystal materials. We therefore extend our approximation formula for β to describe substrate materials with cubic symmetry, since these are the most commonly used in experiments. Crystals with cubic symmetry have three independent density-normalized elastic constants: k_{11} , k_{12} , and k_{44} . The isotropic limit can be obtained from cubic symmetry by setting $k_{12} = k_{11} - 2k_{44}$. Taking advantage of the scaling property given by Eq. (21), we can write

TABLE I. Density-normalized elastic moduli ($10^{10} \text{ cm}^2/\text{s}^2$),^a β_n (computed numerically), β_a (computed using the analytical approximation), and $(\beta_a - \beta_n)/\beta_n$ for several cubic materials. All values of β are given in $10^{-3} \text{ meV}^{-3} \text{ \AA}^{-3}$.

Crystal	k_{11}	k_{12}	k_{44}	β_n	β_a	$(\beta_a - \beta_n)/\beta_n$
Al	39.58	22.40	10.51	1.3635	1.3657	0.16%
Cs	1.25	1.04	0.75	242.75	231.03	-4.83%
Cu	18.84	13.67	8.48	3.6321	3.5586	-2.02%
GaAs	22.34	10.10	11.18	1.7750	1.7835	0.48%
Ge	24.16	9.08	12.55	1.4659	1.4608	-0.35%
Au	9.98	8.45	2.18	23.549	22.361	-5.05%
Ir	25.75	10.75	11.37	1.5337	1.5377	0.26%
Fe	28.73	17.80	14.74	1.4481	1.4374	-0.74%
MgO	83.01	26.64	43.62	0.218 76	0.220 36	0.73%
Ni	27.85	17.38	13.94	1.5574	1.5439	-0.87%
Pd	18.87	14.62	5.96	5.3473	5.1660	-3.39%
Pt	16.13	11.66	3.56	7.9305	7.7329	-2.49%
Rb	1.87	1.58	1.08	142.05	133.94	-5.71%
Si	71.12	27.43	34.16	0.298 20	0.308 18	3.35%
Ag	11.81	8.92	4.39	9.0756	8.7958	-3.08%

^aMass density and elastic constants were taken from Ref. 13.

$$\beta^{-2} = k_{12}^3 h\left(\frac{k_{11}}{k_{12}}, \frac{k_{44}}{k_{12}}\right), \quad (24)$$

where $h(x,y)$ is an unknown function of two variables. Generally, the form of the function $h(x,y)$ may depend on the particular choice of the surface indices. However, numerical calculations of β for different low-index surfaces of the same material show that β is essentially independent of the surface orientation with respect to the crystallographic axes. Thus the same function $h(x,y)$ works well for any low-index surface.

First, we study how $h(x,y)$ depends on x by computing β numerically as a function of k_{11}/k_{12} while keeping k_{44}/k_{12} fixed. We find that $h(x,y)$ depends linearly on x when $x \gg 1$ and goes to zero at $x=1$ as $(x-1)^{3/2}$. We choose the fitting function to have the form

$$h(x,y) = b(y) \frac{(x-1)^{3/2}}{y + (x-1)^{1/2}} \quad (25)$$

which satisfies these asymptotic requirements.

The next step is to find a fitting function for $b(y)$. This can be accomplished by requiring that β for the cubic substrate given by Eq. (24) go to the isotropic limit described by Eq. (22) when $k_{12} = k_{11} - 2k_{44}$. This requirement uniquely specifies that the function $b(y)$ has the form

$$b(y) = \frac{P}{2} y^2 \left[1 + \left(\frac{y}{2}\right)^{1/2} \right] \frac{(y^{-1} + 1)^{3/2}}{3/2 + (y^{-1} + 1)^{3/2}}, \quad (26)$$

where the parameter P is the one determined for the isotropic case, namely $P = 9.14 \times 10^{-11}$.

To check the quality of the approximation given by Eqs. (24) through (26), we have computed β according to this approximation and compared it with β obtained by numerical calculations for 88 different materials with cubic symmetry. The error in the approximated value of β never exceeds 6% for this set of materials, and for the vast majority of cases it is below 4%. Table I shows this comparison for several

important substrate materials.¹³ It should be noted that a given error in β results in a smaller error in the predicted damping rate, γ , due to the β -independent term in Eq. (5).

VI. CONCLUSION

In this paper we have applied the general result of our continuum elastic model² of phonon-mediated adsorbate vibrational relaxation to derive analytic formulas for the FT damping rate when the adsorbates form aggregates on the surface. We have considered two possible forms of adsorbate aggregation: (i) when the adsorbates are aligned along step edges, and (ii) when the adsorbates form well-separated islands. We have derived an expression for the damping rate of an infinite periodic chain of adsorbates, and then shown that the damping rate of a finite locally periodic chain is described by the same expression for all chains above a small threshold length. For the case of an isolated island we have shown that, under mild restrictions on the island geometry, there is a wide range of possible FT resonant frequencies for which the damping rate is essentially the same as for a periodic overlayer with coverage equal to the island's local coverage.

Finally, to facilitate the use of our previously derived expression for the FT damping rate at low coverage, we have developed an analytical formula which approximates the parameter β appearing in the damping law. The formula is valid for both isotropic and cubic materials and achieves remarkable accuracy. We have tested the formula on 88 different cubic materials (*all* of whose elastic constants were readily available) and have found that our analytic approximation predicts β with accuracy better than 6%.

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