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Theoretical studies of the surface phonon linewidth

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Abstract

A brief review of two theoretical methods for calculating the linewidth of surface phonons is presented with specific application to the low-Miller-index surfaces of Ag, Cu, and Al. In the quasi-analytic method, linewidths are calculated by treating the cubic term of a reliable interatomic potential in first-order, time-dependent perturbation theory. In molecular dynamics (MD) simulations, linewidths are obtained from appropriate correlation functions and include the fully anharmonic contribution of the interaction potential. Surface relaxations and phonon frequencies calculated in the harmonic approximation, using selected many-body interatomic potentials, are found to be in good agreement with results from experimental data and *ab initio* calculations. At 300 K, the surface phonon linewidths range approximately between 1 and 0.1 THz, and are found to be in reasonable agreement with the values deduced from experiments. Some disagreement is found between results from perturbative methods and MD simulations. For the low-Miller-index surfaces of Ni, available results from MD simulations also summarized.

1. Introduction

At very low temperatures, phonons are expected to be good eigenstates of lattice vibrations in solids having characteristic frequencies, displacement patterns (polarizations), and infinite lifetime (negligible linewidth). With increasing temperatures, anharmonic effects are expected to shift the phonon frequencies and cause the linewidths to broaden [1]. The interest in studies of phonon linewidth thus stems from the information that it is expected to provide about anharmonicity in the interatomic potential. In the case of surface phonons there is the additional question of whether surface anharmonicity is larger than that in the bulk solid. While experimental observations of phonon linewidth and its temperature dependence are non-trivial because of the inherent difficulties in the extraction of the different contributions to the linewidths, theoretical calculations are also challenging as they require computations

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with higher-order derivatives of a many-body interaction potential, and extensive summations and numerical evaluation of contributions from various parts of the surface Brillouin zone. Additionally, this interaction potential should be capable of providing the actual equilibrium configuration and vibrational dynamics of the surface and bulk atoms of the solid. Demands on the potential aside, the ground work for such calculations was laid some time ago using the one-phonon scattering theory [2–5]. It was shown [4,5] that the phonon linewidth may be obtained from first-order perturbation treatment of the cubic terms of the interaction potential, while the calculation of the frequency shift required inclusion of the quartic term in the anharmonic part of the potential, making the latter a daunting task in quasi-analytic calculations. Perturbative calculation of the cubic terms for realistic systems which need complex and many-body interaction potentials is in itself non-trivial. It is thus not surprising that only a few such studies have been carried out for bulk metals [6–8] and their surfaces [9, 10]. On the other hand, with the advances in computer simulation techniques, extraction of surface phonon linewidth (and frequency shifts) from molecular dynamics (MD) simulations has become much more feasible [11–20]. The advantage of MD simulation is that it takes into account the full anharmonicity afforded by the interaction potential. The drawback is that the extraction of the linewidth from the collected statistics is not straightforward. The very presence of the interactions between the phonons introduces new and overlapping features in the calculated phonon spectral densities making the delineation of the linewidth ambiguous, particularly with increasing temperatures. The availability of the two techniques is thus helpful both in providing verification and in setting the limits of validity, each for the other. In this regard, it is fortunate that both types of technique have been applied to the low-Miller-index surfaces of Ag, Cu, and Al, and that selected experimental data are also available [10, 20–22] for these. To our knowledge, for Ni surfaces such information is available only from MD simulations [17, 19]. The aim in this work is to provide a summary of the status of theoretical calculations of the surface phonon linewidths of these specific metal surfaces. Instead of an exhaustive review in which the wavevector and temperature dependence of the linewidth is included, the objective here is to focus on zone-boundary surface phonons, at 300 K. Details of the wavevector dependence of the linewidths of modes like the Rayleigh wave can be found in particular publications [9, 10, 18, 20]. The temperature dependence of the linewidth may be found in most of the cited publications.

In the next two sections we describe the main features of the theoretical techniques. This is followed in section 4 with the results for surface relaxation, and for the frequencies and linewidths of the zone-boundary surface phonons of the (100), (111), and (110) surfaces of Cu and Ag, and the (100) and (111) surfaces of Al. Also included in section 4 are results for the linewidths of surface phonons of the low-Miller-index surfaces of Ni. The conclusions are summarized in section 5.

2. Linewidth calculations from perturbation theory

As already mentioned, the standard recipe for the calculation of the phonon linewidth quasi-analytically is through the usage of time-dependent perturbation theory. The main idea is to calculate the decay rate of the population of any phonon mode i. At temperature T the mean population of phonon mode i is given by the Bose distribution:

$$\langle n_i \rangle = \left[\exp\left(\frac{\hbar\omega_i}{kT}\right) - 1\right]^{-1}. \tag{1}$$

If the population of a certain mode o is driven out of equilibrium to a value n_o, then the population excess begins to decay according to

$$\frac{\mathrm{d}n_o}{\mathrm{d}t} = -\gamma[n_o - \langle n_o \rangle]. \tag{2}$$

Within the harmonic approximation, there are no phonon–phonon interactions, and the excited phonon state cannot directly transfer its energy excess to other phonon modes. With increasing temperature, the anharmonic terms of the potential become important and phonon–phonon interactions become important. To calculate the decay constant γ by time-dependent perturbation theory, the perturbation is taken to be the third-derivative (so-called cubic) terms in the Taylor series expansion of the interatomic potential Φ with respect to equilibrium atomic coordinates. This is obviously an approximation. In reality, the quartic and higher-order terms may also contribute to the linewidth. However, inclusion of such terms would render the calculations intractable, for the present. A further assumption is that there are no other processes contributing to the linewidth.

For a slab with the Z-axis perpendicular to the surface, we can express the perturbation as

$$\hat{V}_3 = \frac{1}{6} \sum_{\alpha,\beta,\gamma} \sum_{\vec{\ell}_k,\ell_{zk}} \sum_{\vec{\ell}_n,\ell_{zn}} \sum_{\vec{\ell}_p,\ell_{zp}} \left[\frac{\partial^3 \Phi}{\partial u_{p,\gamma}\, \partial u_{n,\beta}\, \partial u_{k,\alpha}} \right]_e \hat{u}_{p,\gamma} \hat{u}_{n,\beta} \hat{u}_{k,\alpha}. \tag{3}$$

Here $\vec{\ell}$ is a lattice vector of the 2D direct lattice, ℓ_z is an index labelling layers, $u_{k,\alpha}$ represents the $\alpha = x$, y or z Cartesian component of the displacement from equilibrium of the atom at site k, and e indicates that the derivative is to be evaluated at the equilibrium configuration. In the above equation, the displacement-coordinate operator for site (ℓ, ℓ_z) is given by

$$\hat{u}_\alpha(\vec{\ell}, \ell_z) = \sum_{\vec{q}} \sum_{j}{}' \left[\frac{\hbar}{2m\omega(\vec{q}, j)N} \right]^{1/2} e_\alpha(\ell_z|\vec{q}, j) \mathrm{e}^{\mathrm{i}\vec{q}\cdot[\vec{\ell}+\vec{K}(\ell_z)]} (\hat{a}^+(-\vec{q}, j) + \hat{a}(\vec{q}, j)). \tag{4}$$

Here $\vec{q}$ is a vector of the 2D reciprocal lattice in the first Brillouin zone, j labels the particular phonon mode for a given $\vec{q}$, the prime on the second sum means excluding the translational modes at $\vec{q} = 0$, $\omega(\vec{q}, j)$ is the angular frequency of the particular mode, N is the number of primitive 2D cells subjected to the periodic boundary conditions, $\vec{K}(\ell_z)$ represents any shift (not a lattice vector) parallel to the slab surface of the atomic sites for layer ℓ_z relative to the lattice of the centre layer of the slab, and a and a^+ are, respectively, the lowering and raising operators for the particular phonon mode. The quantities $e_\alpha(\ell_z|\vec{q}, j)$ are components of the eigenvectors of the dynamical matrix for the $(\vec{q}, j)$ phonon mode.

The detailed expressions given below are those used in [23, 25]. They are similar, in principle, to those employed by Franchini *et al* [9] in related studies. From Fermi's golden rule of time-dependent perturbation theory, we have

$$\frac{\mathrm{d}n_o}{\mathrm{d}t} = \sum_K \frac{2\pi}{\hbar} |\langle K|\hat{V}_3|M\rangle|^2 \delta(E_K - E_M), \tag{5}$$

where M labels an initial state with mode o excited and the sum extends over all final states K. There are two kinds of process [9,25] that contribute to the right-hand side of equation (5): a splitting process having $\omega_o = \omega_a + \omega_b$ and matrix elements of the form

$$\langle n_b + 1, n_a + 1, n_o - 1|\hat{V}_3|n_o n_a n_b\rangle; \tag{6}$$

and a difference process having $\omega_o = \omega_a - \omega_b$ and matrix elements of the form

$$\langle n_b - 1, n_a + 1, n_o - 1|\hat{V}_3|n_o n_a n_b\rangle. \tag{7}$$

One may visualize a splitting process as one in which the phonon mode of interest decays into a pair of phonons of frequency ω_a and ω_b, while in the difference process the phonon mode of interest may fuse with another phonon of frequency ω_b to produce a third phonon of frequency ω_a. There are thus two specific contributions to the decay constant: γ_{dif} and γ_{sp}. In working out expressions for γ_{dif} and γ_{sp}, the inverses of these processes must also be considered. After some algebra, the following expressions are obtained:

$$\begin{aligned}\gamma_{dif} = \frac{36A}{2\pi\hbar}\int_{BZ}\mathrm{d}^2\vec{q}_a\int_{BZ}\mathrm{d}^2\vec{q}_b\sum_{j_a}\sum_{j_b}|M(-\vec{q}_a, j_a; \vec{q}_b, j_b; \vec{q}_o, j_o)|^2\\ \times\left(\sum_{\vec{G}}\delta[(-\vec{q}_a+\vec{q}_b+\vec{q}_o)-\vec{G}]\right)\delta(\hbar\omega_a-\hbar\omega_b-\hbar\omega_o)(\langle n_b\rangle-\langle n_a\rangle),\end{aligned} \tag{8}$$

and

$$\begin{aligned}\gamma_{sp} = \frac{36A}{2\pi\hbar}\int_{BZ}\mathrm{d}^2\vec{q}_a\int_{BZ}\mathrm{d}^2\vec{q}_b\sum_{j_a}\sum_{j_b}|M(-\vec{q}_a, j_a; -\vec{q}_b, j_b; \vec{q}_o, j_o)|^2\\ \times\left(\sum_{\vec{G}}\delta[(\vec{q}_a+\vec{q}_b-\vec{q}_o)-\vec{G}]\right)\delta(\hbar\omega_a+\hbar\omega_b-\hbar\omega_o)(\langle n_a\rangle+\langle n_b\rangle+1)\end{aligned} \tag{9}$$

where A is the area of a primitive cell of the 2D direct lattice, G is a lattice vector of the 2D reciprocal lattice, and the matrix element M is given by

$$\begin{aligned}M(\vec{q}_1, j_1; \vec{q}_2, j_2; \vec{q}_3, j_3) = \frac{1}{6}\left(\frac{\hbar}{2m}\right)^{3/2}(\omega(\vec{q}_1, j_1)\omega(\vec{q}_2, j_2)\omega(\vec{q}_3, j_3))^{-1/2}\\ \times\sum_{\alpha,\beta,\gamma}\sum_{\ell_{zk}}\sum_{\ell_{zn}}\sum_{\ell_{zp}}\sum_{\vec{h}_{nk}}\sum_{\vec{h}_{pk}}\left[\frac{\partial^3\Phi}{\partial u_{p\gamma}\,\partial u_{n\beta}\,\partial u_{k\alpha}}\right]_o \mathrm{e}^{\mathrm{i}\vec{q}_2\cdot\vec{h}_{nk}}\mathrm{e}^{\mathrm{i}\vec{q}_3\cdot\vec{h}_{pk}}\\ \times e_\alpha(\ell_{zk}|\vec{q}_1, j_1)e_\beta(\ell_{zn}|\vec{q}_2, j_2)e_\gamma(\ell_{zp}|\vec{q}_3, j_3)\mathrm{e}^{\mathrm{i}\vec{q}_1\cdot\vec{K}(\ell_{zk})}\mathrm{e}^{\mathrm{i}\vec{q}_2\cdot\vec{K}(\ell_{zn})}\mathrm{e}^{\mathrm{i}\vec{q}_3\cdot\vec{K}(\ell_{zp})}.\end{aligned} \tag{10}$$

Here $\vec{h}_{nk} = \vec{\ell}_n - \vec{\ell}_k$ is the 2D direct-lattice vector locating cell n relative to cell k.

Speaking strictly, equations (8) and (9) are valid only as long as modes a and b maintain their thermal average populations. It is assumed that, at least at the onset, the coupling to the thermal reservoir is strong enough to maintain these populations while nevertheless not providing an important alternative path for decay of the population excess in mode o. The persistent summations in the above equation attest to the complexities of these calculations. Details of evaluations of the lattice sums may be found in [9, 23, 24].

Once the total decay constant is calculated from the above equations, the frequency halfwidth of the phonon mode is readily obtained by considering the halfwidth of the power spectral density of the Fourier transform of a decaying oscillation of the form

$$f(t) = 0, \qquad t < 0; \tag{11}$$

$$f(t) = A\cos(\omega_o t)\mathrm{e}^{-\gamma_{tot}t}, \qquad t > 0. \tag{12}$$

This results in a frequency halfwidth Γ of $\approx 0.1125\gamma$.

3. Linewidth from molecular dynamics simulations

In standard MD simulations the positions and velocities of atoms are collected for a chosen time period by solving numerically Newton's equations of motion using an efficient algorithm like Nordsieck's. For simulations of surface systems the MD cell generally consists of few thousand atoms, arranged in about 10–30 layers with periodic boundary conditions applied parallel to the surface. The exact size of the system is chosen so as to avoid finite-size effects.

For the systems of interest, a time step of about 1 fs is found to be suitable. Initially a constant-temperature, constant-pressure (NPT) simulation is performed for a bulk system to calculate the lattice constant at that temperature. The surface system is then created with the lattice constant corresponding to the temperature of interest. Under conditions of constant volume and constant temperature (NVT) this surface system is equilibrated to the desired temperature. Next, the system is isolated and allowed to evolve in a much longer run of about few hundred picoseconds in which its energy remains constant (NVE) and statistics on the positions and velocities of the atoms are recorded.

Surface phonon spectral densities are calculated in the one-phonon approximation, using

$$g_{\alpha\alpha}(\vec{Q}_\parallel, \omega) = \left| \int \mathrm{e}^{\mathrm{i}\omega t} \left(\sum_{j=1}^{N_l} \mathrm{e}^{\vec{Q}_\parallel \cdot \vec{R}_j^0} v_{j\alpha}(t) \right) \mathrm{d}t \right|^2 \tag{13}$$

where $g_{\alpha\alpha}$ is the spectral density for displacements along direction α ($=x, y, z$) of atoms in layer l, N_l is the number of atoms in the layer, $\vec{Q}_\parallel$ is the two-dimensional wavevector parallel to the surface, $\vec{R}_j^0$ is the equilibrium position of atom j whose velocity is $\vec{v}_j$. Instead of the velocity auto-correlation function in the above equation, phonon spectral densities may also be calculated from the displacement auto-correlation function [18].

The raw spectrum obtained according to the above equation is generally smoothed by convoluting it with a Gaussian function of width δ, which eliminates any noise caused by the finite number of terms in the above summation. In such cases the function

$$f(\omega) = \int g(\omega')\mathrm{e}^{-(\omega'-\omega)^2/\delta^2}\, \mathrm{d}\omega' \tag{14}$$

has peaks of width greater than those in $g(\omega)$. If the original peak in $g(\omega)$ is a Gaussian with width Δ, then it can be shown that the resulting peak in $f(\omega)$ is also a Gaussian, with width Δ'. The exact relation between these widths is

$$\Delta = \sqrt{\Delta'^2 - \delta^2}. \tag{15}$$

An equation like the one above is used to extract the true width of the phonon spectral density Δ, since most of the peaks are Gaussian-like.

3.1. The interaction potential

A vital ingredient for all calculations is the interaction potential Φ, be it for calculating the decay constants via perturbation theory or for solving Newton's equation in MD simulations. In the set of theoretical papers of interest here, the choice of the interaction potential has ranged from those based on pair potentials [9, 10] and parametrized by force constants in a Born–von Karman-like scheme, or simply in a Morse form [20], to those [12–20] obtained from many-body potentials of the embedded-atom (EAM) form [26,27]. In a recent perturbation theoretical calculation [23, 24] usage has been made of an analytic form of the EAM potential by Mei *et al* [28] which facilitates the calculation of the second and third derivatives of the potential Φ for arbitrary choices of the atomic positions. The range of interactions is generally taken to extend to third- or fourth-nearest neighbours, and appears to be adequate. Semiempirical, many-body potentials of the EAM type, for example, are expected to be sufficient for describing the structural and dynamical characteristics of Ag, Cu, and Ni bulk and surfaces [12,13,16,26], and also to a great extent those of Al [18,27]. The same cannot be said of pair potentials, and their application to metals has to be treated with caution.

Table 1. Relaxation of the interlayer spacing of Cu surfaces as an illustrative example.

Surface	Method	Δd_{12} (%)	Δd_{23} (%)	Δd_{34} (%)	Reference
(100)	EAM	−1.25	−0.43	−0.09	[23]
	EAM	−1.44	−0.33		[26]
	FP	−3.02	+ 0.08	−0.24	[33]
	MEIS	−2.0	+ 1.0		[47]
	SPLEED	−1.2	+ 0.9		[48]
	LEED	−2.1	+ 0.45		[49]
(110)	EAM	−4.52	+ 0.10	−0.54	[23]
	EAM	−4.93	+ 0.23		[26]
	FP	−9.27	+ 2.77	−1.08	[33]
	LEED	−8.5	+ 2.3		[50]
	HEIS	−5.3	+ 3.3		[50]
(111)	EAM	−1.23	−0.15	−0.06	[23]
	EAM	−1.39	−0.05		[26]
	FP	−1.27	−0.64	−0.26	[33]
	MEIS	−1.0	−0.2	0.0	[51]

4. Results and discussion

In this section a summary of the results for the low-Miller-index surfaces of Ag, Cu, Ni, and Al is presented. First a brief account of the calculation of the structural properties of the surfaces is provided. This is done to ensure that the surface is fully relaxed and that the equilibrium positions are in reasonable agreement with accepted results. Such agreement implies reliability of the selected interaction potential. Next, a summary of the lattice dynamical calculations, in the harmonic approximation, for the frequencies of the surface phonons at the zone boundaries of the surfaces of interest is provided. Since it would be repetitive to tabulate the results from all related publications for surface relaxation and phonon frequencies, which are of secondary interest to this work, we have chosen to include here the results from our recent calculations as a representative illustration. A very good reason for doing this is that in this set of calculations an analytic form of the EAM potential [28] was used to facilitate the calculation of the cubic term. This particular form of the EAM potentials had previously not been tested for application to surface properties of these metals. The good agreement with previous results attests to the reliability of the interatomic potentials. Finally, results are presented for the calculated linewidths of the surface modes. Results for the bulk modes are not discussed here, as the focus is on surface vibrations.

4.1. Surface relaxations

With the analytic form of the EAM potential [28], equilibrium positions of surface atoms are calculated using standard energy-minimization techniques [29]. The results, together representative values from other calculations and from experiment, are given in table 1 for the (100), (110), and (111) surfaces of Cu. These results are in good agreement with other EAM calculations. The agreement with experiment, where different groups have found somewhat varying values, is less satisfactory for (100) and (110), especially for Δd_{23}. For similar results for all other surfaces of interest here, the reader is referred to the specific publications as cited in table 2.

Table 2. Calculated frequencies (ν) and frequency halfwidths (Γ) for surface phonons of Ag, Cu, Al, and Ni. Also included are results from experiments and MD simulations, where available. All quantities are in units of THz (1 THz = 4.136 meV).

Surface	Point	Mode	ν	ν (MD)	ν (experiment)	Γ	Γ (MD)
Cu(100)	$\bar{M}$	$S_1(z)$	3.95 [24]	3.88 [12]	4.05 [43–45]	0.35 [24]	0.15 [12]
		$S_2(z_2)$	5.16 [24]	4.99 [12]	—	0.05 [24]	0.07 [12]
	$\bar{X}$	$S_1(y)$	2.10 [24]	1.91 [12]	—	0.21 [24]	0.09 [12]
		$S_4(z)$	3.01 [24]	2.91 [12]	3.24 [43–45]	0.10 [24]	0.08 [12]
		$S_6(x)$	6.04 [24]	5.77 [12]	6.10 [43–45]	1.10 [24]	0.25 [12]
Ag(100)	$\bar{M}$	$S_1(z)$	2.68 [24]	2.78 [12]	2.40 [46]	0.11 [24]	0.09 [12]
		$S_2(z_2)$	3.33 [24]	3.48 [12]	—	0.14 [24]	0.11 [12]
	$\bar{X}$	$S_1(y)$	1.45 [24]	1.55 [12]	—	0.08 [24]	0.07 [12]
		$S_4(z)$	1.97 [24]	2.10 [12]	2.10 [46]	0.06 [24]	0.09 [12]
		$S_6(x)$	3.87 [24]	3.95 [12]	—	0.26 [24]	0.17 [12]
Ni(100)	$\bar{M}$	$S_1(z)$	—	4.88 [17]	4.65 [35,36]	—	0.25 [17]
		$S_2(z_2)$	—	6.53 [17]	6.60 [35,36]	—	0.30 [17]
	$\bar{X}$	$S_1(y)$	—	2.62 [17]	0.20 [17]	—	0.22 [17]
		$S_4(z)$	—	3.85 [17]	3.96 [37,38]	—	—
		$S_6(x)$	—	7.60 [17]	7.56 [37,38]	—	—
Al(100)	$\bar{X}$	$S_4(z)$	—	3.94 [20]	3.90 [20]	—	0.12 [6]
Cu(110)	$\bar{Y}$	$S_5(y)$	4.56 [24]	4.40 [13]	—	0.09 [24]	0.15 [13]
		$S_3(z)$	2.96 [24]	2.90 [13]	2.90 [52]	0.13 [24]	0.10 [13]
		$S_2(x)$	2.46 [24]	2.40 [13]	—	0.14 [24]	0.08 [13]
		$S_1(y)$	1.76 [24]	1.60 [13]	—	0.10 [24]	0.10 [13]
Ag(110)	$\bar{Y}$	$S_5(y)$	3.01 [24]	3.14 [15]	3.14 [53]	0.10 [24]	0.07 [15]
		$S_3(z)$	1.94 [24]	1.96 [15]	1.89 [53]	0.09 [24]	0.07 [15]
		$S_2(x)$	1.62 [24]	—	—	0.09 [24]	—
		$S_1(y)$	1.21 [24]	1.32 [15]	1.21 [53]	0.07 [24]	0.08 [15]
Ni(110)	$\bar{X}$	$S_1(z)$	—	3.94	4.11 [37,38]	—	0.20 [17]
		$S_2(y)$	—	4.80	5.07 [37,38]	—	—
		$S_7(x)$	—	7.43	6.80 [37,38]	—	0.30 [17]
		$MS_0(x)$	—	4.18	4.26 [37,38]	—	—
	$\bar{Y}$	$S_1(y)$	—	2.18	2.40 [37,38]	—	0.20 [17]
		$S_2(x)$	—	3.07	3.48 [37,38]	—	—
		$S_3(z)$	—	3.59	3.70 [37,38]	—	0.40 [17]
		$S_5(y)$	—	5.75	—	—	0.30 [17]
Cu(111)	$\bar{M}$	L	6.71 [24]	6.51 [19]	6.77, 6.30 [54,55]	0.61 [24]	0.25 [19]
		SV	3.09 [24]	3.02 [19]	3.16, 3.22 [54,55]	0.08 [24]	0.11 [19]
Ag(111)	$\bar{M}$	L	4.23 [24]	4.33 [19]	—	0.46 [24]	0.20 [19]
		SV	2.03 [24]	2.15 [19]	2.06 [57], 2.10 [56]	0.07 [24]	0.06 [19]
Ni(111)	$\bar{M}$	L	—	8.88 [19]	8.79 [58]	—	0.09 [19]
		SV	—	3.91 [19]	4.01 [58]	—	0.04 [19]
Al(111)	$\bar{M}$	SV	—	—	3.65 [20]	0.07 [9]	—

4.2. Phonon states in the harmonic approximation

Again, as representative calculations of phonon frequencies, we give here details from our latest calculations. Basis states for the perturbation calculation were phonon states in the harmonic approximation obtained by solving the eigenvalue problem for the dynamical matrix using routines for the eigenvalues and eigenvectors of a real, symmetric matrix from numerical recipes [29]. For the slabs, the procedure of Allen and deWette [30, 31] for transforming from the dynamical matrix to a real, symmetric matrix was followed. The surface phonon frequencies and eigenvector polarizations obtained for various special points on the 2D Brillouin zone surface for 31-layer slabs with (100), (110), and (111) surfaces are given in table 2 together with representative values from the literature. The calculated frequencies are in good agreement with those obtained previously.

4.3. Phonon decay constants and linewidth

The results of calculations of the surface phonon linewidth from perturbation calculations are presented in table 2. All results are for a phonon occupancy at 300 K. The table also includes results from MD simulations and experiments, where available.

There are only a few experiments in which the linewidth of the surface phonons of Ag and Cu, at the 2D Brillouin zone boundaries, have been measured. Using high-resolution electron-energy-loss spectroscopy [21], the halfwidth for Cu(110) at $\bar{\mathrm{Y}}$ for the $\mathrm{S}_3(z)$ mode was reported to be 0.77 THz, significantly larger than results from perturbative methods or from MD. However, this large value has remained controversial [42]. Experiments using He scattering with time-of-flight detection [10] to measure the halfwidth for Ag(110) at $\bar{\mathrm{Y}}$ for the $\mathrm{S}_3(z)$ and $\mathrm{S}_1(y)$ modes show a linewidth of 0.04 THz for both modes. These results on Ag(110) are in good agreement with those from calculations.

For surface modes the halfwidth Γ in the calculations appears to be of the order of 0.1 THz unless it is a resonance mode like S_6. The case of S_6 for Cu(100) is, however, puzzling as the perturbation method produces a large value of 1.10 THz, while MD simulations yield 0.25 THz. We do not understand the reason for this disagreement, particularly since the two methods produce very similar results for the same quantity for Ag(100). It is also interesting to note that the longitudinal modes at $\bar{\mathrm{M}}$ have a rather large Γ for on both Cu(111) and Ag(111). Within the framework of the perturbation theory, Al(111) was studied using a different interaction potential [9]. Interestingly, the two sets of perturbative methods produce similar values for the linewidth of the Rayleigh wave for the (111) surfaces of the metals: Ag, Cu, and Al. The table also includes the results from MD simulations for Ni(100), Ni(110), and Ni(111). So far such results have not been obtained for Ni surfaces from either perturbative methods or experiments. It should be noted that for Al surfaces the calculated frequencies of the modes in table 2 are in agreement with those from *ab initio* calculations [32]. *Ab initio* results for Cu and Ag surfaces [33, 43] also confirm the results for the frequencies of the phonons obtained by semiempirical methods, as summarized in table 2. Also, the frequencies for the Ni surface phonons in table 2, from MD simulations, are in good agreement with those from lattice dynamical calculations using model force constants [34].

Table 2 shows that the linewidths calculated at 300 K from perturbation theory and MD simulations are good agreement in most cases. This comparison becomes more difficult at higher temperatures, as shown in a related publication [24]. With increasing temperature, results from MD simulations show a complex behaviour which depends on the surface geometry. On the other hand, the temperature dependence in the perturbation calculations is limited to the temperature dependence of the phonon populations. In view of this, we can only expect a linear dependence of the linewidth on temperature above 300 K.

5. Conclusions

We have presented here a summary of available results for the linewidths of surface phonons of the low-Miller-index surfaces of Cu, Ag, Ni, and Al, at several high-symmetry points in the surface Brillouin zone. As a rule of thumb, for most surface modes, calculations based on perturbation theory produce halfwidths of a few tenths of a THz at 300 K. This result is in general in good agreement with those obtained in related MD simulations. There are some exceptions such as the case of the S_6 mode on Cu(100) where one obtains a large broadening of 1.10 THz in the perturbation calculation and only 0.25 THz in the MD simulations. Modes such as the longitudinal ones at $\bar{M}$ on Cu(111) and Ag(111) also appear to have appreciable, and differing, linewidths in the two types of calculation. It should be remembered that the perturbative calculations do not include a shift in the frequencies of the phonons as a result of anharmonicity, since such calculations involve the quartic term. Proper comparison with experiments and MD simulations would require the inclusion of the frequency shifts together with the changes in the linewidth, as a function of temperature. Nonetheless, quasi-analytic calculations such as the ones included here provide a reasonable approach to calculating the broadenings in the surface phonon linewidth. Such calculations are an alternative to MD simulations, and also a test for the latter. Results obtained here are in reasonable agreement with experimental data which are available for a few of the modes. We await experimental results on the rest of the modes.

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