A Model for the Thermal Expansion of Ag(111) and other Metal Surfaces

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We develop a model to study the thermal expansion of surfaces, wherein phonon frequencies are obtained from *ab initio* total energy calculations. Anharmonic effects are treated exactly in the direction normal to the surface, and within a quasiharmonic approximation in the plane of the surface. We apply this model to the Ag(111) and Al(111) surfaces, and find that our calculations reproduce the experimental observation of a large and anomalous increase in the surface thermal expansion of Ag(111) at high temperatures[1]. Surprisingly, we find that this increase can be attributed to a rapid softening of the *in-plane* phonon frequencies, rather than due to the anharmonicity of the out-of-plane surface phonon modes. This provides evidence for a new mechanism for the enhancement of surface anharmonicity. A comparison with Al(111) shows that the two surfaces behave quite differently, with no evidence for such anomalous behavior on Al(111).

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The equilibrium lattice constant of a crystal is determined by a balance between the various attractive and repulsive forces present within the solid. When the crystal is cleaved to form surfaces, this balance is destroyed, and the atoms at the surface therefore relax either inwards (which is the usual situation for most metal surfaces) or outwards.

However, upon heating the crystal, these relaxations may change dramatically as a function of temperature. The phenomenon of bulk thermal expansion is, of course, a familiar one: upon heating the crystal, the lattice constant changes, reflecting the anharmonicity of the interatomic potentials. Similarly, asymmetries and anharmonicities in surface phonon vibrations will be manifested in a change in interlayer displacements as a function of temperature T. Due to the different asymmetries present at the surface and in the bulk, it is possible that these two quantities (bulk lattice constant and interlayer distances near the surface) may change quite differently upon increasing T.

Indeed, it has long been realized that one would expect all such measures of anharmonicity (e.g., coefficients of thermal expansion α, mean squared displacements (MSDs) of atoms, and the rate of change of phonon frequency with temperature) to be larger at surfaces than in bulk crystals[3] for two reasons: *(i)* the breaking of symmetry due to the presence of the surface makes the interlayer potential more asymmetric at the surface than in the bulk, increasing the size of the odd terms in a Taylor series expansion of the energy in powers of atomic displacements; *(ii)* atomic displacements may be greater at the surface than in the bulk, thus increasing the relative magnitudes of the higher-order anharmonic terms in this series expansion.

Interestingly, studies on metal surfaces have shown that such enhancements of surface anharmonicity, when observed, are strongly dependent on both the element and the orientation of the surface. Early experiments and calculations[4],[5] on metal surfaces suggested that measures of anharmonicity (such as the coefficient of thermal expansion) are typically at most three times larger at the surface than in the bulk, and as a result do not affect surface properties drastically. However, recent experiments have shown a huge enhancement on a few surfaces: for Ni(001)[8] and Pb(110)[7] at high temperatures, the surface coefficient of thermal expansion α_S, defined by:

$$\alpha_S = (d_{12})^{-1}(\partial d_{12}/\partial T), \tag{1}$$

(where d_{12} is the interlayer spacing between the first two planes of atoms at the surface) is 10 to 20 times larger than the bulk coefficient of thermal expansion α_B, while for Cu(110) the surface MSDs are up to six times greater than the bulk MSDs[9].

Perhaps the most interesting case is that of Ag(111): recent experiments[1] show that the contraction of d_{12} is dramatically reversed for the Ag(111) surface as the crystal is heated: Up to $T \approx 670$ K, d_{12} is indeed *contracted* by $\sim 2.5\%$ relative to the bulk separation d_B; but upon increasing T further, d_{12} increases much more rapidly than d_B does, so that by 1150 K it is *expanded* by $\sim 10\%$. Correspondingly, α_S becomes more than ten times as large as α_B[2]. Such a large effect is especially unexpected for a close-packed metal surface, and contradicts the conventional expectation that more open surfaces should exhibit larger surface anharmonicity.

Lewis[6] has carried out EAM simulations to investigate the thermal behavior of Ag(111). The results of these simulations differ significantly from those reported experimentally: the surface layer relaxes inwards at all temperatures, and α_S is less than twice as large as α_B.

Is this disagreement between experiment and calculation on Ag(111) due to inadequacies of the EAM potentials? Or could it be a sign of some hitherto undetected surface phase transition?

To study these questions, we have investigated the harmonic and anharmonic properties of Ag(111) and Al(111) by performing *ab initio* calculations using density functional theory. Fully separable norm-conserving pseudopotentials[12] were used in our calculations, together with a plane wave basis set with an energy cut-off of 60 Ry (20 Ry for Al), and the local-density approximation with Ceperley-Alder exchange-correlation[13]. We note that the relatively high cut-off of the plane-wave basis set is necessary in order to obtain a good description of *anharmonic* effects, even though a lower cut-off may suffice to describe harmonic properties adequately.

Before performing surface calculations, we first verified that the harmonic and anharmonic properties of the bulk materials are satisfactorily described by these pseudopotentials. Some of these results, such as the optimal values of the lattice constant and the bulk modulus, are presented in Table 1. This table also contains the calculated values of two measures of anharmonicity: the pressure derivative of the bulk modulus, and the Grüneisen parameters γ, which describe how the phonon frequencies vary upon changing the lattice constant. Note that the experimental value of γ is an average over all bulk modes, whereas the theoretical values were calculated separately for each band, and at a sample wave-vector along the [111] direction, between the zone-center Γ and the zone-edge L. (These particular bulk modes were chosen because they project on to the zone-center of the surface Brillouin zone, and can therefore be regarded as analogous to the surface zone-center vibrations that we will later investigate for the (111) surface.)

The surface calculations were performed using a repeated slab geometry consisting of six atomic layers separated by a vacuum layer of the same thickness. The **k**-point sets used to sample reciprocal space consisted of a uniform grid centered on the Γ point and containing seven points in the irreducible part of the Brillouin zone for the undistorted surface; the number of **k**-points was correspondingly increased upon breaking symmetries by distorting the lattice in order to calculate phonon frequencies. Convergence of calculated anharmonic quantities with respect to energy cut-off, number of **k**-points and number of layers was carefully tested for.

Our strategy is to compute static energies and phonon frequencies by performing self-consistent calculations at $T = 0$ K, and then extend our results to finite temperatures by using a quasiharmonic approximation.

In order to obtain a qualitative understanding of the mechanisms in operation, and a first estimate of the size of surface thermal effects, we use a simple model of the lattice dynamics of the surface, considering only three phonon modes, in all of which the topmost layer of the slab moves as a whole – i.e., we assume that the displacements are confined to the first layer of atoms at the surface, and consider only those modes with zero wave-vector.

We consider one mode in which the surface atoms vibrate normal to the surface plane (along the z direction), and two modes (along $\mathbf{x} = [1\overline{1}0]$ and $\mathbf{y} = [11\overline{2}]$) in which they vibrate in the plane of the surface. (We emphasize that these displacements do not correspond to any of the actual normal modes of vibration of the surface slab, but may be considered as indicative of the strengths of the various force-constants that would appear in the true dynamical matrix of the system. This proviso should be kept in mind when we refer to "modes" and "phonons" in the rest of this paper.)

We first computed the change in the total energy of the Ag(111) slab upon varying the first two interlayer separations d_{12} and d_{23}, and maintaining the fcc stacking of the bulk crystal. This not only provides the static interlayer potential, but is also equivalent to simulating the vibrational mode along z. Our result for the dependence on d_{12} of the first interlayer potential is plotted in Fig. 1; it is clearly asymmetric about the minimum at $d_{12} = 2.30$ Å. We found that allowing for the relaxation of d_{23} does not have a significant impact on the results for the close-packed (111) surface[14]. For the results presented in Fig. 1 and the rest of this paper, d_{23} is therefore fixed at the bulk interlayer separation of 2.34 Å.

To see how this anharmonicity of the interlayer potential is manifested at finite temperatures, we consider a one-dimensional quantum oscillator vibrating in the interlayer potential of Fig. 1. A numerical solution of the Schrödinger equation for this problem furnishes the eigenstates and eigenvalues of such an oscillator, and the mean displacement $\langle d_{12} \rangle_n$ in the n-th eigenstate is obtained by computing the expectation value of the displacement operator in each state. The average value at a finite temperature T is then obtained by weighting these results with the corresponding partition function.

Our results for $d_{12}(T)$ obtained from this procedure (see the open circles in Fig. 3) indicate a modest enhancement in α_S relative to α_B of ~ 1.7, which is much smaller than that measured experimentally.

We next performed frozen-phonon calculations to study the behavior of the two in-plane modes in our model. At each value of d_{12}, the atoms in the surface layer were displaced along first the x and then the y direction, and the total energy was computed for a series of displacements up to ±0.15 Å. The curvature of the resulting plots of energy versus displacement gives the mode frequency. We find that the frequency of these in-plane modes decreases surprisingly rapidly upon increasing d_{12}; these results are plotted in Fig. 2.

In analogy to the usual bulk Grüneisen parameter γ_B, we can define a surface Grüneisen parameter:

$$\gamma_S \equiv -\partial \mathrm{ln}(\omega)/\partial \mathrm{ln}(d_{12}). \tag{2}$$

The value of the γ_S extracted from our results for the in-plane modes (between 5.5 and 7.5) is significantly larger than the corresponding value of of 2.39 that we obtain for a bulk vibration with an analogous pattern of displacements. Thus, the frequently made assumption[4] that γ is approximately equal for surface and bulk modes is clearly invalid in this case.

The surface can thus reduce its vibrational free energy significantly by expanding outwards, though such an outward expansion would be accompanied by an increase in the static energy. The optimal value of d_{12} is determined by minimizing the free energy function[3]:

$$F(d_{12}, T) = E_{\mathrm{stat}}(d_{12}) + \sum_i F^i_{\mathrm{vib}}(d_{12}, T), \tag{3}$$

at each temperature T . Here, $E_{\mathrm{stat}}(d_{12})$ is the static interlayer potential plotted in Fig. 1, and $F^i_{\mathrm{vib}}(d_{12}, T)$ is the vibrational free energy corresponding to vibrations in the i-th direction, which, in the quasiharmonic approximation, is given by[3]:

$$F^i_{\mathrm{vib}}(d_{12}, T) = k_B T ln \Big\{ 2 sinh \Big(\frac{\hbar \omega_i(d_{12})}{2 k_B T} \Big) \Big\}; \tag{4}$$

where k_B and $\hbar$ are Boltzmann's constant and Planck's constant respectively. The frequency of the mode polarized along the i-th direction, when the first interlayer separation is fixed at d_{12}, is denoted by $\omega_i(d_{12})$. The sum in Eq. (3) runs over all the bands of the phonon spectrum (averaged over the entire surface Brillouin zone); in our case we approximate it by a sum over the 3 zone-center vibrational patterns that we have considered, which are polarized along the x,y and z directions respectively. The variation of $\omega_i(d_{12})$ is obtained directly from our frozen-phonon calculations for the two in-plane modes (see Fig. 2). For the out-of-plane mode, we compute $F^z_{\rm vib}(d_{12},T)$ numerically, in such a way as to reproduce the exact result for $d_{12}(T)$ that we have already obtained by solving the Schrödinger equation when only the mode along z is present.

Our final result for $d_{12}(T)$ in the presence of all three modes, obtained by minimizing the free energy expression given by Eq. (3), is shown by the filled circles in Fig. 3 (note that the temperatures are normalized with respect to the melting temperature T_m). The experimentally measured data points[1] are also plotted; both the experimental and theoretical curves display the same features: there is little or no change up to about $T/T_m = 0.5$, i.e., $T = 617$ K, beyond which there is a rapidly increasing trend towards outwards relaxation of the surface layer. At $T/T_m = 0.85$, i.e., $T = 1049$ K, we find that the surface layer is relaxed outwards by about 15%, whereas the experiments show an outwards relaxation of $\sim 7.5\%$. Given the simplicity of our model, and the large experimental error bars, this is as good an agreement as we can hope for.

The increasing slope of $d_{12}(T)$ reflects a flattening in the minimum of the free-energy curve, and the rapid increase in $d_{12}(T)$ at high T is a precursor to the development of a saddle-point instability in the free-energy curve, similar to that which has been obtained in studies of the surface melting of copper surfaces[16]. We emphasize that the rapid decrease of $\omega_i(d_{12})$ for the in-plane modes is crucial for obtaining the large outwards expansion; if, for example, this rate of decrease were to be halved, the maximum outwards expansion would be drastically reduced to about 2%. In the limit of high T (when all modes are excited), the value of $d_{12}(T)$ is no longer sensitive to the absolute scale of ω_i, but is instead controlled by γ_S, which is a normalized indicator of how rapidly ω_i falls off with increasing d_{12}.

To check whether such behavior is universal or a peculiar property of Ag(111), we repeated the same calculations on bulk aluminum and Al(111). Our results for the relaxation of d_{12} for Al(111) are also plotted in Fig. 3, and it is obvious that there is no evidence for a dramatically increased surface expansion on Al(111). We have also performed calculations on Cu(111)[20] which show that the behavior of Cu(111) is intermediate between that of Ag(111) and Al(111), which has been confirmed by very recent experiments[21].

Our results indicate that in addition to the two well known sources of enhanced surface anharmonicity that we have already mentioned, a third (and hitherto neglected) effect is more important in causing the dramatic enhancement in surface anharmonicity on Ag(111): Not only do interlayer potentials at the surface tail off rapidly with increasing z , they simultaneously *become much flatter in the xy plane* – in other words, the operative effect is not so much a decrease in the absolute magnitudes of interlayer potentials at the surface, but a *reduction in their corrugation parallel to surface.* As a consequence, those surface phonon modes in which atomic dispacements have significant components in the surface plane soften rapidly upon increasing interlayer separations; this drives the outermost layer of atoms to expand outwards at high temperatures.

An accurate description of the in-plane corrugation clearly requires taking into account the correct distribution of the electronic charge density (and the resulting chemical bond formation) at the surface. It seems plausible that when rebonding effects become significant, the EAM (which essentially ignores the relaxation of atomic charge densities and the rehybridization of electronic states) may fail; this may be why Lewis[6] did not observe a large outwards expansion in his simulations.

The rapid decrease in the corrugation of the interlayer potential is evident in Fig. 4, where we have plotted the differences in energies when the outermost layer of atoms occupies various stacking sites. Note that *(i)* the flattening occurs more rapidly for Ag(111) than Al(111) *(ii)* upon allowing for the lighter mass of Al atoms, the *effective* corrugation relevant for phonon frequencies is actually larger for Al(111) than for Ag(111). Both these factors contribute to the enhancement in γ of the in-plane top-layer modes and thus the larger thermal expansion of Ag(111).

Such a decrease in the corrugation of the substrate potential would also tend to favor a top-layer reconstruction of the type that has been observed on Au(111)[18] or Pt(111)[19], where the substrate potential is too weak to prevent a densification of atoms in the topmost layer. However, experiments apparently show no evidence of such a reconstruction on Ag(111)[1]; further calculations of surface stresses and the strength of intralayer couplings should help clarify the situation.

Our conclusion that the enhancement in surface expansion arises mainly from in-plane vibrations is supported by the experimental observation that the amplitude of in-plane vibrations on Ag(111) rises faster than the magnitude of out-of-plane vibrations[21]. Experiments on other surfaces, e.g., Cu(001), have detected in-plane vibrational amplitudes that are larger than out-of-plane amplitudes[22], and it is interesting to speculate whether this (counter-intuitive) result arises from the same cause, i.e., from a rapid softening of in-plane frequencies due to thermal expansion.

Of course, the calculation we have presented above does contain certain approximations: we have restricted ourselves to surface vibrations at the zone-center, we approximate the true electronic exchange-correlation functional by the LDA, and we use a quasiharmonic form for vibrational free energy. We should also allow for expansion in the plane of the surface, but this should in fact reinforce the softening of the in-plane modes. The validity of some of these approximations can be tested by performing *ab initio* molecular dynamics simulations in which all anharmonic contributions are fully included automatically, and in which no assumptions are made about the polarizations of bulk and surface vibrations; work in this direction is in progress.

We expect that our numerical results will change slightly upon including other surface phonon modes and allowing for dispersion through the surface Brillouin zone. Surface vibrations at the zone-center are sensitive only to the strength of *interlayer* force-constants coupling atoms at the surface to atoms in layers below; however, the frequency of a phonon at arbitrary wave-vector also depends on the *intralayer* force-constants, and one may expect these to be less sensitive to d_{12}; we may therefore have over-estimated the degree of surface anharmonicity by restricting ourselves to the zone-center. However, we note that measurements of surface phonon frequency-shifts suggest that the degree of anharmonicity remains approximately constant through a surface phonon band[17].

In conclusion, we have developed a simple model for the study of surface thermal expansion. By applying it to Ag(111), we have demonstrated that the anomalously large surface thermal expansion of Ag(111) can be attributed to a rapid softening of in-plane vibrational modes (related to a rapid flattening of the corrugation of the interlayer potential) upon increasing interlayer distances. We have shown that a similar scenario does not, however, lead to significant enhancement on Al(111).

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Table 1

Quantity	Ag	Al
a_0(Å)	4.06 *(4.09)*	3.94 *(4.05)*
B(MBar)	1.22 *(1.01)*	0.80 *(0.75)*
B'	5.94 *(5.92)*	4.22 *(5.36)*
$\gamma(T)$	2.39 *(2.46)*	2.12 *(2.18)*
$\gamma(L)$	2.95 *(2.46)*	2.05 *(2.18)*

Table 1: Calculated values of bulk properties of Ag and Al: a_0 = the equilibrium lattice constant at $T = 0$, B=bulk modulus, B' = pressure derivative of B, $\gamma(T)$ = Grüneisen parameter for transverse bulk mode along [111], with wave-vector 2/3 of the way between the zone-center and zone-edge, $\gamma(L)$ = Grüneisen parameter for longitudinal bulk mode at the same wave-vector. Experimental values at room temperature, obtained from Reference[23], are given in parentheses.

Figures

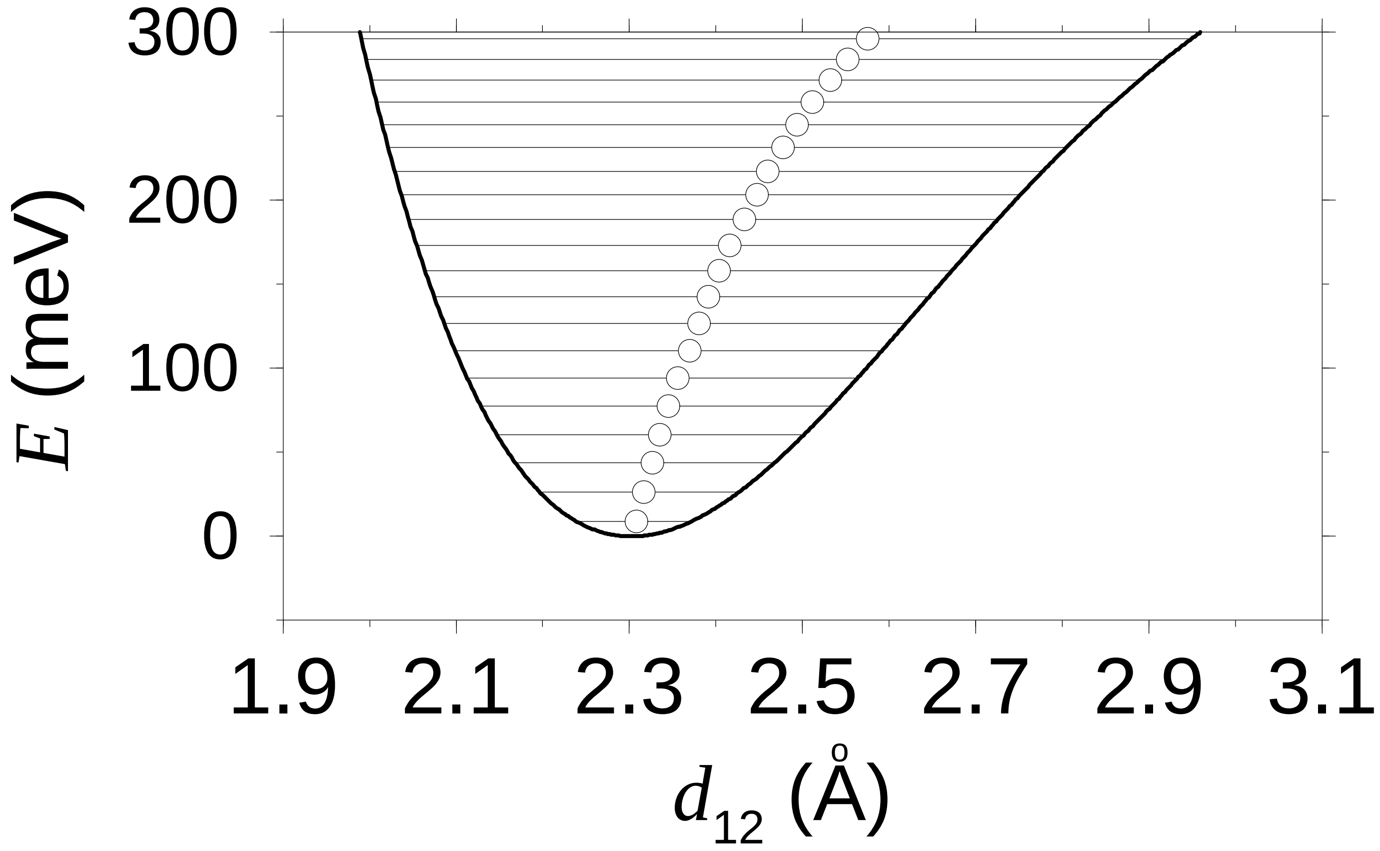

Fig.1: Static interlayer potential between the two outermost layers of Ag(111). The horizontal lines and open circles indicate the energy eigenvalues E_n and the mean displacements $\langle d_{12} \rangle_n$ respectively of an Ag atom vibrating in this potential.

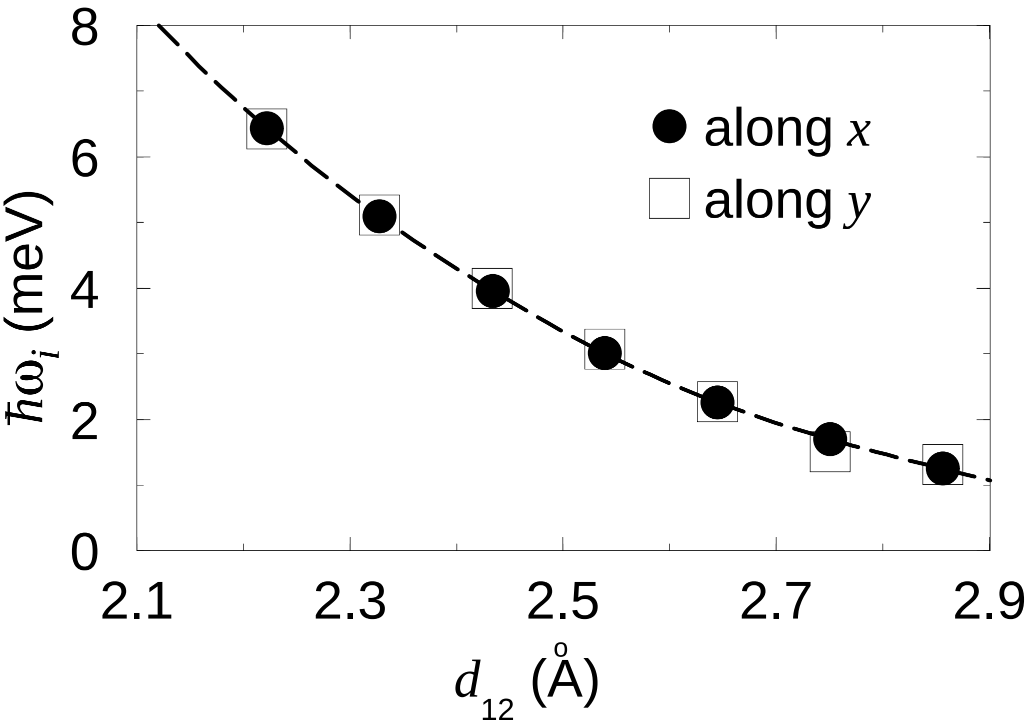

Fig.2: Energy $\hbar\omega_i$ of the top-layer in-plane modes of Ag(111), as a function of the first interlayer separation d_{12}. Circles and squares indicate modes polarized along the x- and y-directions respectively.

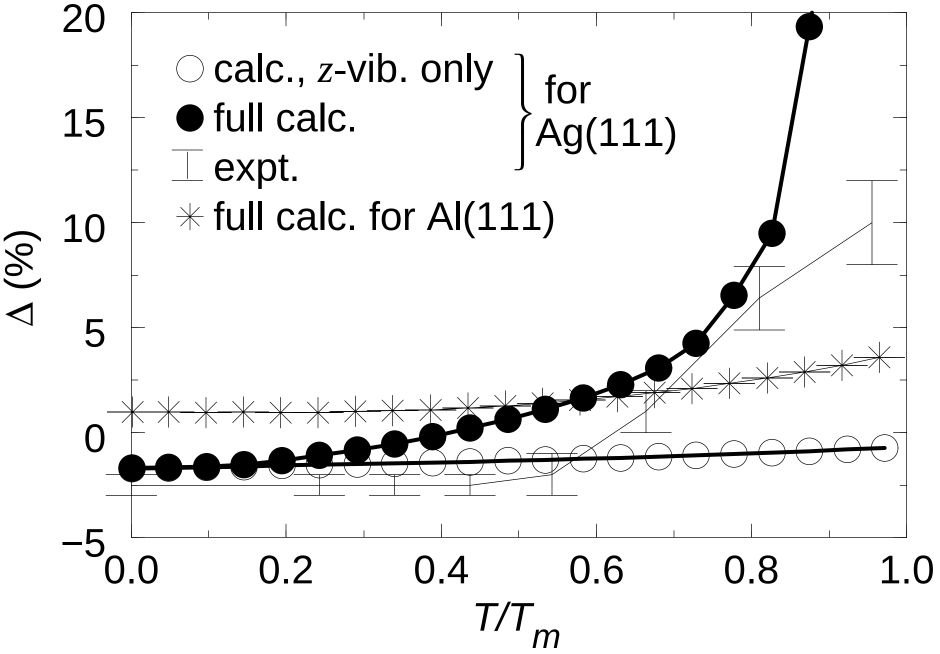

Fig.3: Contraction/expansion of d_{12} relative to d_B, as a function of normalized temperature T/T_m – our calculations for Ag(111) with out-of-plane mode only (open circles), and all three modes (filled circles); experiment[1] on Ag(111) (solid line with error bars); our calculation for Al(111) with all three modes (stars). T_m is the bulk melting temperature ($T_m^{Ag} = 1234$ K, $T_m^{Al} = 933$ K).

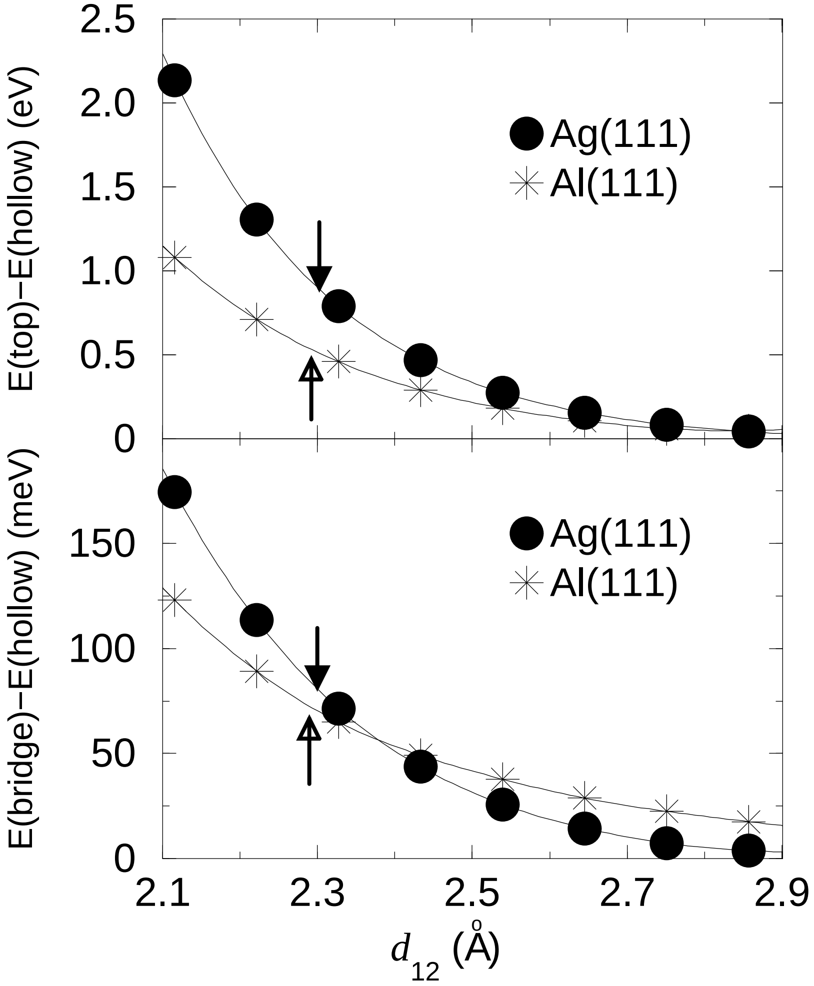

Fig.4: Decrease in the corrugation of the interlayer potential with increasing interlayer separation d_{12}: the graphs show the increase in surface energy when the outermost layer of atoms occupies an atop site or bridge site instead of the favored fcc hollow site, for Ag(111) (filled circles) and Al(111) (stars). Arrows indicate the equilibrium value (neglecting zero-point vibrations) of d_{12} at $T = 0$ K.