

# PRE-MELTING IN CUBIC STRUCTURE WITH RELAXATION

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We study the effect of melting of well-defined crystal surface within the frame of theory of atomic vibrations in harmonic approximation. We find that for two types of cubic crystal lattice: face centered cubic and body centered cubic, we may expect the existence of pre-melting. It is also shown that the occurrence or absence of surface melting depends strongly on the relaxation of lattice constant.

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## 1. Introduction

The phenomena of melting of solid surface have recently been extensively studied. The measurements made by various experimental techniques, such as low energy electron diffraction (LEED) [1, 2], scanning tunnelling microscopy (STM) [3] or medium energy ion scattering (MEIS) [4, 5] show that the top of a solid sample in thermodynamic equilibrium begins to change its state significantly below the temperature of melting, determined for the whole volume of a crystal. There have been developed some theoretical methods devoted to explain these facts, called the pre-melting effect. The first original works on these topics come from Lipovsky [6], who based his theory on the Landau theory of phase transitions. Since then, the most often used approach is based on studying the thermodynamical value  $\Delta\gamma$  which represents the excess of the energy of the dry surface with respect to the free energy of the surface completely wetted by the liquid layer of its own melt.

In our study we use the approach taking into account the dynamics of the vibrations of crystal lattice atoms, which is not the frequently used way for studying melting effects, however, it seems to be very convenient. This approach allows us to point out the difference and connection between two aspects of the problem, i.e., (1) inhomogeneous distribution of mean square displacements of atoms from their equilibrium position, depending on the number of layers below the surface of

a crystal, (2) influence of this distribution on the melting temperature connected with the specific layer of a crystal.

It is most important to find the relationship between the characteristics of vibration, especially the amplitude and the local state of a crystal. This relationship may be easily found when we take into account the Lindemann criterion [7] of melting, which says that we may treat a part of a crystal, as melted, if the mean amplitude of atomic vibration in the whole volume of this part is greater than one fourth of the smallest interatomic distance. According to this criterion we may determine, examining the dynamics of crystal lattice, the temperature in which the melting of separate layers parallel to the crystal surface occurs.

In order to obtain the mean square displacement due to vibrations, first of all we have to obtain the frequencies of phonons. This was done by the root sampling method [8], applied however in the specific form of the crystal SLABS [9–11]. The similar idea, however based on some other approaches, when the amplitudes of vibrations in successive layers are calculated in the self-consistent model without calculating a full phonon spectrum is also presented in Ref. [12]. In this method, we use two-dimensional Fourier transform between the displacement and momentum, instead of usually used three-dimensional one. A special significance of this approach comes from the fact that it allows us to consider not only the infinite crystal, but also the limited one. The sample is considered, as a finite set of planes (SLABS), which separately have to satisfy the requirement of two-dimensional infinity. The values of the third component of the wave vector  $q_z$ , perpendicular to the SLAB's surface are then stored in eigenvectors of the dynamical matrix.

Our interest was also directed at the influence of the relaxation of lattice parameter at the surface on the pre-melting effect. The relaxation is the well-known effect, when the distance between some surface layers is different from that characterising bulk. Calculations were made for two types of cubic structures: fcc and bcc.

## 2. Theoretical background

### 2.1. General remarks

In order to find the effect of crystal surface melting we build the sample as follows. We investigate the sample, which is infinite in two dimensions parallel to the surface. In these two directions the periodic Born-von Karman conditions are also satisfied. In the direction perpendicular to the surface we consider the number of  $n$  monoatomic layers. In our approach the most interesting parameter describing the layer is the mean amplitude of thermal vibration, which should vary with the  $\nu$  number, when  $\nu$  enumerates the layers in the volume of a crystal according to the inhomogeneity of a sample in the direction normal to the surface. Certainly, the amplitude must have the same value for layers labelled from the top, as well as from the bottom of a sample, so the following relation should take place:  $\rho_\nu = \rho_{n+1-\nu}$  ( $n$  is the total number of layers in a sample).

In order to determine the mean square displacement we should determine the frequencies of all the modes of vibrations which the atom in the  $\nu$ -th layer undergoes. The starting point is the Hamiltonian of the system. In harmonic approximation

$$H = \sum_{\alpha r} \frac{p_r^{\alpha 2}}{2M} + \frac{1}{2} \sum_{\alpha r} \sum_{\alpha' r'} A_{rr'}^{\alpha\alpha'} (R_r^\alpha - R_{r'}^{\alpha'}) (R_r^\alpha - R_{r'}^{\alpha'}), \quad (1)$$

where  $r, r'$  number the atoms in lattice,  $\alpha, \alpha'$  are the Cartesian coordinates.  $A_{rr'}^{\alpha\alpha'}$  are the force constants between the  $r$ -th and the  $r'$ -th atom in the volume. They must obey the symmetry relations. The determination of the force constants is always the crucial point of the calculations devoted to study the crystal dynamics. In our study we deduced them from the well-known (6-12) Lennard-Jones (L-J) potential

$$\Phi(r) = 4\epsilon \left[ \left( \frac{\sigma}{R} \right)^{12} - \left( \frac{\sigma}{R} \right)^6 \right]. \quad (2)$$

The coefficient may be obtained easily, using the standard procedure proposed by Lennard-Jones and Ingham [13, 14]. The idea of this method is to find the minimum of the total potential energy of a crystal

$$U_{\text{total}} = \frac{1}{2} N (4\epsilon) \sum_{ij} \left[ \left( \frac{\sigma}{p_{ij} R} \right)^{12} - \left( \frac{\sigma}{p_{ij} R} \right)^6 \right] \quad (3)$$

in a function of the smallest interatomic distance  $R$  ( $i$  and  $j$  number, as usually, all pairs of atoms and  $N$  is the total number of atoms in the crystal). The values of the ratio  $R/\sigma$  are then equal to 1.09 for fcc structure and 1.075 for bcc structure.

The value of parameter is a relative coefficient chosen in such a way as to fit the obtained amplitude of thermal vibration in the bulk of a crystal to the value corresponding to the melting effect, according to the Lindemann criterion.

The values of the force constants are then obtained as the central forces according to the following formula:

$$A_{rr'}^{\alpha\beta} = \frac{R_\alpha R_\beta}{R^2} \left( \Phi''(R) - \frac{1}{R} \Phi'(R) \right) + \frac{\delta_{\alpha\beta}}{R} \Phi'(R), \quad (4)$$

where  $R$  is the distance between atoms numbered  $r$  and  $r'$ . They are not temperature dependent.

Since the method of determining the amplitudes of thermal vibrations in successive layers is in more detail described in Refs. [15, 16], here we point out only the most important information.

From Eq. (1) we may simply obtain the equation of motion of the  $r$ -th atom

$$-M\omega^2 R_r^\alpha = \dot{p}_r^\alpha = - \left( \frac{\partial H}{\partial R_r^\alpha} \right) = - \sum_{\alpha' r'} A_{rr'}^{\alpha\alpha'} (R_r^\alpha - R_{r'}^{\alpha'}). \quad (5)$$

It is obvious that the summation in the equations is over all atoms in a crystal. Assuming that a plane wave with the wave vector  $q$  may propagate in a crystal we can introduce the transform

$$R_r^\alpha = \sum_{\lambda q} T_{qr}^{\alpha\lambda} Q_q^\lambda. \quad (6)$$

Putting (6) into (5)

$$\sum_{\lambda q} \omega^2 T_{qr}^{\alpha\lambda} Q_q^\lambda = \sum_{r'} \sum_{\lambda q} A_{rr'}^{\alpha\alpha'} T_{qr}^{\alpha\lambda} Q_q^\lambda. \quad (7)$$

The transformation matrix  $T_{qr}^{\alpha\lambda}$  may be written in a more evident form

$$T_{qr}^{\alpha\lambda} = T_{\nu\tau}^{\lambda} \exp [i(h_x r_x(j) + h_y r_y(j))], \quad (8)$$

where  $\nu$  denotes the index of layer,  $j$  is the number of an atom lying in the layer  $\nu$ . This formula, using the dependence of matrix element  $T_{\nu\tau}^{\lambda}$  on  $\nu$ , allows us to distinguish the influence of separate layers on the total dynamical effect.

Equation (7) is one of the forms of matrix-type dynamic equation of vibrating lattice, whose eigenvalues are the frequencies of normal modes and the eigenvectors are connected to the polarization vectors. We should point out that the eigenvectors contain information not only about the polarization of mode, but also about the third component of the wave vector  $q_z$ , which is perpendicular to the surface. Having calculated frequencies as well as the elements it is possible to obtain the mean square displacement of atom in the  $\nu$ -th layer

$$\langle (\delta R_{\nu j}^{\alpha}) \rangle = \frac{1}{2M} \sum_{\lambda\tau h} (T_{\nu j\tau h}^{\alpha\lambda})^2 \frac{1}{E_{\tau h}^{\lambda}} \coth \frac{E_{\tau h}^{\lambda}}{2kT}. \quad (9)$$

The details of introducing formula (9) are presented in Ref. [15].

## 2.2. Relaxation

The problem, which we especially want to take into account, is the relaxation of lattice between the surface and the subsurface layers. The results obtained by means of various experimental techniques and connected with determining the magnitude of the effect differ from one another, but the occurrence of the phenomena is obviously observed. As an example, in our calculations we used the coefficients obtained for crystals characterised by significant relaxation values: copper (fcc) and iron (bcc).

TABLE

The typical values of relaxation coefficients for fcc (copper) and bcc (iron) crystals (in percent), from [19].

	$\Delta d_{12}/d_{12}$	$\Delta d_{23}/d_{23}$	$\Delta d_{34}/d_{34}$	$\Delta d_{45}/d_{45}$
fcc (100)	-1.1	+1.7		
fcc (110)	-8.5	+2.3	-0.9	-0.8
fcc (111)	-0.7			
bcc (100)	-5	+5		
bcc (110)	+0.5			
bcc (111)	-16.9	-9.8	+4.2	-2.2

In Table we present the percentage change of interplanar spacing for copper (fcc) and iron (bcc) for three main crystallographic directions perpendicular to the surface, as the typical values of relaxation coefficients for cubic crystals.

In our calculations the relaxation causes the change of values of force constants. In order to determine their corrected values we assumed the same type

of interaction potential, however scaled by the ratio of relaxed and unrelaxed interatomic distance. It should be also noted that we took into account only the relaxation in the direction perpendicular to the surface. For low index crystallographic axes of cubic crystals this approach is valid.

### 3. Numerical results

Our calculations were made for both types of crystal for their three crystallographic orientations listed in Table, i.e., (100), (110) and (111). For all combinations of crystal and directions we made the calculation three times:

(a) calculation for bulk — this corresponds to the situation, when the elements of dynamical matrix do not depend on the number  $n$ , which labels the layers in a sample;

(b) calculation for surface — the values of matrix elements are for surface and subsurface layers reduced by the value connected with the excess of atoms over the surface [17];

(c) calculation for surface with relaxation — the situation is similar to that described in (b), however, we change also the values of force constants, due to the change of the component of displacement between the atoms on surface perpendicular to the surface by the percentage value given in Table.

All calculations were made for SLAB built of 30 layers. Our results [17] show that such a number is sufficient to treat the sample as a macroscopic one, in the sense that inner layers have the properties of bulk of crystal.

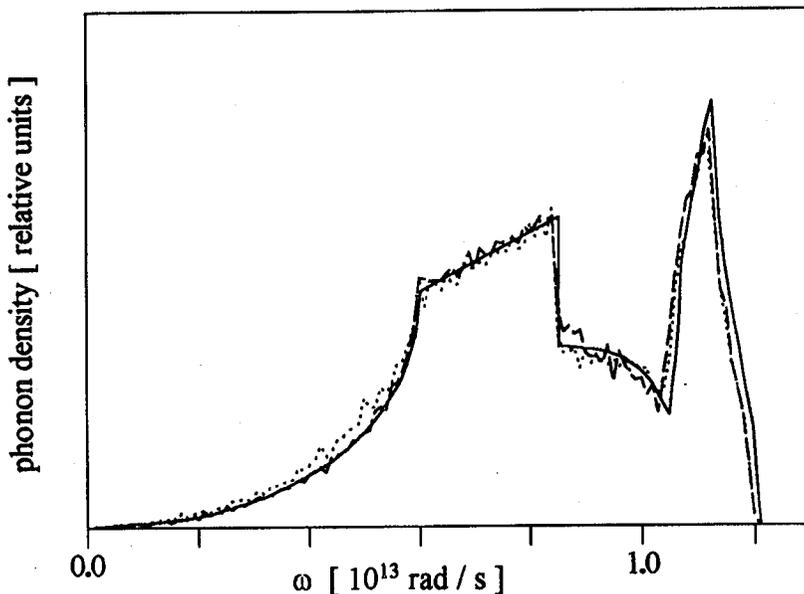


Fig. 1. Typical normalised phonon spectra obtained within the frame of our model for fcc crystal: solid line — calculation for bulk conditions, dashed line — calculation for surface without relaxation, dotted line — calculation for surface with relaxation.

In Fig. 1 we present a comparison of typical plots of normalised density of phonon states for (a) and (b) types of calculation. This plot shows insignificant, though explicit increase in  $g(\omega)$  function for lower frequencies, which should result, according to formula (9), from an increase in the amplitude of thermal vibration.

This situation may be observed in Figs. 2a and b. We present in them the values of mean amplitude of vibration for successive layers in a crystal. The solid line shows the behaviour of bulk calculations, whereas the long-dashed line corresponds to the surface calculation. In all the cases considered the inclusion of the surface effect causes a distinct increase in amplitude in several first layers. As it follows from Lindemann criterion, such an increase may be understood as the situation in which there is a temperature in which the whole volume of a crystal preserves its properties, however, there exists a part of a crystal, a specific layer, which may be treated as a liquid-like one. It seems interesting that the effect of the increase in the amplitude of thermal vibration is relatively stronger for bcc crystal, especially for (111) surface, where it reaches the value of more than 50%.

The third curve in Figs. 2a and b (dotted one) presents the results of calculation made for the surface with relaxation. This effect depends very strongly on the structure of a crystal. The plots obtained for (100) and (110) directions in fcc crystal show that the amplitude slightly changes its value, although in various

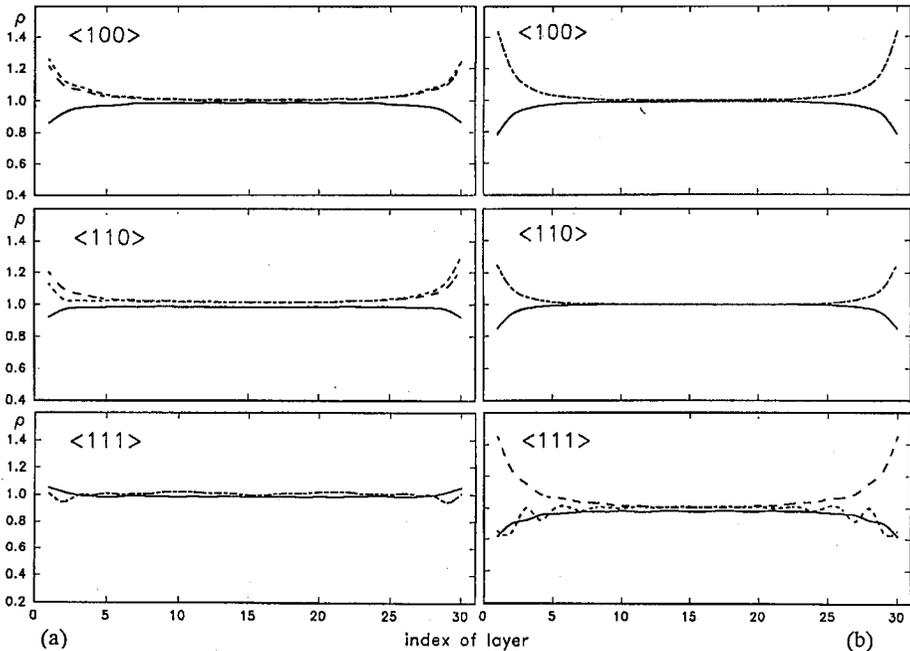


Fig. 2. Dependence of mean amplitude of thermal vibration on the index of layer for fcc (a) and bcc (b) crystals: solid line — bulk, long dashed line — surface without relaxation, short-dashed line — surface with relaxation.

ways. For (100) the magnitude of surface effect rises when including the relaxation. This fact is interesting, especially taking into account that the difference between values of real and theoretical (based on the value of lattice parameter) interplanar spacing is very small, close to 1%. The more significant relaxation for (110) surface produces the inverse effect. The values of amplitudes are here smaller with relaxation than without it.

The most interesting case for fcc crystals is the (111) surface. Experimental researches made for some fcc crystals (Pb [4, 5]) demonstrated that for this direction pre-melting does not occur. We should expect the same behaviour, as the effect of this study. Our calculations show that in order to obtain the expected effect we have to take into account the relaxation effect, even very small (0.7%). It is interesting that for this direction our results qualitatively differ from the results obtained by Broughton and Gilmer using molecular dynamics (MD) methods with truncated L-J potential [18], showing better agreement with experimental data. The reason of it may be the fact that the authors of earlier MD calculations had to restrict the studied structure to small dimensions. Broughton and Gilmer used the sample built of a few hundreds of atoms and applied to it the boundary conditions.

Analogous calculations made for bcc crystal do not show any difference between the effect with and without relaxation for (100) and (110) directions. It is

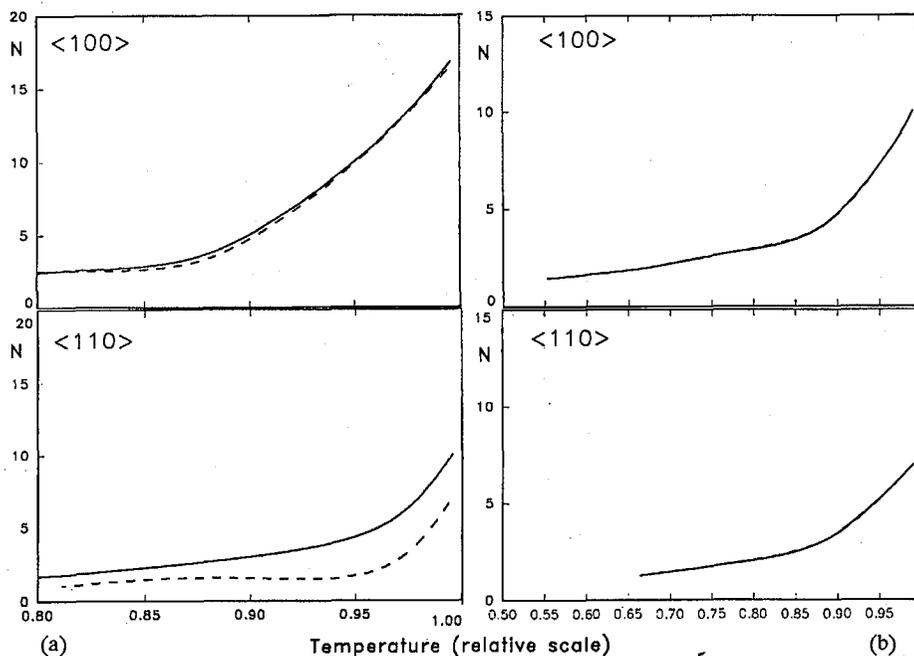


Fig. 3. Dependence of the number of melted layers of fcc (a) and bcc (b) samples with surface perpendicular to the (100) (upper plot) and (110) (lower plot) crystallographic orientation on temperature: solid line — surface without relaxation, dashed line — surface with relaxation, solid vertical line — temperature of melting of bulk.

worthwhile noticing that, although for (110) the relaxation values are small, for (100) they become significant values about +5% and -5%. It means that the second layer is "shifted" with the value of 5% of interplanar spacing between the first and third row. We may say that such a "shift" does not influence the dynamic properties of surface.

For (111) direction we observe the same effect as for fcc, i.e., the relaxation causes the total absence of pre-melting. It should be pointed out that the changes of interplanar spacing are here extremely large, reaching the value of the sixth part of the distance between the layers.

Figures 3a and b present the plots of the number of melted layers in a function of temperature. For an iron crystal we cannot distinguish the curves for the surface and the surface with relaxation. We can only compare the plots for two directions. It may be seen that for (110) surface the melting begins at higher temperatures than for (100). Both surfaces begin to melt in temperatures slightly higher than 1000 K.

For fcc crystal we observe various behaviours dependent on whether or not we consider relaxation. The plot for (100) direction shows that in some regions of temperatures the subsurface layers begin to melt later when taking into account relaxation, although the higher temperature tendency is the same for both cases. For (110) surface in the model with relaxation all layers melt in higher temperatures. The tendency to infinity in bulk melting temperature is the good proof of our calculations.

#### 4. Conclusions

Our calculations show explicit that the relaxation of lattice constant has a significant influence on the dynamic characteristics of a surface. The magnitude of this effect depends strongly on the structure of a crystal and the orientation of surface layer, so in some cases a quite small change may change our picture of the behaviour of surface in high temperatures. The bcc structure seems to be insensitive to relaxation if the coefficients are small, although the effect of the "shift" of a layer may be observed. However, when the effect takes place we may generally observe that it causes the increase in the surface melting temperature. It may be connected to the fact that in our approximation the force constants are, due to relaxation, higher, inducing lower amplitudes of vibrations. This fact, according to the Lindemann criterion, may be responsible for the increase in pre-melting temperatures.

We can see that, if the melting of the surfaces occurs, it begins in temperatures significantly lower than the bulk melting temperature; however, up to the melting point only a very small number of layers stays liquid-like.

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