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## Self-Consistent Einstein Model and Theory of Anharmonic Surface Vibration. I

—*One-Dimensional Model*—

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Softening of the surface lattice vibration and surface lattice relaxation are discussed on the basis of a self-consistent Einstein model, laying emphasis on the anharmonic effect. One-dimensional model is considered for the illustrative purpose. It is shown that the anharmonic effect is much more enhanced on and near the surface than in the interior.

### § 1. Introduction

It has been revealed by the LEED and other experiments that the vibration of atoms on the surface of metal crystal is quite anisotropic and much larger in amplitude than that of interior atoms (a phenomenon is sometimes called softening of surface vibration). There are also many accumulated evidences to show that the effect of anharmonicity is very important in such surface lattice vibrations. Most theoretical calculations of the surface lattice vibrations in the harmonic approximation seem to fail to provide with quantitatively satisfactory results.<sup>1)</sup> In the surface relaxation of lattice constant, the effect of anharmonicity should be also important because both the surface relaxation and the softening of the surface lattice vibrations are closely related.<sup>2)</sup> In order to discuss such anharmonic effects on the surface vibrations in a simple manner, one of the present authors has proposed a self-consistent Einstein model and applied it to a theory of melting of metallic fine particles<sup>3)</sup> and to the surface Debye temperature.<sup>4)</sup> In this model each atom is assumed to perform harmonic oscillation with the frequency which is self-consistently determined from the knowledge of the interatomic potential and the averaged motions of all atoms. The effect of anharmonicity or nonlinear interaction comes in through the self-consistent equations. In the previous applications of the model described in Refs. 3) and 4), the finite size effect of fine particles or surface effect has been properly taken into account, but the self-consistency has not been thoroughly pursued, although its importance was remarked for attaining quantitative agreement between the theory and experiments. The aim of this paper is to demonstrate, using a simple one-dimensional model, the importance of self-consistent treatment of the nonlinear coupling between the softening of frequency and amplitude of thermal motion in the present model. In a forthcoming paper, on the basis of the same model, a more realistic case will

be discussed to give a theory of anharmonic surface vibration of fcc metal crystals together with comparison with experimental data.

The organization of this paper is as follows: In § 2 a general formulation of the model is given and all the basic equations are derived. In § 3 the model is specialized by the use of the Morse function for the atomic potential, and the equations to determine the Einstein frequencies and lattice constants are set up. In the last section the numerical results are shown and discussion on the effect of anharmonicity is given.

Before entering general formulation, it should be pointed out that the one-dimensional lattice is always unstable against the excitation of long wave vibrational modes. If one calculated the thermal average of the squared amplitude of an atom in one-dimensional lattice, it will diverge as the number of atoms in the lattice is increased. In spite of this obvious defect of the model, the present calculation, in which the divergence above mentioned is avoided by taking the Einstein model, will give us some insight about the importance of anharmonicity in the surface vibration problem.

## § 2. Formulation of the model

We consider a simple linear chain of  $N+1$  atoms numerated as in Fig. 1 with atomic mass  $M$ . Let  $a_n$  be the interatomic distance between the  $(n-1)$ -th and  $n$ -th atoms in thermal equilibrium and be given by  $\langle x_n \rangle - \langle x_{n-1} \rangle$ , where  $x_n$  is the coordinate of the  $n$ -th atom and  $\langle \rangle$  denotes a thermal average defined later. The Hamiltonian of this linear system can be taken as

$$H = (M/2) \sum_n (dx_n/dt)^2 + \sum_{n < m} v(x_m - x_n), \quad (1)$$

where  $v(x)$  is interatomic pair potential. When atomic displacement from the thermal equilibrium

$$u_n = x_n - \langle x_n \rangle$$

is introduced, (1) is rewritten as

$$H = (M/2) \sum_n (du_n/dt)^2 + \sum_{n < m} v(u_m - u_n + \sum_{l=n+1}^m a_l). \quad (2)$$

In order to determine the thermal properties of this system, we adopt the variational principle at finite temperatures, using a trial statistical operator ( $\beta = 1/k_B T$ )

$$\rho = \exp(-\beta H_{\text{tr}}) / \text{Tr}[\exp(-\beta H_{\text{tr}})] \quad (3)$$

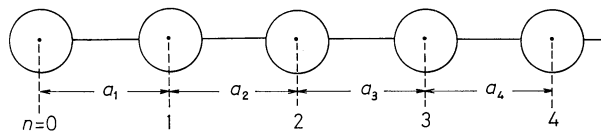


Fig. 1. A model of one-dimensional lattice.

with a trial Hamiltonian

$$H_{\text{tr}} = (M/2) \sum_n (du_n/dt)^2 + \sum_n \phi_n u_n^2/2. \tag{4}$$

Let us define the free energy  $F$  by

$$F = \text{Tr}[\rho(H + \beta^{-1} \ln \rho)] \tag{5}$$

and require to make  $F$  minimum with respect to variation of  $\phi_n$ . If we call

$$F_H = \text{Tr}[\rho(H_{\text{tr}} + \beta^{-1} \ln \rho)], \tag{6}$$

then  $F$  is obviously transformed into

$$\begin{aligned} F &= \langle H \rangle - \langle H_{\text{tr}} \rangle + F_H \\ &= \sum_{n < m} \sum_{i=n+1}^m \langle v(u_m - u_n + \sum_{l=n+1}^m a_l) \rangle - \sum_n \phi_n \langle u_n^2 \rangle / 2 + F_H, \end{aligned} \tag{7}$$

where the thermal average is defined by  $\langle \dots \rangle = \text{Tr}[\rho \dots]$ . The Einstein model characterized by the trial Hamiltonian  $H_{\text{tr}}$  is expected to be a good approximation at high temperatures, and hence we shall confine ourselves hereafter to the high temperature approximation, with which it is easily verified that

$$F_H = \beta^{-1} \sum_n \ln(\beta \hbar \sqrt{\phi_n/M}) \tag{8}$$

and

$$\phi_n \langle u_n^2 \rangle / 2 = \beta^{-1} / 2. \tag{9}$$

Thus, for performing the necessary variation of  $F$  with respect to  $\phi_n$ , the remaining problem is to express  $\langle v(\dots) \rangle$  in Eq. (7) as functions of  $\phi_n$ . For this purpose, it is convenient to decompose  $v(x)$  into Fourier components:

$$v(x) = \int_{-\infty}^{\infty} V(q) \exp(iqx) dq. \tag{10}$$

Since the thermal average with the statistical weight  $\rho$  is essentially the Gaussian average and the equipartition law, Eq. (9), does hold in the present approximation, one can readily obtain

$$\langle \exp[iq(u_m - u_n)] \rangle = \exp[-(q^2/2\beta)(\phi_m^{-1} + \phi_n^{-1})]. \tag{11}$$

Putting (8) ~ (11) into (7), we have

$$\begin{aligned} F &= \sum_{n < m} \sum_{i=n+1}^m \int_{-\infty}^{\infty} dq V(q) \exp(iq \sum_{l=n+1}^m a_l) \exp[-(q^2/2\beta)(\phi_m^{-1} + \phi_n^{-1})] \\ &\quad + (2\beta)^{-1} \sum_n \ln(\beta^2 \hbar^2 \phi_n / Me). \end{aligned} \tag{12}$$

Now the equations to determine  $\{\phi_n\}$  and  $\{a_n\}$  follow from the variation

$$\delta F / \delta \phi_n = 0, \quad n = 0, 1, 2, \dots, N$$

and

$$\delta F / \delta a_n = 0, \quad n = 1, 2, \dots, N.$$

Simple manipulation using Eq. (12) yields  $2N+1$  equations for  $\{\phi_n\}$  and  $\{a_n\}$  in the following forms:

$$\phi_n + \int_{-\infty}^{\infty} dq q^2 V(q) \sum_{m \neq n} \exp(iq \xi_{mn}) \exp[-(q^2/2\beta)(\phi_m^{-1} + \phi_n^{-1})] = 0, \quad n = 0, 1, 2, \dots, N \tag{13}$$

$$\sum_{m \geq p > n} \sum_{l=n+1}^m \int_{-\infty}^{\infty} dq q V(q) \exp(iq \sum_{l=n+1}^m a_l) \exp[-(q^2/2\beta)(\phi_m^{-1} + \phi_n^{-1})] = 0, \quad p = 1, 2, \dots, N \tag{14}$$

where

$$\xi_{mn} = \begin{cases} \sum_{l=n+1}^m a_l & \text{for } m > n, \\ \sum_{l=m+1}^n a_l & \text{for } m < n. \end{cases}$$

These are complicated nonlinear equations and it is very difficult to solve them for general cases. In the next section, therefore, we shall simplify the problem by taking a special potential form for  $v(x)$ . It will be, however, constructive to rewrite Eqs. (13) and (14) so as one can have a clear interpretation of them. Let us define an average potential

$$\phi_{mn}(x) = \langle v(x + u_m - u_n) \rangle, \quad m > n. \tag{15}$$

Then it is not hard to show that

$$\phi'_{mn}(x) \Big|_{x = \sum_{l=n+1}^m a_l} = i \int_{-\infty}^{\infty} dq q V(q) \exp(iq \sum_{l=n+1}^m a_l) \exp[-(q^2/2\beta)(\phi_m^{-1} + \phi_n^{-1})] \tag{16}$$

and

$$\phi''_{mn}(x) \Big|_{x = \xi_{mn}} = - \int_{-\infty}^{\infty} dq q^2 V(q) \exp(iq \xi_{mn}) \exp[-(q^2/2\beta)(\phi_m^{-1} + \phi_n^{-1})]. \tag{17}$$

Therefore Eqs. (13) and (14) may be transcribed as

$$\phi_n = \sum_{m \neq n} [\phi''_{mn}(x)]_{x = \xi_{mn}}, \quad n = 0, 1, 2, \dots, N \tag{13'}$$

and

$$\sum_{m \geq p > n} \sum_{l=n+1}^m [\phi'_{mn}(x)]_{x = \sum_{l=n+1}^m a_l} = 0, \quad p = 1, 2, \dots, N. \tag{14'}$$

The physical meaning of these equations is clear: Eq. (14') is the same as the static equilibrium condition of a lattice composed of atoms interacting with the average potential  $\phi_{mn}(x)$ , while Eq. (13') tells that the Einstein frequency of the  $n$ -th atom is determined from the curvature of the total average potential acting at the equilibrium position obtained from Eq. (14'). Thus the problem

apparently reduces to a static one with the average potential  $\phi_{mn}(x)$  into which all the thermodynamical effects are absorbed.

### § 3. Specialization for Morse potential

In order to reduce the mathematical difficulty, we shall adopt a simple Morse function for  $v(x)$ :

$$v(x) = D\{\exp[-2\alpha(x-r_0)] - 2\exp[-\alpha(x-r_0)]\}. \tag{18}$$

Then the average potential  $\phi_{mn}(x)$  is calculated by taking Gaussian average of  $v(x)$ :

$$\phi_{mn}(x) = \frac{\int \cdots \int \prod_{p=0}^N (du_p \exp[-\beta\phi_p u_p^2/2]) v(x+u_m-u_n)}{\int \cdots \int \prod_{p=0}^N (du_p \exp[-\beta\phi_p u_p^2/2])}$$

The final result for  $\phi_{mn}(x)$  is neat and of a similar form to (18):

$$\phi_{mn}(x) = D_{mn}\{\exp[-2\alpha(x-r_{mn})] - 2\exp[-\alpha(x-r_{mn})]\}, \tag{19}$$

where

$$D_{mn} = D \exp[-(\alpha^2/\beta)(\phi_m^{-1} + \phi_n^{-1})] \tag{20}$$

and

$$r_{mn} = r_0 + (3\alpha/2\beta)(\phi_m^{-1} + \phi_n^{-1}). \tag{21}$$

We observe from Eqs. (19)~(21) that in the thermal average potential the depth of the potential minimum becomes smaller ( $D \rightarrow D_{mn}$ ,  $D > D_{mn}$ ), the equilibrium distance becomes larger ( $r_0 \rightarrow r_{mn}$ ,  $r_0 < r_{mn}$ ), and these shifts are enhanced as temperature is increased. General behaviour of  $\phi_{mn}(x)$  is schematically depicted in Fig. 2. When we use this average potential in the basic equations (13') and (14'), the effect of the anharmonicity is seen in a conspicuous way: Increase of temperature and presence of surface reduce the values of  $\{\phi_n\}$ . Then this causes weakening of the potential  $\phi_{mn}(x)$  and gives rise to reduction of the values of  $\{\phi_n\}$  again through Eq. (13'). At

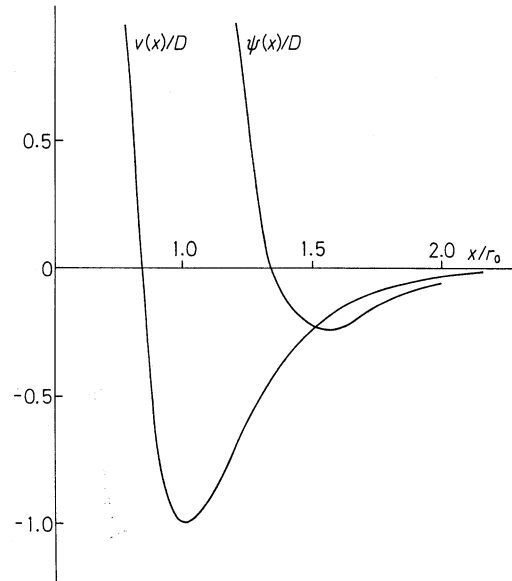


Fig. 2. The Morse function and average potential. The parameters used are:  $\alpha r_0 = 1$ ,  $D_{mn}/D = 2$ .

the same time this cooperative processes go on unevenly when the surface is present, producing both the surface relaxation of lattice constant and the surface softening of atomic vibration.

To see more quantitatively such effects, we simplify the problem further by assuming that  $\psi_{mn}(x)$  is of enough short range that interaction between distances far more than the nearest neighbour can be neglected. Furthermore we consider a semi-infinite lattice, taking limit  $N \rightarrow \infty$ . Then Eqs. (13') and (14') become

$$\begin{aligned} \phi_0 &= \psi''_{10}(a_1), \\ \phi_n &= \psi''_{n-1,n}(a_n) + \psi''_{n+1,n}(a_{n+1}), \quad n \geq 1 \end{aligned} \tag{22}$$

$$\psi'_{n,n-1}(a_n) = 0, \quad n = 1, 2, \dots \tag{23}$$

It is convenient to introduce a reduced mean square displacement defined by

$$\lambda_n = \alpha^2 / \beta \phi_n = \alpha^2 \langle u_n^2 \rangle. \tag{24}$$

Upon using Eq. (19) for  $\psi_{mn}(x)$  and Eq. (21) for  $r_{mn}$ , the solution of Eq. (23) is immediately given as

$$a_n = r_0 + (3/2\alpha) (\lambda_{n-1} + \lambda_n), \quad n = 1, 2, \dots, \tag{25}$$

whereas Eq. (22) can be cast into the forms

$$\begin{aligned} 2\beta D \lambda_0 \exp(-\lambda_0 - \lambda_1) &= 1, \\ 2\beta D \lambda_n \{ \exp(-\lambda_n - \lambda_{n-1}) + \exp(-\lambda_n - \lambda_{n+1}) \} &= 1, \quad n \geq 1. \end{aligned} \tag{26}$$

Let us first examine the limit of bulk state by taking

$$\lim_{n \rightarrow \infty} \lambda_n = \lambda_b \quad \text{and} \quad \lim_{n \rightarrow \infty} a_n = a_b.$$

Both the limits of Eqs. (25) and (26) yield

$$a_b = r_0 + 3\lambda_b / \alpha \tag{27}$$

and

$$\lambda_b \exp(-2\lambda_b) = k_B T / 4D. \tag{28}$$

There are two solutions of Eq. (28) for  $\lambda_b$  as shown in Fig. 3, and the smaller one is a correct solution, giving rise to a finite Einstein frequency as  $T \rightarrow 0$ . Figure 3 also shows that when  $T \geq T_c = 2D / ek_B$  there exists no solution. Thus above  $T_c$  the lattice becomes unstable.<sup>5)</sup> In order to look for the surface effect on  $\lambda_n$ , we rewrite Eq. (26) in the following forms:

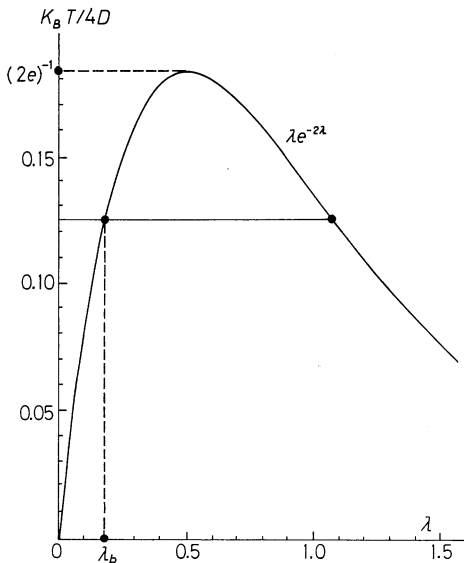


Fig. 3. Graphical solution of Eq. (28).

$$\begin{aligned} \lambda_0 &= (k_B T / 2D) \exp(\lambda_0 + \lambda_1), \\ \lambda_n &= (k_B T / 2D) \exp(\lambda_{n-1} + \lambda_n + \lambda_{n+1}) / \{\exp(\lambda_{n-1}) + \exp(\lambda_{n+1})\}, \\ & n \geq 1. \end{aligned} \tag{29}$$

Now we can solve  $\{\lambda_n\}$  by iteration: First insert the value of  $\lambda_b$  determined from Eq. (28) into the right-hand side of Eqs. (29) to obtain a set of new values of  $\{\lambda_n\}$ , which are used again in the right-hand side of Eqs. (29). This procedure may be repeated to any order until stationary solution for  $\{\lambda_n\}$  is obtained. In the next section, the results of such iteration calculation will be described. In the meanwhile it would be useful to see general trend of  $\{\lambda_n\}$  and  $\{a_n\}$  in analytical forms for particular cases.

When  $k_B T / D \ll 1$  it is not hard to derive approximate solutions of Eqs. (28) and (29). Under this condition it holds that  $\lambda_b \ll 1$ , and hence from Eq. (28) up to order  $(k_B T / D)^2$

$$\lambda_b(1 - 2\lambda_b) = k_B T / 4D$$

or

$$\lambda_b = (k_B T / 4D) (1 + k_B T / 2D). \tag{30}$$

Since  $k_B T / 4D = \lambda_b^b$  is nothing but the value for harmonic oscillator, the effect of anharmonicity is included in the factor  $(1 + k_B T / 2D)$ . The second iteration starting with  $\lambda_b$  yields

$$\begin{aligned} \lambda_0 &= (k_B T / 2D) (1 + 3k_B T / 4D), \\ \lambda_1 &= (k_B T / 4D) (1 + 5k_B T / 8D), \\ \lambda_n &= \lambda_b, \quad n \geq 2. \end{aligned}$$

Further iterations do not change the above results, giving rise to only higher terms, and hence up to order  $(k_B T / D)^2$ , the above results for  $\lambda_n$  are consistent and correct. We can put them into reduced forms dividing by  $\lambda_b$ :

$$\begin{aligned} \lambda_0 / \lambda_b &= 2(1 + k_B T / 4D), \\ \lambda_1 / \lambda_b &= 1 + k_B T / 8D, \\ \lambda_n / \lambda_b &= 1, \quad n \geq 2. \end{aligned} \tag{31}$$

The determination of  $a_b$  and  $\{a_n\}$  is also straightforward. The results are, up to order  $(k_B T / D)^2$ , summarized as

$$\begin{aligned} a_b &= r_0 + (3k_B T / 4\alpha D) (1 + k_B T / 2D), \\ a_1 &= r_0 + (3k_B T / 4\alpha D) (3/2 + 17k_B T / 16D), \\ a_2 &= r_0 + (3k_B T / 4\alpha D) (1 + 9k_B T / 16D), \\ a_n &= a_b, \quad n \geq 3, \end{aligned}$$

or in the reduced forms:

$$\begin{aligned} a_1/a_b &= 1 + (3k_B T/8\alpha r_0 D) + (3k_B T/4\alpha r_0 D)^2 (3\alpha r_0/16 - 1/2), \\ a_2/a_b &= 1 + (\alpha r_0/12) (3k_B T/4\alpha r_0 D)^2, \\ a_n/a_b &= 1, \quad n \geq 3. \end{aligned} \quad (32)$$

It should be noted that the relaxation of the first lattice constant is of order  $(k_B T/\alpha r_0 D)$  while that of the second lattice constant is of order  $(k_B T/\alpha r_0 D)^2$ . If we call

$$\gamma_b = 3k_B T/4\alpha r_0 D = r_0^{-1} (da_b/dT) \quad (33)$$

the thermal expansion coefficient of the bulk lattice, then

$$(a_1/a_b - 1) \cong \gamma_b/2. \quad (34)$$

Therefore, the more thermally expandable the lattice is, the more appreciable the surface relaxation is.

#### § 4. Numerical results and discussion

For the numerical analysis of  $\{a_n\}$ , we have to specify the value of  $\alpha r_0$ , and we choose

$$\alpha = 1.1836 A^{-1}, \quad r_0 = 3.733 A$$

which are the values corresponding to Pb.<sup>6)</sup> The numerical results for  $\{\lambda_n\}$  and  $\{a_n\}$  calculated by the iteration method are listed up in Table I for several values of  $k_B T/D$ . In Fig. 4  $\lambda_0/\lambda_b$  and  $\lambda_1/\lambda_b$  are plotted as functions of  $k_B T/D$ . Figure 5 shows the value of  $a_1/a_b$  as a function of  $k_B T/D$ . As seen from these figures,

Table I.

$k_B T/D$	1/8	1/4	3/8	1/2
$\lambda_b$	0.03341	0.07221	0.11892	0.1787
$\lambda_b^h = k_B T/4D$	0.03125	0.0625	0.09375	0.125
$\lambda_b/\lambda_b^h$	1.069	1.155	1.268	1.430
$\lambda_0/\lambda_b$	2.075	2.187	2.385	2.948
$\lambda_1/\lambda_b$	1.018	1.047	1.095	1.223
$\lambda_2/\lambda_b$	1.000	1.001	1.007	1.025
$\lambda_3/\lambda_b$		1.000	1.001	1.003
$\lambda_4/\lambda_b$			1.000	1.001
$\lambda_5/\lambda_b$				1.000
$a_b/r_0$	1.023	1.049	1.081	1.121
$a_1/a_b$	1.012	1.029	1.055	1.117
$a_2/a_b$	1.000	1.001	1.004	1.013
$a_3/a_b$		1.000	1.000	1.001
$a_4/a_b$				1.000



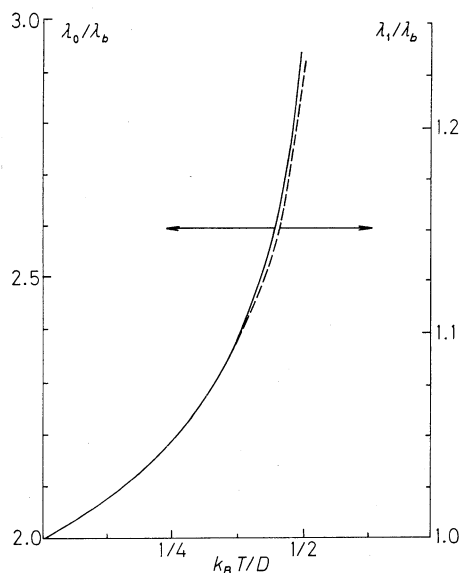


Fig. 4. Ratio of the mean square displacement of surface atom to that corresponding to bulk atom as functions of temperature. The solid line is for the 0-th atom with the left scale and the dotted line for the first atom with the right scale.

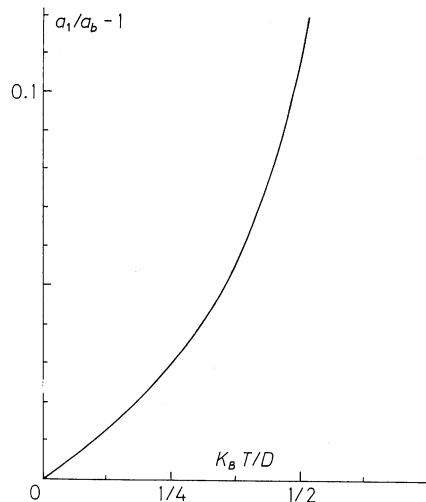


Fig. 5. Surface relaxation of the first lattice constant as a function of temperature.

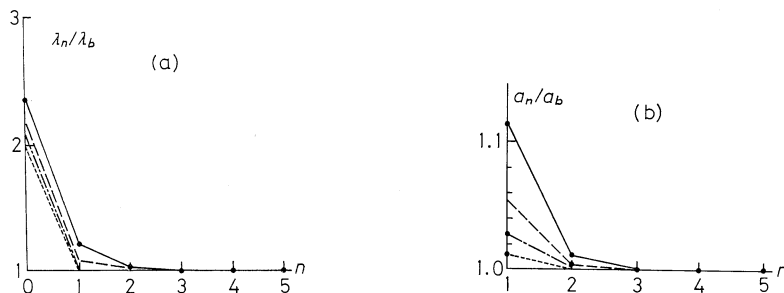


Fig. 6. Site and temperature dependence of (a) mean square amplitude and (b) lattice constant. Four lines correspond from top in order to the values of temperatures  $k_B T/D=1/2, 3/8, 1/4$  and  $1/8$ , respectively.

the amplitude of the surface lattice vibration is very large compared with that of the bulk atoms and the surface relaxation of the lattice constant becomes also appreciable as temperature is increased. Since only the nearest neighbour interactions are taken into account in the present calculation, there should not exist the surface relaxation at all within the harmonic approximation. The observed surface relaxation in Table I is, therefore, entirely due to the effect of anharmonicity. In the Table, the bulk values for the mean square displacement  $\lambda_b$  and

lattice constant  $a_b$ , are expressed in unit of those corresponding to the harmonic approximation. These quantities already deviate from unity and show fairly large temperature dependence. In addition to this anharmonic behaviour of the bulk lattice, there appear remarkable enhancements in the mean square amplitude and the relaxation of lattice constant on and near the surface as summarized in Fig. 6. One can also say that the effect of anharmonicity becomes appreciable on the surface from temperature much lower than that for the bulk atoms.

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