

## Mean-Square Amplitudes of Vibration at a Surface\*

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The ratios of the mean-square amplitudes of vibration at a surface to those in the bulk have been studied in detail for model crystals whose particles interact through a Lennard-Jones potential. Within a quasi-harmonic approximation, the ratio for a particular surface and direction of vibration is approximately a universal function of  $T/\Theta_D$ , where  $T$  is the temperature and  $\Theta_D$  the bulk Debye temperature. The ratio increases rapidly with  $T$  for  $T < \frac{1}{2}\Theta_D$  and then is nearly constant. Three factors increase the ratio above the value it would have in a simple force-constant model: (i) a temperature-independent decrease in the force constants at the surface relative to those in the bulk, (ii) a further temperature-dependent decrease, and (iii) anharmonicity. These factors may account for the tendency of experimental values of this ratio to be larger than values calculated with force-constant models.

WITHIN the past few years, low-energy electron diffraction has proved to be a useful tool for studying a number of surface properties. One subject of investigation has been the vibrations of atoms (or ions) at a surface. These vibrations determine the Debye-Waller factor,<sup>1-7</sup> the one-phonon scattering,<sup>8,9</sup> and the multiphonon scattering.<sup>10,11</sup> The measured quantities which are most directly related to the surface vibrations are the mean-square amplitudes of vibration, which can be determined from the temperature dependence of the Debye-Waller factor.

In this paper, we report a study of the surface mean-square amplitudes of vibration in a model crystal which has an fcc structure and which is composed of particles interacting through a Lennard-Jones (LJ) potential,

$$\phi(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]. \quad (1)$$

Here  $r$  is the distance between the interacting particles and  $\epsilon$  and  $\sigma$  are the potential parameters.

There are two ways of regarding the use of the LJ potential. The first point of view, emphasized elsewhere,<sup>12-15</sup> is that it can be used for quantitative cal-

culations in the case of the noble-gas solids. The second point of view, emphasized here, is that it can be used for general, qualitative studies of surface properties in monatomic crystals. The LJ potential has the advantage of yielding results which, when expressed in dimensionless form, are independent of the atomic mass  $M$  and the potential constants  $\epsilon$  and  $\sigma$ ; i.e., the results depend only upon the shape of the potential. This convenient feature is not present in other potentials, such as the Morse and Buckingham potentials, that have the same general shape but yield results which depend upon particular values of the potential parameters.

Previous calculations<sup>16-23</sup> of the mean-square amplitudes of vibration at a surface have been based upon the use of force-constant models.<sup>24</sup> The advantage of using a potential is that a number of effects can be studied which are beyond the scope of a force-constant model. Among these are (i) the displacements of surface atoms from the positions they would have in the bulk, (ii) the effect of these displacements on the force constants and on dynamical quantities such as the mean-square amplitudes, (iii) thermal expansion at the surface and its effect on the dynamical quantities, and (iv) the importance of anharmonic effects at the surface.

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TABLE I. The ratios  $\langle u_\alpha^2 \rangle_{\text{surface}} / \langle u_\alpha^2 \rangle_{\text{bulk}}$  ( $\alpha = x, y, \text{ or } z$ ) at  $T = 0^\circ\text{K}$  for densities given by  $\sigma/a = 1.30, 1.28, 1.26, \text{ and } 1.24$ .

Surface	Component	1.30	1.28	1.26	1.24
(100)	$\langle u_x^2 \rangle$	1.30	1.30	1.30	1.31
	$\langle u_z^2 \rangle$	1.60	1.60	1.58	1.56
(111)	$\langle u_x^2 \rangle$	1.10	1.10	1.11	1.11
	$\langle u_z^2 \rangle$	1.58	1.56	1.54	1.51
(110)	$\langle u_x^2 \rangle$	1.24	1.24	1.24	1.25
	$\langle u_y^2 \rangle$	1.68	1.68	1.68	1.68
	$\langle u_z^2 \rangle$	1.61	1.61	1.61	1.61

In the quasiharmonic approximation, the surface mean-square amplitudes of vibration  $\langle u_\alpha^2 \rangle_{\text{surface}}$  ( $\alpha = x, y, \text{ or } z$ ) are given by<sup>12</sup>

$$\langle u_\alpha^2 \rangle_{\text{surface}} = \frac{\hbar}{2NM} \sum'_{q,p} |\xi_\alpha(q,p)|_{\text{surface}}^2 \times \frac{\coth[\hbar\omega_p(q)/2k_B T]}{\omega_p(q)}. \quad (2)$$

Here  $T$  is the temperature,  $k_B$  is the Boltzmann constant,  $N$  is the number of surface atoms,  $\omega_p(q)$  is the vibrational frequency for the mode labeled by  $p$  and the two-dimensional wave vector  $q$ , and  $|\xi_\alpha(q,p)|_{\text{surface}}^2$  gives the amplitude of vibration at the surface associated with this frequency. (The prime on the summation indicates that the three zero-frequency modes associated with uniform translations are to be omitted from the summation.) The method for calculating  $\omega_p(q)$  and  $|\xi_\alpha(q,p)|_{\text{surface}}^2$  is described in Ref. 12. The bulk mean-square amplitude  $\langle u_\alpha^2 \rangle_{\text{bulk}}$  is given by an equation similar to Eq. (2).<sup>25</sup>

We begin by considering the dependence of the ratio  $\langle u_\alpha^2 \rangle_{\text{surface}} / \langle u_\alpha^2 \rangle_{\text{bulk}}$  upon the density. It is convenient to represent the density by the dimensionless quantity  $\sigma/a$ , where  $\sqrt{2}a$  is the nearest-neighbor distance. In Tables I and II, calculated values of  $\langle u_\alpha^2 \rangle_{\text{surface}} / \langle u_\alpha^2 \rangle_{\text{bulk}}$  are given both at  $0^\circ\text{K}$  and in the high-temperature limit for densities corresponding to  $\sigma/a = 1.30, 1.28, 1.26, \text{ and } 1.24$ . Since the  $\sigma/a$  ratio for argon is approximately 1.284 at  $0^\circ\text{K}$  and 1.247 at the melting temperature (if the values of  $\epsilon$  and  $\sigma$  are taken to be those given by Horton<sup>26</sup>), this is a rather extreme range of densities. It can be seen, however, that there is only a small variation in  $\langle u_\alpha^2 \rangle_{\text{surface}} / \langle u_\alpha^2 \rangle_{\text{bulk}}$  (less than 10% in all cases).

The smallness of the variation can be understood as follows: The Grüneisen parameter  $\gamma_p(q)$  can be defined by

$$\gamma_p(q) = -d \ln \omega_p(q) / d \ln V, \quad (3)$$

where  $V$  is the volume of the crystal. When  $\gamma_p(q)$  was

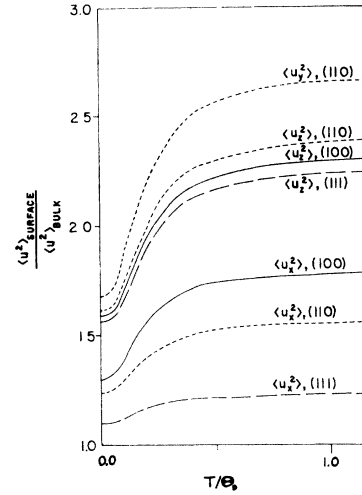


FIG. 1. Temperature dependence of  $\langle u_\alpha^2 \rangle_{\text{surface}} / \langle u_\alpha^2 \rangle_{\text{bulk}}$  for (100), (111), and (110) surfaces.

calculated for crystals with surfaces,<sup>15</sup> it was found, for all values of  $p$  and  $q$ , to be approximately equal to the average Grüneisen parameter calculated for the bulk. As the density changes, therefore, the frequencies for a crystal with surfaces change in proportion to the frequencies for the bulk.

Now suppose that the ratio  $T/\Theta_D$ , where  $\Theta_D$  is the Debye temperature,<sup>27</sup> is kept fixed as the density changes. Since  $\Theta_D$  represents a characteristic vibrational frequency  $\omega_D$  ( $\Theta_D = \hbar\omega_D/k_B$ ), the ratio  $\hbar\omega_p(q)/2k_B T$  in Eq. (2) then remains nearly constant, while  $\omega_p(q)$  is multiplied by a factor which is nearly the same for all frequencies. Consequently,  $\langle u_\alpha^2 \rangle_{\text{surface}} / \langle u_\alpha^2 \rangle_{\text{bulk}}$  remains approximately constant with respect to changes in density.

We thus have the result that the ratio  $\langle u_\alpha^2 \rangle_{\text{surface}} / \langle u_\alpha^2 \rangle_{\text{bulk}}$  is a universal function of  $T/\Theta_D$ , except for variations of a few percent with extreme changes in density. The functional dependence for the (100), (111), and (110) surfaces is shown in Fig. 1. (The results of Fig. 1 were obtained by carrying out calculations for  $\sigma/a = 1.28$  and taking the dimensionless Debye tem-

TABLE II. The ratios  $\langle u_\alpha^2 \rangle_{\text{surface}} / \langle u_\alpha^2 \rangle_{\text{bulk}}$  in the high-temperature limit for densities given by  $\sigma/a = 1.30, 1.28, 1.26, \text{ and } 1.24$ .

Surface	Component	1.30	1.28	1.26	1.24
(100)	$\langle u_x^2 \rangle$	1.79	1.80	1.80	1.80
	$\langle u_z^2 \rangle$	2.35	2.32	2.28	2.24
(111)	$\langle u_x^2 \rangle$	1.24	1.24	1.25	1.26
	$\langle u_z^2 \rangle$	2.30	2.25	2.19	2.12
(110)	$\langle u_x^2 \rangle$	1.56	1.56	1.57	1.59
	$\langle u_y^2 \rangle$	2.70	2.68	2.67	2.66
	$\langle u_z^2 \rangle$	2.42	2.40	2.39	2.38

<sup>25</sup> A. A. Maradudin, E. W. Montroll, and G. H. Weiss, *Theory of Lattice Dynamics in the Harmonic Approximation* (Academic Press Inc., New York, 1963), p. 237.

<sup>26</sup> G. K. Horton, Am. J. Phys. **36**, 93 (1968).

<sup>27</sup> To remove ambiguity, we take  $\Theta_D$  to be the Debye temperature determined from specific-heat measurements as  $T \rightarrow 0$ .

TABLE III. The ratios  $\langle u_\alpha^2 \rangle_{\text{surface}} / \langle u_\alpha^2 \rangle_{\text{bulk}}$  calculated in the high-temperature-limit approximation (valid for  $T > \frac{1}{2}\Theta_D$ ). Four methods were used: (a) simple force-constant model, with force constants at the surface equal to those in bulk (SFC). (b) Quasiharmonic approximation, changes in surface force constants determined at 0°K (QH, 0°K). (c) Quasiharmonic approximation, changes in surface force constants determined at  $\frac{1}{2}$  the melting temperature  $T_M$  (QH,  $\frac{1}{2}T_M$ ). (d) Molecular dynamics computer experiment at  $\frac{1}{2}T_M$ , with all effects including anharmonicity taken into account (MD,  $\frac{1}{2}T_M$ ).

Surface	Component	SFC	QH, 0°K	QH, $\frac{1}{2}T_M$	MD, $\frac{1}{2}T_M$
(100)	$\langle u_x^2 \rangle$	1.46	1.66	2.03	2.23±0.17
	$\langle u_y^2 \rangle$	1.46	1.66	2.03	2.21±0.18
	$\langle u_z^2 \rangle$	1.87	2.17	2.77	3.07±0.15
(111)	$\langle u_x^2 \rangle$	1.30	1.34	1.45	1.27±0.07
	$\langle u_y^2 \rangle$	1.30	1.34	1.45	1.22±0.11
	$\langle u_z^2 \rangle$	1.86	2.09	2.85	3.48±0.18
(110)	$\langle u_x^2 \rangle$	1.50	1.60	1.78	1.89±0.20
	$\langle u_y^2 \rangle$	2.14	2.49	3.21	4.99±0.65
	$\langle u_z^2 \rangle$	1.83	2.20	3.03	3.57±0.25

perature  $(k_B/h)(M\sigma^2/\epsilon)^{1/2}\Theta_D$  to be equal to 26 at this density.<sup>28</sup>

The main features of the temperature dependence of  $\langle u_\alpha^2 \rangle_{\text{surface}} / \langle u_\alpha^2 \rangle_{\text{bulk}}$  are a rapid increase up to about half the Debye temperature and then a leveling off to a constant asymptotic value. This behavior can be explained as follows: At 0°K, the summand in Eq. (2) is proportional to  $|\xi_\alpha(q,p)|_{\text{surface}}^2/\omega$ , and in the high-temperature limit is it proportional to  $|\xi_\alpha(q,p)|_{\text{surface}}^2/\omega^2$ . Therefore, as the temperature increases the lower frequencies are weighted more heavily. There are surface modes of vibration present, and these modes have low frequencies<sup>15</sup>; consequently, the large values of  $|\xi_\alpha(q,p)|_{\text{surface}}^2$  associated with the surface modes are weighted more heavily at high temperatures, and so  $\langle u_\alpha^2 \rangle_{\text{surface}} / \langle u_\alpha^2 \rangle_{\text{bulk}}$  increases with temperature.

The results presented up to this point were obtained with the use of two assumptions: The first is the validity of the quasiharmonic approximation, which takes into account changes in density, but not truly anharmonic effects. The second is the assumption that thermal expansion is uniform throughout the crystal. In fact, however, it was found in Refs. 12 and 13 that both anharmonicity and differential thermal expansion at the surface are of importance at sufficiently high temperatures.

In Table III, we give results in the high-temperature limit ( $T \gg \Theta_D$ ) for the ratio of surface to bulk mean-square amplitudes calculated with four different methods. The first column was obtained with a simple force-constant model. (By a "simple force-constant model" we mean a model in which the force constants

<sup>28</sup> For Ar, Kr, and Xe, the experimental values of the dimensionless Debye temperature at 0°K are respectively 26.3, 26.7, and 27.4. The values of  $\sigma/a$  are 1.284, 1.289, and 1.292. (These values were obtained from the values for  $\sigma$ ,  $\epsilon$ , and  $\Theta_D$  given in Ref. 26.) It is therefore reasonable to take the dimensionless Debye temperature to be equal to 26.0 for  $\sigma/a=1.28$ .

at the surface are equal to those in the bulk.) This model differs from that of Clark, Herman, and Wallis<sup>20</sup> only in that an all-neighbor interaction was used. The second column of results was obtained with the changes in the force constants at the surface determined at 0°K.<sup>29</sup> At higher temperatures it is assumed that the surface region expands in proportion to the interior of the crystal; i.e., thermal expansion is taken into account, but differential thermal expansion at the surface is not. The third column was obtained with the changes in the surface force constants determined at one-half the melting temperature,<sup>30</sup> with the differential thermal expansion taken into account. (The values for the thermal expansion at the surface were taken from Ref. 13, but it has been found that the values obtained with lattice dynamics<sup>12</sup> and molecular dynamics<sup>13</sup> agree very closely.) Finally, the results of the fourth column were obtained in molecular dynamics computer experiments at one-half the melting temperature. Such computer experiments take all effects, including anharmonicity, fully into account. The molecular dynamics values for the surface mean-square amplitudes were taken from Ref. 13, where the method of calculation was described. The error estimates represent the limits of 50% confidence. These estimates were obtained by dividing the total number of time steps in each molecular dynamics calculation into three subgroups, and then using the equation<sup>31</sup>

$$\text{estimated error} = \frac{t_{0.50}}{[n(n-1)]^{1/2}} \times \left[ \sum_{i=1}^n (\langle u^2 \rangle_i - \langle u^2 \rangle)^2 \right]^{1/2}, \quad (4)$$

where  $\langle u^2 \rangle_i$  is the average over the  $i$ th subgroup,  $n=3$ , and  $t_{0.05}=0.816$ .

For consistency, all the results for  $\langle u_\alpha^2 \rangle_{\text{surface}}$  in Table III were calculated using identical model crystals (i.e., identical for a given surface); these crystals were eleven layers thick and contained about 50 atoms in each surface.<sup>13</sup> It should be mentioned that the values of  $\langle u_\alpha^2 \rangle$  obtained with models this smaller differ by several percent from the values obtained with much larger crystals, as can be seen from a comparison of the

<sup>29</sup> We assume that the effect of the zero-point vibrations is negligible in this context. In Ref. 12, it was found that this is a good approximation even for Ar.

<sup>30</sup> According to the values of  $\epsilon$  given in Ref. 26,  $k_B T_M/\epsilon=0.701$ , 0.704, and 0.698 for Ar, Kr, and Xe, respectively, so we can take 0.70 to be the dimensionless melting temperature for an LJ potential. There is no contradiction in using the high-temperature-limit approximation at  $T=\frac{1}{2}T_M$ , since this approximation is valid for  $T > \frac{1}{2}\Theta_D$  (see Fig. 1) and  $T_M \gg \Theta_D$  for most metals. Wallis *et al.* (Ref. 22) have also found the high-temperature-limit approximation to be valid down to  $\frac{1}{2}\Theta_D$ .

<sup>31</sup> See, e.g., P. G. Hoel, *Introduction to Mathematical Statistics* (John Wiley & Sons, Inc., New York, 1954), p. 226. If this equation is to provide the actual probable error (for large  $n$ ), it is necessary that the  $\langle u^2 \rangle_i$  be normally distributed.

results in column two of Table III with the corresponding results for a 21-layer model in Table II.

The results of Table III were obtained with a  $\sigma/a$  ratio of 1.28, which is approximately correct for a classical crystal at half the melting temperature and zero pressure. The value used for  $\langle u_{\alpha}^2 \rangle_{\text{bulk}}$  in the case of the quasiharmonic calculations (columns 1-3) was given by  $(\epsilon/k_B\sigma^2)\langle u_{\alpha}^2 \rangle_{\text{bulk}}/T=0.00602$ . This value was determined by performing an independent calculation for the bulk in the quasiharmonic approximation. The value for  $\langle u_{\alpha}^2 \rangle_{\text{bulk}}$  in the case of the molecular-dynamics calculations (column 4) was obtained from an independent molecular-dynamics calculation for the bulk; a system of 864 particles with periodic boundary conditions in all three directions was used. This calculation yielded the result  $(\epsilon/k_B\sigma^2)\langle u_{\alpha}^2 \rangle_{\text{bulk}}/T=0.00619 \pm 0.00009$ . According to these results, therefore, anharmonicity causes the bulk mean-square amplitudes to be increased by several percent at one-half the melting temperature.<sup>32</sup> Increases of the same order of magnitude were calculated by Maradudin and Flinn<sup>33</sup> for Pb at room temperature and by Wolfe and Goodman<sup>34</sup> for Cu at 300 and 400°K.

The results of Table III can be summarized as follows: There are three factors which cause  $\langle u_{\alpha}^2 \rangle_{\text{surface}}/\langle u_{\alpha}^2 \rangle_{\text{bulk}}$  to be different from the value calculated with a simple force-constant model. The first is a temperature-independent decrease in the force constants at the surface due to static effects (i.e., due to relaxation of the surface atoms at 0°K). The second is a further temperature-dependent decrease in the surface force constants which is due to dynamical effects (differential thermal expansion at the surface). The third factor is anharmonicity, which produces increases in the mean-square amplitudes which are larger at the surface than in the bulk. All three factors lead to increases in the ratio  $\langle u_{\alpha}^2 \rangle_{\text{surface}}/\langle u_{\alpha}^2 \rangle_{\text{bulk}}$ .<sup>35</sup>

<sup>32</sup> V. V. Goldman [Phys. Rev. **174**, 1041 (1968)] obtained a decrease of several percent, but his approximations are open to question.

<sup>33</sup> A. A. Maradudin and P. A. Flinn, Phys. Rev. **129**, 2529 (1963).

<sup>34</sup> G. A. Wolfe and B. Goodman, Phys. Rev. **178**, 1171 (1969).

<sup>35</sup> There is one exception: In the case of  $\langle u_z^2 \rangle$  for the (111) surface, anharmonicity appears to cause a decrease.

Morabito, Steiger, and Somojai<sup>7</sup> have pointed out that experimental values for the ratio  $\langle u_z^2 \rangle_{\text{surface}}/\langle u_{\alpha}^2 \rangle_{\text{bulk}}$  are larger than the values calculated with simple force-constant models. They suggested that the discrepancy might be due to a decrease in the force constants at the surface. This hypothesis is quite reasonable, since a number of calculations with model potentials<sup>36</sup> have indicated that the surface atoms relax outward in static monatomic crystals, and Vail<sup>37</sup> found decreases in the surface force constants using a Morse potential. Furthermore, Wallis *et al.*<sup>21</sup> found that if the force constants coupling atoms in the surface plane to those in the planes below are weakened phenomenologically, then the calculated values for the surface mean-square amplitudes show better agreement with the experimental values for Ni.

The present results provide further evidence for the hypothesis of weakened force constants at the surface, but also suggest that two other factors are involved in the anomalously large experimental values of  $\langle u_z^2 \rangle_{\text{surface}}/\langle u_{\alpha}^2 \rangle_{\text{bulk}}$ —namely, anharmonicity and differential thermal expansion at the surface.

The temperature dependence of the surface mean-square amplitudes has been calculated and discussed previously.<sup>38</sup> It was found that  $\langle u_{\alpha}^2 \rangle_{\text{surface}}$  is not a linear function of temperature at low temperatures, because of the zero-point vibrations, and that there should be some departure from linearity at high temperatures also, because of thermal expansion and anharmonicity. According to the present results,  $\langle u_{\alpha}^2 \rangle_{\text{surface}}/\langle u_{\alpha}^2 \rangle_{\text{bulk}}$  should increase sharply with temperature for  $T < \frac{1}{2}\Theta_D$ , because of the presence of surface modes, and should show some increase with temperature even at high  $T$ , because of anharmonicity and differential thermal expansion. It would be interesting if the temperature dependence of  $\langle u_{\alpha}^2 \rangle_{\text{surface}}/T$  and  $\langle u_{\alpha}^2 \rangle_{\text{surface}}/\langle u_{\alpha}^2 \rangle_{\text{bulk}}$  were observed experimentally.

<sup>36</sup> See, e.g., G. C. Benson and T. A. Claxton, J. Phys. Chem. Solids **25**, 367 (1964); J. J. Burton and G. Jura, J. Phys. Chem. **71**, 1937 (1967).

<sup>37</sup> J. Vail, Can. J. Phys. **45**, 2661 (1967).

<sup>38</sup> In Figs. 8 and 9 of Ref. 12,  $\langle u_{\alpha}^2 \rangle_{\text{surface}}$  was graphed up to about half the Debye temperature as a function of the dimensionless temperature  $(k_B/\hbar)(M\sigma^2/\epsilon)^{1/2}T$ . The temperature variable in these graphs can easily be converted to  $T/\Theta_D$  by using the relation  $(k_B/\hbar)(M\sigma^2/\epsilon)^{1/2}\Theta_D=26.0$ .