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Calculation of Dynamical Surface Properties of Noble-Gas Crystals. II. Molecular Dynamics*

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Various surface properties have been calculated for the (100), (111), and (110) surfaces of noble-gas crystals through the method of molecular dynamics. This method takes complete account of anharmonic effects and mean displacements, both of which are found to be important for surface calculations at high temperatures. The results are compared with those obtained through lattice dynamics in the quasiharmonic approximation. The results for the displacements of the mean atomic positions (from the positions in the bulk) are in good agreement with these found through lattice dynamics. The results for the mean-square amplitudes are in good agreement for atoms a few layers beneath the surface, but indicate that anharmonicity causes a substantial increase in these quantities near the surface at about half the melting temperature (the temperature for which most of the calculations were performed). The Fourier transform of the velocity autocorrelation function is compared with the density-of-states function determined in the quasiharmonic approximation, and the presence of anharmonic effects is again indicated. The static displacements, determined by damping the motion of the atoms, are found to be the same for all atoms in a given plane, thus justifying the usual assumption made in calculating these quantities.

I. INTRODUCTION

THERE has, until the present, been no calculation of the mean-square amplitudes of vibration of atoms near a crystal surface in which anharmonicity is taken into consideration. Since the mean-square amplitudes are much larger at the surface than in the bulk of the crystal,[1] anharmonic effects should be more important at the surface. In this paper we present results obtained with a method which takes anharmonic effects into account completely. These results are compared with those of lattice-dynamics calculations for the same model crystals.

In Sec. II the method of calculation is described, and in Sec. III the results are presented and discussed.

II. METHOD OF CALCULATION

Molecular-dynamics calculations[2] consist in solving Newton's equations of motion for a system of interacting particles. The three systems considered in this paper are slab-shaped, fcc crystals, their two free surfaces being, respectively, (100), (111), or (110) planes of the crystal. In each case the slab consists of 11 layers of particles parallel to the surface. We shall denote by x and y, two suitably chosen orthogonal directions in a plane parallel to the surface, and by z the direction perpendicular to the surface.

The arrangement of lattice points in an fcc crystal is such that the surface planes under consideration have the structures shown in Fig. 1. Since the slab consisted of 11 such layers in each case, the total number N_s of particles in the system differed slightly for the three cases; the values of N_s were 550, 539, and 528 for the (100), (111), and (110) surfaces, respectively. The usual periodic boundary conditions were imposed with respect to translations parallel to the free surface, so that one can visualize the slab as being surrounded by replicas of itself extending to infinity (see Fig. 1).

All calculations were performed for a Lennard-Jones (6, 12) potential of interaction between pairs of particles $\phi(r)$ given by

$$\phi(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^{6}], \tag{2.1}$$

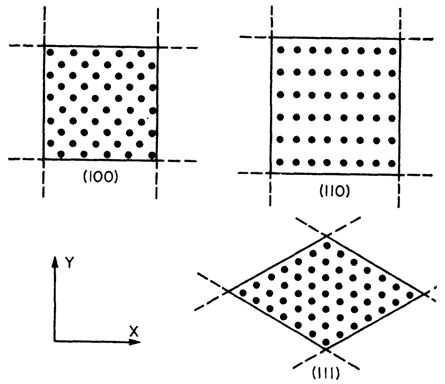

FIG. 1. Structure of (100), (111), and (110) surfaces in an fcc crystal. Each dot represents an atom. The solid lines indicate the boundaries in the xy plane of the slab-shaped models used in the molecular dynamics calculations.

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[1] R. E. Allen and F. W. de Wette, preceding paper, Phys. Rev. **179**, 873 (1969). We refer to this paper as I.

[2] A. Rahman, Phys. Rev. **136**, A405 (1964).

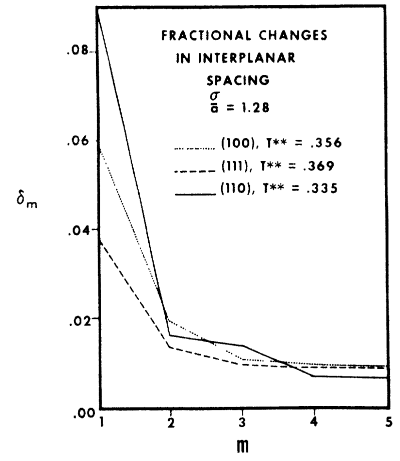

FIG. 2. Dynamic displacements δ_m for (100), (111), and (110) surfaces of noble-gas crystals at about half the melting temperature, expressed as fractional changes in the interplanar spacings.

where ϵ and σ are potential constants, and r is the distance between the particles. We define M to be the atomic mass, t to be the time, and $\mathbf{r}^l$ to be the position vector of the particle labeled by l. We also define the dimensionless quantities $\mathbf{s}^l$ and τ by

$$\mathbf{r}^l=\sigma\mathbf{s}^l \tag{2.2}$$

and

$$t=(M\sigma^2/\epsilon)^{1/2}\tau; \tag{2.3}$$

i.e., we adopt σ as the unit of length and $(M\sigma^2/\epsilon)^{1/2}$ as the unit of time. Then we can use Eq. (2.1) to write Newton's equations of motion for the particle l as

$$\frac{d^2\mathbf{s}^l}{d\tau^2}=24\sum_{l'\neq l}\left(\frac{1}{s^{ll'}}\right)^8\left[2\left(\frac{1}{s^{ll'}}\right)^6-1\right]\mathbf{s}^{ll'}, \tag{2.4}$$

where

$$\mathbf{s}^{ll'}=\mathbf{s}^l-\mathbf{s}^{l'},\quad s^{ll'}=|\mathbf{s}^{ll'}|.$$

The potential $\phi(r)$ was truncated at $r=3.25\ a$, where $\sqrt{2}a$ is the nearest-neighbor distance; for this range of interaction each particle interacts with about 70 neighbors around it. A surface particle, of course, interacts with only a little more than half this number. The total force in the z direction due to the particles outside the sphere of interaction is not negligible, because of the asymmetry in the z direction resulting from the free surface. However, this force can be approximated by a constant "background force," perpendicular to the surface, calculated in advance by taking all the atoms in the slab to be at their static equilibrium positions. Test calculations show that neglecting the background force can lead to an increase of up to 20% in the displacements of the mean positions and the mean-square amplitudes at the surface.

The $3N_s$ coupled equations of motion given by Eq. (2.4) were solved numerically,[3] so as to give the positions and velocities of the N_s particles in the x, y, and z directions as functions of time. The solutions were obtained for $\tau=n\Delta\tau$, where n is an integer, and in the present calculations, $\Delta\tau=0.01$ (corresponding to $\Delta t \sim 10^{-14}$ sec).

There is a wide variety of ways in which initial conditions (positions and velocities of the N_s particles) can be chosen to start off the calculation. We have used the following procedure: The static displacements, calculated as described in I, are used to place the N_s particles in positions which, if not disturbed, would be positions of static equilibrium. At $t=0$ the particles are given small random displacements from these positions and from then on are allowed to move according to the equations of motion (2.4). The potential energy put into the system by the random displacements is gradually released as the particles move, and eventually thermal equilibrium is achieved. The temperature finally attained (we shall define temperature below) depends on the potential energy given to the system at $t=0$.

It must be emphasized, however, that although the time required to reach thermal equilibrium depends on the initial conditions, the final state of equilibrium does not. Since we are interested in the properties of the system while in thermal equilibrium, the details of the starting procedure will not be of further concern. We only mention that, for the above starting conditions, about 100 steps of $\Delta\tau=0.01$ each were sufficient to establish thermal equilibrium.

In a classical system in equilibrium, temperature (in degrees absolute) is a measure of the mean-square velocity or, equivalently, of the mean kinetic energy of the particles. If $\mathbf{v}^l$ denotes the velocity of the particle labeled by l, we have

$$\tfrac{3}{2}k_BT=\frac{1}{N_s}\sum_l \tfrac{1}{2}M(\mathbf{v}^l)^2, \tag{2.5}$$

where k_B is the Boltzmann constant. Using ϵ, the depth of the potential, we have expressed T in terms of a dimensionless quantity

$$T^{**}=(k_B/\epsilon)T, \tag{2.6}$$

so that, in terms of $\mathbf{s}^l$ and τ, we have

$$T^{**}=\frac{1}{3N_s}\sum_l\left(\frac{d\mathbf{s}^l}{d\tau}\right)^2. \tag{2.7}$$

(The unit of temperature ϵ/k_B is 119, 159, and 228°K,[4] respectively, for Ar, Kr, and Xe. The melting points are given by $T=84$, 116, and 161°K, or $T^{**}=0.71$, 0.73, and 0.71, respectively.)

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[3] The details of the algorithm used to solve Eqs. (2.4) will not be described here; we refer the reader to C. W. Gear, Argonne National Laboratory Report No. ANL-7126, 1966 (unpublished). We shall only mention that the solution was accurate enough to keep the total energy of the system constant except for fluctuations of the order of 0.1% of the mean value.

[4] G. L. Pollack, Rev. Mod. Phys. 36, 748 (1964).

Since the purpose of these calculations is to investigate the dynamical behavior of the atoms in the system as a function of the distance from the free surface, we have made all the analyses separately for each layer. However, because there are two equivalent layers in every case (except for the central layer, there being 11 layers in all), we have used the positions and velocities of particles in both of these layers in obtaining the results to be presented below. These results, therefore, represent averages over 96–100 particles, the exact number depending upon the type of surface (see Fig. 1), and over an ensemble of 1500 configurations of the system (each configuration corresponding to a different value of the time).

III. RESULTS AND DISCUSSION

The surface quantities in which we are primarily interested are the displacements of the mean positions of the atoms from the positions they would occupy in the bulk of the crystal, and the mean-square amplitudes of vibration about the displaced positions. Both these quantities can be measured by means of low-energy electron-diffraction (LEED) experiments.[5] We express the displacements in terms of δ_m, the fractional change in the distance between the mth and $(m+1)$th planes. The displacements in a static crystal and in a vibrating crystal we call, respectively, the *static displacements* and the *dynamic displacements*.[6]

Results for the dynamic displacements are shown in Fig. 2.[7] It can be seen that the dynamic displacements at the temperature for which these calculations were carried out ($T^{**}\approx 0.35$, or about half the melting temperature) behave qualitatively in the same way as the static displacements given in I. In particular, the displacements for the (110) surface exhibit the "staircase" behavior pointed out and explained in I. However, the dynamic displacements are roughly twice as large at the surface as the static displacements, and the graph for $T^{**}=0.547$ in Fig. 3 shows that they are still larger at this higher temperature. Figure 3 also shows that there is very good agreement with the displacements (at $\sigma/a=1.28$ and $T^{**}=0.356$) found by minimizing the total free energy in the quasiharmonic approximation.[1]

The fact that the dynamic displacements are larger than the static displacements can be explained as follows: An atom at the surface encounters its neighbors in the next plane upon moving toward the center of the crystal and encounters no other atoms upon moving away. On the average, therefore, an atom will be farther from the center of the crystal when vibrating than when stationary.

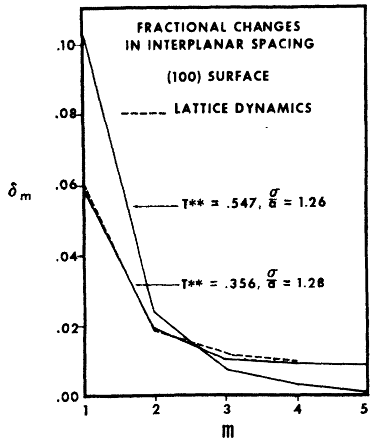

FIG. 3. Dynamic displacements δ_m for (100) surface at about half the melting temperature ($T^{**}=0.356$), as determined with molecular dynamics (solid line) and lattice dynamics (dashed line), and dynamic displacements from molecular dynamics at a higher temperature ($T^{**}=0.547$).

In calculating the static displacements in I, it was assumed that all the atoms in a given plane are displaced equally in a direction perpendicular to the surface. Schmidt and Jura,[8] after studying several possible surface configurations for static semi-infinite noble-gas crystals, concluded that it is unlikely that atoms in the same plane will undergo different displacements. In order to investigate this matter further, we imposed a damping force on the vibrating atoms until they were almost entirely motionless. It was found that for the (100), (111), and (110) surfaces all the atoms in each plane were indeed displaced equally in the direction perpendicular to the surface. One advantage of molecular dynamics for such studies of surface structure is that each atom in the system is allowed to relax independently.

Now we turn to the mean-square amplitudes. The displacement of an atom from its mean position we call $\mathbf{u}$, so that $\langle u_\alpha^2\rangle$ is the mean-square amplitude of vibration in the α direction, with $\alpha=x, y$, or z. It is interesting to compare the results for the mean-square amplitudes obtained through molecular dynamics with those obtained through the completely independent method of lattice dynamics. We have therefore performed lattice-dynamics calculations for the model crystals described above using the procedure outlined in I: The thickness was taken to be 11 layers, and the q points in the Brillouin zone were chosen so as to correspond to the periodicity length and surface structure of the crystals used for the molecular dynamics calculations (see Fig. 1). The displacements were taken to be those shown in Fig. 2 (i.e., those calculated through molecular dynamics), rather than the static displacements which

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[5] See, e.g., A. U. MacRae, Surface Sci. **2**, 522 (1964); I. Marklund and S. Andersson, *ibid.* **5**, 197 (1966).

[6] See Secs. I and VI and Fig. 1 of I.

[7] In performing a molecular-dynamics calculation, one has to assume the density in advance. Since the assumed density (corresponding to $\sigma/a=1.28$) is not precisely correct for the temperatures reached at thermal equilibrium, the displacements in Fig. 2 approach asymptotic values which are not precisely zero.

[8] H. H. Schmidt and G. Jura, J. Phys. Chem. Solids **16**, 60 (1960).

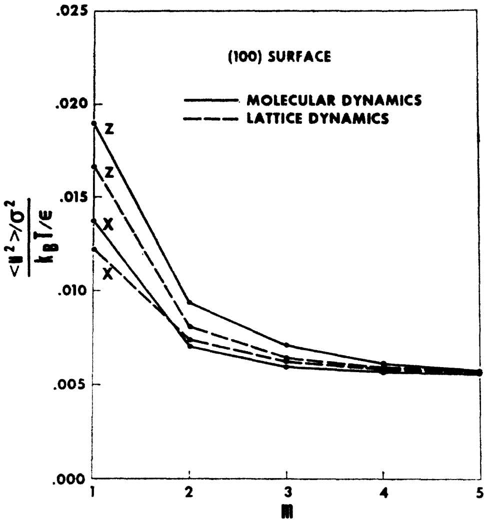

FIG. 4. Mean-square amplitudes $\langle u_x^2 \rangle$ and $\langle u_z^2 \rangle$ for (100) surface at about half the melting temperature ($T^{**}=0.356$ and $\sigma/a=1.28$).

TABLE I. Root-mean-square deviations Δ of the mean-square amplitudes, expressed as percentages of the mean values.

Surface	m	$\langle u_x^2 \rangle$	$\langle u_y^2 \rangle$	$\langle u_z^2 \rangle$
(100)	1	13.3	14.1	8.5
	2	6.8	6.6	9.5
	3	5.7	6.0	7.4
	4	3.2	2.4	4.4
	5	4.9	1.4	2.1
(111)	1	9.9	16.3	9.2
	2	6.5	11.3	5.2
	3	6.6	6.1	3.1
	4	8.0	4.0	4.4
	5	5.6	4.1	5.9
(110)	1	17.9	22.5	12.3
	2	6.6	12.1	6.0
	3	7.8	7.9	7.2
	4	2.0	6.9	8.4
	5	5.7	7.9	10.4

were used in I. The calculations were carried out in the high-temperature limit in order to eliminate the effect of zero-point vibrations.

In Figs. 4–6 the results from both methods are presented. The planes are labeled by m, with $m=1$ for the surface plane, $m=2$ for the next plane, and so on. It can be seen that, in general, the molecular-dynamics and lattice-dynamics results are in good agreement at the center of the crystal, but that there are considerable differences between the results at the surface, particularly in the case of $\langle u_y^2 \rangle$ for the (110) surface.

These differences must be due to anharmonicity,[9] since they are too large to be attributed to statistical fluctuations (see below). Our results indicate, therefore, that at about half the melting temperature anharmonic effects are small in the bulk, but cause substantial increases in the mean-square amplitudes at the surface. At higher temperatures, of course, anharmonic effects will be greater both in the bulk and at the surface.

One matter of importance is the influence of statistical fluctuations upon the final results of the molecular-dynamics calculations. Since these results represent averages over only a finite number of configurations of a system containing relatively few particles (about 50 per plane), they will depart somewhat from the results that would be obtained from averaging over an infinity of configurations. In order to determine the probable error associated with the results presented here, which represent averages over 1500 configurations, one would have to repeat the complete molecular-dynamics calculation a large number of times. Such a procedure is impractical, but one can obtain a rough estimate of the probable error by performing separate averages over several groups of configurations and seeing how well these averages agree. A rough quantitative measure is provided by the rms deviation of these separate averages from the mean which is calculated by taking all the available configurations into account. This rms deviation Δ is, for the mean-square amplitudes, defined by

$$\Delta=\left[\sum_i \left(\langle u^2 \rangle_i-\langle u^2 \rangle\right)^2/N\right]^{1/2}, \tag{3.1}$$

where $\langle u^2 \rangle_i$ is the average over the ith group of configurations, N is the number of such groups, and $\langle u^2 \rangle$

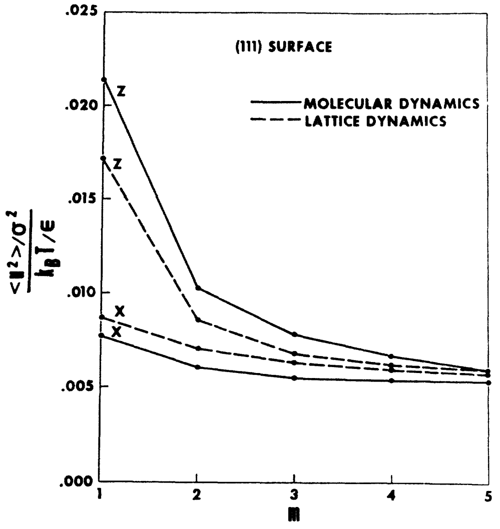

FIG. 5. Mean-square amplitudes $\langle u_x^2 \rangle$ and $\langle u_z^2 \rangle$ for (111) surface at about half the melting temperature ($T^{**}=0.369$ and $\sigma/a=1.28$).

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[9] "Anharmonicity" in this case includes effects due to a linear term in the Taylor-series expansion of the potential energy Φ, as well as the usual cubic, quartic, etc. terms. This linear term vanishes in the strict harmonic approximation, in which the mean positions are taken to be the positions of static equilibrium; it also vanishes because of symmetry in a perfect crystal at any density (provided that every atom is a center of symmetry). However, in the present case (quasiharmonic approximation for a crystal with surfaces), the linear term is in general nonzero and is to be regarded as a perturbation together with the higher-order anharmonic terms. See G. Leibfried and W. Ludwig, Solid State Phys. 12, 275 (1961).

TABLE II. Comparison of $\langle u_x^2\rangle$ and $\langle u_y^2\rangle$ for (100) and (111) surfaces.

	(100)		(111)	
m	$\langle u_x^2\rangle/\sigma^2$	$\langle u_y^2\rangle/\sigma^2$	$\langle u_x^2\rangle/\sigma^2$	$\langle u_y^2\rangle/\sigma^2$
1	0.00492	0.00488	0.00290	0.00279
2	0.00256	0.00249	0.00223	0.00225
3	0.00212	0.00204	0.00197	0.00206
4	0.00202	0.00201	0.00204	0.00197
5	0.00194	0.00202	0.00203	0.00196

is the average calculated over all the configurations. In the present calculations, the 1500 configurations were divided into three groups of 500 each for the purpose of calculating Δ. The results are given in Table I, expressed as percentages of the mean values. It can be seen that the fluctuations are largest at the surface, where Δ ranges from 8.5 to 22.5%. The probable error associated with the results presented here is expected to be smaller than Δ, of course, since these results were obtained by averaging over 1500 rather than 500 steps.

Another test of the importance of fluctuations is provided by comparison of $\langle u_x^2\rangle$ and $\langle u_y^2\rangle$, which should in principle be equal for the (100) and (111) surfaces. Such a comparison is given in Table II, and it can be seen that in all cases there is agreement to within 5%.

Another interesting comparison between lattice dynamics and molecular dynamics involves the Fourier transform of the velocity autocorrelation function, which we call $f(\omega)$. In the quasiharmonic approximation this quantity is proportional to the density-of-states function. $f(\omega)$ is defined as

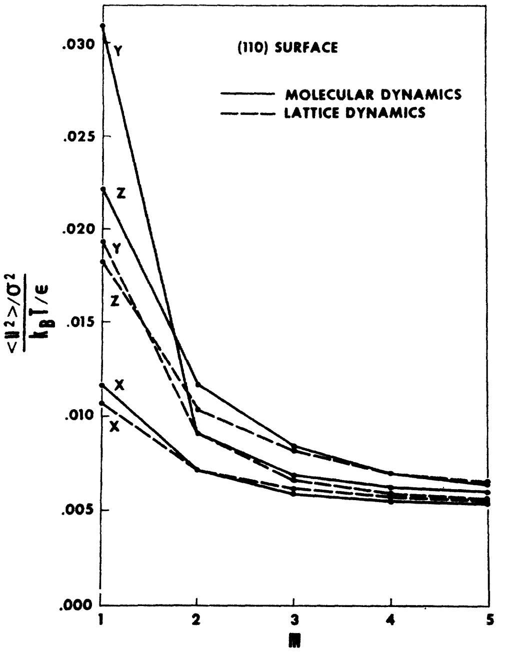

FIG. 6. Mean-square amplitudes $\langle u_x^2\rangle$, $\langle u_y^2\rangle$, and $\langle u_z^2\rangle$ for (110) surface at about half the melting temperature ($T^{**}=0.335$ and $\sigma/a=1.28$).

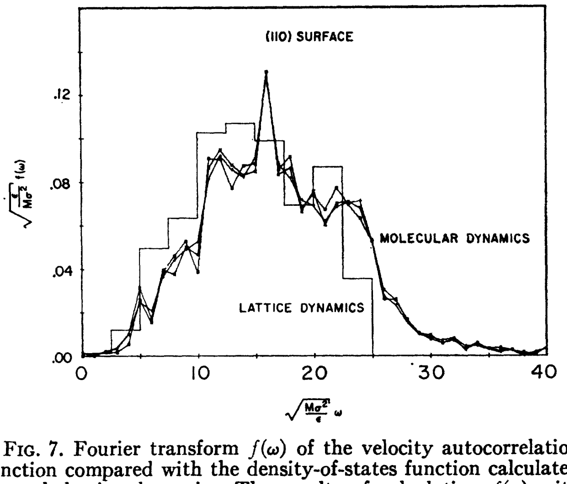

FIG. 7. Fourier transform $f(\omega)$ of the velocity autocorrelation function compared with the density-of-states function calculated through lattice dynamics. The results of calculating $f(\omega)$ with three values of the cutoff time t_c, given by $(\epsilon/M\sigma^2)^{1/2}t_c=7$, 10, and 13, are superimposed in the figure.

$$f(\omega)=\int_0^\infty \frac{\langle \mathbf{v}(t+t_0)\cdot\mathbf{v}(t_0)\rangle_s}{\langle \mathbf{v}(t_0)\cdot\mathbf{v}(t_0)\rangle_s}\cos\omega t\,dt\,, \qquad (3.2)$$

where $\mathbf{v}(t)$ is the velocity of an atom at time t and the subscript s indicates that the average is taken over the whole system, rather than over a single plane. In Fig. 7, $f(\omega)$ is compared with the density-of-states function from a lattice-dynamics calculation for the same model crystal. (The density-of-states function is normalized to an area of $\frac{1}{2}\pi$.) In a practical molecular-dynamics calculation one is, of course, limited to a finite range of the time t in Eq. (3.2), and it is necessary to truncate the integration at some point. In order to determine the effect of disregarding the part of the integral for $t>t_c$, where t_c is some finite cutoff time, we carried out the calculation for three values of t_c. The results are superimposed in Fig. 7. In each case, 20 initial times t_0 were used in calculating the velocity autocorrelation function $\langle \mathbf{v}(t+t_0)\cdot\mathbf{v}(t_0)\rangle_s$. The shift of $f(\omega)$ toward higher frequencies as compared with the quasiharmonic density-of-states function is attributed to anharmonicity.

In attributing differences between the lattice-dynamics and molecular-dynamics results to anharmonicity, we have tacitly assumed that there is no reconstruction of the surface—i.e., that the mean positions of atoms in the surface plane are displaced from the bulk positions by the same amount. This assumption was tested in the case of the (110) surface, for which the differences between the lattice-dynamics and molecular-dynamics results are greatest. It was found that in the present calculations reconstruction of the surface did not occur.

In summary, two significant results have been obtained: First, the dynamic displacements (fractional changes in interplanar spacings calculated with vibrational effects taken into account) increase rapidly with temperature; equivalently, one can say that thermal expansion is greater near the surface than in the bulk. Second, anharmonicity already causes a substantial increase in the surface mean-square amplitudes at about half the melting temperature.

Since both of these effects should be observable by means of LEED, it would be interesting if LEED experiments (on metals or other monatomic materials) could be carried out over a wide range of temperatures to determine the importance of anharmonicity and the dependence of the mean atomic displacements upon temperature.

The method of molecular dynamics used here has two important advantages for surface calculations at temperatures above the Debye temperature, in that both anharmonic effects and mean displacements are taken into account completely. Below the Debye temperature zero-point vibrations become important, and the classical approximation consequently breaks down. But the method described in I is most applicable at low temperatures, since this method involves the quasiharmonic approximation and the approximation of using the static, rather than dynamic, displacements. In this sense, therefore, molecular dynamics and lattice dynamics are complementary methods of investigation. Both methods have considerable potential for theoretical studies of the structure and dynamics of crystal surfaces.

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Dielectric Function of a Model Insulator[†]

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A wave-number– and frequency-dependent dielectric function has been calculated for a model insulator using the random-phase approximation. The model insulator consists of a free-electron conduction band represented by a single orthogonalized plane wave (OPW) and a valence band represented by linear combinations of ionic wave functions. All energy bands are assumed parabolic and isotropic. Numerical results are obtained for Ar, KCl, CsCl, MnS, and Si, in reasonable agreement with previous calculations. Screened exchange potentials have been obtained by using an interpolation formula, and evaluated for the chlorine ion in CsCl.

I. INTRODUCTION

THE dielectric formulation[1,2] of the many-body problem has been found especially attractive in solid-state physics, since it uses mathematical and physical concepts known to most solid-state physicists, and interprets solid-state systems in terms of familiar quantities which are accessible through experiment. Aside from its use in various schemes for calculating correlation contributions to ground-state energies,[3] the dielectric formulation has been used to understand energy loss by fast electrons in solids,[4] plasma energies,[5] and optical properties[6–8] of solids. In addition, the dielectric formalism has been used extensively to study properties of the electron gas,[1] and quasiparticle[9] and collective[10] excitations of an electron gas containing a single point-charge impurity. Recent calculations have considered more carefully effects of the Pauli exclusion principle.[11,12] The formalism has also been used in band theory to develop a theory of self-consistent screened pseudopotentials for semiconductors[13] and more recently to develop a theory of the covalent bond in crystals.[14]

Application of the theory centers around calculation of the dielectric constant tensor $\epsilon(\mathbf{q},\omega)$ as a function of frequency and wave vector for the many-body system under consideration. Longitudinal or transverse components of $\epsilon(\mathbf{q},\omega)$ have been calculated in various approx-

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