PHYSICAL REVIEW B VOLUME 1, NUMBER 2 15 JANUARY 1970

Size and Surface Effects on the Phonon Properties of Small Particles*

J. M. DICKEY
Brookhaven National Laboratory, Upton, New York 11973

AND

ARTHUR PASKIN
Queens College of The City University of New York, Flushing, New York
and
Brookhaven National Laboratory, Upton, New York 11973

(Received 28 August 1969)

Measurements on thin films and surfaces have generated a need for a technique whereby one can calculate the phonon properties of small particles containing only a few hundred atoms. We have used molecular-dynamic techniques to calculate the frequency distribution and various moments for five different particle configurations. Results are compared with the bulk solid. A model extending the Lennard-Jones and Devonshire cell model to surface environments is described. It is shown that this model replicates features of the more exact calculation. The frequency spectrum and various correlation functions are decomposed into contributions from the bulk, surface, and edge of a particle. The differences can be explained in terms of the local environment.

INTRODUCTION

IN recent years, studies of the superconductivity of thin films[1] and low-energy electron-diffraction (LEED) measurements of surfaces,[2] have focused attention on various dynamic properties not amenable to the usual techniques, based on the periodicity of infinite systems. Surfaces alter the boundary conditions, and also allow relaxation of the atoms nearby, thus destroying the lattice periodicity. For a macroscopic system the surface-to-volume ratio is small, and so bulk measurements are well approximated by neglecting the surface. For very small particles of the order of 50 Å wide, thin films up to about five atomic layers thick, and measurements such as LEED which can sample the topmost atomic layers, it is not possible to neglect the influence of the surface on the dynamic properties. Molecular-dynamic techniques allow one to simulate atomic motion in these very small particles and in atomic layered films. Both surface relaxation and the boundary condition can be treated exactly for a classical system. Further, molecular-dynamic calculations provide an accurate treatment of the anharmonic contributions, which are important for the soft surface modes and at high temperatures. Preliminary calculations[3] were reported for the frequency distribution of an infinite crystal and a platelike particle, three atom layers thick. These calculations are here extended to cover a spherical "blob," a five-layer platelike particle, and a three-layer particle bounded by rigid substrates, as well as details for the three-layer system. It is shown that by appropriate mixtures of bulk, surface, and edge frequency distributions one can approximate particular geometries of particles. Using a Lennard-Jones–Devonshire cell approximation it is demonstrated that the surface modes scale as the local neighbor configuration. The cell model can be used to generate the moments for the surface modes in different geometries.

PROCEDURE

The molecular-dynamic technique used here has been described in detail in Dickey and Paskin,[4] hereafter referred to as I. Briefly, the atoms are arranged in a suitable configuration and their motion is followed by solving Newton's equations in a difference form. As we are interested in changes in properties arising from different geometric shapes of particles, the form of the potential is not important and we have used the familiar Lennard-Jones potential

$$V(r)=\epsilon[(\sigma/r)^{12}-2(\sigma/r)^{6}]. \qquad (1)$$

Results in this paper are quoted in the natural units for a Lennard-Jones potential (ϵ, σ, and mass m all equal to 1), and, by appropriate choice of these parameters, can be scaled to describe any simple solid. The main difference in this calculation from usual molecular-dynamic calculations, is that periodic boundary conditions are, of course, not used, as we are explicitly interested in surface effects. Not including the usual periodic boundary conditions made the simulation more realistic, but introduced additional constraints on the motion. In previous calculations the motion was constrained to have a net translational velocity of zero; the particle has the additional requirement that its angular momentum be zero. This affects the procedure for introducing energy into the particle, our "randomiza-

---

* Work performed under the auspices of the U. S. Atomic Energy Commission.

[1] M. Strongin, O. F. Kammerer, J. E. Crow, R. D. Parks, D. H. Douglass, Jr., and M. A. Jensen, Phys. Rev. Letters **21**, 1320 (1968).

[2] A. U. McRae and L. H. Germer, Phys. Rev. Letters **8**, 489 (1962).

[3] J. M. Dickey and A. Paskin, Phys. Rev. Letters **21**, 1441 (1968).

[4] J. M. Dickey and A. Paskin, Bull. Am. Phys. Soc. **13**, 398 (1968); Phys. Rev. (to be published).

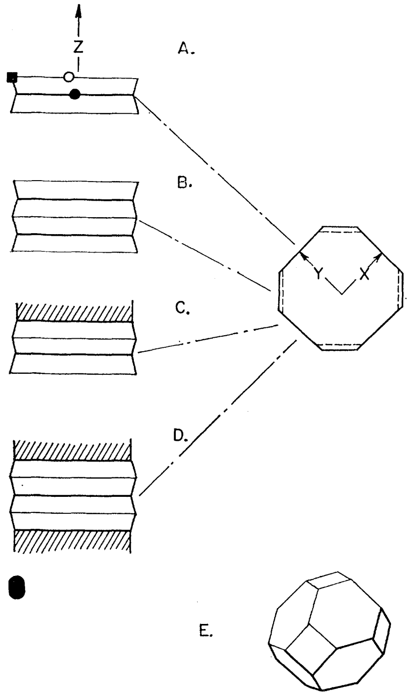

FIG. 1. Schematic representation of the various geometries: A is three-layered plate, B is five-layered plate, C is three-layered plate with one substrate, D is three-layered plate with two substrates, and E is the almost spherical blob. The layers in the platelike particle are not drawn to scale in the z direction. The shaded regions indicate the rigid substrate. In A an "edge" atom is indicated by ■, a "surface" atom by ○, and a "bulk" atom by ●. Within the particles the atoms are arranged on a fcc lattice.

tion procedure." The atoms are given small random displacements and the system allowed to evolve. The random displacements inject potential energy into the system, thus the linear and angular momentum of the particle are identically zero. It might be noted that randomizing the velocities gives the particle a net small angular momentum causing it to rotate. To randomize the phases of the modes, the velocities of the atoms were scaled after an arbitrary interval, and this process was repeated many times. This elaborate procedure of randomization is necessary to optimize equipartition of energy among the modes. At ordinary temperatures the anharmonicity redistributes energy among all modes rapidly. However, these calculations were performed at low temperatures where the potentials behave quite harmonically and there is little redistribution of energy. Our randomization procedure is designed to allow us to distribute the energy uniformly even in the low-temperature harmonic regime. We chose to keep the system at low temperatures to ensure the stability of these small particles. It is known empirically that these small particles must be kept at very low temperatures and probably change their shape (ball up) at higher temperatures.[5] We further calculate the same properties for several different independent initializations, this minimizes the effects of statistical deviations from randomness incurred in using a few hundred random numbers at a time. After following this randomization procedure the system was allowed to come into equilibrium, which, for particles with free surfaces, involved relaxing to a larger interatomic spacing than that in the infinite solid.

The particle geometries are shown in Fig. 1. The boundary conditions were of two types: the free surface and a rigid substrate. Combinations of these can be made to simulate most thin film depositions. The geometric effect comes from the different mixtures of surface and volume, as well as the number of neighbors at some geometric region. For example, in the small particle geometries, surface atoms are of two kinds: Some atoms are surrounded in a plane by other surface atoms but other atoms are at the edge of the particle. It is apparent that the forces are weaker on the edge atoms. As it is the local environment that determines the average forces, the surfaces on different crystallographic faces will have somewhat different neighbor configurations. Further, surfaces of real crystals are not flat to atomic dimensions and one would expect that the surfaces both of crystals and deposited films would exhibit surface roughness, so that some of the atoms on surfaces and just below would have less neighbors than an ideal flat surface. The existence of hillocks and hollows probably has so great an effect on surface vibrational properties that for a large surface, treatment of an ideally flat surface does not constitute a good approximation. It might be more useful to think of even a large semi-infinite surface as a patchwork of small particles.

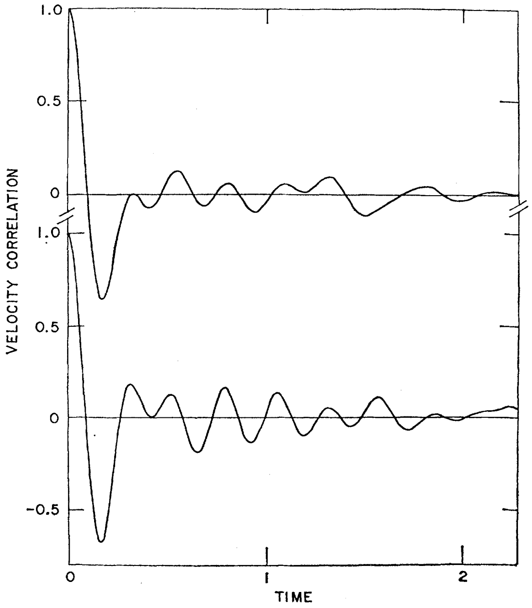

FIG. 2. Velocity correlation of a small particle, the blob (upper curve), compared with that of the bulk solid (lower curve).

---

[5] M. Strongin (private communication).

In these calculations we emphasize not the quantitative details, but try to relate the relative frequency shifts from the bulk values to the local environment of an atom. Thus one can construct the frequency spectrum of a film or a surface by making statistical assumptions about the likely size and orientation of the particles, combined with the frequency shifts associated with different atomic environments. Most materials do not have a Lennard-Jones potential, but empirical frequency spectra are becoming available. Following this scheme one should be able to use bulk spectra to construct surface spectra and calculate surface phonon properties.

RESULTS

There are a number of phonon-determined properties that can be obtained from molecular-dynamic calculations. The distribution of normal modes is probably the most useful. Following the procedure described in detail in I the velocity correlation function $\gamma(t)$,

$$\gamma(t)=\sum_i \langle \mathbf{v}_i(t)\cdot\mathbf{v}_i(0)\rangle/\sum_i \langle \mathbf{v}_i(0)^2\rangle, \qquad (2)$$

is Fourier transformed to give the distribution of normal modes $f(\omega)$,

$$f(\omega)=\int_0^\infty dt\,\gamma(t)\cos\omega t. \qquad (3)$$

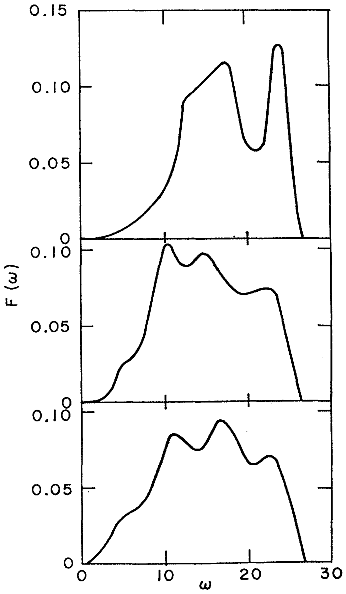

FIG. 3. Frequency spectrum of the bulk solid, the blob, and the five-layer particle, from top to bottom. The relative importance of the bulk modes decreases in this sequence as the surface-to-volume ratio increases.

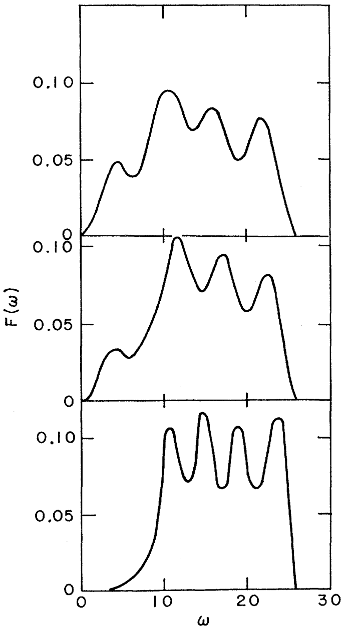

FIG. 4. Frequency spectra of three-layer particles. From top to bottom, the particles have two free surfaces, one free surface and one rigid substrate, and two rigid substrates. The progressive elimination of the edge modes can be seen, as one substrate binds half the edge atoms and with two substrates on either side of the particle there are no loosely bound edge atoms.

In Fig. 2, we show a typical velocity autocorrelation for a small particle (the blob) superimposed with one for the bulk solid, and in Fig. 3 we compare the corresponding $f(\omega)$'s. It is apparent that the small particle has low-frequency structure which does not exist in the solid. The presence of free surfaces not only introduces additional low-frequency modes, but because free surfaces allow relaxation of the surface atoms, anharmonic effects become important. As can be seen in Fig. 2, $\gamma(t)$ decays more rapidly for a small particle than for the bulk solid. For the latter, at the very low temperature at which these calculations were made, the harmonic approximation is valid and the phonon lifetimes are very long.[4]

The main emphasis in presenting the results for the various particle geometries is to understand the origin of the soft frequency modes. While it is customary to lump the low-frequency modes into the loose categories "surface modes" and "edge modes," we show that these modes can be attributed directly to the local atomic environment. Thus in each particle geometry there are atoms with anywhere from 4 to 12 nearest neighbors. To a first approximation each neighbor configuration gives rise to a proportionate frequency. Subsequently, we show how the frequency scales with the number of neighbors, but we first present the general dependence of $f(\omega)$ on particular geometries in Figs. 3 and 4. By comparison with the bulk spectrum, the high-frequency bulk longitudinal and transverse modes can be identified in all of these geometries. The relative amount of the bulklike modes is less in those particles having a large surface-to-volume ratio such as the three-layer particle. The low-frequency modes are more difficult to identify

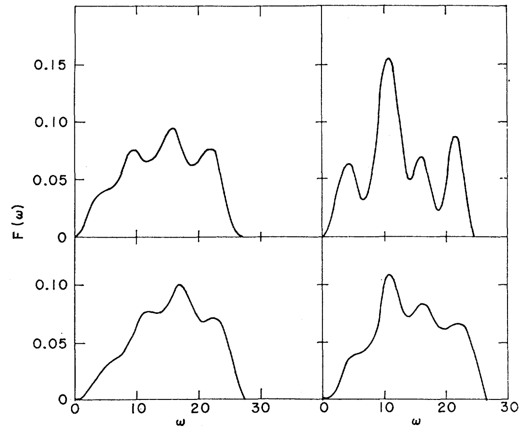

FIG. 5. Components of the frequency spectrum in x (left-hand diagrams) and z (right-hand diagrams) directions. The upper curves correspond to the three-layer particle and the lower curves to the five-layer particle. The surface and edge modes are more prominent in the three-layer particle where about $\frac{2}{3}$ of the atoms are at the surface.

on these spectra averaged over all the atoms in the particle and all directions. In order to identify the origin of the soft modes we first decompose the motions into Cartesian coordinates; taking the z axis at right angles to the plate the motion in the x and y directions is symmetrical (see Fig. 1). The z component of $f(\omega)$ is derived by using only the z component of the velocity in Eq. (2). In Fig. 5, we compare $f(\omega)$ of the three- and five-layer particles in the z and x directions. For the z component it is apparent that the large low-frequency peak at $\omega\sim 11$ arises principally from atoms vibrating at the free planar surfaces. This peak is more prominent in the three-layer particle, where almost $\frac{2}{3}$ of the atoms are in this category, than in the five-layer particle, which has proportionately fewer atoms at the planar surfaces. There is an even softer mode, at $\omega\sim 5$, which arises from the atoms at the edge of the plate. Once again this is more prominent in the three-layer particle where there are proportionately more loosely bound atoms, than in the five-layer particle. These low-frequency modes are also visible in the x component of the frequency spectrum.

As three-layer particles could only occur in nature by vapor deposition onto a substrate, the question arises in such a simulation of how to treat realistically the interaction with the substrate. Atoms which are more tightly bound to each other than to the substrate might be approximated by the two free surfaces. An alternative boundary condition which may be more appropriate when the interaction with the substrate is strong, is to couple the atoms to a rigid boundary. We have taken the structure of this boundary and the interaction to be the same as that of the particle. The effect of this boundary condition is to remove one free surface, as the atoms adjacent to the rigid boundary, to a first approximation, move in the same force field as in the interior of a crystal. In Fig. 4, it can be seen that introducing the substrate changes the relative amount of bulk, surface, and edge modes. In the event that the three-layer particle is sandwiched between two strata [see Fig. 1(D)] only the surface around the rim of the plate remains and the edge modes have disappeared—confirming our identification of these modes.

TABLE I. Mean-square amplitude of vibration of the atoms. $\langle u^2\rangle$ is normalized by dividing by the temperature.

Particle	$\langle u^2\rangle$
Bulk solid	0.14
Blob	0.22
Five-layer	0.35
Three-layer	0.65
Three-layer and one substrate	0.50
Three-layer and two substrates	0.15

The mean-square displacement $\bar{u}^2$ of the atoms, from their equilibrium positions, is very important in interpreting diffraction patterns. We calculated the position autocorrelation function $\beta(t)$,

$$\beta(t)=N^{-1}\langle\sum(\mathbf{r}_i(t)-\mathbf{r}_i(0))^2\rangle \tag{4}$$

as described in I. For large times, $\beta(t)$ tends asymptotically to $2\langle u\rangle^2$. In Fig. 6 are shown some of the curves of $\beta(t)$. The net softening due to the free surface is evident comparing the curves for the bulk solid and the blob. For the three-layer particle we give the x, y, and z components. The mean-square amplitude is larger in the z direction, which is at right angles to the plane of the particle. Because of the symmetry of the particle the average motion in the x and y directions is the same, the slight difference between these two components indicates the accuracy of the statistics. In Table I, the mean-square amplitudes of vibration of the atoms are given for the different particles. The role of the loosely bound atoms at a free surface in increasing the average amplitude can be seen as the amplitude increases rapidly in the sequence bulk solid, blob, five- and three-layer particle, which corresponds to increasing the surface-to-volume ratio. The rigid substrates dampen the vibration of the atoms at the surface of the three-layer particle.

MODEL FOR CALCULATING GEOMETRIC EFFECTS

Given the appropriate pair interaction, one can use the molecular-dynamic technique to calculate classical phonon properties of any small particle geometry. However, this is very time consuming of a computer and just gives the numerical results for the particular geometry and force law, so it is more valuable to have a general technique for synthesizing the frequency spectrum for various geometries. We have found that the following simple model is successful in interpreting and giving various moments for the particle geometries that we have studied, and we suggest that the same model may be combined with empirical bulk frequency spectra to yield appropriate information. The basic idea is to treat each atom as vibrating in a Lennard-Jones–Devonshire cell. That is, in this model each atom moves in an average field arising from the near neighbors. In the usual cell-model calculations one makes a spherical average of the local environment and thus arrives at a spherically symmetrical potential with no directional effects. Our model consists of extending this principle to surface environments. An atom at the surface will have different environments depending on which crystalline face is exposed. For example, whereas a bulk atom has 12 nearest neighbors, an atom in a (111) face is lacking three nearest neighbors, and an atom in a (100) face is lacking four. Atoms on the edge of a small particle or on a rough surface at the pinnacle of a hillock may have as little as four neighbors, whereas atoms in a depression may miss just one or two neighbors. For high temperatures one could follow the calculations for the regular Lennard-Jones–Devonshire cell model and calculate directly the thermodynamic properties of cells appropriate to these situations. At lower temperatures it is more appropriate to know the phonon-frequency distribution. For many applications while a detailed frequency spectrum such as Fig. 3 would be desirable, for most purposes it is sufficient to replace the transverse and longitudinal distributions by an Einstein frequency. The cell model is equivalent to an Einstein oscillator, because one has assumed that the atom in each cell vibrates independently. As the effective potential is proportional to the number of neighbors and as the frequency squared is proportional to the gradient of the potential we would expect the Einstein frequencies to scale as the square root of the number of neighbors. Thus our prescription for obtaining the frequency associated with any local geometry is to scale the known bulk value by the appropriate ratio of neighbors:

$$\omega_i = (n_i/n_0)^{1/2}\omega_0\,, \tag{5}$$

where n_i, n_0 is the number of neighbors, ω_i, ω_0 are the frequencies, in the particular geometry and in the bulk, respectively. The Einstein frequency of the bulk solid is chosen to match some average property, and as the frequency spectrum is not actually an Einstein form, the frequency used depends on the property selected. Thus ω_0, in Eq. (4), will be different if determined from $\langle\omega\rangle$, $\langle\omega^2\rangle$, or $\langle\omega^{-1}\rangle$, etc., and if found from $\langle\omega^n\rangle$ should be written $\omega_0(n)$. The moments of a particle can be readily calculated:

$$\langle\omega^n\rangle = \sum \alpha_i\omega_i^{\,n}\,, \tag{6}$$

where α_i is the fraction of atoms in environment i, and ω_i is obtained by replacing ω_0 in Eq. (4) by the appropriate Einstein frequency.

In order to test this prescription we first decompose our particle into groups of atoms with a given number of neighbors. Table II gives the appropriate neighbor decomposition for each particle. In Table III we show the moments calculated from Eq. (5) compared with

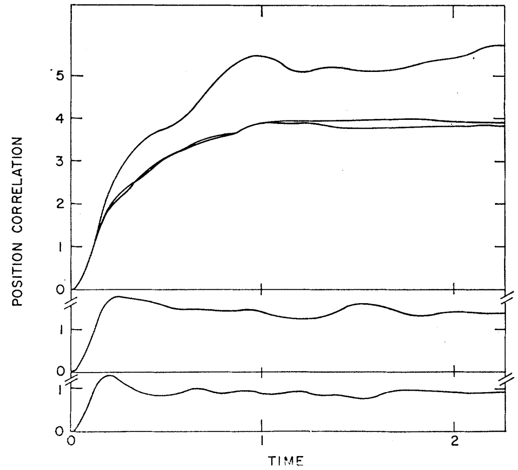

FIG. 6. Position correlation function of the solid, the blob, and the three-layer particle, from bottom to top. For the three-layer particle the components of $\beta(t)$ are shown, the uppermost curve is the z component and the two lower curves are the x and y components. The difference between these two indicates the accuracy of the statistics. The asymptotic value of $\beta(t)$ is the mean-square amplitude of vibration which is larger for particles with high surface areas.

TABLE II. Division of each particle into bulk, surface, and edge atoms, and the number of atoms in each particle with a given number of nearest neighbors.

No. of neighbors	Blob	Five-layer	Three-layer	Three-layer with two substrates	Three-layer with one substrate	Atoms
4		16	16		8	
5	24	24	24		12	Edge
6	24	8		16	8	
7	60	4		8	4	
8	24	106	86	28	57	Surface
9	48					
10	24					
11	24	16	8	8	8	Bulk
12	201	101	32	106	69	
	429	275	166	166	166	All

TABLE III. Moments of the frequency distribution, for different particles, calculated by molecular dynamics and the corresponding values based on the cell model using an Einstein frequency.

	$\langle\omega\rangle$		$\langle\omega^2\rangle$		$\langle\omega^{-1}\rangle$	
Particle	Calculated	Model	Calculated	Model	Calculated	Model
Solid	17.5		335		0.063	
Blob	15.5	15.8	271	275	0.074	0.071
Five-layer	15.1	15.0	262	254	0.084	0.075
Three-layer	13.7	14.2	222	225	0.098	0.079
Three-layer and one substrate	14.7	15.3	252	259	0.086	0.074
Three-layer and two substrates	16.4	16.2	296	292	0.068	0.069

the exact moments from the frequency distribution. Considering the simplifying approximation the agreement is strikingly good. The first and second moments calculated from the model are mainly within 3% of the molecular-dynamic calculations, which have a probable error of about 1%. The fact that Eq. (5) holds to a high approximation for the second moment as well as the first shows that the shape of the frequency distribution is similar in the different environments. The model gives $\langle\omega^{-1}\rangle$ within 5% for the blob and the three-layer particle sandwiched between two substrates. The agreement is less good for the other particles although the model still gives a first approximation. $\langle\omega^{-1}\rangle$ weights more heavily the low frequencies, i.e., the small neighbor configurations, so relaxation and anharmonic effects are largest for this moment. This is borne out by the fact that the discrepancy is smaller for the five-layer particle which has proportionately fewer atoms in low neighbor environments than the three-layer particle.

Having demonstrated that Eq. (4) can be used to deduce the moments associated with a particular geometry, we further show that it reproduces the moments associated with different regions, and so it can be applied to arbitrary geometries composed of different mixtures of surface, edge, and bulk atoms. We have divided the atoms in the blob, three-, and five-layer particles into three groups as shown in Table II; "edge" atoms comprising atoms with 4–6 neighbors, "surface" atoms with 7–9 neighbors, and "bulk" atoms with 10–12 neighbors. We have calculated the moments for each of these groups of atoms using Table II and Eq. (5) and list the moments in Table IV. During the course of the molecular-dynamic calculations we also calculated the correlations for the atoms in each of these groups, severally. Since some of these groups contain only a small number of particles, statistics are poor, and the error in some of the moments is about 5%; the statistics could, of course, be improved if the computations were carried out for longer times. In Table IV we compare the molecular-dynamic and model calculations of the moments. Again the agreement between the two calculations is very good. The only results which have a large discrepancy are the edge atoms in the three- and five-layer particles, which include several very loosely bound atoms with only four neighbors.

For each of the three groups of atoms the $\gamma(t)$ arising from the different particles are very similar. The velocity correlations of the edge atoms in the three- and five-layer particles, however, is softer and decays more rapidly than that of the edge atoms in the blob. This difference between the edge atoms of the blob and the platelike particles arises from the fact that there are the very loosely bound atoms with only four neighbors on the latter particles, but no such atoms on the smoother blob. In Fig. 7 are shown typical frequency spectra: for the edge and surface atoms of the three-layer particle and the bulk atoms of the five-layer particle. Our previous identification of the bulk, surface, and edge modes is confirmed. By comparison with Fig. 3 it can be seen that the spectrum of the "bulk atoms" is very similar to that of the bulk solid, and the "surface atoms" have the additional surface-mode peak at $\omega \sim 11$. For

TABLE IV. Moments of the frequency distribution for edge, surface, and bulk atoms in the blob and the three- and five-layer particles. Values are given from the molecular-dynamic calculation and the cell model.

	$\langle\omega\rangle$		$\langle\omega^2\rangle$		$\langle\omega^{-1}\rangle$		
Particle	Calculated	Model	Calculated	Model	Calculated	Model	Atoms
Blob	12	12	170	160	0.095	0.093	Edge
	14	14	220	210	0.083	0.077	Surface
	17	17	310	330	0.067	0.064	Bulk
Five-layer	10	11	120	140	0.13	0.099	Edge
	14	14	210	230	0.084	0.077	Surface
	18	17	340	330	0.065	0.063	Bulk
Three-layer	9.5	11	120	130	0.148	0.101	Edge
	14	14	220	220	0.090	0.077	Surface
	17	17	330	330	0.070	0.063	Bulk

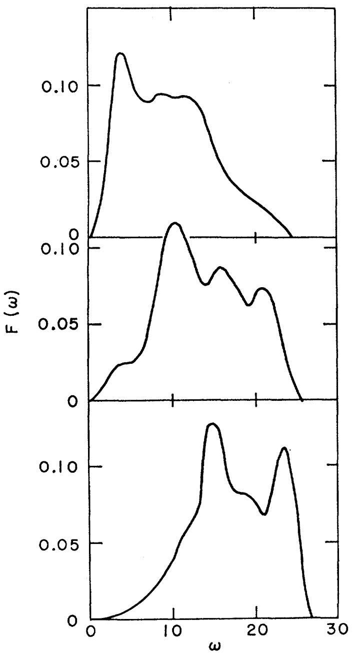

FIG. 7. Frequency distribution of the edge and surface atoms of the three-layer particle, and of the bulk atoms of the five-layer particle, from top to bottom. The surface atoms have the additional surface-mode peak and the edge atoms show only very low-frequency modes.

the edge atoms all the frequencies are shifted to very low values, centered at about $\omega\sim 5$.

For the surface it is illuminating to look at the motion perpendicular and parallel to the surface. The motion along the surface is quite similar to the bulk, whereas the motion at right angles is clearly softer. The Lennard-Jones–Devonshire cell for a surface atom is asymmetrical; in directions parallel to the surface it is similar to a bulk cell, but at right angles to the surface it is asymmetric, being bound only by the soft attractive forces outside the particle. In our model calculation we have used the total number of neighbors to calculate an average frequency. This averaging procedure would not be applicable to properties which can select a given direction, e.g., the Debye-Waller factor which measures mean-square displacements normal to the incident beam. If one wished to extend the model to such directionally dependent quantities one should use the effective number of neighbors in the direction of motion. This would further give rise to crystalline directional effects. In Fig. 8 are shown the z and x components of the frequency spectrum of the surface atoms in the three-layer particle. The dominance of the slow surface vibration at right angles to the surface can be seen, whereas the motion in the plane of the surface has a large component at the bulk frequencies.

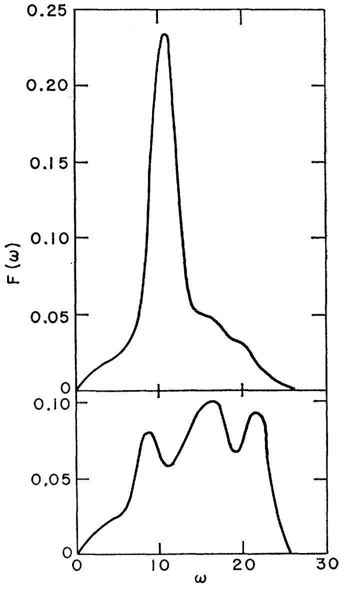

FIG. 8. z component (upper curve) and x component (lower curve) of the frequency spectrum of the three-layer particle. The motion at right angles to the plane of the particle is predominantly the "surface mode."

CONCLUSION

Having calculated frequency distributions for a variety of sizes and shapes of particles with different boundary conditions, we have demonstrated that molecular-dynamic calculations can readily be made to simulate phonon properties, including relaxation and anharmonicity effects. Safeguards must be taken to ensure equilibrium conditions and adequate sampling of the phase space, and time runs must be long enough to ensure good statistics. For many purposes a much simpler procedure involving the Lennard-Jones–Devonshire cell model duplicated moments for the various geometries. The model has the advantage of being extremely simple and phenomenological so it can be applied to any material for which appropriate Einstein frequencies are known. The disadvantage of using Einstein frequencies is that one cannot then, *a priori*, treat anharmonicity and relaxation effects. However, these can be included by using an asymmetric Lennard-Jones–Devonshire cell appropriate to an atom on the surface and calculating a new equilibrium position for a surface atom. Thus, a higher-order approximation of the cell model could be made, but at the expense of the loss of simplicity which is the great virtue of our model.

ACKNOWLEDGMENT

We are indebted to M. Strongin for suggesting that we investigate phonon behavior in small particles.