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COMPARISON OF THE LATTICE-DYNAMICS  
AND CELL-MODEL APPROXIMATIONS  
WITH MONTE-CARLO THERMODYNAMIC PROPERTIES\*

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**Synopsis**

Results from Monte-Carlo computer experiments for energy, pressure, specific heat, Grüneisen  $\gamma$ , and elastic constants are compared with approximate lattice dynamics and cell-model predictions. Comparisons are made for both the Lennard-Jones 6-12 and the exponential-six pair potentials. The elastic constants predicted by lattice dynamics agree best with the Monte-Carlo results. For the other thermodynamic properties the cell model gives more accurate estimates. The effects of increasing the number of particles and of making the calculations according to quantum mechanics instead of classical mechanics are both studied.

1. *Introduction.* Several paths are available for calculating macroscopic thermodynamic properties for a system with given interparticle forces. Most paths are approximate. The lattice dynamics approximation<sup>1)</sup> treats correctly all terms in the energy which are quadratic in the particle displacements. The cell-model approximation<sup>2)</sup> in which a single particle moves in the field of its fixed neighbors modifies the quadratic terms but includes an estimate of anharmonic corrections. More sophisticated theories<sup>3)</sup> treat anharmonic perturbations analytically (the actual calculations require fast computers) but seem complicated enough to attract few followers.

The approximate methods have the important advantage of being quick and inexpensive to calculate. The computer experiments giving exact thermodynamic properties, either by following the motion of the particles or by sampling the configuration space<sup>4)</sup>, are relatively expensive because they require so much computer time, particularly if high precision is necessary. To halve the statistical uncertainty in computer-experiment results requires quadrupling the computer time used up. The precision also depends on the sensitivity of the property measured to fluctuations in pressure and

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energy. Because successively higher derivatives of the free energy involve higher moments of the pressure-tensor component distributions and energy distributions, the time necessary to characterize derivatives increases rapidly with derivative order. Second-order elastic constants and the specific heat involve second moments; third-order elastic constants involve third moments; and so on. So far only first- and second-derivative quantities have been examined. Thus, if the approximations should prove to come close to exact results, they would give us a useful shortcut to accurate thermodynamic properties. It was in the hope of establishing their usefulness that we undertook these calculations.

In this paper we compare the results of solid-phase Monte Carlo experiments on 108 particles interacting with the Lennard-Jones and exponential-six potentials with the predictions of 108-particle lattice dynamics and the cell model. In addition to the energy and pressure, we compare the second-derivative quantities: specific heat, Grüneisen  $\gamma$ , and elastic constants, with approximate predictions. Although either computer method, molecular dynamics or Monte Carlo, can be extended to quantum systems by using the Wigner-Kirkwood Planck's constant expansion of the free energy<sup>5)</sup>, we have made our comparisons using classical mechanics. To find out how important the small size and classical nature of our systems are, we use the lattice-dynamics method to investigate the number dependence of all of the thermodynamic properties and quantum corrections to the elastic constants. Quantum corrections to other thermodynamic properties have been calculated elsewhere<sup>6)</sup>.

In section 2 we describe the lattice-dynamics calculations. The method has been in use for over 50 years, although many so-called lattice-dynamics calculations of elastic constants have actually been calculations of the elastic response of a static lattice. We take lattice vibrations explicitly into account. The first correct harmonic calculation using normal-mode vibrations was announced by Feldman<sup>7)</sup>. He obtained expressions for the second-order elastic constants which involved the vibration frequencies and their strain derivatives. The frequencies were then obtained by the usual method of diagonalizing the dynamical matrix. The frequency-shift derivatives were calculated by means of perturbation theory. We calculate the work of deforming the crystal by the alternative procedure of computing the free energy numerically for several slightly different values of the strain and then fitting the results to a strain polynomial. Besides avoiding the tedious algebra of Feldman's analytic approach, the numerical method is more readily generalized to higher-order elastic constants.

In section 3 we describe the cell-model calculations. The cell model, although actually only appropriate for solids, was first used in an attempt to describe gases and liquids<sup>8)</sup>. In the cell model the effect of heating the crystal lattice is approximated by a "one-particle" model in which a single

particle moves in the field of its fixed neighbors. Neglecting interparticle correlations by approximating an  $N$ -body problem by a one-body problem is, for classical systems, most reasonable at low temperatures and is exact only in the static-lattice limit.

The advantage of the cell model over the harmonic approximation lies in its ability to estimate anharmonic contributions from potential-energy terms beyond the quadratic ones. The cell model has often been used to calculate energy, pressure, and specific heat<sup>9</sup>). Our elastic-constant calculations are a new use of this model. Henkel<sup>10</sup>) has studied a similar model, a quantum cell model in which the potential was expanded in powers of displacement and the quartic contributions were treated by perturbation theory. If the perturbations were ignored, Henkel's work would reduce to the usual harmonic Einstein model.

In section 4 we compare the tabulated results from both approximations and consider the dependence of the results on number of particles. We also discuss some interesting cancellations found in the course of the Monte Carlo calculations. In section 5 we assess the importance of quantum effects on the elastic constants.

2. *Lattice-dynamics calculations.* The lattice dynamics calculations are based on the approximation of truncating a Taylor series expansion of the lattice potential energy  $\Phi$  after the quadratic terms in the particle displacements. Sometimes this is called the "quasi-harmonic" approximation. The coefficients in the Taylor series expansion are calculated from the assumed force law, and the lattice sites are chosen to match the structure of the lattice being described. The expansion is made about a configuration in which each atom is fixed at its average position in a perfect crystal with fixed center of mass. Thus the truncated potential depends upon the size and shape of the assumed static lattice configuration. By changing to normal-mode coordinates the quasi-harmonic Hamiltonian can be rewritten as a sum of  $3N - 3$  independent harmonic oscillator Hamiltonians. The partition function of an oscillator, either quantum or classical, is known<sup>11</sup>) so that the quasi-harmonic thermodynamic properties of the system can be calculated.

The partition function,  $Z = \exp(-A/kT)$ , where  $A$  is the Helmholtz free energy and  $kT$  is Boltzmann's constant times the absolute temperature, can be written as a product of single oscillator partition functions:

$$\begin{aligned}
 Z &= \exp(-\Phi_0/kT) Z_{\text{cm}} \prod_{i=1}^{3N-3} Z_i, \\
 Z_{\text{cm}} &= (V/N)(2\pi Nm kT/h^2)^{\frac{3}{2}}, \\
 Z_i &= (e^{\frac{1}{2}x} - e^{-\frac{1}{2}x})_i^{-1} = x_i^{-1} - \frac{1}{24}x_i + \frac{7}{5760}x_i^3 \dots, \\
 x_i &\equiv hv_i/kT.
 \end{aligned}$$

In the classical limit only the first term in the expansion,  $kT/h\nu$ , is kept.  $\Phi_0$  is the static lattice energy. The vibration frequencies  $\nu_i$  are determined from the quadratic Hamiltonian; the center of mass contribution is  $Z_{\text{cm}}$ . For accurate work on small crystals  $Z_{\text{cm}}$  has to be included if comparisons are made with Monte Carlo calculations in which the center of mass is allowed to move.

Thermodynamic properties can all be derived from the partition function. Temperature derivatives can be evaluated explicitly to compute the energy and specific heat:

$$(E/kT) = (\partial \ln Z / \partial \ln T)_\eta; \quad C_V = (\partial E / \partial T)_\eta.$$

“Strain” derivatives are harder to evaluate. The strains are defined in terms of three vectors colinear with the edges common to one corner of a parallelepiped produced by deforming a cube of crystal with sidelength  $a$ . If  $\mathbf{a}_1$ ,  $\mathbf{a}_2$ , and  $\mathbf{a}_3$  are the vectors, then

$$\begin{aligned} \eta_1 &\equiv \frac{1}{2}[(\mathbf{a}_1/a)^2 - 1], & \eta_4 &\equiv (\mathbf{a}_2/a) \cdot (\mathbf{a}_3/a), \\ \eta_2 &\equiv \frac{1}{2}[(\mathbf{a}_2/a)^2 - 1], & \eta_5 &\equiv (\mathbf{a}_1/a) \cdot (\mathbf{a}_3/a), \\ \eta_3 &\equiv \frac{1}{2}[(\mathbf{a}_3/a)^2 - 1], & \eta_6 &\equiv (\mathbf{a}_1/a) \cdot (\mathbf{a}_2/a), \end{aligned}$$

are the six independent strains. The dynamical matrix then gives a complicated implicit relation for the vibration frequencies as functions of the strains. Because there is no convenient expression for  $\nu(\eta)$  it is easiest to proceed numerically. Both the average pressure tensor component  $\langle P_{11} \rangle \equiv P$  and the elastic constant  $C_{11}^T$  can be determined by evaluating  $A$  for a strain along axis one: a lattice site initially at  $\mathring{\mathbf{r}} = (\mathring{r}_1, \mathring{r}_2, \mathring{r}_3)$  is displaced to  $\mathbf{r}$ , given by

$$r_1 = \mathring{r}_1(1 + 2\eta_1)^{\frac{1}{2}}, \quad r_2 = \mathring{r}_2, \quad r_3 = \mathring{r}_3,$$

where  $r_i$  and  $\mathring{r}_i$  are the Cartesian coordinates of  $\mathbf{r}$  and  $\mathring{\mathbf{r}}$ , and  $\eta_1$  is the only nonzero strain. In the strained configuration the Hamiltonian is again expanded, the quadratic terms kept, and the result diagonalized, giving a new set of frequencies and the free energy  $A(\eta_1)$ . The diagonalization can be visualized in terms of plane-wave solutions of the classical equations of motion. The waves propagate through the crystal with wavelengths and directions imposed by the shape of the crystal and described by wave vectors chosen from a convenient Brillouin zone<sup>12</sup>). If  $\mathring{\mathbf{y}}$  is a wave vector in the unstrained crystal then the corresponding  $\mathbf{y}$  in the strained crystal is:

$$y_1 = \mathring{y}_1(1 - 2\eta_1)^{-\frac{1}{2}}, \quad y_2 = \mathring{y}_2, \quad y_3 = \mathring{y}_3,$$

where  $y_i$  and  $\mathring{y}_i$  are the Cartesian coordinates of  $\mathbf{y}$  and  $\mathring{\mathbf{y}}$ . Applying the Born-von Kármán normal-mode analysis for several values of  $\eta_1$ , the first four or five coefficients in the expansion,

$$A(\eta_1) = A(0) - PV\eta_1 + \frac{1}{2}C_{11}^T V\eta_1^2 + \frac{1}{6}C_{111}^T V\eta_1^3 + \dots,$$

can be determined. By choosing values of  $\eta_1$  separated by 0.0001, both the pressure and  $C_{11}^T$  were determined with four-figure accuracy in this way.

By considering two simultaneous strains along the one axis and the two axis, and analyzing the resulting free energy changes as a series in  $\eta_1$  and  $\eta_2$ , we next determined  $C_{12}^T = (\partial^2 A / \partial \eta_1 \partial \eta_2)_T / V$ .

To calculate  $C_{44} = (\partial^2 A / \partial \eta_6^2)_T / V$  a shear strain can be introduced by changing the angle between the one and two axes:

$$r_1 = \overset{\circ}{r}_1(1 - \eta_6^2)^{\frac{1}{2}}, \quad r_2 = \overset{\circ}{r}_2 + \overset{\circ}{r}_1\eta_6, \quad r_3 = \overset{\circ}{r}_3.$$

The wave vectors become:

$$y_1 = (\overset{\circ}{y}_1 - \overset{\circ}{y}_2\eta_6)(1 - \eta_6^2)^{-\frac{1}{2}}, \quad y_2 = \overset{\circ}{y}_2, \quad y_3 = \overset{\circ}{y}_3.$$

The generalization of this technique to calculation of higher-order elastic constants or to mixed strain-temperature derivatives is straightforward. For crystals of lower symmetry one needs to calculate more elastic constants and hence one considers more different combinations of strain. Other strains would also be needed for cubic crystals to determine the six nonzero third-order constants or the eleven nonzero fourth-order constants and the mixed strain-temperature derivatives.

The adiabatic elastic constants

$$C_{11}^S = (\partial^2 E / \partial \eta_1^2)_S / V \quad \text{and} \quad C_{12}^S = (\partial^2 E / \partial \eta_1 \partial \eta_2)_S / V$$

can be calculated by adding a term to the isothermal constants:

$$\Delta C \equiv C_{11}^S - C_{11}^T = C_{12}^S - C_{12}^T = (\partial S / \partial \eta_1)_T^2 (\partial T / \partial S)_\eta / V,$$

where  $S$  is the entropy of the crystal. Because  $S(\eta_1)$  and  $(\partial T / \partial S)_\eta$  can be calculated exactly for a quasi-harmonic crystal, the correction term can be evaluated numerically.

In order to make a comparison with the 108-particle Monte Carlo calculations<sup>13,14</sup>) we have calculated the thermodynamic properties for a 108-particle system with the same periodic boundaries and Hamiltonian as those used in the Monte Carlo work. Using the nearest-image convention, each particle in the crystal interacts with 107 neighbors according to the Lennard-Jones 6-12 potential

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

or the exponential-six potential

$$\phi = 0.8\epsilon \exp[13.5\{1 - r/r_{\min}\}] - 1.8\epsilon(r_{\min}/r)^6.$$

These potentials have both been used principally to describe rare gases and have shown themselves to fit these real materials well. Although we picked these potentials because of their value in describing rare gases we expect

TABLE I

Calculated thermodynamic properties for classical Lennard-Jones and exponential-six solids. The various  $\Delta$ 's are the 108-particle thermal contributions to the thermodynamic properties which must be added to the infinite static lattice (subscript o) quantities. The column headings indicate temperatures appropriate to solid argon. The *reduced* temperatures,  $kT/\epsilon$ , where  $\epsilon$  is the potential well depth, are 0.3361, 0.5042, and 0.6723 for the Lennard-Jones potential, and 0.3279, 0.4918, and 0.6557 for the exponential-six potential. Reduced volumes,  $\sqrt{2V/Nr_{\min}^3}$ , where  $r_{\min}$  is the minimum in the potential, are 0.972, 0.997, and 1.032 for the Lennard-Jones potential, and 0.946, 0.971, and 1.005 for the exponential-six potential.

	Lennard-Jones			Exponential-six		
	40	60	80	40	60	80
$(E/NkT)_o$	-25.30	-16.66	-12.23	-25.54	-16.89	-12.47
$\Delta$ (Monte Carlo)	2.89	2.85	2.79	2.89	2.89	2.86
$\Delta$ (Lattice dynamics)	3.00	3.00	3.00	3.00	3.00	3.00
$\Delta$ (Cell model)	2.91	2.86	2.80	2.94	2.90	2.85
$(PV/NkT)_o$	-10.11	-9.00	-8.57	-5.65	-6.39	-6.96
$\Delta$ (Monte Carlo)	8.78	8.62	8.49	7.67	7.80	7.83
$\Delta$ (Lattice dynamics)	9.29	9.53	9.89	8.18	8.42	8.77
$\Delta$ (Cell model)	8.88	8.74	8.59	7.97	7.95	7.93
$(C_V/Nk)$ (Monte Carlo)	2.73	2.69	2.79	3.09	2.84	2.87
$(C_V/Nk)$ (Lattice dynamics)	3.00	3.00	3.00	3.00	3.00	3.00
$(C_V/Nk)$ (Cell model)	2.84	2.76	2.67	2.89	2.82	2.75
$\gamma$ (Monte Carlo)	2.82	2.82	2.91	2.73	2.56	2.66
$\gamma$ (Lattice dynamics)	3.10	3.18	3.30	2.73	2.81	2.93
$\gamma$ (Cell model)	2.95	2.90	2.85	2.64	2.62	2.61
$(C_{11}V/NkT)_o$	183.5	97.8	52.5	217.1	120.1	68.5
$\Delta^T$ (Monte Carlo)	12.6	10.2	6.9	-2.6	3.9	1.5
$\Delta^T$ (Lattice dynamics)	6.1	5.2	3.6	1.5	1.0	0.0
$\Delta^T$ (Cell model)	23.4	24.1	24.7	16.2	17.0	17.9
$\Delta^S$ (Monte Carlo)	34.3	31.7	27.5	20.4	22.5	21.8
$\Delta^S$ (Lattice dynamics)	34.9	35.5	32.6	23.9	24.7	25.7
$\Delta^S$ (Cell model)	48.1	47.3	46.4	36.3	36.4	36.6
$(C_{12}V/NkT)_o$	110.7	61.0	34.9	128.9	73.1	43.5
$\Delta_{12}^T$ (Monte Carlo)	0.4	0.9	-2.6	-7.3	-1.8	-3.9
$\Delta_{12}^T$ (Lattice dynamics)	-6.2	-7.4	-9.6	-5.5	-6.4	-8.0
$\Delta_{12}^T$ (Cell model)	-9.8	-8.4	-7.1	-9.5	-8.7	-7.8
$\Delta_{12}^S$ (Monte Carlo)	22.1	22.3	21.0	15.7	16.9	16.4
$\Delta_{12}^S$ (Lattice dynamics)	22.5	22.8	23.1	16.9	17.2	17.6
$\Delta_{12}^S$ (Cell model)	14.9	14.8	14.6	10.7	10.7	11.0
$\Delta_{44}$ (Monte Carlo)	6.0	7.3	7.7	3.5	2.0	3.6
$\Delta_{44}$ (Lattice dynamics)	5.6	5.4	5.1	2.0	2.0	2.0
$\Delta_{44}$ (Cell model)	16.8	16.5	16.2	11.9	12.0	12.2

that our general conclusions in comparing approximate calculations with exact computer experiments will be valid for potentials describing interactions in salts or metals as well.

Table I gives both the Monte Carlo and the lattice-dynamics results. The three temperatures span the range from about  $0.48T_{\text{triple}}$  to  $0.95T_{\text{triple}}$  and the densities correspond closely to zero pressure. Because the static-lattice contributions to the thermodynamic properties present no theoretical problems (they are correctly calculated by any theory) we have tabulated separately the thermal contributions to the thermodynamic properties. The data in the table show that the lattice-dynamics elastic constants are quite close to the Monte Carlo values at three different temperatures and for both potentials tested.

3. *Cell-model calculations.* The cell-model approach incorporates the same static lattice contributions as does the lattice-dynamics method. To these are added thermal corrections estimated by having a single "wanderer" particle move in the potential field of an otherwise static lattice. Using a  $\Delta$  to indicate restriction of the moving particle to a cell of volume  $V/N$  centered on its lattice site, and using  $\delta\phi$  to indicate the change in potential energy of the system as a function of the wanderer's location, the approximate partition function has the form:

$$Z_{\text{cell}} \equiv \exp(-\Phi_0/kT)(2\pi mkT/h^2)^{3N/2} \left[ \int_{\Delta} \exp(-\delta\phi/kT) d\mathbf{r} \right]^N.$$

If only the quadratic terms in  $\delta\phi$  are kept, the so-called "Einstein approximation" results. By keeping the entire potential we get an estimate of the anharmonic contributions to the free energy. This estimate turns out to be amazingly good so far as the first derivative quantities, pressure and energy, are concerned; it is much less accurate for the higher derivatives.

To calculate thermodynamic properties from the cell model one differentiates the cell-model free energy with respect to temperature and strain. If one wants higher-order derivatives then one should instead use a finite-difference method similar to our lattice-dynamics approach. For first and second derivatives it is simple enough to differentiate explicitly (the calculation is nearly identical with that described in ref. 13). Again using  $\delta$  to indicate the difference, from the cell-center value, of a sum over all neighbors of the "wanderer" particle, and the subscript o to indicate a static-lattice property, the thermodynamic quantities can all be written in terms of average values  $\langle \rangle$  of functions of the wanderer's location with weighting function  $\exp(-\delta\phi/kT)$ :

$$\langle F \rangle \equiv \int_{\Delta} F(\mathbf{r}) \exp(-\delta\phi/kT) d\mathbf{r} / \int_{\Delta} \exp(-\delta\phi/kT) d\mathbf{r}.$$

The equations for the thermodynamic properties are:

$$\begin{aligned}
E/NkT &= \Phi_0/NkT + \frac{3}{2} + \langle \delta\phi \rangle / kT, \\
PV/NkT &= P_0V/NkT + 1 - \langle \delta x^2 \phi' / r \rangle / kT, \\
C_V/Nk &= \frac{3}{2} + [\langle (\delta\phi)^2 \rangle - \langle \delta\phi \rangle^2] / (kT)^2, \\
\gamma &= V(\partial P / \partial E)_V = \{1 - [\langle (\delta\phi)(\delta x^2 \phi' / r) \rangle \\
&\quad - \langle \delta\phi \rangle \langle \delta x^2 \phi' / r \rangle] / (kT)^2\} C_V/Nk, \\
C_{11}^T V/NkT &= (C_{11}^T V/NkT)_0 + 2 + (\langle \delta\phi'' x^4 / r^2 \rangle - \langle \delta\phi' x^4 / r^3 \rangle) / kT \\
&\quad + [\langle \delta\phi' x^2 / r \rangle^2 - \langle (\delta\phi' x^2 / r)^2 \rangle] / (kT)^2, \\
C_{12}^T V/NkT &= (C_{12}^T V/NkT)_0 \\
&\quad + (\langle \delta\phi'' x^2 y^2 / r^2 \rangle - \langle \delta\phi' x^2 y^2 / r^3 \rangle) / kT \\
&\quad + [\langle \delta\phi' x^2 / r \rangle^2 - \langle (\delta\phi' x^2 / r)(\delta\phi' y^2 / r) \rangle] / (kT)^2, \\
C_{44} V/NkT &= (C_{12}^T V/NkT)_0 + 1 \\
&\quad + (\langle \delta\phi'' x^2 y^2 / r^2 \rangle - \langle \delta\phi' x^2 y^2 / r^3 \rangle) / kT \\
&\quad - \langle (\delta\phi' xy / r)^2 \rangle / (kT)^2,
\end{aligned}$$

and

$$(C_{11}^S - C_{11}^T) V/NkT = (C_{12}^S - C_{12}^T) V/NkT = \gamma^2 C_V/Nk.$$

For fluids or isotropic solids, these relations (as well as the analogous exact relations) can be simplified. The three elastic constants are replaced by two Lamé constants,  $\lambda^x$  and  $\mu^x$ , equal respectively to  $C_{12}^x$  and  $C_{44} = \frac{1}{2}(C_{11}^x - C_{12}^x)$ , where  $x$  is either  $T$  or  $S$ . The bulk modulus,

$$B^x = -V(\partial P / \partial V)_x = (C_{11}^x + 2C_{12}^x + P)/3,$$

becomes  $(3\lambda^x + 2\mu^x + P)/3$ . The shear modulus,  $\mu^x - P$ , vanishes for fluids.

With modern computers it is easy to get four-figure accuracy in computed cell-model thermodynamic properties. In practice only the first three shells of neighbors are necessary in computing the thermal contributions. Even for the properties most sensitive to the integration mesh, specific heat and Grüneisen  $\gamma$ , 20-point Gaussian integration is sufficient. For sixth-power attraction the lattice sums for the static-lattice properties vary with the number of particles included in the sum as  $1/N$  so that direct summation can be used. The results from the cell-model approximation for both pair potentials at the same three temperatures and densities used in the Monte Carlo and lattice dynamics work are listed in table I. Notice that the cell-model energies and pressures are very close to the exact Monte Carlo results.

4. *Intercomparison and discussion of results.* The data in table I show that cell-model estimates of the energy and pressure are nearly correct;

without faster computers or improved Monte Carlo methods there are only a few applications which justify the expense of improving on cell-model energies and pressures. The errors in the lattice-dynamics approach, without anharmonic corrections, are an order of magnitude greater.

For specific heat and Grüneisen  $\gamma$  the cell model is again the better approximation. The lattice-dynamics method is, however, the better approximation for the adiabatic elastic constants. Neither approximate method successfully reproduces the isothermal elastic constants. It is interesting to see that these isothermal constants are more sensitive to small changes in the interparticle pair potential than are the adiabatic constants. Ideally, the isothermal constants would be useful in determining force laws from experiment. Unfortunately, the  $C_{ij}^T$  are hard to measure in laboratory experiments.

An interesting feature common to the Monte Carlo results and to those of both approximate methods is the near cancellation of the thermal contributions to  $C_{11}^T$  and  $C_{12}^T$ . If the elastic constants are written as the sum of three terms, the "Born" term, the "fluctuation" term, and the "kinetic" term<sup>13</sup>), it is found that at the triple point the thermal contributions to the first two terms are both large, about the same magnitude as the elastic constant itself, but that their sum is nearly zero. This cancellation can be "understood" by examining an idealized model of a solid in which a similar cancellation is *exact*. Consider a classical system of particles interacting with the inverse power potential  $\phi = \epsilon(\sigma/r)^n$ . At temperatures low enough for the quasi-harmonic approximation to be valid, the combination

$$V(C_{11}^T + 2C_{12}^T - 2P) = -3[\partial(PV)/\partial \ln V]_T$$

becomes temperature independent. Separating the "Born" and "fluctuation" terms in pairs of braces, we find the results:

$$\begin{aligned} V(C_{11}^T + 2C_{12}^T - 2P) &= -3[\partial(PV)/\partial \ln V]_0 + \{\langle \sum \phi''r^2 + \sum \phi'r \rangle\} \\ &\quad - \{(1/kT)[\langle (\sum \phi'r)^2 \rangle - \langle \sum \phi'r \rangle^2]\} \\ &= -3[\partial(PV)/\partial \ln V]_0 + \{n^2 \langle \sum \phi \rangle\} \\ &\quad - \{(n^2/kT)[\langle (\sum \phi)^2 \rangle - \langle \sum \phi \rangle^2]\}. \end{aligned}$$

Within the braces the sums are over all pairs of particles, and the static lattice parts have been subtracted out. In the harmonic approximation the last two terms cancel exactly, leaving only the static-lattice derivative indicated by the subscript 0. For potentials other than an inverse power the cancellation is not exact. However, it is quite close. For the Lennard-Jones potential at  $kT/\epsilon = 0.3361$  (about half the triple point temperature) the thermal Born term contribution to  $(C_{11}^T + 2C_{12}^T - 2P)_T V/NkT$  is

$63 + 59 - 16 = 106$ . The thermal fluctuation terms give  $-53 - 58 = -111$ . Thus the total thermal contribution  $-5$  is very small relative to the static-lattice value of 425.

The computer experiments also showed that the adiabatic elastic constants converge about ten times as quickly as the isothermal ones and that the adiabatic constants agree better with the lattice-dynamics and cell-model approximations. The reason for this fast convergence and improved agreement can be seen by again considering the case of a classical inverse-power solid. Calculation shows that approximately two thirds of the slowly convergent fluctuation contributions to  $C_{11}^T + 2C_{12}^T$  is cancelled by the adiabatic correction  $3\Delta C$ .

At first glance it appears strange that the lattice-dynamics calculations, which do poorly in the energy and pressure calculations (at least when compared to the cell model) give good estimates of the adiabatic elastic constants. This fact becomes more easily understood on closer inspection of the results of the calculations. In table II we tabulate the percent deviation of the *thermal part* of  $E$ ,  $P$ , and  $C_{ij}^S$  from the Monte Carlo values for lattice-dynamics and cell-model calculations. The energy, pressure, and elastic constants are respectively zeroth-, first-, and second-order strain derivative thermodynamic properties. From table II one can observe that higher-derivative properties are harder to estimate for both methods. The cell-model calculations deteriorate faster, because the long-wavelength vibrational modes which are poorly described in this Einstein-like calculation become more important in the higher-derivative properties. The saving feature for the adiabatic elastic constants is that the thermal contribution is a small percentage of the total elastic constant, so that a 20% error in the thermal contribution, which would be intolerable in the pressure calculation, leads to an error of only about 5% in the total elastic constant.

Having concluded that lattice dynamics *is* useful for computing adiabatic elastic constants for 108-particle crystals, we now ask how many particles

TABLE II

Percent deviation from Monte Carlo values of the approximate thermal contributions to the thermodynamic properties

	Lattice dynamics						Cell model					
	6-12			e-6			6-12			e-6		
	40	60	80	40	60	80	40	60	80	40	60	80
$\Delta E$	4	5	8	4	4	5	1	0	0	2	0	0
$\Delta P$	6	11	16	7	8	12	1	1	1	4	2	1
$\Delta C_{11}^S$	2	12	19	17	10	18	40	49	69	78	62	68
$\Delta C_{12}^S$	2	2	10	8	2	7	-33	-34	-30	-32	-37	-33
$\Delta C_{44}$	-7	-26	-34	-43	0	-44	180	130	110	240	500	240

need be used (or equivalently, how fine a mesh in the Brillouin zone is necessary) to imitate the properties of infinite crystals. The same question is faced in setting up or interpreting Monte Carlo or molecular-dynamics calculations. To answer this question for classical crystals, we calculated the lattice-dynamics estimates of pressure, Grüneisen  $\gamma$ , and elastic constants for periodic cubic crystals of from 32 to 864 particles. The thermal parts of the pressure and the Grüneisen  $\gamma$  were found to converge to three significant digits for a Brillouin zone of 107 points. The elastic constants require a Brillouin zone of 499 points for three significant digits in the thermal part. The dependence of the elastic constants on  $N$  is more complicated than the  $\ln N/N$  dependence observed<sup>15)</sup> for the entropy and the free energy. Over the range from 31 to 863 points, the convergence is faster than  $1/N$  and increases with  $N$ . Because the thermal part is a small correction to the easily calculated infinite static-lattice results, the error in the total elastic constant due to using 107 points instead of an integration over the Brillouin zone will be less than 2%. By using 499 points one can eliminate the error entirely for calculations which keep only three significant digits.

5. *Quantum-mechanical effects.* In figs. 1 through 4 we show graphs of the adiabatic elastic constants for neon, argon, krypton, and xenon calculated by means of lattice dynamics and using the Lennard-Jones 6-12 potential. We used 500 particles for this calculation. The values of  $\epsilon$  and  $\sigma$  used here are those tabulated by Horton<sup>16)</sup> for describing the solid state of rare gases, except for the argon calculation in which we used the same values as in our other calculations for argon. Our argon parameters are quite close to Horton's. We tabulate  $\epsilon$  and  $\sigma$  in table III. The graphs represent all-neighbor, infinite-lattice calculations, since retaining more neighbors or using more particles will not cause a detectable change in the curves. As before, the contribution of the static lattice is calculated for an infinite number of particles. The zero-pressure lattice spacings used here were taken from Pollack's<sup>17)</sup> compilation of X-ray diffraction data. Except for neon, the intercepts of the quantum-mechanical curves at absolute zero are those

TABLE III

Values of $\epsilon$ and $\sigma$ used in the quantum-mechanical calculations of the elastic constants		
	$\epsilon/k$ (K)	$\sigma$ (Å)
Neon	36.65	2.789
Argon	119.00	3.400
Krypton	164.44	3.638
Xenon	231.08	3.961

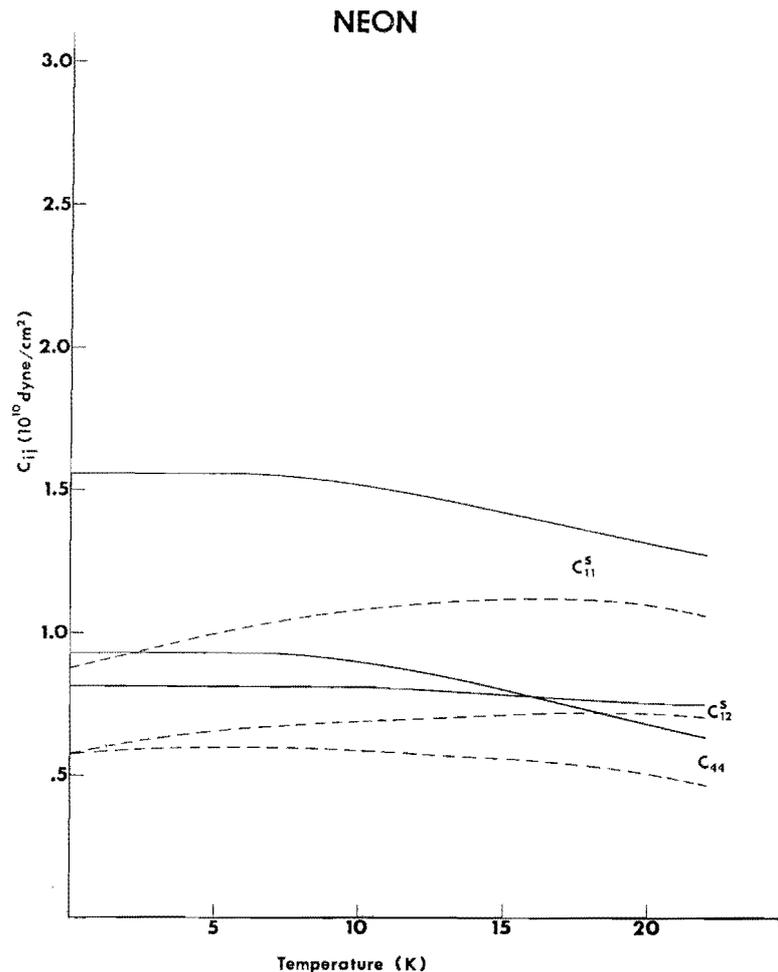


Fig. 1. Adiabatic elastic constants for neon according to the Lennard-Jones 6-12 potential in the quasi-harmonic approximation. Solid curves are the quantum-mechanical calculation and the dashed curves are the classical calculation.

calculated by Barron and Klein<sup>18</sup>). We omit their neon results because they used different values of the potential parameters.

The error introduced by anharmonicities not included in the quasi-harmonic approximation is about 5% near the triple point and about 0.3% at 40 K for argon. Although we have not made Monte Carlo calculations for the other rare gases, the error in those cases would be about the same as that for argon for equal fractions of the triple-point temperature.

We include in each graph both the quantum and classical calculations of the elastic constants. This displays the magnitude of the quantum effect in each case; increasing from xenon which is the most classical, to neon which is the most quantum mechanical of the four. It is interesting to note that the quantum correction for  $C_{44}$  is much larger than that for  $C_{12}^S$  at points near absolute zero. This is a little surprising, since one can estimate these corrections<sup>14</sup>) by means of the Wigner-Kirkwood expansion which predicts,

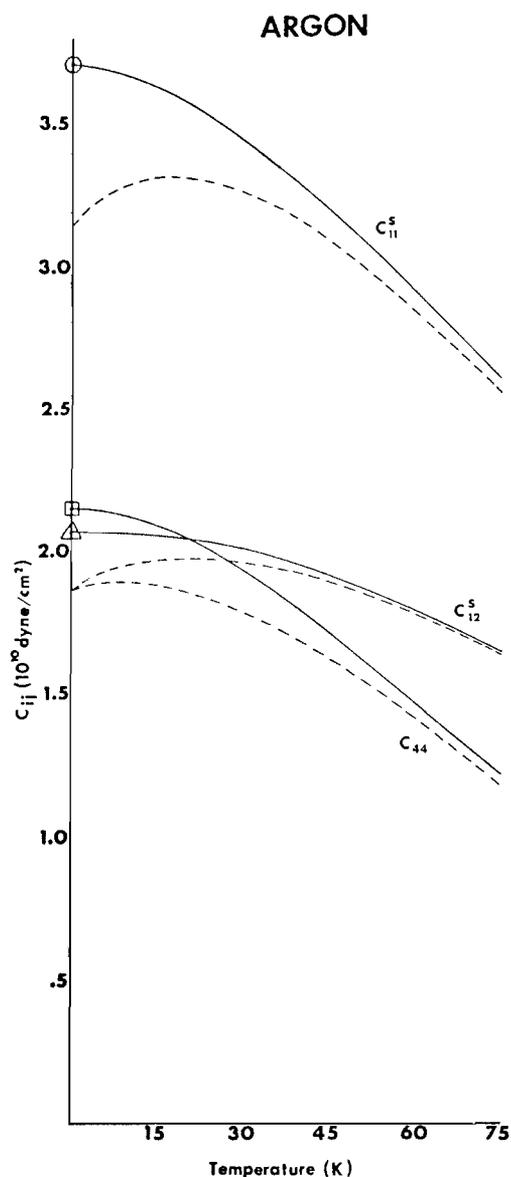


Fig. 2

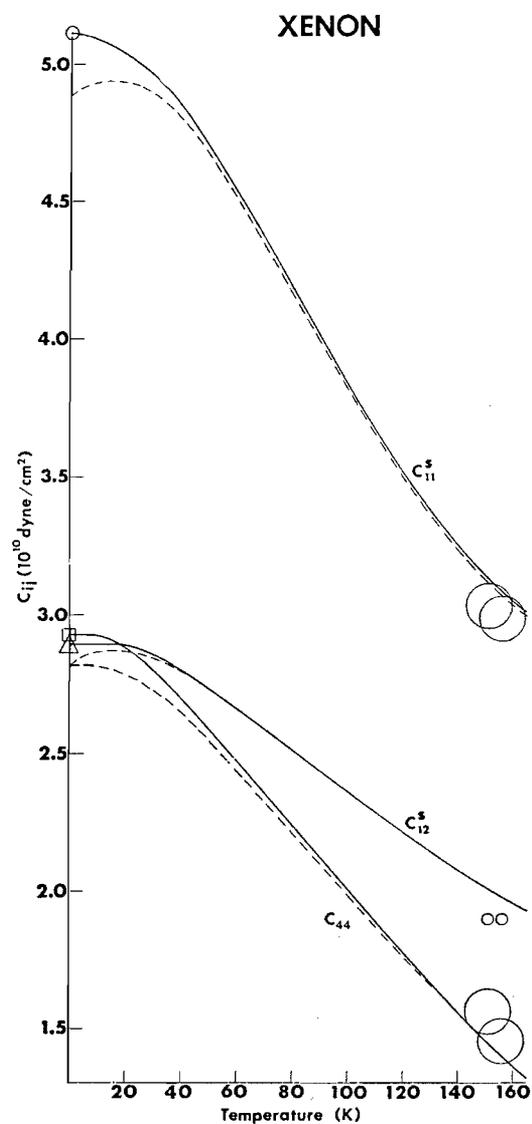


Fig. 3

Fig. 2. Adiabatic elastic constants for argon according to the Lennard-Jones 6-12 potential in the quasi-harmonic approximation. Solid curves are the quantum-mechanical calculation and the dashed curves are the classical calculation. Intercepts at absolute zero are from ref. 18.

Fig. 3. Adiabatic elastic constants for xenon according to the Lennard-Jones 6-12 potential in the quasi-harmonic approximation. Solid curves are the quantum-mechanical calculation and the dashed curves are the classical calculation. Intercepts at absolute zero are from ref. 18.

at least in the static-lattice approximation, that  $C_{44}$  and  $C_{12}^S$  will have identical quantum corrections.

The computer calculations bear out the observation<sup>19)</sup> that solid-phase properties alone cannot be used to predict melting. The molecular-dynamics work<sup>20)</sup> of Hansen and Verlet shows that our highest temperature points

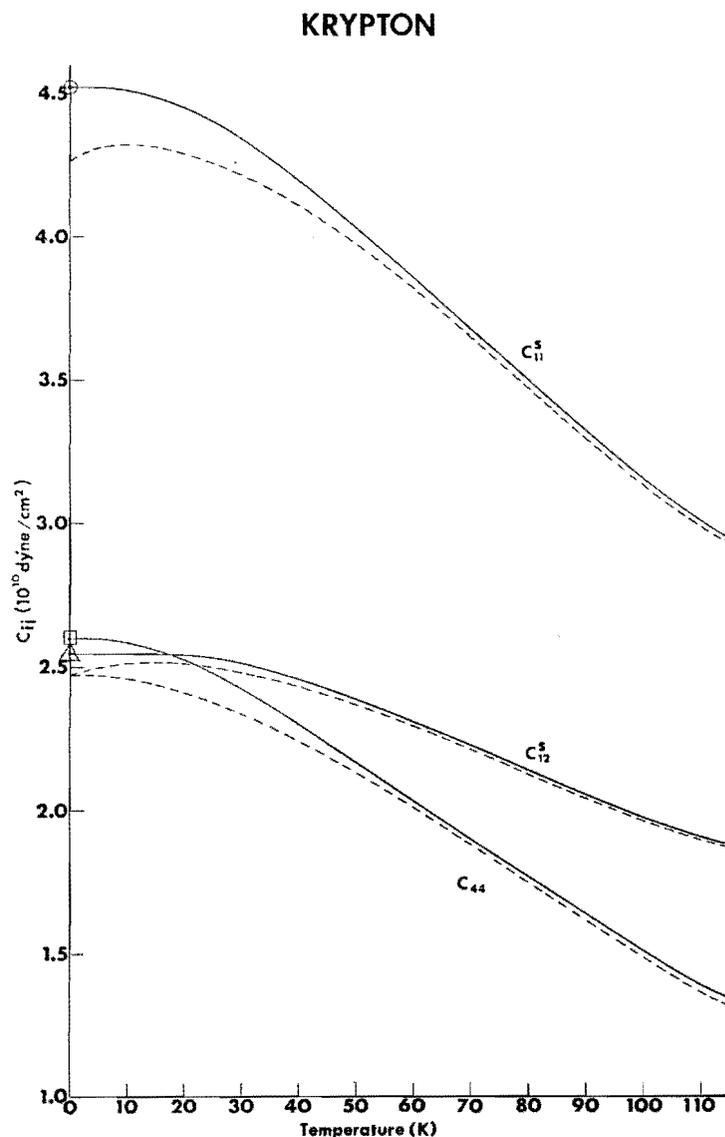


Fig. 4. Adiabatic elastic constants for krypton according to the Lennard-Jones 6-12 potential in the quasi-harmonic approximation. Solid curves are the quantum-mechanical calculation and the dashed curves are the classical calculation. Intercepts at absolute zero are from ref. 18.

for argon lie fairly near the triple point. On the other hand, a common method for predicting melting is to look for the vanishing of a shear modulus, either  $C_{44} - P$  or  $\frac{1}{2}(C_{11} - C_{12}) - P$  for cubic crystals. A long extrapolation of our results for the shear moduli suggests erroneously that the crystal remains stable to shear up to *twice* the triple point temperature. Thus it appears that the vanishing of the shear modulus is not related to the phenomenon of melting, which will occur when the Gibbs free energy of the liquid is less than that for the solid at the same pressure and temperature.

6. *Summary.* In this paper we have compared calculated values of the thermodynamic properties of argon obtained from Monte Carlo calculations

and from two approximate models, the cell-model and the quasi-harmonic approximation. We have considered two different potentials for argon at three temperatures: 40 K, 60 K, and 80 K. Our comparisons confirm earlier reports<sup>21)</sup> which show that the cell model provides an excellent approximation for the energy, pressure, specific heat, and Grüneisen  $\gamma$ . Our most important new result is that the quasi-harmonic approximation, which is not as good as the cell model in estimating other properties, actually does a good job of predicting the adiabatic elastic constants. Neither approximation provides an accurate estimate of the isothermal elastic constants.

We have calculated the adiabatic elastic constants for neon, argon, krypton, and xenon using quantum mechanics and the lattice-dynamics approximation for the full range of temperatures from absolute zero to the triple point at 0 pressure. We hope that these calculations will be useful to experimenters who wish to compare their results with the predictions of the Lennard-Jones 6-12 pair potential. In the future we hope to calculate adiabatic elastic constants for alkali-halide crystals.

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*Note added in proof.* Since we submitted this paper, Gornall and Stoicheff<sup>22)</sup> have reported experimental value of the adiabatic elastic constants for xenon. We have plotted their results in fig. 3 for comparison with our calculated values. The agreement is excellent, and is improved if one makes anharmonic corrections by means of table I.

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