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Lattice Dynamics with Three-Body Forces: Argon

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The specific heat, thermal expansion, and bulk modulus of crystalline argon at low temperatures (up to 12 °K) are calculated using pair potential functions known to be consistent with pair-interaction data, together with the Axilrod-Teller triple-dipole interaction. The methods of lattice dynamics are used and correction for anharmonicity is made. The potential of Barker and Pompe gives good agreement with experimental specific heats and a slight modification of this potential gives excellent agreement. The modified potential also gives excellent agreement with experimental thermal-expansion results, but the calculated bulk modulus is about 9% higher than current experimental estimates. Harmonic calculations are also made using the potential of Dymond and Alder. The resulting harmonic specific heats are in very poor agreement with experiment and there are very large anharmonic effects.

I. INTRODUCTION

Most theoretical calculations of the low-temperature properties of crystalline inert gases[1-6] have used simple-model potentials, in particular the Lennard-Jones 6-12 potential and the exp-6 potential, which are now known to differ considerably from the true pair potential, at least for argon. To test present understanding of the simplest solids, we have calculated low-temperature crystal properties for argon using the best available pair potentials[7-9] together with the Axilrod-Teller[10,11] triple-dipole interaction.

It is commonly assumed that the potential energy of a set of N inert-gas atoms can be written in the form

$$U=\sum_{i<j} u^{(2)}(ij)+\sum_{i<j<k} u^{(3)}(ijk)+\cdots , \qquad (1)$$

in which higher terms would depend on the coordinates of four, five, or more atoms; the functions $u^{(n)}(ijk\cdots)$ are assumed to vanish whenever *one* of the atoms $ijk\cdots$ is remote from the others, and the functions $u^{(2)}(ij)$ depend only on the distance between the two atoms, so that $u^{(2)}(ij)$ may be written $u(R_{ij})$.

The further approximation which is basic to our work is to neglect terms beyond the triplet term in (1) and to replace the triplet function $u^{(3)}(ijk)$ by the long-range Axilrod-Teller form

$$u^{(3)}(ijk)=\nu(1+3\cos\theta_1\cos\theta_2\cos\theta_3)/(R_1R_2R_3)^3 , \qquad (2)$$

in which $\theta_1\ \theta_2\ \theta_3$ and $R_1\ R_2\ R_3$ are the angles and sides of the triangle formed by the three atoms, and the coefficient ν is known to good accuracy from calculations using oscillator strengths derived from the absorption spectrum and sum rules.

Arguments have been given both for[8,12,13] and against[4,9] the usefulness of this approximation; detailed references are given in the papers cited. In our opinion the calculations of Copeland and Kestner,[13] which show explicitly that the neglected terms are small, together with the success with which a wide range of properties of solid, liquid, and gaseous argon can be correlated,[8,12] suggest that it is a good approximation.

Calculations of the effects of the triple-dipole interaction have been made by Chell and Zucker,[14,15] by Goetze and Schmidt,[16] and by Hüller, Goetze, and Schmidt.[17] In all of this work simple 6-12 and exp-6 pair potential functions were considered, and in addition the Einstein approximation was used to evaluate the zero-point energy.

In most of our calculations we have used the analytic form for the pair potential proposed by Barker and Pompe,[8] namely,

$$u(R)=\epsilon\left(e^{\alpha(1-r)}\sum_{i=0}^{L} A_i(r-1)^i-\sum_{i=0}^{2}\frac{C_{2i+6}}{\delta+r^{2i+6}}\right) , \qquad (3)$$

where r is R/R_m, with R_m being the separation at the minimum of the potential, and ϵ the depth at the minimum. The second summation in (3) ensures that the potential has the correct form at large distances where the asymptotic behavior is known to involve (negative) terms proportional to R^{-6}, R^{-8}, etc. The constant δ is included to suppress the divergence of these terms at small R. The coefficient of R^{-6} is known accurately and approximate calculations of the coefficients of R^{-8} and R^{-10} are available.[8] The first summation, intended to describe overlap effects important at small distances, has a form consistent with quantum-mechanical calculations which suggest an exponentially decreasing function multiplied by a relatively slowly varying polynomial. By including sufficient terms in this summation, the potential is given the necessary flexibility in the neighborhood of its minimum.

We have also made calculations for the numerical pair potential of Dymond and Alder.[9] In order to evaluate the derivatives of the potential required in the lattice dynamics calculations, we made least-squares polynomial fits in appropriate ranges of R. The nontrivial amount of work which this involved confirmed us in our preference for flexible analytic potentials rather than numerical potentials.

II. LATTICE DYNAMICS

The sites of a face-centered cubic (fcc) lattice may be specified by

$$\vec{r}(\lambda, \mu, \nu) = (\lambda\vec{a}_1 + \mu\vec{a}_2 + \nu\vec{a}_3)d , \tag{4}$$

where

$$\vec{a}_1 = (1, 1, 0)/\sqrt{2}, \quad \vec{a}_2 = (1, 0, 1)/\sqrt{2}, \quad \vec{a}_3 = (0, 1, 1)/\sqrt{2}, \tag{5}$$

and d is the nearest-neighbor distance; the cubic lattice parameter a is $d\sqrt{2}$. In the quasiharmonic approximation, the three frequencies $\nu_i(\vec{q}), i = 1, 2, 3$ corresponding to waves with wave vector $\vec{q}$ are determined by the eigenvalue equation[2]

$$4\pi^2 m[\nu_i(\vec{q})]^2 u^i_\alpha(\vec{q}) = \sum_{\beta=1}^{3} D_{\alpha\beta}(\vec{q}) u^i_\beta(\vec{q}) , \tag{6}$$

with

$$D_{\alpha\beta}(\vec{q}) = -\sum_{\lambda,\mu,\nu}{}' U_{000\alpha;\lambda\mu\nu\beta} \sin^2[\pi\vec{r}(\lambda, \mu, \nu)\cdot\vec{q}] . \tag{7}$$

In these equations, α, β specify the Cartesian components of the polarization vectors $u^i{}_\alpha(\vec{q})$, and $U_{000\alpha;\lambda\mu\nu\beta}$ is defined by

$$U_{000\alpha;\lambda\mu\nu\beta} = \frac{\partial^2 U}{\partial x_\alpha \partial x'_\beta} , \tag{8}$$

where x_α is the α component of the displacement of the atom at site (0, 0, 0), and x'_β is the β component of the displacement of the atom at site (λ, μ, ν); the derivatives are evaluated at zero displacement. The summation $\sum'$ is taken over all sets (λ, μ, ν) with λ, μ, ν integral (positive, negative, or zero) *except* (0, 0, 0).

The Helmholtz free energy of a crystal of N atoms is given by

$$A = U_0 + 12N\sum_{i=1}^{3} \iiint dU\,dV\,dW[\tfrac{1}{2}h\nu_i + \ln(1 - e^{-h\nu_i/kT})] , \tag{9}$$

where U_0 is the static lattice energy, and we have written

$$\vec{q} = (U, V, W)/a . \tag{10}$$

The integration is taken throughout the "irreducible $\frac{1}{48}$ of the Brillouin zone," defined by

$$0 < U < V < W < 1, \quad U + V + W < 1.5 . \tag{11}$$

The factor 12 is a normalization constant corresponding to this region; ν_i in (9) is understood to be a function of $\vec{q}$ and therefore of $U, V,$ and W. Similarly, the specific heat C_v is given by

$$C_v = 12Nk\sum_{i=1}^{3} \iiint \frac{dU\,dV\,dW(h\nu_i/kT)^2 e^{-h\nu_i/kT}}{(1 - e^{-h\nu_i/kT})^2} . \tag{12}$$

To evaluate other thermodynamic properties (pressure and compressibility), we computed the Helmholtz free energy for several values of the lattice constant and performed numerical differentiations.

To perform the integrations in (9) and (12) with high accuracy at low temperatures we used Gauss-Legendre quadrature with 10-point panels of varying width to provide a fine grid in the neighborhood of the origin. For most of our calculations, we used three panels for the W integration, from 0 to 0.1, 0.1 to 0.5, and 0.5 to 1; and two equal panels for the U and V integration [the limits for the U integration are 0 and min $(V, 1.5 - V - W)$, while those for the V integration are 0 and min $(W, 1.5 - W)$]. We made some calculations in which each of the panels in the above scheme was replaced by two equal panels; the error using this scheme should be negligible compared to that using the first scheme, so that the difference between the results of the two calculations gives a good estimate of the error involved in using the first scheme. The two methods gave calculated Debye temperatures which agreed to better than 0.01 °K at temperatures above 0.4 °K, so that we estimate the integration error in our computed Debye temperatures as less than 0.01 °K. This accuracy is more than sufficient for our purpose.

Note that with these integration schemes the normalization integral $12\iiint dU\,dV\,dW$ is not exactly 1; to ensure high accuracy at high temperatures, we divided our integrals by this factor. The error resulting from this at low temperatures is negligible.

III. THREE-BODY FORCES

The features of our calculation which are specific to three-body forces arise in the evaluation of the derivatives $U_{000\alpha;\lambda\mu\nu\beta}$. For brevity we will denote (λ, μ, ν) by $\vec{\lambda}$ and (0, 0, 0) by $\vec{0}$; we will also divide $U_{\vec{0}\alpha;\vec{\lambda}\beta}$ into two-body and three-body contributions,

$$U_{\vec{0}\alpha;\vec{\lambda}\beta} = U^{(2)}_{\vec{0}\alpha;\vec{\lambda}\beta} + U^{(3)}_{\vec{0}\alpha;\vec{\lambda}\beta} . \tag{13}$$

The vector $\vec{r}_{\vec{\lambda}}$ will denote the position of lattice site $\vec{\lambda}$ and $\vec{x}_{\vec{\lambda}}$ the displacement of the atom at that site, with components $x^\alpha_{\vec{\lambda}}$. For the two-body contribution we find immediately

$$U^{(2)}_{\vec{0}\alpha;\vec{\lambda}\beta}=-\left(\frac{u''(R)}{R^2}-\frac{u'(R)}{R^3}\right)\,x^{\alpha}_{\vec{\lambda}}x^{\beta}_{\vec{\lambda}}-\frac{u'(R)}{R}\,\delta_{\alpha\beta}\,, \tag{14}$$

where $\delta_{\alpha\beta}$ is the Kronecker δ, $x^{\alpha}_{\vec{\lambda}}$ is the α component of the vector $\vec{\mathrm{r}}_{\vec{\lambda}}-\vec{\mathrm{r}}_{\vec{0}}$, and R is $|\vec{\mathrm{r}}_{\vec{\lambda}}-\vec{\mathrm{r}}_{\vec{0}}|$.

The three-body contribution is given by

$$U^{(3)}_{\vec{0}\alpha;\vec{\lambda}\beta}=\sum_{\vec{\lambda}'\neq\vec{0},\,\alpha}\frac{\partial^2u^{(3)}(\vec{0},\vec{\lambda},\vec{\lambda}')}{\partial x^{\alpha}_{\vec{0}}\,\partial x^{\beta}_{\vec{\lambda}}} \tag{15}$$

in which the atoms are numbered by $\vec{0},\vec{\lambda},\vec{\lambda}'$ rather than i,j,k, as in Eq. (1); the derivatives are of course to be evaluated with $x^{\alpha}_{\vec{0}}$ and $x^{\beta}_{\vec{0}}$ zero. We may rewrite Eq. (2) in the form

$$u(\vec{0},\vec{\lambda},\vec{\lambda}')=\nu[z_1z_2z_3+\tfrac{3}{8}(z_1+z_2-z_3)(z_1-z_2+z_3)\times(-z_1+z_2+z_3)]\;(z_1z_2z_3)^{-5/2}, \tag{16}$$

where

$$z_1=|\vec{\mathrm{r}}_{\vec{\lambda}}+\vec{\mathrm{x}}_{\vec{\lambda}}-\vec{\mathrm{r}}_{\vec{0}}-\vec{\mathrm{x}}_{\vec{0}}|^2,\quad z_2=|\vec{\mathrm{r}}_{\vec{\lambda}'}+\vec{\mathrm{x}}_{\vec{\lambda}'}-\vec{\mathrm{r}}_{\vec{0}}-\vec{\mathrm{x}}_{\vec{0}}|^2,$$

$$z_3=|\vec{\mathrm{r}}_{\vec{\lambda}'}+\vec{\mathrm{x}}_{\vec{\lambda}'}-\vec{\mathrm{r}}_{\vec{\lambda}}-\vec{\mathrm{x}}_{\vec{\lambda}}|^2. \tag{17}$$

Then the derivative in (15) is given by

$$\frac{\partial^2u^{(3)}(0,\vec{\lambda},\vec{\lambda}')}{\partial x^{\alpha}_{\vec{0}}\,\partial x^{\beta}_{\vec{\lambda}}}=\sum_{p=1}^{3}\sum_{q=1}^{3}\frac{\partial^2u^{(3)}}{\partial z_p\partial z_q}\,\frac{\partial z_p}{\partial x^{\alpha}_{\vec{0}}}\,\frac{\partial z_q}{\partial x^{\beta}_{\vec{\lambda}}}+\frac{\partial u^{(3)}}{\partial z_1}\,\frac{\partial^2 z_1}{\partial x^{\alpha}_{\vec{0}}\,\partial x^{\beta}_{\vec{\lambda}}}=-4D_{11}X^{\alpha}_{\vec{\lambda}}X^{\beta}_{\vec{\lambda}}-4D_{12}X^{\alpha}_{\vec{\lambda}'}X^{\beta}_{\vec{\lambda}}-4D_{13}X^{\alpha}_{\vec{\lambda}}(X^{\beta}_{\vec{\lambda}}-X^{\beta}_{\vec{\lambda}'})-4D_{23}X^{\alpha}_{\vec{\lambda}'}(X^{\beta}_{\vec{\lambda}}-X^{\beta}_{\vec{\lambda}'})-2D_1\delta_{\alpha\beta}\,, \tag{18}$$

where

$$D_1=\frac{\partial u^{(3)}}{\partial z_1},\quad D_{pq}=\frac{\partial^2u^{(3)}}{\partial z_p\,\partial z_q}\quad. \tag{19}$$

Note that there is only one term involving the first derivative of u because only z_1 depends both on $x^{\alpha}_{\vec{0}}$ and on $x^{\beta}_{\vec{\lambda}}$. The evaluation of the derivatives D_1 and D_{pq} from Eq. (16) is a matter of algebra which will not be given here. We wrote expressions for these derivatives into our computer program and used Eq. (19) to evaluate the summand in (15), which was then summed over $\vec{\lambda}'$ (this is actually a triple summation over λ', μ', ν'). To check our algebra we performed a calculation in which the derivatives D_1, D_{pq} were found by numerical differentiation and found identical results. We actually included in the summations in Eq. (15) all terms (and only those terms) for which z_1, z_2, and z_3 were all less than N_nd^2, where N_n is a parameter which determines the number of neighbor shells considered in the calculation. It can be shown after some algebra that if all such contributions are to be included then λ, μ, ν and λ', μ', ν' must run from $-M_n$ to $+M_n$, where M_n is the integral part of $(\frac{3}{2}N_n)^{1/2}$, with sets for which z_1, z_2, or z_3 is greater than N_nd^2 (or equal to zero) being rejected. The quantities $U^{(3)}_{\vec{0}\alpha;\vec{\lambda}\beta}$ are all proportional to ν/d^{11} so that they can be evaluated once for all if N_n is fixed. We do not give tables because they would be too bulky and the computational effort required to generate values is not excessively large.

In calculating the static lattice energy U_0, we calculated two-body contributions out to $R=(60)^{1/2}d$ directly, using tabulated numbers of neighbors; interactions at larger distances were approximated by an integral. For the three-body contribution, we used the result of Chell and Zucker,[14] which is extrapolated to infinite range.

IV. ANHARMONIC CORRECTIONS

Anharmonic corrections to the free energy may be computed by perturbation theory. According to Klein *et al.*[4] and Feldman and Horton[18] the cubic and quartic anharmonic corrections to the molar Helmholtz free energy for a crystal with nearest-neighbor two-body interactions are given by

$$A_3=(-\tfrac{9}{2}g)\;[a_3^2\,S_1\,(T_R,a_1)+4a_3S_2\,(T_R,a_1)+4S_3(T_R,a_1)], \tag{20}$$

$$A_4=(\tfrac{27}{4}g)\;[a_4I_1\,(T_R,a_1)+2a_3I_2(T_R,a_1)+4I_3\,(T_R,a_1)], \tag{21}$$

where

$$a_n=R^{2n-4}[D^n u(R)]/[D^2u(R)], \tag{22}$$

$$g=(Nh)^2/(MR^2), \tag{23}$$

$$T_R=(kT/hR)\;[N\,D^2u(R)/M]^{-1/2}. \tag{24}$$

In these expressions, D is $(1/R)(d/dR)$ and R is to be replaced by the nearest-neighbor distance d; M is the gram atomic weight (not atomic mass as in Klein *et al.*); and $S_i(T_R,a_1)$ and $I_i(T_R,a_1)$ are certain integrals tabulated by Klein *et al.*[4] and Feldman and Horton.[18]

We have made the approximation of using these results directly in our calculation, thus ignoring (in calculating anharmonic corrections) interactions between non-nearest neighbors and three-body interactions. We estimate that this introduces errors of the order of 10% in the anharmonic corrections; the resulting errors in our calculated Debye temperatures are of the order of 0.4%, and this is our principal source of error.

To use the tabulated values of S_i and I_i in (20) and (22) it is necessary to interpolate both in the variable a_1, which depends on volume or lattice spacing, and in the reduced temperature variable T_R. To interpolate in a_1, we used 5-point Lagrange interpolation. To interpolate in T_R we constructed expressions of the type

$$X=a+T_R^4\,(b+cT_R^2)/(1+dT_R^2+eT_R^4), \tag{25}$$

in which X represents I_i or S_i, and the constants were determined from the results tabulated for zero temperature and for the four-highest nonzero temperatures. We found that these expressions reproduced the values tabulated for the lowest nonzero temperature to within 1 in the last significant figure. This represents a modification of the procedure of Klein *et al.*[4] in that (25) has the correct asymptotic form not only at high temperatures but also at low temperatures. It appears to give good results even at very low temperatures where the unmodified procedure of Klein *et al.* is unsatisfactory. For the Barker-Pompe potential (Sec. V) the extrapolated zero-temperature Debye temperature calculated using (25) was within 0.2 °K of the value calculated by the accurate method of Barron and Klein[3] (also assuming nearest-neighbor interactions). Thus these interpolation procedures do not introduce serious errors.

V. RESULTS: POTENTIAL OF BARKER AND POMPE

This potential is given by Eq. (3) with $L = 3$, $A_0 = 0.2349$, $A_1 = -4.7735$, $A_2 = -10.2194$, $A_3 = -5.2905$, $C_6 = 1.0698$, $C_8 = 0.1642$, $C_{10} = 0.0132$, $\alpha = 12.5$, $\delta = 0.01$, $\epsilon/k = 147.7$ °K, and $R_m = 3.756$ Å. These parameters were determined to be consistent for small R with molecular beam-scattering data and for large R with the known value of C_6 and approximately known values of C_8 and C_{10}. In addition, the potential was constrained to fit (when used in conjunction with the Axilrod-Teller potential) the experimental lattice spacing of crystalline argon at 0 °K, the cohesive energy of crystalline argon (approximately), and the experimental second virial coefficients of gaseous argon.

We investigate first the effect of the number of neighbor shells included in the calculation, which we have denoted by N_n, on the calculated Debye temperatures. We will use throughout the value of the three-body parameter $\nu = 73.2 \times 10^{-84}$ erg cm^9 used by Barker and Pompe and due to Leonard.[19] Some sample results are listed in Table I. It is clear that the accuracy attained with $N_n = 42$ is excellent and that even a value as small as $N_n = 9$ does not lead to serious error; we use the latter value for exploratory calculations and the former for final calculations.

TABLE I. Debye temperatures (anharmonic) for different values of N_n; Barker-Pompe potential.

$N_n = T$ °K	1	9	25	42
0.4	95.94	90.13	89.94	89.91
1.2	95.82	90.03	89.85	89.82
2.4	95.22	89.50	89.35	89.33
4.8	90.61	85.52	85.44	85.43
8.0	84.50	81.12	81.08	81.08
12.0	83.20	80.82	80.79	80.79

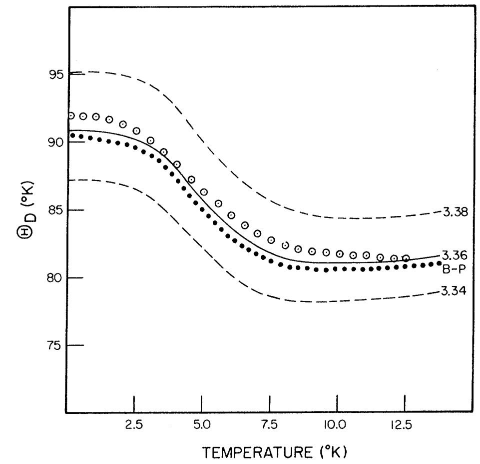

FIG. 1. Calculated and experimental Debye temperatures. Open circles, experimental results of Finegold and Phillips (Ref. 20). Black circles, calculated with the Barker-Pompe potential. The curves are calculated for the potentials of Sec. VI and are labeled with the value of R_0.

The temperature dependence of the calculated Debye temperature is shown in Fig. 1, with the experimental data of Finegold and Phillips[20] (these results are probably more accurate in this temperature range than those of Flubacher *et al.*[21] which lie about 1 °K higher). The integrated thermal expansion is compared with experiment[22,23] in Fig. 2.

The agreement with experiment is very good, considering that the specific-heat data were not used in determining the potential. It is known that this potential gives good agreement with experimental third virial coefficients[8], and fair agree-

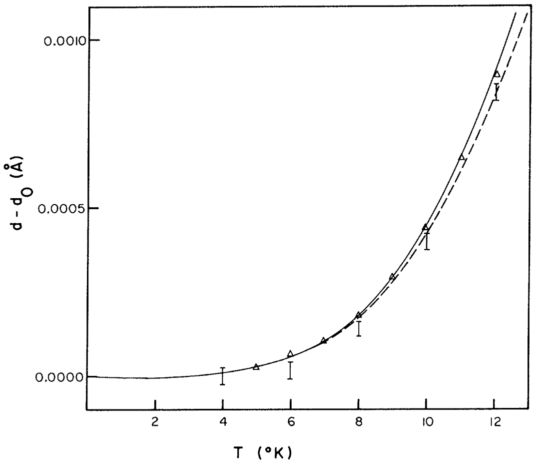

FIG. 2. Integrated thermal expansion $d - d_0$. Dashed curve, calculated for the Barker-Pompe potential. Solid curve, calculated for the final potential of Sec. VI. Triangle, experimental, Tilford and Swenson (Refs. 2 and 3). I, experimental, Peterson *et al.* (Ref. 12).

ment with experimental gas-transport properties[8] and liquid-equilibrium properties.[12] Thus the potential correlates with fair accuracy an extraordinarily wide range of properties of argon. However, it is clear from Fig. 1 that the potential can be improved, and this is undertaken in Sec. VI.

VI. IMPROVED POTENTIAL

To improve on the Barker-Pompe potential we included two extra terms in the polynomial multiplying the exponential in (3); that is we chose $L = 5$. We retained the values $\alpha = 12.5$, $\delta = 0.01$ of Barker and Pompe and used the remaining parameters to fit all the experimental data used by Barker and Pompe, *plus* the value of the Debye temperature at 0 °K; at the same time we attained an essentially exact fit of the cohesive energy at 0 °K, for which the Barker-Pompe potential was in error by about 1.5%. For references to all experimental data we refer to the paper of Barker and Pompe.

The fitting procedure was as follows. For given ϵ and R_m we determined C_6, C_8, and C_{10} to give the desired coefficients of R^{-6}, R^{-8}, and R^{-10} at large distances. For given A_5, we then determined A_2, A_3, and A_4 to give the desired value of the potential and its derivative at $R = 2$ Å, and a desired value of the separation at the zero of the potential R_0. This involved solution of a set of three linear equations. Note that A_0 and A_1 are determined by the fact that the potential has a minimum of depth $-\epsilon$ at $R = R_m$. We then varied A_5 to find the best fit of experimental second virial coefficients. This gave the best potential consistent with the assumed ϵ, R_m, and R_0. We then multiplied R_m and ϵ by the ratio of experimental to calculated lattice spacing and cohesive energy, respectively, and repeated the whole process until convergence was attained, typically within about 10 iterations.

This led to a class of potentials, fitting all the data used by Barker and Pompe, and with different values of R_0. We calculated Debye temperatures for several of these potentials, and the results are shown in Fig. 1. It is clear that the low-temperature specific heats are sensitive to the remaining parameter R_0. By inverse interpolation we estimated that the experimental value of the Debye temperature at 0 °K was fairly closely reproduced with $R_0 = 3.3666$ Å. For this potential the parameters were $\epsilon/k = 140.23$ °K, $R_m = 3.7630$ Å, $A_0 = 0.29214$, $A_1 = -4.41458$, $A_2 = -7.70182$, $A_3 = -31.9293$, $A_4 = -136.026$, $A_5 = -151.000$, $C_6 = 1.11976$, $C_8 = 0.171551$, and $C_{10} = 0.013747$; for completeness we append $L = 5$, $\alpha = 12.5$, and $\delta = 0.01$.

Using these parameters we computed the Helmholtz free energy and specific heat for five values of the nearest-neighbor distance d varying in steps of 1%. From these we computed pressures and used inverse interpolation to find the zero-pressure value of d as a function of temperature. Near 0 °K the value of d was 3.7548 Å compared with the experimental value 3.7552 Å; the calculated cohesive energy was −1844 cal/mole compared with the experimental value −1846 ± 7 cal/mole. This verifies the adequacy of our fitting procedure.

The calculated Debye temperatures are compared with the experimental data of Finegold and Phillips[20] in Fig. 3. The computed results are very close to the experimental results; the temperature dependence is reproduced well, and this was not used in determining the potential.

The computed integrated thermal expansion is shown in Fig. 2 with experimental data for comparison. In this temperature range the direct measurements of Tilford and Swenson[23] are expected to be more accurate than the x-ray results of Peterson *et al.*[22] The agreement with experiment is almost perfect; we note that these data were in no way used in determining the potential. The fact that the present potential and the rather similar Barker-Pompe potential give appreciably different results for the thermal expansion shows that the thermal expansion is sensitive to the form of the potential, so that this agreement must be regarded as significant. It is known[4] that the 6-12 potential gives errors of the order of 20% in the low-temperature thermal expansion.

By numerical differentiation of the pressure we calculated the bulk modulus and found the value 2.92×10^{10} dyn cm^{-2} near 0 °K; this quantity varies only slightly with temperature in the range 0–12 °K. This is about 9% higher than the experimental value 2.67×10^{10} dyn cm^{-2} of Peterson *et al.*[22] derived from x-ray measurements. It is already known[4] that the Barker-Pompe potential also gives a bulk modulus about 10% higher than experiment. The

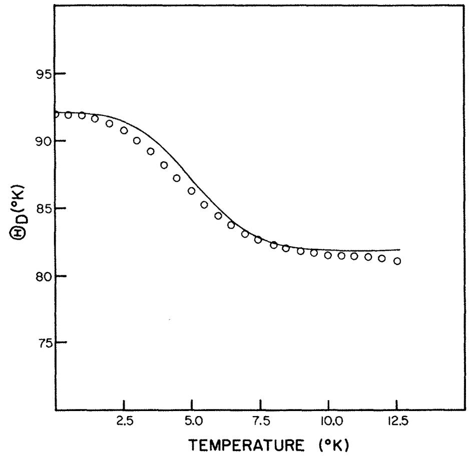

FIG. 3. Calculated and experimental Debye temperatures. The curve gives values for the final potential of Sec. VI, circles are experimental values of Finegold and Phillips (Ref. 20).

sound velocity measurements of Keeler and Batchelder[24] give a bulk modulus agreeing with that of Peterson *et al.*, but this involves an uncertain extrapolation and should be given less weight than the x-ray measurements.

In any case, there is a real discrepancy between theory and experiment on this point. If our basic assumptions (neglect of triplet interactions other than the triple-dipole interactions, and of higher many-body interactions) are correct, then it is difficult to see anything in the theoretical calculations which could lead to such a discrepancy. Clearly these assumptions remain open to question, in spite of the impressive correlation of data to which they lead (in addition to the data discussed here the present potential gives good agreement with experimental phonon disperison curves,[25] third virial coefficients, and gas transport properties[26]).

On the other hand, there is an open question concerning the experiments, in connection with the observed effect of the helium used as pressure fluid on the lattice spacing. In fact, in Fig. 1 of the paper by Peterson *et al.*[22] the points corresponding to the *initial* increase of helium pressure appear to have a slope close to that corresponding to our theoretical bulk modulus. Further theoretical and experimental work is required.

VII. POTENTIAL OF DYMOND AND ALDER

Dymond and Alder have derived a numerical potential which has essentially the same short-range and very long-range behavior as the potentials already discussed, and which give an excellent fit of second virial coefficients and gas-transport properties (but not in fact[26] a better fit than the potential of Sec. VI).

We calculated quasiharmonic specific heats, both with and without the Axilrod-Teller interaction for this potential. The results are shown in Table II. The calculated Debye temperatures are smaller by a factor of 2 than the experimental values (corresponding to specific heats larger than experimental by a factor of 8), and show the wrong temperature dependence. However, when we attempted to compute anharmonic corrections by the method of Sec. IV we found much larger Debye temperatures (around 120 °K) at 0.4 °K and *negative* specific heats at all higher temperatures. This potential is so highly anharmonic that the perturbation theory for anharmonic corrections fails even at the lowest temperatures. One cannot exclude the possibility that a nonperturbative anharmonic calculation would lead to much better agreement with experiment for this potential, but it does seem unlikely that the temperature dependence would come out closely similar to that given by the potentials of Secs. V and VI, for which the temperature dependence is determined largely by the quasiharmonic contributions.

TABLE II. Debye temperatures for the potential of Dymond and Alder.

	Three-body force		No three-body force	
T(K°)	Quasi-harmonic	Anharmonic	Quasi-harmonic	Anharmonic
0.39	46.8	(142.3)	46.5	(122.8)
0.79	47.2		46.9	
1.18	47.7		47.4	
2.37	48.4		48.1	
4.74	48.2		47.9	
7.90	49.6		49.1	
11.85	50.9		50.3	

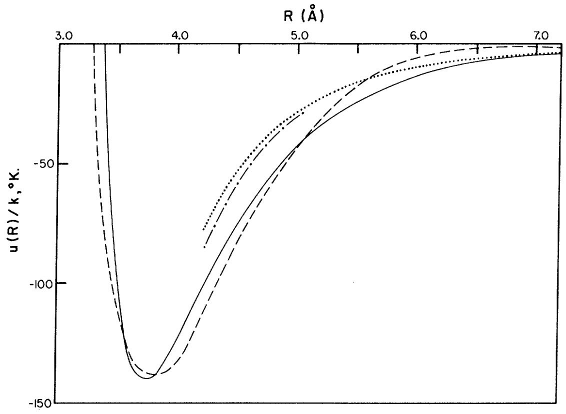

FIG. 4. The potentials of Sec. VI (solid curve) and of Dymond and Alder (dashed curve). The dotted curve shows the R^{-6} dispersion interaction, and the dash-dotted curve shows the sum of the R^{-6}, R^{-8}, and R^{-10} contributions.

The potential of Dymond and Alder is compared in Fig. 4 with the potential of Sec. VI. The dotted curve shows the contribution of the R^{-6} dispersion interaction. The least satisfying feature of the Dymond-Alder potential is that the potential is much less negative than the R^{-6} interaction in a range of separations (beyond 6 Å) in which the positive overlap contributions would be expected to be very small (note that higher multipole dispersion interactions are negative). This fact, together with the specific heats, suggests that the potential of Sec. VI is closer to the truth. Apart from this behavior at large distances and the detailed behavior near the minimum, there is reasonable agreement between the two potentials.

VIII. GENERAL DISCUSSION

It is of some interest to examine qualitatively the effects of the three-body interaction. In Table III we show values of the Debye temperature at 0 °K (extrapolated) and of the zero-point energy, calculated for the potential of Sec. VI both with

TABLE III. Zero-temperature Debye Θ and zero-point energy for the potential of Sec. VI.

	θ_0 (°K) Quasi-harmonic	θ_0 (°K) Anharmonic	U_z (cal/mole) Quasi-harmonic	U_z (cal/mole) Anharmonic
No three-body interaction	88.8	91.8	179.9	186.2
Three-body interaction	89.0	92.1	181.4	187.7

and without the three-body interaction. The effect of the three-body interaction is to increase the Debye temperature by about 0.2% and to increase the zero-point energy by 0.7%. The latter result disagrees with that of Chell and Zucker[14] who found, using the Einstein approximation, that three-body forces *reduce* the zero-point energy. The explanation is that Chell and Zucker omitted a nonzero sum in their calculation in the belief that it vanished because of symmetry; this will be discussed in more detail elsewhere.[27]

The zero-point energy is increased proportionately more than the zero-temperature Debye θ because the low-frequency transverse modes which contribute most to the low-temperature specific heat, and the corresponding elastic shear constants, are almost unaffected by the three-body interaction,[25] while the longitudinal frequencies, which contribute more to the zero-point energy, and the bulk modulus are substantially increased. This also explains why the present calculation with three-body forces leads to a higher bulk modulus than previous calculations with only two-body interactions. The most important effect of the three-body interactions is on the static lattice energy and its volume dependence.

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