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ISOTHERMAL ELASTIC CONSTANTS FOR ARGON. THEORY AND MONTE CARLO CALCULATIONS*

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Synopsis

Exact expressions for the isothermal elastic constants, C_{11}^T, C_{12}^T, and C_{44}^T, are derived for cubic crystals whose molecules interact with pairwise-additive central forces. The exact expressions contain *fluctuation terms*, omitted by Born, which make important contributions at nonzero temperatures.

We use the Monte Carlo technique to evaluate C_{11}^T, C_{12}^T, and C_{44}^T for argon at 40, 60 and 80 K. The isothermal compressibility $\beta_T \doteq 3/(C_{11}^T + 2C_{12}^T)$, calculated from the numerical results, is in good agreement with experiment at all three temperatures.

1. *Introduction.* Both experimentalists and theoreticians are attracted to rare-gas crystals. Because these systems are the simplest available, the hope of understanding their properties on a molecular level and achieving quantitative agreement between experiment and theory is best. Solid-phase properties are slightly more complicated than those of the fluid because *shape* as well as volume and temperature can be changed. The work required to distort a solid is described by the elastic constants, which are analogs of the bulk modulus for a fluid. For the rare-gas crystals, straightforward measurement of the work of distortion is difficult. At low temperatures the crystals are very brittle; at higher temperatures, near melting, they have a mushy consistency. Instead of a direct measurement, an indirect approach is used. High-frequency sound velocities can be measured. In a cubic crystal such as argon, measurement of the longitudinal and transverse sound speeds in a known direction allows the three independent *adiabatic* elastic constants C_{11}^S, C_{12}^S, and C_{44}^S to be determined. These velocities have recently been reported for argon as functions of temperature by Moeller and Squire[1]). The *isothermal* elastic constants, which describe the change in free energy with slow distortion of the crystal, as opposed to the rapid adiabatic dis-

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tortion caused by a sound wave, have never been measured in rare-gas crystals because of the tendency of the crystals either to crack or to flow, depending on the temperature.

The lattice theory of elastic constants was first developed by Born[2]). Since Born had no access to modern computers, his results were restricted to the simplest case, perfect crystals at absolute zero. Computers make it possible to study the more complicated finite-temperature case in detail, without, however, providing a useful analytic theory. It is the lack of a simple theory for treating anharmonic effects in crystals that still hampers quantitative calculations of the elastic constants, as well as other thermodynamic properties, at temperatures different from absolute zero. Limitations of present theories are discussed at length by Leibfried and Ludwig[3]).

Since the Monte Carlo computer method for calculating thermodynamic properties takes all interactions into account exactly (within the assumptions of a given force-law and classical mechanics) it seems to us ideally suited for determining elastic constants for solid argon. We will not describe the Monte Carlo method itself because that has already been done[4,5]).

In section 2 the theoretical development of expressions is given for the isothermal elastic constants as ensemble-average functions of particle coordinates and the interparticle force law. No approximations, such as treating vibrations as small or quasi-harmonic, are made. We follow Born's treatment for the energy, applied to the Helmholtz free energy, deriving expressions for the derivatives of the Helmholtz free energy with respect to strain components (distortions of the lattice structure). The only difference between our expressions and Born's is that ours include *fluctuation terms* which vanish at absolute zero, but which become important, contributing as much as 30% of the simpler *Born terms*, for the solid at high temperatures.

In section 3 the results of the Monte Carlo calculations are presented. It is shown that the results for isothermal compressibility are in good agreement with the experiments of Peterson, Batchelder, and Simmons[6]). In the last section the results are compared to previous work, and the conclusion is drawn that a new theory is needed to calculate the fluctuation terms as well as the high-temperature form of the Born terms. It is hoped that *experiments* on the isothermal elastic constants will eventually be carried out to check further the adequacy of the pair potentials used in theoretical calculations.

2. *Theory*. In this section we derive expressions for the isothermal elastic constants which can be evaluated conveniently by Monte Carlo calculation. The elastic constants describe the change of Helmholtz free energy, which is $-kT$ times the logarithm of the canonical partition function, with changes in the shape of a crystal from an initial cube. In order to derive expressions for these constants in terms of particle coordinates, the partition function is first written for a crystal of general shape. This gives the free energy as

a function of temperature and the so-called strain tensor, which describes the distortion from a perfect cube. Straightforward differentiation then yields the desired expressions for the elastic constants.

Following Born [7]), we describe the crystal lattice with a set of three molar basis vectors, $\boldsymbol{a}_i$, which determine the lattice sites by means of the equation

$$\boldsymbol{r}^{\bar{l}} = l^i \boldsymbol{a}_i. \tag{1}$$

In this equation, and in those that follow, the unbarred indices (i or j) range over the values 1, 2 and 3. An unbarred index which occurs twice in the same term will imply a summation. A barred index ($\bar{l}$ or $\bar{m}$) stands for the three integers used to label the lattice sites in the crystal. For example, $\bar{l}$ stands for $\{l^1, l^2, l^3\}$. We ultimately consider a face-centered cubic argon crystal, for which the only allowed values for the barred indices are those for which the sum of the three components is equal to an even integer. The vector $\boldsymbol{r}^{\bar{l}}$ gives the position of the $\bar{l}$th lattice site.

We restrict ourselves to the description of homogeneous deformations and we allow the molar basis vectors to change as the lattice is deformed. Thus, when the lattice is undeformed, the three vectors $\boldsymbol{a}_i$ are mutually orthogonal and are identical in length; but when the lattice is deformed, the lengths of the $\boldsymbol{a}_i$ and the angles between them may change. We take, as a measure of strain, the tensor

$$\eta_{ij} = \frac{1}{2}\left\{\frac{1}{a^2}\, a_{ij} - \delta_{ij}\right\}, \tag{2}$$

where $a_{ij} = \boldsymbol{a}_i \cdot \boldsymbol{a}_j$ is the metric tensor of the molar basis vectors, δ_{ij} is the Kronecker delta, and a is the length of the molar basis vectors in the unstrained state. The quantity η_{ij}, defined in eq. (2), is the nonlinear Lagrangian strain tensor [8]).

The position vector, $\boldsymbol{x}^{\bar{l}}$ of the $\bar{l}$th particle is the sum of $\boldsymbol{r}^{\bar{l}}$ given by eq. (1) and a vector, $\boldsymbol{q}^{\bar{l}}$, which gives the displacement from the lattice site due to the thermal motion of the particle. If $q^{\bar{l}i}$ are the coordinates of $\boldsymbol{q}^{\bar{l}}$ with respect to the basis vectors $\boldsymbol{a}_i$, then we have

$$\boldsymbol{x}^{\bar{l}} = (l^i + q^{\bar{l}i})\, \boldsymbol{a}_i = x^{\bar{l}i} \boldsymbol{a}_i, \tag{3}$$

where $x^{\bar{l}i}$ are the coordinates of the position vector with respect to the molar basis vectors. As a final geometrical consideration, we can use eqs. (2–3) to express the scalar distance, $r^{\bar{l}\bar{m}}$, between the $\bar{l}$th and $\bar{m}$th particles in the form

$$r^{\bar{l}\bar{m}} = [(x^{\bar{l}j} - x^{\bar{m}j})(x^{\bar{l}i} - x^{\bar{m}i})\, a^2 \cdot (2\eta_{ij} + \delta_{ij})]^{\frac{1}{2}}. \tag{4}$$

We now assume that the particles in the lattice interact in a pairwise fashion and that the interaction depends only on the distance between them. If we use $\phi(r)$ to represent the potential energy of the interaction, then the classical partition function for a perfect lattice will be given by the equation

$$Z = \frac{(2\pi mkT)^{3N/2}}{h^{3N}} \int\limits_{\Delta} \cdots \int\limits_{\Delta} \mathrm{d}\boldsymbol{x}^{\bar{l}} \cdots \mathrm{d}\boldsymbol{x}^{\bar{m}} \exp\left(-\sum \phi(r)/kT\right), \tag{5}$$

where Z is the canonical partition function, m is the particle mass, N is the number of particles in the system, k is Boltzmann's constant, h is Planck's constant, and T is the temperature. The Δ's indicate that in eq. (5) each particle is constrained to stay closer to its own lattice site than to any other. The summation symbol in eq. (5), and in the following equations, denotes a sum over all distinct pairs of particles, and the argument of ϕ is the interparticle distance $r^{\bar{l}\bar{m}}$ of the pair under consideration. Finally, since the Helmholtz free energy is related to Z by the equation

$$A = -kT \ln Z, \tag{6}$$

we can use eqs. (4–6) to obtain the derivatives* of A with respect to η_{ij}. We have

$$\frac{1}{V}\left(\frac{\partial A}{\partial \eta_{ij}}\right)_T = \frac{a^2}{V}\left\langle \sum \frac{\phi'}{r}(x^{\bar{l}i} - x^{\bar{m}i})(x^{\bar{l}j} - x^{\bar{m}j})\right\rangle, \tag{7}$$

and

$$\begin{aligned} C^T_{ijpq} = \frac{1}{V}\left(\frac{\partial^2 A}{\partial \eta_{ij}\,\partial \eta_{pq}}\right)_T = \frac{a^4}{VkT} &\left\{\left\langle \sum \frac{\phi'}{r}(x^{\bar{l}i} - x^{\bar{m}i})(x^{\bar{l}j} - x^{\bar{m}j})\right\rangle \cdot\right. \\ &\cdot\left\langle \sum \frac{\phi'}{r}(x^{\bar{l}p} - x^{\bar{m}p})(x^{\bar{l}q} - x^{\bar{m}q})\right\rangle - \\ &- \left\langle \left[\sum \frac{\phi'}{r}(x^{\bar{l}i} - x^{\bar{m}i})(x^{\bar{l}j} - x^{\bar{m}j})\right] \cdot\right. \\ &\left.\left.\cdot\left[\sum \frac{\phi'}{r}(x^{\bar{l}p} - x^{\bar{m}p})(x^{\bar{l}q} - x^{\bar{m}q})\right]\right\rangle\right\} + \\ &+ \frac{a^4}{V}\left\langle \sum \frac{\phi''}{r^2}(x^{\bar{l}i} - x^{\bar{m}i})(x^{\bar{l}j} - x^{\bar{m}j})(x^{\bar{l}p} - x^{\bar{m}p})(x^{\bar{l}q} - x^{\bar{m}q})\right\rangle - \\ &- \frac{a^4}{V}\left\langle \sum \frac{\phi'}{r^3}(x^{\bar{l}i} - x^{\bar{m}i})(x^{\bar{l}j} - x^{\bar{m}j})(x^{\bar{l}p} - x^{\bar{m}p})(x^{\bar{l}q} - x^{\bar{m}q})\right\rangle. \end{aligned} \tag{8}$$

In eqs. (7–8) the symbol $\langle X \rangle$ stands for the thermal average of X defined

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*) We have left out the "kinetic" contributions to the elastic constants in eqs. (7) and (8) because these are generally negligible for solids. These contributions, which come from the additive term $-NkT \ln V$ in the Helmholtz free energy, are $-NkT\delta_{ij}$ for $(\partial A/\partial \eta_{ij})$ and $2NkT\delta_{iq}\delta_{jp}$ for $(\partial^2 A/\partial \eta_{ij}\partial \eta_{pq})$. These terms are included in eqs. (10) and (12). Note that $C^T_{44} = \frac{1}{4}(C^T_{1212} + C^T_{1221} + C^T_{2112} + C^T_{2121})$.

by the equation

$$\langle X\rangle = \frac{(2\pi mkT)^{3N/2}}{Zh^{3N}} \int_{\Delta}\cdots\int_{\Delta} \mathrm{d}\boldsymbol{x}^{l}\cdots \mathrm{d}\boldsymbol{x}^{m}\, X\cdot\exp(-\textstyle\sum \phi/kT). \tag{9}$$

The quantities C^T_{ijpq} are the second-order isothermal elastic constants of the lattice[9]). For a cubic crystal, only three of the C^T_{ijpq} are nonzero and unique: C^T_{11}, C^T_{12}, and C^T_{44}. The number of subscripts has been reduced by the usual Voigt[10]) notation.

For these particular cases, eq. (8) becomes

$$C^T_{11} = \frac{1}{VkT}\left\{\left\langle \sum \frac{\phi'}{r}(\Delta x)^2\right\rangle^2 - \left\langle\left[\sum \frac{\phi'}{r}(\Delta x)^2\right]^2\right\rangle\right\} + \\ + \frac{1}{V}\left\langle \sum \frac{\phi''}{r^2}(\Delta x)^4\right\rangle - \frac{1}{V}\left\langle \sum \frac{\phi'}{r^3}(\Delta x)^4\right\rangle + \frac{2NkT}{V}, \tag{10}$$

$$C^T_{12} = \frac{1}{VkT}\left\{\left\langle \sum \frac{\phi'}{r}(\Delta x)^2\right\rangle\left\langle \sum \frac{\phi'}{r}(\Delta y)^2\right\rangle - \\ - \left\langle \sum \frac{\phi'}{r}(\Delta x)^2\cdot \sum \frac{\phi'}{r}(\Delta y)^2\right\rangle\right\} + \\ + \frac{1}{V}\left\langle \sum \frac{\phi''}{r^2}(\Delta x)^2(\Delta y)^2\right\rangle - \frac{1}{V}\left\langle \sum \frac{\phi'}{r^3}(\Delta x)^2(\Delta y)^2\right\rangle, \tag{11}$$

$$C^T_{44} = \frac{1}{VkT}\left\{\left\langle \sum \frac{\phi'}{r}\Delta x\,\Delta y\right\rangle^2 - \left\langle\left[\sum \frac{\phi'}{r}\Delta x\,\Delta y\right]^2\right\rangle\right\} + \\ + \frac{1}{V}\left\langle \sum \frac{\phi''}{r^2}(\Delta x)^2(\Delta y)^2\right\rangle - \frac{1}{V}\left\langle \sum \frac{\phi'}{r^3}(\Delta x)^2(\Delta y)^2\right\rangle + \frac{NkT}{V}, \tag{12}$$

where the quantities Δx, Δy, and Δz represent the x, y, and z Cartesian coordinates of $(\boldsymbol{x}^l - \boldsymbol{x}^m)$. In the remainder of the paper we will refer to the term in braces as the "fluctuation term", while the following terms in each of these expressions will constitute the "Born term" and "kinetic" term.

3. *Numerical results.* To calculate the isothermal elastic constants for argon, it is necessary to determine the ensemble averages which appear in eqs. (10–12). We use the pairwise-additive Lennard-Jones potential,

$$\phi(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \tag{13}$$

with the values of ε and σ determined for crystalline argon by Horton and Leech[11]):

$\varepsilon/k = 119$ K, $\sigma = 3.40$ Å.

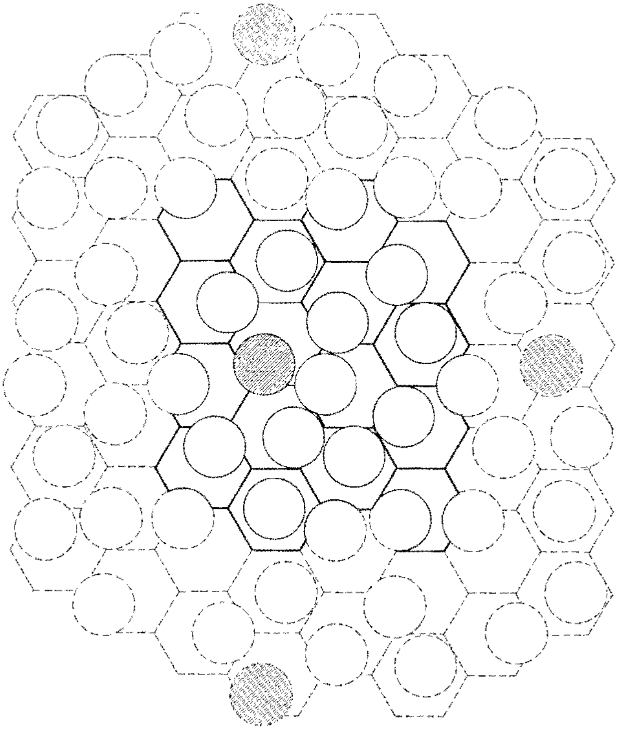

Fig. 1. A two-dimensional single-occupancy system. In this system (heavy lines) each particle is restricted to a cell. In the Monte Carlo calculations periodic boundary conditions were used so that each particle interacted with the $N-1$ particles or periodic images (light lines) closest to it. To illustrate the periodic boundary one particle and three of its images have been shaded.

These values of the parameters, and the Lennard-Jones potential function itself, appear to roughly describe the thermodynamic properties of solid argon. This has been borne out in recent Monte Carlo calculations of the pressure and internal energy in an investigation of thermal defects in solid argon[12]).

The classical system considered for these calculations contained 108 particles initially located at the lattice sites of a face-centered cubic lattice. The x-ray lattice spacing[13]) at the corresponding values of the temperatures were used. Surface effects were eliminated by using periodic boundary conditions, as shown for an analogous two-dimensional system in fig. 1. The molecules were constrained to remain inside spherical cells centered at the lattice sites. The cell radius was one-half the nearest-neighbor distance. The choice of these cells rather than the larger Wigner-Seitz cells has no effect upon the results. Less than 0.01% of the Monte Carlo moves were disallowed by this geometric restraint. Most of these moves would have been rejected anyway because of the resulting high energy.

As the quantities which we are interested in calculating depend upon the lattice being infinite in extent, the results for the actual finite system were corrected by considering the lattice outside the fundamental Monte Carlo cell to be a static lattice. The correction term for a given quantity was determined by taking the difference in the static lattice value of the quantity for the finite system and the static lattice value for the same quantity for the infinite system. This technique was found to be satisfactory in earlier Monte Carlo calculations[12]) on systems containing 32 and 108 particles. The number-dependent corrections gave values for both energy and pressure in good agreement for the two different sized systems.

TABLE I

The isothermal elastic constants (in units of 10^{10} dynes/cm^2) as functions of temperature and lattice spacing for solid argon. The first three sets of data are near zero pressure, while the last two sets describe the solid under tension and compression, respectively. The expected error in the Born terms is about 1%, while the expected error in the fluctuation terms varies from about 5% to 10%. The perfect-lattice nearest-neighbor distance is d.

T (kelvins)	d (ångstroms)	Corrected Born term	Fluctuation Term	Kinetic Term	Corrected constant	Static-lattice constant
40	3.780	3.57	−0.76	0.03	$C_{11}^T = 2.84$	2.654
		2.03	−0.42	0.00	$C_{12}^T = 1.61$	1.601
		2.03	−0.36	0.01	$C_{44}^T = 1.69$	1.60
60	3.813	3.38	−1.14	0.04	$C_{11}^T = 2.28$	2.064
		1.90	−0.59	0.00	$C_{12}^T = 1.31$	1.288
		1.90	−0.48	0.02	$C_{44}^T = 1.44$	1.288
80	3.857	3.12	−1.55	0.05	$C_{11}^T = 1.62$	1.428
		1.72	−0.84	0.00	$C_{12}^T = 0.88$	0.949
		1.72	−0.59	0.03	$C_{44}^T = 1.16$	0.949
40	3.857	2.34	−0.63	0.03	$C_{11}^T = 1.73$	1.428
		1.37	−0.49	0.00	$C_{12}^T = 0.88$	0.949
80	3.780	4.39	−1.61	0.06	$C_{11}^T = 2.83$	2.654
		2.40	−0.89	0.00	$C_{12}^T = 1.51$	1.601

In table I we have tabulated the Born, fluctuation and kinetic terms for eqs. (10–12) at three particular temperatures: 40, 60, and 80 K. The Monte Carlo runs for all results reported were 300 000 configurations in length. The initial 50 000 configurations were excluded in the computation of ensemble averages. In addition, ensemble averages were determined by averaging a given quantity for all three equivalent directions. For example, the ensemble average of $\langle \sum (\phi'/r)(\Delta x)^2 \rangle$ used in calculating C_{11}^T was determined by averaging the result for this expression with the results obtained for $\langle \sum (\phi'/r)(\Delta y)^2 \rangle$ and $\langle \sum (\phi'/r)(\Delta z)^2 \rangle$. The corresponding Born

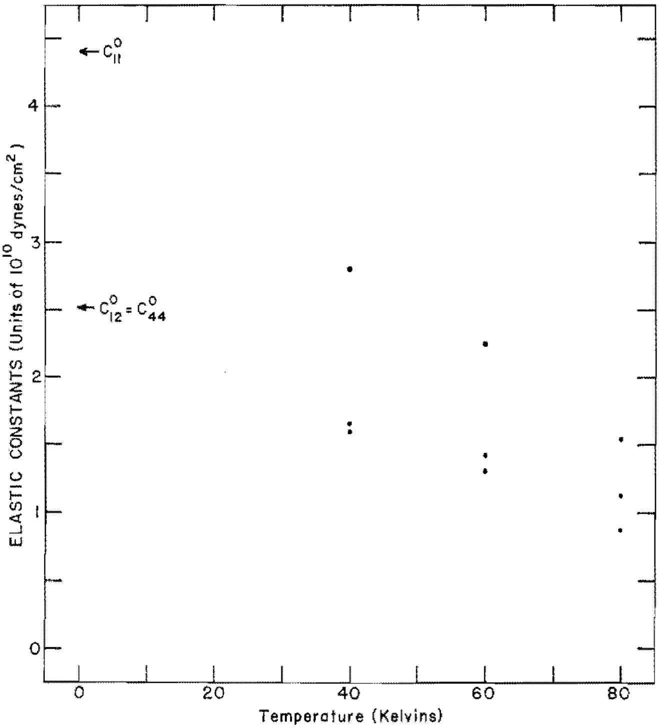

Figure 2. Isothermal Elastic Constants for argon at zero pressure as determined by Monte Carlo calculation. From top to bottom at 40, 60, and 80 K the points represent Monte Carlo values of C_{11}^T, C_{44}^T, and C_{12}^T. The theoretical (classical) zero-degree elastic constants are indicated by arrows.

terms for the various lattice spacings but for an infinite static lattice are also listed in table I. The Monte Carlo isothermal elastic constants for zero pressure are plotted in fig. 2.

The Monte Carlo results for the isothermal compressibility*,

$$\beta^T \doteq \frac{3}{C_{11}^T + 2C_{12}^T} \tag{14}$$

are compared to the zero-pressure results of Peterson *et al.*[6]) in table II. For the compressed lattice the Monte Carlo result at 80 K and 850 atmospheres is compared to Stewart's[14]) experimental result at 77 K and 970 atmospheres.

The compressibility was also computed from the following relation,

$$\beta^T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T, \tag{15}$$

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* Eq. (14) is strictly valid only at zero pressure.

TABLE II

Isothermal compressibility as a function of temperature and lattice spacing. The expected errors in both the Monte Carlo results and in the experimental values of Peterson *et al.*[6]) are 10%. All values for isothermal compressibility β^T are in units of 10^{-12} cm^2/dyne.

T (kelvins)	d (ångstroms)	β^T Monte Carlo	β^T Experiment	β^T Static-Lattice
40	3.780	49	46	51
60	3.813	61	58	65
80	3.857	89	82	90
40	3.857	89	—	90
80	2.780	51	47*	51

* This experimental datum (Stewart[14])) was taken at 77 K.

using the pressure data from the two Monte Carlo runs at 80 K. This method yielded a value of $65 \pm 10 \times 10^{-12}$ cm^2/dyne, in agreement with the static lattice and direct Monte Carlo computation.

4. *Discussion.* We would now like to draw some tentative conclusions from the data given in the preceding section. We note first that the Monte Carlo Born term (table I) greatly exceeds the static-lattice elastic constant (which is just the value of the Born term when the particles are at rest). Most of this excess is offset by the negative fluctuation term so that the final elastic constant differs by only about ten per cent from the zero-degree one. This near cancellation of the Born-term increase and the negative fluctuation term is striking. It would be interesting to study quantitatively the relative sizes of the Born and fluctuation terms from the standpoint of lattice dynamics. We hope that a theory capable of handling both kinds of terms will be forthcoming.

Finally, we notice that the Monte Carlo and static-lattice values for the isothermal compressibility (which depends on both C_{11}^T and C_{12}^T) agree well with each other but exceed experimental values by about ten per cent. The insensitivity of compressibility to temperature deserves further investigation. The disagreement with experimental compressibilities indicates that the two-particle Lennard-Jones potential function is somewhat softer than the effective two-particle potential in argon. In the future we expect to report on applications to adiabatic elastic constants for both quantum and classical solids and fluids.

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