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32

29

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

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Synopsis

Exact expressions for the adiabatic elastic constants, C^S_{11}, C^S_{12} and C^S_{44}, are derived for cubic crystals composed of particles interacting with pairwise additive central forces. Monte Carlo simulation of an argon crystal, using the Lennard-Jones potential, gives results for the elastic constants at 40, 60 and 80 kelvins.

1. *Introduction.* In 1912 Debye, Born and von Kármán used quantum mechanics to explain the peculiar temperature dependence of crystal heat capacities. The outstanding success of this use of quantum mechanics has led to the neglect of classical calculations of solid-phase thermodynamic properties. This is unfortunate today, for the widespread availability of computing machines makes it possible to treat classical many-body problems exactly[1,2]). Practical quantum calculations, on the other hand, can only approximate correlations and anharmonic effects.

Classical systems for which Monte Carlo calculations can be carried out must satisfy two fundamental requirements. First, the intensive properties of small systems, up to a few thousand particles, which the machine can handle must be sufficiently close to the large-system limit. In homogeneous systems with short-range forces this restriction can be accomodated by using periodic boundaries and making lattice-sum corrections. The second requirement is that machine calculation of the potential energy function not be too time-consuming. At present this restriction is not important because existing computers would be capable of studying three-body forces, if only they were known theoretically.

In the classical Monte Carlo calculations the independent variables are temperature and the size and shape of the system. The potential function

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$\Phi(\boldsymbol{r}^N)$ is first specified, giving the potential energy of the system in terms of the particle coordinates. The computer then samples many configurations in the vicinity of the initial one, weighting these with relative probability $\exp[-\Phi/kT]$, corresponding to a canonical-ensemble average. The velocities never enter the classical calculations because their known distribution is independent of configuration $\boldsymbol{r}^N$.

We have already used the Monte Carlo computer method to obtain *isothermal* elastic constants for a classical system. These constants give the change of Helmholtz free energy caused by changing the size and shape of the container at constant temperature[3]). This is straightforward. We carried out such a calculation for crystalline argon[4]). The constant-entropy *adiabatic* elastic constants are more difficult to treat by constant-temperature computer calculation. But the adiabatic elastic constants are much more easily measured in the laboratory. In this paper, in order to compare our results with laboratory experiments, we calculate the adiabatic elastic constants. In the next section the microscopic expressions for the elastic constants are derived, and numerical values for argon are obtained using the Monte Carlo method. The discrepancy between calculation and experiment can be due to our neglect of quantum effects as well as to uncertainties in the potential function Φ. The quantum effect is calculated in section 3.

2. *Expressions for the elastic constants.* We consider a crystal of N particles, interacting with a pairwise-additive potential $\phi(r)$, at temperature T in a volume V. We explicitly consider a perfect crystal, without vacancies, by confining each particle to the region (Wigner-Seitz cell) in space closest to its lattice site. The unstrained crystal is a cube of sidelength a. We define three vectors, $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, and $\boldsymbol{a}_3$, colinear with the three edges at one corner of the cube. If the $\boldsymbol{a}_i$, which specify the location of the lattice sites, change in length and direction, the crystal is said to be *strained*. The changes are conveniently described by the six dimensionless independent strains $\boldsymbol{\eta} = \eta_1, \eta_2, \eta_3, \eta_4, \eta_5$, and η_6:

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

We are not here following the alternative practice of defining nine strains, η_{ij} and then formally treating all nine as independent variables. In that case *the same* results for the elastic constants are obtained, if the definitions of $\eta_{23} \equiv \eta_{32}$, $\eta_{13} \equiv \eta_{31}$, and $\eta_{12} \equiv \eta_{21}$ are exactly half of our expressions for η_4, η_5, and η_6, respectively.

All of the thermodynamic properties of the crystal can be obtained from the Helmholtz free energy, a function of the seven independent variables

T and $\boldsymbol{\eta}$, although we will not explicitly indicate the temperature-dependence in what follows. The Helmholtz free energy A and the internal energy E can be written as follows:

$$\begin{aligned} A(\boldsymbol{\eta}) &= -kT \ln Z(\boldsymbol{\eta}) = \\ &= -kT \ln \{\Lambda^{-3N} \int_{\Delta} \dots \int_{\Delta} \exp[-\Phi(\boldsymbol{\eta})/kT]\, \mathrm{d}\boldsymbol{r}^N\}, \\ E(\boldsymbol{\eta}) &= \tfrac{3}{2}NkT + \langle\Phi(\boldsymbol{\eta})\rangle, \end{aligned} \tag{2}$$

where Z is the canonical partition function, Λ is the thermal de Broglie wavelength $h/(2\pi mkT)^{\frac{1}{2}}$, m is the particle mass, and k and h are Boltzmann's and Planck's constants, respectively. The angular brackets in eqs. (2) indicate a canonical-ensemble average:

$$\langle X(\boldsymbol{r}^N)\rangle \equiv \int_{\Delta} \dots \int_{\Delta} X(\boldsymbol{r}^N) \exp[-\Phi(\boldsymbol{r}^N)/kT]\, \mathrm{d}\boldsymbol{r}^N/[\Lambda^{3N}Z(\boldsymbol{\eta})].$$

The Δ's below the integral signs are reminders that each particle is restricted to its own region of space during the integration over the particle coordinates $\boldsymbol{r}^N$.

We have already shown how the Helmholtz free energy for a strained cubic crystal can be expanded as a power series in the η_i's, *with all expansion coefficients evaluated in the initial unstrained state*:

$$\begin{aligned} A(\boldsymbol{\eta}) = -kT \ln Z(\boldsymbol{\eta}) = A - PV(\eta_1 + \eta_2 + \eta_3) + \\ + \tfrac{1}{2}VC_{11}^T(\eta_1^2 + \eta_2^2 + \eta_3^2) + VC_{12}^T(\eta_1\eta_2 + \eta_1\eta_3 + \eta_2\eta_3) + \\ + \tfrac{1}{2}VC_{44}^T(\eta_4^2 + \eta_5^2 + \eta_6^2) + \mathcal{O}(\eta^3). \end{aligned} \tag{3}$$

The C_{ij}^T's are the isothermal elastic constants, which in conjunction with P describe the reversible work necessary to distort a crystal at constant temperature. If the distortion is carried out rapidly enough to be adiabatic (but slowly enough to be reversible) as in ultrasonic measurements of elastic constants, then the work done can be described by expanding the internal energy in the strains at constant entropy. In place of the isothermal elastic constants C_{ij}^T we have the adiabatic elastic constants C_{ij}^S:*

$$\begin{aligned} E(\boldsymbol{\eta}) = E - PV(\eta_1 + \eta_2 + \eta_3) + \tfrac{1}{2}VC_{11}^S(\eta_1^2 + \eta_2^2 + \eta_3^2) + \\ + VC_{12}^S(\eta_1\eta_2 + \eta_1\eta_3 + \eta_2\eta_3) + \tfrac{1}{2}VC_{44}^S(\eta_4^2 + \eta_5^2 + \eta_6^2) + \mathcal{O}(\eta^3). \end{aligned} \tag{4}$$

In Monte Carlo calculations temperature, rather than entropy, can conveniently be kept constant, so that in order to differentiate at fixed entropy,

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* By expanding the pressure tensor for a strained system in powers of the strain one finds the relations between the C_{ij} and the linear stress-strain coefficients:

$(\partial P_{11}/\partial\eta_1) = -C_{11} + P_{11}$; $(\partial P_{11}/\partial\eta_2) = -C_{12} - P_{11}$; $(\partial P_{12}/\partial\eta_6) = -C_{44} + P_{11}$.

These relations hold for isothermal and for adiabatic strains.

to find the elastic constants defined in eq. (4), an indirect route is required:

$$\left(\frac{\partial}{\partial\eta}\right)_S = \left(\frac{\partial}{\partial\eta}\right)_T - \left(\frac{\partial T}{\partial S}\right)_\eta \left(\frac{\partial S}{\partial\eta}\right)_T \left(\frac{\partial}{\partial T}\right)_\eta,$$

$$\text{where} \qquad S \equiv (E - A)/T. \tag{5}$$

The derivatives in eq. (5) can all be computed in terms of canonical-ensemble averages. The first derivative gives $(\partial E/\partial\eta_i)_S = (\partial A/\partial\eta_i)_T = -VP$ for $i = 1, 2, 3$ where P is the initial hydrostatic pressure. Going on to calculate the second derivatives, and then setting η equal to zero, we find the results:*

$$\Delta C \equiv C^S_{11} - C^T_{11} = C^S_{12} - C^T_{12} =$$

$$= \frac{\dfrac{kT}{V}\left\{N - \dfrac{1}{(kT)^2}\left\langle\Sigma\dfrac{\phi' x^2}{r}\Sigma\phi\right\rangle + \dfrac{1}{(kT)^2}\left\langle\Sigma\dfrac{\phi' x^2}{r}\right\rangle\langle\Sigma\phi\rangle\right\}^2}{\frac{3}{2}N + \dfrac{1}{(kT)^2}\langle[\Sigma\phi]^2\rangle - \dfrac{1}{(kT)^2}\langle\Sigma\phi\rangle^2} =$$

$$= VT(\partial P/\partial T)^2_v/C_v \equiv \gamma^2 T C_v/V, \tag{6}$$

and

$$C^S_{44} = C^T_{44} \equiv C_{44}. \tag{7}$$

The isothermal elastic constants appearing in eqs. (6) and (7) were previously calculated using the following expressions:

$$VC^T_{11} = \frac{1}{kT}\langle\Sigma\phi' x^2/r\rangle^2 - \frac{1}{kT}\langle[\Sigma\phi' x^2/r]^2\rangle +$$

$$+ \langle\Sigma(\phi'' x^4/r^2 - \phi' x^4/r^3)\rangle + 2NkT,$$

$$VC^T_{12} = \frac{1}{kT}\langle\Sigma\phi' x^2/r\rangle\langle\Sigma\phi' y^2/r\rangle - \frac{1}{kT}\langle\Sigma\phi' x^2/r\Sigma\phi' y^2/r\rangle +$$

$$+ \langle\Sigma(\phi'' x^2y^2/r^2 - \phi' x^2y^2/r^3)\rangle,$$

$$VC_{44} = -\frac{1}{kT}\langle[\Sigma\phi' xy/r]^2\rangle +$$

$$+ \langle\Sigma(\phi'' x^2y^2/r^2 - \phi' x^2y^2/r^3)\rangle + NkT. \tag{8}$$

The quantities x, y and z represent the three components of the vector joining the pair of particles in the sum over all pairs and γ is the Grüneisen gamma [5]) of thermodynamics, $V(\partial P/\partial T)_v/C_v$.

Even with the assumption of pairwise-additive forces the fluctuation quantities in eqs. (6) and (8) involve four-particle correlation functions. The expressions are cumbersome to evaluate analytically even in the harmonic

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* The thermodynamic, as opposed to statistical, derivation of eq. (6) appears in several texts.

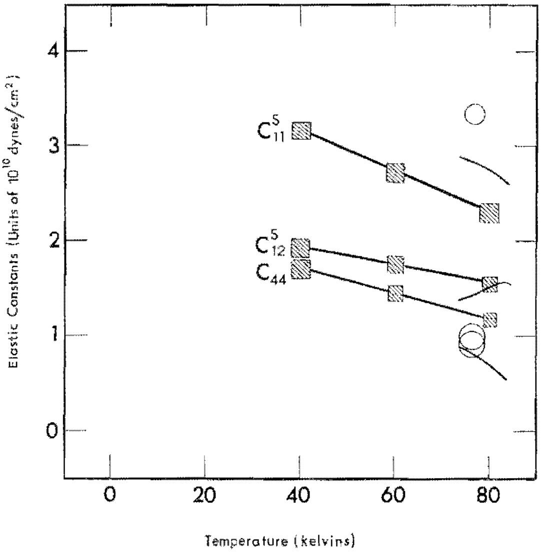

Fig. 1. Comparison of the zero-pressure Monte-Carlo adiabatic elastic constants for argon with experimental data of Moeller and Squire (light lines) and Gsänger, Egger and Lüscher (circles). The Monte-Carlo data (squares) are connected by heavy straight lines. The discrepancy between the Moeller–Squire and Gsänger–Egger–Lüscher data is an indication of the uncertainty in the experimental results. In all cases the elastic constants follow the ordering $C_{11}^S > C_{12}^S > C_{44}$.

TABLE I

Monte Carlo results for specific heat C_v, Grüneisen gamma γ, and the elastic constant correction ΔC for solid argon at zero pressure. These data were calculated using a 108-particle periodic system and have an estimated error of 5%. The nearest-neighbor spacing in the face-centered lattice is d (in ångstroms). The elastic-constant correction ΔC is in units of 10^{10} dynes/cm^2.

T (kelvins)	d	C_v/Nk	γ	ΔC
40	3.780	2.73	2.82	0.32
60	3.813	2.69	2.82	0.45
80	3.857	2.79	2.91	0.67

approximation⁶). Using the Monte Carlo technique, however, none of the sums is more time-consuming to compute than the usual expressions for the pressure and energy, so that machine calculations can be efficiently carried out.

In order to compare the computer results with experiment, we used the Lennard–Jones potential for argon determined by Horton and Leech⁷):

$$\phi(r) = 6.571[(3.4/r)^{12} - (3.4/r)^6] \times 10^{-14} \text{ ergs},$$

where r is in ångströms. We measured the constant-volume specific heat C_v

and the Grüneisen gamma, γ, and from these calculated the elastic-constant correction ΔC, defined by eq. (6). The results are listed in table I, and the adiabatic elastic constants (at zero pressure) are plotted in fig. 1, along with the experimental data of Moeller and Squire[8,9]) and Gsänger *et al.*[10]).

Although the experimental data are still sparse it appears that C_{11}^S from the Lennard–Jones potential definitely lies below the argon data. In the next section we will see that the discrepancy is too large to be explained by quantum effects.

3. *Quantum corrections.* We can easily estimate the effect of quantum mechanics on thermodynamic properties by evaluating coefficients in Wigner and Kirkwood's Planck's-constant expansion of the Helmholtz free energy[11]). If only the first nonvanishing quantum correction is kept, the resulting expressions, averages over the *classical* distribution of configurations, can be readily evaluated numerically. The correction to the Helmholtz free energy (quantum minus classical is denoted by δ) is

$$\begin{aligned}\delta A &= [\Lambda^2/(48\pi)] \sum_{i=1}^{N} \langle \nabla_i^2 \Phi(\boldsymbol{r}^N) \rangle = \\ &= [\Lambda^2/(24\pi)] \sum_{\text{pairs}} \langle \phi'' + 2\phi'/r \rangle, \end{aligned} \tag{9}$$

and differentiation with respect to $\boldsymbol{\eta}$ gives the corresponding corrections to the pressure and to the elastic constants:

$$\begin{aligned}\delta P &= -[\Lambda^2/(24\pi V)]\,\{\langle \Sigma\,(\phi'''/r + 2\phi''/r^2 - 2\phi'/r^3)\,x^2 \rangle + \\ &\quad + (kT)^{-1} \langle \Sigma\,(\phi'' + 2\phi'/r) \rangle \langle \Sigma \phi' x^2/r \rangle - \\ &\quad - (kT)^{-1} \langle \Sigma\,(\phi'' + 2\phi'/r)\, \Sigma \phi' x^2/r \rangle\}, \\ \delta C_{11}^T &\doteq [\Lambda^2/(24\pi V)] \langle \Sigma\,(\phi^{\mathrm{iv}}/r^2 + \phi'''/r^3 - 6\phi''/r^4 + 6\phi'/r^5)\,x^4 \rangle, \\ \delta C_{12}^T &\doteq \delta C_{44} \doteq [\Lambda^2/(24\pi V)] \langle \Sigma\,(\phi^{\mathrm{iv}}/r^2 + \phi'''/r^3 - 6\phi''/r^4 + 6\phi'/r^5)\,x^2 y^2 \rangle. \end{aligned} \tag{10}$$

We have left out unwieldy fluctuation terms (which involve up to six-particle correlations) in the elastic-constant corrections of eqs. (10) to save space. Because the corrections involve the fourth derivative of the pair potential, which is not accurately known, it is sensible to estimate δC_{11}^T and δC_{12}^T by evaluating the contributing lattice sums for a static lattice. Such an approximation is typically within 10% of the thermal-average exact sums.

Using the Lennard–Jones potential the corrections to C_{11} and C_{12} at 80 kelvins are +5% and +4%, respectively. At 40 kelvins the corrections are larger, +8% and +7%, respectively.

These estimates of the quantum corrections suggest that most of the 20% discrepancy between the theoretical results for C_{11}^S and experiment must be ascribed to uncertainties in the potential $\Phi(\boldsymbol{r}^N)$. Götze and Schmidt[12]) have studied how the zero-temperature elastic constants depend on the inclusion of three-body forces. Their results suggest a three-body effect of order 5 to 10%. A direct experimental estimate of the many-body forces could be made by measuring the two elastic constants C_{12} and C_{44} for xenon at temperatures high enough so that quantum effects can be ignored. (The quantum corrections for xenon at its triple point are less than 1%.) Our eq. (8) shows that extrapolating the classical results to zero kelvins will give $C_{12}^0 = C_{44}^0$, a so-called "Cauchy relation" in the event that $\Phi(\boldsymbol{r}^N)$ is a sum of pairwise-additive terms. It is easy to verify that the presence of nonpair terms in Φ destroys the validity of the Cauchy relations, even for a perfect (classical, zero kelvins) crystal.

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