Hard-Sphere Pressure Bound from a Reformulation of Solid-Phase Thermodynamics*

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Two different ways of describing the work necessary to distort an elastic solid result in alternative microscopic expressions for the pressure and the elastic constants. In the case of a hard-sphere solid with nearest-neighbor interactions a lower bound on the pressure can be obtained by comparing the two pressure expressions. This lower bound is identical with the pressure derived from Kirkwood's self-consistent free-volume theory.

I. INTRODUCTION

Fast computers make it possible to measure the thermodynamic properties of classical many body systems by carrying out "computer experiments" on systems of several hundred particles.[1] With reasonable care the compressibility factor PV/NkT and the reduced energy E/NkT can be determined within about 0.01. Although fluids and solids can both be studied using the computers, solids have so far been investigated much less than have fluids. This is, first, because solids seem simpler and, second, because the traditional treatment of solids, lattice dynamics, is quantum mechanical, not classical, and already semiquantitative. Increased interest in computer experiments on solids is accompanying the realization that both the quantum corrections to the classical experiments and anharmonic corrections to the predictions of lattice dynamics can be obtained from computers.

Current solid-phase investigations are no longer restricted to the pressure and energy. In 1968, Squire, Holt, and Hoover[2] formulated the problem of the elastic response of a crystal to strain so that it could be solved numerically on a fast computer. The isothermal elastic constants, second derivatives of the Helmholtz free energy with respect to strain, were expressed as canonical-ensemble averages involving the pair potential $\phi(r)$ and its derivatives $\phi'(r)$ and $\phi''(r)$. The averages were evaluated for the Lennard-Jones and exponential-six pair potentials and compared with the experimental elastic constants for rare gases.[3]

Salsburg independently developed elastic-constant expressions which were somewhat different from those of Squire, Holt, and Hoover. During the summer of 1969 we compared both treatments and convinced ourselves that, despite the apparent differences, *both* were correct. This in itself is interesting because it has happened in the past that different microscopic expressions for a thermodynamic property can converge at different rates in computer calculations.[4] We also noticed an application of the two formulations for which the computer is not required: By combining Salsburg's expression for the pressure with the conventional virial theorem, a rigorous lower bound on the pressure for a hard-sphere solid results.

II. SOLID-PHASE DEFORMATION

In theoretical treatments of solid-phase thermodynamic properties it is convenient to consider an
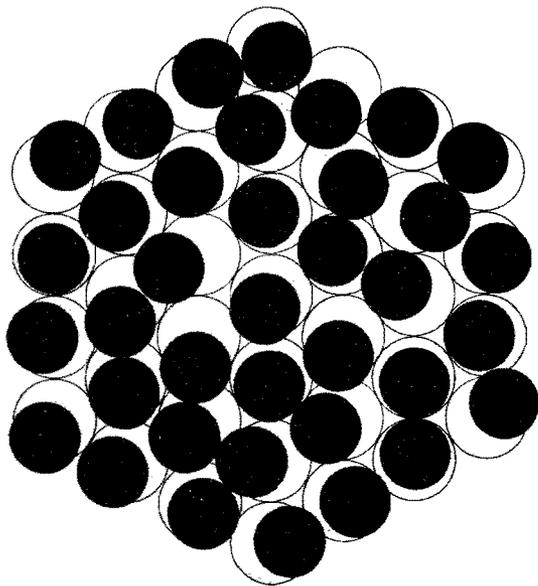
FIG. 1. A single-occupancy solid. The particles, shown as black circles, are free to move as long as the center of each stays in its cell. The cells are shown as larger shaded circles.

idealized crystal in which the distractions caused by vacancies, dislocations, and grain boundaries are absent. The simplest way to make this structural simplification is to restrict the particles to individual cells, as shown in Fig. 1. Because each cell contains only one particle such a crystal can be called a "single-occupancy" solid.[5,6]

With the gross structure of the solid enforced by the cell boundaries, the crystal can be "homogeneously" deformed by changing the size and shape of the cells. Homogeneously means that all cells are distorted in the same way. The resulting deformation is described by the macroscopic strain η:

$$\eta_1 = \tfrac{1}{2}[(\mathbf{a}_1/a)^2 - 1], \qquad \eta_4 = (\mathbf{a}_2/a) \cdot (\mathbf{a}_3/a),$$
$$\eta_2 = \tfrac{1}{2}[(\mathbf{a}_2/a)^2 - 1], \qquad \eta_5 = (\mathbf{a}_1/a) \cdot (\mathbf{a}_3/a),$$
$$\eta_3 = \tfrac{1}{2}[(\mathbf{a}_3/a)^2 - 1], \qquad \eta_6 = (\mathbf{a}_1/a) \cdot (\mathbf{a}_2/a). \quad (1)$$

These strains are the generalization of the thermodynamic variable volume to the case in which properties depend upon shape as well as size. Figure 2 shows how the basis vectors, $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$, change in length and orientation when a crystal is strained.

The amount of thermodynamic work δW required to induce a particular strain η depends upon whether or not the crystal is allowed to exchange heat with its surroundings. Thermodynamics can describe either isothermal (constant temperature T) or adiabatic (constant entropy S) deformations. If we use x to indicate either T or S, the work done can be expressed as a power series in η, with coefficients depending on x. For the simplest interesting case, a cubic crystal under an initial hydrostatic pressure P, the expansion has the

form

$$\delta W^x = -PV(\eta_1 + \eta_2 + \eta_3) + \tfrac{1}{2}C_{11}^x V(\eta_1^2 + \eta_2^2 + \eta_3^2)$$
$$+ C_{12}^x V(\eta_1\eta_2 + \eta_1\eta_3 + \eta_2\eta_3) + \tfrac{1}{2}C_{44} V(\eta_4^2 + \eta_5^2 + \eta_6^2) + \cdots,$$
$$\delta W^T = \delta A, \quad \delta W^S = \delta E. \quad (2)$$

A and E are the Helmholtz free energy and the internal energy. The coefficients in the series, the pressure P and the second-order elastic constants C_{ij}^x, can be expressed as canonical ensemble averages.[2,3] First express the coordinates of all the particles in an N-particle crystal in terms of the orthogonal vectors $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$. All three vectors have length a in the undeformed crystal. Then expand the resulting canonical partition function in powers of η. In carrying out the expansion the location of Particle i is specified as $x_i(\mathbf{a}_1/a) + y_i(\mathbf{a}_2/a) + z_i(\mathbf{a}_3/a)$ and the integration over the configuration space contains $dx_i dy_i dz_i$. The final results are averages, carried out in the initial unstrained configuration:

$$PV = NkT - \langle \sum x^2 \phi'/r \rangle,$$
$$C_{11}^T V = 2NkT + \langle \sum \phi'' x^4/r^2 - \phi' x^4/r^3 \rangle$$
$$- V^2(\langle P_1^2 \rangle - \langle P_1 \rangle^2)/kT,$$
$$C_{12}^T V = \langle \sum \phi'' x^2 y^2/r^2 - \phi' x^2 y^2/r^3 \rangle$$
$$- V^2(\langle P_1 P_2 \rangle - \langle P_1 \rangle^2)/kT,$$
$$C_{44} V = NkT + \langle \sum \phi'' x^2 y^2/r^2 - \phi' x^2 y^2/r^3 \rangle$$
$$- V^2 \langle P_6^2 \rangle/kT, \quad (3)$$

where the sums include all pairs of particles in the crystal, where x, y, z indicate the distances separating a pair of particles in the $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ directions, and where the brackets $\langle \ \rangle$ indicate canonical averages in an unstrained crystal. P_1, P_2, and P_6 indicate instantaneous values of pressure tensor components:

$$P_1 V = NkT - \sum x^2 \phi'/r, \qquad P_4 V = -\sum yz\phi'/r,$$
$$P_2 V = NkT - \sum y^2 \phi'/r, \qquad P_5 V = -\sum xz\phi'/r,$$
$$P_3 V = NkT - \sum z^2 \phi'/r, \qquad P_6 V = -\sum xy\phi'/r. \quad (4)$$

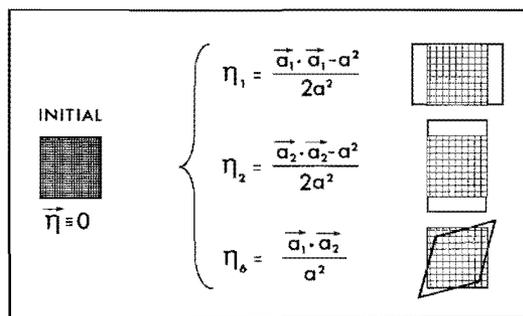Salsburg used a slightly different coordinate system in

FIG. 2. The distortion of a crystal described by the strains η_1, η_2, and η_6.

deriving alternative microscopic expressions for the expansion coefficients P and C_{ij}^{x}. He located the ith particle at $\mathbf{R}_i(\boldsymbol{\eta})+\boldsymbol{\delta r}_i$, where only the lattice-site coordinate $\mathbf{R}_i$ depends upon the strain and the displacement coordinate $\boldsymbol{\delta r}_i$, measuring the displacement of particle i from its lattice-site position, is strain independent. In the solid phase it has been empirically established that the rms displacement of a particle *is* small relative to the nearest-neighbor spacing. Lindemann's relation states that a solid melts when the rms displacement becomes about $1/10$ the nearest-neighbor spacing. Salsburg makes the assumption that the particle vibrations are small enough so that the integration limits on the displacement $\boldsymbol{\delta r}_i$ can be considered strain-independent. He then finds the following expressions for the pressure and the elastic constants:

$$PV = -\langle \sum Xx\phi'/r\rangle,$$

$$C_{11}{}^T V = \langle \sum \phi''X^2x^2/r^2 - \phi'X^2x^2/r^3 + \phi'X(X-x)/r\rangle$$
$$- V^2(\langle P_1{}^2\rangle - \langle P_1\rangle^2)/kT,$$

$$C_{12}{}^T V = \langle \sum \phi''XYxy/r^2 - \phi'XYxy/r^3\rangle$$
$$- V^2(\langle P_1P_2\rangle - \langle P_1\rangle^2)/kT,$$

$$C_{44} V = \langle \sum \phi''X^2y^2/r^2 - \phi'X^2y^2/r^3 + \phi'X(X-x)/r\rangle$$
$$- V^2\langle P_6{}^2\rangle/kT. \quad (5)$$

The capital letters X, Y, Z in (5) stand for components of the interparticle separation in a perfect stationary lattice, measured along the $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ directions. The lower case letters x, y, z stand for the actual varying components which fluctuate around the static-lattice values X, Y, Z. The pressures P_1, P_2, and P_6 in (5) are slightly different from those appearing in (4). Because the expression for the pressure in (5) is different from the more conventional one appearing in (3) it is worth pointing out that it can be derived more directly, and without the assumption of small vibrations.[7] Although the results in (3) and (5) *look* different it is easy enough to work out special cases showing that the two do agree. These special cases also show that the pressure fluctuations, which contribute to the elastic constants, are *not* the same, so that one formulation or the other might be more appropriate for a particular problem. (5) might work best when the pressure is close to zero, so that the two pressure terms in (3) nearly cancel.

III. HARD-SPHERE SOLID PRESSURE BOUND

Apart from the practical consideration that (3) and (5) converge at different rates in computer experiments, so that one or the other might prove better in particular applications, what else can be learned by comparing the two formulations? If the particles under consideration are hard spheres of diameter σ, then (3) and (5) can both be simplified because the hard spheres exert forces on one another only when they are separated by a distance σ. If we indicate the angle between a pair's separation $\mathbf{r}$ and the separation of the corresponding lattice sites $\mathbf{R}$ by $\theta = \cos^{-1}[(\mathbf{r}/r)\cdot(\mathbf{R}/R)]$, and express the nearest-neighbor spacing in the perfect crystal as $\sigma\rho^{-1/3}$, where ρ is the ratio of the density to the close-packed density, then the two pressure expressions can be written:

$$3PV = 3NkT - \sigma\langle \sum \phi'\rangle,$$
$$3PV = -\sigma\rho^{-1/3}\langle \sum \phi' \cos\theta\rangle. \quad (6)$$

Because the maximum value for the cosine is 1, the second expression gives a lower bound for $\langle \sum \phi'\rangle$, which, substituted into the first expression, provides a lower bound on the pressure itself:

$$PV/NkT \geq (1-\rho^{1/3})^{-1}. \quad (7)$$

This lower bound is perfectly rigorous under the assumptions of (1) single occupancy and (2) nearest-neighbor interactions, both of which are certainly reasonable for hard-sphere solids. It is interesting to note that the bound is exactly the same pressure expression that Wood[8] calculated using Kirkwood's self-consistent free volume theory. The bound fits the results of the hard-sphere computer experiments quite well. The maximum error is about 8%. It occurs at an expansion of 36% from the close-packed density, where the hard-sphere solid melts.[6]

ACKNOWLEDGMENT

[1] For a review of the computer experiments see the summary of W. W. Wood, *Physics of Simple Liquids*, edited by H. N. V. Temperley, J. S. Rowlinson, and G. S. Rushbrooke (North-Holland, Amsterdam, 1968), Chap. 5.

[2] D. R. Squire, A. C. Holt, and W. G. Hoover, Physica **42**, 388 (1968).

[3] W. G. Hoover, A. C. Holt, and D. R. Squire, Physica **44**, 437 (1969).

[4] The pressure for hard spheres, for example, can be calculated either from the virial theorem or from the measured collision rate. The fluctuations in the virial theorem pressure are only about one-third the size of the fluctuations in the collision rate pressure. See B. J. Alder and T. E. Wainwright, J. Chem. Phys. **33**, 1439 (1960), and W. G. Hoover and B. J. Alder, *ibid.* **46**, 686 (1967).

[5] J. G. Kirkwood, J. Chem. Phys. **18**, 380 (1950).

[6] W. G. Hoover and F. H. Ree, J. Chem. Phys. **49**, 3609 (1968).

[7] The derivation of (5) for a single-occupancy solid follows that given for a fluid on p. 41 of J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954). Instead of dotting the equation of motion $\mathbf{F}_i = m\ddot{\mathbf{r}}_i$ with $\mathbf{r}_i$ and averaging, dot instead with $\langle \mathbf{r}_i\rangle \equiv \mathbf{R}_i$. The wall forces are assumed to be short ranged so that $\langle \sum \mathbf{r}_i\cdot\mathbf{F}_i^{(\text{ext})}\rangle - \langle \sum \mathbf{R}_i\cdot\mathbf{F}_i^{(\text{ext})}\rangle$ is negligible.

[8] W. W. Wood, J. Chem. Phys. **20**, 1334 (1952).