Elasticity in Rigid-Disk and -Sphere Crystals

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Our previously developed product representation for the partition function of rigid molecules under high compression is generalized to include distorted reference lattices. The resulting strain component variations of free energy then permit extraction of elastic constants, both linear and nonlinear. The high-compression elastic behavior of the two-dimensional rigid-disk crystal is explicitly evaluated through triplet cluster contributions. For rigid spheres in three dimensions in the face-centered-cubic lattice, singlet and pair cluster contributions have been evaluated, and the sound velocity ratio is reported for propagation along the ⟨100⟩ directions. Consideration of singlet and pair contributions for hexagonal packing suggests not only that this structure is more stable than the face-centered-cubic case, but that it exhibits a spontaneous small contraction along the c axis.

I. INTRODUCTION

In an earlier publication[1] a procedure was developed for calculating free energies of rigid-disk and -sphere systems in the close-packed crystalline limit. The reference lattice utilized in definition of the relevant cell-cluster contributions (the leading one of which was the free area or free volume) was chosen to be undistorted from its most symmetrical form. In the present paper, however, we consider the more general situation for which the underlying lattice bears a homogeneous distortion. Since the earlier procedure may be readily adapted to calculation of free energy as an explicit function of strain components, this sequel provides a means for obtaining rigid-disk and -sphere crystal elastic constants in the high-compression regime.

In the same manner as before in the undistorted lattice work, the elastic properties calculated below are expressed as an infinite series of contributions of ever-increasing complexity corresponding to all possible connected figures that may be drawn on the reference lattice with nearest-neighbor bonds. With inclusion of strain components, the cell-cluster evaluations become especially lengthy even in the entirely computer-automated procedure outlined below. For that reason, it has been necessary to truncate calculations at a lower cluster order than in Ref. 1 (the situation is particularly severe for the three-dimensional crystals). As a result the elastic constant calculations have less convincing convergence properties.

Although we intend eventually to push the elastic-constant calculations to inclusion of more complex cell clusters, the low-order results already obtained were deemed worthy of public exposure not only because they illustrate a new method for handling anharmonic solids, but because they also yield qualitatively interesting results. In particular we find tentatively that hexagonal packing is more stable for spheres in three dimensions than the face-centered-cubic packing[2]; furthermore the most stable form of the hexagonal packing appears to involve spontaneous contraction along the hexagonal c axis.

The major advantage in working in the high-compression limit is that curvatures of cell-cluster boundaries are negligible. In addition, vacancies or other lattice defects have such vanishingly small concentrations in this regime as to be also totally negligible, so only perfect crystals are considered below. Although our free-energy series consisting of cell clusters each of which is taken in the high-compression limit demonstrably yields the correct result for a finite system of particles (at least in some density neighborhood of close packing), the same has not yet been demonstrated rigorously for the infinite system limit.[3] We assume, however, that the two limit operations do in fact commute.

With specific regard to elasticity, the high-compression limit for disks or spheres implies that plastic relaxation of the system under an initial shear for example is entirely excluded. The high-compression limit therefore constitutes a regime in which elastic response may be deduced from a suitably arranged equilibrium theory, whereas more generally it must be treated as, say, a zero frequency limit of the real part of a temporal response function.[4]

On account of its relative pictorial and mathematical simplicity, the two-dimensional crystal of rigid disks serves as a convenient starting point, so the general procedure below is first set up and illustrated for this system. The corresponding three-dimensional face-

[1] F. H. Stillinger, Jr., Z. W. Salsburg, and R. L. Kornegay, J. Chem. Phys. **43**, 932 (1965).

[2] This is true in spite of the fact that these two crystal structures have identically the same close-packed density.

[3] This finite-system limitation has been explored in Z. W. Salsburg and W. W. Wood, J. Chem. Phys. **37**, 798 (1962).

[4] That certain general relations may always be established between elastic properties and strict equilibrium properties of the system is demonstrated in F. H. Stillinger, Jr., Phys. Rev. **142**, 237 (1966).

centered-cubic and hexagonal crystals are then treated in turn.

II. RIGID-DISK CRYSTAL

A. General Considerations

Figure 1 illustrates the undistorted regular hexagonal lattice for rigid disks under high lateral compression. The particles have been placed at their nominal equilibrium sites, and the six-sided "free area" for motion of a single particle in the cage formed by its neighbors is bounded by circular arcs whose radii equal the collision diameter a.

Let the vectors $\mathbf{R}_1 \cdots \mathbf{R}_N$ locate the N sites of the underlying lattice, one for each particle of the system. If we imagine the crystal to be contained within rigid boundaries, the restriction to high densities implies that we may regard Disk 1 to be confined to the vicinity of $\mathbf{R}_1$, $\cdots$, and Disk N to the vicinity of $\mathbf{R}_N$ (i.e., particle interchanges are geometrically impossible). Then if $\mathbf{r}_1 \cdots \mathbf{r}_N$ denote the respective disk displacements from the lattice sites, the canonical partition function Q_N and Helmholtz free energy F_N may be expressed in the following way[5]:

$$Q_N = \exp(-F_N/kT)$$
$$= \lambda^{-sN} \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_N \prod_{i<j}^{(\mathrm{nn})} U(|\mathbf{R}_{ij}+\mathbf{r}_j-\mathbf{r}_i|-a);$$
$$\mathbf{R}_{ij} = \mathbf{R}_j - \mathbf{R}_i. \qquad (1)$$

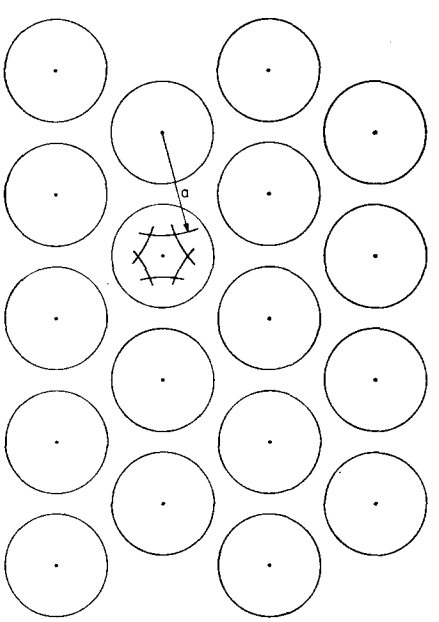

FIG. 1. Undistorted hexagonal lattice of rigid disks. The free area for any particle is formed by arcs of radius a centered about neighboring lattice sites.

[5] Since primary interest centers on bulk phase properties, we suppress explicit occurrence of rigid boundaries in Eq. (1). Indeed it is even possible in principle to use periodic boundary conditions (thus permitting free translation of the entire system) without substantially affecting free energy on a per-particle basis.

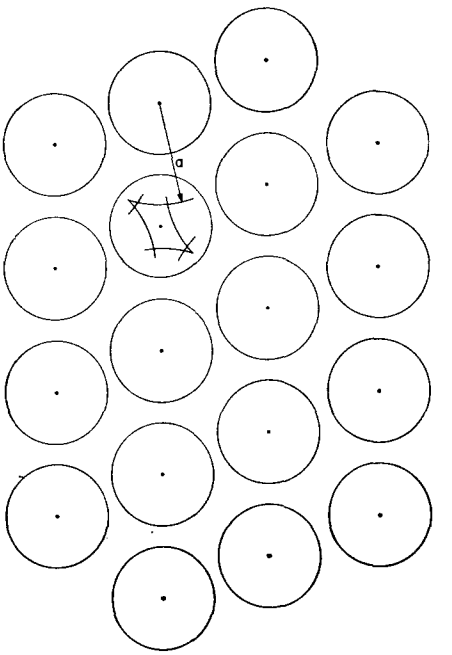

FIG. 2. Reference lattice and free area under the influence of a homogeneous strain.

Here λ is the mean thermal de Broglie wavelength, s the dimensionality (2 for disks, 3 for spheres), U is the unit step function,

$$U(x) = 0 \qquad (x<0)$$
$$= 1 \qquad (x \geq 0), \qquad (2)$$

and the integrand product in Eq. (1) includes all nearest-neighbor (nn) pairs once.

As the crystal is compressed to the high density limit, it is clear from Fig. 1 that the free areas shrink to zero size. Although any given particle may actually wander beyond the limits of the nominal free areas as a result of proper cooperative motion of neighbors, it is nevertheless true that the average displacements $\mathbf{r}_j$ at high compression will be small compared to the lattice spacing. Therefore in the high-compression regime it is valid to simplify step-function arguments thus:

$$U(|\mathbf{R}_{ij}+\mathbf{r}_j-\mathbf{r}_i|-a)$$
$$\cong U[(\mathbf{R}_{ij}/R_{ij})\cdot(\mathbf{R}_{ij}+\mathbf{r}_j-\mathbf{r}_i)-a]; \qquad (3)$$

this operation amounts to replacing exclusion circular arcs by tangent lines perpendicular to the respective lattice directions. Replacements (3) in the partition function (1) constituted the basis of calculations in Ref. 1. In a forthcoming publication we shall show that a more exact development of the step function argument than exhibited in Eq. (3) permits evaluation of

correction terms to F_N which vanish in the high-compression limit, but which become important at lower solid-phase densities.

Under the influence of a homogeneous strain, the reference lattice and free areas might suffer distortions as exhibited for example in Fig. 2. Such homogeneous distortions may generally be described by a position-independent dyadic strain tensor $\mathbf{u}$. Under the influence of $\mathbf{u}$ the shifted lattice-site positions correspond to the vectors $\mathbf{R}_1+\mathbf{u}\cdot\mathbf{R}_1, \cdots, \mathbf{R}_N+\mathbf{u}\cdot\mathbf{R}_N$, so the strain-dependent partition function and free energy generalizing Eq. (1) are thus:

$$Q_N(\mathbf{u})=\exp[-F_N(\mathbf{u})/kT]$$
$$=\lambda^{-sN}\int d\mathbf{r}_1\cdots\int d\mathbf{r}_N\prod_{i<j}^{(nn)}U(|\,\mathbf{R}_{ij}+\mathbf{u}\cdot\mathbf{R}_{ij}+\mathbf{r}_j-\mathbf{r}_i\,|-a). \tag{4}$$

The boundary linearization corresponding to Eq. (3) for this more general case subsequently permits us to write at high compression

$$Q_N(\mathbf{u})\sim\lambda^{-sN}\int d\mathbf{r}_1\cdots\int d\mathbf{r}_N\prod_{i<j}^{(nn)}U\left[\frac{\mathbf{R}_{ij}}{R_{ij}}\cdot(\mathbf{R}_{ij}+\mathbf{u}\cdot\mathbf{R}_{ij}+\mathbf{r}_j-\mathbf{r}_i)-a\right]. \tag{5}$$

In discussion of statistical thermodynamics of rigid particles it is convenient to use a dimensionless density variable θ, which varies between zero and an upper limit unity corresponding to close packing. In terms of θ then,

$$(a/R_{ij})^s=\theta. \tag{6}$$

Now the partition function expression (5) can be rewritten in the $\theta\to1$ limit:

$$Q_N(\mathbf{u})\sim[a(\theta^{-1}-1)/s\lambda]^{sN}Z_N(\mathbf{u}),$$
$$Z_N(\mathbf{u})=\int d\mathbf{t}_1\cdots\int d\mathbf{t}_N\prod_{i<j}^{(nn)}U[1+\mathbf{w}_{ij}\cdot\mathbf{S}\cdot\mathbf{w}_{ij}+\mathbf{w}_{ij}\cdot(\mathbf{t}_j-\mathbf{t}_i)],$$
$$\mathbf{w}_{ij}=\mathbf{R}_{ij}/R_{ij},\qquad \mathbf{t}_j=s\mathbf{r}_j/a(\theta^{-1}-1),\qquad \mathbf{S}=s\mathbf{u}/(\theta^{-1}-1). \tag{7}$$

As the crystal is compressed toward its close-packed limit it of course becomes more and more difficult to distort, and the mathematical manifestation of this behavior in Eq. (7) is the increasing magnitude of the scaled strain tensor $\mathbf{S}$ relative to the actual strain tensor $\mathbf{u}$. In the following we shall actually suppose that the components of $\mathbf{S}$ remain of order unity, so that the passage from Eq. (4) to Eq. (5) above is automatically justified by the consequent vanishing of $\mathbf{u}$ components in the high-compression limit.

Before proceeding to evaluate $Q_N(\mathbf{u})$, it is advantageous to summarize the phenomenological form of linear elasticity theory for crystals with the hexagonal symmetry of the rigid-disk solid. It is thus required to express the free energy per particle as a multinomial in the components of $\mathbf{u}$, retaining terms only through quadratic order. The correct form is the following:

$$\frac{F_N(\mathbf{u})}{NkT}=\frac{F_N(0)}{NkT}-\frac{pA}{NkT}(u_{xx}+u_{yy})+(NkT)^{-1}\{2\lambda_{\xi\eta\xi\eta}(u_{xx}+u_{yy})^2+\lambda_{\xi\xi\eta\eta}[(u_{xx}-u_{yy})^2+4u_{xy}^2]\}+O(u^3), \tag{8}$$

when expressed in terms of $\mathbf{u}$'s Cartesian components. Here we have followed the Landau–Lifshitz[6] notation for elastic constants, instead of the Voigt[7] convention. The pressure term is missing for crystals whose undistorted shape is stress free, but generally this term may be identified as a pressure–area work, since to leading order the fractional area increment is

$$\delta A/A\cong u_{xx}+u_{yy}. \tag{9}$$

The rigid-disk crystal linear elasticity may thus be described by just two elastic constants, $\lambda_{\xi\eta\xi\eta}$ and $\lambda_{\xi\xi\eta\eta}$.

We now proceed to develop $Z_N(\mathbf{u})$ and hence $Q_N(\mathbf{u})$ into a formally exact product [in essentially the same manner as for $Q_N(0)$ in Ref. 1] whose terms, respectively, are the free area approximation, pair cluster corrections, triplet corrections, etc. To do so, we note first that in terms of reduced configuration variables $\mathbf{t}_i$, the free area for

[6] L. D. Landau and E. M. Lifshitz, *Theory of Elasticity*, translated by J. B. Sykes and W. H. Reid (Addison-Wesley Publ. Co., Reading, Mass., 1959), p. 39. To adapt Eq. (10.8) for three-dimensional hexagonal crystals in this reference to the two-dimensional rigid-disk system, it is necessary to suppress terms including $\mathbf{u}$ components with subscripts z.

[7] W. Voigt, *Lehrbuch der Kristallphysik* (B. G. Teubner, Leipzig, 1928).

particle i, $Z_i^{(1)}(\mathbf{u})$, may be written in the high-compression regime as

$$Z_i^{(1)}(\mathbf{u}) = \int d\mathbf{t}_i \prod_{\alpha\epsilon\nu(i)} U(1+\mathbf{w}_{i\alpha}\cdot\mathbf{S}\cdot\mathbf{w}_{i\alpha}-\mathbf{w}_{i\alpha}\cdot\mathbf{t}_i), \tag{10}$$

wherein the integrand product spans the set $\nu(i)$ of nearest neighbors of particle i. In similar fashion a particle pair generalization of the free-area integral, for nearest-neighbor disks i and j, may be defined by

$$Z_{ij}^{(2)}(\mathbf{u}) = \int d\mathbf{t}_i \int d\mathbf{t}_j U[1+\mathbf{w}_{ij}\cdot\mathbf{S}\cdot\mathbf{w}_{ij}+\mathbf{w}_{ij}\cdot(\mathbf{t}_j-\mathbf{t}_i)] \prod_{\alpha\epsilon\nu(i)-j} U(1+\mathbf{w}_{i\alpha}\cdot\mathbf{S}\cdot\mathbf{w}_{i\alpha}-\mathbf{w}_{i\alpha}\cdot\mathbf{t}_i)$$
$$\times \prod_{\beta\epsilon\nu(j)-i} U(1+\mathbf{w}_{j\beta}\cdot\mathbf{S}\cdot\mathbf{w}_{j\beta}-\mathbf{w}_{j\beta}\cdot\mathbf{t}_j). \tag{11}$$

Now the integrand contains step functions corresponding to nonoverlap between (1) disks i and j, (2) between i and its set $\nu(i)-j$ of *fixed* nearest neighbors (thus excluding j), and (3) between j and its set $\nu(j)-i$ of *fixed* nearest neighbors. Analogous higher-order configuration integrals $Z^{(n)}{}_{i_1\cdots i_n}$ may likewise be written down for any set of n disks which form a connected grouping on the lattice; that is, each disk can be reached from any other by nearest-neighbor jumps involving only disks in the set $i_1\cdots i_n$. Of course for large n there will tend to be a very large number of distinct types of connected groupings or clusters.

The desired product representation has the following structure:

$$Z_N(\mathbf{u}) \equiv Z^{(N)}{}_{1\cdots N}(\mathbf{u})$$
$$= [\prod_{i=1}^{N} Z_i^{(1)}(\mathbf{u})]\Big[\prod_{i<j}{}' \frac{Z_{ij}^{(2)}(\mathbf{u})}{Z_i^{(1)}(\mathbf{u})Z_j^{(1)}(\mathbf{u})}\Big]\Big[\prod_{i<j<k}{}' \frac{Z_{ijk}^{(3)}(\mathbf{u})Z_i^{(1)}(\mathbf{u})Z_j^{(1)}(\mathbf{u})Z_k^{(1)}(\mathbf{u})}{Z_{ij}^{(2)}(\mathbf{u})Z_{ik}^{(2)}(\mathbf{u})Z_{jk}^{(2)}(\mathbf{u})}\Big]\cdots$$
$$\equiv [\prod_{i=1}^{N} Y_i^{(1)}(\mathbf{u})][\prod_{i<j}{}' Y_{ij}^{(2)}(\mathbf{u})][\prod_{i<j<k}{}' Y_{ijk}^{(3)}(\mathbf{u})]\cdots[Y^{(N)}{}_{1\cdots N}(\mathbf{u})]. \tag{12}$$

The primes on the pair, triplet, $\cdots$, factor products are to indicate that only connected clusters are included. It is a simple matter to prove by induction that (12) is a rigorous identity if the $Y^{(N)}{}_{i_1\cdots i_n}$ are generally defined to equal the corresponding $Z^{(N)}{}_{i_1\cdots i_n}$ divided by a Y of lower order for each connected proper subset of $i_1\cdots i_n$. It hardly needs to be remarked that the general utility of the product representation rests upon the presumption that terms of ascending order converge rapidly to unity, and that numerical evaluation be feasible for at least the leading members of the product.

Our computations are aided by the translational symmetry of the crystal, for this implies that all $Y^{(n)}$'s for a given species (shape) of cluster of n particles with fixed orientation in the $\mathbf{u}$ field are equal. In view of Eqs. (7) and (12), then, the free energy per particle may be expressed as a series of cluster terms:

$$\frac{F_N(\mathbf{u})}{NkT} = s\ln\Big[\frac{\lambda}{a(\theta^{-1}-1)}\Big] - \ln[s^{-s}Y^{(1)}(\mathbf{u})] - \sum_{n=2}^{N}[\sum_{\alpha}\tau(n,\alpha)\ln Y^{(n,\alpha)}(\mathbf{u})]; \tag{13}$$

particle subscripts on Y's are now unnecessary. α is an index denoting cluster species, and it is presumed that a given cluster of n particles may be formed on the lattice in $\tau(n,\alpha)N$ different ways.[8] After the right member of Eq. (13) is expanded in powers of $\mathbf{u}$ components, it becomes possible to identify the elastic constants of the rigid-disk crystal by comparison with the phenomenological free-energy expression (8).

B. Cluster-Integral Evaluation

For present purposes it is unnecessary to calculate the $Y^{(n,\alpha)}$ for an arbitrary homogeneous strain field. Instead it suffices, to find $\lambda_{\xi\eta\xi\eta}$ and $\lambda_{\xi\xi\eta\eta}$, to consider just two independent strain fields, which can be selected purely for computational convenience. In particular we choose (1) uniform dilation ($u_{xx}=u_{yy}$, $u_{xy}=0$) and (2) uniaxial elongation ($u_{xx}=u_{xy}=0$, $u_{yy}\neq 0$).

We suppose that the x axis coincides with one of the principal crystallographic directions for the undistorted crystal. Then from Fig. 3 one verifies that the unit vectors pointing to nearest neighbors are selected from the set

$$\begin{aligned} &\mathbf{w}_1=\mathbf{i}, && \mathbf{w}_4=-\mathbf{i},\\ &\mathbf{w}_2=\tfrac{1}{2}\mathbf{i}+(\sqrt{3}/2)\mathbf{j}, && \mathbf{w}_5=-\tfrac{1}{2}\mathbf{i}-(\sqrt{3}/2)\mathbf{j},\\ &\mathbf{w}_3=-\tfrac{1}{2}\mathbf{i}+(\sqrt{3}/2)\mathbf{j}, && \mathbf{w}_6=\tfrac{1}{2}\mathbf{i}-(\sqrt{3}/2)\mathbf{j}, \end{aligned} \tag{14}$$

expressed in terms of x- and y-direction unit vectors $\mathbf{i}$ and $\mathbf{j}$. Instead of evaluating cluster integrals in terms

[8] Certain pairs of clusters for given n that are distinguishable with a certain distortion $\mathbf{u}$ may degenerate into indistinguishability for $\mathbf{u}=0$, because the undistorted crystal has higher symmetry. For this reason the topological factors $\tau(n,\alpha)$ constitute a larger set of numbers than the corresponding $t(n,\alpha)$ appearing in Ref. 1.

of Cartesian coordinates, it is far more convenient to introduce an oblique coordinate system z_1, z_2 whose axes as shown in Fig. 3 are parallel to sides of the high-compression, free-area hexagon. The transformation is

$$z_1 = x,$$
$$z_2 = \tfrac{1}{2}x + (\sqrt{3}/2)y, \tag{15}$$

and the Jacobian transformation is found to be

$$\partial(x, y)/\partial(z_1, z_2) = (2/\sqrt{3}). \tag{16}$$

Let u stand for the common value of u_{xx} and u_{yy} in the uniform dilation of the disk crystal. The corresponding scaled strain tensor is just a constant times the unit tensor:

$$\mathbf{S} = \eta \mathbf{1},$$
$$\eta = 2u/(\theta^{-1}-1). \tag{17}$$

With this simplification the free-area integral (10) may be expressed very compactly in terms of the oblique coordinate system:

$$Z^{(1)}(u_{xx}=u_{yy}=u) = \frac{2}{\sqrt{3}}\int_{-\infty}^{+\infty} dz_1 \int_{-\infty}^{+\infty} dz_2 U(1+\eta-z_1)\,U(1+\eta-z_2) \times U(1+\eta+z_1-z_2)\,U(1+\eta+z_1)\,U(1+\eta+z_2)\,U(1+\eta-z_1+z_2). \tag{18}$$

One advantage offered by the oblique coordinates is that some of the step functions may be reinterpreted as integral limits; Expression (18) accordingly becomes elementary to evaluate:

$$\begin{aligned} Z^{(1)}(u_{xx}=u_{yy}=u) &= \frac{2}{\sqrt{3}}\int_{-1-\eta}^{1+\eta} dz_1 \int_{-1-\eta}^{1+\eta} dz_2 U(1+\eta+z_1-z_2)\,U(1+\eta-z_1+z_2) \\ &= \frac{2}{\sqrt{3}}\left(\int_{-1-\eta}^{0} dz_1 \int_{-1-\eta}^{1+\eta+z_1} dz_2 + \int_{0}^{1+\eta} dz_1 \int_{-1-\eta+z_1}^{1+\eta} dz_2\right) \\ &= 2\sqrt{3}(1+\eta)^2. \end{aligned} \tag{19}$$

Under uniform dilation the higher-order cluster quantities $Y^{(n,\alpha)}$ are independent of η since they are homogeneous of degree zero in length-scale shifts[9]; therefore they contribute only to the additive free-energy constant C which was the object of primary concern in Ref. 1.

With the result (19) inserted into the free-energy expression (13), we can then begin to identify terms in the phenomenological free-energy expression (8):

$$pA/NkT = 2/(\theta^{-1}-1); \tag{20}$$
$$\lambda_{\xi\eta\xi\eta} = NkT/2(\theta^{-1}-1)^2. \tag{21}$$

These results are the free-area equation of state presumed to be asymptotically valid in the high-pressure limit for rigid disks, and the corresponding "compressibility" elastic constant.

We therefore establish that only the free-area single-particle integrals need to be considered for one of the two elastic constants for disks, but extraction of the second constant is a fundamentally more difficult task since it involves the entire set of cluster integrals. The next step therefore is to evaluate the leading members of this set under the uniaxial elongation, for which we now set

$$\mathbf{S} = \eta \mathbf{jj},$$
$$\eta = 2u_{yy}/(\theta^{-1}-1). \tag{22}$$

By following the same steps as before, the oblique coordinate system integral is now found to be[10]

$$\begin{aligned} Z^{(1)}(u_{yy}=u) &= \frac{2}{\sqrt{3}}\int_{-1}^{+1} dz_1 \int_{-1-(3/4)\eta}^{1+(3/4)\eta} dz_2 U(1+\tfrac{3}{4}\eta-z_1+z_2)\,U(1+\tfrac{3}{4}\eta+z_1-z_2) \\ &= \frac{2}{\sqrt{3}}\left(\int_{-1}^{0} dz_1 \int_{-1-(3/4)\eta}^{1+(3/4)\eta+z_1} + \int_{0}^{+1} dz_1 \int_{-1-(3/4)\eta+z_1}^{1+(3/4)\eta} dz_2\right) \\ &= 2\sqrt{3}(1+\eta). \end{aligned} \tag{23}$$

Detailed analysis reveals a common pattern when the configuration integrals are expressed in terms of the scaled strain component η. Invariably one finds step-function products as integrands with arguments consisting of linear polynomials in the oblique coordinates and η with rational number coefficients. These step functions then generate possible sets of upper and lower limits on integrals which must be tested for logical consistency, and then treated as separate additive contributions to the desired configuration integral. Aside

[9] In other words they contain as many integrals in numerator as in denominator.

[10] This result actually requires $\eta \geq -\frac{2}{3}$, below which lower limit the free area is no longer hexagonal, but quadrilateral. But since extraction of elastic constants only requires η to be infinitesimal, we disregard this irrelevant restriction.

from transformation Jacobian factors which would be irrational for odd n, the result is a polynomial in η with rational number coefficients.

As n increases the number of logically distinct cases increases rapidly, and so these cases become difficult to enumerate and calculate accurately. For this reason a digital computer program was developed at the Rice University Computer Project to evaluate the η polynomial results exactly for each configuration integral, with step-function linear polynomial coefficients as input. This permitted evaluation of all rigid-disk pair and triplet cluster contributions to the uniaxial stretch mode free energy.

An interesting complication arises in evaluation of cell-cluster integrals involving two or more particles, which is illustrated in Fig. 4 for a pair cluster. As a result of uniaxial stretch, the number of boundaries of the outer limits of possible motion for a given particle depends upon the sign of η, and therefore the polynomials change as η changes sign. This necessitates separate computer runs for positive and for negative η, but combined results may always be expressed as functions of η *and* $|\eta|$.

The pair and triplet configuration integrals for uniaxial strain have been listed in Table I and are found to have the following values:

$$Z^{(2,1)}=(2/\sqrt{3})^2[\tfrac{217}{24}+19\eta+\tfrac{81}{8}\eta^2-\tfrac{9}{16}\eta^2(\eta-|\eta|)-\tfrac{81}{128}\eta^3(\eta-|\eta|)],$$

$$Z^{(2,2)}=(2/\sqrt{3})^2[\tfrac{217}{24}+\tfrac{141}{8}\eta+\tfrac{531}{64}\eta^2+\tfrac{9}{128}\eta^2(|\eta|-4\eta)+\tfrac{27}{2048}\eta^3(2\eta+|\eta|)],$$

$$Z^{(3,1)}=(2/\sqrt{3})^3[\tfrac{32339}{120}+\tfrac{3471}{40}\eta+\tfrac{3057}{32}\eta^2+\tfrac{1107}{32}(\eta+\tfrac{7}{123}|\eta|)\eta^2 -\tfrac{1269}{256}\eta^3(\eta-\tfrac{45}{47}|\eta|)-\tfrac{51803}{12800}\eta^4(\eta-\tfrac{53}{63}|\eta|)-\tfrac{729}{5120}\eta^5(\eta-\tfrac{13}{3}|\eta|)],$$

$$Z^{(3,2)}=(2/\sqrt{3})^3[\tfrac{32339}{120}+\tfrac{3123}{40}\eta+\tfrac{1179}{16}\eta^2+\tfrac{2591}{256}\eta^2(\eta+\tfrac{7}{599}|\eta|) -\tfrac{49095}{40096}\eta^3(\eta-\tfrac{39}{185}|\eta|)+\tfrac{2673}{10240}\eta^4(\eta-\tfrac{1}{11}|\eta|)-\tfrac{243}{81920}\eta^6],$$

$$Z^{(3,3)}=(2/\sqrt{3})^3[\tfrac{2453}{90}+\tfrac{6671}{80}\eta+\tfrac{2703}{32}\eta^2+\tfrac{13071}{512}\eta^2(\eta+\tfrac{351}{4357}|\eta|) -\tfrac{38259}{8192}\eta^3(\eta-\tfrac{11063}{12753}|\eta|)-\tfrac{150417}{81920}\eta^4(\eta-\tfrac{1979}{1857}|\eta|)+\tfrac{51103}{131072}\eta^5(\eta-\tfrac{33}{35}|\eta|)],$$

$$Z^{(3,4)}=(2/\sqrt{3})^3[\tfrac{2453}{90}+\tfrac{3141}{40}\eta+\tfrac{147}{2}\eta^2+\tfrac{3}{256}\eta^2(1765\eta+39|\eta|)+\tfrac{297}{4096}\eta^3(7|\eta|-19\eta) +\tfrac{81}{20480}\eta^4(65\eta+7|\eta|)-\tfrac{81}{163840}\eta^5(37\eta+27|\eta|)],$$

$$Z^{(3,5)}=(2/\sqrt{3})^3[\tfrac{33007}{120}+\tfrac{3307}{40}\eta+\tfrac{5313}{64}\eta^2+\tfrac{861}{32}\eta^3-\tfrac{27}{32}\eta^4+\tfrac{243}{20480}\eta^4(63\eta+46|\eta|)+\tfrac{81}{163840}\eta^5(1093\eta+1126|\eta|)]. \tag{24}$$

These results may be utilized to form next the corresponding $Y^{(n,\alpha)}$ required by free-energy expression (13), with the factors $\tau(n,\alpha)$ taken from Table I. After expansion of the approximate free energy obtained through this cluster order in powers of η, comparison with phenomenological expression (8) and exact result (21) for $\lambda_{\xi\eta\xi\eta}$ finally yields a numerical approximation for the "shear" elastic constant:

$$\begin{aligned}\lambda_{\xi\xi\eta\eta}&=bNkT/(\theta^{-1}-1)^2\\&=(1.000000+0.210559-0.716980+\cdots)\times[NkT/(\theta^{-1}-1)^2]\\&\cong 0.493579[NkT/(\theta^{-1}-1)^2].\end{aligned} \tag{25}$$

The three contributions shown represent, respectively, the free-area approximation, the pair cluster correction, and the totality of triplet cluster corrections. Since $|\eta|$ terms in the Z's in (24) occur only in cubic or higher-order terms, they do not affect the linear-elastic property predictions.

The insistence on going beyond the simple free-area approximation has clearly been necessary in view of the size of the multiple-particle cluster corrections shown in Eq. (25). From the standpoint of error estimation the convergence so far looks poor, and it would eventually be desirable to extend the calculation an order or two. We nevertheless have clearly established already the cooperative character of elastic response in the high-compression, rigid-disk crystal.

TABLE I. List of rigid-disk-crystal pair and triplet clusters under vertical uniaxial strain. The cluster graph shown is intended to symbolize the entire set of clusters yielding the same configuration integral, which is invariant to translation and to reflection about the vertical axis. The $\tau(n,\alpha)$ are the combinatorial weights for the cluster sets, required in Eq. (13).

Strain direction	Cluster graph	Cluster number n,α	$\tau(n,\alpha)$
↕		2, 1	1
		2, 2	2
		3, 1	1
		3, 2	2
		3, 3	4
		3, 4	2
		3, 5	2

C. Sound Velocities

Within the high-compression regime, the phenomenological linear elasticity expression (8) may be compactly rewritten as follows:

$$\frac{F_N(T,\mathbf{u})}{N}=\frac{F_N(T,0)}{N}-\frac{2kT}{\theta^{-1}-1}(u_{xx}+u_{yy})+(2N)^{-1}\lambda_{ijlm}u_{ij}u_{lm}, \quad (26)$$

where the repeated-index summation convention applies to the last term (Latin subscripts stand for x or y). In this expression we use the following linear combinations of Greek-subscript elastic constants:

$$\lambda_{xxxx}=\lambda_{yyyy}=4\lambda_{\xi\eta\xi\eta}+2\lambda_{\xi\xi\eta\eta},$$
$$\lambda_{xxyy}=\lambda_{yyxx}=4\lambda_{\xi\eta\xi\eta}-2\lambda_{\xi\xi\eta\eta},$$
$$\lambda_{xyxy}=\lambda_{yxxy}=\lambda_{xyyx}=2\lambda_{\xi\xi\eta\eta}. \quad (27)$$

Because we are now concerned with propagation of sound waves in the crystal with wavelengths very large compared to the lattice spacing, it is necessary to transform the isothermal elastic constants appearing in Eqs. (8) and (26) to adiabatic elastic constants. Adiabatic transformations are carried out at constant entropy $S(T,\mathbf{u})$:

$$-N^{-1}(\partial F_N/\partial T)_{\mathbf{u}}=S(T,\mathbf{u})/N$$
$$=[S(T,0)/N]+[2k/(\theta^{-1}-1)](u_{xx}+u_{yy})-(2N)^{-1}(\partial\lambda_{ijlm}/\partial T)u_{ij}u_{lm}. \quad (28)$$

It suffices for present purposes to obtain a temperature change linear in the strain components, so for the adiabatic change one has

$$S(T,0)/N\cong[S(T+\delta T,0)/N]+[2k/(\theta^{-1}-1)](u_{xx}+u_{yy})$$
$$\cong[S(T,0)/N]+(C_V/T)\delta T+[2k/(\theta^{-1}-1)](u_{xx}+u_{yy}), \quad (29)$$

where we have let C_V stand for the constant-strain specific heat per particle. The linear temperature change is thus

$$\delta T=-[2kT/C_V(\theta^{-1}-1)](u_{xx}+u_{yy}). \quad (30)$$

The adiabatic change analog of the free-energy-change equation (26), correct through second order in $\mathbf{u}$ components, therefore becomes

$$\frac{F_N(T+\delta T,\mathbf{u})}{N}=\frac{F_N(T,0)}{N}-\frac{2k(T+\delta T)}{\theta^{-1}-1}(u_{xx}+u_{yy})+(2N)^{-1}\lambda_{ijlm}u_{ij}u_{lm}$$
$$=\frac{F_N(T,0)}{N}-\frac{2kT}{\theta^{-1}-1}(u_{xx}+u_{yy})+(2N)^{-1}\lambda^{(\mathrm{ad})}{}_{ijlm}u_{ij}u_{lm}; \quad (31)$$

here the temperature change δT in Eq. (30) has been inserted with the result that adiabatic elastic constants [superscripts (ad)] satisfying linear relations (27) arise, with

$$\lambda^{(\mathrm{ad})}{}_{\xi\eta\xi\eta}=[NkT/(\theta^{-1}-1)^2][\tfrac{1}{2}+(2k/C_V)],$$
$$\lambda^{(\mathrm{ad})}{}_{\xi\xi\eta\eta}=\lambda_{\xi\xi\eta\eta}. \quad (32)$$

The wave equation describing adiabatic motion of the vector strain field (components u_i) in a general linear elastic medium has the form[11]

$$\rho\ddot{u}_i=\lambda^{(\mathrm{ad})}{}_{ijlm}(\partial^2u_m/\partial x_k\partial x_l), \quad (33)$$

with ρ equal to the mass density, and again involving the repeated-index summation. We now write out the detailed form for $\ddot{u}_x$ and $\ddot{u}_y$:

$$\rho\ddot{u}_x=\lambda^{(\mathrm{ad})}{}_{xxxx}\frac{\partial^2u_x}{\partial x^2}+\lambda^{(\mathrm{ad})}{}_{xxyy}\frac{\partial^2u_y}{\partial x\partial y}+\lambda^{(\mathrm{ad})}{}_{xyxy}\frac{\partial^2u_y}{\partial y\partial x}+\lambda^{(\mathrm{ad})}{}_{xyyx}\frac{\partial^2u_x}{\partial^2y}; \quad (34)$$

$$\rho\ddot{u}_y=\lambda^{(\mathrm{ad})}{}_{yyyy}\frac{\partial^2u_y}{\partial y^2}+\lambda^{(\mathrm{ad})}{}_{yyxx}\frac{\partial^2u_x}{\partial y\partial x}+\lambda^{(\mathrm{ad})}{}_{yxyx}\frac{\partial^2u_x}{\partial x\partial y}+\lambda^{(\mathrm{ad})}{}_{yxxy}\frac{\partial^2u_y}{\partial x^2}. \quad (35)$$

[11] Reference 6, p. 103.

In the long-wavelength limit for which the wave equation is appropriate, the rigid-disk crystal permits propagation of both pure longitudinal and pure transverse sound waves. The dispersion relation for the former may be obtained by substituting a plane wave corresponding to a longitudinal wave with frequency ω traveling along the x direction:

$$u_x = u_0 \exp[i(\kappa x - \omega t)],$$
$$u_y = 0, \tag{36}$$

into Eq. (34) to obtain

$$\rho\omega^2 = \lambda^{(\mathrm{ad})}{}_{xxxx}\kappa^2. \tag{37}$$

The propagation velocity (group velocity) then can be computed for this mode:

$$v_l = \partial\omega/\partial\kappa = [(\lambda^{(\mathrm{ad})}{}_{xxxx}/\rho)]^{1/2}. \tag{38}$$

The analogous transverse wave propagating in the x direction

$$u_x = 0,$$
$$u_y = u_0 \exp[i(\kappa x - \omega t)] \tag{39}$$

similarly leads to the dispersion relation

$$\rho\omega^2 = \lambda^{(\mathrm{ad})}{}_{yxxy}\kappa^2 \tag{40}$$

and velocity

$$v_t = [(\lambda^{(\mathrm{ad})}{}_{yxxy}/\rho)]^{1/2}. \tag{41}$$

In terms of the previously computed number b in Eq. (25), the dimensionless sound-velocity ratio has the form

$$v_l/v_t = [1+(1/b)+(4k/bC_V)]^{1/2}. \tag{42}$$

If we take the specific heat C_V to equal k (two translational, no internal, degrees of freedom per disk), and adopt the numerical b value obtained in the triplet cell-cluster approximation,

$$v_l/v_t \cong 3.3362, \tag{43}$$

which may be compared with $(6)^{1/2}=2.4495$ that results from the cruder single-particle, free-area approximation ($b=1$).

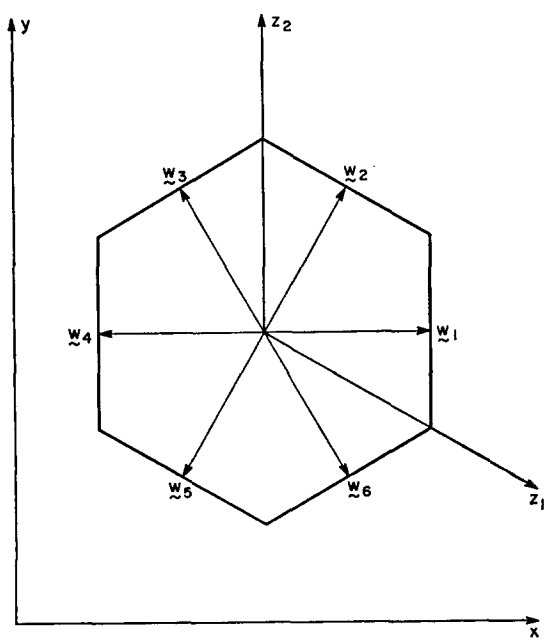

FIG. 3. Undistorted hexagonal flat-sided free area appropriate for the high-compression regime. Unit vectors $\mathbf{w}_1 \cdots \mathbf{w}_6$ point toward nearest neighbors. The oblique coordinate system z_1, z_2 is used in evaluating the cluster integrals.

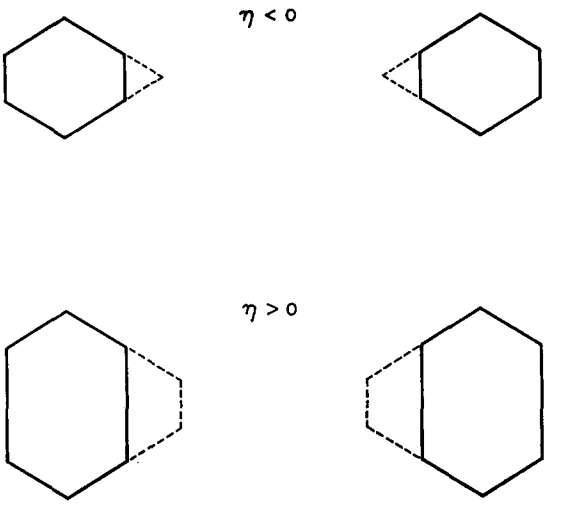

FIG. 4. Effect of vertical uniaxial stretch upon motion of horizontal nearest-neighbor disk pairs. The solid boundaries are the distorted high-compression free areas, and the dotted lines indicate the outer limits of possible disk center excursion, with shapes depending on the sign of distortion η. The free areas shown are of course much expanded relative to the actual near-neighbor separation.

III. FACE-CENTERED-CUBIC SPHERE CRYSTAL

The phenomenological free-energy expression for any cubic crystal, corresponding to rigid-disk Eq. (8), is[12]

$$\frac{F_N(\mathbf{u})}{NkT} = \frac{F_N(0)}{NkT} - \frac{pV}{NkT}(u_{xx}+u_{yy}+u_{zz}) + (NkT)^{-1}[\tfrac{1}{2}\lambda_{xxxx}(u_{xx}^2+u_{yy}^2+u_{zz}^2) + \lambda_{xxyy}(u_{xx}u_{yy}+u_{xx}u_{zz}+u_{yy}u_{zz}) + 2\lambda_{xyxy}(u_{xy}^2+u_{xz}^2+u_{yz}^2)], \tag{44}$$

and in particular applies to the face-centered-cubic crystal of rigid spheres. The occurrence now of three different elastic constants requires separate examination of three distinct homogeneous strains.

Figure 5 exhibits the three basis vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ which generate the face-centered-cubic lattice, with

[12] Reference 6, p. 40.

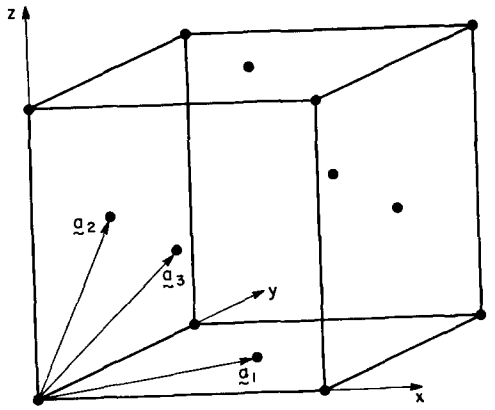

FIG. 5. Basis vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ and the Cartesian coordinate axes for the face-centered-cubic sphere crystal.

the presumption that the ordinary Cartesian x, y, and z axes coincide with the principal crystal axes. The unit vectors pointing toward the 12 nearest neighbors, when expressed in terms of the Cartesian unit vectors $\mathbf{i}$, $\mathbf{j}$, $\mathbf{k}$, are given by

$$\begin{aligned}
\mathbf{w}_1&=\mathbf{a}_1/\,|\,\mathbf{a}_1\,|=(1/\sqrt{2})\,(\mathbf{i}+\mathbf{j}),\\
\mathbf{w}_2&=-\mathbf{w}_1,\\
\mathbf{w}_3&=\mathbf{a}_2/\,|\,\mathbf{a}_2\,|=(1/\sqrt{2})\,(\mathbf{j}+\mathbf{k}),\\
\mathbf{w}_4&=-\mathbf{w}_3,\\
\mathbf{w}_5&=\mathbf{a}_3/\,|\,\mathbf{a}_3\,|=(1/\sqrt{2})\,(\mathbf{i}+\mathbf{k}),\\
\mathbf{w}_6&=-\mathbf{w}_5,\\
\mathbf{w}_7&=\mathbf{w}_1-\mathbf{w}_3,\\
\mathbf{w}_8&=\mathbf{w}_3-\mathbf{w}_1,\\
\mathbf{w}_9&=\mathbf{w}_1-\mathbf{w}_5,\\
\mathbf{w}_{10}&=\mathbf{w}_5-\mathbf{w}_1,\\
\mathbf{w}_{11}&=\mathbf{w}_3-\mathbf{w}_5,\\
\mathbf{w}_{12}&=\mathbf{w}_5-\mathbf{w}_3.
\end{aligned}\tag{45}$$

The partition-function expression (7) and cell-cluster product development (12) are directly applicable to three-dimensional crystals. Of course the number of possible cell clusters for a given number of spheres increases in going from two to three dimensions on account of the variety of possible spatial orientations and conformations. In addition the number of unit step functions in cell clusters of given order increases as well reflecting the increased number of nearest neighbors. However by introducing again an oblique coordinate system z_1, z_2, z_3, whose unit vectors constitute a system reciprocal to $\mathbf{w}_1$, $\mathbf{w}_2$, $\mathbf{w}_3$, the unit step functions may be forced to display arguments in the form of rational polynomials in z_1, z_2, z_3, and the distortion variable η. Thus, again the evaluation of cell-cluster integrals may be performed exactly by the rapid electronic computer scheme utilized already for the disk crystal.

The linear transformation from Cartesian to oblique coordinates leading to rational step function arguments is

$$\begin{aligned}
z_1&=(1/\sqrt{2})\,(x+y),\\
z_2&=(1/\sqrt{2})\,(y+z),\\
z_3&=(1/\sqrt{2})\,(x+z),
\end{aligned}\tag{46}$$

for which the transformation Jacobian is found to be

$$\partial(x,\,y,\,z)/\partial(z_1,\,z_2,\,z_3)=\sqrt{2}.\tag{47}$$

Because the evaluation procedure for cell-cluster integrals involves mostly tedious technical detail rather than conceptual novelty in comparison with the rigid-disk case, we shall only present results.

The first homogeneous strain to be examined is the uniform dilation ($u_{xx}=u_{yy}=u_{zz}=u$):

$$\begin{aligned}
\mathbf{S}&=\eta\mathbf{1},\\
\eta&=3u/(\theta^{-1}-1).
\end{aligned}\tag{48}$$

In exactly the same way as for the previous two-dimensional example the only contribution to the high-compression strain-dependent part of the free energy arises from the "free-volume" single-particle cell integrals. One obtains the result for these:

$$Z^{(1)}(u_{xx}=u_{yy}=u_{zz}=u)=4\sqrt{2}\,(1+\eta)^3.\tag{49}$$

In comparison with Expression (44), this implies an exact high-compression sum rule that must be satisfied by two of the three cubic-crystal elastic constants:

$$\tfrac{1}{2}\lambda_{xxxx}+\lambda_{xxyy}=9NkT/2(\theta^{-1}-1)^2,\tag{50}$$

which may be regarded as a three-dimensional analog of Eq. (21). In the process of comparison of free-energy expressions of course the pressure term in Eq. (44) is found to have the standard free-volume form:

$$pV/NkT=3/(\theta^{-1}-1).\tag{51}$$

The single elastic constant λ_{xxxx} next may separately be obtained from the uniaxial process for which only $u_{yy}=u$ is nonzero, and hence for which

$$\mathbf{S}=\eta\mathbf{jj}.\tag{52}$$

Now in principle all cluster factors $V^{(n,\alpha)}$ should be taken into account for an exact calculation, but on account of computer limitation we are forced to accept as an approximation a truncation after only the pair cell clusters. First, the free-volume integral turns out simply to be

$$Z^{(1)}(u_{yy}=u)=4\sqrt{2}\,(1+\eta).\tag{53}$$

Secondly, there are two distinct types of nearest-neighbor pairs according to whether the connecting link is perpendicular to, or at an oblique (45°) angle

to, the y axis; the respective integrals (weights $\tau_{\perp}=2$ and $\tau_{<}=4$) are

$$Z_{\perp}^{(2)}(u_{yy}=u)=(\sqrt{2})^2[\tfrac{467}{30}+32\eta+\tfrac{55}{3}\eta^2+\tfrac{1}{9}\eta^2(-7\eta+13\mid\eta\mid)$$
$$+\tfrac{1}{12}\eta^3(-31\eta+21\mid\eta\mid)+\tfrac{2}{15}\eta^4(-\eta+3\mid\eta\mid)+\tfrac{1}{18}\eta^5(\eta-\mid\eta\mid)],$$
$$Z_{<}^{(2)}(u_{yy}=u)=(\sqrt{2})^2[\tfrac{467}{30}+\tfrac{307}{10}\eta+\tfrac{61}{4}\eta^2+\tfrac{1}{18}\eta^2(-41\eta+37\mid\eta\mid)$$
$$+\tfrac{1}{192}\eta^3(-397\eta+383\mid\eta\mid)+\tfrac{1}{960}\eta^4(201\eta-140\mid\eta\mid)+\tfrac{1}{23040}\eta^5(4677\eta-5045\mid\eta\mid)]. \quad (54)$$

In combination with Sum Rule (50), the configuration integrals (53) and (54) permit separate deduction of pair–cell approximations to each of λ_{xxxx} and λ_{xxyy}. One finds

$$\lambda_{xxxx}=(9-4.849928+\cdots)[NkT/(\theta^{-1}-1)^2]$$
$$\cong 4.150072[NkT/(\theta^{-1}-1)^2],$$
$$\lambda_{xxyy}=(0+2.424964+\cdots)[NkT/(\theta^{-1}-1)^2]$$
$$\cong 2.424964[NkT/(\theta^{-1}-1)^2]; \quad (55)$$

as before the separate numbers in parentheses are, respectively, the free-volume predictions, and the correlated cell–pair corrections.

The last of the three elastic constants for the face-centered-cubic lattice, λ_{xyxy}, may be obtained by application of a shearing strain which is described for convenience by the unsymmetrical tensor

$$\mathbf{S}=\eta\mathbf{ij}, \quad (56)$$

so that in terms of the conventional symmetrical strain tensor $\mathbf{u}$,

$$\eta=3u/(\theta^{-1}-1)=6u_{xy}/(\theta^{-1}-1), \quad (57)$$

i.e., $u_{xy}=\frac{1}{2}u$ for this case. The result for the sheared free volume is

$$Z^{(1)}(u_{xy}=\tfrac{1}{2}u)=\sqrt{2}(4-\eta^2+(1/32)\mid\eta\mid^3). \quad (58)$$

Figure 6 exhibits the four distinct types of nearest-neighbor pairs; the unit vectors (45) corresponding to each of these types are:

Type 1:	$\mathbf{w}_3$, $\mathbf{w}_4$, $\mathbf{w}_9$, $\mathbf{w}_{10}$	$(\tau=2)$,
Type 2:	$\mathbf{w}_5$, $\mathbf{w}_6$, $\mathbf{w}_7$, $\mathbf{w}_8$	$(\tau=2)$,
Type 3:	$\mathbf{w}_1$, $\mathbf{w}_2$	$(\tau=1)$,
Type 4:	$\mathbf{w}_{11}$, $\mathbf{w}_{12}$	$(\tau=1)$.

(59)

It is clear from Fig. 6 that the pair–cell-cluster integrals for Types 3 and 4 as functions of η should differ only by a sign change of this variable. The machine calculations furthermore show that the integrals for Types 1 and 2 are identical:

$$Z^{(2,1)}(u_{xy}=\tfrac{1}{2}u)=Z^{(2,2)}(u_{xy}=\tfrac{1}{2}u)$$
$$=(\sqrt{2})^2(\tfrac{467}{30}-\tfrac{65}{8}\eta^2+\tfrac{53}{48}\eta^4+\tfrac{1}{160}\mid\eta\mid^5-\tfrac{1}{128}\eta^6),$$
$$Z^{(2,3)}(u_{xy}=\tfrac{1}{2}u)=Z^{(2,4)}(-u_{xy}=-\tfrac{1}{2}u)$$
$$=(\sqrt{2})^2[\tfrac{467}{30}+\tfrac{7}{10}\eta-\tfrac{179}{24}\eta^2-\tfrac{5}{12}\eta^3+\tfrac{1}{96}\eta^3(73\eta+8\mid\eta\mid)$$
$$+\tfrac{1}{480}\eta^4(5\eta+24\mid\eta\mid)+\tfrac{1}{1920}\eta^5(15\eta+8\mid\eta\mid)]. \quad (60)$$

Results (58) and (60) may finally be converted into the last of the three cubic elastic constants[13]:

$$\lambda_{xyxy}=(\tfrac{9}{2}+0.865092+\cdots)[NkT/(\theta^{-1}-1)^2]$$
$$\cong 5.365092[NkT/(\theta^{-1}-1)^2]. \quad (61)$$

[13] It is interesting to notice that the Cauchy relation $\lambda_{xxyy}=\lambda_{xyxy}$ that must be obeyed by central force harmonic crystals fails apparently by more than a factor of 2 in the extremely anharmonic rigid-sphere model.

Each of the face-centered-cubic-lattice pair integrals quoted in Eqs. (54) and (60) of course have a common value$(\sqrt{2})^2(467/30)$ in the limit of zero strain. For the purposes of later comparison with the hexagonal crystal, we note that the limiting undistorted high-compression free energy so implied is

$$F_N(0)/NkT \sim 3\ln[\lambda/a(\theta^{-1}-1)]+C_{\text{fcc}},$$
$$C_{\text{fcc}} = -\ln(4\sqrt{2}/27)-6\ln(467/480)-\cdots$$
$$\cong 1.727710, \tag{62}$$

where the C_{fcc} is imagined arranged according to the $\mathbf{u}=0$ case of Eq. (13).

The last aspect of the rigid-sphere face-centered-cubic lattice will be calculation of sound velocities on the basis of the approximate elastic constants just obtained. We consider only sound propagating along the x axis (the [100] direction). The temperature rise associated with an adiabatic sound wave in the crystal

$$\delta T = -[3kT/C_V(\theta^{-1}-1)](u_{xx}+u_{yy}+u_{zz}) \tag{63}$$

results in the following adiabatic constants:

$$\lambda^{(\text{ad})}{}_{xxxx} = \lambda_{xxxx}+[18Nk^2T/C_V(\theta^{-1}-1)^2],$$
$$\lambda^{(\text{ad})}{}_{xxyy} = \lambda_{xxyy}+[18Nk^2T/C_V(\theta^{-1}-1)^2],$$
$$\lambda^{(\text{ad})}{}_{xyxy} = \lambda_{xyxy}. \tag{64}$$

The general wave equation (33) again permits pure longitudinal,

$$u_x = u_0\exp[i(\kappa x-\omega t)],$$
$$u_y = u_z = 0, \tag{65}$$

and pure transverse modes

$$u_x = u_z = 0,$$
$$u_y = u_0\exp[i(\kappa x-\omega t)]. \tag{66}$$

After evaluating the respective dispersion relations, the sound-velocity ratio is found to be:

$$v_l/v_t = (\lambda^{(\text{ad})}{}_{xxxx}/\lambda^{(\text{ad})}{}_{xyxy})^{1/2}. \tag{67}$$

Finally, setting $C_V = 3k/2$, and accepting approximate values (55) and (61) for the isothermal elastic constants, one obtains

$$v_l/v_t \cong 1.7350, \tag{68}$$

whereas the free-volume approximation yields $(14/3)^{1/2}=2.1602$.

IV. HEXAGONAL SPHERE CRYSTAL

The high symmetry of the face-centered-cubic lattice implies that the stress is isotropic in the undistorted state, i.e., when all 12 nearest-neighbor distances from a given site in the reference lattice are equal. The result in the phenomenological free-energy equation (44) is that the linear terms in strain components all have the same coefficient, $-pV/NkT$, with p the ordinary thermodynamic pressure for the undistorted crystal. The hexagonal crystal however has lower symmetry, and even though it may be constructed from the face-centered lattice by shifting successive close-packed layers of spheres, it does not follow that with the same set of nearest-neighbor reference lattice distances as for the face-centered crystal that the stress will be isotropic.

For reasons of computational convenience nevertheless we elect to define the "undistorted" reference state as the one with equal distances. Then if we choose Cartesian x and y axes to lie in the basal plane, so the z axis coincides with the conventional hexagonal "c axis," the requisite phenomenological free-energy expression must have the following form[6]:

$$\frac{F_N(\mathbf{u})}{NkT} = \frac{F_N(0)}{NkT} - \frac{pV}{NkT}[(u_{xx}+u_{yy}+u_{zz})+\epsilon(2u_{zz}-u_{xx}-u_{yy})]+(NkT)^{-1}\{\tfrac{1}{2}\lambda_{zzzz}u_{zz}^2+2\lambda_{\xi\eta\xi\eta}(u_{xx}+u_{yy})^2$$
$$+\lambda_{\xi\xi\eta\eta}[(u_{xx}-u_{yy})^2+4u_{xy}^2]+2\lambda_{\xi\eta zz}(u_{xx}+u_{yy})u_{zz}+4\lambda_{\xi\eta z}(u_{xz}^2+u_{yz}^2)\}. \tag{69}$$

Here the constant ϵ measures the reference-state stress anisotropy and $-p$ stands for one-third the stress-tensor trace in that state. We do not evaluate all five elastic constants in part because a greater number of homogeneous strains would have to be separately considered, but also our experience has unfortunately shown that evaluation of cell-cluster integrals of given order is far more time consuming for hexagonal than for face-centered-cubic crystals. Instead we are mainly content to examine stability of the crystal with respect

to elongation along the $z(c)$ axis, accompanied by basal plane contraction so as to maintain constant density.

As before, we examine first the homogeneous expansion (48), for which only the free-volume factors in the basic product representation can yield η dependence. It was noted in Ref. 1 that the free volumes of the face-centered-cubic and hexagonal crystals are equal as a result of a geometrically simple transformation relating the two. For that reason the cubic crystal $Z^{(1)}(\eta)$ result quoted in Eq. (49) is equally valid for the hexagonal case. The direct implication is that Eq. (51) once again is the correct high-compression identification for pV/NkT in the free-energy expression (69), and furthermore the hexagonal high-compression elastic constants must obey the exact sum rule:

$$\tfrac{1}{2}\lambda_{zzzz}+8\lambda_{\xi\eta\xi\eta}+4\lambda_{\xi\eta zz}=27NkT/2(\theta^{-1}-1)^2. \quad (70)$$

Figure 7 illustrates the three basic vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ which generate the hexagonal lattice. From them a set of three reciprocal vectors may then be constructed which define as before an oblique coordinate system that can be utilized in evaluation of cell-cluster integrals. We omit details.

It suffices for the cited stability question to examine additionally only the homogeneous c-axis stretch ($u_{zz}=u$, all other components 0):

$$\mathbf{S}=\eta\mathbf{kk},$$
$$\eta=3u/(\theta^{-1}-1). \quad (71)$$

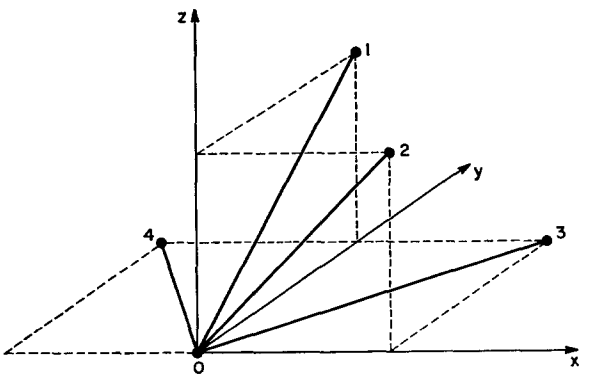

FIG. 6. Examples of the four types of nearest neighbors formed by a particle at the origin 0 in the face-centered-cubic lattice, with $\mathbf{S}=\eta\mathbf{ij}$. To lowest order η with the shearing motion, distance (03) increases, but (04) decreases.

The correspondingly stretched free volume is[14]

$$Z^{(1)}(u_{zz}=u)=(4\sqrt{2})(1+\eta). \quad (72)$$

There are two distinct pair species, oriented, respectively, perpendicular to (such as Vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ in Fig. 7) or obliquely to (vector $\mathbf{a}_3$ in Fig. 7) the stretch axis, with equal numbers of the two species:

$$\tau_\perp=\tau_<=3. \quad (73)$$

Through quadratic terms in the distortion the results may be written as follows:

$$Z_\perp^{(2)}(u_{zz}=u)=(\sqrt{2})^2\,{}^{4\,6\,7}_{3\,0}[1+2.02997859\eta+1.03259576\eta^2+O(\eta^3)],$$
$$Z_<^{(2)}(u_{zz}=u)=(\sqrt{2})^2\,{}^{9\,0\,8\;1\,7\,9}_{5\,8\;3\,2\,0}[1+1.96926377\eta+0.94626720\eta^2+O(\eta^3)]. \quad (74)$$

Although $Z_\perp^{(2)}$ reduces for $\eta=0$ to the common value for undistorted pair cluster integrals for the preceding cubic case, $Z_<^{(2)}$ does not, but instead exhibits a slightly larger value. The undistorted hexagonal free energy to be compared with Eq. (62) (both in the cell–pair approximation) is

$$F_N(0)/NkT\sim 3\ln[\lambda/a(\theta^{-1}-1)]+C_{\text{hex}},$$
$$C_{\text{hex}}=-\ln(4\sqrt{2}/27)-[3\ln({}^{4\,6\,7}_{4\,8\,0})+3\ln({}^{9\,0\,8\;1\,7\,9}_{9\,3\,3\;1\,2\,0})]-\cdots. \quad (75)$$

The implication in this order of approximation is that at least under high compression the hexagonal crystal has a lower free energy per sphere than the face-centered-cubic crystal, with

$$\Delta F_N(0)/NkT\cong 0.00109. \quad (76)$$

The singlet and pair integral η variations shown in Eqs. (72) and (74) permit estimates to be made for ϵ and the single elastic constant λ_{zzzz}:

$$\epsilon=0-0.00113647+\cdots$$
$$\cong -0.00113647;$$
$$\lambda_{zzzz}=(9+1.109348+\cdots)[NkT/(\theta^{-1}-1)^2]$$
$$\cong 10.109348[NkT/(\theta^{-1}-1)^2]. \quad (77)$$

The other two elastic constants appearing in the sum rule (70) may also actually be evaluated with the infor-

[14] That the same result obtains here as for the similarly stretched face-centered free volume, Eq. (53), again reflects the existence of the geometrical transformation between these polyhedra.

mation already at hand. The class of strains for which

$$u_{xx}=u_{yy}=\alpha,$$
$$u_{zz}=\alpha', \tag{78}$$

with α and α' independent variables, and all other u's vanishing, may by virtue of the trivial identity for the stretch-factor product,

$$(1+u_{xx})(1+u_{yy})(1+u_{zz})=(1+\alpha)^2(1+\alpha')\equiv(1+\alpha)^3\{1+[(\alpha'-\alpha)/(1+\alpha)]\}, \tag{79}$$

be regarded as composed of a homogeneous dilation ($u_{xx}=u_{yy}=u_{zz}=\alpha$) followed by a uniaxial strain $\{u_{zz}=[(\alpha'-\alpha)/(1+\alpha)]\}$. We know therefore that the free-volume integral will automatically be

$$Z^{(1)}(\alpha,\alpha')=(4\sqrt{2})\{1+[3\alpha/(\theta^{-1}-1)]\}^3\{1+[3(\alpha'-\alpha)/(1+\alpha)(\theta^{-1}-1)]\}. \tag{80}$$

Furthermore, we know that $Y^{(n)}$ factors for $n\geq 2$ are invariant to uniform dilation, so for Processes (78) it suffices to construct $Y^{(2)}$'s from the uniaxial pair integrals (74) by setting $\eta=3(\alpha'-\alpha)/(1+\alpha)(\theta^{-1}-1)$. After this is done, comparison of the resulting free-energy expression with the basic form (69) for the hexagonal crystal yields the following high-compression values:

$$\begin{aligned}\lambda_{\xi\eta\xi\eta}&=(\tfrac{9}{4}+0.069334+\cdots)[NkT/(\theta^{-1}-1)^2]\\&\cong 2.319334[NkT/(\theta^{-1}-1)^2];\\ \lambda_{\xi\eta zz}&=(-\tfrac{9}{4}-0.277337+\cdots)[NkT/(\theta^{-1}-1)^2]\\&\cong -2.527337[NkT/(\theta^{-1}-1)^2].\end{aligned} \tag{81}$$

The sum rule (70) is satisfied by our pair-cluster approximate elastic constants displayed in (77) and (81).

The final remaining task is examination of crystal stability with respect to that particular distortion of type (78) for which over-all particle density is invariant. This condition requires that α' as a function of α vary in just the proper manner that the stretch factor product remain equal to unity:

$$\begin{aligned}1&=(1+u_{xx})(1+u_{yy})(1+u_{zz})\\&=(1+\alpha)^2[1+\alpha'(\alpha)].\end{aligned} \tag{82}$$

To the requisite quadratic order therefore

$$\alpha'(\alpha)=-2\alpha+4\alpha^2+O(\alpha^3). \tag{83}$$

In view of this manner of coupling the α and α' variations, the free-energy expression (69) may be developed into a quadratic expression in α:

$$F_N(\alpha)/NkT=[F_N(0)/NkT]+[18\epsilon/(\theta^{-1}-1)]\alpha+(NkT)^{-1}(2\lambda_{zzzz}+8\lambda_{\xi\eta\xi\eta}-8\lambda_{\xi\eta zz})\alpha^2. \tag{84}$$

The thermodynamically stable configuration for the hexagonal sphere crystal should correspond to the minimum of this function of α, which is immediately found to be

$$\begin{aligned}\alpha_{\min}&=-\frac{9\epsilon NkT}{2(\theta^{-1}-1)(\lambda_{zzzz}+4\lambda_{\xi\eta\xi\eta}-4\lambda_{\xi\eta zz})}\\&\cong 0.00017338(\theta^{-1}-1).\end{aligned} \tag{85}$$

At least in the cell–pair-cluster approximation, therefore, our theory predicts that the stable configuration of the hexagonal crystal (with isotropic stress) displays slightly larger nearest-neighbor distances within the successive layers of spheres parallel to the basal plane, than for nearest-neighbor pairs inclined obliquely to the c axis. Of course in the close-packed limit $\theta=1$ all distances are forced geometrically to be equal, and (85) vanishes accordingly. Our result may perhaps best be viewed as a small stable distortion of the free-volume dodecahedron amounting to several hundredths of a percent. The corresponding free-energy reduction may be obtained by inserting the quantity (85) into (84):

$$F_N(\alpha_{\min})/NkT=[F_N(0)/NkT]-0.000001773. \tag{86}$$

This very tiny reduction is about three powers of ten less than the free-energy difference obtained in Eq. (76) for undistorted face-centered-cubic and hexagonal crystals.

V. DISCUSSION

One must in fairness question the significance of the low-order results reported here. Although it may never be possible to prove convergence of the very complicated cell-cluster free-energy series, we have proceeded under the tentative assumption that useful results could be derived at least in the sense of asymptotic series. From this point of view we shall in a forthcoming communication extend computation of undistorted crystal additive free-energy constants C_{fcc} and C_{hex} to triplet clusters to see if the relative stability of the hexagonal crystal is maintained. In addition we shall then also report results for hybrid sphere crystals constructed by stacking schemes intermediate between those for pure face-centered cubic and hexagonal.[15]

Unquestionably the most useful assessment of our calculations of the many-body aspects of rigid-sphere-crystal phenomena could be provided by suitably designed electronic computer "experiments," either of the Monte Carlo[16] or the molecular-dynamic variety.[17] In particular it should in principle be possible to investigate the relative stability of the two crystal forms by integrating "measured" equations of state for each by the procedure outlined in Ref. 1, Sec. V. Alternatively, initial conditions could be selected for computer experiments consisting of a composite crystal at high compression, half-face-centered cubic and half-hexagonal, and then to see (by introduction of a few vacancies to enhance diffusion) which half grows at the expense of the other.

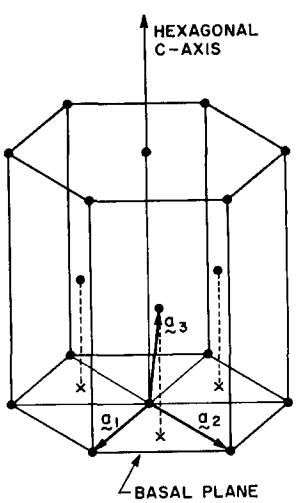

FIG. 7. Basis vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ generating the hexagonal-crystal reference lattice.

It has been traditional in computer experiments to select boundary conditions (usually periodic-boundary conditions) which are consistent with unstrained crystals. The negative value obtained for ϵ in Sec. IV suggests that if a hexagonal crystal were so constrained and "measurements" separately taken of the various mean stress components, the hexagonal c-axis stress p_{zz} should be slightly less than the basal plane $p_{xx}=p_{yy}$. Equivalently, the contact pair correlation function should be larger for basal plane pairs than for oblique pairs. More generally it should be possible to measure each isothermal elastic constant (when the density is sufficiently high to prevent sphere migration) by measuring stress components as the periodicity cell changes shape in various ways.

The molecular-dynamics approach furthermore raises the possibility of direct measurement of sound velocities, and therefore of adiabatic elastic constants. Relevant initial conditions in such an investigation for example might correspond to a sinusoidal density distribution (for subsequent longitudinal standing waves) or a sinusoidal increment of transverse particle velocities (for transverse standing waves).

Beside their implications for macroscopic sound propagation, computations of crystal elasticity bear in an important way on the character of point defects in solids.[18] We therefore anticipate complementary calculations, both by extension of the present paper's technique and by computer experiment, of the free energy and configurational relaxation around vacancies in crystals.

Finally we mention only briefly the conviction that the appearance of absolute values of strain components, for instance in Eqs. (24), for terms in the cell-cluster development contributing to nonlinear elasticity, must surely be an artifact. The source is the fixed set of neighbors constrained to lattice sites for any given cluster under consideration, with the result that multidimensional polyhedra whose content must be evaluated for $Z^{(n)}$ change their numbers of edges and vertices with strain component sign change. In the actual crystal of course neighbors of any set of particles constantly fluctuate in position, so one may crudely say that the sharply delineated cell-cluster polyhedra are smeared on the average. If it were possible to calculate any selected nonlinear elastic response through ascending orders by our procedure, one probably would find the numerical coefficient of the absolute-value portion converging to zero. More practically, it seems reasonable in any finite order simply to average calculated responses for positive and for negative strains.

[15] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, N.Y., 1960), pp. 407–409.

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[17] B. J. Alder and T. E. Wainwright, Phys. Rev. **127**, 359 (1962).

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