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Density-functional theory of elastic moduli: Hard-sphere and Lennard-Jones crystals

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We propose a density-functional method for calculating elastic moduli of crystalline solids. The method is based on the second-order Ramakrishnan-Yussouff (RY) expansion of the variational grand-canonical potential around a uniform liquid state. The densities of the strained and unstrained crystal are represented as sums of narrow Gaussians. We express the crystal moduli in terms of the liquid structure factor its first and second derivatives evaluated at the reciprocal-lattice points of the crystal. We evaluate the elastic moduli for fcc hard-sphere and Lennard-Jones crystals using the Percus-Yevick and computer-simulation liquid structure factors, respectively. An indirect comparison with available experimental and theoretical values shows that although our calculated moduli are accurate to an order of magnitude, higher-order terms in the RY expansion might be significant. We find important contributions from density equilibration within the strained unit cell.

I. INTRODUCTION

The only zero-frequency elastic response which a fluid can exhibit is the compressibility. The isothermal compressibility is related via fluctuation-compressibility theorem to the density fluctuations[1] in a fluid. For solids, the fluctuation-compressibility relation can be generalized[2] to all zero-frequency elastic moduli except those that represent response to a shear stress.

The lattice theory[3] of elastic constants first developed by Born was restricted to perfect crystals at zero temperature. Exact expressions for isothermal elastic moduli that contain fluctuation effects omitted by Born and which made important contribution at nonzero temperature were derived by Squire *et al.*[4] The expressions for elastic moduli were evaluated via Monte Carlo techniques. In this theory, the interparticle potential plays an explicit role while the structure of the crystal plays an implicit role.

Lipkin *et al.*[5] and Ramakrishnan[6] have introduced an approximate theory of elastic moduli based on Ramakrishnan-Yussouff (RY) density-functional theory[7] of solidification. In this theory the role of the structure of the medium is explicit while leaving the role of interparticle potential implicit, buried in the two- (multi-) particle correlation function of a metastable fluid state around which an expansion is developed. In particular, the elastic constants of a solid have been expressed in terms of the curvature at the main peak of the fluid structure factor by assuming that this contribution is dominant. They also implicitly assumed affine density deformation of the strained medium at *all* scales. This is generally not the case below the Cauchy length.[8]

The usual variational calculations of the grand-canonical potential follow from the classical theorems of Gibbs[9] and their quantum generalizations.[10–15] The main result, first established by Lee and Yang,[10] states that the grand partition function of a system of interacting particles is stationary with respect to variations of the single-particle density. Ramakrishnan and Yussouff[7] separated the variational grand-canonical potential into an explicit entropy contribution and a contribution from interparticle interactions. Then, they expanded the interaction part into a functional Taylor series around a uniform fluid state. In this way they could express the grand-canonical potential of the solid in terms of the direct correlation functions of the coexisting or metastable liquid.

This theory resembles a molecular-field theory in which each particle sees an external (chemical) potential and a response potential (molecular field) self-consistently set up by the interparticle interaction. The extremum equation, analogous to the self-consistency condition of a molecular-field theory, is a nonlinear integral equation for the solid density. RY found approximate periodic (crystal) solutions of this equation by expanding the solid density into a Fourier series, then projecting from the resulting equation a set of nonlinear equations for the Fourier amplitudes of the density. Solutions of these nonlinear equations show[7] how correlations in the fluid self-consistently generate a nonuniform density of crystalline periodicity and symmetry.

Recently, several authors realized that sufficient accuracy can often be achieved by a much simpler expansion of the solid density into narrow Gaussians.[16–20] Such an expansion is justified by actual calculations of the Fourier amplitudes and by the experimental fact that even at the melting point of many crystals the atomic motions are small and approximately harmonic.[21,22]

Density-functional theories have been quite successful in predicting solidification parameters for hard-sphere[17,18,22] (HS) and Lennard-Jones[19,23] (LJ) fluids. Such theories were also used to study submonolayer phases of rare gases on graphite,[16] the glass transition,[24]

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and most recently the stability of icosahedral quasicrystals.[20] Several authors have proposed that a similar approach can be used for "first-principles" calculations of such quantities as defect energy,[6,25,26] liquid-solid interface,[27] etc.

In order to calculate the elastic free energy of a strained solid, and thus its elastic moduli, we evaluate its grand-canonical potential and density using the same approximation as when evaluating the grand-canonical potential of the unstrained solid. In this way we take account of the fact that the solid crystal density deforms under a stress in a nonaffine way below the unit-cell scale. This is manifested in a change of the concentration of interstitials and vacancies as well as in a nonaffine change (relaxation) of the Gaussian widths. In many experimental situations the vacancy concentration change can be neglected because of the long diffusion times. However, the relaxation of the widths plays a more fundamental role as we will see in the case of the hard-sphere crystal. Some results of this paper have been summarized in an earlier publication.[28]

We calculated elastic moduli for fcc hard-sphere and Lennard-Jones crystals at the melting point and near the triple point, respectively. For the HS calculation we used Percus-Yevick liquid structure factor, while for the LJ calculation we used a structure factor obtained by computer simulations.[29] Calculated elastic moduli are correct to an order of magnitude. However, a more stringent test of our results is not possible at present since the measured or independently calculated elastic moduli are determined at different points in the phase diagrams. It appears that although third-order terms in RY expansion are not significant for determination of the solid-liquid phase boundary, they are for accuracy of elastic moduli.[30,31] The theory which we developed here can be easily extended to the case when third- or higher-order terms are included.

We review the density-functional formalism in Sec. II. Thermodynamics of elastically deformed media is summarized in Sec. III. In Sec. IV we discuss the Gaussian expansions for the strained and unstrained solids and we derive expressions for the elastic energy and moduli. Results of the application of our theory to HS and LJ solids are presented in Sec. V. The last section is devoted to summary and discussion. In Appendix A we derive a simple molecular-field theory of a classical fluid (and solid) and we emphasize its distinction from the density-functional theory of Ramakrishnan and Yussouff. In Appendix B we derive thermodynamic equations for a crystal at finite strain. Explicit formulas for the elastic modulus tensor, written in terms of reciprocal-lattice sums over the derivatives of the liquid structure factor, are derived in Appendix C.

II. DENSITY-FUNCTIONAL THEORY

In this section we give a short tutorial to the variational formulation of the calculation of the thermodynamic grand-canonical potential.

Generally, the thermodynamic grand-canonical potential G can be variationally determined as

$$G[\mu(\vec{x});V,T]=\min_{\rho}\,\mathrm{tr}\rho\left[k_BT\ln\rho+H_N-\int_v n_N(\vec{x})\mu(\vec{x})d^3x\right]\,, \tag{2.1}$$

where, classically,

$$\mathrm{tr}\equiv\sum_{N=0}^{\infty}\frac{1}{N!}\prod_{i=1}^{N}\frac{1}{h^3}\int_{\infty}d^3p_i\int_V d^3x_i\,, \tag{2.2}$$

h is Planck's constant and $\vec{p}_i$ and $\vec{x}_i$ are momenta and coordinates of N particles at temperature T, restricted to the volume V in the presence of the external (chemical) potential $\mu(\vec{x})$ and interacting via Hamiltonian H_N ($k_BT=\beta^{-1}$ is the Boltzmann factor). The microscopic single-particle density of the N-particle system is

$$n_N(\vec{x})\equiv\sum_{i=1}^{N}\delta(\vec{x}-\vec{x}_i)\,. \tag{2.3}$$

The variation in Eq. (2.1) is to be performed over the *normalized* probability distribution (*density matrix*) ρ. The distribution which minimizes Eq. (2.1) is the Boltzmann distribution

$$\rho_B\equiv\frac{\exp\left[\beta\left[\int_V n_N(\vec{x})\mu(\vec{x})d^3x-H_N\right]\right]}{\mathrm{tr}\exp\left[\beta\left[\int_V n_N(\vec{x})\mu(\vec{x})d^3x-H_N\right]\right]}\,. \tag{2.4}$$

The Boltzmann distribution is explicitly a functional of the chemical potential. However, it can be also viewed as an implicit functional of the equilibrium particle density $n(\vec{x})$,

$$n(\vec{x})=\mathrm{tr}\rho_B n_N(\vec{x})\,. \tag{2.5}$$

Therefore, one may restrict the variation in Eq. (2.1) to $\rho=\rho_B[n(\vec{x})]$, with $n(\vec{x})$ as the variable,

$$G[\mu(\vec{x});V,T]=\min_{n(\vec{x})}\,\mathrm{tr}\rho_B[n(\vec{x})]\left[k_BT\ln\rho_B[n(\vec{x})]+H_N-\int_V n_N(\vec{x})\mu(\vec{x})d^3x\right]\,. \tag{2.6}$$

Clearly, $n(\vec{x})$ which minimizes Eq. (2.6) for a given $\mu(\vec{x})$ will be the equilibrium density which will automatically satisfy Eq. (2.5). In fact, Eq. (2.6) can be written as

$$G[\mu(\vec{x});V,T]=\min_{n(\vec{x})}\left[F[n(\vec{x});V,T]-\int_V n(\vec{x})\mu(\vec{x})d^3x\right]\,, \tag{2.7}$$

in which case it can be recognized as a statement of the familiar fact that the grand-canonical potential $G[\mu(\vec{x});V,T]$ is the Legendre transform of the Helmholtz potential $F[n(\vec{x});V,T]$,

$$F[n(\vec{x});V,T]=\mathrm{tr}\rho_B[n(\vec{x})]\{k_BT\ln\rho_B[n(\vec{x})]+H_N\}\,. \tag{2.8}$$

The chemical potential $\mu(\vec{x})$ can be explicitly determined as a functional of the density $n(\vec{x})$ by

$$\mu(\vec{x})=\frac{\delta F[n(\vec{x});V,T]}{\delta n(\vec{x})} . \tag{2.9}$$

The Helmholtz potential for a system of noninteracting particles is purely entropic

$$F_0[n(\vec{x});V,T]=k_BT\int_V n(\vec{x})\{\ln[n(\vec{x})\lambda_T^3]-1\}d^3x , \tag{2.10}$$

where $\lambda_T\equiv(h^2/2\pi mk_BT)^{1/2}$ is the thermal wavelength of a particle of mass m in a bath at temperature T. Therefore, the Helmholtz potential for an interacting system can be written in the form

$$F[n(\vec{x});V,T]=F_0[n(\vec{x});V,T]+F_{\text{int}}[n(\vec{x});V,T] . \tag{2.11}$$

The functional $F_{\text{int}}[n(\vec{x});V,T]$ contains the full effect of many-body interaction and will be expanded in the functional Taylor series around a liquid state with density $n_l(\vec{x})$ and corresponding chemical potential $\mu_l(\vec{x})$.

The expansion of F_{int} can be carried out by using the following relation:

$$\frac{\delta F_{\text{int}}[n_l(\vec{x})]}{\delta n(\vec{x})}=\mu_l(\vec{x})-k_BT\ln[n_l(\vec{x})\lambda_T^3] , \tag{2.12}$$

and the definition of the m-point ($m\geq 2$) direct correlation function of the liquid

$$\begin{aligned}k_BTC_l^{(m)}(\vec{x}_1,\ldots,\vec{x}_m)&=-\frac{\delta^mF_{\text{int}}[n_l(\vec{x})]}{\delta n(\vec{x}_1)\cdots\delta n(\vec{x}_m)}\\&=-\frac{\delta^mF[n_l(\vec{x})]}{\delta n(\vec{x}_1)\cdots\delta n(\vec{x}_m)}+(-1)^m(m-2)!n_l(\vec{x}_1)^{1-m}\delta(\vec{x}_1-\vec{x}_2)\cdots\delta(\vec{x}_1-\vec{x}_m) .\end{aligned} \tag{2.13}$$

Combining this expansion with Eq. (2.7), we can write

$$G[\mu(\vec{x});V,T]-G_l[\mu_l(\vec{x});V,T]=\min_{n(\vec{x})}\Delta W[n(\vec{x}),\mu(\vec{x});V,T] , \tag{2.14}$$

where the variational potential ΔW is

$$\begin{aligned}\beta\Delta W[n(\vec{x}),\mu(\vec{x});V,T]=&\int_V\left[n(\vec{x})\ln\frac{n(\vec{x})}{n_l(\vec{x})}-\Delta n(\vec{x})-\beta n(\vec{x})\Delta\mu(\vec{x})\right]d^3x\\&-\frac{1}{2}\int_V\int_V C_l^{(2)}(\vec{x}_1,\vec{x}_2)\Delta n(\vec{x}_1)\Delta n(\vec{x}_2)d^3x_1d^3x_2+\cdots ,\end{aligned} \tag{2.15}$$

and $\Delta n(\vec{x})\equiv n(\vec{x})-n_l(\vec{x})$, $\Delta\mu(\vec{x})\equiv\mu(\vec{x})-\mu_l(\vec{x})$. Clearly, the left-hand side of Eq. (2.14) gives the pressure difference $\Delta P\equiv P-P_l$:

$$-V\Delta P=G[\mu(\vec{x});V,T]-G_l[\mu_l(\vec{x});V,T] . \tag{2.16}$$

In the absence of an external potential, the case with which we are concerned, $\mu(\vec{x})$ and $\mu_l(\vec{x})$ are constants and the liquid state has a uniform density n_l. In this case the grand-canonical potential can be expressed as

$$G(\mu,V,T)=\min_N[F(N,V,T)-\mu N] . \tag{2.17}$$

Its Legendre transform $F(N,V,T)$ is obtained from

$$F(N,V,T)=\min_{\substack{n(\vec{x})\\ n=N/V}}F[n(\vec{x}),V,T] , \tag{2.18}$$

where the minimization is over densities whose average is fixed to $n=N/V$. At the coexistence between the reference liquid and a solid it is required that

$$\mu_s=\mu_l , \tag{2.19}$$

and

$$-VP_s=G(\mu_s,V,T)=G_l(\mu_l,V,T)=-VP_l . \tag{2.20}$$

Once the usual thermodynamic grand-canonical potential $G(\mu,V,T)$, or the Helmholtz potential $F(N,V,T)$ are known, we can obtain various quantities of interest from the standard thermodynamic relations[32]

$$dG=-S\,dT-P\,dV-N\,d\mu , \tag{2.21}$$

or

$$dF=-S\,dT-P\,dV+\mu\,dN , \tag{2.22}$$

and from the observation that F, for example, is an extensive quantity,

$$F=Nf(n,T) . \tag{2.23}$$

In the next section we shall generalize these equations to describe the thermodynamics of elastic deformations.

Equations (2.14) and (2.15) are the central equations of RY theory of solidification. They are reminiscent of molecular-field equations but should not be confused with these. Approximations introduced into RY theory by truncating the expansion of the variational potential can, in principle, be as good as one desires, providing the expansion is convergent. The usual molecular-field theory approximates the probability distribution and cannot be improved without invoking multiparticle densities. The molecular-field approximation could be viewed as a truncation of the RY expansion at the second order, combined with the identification of the pair correlation function and the interparticle pair potential. This is the essential and important difference between the molecular-field and RY theories. A derivation of a molecular-field theory is given in Appendix A.

The correlation functions $C_l^{(m)}$ will, in general, depend on the thermodynamic state of the liquid. In particular, the direct pair correlation function is a function only of $|\vec{x}_1-\vec{x}_2|$ for a spatially homogeneous and isotropic liquid state

$$C_l^{(2)}(\vec{x}_1,\vec{x}_2)\equiv C_l(|\vec{x}_1-\vec{x}_2|) . \tag{2.24}$$

The function $C_l(|\vec{x}|)$ can also be viewed in a slightly different way: Instead of simply minimizing over possible density functions, we can regard Eq. (2.15) as the starting point for a kind of coarse-grained statistical mechanics, in the spirit of the Landau-Ginzburg-Wilson theories of critical phenomena.[33] The Boltzmann weight associated with a density configuration $n(\vec{x})$ is $\exp(-\beta\Delta W)$, and the true partition function is obtained by carrying out a functional integral over the possible densities $n(\vec{x})$. Upon truncating Eq. (2.15) at second order in $\Delta n(\vec{x})$, and Fourier transforming, we can easily show using this approach that $C_l(|\vec{x}|)$ is related to the structure function,

$$S_l(|\vec{q}|)=\langle|\Delta n(\vec{q})|^2\rangle\approx[1-C_l(|\vec{q}|)]^{-1} , \tag{2.25}$$

where

$$C_l(|\vec{q}|)\equiv n_l\int C_l(|\vec{x}|)e^{i\vec{q}\cdot\vec{x}}d^3x . \tag{2.26}$$

The structure function at zero $\vec{q}$ is related to the isothermal compressibility κ_T of the liquid by the fluctuation-compressibility theorem,

$$S_l(0)=n_l\kappa_T k_B T . \tag{2.27}$$

Higher-order nonlinearities will give corrections to the result in Eq. (2.25). Provided these effects are small, we can extract C_l from an experimentally measured liquid structure function. We can then return to the expression (2.15) and search for crystalline states with a lower thermodynamic potential. Minimizing $\Delta W[n(\vec{x}),\mu;V,T]$ over possible densities $n(\vec{x})$ is equivalent to neglecting fluctuations about the preferred state in the statistical mechanical treatment sketched above.

If Eq. (2.15) is regarded as arising from a coarse-graining procedure, there will also be a background, singular contribution to the thermodynamic potential. Although this potential plays no role in determining the relative stability of liquid and crystalline states, it can contribute weak temperature and chemical potential dependence to thermodynamic derivatives. Because the translational correlation length (and, hence, coarse-graining scale) in three-dimensional liquids rarely becomes large, corrections due to this effect will be quite small.

III. THERMODYNAMICS OF ELASTIC DEFORMATIONS

In this section we shall first discuss thermodynamics of infinitesimal isothermal elastic deformations from a density-functional point of view. In particular, we shall analyze the effect of nonaffine density deformations below the Cauchy scale, as well as the strain dependence of the vacancy concentration. Then, we shall briefly review the usual thermodynamic relations establishing connection between isothermal and isentropic elastic moduli as well as connection between the moduli at constant chemical potential and constant number of particles. A discussion of thermodynamics at *finite* strain is left for Appendix B.

Consider the uniform change in density $n(\vec{x})$ under a general nonsingular affine coordinate transformation $\mathbf{A}$

$$n(\vec{x})\rightarrow n'(\vec{x})=n(\mathbf{A}^{-1}\cdot\vec{x})/J_A . \tag{3.1}$$

For ordinary materials in the absence of external fields, we can restrict our attention to symmetric linear (homogeneous) transformations (matrices) $\mathbf{A}$, since any inhomogeneous, or antisymmetric parts in $\mathbf{A}$ correspond to energy preserving translations or rotation reflections, respectively. In this case $J_A=\det\mathbf{A}$. More general $\mathbf{A}$'s will be required to describe low-energy deformations of incommensurate and, in particular, icosahedral crystals and will be discussed in Ref. 34. The Jacobian J_A occurs in the denominator in Eq. (3.1) to insure that the total number of particles N remains unchanged by the transformation. Indeed, we have

$$N'=\int_{V'}n'(\vec{x})d^3x=\int_V n(\vec{x}')d^3x'=N , \tag{3.2}$$

where $\vec{x}'=\mathbf{A}^{-1}\cdot\vec{x}$, and V' and V indicate integrations over transformed and untransformed volumes, respectively.

Given a particular equilibrium density $n(\vec{x})$ of a solid, we now ask how the thermodynamic potential changes under a small deformation of the solid characterized by a symmetric constant strain matrix ϵ. If a piece of the material were uniformly strained, the strained density would be given by Eq. (3.1) with[35]

$$\mathbf{A}=1+\epsilon . \tag{3.3}$$

However, we imagine a static experiment in which a strain ϵ is imposed on the surface of a sample so that, initially, the density at the strained surface of the sample is

$$n_\epsilon(\vec{x})=n(\mathbf{A}^{-1}\cdot\vec{x})/J_A , \tag{3.4}$$

while the density in the interior of the sample is allowed to relax to find the minimum of an appropriate thermodynamic potential. In such an experiment the particle number is conserved.

Two cases of density equilibration in a strained solid can be imagined. In the first case we imagine the density at the sample surfaces to be clamped to the reservoir, satisfying Eq. (3.4) at all times. In this case the equilibrium strained density $n_\epsilon(\vec{x})$ will satisfy Eq. (3.4) also at all scales above certain scale. For ordinary crystals this (Cauchy) scale is assumed to coincide with the unit cell scale. The unit cell of the strained crystal is the strained unit cell of the original, unstrained crystal. That is,

$$\mathbf{a}_\epsilon = \mathbf{A}\cdot\mathbf{a} = (1+\boldsymbol{\epsilon})\cdot\mathbf{a} \ , \tag{3.5}$$

where $\mathbf{a}$ and $\mathbf{a}_\epsilon$ are 3×3 matrices whose columns are primitive lattice vectors of the original and the strained crystal, respectively. Clearly, the equilibrium density *within* the strained unit cell will not generally satisfy Eq. (3.4) and must be determined by actual minimization of a thermodynamic potential.

In the second case, we imagine that after the surface is strained the density initially distorts as above. Then, because of vacancy migration (annihilation or creation), the strained density relaxes at all scales, including the surface. After a sufficiently long time, motion of the vacancies, which can leave or enter the crystal, will lead to the strained unit cell defined by a *microscopic* strain $\boldsymbol{\zeta}$,

$$\mathbf{a}_\epsilon = \mathbf{A}_m\cdot\mathbf{a} \equiv (1+\boldsymbol{\zeta})\cdot\mathbf{a} \ , \tag{3.6}$$

which is generally different from the *macroscopic,* fixed strain $\boldsymbol{\epsilon}$. In the limit of large volume and after allowing the strained crystal to relax for infinite time, the microscopic strain should only depend on the volume change, that is on J_A,

$$\frac{\Delta V}{V} = \frac{V_\epsilon - V}{V} = J_A - 1 \ . \tag{3.7}$$

In other words, after a sufficiently long time, the strained crystal will recrystallize with a lattice determined by the density change imposed by the strain and determined by a minimization of the Helmholtz free energy as in Eq. (2.18), where the average density is fixed to $n_{s\epsilon} = N/V_\epsilon$,

$$F(N,V_\epsilon,T) = \min_{\substack{n_\epsilon(\vec{x}) \\ n_{s\epsilon}=N/V_\epsilon}} F[n_\epsilon(\vec{x}),V_\epsilon,T] \ . \tag{3.8}$$

At intermediate times, the relationship between $\boldsymbol{\zeta}$ and $\boldsymbol{\epsilon}$ depends on the precise mechanism by which the vacancies migrate. It is experimentally observed that microscopic and macroscopic strains are generally different,[36] but a systematic investigation seems to be lacking at the present. It is conceivable that there exists a well-defined regime in which $\mathbf{A}_m$ is simply proportional to $\mathbf{A}$,

$$\mathbf{A}_m = \kappa\mathbf{A} \ , \tag{3.9}$$

where κ is a scalar function of $\boldsymbol{\epsilon}$.

The last relationship, Eq. (3.9), has been implicitly assumed in a recent calculation of elastic constants of the hard-sphere solid, albeit the same calculation has not accounted for the full relaxation within the strained unit cell.[37] In the present work, after deriving the general formulas, we shall assume validity of Eq. (3.5), that is, $\mathbf{A}_m = \mathbf{A}$ or, equivalently

$$\boldsymbol{\zeta} = \boldsymbol{\epsilon} \ , \tag{3.10}$$

as required in the first case discussed above. Some results derived using Eq. (3.9) will be presented elsewhere.[31]

Strictly speaking, an experiment on a sufficiently large sample, which is equilibrated for a sufficiently long time, will be, as discussed above, characterized by the usual thermodynamic functions which depend only on the volume V_ϵ of the strained sample,

$$V_\epsilon = VJ_A = V\det(1+\boldsymbol{\epsilon}) \ , \tag{3.11}$$

but are otherwise independent of the macroscopically imposed strain $\boldsymbol{\epsilon}$. In this case Eqs. (2.21) and (2.22) suffice. However, in the cases of two experiments envisioned above, Eqs. (3.9) and (3.10), or when the microscopic strain is a more general function of the macroscopic strain, it is necessary to define a strain-dependent Helmholtz potential

$$F_\epsilon(N,V,T) = \min_{\substack{n_\epsilon(\vec{x}) \\ n_{s\epsilon}=N/V_\epsilon,\mathbf{a}_\epsilon=\mathbf{A}_m\cdot\mathbf{a}}} F[n_\epsilon(\vec{x});V_\epsilon,T] \ , \tag{3.12}$$

where the minimization is over *periodic* densities characterized by the Bravais lattice given in Eq. (3.6) and constrained as in Eq. (3.10) [or, more generally, in Eq. (3.9)], while the average strained density is fixed to

$$n_{s\epsilon} \equiv \frac{1}{V_\epsilon}\int_{V_\epsilon} n_\epsilon(\vec{x})d^3x = N/V_\epsilon \ . \tag{3.13}$$

A reference crystal of volume V is assumed to be only under hydrostatic pressure. The strain-dependent grand-canonical potential is the Legendre transform

$$G_\epsilon(\mu,V,T) = \min_N[F_\epsilon(N,V,T) - \mu N] \ . \tag{3.14}$$

It is important to emphasize that, in general, both V and $\boldsymbol{\epsilon}$ are independent variables. That is, a change in the strain $\boldsymbol{\epsilon}$ which produces a volume change

$$V_\epsilon \rightarrow V_\epsilon + \Delta V_\epsilon \ , \tag{3.15}$$

while the reference volume is kept fixed, is generally *not* equivalent to the appropriate volume-conserving change in the strain, accompanied by the reference volume change

$$V \rightarrow V + \frac{1}{J_A}\Delta V_\epsilon \ . \tag{3.16}$$

The reason is that the two changes generally assume different "boundary" conditions for $n_\epsilon(x)$: The change in Eq. (3.16) can be viewed as if $\mathbf{a}_\epsilon$ were an *unrestricted* variational parameter. Since this difference is not considered in the standard approaches,[32,38] we shall make appropriate generalizations in Appendix B where we shall also explicitly calculate the difference in the Helmholtz potentials caused by the two types of volume changes described above. Here, we shall only quote the results needed for the elastic moduli of a solid under hydrostatic pressure.

As shown in Appendix B, the requisite generalization of Eq. (2.22), at $\epsilon=0$, is

$$\begin{aligned} dF_{\epsilon=0} &= -S\,dT - P\,dV + \mu\,dN + V\sigma_{ij}\,d\epsilon_{ij} \\ &= -S\,dT + \mu\,dN + V^{2/3}\sigma_{ij}\,d(V^{1/3}\epsilon_{ij}) , \end{aligned} \tag{3.17}$$

where σ_{ij} is the symmetric Cauchy stress tensor and the last term represents the work done by the stress in deforming the crystal. Summations over repeated indices are implied. It follows immediately that the ij component of the stress tensor is given by

$$\sigma_{ij} = \frac{1}{V}\frac{\partial F_{\epsilon=0}}{\partial \epsilon_{ij}} , \tag{3.18}$$

while hydrostatic pressure P is defined as usual by

$$P = -\frac{\partial F_{\epsilon=0}}{\partial V} . \tag{3.19}$$

The second equality in Eq. (3.17) follows from the fact that the solid is isotropically compressed at $\epsilon=0$, that is,

$$\sigma_{ij} = -P_\epsilon \delta_{ij} \tag{3.20}$$

and the hydrostatic pressure equals the stress pressure P_ϵ (see Appendix B).

The elastic modulus tensor C_{ijkl} at $\epsilon=0$ is defined via Hooke's law as[32]

$$d\sigma_{ij} = C_{ijkl}\,d\epsilon_{kl} , \tag{3.21}$$

from which it follows that at constant temperature and number of particles (see Appendix B)

$$C^T_{ijkl} = \frac{1}{V}\frac{\partial^2 F_{\epsilon=0}}{\partial\epsilon_{ij}\partial\epsilon_{kl}} + P[\delta_{ij}\delta_{kl} - \tfrac{1}{2}(\delta_{ik}\delta_{jl} + \delta_{jk}\delta_{il})] . \tag{3.22}$$

The last expression can be also derived from the expansion of an elastic free energy defined by

$$E_\epsilon = (F_\epsilon - F) + P(V_\epsilon - V) = \frac{V}{2}\epsilon_{ij}C^T_{ijkl}\epsilon_{kl} + O(\epsilon^3) . \tag{3.23}$$

Note that the second term on the left-hand side of this equation can be interpreted as subtraction of the work against the external pressure P.

The potential $F_\epsilon(N,V,T)$, defined in Eq. (3.12), can be evaluated in a similar way as for unstrained medium, namely, by expanding the interaction part of the Helmholtz potential F_ϵ around a liquid state. Either the unstrained, or the strained liquid, could be used as a reference. We used the former expansion [see Eq. (B25) in Appendix B] which, together with Eqs. (2.14) and (2.15), gives for the elastic energy of Eq. (3.23)

$$E_\epsilon = (P - P_l)V_\epsilon + \Delta W[n_\epsilon(\vec{x}),\mu_s;V_\epsilon,T]_{\text{eq}} . \tag{3.24}$$

ΔW, defined with respect to a liquid whose density and chemical potential are n_l and μ_l, is given by Eq. (2.15), and

$$\Delta W[n_\epsilon(\vec{x}),\mu_s;V_\epsilon,T]_{\text{eq}} \equiv \min_{\substack{n_\epsilon(\vec{x}) \\ n_{s\epsilon}=N/V_\epsilon,\mathbf{a}_\epsilon=\mathbf{A}_m\cdot\mathbf{a}}} \Delta W[n_\epsilon(\vec{x}),\mu_s;V_\epsilon,T] . \tag{3.25}$$

The minimization is over periodic densities $n_\epsilon(\vec{x})$ whose Bravais lattice is $\mathbf{a}_\epsilon$ and average density is fixed to $n_{s\epsilon}=n_s/J_A$. Precisely because of this last constraint the explicit μ_s dependence in Eqs. (3.24) and (3.25) can be made superficial. Clearly, μ_s can be arbitrarily chosen, if Eq. (3.24) is rewritten as

$$\begin{aligned} E_\epsilon = (P - P_l)(V_\epsilon - V) &+ \Delta W[n_\epsilon(\vec{x}),\mu_s;V_\epsilon,T]_{\text{eq}} \\ &- \Delta W[n(\vec{x}),\mu_s;V,T]_{\text{eq}} , \end{aligned} \tag{3.26}$$

where the subscript eq emphasizes evaluation at the equilibrium. A convenient choice is $\mu_s=\mu_l$.

There are two obvious checks on Eqs. (3.23) and (3.24). First, it can be trivially verified (cf. Appendix B) that the zero- and first-order terms in the expansion of E_ϵ indeed vanish. Second, the formulas can be used to evaluate the elastic response of the reference liquid; one should obtain no shear moduli, and the isothermal compressibility must be consistent with Eqs. (2.25)–(2.27). Indeed, substituting $P=P_l$, $\mu_s=\mu_l$, and $n_\epsilon(\vec{x})=n_l/J_A$ into Eq. (3.23) and using Eq. (2.15), we obtain

$$\begin{aligned} \frac{E_\epsilon}{k_BT} &= \frac{V}{2}(\text{tr}\epsilon)^2[1 - C_l(0)]n_l + O(\epsilon^3) \\ &\equiv \frac{V}{2}\left[\frac{\Delta V}{V}\right]^2 \frac{1}{k_BT\kappa_T} + O(\epsilon^3) , \end{aligned} \tag{3.27}$$

which identifies κ_T as in Eq. (2.27).

Since the crystal starts in undeformed state, the stress tensor is $\sigma_{ij}=-P\delta_{ij}$, where P is the equilibrium pressure. Because we also have $G=-PV$ for an undeformed crystal,[32] the potentials for a crystal perturbed by infinitesimal strains obey

$$G_{\epsilon=0}\delta_{ij} = -\frac{\partial F_{\epsilon=0}}{\partial\epsilon_{ij}} . \tag{3.28}$$

This equation is a simple consequence of Eq. (3.14) and the fact that $F_\epsilon(N,V,T)$ is an extensive quantity.

Equations (3.23) and (3.24) give a prescription for calculating isothermal elastic moduli. These are the relevant quantities for comparing with experiments measuring macroscopic elastic constants. It is, however, constant entropy, or isentropic elastic moduli which are relevant for experiments which probe sound propagation velocities, because entropy fluctuations do not have time to relax during one period of a sound wave. Standard thermodynamic manipulations allow us to relate isothermal elastic moduli to isentropic ones. It can be shown that isentropic elastic moduli C^S are related to the isothermal C^T defined in Eq. (3.22) by

$$C^S_{ijkl} = C^T_{ijkl} + \frac{T}{c_v}\left[\frac{\partial P}{\partial T}\right]^2 \delta_{ij}\delta_{kl} , \tag{3.29}$$

where the specific heat c_v and the derivative $\partial P/\partial T$ are at a constant volume and number of particles. Similar relationships can be derived relating elastic moduli at constant number of particles to the moduli at constant chemical potential.

The above discussion of elastic thermodynamics was presented in the context of ordinary crystals. The modifications required for incommensurate crystals and quasicrystals will be presented elsewhere.[34]

IV. ELASTIC CONSTANTS FROM DENSITY FUNCTIONALS

A. Variational calculation for undeformed crystal

To search for crystalline minima of Eq. (2.14) with a lower free energy than the liquid state, the standard procedure is to expand the density into a trial set of reciprocal-lattice vectors $\vec{Q}$,

$$n(\vec{x})=\sum_{\vec{Q}} n(\vec{Q})e^{i\vec{Q}\cdot\vec{x}} , \tag{4.1}$$

where the Fourier coefficients $n(\vec{Q})$ are regarded as variational parameters. The resulting calculations are cumbersome, however, especially if many different reciprocal-lattice vectors play an important role. Excellent results can be obtained by using a more restricted, but physically motivated *Ansatz* which approximates the density by a sum of Gaussians located at the ideal atomic positions.[16–20] For example, for a one-component crystal, with atoms at vertices $\vec{R}$ of a Bravais lattice generated by $\mathbf{a}$,

$$n(\vec{x})=n_G(\vec{x};n_s,\mathbf{a},\boldsymbol{\alpha})\equiv\frac{n_s}{N_c\pi^{3/2}\det\boldsymbol{\alpha}^{1/2}}\sum_{\vec{R}}\exp[-(\vec{x}-\vec{R})\cdot(\mathbf{a}\cdot\boldsymbol{\alpha}\cdot\tilde{\mathbf{a}})^{-1}\cdot(\vec{x}-\vec{R})] , \tag{4.2}$$

where the average density n_s, the lattice-constant matrix $\mathbf{a}$, and the dimensionless, symmetric Gaussian-width matrix $\boldsymbol{\alpha}$ are variational parameters, while N_c is the number of sites per unit cell ($N_c=1$ when $\mathbf{a}$ is primitive). The square roots are assumed positive. Although this gives a total of 16 parameters, since only the relative orientation of $\mathbf{a}$ and $\boldsymbol{\alpha}$ is relevant, the number of independent parameters is, actually, 13. This number can still be reduced if one is restricted to lattices with certain high symmetry.

The average density n_s is restricted to n_l if the liquid is incompressible, but is needed more generally to allow for a difference in the solid and liquid densities. Similarly, in order to allow for the presence of equilibrium vacancies (or interstitials) the average number of particles per unit cell should be generally allowed to differ from one, that is,

$$n_s\neq\frac{1}{v_c}\equiv N_c\det\mathbf{a}^{-1} , \tag{4.3}$$

where v_c is volume of the primitive unit cell.

In this paper we only consider the case of single-component, primitive crystals. A more general case will be investigated elsewhere.[39]

The interaction term in Eq. (2.15) can be written down immediately in terms of $C_l(\vec{q})$ and the $n(\vec{Q})$'s. The nonlinear entropy term is more complicated. However, given the *Ansatz* equation (4.2), it is easy to show that the Fourier coefficients of the density are

$$n(\vec{Q})\equiv\frac{1}{v_c}\int_{v_c} n(\vec{x})e^{-i\vec{Q}\cdot\vec{x}}d^3x=n_s\exp(-\tfrac{1}{4}\vec{Q}\cdot\mathbf{a}\cdot\boldsymbol{\alpha}\cdot\tilde{\mathbf{a}}\cdot\vec{Q}) , \tag{4.4}$$

and the entropy term can be approximately evaluated in the limit of large or small $\boldsymbol{\alpha}$. Upon using the small $\boldsymbol{\alpha}$ (narrow Gaussian) approximation discussed, for example, in Ref. 20, the variational thermodynamic potential Eq. (2.15) in the crystalline state takes the form

$$\begin{aligned}\frac{\Delta W[n(\vec{x}),\mu_s;V,T]}{k_BTn_lV}&=w_G(\xi,\mathbf{b},\boldsymbol{\alpha};\Delta\mu)\equiv\xi\left[\ln\left[\frac{\xi}{N_c\pi^{3/2}\det\boldsymbol{\alpha}^{1/2}}\right]-\frac{3}{2}\right]-(\xi-1)-\beta\xi\Delta\mu\\&\qquad-\tfrac{1}{2}C_l(0)(1-2\xi)-\tfrac{1}{2}\xi^2\sum_{\vec{M}\in\mathbf{Z}^3}C_l(|\mathbf{b}\cdot\vec{M}|)h_M(\boldsymbol{\alpha}) ,\end{aligned} \tag{4.5}$$

where $\xi\equiv n_s/n_l$,

$$h_M(\boldsymbol{\alpha})\equiv\exp(-2\pi^2\vec{M}\cdot\boldsymbol{\alpha}\cdot\vec{M})=\exp(-\tfrac{1}{2}\vec{Q}\cdot\mathbf{a}\cdot\boldsymbol{\alpha}\cdot\tilde{\mathbf{a}}\cdot\vec{Q}) , \tag{4.6}$$

and for future convenience we defined the reciprocal-lattice matrix $\mathbf{b}$,

$$\mathbf{b}=2\pi\tilde{\mathbf{a}}^{-1} , \tag{4.7}$$

which generates the reciprocal-lattice vectors $\vec{Q}$,

$$\vec{Q}=\mathbf{b}\cdot\vec{M} , \tag{4.8}$$

where $\vec{M}\in\mathbf{Z}^3$ is a vector with integer components. It becomes obvious that w_G depends on $\mathbf{b}$ (or $\mathbf{a}$) only implicitly, through the reciprocal-lattice vectors in $C_l(|\vec{Q}|)$. The equation of state, Eq. (2.16), takes the form

$$-\Delta P = k_B T n_l \min_{\xi,\mathbf{b},\boldsymbol{\alpha}} w_G(\xi,\mathbf{b},\boldsymbol{\alpha};\Delta\mu) \ . \tag{4.9}$$

The approximation of narrow Gaussians should be especially good if there is a sizable first-order transition separating the liquid and crystal states.

It is straightforward to numerically minimize (4.5) with respect to the parameters ξ, $\mathbf{b}$, and $\boldsymbol{\alpha}$, at least in the case of cubic symmetry. Explicitly, the equilibrium conditions are

$$\begin{aligned} 0=\frac{\partial w_G}{\partial \xi} &= -\ln(N_c\pi^{3/2}\det\boldsymbol{\alpha}^{1/2})-\tfrac{3}{2}-\beta\,\Delta\mu+C_l(0)+\ln\xi-\xi\sum_{\vec{\mathbf{Q}}} C_l(\,|\vec{\mathbf{Q}}|\,)h_M(\boldsymbol{\alpha}) \\ &= -\ln(N_c\pi^{3/2}\det\boldsymbol{\alpha}^{1/2})-\tfrac{3}{2}-\beta\Delta\mu+C_l(0)+\ln\xi-\xi\sum_{\vec{\mathbf{M}}} C_l(\,|\mathbf{b}\cdot\vec{\mathbf{M}}|\,)h_M(\boldsymbol{\alpha}) \ , \end{aligned} \tag{4.10}$$

$$0=\frac{\partial w_G}{\partial \mathbf{b}} = -\frac{1}{4\pi}\xi^2 \sum_{\vec{\mathbf{Q}}\,(\neq\vec{0})} \dot{C}_l(\,|\vec{\mathbf{Q}}|\,)\frac{\vec{\mathbf{Q}}\vec{\mathbf{Q}}\cdot\mathbf{a}}{|\vec{\mathbf{Q}}|}h_M(\boldsymbol{\alpha}) = -\tfrac{1}{2}\xi^2 \sum_{\vec{\mathbf{M}}\,(\neq\vec{0})} \dot{C}_l(\,|\mathbf{b}\cdot\vec{\mathbf{M}}|\,)\frac{\mathbf{b}\cdot\vec{\mathbf{M}}\vec{\mathbf{M}}}{|\mathbf{b}\cdot\vec{\mathbf{M}}|}h_M(\boldsymbol{\alpha}) \ , \tag{4.11}$$

and

$$0=\frac{\partial w_G}{\partial \boldsymbol{\alpha}} = -\tfrac{1}{2}\xi\boldsymbol{\alpha}^{-1}+\tfrac{1}{4}\xi^2 \sum_{\vec{\mathbf{Q}}\,(\neq\vec{0})} C_l(\,|\vec{\mathbf{Q}}|\,)[\tilde{\mathbf{a}}\cdot(\vec{\mathbf{Q}}\vec{\mathbf{Q}})\cdot\mathbf{a}]h_M(\boldsymbol{\alpha}) = -\tfrac{1}{2}\xi\boldsymbol{\alpha}^{-1}+\pi^2\xi^2 \sum_{\vec{\mathbf{M}}\,(\neq\vec{0})} C_l(\,|\mathbf{b}\cdot\vec{\mathbf{M}}|\,)(\vec{\mathbf{M}}\vec{\mathbf{M}})h_M(\boldsymbol{\alpha}) \ . \tag{4.12}$$

We assumed for convenience that $\mathbf{b}$, rather than $\mathbf{a}$, is the independent variable, and we denoted by a dot above a function the derivative with respect to $|\vec{\mathbf{Q}}|$. Clearly, Eqs. (4.10)–(4.12) cannot generally be solved analytically, although the last equation can be obviously used to eliminate ξ. Therefore, the minimization in Eq. (4.5) is usually performed numerically.

As we have already emphasized, the results of the minimization for HS and LJ systems at the freezing point are in good agreement with computer simulations.

B. Variational calculation for strained crystal

If a crystal were uniformly strained at all scales, its density would be given by Eq. (3.4). Therefore, if the unstrained density would be represented by Gaussians, Eq. (4.2), so would the strained density,

$$\begin{aligned} n_\epsilon(\vec{\mathbf{x}}') &= n_G(\,\mathbf{A}^{-1}\cdot\vec{\mathbf{x}};n_s,\mathbf{a},\boldsymbol{\alpha})/J_A \\ &= n_G(\vec{\mathbf{x}};n_s/J_A,\,\mathbf{A}\cdot\mathbf{a},\boldsymbol{\alpha}) \ . \end{aligned} \tag{4.13}$$

However, because the nonaffine density deformations on scales below the unit-cell scale, and because of the vacancy migration, these equations have to be modified. Nonetheless, for small strains we can still assume an expansion of the strained density into Gaussians,

$$n_\epsilon(\vec{\mathbf{x}}) = n_G(\vec{\mathbf{x}};n_{s\epsilon},\mathbf{a}_\epsilon,\boldsymbol{\alpha}_\epsilon) \ , \tag{4.14}$$

where the average density of the strained solid,

$$n_{s\epsilon} = \frac{n_s}{J_A} \ , \tag{4.15}$$

is fixed by conservation of the total number of particles; the strained lattice

$$\mathbf{a}_\epsilon = \mathbf{A}_m\cdot\mathbf{a} = (1+\boldsymbol{\zeta})\cdot\mathbf{a} \ , \tag{4.16}$$

or its reciprocal lattice (observed in diffraction experiments)

$$\mathbf{b}_\epsilon = \mathbf{A}_m^{-1}\cdot\mathbf{b} = (1+\boldsymbol{\zeta})^{-1}\cdot\mathbf{b} \ , \tag{4.17}$$

is given by the microscopic strain $\boldsymbol{\zeta}$ which may differ from $\boldsymbol{\epsilon}$ because of the vacancy annihilation; the strained Gaussian width,

$$\boldsymbol{\alpha}_\epsilon \equiv \boldsymbol{\alpha} + \Delta\boldsymbol{\alpha}_\epsilon \ , \tag{4.18}$$

generally differs from $\boldsymbol{\alpha}$ because of the nonaffine character of deformations below the unit-cell scale.

The microscopic strain ξ and the Gaussian-width relaxation $\Delta\boldsymbol{\alpha}_\epsilon$ are to be determined by minimization of the elastic free energy, Eqs. (3.23) and (3.24). In analogy with Eq. (4.5), we can determine explicitly $\Delta W[n_\epsilon(\vec{\mathbf{x}}),\mu_s;V_\epsilon,T]$:

$$\frac{\Delta W[n_\epsilon(\vec{\mathbf{x}});\mu_s;V_\epsilon,T]}{k_B T n_l V_\epsilon} = w_G(\xi/J_A,\,\mathbf{A}_m^{-1}\cdot\mathbf{b},\boldsymbol{\alpha}+\Delta\boldsymbol{\alpha}_\epsilon;\Delta\mu) \ . \tag{4.19}$$

With this expression, the elastic energy, Eq. (3.24), becomes

$$\frac{E_\epsilon}{k_B T n_l V} = J_A \left[\min_{\mathbf{A}_m,\Delta\boldsymbol{\alpha}_\epsilon} w_G(\xi/J_A,\,\mathbf{A}_m^{-1}\cdot\mathbf{b},\boldsymbol{\alpha}+\Delta\boldsymbol{\alpha}_\epsilon;\Delta\mu) - w_G(\xi,\mathbf{b},\boldsymbol{\alpha};\Delta\mu) \right] \ , \tag{4.20}$$

where ξ, $\mathbf{b}$, and $\boldsymbol{\alpha}$ are the solutions of Eqs. (4.10)–(4.12) while the dependence of $\mathbf{A}_m$ upon $\mathbf{A}$ is fixed by a relationship such as Eq. (3.9) or (3.10).

It is again straightforward to verify that the zero-order and first-order terms in $\boldsymbol{\epsilon}$ vanish in Eq. (4.20); it is only necessary to apply Eqs. (4.10)–(4.12) and to notice that $\boldsymbol{\epsilon}=0$ implies $\mathbf{A}_m=1$ and $\Delta\boldsymbol{\alpha}_\epsilon=0$.

Since we are interested in the expansion of Eq. (4.20) to order $\boldsymbol{\epsilon}^2$, it is not necessary to perform indicated minimization in Eq. (4.20) for arbitrary $\mathbf{A}$. Instead, it suffices to expand the right-hand side to second order in ϵ, $\Delta\boldsymbol{\alpha}$, and $\Delta\mathbf{A}_m^{-1}=\mathbf{A}_m^{-1}-1\approx-\boldsymbol{\zeta}$; and then to minimize the resulting quadratic form.[40] This is equivalent to the assertion that $\partial\boldsymbol{\alpha}/\partial\boldsymbol{\epsilon}$ and $\partial\boldsymbol{\zeta}/\partial\boldsymbol{\epsilon}$ are finite at $\boldsymbol{\epsilon}=0$; that is, $\Delta\boldsymbol{\alpha}$ and $\boldsymbol{\zeta}$ are both of order $\boldsymbol{\epsilon}$ or higher.

Consequently, the elastic energy E_ϵ can be formally written as

$$\tfrac{1}{2}\boldsymbol{\epsilon}:\mathbf{C}:\boldsymbol{\epsilon}=\min_{\xi,\Delta\boldsymbol{\alpha}}\tfrac{1}{2}(\boldsymbol{\epsilon}\,\boldsymbol{\zeta}\,\Delta\boldsymbol{\alpha}):\mathcal{C}:\begin{bmatrix}\boldsymbol{\epsilon}\\ \boldsymbol{\zeta}\\ \Delta\boldsymbol{\alpha}\end{bmatrix}, \tag{4.21}$$

where the tensorial blocks of $\mathcal{C}$, in units k_BTn_l, are

$$\mathcal{C}^{\epsilon\epsilon}_{ijkl}=\delta_{ij}\delta_{kl}\xi^2\frac{\partial^2 w_G}{\partial\xi^2}, \tag{4.22}$$

$$\mathcal{C}^{\epsilon\zeta}_{ijkl}=\mathcal{C}^{\zeta\epsilon}_{klij}=\tfrac{1}{2}\delta_{ij}\xi\left[\frac{\partial w_G}{\partial\xi\partial b_{kp}}b_{lp}+\frac{\partial^2 w_G}{\partial\xi\partial b_{lp}}b_{kp}\right], \tag{4.23}$$

$$\mathcal{C}^{\epsilon\alpha}_{ijkl}=\mathcal{C}^{\alpha\epsilon}_{klij}=-\delta_{ij}\xi\frac{\partial^2 w_G}{\partial\xi\partial\alpha_{kl}}, \tag{4.24}$$

$$\mathcal{C}^{\zeta\zeta}_{ijkl}=\frac{1}{4}\left[\frac{\partial^2 w_G}{\partial b_{ip}\partial b_{kq}}b_{jp}b_{lq}+\frac{\partial^2 w_G}{\partial b_{jp}\partial b_{kq}}b_{ip}b_{lq}+\frac{\partial^2 w_G}{\partial b_{ip}\partial b_{lq}}b_{jp}b_{kq}+\frac{\partial^2 w_G}{\partial b_{jp}\partial b_{lq}}b_{ip}b_{kq}\right], \tag{4.25}$$

and

$$\mathcal{C}^{\zeta\alpha}_{ijkl}=\mathcal{C}^{\alpha\zeta}_{klij}=-\frac{1}{2}\left[\frac{\partial w_G}{\partial b_{ip}\partial\alpha_{kl}}b_{jp}+\frac{\partial^2 w_G}{\partial b_{jp}\partial\alpha_{kl}}b_{ip}\right], \tag{4.26}$$

$$\mathcal{C}^{\alpha\alpha}_{ijkl}=\frac{\partial^2 w_G}{\partial\alpha_{ij}\partial\alpha_{kl}}. \tag{4.27}$$

The employed notation is

$$\tfrac{1}{2}\boldsymbol{\epsilon}:\mathbf{C}:\boldsymbol{\epsilon}=\tfrac{1}{2}\epsilon_{ij}C_{ijkl}\epsilon_{kl}. \tag{4.28}$$

All the second derivatives are evaluated at the initial, unstrained configuration. Since the initial configuration is assumed to be a local minimum, it follows that the quadratic forms in (4.21) are positive definite.

Given a particular form for $\boldsymbol{\zeta}$, minimization in Eq. (4.21) can be performed. We shall assume here that Eq. (3.10) is valid, that is, $\boldsymbol{\zeta}=\boldsymbol{\epsilon}$ so that minimization over $\boldsymbol{\zeta}$ is completely eliminated. The elastic energy now becomes

$$\tfrac{1}{2}\boldsymbol{\epsilon}:\mathbf{C}:\boldsymbol{\epsilon}=\min_{\Delta\boldsymbol{\alpha}}\tfrac{1}{2}[\boldsymbol{\epsilon}:\mathbf{C}^{\epsilon\epsilon}:\boldsymbol{\epsilon}+2\Delta\boldsymbol{\alpha}:\mathbf{C}^{\alpha\epsilon}:\boldsymbol{\epsilon}+\Delta\boldsymbol{\alpha}:\mathbf{C}^{\alpha\alpha}:\Delta\boldsymbol{\alpha}], \tag{4.29}$$

where, with the help of Eqs. (4.22)–(4.27)

$$\mathbf{C}^{\epsilon\epsilon}=\mathcal{C}^{\epsilon\epsilon}+\mathcal{C}^{\epsilon\zeta}+\mathcal{C}^{\zeta\epsilon}+\mathcal{C}^{\zeta\zeta}, \tag{4.30}$$

$$\tilde{\mathbf{C}}^{\epsilon\alpha}=\mathbf{C}^{\alpha\epsilon}=\mathcal{C}^{\alpha\epsilon}+\mathcal{C}^{\alpha\zeta}, \tag{4.31}$$

and

$$\mathbf{C}^{\alpha\alpha}=\mathcal{C}^{\alpha\alpha}. \tag{4.32}$$

After minimizing Eq. (4.29) we finally obtain the elastic modulus tensor

$$\mathbf{C}=\mathbf{C}^{\epsilon\epsilon}-\mathbf{C}^{\epsilon\alpha}:(\mathbf{C}^{\alpha\alpha})^{-1}:\mathbf{C}^{\alpha\epsilon}. \tag{4.33}$$

The explicit formulas for tensors $\mathbf{C}^{\epsilon\epsilon}$, $\mathbf{C}^{\alpha\epsilon}$, and $\mathbf{C}^{\alpha\alpha}$ are derived in Appendix C. Also, the formulas specialized to the case of crystals with cubic symmetry, necessary since both HS and LJ liquids freeze into fcc structures, are given in Appendix C.

V. RESULTS

Let us first consider a system of particles interacting via a hard-sphere potential. The thermodynamic properties as well as the fluid-solid phase transition of such a system have been extensively studied through computer experiments. We have chosen to investigate the elastic moduli at the phase coexistence for a variety of reasons. First, the predictions of the density-functional theory of freezing could be used as input to the calculation. Second, an accurate structure factor of hard-sphere fluid exists for densities in the range of phase coexistence. Finally, we could test whether the elastic constants of shear vanish at the melting point as predicted by the lattice theory of Born.

For the direct correlation function of the fluid we use the exact solution[41] of the Percus-Yevick integral equation. This is a good solution in the density range of interest and has been successfully used in recent theories of freezing[17,18] in which the freezing parameters are found assuming a simple fcc structure. More recently, it has been verified that fcc structure is both locally stable and more stable than a large class of crystal structures.[39] We reevaluated the freezing parameters and found agreement with previous calculations. We also found the freezing parameters when vacancies are not allowed and the average density is fixed to one per unit cell. In both cases the elastic moduli have been evaluated and are presented in Table I.

The elastic moduli satisfy all the constraints necessary for a stable crystal structure, namely $C_{11}+2C_{12}$, $C_{11}-C_{12}$, and C_{44} are all positive (we use here the Voigt notation). The elastic constant for shear does not vanish at the melting point. The Cauchy relation $C_{12}=C_{44}$ that must be obeyed by central force harmonic crystals fails. In fact, we find an unexpected result that the Poisson ratio for the hard-sphere fcc crystal at melting is negative.[42] In order to test robustness of this result we used a correction to Percus-Yevick structure factor due to Henderson and Grundke.[43] Our preliminary results indicate that although the freezing parameters, as well as elastic moduli change for a few percent, the Poisson ratio remains negative.

Using a cell-cluster free-energy series, Stillinger and Salsburg[44] have developed a theory for the elastic constants of a hard-sphere system in the high-density limit. These authors find that the elastic constants can be asymptotically expressed in terms of a small parameter $\theta\equiv(n_{\mathrm{CP}}/n_s-1)$, where the solid density n_s is fixed to one per unit cell and n_{CP} is the close-packing density of the lattice. Specifically, for the fcc solid they find

TABLE I. Elastic moduli for fcc HS solid at the melting. The solid density n_s is in units σ^{-3}, where σ is the HS diameter, while the solid pressure P_s and the moduli C_{ij} (Voigt notation) are in units $k_B T n_s$. The first four rows correspond to the following freezing parameters: the liquid density $n_l = 0.946\sigma^{-3}$, the cubic lattice parameter $a = 1.506\sigma$, and the inverse of the Gaussian width with respect to the cubic unit cell, $\alpha^{-1} = 1316$. The first row corresponds to equilibration of the strained width, but without vacancy migration. Neither the width nor the vacancy density are equilibrated for results in rows two and three. The vacancy density and only the scalar strained Gaussian width are equilibrated in the fourth row. The fifth and sixth row are obtained by fixing the solid density to precisely one particle per cell with or without equilibrating the strained widths, respectively. The freezing parameters are in this case $n_l = 0.967\sigma^{-3}$, $a = 1.515\sigma$, and $\alpha^{-1} = 1146$. The results in the seventh row are estimated from figures in Ref. 45 at the instability where the bulk modulus becomes zero. The results in the last row are obtained by substituting our melting density ($n_s = 1.052$) into the asymptotic formulas of Ref. 44. The pressure in rows one through six is equal to the liquid pressure calculated in the Percus-Yevick approximation.

Source	n_s	P_s	$C_{11}+2C_{12}$	$C_{11}-C_{12}$	C_{44}
Here	1.052	13.5	78.2	198	141
Here	1.052	13.5	946	228	251
Ref. 37	1.053	13.5	1143	226	252
Ref. 37	1.053	13.5	47.5	224	252
Here	1.151	14.6	34.4	197	122
Here	1.151	14.6	942	234	249
Ref. 45	1.095	10	0	35	36
Ref. 44	1.052	9	75	15	45

$$C_{11} \cong 4.150\theta^{-2} , \tag{5.1}$$

$$C_{12} \cong 2.425\theta^{-2} , \tag{5.2}$$

and

$$C_{44} \cong 5.365\theta^{-2} , \tag{5.3}$$

in units of $k_B T n_s$. Since these results are valid near close-packed densities, neither quantitative nor qualitative predictions obtained at the melting point, where $n_{\rm CP}/n_s \approx 1.344$, can be meaningfully compared with our density-functional approach. For example, at the melting, the pressure correction which is of order θ^{-1}, is approximately equal to the leading term. Moreover, the expressions Eqs. (5.1)–(5.3) are derived neglecting three- and higher-cluster terms. In two dimensions, three-cluster terms give a *negative* contribution to C_{12}, of the same order of magnitude as the one- and two-cluster terms. Such contribution could also be sufficiently negative in three dimensions to make C_{12}, and thus the Poisson ratio, negative.

More recently, Honda *et al.*[45] have developed a molecular-field theory for calculating the free energy of an fcc, hard-sphere crystal near the melting point. Extending their molecular-field theory, these authors compute the elastic constants by evaluating the excess free energy due to a strain. Numerically solving the self-consistency equations they conclude that the crystal becomes unstable (bulk modulus equal zero) at $n_s = 1.095$ (in units of σ^{-3}, σ being the hard-sphere diameter), but that the Poisson ratio ($\sim C_{12}$) turns negative already at somewhat higher density, $n_s = 1.096$. Therefore these results suggest that the Poisson ratio for the hard-sphere crystal might indeed be negative. Unfortunately, the fact that density at the melting, obtained from computer simulations and density-functional calculations, is significantly lower ($n_s \approx 1.052$) seems to cast a serious doubt on reliability of the above results. An important omission from the calculation by Honda *et al.* is the absence of vacancies even at nonzero temperatures. Indeed, elimination of vacancies from our density-functional calculation results in a higher density at the melting, $n_s \approx 1.151$, and, at the same time, in the more negative Poisson ratio (see Table I).

In the case of the Lennard-Jones fluid, we have used the structure factor obtained via molecular-dynamics simulations by Kimura and Yonezawa[29] at temperature $T = 0.68\epsilon/k_B$, slightly below the triple point. At this temperature the supercooled liquid, which is identified with glass, has density $0.807\sigma^{-3}$ and its pressure is $0.0024\epsilon\sigma^{-3}$ [σ and ϵ are, respectively, the bond length and strength of the LJ potential parametrized by $u(r) = 4\epsilon((\sigma/r)^{12} - (\sigma/r)^6)$].

The results of density-functional calculations are very sensitive to the value of the structure factor at the origin. Unfortunately, this number cannot be reliably determined from simulations. For example, by using two different approaches, Kimura and Yonezawa obtain values $S(0) = 0.138$ and 0.078. We decided to use what we believe is a more realistic value $S(0) = 0.04$, compatible with compressibility of argon.[46]

Our variational calculation for the fcc solid, assuming $\mu_s = \mu_l$, gives $n_s = 1.027\sigma^{-3}$, $a = 1.599\sigma$, and $\alpha^{-1} = 628$, at pressure $P_s = 0.342\epsilon\sigma^{-3}$. For comparison, at the same temperature, but at much lower pressure $P_s = 0.002\epsilon\sigma^{-3}$, experimentally observed values for argon are $n_s = 0.968\sigma^{-3}$, $a = 1.607\sigma$ (using the standard argon parameters: $\epsilon/k_B = 119$ K, $\sigma = 3.40$ Å). Because of the pressure difference, we cannot make a sensible comparison between these values.

TABLE II. The elastic moduli for the fcc LJ solid at temperature $T=0.68\epsilon/k_B$, where ϵ is the LJ bond strength (for argon, a standard value is $\epsilon/k_B=119$ K). The solid density n_s is in units σ^{-3}, where σ is the LJ bond length (for argon, $\sigma=3.40$ Å), while the solid pressure P_s and the moduli C_{ij} (Voigt notation) are in units k_BTn_s. The first two rows were calculated using the supercooled liquid structure factor from Ref. 29 extrapolated to the value 0.04 at the origin. The liquid density is given as $n_l=0.806\sigma^{-3}$ and we also assumed that $\mu_s=\mu_l$, $n_s=1.027\sigma^{-3}$, $a=1.599\sigma$, and $\alpha^{-1}=628$. The first row corresponds to equilibration of the strained width, but without vacancy migration. Neither the width nor the vacancy density are equilibrated for results in row two. Rows four and five give calculated and measured (for argon) elastic moduli.

Source	n_s	P_s	$C_{11}+2C_{12}$	$C_{11}-C_{12}$	C_{44}
Here	1.027	0.15	398	24	106
Here	1.027	0.15	440	26	119
Ref. 4	0.952	0	113	25	39
Ref. 47	0.968	0.00	215	51	22

The elastic constants which we calculate are summarized in Table II. Clearly, these elastic constants satisfy the stability criteria. In this table we also summarize the results of Squire *et al.*,[4] who have calculated the isothermal elastic constants for argon via Monte Carlo simulations. Unfortunately, their simulations were done at zero pressure and, therefore, we cannot make a meaningful comparison. A similar difficulty is encountered if we attempt a comparison with the available experimental results for argon, also listed in Table II. An additional difficulty in interpreting the results of the Monte Carlo simulations stems from the fact that the simulations assume absence of vacancies.

VI. SUMMARY

In the present paper we have formulated a density-functional theory of elasticity. The theory was applied to HS and LJ fcc crystals at the melting point and near the triple point, respectively. Neglecting the vacancy relaxation in the strained crystal we then evaluated the elastic moduli. A detailed comparison of our results with other calculations or experiments is not possible at present because the available results are for different points in the phase diagram. Nevertheless, it appears that the eigenmoduli we determine are probably too large, although of correct order of magnitude.

An interesting result of our investigation is the negative Poisson ratio (and C_{12}) for the HS fcc crystal at the melting point. This result will not change by the inclusion of the vacancy effects, which will only reduce the bulk modulus, leaving other eigenmoduli unchanged. It is also conceivable that the three-point correlations contribute significantly to the elastic moduli[31] or that a more accurate density functional is required. Further work is necessary to explore potentially important contributions from the three-point correlations neglected in the lowest-order expansion. Our approach can be easily extended to include such contributions.[31] However, very little is presently understood about three-point correlations in liquids. In order to check the accuracy of our approach it will also be necessary to extend our calculation for the LJ crystal to the entire liquid-solid transition line.

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APPENDIX A: MOLECULAR-FIELD THEORY

Let us consider a system of identical classical particles confined to a volume V, at temperature T, interacting through a pair potential $U(\vec{x},\vec{y})$, and in the presence of an external potential $-\mu(\vec{x})$. The molecular-field approximation for the probability distribution is

$$\rho_{\rm MF}=\frac{\prod_{i=1}^{N}\exp[\beta\mu_{\rm MF}(\vec{x}_i)-\vec{p}_i^{\,2}/2mk_BT]}{{\rm tr}\prod_{i=1}^{N}\exp[\beta\mu_{\rm MF}(\vec{x}_i)-\vec{p}_i^{\,2}/2mk_BT]}\,, \tag{A1}$$

where $\mu_{\rm MF}$ is the effective, molecular field seen by the particles. Substitution of this *Ansatz* into Eq. (2.5) leads to the explicit form of the molecular field

$$\beta\mu_{\rm MF}(\vec{x})=\ln[n(\vec{x})\lambda_T^3]\,, \tag{A2}$$

which in turn gives rise to

$$\rho_{\rm MF}=\exp(-Vn_s)\prod_{i=1}^{N}\lambda_T^3 n(\vec{x}_i)\exp(-\vec{p}_i^{\,2}/2mk_BT)\,, \tag{A3}$$

where n_s is the average density. Therefore, by combining this equation and Eq. (2.1) we determine the molecular-field variational grand-canonical potential

$$\beta W_{\mathrm{MF}}[n(\vec{x}),\mu(\vec{x});V,T]=\int_V n(\vec{x})\{\ln[n(\vec{x})\lambda_T^3]-1-\beta\mu(\vec{x})\}d^3x+\tfrac{1}{2}\int_V\int_V \beta U(\vec{x}_1,\vec{x}_2)n(\vec{x}_1)n(\vec{x}_2)d^3x_1d^3x_2\ . \tag{A4}$$

If we now assume that for a given potential $\mu_l(\vec{x})$ a "liquid" density $n_l(\vec{x})$ extremizes W_{MF}, we can obtain (2.15) with

$$\beta\Delta W=\int_V\left[n(\vec{x})\ln\frac{n(\vec{x})}{n_l(\vec{x})}-\Delta n(\vec{x})-\beta n(\vec{x})\Delta\mu(x)\right]d^3x+\tfrac{1}{2}\int_V\int_V\beta U(\vec{x}_1,\vec{x}_2)\Delta n(\vec{x}_1)\Delta n(\vec{x}_2)d^3x_1d^3x_2\ . \tag{A5}$$

It should be noted, however, that ΔW is ill defined for interactions U similar to the hard-sphere interaction.

APPENDIX B: THERMODYNAMICS AT FINITE STRAIN

Starting from an initially unstrained solid (that is, only under hydrostatic pressure), characterized by a Helmholtz potential $F(N,V,T)$, where N is the number of particles, V is the volume, and T is temperature, we shall strain it by transforming its boundary according to a coordinate transformation

$$x_i\to x_i(\mathbf{A})=A_{ij}x_j\ . \tag{B1}$$

Generally, $\mathbf{A}$ is product of a symmetric matrix and a rotation-reflection (orthogonal) matrix. Since we assume that a rotation-reflection leaves the initial energy unchanged we may assume that A_{ij} is symmetric.[48]

Besides the usual strain matrix ϵ_{ij},

$$\epsilon_{ij}=A_{ij}-\delta_{ij}\ , \tag{B2}$$

one often uses the so-called Lagrangian strain matrix η_{ij}

$$\eta_{ij}=\eta_{ij}=\tfrac{1}{2}(A_{ki}A_{kj}-\delta_{ij})\ . \tag{B3}$$

The last two relationships also imply the differential relationships,

$$d\epsilon_{ij}=\tfrac{1}{2}(\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk})dA_{kl} \tag{B4}$$

and

$$d\eta_{ij}=\tfrac{1}{4}(A_{ki}\delta_{lj}+A_{kj}\delta_{li}+A_{li}\delta_{kj}+A_{lj}\delta_{ki})dA_{kl}\ , \tag{B5}$$

where dA_{ij} differentials are explicitly symmetrized.[48] We can easily evaluate the following useful derivatives:

$$\frac{\partial\epsilon_{ij}}{\partial A_{kl}}=\frac{\partial A_{kl}}{\partial\epsilon_{ij}}=\tfrac{1}{2}(\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk}) \tag{B6}$$

and

$$\frac{\partial\eta_{ij}}{\partial A_{kl}}=\tfrac{1}{4}(A_{ki}\delta_{lj}+A_{kj}\delta_{li}+A_{li}\delta_{kj}+A_{lj}\delta_{ki})\ . \tag{B7}$$

We want to investigate infinitesimal deformations of the *strained* solid. If the strained solid is characterized by the symmetric strain ϵ_{ij} and the symmetric transformation matrix $A_{ij}=\delta_{ij}+\epsilon_{ij}$, then we are interested in the change in the Helmholtz potential due to an infinitesimal change

$$A_{ij}\to A_{ij}+dA_{ij}\ , \tag{B8}$$

where $dA_{ij}=dA_{ji}$. This infinitesimal change corresponds to the infinitesimal transformation

$$du_{ij}=dA_{kl}\frac{\delta_{ik}A_{lj}^{-1}+\delta_{il}A_{kl}^{-1}}{2} \tag{B9}$$

of the *strained* solid. That is,

$$\begin{aligned}x_i(\mathbf{A})\to x_i(\mathbf{A}+d\mathbf{A})&=x_i(\mathbf{A})+dx_i(\mathbf{A})\\&=x_i(\mathbf{A})+x_i(\mathbf{A})du_{ij}\ .\end{aligned} \tag{B10}$$

Since the solid is strained, it is under a stress $\sigma_{ij}(\mathbf{A})$. This is the *symmetric* Cauchy stress, as required by the absence of a net torque on the sample:

$$0=\int_{S_A}\varepsilon_{ijk}x_j\sigma_{kl}dS_l=V_\epsilon\varepsilon_{ijk}\sigma_{kj}\ , \tag{B11}$$

where S_A and V_ϵ are the surface and the volume of the sample. Therefore, the work associated with the infinitesimal deformation du_{ij} is

$$\begin{aligned}\int_{S_A}du_{ij}x_j\sigma_{ik}dS_k&=V_\epsilon\sigma_{ij}du_{ij}\\&=V_\epsilon\,\mathrm{tr}\left[\sigma\cdot\frac{\mathbf{A}^{-1}\cdot d\mathbf{A}+d\mathbf{A}\cdot\mathbf{A}^{-1}}{2}\right]\\&=V_\epsilon\,\mathrm{tr}(\sigma\cdot\mathbf{A}^{-1}\cdot d\eta\cdot\mathbf{A}^{-1})\ ,\end{aligned} \tag{B12}$$

where the last equalities follow from Eqs. (B9) and (B5).

Using the result Eq. (B12) we can now write the differential of the generalized Helmholtz free energy

$$\begin{aligned}dF_\epsilon&=-S\,dT-PJ_A\,dV+\mu\,dN+V_\epsilon\,\mathrm{tr}(\mathbf{A}^{-1}\cdot\sigma\cdot\mathbf{A}^{-1}\cdot d\eta)\\&=-S\,dT-PJ_A\,dV+\mu\,dN\\&\quad+V_\epsilon\,\mathrm{tr}\left[\frac{\sigma\cdot\mathbf{A}^{-1}+\mathbf{A}^{-1}\cdot\sigma}{2}\cdot d\mathbf{A}\right]\ ,\end{aligned} \tag{B13}$$

where $J_A=V_\epsilon/V=\det\mathbf{A}$. It follows immediately that

$$\tfrac{1}{2}(\delta_{ik}A_{jl}^{-1}+\delta_{il}A_{jk}^{-1})\sigma_{ij}(\mathbf{A})=\frac{1}{V_\epsilon}\frac{\partial F_\epsilon}{\partial A_{kl}} \tag{B14}$$

and

$$\sigma_{ij}(\mathbf{A})=\frac{1}{V_\epsilon}A_{ik}A_{jl}\frac{\partial F_\epsilon}{\partial\eta_{kl}}\ . \tag{B15}$$

The last two equations can be related with the help of Eq. (B7) to obtain

$$\frac{\partial F_\epsilon}{\partial A_{ij}}=\tfrac{1}{2}(A_{ki}\delta_{lj}+A_{kj}\delta_{li})\frac{\partial F_\epsilon}{\partial\eta_{kl}}\ . \tag{B16}$$

A strain-induced pressure, which we will call the stress pressure, can be defined as

$$P_\epsilon(\mathbf{A})=-\tfrac{1}{3}\sigma_{ii}(\mathbf{A})=-\tfrac{1}{3}\,\mathrm{tr}\boldsymbol{\sigma}(\mathbf{A})\ , \tag{B17}$$

and calculated from Eq. (B13):

$$P_\epsilon(\mathbf{A})=-\frac{1}{3V_\epsilon}A_{ik}A_{il}\frac{\partial F_\epsilon}{\partial \eta_{kl}}=-\frac{1}{3V_\epsilon}\mathrm{tr}\left[\mathbf{A}\cdot\frac{\partial F}{\partial \boldsymbol{\eta}}\cdot\mathbf{A}\right] . \tag{B18}$$

On the other hand, the usual hydrostatic pressure P, defined in Eq. (B13), is

$$P(\mathbf{A})=-\frac{1}{J_A}\frac{\partial F_\epsilon}{\partial V} . \tag{B19}$$

These two pressures are generally not equal. This is consistent with the fact that the two deformations given by

$$\mathbf{A}\rightarrow\mathbf{A}+d\,\mathbf{A},\quad V=\text{const},\quad N=\text{const},\quad T=\text{const} \tag{B20}$$

and

$$\begin{aligned}&\mathbf{A}\rightarrow\mathbf{A}+d\,\mathbf{A}-\mathbf{A}\tfrac{1}{3}\,\mathrm{tr}(\mathbf{A}^{-1}\cdot d\,\mathbf{A})\ ,\\ &V\rightarrow V+V\,\mathrm{tr}(\mathbf{A}^{-1}\cdot d\,\mathbf{A})\ ,\\ &N=\text{const},\quad T=\text{const}\ ,\end{aligned} \tag{B21}$$

which produce the identical shapes of the sample and identical average densities, will generally produce different changes in the Helmholtz potential. Indeed, the corresponding changes are

$$dF_\epsilon=V_\epsilon\,\mathrm{tr}\left[\frac{\boldsymbol{\sigma}\cdot\mathbf{A}^{-1}+\mathbf{A}^{-1}\cdot\boldsymbol{\sigma}}{2}\cdot d\,\mathbf{A}\right] \tag{B22}$$

and

$$dF_\epsilon=V_\epsilon\,\mathrm{tr}\left[\frac{\boldsymbol{\sigma}\cdot\mathbf{A}^{-1}+\mathbf{A}^{-1}\cdot\boldsymbol{\sigma}}{2}\cdot d\,\mathbf{A}\right]+V_\epsilon(P_\epsilon-P)\mathrm{tr}(\mathbf{A}^{-1}\cdot d\,\mathbf{A})\ , \tag{B23}$$

respectively. Clearly, the difference between Eqs. (B23) and (B22),

$$V_\epsilon(P_\epsilon-P)\mathrm{tr}(\mathbf{A}^{-1}\cdot d\,\mathbf{A})\ , \tag{B24}$$

is proportional to the difference between the stress pressure and the hydrostatic pressure. Note that imposing $P_\epsilon(\mathbf{A})=P(\mathbf{A})$ would make ϵ_{ij} and V mutually dependent variables and require that they be replaced by six independent variables $V^{1/3}A_{ij}$.

In order to explicitly verify that $P_\epsilon(\mathbf{A})$ and $P(\mathbf{A})$ are generally different, we shall first rewrite $F_\epsilon(N,V,T)$ Eq. (3.12), in terms of the *exact* variational potential, Eqs. (2.14)–(2.16). Thus,

$$\begin{aligned}F_\epsilon(N,V,T)-F(N,V,T)=\ &\Delta W[n_\epsilon(\vec{\mathrm{x}}),\mu;V_\epsilon,T]_{\mathrm{eq}}\\ &-\Delta W[n(\vec{\mathrm{x}}),\mu;V,T]_{\mathrm{eq}}\\ &-P_l(V_\epsilon-V)\ ,\end{aligned} \tag{B25}$$

where we used the subscript eq to emphasize that the expressions are to be evaluated at the equilibrium strained and unstrained densities, respectively. The right-hand side of this equation is obtained by adding and subtracting μN and $P_l(V_\epsilon-V)$ from the left-hand side and by identifying

$$G_l(\mu_l,V_\epsilon,T)-G_l(\mu_l,V,T)=-P_l(V_\epsilon-V)\ . \tag{B26}$$

Using the definition (B15), we obtain

$$\sigma_{ij}(\mathbf{A})=\frac{1}{V_\epsilon}A_{ik}A_{jl}\int_{V_\epsilon}\frac{\delta\Delta W[n_\epsilon(\vec{\mathrm{x}}),\mu;V_\epsilon,T]}{\delta n_\epsilon(\vec{\mathrm{x}})}\times\left.\frac{\partial n_\epsilon(\vec{\mathrm{x}})}{\partial\eta_{kl}}\right|_{\mathrm{eq}}d^3x-\delta_{ij}P(\mathbf{A})\ , \tag{B27}$$

where, following Eq. (B19),

$$\frac{\partial\Delta W[n_\epsilon(\vec{\mathrm{x}}),\mu;V_\epsilon,T]_{\mathrm{eq}}}{\partial V_\epsilon}=-P(\mathbf{A})+P_l\ , \tag{B28}$$

and we have used the formula

$$\frac{\partial J_A}{\partial\eta_{ij}}=J_A A_{ij}^{-1}\ . \tag{B29}$$

Combining this result with Eq. (B18) we finally obtain

$$P_\epsilon(\mathbf{A})=-\frac{1}{3V_\epsilon}A_{kl}^2\int_{V_\epsilon}\frac{\delta\Delta W[n_\epsilon(\vec{\mathrm{x}}),\mu;V_\epsilon,T]}{\delta n_\epsilon}\times\left.\frac{\partial n_\epsilon(\vec{\mathrm{x}})}{\partial\eta_{kl}}\right|_{\mathrm{eq}}d^3x+P(\mathbf{A})\ . \tag{B30}$$

Clearly, the first term in this equation is generally nonzero since $\Delta W[n_\epsilon(\vec{\mathrm{x}}),\mu;V_\epsilon,T]$ is stationary at the equilibrium $n_\epsilon(\vec{\mathrm{x}})$ relative to variations with fixed ϵ, whereas the variation in (B30) is, in fact, induced by a change in ϵ. Therefore, the stress pressure and the hydrostatic pressure are generally different at nonzero strain.

However, at zero strain, Eq. (B30) reduces to

$$P_{\epsilon=0}(\mathbf{A}=1)=-\frac{1}{3V}\int_V\frac{\delta\Delta W[n(\vec{\mathrm{x}}),\mu;V,T]}{\delta n(\vec{\mathrm{x}})}\times\left.\frac{\partial n_{\epsilon=0}(\vec{\mathrm{x}})}{\partial\eta_{kl}}\right|_{\mathrm{eq}}d^3x+P\ . \tag{B31}$$

In this case the first term vanishes since at the equilibrium density $n(\vec{\mathrm{x}})$, ΔW is stationary relative to *all* variations $\delta n(\vec{\mathrm{x}})$. Therefore, at $\epsilon=0$

$$P_{\epsilon=0}=P\ . \tag{B32}$$

More generally, by setting $\epsilon=0$ in Eq. (B27) one verifies that

$$\sigma_{ij}=-P\delta_{ij}\ . \tag{B33}$$

It is worth noting that if one is to make an approximation for ΔW, as in Eq. (2.15), at a *finite* strain, it would be better to expand around the strained liquid. However, in this case one would have to know the strain (volume) dependence of liquid pressure and chemical potential in addition to knowing the density dependence of the liquid structure factor. A derivation of the required formulas, which is straightforward but tedious, will not be presented here since we are ultimately interested in the elastic constants at zero strain, in which case either expansion, as long as it is carried to at least second order in δn, gives the identical result.

Next, we would like to evaluate the change $\sigma_{ij}(\mathbf{A})\rightarrow\sigma_{ij}(\mathbf{A})+d\sigma_{ij}$ caused by the infinitesimal deformation du_{ij}. This defines the elastic modulus tensor which is the proportionality constant in the Hooke's law

$$d\sigma_{ij}(\mathbf{A})=C_{ijkl}(\mathbf{A})du_{kl}\ . \tag{B34}$$

Note that at a finite stress $C_{ijkl}(\mathbf{A})$ does not have the full Voigt symmetry.

Starting from Eq. (B15) we can evaluate

$$d\sigma_{kj}=\left[\frac{1}{V_\epsilon}A_{ia}A_{jb}A_{kp}A_{lq}\frac{\partial^2 F_\epsilon}{\partial\eta_{ab}\partial\eta_{pq}}-\delta_{kl}\sigma_{ij}(\mathbf{A})\right.$$
$$\left.+\delta_{ki}\sigma_{lj}(\mathbf{A})+\delta_{kj}\sigma_{li}(\mathbf{A})\right]du_{kl}\ , \tag{B35}$$

where we used Eqs. (B5), (B9), and (B15), as well as

$$\frac{\partial J_A}{\partial A_{ij}}=J_A A_{ji}^{-1}\ . \tag{B36}$$

Therefore, we can identify the elastic modulus tensor as

$$C_{ijkl}(\mathbf{A})=\frac{1}{V_\epsilon}A_{ia}A_{jb}A_{kp}A_{lq}\frac{\partial^2 F_\epsilon}{\partial\eta_{ab}\partial\eta_{pq}}-\delta_{kl}\sigma_{ij}(\mathbf{A})$$
$$+\delta_{ki}\sigma_{lj}(\mathbf{A})+\delta_{kj}\sigma_{li}(\mathbf{A})\ . \tag{B37}$$

If we take an initially unstrained solid, we have to set $\mathbf{A}=1$ and Eq. (B13) reduces to

$$dF_{\epsilon=0}=-SdT-PV^{2/3}d(V^{1/3}\mathrm{tr}\,\mathbf{A})+\mu dN\ , \tag{B38}$$

while the stress σ_{ij}, defined in Eq. (B15), becomes [cf. Eq. (B33)],

$$\sigma_{ij}=\frac{1}{V}\frac{\partial^2 F_{\epsilon=0}}{\partial\eta_{ij}}=\frac{1}{V}\frac{\partial^2 F_{\epsilon=0}}{\partial\epsilon_{ij}}=-P\delta_{ij}=\frac{1}{V}\delta_{ij}\frac{\partial F_{\epsilon=0}}{\partial V}\ . \tag{B39}$$

Similarly, the elastic modulus Eq. (B37) reduces to

$$C_{ijkl}=\frac{1}{V}\frac{\partial^2 F_{\epsilon=0}}{\partial\eta_{ij}\partial\eta_{kl}}+P(\delta_{ij}\delta_{kl}-\delta_{ik}\delta_{jl}-\delta_{il}\delta_{jk})\ , \tag{B40}$$

which clearly has the complete Voigt symmetry. This expression can be further modified by using the identity

$$\frac{\partial^2}{\partial A_{ij}\partial A_{kl}}=\tfrac{1}{4}(A_{ia}\delta_{jb}+A_{ja}\delta_{ib})(A_{kp}\delta_{lq}+A_{lp}\delta_{kq})$$
$$\times\frac{\partial^2}{\partial\eta_{ab}\partial\eta_{pq}}+\frac{1}{4}\left[\delta_{ik}\frac{\partial}{\partial\eta_{jl}}+\delta_{il}\frac{\partial}{\partial\eta_{jk}}\right.$$
$$\left.+\delta_{jk}\frac{\partial}{\partial\eta_{il}}+\delta_{jl}\frac{\partial}{\partial\eta_{ik}}\right]\ , \tag{B41}$$

which, evaluated at $\mathbf{A}=1$, gives

$$\frac{1}{V}\frac{\partial^2 F_{\epsilon=0}}{\partial A_{ij}\partial A_{kl}}=\frac{1}{V}\frac{\partial^2 F_{\epsilon=0}}{\partial\eta_{ij}\partial\eta_{kl}}-\tfrac{1}{2}P(\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk})\ . \tag{B42}$$

Substituting this into Eq. (B40) finally leads to

$$C_{ijkl}=\frac{1}{V}\frac{\partial^2 F_{\epsilon=0}}{\partial\epsilon_{ij}\partial\epsilon_{kl}}+P[\delta_{ij}\delta_{kl}-\tfrac{1}{2}(\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk})]\ . \tag{B43}$$

This last equation can be interpreted as arising from the expansion

$$\frac{1}{V}[F_\epsilon-F+P(V_\epsilon-V)]=\tfrac{1}{2}C_{ijkl}\epsilon_{ij}\epsilon_{kl}+O(\epsilon^3)\ . \tag{B44}$$

This is the main equation derived in this appendix and it will be used in actual calculations of C_{ijkl}.

APPENDIX C: THE ELASTIC MODULUS TENSOR

In this appendix we shall derive explicit formulas for the elastic modulus tensor. As shown in Sec. IV, the elastic modulus tensor can be expressed in terms of the Hessian matrix of $w_G(\xi,\mathbf{b},\boldsymbol{\alpha};\Delta\mu)$ defined in Eq. (4.5). In terms of the reciprocal-lattice sums, this matrix can be evaluated from Eqs. (4.10)–(4.12) which read, in component form,

$$0=\frac{\partial w_G}{\partial\xi}=-\ln(N_c\pi^{3/2}\det\boldsymbol{\alpha}^{1/2})-\tfrac{3}{2}-\beta\Delta\mu+C_l(0)$$
$$+\ln\xi-\xi\sum_{\vec{\mathrm{Q}}}C_l(|\vec{\mathrm{Q}}|)h_M(\boldsymbol{\alpha})\ , \tag{C1}$$

$$0=\frac{\partial w_G}{\partial b_{ij}}=-\frac{1}{4\pi}\xi^2\left[\sum_{\vec{\mathrm{Q}}(\neq\vec{0})}\dot{C}_l(|\vec{\mathrm{Q}}|)\frac{Q_iQ_k}{|\vec{\mathrm{Q}}|}h_M(\boldsymbol{\alpha})\right]a_{kj}\ , \tag{C2}$$

and

$$0=\frac{\partial w_G}{\partial\alpha_{ij}}=-\tfrac{1}{2}\xi\alpha_{ij}^{-1}$$
$$+\tfrac{1}{4}\xi^2\left[\sum_{\vec{\mathrm{Q}}(\neq\vec{0})}C_l(|\vec{\mathrm{Q}}|)Q_kQ_lh_M(\boldsymbol{\alpha})\right]a_{ki}a_{lj}\ . \tag{C3}$$

Starting from the above equations it is straightforward to derive the components of the Hessian matrix:

$$\frac{\partial^2 w_G}{\partial \xi^2}=\frac{1}{\xi}-\sum_{\vec{\mathbf{M}}\in \mathbf{Z}^3} C_l(\,|\mathbf{b}\cdot\vec{\mathbf{M}}|\,)h_M(\boldsymbol{\alpha})$$

$$=\frac{1}{\xi^2}\left[1+\frac{\kappa_T^{-1}+2\Delta P}{k_B T n_l}\right]-\frac{1}{\xi}\ , \tag{C4}$$

where the last equality is a consequence of the definition of w_G, Eq. (4.5), and of the equilibrium condition Eq. (4.10);

$$\frac{\partial^2 w_G}{\partial \xi\,\partial b_{ij}}=-\xi\sum_{\vec{\mathbf{M}}\,(\neq\vec{0})}\dot{C}_l(\,|\mathbf{b}\cdot\vec{\mathbf{M}}|\,)\frac{b_{ik}M_kM_j}{|\mathbf{b}\cdot\vec{\mathbf{M}}|}h_M(\boldsymbol{\alpha})=0\ , \tag{C5}$$

where the last equality follows from Eq. (4.11);

$$\frac{\partial^2 w_G}{\partial \xi\,\partial \alpha_{ij}}=-\tfrac{1}{2}\alpha_{ij}^{-1}+2\pi^2\xi\sum_{\vec{\mathbf{M}}\,(\neq\vec{0})}C_l(\,|\mathbf{b}\cdot\vec{\mathbf{M}}|\,)(M_iM_j)h_M(\boldsymbol{\alpha})$$

$$=\tfrac{1}{2}\alpha_{ij}^{-1}\ , \tag{C6}$$

where the last equality follows from Eq. (4.12);

$$\frac{\partial^2 w_G}{\partial b_{ij}\,\partial b_{kl}}=-\tfrac{1}{2}\xi^2\sum_{\vec{\mathbf{M}}\,(\neq\vec{0})}\left[\ddot{C}_l(\,|\mathbf{b}\cdot\vec{\mathbf{M}}|\,)\frac{(b_{ip}M_pM_j)(b_{kq}M_qM_l)}{|\mathbf{b}\cdot\vec{\mathbf{M}}|^2}+\frac{\dot{C}(\,|\mathbf{b}\cdot\vec{\mathbf{M}}|\,)}{|\mathbf{b}\cdot\vec{\mathbf{M}}|}\left[\delta_{ik}M_jM_l-\frac{(b_{ip}M_pM_j)(b_{kq}M_qM_l)}{|\mathbf{b}\cdot\vec{\mathbf{M}}|^2}\right]\right]h_M(\boldsymbol{\alpha})$$

$$=-\tfrac{1}{2}\xi^2\sum_{\vec{\mathbf{M}}\,(\neq\vec{0})}\left[\frac{\ddot{C}_l(\,|\mathbf{b}\cdot\vec{\mathbf{M}}|\,)}{|\mathbf{b}\cdot\vec{\mathbf{M}}|^2}-\frac{\dot{C}_l(\,|\mathbf{b}\cdot\vec{\mathbf{M}}|\,)}{|\mathbf{b}\cdot\vec{\mathbf{M}}|^3}\right](b_{ip}M_pM_j)(b_{kq}M_qM_l)h_M(\boldsymbol{\alpha})\ , \tag{C7}$$

where the last equality follows from Eq. (4.11) and the fact that **b** is nonsingular; and

$$\frac{\partial^2 w_G}{\partial b_{ij}\,\partial \alpha_{kl}}=\pi^2\xi^2\sum_{\vec{\mathbf{M}}\,(\neq\vec{0})}\dot{C}_l(\,|\mathbf{b}\cdot\vec{\mathbf{M}}|\,)\frac{b_{ip}M_pM_j}{|\mathbf{b}\cdot\vec{\mathbf{M}}|}(M_kM_l)h_M(\boldsymbol{\alpha})\ , \tag{C8}$$

$$\frac{\partial^2 w_G}{\partial \alpha_{ij}\,\partial \alpha_{kl}}=\tfrac{1}{4}\xi(\alpha_{ik}^{-1}\alpha_{jl}^{-1}+\alpha_{jk}^{-1}\alpha_{il}^{-1})-2\pi^4\xi^2\sum_{\vec{\mathbf{M}}\,(\neq\vec{0})}C_l(\,|\mathbf{b}\cdot\vec{\mathbf{M}}|\,)(M_iM_jM_kM_l)h_M(\boldsymbol{\alpha})\ . \tag{C9}$$

Therefore, the components of the tensor $\mathcal{C}$ defined in Eqs. (4.22)–(4.27) can be written as

$$\mathcal{C}^{\epsilon\epsilon}_{ijkl}=\delta_{ij}\delta_{kl}\left[\left[1+\frac{\kappa_T^{-1}+2\Delta P}{k_BTn_l}\right]-\xi\right]\ , \tag{C10}$$

$$\mathcal{C}^{\epsilon\zeta}_{ijkl}=\mathcal{C}^{\zeta\epsilon}_{klij}=0\ , \tag{C11}$$

$$\mathcal{C}^{\epsilon\alpha}_{ijkl}=\mathcal{C}^{\alpha\epsilon}_{klij}=-\tfrac{1}{2}\xi\delta_{ij}\alpha_{kl}^{-1}\ , \tag{C12}$$

$$\mathcal{C}^{\zeta\zeta}_{ijkl}=-\tfrac{1}{2}\xi^2\sum_{\vec{\mathbf{Q}}\,(\neq\vec{0})}\left[\frac{\ddot{C}_l(\,|\vec{\mathbf{Q}}|\,)}{|\vec{\mathbf{Q}}|^2}-\frac{\dot{C}_l(\,|\vec{\mathbf{Q}}|\,)}{|\vec{\mathbf{Q}}|^3}\right]h_M(\boldsymbol{\alpha})Q_iQ_jQ_kQ_l\ , \tag{C13}$$

$$\mathcal{C}^{\zeta\alpha}_{ijkl}=\mathcal{C}^{\alpha\zeta}_{klij}=-\tfrac{1}{4}\xi^2\sum_{\vec{\mathbf{Q}}\,(\neq\vec{0})}\left[\frac{\dot{C}_l(\,|\vec{\mathbf{Q}}|\,)}{|\vec{\mathbf{Q}}|}h_M(\boldsymbol{\alpha})Q_iQ_jQ_pQ_q\right]a_{pk}a_{ql}\ , \tag{C14}$$

$$\mathcal{C}^{\alpha\alpha}_{ijkl}=\tfrac{1}{4}\xi(\alpha_{ik}^{-1}\alpha_{jl}^{-1}+\alpha_{il}^{-1}\alpha_{jk}^{-1})-\tfrac{1}{8}\xi^2\left[\sum_{\vec{\mathbf{Q}}\,(\neq\vec{0})}C_l(\,|\vec{\mathbf{Q}}|\,)h_M(\boldsymbol{\alpha})Q_aQ_bQ_cQ_d\right]a_{ai}a_{bj}a_{ck}a_{dl}\ . \tag{C15}$$

We can specialize these equations to the case of cubic lattices. Using the cubic unit cell we have, by symmetry,

$$\alpha_{ij}=\alpha\delta_{ij} \tag{C16}$$

and

$$a_{ij}=a\delta_{ij}\ , \tag{C17}$$

where α and a are scalars. Equations (C10)–(C15) now reduce to

$$\mathcal{C}^{\epsilon\epsilon}_{ijkl}=\delta_{ij}\delta_{kl}\left[\frac{\kappa_T^{-1}+2\Delta P}{k_B T n_l}+1-\xi\right], \tag{C18}$$

$$\mathcal{C}^{\epsilon\zeta}_{ijkl}=\mathcal{C}^{\zeta\epsilon}_{klij}=0\ , \tag{C19}$$

$$\mathcal{C}^{\epsilon\alpha}_{ijkl}=\mathcal{C}^{\alpha\epsilon}_{klij}=\frac{-\xi}{2\alpha}\delta_{ij}\delta_{kl}\ , \tag{C20}$$

$$\mathcal{C}^{\zeta\zeta}_{ijkl}=-\tfrac{1}{2}\xi^2\sum_{\vec{Q}\,(\neq\vec{0})}\left[\frac{\ddot{C}_l(|\vec{Q}|)}{|\vec{Q}|^2}-\frac{\dot{C}_l(|\vec{Q}|)}{|\vec{Q}|^3}\right]h_M(\alpha)Q_iQ_jQ_kQ_l\ , \tag{C21}$$

$$\mathcal{C}^{\zeta\alpha}_{ijkl}=\mathcal{C}^{\alpha\zeta}_{klij}=-\tfrac{1}{4}\xi^2a^2\sum_{\vec{Q}\,(\neq\vec{0})}\frac{\dot{C}_l(|\vec{Q}|)}{|\vec{Q}|}h_M(\alpha)Q_iQ_jQ_kQ_l\ , \tag{C22}$$

$$\mathcal{C}^{\alpha\alpha}_{ijkl}=\frac{\xi}{4\alpha^2}(\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk})-\tfrac{1}{8}\xi^2a^4\sum_{\vec{Q}\,(\neq\vec{0})}C_l(|\vec{Q}|)h_M(\alpha)Q_iQ_jQ_kQ_l\ . \tag{C23}$$

A typical expression which needs to be evaluated is of the form

$$f_{ijkl}=\sum_{\vec{Q}}f(\vec{Q})Q_iQ_jQ_kQ_l\ , \tag{C24}$$

where $f(\vec{Q})$ is invariant under the crystal's symmetry. A theorem can be proved[48] which allows us to reduce such sums to certain invariant sums, namely

$$f_{ijkl}=\left[\sum_{\vec{Q}}f(\vec{Q})\hat{t}^{\,\nu}(\vec{Q})\right]\hat{t}^{\,\nu}_{ijkl}\ , \tag{C25}$$

where

$$\hat{t}^{\,\nu}(Q)=\hat{t}^{\,\nu}_{ijkl}Q_iQ_jQ_kQ_l \tag{C26}$$

are orthonormalized, basic quartic invariant polynomials. Here, "orthonormalized" means

$$\hat{t}^{\,\mu}_{ijkl}\hat{t}^{\,\nu}_{ijkl}=\delta^{\mu\nu}\ . \tag{C27}$$

For cubic symmetry, there are two independent quartic polynomials, for example, $|\vec{Q}|^4$ and $Q_1^4+Q_2^4+Q_3^4$. An orthonormalized pair we have used is

$$\hat{t}^{\,1}(\vec{Q})=\frac{1}{\sqrt{5}}|Q|^4 \tag{C28}$$

and

$$\hat{t}^{\,2}(\vec{Q})=\frac{1}{\sqrt{30}}[5(Q_1^4+Q_2^4+Q_3^4)-3|\vec{Q}|^4]\ , \tag{C29}$$

or in terms of the tensors $\hat{t}_{ijkl}$,

$$\hat{t}^{\,1}_{ijkl}=\frac{1}{3\sqrt{5}}(\delta_{ij}\delta_{kl}+\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk}) \tag{C30}$$

and

$$\hat{t}^{\,2}_{ijkl}=-\sqrt{3/2}\,\hat{t}^{\,1}_{ijkl}+\begin{cases}(\frac{5}{6})^{1/2} & \text{if } i=j=k=l\ ,\\ 0 & \text{otherwise}\ .\end{cases} \tag{C31}$$

An advantage in using Eq. (C24) is in that one explicitly sees that the sum over $\vec{Q}$ need only be carried over the fundamental region for cubic group, that is,

$$f_{ijkl}=\left[\sum_{M_1=0}^{\infty}\sum_{M_2=0}^{M_1}\sum_{M_3=0}^{M_2}m(\vec{M})f(\vec{Q})\hat{t}^{\,\nu}(\vec{Q})\right]\hat{t}^{\,\nu}_{ijkl}\ , \tag{C32}$$

where $\vec{M}$ is defined in Eq. (4.8) and $m(\vec{M})$ is the appropriate orbit multiplicity and takes the values[50] 1, 6, 8, 12, 24, and 48.

Finally, we would like to point out that Eq. (4.33) can be evaluated after observing that each block of **C** has cubic symmetry so that all blocks can be simultaneously diagonalized. In this way we obtain

$$C_{11}+2C_{12}=(C^{\epsilon\epsilon}_{11}+2C^{\epsilon\epsilon}_{12})-(C^{\alpha\epsilon}_{11}+2C^{\alpha\epsilon}_{12})^2/(C^{\alpha\alpha}_{11}+2C^{\alpha\alpha}_{12})\ , \tag{C33}$$

$$C_{11}-C_{12}=(C^{\epsilon\epsilon}_{11}-C^{\epsilon\epsilon}_{12})-(C^{\alpha\epsilon}_{11}-C^{\alpha\epsilon}_{12})^2/(C^{\alpha\alpha}_{11}-C^{\alpha\alpha}_{12})\ , \tag{C34}$$

and

$$C_{44}=C^{\epsilon\epsilon}_{44}-(C^{\alpha\epsilon}_{44})^2/(C^{\alpha\alpha}_{44})\ , \tag{C35}$$

where we used the Voigt notation. The last three equations verify that any additional equilibration of the strained density will reduce the eigenmoduli.

We have carried out the sums in Eqs. (C21)–(C23) with help of a computer. The results are summarized in Sec. V.

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[1] L. S. Ornstein and F. Zernike, Proc. Akad. Sci. (Amsterdam) **18**, 793 (1914).

[2] F. Stillinger, Phys. Rev. **142**, 237 (1966).

[3] M. Born and K. Huang, *Dynamic Theory of Crystal Lattices* (Oxford University Press, Oxford, 1954); see also, G. Leibfried and W. Ludwig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1961), Vol. 12.

[4] D. R. Squire, A. C. Holt, and W. G. Hoover, Physica **42**, 437

(1969).

[5] M. Lipkin, S. A. Rice, and U. Mohanty, J. Chem. Phys. **82**, 479 (1985).

[6] T. V. Ramakrishnan, Pramana **22**, 365 (1984).

[7] T. V. Ramakrishnan and M. Yussouff, Phys. Rev. B **19**, 2775 (1979); see also, S. Alexander, in *Symmetries and Broken Symmetries in Condensed Matter Physics*, edited by N. Boccara (IDSET, Paris, 1981).

[8] S. Alexander, J. Phys. (Paris) **45**, 1939 (1984).

[9] J. W. Gibbs, *Elementary Principles in Statistical Mechanics* (Yale University Press, New Haven, 1902).

[10] T. D. Lee and C. N. Yang, Phys. Rev. **113**, 1165 (1959).

[11] P. C. Martin and J. Schwinger, Phys. Rev. **115**, 1342 (1959); P. C. Martin (unpublished).

[12] C. DeDominicis, J. Math. Phys. **3**, 983 (1962).

[13] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[14] N. D. Mermin, Phys. Rev. **137**, 1441 (1965).

[15] For a pedagogical review, see H. Falk, Am. J. Phys. **38**, 858 (1970).

[16] D. K. Fairbonet, W. F. Saam, and L. M. Sander, Phys. Rev. B **26**, 179 (1982); L. M. Sander and J. Hautman, *ibid.* **29**, 2171 (1984).

[17] G. L. Jones and U. Mohanty, Mol. Phys. **54**, 1241 (1985).

[18] P. Tarzona, Phys. Rev. A **31**, 2672 (1985).

[19] W. A. Curtain and N. W. Ashcroft, Phys. Rev. Lett. **56**, 2775 (1986).

[20] S. Sachdev and D. R. Nelson, Phys. Rev. B **32**, 4592 (1985).

[21] A. D. J. Haymet, J. Chem. Phys. **78**, 4641 (1983).

[22] A. D. J. Haymet and D. W. Oxtoby, J. Chem. Phys. **84**, 1769 (1986).

[23] C. Marshall, B. B. Laird, and A. D. J. Haymet, Chem. Phys. Lett. **122**, 320 (1985).

[24] M. Baus and J.-L. Colot, J. Phys. C **19**, L135 (1986); Y. Singh, J. Stossel, and P. Wolynes, Phys. Rev. Lett. **54**, 1059 (1985).

[25] M. R. Lakshmi, H. R. Krishnamurthy, and T. V. Ramakrishnan (unpublished).

[26] U. Mohanty (unpublished).

[27] A. D. J. Haymet and D. W. Oxtoby, J. Chem. Phys. **74**, 2559 (1981); D. W. Oxtoby and A. D. J. Haymet, *ibid.* **76**, 6262 (1982).

[28] M. V. Jarić and U. Mohanty, Phys. Rev. Lett. **58**, 230 (1987).

[29] M. Kimura and F. Yonezawa, in *Topological Disorder in Condensed Matter*, edited by F. Yonezawa and T. Ninomiya (Springer-Verlag, Berlin, 1983), Vol. 46, p. 80.

[30] D. Frenkel and A. J. C. Ladd, Phys. Rev. Lett. **59**, 1169 (1987).

[31] M. V. Jarić and U. Mohanty, Phys. Rev. Lett. **59**, 1170 (1987).

[32] H. Callen, in *Thermodynamics* (Wiley, New York, 1960).

[33] See, for example, a review by D. J. Wallace, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, New York, 1976), Vol. 6, p. 293, and references therein.

[34] M. V. Jarić and U. Mohanty (unpublished).

[35] Different definitions of the strain matrix, which describes departures of **A** from the identity, could be used. For example, a strain could be defined by $\epsilon' = \ln \mathbf{A}$. A commonly used, Lagrangian strain η, based on the transformation of the scalar product, is defined by $\eta = \frac{1}{2}(\tilde{\mathbf{A}}\mathbf{A} - 1)$. These definitions differ in second order in the strain and, consequently, lead to different elastic modulus tensors if these are defined as quadratic forms in an energy expansion.

[36] M. A. Krivoglaz, *Theory of X-Ray and Thermal-Neutron Scattering by Real Crystals* (Plenum, New York, 1969).

[37] G. L. Jones, Mol. Phys. **61**, 455 (1987).

[38] D. C. Wallace, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1970), Vol. 25, p. 301; D. C. Wallace, *Thermodynamics of Crystals* (Wiley, New York, 1972).

[39] M. Popović and M. V. Jarić (unpublished).

[40] Again, it is straightforward to verify that the constant and the linear terms all vanish.

[41] E. Thiele, J. Chem. Phys. **39**, 474 (1963); M. S. Wertheim, Phys. Rev. Lett. **10**, 321 (1963).

[42] Given a uniaxial stress whose only nonvanishing component is σ_{11}, we define the Poisson ratio as (transverse compression strain/longitudinal extension strain) $= -\epsilon_{22}/\epsilon_{11} = C_{12}/(C_{11} + C_{12})$.

[43] D. Henderson and W. W. Grundke, J. Chem. Phys. **63**, 601 (1975).

[44] F. Stillinger and Z. W. Salsburg, J. Chem. Phys. **46**, 3962 (1967).

[45] K. Honda, H. Nakano, and K. Nakamura, J. Phys. Soc. Jpn. **49**, 457 (1980).

[46] Henshaw *et al.*, Phys. Rev. **105**, 976 (1956).

[47] *Landolt-Börnstein*, edited by K.-H. Hellwege (Springer-Verlag, Berlin, 1969), New Series, Group III, Vol. 2.

[48] Although A_{ij} is symmetric, we can formally treat it as having nine independent components. However, we must be careful to symmetrize the differential $dA_{ij} \rightarrow \frac{1}{2}(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})dA_{lk}$. That is, a result of differentiation with respect to A_{ij} treated as independent from A_{ji} should, at the end, be symmetrized with respect to indices i and j.

[49] M. V. Jarić, in *Proceedings of the XVth International Colloquium on Group Theoretical Methods in Physics*, edited by R. Gilmore and D. H. Geng (World-Scientific, Singapore, 1987).

[50] See, for example, M. V. Jarić, L. Michel, and R. T. Sharp, J. Phys. (Paris) **45**, 1 (1984).