Correlation functions in classical solids

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(Received 28 October 1996)

By invoking thermodynamic potentials as generating functions for hierarchies of correlation functions, we develop a description of solids written in the same statistical language used to describe inhomogeneous fluids. Important constraints then follow from consideration of the symmetries of the crystalline solid. Considerable insight into the two-particle density is obtained by appealing to the harmonic model of the solid, which motivates the idea of parametrizing the correlation functions using parameters unique to each lattice site. By paralleling the derivation of the Ornstein-Zernike equation we are led to an equivalent relation for the solid between the parameters of the direct correlation function and the parameters of the two-particle density. By similarly paralleling the derivation of Percus identity, we develop an equation for the parametrization of correlation functions of a solid analogous to the hypernetted-chain equation of inhomogeneous fluids. The harmonic model of the solid thus emerges from the appropriate limit of the hypernetted-chain equation for an extremely inhomogeneous fluid. [S1063-651X(97)02604-4]

PACS number(s): 05.20.−y, 61.20.Ne, 05.70.−a, 63.10.+a

I. INTRODUCTION

The dynamics of three-dimensional crystalline solids are traditionally described in terms of small amplitude vibrations of atoms from their equilibrium positions which, when quantized, are the phonons. However, when the atoms make larger excursions from their equilibrium sites, for example, near melting, solid-solid phase transitions, and other extremely anharmonic phenomena, this description is inadequate. To address these problems, phonon-free theories, especially density-functional theories, have been developed and have met with considerable success in describing, for example, the melting of the hard-sphere solid [1]. Density-functional theories of solids require extremely inhomogeneous parametrizations of the one-particle density; the density near a lattice site may be orders of magnitude higher than the density in the interstitial regions. These theories also require as input the Helmholtz free energy of the homogeneous fluid state and information on correlation such as the Ornstein-Zernike function. In effect, the crystalline solid is viewed as an exceedingly inhomogeneous system, with sharp peaks in the one-particle density at a discrete set of sites.

This representation of the solid system as an inhomogeneous system suggests an alternative treatment of the classical solid. Inhomogeneous fluids are described *statistically*, normally in terms of correlation functions, for example, the correlation functions which relate the one-point and two-point densities. These correlation functions can be given as the simultaneous solution of an integral equation, the Ornstein-Zernike equation, and an algebraic closure relation which relates the correlation functions to the pair potential. Well-known approximations to the closure relation are the hypernetted-chain relation, the Percus-Yevick relation, and the mean spherical approximation [2]. In the homogeneous case, the ensuing equations have been used quite successfully to describe the structure of simple fluids. However, similar though more complex relations also describe the correlation functions in, for example, the crystalline solid. No features of the theory inherently prevent it from being used to describe an inhomogeneous ''fluid'' whose one-particle density is sharply peaked at a discrete set of sites; the limit of extreme inhomogeneity is the classical solid but treated from the same point of view as classical density-functional theory.

In this paper we investigate several properties of the two-point density and the direct correlation function of a classical solid which follow from this picture. For simplicity, we restrict our treatment to solids with a single atom associated with each site of a Bravais lattice. We begin by noting that both symmetry considerations and certain aspects of the harmonic model of solids strongly suggest that the correlation functions in a solid can be physically described by focusing on their properties in the vicinity of the lattice sites. We adopt this point of view and with it propose a parametrization of the two-particle density and the direct correlation function, the parameters themselves satisfying a discrete equation analogous to the Ornstein-Zernike equation. By methods similar to the Percus identity, we also develop a parametrized form of the closure relationship. Finally, we show that these results contain the harmonic model of the solid in an appropriate limit.

II. DEFINITIONS

The properties of a classical system of N particles of mass m in a three-dimensional volume V at coordinates $\{\mathbf{r}_i\}$ with momenta $\{\mathbf{p}_i\}$ ($i=1,\ldots,N$) interacting via pairwise potentials $\phi^{(2)}(\mathbf{r},\mathbf{r}')$ and in an external potential $\phi^{(1)}(\mathbf{r})$ are described by the Hamiltonian

$$\hat{\mathcal{H}}_N = \hat{T}_N + \int_V d^3\mathbf{r}\,\hat{\rho}(\mathbf{r})\phi^{(1)}(\mathbf{r})$$

$$+ \tfrac{1}{2}\int_V d^3\mathbf{r}\int_V d^3\mathbf{r}'\,\hat{\rho}^{(2)}(\mathbf{r},\mathbf{r}')\phi^{(2)}(\mathbf{r},\mathbf{r}'), \qquad (1)$$

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where $\hat{T}_N = \Sigma_{i=1}^N \mathbf{p}_i^2/2m$ is the kinetic energy

$$\hat{\rho}(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \qquad (2)$$

is the (one-particle) density operator, and

$$\hat{\rho}^{(2)}(\mathbf{r},\mathbf{r}') = \sum_{i=1}^N \sum_{\substack{j=1 \\ j \neq i}}^N \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j) \qquad (3)$$

is the two-particle density operator. Interactions of three or more particles that cannot be decomposed into pair potentials will be ignored. The evident translational symmetry of Eq. (1) can be broken by the imposition of an arbitrarily weak external potential. We focus our attention on systems and the choice of thermodynamic conditions for which $\langle \hat{\rho}(\mathbf{r}) \rangle$ is periodic, and with the symmetry of a Bravais lattice (no essential physics is lost by this restriction). The grand potential Ω associated with this Hamiltonian is then a generating function for a hierarchy of multipoint densities of the system [3,4], as follows:

$$-\frac{1}{\beta} \frac{\delta(\beta\Omega)}{\delta\phi^{(1)}(\mathbf{r})} = \langle \hat{\rho}(\mathbf{r}) \rangle = \rho^{(1)}(\mathbf{r}), \qquad (4)$$

$$-\frac{1}{\beta^2} \frac{\delta^2(\beta\Omega)}{\delta\phi^{(1)}(\mathbf{r})\delta\phi^{(1)}(\mathbf{r}')} = \langle \hat{\rho}(\mathbf{r})\hat{\rho}(\mathbf{r}') \rangle - \langle \hat{\rho}(\mathbf{r}) \rangle \langle \hat{\rho}(\mathbf{r}') \rangle$$

$$= \rho^{(2)}(\mathbf{r},\mathbf{r}') + \delta(\mathbf{r} - \mathbf{r}')\rho^{(1)}(\mathbf{r})$$

$$- \rho^{(1)}(\mathbf{r})\rho^{(1)}(\mathbf{r}'). \qquad (5)$$

The above correspondence between $\phi^{(1)}(\mathbf{r})$ and $\rho^{(1)}(\mathbf{r})$ suggests that they are thermodynamically conjugate variables, relating two potentials via a Legendre transformation.

In fact, if we define the "intrinsic" Helmholtz free energy by

$$\mathcal{F}[\rho^{(1)}] = \Omega[\rho^{(1)}] - \int d^3\mathbf{r}\, \rho^{(1)}(\mathbf{r})[\phi^{(1)}(\mathbf{r}) - \mu] \qquad (6)$$

then since $\mathcal{F}$ is a unique functional of the one-particle density [5,6]

$$\phi^{(1)}(\mathbf{r}) = \frac{\delta\mathcal{F}}{\delta\rho^{(1)}(\mathbf{r})}. \qquad (7)$$

The intrinsic Helmholtz free energy can be separated into an ideal part $\mathcal{F}_{id}$ (which is the Helmholtz free energy of a non-interacting system at the same temperature and with an identical one-particle density), and an excess part $\mathcal{F}_{ex}$, which arises from the interactions of the particles in the system. Since

$$\beta\mathcal{F}_{id} = \int d^3\mathbf{r}\, \rho^{(1)}(\mathbf{r})\{\ln[\lambda^3\rho^{(1)}(\mathbf{r})] - 1\}, \qquad (8)$$

where $\lambda^2 = \beta h^2/2m\pi$ is the thermal de Broglie wavelength, the excess part is then a generating function for a second hierarchy of correlation functions, namely, the direct correlation functions:

$$c^{(1)}(\mathbf{r}_1) = -\beta \frac{\delta\mathcal{F}_{ex}}{\delta\rho^{(1)}(\mathbf{r}_1)}, \qquad (9)$$

$$c^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = -\beta \frac{\delta^2\mathcal{F}_{ex}}{\delta\rho^{(1)}(\mathbf{r}_1)\delta\rho^{(1)}(\mathbf{r}_2)}.$$

We emphasize that these hierarchies arise from simply regarding the thermodynamic potentials as generating functions for correlation and distribution functions; we distinguish these hierarchies from the Bogoliubov-Born-Green-Kirkwood-Yvon hierarchy, which has also been used to describe distribution functions in solids. (See [7,8], and references therein.) Because

$$\frac{1}{\beta} \frac{\delta\mathcal{F}_{id}}{\delta\rho^{(1)}(\mathbf{r})} = \ln[\lambda^3\rho^{(1)}(\mathbf{r})], \qquad (10)$$

it follows that

$$\rho^{(1)}(\mathbf{r}) = \frac{1}{\lambda^3} e^{-\beta\phi^{(1)}(\mathbf{r}) + c^{(1)}(\mathbf{r})}. \qquad (11)$$

If the particles are noninteracting, $\mathcal{F}_{ex}$ vanishes, and all of its functional derivatives including $c^{(1)}(\mathbf{r})$ vanish. In this circumstance, Eq. (11) becomes the familiar "barometer" formula, the Boltzmann distribution of noninteracting particles at a given temperature in an external potential. Here we see that $c^{(1)}(\mathbf{r})$ plays the role of an effective external potential arising from the interactions of the particles. In the case of solids, $c^{(1)}(\mathbf{r})$ plays an important role in stabilizing the solid even in an arbitrarily small external field, thus breaking the symmetry of the Hamiltonian. The role of $c^{(2)}(\mathbf{r},\mathbf{r}')$ will be elucidated in the next section.

Because of the conjugacy of $\phi^{(1)}(\mathbf{r})$ and $\rho^{(1)}(\mathbf{r})$, their functional derivatives are "matrix" inverses of each other, i.e.,

$$\delta(\mathbf{r}_1 - \mathbf{r}_2) = \int d^3\mathbf{r}_3 \frac{\delta\phi^{(1)}(\mathbf{r}_1)}{\delta\rho^{(1)}(\mathbf{r}_3)} \frac{\delta\rho^{(1)}(\mathbf{r}_3)}{\delta\phi^{(1)}(\mathbf{r}_2)}$$

$$= \int d^3\mathbf{r}_3 \frac{\delta^2\mathcal{F}}{\delta\rho^{(1)}(\mathbf{r}_1)\delta\rho^{(1)}(\mathbf{r}_3)} \frac{\delta^2\Omega}{\delta\phi^{(1)}(\mathbf{r}_3)\delta\phi^{(1)}(\mathbf{r}_2)}. \qquad (12)$$

This equation is equivalent to the Ornstein-Zernike equation.

III. SYMMETRY CONSIDERATIONS

In a homogeneous, isotropic liquid, correlation functions simplify markedly. Because homogeneity implies a continuous translational symmetry, functions of one position satisfy $\rho^{(1)}(\mathbf{r} + \mathbf{r}') = \rho^{(1)}(\mathbf{r})$, for all $\mathbf{r}'$, and hence are constant. By the same symmetry, functions of two positions satisfy $\rho^{(2)}(\mathbf{r},\mathbf{r}') = \rho^{(2)}(\mathbf{r} + \mathbf{r}'',\mathbf{r}' + \mathbf{r}'')$, for all $\mathbf{r}''$, and choosing $\mathbf{r}'' = -\mathbf{r}'$, for all $\mathbf{r}$ we see that two-point functions are functions only of the difference between the two variables. Furthermore, if the liquid is isotropic (rotationally and transla-

tionally invariant), only the magnitude of the difference matters, and $\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2)=\rho^{(2)}(|\mathbf{r}_1-\mathbf{r}_2|)$. Thus a function of six variables has been reduced to a function of one variable.

In an inhomogeneous system, a function of six variables can be reduced to a function of one variable by averaging the function of two positions over all translations and then averaging the resulting function of one vector $\mathbf{r}$ over rotations Ω, e.g.,

$$\widetilde{g}(r)=\int \frac{d\Omega}{4\pi}\int \frac{d^3\mathbf{r}'}{V}\frac{\rho^{(2)}(\mathbf{r}+\mathbf{r}^*,\mathbf{r}')}{\rho_s^2}. \qquad (13)$$

In the homogeneous limit, this function reduces to the familiar radial distribution function, and retains much of its structure even in inhomogeneous systems. Indeed, Rascon *et al.* [9] have exploited this similarity in order to develop a theory of correlations in the solid based on this function. However, it does not satisfy any known equations corresponding to the Ornstein-Zernike and hypernetted-chain equations. We therefore focus instead on the two-particle density itself in order to develop a theory of solids analogous to statistical theories of inhomogeneous fluids.

In crystalline solids, the continuous translational symmetry is broken; the system is invariant only under a discrete set of transformations. We emphasize that the crystals discussed here are dynamic, and that the symmetries refer to the properties of thermodynamic averages, not the instantaneous positions of the particles. The first step toward understanding the structure of correlation functions in solids is thus to determine the constraints that this broken symmetry places upon them. The meaning of translational symmetry for a crystalline solid is that there exists a discrete set of vectors $\mathbf{R}_i$ such that any function of position, such as one-particle density $\rho^{(1)}(\mathbf{r})$, satisfies

$$\rho^{(1)}(\mathbf{r})=\rho^{(1)}(\mathbf{r}+\mathbf{R}_i) \quad \text{for all } \mathbf{R}_i. \qquad (14)$$

This set of vectors necessarily forms a Bravais lattice and the consequent periodic structure implies that one-point functions can be expanded as a Fourier series [10]

$$\rho^{(1)}(\mathbf{r})=\sum_{\mathbf{G}} \rho_{\mathbf{G}}e^{i\mathbf{G}\cdot\mathbf{r}}, \qquad (15)$$

where the Fourier series coefficients $\rho_{\mathbf{G}}$ are defined in terms of an integral over the volume v of a primitive cell C,

$$\rho_{\mathbf{G}}=\frac{1}{v}\int_C d^3\mathbf{r}\ e^{-i\mathbf{G}\cdot\mathbf{r}}\rho^{(1)}(\mathbf{r}). \qquad (16)$$

The $\mathbf{G}$ are reciprocal lattice vectors with the property that $e^{i\mathbf{G}\cdot\mathbf{R}_i}=1$ for all $\mathbf{G}$ and all $\mathbf{R}_i$. Two-point functions in a crystal are not doubly periodic. Any two-point function, for example $\rho^{(2)}$, satisfies the single periodicity requirement

$$\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2)=\rho^{(2)}(\mathbf{r}_1+\mathbf{R}_i,\mathbf{r}_2+\mathbf{R}_i) \quad \text{for all } \mathbf{R}_i. \qquad (17)$$

If we write Eq. (17) in terms of a center of mass variable $\mathbf{r}_+=(\mathbf{r}_1+\mathbf{r}_2)/2$ and a difference variable $\mathbf{r}_-=\mathbf{r}_1-\mathbf{r}_2$ then we see that $\rho^{(2)}(\mathbf{r}_+,\mathbf{r}_-)$ is a periodic function of the center of mass variable, and a continuous function of the difference

variable. It can therefore be written in a Fourier series in the center of mass variable, with coefficients that are functions of the difference, i.e.,

$$\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2)=\sum_{\mathbf{G}} e^{i\mathbf{G}\cdot(\mathbf{r}_1+\mathbf{r}_2)/2}\rho_{\mathbf{G}}^{(2)}(\mathbf{r}_1-\mathbf{r}_2). \qquad (18)$$

The coefficients satisfy $\rho_{\mathbf{G}}^{(2)}(\mathbf{r})=\rho_{-\mathbf{G}}^{(2)}(\mathbf{r})$ since the two-point density is real, and they also satisfy $\rho_{\mathbf{G}}^{(2)}(\mathbf{r})=\rho_{\mathbf{G}}^{(2)}(-\mathbf{r})$ because the two-point density is symmetric with respect to interchange of variables. By definition of a reciprocal lattice vector, $e^{i\mathbf{G}\cdot\mathbf{R}_2}=1$, and therefore $e^{i\mathbf{G}\cdot(\mathbf{R}_1-\mathbf{R}_2)/2}=e^{i\mathbf{G}\cdot(\mathbf{R}_1+\mathbf{R}_2)/2}$. It follows that any two-point function, when evaluated at two lattice sites, is a function only of the *difference* between the two lattice sites. This property holds only for lattice sites and not, of course, for arbitrary points. Furthermore, if the Fourier series Eq. (18) is differentiable with respect to $\mathbf{r}_1$ and $\mathbf{r}_2$, the same arguments continue to apply to its derivatives, which will also be functions of the difference between two lattice points. (In carrying out the differentiation, it is essential to differentiate first, and only then to evaluate the result at lattice sites.) From these properties we deduce that if a two-point function can be written as a Fourier series that is infinitely differentiable, it can be represented as a Taylor expansion about each lattice site, and the coefficients of the Taylor expansion will be functions only of the difference between the lattice sites. Although the two-point correlation functions of a crystalline solid are considerably more complicated than those of an isotropic, homogeneous fluid, they are nevertheless much simpler than those of an arbitrary inhomogeneous fluid.

IV. HARMONIC APPROXIMATION

A great deal can be learned about the multipoint densities of a solid by studying the harmonic approximation to atomic dynamics. In this approximation, we break the continuous translational symmetry of the basic Hamiltonian Eq. (1) by tying each particle to a particular equilibrium site. For convenience, we will continue to assume that the equilibrium sites form a Bravais lattice, although much of the analysis applies in more general situations, such as a Bravais lattice with a basis, or even in the absence of any translational symmetry (such as a nondiffusive glassy system). The relevant dynamical variables are no longer the positions of the particles $\mathbf{r}_i$ but their displacements $\mathbf{u}(i)=\mathbf{r}_i-\mathbf{R}_i$ from a fixed set of lattice sites $\{\mathbf{R}_i\}$. In this section we shall show that the one- and two-point densities describing the harmonic solid have simple functional forms that provide insight into the behavior of these functions in more general situations. Furthermore, the relationship of these functions to correlation functions of displacement will provide a connection between distribution function and phonon-based views of the solid. The Hamiltonian of the harmonic solid is assumed to contain a potential energy that is a general quadratic function of the displacements [10]. To within constant terms, the Hamiltonian takes the well-known form

$$\hat{\mathcal{H}}=\hat{T}+\tfrac{1}{2}\sum_{\mathbf{R}_i,\mathbf{R}_j} \mathbf{u}(i)\cdot\overleftrightarrow{\mathbf{D}}(i,j)\cdot\mathbf{u}(j). \qquad (19)$$

In Eq. (19) the matrix of rank-2 tensors $\overleftrightarrow{\mathrm{D}}(i,j)$, the dynamical matrix, can be written in terms of the second derivative tensor of the pair potentials in the Hamiltonian Eq. (1):

$$\overleftrightarrow{\mathrm{D}}(i,j)_{\mu\nu} = -\phi^{(2)}(\mathbf{R}_i,\mathbf{R}_j)_{\mu\nu} + \delta_{ij}\sum_{\mathbf{R}_k}\phi^{(2)}(\mathbf{R}_i,\mathbf{R}_k)_{\mu\nu},$$
(20)

where

$$\phi^{(2)}(\mathbf{r})_{\mu\nu} = \frac{\partial^2\phi^{(2)}(\mathbf{r})}{\partial r_\mu \partial r_\nu}$$
(21)

(μ and ν are Cartesian components). Note that neither the first derivatives of nor even the actual values of the pair potential enter the harmonic Hamiltonian (19). (The latter enter into a constant that is physically irrelevant in the harmonic model; the first derivatives vanish because the Hamiltonian is expanded about sites which by definition constitute the equilibrium configuration of the particles.)

In order to calculate the one-particle density, it is more convenient to work in terms of its Fourier transform:

$$\rho(\mathbf{k}) = \int d^3\mathbf{r}\, e^{i\mathbf{k}\cdot\mathbf{r}}\rho(\mathbf{r}) = \sum_{\mathbf{R}_i} e^{i\mathbf{k}\cdot\mathbf{R}_i}\langle e^{i\mathbf{k}\cdot\mathbf{u}(i)}\rangle.$$
(22)

It is also convenient to begin with a quantum mechanical description and then to proceed to the classical limit. In the harmonic model, if operators $\hat{A}$ and $\hat{B}$ are linear functions of displacement and momentum, or if the corresponding quantum mechanical operators are linear functions of creation and annihilation operators, then expectation values of exponentials satisfy [11]

$$\langle e^{\hat{A}}e^{\hat{B}}\rangle = e^{(1/2)\langle\hat{A}^2 + 2\hat{A}\hat{B} + \hat{B}^2\rangle},$$
(23)

which enables us to write any expectation value necessary for the calculation of any multipoint density entirely in terms of displacement-displacement correlation functions $\langle\mathbf{u}(\mathbf{R}_i)\mathbf{u}(\mathbf{R}_j)\rangle$. For the one-point density, only the correlation functions involving components of displacements from the same site are needed; more generally, correlation functions between displacements at pairs of sites are needed. Thus

$$\rho^{(1)}(\mathbf{k}) = \sum_{\mathbf{R}_i} e^{i\mathbf{k}\cdot\mathbf{R}_i}e^{-(1/2)\mathbf{k}\cdot\langle\mathbf{u}(i)\mathbf{u}(i)\rangle\cdot\mathbf{k}}$$
(24)

and at this point the average can be reinterpreted under classical conditions. Note that the displacement-displacement autocorrelation function $\langle\mathbf{u}(i)\mathbf{u}(i)\rangle$ is a second rank tensor, but for a crystal of cubic symmetry, it is simply proportional to $\delta_{\mu\nu}$. The correlation functions between displacements at different sites will generally not be proportional to $\delta_{\mu\nu}$, except in the approximation that all three branches of the phonon dispersion relationship are degenerate. These displacement-displacement correlation functions are all easily computed in the Debye approximation, and, as expected are seen to be functions only of the difference between the lattice sites. Now the Fourier transform can be inverted to obtain

$$\rho^{(1)}(\mathbf{r}) = (2\pi)^{-(3/2)}|\alpha|^{(1/2)}\sum_{\mathbf{R}_i} e^{-(1/2)(\mathbf{r}-\mathbf{R}_i)\cdot\overleftrightarrow{\alpha}\cdot(\mathbf{r}-\mathbf{R}_i)},$$
(25)

where $\sum_\nu\alpha_{\mu\nu}\langle\mathbf{u}(i)_\nu\mathbf{u}(i)_\lambda\rangle = \delta_{\mu\lambda}$ is the matrix inverse of the displacement-displacement correlation tensor. It is worth noting that not only is the one-point density of the *harmonic* solid rigorously a sum of Gaussians, but in particular the one-point density of the hard-sphere solid, the most *anharmonic* solid imaginable, is also representative of a sum of Gaussians, as gauged in simulational studies of the moments of displacement [12].

Paralleling the above analysis, the Fourier transform of the two-point density

$$\rho^{(2)}(\mathbf{k}_1,\mathbf{k}_2) = \sum_{\mathbf{R}_i}\sum_{\mathbf{R}_j\neq\mathbf{R}_i} e^{i\mathbf{k}_1\cdot\mathbf{R}_i}e^{i\mathbf{k}_2\cdot\mathbf{R}_j}\langle e^{i\mathbf{k}_1\cdot\mathbf{u}(i)}e^{i\mathbf{k}_2\cdot\mathbf{u}(j)}\rangle$$
(26)

can be written

$$\rho^{(2)}(\mathbf{k}_1,\mathbf{k}_2) = \sum_{\mathbf{R}_i}\sum_{\mathbf{R}_j\neq\mathbf{R}_i} e^{i\mathbf{k}_1\cdot\mathbf{R}_i}e^{i\mathbf{k}_2\cdot\mathbf{R}_j}\exp\{-\tfrac{1}{2}[\mathbf{k}_1\cdot\langle\mathbf{u}(i)\mathbf{u}(i)\rangle\cdot\mathbf{k}_1 + 2\mathbf{k}_1\cdot\langle\mathbf{u}(i)\mathbf{u}(j)\rangle\cdot\mathbf{k}_2 + \mathbf{k}_2\cdot\langle\mathbf{u}(j)\mathbf{u}(j)\rangle\cdot\mathbf{k}_2]\}.$$
(27)

This Fourier transform can also be inverted analytically, the result involving the inverse of a 6×6 matrix. However, by writing the term in the final exponential as a 6×6 matrix but partitioned into 3×3 blocks, i.e.,

$$[\mathbf{k}_1\cdot\langle\mathbf{u}(i)\mathbf{u}(i)\rangle\cdot\mathbf{k}_1 + 2\mathbf{k}_1\cdot\langle\mathbf{u}(i)\mathbf{u}(j)\rangle\cdot\mathbf{k}_2 + \mathbf{k}_2\cdot\langle\mathbf{u}(j)\mathbf{u}(j)\rangle\cdot\mathbf{k}_2] = (\mathbf{k}_1\mathbf{k}_2)\cdot\begin{pmatrix}\langle\mathbf{u}(i)\mathbf{u}(i)\rangle & \langle\mathbf{u}(i)\mathbf{u}(j)\rangle \\ \langle\mathbf{u}(i)\mathbf{u}(j)\rangle & \langle\mathbf{u}(j)\mathbf{u}(j)\rangle\end{pmatrix}\cdot\begin{pmatrix}\mathbf{k}_1 \\ \mathbf{k}_2\end{pmatrix},$$
(28)

the final result for two-point density will also involve only 3×3 matrices. The form for the two-point density is therefore also a Gaussian to be associated with every pair of lattice sites, namely,

$$\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = \frac{|\alpha|}{(2\pi)^3}\sum_{\mathbf{R}_i}\sum_{\mathbf{R}_j\neq\mathbf{R}_i}|n|^{-1/2}\exp\left[-\frac{1}{2}(\mathbf{r}_1-\mathbf{R}_i\mathbf{r}_2-\mathbf{R}_j)\cdot\begin{pmatrix}c & d \\ d & c\end{pmatrix}\cdot\begin{pmatrix}\mathbf{r}_1-\mathbf{R}_i \\ \mathbf{r}_2-\mathbf{R}_j\end{pmatrix}\right],$$
(29)

where

$$n = 1 - \langle \mathbf{u}(i)\mathbf{u}(i) \rangle^{-1} \langle \mathbf{u}(i)\mathbf{u}(j) \rangle \langle \mathbf{u}(i)\mathbf{u}(i) \rangle^{-1} \langle \mathbf{u}(i)\mathbf{u}(j) \rangle,$$
(30)

$$c = n^{-1} \langle \mathbf{u}(i)\mathbf{u}(i) \rangle^{-1},$$
(31)

and

$$d = n^{-1} \langle \mathbf{u}(i)\mathbf{u}(i) \rangle^{-1} \langle \mathbf{u}(i)\mathbf{u}(j) \rangle \langle \mathbf{u}(i)\mathbf{u}(i) \rangle^{-1}$$
(32)

are functions only of the difference between lattice sites. (In the more general case where the equilibrium sites $\mathbf{R}_i$ do not form a Bravais lattice, the one- and two-point densities can also be expressed as Gaussians, but the symmetry properties of the lattice cannot be exploited further in simplifying the expressions.)

Continuing within this approximation, the total correlation function evaluated in the neighborhoods of two distinct lattice sites then follows from the fundamental definition, i.e.,

$$h(\mathbf{R}_i + \mathbf{r}_1, \mathbf{R}_j + \mathbf{r}_2) = \frac{\rho^{(2)}(\mathbf{R}_i + \mathbf{r}_1, \mathbf{R}_j + \mathbf{r}_2)}{\rho^{(1)}(\mathbf{R}_i + \mathbf{r}_1)\rho^{(1)}(\mathbf{R}_j + \mathbf{r}_2)} - 1,$$
(33)

and can be Taylor expanded about those sites,

$$h(\mathbf{R}_i + \mathbf{r}_1, \mathbf{R}_j + \mathbf{r}_2) = h^0 + \mathbf{r}_1 \cdot h^{11} \cdot \mathbf{r}_1 + \mathbf{r}_1 \cdot h^{12} \cdot \mathbf{r}_2$$
$$+ \mathbf{r}_2 \cdot h^{22} \cdot \mathbf{r}_2 + \cdots .$$
(34)

The first derivative terms vanish; the coefficients are functions only of the difference between lattice sites because the displacement-displacement correlation functions are also. Assuming nonoverlapping Gaussians, and if $\langle \mathbf{u}(i)\mathbf{u}(i) \rangle$ is assumed to be diagonal, then the remaining coefficients have convenient Taylor expansions in terms of $\mathcal{B}_{\mu\nu} = \Sigma_\lambda \langle \mathbf{u}(i)_\mu \mathbf{u}(j)_\lambda \rangle \langle \mathbf{u}(i)_\lambda \mathbf{u}(j)_\nu \rangle$, namely,

$$h^0 = \frac{\alpha^2}{2} \mathrm{Tr}\mathcal{B} + \frac{\alpha^4}{8}(\mathrm{Tr}\mathcal{B})^2 + \frac{\alpha^6}{48}(\mathrm{Tr}\mathcal{B})^3 + \cdots ,$$
(35)

$$h^{11} = h^{22} = -\frac{\alpha^3}{2}\mathcal{B} + \cdots ,$$
(36)

$$h^{12} = \alpha^2 \langle \mathbf{u}(i)\mathbf{u}(j) \rangle + \cdots ,$$
(37)

$$\vdots$$

These expressions are Taylor expanded in this particular form because we typically expect $\|\langle \mathbf{u}(i)\mathbf{u}(j) \rangle\| \ll \|\langle \mathbf{u}(i)\mathbf{u}(i) \rangle\|$ for $i \neq j$ where $\|\cdot\|$ is any well-behaved linear norm for rank-2 tensors, for example, the trace of the tensor. In fact, in the Debye approximation $\|\langle \mathbf{u}(i)\mathbf{u}(j) \rangle\|$ decays with separation as $|\mathbf{R}_i - \mathbf{R}_j|^{-1}$. Utilizing the same approximation with all three branches of the phonon dispersion relationship degenerate, it is necessarily positive definite. Thus we can see that if only one particle is displaced from its site, $h(\mathbf{R}_i + \mathbf{u}(i), \mathbf{R}_j + \mathbf{u}(j))$ decreases with displacement. But if both particles are simultaneously displaced in directions with $\mathbf{u}(i) \cdot \mathbf{u}(j) > 0$, h increases with displacement. It follows that h is locally a saddle about pairs of distinct sites in six-dimensional space.

This analysis ceases to apply when both arguments are evaluated in the vicinity of the same site. Because $\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ is proportional to the joint probability density of finding different particles at $\mathbf{r}_1$ and $\mathbf{r}_2$, no Gaussian can be associated with pairs of sites $\mathbf{R}_i = \mathbf{R}_j$. The only contribution to $\rho^{(2)}(\mathbf{R}_i + \mathbf{r}_1, \mathbf{R}_i + \mathbf{r}_2)$ is from the tails of the surrounding Gaussians. Accordingly h will be small (but nonzero) in this case, and will certainly have an analytic expansion about the origin. However, the familiar low-density approximation $h(\mathbf{r}_1 - \mathbf{r}_2) \approx e^{-\beta\phi^{(2)}(\mathbf{r}_1 - \mathbf{r}_2)} - 1$ generally requires h to have an essential singularity about the line $\mathbf{r}_1 = \mathbf{r}_2$ because the pair potential is normally infinite there. (Note that h is continuous and infinitely differentiable through this singularity; however, all derivatives of h vanish along this line and h cannot be reconstructed at other points in space from its Taylor expansion about the origin.) The reason that the harmonic approximation predicts analytic behavior at small separations is that this approximation does not account for the ''hard-core'' repulsions of typical pair potentials, which for typical systems cannot be reconstructed from only the second derivative information contained in Eq. (20).

It should be noted that in the displacement-displacement correlation function calculated in the Debye approximation, the value of

$$\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - \rho^{(1)}(\mathbf{r}_1)\rho^{(1)}(\mathbf{r}_2) = \rho^{(1)}(\mathbf{r}_1)\rho^{(1)}(\mathbf{r}_2)h(\mathbf{r}_1, \mathbf{r}_2)$$
(38)

evaluated at pairs of lattice points $(\mathbf{R}_i, \mathbf{R}_j)$ decays as $|\mathbf{R}_i - \mathbf{R}_j|^{-2}$ for large separation. However, because the coefficient h^{12} decays as $|\mathbf{R}_i - \mathbf{R}_j|^{-1}$, we have $|h^{12}| \gg |h^0|$ for large separation, and the maximum value of $\rho^{(1)}(\mathbf{r}_1)\rho^{(1)}(\mathbf{r}_2)h(\mathbf{r}_1, \mathbf{r}_2)$ occurs slightly *away* from pairs of lattice sites. Furthermore, this maximum value decays as $|\mathbf{R}_i - \mathbf{R}_j|^{-1}$, in accord with the expected asymptotic behavior [13]. This observation further motivates our concentration on the Ornstein-Zernike equation as written in terms of the two-point density

$$\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - \rho^{(1)}(\mathbf{r}_1)\rho^{(1)}(\mathbf{r}_2) - \rho^{(1)}(\mathbf{r}_1)\rho^{(1)}(\mathbf{r}_2)c^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$$

$$= \int d^3\mathbf{r}_3 [\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_3) - \rho^{(1)}(\mathbf{r}_1)\rho^{(1)}(\mathbf{r}_3)]$$

$$\times [\rho^{(1)}(\mathbf{r}_3)\rho^{(1)}(\mathbf{r}_2)c^{(2)}(\mathbf{r}_3, \mathbf{r}_2)],$$
(39)

rather than in the usual form in terms of h.

V. THE ORNSTEIN-ZERNIKE EQUATION FOR A CRYSTAL

Our intent in this section is to examine approximations to the crystalline two-point functions which, via physically motivated parametrizations, will lead to a sitewise equivalent of the Ornstein-Zernike equation. The harmonic solid has a well-known statistical property: because its Hamiltonian is a quadratic form, its partition function is the integral of a Gaussian and can be written down analytically. If the harmonic solid is now placed in a weak external potential, we can take advantage of the fact that the particles are already well localized around lattice sites to Taylor expand the external potential around the same sites. If we retain terms as

high as quadratic, we can still obtain an analytic form for the partition function. Including the external potential, we can write the Hamiltonian

$$\hat{\mathcal{H}} = \hat{T} + \tfrac{1}{2} \sum_{\mathbf{R}_i, \mathbf{R}_j} \mathbf{u}(i) \cdot \overset{\leftrightarrow}{\mathbf{D}}'(i,j) \cdot \mathbf{u}(j) + \sum_{\mathbf{R}_i} \phi^{(1)}(\mathbf{R}_i)$$

$$+ \sum_{\mathbf{R}_i} \boldsymbol{\nabla} \phi^{(1)}(\mathbf{R}_i) \cdot \mathbf{u}(i) + O(\mathbf{u}(i)^3) + O(\mathbf{u}(i)^4),$$

(40)

where $\overset{\leftrightarrow}{\mathbf{D}}'(i,j) = \overset{\leftrightarrow}{\mathbf{D}}(i,j) + (1/2)[\partial^2 \phi^{(1)}(\mathbf{R}_i)/\partial x_\mu \partial x_\nu]$ subsumes the quadratic term arising from external potential. The expansion in powers of displacement must be terminated at an even order in order to be bounded below. The canonical partition function is then

$$\mathcal{Z} = \lambda^{-3N} h^{-3N} \int d^{3N-6} \{\mathbf{u}\} e^{-\beta \hat{\mathcal{H}}}$$

$$= (2\pi)^{(3/2)N} \lambda^{-3N} |\beta \overset{\leftrightarrow}{\mathbf{D}}'|^{-(1/2)} e^{-\beta \phi^{(1)}(\mathbf{R}_i)}$$

$$\times \exp\left(\frac{\beta}{2}, \sum_{\mathbf{R}_i, \mathbf{R}_j} \boldsymbol{\nabla} \phi^{(1)}(\mathbf{R}_i) \cdot \overset{\leftrightarrow}{\mathbf{C}} C(i,j) \cdot \boldsymbol{\nabla} \phi^{(1)}(\mathbf{R}_j) \right)$$

(41)

where $\overset{\leftrightarrow}{\mathbf{C}}$ is the matrix inverse to $\overset{\leftrightarrow}{\mathbf{D}}'$, defined implicitly by

$$\sum_j \overset{\leftrightarrow}{\mathbf{C}}(i,j)_{\mu\nu} \cdot \overset{\leftrightarrow}{\mathbf{D}}(j,k)_{\nu\lambda} = \delta_{ik} \delta_{\mu\lambda}.$$

(42)

The integrations are over all displacement degrees of freedom except the three corresponding to an overall translation of the crystal and the three corresponding to an overall rotation. The set of displacements spanning the six degrees of freedom not integrated out are the null space of the dynamical matrix because there is no restoring force opposing these collective motions. Hence the determinant of the dynamical matrix in the result must be interpreted as the product of the eigenvalues whose eigenvectors span the $(3N-6)$-dimensional space that is the domain of integration. The remaining six eigenvalues are zero. No factor of $1/N!$ appears as is usual in a system of identical particles because states with particles interchanged are not overcounted in the partition function. Because the Hamiltonian is written in terms of displacements of particles tied to particular sites, the state with two particles exchanged [for instance, $\mathbf{u}(i) = \mathbf{R}_j - \mathbf{R}_i$, $\mathbf{u}(j) = \mathbf{R}_i - \mathbf{R}_j$] has much higher energy than the identical state with particles in their ''proper'' location and thus contributes negligibly to the partition function. Neglecting irrelevant constants, the Helmholtz free energy is then

$$F = \frac{1}{2\beta} \ln |\beta \overset{\leftrightarrow}{\mathbf{D}}' \lambda^2| + \sum_{\mathbf{R}_i} \phi(\mathbf{R}_i)$$

$$+ \frac{1}{2} \sum_{\mathbf{R}_i, \mathbf{R}_j} \boldsymbol{\nabla} \phi^{(1)}(\mathbf{R}_i) \cdot \overset{\leftrightarrow}{\mathbf{C}}(i,j) \cdot \boldsymbol{\nabla} \phi^{(1)}(\mathbf{R}_j) + \cdots.$$

(43)

The Helmholtz free energy, which in general is a *functional* of the external potential, is here a *function* of the Taylor series coefficients of the external potential (effectively, the external potential has been parametrized by its Taylor series coefficients). Since we are performing a separate Taylor expansion of the external potential about each site, a set of parameters is thereby uniquely associated with each site.

In order to develop a method of parametrizing distribution functions more systematically, we now explore a somewhat more general system. Consider a Hamiltonian $\hat{\mathcal{H}}_0$ for a system of N^* particles in a volume V^*, which is symmetry broken so that the relevant dynamical variables are the displacements $\mathbf{u}(i)$; otherwise it is arbitrary. We focus on a subsystem of volume $V \ll V^*$ (but still macroscopic) embedded in the larger system. The volume V^* will be subdivided into N^* cells, identified as the Wigner-Seitz cells of equilibrium positions of the N^* particles. To the basic Hamiltonian we add an external potential, regarded as a perturbation term, but defined only within the subvolume V; thus

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0[\mathbf{u}(i), \mathbf{p}(i)] + \sum_{\substack{\text{cells} \\ i}} \sum_{\substack{\text{particles} \\ j}} \Theta_i(j) \phi^{(1)}$$

$$\times (\mathbf{R}_i + (\mathbf{R}_j - \mathbf{R}_i) + \mathbf{u}(j)),$$

(44)

where $\Theta_i(\mathbf{r})$ is unity if $\mathbf{r}$ is in the Wigner-Seitz cell of site $\mathbf{R}_i$, and zero otherwise, and abbreviated here by $\Theta_i(j) = \Theta_i(\mathbf{R}_j + \mathbf{u}(j))$. The sums over cells are taken to be only over those cells comprising the volume of the subsystem. We have written the external potential in this form in order to emphasize that we wish to Taylor expand the contribution of particle i to the potential energy about the site to which it is *nearest*, and not the site of its equilibrium position.

Now, any physical quantity which is local to a region within V and determined from a thermal average over a grand canonical ensemble of configurations of V can just as well be calculated as a thermal average over a canonical ensemble of configurations of V^*. Since partial derivatives of thermodynamic potentials ''pull down'' quantities from the Boltzmann factor in the partition function and compute their thermal averages, it follows that there is a correspondence between partial derivatives of the grand potential Ω of the subsystem in V and the partial derivatives of the Helmholtz free energy of the system in V^*, provided that the variable with respect to which we differentiate is itself local in V. If we therefore Taylor expand the external potential in Eq. (45) about the equilibrium sites $\mathbf{R}_i$, then partial derivatives of the grand potential with respect to the Taylor coefficients of the external potential result in functionals of density which have exact representations as integrals, for example,

$$\frac{\partial \Omega}{\partial \phi_r^{(1)}(\mathbf{R}_i)} = \sum_{\substack{\text{particles} \\ j}} \langle \Theta_i(j) \rangle = \int d^3\mathbf{r} \, \Theta_i(\mathbf{r}) \rho^{(1)}(\mathbf{r}),$$

(45)

$$\frac{\partial \Omega}{\partial \phi^{(1)}(\mathbf{R}_i)_\mu} = \sum_{\substack{\text{particles} \\ j}} \langle \Theta_i(j)(\mathbf{R}_j - \mathbf{R}_i + \mathbf{u}(j)_\mu) \rangle$$

$$= \int d^3\mathbf{r} \, \Theta_i(\mathbf{r})(\mathbf{r} - \mathbf{R}_i)_\mu \rho^{(1)}(\mathbf{r}).$$

$$\vdots$$

This suggests a clear correspondence [5] between parameters of external potential and parameters of a density operator, as follows:

$$\phi^{(1)}(\mathbf{R}_i) \leftrightarrow \hat{\rho}(\mathbf{R}_i) = \sum_{\substack{\text{particles} \\ j}} \Theta_i(j),$$

$$\phi^{(1)}(\mathbf{R}_i)_\mu \leftrightarrow \hat{\rho}(\mathbf{R}_i)_\mu = \sum_{\substack{\text{particles} \\ j}} \Theta_i(j) \mathbf{r}(ij)_\mu, \qquad (46)$$

$$\phi^{(1)}(\mathbf{R}_i)_{\mu \cdots \nu} \leftrightarrow \hat{\rho}(\mathbf{R}_i)_{\mu \cdots \nu} = \sum_{\substack{\text{particles} \\ j}} \Theta_i(j) \mathbf{r}(ij)_\mu \cdots \mathbf{r}(ij)_\nu,$$

where $\mathbf{r}(ij) = \mathbf{R}_j - \mathbf{R}_i + \mathbf{u}(j)$. The set of Taylor coefficients of the external potential about each site is now taken as sufficient to describe any reasonably smooth external potential; it is conjugate to the moments of one-particle density about each site (with integration restricted to the Wigner-Seitz cell of the site) which is a set of variables sufficient to describe any reasonably smooth one-particle density.

In the limit that we parametrize all possible variations completely, we can use the chain rule to write expressions involving *functional* derivatives in terms of corresponding expressions involving *partial* derivatives, for example,

$$\frac{\delta \Omega}{\delta \phi^{(1)}(\mathbf{r})} = \sum_a \frac{\partial \Omega}{\partial \phi_a} \frac{\delta \phi_a}{\delta \phi^{(1)}(\mathbf{r})}, \qquad (47)$$

$$\frac{\delta^2 \Omega}{\delta \phi^{(1)}(\mathbf{r}_1) \delta \phi^{(1)}(\mathbf{r}_2)}$$

$$= \sum_a \sum_b \frac{\partial^2 \Omega}{\partial \phi_a \partial \phi_b} \frac{\delta \phi_a}{\delta \phi^{(1)}(\mathbf{r}_1)} \frac{\delta \phi_b}{\delta \phi^{(1)}(\mathbf{r}_2)}$$

$$+ \sum_a \frac{\partial \Omega}{\partial \phi_a} \frac{\delta^2 \phi_a}{\delta \phi^{(1)}(\mathbf{r}_1) \delta \phi^{(1)}(\mathbf{r}_2)}. \qquad (48)$$

[Here we use $a, b, c, \ldots$ to label parameters that are properly described by a site $\mathbf{R}_i$ and a list of (possibly zero) Cartesian indices.] A similar formula holds for variations with respect to $\rho^{(1)}(\mathbf{r})$. The functional derivatives of parameters with respect to $\phi^{(1)}$ can be evaluated by

$$\frac{\delta \phi^{(1)}(\mathbf{R}_i)_{\mu \cdots \nu}}{\delta \phi^{(1)}(\mathbf{r})} = \frac{\partial_\mu \cdots \partial_\nu}{s} \delta(\mathbf{r} - \mathbf{R}_i),$$

$$\frac{\delta^2 \phi^{(1)}(\mathbf{r}_i)_{\mu \cdots \nu}}{\delta \phi^{(1)}(\mathbf{r}) \delta \phi^{(1)}(\mathbf{r}')} = 0, \qquad (49)$$

$$\frac{\delta \rho(\mathbf{R}_i)_{\mu \cdots \nu}}{\delta \rho^{(1)}(\mathbf{r})} = (\mathbf{r} - \mathbf{R}_i)_\mu \cdots (\mathbf{r} - \mathbf{R}_i)_\nu \Theta(\mathbf{r} - \mathbf{R}_i),$$

$$\frac{\delta^2 \rho(\mathbf{r}_i)_{\mu \cdots \nu}}{\delta \rho^{(1)}(\mathbf{r}) \delta \rho^{(1)}(\mathbf{r}')} = 0, \qquad (50)$$

where s is a symmetry factor accounting for the product of the factorials of the number of occurrences of x, y, and z in

the list of Cartesian coordinates. The choice of a parametrization in which these second and higher functional derivatives actually vanish is now important, because in turn it causes the second term on the right-hand side of Eq. (48) to vanish; the second (and higher) functional derivatives of the thermodynamic potentials have expressions in terms of their parameters similar to the expression for the first derivative. This parametrization has an important orthonormality property, namely,

$$\int d^3\mathbf{r}_3 \frac{\delta \rho_b}{\delta \rho^{(1)}(\mathbf{r}_3)} \frac{\delta \phi_c}{\delta \phi^{(1)}(\mathbf{r}_3)} = \delta_{bc}, \qquad (51)$$

which can be proven by noting that Eq. (51) written in terms of the Cartesian components x, y, and z of $\mathbf{r} - \mathbf{R}_i$ is

$$\int dx\, dy\, dz\, \Theta(x,y,z) \delta^{(m_x)}(x) x^{n_x} \delta^{(m_y)}(y) y^{n_y} \delta^{(m_z)}(z) z^{n_z}, \qquad (52)$$

where m_x, m_y, and m_z are the number of occurrences of x, y, and z, respectively, in the subscripts preceding the derivative, n_x, n_y, and n_z are the number of occurrences of x, y, and z, respectively, in the subscripts of the position vectors, and $\delta^{(m)}(x)$ denotes the mth derivative of the δ function. The x integration vanishes if $n_x > m_x$ because it is the evaluation of a power of x at the origin; it vanishes if $m_x > n_x$ because the m_xth derivative of x^{n_x} is zero; if $m_x = n_x$, then the x integration is $m_x!$. The factor Θ is irrelevant because the origin always lies within the Wigner-Seitz cell; the orthogonality is established because the y and z integrations are identical and the normalization is established because $s = m_x! m_y! m_z!$. Since any parameter of density is a functional of one-particle density with an integral expression, for example,

$$\rho_a^{(1)} = \int d^3\mathbf{r}\, \frac{\delta \rho_a^{(1)}}{\delta \rho^{(1)}(\mathbf{r})} \rho^{(1)}(\mathbf{r}), \qquad (53)$$

we can multiply on both sides by $\delta \phi_b / \delta \phi^{(1)}(\mathbf{r}')$, integrate with respect to $\mathbf{r}'$, and sum on b to obtain an expression for density:

$$\rho^{(1)}(\mathbf{r}) = \sum_a \rho_a^{(1)} \frac{\delta \phi_a^{(1)}}{\delta \phi^{(1)}(\mathbf{r})}. \qquad (54)$$

The result is that for the crystalline solid we have parametrized the one-point density in terms of δ functions and their derivatives. This is a sensible approximation because the one-point density of a solid is known to be sharply peaked about equilibrium sites, and thermodynamic quantities calculated as integrals over the one-point density can now be expressed as sums over the parameters of density. Since the parameters of external potential were obtained simply by Taylor expanding it about each lattice site, Taylor's theorem itself now provides the reconstruction of the external potential in terms of its parameters.

More generally, suppose that the density $\rho^{(1)}(\mathbf{r})$ and external potential $\phi^{(1)}(\mathbf{r})$ are parametrized in such a way that

$$\rho^{(1)}(\mathbf{r}) = \sum_a \Theta^a(\mathbf{r} - \mathbf{R}_i(a)) \Delta^a(\mathbf{r} - \mathbf{R}_i(a)) \rho_a, \qquad (55)$$

$$\phi^{(1)}(\mathbf{r}) = \sum_a \Theta^a(\mathbf{r} - \mathbf{R}_i(a)) P^a(\mathbf{r} - \mathbf{R}_i(a)) \phi_a, \quad (56)$$

where $P^a(\mathbf{r})$ is a polynomial in the vector components of $\mathbf{r}$, $\Theta^a(\mathbf{r})$ is one or zero according to whether $\mathbf{r}$ is or is not in some bounded region associated with the parameter a, and $\mathbf{R}_i(a)$ is an equilibrium site in or near that region. Furthermore $\Delta^a(\mathbf{r}) = P^a(\partial/\partial\mathbf{r})\delta(\mathbf{r})$. In Eq. (56) the sum runs over a set of polynomials P^a whose corresponding parameters are orthonormal in the sense of Eq. (51). Substituting in Eq. (48) into the inverse relation of the functional derivative hierarchy Eq. (12), we can write

$$\delta(\mathbf{r}_1 - \mathbf{r}_2) = \sum_a \sum_b \sum_c \sum_d \int d^3\mathbf{r}_3 \frac{\partial^2 \mathcal{F}}{\partial\rho_a\partial\rho_b} \frac{\partial^2\Omega}{\partial\phi_c\partial\phi_d}$$

$$\times \frac{\delta\rho_a}{\delta\rho^{(1)}(\mathbf{r}_1)} \frac{\delta\rho_b}{\delta\rho^{(1)}(\mathbf{r}_3)} \frac{\delta\phi_c}{\delta\phi^{(1)}(\mathbf{r}_3)} \frac{\delta\phi_d}{\delta\phi^{(1)}(\mathbf{r}_2)}. \quad (57)$$

Using the orthonormality property, Eq. (51), we can multiply Eq. (57) by $\delta\phi_{a'}/\delta\phi^{(1)}(\mathbf{r}_1)$ and $\delta\rho_{d'}/\delta\rho^{(1)}(\mathbf{r}_2)$ and integrate over $\mathbf{r}_1$ and $\mathbf{r}_2$ to obtain

$$\delta_{ad} = \sum_c \frac{\partial^2 \mathcal{F}}{\partial\rho_a\partial\rho_c} \frac{\partial^2\Omega}{\partial\phi_c\partial\phi_d} \quad (58)$$

after dropping primes on the subscripts. Consequently, the parameters ϕ_a and ρ_a of the thermodynamically conjugate fields $\phi^{(1)}(\mathbf{r})$ and $\rho^{(1)}(\mathbf{r})$ are themselves thermodynamically conjugate variables. We have therefore established that Eq. (58) is analogous to the inversion equation in the functional derivative hierarchy Eq. (12). Parametrizations of this form greatly simplify the analysis of the Ornstein-Zernike and hypernetted-chain equations for the crystalline solid. Previous analyses in terms of Fourier components and expansion in powers of density [7] have indicated that solutions of these equations corresponding to solids exist, but otherwise have not illuminated the asymptotic properties of the correlation functions, or their special relation to the harmonic model.

VI. THE DIRECT CORRELATION FUNCTION FOR A CRYSTAL

In this section we further develop the analogy between the hierarchy inversion relationships Eq. (58) and Eq. (12). The Ornstein-Zernike equation is equivalent to Eq. (12). Here we introduce a parametrized direct correlation function which allows us to rewrite Eq. (58) in a form more nearly resembling the Ornstein-Zernike equation. We start from the hierarchy inversion relationship Eq. (58) rewritten to emphasize that each parameter is associated with a unique lattice site, namely,

$$\sum_{\mathbf{R}_k} \frac{\partial^2 \mathcal{F}}{\partial\phi(\mathbf{R}_i)_a\partial\rho(\mathbf{R}_k)_c} \frac{\partial^2 F}{\partial\phi(\mathbf{R}_k)_c\partial\phi(\mathbf{R}_j)_b} = \delta_{\mathbf{R}_i,\mathbf{R}_j}\delta_{ab}. \quad (59)$$

We again separate the intrinsic Helmholtz free energy into ideal and excess parts, $\mathcal{F} = \mathcal{F}_{id} + \mathcal{F}_{ex}$, where the ideal part is

the Helmholtz free energy of an ensemble of noninteracting particles with the same one-point density. Next, we define the analog of the direct correlation function by

$$-\frac{\beta\partial^2 \mathcal{F}}{\partial\rho(\mathbf{R}_i)_a\partial\rho(\mathbf{R}_k)_c} = c^{(2)}(\mathbf{R}_i, \mathbf{R}_k)_{ac} + f(\mathbf{R}_i)_{ac}\delta_{\mathbf{R}_i,\mathbf{R}_k}, \quad (60)$$

where

$$f(\mathbf{R}_i)_{ac} = -\frac{\beta\partial^2 \mathcal{F}_{id}}{\partial\rho(\mathbf{R}_i)_a\partial\rho(\mathbf{R}_i)_c} \quad (61)$$

depends only on the density about one site since interparticle interactions are irrelevant in the ideal gas term. From Eq. (11), the equivalent noninteracting system may be interpreted as a system of noninteracting oscillators with potentials $\beta^{-1}c^{(1)}(\mathbf{r})$. Because they are noninteracting, the canonical partition function for the ensemble is simply the product of the canonical partition functions of the individual oscillators. Hence the (nonintrinsic) Helmholtz free energy of the equivalent ideal gas is

$$-\beta F_{id} = \ln\left(\lambda^{-3N}\prod_{\mathbf{R}_i}\int d^3\mathbf{u}(i)e^{-c^{(1)}(\mathbf{R}_i+\mathbf{u}(i))}\right), \quad (62)$$

where $(1/\beta)c^{(1)}(\mathbf{R}_i+\mathbf{u}(i))$ is the effective external potential that causes the ideal gas to assume the one-point density of the solid. We assume that the $c^{(1)}$ can be parametrized in the same manner as the one-particle density by

$$c^{(1)}(\mathbf{R}_i+\mathbf{u}(i)) = \sum_a c(i)_a \hat{\rho}(i;\mathbf{u}(i))_a. \quad (63)$$

Then $\rho(\mathbf{R}_i)_a = -\beta[\partial/\partial c(i)_a]F_{id}$, and since the intrinsic Helmholtz free energy is the Legendre transformation,

$$\beta\mathcal{F}_{id} = \int d^3\mathbf{r}\, \rho(\mathbf{r})\{\ln[\lambda^3\rho(\mathbf{r})] - 1\}$$

$$= \beta F_{id} + \sum_{\mathbf{R}_i,a} \rho(\mathbf{R}_i)_a c(i)_a, \quad (64)$$

we have

$$\sum_c \frac{\partial^2\beta\mathcal{F}_{id}}{\partial\rho(\mathbf{R}_i)_a\partial(\mathbf{R}_i)_c}[\langle\hat{\rho}(\mathbf{R}_i)_c\hat{\rho}(\mathbf{R}_i)_b\rangle - \langle\hat{\rho}(\mathbf{R}_i)_c\rangle\langle\hat{\rho}(\mathbf{R}_i)_b\rangle]$$

$$= \delta_{ab}. \quad (65)$$

If the density profiles about neighboring sites can be regarded as nonoverlapping, the sitewise analog of the two-point density is simply

$$\rho^{(2)}(\mathbf{R}_i, \mathbf{R}_j)_{ab} = \langle\hat{\rho}(\mathbf{R}_i)_a\hat{\rho}(\mathbf{R}_j)_b\rangle(1 - \delta_{\mathbf{R}_i\mathbf{R}_j}). \quad (66)$$

The usefulness of this definition depends crucially on the nonoverlapping approximation, for it ensures that particles associated with different lattice sites are, in fact, distinct particles. Then

$$-\frac{1}{\beta^2}\frac{\partial^2\beta F}{\partial\phi(\mathbf{R}_i)_a\partial\phi(\mathbf{R}_j)_b} = \rho^{(2)}(\mathbf{R}_i, \mathbf{R}_j)_{ab} - \rho(\mathbf{R}_i)_a\rho(\mathbf{R}_j)_b$$

$$+ \delta_{\mathbf{R}_i\mathbf{R}_j}\rho(\mathbf{R}_i)_{a\otimes b}, \quad (67)$$

where

$$\rho(\mathbf{R}_i)_{a\otimes b} = \langle\hat{\rho}(\mathbf{R}_i)_a\hat{\rho}(\mathbf{R}_i)_b\rangle \qquad (68)$$

is the parameter of density formed by combining two parameters of density multiplicatively. Further,

$$\sum_{\mathbf{R}_{k,c}} c^{(2)}(\mathbf{R}_i,\mathbf{R}_k)_{ac}[\rho^{(2)}(\mathbf{R}_k,\mathbf{R}_j)_{cb} - \rho(\mathbf{R}_k)_c\rho(\mathbf{R}_j)_b]$$

$$+ \sum_c f(\mathbf{R}_i)_{ac}[\rho^{(2)}(\mathbf{R}_i,\mathbf{R}_j)_{cb} - \rho(\mathbf{R}_i)_c\rho(\mathbf{R}_j)_b]$$

$$+ \sum_c c^{(2)}(\mathbf{R}_i,\mathbf{R}_j)_{ac}\rho(\mathbf{R}_i)_{c\otimes b}$$

$$+ \delta_{\mathbf{R}_i\mathbf{R}_j}\sum_c f(\mathbf{R}_i)_{ac}\rho(\mathbf{R}_j)_{c\otimes b}$$

$$= \delta_{\mathbf{R}_i\mathbf{R}_j}\delta_{ab}. \qquad (69)$$

Because of Eq. (65), the δ function terms cancel, so that we finally arrive at

$$\sum_{\mathbf{R}_{k,c}} c^{(2)}(\mathbf{R}_i,\mathbf{R}_k)_{ac}[\rho^{(2)}(\mathbf{R}_k,\mathbf{R}_j)_{cb} - \rho(\mathbf{R}_k)_c\rho(\mathbf{R}_j)_b]$$

$$+ \sum_c f(\mathbf{R}_i)_{ac}[\rho(\mathbf{R}_i,\mathbf{R}_j)_{cb} - \rho(\mathbf{R}_i)_c\rho(\mathbf{R}_j)_b]$$

$$+ \sum_c c^{(2)}(\mathbf{R}_i,\mathbf{R}_j)_{ac}\rho(\mathbf{R}_j)_{c\otimes b} = 0. \qquad (70)$$

This result is the sought-for sitewise analog of the Ornstein-Zernike equation, and is one of our primary results for the crystal.

VII. THE PERCUS IDENTITY FOR MOMENTS

In this section we will develop an identity analogous to the so-called ''Percus trick'' [14], but one that can be used for moments of one- and two-point density. In other words, if $\hat{\rho}(\mathbf{R}_i)_a$ and $\hat{\rho}(\mathbf{R}_j)_b$ $(i\neq j)$ are parameters of the density operator (say vector components of particle displacements) from different sites in an N-particle system, we wish to write

$$\langle\hat{\rho}(\mathbf{R}_i)_a\hat{\rho}(\mathbf{R}_j)_b\rangle = \langle\hat{\rho}(\mathbf{R}_i)_a\rangle^*\langle\hat{\rho}(\mathbf{R}_j)_b\rangle, \qquad (71)$$

where the star indicates that the average is to be carried out in an $(N-1)$-particle ensemble obtained by removing a particular particle from our original N-particle ensemble, and possibly with different interactions. This cannot be achieved in general. We attempt to parallel the derivation of the Percus identity and for convenience, we define a trace over distinguishable particles by

$$\mathrm{Tr} \equiv h^{-3N}\int d^3\mathbf{u}(1)\cdots d^3\mathbf{u}(N)\int d^3\mathbf{p}_1\cdots d^3\mathbf{p}_N. \qquad (72)$$

Now we proceed as before, but with the δ functions of the continuous form of the density operator replaced by density operator parameters:

$$\langle\hat{\rho}(\mathbf{R}_i)_a\hat{\rho}(\mathbf{R}_j)_b\rangle = \frac{\mathrm{Tr}\hat{\rho}(\mathbf{R}_i)_a\hat{\rho}(\mathbf{R}_j)_b e^{-\beta\hat{\mathcal{H}}}}{\mathrm{Tr}e^{-\beta\hat{\mathcal{H}}}}$$

$$= \frac{\mathrm{Tr}\hat{\rho}(\mathbf{R}_i)_a\hat{\rho}(\mathbf{R}_j)_b e^{-\beta\hat{\mathcal{H}}}}{\mathrm{Tr}\hat{\rho}(\mathbf{R}_j)_b e^{-\beta\hat{\mathcal{H}}}}\frac{\mathrm{Tr}\hat{\rho}(\mathbf{R}_j)_b e^{-\beta\hat{\mathcal{H}}}}{\mathrm{Tr}e^{-\beta\hat{\mathcal{H}}}}$$

$$= \frac{\mathrm{Tr}\hat{\rho}(\mathbf{R}_i)_a\hat{\rho}(\mathbf{R}_j)_b e^{-\beta\hat{\mathcal{H}}}}{\mathrm{Tr}\hat{\rho}(\mathbf{R}_j)_b e^{-\beta\hat{\mathcal{H}}}}\langle\hat{\rho}(\mathbf{R}_j)_b\rangle. \qquad (73)$$

We can easily identify the second factor as $\langle\hat{\rho}(\mathbf{R}_j)_b\rangle$. However, when we attempt to identify the first factor, as

$$\langle\hat{\rho}(\mathbf{R}_i)_a\rangle = \frac{\mathrm{Tr}\hat{\rho}(\mathbf{R}_i)_a e^{-\beta\hat{\mathcal{H}}^*}}{\mathrm{Tr}e^{-\beta\hat{\mathcal{H}}^*}} \qquad (74)$$

for some effective Hamiltonian $\hat{\mathcal{H}}^*$ two problems are immediately encountered. The first is minor: the expressions for the density operators, Eq. (46), in terms of the displacements (the actual dynamical variables of the Hamiltonian) are not invertible. However, if the particles in the solid are well localized about their lattice sites, we may assume that the dominant term in each of the sums in Eq. (46) is the $i=j$ term, and continue paralleling the derivation of the Percus identity by writing the effective Hamiltonian as

$$e^{-\beta\hat{\mathcal{H}}^*} \propto \int d^3\mathbf{u}(j)\hat{\rho}(\mathbf{R}_j)_b e^{-\beta\hat{\mathcal{H}}}. \qquad (75)$$

We define the effective Hamiltonian with a proportionality because multiplication by an overall constant is equivalent to adding an overall constant to $\hat{\mathcal{H}}^*$, which is physically irrelevant. However, because the density parameter is a dimensional quantity (typically a power of length), we divide by, for example, an appropriate power of λ in order to ensure that $e^{-\beta\hat{\mathcal{H}}^*}$ is dimensionless.

The second and more serious problem is that since the integration runs through all possible values of $\hat{\rho}(\mathbf{R}_j)_b$, for some configurations of the other particles the integral can be negative. We cannot simply take the absolute value of the integral, because this integral, a function of all other displacements, is itself integrated over, and some configurations are weighted negatively in the outer averaging. Evidently the physical constraint that density be non-negative has a sitewise analog: density must be parametrized in such a way that its parameters are non-negative.

One solution is therefore to divide the *parameter* of the density operator into separate positive and negative parts:

$$\hat{\rho}^+ = \begin{cases} \hat{\rho} & \text{if } \hat{\rho}>0 \\ 0 & \text{if } \hat{\rho}\leq 0 \end{cases}, \quad \hat{\rho}^- = \begin{cases} 0 & \text{if } \hat{\rho}\geq 0 \\ |\hat{\rho}| & \text{if } \hat{\rho}<0 \end{cases}. \qquad (76)$$

Then, identifying the site to be pinned as site $\mathbf{R}_0$, we can easily write $\langle\hat{\rho}(\mathbf{R}_i)_a\hat{\rho}(\mathbf{R}_0)_b\rangle = \langle\hat{\rho}(\mathbf{R}_i)_a\hat{\rho}(\mathbf{R}_0)_b^+\rangle - \langle\hat{\rho}(\mathbf{R}_i)_a\hat{\rho}(\mathbf{R}_0)_b^-\rangle$, and then develop separate effective Hamiltonians for each term. Thus

$$\langle \hat{\rho}(\mathbf{R}_i)_a \hat{\rho}(\mathbf{R}_0)_b^+ \rangle = \langle \hat{\rho}(\mathbf{R}_0)^+ \rangle \langle \hat{\rho}(\mathbf{R}_i)_a \rangle^+, \qquad (77)$$

where

$$\langle \hat{\rho}(\mathbf{R}_i)_a \rangle^+ = \frac{\mathrm{Tr}\hat{\rho}(\mathbf{R}_i)_a e^{-\beta\hat{\mathcal{H}}^+}}{\mathrm{Tr}e^{-\beta\hat{\mathcal{H}}^+}} \qquad (78)$$

and

$$e^{-\beta\hat{\mathcal{H}}^+} \propto \int d^3\mathbf{u}(0)\hat{\rho}(\mathbf{R}_0)_b^+ e^{-\beta\hat{\mathcal{H}}}, \qquad (79)$$

with corresponding averages over the negative part defining a similar effective Hamiltonian $\hat{\mathcal{H}}^-$ for the negative part. Observe that $e^{-\beta\hat{\mathcal{H}}^+}$ and $e^{-\beta\hat{\mathcal{H}}^-}$ are strictly non-negative.

It is important to note that when the Cartesian tensor parameters of the density operator presented in Sec. II C are split into positive and negative parts, the orthonormality relation Eq. (51), and hence the discretized form of the Ornstein-Zernike equation (58), can still be recovered. Furthermore, the external potential is still Taylor expanded about each lattice site, but in a piecewise manner: Taylor series coefficients in each octant are treated as independent variables. Differentiating the grand potential with respect to one of these coefficients produces a correspondence between parameters of external potential and parameters of a density operator analogous to Eq. (46), except that only the split part of a vector appears:

$$\phi^{(1)}(\mathbf{R}_i)_{\mu\cdots\nu} \leftrightarrow \hat{\rho}(\mathbf{R}_i)_{\mu^\pm\cdots\nu^\pm}$$

$$= \sum_{\substack{\mathrm{particles}\\ j}} \Theta_i(j)\mathbf{r}(ij)_{\mu^\pm}\cdots\mathbf{r}(ij)_{\nu^\pm}, \qquad (80)$$

where the choice of plus or minus for each Cartesian index is identical on both sides of the correspondence. The functional derivatives of parameters of external potential and density with respect to the actual external potential and density are similarly analogous to Eqs. (49) and (50), i.e.,

$$\frac{\delta\phi^{(1)}(\mathbf{R}_i)_{\mu^\pm\cdots\nu^\pm}}{\delta\phi^{(1)}(\mathbf{r})} = \frac{\partial_{\mu^\pm}\cdots\partial_{\nu^\pm}}{s}\delta(\mathbf{r}-\mathbf{R}_i),$$

$$\frac{\delta^2\phi^{(1)}(\mathbf{r}_i)_{\mu^\pm\cdots\nu^\pm}}{\delta\phi^{(1)}(\mathbf{r})\delta\phi^{(1)}(\mathbf{r}')} = 0, \qquad (81)$$

and

$$\frac{\delta\rho(\mathbf{R}_i)_{\mu^\pm\cdots\nu^\pm}}{\delta\rho^{(1)}(\mathbf{r})} = (\mathbf{r}-\mathbf{R}_i)_{\mu^\pm}\cdots(\mathbf{r}-\mathbf{R}_i)_{\nu^\pm}\Theta(r-\mathbf{R}_i),$$

$$\frac{\delta^2\rho(\mathbf{r}_i)_{\mu^\pm\cdots\nu^\pm}}{\delta\rho^{(1)}(\mathbf{r})\delta\rho^{(1)}(\mathbf{r}')} = 0, \qquad (82)$$

except that now we must identify ∂_{μ^+} and ∂_{μ^-} with right-hand and left-hand derivative operators [15]. Thus, for example, $\int f(x)\partial_x + \delta(x)dx = -\mathrm{f}'(\epsilon)$, where ϵ is arbitrarily small but positive. The orthonormality relationship analogous to Eq. (51) is proven as before, except that now it is split into six components, and the number of occurrences of

x^+ must separately match the number of occurrences of ∂_x+. Because $x^+x^-=0$, the symmetry factor s is the same as before.

The proposed division into positive and negative parts is not required in the traditional development of the Percus identity because the densities are defined as expectation values of δ functions, and the fact that δ functions (and many approximations to them) are strictly non-negative ensures that the resulting density is always non-negative. When the density is parametrized in terms of *moments* about the sites, the physical requirement that the density be non-negative must be extended here to require that the density be parametrized in terms of non-negative quantities. (In fact, in the continuum case the density can be thought of as parametrized in terms of its value at spatial locations. Since density itself is physically required to be non-negative, it is automatically parametrized in terms of non-negative quantities.) A similar problem can arise in some formulations of density-functional theory which require only reciprocal space information about the density: The absolute positivity of density cannot be ensured if all of the Fourier components of density are regarded as independent variational parameters.

VIII. ANALOG OF THE HYPERNETTED-CHAIN EQUATION

In this section we apply the analog of the Percus identity derived in the preceding section to obtain an algebraic closure relationship analogous to the hypernetted-chain equation. Since any parameter of effective potential introduced in the Percus identity is thermodynamically conjugate to the corresponding parameter of density, we can write that parameter as a functional derivative, provided that the functional derivative is evaluated in the system with one particle integrated out. If we subtract off the corresponding quantity in an unperturbed system, we obtain

$$\widetilde{\phi}(\mathbf{R}_i)_a\big|_{\rho(\mathbf{R}_j)_b} = \frac{\partial\mathcal{F}}{\partial\rho(\mathbf{R}_i)_a}\bigg|_{\rho(\mathbf{R}_j)_b} - \frac{\partial\mathcal{F}}{\partial\rho(\mathbf{R}_i)_a}\bigg|_0, \qquad (83)$$

where the effective potential is the external potential that must be added to the effective Hamiltonian obtained by integrating out $\hat{\rho}(\mathbf{R}_j)_b$ in order to obtain the original Hamiltonian. At this stage, the particle number has changed from N to $N-1$ and therefore when we integrate out the corresponding degrees of freedom it is important that we work with a parametrization of density sufficiently flexible to allow changes in cell occupancy. We will, however, derive a general equation which can then be approximated by restricting the set of parameters considered. Splitting into ideal and excess components of free energy as before, we obtain

$$\widetilde{\phi}(\mathbf{R}_i)_a\big|_{\rho(\mathbf{R}_j)_b} = \frac{\partial\mathcal{F}_{\mathrm{id}}}{\partial\rho(\mathbf{R}_i)_a}\bigg|_{\rho(\mathbf{R}_j)_b} - \frac{\partial\mathcal{F}_{\mathrm{id}}}{\partial\rho(\mathbf{R}_i)_a}\bigg|_0$$

$$+ \sum_{\mathbf{R}_k,c} \frac{\partial^2\mathcal{F}_{\mathrm{ex}}}{\partial\rho(\mathbf{R}_i)_a\partial\rho(\mathbf{R}_k)_c}\bigg|_0$$

$$\times[\rho(\mathbf{R}_k)_c\big|_{\rho(\mathbf{R}_j)_b} - \rho(\mathbf{R}_k)_c\big|_0], \qquad (84)$$

where the $\widetilde{\phi}$ is assumed to include not only the corrections from integrating out one particle, but also the corrections due to the analog of the bridge function [2] [the higher order terms in the expansion of $\partial \mathcal{F}\text{ex}/\partial\rho(\mathbf{R}_i)_a$]: thus

$$\left. \frac{\partial \mathcal{F}_\text{ex}}{\partial\rho(\mathbf{R}_i)_a} \right|_{\rho(\mathbf{R}_j)_b} - \left. \frac{\partial \mathcal{F}_\text{ex}}{\partial\rho(\mathbf{R}_i)_a} \right|_0$$

$$= \sum_{\mathbf{R}_k,c} \left. \frac{\partial^2 \mathcal{F}_\text{ex}}{\partial\rho(\mathbf{R}_i)_a \partial\rho(\mathbf{R}_k)_c} \right|_0$$

$$\times [\rho(\mathbf{R}_k)_c|_{\rho(\mathbf{R}_j)_b} - \rho(\mathbf{R}_k)_c|_0] + b(\mathbf{R}_i,\mathbf{R}_j)_{ab}.$$

$$(85)$$

We will denote the first two terms on the right-hand side of Eq. (84) by $\Delta\mathcal{F}_\text{id}(\mathbf{R}_i;\mathbf{R}_j)_{ab}$. The density difference can be expressed as

$$\rho(\mathbf{R}_k)_c|_{\rho(\mathbf{R}_j)_b} - \rho(\mathbf{R}_k)_c|_0 = \frac{\rho^{(2)}(\mathbf{R}_k,\mathbf{R}_j)_{cb}}{\rho(\mathbf{R}_j)_b} - \rho(\mathbf{R}_k)_c,$$

$$(86)$$

so that

$$\beta\widetilde{\phi}(\mathbf{R}_i)_a|_{\rho(\mathbf{R}_j)_b} = \beta\Delta\mathcal{F}_\text{id}(\mathbf{R}_i;\mathbf{R}_j)_{ab} + \sum_{\mathbf{R}_k,c} c^{(2)}(\mathbf{R}_i,\mathbf{R}_k)_{ac}$$

$$\times \left(\frac{\rho^{(2)}(\mathbf{R}_k,\mathbf{R}_j)_{cb} - \rho(\mathbf{R}_k)_c\rho(\mathbf{R}_j)_b}{\rho(\mathbf{R}_j)_b} \right).$$

$$(87)$$

The second term on the left-hand side can be transformed via the analog of the Ornstein-Zernike equation (70) to yield

$$\beta\Delta\mathcal{F}_\text{id}(\mathbf{R}_i;\mathbf{R}_j)_{ab} - \frac{1}{\rho(\mathbf{R}_j)_b} \sum_c f(\mathbf{R}_i)_{ac}$$

$$\times [\rho(\mathbf{R}_i,\mathbf{R}_j)_{cb} - \rho(\mathbf{R}_i)_c\rho(\mathbf{R}_j)_b]$$

$$- \frac{1}{\rho(\mathbf{R}_j)_b} \sum_c c^{(2)}(\mathbf{R}_i,\mathbf{R}_j)_{ac}\rho(\mathbf{R}_j)_{c\otimes b}$$

$$= \beta\widetilde{\phi}(\mathbf{R}_i)_a|_{\rho(\mathbf{R}_j)_b}.$$

$$(88)$$

This equation, for the lattice case, is the equation analogous to the hypernetted-chain relation [2]

$$\ln g(\mathbf{r}_1,\mathbf{r}_2) = -\beta\phi^{(2)}(\mathbf{r}_1 - \mathbf{r}_2) + h(\mathbf{r}_1,\mathbf{r}_2) - c^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$$

$$(89)$$

familiar for fluids. It is another primary result for the crystal.

IX. RELATION TO HARMONIC MODEL

We will now simplify the sitewise analogs of the Ornstein-Zernike [Eq. (70)] and hypernetted-chain equations [Eq. (88)] presented in the preceding sections as much as possible, and specialize them to the parametrization in terms of positive and negative parts of Cartesian coordinates. We have already seen that in the functional approach to inhomogeneous fluids, the thermodynamic potentials are functionals of $\phi^{(1)}(\mathbf{r})$ and $\rho^{(1)}(\mathbf{r})$; if $\phi^{(1)}$ and $\rho^{(1)}$ are regarded as param-

etrized by their values at all points $\mathbf{r}$, then the thermodynamic potentials depend upon a continuous infinity of parameters. By making strong but entirely physical assumptions about the form of the equilibrium one-particle density, namely, that it is sharply peaked about the sites of a Bravais lattice, we can parametrize the external potential and one-particle density in terms of a number of parameters to be associated with each site. In this view, the thermodynamic potentials then depend upon a discrete infinity of parameters. Since classical density-functional theory has had considerable success with single-parameter Gaussians as a trial density, we likewise simplify the parametrization further by removing from the parametrization of density all moments higher than second, and truncating the Taylor expansion of external potential after the linear term, leaving just four parameters per lattice site.

We now focus on the scalar parameter at each site. The value of the external potential at a lattice site $\phi^{(1)}(\mathbf{R}_i)$ is conjugate to the normalization parameter $\rho^{(1)}(\mathbf{R}_i) = \langle\hat{n}(i)\rangle$ of density. However, in most real solids the density of vacancies and interstitials is very small (even up to melting), for example, experimentally of the order of 10^{-4} in noble gas solids [16], with density-functional calculations yielding similar results [17]. Furthermore, models such as the harmonic crystal that ignore vacancies and interstitials have had considerable success in describing solids. Thus, as a first approximation, we take the normalization of density at each site to be $\hat{n}(i) = 1$ for all $\mathbf{R}_i$. The value of the external potential is thus irrelevant. As can be seen in Eq. (43), the Helmholtz free energy of a single-occupancy harmonic model depends upon the value of the external potential only through an overall constant that is also physically irrelevant. In particular, the one-particle density is not affected by variations in the value of the external potential at the lattice site. This invariance further implies that the Gaussians that describe the two-particle density are also normalized to a joint occupancy of unity [$\langle\hat{n}(i)\hat{n}(j)\rangle = 1$], because

$$-\frac{1}{\beta^2} \frac{\partial^2\beta\Omega}{\partial\phi^{(1)}(\mathbf{R}_i)\partial\phi^{(1)}(\mathbf{R}_j)} = \langle\hat{n}(i)\hat{n}(j)\rangle - \langle\hat{n}(i)\rangle\langle\hat{n}(j)\rangle = 0.$$

$$(90)$$

Furthermore, mixed second derivatives of the grand potential in which one derivative is taken with respect to $\phi^{(1)}(\mathbf{R}_i)$ also vanish in this approximation because

$$-\frac{1}{\beta^2} \frac{\partial^2\beta\Omega}{\partial\phi^{(1)}(\mathbf{R}_i)\partial\phi^{(1)}(\mathbf{R}_j)_\mu}$$

$$= \langle\hat{n}(i)\hat{\rho}(\mathbf{R}_j)_\mu\rangle - \langle\hat{n}(i)\rangle\langle\hat{\rho}(\mathbf{R}_j)_\mu\rangle = 0.$$

$$(91)$$

This relationship implies that even if we relax the single-particle occupancy restriction, the occupancy-occupancy correlation part of the Ornstein-Zernike equation will approximately decouple from the terms involving displacement. The occupancy-occupancy term can then be treated as a lattice gas, for which analogs of the Ornstein-Zernike equation and density-functional theory have already been developed [18,19]. We note that the first direct correlation function $c^{(1)}(\mathbf{r})$ has also been described in crystals with vacancies and interstitials [20]. We now reconsider the Ornstein-Zernike

equation in the form of the hierarchy inverse relationship Eq. (58), except that we now label the parameters separately with the $+$ and $-$ separation introduced above. For notational convenience, introduce an operator $\mathcal{M}$ that turns any component of a second rank tensor (include second partial derivatives) into a 2×2 matrix of split components, such as

$$\overset{\leftrightarrow}{\mathcal{M}}[f_{\mu\nu}] = \begin{pmatrix} f_{\mu^+\nu^+} & f_{\mu^+\nu^-} \\ f_{\mu^-\nu^+} & f_{\mu^-\nu^-} \end{pmatrix}. \qquad (92)$$

We can therefore write the matrix form of the Ornstein-Zernike equation (58) as

$$\begin{pmatrix} \delta_{ij}\delta_{\mu\nu} & 0 \\ 0 & \delta_{ij}\delta_{\mu\nu} \end{pmatrix} = \sum_{\mathbf{R}_k} \sum_{\lambda} \overset{\leftrightarrow}{\mathcal{M}}\left[\frac{\partial^2 \mathcal{F}}{\partial \rho(\mathbf{R}_i)_\mu \partial \rho(\mathbf{R}_j)_\lambda} \right]$$
$$\times \overset{\leftrightarrow}{\mathcal{M}}\left[\frac{\partial^2 \Omega}{\partial \phi^{(1)}(\mathbf{R}_k)_\lambda \partial \phi^{(1)}(\mathbf{R}_j)_\nu} \right]. \qquad (93)$$

Note that for any variable that has been split into positive and negative parts, $x = x^+ - x^-$ and $|x| = x^+ + x^-$. Furthermore, for any two variables x and y that have been separated this way,

$$\frac{1}{2}\begin{pmatrix} |x||y| & -|x|y \\ -x|y| & xy \end{pmatrix} = \overset{\leftrightarrow}{\mathbf{B}}^{-1} \cdot \begin{pmatrix} x^+y^+ & x^+y^- \\ x^-y^+ & x^-y^- \end{pmatrix} \cdot \overset{\leftrightarrow}{\mathbf{B}}, \quad (94)$$

where

$$\overset{\leftrightarrow}{\mathbf{B}} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix} \qquad (95)$$

provides a similarity transformation between the two bases. Note also that the transpose is equivalent to the inverse: $\overset{\leftrightarrow}{\mathbf{B}}^T = \overset{\leftrightarrow}{\mathbf{B}}^{-1}$. Thus an off-diagonal term in

$$\overset{\leftrightarrow}{\mathbf{B}}^{-1}\overset{\leftrightarrow}{\mathcal{M}}\left[\frac{\partial^2 \Omega}{\partial \phi^{(1)}(\mathbf{R}_k)_\lambda \partial \phi^{(1)}(\mathbf{R}_j)_\nu} \right]\overset{\leftrightarrow}{\mathbf{B}} \qquad (96)$$

is given by

$$-\tfrac{1}{2}[\langle|\hat{\rho}(\mathbf{R}_k)_\lambda|\hat{\rho}(\mathbf{R}_j)_\nu\rangle - \langle|\hat{\rho}(\mathbf{R}_k)_\lambda|\rangle\langle\hat{\rho}(\mathbf{R}_j)_\nu\rangle] \qquad (97)$$

and it vanishes in harmonic approximation when we neglect overlap of the density profiles at each site because the two-point density is Gaussian (not because of symmetry considerations). Accordingly, we will neglect the off-diagonal terms of Eq. (96) here. We can then act on Eq. (93) on the left with $\overset{\leftrightarrow}{\mathbf{B}}^{-1}$ and on the right with $\overset{\leftrightarrow}{\mathbf{B}}$ to obtain two separate equations

$$-\delta_{ij}\delta_{\mu\nu} = \sum_{\mathbf{R}_k} \sum_{\lambda} \frac{\beta\partial^2 \mathcal{F}}{\partial \rho(\mathbf{R}_i)_{[\mu]}\partial \rho(\mathbf{R}_k)_{[\lambda]}} [\langle|\hat{\rho}(\mathbf{R}_k)_\lambda||\hat{\rho}(\mathbf{R}_j)_\nu|\rangle$$
$$- \langle|\hat{\rho}(\mathbf{R}_k)_\lambda|\rangle\langle|\hat{\rho}(\mathbf{R}_j)_\nu|\rangle], \qquad (98)$$

$$-\delta_{ij}\delta_{\mu\nu} = \sum_{\mathbf{R}_k} \sum_{\lambda} \frac{\beta\partial^2 \mathcal{F}}{\partial \rho(\mathbf{R}_i)_{(\mu)}\partial \rho(\mathbf{R}_k)_{(\lambda)}} [\langle\hat{\rho}(\mathbf{R}_k)_\lambda\hat{\rho}(\mathbf{R}_j)_\nu\rangle$$
$$- \langle\hat{\rho}(\mathbf{R}_k)_\lambda\rangle\langle\hat{\rho}(\mathbf{R}_j)_\nu\rangle], \qquad (99)$$

where we are using brackets and parentheses to symmetrize and antisymmetrize subscripted expressions, for example, $r_{[\mu]} = r_{\mu^+} + r_{\mu^-}$ and $r_{(\mu)} = r_{\mu^+} - r_{\mu^-}$. We will refer to these rearrangements as cusplike and continuous, respectively. Now, we separate the second derivative of $\mathcal{F}$ into noninteracting and excess parts as in Eq. (60). In order to evaluate the ideal gas free energy, we must make assumptions about the higher moments of the density profile at each site $\sigma(\mathbf{r}-\mathbf{R}_i)$, defined implicitly by

$$\rho(\mathbf{r}) = \sum_{\mathbf{R}_i} \sigma(\mathbf{r}-\mathbf{R}_i). \qquad (100)$$

Next, assume that the density profile is factorable into Cartesian coordinates $\sigma(\mathbf{r}) = \sigma_f(r_x)\sigma_f(r_y)\sigma_f(r_z)$. Since the density profiles about a site are Gaussian for a wide variety of potentials, and, further in crystals of sufficiently high symmetry (including cubic), *one-parameter* Gaussian, this assumption about factorization is not a limitation. The noninteracting free energy associated with that site [in the approximation that overlap integrals of the form $\int d^3\mathbf{r}\,\sigma(\mathbf{r})\sigma(\mathbf{r}-\mathbf{R}_i)$ can be ignored for $\mathbf{R}_i \neq 0$] can be written in the form

$$\beta\mathcal{F}_{\text{id}} = C_1 N - \frac{1}{2}\sum_{\mathbf{R}_i}\left(\ln\frac{\langle|\hat{\rho}(\mathbf{R}_i)_x|\rangle}{\lambda} + \ln\frac{\langle|\hat{\rho}(\mathbf{R}_i)_y|\rangle}{\lambda} \right.$$
$$\left. + \ln\frac{\langle|\hat{\rho}(\mathbf{R}_i)_z|\rangle}{\lambda} \right) \qquad (101)$$

parametrized by the mean absolute displacements in each Cartesian coordinate, where C_1 is a constant that depends upon the form of the density profile, and not on its width. Since the free energy of the noninteracting system depends upon density parameters only through the width $w = \langle|\hat{\rho}(\mathbf{R}_i)_\mu|\rangle$ and not through the particle's mean position $\langle\hat{\rho}(\mathbf{R}_i)_\mu\rangle$ (which is zero, by definition). It follows that the second derivative of the ideal gas free energy appears only in the cusplike equation. Thus the noninteracting contribution simplifies to

$$\frac{\beta\mathcal{F}_{\text{id}}}{N} = C_1 - \frac{3}{2}\ln\frac{w}{\lambda} \qquad (102)$$

and the separate cusplike and continuous Ornstein-Zernike equations become

$$\delta_{ij}\delta_{\mu\nu} = \sum_{\mathbf{R}_k} \sum_{\lambda} [c^{(2)}(\mathbf{R}_i,\mathbf{R}_k)_{[\mu][\lambda]} + \delta_{\mathbf{R}_i,\mathbf{R}_k}f(\mathbf{R}_i)_{[\mu][\lambda]}]$$
$$\times [\langle|\hat{\rho}(\mathbf{R}_k)_\lambda||\hat{\rho}(\mathbf{R}_j)_\nu|\rangle - w^2], \qquad (103)$$

$$\delta_{ij}\delta_{\mu\nu} = \sum_{\mathbf{R}_k} \sum_{\lambda} c^{(2)}(\mathbf{R}_i,\mathbf{R}_k)_{(\mu)(\lambda)}[\langle\hat{\rho}(\mathbf{R}_k)_\lambda\hat{\rho}(\mathbf{R}_j)_\nu\rangle]. \qquad (104)$$

These equations, together with sitewise analog of the hypernetted-chain equation, completely determine the coefficients of left and right derivatives of δ functions in the

two-point density. But because of the similarity transformation, Eq. (94), the left and right derivatives combine in forms that either form the (two-sided) derivative of a δ function in the continuous equation, or extract the change of derivative that occurs at a cusp, in the cusplike equation. When a thermodynamic function is calculated by integrating over the two-point density, the other functions in the integrand almost always have continuous derivatives. Because of this, the coefficients of the two-point density determined by the cusplike equation are rarely of interest. And since the second of these equations is a matrix inverse, it is clear that the continuous quadratic parts of the direct correlation function play a role analogous to the dynamic matrix of the harmonic model.

We can apply the same transformation to the sitewise hypernetted-chain Eq. (88) which we now write in a more symmetrical form,

$$\beta\overleftrightarrow{\mathcal{M}}[\Delta\mathcal{F}_{\mathrm{id}}(\mathbf{R}_i;\mathbf{R}_j)_{\mu\nu}]-\sum_\lambda\,\overleftrightarrow{\mathcal{M}}[f(\mathbf{R}_i)_{\lambda\nu}]\vec{\rho}^{(1)}(\mathbf{R}_j)_\lambda$$

$$\times\overleftrightarrow{\mathcal{M}}[h(\mathbf{R}_i,\mathbf{R}_j)_{\lambda\nu}]-\sum_\lambda\,\overleftrightarrow{C}(i,j)_{\mu\lambda}\vec{\rho}^{(1)}(\mathbf{R}_j)_\lambda\overleftrightarrow{\mathrm{R}}(j)_{\lambda\nu}$$

$$=\beta\overleftrightarrow{\mathcal{M}}[\,\widetilde{\phi}(\mathbf{R}_i)_\mu|_{\rho(\mathbf{R}_j)_\nu}], \tag{105}$$

$$\overleftrightarrow{\rho}\overleftrightarrow{\rho}^{(1)}(\mathbf{R}j)\lambda\overleftrightarrow{\mathrm{R}}(j)\lambda\nu=\beta\overleftrightarrow{\mathcal{M}}[\,\widetilde{\phi}(\mathbf{R}i)\mu|\rho(\mathbf{R}J)\nu], \tag{105}$$

$$\overleftrightarrow{\rho}\overleftrightarrow{\rho}^{(1)}(\mathbf{R}j)\lambda\overleftrightarrow{\mathrm{R}}(j)\lambda\nu=\beta\overleftrightarrow{\mathcal{M}}[\,\widetilde{\phi}(\mathbf{R}i)\mu|\rho(\mathbf{R}J)\nu], \tag{105}$$

where

$$\overleftrightarrow{C}(i,j)_{\mu\lambda}=\overleftrightarrow{\mathcal{M}}[c^{(2)}(\mathbf{R}_i,\mathbf{R}_j)_{\mu\lambda}], \tag{106}$$

$$\overleftrightarrow{\mathrm{R}}(j)_{\lambda\nu}=\overleftrightarrow{\mathcal{M}}\!\left[\frac{\rho(\mathbf{R}_j)_{\lambda\otimes\nu}}{\rho^{(1)}(\mathbf{R}_j)_\lambda\rho^{(1)}(\mathbf{R}_j)_\nu}\right], \tag{107}$$

and

$$h(\mathbf{R}_i,\mathbf{R}_j)_{\lambda\nu}=\frac{\rho^{(2)}(\mathbf{R}_i,\mathbf{R}_j)_{\lambda\nu}-\rho^{(1)}(\mathbf{R}_i)_\lambda\rho^{(1)}(\mathbf{R}_j)_\nu}{\rho^{(1)}(\mathbf{R}_i)_\lambda\rho^{(1)}(\mathbf{R}_j)_\nu}, \tag{108}$$

$$\vec{\rho}^{(1)}(\mathbf{R}_j)_\mu=\begin{pmatrix}\rho(\mathbf{R}_j)_{\mu^+} & 0 \\ 0 & \rho(\mathbf{R}_j)_{\mu^-}\end{pmatrix}. \tag{109}$$

In order to make use of this result, we must estimate the effective potential on the right-hand side, in terms of the effective Hamiltonian that appears in the Percus identity for moments. We carry out this estimate in a mean-field approximation by taking a Hamiltonian composed entirely of pair potentials, as Eq. (1), without the external potential, and estimating the pair potential obtained when $u(0)_z$ (whose equilibrium position $\mathbf{R}_0$ is taken to be the origin) is integrated out, for positive values; thus

$$e^{-\beta\hat{\mathcal{H}}^+}=\int d^3\mathbf{u}(0)u(0)_z \tag{110}$$

$$\times\exp\!\left(-\tfrac{1}{2}\beta\sum_{i\neq j}\,\phi^{(2)}(\mathbf{R}_i-\mathbf{R}_j+\mathbf{u}(i)-\mathbf{u}(j))\right)$$

$$\approx e^{-\beta\hat{\mathcal{H}}'}\int d^3\mathbf{u}(0)u(0)_z$$

$$\times\exp\!\left(\beta\sum_{i\neq 0}\,u(i)_\mu\phi^{(2)}(\mathbf{R}_i)_{\mu\nu}u(0)_\nu\right)$$

$$\times\exp\!\left(-\beta\sum_{i\neq 0}\,u(0)_\mu\phi^{(2)}(\mathbf{R}_i)_{\mu\nu}u(0)_\nu\right)$$

$$\approx e^{-\beta\hat{\mathcal{H}}'}Z\!\left(\langle u(0)_{z^+}\rangle+\beta\sum_{i\neq 0}\,u(i)_\mu\phi^{(2)}\right.$$

$$\left.\times(\mathbf{R}_i)_{\mu z}\langle u(0)_{z^+}^2\rangle+\cdots\right),$$

where Z is a constant of normalization independent of the displacements, there is no summation over subscript z in the final line, and the replacement of the integration variables by their mean values is the mean-field approximation. The primed Hamiltonian contains dynamical variables of all particles except $u(0)$: i.e.,

$$\hat{\mathcal{H}}'=\tfrac{1}{2}\sum_{i\neq j\neq 0}\,\phi^{(2)}(\mathbf{R}_i-\mathbf{R}_j+\mathbf{u}(i)-\mathbf{u}(j))+\sum_{i\neq 0}\,\phi^{(2)}(\mathbf{R}_i)$$

$$+\sum_{i\neq 0}\,u(i)_\mu\phi^{(2)}(\mathbf{R}_i)_\mu+\tfrac{1}{2}\sum_{i\neq 0}\,u(i)_\mu\phi^{(2)}(\mathbf{R}_i)_{\mu\nu}u(i)_\nu. \tag{111}$$

We take the logarithm of the final line of Eq. (110) to obtain

$$\hat{\mathcal{H}}^+=\hat{\mathcal{H}}'-\frac{1}{\beta}\ln Z-\frac{1}{\beta}\ln\langle u(0)_{z^+}\rangle+\sum_{i\neq 0}\,u(i)_\mu\phi^{(2)}$$

$$\times(\mathbf{R}_i)_{\mu z}\frac{\langle u(0)_{z^+}^2\rangle}{\langle u(0)_{z^+}\rangle}+\cdots. \tag{112}$$

Thus we obtain the effective external potential as

$$\widetilde{\phi}(\mathbf{R}_i)_\mu|_{\rho^{(1)}(\mathbf{R}_0)_{z^+}}=\phi^{(2)}(\mathbf{R}_i)_{\mu z}\frac{\langle u(0)_{z^+}^2\rangle}{\langle u(0)_{z^+}\rangle} \tag{113}$$

and the continuous, quadratic parts of the direct correlation function are given by the second derivatives pair potential

$$c^{(2)}(\mathbf{R}_i,\mathbf{R}_J)_{(\mu)(\nu)}=-\beta\phi^{(2)}(\mathbf{R}_i,\mathbf{R}_j)_{\mu\nu}. \tag{114}$$

We arrive at our objective: The continuous, quadratic part of the direct correlation function in a solid of pairwise interacting atoms now seems to be the dynamical matrix of the harmonic model of that solid.

X. CONCLUSION

We have established conjugate parametrizations of the two-point density and direct correlation function of the classical solid. The parameters satisfy a matrix equation analogous to the Ornstein-Zernike equation, as well as an algebraic closure relation. Together these equations determine displacement-displacement correlation functions in a solid, and form a phonon-free theory of simple classical solids. Such a theory will be useful in describing solids under circumstances where phonon-based approaches break down, such as at surfaces and other interfaces, or in melting. We have simplified an approximation to the closure relation that is analogous to the hypernetted-chain relation of inhomogeneous fluids. From these results it is clear that the sitewise analog of the hypernetted-chain equation, when evaluated in terms of a basis of density operators corresponding to particle displacements, reduces to the harmonic model for the solid. There are of course several possible sources of anharmonicity and these will enter into more extended descriptions. First, a more extensive parametrization of the density operator, for example, including higher moments of displacement, or explicitly including occupancy, will include the consequences of nonquadratic parts of the interparticle potential. Second, knowledge of higher moments of displacement that would be included in this more extensive calculation would enable an assessment of how much the density profile about each site deviates from a perfect Gaussian, and would therefore allow for inclusion of coupling between density operators of differing tensor rank, and between the continuous and cusplike moments of density. Finally, the effective external potential used in the Percus identity can be calculated using approximations more sophisticated than Eq. (110).

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