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Consistent integral equations for two- and three-body-force models: Application to a model of silicon

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Functional differentiation of systematic expansions for the entropy, in the grand ensemble [B. B. Laird and A. D. J. Haymet, Phys. Rev. A **45**, 5680 (1992)], leads directly to consistent integral equations for classical systems interacting via two-body, three-body, and even higher-order forces. This method is both a concise method for organizing existing published results and for deriving previously unpublished higher-order integral equations. The equations are automatically consistent in the sense that all thermodynamic quantities may be derived from a minimum on an approximate free-energy surface, without the need to introduce weighting functions or numerically determined crossover functions. A number of existing approximate theories are recovered by making additional approximations to the equations. For example, the Kirkwood superposition approximation is shown to arise from a particular approximation to the entropy. The lowest-order theory is then used to obtain integral-equation predictions for the well-known Stillinger-Weber model for silicon, with encouraging results. Further connections are made with increasingly popular density-functional methods in classical statistical mechanics.

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I. INTRODUCTION

Integral-equation theories continue to play an important role in theories of liquids [1], but have been for the most part restricted to systems with pairwise additive two-body interactions. Therefore, information about model systems with three-body or higher interactions has not been obtainable from such theories, except when the deviations from two-body interactions are small and can be treated perturbatively [2, 3]. This restriction has traditionally excluded from such study many interesting and important materials, such as silicon, for which nonpairwise interactions play a large, if not dominant, role. Here we present integral-equation results for the popular and successful classical model of silicon due to Stillinger and Weber [4]. These results are obtained from a set of three coupled equations described below, which are generalized readily to higher order.

Recently, the systematic expansion of the entropy in terms of correlation functions has been revisited by us [5–7] and Baranyai and Evans [8, 9], and others [10–12]. These expansions lead to numerically useful approximations for both single-component liquids [5] and mixtures [6]. Hence it is not surprising that these expansions lead to an attractive integral-equation formalism [13].

The origin of this approach is stated easily. Consider a classical system with at most n-body contributions to the total potential energy, at fixed temperature T, volume V, and chemical potential μ. Since the energy functional may be expressed exactly in terms of a finite number of correlation functions $g^{(m)}$ $(m \leq n)$, only a consideration of the entropy is required to specify the grand potential $\Omega = \Omega(T, V, \mu)$. Thus, any given level of approximation to the entropy functional leads to an approximate grand free-energy functional, as shown schematically in Fig. 1. If the exact functional were known, the true equilibrium state of the system may be found by minimizing the exact functional. Consequently, an *approximation* to the equilibrium state of the system may be found by minimizing an *approximate* free-energy functional with respect to the various multiparticle correlation functions. This procedure yields both a series of coupled integral equations for the correlation functions themselves, and a self-consistent set of equations for all thermodynamic quantities (pressure, chemical potential, etc.) necessary to describe the equilibrium state of the system.

The advantage of integral-equation theories that are derivable as the minimum of some approximate free-energy functional lies in the existence of an internally self-

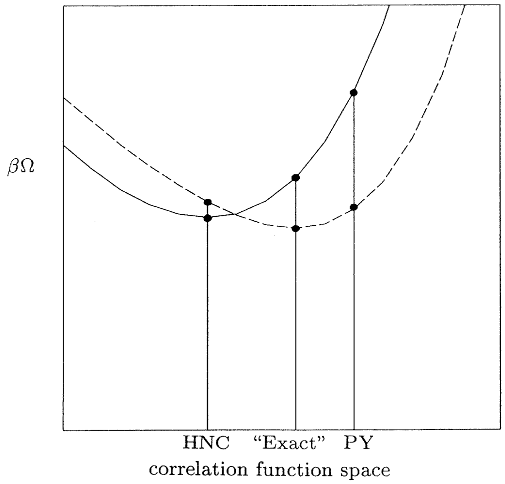

FIG. 1. Illustrative free-energy surfaces for the exact (dashed line) and HNC functionals. The multidimensional $\{g^{(n)}\}$ function space has been represented for simplicity by a one-dimensional axis. The hypothetical positions of the HNC, PY, and exact theories are indicated along the ordinate axis.

consistent set of relations for the thermodynamic variables. If the multiparticle distribution functions are assumed to be known, it is well known [1] that there is often more than one way to calculate a given thermodynamic quantity. For example, the pressure can be calculated either from the virial equation or by integrating the compressibility calculated from the zero-wave-vector limit of the structure factor. If the exact correlation functions are used, all such methods are guaranteed to yield the same result; however, the same is not true of approximate solutions. Therefore, without an underlying free-energy functional to provide a consistent thermodynamic framework, there is no unique way, using an approximate integral-equation theory, to specify the thermodynamic state of the system under study. The need for consistent thermodynamics is especially acute in studies of phase transitions [14].

The role of free-energy functionals can be illustrated by comparing two popular integral-equation theories, namely, the hypernetted chain (HNC) and Percus-Yevick (PY) [15] approximations. As discussed below, the HNC theory may be derived as the minimum of a well-defined approximation to the exact grand potential functional, and therefore a natural, self-consistent thermodynamics can be defined. The PY theory, on the other hand, cannot be derived from any physically reasonable approximate free-energy functional, and no such unique thermodynamic framework can be naturally defined [16]. However, this lack of an underlying functional does not preclude the PY approximation from yielding results that are closer to the exact results than the results of the HNC approximation, since the functional that generates HNC is itself approximate. As illustrated in Fig. 1, it is entirely possible that PY is a better approximation to the minimum of the exact functional than is the HNC theory. This is indeed the case with the hard-sphere system. Hence, as is well documented, the PY approximation is a valuable tool for studying liquid systems.

In Sec. II we examine two ways to generate integral-equation theories from free-energy functionals. The first method, which we call the g representation, considers the free energy to be a functional of the set of n-body multiparticle correlation functions $g^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n)$, $n=1,\ldots,\infty$. This is the grand-ensemble version of the canonical ensemble treatment presented by Schlijper and Kikuchi [17], which has also been pursued by Schlijper, Telo de Gamma, and Ferreira [18]. To a first approximation, this formalism is shown to yield a simple generalization of the HNC equation to systems with three-body interactions, which is denoted the HNC+3 theory. Secondly, we review for comparison the traditional density-functional (DF) technique for generating theories of the homogeneous fluid, which expand the free-energy functional in terms of the multiparticle direct correlation functions $c^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n)$.

In Sec. III, we solve the HNC+3 system of equations for the Stillinger-Weber (SW) model potential for silicon. Silicon is a natural choice for benchmark calculations of such theories, because the three-body interactions are large and cannot be studied using perturbation methods. Connection is made with earlier work by considering a linearized version of the HNC+3 theory in Sec. IV, which includes a further application to the SW silicon model. Our conclusions are summarized in Sec. V. The Appendix collects the formulas for the generalization of this approach to mixtures. The generalization to inhomogeneous systems, which yields a rich array of results, will be presented elsewhere.

II. FREE-ENERGY FUNCTIONALS AND INTEGRAL EQUATIONS

A. g representation

The thermodynamic variables for a system with a known potential energy $u(\{\mathbf{r}_i\})$ may be expressed as *functionals* of the multiparticle correlation functions $g^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n)$, $n=1,\ldots,\infty$, in the grand ensemble. For some quantities, such as the pressure P and average total energy U, the functional dependence is quite simple. For example, for a system with at most three-body interactions, P and U may be evaluated exactly from knowledge of the two- and three-particle correlations alone. However, the corresponding functionals for important quantities such as the entropy (and therefore, the free energy) contain contributions from correlation functions of all orders, independent of the nature of the interaction potential.

Until recently, such functionals (or approximations thereto) have been used primarily to calculate thermodynamic data from known correlation functions. In principle, however, the extremum properties of thermodynamic potentials can be used to invert this procedure and develop integral-equation theories for the correlations functions themselves. The grand potential Ω is the most natural functional to minimize because it avoids the difficulties associated with particle-number constraints that have plagued earlier attempts using the canonical ensemble [12, 17] .

We emphasize that the equations as printed below are not necessarily new. It is the systematic method of derivation which we put forward as being helpful in designing new approximations. We also find that this formalism leads to higher-order theories and theories for inhomogeneous systems, which are not yet published in the literature.

Recent research on functionals for the entropy in the grand ensemble [6] leads naturally to the following analysis. The total grand potential $\Omega=PV$ can be constructed from the total energy, entropy, and chemical potential

$$\begin{aligned}\Omega[g^{(1)},g^{(2)},g^{(3)},...]&=\Omega[\{g^{(n)}\}]\\&=E[\{g^{(n)}\}]-TS[\{g^{(n)}\}]+\mu N.\end{aligned}\quad(1)$$

For a homogeneous fluid interacting via a total potential energy u which is the sum of two- and three-body potential energies,

$$u(\{\mathbf{r}_i\})=\sum_{i,j}u^{(2)}_{ij}(r_{ij})+\sum_{i,j,k}u^{(3)}_{ijk}(r_{ij},r_{jk},r_{ki})\ ,\quad(2)$$

the average total energy E is given exactly by the functional

$$\beta E[\{g^{(n)}\}]V = \tfrac{3}{2}\rho + \tfrac{1}{2}\rho^2 \int dr_{12}\, \beta u^{(2)}(r_{12}) g^{(2)}(r_{12}) + \frac{\rho^3}{6V}\int dr_1 \int dr_2 \int dr_3\, \beta u^{(3)}(r_{12},r_{23},r_{31}) g^{(3)}(r_{12},r_{23},r_{31}) \,, \tag{3}$$

where $\beta^{-1} = kT$.

The functional expansion for the entropy is much more complicated. Using an expansion due to Kirkwood [19], H.S. Green [20] developed an expansion for the entropy in terms of canonical ensemble correlation functions (i.e., for a system with a fixed number of particles). Later, Nettleton and M.S. Green [21] and Raveché [22] derived the corresponding expression for an open system (grand canonical ensemble):

$$\begin{aligned}\frac{S[\{g^{(n)}\}]}{Vk} = {} & \tfrac{5}{2}\rho - \rho \ln(\rho\Lambda^3) - \tfrac{1}{2}\rho^2 \int d\mathbf{r}\, [g^{(2)}(r)\ln g^{(2)}(r) - g^{(2)}(r) + 1] \\ & -\frac{\rho^3}{6V}\int d\mathbf{r}_1 \int d\mathbf{r}_2 \int d\mathbf{r}_3 \left\{ g^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) \ln\left[\frac{g^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)}{g^{(2)}(r_{12})g^{(2)}(r_{23})g^{(2)}(r_{13})}\right] \right. \\ & \left. - g^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) + 3g^{(2)}(r_{12})g^{(2)}(r_{23}) - 3g^{(2)}(r_{12}) + 1 \right\} \\ & + \sum_{i=4}^{\infty} S(i)[\{g^{(m)}\}; m \le i] \,. \end{aligned} \tag{4}$$

Through an elegant rearrangement of terms, Baranyai and Evans [8] showed that the grand canonical expression is, in fact, an ensemble invariant one, namely that it yields the same result whether canonical or grand canonical correlation functions are used.

The functionals $S(i)$ in Eq. (5) contain all terms that are ith order in the density and include contributions for all multiparticle correlation functions up to order i. Hernando [11] has shown that the leading term in each $S(i)$ can be represented, in the language of graph theory, by an ith-order ring diagram with h bonds and black ρ circles. The remaining terms either vanish under the generalized superposition approximation (GSA) [23], or correspond to highly connected diagrams. The subset of ring diagrams can be summed explicitly [12] to infinite order to yield the expansion for the entropy,

$$\begin{aligned}\frac{S[\{g^{(n)}\}]}{Vk} = {} & \tfrac{5}{2}\rho - \rho \ln(\rho\Lambda^3) - \tfrac{1}{2}\rho^2 \int d\mathbf{r}\, [g^{(2)}(r)\ln g^{(2)}(r) - g^{(2)}(r) + 1] \\ & -\frac{\rho^3}{6V}\int d\mathbf{r}_1 \int d\mathbf{r}_2 \int d\mathbf{r}_3 \left\{ g^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) \ln\left[\frac{g^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)}{g^{(2)}(r_{12})g^{(2)}(r_{23})g^{(2)}(r_{13})}\right] \right. \\ & \left. - g^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) + g^{(2)}(r_{12})g^{(2)}(r_{23})g^{(2)}(r_{13}) \right\} \\ & - \frac{1}{2\rho(2\pi)^3}\int d\mathbf{k}\{\rho\tilde{h}(k) - \tfrac{1}{2}\rho^2\tilde{h}^2(k) - \ln[1+\rho\tilde{h}(k)]\} + \sum_{i=4}^{\infty} S'(i)[\{g^{(m)}\}; m \le i] \,, \end{aligned} \tag{5}$$

where the $S'(i)$ are identical to the terms $S(i)$ in Eq. 5 without the ring-diagram contributions.

The lowest-order, nontrivial theory can be obtained by setting the $S'(i)$ to zero for $i \ge 4$. (This and related approximations for the entropy have been evaluated for a variety of systems by Laird and Haymet [5, 6].) Minimization of the resulting grand potential functional $\beta\Omega$ at constant temperature and chemical potential, with respect to $g^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)$, $g^{(2)}(r)$, and ρ yields the set of equations,

$$g^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) = g^{(2)}(r_{12})g^{(2)}(r_{13})g^{(2)}(r_{23}) \times e^{-\beta u^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)} \,, \tag{6}$$

$$\ln g^{(2)}(r) = h(r) - c(r) - \beta u^{(2)}(r) - \beta\bar{u}^{(3)}(r) \,, \tag{7}$$

$$\beta\mu = \ln(\rho\Lambda^3) - \tfrac{1}{2}[h(0) - c(0)] + \rho \int d\mathbf{r}\, \{\tfrac{1}{2}h^2(r) - c(r) - g^{(2)}(r)\beta\bar{u}^{(3)}(r)\} \,, \tag{8}$$

where

$$\beta\bar{u}^{(3)}(r_{12}) \equiv -\rho \int d\mathbf{r}_3\, g^{(2)}(r_{13})g^{(2)}(r_{23}) \times [e^{-\beta u^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)} - 1] \tag{9}$$

is the averaged three-body potential. The direct correlation function $c(r)$ is defined by the Ornstein-Zernicke (OZ) equation

$$h(r_{12}) = c(r_{12}) + \rho \int d\mathbf{r}_3\, c(r_{13})h(r_{23}) \,. \tag{10}$$

This set of three equations is the principal formal result of this paper [24].

Finally, substituting the above three minimum conditions into the original functional for $\beta\Omega$ yields a consistent equation for the equilibrium pressure,

$$\beta P/\rho = 1 + \tfrac{1}{2}\rho^2 \int d\mathbf{r}\{h^2(r) - c(r) - \tfrac{1}{3}g^{(2)}(r)\beta\bar{u}^{(3)}(r)\}$$

$$+\frac{1}{2\rho(2\pi)^3}\int d\mathbf{k}\left\{\ln\left[1+\rho\tilde{h}(k)\right] - \rho\tilde{h}(k)\right\} \ . \quad (11)$$

Note that the first term in the integrand is indeed the square of the total correlation function $h(r)$. All additional thermodynamic functions (such as the Helmholtz free energy) may be derived readily from Eqs. (6) and (11). Therefore, the set of equations (6)–(11) forms a thermodynamically complete and self-consistent approximate theory for liquids with three-body interactions. For completeness, the generalization of this derivation to multicomponent systems is included in the Appendix.

This set of equations will be solved numerically below. First we note a number of important features of these equations. First, the simplicity of the derivation should be compared with the approach in the canonical ensemble [17]. Second, the equation for the triplet correlation function [Eq. (6)] is the usual Kirkwood superposition approximation generalized to take into account three-body interactions. Although it is quite common to make this approximation as an ansatz, the above g-representation procedure is unique in obtaining the superposition approximation as a consequence of an approximation to the entropy.

Finally, the form of the equation for the pair correlation function $g^{(2)}(r)$ [Eqs. (7) and (8)] is familiar. Without the three-body interactions, this is exactly the HNC equation. The effect of the three-body potential is to introduce a correction to the usual pair interaction in the HNC equation, namely an average over the three-body potential. Therefore, the theory defined by Eqs. (6)–(11) may be viewed as a three-body generalization of the HNC theory, and it will be denoted HNC+3.

These equations have occurred several times in the literature. Schlijper, Telo de Gamma, and Ferrerira [18] have pursued this approach. Earlier, Attard [25] presented the equations using a less self-contained approach. For example, the superposition approximation was assumed *a priori*. In addition, there are also many earlier examples in the literature of the use of an effective pair potential (in varying forms and levels of approximation) to represent the effect of three-body interactions in integral-equations [26–32]. In the absence of the three-body interactions, the equations for the HNC thermodynamic functions (presented above) have been known for a long time, but their self-consistent nature has not been emphasized until recently [6, 14, 33].

B. The c representation

A second way to generate thermodynamically self-consistent integral equation theories is the expansion of the free energy in multiparticle direct correlation functions $c^{(n)}(\mathbf{r}_1,...,\mathbf{r}_1)$. This is the standard density-functional theory approach, which was developed primarily for the study of inhomogeneous fluids, as summarized, for example, by Evans [34], but it can be applied to the homogeneous case using a method due to Percus [35]. This development shows clearly that every density-functional approximation (whether for inhomogeneous liquids or freezing) corresponds to an approximate integral-equation theory for bulk liquids, albeit often an unusual theory.

Consider a homogeneous liquid with bulk density $\rho^{\mathcal{B}}$, interacting via a pairwise additive interparticle potential $u^{(2)}(r)$. In the Percus procedure (often called the "bootstrap" method), one particle of the system is considered to be "outside" the system and placed at the origin. This particle generates an external potential $u^{(2)}(r)$ through which the other particles move. The effect of this external potential is to induce an inhomogeneous single-particle density field $\rho(\mathbf{r})$ around the "external" particle. Since this external particle is in reality no different to the other particles, consistency requires that the single-particle density induced around it be related directly to the pair-correlation function $g^{(2)}(r)$ of the original homogeneous system, that is,

$$\rho(r) \to \rho^{\mathcal{B}} g^{(2)}(r) \ , \quad (12)$$

where $\rho^{\mathcal{B}}$ is the bulk liquid density.

In the notation of density-functional theory, the difference in the grand potential $\beta\Omega$ for the system with the artificial external particle, compared to the grand potential of the homogeneous system, may be written as a functional of the single-particle density $\rho(\mathbf{r})$,

$$\Delta\beta\Omega[\rho(\mathbf{r})] = \int d\mathbf{r}\,\rho(\mathbf{r})\beta u^{(2)}(\mathbf{r}) + \int d\mathbf{r}\{\rho(\mathbf{r})\ln[\rho(\mathbf{r})/\rho^{\mathcal{B}}] - [\rho(\mathbf{r}) - \rho^{\mathcal{B}}]\}$$

$$-\tfrac{1}{2}\int d\mathbf{r}_1 \int d\mathbf{r}_2\, c^{(2)}(\mathbf{r}_1,\mathbf{r}_2;\rho^{\mathcal{B}})[\rho(\mathbf{r}_1) - \rho^{\mathcal{B}}][\rho(\mathbf{r}_2) - \rho^{\mathcal{B}}]$$

$$-\sum_{n=3}^{\infty}\frac{1}{n!}\int d\mathbf{r}_1 \cdots \int d\mathbf{r}_n\, c^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n;\rho^{\mathcal{B}})[\rho(\mathbf{r}_1) - \rho^{\mathcal{B}}]\cdots[\rho(\mathbf{r}_n) - \rho^{\mathcal{B}}] \ , \quad (13)$$

where the direct correlation functions may be defined formally as functional derivatives of the excess Helmholtz free energy $\mathcal{F}_{\text{ex}}$,

$$c^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n;\rho) \equiv -\frac{\delta^n \beta\mathcal{F}_{\text{ex}}[\rho]}{\delta\rho(\mathbf{r}_1)\cdots\delta\rho(\mathbf{r}_n)} \,. \tag{14}$$

The equilibrium single-particle density for this inhomogeneous system (and therefore the pair-correlation function for the homogeneous system) may be calculated by minimizing this free-energy functional, that is, from the condition that

$$\frac{\delta^n \beta\Omega[\rho]}{\delta\rho(\mathbf{r}_1)} = 0 \,. \tag{15}$$

We define the last term of Eq. (13) to be the functional $\chi[\rho]$. The minimum condition [Eq. (15)] yields

$$\begin{aligned}\ln[\rho(\mathbf{r})/\rho^{\mathcal{B}}] = &\int d\mathbf{r}_1\, c^{(2)}(|\,\mathbf{r}-\mathbf{r}_1\,|;\rho^{\mathcal{B}})[\rho(\mathbf{r}_1)-\rho^{\mathcal{B}}] \\ &-\beta u^{(2)}(r) - \frac{\delta\chi[\rho]}{\delta\rho(\mathbf{r})} \,.\end{aligned} \tag{16}$$

Using the Percus relation between the single-particle density and the pair-correlation function $g^{(2)}(r)$ of the homogeneous system [Eq. (12)] we obtain

$$\begin{aligned}\ln[g^{(2)}(r)] = \rho^{\mathcal{B}} &\int d\mathbf{r}_1\, c^{(2)}(|\,\mathbf{r}-\mathbf{r}_1\,|)h(r_1) \\ &-\beta u^{(2)}(r) + B(r) \,,\end{aligned} \tag{17}$$

where we define

$$B(\mathbf{r}) = -\frac{\delta\chi[\rho]}{\delta\rho(\mathbf{r})} \,. \tag{18}$$

Using the OZ definition for $c(r)$ [Eq. (10)] to evaluate the integral in Eq. (17), we obtain the final equation for the pair-correlation function

$$\ln[g^{(2)}(r)] = h(r) - c(r) - \beta u^{(2)}(r) + B(r) \,, \tag{19}$$

where the total correlation function $h(r) \equiv g^{(2)}(r) - 1$. Setting $B(r) = 0$ in the above equation, we recover the usual HNC equation. This identifies $B(r)$ as the bridge function.

At its minimum value, $\Delta\beta\Omega$ here represents the amount of work required to insert the external particle into the system, and is therefore equal to the (dimensionless) excess chemical potential $\beta\mu_{\text{ex}}$. Substitution of the minimum condition [Eq. (19)] into the original functional yields, after some manipulation,

$$\begin{aligned}\beta\mu_{\text{ex}} = \rho^{\mathcal{B}} &\int d\mathbf{r}\{\tfrac{1}{2}h^2(r) - c(r) + g^{(2)}(r)B(r)\} \\ &-\tfrac{1}{2}[h(0) - c(0)] \\ &-\rho^{\mathcal{B}}\int_0^1 d\lambda \int d\mathbf{r}\, B(\mathbf{r};[\lambda h(r)])h(r) \,.\end{aligned} \tag{20}$$

For the HNC approximation, here the bridge function $B(r)$ is assumed to be zero, this chemical potential is identical to that given within the g representation [Eq. (8)] provided there is no three-body interaction. A systematic derivation of other thermodynamic variables, such as the Helmholtz free energy and the pressure, results in expressions that are identical to those of the g-representation theory (with no three-body potential) [25].

As will be shown below, the calculation of the three-body correlation function $g^{(3)}$ is neither straightforward nor well defined. This is not a problem in the g representation, since an approximation for $g^{(3)}$ is a natural product of the derivation. To date we have not been able to choose a three-body correlation function which is consistent with all the assumptions of the density-functional derivation.

One way to calculate the three-body correlation functions from the density-functional expansion [Eq. (13)] is to consider *two* external particles at positions $\mathbf{r}_1$ and $\mathbf{r}_2$. Minimizing the grand potential functional with an external potential generated by these two particles yields the conditional particle density $\rho^{(3)}(\mathbf{r}_3\mid\mathbf{r}_1,\mathbf{r}_2)$, which is the (unnormalized) probability that a particle will be found at $\mathbf{r}_3$ given that there are particles at $\mathbf{r}_1$ and $\mathbf{r}_2$. The connection of this quantity to $g^{(3)}$ is given by

$$\rho^2 g^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) = \rho^{(3)}(\mathbf{r}_3\mid\mathbf{r}_1,\mathbf{r}_2)g^{(2)}(|\,\mathbf{r}_1-\mathbf{r}_2\,|) \,. \tag{21}$$

If we use the same approximation for the grand potential functional that leads to the HNC equation (that is, $\chi[\rho] = 0$), we obtain the following equation for $g^{(3)}$:

$$\ln\left\{\frac{g^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)}{g^{(2)}(r_{12})}\exp(\beta[u^{(2)}(r_{13})+u^{(2)}(r_{23})])\right\} = \rho\int d\mathbf{r}_4 c(r_{34})\left[\frac{g^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_4)}{g^{(2)}(r_{12})} - 1\right] \,. \tag{22}$$

This is precisely the HNC2 equation derived in another way by Verlet [36].

Another way to derive an expression for the HNC triplet correlation function is by considering the nature of the approximation to the functional that generates the HNC, namely that $\chi[\rho] = 0$ [and thus the bridge function $B(r) = 0$]. By construction, this is true if and only if

$$c^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n) = 0, \quad n \geq 3 \,. \tag{23}$$

From the definition of $c^{(n)}$ [Eq. (14)], it can be easily seen that it is sufficient that

$$c^{(3)}(\mathbf{r}_1,\ldots,\mathbf{r}_n) = 0 \tag{24}$$

for Eq. (23) to be satisfied. This assumption is known as the *convolution approximation* (which is equivalent to a "superposition" approximation for the k-space structure factors) for the triplet direct correlation functions. Using the triplet analog of the OZ equation, it can be shown [37] that the convolution approximation for $c^{(3)}$ is equivalent to the following expression for the three-body total correlation function:

$$\begin{aligned} h^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) = {} & h(r_{12})h(r_{23}) + h(r_{23})h(r_{13}) \\ & + h(r_{13})h(r_{12}) \\ & + \rho^{\mathcal{B}} \int d\mathbf{r}_4 h(r_{14})h(r_{24})h(r_{34}) \ , \end{aligned} \tag{25}$$

where

$$\begin{aligned} h^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) \equiv {} & g^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) - g^{(2)}(r_{12}) \\ & - g^{(2)}(r_{13}) - g^{(2)}(r_{23}) + 1. \end{aligned} \tag{26}$$

Each of these derived expressions for the HNC $g^{(3)}$ [Eqs. (22) and (26)] are incompatible with the other and with the superposition approximation. The deeper meaning of this inconsistency is not yet clear.

The above discussion of c-representation derivations of integral equations is valid for systems with two-body potentials only. This is because the standard density-functional approach only considers one-body external potentials (which correspond to interparticle pair potentials in the Percus method). Treatment of three-body potentials requires the reformulation of density-functional theory to include two-body external potentials. The free energies will then become functionals of both the single and two-particle density fields. Such a program has been attempted by Iyetomi and Vashishta [38]. Because of the difficulties caused by introducing the two-body external potentials, they were only able to minimize the resulting functional using a perturbative approach where the three-body interaction is assumed to be weak. Interestingly, the integral equation they derived is equivalent to an approximate version of the HNC+3 theory, in which the equation for the averaged three-body potential [Eq. (9)] is linearized with respect to $\beta u^{(3)}$,

$$\begin{aligned} \beta \bar{u}_l^{(3)}(r_{12}) \equiv \rho^{\mathcal{B}} \int & d\mathbf{r}\, g^{(2)}(r_{13}) g^{(2)}(r_{23}) \\ & \times \beta u^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) \ . \end{aligned} \tag{27}$$

In Sec. IV we will solve numerically this linearized HNC+3 theory for a model of silicon.

III. SILICON: HNC+3 THEORY

We have generated above a set of thermodynamically self-consistent integral equations for liquids with multibody interactions. At the simplest level of approximation, the set consists of (i) the superposition approximation [Eq. (6)] for the triplet correlation function, (ii) an integral equation for $g^{(2)}(r)$ that has the form of the hypernetted chain (HNC) equation with an effective pair potential containing information about the three-body interactions, and (ii) a self-consistent formula for the chemical potential. This level of theory will be denoted HNC+3.

In fact these equations have been solved by Attard [25, 39] for a a Lennard-Jones fluid with the Axilrod-Teller [40] (triple dipole) three-body potential. These results show that the HNC+3 theory is accurate at low densities, but less than adequate in the liquid region. The problem at higher densities arises not necessarily from fundamental problems with the treatment of the three-body potential (which are basically just a perturbation), but from the inability of the HNC equation to describe the dominant short-ranged two-body interactions.

In this section we apply the HNC+3 theory to liquid silicon. The interactions between silicon atoms cannot be well approximated by a simple, classical, two-body potential. A correct description of the tendency to bond tetrahedrally requires, at the very least, inclusion of three-body forces. These three-body forces are of the same magnitude as the two-body ones, and therefore they are not amenable to perturbation techniques, in contrast to the Axilrod-Teller potentials studied by Attard. Consequently, without advances in nonperturbative integral-equation theories for systems with three-body potentials, the only current way to obtain structural and thermodynamic information on this system is through time-consuming computer simulations.

A popular and useful classical potential for silicon is due to Stillinger and Weber (SW) [4]. The parameters of this model were chosen to provide a reasonable fit to the experimentally observed thermodynamic and structural properties of crystalline and liquid silicon. The total potential energy is written as the sum of a two-body potential and a three-body potential

$$u_{\mathrm{SW}} = \sum_{(i<j)} u^{(2)}(r_{ij}) + \sum_{(i<j<k)} u^{(3)}(\mathbf{r}_i,\mathbf{r}_j,\mathbf{r}_k) \ . \tag{28}$$

Using $\sigma = 2.0951$ Å and $\varepsilon = 50$ kcal/mole as the units of distance and energy, the SW two-body potential is relatively short-ranged and is assigned the form

$$u^{(2)}(r) \equiv \begin{cases} A[Br^{-4} - 1], \ \ \exp\left[\frac{1}{r-a}\right], & r < a \\ 0, \ \ r \geq a \end{cases} \tag{29}$$

where $A = 7.049\,556\,277$, $B = 0.602\,224\,558\,4$, and $a = 1.8$. The three-body potential is also short ranged, and is given by

$$\begin{aligned} u^{(3)}(\mathbf{r}_i,\mathbf{r}_j,\mathbf{r}_k) \equiv {} & v(r_{ij},r_{ik},\theta_{jik}) + v(r_{ij},r_{jk},\theta_{ijk}) \\ & + v(r_{ik},r_{jk},\theta_{ikj}), \end{aligned} \tag{30}$$

where θ_{jik} is the angle formed by the vectors $\mathbf{r}_{ij}$ and $\mathbf{r}_{ik}$ and

$$\begin{aligned} v(r_{ij},r_{ik},\theta_{ikj}) = {} & \lambda \exp\left[\gamma\left(\frac{1}{r_{ij}-a} + \frac{1}{r_{ik}-a}\right)\right] \\ & \times(\cos\theta_{jik} + \tfrac{1}{3})^2 H(a - r_{ij}) \\ & \times H(a - r_{ik}), \end{aligned} \tag{31}$$

where $\gamma = 1.20$, $\lambda = 21.0$, and $H(x)$ is the usual Heaviside step function. The $[\cos(\theta) + \frac{1}{3}]$ term in the three-body interaction ensures that tetrahedral geometries will be favored.

When simulated via molecular-dynamics or Monte Carlo techniques, the SW potential is successful at reproducing many of the principal features of the silicon liquid structure. For example, it obtains the unusual shoulder on the first peak of the structure factor and a coordination number that is considerably smaller than the icosahedral close-packed value of 12 typical of spherical pairwise additive potentials. The experimental melting temperature of silicon at 1 atm. pressure is 1410 °C (1783 K) with a liquid density of 2.53 g/cm^3—corresponding to a number density of 0.0525 Å^{-3} (0.4832 in reduced units). All calculations in this paper will be at this density. Keeping the mass density fixed at the experimental value, Stillinger and Weber have estimated the equilibrium melting temperature of the model to be slightly high, at about 1740 °C (2013 K).

The solution of the HNC+3 equations is straightforward, since they have the same form as the usual two-body HNC equation, with an effective pair potential induced by the triplet interactions. First, an input guess is made for $g^{(2)}(r)$ from which the effective potential [Eq. (9)] is calculated. Equation (7) is then solved assuming that the total effective potential

$$u^{(2)}_{\text{eff}}(r) = u^{(2)}(r) + \bar{u}^{(3)}(r) \tag{32}$$

is fixed, yielding an updated result for $g^{(2)}(r)$. This process is iterated until the input and output values of $g^{(2)}(r)$ have converged within a preselected tolerance.

If the three-body potential is neglected, the model has no physical connection with silicon, since it yields liquid structures with approximately 12 nearest neighbors. In fact, liquid solutions to the equations may be obtained only above 39 000 K. Including the three-body interactions, a large effect is observed, by comparison of the full solution to that which results when the three-body potential is ignored. Figure 2(b) shows $g^{(2)}(r)$ calculated with and without the three-body interaction at the temperature 39 000 K. The corresponding effective HNC potentials for the two calculations are shown in Fig. 2(a). The most striking feature of Fig. 2 is that, without the three-body correction, the bare two-body potential is very deep, and leads to a $g^{(2)}(r)$ with far too much structure for a fluid at a temperature that is 20 times the equilibrium melting point. With the repulsive three-body correction, the deep well disappears, and there is a corresponding dramatic decrease in the liquid structure.

To illustrate the effect of the three-body potential on the triplet correlations, the superposition approximation [Eq. (6)] to this quantity (at the same temperature and density used in Fig. (2) is shown in Fig. 3 both with (bottom) and without (top) the contribution from the three-particle interactions. The form of the three-body potential induces a strong enhancement of the triplet correlation at tetrahedral geometries.

Inclusion of the three-body contributions lowers considerably the temperature above which reasonable solutions may be found, to about 12 000 K. Figure 4 shows the pair-correlation function and structure factor for this minimum temperature. Below 12 000 K, the structure factor begins to exhibit an unphysical extra peak at about $k = 1$ Å^{-1}. This temperature is still about six times the equilibrium melting point and about 3.5 times the maximum temperature at which computer simulation data has been published. Higher-order theories based on

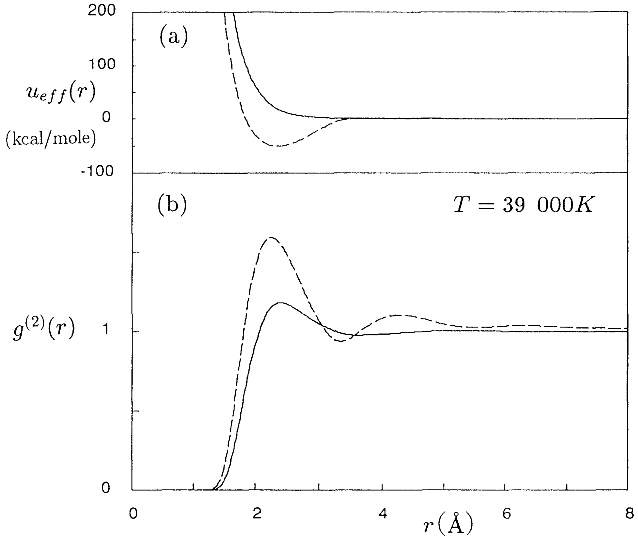

FIG. 2. (a) The effective pair potentials for SW silicon at $T = 39\,000$ K and $\rho = 0.0525$ Å^{-3}, both with (solid line) and without (dashed line) the three-body contribution. (b) The pair-correlation functions for the same system corresponding to the effective pair potentials in (a) (the same line-type conventions are used).

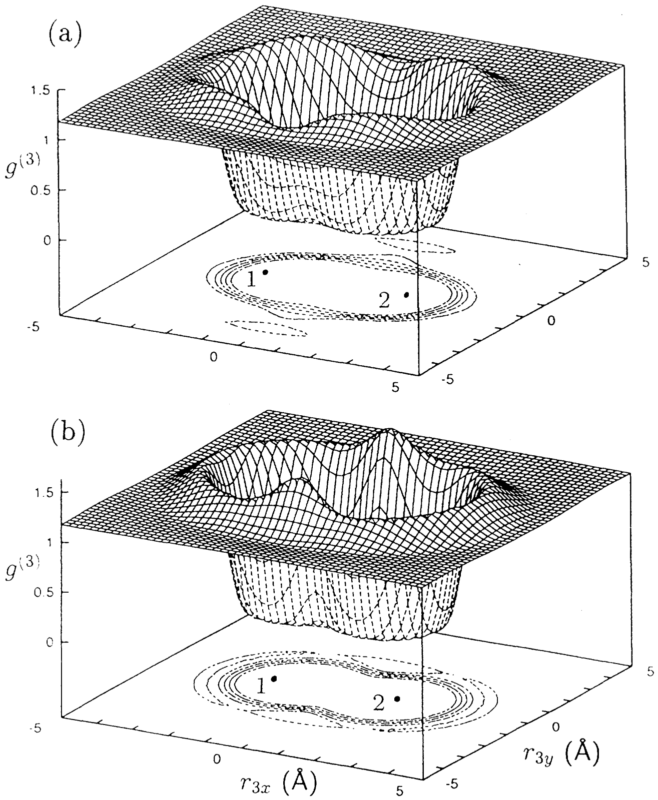

FIG. 3. Superposition approximation [Eq. (6)] for the HNC+3 triplet correlation function at $T = 39\,000$ K and $\rho = 0.0525$ Å^{-3} both (a) without and (b) with the contribution from the three-body interaction. The figures represent $g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ with $\mathbf{r}_1$ and $\mathbf{r}_2$ fixed at a separation corresponding to the minimum in the two-body potential (1.21 Å).

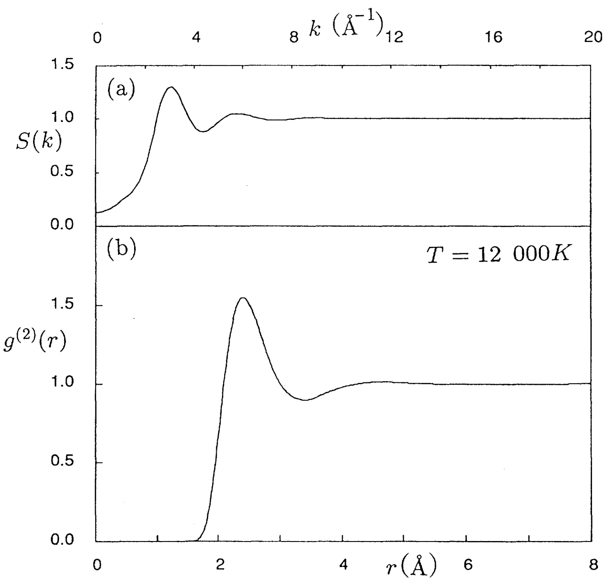

FIG. 4. The functions $g^{(2)}(r)$ and $S(k)$ predicted by the HNC+3 approximation for the SW model at the temperature 12 000 K and density $\rho = 0.0525$ Å^{-3}.

Eq. (5) are being investigated.

In Fig. 5 we show the pressure calculated from the HNC+3 results as a function of temperature, at fixed number density (0.055 25 Å^{-3}). The pressure has been calculated using both the self-consistent HNC+3 pressure relation [Eq. (11)], and the virial equation generalized for three-body potentials,

$$\beta P/\rho = 1 - \tfrac{1}{6}\rho \int d\mathbf{r}\, r g^{(2)}(r) \frac{\partial[\beta u^{(2)}(r)]}{\partial r} - \tfrac{1}{6}\rho^2 \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3\, r_{12}\, g^{(3)}(r_{12}, r_{13}, r_{23}) \times \frac{\partial[\beta u^{(2)}(r_{12}, r_{13}, r_{23})]}{\partial r_{12}}\,. \quad (33)$$

These two methods of calculating the pressure do not yield identical results because the HNC+3 theory is not exact. The HNC+3 pressure equation is the preferred method because the pressure generated is guaranteed to be consistent with the other thermodynamics results produced within the HNC+3 formalism.

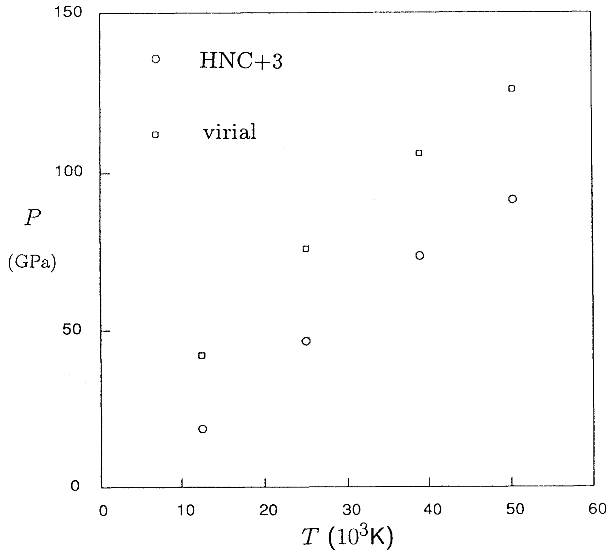

FIG. 5. The predicted pressure for the SW model of silicon at $\rho = 0.0525$ Å^{-3} as a function of temperature, calculated from the HNC+3 approximation, using both the self-consistent pressure equation (11) (squares) and the virial equation (33) (circles). Note that the pressures are large at elevated temperatures because the density is fixed at the triple-point density.

For an additional comparison, we have also applied the HNC+3 theory to another empirical potential for silicon due to Biswas and Hamann (BH) [41]. This potential has two- and three-body interactions which are softer, but of longer range, than the model of Stillinger and Weber. Although the BH potential was not specifically optimized for the liquid state, it is of interest to study the effect of changes in the interactions on the HNC+3 predictions. Within the HNC+3 formalism, the softness of the BH three-body interaction yields an effective, averaged potential which is less repulsive than the SW potential, and it is less effective at reducing the effect of the two-body, deep minimum. Consequently, physical results from the HNC+3 approximation may be obtained for the BH model only above a higher temperature (about 39 000 K) than for the SW model. [Below this temperature the HNC+3 solutions begin to develop the same anomalous peak in S(k) that appear in the SW solutions below 12 000 K.] Note that this is not a criticism of the BH model, merely an observation on the behavior of the HNC+3 theory for softer potentials. A comparison of the HNC+3 results for $g^{(2)}(r)$ and the total effective pair potential [Eq. (32)] for the Biswas-Hamann and Stillinger-Weber models is shown in Fig. 6.

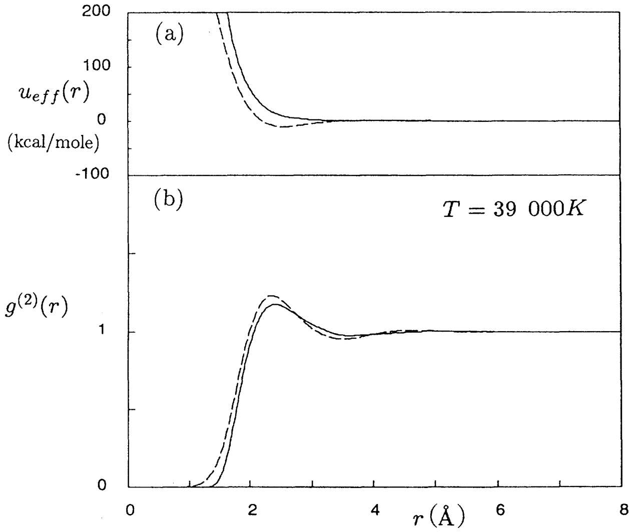

FIG. 6. HNC+3 predictions for silicon at T = 39 000 K and $\rho = 0.0525$ Å^{-3} for the Stillinger-Weber (solid line) and Biswas-Hamann (dashed line) models: (a) effective pair potential and (b) pair-correlation function $g(r)$.

IV. SILICON: RESULTS FOR A LINEARIZED HNC+3 THEORY

As noted above, additional approximate integral-equation theories may be obtained from an approximate grand potential functional by making further approximations once the minimization has been performed. Such theories no longer represent true minima of the approximate free-energy surface. However, for many systems, through a fortuitous cancellation of errors, these approximations may be more representative of the exact solution. An example of such a theory is the well-known Percus-Yevick equation, which may be obtained (among other ways) from the HNC equation by linearizing the exponential of the pair potential, and which yields accurate predictions for systems with short-ranged interactions (such as hard spheres).

In this section we examine the Stillinger-Weber silicon potential using one such approximation to the HNC+3 functional minimum. By linearizing the exponential of the three-body potential in Eq. (9), one obtains the following result for the three-body contribution to the effective HNC potential:

$$\beta \bar{u}_l^{(3)}(r_{12}) \equiv \rho^{\mathcal{B}} \int d\mathbf{r}\, g^{(2)}(r_{13}) g^{(2)}(r_{23}) \times \beta u^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \,. \qquad (34)$$

This is the same equation derived by Iyetomi and Vashishta [38] using a generalized density-functional approach [see Eq. (27) in Sec. II B)]. Together with Eq. (7), this equation comprises the linearized HNC+3 theory, denoted LHNC+3.

For the SW model of silicon, the LHNC+3 equations may also be solved numerically. The LHNC+3 three-body contribution to the effective potential is more repulsive than in the HNC+3 theory, especially at lower temperatures, and appears to dampen the effect of the deep two-body well more effectively than that for the full, unlinearlized theory. Consequently, the calculation may be extended to much lower temperatures, even down to the equilibrium melting temperature where simulation data are available for comparison.

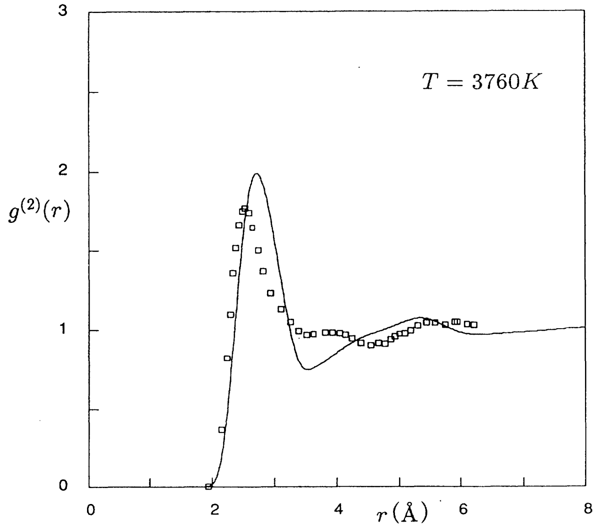

FIG. 7. Predictions for the pair-correlation function $g^{(2)}(r)$ for the SW model of silicon at T = 3760 K (3487 °C): the linearized HNC+3 (LHNC+3) theory (solid line) and molecular-dynamics simulations (squares) of Stillinger and Weber [4].

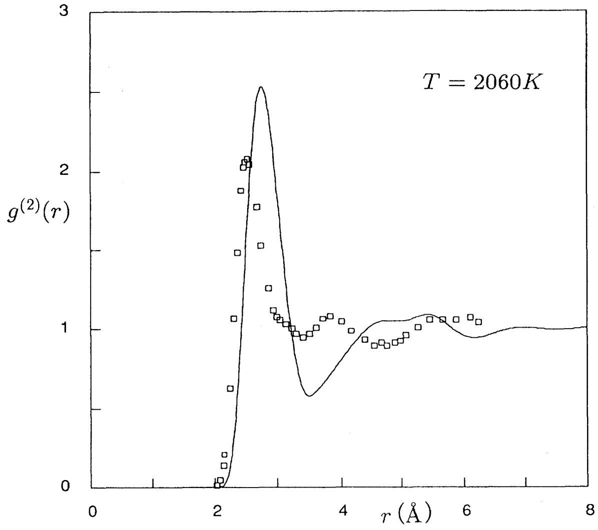

FIG. 8. Predictions for the pair-correlation function $g^{(2)}(r)$ for the SW model of silicon at T = 2060 K (1787 °C): the linearized HNC+3 (LHNC+3) theory (solid line) and molecular-dynamics simulations (squares) of Stillinger and Weber [4].

In Figs. 7 and 8 are shown the pair-correlation functions $g^{(2)}(r)$ for SW silicon from both the LHNC+3 integral-equation and the molecular-dynamics simulations of Stillinger and Weber [4] for T = 3760 K (3487 °C) and T = 2060 K (1787 °C). The lower temperature is very close to the estimated equilibrium melting temperature for the model. To our knowledge, these are the first published integral equation predictions for this model (or similar models). The integral-equation predictions are clearly comparable to the exact computer results, whereas as no solution exists for two-body or perturbative approximations. However, the first-order theory, the LHNC+3 approximation, falls short of being a quantitatively acceptable theory for SW silicon. For example, the observed second peak in the pair-correlation function is absent. The shift in the peak maximum is due to the spherical averaging of the three-body potential, which underestimates the ability of the nearest-neighbor silicon atoms to penetrate into the tetrahedral pockets of the potential. We believe this feature wll be improved substantially by the next level, higher-order treatment of the three-body interaction. In spite of these problems, the results of the LHNC+3 theory are a promising step in the nonperturbative treatment of three-body interactions via integral equations.

V. SUMMARY

Utilizing recent advances in entropy expansions [5, 6, 8, 11], the grand potential may be written as a general functional of multiparticle correlation functions. Minimization of this g representation for the grand potential functional at various levels of approximation provides a systematic way to develop integral-equation theories for the correlation functions themselves. This procedure has two principal advantages. First, because the solutions represent a minimum of a free-energy hypersurface, the system thermodynamics may be obtained in a completely self-consistent manner. Second, the method permits the inclusion of multiparticle interactions in a natural way. For systems with at most three-body interactions, the first level of approximation leads to the HNC+3 theory, which is a generalization of the well-known HNC integral equation to systems with three-body interactions. At this level of approximation, the triplet correlation functions are shown to be given by a generalized Kirkwood superposition approximation, which includes explicitly the three-body interactions.

To illustrate the usefulness of this method, we have applied the HNC+3 equation (and a linearized variant) to the Stillinger-Weber [4] model of silicon. Aside from the obvious technological importance of silicon, this system is an important benchmark for the present study because the three-body interactions are very large and cannot be treated merely as a perturbation on the two-body interaction. These calculations are apparently the first application of an integral-equation theory to such a system. The results represent an important first step in the development of nonperturbative integral-equation theories for systems with multibody interactions. We expect that further effort in this direction will result in the extension of the classical theory of liquids to systems in which directional bonding plays a dominant role, such as semiconductors.

ACKNOWLEDGMENTS

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APPENDIX: EQUATIONS FOR MIXTURES

In this appendix the g-representation energy, entropy, and subsequent integral-equations are generalized for mixtures. Consider a homogeneous fluid mixture with ν components, volume V, and temperature T, interacting via the two- and three-body potentials $u^{(2)}_{\alpha\beta}(\mathbf{r}_{\alpha\beta})$, and $u^{(3)}_{\alpha\beta\gamma}(\mathbf{r}_\alpha,\mathbf{r}_\beta,\mathbf{r}_\gamma)$, where α, β, and γ index component types. The average total energy for this system is given exactly by the functional

$$\begin{aligned}\frac{\beta E[\{g^{(n)}\}]}{V} &= \tfrac{3}{2}\rho^{\mathcal{B}} + \tfrac{1}{2}\sum_{\alpha=1}^{\nu}\sum_{\beta=1}^{\nu}\rho_\alpha\rho_\beta\int dr_{\alpha\beta}\, u^{(2)}_{\alpha\beta}(r_{\alpha\beta})g^{(2)}_{\alpha\beta}(r_{\alpha\beta}) \\ &\quad + \sum_{\alpha=1}^{\nu}\sum_{\beta=1}^{\nu}\sum_{\gamma=1}^{\nu}\frac{\rho_\alpha\rho_\beta\rho_\gamma}{6V}\int dr_\alpha\int dr_\beta\int dr_\gamma\, u^{(3)}_{\alpha\beta\gamma}(r_{\alpha\beta},r_{\alpha\gamma},r_{\beta\gamma})g^{(3)}_{\alpha\beta\gamma}(r_{\alpha\beta},r_{\alpha\gamma},r_{\beta\gamma})\ ,\end{aligned} \tag{A1}$$

where ρ_α is the partial number density of component α, and $\rho^{\mathcal{B}} = \sum_{\alpha=1}^{\nu}\rho_\alpha$ is the total number density.

The entropy functional for this mixture may be derived by generalizing Hernando's result for the ring entropy contribution [12]. After some matrix algebra, one obtains

$$\begin{aligned}\frac{S[\{g^{(n)}\}]}{Vk} &= \tfrac{5}{2}\rho^{\mathcal{B}} - \sum_{\alpha=1}^{\nu}\rho_\alpha\ln(\rho_\alpha\Lambda_\alpha^3) - \sum_{\alpha=1}^{\nu}\sum_{\beta=1}^{\nu}\frac{\rho_\alpha\rho_\beta}{2}\int d\mathbf{r}_{\alpha\beta}[g^{(2)}_{\alpha\beta}(r_{\alpha\beta})\ln g^{(2)}_{\alpha\beta}(r_{\alpha\beta}) - g^{(2)}_{\alpha\beta}(r_{\alpha\beta}) + 1] \\ &\quad - \sum_{\alpha=1}^{\nu}\sum_{\beta=1}^{\nu}\sum_{\gamma=1}^{\nu}\frac{\rho_\alpha\rho_\beta\rho_\gamma}{6V}\int d\mathbf{r}_\alpha\int d\mathbf{r}_\beta\int d\mathbf{r}_\gamma\,\Bigg\{g^{(3)}_{\alpha\beta\gamma}(\mathbf{r}_\alpha,\mathbf{r}_\beta,\mathbf{r}_\gamma)\ln\left[\frac{g^{(3)}_{\alpha\beta\gamma}(\mathbf{r}_\alpha,\mathbf{r}_\beta,\mathbf{r}_\gamma)}{g^{(2)}_{\alpha\beta}(\mathbf{r}_{\alpha\beta})g^{(2)}_{\beta\gamma}(\mathbf{r}_{\beta\gamma})g^{(2)}_{\alpha\gamma}(\mathbf{r}_{\alpha\gamma})}\right] \\ &\qquad - g^{(3)}_{\alpha\beta\gamma}(\mathbf{r}_\alpha,\mathbf{r}_\beta,\mathbf{r}_\gamma) + g^{(2)}_{\alpha\beta}(r_{\alpha\beta})g^{(2)}_{\beta\gamma}(r_{\beta\gamma})g^{(2)}_{\alpha\gamma}(r_{\alpha\gamma})\Bigg\} \\ &\quad + \frac{1}{2\rho^{\mathcal{B}}(2\pi)^3}\int d\mathbf{k}[\ln|\,\mathbf{I}+\tilde{\mathbf{H}}(k)\,| + \tfrac{1}{2}\,\mathrm{Tr}\tilde{\mathbf{H}}^2(k) - \mathrm{Tr}\tilde{\mathbf{H}}(k)] + \sum_{i=4}^{\infty}S'_{\mathrm{mix}}(i)[\{g^{(m)}_{\alpha\beta\ldots}\};\ m\le i]\ ,\end{aligned} \tag{A2}$$

where $\mathbf{I}$ is the $\nu\times\nu$ identity matrix,

$$\tilde{\mathbf{H}}(k)_{\alpha\beta} \equiv \rho_\alpha^{1/2}\tilde{h}_{\alpha\beta}(k)\rho_\beta^{1/2}$$

is the total correlation function, and $S'_{\mathrm{mix}}(i)$ is the multicomponent analog of the remainder term $S'(i)$ in Eq. (6).

Using the multicomponent version of Eq. (1), the grand potential functional may be constructed from the above energy and entropy functionals and the chemical potentials of the ν components. Setting the $S'_{\mathrm{mix}}(i)$ equal to zero for $i \geq 4$, and minimizing the resulting $\beta\Omega$ with respect to $g^{(3)}_{\alpha\beta\gamma}(\mathbf{r}_\alpha, \mathbf{r}_\beta, \mathbf{r}_\gamma)$, $g^{(2)}_{\alpha\beta}(r_{\alpha\beta})$, and the component densities yields (1) the superposition approximation

$$g^{(3)}_{\alpha\beta\gamma}(\mathbf{r}_\alpha, \mathbf{r}_\beta, \mathbf{r}_\gamma) = g^{(2)}_{\alpha\beta}(r_{\alpha\beta}) g^{(2)}_{\beta\gamma}(r_{\beta\gamma}) g^{(2)}_{\alpha\gamma}(r_{\alpha\gamma}) e^{-\beta u^{(3)}_{\alpha\beta\gamma}(\mathbf{r}_\alpha, \mathbf{r}_\beta, \mathbf{r}_\gamma)} \, , \tag{A3}$$

(2) the HNC+3 equation for mixtures

$$\ln g^{(2)}_{\alpha\beta}(r_{\alpha\beta}) = h_{\alpha\beta}(r_{\alpha\beta}) - c_{\alpha\beta}(r_{\alpha\beta}) - \beta u^{(2)}_{\alpha\beta}(r_{\alpha\beta}) - \beta \bar{u}^{(3)}_{\alpha\beta}(r_{\alpha\beta}) \, , \tag{A4}$$

where $c_{\alpha\beta}$ is defined via the OZ equation for mixtures

$$h_{\alpha\beta}(r_{\alpha\beta}) = c_{\alpha\beta}(r_{\alpha\beta}) + \sum_{\gamma=1}^{\nu} \rho_\gamma \int d\mathbf{r}_\gamma h_{\alpha\gamma}(r_{\alpha\gamma}) c_{\beta\gamma}(r_{\beta\gamma}) \, , \tag{A5}$$

(3) and the chemical potentials

$$\beta\mu_\alpha = \ln(\rho_\alpha \Lambda^3_\alpha) - \tfrac{1}{2}[h_{\alpha\alpha}(0) - c_{\alpha\alpha}(0)] - \sum_\beta \rho_\beta \int d\mathbf{r}_{\alpha\beta} \{ \tfrac{1}{2} h^2_{\alpha\beta}(r_{\alpha\beta}) - c_{\alpha\beta}(r_{\alpha\beta}) - \tfrac{1}{2} g_{\alpha\beta}(r_{\alpha\beta}) \beta \bar{u}^{(3)}_{\alpha\beta}(r_{\alpha\beta}) \} \, , \tag{A6}$$

where

$$\beta \bar{u}^{(3)}_{\alpha\beta}(r_{\alpha\beta}) \equiv \sum_\gamma \rho_\gamma \int d\mathbf{r}_\gamma g_{\alpha\gamma}(r_{\alpha\gamma}) g_{\beta\gamma}(r_{\beta\gamma}) [e^{-\beta u^{(3)}_{\alpha\beta\gamma}(\mathbf{r}_\alpha, \mathbf{r}_\beta, \mathbf{r}_\gamma)} - 1] \, . \tag{A7}$$

Finally, substituting the above three minimum conditions into the original functional for $\beta\Omega$ yields the consistent equation for the equilibrium pressure,

$$\begin{aligned} \frac{\beta P}{\rho^{\mathcal{B}}} &= 1 + \frac{1}{2\rho^{\mathcal{B}}} \sum_{\alpha\beta} \rho_\alpha \rho_\beta \int d\mathbf{r}_{\alpha\beta} \{ h^2_{\alpha\beta}(r_{\alpha\beta}) - c_{\alpha\beta}(r_{\alpha\beta}) - \tfrac{1}{3} g_{\alpha\beta}(r_{\alpha\beta}) \beta \bar{u}^{(3)}_{\alpha\beta}(r_{\alpha\beta}) \} \\ &\quad + \frac{1}{2\rho^{\mathcal{B}}(2\pi)^3} \int d\mathbf{k} [\ln | \mathbf{I} + \tilde{\mathbf{H}}(k) | - \mathrm{Tr} \tilde{\mathbf{H}}(k)] \, . \end{aligned} \tag{A8}$$

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