

Statistical mechanical models with effective potentials: Definitions, applications, and thermodynamic consequences

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Realistic interactions that operate in condensed matter systems can exhibit complicated many-particle characteristics. However, it is often useful to seek a more economical description using at most singlet and pair effective interactions that are density dependent, to take advantage of the theoretical and computational simplifications that result. This paper analyzes the statistical mechanical formalism required to describe thermal equilibrium in that kind of approach. Two distinct interpretations are available for the role of density dependence. Either one can be treated with internal consistency, but generally they lead to differing thermodynamic predictions. One regards the density dependence of effective interactions as merely a passive index for the state at which the optimal choice of those effective interactions was determined (Case I). The other treats the density as an active variable on the same footing as particle coordinates (Case II). Virial pressure and isothermal compressibility expressions in terms of particle distribution functions are displayed for both cases. Under special circumstances it is possible for the two interpretations to yield the same pressure isotherms; the conditions producing this coincidental concordancy have been explored by means of density expansions. © 2002 American Institute of Physics.

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I. INTRODUCTION AND HISTORICAL BACKGROUND

Regardless of whether it is close to, or far from, a state of equilibrium, the behavior of any material sample depends fundamentally on the structure of its constituent particles and on their mutual interactions. For the majority of substances that command research attention in the physical and biological sciences, those structures and interactions tend to be very complex. In theory, a full characterization would require solving the Schrödinger equation for all electrons, in an arbitrary configuration of the system's nuclei, at least for the ground electronic state. In practice this is a difficult or impossible task. Both conceptual understanding and numerical studies motivate the search for a more economical description.

Quite generally, the many-particle interaction potential Φ_N that emerges from solving the Schrödinger equation for electrons can be resolved into separate one-body, two-body, ..., N -body contributions:

$$\begin{aligned} \Phi_N(\mathbf{r}_1 \cdots \mathbf{r}_N) = & \sum_i u_1(\mathbf{r}_i) + \sum_{i < j} u_2(\mathbf{r}_i, \mathbf{r}_j) \\ & + \sum_{i < j < k} u_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + \cdots + u_N(\mathbf{r}_1 \cdots \mathbf{r}_N). \end{aligned} \quad (1.1)$$

We have assumed for simplicity here that only a single species is present (the multicomponent generalization is straightforward), and \mathbf{r}_i comprises all nuclear positions of the i th particle. Also, the zero of energy for Φ_N has been chosen to correspond to widely separated particles, all in their lowest-energy conformation. In the event that structureless particles were under consideration, u_1 would vanish identically except near confining container walls. The requirement that Eq. (1.1) be satisfied identically for all N , with the same functions u_i , uniquely determines these component functions.

The scientific literature reveals many theoretical proposals to replace the exact many-body potential (1.1) with a mathematically simpler, and therefore more tractable, form Φ_N^* while attempting to retain physical essentials. The most popular approach approximates Φ_N with a linear combination of (at most) "effective" one-body and two-body interactions,

$$\Phi_N \cong \Phi_N^* = \sum_i u_1^*(\mathbf{r}_i) + \sum_{i < j} u_2^*(\mathbf{r}_i, \mathbf{r}_j). \quad (1.2)$$

Of course some criterion must be advanced for the selection of the u_i^* 's, including specification of the function search space. The results generally will depend on temperature T , system volume V , and either N (closed system) or chemical potential μ (open system), presuming that the system is close

to a state of thermal equilibrium. So far as the present investigation is concerned, we shall assume that isothermal conditions apply, and thus shall concentrate on the effects of V and N . The implications of temperature dependence for effective interactions will be reserved for later consideration.

Early proposals for effective pair potentials assumed that the full expansion (1.1) converged rapidly with respect to order, and that terms beyond three-body contributions could be neglected. This assumption was viewed as well justified for insulating atomic and molecular systems (e.g., noble gases, water, saturated hydrocarbons). One of the first proposals to invoke density-dependent pair potentials in this context was put forward by Sinanoğlu;¹⁻³ it utilized invariance of the thermodynamic energy as its basic criterion. Rushbrooke and Silbert⁴ adopted a contrasting strategy, which was also followed by Rowlinson and collaborators,⁵⁻⁷ that the effective pair interaction should reproduce the pair correlation function of the system with the full many-body potential. Neither of these approaches assumed that it was necessary to consider a u_1^* differing from u_1 .

In the event that the particles of the system bear permanent electrostatic charges, local polarization effects become important, and confer an intrinsically many-body character on the true interaction Φ . For molten salts⁸ the obvious and traditional way to simplify induced polarization involves renormalizing the bare Coulomb interactions by the inverse of D_∞ , the density-dependent high-frequency dielectric constant. For some purposes it may be desirable to include Born cavity energies for each ion.⁹

The case of highly polar, but electrostatically neutral, molecules presents an analogous situation. The modeling of water and aqueous solutions provides an obvious and significant application area. The presence of large multipole moments on the bare molecules induces excess electrostatic moments, whose influence affects the choice of an effective pair potential, and requires inclusion of effective self-energy terms.¹⁰

Molten metals¹¹⁻¹³ and semiconductors^{14,15} present another broad class of substances for which effective interactions offer a useful modeling tool. For these cases, valence and conduction band electrons dominate the underlying physics, and their thermal excitations (to excited electronic states) generally confer additional temperature dependence upon the effective interactions, beyond what would be present for insulating substances.

Assuming that nuclear motions and local order in a substance of interest obey classical statistical mechanics, the corresponding canonical partition function can be interpreted as an inner product. This tactic generates a variational criterion for selection of a “best” effective pair potential, regardless of how rapidly expression (1.1) converges.¹⁶ Such a variational approach in principle accounts for particle correlations of all orders by optimally approximating the full-potential multidimensional Boltzmann factor. Furthermore it can serve as the basis for developing density expansions of effective interactions.¹⁷

In addition to the examples just mentioned, another source of density-dependent pair interactions arises in a purely theoretical context. This is the “iso- $g^{(2)}$ ” process that

seeks a continuous variation in the pair potential, as the number density ρ of the entire system changes, so that the short-range order expressed by the pair correlation function $g^{(2)}$ remains invariant.¹⁸ The density range over which this invariance can be maintained offers some insight into the statistical geometry of particle packing.

Yet another source of density-dependent effective pair potentials has emerged from an adaptation^{19,20} of the so-called “reverse Monte Carlo” procedure.^{21,22} This approach starts with a given pair distribution function at fixed number density, often determined experimentally for a real substance, and then applies an iterative statistical algorithm to extract a pair potential that would produce the given distribution function at the same temperature and density. Consequently, the final objective is the same as that of the Rushbrooke and Silbert work mentioned above.⁴ The presence of many-body interactions in the initial system can be expected to induce temperature and density effects on the outcome of this procedure.

A substantial group of published works²³⁻²⁶ has dealt with consistency issues that appear to arise in statistical mechanics in the presence of density-dependent effective interactions. Specifically, this involves reconciling the Ornstein–Zernike expression for isothermal compressibility²⁷ [i.e., the structure function $S(k)$ for $k \rightarrow 0$] with the Clausius virial theorem for pressure, extended to the case of density-dependent pair interactions. This issue also forms a major subject of the present paper.

Two opposing viewpoints are possible when using nominally density-dependent effective interactions. On the one hand, if interest only requires modeling a given substance over a narrow density range, it may suffice to determine an effective interaction only at the midpoint of that range, and then subsequently to treat the resulting effective interaction as though it were density independent. Within this interpretation the compressibility formula and the Clausius virial theorem in its conventional form are automatically consistent. On the other hand, density dependence of effective interactions can be regarded as an intrinsic property of a model, under experimental control by varying the system volume (closed system), or by varying the chemical potential (open system). This second viewpoint requires modification of the Clausius virial relation,^{8,23-27} and thus requires a reinterpretation of the Ornstein–Zernike compressibility formula. Both viewpoints can be independently developed as thermodynamically consistent formalisms, but they generally yield distinct predictions. It is not always possible *a priori* to decide which approach is preferable; the choice depends on the application.

The principal objective of the present paper is to examine formal aspects of these contrasting viewpoints, and to show that each is internally consistent. The following Sec. II reviews some general statistical mechanical formulas needed for our analysis. Section III considers the well-known mean-field approximation, perhaps the simplest example of an effective interaction model. The aforementioned iso- $g^{(2)}$ process is revisited in Sec. IV, emphasizing how the two interpretations (viewpoints) lead to different thermodynamic predictions. Section V demonstrates the existence of a math-

emathical constraint on effective interactions that, if implemented, would enforce equality between the thermodynamic predictions that emerge from the two alternative viewpoints. The final Sec. VI presents conclusions and discusses some related matters. We have also included an Appendix devoted to rigid sphere models with density-dependent effective collision diameters.

II. GENERAL RELATIONS

The canonical ensemble offers the most convenient statistical mechanical setting in which to develop our analysis. In the interest of simplicity, it will be supposed in the following that N identical structureless particles reside in volume V , at inverse temperature $\beta = 1/k_B T$, and that they are subject to periodic boundary conditions. Given an effective potential Φ_N^* , the corresponding canonical partition function has the following form:²⁸

$$Z_N(\beta, V) = (\lambda_T^{3N} N!)^{-1} Y_N(\beta, V), \quad (2.1)$$

$$Y_N(\beta, V) = \int_V d\mathbf{r}_1 \cdots \int_V d\mathbf{r}_N \exp[-\beta \Phi_N^*(\mathbf{r}_1 \cdots \mathbf{r}_N)],$$

where λ_T is the mean thermal deBroglie wavelength. Connection to thermodynamics occurs through the Helmholtz free energy F , which is obtained from Z_N ,

$$-\beta F(N, \beta V) = \ln Z_N(\beta, V). \quad (2.2)$$

In particular, this connection can serve as the starting point for developing various thermodynamic functions in density power series, i.e., in cluster expansions.²⁹

As a result of the free translation permitted by the periodic boundary conditions, the particle density will be strictly constant throughout the system. This will be true for all phases that might be present, either singly or in coexistence, and whether those phases are fluid or crystalline. Particle configurational order is revealed by the correlation functions $g^{(n)}$ of orders $n > 1$, whose definition in the effective-interaction canonical ensemble is substantially identical in form to that for conventional (density independent) interactions:³⁰

$$g^{(n)}(\mathbf{r}_1 \cdots \mathbf{r}_N) = \frac{V^n N!}{N^n (N-n)! Y_N} \int_V d\mathbf{r}_{n+1} \cdots \int_V d\mathbf{r}_N \times \exp[-\beta \Phi_N^*(\mathbf{r}_1 \cdots \mathbf{r}_N)]. \quad (2.3)$$

Periodic boundary conditions ensure that all $g^{(n)}$ possess translational invariance; rotational invariance can only be expected for homogeneous fluid phases in the large system limit.

As pointed out in Sec. I, two distinct meanings, or interpretations, can be attached to the density dependence of effective interactions Φ_N^* . To keep these cases separate, we shall use correspondingly distinct notations.

Case I. This involves prior determination of an optimal effective interaction, using input data for the system of interest, at number density ρ_d . We denote that effective interaction by $\Phi_N^*(\mathbf{r}_1 \cdots \mathbf{r}_N | \rho_d)$. The vertical bar isolates ρ_d from the configurational variables to emphasize that this quantity serves only as an index or identifier for the optimization

process. Subsequent usage of $\Phi_N^*(\mathbf{r}_1 \cdots \mathbf{r}_N | \rho_d)$ for theoretical modeling or computer simulation would not necessarily be restricted to number density ρ_d , but could in principle entail any other number density $\rho \neq \rho_d$. One must also bear in mind that a series of similar optimizations could also be accomplished, each belonging to a discrete set or a continuous range of ρ_d 's; but for any one of these the corresponding ρ_d serves only as an index to the optimization, and implies no density commitment for subsequent application. For that reason, we can refer to ρ as merely a "passive" variable.

Case II. This alternative treats ρ as a true independent variable for the effective interactions, on the same mathematical footing as $\mathbf{r}_1 \cdots \mathbf{r}_N$. Consequently, for this case we write $\Phi_N^*(\mathbf{r}_1 \cdots \mathbf{r}_N, \rho)$. "Experimental" control over this ρ can be exercised by varying either N , or V , or both. By contrast with the preceding Case I, ρ now plays the role of an "active" variable.

Suppose for the moment that the passive- ρ Case I interpretation is applicable, with just one-particle and two-particle effective interactions, as suggested earlier in Eq. (1.2), and which we now rewrite as follows:

$$\Phi_N^*(\mathbf{r}_1 \cdots \mathbf{r}_N | \rho_d) = N u_1^*(|\rho_d) + \sum_{i < j} u_2^*(r_{ij} | \rho_d). \quad (2.4)$$

In writing this expression we have recognized that all u_1^* 's are identical and position independent, and we have followed the conventional assumption that the u_2^* 's are spherically symmetric. In this circumstance, the usual Clausius virial relation gives the pressure p , with no contribution from the singlet interactions u_1^* . Whether it is inferred from a time-averaged virial quantity, or by applying a volume scaling to the canonical partition function,³¹ the resulting expression for the pressure is the following:

$$\beta p = \rho - (\beta \rho^2 / 6) \int d\mathbf{r}_{12} r_{12} [du_2^*(r_{12} | \rho_d) / dr_{12}] \times g^{(2)}(r_{12}, \rho, \beta). \quad (2.5)$$

Furthermore, the Ornstein-Zernike relation²⁷ that connects the isothermal compressibility

$$\kappa_T = -(\partial \ln V / \partial p)_{N, \beta} \quad (2.6)$$

to local density fluctuations via $g^{(2)}$ is also valid for Case I:

$$\rho \kappa_T / \beta = 1 + \rho \int d\mathbf{r}_{12} [g^{(2)}(\mathbf{r}_{12}, \rho, \beta) - 1]. \quad (2.7)$$

It must be stressed that the pair correlation function $g^{(2)}$ to be inserted in this relation must be the infinite-system limit function (for which the large- r_{12} asymptote is indeed 1), and the upper integration limit is then allowed to pass to infinity. The logical consistency between the two expressions (2.5) and (2.7) that involve the pressure is just the same as for conventional statistical mechanical models with true density-independent pair potentials (e.g., the Lennard-Jones 12-6 potential model).

The active- ρ Case II provides an illuminating contrast. The analog of Eq. (2.4) for this alternative is

$$\Phi_N^*(\mathbf{r}_1 \cdots \mathbf{r}_N, \rho) = N u_1^*(\rho) + \sum_{i < j} u_2^*(r_{ij}, \rho). \quad (2.8)$$

The explicit density dependences of the effective singlet and pair interactions appearing here generate additional terms contributing to the pressure in its virial-theorem form^{8,23,24,26}

$$\beta p = \rho + \beta \rho^2 \frac{d u_1^*(\rho)}{d \rho} + \frac{\beta \rho^3}{2} \int d\mathbf{r}_{12} \left[\frac{\partial u_2^*(r_{12}, \rho)}{\partial \rho} - \frac{r_{12}}{3 \rho} \frac{\partial u_2^*(r_{12}, \rho)}{\partial r_{12}} \right] g^{(2)}(r_{12}, \rho, \beta). \quad (2.9)$$

The existence of the new terms reflects the additional isothermal reversible work that must be performed, while changing volume V , in order to modify the interactions among any fixed set of particles in the interior of the system.

Unless the new Case II (active ρ) contributions to the pressure accidentally sum to zero over the density range of interest (see Sec. V below), the isothermal compressibility κ_T will be modified from its Case I (passive ρ) counterpart. However it is important to realize that correlation functions $g^{(n)}$, Eq. (2.3), are identical for the two classes of effective interactions $\Phi_N^*(\mathbf{r}_1 \cdots \mathbf{r}_N | \rho_d = \rho)$ and $\Phi_N^*(\mathbf{r}_1 \cdots \mathbf{r}_N, \rho)$, provided that the configuration-variable dependences of these two alternatives are the same. In other words, short- and long-range particle order in the system under fixed N, V, β conditions cannot depend on whether the effective interactions would, or would not, change if V were to be changed. The implication is that the Ornstein–Zernike relation (2.7) generally will not yield the correct κ_T for Case II.

III. MEAN FIELD APPROXIMATION

One of the simplest, and most familiar, examples of effective interactions emerges from the mean field approximation. Within the domain of classical statistical mechanics for continuum systems, this approximation usually appears in connection with a strategy to separate the full N -body potential into short-range (s) and long-range (l) components. Such a separation implicitly underlies the venerable van der Waals equation of state,³² as well as the more modern revision created by Longuet-Higgins and Widom.³³

Suppose that the initial N -body potential consisted only of pair terms, and let the separated form be written

$$\Phi_N(\mathbf{r}_1 \cdots \mathbf{r}_N) = \sum_{i < j} [u_2^{(s)}(r_{ij}) + u_2^{(l)}(r_{ij})]. \quad (3.1)$$

Here it will be supposed that $u_2^{(l)}$ comprises of primarily attractive interactions, and is bounded and integrable,

$$4 \pi \int_0^\infty r^2 u_2^{(l)}(r) dr = -2A. \quad (3.2)$$

The basic idea of the mean field approximation is to postulate that $u_2^{(l)}$ is pointwise sufficiently weak so as to have negligible effect on structure, but sufficiently long ranged so that it encompasses a macroscopic domain of neighbor particles (whose number therefore scales with the overall density ρ). If that is the case, then the entire set of long-range

pair interactions appearing in Eq. (3.1) can be replaced by density-dependent singlet effective interactions,

$$\sum_{i < j} u_2^{(l)}(r_{ij}) \cong \sum_{i=1}^N u_1^*(i), \quad (3.3)$$

$$u_1^*(i) = -A\rho.$$

This approximation can be generated as the leading perturbation term in a suitably crafted systematic expansion, the so-called γ expansion.^{34,35}

In view of the fact that u_1^* is independent of position within the system, an alternative (but equivalent) formulation of the mean field approximation is to replace Eq. (3.3) by the following:

$$\sum_{i < j} u_2^{(l)}(r_{ij}) \cong \sum_{i < j} u_2^{(l)*}(i, j), \quad (3.4)$$

$$u_2^{(l)*}(i, j) = [u_1^*(i) + u_1^*(j)] / (N - 1) = -2A\rho / (N - 1).$$

In other words, the collection of long-range attractive interactions becomes replaced by position-independent, very weak pair interactions. For either formulation, the effective interaction for the entire N -body system is

$$\Phi_N^* = \sum_{i < j} u_2^{(s)}(r_{ij}) - NA\rho. \quad (3.5)$$

The standard interpretation of the mean field approximation conforms to Case II of the preceding Sec. II. That is, ρ becomes a true “active” variable in the N -body potential function, which in the notational convention introduced earlier would be written $\Phi_N(\mathbf{r}_1 \cdots \mathbf{r}_N, \rho)$. Consequently the pressure should be evaluated from the extended form of the virial expression, Eq. (2.9), with the familiar result equal to that for the short-range-interaction system ($p^{(s)}$) supplemented by the mean field correction

$$p(\rho, \beta) = p^{(s)}(\rho, \beta) - A\rho^2. \quad (3.6)$$

Under the assumption that the short-range interactions are those for rigid spheres, this is just the result produced by Longuet-Higgins and Widom in their extension of the van der Waals equation.³³

The passive- ρ Case I interpretation (that is unnatural for the mean field approximation) would establish the effective interactions, whether singlet or pair, at a chosen distinguished density ρ_d , and then insist on maintaining exactly the same effective interactions at any subsequently used system number density ρ . In the notational convention defined earlier, one would write

$$\Phi_N^*(\mathbf{r}_1 \cdots \mathbf{r}_N | \rho_d) = \sum_{i < j} u_2^{(s)}(r_{ij}) - NA\rho_d. \quad (3.7)$$

The last term on the right-hand side of this expression merely amounts to a constant downward shift of all configurational energies, and can have no influence on the pressure, which is just that of the short-range-interaction system, $p^{(s)}$. The corresponding isothermal compressibility $\kappa_T^{(s)}$ would be given by the Ornstein–Zernike formula, Eq. (2.7), using the

pair correlation function for the short-range-interaction system. Note that the relation between the Case I and Case II isothermal compressibilities is as follows:

$$1/\kappa_T = 1/\kappa_T^{(s)} - 2A\rho^2. \quad (3.8)$$

In spite of the fact that the pair correlation function is the same regardless of which of Case I or Case II is invoked, it is directly relevant for evaluating isothermal compressibility only for the former; Eq. (3.8) must be used for the latter.

IV. ISO- $g^{(2)}$ PROCESSES

The introduction and examination of “iso- $g^{(2)}$ processes”^{18,36} has been motivated by the need to understand more deeply and in technical detail the connections between interparticle interactions and the equilibrium statistical correlations that they induce. As the name suggests, these processes seek to identify changes in pair potentials that manage exactly to preserve pair correlation functions as invariants as the system number density varies isothermally. Put another way, the objective is to have density change and pair potential change exert precisely canceling effects on the pair correlation function $g^{(2)}(r)$. No singlet effective interactions u_1^* are involved. Detailed studies have thus far been carried out for the rigid rod, disk, and sphere systems,¹⁸ as well as the square-well system in three dimensions.³⁶ One straightforward example of an iso- $g^{(2)}$ process would be to maintain the exact zero-density form of the pair correlation function (i.e., the Boltzmann factor for the initial pair potential) as the density increases from zero, and to inquire whether this condition can only be applied up to some maximum density $\rho^* > 0$. In the following, we will assume for convenience that the pair correlation function to be held constant has emerged from a system with pair interactions of finite range.

The pair potentials created by an iso- $g^{(2)}$ process are not effective interactions in the usual sense of having emerged from an approximation method. Nevertheless, they are density dependent, and the resulting many-body systems can be interpreted according to either the passive- ρ Case I or the active- ρ Case II protocol. The former involves a sequence of model systems with pair interactions $u_2^*(r_{ij}|\rho_d)$, each created specifically to reproduce the target $g^{(2)}$ at a given ρ_d , but only at that ρ_d . The latter envisions a single model system with pair interactions $u_2^*(r_{ij}, \rho)$ that continuously change form as the system volume varies continuously.

The structure factor is defined by

$$S(k) = 1 + \rho G(k), \quad (4.1)$$

$$G(k) = \rho \int d\mathbf{r}_{12} \exp(i\mathbf{k} \cdot \mathbf{r}_{12}) [g^{(2)}(r_{12}) - 1].$$

In an iso- $g^{(2)}$ setting, $S(k)$ becomes strictly a linear function of ρ , as does its $k \rightarrow 0$ limit, the Case I quantity $\rho\kappa_T/\beta$, Eq. (2.7). Under thermal equilibrium conditions, the structure factor obeys the restriction

$$S(k) \geq 0. \quad (4.2)$$

Consequently, if $G(k)$ has an absolute minimum that is negative at some k_{\min} ,

$$G(k_{\min}) < 0, \quad (4.3)$$

then restriction (4.2) would be violated at k_{\min} if ρ were to exceed the upper limit

$$\rho^* = -1/G(k_{\min}). \quad (4.4)$$

An important group of applications leading to an upper density limit ρ^* of the form (4.4) have $k_{\min} = 0$. In particular this occurs for the rigid sphere model where the invariant $g^{(2)}$ is that for low or vanishing density.¹⁸ This implies that the passive- ρ Case I isothermal compressibility continuously approaches zero as ρ approaches ρ^* from below, i.e., the iso- $g^{(2)}$ system becomes arbitrarily “stiff” at ρ^* . Evidently this indicates that at ρ^* the many body system has run out of particle arrangements that would be required to maintain the invariant pair correlation pattern under further density increase.

In those instances where $k_{\min} = 0$, we can expand $G(k)$ around the origin of k space as follows:

$$G(k) = G_0 + G_2 k^2 + O(k^4), \quad (4.5)$$

$$G_0 < 0, \quad G_2 > 0.$$

This can then be related to the small- k behavior of the Fourier transform of the direct correlation function, $C(k)$,³⁷

$$C(k) = \frac{G(k)}{1 + \rho G(k)} = \frac{-1}{\delta\rho + (G_2/G_0^2)k^2} + O(k^4). \quad (4.6)$$

Here we have set the density deficit below ρ^* equal to $\delta\rho$,

$$\rho = \rho^* - \delta\rho. \quad (4.7)$$

When $\delta\rho$ is small, only the leading term on the right-hand side of Eq. (4.6) needs to be considered, and this term produces a large and narrow peak at the origin. An inverse Fourier transform applied to that leading term then yields the r -space form of the direct correlation function

$$\begin{aligned} c(r_{12}, \rho) &\cong (2\pi)^{-3} \int d\mathbf{k} \exp(-i\mathbf{k} \cdot \mathbf{r}_{12}) \\ &\times \{-1/[\delta\rho + (G_2/G_0^2)k^2]\} \\ &= -(G_0^2/4\pi G_2 r_{12}) \exp[-|G_0|(\delta\rho/G_2)^{1/2} r_{12}]. \end{aligned} \quad (4.8)$$

This Yukawa function continuously loses its exponential damping upon approach to the upper density limit ρ^* . The $O(k^4)$ terms neglected in Eq. (4.8) can be expected to add short-range corrections to this long-range Yukawa result.

The Percus–Yevick (PY)³⁸ and the hypernetted chain (HNC)³⁹ approximations supply connections between the direct correlation function and the pair interactions that are present to produce it. Both approximations agree that in the asymptotic large-distance regime,

$$c(r_{12}, \rho) \sim -\beta u_2^*(r_{12}). \quad (4.9)$$

Equation (4.8) above then implies that u_2^* will adopt a repelling Yukawa form at large separations, which in the $\rho \rightarrow \rho^*$ limit becomes Coulombic,

$$u_2^*(r_{12}|\rho), u_2^*(r_{12}, \rho) \sim (G_0^2/4\pi\beta G_2 r_{12}) \times \exp[-|G_0|(\delta\rho/G_2)^{1/2}r_{12}]. \tag{4.10}$$

With either the Case I or Case II interpretation, this long-range effective pair potential has a dominating influence on the system pressure. For the passive- ρ Case I, insertion of form (4.10) into the conventional virial expression (2.5) generates a pressure contribution that has the character of a simple-pole divergence:

$$\beta p(\rho, \beta) \sim (\rho^*)^2/2\delta\rho \quad (\text{Case I}). \tag{4.11}$$

This simple pole contribution is also present in the active- ρ Case II interpretation, of course, but it is itself dominated by a double-pole contribution that arises from the $\partial u_2^*/\partial\rho$ contribution appearing in the extended virial relation (2.9):

$$\beta p(\rho, \beta) \sim (\rho^*)^3/2(\delta\rho)^2 \quad (\text{Case II}). \tag{4.12}$$

This contrasting pair of pressure results vividly illustrates the different thermodynamic implications that can emerge from the alternative interpretations. We remind the reader that Eq. (4.11) expresses the pressure behavior of a sequence of systems indexed by ρ and each examined at its indexing ρ , whereas Eq. (4.12) refers to a single system for which ρ is a fundamental variable of the potential energy function. In view of this distinction, note that the vanishing at ρ^* of the sequence of isothermal compressibilities for Case I cannot correctly be inferred from asymptote (4.11) by differentiation with respect to density [which would erroneously suggest proportionality to $(\delta\rho)^2$]; in fact it follows from Eq. (4.1) above that the proportionality is linear in $\delta\rho$ at ρ^* :

$$\rho\kappa_T/\beta = |G_0|\delta\rho \quad (\text{Case I}). \tag{4.13}$$

V. CONCORDANCY CONDITION

Although Case I and Case II interpretations generally will produce distinct pressure predictions, special circumstances exist under which those distinctions will vanish. Identifying those circumstances proceeds from the requirement that the conventional and the extended forms of the virial expression for pressure, Eqs. (2.5) and (2.9), respectively, produce the same result. This is equivalent to demanding that the Case II interactions satisfy the condition

$$\frac{du_1^*(\rho)}{d\rho} = \frac{\rho}{2} \int d\mathbf{r}_{12} \frac{\partial u_2^*(r_{12}, \rho)}{\partial\rho} g^{(2)}(r_{12}, \rho). \tag{5.1}$$

As pointed out in Sec. III above, the singlet effective interactions u_1^* could formally be absorbed into the definition of u_2^* . Thus the concordancy condition for the two interpretations would reduce to the following:

$$0 = \int d\mathbf{r}_{12} \frac{\partial u_2^*(r_{12}, \rho)}{\partial\rho} g^{(2)}(r_{12}, \rho). \tag{5.2}$$

For the purposes of this section, however, Eq. (5.1) offers the more convenient starting point.

The singlet and pair effective interactions can both be developed into density power series

$$u_1^*(\rho) = u_{1,1}\rho + u_{1,2}\rho^2 + u_{1,3}\rho^3 + \dots, \tag{5.3}$$

$$u_2^*(r_{12}, \rho) = u_{2,0}(r_{12}) + u_{2,1}(r_{12})\rho + u_{2,2}(r_{12})\rho^2 + \dots. \tag{5.4}$$

Notice that the first of these should have no constant (ρ^0) term. The leading term of the second simply represents the “bare” pair interaction of two particles in isolation.

Under the conventional circumstances, where “true” interactions are involved that are short ranged and density independent, the pair correlation function can also be developed in a density power series using the cluster expansion technique.^{39,40} The resulting expansion can be represented in the following manner:

$$g^{(2)}(r_{12}, \rho) = \exp[-\beta u_2(r_{12})] \{1 + C^{(2,1)}(r_{12})\rho + C^{(2,2)}(r_{12})\rho^2 + \dots\}. \tag{5.5}$$

Here the $C^{(2,j)}(r_{12})$ would be ρ independent, and u_2 would be identified with $u_{2,0}$ in Eq. (5.4) above. But when ρ -dependent effective interactions are under consideration, and the cluster sums are themselves constructed using those effective interactions, a strict power series for $g^{(2)}$ would require expanding each $C^{(2,j)}$, and then collecting all terms in Eq. (5.5) with a common order in ρ . Once this is done, and all power series are inserted in Eq. (5.1) above, each ρ order generates its own constraint to enforce Case I–Case II concordancy. All constraints of orders up to ρ^n extracted from Eq. (5.1), when enforced, assure that Case I and Case II pressures will agree through order ρ^{n+2} .

The leading-order constraint [$O(\rho^0)$] from Eq. (5.1) is trivial:

$$u_{1,1} = 0, \tag{5.6}$$

and simply shows that the series (5.3) begins at quadratic order. The next order [$O(\rho)$] leads straightforwardly to the condition:

$$u_{1,2} = \frac{1}{4} \int d\mathbf{r}_{12} u_{2,1}(r_{12}) \exp[-\beta u_{2,0}(r_{12})]. \tag{5.7}$$

This last relation can be viewed as a specification of the constant $u_{1,2}$ once that $u_{2,1}(r_{12})$ has been selected. Alternatively, if interest lies in the subset of effective potentials that have only short-range pair terms (and no singlet effective interactions), then Eq. (5.7) reduces to

$$0 = \int d\mathbf{r}_{12} u_{2,1}(r_{12}) \exp[-\beta u_{2,0}(r_{12})], \tag{5.8}$$

which requires that $u_{2,1}$ be orthogonal to the bare-pair-potential Boltzmann factor.

Proceeding to the next order [$O(\rho^2)$], it is necessary to account for contributions to $g^{(2)}$ that (a) arise from $C^{(2,1)} \times (r_{12})$, and (b) arise from the already-constrained effective pair function $u_{2,1}(r_{12})$. One finds

$$u_{1,3} = \frac{1}{6} \int d\mathbf{r}_{12} \exp[-\beta u_{2,0}(r_{12})] \left\{ [2u_{2,2}(r_{12}) - \beta(u_{2,1}(r_{12}))^2] + u_{2,1}(r_{12}) \int d\mathbf{r}_3 f(r_{13})f(r_{32}) \right\}, \quad (5.9)$$

where f is the Mayer cluster bond for the bare pair interaction

$$f(r_{ij}) = \exp[-\beta u_{2,0}(r_{ij})] - 1. \quad (5.10)$$

Only the two quantities $u_{1,3}$ and $u_{2,2}(r_{12})$ make their first appearance in Eq. (5.9), and are thus constrained for the first time.

It is clear that this systematic process could be continued to higher orders, though the outcomes rise rapidly in complexity with increasing order. At $O(\rho^n)$, one has first appearances of $u_{1,n}$ and $u_{2,n-1}$. If in fact the various density expansions (5.3)–(5.5) are convergent, the resulting constrained effective interactions u_1^* and u_2^* as represented by density series (5.3) and (5.4) should produce concordant results for Case I and Case II pressures, at least up to the density of a phase transition. It should also be pointed out that if the effective pair potential $u_2^*(r_{12}, \rho)$ were a given quantity, then Eq. (5.1) could be used to determine that singlet function $u_1^*(\rho)$ which would produce Case I–Case II pressure agreement, even across phase transitions.

We close this Sec. V with a brief examination of the result obtained by applying the concordancy constraint to the iso- $g^{(2)}$ process discussed in Sec. IV. In this circumstance, the usual compressibility expression, Eq. (2.7) applies to both Case I and Case II by construction. It can be written in the form

$$\beta \left(\frac{\partial p}{\partial \rho} \right)_\beta = [1 + \rho G(0)]^{-1}, \quad (5.11)$$

where $G(0)$ is the excess pair correlation function spatial integral [Eq. (4.1)]. In view of the fact that $G(0)$ is density independent for iso- $g^{(2)}$ processes, the preceding Eq. (5.11) can immediately be integrated to yield

$$\beta p = [G(0)]^{-1} \ln[1 + \rho G(0)]. \quad (5.12)$$

In other words, the constrained version of the iso- $g^{(2)}$ process possesses an elementary explicit pressure equation of state over its full density range. Finally, it should be noted that in the limit of vanishing $G(0)$, the expression shown in Eq. (5.12) reduces identically to the ideal gas equation of state.

VI. CONCLUSIONS AND DISCUSSION

The desire to construct and analyze realistic models for technologically important substances is hindered by the complexity of the constituent particles and their interactions. For reasons of practicality, it is desirable to limit the mathematical representation of interactions to low order in particle number, for example to singlet and pair functions only. In-

corporation of the effects of real many-body interactions can often be well approximated by adroit choice of “effective” singlet and pair potentials, which generally can be expected to display both temperature and density dependence.

The present study has been concerned with the consequences of density dependence in effective potentials. Two distinct viewpoints, or interpretations, have been identified. The first (Case I) involves determination of effective interactions at a set of one or more fixed densities ρ_d , and then treating each such determination as though ρ_d were simply a nonvarying parameter; the number density ρ in a theoretical or simulational application of interest is then permitted to vary from ρ_d while treating the interaction functions as invariant quantities. The second (Case II) treats the density dependence of effective interactions as a legitimate variable in the Hamiltonian of the many-particle system, on a mathematical footing equivalent to that of particle configurational coordinates. These separate viewpoints generally produce distinct thermodynamic functions. In particular, the virial pressure appears in two different forms, Eqs. (2.5) and (2.9) for Case I and for Case II, respectively. But in spite of this distinction, both interpretations enjoy internal consistency. Which of Case I or Case II is to be the preferred interpretation in any given application cannot be decided *a priori*, but must rest upon physical details of the specific materials and phenomena under consideration.

Section V explores the possibility that imposition of suitable constraints on the space of effective interactions, at least at the singlet plus pair level, might cause the virial pressures for the Case I and Case II interpretations to become equal functions of the density. This special circumstance indeed seems to be realizable, and in the event that only short-range interactions are present, the constraints can be stepwise implemented in increasing integer orders in density. The situation is less straightforward if the particles comprised in the system bear electrostatic charges (e.g., fused salts, electrolytic solutions), because density expansions are inappropriate. This aspect of the subject deserves an in-depth examination in a future study.

Although the present work has concentrated on density as a variable, we recognize that parallel issues exist concerning temperature dependence that could arise from any procedure used to assign effective interactions. The analogs of our Case I and Case II interpretations would hinge on whether the temperature in the effective interactions were to be treated simply as an indexing parameter T_d similar to ρ_d above (from which the operative temperature could depart), or whether T were to be regarded as a “true” variable of the effective interactions, controllable through the total energy in a microcanonical ensemble. It is clear that the respective predictions of the heat capacities generally would differ, although suitably constraining the space of effective interactions should once again produce concordancy. This is another feature of the general subject whose full analysis must await a later examination.

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APPENDIX: EFFECTIVE INTERACTIONS FOR RIGID SPHERES

The purpose of this Appendix is to record a few results for the specific model of rigid spheres with density-dependent collision diameters $a(\rho)$. The conventional rigid sphere model, with a fixed collision diameter, provides the natural backdrop. The pressure for that fixed- a model can be expressed in the following form:

$$\beta p = \rho f(\rho a^3), \quad (\text{A1})$$

where f possesses a convergent power series that generates the virial series for the pressure

$$f(x) = 1 + f_1 x + f_2 x^2 + \dots \quad (\text{A2})$$

This function is related to the contact value of the rigid sphere pair correlation function as follows:⁴¹

$$f(\rho a^3) = 1 + (2\pi/3)\rho a^3 g^{(2)}(r_{12}=a, \rho a^3). \quad (\text{A3})$$

The isothermal compressibility can simply be expressed in terms of f ,

$$\rho \kappa_T / \beta = [f(\rho a^3) + \rho a^3 f'(\rho a^3)]^{-1}. \quad (\text{A4})$$

The first-order freezing transition from isotropic fluid to face-centered-cubic crystal occurs over the density range:⁴²

$$0.943 < \rho a^3 < 1.014, \quad (\text{A5})$$

and over that coexistence range f must be inversely proportional to ρ so that the pressure is constant.

The Case I interpretation simply utilizes expressions (A1)–(A5) with insertion of the density-dependent collision diameter $a(\rho)$. If this kind of effective-diameter rigid sphere model is to be realistic in its description of the freezing transition, $a(\rho)$ would have to be a constant across the coexistence range in order for the pressure to remain constant. But within either homogeneous phase interval of density, this effective diameter could have nontrivial density variation. The only requirements that must be obeyed by $a(\rho)$ are that it have a convergent density expansion,

$$a(\rho) = a_0 + a_1 \rho + a_2 \rho^2 + \dots, \quad (\text{A6})$$

to permit a pressure virial series to exist, and that the obvious close-packing condition be satisfied,

$$\rho [a(\rho)]^3 \leq 2^{1/2}. \quad (\text{A7})$$

Analysis of the Case II interpretation for the effective-diameter rigid sphere model begins with the extended form of the pressure virial expression, Eq. (2.9). The new contribution to be considered involves the density derivative of the effective pair interaction $u_2^*(r_{12}, \rho)$. Because the singular rigid sphere interaction is involved, the entire contribution to

the virial integral is concentrated at pair contact. Consequently we can make the following formal replacement involving the Dirac delta function:

$$\left(\frac{\partial \beta u_2^*(r_{12}, \rho)}{\partial \rho} \right) g^{(2)}(r_{12}, \rho) \rightarrow g^{(2)}[a(\rho)] \left(\frac{da(\rho)}{d\rho} \right) \delta[r_{12} - a(\rho)], \quad (\text{A8})$$

which is analogous to the replacement that converts the usual virial expression Eq. (2.5) to an expression involving just the contact pair correlation function Eq. (A3) above.⁴³ Equation (A8) converts Eq. (2.9) to the following:

$$\beta p = \rho \left\{ 1 + (2\pi/3)\rho a^3(\rho) g^{(2)}[a(\rho), \rho] \left[1 + \frac{d \ln a^3(\rho)}{d \ln \rho} \right] \right\} \equiv \rho F[\rho a^3(\rho)]. \quad (\text{A9})$$

From this expression it follows that the Case II compressibility is given by

$$\rho \kappa_T / \beta = \left\{ F[\rho a^3(\rho)] + \rho a^3(\rho) F'[\rho a^3(\rho)] \frac{d \ln \rho a^3(\rho)}{d \ln \rho} \right\}^{-1}. \quad (\text{A10})$$

¹O. Sinanoğlu, Chem. Phys. Lett. **1**, 340 (1967).

²O. Sinanoğlu, Adv. Chem. Phys. **12**, 283 (1967).

³T. Halcioglu and O. Sinanoğlu, J. Chem. Phys. **49**, 996 (1968).

⁴G. S. Rushbrooke and M. Silbert, Mol. Phys. **12**, 505 (1967).

⁵J. S. Rowlinson, Mol. Phys. **12**, 513 (1967).

⁶G. Casanova, R. J. Dulla, D. A. Jonah, J. S. Rowlinson, and G. Saville, Mol. Phys. **18**, 589 (1970).

⁷R. J. Dulla, J. S. Rowlinson, and W. R. Smith, Mol. Phys. **21**, 299 (1971).

⁸F. H. Stillinger, in *Molten Salt Chemistry*, edited by M. Blander (Interscience-Wiley, New York, 1964), p. 1. Note that a factor β is missing from the second term on the right-hand side of Eq. (47), p. 36.

⁹Reference 8, p. 21.

¹⁰H. J. C. Berendsen, J. R. Grigera, and T. P. Straatsma, J. Phys. Chem. **91**, 6269 (1987).

¹¹W. A. Harrison, *Pseudopotentials in the Theory of Metals* (W. A. Benjamin, New York, 1966).

¹²P. Egelstaff, *An Introduction to the Liquid State* (Academic, New York, 1967).

¹³D. Stroud and N. W. Ashcroft, Phys. Rev. B **5**, 371 (1972).

¹⁴A. Arnold, N. Mauser, and J. Hafner, J. Phys.: Condens. Matter **1**, 965 (1989).

¹⁵W. Jank and J. Hafner, Phys. Rev. B **41**, 1497 (1990).

¹⁶F. H. Stillinger, J. Phys. Chem. **74**, 3677 (1970).

¹⁷F. H. Stillinger, J. Chem. Phys. **57**, 1780 (1972).

¹⁸F. H. Stillinger, S. Torquato, J. M. Eroles, and T. M. Truskett, J. Phys. Chem. **105**, 6592 (2001).

¹⁹A. P. Lyubartsev and A. Laaksonen, Phys. Rev. E **52**, 3730 (1995).

²⁰A. P. Lyubartsev and A. Laaksonen, Comput. Phys. Commun. **121–122**, 57 (1999).

²¹R. L. McGreevy and L. Pusztai, Mol. Simul. **1**, 359 (1988).

²²D. A. Keen and R. L. McGreevy, Nature (London) **344**, 423 (1990).

²³P. Ascarelli and R. J. Harrison, Phys. Rev. Lett. **22**, 385 (1969).

²⁴W. Jones, J. Phys. C **6**, 2833 (1973).

²⁵N. G. Almarza, E. Lomba, G. Ruiz, and C. F. Tejero, Phys. Rev. Lett. **86**, 2038 (2001).

²⁶J. Hafner, *From Hamiltonians to Phase Diagrams* (Springer-Verlag, New York, 1987), p. 342.

²⁷L. S. Ornstein and F. Zernike, Phys. Z. **27**, 761 (1926).

²⁸T. L. Hill, *Statistical Mechanics* (McGraw-Hill, New York, 1956), p. 91, Eq. (16.67).

- ²⁹J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (Wiley, New York, 1940), Chap. 13.
- ³⁰Reference 27, Chap. 6.
- ³¹J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954), p. 134.
- ³²Reference 27, Chap. 12.
- ³³H. C. Longuet-Higgins and B. Widom, *Mol. Phys.* **8**, 549 (1964).
- ³⁴P. C. Hemmer, *J. Math. Phys.* **5**, 75 (1964).
- ³⁵J. L. Lebowitz, G. Stell, and S. Baer, *J. Math. Phys.* **6**, 1282 (1965).
- ³⁶H. Sakai, S. Torquato, and F. H. Stillinger, *J. Chem. Phys.* **117**, 297 (2002), following paper.
- ³⁷J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, New York, 1976), p. 101.
- ³⁸J. K. Percus and G. J. Yevick, *Phys. Rev.* **110**, 1 (1958).
- ³⁹J. M. J. Van Leeuwen, J. Groeneveld, and J. De Boer, *Physica (Amsterdam)* **25**, 792 (1959).
- ⁴⁰S. A. Rice and P. Gray, *The Statistical Mechanics of Simple Liquids* (Interscience, New York, 1965), Chap. 2.
- ⁴¹Reference 28, p. 216.
- ⁴²W. G. Hoover and F. H. Ree, *J. Chem. Phys.* **49**, 3609 (1968).
- ⁴³Reference 28, p. 214.