

Density Expansions for Effective Pair Potentials

FRANK H. STILLINGER

Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey 07974

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The leading density dependence for the variationally defined effective pair potential v is derived, using van Kampen's product technique to evaluate the multidimensional configuration integrals that arise. This function v is compared in that density order to two other effective pair potentials that have been proposed, and it is shown to be the only one that simultaneously reduces both free energy and pair correlation errors to quadratic order in the magnitude of triplet nonadditivity. The signs of density shifts in v at low temperature are analyzed for noble gases and for water in various configurations, and a reasonable arbitrary-density approximation to v is suggested that may have utility in simulation of liquids by rapid electronic computer.

I. INTRODUCTION

The interaction potential V_N for a system of N molecules possesses an unique resolution into inherent pair ($V^{(2)}$), triplet ($V^{(3)}$), quadruplet ($V^{(4)}$), \dots contributions,

$$V_N(\mathbf{x}_1 \cdots \mathbf{x}_N) = \sum_{i < j=1}^N V^{(2)}(\mathbf{x}_i, \mathbf{x}_j) + \sum_{i < j < k=1}^N V^{(3)}(\mathbf{x}_i, \mathbf{x}_j, \mathbf{x}_k) \\ + \sum_{i < j < k < l=1}^N V^{(4)}(\mathbf{x}_i, \mathbf{x}_j, \mathbf{x}_k, \mathbf{x}_l) + \cdots \\ + V^{(N)}(\mathbf{x}_1 \cdots \mathbf{x}_N). \quad (1.1)$$

Here the vector \mathbf{x}_i comprises components describing all relevant position and orientation coordinates for molecule i . The separate functions $V^{(n)}$, $2 \leq n$, may be defined recursively in terms of the total N -molecule potentials V_N , by requiring $V^{(n)}$ to represent the portion of V_N not attributable to proper subsets of the chosen n molecules. Specifically, one has

$$V^{(2)}(\mathbf{x}_i, \mathbf{x}_j) = V_2(\mathbf{x}_i, \mathbf{x}_j), \quad (1.2)$$

$$V^{(3)}(\mathbf{x}_i, \mathbf{x}_j, \mathbf{x}_k) = V_3(\mathbf{x}_i, \mathbf{x}_j, \mathbf{x}_k) - V^{(2)}(\mathbf{x}_i, \mathbf{x}_j) \\ - V^{(2)}(\mathbf{x}_i, \mathbf{x}_k) - V^{(2)}(\mathbf{x}_j, \mathbf{x}_k), \quad (1.3)$$

and in general ($1 \leq i_a \leq n$)

$$V^{(n)}(i_1, i_2, \dots, i_n) = V_n(i_1, i_2, \dots, i_n) \\ - \sum_{j=2}^{n-1} \sum_{\alpha_1 < \alpha_2 < \dots < \alpha_j=1}^n V^{(j)}(\alpha_1, \alpha_2, \dots, \alpha_j). \quad (1.4)$$

A basic tenet in conventional statistical mechanics of the condensed states is that the series (1.1) is dominated by its leading terms, the pair interactions, so that succeeding terms may be neglected. Of course this is never strictly valid, but still it seems plausible that for an important class of nonpolar substances the major qualitative aspects of molecular motions and arrangements as well as thermodynamic properties can be accounted for with $V^{(2)}$ alone. By suppressing nonadditivity in V_N for these simple materials, the formal statistical mechanical theory may be developed in relatively compact form.^{1,2} Furthermore the computer simulation of classical many-body systems by either the Monte Carlo³ or the molecular dynamics⁴ method is

substantially facilitated by assuming V_N to be pairwise additive.

In view of these facts it is hardly surprising to see the emergence of attempts to retain many-molecule interactions for precision within the convenient format of pair additivity, using "effective pair potentials." The first direct approach along these lines seems to have been initiated by Sinanoğlu and his collaborators.⁵⁻⁸ Their basic requirement was that the correct mean energy be reproduced by using their effective pair potential v_S . In the event that nonadditivity arises solely from the triplet potential $V^{(3)}$, they propose for a pure substance to set

$$v_S(\mathbf{x}_1, \mathbf{x}_2) = V^{(2)}(\mathbf{x}_1, \mathbf{x}_2) + (\rho^{(1)}/3) \int V^{(3)}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) \\ \times [g^{(3)}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3)/g^{(2)}(\mathbf{x}_1, \mathbf{x}_2)] d\mathbf{x}_3, \quad (1.5)$$

where $\rho^{(1)}$ is the singlet molecular density,

$$\rho^{(1)} = N/\Omega, \quad \Omega = \int d\mathbf{x}, \quad (1.6)$$

and the $g^{(n)}$ are the infinite-system-limit molecular correlation functions,⁹ which refer to the initial system with nonadditivity. Equation (1.5) illustrates the general density and (through $g^{(2)}$ and $g^{(3)}$) temperature dependence to be expected for effective pair potentials.

It was pointed out in Ref. 8 that the formal partition function $Z_N\{\sum v_S\}$ constructed from the effective pair potential leads to mean energy and entropy which differ from the system's exact quantities only in second and higher orders in the difference.

$$V_N - \sum v_S(ij). \quad (1.7)$$

Although this may bring assurance for most cases of interest that thermodynamic behavior is adequately handled, it still leaves open the question about how realistic the molecular correlation functions produced by $\sum v_S$ will be. This problem is particularly vexing in the face of realization that the specific form (1.5) is not unique in reproducing the thermodynamic energy.

For purposes of later comparison, we note that v_S has the following density development ($\beta = 1/k_B T$):

$$v_S(\mathbf{x}_1, \mathbf{x}_2) = V^{(2)}(\mathbf{x}_1, \mathbf{x}_2) + (\rho^{(1)}/3) \int V^{(3)}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) \\ \times \exp[-\beta V^{(2)}(\mathbf{x}_1, \mathbf{x}_3) - \beta V^{(2)}(\mathbf{x}_2, \mathbf{x}_3) - \beta V^{(3)}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3)] d\mathbf{x}_3 \\ + O[(\rho^{(1)})^2]. \quad (1.8)$$

The opposite philosophy in definition of an effective pair potential was advocated by Rushbrooke and Silbert,¹⁰ and exploited by Rowlinson and his co-workers.¹¹⁻¹³ They required that the model system interacting through the pairwise sum of effective pair potentials v_R possess the same pair correlation function that obtains in the starting system with the full V_N . The density development, corresponding to Eq. (1.8) for v_S , was found to be¹⁴

$$\begin{aligned} v_R(\mathbf{x}_1, \mathbf{x}_2) &= V^{(2)}(\mathbf{x}_1, \mathbf{x}_2) - (\rho^{(1)}/\beta) \\ &\times \int \exp[-\beta V^{(2)}(\mathbf{x}_1, \mathbf{x}_3) - \beta V^{(2)}(\mathbf{x}_2, \mathbf{x}_3)] \\ &\times \{ \exp[-\beta V^{(3)}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3)] - 1 \} d\mathbf{x}_3 + O[(\rho^{(1)})^2]. \end{aligned} \quad (1.9)$$

Obviously Eqs. (1.8) and (1.9) do not agree, and in particular the formal partition function $Z_N\{ \sum v_R \}$ will commit first-order errors in energy and entropy with respect to the difference,

$$V_N - \sum v_R(ij). \quad (1.10)$$

That different choices of basic properties for the starting system would lead to distinct definitions of effective pair potentials was discussed in detail in Ref. 12.

A way out of this apparent nonuniqueness problem was recently proposed,¹⁵ which leads to yet another effective pair potential definition. This proposal is based upon a representation of the exact partition function $Z_N\{ V_N \}$ in terms of an inner product,

$$\begin{aligned} Z_N\{ V_N \} &= Z_N\{ 0 \} [\Omega^{-N} \int d\mathbf{x}_1 \cdots \int d\mathbf{x}_N \exp(-\beta V_N)] \\ &= Z_N\{ 0 \} \{ \exp(-\beta V_N/2), \exp(-\beta V_N/2) \}, \end{aligned} \quad (1.11)$$

where $Z_N\{ 0 \}$ is the partition function for noninteracting molecules, and the inner product is defined by¹⁶

$$\langle h_1, h_2 \rangle = \Omega^{-N} \int d\mathbf{x}_1 \cdots \int d\mathbf{x}_N h_1(\mathbf{x}_1 \cdots \mathbf{x}_N) h_2(\mathbf{x}_1 \cdots \mathbf{x}_N). \quad (1.12)$$

The importance of the inner product is that it implies a natural definition of the "distance" D between two functions,¹⁶

$$\begin{aligned} D(h_1, h_2) &\geq 0, \\ D^2(h_1, h_2) &= \{ h_1 - h_2, h_1 - h_2 \} \\ &= \Omega^{-N} \int d\mathbf{x}_1 \cdots \int d\mathbf{x}_N [h_1(\mathbf{x}_1 \cdots \mathbf{x}_N) \\ &\quad - h_2(\mathbf{x}_1 \cdots \mathbf{x}_N)]^2. \end{aligned} \quad (1.13)$$

In particular, then, we can assess the quality of an approximation to the function,

$$h_1(\mathbf{x}_1 \cdots \mathbf{x}_N) = \exp[-\beta V_N(\mathbf{x}_1 \cdots \mathbf{x}_N)/2], \quad (1.14)$$

in the form of the equivalent Boltzmann factor for an additive effective potential,

$$h_2(\mathbf{x}_1 \cdots \mathbf{x}_N) = \exp[-\beta \sum_{i < j=1}^N v(\mathbf{x}_i, \mathbf{x}_j)/2], \quad (1.15)$$

by computing the distance $D(h_1, h_2)$.

Through the expression (1.11) for the partition function, we can regard the Boltzmann function h_1 in Eq. (1.14) as the fundamental generating function for the classical many-body problem in hand. Subsequently it is obvious that the optimal choice for an effective pair potential v will be the one which minimizes $D^2(h_1, h_2)$. Hence it was suggested in Ref. 15 that v should be determined by the explicit variational criterion,

$$\begin{aligned} \min &= \Omega^{-N} \int d\mathbf{x}_1 \cdots \int d\mathbf{x}_N \{ \exp\{-\frac{1}{2}\beta V_N(\mathbf{x}_1 \cdots \mathbf{x}_N)\} \\ &\quad - \exp\{-\frac{1}{2}\beta \sum_{i < j=1}^N v(\mathbf{x}_i, \mathbf{x}_j)\} \}^2. \end{aligned} \quad (1.16)$$

After carrying out the functional derivative with respect to v , one obtains the following Euler equation for determination of v :

$$\begin{aligned} \Omega^{2-N} \int d\mathbf{x}_3 \cdots \int d\mathbf{x}_N \\ \times \exp\{-\frac{1}{2}\beta [V_N(\mathbf{x}_1 \cdots \mathbf{x}_N) + \sum_{i < j=1}^N v(\mathbf{x}_i, \mathbf{x}_j)]\} \\ = \Omega^{2-N} \int d\mathbf{x}_3 \cdots \int d\mathbf{x}_N \exp[-\beta \sum_{i < j=1}^N v(\mathbf{x}_i, \mathbf{x}_j)]. \end{aligned} \quad (1.17)$$

The primary goal in this paper is to derive a density expansion for v to compare with those for v_S and v_R .

It is easy to show¹⁵ that the v defined by criterion (1.17) eliminates from thermodynamic functions first-order errors in the difference

$$V_N - \sum v(ij), \quad (1.18)$$

and to that extent v enjoys the same advantage that v_S does. But additionally the variational requirement (1.16) forces v to regenerate molecular correlations optimally over the full multidimensional configuration space for the system. No equivalent restraint operates on v_S .

Although v_R formally reproduces the correct $g^{(2)}$, it is rather uncertain to what degree $g^{(3)}$, $g^{(4)}$, \dots are distorted by replacement of V_N by $\sum v_R$. By contrast v treats all $g^{(n)}$ without special bias, since it is the fundamental Boltzmann function h_1 from which all are obtained by contraction that is being globally approximated. In view of application of the effective pair potential concept to highly structured materials such as water,¹⁷ it seems unwise to place full emphasis on $g^{(2)}$ to the exclusion of the more informative higher-order $g^{(n)}$.

Section II provides the formal density expansion for the Helmholtz free energy in the presence of non-additivity. Although this result is hardly new, its derivation here provides a didactically convenient entry point to our subject, and serves in the interest of expository unity. We follow this in Sec. III with the actual deduction of the v density series leading terms. Section IV judges the merit of each of v_S , v_R , and v in terms of the corresponding Hilbert space distance D . The final section, V provides some further ideas on the

general character of v and its application to specific materials.

II. HELMHOLTZ FREE ENERGY EXPANSION

The partition function (1.11) determines the Helmholtz free energy F ,

$$\beta F\{V_N\} = \beta F\{0\} - \ln[\Omega^{-N} \int d\mathbf{x}_1 \cdots \int d\mathbf{x}_N \exp(-\beta V_N)]$$

$$\equiv \beta F\{0\} - \ln \langle \exp(-\beta V_N) \rangle; \tag{2.1}$$

$$\beta F\{0\} = -\ln Z_N\{0\}; \tag{2.2}$$

$$\langle l \rangle = \Omega^{-N} \int d\mathbf{x}_1 \cdots \int d\mathbf{x}_N l(\mathbf{x}_1 \cdots \mathbf{x}_N). \tag{2.3}$$

In order to generate the density expansion for the excess (nonideal) part of F , we shall employ a product representation of the type originated by van Kampen¹⁸ for the average value appearing in Eq. (2.1)¹⁹:

$$\langle \exp(-\beta V_N) \rangle = \prod_{i<j=1}^N \langle \exp[-\beta V_2(ij)] \rangle \prod_{i<j<k=1}^N \frac{\langle \exp[-\beta V_3(ijk)] \rangle}{\langle \exp[-\beta V_2(ij)] \rangle \langle \exp[-\beta V_2(ik)] \rangle \langle \exp[-\beta V_2(jk)] \rangle}$$

$$\times \prod_{i<j<k<l=1}^N \frac{\langle ijkl \rangle \langle ij \rangle \langle ik \rangle \langle il \rangle \langle jk \rangle \langle jl \rangle \langle kl \rangle}{\langle ijk \rangle \langle ijl \rangle \langle ikl \rangle \langle jkl \rangle} \times \cdots \tag{2.4}$$

This identity at first estimates the full average by a product of independent pair averages, then sequentially provides triplet, quadruplet, quintuplet, \cdots , corrections. The correction factor for particles $\alpha_1 \cdots \alpha_n$ consists of an averaged Boltzmann factor for those particles, divided by lower-order correction factors for each proper subset of $\alpha_1 \cdots \alpha_n$; under that circumstance it is straightforward to show by induction that (2.4) is indeed an identity.

That development (2.4) is appropriate in the low density regime is obvious, for isolated pair collisions

are the predominant dynamical event. Three-body collisions will be correspondingly rarer, and so triplet corrections to an assumed independent pair set should indeed have modest magnitude (i.e., the triplet correction factors should all be close to unity). Four-particle encounters would be even rarer, etc.

The Helmholtz free energy expression (2.1) requires the negative logarithm of product (2.4), and hence the factors corresponding to sets of particles of ascending size (pairs, triplets, quadruplets, \cdots) contribute additively to F . On account of the identity of particles, all $N!/n!(N-n)!$ n -tuple contributions will be identical, and may be lumped together.

Consider first the independent pair contributions,

$$-\ln \prod_{i<j=1}^N \langle \exp[-\beta V_2(ij)] \rangle$$

$$= -\frac{1}{2}N(N-1) \ln \langle \exp[-\beta V_2(12)] \rangle$$

$$= -\frac{1}{2}N(N-1) \ln [1 + \langle f(12) \rangle], \tag{2.5}$$

where we have introduced the Mayer f function,

$$f(ij) = \exp[-\beta V_2(ij)] - 1. \tag{2.6}$$

Since

$$\langle f(12) \rangle = \Omega^{-2} \int d\mathbf{x}_1 \int d\mathbf{x}_2 f(12) \tag{2.7}$$

will be inversely proportional to the system volume in the conventional large-volume limit, we can surely expand the logarithm in Eq. (2.5) to obtain

$$-\frac{1}{2}N\rho^{(2)}\Omega^{-1} \int d\mathbf{x}_1 \int d\mathbf{x}_2 f(12) + O(N^0) \tag{2.8}$$

for the pair contributions to F . Following the usual convention, we have explicitly retained only the part proportional to N in the large-system limit, since that is the part which provides the limiting free energy per particle.

The triplet contributions may be treated in a similar manner,

$$-\ln \left\{ \prod_{i<j<k=1}^N \frac{\langle \exp[-\beta V_3(ijk)] \rangle}{\langle \exp[-\beta V_2(ij)] \rangle \langle \exp[-\beta V_2(ik)] \rangle \langle \exp[-\beta V_2(jk)] \rangle} \right\}$$

$$= -\frac{1}{6}N(N-1)(N-2) \ln \left\{ \frac{\langle \exp[-\beta V_3(123)] \rangle}{[1 + \langle f(12) \rangle][1 + \langle f(13) \rangle][1 + \langle f(23) \rangle]} \right\}. \tag{2.9}$$

The averaged triplet Boltzmann factor remaining here can be manipulated into a more convenient form,²⁰

$$\langle \exp[-\beta V_3(123)] \rangle = 1 + \langle f(12) \rangle + \langle f(13) \rangle + \langle f(23) \rangle + \langle f(12) \rangle \langle f(13) \rangle + \langle f(12) \rangle \langle f(23) \rangle$$

$$+ \langle f(13) \rangle \langle f(23) \rangle + \langle f(12) \rangle \langle f(13) \rangle \langle f(23) \rangle + \langle \exp[-\beta V_3(123)] \rangle - \exp[-\beta V_2(12) - \beta V_2(13) - \beta V_2(23)]. \tag{2.10}$$

Each of the averages in the right member is small (i.e., proportional to Ω^{-1} or Ω^{-2}). Thus after inserting (2.10) into (2.9) the logarithm may be expanded to yield

$$-\frac{1}{6}N(\rho^{(1)})^2\Omega^{-1} \left(\int d\mathbf{x}_1 \int d\mathbf{x}_2 \int d\mathbf{x}_3 f(12)f(13)f(23) + \int d\mathbf{x}_1 \int d\mathbf{x}_2 \int d\mathbf{x}_3 \right.$$

$$\left. \times \{ \exp[-\beta V_3(123)] - \exp[-\beta V_2(12) - \beta V_2(13) - \beta V_2(23)] \} \right) + O(N^0). \tag{2.11}$$

for the triplet contribution.

From these considerations it becomes clear that the quadruplet factors in (2.4) would produce free energy terms of the type $N(\rho^{(1)})^3$, quintuplet factors would produce those of type $N(\rho^{(1)})^4$, etc. Through second order in $\rho^{(1)}$,

therefore, the limiting free energy density must be

$$N^{-1}\beta F\{V_N\} = N^{-1}\beta F\{0\} - \frac{1}{2}\rho^{(1)}\int d\mathbf{x}_2 f(12) - \frac{1}{6}(\rho^{(1)})^2\int d\mathbf{x}_2\int d\mathbf{x}_3 f(12)f(13)f(23) \\ - \frac{1}{6}(\rho^{(1)})^2\int d\mathbf{x}_2\int d\mathbf{x}_3\{\exp[-\beta V_3(123)] - \exp[-\beta V_2(12) - \beta V_2(13) - \beta V_2(23)]\} + O[(\rho^{(1)})^3]. \quad (2.12)$$

The free energy densities that are generated by partition functions $Z_N\{\sum v_S\}$ and $Z_N\{\sum v_R\}$, using effective pair potential sums in place of the exact V_N , may be evaluated easily from the general formula (2.12). Of course it is necessary to take the density variations of v_S [Eq. (1.8)] and v_R [Eq. (1.9)] into account in collecting terms of equivalent order. One finds the following results:

$$N^{-1}\beta F\{\sum v_S\} = N^{-1}\beta F\{0\} - \frac{1}{2}\rho^{(1)}\int d\mathbf{x}_2 f(12) - \frac{1}{6}(\rho^{(1)})^2\int d\mathbf{x}_2\int d\mathbf{x}_3 f(12)f(13)f(23) \\ + \frac{1}{6}\beta(\rho^{(1)})^2\int d\mathbf{x}_2\int d\mathbf{x}_3 V^{(3)}(123) \exp[-\beta V_3(123)] + O[(\rho^{(1)})^3]; \quad (2.13)$$

$$N^{-1}\beta F\{\sum v_R\} = N^{-1}\beta F\{0\} - \frac{1}{2}\rho^{(1)}\int d\mathbf{x}_2 f(12) - \frac{1}{6}(\rho^{(1)})^2\int d\mathbf{x}_2\int d\mathbf{x}_3 f(12)f(13)f(23) \\ - \frac{1}{2}(\rho^{(1)})^2\int d\mathbf{x}_2\int d\mathbf{x}_3 \exp[-\beta V_2(12) - \beta V_2(13) - \beta V_2(23)]\{\exp[-\beta V^{(3)}(123)] - 1\} + O[(\rho^{(1)})^3]. \quad (2.14)$$

Although the first of these is correct for small $\beta V^{(3)}$, the second overestimates the effect of triplet nonadditivity. On the other hand, the latter may have a more reasonable behavior than the former when large $\beta V^{(3)}$ magnitudes are involved.

III. EFFECTIVE PAIR POTENTIAL SERIES

Let us define a partial configuration average,

$$\langle l \rangle_{12} = \Omega^{2-N} \int d\mathbf{x}_3 \cdots \int d\mathbf{x}_N l(\mathbf{x}_1 \cdots \mathbf{x}_N). \quad (3.1)$$

The Euler equation (1.17) for determination of our variationally optimal v hence may be rewritten,

$$\langle \exp[-\beta \sum_{i<j=1}^N v(ij)] \rangle_{12} = \langle \exp[-\frac{1}{2}\beta V_N(1 \cdots N) - \frac{1}{2}\beta \sum_{i<j=1}^N v(ij)] \rangle_{12}. \quad (3.2)$$

By means of an extension of van Kampen's product technique, both members in Eq. (3.2) can be evaluated as $\rho^{(1)}$ power series, with coefficients that are functions of \mathbf{x}_1 and \mathbf{x}_2 . We must keep in mind that v itself ultimately will be a $\rho^{(1)}$ power series.

We shall first operate on the left side (L) of Eq. (3.2). It will suffice for present purposes merely to carry the product through triplet terms. Thus we write

$$L = \prod_{i<j=1}^N \langle \exp[-\beta v(ij)] \rangle_{12} \prod_{i<j<k=1}^N \frac{\langle \exp[-\beta v(ij) - \beta v(ik) - \beta v(jk)] \rangle_{12}}{\langle \exp[-\beta v(ij)] \rangle_{12} \langle \exp[-\beta v(ik)] \rangle_{12} \langle \exp[-\beta v(jk)] \rangle_{12}}. \quad (3.3)$$

With regard to the pair factors, only the one with $i, j = 1, 2$ is distinct; all the others equal

$$1 + \langle \exp[-\beta v(ij)] - 1 \rangle. \quad (3.4)$$

Similarly, the triplet factors are of two types, depending on whether or not i, j, k includes *both* 1 and 2. After taking logarithms in (3.3), transforming integrals, and expanding through the requisite order, one obtains²¹

$$\ln L = -\beta v(12) + [\frac{1}{2}N(N-1) - 1]\Omega^{-1}\int d\mathbf{x}_3\{\exp[-\beta v(13)] - 1\} + (N-2)\Omega^{-1}\int d\mathbf{x}_3\{\exp[-\beta v(13)] - 1\} \\ \times \{\exp[-\beta v(23)] - 1\} + [\frac{1}{6}N(N-1)(N-2) - (N-2)]\Omega^{-2}\int d\mathbf{x}_3\int d\mathbf{x}_4\{\exp[-\beta v(13)] - 1\} \\ \times \{\exp[-\beta v(14)] - 1\}\{\exp[-\beta v(34)] - 1\}. \quad (3.5)$$

Exactly the same types of considerations apply in reduction of the right member (R) of Eq. (3.2). One finally finds²¹

$$\ln R = -\frac{1}{2}\beta[V_2(12) + v(12)] + [\frac{1}{2}N(N-1) - 1]\Omega^{-1}\int d\mathbf{x}_3\{\exp[-\frac{1}{2}\beta V_2(13) - \frac{1}{2}\beta v(13)] - 1\} + (N-2)\Omega^{-1} \\ \times \int d\mathbf{x}_3\{\exp[-\frac{1}{2}\beta V_2(13) - \frac{1}{2}\beta v(13)] - 1\}\{\exp[-\frac{1}{2}\beta V_2(23) - \frac{1}{2}\beta v(23)] - 1\} + (N-2)\Omega^{-1} \\ \times \int d\mathbf{x}_3\{\exp[-\frac{1}{2}\beta V^{(3)}(123)] - 1\} \exp\{-\frac{1}{2}\beta[V_2(13) + V_2(23) + v(13) + v(23)]\} \\ + [\frac{1}{6}N(N-1)(N-2) - (N-2)]\Omega^{-2}\int d\mathbf{x}_3\int d\mathbf{x}_4\{\exp[-\frac{1}{2}\beta V_2(13) - \frac{1}{2}\beta v(13)] - 1\} \\ \times \{\exp[-\frac{1}{2}\beta V_2(14) - \frac{1}{2}\beta v(14)] - 1\}\{\exp[-\frac{1}{2}\beta V_2(34) - \frac{1}{2}\beta v(34)] - 1\} + [\frac{1}{6}N(N-1)(N-2) - (N-2)]\Omega^{-2} \\ \times \int d\mathbf{x}_3\int d\mathbf{x}_4\{\exp[-\frac{1}{2}\beta V^{(3)}(134)] - 1\} \exp\{-\frac{1}{2}\beta[V_2(13) + V_2(14) + V_2(34) + v(13) + v(14) + v(34)]\}. \quad (3.6)$$

The leading, density-independent, term in the $\rho^{(1)}$ series for v will naturally be V_2 . Our task is to find the contribution linear in $\rho^{(1)}$,

$$v(ij) = V_2(ij) + \rho^{(1)}\phi(ij) + O[(\rho^{(1)})^2]. \tag{3.7}$$

In order to calculate ϕ , this expression must be inserted in each of $\ln L$, Eq. (3.5), and $\ln R$, Eq. (3.6) and the resulting functions expanded through first order in $\rho^{(1)}$.

The manipulations leading to deduction of the function ϕ are necessarily complex. It is therefore advisable first to examine the simplest possible case, namely that for which the true pair interaction V_2 vanishes. The effective pair potential $v = \rho^{(1)}\phi$ then arises solely from the triplet function $V^{(3)}$. By equating the corresponding simplified expressions for $\ln L$ and $\ln R$, followed by expansion of integrands to linear order in $\rho^{(1)}\phi$, we obtain

$$-\frac{1}{2}\beta\rho^{(1)}\phi(12) - \frac{1}{2}\beta\rho^{(1)}\left(\frac{1}{2}N\rho^{(1)} - \frac{1}{2}\rho^{(1)} - \Omega^{-1}\right) \int d\mathbf{x}_3 \phi(13) = [\rho^{(1)} - (2/\Omega)] \int d\mathbf{x}_3 \{ \exp[-\frac{1}{2}\beta V^{(3)}(123)] - 1 \} \\ + [\frac{1}{6}N(\rho^{(1)})^2 - \frac{1}{2}(\rho^{(1)})^2 - (2\rho^{(1)}/3\Omega) + (2/\Omega^2)] \int d\mathbf{x}_3 \int d\mathbf{x}_1 \{ \exp[-\frac{1}{2}\beta V^{(3)}(134)] - 1 \}. \tag{3.8}$$

It is important to notice that this equation contains some terms proportional to N (i.e., to the system size), as well as others which remain bounded as the system size diverges. Clearly the former class of terms must independently cancel; as a result we have the condition

$$\beta \int d\mathbf{x}_3 \phi(13) = -\frac{2}{3} \int d\mathbf{x}_3 \int d\mathbf{x}_1 \{ \exp[-\frac{1}{2}\beta V^{(3)}(134)] - 1 \}, \tag{3.9}$$

which must be obeyed by ϕ .

One can also see from Eq. (3.8) that the relative changes in $\phi(12)$ as \mathbf{x}_1 and \mathbf{x}_2 vary arise entirely from the first integral in this equation's right member. In a macroscopically large system therefore we must have

$$\beta\phi(12) = -2 \int d\mathbf{x}_3 \{ \exp[-\frac{1}{2}\beta V^{(3)}(123)] - 1 \} + C. \tag{3.10}$$

The additive constant C may easily be determined by applying condition (3.9); consequently

$$\beta\phi(12) = -2 \int d\mathbf{x}_3 \{ \exp[-\frac{1}{2}\beta V^{(3)}(123)] - 1 \} \\ + (4/3\Omega) \int d\mathbf{x}_3 \int d\mathbf{x}_1 \{ \exp[-\frac{1}{2}\beta V^{(3)}(134)] - 1 \}. \tag{3.11}$$

The novel feature which arises here is the weak (proportional to Ω^{-1}), long-ranged tail in ϕ . Although this tail vanishes pointwise in the $\Omega \rightarrow \infty$ limit, its free-energy consequences do not. All molecular pairs in the system are subject to this tail, regardless of their distance; with $\frac{1}{2}N(N-1)$ pairs the aggregate "tail" interaction will be proportional to $N\rho^{(1)}$, and will be a significant part of the total extensive free energy. Although result (3.11) refers specifically to the $V_2=0$ special case, we must expect that the more general ϕ will also exhibit a weak, long-ranged tail.

Returning now to the general case of nonvanishing V_2 , we can first identify the generalization of condition (3.9) by equating terms proportional to N in the relation,

$$\ln L = \ln R. \tag{3.12}$$

By referring to the earlier expressions (3.5) and (3.6), one deduces that

$$\beta \int d\mathbf{x}_3 \exp[-\beta V_2(13)] \phi(13) = -\frac{2}{3} \int d\mathbf{x}_3 \int d\mathbf{x}_1 \\ \times \exp[-\beta V_2(13) - \beta V_2(14) - \beta V_2(34)] \\ \times \{ \exp[-\frac{1}{2}\beta V^{(3)}(134)] - 1 \}. \tag{3.13}$$

Furthermore it is possible as before to identify the source of relative variation of $\phi(12)$ with $\mathbf{x}_1, \mathbf{x}_2$. Hence one concludes, analogous to Eq. (3.10), that

$$\beta\phi(12) = -2 \int d\mathbf{x}_3 \exp[-\beta V_2(13) - \beta V_2(23)] \\ \times \{ \exp[-\frac{1}{2}\beta V^{(3)}(123)] - 1 \} + C. \tag{3.14}$$

After using Eq. (3.13) to determine C , we have

$$\beta\phi(12) = -2 \int d\mathbf{x}_3 \exp[-\beta V_2(13) - \beta V_2(23)] \\ \times \{ \exp[-\frac{1}{2}\beta V^{(3)}(123)] - 1 \} + (4/3\Omega) \int d\mathbf{x}_3 \int d\mathbf{x}_1 \\ \times \exp[-\beta V_2(13) - \beta V_2(14) - \beta V_2(34)] \\ \times \{ \exp[-\frac{1}{2}\beta V^{(3)}(134)] - 1 \}. \tag{3.15}$$

Through order $\rho^{(1)}$, therefore, the effective pair potential v has the following form:

$$v(12) = V_2(12) - (2\rho^{(1)}/\beta) \int d\mathbf{x}_3 \\ \times \exp[-\beta V_2(13) - \beta V_2(23)] \{ \exp[-\frac{1}{2}\beta V^{(3)}(123)] - 1 \} \\ + (4\rho^{(1)}/3\Omega\beta) \int d\mathbf{x}_3 \int d\mathbf{x}_1 \\ \times \exp[-\beta V_2(13) - \beta V_2(14) - \beta V_2(34)] \\ \times \{ \exp[-\frac{1}{2}\beta V^{(3)}(134)] - 1 \} + O[(\rho^{(1)})^2]. \tag{3.16}$$

This may be compared with the preceding expansions for v_S , Eq. (1.8), and for v_R , Eq. (1.9).

Next we can insert the v result into the generic Helmholtz free energy series (2.12). The result is the following:

$$N^{-1}\beta F\{\sum v\} = N^{-1}\beta F\{0\} - \frac{1}{2}\rho^{(1)} \int d\mathbf{x}_2 f(12) - \frac{1}{6}(\rho^{(1)})^2 \\ \times \int d\mathbf{x}_2 \int d\mathbf{x}_3 f(12)f(13)f(23) - \frac{1}{3}(\rho^{(1)})^2 \\ \times \int d\mathbf{x}_2 \int d\mathbf{x}_3 \exp[-\beta V_2(12) - \beta V_2(13) - \beta V_2(23)] \\ \times \{ \exp[-\frac{1}{2}\beta V^{(3)}(123)] - 1 \} + O[(\rho^{(1)})^3]. \tag{3.17}$$

In the event that $\beta V^{(3)}$ is small enough that exponential function linearization is in order, both $F\{\sum v_S\}$ and $F\{\sum v\}$ agree with the exact free energy $F\{V_N\}$. More generally, we can establish that $F\{\sum v\}$ bounds $F\{V_N\}$ from above,¹⁵

$$F\{\sum v\} \geq F\{V_N\}. \tag{3.18}$$

Notice that

$$\begin{aligned} [\exp(x) - 1] - 2[\exp(\frac{1}{2}x) - 1] &= \exp(x) - 2\exp(\frac{1}{2}x) + 1 \\ &= [\exp(\frac{1}{2}x) - 1]^2 \geq 0; \end{aligned} \quad (3.19)$$

hence

$$\exp(x) - 1 \geq 2[\exp(\frac{1}{2}x) - 1]. \quad (3.20)$$

This clearly implies that

$$\begin{aligned} -\frac{1}{3} \int d\mathbf{x}_2 \int d\mathbf{x}_3 \exp[-\beta V_2(12) - \beta V_2(13) - \beta V_2(23)] \\ \times \{ \exp[-\frac{1}{2}\beta V^{(3)}(123)] - 1 \} \geq -\frac{1}{6} \int d\mathbf{x}_2 \int d\mathbf{x}_3 \\ \times \exp[-\beta V_2(12) - \beta V_2(13) - \beta V_2(23)] \\ \times \{ \exp[-\beta V^{(3)}(123)] - 1 \}, \end{aligned} \quad (3.21)$$

from which inequality (3.18) follows through $O[(\rho^{(u)})^2]$. The alternative effective pair potentials v_S and v_R have no corresponding free energy bound property.

IV. STRUCTURAL FIDELITY

Section I offered the comment that effective pair potentials could be judged by examining the magnitude of the function-space distance D . For effective potential v , we have

$$\begin{aligned} D^2(h_1, h_2) &= \langle \{ \exp[-\frac{1}{2}\beta V_N] - \exp[-\frac{1}{2}\beta \sum_{i < j=1}^N v(ij)] \}^2 \rangle \\ &= \langle \exp[-\beta V_N] \rangle - 2 \langle \exp[-\frac{1}{2}\beta V_N - \frac{1}{2}\beta \sum_{i < j=1}^N v(ij)] \rangle \\ &\quad + \langle \exp[-\beta \sum_{i < j=1}^N v(ij)] \rangle. \end{aligned} \quad (4.1)$$

By integration over \mathbf{x}_1 and \mathbf{x}_2 , the Euler equation (3.2) satisfied by v implies that

$$\begin{aligned} \langle \exp[-\beta \sum_{i < j=1}^N v(ij)] \rangle \\ = \langle \exp[-\frac{1}{2}\beta V_N - \frac{1}{2}\beta \sum_{i < j=1}^N v(ij)] \rangle; \end{aligned} \quad (4.2)$$

therefore D^2 may be put into the alternative forms

$$\begin{aligned} D^2(h_1, h_2) &= \langle \exp[-\beta V_N] \rangle - \langle \exp[-\beta \sum_{i < j=1}^N v(ij)] \rangle \\ &= \langle \exp(-\beta V_N) \rangle [1 - \exp(-\beta \Delta F)], \end{aligned} \quad (4.3)$$

in which

$$\Delta F = F\{\sum v\} - F\{V_N\} \quad (4.4)$$

is the nonnegative free energy increment resulting from replacement of the actual potential by its effective pairwise analog. Of course ΔF will be an extensive quantity, that is, it will be proportional to N . In most cases of practical interest, in which N compares in magnitude with Avogadro's number,

$$\exp(-\beta \Delta F) \ll 1, \quad (4.5)$$

so that D^2 differs insignificantly from $\langle \exp(-\beta V_N) \rangle$. It must be kept in mind however that ΔF is formally quadratic to lowest order in the magnitude of $\beta V^{(3)}$. Thus for any finite N , we have for very small $\beta V^{(3)}$

$$\begin{aligned} D^2 &= O[(\beta V^{(3)})^2], \\ D &= O[\beta V^{(3)}]. \end{aligned} \quad (4.6)$$

In the case of other proposed effective pair potentials v_α ($\alpha = S, R$, or other possibilities), a relationship of type (4.2) is not generally available, so

$$\begin{aligned} D^2 &= \langle \exp[-\beta V_N] \rangle - 2 \langle \exp[-\frac{1}{2}\beta V_N - \frac{1}{2}\beta \sum_{i < j=1}^N v_\alpha(ij)] \rangle \\ &\quad + \langle \exp[-\beta \sum_{i < j=1}^N v_\alpha(ij)] \rangle. \end{aligned} \quad (4.7)$$

Since a free energy bounding property does not exist for arbitrary v_α , two distinct cases arise depending on which of the two positive terms in Eq. (4.7) dominates the positive quantity D^2 . For both cases, the Schwartz inequality²² requires

$$\begin{aligned} \langle \exp(-\beta V_N) \rangle \langle \exp(-\beta \sum v_\alpha) \rangle \\ \geq \langle \exp(-\frac{1}{2}\beta V_N - \frac{1}{2}\beta \sum v_\alpha) \rangle^2. \end{aligned} \quad (4.8)$$

If the last term on the right in Eq. (4.7) dominates, then

$$\begin{aligned} D^2 &= \langle \exp(-\beta \sum v_\alpha) \rangle \\ &\times \left\{ 1 - \frac{2 \langle \exp(-\frac{1}{2}\beta V_N - \frac{1}{2}\beta \sum v_\alpha) \rangle}{\langle \exp(-\beta \sum v_\alpha) \rangle} + \frac{\langle \exp(-\beta V_N) \rangle}{\langle \exp(-\beta \sum v_\alpha) \rangle} \right\}. \end{aligned} \quad (4.9)$$

The last term in the $\{\dots\}$ factor is negligible by assumption, and the Schwartz inequality (4.8) suffices to show that the negative term preceding it is also negligible. Thus for this case

$$D^2 \cong \exp[-\beta(F\{\sum v_\alpha\} - F\{V_N\})] \langle \exp(-\beta V_N) \rangle. \quad (4.10)$$

In virtue of the extensive character and the positivity of the free energy exponent occurring here, this squared-distance result will be incomparably greater (for large N) than the preceding result (4.3) for v .

For the alternative possibility that the first term on the right side of Eq. (4.7) dominates,

$$\begin{aligned} D^2 &= \langle \exp[-\beta V_N] \rangle \\ &\times \left\{ 1 - \frac{2 \langle \exp(-\frac{1}{2}\beta V_N - \frac{1}{2}\beta \sum v_\alpha) \rangle}{\langle \exp(-\beta V_N) \rangle} + \frac{\langle \exp(-\beta \sum v_\alpha) \rangle}{\langle \exp(-\beta V_N) \rangle} \right\} \end{aligned} \quad (4.11)$$

will be very close to $\langle \exp(-\beta V_N) \rangle$ itself, and hence close to D^2 for v shown in Eq. (4.3). However, we know that the variational definition of v has forced its D^2 to be less than that for any other function v_α , so we must

have

$$\begin{aligned} & \exp[-\beta(F\{\sum v\} - F\{V_N\})] \\ & \geq 2 \exp[-\beta(F\{\frac{1}{2}V_N + \frac{1}{2}\sum v_\alpha\} - F\{V_N\})] \\ & \quad - \exp[-\beta(F\{\sum v_\alpha\} - F\{V_N\})], \quad (4.12) \end{aligned}$$

with equality obtaining only when $v_\alpha = v$. Inequality (4.12) is equivalent to the result,

$$\begin{aligned} \exp(-\beta F\{\frac{1}{2}V_N + \frac{1}{2}\sum v_\alpha\}) & \leq \frac{1}{2} \exp(-\beta F\{\sum v_\alpha\}) \\ & \quad + \frac{1}{2} \exp(-\beta F\{\sum v\}). \quad (4.13) \end{aligned}$$

The van Kampen product technique can be applied directly to evaluation of the molecular pair correlation function,

$$g^{(2)}(\mathbf{x}_1, \mathbf{x}_2) = \langle \exp(-\beta V_N) \rangle_{12} / \langle \exp(-\beta V_N) \rangle \quad (4.14)$$

as a density series.¹⁸ The generic result through $O(\rho^{(1)})$ has the following form²³:

$$\begin{aligned} g^{(2)}(12) & = \exp[-\beta V_2(12)] [1 + \rho^{(1)} \int d\mathbf{x}_3 f(13) f(23) \\ & \quad + \rho^{(1)} \int d\mathbf{x}_3 \exp[-\beta V_2(13) - \beta V_2(23)] \\ & \quad \times \{\exp[-\beta V^{(3)}(123)] - 1\} + O[(\rho^{(1)})^2]]. \quad (4.15) \end{aligned}$$

By construction, of course, the effective potential v_R reproduces this expression. The alternative quantity v_S however generates an inexact form,²³

$$\begin{aligned} g^{(2)}(12, \{v_s\}) & = \exp[-\beta V_2(12)] \\ & \quad \times \{1 + \rho^{(1)} \int d\mathbf{x}_3 f(13) f(23) - \frac{1}{3} \beta \rho^{(1)} \int d\mathbf{x}_3 V^{(3)}(123) \\ & \quad \times \exp[-\beta V_2(13) - \beta V_2(23) - \beta V^{(3)}(123)] + O[(\rho^{(1)})^2]\}. \quad (4.16) \end{aligned}$$

For small $\beta V^{(3)}$, this approximation underestimates the structural influence of triplet nonadditivity by a factor of 3.

Finally, we display the pair correlation function produced by the variationally defined function v ,²³

$$\begin{aligned} g^{(2)}(12, \{v\}) & = \exp[-\beta V_2(12)] \\ & \quad \times \{1 + \rho^{(1)} \int d\mathbf{x}_3 f(13) f(23) + 2\rho^{(1)} \int d\mathbf{x}_3 \\ & \quad \times \exp[-\beta V_2(13) - \beta V_2(23)] \\ & \quad \times \{\exp[-\frac{1}{2}\beta V^{(3)}(123)] - 1\} + O[(\rho^{(1)})^2]\}. \quad (4.17) \end{aligned}$$

Inequality (3.20) above implies, through $O(\rho^{(1)})$, that

$$g^{(2)}(12, \{V_N\}) \geq g^{(2)}(12, \{v\}). \quad (4.18)$$

The pair correlation error committed by the effective pair potential v in order $\rho^{(1)}$ is therefore quadratic in $\beta V^{(3)}$. Although the pointwise inequality (4.17) may not persist to all $\rho^{(1)}$ orders, it has been established¹⁸ that the quadratic nature of the pair correlation error does so persist. Hence v , unlike v_S and v_R , produces only quadratic errors in both F and $g^{(2)}$.

V. DISCUSSION

Three-body nonadditivities $V^{(3)}$ that have been established for real substances tend to be nonuniform in sign. The Axilrod-Teller triple-dipole interaction²⁴ that is relevant to the noble gases provides a well-known example,

$$\begin{aligned} V^{(3)}(123) & = \nu(1 + 3 \cos\theta_1 \cos\theta_2 \cos\theta_3) / r_{12}^3 r_{13}^3 r_{23}^3, \quad \nu > 0, \quad (5.1) \end{aligned}$$

where the θ_i 's are the internal angles, and the r_{ij} 's the side lengths, for the triangle of centers. The most stable configuration for three noble-gas atoms surely will be an equilateral triangle, but the Axilrod-Teller interaction (5.1) will tend to reduce its binding energy somewhat, as well as to increase the triangle side slightly. On the other hand, this interaction tends to increase the magnitude of the binding energy (i.e., V_3 decreases) for linear configurations.

At low temperature, the integral which determines the sign and magnitude of the long-ranged tail of v in order $\rho^{(1)}$,

$$\begin{aligned} (4\rho^{(1)}/3\beta) \int d\mathbf{x}_3 \int d\mathbf{x}_4 \exp[-\beta V_2(13) - \beta V_2(14) - \beta V_2(34)] \\ \times \{\exp[-\frac{1}{2}\beta V^{(3)}(134)] - 1\}, \quad (5.2) \end{aligned}$$

will obviously be dominated by the contribution of configurations near the one with absolute minimum energy. Since the last integrand factor is negative for those configurations, the long-ranged tail will likewise be negative. The order- $\rho^{(1)}$ part of the $v(12)$ which actually changes with configuration of 1 and 2,

$$\begin{aligned} -(2\rho^{(1)}/\beta) \int d\mathbf{x}_3 \exp[-\beta V_2(13) - \beta V_2(23)] \\ \times \{\exp[-\frac{1}{2}\beta V^{(3)}(123)] - 1\}, \quad (5.3) \end{aligned}$$

will be determined at low temperature by the minimum energy configuration for fixed r_{12} . When r_{12} lies close to the $V_2(r_{12})$ minimum, this constrained configuration will be substantially the same as the unconstrained one, so (5.3) will be positive. However when r_{12} is roughly twice as large so that the third particle neatly fits in the middle, (5.3) will be negative. The net low-temperature effect for noble gases then would be to make $v(r_{12})$ shallower and broader than $V_2(r_{12})$.

In the case of water, the analog of triple-dipole interaction (5.1) should still be present, but other effects of greater chemical significance predominate, stemming from the tendency of neighbors to form linear hydrogen bonds. Considerable recent effort has been devoted to understanding hydrogen-bond nonadditivity in water, by means of all-electron Hartree-Fock calculations.²⁵⁻²⁸ As is the case with the Axilrod-Teller potential, $V^{(3)}$ for water varies in sign depending upon the configuration of the three molecules. The dependence upon angles is unlike that displayed in Eq. (5.1); in particular it depends crucially upon the hydrogen-bond pattern.

The available evidence indicates that the most stable configuration for three water molecules is unsymmetrical, and involves three hydrogen bonds in ordered sequence around a triangle.²⁷ Furthermore $V^{(3)}$ is definitely negative in this configuration. At low temperature therefore the integral (5.2) will be positive,²⁹ so that the long-ranged tail of v will have positive sign, contrary to the noble-gas case.

If the configurations \mathbf{x}_1 and \mathbf{x}_2 for two water molecules correspond to the formation of an undistorted linear hydrogen bond, the relevant constrained triplet energy minimum should involve a sequential pair of hydrogen bonds. Again $V^{(3)}$ would be negative, as then would be the integral (5.3) at low temperature. The effect on $v(12)$ would therefore be to strengthen and compress the "effective hydrogen bond" by comparison with V_2 . On the other hand if \mathbf{x}_1 and \mathbf{x}_2 corresponded to the configurations of second neighbors in an ice or clathrate lattice, the part of the shift $v(12)-V_2(12)$ determined by integral (5.3) at low temperature would be: (a) negative if a third molecule could be a proton donor to one of 1 and 2, and a proton acceptor to the other (to form a sequence of two equivalently ordered hydrogen bonds); (b) positive if a third molecule could act as a simultaneous double donor or acceptor of protons.

The extent to which these sign assignments both for noble gases and water would persist to intermediate and high temperature could only be established by detailed numerical studies of expressions (5.2) and (5.3).

If the effective pair potential concept is to have substantial impact on electronic computer simulations of liquids, a practical method for estimating v at high density will be required. In principle, the Monte Carlo method could be used to evaluate D^2 directly, and to identify that function v out of a test group for which D^2 is minimized. But the practical difficulty inherent in this direct assault was pointed out in Sec. IV: For a wide class of test functions v_α the quantity D^2 will be substantially invariant.

A full analytical solution to the variational problem (1.16) will probably not become available in the near future. For the interim period, it may be worth pointing out that a plausible generalization of our low-density result (3.16) to arbitrary density would be the following:

$$v(12) \cong V_2(12) - (2\rho^{(1)}/\beta) \int d\mathbf{x}_3 \\ \times [g^{(3)}(123, \{\sum v\})/g^{(2)}(12, \{\sum v\})] \\ \times \{\exp[-\frac{1}{2}\beta V^{(3)}(123)] - 1\} + (4\rho^{(1)}/3\Omega\beta) \int d\mathbf{x}_3 \int d\mathbf{x}_4 \\ \times g^{(3)}(134, \{\sum v\}) \{\exp[-\frac{1}{2}\beta V^{(3)}(134)] - 1\}, \quad (5.4)$$

assuming that the $V^{(n)}$, $n > 3$, are negligible. The

correlation functions occurring here have purposely been chosen as those generated by the effective pair interaction itself, for they are the ones which would arise in a typical computer simulation. As it stands, the relation (5.4) would constitute a condition of self-consistency on v . In practice however a more likely use would involve computer generation of the correlation functions and evaluation of the integrals in (5.4) with an initial estimate v_0 to v , for which (5.4) would then suggest a correction. A recycling of this procedure might then be carried out to seek convergence to a self-consistent v .

¹ T. L. Hill, *Statistical Mechanics* (McGraw-Hill, New York, 1956).

² S. A. Rice and P. Gray, *The Statistical Mechanics of Simple Liquids* (Interscience, New York, 1965).

³ W. W. Wood, *J. Chem. Phys.* **48**, 415 (1968).

⁴ A. Rahman, *Phys. Rev.* **136**, A405 (1964).

⁵ N. R. Kestner and O. Sinanoğlu, *J. Chem. Phys.* **38**, 1730 (1963).

⁶ O. Sinanoğlu, *Chem. Phys. Letters* **1**, 340 (1967).

⁷ O. Sinanoğlu, *Advan. Chem. Phys.* **12**, 283 (1967).

⁸ T. Halcioğlu and O. Sinanoğlu, *J. Chem. Phys.* **49**, 996 (1968).

⁹ Following the usual convention the $g^{(n)}$ used in this paper are normalized so as to equal unity when all n molecules are widely separated.

¹⁰ G. S. Rushbrooke and M. Silbert, *Mol. Phys.* **12**, 505 (1967).

¹¹ J. S. Rowlinson, *Mol. Phys.* **12**, 513 (1967).

¹² G. Casanova, R. J. Dulla, D. A. Jonah, J. S. Rowlinson, and G. Saville, *Mol. Phys.* **18**, 589 (1970).

¹³ R. J. Dulla, J. S. Rowlinson, and W. R. Smith, *Mol. Phys.* **21**, 299 (1971).

¹⁴ If quadruplet contributions $V^{(4)}$ were present in V_N , only the $O[(\rho^{(1)})^2]$ terms in Eqs. (1.8) and (1.9) would be affected. Similarly $V^{(6)}$ would appear in order $(\rho^{(1)})^3$ and beyond, etc.

¹⁵ F. H. Stillinger, *J. Phys. Chem.* **74**, 3677 (1970).

¹⁶ This definition differs only trivially from the one given in Ref. 15, by inclusion of the convenient factor Ω^{-N} .

¹⁷ A. Rahman and F. H. Stillinger, *J. Chem. Phys.* **55**, 3336 (1971).

¹⁸ N. G. van Kampen, *Physica* **27**, 783 (1961).

¹⁹ An obvious shorthand notation has been used to indicate the structure of the quadruplet terms.

²⁰ In obtaining this relation we have used the fact that $\langle f(ij) \rangle \langle f(jk) \rangle = \langle f(ij)f(jk) \rangle$. If the molecular coordinate vectors \mathbf{x}_i were to have included internal conformational degrees of freedom, this identity would be invalid, and a somewhat more elaborate analysis would be required.

²¹ Some of the terms varying as Ω^{-1} in the large-system limit have been disregarded here. Their neglect in no way affects the final conclusion concerning the v density expansion.

²² F. Riesz and B. Sz. Nagy, *Functional Analysis* (Frederick Ungar, New York, 1955), pp. 40-43.

²³ The results quoted here refer to the conventional infinite system limit.

²⁴ B. M. Axilrod and E. Teller, *J. Chem. Phys.* **11**, 299 (1943); a convenient table of v values is provided in A. Dalgarno, *Advan. Chem. Phys.* **12**, 143 (1967).

²⁵ J. Del Bene and J. A. Pople, *Chem. Phys. Letters* **4**, 426 (1969).

²⁶ D. Hankins, J. W. Moskowitz, and F. H. Stillinger, *Chem. Phys. Letters* **4**, 527 (1970).

²⁷ J. Del Bene and J. A. Pople, *J. Chem. Phys.* **52**, 4858 (1970).

²⁸ D. Hankins, J. W. Moskowitz, and F. H. Stillinger, *J. Chem. Phys.* **53**, 4544 (1970).

²⁹ On account of the minimum-energy arrangement's asymmetry, six equivalent classes of configurations will contribute equally to integral (5.2).