

Pair Distribution in the Rigid-Sphere System by the Method of Particle Scaling* †

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By use of the scale of interaction distance as a coupling constant, integral equations for the molecular distribution functions are derived and discussed with particular reference to the calculation of the pair distribution for rigid-sphere systems. It is shown that considerable improvement over the usual superposition approach results upon retention of the superficial form of the superposition approximation, but with a suitably defined effective local density. Specifically, the equation becomes exact over half the range of the coupling parameter. The fourth virial coefficient in the equation of state is correct in this theory, in comparison with an ordinary superposition value 61% low. Generalization of the effective density analysis to the case of arbitrary potentials is briefly discussed.

I. INTRODUCTION

IT has long been recognized that a convenient model for picturing the microscopic structure of liquids and dense gases is the rigid-sphere system. At high temperatures, where the attractive portion of the intermolecular potential curve is shallow by comparison with kT , the particle distribution is determined alone by the very steep repulsive electron core interactions; replacement of the actual potential by the singular rigid-sphere interaction involves little actual modification. At lower temperatures, furthermore, the attractive forces apparently play a relatively minor role in producing the molecular distribution at liquid densities; they only serve to provide a fairly uniform negative potential over the entire system, in which the otherwise strongly repelling particles appear to move under thermal agitation. Consequently, the excess entropy is determined primarily by the nearly rigid (and rather sharply defined) cores, and the liquid cohesive energy may be computed with fair accuracy by assuming the pair correlation function is adequately approximated by that for a fluid at the same density, but whose particles interact only via the repulsive core forces.¹ A result is the observation that these excess quantities are nearly temperature independent in liquids at constant volume. The weight of evidence furthermore indicates that even the rigid-sphere fluid exhibits a fluid-solid phase transition² as a result, roughly speaking, of the unavailability of sufficient room for the spheres at high density in any but a regular close-packed arrangement.

* A portion of this work is based upon material contained in an unpublished dissertation presented by F. H. S. (1958) to the Graduate School Faculty of Yale University in pursuit of the degree of Doctor of Philosophy.

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¹ In this connection, it might be remarked that the hardsphere radial distribution function forms a very convenient starting point for precise iterative computation of the same quantity for attracting molecules: J. G. Kirkwood, V. A. Lewinson, and B. J. Alder, *J. Chem. Phys.* **20**, 929 (1952).

² B. J. Alder and T. E. Wainwright, *J. Chem. Phys.* **27**, 1208 (1957).

In view of these several physically interesting features exhibited by this idealized system, as well as the simple geometrical picture offered by the rigid-sphere interaction, there is considerable motivation for determination of the properties of this model from the fundamentals of statistical mechanics. In the following, a procedure is evolved for computation of the radial distribution function $g^{(2)}(r)$ in the rigid-sphere system which appears to be significantly more accurate than previous similar approaches. The most striking feature of the deduced functional equation for $g^{(2)}(r)$ is the fact that it can be cast into a form which bears an outward resemblance to the Kirkwood superposition integral equation (in the interaction range variation approach), but differing by inclusion of a suitably defined local effective density ρ^* . This quantity varies appropriately from the macroscopic density ρ , thereby absorbing in such variation much of the error generated in the usual superposition formalism.

The effective density ρ^* is defined as an average, over a certain finite geometrical region, of the variable molecular density induced in the medium by introduction of a fixed particle. Strictly speaking, ρ^* is thereby a nonlocalized property of the molecular system. Its use in the $g^{(2)}$ integral equation may be seen to free the theory from the restrictive procedure of approximating the triplet distribution function by a product of spherically symmetric pair functions (specifically, the $g^{(2)}$'s themselves). An effect of the increased power of the technique outlined here is prediction of a rigorously exact fourth virial coefficient.

The theory is based upon the use of the scaling of the distance of interaction as a coupling procedure³⁻⁵; i.e., it is assumed that particle 1 interacts with any other particle i in the fluid with a potential $v(r_{1i}/\lambda)$, whereas the interaction of i with j is $v(r_{ij})$. Thus when $\lambda=0$ particle 1 is effectively decoupled; and letting λ grow to unity fully couples it into its surroundings.

³ F. H. Stillinger, Ph.D. dissertation, Yale University, 1958.

⁴ H. Reiss, H. L. Frisch, and J. L. Lebowitz, *J. Chem. Phys.* **31**, 369 (1959).

⁵ E. Helfand, H. Reiss, H. L. Frisch, and J. L. Lebowitz, *J. Chem. Phys.* **33**, 1379 (1960).

This procedure has the advantage that even singular potentials may be thus handled.

For rigid-sphere systems an exact integral equation can be derived relating the pair distribution function for $\lambda < \frac{1}{2}$ to the pair distribution for $\lambda = 1$. For $\lambda > \frac{1}{2}$ an integral equation, based on our specific effective density approximation is presented. The error in the effective density can be shown to begin as $(\lambda - \frac{1}{2})^2$.

A brief section (IV) is devoted to extension of the effective density theory to fluids interacting with a general spherically symmetric potential function.

II. EFFECTIVE DENSITY INTEGRAL EQUATION

One approach to the calculation of the pair correlation function is through one of a class of integral equations relating the derivative of the pair potential of mean force, with respect to a variable upon which it depends, to the pair and higher order (usually triplet) correlation functions.^{6,7} In the past, derivatives with respect to the pair separation, the concentration, the temperature, and the strength of interaction of particle 1 with the remainder of the fluid have been considered. This last coupling procedure, due to Kirkwood,⁸ has certain conceptual shortcomings in the case of singular potential functions such as that between rigid spheres. If one considers the partially coupled particle 1 to interact with particle i according to the law

$$v(r_{1i}, \xi) = \xi v(r_{1i}), \tag{1}$$

where

$$\begin{aligned} v(r) &= \infty, & r < a, \\ &0, & r > a, \end{aligned} \tag{2}$$

then particle 1 is decoupled from the system for $\xi = 0$, but is fully coupled for any finite ξ .

In this paper a coupling procedure which does not suffer from this shortcoming is presented. In addition, the method lends itself to a number of interesting, new developments of the integral equation technique. Consider that the scale of distance for the interaction of particle 1 with other molecules is determined by a parameter λ , so that the total potential of interaction of the system is

$$v_N(1 \dots N, \lambda) = \sum_{i=2}^N v\left(\frac{r_{1i}}{\lambda}\right) + \sum_{i < j=2}^N v(r_{ij}). \tag{3}$$

When $\lambda = 0$ the potential of interaction between particle 1 (which, because it is coupled to the extent λ , we call the "lambdacule") and i has argument ∞ and thus vanishes. Increasing λ from 0 to 1 gradually couples in the lambdacule to the full extent, and corresponds in a sense to the growth of particle 1.

In the case of the rigid-sphere potential this coupling scheme has a particularly clear physical significance;

namely, that if the normal spheres have diameter a and the lambdacule corresponds to a sphere of diameter b , then one has the relation

$$\frac{1}{2}(a+b) = \lambda a.$$

Note that for $\lambda < \frac{1}{2}$ the diameter b is negative. This is to be expected since even a point placed in such a fluid has an excluded volume, and it means that the centers of the lambdacule can penetrate into normal particles to a depth $|b|$.

The equation which we desire for the n -particle correlation function is most readily derived from canonical ensemble theory. The correlation functions $g^{(n)}$ and potentials of mean force $w^{(n)}$ have definitions as partial phase space integrals of the canonical configurational density

$$\begin{aligned} g^{(n)}(1 \dots n, \lambda) &= \exp[-w^{(n)}(1 \dots n, \lambda)/kT], \\ &= V^n [Z_N(\lambda)]^{-1} \\ &\times \int \dots \int \exp\frac{-v_N(1 \dots N, \lambda)}{kT} d^3r_{n+1} \dots d^3r_N, \\ Z_N(\lambda) &= \int \dots \int \exp\frac{-v_N(1 \dots N, \lambda)}{kT} d^3r_1 \dots d^3r_N, \end{aligned} \tag{4}$$

where V is the volume. A λ differentiation of Eq. (4) leads to the relation (this sequence of manipulations is standard^{7,8})

$$\begin{aligned} -kT[\partial \log g^{(n)}(1 \dots n, \lambda)/\partial \lambda] &= \partial w^{(n)}(1 \dots n, \lambda)/\partial \lambda \\ &= \sum_{i=2}^n \frac{\partial v(1i, \lambda)}{\partial \lambda} \\ &+ \rho \int \frac{\partial v(1, n+1, \lambda)}{\partial \lambda} \\ &\times \{ [g^{(n+1)}(1 \dots n+1, \lambda)/g^{(n)}(1 \dots n, \lambda)] \\ &- g^{(2)}(1, n+1, \lambda) \} d^3r_{n+1}. \end{aligned} \tag{5}$$

This integro-differential equation expresses the scale-parameter variation of $w^{(n)}$ as the change in potential of the isolated set n , plus a term which represents the rate of change of interaction energy with the remainder of the medium.

As already remarked, $\lambda = 0$ results in complete decoupling of particle 1 from its neighbors, so that no position correlation can occur between 1 and the set $2 \dots n$; specifically

$$\begin{aligned} g^{(n)}(1 \dots n, \lambda = 0) &= g^{(1)}(1, \lambda = 0) g^{(n-1)}(2 \dots n) \\ &= g^{(n-1)}(2 \dots n), \end{aligned} \tag{6}$$

since in the absence of external forces, particle 1 may be found anywhere in V with equal probability. A convenient form for the expression (5) is obtained by

⁶ J. E. Mayer, *J. Chem. Phys.* **15**, 187 (1947).
⁷ T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, New York, 1956), Chap. 6.
⁸ J. G. Kirkwood, *J. Chem. Phys.* **3**, 300 (1935).

integration over λ , subject to the condition (6)

$$\begin{aligned}
 & -kT \log [g^{(n)}(1 \cdots n, \lambda) / g^{(n-1)}(2 \cdots n)] \\
 & = \sum_{i=2}^n v(i, \lambda) + \rho \int_0^\lambda d\lambda' \int d^3\mathbf{r}_{n+1} \frac{\partial v(1, n+1, \lambda)}{\partial \lambda} \\
 & \quad \times \{ [g^{(n+1)}(1 \cdots n+1, \lambda) / g^{(n)}(1 \cdots n, \lambda)] \\
 & \quad - g^{(2)}(1, n+1, \lambda) \}. \quad (7)
 \end{aligned}$$

Hill⁹ and Buff and Stillinger⁹ have pointed out that it is possible to present a consistent definition of local chemical potentials in a fluid in the vicinity of a fixed set of molecules, the latter providing in essence an external force field. Under equilibrium conditions it is necessary to demand that this local chemical potential equal the bulk chemical potential, and Hill's analysis shows that such requirement is equivalent to the result (7), upon use of the interaction range scaling method. One may see in this connection that the equilibrium distribution for particle 1, when the "external force-supplying" particles $2 \cdots n$ are known to have positions $\mathbf{r}_2 \cdots \mathbf{r}_n$ depends directly upon the reversible work of "charging up" particle 1 at various positions in the system, accomplished by changing λ . One may in fact make precisely such identifications with the individual terms appearing in Eq. (7), as is now demonstrated for a special case.

The major interest, so far as deduction of thermodynamic properties is concerned, lies in the pair distribution equation, obtained by setting $n=2$ in Eq. (7),

$$\begin{aligned}
 & -kT \log g^{(2)}(12, \lambda) = w^{(2)}(12, \lambda) \\
 & = v(12, \lambda) + \int_0^\lambda d\lambda' \int d^3\mathbf{r}_3 \frac{\partial v(13, \lambda')}{\partial \lambda'} \\
 & \quad \times [\rho_{12}(\mathbf{r}_3, \lambda) - \rho_1(\mathbf{r}_3, \lambda)], \\
 & \rho_{12}(\mathbf{r}_3, \lambda') = \rho g^{(3)}(123, \lambda') / g^{(2)}(12, \lambda'), \\
 & \rho_1(\mathbf{r}_3, \lambda') = \rho g^{(2)}(13, \lambda'). \quad (8)
 \end{aligned}$$

We have supposed that the boundary conditions on our system allow translation invariance, so that $g^{(i)} \equiv 1$ even in the solid-state region of the phase diagram. As the notation indicates, $\rho_1(\mathbf{r}_3, \lambda)$ and $\rho_{12}(\mathbf{r}_3, \lambda)$ are the average particle densities at position \mathbf{r}_3 in the neighborhood of fixed particle 1, or the fixed pair 12, respectively. The various contributions to the pair potential of mean force appearing in Eq. (8) represent separate steps in the reversible process:

(A1) When particles 1 and 2 are far apart [$w^{(2)}(12) = 0$], decrease λ to 0; the "cavity" or "hole" which 1 punches out of the surroundings collapses reversibly with work $-W^{(2)}(\lambda)$ done on the system. $W^{(2)}(\lambda)$ is determined by multiplying the work of altering λ by $d\lambda$ in the presence of only another particle

at \mathbf{r}_3 , multiplied by the equilibrium density at \mathbf{r}_3 when the particle at \mathbf{r}_1 has parameter λ , integrated over all positions \mathbf{r}_3 , and then integrated over λ to create the hole (it is the cavity creation work):

$$W^{(2)}(\lambda) = \int_0^\lambda d\lambda' \int d^3\mathbf{r}_3 \frac{\partial v(13, \lambda')}{\partial \lambda'} \rho_1(\mathbf{r}_3, \lambda'). \quad (9)$$

(A2) Bring discharged particle 1 to distance r_{12} of particle 2 (no work required).

(A3) Recharge 1 by increasing λ to its initial value, which requires work

$$\begin{aligned}
 & \int_0^\lambda d\lambda' \int d^3\mathbf{r}_3 \frac{\partial v(13, \lambda')}{\partial \lambda'} [\delta(\mathbf{r}_3 - \mathbf{r}_2) + \rho_{12}(\mathbf{r}_3, \lambda')] \\
 & = v(13, \lambda) + W_2^{(2)}(12, \lambda),
 \end{aligned}$$

$$W_2^{(2)}(12, \lambda) = \int_0^\lambda d\lambda' \int d^3\mathbf{r}_3 \frac{\partial v(13, \lambda')}{\partial \lambda'} \rho_{12}(\mathbf{r}_3, \lambda'). \quad (10)$$

At zero density, the only work performed occurs in step (3), $v(12, \lambda)$. However, at finite density, the average surroundings of 1 are spherically symmetric in step (1), but are perturbed nonspherically in step (3) by the presence of particle 2. It is the difference in the works of rearrangement for these two environments that gives rise to the nonvanishing density dependent, integral term in Eq. (8). This integral equation then may be abbreviated

$$w(12, \lambda) = v(12, \lambda) + W_2^{(2)}(12, \lambda) - W^{(2)}(\lambda). \quad (11)$$

For the hard-sphere form of $v(r)$, only those configurations \mathbf{r}_3 contribute to the integral appearing in Eq. (8), which correspond to "contact" between particles 1 and 3; this condition amounts to the equality $r_{13} = \lambda'a$.⁷ As a result, we may rewrite Eq. (8), for $r_{12} \geq \lambda a$,

$$\begin{aligned}
 -\log g^{(2)}(12, \lambda) & = a \int_0^\lambda d\lambda' \int_{S(\lambda')} d^2\mathbf{r}_3 [\rho_{12}(\mathbf{r}_3, \lambda') \\
 & \quad - \rho_1(\mathbf{r}_3, \lambda')], \quad (12)
 \end{aligned}$$

where $S(\lambda')$ is the spherical surface of radius $\lambda'a$, centered on particle 1.

The cavity creation works appearing in Eq. (11) may be obtained very simply in the case when $\lambda \leq \frac{1}{2}$. This observation is one of the key steps in the highly successful calculations of the thermodynamic properties of the rigid-sphere fluid by Reiss, Frisch, and Lebowitz.⁴ The work of creating a spherical cavity of radius λa about position 1 is related to the probability of spontaneously finding such a cavity in the fluid $p_0(\lambda)$ by the Boltzmann factor

$$p_0(\lambda) = \exp[-W^{(2)}(\lambda)/kT], \quad (13)$$

$$= 1 - p'(\lambda), \quad (14)$$

where $p'(\lambda)$ is the probability that the cavity is occupied. For $\lambda \leq \frac{1}{2}$ the region within $S(\lambda)$ can be

⁹ T. L. Hill, *J. Chem. Phys.* **30**, 1521 (1959); F. P. Buff and F. H. Stillinger, Jr., *ibid.* **25**, 312 (1956).

occupied by at most one particle, since this particle's exclusion sphere always blocks the entry of a second particle. The probability of occupation is then the average number of particles to be found in such a region, so that⁴

$$\exp[-W^{(c)}(\lambda)/kT] = 1 - 4\pi\rho a^3\lambda^3/3, \quad \lambda \leq \frac{1}{2}. \quad (15)$$

The result for $W_2^{(c)}(12, \lambda)$ is similar, but now one must account for the mean density variations surrounding particle 2. Therefore, the formula analogous to (15) is

$$\exp\left[\frac{-W_2^{(c)}(12, \lambda)}{kT}\right] = 1 - \rho \int_{\omega(\lambda)} g^{(2)}(23) d^3\mathbf{r}_3, \quad (16)$$

$$= 1 - 4\pi\rho^*(\lambda) a^3\lambda^3/3, \quad \lambda \leq \frac{1}{2}, \quad (17)$$

where $\omega(\lambda)$ is the spherical volume element bounded by $S(\lambda)$. The effective density $\rho^*(\lambda)$ has been introduced to preserve the form of the previous result (15). It is the average density inside ω , and differs from ρ because of the disturbing influence of particle 2. It is quite clear that (16) reduces to (15) as the distance r_{12} becomes large, and in this limit, the effective density ρ^* is identical with the actual macroscopic density ρ .

It has been pointed out before^{3,4} that in the present context of variably sized rigid spheres, the cavity work $W^{(c)}(\lambda)$ is directly related to the contact values of the pair correlation function $g^{(2)}(\lambda a, \lambda)$. Upon direct evaluation of the kinetic stress acting at the surface $S(\lambda)$, one finds

$$W^{(c)}(\lambda) = 4\pi\rho a^3 kT \int_0^\lambda \lambda'^2 g^{(2)}(\lambda' a, \lambda') d\lambda', \quad (18)$$

valid for all λ . This relationship provides an independent means of computing the cavity creation work. Alternatively, it may be combined with Eq. (17) to obtain the $\lambda \leq \frac{1}{2}$ values of the contact pair distribution⁴

$$g^{(2)}(\lambda a, \lambda) = 1/[1 - 4\pi\rho a^3\lambda^3/3], \quad \lambda \leq \frac{1}{2}. \quad (19)$$

In the event, then, that $0 \leq \lambda \leq \frac{1}{2}$, the pair distribution integral equation assumes precisely the form

$$\begin{aligned} -\log g^{(2)}(12, \lambda) &= w^{(2)}(12, \lambda)/kT \\ &= v(12, \lambda)/kT \\ &+ \log\left\{ \frac{1 - \frac{4}{3}\pi\rho a^3\lambda^3}{1 - \frac{4}{3}\pi\rho^*(\lambda) a^3\lambda^3} \right\} \\ &= v(12, \lambda)/kT \\ &+ [w^{(2)}(\lambda a, \lambda) - w^{(2)}(\lambda a, \lambda, \rho^*)]/kT. \quad (20) \end{aligned}$$

The last manner of writing has made use of Eqs. (15), (17), and (18). We have adopted the notation here and in the following, that unless otherwise indicated by inclusion of ρ^* , the quantities appearing in our equations are to be evaluated at the macroscopic density ρ . Over the indicated λ interval, as thus shown, it has been possible exactly to replace the integrals

appearing in Eq. (12) by a simple difference of mean pair potentials, involving the suitably defined effective density ρ^* . This gives $g^{(2)}(12, \lambda \leq \frac{1}{2})$ in terms of $g^{(2)}(12, \lambda=1)$. Another form of Eq. (20) is presented in the next section.

Much the same probabilistic analysis leads to an alternative but more complicated expression for $w^{(2)}$, utilizing the same effective density. When once again the variable range parameter is less than $\frac{1}{2}$, the average density in the neighborhood of particles 1 and 2, $\rho_{12}(\mathbf{r}_3, \lambda)$, may readily be evaluated for the configurations of interest in Eq. (12). When a particle is located at \mathbf{r}_3 on the surface $S(\lambda)$, its exclusion sphere entirely covers that for the shrunken particle 1. As a result, ρ_{12} may be expressed as the macroscopic ρ times a simply computable Boltzmann factor, by considering a second process:

(B1) Move particle 3 from a large distance to the required \mathbf{r}_{23} in the environment of 2; this necessitates, by definition, expenditures of reversible work $w^{(2)}(23)$.

(B2) Discharge 1 at a large distance from both 2 and 3, with associated cavity collapse work $-W^{(c)}(\lambda)$.

(B3) Charge up 1 to its initial state (size ϵ) at distance λa from 3 so that 1 and 3 end up in contact. This last step would entail work $v(12, \lambda)$ for a general pair interaction potential.

From the sum of reversible works performed in steps 1-3 it is necessary to subtract the pair potential of mean force $w^{(2)}(12, \lambda)$, since ρ_{12} is a local particle density *conditional* upon the presence of particles 1 and 2, separated by distance r_{12} . Finally, therefore,

$$\begin{aligned} \rho_{12}(\mathbf{r}_3, \lambda) &= \rho \exp\{-[w^{(2)}(23) - W^{(c)}(\lambda) + v(12, \lambda) \\ &- w^{(2)}(12, \lambda)]/kT\}, \quad r_{13} = \lambda a, \quad \lambda \leq \frac{1}{2}. \quad (21) \end{aligned}$$

The result (11) may be utilized in elimination of $w^{(2)}(12, \lambda)$, from (21). In view of Eq. (17) for $W_2^{(c)}(12, \lambda)$, one finds ($\lambda \leq \frac{1}{2}$)

$$\begin{aligned} \rho_{12}(r_{13} = \lambda a, \lambda) &= \rho g^{(2)}(23)/\frac{3}{2}[1 - 4\pi\rho^*(\lambda) a^3\lambda^3] \\ &= \rho g^{(2)}(23) g^{(2)}[r_{13} = \lambda a, \lambda, \rho^*(\lambda)], \quad (22) \end{aligned}$$

where (19) has been used to introduce the pair distribution function for particles 1 and 3, evaluated at the effective density ρ^* . [Equation (22) and all other results in this paper may be obtained by formal manipulation of the canonical ensemble distribution function, but we have chosen to present physical derivations instead.]

Likewise, the local density $\rho_1(r_{13} = \lambda a, \lambda)$ may be obtained simply by removing particle 2 to an essentially infinite distance. Equation (22) then reduces to

$$\begin{aligned} \rho_1(r_{13} = \lambda a, \lambda) &= \lim_{r_{2 \rightarrow \infty}} \rho_{12}(r_{13} = \lambda a, \lambda) \\ &= \rho g^{(2)}(13, \lambda, \rho^* = \rho), \quad (23) \end{aligned}$$

since ρ^* becomes equal, in this limit, to ρ , and $g^{(2)}(23)$ is just unity.

An important observation follows insertion of our expressions for ρ_{12} and ρ_1 into the integral equation (12)

$$-\log g^{(2)}(12, \lambda) = \rho a \int_0^\lambda d\lambda' \int_{S(\lambda')} d^3\mathbf{r}_3 \times [g^{(2)}(23)g^{(2)}[13, \lambda', \rho^*(\lambda')] - g^{(2)}(13, \lambda')]. \quad (24)$$

One sees that this integral equation, which is an exact relation for $0 \leq \lambda \leq \frac{1}{2}$ with definition (17) of ρ^* , has the same appearance as the Kirkwood superposition equation¹⁰ for this interaction range variation approach, but modified only by inclusion of a suitable effective density ρ^* . Stated in another way, the error committed in use of the usual superposition approximation may be compensated completely (at least for $\lambda \leq \frac{1}{2}$) by introduction of a simply modified density for particle separation distances comparable to molecular dimensions.

The physically interesting situation naturally demands that λ be unity. There probably exists some quantity $\rho^*(\lambda)$, for all values of the size parameter, which renders Eq. (24) an exact relation for $g^{(2)}$ with arbitrary λ . The problem is to formulate a reliable, if not exact, definition of ρ^* for all λ . When this parameter begins to exceed the value $\frac{1}{2}$, one major fact starts to invalidate the preceding analysis. It is the possibility of having two or more fully sized rigid-sphere molecules within $S(\lambda)$. As a result, our simple form for $W^{(e)}(\lambda)$ and $W_2^{(e)}(12, \lambda)$ are no longer correct.

The local density ρ_{12} may also be built up by a third virtual process which amounts to a permutation of the

steps in process B:

(C1) Discharge 1 at distance r_{12} from 2 which involves a cavity work of $-W_2^{(e)}(12, \lambda)$.

(C2) Bring up particle 3 from infinity to the desired distance from 2 with work $w^{(2)}(23)$.

(C3) Recharge 1 at its original position, now under the joint perturbing influence of both particles 2 and 3 which requires a cavity work denoted by $+W_{23}^{(e)}(123, \lambda)$.

As a result, one has ($r_{13} \geq \lambda a$)

$$\rho_{12}(\mathbf{r}_3, \lambda) = \rho \exp\{-[w^{(2)}(23) + W_{23}^{(e)}(123, \lambda) - W_2^{(e)}(12, \lambda)]/kT\}. \quad (25)$$

The cavity free energies appearing here and previously may be computed⁴ in principle from the results of Mayer and Montroll.¹¹ By way of obtaining a general ρ^* , applicable to all values of λ , we desire to replace the factor

$$\exp\{-[W_{23}^{(e)}(123, \lambda) - W_2^{(e)}(12, \lambda)]/kT\}, \quad (26)$$

where evaluation is at density ρ , by the expression

$$\exp\{-[W_3^{(e)}(13, \lambda, \rho^*) - W^{(e)}(\lambda, \rho^*)]/kT\} = g^{(2)}(13, \lambda, \rho^*), \quad (27)$$

with quantities now referring to effective density ρ^* . It is clear that upon doing so, the previous integral equation (24), with exactly the superficial structure of the Kirkwood superposition equation, is valid for all λ . When explicit use is made of the Mayer-Montroll series, $\rho^*(\lambda)$ is found to be given implicitly by the expression

$$1 - \frac{\rho}{1! \int_{\omega(\lambda)} g^{(3)}(23i) d^3\mathbf{r}_i} + \frac{\rho^2}{2! \int_{\omega(\lambda)} g^{(4)}(23ij) d^3\mathbf{r}_i d^3\mathbf{r}_j} - \dots = 1 - \frac{\rho^*}{1! \int_{\omega(\lambda)} g^{(2)}(3i, \rho^*) d^3\mathbf{r}_i} + \frac{(\rho^*)^2}{2! \int_{\omega(\lambda)} g^{(3)}(3ij, \rho^*) d^3\mathbf{r}_i d^3\mathbf{r}_j} - \dots$$

$$1 - \frac{\rho}{1! \int_{\omega(\lambda)} g^{(2)}(2i) d^3\mathbf{r}_i} + \frac{\rho^2}{2! \int_{\omega(\lambda)} g^{(3)}(2ij) d^3\mathbf{r}_i d^3\mathbf{r}_j} - \dots = 1 - \frac{\rho^*}{1! \int_{\omega(\lambda)} d^3\mathbf{r}_i} + \frac{(\rho^*)^2}{2! \int_{\omega(\lambda)} g^{(2)}(ij, \rho^*) d^3\mathbf{r}_i d^3\mathbf{r}_j} - \dots \quad (28)$$

This reduces to the previous definition ρ^* when $\lambda \leq \frac{1}{2}$, since then only one particle can be in $\omega(\lambda)$ at a time.

Even if it were known that a unique quantity $\rho^*(\lambda)$ existed as the inversion of relation (28), this method of determination defeats the ultimate desire to obtain a closed functional relation for the pair distribution

¹⁰ The Kirkwood approximate integral equation is obtained from (12), upon replacement of $g^{(3)}(123, \lambda)$ in ρ_{12} , Eq. (8), by a superposition of pair correlation functions

$$g^{(3)}(123, \lambda) \cong g^{(2)}(12, \lambda)g^{(2)}(13, \lambda)g^{(2)}(23).$$

Each of the $g^{(2)}$'s is evaluated at the macroscopic density ρ .

function, involving no other unknowns, since $g^{(n)}$'s of all orders appear in Eq. (28). Nevertheless, it does appear possible to use this last equation as a guide in approximate practical definition of ρ^* , in which only $g^{(2)}$ occurs.

For this reason, we examine the zero density asymptote for ρ^* , and any value of λ . Thus it is necessary to retain only the leading terms in each numerator and denominator of (28), and to replace each correlation function by its zero density form. Taking logarithms

¹¹ J. E. Mayer and E. Montroll, J. Chem. Phys. 9, 2 (1941).

in (28), one first obtains

$$\begin{aligned}
 &-\rho \int_{\omega(\lambda)} \left[\frac{g^{(3)}(23i)}{g^{(2)}(23)} - g^{(2)}(2i) \right] d^3\mathbf{r}_i + \frac{(-\rho)^2}{2!} \\
 &\times \int_{\omega(\lambda)} \{ \} d^3\mathbf{r}_i d^3\mathbf{r}_j + \dots = -\rho^* \int_{\omega(\lambda)} [g^{(2)}(3i, \rho^*) - 1] d^3\mathbf{r}_i \\
 &\quad + \frac{(-\rho^*)^2}{2!} \int_{\omega(\lambda)} [\] d^3\mathbf{r}_i d^3\mathbf{r}_j + \dots \quad (29)
 \end{aligned}$$

Passing to the $\rho=0$ limit, one finds

$$\frac{\rho^*}{\rho} = \frac{\int_{\omega(\lambda)} \exp\left[-\frac{v(2i)}{kT}\right] \left[\exp\left[-\frac{v(3i)}{kT}\right] - 1 \right] d^3\mathbf{r}_i}{\int_{\omega(\lambda)} \left\{ \exp\left[-\frac{v(3i)}{kT}\right] - 1 \right\} d^3\mathbf{r}_i} \quad (30)$$

Since the factor $\{\exp[-v(3i)/kT]-1\}$ vanishes for positions \mathbf{r}_i outside the exclusion sphere of particle 3, we see that the effective density amounts to an average of $\rho \exp[-v(2i)/kT]$, which is the low-density limit of $\rho g^{(2)}(2i)$, over the volume $\omega_{13}(\lambda)$ common to the exclusion spheres of both particles 1 and 3. Unlike the previous $\lambda \leq \frac{1}{2}$ situation, $\omega(\lambda)$ is not entirely encased within 3's sphere. In this latter case one obviously has $\omega_{13}(\lambda) = \omega(\lambda)$. These regions are illustrated in Fig. 1.

The effective density definition that is immediately suggested as an approximate formulation at *all* values of *both* ρ and λ , is the average of $\rho g^{(2)}(2i)$ over the region $\omega_{13}(\lambda)$

$$\rho^*(\lambda) = \rho \left[\int_{\omega_{13}(\lambda)} g^{(2)}(2i) d^3\mathbf{r}_i \right] / \left[\int_{\omega_{13}(\lambda)} d^3\mathbf{r}_i \right] \quad (31)$$

As we have seen, Eq. (31) becomes exact in the two simply solved cases, $\lambda \leq \frac{1}{2}$ (with any ρ), and $\rho \rightarrow 0$ (any λ). It is of interest to note, furthermore, for λ just above $\frac{1}{2}$, definition (31) can be in error only by terms of order $(\lambda - \frac{1}{2})^2$. Therefore, the simplified ρ^* definition, Eq. (31) "starts out" toward $\lambda=1$ properly at any density ρ , since the error cannot immediately and discontinuously jump to a large value. On this crude basis, one might reasonably expect that perhaps the error in this extrapolation formula has not much opportunity to build up to significant size by the time that λ reaches unity.

One immediate advantage of the use of ρ^* , even in the unsophisticated approximation (31), is clear. Since ρ^* as defined is correct to lowest order in ρ , the corresponding $g^{(2)}$ computed from the effective density integral equation is given correctly to order ρ^2 . As a result, the fourth virial coefficient B_4 in density expansion of the pressure of the rigid-sphere system is obtained exactly, when use is made specifically of the predicted $g^{(2)}(a, 1)$. A little reflection will show that

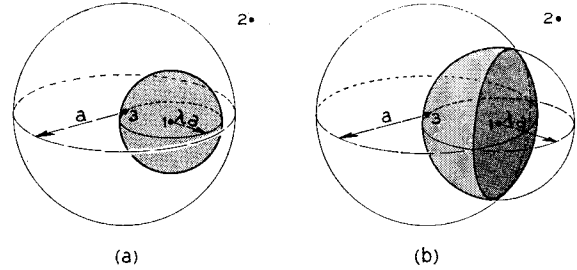


FIG. 1. The region of integration ω for (a) $\lambda \leq \frac{1}{2}$ and (b) $\lambda \geq \frac{1}{2}$ is shown by shading. The light spheres are the exclusion spheres of the particle at 3 and the lambda-dacule at 1. A typical location of the point 2 is indicated.

the geometrical region ω_{13} is just what should arise in the rather troublesome three-center integrals encountered in the cluster-theoretical evaluation of B_4 . The exactness of specific virial coefficients, though, cannot be construed as direct evidence for an adequate microscopic description of the system at typical liquid or solid densities. It is nevertheless gratifying that an excellent account of the moderately dense gas automatically appears in this formalism. On the ordinary superposition basis, where $\rho^* = \rho$, one finds the predicted B_4 is 61% low.

III. FURTHER DEVELOPMENT OF THE INTEGRAL EQUATION

In the previous section the integral equations were handled in a manner which was most suitable for the development of the theory. For computational and certain conceptual purposes it may be useful to present the equations in another guise.

A differentiation of Eq. (12) with respect to λ yields

$$\begin{aligned}
 \frac{dg^{(2)}(12, \lambda)}{d\lambda} &= \rho a \int_{S(\lambda)} d^2\mathbf{r}_3 \\
 &\times [g^{(3)}(r_{12}, r_{23}, r_{13} = \lambda a, \lambda) - g^{(2)}(12, \lambda) g^{(2)}(r_{13} = \lambda a, \lambda)]. \quad (32)
 \end{aligned}$$

Equation (22) illustrated how this equation can be closed entirely in terms of $g^{(2)}$'s for $\lambda \leq \frac{1}{2}$, but there is actually another exact form of closure which has a simpler aspect. The $g^{(3)}$ which enters into Eq. (32) requires that the lambda-dacule 1 be in contact with 3. For $\lambda \leq \frac{1}{2}$ this means that the lambda-dacule is completely inside the exclusion sphere of 3, so that particle 2 has no way of knowing whether the lambda-dacule is there or not. Thus, 1 and 2 are uncorrelated. The $g^{(3)}$ of interest is simply a product of two independent correlation factors [cf. Eq. (21)]

$$g^{(3)}(r_{12}, r_{23}, r_{13} = \lambda a, \lambda) = g^{(2)}(23) g^{(2)}(r_{13} = \lambda a, \lambda), \quad \lambda \leq \frac{1}{2}. \quad (33)$$

This last equation is directly related to (22) through Eqs. (19) and (20). When Eq. (33) is inserted in (32)

one obtains a relation which may be explicitly integrated, since $g^{(2)}(r_{12}=\lambda a, \lambda \leq \frac{1}{2})$ is known. The result, after considerable manipulation, is

$$g^{(2)}(r_{12}, \lambda) = \frac{1}{(1 - \frac{4}{3}\pi\rho a^3\lambda^3)} \left[1 + \frac{\pi\rho}{r_{12}} \int_1^\infty \{ |r_{12} - r_{23}|^2 - (\lambda a)^2 \} A(\lambda a - |r_{12} - r_{23}|) r_{23} g^{(2)}(r_{23}) dr_{23} \right], \quad \lambda \leq \frac{1}{2}, \quad r_{12} \geq \lambda a, \quad (34)$$

where A is the unit step function. This exact expression relating $g^{(2)}$ for $\lambda \leq \frac{1}{2}$ to its value for $\lambda=1$ is to be considered as an equation coupled, but only in an almost trivial sense, to the effective density equation which now need be integrated only from $\lambda = \frac{1}{2}$ to 1; viz.,

$$-\log[g^{(2)}(12, \lambda)/g^{(2)}(12, \lambda = \frac{1}{2})] = \rho a \int_{\frac{1}{2}}^\lambda d\lambda' \int_{S(\lambda')} d^2\mathbf{r}_3 \times \{ g^{(2)}(r_{23}) g^{(2)}[r_{13} = \lambda' a, \lambda', \rho^*(\lambda')] - g^{(2)}(r_{13} = \lambda' a, \lambda') \}. \quad (35)$$

At first sight it would seem that the most imposing obstruction to a numerical solution of (35) is the fact that the radial distribution functions at various densities are coupled in an unpleasant fashion. This occurs however, only through the density dependence of the contact distribution function, for which a functional form, which is probably quite good, has been presented by Reiss, Frisch, and Lebowitz.⁴

Finally, we wish to mention that a more reasonable independent variable than r_{12} to employ in Eq. (32) is

$$s_{12} = r_{12} - \lambda a. \quad (36)$$

The integration over λ should then be performed at constant s_{12} rather than r_{12} by use of the relation

$$(\partial/\partial\lambda)_{s_{12}} = (\partial/\partial\lambda)_{r_{12}} + a(\partial/\partial r_{12})_\lambda. \quad (37)$$

The required expression for $[\partial \log g(12, \lambda)/\partial r_{12}]_\lambda$ may be obtained by deriving a Born-Green integral equation with λ coupling. The advantage of this procedure is that one expects the derivative of the potential of mean force at constant s_{12} to be smoother and smaller than at constant r_{12} , as is evident for example for contact $r_{12} = \lambda a$. A fuller discussion of these points, and other purely computational matters, will be reserved for a future publication.

IV. GENERALIZATION

The advantage of using the hard-sphere model in constructing the effective density integral equation to a large extent lies in the fact that the configuration integrals encountered span sharply defined geometrical regions. Such clear-cut regions, which thereby have the

attraction of ready visualization, arose precisely from the discontinuous nature of the rigid-sphere interaction potential, Eq. (2). A more realistic interaction, in the interests of better numerical correspondence with real systems at low or intermediate temperatures, would necessarily exhibit the attractive well and the core "softness" such as possessed by the usual semiempirically determined molecular potential functions. As a consequence, it is desirable to indicate here the method of generalizing the effective density procedure to handle this larger class of model systems.

In spite of relaxation of the sharp and singular hard-sphere picture, one still must acknowledge that realistic sphericalized molecular potentials possess very powerful repulsive forces at small distances of separation giving rise to a meaningful concept of molecular "size." As a consequence, our former comments concerning the simple form of $W^{(e)}$ and $g^{(2)}$, when the size parameter λ is sufficiently small, still bear the force of excellent approximation. Now, though, there does not necessarily exist a uniquely defined analog to the previous value $\lambda = \frac{1}{2}$, below which the elementary analysis is exact.⁵

Reference to Eq. (8), which is valid for arbitrary interaction potentials v , shows that the relative configurations of particles 1 and 3 which contribute the major portion of the integral are those for which $v(13, \lambda')$ is either at the sides of the attractive well, or on the steeply rising repulsive part. When λ' is small, and when these configurations obtain, particle 3 effectively shields 1 from the influence of others. In order that any passing particles get close enough to 1 to interact strongly, it must necessarily move well into the powerfully repelling core of 3, a statistically unlikely event.

The appropriate generalization procedure follows immediately upon examining the Mayer-Montroll series for the more realistic interactions.¹¹ Here it is found that the only modification is replacement of integrals over the finite region $\omega(\lambda)$ in Eq. (21) by integrals over the entire system volume, but with a weighting factor

$$-f(1j, \lambda) = 1 - \exp[-v(1j, \lambda)/kT]. \quad (38)$$

The former case is recovered for a rigid sphere v , since then $-f$ is a unit step function, vanishing identically outside the region of singular repulsion. Adaptation of the previous analysis therefore is straightforward, and yields a $\rho^*(\lambda)$ defined by

$$\rho^*(\lambda) = \rho \left[\int f(1i, \lambda) f(3i) g^{(2)}(2i) d^3\mathbf{r}_i / \int f(1i, \lambda) f(3i) d^3\mathbf{r}_i \right]. \quad (39)$$

The functional equation determining the pair distribution is of course once again the superposition integral

equation, including ρ^*

$$-kT \log g^{(2)}(12, \lambda) = v(12, \lambda) + \rho \int_0^\lambda d\lambda' \int d^3\mathbf{r}_3 (\partial v(13, \lambda') / \partial \lambda') \times \{g^{(2)}(23)g^{(2)}[13, \lambda', \rho^*(\lambda')] - g^{(2)}(13, \lambda')\}. \quad (40)$$

Unfortunately it is no longer possible to make use of the reduction of the $d^3\mathbf{r}_3$ integration as in Eq. (12) to a surface integral. Consequently, detailed numerical solution for $g^{(2)}$ in the general situation is a somewhat more difficult task than for the hard-sphere model.

Once again, the fourth virial coefficient is predicted correctly as a result of using the effective density ρ^* .

V. DISCUSSION

The object of the preceding analysis consists in suggesting use of certain statistical mechanical information in improving existing methods for computation of molecular distribution functions. That an effective density ρ^* should arise is not surprising; any particle in the system possesses an interaction potential of finite range and therefore is capable of "sampling" its surroundings over some finite region of molecular extent. Replacement of the local density average ρ^* by the macroscopic ρ , as one now sees has been traditional, is a moderately crude procedure which entails distortion of the microscopic description. This loss of molecular structure information is already evident in the fourth virial coefficient predictions.

To state the situation somewhat differently, one might remark that previously it was customary to approximate the three-particle correlation functions by a product ("superposition") of spherically symmetric pair functions. It is quite clear that the resulting approximate $g^{(3)}$ belongs to a very special class of functions of three position variables. That is, the mathematical restriction on $g^{(3)}$ imposed merely by demanding it be a product of radial functions is probably quite severe so far as correspondence with the physical situation is concerned. The introduction of

an effective density, even by the simple definition (39), however, has removed this restriction. That the computed B_4 is exact already shows that in moderately dense gases our $g^{(3)}$ is more accurate than previously.

We do not claim to have made an exhaustive analysis of possible effective density procedures. The elementary ρ^* considered here, though, does seem to represent sufficient improvement on the theory to warrant somewhat more than superficial investigation. One can, of course, set forth a sequence of more and more complicated ρ^* 's which yield exact B_n 's of higher and higher orders. It must nevertheless be stressed that one cannot thereby be assured that such extra work is profitable in providing an increasingly precise account of the condensed phases' properties.

On physical grounds one might imagine that more symmetric effective density approximations may be of interest. If the presence of particle 2 at \mathbf{r}_2 requires that $g^{(2)}(13)$ be evaluated at some effective density characteristic of the neighborhood of 2 where 1 and 3 are located, should not the presence of 1 similarly influence 2 and 3? This may be a fertile field for investigation. The authors have given some consideration to this problem from the point of view of the diagrammatic expansion of $g^{(3)}$, and the difficulties in symmetrizing become immediately apparent.

The effective density scheme may be adapted to systems of molecules without spherical symmetry, and with internal coordinates. It is likewise possible to consider mixtures of several different species. In such elaborations of the theory, the major difficulty is one of notation, rather than novelty in concept.

The special features of the particle scaling procedure have been particularly useful in leading to the effective density formulation. It is certainly true that the Mayer-Montroll series could be employed to suggest a suitable effective density in the context of Kirkwood's original interaction *strength* variation method.⁸ Here, however, it is not possible to give a straightforward account of the singular rigid-sphere case, which is so conveniently handled by the technique of this article.