

## Approximations in the Theory of Dense Fluids\*

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A fluid of rigid spheres in equilibrium is considered from a viewpoint which allows the deduced equation of state to reflect very sensitively the accuracy of two approximations to the triplet distribution function. Specifically, these approximations are: (1) the usual Kirkwood superposition scheme, and (2) assumption that the correlation of excess particles near a fixed particle pair is additively composed of the excesses induced individually by each member of the pair (linear correlation field hypothesis). Granted only these hypotheses, each in turn, the rigorous statistical mechanical relations between rigid-sphere distribution functions and the thermodynamic pressure and compressibility lead unambiguously to nonlinear first-order differential equations for the pressure as a function of density. The simply obtained numerical solutions clearly demonstrate that assumption (1) is considerably superior to (2).

### I. INTRODUCTION

THE central quantity in analysis of the equilibrium properties of liquids and dense gases is the pair correlation function  $g^{(2)}$ . If the constituent molecules may be regarded as interacting in pairs, a complete knowledge of this function allows deduction of all thermodynamic properties, as well as x-ray scattering patterns. Furthermore, the equilibrium pair correlations may serve as the starting point for evaluation of dense fluid transport properties.<sup>1</sup>

The function  $g^{(2)}$  is experimentally accessible by Fourier inversion of scattering patterns. But due to the extreme sensitivity of computed thermodynamic properties (such as the isothermal compressibility) upon the exact form of  $g^{(2)}$ , as well as inherent interest in the statistical problem, it has been desirable to seek accurate and practical theoretical determinations of this function. A number of investigators<sup>2-5</sup> have shown that  $g^{(2)}$ , as well as higher-order correlation functions, rigorously satisfy hierarchies of coupled functional equations. The relation for  $g^{(2)}$  typically involves the triplet correlation function  $g^{(3)}$ , so that the former quantity is not directly determined by such analyses.

It has therefore been necessary to seek suitable approximations which, in the first place, would

supplant the hierarchies by functional equations involving only  $g^{(2)}$ . Secondly, these approximations should be based upon sufficient physical evidence, or arguments by close analogy, to ensure (at least on an intuitive basis) that the resulting  $g^{(2)}$  are fairly close to their exact forms.

Unfortunately, the microscopic structure of dense fluids is complicated to the extent that such approximations are hard to justify in a convincing manner. The purpose of the present paper is to examine, for the idealized fluid consisting of rigid spheres, the results of utilizing each of two approximations to the triplet correlation function. The first of these is the well-known Kirkwood superposition approximation, wherein it is supposed that the potential of mean force for three particles is pairwise decomposable, similar to what is generally supposed for the interaction potentials themselves. The alternative hypothesis investigated appears to rest no less firmly upon the presumptive evidence for superposition. It claims essentially that the excess density local to a fixed particle plays the role of a linear scalar field; the excess density near a fixed pair, then, is additively composed of the two single particle contributions.

The rigid-sphere fluid is convenient for illustration's sake for two reasons. The equation of state for this model may be reduced, in both the superposition approximation, and linear correlation field cases, to nonlinear first-order differential equations. The other motivation for such choice, also a result of the singular potential, is that the particle configurations which contribute to the deduced equations of state are precisely those for which the relevant approximations are expected to be poor, namely, when particles are in contact. Thus, by

\* This work is based partly upon a section contained in a dissertation presented by the author in 1958 to the Graduate School Faculty of Yale University.

<sup>1</sup> J. G. Kirkwood, F. P. Buff, and M. S. Green, *J. Chem. Phys.* **17**, 988 (1949).

<sup>2</sup> J. G. Kirkwood, *J. Chem. Phys.* **3**, 300 (1935).

<sup>3</sup> J. Yvon, *Actualités Scientifique et Industrielles* (Hermann & Cie, Paris, France, 1935).

<sup>4</sup> M. Born and H. S. Green, *A General Kinetic Theory of Liquids* (Cambridge University Press, Cambridge, England, 1949).

<sup>5</sup> L. Sarolea and J. E. Mayer, *Phys. Rev.* **101**, 1627 (1956).

choosing to aggravate imprecision in the approximations, the corresponding inaccurate equations of state serve as sensitive indicators of the value of those approximations; the results must be compared to the known behavior of the system, determined accurately by independent means.

The nonlinear differential equations have been solved numerically, subject to the appropriate boundary conditions. One concludes that the superposition approximation has greater validity than the linear correlation field hypothesis.

## II. GENERAL RELATIONS

In this section, an integral equation technique for the pair correlation function is reviewed briefly in slightly generalized form. One considers, in a appropriate container of volume  $V$ , a set of  $N$  identical particles which interact through pairwise additive central forces. At absolute temperature  $T$ , the unnormalized configuration probability for a canonically distributed ensemble of such systems is

$$\exp \left[ -\frac{1}{kT} \sum_{i < j=1}^N v(ij) \right], \quad v(ij) \equiv v(r_{ij}), \quad (1)$$

with  $v(ij)$  the pair potential for particles  $i$  and  $j$ , and where  $k$  is Boltzmann's constant.

The correlation function for a set of  $n \ll N$  particles,  $g^{(n)}(1 \cdots n)$ , is defined to be proportional to the probability that the indicated  $n$  particles simultaneously occupy positions  $\mathbf{r}_1 \cdots \mathbf{r}_n$ , irrespective of the configuration of the remaining  $N - n$  particles. For the present purposes it is sufficient to suppose that  $g^{(n)}$  is normalized to unity when all the  $n$  particles are far from one another with respect to the range of intermolecular forces. Consequently,  $g^{(n)}$  may be written as a partial phase space integral of the density (1) over the coordinates of the residual  $N - n$  particles in  $V$ . Neglecting insignificant terms of order  $N^{-1}$ ,<sup>6</sup> one finds

$$\begin{aligned} g^{(n)}(1 \cdots n) &= \exp \left[ -\frac{1}{kT} w^{(n)}(1 \cdots n) \right] \\ &= \frac{V^n}{Z_N} \int \cdots \int \exp \left[ -\frac{1}{kT} \right. \\ &\quad \left. \cdot \sum_{i < j=1}^N v(ij) \right] d^3\mathbf{r}_{n+1} \cdots d^3\mathbf{r}_N, \quad (2) \end{aligned}$$

$$Z_N = \int \cdots \int \exp \left[ -\frac{1}{kT} \sum_{i < j=1}^N v(ij) \right] d^3\mathbf{r}_1 \cdots d^3\mathbf{r}_N.$$

Here,  $w^{(n)}$  is the potential of mean force for  $n$  particles.

The procedure for derivation of the  $g^{(2)}$  integral equation (involving  $g^{(3)}$ ) follows through use of an artifice introduced by Kirkwood.<sup>2</sup> For one of the  $N$  particles (chosen to be particle 1), an accessory parameter  $\lambda$  is introduced which serves to decouple this particle from the  $N - 1$  others. Thus one replaces the pair interaction  $v(r_{1i})$ , for the chosen particle 1 and each of the  $N - 1$  others, by a new function  $v(r_{1i}, \lambda)$  satisfying

$$\begin{aligned} v(r_{1i}, \lambda = 0) &= 0, \\ v(r_{1i}, \lambda = 1) &= v(r_{1i}). \end{aligned} \quad (3)$$

Therefore, vanishing  $\lambda$  corresponds to complete decoupling of 1 from the remaining particles; setting  $\lambda = 1$ , however, produces the full coupling of  $N$  identically interacting molecules and hence represents the "real" system. For the moment,  $v(r, \lambda)$  may be arbitrarily chosen, provided it is once differentiable in  $\lambda$ , and satisfies Eq. (3).

In view of the use of  $\lambda$ , the pair correlation function for particles 1 and 2 must now be written to indicate  $\lambda$  dependence. When the appropriate modifications are introduced in definition (2), with  $n = 2$ , a  $\lambda$  differentiation, followed by rearrangement and integration over  $\lambda$ ,<sup>7</sup> finally yields the desired integral equation,

$$\begin{aligned} -kT \log g^{(2)}(12, \lambda) &= w^{(2)}(12, \lambda) \\ &= v(12, \lambda) + \rho \int_0^\lambda d\lambda' \int d^3\mathbf{r}_3 \frac{\partial v(13, \lambda')}{\partial \lambda'} \\ &\quad \cdot \left\{ \frac{g^{(3)}(123, \lambda')}{g^{(2)}(12, \lambda')} - g^{(2)}(13, \lambda') \right\}, \quad (4) \end{aligned}$$

where

$$\rho = N/V.$$

The terms on the right side of Eq. (4) may readily be identified in a physically understandable sense. The leading term is of course the contribution to the pair potential of mean force,  $w^{(2)}$ , remaining at zero fluid density; it is precisely the interaction potential for the pair 12. The integral term, in two parts, represents at finite  $\rho$  the nonvanishing effect of fluctuating forces on 1 and 2, provided by the surrounding medium of  $N - 2$  particles.

In general, a certain amount of reversible (isothermal) work is performed if the coupling parameter  $\lambda$  slowly varies. The local particle density at  $\mathbf{r}_3$

<sup>6</sup> T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956), Chap. 6.

<sup>7</sup> The derivation is covered in detail in Chap. 6 of reference 6 for a special  $v(r, \lambda)$ . Generalization to the present case is trivial.

surrounding 1, when a second particle 2 is held fixed a distance  $r_{12}$  away, is given by the expression

$$\rho \frac{g^{(3)}(123, \lambda)}{g^{(2)}(12, \lambda)} = \rho_{12}(\mathbf{r}_3, \lambda), \quad (5)$$

which follows from definition of the correlation functions. The reversible work done on volume element  $d^3\mathbf{r}_3$  at  $\mathbf{r}_3$ , when the coupling parameter changes from  $\lambda$  to  $\lambda + d\lambda$  is therefore equal to

$$\rho \frac{\partial v(13, \lambda)}{\partial \lambda} \frac{g^{(3)}(123, \lambda)}{g^{(2)}(12, \lambda)} d^3\mathbf{r}_3 d\lambda; \quad (6)$$

this is precisely the combination occurring in Eq. (4). When Eq. (6) is integrated over all positions  $\mathbf{r}_3$ , one obtains the total reversible work performed on the surroundings of 1 and 2. If particle 2 were sufficiently far from 1 (at "infinity," but still within the system, of course), the quantity in Eq. (5) reduces to

$$\begin{aligned} \rho \lim_{r_2 \rightarrow \infty} \frac{g^{(3)}(123, \lambda)}{g^{(2)}(12, \lambda)} &= \rho g^{(2)}(13, \lambda) \\ &= \rho_1(\mathbf{r}_3, \lambda), \end{aligned} \quad (7)$$

with a differential work, corresponding to Eq. (6), which is

$$\rho \frac{\partial v(13, \lambda)}{\partial \lambda} g^{(2)}(13, \lambda) d^3\mathbf{r}_3 d\lambda. \quad (8)$$

Aside from a minus sign, this is the second term under the integral in Eq. (4).

The contribution of the ambient medium to the pair potential of mean force, acting between a pair of particles at distance  $r_{12}$ , therefore has a clear interpretation. It is the net work that must be done to discharge one of the particles at very large separation from the other ( $\lambda$  decreasing from 1 to 0), followed next by relocation of this discharged particle at distance  $r_{12}$  (no work is done in this step, since  $\lambda \rightarrow 0$  removes the relevant forces), and finally charging up the particle in its new location ( $\lambda$  increasing from 0 to 1) with the pair interaction  $v(12, \lambda)$  subtracted out of the last step since it does not refer to the medium contribution. A nonvanishing net reversible work reflects the fact that particle 2 at finite distance from 1 disturbs the average composition in the environment of particle 1.

We next take note of two well-known relations,<sup>6</sup> which will subsequently be used to connect the pair correlation functions to the thermodynamic pressure  $p$ . From the virial theorem, one establishes that

$$\frac{p}{\rho kT} = 1 - \frac{2\pi\rho}{3kT} \int_0^\infty r^3 \frac{\partial v(r)}{\partial r} g^{(2)}(r, \lambda = 1) dr. \quad (9)$$

In addition, the compressibility may be obtained directly from fluctuation theory without recourse to differentiation of Eq. (9). One finds

$$\begin{aligned} kT \left( \frac{\partial \log \rho}{\partial p} \right)_T \\ = \frac{1}{\rho} + 4\pi \int_0^\infty r^2 [g^{(2)}(r, \lambda = 1) - 1] dr. \end{aligned} \quad (10)$$

It is our purpose to examine the integral, Eq. (4), for a fluid of rigid spheres. With this system, the pair interactions are either infinite, or zero, depending on whether or not the chosen pair of spheres (each with diameter  $a$ ) overlap. It is especially convenient, for these rigid spheres, to specify the  $\lambda$ -parameterized interaction by

$$\begin{aligned} v(r, \lambda) &= v(r/\lambda); \\ v(s) &= \infty \quad s < a, \\ &= 0 \quad s \geq a. \end{aligned} \quad (11)$$

The effect of changes in  $\lambda$  hence is variation in the range (rather than strength) of the interaction. As  $\lambda$  decreases to zero, the region of repulsion in relative pair space shrinks finally to a point, so the pair interaction has in essence been removed.<sup>8</sup>

In terms of the local densities  $\rho_{12}$  and  $\rho_1$ , the general integral equation for our special fluid is

$$\begin{aligned} -\log g^{(2)}(12, \lambda) &= \frac{v(12, \lambda)}{kT} + \frac{1}{kT} \int_0^\lambda d\lambda' \\ &\cdot \int d^3\mathbf{r}_3 \frac{\partial v(r_{13}/\lambda')}{\partial \lambda'} [\rho_{12}(\mathbf{r}_3, \lambda') - \rho_1(\mathbf{r}_3, \lambda')]. \end{aligned} \quad (12)$$

The  $\lambda'$  derivative of  $v$  appearing in the integrand of Eq. (12), with the singular definition, Eq. (11), only has proper meaning when combined with the square-bracketed factor. In this connection, note that each  $\rho_{12}(\mathbf{r}_3, \lambda')$  and  $\rho_1(\mathbf{r}_3, \lambda')$  may be expressed as a function of  $\mathbf{r}_3$  continuous at  $r_{13} = \lambda a$  (denoted by bars), multiplied by the appropriate discontinuous Boltzmann factor (which is either 0 or 1).<sup>9</sup>

$$\begin{aligned} \rho_{12}(\mathbf{r}_3, \lambda') &= \exp \left[ -\frac{1}{kT} v(13, \lambda') \right] \bar{\rho}_{12}(\mathbf{r}_3, \lambda'), \\ \rho_1(\mathbf{r}_3, \lambda') &= \exp \left[ -\frac{1}{kT} v(13, \lambda') \right] \bar{\rho}_1(\mathbf{r}_3, \lambda'). \end{aligned} \quad (13)$$

<sup>8</sup> This coupling scheme has recently been used also to obtain accurate thermodynamic results for the hard-sphere fluid by a somewhat different approach; see H. Reiss, H. L. Frisch, and J. L. Lebowitz, *J. Chem. Phys.* **31**, 369 (1959).

<sup>9</sup> Cf. *Phase Transformations in Solids*, edited by R. Smoluchowski (John Wiley & Sons, Inc., New York, 1951), p. 72.

Upon acknowledging the identity

$$\begin{aligned} \exp \left[ -\frac{1}{kT} v(13, \lambda') \right] \frac{\partial v(13, \lambda')}{\partial \lambda'} \\ = -kT \frac{\partial}{\partial \lambda'} \exp \left[ -\frac{1}{kT} v(13, \lambda') \right] \\ = akT \delta(r_{13} - \lambda a) \end{aligned} \tag{14}$$

[this follows from Eq. (11)], the pair correlation integral equation may be written

$$\begin{aligned} -\log g^{(2)}(12, \lambda) = \frac{v(12, \lambda)}{kT} \\ + a \int_0^\lambda d\lambda' \int_{S(\lambda')} d^2\mathbf{r}_3 [\bar{\rho}_{12}(\mathbf{r}_3, \lambda') - \bar{\rho}_1(\mathbf{r}_3, \lambda')]. \end{aligned} \tag{15}$$

One is left with an  $\mathbf{r}_3$  integral over just the two-dimensional surface,  $S(\lambda')$ , of the sphere surrounding particle 1, with radius  $\lambda'a$ . It is precisely at the surface of this exclusion sphere that work of displacement is performed in creating cavities of the proper size to contain the impenetrable particle; for this reason, only those values of the local density exactly at the surface  $S(\lambda')$  are of significance in Eq. (15).

Essentially the same considerations for this rigid-sphere fluid show that only the value of  $g^{(2)}(r)$  at contact ( $r = a$ ) contributes to the pressure. Equation (9) therefore appears,

$$\frac{p}{\rho kT} = 1 + \frac{2\pi\rho a^3}{3} g^{(2)}(a, 1). \tag{16}$$

### III. THE SUPERPOSITION APPROXIMATION

The average density surrounding a fixed particle, with associated "size" parameter  $\lambda$ , is the quantity  $\rho_1$  in Eq. (7), which we may exhibit in the form

$$\rho_1(r_3, \lambda) = \rho \exp \left[ -\frac{1}{kT} v(13, \lambda) \right] [1 + \varphi(13, \lambda)]. \tag{17}$$

As the density of our fluid decreases to zero,  $\varphi$  vanishes to yield the Boltzmann factor representative of the pair interaction  $v$ , and unmodified by any surrounding medium. Similarly,  $\rho_{12}$ , the density near a pair, can be expressed as

$$\begin{aligned} \rho_{12}(\mathbf{r}_3, \lambda) = \rho \exp \left\{ -\frac{1}{kT} [v(13, \lambda) + v(23)] \right\} \\ \cdot [1 + \varphi(13, \lambda) + \varphi(23) + \epsilon(123, \lambda)], \\ \varphi(23) = \varphi(23, \lambda = 1), \end{aligned} \tag{18}$$

thereby defining  $\epsilon$ . When the distance  $r_{12}$  is large compared to the range of intermolecular forces,  $\epsilon$  must be zero, since then only separate density

fluctuations occur in the neighborhoods of 1 and 2.

There is a further condition on  $\epsilon$ , when  $\lambda$  is set equal to unity, that may be recognized. This arises from the fact that the triplet correlation function is unchanged upon permutation of its configuration arguments. By combining Eqs. (5), (17), and (18), we must have that

$$[1 + \varphi(12)][1 + \varphi(13) + \varphi(23) + \epsilon(123)] \tag{19}$$

be symmetric in its three arguments.

Unfortunately, these considerations are not in themselves quantitatively illuminating; it is essentially the unknown character of  $\epsilon$  which prevents one from computing the exact behavior of  $g^{(2)}$ . It has been Kirkwood's suggestion that the triplet potential of mean force  $w^{(3)}$  is approximated adequately by the sum of the three mean pair potentials,

$$\begin{aligned} w^{(3)}(123, \lambda) \cong w^{(2)}(12, \lambda) \\ + w^{(2)}(13, \lambda) + w^{(2)}(23). \end{aligned} \tag{20}$$

This superposition approximation in triplet configuration space is equivalent to the statement

$$\epsilon(123, \lambda) \cong \varphi(13, \lambda)\varphi(23). \tag{21}$$

The hypothesis (20) is suggested by analogy with the zero gas density situation, in which  $w^{(3)}$  reduces to precisely the sum of the three pair interactions  $v$ . By employing a cluster expansion, furthermore, it may be established that the lowest-order correction in density to  $w^{(3)}$  still satisfies Eq. (20). In addition, if any one of the three particles 1, 2, 3 is sufficiently far from the other two, Eq. (20) reduces to just the remaining pair potential, as rigorously it must. Finally, Eq. (20) is symmetric in  $\mathbf{r}_1$ ,  $\mathbf{r}_2$ , and  $\mathbf{r}_3$  (when  $\lambda = 1$ ), so the proposed approximation to  $\epsilon$  satisfies condition (19).

We now introduce the superposition approximation into Eq. (15). When  $r_{12} \geq \lambda a$ ,

$$\begin{aligned} -\log g^{(2)}(12, \lambda) = \rho a \int_0^\lambda d\lambda' \\ \cdot \int_{S(\lambda')} d^2\mathbf{r}_3 g^{(2)}(13, \lambda') [g^{(2)}(23) - 1]. \end{aligned} \tag{22}$$

The configuration integration simplifies considerably upon introduction of dipolar coordinates; in terms of reduced distances, one finds

$$\begin{aligned} -\log g(s, \lambda) \\ = \frac{2\pi\rho a^3}{s} \int_0^\infty dt K(s-t) t [g(t) - 1], \quad s \geq \lambda; \end{aligned}$$

$$K(q, \lambda) = \int_{|q|}^{\lambda} d\lambda' \lambda' g(\lambda', \lambda') \quad \text{if } |q| \leq \lambda, \tag{23}$$

$$= 0 \quad \text{if } |q| \geq \lambda;$$

$$s = r_{12}/a, \quad t = r_{23}/a, \quad g(s, \lambda) = g^{(2)}(r_{12}, \lambda), \quad \text{etc.}$$

The kernel  $K$  involves, for this rigid-sphere fluid, only those values of the pair correlation function corresponding to contact with the particle of "size"  $\lambda'a$ .

Suppose next that  $\lambda$  becomes very large. In this circumstance, the interaction potential, Eq. (11), would produce singular repulsion over an increasingly large sphere surrounding the center of particle 1. The surface of this expanding sphere displaces the other particles as it moves outward; eventually, a "bubble" of macroscopic extent could be produced containing only the swollen particle 1.

When  $\lambda \gg 1$ , the surface of the expanding molecule 1 acts, from the standpoint of those particles near it, as a planar impenetrable wall. Thus, when  $\lambda$  is perhaps an order of magnitude or more larger than unity, the value of  $g(\lambda, \lambda)$  is for all intensive purposes constant, and equal to the contact value for a flat wall,  $g_w$ . Aside, then, from terms of lower order in  $\lambda$  than those retained, it is permissible to replace  $g(\lambda', \lambda')$  by  $g_w$  in  $K$

$$K(q, \lambda) \cong \frac{1}{2} g_w (\lambda^2 - u^2) \quad |q| \leq \lambda, \tag{24}$$

$$= 0, \quad |q| \geq \lambda.$$

As  $\lambda$  approaches infinity, introduce the following definitions:

$$g^{(1)}(u) = \lim_{\lambda \rightarrow \infty} g(\lambda + u, \lambda), \tag{25}$$

$$x = \lambda + u, \quad g^{(1)}(0) = g_w.$$

Here,  $g^{(1)}(u)$  is the correlation function for spherical particles near a hard wall; it becomes unity at large normal distances to the wall  $u$ .  $u = 0$  corresponds to the position of closest approach to this wall. In view of relations, Eqs. (24) and (25), the integral, Eq. (23), leads to an expression for the surface correlation function  $g^{(1)}$  involving only a quadrature of the bulk pair correlation,  $g$ ,

$$-\log g^{(1)}(u) = 2\pi\rho a^3 g_w \int_u^\infty t(t-u)[g(t) - 1] dt. \tag{26}$$

Upon inserting known values for the bulk  $g(t)$  into Eq. (26), the resulting approximate surface correlations, like their bulk analogs, would be found to possess alternate peaks and valleys, which be-

come less and less pronounced as  $u$  increases. This corresponds in dense fluids to virtual crystallographic planes arranged parallel to the hard surface. In this manner one observes the tendency toward local lattice-like structure in dense fluids.

The crucial result of this section is obtained by setting  $u = 0$  in Eq. (26). One obtains thereupon an implicit relation for  $g_w$ ,

$$-\log g_w = 2\pi\rho a^3 g_w \int_0^\infty t^2 [g(t) - 1] dt. \tag{27}$$

Two points may be noticed in connection with this last result. First, the integral involving  $g(t)$  is the same one occurring in the compressibility expression (10). Furthermore,  $g_w$  itself is directly related to the pressure, since it gives the kinetic stress acting at the impenetrable wall.<sup>8</sup> Specifically,

$$p/kT = \rho g_w. \tag{28}$$

In view of these relations, therefore, Eq. (27) is seen to be equivalent to a differential equation for the pressure in terms of the fluid's density. Upon performing the requisite elementary substitutions, one finds

$$\frac{dx}{dz} = \frac{x(z - 2 \log z)}{z(2 \log z - z + 1)}, \tag{29}$$

$$z = p/\rho kT, \quad x = \rho a^3.$$

The superposition approximation has therefore led, by the requirement of consistency between essentially independent expressions for pressure and compressibility, to a nonlinear first-order differential relation giving the equation of state.

#### IV. LINEAR CORRELATION FIELD

The next object is to obtain a differential equation corresponding to Eq. (29), but deduced by use of the linear correlation hypothesis, rather than the superposition approximation. This hypothesis is equivalent to neglect of  $\epsilon$  in Eq. (18).  $\epsilon$  clearly cannot be identically zero, for then condition (19) would be violated. But on an *a priori* basis, it would appear no less reasonable to make this supposition that  $\epsilon$  is small, than it is equal to the specific form, Eq. (21). One must remember in this connection that the superposition approximation follows by analogy with the low-density result. In this case the function  $\phi$  is first order in  $\rho$ , whereas  $\epsilon$  is second order; the latter is, by comparison, negligibly small. The linear correlation field hypothesis therefore attempts to extend this relationship to large values

of  $\rho$ , as being at least as reasonable an inference as superposition.

By utilization of this alternative hypothesis, the integral, Eq. (12), is replaced by ( $r_{12} \geq \lambda a$ )

$$\begin{aligned}
 -\log g^{(2)}(12, \lambda) &= \frac{\rho}{kT} \int_0^\lambda d\lambda' \\
 &\cdot \int d^3\mathbf{r}_3 \frac{\partial v(13, \lambda')}{\partial \lambda'} \exp \left[ -\frac{1}{kT} v(13, \lambda') \right] \\
 &\cdot \left\{ \exp \left[ -\frac{1}{kT} v(23) \right] [1 + \varphi(13, \lambda') + \varphi(23)] \right. \\
 &- [1 + \varphi(13, \lambda')] \left. \right\} = -\rho\tau(12, \lambda) + \frac{\rho}{kT} \int_0^\lambda d\lambda' \\
 &\cdot \int d^3\mathbf{r}_3 \frac{\partial v(13, \lambda')}{\partial \lambda'} \exp \left[ -\frac{1}{kT} v(13, \lambda') \right] \\
 &\cdot \left\{ \varphi(13, \lambda') \left[ \exp \left( -\frac{1}{kT} v(23) \right) - 1 \right] \right. \\
 &+ \left. \exp \left[ -\frac{1}{kT} v(23) \right] \varphi(23) \right\}. \tag{30}
 \end{aligned}$$

The leading term is precisely the first cluster integral obtained in rigorous expansion of  $-\log g^{(2)}$  in a density series:

$$\begin{aligned}
 \tau(12, \lambda) &= \int d^3\mathbf{r}_3 \left\{ \exp \left[ -\frac{1}{kT} v(13, \lambda) \right] - 1 \right\} \\
 &\cdot \left\{ \exp \left[ -\frac{1}{kT} v(23) \right] - 1 \right\}. \tag{31}
 \end{aligned}$$

The second term may be transformed, as before, by use of Eq. (14). As a result, the position  $\mathbf{r}_3$  is once again constrained to the surface  $S(\lambda')$ . If we denote by  $S'(12, \lambda')$  the magnitude of that part of the area  $S$  inside the exclusion sphere of particle 2 (this is the only region of  $S$  where  $\{\exp [-(1/kT)v(23)] - 1\}$  is nonvanishing), and by  $S''(12, \lambda')$  the area outside ( $S''$  is thus the complement of  $S'$  on  $S$ ), one then has

$$\begin{aligned}
 -\log g^{(2)}(12, \lambda) &= -\rho\tau(12, \lambda) \\
 &- \rho a \int_0^\lambda d\lambda' S'(12, \lambda') \varphi(a\lambda', \lambda') \\
 &+ \rho a \int_0^\lambda d\lambda' \int_{S''(12, \lambda')} d^2\mathbf{r}_3 \varphi(23). \tag{32}
 \end{aligned}$$

In accord with the previous section,  $\lambda$  is chosen to be very large relative to unity, and  $r_{12}$  is set equal to  $\lambda a$  to yield contact between particle 2 and the "hard wall." Under this circumstance,  $\tau$  is easily found to be  $\frac{2}{3}\pi a^3$ . In addition,  $S'(12, \lambda')$  vanishes unless  $\lambda - 1 < \lambda' \leq \lambda$ ; as  $\lambda'$  covers this interval,

$\varphi(a\lambda', \lambda')$  is essentially equal to  $g_w - 1$ , and  $S'$  sweeps out half the exclusion volume of particle 2. Finally, the elementary  $\mathbf{r}_3$  integration over the planar surface  $S''$  may be carried out to give

$$\begin{aligned}
 \log g_w &= \frac{2\pi\rho a^3}{3} [g_w - 1] \\
 &- 2\pi\rho a^3 \int_0^\infty t^2 [g(t) - 1] dt. \tag{33}
 \end{aligned}$$

Once again it is possible to relate the integral occurring here to the compressibility, Eq. (10), and  $g_w$  to the pressure. The resulting nonlinear first-order differential equation is not, however, identical to that obtained previously. One finds

$$\begin{aligned}
 \frac{dx}{dy} &= 1 + \left[ \frac{4\pi}{3} y - 2 \log y \right] \\
 &- \left[ \frac{4\pi}{3} x - 2 \log x \right], \tag{34} \\
 y &= \rho a^3 / kT.
 \end{aligned}$$

The difference obviously reflects the inequivalence of the two approximations used.

V. DISCUSSION AND NUMERICAL ANALYSIS

By restricting the preceding development to a fluid of impenetrable spheres, it has been necessary to consider values of the local density in the neighborhood of a fixed pair, which correspond to contact with one member of this pair. Since the fixed pair itself was eventually set in contact, the relevant particle triplet configurations invariably had all three particles close to one another. Accordingly, the triplet potential of mean force was about as large in magnitude as possible, so that the three particles were strongly correlated. Under such a circumstance, on the one hand, the superposition approximation would be as far from accuracy as possible, and on the other hand, nonlinear correlation effects should be maximized. Put another way, one could say that since the triplet configurations amount not to isolated, but mutually influential, pairs, the errors in the approximations utilized should be large.

In addition, use has been made of the relation of the system's pressure to the contact value of the pair correlation function when  $\lambda = 1$ , Eq. (16), and in the case  $\lambda = \infty$  to the wall correlation,  $g_w$ , by Eq. (28). Now if, for arbitrary  $\lambda$ ,  $g^{(2)}(r, \lambda)$  were accurate to order  $\rho^n$ , but in error in the next order in  $\rho$ , Eq. (16) would yield the first  $n + 2$  virial coefficients in expansion of the pressure correctly,

but Eq. (28) produces only  $n + 1$  correct coefficients. In this sense it may be argued that Eq. (28) is a relatively efficient "error producer." Any use of this equation therefore would be expected to give deviations at lower density than might otherwise be found.

Finally, it should be realized that the differential equations produced by the consistency requirements, which appear in the form

$$d\alpha/d\beta = f(\alpha, \beta), \quad (35)$$

are themselves capable of compounding errors introduced during their derivation. It is probably true that if an accurate pair of simultaneous values  $\alpha$  and  $\beta$ , obtained by some independent means, is inserted into  $f(\alpha, \beta)$ , the number computed would check closely with the expected value for  $d\alpha/d\beta$ . But if Eq. (35) is alone integrated over a sizable interval subject to zero gas density boundary conditions, the results can easily differ even qualitatively from the exact equation of state. This fact can readily be appreciated in view of the usual numerical procedures for solving differential equations of type Eq. (35): The result of extending the solution for a given increment in the independent variable depends upon values obtained in previous extensions. Errors thus tend to feed on themselves, often catastrophically.

The (obvious) implication of these facts is that the method outlined in this article is by no means well designed to predict the equation of state for the rigid-sphere fluid. The method's considerable sensitivity to the inexactness of individual approximations employed, however, can be used to good advantage as a test for the extent to which these approximations are in error. Probably the best hard-sphere equation of state obtainable from the foregoing integral equation formulation of distribution function theory would follow from solution of the integral equation, Eq. (23), with  $\lambda = 1$ , then substitution into Eq. (16).

It is solely for the purpose of comparing the exactness of the superposition approximation, and the linear correlation field hypothesis, that the numerical solutions to the differential equations, Eqs. (29) and (34), have been obtained. As previously implied, the solutions proceed from the known dilute gas values of the pressure as initial condition. Although each of the differential equations is first order, their singular nature at zero density necessitates specification of two arbitrary constants at  $\rho = 0$  to define unique solutions. The choice of constants amount to fixing the first two coefficients

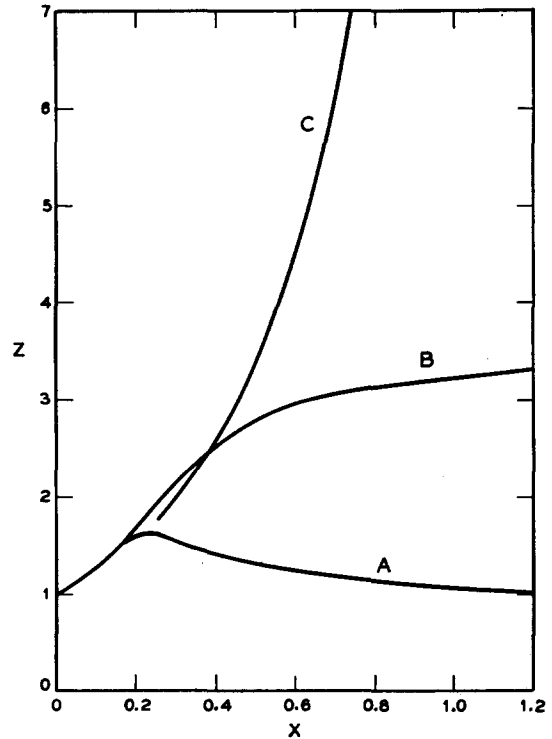


FIG. 1. Distortions in the equation of state as a result of the linear correlation hypothesis (curve A), and the superposition approximation (curve B). Curve C represents the exact behavior.

in density expansion of  $p$ ;

$$p/kT = \rho + B\rho^2 + \dots \quad (36)$$

The well-known value of the second virial coefficient  $B$  can be obtained from Eq. (16),

$$B = \frac{2}{3}\pi a^3. \quad (37)$$

The predicted virial expansion in the low-density region may readily be found by substitution of the series

$$\begin{aligned} z(x) &= 1 + bx + cx^2 + dx^3 + ex^4 + \dots, \\ y(x) &= x + bx^2 + cx^3 + dx^4 + ex^5 + \dots, \end{aligned} \quad (38)$$

$$b = \frac{2}{3}\pi,$$

into the respective differential equations. Upon equating coefficients of the same powers of  $x$ , one finds for the superposition approximation

$$\begin{aligned} c &= b^2, \\ d &= 5b^3/6, \\ e &= 7b^4/18, \end{aligned} \quad (39)$$

and for linear correlation fields,

$$\begin{aligned} c &= b^2, \\ d &= b^3/3, \\ e &= -13b^4/6. \end{aligned} \quad (40)$$

Already the third virial coefficients are incorrect; the exact value is  $c = 5b^2/8$ . This results from use of the relation between  $p$  and  $g_w$ , as already pointed out.

The numerically obtained solutions to Eqs. (29) and (34) are presented in Fig. 1, along with a curve from reference 8, which is in accord with the accurate Monte Carlo results of Alder and Wainwright.<sup>10</sup> At high density, both solutions predict values for the pressure which are too small. But whereas the linear correlation field solution loses significance about the low density of  $x \cong 0.2$  ( $x = 1.414$  gives close packing), the superposition curve is semi-quantitatively correct to at least twice this value. The latter, furthermore, is at least monotonically increasing over the whole fluid density range,

<sup>10</sup> W. W. Wood and J. D. Jacobsen, *J. Chem. Phys.* **27**, 1207 (1957).

but the former displays the unphysical behavior of negative compressibility above about  $x = 0.23$ .

The conclusion to be drawn is simply that correlations induced by two or more particles in a dense fluid are not at all additive: the function  $\epsilon$  is far from negligible. Even the superposition approximation appears to underestimate the magnitude of this quantity. In light of the rather sensitive test that has been devised, it would perhaps be worth investigating the class of functions  $\epsilon$  which lead to analyses similar to those preceding, with a view toward distinguishing accurate approximation schemes.

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## On the Boltzmann Equation and the Structure of Shock Waves

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The methods of Mott-Smith and Rosen for the shock structure problem are correlated. It is found that the application of Rosen's restricted variational technique to the Boltzmann equation yields the transport equation used by Mott-Smith, and in addition determines a transport function. The expression for the average translational temperature profile, as derived by Mott-Smith, is examined for the existence of relative minima or maxima. For a monatomic gas the temperature profiles have no relative extrema inside the shock wave for any Mach number. For a diatomic gas the temperature profiles are smooth for Mach numbers below 1.89, but above that a hump appears.

THE method used by Mott-Smith<sup>1</sup> to investigate the structure of a normal shock wave was based on the Boltzmann transport equation. This equation is of the following form for the one-dimensional time-independent case:

$$\int \varphi u \frac{\partial f}{\partial x} dc = \iiint \varphi (f'f'_1 - ff_1) g d\Omega dc_1 dc$$

$$\equiv \int \varphi \left( \frac{\partial \epsilon f}{\partial t} \right) dc. \quad (1)$$

The distribution function  $f(c, x)$  was taken to be

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<sup>1</sup> H. M. Mott-Smith, *Phys. Rev.* **82**, 885 (1951).

the sum of two locally Maxwellian distribution functions, each of which had constant but different values of temperature and mass velocity. The number density in each of these two distributions was taken to be a function of position. Thus the velocity dependence of the distribution function was specified, and substitution into Eq. (1) provided an ordinary differential equation which was solved for the density profile once the transport function had been chosen.

A restricted variational technique was used by Rosen<sup>2,3</sup> to study the same problem. The advantage

<sup>2</sup> P. Rosen, *J. Appl. Phys.* **25**, 336 (1954).

<sup>3</sup> P. Rosen, *J. Chem. Phys.* **22**, 1045 (1954).