

## Statistical Mechanics of Rigid Spheres

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An equilibrium theory of rigid sphere fluids is developed based on the properties of a new distribution function  $G(r)$  which measures the density of rigid sphere molecules in contact with a rigid sphere solute of arbitrary size. A number of *exact* relations which describe rather fully the functional form of  $G(r)$  are derived. These are based on both geometrical considerations and the virial theorem. A knowledge of  $G(a)$  where  $a$  is the diameter of a rigid sphere enables one to arrive at the equation of state. The resulting analytical expression which is exact up to the third virial coefficient gives the fourth virial coefficient within 3% and the fifth, insofar as it is known, within 5%. Furthermore over the entire range of fluid density, the equation of state derived from theory agrees with that computed using machine methods. Theory also gives an expression for the surface tension of a hard sphere fluid in contact with a perfectly repelling wall. The dependence of surface tension on curvature is also given. The expressions obtained correlate nicely with those adduced by other thermodynamic and statistical mechanical theories. They also suggest that macroscopic consideration on surface tension can sometimes be successfully extrapolated to molecular dimensions.

### 1. INTRODUCTION

FLUIDS of rigid spheres have been the subject of many investigations. Through the application of cluster theory<sup>1</sup> and a certain amount of numerical analysis<sup>2,3</sup> one is now in possession of the first five virial coefficients for any such fluid. Recently the equation of state has been investigated by machine calculations, both by application of the Monte Carlo method<sup>4,5</sup> and by direct integration of the equations of motion of several hundreds of interacting rigid spheres.<sup>6</sup>

Aside from the application of cluster theory the problem has been attacked analytically by the distribution function method.<sup>7</sup> This has the disadvantage of invoking the superposition approximation<sup>8</sup> whose accuracy has never been clearly defined. Furthermore, the calculation of the *entire* radial distribution function is not required for the determination of the equation of state. For rigid spheres this equation can be shown through use of the virial theorem<sup>9</sup> to have the form<sup>10</sup>

$$(p/kT) = \rho + \frac{2}{3}\pi a^3 \rho^2 g(a). \quad (1.1)$$

Here  $p$  is the pressure,  $T$  the temperature,  $\rho$  the number density of particles,  $k$  the Boltzmann constant,  $a$  the diameter of a rigid sphere, and  $g(r)$  the radial distribu-

tion function at separation  $r$ . It is evident from (1.1) that  $g(r)$  is not required for all values of  $r$  and that all we need is  $g(a)$  the value of  $g$  corresponding to two spheres in contact, i.e., when their centers are separated by the distance  $a$ .

If one is only interested in the equation of state, it would seem worthwhile to look for new methods which give information about  $g(a)$ . The present paper will offer an analysis of this sort. It will appear that a certain number of exact relations can be derived which go a long way toward determining the equation of state. Furthermore, the degree by which they fail in the full determination can be understood.

### 2. AN INTEGRAL EQUATION

We shall begin with a fluid of  $N$  rigid spheres of diameter  $a$  contained in the volume  $V$ . To this system another sphere of the same type can be added by means of a coupling parameter.<sup>11</sup> The more usual type<sup>12</sup> of coupling parameter has the following properties. Assume that the potential energy  $\Phi_{N+1}$  of the system is composed of terms  $u_{ij}$  signifying the pairwise interaction of particles  $i$  and  $j$ ,

$$\Phi_{N+1} = \sum_{1 \leq i < j \leq N+1} u_{ij}. \quad (2.1)$$

By assigning to say particle 1 the parameter  $\xi$ , in the sense that each pairwise term containing the index 1 in (2.1) is to be multiplied by  $\xi$ , we obtain

$$\begin{aligned} \Phi_{N+1}(\xi) &= \sum_{j=1}^{j=N} u_{1j}(\xi) + \sum_{2 \leq i < j \leq N+1} u_{ij}, \\ u_{1j}(\xi) &= \xi u_{1j}(1). \end{aligned} \quad (2.2)$$

By permitting  $\xi$  to go to unity we recover (2.1) while by setting  $\xi=0$  we are left with only the second term on

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<sup>1</sup> T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956), Chapter 5.

<sup>2</sup> R. Majumdar, *Bull. Calcutta Math. Soc.* **21**, 107 (1929).

<sup>3</sup> Hirschfelder, Curtiss, and Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), p. 157.

<sup>4</sup> M. N. Rosenbluth and A. W. Rosenbluth, *J. Chem. Phys.* **22**, 881 (1954).

<sup>5</sup> W. W. Wood and J. D. Jacobsen, *J. Chem. Phys.* **27**, 1207 (1957).

<sup>6</sup> T. E. Wainwright and B. J. Alder, AEC Report Contract No. W-7405-eng-48, Radiation Laboratory at Livermore, University of California.

<sup>7</sup> See reference 1, Chapter 6.

<sup>8</sup> See reference 1, p. 195.

<sup>9</sup> See reference 3, pp. 41, 134.

<sup>10</sup> See reference 1, p. 216.

<sup>11</sup> L. Onsager, *Chem. Revs.* **13**, 73 (1933); J. G. Kirkwood, *J. Chem. Phys.* **3**, 300 (1935).

<sup>12</sup> See reference 1, pp. 191, 192.

the right of (2.2) which clearly represents the potential energy  $\phi_N$  of the system of  $N$  particles, which remains if particle 1 is removed. Thus by allowing  $\xi$  to go from zero to unity we can formally add an additional particle to a system of  $N$  particles. Evidently  $\xi$  is the coupling parameter and it should be noticed that with this type of coupling

$$\partial u_{1j}(\xi)/\partial \xi = u_{1j}(1). \quad (2.3)$$

Now the chemical potential  $\mu$  for a system of particles interacting in a pairwise fashion can be written in terms of the coupling parameter in the following form<sup>13</sup>

$$\mu = kT \ln \rho \Lambda^3 + \rho \int_0^1 d\xi \int_0^\infty \frac{\partial u}{\partial \xi} 4\pi r^2 g(r, \xi) dr, \quad (2.4)$$

where  $u$  stands for any  $u_{1j}$ , the same for all  $j$ , and where we have replaced the  $u(1)$  in the formula of reference 13 by  $\partial u/\partial \xi$  in accordance with (2.3).  $\Lambda^3$  is the reciprocal of the momentum partition function and is given by

$$\Lambda^3 = h^3 / (2\pi m kT)^{3/2}, \quad (2.5)$$

where  $h$  is Planck's constant and  $m$  is the mass of a particle.

Equation (2.4) is true generally in the case of systems involving pairwise interaction for any coupling parameter which is able to remove the contribution of a given particle from  $\Phi_{N+1}$ . The upper limit on the integration over the coupling parameter may not be 1 as in (2.4), however, but some appropriate number which signifies the complete coupling of the added particle to the rest of the system. Suppose for example that we wish to add an additional rigid sphere of diameter  $b$  to a fluid of  $N$  spheres of diameter  $a$ . The pairwise interaction of this sphere with any of the original is specified by

$$\begin{aligned} u &= \infty, & r \leq (a+b)/2 = \lambda \\ u &= 0, & r > (a+b)/2 = \lambda. \end{aligned} \quad (2.6)$$

Notice that  $u$ , could be made zero everywhere by setting  $\lambda=0$ . Therefore,  $\lambda$  can be made to play the role of a coupling parameter; complete coupling being achieved when  $\lambda=a$ .

It should be observed that  $\lambda=0$  implies  $b=-a$ . In other words it is not sufficient to set  $b=0$  in order to decouple the added particle but we must assign it a negative diameter. This is so because with  $b=0$  we still have a *point* molecule which is capable of excluding the centers of other molecules from a sphere of radius  $a/2$  surrounding it. Making  $b$  negative need not be regarded as adding a molecule with negative dimensions but merely as adding a point molecule capable of penetrating the rigid cores of the original molecules.

It will be convenient to think of the added molecule as a *solute* when  $b \neq a$ , while the original molecules constitute the *solvent*.

Inserting (2.6) into the integral on the right of (2.4) gives

$$\rho \int_0^a d\lambda \int_0^\infty \frac{\partial u}{\partial \lambda} 4\pi r^2 g(r, \lambda) dr. \quad (2.7)$$

Now

$$\begin{aligned} &(\partial/\partial \lambda)[\exp(-u/kT)] \\ &= -(1/kT)(\partial u/\partial \lambda) \exp(-u/kT) = -\delta(\lambda-r), \end{aligned} \quad (2.8)$$

where  $\delta(\lambda-r)$  is the Dirac delta function.<sup>14</sup> From Eq. (2.6) and the left member of (2.7) it is seen that the delta function is properly normalized so that its integral over the infinite range is unity. Solving for  $\partial u/\partial \lambda$  from the right-hand equation of (2.8) and substitution in (2.7) yields, after the latter is placed in (2.4),

$$\mu = kT \ln \rho \Lambda^3 + kT \rho \int_0^a 4\pi \lambda^2 g(\lambda, \lambda) d\lambda. \quad (2.9)$$

Now  $g(\lambda, \lambda)$  is the value of the radial distribution function for solvent molecules around a solute molecule on contact between solvent and solute, i.e., when their centers are separated by the distance  $\lambda = (a+b)/2$ . It is convenient to denote  $g(\lambda, \lambda)$  simply by  $G(\lambda)$ . Thus  $\rho G(\lambda)$  measures the average density of solvent molecules in contact with the solute, and in particular

$$G(a) = g(a). \quad (2.10)$$

For the case of rigid spheres it is instructive to derive (2.9) by another method which provides more physical insight. Suppose the added solute molecule of diameter  $b$  is placed with its center at some *fixed* point  $\mathbf{R}$  in the fluid. Then about  $\mathbf{R}$  will exist a spherical region of radius  $\lambda = (a+b)/2$  from which the centers of all  $N$  solvent molecules will be excluded. The presence of the solute at  $\mathbf{R}$  is evidently equivalent to the existence of a spherical cavity at  $\mathbf{R}$  in the solvent of at least radius  $\lambda$ . For this reason the reversible work which would be expended in the production of such a cavity must be identical with that required for the addition of the fixed solute molecule. If this work is increased by the free energy of mixing which would attend the liberation of the solute so that it could wander from the point  $\mathbf{R}$ , the result would equal the reversible work involved in the addition of a real solute molecule, and so would equal the chemical potential of the solute. In the special case  $b=a$  we would derive  $\mu$ , the chemical potential of the solvent, given presumably by (2.9). Our program then will be to compute  $\mu$  through consideration of the reversible work required for the production of a cavity of radius  $a$ .

It is a general result<sup>15</sup> of statistical mechanics that if  $W(\lambda)$  is the reversible work required for the creation of a cavity of radius at least  $\lambda$ , then the probability

<sup>14</sup> V. Rojansky, *Introductory Quantum Mechanics* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1942), p. 68.

<sup>15</sup> R. C. Tolman, *The Principles of Statistical Mechanics* (Oxford University Press, London, 1938), Sec. 141.

<sup>13</sup> See reference 1, Eq. (30.36).

$p_0(\lambda)$  of observing a fluctuation in which such a cavity forms is given by

$$p_0(\lambda) = \exp(-W(\lambda)/kT). \quad (2.11)$$

Thus knowledge of  $p_0(\lambda)$  is equivalent to knowledge of  $W(\lambda)$ .

Now  $p_0(\lambda)$  can be expressed in terms of  $G(\lambda)$  by the following device. Introduce the auxiliary function  $h(\lambda)$  which has the following meaning;  $h(\lambda)d\lambda$  is the probability that at an arbitrary point in the fluid the center of the *nearest* molecule is a distance  $\lambda$  away, in the range  $d\lambda$ . Then  $h(\lambda)d\lambda$  must be given by

$$h(\lambda)d\lambda = p_0(\lambda)4\pi\lambda^2\rho G'(\lambda)d\lambda. \quad (2.12)$$

The factor  $p_0(\lambda)$  on the right is the probability that the *nearest* molecule is *at least* a distance  $\lambda$  away (i.e., the probability of having a spherical cavity of radius at least  $\lambda$ ) while  $4\pi\lambda^2\rho G'(\lambda)d\lambda$  is the conditional probability that the spherical shell of volume  $4\pi\lambda^2d\lambda$  enveloping the cavity of radius  $\lambda$  contains the center of at least one molecule. From the definition of  $h(\lambda)$ ,  $\rho G'(\lambda)$  is the average density of molecular centers just outside the cavity of radius  $\lambda$  (or the average density of molecules in contact with the solute of radius  $b$ ) or  $G'(\lambda) = G(\lambda)$ .

It should also be clear that

$$p_0(\lambda) = 1 - \int_0^\lambda h(\lambda')d\lambda' \quad (2.13)$$

since the integral on the right is the probability that the center of at least one molecule *is* in the spherical region of radius  $\lambda$ . Differentiating (2.13) with respect to  $\lambda$  we have

$$h(\lambda) = -\partial p_0/\partial\lambda. \quad (2.14)$$

Substituting this result into (2.12) then yields

$$G(\lambda) = -(1/4\pi\lambda^2\rho)(\partial \ln p_0/\partial\lambda) \quad (2.15)$$

or, since  $p_0(0) = 1$ ,

$$-\ln p_0(\lambda) = \rho \int_0^\lambda 4\pi\lambda'^2 G(\lambda')d\lambda' \quad (2.16)$$

which in combination with (2.11) gives

$$W(\lambda) = kT\rho \int_0^\lambda 4\pi\lambda'^2 G(\lambda')d\lambda'. \quad (2.17)$$

The free energy of mixing of the solute molecule with solvent is the well-known expression  $kT \ln(\Lambda_b^3/V)$ . The factor  $(1/V)$  is essentially the density  $\rho_b$  of solute molecules. In case there is more than one solute molecule present the free energy of mixing can still be expressed as  $kT \ln(\rho_b\Lambda_b^3)$  provided the solution is dilute enough so that solutes do not interact. Adding this contribution to (2.17) we obtain for  $\mu_b$  the chemical potential of the solute

$$\mu_b = kT \ln(\rho_b\Lambda_b^3) + kT\rho \int_0^{(a+b)/2} 4\pi\lambda^2 G(\lambda)d\lambda. \quad (2.18)$$

Equation (2.18) is the expression for the chemical potential of a molecule of radius  $b/2$  in a mixture of  $b$  and  $a$  molecules with  $\rho_b b^3 \ll 1$ .

If our single additional "solute" molecule has a diameter  $a$  and is indistinguishable from the "solvent" molecules then clearly its entropy of mixing is  $kT \ln(\Lambda_a^3\rho)$ . Hence its chemical potential, which is now identically that of a "solvent molecule," is given by (2.18), (without reference to any solutions), when we set  $b = a$ ,  $\rho_b = \rho$ . When these replacements are made (2.18) becomes identical with (2.9) which completes the alternative mode of derivation.

Combining (2.16) with (2.12) and (2.13) yields

$$h(\lambda) = 4\pi\lambda^2\rho G(\lambda) \exp\left\{-\int_0^\lambda 4\pi\lambda'^2\rho G(\lambda')d\lambda'\right\}. \quad (2.19)$$

The function  $h(\lambda)$  is related to the Hertz or *nearest neighbor* distribution.<sup>16</sup> This function and its close relatives have found application in other problems in physics.<sup>17-19</sup>

The next step involves computing the pressure  $p$  from  $\mu$  given by (2.9). In this connection we employ the straightforward thermodynamic relation

$$p = \int_0^\rho \rho \left( \frac{\partial \mu}{\partial \rho} \right)_T d\rho. \quad (2.20)$$

Substitution of (2.9) into (2.20) yields, after an integration by parts,

$$\frac{p}{kT} = \rho + \rho^2 \int_0^a 4\pi r^2 G(r, \rho) dr - \int_0^\rho \rho' d\rho' \int_0^a 4\pi r^2 G(r, \rho') dr, \quad (2.21)$$

in which we now use  $r$  in place of  $\lambda$ . Introduction of (2.10) into (1.1) and equating the right-hand sides of (1.1) and (2.21) then gives

$$\frac{2}{3}\pi a^3 \rho^2 G(a, \rho) = \rho^2 \int_0^a 4\pi r^2 G(r, \rho) dr - \int_0^\rho \rho' d\rho' \int_0^a 4\pi r^2 G(r, \rho') dr, \quad (2.22)$$

which is an integral equation on  $G(r, \rho)$ .

It is worthwhile to pause at this stage to consider the implications of (2.22). First we notice that because it contains definite integrals it cannot determine  $G(a, \rho)$  uniquely. Nevertheless, it may provide a considerable amount of information concerning  $G(a, \rho)$ . It is *exact*, and together with other exact conditions may lead to a powerful method for getting at  $G(a, \rho)$  and

<sup>16</sup> S. Chandrasekhar, *Revs. Modern Phys.* **15**, 1 (1943).

<sup>17</sup> Holtzmark, *Ann. Physik* **58**, 577 (1919); *Physik. Z.* **20**, 162 (1919); **25**, 73 (1924); S. Chandrasekhar, *Revs. Modern Phys.* **15**, 1 (1943).

<sup>18</sup> R. M. Fuoss, *Trans. Faraday Soc.* **30**, 967 (1934).

<sup>19</sup> H. Reiss, *J. Chem. Phys.* **25**, 400, 408 (1956).

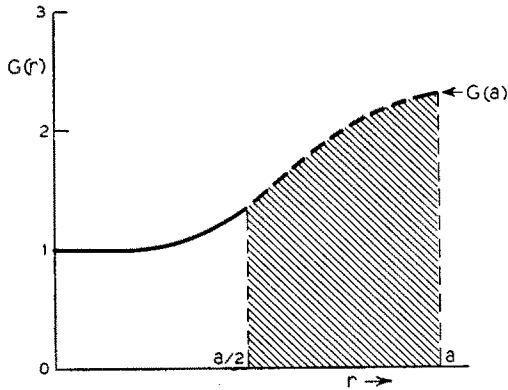


FIG. 1. The behavior of the distribution function  $G(r)$  in  $0 \leq r \leq a$ .

thus, through (1.1), at the equation of state. We shall see that this is the case.

On the other hand there is a deeper significance to which attention should be directed. This is that Eq. (2.22) has been derived with the aid of the virial theorem. Conventionally, the virial theorem has been used to obtain information concerning the *macroscopic* properties of a system. In (2.22) it provides information on the *microstructure* of the system. In fact by using other types of coupling parameters together with the virial theorem it is actually possible to derive other integral equations which give information on various aspects of the radial distribution function. The elucidation of these is not however within the domain of this paper. It suffices to mention that it may be profitable to investigate them.

### 3. FURTHER CONDITIONS ON $G(r, \rho)$

Additional exact conditions on  $G(r, \rho)$  can be obtained. Consider for example  $p_0(r)$  for  $r \leq a/2$ . A spherical region whose radius lies in this range can contain at the most the center of *one* rigid sphere at a time. The probability that it is so occupied is therefore  $(\frac{4}{3})\pi r^3 \rho$ , and the probability that it is empty is just one minus this quantity, so

$$p_0(r) = 1 - \frac{4}{3}\pi r^3 \rho, \quad r \leq a/2. \quad (3.1)$$

Substitution of this result into (2.14) then yields

$$G(r) = (1 - \frac{4}{3}\pi r^3 \rho)^{-1}, \quad r \leq a/2. \quad (3.2)$$

Therefore,  $G(r, \rho)$  is actually known up to  $r = a/2$ .

It has been pointed out that the condition  $r = a/2$  corresponds to the presence of a point molecule. It may be of interest to compute the work  $W(a/2)$  expended in the introduction of a fixed point molecule into the fluid. This is accomplished by inserting (3.2) in (2.17), setting the limit  $\lambda$  equal to  $a/2$ .

$$W(a/2) = -kT \ln[1 - (\pi a^3 \rho / 6)]. \quad (3.3)$$

According to (3.2)  $G(r)$  is a monotone increasing function of  $r$  in the range  $r \leq a/2$  [except when  $(\frac{4}{3})\pi r^3 \rho > 1$ ,

a condition which cannot be realized at densities less than close packing]. There are strong grounds for believing that  $G(r)$  is monotone increasing over the whole range of  $r$  as long as the system remains in the fluid state, but we have not been able to prove this. For large values of  $r$ , however, a strong plausibility argument can be given. This is based on the fact that for large  $r$  the cavity is essentially a bubble and its work of formation can be represented as the sum of surface and volume terms. Thus

$$W(r) = \omega v - \gamma v^{2/3}, \quad r \text{ large} \quad (3.4)$$

where  $v = (\frac{4}{3})\pi r^3$  is the volume of the cavity and  $\omega$  and  $\gamma$  are positive and independent of  $v$ . The term in  $v$  is the volume term and that in  $v^{2/3}$  is the surface work. The surface work is negative because for hard spheres the surface tension is negative.

Differentiation of (2.17), with  $v = (\frac{4}{3})\pi r^3$ , and also (3.4),

$$\partial W / \partial v = kT \rho G = P$$

$$\partial^2 W / \partial v^2 = kT \rho (\partial G / \partial v) = \frac{2}{3} \gamma v^{-4/3} > 0. \quad (3.5)$$

In the first of these equations  $P$  is the stress normal to the surface of the cavity which since it is wholly kinetic is equal to  $kT$  times the density  $\rho G$  at the surface of the cavity. We could have derived the relation between  $p_0$  and  $G$  directly from this fact. The second of Eqs. (3.5) shows that  $\partial G / \partial v$  is positive and therefore  $G$  increases monotonically with  $v$  or  $r$ .†

If the cavity is allowed to grow to infinite size, its bounding surface will behave like a plane wall, and  $\rho G(\infty, \rho)$  is therefore the average density  $\rho_{\text{wall}}$  of molecules next to a plane wall. Now according to (3.5)

$$p/kT = \rho_{\text{wall}} = \rho G(\infty, \rho). \quad (3.6)$$

Comparing this with (1.1) after taking notice of (2.8) yields

$$G(\infty, \rho) = 1 + \frac{2}{3}\pi a^3 \rho G(a, \rho) \quad (3.7)$$

which is another exact condition on the behavior of  $G(r, \rho)$ .

Some perspective on the entire problem can now be had. For the equation of state we require  $G(a, \rho)$ , and this is available from Eq. (2.22) provided the integrals on the right are known. In essence we need to know the area under the curve in Fig. 1. Now we are exactly cognizant of this area up to the point  $r = a/2$  in view of (3.2). What is lacking is the shaded area in Fig. 1. But if  $G(r)$  is a fairly smooth and simple curve we might connect the points  $a/2$  and  $a$  by some elementary function having undetermined parameters which do not depend on  $r$ . If the parameters are then determined by whatever exact information on  $G(r)$  is available we arrive at a fairly accurate specification of  $G(a)$ .

† The authors are indebted to G. H. Wannier for suggesting that a proof of monotone behavior might be obtained through consideration of the work.

We have not exhausted the store of possible exact conditions on  $G(r, \rho)$ . Suppose  $p_1(r)$ ,  $p_2(r)$ , etc., represent the probabilities that the centers of *exactly* one particle, *exactly* two particles, etc., lie in the spherical region of radius  $r$ . Then

$$p_0 + p_1 + p_2 + p_3 + \dots = 1. \tag{3.8}$$

This can also be written as

$$\begin{aligned} p_0 + \sum_{m=1}^{\infty} p_m &= p_0 - \sum_{m=1}^{\infty} \{ [1 + (-1)]^m - 1 \} p_m \\ &= p_0 - \sum_{m=1}^{\infty} p_m \sum_{n=1}^{\infty} (-1)^n C_n^m \\ &= p_0 - \sum_{n=1}^{\infty} (-1)^n \sum_{m=n}^{\infty} C_n^m p_m = 1 \end{aligned} \tag{3.9}$$

where  $C_n^m$  are the binomial coefficients.

Solving for  $p_0$  we have

$$\begin{aligned} p_0 &= 1 - (p_1 + 2p_2 + 3p_3 + \dots) + (p_2 + 3p_3 + 6p_4 + \dots) \\ &\quad - (p_3 + 4p_4 + \dots) + \dots \end{aligned} \tag{3.10}$$

Now in (3.10) the first sum in brackets represents the average number of individual particles to be found in the region of radius  $r$ . The second sum represents the average number of pairs, the third the average number of triplets, etc. From this it is obvious that

$$\begin{aligned} p_0(r) &= 1 + \sum_{m=1}^{\infty} \frac{(-1)^m \rho^m}{m!} \int_{[\text{region of radius } r]} g^{(m)} d\tau_1 d\tau_2 \dots d\tau_m \\ &= 1 + \sum_{m=1}^{\infty} (-1)^m F_m \end{aligned} \tag{3.11}$$

where  $g^{(m)}$  is the  $m$ -particle correlation function<sup>20</sup> and  $d\tau_1$  etc., are the volume elements for the coordinates of the different particles. The  $F_m$  are quantities defined by the last equality. It will be noticed that  $g^{(2)}$  is just  $g$ , the radial distribution function.

Equation (3.11) is derivable by purely statistical mechanical means, beginning with the partition function, but we have chosen to use probabilistic arguments because they are simpler to develop,<sup>‡</sup> and also furnish more insight into the problem. The equation in more general form was derived essentially, by using statistical mechanics, by Mayer and Montroll.<sup>21</sup> It is in fact Eq. (60) of their paper if for the activity which they call  $Z$  we substitute  $(p_0 \Lambda^3)^{-1}$  which can be shown to represent the activity.

Equation (3.11) is exceedingly useful for the development of exact conditions on  $G(r, \rho)$ . Thus suppose  $r$  is just large enough so that the region can accom-

modate two but not three particles. This condition arises when

$$a/2 < r \leq a/\sqrt{3}. \tag{3.12}$$

Then  $g^{(m)}$  for  $m \geq 3$  must be zero everywhere in the spherical region, so that according to (3.11)

$$\begin{aligned} p_0 &= 1 - \frac{4}{3} \pi r^3 \rho + (\rho^2/2) \int_{(\text{region of radius } r)} g d\tau_1 d\tau_2 \\ &= 1 - F_1 + F_2 \end{aligned} \tag{3.13}$$

where we have used the fact that  $g^{(1)} = 1$ .

Although the functions  $F_m$  defined in (3.11) relate to integrals over the limited region of radius  $r$  they can be given an alternative form in terms of integrals taken over the whole of the volume  $V$  in which the system is contained. This form is in fact used in Eq. (60) of reference 21. Consider  $m$  particles of diameter  $a$  with their centers respectively at the points  $\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_m$ . Around each of these centers describe a sphere of radius  $r$ . Then  $\Omega_m(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_m, r)$  is defined as the total volume of overlap of the  $m$  spheres of radius  $r$  when their centers are at the stated positions. We will now show that

$$\begin{aligned} F_m &= (\rho^m/m!) \int \dots \int_V g^{(m)}(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_m) \\ &\quad \times \frac{\Omega_m(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_m, r)}{V} d\mathbf{R}_1 d\mathbf{R}_2 \dots d\mathbf{R}_m, \end{aligned} \tag{3.14}$$

where the integration now proceeds over the entire volume  $V$ .

Equation (3.14) can be justified by a simple interpretation in terms of  $p_0(r)$ . If a sphere of radius  $r$  is drawn about the center of each molecule in the system, then the probability  $p_0(r)$  that there is no molecule within a distance  $r$  of an arbitrary point in the fluid is just equal to the fraction of  $V$  outside all the spheres. If the spheres did not overlap this fraction would be

$$p_0(r) = \frac{V - N \frac{4}{3} \pi r^3}{V} = 1 - \rho \int_V \Omega_1(\mathbf{R}_1, r) d\mathbf{R}_1. \tag{3.15}$$

This is exactly the case for  $r \leq a/2$  since then the spheres of radius  $r$  are all inside the rigid sphere molecules and cannot possibly overlap. Since  $N/V = \rho$ , (3.15) is identical, as expected, with (3.1).

For  $r > a/2$  there will be some overlap to be accounted for. Thus to  $V - N \frac{4}{3} \pi r^3$  in (3.15) would have to be added the volume of overlap of all pairs of spheres (some of these pairs may be part of a triple overlap configuration etc.) which has been subtracted twice through the term  $N \frac{4}{3} \pi r^3$ . But now the volume of triple overlaps will have been added once too often and we have to subtract it. The process of adding and subtracting may be continued through consideration of all higher

<sup>20</sup> See reference 1, p. 183.

<sup>‡</sup> Equation (3.11) is not limited to a gas of rigid spheres but holds for cavities in all fluids.

<sup>21</sup> J. E. Mayer and E. Montroll, J. Chem. Phys. 9, 2 (1941).

order overlappings with the result [in extension of (3.15)],

$$\begin{aligned}
 p_0(r) &= \frac{V - \rho \int_V \Omega_1(\mathbf{R}_1, r) d\mathbf{R}_1 + (\rho^2/2) \iint_V g^{(2)}(\mathbf{R}_1, \mathbf{R}_2) \Omega_2(\mathbf{R}_1, \mathbf{R}_2, r) d\mathbf{R}_1 d\mathbf{R}_2 + \dots}{V}, \\
 &= 1 + \sum_{m=1}^{\infty} (-1)^m F_m
 \end{aligned}
 \tag{3.16}$$

which identifies  $F_m$  in the form (3.14).

In particular since both  $g^{(2)}(\mathbf{R}_1, \mathbf{R}_2, r)$  and  $\Omega_2(\mathbf{R}_1, \mathbf{R}_2, r)$  depend on  $\mathbf{R}_1$  and  $\mathbf{R}_2$  only through  $|\mathbf{R}_1 - \mathbf{R}_2|$  it follows that

$$\begin{aligned}
 F_2(r) &= \rho^2/2 \iint_V g(\mathbf{R}_1, \mathbf{R}_2) \frac{\Omega_2(\mathbf{R}_1, \mathbf{R}_2)}{V} d\mathbf{R}_1 d\mathbf{R}_2 \\
 &= (\rho^2/2) \int_0^{2r} g(s) \Omega_2(s, r) 4\pi s^2 ds.
 \end{aligned}
 \tag{3.17}$$

Here  $s = |\mathbf{R}_1 - \mathbf{R}_2|$  and the upper limit  $2r$  is derived from the fact that  $\Omega(s, r) = 0$  for  $s \geq 2r$  since two spheres of radius  $r$  cannot overlap when their centers are separated by a distance greater than  $2r$ . Differentiation of (3.17) with respect to  $r$  yields

$$\begin{aligned}
 \partial F_2/\partial r &= (\rho^2/2) \int_0^{2r} g(s) (\partial \Omega_2/\partial r) 4\pi s^2 ds \\
 &\quad + \rho^2 g(2r) \Omega(2r, r) 16\pi r^2.
 \end{aligned}
 \tag{3.18}$$

The second term on the right vanishes because, as mentioned,  $\Omega(2r, r) = 0$ . Furthermore,  $\partial \Omega_2/\partial r$  in the first term is nothing more than  $S_2(s, r)$ , the surface area of the overlapping volume of two spheres. This last follows from the fact that by  $(\partial \Omega_2/\partial r) dr$  we mean a volume increment achieved by moving the surface of overlap a distance  $r$  normal to itself. Thus we have

$$\partial F_2/\partial r = (\rho^2/2) \int_0^{2r} g(s) S_2(s, r) 4\pi s^2 ds,
 \tag{3.19}$$

and it is shown easily by simple geometry that

$$S_2(s, r) = 4\pi r[r - (s/2)].
 \tag{3.20}$$

From this we see that  $S_2(2r, r) = 0$ , so that by reasoning analogous to that used in deriving (3.19) we obtain

$$\partial^2 F_2/\partial r^2 = (\rho^2/2) \int_0^{2r} g(s) (\partial S_2/\partial r) 4\pi s^2 ds.
 \tag{3.21}$$

Since

$$g(s) = 0, \quad s \leq a
 \tag{3.22}$$

it follows from (3.19) and (3.21) that

$$(\partial F_2/\partial r)_{r=a/2} = (\partial^2 F_2/\partial r^2)_{r=a/2} = 0.
 \tag{3.23}$$

This means that in spite of the sudden appearance of of  $F_2$  in  $p_0$  [see (3.13)] at  $r = a/2$  both  $\partial p_0/\partial r$  and  $\partial^2 p_0/\partial r^2$  are continuous at  $r = a/2$ . Differentiating

(3.21) making use of (3.20) and (3.22) yields

$$(\partial^3 F_2/\partial r^3)_{r=a/2} = 8\pi^2 \rho^2 a^3 g(a)
 \tag{3.24}$$

so that  $\partial^3 p_0/\partial r^3$  is not continuous at  $r = a/2$ , but contains a jump proportional to  $g(a)$ .

Since  $G(r)$  is determined according to (2.15) by the derivative of  $p_0$ , (3.23) implies that both  $G$  and its first derivative are continuous at  $r = a/2$ , while (3.24) requires that the second derivative of  $G$  be discontinuous. The exact relations for  $G$  and its derivatives are

$$G = \frac{1}{1 - (\pi a^3 \rho/6)}, \quad r = a/2
 \tag{3.25}$$

$$\left(\frac{\partial G}{\partial r}\right)_{r=a/2} = \frac{\pi a^2 \rho}{[1 - (\pi a^3 \rho/6)]^2}
 \tag{3.26}$$

$$\begin{aligned}
 \left(\frac{\partial^2 G}{\partial r^2}\right)_{r=a/2} &= \frac{4\pi a \rho}{[1 - (\pi a^3 \rho/6)]^2} + \frac{2\pi^2 a^4 \rho^2}{[1 - (\pi a^3 \rho/6)]^3} \\
 &\quad - \frac{8\pi a \rho}{[1 - (\pi a^3 \rho/6)]} G(a).
 \end{aligned}
 \tag{3.27}$$

The derivative in (3.27) is taken to the right of  $r = a/2$ , the last term representing the discontinuity proportional to  $G(a)$ . In (3.27)  $G(a)$  has been used for  $g(a)$ . Both (3.26) and (3.27) are further *exact* conditions on the behavior of  $G(r, \rho)$ .

The function  $G$  is obviously not analytic since discontinuities in its higher derivatives occur at points where  $r$  becomes large enough so that the spherical region can accommodate more particles. These are the points  $a/2, a/\sqrt{3}$ , etc., at which two, three, etc., particles can be accommodated. The discontinuities are associated with the appearance of the new processes associated with the additional particles. Between  $a/2$  and  $a$ , for example,  $G(r)$  is not analytic at twelve points, at least, because up to twelve particles can be accommodated.

Nevertheless  $G$  is a smooth function because the discontinuity occurs in high order derivatives. For example, at  $a/2$  it first occurs in the second derivative. By an analysis similar to that given previously it can be shown that at  $a/\sqrt{3}$

$$F_3(r) = A[r - (a/\sqrt{3})]^{11/2} g^{(3)}(a, a, a)
 \tag{3.28}$$

plus higher order terms in  $[r - (a/\sqrt{3})]$ , and where  $A$  is independent of  $r$ . From this it follows that at  $r = a/\sqrt{3}$  the first five derivatives of  $p_0(r)$  are continuous, the discontinuity occurring in the sixth. Therefore, the first

four derivatives of  $G$  are continuous, the discontinuity occurring in the fifth. In general the order of the derivative at which the discontinuity occurs increases by at least two at each successive value of  $r$  at which another particle can be accommodated.

The results contained in (3.26) and (3.27) could have been deduced by performing integrations by parts in the integral of (3.13). These integrations have been performed by Hill<sup>22</sup> and yield§

$$p_0(r) = 1 - \frac{4}{3}\pi r^3 \rho + \frac{\rho^2}{2} \int_0^{2r} 4\pi s^2 g(s) \left[ \frac{\pi r^3}{3} \left\{ 4 - \frac{3s}{r} + \frac{s^3}{4r^3} \right\} \right] ds \tag{3.29}$$

[ $\Omega_2(s, r)$  is equal to the terms in the bracket under the integral sign in (3.29)] which can be differentiated to yield (3.26) and (3.27). Although (3.29) will prove useful later in a discussion of the relation between  $g(r)$  and  $G(r)$  for a range of values of  $r$  it is not the most efficient means of arriving at (3.26) and (3.27), and in fact a similar technique could probably not be employed for the derivation of (3.28).

In closing this section we shall find  $G(r, \rho)$  to the first order in  $\rho$  for all values of  $r$ . This will also give an illustration of the validity of Eq. (2.22). This is accomplished by finding an exact expression for  $G(r, \rho)$  to the appropriate order in  $\rho$ . It is convenient to work in terms of the reduced variables||

$$\begin{aligned} \xi &= r/a, \\ x &= a^3 \rho, \end{aligned} \tag{3.30}$$

instead of  $r$  and  $\rho$ . When these new variables are substituted into (2.22) and the integrations up to  $a/2$  (or up to  $\frac{1}{2}$  in terms of  $\xi$ ) are performed with the aid of (3.2) we obtain

$$\begin{aligned} \frac{x^2}{6} G(1, x) + \frac{3}{2\pi^2} \left\{ \ln \left( 1 - \frac{\pi x}{6} \right) + \frac{\pi x}{6} \right\} \\ = x^2 \int_{\frac{1}{2}}^1 \xi^2 G(\xi, x) d\xi - \int_0^x zdz \int_{\frac{1}{2}}^1 \xi^2 G(\xi, z) d\xi. \end{aligned} \tag{3.31}$$

According to (3.11)  $p_0(r)$  is determined up to terms in  $\rho^2$  for all values of  $r$  by the part of (3.11) which appears in (3.29). This follows from the fact that the integrals in  $g^{(m)}$  for  $m \geq 3$  in (3.11) are preceded by  $\rho$  raised to a higher power than 2. Furthermore,  $g$  can be expanded<sup>23</sup> in a power series in  $\rho$  the first term of which is always unity. We will only be interested in  $p_0(r)$  to

<sup>22</sup> T. L. Hill, J. Chem. Phys. **28**, 1179 (1958).

§ The present authors wish to signify their indebtedness to Hill's paper for having planted some of the germinal ideas of the present work. There is apparently however an error in Hill's equation which appears to express  $p_0(r)$  exclusively in terms of  $g(r)$  for all values of  $r$ .

|| The  $\xi$  introduced here should not be confused with the coupling parameter mentioned in Sec. 2. The latter does not appear in this paper beyond Sec. 2.

<sup>23</sup> J. DeBoer, Repts. Progr. in Phys. **12**, 305 (1949).

terms in  $\rho^2$  so that in (3.29) we can use

$$\begin{aligned} g &= 0, & s &\leq a \\ g &= 1, & s &> a \end{aligned} \tag{3.32}$$

and obtain a value of  $p_0(r)$  up to powers in  $\rho^2$  and valid for  $r > a/2$ . Using this in (2.15) provides a value for  $G(r, \rho)$  up to the first power in density, and valid for  $r > a/2$ . Written in terms of  $\xi, x$  this is

$$G(\xi, x) = 1 + (\pi x/24)[16 - (6/\xi)] + 0(x^2), \quad \xi > \frac{1}{2}. \tag{3.33}$$

Substitution of (3.33) into the integrals of (3.31) with expansion of the logarithmic term in powers of  $x$  and subsequent collection of powers yields up to terms in  $x$

$$G(1, x) = 1 + \frac{5}{12}\pi x + 0(x^2) = g(a), \tag{3.34}$$

which is the same as (3.33) for  $\xi = 1$ . This also agrees with the well-known virial expansion for  $g(a)$ .<sup>24</sup>

#### 4. EVALUATION OF $G(1, x)$ BY POLYNOMIAL METHOD

In this section we shall attempt to evaluate  $G(1, x)$  and hence the equation of state through manipulation of the exact relations derived in the preceding sections. In particular we shall make use of (3.31), (3.25), (3.26), and (3.27). As we have mentioned earlier in connection with Fig. 1, we require information concerning the area below the curve  $G(r, \rho)$  between  $r = a/2$  and  $r = a$ . This region corresponds to the integrals in (3.31). It has been shown that  $G(r, \rho)$  is a smooth curve with discontinuities only in the higher derivatives, and also is probably monotone increasing. We shall therefore try to approximate  $G(r, \rho)$  in the short range between  $a/2$  and  $a$  by some simple function of  $r$  with four parameters which may be functions of  $\rho$ .

Almost any simple function will do and for convenience we choose the cubic polynomial

$$\begin{aligned} G(\xi, x) &= \alpha_0(x) + \alpha_1(x) \left( \xi - \frac{1}{2} \right) + [\alpha_2(x)/2!] \left( \xi - \frac{1}{2} \right)^2 \\ &\quad + [\alpha_3(x)/3!] \left( \xi - \frac{1}{2} \right)^3, \end{aligned} \tag{4.1}$$

where the reduced variables  $\xi$  and  $x$  are used in place of  $r$  and  $\rho$ . By the straightforward substitution of (4.1) into (3.31), (3.25), (3.26), and (3.27) a set of simultaneous equations for the coefficients  $\alpha_0, \alpha_1, \alpha_2,$  and  $\alpha_3$  are obtained which can be solved, and in fact  $G(1, x)$  can be represented by a single quadrature.

$$\begin{aligned} G(1, x) &= t^{-\delta} \exp[H_1(t)] \int_0^t u^\delta \\ &\quad \times \exp[-H_1(u)] [(\delta/u) + H_2(u)] du, \end{aligned} \tag{4.2}$$

where

$$t = \pi x/6, \tag{4.3}$$

$$\delta = 111/31 = 3.5806452, \tag{4.4}$$

$$H_1(t) = \ln(1-t) + [4783/31(47)] \ln[1 + (47t/31)], \tag{4.5}$$

$$H_2(t) = \frac{6718 + 11776t - 12830t^2 + 5217t^3}{31(1-t^3)(31+47t)}. \tag{4.6}$$

<sup>24</sup> See reference 1, p. 211.

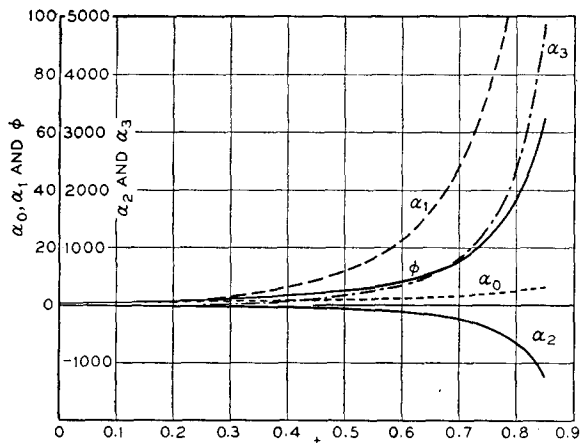


FIG. 2. Plots of the coefficients of the polynomial method [Eq. (4.1)] versus the reduced density.

The quadrature in (4.2) was performed numerically using the IBM 704 computer at Bell Laboratories. With  $G(1, x)$  known the set of simultaneous equations permits the immediate evaluation of  $\alpha_0$ ,  $\alpha_1$ ,  $\alpha_2$ , and  $\alpha_3$  by algebraic manipulation. Figure 2 contains plots of  $G(1, t)$ ,  $\alpha_0(t)$ ,  $\alpha_1(t)$ ,  $\alpha_2(t)$ , and  $\alpha_3(t)$  determined in this manner up to  $t=0.85$  or  $x=1.62$ . Knowledge of the  $\alpha$ 's is not only equivalent to  $G(1, x)$  but also to  $G(\xi, x)$  according to (4.1), at least in the interval  $a/2$  to  $a$ . This means that we can treat rigid sphere solutions with solutes having diameters  $b < a$ , through application of (2.17). As a matter of interest we give in Fig. 3 a plot of  $G(\xi, x)$  for  $x=0.574$  between  $\xi=0$  and  $\xi=1$ . Between  $\xi=\frac{1}{2}$  and  $\xi=1$  the curve is concave downward and does not depart appreciably from a straight line.

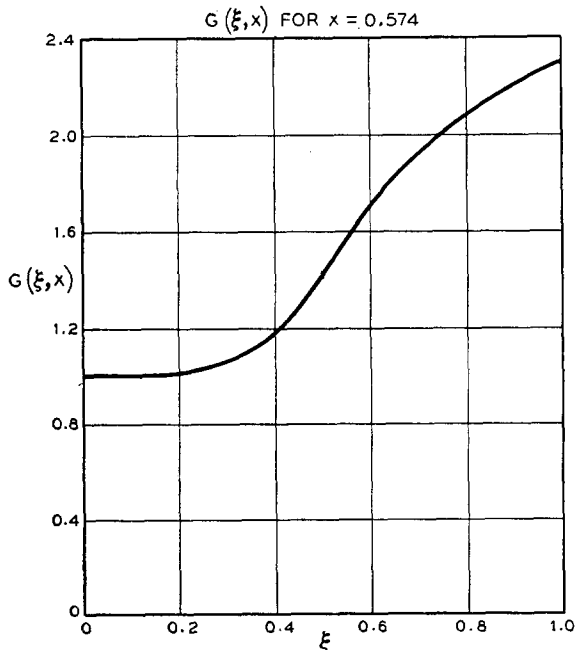


FIG. 3. Plot of  $G(\xi, x)$  from the polynomial method.

Our value of  $G(1, x) = g(a)$  can now be compared with the most reliable previous estimates. These are the Monte Carlo calculations of Rosenbluth and Rosenbluth<sup>4</sup> and Wood and Jacobsen<sup>5</sup> and the dynamical equations calculations of Alder and Wainwright.<sup>6</sup> Wood and Jacobsen and Alder and Wainwright are in agreement with respect to their computed equations of state, but Rosenbluth and Rosenbluth arrive at values of  $p/\rho kT$  which in the high-density range fall from 5 to 10% below those of the first authors. Since Wood and Jacobsen eliminated some possible sources of error in the procedure of Rosenbluth and Rosenbluth, and in addition agree with Alder and Wainwright it is reasonable to assume that both they and Alder and Wainwright are in possession of the more reliable equation of state.

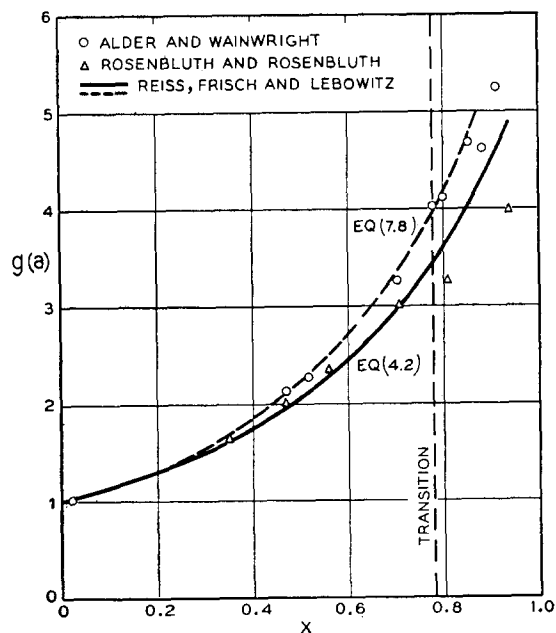


FIG. 4. Comparison of theory with machine calculations.

The full line in Fig. 4 is a plot of our value of  $G(1, x)$  while the open circles represent the data of Alder and Wainwright and the triangles that of Rosenbluth and Rosenbluth. The broken vertical line denotes the value of  $x$  at which the so-called fluid to solid phase transition makes its first appearance. We use the terminology "first appearance" rather than anything more definite because in Alder and Wainwright's calculations there is a transition range rather than point within which the system fluctuated with time between fluid and solid states. These fluctuations are presumably a result of the small number of particles used for the calculation. In Fig. 4 those results of Alder and Wainwright which lie to the right of the dashed line refer to the system in the "metastable" fluid condition.

Rosenbluth and Rosenbluth also saw signs of a transition to the right of the dashed line. However, the change of state appeared to be gradual, the calculated



radial distribution function changing smoothly with increasing density from that characteristic of a fluid to that for a solid.

As can be seen from Fig. 4 our results agree with those of Rosenbluth and Rosenbluth to within about 1%, below the transition line. At densities beyond this line, however, Rosenbluth and Rosenbluth's results fall below ours. Presumably this happens because the latter authors have observed the transition while due to the smoothing effects inherent in our use of the analytic polynomial (4.1) we have removed the possibility of transition. Thus our pressure [and therefore  $g(a)$ ] refers to a metastable fluid while Rosenbluth and Rosenbluth's is that of a solid and should be lower. For the purpose of orientation it should be mentioned that close packing corresponds to the density  $x = \sqrt{2}$ .

It may be of interest to expand  $G(1, x)$  in powers of  $x$  to see how our first five coefficients compare with the known exact ones. Equation (4.7) is the exact expression, while (4.8) is derived from our  $G(1, x)$ . For comparison we have also shown in (4.9) the expansion which results when in place of (4.1) the linear expression

$$G(\xi, x) = \alpha_0(x) + \alpha_1(x)\xi$$

is used, together with Eqs. (3.31) and (3.25). This corresponds to connecting the points at  $a/2$  and  $a$  by a straight line.

$$G(1, x) = g(a, \rho) = 1 + 0.417\pi x + 0.1275(\pi x)^2 + (0.0341 \pm 0.0015)(\pi x)^3 \quad (4.7)$$

$$G(1, x) = g(a, \rho) = 1 + 0.399\pi x + 0.1174(\pi x)^2 + 0.0266(\pi x)^3 \quad (4.8)$$

$$G(1, x) = g(a, \rho) = 1 + 0.31\pi x + 0.079(\pi x)^2 + 0.0185(\pi x)^3. \quad (4.9)$$

Although only terms up to  $x^3$  are included in the above expressions they represent expansions including the fifth virial coefficient since in (1.1)  $g(a)$  is multiplied by the density squared. Comparison of (4.8) and (4.9) shows the expected improvement as we go from a linear to a cubic polynomial, but the final result is still low by a few percent. Since our  $G(1, x)$  agrees with that of Rosenbluth and Rosenbluth this adds support to the contention that theirs is low.

### 5. A MORE GENERAL INTEGRAL EQUATION

We have indicated that Eq. (2.22) suffers from the defect that the integrals over  $r$  are definite, and therefore  $G(r, \rho)$  is only determined to a limited degree. In this section we shall derive an equation with indefinite integrals. This can be employed together with other information to derive a more precise value of  $G(1, x)$ . We shall in fact obtain analytic forms for both  $G(1, x)$  and  $G(\xi, x)$ . Furthermore we also obtain expressions for the surface tension  $\sigma_0$  of a rigid sphere

fluid as well as for the distance  $\delta$  separating the Gibbs surface of tension<sup>25</sup> from the dividing surface for which the superficial density of matter<sup>25</sup> vanishes.

Consider a fluid containing solutes of diameter  $b$  and solvent molecules of diameter  $a$ . In particular assume that the solution is dilute so that the concentration of solute  $\rho_b$  is small. The generalization of Eq. (1.1) for the pressure of this solution is easily shown to be<sup>26</sup>

$$\frac{p}{kT} = \rho_a + \rho_b + \frac{2}{3}\pi a^3 \rho_a^2 g_{aa}(a) + \frac{4}{3}\pi \left(\frac{a+b}{2}\right)^3 \rho_a \rho_b g_{ab}\left(\frac{a+b}{2}\right) + \frac{2}{3}\pi b^3 \rho_b^2 g_{bb}(b), \quad (5.1)$$

where  $g_{aa}(a)$  is the radial distribution function on contact between two solvent molecules,  $g_{bb}(b)$  the radial distribution function on contact between two solute molecules, and  $g_{ab}[(a+b)/2]$  the similar quantity between a solute and solvent.  $\rho_a$  is the concentration of the solvent, formerly denoted by  $\rho$ .

The chemical potential  $\mu_b$  of the solute is given by (2.18) with  $\rho$  replaced by  $\rho_a$ . Introducing (2.16) into (2.18) yields the alternative form

$$\mu_b = kT \ln \{ \rho_b \Lambda^3 / p_0 [(a+b)/2] \}. \quad (5.2)$$

By straightforward thermodynamic methods it can be shown that

$$\left(\frac{\partial p}{\partial \rho_b}\right)_{\rho_a} = \rho_b \left(\frac{\partial \mu_b}{\partial \rho_b}\right)_{\rho_a} + \rho_a \left(\frac{\partial \mu_b}{\partial \rho_a}\right)_{\rho_b}. \quad (5.3)$$

Then by differentiation of (5.2) and substitution of (5.3) we have

$$-\frac{1}{kT} \left(\frac{\partial \mu_b}{\partial \rho_a}\right)_{\rho_b} = \left(\frac{\partial \ln p_0}{\partial \rho_a}\right)_{\rho_b} = -\frac{1}{kT \rho_a} \left\{ \left(\frac{\partial p}{\partial \rho_b}\right)_{\rho_a} - \rho_b \left(\frac{\partial \mu_b}{\partial \rho_b}\right)_{\rho_a} \right\}. \quad (5.4)$$

Substitution of (5.1) into the right-hand member of (5.4) yields

$$\left(\frac{\partial \ln p_0}{\partial \rho_a}\right)_{\rho_b} = -\frac{1}{\rho_a} \left\{ 1 + \frac{2}{3}\pi a^3 \rho_a^2 \left(\frac{\partial g_{aa}(a)}{\partial \rho_b}\right)_{\rho_a} + \frac{4}{3}\pi \left(\frac{a+b}{2}\right)^3 \rho_a g_{ab}\left(\frac{a+b}{2}\right) + \frac{4}{3}\pi \left(\frac{a+b}{2}\right)^3 \rho_a \rho_b \left(\frac{\partial g_{ab}[(a+b)/2]}{\partial \rho_b}\right)_{\rho_a} - \frac{\rho_b}{kT} \left(\frac{\partial \mu_b}{\partial \rho_b}\right)_{\rho_a} \right\}, \quad (5.5)$$

where the term in  $g_{bb}$  has been omitted because we shall be interested in the case  $\rho_b \rightarrow 0$  and it is of higher order in  $\rho_b$ . In the limit  $\rho_b \rightarrow 0$

$$g_{ab}\left(\frac{a+b}{2}\right) \rightarrow G\left(\frac{a+b}{2}, \rho\right) \\ g_{aa}(a) \rightarrow G(a, \rho) \quad (5.6)$$

<sup>25</sup> R. C. Tolman, *J. Chem. Phys.* **16**, 758 (1948); **17**, 118, 333 (1949).

<sup>26</sup> H. S. Green, *The Molecular Theory of Fluids* (North-Holland Publishing Company, Amsterdam, 1952), p. 171.

and

$$(\partial\mu_b/\partial\rho_b)_{\rho_a} \rightarrow (kT/\rho_b), \tag{5.7}$$

since  $\mu_b$  is given by (5.2) and in the limit  $p_0[(a+b)/2]$  is independent of  $\rho_b$ . Substituting (5.6) and (5.7) into (5.5) and writing  $\rho$  for  $\rho_a$  we then have in the limit  $\rho_b \rightarrow 0$ .

$$\begin{aligned} \frac{\partial \ln p_0}{\partial \rho} &= -\frac{2}{3}\pi a^3 \rho \left( \frac{\partial G(a, \rho)}{\partial \rho_b} \right)_{\rho_b=0} - \frac{4}{3}\pi \left( \frac{a+b}{2} \right)^3 G\left( \frac{a+b}{2}, \rho \right) \\ &= \frac{Q(b, a, \rho)}{\rho} - \frac{4}{3}\pi \left( \frac{a+b}{2} \right)^3 G\left( \frac{a+b}{2}, \rho \right). \end{aligned} \tag{5.8}$$

It is evident from (5.8) that

$$Q(b, a, \rho) = -\frac{2}{3}\pi a^3 \rho^2 \left( \frac{\partial G(a, \rho)}{\partial \rho b} \right)_{\rho_b=0}. \tag{5.9}$$

At this stage it is again convenient to introduce the transformation

$$\begin{aligned} \xi &= (a+b)/2a, \\ x &= a^3 \rho. \end{aligned} \tag{5.10}$$

From (5.8) and (2.15) one can then derive

$$\begin{aligned} Q(\xi, x) &= x \frac{\partial \ln p_0}{\partial x} - \frac{\xi}{3} \frac{\partial \ln p_0}{\partial \xi} \\ &= -x \frac{\partial}{\partial x} \left\{ x \int_0^\xi 4\pi \xi^2 G(\xi, x) d\xi \right\} + \frac{4}{3}\pi x \xi^3 G(\xi, x). \end{aligned} \tag{5.11}$$

This is an integral equation on  $G(\xi, x)$  containing indefinite integrals.<sup>¶</sup> However the function  $Q(\xi, x)$  defined by (5.4) is not immediately available in useful form, and the utility of (5.11) will depend on how explicitly  $Q(\xi, x)$  can be determined.

Introducing (3.1) into (5.11) together with the additional knowledge that  $\partial p_0/\partial \xi$  and  $\partial^2 p_0/\partial \xi^2$  are continuous at  $\xi = \frac{1}{2}$  we obtain

$$Q = \partial Q/\partial \xi = 0, \quad \xi \leq \frac{1}{2}. \tag{5.12}$$

This implies that an expansion of  $Q$  in powers of  $(\xi - \frac{1}{2})$  begins with a quadratic term whose coefficient is  $\frac{1}{2}(\partial^2 Q/\partial \xi^2)_{\xi=\frac{1}{2}}$ . In fact this coefficient can be determined by differentiating (5.11) three times with respect to  $\xi$  and making use of (3.27). The result for the quadratic term is then

$$\lim_{\xi \rightarrow \frac{1}{2}} Q(\xi, x) = -\frac{2\pi^2 x^2}{3[1 - (\pi x/6)]} G(1, x) (\xi - \frac{1}{2})^2. \tag{5.13}$$

It can also be shown that the dominant term in  $Q$  as  $\xi \rightarrow \infty$  is

$$Q_{dom} = -\frac{4}{3}\pi \xi^3 x^2 [\partial G(\infty, x)]/\partial x. \tag{5.14}$$

This varies with the third power of  $\xi$ .

<sup>¶</sup> For  $\xi=1$  (5.11) is equivalent to (2.22) since according to (5.9)  $Q(1, x) = -\frac{2}{3}\pi x^2 [\partial G(1, x)]/\partial x$ .

Although  $Q$  and  $G$  are not analytic functions of  $\xi$  it may be possible to approximate them closely by analytic functions. An analytic approximation to  $Q$  which interpolates the proper limiting behavior indicated by (5.13) and (5.14) is

$$Q(\xi, x) = \omega_2(x) (\xi - \frac{1}{2})^2 + \omega_3(x) (\xi - \frac{1}{2})^3, \quad \xi > \frac{1}{2} \tag{5.15}$$

where  $\omega_2(x)$  and  $\omega_3(x)$  are the coefficients of the powers of  $\xi - \frac{1}{2}$  (and  $\xi$ ) in (5.13) and (5.14).

If (5.15) is substituted into (5.11), and the result differentiated once with respect to  $\xi$ , the following equation is obtained

$$\begin{aligned} \frac{1}{2\pi} \omega_2(x) (\xi - \frac{1}{2}) + \frac{3}{4\pi} \omega_3(x) (\xi - \frac{1}{2})^2 \\ = -x^2 \xi^2 \frac{\partial G}{\partial x} + \frac{1}{3} x \xi^3 \frac{\partial G}{\partial \xi}. \end{aligned} \tag{5.16}$$

Now it is easily shown that the solution of (5.16) must be of the form (if we assume in approximation that  $G$  is analytic in  $\xi > \frac{1}{2}$ ).

$$G(\xi, x) = \phi(\xi^3 x) + \frac{\alpha_{-2}(x)}{\xi^2} + \frac{\alpha_{-1}(x)}{\xi} + \alpha_0(x) \tag{5.17}$$

where  $\phi$  is some function of the single variable  $\xi^3 x$ . This can be proved by direct substitution of an arbitrary form of  $G(\xi, x)$  containing all possible powers of  $\xi$  as well as the part shown in (5.17).

The function of  $\phi(\xi^3 x)$  must vanish as  $\xi \rightarrow \infty$  since  $G(\infty, x)$  is a function of  $x$  alone, that is  $\alpha_0(x) = G(\infty, x)$ . But the limit of (5.17) as  $\xi \rightarrow \infty, x \rightarrow 0$  in such a way that  $\xi^3 x \rightarrow y$ , a finite but arbitrary number, shows that  $\phi(y)$  must vanish. This leaves the suggested form

$$G(\xi, x) = \alpha_0(x) + \frac{\alpha_{-1}(x)}{\xi} + \frac{\alpha_{-2}(x)}{\xi^2}. \tag{5.18}$$

We shall see that thermodynamic considerations suggest the same form.

### 6. THERMODYNAMIC CONSIDERATIONS, A MORE PRECISE $G(1, x)$ AND SURFACE TENSION

By differentiation of (2.17), expressed in terms of  $\xi$  and  $x$ , one obtains

$$G(\xi, x) = (1/4\pi \xi^2 kTx) (\partial W/\partial \xi). \tag{6.1}$$

When the spherical cavity is sufficiently large ( $\xi$  large)  $W$  can be represented by<sup>25, 27, 28</sup>

$$W = a^3 p \frac{4}{3} \pi \xi^3 + a^2 4\pi \xi^2 \sigma_0(x) \left( 1 - \frac{2\delta(x)}{\xi} \right). \tag{6.2}$$

Here the first term on the right is the pressure-volume work expended in creating the cavity and the second term is the surface work. The quantity

$$\sigma_0 [1 - (2\delta/\xi)] \tag{6.3}$$

<sup>27</sup> J. S. Kirkwood and F. P. Buff, J. Chem. Phys. **17**, 338 (1949).  
<sup>28</sup> F. P. Buff, J. Chem. Phys. **23**, 419 (1955).

is the surface tension.  $\delta(x)$  is the distance, (divided by  $a$ ), between the dividing surface for which the superficial density of matter vanishes and the Gibbs surface of tension,<sup>25,27,28</sup> while  $\sigma_0(x)$  is the surface tension at infinite  $\xi$ , i.e. infinite radius of curvature.

The pressure in (6.2) can be replaced by a function of  $G(1, x)$  through use of (1.1). When this is done and (6.2) is substituted into (6.1) we obtain

$$G(\xi, x) = \left\{ 1 + \frac{2}{3}\pi x G(1, x) \right\} + \left\{ \frac{2a^2\sigma_0(x)}{kTx} \right\} \frac{1}{\xi} - \left\{ \frac{2a^2\sigma_0(x)\delta(x)}{kTx} \right\} \frac{1}{\xi^2}. \quad (6.4)$$

This is identical in form with (5.18), but is exact in the region in which  $\xi$  is *very large*, while (5.18) refers to  $\xi$  *small*. This lends support to the idea that (5.18) is a good approximation over the entire range between  $\xi = \frac{1}{2}$  and  $\xi = \infty$ . Equation (3.7) shows that the first bracketed expression on the right of (6.4) is nothing more than  $G(\infty, x)$  so that  $G$  given by (6.4) approaches the correct limit for  $\xi \rightarrow \infty$ .

If we do assume that (6.4) is valid right down to  $\xi = \frac{1}{2}$  we can substitute it into the exact relation (3.25) and (3.26). The result is two equations on the three unknowns  $G(1, x)$ ,  $\sigma_0(x)$ , and  $\delta(x)$ . A third equation is obtained by simply setting  $\xi$  in (6.4) equal to unity.\*\* The three equations are

$$\frac{1}{1 - (\pi x/6)} = 1 + \frac{2}{3}\pi x G(1, x) + \frac{4a^2\sigma_0(x)}{kTx} - \frac{8a^2\sigma_0(x)\delta(x)}{kTx}. \quad (6.5)$$

$$\frac{\pi x}{[1 - (\pi x/6)]^2} = -\frac{8a^2\sigma_0(x)}{kTx} + \frac{32a^2\sigma_0(x)\delta(x)}{kTx}. \quad (6.6)$$

$$(1 - \frac{2}{3}\pi x)G(1, x) = 1 + \frac{2a^2\sigma_0(x)}{kTx} - \frac{2a^2\sigma_0(x)\delta(x)}{kTx}. \quad (6.7)$$

These can be solved simultaneously to yield

$$G(1, x) = \frac{1}{4[1 - (\pi x/6)]} + \frac{3}{4[1 - (\pi x/6)]^2} + \frac{\pi x}{8[1 - (\pi x/6)]^3}. \quad (6.8)$$

$$\sigma_0(x) = -\frac{kT\pi x^2[1 + (\pi x/6)]}{8a^2[1 - (\pi x/6)]^3}. \quad (6.9)$$

$$\delta(x) = \frac{1}{4} - \frac{1}{4} \left\{ \frac{1 - (\pi x/6)}{1 + (\pi x/6)} \right\}. \quad (6.10)$$

\*\* Note added in proof.—A third equation can also be obtained by merely substituting (6.4) into (3.31). The result is a value for  $G(1, x)$  different from that given in (6.8), and which in fact gives more accurate virial coefficients. Of course, before (6.4) is substituted in (3.31), the first term is represented as  $G(\alpha, x)$ , i.e., (3.7) is not satisfied by the resulting  $G(1, x)$ .

We have thus not only determined the equation of state, but the surface tension and its dependence on curvature as well.

The expression (6.8) is remarkable in a number of respects: Expanded in powers of  $x$  it yields

$$G(1, x) = 1 + 0.417\pi x + 0.1319(\pi x)^2 + 0.0359(\pi x)^3 + \dots \quad (6.11)$$

This is to be compared with (4.7). It is seen that up to and including the third virial coefficient (6.11) is exact. (The 0.417 is actually the fraction (5/12) which is known to be exact.) The error in the fourth virial coefficient is only about 3% and in the fifth only 5%. In fact the exact fifth virial coefficient is not known to within better than 5%.<sup>3</sup> Inspection of (6.8) shows that all the coefficients of its expansion in powers of  $x$  are positive. This supports the idea that for hard spheres all the virial coefficients are positive.

However, it must be understood that Eq. (6.4) is an interpolation formula whose functional form is suggested by previous considerations. Since this "best" functional form contains only three parameters, we cannot use all the information we possess concerning  $G$  (e.g.,  $G''(\frac{1}{2})$ , Eq. (2.22)). Thus we do not expect Eq. (6.4) to give reliably higher derivatives of  $G$ . Equation (6.4) does, however, give  $G(\xi, x)$  exactly to terms linear in  $x$ .

The dashed line in Fig. 4 is a plot of  $G(1, x)$  as given by (6.8). The results are almost indistinguishable from the data of Alder and Wainwright over the entire range of density. In fact agreement is maintained even beyond the transition line showing that Alder and Wainwright's points do indeed correspond to a metastable fluid.

Equation (6.9) shows that the surface tension  $\sigma_0$  for a rigid sphere fluid is indeed negative. Furthermore, for  $x \rightarrow 0$ ,

$$\sigma_0 = -\frac{kT\pi x^2}{8a^2} = -\frac{kT\pi a^4 \rho^2}{8}, \quad (6.12)$$

which is identical with the result derived from an equation due to Kirkwood and Buff<sup>27</sup> [Eq. (29) of their paper] when for the gradient of the potential is substituted  $-kT\delta(r-a)$  [see Eq. (2.6)]. Since Kirkwood and Buff's result must be exact in the limit of zero density this is further confirmation of the validity of (6.9).

Equation (6.10) shows that  $\delta$  lies between 0 and  $\frac{1}{2}$ . This shows according to (6.3) that the surface tension does not vary strongly with curvature until a cavity of molecular dimensions is involved. In fact at zero density  $\delta = 0$  and within the framework of the approximation there is no dependence on curvature.

## 7. RELATION BETWEEN $G(r, \rho)$ AND $g(r)$

The foregoing analysis has been aimed primarily at determining, to a sufficient approximation,  $g(a)$  from which the thermodynamic properties of the rigid sphere

fluid follow. One expects though that a knowledge of  $G(r, \rho)$  will not only specify  $g(a)$  but to some extent at least  $g(r)$  for  $r > a$ . We will show that in the range  $(a/2) \leq r < a/\sqrt{3}$  a knowledge of  $G(r, \rho)$  determines  $g(r)$  exactly in  $a \leq r < 2a/\sqrt{3}$ .

Consider Eq. (3.29) which applies in this range.  $p_0(r)$  on the left-hand side can be written by virtue of (2.16) as a negative exponential of a quadrature of  $G(r, \rho)$ . Thus (3.29) can be rewritten as

$$F(r) = 4 \int_0^{2r} s^2 g(s) ds - \frac{3}{r} \int_0^{2r} s^3 g(s) ds + \frac{1}{4r^3} \int_0^{2r} s^5 g(s) ds, \quad (7.1)$$

where

$$F(r) = \frac{p_0(r) - 1 + \frac{4}{3}\pi r^3 \rho}{\frac{2}{3}\pi^2 r^3 \rho^2} \\ = \frac{\exp\left\{-\rho \int_0^r 4\pi s^2 G(s, \rho) ds\right\} - 1 + \frac{4}{3}\pi r^3 \rho}{\frac{2}{3}\pi^2 r^3 \rho^2}. \quad (7.2)$$

After differentiating (7.2) three times with respect to  $r$ , one notes that the three derivatives  $F'(r)$ ,  $F''(r)$ ,  $F'''(r)$  can be written in terms of  $g(2r)$  and the last two integrals over  $g(s)$  on the right-hand side of (7.1) (i.e., no other terms containing  $g(s)$  are present). On eliminating these integrals we find that

$$g(2r) = [F'''(r)/96] + (1/96r) \{(8/r)F'(r) + 7F''(r)\}, \quad (7.3)$$

for

$$a/2 \leq r < a/\sqrt{3},$$

as was to be shown.

Although Eq. (7.3) only allows us to determine  $g(r)$  exactly up to  $r = 2a/\sqrt{3}$  in terms of  $G(r, \rho)$  it may approximate  $g(r)$ , for certain purposes, sufficiently well

beyond this point. In any case the investigation of the analytic form of  $G(r, \rho)$  beyond  $r = a/\sqrt{3}$  will be postponed for a later discussion, as will the validity of (7.3) beyond  $r = a/\sqrt{3}$  and possible extensions of (7.3).

## 8. CONCLUDING REMARKS

In this paper we have presented two schemes for arriving at the equation of state for a system of rigid spheres. These are the polynomial method of Sec. 4, and the method based on the second integral equation (5.11). Whereas the polynomial method leads to a less precise result it has the advantage of being entirely free of thermodynamic considerations, while the second method though largely statistical requires some thermodynamic argument to support the form of  $G(\xi, x)$  suggested by statistical investigation.

Nevertheless the second method yields far more information than the polynomial method and should, in fact, be capable of giving a completely nonthermodynamic theory. The next step ought to be aimed along these lines. An attempt must be made to express  $Q$  defined as (5.9) as a function of  $G[(a+b)/2, \rho]$ . This would render Eq. (5.11) more determinate.

A considerable amount of interesting discussion concerning solutions can be given. We have omitted this here but intend to include it in a later paper.

Finally we remark that it is possible to treat molecules with attractive potentials by the techniques described here. This too will be reserved for a later paper.

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