

# Theory of the Two- and One-Dimensional Rigid Sphere Fluids

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The approximate theory of the three-dimensional hard sphere fluid developed by Reiss, Frisch, and Lebowitz has given astonishingly good predictions with little labor. In an attempt to investigate the reason for this result we adduce, in this paper, further evidence for the internal consistency of the approximations of this theory. Thus it is noted that the same equation of state of hard sphere fluid is obtained when one uses the "integral condition" as when the "infinity condition" is used. We have then applied the theory to study the thermodynamic properties, in particular the equation of state, of the rigid sphere fluid in two and one dimensions. The approximate equation of state of the two-dimensional rigid sphere fluid is in good agreement over the range of fluid densities with the results of the machine Monte Carlo calculations by Jacobson and Wood and dynamical machine calculations of Wainwright and Alder. The exact Tonks' equation of state of the one-dimensional rigid sphere fluid is derived in a particularly simple manner.

## I. INTRODUCTION

THE thermodynamic properties of systems of particles interacting only with rigid core repulsive forces are determined completely by the value of certain contact correlation functions. Reiss, Frisch, and Lebowitz<sup>1</sup> (hereinafter referred to as I) have recently made significant progress in the theory of such systems by focusing attention on these required unknowns, rather than attempting to determine all the information contained in the full radial distribution function. The theoretical basis of I has been viewed in a somewhat different manner and extended to provide the basis for the treatment of real fluids in a paper by Helfand, Reiss, Frisch, and Lebowitz.<sup>2</sup> Unfortunately these investigations do not seem to supply the complete reason why these simple theories make as accurate predictions as they do. A very partial answer to this question, which we obtain in the first part of this paper, is that there exists further evidence of the inner consistency of the theory as developed for three-dimensional fluids. In the attempt to investigate further this question we consider in the main part of this paper the extension of the theory to two and one dimensions to see how well and possibly why it works in these cases.

The basic technique is to define a function  $G(\lambda, \rho)$  such that  $\rho G(\lambda, \rho)$  is the density of rigid sphere molecules of diameter  $a$  in contact with a single "solute" sphere (this single particle may, alternatively, be viewed as a hole) of diameter  $b$ , where  $\lambda a = \frac{1}{2}(a+b)$  and  $\rho$  is the particle number density ( $N/V$  in three

dimensions,  $N/A$  in two dimensions, and  $N/L$  in one dimension). The significance of  $\lambda$  is that if the normal molecule-molecule potential function is  $u(r)$ , the molecule-solute interaction potential is  $u(r/\lambda)$ . Thus, even for more general potentials, the solute is essentially a size-scaled version of the normal molecules. We have termed such a scaled particle a  $\lambda$ -cule. The value of  $\lambda$  may range from zero to infinity. When  $\lambda=0$  the  $\lambda$ -cule can completely penetrate all molecules so that it is a free particle. The value  $\lambda=\frac{1}{2}$  plays a role of central importance since it is the first point at which the  $\lambda$ -cule can interact with more than one molecule at a time. When  $\lambda=1$  we see that  $b=a$ , so that the  $\lambda$ -cule is identical with the other molecules. Thus  $G(1, \rho)$  is the contact radial distribution function for a pure system of diameter  $a$  particles. Finally, when  $\lambda=\infty$  the  $\lambda$ -cule may be regarded as a plane rigid wall.

The method of determining the  $G$  function for a three-dimensional system as developed in I is reviewed in the next section, and a new observation relating to the consistency of the assumed form of  $G$  is made. We then extend this technique to allow for the treatment of a two-dimensional hard sphere system, where some additional complications enter. An equation of state in close agreement with machine calculations is derived. Next we show that the method may be simply applied to a one-dimensional system to yield the exact equation of state. Finally, in appendices, we consider the application of the theory to the simplest cases of the perfect gas and the hard sphere lattice gas.

## II. THREE DIMENSIONS

In three dimensions the equation of state of a hard sphere fluid is

$$\rho/\rho k T = 1 + \frac{2}{3}\pi\rho a^3 G(1, \rho), \quad (2.1)$$

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<sup>1</sup> H. Reiss, H. L. Frisch, and J. L. Lebowitz, *J. Chem. Phys.* **31**, 369 (1959).

<sup>2</sup> E. Helfand, H. Reiss, H. L. Frisch, and J. L. Lebowitz, *J. Chem. Phys.* **33**, 1379 (1960).

while the chemical potential is

$$\mu/kT = \ln \rho \Lambda^3 + 4\pi \rho a^3 \int_0^1 \lambda^2 G(\lambda, \rho) d\lambda, \quad (2.2)$$

where  $\Lambda^3 = h^3 / (2\pi m k T)^{3/2}$ . As a generalization of (2.2) one has for the work of introducing a  $\lambda$ -cule at a fixed point in a system of molecules

$$W(\lambda) = 4\pi \rho a^3 k T \int_0^\lambda \lambda'^2 G(\lambda', \rho) d\lambda', \quad (2.3)$$

( $W$  is also  $\rho$ -dependent but here and at various other points later we will leave the functional dependence on  $\rho$  implicit when it is obvious), from which one obtains by differentiating

$$G(\lambda, \rho) = (4\pi \rho a^3 k T)^{-1} [\partial W(\lambda) / \partial \lambda]. \quad (2.4)$$

A relation exists between the work of introducing a  $\lambda$ -cule (or equivalently the work of creating a hole of radius  $\lambda a$ ) and the probability of finding a hole of at least size  $\lambda a$  as a result of a spontaneous fluctuation,  $p_0(\lambda)$ ; it is

$$p_0(\lambda) = \exp[-W(\lambda) / kT]. \quad (2.5)$$

This allows the discussion to be carried through in terms of certain physically defined probabilities. The probability of a vacant hole of radius  $\lambda a$  is equal to

$$p_0 = 1 - p_1 - p_2 - p_3 - \dots, \quad (2.6)$$

where  $p_k$  is the probability of finding exactly  $k$  molecules in this region. Equation (2.6) may be rearranged as

$$p_0 = 1 - (p_1 + 2p_2 + 3p_3 + \dots) + (p_2 + 3p_3 + 6p_4) - (p_3 + 4p_4 + \dots) + \dots, \quad (2.7)$$

where the first sum in parentheses represents the average number of individual particles in the region of radius  $\lambda a$ , the second sum represents the average number of pairs, the third the average number of triplets, etc. (See Appendix A for the case of the ideal gas.) The series (2.7) may be written in terms of  $m$ -particle correlation functions,<sup>3</sup>  $g^{(m)}$ , as

$$p_0(\lambda) = 1 + \sum_{m=1}^{\infty} [(-1)^m \rho^m / m!] \int_{[\text{region of radius } \lambda a]} g^{(m)}(\mathbf{r}_1, \dots, \mathbf{r}_m) d\mathbf{r}_1 \dots d\mathbf{r}_m. \quad (2.8)$$

The convenience of Eq. (2.8) arises from the fact that the series on the right-hand side terminates at a value  $m$  equal to the number of molecules which may be packed into the region of radius  $\lambda a$ . For  $\lambda \leq \frac{1}{2}$  the only term is  $m=1$ ; i.e., the center of only one molecule may be in a cavity of radius less than  $\frac{1}{2}a$ , and the probability of a molecule being there is the density times the

<sup>3</sup> T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956), Section 29.

cavity volume.<sup>4</sup> Therefore we have

$$p_0(\lambda) = 1 - \frac{4}{3}\pi \rho a^3 \lambda^3, \quad \lambda \leq \frac{1}{2}, \quad (2.9)$$

which leads through Eqs. (2.4)–(2.5) to

$$G(\lambda) = 1 / (1 - \frac{4}{3}\pi \rho a^3 \lambda^3), \quad \lambda \leq \frac{1}{2}. \quad (2.10)$$

By examination of the series (2.8) it is also shown in I that both  $G(\lambda)$  and  $\partial G(\lambda) / \partial \lambda$  are continuous for all  $\lambda$  and that the discontinuity of the second derivative of  $G$  at  $\lambda = \frac{1}{2}$  is given by

$$(\partial^2 G / \partial \lambda^2)_{\lambda=\frac{1}{2}+} - (\partial^2 G / \partial \lambda^2)_{\lambda=\frac{1}{2}-} = - \frac{8\pi \rho a^3}{1 - (\pi \rho a^3 / 6)} G(1). \quad (2.11)$$

A further condition which  $G(\lambda)$  must satisfy arises from the fact that from the chemical potential of Eq. (2.2) one may calculate a pressure which must be equal to that given by Eq. (2.1). Explicitly, the thermodynamic equality

$$p = \int_0^\rho \rho' (\partial \mu / \partial \rho') T d\rho', \quad (2.12)$$

leads to

$$\frac{2}{3}\pi \rho^2 G(1, \rho) = \rho^2 \int_0^1 4\pi \lambda^2 G(\lambda, \rho) d\lambda - \int_0^\rho \rho' d\rho' \int_0^1 4\pi \lambda^2 G(\lambda, \rho') d\lambda. \quad (2.13)$$

Because of the definite limits on the  $\lambda$  integration this is not a deterministic equation but rather a condition on  $G$ . It relates the value of  $G$  at  $\lambda=1$  to an integral over the range  $0 < \lambda < 1$ . The fact that  $G$  is known exactly for  $\lambda \leq \frac{1}{2}$  makes this an even narrower range.

A condition on  $G(\lambda)$  exists for large values of  $\lambda$ . Under these circumstances the surface of the cavity may be considered as a hard flat wall. The density near such a wall  $\rho G(\infty)$  is proportional to the pressure,

$$p/kT = \rho G(\infty), \quad (2.14)$$

so that  $G(\infty)$  may be related to  $G(1)$  by Eq. (2.1):

$$G(\infty) = 1 + \frac{2}{3}\pi \rho a^3 G(1). \quad (2.15)$$

In this limit, as the size of the system goes to infinity, the density of the system remains constant and is unaffected by the presence of the cavity. Equation (2.14) may then also be derived by treating the cavity as a system of volume  $v = \frac{4}{3}\pi \lambda^3 a^3$  in contact with a particle bath (represented by the rest of the system). This system is then represented by a grand canonical ensemble

$$p_n = z^n Q_n / \Xi,$$

<sup>4</sup> For  $\lambda=1$ ,  $m=12$ , the number of molecules in contact with a given one at close packing, while for  $\lambda \gg 1$ ,  $m(\lambda) \sim (\frac{4}{3}\pi \sqrt{2}) \lambda^3 + 0(\lambda^2)$ .

where  $z$  is the activity,  $\Xi$  the grand partition function, and  $Q_n$  the canonical partition function of  $n$  particles in the cavity. This yields

$$p_0 = \Xi^{-1} = \exp(-pv/kT),$$

which combined with (2.4) and (2.5) leads to (2.15).

In summary one has the following exact information about the function  $G(\lambda)$ : (a) the value of  $G(\lambda)$  for  $\lambda \leq \frac{1}{2}$ , Eq. (2.10); (b)-(c) the continuity of  $G(\lambda)$  and its first derivative; (d) the magnitude of the discontinuity of  $G''(\lambda)$  at  $\lambda = \frac{1}{2}$ ; (e) the integral condition (2.13); (f) the infinity condition (2.15).

A quasi-thermodynamic argument is used in I to determine the form of  $G(\lambda)$  for large values of the argument  $\lambda$ . The work of expanding a cavity in a fluid is given by a pressure-volume and a surface tension-surface area term:

$$dW = p dV + \sigma dS. \quad (2.16)$$

As a first approximation to the Gibbs-Tolman-Koenig<sup>5</sup> relation for the surface tension of a surface of radius of curvature  $\lambda a$ , one has

$$\sigma = \sigma_0 [1 - (2\delta/\lambda)], \quad (2.17)$$

where  $\delta a$  is the distance between the surface for which the superficial density vanishes and the surface of tension. Equation (2.16) may thus be written

$$dW = [4\pi p a^3 \lambda^2 + 8\pi \sigma_0 a^2 \lambda + 16\pi \sigma_0 \delta a^2] d\lambda, \quad (2.18)$$

so that by Eq. (2.4) the suggested form for  $G(\lambda)$  is

$$G(\lambda, \rho) = A(\rho) + [B(\rho)/\lambda] + [C(\rho)/\lambda^2], \quad (2.19)$$

where  $A, B, C$  may be written in terms of  $p, \sigma$ , and  $\delta$ .

By examining the properties of mixtures of molecules and  $\lambda$ -cules Reiss, Frisch, and Lebowitz show how further insight into  $G$  may be gained. Their considerations suggest the form (2.19) for  $G$  is a good, analytic approximation over the entire range  $\frac{1}{2} < \lambda < \infty$ , and is in fact exact not only at the upper limit as indicated in the previous paragraph but also at the lower limits. Details of this argument as applied to the two-dimensional fluid are presented in the following section.

The three unknown functions of density which appear in Eq. (2.19) may be determined from a combination of any three of the five exact conditions (b) to (f) in combination with (a). In I the continuity of  $G$  and  $G'$  conditions, and the infinity condition are used to derive the three-dimensional equation of state

$$p/\rho kT = (1 + y_3 + y_3^2)/(1 - y_3)^3, \quad (2.20)$$

where  $y_3 = \pi \rho a^3/6$  ( $y_3$  ranges from 0 to 0.740 for close packing). This is in remarkably good agreement with the machine calculations of Wood and Jacobson<sup>6</sup> and

Wainwright and Alder.<sup>7</sup> Equation (2.20) has the virial development

$$p/\rho kT = 1 + 4y_3 + 10y_3^2 + 19y_3^3 + 31y_3^4 + \dots, \quad (2.21)$$

which compares well with the exact virial series<sup>8</sup>

$$p/\rho kT = 1 + 4y_3 + 10y_3^2 + 18.36y_3^3 + (29.4 \pm 1.3)y_3^4 + \dots. \quad (2.22)$$

We have tried also to calculate  $G$  using the continuity of  $G$  and  $G'$  and the integral condition (2.13). The same equation of state is found, so that with the three coefficient form (2.19) the four conditions (b), (c), (e), and (f) are compatible. This lends further weight to (2.19) as an analytic approximation for  $G$  since with this form the theory possesses added internal consistency.

On the other hand when one of the four conditions used above is replaced by the discontinuity condition (d) the resulting virial series is in poor agreement with the exact virial expansion.

### III. TWO DIMENSIONS

The pressure and chemical potential of a two-dimensional fluid of rigid spheres are given, respectively, by

$$p/\rho kT = 1 + \frac{1}{2}\pi \rho a^2 G(1, \rho), \quad (3.1)$$

$$\mu/kT = \ln \rho \Lambda^2 + 2\pi \rho a^2 \int_0^1 \lambda G(\lambda, \rho) d\lambda. \quad (3.2)$$

The contact correlation function of molecules touching a  $\lambda$ -cule is related to the work of expanding the  $\lambda$ -cule by

$$G(\lambda, \rho) = (2\pi \rho a^2 \lambda kT)^{-1} [\partial W(\lambda)/\partial \lambda]. \quad (3.3)$$

The work is given by the series (2.8) in conjunction with (2.5) so that we can show that for  $\lambda \leq \frac{1}{2}$ , where the series terminates after  $m=1$ ,  $G(\lambda, \rho)$  is given exactly by

$$G(\lambda, \rho) = 1/(1 - \pi \rho a^2 \lambda^2), \quad \lambda < \frac{1}{2}. \quad (3.4)$$

Furthermore,  $G(\lambda)$  and  $[\partial G/\partial \lambda]$  may again be shown through examination of (2.8) to be continuous. The second derivative, however, diverges this time as  $(\lambda - \frac{1}{2})^{-1}$  as  $\lambda \rightarrow \frac{1}{2}$ . The second derivative condition was not used in three dimensions and likewise in two dimensions we will not find that there is a necessity to employ it. (The final solution will not have the correct second derivative at  $\lambda = \frac{1}{2}$  but this does not seem to greatly affect the equation of state.)

<sup>5</sup> J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), p. 351.

<sup>6</sup> W. W. Wood and J. D. Jacobson, *J. Chem. Phys.* **27**, 1207 (1957).

<sup>7</sup> T. E. Wainwright and B. J. Alder, U. S. Atomic Energy Commission Report Contract No. W-7405-eng-48, Lawrence Radiation Laboratory, Livermore, University of California.

<sup>8</sup> Reference 5, p. 157.

The condition on  $G$  arising from the thermodynamic relation (2.12) between  $p$  and  $\mu$  is [cf. (2.13)]

$$\frac{1}{2}\pi\rho^2G(1, \rho) = \rho^2 \int_0^1 2\pi\lambda G(\lambda, \rho) d\lambda - \int_0^\rho \rho' d\rho' \int_0^1 2\pi\lambda G(\lambda, \rho') d\lambda. \quad (3.5)$$

This equation may be put into a more useful form by inserting (3.4) and differentiating with respect to  $\rho$ :

$$\rho^2[\partial G(1, \rho)/\partial\rho] + 2\rho G(1, \rho) = \frac{1}{2}\{\rho/[1 - (\pi\rho/4)]\} + 4\rho \int_{\frac{1}{2}}^1 \lambda G(\lambda, \rho) d\lambda + 4\rho^2 \int_{\frac{1}{2}}^1 \lambda [\partial G(\lambda, \rho)/\partial\rho] d\lambda. \quad (3.6)$$

Finally, we again find an infinity condition by equating Eq. (3.1) to Eq. (2.14) which holds also in two dimensions. This yields

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

These conditions may be used to determine the equation of state if we have a form of  $G$  in  $\lambda$ . As in three dimensions we may obtain some information by a consideration of mixtures. By the technique presented in I,  $G$  may be related to a function  $Q$  by the equation

$$Q(\lambda, \rho) = -\rho a^2 \int_0^\lambda 2\pi\lambda' G(\lambda', \rho) d\lambda' - \rho^2 a^2 \int_0^\lambda 2\pi\lambda' [\partial G(\lambda', \rho)/\partial\rho] d\lambda' + \pi\rho a^2 \lambda^2 G(\lambda, \rho). \quad (3.8)$$

$Q$  is given by

$$Q(\lambda, \rho) = -\frac{1}{2}\pi\rho^2 a^2 [\partial G(1, \rho, \rho_\lambda)/\partial\rho_\lambda]_{\rho_\lambda} = 0, \quad (3.9)$$

where  $G(1, \rho, \rho_\lambda)$  in this definition is the contact radial distribution function between two normal molecules in a system with molecule density  $\rho$  and  $\lambda$ -cule density  $\rho_\lambda$ . We see that Eq. (3.6) is the special case of (3.8–9) with  $\lambda=1$ . From the properties of  $p_0$  it follows, as in I, that

$$Q = \partial Q/\partial\lambda = 0, \quad \lambda \leq \frac{1}{2}. \quad (3.10)$$

Furthermore for large  $\lambda$  we find from Eq. (3.8) that the dominant term of  $Q$  is

$$Q_{\text{dom}} = -\pi\rho^2 a^2 \lambda^2 [\partial G(\infty, \rho)/\partial\rho],$$

which varies as  $\lambda^2$ .

The functions  $G$  and  $Q$  have discontinuities in certain of their derivatives with respect to  $\lambda$  but the indications of I are that these functions may be approximated closely by analytic functions. A form which interpolates the  $\lambda = \frac{1}{2}$  and  $\lambda \rightarrow \infty$  limiting behavior of  $Q$  is

$$Q(\lambda, \rho) = \omega_2(\rho) (\lambda - \frac{1}{2})^2. \quad (3.11)$$

Using Eq. (3.8) such a  $Q$  may be shown to be com-

patible with a  $G$  of the form

$$G = \phi(\rho\lambda^2) + A(\rho) + [B(\rho)/\lambda]. \quad (3.12)$$

As in I the function  $\phi(\rho\lambda^2)$  must vanish, since it vanishes in the limit  $\lambda \rightarrow \infty$ ,  $\rho\lambda^2 \rightarrow \text{const}$ . In two dimensions, therefore, the indicated form for  $G$  is

$$G = A(\rho) + [B(\rho)/\lambda]. \quad (3.13)$$

This form may also be arrived at by the quasi-thermodynamic argument. The three-dimensional considerations may be employed directly if we regard the two-dimensional fluid as a system of infinite cylinders with parallel axes and take the properties for unit length in the axial direction. Equation (2.16) for the work of expanding a  $\lambda$ -cule becomes

$$dW = 2\pi\rho a^2 \lambda d\lambda + 2\pi\sigma a d\lambda. \quad (3.14)$$

With a surface tension  $\sigma$  independent of  $\lambda$  this, by Eq. (3.3), goes over into the form (3.13) for  $\lambda$ . For large  $\lambda$  the surface tension should have the form  $\sigma_0[1 - (\delta/\lambda)]$  which would add a  $C/\lambda^2$  term to (3.13) but since such a term is not applicable to the small  $\lambda$  limits, as indicated by the  $Q$  function argument, and since  $C/\lambda^2$  is small for large  $\lambda$ , it is not appropriate to include a curvature term.

The parametric functions of  $\rho$ ,  $A(\rho)$  and  $B(\rho)$ , may be determined by using the continuity of  $G$  to match (3.13) to (3.4) at  $\lambda = \frac{1}{2}$ , and by employing the infinity condition, (3.7). Instead of the infinity condition the integral equation, (3.5), may be used as a second condition. As in three dimensions the result is the same, which again adds weight to this form for  $G$ .<sup>9</sup>

The equation of state found in this way is

$$p/\rho kT = 1/(1 - y_2)^2, \quad (3.15)$$

where  $y_2 = \pi\rho a^2/4$  ( $y_2$  ranges from 0 to 0.907 for close packing). This has as a virial development

$$p/\rho kT = 1 + 2y_2 + 3y_2^2 + 4y_2^3 + 5y_2^4 + \dots, \quad (3.16)$$

to be compared with the exact virial series

$$p/\rho kT = 1 + 2y_2 + 3.128y_2^2 + 4.262y_2^3 + (4.95 \pm 0.25)y_2^4 + \dots. \quad (3.17)$$

In Fig. 1 the equation of state over the entire range of accessible fluid densities is compared with the results of machine Monte Carlo calculations by Jacobson and

<sup>9</sup> We have not found any other functional forms which exhibit this property. For instance if one uses  $G = A + B/\lambda + C/\lambda^2$  with the continuity of  $G$  and  $G'$  at  $\lambda = \frac{1}{2}$  and either the infinity condition or the integral condition, one obtains two different answers, both poor.

Wood<sup>10,11</sup> and dynamical machine calculations by Wainwright and Alder.<sup>11,12</sup> The agreement is good. For comparison the results of the simple Lennard-Jones-Devonshire cell theory are included on the same graph. Various extended cell calculations, such as Cohen and Rethmeier's<sup>13</sup> double cell cluster theory with exact cell shape, do not substantially better the agreement over the entire range of densities. The cell theories, however, seem to be in agreement with the low pressure ordered phase which is observed<sup>10,12</sup> at densities greater than  $\rho a^2 \approx 0.8$ . Close packing corresponds to  $\rho a^2 = 2/\sqrt{3} = 1.15$ .

The complete  $G(\lambda, \rho)$  determined in the above calculation is

$$G(\lambda, \rho) = [(1-y_2)^2]^{-1} + \frac{1}{2} \{ (1-y_2)^{-1} - [(1-y_2)^2]^{-1} \} \lambda^{-1}. \quad (3.18)$$

By Eqs. (3.3), (3.13), and (3.14) this corresponds to a surface tension

$$\sigma/\rho a k T = \frac{1}{2} [(1-y_2)^{-1} - (1-y_2)^{-2}]. \quad (3.19)$$

#### IV. ONE DIMENSION

An extremely simple treatment of the properties of a one-dimensional system of rigid spheres may be achieved by application of the Reiss, Frisch, and Lebowitz techniques. The thermodynamic properties of the system are derivable from the equation of state,

$$p/\rho k T = 1 + \rho a G(1, \rho), \quad (4.1)$$

and the chemical potential

$$\mu/k T = \ln \rho \Lambda + 2 \rho a \int_0^1 G(\lambda, \rho) d\lambda. \quad (4.2)$$

The pressure is also related to the density at the wall by [cf. Eq. (2.14)]

$$p/\rho k T = G(\infty, \rho). \quad (4.3)$$

We can derive the equation of state in essentially one step by realizing that since no two particles on opposite sides of a  $\lambda$ -cule with  $\lambda > \frac{1}{2}$  can ever interact, molecules cannot tell what size  $\lambda$ -cule they are next to for  $\lambda > \frac{1}{2}$ . Thus  $G(\lambda, \rho)$  must be independent of  $\lambda$  for  $\lambda > \frac{1}{2}$ , and as a special case the molecule-molecule contact density must equal the wall density, i.e.,

$$G(1, \rho) = G(\infty, \rho). \quad (4.4)$$

<sup>10</sup> J. D. Jacobson and W. W. Wood, Los Alamos Scientific Laboratory of the University of California, Report GMX-10-37.

<sup>11</sup> We thank Dr. Jacobson, Dr. Wood, Dr. Wainwright, and Dr. Alder for making available and allowing us to include the results of their calculations which are not fully completed. These authors have cautioned us that there may be some changes in individual points upon further refinement. Nevertheless we have felt that it is worthwhile to include these data in order to provide an indication of the degree of reliability of the present calculation.

<sup>12</sup> T. E. Wainwright and B. J. Alder, private communication.

<sup>13</sup> E. G. D. Cohen and B. C. Rethmeier, *Physica* **24**, 959 (1958).

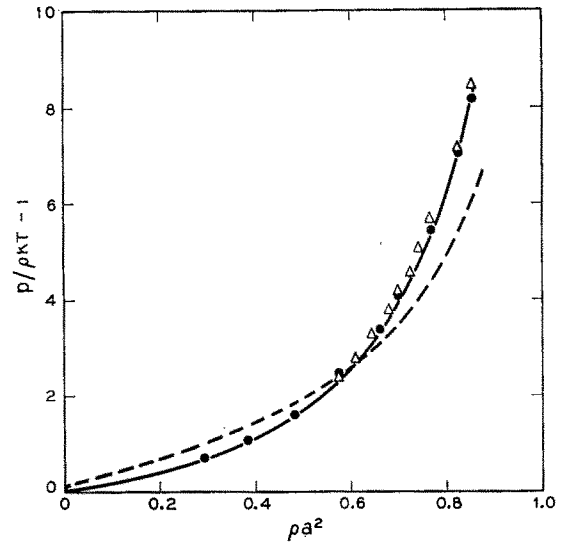


Fig. 1. The equation of state of a two-dimensional hard sphere fluid: ——— this work; ● Monte Carlo calculations of Wood; △ dynamical calculations of Alder and Wainwright; - - - - Lennard-Jones-Devonshire cell theory.

This equation in conjunction with Eqs. (4.1) and (4.3) yields the well-known Tonks' equation of state<sup>14</sup> for a one-dimensional hard sphere system

$$p/\rho k T = 1/(1-\rho a), \quad (4.5)$$

which is exact.

Equation (4.5) may be derived in another simple manner. For  $\lambda \leq \frac{1}{2}$ , at most one molecule can be in a cavity. The probability that the cavity is vacant is, therefore, one minus the density times the cavity volume, or

$$p_0(\lambda) = 1 - \rho(2a\lambda), \quad \lambda \leq \frac{1}{2}. \quad (4.6)$$

The work of forming such a cavity is again [cf. (2.5)]

$$W(\lambda) = -k T \ln p_0, \quad (4.7)$$

and  $G$  is related to this work by

$$G(\lambda, \rho) = (2\rho a k T)^{-1} [\partial W(\lambda)/\partial \lambda], \quad (4.8)$$

so that

$$G(\lambda, \rho) = 1/(1-2\rho a\lambda), \quad \lambda \leq \frac{1}{2}. \quad (4.9)$$

For  $\lambda > \frac{1}{2}$  we saw in the last paragraph that  $G$  is constant so using the continuity of  $G$ , which is easily established as in I or previous sections, we have

$$G(\lambda \geq \frac{1}{2}, \rho) = G(1, \rho) = G(\infty, \rho) = 1/(1-\rho a). \quad (4.10)$$

By Eq. (4.1) or (4.3) this leads immediately to the Tonks' equation, (4.5).

The fact that  $G$  is constant for  $\lambda > \frac{1}{2}$  follows also from Eq. (4.8). For  $\lambda > \frac{1}{2}$  the work of expanding a

<sup>14</sup> L. Tonks, *Phys. Rev.* **50**, 955 (1936).

cavity (or  $\lambda$ -cule) is all pressure-volume work so that

$$dW = p(2ad\lambda), \quad \lambda > \frac{1}{2} \quad (4.11)$$

which implies  $G(\lambda > \frac{1}{2}, \rho) = \text{constant} = p/\rho kT$ .

In I it was shown how a knowledge of the cavity probability  $p_0$  could be used to determine the radial distribution function over part of the range. To develop this theory for one dimension we must write the series (2.8) for  $p_0$  in the range  $\frac{1}{2} < \lambda < 1$ , wherein the series terminates at  $m=2$ :

$$\begin{aligned} p_0(\lambda) &= 1 - 2\rho a\lambda + \frac{1}{2}\rho^2 a^2 \int_{-\lambda a}^{\lambda a} \int_{-\lambda a}^{\lambda a} g(|r_1 - r_2|) dr_1 dr_2, \\ &= 1 - 2\rho a\lambda + \rho^2 a^2 \int_0^{2\lambda} (2\lambda - x) g(ax) dx, \quad \lambda \leq 1. \end{aligned} \quad (4.12)$$

Differentiating twice with respect to  $\lambda$ , one finds that

$$\partial^2 p_0 / \partial \lambda^2 = 4\rho^2 a^2 g(2\lambda a), \quad \lambda < 1. \quad (4.13)$$

The function  $p_0$  is related to  $G$  through Eqs. (4.7)–(4.8) and is given by

$$\begin{aligned} p_0(\lambda) &= \exp\left[-2\rho a \int_0^\lambda G(\lambda', \rho) d\lambda'\right] \\ &= (1 - \rho a) \exp[-\rho a(2\lambda - 1)/(1 - \rho a)], \quad \lambda > \frac{1}{2}. \end{aligned} \quad (4.14)$$

The combination of Eqs. (4.13) and (4.14) allow us to write for the radial distribution function in the range  $a < r < 2a$

$$g(r) = (1 - \rho a)^{-1} \exp[-\rho(r - a)/(1 - \rho a)], \quad a < r < 2a, \quad (4.15)$$

in agreement with other theories of the pair correlation function.<sup>15</sup> The range of  $r$  may be extended by considering further terms in the  $p_0$  series, (2.8). The higher order correlation functions which enter may be written in terms of products of pair correlations exactly in one dimension.<sup>15</sup>

Interestingly enough Eq. (4.15) can be extended, partly at least, to the case where the molecules have in addition to their hard cores also a soft potential  $\phi_s$ . When  $\phi_s$  has a finite range  $\gamma a$ ,  $\gamma > 1$ , then for  $\lambda > \frac{1}{2}\gamma$  the molecules will again be unable to “feel” across the cavity and we will have

$$\begin{aligned} dW &= p2ad\lambda, \quad \lambda > \frac{1}{2}\gamma \\ G(\lambda) &= p/\rho kT, \quad \lambda > \frac{1}{2}\gamma. \end{aligned} \quad (4.16)$$

If further  $\gamma < 2$  then the above arguments yield

$$g(r) = (p/\rho kT)^2 p_0(\gamma a/2) \exp[-(p/kT)(r - \gamma a)], \quad \gamma a < r < 2a, \quad (4.17)$$

where  $g(r)$  is the radial distribution function between two molecules in the fluid. The nature of the soft potential  $\phi_s$  enters here only through the value of the pressure  $p$  and the work necessary to make a hole of size  $(\gamma a/2)$ :

$$p_0(\gamma a/2) = \exp[-W(\frac{1}{2}\gamma a)/kT]. \quad (4.18)$$

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#### APPENDIX I. IDEAL GAS

We give a simple illustration of the ideas discussed in Sec. 2 by considering the case of an ideal gas. For this gas it is well known that  $p_N$  satisfies the Poisson distribution<sup>16</sup>

$$p_n = (v^n/n!) e^{-v}, \quad (A.1)$$

where  $v = \frac{4}{3}\pi\rho a^3 \lambda^3 = \langle n \rangle$ . In particular

$$p_0 = \exp(-\frac{4}{3}\pi\rho a^3 \lambda^3) = \exp[-W(\lambda)/kT], \quad (A.2)$$

and

$$dW = \rho kT dV = p dV.$$

#### APPENDIX II. RIGID LATTICE GAS

Another simple illustration of our ideas can be obtained by considering a lattice of  $\eta$  sites on which  $N$  particles are to be placed. The volume per site is taken to be unity. The particles behave like rigid spheres in that not more than one particle can be placed on one site and that otherwise the particles do not interact. A hole will now mean an empty lattice site and according to Eqs. (2.5)–(2.7) we find

$$p_0 = \exp(-W/kT) = 1 - \rho, \quad (B.1)$$

with  $\rho = N/\eta$ . This yields for the chemical potential  $\mu$  in accordance with Eqs. (2.2) and (2.3)

$$\mu = kT \ln(\rho \Lambda^3) + W = kT \ln\{\rho/(1 - \rho)\} \Lambda^3, \quad (B.2)$$

while the pressure is given by

$$p = \int_0^\rho \rho (\partial \mu / \partial \rho) d\rho = -kT \ln(1 - \rho). \quad (B.3)$$

<sup>15</sup> Z. W. Salsburg, R. W. Zwanzig, and J. G. Kirkwood, J. Chem. Phys. **21**, 1098 (1953).

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