

Asymptotic Value of the Pair Distribution Near a Wall

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We calculate the asymptotic value of the pair probability density $\rho_2(\mathbf{r}_2, \mathbf{r}_1)$ for finding a fluid particle at a point \mathbf{r}_2 far in the interior of a fluid, when it is known that there is a particle at \mathbf{r}_1 in contact with the walls (rigid) of the container. This value is different from the well-known expression for the asymptotic value of $\rho_2(\mathbf{r}_2, \mathbf{r}_1)$ when both \mathbf{r}_2 and \mathbf{r}_1 are in the interior of the fluid. Our derivation is based on the virial theorem for total momentum fluctuations in an equilibrium system and makes use of the assumption that there are no long range correlations in a fluid. Application is made of our result to re-derive simply the expression for the second virial coefficient and the exact equation of state of a hard-sphere gas in one dimension. Quantum systems are also treated.

INTRODUCTION

ALMOST all of the equilibrium properties of a simple fluid are expressible in terms of the pair density $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$, which gives the probability density for the simultaneous presence of particles at \mathbf{r}_1 , and \mathbf{r}_2 . For a system in equilibrium, ρ_2 is known in principle from Gibbsian statistical mechanics. However, its explicit evaluation presents insurmountable difficulties. We are forced, therefore, to use expansions in powers of the density and various approximate integral equations to get theoretical insight into the nature of this important function. Fortunately ρ_2 also may be determined explicitly from x-ray scattering data. In particular, there is a relation between long wavelength (visible light) scattering and the asymptotic value of ρ_2 when \mathbf{r}_1 and \mathbf{r}_2 are far from each other and from the walls of the fluid container.^{1,2} This asymptotic value in turn, is related to the isothermal compressibility χ .

In this note we find the asymptotic value of $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$ when \mathbf{r}_1 is located at the rigid wall of the fluid container, and \mathbf{r}_2 is far in the interior. This value is found to differ from that obtained when \mathbf{r}_1 and \mathbf{r}_2 are both far in the interior. We make use in our derivation of the assumption that there is no long range correlation in a fluid. It is one of the purposes of this note to emphasize this assumption by making explicit use of it.

The absence of long range correlations in a fluid usually is assumed to be the feature which distinguishes a fluid from a crystal.^{1,3} Intuitively,

¹ For a general reference see H. S. Green, *The Molecular Theory of Fluids* (Interscience Publishers, Inc., New York, 1952).

² L. S. Ornstein and F. Zernicke, *Proc. Acad. Sci. Amsterdam*, **17**, 793 (1914).

³ O. Penrose and L. Onsager, *Phys. Rev.* **104**, 576 (1956); J. E. Mayer and E. W. Montroll, *J. Chem. Phys.* **9**, 2 (1941).

this means that the presence of a particle at \mathbf{r}_2 is not correlated to the presence of a different particle at \mathbf{r}_1 if r_{12} is sufficiently large, by molecular standards. This may be stated a little more precisely in terms of the function $w(\mathbf{r}_2, \mathbf{r}_1)$,

$$w(\mathbf{r}_2, \mathbf{r}_1) = \rho_2(\mathbf{r}_2, \mathbf{r}_1) / \rho(\mathbf{r}_1), \quad (1)$$

which gives the conditional probability density for finding a particle at \mathbf{r}_2 when it is known that there is a particle at \mathbf{r}_1 , $\rho(\mathbf{r}_1)$ being the density of particles at \mathbf{r}_1 . When there are no long range correlations then

$$\lim_{r_{12} \rightarrow \infty} w(\mathbf{r}_2, \mathbf{r}_1) = \rho(\mathbf{r}_2) \{1 - b/N[1 + O(1/N)]\}. \quad (2)$$

Here N is the total number of particles in the fluid which is permitted to become very large while the average density $\rho = N/V$ is kept constant, and b is independent of N . In the simplest case, i.e., an ideal gas, the only effect of the presence of a particle at \mathbf{r}_1 is to reduce to $(N - 1)$ the number of particles which could possibly be at \mathbf{r}_2 . Thus

$$w(\mathbf{r}_2, \mathbf{r}_1) = \rho(\mathbf{r}_2)[1 - 1/N], \quad (3)$$

for an ideal gas. In a real fluid the presence of a particle at \mathbf{r}_1 rearranges the density of other molecules in its neighborhood in a way which depends on its microscopic structure.⁴

The value of b may be found generally by considering the fluctuations in the number of particles N_A in a macroscopic volume element V_A ; $\rho^{-1} \ll V_A \ll V$. When these fluctuations are computed in two different ways, one purely statistical and one quasithermodynamic, there results the

⁴ R. P. Feynman and M. Cohen, *Phys. Rev.* **102**, 1189 (1956).

relation¹

$$\langle (N_A - \langle N_A \rangle)^2 \rangle = \langle N_A \rangle + \int_{V_A}^{d\mathbf{r}_1} \rho(\mathbf{r}_1) \cdot \int_{V_A} [w(\mathbf{r}_2, \mathbf{r}_1) - \rho(\mathbf{r}_2)] d\mathbf{r}_2 = kT\chi \langle N_A \rangle \rho, \quad (4)$$

where χ is the isothermal compressibility. For the second equality we have to neglect surface terms S_A in comparison to V_A and terms of $O(V_A/V)$. Now

$$\begin{aligned} \int_{V_A} [w(\mathbf{r}_2, \mathbf{r}_1) - \rho(\mathbf{r}_2)] d\mathbf{r}_2 &= \int_V [w(\mathbf{r}_2, \mathbf{r}_1) - \rho(\mathbf{r}_2)] d\mathbf{r}_2 \\ &\quad - \int_{V_B} [w(\mathbf{r}_2, \mathbf{r}_1) - \rho(\mathbf{r}_2)] d\mathbf{r}_2, \end{aligned} \quad (5)$$

where $V_B = V - V_A$ is the volume outside V_A . Because of normalization the first term on the right-hand side of Eq. (5) is just $[(N - 1) - N]$ while if \mathbf{r}_1 is in the interior of V_A the integrand in the second term may be replaced by its asymptotic value to yield $(-bV_B/N)$. For this second replacement we have to assume that w approaches its asymptotic value sufficiently rapidly. It generally is assumed that this approach is exponential for finite temperatures, $T \neq 0$.⁴ When Eq. (5), with the substitutions, is put back into Eq. (4) we get

$$b = \rho kT\chi, \quad (6)$$

which reduces to Eq. (3) for an ideal gas. Equation (6) also may be obtained directly from the virial expansion for a dilute gas.⁵

PAIR DENSITY NEAR A WALL

We turn now to the derivation of the asymptotic value of $\rho_2(\mathbf{r}_2, \mathbf{r}_1)$ when \mathbf{r}_1 is near a wall. Our system consists of N identical particles whose Hamiltonian has the form,

$$H = \sum_{i=1}^N \mathbf{p}_i^2 / 2m + \frac{1}{2} \sum_{i,j} \phi(r_{ij}) + \sum_{i=1}^N U(\mathbf{r}_i). \quad (7)$$

Here $U(\mathbf{r})$ is the potential of the external forces acting on the system. These forces keep the fluid confined to a bounded region in space. The virial theorem for the total momentum states that

$$\langle \mathbf{P}\mathbf{P} \rangle_{Av} = \sum_{i,j} \left\langle m\mathbf{r}_i \cdot \frac{\partial U}{\partial \mathbf{r}_i}(\mathbf{r}_i) \right\rangle_{Av}. \quad (8)$$

⁴ J. de Boer, Thesis, Amsterdam, 1940 quoted in T. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956), Appendix 7.

Here $\mathbf{P} = \sum \mathbf{p}_i$ is the total momentum of the system, and $\langle \rangle_{Av}$ is an infinite time average along the systems trajectory in its phase space.

When our fluid is in a stationary state, the time average may be replaced by an average over an appropriate stationary ensemble, denoted by $\langle \rangle$. For an equilibrium system this average is over a canonical ensemble. When the only external forces are those due to the walls, and act only in the neighborhood of the walls,⁶

$$\langle \mathbf{P}\mathbf{P} \rangle = m \left\{ pV\mathbf{1} + \iint \mathbf{r}_2 \cdot \frac{\partial}{\partial \mathbf{r}_1} U(\mathbf{r}_1) \cdot \rho_2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \right\}, \quad (9)$$

where p is the pressure and V the volume of the fluid, and $\mathbf{1}$ is the unit tensor. Equation (3) holds for both classical and quantum systems. For classical systems we have the further relation from the definition of the canonical ensemble, that

$$\langle \mathbf{P}\mathbf{P} \rangle = Nm kT\mathbf{1}, \quad (10)$$

which is the equipartition law for the kinetic energy associated with the center of mass motion.

An inspection of Eq. (9) shows that only those regions of space where \mathbf{r}_1 is very close to the walls will contribute to the integral there. In such a region of space $\rho(\mathbf{r}_1)$ and $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$ may be expected to differ greatly from their value in the interior of the fluid. I shall consider here the limiting case of rigid wall boundaries. Further, to avoid any extraneous complications, I shall treat explicitly only the case of a spherical container,

$$U(\mathbf{r}) = \begin{cases} 0, & r < R, \\ \infty, & r > R, \end{cases} \quad V = \frac{4}{3} \pi R^3. \quad (11)$$

The density of particles at the wall $\rho^w = \rho(\mathbf{r}), r = R$ is now simply related to the pressure of the fluid,

$$\rho^w = p/kT. \quad (12)$$

Equation (12) may be derived by considering Eq. (11) as the limit of a continuous potential which rises sharply in the neighborhood of R . We then have

$$4\pi R^2 p = \int \rho(\mathbf{r}) \frac{\partial}{\partial r} U(r) dr. \quad (13)$$

The integrand will be different from zero only near

⁶ J. L. Lebowitz, Phys. Rev. 109, 1464 (1958).

R where we may write (for the canonical distribution)

$$\rho(r) = A(r)e^{-U(r)/kT}. \quad (14)$$

Passing now to the limit of a hard wall $A(r)$ will remain continuous and we obtain Eq. (12).⁷

An alternative derivation of Eq. (12) may be based on the usual arguments which lead to the equation of state of a very dilute gas.⁸ Since the stress which the fluid exerts on a rigid wall is purely kinetic, it follows rigorously that

$$p = \frac{2}{3}\langle K \rangle^w, \quad (15)$$

where $\langle K \rangle^w$ is the mean kinetic energy density at the wall. This leads again to Eq. (12).

The trace of Eq. (3) may now be written in the form

$$\langle P^2 \rangle / m = 3Nkt = 3pV + \rho^w kT \cdot \int \frac{\mathbf{r}_2 \cdot \mathbf{r}_1}{r_1} w(\mathbf{r}_2, \mathbf{r}_1) \delta(r_1 - R) d\mathbf{r}_1 d\mathbf{r}_2, \quad (16)$$

where we again have used the argument of starting with a continuous potential and going to the limit which led to Eq. (12). The spherical symmetry of our problem enables us to perform the integration over \mathbf{r}_1 in Eq. (16) yielding

$$p/\rho kT = 1 - (p/\rho kT) \left\{ 1/R \int w(\mathbf{r}_2) z_2 d\mathbf{r}_2 \right\}, \quad (17)$$

where $w(\mathbf{r}_2) = w(\mathbf{r}_2, \mathbf{r}_1)$ for $r_1 = R$.

Now let us shift the origin of our coordinates to the point $(0, 0, -R)$, and

$$\int w(\mathbf{r}_2) z_2 d\mathbf{r}_2 = \int (R - z) \bar{w}(\mathbf{r}) d\mathbf{r} = (N - 1)R - \int z \bar{w}(\mathbf{r}) d\mathbf{r}. \quad (18)$$

Here $\bar{w}(\mathbf{r})$ is the probability density for finding a particle at \mathbf{r} when there is a particle at the origin in contact with the wall. The second equality follows from the fact that the integral of \bar{w} is $(N - 1)$.

We now write the asymptotic value of \bar{w} as

$$\bar{w}(\mathbf{r}) \xrightarrow{|\mathbf{r}| \rightarrow \infty} \rho(\mathbf{r}) \{ 1 - b^w/N[1 + O(1/N)] \} \quad (19)$$

and make the basic assumption about the absence of long range order in fluids in the following mild form:

⁷ See, for example, the derivation of the virial theorem for a hard-sphere gas in T. Hill (reference 5), p. 216.

⁸ E. M. Kennard, *Kinetic Theory of Gases* (McGraw-Hill Book Company, Inc., New York, 1938).

$$\lim_{R \rightarrow \infty} \left\{ \frac{1}{R} \int z [\bar{w}(\mathbf{r}) - \rho(\mathbf{r})(1 - b^w/N)] d\mathbf{r} \right\} = 0. \quad (20)$$

This limit is to be taken with (N/V) remaining fixed. In order for Eq. (20) to hold it is only necessary for $\bar{w}(\mathbf{r})$ to approach its asymptotic value as $(1/r^{4+\epsilon})$. When Eq. (20) holds, we may replace \bar{w} in Eq. (18) by its asymptotic value,

$$\begin{aligned} \frac{1}{R} \int z \bar{w}(\mathbf{r}) d\mathbf{r} &= [1 - b^w/N] \frac{1}{R} \\ &\cdot \int (z - R + R) \rho(\mathbf{r}) d\mathbf{r} + O(1/R) \\ &= [1 - b^w/N] N + O(1/R), \end{aligned} \quad (21)$$

where we have used the symmetry of $\rho(\mathbf{r})$ about the center of the sphere. Combining Eqs. (17), (18), and (21), leads to the desired result

$$b^w = (\rho kT/p) = \rho/\rho^w \quad (22)$$

or

$$\bar{w}(\mathbf{r}) \rightarrow \rho(\mathbf{r}) [1 - (\rho/\rho^w)/N]. \quad (23)$$

This final formula has a simple interpretation. The greater the value of ρ^w the closer does $\bar{w}(\mathbf{r})$ approach the density $\rho(\mathbf{r})$, since the difference between certain knowledge that there is a particle at the surface and no information which is the difference between \bar{w} and ρ becomes smaller as ρ^w increases.

Our argument can be extended without difficulty to cubical volumes and probably holds for arbitrary shaped containers (as long as the ratio of surface area to volume goes to zero). We may also write now in analogy to Eq. (4)

$$\begin{aligned} b^w = \frac{\rho kT}{p} &= \left\{ 1 + \int_{V_A} [\bar{w}(\mathbf{r}) - \rho(\mathbf{r})] d\mathbf{r} \right\} \\ &+ O(V_A/V) + O(S_A/V_A), \end{aligned} \quad (24)$$

where V_A contains a point on the boundary from which r is measured and $\rho^{-1} \ll V_A \ll V$ so that the ratio of the surface of V_A , S_A , to V_A and of V_A to V both go to zero. We must think of Eq. (24) in terms of some limit of V_A and V both becoming very large while ρ is kept fixed. Further, V_A becomes large in such a way that each point on S_A is very far from the origin. We may note that the terms in the curly bracket on the right side of Eq. (24) are simply the difference between the average number of particles in V_A , when it is known that there is a particle at the origin, and when nothing is known.

Equation (24) may be used in principle for developing the pressure in a power series in the density

(virial expansion), by first expanding $\bar{w}(\mathbf{r})$ and $\rho(\mathbf{r})$ in such a series.⁶ This appears, however, to be even more complicated than the usual methods. Therefore, we shall consider here only the case of dilute gases and obtain very simply the second virial coefficient. For a dilute gas,

$$\bar{w}(\mathbf{r}) = \rho(\mathbf{r}) \exp [\phi(r)/kT] + O(\rho^2) + O(1/N). \quad (25)$$

Also, since the only external forces acting on the system are those due to the rigid walls we have

$$\rho(\mathbf{r}) = \rho + O(\rho^2), \quad (26)$$

inside the container and zero outside. Substitution of Eqs. (25) and (26) into Eq. (24) yields

$$\begin{aligned} \rho kT/p &= 1 + \rho \int_{V_A} [e^{-\phi/hT} - 1] d\mathbf{r} \\ &= 1 + \frac{1}{2}\rho \int_0^\infty [e^{-\phi/hT} - 1] 4\pi r^2 dr, \end{aligned} \quad (27)$$

where we have used the fact that, since the origin of \mathbf{r} is at the wall, the integral over V_A is just half of that obtained from integrating over all \mathbf{r} , when $\phi(r)$ falls off sufficiently rapidly. On computing the pressure from Eq. (27) we find

$$p = \rho kT \left\{ 1 + 2\pi\rho \int_0^\infty [1 - e^{-\phi/kT}] r^2 dr + O(\rho^2) \right\}, \quad (28)$$

which agrees with the usual derivation of the second virial coefficient.⁷ A similar result may be arrived at from Eq. (4). We are now investigating the possibility of finding an approximate equation of state for a fluid by making reasonable assumptions about the behavior of $\bar{w}(\mathbf{r})$ and $\rho(\mathbf{r})$ in Eqs. (24) and (4).

QUANTUM SYSTEMS

It was shown in reference 5 that Eq. (9) holds also for a quantum system. There is no simple proof available though for the validity of Eq. (10) in such a system. It was shown however by Lebowitz and Onsager⁹ on the basis of very reasonable assumptions that Eq. (10) holds for liquid helium II, and extreme quantum fluid, and Blatt, Butler, and Schefthroth¹⁰ have argued that Eq. (10) should always hold. We may therefore expect that, at last, when

⁹ J. L. Lebowitz and L. Onsager, *Low Temperature Physics and Chemistry*, (The University of Wisconsin Press, Madison, Wisconsin, 1958).

¹⁰ Blatt, Butler, and Schefthroth, *Phys. Rev.* **100**, 481 (1955).

the trace is taken in Eq. (10) yielding the equipartition law for the center of mass motion, a macroscopic quantity, it remains valid for quantum systems (up to terms of a lower order than N).

When the walls are treated as rigid, the potential $U(\mathbf{r})$ is replaced by the requirement that the wave function $\psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$ of the system vanishes at the boundaries. This implies that the density $\rho(\mathbf{r})$ as well as its first derivative (since $\rho(\mathbf{r})$ is quadratic in ψ) vanish at the walls of the container. The pressure now is related to the second derivative of $\rho(\mathbf{r})$ at the wall,¹¹

$$p = \frac{\hbar^2}{4m} \frac{d^2 \rho(r)}{dr^2}, \quad (29)$$

at $r = R$ for a spherical container. Equation (16) now assumes the form⁵

$$\begin{aligned} \langle \mathbf{P}^2 \rangle &= 3mpV + \frac{\hbar^2}{4} \\ &\cdot \int \frac{\mathbf{r}_1 \cdot \mathbf{r}_2}{r_1} \frac{\partial^2}{\partial r_1^2} \rho_2(\mathbf{r}_2, \mathbf{r}_1) \delta(r_1 - R) d\mathbf{r}_1 d\mathbf{r}_2 \\ &= 3mpV + p \\ &\cdot \int \frac{\mathbf{r}_1 \cdot \mathbf{r}_2}{r_1} w(\mathbf{r}_2, \mathbf{r}_1) \delta(r_1 - R) d\mathbf{r}_1 d\mathbf{r}_2. \end{aligned} \quad (30)$$

This may be brought in a form similar to Eq. (17) with ρkT replaced by $[\langle \mathbf{P}^2 \rangle / 3mV]$. However, as mentioned in the beginning of this section, Eq. (10) may be expected to hold also for quantum systems and hence the asymptotic value of \bar{w} is identical classically and quantum mechanically when expressed in terms of p . This is also true for the asymptotic value of w given by Eq. (6). It was pointed out by Feynman and Cohen⁴ that at $T = 0$ the coefficient b , and as we see now b^w also, is zero. This means that there is complete adjustment of the density in the neighborhood of the point where a molecule is known to be present, and no effect is felt very far away. We must, however, admit that the meaning of \bar{w} while formally defined by Eq. (1) is not completely obvious here. It represents the ratio of two numbers whose value is zero when \mathbf{r} is at the wall. One has, therefore, to be very careful in the interpretation of our formulas for a quantum system.¹²

ONE-DIMENSIONAL HARD SPHERE GAS

We will now illustrate the result of this note by using it to derive the well-known equation of state

¹¹ M. Fierz, *Phys. Rev.* **106**, 412 (1957); **107**, 1736 (1957).
¹² R. Mazo and J. Kirkwood, *Proc. Natl. Acad. Sci.* **41**, 204 (1955).

of a one-dimensional hard sphere gas.¹³ Let a be the diameter of our particles and L the length of the container bounded by hard walls. It is clear that holding one particle in contact with the wall of the container is completely equivalent to treating a gas of $(N - 1)$ particles in a container of size $(L - a)$. Hence the conditional probability density $\bar{w}(x)$ for finding a particle a distance x from the edge of the particle in contact with the wall must be identical to the density $\rho'(x)$ of $(N - 1) = N'$ molecules in a container of size $(L - a) = L'$, with a corresponding origin. Now far away from the edge of the container we will have

$$\begin{aligned} \bar{w}(x) &= \rho'(x) \\ &= \rho' \left[1 + \frac{c}{N'} + O\left(\frac{1}{N'^2}\right) \right], \quad \rho' = N'/L'. \end{aligned} \quad (31)$$

¹³ A. Muenster, *Statistische Thermodynamik* (Springer Verlag, Berlin, Germany, 1956), Sec. 7.7 and references cited there.

Similarly the density $\rho(x)$ of our system will be, for large x ,

$$\rho(x) = \rho \left[1 + (c/N) + O(1/N^2) \right], \quad \rho = N/L. \quad (32)$$

We therefore have

$$\lim_{x \rightarrow \infty} [\bar{w}(x) - \rho(x)] = (a\rho - 1)/N + O(1/N^2). \quad (33)$$

This yields

$$b^w = 1 - a\rho = \rho kT/p, \quad (34)$$

which is the correct equation of state for this system. We cannot apply this result to a quantum system for the reason stated at the end of the last section.

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Remark on Dilute Bose Systems

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Some results are given on the connection existing between the Lee-Huang-Yang theory for the interacting Bose systems, and the Bogoliubov theory.

1. INTRODUCTION

THE low-temperature properties of a dilute system of Bose particles with hard-sphere interactions have been investigated by Lee, Huang, and Yang¹ who gave the motivation underlying such a study. The assumption that a condensed phase exists even when a strong interaction is present, provided the system is very dilute, leads these authors to consider that the more important effects of the interaction is the creation or annihilation of pairs of particles with opposite momenta. On this basis, they developed a rigorous mathematical method which gave the expected properties of the system.

On the other hand, Bogoliubov² has used a quite different method to deal with the similar problem of a system of Bose particles with a weak repulsive interaction. With this assumption, and its corollary that the condensed phase is affected only slightly by this kind of interaction, he was able to prove that (in a first approximation) the system behaves like a gas of free Bose "quasi particles." The starting point of this theory is the reduced Hamiltonian

$$\begin{aligned} H_{\text{red.}} &= \frac{N^2}{\Omega} \nu(0) + \sum \frac{p^2}{2m} b_p^* b_p \\ &+ \frac{N_0}{2\Omega} \sum_{p \neq 0} \nu(p) [b_p^* b_{-p}^* + b_p b_{-p} + 2b_p^* b_p], \end{aligned}$$

where $\nu(q)$ is the Fourier transform of the potential,

² N. N. Bogoliubov, *J. Phys. U.S.S.R.* **9**, 23 (1947).

¹ Lee, Huang, and Yang, *Phys. Rev.* **106**, 1135 (1957). Cf also K. A. Brueckner and K. Sawada, *Phys. Rev.* **106**, 1117 (1957).