THE STRUCTURE OF QUANTUM FLUIDS: HELIUM AND NEON

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Abstract

A procedure for the evaluation of the path integrals for the two-particle statistical density matrix at low temperatures is described. It is applied to both helium and neon, the first being the paradigm of a quantum mechanical gas and the second exhibiting weaker, but still significant, quantum effects at temperatures above the triple point. The density independent part of the pair-correlation functions and the second virial coefficients are obtained from these quantities. Three- and many-particle quantum properties are examined by approximating the Slater sum by a product of Boltzmann factors, each factor containing an effective pair-potential defined from the results of the two-particle case. The radial distribution function, obtained from a Percus–Yevick equation using this effective potential, demonstrates the validity of using the effective potential approximation as a tool for studying quantum properties by giving satisfactory results for helium and good agreement with experiment for neon.

I. Introduction

The statistical density matrix plays a fundamental role in quantum statistical mechanics. Through it the observed value of any observable of a quantum mechanical system of interest can be found. It is the operator which connects quantum mechanics with the statistical mechanics of many-particle systems. The density operator ρ (of which the density matrix is just a description in a particular representation) can be found by solving the Bloch equation

$$\partial\rho/\partial\beta = -H\rho, \tag{1}$$

with the boundary condition

$$\lim_{\beta\to 0} \rho = 1 \quad \text{(unit operator)}, \tag{2}$$

where $\beta = 1/kT$ and H is the Hamiltonian of the system being considered. The formal solution of this equation is $\rho = \exp(-\beta H)$. It can be solved analytically in several instances, in particular when a single particle is considered, the result being applicable to a system of many non-interacting particles. However, in most cases we have to resort to approximations or numerical procedures, or often both.

A direct evaluation of the density independent part of the pair-correlation function for helium via the Slater sum was performed by Larsen et al. (1966) who, in their evaluation, used expressions which were formally derived by Blatt (1956). The sum over orbital angular momentum restricted the temperature to below 2 K.

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This method has also been applied to hydrogen by Poll and Miller (1971). An alternative method, based on a Monte Carlo evaluation of the path integrals for the Slater sum, was presented by Fosdick and Jordan (1966) who used an idea originally put forward by Butler and Friedman (1955). However, the Monte Carlo sampling errors increased with decreasing temperature, with the result that the pair-correlation function became increasingly indeterminate below about 30 K.

A procedure is outlined here which provides a method of finding the pair-correlation function in the temperature range where it has not been determined with accuracy before and also provides a consistency check with the other two methods, at each end of the temperature range. The density matrix is obtained for both helium and neon and then applied to multiple-particle effects, the first of these being the third virial coefficient and the associated contribution to the radial distribution function from the term of first order in the density. The required three-particle diagonal elements of the density matrix are approximated by a product of two-particle diagonal elements. This reduction to effective pair-potentials permits the use of an effective quantum mechanical Percus–Yevick equation to study the radial distribution function of a quantum liquid.

II. Density Matrix of a Two-particle System

Consider a system consisting of two nonidentical particles, the system being open (i.e. unbounded) within a statistical mechanical framework. The coordinate representation of the Hamiltonian operator for this system is

$$H = -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} + V(|r|) \tag{3}$$

$$= H_x + H_r,$$

where x is the coordinate of the centre of mass, M the total mass, r the relative coordinate, and μ the reduced mass. Since the Hamiltonian for the centre of mass motion commutes with the Hamiltonian for the relative motion, the density matrix for relative motion $\rho(r, r'; \beta)$ can be defined by the equation

$$\langle x, r | \exp(-\beta H) | x', r' \rangle$$
$$= (2\pi\hbar^2\beta/M)^{-3/2} \exp\{-(x-x')^2/(2\hbar^2\beta/M)\}\langle r | \exp(-\beta H_r) | r' \rangle, \tag{4}$$

where

$$\rho(r, r'; \beta) = \langle r | \exp(-\beta H_r) | r' \rangle. \tag{5}$$

The potential used in this paper is the Lennard-Jones potential

$$V(r) = 4\varepsilon\{(\sigma/r)^{12} - (\sigma/r)^6\}, \tag{6}$$

with the de Boer–Michels parameters appropriate to helium-4 (de Boer 1949)

$$\varepsilon/k = 10\cdot22 \quad \text{K} \quad \text{and} \quad N_0\sigma^3 = 10\cdot06 \times 10^{-6} \quad \text{m}^3, \tag{7}$$

where N_0 is Avogadro's number, and parameters calculated by Nicholson and

Schneider (1955) for neon

$$\varepsilon/k = 33 \cdot 74 \quad \text{K} \quad \text{and} \quad N_0 \sigma^3 = 12 \cdot 607 \times 10^{-6} \quad \text{m}^3. \tag{8}$$

For the Lennard-Jones potential there is a particularly convenient method of choosing dimensionless variables: let $r^* = r/\sigma$ and define new parameters β^* and ε^* by

$$\beta^* = (\hbar^2/2\mu\sigma^2 k)T^{-1} \quad \text{and} \quad \varepsilon^* = 4\varepsilon 2\mu\sigma^2/\hbar^2. \tag{9}$$

These shall determine the units to be used in the remainder of the paper and so, for convenience, the asterisks will be discarded.

The density matrix for any central potential can be expanded in terms of con tributions from all partial waves

$$\rho(r, r'; \beta) = \sum_{l=0}^{\infty} \{(2l+1)/4\pi rr'\} \rho_l(r, r'; \beta) P_l(\cos\theta), \tag{10}$$

where θ is the angle between r and r'. Since helium and neon are Bose–Einstein gases the pair-correlation function $g(r)$ is the sum of a direct and an exchange contribution:

$$g(r) = g_d(r) + g_{ex}(r), \tag{11}$$

where

$$g_d(r) = (4\pi\beta)^{3/2} \sum_{l=0}^{\infty} \{(2l+1)/4\pi r^2\} \rho_l(r, r; \beta) = \sum_{l=0}^{\infty} g_l(r) \tag{12}$$

and

$$g_{ex}(r) = (4\pi\beta)^{3/2} \rho(r, -r; \beta) = \sum_{l=0}^{\infty} (-1)^l g_l(r). \tag{13}$$

The free-particle density matrix $\rho^{(0)}(r, r'; \beta)$ can be expanded in terms of partial waves in similar manner to equation (10) (see Storer 1968a, 1968b)

$$\rho^{(0)}(r, r'; \beta) = (4\pi\beta)^{-3/2} \exp\{-(r-r')^2/4\beta\}$$

$$= \sum_{l=0}^{\infty} \{(2l+1)/4\pi rr'\} \rho_l^{(0)}(r, r'; \beta) P_l(\cos\theta) \tag{14}$$

$$= (4\pi\beta)^{-3/2} \sum_{l=0}^{\infty} (2l+1) \exp\left(-\frac{r^2+r'^2}{4\beta}\right) i_l\left(\frac{rr'}{2\beta}\right) P_l(\cos\theta), \tag{15}$$

where i_l is the modified spherical Bessel function, that is, $i_l(z) = (\pi/2z)^{\frac{1}{2}} I_{l+\frac{1}{2}}(z)$.

III. High Temperature Approximation

There are several approaches that can be made to obtain approximations to the density matrix (see e.g. Blatt 1956; Fosdick and Jordan 1966) but our technique is to use the properties of an expansion of the exponential of the sum of two noncommuting operators. From equation (3) it can be seen that we can write the Hamiltonian operator for relative motion as the sum of two noncommuting operators,

$$H_r = H_0 + H_1. \tag{16}$$

It is usual for the operator H_1 to contain the potential energy term $V(r)$ since it is nearly always this term which prevents an exact solution of the density matrix of the original Hamiltonian.

For sufficiently small β we may expand the exponentials involving terms of order β^2 or higher, to obtain the approximation (Grimm and Storer 1969)

$$\exp\{-\beta(H_0+H_1)\} \approx \exp(-\tfrac{1}{2}\beta H_1)\exp(-\beta H_0)\exp(-\tfrac{1}{2}\beta H_1)$$

$$-2\beta^3\exp(-\tfrac{1}{2}\beta H_1)\exp(-\tfrac{1}{2}\beta H_0)$$

$$\times c_3\exp(-\tfrac{1}{2}\beta H_0)\exp(-\tfrac{1}{2}\beta H_1)+\dots,\qquad(17)$$

where

$$c_3 = \tfrac{1}{48}[H_1,[H_1,H_0]]+\tfrac{1}{24}[H_0,[H_1,H_0]].\qquad(18)$$

Thus we have an approximation for the density operator for relative motion, defined by equation (4), which is correct to order β^2

$$\rho = \exp(-\beta H_r) \approx \exp(-\tfrac{1}{2}\beta H_1)\exp(-\beta H_0)\exp(-\tfrac{1}{2}\beta H_1),\qquad(19)$$

where the operators $\rho_1 = \exp(-\tfrac{1}{2}\beta H_1)$ and $\rho^{(0)} = \exp(-\beta H_0)$ satisfy the differential equations

$$\tfrac{1}{2}H_1\rho_1 = -\partial\rho_1/\partial\beta \qquad\text{and}\qquad H_0\rho^{(0)} = -\partial\rho^{(0)}/\partial\beta\qquad(20)$$

respectively, with boundary conditions

$$\lim_{\beta\to0}\rho^{(0)} = \lim_{\beta\to0}\rho_1 = 1.\qquad(21)$$

The importance of this result lies in the fact that, although it may be impossible to write down a closed form for the density operator, it may be possible to divide the Hamiltonian operator H_r into two parts H_0 and H_1 for which the exact solutions of the equations (20) can be found.

The lth partial wave Hamiltonian operator can be divided into a sum of two noncommuting operators $H_l = H_l^0 + H_l^1$, where $H_l^0 = -(\partial^2/\partial r^2)+l(l+1)/r^2$, in an analogous manner to equation (16), and so by the same procedure as before we obtain

$$\rho_l(r,r';\beta) \approx \exp\{-\tfrac{1}{2}\beta H_l^1(r)\}\,\rho_l^{(0)}(r,r';\beta)\exp\{-\tfrac{1}{2}\beta H_l^1(r')\}+o(\beta^3),\qquad(22)$$

with $\rho_l^{(0)}$ as defined in equation (15).

This approximation relies on the value of β being small, i.e. it is a high temperature expansion (although it should be pointed out that the error is also proportional to the operator c_3, which allows the approximation to remain valid under less stringent conditions in particular cases). The basic procedure used in this paper is to extend the solution to low temperature regions, where quantum effects are important, by recognizing that the operator equation (Storer 1968a, 1968b)

$$\exp(-2\beta H) = \exp(-\beta H)\exp(-\beta H)\qquad(23)$$

is an exact relation. In coordinate space representation for $\rho_l(r, r'; \beta)$, this is simply

$$\rho_l(r, r'; 2\beta) = \int_0^\infty dr_2 \, \rho_l(r, r_2; \beta) \rho_l(r_2, r'; \beta). \tag{24}$$

We can then use the high temperature approximation (22), at a temperature T, as a starting point for an iteration procedure based on this equation to find the density matrix at a series of temperatures T, $T/2$, $T/4$, etc. The detailed equivalence between this procedure and the path integral formulation for the density matrix (Fosdick and Jordan 1966) has been pointed out by Storer (1968a).

IV. NUMERICAL CALCULATIONS

The most obvious choice of division of the Hamiltonian operator is to let

$$H_l^0 = -(\partial^2/\partial r^2) + l(l+1)/r^2 \quad \text{and} \quad H_l^1 = V(r).$$

The solution of the relevant Bloch equation (20) is the lth partial wave contribution to the free-particle density matrix

$$\rho_l^{(0)}(r, r'; \beta) = (4\pi\beta)^{-3/2} 4\pi r r' \exp\{-(r^2 + r'^2)/4\beta\} \, i_l(rr'/2\beta). \tag{25}$$

The modified spherical Bessel functions were computed by using the standard backwards recurrence relation (Abramowitz and Stegun 1965) or the power series for small $z = rr'/2\beta$ ($z \leqslant 1$). For large z ($\geqslant 50$) the asymptotic expansion used was

$$i_l(z) = \frac{1}{2z} \exp\left(z - \frac{l(l+1)}{2z}\right)\left(1 - \frac{l(l+1)}{(2z)^2} + \frac{l(l+1)(l-2)(l+3)}{3(2z)^3}\right.$$
$$\left. + \frac{l(l+1)(5l^2 + 5l - 12)}{2(2z)^4}\right). \tag{26}$$

The explicit inclusion of the term $\exp\{-l(l+1)/2z\}$ was found to give much better results than using the standard asymptotic expansion for modified Bessel functions (Abramowitz and Stegun 1965). Thus we can make the initial high temperature approximation (22) over a grid of any size, and for any l value, and it remains to extend this approximation to low temperatures using numerical integration techniques to implement the iteration procedure.

The range of the integration given by equation (24) is $(0, \infty)$ but this can be restricted to a finite interval because of two properties. The first is that off-diagonal terms decrease as $\exp(-r^2/2\beta)$, which means that for any fixed r and r' the integration over r_2 can be restricted to a finite range. The second property restricting the iteration procedure is that, although we have infinite matrices (with a limited number of off-diagonal terms), the solution for $r, r' > R$, where R is some chosen finite range dependent on β, can be approximated by the known expression

$$\exp\{-\beta V(r)\} \rho_l^{(0)}(r, r'; 2\beta) \exp\{-\beta V(r')\}$$

to a predetermined accuracy. It is thus unnecessary to extend the ranges of r and r'

which determine the size of the resultant matrix beyond this value. Because the Lennard-Jones potential can be effectively replaced by a hard core for radial separations $r < \gamma$, where γ is of the order of $0 \cdot 6 \sigma$, all matrix elements within this barrier are zero and so no contribution is made by these elements to the integration.

Formally then, if the range of r and r' over which we wish to find values for the density matrix is $R = N\Delta$, the integral (24) can be written in terms of the trapezoidal rule as

$$[\rho_l(2\beta)]_{pq} = \sum_k [\rho_l(\beta)]_{pk} [\rho_l(\beta)]_{kq} \Delta \qquad (27)$$

for $p, q \leqslant N$, where we have defined

$$[\rho_l(\beta)]_{pq} = \rho_l(p\Delta, q\Delta; \beta). \qquad (28)$$

This iteration procedure is thus equivalent to a matrix squaring operation.

Beginning with the initial approximation given by equation (22) the above procedure will result in the calculation of $\rho_l(r, r'; 2\beta)$ within the range $r, r' \leqslant R$. In the small region, where r or r' is within a distance of the order the thermal wavelength λ from R, there will be some error because the integral (24) has been truncated at a finite point R. When both $r \geqslant R - \lambda$ and $r' \geqslant R - \lambda$, this can be remedied simply by noting that the approximation

$$\rho_l(r, r'; 2\beta) = \exp\{-\beta V(r)\} \rho_l^{(0)}(r, r'; 2\beta) \exp\{-\beta V(r')\}$$

is valid for large r and r', and the erroneous values can be corrected to this expression. When r' is large ($\geqslant R - \lambda$) but r is small (or vice versa), it is found satisfactory to use the replacement

$$\rho_l(r, r'; 2\beta) = \exp\{-\beta V_{\text{eff}}(r; \beta) - \beta V(r')\} \rho_l^{(0)}(r, r'; 2\beta), \qquad (29)$$

where $V_{\text{eff}}(r; \beta)$ is defined by

$$\exp\{-\beta V_{\text{eff}}(r; \beta)\} = \rho_l(r, r; \beta) / \rho_l^{(0)}(r, r; \beta). \qquad (30)$$

These modifications, however, only affect the narrow strip within a distance λ from R.

By repetition of this procedure the lth partial wave contribution to the density matrix is evaluated at temperatures $T/2^m$, where T is the initial temperature and m the number of times the matrix is squared. In principle the direct and exchange contributions to the pair-correlation function result simply from the summation of the partial wave contributions at a particular temperature according to equations (12) and (13) respectively. However, for helium the highest temperatures for which the pair-correlation function could be found to sufficient accuracy by direct summation was about 10 K. These summations required partial waves up to $l \approx 17$ while, for temperatures higher than this, evaluation of the extra partial waves needed would have required unreasonable computing times.

It is interesting to compare the result at 2 K with those of Larsen *et al.* (1966) and Fosdick and Jordan (1966), since both groups evaluated the same quantity with identical potential parameters but used different numerical techniques. This was the
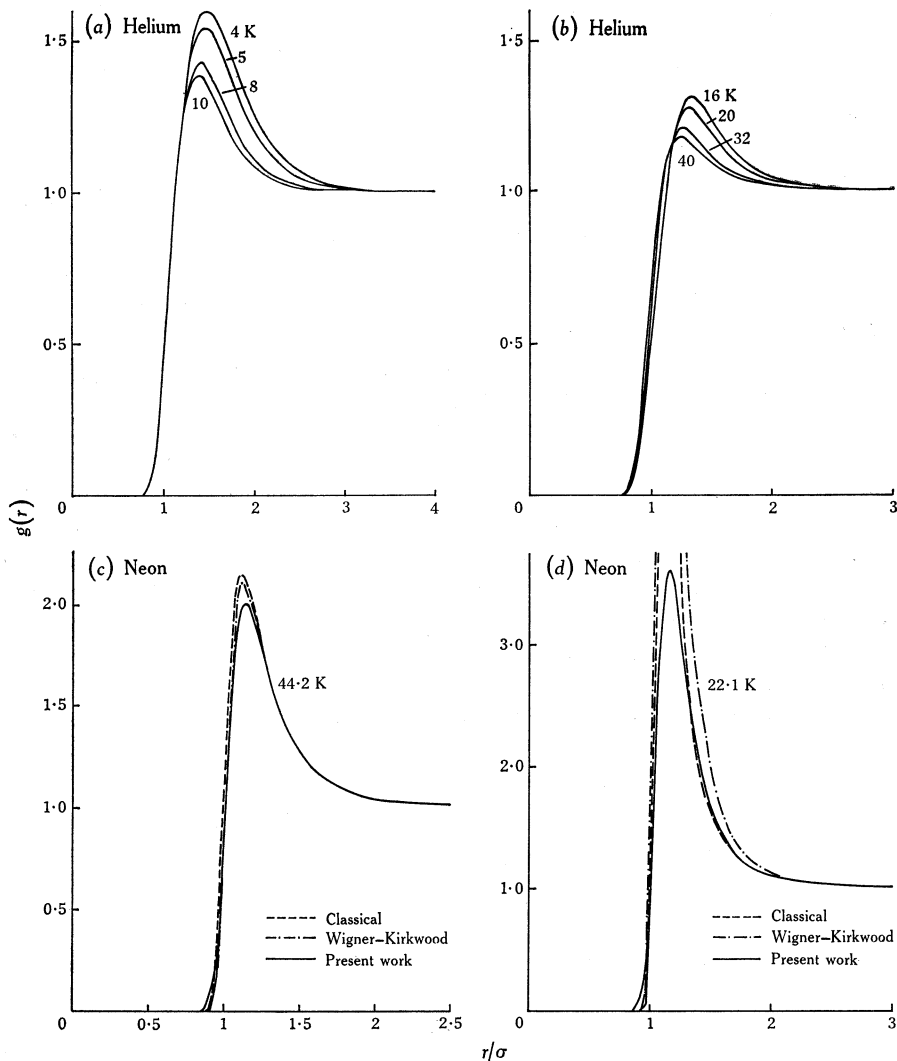
Fig. 1.—Pair-correlation functions $g(r)$ for helium and neon at the indicated temperatures. In (a) only the density independent contribution is shown. In (b)–(d) the terminated expansion method (see text) has been used to obtain $g(r)$ from the present work. A comparison with the classical and Wigner–Kirkwood equivalent expressions is given in (c) and (d).

highest temperature considered by Larsen *et al.*, while Fosdick and Jordan forced their calculations down to 2 K for comparison, their procedure encountering large Monte Carlo sampling errors at this temperature. The result for the present work at 2 K follows closely that of Larsen *et al.*, the largest variation occurring at the maximum where we differ only in the third significant figure, this difference being too small to allow graphical comparison. The same relationship exists at 1 K. This comparison inspires confidence in the accuracy of the present results at higher temperatures.

The exchange term, found by summing g_l according to equation (13) follows closely the results of Larsen *et al.* (1966) at 2 K but differs considerably from those of Fosdick and Jordan (1966). In this case, however, their errors are even greater than the magnitude of $g_{ex}(r)$. In Figure 1(*a*) we show the density independent part of the pair-correlation function for the temperatures 4, 5, 8, and 10 K.

The direct contribution to the pair-correlation function can be adequately represented by the Wigner–Kirkwood approximation (see Uhlenbeck and Beth 1936, 1937; Green 1951) for temperatures above about 100 K for both helium and neon but for lower temperatures the approximation worsens quickly. We extend the calculation of the pair-correlation function to the temperature range between that for which a simple partial wave summation can be performed and that for which the Wigner–Kirkwood approximation is valid, by using the following technique. The speed of convergence of the sums in equations (12) and (13) depends not only on the temperature but also on the distance between the two particles, the smaller the separation the faster the convergence. Consequently the number of the partial wave terms evaluated (17 for helium and 51 for neon) is sufficient for all temperatures, provided the value of r concerned is small enough in each case. Also, the higher the temperature the smaller is the choice of r, which we will denote by r_c. Similarly the approximation given by equation (22) depends not only on the temperature but also on the radial separation via the commutators of H_l^0 and H_l^1, the higher the temperature the smaller the distance r_a required for the approximation to be accurate to within a definite number of significant figures.

If the number L of partial waves taken is enough to satisfy the criterion $r_c \geqslant r_a$ for the partial sum so formed then for $r > r_c$ equation (12) can be approximated by

$$g_d(r) \approx \sum_{l=0}^{L} g_l(r) + \exp\{-\beta V(r)\} \sum_{l=L+1}^{\infty} g_l^{(0)}(r), \qquad (31)$$

where

$$g_l^{(0)}(r) = (4\pi\beta)^{3/2}\{(2l+1)/4\pi r^2\}\, \rho_l^{(0)}(r, r; \beta). \qquad (32)$$

This expression can be rewritten in the form

$$g_d(r) \approx \sum_{l=0}^{L} [g_l(r) - \exp\{-\beta V(r)\} g_l^{(0)}(r)] + \exp\{-\beta V(r)\}, \qquad (33)$$

since

$$\sum_{l=0}^{\infty} g_l^{(0)}(r) = 1. \qquad (34)$$

We call approximation by equation (33) the terminated expansion method. A similar expression can be derived for the exchange term (unlike the Wigner–Kirkwood expansion), although at the temperatures for which we have applied the method the exchange term can be neglected.

Figure 1(*b*) shows the pair-correlation function for helium at the four temperatures 40, 32, 20, and 16 K as evaluated by the above method. The pair-correlation function was also evaluated at 8 and 10 K by this approximation to enable a comparison to be made between it and the direct sum. In the latter case the magnitude of the tail is low due to the incomplete sum, while the semiclassical approximation for the

tail in the former case increases its value, thus putting an upper and lower limit on the tail. The difference is too small to be shown graphically but comparison of the second virial coefficients, found by integrating the curves, indicates the numerical differences to be of the order of 10^{-7} m³ mole⁻¹.

The pair-correlation functions for neon at the temperatures 44·2 and 22·1 K are shown in Figures 1(c) and 1(d) together with the classical and Wigner–Kirkwood approximations, demonstrating the large quantum effects that exist at these temperatures.

V. SECOND VIRIAL COEFFICIENT

The above results can be used to calculate the second virial coefficient. This serves, in the case of helium, as a check on the accuracy of our evaluation of the pair-correlation function by comparison with the phase shift method (see e.g. de Boer and Michels 1939; Green 1951, 1952a, 1952b; Boyd et al. 1969). For neon these results go below the temperature where the Wigner–Kirkwood results are accurate.

The second virial coefficient has the same form in quantum mechanics as in classical mechanics,

$$B = -2\pi N_0 \sigma^3 \int_0^\infty dr\, r^2 \{g(r) - 1\}. \tag{35}$$

After substitution from equation (11), the second virial coefficient can be separated into a contribution due to Boltzmann statistics and one due to exchange effects,

$$B_d = -2\pi N_0 \sigma^3 \int_0^\infty dr\, r^2 (g_d - 1) \tag{36}$$

and

$$B_{ex} = -2\pi N_0 \sigma^3 \int_0^\infty dr\, r^2 g_{ex}. \tag{37}$$

The second virial coefficient results from the evaluation of these two integrals. The direct term can be written as the sum of three parts; the first

$$\tfrac{2}{3}\pi N_0 \sigma^3 \gamma^3 \tag{38}$$

is the contribution due to the "hard core"; the expression

$$-2\pi N_0 \sigma^3 \int_\gamma^R dr\, r^2 (g_d - 1) \tag{39}$$

gives the contribution due to the effect of quantum mechanics. By using equation (12) and diagonal values of equation (14) this expression can be rewritten as

$$-2\pi N_0 \sigma^3 \sum_{l=0}^\infty \int_\gamma^R dr\, r^2 \{g_l(r) - g_l^{(0)}(r)\}, \tag{40}$$

this second form being applicable in the low temperature region where the sum can be accurately terminated. The limit R is the point at which g_d differs insignificantly from $\exp(-\beta V)$, so that the final part is

$$-2\pi N_0 \sigma^3 \int_R^\infty dr\, r^2 [\exp\{-\beta V(r)\} - 1]. \tag{41}$$

The exchange term of the second virial coefficient also simplifies, but to the single term

$$-2\pi N_0 \sigma^3 \int_\gamma^{R'} dr\, r^2 g_{ex}(r), \tag{42}$$

which can be rewritten as

$$-2\pi N_0 \sigma^3 \sum_{l=0}^\infty (-1)^l \int_\gamma^{R'} dr\, r^2 g_l(r), \tag{43}$$

where R' is the range at which g_{ex} differs insignificantly from zero.

Equations (40) and (43) imply that, in the low temperature region where sufficient l values can be summed over, the contribution from each orbital angular momentum

TABLE 1

SECOND VIRIAL COEFFICIENTS FOR HELIUM

The second virial coefficients are expressed in units of 10^{-6} m^3 mole^{-1}

Temp. T (K)	Present work			Boyd et al. (1969)		
	B_{ex}	B_d	B	B_{ex}	B_d	B
1	$-53\cdot13$	$-383\cdot27$	$-436\cdot40$	$-52\cdot400$	$-376\cdot630$	$-429\cdot030$
2	$-3\cdot477$	$-176\cdot10$	$-179\cdot58$	$-3\cdot427$	$-173\cdot992$	$-177\cdot419$
2·5	$-1\cdot113$	$-137\cdot68$	$-138\cdot79$	$-1\cdot113$	$-135\cdot282$	$-136\cdot395$
4	$-0\cdot061$	$-78\cdot66$	$-78\cdot72$	$-0\cdot060$	$-78\cdot045$	$-78\cdot105$
5	$-0\cdot011$	$-59\cdot98$	$-59\cdot99$	$-0\cdot011$	$-59\cdot114$	$-59\cdot125$
8	$0\cdot000$	$-30\cdot11$	$-30\cdot11$	$0\cdot000$	$-30\cdot767$	$-30\cdot767$
10	$0\cdot000$	$-20\cdot95$	$-20\cdot95$	$0\cdot000$	$-21\cdot321$	$-21\cdot321$

to the second virial coefficient can be directly evaluated, and this has been done in these cases. The contribution to the direct second virial coefficient by the hard core is independent of the temperature and has the constant value $B_{hc} = 4\cdot551 \times 10^{-6}$ m^3 mole^{-1} for helium. Adding to this the total contribution from expression (40) and the contribution from the classical tail gives the direct second virial coefficient. This, and the exchange second virial coefficient are given in Table 1, where they are compared with the results of Boyd et al. (1969). The results agree to within 2% with their very accurate values. The discrepancies that do exist are justified in that the aim was to evaluate the pair-correlation function, the virial coefficient integrals being a reasonable test of the accuracy of the results without demanding precision. The results obtained for higher temperatures by integrating equation (33), together with experimental data, are plotted in Figure 2(a). It should be pointed out that the Wigner–Kirkwood results do not continue to diverge from the true values in the gentle curve shown. Instead they quickly diverge upwards towards infinity as the temperature decreases further.

The three values obtained for neon by integrating over the appropriate approximate pair-correlation functions are compared in Figure 2(b) with low temperature experimental evaluations. The low temperature values of Keesom and Van Lammeren (1934) were ignored by Nicholson and Schneider (1955) in all attempts to find the parameters of the Lennard–Jones potential by fitting the data. The reason for this appears to be that, when the results of Keesom and Van Lammeren and of Holborn and Otto (see Otto 1929) were the only experimental values for neon, the former were

about 10% less in the region of overlap which is presented in Figure 2(b), the latter work being used to obtain an accepted set of values. Thus it was deemed that the compressibility measurements in the former case were incorrect especially when comparisons of third virial coefficient data were made. There is obviously a great need for a second series of measurements in this region.
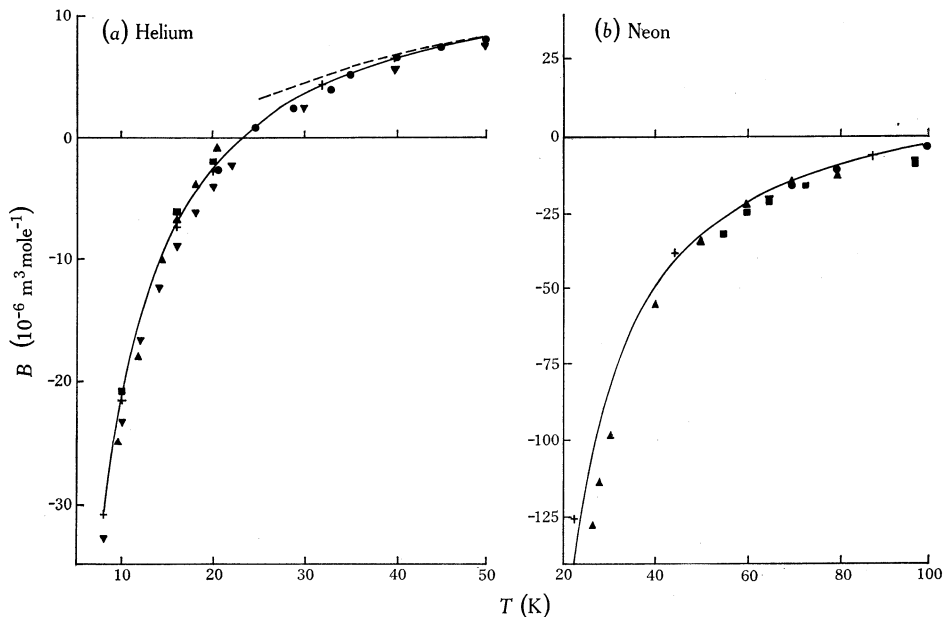

Fig. 2.—Second virial coefficient B for helium and neon as a function of temperature. Results of the present work are indicated by crosses. (a) The continuous curve is from Boyd et al. (1969) and the dashed curve from the Wigner–Kirkwood expansion. The experimental points are: inverted triangles, Keesom (1942) "adopted values"; triangles, Keesom and Walstra (1947); circles, White et al. (1960); squares, Boyd et al. (1968). (b) The continuous curve is the classical relation obtained by substituting Nicholson and Schneider's (1955) potential parameters into the reduced values tabulated by Hirschfelder et al. (1954). The experimental points are: squares, Kamerlingh-Onnes et al. and Palacios Martinez and Kamerlingh-Onnes (see Otto 1929); inverted triangles, Otto (1929); triangles, Keesom and Van Lammeren (1934); circles, Sullivan and Sonntag (1967).

VI. Effective Potentials and Three-particle Effects

In practice the solution of even the three-body problem is very difficult and it is inevitable that for more than three particles approximations have to be made. We introduce here an effective potential $V_{\text{eff}}(r; \beta)$ defined by

$$g(r) = \exp\{-\beta V_{\text{eff}}(r; \beta)\}, \qquad (44)$$

where $g(r)$ is the density independent part of the pair-correlation function. We then assume that the many-body density matrix ρ can be written in the form

$$\rho(r_1, \ldots, r_N; r'_1, \ldots, r'_N; \beta)$$

$$= \rho^{(0)}(r_1, \ldots, r_N; r'_1, \ldots, r'_N; \beta) \exp\left(-\tfrac{1}{2}\beta \sum_{i<j} \{V_{\text{eff}}(r_{ij}; \beta) + V_{\text{eff}}(r'_{ij}; \beta)\}\right), \quad (45)$$

where $\rho^{(0)}$ is the free-particle density matrix. Since $V_{\text{eff}}(r; \beta) \to V(r)$ as $\beta \to 0$, this equation is certainly valid for high temperatures (see equation (17)) and, by looking in detail at the consequences of this approximation for the three-body system, we hope to be able to investigate its validity at temperatures where quantum effects are important. It is similar in spirit to the Bijl–Jastrow approximation (Jastrow 1955) which has been applied to the ground state of many-particle systems, and to the approximation of Dunn and Broyles (1967) which has been applied to the electron gas and the hydrogen plasma (Broyles *et al.* 1969). Fosdick and Jacobson (1971) and Klemm (1971) have both applied the present approximation to the three-body problem in order to test its validity.

If we define

$$F_{ij} = \exp\{-\beta V_{\text{eff}}(r_{ij}; \beta)\} - 1 \qquad (46)$$

by analogy with Mayer's classical function f_{ij}, we obtain the following expression for the third virial coefficient in terms of F_{ij}

$$C(T) = -\frac{(N_0 \sigma^3)^2}{3V} \iiint F_{12} F_{23} F_{13} \, d\boldsymbol{r}_1 \, d\boldsymbol{r}_2 \, d\boldsymbol{r}_3, \qquad (47)$$

which can be reduced to

$$C(T) = -\frac{(N_0 \sigma^3)^2}{6\pi^2} \int_0^\infty G^3(k) k^2 \, dk,$$

where $G(k)$ is given by the Fourier transform expression

$$G(k) = 4\pi \int_0^\infty F(r)(\sin kr/kr) r^2 \, dr. \qquad (48)$$

Thus the number of integrations necessary to find the third virial coefficient has been reduced from nine to two.

We can also find the contribution to the pair-correlation function from the term linear in the density, since this can be evaluated in a similar manner. It has the form

$$g_1(r_{12}) = \int F_{13} F_{23} \, d\boldsymbol{r}_3 \qquad (49)$$

and, applying the inverse Fourier transform (48), it becomes

$$g_1(r) = (\sigma/2\pi)^3 4\pi \int_0^\infty G^2(k)(\sin kr/kr) k^2 \, dk, \qquad (50)$$

which is just the Fourier transform of G^2. Thus we can also find an approximation to the pair-correlation function correct to the first power of the number density.

In Figure 3(*a*) we compare the Monte Carlo results of Jordan and Fosdick (1968) for the third virial coefficient of helium with the results obtained using the approximation (45) by Fosdick and Jacobson (1971) and Klemm (1971). The slight difference between these two results most likely arises from the uncertainty in the value of the $g(r)$ used by Fosdick and Jacobson due to Monte Carlo sampling. Included in the
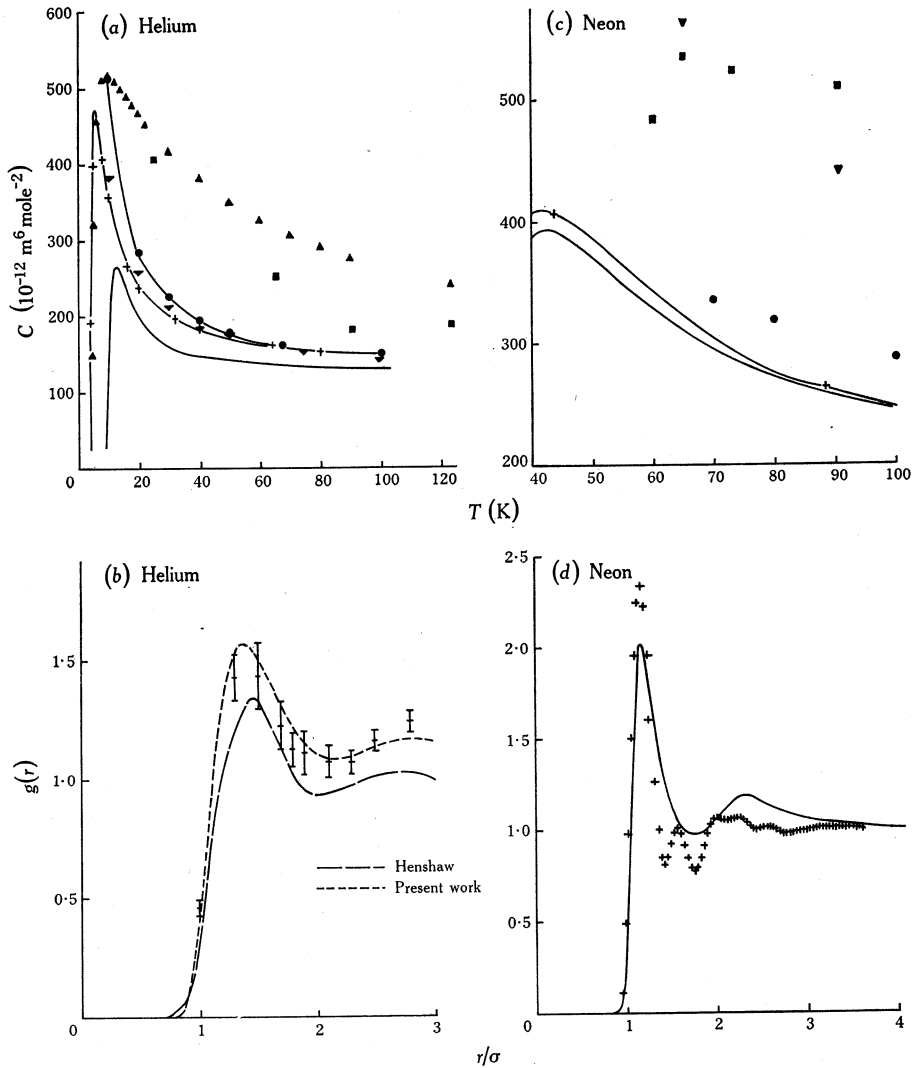
Fig. 3.—Third virial coefficient C, as a function of temperature, and radial distribution function $g(r)$ to first order in the density, for helium and neon. In (a) and (c) the results of the present work are indicated by crosses. In (b) and (d) the results are for helium at 5 K, $\rho = 95$ kg m^{-3} and neon at 44·2 K, $\rho = 670$ kg m^{-3} respectively. The symbols used are: (a) Squares, Otto (1929); triangles, Keesom (1942) "adopted values"; continuous curve, classical solution for a Lennard-Jones potential; circles, Jordan and Fosdick (1968); inverted triangles, Fosdick and Jacobson (1971). (b) Crosses with error bars, Monte Carlo calculations of Jordan and Fosdick (1968). (c) Squares, Kamerlingh-Onnes *et al.* (see Otto 1929); inverted triangles, Otto (1929); circles, Sullivan and Sonntag (1967), full curve, classical solution for a Lennard-Jones potential assuming additive two-body forces. (d) Crosses, experimental results of Stirpe and Tompson (1962); continuous curve, present results,

figure are the experimental results of Keesom (1942) (adopted values) and Otto (1929). It is interesting to note the marked discrepancy between the two sets of data, especially since they are the only experimental results available except for some very low temperature points evaluated by Keller (1955) from pressure–volume isotherms. Indeed Otto has an additional point at $15 \cdot 19$ K which is not included because it is too far off scale (his value being 1063×10^{-12} m^6 $mole^{-2}$).

The radial distribution function in liquid helium has been derived from experimental neutron and X-ray scattering data for a variety of densities at several temperatures in helium. In particular Henshaw (1960) published some results up to $5 \cdot 04$ K derived from neutron scattering data. In Figure 3(b) the experimental result at this temperature and a density of 95 kg m^{-3} is shown together with the linear approximation to the radial distribution function at this density and a temperature of 5 K as derived by Jordan and Fosdick (1968). Our curve, in the same figure, follows closely Jordan and Fosdick's results and thereby demonstrates the feasibility of making the approximation (45) in order to obtain qualitative estimates of thermodynamic properties when the system is described by quantum statistical mechanics. Figure 3(c) compares the classical third virial coefficient with our results in the temperature range between 40 and 100 K for neon. The additional point found by us at $22 \cdot 1$ K is not shown because it has a large negative value, namely -2355×10^{-12}, as compared with -4335×10^{-12} m^6 $mole^{-2}$ in the classical case. The only experimental results around this temperature are two points evaluated by Keesom and Van Lammeren (1934): 5116×10^{-12} and 4017×10^{-12} m^6 $mole^{-2}$ at $26 \cdot 2$ and $27 \cdot 8$ K respectively.

The theoretical and experimental turning points for helium occur at similar temperatures and this would be expected to be the case for neon. Thus there is no explanation for the huge discrepancy present between experimental and theoretical values, the classical turning point occurring between 40 and 44 K. Figure 3(c) shows that only the recent measurements of Sullivan and Sonntag (1967) are near the theoretical results, the earlier measurements being about twice the magnitude and following no discernible pattern. These include the values of Kamerlingh-Onnes et al. (see Otto 1929), since an unplotted point of theirs at $55 \cdot 63$ K has a value of $900 \cdot 55 \times 10^{-12}$ m^6 $mole^{-2}$. Thus it would appear that there is an almost complete lack of experimental data that can be taken as correct for the temperature region immediately above the turning point. This poses a serious difficulty in obtaining the effects of nonadditive three-body forces, not to mention improvements in two-body additive potentials. It should also be noted (see Fig. 3(a)) that, although there does exist a curve of smoothed values of the third virial coefficient for helium, it is of similar antiquity to the above results and conflicts with the only other experimental points available.

The contribution to the radial distribution function from the term linear in the density at $44 \cdot 2$ K is shown in Figure 3(d) at a density of 670 kg m^{-2}. This is compared with the experimental determination by Stirpe and Tompson (1962) for the same density and temperature in liquid neon. Terminating the expansion at the first term gives excessive weight to the second distribution peak, the many-particle effects present in a liquid not being included in our results (c.f. Fig. 4(b)). A series of tests conducted by Stirpe and Tompson strongly suggest that the peak in the experimental curve at about $1 \cdot 7 \sigma$ was an artifact from the Fourier transformation and did not represent structure in liquid neon. Schmidt and Tompson (1968) noted that the scattered intensity in this experiment was very low and the results must be considered with this defect in mind.
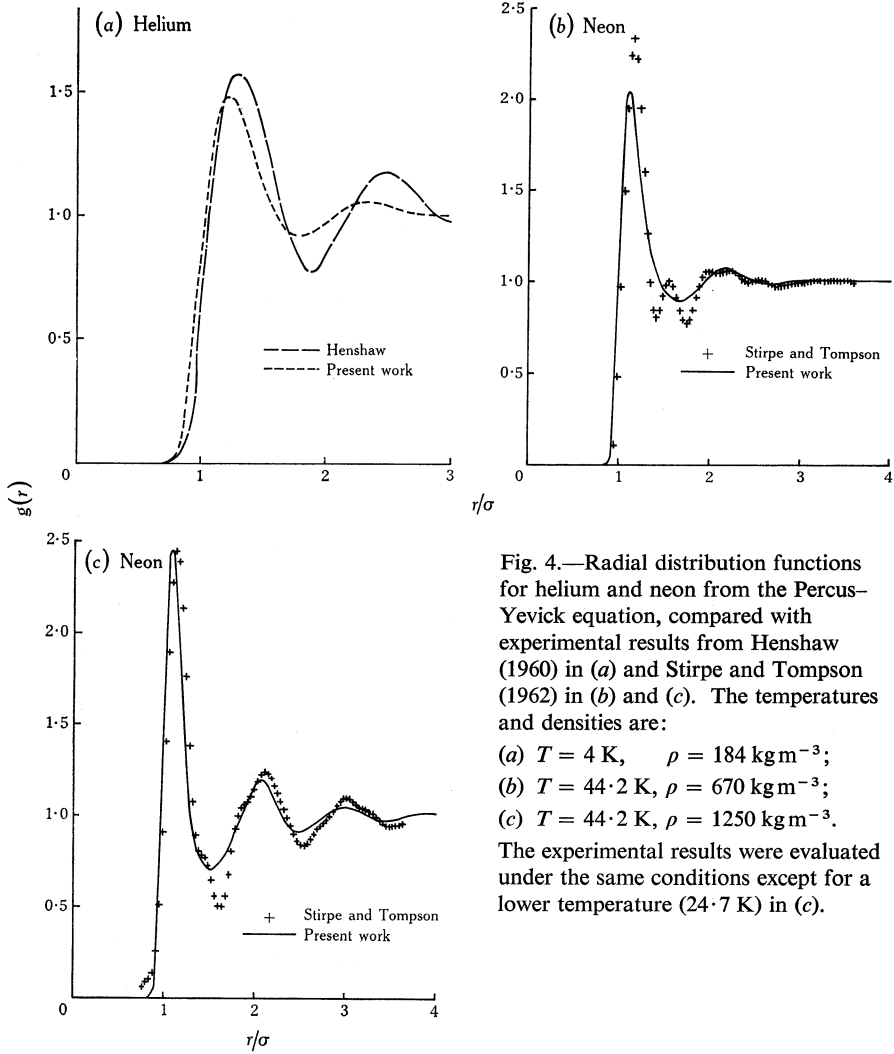
Fig. 4.—Radial distribution functions for helium and neon from the Percus–Yevick equation, compared with experimental results from Henshaw (1960) in (a) and Stirpe and Tompson (1962) in (b) and (c). The temperatures and densities are:

(a) $T = 4$ K, $\rho = 184$ kg m^{-3};

(b) $T = 44 \cdot 2$ K, $\rho = 670$ kg m^{-3};

(c) $T = 44 \cdot 2$ K, $\rho = 1250$ kg m^{-3}.

The experimental results were evaluated under the same conditions except for a lower temperature (24·7 K) in (c).

VII. RADIAL DISTRIBUTION FUNCTION

A quantum fluid has a radial distribution function which has the same shape as the corresponding classical quantity. It differs only in the magnitude and position of the various maxima and minima and has the same property that $g(r) \to 1$ as $r \to \infty$. It is satisfactory therefore to introduce a quantum mechanical direct correlation function $c(r)$ and if we assume pair-wise additivity of effective potentials, so that we can write

$$F(r) = \exp\{-\beta V_{\text{eff}}(r; \beta)\} - 1, \tag{51}$$

then by a similar procedure to Percus and Yevick (1958) we can obtain the quantum analogue to the Percus–Yevick approximation

$$\{F(r) + 1\}c(r) = g(r)F(r). \tag{52}$$

Combining this with the definition of $c(r)$ we can write the approximation as

$$y(r) = 1 + n \int y(r') F(r') \{ y(|r-r'|) F(|r-r'|) + y(|r-r'|) - 1 \} \, dr', \qquad (53)$$

where

$$y(r) = g(r) \exp\{\beta V_{\text{eff}}(r; \beta)\}. \qquad (54)$$

We have used the method devised by Broyles (1961) to solve the Percus–Yevick equation with the effective potentials in place of the classical Lennard-Jones potential (c.f. Mandel *et al.* 1970). In Figure 4(*a*) we compare our solution for helium at a temperature of 4 K and a density of 184 kg m^{-3} with an experimental evaluation by Henshaw (1960) at a temperature of $4 \cdot 02$ K and the same density. Since our result in Figure 3(*b*) follows Jordan and Fosdick's (1968) results reasonably closely it is not likely that the deviation from experimental values here is due to our approximation. It is more likely due to either the choice of potential or the inherent approximation involved in choosing pair-wise additive forces. The latter possibility is also indicated by the results for the third virial coefficient given in Section VI. This factor is also suspect because we are going from gas to liquid temperatures and densities.

The result of applying the Percus–Yevick approximation to neon at $44 \cdot 2$ K and a density of 670 kg m^{-3} is shown in Figure 4(*b*), where it is compared with the experimental results of Stirpe and Tompson (1962) for identical conditions. It should be noted that the fit to the secondary peaks is far better than in Figure 3(*d*), where the three-particle contribution only is graphed. Stirpe and Tompson also obtained results at a temperature of $24 \cdot 7$ K and a density of 1250 kg m^{-3}. In Figure 4(*c*) we compare the results obtained from the Percus–Yevick equation at this density and a temperature of $44 \cdot 2$ K since some difficulty was encountered at the low temperature (probably due to the proximity of the triple point). However, because neon is a liquid in this range the structure should not depend critically on the temperature. There is good agreement with the first peak, although the second peak is low, a probable consequence of the closer packing which occurs at lower temperatures.

These results give confidence that an effective potential approach to the study of the structure of many-body systems which have to be described by quantum statistical mechanics is a fruitful one. It certainly has the major advantage of enabling the many techniques developed for classical statistical mechanics to be applied to quantum systems.

VIII. Acknowledgment

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