Quantum Statistical Mechanics of a Many-Body System of Interacting Particles

R.K. PATHRIA* and M.P. KAWATRA

Department of Physics
University of Delhi, Delhi-6, India

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The binary collision method of Lee and Yang is applied to investigate the equilibrium properties of a many-body system of particles interacting through a generalized two-body potential. It is found that, to the order $a^2/\lambda^2$ where $a$ and $\lambda$ represent respectively the range of the two-body interaction and the mean thermal wavelength of the particles, the final results can be written down explicitly in terms of the relevant phase shift for the $s$-waves. Ground state properties of a few systems of particles interacting through certain typical potentials and obeying Fermi-Dirac or Bose-Einstein statistics are studied.

§ 1. Introduction

In an earlier paper (hereafter referred to as I) the binary collision method of Lee and Yang was applied to investigate the equilibrium properties of a system of particles interacting through the Herzfeld potential, viz. a hard repulsive core surrounded by an attractive square well. It was found that, to the second order of approximation, the final expressions for the various quantities pertaining to the system could be written down explicitly in terms of the phase shift corresponding to the interparticle potential. In view of this result one feels inclined to expect that the same situation might hold in the case of still more realistic potentials provided that they conform to certain plausible conditions such as were imposed on the parameters of the potential considered in I.

In this connection it appears worthwhile to mention that Pais and Uhlenbeck, in their recent investigation of the virial coefficients of a quantum-mechanical system of interacting particles, obtained results consistent with this expectation when they considered interactions which do not lead to the formation of two-body bound states.

In the present paper we have investigated the case of a system of particles interacting through a two-body potential of an 'arbitrary' form. The various parameters of the potential, however, are subject to the conditions that (i) the interaction between a pair of particles is not strong enough for a bound state to form and (ii) the kinetic energy of relative motion of two particles is much smaller than the potential energy of their mutual interaction on a close approach.

* Senior Research Fellow of the National Institute of Sciences of India.

** It is obvious that at low temperatures this condition is quite generally satisfied; for high temperatures, however, it does become a definite restriction on the potential.
These two conditions are not incompatible with each other; in practice, cases do occur where both of them are simultaneously satisfied. The solution of this generalized problem does not appear to be a straightforward one, for the simple reason that the form of the potential energy term $V(r)$ is left quite arbitrary. We have, however, rendered the problem amenable to a comparatively simple treatment by adopting the following recipe.

Since the solutions of the two-particle Schrödinger wave equation, from which the relevant binary kernel is obtained, depend explicitly on the function $V(r)$ itself and not on its derivatives, the various results obtained by making use of these solutions would not be materially affected if we replace the actual potential by one that takes precisely the same values at the various points of the interparticle range as the actual one does; as regards the first derivative, the two potentials might agree just to the extent of a 'smoothed out' value thereof. One may, for instance, consider a potential consisting of a finite number of suitable steps of the square-well type, solve the problem in terms of that and thereafter take the limit of this procedure to an infinitely large number of steps in such a way that this (artificial) potential simulates the real one satisfactorily. It is quite likely that the final results, up to a certain order, turn out to be insensitive to the finer details of the function $V(r)$, i.e. they depend merely on a certain physical parameter which represents the interparticle potential in an overall manner. It is found that this indeed is the case with the problem investigated here.

In order to make a smooth transition from the procedure of our earlier paper to the one indicated in the preceding paragraph, it appears worthwhile to consider first the case of a potential consisting of two steps of the square-well type. This is done in § 2. Next, in § 3, the treatment is extended to the case of a multi-step potential. We find that in each case the final results, to the order $\langle a/\hbar \rangle^2$, depend directly on the phase shift corresponding to the potential considered—a result which on grounds of plausibility was already expected. Once this is established the problem of determining the thermodynamical properties of a system of interacting particles reduces simply to that of evaluating the corresponding phase shift which, as is well known, can be obtained in a straightforward manner from the asymptotic solution of the radial part of the two-body wave equation.

In § 4, we have discussed the properties of a few systems consisting of particles interacting through different types of potentials. A comparative study of these cases is made with the help of graphical representation of certain quantities such as the zero-point energy, the zero-point pressure, etc., both for a system of fermions with spin half and for a system of bosons with spin zero.

An extension of the binary collision method to many-body systems consisting of particles of more than one type has been carried out and is being reported shortly.
§ 2. Binary kernel for a double-step square-well interaction

We consider a system of $N$ identical particles interacting pair-wise through a double-step square-well potential

$$V(r) = +\infty \quad \text{for } r \leq a,$$
$$= -\epsilon_1 \quad \text{for } a < r \leq g_1 a,$$
$$= -\epsilon_2 \quad \text{for } g_1 a < r \leq g_2 a,$$
$$= 0 \quad \text{for } g_2 a < r,$$

(1)

where $r$ is the interparticle distance, $\epsilon_1$ and $\epsilon_2$ the respective depths of the two wells, $a$ the diameter of the hard core and $g_1$ and $g_2$ certain numbers which specify the positions of the interfaces between the various potential regions; $(g_2 > g_1 > 1)$. We assume that the depths and the widths of the potential wells are such that the formation of two-body bound states is not possible. The radial part of the wave function corresponding to the two-body continuum states is readily obtained by solving the relevant Schrödinger equation. One obtains for the $S$-state ($l=0$)

$$R_k(r) = 0 \quad \text{for } r \leq a,$$
$$= A_1 \sin \nu_1 (r-a_1) \quad \text{for } a < r \leq g_1 a,$$
$$= A_2 \sin \nu_2 (r-a_2) \quad \text{for } g_1 a < r \leq g_2 a,$$
$$= \sin k(r-a_3) \quad \text{for } g_2 a < r,$$

(2)

where

$$\nu_i^2 = \Delta_i^2 + k^2, \quad \Delta_i = (\epsilon_i/2)^{1/2}; \quad i = 1, 2.$$

(3)

We further assume, as was done in I, that $(k/\Delta_i) \ll 1$. Thus

$$\nu_i \cong \Delta_i. \quad (3')$$

We follow here, in all essential details, the notation of I. Eqs. (1)–(8) of that paper hold equally well for the present one.

** See Eqs. (8) and (11)–(13) of I.
From the last two equations it is clear that the magnitude of the amplitude $A_1$ or $A_2$ is much less than unity and is in fact of the order $k a^2$ ($\cdot \cdot a = O(1)$). This is so because the states being considered here belong to the continuum; the probability amplitude for the two particles to be so close to each other as to fall into the attractive well should consequently be small. This situation reflects itself very clearly when we calculate the various contributions to the binary kernel arising from the different regions of the $(r', r)$-domain.

Next, we evaluate the matrix elements of the binary kernel $B(\beta ; 1, 2)$ for a pair of particles belonging to the system under investigation. We follow exactly the same procedure as in I and write

$$\langle k'_1, k'_2 | B | k_1, k_2 \rangle = \frac{\partial}{\partial k} \langle k'_1, k'_2 | U_2 | k_1, k_2 \rangle + E' \langle k'_1, k'_2 | U_3 | k_1, k_2 \rangle, \quad (7)$$

where

$$\langle k'_1, k'_2 | U_2 | k_1, k_2 \rangle = (8\pi^3)^{-1} \exp \left\{-i \left( k'_1 \cdot r'_1 + k'_2 \cdot r'_2 - k_1 \cdot r_1 - k_2 \cdot r_2 \right) \right\} \times \langle r'_1, r'_2 | U_3 | r_1, r_2 \rangle d^3 r'_1 d^3 r'_2 d^3 r_1 d^3 r_2. \quad (8)$$

Here

$$\langle r'_1, r'_2 | U_3 | r_1, r_2 \rangle = 8^{3/2} i^{-3} \exp \left[ - \left( (r'_1 + r'_2 - r_1 - r_2)^2 / 8\beta \right) \right] \times (2\pi r')^{-3} [I_{\text{real}} - I_{\text{ideal}}], \quad (9)$$

where

$$r' = |r'_1| = |r'_2 - r'_1|, \quad r = |r| = |r_1 - r_2|,$$

$$I_{\text{real}} = \int_0^a dk \exp (-2\beta k^2) \{ R_k (r') R_k (r) \}, \quad \text{real} \quad (10)$$

and

$$I_{\text{ideal}} = \int_0^a dk \exp (-2\beta k^2) \{ R_k (r') R_k (r) \}, \quad \text{ideal}. \quad (11)$$

Substituting (9), (10) and (11) in (8) and carrying out integrations over the
centre-of-mass coordinates \((r'_1 + r'_2)/2\) and \((r_1 + r_2)/2\) and over the directions of the relative coordinates \(r'\) and \(r\), we are left with

\[
\langle k'_1, k'_2 | U | k_1, k_2 \rangle
\]

\[
= (\pi^3 k' k)^{-1} \delta^3 (k'_1 + k'_2 - k_1 - k_2) \exp \{-\beta/2 |k_1 + k_2|^3\}
\]

\[
\times [F_{\text{real}} - F_{\text{ideal}}],
\]

where

\[
k' = \frac{1}{2} |k'_1 - k'_2|, \quad k = \frac{1}{2} |k_1 - k_2|
\]

and

\[
F = \iint_{0}^{\infty} \sin k' r' \sin k r \ I(r', r) \ dr' \ dr.
\]

For the corresponding ideal system, we have

\[
R_k(r) = \sin kr \quad \text{for all } r.
\]

Consequently one obtains from Eq. (11)

\[
I_{\text{ideal}} = (1/4) (\pi/2\beta)^{1/n} \left[ \exp \{- (r' - r)^2/8\beta\} - \exp \{- (r' + r)^2/8\beta\} \right],
\]

which, on substitution in Eq. (13), gives, after integration over \(r'\) and \(r\) is carried out, the appropriate expression for \(F_{\text{ideal}}\).

For the real system, on the other hand, the relevant expressions for the function \(R_k(r)\), for various ranges of the values of \(r\), are given by Eqs. (2)–(6). However, in the \(r', r\)-domain we have to consider separately the following four classes into which the various regions of this domain can be grouped:

(i) When at least one of the two variables \(r'\) and \(r\) is in the region of the hard core; we have in this case seven contributions to \(F_{\text{real}}\) and all of them are identically zero.

(ii) When each one of the two variables \(r'\) and \(r\) is in one or the other of the two wells; we have here four contributions to \(F_{\text{real}}\) and they are found\(^{1}\) to be each of the order \(a^2\).

(iii) When one of the variables \(r'\) and \(r\) is in one of the two wells while the other is in the potential-free region; we have in this case again four contributions to \(F_{\text{real}}\) which are found to be each of the order \(a^3\).

(iv) When both the variables are in the potential-free region; it is in this

\(^{1}\) This is seen on the basis of considerations similar to the ones employed in the appendix of I.

\(^{2}\) Here, and throughout in the sequel, the expression 'of the order \(a^n\)' is understood to mean 'of the order \((a/\lambda)^n\)' where \(\lambda\) is the mean thermal wavelength of the particles.
case that the contribution to $F_{\text{real}}$ is of the order $a$.

Since, in the present investigation, we do not propose to go beyond the order $a^2$, we have to consider only the last mentioned region of the $(r', r)$-domain. This gives

$$F_{\text{real}} = \left(\frac{1}{4}\right) \frac{(\pi/2)^{1/2}}{\sin k'r' \sin kr} \int_{g_a}^{\infty} \exp\left\{-(r'-r)^2/8\beta\right\} dr' dr.$$

(16)

Carrying out the integration, we obtain to the second order in $a$ (see the Appendix),

$$F_{\text{real}} - F_{\text{ideal}} = \frac{\pi}{2} k'k (k'^2 - k^2)^{-1} g_a a \left\{ \exp(-2\beta k'k) - \exp(-2\beta k^2) \right\}$$

$$- \frac{2}{\pi^{1/8}} g_a a \left\{ k'M(\sqrt{2\beta k}) \exp(-2\beta k'^2) - kM(\sqrt{2\beta k}) \exp(-2\beta k^2) \right\},$$

(17)

where

$$M(y) = \int_{0}^{y} \exp(x^2) dx.$$

(18)

It is remarkable that the foregoing result (17) does not depend explicitly on the quantity $g_2$. Substituting (17) in (8') one gets, to the same order,

$$\langle k_1', k_2'|U_2|k_1, k_2 \rangle$$

$$= \frac{2\pi^2 (k'^2 - k^2)^{-1}}{\beta^2} \delta^2 (k_1' + k_2' - k_1 - k_2)$$

$$\times g_a a \left\{ \exp(-\beta E') - \exp(-\beta E) \right\}$$

$$- \frac{2}{\pi^{1/8}} g_a a \left\{ k'M(\sqrt{2\beta k}) \exp(-2\beta k'^2) - kM(\sqrt{2\beta k}) \exp(-2\beta k^2) \right\},$$

(19)

where

$$E' = k_1'^2 + k_2'^2 \text{ and } E = k_1^2 + k_2^2.$$

From Eqs. (7) and (19), one readily obtains for the binary kernel

$$\langle k_1', k_2'|B|k_1, k_2 \rangle$$

$$= -\delta^2 (k_1' + k_2' - k_1 - k_2) \pi^{-2} \exp(-\beta E)$$

$$\times g_a a \left\{ 1 - \frac{2}{\pi^{1/8}} g_a a \left( kM(\sqrt{2\beta k}) - (8\beta)^{-1/2} \exp(2\beta k^2) \right) \right\},$$

(20)
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correct to the second order in \( a \).

A comparison of expressions (19) and (20) with the corresponding ones for the case of hard-sphere interaction (Eqs. (67) and (71) of reference 2)) and square-well interaction (Eqs. (24) and (28) of I) clearly shows that, to the second order in \( a \), the final results depend directly on the phase shift that arises from the interparticle potential. In the present case the phase shift \( \gamma_0 \) for the \( S \)-wave is given by \(-ka_0 \) or \(-ka_0' \) (see Eqs. (2) and (4)) and it is precisely this quantity which, for our purpose, fully represents the actual potential. It may, however, be mentioned that \( g_0' \) is the scattering length for the potential under consideration.

§ 3. Binary kernel for a multi-step square-well interaction

We now extend the foregoing treatment to the case of a generalized potential consisting of a number of rectangular steps, bounded on one side by a hard core and on the other side by a potential-free region:

\[
V(r) = +\infty \quad \text{for} \quad r \leq a,
\]

\[
= -\epsilon_s \quad \text{for} \quad g_{s-1}a < r \leq g_se, \quad \text{for} \quad g_{s-1}a < r \leq g_se a,
\]

\[
(s = 1, 2, \ldots, n; \quad g_0 = 1)
\]

\[
= 0 \quad \text{for} \quad g_se a < r. \quad (21)
\]

Here again we assume that the various parameters of the potential, though otherwise arbitrary, are such that two-body bound states do not form. We then have, corresponding to expressions (2) of the previous case,

\[
R_k(r) = 0 \quad \text{for} \quad r \leq a,
\]

\[
= A_s \sin \nu_s (r-a_s) \quad \text{for} \quad g_{s-1} a < r \leq g_s a,
\]

\[
(s = 1, 2, \ldots, n; \quad g_0 = 1)
\]

\[
= \sin k (r-a_{s+1}) \quad \text{for} \quad g_se a < r, \quad (22)
\]

where

\[
\nu_s^2 = \Delta_s^2 + k^2, \quad \Delta_s = (\epsilon_s/2)^{1/2}; \quad s = 1, 2, \ldots, n. \quad (23)
\]

Assuming the various depths to be such that

\[
(k/\Delta_s) \ll 1 \quad \text{for all} \quad s,
\]

we have

\[
\nu_s \ll \Delta_s. \quad (23')
\]

Applying the conditions of continuity, at the various interfaces between the different potential regions, of the wave function and of its first derivative, one gets in view of (23')
\[ a_s = a \left[ g_{s-1} - \frac{1}{ad_s} \tan^{-1} \left( \frac{d_s}{d_{s-1}} \tan \theta_{s-1} \right) \right] \]
\[ = ag'_{s-1}; \ s = 1, 2, \ldots, n \] (24)

and

\[ a_{n+1} = a \left[ g_n - \frac{1}{ad_n} \tan \theta_n \right] \]
\[ = ag'_n, \] (25)

where

\[ \theta_s = d_s (g_s - g'_{s-1}) a; \ s = 1, 2, \ldots, n. \]

Obviously, we have for the first interface \( a_1 = a \), hence \( g'_0 = 1 \). Further, we also find that, under the approximation (23'),

\[ A_{s-1} = A_s d_s \left( d_s^2 \sin^2 \theta_{s-1} + d_{s-1}^2 \cos^2 \theta_{s-1} \right)^{-1/2}; \]
\[ s = 2, 3, \ldots, n \] (26)

and

\[ A_n = (k/d_n) \sec \theta_n, \] (27)

which show that the various \( A_s \) are all of the same order, viz. \((ka)\), i.e. much less than unity.

We now calculate the matrix elements of the operators \( U_\alpha \) and \( B \) in the present case. Following the same procedure as before, we first note that in the \((r', r)\)-domain, we are to deal with \((n+2)^2 \) different regions which can be grouped into the four classes, (i)–(iv), in the same manner as was done in § 2. In class (i) we have \((2n+3)\) contributions which all vanish identically; in class (ii) we have \(n^3\) contributions, each of the order \((a^3)\); in class (iii) we have \(2n\) contributions each of the order \((a^3)\) and finally in class (iv) we have a single contribution that gives results of the order \(a\). We have therefore to consider only the last contribution; this gives for \( F_{\text{real}} \) an expression of the same form as (16), except that the quantities \( g_2 \) and \( g_3' \) are replaced by \( g_n \) and \( g_n' \) respectively. For \( F_{\text{ideal}} \), however, we have the same expression as before. The final expressions for \( \langle k_1', k_2' | U_\alpha | k_1, k_2 \rangle \) and \( \langle k_1', k_2' | B | k_1, k_2 \rangle \) therefore turn out to be exactly the same as we have in (19) and (20), except that again \( g_3' \) gets replaced by \( g_n' \). A reference to Eqs. (22) and (25) shows that in the present case too the final results, to the second order of approximation, depend exclusively on the phase shift corresponding to the actual interparticle potential.

Once this result is established, we can immediately apply it to the case of any real potential operating between the particles, provided that it satisfies the conditions mentioned above. This can be done on the basis of the consideration that any real potential, whatever its mathematical form may be, can always be
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represented, as closely as we like by a chain of rectangular steps whose heights and widths are suitably chosen. The foregoing treatment would remain valid even when we take the limiting case of an infinitely large number of steps. Actually, as we increase the number of steps, the wave equation and its solutions come closer and closer to those appropriate to the actual case. In the limit, although the actual slope of the potential curve at various points is still either zero or infinite, its mean value (taken in a suitable manner) would finally approach the actual one. It appears therefore quite legitimate to carry out such a limiting process. This becomes all the more justifiable because of the result obtained above that, to the order ($a^2$), the final results depend exclusively on the phase shift and not on the detailed form of the potential. Therefore, in order to study the thermodynamical properties of a many-body system to this order of approximation, one may take the relevant phase shift as the sole representative of the interparticle potential.

It may be pointed out that in the limit of an infinitely large number of steps the condition (23') will no longer be valid for those steps which are on the outer portions of the attractive part of the potential. We note, however, that the error introduced by this will finally be of no practical significance if this condition holds for the average depth of the attractive part.

§ 4. Thermodynamical properties at absolute zero

We now study the ground state properties of a few systems in which the constituent particles interact through certain specified potentials. For this purpose we require in each case the relevant expression for the phase shift, in the $S$-wave, appropriate to the potential under study. We shall take for the sake of illustration and intercomparison, apart from the simplest case of hard spheres, the following four potentials:

(i) A hard core followed by a single step of the square-well type, viz. the Herzfeld potential.
(ii) A hard core followed by two steps of the square-well type.
(iii) A hard core followed by an attractive part of the exponential type.
(iv) A hard core followed by a single step of the square-well type and a subsequent attractive part of the exponential type.

Phase shifts for the first two potentials are already available from the preceding sections. In order to determine those for the remaining ones we first investigate the case (iv); the result for (iii) will be readily obtainable from that for (iv).

We now consider the interparticle potential corresponding to the case (iv):

*) It may be added here that, within the limit of approximation considered, the process of going over to a continuous potential appears fully justified on physical grounds. A critical mathematical analysis of this transition, however, is still called for.
\[ V(r) = \begin{cases} +\infty & \text{for } r \leq a, \\ -\varepsilon_0 & \text{for } a < r \leq ga, \\ -\varepsilon_0 \exp\left\{ -\alpha (r - ga)/a \right\} & \text{for } ga < r. \end{cases} \]  

(28)

Corresponding differential equation for the radial part of the two-body wave function is

\[ \frac{d^2R}{dr^2} + \left\{ 2k^2 + V(r) \right\} R = 0, \]

(29)

where we have put

\[ E_0 = 2k^2. \]

Substituting (28) in the foregoing equation and solving separately for the three regions of the potential, we get for the radial function (yet to be normalized)

\[ R_k(r) = \begin{cases} 0 & \text{for } r \leq a, \\ A \sin \nu (r - a) & \text{for } a < r \leq ga, \\ J_1(x) + BJ_{-1}(x) & \text{for } ga < r, \end{cases} \]

(30)

where

\[ \nu = (\Delta_0^2 + k^2)^{1/2}; \quad \Delta_0 = (\varepsilon_0/2)^{1/2} \]

(31)

and \( J_{\pm l}(x) \) are Bessel functions of imaginary orders \( \pm l \); \( l \) and \( x \) are given by

\[ l = 2kai/\alpha \quad \text{and} \quad x = (2\Delta_0a/\alpha) \exp\left\{ -\alpha (r - ga)/2a \right\}. \]

(32)

Applying the conditions of continuity of the wave function and of its first derivative at \( r = ga \) and taking the asymptotic form of the wave function, \( \nu \rightarrow \infty \), we obtain the following expression for the phase shift \( \gamma_0 \):

\[ \gamma_0 = \frac{ka}{\varepsilon_0} \left\{ g + (2/\alpha) \ln (\Delta_0a/\alpha) \right\} \]

\[ + \frac{1}{2i} \ln \left[ \frac{\Gamma(1+l)}{\Gamma(1-l)} \right] \frac{(2\nu a/\alpha) \cot \theta \cdot J_0(2\Delta_0a/\alpha) - l J_0(2\Delta_0a/\alpha) - (2\Delta_0a/\alpha) J_1(2\Delta_0a/\alpha)}{(2\nu a/\alpha) \cot \theta \cdot J_{-1}(2\Delta_0a/\alpha) - l J_{-1}(2\Delta_0a/\alpha) - (2\Delta_0a/\alpha) J_{-1}(2\Delta_0a/\alpha)} \right], \]

(34)

where \( l \) was defined in (32). Since we are working under the condition \( ka \ll 1 \), we may expand the logarithmic term in (34) as a Maclaurin series in \( ka \) or, what is the same thing, in \( l \) and retain only the first order term.\(^{*}\) One obtains, after a little algebra that involves the use of certain properties of the Bessel functions and the Gamma functions, the following result:

\(^{*}\) In this expansion the second order term, beyond which we do not propose to go in the present investigation, identically vanishes. This is because of the simple reason that the logarithmic term in question is an odd function of \( l \).
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\[ 
\gamma_0 = -\alpha a \left[ g + \frac{1}{\alpha} \left\{ 2 \ln \left( \frac{\Delta_0 a}{\alpha} \right) - 2Z'(1) \right\} \right], 
\]

where

\[ Z'(1) = \left\{ \frac{\partial}{\partial x} \ln \Gamma'(1 + x) \right\}_{x=0} = -0.5772; \]

\( \theta \), as before, is equal to \( \Delta_0 (g-1)a \), while \( Y_0 \) and \( Y_1 \) are Weber's functions of order 0 and 1 respectively.

Having obtained the desired expression for the phase shift corresponding to the potential (iv), we readily obtain one for the potential (iii). This is done by making the square well in (iv) (see Eq. (28)) disappear by letting \( g \to 1 \). Consequently \( \gamma \to 0 \) and \( \cot \theta \to \infty \) in the manner \( 1/\theta \). Expression (35) then becomes

\[ \gamma_0 = -\alpha a \left[ 1 + \frac{1}{\alpha'} \left\{ 2 \ln \left( \frac{\Delta_0 a}{\alpha'} \right) - 2Z'(1) - \pi \frac{Y_0(2\Delta_0 a/\alpha')}{J_0(2\Delta_0 a/\alpha')} \right\} \right], \]

where parameters \( \alpha \) and \( \Delta_0 \), in this limiting case, have been specified by primed symbols.

We are now in a position to study the thermodynamical properties of the various systems introduced above. In order to make a semi-quantitative comparison of the different potentials we must choose the various parameters characterizing them in a certain consistent manner. In the present study we have made this choice (partially) by imposing the semi-empirical condition (see reference 4), § 3.9) that the areas under the attractive parts of the various potential curves are equal. By arranging this, one expects that the mean depth and the effective range, taken together, of the various potentials have been so chosen that the differences in the final results would now arise mainly due to the differences in their mathematical form. In order to remove further the ambiguity still left in selecting the various parameters, we again follow the choice made by earlier workers (see reference 4), § 3.5). Thus, for a fixed value of the depth \( \epsilon_{0}' \) of the exponential potential (iii) we choose for the single-step square-well potential (i), \( \epsilon = 0.56 \epsilon_{0}' \). Further, for the potential (i) we take the width of the well \( (g-1)a=0.8a \), while \( a \), the diameter of the hard core, is taken to be the same for all the potentials studied here. Our condition of equal areas, when applied to the potentials (i) and (iii), then fixes the value of \( \alpha' \) for the latter at 2.23.

For the double-step potential (ii), see Eq. (1), we choose

\[ g_1 = 1.5, \quad g_2 = 2.2; \]
\[ \epsilon_1 = \frac{12}{11} \epsilon, \quad \epsilon_2 = \frac{4}{11} \epsilon; \]

here \( \epsilon \) is the depth chosen for the single-step potential. Finally, for the potential (iv), see Eq. (28), we take

\[ g = 1.25 \quad \text{and} \quad \epsilon_0 = \frac{4}{3} \epsilon, \]

whence the condition of equal areas fixes the value of \( \alpha \) at 2.86.

The four potentials being considered here are shown diagramatically in Fig. 1 where the various dimensions are drawn to scale. A perusal of the

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Fig. 1. A sketch of the various interparticle potentials, \( V(r/a) \), considered. Here, \( a \) stands for the hard-core diameter which is taken to be common to all the potentials. For the attractive parts we have the notation:

- Single-step square-well: 
- Double-step square-well: 
- Exponential: 
- Single-step followed by an exponential part:

The general shape of these curves clearly shows that the overall effectiveness of the attractive parts of these potentials is most pronounced in the case of the simple exponential type and least pronounced in the case of the single-step square-well type, whereas for the other two potentials the overall effectiveness of the attractive part is intermediate. This reveals itself very prominently when we study the corresponding scattering lengths \( g' a \). The respective values of the quantity \( g' \), as computed from the relevant equations given above, are plotted in Fig. 2. The abscissa in this figure is the parameter \( \theta \) which, by virtue of its defining relation
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\[ \theta = \{(g-1) \Delta a\}_\text{square well} \]
\[ = 0.8 (\epsilon/2)^{1/2} a, \]

is a measure of the depth \( \epsilon \) of the square well. Thus, to each value of \( \theta \) there corresponds a definite value of \( \epsilon a^2 \), whence we can fix the values of \( \epsilon_1 a^2, \epsilon_2 a^2, \epsilon_3 a^2 \) and \( \epsilon_4 a^2 \) required for the determination of the scattering lengths for the other potentials. In this manner we compute for all the four potentials the values of \( g' \) as a function of the parameter \( \theta \). The value of this quantity in the case of a pure hard-core potential is equal to unity. A comparative study of the various curves brings out clearly the relative effectiveness of the attractive parts of these potentials. It may be pointed out here that beyond a certain value of the parameter \( \theta \), which is different for different potentials, \( g' \) becomes negative, i.e. the phase shift becomes positive. This represents the situation where the attractive part of the potential becomes dominant over the hard core. Some of the subsequent expressions give, in this case, unphysical results, the reason for which is not clearly understood by the authors. In the present investigation, therefore, discussion is confined only to those situations for which \( g' \) is positive.

We have plotted in Figs. 3, 4 and 5 the values of the following thermodynamical quantities, pertaining to a Fermi-Dirac system (at \( T=0 \)°K) of particles with spin half, as functions of the parameter \( \rho a^3 (\rho = N/\Omega, \text{the particle density}) \):

![Fig. 2. Variation of the factor \( g' \) with the parameter \( \theta \), defined in the text. Otherwise as in Fig. 1.](image-url)
\[ \frac{p}{p_{\text{ideal}}} = 1 + \frac{5}{3} (3\pi)^{1/3} g' (\rho a^3)^{1/3} + \frac{8}{21} (11 - 2 \ln 2) (3/\pi)^{2/3} g' (\rho a^3)^{2/3}, \quad (39) \]

\[ \frac{E - E_{\text{ideal}}}{2\pi \rho a} = g' \left[ 1 + \frac{6}{35} (11 - 2 \ln 2) (3/\pi)^{1/3} g' (\rho a^3)^{1/3} \right] \quad (40) \]

and

\[ \frac{\delta E_F}{4\pi \rho a} = g' \left[ 1 + \frac{11 - 2 \ln 2}{5} (3/\pi)^{1/3} g' (\rho a^3)^{1/3} \right], \quad (41) \]

where \( p \) is the equilibrium pressure, \( E \) the energy per particle and \( \delta \) the increase in the energy content of the system arising from the introduction of one more particle into it, i.e., the chemical potential. The quantity \( E_F \) here is the Fermi energy given by

\[ E_F = (3\pi^2 \rho)^{2/3}. \]

For each of the three quantities given by (39), (40) and (41) curves are plotted for all the four potentials, (i) to (iv), and for three different values of the parameter \( \theta \), viz. 20°, 40° and 53° 36’. Results for the case of hard spheres

![Graph](https://academic.oup.com/ptp/article-abstract/27/6/1085/1906643/1061-9966-43)

Fig. 3. Variation with \( \rho a^3 \) of the ratio of the zero-point pressure of a Fermi-Dirac system of interacting particles, with spin half, to that of a similar system of free particles. Sets I, II and III correspond to three values of the parameter \( \theta \), viz. 20°, 40° and 53° 36’ respectively. Otherwise as in Fig. 1.
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Fig. 4. Variation with $\rho a^3$ of the difference between the mean zero-point energy per particle of a Fermi-Dirac system of interacting particles, with spin half, and the corresponding quantity for a similar system of free particles. Otherwise as in Fig. 3.

Fig. 5. Variation with $\rho a^3$ of the quantity $(\beta - E_F)/4\pi \rho a$, defined in the text, for a Fermi-Dirac system of interacting particles with spin half. Otherwise as in Fig. 3.
(g' = 1) are also included. By a comparative study of the various curves, one can appreciate quite clearly the effect of the particle interactions, especially of the attractive parts thereof, on the various thermodynamical properties of the assembly under consideration. The salient features of these curves, as regards their dependence on the form of the potential of the two-particle interaction, are self-explanatory.

Next, we have plotted in Figs. 6, 7 and 8 the values of the following thermodynamical quantities, pertaining to a Bose-Einstein system (at T = 0 °K) of particles with spin zero, as functions of the parameter \( \rho a^3 \):

\[
\frac{p}{4\pi \rho^2 a} = g' \left[ 1 + \frac{64}{5\pi^{1/2}} (g'^3 \rho a^3)^{1/2} \right],
\]

(42)

\[
\frac{E}{4\pi \rho a} = g' \left[ 1 + \frac{128}{15\pi^{1/2}} (g'^3 \rho a^3)^{1/2} \right]
\]

(43)

and

\[
\delta/8\pi \rho a = g' \left[ 1 + \frac{32}{3\pi^{1/2}} (g'^3 \rho a^3)^{1/2} \right],
\]

(44)

![Fig. 6. Variation with \( \rho a^3 \) of the zero-point pressure of a Bose-Einstein system of interacting particles with spin zero. Otherwise as in Fig. 3.](image1)

![Fig. 7. Variation with \( \rho a^3 \) of the zero-point energy per particle of a Bose-Einstein system of interacting particles with spin zero. Otherwise as in Fig. 3.](image2)
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where the various symbols have their usual meaning. Again, for each of the three quantities given by Eqs. (42), (43) and (44) curves have been plotted for all the four potentials considered above and for all the three values of \( \theta \) taken earlier. Corresponding curves for the case of hard spheres are also included. The relative influence of the attractive parts of the various potentials on the physical properties of the system under study is brought out clearly in these figures.

Fig. 8. Variation with \( \rho a^3 \) of the quantity \( \delta \beta \pi a \), defined in the text, for a Bose-Einstein system of interacting particles with spin zero. Otherwise as in Fig. 3.

Appendix

We outline, in this appendix, the derivation of expression (17) of the text. One has from Eqs. (13), (15) and (16)

\[
F_{\text{real}} - F_{\text{ideal}} = \frac{1}{4} (\pi/2\beta)^{1/2} 
\times \left[ \int_0^{\infty} \int_0^{\infty} \sin k'r' \sin kr \left\{ \exp \left[ -\frac{(r'-r)^2}{8\beta} \right] - \exp \left[ -\frac{(r'+r-2g_4a)^2}{8\beta} \right] \right\} dr'dr 
- \int_0^{\infty} \int_0^{\infty} \sin k'r' \sin kr \left\{ \exp \left[ -\frac{(r'-r)^2}{8\beta} \right] - \exp \left[ -\frac{(r'-r)^2}{8\beta} \right] \right\} dr'dr \right].
\]  

(1)

Since our interest in the present investigation lies in results up to the order \( a^2 \) only, we expand the right-hand side of (1), after making the transformation \( r' \to r' + g_4a \) and \( r \to r + g_4a \) in the first integral, in the form of a Maclaurin series in \( a \). The main term in this expansion obviously vanishes whereas the next two terms are
\[
\frac{1}{4} \left( \frac{\pi}{2\beta} \right)^{1/2} a \int_0^\infty \int_0^\infty \left\{ \frac{g-g'}{2\beta} (r'+r) \sin k' r' \sin kr \exp\left[ -\frac{(r'+r)^2}{8\beta} \right] \right.
\]
\[+ g \left[ k \sin k' r' \cos kr + k' \cos k' r' \sin kr \right] \times \left[ \exp\left\{ -\frac{(r'-r)^2}{8\beta} \right\} - \exp\left\{ -\frac{(r'+r)^2}{8\beta} \right\} \right] \, dr' \, dr \quad (\text{II})
\]

and
\[
\frac{1}{4} \left( \frac{\pi}{2\beta} \right)^{1/2} a^2 \int_0^\infty \int_0^\infty \left[ \frac{(g-g')^2}{2\beta} \{4\beta - (r'+r)^2\} \sin k' r' \sin kr \exp\left[ -\frac{(r'+r)^2}{8\beta} \right] \right.
\]
\[+ g \frac{(g-g')}{\beta} (r'+r) \{ k \sin k' r' \cos kr + k' \cos k' r' \sin kr \} \exp\left[ -\frac{(r'+r)^2}{8\beta} \right] \]
\[+ g^2 \{2k' k \cos k' r' \cos kr - (k'^2 + k^2) \sin k' r' \sin kr \}
\]
\[\times \left\{ \exp\left[ -\frac{(r'-r)^2}{8\beta} \right] - \exp\left[ -\frac{(r'+r)^2}{8\beta} \right] \right\} \, dr' \, dr, \quad (\text{III})
\]

respectively. Evaluating (II) and (III) by elementary means we obtain the desired result.

References