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On the Quantum Theory of the Third Virial Coefficient

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The quantum theory of the third virial coefficient C is discussed. Three types of intermolecular pair forces must be distinguished. (1) No bound or low-lying two- and/or three-body states exist. The first four terms of the low-temperature expansion of C_{BE} are obtained. They depend on the scattering length, the effective range, and a third length which cannot be inferred from scattering data. The limitations of the applicability of such expansions are discussed, both for He^4 and He^3, by means of a comparison of the corresponding expansion for the second virial coefficient B with detailed numerical results known for specific potentials. (2) Existence of a near zero energy level both for the two- and the three-body system. It is shown how in this case the actual potentials may be replaced by suitably matched boundary conditions on the two- and the three-body wave functions near the respective coordinate origins. It is first explained how the method applies to B. Then the leading term of C is explicitly determined. (3) Existence of strongly bound two- and three-body states. An approximate expression for C is given by treating the single atoms and the binary and ternary compounds as a system of three ideal gases in chemical equilibrium.

I. INTRODUCTION

THE virial coefficients $B(T)$, $C(T)$, $\cdots$ are defined by the Kamerlingh Onnes virial expansion:

$$pV=RT\left[1+\frac{B(T)}{V}+\frac{C(T)}{V^2}+\cdots\right], \tag{1}$$

for the equation of state of a dilute gas. It is well known that in the classical theory, that is for high temperatures, the virial coefficients can be found explicitly in terms of the intermolecular forces. These expressions are simplest and most familiar when (a) the forces are additive and (b) the two-particle force is central, and these properties will also be assumed throughout the present work. For a discussion of the classical theory for special intermolecular potentials we refer to the review by Kihara.[1]

In the quantum theory, that is for sufficiently low temperatures, the picture is very much less complete. There exist explicit expressions for the first quantum mechanical corrections to the classical results,[2] but only for the *second* virial coefficient $B(T)$ is an exact expression known by means of which one can discuss the entire temperature range.[3] We will come back to this in Sec. III but it may be well to point out already here that this expression relates $B(T)$ to the discrete energy levels of the two-body system and to the phase shifts of the two-body continuum wave functions. The continuum part can thus be found in principle from scattering experiments.

In recent times the quantum theory of the nonideal gas has advanced considerably by the work of Lee, Yang, and their collaborators.[4,5] The methods these authors developed were applied by them mainly to the investigation of the low-temperature behavior of a dilute Bose-Einstein (BE) gas or a dilute Fermi-Dirac (FD) gas of hard spheres, but they have a wider validity of which the limits at present are still unclear.

Two aspects of the work of Lee and Yang are of particular interest for what follows: First, they showed how to relate the so-called cluster functions of a BE or an FD gas to the corresponding functions for a Boltzmann system (see also Sec. II). A second essential feature is their binary expansion method, in which one arrives at a formal reduction of the properties of an n-body Boltzmann system to the corresponding two-body system. A short review of this method, with some emphasis on the relation to the classical Ursell expansion, will be given in Sec. V. We only note here that, thus far, the influence of the existence of bound two- and/or more-body states on the binary expansion procedure has not been clarified.

The study of the binary expansion method led us to ask two questions, the answer to both of which is known where $B(T)$ is concerned: To what extent are the higher virial coefficients determined by two-body *scattering* data? Is it possible to discuss to some extent in which way these coefficients are affected by the existence of two- and/or more-body bound states? It is the purpose of this paper to analyze these questions specifically for the third virial coefficient $C(T)$.

It turns out that it is essential to distinguish three cases depending on the form of the intermolecular potential.

(α) *The case of repulsive forces.*—Assuming that the intermolecular force is purely repulsive, or if in addition some attraction is present, that the attractive force is so weak that *no* two- and/or three-body bound states or

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[1] T. Kihara, Revs. Modern Phys. **25**, 831 (1953); **27**, 412 (1955).

[2] See reference 1, Secs. 14–16.

[3] E. Beth and G. E. Uhlenbeck, Physica, **3**, 729 (1936); **4**, 915 (1937). See also B. Kahn, dissertation, Utrecht, 1938 (unpublished), Chap. IV.

[4] K. Huang and C. N. Yang, Phys. Rev. **105**, 767 (1957); Huang, Yang, and Luttinger, Phys. Rev. **105**, 776 (1957); T. D. Lee and C. N. Yang, Phys. Rev. **105**, 1119 (1957); Lee, Huang, and Yang, Phys. Rev. **106**, 1135 (1957).

[5] T. D. Lee and C. N. Yang, Phys. Rev. **113**, 1165 (1959).

low-lying virtual states exist, the method of Lee and Yang[5] can be applied and leads to a low-temperature expansion of $C(T)$. In Sec. VI the first four terms of this expansion are given; see Eq. (121). To this order the characteristic lengths of the two-body system which appear successively are: the scattering length a, the effective range r_0, and a third length d, which cannot be inferred from scattering data[6]; see Eq. (96).

(β) *The case of weak binding.*—Here we consider the situation when the attractive forces allow just one low-lying energy level (either real or virtual) both for the two-body and the three-body systems. More precisely, we mean by this that the energy levels in question are so close to zero that a temperature regime exists in which the ratio, binding energy over kT, is much less than one, while at the same time the ratio, range of the forces over the thermal wavelength $\lambda=h(2\pi mkT)^{-\frac{1}{2}}$, is also much smaller than one. We shall show in Sec. VII that in this case the leading term in C is of the form const$\times\lambda^6$, where the constant is independent of the precise shape of the intermolecular potential and can be determined by replacing the actual potential by a suitable boundary condition. The final result is given in Eq. (181).

(γ) *The case of strong binding.*—In this case we assume that two- and three-body bound states exist and that we are in a range of such low temperatures that the ratio of the binding energies to kT is much larger than one. Here the method of Lee and Yang[5] is not directly applicable. For this regime of binding, our results will be presented in Sec. VIII.

It is, of course, possible and also sometimes convenient to consider the above three cases for the second virial coefficient. However, for $B(T)$ all expansions can be obtained from the exact expression, whereas, to our knowledge, for $C(T)$ one has to start afresh for each of the three cases. Since the weak-binding case (where the leading term of B is of the form const$\times\lambda^3$) seemed of special interest to us, we shall give in Sec. IV a new derivation of the value of the constant, in which we do not start from the exact expression for $B(T)$, but also for B treat the problem as one with boundary conditions replacing the intermolecular potential.

The experimental validity of the low-temperature expansions of the virial coefficients is very probably quite limited. In this connection the isotherms of He^4 and He^3 are, of course, of special interest. Recently Keller[7] has made new measurements of the isotherms both for He^4 and He^3 at temperatures below 4°K, and there are also recent numerical calculations of $B(T)$ based on the Lennard-Jones (12,6) potential[8] and on the (exp,6) potential.[9] We will make some comments on these results in Sec. III. Here we only state that with regard to the third virial coefficient no dependable low-temperature data exist so far for He^4, as Keller has pointed out.[7] In the case of He^3 the same author gives experimental values for C at 3.8° and 3°K. However, as we shall see in Sec. VI, the binary expansion result for He^3 is already rather dubious at these temperatures. The practical usefulness, if any, of our results for $C(T)$ remains therefore to be seen, but we believe, at any rate, that the considerations which follow may be of some methodical interest.

II. GENERAL PRELIMINARIES

We recall that the virial coefficients can be expressed in terms of the so-called cluster functions b_l through the Mayer equations:

$$\frac{p}{kT}=\lim_{V\to\infty}\sum_{l=1}^{\infty} b_l(V,T)z^l,$$
$$\frac{N}{V}=\lim_{V\to\infty}\sum_{l=1}^{\infty} lb_l(V,T)z^l, \tag{2}$$

by elimination of z. For large volume V the $b_l(V,T)$ become independent of V and in the gas region the sum and the limit in (2) can be interchanged. Calling $b_l=\lim b_l(V)$ (we will always suppress the argument T), one obtains

$$B=-\frac{Nb_2}{b_1{}^2},\quad C=\frac{N^2}{b_1{}^4}(-2b_3b_1+4b_2{}^2),\text{ etc.} \tag{3}$$

The $b_l(V)$ are defined in terms of the trace of the l-body cluster operator U_l which in turn is expressed in terms of operators W_n, defined by

$$W_n=\exp(-\beta H^{(n)}),\quad \beta=1/kT, \tag{4}$$

where $H^{(n)}$ is the n-body Hamiltonian. One has

$$\begin{aligned}
&U_1(1)=W_1(1),\\
&U_2(1,2)=W_2(1,2)-W_1(1)W_1(2),\\
&U_3(1,2,3)=W_3(1,2,3)-W_2(1,2)W_1(3)\\
&\qquad -W_2(2,3)W_1(1)-W_2(3,1)W_1(2)\\
&\qquad\qquad +2W_1(1)W_1(2)W_1(3);
\end{aligned} \tag{5}$$

then

$$Vl!b_l(V)=\mathrm{Tr}(U_l). \tag{6}$$

All these definitions and relations hold irrespective of the statistics. The statistics enters *only* in the choice of

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[6] Lee and Yang have shown that the ground-state energy per particle of a dilute BE system of hard spheres with diameter a is given by $\epsilon=4\pi a\rho[1+128(\rho a^3)^{\frac{1}{2}}/15\pi^{\frac{1}{2}}+\cdots]$. By means of the methods of Sec. VI, it is easy to give a direct proof of the rather obvious fact that this formula for ϵ also holds for an arbitrary repulsive force, provided one replaces the hard-sphere diameter by the scattering length. We have also found that beyond this order, terms in the square bracket proportional to $\rho a^2 r_0$ and to ρd^3 must appear.

[7] W. E. Keller, Phys. Rev. **97**, 1 (1955): He^4; **98**, 1571 (1955): He^3.

[8] de Boer, van Kranendonk, and Compaan, Physica **16**, 545 (1950): He^3; J. E. and M. F. Kilpatrick, J. Chem. Phys. **19**, 1930 (1951): He^4; Kilpatrick, Keller, Hammel, and Metropolis, Phys. Rev. **94**, 1103 (1954): He^3 and He^4.

[9] Kilpatrick, Keller, and Hammel, Phys. Rev. **97**, 9 (1955): He^3 and He^4.

the l-particle states in the volume V (with prescribed boundary conditions on the surface of V) with respect to which the matrix elements of W_l and U_l are formed. We have:

(1) Boltzmann statistics,

$$\langle 1'\cdots N'|W_N|1\cdots N\rangle =\sum_i\psi_i(1'\cdots N')\psi_i^*(1\cdots,N)\exp(-\beta E_i^{(N)}); \quad (7)$$

(2) BE statistics,

$$\langle 1'\cdots N'|W_N^{\mathrm{BE}}|1\cdots N\rangle=N!\times\sum_{i,\mathrm{symm}}\psi_i(1'\cdots N')\psi_i^*(1\cdots,N)\exp(-\beta E_i^{(N)}), \quad (8)$$

(3) FD statistics: same as Eq. (8) but with a summation over antisymmetric states.

Of course, the operator W_N itself does not depend on the symmetry properties of the ψ's. However, it is convenient to hang a label BE or FD on W_N and likewise on U_l. Without labels the corresponding symbols shall always refer to the Boltzmann case. The arguments $1,\cdots,N$ of the ψ's in Eqs. (7), (8) refer to the coordinates and, where necessary, to the spins of the N particles. It may be recalled that Eqs. (2)–(6) hold true for arbitrary spin.

It has been observed by Lee and Yang[5] that W_N^{BE} and W_N^{FD} can be expressed in terms of the corresponding Boltzmann matrix elements W_N, as follows:

$$\langle 1'\cdots,N'|W_N^{\mathrm{BE}}|1\cdots N\rangle =\sum_{P'}P'\langle 1',\cdots,N'|W_N|1,\cdots,N\rangle, \quad (9)$$

$$\langle 1'\cdots,N'|W_N^{\mathrm{FD}}|1\cdots N\rangle =\sum_{P'}P'\epsilon_{P'}\langle 1',\cdots,N'|W_N|1,\cdots,N\rangle, \quad (10)$$

where P' is any one of the $N!$ operators that permute the variables $1',\cdots,N'$. $\epsilon_{P'}=+1(-1)$ if the permutation of the normal order is even (odd). Thus one has a scheme to go from U^{BE} to U which goes via the sequence

$$U^{\mathrm{BE}}\rightarrow W^{\mathrm{BE}}\rightarrow W\rightarrow U, \quad (11)$$

and similarly for FD. It turns out that the relation (11) between U^{BE} and U can be expressed most simply by means of quantities $\mathfrak{U}^S$ defined as follows:

$$(a_1,a_2,\cdots,a_l|\mathfrak{U}_l^S|1,2,\cdots l) =\sum_P P_i(a_1,\cdots,a_l|U_l|1,\cdots,l). \quad (12)$$

For example, one finds from Eqs. (9) and (12)

$$(1'|U_1^{\mathrm{BE}}|1)=(1'|\mathfrak{U}_1^S|1)=(1'|U_1|1), \quad (13)$$

$$\begin{aligned}(1'2'|U_2^{\mathrm{BE}}|1,2)&=(1',2'|\mathfrak{U}_2^S|1,2)+(2'|\mathfrak{U}_1^S|1)(1'|\mathfrak{U}_1^S|2)\\&=(1',2'|U_2|1,2)+(2',1'|U_2|1,2)\\&\quad+(2'|U_1|1)(1'|U_1|2),\end{aligned} \quad (14)$$

$$\begin{aligned}&(1'2'3'|U_3^{\mathrm{BE}}|123)\\&=(1'2'3'|\mathfrak{U}_3^S|123)+(1'3'|\mathfrak{U}_2^S|12)(2'|U_1|3)\\&\quad+(2'3'|\mathfrak{U}_2^S|12)(1'|U_1|3)+(2'3'|\mathfrak{U}_2^S|13)\\&\quad\times(1'|U_1|2)+(1'2'|\mathfrak{U}_2^S|13)(3'|U_1|2)\\&\quad+(1'3'|\mathfrak{U}_2^S|23)(2'|U_1|1)+(1'2'|\mathfrak{U}_2^S|23)\\&\quad\times(3'|U_1|1)+(2'|U_1|1)(3'|U_1|2)(1'|U_1|3)\\&\quad+(3'|U_1|1)(1'|U_1|2)(2'|U_1|3).\end{aligned} \quad (15)$$

A corresponding procedure can also be worked out for the FD case.[5]

We will adopt units for which $\hbar=1$ and the mass of the particle $m=\frac{1}{2}$; the thermal wavelength λ is then $(4\pi\beta)^{\frac{1}{2}}$. With these units

$$H^{(n)}=-\sum_{i=1}^{n}\Delta_i+\sum_{i<j}\Phi_{ij}, \quad (16)$$

where Φ_{ij} is the (central) two-body potential.

III. REVIEW OF THE QUANTUM THEORY OF $B(T)$

From Eqs. (4) and (6), one finds

$$b_1=\lim\frac{1}{V}\operatorname{Tr}(W_1)=\frac{1}{\lambda^3}, \quad (17)$$

$$b_2=\lim\frac{1}{2V}\Big[\sum_i\exp(-\beta E_i^{(2)})-\sum_i\exp(-\beta E_i^{(0)})\Big], \quad (18)$$

where $E_i^{(2)}$, $E_i^{(0)}$ are the energy states of the two-particle system, enclosed in V, with and without interaction, respectively. By separating the different angular momenta and the possible discrete states from the continuum states, Eq. (18) can be transformed into

$$b_2=\frac{2^{\frac{1}{2}}}{\lambda^3}\sum_{l=0}^{\infty}(2l+1)B_l, \quad (19)$$

$$B_l=\sum_n e^{\beta\epsilon_{nl}}+2\int_0^\infty dr\times\int_0^\infty dk\exp(-2\beta k^2)[R_{kl}^2(r)-R_{k,l}^{(0)2}(r)], \quad (20)$$

where ϵ_{nl} are the binding energies of the possible states for given l, and $R_{kl}(r)$, $R_{k,l}^{(0)}(r)$ are the radial wave functions, with and without interaction, for the relative motion of the two-body system. The normalization of these radial functions is so chosen that for $r\rightarrow\infty$

$$\begin{aligned}R_{kl}&\rightarrow\sin[kr-\tfrac{1}{2}l\pi+\delta_l(k)],\\R_{kl}^{(0)}&=(\pi kr/2)^{\frac{1}{2}}J_{l+\frac{1}{2}}(kr)\rightarrow\sin(kr-\tfrac{1}{2}l\pi).\end{aligned} \quad (21)$$

In Eq. (20) the integral over r can be carried out, and from Eqs. (3), (17), and (18) we obtain the final formula, always for Boltzmann statistics:

$$B=-2^{\frac{1}{2}}N\lambda^3\sum_{l=0}^{\infty}(2l+1)B_l,$$
$$B_l=\sum_n e^{\beta\epsilon_{nl}}+\frac{1}{\pi}\int_0^{\infty}dk\frac{d\delta_l}{dk}\exp(-2\beta k^2). \tag{22}$$

The generalization to BE or FD statistics is straightforward and also the influence of an intrinsic spin s of the particles is easily taken into account. One obtains

$$B_{\mathrm{BE}}{}^{(s)}=\frac{s+1}{2s+1}B_{\mathrm{BE}}+\frac{s}{2s+1}B_{\mathrm{FD}},$$
$$B_{\mathrm{FD}}{}^{(s)}=\frac{s+1}{2s+1}B_{\mathrm{FD}}+\frac{s}{2s+1}B_{\mathrm{BE}}, \tag{23}$$

where B_{BE} and B_{FD} refer to zero spin and are given by

$$B_{\mathrm{BE}}=-2^{\frac{1}{2}}N\lambda^3\Big[\tfrac{1}{8}+2\sum_{l\text{ even}}(2l+1)B_l\Big],$$
$$B_{\mathrm{FD}}=-2^{\frac{1}{2}}N\lambda^3\Big[-\tfrac{1}{8}+\sum_{l\text{ odd}}(2l+1)B_l\Big], \tag{24}$$

with B_l given in Eq. (22).

Since in this paper we are mainly interested in the very-low-temperature behavior of $B(T)$, and since we always will have the application to He^4 and He^3 in mind, the equations can be simplified by considering only S states, at most one discrete state and $s=0$ for BE (He^4), $s=\frac{1}{2}$ for FD (He^3). Then

$$B_{\mathrm{BE}}=-2^{\frac{1}{2}}N\lambda^3\big[\tfrac{1}{8}+2B_0\big],$$
$$B_{\mathrm{FD}}{}^{(\frac{1}{2})}=-2^{\frac{1}{2}}N\lambda_{\frac{1}{2}}{}^3\big[-\tfrac{1}{16}+\tfrac{1}{2}B_0\big],$$
$$B_0=e^{\beta\epsilon}+B_0{}';\quad B_0{}'=\frac{1}{\pi}\int_0^{\infty}dk\frac{d\delta}{dk}\exp(-2\beta k^2). \tag{25}$$

To account for the differences in the mass of He^3 and He^4 we have introduced in (25) two thermal wavelengths λ and $\lambda_{\frac{1}{2}}$. It is understood that the quantities ϵ and δ should be labeled correspondingly.

The most recent measurements of $B(T)$ for He^3 and He^4 at temperatures below 4°K are due to Keller.[7] The theoretical discussion, which was started by de Boer,[10] assumes an empirical potential $\Phi(r)$ with parameters adapted so as to represent the high-temperature behavior of $B(T)$. For instance, de Boer used the Lennard-Jones potential,

$$\Phi(r)=4\eta[(\sigma/r)^{12}-(\sigma/r)^6], \tag{26}$$

with parameters $\eta/k=10.2$°K, $\sigma=2.56$ A, but also other forms of the potential have been used. For a recent review of this work we refer to the report of de Boer[11] at the Kamerlingh Onnes Conference. We note that the numerical calculations based on potentials like (26) show that even at 1°K the D-state contributions in (22) are already appreciable. Since the lowest temperature for which B has been measured is 1.5°K, the validity of Eq. (25) and of the expansions for the three regimes of binding defined in the introduction is extremely limited. Nevertheless, these expansions may perhaps be useful as a check on numerical calculations.

(α) The Case of Repulsive Forces

Now the bound state term in B_0 is absent, while for δ we may use the expansion[12]

$$k\cot\delta=-\frac{1}{a}+\tfrac{1}{2}r_0k^2+O(k^4), \tag{27}$$

where a is the scattering length and r_0 the effective range. This leads to

$$B_0=2^{-\frac{1}{2}}\left[-\frac{a}{\lambda}+\frac{\pi}{\lambda^3}a^2(a-\tfrac{3}{2}r_0)+O(\lambda^{-5})\right], \tag{28}$$

which when inserted into Eq. (25) gives the low-temperature expansions for the B's. Note that only in the BE case the term $\sim 1/\lambda^3$ has meaning since D-states give an $O(\lambda^{-5})$ contribution. For the FD case one must stop at the first term in Eq. (28) unless the P-wave contribution is taken into account. Only for He^3 it seems certain that no discrete state exists, so that the expansion (28) might be tried. From $\delta(k)$, computed numerically[8] with the use of Eq. (16), it can be estimated[13] that for He^3, $a_{\frac{1}{2}}\cong -6.4$ A, which leads to

$$B(\mathrm{He}^3)=\left(+\frac{53.5}{T^{\frac{3}{2}}}-\frac{170}{T}+\text{const}\right)\ \mathrm{cm}^3/\text{mole}. \tag{29}$$

Thus for $T\to 0$, $B(\mathrm{He}^3)$ should go to $+\infty$. $B(\mathrm{He}^3)$ has been measured[7] at temperatures ranging from 3.8 to 1.5°K and all experimental values found in this interval are negative. Numerical computations of $B(\mathrm{He}^3)$, published both for Lennard Jones potentials[8] and for exp-six potentials,[9] go down to 0.3°K where $B(\mathrm{He}^3)$ is still negative. However, Keller has communicated to us unpublished numerical results obtained in collaboration with J. E. Kilpatrick and E. F. Hammel for $B(\mathrm{He}^3)$ at 0.1 and 0.2°K from which it is seen that at $\sim$0.1°K the $B(\mathrm{He}^3)$, for either type of potential, is still negative but begins to exhibit an upturn which presumably leads to positive values for $B(\mathrm{He}^3)$ at still lower temperatures.

It may further be noted that if one uses the first two terms of Eq. (29) only, one would get negative values

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[10] See the contribution of J. de Boer and R. B. Bird, in Hirschfelder, Curtiss, and Bird, *Molecular Theory of Gases* (John Wiley and Sons, Inc., New York, 1954).

[11] J. de Boer, Physica **24**, 90 (1958).

[12] See for instance J. Blatt and V. Weisskopf, *Theoretical Nuclear Physics* (John Wiley and Sons, Inc., New York, 1952), p. 62.

[13] J. de Boer (private communication).

for $B(\mathrm{He}^3)$ from $T \sim 0.1°\mathrm{K}$ on upward. However, de Boer has pointed out to us[13] that from temperatures as low as $\sim 0.05°\mathrm{K}$ on up the P-states contributions become quite important, so that the two term S-wave Eq. (29) does not have much meaning beyond that point. In that connection it is also interesting to quote a further unpublished result due to de Boer: using the potential (26) he finds that for wave numbers up to $\sim 0.2\ \mathrm{A}^{-1}$ the two-term formula (27) gives a reasonable account of the behavior of δ provided one takes $r_0 \cong 22.6$ A.

The large values of a and r_0 clearly show that for temperatures of, say, 1°K on up the expansion of $B(\mathrm{He}^3)$ of the type (27)–(29) must be very slowly, if at all, convergent. The scattering objects are so big that the regime of practical usefulness of the scattering length and effective range concepts is extremely limited. It will moreover become clear from the discussion of the weak-binding case, to which we turn next, that for He^4 the notion of scattering length is in fact meaningless for all practical purposes.

(β) The Weak-Binding (WB) Case

As was stated in the introduction, this regime is defined by the simultaneous conditions,

$$\beta\epsilon \ll 1, \quad \sigma/\lambda \ll 1, \tag{30}$$

where ϵ is the absolute value of the bound state, or the energy of the low-lying virtual state, whatever the case may be, and where σ is a measure for the range of the forces. In this case there is a well-known argument[3] which allows us to put

$$B_0 \cong \tfrac{1}{2}, \tag{31}$$

and which runs as follows: for a level close to zero, the corresponding wave function develops for very nearly a quarter wavelength up to the range of the forces. On the other hand, the phase shift δ starts from zero or π for $k=0$ if the level is virtual or real. Thus if we now entirely neglect the range of the forces, we may in first instance replace $d\delta/dk$ in Eq. (25) by $\pm\pi/2$ at $k=0$, where the plus (minus) sign corresponds to the virtual (real) case. Of course, the term $e^{\beta\epsilon}$ in B_0 is present only for the real case. Then Eq. (31) follows immediately. Substituting Eq. (31) into Eq. (25), one gets in the WB limit

$$B_{\mathrm{BE}} \cong -9N\lambda^3/2^{\frac{5}{2}}, \quad B_{\mathrm{FD}}{}^{(\frac{1}{2})} \cong -3N\lambda_{\frac{1}{2}}{}^3/2^{7/2}. \tag{32}$$

It is possible to refine this result somewhat by using an argument similar to the one leading to Eq. (27). One finds in the WB limit

$$\delta(k) = \frac{\pi}{2} S_{\pm}(k) - k \lim_{k\to 0} \int_0^\infty dr\,(1 - R_k{}^2(r)) + \cdots, \tag{33}$$

where $S_{\pm}(k)$ is the unit step function going up (down) in the virtual (real) case. Thus the correction to the phase jump of $\pi/2$ clearly depends on the force law.

The WB case seems to be applicable to He^4. All numerical calculations[8,9] based on empirical potentials have shown that, if a discrete level exists at all, ϵ/k is less than 0.05°K. In fact, on the basis of the present available data one cannot decide whether the level close to zero is real or virtual. Since for He^4, $\lambda \cong 8.7/T^{\frac{1}{2}}$ A, and since the range of the forces is of the order of 5 A, there is a small range of temperatures below say 0.5°K, for which both inequalities (30) are fulfilled.

For He^4 Eq. (32) gives $B_{\mathrm{BE}} = -625/T^{\frac{3}{2}}$ cm^3/mole. From the published numerical tables,[14] one finds at 0.3°K $B(\mathrm{He}^4)T^{\frac{3}{2}} \cong -445$. From the unpublished results of Keller *et al.* mentioned previously, one finds $B(\mathrm{He}^4)T^{\frac{3}{2}} = -466$ and -454 at 0.1 and 0.2°K, respectively.[15] Using Eq. (23) with the Lennard-Jones potential (16), one gets $\delta(k) = \frac{1}{2}\pi - 1.34k\sigma$, which at 0.3°K reduces the theoretical value -625 for $B_{\mathrm{BE}}T^{\frac{3}{2}}$ to -540. We quote these numbers not from the point of view of getting quantitive agreement, but rather to emphasize that for He^4 the WB limit seems a considerably better leading approximation than the ideal Bose gas, for which $B(\mathrm{He}^4)T^{\frac{3}{2}}$ would approach the value -69.5.

If He^4 has an S-state close to zero, then the same cannot be true for He^3. This is also clearly seen from the S-phase behavior of He^3 computed by de Boer *et al.*[7] This phase rises more slowly with increasing k than the one of He^4 and never reaches $\pi/2$.

(γ) The Case of Strong Binding

In this case $\beta\epsilon \gg 1$ and therefore the low-temperature behavior of B will be dominated by the bound-state contribution. It has been pointed out[3] that this approximate expression for B can also be derived directly by considering the total system to be a state of chemical equilibrium between "atoms" and "binary molecules." Since neither for He^3 nor for He^4 is this case applicable, we will not make any further comments here. However, the strong-binding treatment may be of relevance for other particles, like for example the heavier noble gases, where, for suitable temperatures, it may be better than either the repulsive or the WB method.

In concluding this section we would like to express our sincere appreciation to Dr. W. E. Keller and to Dr. J. de Boer. Their communications of some unpublished results has been of great help to us.

IV. NEW DERIVATION OF THE WB LIMIT FOR B

Since in the WB limit the range of the forces is neglected in first approximation, the result of Eq. (31) clearly only depends on the properties of the wave function outside the interaction region. In this section

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[14] See the last of references 8 and 9.

[15] It is a bit surprising that the numerical values even at the lowest temperatures do not approach closer to the theoretical value. This is perhaps an indication of the sensitivity of the numerical calculations at these temperatures.

we show how to obtain the WB limit by replacing the actual two-particle problem which involves a potential by a suitable boundary-value problem.[16]

In order to state the problem in this way we return to the expression (18) for b_2. In the limit $V\rightarrow\infty$ the eigenfunctions corresponding to $E_n^{(i)}$ are denoted by $\phi_n^{(i)}(\mathbf{R},\mathbf{r})$, $i=2$ or 0, where $\mathbf{R}$, $\mathbf{r}$ are the center-of-mass and the relative coordinates, respectively. The $\phi_n^{(i)}$ are supposed to be an orthonormal set. Define

$$P^{(i)}(\mathbf{R}^0,\mathbf{r}^0|\mathbf{R},\mathbf{r},\beta) =\textstyle\sum_n \phi_n^{(i)*}(\mathbf{R}^0,\mathbf{r}^0)\phi_n^{(i)}(\mathbf{R},\mathbf{r}) \exp(-\beta E_n^{(i)}) \quad (34)$$

with $i=2$ or 0. The formal symbol $\sum_n$ stands, of course, for a summation over possible discrete states and a multiple integral over the continuum wave numbers. Put

$$P=P^{(2)}-P^{(0)}. \quad (35)$$

Then, from Eq. (18)

$$b_2=\lim_{V=\infty}\frac{1}{2V}\int d\mathbf{R}\, d\mathbf{r}\, P(\mathbf{R},\mathbf{r}|\mathbf{R},\mathbf{r},\beta). \quad (36)$$

There is an apparant contradiction in Eq. (36): On the one hand, the limit $V=\infty$ still has to be taken; on the other hand, the ϕ_n entering in the definition of P already refer to infinite volume. Still, the interpretation of Eq. (36) is quite obvious: Only for infinite volume is the separation of center-of-mass and relative motion strictly possible. As we shall see in a moment, this separation reduces the $\mathbf{R}$-integration simply to const $\int d\mathbf{R}$ and this integral has then to be interpreted as V. All subsequent integrations are V-independent. The purpose of this device is merely to bypass the rather irrelevant question of the inseparability of $\mathbf{R}$ and $\mathbf{r}$ for finite volume.

From Eq. (34) it follows that the $P^{(i)}$ satisfy the respective Bloch equations

$$\partial P^{(2)}/\partial\beta=(\tfrac{1}{2}\Delta_R+2\Delta_r)P^{(2)}-\Phi(r)P^{(2)}, \quad (37)$$

$$\partial P^{(0)}/\partial\beta=(\tfrac{1}{2}\Delta_R+2\Delta_r)P^{(0)}, \quad (38)$$

whereas from the completeness of the ϕ_n we have

$$P^{(i)}(\mathbf{R}^0,\mathbf{r}^0|\mathbf{R},\mathbf{r},0)=\delta(\mathbf{R}-\mathbf{R}^0)\delta(\mathbf{r}-\mathbf{r}_0). \quad (39)$$

It remains to specify boundary conditions. With respect to $\mathbf{R}$ the answer is simply that there are none. As moreover the equations for the $P^{(i)}$ as well as the initial conditions are separable in $\mathbf{R}$ and $\mathbf{r}$, we have

$$P^{(i)}=\frac{\exp[-(\mathbf{R}-\mathbf{R}_0)^2/2\beta]}{(2\pi\beta)^{\frac{3}{2}}}Q^{(i)}(\mathbf{r}_0|\mathbf{r},\beta), \quad (40)$$

where the cofactor of $Q^{(i)}$ is the fundamental solution of the diffusion equation

$$\partial F/\partial\beta=\tfrac{1}{2}\Delta_R F.$$

Doing the $\mathbf{R}$-integration in the sense explained above we get

$$2b_2=(2\pi\beta)^{-\frac{3}{2}}\int d\mathbf{r}\, Q(\mathbf{r}|\mathbf{r},\beta), \qquad Q=Q^{(2)}-Q^{(0)}. \quad (41)$$

Next we decompose the $Q^{(i)}$ with respect to states with angular momentum l, and we assume that the contributions to $Q^{(2)}$ from $l>0$ are "free," that is, equal to the corresponding ones for $Q^{(0)}$ so that Q of Eq. (41) becomes

$$Q_0=Q_0^{(2)}-Q_0^{(0)}, \quad (42)$$

where the subscript 0 refers to the S-state part. In principle we introduce here an error, but one which is negligible for $\beta\rightarrow\infty$ $(T\rightarrow 0)$, the limiting case we are interested in. The $Q_0^{(i)}$ depend only on the respective magnitudes r_0, r of $\mathbf{r}_0$, $\mathbf{r}$. Put

$$Q_0^{(i)}(r_0|r,\beta)=\frac{q_0^{(i)}(r_0|r,\beta)}{4\pi r r_0}. \quad (43)$$

It follows from Eqs. (37)–(40) that

$$\partial q_0^{(2)}/\partial\beta=2(\partial^2 q_0^{(2)}/\partial r^2)-\Phi(r)q_0^{(2)}, \quad (44)$$

$$\partial q_0^{(0)}/\partial\beta=2(\partial^2 q_0^{(0)}/\partial r^2), \quad (45)$$

while

$$q^{(i)}(r_0|r,0)=\delta(r_0-r). \quad (46)$$

From Eqs. (41) and (43) we obtain

$$2b_2=(2\pi\beta)^{-\frac{3}{2}}\int dr[q_0^{(2)}(r|r,\beta)-q_0^{(0)}(r|r,\beta)]. \quad (47)$$

Except for the S-wave approximation, this expression is still exact. In fact from the general definition (34) it follows that

$$\begin{aligned} q_0^{(2)}(r_0|r,\beta)-q_0^{(0)}(r_0|r,\beta) &=R(r_0)R(r)e^{\beta\epsilon}+\frac{2}{\pi}\int_0^\infty dk\,\exp(-2\beta k^2) \\ &\quad\times[R_k(r_0)R_k(r)-R_k^{(0)}(r_0)R_k^{(0)}(r)], \end{aligned} \quad (48)$$

where we assume that there is only one discrete state of energy $-\epsilon$ and with wave function $R(r)$. Inserting (48) into (47) gives $b_2=2^{\frac{1}{2}}\lambda^{-3}B_0$; see Eqs. (19) and (20).

At this stage we specifically turn to the WB limit and argue as follows: Let the interaction Φ be zero for $r>\sigma$. Then if there exists an energy level, either real or virtual, very close to zero, the derivative of the corresponding wave functions must almost vanish for $r=\sigma$. Now $q_0^{(2)}$ is proportional to an integral over the relative wave number k of all S-states specified by k where, according to Eq. (48), each state k has the weight $\exp(-2\beta k^2)$. As for $\beta\rightarrow\infty$ the main contribution comes from the region near $k=0$ we are therefore led, in the WB limit, to

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[16] We are indebted to Professor Marc Kac for a private communication in which he pointed out to us the connection between the present formulation of the problem and diffusion theory.

substitute for Eq. (44) the new equation

$$\partial q_0^{(2)}/\partial\beta = 2(\partial^2 q_0^{(2)}/\partial r^2). \tag{49}$$

Finally, as in the WB limit σ is neglected, we shall adjoin to (49) the boundary condition obtained by letting $\sigma \to 0$:

$$(\partial q_0^{(2)}/\partial r)_{r=0} = 0. \tag{50}$$

It remains to specify the boundary condition for Eq. (45). Since the choice of polar coordinates makes $r=0$ a singular point, we must require

$$q_0^{(0)}(r=0) = 0. \tag{51}$$

The solution of the two diffusion problems (45), (49) with respective boundary conditions (51), (50) and with common initial condition (46) are

$$\begin{gathered} q_0^{(2)}(r_0|r,\beta) = (8\pi\beta)^{-\frac{1}{2}}(\alpha_- + \alpha_+), \\ q_0^{(0)}(r_0|r,\beta) = (8\pi\beta)^{-\frac{1}{2}}(\alpha_- - \alpha_+), \\ \alpha_\pm = \exp[-(r \pm r_0)^2/8\beta]. \end{gathered} \tag{52}$$

Hence

$$q_0 = q_0^{(2)} - q_0^{(0)} = 2(8\pi\beta)^{-\frac{1}{2}}\alpha_+. \tag{53}$$

It follows that the integrand of the r-integral in Eq. (47) is $(4\pi r^2)^{-1} q_0(r|r\beta)$. Note how essential the cancelation of α_- is in obtaining q_0 from Eq. (52): a term in q_0 proportional to α_- would have produced a contribution that would diverge for $V \to \infty$. Thus we have now verified that the limit in Eq. (18) exists and the final answer is

$$b_2 = \sqrt{2}/(2\lambda^3), \tag{54}$$

which is equivalent to Eq. (31).

The present procedure of treating the WB limit by means of a set of diffusion equations with specified initial and boundary conditions will serve as a muster for the treatment of the corresponding problem for the third virial coefficient, see Sec. VII.

Finally it may be good to note here that also in the repulsive case the quantity B_0, in the limit $T \to 0$, again depends only on the behavior of the wave function outside the range of interaction. This can be seen as follows. B_0 [see Eq. (20)] can be written as

$$\begin{aligned} B_0 &= 2\int_0^\infty dk \exp(-2\beta k^2)(I_k^{\text{out}} + I_k^{\text{in}}), \\ I_k^{\text{out}} &= \int_0^\infty dr[R_k^{(as)2}(r) - R_k^{(0)2}(r)], \\ I_k^{\text{in}} &= \int_0^\infty dr[R_k^2(r) - R_k^{(as)2}(r)], \\ R_k^{(as)} &= \sin(kr+\delta). \end{aligned} \tag{55}$$

Observe that I_k^{out} is an improper integral. Let us give it a precise meaning by inserting a factor $e^{-\alpha r}$ in the integrand and letting $\alpha \to 0$ after integration. This gives

$$I^{\text{out}}(k) = \sin 2\delta/4k. \tag{56}$$

Now consider I^{in} and I^{out} near $k=0$ which is the relevant region for the low-temperature behavior of B_0. We have

$$\lim_{k=0} I^{\text{out}} = \frac{1}{2}\left(\frac{d\delta}{dk}\right)_0, \tag{57}$$

$$\lim_{k=0} I^{\text{in}} = \int_0^\infty dr \lim_{k=0}[R_k^2(r) - R_k^{(as)2}(r)] = 0, \tag{58}$$

where in Eq. (58) we have legitimately interchanged the r-integration and the limit operation. Equation (57) is valid for $\delta(k=0) = n\pi$ where n is the number of bound states. Thus we find that when $T \to 0$ the contributions to B come entirely from the outer region. It is easily seen that an expansion of I^{out} near $k=0$ yields correctly the first and only the first term of Eq. (28). Thus, from the term $\sim\lambda^{-3}$ in Eq. (28) on, the inner region is being explored as is also obvious from the definition of r_0:

$$-a^2 r_0 = 2 \lim_{k=0} \frac{1}{k^2} I^{\text{in}}(k). \tag{59}$$

V. THE BINARY EXPANSION METHOD

Lee and Yang[5] have shown how to express the cluster operators U_l in terms of certain two-body operators. In this binary expansion procedure one conveniently makes use of a representation by graphs. We shall here give the results in the form of a set of recipes which especially emphasize that the graphs in question may be considered as "blown-up" versions of the Ursell graphs of classical theory, in a sense now to be described.

First let us recall how the Ursell graphs are defined. Since in the classical theory the trace operation becomes an integration over phase space, Eq. (6) becomes, in our units,

$$Vl!b_l^c(V) = \frac{1}{(2\pi)^{3l}} \int d\mathbf{p}_1 \cdots d\mathbf{p}_l d\mathbf{r}_1 \cdots d\mathbf{r}_l U_l^c, \tag{60}$$

where U_l^c is expressed in W_n^c as before, see Eq. (5). Put

$$\begin{gathered} W_n^c = \exp(-\beta H^{(n)c}) = e^{-\beta T_n} \prod_{i>j=1}^{n} (1+f_{ij}), \\ f_{ij} = \exp(-\beta\Phi_{ij}) - 1, \end{gathered} \tag{61}$$

where $T_n = \sum p_k^2$ is the kinetic energy. Then it turns out that U_l^c is given by[17]

$$U_l^c = \sum_{(G)} U_l^c(G), \tag{62}$$

$$U_l^c(G) = e^{-\beta T_l} \prod_{(G)} f_{ij}, \tag{63}$$

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[17] It follows from the definition of U_l^c that the $\mathbf{p}$-integrations in Eq. (60) can trivially be done. In fact, one usually defines U_l^c without the factor $\exp(-\beta T_l)$. For the present it is convenient to use the definition just given for the purpose of a comparison with quantum theory.

where G is a connected graph of l labeled points. To a line of G between the points i and j one associates the factor f_{ij}. The summation in Eq. (62) goes over all such graphs. For example, for $l=3$ the graphs are those drawn in Fig. 1 and we have

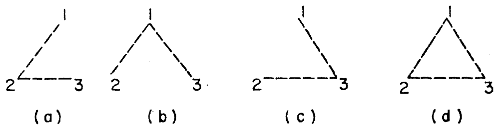
$$U_3{}^c = e^{-\beta T_3}(f_{12}f_{23}+f_{23}f_{31}+f_{31}f_{12}+f_{12}f_{23}f_{31}). \quad (64)$$

Let us now turn to the U_l, that is, the quantum case with Boltzmann statistics. As a first example we take U_3. By following the Lee-Yang procedure it can be seen that this operator can again be represented as the sum of four operators, to each of which corresponds one of the Ursell graphs of Fig. 1. In detail the procedure is as follows.

Draw one of these Ursell graphs, for example Fig. 1(b). Then draw lines through the vertices 1, 2, 3 perpendicular to the plane of the graph which in the example yields two intersecting planes. Then proceed by the following set of recipes.

(1) Starting from the bottom, draw a block in one of the planes. Example: see Fig. 2(a) where the shaded area between 1 and 3 represents a block.

(2) Then draw a block in the other plane starting from the top of the previous block. A graph which has at least one block in each plane will be called a connected quantum graph.



(a) (b) (c) (d)

FIG. 1. Classical Ursell graphs for $l=3$.

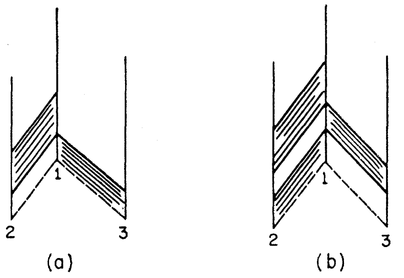
(3) Thus Fig. 2(a) represents a connected quantum graph of two blocks. There are two of those two-block graphs as one might alternatively have started with the lower block in the (1,2)-plane. Figure 2(b) also represents a connected quantum graph, where now an additional block has been drawn, again starting upward from the previous block. Again there are two three-block graphs. Continue to build such graphs with higher numbers of blocks N_b.

(4) To the Ursell graph of Fig. 1(b) we associate the infinite sum of all connected quantum graphs where the summation goes over $2 \leq N_b < \infty$. This infinite sum we call the Ursell quantum graph. For each N_b we get two summands corresponding to the two ways in which the blocks can be arranged, as indicated above for $N_b=2$.

(5) Proceed in the same way for each of the graphs of Fig. 1. One further example is given in Fig. 3 where one of the six connected quantum graphs for $N_b=3$ (the minimal number in this case) is drawn corresponding to Fig. 1(d).

(6) To the operator U_3 we associate the sum of the four Ursell quantum graphs.

We proceed likewise for general U_l: first draw the associated Ursell graphs, then draw lines upward perpendicular to their planes. In each such figure put in blocks in such a way that (1) one starts from the bottom; (2) one builds the $(n+1)$th block starting from the top of the nth block; (3) if the nth block is in the plane of the particles (i,j), then the $(n+1)$th must be in a different plane; (4) for each N_b one distinguishes the orders in which the blocks are built up; (5) one associates to an Ursell graph an Ursell quantum graph by summing over all N_b; (6) one associates to U_l the sum of all Ursell quantum graphs so constructed.



(a) (b)

FIG. 2. Two examples of connected quantum graphs corresponding to the Ursell graph of Fig. 1(b).

Suppose that by building up the blocks, we have a particular quantum graph with kth block in the (ij) plane. To this block we associate the operator

$$C(\beta_k; ij) = B(\beta_k; ij) \exp(-\beta_k \sum_{n=1}{}' p_n{}^2), \quad (65)$$

where B is the binary operator introduced by Lee and Yang[5]:

$$B(\beta_k, ij) = -\Phi_{ij} \exp[-\beta_k(p_i{}^2+p_j{}^2+\Phi_{ij})]. \quad (66)$$

The prime on the summation sign in Eq. (65) means that $n \neq i, j$; β_k is an auxiliary parameter.

To the sequence of blocks of a given connected quantum graph we associate an ordered product of C's such that the sequence of blocks from bottom to top is represented by the corresponding product of C's from right to left. Next we associate to a connected quantum graph of n blocks $(n \geq l-1)$, the operator

$$\int \cdots \int d\beta_1 \cdots d\beta_n \exp[-(\beta - \sum_{i=1}^{n} \beta_i) T_l]$$
$$\times C(\beta_n; i_n j_n) C(\beta_{n-1}; i_{n-1}, j_{n-1}) \cdots C(\beta_1; i_1, j_1), \quad (67)$$

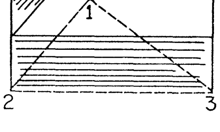


FIG. 3. Example of a connected quantum graph corresponding to the Ursell graph of Fig. 1(d).

where the integration domain of the β_k is restricted by

$$\sum_{k=1}^{n} \beta_k \leq \beta. \tag{68}$$

We are thus led to associate to each Ursell graph G the operator

$$U_l(G) = e^{-\beta T_l} \mathbf{S} \int \cdots \int d\beta_1 \cdots d\beta_N \exp(T_l \sum_{k=1}^{N} \beta_k)$$
$$\times C(\beta_N; i_N j_N) \cdots C(\beta_1; i_1, j_1), \tag{69}$$

where the round summation $\mathbf{S}$ means: (1) summation over all numbers $n(i,j)$ of blocks between particles i and j from $n(i,j)=1$ to ∞; $N=\sum_{i,j} n(i,j)$; (2) for given $n(i,j)$ one also sums over all allowed permutations of the blocks. Remember that some permutations are forbidden as one can never have two C's as nearest neighbors which refer to the same point pair. The number $\mathfrak{N}(n(i,j))$ of connected quantum graphs for given $n(i,j)$, or in other words the number of allowed permutations is computed in Appendix I. The fact that we consider one specific Ursell graph G of l points is implicitly dictated by the choice of point pairs (i_k, j_k) in Eq. (69). Finally we have

$$U_l = \sum_{(G)} U_l(G), \tag{70}$$

which is the quantum analog of the classical relation (62).

Note the following special cases. For $l=1$ there is but one Ursell graph consisting of one point so $U_1 = \exp(-\beta T_1)$. For $l=2$, the Ursell graph is just one link between points 1 and 2. Thus the Ursell quantum graph is just one one-block graph and

$$U_2(1,2) = e^{-\beta T_2} \int_0^\beta d\beta_1\, e^{\beta_1 T_2} (-\Phi_{12}) e^{-\beta_1 (T_2 + \Phi_{12})}. \tag{71}$$

This equation is very instructive for a comparison with classical theory. In fact, Eq. (69) must also be valid if we ignore the noncommutativity of kinetic and potential energies, that is to say in the classical limit. Proceeding in this way with Eq. (71), we get

$$U_2 \rightarrow U_2{}^c = e^{-\beta T_2} f_{12}, \tag{72}$$

in accordance with Eqs. (62), (63) for $l=2$. See also Appendix I. From $l=3$ on, every Ursell quantum graph consists of an infinite number of terms.

Equation (69) as it stands is nothing more nor less than a formal operator identity which relates the l-body cluster operator $U_l(G)$ to sums of products of the two-body operators B of Eq. (66). It is this Eq. (69) which forms the starting point for the binary expansion computation of such quantities as the b_l. We collect here a few general formulas which are constantly needed for such calculations.

To obtain the general matrix element of a C-operator we need, according to Eq. (65): first the matrix elements of $\exp(-\beta p^2)$, where p^2 is the kinetic energy of one particle. We have, in coordinate space (for $V \rightarrow \infty$)

$$\langle \mathbf{r}_1 | \exp(-\beta p^2) | \mathbf{r}_2 \rangle$$
$$= \langle \mathbf{r}_1 | U_1 | \mathbf{r}_2 \rangle = \lambda^{-3} \exp[-(\mathbf{r}_1 - \mathbf{r}_2)^2 / 4\beta]. \tag{73}$$

Secondly we need the matrix elements of $B(\beta, ik)$. According to[18] Eqs. (66) and (5),

$$B(\beta, ik) = \partial U_2(\beta, ik)/\partial\beta + (p_i^2 + p_k^2) U_2(\beta, ik). \tag{74}$$

Hence the matrix elements of U_2 are required. With

$$\mathbf{R} = \tfrac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2), \quad \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2, \tag{75}$$

we have, again for $V \rightarrow \infty$

$$\langle \mathbf{r}_1', \mathbf{r}_2' | U_2 | \mathbf{r}_1, \mathbf{r}_2 \rangle$$
$$= (2\pi\beta)^{-\frac{3}{2}} \exp[-1/2\beta (\mathbf{R} - \mathbf{R}')^2] \langle \mathbf{r}' | u | \mathbf{r} \rangle, \tag{76}$$

where the relative motion part $\langle \mathbf{r}' | u | \mathbf{r} \rangle$ is given by

$$\langle \mathbf{r}' | u | \mathbf{r} \rangle = (2\pi^2 r r')^{-1} \sum_l (2l+1) \mathcal{P}_l(\theta)$$
$$\times \Big[\tfrac{1}{2}\pi \sum_n R_{nl}(r) R_{nl}(r') e^{\beta \epsilon_{nl}}$$
$$+ \int_0^\infty dk \exp(-2\beta k^2) \{ R_{kl}(r) R_{kl}(r')$$
$$- R_{kl}{}^{(0)}(r) R_{kl}{}^{(0)}(r') \} \Big]. \tag{77}$$

The continuum wave functions $R_{kl}(r)$ and $R_{kl}{}^{(0)}(r)$ are defined as in Sec. III; the discrete radial functions R_{nl} are normalized to unity.

From Eq. (76) it follows that in the momentum representation

$$\langle \mathbf{q}_1', \mathbf{q}_2' | U_2 | \mathbf{q}_1, \mathbf{q}_2 \rangle = \delta(\mathbf{Q} - \mathbf{Q}') \langle \mathbf{q}_1', \mathbf{q}_2' | u_2 | \mathbf{q}_1, \mathbf{q}_2 \rangle, \tag{78}$$

where

$$\langle \mathbf{q}_1', \mathbf{q}_2' | u_2 | \mathbf{q}_1, \mathbf{q}_2 \rangle$$
$$= \exp[-\tfrac{1}{8}\beta (\mathbf{Q} - \mathbf{Q}')^2] \times (2\pi)^{-3} \int\int d\mathbf{r} d\mathbf{r}'$$
$$\times e^{-i[\mathbf{q}'\mathbf{r}' - \mathbf{q}\mathbf{r}]} \langle \mathbf{r}' | u | \mathbf{r} \rangle, \tag{79}$$
$$\mathbf{Q} = \mathbf{q}_1 + \mathbf{q}_2, \quad \mathbf{q} = \tfrac{1}{2}(\mathbf{q}_1 - \mathbf{q}_2).$$

With the help of the matrix elements of C, the general Eqs. (69) and (70) lead to expressions for the b_l in the form of an infinite series. About the convergence of this series nothing is known at present. Since the expansion goes in some sense in the number of blocks or binary kernels, its usefulness clearly depends on whether a

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[18] See also reference 5. In the further use of Eq. (74) we will always understand that the operator identity $U_2(0,ik)=0$ holds true in all representations. Note that this identity is not always valid for singular potentials! However, in this paper we will always have regular potentials.

successive increase of the number of blocks or binary kernels gives contributions that fall off sufficiently rapidly. From Eq. (77) it is clear that if bound states are present, grave convergence difficulties may arise[19] in the temperature regime where $\beta\epsilon_{nl}\gg 1$. Therefore till now the expansion has only been used in the repulsive case, but even here the convergence question is open. It is noteworthy that in the classical limit the series for b_l converges whatever the potential is; see Appendix I.

VI. $C(T)$ AT LOW TEMPERATURES FOR THE REPULSIVE CASE

We recall that for any statistics C is expressible in terms of the corresponding b's by Eq. (3). In this section we shall be mainly concerned with the BE case; at the end we shall make a brief comment on C_{FD}.

Thus we must find b_l^{BE}, $l=1, 2, 3$. From Eq. (17) we have $b_1^{\mathrm{BE}}=b_1=\lambda^{-3}$. Next we recall that at low temperatures b_2^{BE} is given by

$$b_2^{\mathrm{BE}}=2^{\frac{1}{2}}\lambda^{-3}[\tfrac{1}{8}+2B_0],$$

as was seen in connection with Eq. (25). As explained in Sec. III we may use the expansion (28) in the repulsive case, so that

$$b_2^{\mathrm{BE}}=\lambda^{-3}\left[2^{-\frac{5}{2}}-\frac{2a}{\lambda}+\frac{2\pi a^2}{\lambda^3}(a-\tfrac{3}{2}r_0)+O(\lambda^{-5})\right]. \tag{80}$$

Next we turn to b_3^{BE} for which we have, from Eqs. (6) and (15),

$$b_3^{\mathrm{BE}}=b_{3,(0)}^{\mathrm{BE}}+b_{3,(1)}^{\mathrm{BE}}+b_{3,(2)}^{\mathrm{BE}}, \tag{81}$$

$$b_{3(0)}^{\mathrm{BE}}=\frac{2}{3!}\lim\frac{1}{V}\operatorname{Tr}(2|U_1|1)(3|U_1|2)(1|U_1|3)$$
$$=\lambda^{-3}3^{-\frac{5}{2}}, \tag{82}$$

$$b_{3(1)}^{\mathrm{BE}}=\frac{2}{3!}\lim\frac{1}{V}\operatorname{Tr}[(12|U_2|13)+(21|U_2|13)$$
$$+(12|U_2|31)+(21|U_2|31)](3|U_1|2), \tag{83}$$

$$b_{3(2)}^{\mathrm{BE}}=\frac{1}{3!}\lim\frac{1}{V}\operatorname{Tr}(123|\mathfrak{U}_3{}^S|123). \tag{84}$$

In order to get the ideal gas contribution (82), we have used Eq. (73). In the expression (83) some simplifications have been made which follow from the definition (12) and the symmetry of the trace operation.

We first treat Eq. (83) in more detail. From Eqs. (73) and (76), we have

$$b_{3(1)}^{\mathrm{BE}}=\frac{2^{\frac{1}{2}}}{\lambda^6}\int d\mathbf{r}d\mathbf{r}'[(\mathbf{r}|u|\mathbf{r}')+(\mathbf{r}|u|-\mathbf{r}')+(-\mathbf{r}|u|\mathbf{r}')$$
$$+(-\mathbf{r}|u|-\mathbf{r}')]\exp\left[-\frac{3}{8\beta}(\mathbf{r}-\mathbf{r}')^2\right], \tag{85}$$

which is still rigorous. Now just as we went to the S-wave approximation in discussing b_2, we must do likewise for $(\mathbf{r}|u|\mathbf{r}')$, given by Eq. (77). In this way we get, after integrating over angles,

$$b_{3(1)}^{\mathrm{BE}}=\frac{2^{9/2}}{3\pi\lambda^4}\int_0^\infty\int_0^\infty drdr'\left\{\exp\left[-\frac{3}{8\beta}(r-r')^2\right]\right.$$
$$\left.-\exp\left[-\frac{3}{8\beta}(r+r')^2\right]\right\}$$
$$\times\int_0^\infty dk\exp(-2\beta k^2)\eta(k,r,r'),$$

$$\eta(k,r,r')=R_k(r)R_k(r')-R_k{}^{(0)}(r)R_k{}^{(0)}(r'). \tag{86}$$

We treat η by a similar method as used in connection with Eq. (55). Put

$$\eta=\eta_{\mathrm{out}}+\eta_{\mathrm{in}}, \tag{88}$$

$$\eta_{\mathrm{out}}=R_k{}^{(as)}(r)R_k{}^{(as)}(r')-R_k{}^{(0)}(r)R_k{}^{(0)}(r'), \tag{89}$$

$$\eta_{\mathrm{in}}=R_k(r)R_k(r')-R_k{}^{(as)}(r)R_k{}^{(as)}(r'), \tag{90}$$

with $R_k{}^{(as)}=\sin(kr+\delta)$, as in Sec. IV. Thus

$$\eta_{\mathrm{out}}(k,r,r')=\frac{\cos k(r+r')+\cot\delta\,\sin k(r+r')}{1+\cot^2\delta}$$
$$=-ka\sin k(r+r')+k^2a^2\cos k(r+r')$$
$$+k^3a^2(a-\tfrac{1}{2}r_0)\sin k(r+r')+\cdots. \tag{91}$$

Here we have once more used the expansion (27) which is again broken off at $O(k^3)$ because beyond this order the D-wave contributions must also be taken into account. Inserting Eq. (91) into Eq. (86), we find for the contribution of η_{out} to $b_{3(1)}^{\mathrm{BE}}$,

$$\frac{-2^{\frac{1}{2}}a}{\lambda^4}-\frac{2a^2}{\lambda^5}+\frac{\pi}{2^{\frac{3}{2}}\lambda^6}a^2(a-\tfrac{1}{2}r_0). \tag{92}$$

We must now find the contribution from η_{in}. As the integrand of Eq. (86) is symmetrical in r and r', we may write this contribution as

$$\frac{2^{9/2}}{3\pi\lambda^4}\int_0^\infty\int_0^\infty drdr'\left\{\exp\left[-\frac{3}{8\beta}(r-r')^2\right]\right.$$
$$\left.-\exp\left[-\frac{3}{8\beta}(r+r')^2\right]\right\}\int_0^\infty dk\exp(-2\beta k^2)$$
$$\times\{R_k(r)+R_k{}^{(as)}(r)\}\{R_k(r')-R_k{}^{(as)}(r')\}. \tag{93}$$

Because of the last factor the r'-integration is restricted to the range of the forces. Since for low temperatures the main contribution of the k-integral comes from small k, and since for small k and small r' both R_k and $R_k{}^{(as)}$ are

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[19] The existence of many-body bound states will give rise to additional complications.

proportional to k, we may put

$$R_k(r')-R_k^{(as)}(r')\simeq -k\phi(r'), \tag{94}$$

where $\phi(r')$ tends rapidly to zero for $r'\rightarrow\infty$. The r-integration, on the other hand still extends over the full range. However, it can be seen that the contribution coming from the r-region inside the range is of order $(\text{range})^6\cdot\lambda^{-9}$ which is negligible in our approximation. Furthermore, for r beyond the force range it is readily seen that, to our approximation, $R_k(r)+R_k^{(as)}(r)\simeq 2\sin kr$. One may also approximate the factor in square brackets of Eq. (93) by

$$(3rr'/2\beta)\exp(-3r^2/8\beta).$$

The k- and r-integrations can now be performed and one obtains for the contribution of η_{in} to $b_{3(1)}{}^{\text{BE}}$:

$$2^{\frac{3}{2}}\pi d^3/3\lambda^6, \tag{95}$$

where, according to Eq. (94),

$$\frac{d^3}{6}=\int_0^\infty dr\, r\lim_{k=0}\frac{1}{k}[R_k(r)-R_k^{(as)}(r)]. \tag{96}$$

For the special case of a hard sphere potential, our scattering length a is equal to the diameter of the sphere. Furthermore, in this case $r_0=2a/3$, while it is seen from Eq. (96) that $d=a$. Hence

$$b_{3(1)}{}^{\text{BE}}=-\frac{2^{\frac{1}{2}}a}{\lambda^4}-\frac{2a^2}{\lambda^5}+\frac{5\pi a^3}{3(2)^{\frac{1}{2}}\lambda^6},\ \text{(hard spheres)}, \tag{97}$$

which can be checked by a direct calculation using the exact expression for $(r|u|r')$; see Appendix II.

We now come to $b_{3(2)}{}^{\text{BE}}$. It is here that three-body effects begin to play a role; it is also here that we need the binary expansion for the first time. It is convenient to evaluate the necessary traces in momentum space. Since we only ask for $b_3{}^{\text{BE}}$ up to the order $(\text{characteristic length})^3\times\lambda^{-6}$, we shall need, besides the expansion of U_3 *in* blocks, the expansion of a block or binary operator in terms of the characteristic lengths. As a preparation we collect first the matrix elements of $B(\beta,ik)$ in momentum space and up to the second order in these lengths—which is as far as we shall need them here.

Using the same notations as in Eq. (79), we put

$$\langle\mathbf{q}_1'\mathbf{q}_2'|B|\mathbf{q}_1,\mathbf{q}_2\rangle=\delta(\mathbf{Q}'-\mathbf{Q})\langle\mathbf{q}_1',\mathbf{q}_2'|b|\mathbf{q}_1,\mathbf{q}_2\rangle, \tag{98}$$

and expand

$$\begin{aligned}&\langle\mathbf{q}_1',\mathbf{q}_2'|b|\mathbf{q}_1,\mathbf{q}_2\rangle\\&\quad=\langle\mathbf{q}_1'\mathbf{q}_2'|b^{(1)}|\mathbf{q}_1,\mathbf{q}_2\rangle+\langle\mathbf{q}_1',\mathbf{q}_2'|b^{(2)}|\mathbf{q}_1,\mathbf{q}_2\rangle+\cdots.\end{aligned} \tag{99}$$

From Eqs. (74) and (79) we find, using the first two terms in the expansion of $(r|u|r')$, exactly as in the discussion of Eq. (86),

$$\langle\mathbf{q}_1',\mathbf{q}_2'|b^{(1)}|\mathbf{q}_1,\mathbf{q}_2\rangle=\frac{-a}{\pi^2}\exp[-\beta(\mathbf{q}_1{}^2+\mathbf{q}_2{}^2)], \tag{100}$$

$$\begin{aligned}&\langle\mathbf{q}_1',\mathbf{q}_2'|b^{(2)}|\mathbf{q}_1,\mathbf{q}_2\rangle\\&\quad=\frac{a^2}{\pi^{\frac{5}{2}}}\{\exp[-\beta(\mathbf{q}_1{}^2+\mathbf{q}_2{}^2)]\}\\&\qquad\times[2qM\{q(2\beta)^{\frac{1}{2}}\}-(2\beta)^{-\frac{1}{2}}\exp(2\beta q^2)],\\&\qquad q=\tfrac{1}{2}|\mathbf{q}_1-\mathbf{q}_2|,\quad M(x)=\int_0^x\exp(t^2)dt.\end{aligned} \tag{101}$$

Thus, up to this order (and not any further), the general expansion of the binary operator is identical with the special case of hard spheres,[5] always provided that one identifies sphere diameter and scattering length.

According to the definition (12), $b_{3(2)}{}^{\text{BE}}$ consists of six terms one of which is the Boltzmann b_3,

$$b_3=\frac{1}{3!}\lim\frac{1}{V}\operatorname{Tr}U_3. \tag{102}$$

We shall calculate b_3 first. From the general prescription of constructing connected quantum graphs, the minimal number of blocks involved in the graphs which make up U_3 is equal to two. This minimal case is just the one drawn in Fig. 2(a). As we need b_3 up to order $a^3\lambda^{-6}$, it is clear that all the graphs we need are: (α) the one of Fig. 2(a) with the binary kernel developed up to at most a^2; (β) the graph of Fig. 2(b), with B everywhere approximated by its term $\sim a$; (γ) the graph of Fig. 3, with B treated as in case (β). The results are as follows.

Case (α).—Whenever, as in the graph of Fig. 2(a), we have only one block between each pair of lines it is readily seen that only the diagonal elements $\langle\mathbf{q}_1,\mathbf{q}_2|b|\mathbf{q}_1,\mathbf{q}_2\rangle$ enter the trace calculation. Observe further that there are six graphs of the type of Fig. 2(a), since there are three Ursell graphs of this type, in each of which we can order the blocks in two ways. Thus the contribution to b_3 can be written as

$$\begin{aligned}\frac{6}{3!(2\pi)^3}&\int d\mathbf{q}_1d\mathbf{q}_2d\mathbf{q}_3\exp[-\beta(q_1{}^2+q_2{}^2+q_3{}^2)]\int\int d\beta_1d\beta_2\\&\times\exp[\beta_1(q_1{}^2+q_2{}^2)+\beta_2(q_2{}^2+q_3{}^2)]\\&\times\langle\mathbf{q}_2,\mathbf{q}_3|b(\beta_2)|\mathbf{q}_2,\mathbf{q}_3\rangle\langle\mathbf{q}_1,\mathbf{q}_2|b(\beta_1)|\mathbf{q}_1,\mathbf{q}_2\rangle,\end{aligned} \tag{103}$$

where

$$\beta_1+\beta_2\leq\beta.$$

We get two kinds of contributions to b_3: one $\propto a^2$, obtained by replacing in (103) both b's by $b^{(1)}$ as given by Eq. (100). It is easily seen that this contributes an amount

$$2a^2/\lambda^5 \tag{104}$$

to b_3. Secondly we can, in two ways, replace one b by $b^{(1)}$, the other by $b^{(2)}$. These two choices give equal contributions, the sum of which can be written as

$$\frac{-a^3}{4\pi^{15/2}}\int d\mathbf{q}_1 d\mathbf{q}_2 d\mathbf{q}_3 \exp[-\beta(q_1^2+q_2^2+q_3^2)]\int_0^\beta d\beta_2(\beta-\beta_2)$$
$$\times[2qM(q(2\beta_2)^{\frac{1}{2}})-(2\beta_2)^{-\frac{1}{2}}\exp(2\beta_2 q^2)], \quad (105)$$

where $q=|\mathbf{q}_1-\mathbf{q}_2|/2$. Introducing again $\mathbf{Q}$ and $\mathbf{q}$ of Eq. (79), this becomes

$$\frac{-2^{\frac{3}{2}}a^3}{\beta^3\pi^{7/2}}\int_0^\beta d\beta_2(\beta-\beta_2)I(\beta,\beta_2), \quad (106)$$

where

$$I(\beta,\beta_2)=\int_0^\infty q^2dq\exp(-2\beta q^2)\{2qM[q(2\beta_2)^{\frac{1}{2}}]$$
$$-(2\beta_2)^{-\frac{1}{2}}\exp(2\beta_2q^2)\}=\frac{\pi^{\frac{1}{2}}(2\beta_2-\beta)}{16\beta_2^{\frac{1}{2}}(\beta-\beta_2)^{\frac{1}{2}}}. \quad (107)$$

It is then readily verified that the contribution $\propto a^3$ to b_3 becomes

$$2^{\frac{3}{2}}\pi a^3/\lambda^6. \quad (108)$$

Case (β).—Again there are six equivalent contributions of the type of Fig. 2(b). Each of the three blocks is approximated by $b^{(1)}$. We get

$$\frac{6}{3!(2\pi)^3}\left(\frac{-a}{\pi^2}\right)^3\int d\mathbf{q}_1d\mathbf{q}_2d\mathbf{q}_3\exp[-\beta(q_1^2+q_2^2+q_3^2)]$$
$$\times\int\int\int d\beta_1d\beta_2d\beta_3\int d\mathbf{p}\, g_{12}(\beta_1,\mathbf{p})g_{12}(\beta_2,\mathbf{p}), \quad (109)$$

where

$$g_{ij}(\beta,\mathbf{p})=\exp[-2\beta(p^2-(\mathbf{q}_i+\mathbf{q}_j)\mathbf{p}+\mathbf{q}_i\mathbf{q}_j)], \quad (110)$$

and $\beta_1+\beta_2+\beta_3\leq\beta$. Integrating first over p, then over the q_i, and finally over the β's, the result is

$$-\pi(2^{\frac{3}{2}}a^3)/\lambda^6. \quad (111)$$

Case (γ).—Here the integral to be considered is

$$\frac{6}{3!(2\pi)^3}\left(\frac{-a}{\pi^2}\right)^3\int d\mathbf{q}_1d\mathbf{q}_2d\mathbf{q}_3\exp[-\beta(q_1^2+q_2^2+q_3^2)]$$
$$\times\int\int\int d\beta_1d\beta_2d\beta_3\int d\mathbf{p}\, g_{12}(\beta_1,\mathbf{p})g_{13}(\beta_2,\mathbf{p}). \quad (112)$$

Doing the integrals in the same order as before, the contribution is

$$-\pi(2^{\frac{3}{2}}a^3)/3\lambda^6. \quad (113)$$

This concludes the calculation of b_3 to our order, and we must now turn to the other terms in $b_{3(2)}{}^{\mathrm{BE}}$. The various terms of $\mathcal{U}_3{}^S$ can be represented by the same connected quantum graphs used for U_3. However, while for U_3 the labels at the top of the lines must be the same as those at the bottom, for $\mathcal{U}_3{}^S$ one must sum over all permutations of the labels at the top for given labels at the bottom. We shall again consider separately the three cases (α), (β), (γ).

Case (α).—To the order considered, $\langle ij|b|kl\rangle$ is symmetrical both in (i,j) and in (k,l). From this it is easily seen that four of the six permutations give the same result as for the Boltzmann case, while the remaining two permutations are equal to each other and are each given by

$$\frac{6}{3!(2\pi)^3}\int d\mathbf{q}_1d\mathbf{q}_2d\mathbf{q}_3\exp[-\beta(q_1^2+q_2^2+q_3^2)]$$
$$\times\int\int d\beta_1d\beta_2\exp[+(\beta_1+\beta_2)(q_1^2+q_2^2)]$$
$$\times\langle\mathbf{q}_1,\mathbf{q}_2|b(\beta_2)|\mathbf{q}_1+\mathbf{q}_2-\mathbf{q}_3,\mathbf{q}_3\rangle$$
$$\times\langle\mathbf{q}_1+\mathbf{q}_2-\mathbf{q}_3,\mathbf{q}_3|b(\beta_1)|\mathbf{q}_1,\mathbf{q}_2\rangle. \quad (114)$$

Thus, although no integration over virtual momenta is involved, we nevertheless meet in (114) the occurrence of off-diagonal elements of b, due to three-body exchange effects.

The further evaluation of (114) becomes particularly simple by introducing the following linear combination of the q's, characteristic for three-body problems:

$$\begin{aligned}\mathbf{q}_1+\mathbf{q}_2-2\mathbf{q}_3&=2\mathbf{q},\\ \mathbf{q}_1-\mathbf{q}_2&=\mathbf{Q},\\ \mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3&=3\mathbf{p}.\end{aligned} \quad (115)$$

Introducing these into (114) it is easily seen that to order a^2, each of the two permutations represented by (114) gives again the contribution (104). Thus the a^2-term of $b_{3(2)}{}^{\mathrm{BE}}$ is

$$12a^2/\lambda^5. \quad (116)$$

There are two a^3-contributions from (114): The one with the lower block replaced by $b^{(2)}$, the upper one by $b^{(1)}$ gives

$$\frac{-a^3}{2^{\frac{5}{2}}\pi^{7/2}\beta^{\frac{3}{2}}}\int\int\frac{d\beta_1d\beta_2}{(\beta+3\beta_2)}I(\tfrac{1}{4}\beta-\tfrac{1}{4}\beta_2,\beta_1),$$

while the one with the upper block replaced by $b^{(1)}$, the lower by $b^{(2)}$ gives

$$\frac{-2^{\frac{1}{2}}a^3}{\pi^{7/2}(3\beta)^{\frac{3}{2}}}\int\int d\beta_1d\beta_2\,I(\tfrac{1}{3}\beta+\beta_2,\beta_2).$$

The evaluation of these two expressions with the help of Eq. (107) gives the same value for both, namely $\pi a^3/2^{\frac{1}{2}}\lambda^6$. We did not succeed in finding a simple reason to show that these two expressions should be equal.

Combining this last result with the one stated in expression (108), we therefore see that the graph of

Fig. 2(a) gives a contribution to $b_{3(2)}{}^{\mathrm{BE}}$ which is equal to

$$2^{\frac{1}{2}}(10\pi a^3)/\lambda^6. \qquad (117)$$

Case (β).—By following the prescription given above, it is readily seen that the contribution to $b_{3(2)}{}^{\mathrm{BE}}$ is obtained from (109) by replacing in that integral $g_{12}(\beta_1,\mathbf{p})g_{12}(\beta_2,\mathbf{p})$ by

$$\sum_{i\neq j=1}^{3} g_{ij}(\beta_1,\mathbf{p})g_{12}(\beta_2,\mathbf{p}).$$

Comparing the integrals (109) and (112), it is clear that one obtains in this way twice the contribution (111) plus four times the contribution (113). Thus the graph of Fig. 2(b) contributes

$$-7\pi(2^{\frac{5}{2}}a^3)/3\lambda^6. \qquad (118)$$

Case (γ).—By the same method as used for the previous graph the reader will verify that one again obtains the result (118). Hence from (116), (117), and (118) we have

$$b_{3(2)}{}^{\mathrm{BE}}=\frac{12a^2}{\lambda^5}-\frac{26}{3}\left(\frac{2^{\frac{1}{2}}\pi a^3}{\lambda^6}\right). \qquad (119)$$

From this result and from Eqs. (82), (92), and (95) we finally get

$$b_3{}^{\mathrm{BE}}=\frac{1}{\lambda^3}\left[\frac{1}{3^{\frac{5}{2}}}-\frac{2^{\frac{1}{2}}a}{\lambda}+\frac{10a^2}{\lambda^2}\right.$$
$$\left.-\frac{2^{\frac{1}{2}}\pi}{24\lambda^3}(202a^3+3a^2r_0-16d^3)\right]. \qquad (120)$$

Using also Eq. (80), the low-temperature expansion of the third virial coefficient is therefore

$$C_{\mathrm{BE}}=N^2\lambda^6\left[\left(\frac{1}{8}-\frac{2}{3^{\frac{5}{2}}}\right)-\frac{4a^2}{\lambda^2}\right.$$
$$\left.+\frac{\pi(2)^{\frac{1}{2}}}{12\lambda^3}(226a^3-33a^2r_0-16d^3)\right]. \qquad (121)$$

We remind that this is as far as one can expand without taking D-wave contributions into account.

For the FD case (spin s) Lee and Yang[4] have shown for the hard sphere gas that

$$C_{\mathrm{FD}}{}^{(s)}=\frac{N^2\lambda^6}{(2s+1)^2}\left[\left(\frac{1}{8}-\frac{2}{3^{\frac{5}{2}}}\right)+4s\frac{a^2}{\lambda^2}+\cdots\right]. \qquad (122)$$

It is obvious from the above arguments that this expression is also valid in the general repulsive case with a again denoting the scattering length. Here we cannot expand further without taking P-waves into account.

As stated in Sec. III, only for He^3 might the repulsive case perhaps have some applicability. In this case Eq. (122) becomes

$$\tfrac{1}{4}N^2\lambda_{\frac{1}{2}}{}^6[-0.003+2(a_{\frac{1}{2}}/\lambda_{\frac{1}{2}})^2]. \qquad (123)$$

Clearly the ideal gas term is quite negligible and so one would expect that at very low temperatures C would be positive and proportional to T^{-2}.

Keller[7] gives values for C(He^3) at 3.8° and 3°K which are positive; their ratio approximately corresponds to a T^{-2} dependence and the same order of magnitude as follows from $a_{\frac{1}{2}}\simeq 6.4$ A (see Sec. III). However, as already noted in Sec. III, at these temperatures the validity of expansions like (123) is dubious.

VII. C_{BE} IN THE WB LIMIT

In the treatment of C, the notion of weak binding has reference to the properties both of two-body and of three-body systems. We discuss these two aspects separately.

(*a*) *The two-body aspect.*—Here the WB limit will be defined exactly as was done in Sec. IV. This has two consequences inasfar as C is concerned: first, C_{BE} depends on $b_2{}^{\mathrm{BE}}$, see Eq. (3). According to Eqs. (3) and (32), we have in the present limit

$$b_2{}^{\mathrm{BE}}=9/2^{\frac{5}{2}}\lambda^3. \qquad (124)$$

Secondly, our WB definition for the two-body system enables us to give an expression for the part $b_{3(1)}{}^{\mathrm{BE}}$ of $b_3{}^{\mathrm{BE}}$; see Eq. (81). [Of course $b_{3(0)}{}^{\mathrm{BE}}$ is again given by Eq. (82).] In the spirit of the WB limit we assume that there exists at most one bound two-body S-state. Correspondingly we must modify the expression (86) for $b_{3(1)}{}^{\mathrm{BE}}$ and it is readily seen that we now get

$$b_{3(1)}{}^{\mathrm{BE}}=\frac{2^{9/2}}{3\pi\lambda^4}\int\int drdr'\left[\exp\left(-\frac{3}{8\beta}(r-r')^2\right)\right.$$
$$\left.-\exp\left(-\frac{3}{8\beta}(r+r')^2\right)\right]\times\left\{\frac{\pi}{2}R(r)R(r')e^{\beta\epsilon}\right.$$
$$\left.+\int_0^\infty dk\exp(-2\beta k^2)\eta(k,r,r')\right\}, \qquad (125)$$

where the notations are as in Eqs. (87) and (48). From the latter equation we see that the quantity in curly brackets is equal to $(2/\pi)\{q_0{}^{(2)}(r|r',\beta)-q_0{}^{(0)}(r|r',\beta)\}$. It was shown in Sec. IV that the $q_0{}^{(i)}$ are given by Eq. (52). Substituting all this information into Eq. (125), we find

$$b_{3(1)}{}^{\mathrm{BE}}=\left(\frac{8}{3^{\frac{3}{2}}}-\frac{4}{3\pi}\right)\frac{1}{\lambda^3}. \qquad (126)$$

(*b*) *The three-body aspect.*—It was noted in Sec. VI that in the remaining part $b_{3(2)}{}^{\mathrm{BE}}$ of $b_3{}^{\mathrm{BE}}$ three-body effects become important. As was done in that section, we first concentrate on the Boltzmann part b_3 of $b_{3(2)}{}^{\mathrm{BE}}$, given by Eq. (102). Our procedure will now be quite similar to that of Sec. IV: Corresponding to each term of U_3 expressed in the W's [see Eq. (5)], we shall again introduce a P-function.

First a few definitions. The coordinates of the three particles are $\mathbf{r}_k$, $k=1, 2, 3$. The eigenfunctions for the state n of the Hamiltonian $H^{(3)}$ [see Eq. (16)] will be denoted by $\phi_n^{(3)}(\mathbf{r}_i)$ and the eigenvalues by $E_n^{(3)}$. If only one pair interaction Φ_{jk} is present, as in the mixed terms $W_2(jk)W_1(i)$ of Eq. (5), the corresponding eigenfunctions and eigenvalues will be called $\phi_n^{(2,i)}$, $E_n^{(2,i)}$ where i, j, $k=1, 2, 3$ cyclically. Finally $\phi_n^{(0)}$, $E_n^{(0)}$ will denote the corresponding quantities in the absence of all interaction. All eigenfunctions shall refer to the limit of infinite volume.

We now define the P-functions:

$$P^{(3)}(\mathbf{r}_k{}^0|\mathbf{r}_k,\beta)=\sum_n \phi_n{}^{(3)*}(\mathbf{r}_k{}^0)\phi_n{}^{(3)}(\mathbf{r}_k)\exp(-\beta E_n{}^{(3)}), \quad (127)$$

$$P^{(2,i)}(\mathbf{r}_k{}^0|\mathbf{r}_k,\beta)=\sum_n \phi_n{}^{(2,i)*}(\mathbf{r}_k{}^0)\phi_n{}^{(2,i)}(\mathbf{r}_k)\exp(-\beta E_n{}^{(2,i)}), \quad (128)$$

$$P_n{}^{(0)}(\mathbf{r}_k{}^0|\mathbf{r}_k,\beta)=\sum_n \phi_n{}^{(0)*}(\mathbf{r}_k{}^0)\phi_n{}^{(0)}(\mathbf{r}_k)\exp(-\beta E_n{}^{(0)}), \quad (129)$$

in terms of which

$$b_3=\lim_{V=\infty}\frac{1}{3!V}\int d\mathbf{r}_1d\mathbf{r}_2d\mathbf{r}_3\Big[P^{(3)}(\mathbf{r}_i|\mathbf{r}_i,\beta)-\sum_{i=1}^{3}P^{(2,i)}(\mathbf{r}_i|\mathbf{r}_i,\beta)+2P^{(0)}(\mathbf{r}_i|\mathbf{r}_i,\beta)\Big]. \quad (130)$$

Insofar as the limit $V=\infty$ is concerned, we shall proceed presently in a manner similar to that discussed after Eq. (36). The $P^{(\alpha)}$ satisfy the respective Bloch equations

$$\partial P^{(\alpha)}/\partial\beta=\Big[\sum_i \Delta_i-\Phi^{(\alpha)}\Big]P^{(\alpha)}, \quad (131)$$

where we have used the convenient shorthand

$$\Phi^{(3)}=\sum_{i>j}\Phi_{ij}, \quad \Phi^{(2,i)}=\Phi_{jk}, \quad \Phi^{(0)}=0. \quad (132)$$

Furthermore, for all $P^{(\alpha)}$ the initial condition

$$P^{(\alpha)}(\mathbf{r}_i{}^0|\mathbf{r}_i,0)=\prod_i\delta(\mathbf{r}_i-\mathbf{r}_i{}^0) \quad (133)$$

holds true.

Next we define the following three-body coordinates:

$$\begin{aligned}\mathbf{R}&=\tfrac{1}{3}(\mathbf{r}_1+\mathbf{r}_2+\mathbf{r}_3),\\ \mathbf{r}&=\mathbf{r}_1-\mathbf{r}_2,\\ \boldsymbol{\varrho}&=\mathbf{r}_3-\tfrac{1}{2}(\mathbf{r}_1+\mathbf{r}_2).\end{aligned} \quad (134)$$

We shall also need the combinations

$$\begin{aligned}\mathbf{r}'&=\mathbf{r}_2-\mathbf{r}_3=-\tfrac{1}{2}\mathbf{r}-\boldsymbol{\varrho},\\ \boldsymbol{\varrho}'&=\mathbf{r}_1-\tfrac{1}{2}(\mathbf{r}_2+\mathbf{r}_3)=\tfrac{3}{4}\mathbf{r}-\tfrac{1}{2}\boldsymbol{\varrho},\\ \mathbf{r}''&=\mathbf{r}_3-\mathbf{r}_1=-\tfrac{1}{2}\mathbf{r}+\boldsymbol{\varrho},\\ \boldsymbol{\varrho}''&=\mathbf{r}_2-\tfrac{1}{2}(\mathbf{r}_3+\mathbf{r}_1)=-\tfrac{3}{4}\mathbf{r}-\tfrac{1}{2}\boldsymbol{\varrho}.\end{aligned} \quad (135)$$

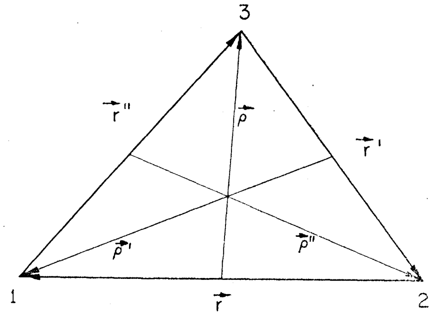

FIG. 4. The three-body variables of Eqs. (134), (135).

The various $\mathbf{r}$, $\boldsymbol{\varrho}$ variables are displayed in Fig. 4. The momenta $(\mathbf{K},\mathbf{k},\boldsymbol{\kappa})$ conjugate to $(\mathbf{R},\mathbf{r},\boldsymbol{\varrho})$ are expressed in terms of the momenta $\mathbf{k}_i$ conjugate to $\mathbf{r}_i$ in the following way:

$$\begin{aligned}\mathbf{K}&=\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3,\\ \mathbf{k}&=\tfrac{1}{2}(\mathbf{k}_1-\mathbf{k}_2),\\ \boldsymbol{\kappa}&=\tfrac{1}{3}(2\mathbf{k}_3-\mathbf{k}_1-\mathbf{k}_2).\end{aligned} \quad (136)$$

Therefore, in obvious notation,

$$\textstyle\sum_i \Delta_i=\tfrac{1}{3}\Delta_R+2\Delta_r+\tfrac{3}{2}\Delta_\rho. \quad (137)$$

Equation (133) may be written as

$$P^{(\alpha)}(\mathbf{r}_i{}^0|\mathbf{r}_i,0)=\delta(\mathbf{R}-\mathbf{R}^0)\delta(\mathbf{r}-\mathbf{r}^0)\delta(\boldsymbol{\varrho}-\boldsymbol{\varrho}^0). \quad (138)$$

We can now immediately separate off the center-of-mass motion. Proceeding similarly to the transition from Eq. (36) to Eq. (41) one finds

$$b_3=\frac{3^{\frac{3}{2}}}{3!\lambda^3}\int d\mathbf{r}d\boldsymbol{\varrho}\,Q(\mathbf{r},\boldsymbol{\varrho}|\mathbf{r},\boldsymbol{\varrho},\beta), \quad (139)$$

where

$$Q(\mathbf{r}_0,\boldsymbol{\varrho}_0|\mathbf{r},\boldsymbol{\varrho},\beta)=Q^{(3)}(\mathbf{r}_0,\boldsymbol{\varrho}_0|\mathbf{r},\boldsymbol{\varrho},\beta)-\sum_{i=1}^{3}Q^{(2,i)}(\mathbf{r}_0,\boldsymbol{\varrho}_0|\mathbf{r},\boldsymbol{\varrho},\beta)+2Q^{(0)}(\mathbf{r}_0,\boldsymbol{\varrho}_0|\mathbf{r},\boldsymbol{\varrho},\beta). \quad (140)$$

The $Q^{(\alpha)}$ satisfy

$$\partial Q^{(\alpha)}/\partial\beta=\big[2\Delta_r+\tfrac{3}{2}\Delta_\rho-\Phi^{(\alpha)}(\mathbf{r},\boldsymbol{\varrho})\big]Q^{(\alpha)}, \quad (141)$$

with the common initial condition

$$Q^{(\alpha)}(\mathbf{r}_0,\boldsymbol{\varrho}_0|\mathbf{r},\boldsymbol{\varrho},\beta)=\delta(\mathbf{r}-\mathbf{r}_0)\delta(\boldsymbol{\varrho}-\boldsymbol{\varrho}_0). \quad (142)$$

The angular momentum operator $\mathbf{L}$ (referring to the relative motion) is given by

$$\mathbf{L}=\mathbf{L}_r+\mathbf{L}_\rho, \quad (143)$$

and commutes, of course, with the operator on the right-hand side of Eq. (141), for all (α). Thus we can decompose each $Q^{(\alpha)}$ with respect to angular momentum:

$$Q^{(\alpha)}=\sum_{L=0}^{\infty}Q_L{}^{(\alpha)}. \quad (144)$$

The S-state part $Q_0^{(\alpha)}$ of $Q^{(\alpha)}$ can be written as

$$Q_0^{(\alpha)}=\sum_{l=0}^{\infty} Q_{0,l}^{(\alpha)}, \tag{145}$$

where, according to Eq. (143),

$$\mathbf{L}_r^2 Q_{0,l}^{(\alpha)}=\mathbf{L}_\rho^2 Q_{0,l}^{(\alpha)}=l(l+1)Q_{0,l}^{(\alpha)}. \tag{146}$$

Observe that, depending on the $\Phi^{(\alpha)}$, the individual $Q_{0,l}^{(\alpha)}$ may or may not be coupled to each other by Eq. (141).

The formalism developed from Eq. (127) on is general and rigorous. We now turn to the definition of the WB limit for the three-body part of the problem and to the treatment of the Q-equations in this special case.

So far the WB limit has been specified by the two relations (30), where ϵ is the absolute value of the two-body bound state or the energy of the two-body virtual state, whatever the case may be. We shall now in addition assume that, under these circumstances, the three-body system as well has a level close to zero with energy ϵ_3, where ϵ_3 may either be a binding energy or a virtual level energy; and that, simultaneously with Eq. (30), we can also satisfy

$$\beta\epsilon_3 \ll 1. \tag{147}$$

If the two-body system has a level ϵ near zero, it is clear that, with the additivity of forces always assumed in this paper, the corresponding three-body system will be bound more strongly. It seems physically plausible, however, that when ϵ is very close to zero, ϵ_3 will not be far from zero either.

The treatment of the $Q^{(\alpha)}$ in the WB limit, now fully defined, proceeds in two steps:

(1) Only the S-state part $Q_0^{(\alpha)}$ of the various $Q^{(\alpha)}$'s are considered to be different for different α. The corresponding neglect of the differences in the $Q_L^{(\alpha)}$, $L\geq 1$ for various α is entirely reasonable in the extreme low-temperature regime we are interested in, as long as the forces are not too strong. In this situation the $Q_L^{(\alpha)}$-terms for $L\geq 1$ cancel each other in Eq. (140) so that Eq. (139) may be written as

$$b_3=\frac{3^{\frac{3}{2}}}{3!\lambda^3}\int d\mathbf{r}d\boldsymbol{\varrho}\, Q_0(\mathbf{r},\boldsymbol{\varrho}|\mathbf{r},\boldsymbol{\varrho},\beta), \tag{148}$$

where Q_0 is the algebraic sum of the S-state parts of the $Q^{(\alpha)}$ in Eq. (140). However, in the case of S-states, $Q_0^{(\alpha)}(\mathbf{r}_0,\boldsymbol{\varrho}_0|\mathbf{r},\boldsymbol{\varrho},\beta)$ depends only on the respective magnitudes r, ρ of $\mathbf{r}$ and $\boldsymbol{\varrho}$ and on the angle θ between these vectors; likewise for the dependence on the $\mathbf{r}_0$ and $\boldsymbol{\varrho}_0$ variables. Put

$$\begin{aligned}Q_0^{(\alpha)}&=Q_0^{(\alpha)}(r_0,\rho_0,z_0|r,\rho,z,\beta)\\&=\frac{1}{8\pi^2 r r_0\rho\rho_0}q_0^{(\alpha)}(r_0,\rho_0,z_0|r,\rho,z,\beta),\end{aligned} \tag{149}$$

where $z=\cos\theta$, $z_0=\cos\theta_0$. Then

$$b_3=\frac{3^{\frac{3}{2}}}{3!\lambda^3}\int_0^\infty dr\int_0^\infty d\rho\int_{-1}^{+1} dz q_0(r,\rho,z|r,\rho,z,\beta), \tag{150}$$

where, according to Eq. (140),

$$q_0=q_0^{(3)}-\textstyle\sum_i q_0^{(2,i)}+2q_0^{(0)}. \tag{151}$$

All $q_0^{(\alpha)}$ satisfy the initial condition

$$q_0^{(\alpha)}(r_0,\rho_0,z_0|r,\rho,z,0)=\delta(r-r_0)\delta(\rho-\rho_0)\delta(z-z_0), \tag{152}$$

as is seen by projecting out the S-wave part of the right-hand side of Eq. (142).

(2) The potentials $\Phi^{(3)}$ and $\Phi^{(2,i)}$ are replaced by appropriate boundary conditions and all terms $O(\sigma/\lambda)$ [see Eq. (30)] are neglected. Thus if we put[20]

$$q_0^{(\alpha)}=\textstyle\sum_l \mathcal{P}_l(z)q_{0,l}^{(\alpha)}(r,\rho), \tag{153}$$

it follows from Eqs. (141), (144), (145), and (149) that

$$\frac{\partial q_{0,l}^{(\alpha)}(r,\rho)}{\partial\beta}=\left[2\left(\frac{d^2}{dr^2}-\frac{l(l+1)}{r^2}\right)+\frac{3}{2}\left(\frac{d^2}{d\rho^2}-\frac{l(l+1)}{\rho^2}\right)\right]q_{0,l}^{(\alpha)}(r,\rho). \tag{154}$$

Here the q's for different l appear not to be coupled to each other. As follows from the remark after Eq. (146), such couplings may nevertheless appear due to the nature of the boundary conditions which now are going to be substituted for the potentials. We next proceed to the specification of these conditions.

Although ultimately we shall employ the boundary conditions only in the limit where the range σ of the pair interaction is neglected, it is nevertheless necessary first to state these conditions for finite σ. In this case the six-dimensional phase space region ν of common interaction of all three particles (for fixed but arbitrary center of mass) can be visualized as in Fig. 5. Here the two circles with center 1 and 2, respectively, and with radius σ denote a plane cross section of the interaction spheres centered on particles 1 and 2. The distance 12 is equal to r, the variable ρ is measured from the point 0, see Eq. (134); and the angle θ is measured as indicated in

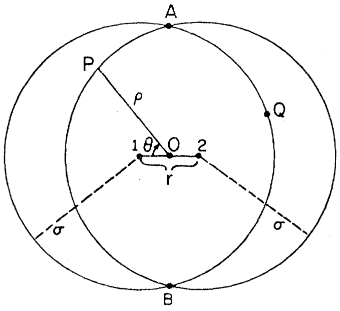

FIG. 5. Region of common interaction of three particles.

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[20] $\mathcal{P}_l(z)$ is the lth Legendre polynomial.

the figure. As long as $r\leq\sigma$, the particles 1 and 2 are within each others' force range and as long as particle 3 is anywhere inside the overlap *APBQ* of the two spheres (we shall call this region of overlap "the lens") then, always for $r\leq\sigma$, all three particles are in common interaction. v is obtained by integrating the lens volume for given r with respect to $d\mathbf{r}$, with $0\leq r\leq\sigma$. (One finds $v=5\pi^2\sigma^6/6$.)

Note that the surface of v consists of three parts: (1) The "r-part," $s(r)$. This is reached when $r=\sigma$, and each inner point of the special lens $r=\sigma$ is a surface point.

$$s(r):\quad r=\sigma;\quad 0\leq\theta\leq\pi;\quad 0\leq\rho\leq\tfrac{1}{2}\sigma\sqrt{3}. \tag{155}$$

(2) The r'-part, $s(r')$. For $r<\sigma$, any point on the surface part *APB* of the lens is a surface point of v. The distance *P*2 is just equal to σ. Thus, using also Eq. (135),

$$s(r'):\quad r'=\sigma;\quad 0<r/\sigma<1;\quad 0\leq\theta\leq\tfrac{1}{2}\pi;\quad 0\leq\rho\leq(\sigma^2-\tfrac{1}{4}r^2)^{\frac{1}{2}}. \tag{156}$$

(3) The r''-part, $s(r'')$. For $r<\sigma$, any point on the surface part *AQB* of the lens is a surface point of v. The distance *Q*1 is equal to r''; see Eq. (135).

$$s(r''):\quad r''=\sigma;\quad 0<r/\sigma<1;\quad \tfrac{1}{2}\pi\leq\theta\leq\pi;\quad 0\leq\rho\leq(\sigma^2-\tfrac{1}{4}r^2)^{\frac{1}{2}}. \tag{157}$$

These three surface parts do not overlap (they are each equal to $5\pi^2\sigma^5/3$). The total surface is

$$s=s(r)+s(r')+s(r''). \tag{158}$$

For any α, the solution of the diffusion equation (154) is completely determined if boundary conditions on s (and at ∞) are specified. We first state the conditions for $q^{(3)}$.

In the WB limit the 3-body system has an energy level, real or virtual, close to zero. According to Eq. (154), the corresponding function $q_{0,0}{}^{(3)}$ will spill out of v with a normal derivative which will be close to zero everywhere on s. We shall assume[21] that the same property holds for $q_{0,l}{}^{(3)}$, $l>0$. Proceeding in analogy with the treatment of the two-body problem of Sec. IV, we shall therefore require that the normal derivative of $q^{(3)}$ vanish on s, that is to say

$$\left(\frac{\partial q_0{}^{(3)}}{\partial r}\right)_{s(r)}=\left(\frac{\partial q_0{}^{(3)}}{\partial r'}\right)_{s(r')}=\left(\frac{\partial q_0{}^{(3)}}{\partial r''}\right)_{s(r'')}=0. \tag{159}$$

Here we must re-express the variables r', r'' in terms of r, ρ, θ. A simple geometrical consideration shows that Eq. (159) is equivalent to

$$\begin{aligned}\left(\frac{\partial q_0{}^{(3)}}{\partial r}\right)_{s(r)}&=0,\\ \left(\cos\alpha\frac{\partial q_0{}^{(3)}}{\partial\rho}-\frac{\sin\alpha}{\rho}\frac{\partial q_0{}^{(3)}}{\partial\theta}\right)_{s(r')}&=0,\\ \left(\cos\alpha\frac{\partial q_0{}^{(3)}}{\partial\rho}+\frac{\sin\alpha}{\rho}\frac{\partial q_0{}^{(3)}}{\partial\theta}\right)_{s(r'')}&=0,\end{aligned} \tag{160}$$

where

$$\cos\alpha=(\sigma^2+\rho^2-\tfrac{1}{4}r^2)/2\sigma\rho,\quad \sin\alpha=(r/2\sigma)\sin\theta. \tag{161}$$

$q_0{}^{(3)}$ is now completely determined by Eqs. (152–154) and (160, 161). As regards the latter two, we shall actually only wish to apply them for $\sigma=0$. In this limit we now show that

$$q_0{}^{(3)}=\sum_{l=0}^{\infty}\frac{2l+1}{2}\mathcal{P}_l(z)\mathcal{P}_l(z_0)G_l(r_0|r,\beta)\Gamma_l(\rho_0|\rho,\beta), \tag{162}$$

where

$$G_l(r_0|r,\beta)=(rr_0)^{\frac{1}{2}}\int_0^\infty dk\exp(-2\beta k^2)k\xi_l(kr)\xi_l(kr_0), \tag{163}$$

$$\Gamma_l(\rho_0|\rho,\beta)=(\rho\rho_0)^{\frac{1}{2}}\int_0^\infty d\kappa\exp(-3\beta\kappa^2/2)\kappa\eta_l(\kappa\rho)\eta_l(\kappa\rho_0). \tag{164}$$

The ξ_l, η_l are defined as follows:

$$\xi_l=J_{l+\frac{1}{2}}(kr),\quad \eta_l=J_{l+\frac{1}{2}}(\kappa\rho),\quad l>0; \tag{165}$$

while, for $l=0$,

$$q_0{}^{(3)}\text{ case:}\qquad \xi_0=J_{-\frac{1}{2}}(kr),\quad \eta_0=J_{-\frac{1}{2}}(\kappa\rho). \tag{166}$$

The expression (162) clearly satisfies the Eq. (154). It also satisfies the initial condition (152). We have in fact

$$G_l(r_0|r,0)=\delta(r-r_0);\quad \Gamma_l(\rho_0|\rho,0)=\delta(\rho-\rho_0), \tag{167}$$

independently of l (Fourier-Bessel identity). Insert this in Eq. (162); then Eq. (152) follows from the completeness of the $\mathcal{P}_l$.

Now we turn to Eq. (160) for $\sigma=0$. There the first relation is satisfied because,[22] for $l>0$, $(r^{\frac{1}{2}}\xi_l)'\sim r^l$ for $r\rightarrow 0$, while for $l=0$ we have $(\cos kr)'_{r=0}=0$. The second and third relation couple the various l-parts to each other, but only for finite σ. For $\sigma=0$ Eqs. (162–166) would in fact not satisfy all boundary conditions. How-

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[21] Since there is an energy level close to zero, the corresponding $q_{0,l}{}^{(3)}$ will be nearly flat for $r\rightarrow\infty$, $\rho\rightarrow\infty$, for any l. However, it is clear that for large l (and perhaps already for $l\geq 1$) this flatness does not extend toward the boundary of v. Thus the assumption of vanishing derivative of $q_{0,l}{}^{(3)}$ on the boundary of v is quite sensible for $l=0$, but gets worse and worse for increasing l.

On the other hand, it will be seen from what follows that *in the limit* $\sigma=0$ the precise form of the boundary condition on $q_{0,l}{}^{(3)}$, $l>0$ is immaterial, as long as the replacement of the potentials by boundary conditions is done in the same way for the three-body problem described by $q_0{}^{(3)}$ as for the three associated two-body problems described by the $q_0{}^{(2,i)}$. In fact if one were to require $q_{0,l}{}^{(\alpha)}=0$ on the boundary of v, for all $l>0$ and all α (which is perhaps more plausible) the final answer would remain the same, always in the limit $\sigma=0$.

[22] In this paragraph a prime will denote differentiation with respect to r or to ρ, whatever the case may be.

ever, for $\sigma=0$ one easily sees that all is well: First, the $l>0$ terms are all right because, for $\rho\rightarrow 0$, $(\rho^{\frac{1}{2}}\eta_l)'\sim\rho^l$ and $\rho^{-\frac{1}{2}}\eta_l\sim\rho^l$. Secondly, the $l=0$ terms do not depend on θ so that the relations in question are again satisfied as $(\rho^{\frac{1}{2}}\eta_0)'=0$ at $\rho=0$.

Next we turn to the quantities $q_0^{(2,i)}$ and consider first $q_0^{(2,3)}$. According to the definitions (132) only the particles (1,2) are here in interaction while particle 3 is free. The boundary conditions appropriate to the WB limit therefore now have reference to the two-body system (1,2). Here the part $s(r)$ of s is in a special position, as $s(r)$ denotes the boundary of the (1,2) interaction, wherever 3 may be. We shall therefore require analogously to Sec. IV that

$$(\partial q_0^{(2,3)}/\partial r)_{s(r)}=0. \tag{168}$$

The parts $s(r')$, $s(r'')$ contract, like $s(r)$, to the (r,ρ) origin for $\sigma\rightarrow 0$. Due to the choice of coordinates the origin is a singular point, and we must require

$$(q_0^{(2,3)})_{s(r')}=(q_0^{(2,3)})_{s(r'')}=0, \tag{163}$$

just as we used Eq. (51) in the discussion of b_2. It is readily verified that, always for $\sigma\rightarrow 0$, $q_0^{(2,3)}$ is also given by Eqs. (162–165), but (166) must now be replaced by

$$q_0^{(2,3)}\text{ case:}\qquad \xi_0=J_{-\frac{1}{2}}(kr),\quad \eta_0=J_{\frac{1}{2}}(\kappa\rho). \tag{170}$$

Also for $q_0^{(2,1)}$ and $q_0^{(2,2)}$ one of the three parts of s is in a special position, namely $s(r')$ and $s(r'')$, respectively; see Eq. (135). By the same reasoning as for $q_0^{(2,3)}$, we have

$$\begin{aligned}(\partial q_0^{(2,1)}/\partial r')_{s(r')}=(\partial q_0^{(2,2)}/\partial r'')_{s(r'')}&=0,\\ (q_0^{(2,1)})_{s(r)}=(q_0^{(2,1)})_{s(r'')}&=0,\\ (q_0^{(2,2)})_{s(r)}=(q_0^{(2,2)})_{s(r')}&=0.\end{aligned} \tag{171}$$

The solutions are once more given by Eqs. (162–165) while (166) now becomes

$$\begin{aligned}q_0^{(2,1)}\text{ case: }\xi_0=J_{\frac{1}{2}}(kr),\ \eta_0&=J_{-\frac{1}{2}}(\kappa\rho)\text{ for }0\leq\theta\leq\tfrac{1}{2}\pi,\\ &=J_{\frac{1}{2}}(\kappa\rho)\text{ for }\tfrac{1}{2}\pi\leq\theta\leq\pi.\end{aligned} \tag{172}$$

$$\begin{aligned}q_0^{(2,2)}\text{ case: }\xi_0=J_{\frac{1}{2}}(kr),\ \eta_0&=J_{\frac{1}{2}}(\kappa\rho)\text{ for }0\leq\theta\leq\tfrac{1}{2}\pi,\\ &=J_{-\frac{1}{2}}(\kappa\rho)\text{ for }\tfrac{1}{2}\pi\leq\theta\leq\pi.\end{aligned} \tag{173}$$

The θ-intervals specified in Eqs. (172–173) follow[23] from the detailed definitions (156–157) of $s(r')$ and $s(r'')$. Clearly while for $\sigma\rightarrow 0$ the r and ρ regions entering in the definition of s tend to zero, θ will continue to run from 0 to π. It is essentially this θ-dependence of the boundary conditions which makes it hard to formulate these conditions from the start with $\sigma=0$.

Finally, it will be clear that for $q_0^{(0)}$

$$(q_0^{(0)})_s=0 \tag{174}$$

is the proper boundary condition, so that also $q_0^{(0)}$ is given by Eqs. (162–165) while

$$q_0^{(0)}\text{ case:}\qquad \xi_0=J_{\frac{1}{2}}(kr),\quad \eta_0=J_{\frac{1}{2}}(\kappa\rho). \tag{175}$$

We now have the answer for the quantity q_0 defined by Eq. (151). A great simplification occurs because all $q_0^{(\alpha)}$ have the same $l>0$ part. Note that this is an automatic consequence of taking the limit $\sigma=0$. For $\sigma\neq 0$, things are much more complex. Thus all $l>0$ parts cancel in Eq. (151) and we get from Eqs. (162–175), after integrating over k and κ *and over z*:

$$3^{\frac{1}{2}}\lambda^2\int_{-1}^{+1}dzq(r_0,\rho_0,z_0|r,\rho,z,\beta)=\alpha_{++}-\alpha_{+-}-\alpha_{-+}+\alpha_{--}, \tag{176}$$

$$\alpha_{\pm\pm}=\left[\exp\left(-\frac{(r-r_0)^2}{8\beta}\right)\pm\exp\left(-\frac{(r+r_0)^2}{8\beta}\right)\right]\times\left[\exp\left(-\frac{(\rho-\rho_0)^2}{6\beta}\right)\pm\exp\left(-\frac{(\rho+\rho_0)^2}{6\beta}\right)\right], \tag{177}$$

where the α_{++} term stems from $q_0^{(3)}$, the $\alpha_{\pm\mp}$ terms from the $q^{(2,i)}$ and the α_{--} term from $q_0^{(0)}$. Hence finally, from Eq. (150),

$$b_3=3^{\frac{1}{2}}/12\lambda^3. \tag{178}$$

At this stage we would like to make one general comment on the procedure followed in this section. Let us return for a moment to Eq. (130) for b_3. The 9-dimensional integration domain in that equation consists of the following parts: first a region $\sim\sigma^6V$ corresponding to the domain of phase space where all three particles interact. This domain is the common intersection of three "tubes" with volume $\sim\sigma^3V^2$ where each "tube" corresponds to a phase space domain in which a pair of particles is within the range σ while the remaining particle is free. Finally, there is the domain $\sim V^3$ where all particles are outside each other's range. Each $P^{(\alpha)}$, when integrated separately, yields a result that tends to infinity as V^3. Here one factor V is trivially accounted for by the center-of-mass motion. There still remains an individual divergence $\sim V^2$, however. This divergence finds its reflection in the fact that if in Eq. (176) we put $r=r_0$, $\rho=\rho_0$, and then integrate an individual α separately, the result diverges like $V^{\frac{2}{3}}$. The fact that we find a $V^{\frac{2}{3}}$—rather than a V^2—behavior is due to the circumstance that we have been able to restrict our problem first to the consideration of $L=0$ states only, see Eq. (148), and thereupon to $l=0$ only, see the remarks after Eq. (175).

It will therefore be clear, and this is the point we wish to emphasize particularly, that the finite result (178), due to cancelations of the singularities $\sim V^{\frac{2}{3}}$ and $\sim V^{\frac{1}{3}}$ of the integration over the individual α's of Eq. (176) has been obtained by means of *a proper matching of three-body to two-body boundary conditions.* That b_3 may not depend on V is, of course, nothing but the cluster property of U_3. Whenever in a many-body

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[23] Wherever in the definition of ξ's and η's no explicit specification of the θ-interval is made, it is always understood that $0\leq\theta\leq\pi$.

problem potentials are replaced by suitable boundary conditions, this question of a matching of the various conditions must necessarily arise.

We now must go from b_3 to $b_{3(2)}{}^{\mathrm{BE}}$. In the WB limit the result is simply

$$b_{3(2)}{}^{\mathrm{BE}}=6b_3=3^{\frac{1}{2}}/2\lambda^3. \tag{179}$$

The proof goes as follows. From the definitions (84) of $b_{3(2)}{}^{\mathrm{BE}}$ and (12) of $\mathfrak{U}_3{}^S$, one readily sees that for each of the six terms of $\mathrm{Tr}\mathfrak{U}_3{}^S$ one can define corresponding functions $P^{(3)}$, $P^{(2,i)}$, $P^{(0)}$ which always satisfy Eqs. (131–132). Also in all six cases the sequence $P^{(\alpha)}\rightarrow Q^{(\alpha)}\rightarrow q_0{}^{(\alpha)}$ is the same as for the normal permutation to which b_3 corresponds. Again the boundary conditions are identical to those previously given, for all six instances. Each of the six terms has its own characteristic initial condition, however. Indeed, the right-hand side of Eq. (142) reads as follows [see also Eq. (135)]:

$$\begin{aligned}
(1\,2\,3):&\quad \delta(\mathbf{r}-\mathbf{r}_0)\delta(\boldsymbol{\varrho}-\boldsymbol{\varrho}_0),\\
(2\,1\,3):&\quad \delta(\mathbf{r}+\mathbf{r}_0)\delta(\boldsymbol{\varrho}-\boldsymbol{\varrho}_0),\\
(2\,3\,1):&\quad \delta(\mathbf{r}'-\mathbf{r}_0')\delta(\boldsymbol{\varrho}'-\boldsymbol{\varrho}_0'),\\
(3\,2\,1):&\quad \delta(\mathbf{r}'+\mathbf{r}_0')\delta(\boldsymbol{\varrho}'-\boldsymbol{\varrho}_0'),\\
(3\,1\,2):&\quad \delta(\mathbf{r}''-\mathbf{r}_0'')\delta(\boldsymbol{\varrho}''-\boldsymbol{\varrho}_0''),\\
(1\,3\,2):&\quad \delta(\mathbf{r}''+\mathbf{r}_0'')\delta(\boldsymbol{\varrho}''-\boldsymbol{\varrho}_0'').
\end{aligned} \tag{180}$$

Here (1 2 3), (2 1 3), etc. denote the permutations that label the individual terms of $\mathrm{Tr}(1\,2\,3|\mathfrak{U}_3{}^S|1\,2\,3)$. The first line of Eq. (180) corresponds to the case of b_3 previously treated. As to the second line, the only difference is that now in Eq. (162) the contributions for odd l enter with opposite sign. Thus in combining the (1 2 3) and (2 1 3) terms the terms odd in l cancel, as is characteristic for a BE system. We could confine ourselves previously to the contributions $l=0$, however, so that (2 1 3) contributes as much as (1 2 3) does. Finally, since $b_{3(2)}{}^{\mathrm{BE}}$ is additively composed of the six contributions corresponding to all permutations, the (r',ρ')- and (r'',ρ'')-pairs of Eq. (180) contribute as much as the (r,ρ)-pair does.

Using Eqs. (3), (82), (124), (126), and (179) we find for the third virial coefficient for a BE gas, in the WB limit,

$$\begin{aligned}
C_{\mathrm{BE}}&=N^2\lambda^6\left[\frac{81}{8}-\frac{77}{9\sqrt{3}}+\frac{8}{3\pi}\right]\\
&=9.4\times10^5/T^3\ \mathrm{cm}^6/\mathrm{mole}.
\end{aligned} \tag{181}$$

Hence if the WB limit is applicable to He^4, the third virial coefficient should be large and positive at temperatures of, say, below 1°K. We have made no estimate of how potential-dependent terms would correct the answer (181).

VIII. $C(T)$ FOR THE CASE OF STRONG BINDING

From the definition of strong binding, given in Sec. I, it follows that this regime has no applicability for He. The main interest of this section is therefore a methodical one. We are now in a situation in which the binary expansion method is not applicable, see Sec. V. The method to be considered here is a generalization of the chemical equilibrium approach which has also been used[3] for the second virial coefficient in the presence of a strongly bound two-body state.

Let us call the atoms of the gas X_1, and their binary and ternary bound systems X_2 and X_3, with binding energies ϵ_2 and ϵ_3, respectively. We shall assume that there exists only one such two-body and one three-body bound state, each with unit weight. The extension of what follows to more bound states will be obvious. We shall furthermore assume that the particles X_1 satisfy BE statistics; the extension to the FD case will also be straightforward.

In the strong-binding approach we consider the gas as a mixture of N_i particles of kind X_i in chemical equilibrium. If in addition we assume that the three BE gases X_i are ideal, the equation of state of the system is

$$\frac{pV}{kT}=\sum_{i=1}^{3}\left[N_i+\frac{\beta_iN_i{}^2}{V}+\gamma_i\frac{N_i{}^3}{V^2}+\cdots\right]. \tag{182}$$

Here β_iN_i, $\gamma_iN_i{}^2$ are the second and third virial coefficients, respectively, of the gas of kind i. Although the gases are ideal there do, of course, exist nonvanishing virial coefficients due to their BE character. As the gases are supposed to be interacting *only* via the equilibrium reactions

$$X_3\rightleftharpoons X_2+X_1\rightleftharpoons X_1+X_1+X_1; \tag{183}$$

there are no terms $\sim N_iN_j$ $(i\neq j)$ present in Eq. (182).

The N_i can be found from the BE-distribution

$$N_n=\frac{V}{8\pi^3}\int d\mathbf{p}\bigg/\left\{\frac{1}{A_n}\exp\left[\beta\left(\frac{p^2}{n}-\epsilon_n\right)\right]-1\right\}, \tag{184}$$

(with $\epsilon_1\equiv0$). Here $A_n=\exp(\beta\mu_n)$, where μ_n is the chemical potential of X_n. Chemical equilibrium implies that

$$A_n=A_1{}^n. \tag{185}$$

Finally, if N is the total number of X atoms in the system, then

$$N_1+2N_2+3N_3=N. \tag{186}$$

From Eq. (184) we can find A_n in terms of N_n and then from Eqs. (185), (186) the N_n can be expressed as functions of N. Developing in both stages up to terms $\sim V^{-2}$, we find

$$\begin{aligned}
N_1&=N-2aN^2+(8a^2-3b+2c)N^3,\\
N_2&=aN^2-(4a^2+c)N^3,\\
N_3&=bN^3,
\end{aligned} \tag{187}$$

where

$$a=2^{\frac{3}{2}}\lambda^3e^{\beta\epsilon_2}/V,\quad b=3^{\frac{3}{2}}\lambda^6e^{\beta\epsilon_3}/V^2,\quad c=a\lambda^3/(2^{\frac{1}{2}}V). \tag{188}$$

It will be seen that if we insert Eqs. (187), (188) into Eq. (182), and again expand the right-hand side of that equation up to $O(V^{-2})$, the terms $\sim\beta_i$, γ_i with $i>1$ must be dropped. From Eqs. (25) and (121) it follows that

$$\beta_1=\lambda^3/2^{\frac{5}{2}}, \quad \gamma_1=\lambda^6(\tfrac{1}{8}-2/3^{\frac{5}{2}}). \tag{189}$$

Thus upon rearrangement in powers of V^{-1},

$$\frac{pV}{kT}=N\left[1+\frac{B}{V}+\frac{C}{V^2}+\cdots\right], \tag{190}$$

where

$$B=-N\lambda^3[2^{\frac{3}{2}}e^{\beta\epsilon_2}+1/2^{\frac{5}{2}}], \tag{191}$$

$$C=2N^2\lambda^6[2e^{\beta\epsilon_2}+16e^{2\beta\epsilon_2}-3^{\frac{3}{2}}e^{\beta\epsilon_3}+(\tfrac{1}{16}-1/3^{\frac{5}{2}})]. \tag{192}$$

The "nonexponential" terms of Eqs. (191), (192) are of course the ideal BE contributions. Note that these last two equations could also have been obtained from Eq. (3), where the Mayer b's are taken to be

$$\begin{aligned} b_1&=\lambda^{-3}, \quad b_2=\lambda^{-3}[2^{-\frac{5}{2}}+2^{\frac{3}{2}}e^{\beta\epsilon_2}], \\ b_3&=\lambda^{-3}[3^{-\frac{5}{2}}+3^{\frac{3}{2}}e^{\beta\epsilon_3}], \end{aligned} \tag{193}$$

corresponding to the neglect of all contributions but the ideal and discrete ones. We further observe:

(1) If we had taken for β_1 the ideal contribution [see Eq. (189)] plus the two-body continuum state terms, we would have arrived at the exact expression for B_{BE} in which the bound-state term appears by the separate equilibrium argument.

(2) One might perhaps try to estimate the effect of the nonideality of the BE gases, inasfar as their *mutual* interaction is concerned, by including in Eq. (182) terms like $\beta_{12}N_1N_2V^{-1}$, which are present in the general virial expansion for nonideal mixtures. From Eq. (187) it is seen that the term just mentioned has a $O(V^{-2})$ part which contributes to C. The physical effect here considered is the scattering of X_1 on X_2 and the leading order of contribution to C is

$$\sim\frac{a_{12}}{\lambda}e^{\beta\epsilon_2}\lambda^6N^2, \tag{194}$$

where a_{12} is the scattering length for (X_1,X_2)-scattering.

(3) One might perhaps also try to include in γ_1, besides the ideal gas term, the complete continuum part of the three-body BE interaction as treated by binary expansion which gives a leading term in C

$$\sim a^2/\lambda^2; \tag{195}$$

see Eq. (121). In addition terms will appear $\sim a^2\lambda^{-2}e^{\beta\epsilon_2}$, etc.

However, the remarks in connection with the expressions (194), (195) are only of a heuristic character. A systematic simultaneous treatment of bound-state and continuum contributions needs a further thorough investigation.

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APPENDIX I. FURTHER REMARKS ABOUT $U_l(G)$

$U_l(G)$ is given by Eq. (69) with the constraint (68) on the integration variables β_k. We can formally replace this constraint by an auxiliary integration

$$U_l(G)=e^{-\beta T_l}\frac{1}{2\pi i}\int\frac{e^{\beta t}}{t}dt\,\mathbf{S}\int_0^\infty\cdots\int_0^\infty d\beta_1\cdots d\beta_N \times\exp[(T_l-t)\sum\beta_k]C(\beta_N)\cdots C(\beta_1), \tag{A.1}$$

where the path of the newly introduced t-integration is from $-i\infty$ to $+i\infty$ in the t-plane and to the right of all singularities (in t) of the integrand.

Equation (A.1) can conveniently be used to find the number $\mathfrak{N}(n(ij))$ defined after Eq. (69). The procedure is to go to the classical limit where $U_l(G)$ reduces to $U_l^c(G)$, as exemplified for $l=2$ by the transition from Eq. (71) to Eq. (72). With the help of the definition of $U_l^c(G)$, see Eq. (63), and of Eq. (A.1) one thus arrives at the identity

$$f_{i_1j_1}f_{i_2j_2}\cdots f_{i_mj_m} = \sum_{n(i_1j_1)=1}^{\infty}\chi(n(i_1,j_1),\cdots,n(i_m,j_m)) \times\frac{1}{2\pi i}\int\frac{e^{\beta t}}{t}dt\prod_{\lambda=1}^{m}\left[\frac{-\Phi_{i_\lambda j_\lambda}}{t+\Phi_{i_\lambda j_\lambda}}\right]^{n(i_\lambda,j_\lambda)}, \tag{A.2}$$

where the point pairs labeling the f's are characteristic for the Ursell graph under consideration. Observe that in the classical limit we may replace the operation S defined after Eq. (69) by the summation $\sum$ of Eq. (A.2) with a weight χ. This is so because in this limit, where the order of the C-factors in Eq. (A.1) becomes irrelevant, each of the allowed permutations of C-factors must contribute equally. Thus the number $\mathfrak{N}(n(ij))$ is equal to the absolute value of χ. To find χ we use the definition (61) of f_{ij} and also the identity

$$\prod_{\lambda=1}^{m}[\exp(-\beta x_\lambda)-1] =\frac{1}{2\pi i}\int dt\, e^{\beta t}\left[\frac{(-1)^m}{t}+(-1)^{m-1}\sum_\lambda\frac{1}{t+x_\lambda}+(-1)^{m-2} \times\sum_{\lambda>\mu}\frac{1}{t+x_\lambda+x_\mu}+\cdots+\frac{1}{t+x_1+\cdots+x_m}\right]. \tag{A.3}$$

From Eqs. (A.2) and (A.3) one finds, after some rearrangement,

$$\chi(n_1,\cdots,n_m)=\int_0^\infty dz\, e^{-z}\prod_{\lambda=1}^{m} L_{n_\lambda}{}^{(-1)}(z), \qquad \text{(A.4)}$$

where $L_n{}^{(-1)}$ is an associated Laguerre polynomial.[24] Examples: $\chi(1,1,1)=-6$; $\chi(2,1,1)=6$; $\chi(2,2,2)=30$. Thus the corresponding $\mathfrak{N}$ values are 6, 6, 30 as can be verified by drawing the quantum graphs in question.

We could also have obtained the number $\mathfrak{N}$ directly by purely combinatorial methods. Thus the above argument also provides proof of the convergence to $b_l{}^c$ of the binary expansion series for b_l in the classical limit.

Finally, we note that the expression (A.1) is also suited to give an alternative formal expression for the trace in momentum space of $U_l(G)$. It follows from Eqs. (65) and (A.1) that

$$\begin{aligned}\mathrm{Tr}U_l(G)&\\ &=\int dq_1\cdots dq_l\, e^{-\beta T_l(q)}\times\frac{1}{2\pi i}\int dt\frac{e^{\beta t}}{t}\mathsf{S}\\ &\qquad\times\langle q|D_q(i_Nk_N)|q'\rangle\langle q'|D_q(i_{N-1}k_{N-1})|q''\rangle\cdots\\ &\qquad\qquad\times\langle q^{(N-1)}|D_q(i_1k_1|q\rangle, \qquad \text{(A.5)}\end{aligned}$$

where $|q\rangle=|q_1,\cdots,q_l\rangle$ and

$$\begin{aligned}&\langle q'|D_q(ik)|q''\rangle\\ &=\left\langle q'\right|\int_0^\infty d\beta\, e^{\beta(T_l(q)-t)}B(\beta,ik)\\ &\qquad\times\exp\{-\beta[T_l(q'')-q_i{}''^2-q_k{}''^2]\}\left|q''\right\rangle. \qquad \text{(A.6)}\end{aligned}$$

Here $T_l(q)$ denotes the c-number kinetic energy of l particles with momenta $(q_1,\cdots,q_l)$. We now make use of Eq. (74) and integrate the $\partial U_2/\partial\beta$-term by parts. The integrated term gives no contribution at $\beta=0$ as $U_2(0)=0$ and no contribution at $\beta=\infty$ as $\mathrm{Re}(t)$ may be taken arbitrarily large and positive. In this way one finds, with the help of the definition of U_2,

$$\begin{aligned}&\langle q'|D_q(ik)|q''\rangle\\ &=-\left\langle q'\right|\Phi_{ik}\frac{1}{t+H_{ik}+T_l(q'')-q_i{}''^2-q_k{}''^2-T_l(q)}\left|q''\right\rangle. \qquad \text{(A.7)}\end{aligned}$$

This expression and the corresponding form of $\mathrm{Tr}U_l(G)$ may perhaps be of interest for a comparison between various formal expansion techniques currently used for many-body problems.

APPENDIX II. $b_{3(1)}{}^{\mathrm{BE}}$ FOR HARD SPHERE GAS

For hard spheres the relative motion matrix $(r|u|r')$ [see Eq. (77)] becomes, in the S-wave approximation,[5]

$$(r|u|r')=\frac{1}{2^{\frac{5}{2}}\pi\lambda rr'}\xi(r,r'),$$

$$\xi(r,r')=\begin{cases}\exp\left[\dfrac{-(r+r')^2}{8\beta}\right]-\exp\left[\dfrac{-(r+r'-2a)^2}{8\beta}\right], & r>a,\quad r'>a,\\[2ex] \exp\left[\dfrac{-(r+r')^2}{8\beta}\right]-\exp\left[\dfrac{-(r-r')^2}{8\beta}\right], & \text{otherwise.}\end{cases}$$

Inserting this in Eq. (85), we get

$$b_{3(1)}{}^{\mathrm{BE}}=-\frac{8}{3\lambda^5}G(a), \qquad \text{(A.8)}$$

where

$$\begin{aligned}G(a)=\int\int drdr'\Bigg\{&\exp\left[-\frac{3}{8\beta}(r+r')^2\right]\\ &-\exp\left[-\frac{3}{8\beta}(r-r')^2\right]\Bigg\}\xi(r,r').\end{aligned}$$

The expansion in powers of a is much facilitated by noting that

$$\frac{\partial G}{\partial a}=2^{-\frac{1}{2}}\lambda-\frac{4}{\beta}\int_0^\infty dt\, t^2\exp\left[-\frac{t^2}{2\beta}-\frac{3}{2\beta}(t+a)^2\right],$$

$$t=\tfrac{1}{2}(r+r')-a,$$

from which one immediately obtains

$$\begin{aligned}(\partial G/\partial a)_{a=0}&=3\lambda/2^{\frac{5}{2}},\\ (\partial^2G/\partial a^2)_{a=0}&=\tfrac{3}{2},\\ (\partial^3G/\partial a^3)_{a=0}&=-15\pi/2^{\frac{5}{2}}\lambda.\end{aligned}$$

The first three terms of the Taylor expansion of $b_{3(1)}{}^{\mathrm{BE}}$ as given by Eq. (A.8) immediately gives Eq. (97).[25]

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[24] The following definition is used:

$$L_n{}^{(-1)}(z)=\sum_{k=1}^{n}(-1)^k\frac{z^k}{k!}\binom{n-1}{n-k}.$$

[25] $b_3{}^{\mathrm{BE}}$ up to order a^2 has previously been obtained by Huang, Yang, and Luttinger with the help of the pseudopotential method; see reference 4. See also T. D. Lee and C. N. Yang, Phys. Rev. **116**, 25 (1959).