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Low-Temperature Expansion of the Third-Cluster Coefficient of a Quantum Gas

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The low-temperature behavior of the third-quantum-cluster coefficient is investigated using the multiple-scattering form of the binary-collision expansion. For hard spheres and Boltzmann statistics we find

$$b_3 = 2(a/\lambda)^2 - \frac{4}{3}\sqrt{2} \pi (a/\lambda)^3 - \frac{16}{3}(4\pi - 3\sqrt{3})(a/\lambda)^4 \ln(a/\lambda) + O((a/\lambda)^4),$$

where a is the sphere diameter and λ is the thermal wavelength. The first two terms were obtained some time ago by Lee and Yang and by Pais and Uhlenbeck. The occurrence of a term of the form $\lambda^{-4} \ln \lambda$ was predicted recently by Adhikari and Amado. The expansion is also given for Bose-Einstein and Fermi-Dirac statistics, and for the case of an intermolecular potential without bound states. The limitations of such low-temperature expansions are discussed.

I. INTRODUCTION

For a classical gas, the cluster coefficients b_l (and hence the virial coefficients) can be expressed as integrals over functions of the two-body potential. Thus their evaluation involves a series of quadratures.

In the quantum case, the connection between the cluster coefficients and the intermolecular potential is not nearly so direct. Only for the second coefficient b_2 is there available an exact expression¹ which allows its computation over a wide temperature range. There exist formal expressions for the third²⁻⁴ and higher⁵⁻⁸ coefficients, but these have not as yet been used for any extensive calculations.

The limiting case of low temperatures has been studied using the binary-collision expansion⁹ and the related pseudopotential method.¹⁰ For the hard-sphere gas Lee and Yang¹¹ evaluated b_l as a series in powers of a/λ as far as the term in $(a/\lambda)^2$. [a is the sphere diameter and $\lambda = (2\pi\hbar^2/mkT)^{1/2}$ is the thermal wavelength.] Pais and Uhlenbeck¹² extended this to the term in $(a/\lambda)^3$ for b_3 . From this

it might appear that we have the leading terms of an expansion for b_l in powers of (a/λ) .¹³ However, Adhikari and Amado¹⁴ have recently shown that the low-temperature expansions of cluster coefficients higher than the second¹⁵ involve $\ln \lambda$ as well as powers of λ . In particular, the third-cluster coefficient (for Boltzmann statistics) has the expansion

$$b_3 = c_1/\lambda^2 + c_2/\lambda^3 + c_3(\ln \lambda)/\lambda^4 + O(\lambda^{-4}), \quad (1)$$

where the c_i depend only on the hard-sphere diameter, or more generally on the two-body s -wave scattering length. The coefficient c_3 can be found from the leading terms of the binary-collision expansion, and we shall present its explicit calculation below. However this is as far as we can go by present methods. The evaluation of the coefficient of the λ^{-4} term involves a solution of the full three-body problem, and this is a calculation of a higher order of difficulty.

It should be mentioned that other quantities relating to many-particle systems have logarithmic terms in their expansions. In particular, the low-density expansion of the ground-state energy of a system of bosons¹⁶ or of fermions^{17,18} contains a

term of the type $a^4 \ln a$. We return to this point in Sec. VI.

In this paper we calculate the expansion coefficients for b_3 (for all types of statistics) up to and including that of the logarithmic term.¹⁹ These are given first for the hard-sphere case, and then for the more general case where the particles interact through a potential without bound states. In the latter case several parameters besides the s -wave scattering length have to be introduced. Instead of using the original form of the binary-collision expansion,⁹ we use the equivalent form based on the Watson multiple-scattering expansion of the T matrix.^{20,21} This has some advantages for the present calculation.

II. BASIC EQUATIONS

Consider a system of N identical particles each of mass m in a container of volume V . Let the Hamiltonian be

$$H_N = H_N^0 + \sum_{i>j} v_{ij}, \quad (2)$$

where H_N^0 is the kinetic energy of the N particles and v_{ij} is a pair potential. The cluster coefficients $b_l(V)$ occur in the expansion of the logarithm of the grand partition function in powers of the fugacity z :²²

$$\frac{1}{V} \ln Z_{gr} = \frac{1}{\lambda^3} \sum_{l=1}^{\infty} b_l(V) z^l. \quad (3)$$

From this one obtains the equation of state in parametric form;

$$\beta p = \lim_{V \rightarrow \infty} \frac{1}{\lambda^3} \sum_{l=1}^{\infty} b_l(V) z^l, \quad (4)$$

$$\frac{N}{V} = \lim_{V \rightarrow \infty} \frac{1}{\lambda^3} \sum_{l=1}^{\infty} l b_l(V) z^l,$$

where p is the pressure and $\beta = 1/kT$. The virial series is obtained by eliminating z between these two equations. In the gas region the limit and sum in (4) can be interchanged, so the quantity we are interested in is

$$b_l = \lim_{V \rightarrow \infty} b_l(V). \quad (5)$$

In the usual theory,²² $b_l(V)$ is given by

$$b_l(V) = (\lambda^3/l!V) \text{Tr}(U_l), \quad (6)$$

where the Ursell operator U_l is defined in terms of $W_n = e^{-\beta H_n}$. More concisely, $b_l(V)$ can be expressed directly in terms of $e^{-\beta H_l}$ according to

$$b_l(V) = (\lambda^3/l!V) (\text{Tr} e^{-\beta H_l})_c. \quad (7)$$

Here we are thinking of $\text{Tr} e^{-\beta H_l}$ expanded in a perturbation series and the various terms represented by diagrams. The suffix c then indicates that only connected diagrams are to be used in

evaluating $b_l(V)$. The basic perturbation expansion is in powers of the pair potential v . A partial summation of this series leads to the Lee-Yang binary-collision expansion,⁹ in which the place of the potential is taken by the binary kernel

$$B(\beta) = -v e^{-\beta H_2}. \quad (8)$$

$B(\beta)$ can be calculated from the solution of the two-body Schrödinger equation, and it has the advantage of existing even for interactions with a hard core.

The above may be looked upon as a "time-dependent" formulation of the problem, with $-i\beta$ playing the role of the time. The "time-independent" counterpart is obtained by taking an inverse Laplace transform with respect to β . The basic relation is²⁰

$$e^{-\beta H_l} = \mathcal{L}_\beta^{-1} G(z) \equiv (1/2\pi i) \int_C dz e^{-\beta z} G(z), \quad (9)$$

where

$$G(z) = (z - H_l)^{-1}. \quad (10)$$

The contour C surrounds the spectrum of H_l on the real axis and is traversed counterclockwise. In this formulation Eq. (7) is replaced by

$$b_l(V) = (\lambda^3/l!V) [\text{Tr} \mathcal{L}_\beta^{-1} G(z)]_c. \quad (11)$$

$G(z)$ is related to the l -body T matrix $T(z)$ by²³

$$G(z) = G_0(z) + G_0(z)T(z)G_0(z), \quad (12)$$

where $G_0(z) = (z - H_l^0)^{-1}$. Inserting this in (11) gives

$$b_l(V) - b_l^{(0)}(V) = (\lambda^3/l!V) [\text{Tr} \mathcal{L}_\beta^{-1} G_0(z)T(z)G_0(z)]_c, \quad (13)$$

where

$$b_l^{(0)}(V) = (\lambda^3/l!V) [\text{Tr} \mathcal{L}_\beta^{-1} G_0(z)]_c. \quad (14)$$

is the ideal-gas term. This expresses $b_l(V)$ in terms of the completely off-shell T matrix. Dashen, Ma, and Bernstein⁷ have gone further and shown that $b_l(V)$ can be expressed entirely in terms of on-shell quantities by the formula

$$b_l(V) = \frac{\lambda^3}{l!V} \int_0^\infty dE e^{-\beta E} \frac{1}{2\pi} \frac{\partial}{\partial E} \text{Im} [\text{Tr} \ln S(E)]_c, \quad (15)$$

where $S(E)$ is the l -particle S matrix. However, considerable care is required in handling this expression, since singular integrals arise as soon as one attempts an actual evaluation of terms. In the present case we prefer to work with (13) which avoids this complication at the expense of introducing off-shell quantities.

If in (13) we separate out the center-of-mass momentum and take the limit $V \rightarrow \infty$, we get

$$b_l - b_l^{(0)} = (l^3/2!l!) [\text{Tr}_{\text{c.m.}} \mathcal{L}_\beta^{-1} G_0(z)T(z)G_0(z)]_c, \quad (16)$$

where $b_l^{(0)} = l^{-5/2}$. The trace is now to be performed in the center-of-mass system. The l -body T matrix can be expanded in a multiple-scattering series according to²⁰

$$T(z) = \sum_{\alpha} t_{\alpha} + \sum_{\alpha} t_{\alpha} G_0 \sum_{\beta \neq \alpha} t_{\beta} + \dots, \quad (17)$$

where the summations run from 1 to l . $t_{\alpha} \equiv t_{\alpha}(z, H_l^0)$ is the T matrix satisfying the equation

$$t_{\alpha} = v_{\alpha} + v_{\alpha}(z - H_l^0)^{-1} t_{\alpha}. \quad (18)$$

Inserting (17) in (16) gives a series for b_l . This is just the "time-independent" counterpart of the binary-collision expansion,^{21,24} and indeed the binary kernel and the T matrix are related by

$$B(\beta) = -\mathcal{L}_{\beta}^{-1} [t(z, H_2^0)(z - H_2^0)^{-1}]. \quad (19)$$

Although the two expansions are equivalent, there do seem to be some advantages in using the multiple-scattering form. The quantities used are already familiar from scattering theory. The two-body T matrix possesses certain symmetries which the binary kernel does not, and this reduces the number of different terms to be calculated. Also in the actual calculation one obtains the integrals in a more flexible form, and this can facilitate their evaluation. (For an example of this see Appendix A.)

The trace in (16) is the best evaluated using the free-particle momentum eigenstates $|\vec{k}_1 \vec{k}_2 \dots \vec{k}_l\rangle$ (with $\sum_{\alpha} \vec{k}_{\alpha} = \vec{0}$ since we are in the center-of-mass system):

$$b_l - b_l^{(0)} = (l^{3/2}/l!) \sum_P \epsilon^P \int d^{3l-3} k \mathcal{L}_{\beta}^{-1} \\ \times \langle \vec{k}_1 \dots \vec{k}_l | G_0(z) T(z) G_0(z) P | \vec{k}_1 \dots \vec{k}_l \rangle_c. \quad (20)$$

The sum is over all permutations P of the l particles, and

$$\epsilon = \begin{cases} 1 & \text{for bosons} \\ -1 & \text{for fermions} \end{cases}.$$

We are interested in the case $l=3$. It is convenient to introduce the combinations

$$\vec{k}_{23} = \frac{1}{2}(\vec{k}_2 - \vec{k}_3), \text{ etc.} \quad (21)$$

The total energy is (in units where $\hbar = m = 1$)

$$E = \frac{1}{2}(k_1^2 + k_2^2 + k_3^2), \quad (22)$$

with the k 's restricted by $\sum_{\alpha} \vec{k}_{\alpha} = \vec{0}$. Thus

$$E = k_1^2 + \vec{k}_1 \cdot \vec{k}_2 + k_2^2 \quad (23)$$

and

$$E = k_{23}^2 + \frac{3}{4}k_1^2. \quad (24)$$

The matrix elements of $t_{\alpha}(z, H_3^0)$ in the space of three-particle states are

$$\langle \vec{k}'_1 \vec{k}'_2 \vec{k}'_3 | t_{\alpha}(z, H_3^0) | \vec{k}_1 \vec{k}_2 \vec{k}_3 \rangle \\ = \langle \vec{k}'_{\beta} | t(z - \frac{3}{4}k_{\alpha}^2) | \vec{k}_{\beta} \rangle \delta(\vec{k}'_{\alpha} - \vec{k}_{\alpha}), \quad (25)$$

where $t(z)$ is the two-body T matrix. It satisfies the Lippmann-Schwinger equation

$$t(z) = v + v(z - h_0)^{-1} t(z), \quad (26)$$

where h_0 is the Hamiltonian for the relative motion of two free particles.

III. b_3 FOR HARD SPHERES: BOLTZMANN STATISTICS

For hard spheres, the off-shell two-body T matrix has the following expansion in powers of the sphere diameter a :

$$\langle \vec{k}' | t(z) | \vec{k} \rangle = (2\pi^2)^{-1} [a + a^2(-z)^{1/2} - \frac{1}{3}a^3(2z + k'^2 + k^2) \\ + a^3 \vec{k}' \cdot \vec{k} + O(a^4)]. \quad (27)$$

This can be obtained from the explicit expression for the hard-sphere t matrix,²⁵ or as a special case of the general expansion derived in Appendix C.

From (20), b_3 for Boltzmann statistics is

$$b_3 = (3^{3/2}/3!) \int d^6 k \mathcal{L}_{\beta}^{-1}(z - E)^{-2} \langle \vec{k}_1 \vec{k}_2 \vec{k}_3 | T(z) | \vec{k}_1 \vec{k}_2 \vec{k}_3 \rangle_c. \quad (28)$$

We now look at the individual terms that arise when the multiple-scattering series for $T(z)$ is inserted in (28). There are no connected diagrams involving one t matrix, so we need only consider terms with two or more t matrices.

A. Two t Matrices

The multiple-scattering series contains six terms involving two t matrices. These give equal contributions (as is seen by relabeling the particles), so the total contribution to b_3 is

$$(b_3)_2 = 3\sqrt{3} \int d^6 k \mathcal{L}_{\beta}^{-1} \langle \vec{k}_1 \vec{k}_2 \vec{k}_3 | G_0 t_1 G_0 t_2 G_0 | \vec{k}_1 \vec{k}_2 \vec{k}_3 \rangle \\ = 3\sqrt{3} \int d^6 k \mathcal{L}_{\beta}^{-1}(z - E)^{-3} \langle \vec{k}_{23} | t(z - \frac{3}{4}k_1^2) | \vec{k}_{23} \rangle \\ \times \langle \vec{k}_{31} | t(z - \frac{3}{4}k_2^2) | \vec{k}_{31} \rangle. \quad (29)$$

The expansion (27) for the t matrices is now inserted, and the inverse transform and momentum integrals are performed, giving

$$(b_3)_2 = 2(a/\lambda)^2 + 2\sqrt{2}\pi (a/\lambda)^3 + O((a/\lambda)^4). \quad (30)$$

The details are given in Appendix A.

B. Three t Matrices

In this category we have twelve terms giving contributions of two types. The total contribution to b_3 from the six terms of the first type is

$$\begin{aligned}
(b_3)_{3a} &= 3\sqrt{3} \int d^3k \mathcal{L}_\beta^{-1} \langle \bar{\mathbf{k}}_1 \bar{\mathbf{k}}_2 \bar{\mathbf{k}}_3 | G_0 t_1 G_0 t_2 G_0 t_1 G_0 | \bar{\mathbf{k}}_1 \bar{\mathbf{k}}_2 \bar{\mathbf{k}}_3 \rangle \\
&= 3\sqrt{3} \int d^3k_{23} d^3k_1 d^3k_2' \mathcal{L}_\beta^{-1} [z - (k_{23}^2 + \frac{3}{4}k_1^2)]^{-2} [z - (k_1^2 + \bar{\mathbf{k}}_1 \cdot \bar{\mathbf{k}}_2' + k_2'^2)]^{-2} \\
&\quad \times \langle \bar{\mathbf{k}}_{23} | t(z - \frac{3}{4}k_1^2) | -\bar{\mathbf{k}}_2' - \frac{1}{2}\bar{\mathbf{k}}_1 \rangle^2 \langle \bar{\mathbf{k}}_1 + \frac{1}{2}\bar{\mathbf{k}}_2' | t(z - \frac{3}{4}k_2'^2) | \bar{\mathbf{k}}_1 + \frac{1}{2}\bar{\mathbf{k}}_2' \rangle. \quad (31)
\end{aligned}$$

Inserting the expansion for the t matrices leads to

$$(b_3)_{3a} = I_1 a^3 + (I_2 + I_3) a^4 + \dots, \quad (32)$$

where

$$\begin{aligned}
I_\alpha &= 3\sqrt{3} (2\pi^2)^{-3} \int d^3k d^3p d^3q \mathcal{L}_\beta^{-1} [z - (k^2 + \frac{3}{4}p^2)]^{-2} \\
&\quad \times [z - (p^2 + \vec{p} \cdot \vec{q} + q^2)]^{-2} f_\alpha. \quad (33)
\end{aligned}$$

Here we have set $\bar{\mathbf{k}}_{23} = \bar{\mathbf{k}}$, $\bar{\mathbf{k}}_1 = \vec{p}$, $\bar{\mathbf{k}}_2' = \vec{q}$, and

$$f_1 = 1, \quad (34)$$

$$f_2 = 2(\frac{3}{4}p^2 - z)^{1/2}, \quad (35)$$

$$f_3 = (\frac{3}{4}q^2 - z)^{1/2}. \quad (36)$$

To evaluate I_1 , make the change of variable $\vec{q} = \vec{s} - \frac{1}{2}\vec{p}$. Then

$$\begin{aligned}
I_1 &= 3\sqrt{3} (2\pi^2)^{-3} \int d^3p e^{-3\beta p^2/4} \mathcal{L}_\beta^{-1} \int d^3k (z - k^2)^{-2} \\
&\quad \times \int d^3s (z - s^2)^{-2}. \quad (37)
\end{aligned}$$

The integrals are now easily done (provided one does the k and s integrals first), with the result

$$I_1 = -2\sqrt{2}\pi\lambda^{-3}. \quad (38)$$

I_2 is readily evaluated in the same manner. However, all we require is the result that I_2 is finite, and thus

$$I_2 a^4 = O((a/\lambda)^4). \quad (39)$$

On the other hand I_3 is divergent: The q integral diverges logarithmically at its upper limit. This occurs because a small-momentum expansion has been used for the t matrices, but the integration range is still taken from zero to infinity. The expression (31) for $(b_3)_{3a}$ with the full t matrices in it is convergent, and to obtain the complete low-temperature series we would have to work with this. However, the next term in the series can be obtained from I_3 by the device of introducing a cutoff on the q integration. From the explicit expression for $\langle \bar{\mathbf{k}}' | t(z) | \bar{\mathbf{k}} \rangle$,²⁵ it is apparent that the major contribution comes from the region where ak is small. Thus the low-temperature behavior of I_3 can be found by cutting off the q integral at a momentum of order $1/a$. Specifically, we restrict q to be less than d_1/a where d_1 is a number independent of q and a . Then

$$\begin{aligned}
I_3 &\sim 3\sqrt{3} (2\pi^2)^{-3} \int d^3k d^3p \mathcal{L}_\beta^{-1} \\
&\quad \times [z - (k^2 + \frac{3}{4}p^2)]^{-2} J_1(p, z), \quad (40)
\end{aligned}$$

where

$$J_1(p, z) = \int_{q < d_1/a} d^3q [z - (p^2 + \vec{p} \cdot \vec{q} + q^2)]^{-2} (\frac{3}{4}q^2 - z)^{1/2}. \quad (41)$$

As $p \rightarrow 0$ and $z \rightarrow 0$,

$$\begin{aligned}
J_1(p, z) &\sim \int_{q < d_1/a} d^3q (z - q^2)^{-2} (\frac{3}{4}q^2)^{1/2} \\
&\sim -\sqrt{3}\pi \ln(-a^2 z). \quad (42)
\end{aligned}$$

{A more careful analysis gives $-\sqrt{3}\pi \ln[a^2(p^2 - z)]$ but this does not affect the final result.} Inserting (42) into (40) and making the changes of variable $\beta z = \zeta$, $\beta^{1/2}k = x$, $\beta^{1/2}p = y$ gives

$$\begin{aligned}
I_3 &= -3\sqrt{3} (2\pi^2)^{-3} \sqrt{3}\pi\beta^{-2} \ln\left(\frac{a^2}{\beta}\right) \int d^3x d^3y \\
&\quad \times \frac{1}{2\pi i} \int_c d\zeta e^{-\zeta} [\zeta - (x^2 + \frac{3}{4}y^2)]^{-2} + O\left(\frac{a^4}{\beta^2}\right) \\
&= 8\sqrt{3}\lambda^{-4} \ln\left(\frac{a}{\lambda}\right) + O\left(\left(\frac{a}{\lambda}\right)^4\right). \quad (43)
\end{aligned}$$

From (32), (38), (39), and (43) we have the result

$$(b_3)_{3a} = -2\sqrt{2}\pi(a/\lambda)^3 + 8\sqrt{3}(a/\lambda)^4 \ln(a/\lambda) + O((a/\lambda)^4). \quad (44)$$

The contribution from the second six terms containing three t matrices is

$$(b_3)_{3b} = 3\sqrt{3} \int d^3k \mathcal{L}_\beta^{-1} \langle \bar{\mathbf{k}}_1 \bar{\mathbf{k}}_2 \bar{\mathbf{k}}_3 | G_0 t_1 G_0 t_2 G_0 t_3 G_0 | \bar{\mathbf{k}}_1 \bar{\mathbf{k}}_2 \bar{\mathbf{k}}_3 \rangle. \quad (45)$$

This is treated in the same way as $(b_3)_{3a}$, with the result

$$(b_3)_{3b} = -\frac{4}{3}\sqrt{2}\pi(a/\lambda)^3 + 8\sqrt{3}(a/\lambda)^4 \ln(a/\lambda) + O((a/\lambda)^4). \quad (46)$$

Thus the total contribution to b_3 from terms containing three t matrices is

$$\begin{aligned}
(b_3)_3 &= -(2\sqrt{2}\pi + \frac{4}{3}\sqrt{2}\pi)(a/\lambda)^3 + 16\sqrt{3}(a/\lambda)^4 \ln(a/\lambda) \\
&\quad + O((a/\lambda)^4). \quad (47)
\end{aligned}$$

C. Four t Matrices

The multiple-scattering series gives rise to 24 terms containing four t matrices. If we use only the first term of expansion (27) for the t matrices, the contribution to b_3 can be expressed in terms of two different integrals:

$$(b_3)_4 = 3\sqrt{3} (2\pi^2)^{-4} (I_4 + 3I_5) a^4 + \dots, \quad (48)$$

where

$$\begin{aligned}
I_4 &= \int d^3k d^3p d^3q d^3s \mathcal{L}_\beta^{-1} [z - (k^2 + \frac{3}{4}p^2)]^{-2} \\
&\quad \times [z - (p^2 + \vec{p} \cdot \vec{q} + q^2)]^{-1} [z - (q^2 + \vec{q} \cdot \vec{s} + s^2)]^{-1}
\end{aligned}$$

$$\begin{aligned} & \times [z - (p^2 + \vec{p} \cdot \vec{s} + s^2)]^{-1}, \quad (49) \\ I_5 = & \int d^3k d^3p d^3q d^3s \mathcal{L}_B^{-1} [z - (k^2 + \vec{k} \cdot \vec{p} + p^2)]^{-2} \\ & \times [z - (k^2 + \vec{k} \cdot \vec{q} + q^2)]^{-1} [z - (s^2 + \vec{s} \cdot \vec{q} + q^2)]^{-1} \\ & \times [z - (s^2 + \vec{s} \cdot \vec{p} + p^2)]^{-1}. \quad (50) \end{aligned}$$

Both I_4 and I_5 are divergent as they stand. We adopt the same procedure as before, and introduce a cutoff on the momentum:

$$I_4 \sim \int d^3k d^3p \mathcal{L}_B^{-1} [z - (k^2 + \frac{3}{4} p^2)]^{-2} J_2(p, z), \quad (51)$$

where

$$\begin{aligned} J_2(p, z) = & \int_{s < a_2/a} d^3q d^3s [z - (p^2 + \vec{p} \cdot \vec{q} + q^2)]^{-1} \\ & \times [z - (q^2 + \vec{q} \cdot \vec{s} + s^2)]^{-1} \\ & \times [z - (p^2 + \vec{p} \cdot \vec{s} + s^2)]^{-1}. \quad (52) \end{aligned}$$

We need only the behavior of $J_2(p, z)$ as $p \rightarrow 0$ and $z \rightarrow 0$. In Appendix B it is shown that

$$J_2(p, z) \sim \frac{4}{3} \pi^4 \ln(-a^2 z). \quad (53)$$

Inserting this in (51) leads to

$$I_4 \sim -2^8 3^{-5/2} \pi^9 \lambda^{-4} \ln(a/\lambda) + O(\lambda^{-4}). \quad (54)$$

I_5 is treated in a similar way, and an identical logarithmic contribution is obtained. Thus

$$(b_3)_4 = -\frac{1}{3} 2^6 \pi (a/\lambda)^4 \ln(a/\lambda) + O((a/\lambda)^4). \quad (55)$$

D. Higher-Order Terms

Consider a term with five t matrices. The leading contribution has the general form

$$L_5 = a^5 \int (d^3k)^2 \mathcal{L}_B^{-1}(z-E)^{-2} \int (d^3k)^3 \prod_{i=1}^4 (z-E_i)^{-1}. \quad (56)$$

This is divergent, but proceeding as usual and cutting off the integrals at a momentum of order $1/a$ gives

$$\begin{aligned} L_5 \sim & a^5 \int (d^3k)^2 \mathcal{L}_B^{-1}(z-E)^{-2} \int_{z^{1/2}}^{1/a} (d^3k)^3 k^{-8} \\ \sim & a^5 \int (d^3k)^2 \mathcal{L}_B^{-1}(z-E)^{-2} a^{-1} \sim (a/\lambda)^4. \quad (57) \end{aligned}$$

Similarly, for a term containing n t matrices we find the general behavior

$$L_n \sim a^n \int (d^3k)^2 \mathcal{L}_B^{-1}(z-E)^{-2} \int_{z^{1/2}}^{1/a} (d^3k)^{n-2} k^{2-2n} \sim (a/\lambda)^4. \quad (58)$$

Thus all the higher terms give contributions of order $(a/\lambda)^4$, and to find the total contribution to b_3 it would be necessary to sum this infinite series.²⁶ The $(a/\lambda)^4$ term corresponds to a true three-body collision, and its determination would involve a solution of the three-body problem. The same conclusion is reached by Adhikari and Amado¹⁴ on the basis of the low-energy behavior of the three-body scattering amplitude as given by Amado and Rubin.²⁷ However, here we are only concerned with contributions to order $\lambda^{-4} \ln \lambda$, and these are completely determined by terms in the

multiple-scattering series involving fewer than five t matrices.

From (30), (47), and (55) we have the final result:

$$\begin{aligned} b_3 = & 2 \left(\frac{a}{\lambda} \right)^2 - \frac{4}{3} \sqrt{2} \pi \left(\frac{a}{\lambda} \right)^3 \\ & - \frac{16}{3} (4\pi - 3\sqrt{3}) \left(\frac{a}{\lambda} \right)^4 \ln \left(\frac{a}{\lambda} \right) + O \left(\left(\frac{a}{\lambda} \right)^4 \right). \quad (59) \end{aligned}$$

IV. b_3 FOR HARD SPHERES: BOSE-EINSTEIN AND FERMI-DIRAC STATISTICS

Let

$$\begin{aligned} M(1'2'3') = & (3\sqrt{3}/3!) \int d^3k \mathcal{L}_B^{-1}(z-E)^{-2} \\ & \times \langle \vec{k}_1 \vec{k}_2 \vec{k}_3 | T(z) | \vec{k}_1' \vec{k}_2' \vec{k}_3' \rangle_c. \quad (60) \end{aligned}$$

Then, from (20),

$$b_3^{\text{BE (FD)}} = b_3^{(0)} + \sum_P \epsilon^P PM(123). \quad (61)$$

It is convenient to separate b_3 into direct and exchange parts.⁹ If the particles have an intrinsic spin s and the interaction is spin independent, we can write

$$b_3^{\text{BE (FD)}} = (2s+1)^3 b_3^{\text{dir}} \pm (2s+1)^2 b_3^{\text{exch},1} + (2s+1) b_3^{\text{exch},2}, \quad (62)$$

where

$$b_3^{\text{dir}} = M(123), \quad (63)$$

$$b_3^{\text{exch},1} = M(132) + M(213) + M(321), \quad (64)$$

$$b_3^{\text{exch},2} = b_3^{(0)} + M(231) + M(312). \quad (65)$$

In (62) the plus sign refers to the Bose-Einstein (BE) case and the minus sign to the Fermi-Dirac (FD) case. b_3^{dir} is the same as b_3 for Boltzmann statistics. The other terms contain the effects of the statistics, $b_3^{\text{exch},1}$ coming from processes in which two particles interchange and $b_3^{\text{exch},2}$ from processes in which all three particles interchange.

We now proceed as before and substitute the multiple-scattering expansion for $T(z)$. In this case there are connected diagrams involving one t matrix, and a straightforward calculation gives the contributions

$$(b_3^{\text{exch},1})_1 = -\frac{1}{2} \sqrt{2} \frac{a}{\lambda} - \left(\frac{a}{\lambda} \right)^2 - \frac{17}{24} \sqrt{2} \pi \left(\frac{a}{\lambda} \right)^3 + O \left(\left(\frac{a}{\lambda} \right)^4 \right), \quad (66)$$

$$(b_3^{\text{exch},2})_1 = -\frac{1}{2} \sqrt{2} \frac{a}{\lambda} - \left(\frac{a}{\lambda} \right)^2 + \frac{37}{24} \sqrt{2} \pi \left(\frac{a}{\lambda} \right)^3 + O \left(\left(\frac{a}{\lambda} \right)^4 \right). \quad (67)$$

The remaining contributions from terms involving two, three, and four t matrices can all be expressed in terms of integrals already evaluated in the Boltzmann case. The results are

$$(b_3^{\text{exch},1})_2 = 6(a/\lambda)^2 + 5\sqrt{2} \pi (a/\lambda)^3 + O((a/\lambda)^4), \quad (68)$$

$$(b_3^{\text{exch},2})_2 = 4(a/\lambda)^2 + 3\sqrt{2} \pi (a/\lambda)^3 + O((a/\lambda)^4), \quad (69)$$

$$(b_3^{\text{exch},1})_3 = -\frac{28}{3}\sqrt{2}\pi(a/\lambda)^3 + 48\sqrt{3}(a/\lambda)^4 \times \ln(a/\lambda) + O((a/\lambda)^4), \quad (70)$$

$$(b_3^{\text{exch},2})_3 = -6\sqrt{2}\pi(a/\lambda)^3 + 32\sqrt{3}(a/\lambda)^4 \times \ln(a/\lambda) + O((a/\lambda)^4), \quad (71)$$

$$(b_3^{\text{exch},1})_4 = -64\pi(a/\lambda)^4 \ln(a/\lambda) + O((a/\lambda)^4), \quad (72)$$

$$(b_3^{\text{exch},2})_4 = -\frac{128}{3}\pi(a/\lambda)^4 \ln(a/\lambda) + O((a/\lambda)^4), \quad (73)$$

giving

$$b_3^{\text{exch},1} = -\frac{1}{2}\sqrt{2}\frac{a}{\lambda} + 5\left(\frac{a}{\lambda}\right)^2 - \frac{121}{24}\sqrt{2}\pi\left(\frac{a}{\lambda}\right)^3 - 16(4\pi - 3\sqrt{3})\left(\frac{a}{\lambda}\right)^4 \ln\left(\frac{a}{\lambda}\right) + O\left(\left(\frac{a}{\lambda}\right)^4\right), \quad (74)$$

$$b_3^{\text{exch},2} = 3^{-5/2} - \frac{1}{2}\sqrt{2}\frac{a}{\lambda} + 3\left(\frac{a}{\lambda}\right)^2 - \frac{35}{24}\sqrt{2}\pi\left(\frac{a}{\lambda}\right)^3 - \frac{32}{3}(4\pi - 3\sqrt{3})\left(\frac{a}{\lambda}\right)^4 \ln\left(\frac{a}{\lambda}\right) + O\left(\left(\frac{a}{\lambda}\right)^4\right). \quad (75)$$

The region of validity of expansions (74) and (75) for the exchange terms is probably much more limited than that of (59) for the direct term. This is suggested by the behavior of the direct and exchange parts of the second-cluster coefficient. In this case the expansions are¹⁵

$$b_2^{\text{dir}} = -(a/\lambda) - 3\pi(a/\lambda)^3 + O((a/\lambda)^5), \quad (76)$$

$$b_2^{\text{exch}} = \frac{1}{8}\sqrt{2} - (a/\lambda) + 3\pi(a/\lambda)^3 + O((a/\lambda)^5). \quad (77)$$

A comparison with the exact values²⁸ shows that both these expansions give quite accurate values (within 1%) up to $a/\lambda = 0.1$. However, for larger values of a/λ , whereas (76) still represents the general trend of b_2^{dir} , (77) bears no relation at all to the actual values of b_2^{exch} , which decrease very sharply and are negligible by the time $a/\lambda = 0.5$. Physically, this rapid suppression of b_2^{exch} with rising temperature occurs because exchange effects are only significant when the particles can approach closer than their thermal wavelength λ . If the particles are prevented from doing this by the presence of a hard or repulsive core, then exchange effects are negligible.²⁹ For hard spheres, Lieb³⁰ has shown that

$$b_2^{\text{exch}} = \frac{1}{8}\sqrt{2} \exp\left[-\frac{1}{2}\pi^3(a/\lambda)^2 + O((a/\lambda)^{2/3})\right], \quad (78)$$

and Hill³¹ has extended this to general potentials with repulsive cores. The same arguments apply to b_3^{exch} ,³² and although the analog of (78) has not been obtained, it is clear that b_3^{exch} decreases rapidly with increasing temperature, and that (74) and (75) are only valid for very small a/λ .

V. b_3 FOR GENERAL INTERACTION

In this section we allow the particles to interact through a more general potential, with, however, the restriction that no two- and/or three-body

bound states or low-lying resonances exist. In Appendix C it is shown that the off-shell t matrix has the following expansion:

$$\langle \mathbf{k}' | t(z) | \mathbf{k} \rangle = (2\pi^2)^{-1} \{ a_0 + a_0^2(-z)^{1/2} - [a_0^2(a_0 - \frac{1}{2}r_0) - 2\chi_0]z - \chi_0(k'^2 + k^2) + a_1^3 \mathbf{k}' \cdot \mathbf{k} + \dots \}, \quad (79)$$

where terms of order (momentum)³ have been omitted. a_0 , a_1 are the scattering lengths for s and p waves, respectively, and r_0 is the effective range. χ_0 is a further parameter with the dimension (length)³, and it cannot be expressed in terms of the two-body phase shifts. It is given in terms of the two-body wave function by (C16) and is identical to the parameter $(a^3/6)$ introduced by Pais and Uhlenbeck.¹²

If we now use this expansion in (60) we find that the contributions from terms containing two, three, and four t matrices are the same as before, provided the hard-sphere diameter a is replaced by the s -wave scattering length a_0 . In particular, the logarithmic terms are still present in the general case, and are not just a peculiarity of the hard-sphere interaction. However, the contribution from terms containing one t matrix must be modified. We find

$$(b_3^{\text{exch},1})_1 = -\frac{1}{2}\sqrt{2}(a_0/\lambda) - (a_0/\lambda)^2 + \frac{1}{8}\sqrt{2}\pi \times [a_0^2(a_0 - \frac{1}{2}r_0) + 16\chi_0 - 9a_1^3] \lambda^{-3} + O(\lambda^{-4}), \quad (80)$$

$$(b_3^{\text{exch},2})_1 = -\frac{1}{2}\sqrt{2}(a_0/\lambda) - (a_0/\lambda)^2 + \frac{1}{8}\sqrt{2}\pi \times [a_0^2(a_0 - \frac{1}{2}r_0) + 16\chi_0 + 9a_1^3] \lambda^{-3} + O(\lambda^{-4}). \quad (81)$$

The final results are

$$b_3^{\text{dir}} = 2\left(\frac{a_0}{\lambda}\right)^2 - \frac{4}{3}\sqrt{2}\pi\left(\frac{a_0}{\lambda}\right)^3 - \frac{16}{3}(4\pi - 3\sqrt{3})\left(\frac{a_0}{\lambda}\right)^4 \ln\left(\frac{a_0}{\lambda}\right) + O(\lambda^{-4}), \quad (82)$$

$$b_3^{\text{exch},1} = -\frac{1}{2}\sqrt{2}\frac{a_0}{\lambda} + 5\left(\frac{a_0}{\lambda}\right)^2 - \frac{1}{48}\sqrt{2}\pi(202a_0^3 + 3a_0^2r_0 - 96\chi_0 + 54a_1^3)\lambda^{-3} - 16(4\pi - 3\sqrt{3})\left(\frac{a_0}{\lambda}\right)^4 \ln\left(\frac{a_0}{\lambda}\right) + O(\lambda^{-4}), \quad (83)$$

$$b_3^{\text{exch},2} = 3^{-5/2} - \frac{1}{2}\sqrt{2}\left(\frac{a_0}{\lambda}\right) + 3\left(\frac{a_0}{\lambda}\right)^2 - \frac{1}{48}\sqrt{2}\pi(138a_0^3 + 3a_0^2r_0 - 96\chi_0 - 54a_1^3)\lambda^{-3} - \frac{32}{3}(4\pi - 3\sqrt{3})\left(\frac{a_0}{\lambda}\right)^4 \ln\left(\frac{a_0}{\lambda}\right) + O(\lambda^{-4}). \quad (84)$$

VI. DISCUSSION

As mentioned before, logarithmic terms also appear in the low-density expansion of the ground-state energy of a many-particle system. For hard sphere bosons the term is¹⁶

$$N2\pi a\rho^{\frac{3}{2}}(4\pi - 3\sqrt{3})(a^3\rho)\ln(a^3\rho), \quad (85)$$

where $\rho = N/V$, and for fermions it is^{17,18}

$$N\frac{\pi}{27}\pi^{-3}p_F^2(4\pi - 3\sqrt{3})2s(2s-1)(p_F a)^4\ln(p_F a), \quad (86)$$

where p_F is the Fermi momentum. It is notable that the same number $(4\pi - 3\sqrt{3})$ appears multiplying the logarithmic term in both the ground-state energy and the expansion of b_3 [Eq. (59)]. Lee and Yang³³ have shown how to obtain the ground-state energy from the cluster expansion, but since this involves taking the limit $z \rightarrow \infty$ in $\sum_i b_i z^i$, it is necessary to calculate all the b_i 's to a specified order in a/λ . Possibly the same number $(4\pi - 3\sqrt{3})$ occurs multiplying a logarithmic term in all the higher b_i 's, but we have not attempted to check this.³⁴

As Adhikari and Amado¹⁴ have pointed out, the occurrence of logarithmic terms in the low-temperature expansion of b_i conflicts with a claim by Mascheroni⁸ that for an everywhere-finite short-ranged potential without bound states, the low-temperature behavior is³⁵

$$b_l = \sum_{\alpha=0}^{l-1} C_{l,\alpha} \lambda^{-\alpha}, \quad (87)$$

where the $C_{l,\alpha}$ are constants. The restrictions on the potential exclude the hard-sphere case, but as we have seen, the logarithmic terms are still present in the general case. It would seem necessary to investigate the convergence of the expressions for the $C_{l,\alpha}$.

We have not performed the above calculations with any hope of being able to make comparisons with experimental results.³⁶ Rather our work emphasizes the limitations of the binary-collision expansion as a method of calculating cluster coefficients at any but the lowest temperatures. The term in $\lambda^{-4} \ln \lambda$ is the limit to which we can go by such expansion methods—to improve on this involves tackling the full three-body problem. It would seem that any attempt to calculate b_3 at higher temperatures should treat it as a genuine three-body problem from the outset, and not try to approach it via an expansion in terms of two-body functions.

APPENDIX A: EVALUATION OF INTEGRALS IN TWO- t -MATRIX TERMS

Inserting the expansion (27) in (29) gives

$$(b_3)_2 = F_1 a^2 + F_2 a^3 + \dots, \quad (A1)$$

where

$$F_1 = 3\sqrt{3} (2\pi^2)^{-2} \int d^3k \mathcal{L}_\beta^{-1}(z-E)^{-3}, \quad (A2)$$

$$F_2 = 3\sqrt{3} (2\pi^2)^{-2} 2 \int d^3k \mathcal{L}_\beta^{-1}(z-E)^{-3} (\frac{3}{4}k_1^2 - z)^{1/2}. \quad (A3)$$

In F_1 we do the inverse transform first, using

$$\mathcal{L}_\beta^{-1}(z-a)^{-n} = (-\beta)^{n-1} e^{-\beta a} / (n-1)!. \quad (A4)$$

Taking

$$E = k_{23}^2 + \frac{3}{4}k_1^2 \equiv k^2 + \frac{3}{4}p^2$$

then gives

$$F_1 = 3\sqrt{3} (2\pi^2)^{-2} [(-\beta)^2/2!] \int d^3k d^3p e^{-\beta(k^2 + 3p^2/4)} = 2\lambda^{-2}. \quad (A5)$$

F_2 can be evaluated by making use of the convolution property

$$\mathcal{L}_\beta^{-1}[g_1(z)g_2(z)] = -\int_0^\beta d\beta' G_1(\beta') G_2(\beta - \beta'), \quad (A6)$$

where $G_\alpha(\beta) = \mathcal{L}_\beta^{-1} g_\alpha(z)$. However this leads to an expression in terms of error functions, and the whole calculation is rather tedious (cf. Refs. 12 and 21). It is much easier to write

$$F_2 = 3\sqrt{3} (2\pi^2)^{-2} 2 \int d^3p e^{-3\beta p^2/4} \mathcal{L}_\beta^{-1}(-z)^{1/2} \times \int d^3k (z - k^2)^{-3}, \quad (A7)$$

where we have used the translation property of the inverse transform

$$\mathcal{L}_\beta^{-1} g(z-a) = e^{-\beta a} \mathcal{L}_\beta^{-1} g(z), \quad (A8)$$

and then do the k integral first, using

$$\int d^3k (z - k^2)^{-3} = -\frac{1}{4} \pi^2 (-z)^{-3/2}. \quad (A9)$$

The remaining integrals are trivial, and the result

$$F_2 = 2\sqrt{2} \pi \lambda^{-3} \quad (A10)$$

follows immediately.

The above calculation illustrates one advantage that the multiple-scattering expansion has over the binary-collision expansion. If the latter had been used, the integrals obtained would already be in the form which results when the convolution property is applied to our integrals. As we have seen this is not always the most convenient form for their evaluation.

APPENDIX B: LOGARITHMIC TERM FROM FOUR- t MATRICES

We require the behavior of $J_2(p, z)$ as $p \rightarrow 0$ and $z \rightarrow 0$. From (52),

$$J_2(p, z) \sim \int_{s < a_{2/a}} d^3q d^3s (z - q^2)^{-1} \times [z - (q^2 + \vec{q} \cdot \vec{s} + s^2)]^{-1} (z - s^2)^{-1}. \quad (B1)$$

Using the Feynman identity³⁷

$$(abc)^{-1} = \int_0^1 2t_1 dt_1 \int_0^1 dt_2 \times [at_1 t_2 + bt_1(1-t_2) + c(1-t_1)]^{-3}, \quad (B2)$$

the above integral becomes

$$\int_{s < a_2/a} d^3 q d^3 s \int_0^1 2t_1 dt_1 \int_0^1 dt_2 \times [z - t_1 t_2 \vec{q} \cdot \vec{s} - (1 - t_1 + t_1 t_2) q^2 - t_1 s^2]^{-3}. \quad (\text{B3})$$

The q integration can be done, giving

$$-4\pi^2 \int_{s < a_2/a} d^3 s \int_0^1 t_1 dt_1 \int_0^1 dt_2 \times \{ [4t_1(1 - t_1 + t_1 t_2) - t_1^2 t_2^2] s^2 - 4(1 - t_1 + t_1 t_2) z \}^{-3/2}. \quad (\text{B4})$$

We now use the result that, as $z \rightarrow 0$,

$$\int_0^{a_2/a} s^2 ds (As^2 - Bz)^{-3/2} \sim -\frac{1}{2} A^{-3/2} \ln(-a^2 z). \quad (\text{B5})$$

Therefore

$$J_2(p, z) \sim 8\pi^3 \ln(-a^2 z) \int_0^1 t_1 dt_1 \int_0^1 dt_2 \times [4t_1(1 - t_1 + t_1 t_2) - t_1^2 t_2^2]^{-3/2} = \frac{4}{3} \pi^4 \ln(-a^2 z). \quad (\text{B6})$$

APPENDIX C: LOW-ENERGY EXPANSION OF OFF-SHELL t MATRIX

We wish to extend the usual effective-range expansion of the t matrix to the off-shell case. We start by deriving a general relation between the off-shell t matrix and the half-off-shell t matrix.

Introduce the wave operator $\omega(z)$ defined by

$$t(z) = v\omega(z). \quad (\text{C1})$$

Using (26),

$$\omega(z) = 1 + (z - h_0)^{-1} v\omega(z), \quad (\text{C2})$$

$$\omega(z) = 1 + (z - h_0)^{-1} t(z). \quad (\text{C3})$$

We choose as basis the free-particle momentum eigenstates $|\vec{k}\rangle$ whose space representation is

$$\langle \vec{r} | \vec{k} \rangle = (2\pi)^{-3/2} e^{i\vec{k} \cdot \vec{r}}. \quad (\text{C4})$$

We also need the partial-wave expansions

$$\langle \vec{r} | \vec{k} \rangle = (2\pi)^{-3/2} \sum_{l=0}^{\infty} (2l+1) P_l(\hat{r} \cdot \hat{k}) i^l j_l(kr), \quad (\text{C5})$$

$$\langle \vec{r} | \omega(z) | \vec{k} \rangle = (2\pi)^{-3/2} \sum_{l=0}^{\infty} (2l+1) P_l(\hat{r} \cdot \hat{k}) i^l \omega_l(r, k; z), \quad (\text{C6})$$

$$\langle \vec{k}' | t(z) | \vec{k} \rangle = (2\pi^2)^{-1} \sum_{l=0}^{\infty} P_l(\hat{k}' \cdot \hat{k}) t_l(k', k; z). \quad (\text{C7})$$

From (C2), ω_l satisfies the differential equation

$$\left[z + \left(\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{l(l+1)}{r^2} \right) - v(r) \right] \omega_l(r, k; z) = (z - k^2) j_l(kr), \quad (\text{C8})$$

and from (C3) its asymptotic form is

$$\omega_l(r, k; s^2)_{r \rightarrow \infty} \sim (kr)^{-1} \sin(kr - \frac{1}{2}l\pi) - r^{-1} e^{i(sr - l\pi/2)} t_l(s, k; s^2), \quad (\text{C9})$$

where $s = z^{1/2}$ and we are assuming that $\text{Im}s > 0$.

We also introduce the function

$$\bar{\omega}_l(r, k; s^2) = j_l(kr) - is h_l^{(1)}(sr) t_l(s, k; s^2), \quad (\text{C10})$$

which again has the asymptotic form (C9).

From (C3)

$$\langle \vec{k}' | t(z) | \vec{k} \rangle = (z - k'^2) \int d^3 r \langle \vec{k}' | \vec{r} \rangle \times [\langle \vec{r} | \omega(z) | \vec{k} \rangle - \langle \vec{r} | \bar{\omega} \rangle]. \quad (\text{C11})$$

Expanding the matrix elements in partial waves, making use of (C10) and the result

$$\int_0^{\infty} r^2 dr j_l(k'r) h_l^{(1)}(sr) = is^{-1} (s^2 - k'^2)^{-1} (k'/s)^l, \quad (\text{C12})$$

$$t_l(k', k; s^2) = (k'/s)^l t_l(s, k; s^2) + (s^2 - k'^2) \int_0^{\infty} r^2 dr j_l(k'r) \times [\omega_l(r, k; s^2) - \bar{\omega}_l(r, k; s^2)]. \quad (\text{C13})$$

This expresses the off-shell matrix $t_l(k', k; s^2)$ in terms of the half-off-shell matrix $t_l(s, k; s^2)$ and the "off-shell wave function" $\omega_l(r, k; s^2)$.³⁸ Setting $k = s$ in (C13) gives the relation between the half-off-shell t matrix and the on-shell t matrix³⁹:

$$t_l(k', s; s^2) = (k'/s)^l t_l(s, s; s^2) + (s^2 - k'^2) \int_0^{\infty} r^2 dr j_l(k'r) \times [\omega_l(r, s; s^2) - \bar{\omega}_l(r, s; s^2)]. \quad (\text{C14})$$

$\omega_l(r, s; s^2)$ is just the ordinary radial wave function with asymptotic form

$$\omega_l(r, s; s^2)_{r \rightarrow \infty} \sim (sr)^{-1} e^{i\delta_l(s)} \sin(sr - \frac{1}{2}l\pi + \delta_l), \quad (\text{C15})$$

where δ_l is the phase shift.

We require the behavior of the t matrix at low energies in the case where there are no two-body bound states or zero-energy resonances. Define

$$\chi_0 = \lim_{s \rightarrow 0} \int_0^{\infty} r^2 dr [\omega_0(r, s; s^2) - \bar{\omega}_0(r, s; s^2)]. \quad (\text{C16})$$

This is identical to the parameter ($d^3/6$) introduced by Pais and Uhlenbeck.⁴⁰ From (C13)

$$t_0(k', k; s^2) = t_0(s, k; s^2) + (s^2 - k'^2) \chi_0 + \dots, \quad (\text{C17})$$

where terms of order (momentum)³ have been neglected. From (C14) and (C17),

$$t_0(k', k; s^2) = t_0(s, s; s^2) + (2s^2 - k'^2 - k^2) \chi_0 + \dots \quad (\text{C18})$$

The on-shell matrix is related to the phase shift by

$$t_l(s, s; s^2) = -s^{-1} e^{i\delta_l(s)} \sin \delta_l(s). \quad (\text{C19})$$

Thus its low-energy behavior can be found from the usual effective-range expansions

$$s \cot \delta_0 = -a_0^{-1} + \frac{1}{2} r_0 s^2 + O(s^4), \quad (\text{C20})$$

$$s^3 \cot \delta_1 = -3a_1^3 + O(s^2), \quad (\text{C21})$$

where a_0 , a_1 are the scattering lengths for s and p waves, respectively, and r_0 is the effective range. From (C18)–(C20)

$$t_0(k', k; s^2) = a_0 - ia_0^2 s - [a_0^2(a_0 - \frac{1}{2}r_0) - 2\chi_0] s^2$$

$$- \chi_0(k'^2 + k^2) + \dots, \quad (\text{C22})$$

and from (C13), (C19), and (C21)

$$t_1(k', k; s^2) = \frac{1}{3} a_1^3 k' k + \dots \quad (\text{C23})$$

The expansion for the hard-sphere case can be obtained from (C22) and (C23) by setting $a_0 = a_1 = a$, $r_0 = \frac{2}{3} a$, and $\chi_0 = \frac{1}{6} a^3$.

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