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Third Virial Coefficient for Quantum Hard Spheres: Two-Point Padé Approximants for Direct and Exchange Parts

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The method of two-point Padé approximants is used to interpolate between the low-temperature and high-temperature expansions of the second and third cluster integrals (b_2 and b_3) of a quantum hard-sphere gas. b_2 is used as a test case, since accurate numerical values are available. Using only a limited number of terms from the series (about as many as are available for b_3), we are able to represent both the direct and exchange parts to better than 1% over the entire temperature range. For b_3 there are no accurate values available, but the qualitative similarity of the results to those for b_2 leads us to believe that we have a reasonably good representation of both the direct and exchange parts of b_3.

KEY WORDS: Third virial coefficient; third cluster integral; quantum hard spheres; two-point Padé approximant.

1. INTRODUCTION

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

In the quantum case, the connection between the b_l's and the intermolecular potential is not nearly so direct. Only for the second integral b_2 is there available an exact expression[(1)] which allows its accurate computation over a complete temperature range. The evaluation of the third (and higher) cluster integrals has proved particularly intractable, involving many

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of the complexities of the full quantum mechanical N-body problem. (For a recent theoretical treatment, and references to earlier work, see Ref. 2.)

The above is true even for a gas of hard spheres. For b_2 there is no problem, and accurate numerical values have been calculated by Boyd *et al.*,[3] but there is no corresponding set of values available for b_3 or higher integrals. However, for b_3 we do have some exact information available in the form of the first few terms of the high-temperature (high-T) and low-temperature (low-T) expansions (see the Appendix). It seems worthwhile to try to extract as much information as possible from these series.

Various techniques are available for the acceleration of the convergence of series. Recently, Thakkar[4] has tested a number of these on the high-T expansion for the second virial coefficient of a Lennard–Jones gas (the Wigner–Kirkwood series) for which four terms are available, and found that in particular the CREPE algorithm gives a marked improvement in convergence. We have found that a number of these techniques work quite well for the direct part of b_2 for hard spheres, but fail completely for b_3.[2]

In the present work we use the method of two-point Padé approximants.[5–16] This enables us to make simultaneous use of the information available in both the low-T and high-T series, and the Padé approximant interpolates between these limits. Essentially, we are assuming that these series are expansions (about zero and infinity, respectively) of the same function, and we are attempting to represent this function by the ratio of two polynomials.

We use the second cluster integral as a test case. Taking about as many terms as are available for b_3, we find that both the direct and exchange parts of b_2 are represented to better than 1% accuracy over the entire temperature range. This is quite remarkable in the case of the exchange integral, as any extrapolation procedure based entirely on the low-T or on the high-T series leads to complete nonsense.

We then apply the same technique to the third cluster integral. The principal results of this paper are the Padé approximants for b_3: Eq. (10) for b_3(dir), Eq. (14) for b_3(exch $-$ 1), and Eq. (15) for b_3(exch $-$ 2). The presence of logarithmic terms gives these a somewhat different appearance to the corresponding approximants for b_2(dir), [Eq. (8)] and b_2(exch) [Eq. (12)], but a comparison of the graphs (Figs. 1–5) shows that there is a close qualitative similarity. This leads us to believe that the third cluster integral

[2] The principal reason for this failure is the limited number of terms available in the series—even though there are four terms known in the high-T series for b_3(dir), these all have the same sign and fall off more slowly than the corresponding terms in b_2(dir). In the low-T series, the presence of logarithmic terms is an additional complication.

is not too different in general behavior to the second, and that the application of the Padé approximant method is also legitimate here.

2. THE CLUSTER INTEGRALS

We consider a system of N identical particles each of mass m in a container of volume V. The cluster integrals appear in the expansion of the pressure p and the number density N/V in powers of the fugacity z[3]:

$$\beta p = \frac{1}{\lambda^3} \sum_{l=1}^{\infty} b_l z^l \tag{1a}$$

$$\frac{N}{V} = \frac{1}{\lambda^3} \sum_{l=1}^{\infty} l b_l z^l \tag{1b}$$

Here, $\beta = 1/kT$ and $\lambda = (2\pi\hbar^2/mkT)^{1/2}$. Elimination of z between (1a) and (1b) gives the equation of state in virial form:

$$\frac{pV}{NkT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \cdots \tag{2}$$

where

$$B = -N\lambda^3 b_2/b_1^2 \tag{3a}$$

$$C = N^2\lambda^6\left(4b_2^2/b_1^4 - 2b_3/b_1^3\right) \tag{3b}$$

It is convenient to separate out the effect of the particle statistics, and write each cluster integral as the sum of a direct term, which describes particles obeying Boltzmann statistics, and exchange terms, which account for the extra contributions from the Bose–Einstein or Fermi–Dirac statistics.[18] For particles of spin s we get[18,19]

$$b_1 = 2s + 1 \tag{4a}$$

$$b_2 = (2s+1)^2 b_2(\text{dir}) \pm (2s+1) b_2(\text{exch}) \tag{4b}$$

$$b_3 = (2s+1)^3 b_3(\text{dir}) \pm (2s+1)^2 b_3(\text{exch}-1) + (2s+1) b_3(\text{exch}-2) \tag{4c}$$

The upper (plus) sign is for bosons and the lower (minus) sign is for fermions. In (4c), the exchange contribution to b_3 is divided into a single transposition term $b_3(\text{exch}-1)$, which comes from processes in which two particles interchange, and a cyclic permutation term $b_3(\text{exch}-2)$, which comes from processes in which all three particles interchange.

[3] We adopt Huang's[17] definition of b_l, which differs by a factor λ^3 from the usual convention. Huang's definition has the advantage of making b_l dimensionless.

3. PADÉ APPROXIMANTS FOR DIRECT TERMS

3.1. b_2(dir)

Many terms have been calculated in both the high-T and low-T series [see the Appendix, Eqs. (A1) and (A2)], and in fact one can find b_2(dir) to good accuracy simply by summing these series.[20] We could use all the available terms to construct the Padé approximant, and presumably this would give a very accurate representation of b_2(dir). However, our purpose here is not to find the best possible representation of b_2(dir), but rather to investigate how well the Padé method works with only a small number of terms, such as are available for b_3(dir). Thus we start from

$$b_2(\mathrm{dir}) = -\frac{2\pi}{3}\Lambda^{-3} - \frac{\pi}{\sqrt{2}}\Lambda^{-2} - \frac{2}{3}\Lambda^{-1} + O(1), \qquad \Lambda \to 0 \tag{5a}$$

$$b_2(\mathrm{dir}) = -\Lambda^{-1} - 3\pi\Lambda^{-3} + O(\Lambda^{-5}), \qquad \Lambda \to \infty \tag{5b}$$

where $\Lambda \equiv \lambda/a$, a being the hard sphere diameter. We could fit a Padé approximant directly to these series; however, it is more convenient to work with the quantity $F_1(\Lambda)$ defined by

$$F_1(\Lambda) \equiv \Lambda^3 b_2(\mathrm{dir}) + \Lambda^2 \tag{6}$$

Since $F_1(\Lambda) \sim \mathrm{const}$ as $\Lambda \to 0$ or ∞, it is appropriate to fit an $[n/n]$ approximant. Setting

$$F_1(\Lambda) \simeq \frac{p_0 + p_1\Lambda + p_2\Lambda^2}{1 + q_1\Lambda + q_2\Lambda^2} \tag{7}$$

and requiring this to agree with (5a) as $\Lambda \to 0$ and with (5b) as $\Lambda \to \infty$ leads to

$$b_2(\mathrm{dir}) \simeq -\Lambda^{-1} + \Lambda^{-3}\frac{(-2\pi/3) + (-9\pi/7\sqrt{2})\Lambda + ((42 - 27\pi)/98)\Lambda^2}{1 + (3/7\sqrt{2})\Lambda + ((9\pi - 14)/98\pi)\Lambda^2} \tag{8a}$$

$$\simeq -\Lambda^{-1} + \Lambda^{-3}\frac{-2.094395 - 2.856139\Lambda - 0.436969\Lambda^2}{1 + 0.303046\Lambda + 0.046364\Lambda^2} \tag{8b}$$

Table I shows values calculated from (8b) compared with the accurate numerical values of Boyd *et al.*[3] Agreement is good, being excellent in the low-T and high-T regions, and no more than 1% in error in the intermediate region.

Figure 1 shows $\log_{10}[-b_2(\mathrm{dir})]$ plotted against Λ^{-1}. It is seen that the Padé approximant interpolates smoothly between the low-T and high-T series, as calculated from (5a) and (5b), respectively.

Table I. Comparison of Padé Values and Accurate Numerical Values of b_2

	b_2(dir)		$\ln[b_2(\text{exch})]$	
Λ	Exact[a]	Padé[b]	Exact[a]	Padé[c]
30.0	−0.0337	−0.0337	−1.9394	−1.9394
20.0	−0.0512	−0.0511	−2.0563	−2.0563
10.0	−0.1088	−0.1086	−2.4619	−2.4619
5.0	−0.2614	−0.259	−3.5161	−3.5169
3.0	−0.5714	−0.566	−5.4141	−5.417
2.0	−1.1766	−1.167	−8.5582	−8.575
1.0	−5.0101	−4.992	−23.089	−23.223
0.5	−27.003	−26.969		−75.78
0.25	−172.28	−172.25		−1612

[a] From Boyd *et al.*[3]
[b] Equation (8).
[c] Equation (12).

3.2. b_3(dir)

Expansions for b_3(dir) are given in the Appendix. Define $F_2(\Lambda)$ by

$$F_2(\Lambda) \equiv \Lambda^4 b_3(\text{dir}) - \frac{3\pi^2}{4}\Lambda^{-2} - \frac{9\sqrt{2}\,\pi^2}{8}\Lambda^{-1} - 13.113835 - 2\Lambda^2 \qquad (9)$$

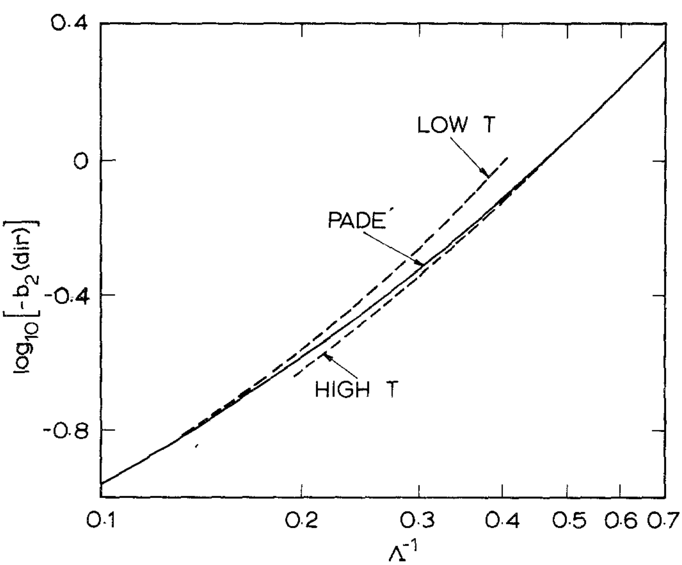

Fig. 1. Direct second cluster integral for hard spheres. The full curve is the Padé approximant (8). The broken curves are the high-T expansion (5a) and the low-T expansion (5b).

The $\ln \Lambda$ term in (9) [see Eq. (A6)] precludes the direct fitting of a Padé approximant, but this problem is easily circumvented by considering $dF_2/d\Lambda$ (cf. Ref. 8). Fitting a [1/1] Padé approximant and then integrating leads to

$$b_3(\mathrm{dir}) \simeq \frac{3\pi^2}{4}\Lambda^{-6} + \frac{9\sqrt{2}\,\pi^2}{8}\Lambda^{-5} + 13.113835\Lambda^{-4} - \frac{4\sqrt{2}\,\pi}{3}\Lambda^{-3} + 2\Lambda^{-2} + \frac{16}{3}(4\pi - 3\sqrt{3})\Lambda^{-4}\ln(1 + 0.2857\Lambda) \tag{10a}$$

$$\simeq 7.402203\Lambda^{-6} + 15.702444\Lambda^{-5} + 13.113835\Lambda^{-4} - 5.923844\Lambda^{-3} + 2\Lambda^{-2} + 39.307830\Lambda^{-4}\ln(1 + 0.2857\Lambda) \tag{10b}$$

It is easily checked that this reproduces (A5) as $\Lambda \to 0$ and (A6) as $\Lambda \to \infty$.

In Fig. 2, $\log_{10}[b_3(\mathrm{dir})]$ is plotted against Λ^{-1}. Comparison with Fig. 1 shows that the Padé approximant again gives the same type of smooth interpolation between the low-T and the high-T series. This qualitative similarity gives us some confidence that the $b_3(\mathrm{dir})$ Padé values are reasonably accurate. Hopefully, matters are no more than an order-of-magnitude

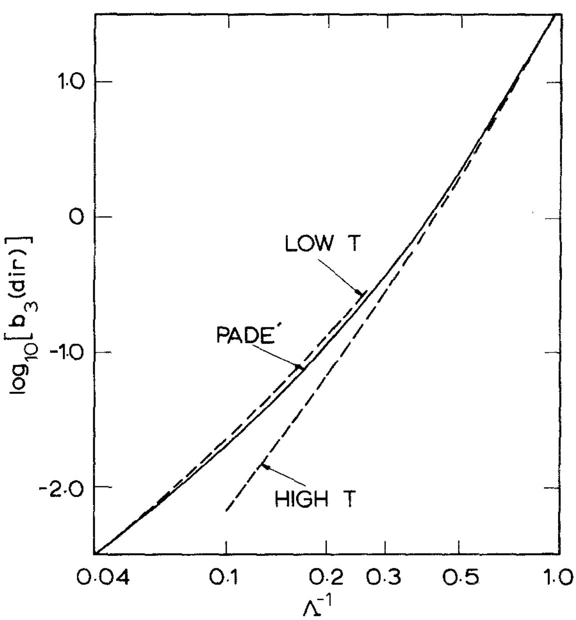

Fig. 2. Direct third cluster integral for hard spheres. The full curve is the Padé approximant (10). The broken curves are the high-T expansion (A5) and the low-T expansion (A6).

worse than in the $b_2(\text{dir})$ case, and thus we could expect a maximum error of less than 10%.

Previously,[21] we applied the Padé method to the direct part of the third virial coefficient C, with the result[21]

$$C_{\text{dir}} \simeq \frac{5\pi^2 a^6}{18}\left[1 + \frac{3\sqrt{2}}{2}\Lambda + 1.707660\Lambda^2 + \frac{48\sqrt{2}}{5\pi}\Lambda^3 - \frac{192}{5\pi^2}(4\pi - 3\sqrt{3})\Lambda^2 \ln(1 + 0.1287\Lambda)\right] \tag{11}$$

This is not identical to calculating C_{dir} from (3b), using (10). [The reason for the difference is that in deriving (11) expansions for $b_2(\text{dir})$, as well as for $b_3(\text{dir})$, have been used.] However, values calculated from the two expressions [using accurate values of $b_2(\text{dir})$] differ by less than 10%, and this is consistent with our estimate of the overall accuracy of (10). We do believe that the present expression (10) is more accurate than (11), as the low-T and high-T series show greater agreement in this case. (Compare Fig. 2 with the figure of Ref. 21.)

A standard method of checking the accuracy of a Padé approximant is to calculate the one of next higher order and see how much the values change. In the present case, we would have to use a [2/2] approximant for $dF_2/d\Lambda$, and this needs an additional two coefficients between series (A5) and (A6). In the Appendix we indicate the difficulties involved in finding more terms in either series, and for the moment we cannot improve on the present calculation.

4. PADÉ APPROXIMANTS FOR EXCHANGE TERMS

At very low temperatures, exchange and direct terms are of comparable (absolute) magnitudes. As the temperature increases, direct terms show a gradual variation, but exchange terms decrease very rapidly. This effect has been investigated in detail for b_2 and b_3, and the results, together with references, are given in the Appendix. This suppression of exchange effects is of an exponential nature, and rather than dealing directly with the series for $b_l(\text{exch})$, it is more appropriate to first take logarithms. Thus we fit the Padé approximants to the series for $\ln|b_l(\text{exch})|$.

4.1. b_2(exch)

Again, we use the second cluster integral as a test case for our approximation scheme. We use all the terms from the low-T series (A4), but only the leading term from the high-T series (A3). Fitting the appropriate Padé approximant [the details are similar to those for $b_2(\text{dir})$ above] leads to

$$\ln\left[b_2(\text{exch})\right] \simeq \ln(2^{-5/2}) - 2^{5/2}\Lambda^{-1} + \Lambda^{-2}\frac{-15.503138 - 3.452068\Lambda - 0.661522\Lambda^2}{1 + 0.197601\Lambda + 0.041345\Lambda^2} \tag{12}$$

Table I shows values calculated from (12) compared with the accurate numerical values. Agreement is excellent—even better than for b_2(dir). For $\Lambda > 2.0$, which is the only region where b_2(exch) is at all significant compared to b_2(dir), the error in b_2(exch) is at most 0.2%.

Figure 3 shows $\ln[b_2(\text{exch})]$ plotted against Λ^{-1}. We show two low-T expansions: low $T(1)$ is obtained by summing (A4), and then taking the logarithm; low $T(2)$ comes from the series for $\ln[b_2(\text{exch})]$. There are also two high-T curves: high $T(1)$ uses the leading term only, while high-$T(2)$ uses all the terms in (A3).

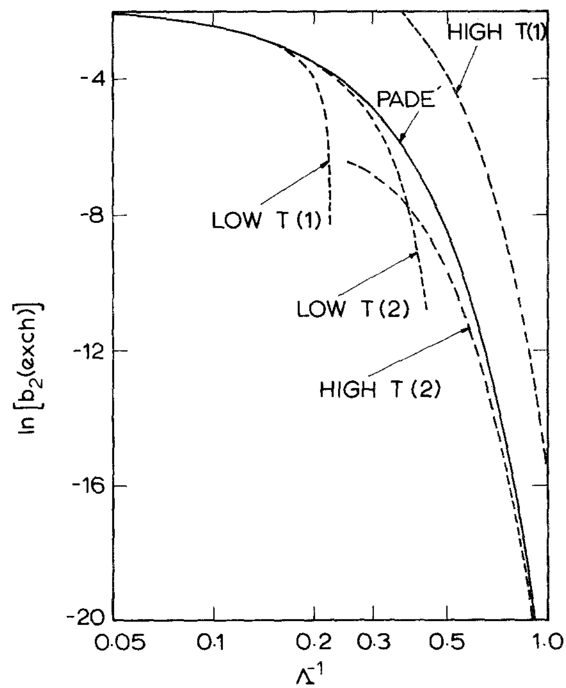

Fig. 3. Exchange second cluster integral for hard spheres. The full curve is the Padé approximant (12). The broken curves come from high-T and low-T expansions: high-$T(1)$ uses only the leading term of the high-T expansion; high-$T(2)$ uses the complete expression (A3); low-$T(1)$ is obtained by summing (A4) and then taking the logarithm; low-$T(2)$ comes from the series for $\ln[b_2(\text{exch})]$.

It is remarkable that the two-point Padé approximant gives such a good representation of $b_2(\text{exch})$. A one-point Padé approximant fitted at $\Lambda^{-1} = 0$ gives only marginal improvement over the low-T expansion. Also, more sophisticated methods, such as the CREPE algorithm,[4] applied to either the $b_2(\text{exch})$ or the $\ln[b_2(\text{exch})]$ series, are of little use. By simply making the additional requirement that the approximant have the correct asymptotic form at $\Lambda^{-1} = \infty$, we are able to represent $b_2(\text{exch})$ accurately over the complete temperature range.

4.2. $b_3(\text{exch} - 1)$

Guided by the case of $b_2(\text{exch})$, we keep only the leading term in the high-T expansion (A7). To handle the logarithmic terms in (A9), we define $F_3(\Lambda)$ by

$$\Lambda^{-3}F_3(\Lambda) \equiv \ln\left[-b_3(\text{exch}-1)\right] + \ln\Lambda + \ln\sqrt{2} + 5\sqrt{2}\,\Lambda^{-1} \tag{13}$$

and then fit a [1/1] approximant to $dF_3/d\Lambda$. The final result is

$$\begin{aligned}\ln\left[-b_3(\text{exch}-1)\right] &\simeq -\ln\Lambda - \ln\sqrt{2} - 5\sqrt{2}\,\Lambda^{-1} + \left(\frac{121\pi}{12} - 25\right)\Lambda^{-2} \\ &\quad - 16\sqrt{2}\,(4\pi - 3\sqrt{3}\,)\Lambda^{-3}\ln(1 + 0.133004\Lambda) \qquad (14\text{a}) \\ &\simeq -\ln\Lambda - 0.346574 - 7.071068\Lambda^{-1} + 6.677726\Lambda^{-2} \\ &\quad - 166.769000\Lambda^{-3}\ln(1 + 0.133004\Lambda) \qquad (14\text{b})\end{aligned}$$

Figure 4 shows $\ln[-b_3(\text{exch} - 1)]$ plotted against Λ^{-1}. Again, the qualitative similarity with the second cluster integral case (cf. Fig. 3) gives us confidence in the interpolation scheme.

4.3. $b_3(\text{exch} - 2)$

The calculation for $b_3(\text{exch} - 2)$ parallels that for $b_3(\text{exch} - 1)$. We find

$$\begin{aligned}\ln\left[b_3(\text{exch}-2)\right] &\simeq \ln 3^{-5/2} - \frac{3^{5/2}}{\sqrt{2}}\Lambda^{-1} + \left(3^{7/2} - \frac{3^5}{4}\right)\Lambda^{-2} \\ &\quad + \left(\frac{3^6}{\sqrt{2}} - \frac{3^{13/2}}{2\sqrt{2}} - \frac{105\sqrt{6}\,\pi}{8}\right)\Lambda^{-3} \\ &\quad - 2499.572\Lambda^{-4}\ln(1 - 0.012778\Lambda) \qquad (15\text{a}) \\ &\simeq -2.746531 - 11.022704\Lambda^{-1} - 13.984628\Lambda^{-2} \\ &\quad - 31.939461\Lambda^{-3} - 2499.572\Lambda^{-4}\ln(1 - 0.012778\Lambda) \qquad (15\text{b})\end{aligned}$$

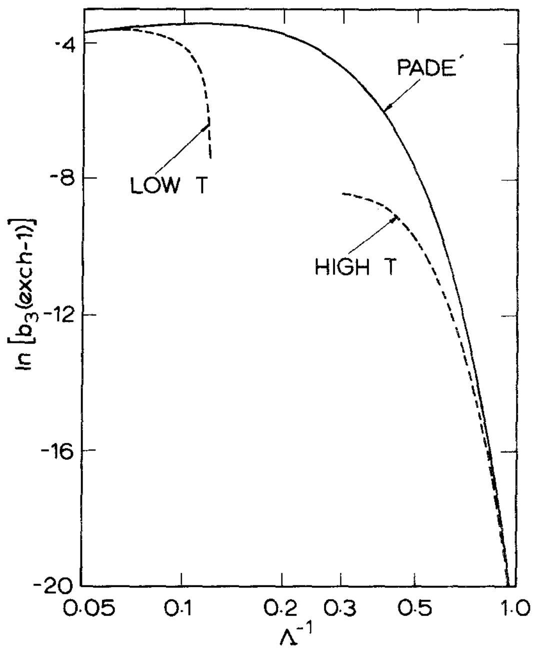

Fig. 4. Exchange third cluster integral (single transposition) for hard spheres. The full curve is the Padé approximant (14). The broken curves are the high-T expansion (A7) and the low-T expansion (A9). (In relation to the high-T curve, see the Appendix, Footnote 4.)

Note that, in contrast to all the previous Padé approximants calculated here, this one does have a singularity on the positive real axis, at $\Lambda^{-1} = 0.012778$. However, this is in a region where the low-T series is certainly valid and should be used instead of (15).

Figure 5 shows the graph of $\ln[b_3(\text{exch} - 2)]$. It is qualitatively similar to Fig. 3 for $\ln[b_2(\text{exch})]$ and Fig. 4 for $\ln[b_3(\text{exch} - 1)]$. The convergence of the high-T series appears to be slower in this case, but this could be largely due to the fact that we have one term less [cf. (A8) with (A7)], and also there is some uncertainty in the value of the quantity γ appearing in (A8).

APPENDIX. EXPANSIONS FOR THE CLUSTER INTEGRALS

For convenience, we collect together the high-T and low-T expansions for the second and third cluster integrals.

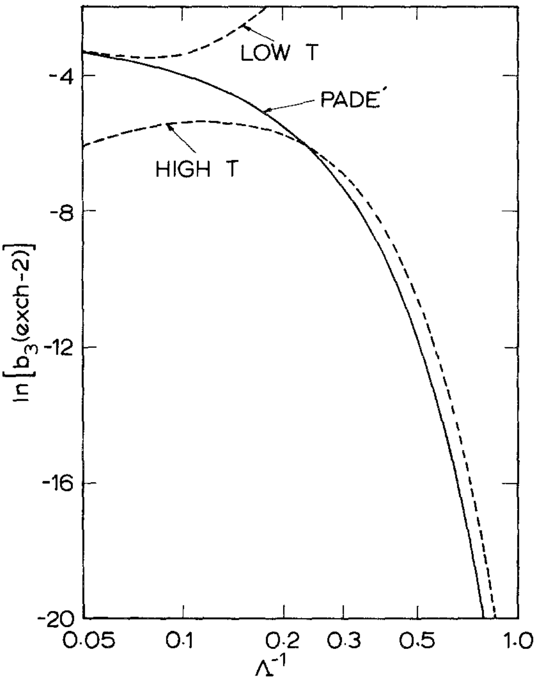

Fig. 5. Exchange third cluster integral (cyclic permutation) for hard spheres. The full curve is the Padé approximant (15). The broken curves are the high-T expansion (A8) and the low-T expansion (A10).

b_2(dir): **High-** T. We have

$$b_2(\mathrm{dir}) = -\frac{2\pi}{3}\Lambda^{-3} - \frac{\pi}{\sqrt{2}}\Lambda^{-2} - \frac{2}{3}\Lambda^{-1} - \frac{1}{24\sqrt{2}} + \frac{2}{315\pi}\Lambda - \frac{1}{960\pi\sqrt{2}}\Lambda^2 + \frac{4}{9009\pi^2}\Lambda^3 - \frac{47}{322{,}560\pi^2\sqrt{2}}\Lambda^4 + O(\Lambda^5), \qquad \Lambda \to 0 \qquad \text{(A1)}$$

The first term is just the classical contribution. The leading quantum correction was obtained by Uhlenbeck and Beth.[22] Subsequent contributions have come from Mohling,[23] Boyd *et al.*,[3] Handelsman and Keller,[24] Hemmer and Mork,[25] Hill,[26] Nilsen,[20] Gibson,[27] and D'Arruda and Hill.[28] The last paper contains all the terms of series (A1).

b_2(dir): **Low** T. We have

$$b_2(\mathrm{dir}) = -\Lambda^{-1} - 3\pi\Lambda^{-3} + \frac{22\pi^2}{3}\Lambda^{-5} - \frac{1921\pi^3}{45}\Lambda^{-7} + \frac{165673\pi^4}{525}\Lambda^{-9} - \frac{472231931\pi^5}{165375}\Lambda^{-11} + O(\Lambda^{-13}), \qquad \Lambda \to \infty \qquad \text{(A2)}$$

The first four terms were obtained by Uhlenbeck and Beth[22]; the remaining two by Ebeling *et al.*[29]

b_2(exch): **High** T. We have

$$b_2(\text{exch}) = 4\pi^3\Lambda^{-3}\exp\left(-\frac{\pi^3}{2}\Lambda^{-2} - \pi^{5/3}\beta_1\Lambda^{-2/3} - \frac{4\pi^{1/3}}{45}\beta_1^2\Lambda^{2/3}\right)$$
$$\times\left[1 + O(\Lambda^{4/3})\right], \qquad \Lambda\to 0 \tag{A3}$$

where $\beta_1 \simeq 1.85576$. The exponential suppression of exchange terms with increasing temperature was first discussed by Larsen *et al.*[30] The leading term in (A.3) was obtained by Lieb[31] using path integral methods. Hill[26] developed a systematic method for obtaining higher terms, and actually calculates many more terms than we have included in (A3).

b_2(exch): **Low** T. We have

$$b_2(\text{exch}) = 2^{-5/2} - \Lambda^{-1} + 3\pi\Lambda^{-3} - \frac{2^5\pi^2}{3}\Lambda^{-5} + O(\Lambda^{-7}), \qquad \Lambda\to\infty \tag{A4}$$

This is from Boyd *et al.*,[3] Eq. (31). We have corrected the sign of the last term.

b_3(dir): **High** T. We have

$$b_3(\text{dir}) = \frac{3\pi^2}{4}\Lambda^{-6} + \frac{9\sqrt{2}\,\pi^2}{8}\Lambda^{-5} + 13.113835\Lambda^{-4}$$
$$+ 5.306\Lambda^{-3} + O(\Lambda^{-2}), \qquad \Lambda\to 0 \tag{A5}$$

The first term is just the classical contribution. The leading correction term was obtained by Jancovici[32] and by Hemmer.[33] The last two terms are the work of Jancovici[34] and Jancovici and Merkuriev,[35] respectively. The latter paper gives a systematic method of constructing the high-T series, but the calculation of the Λ^{-3} term is already very difficult.

b_3(dir): **Low** T. We have

$$b_3(\text{dir}) = 2\Lambda^{-2} - \frac{4\sqrt{2}\,\pi}{3}\Lambda^{-3} + \frac{16}{3}(4\pi - 3\sqrt{3})\Lambda^{-4}\ln\Lambda$$
$$+ O(\Lambda^{-4}), \qquad \Lambda\to\infty \tag{A6}$$

The first and second terms were derived by Lee and Yang[36] and Pais and Uhlenbeck,[37] respectively. The existence of the logarithmic term was established by Adhikari and Amado,[38] and the coefficient was calculated by Gibson.[39] These calculations used the Lee–Yang binary collision expansion (or, equivalently, the inverse Laplace transform of the Watson multiple-scattering expansion), in which three-body functions are expanded in a series of two-body functions. Equation (A6) comes from the first few terms in this series, but it is difficult to go any further. The logarithmic term is a precursor to a full three-body contribution (of order Λ^{-4}), and in order to get this coefficient by the above method it would be necessary to sum an infinite series, since every subsequent term contributes to order Λ^{-4}. (See the discussion in Ref. 39.)

b_3(exch): **High T.**[4] We have

$$b_3(\text{exch}-1) = -9\pi^4\Lambda^{-6}\exp\left[-\pi\left(\frac{1}{2}\pi^2\Lambda^{-2} + \beta_1\pi^{2/3}\Lambda^{-2/3} + \frac{4}{45}\beta_1^2\pi^{-2/3}\Lambda^{2/3}\right)\right]\left[1 + O(\Lambda)\right], \qquad \Lambda\to 0 \tag{A7}$$

$$b_3(\text{exch}-2) = \frac{16\pi^3}{3}\Lambda^{-3}\exp\left(-\frac{4\pi^3}{9}\Lambda^{-2} - \frac{2^{4/3}\pi^{5/3}}{9}\gamma_1\Lambda^{-2/3}\right) \times\left[1 + O(\Lambda^{2/3})\right], \qquad \Lambda\to 0 \tag{A8}$$

where $\beta_1 \simeq 1.85576$ and $\gamma_1 = 8.53 \pm 0.31$. These expressions are due to Hill.[19] The leading terms were also obtained by Bruch.[42]

b_3(exch): **Low T.** We have

$$b_3(\text{exch}-1) = -\frac{\sqrt{2}}{2}\Lambda^{-1} + 5\Lambda^{-2} - \frac{121\sqrt{2}\,\pi}{24}\Lambda^{-3} + 16(4\pi - 3\sqrt{3})\Lambda^{-4}\ln\Lambda + O(\Lambda^{-4}), \qquad \Lambda\to\infty \tag{A9}$$

$$b_3(\text{exch}-2) = 3^{-5/2} - \frac{\sqrt{2}}{2}\Lambda^{-1} + 3\Lambda^{-2} - \frac{35\sqrt{2}\,\pi}{24}\Lambda^{-3} + \frac{32}{3}(4\pi - 3\sqrt{3})\Lambda^{-4}\ln\Lambda + O(\Lambda^{-4}), \qquad \Lambda\to\infty \tag{A10}$$

The references and comments are the same as for b_3(dir): Low T.

[4] It has been pointed out to me[40, 41] that expression (A7) is in error, at least in the coefficient $9\pi^4$. However, the leading term is certainly correct, and since that is all we use in calculating the Padé approximant (14), this error is of no consequence as far as the present work is concerned. The only place in which we use the full expression (A7) is in drawing the high-T curve in Fig. 4; presumably the good agreement with the Padé curve indicates that the correct expression is not too different from (A7).

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