

QUANTUM CORRECTIONS TO THE THIRD AND FOURTH VIRIAL COEFFICIENTS USING THE 6:12 POTENTIAL*

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To order \hbar^2 , the quantum correction to the Helmholtz free energy is

$$A = A(\text{classical}) + \frac{\hbar^2}{24\pi mkT} N \rho \int_0^\infty g(r) \nabla^2 u r^2 dr, \quad (1)$$

where $\rho = N/V$, $g(r)$ is the classical radial distribution function, and $u(r)$ is the intermolecular potential.

If $g(r)$ is expanded in powers of the density, it is found that

$$g(r) = e^{-u/kT} \{1 + \rho g_1(r) + \rho^2 g_2(r) + \dots\}, \quad (2)$$

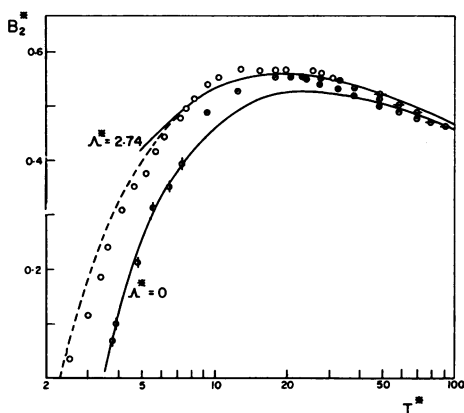


FIG. 1.—Second virial coefficient of He^4 ($\Lambda^* = 2.74$) and classical gases ($\Lambda^* = 0$). Solid lines give theoretical results which are accurate to order \hbar^2 . Broken line gives theoretical results of Kilpatrick *et al.*⁵ correct to all orders in \hbar . Experimental points labeled \circ , \bullet , \oplus , \odot , and ϕ are taken from refs. 11–14, respectively.

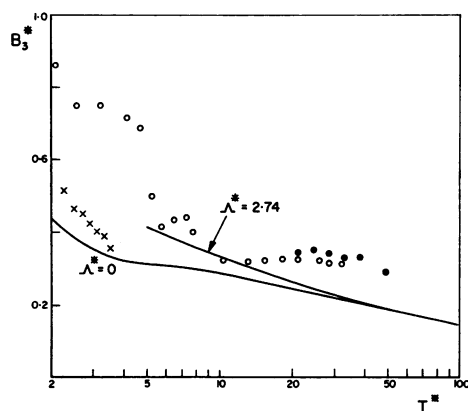


FIG. 2.—Third virial coefficient of He^4 ($\Lambda^* = 2.74$) and classical gases ($\Lambda^* = 0$). Solid lines give theoretical results which are accurate to order \hbar^2 . Experimental points labeled \bullet , \circ , and \times are taken from refs. 11, 13, and 15, respectively.

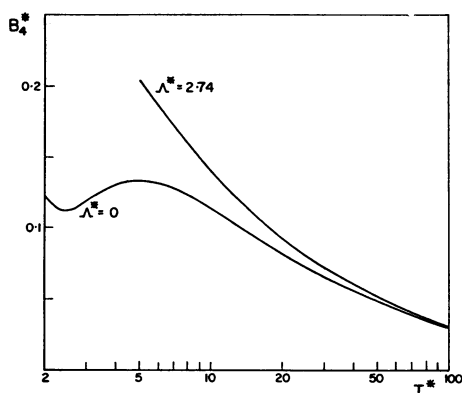


FIG. 3.—Fourth virial coefficient of He^4 ($\Lambda^* = 2.74$) and classical gases ($\Lambda^* = 0$).

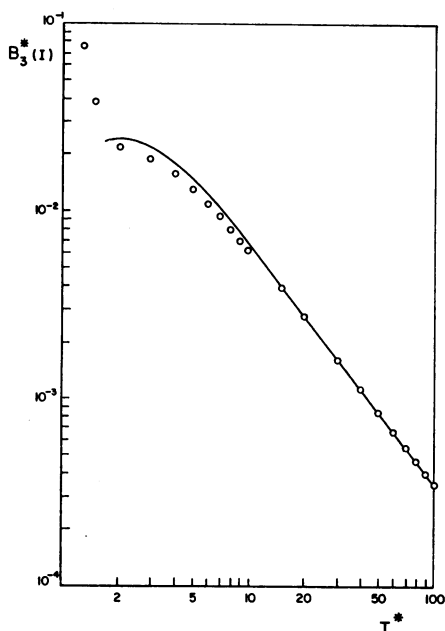


FIG. 4.—Quantum correction to the third virial coefficient. The curve gives the approximate results obtained by Chen *et al.*¹⁶ and the points give the exact results.

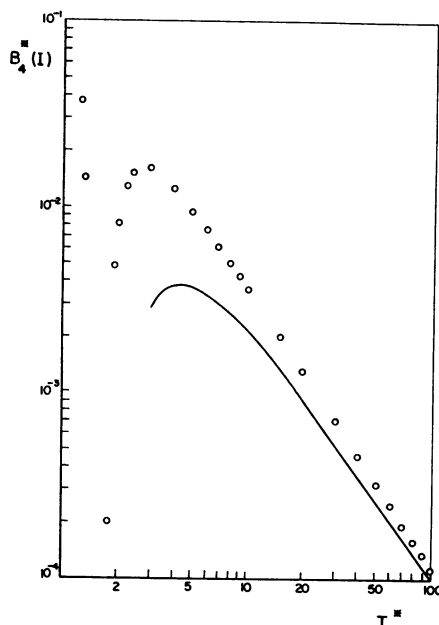


FIG. 5.—Quantum correction to the fourth virial coefficient. The curve gives the approximate results obtained by Chen *et al.*¹⁶ and the points give the exact results.

where

$$g_1(\tau) = \text{---} \bigcirc \text{---} \bigcirc \text{---} \quad (3)$$

and

$$g_2(\tau) = \frac{1}{2} \left[\text{---} \bigcirc \text{---} \bigcirc \text{---} + \text{---} \bigcirc \text{---} \bigcirc \text{---} + 2 \text{---} \bigcirc \text{---} \bigcirc \text{---} + \frac{1}{2} \text{---} \bigcirc \text{---} \bigcirc \text{---} \right] \quad (4)$$

In equations (3) and (4) the presence of a bar linking molecules i and j denotes the factor

$$f(r_{ij}) = e^{-u(r_{ij})/kT} - 1. \quad (5)$$

Each joint between bars denotes a molecule whose coordinates are integrated, and each circle at the end of a bar denotes a molecule whose position remains fixed.

Substitution of equation (2) into (1) yields

$$A = A(\text{classical}) + \frac{h^2}{24\pi m kT} N \sum_{n=0}^{\infty} \rho^{n+1} \int_0^{\infty} e^{-u/kT} g_n(r) \nabla^2 u r^2 dr, \quad (6)$$

where $g_0 = 1$. Differentiating equation (6) with respect to V yields

$$\frac{pV}{NkT} = \frac{pV}{NkT}(\text{classical}) + \frac{h^2}{24\pi m (kT)^2} \sum_{n=0}^{\infty} (n+1) \rho^{n+1} \int_0^{\infty} e^{-u/kT} g_n(r) \nabla^2 u r^2 dr. \quad (7)$$

TABLE 1
 QUANTUM CORRECTIONS TO THE SECOND, THIRD, AND FOURTH VIRIAL COEFFICIENTS

T^*	$B_2^*(I)$	$B_3^*(I)$	$B_4^*(I)$	T^*	$B_2^*(I)$	$B_3^*(I)$	$B_4^*(I)$
0.6	1.67261	15.2025	343.73	4.5	0.02742	0.01439	0.0109
0.7	1.05448	4.92392	64.088	5.0	0.02359	0.01312	0.0*960
0.8	0.72907	1.90654	15.511	6.0	0.01830	0.01103	0.0*756
0.9	0.53763	0.83678	4.395	7.0	0.01485	0.0*9418	0.0*612
1.0	0.41558	0.40434	1.3508	8.0	0.01244	0.0*8158	0.0*507
1.1	0.33287	0.21218	0.4163	9.0	0.01067	0.0*7158	0.0*429
1.2	0.27411	0.12060	0.1124	10.0	0.0*9315	0.0*6350	0.0*368
1.3	0.23076	0.07462	+0.0144	15.0	0.0*5604	0.0*3935	0.0*203
1.4	0.19778	0.05061	-0.0130	20.0	0.0*3947	0.0*2767	0.0*132
1.5	0.17205	0.03769	-0.0161	25.0	0.0*3022	0.0*2097	0.0*946
1.6	0.15153	0.03058	-0.0117	30.0	0.0*2437	0.0*1668	0.0*718
1.7	0.13489	0.02659	-0.0*561	40.0	0.0*1741	0.0*1158	0.0*464
1.8	0.12116	0.02431	+0.0*203	50.0	0.0*1345	0.0*8696	0.0*329
1.9	0.10969	0.02298	0.0*480	60.0	0.0*1091	0.0*6874	0.0*249
2.0	0.09998	0.02216	0.0*836	70.0	0.0*9152	0.0*5632	0.0*196
2.2	0.08453	0.02125	0.0129	80.0	0.0*7865	0.0*4737	0.0*160
2.4	0.07284	0.02066	0.0152	90.0	0.0*6883	0.0*4064	0.0*133
2.6	0.06374	0.02012	0.0161	100.0	0.0*6110	0.0*3543	0.0*113
2.8	0.05648	0.01955	0.0162	200.0	0.0*2811	0.0*1432	0.0*386
3.0	0.05058	0.01895	0.0158	500.0	0.0*1019	0.0*4276	0.0*921
3.5	0.03980	0.01736	0.0142	1000.0	0.0*4753	0.0*1705	0.0*309
4.0	0.03257	0.01581	0.0125				

Note: 0.0*4753 = 0.00004753.

Thus, the n th virial coefficient is

$$B_n = B_n(\text{classical}) + \frac{(n-1)h^2}{24\pi m(kT)^2} \int_0^\infty e^{-u/kT} g_{n-2}(r) \nabla^2 u r^2 dr. \tag{8}$$

Recently, we have calculated $g_1(r)^1$ and $g_2(r)^2$ for the 6:12 potential:

$$u(r) = 4\epsilon \left\{ \left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right\}. \tag{9}$$

In this note these results are used to calculate quantum corrections to B_3 and B_4 . Quantum corrections to B_2 have been calculated previously.³⁻⁷ The classical values of B_2 , B_3 , and B_4 have also been calculated previously.^{1, 2, 8, 9}

It is convenient to write equation (8) in reduced form:

$$B_n^* = B_n^*(\text{classical}) + \Lambda^{*2} B_n(I), \tag{10}$$

where

$$B_n^* = \left(\frac{3}{2\pi\sigma^3} \right)^{n-1} B_n, \quad \Lambda^* = h/\sigma\sqrt{m\epsilon},$$

$$B_n^*(I) = \left(\frac{3}{2\pi} \right)^{n-1} \frac{n-1}{24\pi T^{*2}} \int_0^\infty e^{-u^*/T^*} g_{n-2}^*(\rho) \nabla^2 u^* \rho^2 d\rho, \tag{11}$$

$T^* = kT/\epsilon$, $u^* = u/\epsilon$, and $g_n^* = g_n/\sigma^{3n}$.

In Table 1, $B_3^*(I)$ and $B_4^*(I)$ are listed. Values of $B_2^*(I)$ are also listed in Table 1 for comparison. Using these results we have computed B_3^* and B_4^* for He⁴ using the parameters

$$\epsilon/k = 9.66^\circ\text{K}, \quad N\sigma^3 = 10.24 \text{ cm}^3/\text{mole}, \quad \Lambda^* = 2.74,$$

which have been proposed by Haberlandt.⁷ In Figure 1 we have plotted the theo-

retical values of B_2^* for He^4 ($\Lambda^* = 2.74$) and for classical gases ($\Lambda^* = 0$). The agreement of the quantum values of B_2^* with the experimental¹⁰⁻¹³ results for He^4 is reasonable but is not as good as is the agreement of the classical values of B_2^* with the experimental¹⁴ results for Ar. In Figure 2 we have plotted the theoretical values of B_3^* for He^4 and for classical gases. The agreement with experiment^{11, 13, 15} is only fair. In Figure 3 we have plotted the theoretical values of B_4^* for He^4 and for classical gases.

Recently, we have proposed approximate expressions for the $B_n^*(I)$.¹⁶ It is of interest to compare these approximate results with the exact results reported in this note. In Figure 4 the approximate and exact values for $B_3^*(I)$ are plotted. In Figure 2 of our previous publication,¹⁶ we made a comparison of the exact and approximate values of $B_3^*(I)$. That comparison is in error. Our approximate expressions are quite correct but, unfortunately, we made a slight error in what we termed our exact calculations. When the correct values are used, the agreement between the exact and approximate values of $B_3^*(I)$ is improved and becomes very good. In Figure 5 the approximate and exact values of $B_4^*(I)$ are compared.

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¹ Henderson, D., *Mol. Phys.*, **10**, 73 (1965).

² Henderson, D., and L. Oden, *Mol. Phys.*, **10**, in press.

³ Uhlenbeck, G. E., and E. Beth, *Physica*, **3**, 729 (1936).

⁴ de Boer, J., and A. Michels, *Physica*, **5**, 945 (1938).

⁵ Kilpatrick, J. E., E. E. Keeler, E. F. Hammel, and N. Metropolis, *Phys. Rev.*, **94**, 1103 (1954).

⁶ Kihara, T., Y. Midzuno, and T. Shizume, *J. Phys. Soc. Japan*, **10**, 249 (1955).

⁷ Haberlandt, R., *Phys. Letters*, **8**, 172 (1964); *ibid.*, **14**, 197 (1965).

⁸ Bird, R. B., E. L. Spatz, and J. O. Hirschfelder, *J. Chem. Phys.*, **18**, 1395 (1950).

⁹ Barker, J. A., and J. J. Monaghan, *J. Chem. Phys.*, **36**, 2564 (1962).

¹⁰ Holborn, L., and J. Otto, *Z. Physik*, **33**, 1 (1925).

¹¹ Wiebe, R., V. L. Gaddy, and C. Heins, Jr., *J. Am. Chem. Soc.*, **53**, 1724 (1931).

¹² Yntema, J. L., and W. G. Schneider, *J. Chem. Phys.*, **18**, 641 (1950).

¹³ White, D., T. Rubin, P. Camky, and H. L. Johnston, *J. Phys. Chem.*, **64**, 1607 (1960).

¹⁴ Whalley, E., and W. G. Schneider, *J. Chem. Phys.*, **23**, 1644 (1955).

¹⁵ Michels, A., Hub. Wijker, and Hk. Wijker, *Physica*, **15**, 627 (1949).

¹⁶ Chen, R., D. Henderson, and S. G. Davison, these PROCEEDINGS, **54**, 1514 (1965).

A SPIN-LABELED SUBSTRATE FOR α -CHYMOTRYPSIN*

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In previous work there has been introduced the technique of "spin labeling" whereby the paramagnetic resonance of synthetic organic free radicals is used to probe the structure and function of biomolecules.¹⁻⁴ The paramagnetic nitroxide radicals, $\text{RR}'\text{NO}$, are particularly suitable for this purpose when R and R' are bonded to the NO nitrogen atom through tertiary carbon atoms, since such radi-