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On the Calculation of Second Virial Coefficients for Nonspherical Molecules

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A self-consistent scheme is given for the calculation of the contributions of nonspherical molecular interactions to second virial coefficients. The usual long-range nonspherical interactions, which are asymptotically valid only at large separations, are modified by damping functions that render them valid at small separations as well. Numerical tables of new auxiliary functions $J_n^D(T^*)$ are given for $6 \leqslant n \leqslant 30$ and $0.5 \leqslant T^* \leqslant 10$. These are designed to be used in the identical statistical-mechanical formalism for the second virial coefficient that had been developed for the undamped long-range nonspherical interactions.

KEY WORDS: equation of state; molecular gases; nonspherical interactions; second virial coefficients.

1. INTRODUCTION

A standard method for the calculation of the second virial coefficients of nonspherical molecules is the perturbation scheme developed by Pople and Buckingham [1, 2], in which the intermolecular potential is represented as a spherically symmetric core plus terms for the long-range nonspherical interactions, such as dipole–dipole, dispersion anisotropy, etc. The nonspherical terms are then treated as perturbations, and the statistical-mechanical expression for the second virial coefficient is expanded accordingly to produce an expression that gives corrections to the spherical contribution in the form of series that converge rapidly for high temperatures. The coefficients of the series are integrals that are functions of temperature, which are usually evaluated numerically and tabulated [1–4].

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A weak point in the foregoing development is the form usually assumed for the long-range nonspherical terms in the potential. These terms are given by various inverse powers of the intermolecular separation, a form which is valid only asympotically for large separations but which is, nevertheless, kept in the subsequent integrations even down to $r = 0$. Physically, the magnitude of the long-range terms should be decreased as r is decreased, in order to account for electron overlap and exchange. Thus in a sense the results are inconsistent: the formulas are convergent for high temperatures, but it is at high temperatures that effects occurring at small intermolecular separations might be expected to be most important.

This difficulty was recognized quite early by Castle et al. [5], who carried out exploratory calculations using a Lennard-Jones (12, 6) spherical-core potential with a number of added nonspherical interaction terms. In the absence at that time of any information on the quantitative nature of the damping of the long-range terms as r decreased, they used a simple cutoff at $r = \sigma_0$, the separation at which the spherical potential is zero. They found that the coefficients of the series expression were reduced by roughly 20% at $kT/\varepsilon_0 \equiv T^* = 1$ and by roughly a factor of 2 at $T^* = 10$, where ε_0 is the depth of the spherical potential well. These apparently rather large changes appeared as only relatively small effects on the total second virial coefficient, however, since the nonspherical contributions amounted to less than 6% at $T^* = 1$ and less than 1% at $T^* = 10$. Thus the overall effect of cutting off the asymptotic long-range nonspherical potentials was small but not negligible.

Since that time the nature of the damping of the long-range terms has been greatly clarified, and multiplicative damping functions have been developed that convert the asymptotic formulas valid at large r into ones valid at all r. Such damping functions by now have a fairly elaborate history, which has been reviewed by Tang and Toennies [6] and does not need to be repeated here.

The purpose of this paper is to use these damping functions to produce a self-consistent calculation of the second virial coefficients of nonspherical molecules. The results have the same mathematical form as those obtained earlier with the undamped asymptotic long-range terms, but the functions that serve as coefficients in the high-temperature expression are now different. Our results are qualitatively similar to those of Castle *et al.*, but the smooth damping functions produce a smaller effect on the final second virial coefficients than does the sharp cutoff.

The fact that the effects of the damping functions on the second virial coefficients are small greatly simplifies the numerical calculations. A single damping function can thus be used for all the long-range terms, including those in the spherical potential. In principle, a somewhat different damping function should be used for each long-range term [6], but this refinement greatly increases the number of parameters and the numerical labor involved, without producing any appreciable change in the final second virial coefficients. In practice, we have used a damping function of the form recommended by Ahlrichs *et al.* [7],

$$F(x) = \exp\left[-\left(\frac{D}{x} - 1\right)^2\right], \qquad x < D \tag{1a}$$

$$F(x) = 1, \qquad x \geqslant D \tag{1b}$$

$$x = r/r_m \tag{1c}$$

where r_m is the position of the minimum in the spherical potential, and D is the cutoff or damping parameter. Our final numerical tables were obtained with $D = 1.28$ and the HFD-I spherical potential used by Aziz and Chen [8]. Some exploratory calculations were also made with a (12, 6) spherical potential and with $D = 1.4$.

The final results are presented as a set of functions $J_n^D(T^*)$, which serve as coefficients in the perturbation expansion for the second virial coefficient. These functions should be used for accurate work in preference to those presented earlier [1–4], which did not include any damping function. However, work of an essentially correlation nature does not need to be revised on this account, because the effects of the damping function are sufficiently small that they can be compensated by the adjustable quantities in a correlation [9, 10], such as the parameters σ_0 and ε_0 of the spherical potential.

Finally, it should be mentioned that the functions $J_n^D(T^*)$ can be regarded as essentially universal, although they do depend on both the damping function and the spherical potential. The reason is that the nonspherical effects on the second virial coefficient are sufficiently small at high temperatures that these dependences are almost always less than the experimental uncertainties involved.

2. CALCULATIONS

We write the intermolecular pair potential as the sum of a spherical potential V_0 and a damped nonspherical portion V_{ns},

$$V(r) = V_0(r) + V_{\text{ns}} \cdot F(x) \tag{2}$$

where $F(x)$ is given by Eq. (1). The nonspherical contributions contained in V_{ns} are all of the form of r^{-n} multiplied by a function of the relative molecular orientation. The most important components of V_{ns} are tabulated in Refs. 3 and 4 for the interaction of linear molecules, and there is no need to repeat all those formulas here. As an example, the quadrople–quadrupole interaction between two linear molecules is

$$V_{\text{ns}}(\Theta\Theta)=\frac{3\Theta_1\Theta_2}{4r^5}\left[1-5c_1^2-5c_2^2-15c_1^2c_2^2+2(4c_1c_2-s_1s_2c)^2\right] \quad (3)$$

where Θ_1 and Θ_2 are the two quadrupole moments, and c_1, c_2, s_1, s_2, and c are cosines and sines of the angles describing the relative orientation [3].

The perturbation expansion for the second virial coefficient, $B(T)$, then leads to

$$B(T)=\frac{2\pi N_{\text{A}}}{3}\sigma_0^3[B_0^*(T^*)+B_{\text{ns}}^*(T^*)] \quad (4)$$

where N_{A} is Avogadro's number, B_0^* is the (dimensionless) contribution from $V_0(r)$, and B_{ns}^* is the (dimensionless) contribution due to V_{ns}. Expressions for the first few terms in each of the major contributions to B_{ns}^* are given in Refs. 3 and 4 for like molecules and in Ref. 10 for unlike molecules. For example, the quadrupole–quadrupole contribution to the interaction second virial coefficient of two unlike molecules is

$$\begin{aligned}B_{\text{ns}}^*(\Theta\Theta)_{12}= &-\frac{6}{5}\left(\frac{\Theta_1^*\Theta_2^*}{T_{12}^*}\right)^2\\ &\times\left[J_{10}^D(T_{12}^*)-\frac{6}{49}\left(\frac{\Theta_1^*\Theta_2^*}{T_{12}^*}\right)J_{15}^D(T_{12}^*)+\cdots\right]\end{aligned} \quad (5)$$

where $\Theta_i^*=\Theta_i/(\varepsilon_0\sigma_0^5)_{12}^{1/2}$ are dimensionless quadrupole moments and $T_{12}^*=kT/(\varepsilon_0)_{12}$ is a dimensionless temperature. The subscripts "12" refer to the interaction of species 1 and 2.

The dimensionless integrals $J_n^D(T^*)$ that appear in the expressions for the various contributions to B_{ns}^* are defined as

$$J_n^D(T^*)\equiv\frac{n-3}{2}\left(\frac{\sigma_0}{r_m}\right)^{n-3}\int_0^\infty\frac{dx}{x^{n-2}}F(x)\exp(-V_0^*/T^*) \quad (6)$$

where $x\equiv r/r_m$ and $V_0^*(x)\equiv V_0/\varepsilon_0$. The only difference between these $J_n^D(T^*)$ and the $J_n(T^*)$ previously tabulated [3, 4] is the presence of $F(x)$ in the integrand. (Notice that the distance scale parameter used for making B and J_n^D dimensionless is σ_0 and not r_m.) The form chosen for V_0 was the HFD-I potential used by Aziz and Chen [8] in connection with argon,

$$V_0^*(x)\equiv\frac{V_0}{\varepsilon_0}=Ae^{-\alpha x}-\left(\frac{C_6}{x^6}+\frac{C_8}{x^8}+\frac{C_{10}}{x^{10}}\right)F_0(x) \quad (7)$$

where $F_0(x)$ is the same as the $F(x)$ of Eq. (1) except that its parameter D_0 does not have to be the same as the D in $F(x)$. Although this form was originally used specifically for Ar–Ar interactions, it should be regarded here as simply a realistic general model for V_0; we are adopting only its shape, and the scale parameters ε_0 and σ_0 (or r_m) remain arbitrary. The dimensionless parameters of the dimensionless $V_0^*(x)$ have the following values:

$$\begin{aligned} A &= 7.783990 \times 10^5 \\ \alpha &= 13.722590 \\ C_6 &= 1.213008 \\ C_8 &= 0.509989 \\ C_{10} &= 0.280887 \\ D_0 &= 1.28 \\ r_m/\sigma_0 &= 1.121799 \end{aligned} \tag{8}$$

Values of $J_n^D(T^*)$ were calculated by numerical integration and are given in Table AI for $0.5 \leqslant T^* \leqslant 10$ and $6 \leqslant n \leqslant 30$. Experience with similar previous calculations [3, 4] leads us to believe that the accuracy of the tabulated values is not worse than about 1 part in 10^4.

The values of the spherical contribution $B_0^*(T^*)$ can come from any accurate source, since the $B_{\text{ns}}^*(T^*)$ are insensitive to the choice of $V_0(r)$ [3, 4]. For convenience (and possible consistency), however, values of $B_0^*(T^*)$ corresponding to the V_0^* of Eq. (7) are tabulated in Ref. 4 for the range $0.30 \leqslant T^* \leqslant 30$.

3. RESULTS AND DISCUSSION

The effects of cutoff and damping on the nonspherical contributions are illustrated in Fig. 1 for the typical case of $n = 8$. The ratio J_8^D/J_8 is shown as a function of T^* for a (12, 6) spherical potential, with $D = 1.28$, $D = 1.4$, and the sharp cutoff at σ_0 used by Castle *et al.* As expected, the effects of damping and cutoff (deviation of the ratio from unity) increase with increasing T^*. However, this effect is compensated by the decrease in the nonspherical contributions themselves as T^* increases. The sharp cutoff has a markedly stronger effect than the smooth damping.

The results of damping for several values of n are shown in Fig. 2 for the more realistic case of the HFD-I spherical potential with $D_0 = D = 1.28$. The effect of damping increases with increasing n.

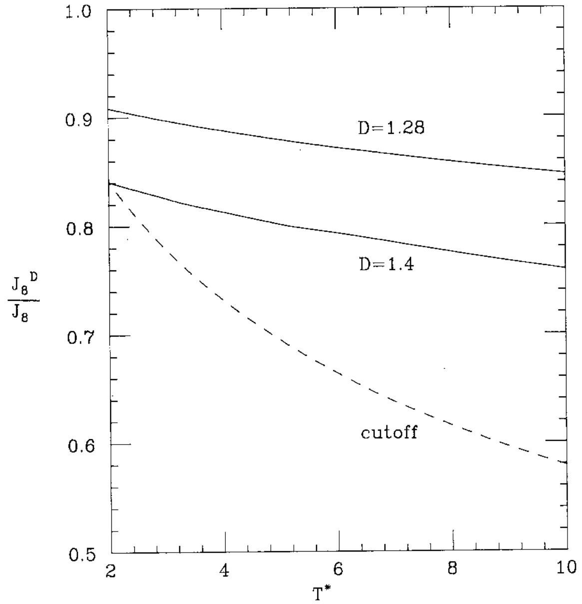

Fig. 1. Effect of damping and cutoff for the typical case of $n = 8$, with the spherical-core potential represented by a (12, 6) model.

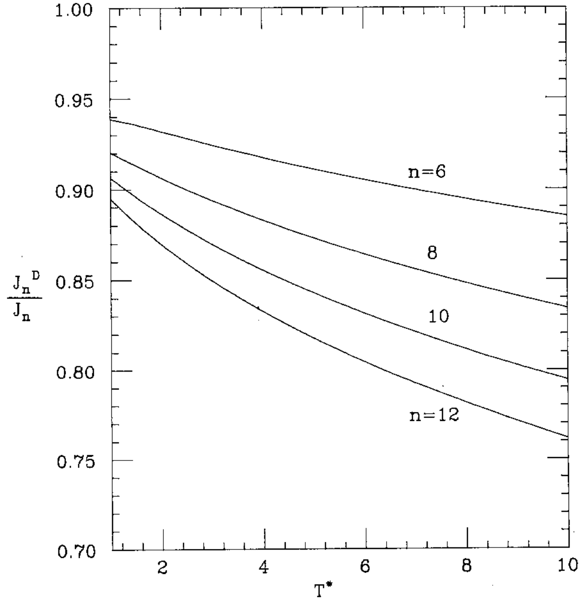

Fig. 2. Effect of damping for several values of n, with the spherical-core potential represented by an HFD-I model.

Table I. Example of the Effect of Damping on the Calculated Nonspherical Contributions to Second Virial Coefficients (CO_2^a)

	$T^*=1$		$T^*=5$	
Contribution	Undamped	Damped	Undamped	Damped
$B^*_{ns}(\Theta\Theta)$	-0.6339	-0.5760	-0.0243	-0.0206
$B^*_{ns}(\Theta, \text{ind } \mu)$	-0.0006	-0.0005	-0.00003	-0.00003
$B^*_{ns}(C_6 \text{ anis})$	-0.0689	-0.0616	-0.0029	-0.0023
$B^*_{ns}(\Theta\Theta \times C_6 \text{ anis})$	$+0.1485$	$+0.1339$	$+0.0057$	$+0.0047$
$B^*_{ns}(\Theta, \text{ind } \mu \times C_6 \text{ anis})$	-0.0100	-0.0088	-0.0005	-0.0004
$B^*_{ns}(\text{total})$	-0.5649	-0.5130	-0.0220	-0.0186
$B^*_0(\text{spherical})$	-2.0716		$+0.3126$	

[a] $\Theta^* = 0.8473$; $\kappa = 0.2664$; $\alpha^*_d = 0.0491$; $C^*_6 = 2.328$.

The effects of the damping on the various nonspherical contributions are illustrated in Table I for CO_2 at reduced temperatures $T^* = 1$ and 5, as calculated with the tables in Ref. 4 and the present tables. Damping reduces the total B^*_{ns} by roughly 10–15%, but the overall effect on the full B^* is only about 1–2%, because of the dominant contribution of the spherical term, B^*_0. Thus the overall effects of damping are small but not negligible. They should be included in accurate work but can be ignored if only rough estimates are needed. The convergence of the perturbation expansion for the nonspherical contributions deteriorates for $T^* < 1$, and the relative contributions themselves diminish rapidly for $T^* > 5$.

The present tables are designed to be used in exactly the same way as the tables in Refs. 3 and 4 for the undamped nonspherical potentials. The only difference is that the present damped functions $J^D_n(T^*)$ replace the previous undamped functions $J_n(T^*)$ in the formulas.

APPENDIX

Table AI. The Functions $J^D_n(T^*)$ for Damped Nonspherical Contributions ($D = 1.28$); the Core Potential is HFD-I

T^*	J^D_6	J^D_7	J^D_8	J^D_9	J^D_{10}
0.5	1.6771	1.8512	1.9669	2.0408	2.0842
0.6	1.3307	1.4524	1.5338	1.5865	1.6188
0.7	1.1376	1.2310	1.2942	1.3361	1.3630
0.8	1.0168	1.0932	1.1456	1.1814	1.2055
0.9	0.9352	1.0004	1.0460	1.0782	1.1010
1.0	0.8770	0.9345	0.9756	1.0055	1.0279

Table AI. *(Continued)*

T^*	J_6^D	J_7^D	J_8^D	J_9^D	J_{10}^D
1.2	0.8004	0.8485	0.8844	0.9123	0.9349
1.4	0.7534	0.7962	0.8296	0.8571	0.8809
1.6	0.7221	0.7619	0.7944	0.8224	0.8478
1.8	0.7004	0.7385	0.7707	0.7997	0.8270
2.0	0.6846	0.7218	0.7544	0.7846	0.8140
2.5	0.6607	0.6976	0.7321	0.7662	0.8010
3.0	0.6485	0.6866	0.7239	0.7622	0.8025
3.5	0.6423	0.6822	0.7227	0.7653	0.8112
4.0	0.6394	0.6814	0.7252	0.7722	0.8236
4.5	0.6385	0.6829	0.7300	0.7813	0.8381
5.0	0.6389	0.6857	0.7361	0.7917	0.8539
6.0	0.6420	0.6935	0.7505	0.8144	0.8870
7.0	0.6466	0.7028	0.7661	0.8382	0.9209
8.0	0.6520	0.7128	0.7821	0.8620	0.9545
9.0	0.6577	0.7228	0.7980	0.8854	0.9876
10.0	0.6634	0.7329	0.8137	0.9084	1.0199

T^*	J_{11}^D	J_{12}^D	J_{13}^D	J_{14}^D	J_{15}^D
0.5	2.1056	2.1110	2.1048	2.0904	2.0703
0.6	1.6363	1.6433	1.6428	1.6372	1.6280
0.7	1.3792	1.3879	1.3914	1.3914	1.3892
0.8	1.2216	1.2320	1.2387	1.2430	1.2458
0.9	1.1175	1.1297	1.1391	1.1469	1.1538
1.0	1.0451	1.0590	1.0710	1.0818	1.0922
1.2	0.9542	0.9716	0.9880	1.0043	1.0210
1.4	0.9026	0.9234	0.9441	0.9653	0.9876
1.6	0.8721	0.8963	0.9210	0.9469	0.9746
1.8	0.8540	0.8815	0.9102	0.9407	0.9735
2.0	0.8437	0.8745	0.9072	0.9422	0.9801
2.5	0.8375	0.8766	0.9189	0.9650	1.0157
3.0	0.8459	0.8931	0.9450	1.0022	1.0657
3.5	0.8613	0.9166	0.9780	1.0464	1.1229
4.0	0.8804	0.9437	1.0146	1.0943	1.1840
4.5	0.9016	0.9728	1.0532	1.1442	1.2473
5.0	0.9238	1.0030	1.0929	1.1952	1.3120
6.0	0.9698	1.0646	1.1735	1.2989	1.4436
7.0	1.0162	1.1265	1.2545	1.4032	1.5765
8.0	1.0622	1.1879	1.3348	1.5072	1.7098
9.0	1.1074	1.2482	1.4143	1.6105	1.8430
10.0	1.1516	1.3075	1.4927	1.7130	1.9760

Table AI. *(Continued)*

T^*	J_{16}^D	J_{17}^D	J_{18}^D	J_{19}^D	J_{20}^D
0.5	2.0463	2.0198	1.9920	1.9636	1.9352
0.6	1.6166	1.6038	1.6905	1.5770	1.5640
0.7	1.3856	1.3813	1.3770	1.3729	1.3695
0.8	1.2479	1.2498	1.2520	1.2548	1.2585
0.9	1.1604	1.1673	1.1748	1.1832	1.1927
1.0	1.1028	1.1140	1.1261	1.1394	1.1541
1.2	1.0385	1.0572	1.0774	1.0994	1.1234
1.4	1.0114	1.0369	1.0646	1.0948	1.1276
1.6	1.0043	1.0364	1.0714	1.1095	1.1510
1.8	1.0090	1.0477	1.0898	1.1359	1.1864
2.0	1.0214	1.0665	1.1159	1.1701	1.2297
2.5	1.0715	1.1330	1.2011	1.2764	1.3599
3.0	1.1363	1.2149	1.3024	1.4002	1.5095
3.5	1.2086	1.3048	1.4129	1.5346	1.6717
4.0	1.2853	1.3997	1.5293	1.6763	1.8432
4.5	1.3645	1.4979	1.6500	1.8236	2.0222
5.0	1.4456	1.5985	1.7739	1.9755	2.2077
6.0	1.6109	1.8046	2.0294	2.2909	2.5956
7.0	1.7788	2.0155	2.2931	2.6193	3.0036
8.0	1.9484	2.2301	2.5636	2.9592	3.4297
9.0	2.1191	2.4477	2.8400	3.3095	3.8726
10.0	2.2906	2.6679	3.1219	3.6694	4.3316

T^*	J_{21}^D	J_{22}^D	J_{23}^D	J_{24}^D	J_{25}^D
0.5	1.9073	1.8803	1.8543	1.8297	1.8066
0.6	1.5516	1.5401	1.5297	1.5206	1.5128
0.7	1.3669	1.3654	1.3651	1.3661	1.3685
0.8	1.2632	1.2692	1.2766	1.2855	1.2960
0.9	1.2036	1.2159	1.2299	1.2456	1.2632
1.0	1.1704	1.1884	1.2084	1.2304	1.2547
1.2	1.1497	1.1783	1.2097	1.2439	1.2812
1.4	1.1634	1.2025	1.2451	1.2915	1.3422
1.6	1.1965	1.2461	1.3003	1.3596	1.4243
1.8	1.2416	1.3022	1.3686	1.4414	1.5212
2.0	1.2951	1.3671	1.4462	1.5333	1.6293
2.5	1.4524	1.5552	1.6693	1.7962	1.9374
3.0	1.6319	1.7689	1.9225	2.0950	2.2890
3.5	1.8265	2.0013	2.1991	2.4232	2.6775
4.0	2.0330	2.2492	2.4958	2.7775	3.0999
4.5	2.2497	2.5107	2.8107	3.1562	3.5547
5.0	2.4754	2.7848	3.1429	3.5582	4.0407

Table AI. *(Continued)*

T^*	J^D_{21}	J^D_{22}	J^D_{23}	J^D_{24}	J^D_{25}
6.0	2.9513	3.3676	3.8557	4.4291	5.1043
7.0	3.4571	3.9938	4.6301	5.3866	6.2877
8.0	3.9905	4.6608	5.4638	6.4283	7.5894
9.0	4.5501	5.3671	6.3550	7.5527	9.0085
10.0	5.1347	6.1113	7.3024	8.7589	10.5448

T^*	J^D_{26}	J^D_{27}	J^D_{28}	J^D_{29}	J^D_{30}
0.5	1.7849	1.7649	1.7466	1.7300	1.7151
0.6	1.5064	1.5015	1.4981	1.4963	1.4961
0.7	1.3724	1.3779	1.3850	1.3939	1.4045
0.8	1.3082	1.3222	1.3381	1.3560	1.3760
0.9	1.2828	1.3045	1.3285	1.3549	1.3838
1.0	1.2813	1.3105	1.3424	1.3772	1.4150
1.2	1.3218	1.3660	1.4141	1.4663	1.5230
1.4	1.3974	1.4575	1.5230	1.5943	1.6720
1.6	1.4951	1.5725	1.6571	1.7496	1.8508
1.8	1.6088	1.7049	1.8105	1.9266	2.0541
2.0	1.7351	1.8516	1.9803	2.1223	2.2793
2.5	2.0984	2.2702	2.4661	2.6849	2.9298
3.0	2.5072	2.7532	3.0308	3.3444	3.6993
3.5	2.9664	3.2951	3.6698	4.0975	4.5863
4.0	3.4695	3.8938	4.3817	4.9438	5.5924
4.5	4.0151	4.5481	5.1662	5.8842	6.7200
5.0	4.6025	5.2578	6.0235	6.9202	7.9721
6.0	5.9011	6.8432	7.9597	9.2854	10.8631
7.0	7.3638	8.6518	10.1968	12.0543	14.2927
8.0	8.9908	10.6863	12.7426	15.2424	18.2887
9.0	10.7827	12.9502	15.6052	18.8655	22.8789
10.0	12.7405	15.4473	18.7930	22.9392	28.0908

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