SECOND VIRIAL COEFFICIENTS OF NONSPHERICAL MOLECULES WITH INDIVIDUAL DAMPING OF HFDID1 POTENTIAL

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Abstract

The second virial coefficients are given as a spherical-core contribution plus a series of nonspherical perturbation terms. A revised analysis is given of the effect of long-range nonspherical terms in the intermolecular potential on the second virial coefficient given by a preferred HFDID1 spherical core treatment of the integration for small intermolecular distances. This effect is considered by damping functions.

Introduction

The potential energy of interaction between two polyatomic molecules is usually assumed to consist of a spherically symmetric component plus a contribution due to the asphericity of the molecular charge distribution. The latter contribution is conveniently divided into terms representing the classical electrostatic interaction between the two charge distributions, the anisotropy of the quantum-mechanical dispersion forces, and the shape of the molecular core (i.e. the anisotropy of the repulsive part of the potential). Parts of the potential contribute more significantly to some properties of the molecular gas than to others. For example, the viscosity of a quadrupolar gas can usually be adequately described by a potential function consisting only of the spherical component plus the contribution due to the quadrupole moments, whereas the second virial coefficient of the same gas depends significantly on all parts of the potential function.

A method for the calculation of the second virial

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coefficients of non-spherical molecules is the perturbation procedure developed by Pople and Buckingham [1,2]. They proposed that in addition to the interaction of permanent dipoles, other oriented intermolecular forces such as dipole-induced dipole interaction, and quadrupole forces, may be important.

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 a series that converge rapidly at high temperatures. The coefficients of the series are some integrals. These integrals are functions of temperature, which are usually evaluated numerically and tabulated [1-4].

The weak point in the above development usually is the form for the long-range nonspherical terms in the potential; this form is kept in the subsequent integrations even down to $r = 0$ (r is the radial coordinate). The formulas are convergent at high temperatures, but it is at high temperatures that effects occurring at small intermolecular separation might be expected to be most important.

Such 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 [5].

In the previous works of Boushehri *et al.* [3,4,6], a single damping function for all the long-range terms, including those in the spherical potential, was used. In principle, a somewhat different damping function should be used for each long-range term, but Absardi *et al.* [7] found that this refinement did not produce any appreciable change in the final second virial coefficients. In this paper, we use a modified potential HFDID1 [8] based on the individual and general damping function and show the effect of these damping functions on the B_{sph} and also B_{ns}.

Calculations

If two nonspherical moelcules interact, the potential energy will depend on the relative spatial orientations of the molecules, V_{ns}, as well as on their distance apart, $V_o(r)$.

All HFD potentials are based on partitioning the interaction energy V_o into uncorrelated (V_{SCF}, Hartree-Fock) and correlated (V_{cor}) parts [9-11].

$$V_o(r) = V_{SCF} + V_{cor} \qquad (1)$$

Here V_{SCF} is the (SCF) Hartree-Fock interaction energy for the rare gas dimers, which is often represented by [10-12]

$$V_{SCF} \text{ (HFD-B)} = A \exp(-\alpha R + \beta R^2) \qquad (2)$$

where the parameters A, α, and β are adjusted to fit experimentally-determined properties for the system of interest.

Douketis *et al.* [9] modified the original HFD-A potential by representing V_{cor} by a doubly-corrected dispersion series of the form

$$V_{cor} = - [\sum C_n R^{-n} g_n(\rho R)] f(\rho R), \qquad (3)$$
$$n = 6,8,10,12,14$$

where

$$g_n(\rho R) = [1 - \exp(-2.1 \, \rho R/n - 0.109 \rho^2 R^2/n^{1/2})]^n \qquad (4)$$

$$f(\rho R) = 1 - (\rho R)^{1.68} \exp(-0.78 \rho R) \qquad (5)$$

with R in atomic unit.

Here, C_n represents the dispersion coefficients; the universal damping functions $g_n(\rho R)$ correct the individual terms of the expansion for charge overlap effects, and the universal function $f(\rho R)$ corrects the expansion for exchange overlap. The quantity ρ is a scaling parameter that accounts for the different range of different

interactions.

This potential is dubbed the HFDID1 (Hartree-Fock Dispersion Individually Damped). The parameters of this potential, which is usually expressed in reduced form, are given in Reference 8.

The perturbation expansion for the second virial coefficient, B(T), then leads to [3]

$$B(T) = \frac{2\Pi N_A}{3\sigma_0^3} [B_0 \, {}^*(T^*) + B_{ns} \, {}^*(T^*)] \qquad (6)$$

where N_A is Avogadro's number; B_0^* is the (dimensionless) contribution from $V_0(r)$; B_{ns}^* is reduced nonspherical contribution to the second virial coefficient, it depends only on $T^* = k_B T/\varepsilon_0$ where ε_0 is the depth of the potential well; T is temperature; k_B is the Boltzman constant; and σ_0 is the separation at which the spherical potential is zero.

Our goal in this work is to calculate the nonspherical contribution to the second virial coefficient of the polyatomic gases by considering the contributions of the following terms of the HFDID1 potential model:

$$B_{ns}^* = B_{ns}^* \, (\theta\theta) + B_{ns}^* \, (\theta, \text{ind} \, \mu) + B_{ns}^* \, (C_6 \text{ anis}) +$$
$$B_{ns}^* \, (\theta\theta \times C_6 \text{ anis}) + B_{ns}^* \, (\theta, \text{ind} \, \mu \times C_6 \text{ anis}) \quad (7)$$

The terms in Equation 7 are defined in the Appendix of Reference 6.

The values of κ (the polarisability anisotropies), θ^*, C_6 and α^* are taken from Reference 7.

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

$$J_n (T^*) = \frac{n-3}{2} \left(\frac{\sigma_0}{r_m}\right)^{n-3} \int_0^\infty x^{2-n} \exp\left(-\frac{V_0^*}{T^*}\right) dx \qquad (8)$$

where V_0^* (r) $\equiv V_0 / \varepsilon_0$ (V_0 is the spherical potential), and $x \equiv r/r_m$. The value of these integrals is calculated for $6 \leq n \leq 30$ and T^* in the range 1-10. Also we represent the dimensionless integrals $J_n^D (T^*)$.

$$J_n^D (T^*) = \frac{n-3}{2} \left(\frac{\sigma_0}{r_m}\right)^{n-3} \int_0^\infty \frac{dx}{x^{n-2}} f(x) \exp\left(-\frac{V_0^*}{T^*}\right) \qquad (9)$$

where f(x) is the same as $f(\rho R)$ given in Equation 5.

The only difference between the $J_n^D (T^*)$ and the $J_n (T^*)$ is the presence of f(x) in the integrand.

It should be noted that the precise form of the short-

Table I. Example of the effect of damping on the calculated nonspherical contributions to second virial coefficients (CO_2^*). The core potential is HFDID1.

Contribution	$T^* = 1$		$T^* = 5$	
	Undamped	Damped	Undamped	Damped
$B_{ns}^*(\theta\theta)$	-0.6414	-0.5941	-0.0252	-0.0226
$B_{ns}^*(\theta, ind\mu)$	-0.0007	-0.0006	-0.0004	-0.00004
$B_{ns}^*(C_6$ anis$)$	-0.0461	-0.0423	-0.0020	-0.0017
$B_{ns}^*(\theta\theta \times C_6$ anis$)$	0.1231	0.1134	0.0049	0.0043
$B_{ns}^*(\theta, ind \mu \times C_6$ anis$)$	-0.0092	-0.0084	-0.0005	-0.0004
B_{ns}^* (total)	-0.5743	-0.5320	-0.0232	-0.0204
B_0^* (spherical)[b]	-1.9912		+0.3212	

[a] $\theta^* = 0.85$; $\kappa = 0.268$; $\alpha_d^* = 0.0547$; $C_6^* = 1.89$

[b] HFDID1 also used for calculation of B_0^* (spherical)

range directional forces is as yet unknown. Therefore, we only consider the contribution to the second virial coefficient resulting from long-range directional forces.

Table I gives the nonspherical contribution to the second virial coefficient of carbon dioxide as a function of temperature, the values were calculated from Equation 7. The effects of the damping on the various nonspherical contributions at reduced temperature $T^* = 1$ and $T^* = 5$ are also shown in this table.

Results and Discussion

The values of function $J_n^D(T^*)$, which serves as coefficients in the perturbation expansion for the second virial coefficient, are available on request. These values are designed to be used in exactly the same way as those of Reference 7 for the damped nonspherical potentials. The differences arise from the use of the preferred accurate pair potential model, HFDID1, in calculating $J_n^D(T^*)$ functions.

The damping effect of the more realistic case of the HFDID1 spherical on the nonspherical contributions for several values of n is illustrated in Figure 1.

The plot in Figure 2 shows the deviation in second virial coefficients of carbon dioxide as predicted by the
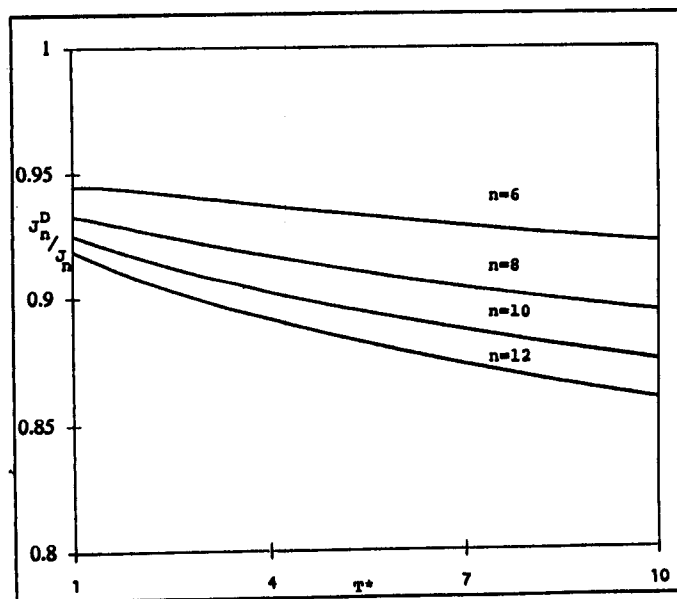
Figure 1. Effect of damping for several values of n, with the spherical-core potential represented by an HFDID1 model
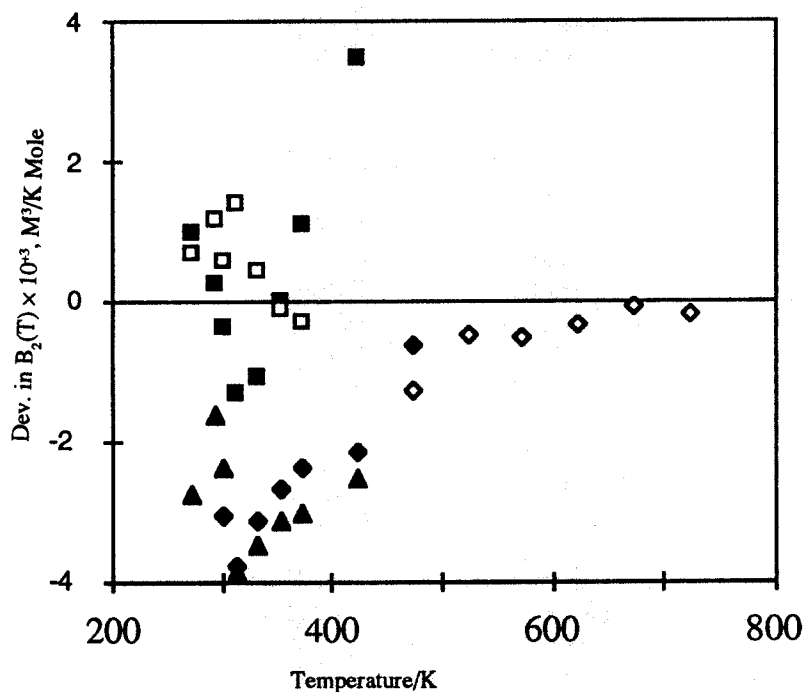
Figure 2. Deviation plot for the second virial coefficient of carbon dioxide. The points are ▲Ref. 13; ◆Ref. 14; ■Ref. 15; ◇Ref. 16; □Ref. 17.

present procedure. As the figure shows, the error, within 4%cc/mol, is in good agreement with experimental uncertainties for a wide range of temperatures.

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