IN THE NAME OF GOD

CALCULATION OF THE SECOND VIRIAL COEFFICIENT OF NONSPHERICAL MOLECULES

BY

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Dedicated to

My family who has contributed much to this thesis, especially my

father and mother

and

my husband

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ABSTRACT

CALCULATION OF THE SECOND VIRIAL COEFFICIENT OF NONSPHERICAL MOLECULES

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A method for the calculation of the second virial coefficients of the nonspherical interactions, which are only asymptotically valid at large separation are improved by damping functions that make them to be valid at small separations as well.

An accurate Hartree-Fock dispersion individually damped (HFD-ID) potential type improved by Boyes for argon has been used as a core potential to calculate both the spherical and nonspherical contributions to the second virial coefficient of simple molecules.

The auxiliary functions that occur in the perturbation terms for calculating the nonspherical contributions, have been calculated numerically and are tabulated over a wide range of temperatures from $T^*=0.5$ to $T^*=10$, where $T^*=kT/\varepsilon$ and ε is the potential well-depth. By fitting the well-depth and the position of the minimum in the core potential, we have calculated the second virial coefficient of N_2, O_2, CO, NO, and CO_2 over the whole temperature range reported in the literature. The calculated results are compared with the large body of experimental data in the literature, and with the pervious calculations by Boushehri et al. (1989). The agreement with both experimental data and theoretical calculations is quite good.

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Nomenclature

B	second virial coefficient	$Cm^3.mol^{-1}$
C_6-C_{14}	dispersion coefficients	$J.m^6$-$J.m^{14}$
$\mathbf{I}$		unit vector
J_n	auxiliary function defined by equation (2.3.1)	
k	Boltzmann constant	$J.K^{-1}$
N	Avogadro's number	mol^{-1}
r	interparticle distance	nm
$\mathbf{r}$	vector separating molecular centers	nm
T	absolute temperature	K
$\mathbf{T}$	dipole-dipole interaction tensor	nm^{-2}
V	potential energy function	J

Greek symbols

α	polarizability	nm^3
θ , φ	Eulerian angles	°
Θ	quadrupole moment	$J^{1/2}m^{5/2}$
σ	the position at which V_0=0	nm
ε	potential well-depth	J
μ	dipole moment	$J^{1/2}m^{3/2}$
$\boldsymbol{\mu}$	dipole moment vector	$J^{1/2}m^{3/2}$
κ	anisotropy of dipole polarizability	

Subscripts

0	spherical contribution
ns	nonspherical contribution
ind	induced
d	dipole

Nomenclature(Continued)

Superscripts

$*$	reduced quantity
$\perp$	vertical component
$\parallel$	parallel component

Chapter one

INTRODUCTION

1-1 Equation of State of Gases

An equation of state of a gas merely given a mathematical relation among the pressure, volume, temperature and number of moles (P,V,T,n) at equilibrium. The simplest equation of state is that for the perfect gas, as, PV=nRT.

1-2 The Equation of State in the Virial Form

Several authors have proposed the modifications of the perfect gas equation of state. K.Onnes in 1901 suggested the idea of expressing the pressure in a convergent series in terms of the reciprocal molar volume and the absolute temperature. In this suggestion the equation of state of a gas expressed in virial form:

$$PV = RT(1+\frac{B}{V}+\frac{C}{V^2}+\frac{D}{V^3}+\ldots) \qquad (1.2.1)$$

where P,V and T are parameters of state , R is the gas constant, and B,C,D,... are called the second , third, fourth,... virial coefficients depending on the temperature only.

It has been known that deviations in the behavior of real gases from that of a perfect gas are essentially due to molecular interactions. From the statistical mechanical expressions for the virial coefficients it becomes evident that the second, third,... virial coefficients represent deviations from ideal behavior, and are due to two body, three body,... molecular collisions.

At not too high densities the third and higher order terms might be neglected. Furthermore, at high densities many terms of the series must be included to obtain satisfactory accuracy, and this means that many parameters (the virial coefficients) have to be determined experimentally.

The reason for the special importance of the virial equation of state is that it is the equation of state known which has been obtained from a theoretical foundation. There is a definite interpretation for each virial coefficient in terms of molecular properties. The second virial coefficient represents the interactions between two molecules; the third represents the interactions among three molecules, and so on. Thus the virial equation of state forms the connection between experimental values of the second virial coefficients have often been employed to determine the parameters in different expressions of the intermolecular potentials and knowledge interactions. The well known statistical mechanical expression for the second virial coefficient reads as:[1]

$$B(T)=\frac{N}{8\pi}\int_0^{\infty}\int_0^{\pi}\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi}[1-\exp(-V/kT)]r^2\,dr\,\sin\theta_1\,d\theta_1\,\sin\theta_2\,d\theta_2\,d\varphi_1\,d\varphi_2 \tag{1.2.2}$$

where N is the Avogadro 's number, k is the Boltzmann 's constant, T is the absolute temperature, and θ and φ are the usual Eulerian angels.

There are two reasons on the importance of calculation of the second virial coefficient: The first reason is its use in the construction of equation of state of gases. The second reason is the relation between the second virial coefficient, which is a macroscopic property, and the intermolecular potential energy function of gases which is a microscopic property via statistical thermodynamics, Eq(1.2.2).

1-3 The intermolecular potential energy of polyatomic molecules

The intermolecular potential energy of polyatomic molecules is usually assumed to consist of a spherically symmetric component plus a contribution due to the asphericity of the molecular charge distribution, so that

$$V(r) = V_0(r) + V_{ns}(r) \qquad (1.3.1)$$

in which V_0 depends only on the distance r between the molecular center of mass, and V_{ns} depends also on the angle ω that specifies the relative orientation of the molecular pair.

One of the most famous intermolecular potential functions which gives a fairly simple and realistic representation for spherical charge distribution calculations is the Lennard-Jones (12-6) potential energy function introduced in 1924 and is described[2] as:

$$V_0(r) = 4\varepsilon_0\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \qquad (1.3.2)$$

where ε_0 is the potential well depth and σ indicates the intermolecular distance at which repulsive and attractive forces are equal in magnitude, and thus cancel each other.

1-4 Calculation of the second virial coefficients of the nonspherical molecules

A common method for the calculation of the second virial coefficients of the nonspherical molecules is the perturbation procedure developed by Pople[3] and by Buckinghom and Pople,[4] who represent the intermolecular potential function as a spherically symmetric core plus terms representing various nonspherical interactions such as dipole-dipole, quadrupole-quadrupole, and dispersion anisotropy interactions.

The nonspherical terms are then treated as perturbations, and the statistical mechanical expressions that given corrections to the spherical contributions in the form of series that converge rapidly for high temperatures. The coefficient of the series are integrals that are functions of temperature and are tabulated.[3-6]

A difficulty in the foregoing development is the form, which is usually assumed for the long-range nonspherical terms in the potential function. These terms are given by various inverse power of the intermolecular separation, but is nevertheless kept in the subsequent integration even down to r=0 separation. Evidently the magnitude of the long-range terms should be decreased, as r decreases in order to account for electron overlap and exchange.

This point was recognized quite early by castle et al.[7] who did exploratory calculations, using a Lennard-Jones (12-6) spherical-core potential function with a number of added nonspherical interaction terms. In the absence of at that time of any information of the quantitative nature of the damping of long-range terms as r decreased, they used a simple cut off at $r=\sigma_0$, the separation at which the spherical potential is zero. They found that the coefficient of the series expression were reduced by roughly 20% at $T^*=\frac{kT}{\varepsilon_0}=1$ and by a factor of about 2 at $T^*=10$, where ε_0 is the depth of spherical potential well, k is the Boltzmann constant, and T is absolute temperature.

The effect of nonspherical contributions to the total second virial coefficients 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 damping of the long-range terms has been greatly understood, and multiplicative damping functions that convert the asymptotic formulas valid at large separation r, into those valid at all r have been developed.