

Intermolecular Forces in Globular Molecules. II. Multipolar Gases with a Spherical-Shell Central Potential*

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The integrals appropriate to the classical second virial coefficient for a molecule obeying a spherical-shell central potential and including either a dipole moment or a quadrupole moment are calculated for a wide range of values of r_0^* , T^* . The functions $H_k(r_0^*, T^*)$ are available for $k=6, 10, 12, 15, 18, 20$, and 24 . The results are used to investigate the intermolecular forces in methyl chloride and benzene. In both cases a significant improvement in fit with experimental data is noted upon inclusion of multipolar forces. For benzene, treated as an axial molecule, a quadrupole moment Θ_{zz} of $\pm 15 \times 10^{-28}$ esu is deduced.

I. INTRODUCTION

A DESCRIPTION of the forces between quasi-spherical polyatomic molecules (globular molecules) can be conveniently made in terms of a model of uniformly dense bireciprocal point centers of interaction, e.g., m - n , spread over the surface of a spherical shell of vanishing thickness. Interior to the shell is a core of hard repulsion.

The spherical-shell potential, previously elaborated in Paper I of this series by De Rocco and Hoover,¹ is obtained by the integration of the point by point interactions between two such shells. The effect of this procedure is to narrow the width of the potential well and to harden the repulsion; a result similarly obtained by adjusting the powers m and n in the Mie potential,² by use of a Morse or Rydberg potential,^{3,4} or by use of the core potential introduced by Kihara.⁵ Of these several models, the spherical-shell potential has the advantages that it depends on the explicit core size of a molecule (the sphericalized geometry of interaction) and takes into account interactions of all parts of one molecule with another (contrast with the Kihara potential, where the critical distance for interaction is the distance of closest approach of the cores).

Interest in the spherical-shell potential comes from two sources. First, it has been approximated by the 28-7 potential for the study both of equilibrium^{2a} and of transport properties.^{2b,2c} Although the viscosity com-

puted for a 28-7 potential is not radically different than that computed for a 12-6 potential, the differences noted in the isotopic thermal-diffusion factors by Smith, Mason, and Munn,^{2c} prompt further attention to the full spherical-shell potential.

A second reason for interest in the spherical-shell model stems from the observation that the "best" core size is intimately related to the equivalent sphere generated by a radius drawn from the center of the globular cluster to those peripheral atoms over which the shell integration is performed.¹ It is striking to obtain exceedingly good internal dimensions for moderately complex molecules from a best fit of second virial coefficients. This observation has been made for quite a variety of molecules, and it has been found to hold with the one interesting exception of peripheral hydrogen atoms, where the core size is always smaller than the interatomic distance.¹ This latter fact is evidence for the softness of hydrogenic repulsions.

Thus the core size in the spherical-shell potential can be regarded not as a free parameter, but rather as a geometrical attribute of the molecule under consideration. With this practice in mind, the central potential is a two-parameter model. This feature of the potential has been discussed recently by McKinley and Reed.⁶

In this paper we extend the spherical-shell potential by including the terms necessary for molecules possessing a permanent dipole or quadrupole moment.

This potential is then integrated in the manner appropriate to the classical second virial coefficient, and the results fitted to experimental data for methyl chloride and benzene. The fits obtained are improvements over previous efforts, even though the shape of the potential well is predetermined in each case by the molecular geometry and the interatomic distances.

II. INTERMOLECULAR POTENTIAL MODEL

We have assumed that the interaction of two globular molecules can be represented by additive contributions from the central potential (which we take to be a

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¹ A. G. De Rocco and W. G. Hoover, *J. Chem. Phys.* **36**, 916 (1962), hereafter referred to as I.

² (a) S. D. Hamann and J. A. Lambert, *Australian J. Chem.* **7**, 1 (1954); (b) J. C. McCoubrey and N. M. Singh, *Trans. Faraday Soc.* **55**, 1826 (1959); (c) F. J. Smith, E. A. Mason, and R. J. Munn, *J. Chem. Phys.* **42**, 1334 (1965).

³ D. D. Konowalow, *Phys. Fluids* **9**, 23 (1966), and references cited therein.

⁴ O. Sinanoğlu and K. S. Pitzer, *J. Chem. Phys.* **31**, 960 (1959).

⁵ T. Kihara, *Rev. Mod. Phys.* **25**, 831 (1953). For a recent example of the use of this model see A. E. Sherwood and J. M. Prausnitz, *J. Chem. Phys.* **41**, 429 (1964).

⁶ M. D. McKinley and T. M. Reed III, *J. Chem. Phys.* **42**, 3891 (1965).

spherical-shell potential) and additional terms appropriate to the interaction of dipoles or quadrupoles situated at the centers of the molecules.

The central part is known to be given by¹

$$u_0(r^*) = \frac{\epsilon[(3r_0^*P_0^{*(4)}+P_0^{*(3)})P^{*(9)} - (9r_0^*P_0^{*(10)}+P_0^{*(9)})P^{*(3)}]}{(9P_0^{*(3)}P_0^{*(10)} - 3P_0^{*(4)}P_0^{*(9)})r^*}, \quad (1)$$

where $(r_0, -\epsilon)$ characterize the range and strength of the minimum. The core has diameter d , in terms of which $r^*=r/d$, and $P_0^{*(N)}=P_0^{(N)}d^N$. The function $P^{(N)}$ is defined as

$$P^{(N)} \equiv (r+d)^{-N} - 2r^{-N} + (r-d)^{-N}. \quad (2)$$

If such a molecule is further characterized by a dipole moment μ or a quadrupole moment Θ at its center, then the total potential is written either as

$$u = u_0(r^*) + (\mu^2/r^3)G_\mu(\theta_1, \theta_2, \phi_1, \phi_2) \quad (3)$$

or

$$u = u_0(r^*) + (3\Theta^2/4r^5)G_\Theta(\theta_1, \theta_2, \phi_1, \phi_2), \quad (4)$$

where the functions G_μ and G_Θ are expressed in terms of the polar (θ) and azimuthal (ϕ) angles as

$$G_\mu = 2 \cos\theta_1 \cos\theta_2 + \sin\theta_1 \sin\theta_2 \cos(\phi_1 + \phi_2), \quad (5)$$

$$G_\Theta = 1 - 5 \cos^2\theta_1 - 5 \cos^2\theta_2 - 15 \cos^2\theta_1 \cos^2\theta_2 + 2[\sin\theta_1 \sin\theta_2 \cos(\phi_1 + \phi_2) + 4 \cos\theta_1 \cos\theta_2]^2. \quad (6)$$

In expressing the interaction energies we have followed the conventions employed by Buckingham.^{7,8} Strictly speaking, we should write Θ_{zz} , to indicate our implicit assumption that we are dealing with molecules possessing axial symmetry.

III. CALCULATIONS

The second virial coefficient for an angular-dependent potential is given by the following well-known expression of classical statistical mechanics:

$$B(T) = \frac{\tilde{N}}{8\pi} \int_0^\infty r^2 dr \int_0^\pi \sin\theta_1 d\theta_1 \int_0^{2\pi} d\phi_1 \int_0^\pi \sin\theta_2 d\theta_2 \int_0^{2\pi} d\phi_2 \left[1 - \exp\left(-\frac{u}{kT}\right) \right], \quad (7)$$

where u is the total two-body potential, k is the Boltzmann constant, T is the absolute temperature, and \tilde{N} represents the Avogadro number.

Detailed expressions for the dipolar and quadrupolar cases are obtained by substituting Eqs. (3) or (4) into Eq. (7), expanding the exponential term, and integrating term by term. The following equations result:

$$\text{(dipole)} \quad \frac{B(T)}{b_0} = \frac{3}{r_0^{*3}} \int_0^\infty r^{*2} \left[1 - \exp\left(-\frac{u_0^*}{T^*}\right) \right] dr^* - \frac{3}{4} \sum_{l=1}^\infty \left(\frac{\tau}{T^*}\right)^l A(l) H_{3l}(r_0^*, T^*), \quad (8)$$

$$\text{(quadrupole)} \quad \frac{B(T)}{b_0} = \frac{3}{r_0^{*3}} \int_0^\infty r^{*2} \left[1 - \exp\left(-\frac{u_0^*}{T^*}\right) \right] dr^* - \frac{3}{4} \sum_{l=1}^\infty \left(\frac{\lambda}{T^*}\right)^l B(l) H_{5l}(r_0^*, T^*). \quad (9)$$

In these expressions the following abbreviations apply: $b_0 = \frac{2}{3}\tilde{N}\pi r_0^3$, $T^* = kT/\epsilon$, $u_0^* = u_0/\epsilon$, $\tau = \mu^2/\epsilon r_0^3$, $\lambda = \Theta^2/\epsilon r_0^5$. The remaining quantities are the H functions which are given by

$$H_k(r_0^*, T^*) = r_0^{*(k-3)} \int_0^\infty r^{*(2-k)} \exp\left(-\frac{u_0^*}{T^*}\right) dr^*, \quad (10)$$

and the coefficients $A(l)$ and $B(l)$,

$$A(l) = \frac{1}{(2\pi)^2} \int_0^\pi \sin\theta_1 d\theta_1 \int_0^{2\pi} d\phi_1 \int_0^\pi \sin\theta_2 d\theta_2 \int_0^{2\pi} d\phi_2 G_\mu^l, \quad (11)$$

$$B(l) = \frac{1}{(2\pi)^2} \int_0^\pi \sin\theta_1 d\theta_1 \int_0^{2\pi} d\phi_1 \int_0^\pi \sin\theta_2 d\theta_2 \int_0^{2\pi} d\phi_2 G_\Theta^l. \quad (12)$$

⁷ A. D. Buckingham, *Quart. Rev. (London)* **13**, 183 (1959).

⁸ A. D. Buckingham and J. A. Pople, *Trans. Faraday Soc.* **51**, 1173 (1955). See also, A. L. McClellan, *Tables of Experimental Dipole Moments* (W. H. Freeman and Co., San Francisco, Calif., 1963).

TABLE I. Values of the coefficients $A(l)$ and $B(l)$ for initial values of l .

l	$A(l)$	$B(l)$
1	0.0	0.0
2	1.333	9.9555
3	0.0	-2.786394
4	0.159999	10.99907
5	0.0	-6.1134833
6	0.105215×10^{-1}	8.493999
7	0.0	-5.7804156
8	0.4434366×10^{-3}	5.027545
9	0.0	-3.321579
10	0.1299325×10^{-4}	2.241094
11	0.0	
12	0.279277×10^{-6}	

The first integral appearing in Eqs. (8) and (9) represents the second virial coefficient for the nonpolar, central part of the potential. Values of this integral have been tabulated in Paper I. We have evaluated the second integral numerically by Simpson's rule for a wide range of (r_0^*, T^*) and for $k=6, 10, 12, 15, 18, 20,$ and 24 . The results of this integration, estimated to be accurate to one part in 10^4 , have been deposited with the American Documentation Institute.⁹

The coefficients $A(l)$ and $B(l)$ were obtained by evaluating the sums that result from a binomial expansion of the integrands of Eqs. (11) and (12). The first few values of these coefficients are given in Table I.

The potential parameters r_0 and ϵ/k for a given shell size d were chosen automatically to minimize the quantity

$$\sigma^2 = \frac{1}{N-1} \sum_{j=1}^N [\ln B_j(T_j)_{\text{exptl}} - \ln B_j(T_j^*, r_0^*)_{\text{calc}}]^2. \quad (13)$$

IV. APPLICATION TO METHYL CHLORIDE AND TO BENZENE

The choices of methyl chloride and benzene were made on two grounds. First the experimental values of the second virial coefficients are known over a fairly wide range of temperatures (CH_3Cl 0° - 350°C , benzene 20° - 355°C), and second the selection of a core size can be made on a reasonable basis in each case.

In the latter connection, the assignment of a shell

size from structural information alone is necessarily somewhat arbitrary. For methyl chloride we took a value of 2.8 \AA (the arithmetic average of the CH and C-Cl bond distances) rather than 2.5 \AA (obtained by weighting each of the four distances evenly) or 3.4 \AA (twice the C-Cl bond distance). The shell size for benzene was taken as 2.78 \AA . This value is twice the C-C distance and takes into account the observation (see Paper I) that hydrogenic repulsions are quite soft. Earlier studies on benzene made no provision for the effects of quadrupole interactions and the fitted value of the shell size was found to be considerably higher (5.61 \AA).¹ The dipole moment for methyl chloride (1.86 D) was taken from Buckingham and Pople.⁸ The remaining potential parameters were fitted according to the recipe provided by Eq. (13). The results are listed in Table II.

The fit with experimental data for each substance was enhanced by inclusion of the appropriate multipole term. For methyl chloride the fit was nearly an order of magnitude better than that obtained with a Stockmayer potential. Furthermore, the parameters derived here are significantly different from those found for (18-6-3) and (12-6-3) Stockmayer potentials.¹⁰ An additional improvement can probably be obtained by inclusion of dipole-quadrupole, induction, and quadrupole-quadrupole terms in the potential function, but this was not thought to justify the large amount of computing time necessary. In an earlier study based on the Lennard-Jones (12-6) central potential the inclusion of a term corresponding to dipole-induced-dipole forces led to only a minor effect on the force constants.⁸ We anticipate the same conclusion to hold for a spherical-shell potential. The existing computer programs can, however, easily be extended should data become available for a more numerous sampling of polar molecules. It is especially important to have accurate virial coefficients over as wide a temperature range as possible.

For benzene the improvement in the fit obtained by inclusion of quadrupolar forces was impressive. Strictly speaking, of course, the conventions employed here for Θ apply only to axially symmetric molecules, but the situation in benzene is not thought to be sufficiently far from axial to severely limit these results.

For benzene no independent measurement of Θ is known to us. The value given is the one which best fits the data when Θ , ϵ/k , and r_0 are varied together. The shell size is fixed, unlike the assignment of benzene parameters made in Paper I. If the potential is treated as a four-parameter model, then the "best" value of d is likely not to be very different from that cited. In an earlier study¹¹ on benzene a quadrupole moment of

⁹ A more detailed form of this paper, containing these tables, has been deposited as Document No. 9120 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D.C. A copy may be secured by citing the document number and by remitting \$3.75 for photoprints, or \$2.00 for 35-mm microfilm. Advance payment is required. Make check or money orders payable to: Chief, Photoduplication Service, Library of Congress.

¹⁰ S. C. Saxena and K. M. Joshi, *Phys. Fluids* **5**, 1217 (1962).

¹¹ G. A. Bottomley and T. H. Spurling, *Australian J. Chem.* **19**, 1331 (1966).

TABLE II. Potential parameters for methyl chloride and benzene.

Substance	d (Å)	ϵ/k (°K)	r_0 (Å)	μ (D)	$\Theta \times 10^{26}$ (esu)	σ^2	Ref.
Methyl chloride	2.8	580	4.700	0	0	2.0×10^{-2}	b
	2.8	560.9	4.491	1.86	0	6.2×10^{-3}	b
	0 ^a	305.3	3.070	1.86	0	2.4×10^{-2}	b
Benzene	2.78	546	6.500	0	0	1.5×10^{-2}	c
	2.78	519	6.050	0	± 15	3.2×10^{-5}	c

^a Corresponds to a Stockmayer potential.

^b R. Whytlaw-Gray, C. G. Reeves, and G. A. Bottomley, *Nature* **181**, 1004 (1958); T. Batuecas, *Compt. Rend.* **181**, 40 (1925); C. C. Hsu and J. J. McKetta, *J. Chem. Eng. Data* **9**, 45 (1964); S. D. Hamann and J. F. Pearse, *Trans. Faraday Soc.* **48**, 101 (1952); T. H. Spurling, Ph.D. thesis, University of Western Australia, 1965; T. S. Storvick and K. W. Suh, "Gas Compressibility Factors at High Temperature and High Pressure by the Burnett Method: Methyl Chloride," *Am. Inst. Chem. Eng. J.* (to be published).

^c J. F. Connolly and G. A. Kandalic, *Phys. Fluids* **3**, 463 (1960); G. A. Bottomley, C. G. Reeves, and R. Whytlaw-Gray, *Proc. Roy. Soc. (London)* **A246**, 504 (1958); E. J. Gornowski, E. H. Amick, and N. Hixson, *Ind. Eng. Chem.* **32**, 957 (1947); G. A. Bottomley and T. H. Spurling, *Australian J. Chem.* **19**, 1331 (1966).

$\pm 15.7 \times 10^{-26}$ esu in conjunction with an (18-6) potential was found to give a better fit than either a (12-6) with a much larger quadrupole moment or a (28-7) with zero quadrupole. Since an (18-6) potential is quite similar to a spherical-shell potential having $r_0^* = 2.2$, we expect that the value of Θ so obtained reflects the most efficient use of this procedure. Quadrupole moments deduced from such studies of virial coefficients and viscosities are known to be in sensible agreement with values obtained by other methods, when available.¹²

The results obtained in this study reinforce the earlier conclusions that for globular molecules of modest complexity and size the spherical-shell potential is a very useful representation for the central part of the intermolecular potential field. In the present work we have

extended its usefulness to include dipolar and quadrupolar molecules, and have shown by example in methyl chloride and benzene that significantly better fits with second virial coefficient data can be obtained using structural parameters deduced independently of the fitting procedure. Our results suggest an increased need for additional experimental determinations of second virial coefficients for globular molecules having multipolar interactions.

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¹² T. H. Spurling and E. A. Mason, *J. Chem. Phys.* **46**, 322 (1967).