International Journal of Thermophysics, Vol. 1, No. 2, 1980

Optimized Parameters and Exponents of Mie (n,m) Intermolecular Potential Energy Function Based on the Shape of Molecules

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Received December 3, 1979

Through the use of the second virial coefficient data, optimized parameters and exponents of the Mie (n,m) potential energy function are derived for a number of symmetric groups of molecules. In the optimizations performed, parameters of the potential function are varied for each molecule, but the exponents of the potential function are taken as functions of the shape of the groups of molecules considered. It is concluded that the attractive exponent, $m = 7$, is shared by all the symmetric groups considered. The repulsive exponent, n, is varied according to the shape of the molecules. Also, in this report, newly calculated parameters of the Lennard-Jones (12,6) and Mie (14,7) potential energy functions for 33 different symmetric and nonsymmetric molecules are reported. Results indicate that, generally, the Mie (14,7) pair-potential energy function is a better fit for the second virial coefficient data than the Lennard-Jones (12,6) function.

KEY WORDS: intermolecular potential energy function; second virial coefficient; Mie potential function; Lennard-Jones potential function.

1. INTRODUCTION

There exists a great deal of interest in the scientific community for development of intermolecular potential energy functions to be used in statistical mechanical prediction of properties of matter. Potential energy functions of simple spherical molecules are very well known [1]. For nonspherical molecules, attempts are under way to develop realistic potential energy functions

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0195-928X/80/0600-0177$03.00/0

that are generally dependent on both distances and orientations of the segments of interacting molecules [1–4]. But, the more sophisticated a potential energy function is, the less likely it will be a candidate for use in practical problems of statistical mechanical predictions.

In the present report, an optimization technique is presented through which we are able to modify the exponents of simple potential energy functions in order to make them applicable for nonspherical molecules. Specifically, the Mie (n,m) potential energy function is used in this study. In order to draw a conclusion about the variation of exponents of the potential function with the shape of molecules, this study is made about the symmetric molecules only. Also, due to the abundance of the second virial coefficient data for a variety of molecules, the present optimization study is based merely on the least-square fitting of the second virial coefficient data. However, the technique presented here can be also applied to other potential energy functions and with the use of other thermophysical properties, when they become available.

2. WORKING EQUATIONS

The Lennard-Jones potential function has been most widely used for thermodynamic and transport property prediction of simple substances in both pure and mixture states and in all phases of matter. However, the Lennard-Jones potential function [5],

$$\phi(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{1}$$

is a special case of the Mie (n,m) potential model [6],

$$\phi(r) = \left(\frac{n}{n-m}\right)\left(\frac{n}{m}\right)^{m/(n-m)} \epsilon\left[\left(\frac{\sigma}{r}\right)^{n} - \left(\frac{\sigma}{r}\right)^{m}\right] \tag{2}$$

when n and m are replaced by 12 and 6. In Eqs. (1) and (2), ϵ is the intermolecular energy parameter for which $\phi_{\min} = -\epsilon$, σ is the intermolecular length parameter, for which $\phi(\sigma) = 0$ is the intermolecular distance. In the Lennard-Jones potential function, the choice of exponent "6" is consistent with the lowest exponent of the London dispersion forces between spherical-nonpolar molecules, while exponent "12" is rather arbitrary and is chosen for simplicity. In other words, instead of exponent "12" in Eq. (1), one may choose an exponent that is larger than "6" in order to have a model potential to be fitted to pair-intermolecular potential data or to be used in thermophysical property computations [1, 7, 8].

Since exponent "6" in Eq. (1) is only a good approximation to London dispersion forces for spherical nonpolar molecules, and since exponent "12" is an arbitrary number, it seems more appropriate to choose Eq. (2) for pair-potential models of nonspherical molecules. Then one may find exponents n and m, as well as coefficients ϵ and σ, for every interacting pair of nonspherical molecules, by fitting pair-potential data to Eq. (2) or by using Eq. (2) in fitting thermophysical property data. It should be, however, pointed out that while coefficients ϵ and σ in Eq. (2) are expected to be different for different molecules, exponents n and m should be dependent only on the shape of molecules considered. As a result in using Eq. (2) for fitting purposes, one shold develop an algorithm through which unique values of n and m are obtained for different molecules with similar shapes. In the present report, the second virial coefficient data are used to find the most approriate exponents of Eq. (2) for different groups of symmetric molecules with similar shapes and the most appropriate values of ϵ and σ for each individual molecule.

Similar to the case of the Lennard-Jones potential function [1, 7, 8], by replacing Eq. (2) in the second virial coefficient relation,

$$B(T) = -\frac{2\pi N_A}{3}\left(\frac{1}{kT}\right)\int_0^\infty r^3\,dr\, e^{-\phi(r)/kT}\frac{\partial\phi(r)}{\partial r} \tag{3}$$

we obtain the following power series for the second virial coefficient of the Mie (n,m) potential function [9]:

$$B(T) = \frac{3}{n}b_0\sum_{j=0}^{\infty}\frac{1}{j!}\left(\frac{a}{T^*}\right)^{[j(n-m)+3]/n}\cdot\Gamma\left(\frac{jm-3}{n}\right) \tag{4}$$

where

$$b_0 \equiv \frac{2}{3}\pi N_A\sigma^3 \tag{5}$$

$$a \equiv \left(\frac{n}{n-m}\right)\left(\frac{n}{m}\right)^{m/(n-m)} \tag{6}$$

$$T^* \equiv kT/\epsilon \tag{7}$$

N_A is the Avogadro's number and T is a gamma-function. For the case of the Lennard-Jones potential function, Eq. (4) reduces to the following relation:

$$B(T) = \frac{b_0}{4}\sum_{j=0}^{\infty}\frac{1}{j!}\left(\frac{1}{T^*}\right)^{(2j-1)/4}\cdot\Gamma\left(\frac{2j-1}{4}\right) \tag{8}$$

The power series convergences of Eqs. (4) and (8) are good for large values of T^*, while many terms are needed when $T^* < 1$ in order for the above power series to converge [10–17].

In least-square fitting of Eq. (4) to the second virial coefficient data of a substance, and with a priori knowledge of exponents n and m, it is necessary to minimize

$$\Delta = \sum_{i=1}^{n} [B_{\mathrm{exp}}(T_i) - B(T_i)]^2 \tag{9}$$

with respect to ϵ and σ, where $B_{\mathrm{exp}}(T_i)$ is the experimental second virial coefficient data at temperature T_i, and n is the number of data available for a substance. This minimization will result in the following relation for σ:

$$\sigma = \left\{ \frac{3}{2\pi N_A} \sum_{i=1}^{n} B_{\mathrm{exp}}(T_i) B^*(T_i) \Bigg/ \sum_{i=1}^{n} [B^*(T_i)]^2 \right\}^{1/3} \tag{10}$$

The right-hand side of Eq. (10) contains ϵ, which can be calculated by solving the following nonlinear equation:

$$\left\{ \sum_{i=1}^{n} B_{\mathrm{exp}}(T_i) B^{*\prime}(T_i) \right\} \left\{ \sum_{i=1}^{\mathrm{n}} [B^*(T_i)]^2 \right\} - \left\{ \sum_{i=1}^{n} B^*(T_i) B^{*\prime}(T_i) \right\} \left\{ \sum_{i=1}^{n} B_{\mathrm{exp}}(T_i) B^*(T_i) \right\} = 0 \tag{11}$$

In Eqs. (9) and (10),

$$B^*(T_i) = B(T_i)/b_0 \tag{12}$$

and

$$B^{*\prime}(T_i) = \epsilon \frac{\partial B^*(T_i)}{\partial \epsilon} = \frac{3}{n^2} \sum_{j=0}^{\infty} \frac{j(n-m)+3}{j!} \left(\frac{a}{T^*} \right)^{[j(n-m)+3]n} \cdot \mathrm{T} \left(\frac{jm-3}{n} \right), \tag{13}$$

3. CALCULATIONS AND RESULTS

Equations (10) and (11) can be used for calculation of ϵ and σ when exponents n and m are already available. In the case when exponents n and m are not known in advance, one should minimize Δ, given by Eq. (9), with respect to ϵ, σ, n, and m. In the case when we want to find the best values of n and m for a number of substances with similar shapes, we should minimize Δ of each substance with respect to ϵ and σ and minimize

$$\Delta_1 + \Delta_2 + \ldots + \Delta_s$$

of all the s substances with respect to n and m.

In order to observe the trend of any change in n and m with the shape of the molecules considered, only symmetrical molecules (molecules with central forces) are picked for the present study. In the minimizations performed, integer values for n and m were chosen, while values for ϵ and σ

Table I. Most Appropriate Exponents and Coefficients of the Mie (n,m) Potential Functions for Different Groups of Symmetric Molecules with Similar Shapes

		Formula	ϵ/k(K)	σ(Å)
Group I	$(n,m) = (12,7)$	Ar	150.7	3.298
	RMSD = 0.88	Kr	210.9	3.541
	RMSD (LJ) = 2.40	Xe	282.4	3.939
	No. of data = 185[a]			
Group II	$(n,m) = (14,7)$	N_2	134.9	3.544
	RMSD = 0.62	O_2	169.3	3.247
	RMSD (LJ) = 1.01			
	No. of data = 107[a]			
Group III[b]	$(n,m) = (14,7)$	NH_3	1100	1.942
	RMSD = 6.00	PH_3	204.1	5.782
	RMSD (LJ) = 10.30			
	No. of data = 44[a]			
Group IV[c]	$(n,m) = (28,7)$	CH_4	308.8	3.359
	RMSD = 25.50	CF_4	313.1	4.260
	RMSD (LJ) = 30.22	CCl_4	839.2	5.270
	No. of data = 116[a]	S_iF_4	313.9	4.940
Group V[d]	$(n,m) = (35,7)$	$C(CH_3)_4$	790.0	4.777
	RMSD = 18.90	$Si(CH_3)_4$	605.6	6.295
	RMSD (LJ) = —[e]			
	No. of Data = 50[a]			

[a] The second virial coefficient data are reported by J. H. Dymond and E. B. Smith, *Second Virial Coefficients of Gases* (Oxford University Press, Oxford, U.K., 1969); and E. A. Mason and T. H. Spurling. *The Virial Equation of State* (Pergamon, London, 1968).

[b] For (n,m) values in the range of (14,7)–(21,7), RMSD was insensitive to n. As a result, (14,7) was chosen for this group.

[c] For (n,m) values in the range of (24,7)–(30,7), RMSD was insensitive to n. As a result, (28,7), which is also recommended by Hamon and Lambert [16], was chosen.

[d] For (n,m) values in the range of (31,7)–(39,7), RMSD was insensitive to n. As a result, (35,7) was chosen.

[e] There exists no solution for this group with the use of the Lennard-Jones potential function.

were allowed to have significant figures consistent with the accuracy of the second virial coefficient data. The data points for which the deviation from predicted values based on the Lennard-Jones potential exceeded three times the root-mean-square deviation were eliminated. The remaining data points were used in the optimization calculations. The results of computations for five different groups of molecules with similar shapes are reported in Table I. For example, according to this table, the best exponents for the Mie potential function for spherical rare gas molecules (Ar, Kr, Xe) are "12" and "7". The root-mean-square deviation (RMSD) for this potential function, as defined by

$$\mathrm{RMSD} = \left\{\frac{\Delta_{\mathrm{Ar}} + \Delta_{\mathrm{Kr}} + \Delta_{\mathrm{Xe}}}{n_{\mathrm{Ar}} + n_{\mathrm{Kr}} + n_{\mathrm{Xe}}}\right\}^{1/2} \tag{14}$$

is lower than the RMSD of the Lennard-Jones functions and any other Mie (n,m) potential function chosen. It should be pointed out that $m = 7$ is still in the range of the exponents of the London dispersion forces for spherical molecules [1, 7, 8].

Similar observations can be made for the other four groups of molecules reported in Table I. One interesting result of the coumputation presented in Table I is that the attractive parameter $m = 7$ is in common between all the groups of molecules considered. Also, it seems that the more the molecules deviate from sphericity, the repulsive parameter n increases further. However, one should not place too much significance on this trend of the repulsive parameter n with the shape of the molecules. For a thorough understanding of intermolecular forces, a multiproperty correlation approach should be used [11, 18]. But for the correlation of the second virial coefficient data to the Mie (n,m) potential function and the use of the resulting potential function in thermodynamic property calculations, the choice of the attractive parameter $m = 7$ seems to be consistently superior over $m = 6$. To make the matter simple, we would like to propose a Mie (14,7) potential function,

$$\phi(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{14} - \left(\frac{\sigma}{r}\right)^{7}\right] \tag{15}$$

for nonpolar-simple molecules. In Table II, the pair-potential parameters of 33 different substances according to the Mie (14,7) and Lennard-Jones (12,6) potential functions are reported. The molecules chosen for Table II are those for which an adequate number of virial coefficient data are available in the literature. According to Table II, the least-square fits of the Mie (14,7) potential function for 28 out of the 33 molecules chosen are better than those of the Lennard-Jones potential function.

Table II. Intermolecular Potential Parameters for Lennard-Jones (12,6) and Mie (14,7) Potential Functions

	Lennard-Jones (12,6)			Mie (14,7)			
Formula	ϵ/k (K)	σ (Å)	RMSD[a]	ϵ/k (K)	σ (Å)	RMSD[a]	No. of Data[b]
Ar	119.0	3.438	0.66	170.0	3.219	0.68	82
Kr	158.9	3.883	3.92	237.2	3.421	2.82	62
Xe	220.3	4.135	1.34	320.7	3.830	1.02	41
CH_4	148.4	3.812	0.34	210.9	3.619	0.32	66
CF_4	151.4	4.750	0.92	214.7	4.520	0.53	23
SiF_4	147.5	5.650	0.65	211.6	5.320	0.61	8
CCl_4	397.7	6.570	74.53	453.0	6.940	68.48	19
N_2	95.48	3.736	0.69	134.9	3.544	0.36	79
O_2	115.7	3.535	1.59	169.3	3.247	1.04	28
NO	99.8	4.294	6.48	145.6	3.977	5.78	23
CO	100.5	3.926	1.30	142.3	3.628	0.65	23
CS_2	262.8	6.661	55.65	475.8	5.325	55.63	21
CO_2	196.0	4.359	2.77	282.3	4.081	2.12	80
SO_2	171.6	7.253	14.96	248.5	6.774	13.89	31
N_2O	155.7	5.450	9.89	229.7	5.009	9.05	38
H_2O	296.1	5.317	16.04	425.8	4.992	14.90	50
NH_3	900.0	2.108	13.50	1100	2.118	14.05	19
PH_3	136.5	6.352	6.84	279.1	5.262	6.79	25
CH_3F	173.7	5.680	4.10	253.1	5.279	3.75	30
CH_3Cl	940.9	2.378	17.86	891.3	2.740	16.39	32
CH_3Br	950	2.563	40.43	950.0	2.812	37.76	16
CH_3I	1050	2.665	18.29	1050	2.926	18.21	10
CH_2F_2	186.9	6.254	6.52	283.3	5.646	6.23	11
CH_2Cl_2	175.5	8.791	27.21	253.2	8.247	26.69	12
CF_2Cl_2	253.7	5.622	5.41	343.7	4.093	7.91	21
$CClF_3$	186.3	5.538	1.85	271.9	5.141	1.59	7
$CFCl_3$	240.0	7.098	5.62	394.8	6.021	15.64	9
$CHCl_3$	210.7	8.757	42.94	316.7	7.956	43.01	26
$CHCl_2F$	348.4	5.076	19.17	422.8	5.130	38.02	9
CH_3CH_3	182.2	5.388	14.53	279.7	4.800	12.19	83
CH_3CH_2Cl	158.1	9.701	68.09	227.8	9.108	67.47	16
CH_2CH_2	159.5	5.378	10.73	238.8	4.885	9.32	81
CHCH	109.4	8.288	6.50	156.9	7.817	6.02	27

[a] Root-mean-square deviation, RMSD, is defined as RMSD $\equiv \{\Delta/N\}^{1/2}$, and Δ is defined by Eq. (9).

[b] The data chosen for each compound are the ones that have an acceptable consistency as explained in the text. The source of the data is the same as in Table I.

ACKNOWLEDGMENTS

The authors would like to thank Prof. S. C. Saxena for his reading of the paper and his constructive comments. This research is supported by the U.S. National Science Foundation, Grant GK43139. Additional computing services were provided by the University of Illinois Computer Center.

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