Revista Brasileira de Física, Vol. 10, Nº 3, 1980

A Modified Form of L-J (12-6) Potential Energy Function for Polyatomic Molecules at Moderately High Temperatures

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Recebido em 12 de Fevereiro de 1980

Using a modified form of the L-J (12-6) potential energy function an expression for the second virial coefficient is derived under some physically realistic assumptions. To test the suitability of the resulting expression the force constants for Ar, N_2, CO_2, CH_4, C_2H_6, neo-C_5H_{12} and SF_6 gases are determined through the minimisation of an error discriminant. The agreement between the experimental second virial data and the theoretical predictions in case of polyatomic quasi-spherical molecules is found to be very satisfactory.

Usando uma forma modificada de função L-J (12-6) para a energia potencial, uma expressão para o segundo coeficiente visial é derivada sob algumas hipóteses fisicamente realistas. Para testar a adeauação da expressão resultante as constantes de força para os gases Ar, N_2, CO_2, CH_4, C_2H_6, Neo-C_5H_{12} e SF_6 são determinados através da minimisação de um discriminante de erro. A concordância entre os dados experimentais do coeficiente de segundo virial e as predições teóricas nos casos de moléculas poliatomicas quasi-esféricas é bastante satisfatória.

1. INTRODUCTION

It is usual to describe the interaction between a pair of spherically symmetrical molecules in terms of the potential energy of the system, $\phi(r)$. This is the so-called intermolecular pair potential energy function, which is related to the force between the molecules $F(r)$ by

$$\phi(r) = \int_r^{\infty} F(r)\,dr$$

where r is the separation between the centres of the molecules.

Generally three principal methods have been used for the determination of the potential energy function.

1. Direct rigorous quantum mechanical calculations for the real systems.
2. The measurement of the equilibrium and transport macroscopic properties that can be related directly to the intermolecular forces. A model is assumed and its disposable parameters are determined through the comparison between experimental data and theoretical predictions. More recently, two additional improved modificationsto this technique have been incorporated:
   a) Inversion of the theoretical formulas involving bulk properties has given very valuable information in the form of a numerical potential which in turn can be fitted to a convenient and realistic functional form. b) The combination of (1) and (2) i.e. accurately known direct calculations in the short and long range portions combined with a realistic functional form in the intermediate regions, such that the sensitive dependence of the related experimental property fixes the shape of the potential energy function.
3. The study of the interactions of molecules in pairs by experiments on the scattering of molecular beams - recently techniques have been developed for the inversion of the differential cross -section data to directly obtain the potential energy curve.

Seventies may be hailed as a milestone in the determination of realistic intermolecular pair potentials for the noble gases. With competitive and often collaborative efforts of the various research groups the intermolecular potential functions for the noble gases are now considered to be kwnow within 1 to 2 percent of the true potential. Because of a large number of articles written on this topic we limit ourselves here to the references of more recent publications of our group[1]. The work of other groups has been extensively referred in our articles. We follow the same practice to refer the literature on the noble gas mixture[2] as well. In the latter case a remarkable progress has been made in the determination of intermolecular pair potential energy functions in spite of the lack of the elaborate experimental data on these systems. The progress in the determination of $\phi(r)$ for noble gases and their mixtures came largely as a result of their being "simple" systems i.e. existence of almost central force fields between molecular pairs. The situation becomes very complicated when we study the polyatomic molecules because of the multibody interactions and the orientation dependent additional parameters. That is why applications of the quantum mechanical methods have not made much headway to perform the ab initio calculations for these systems. We need to continue to use the physically realistic models of the potential energy functions to explain the nature of the intermolecular interactions between polyatomic molecules until the more accurate computational techniques based on the first principies are developed and perfected to satisfactory levels. The Lennard-Jones (12-6) potential model shows probably the best compromise between accuracy and simplicity and is the most extensively studied. Kihara[3] through the calculation of second and third virial coefficients and viscosity on almost structureless, spherically symmetric, nonpolar and nonquantum gases has, however, criticised this function and has concluded that the real intermolecular potential for rare gases has a wider bowl and a harder repulsive wall than that of the L-J (12-6) potential. To improve upon this Kihara[3] assumed the presence of a convex hard core inside each molecule and replaced the separation between the centres of the molecules by the shortest distance between the cores.

Pitzer[4] extended the Kihara core idea to the nonpolar, globular and nonspherical molecules with the view that the application of the Kihara central potential function in case of complicated molecules where the interactions are more dependent on the peripheral atoms or the methyl groups and also to some extent on the orientations of the molecules, will be an oversimplification. It is observed that the overall effect of the nonspherical and globular nature of the molecules is to narrow and deepen the potential well. Balescu[5], Connolly[6] and others$^{7-11}$ have also shown that Kihara as well as other three parameter potentials exhibit the narrowing and the despening of the potential well with increasing molecular asymmetry. The L-J (12-6) potential as such does not involve any molecular parameter depending upon its structure which may account the nonsphericity or asymmetry of the polyatomic molecules and is thus supposed to be insufficiently flexible to reproduce the experimental macroscopic data on complicated molecules.

It is in this light. that in the present article we suggest and test a modified form of the Lennard-Jones, L-J (12-6) potential where we assume the existence of a spherical impenetrable hard core at the centre of each molecule. This modification rectifies the physical deficiency of the L-J (12-6) model by making the potential energy values infinitely large at finite values of intermolecular separation and not at zero separation as in the case of L-J (12-6). The latter implicitly assumes the molecules to be dimensionless (or say, dimensions which are infinitely compressible) which particularly in case of polyatomic molecules is not the correct description of the real physical situation. This modified L-J (12-6) model may be written in the following form.

$$\phi(r) = 4\varepsilon \left[\frac{\sigma^{12}}{r^{12}} - \frac{\sigma^{6}}{r^{6}} \right] \quad \text{for } r \geq a\sigma \qquad (1)$$

and $\phi(r) = \infty$ for $r \lesssim a\sigma$.

Here $\phi(r)$ = potential energy at an intermolecular separation
ε = depth of the potential energy minimum
σ = value of $\underline{r}$ at which $\phi(r) = 0$
$a\sigma$ = diameter of the spherical impenetrable hard core assumed in each molecule.

that is, $a = \dfrac{\text{core diameter}}{\text{collision diameter}}$

Thus we have assumed a direct proportionality between core-diameter and collision-diameter. Consequently, the parameter "a" makes the modified L-J (12-6) potential function dependent upon the molecular dimension. A simplified expression for the second virial coefficient based on the above Eq.(1) is derived. To determine the success of this expression we have determined the potential parameters by the minimization of an error discriminant for Ar, N_2, CO_2, CH_4, C_2H_6, neo-C_5H_{12} and SF_6 gases. We also tabulate [†] the reduced second virial coefficient $(B^*(T^*) = B(T)/(\frac{2}{3}\pi N\sigma^3))$ as a function of T* and reduced core diameter "a".

2. THEORY

According to statistical mechanics the expression[12] for second virial coefficient, $B(T)$, for central potentials is given by

$$B(T) = 2\pi N \int_0^\infty \left[1-\exp\left(-\frac{\phi(r)}{kT}\right)\right] r^2 dr \qquad (2)$$

where N = Avogrado number
k = Boltzmann constant

Now using the physical picture embedded in the potential function given by Eq. (1) and splitting up the integral of Eq.(2) into two parts corresponding to the short range ($a\sigma$ to a) and the long range (σ to ∞), one may modify Eq. (2) as:

$$\begin{aligned} B(T) &= 2\pi N \left[\int_{a\sigma}^{\infty} \left\{1-\exp\left(-\frac{\phi(r)}{kT}\right)\right\} r^2 dr \right. \\ &\quad \left. + \int_{\sigma}^{\infty} \left\{1-\exp\left(-\frac{\phi(r)}{kT}\right)\right\} r^2 dr \right] \\ &\equiv 2\pi N \left[I_1 + I_2\right] \end{aligned} \qquad (3)$$

Where I_1 refers to the first integrand and I_2 to the second in the above equation. The integral I_2 can be solved analytically by expanding the exponential term to yield

$$I_2 = -\frac{\sigma^3}{3}\left[2.667\left(\frac{\varepsilon}{kT}\right) + 0.6095\left(\frac{\varepsilon}{kT}\right)^2 + 0.1478\left(\frac{\varepsilon}{kT}\right)^3 + 0.0384\left(\frac{\varepsilon}{kT}\right)^4 + \ldots\right]$$

[†] These tabulations can be had from the author directly on request.

Or in terms of the reduced temperatures $T^* = \left(\frac{T}{\varepsilon/k} \right)$

$$I_2 = -\frac{\sigma^3}{3}\left[\frac{2.667}{T^*} + \frac{0.6095}{T^{*2}} + \frac{0.1478}{T^{*3}} + \frac{0.0384}{T^{*4}} + \dots\right] \qquad (4)$$

Where T is the tempcrature in degrees Kelvins.

If we consider the temperature range for which T* is greater than unity the series can be terminated after the fourth term without introducing an appreciable error. This assurnption makes the final expression valid only above room ternperature.

The integral I_1 can be written as

$$I_1 = \left[\frac{\sigma^3}{3}(1-a^3) - \int_{a\sigma}^{\sigma} \exp\left(-\frac{\phi(r)}{kT}\right) r^2 dr\right] \qquad (5)$$

3. SOLUTION OF I_1

a) The solution of the second term of the right hand side of Eq. (5) is not very straight forward. It may be noted that its contribution as cornpared to the contribution of the other terms is considerably small. Moreover, in the short range region the repulsive energy term of Eq.(1) is predominant and the dispersion energy contribution in this region can be safely neglected. Hence we can write

$$\int_{a\sigma}^{\sigma} \exp\left(-\frac{\phi(r)}{kT}\right) r^2 dr = \int_{ao}^{\sigma} \exp\left\{-\frac{4\varepsilon}{kT}\left(\frac{\sigma}{r}\right)^{12}\right\} r^2 dr \equiv I3 \qquad (6)$$

b) By putting $r = \sigma - X$ where x is the distance measured from the position at which $\phi(r) = 0$ so that

$$I_3 = \int_0^{\sigma(1-a)} \exp\left\{-\frac{4\varepsilon}{kT}\left(\frac{\sigma}{\sigma-x}\right)^{12}\right\} (\sigma-x)^2\, dx \qquad (7)$$

It is obvious that unless we go to very high temperatures the values of x are bound to be very srnall as compared to r or σ. Under this approximation the integral I_3 reduces to the following form

$$I_3 = \sigma^2 \exp\left(-\frac{4\varepsilon}{kT}\right)\int_0^{\sigma(1-a)} \left(1-\frac{2x}{\sigma}\right)\exp\left(-\frac{48\varepsilon}{kT}\cdot\frac{x}{\sigma}\right) dx \qquad (8)$$

In writing equation (8) we have neglected all term containing $\frac{x^2}{\sigma^2}$ and its higher powers. The integration of Eq. (8) by parts yields

$$I_3 = \frac{\sigma^3 kT}{48\varepsilon}\exp\left(-\frac{4\varepsilon}{kT}\right)\left[\left\{1-2a+\frac{2kT}{48\varepsilon}\right\}\exp\left\{-\frac{48\varepsilon}{kT}(1-a)\right\}+\left\{1-\frac{2kT}{48\varepsilon}\right\}\right] \qquad (9)$$

$$\simeq \left(\frac{\sigma^3 kT}{48\varepsilon}\right)\left[1-\frac{2kT}{48\varepsilon}\right]\exp\left(-4/T^*\right) \qquad (10)$$

The contribution of the term involving $\exp\left\{-\frac{48\varepsilon}{kT}(1-a)\right\}$ is negligible even for sufficiently large values of T or T^* so that it can also be omitted.

Combining Eqs. (3), (4), (5) and (10) we get an expression for the second virial coefficient

$$B(T) = \frac{2\pi}{3}N\sigma^3\left[1-a^3-\frac{T^*}{16}\left(1-\frac{T^*}{24}\right)\exp\left(-4/T^*\right) - \frac{2.667}{T^{*1}} - \frac{0.6095}{T^{*2}} - \frac{0.1478}{T^{*3}} - \frac{0.0384}{T^{*4}}\right] \qquad (11)$$

The assumptions used in the derivation of the above equation limit its validity in the temperature range $T^* > 1$.

4. DETERMINATION OF POTENTIAL PARAMETERS AND DISCUSSION

1) We determine the potential parameters ε/k, σ and "a" through the experimental data on $B(T)$ in conjunction with the theoretical relation (11) developed on the basis of the potential given by Eq. (1). Three pararneters are chosen so that the error discriminant

$$P = \sum_{i=1}^{n} \left[\frac{B_{(cal)_i} - B_{(exp)_i}}{B_{(exp)_i}} \right]^2 \qquad (12)$$

that is, the sum of the squares of the relative deviation (P) between predicted (B_{cal}) and meaured virial coefficient (B_{exp}), is minimum, or in other words when Eq. (12) gives the minimum value with respect to variation of all three parameters of Eq. (11). Here n is the number of the experimental points.

In achieving this we started with the L-J (12-6) potential parameters as the initial values of ε/k and σ and explored their optimimum values in both directions. For "a" the values reported by Kihara[3], Pitzer[4] and Bae and Reed[11] have proven as a great help in their choice as the starting values. The values of three parameterã thus determined are listea in Table 1.

Here the values of "a" are 'larger than the corresponding values for the Kihara potential. It may be pointed out here that a similar study using the Morse potential has been made by Bae and Reed[11]. They also observed that the core sizes for Ar and CO_2 given by Sherwood and Prausnitz[9] according to the Kihara potential are too small considering the structure of the molecules. Further, the large values of "a" which we have fixed throuçh the simultaneous variation of all the three parameters in Eq. (11), seem to be physically justified as the present model wili heve a definite potential energy at r = ao. Hence to have the same repulsion contribution to $B(T)$ as given by Kihara potential the value of "a" must be correspondingly larger.

To test the suitability of the presently proposed model we compare the predictions of expression (11) with the experimental $B(T)$ values and with those on other methods of calculations for Ar, N_2, CO_2, CH_4, C_2H_6, neo-C_5H_{12} and SF_6. The results are listed in the tables 2-8 for the various gases. A brief description of the calculations is a5 follows:

1) The predictions based on expression (11) using the potential parame-

ters, ε/k, σ and "a" determined in the present study through the minimization process, are reported in column three of the Tables 2-8.

2) The calculated $B(T)$ values based on expression (11), using the L-J (12-6) values for the parameters ε/k, σ as reported by H C B[13] and judiciously choosing a fixed of the third parameter "a" (=0.48), are reported in column four of the Tables 2-5.

3) The above two sets of calculated $B(T)$ values are compared with the predictions of the L-J (12-6) potential and the experimental data.

'rhe average absolute deviations ($\bar{x}$) of the three sets of calculated values frorn the experimental ones are 0.95, 1.47 ànd 0.95 for Ar; 0.61, 1.24 and 0.42 for N_2; 4.03, 5.19 and 5.62 for CO_2; 0.29, 0.29 and 0.75 for CH_4, respectively. As we go to more complicated molecules of C_2H_6, neo-C_5H_{12} and SF_6 the expression (11) in conjunction with the potential parameters of Table 1 determined here gives promising results. The failure of the (12-6) potential function in caseof Neo-C_5H_{12} has already been established by Saxena and Joshi[13] and Hamann and Lambert[14]. The present calculations on CO_2 and SF_6 are in good agreement with those of Robinson and Ferron[16] who have determined the potential parameters through the minimization of an error discriminant similar to Eq. (12) from rhe direct determination of the intermolecular potential by numerically inverting the statistical mechanical expression (12) for second virial coefficient. The second virial data on all the polyatomic gases considered here are far better reproduced than the Pitzer's[16,17] equarion of state involving an acentric factor to take care of the asymmetry of the non-spherical molecules.

5. CONCLUSIONS

i) Expression (11) derived on the semi-theoretical basis stands a good test to predict the second virial data for complicated molecules particularly at moderately high temperatures where the experimental data for such type of molecules sre scanty.

2) Complicated numerical integration is easily bypassed in

the calculations of the $B(T)$ without introducing errors beyond the experimental uncertainly involved in the measurements of data.

3) Thus the assumption for the existence of an impenetrable hard core inside a polyatomic molecule indirectly accounts for the non-sphericity of the molecule.

4) Growing evidence in literature is reconfirmed that the L-J (12-6) potential is too simple to account for the force field between complicated molecules.

5) Calculation taking into account the orientations of the hard cores with respect to the axis joining the centres of the cores in the adjoining molecules, may further improve the suitability of expression (11) for interpolation and extrapolation purposes.

Gas	ε/k °K	σ A°	a
Ar	122.9	3.42	0.436
N_2	97.0	3.70	0.454
CO_2	177.6	4.41	0.582
CH_4	148.4	3.82	0.477
C_2H_6	241.5	4.31	0.420
neo-C_5H_{12}	235.3	7.49	0.350
SF_6	187.5	5.97	0.445

Table 1 - Potential parameters for Ar, N_2, CO_2, CH_4, C_2H_6, neo-C_5H_{12} and SF_6 *determined by minimization* of the error discriminant given by Eq. (12)

Gas	Temperature °K	$B(T)$ cc/mole experimental	$B(T)$ cc/mole calc. by parameters of Table 1	$B(T)$ cc/mole calc. by (L-J) Parameters and fixed a	$B(T)$ cc/mole calc. by (L-J) Potential.	References Experimental Data
Ar	173.2	-68.82;-65.21	-68.07	-66.83	-66.44	18, 19, 20
	223.2	-36.79;-37.43	-39.14	-39.02	-38.77	
	273.2	-22.10;-21.45	-22.28	-22.71	-22.56	
	298.2	-16.06;-15.76	-16.30	-16.91	-17.05	
	323.2	-11.17;-11.24	-11.40	-12.1	-12.15	
	348.2	- 7.37;- 7.25	- 7.33	- 8.23	- 8.06	
	373.2	- 4.14;- 4.00	- 3.90	- 4.90	- 4.71	
	447.2	+ 3.72	+ 3.56	+ 2.38	+ 2.68	
	473.2	+ 4.99	+ 5.50	+ 4.31	+ 4.66	
	573.2	+10.77	+10.89	+ 9.52	+10.51	
	673.2	+15.74	+14.20	+12.64	+14.18	
	773.2	+17.76	+16.32	+14.77	+17.06	
	873.2	+19.48	+17.71	+17.11	+18.94	
$\bar{x}$			0.95	1.47	0.95	

Table 2 - Comparison of the experimental and calculated $B(T)$ values for Ar.

Gas	Temperature °K	$B(T)$ cc/mole experimental	$B(T)$ cc/mole calc. by parameters of Table 1	$B(T)$ cc/mole calc. by (L-J) Parameters and fixed a	$B(T)$ cc/mole calc. by (L-J) Potential	References Experimental Data
N_2	277.6	- 8.50	- 9.30	- 9.73	- 9.66	
	298.2	- 4.84	- 4.89	- 5.05	- 5.31	
	310.9	- 2.00	- 2.53	- 3.03	- 2.80	21
	323.2	- 0.52	- 0.46	- 0.90	- 0.77	
	348.2	+ 3.31	+ 3.20	+ 2.64	+ 2.98	
	373.2	+ 6.19	+ 6.25	+ 5.69	+ 6.20	
	398.2	+ 9.05	+ 8.81	+ 8.23	+ 8.89	
	427.6	+11.60	+11.33	+ 9.41	+11.72	
	444.3	+13.10	+12.56	+11.90	+13.14	
	460.9	+14.20	+13.67	+13.01	+14.30	
	477.6	+15.40	+14.67	+14.00	+15.59	
	510.9	+17.40	+16.40	+15.71	+17.39	
	573.2	+20.36	+18.86	+18.18	+21.24	
	673.2	+23.46	+21.44	+20.69	+24.21	
$\bar{x}$			0.61	1.24	0.42	

Table 3 - Comparison of the experimental and calculated $B(T)$ values for N_2.

Gas	Temperature °K	$B(T)$ cc/mole experimental	$B(T)$ cc/mole calc. by Parameters of Table 1	$B(T)$ cc/mole calc. by (L-J) Parameters and fixed a	$B(T)$ cc/mole calc. by (L-J) Potential	References Experimental Data
CO_2	273.2	-145.00	-134.37	-129.4	-128.76	21,22
	298.2	-124.60	-113.19	-109.36	-108.43	
	310.9	-112.70	-103.97	-100.62	- 99.93	
	323.2	-103.00	- 95.85	- 92.92	- 92.28	
	344.3	- 88.80	- 83.50	- 81.14	- 80.71	
	377.6	- 70.70	- 67.27	- 65.83	- 65.49	
	398.2	- 61.20	- 58.81	- 57.80	- 57.41	
	410.9	- 56.50	- 54.09	- 53.32	- 53.15	
	444.3	- 44.60	- 43.18	- 42.96	- 43.12	
	477.6	- 34.90	- 34.08	- 34.27	- 34.0	
	510.9	- 26.40	- 26.39	- 26.92	- 26.96	
	573.2	- 13.58	- 14.84	- 15.84	- 15.73	
	673.2	- 1.58	- 1.67	- 2.97	- 2.80	
	773.2	+ 6.05	+ 7.28	+ 5.78	+ 6.46	
	873.2	+ 12.11	+ 13.58	+ 12.08	+ 13.18	
$\bar{x}$			4.00	5.19	5.62	

Table 4 - Comparison of the experimental and calculated $B(T)$ values for CO_2

Gas	Temperature °K	$B(T)$ cc/mole experimental	$B(T)$ cc/mole calc. by Parameters of Table 1	$B(T)$ cc/mole calc. by (L-J) Parameters and fixed a	$B(T)$ cc/mole calc. by (L-J) Potential	References Experimental Data
CH_4	273.2	-54.1	-54.5	-53.5	-54.0	
	303.2	-41.6	-41.8	-41.6	-41.6	
	323.2	-34.3	-34.9	-34.8	-34.7	
	343.2	-29.1	-28.9	-28.8	-28.7	
	363.2	-24.2	-23.7	-23.6	-23.7	21, 23
	383.2	-19.5	-19.2	-19.1	-19.3	
	402.2	-15.4	-15.1	-15.1	-15.1	
	444.3	- 8.1	- 8.2	- 8.2	- 8.1	
	477.6	- 3.6	- 3.6	- 3.6	- 3.5	
$\bar{x}$			0.29	0.29	0.75	

Table 5 - Comparison of the experimental and calculated $B(T)$ values for CH_4.

Gas	Temperature °K	$B(T)$ cc/mole experimental	$B(T)$ cc/mole calc. by Parameters of Table 1	References Experimental Data
C_2H_6	331.5	-144.3	-142.6	
	351.3	-127.3	-126.9	
	371.2	-113.0	-113.2	
	391.0	-100.7	-101.1	
	410.9	- 89.9	- 90.4	
	430.8	- 80.3	- 80.9	24
	450.6	- 71.5	- 72.4	
	470.5	- 63.4	- 64.6	
	490.3	- 56.0	- 57.7	
	510.2	- 49.0	- 51.3	
$\bar{x}$			0.99	

Table 6 - Comparison of the experimental and calculated $B(T)$ values for C_2H_6.

Gas	Temperature °K	$B(T)$ cc/mole experimental	$B(T)$ cc/mole calc. by parameters of Table 1	References Experimental Data
neo-C_5H_{12}	303.2	-842	-829.7	
	323.2	-734	-731.0	
	343.2	-643	-646.1	
	363.2	-566	-572.3	21
	383.2	-507	-507.6	
	403.2	-452	-450.5	
$\bar{x}$			3.83	

Table 7 - Comparison of the experimental and calculated $B(T)$ values for neo-C_5H_{12}.

Gas	Temperature ^{o}K	$B(T)$ cc/mole experimental	$B(T)$ cc/mole calc. by parameters of Table 1	References Experimental Data
SF_6	313.2	-253	-254.5	
	333.2	-223	-220.7	
	353.2	-192	-191.5	
	373.2	-163	-165.8	23
	393.2	-145	-143.3	
$\bar{x}$			1.76	

Table 8 - Comparison of the experimental and calculated $B(T)$ values for SF_6.

The author wishes to express his thanks to Conselho Nacional de Pesquisas and Comissão Nacional de Energia Nuclear for the financial assistance. Thanks are also due to Prof. Mirabeau Dias, Head, Department of Physics, U. F.Pb, Campina Grande, Paraíba for general encouragement and stimulating discussions during the progress of this work.

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