



A hard-core Exp-6 intermolecular potential function for determining virial coefficients of pure nonpolar and slightly-polar molecules

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ABSTRACT

In this work, we have applied the hard-core term to the Exp-6 intermolecular potential function, in order to obtain a more realistic model for determining the values of second virial coefficients of nonpolar and slightly-polar gases. The second virial coefficients of 24 nonpolar and slightly-polar gases of quite differing natures, including hydrocarbons from the alkane, alkene, and aromatic families, as well as non-hydrocarbons such as carbon dioxide, were calculated using the proposed hard-core Exp-6 intermolecular potential function. The results showed that this integrated approach significantly improves the Exp-6 model, bringing it closer to reality. The average errors in calculated second virial coefficients, over the 564 data points considered, is just 1.5%. In addition, the third virial coefficients of non-polar or slightly-polar gases can be accurately predicted using this proposed potential function. For example, the AAD% of the predicted third virial coefficients of 327 data points corresponding to 11 gases by the proposed model is 50.5%, which is much smaller than the AAD% of the original Exp-6 (80.6%), Lennard-Jones (94.3%) and Kihara (73.5%) models.

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1. Introduction

The most important feature of the virial equation of state is that it has a theoretical basis, therefore, its coefficients have physical significance. For example, the second virial coefficient, B , considers the interaction between a pair of molecules, whereas the third virial coefficient, C , takes into account the three-body interactions of three molecules. Similarly, the higher virial coefficients reflect the complex intermolecular interactions of molecular sets containing higher numbers of molecules. Therefore, the coefficients of the virial equation can directly be related to the intermolecular forces [1]. Thus, using statistical mechanics, it is possible to derive the relations between the virial coefficients and the intermolecular potential functions, $I(r)$ [2]. For example, the second virial coefficient of a gas composed of simple molecules is given as a function of $I(r)$ and temperature, T , by

$$B = 2\pi N_A \int_0^{\infty} \left[1 - e^{-\Gamma(r)/kT} \right] r^2 dr \quad (1)$$

where r is the distance between the molecular centers, k is the

Boltzmann's constant, and N_A is Avogadro's constant [3]. Eq. (1) gives the relation between the second virial coefficient, B , and the intermolecular potential function, $I(r)$, for spherically symmetrical molecules.

Based on the types of intermolecular forces existing between nonpolar molecules (attraction and repulsion forces), a number of intermolecular potential functions have been proposed in the literature. Some have greatly oversimplified the behavior of real molecules, for example, the ideal-gas or hard-sphere potential models [4]. Some others consider molecules with point centers surrounded by soft electron clouds, such as the Lennard-Jones [5] or the Exp-6 potentials [6]. According to this class of models, two molecules can interpenetrate completely within one another, given that they have the necessary energy. In addition, with the Lennard-Jones potential, although the power of six of the inverse of the separation distance in the attraction term has a theoretical basis, the power of twelve of the separation distance in the repulsion term does not. This shortcoming of the repulsion term of the Lennard-Jones potential has been modified through the Exp-6 model by considering an exponential function for the repulsion term. On the other hand, Kihara [7] proposed a potential function, identical in form to the Lennard-Jones potential, with the modification that each molecule has a hard core surrounded by soft electron clouds. Therefore, the intermolecular distance was not taken as the distance between the molecular centers, but rather, as

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the distance between the surfaces of the molecules' cores. In this way, Kihara dealt with the problem of point centers of the Lennard-Jones potential. Although, there are different empirical equations for calculating the virial coefficients [8], calculation of these coefficients using potential functions has an advantage over empirical equations: the calculations of all virial coefficients and other thermodynamic properties can be carried out using the same model. Also, the empirical equations usually have a number of fitting parameters which need to be determined using experimental data, while potential functions have much less fitting parameters [9].

2. The proposed hard-core Exp-6 intermolecular potential function

In this work, we have considered a hard core with a diameter “ a ”, together with a soft shell, and applied it to the Exp-6 model [6] for spherically symmetrical molecules. The proposed modification is:

$$\Gamma = \begin{cases} \infty & r \leq a \\ \frac{\varepsilon}{\left(1 - \frac{6}{s}\right)} \left[\frac{6}{s} \cdot \exp \left[s \left(1 - \frac{r-a}{R-a} \right) \right] - \left(\frac{R-a}{r-a} \right)^6 \right] & r > a \end{cases} \quad (2)$$

where $-\varepsilon$ is the minimum value of potential energy, at the intermolecular separation of R . The parameter s shows the steepness of the repulsive wall. Fig. 1 illustrates the schematic diagram of this model. The collision diameter (σ , the intermolecular distance where $\Gamma = 0$) is slightly smaller than the intermolecular distance R , and slightly larger than the hard-core diameter, a . By bringing into the model a hard-core diameter, we aim to model the impenetrable core of a real molecule, which is neglected in the Exp-6 potential function. Similar to the original Exp-6 model, the proposed model has a false maximum at a short distance of “ $a + d$ ”, where “ d ” is a very short distance which has no physical meaning nor importance [1].

According to Eq. (1), the integration of the proposed potential function to determine the second virial coefficient will take the form:

$$B = 2\pi N_A \left(\frac{a^3}{3} + \int_a^\infty \left[1 - \exp \left(-\frac{\Gamma}{kT} \right) \right] r^2 dr \right) \quad (3)$$

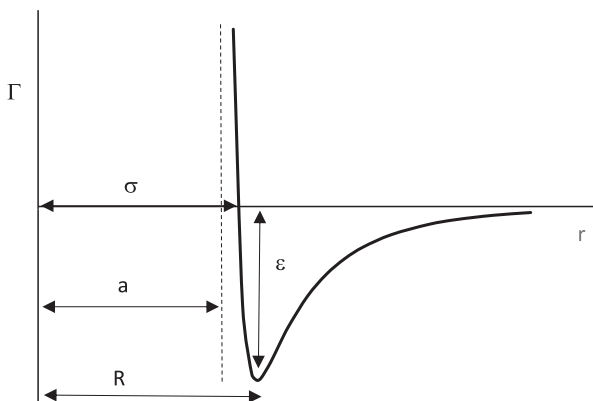


Fig. 1. Schematic diagram of the proposed potential function for a moderate value of s .

The first term of the right hand side of Eq. (3) is related to the hard core of a molecule, while the second term is related to the surrounding soft shell of the spherically symmetrical electron clouds. Based on the complex form of the proposed potential function, the integral in Eq. (3) does not have an analytical solution. Therefore, we have applied trapezoidal-rule numerical integration using MATLAB software to determine the second virial coefficient from Eq. (3). In order to find the parameters of the proposed model, the fmincon optimization tool of MATLAB software which uses constrained nonlinear multivariable function with interior-point algorithm, was applied to minimize the following objective function (OF):

$$OF = \frac{1}{N} \sum_{i=1}^N \frac{|B_{exp\ i} - B_{cal\ i}|}{|B_{exp\ i}|} \quad (4)$$

where B_{exp} , B_{cal} and N are the experimental second virial coefficient, the calculated second virial coefficient, and the number of data, respectively.

3. Results and discussion

In this work, a total of 564 second virial coefficient data points of 24 nonpolar and slightly-polar gases, including hydrocarbons from the alkane, alkene, and aromatic families, as well as non-hydrocarbons such as carbon dioxide, were used [8], in order to optimize the proposed model parameters. Tables 1–4 present the optimized values of ε , a , R , and s for the studied gases for the proposed hard-core Exp-6, original Exp-6, Kihara, and Lennard-Jones models, respectively.

Based on the trends of the optimized proposed model parameters in Table 1, for certain families of components, such as alkanes and alkenes, by increasing the molecular weight of the molecule, the hard-core diameter and R , will also increase. The relations between the molecular weight and the parameters of the proposed model are presented in Eqs. (5) and (6):

For alkanes:

Table 1
The optimized parameters of the proposed model for the investigated nonpolar and slightly-polar gases.

Component	$a/2$ (Å)	R (Å)	ε/k (K)	s
Methane	0.042	3.888	223.2	22
Ethane	0.198	4.553	384.7	24
Propane	0.404	5.158	497.4	24
Butane	0.661	5.517	642.6	24
Pentane	0.821	5.630	801.1	24
Hexane	0.952	5.722	1041.4	40
Heptane	1.034	6.101	1116.2	40
Octane	1.333	6.356	1283.6	40
Benzene	0.706	5.291	910.5	22
Toluene	0.756	6.216	1004.9	50
Tetrafluoromethane	0.081	4.171	428.8	310
Oxygen	0.051	3.740	151.6	17
Carbon dioxide	0.572	3.911	469.3	20
Boron trifluoride	0.049	4.159	478.4	350
Hydrogen	0.020	2.742	73.7	100.2
Fluorine	0.042	3.486	162.9	21.7
Chlorine	0.371	3.551	782.9	24.5
Ethene	0.068	4.335	357.2	29
Propene	0.423	4.555	595.0	29
1-Butene	0.499	4.597	793.2	29
1-Pentene	0.502	4.996	866.7	29
1-Hexene	0.526	5.509	983.3	50
1-Heptene	0.651	5.766	1105.0	50
1-Octene	0.716	6.175	1167.4	50

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