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Analytical Evaluation of Second Virial Coefficient Using Sutherland Potential and Its Application to Real Gases

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Abstract

Keywords
Second virial coefficient; Sutherland potential; Thermodynamics

A simple and efficient analytical formula for the calculation of second virial coefficient over Sutherland potential is derived. The compute conclusions of the second virial coefficient determined for Sutherland potential are compared with calculations of second virial coefficient using Lennard-Jones (12-6) potential and Exp-6 potential. The accuracy of the analytical formula is tested by application to molecules Kr, Xe, Ne and Ar. The results of the calculations for wide temperature range show excellent agreement with the data existing in the literature.

Sutherland Potansiyeli Kullanılarak İkinci Virial Katsayısının Analitik Belirlenmesi ve Gerçek Gazlara Uygulamaları

Özet

Anahtar Kelimeler
İkinci virial katsayısı; Sutherland potansiyeli; Termodinamik

Sutherland potansiyeli kullanılarak ikinci virial katsayısının hesaplanması için basit ve etkili analitik formül türetildi. İkinci virial katsayısı için Sutherland potansiyeli kullanılarak elde edilen hesaplama sonuçları Lennard-Jones (12-6) ve Exp-6 potansiyelinden elde edilen hesaplama sonuçları ile karşılaştırıldı. Analitik formülün doğruluğu Kr, Xe, Ne ve Ar moleküllerine uygulanarak test edildi. Geniş sıcaklık aralığında hesaplama sonuçlarının literatürdeki veriler ile mükemmel bir uyum göstermektedir.

1. Introduction

The virial coefficients are important in many aspects including the determination of intermolecular interaction with the variation of temperature and the definitions of thermodynamic properties of real gases (heat capacity, Joule-Thomson coefficient, internal energy, sound velocity,…) (Fender and Halsey, 1962; Patria, 1996; McQuarrine and Simon, 1997; Abdulagatov, 2002; Widom, 2002; Ramos-Estrada *et.al., 2004;* Kaplan, 2006; Garberoglio *et.al.,* 2011; Meng and Duan, 2012). It is common knowledge that the second virial coefficient is widely used in the determination of thermodynamic quantities (Mayer and Mayer, 1948; McQuarrine, 1973; Gibson, 1981). The second virial coefficient is of great interest in many industrial applications (Oh, 2010; Garberoglio *et. al.*, 2012). The second virial coefficient has been determined using intermolecular potentials such as Lennard-Jones (12-6), Exp-6 and Kihara potentials (Hirschfelder *et. al.,* 1954; Vargas *et. al.,* 2001; Mamedov and Somuncu, 2015). Many experimental and theoretical studies have been developed to precisely determine the second virial coefficient of real gases (Vargas *et. al.,* 2001; Glasser , 2002; Vega *et. al.,* 2004; Deszczynski *et. al.,* 2006; Hutem and

Boonchui, 2012). In spite of many improvements, the accurate evaluation of the second virial coefficient is still one of the main problems in physics and biophysical chemistry (McCarty and Babu, 1970; Garberoglio *et. al.*, 2012; Mohammadi *et. al.*, 2012).

In this study, we proposed a simple and effective analytical formula for the second virial coefficient over Sutherland potential. The obtained results and the implementation of various real gases show a good rate of convergence and numerical stability. Compared to previous analytical methods, our obtained analytical formula is simple and is more appropriate for studying a wide range temperature.

2. Materials and Methods

2.1. Definitions

The virial equation of state of real gases may be written in the general a series form

$$\frac{PV}{nRT} = Z = 1 + B_2(\mathrm{T})\frac{n}{V} + B_3(\mathrm{T})\frac{n^2}{V^2} + \dots , \qquad (1)$$

which is expansion in powers of the number of molecules per unit volume n/V (Hirschfelder *et. al.,* 1954; McQuarrine and Simon, 1997). The Eq. (1) is called the “virial expansion”, and $B_2(\mathrm{T})$, $B_3(\mathrm{T})$,... are called the second and the third virial coefficient, respectively. These coefficients are depend on temperature and on the potential energy between molecules (Hirschfelder *et. al.,* 1954; McQuarrine, 1973). For an ideal gas $B_2(\mathrm{T}) = B_3(\mathrm{T}) = \dots = 0$ (Reif, 1965). The second virial coefficient in terms of intermolecular potential $u(\vec{r})$ describes in the as following,

$$f(r_{ij}) = Exp[-\frac{u(r_{ij})}{k_B T}] - 1 \qquad (2)$$

$$B_2(T) = -\frac{1}{2}\int f(r_{12})d\tau_1 \qquad (3)$$

where $f(r_{ij})$, k_B, T is Mayer function, the Boltzmann constant, and the temperature, respectively (Kihara, 1953).

2.2. Expression for the second virial coefficient over Sutherland potential

To determine the second virial coefficient, we use the Sutherland potential in the following form (Prausinitz *et. al.,* 1999; Kaplan, 2006):

$$u(r) = \begin{cases} \infty & r \le \sigma \\ -\varepsilon\left(\dfrac{\sigma}{r}\right)^6 & r > \sigma \end{cases}, \qquad (4)$$

where ε is the depth of the potential well, σ is the finite distance at which the inter-particle potential is zero, and r is the distance between the particles. The second virial coefficient $B_2(T)$, in terms of intermolecular potential between particles is defined as (Hutem and Boonchui, 2012)

$$B_2(T) = -2\pi N_A 10^{-24}\int_0^\infty \left(e^{-\frac{u(r_{12})}{k_B T}} - 1\right) r_{12}^2 dr_{12} , \qquad (5)$$

where, N_A is the Avogadro constant. If the Sutherland potentials substituted into Eq. (5), one gets

$$B_2(T) = -2\pi N_A \left(\int_0^\sigma \left(e^{-\left(\frac{\infty}{k_B T}\right)} - 1 \right) r^2 dr + \int_\sigma^\infty \left(e^{\frac{\varepsilon}{k_B T}\left(\frac{\sigma}{r}\right)^6} - 1 \right) r^2 dr \right) \qquad (6)$$

the following series expansion relations is used to integrate as $B_2(T)$ analytically (Gradshteyn and Ryzhik, 1965)

$$e^{\pm x} = \sum_{n=0}^{\infty} (-1)^{\pm n} \frac{x^n}{n!} . \qquad (7)$$

which was applied before theoretical studies (Mamedov and Somuncu, 2014; Mamedov and Somuncu, 2015). Then, we obtain the following simply structured formula:

$$B_2\left(T\right)=\frac{2\pi N_A 10^{-24}\sigma^3}{3}\left(e^{\frac{\varepsilon}{k_BT}}-\lim_{N\to\infty}\sum_{n=0}^{N}\frac{1}{n!}\left(\frac{\varepsilon}{k_BT}\right)^n\left(n+\frac{1}{2}\right)^{-1}\right) \qquad (8)$$

In Eq. (8), the indice N is the upper limit of summations.

3. Numerical Results

The parameters $\varepsilon/k_BT,\sigma,\gamma$ and r_m correspond to diffirent potential are used to describe Kr, Xe, Ne and Ar molecules given in Table 1.

Table 1. Potential parameters for some non-polar molecules (Mason and William, 1954; Konowalow and Hirschfelder, 1961; Graben *et. al.,* 1964)

	Lennard-Jones (12-6)		Exp-6			Sutherland (∞ -6)	
Gas	σ (A)	$\frac{\varepsilon}{k_BT}$ (K)	γ	r_m (A)	$\frac{\varepsilon}{k_BT}$ (K)	σ (A)	$\frac{\varepsilon}{k_BT}$ (K)
Kr	4.04	159	12.3	4.056	158.3	3.20	491
Xe	4.46	228	13	4.450	231.2	3.62	632
Ne	3.16	36.3	14.5	3.147	38	2.4	103
Ar	3.87	119.3	14	3.866	123.2	2.95	351

The examples of calculations obtained for various values of the parameters are shown in Tables (2-5).

Table 2. Comparative of calculated values of the second virial coefficients of Kr for different potentials

T(K)	Eq. (8)	Lennard-Jones (12-6) Refs. (Glasser, 2002; Mamedov and Somuncu, 2014)	Exp-6 Ref. (Hirschfelder *et. al.,* 1954)
100	-901.592	-473.506	-352.246
200	-135.982	-140.069	-108.061
300	-53.1431	-60.4112	-50.1452
400	-23.0154	-25.368	-24.7948
500	-7.47216	-5.93586	-10.804
600	2.01426	6.26856	-2.05959
700	8.4086	14.5563	3.84815
800	13.0117	20.494	8.05762
900	16.4843	24.9171	11.1749
1000	19.1975	28.3105	13.5513
1500	27.0116	37.4339	19.8168
2000	30.7466	41.0746	22.1888
2500	32.9358	42.747	23.186

Table 2. Comparative of calculated values of the second virial coefficients of Kr for different potentials **(**Continued)

Table 3. Comparative of calculated values of the second virial coefficients of Xe for different potentials

T(K)	Eq. (8)	Lennard-Jones (12-6) Refs. (Glasser, 2002; Mamedov and Somuncu, 2014)	Exp-6 Ref. (Hirschfelder *et. al.,* 1954)
100	-3776.51	-1268.75	-920.917
200	-356.514	-356.413	-257.972
300	-139.307	-173.286	-127.302
400	-70.373	-96.35	-72.7956
500	-36.8798	-54.416	-43.2256
600	-17.108	-28.2309	-24.8314
700	-4.05873	-10.4471	-12.3825
800	5.20011	2.34119	-3.46094
900	12.1117	11.9258	3.20277
1000	17.4688	19.338	8.33808
1500	32.6915	39.8439	22.4029
2000	39.8628	48.6861	28.3269
2500	44.0356	53.2437	31.286

Table 4. Comparative of calculated values of the second virial coefficients of Ne for different potentials

$T(K)$	**Eq. (8)**	**Lennard-Jones (12-6) Refs. (Glasser, 2002; Mamedov and Somuncu, 2014)**	**Exp-6 Ref. (Hirschfelder *et. al.*, 1954)**
100	-252.395	-251.85	-177.505
200	-49.3811	-69.6099	-48.8305
300	-15.0598	-22.3355	-15.9376
400	-1.05016	-1.15357	-1.31103
500	6.56388	10.627	6.77125
600	11.3499	17.9993	11.7964
700	14.6375	22.9693	15.1607
800	17.0355	26.4952	17.5294
900	18.8621	29.0907	19.2584
1000	20.2999	31.0549	20.5546
1500	24.4931	36.101	23.7808
2000	26.525	37.8649	24.7939
2500	27.7243	38.4938	25.0589

Table 5. Comparative of calculated values of the second virial coefficients of *Ar* for different potential

$T(K)$	**Eq. (8)**	**Lennard-Jones (12-6) Refs. (Glasser, 2002; Mamedov and Somuncu, 2014)**	**Exp-6 Ref. (Hirschfelder *et. al.*, 1954)**
100	-4.3687	-8.02982	-5.24466
200	7.57936	11.4683	8.00672
300	11.0543	16.773	11.5301
400	12.7112	18.9669	12.9424
500	13.6812	20.0318	13.5957

Table 5. Comparative of calculated values of the second virial coefficients of *Ar* for different potential (Continued)

600	14.3182	20.5818	13.9068
700	14.7685	20.8639	14.0422
800	15.1037	20.9944	14.0798
900	15.363	21.034	14.0602
1000	15.5695	21.017	14.0057
1500	16.1842	20.5865	13.5391
2000	16.4888	20.0241	13.0263
2500	16.6708	19.4893	12.5585

The results of calculated from the Eq. (8) and literature for the second virial coefficient with Lennard-Jones (12-6) and Exp-6 potentials are plotted in Figures (1–4).

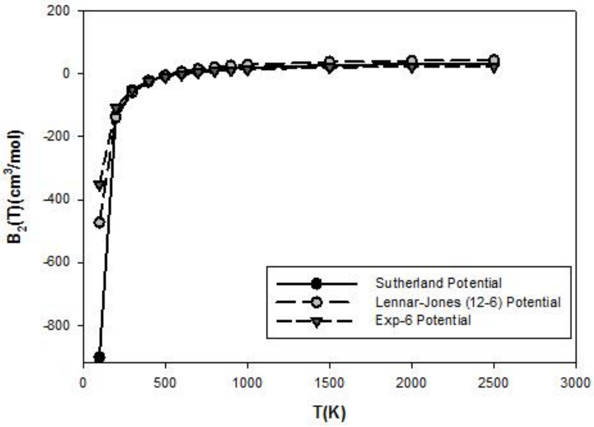

Figure 1. The second virial coefficient of *Kr* plotted against temperature

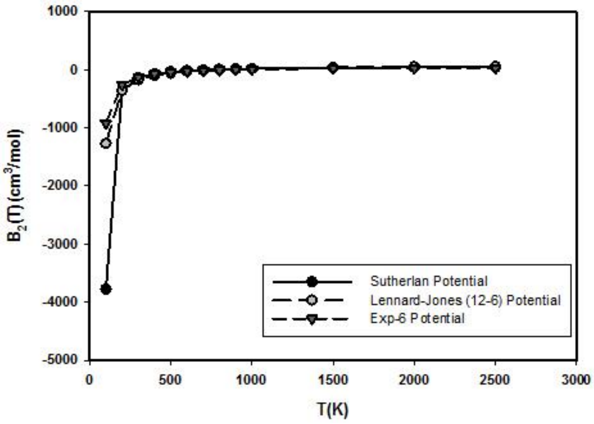

Figure 2. The second virial coefficient of *Xe* plotted against temperature

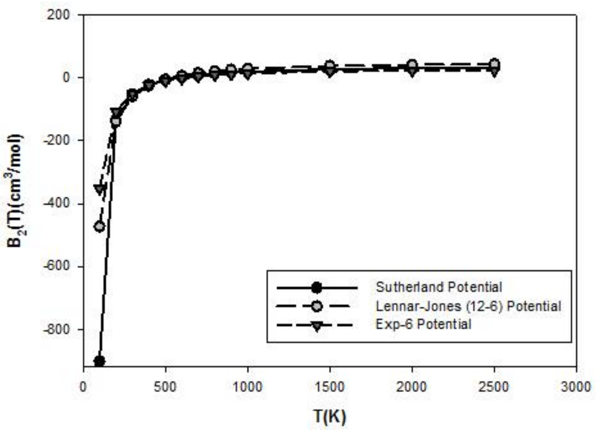

Figure 3. The second virial coefficient of Ne plotted against temperature

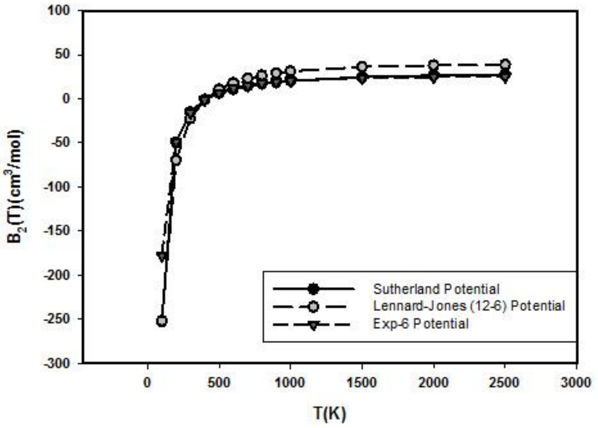

Figure 4. The second virial coefficient of Ar plotted against temperature

4. Discussion and Conclusion

In this paper, a simple approximate analytical expression for second virial coefficient derived using Sutherland potential. The obtained formula is completely general and can be used to calculate some of the thermodynamic properties of real gases for the arbitrary values temperature. Note that this expression gives very accurate results for a wide range of temperature. This should prove their usefulness not only for checking the accuracy of numerical values of the second virial coefficient computed by other types of approximations but also as a practical computational tool in applications. The Mathematica 7.0 international mathematical software was used to calculate the analytical expression obtained in this paper.

The results obtained for $B_2(T)$ are showed an excellent agreement with the literature data (Hirschfelder *et. al.,* 1954; Hostettler and Bernstein, 1959; Graben *et. al.,* 1964; Levi and Llano, 1975; Mi, *et. al.,* 2008; Mamedov and Somuncu, 2014; Mamedov and Somuncu, 2015). Tables (2–5) show the calculated results of the second virial coefficients for molecules Kr, Xe, Ne and Ar.

The results obtained from the Eq. (8) and literature for second virial coefficient over Lennard-Jones (12-6) (Glasser, 2002; Mamedov and Somuncu, 2014) and Exp-6 potentials (Hirschfelder *et. al.,* 1954) are plotted in Figures (1–4). Notice that in Figures (1-4), although the intermolecular potentials have different, the gases do so with nearly the same slopes. It is understood from the compatibility of the graphics that the results are in good agreement with literature data (Hirschfelder *et. al.,* 1954; Hostettler and Bernstein, 1959; Graben *et. al.,* 1964; Levi and Llano, 1975; Vargas, *et. al.,* 2001; Glasser, 2002; Mi, *et. al.,* 2008; Hutem and Boonchui, 2012; Mamedov and Somuncu, 2014; Mamedov and Somuncu, 2015).

The Lennard-Jones (12-6), Exp-6 and Sutherland potentials include the theoretically sound r^{-6} long-range interaction. Sutherland potential can be useful for investigating simple and complex molecules and it is a special case of the Lennard-Jones potential with infinitely steep repulsion. As can be seen Tables (2-5) and Figures (1-4), second virial coefficient takes positive values at high temperature and negative values at low temperature. The positive values indicate that two molecules repulsive each other. The negative values indicate that two molecules attract each other in the low velocity collisions. The attraction is what reasons molecules to condense at sufficiently low temperatures. Over a wide temperature range, the analytical formula offers the advantage of direct and precise calculation of second virial coefficient.

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