

Evaluation of Quantum Corrections to Second Virial Coefficient with Lennard-Jones (12-6) Potential

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Abstract. The efficient method is developed for analytical evaluation of quantum corrections to second virial coefficient with Lennard-Jones (12-6) potential. The quantum corrections to second virial coefficient played a significant role in the investigation of real gases in the low temperatures range. In this paper, we obtained a series of formula in terms of gamma and exponential integral functions which is one of the useful approaches for analytical evaluation of quantum corrections to second virial coefficient. The calculation results excellently agreement with of the literature data.

1. Introduction

A comprehensive study of quantum corrections to the second virial coefficient is very important for understanding of the thermodynamic and other properties of fluids [1-2]. The accurate investigation of the temperature dependence of the intermolecular integration potentials is of central importance for studying behavior of fluids at low temperature [3-7]. Various analytical methods on the evaluation of quantum corrections to the second virial coefficient have been proposed in literatures [8-12]. Gropper et al. [13-15] have done detailed work on the of quantum corrections to the second virial coefficient, which has been successfully applied to the light molecules at low temperature. Also, some researchers proposed analytical and numerical approaches for quantum corrections to the second virial coefficient [16-19]. Although important progress has been made in calculation of quantum corrections to the second virial coefficient, a number of new analytical methods are very important in understanding of various properties of fluids.

In this work, a general method is proposed for evaluating of quantum corrections to the second virial coefficient with the some applications. Compared to previous analytical methods, our obtained expression is more appropriate for studying at low temperature. The proposed algorithm gives a good rate of convergence and numerical stability under a wide range of values of parameters.

2. Expressions for the quantum corrections to second virial coefficient of the Lennard-Jones (12- 6) potential

For evaluation of the quantum corrections to second virial coefficient, we use the Lennard-Jones (12-6) potential and the corresponding intermolecular force in the following forms [20]

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

$$F(r) = \frac{4\epsilon}{\sigma} \left[12 \left(\frac{\sigma}{r} \right)^{13} - 6 \left(\frac{\sigma}{r} \right)^7 \right], \quad (2)$$



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. Note that the locations where the intermolecular potential $u(r)$ is a minimum and intermolecular force $F(r)$ is exactly zero are given by $r_{\min}$ and σ , respectively and the two parameters are related by $r_{\min} = 2^{1/6}\sigma$ [21]. In this study the quantum corrections to second virial coefficient $B_q(T)$ defined as [22]

$$B_q(T) = \frac{h^2 N_A}{24\pi m (k_B T)^3} \int_0^\infty F^2(r) [f(r, T) + 1] r^2 dr, \quad (3)$$

where the symbols N_A , h , m and k_B denote the number of molecules Avogadro's number, Planck's constant, the molecular mass and Boltzmann constant, respectively. In Eq. (3) the function $f(r, T)$ is the Mayer function and defined as [23]

$$f(r, T) = \exp\left(\frac{u(r)}{k_B T}\right) - 1. \quad (4)$$

The intermolecular force $F(r)$ is correlated to intermolecular potential energy $u(r)$ and written as

$$F(r) = -\frac{du(r)}{dr}. \quad (5)$$

Eq. (3) is defined in non-dimensional and given by

$$B_q^*(T^*) = \Lambda^* B_q(T^*), \quad (6)$$

for convenience, where

$$B_q^*(T^*) = \Lambda^* B_q(T^*) / b_0, \quad b_0 = 2\pi r_{\min}^3 / 3, \quad (7)$$

and b_0 is known as the co-volume. The quantum correction to second virial coefficient

$$B_q(T^*) = \frac{3}{T^{*3}} \int_0^\infty F^2(r^*) [f(r^*, T^*) + 1] r^{*2} dr^*, \quad (8)$$

where $T^* = k_B T / \varepsilon$, $r^* = r / r_{\min}$. The quantum mechanical parameter Λ^* given by

$$\Lambda^* = \frac{\hbar^2 R}{12 M k_B \varepsilon r_{\min}^2}, \quad (9)$$

in which $M = mR / k_B$ molar mass, and $\hbar = h / 2\pi$.

Substituting Eqs. (1)- (2) into Eq.(8) we obtain

$$B_q(T^*) = \frac{36}{T^*} \sum_{m=0}^N (-1)^m F_m(2) \sum_{k=0}^{N'} \frac{(2/T^*)^k}{k!} \left[\left(\frac{1}{T^*} \right)^{\frac{23}{12} + \frac{m}{2} + \frac{k}{2}} \left(\Gamma \left[\frac{23}{12} - \frac{m}{2} + \frac{k}{2} \right] - \Gamma \left[\frac{23}{12} - \frac{m}{2} + \frac{k}{2}, \frac{1}{T^*} \right] \right) + E_{\left(-\frac{11}{12} + \frac{m}{2} - \frac{k}{2} \right)} \left(\frac{1}{T^*} \right) \right]. \quad (10)$$

In Eq. (10) the indices N and N' are the upper limits of summations respectively. The $\Gamma(\alpha)$, $\Gamma(\alpha, u)$ and the $E_n(z)$ in the Eq.(10) are well known gamma and incomplete gamma functions and exponential integral functions defined by [24]

$$\Gamma(\alpha) = \int_0^{\infty} t^{\alpha-1} e^{-t} dt, \quad (11)$$

$$E_n(z) = \int_1^{\infty} t^{-n} e^{-zt} dt, \quad (12)$$

$$\Gamma(\alpha, u) = \int_u^{\infty} t^{\alpha-1} e^{-t} dt. \quad (13)$$

3. Numerical Results and Discussion

Closed analytical formula for quantum corrections to the second virial coefficient with Lennard-Jones (12-6) potential is developed. The obtained expression is formulated in terms of infinite summations involving special functions. Our calculation results, generated using Turbo Pascal 7.0 compiler, are demonstrated in Table 1.

Table 1. Quantum correction to second virial coefficient [2, 25-26]

T^*	$B_q(T^*)$	T^*	$B_q(T^*)$
9.9343	3.9654	3.4324x10 ²	0.0651322
1.3124x10 ¹	2.79024	4.6581x10 ²	0.0464939
1.7429 x10 ¹	1.96814	6.3235x10 ²	0.0332084
2.3243x10 ¹	1.39147	8.5844x10 ²	0.0237382
3.1105x10 ¹	0.985627	1.1664x10 ³	0.0216798
4.1731x10 ¹	0.699579	15852.x10 ¹	0.0121265
5.6123x10 ¹	0.497188	2.1543x10 ¹	0.00867326
7.5617x10 ¹	0.353803	2.9270x10 ¹	0.0062076
1.0212x10 ²	0.251808	3.9784x10 ¹	0.00444256
1.3802x10 ²	0.179476	5.4104x10 ¹	0.00317847
1.8682x10 ²	0.127955	7.3544x10 ³	0.00227581
2.5313x10 ²	0.0912692	1.0000x10 ⁴	0.0016293

The temperature dependence of the quantum correction second virial coefficients are shown in Fig.1.

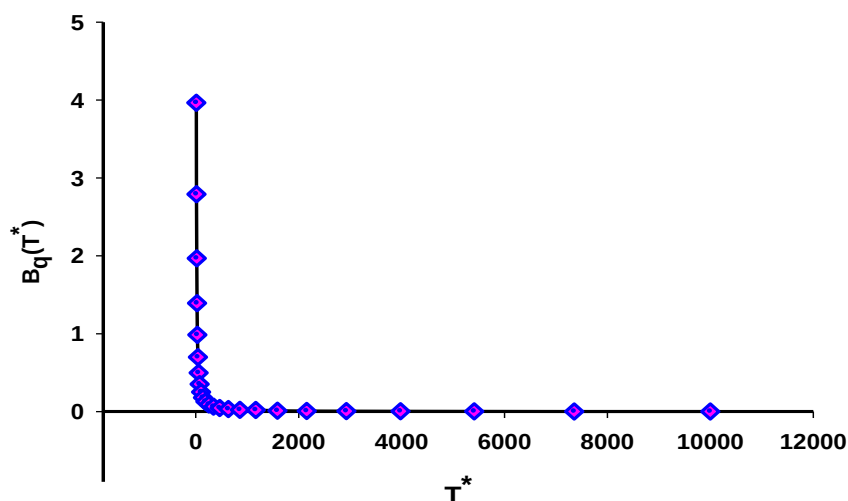


Figure 1. The quantum correction to second virial coefficient

As seen from Table 1 and Fig.1, the method of the present calculation is the useful approximation for analytical evaluation of quantum corrections to the second virial coefficient. The comparison between our results with the literature approximation calculations by Ref. [2, 25-26] is satisfactory. The approach is based on the efficient analytical formula and can be easily implemented to the atom and molecules.

3. References

- [1] Gray C G, Gubbins K E, Joslin C G 2011 *Theory of Molecular Fluids* (Oxford University Press)
- [2] Hirschfelder J O, Curtiss C F and Bird R B 1954 *Molecular Theory of Gases and Liquids* (Jonh Wiley & Sons)
- [3] Lucas K 1991 *Applied Statistical Thermodynamics* (Springer-Verlag)
- [4] Uhlenbeck G E and Gropper L 1932 *Phys. Rev.* **41** 79
- [5] Gropper L 1936 *Phys. Rev.* **50**, 963
- [6] Buckingham R A and Corner J 1947 *Proc. R. Soc. Lond. A* **189**, 118
- [7] Kihara T 1955 *Rev. Mod. Phys.* **27** 412
- [8] Corbin N, Meath W J and Allnatt A R 1984 *Mole. Phys.* **53** 225
- [9] Nilsen T S 1969 *Phys. Rev.* **186** 262
- [10] D'Arruda J J and Hill R N 1970 *Phys. Rev. A* **1** 1791
- [11] McCarty M and Babu S V K 1970 *J. Phys. Chem.* **74** 1113
- [12] Ghassib H B, Sandouqa A S, Joudeh B R and Mosameh S M 2014 *Can. J. Phys.* **92** 997
- [13] Gropper L 1937 *Theory, Phys. Rev.* **51** 1108
- [14] Beth E and Uhlenbeck G E 1937 *Physica* **4** 915
- [15] Uhlenbeck G E and Beth E 1936 *Physica* **3** 729
- [16] Bruch L W and Kariotis R 2006 *Phys. Rev. B* **73** 193404

- [17] Akin-Ojo O, Harvey A H and Szalewicz K 2006 *J. Chem. Phys.* **125** 014314
- [18] Marun R A B, Coronada E A and Ferrero J C 2005 *Chem. Phys. Lett.* **405**, 203
- [19] Wang W F 2003 *J. Quant. Spec. and Rad. Transfer* **76** 23
- [20] Kaplan I G 2006 *Intermolecular Interactions: Physical Picture, Computational Methods and Model Potentials* (Jonh Wiley & Sons)
- [21] Hutem A and Boonchui S 2012 *J. Math. Chem.* **50** 1262
- [22] Lucas K 1991 *Applied Statistical Thermodynamics* (Springer-Verlag)
- [23] McQuarrie D A 1973 *Statistical Mechanics* (Harper & Row)
- [24] Gradshteyn I S and Ryzhik I M 1965 *Tables of Integrals, Series and Products* (Acedemic, London)
- [25] Fowler R H 1936 *Statistical Mechanic: The Theory of the Properties of Matter in Equilibrium* (Cambridge University Press)
- [26] Kim S and Henderson D 1966 *Proc. Natl. Acad. Sci. U.S.A.* **55**