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Analytical Evaluation of Third Virial Coefficient with Lennard-Jones (12-6) Potential and Its Applications

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Abstract. An efficient analytical method to evaluate the third virial coefficient with Lennard-Jones (12-6) type potential is presented. Proposed approach is particularly suitable for analysis of various properties of three body systems. To conform the correctness of the calculation result, a comparison is given with the literature for NO_2, SF_6 and C_2H_2 molecules. Calculation results show that obtained formulae provide higher accuracy and efficiency than the proposed approaches in literature.

INTRODUCTION

It is well known that the virial coefficients are exploited in many aspects of physics such as the deviation of a real equation of state from that of the ideal gas [1–3], the calculation of the thermodynamical properties of gases and liquids [4,5], and the evaluation of intermolecular interaction with variation of temperature [6-9]. In studies the authors [9-13] have proposed useful numerical and theoretical models for evaluation third virial coefficient. The authors Hutem and Boonchui developed algorithm to numerical evaluate of the third virial coefficient for Argon gas by using bipolar coordinate integration [10]. As indicated in study, the proposed algorithm is not general including the obtained formula are not valid the very higher temperature for some molecules. The numerical method based on calculation of third virial coefficient with to center Lennard-Jones quadrupolar molecules are proposed by authors [11]. Another interesting calculation method has been developed for the third virial coefficient for non-polar gases by means of punched-card models [12]. Although the theoretical approaches, there has been no sufficiently analytical formulae attempts so far for third and higher order virial coefficient for arbitrary values of parameters [13].

In this paper, we established analytical formulae for the third virial coefficient with Lennard-Jones (12-6) potential which make possible the fast accuracy calculation. Note that the established analytical formulae in terms of basic integral and gamma functions. The accuracy of proposed algorithm is tested and their usefulness illustrated with practical applications, including the computation of the third virial coefficients of molecules NO_2, SF_6 and C_2H_2.

DEFINITION AND EXPANSIONS RELATIONS FOR THE THIRD VIRIAL COEFFICIENT WITH LENNARD-JONES (12-6) POTENTIAL

The virial equation describing the imperfect gases with the virial expansions is given by

$$\frac{PV}{NRT} = Z = 1 + B_2(\mathrm{T})\frac{N}{V} + B_3(\mathrm{T})\frac{N^2}{V^2} + \ldots, \tag{1}$$

where N is the number of moles, V is the volume, P is pressure, T is temperature and Z is compressibility factor [14-16]. In Eq. (1) the quantities $B_2(\mathrm{T})$ and $B_3(\mathrm{T})$ are second and third virial coefficients and defined as

$$B_2(T) = -\frac{N_A 10^{-24}}{2}\int f(r_{12})dr_{12}, \tag{2}$$

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$$B_3(T) = -\frac{N_A^2 10^{-48}}{3}\iiint f(r_{12}) f(r_{13}) f(r_{23})\, dr_{12} dr_{13} \tag{3}$$

$$f(r_{ij}) = exp\,[-\frac{u(r_{ij})}{k_B T}] - 1 \tag{4}$$

where $f(r_{ij})$ is Mayer function, $u(r_{ij})$ is the interaction potential of two molecules [17].

In this section we have established the analytical formula in the elliptic coordinate system. For evaluation third virial coefficient with Lennard-Jones (12-6) potential, the three body systems are illustrated in Fig. 1.

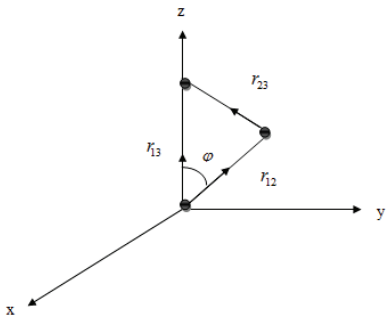

FIGURE 1. The interaction of three atoms

From the Fig. 1, the relations between of parameters r_{12}, r_{13} and r_{23} can be obtained from as

$$\begin{aligned} |r_{13} - r_{12}| = r_{23} &= \sqrt{r_{12}^2 + r_{13}^2 - 2r_{12} r_{13}\cos\varphi} \\ dr_{13} &= 4\pi r_{13}^2 dr_{13} \\ dr_{12} &= 2\pi r_{12}^2 dr_{12} \sin\varphi d\varphi \end{aligned} \tag{5}$$

Substituting Eqs. (5) into Eq. (3) we obtain

$$B_3(T) = 8\pi^2 \frac{N_A^2}{3} 10^{-48} \left[\int_0^\infty r_{12}^2 f(r_{12}) \int_0^\infty r_{13}^2 f(r_{13}) \int_{-\pi}^{\pi} f\left(\sqrt{r_{12}^2 + r_{13}^2 - 2r_{12} r_{13}\cos\varphi}\right) d(\cos\varphi)\, dr_{12} dr_{13} \right]. \tag{6}$$

Finally, using the relation $f(r_{ij})$ Mayer function for B_3(T) we have

$$B_3(T^*) = 6\sigma^{-6}\left[2\, I(T^*) - K(T^*)\right], \tag{7}$$

where $I(T^*)$ and $K(T^*)$ defined as respectively

$$I(T^*) = \int_0^\infty r_{12}^2 \left(1 - e^{\frac{4}{T^*}\left[\left(\frac{\sigma}{r_{12}}\right)^{12} - \left(\frac{\sigma}{r_{12}}\right)^{6}\right]}\right) \int_0^\infty r_{13}^2 \left(1 - e^{\frac{4}{T^*}\left[\left(\frac{\sigma}{r_{13}}\right)^{12} - \left(\frac{\sigma}{r_{13}}\right)^{6}\right]}\right) dr_{12} dr_{13}, \tag{8}$$

$$\begin{aligned} K(T^*) = &\int_0^\infty r_{12}^2 \left(1 - e^{\frac{4}{T^*}\left[\left(\frac{\sigma}{r_{12}}\right)^{12} - \left(\frac{\sigma}{r_{12}}\right)^{6}\right]}\right) \int_0^\infty r_{13}^2 \left(1 - e^{\frac{4}{T^*}\left[\left(\frac{\sigma}{r_{13}}\right)^{12} - \left(\frac{\sigma}{r_{13}}\right)^{6}\right]}\right) \\ &\times \int_{-\pi}^{\pi} e^{\frac{4}{T^*}\left[\left(\frac{\sigma}{\sqrt{r_{12}^2 + r_{13}^2 - 2r_{12} r_{13}\cos\varphi}}\right)^{12} - \left(\frac{\sigma}{\sqrt{r_{12}^2 + r_{13}^2 - 2r_{12} r_{13}\cos\varphi}}\right)^{6}\right]} d(\cos\varphi)\, dr_{12} dr_{13} \end{aligned} \tag{9}$$

In Eq. (6) $T^* = k_B T/\varepsilon$, $b_0 = 2\pi N_A 10^{-24}\sigma^3/3$. We obtain the analytical formula for $I\left(T^*\right)$ in terms of gamma function following from

$$I\left(T^*\right) = \left(\frac{8\sigma^3}{3\sqrt{2}T^*} \lim_{N^{'}\to\infty} \sum_{k=0}^{N^{'}} \frac{\left(2/T^*\right)^k}{k!} \left[\frac{1}{4}\left(1/T^*\right)^{-\frac{3}{4}-\frac{k}{2}} \Gamma\left(\frac{3}{4}+\frac{k}{2}\right) - \frac{1}{4}\left(1/T^*\right)^{\left(-\frac{1}{4}-\frac{k}{2}\right)} \Gamma\left(\frac{1}{4}+\frac{k}{2}\right) \right] \right)^2, \tag{10}$$

where $N^{'}$ is upper limits summations. The obtained formulas are practical simple and they offer some advantages over currently available methods.

NUMERICAL RESULTS AND DISCUSSION

In this paper, we have investigated the third virial coefficient with Lennard-Jones (12-6) potential, which describes various properties of three body system. On the basis of obtained formula, we constructed the program for calculations using the Turbo Pascal 7 program languace. The our calculation results are listed in Table 1 for NO_2, SF_6 and C_2H_2 molecules. Note that our results are in very good agreement with literature [12,18]. In Fig. 2, we plot the third virial coefficient as a function of temperature. The method described here can be applied to the calculation the other thermodynamic properties of imperfect gases. The parameters for NO_2, SF_6 and C_2H_2 molecules are as following $\varepsilon/k_B = 121\,K$, σ =3.481 A°, $\varepsilon/k_B = 202.7\,K$, σ =5.829 A° and $\varepsilon/k_B = 221.4\,K$, σ =4.078 A° [19-21].

TABLE 1. The calculation results of the third virial coefficient for Eq. (7)

T^*	NO_2	SF_6	C_2H_2
0.70	-3.376723494180066	-3.376719196470809	-3.37638952168815
0.80	-0.8490658179020762	-0.8490834794850564	-0.84871377535285072
0.90	0.07667470485253247	0.07669864345069399	0.07667999166841355
5	0.31505601262504754	0.31505840828860465	0.31506404400435367
10	0.2860678408913347	0.2860678664847104	0.2860678173426514
20	0.24641298321866129	0.24641296660512163	0.24641307199788426
30	0.21951114601016233	0.21951102661032235	0.21651104582503536
40	0.20010142749633125	0.20010072835796366	0.2001011352634651
50	0.18527859091036833	0.18527686582656233	0.18527683417097132
60	0.17347129154914243	0.17347124427722996	0.17347126587787554
100	0.1425346828615837	0.14253480722101022	0.14253464590313686
200	0.1068189709073302	0.10682070618925128	0.10681901026801381
300	0.08945450036806166	0.08945939507489307	0.08945481765473631
400	0.07863839895794383	0.07864735672007782	0.07863929999481449

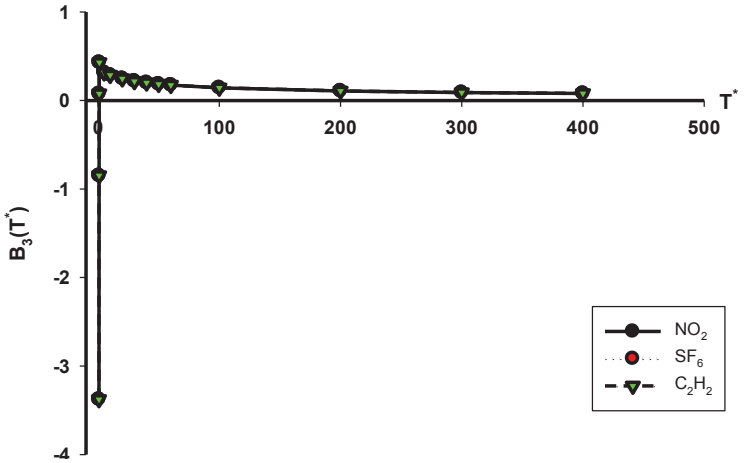

FIGURE 2. The temperature dependence of third virial coefficient NO_2, SF_6 and C_2H_2

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