

Numerical evaluation of second and third virial coefficients of some inert gases via classical cluster expansion

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Abstract In this project we evaluate second virial coefficient of some inert gases via classical cluster expansion, assuming each atomic pair interaction is of Lennard-Jones type. We also try to numerically evaluate the third virial coefficient of Argon gas based on bipolar-coordinate integration (Mas et al. in J Chem Phys 10:6694, 1999), assuming the same Lennard-Jones potential as before. The second virial coefficient (Vega et al. in Phys Chem Chem Phys 4:3000–3007, 2002) calculated from our model are compatible to the experimental data [19] The temperature at which $B_2(T) \rightarrow 0$ is called the Boyle's temperature T_B (Vega et al. in Phys Chem Chem Phys 4:3000–3007, 2002) for the Lennard-Jones (12-6) potential. For the second virial coefficient of He, we obtain the Boyle's temperature as follow: $T_B = 34.9312438964844$ (K) $B_2(T) = 9.82958 \times 10^{-6}$ (cm³/mol).

Keywords The second virial coefficient · The third virial coefficient · Cluster expansion · Inert gases

1 Introduction

In this work, we have considered the (classical) ideal gases of noninteracting particles for which the equation of state is given by $PV = Nk_B T$. This is valid when the gas is very rarefied and particles are far apart from one another, so that the effect of interaction is negligible. For real systems, deviations from the ideal gas law were observed experimentally and interpreted by taking the interaction between the particles of the system into consideration.

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Many attempts were made to obtain an empirical equation of state which would give good agreement with the experimental results.

One important relation is the virial equation of state, which is generally expressed as

$$\frac{P}{k_B T} = \frac{N}{V} \left(1 + B_2(T) \frac{N}{V} + B_3(T) \frac{N^2}{V^2} + B_4(T) \frac{N^3}{V^3} + \dots \right), \quad (1)$$

where P , T , k_B and V is pressure, temperature, Boltzmann constant, molar volume, and N is equal to N_A the Avagadro constant, and $B_2(T)$ and $B_3(T)$ is the second, third, and fourth... virial coefficients, respectively.

Deviations from the ideal state were first interpreted qualitatively by van der waals [1] in terms of intermolecular interaction, which led to the famous equation of state. However, the quantitative interpretation can be given in terms of the virial coefficients, which can be expressed in terms of intermolecular interaction. At low densities, the deviation from the ideal state are adequately explained by the second virial coefficient, but at higher densities, higher virial coefficients must be taken into account.

Edalat et al. [2] used the second virial coefficient to evaluate the Lennard-Jones potential parameter (ϵ^* , σ) and the Mie(n,m) potential. Stigter et al. presented that the second and third coefficients for these interaction can be explained by: (a) steric repulsions among the PC head groups, and (b) a tilting of the $P-N^+$ dipole of PC so that the N^+ end enter the oil phase [4]. For calculation of the classical second and third virial coefficient of helium, argon at temperatures 113.15–1,223.15 K, see Mass et al. [5], Vega et al. [6], Putintsev and Ptintsev [7], Christof and Bernd [8]. The evaluation of the virial coefficient can be obtained from the experiment. However, the study chose to the theory and calculate the virial coefficient of the inert gases. Due to the inert gas with properties similar to real gases.

The scheme of the paper is as follows. In Sect. 2 detailing with the classical fluids with spherical symmetric molecules and the calculation of $B_2(T)$ and $B_3(T)$ are given. In Sect. 3, results for $B_2(T)$ and $B_3(T)$ for inert gases. The conclusion and discussion is given in Sect. 4.

2 Basic theory

In this work, we obtain the expansion of the equation of state in the form [9–11]

$$\beta P = \sum_{\ell=1}^{\infty} B_{\ell} \rho^{\ell}, \quad (2)$$

which is known as the virial expansion of the equation of state and P , ρ , B_{ℓ} and β are call the pressure, the number density ($\rho = N/V$), the ℓ th virial coefficient and irreducible cluster integral [12] respectively. Equation (2) can be obtained by eliminating the fugacity (z) [12] between

$$\beta P = \lim_{V \rightarrow \infty} \frac{\ln G}{V} = \sum_{\ell \geq 1} b_{\ell} z^{\ell}, \quad (3)$$

and

$$\rho = \frac{z}{V} \left(\frac{\partial \ln G}{\partial z} \right)_{T,V} = \sum_{\ell \geq 1} \ell b_{\ell} z^{\ell} \quad (4)$$

where G is the grand partition function. Equation (4) can be rewritten as

$$z = \rho \left(1 + \sum_{\ell=2} \ell b_{\ell} z^{\ell-1} \right)^{-1}. \quad (5)$$

Taking help of Eq. (5), it can be expanded in the form

$$z = \rho \left\{ 1 - \beta_1 z - \left(\frac{1}{2} \beta_1^2 + \beta_2 \right) z^2 - \left(\frac{2}{3} \beta_1^3 + 2\beta_1 \beta_2 + \beta_3 \right) z^3 - \dots \right\}. \quad (6)$$

This can be solved by the method of iteration. Thus,

$$z = \rho \left\{ 1 - \beta_1 \rho + \left(\frac{1}{2} \beta_1^2 - \beta_2 \right) \rho^2 - \left(\frac{1}{6} \beta_1^3 - \beta_1 \beta_2 + \beta_3 \right) \rho^3 + \dots \right\}, \quad (7)$$

or in general

$$z = \rho \exp \left(- \sum_{\ell=1}^{\infty} \beta_{\ell} \rho^{\ell} \right) \quad (8)$$

where the β_{ℓ} are the irreducible cluster integral equation (8) expresses the fugacity as a function of the density ρ . Next we eliminate z from Eq. (3).

Substituting Eqs. (5) and (8) into Eq. (3), we have

$$\beta P = \left(\rho - \frac{1}{2} \beta_1 \rho^2 - \frac{2}{3} \beta_2 \rho^3 - \dots \right). \quad (9)$$

This can also be obtained in an easy way, starting from the probability that an open system contains N molecules ($P_N = z^N Z_N / N! G$). We can now express the configurational integral Z_N ($Z_N = N! \prod_{\ell=1}^N \frac{(V b_{\ell})^{m_{\ell}}}{m_{\ell}!}$, where we consider a system of N particles. Let it consist of a number of clusters which represent m_1 unit clusters, m_2 clusters of two molecules..., m_{ℓ} clusters of ℓ molecules) in terms of the cluster integral b_{ℓ}

$$\beta P = \frac{\ln G}{V}. \quad (10)$$

Differentiating Eq. (10) with respect to z , we obtain

$$\beta \frac{dP}{dz} = \frac{1}{VG} \frac{dP}{dz} = \frac{1}{VG} \frac{d}{dz} \left(\sum_{N=0}^{\infty} \frac{z^N Z_N}{N!} \right) = \frac{1}{VG} \sum_{N=0}^{\infty} \left(\frac{N z^{N-1}}{N!} Z_N \right). \quad (11)$$

Equation (11) can be rewritten as

$$\beta \frac{dP}{dz} = \frac{\langle N \rangle}{Vz} = \frac{\rho}{z}, \tag{12}$$

where

$$\langle N \rangle = G^{-1} \sum_{N=0}^{\infty} \left(\frac{Nz^{N-1}}{N!} Z_N \right).$$

Then,

$$\beta \frac{dP}{d\rho} = \frac{\rho}{z} \frac{dz}{d\rho} = \rho \frac{d(\ln z)}{d\rho}$$

or

$$\beta P = \int_0^{\rho} \dot{\rho} \frac{d(\ln z)}{d\dot{\rho}} d\dot{\rho}. \tag{13}$$

Substituting Eq. (8) into Eq. (13) and using expand Taylor series, we get

$$\beta P = \rho - \sum_{\ell=1}^{\infty} \left(\frac{\ell}{\ell + 1} \right) \beta_{\ell} \rho^{\ell+1}. \tag{14}$$

Comparing Eqs. (2) and (14), the virial coefficients are defined as

$$\begin{aligned} \sum_{\ell=1}^{\infty} B_{\ell} \rho^{\ell} &= \rho - \sum_{\ell=1}^{\infty} \left(\frac{\ell}{\ell + 1} \right) \beta_{\ell} \rho^{\ell+1}, \\ B_1 &= 1, \\ B_{\ell} &= -\left(\frac{\ell - 1}{\ell} \right) \beta_{\ell-1}; \quad \ell \geq 2. \end{aligned} \tag{15}$$

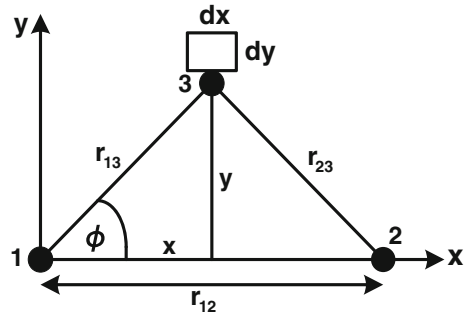
From Eq. (15), the second virial coefficients are [13]

$$B_2(T) = 2\pi N_A 10^{-24} \int_0^{\infty} r^2 \left(1 - \exp\left(-\frac{U(r)}{kT}\right) \right) dr. \tag{16}$$

From Eq. (15), the third virial coefficients are [14]

$$B_3 = -\frac{2}{3} \beta_2 = -\frac{1}{3} \int f_{12} f_{13} f_{23} d\mathbf{r}_3 d\mathbf{r}_2. \tag{17}$$

Fig. 1 Bipolar coordinates for three particles [4]



we introduce the Mayer function f_{ij} defined by the relationship $f_{ij} = 1 - \exp(-\frac{U(r_{ij})}{kl})$ [13], where $U(r_{ij})$ is the pair potential between molecules i and j . In terms of Mayer f-function [3, 12], we form a cluster which is a collection of points (molecules) connected directly or indirectly by the f-function. For example, a cluster of three particles, 1, 2, 3, may be formed in any of the four ways (see Fig. 1). Equation (15) has been confirmed that the contribution of higher order virial coefficients increases with density ρ . At liquid density, one has to consider several terms of the series. However, the expansion diverges at high density. Hence, this expansion approach to the equation of state is suitable at low density where the series converges.

In order to evaluate Eq. (17), we introduce bipolar coordinates (see Fig. 1); we fix the positions of the particles 1 and 2 and let particle 3 take all possible position. Rotation of the element of area $dx dy$ about the x axis sweeps out $d\mathbf{r}_3$, so that

$$d\mathbf{r}_3 = 2\pi y dx dy. \quad (18)$$

The coordinates x and y can be transformed to r_{13} and r_{23} by relation

$$\begin{aligned} r_{13}^2 &= x^2 + y^2, \\ r_{23}^2 &= y^2 + (r_{12} - x)^2 \end{aligned} \quad (19)$$

and

$$r_{23} = \sqrt{r_{13}^2 + r_{12}^2 - 2 r_{12} r_{13} \cos(\phi)}. \quad (20)$$

Using the Jacobian transformation [15], we get

$$\begin{aligned} dx dy &= \frac{r_{13} r_{23}}{y r_{12}} dr_{13} dr_{23} \\ d\mathbf{r}_3 &= \frac{2\pi r_{13} r_{23}}{r_{12}} dr_{13} dr_{23} \end{aligned} \quad (21)$$

Substituting Eq. (21) into Eq. (17), we obtain

$$B_3(T) = \frac{2\pi}{3} \int a_{12} f_{12} d\mathbf{r}_{12} \quad (22)$$

where

$$a_{12} = \frac{1}{r_{12}} \iiint r_{13} r_{23} f_{13} f_{23} dr_{23} dr_{13}. \tag{23}$$

Differentiating Eq. (20) with respect to $\phi \in [0, \pi]$, we obtain

$$\begin{aligned} 2 r_{23} \left(\frac{dr_{23}}{d\phi} \right) &= 2 r_{13} r_{12} \sin(\phi) \\ dr_{23} &= \left(\frac{r_{13} r_{12}}{r_{23}} \right) \sin(\phi) d\phi. \end{aligned} \tag{24}$$

Substituting Eq. (24) into Eq. (23), we have

$$\begin{aligned} a_{12} &= \frac{1}{r_{12}} \int_{allr_{13}} r_{13} f(r_{13}) dr_{13} \left(\int_{allr_{12}} r_{23} \frac{r_{13} r_{12}}{r_{23}} \sin(\phi) f(r_{23}) d\phi \right) dr_{13} \\ a_{12} &= \int_{allr_{13}} r_{13}^2 f(r_{13}) \int_{-1}^1 f \left(\sqrt{r_{13}^2 + r_{12}^2 - 2r_{13}r_{12} \cos(\phi)} \right) d \cos(\phi) dr_{13} \end{aligned} \tag{25}$$

Inserting Eq. (25), $\eta = \cos(\phi)$ and the Lennard-Jones (12-6) potential [13] into Eq. (22), we finally obtain the third virial coefficient

$$\begin{aligned} B_3(T) &= \frac{8\pi^2}{3} (N_A)^2 10^{-48} \int_0^\infty r_{12}^2 f(r_{12}) \int_0^\infty r_{13}^2 f(r_{13}) \\ &\quad \times \int_{-1}^1 f \left(\sqrt{r_{12}^2 + r_{13}^2 - 2r_{12}r_{13}\eta} \right) d\eta dr_{12} dr_{13}. \end{aligned} \tag{26}$$

The special potential given by Lennard-Jones potential with $n = 12, m = 6$ [13] has been used in calculate $B_2(T)$ and $B_3(T)$ in Mathematica program [16, 17].

3 Calculations and result

To again a feeling for the temperature dependence of $B_2(T)$, $B_3(T)$ and its dependence on the form of the interaction, let us look at a particular interaction potential:

$$U(r) = 4\varepsilon^* \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \tag{27}$$

which is known as a generalized Lennard-Jones potential. This potential has a minimum value of $-\varepsilon^*$ at $r = 2^{\frac{1}{6}}\sigma$. For inert gases, appropriate values of ε^* and σ show in Table 1 (see Table 1).

Table 1 Lennard-Jones potential parameter [2,7,18]

Gases	(ϵ^*/k_B) (K)	σ (Å)
He	10.22	2.56
Ne	35.6	2.75
Ar	120	3.40
Kr	171	3.60
Xe	220	4.10
N ₂	95.5	3.74
CH ₄	148.4	3.81
CF ₄	151.4	4.75

Table 2 The second virial coefficient calculation

T (K)	He	Ne	Ar	Kr	Xe	N ₂	CH ₄	CF ₄
293.15	11.16	11.03	-16.90	-53.34	-131.41	-6.14	-45.25	-92.09
400.00	10.99	12.57	-1.02	-23.35	-68.94	9.54	-15.75	-33.48
500.00	10.78	13.24	7.02	-8.25	-37.88	17.45	-0.82	-3.85
600.00	10.57	13.59	12.06	1.23	-18.47	22.36	8.55	14.76
700.00	10.37	13.76	15.46	7.68	-5.29	25.63	14.91	27.39
800.00	10.18	13.84	17.86	12.29	4.19	27.92	19.46	36.43
900.00	10.01	13.86	19.64	15.75	11.30	29.58	22.84	43.15
1,000.00	9.85	13.84	20.98	18.40	16.79	30.82	25.42	48.29
1,200.00	9.57	13.75	22.84	22.17	24.66	32.46	29.06	55.55
1,400.00	9.32	13.62	24.01	24.66	29.94	33.45	31.44	60.29
1,600.00	9.10	13.47	24.79	26.38	33.68	34.05	33.05	63.53
1,800.00	8.91	13.31	25.30	27.62	36.41	34.41	34.19	65.81
2,000.00	8.74	13.16	25.65	28.53	38.47	34.62	35.00	67.45
2,400.00	8.44	12.88	26.04	29.71	41.28	34.75	36.03	69.53

3.1 Logic of the second virial coefficient

By substituting Eq. (27) into Eq. (16), we finally obtain the second virial coefficient as

$$B_2(T) = 2\pi N_A 10^{-24} \int_0^{\infty} r^2 \left(1 - \exp \left(-\frac{4\epsilon^*}{k_B T} \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \right) \right) dr, \quad (28)$$

where $N_A = 6.02 \times 10^{23}$. We obtain the numerical values the second virial coefficient for inert gases as displayed in table (see Tables 2–9). In Figs. 2 and 3 the second virial coefficient for He, Ne, Ar, Kr, Xe, N₂, CH₄, CF₄ are presented.

Table 3 Comparison of the second virial coefficient obtain cluster expansion theory and experimental for He

T (K)	Experiment [19]	Calculation	% difference
293.15	11.15	11.16	0.09
400.00	10.94	10.99	0.46
500.00	10.72	10.78	0.56
600.00	10.51	10.57	0.57
700.00	10.32	10.37	0.48
800.00	10.13	10.18	0.49
900.00	9.97	10.01	0.40
1,000.00	9.81	9.85	0.40
1,200.00	9.58	9.57	0.10
1,400.00	9.37	9.32	0.53
1,600.00	9.15	9.10	0.54
1,800.00	8.93	8.91	0.22
2,000.00	8.72	8.74	0.23
2,400.00	8.44	8.44	0.00

Table 4 Comparison of the second virial coefficient obtain cluster expansion theory and experimental for Ne

T (K)	Experiment [19]	Calculation	% difference
293.15	11.02	11.03	0.09
400.00	12.47	12.57	0.08
500.00	13.19	13.24	0.37
600.00	13.62	13.59	0.22
700.00	13.77	13.76	0.07
800.00	13.87	13.84	0.22
900.00	13.91	13.86	0.36
1,000.00	13.88	13.84	0.29
1,200.00	13.75	13.75	0.00
1,400.00	13.61	13.62	0.07
1,600.00	13.46	13.47	0.07
1,800.00	13.31	13.31	0.00
2,000.00	13.16	13.16	0.00
2,400.00	12.87	12.88	0.08

Logic of the second virial coefficient

- Input values (ϵ^*/k_B), σ (Å) and temperature in Mathematica programm.
- Input Eq. (28) into Mathematica programm.
- Calculate $B_2(T)$

For example, numerical evaluation of second virial coefficient for He

- $\epsilon^* = 10.22$; $\sigma = 2.56$; $T = 2, 400$;
- $$\text{NIntegrate}\left[2\pi N_A 10^{-24} r^2 \left(1 - \exp\left(-\frac{410.22}{k_B 2,400} \left[\left(\frac{2.56}{r}\right)^{12} - \left(\frac{2.56}{r}\right)^6\right]\right)\right)\right]$$
- $B_2(T) = 8.43987$

Table 5 Comparison of the second virial coefficient obtain cluster expansion theory and experimental for Ar

T (K)	Experiment [19]	Calculation	% difference
293.15	-16.85	-16.90	0.29
400.00	-0.82	-1.02	24.29
500.00	7.17	7.02	2.09
600.00	12.25	12.06	1.55
700.00	15.67	15.46	1.34
800.00	18.09	17.86	1.27
900.00	19.84	19.64	1.01
1,000.00	21.19	20.98	0.99
1,200.00	23.01	22.84	0.74
1,400.00	24.03	24.01	0.08
1,600.00	24.86	24.79	0.28
1,800.00	25.49	25.30	0.74
2,000.00	25.91	25.65	1.00
2,400.00	26.24	26.04	0.76

Table 6 Comparison of the second virial coefficient obtain cluster expansion theory and experimental for Kr

T (K)	Experiment [19]	Calculation	% difference
293.15	-53.79	-53.34	0.08
400.00	-22.88	-23.35	2.05
500.00	-7.25	-8.25	13.79
600.00	2.56	1.23	52.57
700.00	9.23	7.68	16.79
800.00	14.01	12.29	12.28
900.00	17.60	15.75	10.51
1,000.00	20.32	18.40	9.44
1,200.00	24.20	22.17	8.38
1,400.00	26.76	24.66	7.85
1,600.00	28.53	26.38	7.53
1,800.00	29.65	27.62	6.84
2,000.00	30.49	28.53	6.43
2,400.00	31.84	29.71	6.69

3.2 Logic of the third virial coefficient

By substituting Eq. (27) into Eq. (26), we finally obtain the third virial coefficient as

$$\begin{aligned}
 B_3(T) = & \frac{8\pi^2}{3} N_A^2 10^{-48} \int_0^{150} \int_0^{150} \int_0^{150} r_{12}^2 \left(1 - \exp\left(-\frac{U(r_{12})}{k_B T}\right) \right) r_{13}^2 \left(1 - \exp\left(-\frac{U(r_{13})}{k_B T}\right) \right) \\
 & \times \left(1 - \exp\left(-\frac{U(\sqrt{r_{12}^2 + r_{13}^2 - 2r_{12}r_{13}\eta})}{k_B T}\right) \right) dr_{13} dr_{12} d\eta, \quad (29)
 \end{aligned}$$

Table 7 Comparison of the second virial coefficient obtain cluster expansion theory and experimental for Xe

T(K)	Experiment [19]	Calculation	% difference
293.15	-131.41	-134.59	2.42
400.00	-68.94	-70.79	2.68
500.00	-37.88	-39.83	5.15
600.00	-18.47	-20.40	10.45
700.00	-5.29	-6.92	16.89
800.00	4.19	2.55	39.14
900.00	11.30	9.67	14.42
1,000.00	16.79	15.29	8.93
1,200.00	24.66	23.25	5.72
1,400.00	29.94	28.53	4.71
1,600.00	33.68	32.32	4.04
1,800.00	36.41	35.10	3.59
2,000.00	38.47	37.19	3.33
2,400.00	41.28	39.91	3.32

Table 8 Comparison of the second virial coefficient obtain cluster expansion theory and experimental for N₂

T(K)	Experiment [19]	Calculation	% difference
293.15	-4.96	-6.14	21.21
400.00	9.48	9.54	0.62
500.00	16.65	17.45	4.62
600.00	21.14	22.36	5.63
700.00	24.19	25.63	5.78
800.00	26.41	27.92	5.58
900.00	28.08	29.58	5.20
1,000.00	29.39	30.82	4.72
1,200.00	31.31	32.47	3.62
1,400.00	32.64	33.45	2.45
1,600.00	33.62	34.05	1.28
1,800.00	34.37	34.41	0.13
2,000.00	34.96	34.63	0.99
2,400.00	35.84	34.75	3.09

where

$$U(r_{12}) = 4\varepsilon^* \left(\left(\frac{\sigma}{r_{12}} \right)^{12} - \left(\frac{\sigma}{r_{12}} \right)^6 \right),$$

$$U(r_{13}) = 4\varepsilon^* \left(\left(\frac{\sigma}{r_{13}} \right)^{12} - \left(\frac{\sigma}{r_{13}} \right)^6 \right),$$

Table 9 Comparison of the second virial coefficient obtain cluster expansion theory and experimental for CH₄

T (K)	Experiment [19]	Calculation	% difference
293.15	-44.95	-45.25	0.67
400.00	-15.09	-15.75	4.26
500.00	0.39	-0.82	71.96
600.00	10.43	8.55	19.82
700.00	17.51	14.91	16.02
800.00	22.77	19.46	15.67
900.00	26.83	22.84	16.08
1,000.00	30.07	25.42	16.75
1,200.00	34.92	29.06	18.29
1,400.00	38.37	31.44	19.86
1,600.00	40.95	33.05	21.34
1,800.00	42.96	34.19	22.72
2,000.00	44.56	35.00	24.03
2,400.00	46.97	36.02	26.04

$$U(\sqrt{r_{12}^2 + r_{13}^2 - 2r_{12}r_{13}\eta}) = 4\varepsilon^* \left(\left(\frac{\sigma}{\sqrt{r_{12}^2 + r_{13}^2 - 2r_{12}r_{13}\eta}} \right)^{12} - \left(\frac{\sigma}{\sqrt{r_{12}^2 + r_{13}^2 - 2r_{12}r_{13}\eta}} \right)^6 \right). \quad (30)$$

We obtain the numerical values the third virial coefficient for inert gases as displayed in table (see Table 10). In Figs. 4 and 5 the third virial coefficient for He, Ne, Ar, Kr, Xe, N₂, CH₄, CF₄ are presented.

Logic of the third virial coefficient

- Input $r_{12} = 0.01$, $r_{13} = 0.01$, $\Delta r_{12} = 0.01$, $\Delta r_{13} = 0.01$ in Mathematica program.
- Input The Lennard-Jones potential in Mathematica programm.
- Input ε^* , σ into the Lennard-Jones potential in Mathematica program.
- Input f-function in Mathematica program.
- We used command. The While loop continues until the condition fails.

For example, numerical evaluation of third virial coefficient for N₂

- $In[1] := r_{13} = 0.01$; $sum1 := 0.0$;
- $In[2] := \Delta r_{12} = 0.01$; $\Delta r_{13} = 0.01$; $\Delta \eta = 0.1$;
- $In[3] := u[a_] := \left(\frac{4 \times 95.48}{2,400} \right) \left(\left(\frac{3.736}{a} \right)^{12} - \left(\frac{3.736}{a} \right)^6 \right)$;

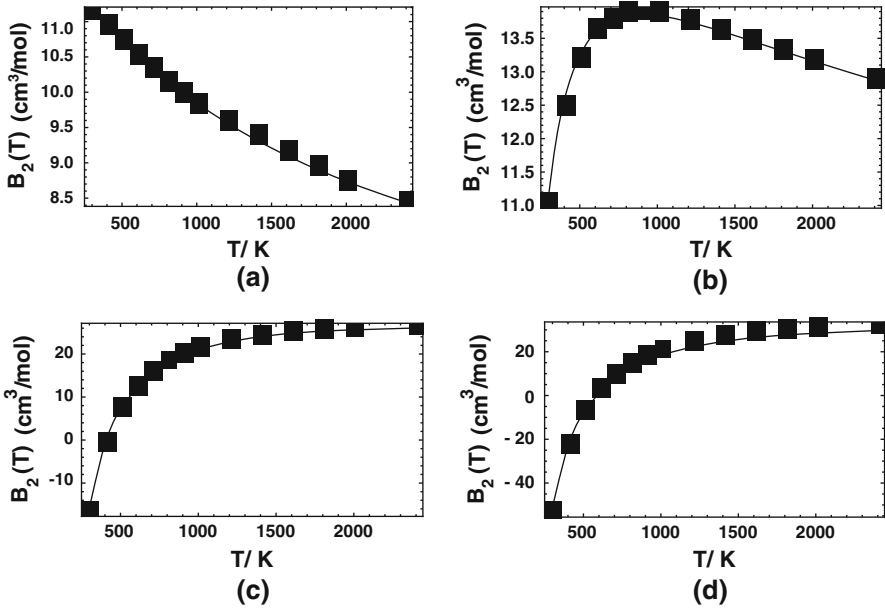


Fig. 2 The second virial coefficient of He, Ne, Ar, Kr as from experiment (*symbols*) [19] and from the calculations of this work for He, Ne, Ar [6], Kr (*solid line*). The parameter (ϵ^* , σ) used to describe He, Ne, Ar, Kr in Table 1. **a** He, **b** Ne, **c** Ar, **d** Kr

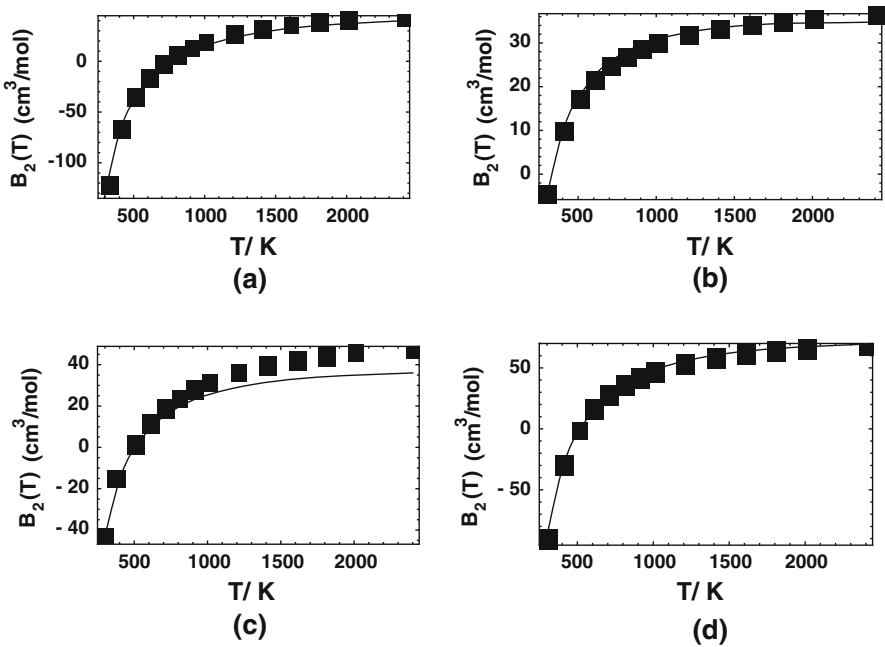
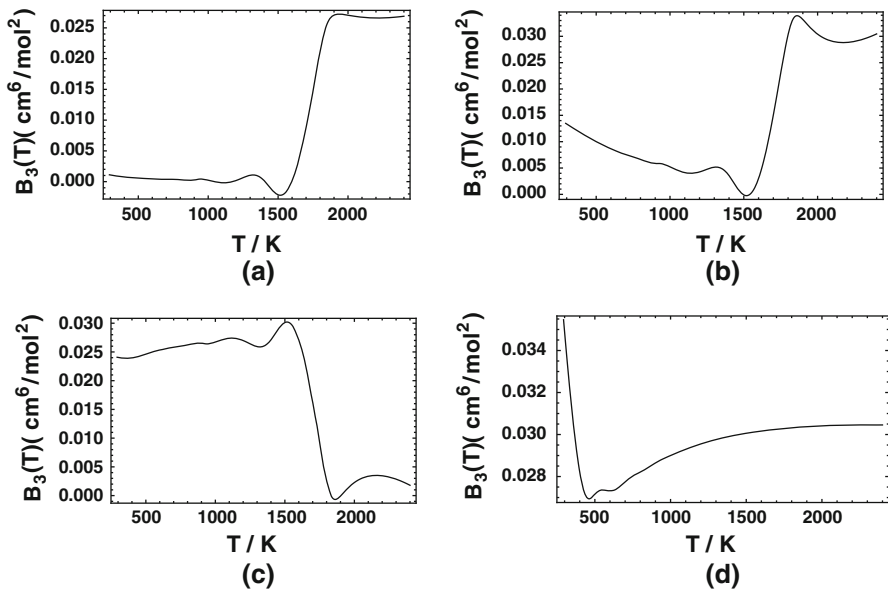


Fig. 3 The second virial coefficient of Xe, N_2 , CH_4 , CF_4 as from experiment (*symbols*) [19] and from the calculations of this work for Xe, N_2 , CH_4 , CF_4 (*solid line*). The parameter (ϵ^* , σ) used to describe Xe, N_2 , CH_4 , CF_4 in Table 1. **a** Xe, **b** N_2 , **c** CH_4 , **d** CF_4

Table 10 The third virial coefficient calculation

T (K)	He	Ne	Ar	Kr	Xe	N ₂	CH ₄	CF ₄
293.15	0.001111	0.013480	0.024080	0.035466	0.0245912	0.0245905	0.0245912	0.0245912
400.00	0.000756	0.011610	0.023955	0.028213	0.0245912	0.0245857	0.0245912	0.0245912
500.00	0.000572	0.010010	0.024643	0.027158	0.0245912	0.0245735	0.0245912	0.0245912
600.00	0.000454	0.008660	0.025314	0.027317	0.0245912	0.0245517	0.0245906	0.0245912
700.00	0.000373	0.007550	0.025827	0.027748	0.0245912	0.0245199	0.0245893	0.0245912
800.00	0.000315	0.006635	0.026224	0.028213	0.0245912	0.0244791	0.0245868	0.0245912
900.00	0.000271	0.005874	0.026515	0.028645	0.0245912	0.0244305	0.0245826	0.0245912
1,000.00	0.000237	0.005230	0.026723	0.028997	0.0245912	0.0243753	0.0245763	0.0245912
1,200.00	0.000187	0.004257	0.026984	0.029556	0.0245912	0.0242502	0.0245570	0.0245912
1,400.00	0.000154	0.003547	0.027119	0.029923	0.0245912	0.0241121	0.0245283	0.0245912
1,600.00	0.000129	0.003016	0.027138	0.030165	0.0245912	0.0239667	0.0244908	0.0245912
1,800.00	0.021150	0.030315	0.002596	0.030317	0.0245910	0.0238183	0.0244454	0.0245912
2,000.00	0.027060	0.030410	0.002275	0.030418	0.0245909	0.0236687	0.0243934	0.0245912
2,400.00	0.026890	0.030455	0.001798	0.030456	0.0245907	0.0233741	0.0242743	0.0245912

**Fig. 4** Third virial coefficient of He, Ne, Ar, Kr as obtained from the calculations are presented *solid line*. **a** He, **b** Ne, **c** Ar, **d** Kr

- $In[4] := f[b_-, c_-, \xi_-] := \frac{8\pi^3}{3}(6.022)^2 0.01(150 b)^2(150 c)^2(1 - e^{-U[150 b]})$
 $(1 - e^{-U[150 c]})$
 $(1 - \exp(-U[\sqrt{(150 b)^2 + (150 c)^2 - 2(150 b)(150 c)\xi}]))$;
- $In[5] := \text{While}[r_{13} < 1.01; r_{13} = r_{13} + \Delta r_{13}; r_{12} = 0.01;$
 $\text{While}[r_{12} < 1.01; r_{12} = r_{12} + \Delta r_{12}; \eta = -1.0;$

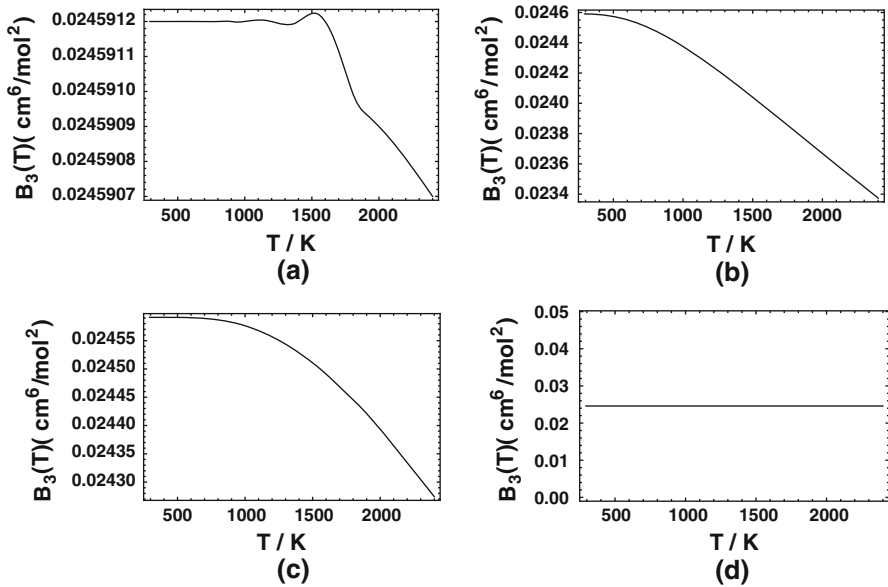


Fig. 5 Third virial coefficient of Xe, N₂, CH₄, CF₄ as obtained from the calculations are presented *solid line*. **a** Xe, **b** N₂, **c** CH₄, **d** CF₄

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While[η < 1, η = η + Δη; sum1 = sum1 + Δr12 Δr13 Δη
f [(r13 - Δr13/2), (r12 - Δr12/2), (η - Δη/2)]
- In[6] := Print[sum1]
- out[6] := 0.0233741
    
```

4 Conclusion

The second virial coefficients is compared with experimental values of Inert gases (see Tables 3, 4, 5, 6, 7, 8, 9), for which the intermolecular pair potential is a function of the interparticle separation. The agreement is good. At high temperature ($T \geq 500$ (K)), where the repulsive part of the interaction dominates, the virial coefficients $B_2(T)$ is positive. However, at low temperatures ($T \leq 500$ (K)), where the attractive part of the interaction dominates, the virial coefficient is negative. The temperature at which $B_2(T) \rightarrow 0$ is called the Boyle's temperature T_B [6] for the Lennard-Jines (12-6) potential. For the second virial coefficient of He, we obtain the Boyle's temperature as follow: $T_B = 34.9312438964844$ (K) $B_2(T) = 9.82958 \times 10^{-6}$ (cm³/mol). For the second virial coefficient of Ne, we get $T_B = 121.67828369140625$ (K) $B_2(T) = 8.31197 \times 10^{-6}$ (cm³/mol). For the second virial coefficient of Ar, we obtain the Boyle's temperature as follow: $T_B = 410.1513671875$ (K) $B_2(T) = 8.85635 \times 10^{-7}$ (cm³/mol). For the second virial coefficient of Kr, we have $T_B = 584.465698242188$ (K) $B_2(T) = 1.20463 \times 10^{-6}$ (cm³/mol). For the second virial coefficient of Xe, we obtain the Boyle's temperature as follow: $T_B = 751.944213867188$ (K) $B_2(T) = 5.32385 \times 10^{-6}$ (cm³/mol).

For the second virial coefficient of N_2 , we obtain the Boyle's temperature as follow: $T_B = 326.34381103515625$ (K) $B_2(T) = 7.75205 \times 10^{-6}$ (cm^3/mol). For the second virial coefficient of CF_4 , we obtain the Boyle's temperature as follow: $T_B = 517.474334716796875$ (K) $B_2(T) = 8.99378 \times 10^{-6}$ (cm^3/mol). For the second virial coefficient of CH_4 , we obtain the Boyle's temperature as follow: $T_B = 507.2205796875$ (K) $B_2(T) = 7.45381 \times 10^{-6}$ (cm^3/mol). From Tables 3, 9, the second virial coefficients of the experimental a little is different from the calculation for He, Ne, Ar, Kr, N_2 , CF_4 . The second virial coefficients of the experimental is different from the calculation for Xe, CH_4 . From Eq. 1, if the higher temperature (T) but very low density ($\frac{N}{V}$)², this the third virial coefficients ($B_3(T)$) must be minimal. He, Ne, CF_4 have the third virial coefficients values not corresponded to Eq. 1, at the very higher temperature (see Table 10). Ar, Kr, N_2 , He, Xe, CH_4 have the third virial coefficients values corresponded to Eq. 1, at the very higher temperature (see Table 10).

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