Virial equations of state of d-dimensional semi classical Lennard-Jones fluid mixture

MANOJ KUMAR[1] and JYOTISH KUMAR[2]

[1.] Madanani Gali, Dashrath Nagar, Mithanpura, Muzaffarpur - 842 002 (India).
[2.]Ramani Mohan Garden, Kalambag Road Chowk, Muzaffarpur - 842 002 (India).

(Received: October 10, 2007; Accepted: November 24, 2007)

ABSTRACT

The virial coefficient of d-dimensional Lennard-Jones (LJ) (12-6) fluid mixture in the semi classical limit are studied. Explicit expressions for classical and first quantum correction of the second virial coefficient of the LJ (12-6) fluid mixture are derived. The results are discussed. The excess second virial coefficient depends on the dimensionality 'd'.

Key words: Semiclassical fluid mixture, quantum correction, second virial coefficient.

INTRODUCTION

In recent years, d-dimensional fluids have been a subject of considerable inherent. However, this is confined to the one- component fluid[1,2]. No attempt have been made to study the equilibrium properties of d-dimensional fluid mixture.

In the present paper, we investigate the classical and quantum corrections to the virial coefficient of the d-dimensional fluid mixture. The usual way of studying the properties of the semi classical system is to expand them in the ascending power of Planck's constant $\hbar$ [3]. Extensive work has been done for three-dimensional fluid[3]. However, no work is available for d-dimensional fluid mixture.

The purpose of present investigation is to derive unified expressions for the virial coefficient of the d-dimensional fluid mixture, whose molecules interact via the Lennard-Jones (LJ) (12-6) potential.

Virial expansion of equation of state of fluid mixture

In this low density limit, the equation of state is given by 3.

$$\beta P/\rho = 1+\sum_{n=2}^{\infty} B_n(d)\rho^{n-1} \quad \text{... (1)}$$

where $B_n(d)$ is the nth virial coefficient of d-dimensional fluid mixture and ρ is the number density. The virial coefficient B_n can be written as

$$B_n(d) = B^c{}_n(d)+h^2B^1{}_n(d)+o(h^4) \quad \text{... (2)}$$

where $B^c{}_n$ (d) and $B^1{}_n$ (d) are the classical and first quantum correction values of B_n(d), respectively.

Thus, for n = 2, we have

$$B_2^c(d) = \quad 1(½)\sum_{\alpha,\beta} x_\alpha x_\beta \int (\exp[-\beta u_{\alpha\beta}(r)]-1)dr \quad \text{...(3)}$$

$$B_2^{q}(d) = -(\beta^3/24)\sum_{\alpha\beta} X_\alpha X_\beta \left(\frac{1}{m_{\alpha\beta}}\right)\int \{\exp[-\beta u_{\alpha\beta}(r)]\nabla^2 u_{\alpha\beta}(r)\} dr \quad ..(4)$$

here $X_\alpha = N_\alpha/N$ is the concentration of species α, and

$$M_{\alpha\beta} = 2m_{\alpha\alpha}\, m_{\beta\beta}\,/(m_{\alpha\beta} + m_{\beta\beta})$$

where $m_{\alpha\alpha} = m_\alpha$ is the mass of a molecule of species.

Second virial coefficient for d-dimensional Lennard-Jones (12-6) fluid mixture

We consider a fluid mixture whose molecules interact via the LJ (12-6) potential.

$$U_{\alpha\beta}(r) = 4\,\epsilon_{\alpha\beta}\,[\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r^6] \quad ...(5)$$

where ϵ_{ab} represents the depth of the potential well and σ_{ab} the diameter of the molecule. For the unlike species, σ_{12} and ϵ_{12} are given by

$$\sigma_{12} = (\sigma_{11} + \sigma_{12})\,/2 \quad ..(6a)$$
$$\epsilon_{12} = \xi_{12}\,(\sigma_{11} + \sigma_{12})\,/2 \quad ..(6b)$$

where ϵ_{12} is an adjustable parameter, which is fairly close to unity. using the relation[1]

$$\int dr\, f(r) = S_d \int dr\, r^{d-1}\, f(r) \quad ... (7)$$

where the function f(r) depends on the distance r=|r| and S_d is the surface area of the unit sphere, given by[1,4]

$$S_d = d\pi^{d/2}\,\Gamma(1+d/2) \quad ...(8)$$

Here $\Gamma(1)$ =1! is the Gamma function. The Eq. (3) and (4) can be written as

$$B_2^c(d) = -(\beta S_d/2d)\sum_{\alpha\beta} x_\alpha x_\beta \int_0^\infty \exp[-\beta u_{\alpha\beta}(r)](\partial u_{\alpha\beta}(r)/\partial r) r^d dr \quad ...(9)$$

$$B_2^q(d) = -(\beta^3 S_d/24\sum_{\alpha\beta} x_\alpha x_\beta (1/m_{\alpha\beta})\int_0^\infty \exp[-\beta u_{\alpha\beta}(r)](\nabla_r^2 u_{\alpha\beta}(r)^{d-1} dr \quad ...(10)$$

where in d-dimensional space[4]

$$\nabla_r^2 = \frac{1}{r^{d-1}}\frac{\partial}{\partial r}\left(r^{d-1}\frac{\partial}{\partial r}\right)$$

Classical second virial coefficient Using the reduced quantities

Using the reduced quantities,

$$r^* = r/\sigma_{\alpha\beta},\ u^*_{\alpha\beta} = u_{\alpha\beta}/\epsilon_{\alpha\beta} \text{ and } T^*_{\alpha\beta} = kT/\epsilon_{\alpha\beta}$$

Eq. (9) can be written

$$B^{c*}_2(d) = (S_d/d)\sum_{\alpha,\beta} x_\alpha x_\beta \sigma^d_{\alpha\beta} B^{c*}_{\alpha\beta}(d) \quad ...(11)$$

where

$$B^{c*}_{\alpha\beta}(d) = -\left(4/T^*_{\alpha\beta}\right)\int_0^\infty d^* r^{*d-1}\left[-12r^{*-12} + 6r^{*-6}\right]\exp\left[-\left(4/T^*_{\alpha\beta}\right)\left(r^{*-12} - r^{*-6}\right)\right] \quad ..(12)$$

One can evaluate Eq. (12) in the series form by expanding exp $[(4/T^*_{\alpha\beta})r^{*-6}]$ as

$$B^{c*}_{\alpha\beta}(d) = T_{\alpha\beta}^{-d/12}\sum_{i=0}^{\infty} b_i^c(d) T_{\alpha\beta}^{*1/2} \quad ...(13)$$

where

$$b_i^c(d) = -\left(\frac{d}{12i}\right)2^{(6i+d)/6}\left(\frac{6i-d}{12}\right) \quad ..(14)$$

Using Eq. (13) in Eq. (11), one can calculate the classical second visual coefficient for α-dimensional LJ (12-6) fluid mixture.

Quantum correction to the second virial coefficient

We introduce the reduced quantum parameters $\Lambda^*_{\alpha\beta}$ defined as [3]

$$\Lambda^*_{\alpha\beta} = h/\sigma_{\alpha\beta}\sqrt{m_{ab}\,\epsilon_{ab}} \quad ...(15)$$

In terms of the reduced quantum parameter $\Lambda^*_{\alpha\beta}$, the second virial coefficient of the d-dimensional LJ (12-6) fluid mixture correct to the first order quantum correction, can be written as

$$B_2(d) = (s_\alpha/d)\sum_{\alpha,\beta} x_\alpha x_\beta \sigma^d_{ab}\,[B^{c*}_{\alpha\beta}(d) + \Lambda^{*2}_{\alpha\beta} B^{*2}_{\alpha\beta}(d)] \quad ...(16)$$

where

$$B^{l*}_{\alpha\beta}(d) = \frac{d}{48\pi^2 T^{*2}_{\alpha\beta}}\int_0^\infty \exp\left[-u^*_{\alpha\beta}(r^*)/T^*_{\alpha\beta}\right]\Lambda_r^2 u^*_{\alpha\beta} r^{*d-1} dr^* \quad ...(17)$$

Substituting Eq. (5) in Eq. (17) and following the method of evaluating $B^{c*}_{\alpha\beta}(d)$, we get

$$B^{I*}_{\alpha\beta}(d)=T^{8(d+10)/12}_{\alpha\beta}\sum_{i=0}^{\infty} b^{I}_{i}(T^{*-i/2}_{\alpha\beta}) \quad ...(18)$$

where

$$b^{I}_{i}(d)=\left(\frac{d}{576\pi^2}\right)\left[\frac{(d-2)(d-14)+36i}{i!}\right]2^{(6i+d+2)/6}\Gamma\left(\frac{6i-d+2}{12}\right) \quad ...(19)$$

Finally, the second virial coefficient of the d-dimensional LJ (12-6) fluid mixture in the semiclassical limit can be expressed as

$$B_2(d)=(s_d/d)\sum_{\alpha,\beta} xaxbs^{d}_{\alpha\beta}B^{*}_{\alpha\beta}(d) \quad ...(20)$$

Where

$$B^{*}_{\alpha\beta}(d)=T^{*-d/12}_{\alpha\beta}\sum_{i=0}^{\infty} b_i(T)^{*-i/2}_{\alpha\beta} \quad ...(22)$$

With

$$b_i(d)=b^{c}_{i}(d)+\Lambda^{*2}_{\alpha\beta}T^{*-5/6}_{\alpha\beta}b^{I}_{i}(d) \quad ...(23)$$

RESULTS AND DISCUSSION

We have calculated the reduced second virial Table 1 coefficient $B^{*}_{\alpha\beta}(d)$ for d-dimensional He_4 -He_3 mixture for 1≤d≤5 as reported in Table 1. B^{*}_{43} lies between B^{*}_{44} and B^{*}_{33}. We have also calculated the excess second virial coefficient $B^{*}_{43}(d)=(2s_{\alpha}/d)x_4x_3\ \ \sigma^{d}_{43}B^{*}_{43}(d)$, which are reported in Table 2. We see that the excess second virial coefficient depends on the dimensionality 'd'.

Summary

We have given as explicit unified expressions for the second virial coefficient for the d-dimensional LJ (12-6) model in the semi classical limit. From the study, we find that the second virial coefficient depends on the dimensionality.

The quantum effect increases with decrease of temperature and at lower temperature one should take the higher order terms to estimate the quantum effects for He_4 - He_3 mixture for which the quantum parameters are large.

Table 1: The reduced second virial coefficient $B^{*}_{\alpha\beta}$ (d)for He_4- He_4, He_3 - He_3 and He_4 - He_3

D	T*	B^*_{44}(D)	B^*_{33}(D)	B^*_{43}(D)
1	50	0.817	0.819	0.818
	30	0.841	0.844	0.843
	10	0.884	0.894	0.889
2	50	0.661	0.664	0.663
	30	0.695	0.699	0.697
	10	0.739	0.756	0.748
3	50	0.518	0.521	0.520
	30	0.544	0.550	0.547
	10	0.527	0.547	0.533
4	50	0.359	0.362	0.361
	30	0.347	0.354	0.351
	10	0.132	0.158	0.145
5	50	0.061	0.064	0.063
	30	-0.097	-0.091	-0.094
	10	-0.019	-0.984	-1.002

Table 2 : The excess second virial coefficient B^*_{43} (d)for He_4–He_3 in A^0 units

T*/D	**1**	**2**	**3**	**4**	**5**
50	1.046	3.400	9.515	18.988	9.001
30	1.077	3.576	10.013	18.456	-13.452
10	1.136	3.836	9.852	7.625	-143.846

REFERENCES

1. Baus, M. and Colot, J.L., *Phys. Rev.* **A36**: 3912 (1987).
2. Sinha, S.K., *Mol. Phys.* **69**: 537 (1990).
3. Singh, Y. and Sinha, S.K., *Phys. Rep.* **79**: 13 (1981).
4. Kumar, M. and Sinha, S.K., Proc. of 51th Congress of ISTAM, pp. 134-139 (2006).