Journal of Atomic, Molecular, Condensate & Nano Physics
Vol. 4, Nos. 1 – 3, pp. 7–13, 2017
ISSN 2349-2716 (online); 2349-6088 (print)
Published by RGN Publications

http://www.rgnpublications.com

Theoretical Study of Non-additive Hard Convex Body Fluid Mixtures

Research Article

Tarun Kumar Dey

Post Graduate Department of Physics, L.S. College, B.R.A. Bihar University, Muzaffarpur 842001, India
Corresponding author: tkdeyphy@gmail.com

Abstract. The structure of a dense fluid or liquid is largely determined by the repulsive intermolecular forces, so the hard core potential has been extensively employed to model real fluids and fluid mixtures. The properties of two dimensional hard body fluids and fluids mixtures have aroused a considerably interest in recent years. This is because they are treated as models of real fluids or fluid mixtures absorbed onto surfaces. The 2D hard-body fluids and fluid mixtures like their three-dimensional counter part are useful reference system in framing a perturbation theory for 2D real fluids and fluid mixtures of non-spherical molecules. The 2D hard-body systems are convex body (HCB) systems such as ellipse (HE) and hard discorectangles (HDR) and hard non-convex body systems i.e., fused hard discs (FHD) and planar hard dumbbell (HDB) systems. The equation of state of hard convex body fluid mixtures (HCB) is studied. Analytic expressions are given for the equation of state of the fluid mixture of the non-additive HCB. The numerical results are discussed for the non-additive hard dumbbell (HDB) fluid mixtures under different conditions for different values of non-additivity Δ. They depend on the conditions, shape parameters L_{11}^* and L_{22}^*, mole fractions x_1 and x_2 and Δ in general and increase with the increase of packing fraction η.

Keywords. Hard body fluid mixture; Non additive dumbbell; Shape parameters

PACS. 64.10.+h

Received: December 27, 2017 **Accepted:** December 30, 2017

1. Introduction

The purpose of present work is to develop a theory for calculating the equation of state of fluid mixtures of hard-body molecules, which is of current interest. This is because they are treated

as a model of real fluid mixture. Considerable progress has been made in understanding the thermodynamic properties of hard-body fluid mixtures [1–5] Almost all these attempts, however, have been confined to the fluid mixture of additive hard-body molecules, where the distance of closest approach between particles of different species is the arithmetic mean of the diameters of both particles. On the other hand, non-additive hard-core mixtures, where the distance of closest approach between particles of different species is no longer arithmetic mean, have received less attention. However, they can be used to deal with interesting aspects occurring in real systems (such as liquid-vapour equilibrium).

Recently, Kumar et al. [5] have developed a simple accurate method to calculate the equation of state for the fluid mixture of additive hard convex body (HCB). This method can be extended to derive the equation of state of the non-additive HCB fluid mixture.

In the present paper, we calculate the equation of state of the non-additive HCB fluid mixture.

2. Basic Theory

We consider a fluid mixture of the hard non-sphere molecules of species 1 and 2. For such a system, the pair interaction is the hard Gausian overlap (HGO) potential defined by

$$\begin{aligned} u_{ab}(r\omega_1\omega_2) &= \infty, \quad r < \sigma_{ab}(\omega_1\omega_2), \\ &= 0, \quad r > \sigma_{ab}(\omega_1\omega_2), \end{aligned} \tag{2.1}$$

where $r = |\mathbf{r}_1 - \mathbf{r}_2|$ is the centre-to-centre distance, ω_i represents the orientational coordinate of molecule i, and $\sigma_{ab}(\omega_1\omega_2)$ is the distance of closest approach between two hard-core molecules of species a and b. It can be expressed in terms of the Euler angles [5].

$$\sigma_{ab}(\omega_1\omega_2) = \sigma^0_{ab}[1-\chi_{ab}(\cos^2\theta_1+\cos^2\theta_2-2\chi_{ab}\cos\theta_1+\cos\theta_2\cos\theta_{12})(1-\chi_{ab}\cos^2\theta_{12})^{-1}]^{-1/2}, \tag{2.2}$$

where σ^0_{ab} is a constant with the unit of length and the shape parameters χ_{ab} is defined as

$$\chi_{ab} = (K^2_{ab} - 1)/(K^2_{ab} + 1). \tag{2.3}$$

Here $\sigma^0_{ab} = 2b_{ab}$ is the width of the molecule of species a and $K_{aa} = 2a_{aa}/2b_{aa}$ is the length-to-breadth ratio of the molecule of species a. The effective values of σ^0_{12} and K_{12} of the molecules of unlike species can be given by [1, 2]

$$\sigma^0_{12} = \sigma^a_{12}(1+\Delta), \tag{2.4a}$$

$$K_{12} = (K_{11}\sigma^0_{11} + K_{22}\sigma^0_{22})/(K_{11}\sigma^0_{22}), \tag{2.4b}$$

where $\sigma^a_{12} = (\sigma^0_{11}+\sigma^0_{22})/2$, and $\Delta = 0$ for a binary mixture of additive hard-core molecule, whereas $\Delta \neq 0$ for non-additive hard-core mixture.

The equation of state of the HCB fluid mixture can be expressed in terms of radial distribution function (RDF) of the hard sphere (HS) fluid mixture at contact g^{HS}_{ab} (σ^{HS}_{ab}) as [5].

$$\beta P/\rho = 1 + (2\pi/3)\rho \sum_{a,b} x_a x_b \alpha_{ab}(\sigma^{HS}_{ab})^3 g^{HS}_{ab}(\sigma^{HS}_{ab}), \tag{2.5}$$

where $\rho = N/V$ is the number density and $x = N_a/N$ is the mole fraction of species a.

Here $\sigma_{ab}^{HS} = \sigma_{ab} K_{ab}^{1/3}$ is the effective diameter of the HS molecule of species a and b. In eq. (2.5), the shape factor α_{ab} is define as [5,6]

$$\alpha_{ab} = R_{ab} S_{ab} / 3 v_{ab}^{m}, \tag{2.6}$$

where $v_{ab}^{m} = (\pi/6)(\sigma_{ab}^{HS})$ is the volume, S_{ab} is the surface and R_{ab} the mean radius of curvature of species a and b.

3. Equation of State of Dense Hard-Core Fluid Mixture

Eq. (2.5) can be used to estimate the equation of state for the dense HCB fluid mixture. It is valid for both additive and non-additive hard-core molecules.

3.1 Additive Fluid Mixture

We extend the van der Waals one (vdW1) fluid theory of mixture to the hard-body mixture. In this theory, we approximates the properties of a mixture by those of a fictitious hard-body fluid with the following parameters [5,9]

$$(\sigma_0^{HS})^3 = \sum_{a,b} x_a x_b (\sigma_{ab}^{HS})^3, \tag{3.1a}$$

$$\alpha_0 (\sigma_0^{HS})^3 = \sum_{a,b} x_a x_b \alpha_{ab} (\sigma_{ab}^{HS})^3. \tag{3.1b}$$

In the vdW1 theory of mixture, it is assumed that

$$g_{ab}^{HS}(\sigma_{ab}^{HS}) = g^{HS}(\sigma_0^{HS}) \tag{3.2}$$

for all a and b, where $g^{HS}(\sigma_0^{HS})$ is the RDF of the HS fluid at the contact with the effective diameter $\sigma_0^{HS} = K_0^{1/3}\sigma_0$. Then eq. (2.5) can be written as

$$\beta P/\rho = 1 + \alpha_0 \left(\frac{\beta P^{HS}}{\rho} - 1 \right), \tag{3.3}$$

where $\beta P^{HS}/\rho$ is the equation of state of the HS fluid, given by [5]

$$\beta P^{HS}/\rho = (1 + \eta_0 + \eta_0^2 - \eta_0^3)/(1-\eta_0)^3, \tag{3.4}$$

where

$$\eta_0 = (\pi/6)\rho(\sigma_0^{HS})^3 = (\pi/6)\rho \sum x_a x_b K_{ab} (\sigma_{ab}^{0})^3, \tag{3.5}$$

and α_0 is obtained from Eq. (3.1).

For the binary mixture of additive HCB, η_0 can be expressed as

$$\eta_0^a = \eta[1 + x_1 x_2 (2K_{12}\sigma_{12}^{0^3} - K_{11}\sigma_{11}^{0^3} - K_{22}\sigma_{22}^{0^3})/(x_1 x_{11}\sigma_{11}^{0^3} + x_2 K_{22}\sigma_{22}^{0^3})], \tag{3.6}$$

where

$$\eta_0 = (\pi/6)\rho(x_1 K_{11}\sigma_{11}^{0^3} + x_2 K_{22}\sigma_{22}^{0^3})^3. \tag{3.7}$$

When applying the theory, we first define the corresponding HGO for a given HDB such that $\sigma^0_{HGO} = \sigma^0_{HDB}$ and $\nu_{HGO} = \nu_{HDB}$. Then K is given by

$$K = 1 + (3L*/2) - (L*^3/2). \tag{3.8}$$

Table 1. The equation of state $\beta P/\rho$ of the fluid mixture of the additive HDB for different values of x_1 under different conditions

Condition	L^*_{11}/L^*_{22}	η	Method	$\beta P/\rho$		
				$x_1 = 0.25$	$x_1 = 0.50$	$x_1 = 0.50$
$\sigma^0_{11} = \sigma^0_{22}$	0.6/0.0	0.30	Theory		4.15	
			Exact [1]		4.20	
		0.45	Theory	9.52	9.89	10.48
			Exact [1]	9.78	10.15	10.76
$\nu_1 = \nu_2$	0.6/0.0	0.30	Theory	4.16		
			Exact [1]	4.25		
		0.45	Theory	9.49	9.99	10.50
			Exact [1]	9.76	10.27	10.82
	0.6/0.3	0.30	Theory	4.23		
			Exact [1]	4.30		
		0.45	Theory	10.12		
			Exact [1]	10.52		

We calculate the equation of state $\beta P/\rho$ of fluid mixture of the additive HDB at $x_1 = 0.25$, 0.50 and 0.75 under the conditions of (i) $\sigma^0_{11} = \sigma^0_{22}$ and (ii) $\nu_1 - \nu_2$. The calculated results are compared with the 'exact' simulation data [1] in Table 1. The agreement is good.

3.2 Non-additive Fluid Mixture

For the non-additive HCB fluid mixture, Eq. (2.5) can be written as

$$\beta(P - P^a)/\rho = (4\pi/3)x_1 x_2 \alpha_{12}\rho\left[(\sigma_{12}^{HS})^3 g_{12}^{HS}(\sigma_{12}^{HS}) - (\sigma_{12}^{HSa})^3 g_{12}^{HSa}(\sigma_{12}^{HSa})\right], \tag{3.9}$$

where P^a is the pressure of the additive fluid mixture and the superscript 'HSa' refers to the properties of the additive HS mixture. Eq. (3.9) can be written as

$$\beta(P - P^a)/\rho = \alpha_{12}\beta(P^{HS} - P^{HSa})/\rho, \tag{3.10}$$

where $\beta P^{HS}/\rho$ is the equation of state for the non-additive HS fluid mixture, which is given by [7, 8]

$$\beta(P^{HS} - P^{HSa})/\rho = 24x_1x_2\eta_a \left[\frac{1}{(1-\eta)^2} + \frac{6\xi\mu}{(1-\eta)^3}\right]\Delta + 0(\Delta^2), \tag{3.11}$$

where

$$\eta_a = (\pi/6)\rho(\sigma_{12}^{HSa})^3 = (\pi/6)\rho K_{12}(\sigma_{12}^{a})^3, \tag{3.12}$$

$$\eta = (\pi/6)\rho[x_1K_{11}(\sigma_{11}^{0})^3 + x_2K_{22}(\sigma_{22}^{0})^3], \tag{3.13}$$

$$\xi = (\pi/6)\rho[x_1K_{11}^{2/3}(\sigma_{11}^{0})^2 + x_2K_{22}^{2/3}(\sigma_{22}^{0})^2], \tag{3.14}$$

$$\mu = (K_{11}K_{22})^{1/3}\sigma_{11}^{0}\sigma_{22}^{0}/(K_{11}^{1/3}\sigma_{11}^{0} + K_{22}^{1/3}\sigma_{22}^{0}). \tag{3.15}$$

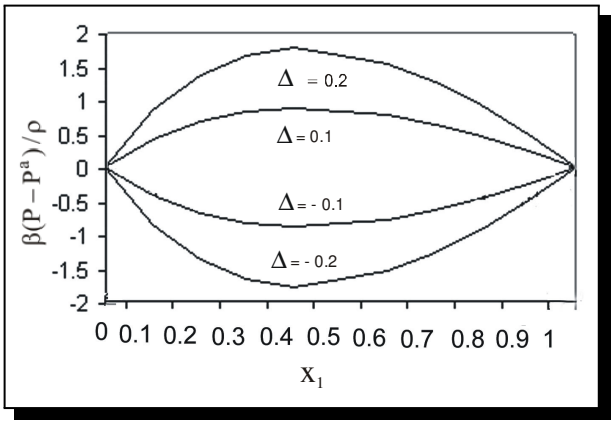

Figure 1. $\beta(P - P^a)/\rho$ of the non additive HDB fluid mixture as a function of the mole fraction x_1 at $\eta = 0.3$ for $\sigma_{11}^0 = \sigma_{22}^0$ and for $L_{11}^*/L_{22}^* = 0.6/0.0$

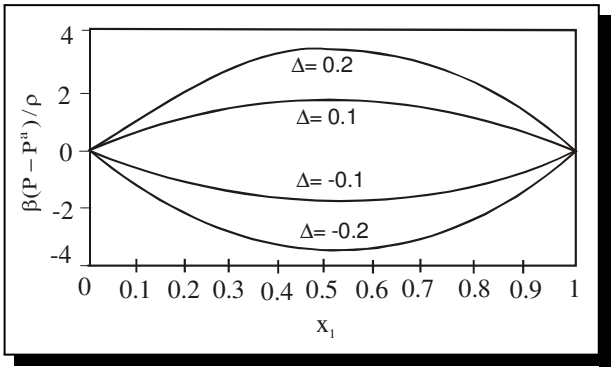

Figure 2. $\beta(P - P^a)/\rho$of the non-additive HDB fluid mixture as a function of the mole fraction x_1 at $\eta = 0.3$ for $\nu_1 = \nu_2$ and for $L_{11}^*/L_{22}^* = 0.6/0.0$

The excess equation of state, $\beta(P - P^a)/\rho$, of the non-additive HDB fluid mixture (Relative to the additive HDB fluid mixture) is calculated at $\eta = 0.3$ for $L_{11}^*/L_{22}^* = 0.6/0.0$ for different values

of Δ. It is shown in Figures 1 and 2, respectively for $\sigma_{11}^0 = \sigma_{22}^0$ and $\nu_1 = \nu_2$ as a function of x_1. They are zero at $x_1 = 0.0$ and 1.0 and finite in the intermediate range of x_1.

We calculate the equation of state, $\beta P/\rho$, of the equimolar fluid mixture of the non-additive HDB under the conditions of (i) $\sigma_{11}^0 = \sigma_{22}^0$ and (ii) $\nu_1 = \nu_2$ for different values of Δ. The calculated results are reported in Table 2. They increase with increase of Δ.

Table 2. The equation of state $\beta P/\rho$ of the equimolar fluid mixture of the non-additive HDB under different conditions and different values of Δ

Condition	L_{11}^*/L_{22}^*	η	$\beta P/\rho$				
			Δ	−0.3	−0.1	0.0	0.1	0.3
$\sigma_{11}^0 = \sigma_{22}^0$	0.6/0.0	0.30		1.67	3.32	4.15	4.98	6.29
		0.45		0.82	6.87	9.89	12.91	18.96
	0.6/0.3	0.30		1.51	3.32	4.23	5.14	6.95
		0.45		0.11	6.78	10.11	13.44	20.10
$\nu_1 = \nu_2$	0.6/0.0	0.30		−1.21	2.37	4.16	5.95	9.53
		0.45		−68.83	−16.28	9.99	36.26	88.81
	0.6/0.3	0.30		0.76	3.07	4.23	5.39	7.70
		0.45		−2.62	5.87	10.12	14.37	22.86

4. Conclusions

The purpose of the present work is to calculate the equation of state of the non-additive HCB fluid mixture. The theory is extension of the previous work for the additive HCB fluid mixture [5]. It is found that the properties depend on the conditions shape parameters L_{11}^*, L_{22}^*, mole fractions x_1, x_2 and non-additivity Δ in general and on packing fraction η. The theory is applied to the HDB fluid mixture. For the additive HDB fluid mixture the agreement with the simulation data is found to be good.

Competing Interests

The author declares that he has no competing interests.

Authors' Contributions

The author wrote, read and approved the final manuscript.

References

[1] T. Boublik and I. Nezbeda, P-V-T Behaviour of hard-body fluids, Theory and experiment, *Collect. Czech. Chem. Commun.* **51**, 230 (1986).

[2] T.P. Singh, J.P. Sinha and S.K. Sinha, Equilibrium properties of hard non-sphere fluids, *Pramana – J. Phys.* **31**, 289 (1988).

[3] R. Kumari and S.K. Sinha, Quantum corrections to thermodynamics of hard Gaussian-overlap fluid mixtures, *Physica* **A211**, 43 (1994).

[4] T.K. Dey, S.C. Singh and S.K. Sinha, Quantum corrections to equation of state of fluid mixtures of hard non-spherical molecules, *Indian J. Phys.* **77B**, 291 (2003).

[5] J. Kumar, T.K. Dey and S.K. Sinha, Semiclassical statistical mechanics of hard-body fluid mixtures, *J. Chem. Phys.* **122**, 224504 (2005).

[6] M.J. Maeso and J.R. Solana, An accurate equation of state for fluids of linear homonuclear fused hard spheres, *J. Chem. Phys.* **101**, 9864 (1994).

[7] U.N. Singh and S.K. Sinha, Equilibrium properties of a non-additive hard-sphere mixture in the semiclassical limit, *J. Chem. Phys.* **78**, 3191 (1983).

[8] S.H. Lee, *Bull. Kor. Chem. Soc.*, **28**, 1371 (2007).

[9] G.A. Fernandez, J. Vrabec and H. Hasse, *H. Mol. Sim.* **31**, 787 (2005).