

## Thermodynamics of polar fluid mixtures of hard non-spherical molecules

Shiv Pujan Singh and Suresh K Sinha\*

Department of Physics, L. S. College,  
B. B. A. Bihar University, Muzaffarpur-842 001, Bihar, India

Received 27 May 2002, accepted 22 May 2003

**Abstract** The problem of calculating the thermodynamic properties of polar fluid mixtures of hard non-spherical molecules is studied. Explicit analytic expressions for the virial coefficients and Helmholtz free energy are given. Numerical results are estimated for the third virial coefficient, equation of state and excess internal energy of quadrupolar hard gaussian overlap fluid mixtures. They are found to depend on the conditions and shape parameters.

**Keywords** Polar fluid mixture, virial coefficients, equations of state

**PACS Nos.** 61.25.Em, 64.10.+h, 31.15.Md, 05.70.Cc

The present work is concerned with the thermodynamic properties of polar fluid mixtures of hard non-spherical molecules. The hard Gaussian overlap (HGO) model has been used by many authors for molecular fluids of hard non-spherical molecules [1]. This is because the HGO model has a close connection with the hard ellipsoid of revolution (HER) and is a useful reference system for molecular fluids of non-spherical molecules.

Considerable progress has been made in the study of molecular fluids and fluid mixtures of the HGO molecules with imbedded point dipoles and quadrupoles [2-4]. However, no attempt has been made to investigate the equation of state of hard non-spherical molecular fluid mixture with electrostatic interactions.

In the present work, we calculate the equation of state and other thermodynamic properties of a polar HGO fluid mixture. We employ the perturbation theory, where the HGO model is taken as a reference and electrostatic interaction as a perturbation.

We consider a fluid mixture of non-spherical molecules interacting via the pair potential written as

$$u_{\alpha\beta}(r\omega_1\omega_2) = u_{\alpha\beta}^{HGO}(r\omega_1\omega_2) + u_{\alpha\beta}^{ES}(r\omega_1\omega_2), \quad (1)$$

where  $u_{\alpha\beta}^{HGO}$  is the hard Gaussian overlap (HGO) potential and  $u_{\alpha\beta}^{ES}$  is the electrostatic potential acting between two molecules of species  $\alpha$  and  $\beta$ . Here  $r = |r_1 - r_2|$  is the centre-to-centre distance and  $\omega_i$  represents the orientational coordinate of molecule  $i$ . The HGO potential is defined as

$$u_{\alpha\beta}^{HGO}(r\omega_1\omega_2) = \begin{cases} \infty, & r < \sigma_{\alpha\beta}(\omega_1\omega_2), \\ 0, & r \geq \sigma_{\alpha\beta}(\omega_1\omega_2), \end{cases} \quad (2)$$

where  $\sigma_{\alpha\beta}(\omega_1\omega_2)$  is the distance of closest approach between two molecules of species  $\alpha$  and  $\beta$  and is expressed in terms of the Euler angles [5] as

$$\sigma_{\alpha\beta}(\omega_1\omega_2) = \sigma_{\alpha\beta}^0 \left[ 1 - \chi_{\alpha\beta} (\cos^2 \theta_1 + \cos^2 \theta_2 - 2\chi_{\alpha\beta} \cos \theta_1 \cos \theta_2 \cos \theta_{12}) / (1 - \chi_{\alpha\beta}^2 \cos^2 \theta_{12}) \right]^{-1/2}. \quad (3)$$

Here  $\sigma_{\alpha\beta}^0$  is a width and  $\chi_{\alpha\beta}$  is the shape parameter defined by

$$\chi_{\alpha\beta} = (K_{\alpha\beta}^2 - 1) / (K_{\alpha\beta}^2 + 1). \quad (4)$$

\*Corresponding Author

Address for correspondence ; Ramani Mohan Garden, Kalambag Road Chowk, Muzaffarpur-842 002, Bihar, India

$K_{\alpha\beta}$  being the length-to-breadth ratio of the molecule. The effective values of  $\sigma_{\alpha\beta}^0$  and  $K_{\alpha\beta}$  between the HGO molecules of unlike species can be given by [6]

$$\sigma_{12}^0 = (\sigma_{11}^0 + \sigma_{22}^0) / 2, \quad (5a)$$

$$K_{12} = (K_{11} \sigma_{11}^0 + K_{22} \sigma_{22}^0) / (\sigma_{11}^0 + \sigma_{22}^0). \quad (5b)$$

$u_{\alpha\beta}^{ES}$  of eq.(1) is the electrostatic interaction due to the permanent multipole moments [1,7]

$$\begin{aligned} u_{\alpha\beta}^{ES}(r\omega_1\omega_2) &= (\mu_\alpha\mu_\beta / r^3) \phi_{\alpha\beta}^{dd}(\omega_1\omega_2) + (3/4 r^2) \\ &[\mu_\alpha Q_\beta \phi_{\alpha\beta}^{dq}(\omega_1\omega_2) + \mu_\beta Q_\alpha \phi_{\alpha\beta}^{dq}(\omega_1\omega_2)] \\ &+ (3/4) (Q_\alpha Q_\beta / r^5) \phi_{\alpha\beta}^{qq}(\omega_1\omega_2). \end{aligned} \quad (6)$$

Here,  $\phi_{\alpha\beta}$  are angle-dependent part of interactions.  $\mu_\alpha$  and  $Q_\alpha$  are, respectively, the dipole moment and quadrupole moment of a molecule of species  $\alpha$ .

Using this division of the pair potential where the HGO potential is taken as a reference, the perturbation expansion of the residual Helmholtz free energy can be written as

$$\begin{aligned} [A - A^*] / NkT &= ([A^{HGO} - A^*] / NkT) + (A_2^{ES} / NkT) \\ &+ (A_3^{ES} / NkT) + \dots, \end{aligned} \quad (7)$$

where  $A^*$  represents the Helmholtz free energy of an ideal gas and  $A^{HGO} - A^*$  the residual free energy of the reference (HGO) fluid mixture.  $A_n^{ES}$  is the n-th order perturbation term due to the electrostatic interactions. Analytic expressions of  $A_2^{ES}$  and  $A_3^{ES}$  are given by Gokhul and Sinha [4].

The total electrostatic contribution to the Helmholtz free energy is obtained from the Pade' approximant [8]

$$\Delta A^{ES} = A_2^{ES} / (1 - A_3^{ES} / A_2^{ES}). \quad (8)$$

Then the total residual Helmholtz free energy of the polar HGO fluid mixture is given as

$$[A - A^*] / NkT = ([A^{HGO} - A^*] / NkT) + (\Delta A^{ES} / NkT). \quad (9)$$

The other thermodynamic properties such as the equation of state  $P / \rho kT$  and excess internal energy  $U - U^*$  can be obtained from the respective derivative of  $A$ .

The equation of state for the polar HGO fluid mixture, obtained from eq.(7), can be expressed in the virial form *i.e.* in the power of  $\rho$

$$P / \rho kT = A + B\rho + C\rho^2, \quad (10)$$

where  $A = 1$ ,  $B$  and  $C$  are the second and third virial coefficient, respectively. For the fluid mixture they are expressed as

$$B = \sum_{\alpha\beta} x_\alpha x_\beta B_{\alpha\beta}, \quad (11)$$

$$C = \sum_{\alpha,\beta,\gamma} x_\alpha x_\beta x_\gamma C_{\alpha\beta\gamma}, \quad (12)$$

where  $x_\alpha = N_\alpha / N$  is the concentration of species  $\alpha$ .

In order to obtain expressions for  $B_{\alpha\beta}$  and  $C_{\alpha\beta\gamma}$ , the radial distribution function (RDF)  $g_{\alpha\beta}^{HS}(r)$  of the hard sphere fluid mixture is expanded in powers of  $\rho$  as [9]

$$g_{\alpha\beta}^{HS}(r) = \exp[-\beta u_{\alpha\beta}^{HS}(r)] \{ 1 + \rho \sum_\gamma x_\gamma a_{\alpha\beta\gamma}^{HS}(r) + \dots \} \quad (13)$$

where  $a_{\alpha\beta}^{HS}(r)$  is the cluster integral for the hard sphere (HS) mixture of the effective diameter  $d_{\alpha\beta} = K_{\alpha\beta}^{1/3} \sigma_{\alpha\beta}^0$  and  $\rho = N/V$  is the number density. An analytic expression for  $a_{\alpha\beta}^{HS}(r^*)$  is given by [10]

$$\begin{aligned} a_{\alpha\beta}^{HS}(r) &= (2\pi/3) [(d_{\alpha\gamma}^3 + d_{\beta\gamma}^3) - (3/4)(d_{\alpha\gamma}^2 + d_{\beta\gamma}^2)r \\ &+ (1/8)r^3 - (3/8)(d_{\alpha\gamma}^2 + d_{\beta\gamma}^2)^2 / r \\ &\text{for } d_{\alpha\beta} \leq r \leq d_{\alpha\gamma} + d_{\beta\gamma}, \\ &= 0 \quad \text{for } r > d_{\alpha\gamma} + d_{\alpha\beta} + d_{\beta\gamma}. \end{aligned} \quad (14)$$

Substituting eq.(13) in eq.(7), we obtain expressions for  $B_{\alpha\beta}$  and  $C_{\alpha\beta\gamma}$ . Thus, the second virial coefficient  $B_{\alpha\beta}$  can be written as

$$B_{\alpha\beta} = B_{\alpha\beta}^{HGO} + B_{\alpha\beta}^2 + B_{\alpha\beta}^3 + \dots \quad (15)$$

Here,  $B_{\alpha\beta}^{HGO}$  is the second virial coefficient of the HGO fluid mixture which is expressed as [11]

$$B_{\alpha\beta}^{HGO} = (1/2) [v_\alpha + v_\beta + R_\alpha L_\beta + R_\beta L_\alpha] \quad (16)$$

giving

$$B_{11}^{HGO} = v_1 + R_1 L_1 = v_1 [1 + 3\alpha_1] \quad (17)$$

and

$$\begin{aligned} B_{12}^{HGO} &= (1/2) [v_1 + v_2 + R_1 L_2 + R_2 L_1] \\ &= (1/2) B_{11}^{HGO} + (1/2) B_{22}^{HGO} + \Delta B^{HGO} \end{aligned} \quad (18)$$

with

$$\Delta B = (3/2) v_1 \alpha_1 [(R_2 / R_1) - 1] + (3/2) v_2 \alpha_2 [(R_1 / R_2) - 1]. \quad (19)$$

Here,  $R_\alpha$  is the  $(1/4\pi)$  multiple of the mean curvature integral,  $L_\alpha$  the surface integral and  $v_\alpha$  is the volume of the HGO molecule of species  $\alpha$ .  $\alpha_\alpha = R_\alpha L_\alpha / 3v_\alpha$  is the shape parameter of the molecule of species  $\alpha$ .  $B_{\alpha\beta}^2$  and  $B_{\alpha\beta}^3$  are, respectively, the second and third order perturbation terms due to the electrostatic interaction. They are given by

$$B_{\alpha\beta}^2 = -(2\pi/3) \sigma_{\alpha\beta}^{03} \left[ (1/2) (\mu_{\alpha\beta}^{*2})^2 J_{\alpha\beta}^6 + (27/40) (\mu_{\alpha\beta}^* Q_{\alpha\beta}^*)^2 J_{\alpha\beta}^8 + (27/224) (Q_{\alpha\beta}^{*2})^2 J_{\alpha\beta}^{10} \right], \quad (20)$$

$$B_{\alpha\beta}^3 = (2\pi/3) \sigma_{\alpha\beta}^{01} \left[ (9/64) (\mu_{\alpha\beta}^{*2})^2 (Q_{\alpha\beta}^{*2}) (J_{\alpha\beta}^{11(1)} + J_{\alpha\beta}^{11(2)}) + (81/320) (\mu_{\alpha\beta}^{*2}) (Q_{\alpha\beta}^{*2})^2 J_{\alpha\beta}^{13} + (9/512) (Q_{\alpha\beta}^{*2})^3 J_{\alpha\beta}^{15} \right], \quad (21)$$

where

$$\sigma_{\alpha\beta}^{nm} = \left\langle \phi_{\alpha\beta}^m(\omega_1, \omega_2) \left[ \sigma_{\alpha\beta}(\omega_1, \omega_2) / \sigma_{\alpha\beta}^0 \right]^{-nm+1} \right\rangle$$

$$\mu_{\alpha\beta}^{*2} = \mu_\alpha \mu_\beta / kT \sigma_{\alpha\beta}^{01},$$

$$Q_{\alpha\beta}^{*2} = Q_\alpha Q_\beta / kT \sigma_{\alpha\beta}^{01}.$$

The third virial coefficient can be expressed in a similar way

$$C_{\alpha\beta\gamma} = C_{\alpha\beta\gamma}^{HGO} + C_{\alpha\beta\gamma}^2 + C_{\alpha\beta\gamma}^3 + \dots, \quad (22)$$

where  $C_{\alpha\beta\gamma}^{HGO}$  is the third virial coefficient of the HGO fluid mixture, and  $C_{\alpha\beta\gamma}^2$  and  $C_{\alpha\beta\gamma}^3$  are, respectively, the second and third order perturbation terms due to the electrostatic interactions.  $C_{\alpha\beta\gamma}^{HGO}$  is expressed as [11,12]

$$C_{\alpha\beta\gamma}^{HGO} = (1/3) \left[ v_\alpha v_\beta + v_\beta v_\gamma + v_\alpha v_\gamma \right] + \left[ v_\alpha (R_\beta L_\gamma + R_\gamma L_\beta) + v_\beta (R_\gamma L_\alpha + R_\alpha L_\gamma) + v_\gamma (R_\alpha L_\beta + R_\beta L_\alpha) \right] + (1/3) \left[ R_\alpha^2 L_\beta L_\gamma + R_\beta^2 L_\gamma L_\alpha + R_\gamma^2 L_\alpha L_\beta \right]. \quad (23)$$

The second order perturbation correction  $C_{\alpha\beta\gamma}^2$  can be written as

$$C_{\alpha\beta\gamma}^2 = -(2\pi/3) \left[ \sigma_{\alpha\beta}^{01} N_{\alpha\beta}^2 + \sigma_{\alpha\gamma}^{01} N_{\alpha\gamma}^2 + \sigma_{\beta\gamma}^{01} N_{\beta\gamma}^2 \right], \quad (24)$$

where

$$N_{\alpha\beta\gamma}^2 = \left[ (\mu_{\alpha\beta}^{*2})^2 J_{\alpha\beta}^6 Y_{\alpha\beta}^2 + (3\mu_{\alpha\beta}^* Q_{\alpha\beta}^* / 2)^2 J_{\alpha\beta}^8 Y_{\alpha\beta}^8 + (3Q_{\alpha\beta}^{*2} / 4)^2 J_{\alpha\beta}^{10} Y_{\alpha\beta}^{10} \right] \quad (25)$$

with

$$Y_{\alpha\beta}^n = \int_1^\infty \exp \left[ -\beta u_{\alpha\beta}^{HS}(r^*) \right] a_{\alpha\beta}^{HS}(r^*) (r^*)^{-n+2} dr^*. \quad (26)$$

Here,  $a_{\alpha\beta}^{HS}(r^*)$  is given by eq (14). Substituting eq.(14) in eq.(26), we can obtain  $Y_{\alpha\beta}^n$  for  $n \geq 6$ .

The third order perturbation correction  $C_{\alpha\beta\gamma}^3$  can be written as

$$C_{\alpha\beta\gamma}^3 = C_{\alpha\beta\gamma}^{32} + C_{\alpha\beta\gamma}^{33}, \quad (27)$$

where

$$C_{\alpha\beta\gamma}^{32} = (2\pi/3) \left[ \sigma_{\alpha\beta}^{01} N_{\alpha\beta}^3 + \sigma_{\alpha\gamma}^{01} N_{\alpha\gamma}^3 + \sigma_{\beta\gamma}^{01} N_{\beta\gamma}^3 \right] \quad (28)$$

with

$$N_{\alpha\beta\gamma}^3 = \left[ 3 \left\{ (\mu_{\alpha\beta}^{*2})^2 (3Q_{\alpha\beta}^{*2} / 4) J_{\alpha\beta}^{11(1)} + (\mu_{\alpha\beta}^{*2}) (3\mu_{\alpha\beta}^* Q_{\alpha\beta}^* / 2)^2 J_{\alpha\beta}^{11(2)} \right\} Y_{\alpha\beta}^{11} + 3(\mu_{\alpha\beta}^{*2}) (3Q_{\alpha\beta}^{*2} / 4)^2 J_{\alpha\beta}^{13} Y_{\alpha\beta}^{13} + (3Q_{\alpha\beta}^{*2} / 4)^3 J_{\alpha\beta}^{15} Y_{\alpha\beta}^{15} \right], \quad (29)$$

$$C_{\alpha\beta\gamma}^{33} = (8\pi^2/3) \left( \sigma_{\alpha\beta}^{01} \sigma_{\beta\gamma}^{01} \sigma_{\alpha\gamma}^{01} \right) \left[ (\mu_{\alpha\beta}^{*2} \mu_{\beta\gamma}^{*2} \mu_{\alpha\gamma}^{*2}) T_{\alpha\beta\gamma}^{\mu\mu\mu} + 3(\mu_{\alpha\beta}^{*2} \mu_{\beta\gamma}^{*2} (3Q_{\alpha\gamma}^{*2} / 4)) T_{\alpha\beta\gamma}^{\mu\mu Q} + 3(\mu_{\alpha\beta}^{*2} (3Q_{\beta\gamma}^{*2} / 4) (3Q_{\alpha\gamma}^{*2} / 4)) T_{\alpha\beta\gamma}^{\mu Q Q} + ((3Q_{\alpha\beta}^{*2} / 4) (3Q_{\beta\gamma}^{*2} / 4) (3Q_{\alpha\gamma}^{*2} / 4)) T_{\alpha\beta\gamma}^{Q Q Q} \right], \quad (30)$$

where

$$T_{\alpha\beta\gamma}^{nmp} = \iiint_{\Delta} M_{\alpha\beta\gamma}^{nmp} \exp \left[ -\beta \left\{ u_{\alpha\beta}^{HS}(r_{12}^*) + U_{\beta\gamma}^{HS}(r_{23}^*) + u_{\alpha\gamma}^{HS}(r_{13}^*) \right\} \right] (r_{12}^*)^{-n+1} (r_{23}^*)^{-m+1} (r_{13}^*)^{-p+1} dr_{12}^* dr_{23}^* dr_{13}^*, \quad (31)$$

$$M_{\alpha\beta\gamma}^{nmp} = (4\pi)^{-3} \iiint \Psi_{\alpha\beta}^n(\omega_1, \omega_2) \Psi_{\beta\gamma}^m(\omega_1, \omega_2) \Psi_{\alpha\gamma}^p(\omega_1, \omega_2) d\omega_1 d\omega_2 d\omega_3 \quad (32a)$$

and

$$\Psi_{\alpha\beta}^n(\omega_i, \omega_j) = \phi_{\alpha\beta}(\omega_i, \omega_j) \left[ \sigma_{\alpha\beta}(\omega_i, \omega_j) / \sigma_{\alpha\beta}^0 \right]^{-n+2}. \quad (32b)$$

Here,  $\Delta$  denotes integration over  $r_{12}^*$ ,  $r_{23}^*$  and  $r_{13}^*$ , which form a triangle. It can be approximately written as [4]

$$\Psi_{\alpha\beta}^n(\omega_i, \omega_j) \approx K_{\alpha\beta}^{-(n-2)/3} \phi_{\alpha\beta}(\omega_i, \omega_j). \quad (33)$$

Under this approximation, eq.(31) can be written as

$$T_{\alpha\beta\gamma}^{nmp} \approx K_{\alpha\beta}^{(n-2)/3} K_{\beta\gamma}^{-(m-2)/3} K_{\alpha\gamma}^{-(p-2)/3} T_{\alpha\beta\gamma}^{nmp}(HS). \quad (34)$$

$T_{\alpha\beta\gamma}^{nmp}(HS)$  is the three-body integral for the hard sphere (HS) fluid mixture. We adopt the van der Waals one (vdW1) fluid theory of mixture [6,13], which approximates the properties of a mixture by those of a fictitious pure fluid with the interaction parameter

$$\sigma_0^3 = \sum_{\alpha\beta} \lambda_\alpha \lambda_\beta \sigma_{\alpha\beta}^0. \quad (35)$$

Then  $T_{\alpha\beta\gamma}^{nmp}(HS)$  can be expressed as

$$T_{\alpha\beta\gamma}^{nmp}(HS) = \left(\sigma_{\alpha\beta}^0 / \sigma_0\right)^{n-2} \left(\sigma_{\beta\gamma}^0 / \sigma_0\right)^{m-2} \left(\sigma_{\alpha\gamma}^0 / \sigma_0\right)^{p-2} T_0^{nmp}(HS). \quad (36)$$

The values of  $T_0(HS)$  for  $\mu - \mu - \mu$ ,  $\mu - \mu - Q$ ,  $\mu - Q - Q$  and  $Q - Q - Q$  interactions may be obtained by the method of Larsen *et al* [14]. Thus, the results are

$$T_{111}^{nmp} = K_{11}^{(n+m+p)/3+2} T_0^{nmp}(HS), \quad (37a)$$

$$T_{112}^{nmp} = K_{11}^{-(n-2)/3} K_{12}^{-(m+p-4)/3} \left(\sigma_{11}^0 / \sigma_0\right)^n \tau_{12}^0 / \sigma_0^{(m+p-4)} T_0^{nmp}(HS), \quad (37b)$$

$$T_{122}^{nmp} = K_{12}^{(n+p-4)/3} K_{22}^{-(m-2)/3} \left(\sigma_{22}^0 / \sigma_0\right)^m \left(\sigma_{12}^0 / \sigma_0\right)^{(n+p-4)} T_0^{nmp}(HS), \quad (37c)$$

$$T_{222}^{nmp} = K_{22}^{(n+m+p)/3+2} T_0^{nmp}(HS), \quad (37d)$$

where [14]

$$T_0^{\mu\mu\mu}(HS) = 0.0235,$$

$$T_0^{\mu\mu Q}(HS) = 0.0118,$$

$$T_0^{\mu Q Q}(HS) = 0.0118,$$

$$T_0^{Q Q Q}(HS) = 0.0155.$$

The knowledge of  $B_{\alpha\beta}^2$  and  $B_{\alpha\beta}^3$ , and  $C_{\alpha\beta}^2$  and  $C_{\alpha\beta}^3$  allows us to write the Pade' approximant [8], which may be employed to determine the whole polar contribution to the virial coefficients.

We first calculate the third virial coefficient of the mixture of hard dumbell (HDB) (with the site-site elongation  $L^* = (L / \sigma_0)$ ). When applying the proposed theory, we first define the corresponding HGO, for a given HDB, such that  $\sigma_{HGO}^0 = \sigma_{HDB}^0$  and  $v_{HGO} = v_{HDB}$  i.e.

$$(\pi/6)K\sigma_{HGO}^0 = (\pi/6)\sigma_{HDB}^0 \left[1 + 3L^*/2 - L^{*3}/2\right] \quad (38)$$

From this, one obtains  $K$  for a given value of  $L^*$ . We employ eq.(23) to calculate the third virial coefficient  $C_{\alpha\beta\gamma}^{HDB}$  for the mixture of the HDB. They are compared with the 'exact' simulation data [11,15] in Table 1. The agreement is fairly good except when  $L^*$  is large (i.e.  $L^* = 1.0$ ).

Next, we apply the theory to calculate the third virial coefficient  $C_{\alpha\beta\gamma}$  for some polar hard Gaussian overlap mixtures such as binary mixture of (i) hard Gaussian overlap (HGO) and dipole hard Gaussian overlap (DHGO) ( $\mu_1 = 0, \mu_1 = \mu$  and  $Q_1 = Q_1 = 0$ ) and (ii) hard Gaussian overlap (HGO) and quadrupole hard Gaussian overlap (QHGO) ( $\mu_1 = \mu_2 = 0$  and  $Q_1 = 0, Q_2 = Q$ ). In both these cases, the electrostatic contribution to  $C_{111}$  and  $C_{112}$  are zero, while finite and negative for  $C_{122}$  and  $C_{222}$ .

**Table 1.** Comparison of the third virial coefficient  $C_{\alpha\beta\gamma} / \sigma_{11}^0$  of mixture of the hard dumbell ( $L_i^* = L_i / \sigma_0^0$ ) with exact results

Condition	$L_1^* / L_2^*$	$C_{111}^{HDB} / \sigma_{12}^0$		$C_{112}^{HDB} / \sigma_{12}^0$		$C_{122}^{HDB} / \sigma_{12}^0$		$C_{222}^{HDB} / \sigma_{12}^0$	
		Theory	Exact	Theory	Exact	Theory	Exact	Theory	Exact
$\sigma_{11}^0 = \sigma_{12}^0$	0.6 / 0.0	10.17	10.64	6.42	6.82	4.05	4.34	2.74	2.74
	0.6 / 0.3	10.17	10.64	8.47	8.78	7.19	7.22	5.98	5.93
	1.0 / 0.0	13.43	18.68	7.82	9.88	4.80	5.22	2.74	2.74
	1.0 / 0.6	13.43	18.68	12.21	15.47	11.19	12.85	10.17	10.64
$v_1 = v_2$	0.6 / 0.0	5.52	5.77	5.26	5.43	5.00	5.08	4.78	4.78
	1.0 / 0.0	6.45	8.98	6.04	7.50	5.63	6.29	5.27	5.27
$v_1 = (2/3)v_2$	0.6 / 0.0	3.49	3.65	4.44	4.54	5.39	5.57	6.79	6.79
	1.0 / 0.0	4.05	5.64	5.07	6.24	6.02	6.85	7.44	7.44

We have calculated  $C_{\alpha\beta\gamma}$  for mixture of (i) HGO and DHGO and (ii) HGO and QHGO, having the same diameter is  $\sigma_{11}^0 = \sigma_{22}^0$ . They are reported in Figures 1 and 2 as a function of  $\mu^{*2}/Q^{*2}$  for  $K_1/K_2 = 1.792/1.0$  and  $1.792/1.436$ , respectively.  $C_{111}$  and  $C_{112}$  do not depend on  $\mu^{*2}/Q^{*2}$  and not shown in figures, while  $C_{122}$  and  $C_{222}$  decrease with increase of  $\mu^{*2}/Q^{*2}$  and shown in figures.

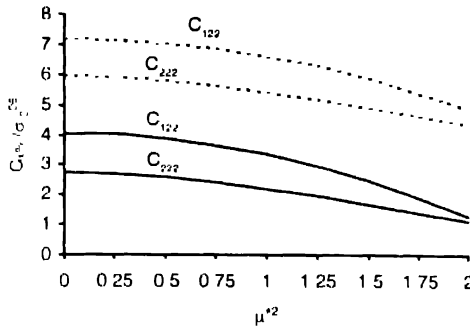


Figure 1. The third virial coefficient  $C_{\alpha\beta\gamma}$  of the binary mixture of HGO and DHGO with  $\sigma_{11}^0 = \sigma_{22}^0$  as a function of  $\mu^{*2}$ . The dotted line represents  $K_{11}/K_{22} = 1.792/1.436$  and thick line  $K_{11}/K_{22} = 1.792/1.0$ .

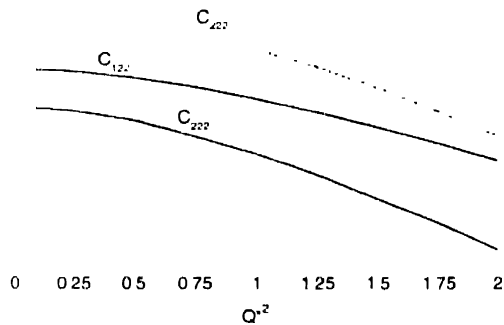


Figure 2. The third virial coefficient  $C_{\alpha\beta\gamma}$  of the binary mixture of HGO and DHGO with  $\sigma_{11}^0 = \sigma_{22}^0$  as a function of  $Q^{*2}$ . Key parameters are same as in Figure 1.

Next, we estimate the thermodynamic properties of the mixture of the HGO and QHGO ( $\mu_1 = \mu_2 = 0$  and  $Q_1 = 0, Q_2 = Q$ ). For this, we first consider the HGO fluid mixture.

Singh *et al* [6] used the extended van der Waals one (vdW1) fluid theory of mixture, which approximates the properties of a mixture by those of a fictitious hard-body fluid with the parameters

$$v_0 = \sum_{\alpha\beta} x_\alpha x_\beta v_{\alpha\beta} \quad (39a)$$

$$v_0 F^0(x) = \sum_{\alpha\beta} x_\alpha x_\beta v_{\alpha\beta} F_{\alpha\beta}^0 \quad (39b)$$

In case of the HGO fluid,  $v_{\alpha\beta} = \pi \sigma_{\alpha\beta}^3 K/6$  and

$$F_{\alpha\beta}^0 = \left(1 - \chi_{\alpha\beta}^2\right)^{-1/2} \left[1 - (1/6) \chi_{\alpha\beta}^2 - (1/40) \chi_{\alpha\beta}^4 - (1/112) \chi_{\alpha\beta}^6 - \dots\right] \quad (40)$$

In the vdW1 fluid theory of mixture, the pressure of the HGO fluid mixture can be given by [6]

$$P^{HGO} / \rho kT = 1 + (2\eta_0(2 - \eta_0) / (1 - \eta_0)^3) F^0(x) \quad (41)$$

where

$$\eta_0 = \rho v_0 = \rho \sum_{\alpha\beta} x_\alpha x_\beta v_{\alpha\beta} \quad (42)$$

which can be expressed for a binary mixture as

$$\eta_0 = \eta \left[1 + x_1 \lambda_2 (2v_{12} - v_{11} - v_{22}) / (x_1 v_{11} + \lambda_2 v_{12})\right] \quad (43)$$

with

$$\eta = \rho (x_1 v_{11} + \lambda_2 v_{12}) \quad (44)$$

Boublik and coworker [11,12] derived another expression for the equation of state for the HGO mixtures

$$P^{HGO} / \rho kT = 1 / (1 - \eta) + rs / \rho(1 - \eta)^2 + [qs^2(1 - 2\eta) + 5rs\eta^2] / 3\rho(1 - \eta)^3 \quad (45)$$

where

$$r = \sum_{\alpha} \rho_{\alpha} R_{\alpha} = \rho \sum_{\alpha} \lambda_{\alpha} R_{\alpha}$$

$$q = \sum_{\alpha} \rho_{\alpha} R_{\alpha}^2 = \rho \sum_{\alpha} x_{\alpha} R_{\alpha}^2 \quad (46)$$

$$s = \sum_{\alpha} \rho_{\alpha} L_{\alpha} = \rho \sum_{\alpha} x_{\alpha} L_{\alpha}$$

Table 2. The equation of state,  $P / \rho kT$  of the equimolar mixture of HDB under different conditions

Condition	$L_1^* / L_2^*$		$P / \rho kT$		
			Eq (41)	Eq (45)	Exact
$\sigma_{11}^0 = \sigma_{12}^0$	0.6 / 0.0	0.30	4.14	4.13	4.20
		0.45	9.36	9.80	10.15
	0.6 / 0.3	0.30	4.22	4.10	
		0.45	10.07	9.68	
$v_1 = v_2$	0.6 / 0.0	0.30	4.39	4.19	4.25
		0.45	10.85	9.47	10.27
	0.6 / 0.3	0.30	4.28	4.23	4.30
		0.45	10.28	10.08	10.52

To test the accuracy of the theory, we first calculate the equation of state  $P / \rho kT$  of the equimolar mixture of the HDB

using eqs.(41) and (45) for (i)  $\sigma_{11}^0 = \sigma_{22}^0$  and (ii)  $v_1 = v_2$ . The calculated results are compared with the 'exact' simulation data [11,15] in Table 2. The agreement with the simulation data is good. The results obtained by eqs.(41) and (45) are comparable to each other. In Table 3, we compare the equation of state  $P / \rho kT$  of the equimolar mixture of hard sphere (HS) and prolate spherocylinders (PSC) with  $\gamma = 2$  obtained with eqs.(41) and (45) with the 'exact' simulation data [11,16]. The results obtained by eq.(45) are in better agreement with the simulation results. We use eq.(45) for further calculation in the present work.

**Table 3.** The equation of state,  $P / \rho kT$  of the equimolar mixture of hard sphere and prolate spherocylinders with  $\gamma = 2$

Conditions		$P / \rho kT$		
		Eq (41)	Eq (46)	Exact
$\sigma_{11}^0 = \sigma_{12}^0$	0.20	2.63	2.51	2.50
	0.30	4.46	4.19	4.11
	0.40	7.90	7.35	7.31
	0.45	10.77	9.97	9.87
$V_{HS} = v_{PSC}$	0.20	2.68	2.53	2.52
	0.30	4.62	4.26	4.20
	0.40	8.40	7.79	7.39
	0.45	11.63	10.16	10.22

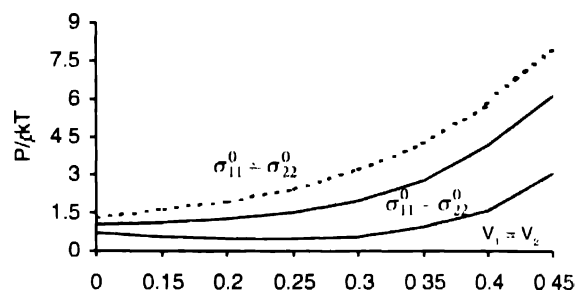
**Table 4.** Contribution of quadrupole interactions to the Helmholtz free energy of equimolar mixtures of the HGO and QHGO under different condition at  $\eta = 0.30$

$Q^{*2}$	$NkT$	$A_{32} / NkT$	$A_{33} / NkT$	$A_3 / NkT$	$\Delta A_{pade} / NkT$
$\sigma_{11}^0 = \sigma_{12}^0$					
0.50	-0.4970	0.0314	0.0003	0.0317	-0.4672
1.50	-4.4729	0.8477	0.0091	0.8568	-3.7538
$v_1 = v_2, K_1 / K_2 = 1.792/1.0$					
0.50	-0.7540	0.0314	0.0003	0.0317	-0.7236
1.50	-6.7857	0.8477	0.0091	0.8568	-6.0250
$\sigma_{11}^0 = \sigma_{22}^0, K_1 / K_2 = 1.792/1.4365$					
0.50	-0.1804	0.0034	0.0004	0.0038	-0.1767
1.50	-1.6234	0.0921	0.0111	0.1032	-1.5264
$v_1 = v_2, K_1 / K_2 = 1.792/1.4365$					
0.50	-0.2094	0.0040	0.0001	0.0041	-0.2054
1.50	-1.8848	0.1076	0.0039	0.1115	-1.7795

We estimate the contribution of the quadrupole interaction to the Helmholtz free energy of the equimolar binary mixture of the HGO and QHGO under two different conditions namely (i) when the diameters of each species are same (i.e.  $\sigma_{11}^0 = \sigma_{22}^0$ ) and (ii) when volume of each species are same (i.e.  $v_1 = v_2$ ). The results for  $\eta = 0.30$  are shown in Table 4. The magnitude of the

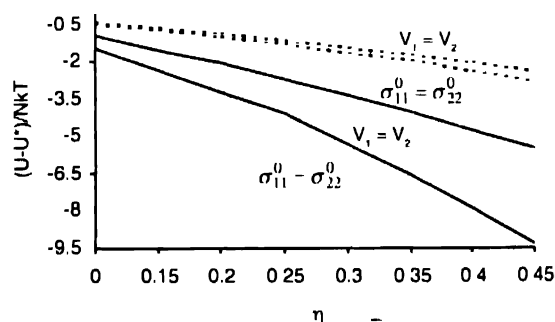
perturbation terms increases with increase of  $Q^{*2}$ . From the table, we find that the series is fast convergent and  $A_{33} \ll A_{32}$ . When  $\Delta A_{pade} / NkT$  is calculated with and without  $A_{33}$  term, the error is less than 1.0%. However, the relative contribution of the  $A_{33}$  term increase with increase of  $Q^{*2}$ .

We have calculated the equation of state  $P / \rho kT$  of the equimolar mixtures of the HGO and QHGO with  $Q^{*2} = 1.0$ . They are demonstrated as a function of  $\eta$  in Figure 3, for (i)  $\sigma_{11}^0 = \sigma_{22}^0$  and (ii)  $v_1 = v_2$  at  $K_{11} / K_{22} = 1.792/1.0$  and  $1.792/1.436$ . The value of  $P / \rho kT$  increases with increase of  $\eta$ .



**Figure 3.** The equation of state  $P / \rho kT$  of the equimolar mixture of HGO and QHGO with  $Q^{*2} = 1.0$  as a function of  $\eta$ . Key parameters are same as in Figure 1

In Figure 4, the excess internal energy  $(U - U^*) / NkT$  of the equimolar mixture of the HGO and QHGO with  $Q^{*2} = 1.0$  are reported as a function of  $\eta$ . The magnitude of  $(U - U_{HGO}) / NkT$  increases with increase of  $\eta$ .



**Figure 4.** The excess internal energy  $(U - U^*) / NkT$  of the equimolar mixture of HGO and QHGO with  $Q^{*2} = 1.0$  as a function of  $\eta$ . Key parameters are same as in Figure 1

The purpose of this work has been to develop a theory for evaluating the virial coefficients and thermodynamic properties of the polar HGO fluid mixtures. We have employed the perturbation theory where the HGO fluid mixture is taken as a reference and perturbation terms as a correction. We have derived explicit expressions for the virial coefficients and Helmholtz free energy for the polar HGO fluid mixtures. It is found that the contribution of the multipole interactions depends on the conditions, the shape parameter  $K$  and the concentration  $x_1, x_2$  in general and on the packing fraction  $\eta$  in particular

## References

- [1] C G Gray and K E Gubbins *Theory of Molecular Fluids* (Oxford · Clarendon) Vol.1 (1984)
- [2] T Boublik *Mol. Phys.* **69** 497 (1990)
- [3] T Boublik, C Vega, S Laga and M Siazpena *Mol. Phys.* **71** 1193 (1990)
- [4] S K Gokhul and S K Sinha *Pramana- J. Phys.* **56** 75 (1996)
- [5] B J Berne and P Pechukas *J Chem Phys* **56** 4213 (1972)
- [6] T P Singh, J P Sinha and S K Sinha *Pramana- J Phys* **31** 289 (1988)
- [7] J O Hirschfelder, C F Curtis and R B Bird *Molecular theory of gases and liquids* (New York · Wiley) (1954)
- [8] G Stell, J C Rasaiah and H Narang *Mol. Phys.* **27** 1393 (1974)
- [9] S A Rice and P Gray *The Statistical Mechanics of Simple Liquids* (New York · Interscience) (1965)
- [10] U N Singh and S K Sinha *J Chem Phys* **77** 5784 (1982)
- [11] T Boublik and I Nezbeda *Colln Czech Chem Commun* **51** 230 (1986)
- [12] T Boublik *Mol. Phys.* **42** 209 (1981)
- [13] T W Leland Jr., J S Rowlinson and G A Sether *Trans Faraday Soc* **64** 1447 (1968)
- [14] B Larsen, J C Rasaiah and G Stell *Mol. Phys.* **33** 987 (1977)
- [15] M Wojcik and K E Gubbins *Mol. Phys.* **49** 1401 (1983)
- [16] P A Monson and M Rigby *Mol. Phys.* **39** 977 (1980)