Pramāṇa - J. Phys., Vol. 28, No. 4, April 1987, pp. 343–353. © Printed in India.

Thermodynamic properties of molecular fluid mixtures of hard ellipsoids

A K SINGH,* U N SINGH and S K SINHA†

Department of Physics, L S College, Bihar University, Muzaffarpur 842001, India

*Permanent address: Department of Physics, S R K Goenka College, Sitamarhi 843 301, India

MS received 29 September 1986; revised 3 February 1987

Abstract. Thermodynamic properties of molecular fluid mixtures of hard ellipsoids are calculated. Numerical results are given for equation of state and excess-free energy of the binary mixture of both additive and non-additive hard ellipsoids. It is found that the equation of state and free energy of mixtures increase with increase of anisotropy parameter χ_0.

Keywords. Hard ellipsoid; equation of state; excess free energy; anisotropy; binary mixture.

PACS No. 61·25

1. Introduction

This paper is concerned with the evaluation of thermodynamic properties of a molecular fluid mixture, whose molecules interact via hard ellipsoid potential. We consider the case where the constituent molecules have the same length to width ratio χ_0.

Many theoretical attempts such as van der Waals one- and two-fluid theories (Leland *et al* 1968; Henderson and Leonard 1971a, b) and perturbation theory (Henderson and Barker 1968; Smith 1971; Smith and Henderson 1972) have been made to understand the structural and thermodynamic properties of simple atomic fluid mixture of hard spheres, where the length-to-width ratio χ_0 is unity. The basis of the perturbation theory is to expand the properties of a hard sphere mixture about that of a one-component fluid of hard spheres of diameter d_0 in power of $(d_{\alpha\gamma}^n - d_0^n)$. It is found that the first order perturbation theory becomes identical to the van der Waals one-fluid (vdW 1) theory, when $n = 3$ (Smith and Henderson 1972; Adams and McDonald 1975) and gives good results for the thermodynamic properties (Smith 1971; Henderson and Leonard 1971b). This method can be extended to the molecular fluid mixture of hard ellipsoids.

In this paper, we examine the theory for a molecular binary mixture of hard ellipsoids and calculate the thermodynamic properties of the system. In § 2, we discuss the theory for calculating the thermodynamic properties of a binary mixture of hard ellipsoids.

† To whom correspondence should be addressed.

The results for additive and non-additive mixtures are discussed in §§3 and 4 respectively.

2. Basic theory

We consider a binary mixture of N_1 hard ellipsoid molecules of species 1 and N_2 hard ellipsoid molecules of species 2, such that the total number of molecules is $N = N_1 + N_2$. Further we assume that the constituent molecules have the same shape but differ in size, so that the parameter χ_0 is the same for all constituent molecules, where χ_0 is the length $(2a_i)$ to width $(2b_i)$ ratio of molecule of species i (i.e. $\chi_0 = a_i/b_i$ for $i = 1, 2$). The potential energy is assumed to be pair-wise additive. Thus

$$U(\bar{X}_1, \bar{X}_2, \ldots, \bar{X}_N) = \sum_{\alpha, \gamma = 1}^{2} \sum_{i<j} u_{\alpha\gamma}(\bar{X}_i, \bar{X}_j), \tag{1}$$

where $u_{\alpha\gamma}(\bar{X}_i, \bar{X}_j)$ is the pair potential between molecules i of species α and molecules j of species γ and is given by

$$\begin{aligned} u_{\alpha\gamma}(\bar{X}_i, \bar{X}_j) &\equiv u_{\alpha\gamma}(r_{ij}, \Omega_i^\alpha, \Omega_j^\gamma) \\ &= \infty \qquad r_{ij} < d_{\alpha\gamma}(\hat{r}_{ij}^{\alpha\gamma}, \Omega_{ij}^{\alpha\gamma}) \\ &= 0 \qquad r_{ij} > d_{\alpha\gamma}(\hat{r}_{ij}^{\alpha\gamma}, \Omega_{ij}^{\alpha\gamma}), \end{aligned} \tag{2}$$

where Ω_i^α and Ω_j^γ denote the orientation of molecule i of species α and molecule j of species γ respectively,

$$r_{ij}^{\alpha\gamma} = |\bar{r}_i^\alpha - \bar{r}_j^\gamma| \quad \text{and} \quad d_{\alpha\gamma}(\hat{r}_{ij}^{\alpha\gamma}, \Omega_{ij}^{\alpha\gamma})$$

is the distance of closest approach between two hard ellipsoids of species α and γ. There is no simple expression for the distance of closest approach between two hard ellipsoids of revolution with arbitrary orientation. We take the Berne and Pechukas (1972) expression for $d_{\alpha\gamma}$

$$\begin{aligned} d_{\alpha\gamma}(\hat{r}_{ij}^{\alpha\gamma}, \Omega_{ij}^{\alpha\gamma}) = d_{\alpha\gamma}^0 [1 - \chi\{ & (\hat{r}_{ij}^{\alpha\gamma} \cdot \hat{e}_i^\alpha)^2 + (\hat{r}_{ij}^{\alpha\gamma} \cdot \hat{e}_j^\gamma)^2 \\ & - 2\chi(\hat{r}_{ij}^{\alpha\gamma} \cdot \hat{e}_j^\alpha)(\hat{r}_{ij}^{\alpha\gamma} \cdot \hat{e}_j^\gamma)(\hat{e}_i^\alpha \cdot \hat{e}_j^\gamma)\}\{1 - \chi^2(\hat{e}_i^\alpha \cdot \hat{e}_j^\gamma)^2\}^{-1}]^{-1/2}, \end{aligned} \tag{3}$$

where $\hat{e}_i^\alpha$ and $\hat{e}_j^\gamma$ are unit vectors along the symmetry axes of two interacting molecules and $\hat{r}_{ij}^{\alpha\gamma}$ is the unit vector along the intermolecular axis $\hat{r}_{ij}^{\alpha\gamma}$. Here $d_{\alpha\gamma}^0 = 2b_{\alpha\gamma}$ is constant with the unit of length and

$$\chi = (\chi_0^2 - 1)/(\chi_0^2 + 1), \tag{4}$$

is an anisotropy parameter. This is a legitimate model for non-spherical molecules, oblate as well as prolate shapes of arbitrary anisotropy. The Berne-Pechukas model represents the hard-ellipsoid model correctly when the difference of length and width $(a_i - b_i)$ is small, but it cannot be exact in general when the difference is large. However, this model is used to calculate the compressibility factor for hard spherocylinders (Singh and Singh 1982) which are in very good agreement with machine simulation results (Mason and Rigby 1978). It has also been used for hard ellipsoids of revolution (Singh and Singh 1986, Singh and Sinha 1986). In general the effective value of $d^0_{\alpha\gamma}$ between hard ellipsoids of unlike species may be given by

$$d^0_{12} = (1/2)(d^0_{11} + d^0_{22})(1 + \Delta), \tag{5}$$

where $d^0_{\alpha\alpha} = 2b_{\alpha\alpha}$ is the width of species α and Δ is the non-additive parameter, $\Delta = 0$ for additive mixture and $|\Delta| > 0$ for non-additive mixture.

In order to calculate the thermodynamic properties of hard ellipsoid mixture, we begin with the pressure equation

$$\frac{\beta P}{\rho} = 1 - \frac{\beta\rho}{6} \sum_{\alpha,\gamma} C_\alpha C_\gamma \int d\bar{r}_{12} r_{12} \Big\langle g_{\alpha\gamma}(r_{12}, \Omega^\alpha_1, \Omega^\gamma_2) \times \frac{\partial u_{\alpha\gamma}(r_{12}, \Omega^\alpha_1, \Omega^\gamma_2)}{\partial r_{12}} \Big\rangle_{\Omega^\alpha_1 \Omega^\gamma_2}, \tag{6}$$

where $g_{\alpha\gamma}(r_{12}, \Omega^\alpha_1, \Omega^\gamma_2)$ is the pair correlation function (PCF) of the hard ellipsoid mixture, $\rho = N/V$ is the number density and $C_\alpha \equiv N_\alpha/N$ is the concentration of species α. Here $\langle \ldots \rangle_{\Omega^\alpha_1 \Omega^\gamma_2}$ represents an unweighted average over the molecular orientations Ω^α_1 and Ω^γ_2 for the quantity within the angular bracket i.e.

$$\langle (\ldots) \rangle_{\Omega^\alpha_1 \Omega^\gamma_2} = \frac{1}{\Omega^\alpha \Omega^\gamma} \int d\Omega^\alpha_1 \int d\Omega^\gamma_2 (\ldots). \tag{7}$$

Ω^α is the normalization constant. For the linear molecule, $\Omega^\alpha = 4\pi$ and

$$d\Omega^\alpha_i = \sin\theta^\alpha_i \, d\theta^\alpha_i \, d\phi^\alpha_i.$$

The hard ellipsoid potential $u_{\alpha\gamma}(r_{12}, \Omega^{\alpha\gamma}_{12})$ satisfies the relation

$$\begin{aligned} u_{\alpha\gamma}(r_{12}, \Omega^\alpha_1, \Omega^\gamma_2) &= u_{\alpha\gamma}(r_{12}/d_{\alpha\gamma}(\hat{r}^{\alpha\gamma}_{12}, \Omega^{\alpha\gamma}_{12})) \\ &= u^{\mathrm{HS}}_{\alpha\gamma}(r^*_{12}) = \infty \qquad r^*_{12} < 1 \\ &= 0 \qquad r^*_{12} > 1, \end{aligned} \tag{8}$$

where

$$r^*_{12} = r_{12}/d_{\alpha\gamma}(\hat{r}^{\alpha\gamma}_{12}, \Omega^{\alpha\gamma}_{12}).$$

Then

$$-\beta \frac{\partial u_{\alpha\gamma}(r_{12}, \Omega^\alpha_1, \Omega^\gamma_2)}{\partial r^*_{12}} = \delta(r^*_{12} - 1). \tag{9}$$

Using the decoupling approximation (Parson 1979), we can write

$$\begin{aligned} g_{\alpha\gamma}(r_{12}, \Omega^\alpha_1, \Omega^\gamma_2) &= g_{\alpha\gamma}[r_{12}/d_{\alpha\gamma}(\hat{r}^{\alpha\gamma}_{12}, \Omega^{\alpha\gamma}_{12})] \\ &= g^{\mathrm{HS}}_{\alpha\gamma}(r^*_{12}), \end{aligned} \tag{10}$$

where $g^{\mathrm{HS}}_{\alpha\gamma}(r^*_{12})$ is the PCF for the hard sphere mixture. Thus the values of $g_{\alpha\gamma}(r_{12}, \Omega^\alpha_1, \Omega^\gamma_2)$ of the hard ellipsoid under this approximation will be obtained from the values of $g^{\mathrm{HS}}_{\alpha\gamma}(r^*_{12})$ of hard sphere mixture at packing fraction

$$\eta_{\alpha\gamma} = \rho V^{\mathrm{HF}}_{\alpha\gamma} = \frac{\pi}{6} \rho d^{0^3}_{\alpha\gamma} \chi_0, \tag{11}$$

where

$$V_{\alpha\gamma}^{\mathrm{HF}} = \frac{\pi}{6} d_{\alpha\gamma}^{0^3} \chi_0 .$$

The decoupling approximation has been found to give compressibility factor in good agreement (Singh and Singh 1986; Singh and Sinha 1986) with computer simulation results (Frenkel and Mulder 1985; Mulder and Frenkel 1985) for a one-component system. It is expected to provide good results even for a mixture. In the decoupling approximation, the orientational and positional degrees of freedom are completely decoupled.

Substituting (9) and (10) in (6) we obtain

$$\frac{\beta P}{\rho} = 1 + \frac{2\pi\rho}{3} \chi_0 F_1(\chi) \sum_{\alpha, \gamma} C_\alpha C_\gamma d_{\alpha\gamma}^{0^3} g_{\alpha\gamma}^{\mathrm{HS}}(1), \tag{12}$$

where $g_{\alpha\gamma}^{\mathrm{HS}}(1)$ is the value of the radial distribution function (RDF) of the hard sphere mixture at the core; and,

$$F_1(\chi) = (1-\chi^2)^{-1/2}(1 - \tfrac{1}{6}\chi^2 - \tfrac{1}{40}\chi^4 - \tfrac{1}{112}\chi^6 - \dots). \tag{13}$$

The vdW 1 fluid theory of mixture (Leland *et al* 1968) originally developed for the hard-sphere system, can be extended in the case of hard ellipsoid mixture. This theory approximates the properties of a mixture by those of fictitious pure hard ellipsoid fluid with the parameter

$$d_0^3 = \sum_{\alpha, \gamma} C_\alpha C_\gamma d_{\alpha\gamma}^{0^3}. \tag{14}$$

In the vdW 1 theory of mixture, it is assumed that

$$g_{\alpha\gamma}^{\mathrm{HS}}(1) = g^{\mathrm{HS}}(d_0) \tag{15}$$

for all α and γ. With the help of (14) and (15), (12) can be written as

$$\beta P/\rho = 1 + 4\eta_0 g^{\mathrm{HS}}(d_0) F_1(\chi), \tag{16}$$

where

$$\eta_0 = \frac{\pi}{6} \rho d_0^3 \chi_0 \tag{17}$$

and $g^{\mathrm{HS}}(d_0)$ is the RDF of the hard-sphere system at the core and is given by

$$g^{\mathrm{HS}}(d_0) = (1 - \eta_0/2)/(1-\eta_0)^3. \tag{18}$$

From (16), we get

$$\beta P/\rho = 1 + \{2\eta_0(2-\eta_0)/(1-\eta_0)^3\} F_1(\chi). \tag{19}$$

The Helmholtz free energy per particle for the mixture is given by

$$\beta A/N = [\ln \rho - 1] + \sum_\alpha C_\alpha \ln C_\alpha + H[\rho, U], \tag{20}$$

where the first two terms represent the free energy of an ideal gas mixture and H is the excess free energy arising from the interparticle interaction. Thus

$$H[\rho, U] = \int_0^{\rho} \{(\beta P/\rho) - 1\}\, \mathrm{d}\rho/\rho. \tag{21}$$

This can be solved using (19). Finally, we obtain an expression for the free energy as

$$\beta A/N = (\ln \rho - 1) + \sum_{\alpha} C_\alpha \ln C_\alpha + \{\eta_0(4 - 3\eta_0)/(1-\eta_0)^2\}\, F_1(\chi). \tag{22}$$

Other thermodynamic properties can be calculated by using (19) and (22).

These equations can be used to calculate the thermodynamic properties of a binary mixture of both additive and non-additive hard ellipsoids.

3. Binary mixture of additive hard ellipsoids

We derive expressions for the thermodynamic properties of binary mixture of additive hard ellipsoids. Using the relation

$$d^3 = C_1 d_{11}^{0^3} + C_2 d_{22}^{0^3}, \tag{23}$$

we get the following relation for the binary mixture of additive hard ellipsoids

$$\eta_0 = \eta[1 - \tfrac{3}{4}C_1C_2(1+R)(1-R)^2/(C_1 + C_2R^3)], \tag{24}$$

where

$$\eta = \frac{\pi}{6}\rho\, d^3\chi_0 = \frac{\pi}{6}\rho\chi_0(C_1 d_{11}^{0^3} + C_2 d_{22}^{0^3}), \tag{25}$$

and $R = d_{22}^0/d_{11}^0$. Using (24) in (19) and (22) we obtain expressions for the pressure and free energy for the additive hard ellipsoid mixture

$$\begin{aligned}\beta P/\rho = {} & 1 + \{2\eta(2-\eta)/(1-\eta)^3\}\, F_1(\chi) \\ & - 6C_1C_2\{\eta_a(4 + 4\eta - 2\eta^2)/(1-\eta)^4\} \\ & \times \{(d_{11}^0 - d_{22}^0)/(d_{11}^0 + d_{22}^0)\}\, F_1(\chi) + O(C_1^2C_2^2),\end{aligned} \tag{26}$$

and

$$\begin{aligned}\beta A/N = {} & (\ln \rho - 1) + \sum_{\alpha} C_\alpha \ln C_\alpha + \{\eta(4-3\eta)/(1-\eta)^2\}F_1(\chi) \\ & - 6C_1C_2\{\eta_a(2-\eta)/(1-\eta)^3\} \\ & \times \{(d_{11}^0 - d_{22}^0)/(d_{11}^0 + d_{22}^0)\}\, F_1(\chi) + O(C_1^2C_2^2),\end{aligned} \tag{27}$$

where

$$\eta_a = \frac{\pi}{6}\rho\chi_0 d_{12}^{a^3}, \tag{28}$$

$$d_{12}^a = (d_{11}^0 + d_{22}^0)/2. \tag{29}$$

However, we prefer to use (19) and (22) for calculating the pressure and free energy of the binary mixture.

We have calculated the equation of state $\beta P/\rho$ and excess free energy per particle $\beta f (\equiv \beta A_E/N)$ for the binary mixture of additive hard ellipsoids with different values of anisotropy parameter χ_0 and different values of R, using (19) and (22). $\chi_0 = 1{\cdot}0$ corresponds to the simple atomic fluid mixture. Here βf is the excess free energy with respect to the ideal gas at the same temperature and density.

We examine the effect of anisotropy on the thermodynamic properties of binary mixture. The value of the equation of state $\beta P/\rho$ and excess free energy per particle βf as a function of χ_0 are reported in figures 1 and 2 respectively for $C_1 = C_2 = 0{\cdot}5$ and $\rho^* = 0{\cdot}3$ and $0{\cdot}5$ at $R = 1{\cdot}1$ and $3{\cdot}0$. The quantity

$$\rho^* = \rho(C_1 d_{11}^{0^3} + C_2 d_{22}^{0^3}).$$

The results for $R = 3{\cdot}0$ are less than those for $R = 1{\cdot}1$ throughout the range of χ_0. From the figures, we find that the equation of state and free energy increase with increase of density ρ^* and with increase of χ_0. Figures 3 and 4 demonstrate the equation of state $\beta P/\rho$ and free energy βf respectively for $C_1 = C_2 = 0{\cdot}5$ and $R = 1{\cdot}1$ and $5/3$ at $\eta = 0{\cdot}3$ (with different values of ρ^*). From these figures we see that the thermodynamic properties such as pressure and free energy at given η are minimum at $\chi_0 = 1{\cdot}0$ and increase when χ_0 either increases or decreases.

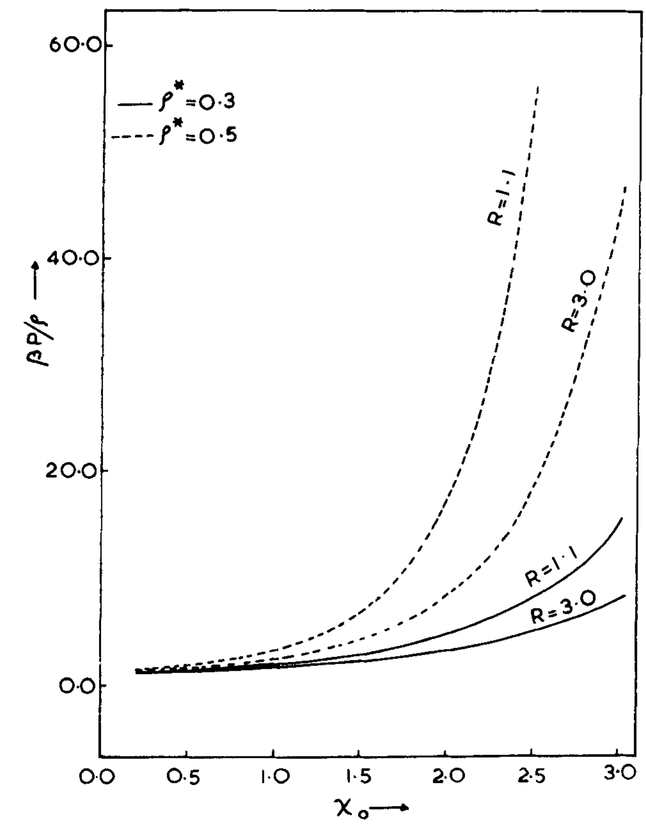

Figure 1. Equation of state $\beta P/\rho$ for binary mixture of additive hard ellipsoids as a function of χ_0 for $C_1 = C_2 = 0{\cdot}5$ and $\rho^* = 0{\cdot}3$ and $0{\cdot}5$ and for $R = 1{\cdot}1$ and $3{\cdot}0$.

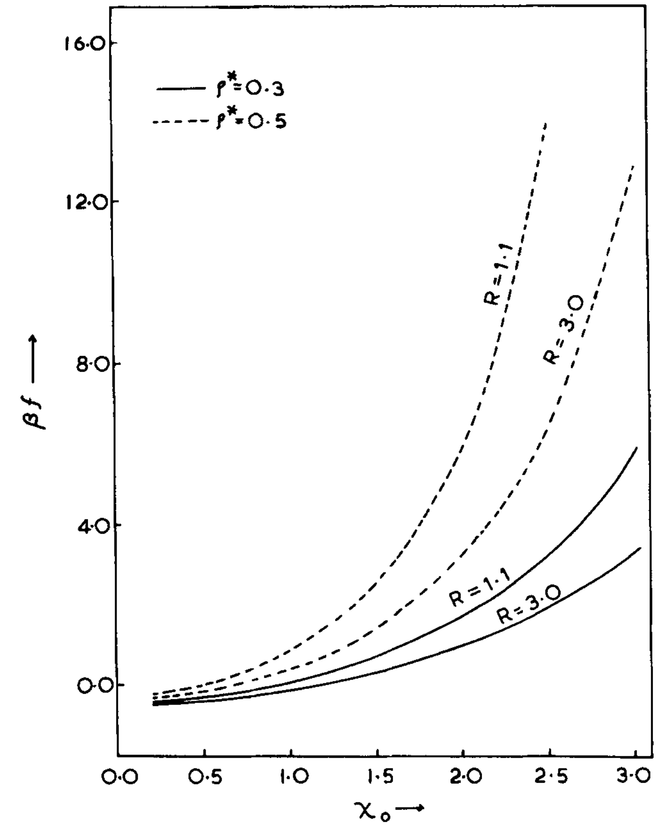

Figure 2. Excess free energy βf for binary mixture of additive hard ellipsoids as a function of χ_0 for $C_1 = C_2 = 0{\cdot}5$ and $\rho^* = 0{\cdot}3$ and $0{\cdot}5$ and for $R = 1{\cdot}1$ and $3{\cdot}0$.

4. Binary mixture of non-additive hard ellipsoids

For non-additive hard ellipsoids, (5) can be written as

$$d_{12}^0 = d_{12}^a(1+\Delta), \tag{30}$$

where

$$d_{12}^a = (d_{11}^0/d_{22}^0)/2.$$

Equations (19) and (22) can be written as

$$\frac{\beta(P-P^a)}{\rho} = 6C_1C_2\eta_a\{(4+4\eta-2\eta^2)/(1-\eta)^4\} \times F_1(\chi)\Delta(1+\Delta)+O(C_1^2C_2^2), \tag{31}$$

$$\frac{\beta(A-A^a)}{N} = 12C_1C_2\eta_a\{(2-\eta)/(1-\eta)^3\} \times F_1(\chi)\Delta(1+\Delta)+O(C_1^2C_2^2). \tag{32}$$

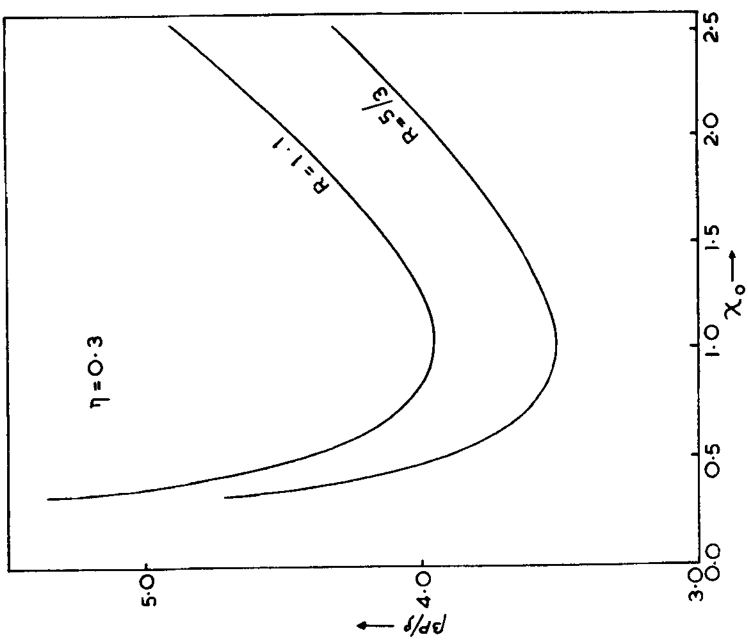

Figure 3. Equation of state $\beta P/\rho$ for binary mixture of additive hard ellipsoids as a function of χ_0 for $C_1 = C_2 = 0{\cdot}5$ and $R = 1{\cdot}1$ and 5/3 at $\eta = 0{\cdot}3$.

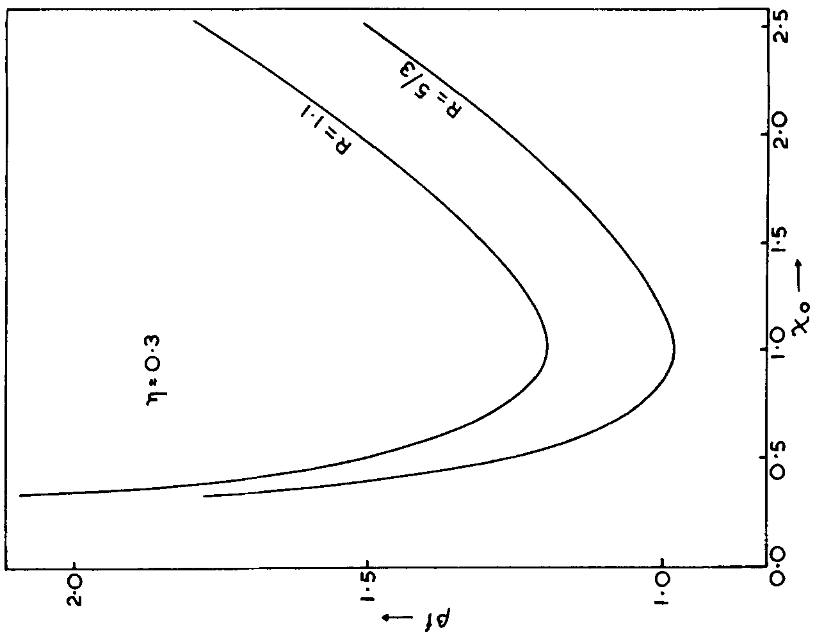

Figure 4. Excess free energy βf for binary mixture of additive hard ellipsoids as a function of χ_0 for $C_1 = C_2 = 0{\cdot}5$ and $R = 1{\cdot}1$ and 5/3 at $\eta = 0{\cdot}3$.

We have calculated $\beta P/\rho$ from (19) for a binary mixture of non-additive hard ellipsoids for $\Delta = 0{\cdot}0$, $-0{\cdot}1$ and $-0{\cdot}5$ at $R = 1{\cdot}0$. These values of $\beta P/\rho$ are reported in figure 5 as a function of χ_0 for $C_1 = C_2 = 0{\cdot}5$ and $\rho^* = 0{\cdot}3$ and $0{\cdot}5$. $\Delta = 0{\cdot}0$ corresponds to the one-component hard ellipsoid fluid. The results obtained for the one-component fluid is in good agreement with experimental results (Singh and Singh 1986). For binary mixture, computer simulation results are not available except for $\chi_0 = 1{\cdot}0$, which corresponds to the simple hard sphere mixture, where the agreement is good (Adams and McDonald 1975). However, this method is expected to provide good results even for other values of χ_0. We see that the pressure increases with increase of χ_0 and with increase of Δ.

In figure 6, the values of βf, obtained from (22), are demonstrated as a function of χ_0 for $C_1 = C_2 = 0{\cdot}5$; $\rho^* = 0{\cdot}3$ and $0{\cdot}5$ and $\Delta = 0{\cdot}0$, $-0{\cdot}1$ and $-0{\cdot}5$ at $R = 1{\cdot}0$. We see that the behaviour of free energy is identical to that of pressure.

Thus we conclude that the equation of state and free energy of the hard ellipsoid mixture increase with increase of anisotropy parameter χ_0.

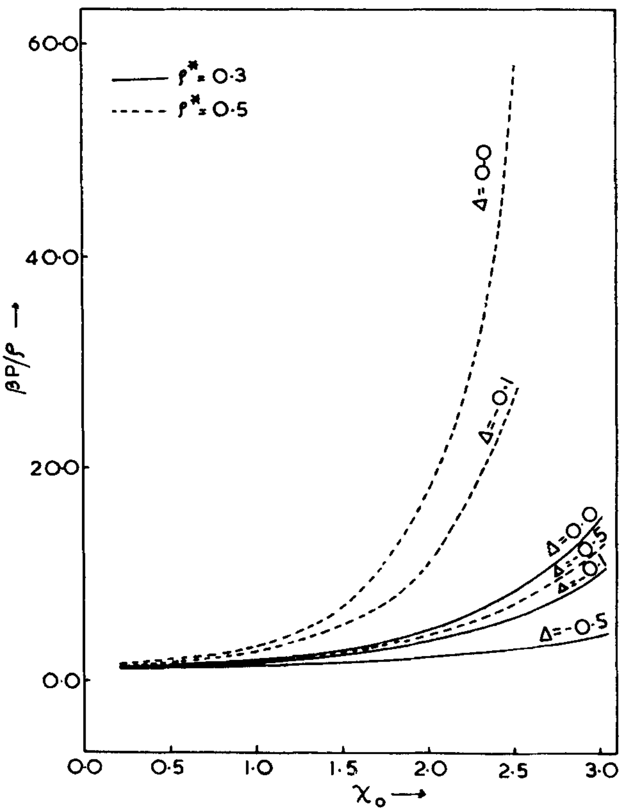

Figure 5. Equation of state $\beta P/\rho$ for binary mixture of non-additive hard ellipsoids as a function of χ_0 for $C_1 = C_2 = 0{\cdot}5$ and $\rho^* = 0{\cdot}3$ and $0{\cdot}5$ and for $\Delta = 0{\cdot}0$, $-0{\cdot}1$ and $-0{\cdot}5$ at $R = 1{\cdot}0$.

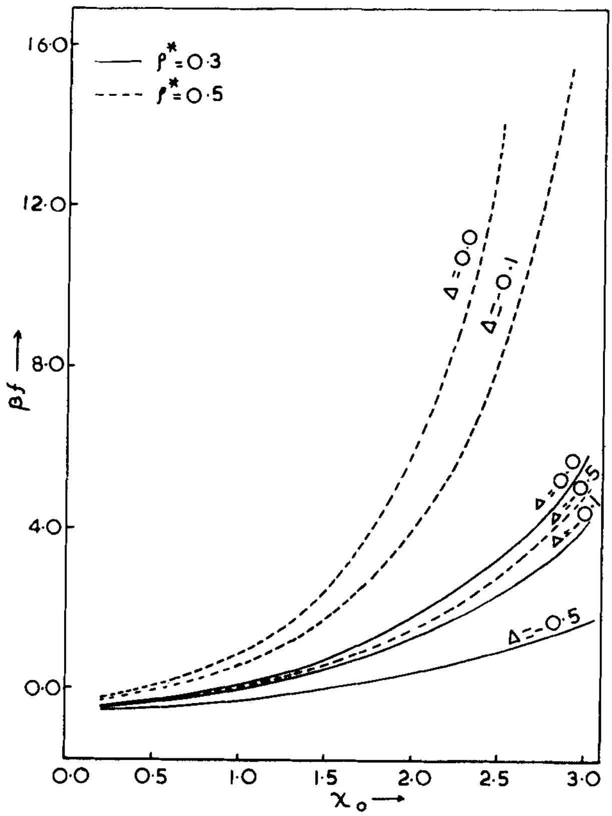

Figure 6. Excess free energy for binary mixture of non-additive hard ellipsoids as a function of χ_0 for $C_1 = C_2 = 0{\cdot}5$ and $\rho^* = 0{\cdot}3$ and $0{\cdot}5$ and for $\Delta = 0{\cdot}0$, $-0{\cdot}1$ and $-0{\cdot}5$ at $R = 1{\cdot}0$.

Acknowledgement

One of us (AKS) acknowledges financial support from UGC, New Delhi.

References

Adams D J and McDonald I R 1975 *J. Chem. Phys.* **63** 1900
Berne B J and Pechukas P 1972 *J. Chem. Phys.* **56** 4213
Frenkel D and Mulder B M 1985 *Mol. Phys.* **55** 1171
Henderson D and Barker J A 1968 *J. Chem. Phys.* **49** 3377
Henderson D and Leonard P J 1971a *Physical chemistry – An advance treatise* (New York: Academic press) Vol. **B8**
Henderson D and Leonard P J 1971b *Proc. Natl Acad. Sci.* (*U.S.A.*) **68** 2354
Leland T W, Rowlinson J S and Sather G A 1968 *Trans. Faraday Soc.* **64** 1447
Mason P A and Rigby M 1978 *Mol. Phys.* **35** 1337
Mulder B M and Frenkel D 1985 *Mol. Phys.* **55** 1193
Parson J D 1979 *Phys. Rev.* **A19** 1225

Singh U P and Sinha S K 1986 *Physica* (in press)
Singh S and Singh Y 1982 *Mol. Cryst. Liq. Cryst.* **87** 211
Singh U P and Singh Y 1986 *Phys. Rev.* **33** 2725
Smith W R 1971 *Mol. Phys.* **21** 105
Smith W R and Henderson D 1972 *Mol. Phys.* **24** 773