

Thermodynamic properties of hard ellipsoid square-well fluid

A K SINGH*, T K DEY 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, Bihar University, Sitamarhi 843301, India

MS received 24 June 1987; revised 5 September 1989

Abstract. The perturbation theory with non-spherical reference system is used for molecular fluid with angle-dependent square-well type potential. Simple analytic expressions are given for the thermodynamic properties such as the equation of state, excess free energy per particle, internal energy and internal heat capacity. The effects of anisotropy on the thermodynamic properties are discussed. The anisotropy effects increase with increase of density and decrease of temperature and depends on the anisotropy parameter x_0 .

Keywords. Perturbation theory; equation of state; excess free energy; internal energy; internal heat capacity; anisotropy parameter; hard ellipsoid.

PACS No. 61-25

1. Introduction

The present paper is concerned with the evaluation of thermodynamic properties of axially symmetric molecular fluids, whose molecules interact via square-well (SW) type potential, defined as

$$\begin{aligned} u(r, \Omega_1, \Omega_2) &= \infty, & r < \sigma(\Omega_1, \Omega_2) \\ &= -\varepsilon(\Omega_1, \Omega_2), & \sigma(\Omega_1, \Omega_2) < r < \lambda\sigma(\Omega_1, \Omega_2) \\ &= 0, & r > \lambda\sigma(\Omega_1, \Omega_2), \end{aligned} \quad (1)$$

where $\sigma(\Omega_1, \Omega_2)$ is the distance of closest approach between two molecules and λ is the potential cut off. Here Ω_1 and Ω_2 denote the orientations of molecules 1 and 2, respectively and $r = |\bar{r}_1 - \bar{r}_2|$. In (1), $\varepsilon(\Omega_1, \Omega_2)$ and $\sigma(\Omega_1, \Omega_2)$ are angle-dependent strength and range parameters respectively. They are assumed to be of forms (Berne and Pechukas 1972)

$$\begin{aligned} \varepsilon(\Omega_1, \Omega_2) &\doteq \varepsilon_0 [1 - x^2(\hat{e}_1 \cdot \hat{e}_2)^2]^{-1/2}, \\ \sigma(\Omega_1, \Omega_2) &= \sigma_0 [1 - x\{(\hat{f} \cdot \hat{e}_1)^2 + (\hat{f} \cdot \hat{e}_2)^2 \\ &\quad - 2x(\hat{f} \cdot \hat{e}_1)(\hat{f} \cdot \hat{e}_2)(\hat{e}_1 \cdot \hat{e}_2)\} \{1 - x^2(\hat{e}_1 \cdot \hat{e}_2)^2\}^{-1}]^{-1/2}, \end{aligned} \quad (2)$$

where \hat{e}_1 and \hat{e}_2 are unit vectors along the symmetry axes of two interacting molecules and \hat{f} the unit vector along the intermolecular axis r . Here ε_0 and σ_0 are constants with units of energy and length respectively, and

$$x = (x_0^2 - 1)/(x_0^2 + 1) \quad (4)$$

is an anisotropy parameter, x_0 being the length ($2a$) to width ($2b$) ratio of the molecule and $\sigma_0 = 2b$. The SW potential is the simplest model which takes into account strong anisotropy in both intermolecular repulsion and attraction and represents, at least qualitatively, the shape of the molecular core.

At present one of the most successful approaches for dealing with molecular fluids is the perturbation theory (Gray and Gubbins 1984). For molecular fluid, whose molecules interact via the angle-dependent pair potential, the perturbation expansion is made about the hard-convex body reference system (Boublik 1976). Recently Boublik (1987) has used the Barker-Henderson (BH) theory in the macroscopic compressibility approximation (Barker and Henderson 1967; Fischer 1980) to calculate the equilibrium properties of the molecular fluids. One may, however, expect to obtain better results by using the local compressibility approximation (Barker and Henderson 1967) in place of the macroscopic compressibility.

In this work we generalize the BH perturbation theory in the local compressibility (l.c.) approximation for non-spherical molecule fluids employing the hard convex body as reference.

In §2 we discuss the second order perturbation theory of hard convex-molecule fluids. The properties of the reference system are given and the angle-integrations of the perturbation parts are performed. Section 3 is devoted to the square-well type of fluid. Analytic expressions for the first and second perturbation corrections to the free energy and pressure are reported there. Results and discussions are presented in §4.

2. Perturbation expansion

We divide the pair potential $u(r\Omega_1\Omega_2)$ as

$$u(r\Omega_1\Omega_2) = u_{hc}(r\Omega_1\Omega_2) + u_p(r\Omega_1\Omega_2), \quad (5)$$

where

$$\begin{aligned} u_{hc}(r\Omega_1\Omega_2) &= \infty, & r < \sigma(\Omega_1\Omega_2) \\ &= 0, & r > \sigma(\Omega_1\Omega_2) \end{aligned} \quad (6)$$

is the hard-convex (HC) potential treated as a reference potential and $u_p(r\Omega_1\Omega_2)$ is perturbation. (Here $r = |\bar{r}_1 - \bar{r}_2|$.)

Using this division of pair potential in the Barker-Henderson-like (BH) perturbation theory in the l.c. approximation, the free energy per particle is given by

$$\begin{aligned} \beta f &= \beta f_{hc} + \frac{1}{2} \beta \rho \int d\bar{r} \langle g_{hc}(r\Omega_1\Omega_2) u_p(r\Omega_1\Omega_2) \rangle \\ &\quad - \frac{1}{4} \beta \rho \left(\frac{\partial \rho}{\partial P_{hc}} \right) \frac{\partial}{\partial \rho} \left[\rho \int d\bar{r} \langle g_{hc}(r\Omega_1\Omega_2) u_p^2(r\Omega_1\Omega_2) \rangle \right], \end{aligned} \quad (7)$$

where $g_{hc}(r\Omega_1\Omega_2)$ is the pair correlation function (PCF) of the HC fluid and $\rho \equiv N/V$ is the number density. Here $\langle \dots \rangle$ represents an unweighted average over the molecular orientations Ω_1 and Ω_2 for the quantity within the angular bracket i.e.

$$\langle \dots \rangle = \frac{1}{\Omega^2} \int d\Omega_1 \int d\Omega_2 (\dots). \quad (8)$$

Ω is the normalisation constant. For the linear molecules $\Omega = 4\pi$ and

$$d\Omega_i = \sin \theta_i d\theta_i d\phi_i.$$

The thermodynamic properties of the HC fluid can be calculated from the equation of state (Singh and Singh 1986; Singh *et al* 1988)

$$\frac{\beta P_{hc}}{\rho} = 1 + \frac{2\eta(2-\eta)}{(1-\eta)^3} F_1(x), \quad (9)$$

where

$$F_1(x) = (1-x^2)^{-1/2} \left[1 - \frac{1}{6}x^2 - \frac{1}{40}x^4 - \frac{1}{112}x^6 + \dots \right] \quad (10)$$

and

$$\begin{aligned} \eta &= \rho V_{hc} = \pi \rho \sigma_0^3 x_0 / 6 \quad (\text{for hard ellipsoids}) \\ &= \frac{1}{12} \pi \rho \sigma_0^3 (3x_0 - 1) \quad (\text{for prolate hard spherocylinder}), \end{aligned}$$

V_{hc} being the volume of a hard non-sphere molecule. Then the expression for free energy per particle of the HC fluid is (Singh *et al* 1988)

$$\beta f_{hc} = \frac{\eta(4-3\eta)}{(1-\eta)^2} F_1(x). \quad (11)$$

Using (9), the compressibility equation for the HC fluid is given by

$$\left(\frac{\partial \rho}{\partial P_{hc}} \right) = \frac{\beta}{a_{hc}}, \quad (12)$$

where

$$a_{hc}(x) = 1 + \frac{2\eta(4-\eta)}{(1-\eta)^4} F_1(x). \quad (13)$$

In order to evaluate the perturbation correction terms, we use the decoupling approximation (Parson 1979) and write

$$g_{hc}(r\Omega_1\Omega_2) = g_{hc}(r/\sigma(\Omega_1\Omega_2)) = g_{hs}(r^*), \quad (14)$$

where $g_{hs}(r^*)$ is the PCF for the hard sphere (HS) system at the packing fraction $\eta = \rho v_{hc}$. In the decoupling approximation, the orientational and positional degrees of freedom are completely decoupled. Then the free energy per particle of the system is expressed in a simpler form

$$\begin{aligned} \beta f - \beta f^c &= \frac{12(1-x^2)^{-1/2}}{T^*} \eta \int_1^\infty dr^* r^{*2} u_p^*(r^*) g_{hs}(r^*) \\ &\quad - \frac{6\Delta(x)}{T^{*2} a_{hc}} \eta \frac{\partial}{\partial \eta} \left[\eta \int_1^\infty dr^* r^{*2} u_p^{*2}(r^*) g_{hs}(r^*) \right], \end{aligned} \quad (15)$$

where

$$\begin{aligned} \Delta(x) &= (1-x^2)^{-1/2} \Omega^{-2} \int d\Omega_1 \int d\Omega_2 (1-x^2 \cos^2 \theta_{12})^{-1/2} \\ &= (1-x^2)^{-1/2} \left[1 + \frac{1}{6}x^2 + \frac{3}{40}x^4 + \frac{5}{112}x^6 + \dots \right], \end{aligned} \quad (16)$$

$$T^* = kT/\varepsilon_0 \equiv (\beta\varepsilon)^{-1} \text{ and } u_p^* = u_p/\varepsilon_0$$

3. Square-well potential

For the square-well potential (Eq. (1)), u_p^* is given by

$$\begin{aligned} u_p^*(r^*) &= -1, & 1 \leq r^* \leq \lambda \\ &= 0, & r^* \geq \lambda, \end{aligned} \quad (17)$$

where λ determines the width of the well in relation to the hard core. This is a very useful model for testing theory of fluids, as the complicating effects of a soft core are not present for this model. Since the classical square well potential with $\lambda = 1.5$ is a qualitatively reasonable model for real simple fluids (Henderson *et al* 1976), we choose $\lambda = 1.5$ in our calculations. In this case, (15) reduces to

$$\beta f - \beta f_{hc} = \beta f_1 + \beta f_2, \quad (18)$$

where

$$\beta f_1 = -\frac{12\eta(1-x^2)^{-1/2}}{T^*} Q(\eta) \quad (19)$$

$$\beta f_2 = -\frac{6\eta\Delta(x)}{T^{*2}a_{hc}} \frac{\partial}{\partial \eta} [\eta Q(\eta)], \quad (20)$$

where

$$Q(\eta) = \int_1^\lambda dr^* r^{*2} g_{hs}(r^*), \quad (21)$$

which can be solved analytically to give (Ponce and Renon 1976)

$$Q(\eta) = \frac{1}{3} \left[\lambda^3 + \left(\frac{1-a_{hs}}{8\eta a_{hs}} \right) \right], \quad (22)$$

where $a_{hs} = (\partial P_{hs} / \partial \rho)$, which can be obtained from (13) by putting $F_1(x) = 1$ i.e.

$$a_{hs} = 1 + \frac{2\eta(4-\eta)}{(1-\eta)^4}. \quad (23)$$

Substituting (22) in (19) and (20) we obtain an analytic expression for the free energy of the square-well molecular fluid

$$\beta f = \beta f_{hc} + \frac{f_1^*}{T^*} + \frac{f_2^*}{T^{*2}}, \quad (24)$$

where

$$f_1^* = -4\eta \left[\lambda^3 + \left(\frac{1-a_{hs}}{8\eta a_{hs}} \right) \right] (1-x^2)^{-1/2} \quad (25)$$

$$f_2^* = -2\eta a_{hc}^{-1} \left[\lambda^3 - \frac{1}{8} a_{hs}^{-2} \left(\frac{\partial a_{hs}}{\partial \eta} \right) \right] \Delta(x). \quad (26)$$

Other thermodynamic properties such as equation of state, internal energy and internal heat capacity can be obtained from (24) using the standard thermodynamic relations.

Expanding the equation of state $\beta P/\rho$ in power of η , we obtain expressions for the second and third virial coefficient for the molecular square well fluid

$$B_2 = b_0 \left[1 - (\lambda^3 - 1) \left\{ \frac{(1-x^2)^{-1/2}}{T^*} + \frac{\Delta(x)}{2T^{*2}} + \dots \right\} \right] \quad (27)$$

$$B_3 = b_0^2 \left[\frac{5}{8} + \frac{2}{T^{*2}} \left\{ (\lambda^3 - 1)F_1(x) - \frac{17}{16} \right. \right. \\ \left. \left. - \frac{17}{16} T^*(1-x^2)^{-1/2} \right\} \right], \quad (28)$$

where

$$b_0 = 4v_{hc} = \frac{2\pi}{3} \sigma_0^3 x_0 \quad (\text{hard ellipsoid}) \\ = \frac{\pi}{3} \sigma_0^3 (2x_0 - 1) \quad (\text{hard prolate spherocylinder}). \quad (29)$$

For hard sphere ($x_0 = 1$), $b_0 = 2\pi\sigma_0^3/3$ and $F_1(x) = \Delta = 1$ and (27) and (28) reduce to (Ponce and Renon 1976)

$$B_2 = b_0 \left[1 - (\lambda^3 - 1) \left(\frac{1}{T^*} + \frac{1}{2T^{*2}} + \dots \right) \right] \quad (30)$$

$$B_3 = b_0^2 \left[\frac{5}{8} + \frac{2}{T^{*2}} \left\{ (\lambda^3 - 1) - \frac{17}{16}(1 + T^*) \right\} \right]$$

The theory developed here for the S W fluid is valid for molecules of oblate ($x_0 < 1$) as well as prolate ($x_0 > 1$) shapes of arbitrary symmetry. $x_0 = 1$ corresponds to the simple fluid whose molecules are spherically symmetric.

4. Results and discussion

In this section we calculate the thermodynamic properties such as equation of state, excess free energy per particles, the internal energy and internal heat capacity of the SW molecular fluid for different values of anisotropy parameter x_0 (i.e. $0 < x_0 < 3.0$).

The Monte Carlo values of the thermodynamic properties such as pressure and free energy of the SW fluid with $\lambda = 1.5$ are available only for $x_0 = 1.0$, where the agreement was found to be good (Ponce and Renon 1976). This method is expected to provide good results even for other values of x_0 . We calculate the results for $\lambda = 1.5$, which is qualitatively a reasonable model for simple fluids.

Figure 1 shows the values of f_1^* and f_2^* as a function of parameter x_0 at $\eta = 0.3$ and 0.4 for $\lambda = 1.5$ using (25) and (26), respectively. They are maximum at $x_0 = 1.0$ and decreases steadily as x_0 moves away from 1.0 . For a given η each of f_1^* and f_2^* has the same value at $x_0 = l$ and $x_0 = l^{-1}$ (l being any value of $x_0 > 1.0$). For example f_1^* at a given η has the same value at $x_0 = 2.0$ and $x_0 = 0.50$.

The values of the equation of state, $\beta P/\rho$, are reported in figure 2 as a function of x_0 for $\eta = 0.45$ at the isotherms $T^* = 2.0, 1.333, 1.0$ and 0.667 . At high temperatures

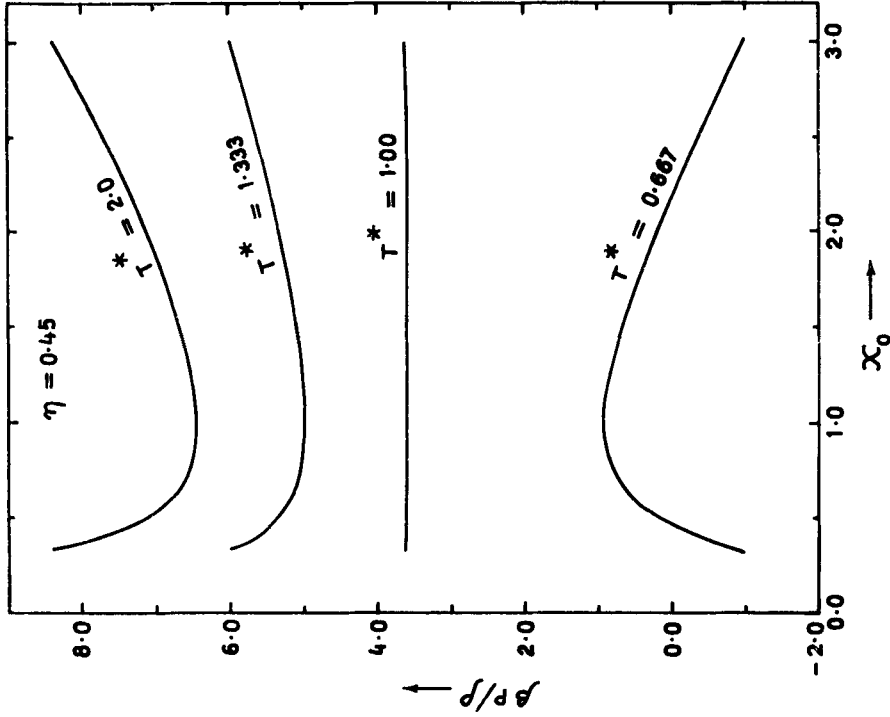


Figure 2. The equation of state, $\beta P/\rho$ of the hard ellipsoid S W fluid with $\lambda = 1.5$ as a function of x_0 for $\eta = 0.45$ at $T^* = 2.0, 1.333, 1.0$ and 0.667 .

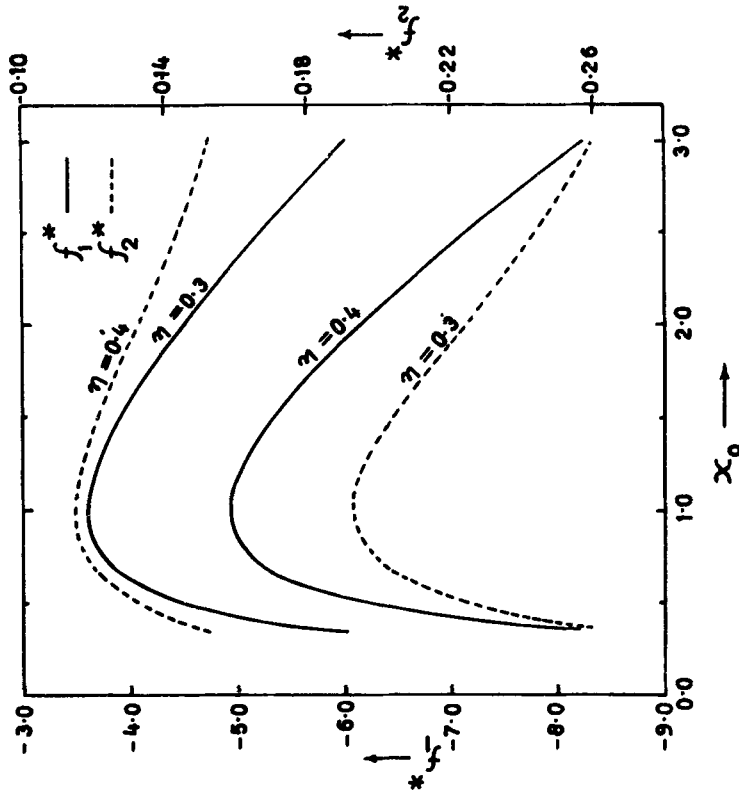


Figure 1. Values of f_1^* and f_2^* of the hard ellipsoid S W fluid with $\lambda = 1.5$ as a function of x_0 for $\eta = 0.3$ and 0.4 .

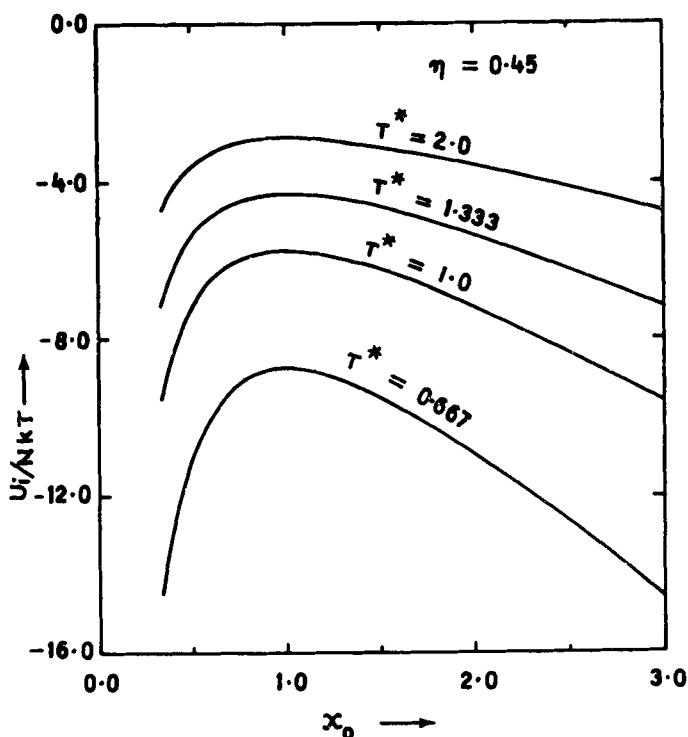


Figure 3. The internal energy, $U_i/N kT$ of the hard ellipsoid S W fluid with $\lambda = 1.5$ as a function of x_0 for $\eta = 0.45$ at $T^* = 2.0, 1.333, 1.0$ and 0.667 .

$T^* \geq 1.0$, $\beta P/\rho$ is minimum at $x_0 = 1.0$ and increases steadily as x_0 moves away from 1.0. However the rate of variation of $\beta P/\rho$ with x_0 decreases with decrease of T^* and at low temperature $T^* < 1.0$ $\beta P/\rho$ begins to decrease as x_0 goes away from 1.0. To explain this behaviour, we consider the contributions of the hard core potential and perturbation corrections which are of opposite signs. However the magnitudes of these contributions increase as x_0 moves away from 1.0. At high temperatures $T^* > 1.0$ the hard-core contribution is dominant and $\beta P/\rho$ increases when x_0 moves away from 1.0. On the other hand at low temperatures it is perturbation effect which dominates and $\beta P/\rho$ decreases when x_0 goes away from 1.0. For a given η , $\beta P/\rho$ has the same value at $x_0 = l$ and $x_0 = l^{-1}$. However it is clear from the expressions of $\beta P_{hc}/\rho$, P_1^* and P_2^* that for a given reduced density $\rho^* = \rho\sigma_0^3$, it cannot have the same value at $x_0 = l$ and $x_0 = l^{-1}$.

Figure 3 demonstrates the variation of the internal energy $U_i/N kT$ as a function of x_0 for $\eta = 0.45$ at $T^* = 2.0, 1.333, 1.0$ and 0.667 . It is maximum at $x_0 = 1.0$ and decreases steadily as x_0 moves away from 1.0. Here U_i is the excess internal energy with respect to the ideal gas at the same temperature and density. Like the equation of state the internal energy is also symmetric about $x_0 = 1.0$, i.e. it has the same value at $x_0 = l$ and $x_0 = l^{-1}$.

In figure 4 the values of the excess free energy per particle, βf , are plotted as a function of $1/T^*$ for $\eta = 0.4$ at $x_0 = 1.0, 1.5$ and 2.0 . The excess free energy increases with increase of temperature and also depends on x_0 . At high temperature ($1/T^* \lesssim 0.5$), βf is minimum and increases as x_0 increases from 1.0, where as at lower temperature

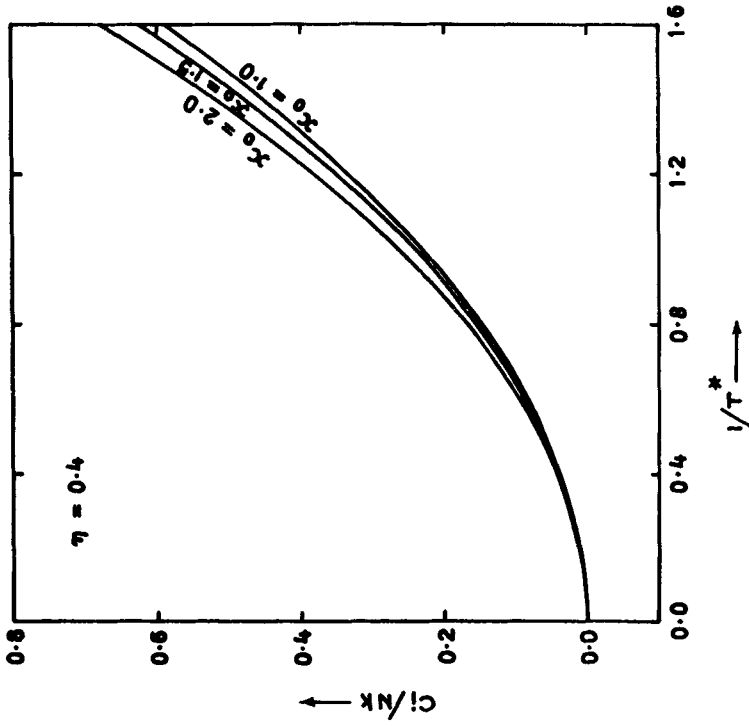


Figure 5. The internal heat capacity, C_i/Nk of the hard ellipsoid SW fluid with $\lambda = 1.5$ as a function of $1/T^*$ for $\eta = 0.4$ at $x_0 = 1.0, 1.5$ and 2.0 .

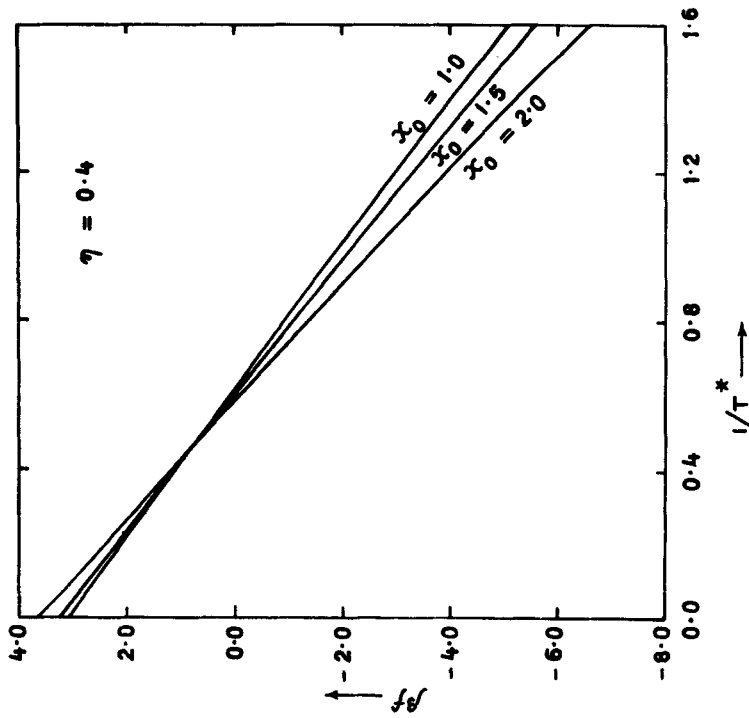


Figure 4. The excess free energy per particle βf of hard ellipsoid SW fluid with $\lambda = 1.5$ as a function of $1/T^*$ for $\eta = 0.4$ at $x_0 = 1.0, 1.5$ and 2.0 .

($1/T^* \gtrsim 0.5$) it begins to decrease when x_0 increases from 1.0. This behaviour of βf can also be explained, like that of the equation of state, by considering the contributions of the hard-core potential and perturbation corrections, which are of opposite signs in this case also.

Figure 5 demonstrates the variation of the internal heat capacity (i.e. heat capacity with respect to the ideal gas at the same density and temperature) C_i/Nk as a function of $1/T^*$ for $\eta = 0.4$ at $x_0 = 1.0, 1.5$ and 2.0 . It increases with decrease of T^* and increase of x_0 .

Acknowledgement

We acknowledge the financial support from University Grants Commission, New Delhi.

References

- Barker J A and Henderson D 1967 *J. Chem. Phys.* **47** 2856
Berne B J and Pechukas P 1972 *J. Chem. Phys.* **56** 4213
Boublik T 1976 *Mol. Phys.* **32** 1737
Boublik T 1987 *J. Chem. Phys.* **87** 1751
Fischer J 1980 *J. Chem. Phys.* **72** 5371
Gray C G and Gubbins K E 1984 *Theory of Molecular Physics* (Oxford: Clarendon press) p. 248
Henderson D, Madden W G and Fitts D D 1976 *J. Chem. Phys.* **64** 5026
Parson J D 1979 *Phys. Rev.* **A19** 1225
Ponce L and Renon H 1976 *J. Chem. Phys.* **64** 638
Singh U P and Singh Y 1986 *Phys. Rev.* **A33** 2725
Singh T P, Sinha J P and Sinha S K 1988 *Pramana - J. Phys.* **31** 289