

Equilibrium properties of hard non-sphere fluids

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Abstract. Derivation of the thermodynamic properties of fluids of hard non-spherical molecules of arbitrary symmetry is based on the decoupling approximation. Theoretical expressions are given and calculations made for the equation of state and virial coefficients for hard ellipsoids. These results are compared with Monte Carlo values and show fair agreement in all cases. The theoretical predictions for the equation of state for binary mixtures are compared with the Monte Carlo results for hard spheres and hard prolate spherocylinders. Theoretical expressions for the first order quantum correction to the free energy, pressure and virial coefficients are also given. The quantum effects increase with increase of density and with increase of anisotropy parameter.

Keywords. Hard ellipsoid; hard spherocylinder; anisotropy; equation of state; quantum correction.

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1. Introduction

Properties of a fluid of hard non-spherical molecules have aroused considerable interest in recent years (Boublik 1983; Boublik and Nezbeda 1986). This is because hard non-spheres would be useful reference systems for molecular fluids like hard spheres for simple atomic fluids. Several theoretical and experimental efforts have been made for understanding the structural and thermodynamic properties of hard non-sphere fluids such as hard spherocylinders and hard ellipsoids (Freasier and Bearman 1976; Monson and Rigby 1980; Frenkel *et al* 1984; Frenkel and Mulder 1985; Mulder and Frenkel 1985; Singh and Singh 1986; Boublik and Nezbeda 1986; Singh *et al* 1987). However, quantum fluids of hard non-sphere molecules have not been studied.

At high temperature (i.e. in the semi-classical limit), when the quantum effects are small and treated as a correction to the classical behaviour, the usual way of studying the properties of the hard sphere fluid is the Hemmer–Jancovici (HJ) method (Hemmer 1968; Jancovici 1969). Extensive work has been done to calculate the equilibrium properties of a hard-sphere fluid in the semi-classical limit (Singh and Sinha 1981). This approach can be extended to hard non-spherical fluids. However, to the best of our knowledge, no work is available for molecular fluids of hard spherocylinders and hard ellipsoids.

In this paper, we evaluate the thermodynamic properties of hard body fluids and their mixture. We consider hard ellipsoids and hard spherocylinders. The pair potential between molecule i of species α and molecule j of species γ for such a system is given

by

$$\begin{aligned} u_{\alpha\gamma}(r_{ij}, \Omega_i^\alpha, \Omega_j^\gamma) &= \infty, & r_{ij} < \sigma_{\alpha\gamma}(\hat{r}_{ij}^{\alpha\gamma}, \Omega_{ij}^{\alpha\gamma}) \\ &= 0, & r_{ij} > \sigma_{\alpha\gamma}(\hat{r}_{ij}^{\alpha\gamma}, \Omega_{ij}^{\alpha\gamma}), \end{aligned} \quad (1)$$

where $r_{ij}^{\alpha\gamma} = |\bar{r}_i^\alpha - \bar{r}_j^\gamma|$, Ω_i^α and Ω_j^γ denote the orientation of molecule i of species α and molecule j of species γ ; and $\sigma_{\alpha\gamma}(\hat{r}_{ij}^{\alpha\gamma}, \Omega_{ij}^{\alpha\gamma})$ is the distance of closest approach between two hard bodies of species α and γ . There is no simple expression for the distance of closest approach between two hard bodies with arbitrary orientation. We take the Berne-Pechukas expression for $\sigma_{\alpha\gamma}$ (Berne and Pechukas 1972)

$$\begin{aligned} \sigma_{\alpha\gamma}(\hat{r}_{ij}^{\alpha\gamma}, \Omega_{ij}^{\alpha\gamma}) &= \sigma_{\alpha\gamma}^0 [1 - x_{\alpha\gamma} \{ (\hat{r}_{ij}^{\alpha\gamma} \cdot \hat{e}_i^\alpha)^2 + (\hat{r}_{ij}^{\alpha\gamma} \cdot \hat{e}_j^\gamma)^2 \\ &\quad - 2x_{\alpha\gamma} (\hat{r}_{ij}^{\alpha\gamma} \cdot \hat{e}_i^\alpha) (\hat{r}_{ij}^{\alpha\gamma} \cdot \hat{e}_j^\gamma) (\hat{e}_i^\alpha \cdot \hat{e}_j^\gamma) \} \\ &\quad \times \{ 1 - x^2 (\hat{e}_i^\alpha \cdot \hat{e}_j^\gamma)^2 \}^{-1}]^{-1/2}, \end{aligned} \quad (2)$$

where \hat{e}_i^α , and \hat{e}_j^γ 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 $r_{ij}^{\alpha\gamma}$. Here $\sigma_{\alpha\gamma}^0$ is constant with the unit of length and

$$x_{\alpha\gamma} = (x_{\alpha\gamma}^{02} - 1)/(x_{\alpha\gamma}^{02} + 1) \quad (3)$$

is an anisotropy parameter. The parameter $x_{\alpha\gamma}^0$ is the length ($2a_{\alpha\alpha}$) to width ($2b_{\alpha\alpha}$) ratio of a molecule of species α . The effective value of $x_{\alpha\gamma}^0$ between hard molecules of unlike species may be given as

$$x_{12}^0 = \frac{a_{11} + a_{22}}{b_{11} + b_{22}} = \frac{x_{11}^0 \sigma_{11}^0 + x_{22}^0 \sigma_{22}^0}{\sigma_{11}^0 + \sigma_{22}^0}, \quad (4)$$

where $\sigma_{\alpha\alpha}^0 = 2b_{\alpha\alpha}$ is the width of species α . The effective value of $\sigma_{\alpha\gamma}^0$ between hard bodies of unlike species can be given by

$$\sigma_{12}^0 = \frac{1}{2}(\sigma_{11}^0 + \sigma_{22}^0). \quad (5)$$

This model is valid for oblate as well as prolate shapes of arbitrary symmetry. This model has been used to calculate the compressibility factor for hard spherocylinders (Singh and Singh 1982, 1986), which are in good agreement with machine simulation results (Monson and Rigby 1980). We adopt this model to calculate the thermodynamic properties for hard non-sphere fluids both in classical and semi-classical limit.

In § 2, we discuss the basic theory for calculating the thermodynamic properties of hard non-sphere fluids in the semi-classical limit. Section 3 is confined to the classical fluids. The properties of the classical binary mixtures are calculated in § 4 and in § 5 we derive expressions for the first order quantum correction to the free energy and equation of states. The results are discussed in § 6.

2. Basic theory

We consider molecular fluid of hard-body molecules which are permanently in their ground electronic and ground vibrational states. The quantity of central importance

for constructing the theory of quantum fluid is the Slater sum, which may be defined in this case as

$$W_N(\bar{x}_1, \bar{x}_2, \dots, \bar{x}_N) = N! \lambda_t^{3N} q_r^{-N} \sum_x \psi_x^* \exp(-\beta \hat{H}_N) \psi_x \quad (6)$$

where

$$\lambda_t = (2\pi\hbar^2\beta/m)^{1/2}, \quad (7a)$$

$$q_r = \sum_J (2J+1) \exp(-\beta J(J+1)\hbar^2/2I). \quad (7b)$$

Here m is the mass, $I_x = I_y = I$ is the moment of inertia of a molecule and $\beta = (kT)^{-1}$. In (6), ψ_x 's are a complete set of orthonormal N -particle wave function. The summation in (6) extends over all states. \hat{H}_N is the Hamiltonian of the system

$$\hat{H}_N = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + \sum_{i<j} u(\bar{x}_i, \bar{x}_j), \quad (8)$$

where ∇_i^2 is the generalized Laplacian operator in an s -dimensional space and $u(\bar{x}_i, \bar{x}_j)$ is a pair potential between molecules i and j . q_r is the single-molecule rotational partition function.

In the semi-classical limit, where the quantum effects are small and treated as a correction to the classical value, we follow the method of Hemmer (1968) and Jancovici (1969) for hard-core system and write

$$W_N = W_N^c W_N^m, \quad (9)$$

where

$$W_N^c(\bar{x}_1, \bar{x}_2, \dots, \bar{x}_N) = \exp[-\beta \sum_{i<j} u(\bar{x}_i, \bar{x}_j)] \quad (10)$$

is the Boltzmann factor and W_N^m is a function which measures the deviations from classical behaviour. In the case of a hard sphere fluid, W_N^m is expressed in terms of 'modified' Ursell function U_l^m . In an analogous way, we can express W_N^m of a hard-body fluid in terms of U_l^m . Thus

$$\begin{aligned} W_N^m(\bar{x}_1, \bar{x}_2, \dots, \bar{x}_N) = & [1 + \sum_{i<j} U_2^m(\bar{x}_i, \bar{x}_j) \\ & + \sum_{i<j<k} U_3^m(\bar{x}_i, \bar{x}_j, \bar{x}_k) \\ & + \sum_{i<j} \sum_{k<l} U_2^m(\bar{x}_i, \bar{x}_j) U_2^m(\bar{x}_k, \bar{x}_l) + \dots]. \end{aligned} \quad (11)$$

Equation (11) can be solved successively for U_2^m, U_3^m, \dots ,

$$U_2^m(\bar{x}_1, \bar{x}_2) = W_2^m(\bar{x}_1, \bar{x}_2) - 1, \quad (12)$$

$$\begin{aligned} U_3^m(\bar{x}_1, \bar{x}_2, \bar{x}_3) = & W_3^m(\bar{x}_1, \bar{x}_2, \bar{x}_3) - W_2^m(\bar{x}_1, \bar{x}_2) \\ & - W_2^m(\bar{x}_1, \bar{x}_3) - W_2^m(\bar{x}_2, \bar{x}_3) + 2. \end{aligned} \quad (13)$$

From (9) and (11), we obtain expression for W_N

$$\begin{aligned} W_N(\bar{x}_1, \bar{x}_2, \dots, \bar{x}_N) = & W_N^c(\bar{x}_1, \bar{x}_2, \dots, \bar{x}_N) [1 + \sum_{i<j} U_2^m(\bar{x}_i, \bar{x}_j) \\ & + \sum_{i<j<k} U_3^m(\bar{x}_i, \bar{x}_j, \bar{x}_k) + \sum_{i<j} \sum_{k<l} U_2^m(\bar{x}_i, \bar{x}_j) U_2^m(\bar{x}_k, \bar{x}_l) \\ & + \dots]. \end{aligned} \quad (14)$$

The term U_l^m appearing in (14) can, in principle, be found from the solution of the quantum mechanical l -body problem. U_2^m is known only for the hard sphere system (Gibson and Byrnes 1975). In deriving (14) we have considered only the one-component fluid. However, its extension for mixture is straightforward.

The quantum-mechanical canonical partition function for a molecular fluid is defined as

$$Q_N = [N! \lambda_i^{3N} q_r^{-N} \Omega^N]^{-1} \int \cdots \int W_N(\bar{x}_1, \dots, \bar{x}_N) \prod_{i=1}^N d\bar{x}_i, \quad (15)$$

where

$$d\bar{x}_i \equiv d\bar{r}_i d\Omega_i = d\bar{r}_i \sin \theta_i d\theta_i d\phi_i$$

and $\Omega = 4\pi$ for linear molecule. Substituting (14) in (15), one can obtain an expression for the free energy. The result is

$$\frac{\beta A}{N} = \frac{\beta A^c}{N} - \frac{1}{2} \rho \int d\bar{r} \langle g^c(\bar{x}_1, \bar{x}_2) U_2^m(\bar{x}_1, \bar{x}_2) \rangle_{\Omega_1 \Omega_2}, \quad (16)$$

where $g^c(\bar{x}_1, \bar{x}_2)$ is the pair correlation function (PCF) of the classical fluid and $\rho = N/V$ is the number density. Here $\langle (\dots) \rangle_{\Omega_1 \Omega_2}$ represents an unweighted average over the molecular orientations Ω_1 and Ω_2 for the quantity within the angular bracket i.e.

$$\langle (\dots) \rangle_{\Omega_1 \Omega_2} = \frac{1}{\Omega_2} \int d\Omega_1 \int d\Omega_2 (\dots). \quad (17)$$

Other thermodynamic properties can be obtained from the free energy. Thus the equation of state is given by

$$\begin{aligned} \frac{\beta P}{\rho} = \frac{\beta P^c}{\rho} - \frac{1}{2} \rho \int d\bar{r}_2 \left\langle \left[g^c(\bar{x}_1, \bar{x}_2) \right. \right. \\ \left. \left. + \rho \frac{\partial g^c(\bar{x}_1, \bar{x}_2)}{\partial \rho} \right] U_2^m(\bar{x}_1, \bar{x}_2) \right\rangle_{\Omega_1 \Omega_2}. \end{aligned} \quad (18)$$

For a mixture of hard non-spheres, the expressions for the free energy and pressure are modified as

$$\begin{aligned} \frac{\beta A}{N} = \frac{\beta A^c}{N} - \frac{1}{2} \rho \sum_{\alpha, \gamma} c_\alpha c_\gamma \int d\bar{r}_2 \left\langle g_{\alpha\gamma}^c(\bar{x}_1, \bar{x}_2) \right. \\ \left. U_{2\alpha\gamma}^m(\bar{x}_1, \bar{x}_2) \right\rangle_{\Omega_1 \Omega_2} \end{aligned} \quad (19)$$

and

$$\begin{aligned} \frac{\beta P}{\rho} = \frac{\beta P^c}{\rho} - \frac{1}{2} \rho \sum_{\alpha, \gamma} c_\alpha c_\gamma \int d\bar{r}_2 \left\langle \left[g_{\alpha\gamma}^c(\bar{x}_1, \bar{x}_2) \right. \right. \\ \left. \left. + \rho \frac{\partial g_{\alpha\gamma}^c(\bar{x}_1, \bar{x}_2)}{\partial \rho} \right] U_{2,\alpha\gamma}^m(\bar{x}_1, \bar{x}_2) \right\rangle_{\Omega_1 \Omega_2}, \end{aligned} \quad (20)$$

where $g_{\alpha\gamma}^c(r_{12}, \Omega_1^\alpha, \Omega_2^\gamma)$ is the PCF of the hard-body mixture and $c_\alpha = N_\alpha/N$ is the concentration of species α .

The PCF can be expanded in power of density ρ as (Rice and Gray 1965)

$$g^c(\bar{x}_1, \bar{x}_2) = \exp[-\beta u(\bar{x}_1, \bar{x}_2)] \left[1 + \sum_{l=1}^{\infty} a_l^c(\bar{x}_1, \bar{x}_2) \rho^l \right], \quad (21)$$

where the coefficient $a_l^c(1, 2)$ is the cluster integral of the classical fluid involving two base points and l field points. Substituting (21) in (18) we obtain an expression for the equation of state in the virial form

$$\beta P = \rho + \sum_{n=2}^{\infty} B_n \rho^n, \quad (22)$$

where B_n is the n th virial coefficient for a system in the semiclassical limit. The first few virial coefficients can be written as

$$B_2 = B_2^c - \frac{1}{2} \int \langle \exp[-\beta u(\bar{x}_1, \bar{x}_2)] U_2^m(\bar{x}_1, \bar{x}_2) \rangle_{\Omega_1 \Omega_2} d\bar{r}_2 \quad (23)$$

and for $n > 2$

$$B_n = B_n^c - \frac{1}{2}(1+n) \int \langle \exp[-\beta u(\bar{x}_1, \bar{x}_2)] a_{n-2}^c(\bar{x}_1, \bar{x}_2) U_2^m(\bar{x}_1, \bar{x}_2) \rangle_{\Omega_1 \Omega_2} d\bar{r}_2, \quad (24)$$

where B_n^c is the n th virial coefficient for a classical fluid.

3. Classical system

In this section we consider the classical fluid mixture consisting of N_1 hard non-sphere molecules of species 1, N_2 hard non-sphere molecules of species 2, ..., N_s hard non-sphere molecules of species s , such that

$$N = \sum_{i=1}^s N_i.$$

We assume that the constituent molecules have, different shape and size.

In order to calculate the thermodynamic properties, we begin with the pressure equation for classical hard body mixture

$$\frac{\beta P^c}{\rho} = 1 - \frac{2\pi}{3} \beta \rho \sum_{\alpha, \gamma} c_\alpha c_\gamma \int dr_{12} r_{12}^3 \langle g_{\alpha\gamma}^c(r_{12}, \Omega_1^\alpha, \Omega_2^\gamma) [\partial u_{\alpha\gamma}(r_{12}, \Omega_1^\alpha, \Omega_2^\gamma)] / \partial r_{12} \rangle_{\Omega_1^\alpha \Omega_2^\gamma}. \quad (25)$$

The hard body potential can be written as

$$\begin{aligned} u_{\alpha\gamma}(r_{12}, \Omega_1^\alpha, \Omega_2^\gamma) &= u_{\alpha\gamma}(r_{12}/\sigma_{\alpha\gamma}(r_{12}^{\alpha\gamma}, \Omega_{12}^{\alpha\gamma})) \\ &= u_{\alpha\gamma}^{\text{HS}}(r_{12}^*) = \infty, \quad r_{12}^* < 1, \\ &= 0, \quad r_{12}^* > 1, \end{aligned} \quad (26)$$

where $r_{12}^* = r_{12}/\sigma_{\alpha\gamma}(r_{12}^{\alpha\gamma}, \Omega_{12}^{\alpha\gamma})$. We assume that the PCF $g_{\alpha\gamma}^c(r_{12}, \Omega_1^\alpha, \Omega_2^\gamma)$ obeys the simple scaling rule, generally known as the decoupling approximation (Parson 1979)

$$\begin{aligned} g_{\alpha\gamma}^c(r_{12}, \Omega_1^\alpha, \Omega_2^\gamma) &= g_{\alpha\gamma}^c(r_{12}/\sigma_{\alpha\gamma})(r_{12}, \Omega_{12}^{\alpha\gamma}) \\ &= g_{\alpha\gamma}^{c,HS}(r_{12}^*), \end{aligned} \quad (27)$$

where $g_{\alpha\gamma}^{c,HS}(r_{12}^*)$ is the PCF for the classical hard sphere mixture. Thus, the values of $g_{\alpha\gamma}^c(r_{12}, \Omega_1^\alpha, \Omega_2^\gamma)$ of the non-spherical hard body system under this approximation will be obtained from the values of $g_{\alpha\gamma}^{c,HS}(r_{12}^*)$ of the hard sphere mixture at packing fraction

$$\eta_{\alpha\gamma} = \rho V_{\alpha\gamma}, \quad (28)$$

where $v_{\alpha\gamma}$ is the volume of a hard body. This approximation introduces anisotropy in pair correlation but is not exact at high density. However, the equation of state obtained under the decoupling approximation is in good agreement with computer simulation results for one-component hard-spherocylinder fluid (Singh and Singh 1982, 1986). It is expected to provide good results for hard-body systems as well as their mixtures.

In the decoupling approximation, the orientational and positional degrees of freedom are completely decoupled. Using (27), we can evaluate (21) as

$$\beta P^c/\rho = 1 + 4\rho \sum_{\alpha,\gamma} c_\alpha c_\gamma v_{\alpha\gamma} F_1(x_{\alpha\gamma}) g_{\alpha\gamma}^{c,HS}(1), \quad (29)$$

where $g_{\alpha\gamma}^{c,HS}(1)$ is the radial distribution function (RDF) of the classical hard-sphere mixture and

$$F_1(x_{\alpha\gamma}) = (1 - x_{\alpha\gamma}^2)^{-1/2} \left[1 - \frac{1}{6} x_{\alpha\gamma}^2 - \frac{1}{40} x_{\alpha\gamma}^4 - \frac{1}{112} x_{\alpha\gamma}^6 - \dots \right]. \quad (30)$$

3.1 One-component fluid

For the classical (one-component) hard sphere fluid, the RDF at the core is given by (Carnehan and Starling 1969)

$$g^{c,HS}(1) = (1 - \eta/2)/(1 - \eta)^3 \quad (31)$$

and then (29) becomes

$$\beta P^c/\rho = 1 + [2\eta(2 - \eta)/(1 - \eta)^3] F_1(x), \quad (32)$$

where

$$\begin{aligned} \eta &= \rho v = \pi \rho \sigma_0^3/6 && \text{(for hard sphere)} \\ &= \pi \rho \sigma_0^3 x^0/6 && \text{(for hard ellipsoids)} \\ &= \frac{1}{12} \pi \rho \sigma_0^3 (3x^0 - 1) && \text{(for prolate hard spherocylinders).} \end{aligned} \quad (33)$$

Using the relation

$$\beta A_{EX}^c/N = \int_0^\rho [(\beta P^c/\rho) - 1] d\rho/\rho,$$

Table 1. Values of the virial co-efficients B_n^* ($\equiv B_n/V_{HE}^{n-1}$) for the classical hard ellipsoid fluid.

B_n^*	$1/x_0$	Present theory	Value of	
			Freasier and Bearman	Monte Carlo value
B_3^*	1.5	10.56	10.72	10.69
	2.0	11.70	12.25	12.09
	0.67	10.56	10.72	10.73
	0.50	11.70	12.25	12.30
B_4^*	1.5	19.39	19.20	19.73
	2.0	21.50	21.69	21.57
	0.67	19.39	19.20	19.62
	0.50	21.50	21.69	22.81
B_5^*	1.5	29.82	29.61	29.88
	2.0	33.06	32.85	31.87
	0.67	29.82	29.61	29.51
	0.50	33.06	32.85	33.18

the excess free energy per particle for the classical hard-body system is given by

$$\beta A_{EX}^c/N = \frac{\eta(4 - 3\eta)}{(1 - \eta)^2} F_1(x). \tag{34}$$

Expanding (32) in power of η we can obtain an expression for the equation of state in the form

$$\beta P^c = \rho + \sum_{n=2}^{\infty} \rho^n B_n^c, \tag{35}$$

Table 2. Equation of state, $\beta P^c/\rho$ for classical hard ellipsoid fluids.

η	Present	Monte Carlo	η	Present	Monte Carlo
$x_0 = 2$			$x_0 = \frac{1}{2}$		
0.1974	2.6111	2.6525	0.1969	2.6041	2.6596
0.3712	6.6939	7.0521	0.3163	4.8994	4.9669
0.4869	13.7710	13.9785	0.3937	7.6442	7.9787
0.5241	17.8024	17.9820	0.4660	11.9893	12.3596
0.5498	21.4512	21.9047	0.5262	18.0700	18.9055
$x_0 = 3$			$x_0 = \frac{1}{3}$		
0.1885	2.8759	2.7778	0.1827	2.7860	2.8653
0.2958	5.2390	5.3097	0.2948	5.2078	5.3286
0.3560	7.4353	7.3529	0.3267	6.2591	6.4103
0.4712	15.3066	14.9811	0.4194	10.9440	11.2360
0.5236	21.9902	21.3220	0.4712	14.3066	15.5556

where B_n^c is the n th virial coefficient for a classical hard ellipsoid system and is given by

$$B_n^c = B_n^{\text{CHS}} F_1(x), \quad (36)$$

where B_n^{CHS} is the value for the classical hard sphere system. The second virial coefficient is exact while the higher virial coefficients are approximate. The values of the third, fourth and fifth virial coefficients for the hard ellipsoids are given in table 1. The Monte Carlo (MC) values (Boublik 1983) along with values obtained by Freasier and Bearman (1976) are also reported in table 1. The agreement is good in all cases.

The values of the equation of states, $\beta P^c/\rho$ for the hard ellipsoids are given in table 2, along with the Monte Carlo values of Frenkel and Mulder (1985).

3.2 Mixtures

We extend the van der Waals one-(vdW 1-) fluid theory of mixture (Leland *et al* 1968), originally developed for the hard sphere system, to the hard-body mixture. This theory approximates the properties of a mixture by those of a fictitious hard-body fluid with the parameter

$$v_0 = \sum_{\alpha, \gamma} c_\alpha c_\gamma v_{\alpha\gamma} \quad (37)$$

We further assume that

$$v_0 F_1(x) = \sum_{\alpha, \gamma} c_\alpha c_\gamma v_{\alpha\gamma} F_1(x_{\alpha\gamma}). \quad (38)$$

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

$$g_{\alpha\gamma}^{\text{HS}}(1) = g^{\text{HS}}(d_0) \quad (39)$$

for all α and γ , where $g^{\text{HS}}(d_0)$ is the RDF of the hard sphere system at the core.

Substituting (38) and (39) (29) can be written as

$$\beta P/\rho = 1 + 4\eta_0 g^{\text{HS}}(d_0) F_1(x), \quad (40)$$

where

$$\eta_0 = \rho v_0 = \rho \sum_{\alpha, \gamma} c_\alpha c_\gamma v_{\alpha\gamma} \quad (41)$$

and

$$g^{\text{HS}}(d_0) = (1 - \eta_0/2)/(1 - \eta_0)^3. \quad (42)$$

Thus the pressure equation for the hard-body mixture is written as

$$\beta P/\rho = 1 + \frac{2\eta_0(2 - \eta_0)}{(1 - \eta_0)^3} F_1(x). \quad (43)$$

The Helmholtz free energy per particle for the mixture can be given by

$$\beta f = (\ln \rho - 1) + \sum c_\alpha \ln c_\alpha + \frac{\eta_0(4 - 3\eta_0)}{(1 - \eta_0)^2} F_1(x). \quad (44)$$

Equations (43) and (44) can be used for a binary mixture of both additive and non-additive hard bodies.

For a binary mixture of additive hard-body, η_0 can be expressed as

$$\begin{aligned}\eta_0 &= \rho [c_1^2 v_{11} + c_2^2 v_{22} + 2c_1 c_2 v_{12}] \\ &= \eta \left[1 + c_1 c_2 \left(\frac{2v_{12} - v_{11} - v_{22}}{c_1 v_{11} + c_2 v_{22}} \right) \right],\end{aligned}\quad (45)$$

where

$$\eta = \rho (c_1 v_{11} + c_2 v_{22}) \quad (46)$$

and $F_1(x)$ is obtained from (38)

$$F_1(x) = \left[\sum_{\alpha, \gamma} c_\alpha c_\gamma v_{\alpha\gamma} F_1(x_{\alpha\gamma}) \right] / \left[\sum_{\alpha, \gamma} c_\alpha c_\gamma v_{\alpha\gamma} \right]. \quad (47)$$

We now consider the binary mixture consisting of different constituent particles.

4. Classical binary mixtures

In this section, we apply the theory developed in §3.2 to calculate the thermodynamic properties of the classical binary mixture of hard non-sphere molecules.

4.1 A binary mixture of hard prolate spherocylinders

We consider a binary mixture of hard prolate spherocylinder of length $(l_{11} + d_{11})$ and breadth d_{11} (species 1) and hard prolate spherocylinder of length $(l_{22} + d_{22})$ and breadth d_{22} (species 2). For such a system, the volume of a molecule is

$$v_{\alpha\gamma} = (\pi d_{\alpha\gamma}^3 / 12) (3x_{\alpha\gamma}^0 - 1), \quad (48)$$

where

$$x_{\alpha\gamma}^0 = (l_{\alpha\gamma} + d_{\alpha\gamma}) / d_{\alpha\gamma}. \quad (49)$$

The effective values of $d_{\alpha\gamma}$, $l_{\alpha\gamma}$ and $x_{\alpha\gamma}^0$ for the hard prolate spherocylinder of unlike species may be written as

$$\begin{aligned}d_{12} &= (d_{11} + d_{22}) / 2, \\ l_{12} &= (l_{11} + l_{22}) / 2\end{aligned}\quad (50)$$

and

$$\begin{aligned}x_{12}^0 &= (l_{12} + d_{12}) / d_{12} = (x_{11}^0 d_{11} + x_{22}^0 d_{22}) / (d_{11} + d_{22}) \\ &= (x_{11}^0 + x_{22}^0 R) / (1 + R),\end{aligned}\quad (51)$$

where

$$R = d_{22} / d_{11}.$$

Using these values in (45) and (47), we obtain

$$\eta_0 = \eta \left[1 + c_1 c_2 \left\{ \frac{\frac{1}{4}(1+R)^3(3x_{12}^0 - 1) - (3x_{11}^0 - 1) - R^3(3x_{22}^0 - 1)}{c_1(3x_{11}^0 - 1) + c_2 R^3(3x_{22}^0 - 1)} \right\} \right], \quad (52)$$

$$\begin{aligned}
 F_1(x) = & [c_1^2(3x_{11}^0 - 1)F_1(x_{11}) + c_2^2R^3(3x_{22}^0 - 1)F_1(x_{22}) \\
 & + \frac{1}{4}c_1c_2(1 + R)^3(3x_{12}^0 - 1)F_1(x_{12})][c_1^2(3x_{11}^0 - 1) \\
 & + c_2^2R^3(3x_{22}^0 - 1) + \frac{1}{4}c_1c_2(1 + R)^3(3x_{12}^0 - 1)]^{-1}. \quad (53)
 \end{aligned}$$

When one of the species, say species 1, is a hard-sphere,

$$x_{11}^0 = 1,$$

$$x_{12}^0 = (1 + x_{22}^0R)/(1 + R)$$

and

$$F_1(x_{11}) = 1.$$

Then (52) and (53) take the form

$$\eta_0 = \eta \left[1 + c_1c_2 \left\{ \frac{\frac{1}{4}(1 + R)^3(3x_{12}^0 - 1) - 2 - R^3(3x_{22}^0 - 1)}{2c_1 + c_2R^3(3x_{22}^0 - 1)} \right\} \right] \quad (54)$$

and

$$\begin{aligned}
 F_1(x) = & [2c_1^2 + c_2^2R^3(3x_{22}^0 - 1)F_1(x_{22}) \\
 & + \frac{1}{4}c_1c_2(1 + R)^3(3x_{12}^0 - 1)F_1(x_{12})] \\
 & \times [2c_1^2 + c_2^2R^3(3x_{22}^0 - 1) + \frac{1}{4}c_1c_2(1 + R)^3(3x_{12}^0 - 1)]^{-1}. \quad (55)
 \end{aligned}$$

Using (54) and (55) in (43) and (44), we can calculate the equation of state and Helmholtz-free energy of binary mixture of hard spheres and hard prolate spherocylinder.

We now discuss some limiting cases. When both species have the same breadth $R = 1$ and $x_{12}^0 = (1 + x_{22}^0)/2$, then (54) reduces to

$$\eta_0 = \eta. \quad (56)$$

On the other hand, both species have the same volume, i.e.

$$v_{11} = v_{22},$$

we have

$$R^3 = 2/(3x_{22}^0 - 1)$$

and hence η_0 is given by

$$\eta_0 = \eta [1 + c_1c_2 \{ \frac{1}{8}(1 + R)^3(3x_{12}^0 - 1) - 2 \}]. \quad (57)$$

We can calculate the thermodynamic properties of a binary mixture of hard sphere and hard prolate spherocylinders. Simulation results are available only for two limiting cases (a) when both species have the same width, $R = 1$ and $x_{12}^0 = (1 + x_{22}^0)/2$ and (b) when both species have the same volume i.e. $v_{11} = v_{22}$ giving

$$R^3 = 2/(3x_{22}^0 - 1).$$

We have used (43) to calculate the equation of state $\beta P/\rho$ for a mixture of hard spheres (HS) and hard prolate spherocylinder (HSC) ($x^0 = 2$) in these two limiting cases. The results are compared with Monte Carlo (MC) values (Pavlicek *et al* 1979; Monson and

Table 3. Equation of state of binary mixtures of hard spheres and hard prolate spherocylinder with $x_0 = 2$.

		Mixture A		
C_1	η	Present	Boublik	Monte Carlo
0.20	0.33	5.171	5.13	5.17
	0.44	8.897	9.68	9.89
	0.50	14.658	14.43	14.34
0.50	0.20	2.531	2.51	2.50
	0.30	4.238	4.19	4.10
	0.40	7.453	7.36	7.31
	0.45	10.130	9.97	9.87
0.71	0.30	4.132	4.02	4.03
	0.40	7.240	6.96	7.02
	0.45	9.830	9.81	9.70
		Mixture B		
0.50	0.20	2.584	2.53	2.52
	0.30	4.408	4.26	4.20
	0.40	7.953	7.49	7.39
	0.45	10.989	10.16	10.22

Rigby 1980; Boublik and Nezbeda 1980) and values obtained by Boublik (1983) in table 3. The agreement is found to be good.

4.2 Binary mixture of hard ellipsoids

In this section, we consider a binary mixture of hard ellipsoids. The volume of a hard ellipsoid is

$$v_{\alpha\gamma} = \frac{\pi}{6} d_{\alpha\gamma}^3 x_{\alpha\gamma}^0 \tag{58}$$

where $x_{\alpha\alpha}^0$ is the length-to-breadth ratio of a hard ellipsoid of species α . The effective value of $x_{\alpha\gamma}^0$ between hard ellipsoids of unlike species is given by (51).

Substituting (58) in (52) and (53), we get

$$\eta_0 = \eta \left[1 + c_1 c_2 \left\{ \frac{\frac{1}{4}(1+R)^2(x_{11}^0 + x_{22}^0 R) - x_{11}^0 - x_{22}^0 R^3}{c_1 x_{11}^0 + c_2 x_{22}^0 R^3} \right\} \right], \tag{59}$$

$$F_1(x) = [c_1^2 x_{11}^0 F_1(x_{11}) + c_2^2 R^3 x_{22}^0 F_1(x_{22}) + \frac{1}{4} c_1 c_2 (1+R)^2 (x_{11}^0 + x_{22}^0 R) F_1(x_{12})] \times [c_1^2 x_{11}^0 + c_2^2 R^3 x_{22}^0 + \frac{1}{4} c_1 c_2 (1+R)^2 (x_{11}^0 + x_{22}^0 R)]^{-1}. \tag{60}$$

When the species 1 is a hard sphere, (59) and (60) reduce to

$$\eta_0 = \eta \left[1 + c_1 c_2 \left\{ \frac{\frac{1}{4}(1+R)^2(1+x_{22}^0 R) - 1 - x_{22}^0 R^3}{c_1 + c_2 x_{22}^0 R^3} \right\} \right], \tag{61}$$

$$F_1(x) = [c_1^2 + c_2^2 R^3 x_{22}^0 F_1(x_{22}) + \frac{1}{4} c_1 c_2 (1 + R)^2 (1 + x_{22}^0 R) F_1(x_{11})] \times [c_1^2 + c_2^2 R^3 x_{22}^0 + \frac{1}{4} c_1 c_2 (1 + R)^2 (1 + x_{22}^0 R)]^{-1}. \quad (62)$$

Values of η_0 and $F_1(x)$ depend on the values of R and x_{22}^0 . For example, when both species have the same breadth we have

$$\eta_0 = \eta \quad (63)$$

and

$$F_1(x) = \frac{c_1^2 + c_2^2 x_{22}^0 F_1(x_{22}) + c_1 c_2 (1 + x_{22}^0) F_1(x_{11})}{c_1 + c_2 x_{22}^0}. \quad (64)$$

On the other hand, when both species have the same volume,

$$R^3 x_{22}^0 = 1.$$

Hence η_0 in this case is given by

$$\eta_0 = \eta [1 + c_1 c_2 \{ \frac{1}{4} (1 + R)^3 (1 + x_{22}^0 R) - 2 \}] \quad (65)$$

and

$$F_1(x) = [c_1^2 + c_2^2 F_1(x_{22}) + \frac{1}{4} c_1 c_2 (1 + R)^2 (1 + x_{22}^0 R) \times F_1(x_{12})] [c_1^2 + c_2^2 + \frac{1}{4} c_1 c_2 (1 + R)^2 (1 + x_{22}^0 R)]^{-1}. \quad (66)$$

We have calculated the equation of state $\beta P/\rho$ of binary mixture of HS and hard ellipsoids (HE) with $x^0 = 2$ in the two limiting cases (A) when both species have the

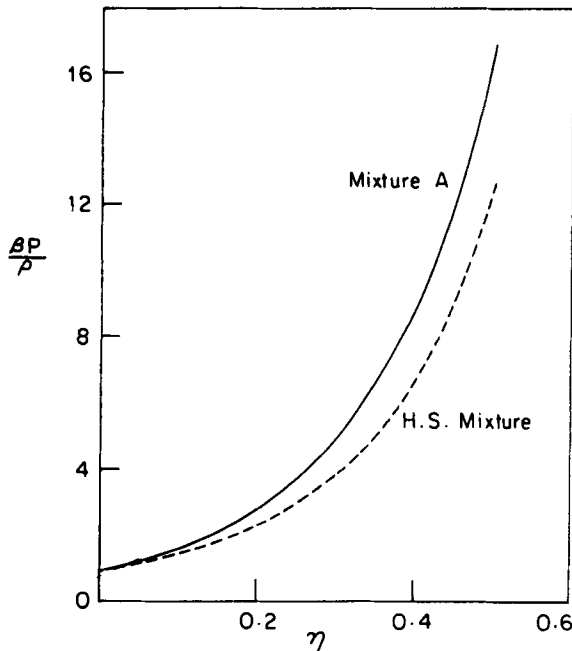


Figure 1. Equation of state of mixture A of hard spheres and hard ellipsoids with $x^0 = 2$ as a function of η . The equation of state of hard sphere mixture is indicated by a dashed line.

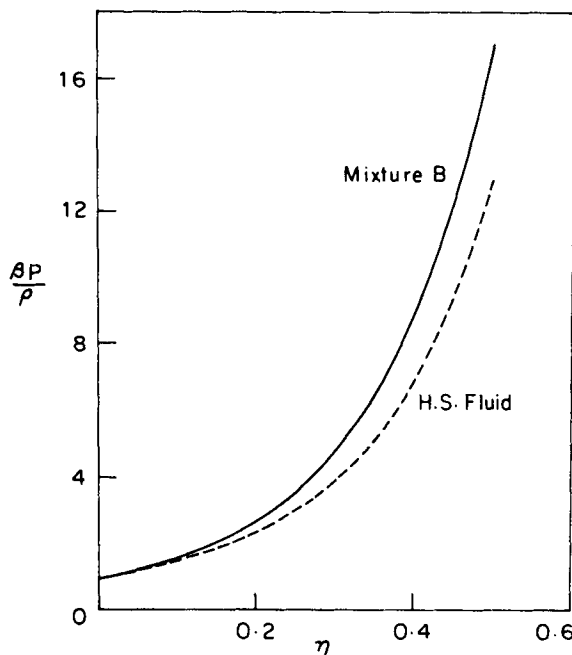


Figure 2. Equation of state of mixture B of hard spheres and hard ellipsoids with $x^0 = 2$ as a function of η . The equation of state of hard sphere fluid is indicated by a dashed line.

same width and (B) when both species have the same volume. The equation of state of mixture A is reported in figure 1 as a function of η . Values of the equation of state of the hard sphere mixture (whose species have the volumes equal to those of species of mixture A) are also shown in the figure. The equation of state of the mixture A is greater than the HS mixture.

In figure 2, we have compared the equation of state of mixture B with that of the HS fluid.

5. First quantum correction

U_2^m for the hard body is not known. In order to calculate the first order quantum correction to the thermodynamic properties, we make use of decoupling approximation for U_2^m as

$$U_2^m(r_{12}, \Omega_1, \Omega_2) = U_2^m(r_{12}/\sigma(f_{12}, \Omega_{12})) = U_{2,HS}^m(r_{12}^*), \quad (67)$$

where $U_{2,HS}^m(r_{12}^*)$ is the two-particle modified Ursell function for the hard spheres and is given by (Gibson and Byrnes 1975)

$$U_2^m(r_{12}^*) = -\frac{\lambda/\sigma(f_{12}, \Omega_{12})}{2\sqrt{2}} \delta(r_{12}^* - 1) + O(\lambda^2). \quad (68)$$

We also assume that the PCF $g^c(r_{12}, \Omega_1, \Omega_2)$ obeys the simple scaling rule

$$g^c(r_{12}, \Omega_1, \Omega_2) = g^c(r_{12}/\sigma(f_{12}, \Omega_{12})) = g_{HS}^c(r_{12}^*, \eta), \quad (69)$$

Table 4. Values of the coefficients A_n of (72) as a function of x_0 .

x_0	A_0	A_2	A_4	A_6	A_8	A_{10}
1.00	1.00000	0.00000	0.00000	0.00000	0.00000	0.00000
1.25	1.17050	-0.01517	-0.00009	0.00000	-0.00000	-0.00000
1.50	1.34771	-0.05543	-0.00103	-0.00003	-0.00000	-0.00000
1.75	1.53060	-0.11439	-0.00394	-0.00019	-0.00001	-0.00000
2.00	1.71844	-0.18734	-0.00965	-0.00070	-0.00006	-0.00001
2.25	1.91064	-0.27078	-0.01854	-0.00180	-0.00020	-0.00002
2.50	2.10668	-0.36215	-0.03072	-0.00369	-0.00050	-0.00008
2.75	2.30610	-0.45951	-0.04611	-0.00656	-0.00106	-0.00019
3.00	2.50851	-0.56141	-0.06447	-0.01051	-0.00195	-0.00041
3.25	2.71358	-0.66678	-0.08557	-0.01560	-0.00324	-0.00077
3.50	2.92100	-0.77477	-0.10912	-0.02187	-0.00498	-0.00132
3.75	3.13052	-0.88477	-0.13485	-0.02928	-0.00724	-0.00211
4.00	3.34191	-0.99627	-0.16250	-0.03781	-0.01003	-0.00318

where $g_{HS}^c(r_{12}^*, \eta)$ is the PCF for the classical hard spheres at the packing fraction $\eta = \rho v$.

Substituting (67) and (69) in (16) we obtain

$$\frac{\beta A}{N} - \frac{\beta A^c}{N} = \frac{\lambda}{2\sqrt{2}} \rho g_{HS}^c(1) \int d\Omega_1 \int d\Omega_2 E = \frac{\lambda}{2\sqrt{2}} \rho g_{HS}^c(1) \langle E \rangle + O(\lambda^2), \quad (70)$$

where

$$E = \frac{1}{2} \int d\hat{r}_{12} \sigma^2(\hat{r}_{12}, \Omega_{12}). \quad (71)$$

In order to evaluate $\langle E \rangle$, we expand $E(\Omega_{12})$ in terms of even Legendre polynomials $P_n(\cos \theta_{12})$, where $\cos \theta_{12} = \hat{e}_1 \cdot \hat{e}_2$. Thus the function $E(\Omega_{12})$ can be expressed as

$$E(\Omega_{12}) = 2\pi\sigma_0^2 \sum'_{n \geq 0} A_n P_n(\cos \theta_{12}), \quad (72)$$

where the prime over the summation indicates that only the even values of n are considered in the summation and the coefficient A_0 gives the average $\langle E \rangle$.

The convergence of the series of E is tested for a range of x_0 considered here. The values of the constants A_n of (72) as function of x_0 are given in table 4. We find that the series is fast convergent and only a few coefficients are needed to represent the series (72). Thus (70) gives

$$\beta A/N = (\beta A^c/N) + A_1^*(\lambda/\sigma), \quad (73)$$

where

$$A_1^* = \frac{\pi}{\sqrt{2}} A_0 (\rho\sigma_0^3) (1 - \eta/2)/(1 - \eta)^3, \quad (74)$$

where A_0 is given by (72). For hard sphere fluid, where $x_0 = 1$ the value of A_0 reduces to unity.

From (22), the equation of state for the hard body fluid, correct to the first order

quantum correction, is given by

$$\beta P/\rho = (\beta P^c/\rho) + P_1^*(\lambda/\sigma_0), \tag{75}$$

where

$$P_1^* = \frac{\pi}{\sqrt{2}} A_0 (\rho \sigma_0^3) (1 + \eta - \frac{1}{2} \eta^2) / (1 - \eta)^4 \tag{76}$$

and P^c is given by (32). Here η is the packing fraction given by (33).

Expanding (75) in power of η , we obtain expressions for the first few virial coefficients for the hard-body fluid

$$B_2 = B_2^c \left[1 + \frac{3}{2\sqrt{2}} S(x_0)(\lambda/\sigma_0) \right], \tag{77}$$

$$B_3 = B_3^c \left[1 + \frac{3}{\sqrt{2}} S(x_0)(\lambda/\sigma_0) \right], \tag{78}$$

and, in general, the expression for the n th virial coefficient is

$$B_n = B_n^c \left[1 + \frac{3}{2\sqrt{2}} (n-1) S(x_0)(\lambda/\sigma_0) \right], \tag{79}$$

where B_n^c is the n th virial coefficient of the classical hard-body fluid, and the quantity $S(x_0)$ is

$$\begin{aligned} S(x_0) &= \frac{A_0}{x_0 F(x)} \text{ (hard ellipsoid),} \\ &= \frac{2A_0}{(3x_0 - 1)F_1(x)} \text{ (hard prolate spherocylinder).} \end{aligned}$$

For hard spheres, $S(x_0)$ reduces to unity.

6. Results and discussion

We have calculated the excess free energy per particle, pressure and virial coefficients for the hard ellipsoid fluid in the semiclassical limit for different values of x_0 ($0.0 \leq x_0 \leq 3.0$). We have considered the first order quantum correction only.

Table 5. Values of the first order coefficients A_1^* and P_1^* for the hard ellipsoid fluid.

$x_0 \eta \rightarrow$	A_1^*			P_1^*		
	0.1	0.3	0.5	0.1	0.3	0.5
1/3	4.161	23.737	95.784	5.329	50.066	351.209
1/2	1.900	10.840	43.744	2.431	22.865	160.396
1.0	0.553	3.154	12.728	0.708	6.653	46.670
2.0	0.475	2.710	10.939	0.608	5.716	40.099
3.0	0.462	2.637	10.643	0.592	5.563	39.023

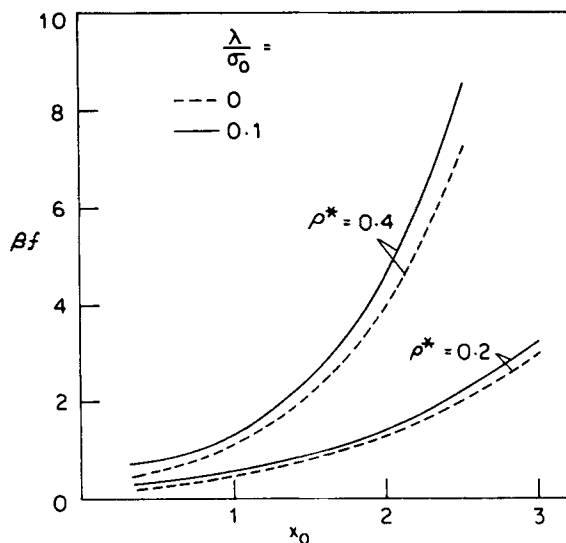


Figure 3. Excess free energy βf as a function of x_0 for $\rho^* = 0.2$ and 0.4 at $\lambda/\sigma_0 = 0.0$ and 0.1 .

The values of the first order coefficients A_1^* and P_1^* listed in table 5 show that these coefficients are positive and increase with increase of the packing fraction η and increase of the parameter x_0 .

The excess free energy per particles $\beta f (\equiv \beta A/N)$ as a function of x_0 is shown in figure 3 at $\rho^* = 0.2$ and 0.4 for $\lambda/\sigma_0 = 0.0$ and 0.1 . This shows that the quantum effect increases with increase of x_0 and increase of ρ^* .

Figure 4 demonstrates the variation of equation of state $\beta P/\rho$ as a function of x_0 for

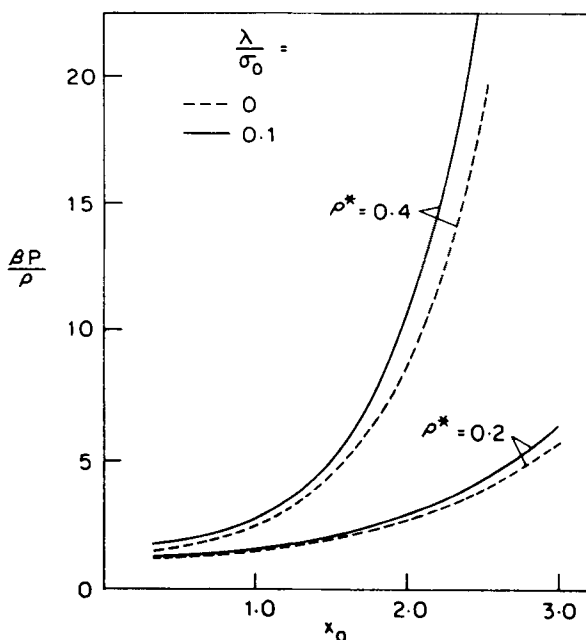


Figure 4. Equation of state $\beta P/\rho$ as a function of x_0 for $\rho^* = 0.2$ and 0.4 at $\lambda/\sigma_0 = 0.0$ and 0.1 .

$\lambda/\sigma_0 = 0.0$ and 0.1 at $\rho^* = 0.2$ and 0.4 . Its behaviour is similar to that of free energy. Table 6 demonstrates the excess free energy βf and equation of state $\beta P/\rho$ for different values of x_0 at $\eta = 0.1, 0.3$ and 0.5 . From this we see that the thermodynamic properties such as free energy and pressure of the fluid at given η are minimum at $x_0 = 1.0$ and increase when x_0 either increases or decreases.

In table 7, we report the percentage contribution of quantum correction to the free energy and pressure of HE fluid at $\lambda/\sigma_0 = 0.1$. We find that the quantum correction increases with increase of η and depends on the value of x_0 . We further find that the upper limit of density to which the first order quantum correction term is sufficient to calculate the free energy and pressure, for a given λ/σ_0 also depends on the value of x_0 .

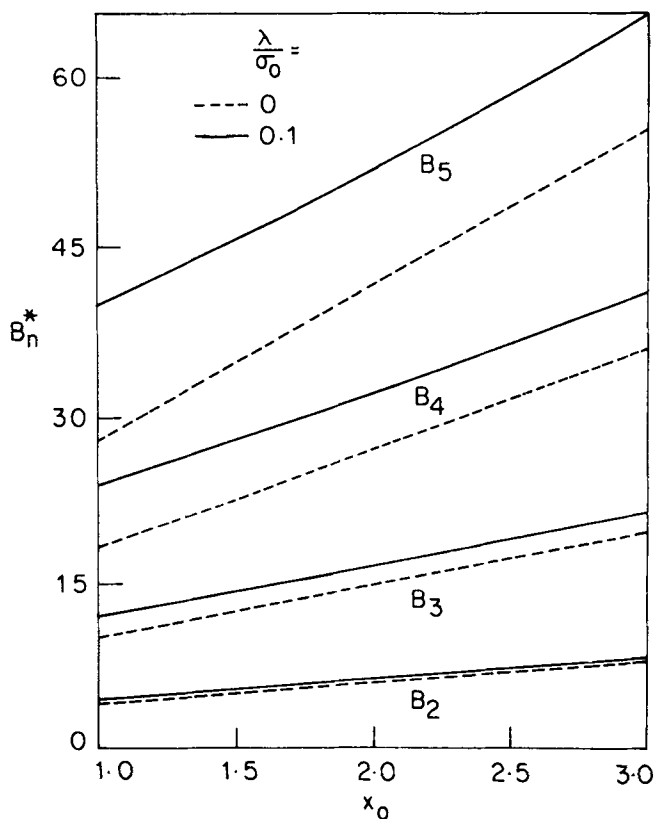
The virial coefficients $B_2^* - B_3^*$ for the HE fluid are shown in figure 5 as a function of x_0 for $\lambda/\sigma_0 = 0.0$ and 0.1 . From this, we find that the virial coefficients increase with x_0 .

Table 6. Excess free energy βf and equation of state $\beta P/\rho$ for the hard ellipsoid fluid.

x_0	η	βf		$\beta P/\rho$	
		$\lambda/\sigma = 0.0$	$\lambda/\sigma = 0.1$	$\lambda/\sigma = 0.0$	$\lambda/\sigma = 0.1$
1/3	0.1	0.671	1.087	1.765	2.298
	0.2	1.560	2.682	3.064	4.904
	0.3	2.706	5.160	5.365	10.372
	0.4	4.567	9.297	9.699	22.707
	0.5	7.340	16.918	18.615	53.736
	0.6	12.110	33.063	39.533	145.796
1/2	0.1	0.535	0.725	1.610	1.853
	0.2	1.244	1.756	2.646	3.486
	0.3	2.221	3.305	4.481	6.767
	0.4	3.641	5.802	7.936	13.876
	0.5	5.852	10.227	15.045	31.085
	0.6	9.656	19.225	31.724	130.253
1.0	0.1	0.457	0.512	1.521	1.592
	0.2	1.063	1.212	2.406	2.651
	0.3	1.898	2.213	3.974	4.639
	0.4	3.111	3.740	6.926	8.654
	0.5	5.000	6.273	13.000	17.667
	0.6	8.250	11.034	27.250	41.370
2.0	0.1	0.535	0.582	1.610	1.671
	0.2	1.244	1.372	2.646	2.856
	0.3	2.221	2.492	4.481	5.052
	0.4	3.641	4.181	7.936	9.421
	0.5	5.852	6.946	15.045	19.055
	0.6	9.656	12.048	31.724	43.856
3.0	0.1	0.671	0.717	1.765	1.824
	0.2	1.560	1.684	3.064	3.269
	0.3	2.786	3.050	5.365	5.922
	0.4	4.567	5.092	9.699	11.144
	0.5	7.340	8.404	18.615	22.517
	0.6	12.110	14.438	39.533	51.340

Table 7. Percentage of quantum correction for the free energy and pressure of the hard ellipsoid fluid at $\lambda/\sigma_0 = 0.1$.

x_0	$[(f - f^c)/f^c] \times 100$		$[(P - P^c)/P^c] \times 100$	
	$\eta = 0.2$	$\eta = 0.3$	$\eta = 0.2$	$\eta = 0.3$
1/3	71.923	85.212	60.052	93.327
1/2	41.158	48.807	31.746	51.015
1.0	14.017	16.596	10.183	16.734
2.0	10.289	12.202	7.937	12.743
3.0	7.949	9.476	6.691	10.382

**Figure 5.** Virial coefficients B_2^* , B_3^* , B_4^* and B_5^* as function of x_0 at $\lambda/\sigma_0 = 0.0$ and 0.1 .

We thus conclude that the quantum effect increases with increases of anisotropy parameter x_0 .

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