

## Quantum corrections to thermodynamics of polar hard sphere fluids

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**Abstract.** The quantum corrections to the thermodynamic properties of polar hard sphere fluids and fluid mixtures are estimated taking into account the influence of dipole and quadrupole moments. Expressions are given for the second virial coefficient, free energy and pressure and results are given for different values of  $\mu^*$  and  $\theta^*$ . The first order quantum correction arises due to the translational contribution only. The quantum effect increases with density,  $\mu^*$  and  $\theta^*$ . Numerical results are also estimated for binary mixtures of (i) hard spheres and dipole hard spheres and (ii) hard spheres and quadrupole hard spheres. The 'excess' free energy for dipole hard sphere binary mixture is also reported. It is found that the 'excess' quantum effect depends on the concentration and the particle diameter ratio and increases with increase of  $\mu^*$  and  $\theta^*$ .

**Keywords.** Polar hard sphere fluid; dipole moments; quadrupole moments; semiclassical fluid; quantum corrections; free energy; equation of state.

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### 1. Introduction

This paper estimates the quantum corrections to the thermodynamic properties of simple polar fluid and fluid mixtures. The simplest model for such fluids is hard spheres with imbedded point dipoles and point quadrupoles. The pair potential for such a system is given by

$$u_{\alpha\gamma}(x_1, x_2) = u_{\alpha\gamma}^{\text{HS}}(r_{12}) + u_{\alpha\gamma}^a(x_1, x_2), \quad (1)$$

where  $u_{\alpha\gamma}^{\text{HS}}(r_{12})$  is the hard sphere potential and  $u_{\alpha\gamma}^a(x_1, x_2)$  is the angle dependent part of the pair potential. In (1) the vector  $x_i \equiv (\bar{r}_i, \omega_i)$  represents both the position of the centre of mass and orientation of the  $i$ th molecule. For polar fluids we take

$$u_{\alpha\gamma}^a = u_{\alpha\gamma}^{dd} + u_{\alpha\gamma}^{dq} + u_{\alpha\gamma}^{qq}, \quad (2)$$

where  $u_{\alpha\gamma}^{dd}$  is the interaction between the permanent dipole moment of molecules of species  $\alpha$  and  $\gamma$ ,  $u_{\alpha\gamma}^{dq}$  is the interaction between the dipole moment in one molecule and the quadrupole moment in other molecule and  $u_{\alpha\gamma}^{qq}$  is the interaction between the quadrupole moments of the molecules. They are expressed as

$$u_{\alpha\gamma}^{dd} = \frac{\mu_\alpha \mu_\gamma}{r^3} [\sin \theta_\alpha \sin \theta_\gamma \cos \phi_{\alpha\gamma} - 2 \cos \theta_\alpha \cos \theta_\gamma], \quad (3)$$

$$u_{\alpha\gamma}^{dq} = \frac{3}{4r^4} \{ \mu_\alpha \theta_\gamma [\cos \theta_\alpha (3 \cos^2 \theta_\gamma - 1) - 2 \sin \theta_\alpha \sin \theta_\gamma \cos \theta_\gamma \cos \phi_{\alpha\gamma}] \\ + \mu_\gamma \theta_\alpha [\cos \theta_\gamma (3 \cos^2 \theta_\alpha - 1) - 2 \sin \theta_\gamma \sin \theta_\alpha \cos \theta_\alpha \cos \phi_{\alpha\gamma}] \}, \quad (4)$$

$$u_{\alpha\gamma}^{qq} = \frac{3}{4} \frac{\theta_\alpha \theta_\gamma}{r^5} [1 - 5(\cos^2 \theta_\alpha + \cos^2 \theta_\gamma) - 15 \cos^2 \theta_\alpha \cos^2 \theta_\gamma \\ + 2(\sin \theta_\alpha \sin \theta_\gamma \cos \phi_{\alpha\gamma} - 4 \cos \theta_\alpha \cos \theta_\gamma)^2], \quad (5)$$

where  $\theta_\alpha, \theta_\gamma$  and  $\phi_{\alpha\gamma} \equiv \phi_\alpha - \phi_\gamma$  are the angles which determine the orientation of the molecule with respect to the line joining the centres of the molecules.  $\mu_\alpha$  and  $\theta_\alpha$  are, respectively, the dipole moment and quadrupole moment of a molecule of species  $\alpha$ .

A considerable progress has been made for classical polar fluids (Rushbrooke *et al* 1973; Stell *et al* 1972, 1974; Larsen *et al* 1977; Singh and Gupta 1970; Singh and Singh 1974) and fluid mixtures (Adelman and Deutch 1973; Melnyk and Smith 1974). However our understanding of the quantum polar fluids is far from satisfactory (Poweles and Rickaygen 1978; Berne and Thirumalai 1986). Quantum effects on the structure of liquid water have been studied by Kuharski and Rossky (1985a, b) and Wallqvist and Berne (1985).

In the semiclassical limit i.e. at high temperature, where the quantum effects are small and can be treated as a correction to the classical behaviour, the usual method for calculating the quantum corrections is the Wigner-Kirkwood (WK) expansion (Wigner 1932; Kirkwood 1933). This method has been used to calculate the equilibrium properties of molecular fluids (Singh and Sinha 1984, 1987) and molecular fluid mixtures (Singh and Sinha 1987). However this method fails (Singh and Sinha 1981) where the intermolecular potential has a hard core since it requires the potential to be differentiable.

Another method is the 'modified' WK expansion (Singh and Sinha 1978; Derderian and Steele 1971, 1973) in which the hard sphere basis functions are used rather than the free particle basis functions. This method has been extensively used to calculate the equilibrium properties of hard-core fluid of spherical molecules (Singh and Sinha 1981). This method can be extended to the case of the polar hard sphere fluids.

In this paper we calculate the quantum correction to the thermodynamic properties of the polar hard sphere fluids and fluid mixtures. We consider the pair potential defined by (1).

In §2 we discuss the basic formalism for calculating the thermodynamic properties of polar hard sphere fluid mixtures in the semiclassical limit. Expressions are given for the free energy and equation of state for fluid mixtures. Section 3 is devoted to obtain expressions for the second virial coefficient of the polar hard sphere fluid in the semiclassical limit. In §4 we give explicit expressions for the free energy and equation of state. We simplify these expressions for one-component polar fluid and binary mixture in §§5 and 6, respectively. The results are discussed in §7. The summary is given in §8.

## 2. Basic formalism

We consider a polar hard sphere fluid mixture, consisting of  $N_1$  molecules of species 1,  $N_2$  molecules of species 2, ...,  $N_s$  molecules of species  $s$ , such that the total number

of molecules is  $N = \sum_{\alpha=1}^s N_{\alpha}$ . In quantum statistical mechanics, the canonical partition function may be defined in this case as (Singh and Sinha 1987)

$$Q_N = \left[ \prod_{\alpha} (N_{\alpha}! \lambda_{\alpha}^{3N_{\alpha}} q_{\alpha}^{-N_{\alpha}} \Omega^{N_{\alpha}}) \right]^{-1} \int \cdots \int W_N(x_1, x_2, \dots, x_N) \prod_{i=1}^N dx_i, \quad (6)$$

where

$$dx_i = d\bar{r}_i d\omega_i = d\bar{r}_i \sin \theta_i d\theta_i d\phi_i,$$

$\Omega = 4\pi$  for linear molecules and

$$W_N(x_1, x_2, \dots, x_N) = \prod_{\alpha=1}^s (N_{\alpha}! \lambda_{\alpha}^{3N_{\alpha}} q_{\alpha}^{-N_{\alpha}}) \sum_x \psi_x^* \exp(-\beta \hat{H}_N) \psi_x \quad (7)$$

is known as the Slater sum of a system, whose Hamiltonian is given by

$$\hat{H}_N = - \sum_{\alpha=1}^s \frac{\hbar^2}{2m_{\alpha}} \sum_{i=1}^{N_{\alpha}} \nabla_i^2 + U(x_1, x_2, \dots, x_N), \quad (8)$$

where  $\nabla_i^2$  is the generalized Laplacian operator in a  $s$ -dimensional space and  $U$  is the total interaction potential. In (7),  $\psi_x$ 's are the complete set of orthogonal  $N$ -particle wave function. The summation in (7) extends over all states. Here  $\lambda_{\alpha}$  is the thermal wavelength and  $q_{\alpha}$  is the single molecule rotational partition function of component  $\alpha$

$$\lambda_{\alpha} = (2\pi\hbar^2 \beta / m_{\alpha})^{1/2}. \quad (9)$$

$$q_{\alpha} = \sum_{J_{\alpha}} (2J_{\alpha} + 1) \exp[-\beta J_{\alpha}(J_{\alpha} + 1)\hbar^2 / 2I_{\alpha}]. \quad (10)$$

Here  $m_{\alpha}$  is the mass and  $I_{\alpha}$  is the moment of inertia of a molecule of species  $\alpha$  and  $\beta = (kT)^{-1}$ .

In the semiclassical limit,  $q_{\alpha}$  for linear molecule is given by (Gray and Gubbin 1984)

$$q_{\alpha} = \Lambda_{\alpha}^{-2} [1 + \frac{1}{6}(\beta\hbar^2 / I_{\alpha})], \quad (11)$$

where

$$\Lambda_{\alpha}^{-2} = (\beta\hbar^2 / 2I_{\alpha})^{-1} \quad (12)$$

is the classical value for the single-molecule rotational partition of species  $\alpha$ .

Assuming that the quantum effects are largely determined by the repulsion due to the hard-core, we choose the basic functions which are the eigen functions of the hard sphere Hamiltonian, defined as

$$\hat{H}_N^0 = - \sum_{\alpha=1}^s \frac{\hbar^2}{2m_{\alpha}} \sum_{i=1}^{N_{\alpha}} \nabla_i^2 + U_{\text{hs}}(\bar{r}_1, \bar{r}_2, \dots, \bar{r}_N). \quad (13)$$

Let  $\psi_x^0$  be the eigen function for the hard-sphere Hamiltonian. Thus

$$\begin{aligned} \psi_x^0 &= 0, & r_{ij} < \sigma_{\alpha\gamma} \\ &= \phi_K(\bar{r}_1, \bar{r}_2, \dots, \bar{r}_N) \chi_m(\theta_1, \phi_1, \dots, \theta_N, \phi_N), & r_{ij} > \sigma_{\alpha\gamma}, \end{aligned} \quad (14)$$

where  $\sigma_{\alpha\gamma}$  is the hard sphere diameter of molecules of species  $\alpha$  and  $\gamma$ ,  $\phi_K$  is the eigen function of the Hamiltonian

$$\hat{H}_{\text{tr}}^0 = - \sum_{\alpha=1}^s \frac{\hbar^2}{2m_{\alpha}} \sum_{i=1}^{N_{\alpha}} \nabla_{r_i}^2 + U_{\text{hs}}, \quad (15)$$

and  $\chi_m$  is the eigen function of the rotational kinetic energy

$$\hat{H}_{\text{rot}}^0 = - \sum_{\alpha=1}^s \frac{\hbar^2}{2I_\alpha} \sum_{i=1}^{N_\alpha} \nabla_{\omega_i}^2. \quad (16)$$

Then

$$\hat{H}_N^0 \phi_K \chi_m = \left[ \sum_{\alpha} \sum_i \frac{p_i^2}{2m_\alpha} + \sum_{\alpha} \sum_i e_\alpha^i \right] \phi_K \chi_m, \quad (17)$$

where

$$e_\alpha^i = J_\alpha(J_\alpha + 1)\hbar^2/2I_\alpha$$

is the energy eigen value corresponding to the rotational kinetic energy. We regard the attractive interaction as a perturbation on the hard sphere system and write

$$\hat{H}_N = \hat{H}_N^0 + U_P(x_1, x_2, \dots, x_N), \quad (18)$$

where

$$U_P(x_1, x_2, \dots, x_N) = \sum_{\alpha, \gamma=1}^s \sum_{i < j} u_{\alpha\gamma}^p(x_i, x_j), \quad (19)$$

where  $u_{\alpha\gamma}^p(x_i, x_j)$  is the intermolecular perturbation potential which is zero for  $r_{ij} < \sigma_{\alpha\gamma}$ .

In terms of the hard sphere wave function  $\psi_x^0$ , the Slater sum can be written as

$$W_N(x_1, x_2, \dots, x_N) = \prod_{\alpha=1}^s [N_\alpha! \lambda_\alpha^{3N_\alpha} q_\alpha^{-N_\alpha}] \sum_x \psi_x^{0*} \exp[-\beta(\hat{H}_0 + U)] \psi_x^0. \quad (20)$$

Following Friedmann's treatment (Friedmann 1962), we write

$$\exp[-t\beta(\hat{H}_N^0 + U_P)] = \exp[-t\beta U_P] T(t) \exp[-t\beta \hat{H}_N^0], \quad (21)$$

where

$$T(t) = 1 + T_1(t) + T_2(t) + \dots \quad (22)$$

with

$$T_1(t) = \int_0^t dt_1 \exp(t_1 \beta U_P) [\exp(-t_1 \beta U_P), \beta \hat{H}_N^0] \quad (23a)$$

$$T_2(t) = \int_0^t dt_1 \exp(t_1 \beta U_P) [\exp(-t_1 \beta U_P) T_1(t_1), \beta \hat{H}_N^0]. \quad (23b)$$

Substituting (21) and (22) in (20) we obtain

$$W_N = W_N^0 + W_N^1 + W_N^2 + \dots, \quad (24)$$

where

$$\begin{aligned} W_N^0(x_1, x_2, \dots, x_N) &= \prod_{\alpha=1}^s [N_\alpha! \lambda_\alpha^{3N_\alpha} q_\alpha^{-N_\alpha}] \sum_x \psi_x^{0*} \exp[-\beta(\hat{H}_N^0 + U_P)] \psi_x^0 \\ &= \exp(-\beta U_P) W_N^{\text{hs}}(\bar{r}_1, \bar{r}_2, \dots, \bar{r}_N) \end{aligned} \quad (25)$$

$$\begin{aligned} W_N^1(x_1, x_2, \dots, x_N) &= \prod_{\alpha=1}^s [N_\alpha! \lambda_\alpha^{3N_\alpha} q_\alpha^{-N_\alpha}] \sum_x \psi_x^{0*} \\ &\quad \times \exp(-\beta U_P) T_1(1) \exp(-\beta \hat{H}_N^0) \psi_x^0 \\ &= -\exp(-\beta U_P) \sum_{\alpha=1}^s \left\{ \left( \frac{\hbar^2 \beta^2}{2m_\alpha} \right) \sum_{i=1}^{N_\alpha} [\frac{1}{2} \nabla_{r_i}^2 U_P \right. \end{aligned}$$

$$-\frac{1}{3}\beta(\nabla_{r_i} U_P)^2 + \nabla_{r_i} U_P \cdot \nabla_{r_i}] W_N^{hs}(\bar{r}_1, \dots, \bar{r}_N) + \left(\frac{\hbar^2 \beta^2}{2I_\alpha}\right) \times \sum_{i=1}^{N_\alpha} \left[\frac{1}{2}\nabla_{\omega_i}^2 U_P - \frac{1}{3}\beta(\nabla_{\omega_i} U_P)^2\right] \left. \right\} W_N^{hs}(\bar{r}_1, \dots, \bar{r}_N) \quad (26)$$

$$W_N^2(x_1, x_2, \dots, x_N) = \prod_{\alpha=1}^s [N_\alpha! \lambda_\alpha^{3N_\alpha} q_\alpha^{-N_\alpha}] \sum_x \psi_x^{0*} \times \exp(-\beta U_P) T_2(1) \exp(-\beta \hat{H}_N^0) \psi_x^0 \quad (27)$$

and

$$W_N^{hs}(\bar{r}_1, \dots, \bar{r}_N) = \prod_{\alpha=1}^s [N_\alpha! \lambda_\alpha^{3N_\alpha}] \sum_K \phi_K^* \exp(-\beta \hat{H}_N^0) \phi_K \quad (28)$$

is the Slater sum of the hard sphere mixture.

Recently Singh *et al* (1990) have used the superposition approximation to evaluate  $W_N^2$  for one-component molecular fluid. Its extension for fluid mixture is straightforward. Thus the result is

$$W_N^2(x_1, x_2, \dots, x_N) = \exp(-\beta U_P) W_N^{hs}(\bar{r}_1, \dots, \bar{r}_N) \sum_{\alpha, \gamma} \left\{ \left(\frac{\hbar^2 \beta^2}{m_{\alpha\gamma}}\right) \times \sum_{i < j} \left[ \frac{1}{3} \nabla_{r_{ij}}^2 u_{\alpha\gamma}^p(x_i, x_j) - \frac{1}{4} \beta \left(\frac{\partial u_{\alpha\gamma}^p(x_i, x_j)}{\partial r_{ij}}\right)^2 \right] + \left(\frac{\hbar^2 \beta^2}{2I_{\alpha\gamma}}\right) \sum_i \left[ \frac{1}{3} \nabla_{\omega_i}^2 u_{\alpha\gamma}^p(x_i, x_j) - \frac{1}{4} (\nabla_{\omega_i} u_{\alpha\gamma}^p(x_i, x_j))^2 \right] \right\}, \quad (29)$$

where  $m_{\alpha\alpha} = m_\alpha$  is the mass of a molecule of species  $\alpha$  and  $m_{\alpha\gamma} = 2m_{\alpha\alpha}m_{\gamma\gamma}/(m_{\alpha\alpha} + m_{\gamma\gamma})$ , and  $I_{\alpha\alpha} = I_\alpha$  is the moment of inertia of a molecule of species  $\alpha$  and  $I_{\alpha\gamma} = 2I_{\alpha\alpha}I_{\gamma\gamma}/(I_{\alpha\alpha} + I_{\gamma\gamma})$ .

In the semiclassical limit,  $W_N^{hs}$  can be expressed as (Hemmer 1968; Jancovici 1969; Singh and Sinha 1982)

$$W_N^{hs}(\bar{r}_1, \dots, \bar{r}_N) = \exp\left[-\beta \sum_{\alpha, \gamma} \sum_{i < j} u_{\alpha\gamma}^{hs}(\bar{r}, \bar{r})\right] \left[ 1 + \sum_{\alpha, \gamma} \sum_{i < j} U_{\alpha\gamma}^{m,hs}(\bar{r}_i, \bar{r}_j) + \sum_{\alpha, \gamma, \delta} \sum_{i < j < k} U_{\alpha\gamma\delta}^{m,hs}(\bar{r}_i, \bar{r}_j, \bar{r}_k) + \dots \right], \quad (30)$$

where  $U_{\alpha\gamma, \dots, \delta}^{m,hs}(\bar{r}_1, \bar{r}_2, \dots, \bar{r}_l)$  is the  $l$ -particle modified Ursell function for hard sphere fluid mixture. The two-body modified Ursell function for hard sphere fluid mixture is given by (Gibson and Byrnes 1975)

$$U_{\alpha\gamma}^{m,hs}(r) = \phi_{\alpha\gamma}^0(r) + \phi_{\alpha\gamma}^1(r) + \dots \quad \gamma > \sigma_{\alpha\gamma} \quad (31)$$

where

$$\phi_{\alpha\gamma}^0(r) = -\exp(-\xi_{\alpha\gamma}^2) \quad (32a)$$

$$\phi_{\alpha\gamma}^1(r) = \frac{1}{\sqrt{2}} (\lambda_{\alpha\gamma}/\sigma_{\alpha\gamma}) \xi_{\alpha\gamma}^2 \operatorname{erfc}(\xi_{\alpha\gamma}). \quad (32b)$$

Here  $\xi_{\alpha\gamma} = [(2\pi)^{1/2}/(\lambda_{\alpha\gamma}/\sigma_{\alpha\gamma})][(r/\sigma_{\alpha\gamma}) - 1]$  and  $\text{erfc}(\xi_{\alpha\gamma})$  is the complimentary error function.  $\lambda_{\alpha\gamma}$  is the thermal wave length of molecules of species  $\alpha$  and  $\gamma$  defined as

$$\lambda_{\alpha\gamma} = (2\pi\hbar^2\beta/m_{\alpha\gamma})^{1/2}.$$

Thus we have (Singh and Sinha 1982)  $\lambda_{\alpha\gamma} = [(\lambda_{\alpha\alpha}^2 + \lambda_{\gamma\gamma}^2)/2]^{1/2}$ .

Substituting (4) in (6) and integrating by parts, we obtain an expression for free energy of a semiclassical fluid mixture

$$\frac{\beta A}{N} = \frac{\beta A^c}{N} + A_1 + A_2 + \dots, \quad (33)$$

where

$$A_1 = -\frac{1}{2}\rho \sum_{\alpha,\gamma} c_\alpha c_\gamma \int d\bar{r}_2 U_{\alpha\gamma}^{m,hs}(\bar{r}_1, \bar{r}_2) \langle g_{\alpha\gamma}^c(x_1, x_2) \rangle_{\omega_1\omega_2} \quad (34)$$

$$A_2 = A_2^{\text{tr}} + A_2^{\text{rot}} - \sum_{\alpha} c_\alpha \left( \frac{\hbar^2\beta}{2I_\alpha} \right), \quad (35)$$

with

$$\begin{aligned} A_2^{\text{tr}} = & -\frac{1}{2}\rho \sum_{\alpha,\gamma} c_\alpha c_\gamma \int d\bar{r}_2 \langle g_{\alpha\gamma}^c(x_1, x_2) U_{\alpha\gamma, \text{tr}}^m(x_1, x_2) \rangle_{\omega_1\omega_2} \\ & -\frac{1}{6}\rho^2 \sum_{\alpha,\gamma,\delta} c_\alpha c_\gamma c_\delta \int d\bar{r}_2 d\bar{r}_3 \langle g_{\alpha\gamma\delta}^c(x_1 x_2 x_3) U_{\alpha\gamma\delta, \text{tr}}^m(x_1 x_2 x_3) \rangle_{\omega_1\omega_2\omega_3} \\ & -\frac{1}{8}\rho^3 \sum_{\alpha,\gamma,\delta,\xi} c_\alpha c_\gamma c_\delta c_\xi \int d\bar{r}_2 d\bar{r}_3 d\bar{r}_4 \langle [g_{\alpha\gamma\delta\xi}^c(x_1, x_2, x_3, x_4) \\ & - g_{\alpha\gamma}^c(x_1 x_2) g_{\delta\xi}^c(x_3 x_4)] \rangle_{\omega_1 \dots \omega_4} U_{\alpha\gamma}^{m,hs}(x_1 x_2) U_{\delta\xi}^{m,hs}(x_3 x_4) \end{aligned} \quad (36a)$$

and

$$A_2^{\text{rot}} = -\frac{1}{2}\rho \sum_{\alpha,\gamma} c_\alpha c_\gamma \int d\bar{r}_2 \langle g_{\alpha\gamma}^c(x_1, x_2) U_{\alpha\gamma, \text{rot}}^m(x_1 x_2) \rangle_{\omega_1\omega_2}, \quad (36b)$$

where

$$U_{\alpha\gamma, \text{tr}}^m(x_1, x_2) = U_{\alpha\gamma}^{m,hs}(\bar{r}_1, \bar{r}_2) + [1 + U_{\alpha\gamma}^{m,hs}(\bar{r}_1, \bar{x}_2)] U_{\alpha\gamma, \text{tr}}^{m,P}(x_1 x_2) \quad (37a)$$

$$\begin{aligned} U_{\alpha\gamma\delta, \text{tr}}^m(x_1, x_2, x_3) = & U_{\alpha\gamma\delta}^{m,hs}(\bar{r}_1, \bar{r}_2, \bar{r}_3) + [1 + U_{\alpha\gamma\delta}^{m,hs}(\bar{r}_1, \bar{r}_2, \bar{r}_3)] \\ & \times U_{\alpha\gamma\delta}^{m,P}(x_1, x_2, x_3) \end{aligned} \quad (37b)$$

and

$$U_{\alpha\gamma, \text{rot}}^m(x_1, x_2) = U_{\alpha\gamma, \text{rot}}^{m,P}(x_1, x_2). \quad (38)$$

Here  $U_{\alpha\gamma, \text{tr}}^{m,P}$  and  $U_{\alpha\gamma, \text{rot}}^{m,P}$  are the modified Ursell functions due to translational and rotational contributions of perturbation potential, respectively, and are given by

$$U_{\alpha\gamma, \text{tr}}^{m,P}(x_1 x_2) = \left( \frac{\hbar^2\beta^2}{2m_{\alpha\gamma}} \right) \left[ \nabla_{r_{12}}^2 u_{\alpha\gamma}^P(x_1, x_2) - \frac{5}{4}\beta \left( \frac{\partial u_{\alpha\gamma}^P(x_1 x_2)}{\partial r_{12}} \right)^2 \right] + O(\hbar^4) \quad (39)$$

$$U_{\alpha\gamma, \text{rot}}^{m,P}(x_1, x_2) = - \left( \frac{\hbar^2\beta^2}{24I_{\alpha\gamma}} \right) [\nabla_{\omega_1}^2 u_{\alpha\gamma}^P(x_1, x_2) + \nabla_{\omega_2}^2 u_{\alpha\gamma}^P(x_1 x_2)] + O(\hbar^4). \quad (40)$$

Here  $A^c$  and  $g_{\alpha,\gamma,\dots,\delta}^c(x_1, \dots, x_l)$  are, respectively, the free energy and  $l$ -particle distribution function for a classical fluid mixture,  $\rho = N/V$  is the number density and

$c_\alpha = N_\alpha/N$  is the concentration of species  $\alpha$ ,  $\langle (\dots) \rangle_{\omega_1, \dots, \omega_l}$  represents an unweighted average over the molecular orientations  $\omega_1, \omega_2, \dots, \omega_l$ .

It is clear that the first quantum correction of order  $\hbar$  comes only from the translational contribution while the second quantum correction contains three terms—the first two arise from the translational and rotational potential energy effects; respectively, and last term in (35) is due to the rotational kinetic energy.

### 3. Virial coefficients of the equation of state of dilute polar hard sphere fluid

The  $l$ -particle distribution function for a classical fluid mixture can be expanded in power of  $\rho$  as (Singh and Sinha 1983; Rice and Gray 1965)

$$g_{\alpha\gamma}(x_1, x_2, \dots, x_l) = \exp \left[ -\beta \sum_{\alpha, \gamma} \sum_{i < j} u_{\alpha\gamma}(x_i, x_j) \right] \times \left[ 1 + \sum_{n=1} \rho^n \sum_{\delta, \xi, \dots} x_\delta x_\xi \dots a_{\alpha \dots \gamma}^{(n)}(x_1, x_2, \dots, x_l) \right], \quad (41)$$

where the coefficient  $a_{\alpha \dots \gamma}^{(n)}(x_1, \dots, x_l)$  is the cluster integral involving  $n$  field points and  $l$ -base points. Thus

$$a_{\alpha\delta\gamma}^{(1)}(x_1, x_2) = \int f_{\alpha\delta}(x_1, x_3) f_{\delta\gamma}(x_3, x_2) dx_3, \quad (42)$$

where

$$f_{\alpha\gamma}(x_i, x_j) = \exp[-\beta u_{\alpha\gamma}(x_i, x_j)] - 1.$$

Substituting (33) and (41) in the relation

$$P = \frac{\rho^2}{N} \left( \frac{\partial A}{\partial \rho} \right),$$

we obtain an expression for the equation of state in the virial form

$$\beta P = \rho + \sum_{n=2} B_n \rho^n, \quad (43)$$

where  $B_n$  is the  $n$ th virial coefficient for the fluid mixture in the semiclassical limit. The second virial coefficient can be written as

$$B_2 = B_2^c + (B_2^{qc})_{tr} + (B_2^{qc})_{rot}. \quad (44)$$

where

$$B_2^c = -\frac{1}{2} \sum_{\alpha, \gamma} c_\alpha c_\gamma \int d\bar{r}_2 \langle \exp[-\beta u_{\alpha\gamma}(x_1, x_2)] - 1 \rangle_{\omega_1, \omega_2} \quad (45)$$

$$(B_2^{qc})_{tr} = -\frac{1}{2} \sum_{\alpha, \gamma} c_\alpha c_\gamma \int d\bar{r}_2 \langle \exp[-\beta u_{\alpha\gamma}(x_1, x_2)] U_{\alpha\gamma, tr}^m(x_1, x_2) \rangle_{\omega_1, \omega_2} \quad (46)$$

$$(B_2^{qc})_{rot} = -\frac{1}{2} \sum_{\alpha, \gamma} c_\alpha c_\gamma \int d\bar{r}_2 \langle \exp[-\beta u_{\alpha\gamma}(x_1, x_2)] U_{\alpha\gamma, rot}^m(x_1, x_2) \rangle_{\omega_1, \omega_2}. \quad (47)$$

Here  $B_2^c$  is the second virial coefficient for the classical fluid mixture, and  $(B_2^{qc})_{tr}$  and  $(B_2^{qc})_{rot}$  are the quantum corrections due to the translational and rotational contribution, respectively.

Substituting (1) in (45) and evaluating the integrals, the classical second virial coefficient of the polar hard sphere fluid mixture can be written as

$$B_2^c = [B_2^c]_{hs} + [B_2^c]_2 + [B_2^c]_3 + \dots \quad (48)$$

where

$$[B_2^c]_{hs} = \frac{2\pi}{3} \sum_{\alpha,\gamma} c_\alpha c_\gamma \sigma_{\alpha\gamma}^3 \quad (49)$$

is the second virial coefficient for the classical hard sphere mixture, and  $[B_2^c]_n$  is the  $n$ th order perturbation correction to it. Thus

$$[B_2^c]_2 = -\frac{2\pi}{3} \sum_{\alpha,\gamma} c_\alpha c_\gamma \sigma_{\alpha\gamma}^3 \left[ \frac{1}{3}(\mu_{\alpha\gamma}^{*2})^2 + \frac{3}{5}(\mu_{\alpha\gamma}^{*2})(\theta_{\alpha\gamma}^{*2}) + \frac{3}{5}(\theta_{\alpha\gamma}^{*2})^2 \right] \quad (50)$$

$$[B_2^c]_3 = \frac{2\pi}{3} \sum_{\alpha,\gamma} c_\alpha c_\gamma \sigma_{\alpha\gamma}^3 \left[ \frac{3}{10}(\mu_{\alpha\gamma}^{*2})^2(\theta_{\alpha\gamma}^{*2}) + \frac{36}{175}(\mu_{\alpha\gamma}^{*2})(\theta_{\alpha\gamma}^{*2})^2 + \frac{18}{245}(\theta_{\alpha\gamma}^{*2})^3 \right], \quad (51)$$

where

$$\mu_{\alpha\gamma}^{*2} = \mu_\alpha \mu_\gamma / kT \sigma_{\alpha\gamma}^3, \quad \theta_{\alpha\gamma}^{*2} = \theta_\alpha \theta_\gamma / kT \sigma_{\alpha\gamma}^5. \quad (52)$$

In order to evaluate (46), we make use of a Taylor expansion of  $u_a(r\omega_1\omega_2)$  about  $\sigma_{\alpha\gamma}$  i.e.

$$u_a(r\omega_1\omega_2) = u_a(\sigma_{\alpha\gamma}\omega_1\omega_2) + (r - \sigma_{\alpha\gamma})u'_a(\sigma_{\alpha\gamma}\omega_1\omega_2) + \dots \quad (53)$$

where  $u'_a(\sigma_{\alpha\gamma}\omega_1\omega_2) = (\partial u_a / \partial r)_{r=\sigma_{\alpha\gamma}}$ . Substituting (37a) and (53) in (46), we obtain an expression for  $(B_2^{qc})_{tr}$  as

$$(B_2^{qc})_{tr} = \frac{2\pi}{3} \sum_{\alpha,\gamma} c_\alpha c_\gamma \sigma_{\alpha\gamma}^3 \left[ \frac{3}{2\sqrt{2}} (B_{\alpha\gamma}^I)_{tr}(\lambda_{\alpha\gamma}/\sigma_{\alpha\gamma}) + \frac{1}{\pi} (B_{\alpha\gamma}^{II})_{tr}(\lambda_{\alpha\gamma}/\sigma_{\alpha\gamma})^2 + \dots \right], \quad (54)$$

where

$$(B_{\alpha\gamma}^I)_{tr} = \langle \exp[-\beta u_{\alpha\gamma}^a(\sigma_{\alpha\gamma}\omega_1\omega_2)] \rangle_{\omega_1\omega_2} \quad (55)$$

$$(B_{\alpha\gamma}^{II})_{tr} = \langle \exp[-\beta u_{\alpha\gamma}^a(\sigma_{\alpha\gamma}\omega_1\omega_2)] \rangle_{\omega_1\omega_2}$$

$$- \frac{1}{4} \langle \beta \sigma_{\alpha\gamma} u_{\alpha\gamma}^{\prime a}(\sigma_{\alpha\gamma}\omega_1\omega_2) \exp[-\beta u_{\alpha\gamma}^a(\sigma_{\alpha\gamma}\omega_1\omega_2)] \rangle_{\omega_1\omega_2}$$

$$+ \frac{1}{8} \int_1^\infty dr^* r^{*2} \langle \beta u_{\alpha\gamma}^{\prime a}(r^*\omega_1\omega_2) \exp[-\beta u_{\alpha\gamma}^a(r^*\omega_1\omega_2)] \rangle_{\omega_1\omega_2}, \quad (56)$$

where  $r^* = r/\sigma_{\alpha\gamma}$ .

Similarly substituting (38) in (47) we get

$$(B_2^{qc})_{rot} = \frac{2\pi}{3} \sum_{\alpha,\gamma} c_\alpha c_\gamma \sigma_{\alpha\gamma}^3 \left[ \frac{1}{\pi I_{\alpha\gamma}^*} (B_{\alpha\gamma}^{II})_{rot}(\lambda_{\alpha\gamma}/\sigma_{\alpha\gamma})^2 + \dots \right], \quad (57)$$

where

$$(B_{\alpha\gamma}^{II})_{rot} = \frac{1}{8} \int_1^\infty dr^* r^{*2} \langle \nabla_{\omega_1}^2 u_{\alpha\gamma}^a(r^*\omega_1\omega_2) \exp[-\beta u_{\alpha\gamma}^a(r^*\omega_1\omega_2)] \rangle_{\omega_1\omega_2} \quad (58)$$

and  $I_{\alpha\gamma}^* = I_{\alpha\gamma}/m_{\alpha\gamma}\sigma_{\alpha\gamma}^2$ .



Finally (44) can be written in the form

$$B_2 = B_2^c + \frac{2\pi}{3} \sum_{\alpha, \gamma} c_{\alpha} c_{\gamma} \sigma_{\alpha\gamma}^3 \left[ \frac{3}{2\sqrt{2}} B_{\alpha\gamma}^I(\lambda_{\alpha\gamma}/\sigma_{\alpha\gamma}) + \frac{1}{\pi} B_{\alpha\gamma}^{II}(\lambda_{\alpha\gamma}/\sigma_{\alpha\gamma})^2 + \dots \right], \quad (59)$$

where

$$B_{\alpha\gamma}^I = (B_{\alpha\gamma}^I)_{tr} \quad (60a)$$

$$B_{\alpha\gamma}^{II} = (B_{\alpha\gamma}^{II})_{tr} + (I_{\alpha\gamma}^*)^{-1} (B_{\alpha\gamma}^{II})_{rot}. \quad (60b)$$

Thus the first order quantum correction arises from the translational part only whereas the second order quantum correction is due to both the translational and rotational contributions.

For potential model given by (2) the quantum correction terms are given by

$$(B_{\alpha\gamma}^I)_{tr} = 1 + \left[ \frac{1}{3}(\mu_{\alpha\gamma}^{*2})^2 + (\mu_{\alpha\gamma}^{*2})(\theta_{\alpha\gamma}^{*2}) + \frac{7}{5}(\theta_{\alpha\gamma}^{*2})^2 \right] + \dots \quad (61)$$

$$(B_{\alpha\gamma}^{II})_{tr} = 1 + \left[ \frac{19}{120}(\mu_{\alpha\gamma}^{*2})^2 + \frac{2}{7}(\mu_{\alpha\gamma}^{*2})(\theta_{\alpha\gamma}^{*2}) + \frac{49}{360}(\theta_{\alpha\gamma}^{*2})^2 \right] + \dots \quad (62)$$

and

$$(B_{\alpha\gamma}^{II})_{rot} = \left[ \frac{1}{18}(\mu_{\alpha\gamma}^{*2})^2 + \frac{1}{200}(\mu_{\alpha\gamma}^{*2})(\theta_{\alpha\gamma}^{*2}) - \left\{ \frac{1}{48}(\theta_{\alpha\gamma}^{*2}) - \frac{106}{189}(\theta_{\alpha\gamma}^{*2})^2 \right\} \right] + \dots \quad (63)$$

For one-component polar hard sphere fluid, (59) becomes

$$B_2 = B_2^c + [B_2^c]_{hs} \left[ \frac{3}{2\sqrt{2}} B^I(\lambda/\sigma) + B^{II}(\lambda/\sigma)^2 + \dots \right], \quad (64)$$

where  $B_2^c$  is the classical second virial coefficient for the polar hard sphere fluid and is given by (48) with

$$[B_2^c]_{hs} = 2\pi\sigma^3/3 \quad (65a)$$

$$[B_2^c]_2 = - [B_2^c]_{hs} \left[ \frac{1}{3}(\mu^{*2})^2 + \frac{3}{5}(\mu^{*2})(\theta^{*2}) + \frac{3}{5}(\theta^{*2})^2 \right] \quad (65b)$$

$$[B_2^c]_3 = [B_2^c]_{hs} \left[ \frac{3}{10}(\mu^{*2})^2(\theta^{*2}) + \frac{36}{175}(\mu^{*2})(\theta^{*2})^2 + \frac{18}{45}(\theta^{*2})^3 \right]. \quad (65c)$$

and  $B^I$  and  $B^{II}$  are respectively, the first and second quantum coefficients for polar hard sphere fluid. Thus

$$B^I = (B^I)_{tr} \equiv 1 + \left[ \frac{1}{3}(\mu^{*2})^2 + (\mu^{*2})(\theta^{*2}) + \frac{7}{5}(\theta^{*2})^2 \right] + \dots \quad (66a)$$

$$B^{II} = (B^{II})_{tr} + (I^*)^{-1} (B^{II})_{rot} \quad (66b)$$

with

$$(B^{II})_{tr} = 1 + \left[ \frac{19}{120}(\mu^{*2})^2 + \frac{2}{7}(\mu^{*2})(\theta^{*2}) + \frac{49}{360}(\theta^{*2})^2 \right] + \dots \quad (67a)$$

$$(B^{II})_{rot} = \left[ \frac{1}{18}(\mu^{*2})^2 + \frac{1}{200}(\mu^{*2})(\theta^{*2}) - \left\{ \frac{1}{48}(\theta^{*2}) - \frac{106}{189}(\theta^{*2})^2 \right\} \right] + \dots \quad (67b)$$

For one-component fluid, we have taken the reduced quantities

$$\mu^{*2} = \mu^2/kT\sigma^3; \quad \theta^{*2} = \theta^2/kT\sigma^5; \quad I^* = I/m\sigma^2.$$

#### 4. Thermodynamic properties of dense polar hard sphere fluid

In this section we evaluate the thermodynamic properties of polar hard sphere fluid in the semiclassical limit.

Using (3) we can evaluate (34). Then the expression for the free energy correct to the first quantum correction can be written as

$$\frac{\beta A}{N} = \frac{\beta A^c}{N} + \sum_{\alpha, \gamma} c_\alpha c_\gamma A_{\alpha\gamma}^I(\lambda_{\alpha\gamma}/\sigma_{\alpha\gamma}) + O(\lambda_{\alpha\gamma}^2), \quad (68)$$

where

$$A_{\alpha\gamma}^I = \frac{\pi}{\sqrt{2}} \rho \sigma_{\alpha\gamma}^3 \langle g_{\alpha\gamma}^c(\sigma_{\alpha\gamma}, \omega_1, \omega_2) \rangle_{\omega_1, \omega_2}. \quad (69)$$

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

$$\frac{\beta P}{\rho} = \frac{\beta P^c}{\rho} + \sum_{\alpha, \gamma} c_\alpha c_\gamma P_{\alpha\gamma}^I(\lambda_{\alpha\gamma}/\sigma_{\alpha\gamma}) + O(\lambda_{\alpha\gamma}^2), \quad (70)$$

where

$$P_{\alpha\gamma}^I = \frac{\pi}{\sqrt{2}} \rho \frac{\partial}{\partial \rho} [\rho \sigma_{\alpha\gamma}^3 \langle g_{\alpha\gamma}^c(\sigma_{\alpha\gamma}, \omega_1, \omega_2) \rangle_{\omega_1, \omega_2}]. \quad (71)$$

Here  $g_{\alpha\gamma}^c(\sigma_{\alpha\gamma}, \omega_1, \omega_2)$  is the RDF for classical polar hard sphere fluid mixture at the contact. Using the perturbation theory where  $u_{\alpha\gamma}^{\text{hs}}$  is treated as the reference potential and  $u_{\alpha\gamma}^a$  is the perturbation,  $g_{\alpha\gamma}^c(x_1, x_2)$  can be expanded as (Gubbins and Gray 1972)

$$g_{\alpha\gamma}^c(x_1, x_2) = g_{\alpha\gamma}^{\text{CHS}}(r_{12}) [1 - \beta u_{\alpha\gamma}^a(x_1, x_2) + \frac{1}{2} \beta^2 u_{\alpha\gamma}^{a^2}(x_1, x_2)] + \dots \quad (72)$$

The corresponding perturbation expansion for the free energy per particle,  $f^c$  ( $\equiv A^c/N$ ) for the classical fluid mixture is given by (Shukla and Singh 1980)

$$f^c = f_{\text{HS}}^c + f_2^c + f_3^c + \dots, \quad (73)$$

where  $f_{\text{HS}}^c$  is the free energy per particle of the classical hard sphere fluid,  $f_2^c$  and  $f_3^c$  are, respectively, the second and third order perturbation corrections to the free energy. For the polar fluid mixture  $f_2^c$  and  $f_3^c$  are expressed as

$$\beta f_2^c = - \sum_{\alpha, \gamma} c_\alpha c_\gamma \rho_{\alpha\gamma}^* \left[ \frac{1}{6} \mu_{\alpha\gamma}^{*4} I_{\alpha\gamma}^{(6)}(\rho_{\alpha\gamma}^*) + \frac{1}{2} \mu_{\alpha\gamma}^{*2} \theta_{\alpha\gamma}^{*2} I_{\alpha\gamma}^{(8)}(\rho_{\alpha\gamma}^*) + \frac{7}{10} \theta_{\alpha\gamma}^* I_{\alpha\gamma}^{(10)}(\rho_{\alpha\gamma}^*) \right], \quad (74)$$

$$\beta f_3^c = \beta f_{3,2}^c + \beta f_{3,3}^c, \quad (75)$$

where

$$\begin{aligned} \beta f_{3,2}^c = & \sum_{\alpha, \gamma} c_\alpha c_\gamma \rho_{\alpha\gamma}^* \left[ \frac{2}{5} \mu_{\alpha\gamma}^{*4} \theta_{\alpha\gamma}^{*2} I_{\alpha\gamma}^{(11)}(\rho_{\alpha\gamma}^*) \right. \\ & \left. + \frac{12}{35} \mu_{\alpha\gamma}^{*2} \theta_{\alpha\gamma}^{*4} I_{\alpha\gamma}^{(13)}(\rho_{\alpha\gamma}^*) + \frac{36}{245} \theta_{\alpha\gamma}^{*6} I_{\alpha\gamma}^{(15)}(\rho_{\alpha\gamma}^*) \right] \end{aligned} \quad (76)$$

and

$$\begin{aligned} \beta f_{3,3}^c = & \rho \sum_{\alpha, \gamma, \delta} c_\alpha c_\gamma c_\delta \left[ \mu_{\alpha\gamma}^{*2} \mu_{\alpha\delta}^{*2} \mu_{\gamma\delta}^{*2} \left( \frac{\sigma_{\alpha\alpha}^3 \sigma_{\gamma\gamma}^3 \sigma_{\delta\delta}^3}{\sigma_{\alpha\gamma} \sigma_{\alpha\delta} \sigma_{\gamma\delta}} \right) k_{\alpha\gamma\delta}^{333} \right. \\ & + \frac{1}{480} \mu_{\alpha\alpha}^{*2} \mu_{\gamma\gamma}^{*2} \theta_{\delta\delta}^{*2} \left( \frac{\sigma_{\alpha\alpha}^3 \sigma_{\gamma\gamma}^3 \sigma_{\delta\delta}^5}{\sigma_{\alpha\gamma} \sigma_{\alpha\delta} \sigma_{\gamma\delta}^2} \right) k_{\alpha\gamma\delta}^{334} \\ & + \frac{1}{640} \mu_{\alpha\alpha}^{*2} \theta_{\gamma\gamma}^{*2} \theta_{\delta\delta}^{*2} \left( \frac{\sigma_{\alpha\alpha}^3 \sigma_{\gamma\gamma}^5 \sigma_{\delta\delta}^5}{\sigma_{\alpha\gamma} \sigma_{\alpha\delta}^2 \sigma_{\gamma\delta}^2} \right) k_{\alpha\gamma\delta}^{344} \\ & \left. + \frac{1}{6400} \theta_{\alpha\alpha}^{*2} \theta_{\gamma\gamma}^{*2} \theta_{\delta\delta}^{*2} \left( \frac{\sigma_{\alpha\alpha}^5 \sigma_{\gamma\gamma}^5 \sigma_{\delta\delta}^5}{\sigma_{\alpha\gamma}^2 \sigma_{\alpha\delta}^2 \sigma_{\gamma\delta}^2} \right) k_{\alpha\gamma\delta}^{444} \right], \end{aligned} \quad (77)$$

where

$$I_{\alpha\gamma}^{(n)}(\rho_{\alpha\gamma}^*) = 4\pi \int_0^\infty g_{\alpha\gamma}^{\text{CHS}}(r_{\alpha\gamma}^*, \rho_{\alpha\gamma}^*) r_{\alpha\gamma}^{*2-n} dr_{\alpha\gamma}^* \quad (78)$$

and

$$I_{\alpha\gamma\delta}^{nn'n''} = \int g_{\alpha\gamma\delta}^{\text{CHS}}(r_{\alpha\gamma}^*, r_{\alpha\delta}^*, r_{\gamma\delta}^*) (r_{\alpha\gamma}^{*-n} r_{\alpha\delta}^{*-n'} r_{\gamma\delta}^{*-n''}) d\bar{r}_{\alpha\delta}^* d\bar{r}_{\gamma\delta}^*. \quad (79)$$

Here we have used the reduced variable

$$r_{\alpha\gamma}^* = r/\sigma_{\alpha\gamma}; \quad \rho_{\alpha\gamma}^* = \rho\sigma_{\alpha\gamma}^3.$$

One can use Pade's approximant to calculate the higher order terms beyond  $f_3^c$ . We use these expressions to calculate the free energy of the classical polar hard sphere fluid mixtures. Other thermodynamic properties can be calculated from (73). Then the equation of state of the classical polar hard sphere fluid is given by

$$\frac{\beta P^c}{\rho} = \frac{\beta P_{\text{HS}}^c}{\rho} + P_2^c + P_3^c + \dots, \quad (80)$$

where  $P_{\text{HS}}^c$  is the pressure of the classical hard sphere fluid and  $P_n^c$  is the  $n$ th order perturbation correction to it.

$$P_n^c = \rho \frac{\partial f_n^c}{\partial \rho}. \quad (81)$$

Substituting (72) in (69), we obtain an expression for the first order quantum correction to the free energy

$$A_{\alpha\gamma}^I = [A_{\alpha\gamma}^I]_{\text{HS}} + [A_{\alpha\gamma}^I]_2 + [A_{\alpha\gamma}^I]_3 + \dots, \quad (82)$$

where

$$[A_{\alpha\gamma}^I]_{\text{HS}} = \frac{\pi}{\sqrt{2}} \rho \sigma_{\alpha\gamma}^3 g_{\alpha\gamma}^{\text{CHS}}(\sigma_{\alpha\gamma}) \quad (83a)$$

$$[A_{\alpha\gamma}^I]_2 = [A_{\alpha\gamma}^I]_{\text{HS}} \left[ \frac{1}{3}(\mu_{\alpha\gamma}^{*2})^2 + (\mu_{\alpha\gamma}^{*2})(\theta_{\alpha\gamma}^{*2}) + \frac{7}{5}(\theta_{\alpha\gamma}^{*2})^2 \right] \quad (83b)$$

$$[A_{\alpha\gamma}^I]_3 = [A_{\alpha\gamma}^I]_{\text{HS}} \left[ \frac{4}{5}(\mu_{\alpha\gamma}^{*2})^2(\theta_{\alpha\gamma}^{*2}) + \frac{24}{35}(\mu_{\alpha\gamma}^{*2})(\theta_{\alpha\gamma}^{*2})^2 + \frac{72}{245}(\theta_{\alpha\gamma}^{*2})^3 \right]. \quad (83c)$$

Here  $g_{\alpha\gamma}^{\text{CHS}}(\sigma_{\alpha\gamma})$  is the RDF of the classical hard sphere fluid mixture at the contact.

Similarly substituting (72) in (71) one can obtain expression for the first order quantum correction to the pressure.

## 5. One-component polar hard sphere fluid

In this section we consider one component fluid of polar hard spheres. The excess free energy per particles for the classical hard sphere fluid is (Carnahan and Starling 1969)

$$\beta f_{\text{HS}}^c \cong \frac{\beta A_{\text{HS}}^c}{N} = \eta(4 - 3\eta)/(1 - \eta)^2, \quad (84)$$

where  $\eta = \pi\rho\sigma^3/6$ . For molecules having the angle-dependent potential (2), Larsen *et*

al (1977) have given analytic expressions for  $\beta f_2^c$  and  $\beta f_3^c$  in terms of the reduced variables defined as

$$\rho^* = \rho\sigma^3; \quad \mu^{*2} = \mu^2/\sigma^3 kT; \quad \theta^{*2} = \theta^2/\sigma^5 kT.$$

Higher order terms beyond  $f_3$  is evaluated using Stell *et al* (1972, 1974) Pade approximant. We use these expressions to calculate the free energy of the classical hard sphere polar fluids. Other thermodynamic properties of the classical polar fluid can be calculated from (73). Thus the equation of state of the classical hard sphere polar fluid is given by

$$\frac{\beta P^c}{\rho} = \frac{\beta P_{\text{HS}}^c}{\rho} + P_2^c + P_3^c + \dots, \quad (85)$$

where (Carnahan and Starling (1969)

$$\frac{\beta P_{\text{HS}}^c}{\rho} = (1 + \eta + \eta^2 - \eta^3)/(1 - \eta)^3 \quad (86)$$

is the equation of state for the classical hard sphere fluid and  $P_n^c$  is the  $n$ th order perturbation correction to it and is given by (81).

For one-component polar hard sphere fluid, (68) can be written as

$$\frac{\beta A}{N} = \frac{\beta A^c}{N} + A_I^*(\lambda/\sigma), \quad (87)$$

where

$$A_I^* = A_{\text{HS}}^{I^*} + A_2^{I^*} + A_3^{I^*} + \dots \quad (88)$$

with

$$A_{\text{HS}}^{I^*} = 3\sqrt{2}\eta g_{\text{HS}}^c(\sigma) \quad (89a)$$

$$A_2^{I^*} = A_{\text{HS}}^{I^*}[\frac{1}{3}\mu^{*4} + \mu^{*2}\theta^{*2} + \frac{7}{3}\theta^{*4}] \quad (89b)$$

$$A_3^{I^*} = A_{\text{HS}}^{I^*}[\frac{4}{3}\mu^{*4}\theta^{*2} + \frac{24}{35}\mu^{*2}\theta^{*4} + \frac{72}{245}\theta^{*6}]. \quad (89c)$$

Here  $g_{\text{HS}}^c(\sigma)$  is the RDF of the classical hard sphere fluid at the contact and is given as (Carnahan and Starling 1969)

$$g_{\text{HS}}^c(\sigma) = (1 - \frac{1}{2}\eta)/(1 - \eta)^3. \quad (90)$$

Similarly (70) reduces to

$$\frac{\beta P}{\rho} = \frac{\beta P^c}{\rho} + P_I^*(\lambda/\sigma). \quad (91)$$

where

$$P_I^* = P_{\text{HS}}^{I^*} + P_2^{I^*} + P_3^{I^*}, \quad (92)$$

with

$$P_{\text{HS}}^{I^*} = 3\sqrt{2}\eta(1 + \eta - \frac{1}{2}\eta^2)/(1 - \eta)^4 \quad (93a)$$

$$P_2^{I^*} = P_{\text{HS}}^{I^*}[\frac{1}{3}\mu^{*4} + \mu^{*2}\theta^{*2} + \frac{7}{3}\theta^{*4}] \quad (93b)$$

$$P_3^{I^*} = P_{\text{HS}}^{I^*}[\frac{4}{3}\mu^{*4}\theta^{*2} + \frac{24}{35}\mu^{*2}\theta^{*4} + \frac{72}{245}\theta^{*6}]. \quad (93c)$$

The values of the first order coefficients  $A_1^*$  and  $P_1^*$  as a function of  $\mu^{*2}$  and  $\theta^{*2}$  are reported in Figures 1 and 2 respectively. These coefficients are positive and increase with increase of  $\mu^{*2}$  and  $\theta^{*2}$  and increase of density  $\rho^* \equiv \rho\sigma^3$ . For the quadrupole the quantum correction coefficients are larger.

**6. Binary mixture**

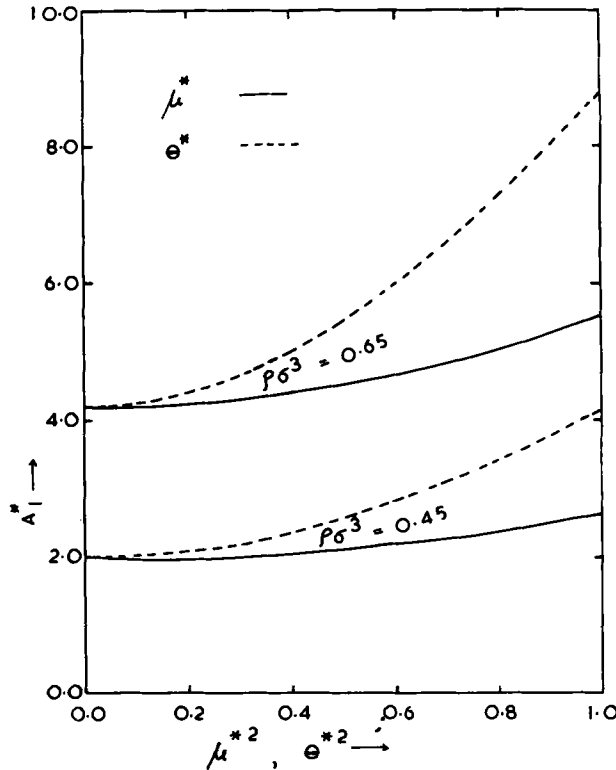
Equation (73) can be used to calculate the free energy of a binary mixtures of polar hard spheres. For such a system  $\sigma_{12}$  is given by

$$\sigma_{12} = (\sigma_{11} + \sigma_{22})/2. \tag{94}$$

We adopt the van der Waals one (vdW 1) fluid theory of mixture (Leland *et al* 1968) to calculate the properties of the classical hard sphere system. This theory approximates the properties of a mixture by those of a fictitious pure fluid with the interaction parameter,

$$\sigma_0^3 = \sum_{\alpha,\gamma} c_\alpha c_\gamma \sigma_{\alpha\gamma}^3. \tag{95}$$

In the vdW 1 theory of mixtures, the free energy and pressure of the classical hard



**Figure 1.** The first order quantum coefficient  $A_1^*$  as a function of  $\mu^{*2}$  and  $\theta^{*2}$  at  $\rho\sigma^3 = 0.45$  and  $0.65$ .

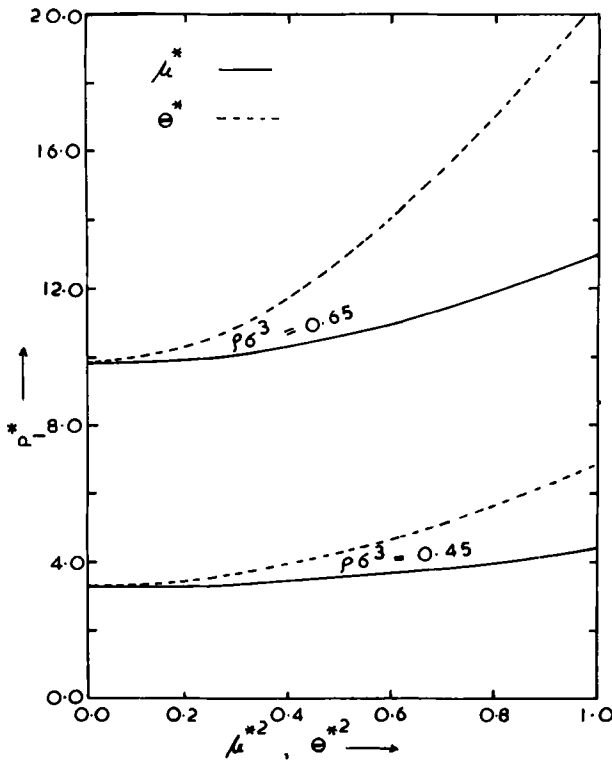


Figure 2. The first order quantum coefficient  $P_1^*$  as a function of  $\mu^{*2}$  and  $\theta^{*2}$  at  $\rho\sigma^3 = 0.45$  and  $0.65$ .

sphere mixture are given by

$$A_{HS}^c = A_0^c + NkT \sum_{\alpha} c_{\alpha} \ln c_{\alpha} + \text{second order terms} \tag{96}$$

$$P_{HS}^c = P_0^c + \text{second order terms}, \tag{97}$$

where  $A_0^c$  and  $P_0^c$  are the values of the free energy and pressure for pure hard sphere fluid containing  $N$  molecules in volume  $V$  at temperature  $T$ . For a hard sphere model having diameter  $\sigma_0$  given by (95),  $A_0^c$  and  $P_0^c$  are given by (84) and (86), respectively, with  $\eta$  defined in this case as

$$\eta = \pi\rho\sigma_0^3/6. \tag{98}$$

The vdW 1 theory has been found to be in good agreement with the machine simulation results.

The angle dependent parts of free energy involve the integrals  $I_{\alpha\gamma}^{(n)}$  and  $K_{\alpha\gamma\delta}^{nn'n''}$ . In order to evaluate the integrals  $I_{\alpha\gamma}^{(n)}$  we use as approximation in which the mixture RDF  $g_{\alpha\gamma}^{CHS}$  is equal to the zero order term in a confirmal solution expansion of Mo *et al* (1974)

$$g_{\alpha\gamma}^{CHS}\left(\frac{r}{\sigma_{\alpha\gamma}}, \rho\sigma_{\alpha\gamma}^3\right) \simeq g_0^{CHS}\left(\frac{r}{\sigma_0}, \rho\sigma_0^3\right), \tag{99}$$

where  $g_0^{\text{CHS}}$  is the RDF of a pure hard sphere fluid at the reduced density  $\rho_0^* = \rho_0 \sigma^3$ . Thus the integral  $I_{\alpha\gamma}^{(n)}$  can be expressed as

$$I_{\alpha\gamma}^{(n)}(\rho_{\alpha\gamma}^*) = \left( \frac{\sigma_{\alpha\gamma}}{\sigma_0} \right)^{n-3} I_0^{(n)}(\rho_0^*), \quad (100)$$

where  $I_0^{(n)}(\rho_0^*)$  is the integral of the pure hard sphere fluid at density  $\rho_0^*$  which can be evaluated using the equation of Larsen *et al* (1977).

To evaluate the three-body integrals  $K_{\alpha\gamma\delta}^{nn'n''}$  we make use of the superposition approximation (Kirkwood 1935) for the three body distribution function of the hard sphere mixture i.e.

$$g_{\alpha\gamma\delta}^{\text{CHS}}(r_{12}, r_{12}, r_{23}) \approx g_{\alpha\gamma}^{\text{CHS}}(r_{12}) g_{\alpha\delta}^{\text{CHS}}(r_{13}) g_{\gamma\delta}^{\text{CHS}}(r_{23}). \quad (101)$$

For each of  $g_{\alpha\gamma}^{\text{CHS}}(r_{ij})$ , we use the value obtained from (99). Then the three-body integrals  $K_{\alpha\gamma\delta}^{nn'n''}$  can be expressed as (Flytzani-Stephanopoulos *et al* 1975)

$$K_{\alpha\gamma\delta}^{nn'n''} \approx \left( \frac{\sigma_{\alpha\gamma}}{\sigma_0} \right)^{n-2} \left( \frac{\sigma_{\alpha\delta}}{\sigma_0} \right)^{n'-2} \left( \frac{\sigma_{\gamma\delta}}{\sigma_0} \right)^{n''-2} K_0^{nn'n''} \quad (102)$$

where  $K_0^{nn'n''}$  is the pure fluid integral at the reduced density  $\rho_0^*$ . The values of integrals have been given in terms of the reduced density by Larsen *et al* (1977).

With the help of (99),  $g_{\alpha\gamma}^{\text{CHS}}(\sigma_{\alpha\gamma})$  is given by (Carnahan and Starling 1969)

$$g_{\alpha\gamma}^{\text{CHS}}(\sigma_{\alpha\gamma}) \approx g_0^{\text{CHS}}(\sigma_0) = (1 - \eta/2)/(1 - \eta)^3 \quad (103)$$

for all  $\alpha$  and  $\gamma$ . The vdW 1 theory has been extended to include the quantum effect (Singh and Sinha 1982)

$$\sigma_0^2 \lambda_0 = \sum_{\alpha, \gamma} c_{\alpha} c_{\gamma} \sigma_{\alpha\gamma}^2 \lambda_{\alpha\gamma} \quad (104)$$

We further assume that

$$\sigma_0^2 \lambda_0 L_0 = \sum_{\alpha, \gamma} c_{\alpha\gamma} \sigma_{\alpha\gamma}^2 \lambda_{\alpha\gamma} L_{\alpha\gamma}, \quad (105)$$

where

$$L_{\alpha\gamma} = \frac{1}{3} \mu_{\alpha\gamma}^{*4} + \mu_{\alpha\gamma}^{*2} \theta_{\alpha\gamma}^{*2} + \frac{7}{5} \theta_{\alpha\gamma}^{*4}. \quad (106)$$

Thus (68) can be expressed as

$$\frac{\beta A}{N} = \frac{\beta A^c}{N} + A_I^*(\lambda/\sigma) + O((\lambda/\sigma)^2), \quad (107)$$

where

$$A_I^* = 3\sqrt{2}F\eta_1(1 - \frac{1}{2}\eta)(1 - \eta)^{-3}[1 + L_0]. \quad (108)$$

Similarly using (70) and (71), we can obtain an expression for pressure valid to the first order of  $(\lambda/\sigma)$

$$\frac{\beta P}{\rho} = \frac{\beta P^c}{\rho} + P_I^*(\lambda/\sigma) + O(\lambda/\sigma^2) \quad (109)$$

where

$$P_I^* = 3\sqrt{2}F\eta_1(1 + \eta - \frac{1}{2}\eta^2)(1 - \eta)^{-4}[1 + L_0]. \quad (110)$$

In deriving these expressions we have used the following notation

$$\eta_1 = \frac{\pi}{6} \rho \sigma^3 = \frac{\pi}{6} \rho (c_1 \sigma_{11}^3 + c_2 \sigma_{22}^3) \quad (111)$$

$$F = \sigma_0^2 \lambda_0 / \sigma^2 \lambda, \quad (112)$$

where

$$\sigma^3 = c_1 \sigma_{11}^3 + c_2 \sigma_{22}^3 \quad (113a)$$

$$\sigma^2 \lambda = c_1 \sigma_{11}^2 \lambda_{11} + c_2 \sigma_{22}^2 \lambda_{22}. \quad (113b)$$

In terms of  $\eta_1, \eta$  can be expressed as (Singh and Sinha 1982)

$$\eta = \eta_1 [1 - \frac{3}{4} c_1 c_2 (1 + R)(1 - R^2) / (c_1 + c_2 R^3)], \quad (114)$$

where  $R = \sigma_{22} / \sigma_{11}$ .

In the theory of mixture, one prefers to estimate the 'excess' thermodynamic properties of the system. Thus the 'excess' free energy for a polar hard sphere fluid mixture, correct to the first order quantum correction, is given by

$$\frac{\beta A_E}{N} = \frac{\beta A_E^c}{N} + A_E^I(\lambda/\sigma) + O(\lambda/\sigma)^2, \quad (115)$$

where

$$A_E^I = \sqrt{2} \pi \rho c_1 c_2 \sigma_{12}^3 g_{12}^{\text{CHS}}(\sigma_{12}) [1 + L_{12}] E. \quad (116)$$

Here  $E$  is given by (Singh and Sinha 1982)

$$E = \sqrt{2} \frac{(1 + R^{-3})^{1/3}}{(1 + R)} \frac{(c_1 + c_2 R^3)}{(c_1 + c_2 R^{1/2})} \quad (117)$$

and  $g_{12}^{\text{CHS}}(\sigma_{12})$  for additive hard sphere is given by (Henderson and Leonard 1971)

$$g_{12}^{\text{CHS}}(\sigma_{12}) = \frac{1}{(1 - \eta_1)} + \frac{3\xi}{(1 - \eta_1)^2} \mu, \quad (118)$$

where

$$\xi = \frac{\pi}{6} \rho (c_1 \sigma_{11}^2 + c_2 \sigma_{22}^2) \quad (119)$$

$$\mu = \sigma_{11} \sigma_{22} / (\sigma_{11} + \sigma_{22}). \quad (120)$$

## 7. Results and discussions

### 7.1 Polar hard sphere fluids

We calculate the numerical results for the hard spheres with point-dipoles and point-quadrupoles in the semiclassical limit. We consider the first order quantum correction only.

Figures 3 and 4, respectively, demonstrate the variation of the excess free energy per particles  $\beta f$  and equation of state  $\beta \rho / \rho$  as a function of  $\mu^{*2}$  and  $\theta^{*2}$  at  $\rho^* = 0.45$  and 0.65 for  $\lambda/\sigma = 0.0$  and 0.1. The results with  $\lambda/\sigma = 0.0$  correspond to the classical



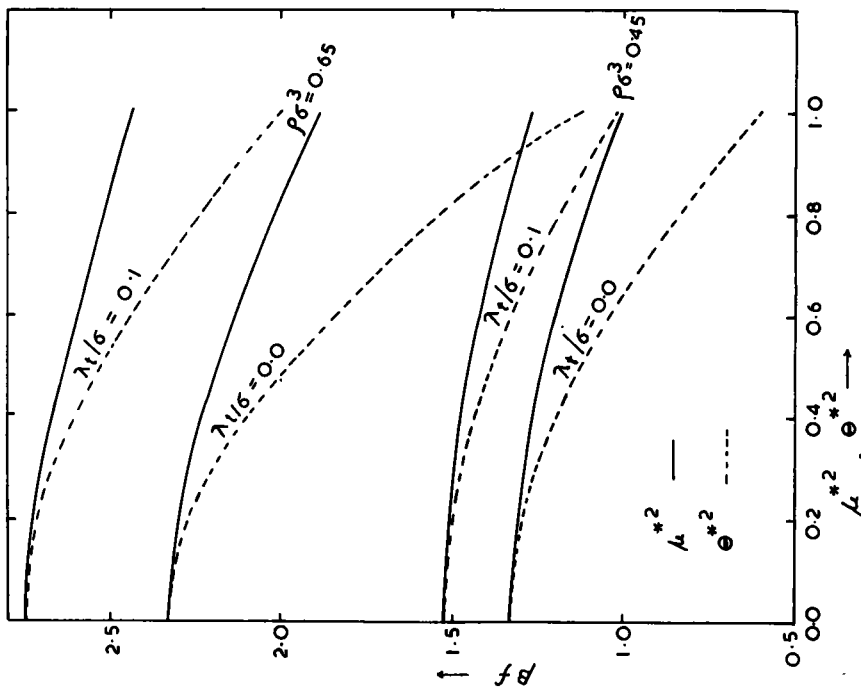


Figure 3. Excess free energy per particle  $\beta f$  as a function of  $\mu^{*2}$  and  $\theta^{*2}$  at  $\rho^* = 0.65$  for  $\lambda/\sigma = 0.0$  and  $0.1$ .

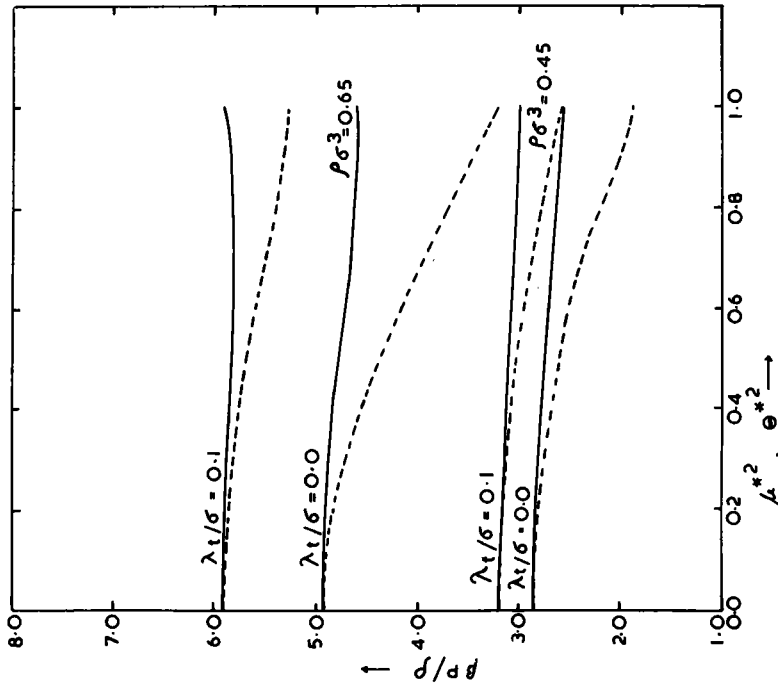


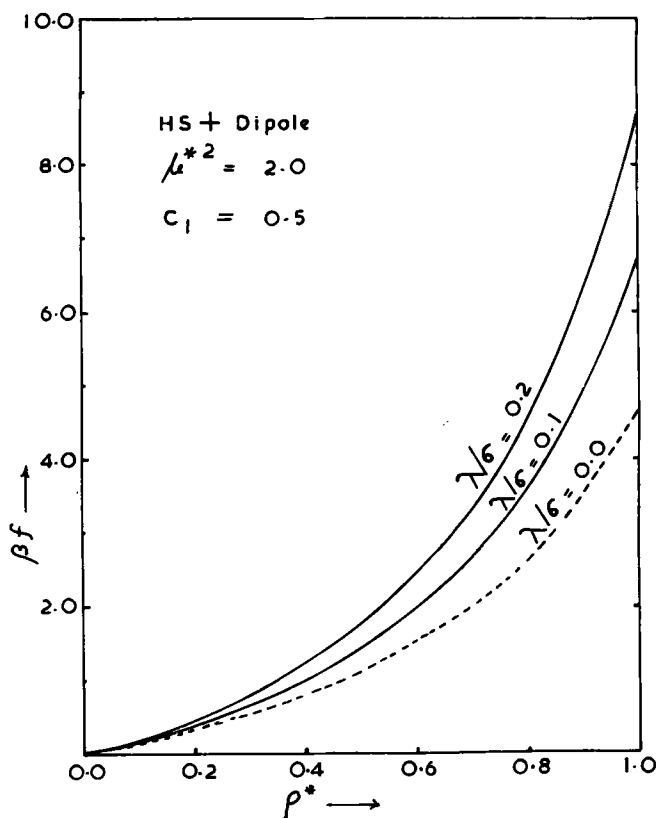
Figure 4. Equation of state  $\beta P/\rho$  as function of  $\mu^{*2}$  and  $\theta^{*2}$  at  $\rho^* = 0.45$  and  $0.65$  for  $\lambda/\sigma = 0.0$  and  $0.1$ .

values. From these figures we see that the difference between classical and semiclassical values of free energy and pressure increases with increase of  $\mu^{*2}$  and  $\theta^{*2}$  as well as increase of density.

In table 1, we report the percentage contribution of quantum correction to the free

**Table 1.** Percentage of quantum correction for the free energy and pressure of the hard sphere polar fluid at  $\lambda/\sigma = 0.1$ .

$\mu^{*2}/\theta^{*2}$	$\frac{f - f^c}{f^c} \times 100$		$\frac{P - P^c}{P^c} \times 100$	
	$\rho\sigma^3 = 0.45$	$\rho\sigma^3 = 0.65$	$\rho\sigma^3 = 0.45$	$\rho\sigma^3 = 0.65$
$\mu^{*2}$				
0.4	16.42	19.69	12.37	21.37
0.8	21.55	25.17	15.05	25.60
1.0	26.14	29.46	17.03	28.38
$\theta^{*2}$				
0.4	19.90	23.96	14.74	25.83
0.8	40.97	48.47	26.11	45.17
1.0	69.10	78.69	36.61	64.46



**Figure 5.** The configurational free energy per particle,  $\beta f$ , for hard sphere and dipole binary mixture as a function of  $\rho^*$  for  $c_1 = c_2 = 0.5$  and  $\mu^{*2} = 2.0$  for  $\lambda/\sigma = 0.0, 0.1$  and  $0.2$ .

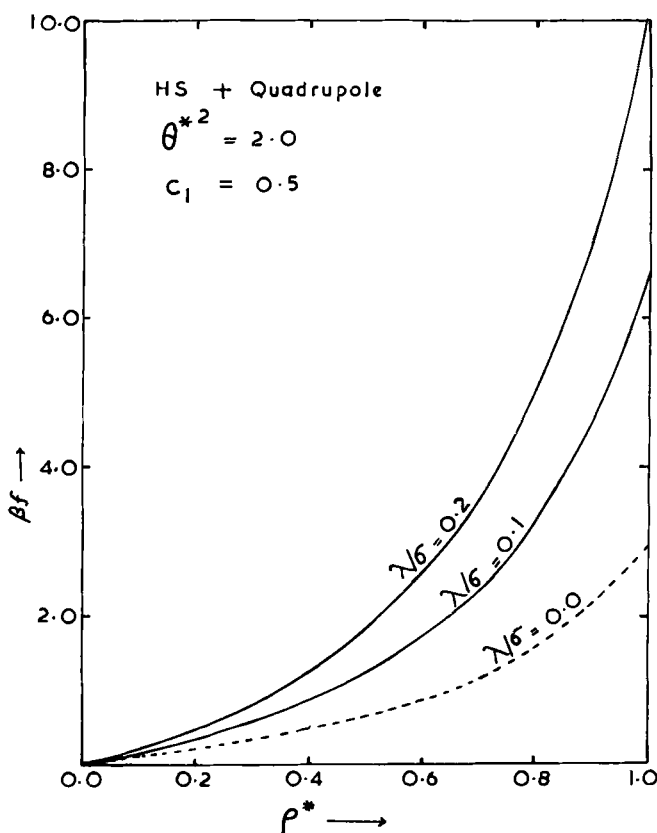


Figure 6. The configurational free energy per particle,  $\beta f$ , for hard sphere and quadrupole binary mixture as a function of  $\rho^*$  for  $c_1 = c_2 = 0.5$  and  $\theta^{*2} = 2.0$  for  $\lambda/\sigma = 0.0, 0.1$  and  $0.2$ .

energy and pressure for the hard sphere polar fluids at  $\lambda/\sigma = 0.1$ . We find that the quantum correction increases with increase of density and increase of  $\mu^{*2}$  and  $\theta^{*2}$ .

We thus come to the conclusion that the quantum effect increases with increase of parameter  $\mu^*$  and  $\theta^*$  and for quadrupole the quantum effect is larger.

### 7.2 Polar hard sphere mixtures

We calculate the numerical results for some polar hard sphere mixtures such as binary mixture (i) hard sphere (HS) and dipole hard sphere (DHS) ( $\mu_1 = 0, \mu_2 = \mu$  and  $\theta_1 = \theta_2 = 0$ ), (ii) hard spheres (HS) and quadrupole hard sphere (QHS) ( $\mu_1 = \mu_2 = 0$  and  $\theta_1 = 0, \theta_2 = \theta$ ) and (iii) dipole and dipole ( $\mu_1 \neq 0, \mu_2 \neq 0$  and  $\theta_1 = \theta_2 = 0$ ) in the semiclassical limit. We consider the first quantum correction only.

The values of the configurational free energy per particles  $\beta f$  for the binary mixture of (i) HS and DHS with  $\mu^{*2} = 2$  and (ii) HS and QHS with  $\theta^{*2} = 2$  are demonstrated as a function of  $\rho^*$  at  $c_1 = c_2 = 0.5$  in figures 5 and 6, respectively, for  $\lambda/\sigma = 0.0, 0.1$  and  $0.2$ . The results with  $\lambda/\sigma = 0.0$  correspond to the classical values. We see that the quantum effects increase with density  $\rho^*$ .

Figures 7 and 8 demonstrate the variation of the reduced pressure  $P^*$  as a function

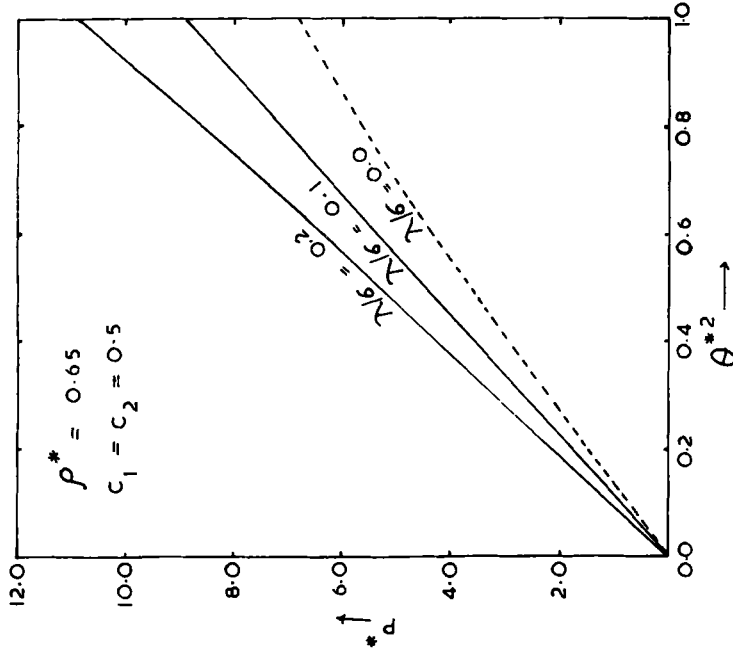


Figure 8. The reduced pressure,  $P^* = P\sigma^8/\theta^2$ , for hard sphere and quadrupole binary mixture as a function of  $\theta^{*2}$  for  $c_1 = c_2 = 0.5$  at  $\rho^* = 0.65$  for  $\lambda/\sigma = 0.0, 0.1$  and  $0.2$ .

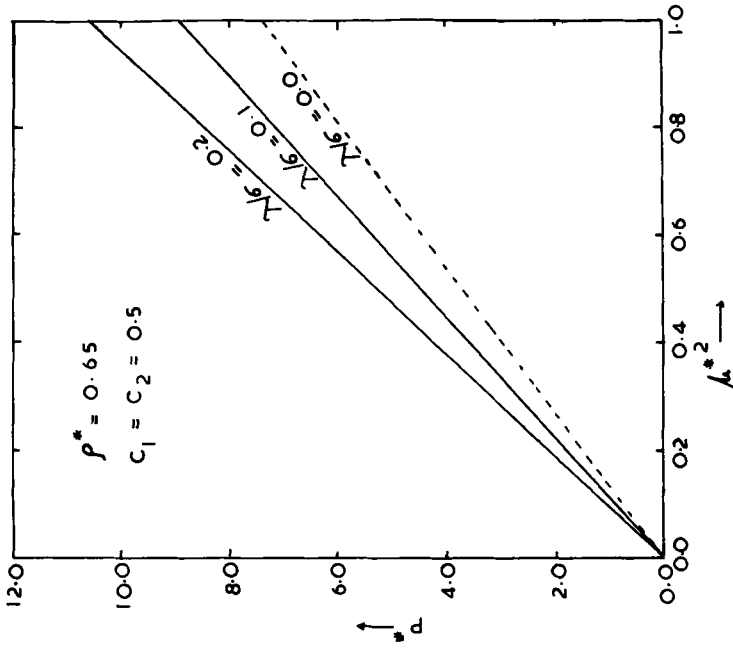


Figure 7. The reduced pressure,  $P^* = P\sigma^6/\mu^2$ , for hard sphere and dipole binary mixture as a function of  $\mu^{*2}$  for  $c_1 = c_2 = 0.5$  at  $\rho^* = 0.65$  for  $\lambda/\sigma = 0.0, 0.1$  and  $0.2$ .

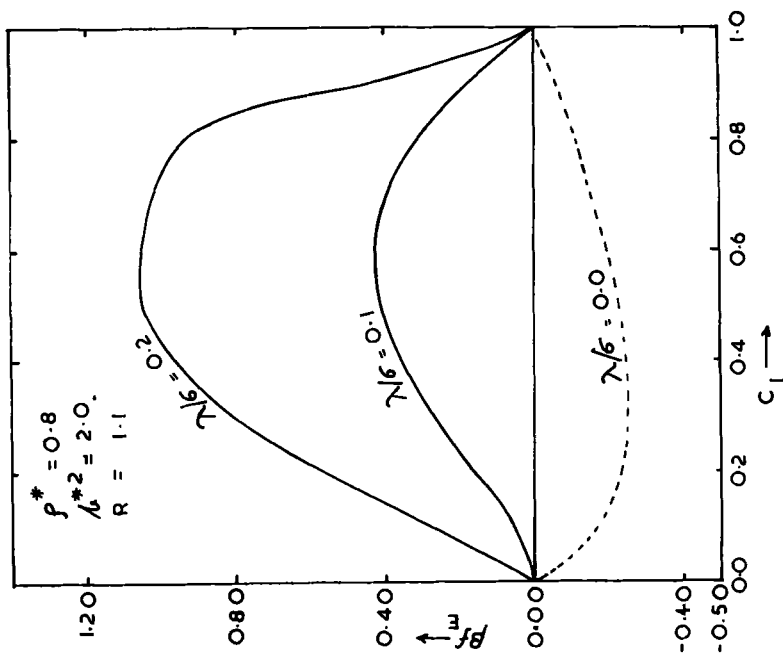


Figure 10. The 'excess' free energy for binary mixture of hard sphere dipoles as a function of  $c_1$  for  $\rho^* = 0.8$ ,  $\mu^{*2} = 2.0$  and  $R = 1.1$  at  $\lambda/\sigma = 0.0, 0.1$  and  $0.2$ .

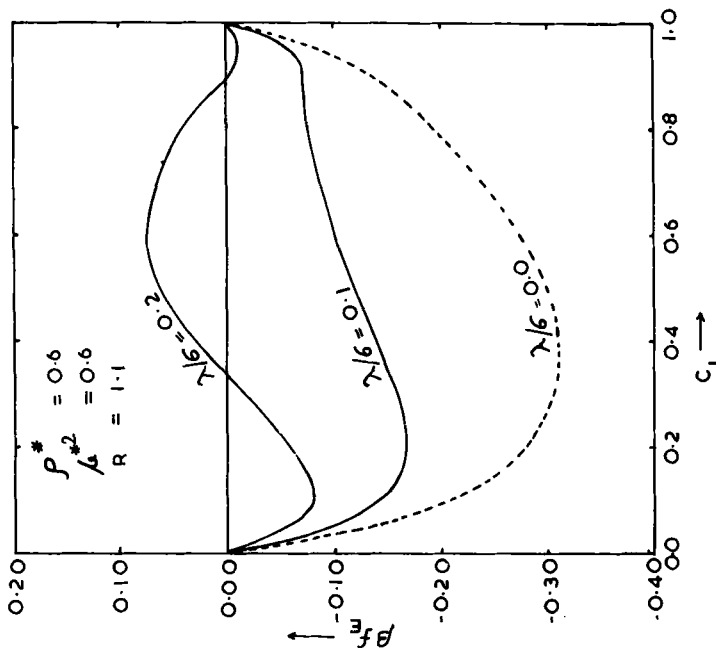


Figure 9. The 'excess' free energy for binary mixture of hard sphere dipole as a function of  $c_1$  for  $\rho^* = 0.6$ ,  $\mu^{*2} = 0.6$  and  $R = 1.1$  at  $\lambda/\sigma = 0.0, 0.1$  and  $0.2$ .

of  $\mu^{*2}$  and  $\theta^{*2}$ , respectively, for  $c_1 = c_2 = 0.5$  at  $\rho^* = 0.65$  for  $\lambda/\sigma = 0.0, 0.1$  and  $0.2$ , where in the first case  $P^* = P\sigma^6/\mu^2$  and in the second case  $P^* = P\sigma^8/\theta^2$ . We see that the quantum effects increase with increase of  $\mu^{*2}$  and  $\theta^{*2}$  as well as density  $\rho^*$ .

We have also calculated the excess free energy per particle,  $\beta f_E$ , ( $\equiv \beta A_E/N$ ) for a DHS-DHS binary mixture where both species have different diameters (i.e.  $\sigma_{11} \neq \sigma_{22}$ ) but same dipole moments (i.e.  $\mu_1 = \mu_2$ ). In figures 9 and 10, the values of  $\beta f_E$  of the DHS-DHS mixture for  $R_2 = 1.1$  are reported as a function of  $c_1$  for  $\rho^* = 0.60$ ,  $\mu_1^{*2} = 0.60$  and  $\rho^* = 0.8$ ,  $\mu_1^{*2} = 2.0$ , respectively for  $\lambda/\sigma = 0.0, 0.1$  and  $0.2$ . The quantity  $\rho^* = \rho(c_1\sigma_{11}^3 + c_2\sigma_{22}^3)$  in this case. It is found that 'excess' classical as well as semiclassical values are zero at  $c_1 = 0.0$  and  $c_1 = 1.0$  and non-zero in the intermediate range of  $c_1$ .

Thus we come to the conclusion that the 'excess' quantum effect depends on the concentration  $c_1$  and  $c_2$  and particle diameter ratio  $R = \sigma_{22}/\sigma_{11}$  and increases with increase of parameter  $\mu^{*2}$ .

## 8. Summary

The purpose of the present paper is to develop a theory for calculating the equilibrium properties of polar hard sphere fluid (in the semiclassical limit), whose molecules interact via a pair potential of the type  $u = u_{HS} + u_a$  where  $u_{HS}$  is a hard sphere potential and  $u_a$  an angle dependent potential. We have given explicit expressions for the first and second quantum corrections for the second virial coefficient and for the first quantum correction to the free energy and equation of state for polar hard sphere fluid and fluid mixture. In this calculation we have considered the permanent multipole interaction only. In polar fluid the polarization of molecules may play an important role in estimating the quantum effects (Pratt 1980). Introduction of the polarizability to some real fluids will be discussed in future publications.

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