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Semiclassical statistical mechanics of ν-dimensional fluid mixture of hard ν-spheres

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Abstract. The problem of calculating the equilibrium properties of ν-dimensional fluid mixture of hard ν-spheres is studied. High temperature expansion for the density independent radial distribution function is derived for a hard ν-sphere mixture. The 'excess' quantum corrections to the second virial coefficient and the excess free energy are also studied. Significant features are the large increase in 'excess' quantum correction with increasing dimensionality.

Keywords. Semiclassical fluid; quantum corrections; equation of state; free energy; dimensionality.

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1. Introduction

The present paper is concerned with the evaluation of thermodynamics of ν-dimensional fluid mixture of hard ν-spheres both in classical and semiclassical limits. This is because the hard ν-sphere mixture is as important in framing a theory of ν-dimensional fluid mixture as the hard ν-sphere fluid is in case of one-component ν-dimensional fluid. The problem of calculating the equilibrium properties of ν-dimensional fluid of hard ν-spheres has been a subject of considerable interest in recent years (Baus and Colot 1987; Sinha 1990; Sinha and Sinha 1990a). However a ν-dimensional fluid mixture has not yet been investigated systematically.

In the semiclassical limit (i.e. at high temperature limit) where the quantum effects are small and treated as a correction to the classical system, the usual procedure is based on an expansion of the physical properties of interest about the classical values (Singh and Sinha 1981). The hard ν-sphere system may be dealt with the Hemmer-Jancovici (HJ) method (Hemmer 1968; Jancovici 1969). Considerable work has been done for hard ν-sphere fluids (with $1 \leqslant \nu \leqslant 5$). This approach has been extended to mixtures of hard discs (Mishra and Sinha 1985) and hard spheres (Singh and Sinha 1982, 1983a). However no work is available for general hard ν-sphere mixture.

The thermodynamics of a classical hard ν-sphere mixture may be evaluated using the perturbation method (Henderson and Leonard 1971; Smith 1971), originally developed for hard sphere mixture. This basis of the perturbation theory is to expand the properties of a hard ν-sphere mixture about those of one component fluid of hard spheres of diameter d_0 defined by (35). This approach has been found to provide good results for hard sphere mixture (Smith and Henderson 1972; Adam and McDonald 1975) and hard disc mixture (Singh and Sinha 1983b).

The purpose of the present investigation is to derive unifined expressions for the thermodynamics and quantum corrections for the ν-dimensional fluid mixture of hard ν-spheres.

In § 2, we describe a basic theory for calculating the equilibrium properties of a ν-dimensional fluid mixture. Section 3 is devoted to derive expressions for the density independent radial distribution function and second virial coefficient for the hard ν-sphere fluid mixture in the semiclassical limit. Section 4 is concerned with the calculation of the thermodynamic properties of dense hard ν-sphere mixture. The thermodynamics of the classical system are discussed in § 5. In § 6, we calculate the quantum corrections to the thermodynamic properties of the fluid mixture. The paper ends with concluding remarks in § 7. The exchange effect is not considered in the paper.

2. Basic theory

We consider a quantum mechanical ν-dimensional mixture, made up of N_1 molecules of species 1, N_2 molecules of species 2,..., N_s moleclues of species S, such that the total number of molecules is $N = \Sigma_{\alpha=1}^{S} N_\alpha$. The quantity of central importance in constructing the theory of quantum fluid is the Slater sum. For ν-dimensional fluid mixture, it may be defined as

$$W_N(1,2,\ldots,N) = \prod_{\alpha=1}^{S} [N_\alpha! \lambda_\alpha^{\nu N_\alpha}] \sum_x \psi_x^*(1,\ldots,N) \exp[-\beta \hat{H}_N] \psi_x(1,\ldots,N), \quad (1)$$

where

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

is the thermal wavelength of species α, $\beta = (kT)^{-1}$ and $\hat{H}_N$ is the Hamiltonion of the system

$$\hat{H}_N = -\frac{\hbar^2}{2} \sum_{\alpha=1}^{S} \frac{1}{m_\alpha} \sum_{i=1}^{N_s} \nabla_i^2 + \sum_{\alpha,\gamma} \sum_{i<j} u_{\alpha\gamma}(i,j). \quad (2)$$

Here $u_{\alpha\gamma}(i,j)$ is the pair potential between the particle i of species α and particle j of species γ.

In the semiclassical limit (i.e. at high temperature), the Slater sum can be written as (Hemmer 1968; Jancovici 1969; Sinha 1990)

$$W_N = W_N^c W_N^m, \quad (3)$$

where

$$W_N^c(1,2,\ldots,N) = \exp\left[-\beta \sum_{\alpha,\gamma} \sum_{i<j} u_{\alpha\gamma}(i,j)\right] \quad (4)$$

is the Boltzmann factor and W_N^m is a function which measures the deviations from classical behaviour. In the case of ν-dimensional (one-component) fluid, W_N^m is expressed in terms of 'modified' Ursell functions U_l^m (Sinha 1990). In an analogous way, we can express W_N^m of a ν-dimensional fluid mixture in terms of $U_{\alpha,\gamma}^m, \ldots \delta$. Thus

$$W_N^m(1,2,\ldots,N) = 1 + \sum_{\alpha,\gamma} \sum_{i<j} U_{\alpha\gamma}^m(i,j) + \sum_{\alpha,\gamma,\delta} \sum_{i<j<k} U_{\alpha\gamma\delta}^m(i,j,k) + \ldots. \quad (5)$$

The $U^m_{\alpha\gamma,\ldots,\delta}(1,2,\ldots,l)$ appearing in (5) can, in principle, be found from the solution of the quantum mechanical l-body problem. Unfortunately the actual solution in general is not possible. Recently Sinha (1990) solved two-body problem to obtain U^m_2 for a hard ν-sphere system. Its extension for the hard ν-sphere mixture is straightforward and evaluated in the next section.

In quantum statistical mechanics, the grand canonical partition function and radial distribution function are defined as

$$\Xi = \sum_{(N_s)} \left(\prod_j \frac{z_j^{N_j}}{N_j!} \right) \int \ldots \int W_N(1,2,\ldots,N) \prod_{i=1}^{N} \mathrm{d}\bar{r}_i \tag{6}$$

and

$$\rho_\alpha \rho_\gamma g_{\alpha\gamma}(1,2) = \Xi^{-1} \sum_{N_j=\delta_{\alpha j}+\delta_{\gamma j}} \left[\prod_j \frac{z_j^{N_j}}{(N_j - \delta_{\alpha j} - \delta_{\gamma j})!} \right] \times \int \ldots \int W_N(1,2,\ldots,N) \prod_{i=3}^{N} \mathrm{d}\bar{r}_i, \tag{7}$$

where

$$z_j = \lambda_j^{-\nu} \exp[\beta \mu_j] \tag{8}$$

is the fugacity of species j and μ_j is the chemical potential.

Substituting (3) and (5) in (6) and (7) we obtain expressions for free energy and radial distribution function (RDF) for the ν-dimensional fluid mixture. Thus the results are

$$\begin{aligned}
\frac{\beta A}{N} = \frac{\beta A^c}{N} &- \frac{1}{2}\rho \sum_{\alpha,\gamma} x_\alpha x_\gamma \int U^m_{\alpha\gamma}(1,2) g^c_{\alpha\gamma}(1,2) \mathrm{d}\bar{r}_2 \\
&- \frac{1}{6}\rho^2 \sum_{\alpha,\gamma,\delta} x_\alpha x_\gamma x_\delta \int U^m_{\alpha\gamma\delta}(1,2,3) g^c_{\alpha\gamma\delta}(1,2,3) \mathrm{d}\bar{r}_2 \mathrm{d}\bar{r}_3 \\
&- \frac{1}{8}\rho^3 \sum_{\alpha,\gamma,\delta,\xi} x_\alpha x_\alpha x_\delta x_\xi \int U^m_{\alpha\gamma}(1,2) U^m_{\delta\xi}(3,4) \\
&\times [g^c_{\alpha\gamma\delta\xi}(1,2,3,4) - g^c_{\alpha\gamma}(1,2) g^c_{\delta\xi}(3,4)] \mathrm{d}\bar{r}_2 \mathrm{d}\bar{r}_3 \mathrm{d}\bar{r}_4 \\
&+ \frac{\rho}{8\beta} K^c \sum_{\alpha,\gamma,\delta} x_\alpha x_\gamma x_\delta \left\{ \int U^m_{\alpha\gamma}(1,2) \frac{\partial}{\partial\rho} \rho^2 g^c_{\alpha\gamma}(1,2) \mathrm{d}\bar{r}_2 \right\} \\
&\times \left\{ \int U^m_{\alpha\delta}(3,4) \frac{\partial}{\partial\rho} [\rho^2 g^c_{\alpha\delta}(3,4)] \mathrm{d}\bar{r}_4 \right\} + 0(\lambda^3_{\alpha\gamma}),
\end{aligned} \tag{9}$$

$$\begin{aligned}
g_{\alpha\gamma}(1,2) = [1 + U^m_{\alpha\gamma}(1,2)] g^c_{\alpha\gamma}(1,2) &+ \rho \sum_\delta x_\delta \int [U^m_{\alpha\gamma\delta}(1,2,3) + U^m_{\alpha\delta}(1,3) \\
&+ U^m_{\alpha\delta}(2,3)] g_{\alpha\gamma\delta}(1,2,3) \mathrm{d}\bar{r}_3 + \frac{1}{2}\rho^2 [1 + U^m_{\alpha\gamma}(1,2)] \\
&\times \sum_{\delta,\xi} x_\delta x_\xi \int U^m_{\delta\xi}(3,4) [g^c_{\alpha\gamma\delta\xi}(1,2,3,4) - g^c_{\alpha\gamma}(1,2) g^c_{\delta\xi}(3,4)] \mathrm{d}\bar{r}_3 \mathrm{d}\bar{r}_4 \\
&- \frac{1}{4\beta} K^c [1 + U^m_{\alpha\gamma}(1,2)] \left[\frac{\partial}{\partial\rho} [\rho^2 g^c_{\alpha\gamma}(1,2)] \right.
\end{aligned}$$

$$\times\left(\sum_{\delta} x_{\delta}\left\{\int U^{m}_{\alpha\delta}(3,4)\frac{\partial}{\partial\rho}[\rho^2 g^{c}_{\alpha\delta}(3,4)]\mathrm{d}\bar{r}_4 + \int U^{m}_{\gamma\delta}(3,4)\frac{\partial}{\partial\rho}[\rho^2 g^{c}_{\gamma\delta}(3,4)]\mathrm{d}\bar{r}_4\right\}\right)\Bigg] + 0(\lambda^2_{\alpha\gamma}), \tag{10}$$

where

$$K^c = \frac{1}{\rho}\left(\frac{\partial\rho}{\partial P^c}\right)_{\beta} \tag{11}$$

is the isothermal compressibility of the classical fluid mixture and given by the relation (Singh and Sinha 1982)

$$\frac{\rho K^c}{\beta} = 1 + \rho\sum_{\alpha,\gamma} x_{\alpha}x_{\gamma}\int[g^{c}_{\alpha\gamma}(r) - 1]\mathrm{d}\bar{r}. \tag{12}$$

A^c and $g^{c}_{\alpha,\gamma,\ldots,\delta}(1,2,\ldots l)$ are the free energy and l-particle distribution function of the classical fluid mixture respectively. Here ρ is the number density and $x_{\alpha} = N_{\alpha}/N$ is the concentration of the species α. Equations (9) and (10) are similar in their functional forms to those for three and two-dimensional fluid mixture (Singh and Sinha 1982; Mishra and Sinha 1985).

3. Equilibrium properties of dilute hard υ-sphere mixture

We consider a quantum mechanical system of hard ν-sphere fluid mixture. For such a system, the pair interaction is given by

$$\begin{aligned} u_{\alpha\gamma}(r) &= \infty, \qquad r < d_{\alpha\gamma} \\ &= 0, \qquad r > d_{\alpha\gamma}, \end{aligned} \tag{13}$$

where $d_{\alpha\gamma}$ is the diameter of hard ν-sphere of species α and γ and r denotes the ν-dimensional distance. For the unlike interaction, d_{12} is given by (Adam and McDonald 1975).

$$d_{12} = \frac{1}{2}(d_{11} + d_{22})(1 + \Delta) = d^{a}_{12}(1 + \Delta) \tag{14a}$$

with

$$d^{a}_{12} = \frac{1}{2}(d_{11} + d_{12}), \tag{14b}$$

where $\Delta = 0$ for a binary mixture of additive hard ν-spheres whereas $|\Delta| > 0$ for a non-additive hard ν-spheres.

The density independent RDF for a ν-dimensional mixture is given by

$$g_{\alpha\gamma}(r) = 2^{\nu/2}\lambda^{\nu}_{\alpha\gamma}\langle r|\exp(-\beta\hat{H}_{\mathrm{rel}})|\bar{r}\rangle, \tag{15}$$

where $\hat{H}_{\mathrm{rel}}$ is the relative Hamiltonian of two particles of masses m_{α} and m_{γ}

$$\hat{H}_{\mathrm{rel}} = -(\hbar^2/m_{\alpha\gamma})\nabla^2 + u_{\alpha\gamma}(r). \tag{16}$$

Here $\lambda_{\alpha\gamma}$ is the thermal wavelength of the molecules of species α and γ, defined as

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

where $m_{\alpha\alpha} \equiv m_\alpha$ is the mass of the molecule of species α and $m_{\alpha\gamma} = 2m_{\alpha\alpha}m_{\gamma\gamma}/(m_{\alpha\alpha} + m_{\gamma\gamma})$. Thus we have (Singh and Sinha 1982)

$$\lambda_{\alpha\gamma} = [(\lambda_{\alpha\alpha}^2 + \lambda_{\gamma\gamma}^2)/2]^{1/2} \tag{17}$$

Equation (15) can be solved to give (Sinha 1990)

$$g_{\alpha\gamma}(r) = \exp[-\beta u_{\alpha\gamma}(r)][1 + U_{\alpha\gamma}^m(r)], \tag{18}$$

where

$$U_{\alpha\gamma}^m(r) = \phi_{\alpha\gamma}^0 + \phi_{\alpha\gamma}^1 + \phi_{\alpha\gamma}^2 + \dots \tag{19}$$

with

$$\phi_{\alpha\gamma}^0 = -\exp[-\xi_{\alpha\gamma}^2] \tag{20a}$$

$$\phi_{\alpha\gamma}^1 = \frac{(\nu-1)}{2\sqrt{2}}(\lambda_{\alpha\gamma}/d_{\alpha\gamma})\xi_{\alpha\gamma}^2 \operatorname{erfc}(\xi_{\alpha\gamma}) \tag{20b}$$

$$\phi_{\alpha\gamma}^2 = \frac{(\nu-1)}{24\pi}(\lambda_{\alpha\gamma}/d_{\alpha\gamma})^2\xi_{\alpha\gamma}^2[\xi 4(\nu-2) + (\nu+1)\xi_{\alpha\gamma}^2]\exp(-\xi_{\alpha\gamma}^2)$$

$$-\sqrt{\pi}\,\xi_{\alpha\gamma}\{6(\nu-1) + (\nu+1)\xi_{\alpha\gamma}^2\}\operatorname{erfc}(\xi_{\alpha\gamma})], \tag{20c}$$

where

$$\xi_{\alpha\gamma} = \frac{(2\pi)^{1/2}}{(\lambda_{\alpha\gamma}/d_{\alpha\gamma})}[(r/d_{\alpha\gamma}) - 1]$$

and erfc (x) is the complimentary error function.

The second virial coefficient $B_2(\nu)$ for ν-dimensional fluid mixture in the semiclassical limit is given by

$$B_2(\nu) = -\frac{1}{2}\sum_{\alpha,\gamma} x_\alpha x_\gamma \int [g_{\alpha\gamma}(r) - 1]\mathrm{d}\bar{r}. \tag{21}$$

Using the relation (Baus and Colot 1987)

$$\int \mathrm{d}\bar{r} f(r) = S_\nu \int_0^\infty \mathrm{d}r r^{\nu-1} f(r),$$

where S_ν is the surface area of the unit sphere, in (21), we get

$$B_2(\nu) = B_2^c(\nu) + B_2^{qc}(\nu), \tag{22}$$

where $B_2^c(\nu)$ and $B_2^{qc}(\nu)$ are, respectively, the classical and quantum correction values of the second virial coefficient. Thus

$$B_2^c(\nu) = -\frac{1}{2}S_\nu\sum_{\alpha,\gamma} x_\alpha x_\gamma \int_0^\infty \mathrm{d}r r^{\nu-1}(\exp[-\beta u_{\alpha\gamma}(r)] - 1) \tag{23}$$

$$B_2^{qc}(\nu) = -\frac{1}{2}S_\nu\prod_{\alpha,\gamma} x_\alpha x_\gamma \int_{d_{\alpha\gamma}}^\infty \mathrm{d}r r^{\nu-1} U_{\alpha\gamma}^m(r), \tag{24}$$

where (Baus and Colot 1987)

$$S_\nu = \nu\pi^{\nu/2}/\Gamma(1+\nu/2)$$

and $\Gamma(l)$ is the Gamma function.

Substituting (13) and (19) in (23) and (24), we get the following expression for the second virial coefficient for hard ν-sphere fluid mixture in the semiclassical limit.

$$B_2(\nu) = \frac{\pi^{\nu/2}}{2\Gamma(1+\nu/2)} \sum_{\alpha,\gamma} x_\alpha x_\gamma d_{\alpha\gamma}^\nu \Bigg[1 + \frac{\nu}{2\sqrt{2}}(\lambda_{\alpha\gamma}/d_{\alpha\gamma}) + \frac{\nu(\nu-1)}{6\pi}(\lambda_{\alpha\gamma}/d_{\alpha\gamma})^2 + \frac{\nu(\nu-1)(7\nu-17)}{384\sqrt{2\pi}}(\lambda_{\alpha\gamma}/d_{\alpha\gamma})^3 + \dots \Bigg], \tag{25}$$

where the first term is the second virial coefficient for the classical hard ν-sphere fluid mixture.

We are interested here to estimate the 'excess' virial coefficient of a binary mixture of hard ν-spheres (relative to the pure components) in the semiclassical limit. The 'excess' second virial coefficient of a binary hard ν-sphere mixture in the semiclassical limit is obtained from (25) as

$$\Delta B_2(\nu) = \frac{\pi^{\nu/2} d^\nu}{\Gamma(1+\nu/2)}(d_{12}/\mathrm{d})^\nu x_1 x_2 \Bigg[1 + \frac{\nu}{2\sqrt{2}} E_\nu(\lambda/\mathrm{d}) + \frac{\nu(\nu-1)}{6\pi} E_\nu^2 (\lambda/\mathrm{d})^2 + \frac{\nu(\nu-1)(7\nu-17)}{384\sqrt{2\pi}} E_\nu^3 (\lambda/d)^3 + \dots \Bigg], \tag{26}$$

where

$$d^\nu = x_1 d_{11}^\nu + x_2 d_{22}^\nu, \tag{27}$$

$$d^{\nu-1}\lambda = x_1 d_{11}^{\nu-1}\lambda_{11} + x_2 d_{22}^{\nu-1}\lambda_{22} \tag{28}$$

and

$$E_\nu(\lambda/d) = \lambda_{12}/d_{12}. \tag{29}$$

The first term in (26) is the classical value. From (27) and (28), we have

$$(\lambda/d) = \left[\frac{x_1 + x_2 R^{\nu-1}(m_{11}/m_{22})^{1/2}}{x_1 + x_2 R^\nu} \right] (\lambda_{11}/d_{11}). \tag{30}$$

From (29) E_ν is given by

$$E_\nu = \sqrt{2}\left[\frac{(1+(m_{11}/m_{22}))^{1/2}}{(1+R)(1+\Delta)} \right]\left[\frac{x_1 + x_2 R^\nu}{x_1 + x_2 R^{\nu-1}(m_{11}/m_{22})} \right], \tag{30a}$$

where the ratio $R = d_{22}/d_{11}$. For simplicity, we may assume that the atomic mass $m_{\alpha\alpha}$ of hard ν-sphere is proportional to $d_{\alpha\alpha}^\nu$. Then (30a) reduces to

$$E_\nu = \sqrt{2}\left[\frac{(1+R^{-\nu})^{1/2}}{(1+R)(1+\Delta)} \right]\left[\frac{x_1 + x_2 R^\nu}{x_1 + x_2 R^{(\nu/2)} - 1} \right]. \tag{31}$$

Equation (26) is valid for both additive and non-additive hard ν-sphere mixture. From this expression it is clear that the 'excess' second virial coefficient depends on x_1 and R as well as on the dimension ν.

Equation (26) is the general expression for the binary mixture of hard ν-spheres and reproduces the results for the hard spheres (Singh and Sinha 1982) and hard discs (Mishra and Sinha 1985).

4. Thermodynamics of a dense hard ν-sphere mixture

The free energy of a hard ν-sphere mixture, correct to the first order quantum correction, is obtained from (9)

$$\frac{\beta A}{N} = \frac{\beta A^c}{N} - \frac{1}{2}\rho \sum_{\alpha,\gamma} x_\alpha x_\gamma \int U^m_{\alpha\gamma}(r) g^c_{\alpha\gamma}(r) \mathrm{d}\bar{r} + 0(\lambda^2_{\alpha\gamma}). \tag{32}$$

Using (19), it can be evaluated as

$$\frac{\beta A}{N} = \frac{\beta A^c}{N} + 2^{\nu - 5/2}\nu \sum_{\alpha,\gamma} x_\alpha x_\gamma \eta_{\alpha\gamma} g^c_{\alpha\gamma}(d_{\alpha\gamma})(\lambda_{\alpha\gamma}/d_{\alpha\gamma}) + 0((\lambda_{\alpha\gamma}/d_{\alpha\gamma})^2), \tag{33}$$

where

$$\eta_{\alpha\gamma} = \frac{\pi^{\nu/2}}{2^\nu \Gamma(1+\nu/2)} \rho d^\nu_{\alpha\gamma}. \tag{34}$$

Here $g^c_{\alpha\gamma}(d_{\alpha\gamma})$ is the classical RDF of the hard ν-spheres at contact. This expression can be applied to additive as well as non-additive hard ν-sphere mixture.

We extend the van der Waals one (*v d Wl*) fluid theory of mixture (Leland *et al* 1968), originally developed for the hard sphere mixture, to calculate the properties of the classical hard ν-sphere mixture. This theory approximates the properties of a mixture by those of a fictitious pure fluid with the diameter d_0 defined as

$$d^\nu_0 = \sum_{\alpha,\gamma} x_\alpha x_\gamma d^\nu_{\alpha\gamma}. \tag{35}$$

In the *v d Wl* theory of mixture, the free energy and pressure of the classical fluid mixture are given by

$$\frac{\beta A^c}{N} = \frac{\beta A^c_0}{N} + \sum_\alpha x_\alpha \ln x_\alpha + \text{second order term} \tag{36}$$

$$\frac{\beta P^c}{\rho} = \frac{\beta P^c_0}{\rho} + \text{second order term}, \tag{37}$$

where A^c_0 and P^c_0 are, respectively, the free energy and pressure for pure classical fluid containing N molecules in volume V at temperature T. They will be discussed in the following section.

In the *v d Wl* theory it is assumed that

$$g^c_{\alpha\gamma}(d_{\alpha\gamma}) = g^c_0(d_0). \tag{38}$$

Further we assume

$$d_0^{\nu-1}\lambda_0 = \sum_{\alpha,\gamma} x_\alpha x_\gamma d_{\alpha\gamma}^{\nu-1}\lambda_{\alpha\gamma} \tag{39}$$

for all α and γ. Then (33) can be written as

$$\frac{\beta A}{N} = \frac{\beta A^c}{N} + 2^{\nu-5/2}\nu\eta_0 g_0^c(d_0)(\lambda_0/d_0), \tag{40}$$

where η_0 is the packing fraction given by (Baus and Colot 1987)

$$\eta_0 = \frac{\pi^{\nu/2}}{2^\nu\Gamma(1+\nu/2)}\rho d_0^\nu = \sum_{\alpha,\gamma} x_\alpha x_\gamma \eta_{\alpha\gamma}. \tag{41}$$

Other thermodynamic properties can be calculated from the expression of the free energy. Thus the equation of state for the hard ν-sphere mixture is given by

$$\frac{\beta P}{\rho} = \frac{\beta P^c}{\rho} + 2^{\nu-5/2}\nu\eta_0\left[g_0^c(d_0) + \rho\frac{\partial g_0^c(d_0)}{\partial\rho}\right](\lambda_0/d_0). \tag{42}$$

Equations (40) and (42) involve the classical RDF at the contact, which can be evaluated using the equation of state for the classical hard ν-sphere fluid mixture, given by (Sinha 1990)

$$\frac{\beta P^c}{\rho} = 1 + 2^{\nu-1}\sum_{\alpha,\gamma} x_\alpha x_\gamma \eta_{\alpha\gamma} g_{\alpha\gamma}^c(d_{\alpha\gamma}) = 1 + 2^{\nu-1}\eta_0 g_0^c(d_0). \tag{43}$$

In terms of the following notations

$$\eta = \frac{\pi^{\nu/2}}{2^\nu\Gamma(1+\nu/2)}\rho d^\nu = \frac{\pi^{\nu/2}}{2^\nu\Gamma(1+\nu/2)}\rho^* \tag{44}$$

and

$$F = d_0^{\nu-1}\lambda_0/d^{\nu-1}\lambda, \tag{45}$$

where d and λ are given by (27) and (28), respectively, (40) can be written as

$$\frac{\beta A}{N} = \frac{\beta A^c}{N} + A_1(\lambda/d) + 0((\lambda/d)^2), \tag{46}$$

where

$$A_1 = 2^{\nu-5/2}\nu F\eta g_0^c(d_0). \tag{47}$$

Similarly (42) can be given by

$$\frac{\beta P}{\rho} = \frac{\beta P^c}{\rho} + P_I(\lambda/d) + 0((\lambda/d))^2 \tag{48}$$

where

$$P_I = 2^{\nu-5/2}\nu F\eta\left[g_0^c(d_0) + \rho\frac{\partial g_0^c(d_0)}{\partial\rho}\right]. \tag{49}$$

In a theory of mixture, usually the 'excess' thermodynamic properties of the system are estimated rather than the absolute values. From (33), the 'excess' free energy for the hard ν-sphere mixture is given by

$$\frac{\beta A_E}{N} = \frac{\beta A_E^c}{N} + A_E^I(\lambda/d) + O((\lambda/d)^2), \tag{50}$$

where

$$A_E^I = 2^{\nu-3/2}\nu x_1 x_2 \eta_{12} E_\nu g_{12}^0(d_{12}). \tag{51}$$

E_ν is given by (31) and $g_{12}^c(d_{12})$ can be obtained from (43) as

$$2^\nu x_1 x_2 \eta_{12} g_{12}^c(d_{12}) = \frac{\beta P^c}{\rho} - \left[x_1 \frac{\beta P_1^c}{\rho_1} + x_2 \frac{\beta P_2^c}{\rho_2}\right], \tag{52}$$

where P_α^c is the pressure of species α at density

$$\rho_\alpha = x_\alpha \rho.$$

5. Equilibrium properties of classical hard v-sphere mixture

For hard ν-sphere model having the diameter d_0 given by (4.4), P_0^c is given by (Baus and Colot 1987)

$$\frac{\beta P_0^c}{\rho} = \left[1 + \sum_n C_n \eta_0^n\right][1 - \eta_0]^{-\nu}, \tag{53}$$

where the coefficients C_n for $1 \leqslant \nu \leqslant 5$ are given in table 1.

Using the relation

$$\frac{\beta A_0^c}{N} = \int_0^{\eta_0} \left(\frac{\beta P_0^c}{\rho} - 1\right)\frac{d\eta'}{\eta'}, \tag{54}$$

One can calculate the free energy of the system. Sinha and Sinha (1990b) have given explicit expressions of the free energy for $1 \leqslant \nu \leqslant 5$. These equations can be used to calculate the pressure and free energy of a binary mixture of both additive and non-additive hard ν-spheres.

Table 1. Values of coefficients C_n.

ν \ C_n	C_1	C_2	C_3	C_4
1	0	0	0	0
2	0	0·1250	0	0
3	1	1	−1	0
4	4	6·4057	−8·1170	0
5	11	36	−74·4380	347·12

5.1 *Binary mixture of additive hard ν-spheres*

For a binary mixture of additive hard ν-sphere, $\Delta = 0$ in (14a) and d_0 can be expressed as

$$d_0^\nu = d^\nu + x_1 x_2[2^{1-\nu}(d_{11} + d_{22})^\nu - (d_{11}^\nu + d_{22}^\nu)], \tag{55}$$

where d is given by (27). Then

$$\eta_0 = \eta + x_1 x_2 \Delta\eta, \tag{55a}$$

where η is given by (44) and

$$\Delta\eta = \frac{\pi^{\nu/2}}{2^\nu \Gamma(1+\nu/2)} \rho[2^{1-\nu}(d_{11} + d_{22})^\nu - (d_{11}^\nu + d_{22}^\nu)]. \tag{56}$$

Then (53) can be simplified in the form

$$\frac{\beta P_0^c}{\rho} = \frac{(1 + \Sigma_n C_n \eta^n)}{(1-\eta)^\nu} + x_1 x_2 \xi_\nu \eta \left[\frac{\nu + \Sigma_n C_n\{(\nu - n)\eta^n + n\eta^{n-1}\}}{(1-\eta)^{\nu+1}}\right]$$
$$+ 0((x_1 x_2)^2), \tag{57}$$

where

$$\xi_\nu = \frac{2^{1-\nu}(1+R)^\nu - (1+R^\nu)}{x_1 + x_2 R^\nu}. \tag{58}$$

With the help of (52) and (53), $g_{12}^c(d_{12})$ for the additive hard ν-sphere mixture can be given by

$$g_{12}^c(d_{12}) = 2^{1-\nu}\left[\frac{\Sigma_n n C_n \eta^{n-1}}{(1-\eta)^\nu} + \nu \frac{1 + \Sigma_n C_n \eta^n}{(1-n)^{\nu+1}}\right]$$
$$- \frac{1}{\eta}\left[1 - \frac{1 - \Sigma_n C_n (n-1)\eta^n}{(1-\eta)^\nu} + \nu_\eta \frac{1 + \Sigma_n C_n \eta^n}{(1-\eta)^{\nu+1}}\right]\mu_\nu, \tag{59}$$

where

$$\mu_\nu = \frac{(x_1 + x_2 R^{2\nu})}{(x_1 + x_2 R^\nu)(1+R)^\nu}. \tag{60}$$

5.2 *Binary mixture of non-additive hard ν-spheres*

For a binary mixture of non-additive hard ν-spheres, $\Delta \neq 0$ in (14a) and d_0 can be written as

$$d_0^\nu = d^\nu + x_1 x_2[2^{1-\nu}(d_{11} + d_{22})^\nu - (d_{11}^\nu + d_{22}^\nu)]$$
$$+ 2^{1-\nu} x_1 x_2 [d_{11} + d_{22})^\nu [(1+\Delta)^\nu - 1]. \tag{61}$$

Then η_0 can be expressed as

$$\eta_0 = \eta + x_1 x_2[\Delta\eta + \delta\eta], \tag{62}$$

where

$$\delta\eta = 2^{1-\nu}\eta\left[\frac{(1+2)^\nu}{x_1 + x_2 R^\nu}\right][(1+\Delta)^\nu - 1]. \tag{63}$$

Using this expression for η_0, one can obtain expressions for the equation of state and free energy for a binary of non-additive hard ν-spheres. Thus for a binary mixture of non-additive hard ν-spheres, (53) can be written as

$$\frac{\beta(P^c - P^c_a)}{\rho} = 2x_1x_2\eta^a_{12}\left[\frac{\nu + \Sigma_n C_n\{(\nu-n)\eta^n + n\eta^{n-1}\}}{(1-\eta)^{\nu+1}}\right][(1+\Delta)^\nu - 1]$$
$$+ 0((x_1^2x_2^2)), \tag{64}$$

where P^c_a is the pressure of a classical binary mixture of additive hard ν-spheres and given by (57). However we prefer to use (53) for calculating the pressure of the classical binary mixture.

With the help of (43), we get

$$\frac{\beta(P^c - P^c_a)}{\rho} = \frac{\pi^{\nu/2}}{\Gamma(1+\nu/2)} x_1x_2\rho[d^\nu_{12}g^c_{12}(d_{12}) - (d^a_{12})^\nu g^c_{12}(d^a_{12})], \tag{65}$$

where $d^a_{12} = (d_{11} + d_{22})/2$. Expanding the right hand side of (65) in the power of Δ, we obtain

$$\frac{\beta(P^c - P^c_a)}{\rho} = 2^\nu x_1x_2\eta^a_{12}[g^c_{12}(d_{12}) - g^c_{12}(d^a_{12}) + \nu\Delta g^c_{12}(d^a_{12}) + 0(\Delta^2)]. \tag{66}$$

Comparing (64) and (66) and using (59), we get

$$g^c_{12}(d_{12}) - g^c_{12}(d^a_{12}) = \frac{\nu}{\eta}\left[1 - \frac{1 - \Sigma_n C_n(n-1)\eta^n}{(1-\eta)^\nu} + \nu\eta\frac{1 + \Sigma_n C_n\eta^n}{(1-\eta)^{\nu+1}}\right]\mu_\nu\Delta$$
$$+ 0(\Delta^2). \tag{67}$$

6. Quantum correction to thermodynamics for a binary mixture of hard ν-spheres

In this section, we estimate the leading quantum correction to the free energy of the binary mixture of hard ν-spheres of both additive and non-additive diameters.

6.1 *Additive hard ν-sphere mixture*

For additive hard ν-sphere mixture, the excess free energy, correct to the first order quantum correction, is given by (50) when A^I_E is expressed in terms of $g^c_{12}(d_{12})$. For additive hard ν-spheres mixture, $g^c_{12}(d_{12})$ is given by (59). From this it is clear that the value of A^I_E depends on the concentration x_1 and the ratio R as well as on the dimension ν.

The values of the coefficient A^I_E for a binary mixture of additive ν-spheres with $1 \leqslant \nu \leqslant 5$ are reported as a function of η in figure 1 for $R = 1{\cdot}1$ and $x_1 = x_2 = 0{\cdot}5$. The coefficient A^I_E is positive and increases with ν and η.

Figure 2 demonstrates the variation of A^I_E for $\eta = 0{\cdot}25$ and $R = 1{\cdot}1$ with the concentration x_1. It is found that A^I_E is zero at $x_1 = 0$ and $x_1 = 1$ and finite in the intermediate range of x_1.

The thermodynamic properties have been studied for a binary mixture of hard spheres (Singh and Sinha 1982, 1983) and hard discs (Mishra and Sinha 1985). In the present paper, we consider the properties for $\nu = 4$ and 5 only.

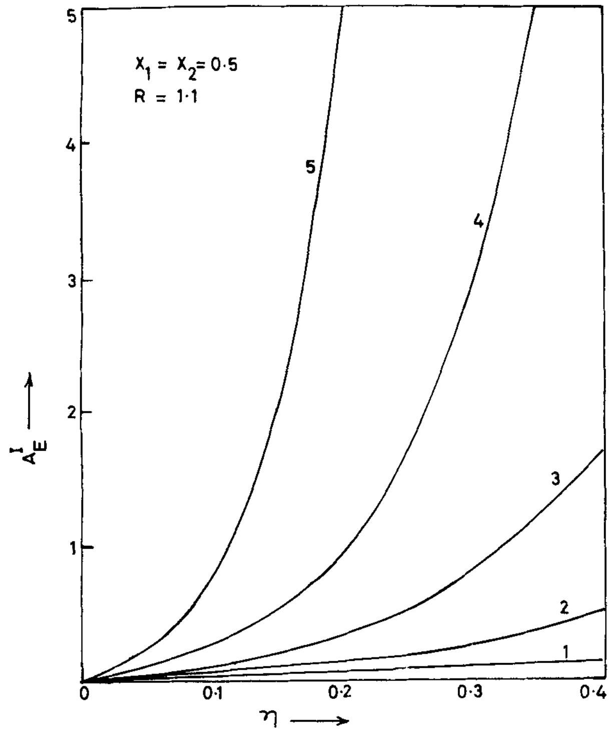

Figure 1. The quantum coefficient A_E^I for a binary mixture of additive hard ν-spheres (with $1 \leqslant \nu \leqslant 5$) as a function of η for $R = 1.1$ and $x_1 = x_2 = 0.5$. The number shown on curves indicates value of ν.

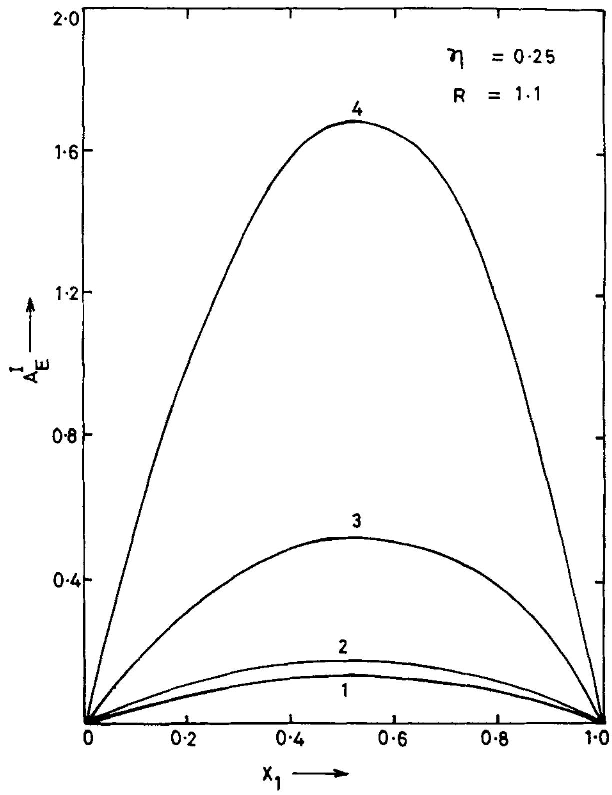

Figure 2. The quantum coefficient A_E^I for a binary mixture of additive hard ν-spheres (with $1 \leqslant \nu \leqslant 4$) as a function of x_1 for $R = 1.1$ at $\eta = 0.25$.

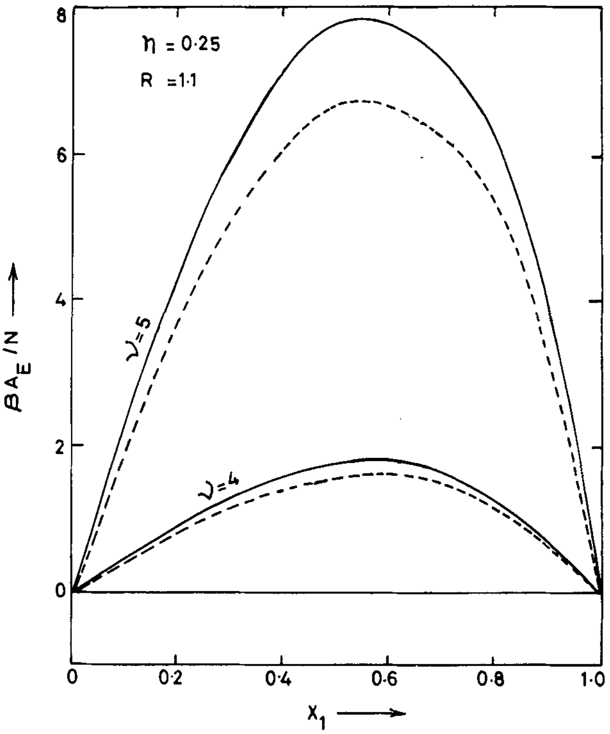

Figure 3. The excess free energy $\beta A_E/N$ of a binary mixture of hard ν-spheres with $\nu = 4$ and 5 as a function of x_1 for $\lambda/d = 0{\cdot}0$ and $0{\cdot}1$. The dashed curves represent the classical value.

The excess free energy, $\beta A_E/N$ of the binary mixture of the additive hard ν-spheres with $\nu = 4$ and 5 at $\eta = 0{\cdot}25$ for $R = 1{\cdot}1$ are shown in figure 3 as a function of x_1 for $\lambda/d = 0{\cdot}0$ and $0{\cdot}1$. $\lambda/d = 0{\cdot}0$ corresponds to the classical values. The excess quantum effect increases with ν. It is zero at $x_1 = 0{\cdot}0$ and $x_1 = 1{\cdot}0$ and finite in the intermediate range of x_1.

6.2 *Non-additive hard ν-sphere mixture*

This section is concerned with the evaluation of the excess properties of the binary mixture of non-additive hard ν-spheres. For such a mixture, (33) can be written in the form

$$\frac{\beta(A - A_a)}{N} = \frac{\beta(A^c - A_a^c)}{N} + \frac{\pi^{\nu/2}\nu}{2^{3/2}\Gamma(1+\nu/2)} x_1 x_2 \rho \times [d_{12}^{\nu-1} g_{12}^c(d_{12}) - (d_{12}^a)^{\nu-1} g_{12}^c(d_{12}^a)]\lambda_{12}, \tag{68}$$

where the subscript '*a*' refers to the properties of the additive hard ν-sphere mixture. $g_{12}^c(d_{12}^a)$ is given by (59) where as $g_{12}^c(d_{12})$ can be obtained from (67).

Substituting the values of $g_{12}^c(d_{12})$ and $g_{12}^c(d_{12}^a)$ in (68), we can obtain the final result for the free energy, correct to the first order quantum correction. Thus,

$$\frac{\beta(A - A_a)}{N} = \frac{\beta(A^c - A_a^c)}{N} + A_E^\lambda(\lambda/d), \tag{69}$$

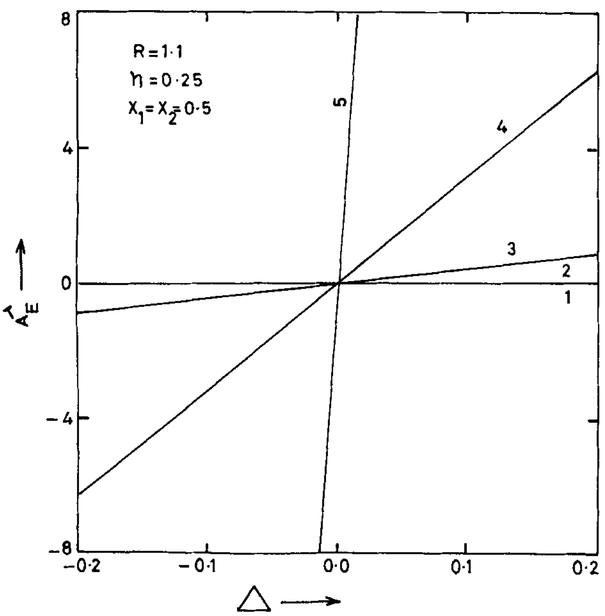

Figure 4. The quantum coefficient A_E^λ for a binary mixture of non-additive hard ν-spheres (with $1 \leqslant \nu \leqslant 5$) as a function of Δ for $\eta = 0{\cdot}25$, $R = 1{\cdot}1$ and $x_1 = x_2 = 0{\cdot}5$.

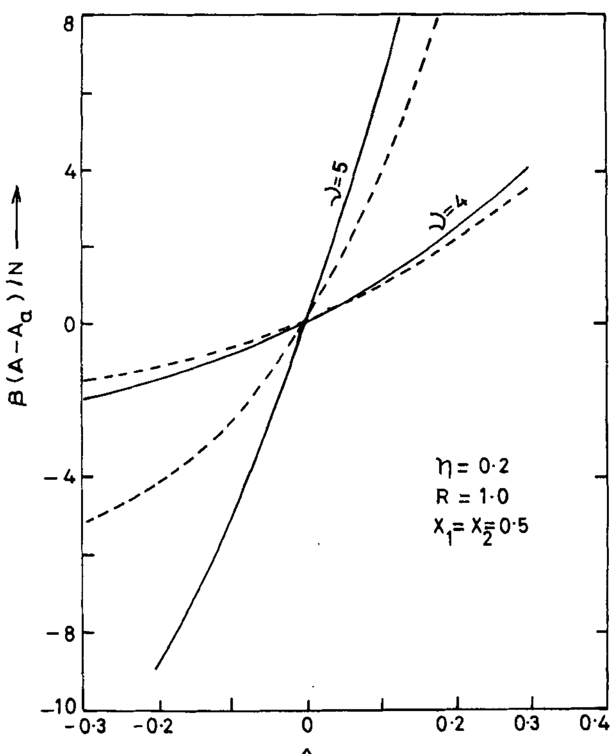

Figure 5. The values of $\beta(A - A_a)/N$ for a binary mixture of non-additive hard ν-spheres with $\nu = 4$ and 5 as a function of Δ for $\lambda/d = 0{\cdot}0$ and $0{\cdot}1$. The dashed curves represent the classical values.

$$A_E^\lambda = 2^{\nu-3/2}\nu x_1 x_2 E_\nu \eta_{12}^a \left(2^{1-\nu}\left[\frac{\nu+\Sigma_n C_n\{\nu-n\}\eta^n + n\eta^{n-1}\}}{(1-\eta)^{\nu+1}}\right]\right.$$
$$\left.+\frac{1}{n}\left[1-\frac{1-\Sigma_n C_n(n-l)\eta^n}{(1-\eta)^\nu}+\nu_\eta\frac{1+\Sigma_n C_n\eta^n}{(1-\eta)^{\nu+1}}\right]\mu_\nu\right)\Delta. \quad (70)$$

We have calculated the coefficient A_E^λ for a binary mixture of non-additive hard ν-spheres with $1 \leqslant \nu \leqslant 5$ for $x_1 = x_2 = 0{\cdot}5$ and $R = 1{\cdot}1$ at $\eta = 0{\cdot}25$. These results are shown in figure 4 as a function of Δ, non-additive parameter. The value of A_E^λ is positive when $\Delta > 0$ and negative when $\Delta < 0$. The magnitude of A_E^λ increases with ν.

In figure 5, the values of $\beta(A - A_a)N$ for a binary mixture of non-additive hard ν-spheres with $\nu = 4$ and 5 for $x_1 = x_2 = 0{\cdot}5$ and $R = 1{\cdot}0$ at $\eta = 0{\cdot}2$ are demonstrated as a function of Δ for $\lambda/d = 0{\cdot}0$ and $0{\cdot}1$. Both classical and semiclassical values are positive for $\Delta > 0$ and negative for $\Delta < 0$. They reduce to zero at $\Delta = 0$.

7. Conclusion

The purpose of this paper is to develop a unified theory for evaluating the equilibrium properties of a ν-dimensional fluid mixture of hard ν-spheres in the semiclassical limit. Analytic expressions for the first order quantum corrections to the second virial coefficient and free energy are given. From these studies, we come to the conclusion that the (excess) quantum effects to the thermodynamic properties of the hard ν-sphere mixture, which depend on the concentration x_1, the diameter ratio R, increase with the dimensionality ν.

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