

Advances in semiclassical statistical mechanical theory of molecular fluids

Suresh K Sinha

Department of Physics, L. S. College, B.B.A. Bihar University, Muzaffarpur-842 001, Bihar, India

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Abstract : The equilibrium properties of molecular fluids in the semiclassical limit, when the quantum effects are small, are studied. The physical properties are defined in terms of the Slater sum and methods for evaluating the Slater sum are discussed. The expansion series of the Helmholtz free energy is derived and employed to estimate the virial coefficients and thermodynamic properties of molecular fluids. Further the effective pair potential is expressed in the Lennard Jones (12–6) potential form, which is used to calculate the thermodynamic properties of molecular fluids.

Keywords : Semiclassical fluids, quantum effects, thermodynamic properties.

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Plan of the Article

1. Introduction
2. Molecular interactions
 - 2.1. Central potential model
 - 2.2. Generalised Stockmayer model
3. Density matrix and the Slater sum
 - 3.1. Canonical ensemble
 - 3.2. Grand canonical ensemble
4. Expansion of rotational partition function and the Slater sum
 - 4.1. Expansion of rotational partition function
 - 4.2. Expansion of Slater sum in power of \hbar
 - 4.2.1. Cluster expansion
 - 4.2.2. Perturbation expansion
5. Expansion formalism for semiclassical molecular fluids
 - 5.1. Density-independent pair distribution function
 - 5.2. Pair distribution function for dense fluids
 - 5.3. Thermodynamic properties of molecular fluids
6. Virial equation of state for dilute molecular fluids
 - 6.1. Analytic potentials
 - 6.1.1. Second virial coefficient
 - 6.1.2. Third virial coefficient
 - 6.2. Hard-core plus attractive tail potential
7. Thermodynamics of dense molecular fluids
 - 7.1. Classical molecular fluids
 - 7.2. Quantum corrections to thermodynamic properties
 - 7.3. Applications
 - 7.4. Concluding remarks
8. Effective pair potential method
 - 8.1. Introduction
 - 8.2. Effective pair potential for semiclassical molecular fluids
 - 8.2.1. Classical molecular fluids
 - 8.2.2. Classical polar fluids
 - 8.3. Thermodynamic properties of molecular fluids
 - 8.3.1. Virial equation of state for dilute molecular fluids
 - 8.3.2. Thermodynamics for dense molecular fluids
 - 8.4. Concluding remarks
9. Theory of corresponding state for semiclassical molecular fluids
 - 9.1. Critical point location
 - 9.2. Surface tension
 - 9.3. Liquid-vapour coexistence curve
 - 9.4. Conclusions
10. Some concluding remarks

1. Introduction

The statistical theory of fluids provides means for accurately predicting the thermophysical properties of fluids from a few well-defined characteristics of constituent molecules. These characteristics typically include the geometrical structure of the individual molecules, the nature of the intermolecular potential acting among different molecules and the nature of the intramolecular potential acting among sites on individual molecules. The thermophysical properties include the thermodynamic properties, transport properties and phase equilibrium behaviour. Thus, these properties may be referred either to equilibrium or non-equilibrium situation. These are important and active area of current research. The development in molecular theory of fluids are very important, as the molecular-based study of fluids has been motivated not only by scientific demands for improving the existing knowledge, but also by practical demands from increasingly sophisticated industry [1].

Most of the fluids found in the nature can be treated classically, because the molecular thermal de Broglie wavelength λ associated with a molecule is much smaller than the mean intermolecular spacing $a = (6/\pi\rho)^{1/3}$, (where $\rho = N/V$ is the fluid number density). Here λ is defined as

$$\lambda = (2\pi\hbar^2/mkT)^{1/2}, \quad (1.1)$$

where m is the molecular mass, k is the Boltzmann constant, T absolute temperature and $\hbar = h/2\pi$ (h being Planck's constant). However, there are some fluids like H_2 , HD, D_2 , H_2O for which deviations from classical behaviour are observed at low temperatures. When λ is of the order of magnitude of a , there are two types of quantum effects—(i) diffraction effects, which are linked with the wave nature of molecules in the fluid and (ii) exchange (or symmetry) effects due to the Bose-Einstein or Fermi Dirac statistics obeyed by the molecules. The exchange or symmetry effects are important, when the de Broglie wavelength of the molecules is of the order of magnitude of the average distance between molecules in the fluid and therefore are very small for all fluids except for liquid helium below $5^\circ K$ [2,3]. On the other hand, the diffraction effects are appreciable even at moderately high temperature. For rigid molecules, one expects three types of the diffraction effects : (i) translational diffraction effect, (ii) rotational potential energy effects and (iii) rotational kinetic energy effects. The quantum deviation due to the translational contributions is measured by Λ^* introduced by de Boer and Michels [4] and that due to the rotational contributions is measured by δ^* [5]. These dimensionless quantum parameters are defined as [4,5]

$$\begin{aligned} \Lambda^* &= h/\sigma\sqrt{(m\epsilon)}, \\ \delta^* &= h/\sqrt{(I\epsilon)}, \end{aligned} \quad (1.2)$$

where I is the moment of inertia (with respect to the centre of mass) and ϵ and σ are, respectively, measures of the strength and range of the interaction potential. Some typical values are listed in Table 1 for λ , λ/a , Λ^* , θ_r/k and δ^* , where $\theta_r = \hbar^2/2Ik$ is the characteristic rotation temperature. The values of λ and λ/a are found at the triple point T_{tr} which is also reported in the Table 1. From Table 1, we see that the quantum effects can be significant for some molecular fluids at low temperatures.

Table 1. Values of quantities for estimating the importance of quantum effects in fluids at their triple point temperature T_{tr} .

| Fluids | $T_{tr}(K)$ | $\lambda(\text{\AA})$ | λ/a | $\theta_r(K)$ | Λ^* | δ^* |
|---------|-------------|-----------------------|---------------|---------------|-------------|------------|
| He | ~ 0 | $\sim \infty$ | $\sim \infty$ | — | 2.67 | — |
| Ne | 24.5 | 0.780 | 0.209 | — | 0.593 | — |
| Ar | 84.6 | 0.300 | 0.967 | — | 0.186 | — |
| H_2 | 14.05 | 3.300 | 0.782 | 85.4 | 1.729 | 13.4997 |
| HD | 16.60 | 2.466 | | 64.3 | 1.414 | 11.7138 |
| D_2 | 18.72 | 2.008 | | 43.0 | 1.223 | 9.5792 |
| N_2 | 63.3 | 0.415 | 0.089 | 2.88 | 0.226 | 1.4889 |
| O_2 | 54.8 | 0.417 | 0.098 | 2.07 | 0.201 | 1.1658 |
| CO | 68.2 | 0.398 | 0.084 | 2.27 | 0.220 | 1.4774 |
| HCl | 159.05 | 0.286 | | 15.02 | 0.144 | 1.8138 |
| CH_4 | 90.7 | 0.460 | 0.097 | 7.54 | 0.239 | 2.0785 |
| CCl_4 | 250.28 | 0.096 | | 0.0823 | 0.033 | 0.1151 |

The present article aims to review the equilibrium properties of molecular fluids of non-spherical molecules in the semiclassical limit. The theory described here is applicable mainly to simple molecular fluids *i.e.* fluids of the homogeneous diatomic molecules. Its extension to complex molecular fluids is not attempted here.

In recent years, a considerable progress has been made in the theory for predicting the equilibrium properties of fluids composed of either spherical or non-spherical molecules. This progress is confined mostly to the classical fluids [6,7]. However, when dealing with molecular fluids in which the deviation takes place at a microscopic level from the classical law, our theoretical understanding is not satisfactory. In recent years, some theoretical methods have been developed to deal with such fluids. The present article is devoted to review these methods. In the present work, we consider the diffraction effects only and confine ourselves to the density and temperature regions where the quantum effects are small and can be treated as a correction to the classical system. The fluid is treated semiclassically under these conditions. The task of a semiclassical theory of fluids

with which we are concerned in this work is two fold : one is to determine the thermodynamic and transport properties of molecular fluids at moderately high temperature, where the quantum effects are small and another is to ascertain the density and temperature range in which the fluid can be treated semiclassically. Apart from direct application of such study to real systems, they may help in framing a theory for quantum fluids.

The earlier review articles by de Boer and Bird [8] and Sinha [9] contain many useful informations about the equilibrium theory of the molecular fluids in the semiclassical limit. The present article is concerned mainly with development of methods of computing the thermodynamic properties of semiclassical molecular fluids in the past 25 years, although some reference is made to earlier papers.

In case of molecular fluids composed of the rigid molecules, the intermolecular potentials depend on the separation as well as orientation of the molecules. This orientation leads to quantitatively new features in fluid properties, when compared to atomic fluids. The intermolecular interaction potentials are discussed in Section 2

The quantity of central importance for constructing the theory of quantum and semiclassical fluids is the Slater sum, used to develop theory of atomic fluids [3,10,11]. This method was extended to develop theory for molecular fluids. We give a brief account of the Slater sum in Section 3. Particle distribution functions and thermodynamic quantities are defined in terms of the Slater sum in both the canonical and the grand canonical ensembles.

At high temperatures, where the quantum effects are small and treated as a correction to the classical behaviour, usual method is to expand the Slater sum in powers of \hbar^2 (for analytic potential) or in powers of \hbar (for non analytic potential). This is discussed in Section 4 and used in following sections.

We use the expansion of the Slater sum for obtaining expressions of the quantum corrections to the pair distribution function and thermodynamic properties of molecular fluids in Section 5 in terms of classical distribution functions. The virial coefficients and thermodynamic properties of semiclassical molecular fluids are discussed in Sections 6 and 7, respectively.

Effective pair potential method is discussed in Section 8. It is used to evaluate the virial coefficients and thermodynamic properties of the semiclassical molecular fluids. In Section 9, we give a brief outline of the theory of corresponding state of the molecular fluids. Some concluding remarks are given in Section 10.

2. Molecular interactions

We consider a fluid consisting of N molecules which are in their ground electronic and ground vibrational states. The total potential energy of such system can be written as

$$\Phi(x_1, x_2, \dots, x_N) = \sum_{i < j} u(x_i, x_j) + \sum_{i < j < k} V(x_i, x_j, x_k) \quad (2.1)$$

where $u(x_i, x_j)$ is the pair interaction potential between molecules i and j and $V(x_i, x_j, x_k)$ is the three body non additive interaction. Here, $x_i \equiv (r_i, \omega_i)$ is the vector describing both the position r_i of the centre of mass and the orientation ω_i of molecules i .

It is supposed [12] that the successive terms of Φ in eq. (2.1) decrease in magnitude

$$\sum_i u(x_i, x_j) > \sum V(x_i, x_j, x_k) > \dots \quad (2.2)$$

The three- and higher-body interactions whose contributions are expected to be small [12] are not considered in the present study and the total potential is assumed to be pairwise additive.

Many potential models were used for statistical mechanical calculations for fluids. We briefly discuss some of the models in this section.

2.1. Central potential model :

The simplest potential model is the hard sphere (HS) potential defined as

$$u_{HS}(r) = \begin{cases} \infty & \text{for } r < \sigma, \\ 0 & \text{for } r > \sigma, \end{cases} \quad (2.3)$$

where σ is the hard sphere diameter. This model, frequently used due to its simplicity, gives a crude representation of the strong, short-range repulsive forces.

For non-polar molecules, a commonly used intermolecular potential is the Lennard-Jones (LJ) (12-6) potential defined as

$$u_{LJ}(r) = 4 \left[(\sigma/r)^{12} - (\sigma/r)^6 \right], \quad (2.4)$$

where ϵ and σ are the well-depth and diameter, respectively and $r = |\mathbf{r}_1 - \mathbf{r}_2| \cdot \sigma$ is the value of r at which $u(r) = 0$ and ϵ is the depth of the potential well which occurs at $r_{\min} = 2^{1/6} \sigma$. This potential function gives a fairly simple and realistic representation for spherical non-polar molecules, such as He, Ne, Ar *etc.*

2.2. Generalised Stockmayer model :

This potential model is assumed to consist of a spherically symmetric potential and a contribution due to the non-sphericity of the molecular charge distribution. That is

$$u(r_1, \omega_1, \omega_2) = u_0(r) + u_a(r_1, \omega_1, \omega_2), \quad (2.5)$$

where $u_0(r)$ is the central potential between molecules 1 and 2, and $u_a(r_1, \omega_1, \omega_2)$, arising from the tensor forces

contains all of the angle dependence of the pair interactions. For the central potential, we use either HS or LJ(12-6) potential. For the tensor interaction between two molecules, we write

$$u_a = u_{\text{perm}} + u_{\text{in}} + u_{\text{dis}} + u_{\text{shape}}, \quad (2.6)$$

where u_{perm} is the interaction between permanent multipole moment of molecules, u_{in} is the interaction of the induced multipole moment in one molecule with the permanent moment in the other molecule, u_{dis} is the interaction between anisotropic dispersion forces of the molecules and u_{shape} is the interaction between anisotropic overlap forces of molecules. These interaction potentials can be expressed as an expansion in spherical harmonics [6,13,14]. For numerical calculation, however, we use the explicit angle-dependent form of interaction [15-19]

$$u_{\text{perm}} = (\mu^2/r^3)\phi_{\mu\mu}(\omega_1\omega_2) + (3\mu Q/2r^4)\phi_{\mu Q}(\omega_1\omega_2) + (3Q^2/4r^5)\phi_{QQ}(\omega_1\omega_2) \quad (2.7)$$

$$\text{with } \phi_{\mu\mu}(\omega_1\omega_2) = \sin\theta_1 \sin\theta_2 \cos\phi + 2\cos\theta_1 \cos\theta_2, \quad (2.8a)$$

$$\phi_{\mu Q}(\omega_1\omega_2) = \cos\theta_1(3\cos^2\theta_2 - 1) - 2\sin\theta_1 \sin\theta_2 \cos\theta_2 \cos\phi, \quad (2.8b)$$

$$\phi_{QQ}(\omega_1\omega_2) = 1 - 5(\cos^2\theta_1 + \cos^2\theta_2) - 15\cos^2\theta_1 \cos^2\theta_2 + 2(\sin\theta_1 \sin\theta_2 \cos\phi - 4\cos\theta_1 \cos\theta_2)^2, \quad (2.8c)$$

$$u_{\text{in}} = -(\alpha\mu^2/4r^6)\phi_{\alpha\mu}(\omega_1\omega_2) - (9\alpha Q^2/8r^8)\phi_{\alpha Q}(\omega_1\omega_2) \quad (2.9)$$

$$\text{with } \phi_{\alpha\mu}(\omega_1\omega_2) = 2 + 3\cos^2\theta_1 + 3\cos^2\theta_2, \quad (2.10a)$$

$$\phi_{\alpha Q}(\omega_1\omega_2) = \sin^4\theta_1 + \sin^4\theta_2 + 4\cos^2\theta_1 + 4\cos^2\theta_2, \quad (2.10b)$$

$$u_{\text{dis}} = 4\epsilon(\sigma/r)^6\phi_{KK}(\omega_1\omega_2) \quad (2.11)$$

$$\text{with } \phi_{KK}(\omega_1\omega_2) = K - (3/2)K(1-K)(\cos^2\theta_1 + \cos^2\theta_2) - (3/2)K^2(\sin\theta_1 \sin\theta_2 \cos\phi - 2\cos\theta_1 \cos\theta_2)^2 \quad (2.12)$$

$$\text{and } u_{\text{shape}} = 4\epsilon(\sigma/r)^{12}\phi_{ss}(\omega_1\omega_2) \quad (2.13)$$

$$\text{with } \phi_{ss}(\omega_1\omega_2) = 3\cos^2\theta_1 + 3\cos^2\theta_2 - 2, \quad (2.14)$$

where θ_1 , θ_2 and $\phi = \phi_1 - \phi_2$ are the Euler angles, which determine the orientation of the molecules with respect to the line joining the centres of the molecules, μ and Q are, respectively, the dipole and quadrupole moment of the molecule, α is the mean polarizability, K is the anisotropy in the polarizability and D is the dimensionless shape parameter of molecule. For linear or symmetric top molecules,

with z chosen as the mean symmetric axes, α and K are defined as [6]

$$\alpha = (\alpha_{\parallel} + 2\alpha_{\perp})/3$$

$$\text{and } K = (\alpha_{\parallel} - \alpha_{\perp})/3\alpha,$$

where $\alpha_{\parallel} = \alpha_{zz}$, $\alpha_{\perp} = \alpha_{xx} = \alpha_{yy}$. The potential parameters ϵ and σ are characteristic of the LJ (12-6) model representing the central potential. This potential model has been used to simple molecular fluids (e.g. N₂, O₂, HCl and H₂), where the non-sphericity is small. In case of CH₄ and CCl₄, both dipole and quadrupole moments are zero, one considers octopole and hexapole moments only. The force parameters of some systems of present interest are reported in Table 2.

Table 2. Force parameters of some fluids of interest.

| System | $\alpha(A)$ | $\epsilon/k(K)$ | $\alpha/10^{-24}$ (cm ³) | $\mu/10^{-18}$ (e.s.u.-cm) | $Q/10^{-26}$ (e.s.u.-cm ²) | K | D |
|-----------------|-------------|-----------------|---|-------------------------------|---|-------|------|
| He ₄ | 2.556 | 10.22 | 0.206 | | | | |
| Ne | 2.749 | 35.60 | 0.396 | | | | |
| Ar | 3.405 | 119.80 | 1.642 | | | | |
| H ₂ | 2.928 | 37.00 | 0.806 | | 0.650 | 0.125 | 0.10 |
| HD | 2.928 | 37.00 | | 5.85×10^{-4} | 0.642 | | |
| D ₂ | 2.928 | 37.00 | 0.795 | | 0.649 | 0.115 | 0.10 |
| N ₂ | 3.620 | 100.15 | 1.730 | | -1.400 | 0.176 | 0.08 |
| O ₂ | 3.388 | 122.44 | 1.600 | | -0.390 | 0.239 | 0.12 |
| HCl | 3.305 | 360.00 | 2.630 | 1.03 | 3.800 | 0.034 | 0.15 |

3. Density matrix and the Slater sum

In statistical mechanics, the state of the quantum ensemble is described by the density operator (or statistical operator) $\hat{\rho}$. Any matrix representing this operator is called a density matrix. Nature of the density operator $\hat{\rho}$ depends on the choice of ensemble.

3.1. Canonical ensemble :

We consider a quantum mechanical system of N identical molecules, each of mass m in their ground electronic and ground vibration state. The Hamiltonian of the system is

$$\hat{H}_N = -(\hbar^2/2m)\sum_{i=1}^N \nabla_i^2 + \Phi(x_1, x_2, \dots, x_N), \quad (3.1)$$

where ∇_i^2 is the generalised Laplacian operator in a s -dimensional space and Φ is the total interaction potential which is assumed to be pair-wise additive *i.e.*

$$\Phi = \sum_{i < j} u(x_i, x_j) \quad (3.2)$$

where $u(x_i, x_j)$ is the pair potential between molecules i and j and the vector $x_i \equiv (r_i, \omega_i)$ represents both the position of the centre of mass and orientation of the molecules i . (For linear molecules, $\omega_i = \theta_i \phi_i$ and for non-linear molecules $\omega_i = \theta_i \phi_i \psi_i$).

For a closed system, the density operator $\hat{\rho}$ is defined as

$$\hat{\rho} = \exp[-\beta\hat{H}_N] / Q_N, \quad (3.3)$$

where $\beta = (kT)^{-1}$ (k being the Boltzmann constant and T the absolute temperature) and Q_N is the normalization factor, known as the quantum mechanical canonical partition function. Since

$$\text{Tr}\hat{\rho} = 1,$$

where 'Tr' indicates the trace, which is the sum of the diagonal elements,

$$Q_N = \text{Tr}(\exp[-\beta\hat{H}_N]). \quad (3.4)$$

If $\{\Psi_x\}$ represents a complete set of (properly symmetrized) orthonormal wave function of the system, then

$$Q_N = \sum \int \Psi_x^*(x_1, \dots, x_N) \exp[-\beta\hat{H}_N] \times \Psi_x(x_1, \dots, x_N) \prod_{i=1}^N dx_i, \quad (3.5)$$

where $dx_i = \Omega^{-1} dr_i d\omega_i$ (3.6)

and $\Omega = 4\pi$ (for linear molecules),
 $= 8\pi^2$ (for non-linear molecules). (3.7)

Now we introduce a quantity known as the Slater sum, which is defined in this case as

$$W_N(x_1, x_2, \dots, x_N) = N! \lambda^{3N} q_r^{-N} \sum \Psi_x^*(x_1, \dots, x_N) \times \exp[-\beta\hat{H}_N] \Psi_x(x_1, \dots, x_N) \quad (3.8)$$

where the summation in eq. (3.8) extends over all states. Here λ is the thermal wavelength and q_r is the single-molecule rotational partition function. The classical counterpart of the Slater sum is the Boltzmann factor

$$W_N^c(x_1, x_2, \dots, x_N) = \exp[-\beta\Phi(x_1, \dots, x_N)]. \quad (3.9)$$

The rotational partition function for a single rigid molecule of arbitrary shape is defined as [6]

$$q_r = \text{Tr}(\exp[-\beta K_r]), \quad (3.10)$$

where K_r is the rotational kinetic energy of a single molecule

$$K_r = aJ_x^2 + bJ_y^2 + cJ_z^2, \quad (3.11)$$

J_x, J_y, J_z are the body-fixed principal axes components of J and $a = 1/2I_{xx}$, etc. For a linear molecule, the term cJ_z^2 is absent (i.e. $K_r = aJ^2 = J^2/2I$). For a non-linear molecule, we have three cases (i) spherical top ($a = b = c$), (ii) symmetric top ($a = b \neq c$) (iii) asymmetric top ($a \neq b \neq c$). Hence for example the single molecule rotational partition function for a linear molecule is given by [6]

$$q_r = \sum (2J+1) \exp[-\beta J(J+1)\hbar^2/2I] \quad (3.12)$$

and for spherical top molecule

$$q_r = \sum (2J+1)^2 \exp[-\beta J(J+1)\hbar^2/2I]. \quad (3.13)$$

In terms of the Slater-sum, the canonical partition function is written as

$$Q_N = Z_N / (N! \lambda^{3N} q_r^{-N}), \quad (3.14)$$

where Z_N is the configurational integral which is defined in this case as

$$Z_N = \int \dots \int W_N(x_1, x_2, \dots, x_N) \prod_{i=1}^N dx_i. \quad (3.15)$$

The 1-particle distribution function is defined as

$$n_N(x_1, x_2, \dots, x_1) = [(n-1)! \lambda^{3N} q_r^{-N} Q_N]^{-1} \times \int \int W_N(x_1, x_2, \dots, x_1) \prod_{i=1}^N dx_i. \quad (3.16)$$

All thermodynamic properties of the system can be obtained from a knowledge of the partition function. Thus, the Helmholtz free energy is

$$\beta A = -\ln Q_N, \quad (3.17)$$

the pressure

$$P = (\rho^2 / N) (\partial A / \partial \rho)_\beta \quad (3.18)$$

and the internal energy

$$U = \partial(\beta A) / \partial \beta. \quad (3.19)$$

3.2. Grand canonical ensemble :

The canonical ensemble is approximate to an equilibrium system having a fixed number of molecules N . For an open system, the density operator $\hat{\rho}$ commute with the Hamiltonian operator \hat{H} as well as the number operator \hat{N} , whose eigen values are 0, 1, 2, The density operator $\hat{\rho}$ in this case is defined as

$$\hat{\rho} = \exp[-\beta(\hat{H} - \mu\hat{N})] / \Xi, \quad (3.20)$$

where $\Xi = \{\exp[-\beta(\hat{H} - \mu\hat{N})]\}$ (3.21)

is the grand canonical partition function and μ the chemical potential. In terms of the Slater sum, eq. (3.21) can be expressed as

$$\Xi = \sum_{N=0}^{\infty} (z^N / N!) \int \dots \int W_N(x_1, x_2, \dots, x_N) \prod_{i=1}^N dx_i, \quad (3.22)$$

where $z = \lambda^{-3} q_r \exp[\beta\mu]$ (3.23)

is the fugacity of the system. The link with thermodynamics is given by the relation

$$\beta P = \lim_{V \rightarrow \infty} V^{-1} \ln \Xi, \quad (3.24)$$

where P is the pressure of the system.

In the grand canonical ensemble, the 1-particle distribution function is written as

$$n(x_1, x_2, \dots, x_1) = \Xi^{-1} \sum_{n=1}^{\infty} (z^N / (N-1)!) \times \int \dots \int W_N(x_1, x_2, \dots, x_N) \prod_{i=1}^N dx_i. \quad (3.25)$$

The pair distribution function $n(x_1, x_2)$, which is frequently used, gives the probability of finding a molecule at $x_1 \equiv r_1 \omega_1$ and another at $x_2 \equiv r_2 \omega_2$.

Instead of using $n(x_1, x_2, \dots, x_1)$, we often find it convenient to use related function known as the correlation function defined by the equation

$$g(x_1, x_2, \dots, x_1) = (\Omega / \rho)^1 n(x_1, x_2, \dots, x_1), \quad (3.26)$$

where $\rho = N/V$ is the number density.

The most important distribution function is the pair distribution function (PDF) $g(r, \omega_1 \omega_2)$ which is a function of $r = |r_1 - r_2|$ as well as the function of ω_1 and ω_2 . For a simple uniform fluid, $g(r)$ depends only on r and is called the radial distribution function (RDF).

Thus the quantity of central importance for constructing the theory of quantum and semiclassical fluids is the Slater sum.

4. Expansion of rotational partition function and the Slater sum

4.1. Expansion of rotation partition function :

At moderately high temperature, when the quantum effects are small, the single-molecule rotational partition function q_r for a linear molecule (moment of inertia $I_1 = I_2 = I$) is given by [6]

$$q_r = q_r^c [1 + (1/6)(\beta \hbar^2 / I)], \quad (4.1)$$

$$\text{where } q_r^c = (2I / \beta \hbar^2) \quad (4.2)$$

and for a symmetric top molecule (with $I_1 = I_2 \neq I_3$) is

$$q_r = q_r^c [1 + (1/12)(\beta \hbar^2 / 2I_1)(4 - I_1 / I_3)], \quad (4.3)$$

$$\text{where } q_r^c = \pi^{1/2} (2I_1 / \beta \hbar^2) (2I_3 / \beta \hbar^2)^{1/2} \quad (4.4)$$

and I_1, I_2 and I_3 are the principal moment of inertia of a molecule. For a spherical top molecule ($I_1 = I_2 = I_3$),

Eq. (4.3) reduces to

$$q_r = q_r^c [1 + (1/8)(\beta \hbar^2 / I)], \quad (4.5)$$

$$\text{where } q_r^c = \pi^{1/2} (2I / \beta \hbar^2)^{1/2}. \quad (4.6)$$

4.2. Expansion of the Slater sum in powers of \hbar :

4.2.1. Cluster expansion

The cluster expansion method originally developed for the atomic fluid [20,21], can be employed for the molecular

fluid. At moderately high temperatures, when the deviation from the classical behaviour is small, we can write [3]

$$W_N = W_N^c W_N^m, \quad (4.7)$$

where W_N^c is the Boltzmann factor (eq. 3.9) and W_N^m is a function, which measures the deviation from the classical behaviour. When the pair potential has a hard core, both W_N and W_N^c vanish for molecular configuration in which hard cores overlap. In this case, W_N^m can also be taken as zero

Now we express W_N^m in terms of the 'modified' Ursell function U_1^m . Thus,

$$W_1^m(x_1) = U_1^m(x_1) = 1, \quad (4.8a)$$

$$W_2^m(x_1 x_2) = 1 + U_2^m(x_1 x_2), \quad (4.8b)$$

$$W_3^m(x_1 x_2 x_3) = 1 + U_2^m(x_1 x_2) + U_2^m(x_1 x_3) + U_2^m(x_2 x_3) + U_3^m(x_1 x_2 x_3), \quad (4.8c)$$

$$W_N^m(x_1, x_2, \dots, x_N) = 1 + \sum U_2^m(x_i x_j) + \sum_{i < j < k} U_3^m(x_i x_j x_k) + \dots \quad (4.8d)$$

Eq. (4.8d) is obtained by taking all possible partitions of the N molecules in groups, making the corresponding product of U_1^m functions and summing over all partitions. The above equations can be solved successively for U_2^m, U_3^m, \dots . Thus,

$$U_2^m(x_1 x_2) = W_2^m(x_1 x_2) - 1, \quad (4.9a)$$

$$U_3^m(x_1 x_2 x_3) = W_3^m(x_1 x_2 x_3) - W_2^m(x_1 x_2) - W_2^m(x_1 x_3) - W_2^m(x_2 x_3) + 2. \quad (4.9b)$$

From eqs. (4.7) and (4.8d), we obtain the expression for W_N

$$W_N(x_1, x_2, \dots, x_N) = W_N^c(x_1, \dots, x_N) [1 + \sum U_2^m(x_i x_j) + \sum U_3^m(x_i x_j x_k) + \dots]. \quad (4.10)$$

The function U_1^m appearing in eq. (4.10) can, in principle, be found from the solution of the quantum mechanical 1-body problem. Unfortunately, the actual calculation is too involved to be feasible. It is only for hard sphere systems that U_2^m have been evaluated as [22]

$$U_2^m(r) = \phi_0 + \phi_1 + \dots, \quad r > \sigma, \quad (4.11)$$

$$\text{where } \phi_0 = -\exp[-X^2], \quad (4.12a)$$

$$\phi_1 = (1/\sqrt{2})(\lambda/\sigma) X^2 \operatorname{erfc}(X) \quad (4.12b)$$

Here $X = (2/\pi)^{1/2}((r/\sigma) - 1)/(\lambda/\sigma)$

$$\text{and } \operatorname{erfc}(X) = (2/\pi)^{1/2} \int_x^{\infty} \exp(-t^2) dt$$

is the complimentary error function.

For potentials, which have an attractive tail, the solution of even a two-body problem becomes difficult. However, for such a potential a different type of expansion known as perturbation expansion can be adopted. We describe this method in Section 4.2.2.

4.2.2. Perturbation expansion

In this section, we discuss the expansion of the Slater sum in powers of \hbar using a method known as perturbation expansion. With a suitable choice of the reference system, this method can be applied to any potential.

(A) Hard sphere basis function

We treat the attractive interaction as a perturbation on the hard sphere system and write the Hamiltonian \hat{H}_N of eq (3.1) in the form

$$\hat{H}_N = \hat{H}_N^0 + \Phi_a, \quad (4.13)$$

$$\text{where } \hat{H}_N^0 = \hat{H}_{N,\text{tr}}^0 + \hat{H}_{N,\text{rot}}^0 \quad (4.14)$$

with

$$\hat{H}_{N,\text{tr}}^0 = (-\hbar^2/2m) \sum_{i=1}^N \nabla_r^2 + \Phi_{HS}(r_1, r_2, \dots, r_N), \quad (4.15a)$$

$$\hat{H}_{N,\text{rot}}^0 = (-\hbar^2/2I) \sum_{i=1}^N \nabla_{\omega_i}^2, \quad (4.15b)$$

$$\text{and } \Phi_a = \sum_{i < j} u_a(x_i, x_j) \quad (4.16)$$

is the total angle dependent potential treated as a perturbation. We choose the basis functions, which are the eigen function of the reference hard sphere Hamiltonian. Let Ψ_i^0 be the eigen function for the Hamiltonian \hat{H}_N^0 . Thus,

$$\begin{aligned} \Psi_x^0(x_1, x_2, \dots, x_N) &= \Phi_K^0(r_1, r_2, \dots, r_N) X_m(\omega_1, \dots, \omega_N) \\ &\quad \text{for } r_{ij} > \sigma \\ &= 0 \quad \text{for } r_{ij} < \sigma, \end{aligned} \quad (4.17)$$

where Φ_K^0 is the eigen function of the translatory hard-sphere Hamiltonian and X_m is the eigen function of the rotational kinetic energy. In terms of the hard sphere wave function, the Slater sum can be written as

$$\begin{aligned} W_N(x_1, \dots, x_N) &= N! \lambda^{3N} q_r^{-N} \sum \Psi_x^{0*} \\ &\quad \times \exp[-\beta \hat{H}_N^0 + \Phi_a] \Psi_x^0. \end{aligned} \quad (4.18)$$

Following the method of Friedmann [23], we obtain the expansion of W_N [24]

$$W_N = W_N^0 + W_N^1 + W_N^2 + \dots, \quad (4.19)$$

where

$$W_N^0(x_1, \dots, x_N) = \exp[-\beta \Phi_a] W_N^{HS}(r_1, \dots, r_N), \quad (4.20)$$

$$\begin{aligned} W_N^1(x_1, \dots, x_N) &= \exp[-\beta \Phi_a] \left[(\hbar^2 \beta^2 / 2m) \right. \\ &\quad \times \sum_i \left((1/2) \nabla_r^2 \Phi_a - (1/3) \beta (\nabla_r \Phi_a)^2 \right. \\ &\quad \left. \left. + (1/2) \nabla_r \Phi_a \cdot \nabla_r \right) W_N^{HS} + (\hbar^2 \beta^2 / 2I) \right. \\ &\quad \left. \times \sum_i \left((1/2) \nabla_{\omega_i}^2 \Phi_a - (1/3) \beta (\nabla_{\omega_i} \Phi_a)^2 \right) \right. \\ &\quad \left. \times W_N^{HS} \right], \end{aligned} \quad (4.21)$$

$$\begin{aligned} W_N^2(x_1, \dots, x_N) &= \exp[-\beta \Phi_a] \left\{ (\hbar^2 \beta^2 / m) \right. \\ &\quad \times \sum \left[(1/3) \nabla_{r_{ij}}^2 u_a(x_i, x_j) \right. \\ &\quad \left. (1/4) \beta (\partial u_a(x_i, x_j) / \partial x_{ij})^2 \right. \\ &\quad \left. - (\hbar^2 \beta^2 / 2I) \sum_{i=1}^N \left[(1/3) \nabla_{\omega_i}^2 u_a(x_i, x_j) \right. \right. \\ &\quad \left. \left. - (1/4) (\nabla_{\omega_i} u_a(x_i, x_j))^2 \right] \right\} W_N^{HS} \end{aligned} \quad (4.22)$$

$$\begin{aligned} \text{and } W_N^{HS}(r_1, \dots, r_N) &= N! \lambda^{3N} \sum_K \Phi_K^{0*} \\ &\quad \times \exp[-\beta \hat{H}_{N,\text{tr}}^0] \Phi_K^0 \end{aligned} \quad (4.23)$$

is the hard sphere Slater sum. In deriving eq. (4.22), we have used the superposition approximation [3] for W_N . In the semiclassical limit, W_N^{HS} can be expressed in the form of eq. (4.10) when U_1^m is the 1-particle 'modified' Ursell function for a hard sphere system. Explicit expression for $U_2^m(r)$ for hard sphere is given by eq. (4.11).

(B) Free particle basis function :

When the potential energy Φ is treated as a perturbation over the kinetic energy, we chose the free particle basis functions, which are the eigen function of the reference Hamiltonian. Then the expansion of the Slater sum W_N can be written as

$$\begin{aligned} W_N &= \exp[-\beta \Phi] \left[1 - \left\{ (\beta^2 \hbar^2 / 12m) \right. \right. \\ &\quad \times \sum_{i=1}^N \left(\nabla_r^2 \Phi - (1/2) \beta (\nabla_r \Phi)^2 \right) + (\beta^2 \hbar^2 / 12I_1) \\ &\quad \left. \left. \times \sum_{i=1}^N \left(\nabla_{\omega_i}^2 \Phi - (1/2) \beta (\nabla_{\omega_i} \Phi)^2 \right) + O(\hbar^4) \right\} \right]. \end{aligned} \quad (4.24)$$

For the spherical top molecules $I_1 = I_2 = I_3$, whereas in the case of the rigid linear molecules $I_1 = I_2 = I$ and Φ does not depend on Ψ_i .

5. Expansion formalism for semiclassical molecular fluids

In the semiclassical limit (*i.e.* at high temperature), when the quantum effects are small and can be treated as a correction

to the classical system, the usual way of studying the properties of the system is to expand them in a series of Plank's constant \hbar . The first term of the series is the classical values and other terms arise due to the quantum effects.

5.1. Density independent pair distribution function :

It was shown by deBoer [25] that the pair distribution function $n(x_1, x_2)$ can be expanded in terms of the number density ρ

$$n(x_1, x_2) = \rho^2 W_2(x_1, x_2) + O(\rho^3), \quad (5.1)$$

where $W_2(x_1, x_2)$ is the two-particle Slater sum. In the low density limit, pair distribution function (PDF) $g^0(x_1, x_2)$ for a molecular fluid of rigid linear molecules is defined as

$$\begin{aligned} g^0(x_1, x_2) &= W_2(x_1, x_2) \\ &= 2! \lambda^6 q_r^{-2} \sum \Psi_\alpha^*(x_1, x_2) \\ &\quad \times \exp[-\beta \hat{H}_2] \Psi_\alpha(x_1, x_2), \end{aligned} \quad (5.2)$$

where $\Psi_\alpha(x_1, x_2)$ is a set of orthonormal two particle wave functions and \hat{H}_2 the two-particle Hamiltonian. Using the centre of mass and relative coordinates R and $r (= |\mathbf{r}_1 - \mathbf{r}_2|)$, we can write eq. (5.2) as

$$\begin{aligned} g^0(r\omega_1\omega_2) &= 2^{3/2} \lambda^3 q_r^{-2} \sum_\alpha \Psi_\alpha^*(r\omega_1\omega_2) \\ &\quad \times \exp[-\beta \hat{H}_{\text{rel}}] \Psi_\alpha(r\omega_1\omega_2), \end{aligned} \quad (5.3)$$

where $\hat{H}_{\text{rel}} = -(\hbar^2/m)\nabla_r^2 - (\hbar^2/2I)(\nabla_{\omega_1}^2 + \nabla_{\omega_2}^2) + u(r\omega_1\omega_2)$

is the relative Hamiltonian of two molecules.

(A) Hard sphere basis function

When the potential has a hard core plus attractive tail, such as polar hard sphere potential, we choose hard-sphere basis function which are eigen function of the hard sphere Hamiltonian. As discussed in the previous section, eq. (5.3) can be expressed in the form [24]

$$\begin{aligned} g^0(r\omega_1\omega_2) &= \exp[-\beta u(r\omega_1\omega_2)] \\ &\quad \times [1 + U_2^m(r\omega_1\omega_2)] \end{aligned} \quad (5.4)$$

$$\text{with } U_2^m = U_{2,\text{tr}}^m + U_{2,\text{rot}}^m, \quad (5.5)$$

$$\text{where } U_{2,\text{tr}}^m(r\omega_1\omega_2) = \gamma_0(r) + \gamma_1(r\omega_1\omega_2), \quad r > \sigma \quad (5.6)$$

$$\text{with } \gamma_0(r) = \phi_0(r), \quad (5.7a)$$

$$\begin{aligned} \gamma_1(r\omega_1\omega_2) &= \phi_0(r) - (\hbar^2 \beta^2 / 6m) \\ &\quad \times [\nabla_r^2 u_a - (1/2)\beta(\partial u_a / \partial r)^2 \\ &\quad + 3(\partial u_a / \partial r)\delta(r - \sigma)], \end{aligned} \quad (5.7b)$$

$$\begin{aligned} U_{2,\text{rot}}^m(r\omega_1\omega_2) &= -(\hbar^2 \beta^2 / 12I) \\ &\quad \times \left[\sum_{i=1}^N \nabla_{\omega_i}^2 u_a - (1/2)\beta(\nabla_{\omega_i} u_a)^2 \right]. \end{aligned} \quad (5.8)$$

Here, ϕ_0 and ϕ_1 are given by eq. (4.12) and

$$(\partial / \partial r)[g_{HS}^0(r)] = \delta(r - \sigma) + (\lambda / \sigma),$$

where δ is the Dirac δ -function.

(B) Free particle basis function

When the pair potential is analytic, eq. (5.3) can be expanded in the form

$$\begin{aligned} g^0(r\omega_1\omega_2) &= \exp[-\beta u(r\omega_1\omega_2)] \left[1 - \{(\hbar^2 \beta^2 / 6m) \right. \\ &\quad \times [\nabla_r^2 u - (1/2)\beta(\nabla_r u)^2] + (\hbar^2 \beta^2 / 12I) \\ &\quad \times \left. \sum_{i=1}^2 \left[\left(\nabla_{\omega_i}^2 u - (1/2)\beta(\nabla_{\omega_i} u)^2 \right) \right] + O(\hbar^2) \right]. \end{aligned} \quad (5.9)$$

This equation can be expressed in an alternative form as

$$\begin{aligned} g^0(r\omega_1\omega_2) &= \exp[-\beta u(r\omega_1\omega_2)] \left[1 - \{(\hbar^2 \beta^2 / 12m) \right. \\ &\quad \times \nabla_r^2 u + (\hbar^2 \beta^2 / 12I)\nabla_{\omega_i}^2 u \} \\ &\quad + \left[(\hbar^2 \beta^2 / 12m)\nabla_r^2 + (\hbar^2 \beta^2 / 12I)\nabla_{\omega_i}^2 \right] \\ &\quad \times \exp[-\beta u(r\omega_1\omega_2)]. \end{aligned} \quad (5.10)$$

Eqs. (5.4) and (5.9) are valid for polar as well as non-polar fluids.

5.2. Pair distribution function for dense fluids :

In order to obtain a simple expression for the first order quantum correction to the PDF, eq. (4.24) of the Slater sum for the linear molecular fluid can be expressed in the form

$$\begin{aligned} W_N &= \exp[-\beta \Phi] \left[1 - \left\{ (\beta^2 \hbar^2 / 24m) \sum_i \nabla_i^2 \Phi \right. \right. \\ &\quad \left. \left. + (\beta^2 \hbar^2 / 24I) \sum_i \nabla_{\omega_i}^2 \Phi \right\} \right] + \left\{ (\beta \hbar^2 / 24m) \sum_i (\nabla_i^2 \right. \\ &\quad \left. + (\beta \hbar^2 / 24I) \sum_i \nabla_{\omega_i}^2) \right\} \exp[-\beta \Phi]. \end{aligned} \quad (5.11)$$

Substituting eq. (5.11) in eq. (3.25), we get

$$\begin{aligned} g(x_1, x_2) &= g^c(x_1, x_2) + (\beta \hbar^2 / m) g_{\text{tr}}^l(x_1, x_2) \\ &\quad + (\beta \hbar^2 / I) g_{\text{rot}}^l(x_1, x_2), \end{aligned} \quad (5.12)$$

where $g^c(x_1, x_2)$ is the PDF of the classical molecular fluid, $g_{\text{tr}}^l(x_1, x_2)$ and $g_{\text{rot}}^l(x_1, x_2)$ are the first order quantum corrections to the PDF due to the translation and

rotational contribution, respectively. They are expressed as

$$\begin{aligned}
 g_x^l(x_1, x_2) = & (1/12) \left[-\beta \nabla_{\alpha_i}^2 u(x_1, x_2) + \nabla_{\alpha_i}^2 \right] g^c(x_1, x_2) \\
 & - (\beta \rho / 6) \int \left\langle g^c(x_1 x_2 x_3) \nabla_{\alpha_i}^2 u(x_1 x_3) \right\rangle_{\omega_1} dr_3 \\
 & - (\beta \rho^2 / 24) \int \left\langle g^c(x_1, \dots, x_4) - g^c(x_1, x_2) \right. \\
 & \times \left. g^c(x_3 x_4) \right\rangle_{\omega_1, \omega_4} \nabla_{\alpha_i}^2 u(x_3 x_4) dr_3 dr_4 \\
 & + (K^c / 24) (\partial / \partial \rho) \left[\rho^2 g^c(x_1, x_2) \right] \\
 & \times \int \left\langle (\partial / \partial \rho) \left[g^c(x_3 x_4) \right] \nabla_{\alpha_i}^2 u(x_3 x_4) \right\rangle_{\omega_1, \omega_4} dr_4, \quad (5.13)
 \end{aligned}$$

$$\text{where } K^c = (1/\rho) (\partial \rho / \partial P^c)_\beta. \quad (5.14)$$

Here, K^c and $g^c(x_1, \dots, x_1)$ are, respectively, the isothermal compressibility and 1-particle distribution function of the classical system. In eq. (5.13), 'x' stands for 'tr' and 'rot' and α_i represents r_i and ω_i , which are associated with the translational and rotational contribution, respectively. This equation contains classical distribution functions only up to four molecule one.

There have been no calculation of the effect of quantum corrections in the PDF of molecular fluids.

5.3 Thermodynamic properties of molecular fluids :

When quantum corrections are small, as is expected for most fluids except He and H₂ (which one can see from Table 1), the quantum effects on the thermodynamic properties can be treated as a correction in powers of \hbar (for non-analytic potentials) or in powers of \hbar^2 (for analytic potentials).

(A) Non-analytic potential

Substituting eq. (4.19) in eq. (3.14) and integrating by parts, we obtain an expression for the free energy of the molecular fluid of linear molecules

$$\beta A / N = (\beta A^c / N) + A_1 + A_2 + \dots, \quad (5.15)$$

$$\text{where } A_1 = -(1/2) \rho \int dr_2 U_{HS}^m(r_{12}) \langle g^c(x_1 x_2) \rangle_{\omega_1, \omega_2}, \quad (5.16)$$

$$A_2 = A_2^{\text{tr}} + A_2^{\text{rot}} - (\hbar^2 \beta / 6 I) \quad (5.17)$$

with

$$\begin{aligned}
 A_2^{\text{tr}} = & -(1/2) \rho \int dr_2 \left\langle g^c(x_1 x_2) U_{2,\text{tr}}^m(x_1 x_2) \right\rangle_{\omega_1, \omega_2} \\
 & - (1/6) \rho^2 \int dr_2 dr_3 \left\langle g^c(x_1 x_2 x_3) U_{3,\text{tr}}^m(x_1 x_2 x_3) \right\rangle_{\omega_1, \omega_2, \omega_3} \\
 & - (1/8) \rho^3 \int dr_2 dr_3 dr_4 \left\langle \left[g^c(x_1 x_2 x_3 x_4) \right. \right. \\
 & \left. \left. - g^c(x_1 x_2) g^c(x_3 x_4) \right] \right\rangle_{\omega_1, \dots, \omega_4} U_{HS}^m(r_{12}) U_{HS}^m(r_{34}) \quad (5.18)
 \end{aligned}$$

$$\text{and } A_2^{\text{rot}} = -(1/2) \rho \int dr_2 \left\langle g^c(x_1 x_2) U_{2,\text{rot}}^m(x_1 x_2) \right\rangle_{\omega_1, \omega_2} \quad (5.19)$$

where

$$U_{2,\text{tr}}^m(x_1 x_2) = U_{HS}^m(r_{12}) + [1 + U_{HS}^m(r_{12})] U_a^{\text{tr}}(x_1 x_2), \quad (5.20a)$$

$$\begin{aligned}
 U_{3,\text{tr}}^m(x_1 x_2 x_3) = & U_{HS}^m(r_1, r_2, r_3) + [1 + U_{HS}^m(r_1, r_2, r_3)] \\
 & \times U_a^{\text{tr}}(x_1 x_2 x_3) \quad (5.20b)
 \end{aligned}$$

$$\text{and } U_{2,\text{rot}}^m(x_1 x_2) = U_a^{\text{rot}}(x_1 x_2). \quad (5.20c)$$

Here, U_a^{tr} and U_a^{rot} are the 'modified' Ursell functions due to the translational and rotational contributions of the angle-dependent potential u_a , respectively. They are given by

$$\begin{aligned}
 U_a^{\text{tr}}(x_1 x_2) = & (\hbar^2 \beta^2 / 2m) \left[\nabla_{r_2}^2 u_a(x_1 x_2) \right. \\
 & \left. - (5/4) \beta (\partial u_a(x_1 x_2) / \partial r_{12})^2 \right] + 0(\hbar^4), \quad (5.21a)
 \end{aligned}$$

$$\begin{aligned}
 U_a^{\text{tr}}(x_1 x_2 x_3) = & -(\hbar^2 \beta^3 / 12m) \left[\nabla_{r_1} u_a(x_1 x_2) \cdot \nabla_{r_1} u_a(x_1 x_3) \right. \\
 & + \nabla_{r_1} u_a(x_1 x_3) \cdot \nabla_{r_2} u_a(x_1 x_2) \cdot \nabla_{r_2} u_a(x_2 x_3) \\
 & \left. + \nabla_{r_1} u_a(x_1 x_3) \cdot \nabla_{r_1} u_a(x_2 x_3) \right] + 0(\hbar^4) \quad (5.21b)
 \end{aligned}$$

$$\begin{aligned}
 \text{and } U_a^{\text{rot}}(x_1 x_2) = & (\hbar^2 \beta^2 / 24 I) \left[\nabla_{\omega_1}^2 u_a(x_1 x_2) \right. \\
 & \left. + \nabla_{\omega_2}^2 u_a(x_1 x_2) \right] + 0(\hbar^4). \quad (5.21c)
 \end{aligned}$$

Here, A^c and $g^c(x_1 \dots x_1)$ are, respectively, the free energy and the 1-particle distribution function for a classical molecular fluid and ρ is the number density. Here $\langle (\dots) \rangle_{\omega_1, \dots, \omega_1}$ is defined as

$$\langle (\dots) \rangle_{\omega_1, \dots, \omega_1} = (\Omega)^{-1} \int (\dots) d\omega_1 \dots d\omega_1. \quad (5.22)$$

It is clear from the above discussion 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 of eq. (5.17) arise from the translational and rotational potential energy effects, respectively, and the last term arises from the rotational kinetic energy.

Eq. (5.15) is given by Singh *et al* [24] and valid for non-analytic potential with a hard-core.

(B) Analytic potential

For analytic potential, using eq. (4.24) in eq. (3.14), we obtain an expression for the free energy of the molecular fluid, correct to the first order of \hbar^2 [16]

$$\begin{aligned}
 \beta A / N = & (\beta A^c / N) + (\beta \hbar^2 / m) (A_{\text{tr}}^l / N) \\
 & + (\beta \hbar^2 / I_a) (A_{\text{rot}}^l / N) - \nabla^l A_{\text{rot}} + 0(\hbar^4), \quad (5.23)
 \end{aligned}$$

$$\begin{aligned} \text{where } \Delta^l A_{\text{rot}} &= \beta\hbar^2/6I \quad \text{for a linear molecule,} \\ &= \beta\hbar^2/8I \quad \text{for a spherical top molecule,} \\ &= \beta\hbar^2/8I_1 \left((4/3) - (1/3)(I_1/I_3) \right) \quad (5.24) \\ &\quad \text{for a symmetric top molecule} \end{aligned}$$

and $I_\alpha = I$ for linear and spherical top molecules while $I_\alpha = I_1$ for a symmetric top molecule. In eq. (5.23), A_{tr}^l and A_{rot}^l are the first order quantum correction to the free energy due to translational and rotational contributions, respectively. They are given by

$$A_{\text{tr}}^l/N = (\rho\beta/24) \int \left\langle g^c(r\omega_1\omega_2) \times \nabla_r^2 u(r, \omega_1\omega_2) \right\rangle_{\omega_1\omega_2} dr, \quad (5.25)$$

$$A_{\text{rot}}^l/N = (\rho\beta/24) \int \left\langle g^c(r\omega_1\omega_2) \times \nabla_{\omega_1}^2 u(r\omega_1\omega_2) \right\rangle_{\omega_1\omega_2} dr, \quad (5.26)$$

where $r = r_1 - r_2$. Here A^c and $g^c(r\omega_1\omega_2)$ are, respectively, the free energy and PDF for the classical molecular fluid.

Eq. (5.23) is the usual expression for the Helmholtz free energy for the semiclassical molecular fluids. It is given by Dey and Sinha [26]. Singh and Sinha [27,28] have derived similar expression for linear molecules. Powles and Rickayzen [29] gave an alternative expression for the Helmholtz free energy in terms of $\langle F^2 \rangle$ and $\langle \tau^2 \rangle$, where $\langle F^2 \rangle$ and $\langle \tau^2 \rangle$ are the classical mean square force and mean square torque of a molecule. For example, an expression for the Helmholtz free energy for the molecular fluid of linear and spherical top molecules is given by

$$\begin{aligned} \beta A/N &= \beta A^c/N + (\hbar^2/24)(kT)^3 \\ &\times \left[(\langle F^2 \rangle/m) - (\langle \tau^2 \rangle/I) \right] \\ &- \nabla^l A_{\text{rot}} + O(\hbar^4), \quad (5.27) \end{aligned}$$

where $\nabla^l A_{\text{rot}}$ is given by eq. (5.24). On comparison, we find that

$$\langle F^2 \rangle = kT\rho \int \left\langle g^c(r\omega_1\omega_2) \nabla_r^2 u(r, \omega_1\omega_2) \right\rangle_{\omega_1\omega_2} dr, \quad (5.28)$$

$$\langle \tau^2 \rangle = kT\rho \int \left\langle g^c(r\omega_1\omega_2) \nabla_{\omega_1}^2 u(r, \omega_1\omega_2) \right\rangle_{\omega_1\omega_2} dr. \quad (5.29)$$

Other thermodynamic properties can be obtained from eq. (5.23) (or eq. (5.27)). Thus, the expression for pressure is

$$\beta P/\rho = \beta P^c/\rho + (\beta\hbar^2/m)(P_{\text{tr}}^l) + (\beta\hbar^2/I_\alpha)(P_{\text{rot}}^l), \quad (5.30)$$

$$\begin{aligned} \text{where } P_{\text{tr}}^l &= (\beta\rho/24)(\partial/\partial\rho)\rho \int \left\langle g^c(r\omega_1\omega_2) \right. \\ &\times \nabla_r^2 u(r, \omega_1\omega_2) \left. \right\rangle_{\omega_1\omega_2} dr, \quad (5.31) \end{aligned}$$

$$\begin{aligned} P_{\text{rot}}^l &= (\rho\beta/24)(\partial/\partial\rho)\rho \int \left\langle g^c(r\omega_1\omega_2) \right. \\ &\times \nabla_{\omega_1}^2 u(r, \omega_1\omega_2) \left. \right\rangle_{\omega_1\omega_2} dr. \quad (5.32) \end{aligned}$$

Since the quantum corrections are small, it is sufficient to use an expansion of the free energy in powers of \hbar . This method was introduced by Wigner [30] and Kirkwood [31] for atomic fluid. Exchange corrections are exponentially vanishing [32] due to the repulsive core interactions for atoms and molecules. Eqs. (5.23) and (5.30) are for rigid molecules.

6. Virial equation of state for dilute molecular fluids

In the low density limit, the equation of state can be expressed in the virial form

$$\beta P/\rho = A + (B/V) + (C/V^2) + \dots, \quad (6.1)$$

where $A = 1$, B and C are the second and third virial coefficient, respectively.

In this section, we obtain expressions for virial coefficients. In general $g^c(x_1, x_2)$ may be expanded in powers of ρ [33]

$$\begin{aligned} g^c(x_1, x_2) &= \exp[-\beta u(x_1, x_2)] \\ &\times \left| 1 + \sum_{n=1} \rho^n a_n^c(x_1, x_2) \right| \quad (6.2) \end{aligned}$$

where the coefficient $a_n^c(x_1, x_2)$ is the cluster integral of the classical molecular fluid, involving n field point and two base points. For example

$$a_1^c(x_1, x_2) = \int \left\langle f^c(x_1, x_3) f^c(x_2, x_3) \right\rangle_{\omega_3} dr_3, \quad (6.3)$$

$$\text{where } f^c(x_i, x_j) = \exp[-\beta u(x_i, x_j)] - 1 \quad (6.4)$$

is the Mayer function.

6.1. Analytic potentials :

When eq. (6.2) is substituted in eq. (5.30), we obtain expressions of B and C for molecular fluid of linear molecules as

$$B = B^c + (\beta\hbar^2/m)(B_{\text{tr}}^l) + (\beta\hbar^2/I)(B_{\text{rot}}^l), \quad (6.5)$$

$$C = C^c + (\beta\hbar^2/m)(C_{\text{tr}}^l) + (\beta\hbar^2/I)(C_{\text{rot}}^l), \quad (6.6)$$

where B^c and C^c are the classical second and third virial coefficients, B_{tr}^l , B_{rot}^l and C_{tr}^l , C_{rot}^l are the first order quantum corrections due to the translational and rotational contributions to the second and third virial coefficients. They are given as

$$B^c = -(1/2)N \int \left\langle f^c(x_1, x_3) \right\rangle_{\omega_1\omega_3} dr_3, \quad (6.7a)$$

$$\begin{aligned} (B_{\text{tr}}^l) &= (\beta/24)N \int \left\langle \exp[-\beta u(x_1, x_2)] \right. \\ &\times \nabla_r^2 u(x_1, x_2) \left. \right\rangle_{\omega_1\omega_2} dr_2, \quad (6.7b) \end{aligned}$$

$$\begin{aligned} (B_{\text{rot}}^l) &= (\beta/24)N \int \left\langle \exp[-\beta u(x_1, x_2)] \right. \\ &\times \nabla_{\omega_1}^2 u(x_1, x_2) \left. \right\rangle_{\omega_1\omega_2} dr_2. \quad (6.7c) \end{aligned}$$

$$C^c = -(1/3)N^2 \int \langle f^c(x_1, x_2) f^c(x_1, x_3) \times f^c(x_2, x_3) \rangle_{\omega_1 \omega_2 \omega_3} d\mathbf{r}_2 d\mathbf{r}_3, \quad (6.8a)$$

$$(C_{tr}^I) = (\beta/12)N^2 \int \langle \exp[-\beta u(x_1, x_2)] a_1^c(x_1, x_2) \times \nabla_{\mathbf{r}}^2 u(x_1, x_2) \rangle_{\omega_1 \omega_2} d\mathbf{r}_2, \quad (6.8b)$$

$$(C_{rot}^I) = (\beta/12)N^2 \int \langle \exp[-\beta u(x_1, x_2)] a_1^c(x_1, x_2) \times \nabla_{\omega_i}^2 u(x_1, x_2) \rangle_{\omega_1 \omega_2} d\mathbf{r}_2. \quad (6.8c)$$

These equations are valid for both polar and non-polar potentials. Wang Chang [34] obtained an expression for the quantum corrections to the second virial coefficient of molecular fluid. Calculations of B^c and C^c have been reviewed by Hirschfelder *et al* [15], Rowlinson [35], Kihara [36], Mason and Spurling [37], Dymond and Smith [38] and Barker and Henderson [39].

6.1.1 Second virial coefficient

Using eq. (2.5) in eq. (6.4), we get

$$f^c(x_1, x_0) = f_0^c(r_{12}) + \exp[-\beta u_0(r_{12})] \times \sum_{n=1}^{\infty} (-\beta u_n(x_1, x_2))^n. \quad (6.9)$$

Substituting eq. (6.9) in eq. (6.5) and using the reduced quantities $r^* = r/\sigma$, $T^* = kT/\epsilon$, $u^* = u/\epsilon$ and $B^* = B/b_0$, where $b_0 = 2\pi N\sigma^3/3$, we can write the reduced second virial coefficient B^* of the semiclassical molecular fluid in terms of the reduced quantum parameters A^* and δ^*

$$B = B^* + (A^*)^2 (B_{tr}^I)^* + (\delta^*)^2 (B_{rot}^I)^* \\ = B^* + (A^*)^2 (B^I)^* \quad (6.10)$$

with

$$(B^I)^* = (B_{tr}^I)^* + (I^*)^{-1} (B_{rot}^I)^*, \quad (6.11)$$

$$\text{where } (B_{tr}^I)^* = (16\pi^2 T^{*2})^{-1} \int_0^{\infty} \exp[-u_0^*(r^*)/T^*] \\ \times \langle [1 - (1/T^*) u_a^*(r^* \omega_1 \omega_2) + \dots] \\ \times \nabla_{\mathbf{r}}^2 u^*(r^* \omega_1 \omega_2) \rangle_{\omega_1 \omega_2} r^{*2} dr^*, \quad (6.12)$$

$$(B_{rot}^I)^* = (16\pi^2 T^{*2})^{-1} \int_0^{\infty} \exp[-u_0^*(r^*)/T^*] \\ \times \langle [1 - (1/T^*) u_a^*(r^* \omega_1 \omega_2) + \dots] \\ \times \nabla_{\omega_i}^2 u^*(r^* \omega_1 \omega_2) \rangle_{\omega_1 \omega_2} r^{*2} dr^* \quad (6.13)$$

and $I^* = I/m\sigma^2$. Here B^c is the second virial coefficient of the classical molecular fluid. When eq. (2.6) is used, B^c is given by

$$B^c = B^c(\text{LJ}) + [B_1^c]^* + [B_2^c]^* + [B_3^c]^*, \quad (6.14)$$

$$\text{where } B^c(\text{LJ}) = -3 \int_0^{\infty} dr^* r^{*2} g_0^{\text{LJ}}(r^*) \quad (6.15)$$

$$[B_1^c]^* = (3/T^*) \int_0^{\infty} dr^* r^{*2} g_0^{\text{LJ}}(r^*) \\ \times \langle u_a^*(r^* \omega_1 \omega_2) \rangle_{\omega_1 \omega_2}, \quad (6.16)$$

$$[B_2^c]^* = -(3/2T^{*2}) \int_0^{\infty} dr^* r^{*2} g_0^{\text{LJ}}(r^*) \\ \times \langle u_a^*(r^* \omega_1 \omega_2) \rangle_{\omega_1 \omega_2}^2, \quad (6.17)$$

$$[B_3^c]^* = -(1/2T^{*3}) \int_0^{\infty} dr^* r^{*2} g_0^{\text{LJ}}(r^*) \\ \times \langle u_a^*(r^* \omega_1 \omega_2) \rangle_{\omega_1 \omega_2}^3 \quad (6.18)$$

Here, $g_0^{\text{LJ}}(r^*) = \exp[-\beta u_{\text{LJ}}(r^*)]$. $B^c(\text{LJ})$ is the reduced second virial coefficient of classical LJ(12-6) fluid and $[B_n^c]^*$ is the n -th order perturbation term due to the angle-dependent interaction potential u_a . The angle integral involved in eqs. (6.16)–(6.18) have been evaluated analytically [40], when eq. (2.6) is used.

The contribution to the second virial coefficient beyond $[B_3^c]^*$ is calculated using the Pade' approximant [41]

$$B^c = B^c(\text{LJ}) + [B_1^c]^* + [B_2^c]^* / (1 - [B_3^c]^* / [B_2^c]^*) \quad (6.19)$$

In eq. (6.19), the term $[B_1^c]^*$ is the contribution due to the potential u_{in} only, while the term $[B_2^c]^*$ is the contribution due to the potential u_{perm} only. The term $[B_3^c]^*$ vanishes for dipole-dipole (dd) potential, so that eq. (6.19) reduces to the second order series for this case. However, $[B_3^c]^*$ contributes for quadrupolar gas.

Substituting eq. (2.6) in eqs. (6.12) and (6.13), the first order quantum correction to the second virial coefficient due to the translational and rotational contributions are given by Singh and Datta [5] and Singh *et al* [24]. Singh and Datta considered the quadrupole-quadrupole (QQ) potential.

We first consider B^* for dipolar fluid, where u_0 is the LJ(12-6) and u_a is the dipole-dipole (dd) interaction. From eq. (6.11), it is clear that the first order quantum correction to the second virial coefficient is the sum of the translational and rotational parts. Singh *et al* [24] have calculated the quantum corrections for $I^* = 0.001$ and 0.007. The values of $(B_{rot}^I)^*/I^*(B_{tr}^I)^*$ are shown in Table 3. When $I^* = 0.001$, the rotational quantum correction dominates, while for $I^* = 0.07$, the translational quantum correction is dominating. Further, the quantum correction increases with increase of μ^{*2} .

Table 2. Values of $(B_{\text{rot}}^l)^* / I^* (B_{\text{tr}}^l)^*$ for the dipolar fluid (Taken from Ref [24])

| T^* | | $I^* = 0.001$ | $I^* = 0.07$ |
|-------|-----|---------------|--------------|
| 1.0 | 1.0 | 14.56 | 0.21 |
| | 2.0 | 40.25 | 0.57 |
| | 3.0 | 59.79 | 0.85 |
| 3.0 | 1.0 | 11.10 | 0.06 |
| | 2.0 | 14.72 | 0.21 |
| | 3.0 | 28.23 | 0.40 |
| 5.0 | 1.0 | 1.68 | 0.02 |
| | 2.0 | 6.50 | 0.09 |
| | 3.0 | 13.36 | 0.19 |

Earlier, eqs. (6.7b) and (6.7c) are employed for estimating the $O(\hbar)$ quantum correction to the second virial coefficient for H_2 and HCl [34,42]. However, these calculations are based on the intermolecular potential models :

$$\text{H}_2 : u(r\omega_1\omega_2) = -(a/r^6) + (b/r^{12}) + (c/r^{12})(\cos^2\theta_1 + \cos^2\theta_2), \quad (6.20)$$

$$\text{HCl} : u(r\omega_1\omega_2) = \sum_{\alpha,\beta} u_{\alpha\beta}^{\text{LJ}}(r_{\alpha\beta}) + u_{\mu\mu} + u_{\mu Q} + u_{QQ}, \quad (6.21)$$

where a, b, c , are adjustable constants [15], $u_{\alpha\beta}^{\text{LJ}}$ is the site-site LJ(12-6) potential for a two-site model, and $u_{\mu\mu}, u_{\mu Q}$ and u_{QQ} are the dipole-dipole, dipole-quadrupole and quadrupole-quadrupole terms. The results are reported in Table 4 for H_2 [15] and HCl [42]. Recently Singh *et al* [24] have used eqs. (2.4) and (2.6) in eqs. (6.12) and (6.13) to estimate the influence of quantum effects on the second virial coefficient of H_2 and HCl whose force and quantum parameters are given in Tables 1 and 2. These calculated results are also shown in Table 4 and compared with the experimental data [38]. For H_2 , the agreement is found to be excellent.

Table 4. The second virial coefficient $B = (2\pi N\sigma^3/3)B^*$ (in unit of $\text{cm}^3\text{-mol}^{-1}$) for H_2 and HCl gases.

| Gas | $T(\text{k})$ | $B^*[24]$ | $B_{\text{Th}}[24]$ | $B_{\text{Th}}[15,42]$ | $B_{\text{Exp}}[39]$ |
|--------------|---------------|-----------|---------------------|------------------------|----------------------|
| H_2 | 123 | -2.77 | 2.94 | 2.17 | 2.56 |
| | 173 | 5.63 | 8.70 | 8.72 | 9.16 |
| | 223 | 9.58 | 11.60 | 11.53 | 12.10 |
| | 323 | 13.30 | 14.48 | 14.43 | 15.17 |
| | 423 | 14.92 | 15.72 | 15.94 | 15.71 |
| HCl | 190 | -719.62 | -700.60 | -452.60 | -456.00 |
| | 250 | -385.76 | -280.94 | -226.90 | -221.00 |
| | 330 | -220.24 | -218.39 | -121.90 | -216.00 |

When compared with the classical values, the quantum effects are appreciable even at high temperature ($T = 423 \text{ K}$) and large below 300 K . The second order quantum correction is appreciable at lower temperature [15]. Thus for H_2 ,

$O(\hbar^2)$ expansion breaks down at lower temperature (*i.e.* below $T = 123 \text{ K}$). For very low temperature, full quantum calculation may be used. In case of HCl , the results obtained by Murad [42] are relatively better. This is probably due to the potential model taken in the calculation. In this case the quantum effects are small but not negligible. From Table 5, it is seen that for H_2 the translational quantum correction is dominant one, whereas for HCl , the rotational quantum correction dominates.

Table 5. Quantum corrections to the second virial coefficient for H_2 and HCl gases (Taken from Ref. [24]).

| Gas | $T(\text{k})$ | $(B_{\text{tr}}^l)^*$ | $(B_{\text{rot}}^l)^*$ | $\frac{(B_{\text{rot}}^l)^*}{(B_{\text{tr}}^l)^*}$ |
|--------------|---------------|-----------------------|------------------------|--|
| H_2 | 123 | 0.04200 | 0.00030 | 0.435 |
| | 173 | 0.02539 | 0.00012 | 0.288 |
| | 223 | 0.01782 | 0.00006 | 0.205 |
| | 323 | 0.01088 | 0.00003 | 0.168 |
| | 423 | 0.00771 | 0.00001 | 0.019 |
| HCl | 190 | 2.23878 | 0.08016 | 5.681 |
| | 250 | 0.98422 | 0.02601 | 4.193 |
| | 330 | 0.47972 | 0.00930 | 3.076 |

Similar results are given for other molecules by Singh and Dutta [5], McCarty and Babu [43]. Pompe and Spurling [44] and Macrury and Steele [45].

6.1.2. Third virial coefficient

Substituting eq. (6.9) in eq. (6.6), the reduced third virial coefficient $C^* = C/b_0^2$ of the semiclassical molecular fluid, correct to the first order quantum correction, is written as

$$C^* = C^c + (\Lambda^*)^2 (C_{\text{tr}}^l)^* + \delta^{*2} (C_{\text{rot}}^l)^*, \quad (6.22)$$

where

$$(C_{\text{tr}}^l)^* = (3/16\pi^3 T^{*2}) \int_0^\infty \exp[-u_0^*(r^*)/T^*] a_{\text{LJ}}^c(r^*) \times \left\langle [1 - (1/T^*) u_a^*(r^*\omega_1\omega_2)] \nabla_r^2 u^*(r^*\omega_1\omega_2) \right\rangle_{\omega_1\omega_2} \times r^{*2} dr^*, \quad (6.23)$$

$$(C_{\text{rot}}^l)^* = (3/16\pi^3 T^{*2}) \int_0^\infty \exp[-u_0^*(r^*)/T^*] a_{\text{LJ}}^c(r^*) \times \left\langle [1 - (1/T^*) u_a^*(r^*\omega_1\omega_2)] \nabla_{\omega}^2 u^*(r^*\omega_1\omega_2) \right\rangle_{\omega_1\omega_2} \times r^{*2} dr^*. \quad (6.24)$$

Here, $a_{\text{LJ}}^c(r^*)$ is the value of a_{LJ}^c for the LJ(12-6) fluid, and C^c is the reduced third virial coefficient of the classical molecular fluid. Using eq. (2.6) in eq. (6.8a) C^c is given by

$$C^c = C^c(\text{LJ}) + [C_1^c]^* + [C_2^c]^* + [C_3^c]^*, \quad (6.25)$$

where C^c (LJ) is the reduced third virial coefficient of the classical LJ(12-6) fluid and $[C_n^c]^*$ is the n -th order perturbation term due to the angle-dependent potential. The contribution to the third virial coefficient of the permanent interactions beyond $[C_3^c$ (perm)] is calculated using the Pade approximant [41].

Substituting eq. (2.6) in eqs. (6.23) and (6.24), the first order quantum correction to the third virial coefficient due to the translational and rotational contribution can be obtained.

However, no calculation has been made to estimate the quantum corrections to the third virial coefficient of the molecular fluids. Earlier, Singh and Singh [46] calculated the third virial coefficient of classical molecular fluids in the presence of three body non-additive interaction potential.

6.2 Hard-core plus attractive tail potential :

We consider the virial coefficient for a molecular fluid of hard sphere plus angle dependent potential. In this case, the pair potential is given by

$$u(r\omega_1\omega_2) = u_{HS}(r) + u_a(r\omega_1\omega_2), \quad (6.26)$$

where $u_{HS}(r)$ is the hard sphere potential and $u_a(r\omega_1\omega_2)$ is the angle-dependent potential, which is regarded as a perturbation of the hard sphere potential.

Substituting eq. (6.2) in eq. (5.15) and using eq. (3.18), we obtain expressions of B and C for molecular fluid of hard-core molecules.

$$B = B^c + B^{qc}, \quad (6.27)$$

$$C = C^c + C^{qc}, \quad (6.28)$$

where B^c and C^c are the classical values of B and C , respectively and given by eqs. (6.7a) and (6.8a), B^{qc} and C^{qc} are the quantum correction values, which are expressed as

$$B^{qc} = -(1/2)N \int \langle \exp[-\beta u(x_1, x_2)] \times U_{2, tr}^m(x_1, x_2) \rangle_{\omega_1\omega_2} dr_2, \quad (6.29)$$

$$C^{qc} = -N^2 \int \langle \exp[-\beta u(x_1, x_2)] a_1^c(x_1, x_2) \times U_{2, tr}^m(x_1, x_2) \rangle_{\omega_1\omega_2} dr_2 - N^2 \int \langle \exp[-\beta \{u(x_1, x_2) + u(x_2, x_3) + u(x_1, x_3)\}] \times U_{3, tr}^m(x_1, x_2, x_3) \rangle_{\omega_1\omega_2\omega_3} dr_2 dr_3, \quad (6.30)$$

$$\text{where } U_1^m = U_{1, tr}^m + U_{1, rot}^m. \quad (6.31)$$

Singh *et al* [24] have evaluated the quantum corrections to the second virial coefficient for the hard sphere dipolar

fluid. Using eq. (6.9) in eq. (6.7a), one can evaluate B^c . The contribution of the perturbation terms with odd powers of u_{dd} are zero. The result is written as [47]

$$B^c = B_{HS}^c \left[1 - (1/3)(\mu^{*2})^2 - (1/75)(\mu^{*2})^4 - (29/55125)(\mu^{*2})^6 - \dots \right], \quad (6.32)$$

where $\mu^{*2} = \mu^2/kT\sigma^3$ and $B_{HS}^c = 2\pi N\sigma^3/3$ is the second virial coefficient for the classical hard sphere fluid. This is monotonically decreasing function of μ^{*2} .

We can employ the Pade' approximant [41] using the third and fourth terms of the series to obtain the results for B^c . Thus,

$$B^c = B_{HS}^c \left[1 - (1/3)(\mu^{*2})^2 - (1/75)(\mu^{*2})^4 \times \left(1 - (29/735)(\mu^{*2})^2 \right)^{-1} \right]. \quad (6.33)$$

Using eq. (6.31), eq. (6.29) can be written as

$$B^{qc} = (B^{qc})_{tr} + (B^{qc})_{rot}, \quad (6.34)$$

$$\text{where } (B^{qc})_{tr} = -2\pi N \int_0^\infty \langle \exp[-\beta u(r\omega_1\omega_2)] \times U_{2, tr}^m(r\omega_1\omega_2) \rangle_{\omega_1\omega_2} r^2 dr, \quad (6.35)$$

$$(B^{qc})_{rot} = -2\pi N \int_0^\infty \langle \exp[-\beta u(r\omega_1\omega_2)] \times U_{2, rot}^m(r\omega_1\omega_2) \rangle_{\omega_1\omega_2} r^2 dr. \quad (6.36)$$

In order to evaluate eq. (6.35), we make use of a Taylor expansion of $u_{dd}(r\omega_1\omega_2)$ about σ , that is

$$u_{dd}(r\omega_1\omega_2) = u_{dd}(\sigma\omega_1\omega_2) + (r - \sigma)u'_{dd}(\sigma\omega_1\omega_2) + \dots \quad (6.37)$$

$u'_{dd}(\sigma\omega_1\omega_2) = [\partial u(r\omega_1\omega_2)/\partial r]_{r=\sigma}$. Substituting eqs. (5.6) and (6.37) in eq. (6.35), we obtain an expression for $(B^{qc})_{tr}$ for a hard sphere dipolar fluid [24]

$$(B^{qc})_{tr} = B_{HS}^c \left[(3/2\sqrt{2})(B^I)_{tr}(\lambda/\sigma) + (1/\pi)(B^{II})_{tr}(\lambda/\sigma)^2 + \dots \right], \quad (6.38)$$

$$\text{where } (B^I)_{tr} = 1 + (1/3)(\mu^{*2})^2 + (1/25)(\mu^{*2})^4 + (29/11025)(\mu^{*2})^6 + \dots, \quad (6.39a)$$

$$(B^{II})_{tr} = 1 - (1/60)(\mu^{*2})^2 - (17/550)(\mu^{*2})^4 - (29/11900)(\mu^{*2})^6 + \dots \quad (6.39b)$$

Similarly, substituting eq. (5.21c) in eq. (4.36), we get [24]

$$(B^{qc})_{rot} = B_{HS}^c \left[(3/\pi^*) (B^{II})_{rot}(\lambda/\sigma)^2 + \dots \right], \quad (6.40)$$

$$\text{where } (B^{II})_{\text{rot}} = (1/12) \left[(2/3)(\mu^{*2})^2 + (4/75)(\mu^{*2})^4 + (58/18375)(\mu^{*2})^6 + \dots \right]. \quad (6.41)$$

Finally, eq. (6.27) can be written in the form

$$B = B^t + B_{\text{fIS}}^t \left[(3/2\sqrt{2})B^l(\lambda/\sigma) + (1/\pi)B^{II}(\lambda/\sigma)^2 + \dots \right], \quad (6.42)$$

$$\text{where } B^l = (B^I)_{\text{tr}}, \quad (6.43a)$$

$$B^{II} = (B^{II})_{\text{tr}} + (I^*)^{-1}(B^{II})_{\text{rot}}. \quad (6.43b)$$

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 parts.

When $u_{\text{dd}} = 0$, we have

$$B^l = (B^I)_{\text{tr}} = 1, \quad (6.44a)$$

$$B^{II} = (B^{II})_{\text{tr}} = 1, \quad (6.44b)$$

which is correct for pure hard sphere fluid [3].

7. Thermodynamics of dense molecular fluids

Singh and Sinha [27,28] have calculated the first quantum correction to the thermodynamic properties of the molecular fluids of rigid linear molecules interacting via the pair potential of the type given by eq. (2.5). Dey and Sinha [26] have extended the theory for rigid non-linear molecule. Its extension to the fluid mixtures is straight forward [48]. However, it is not considered in this article. Clancy and Gubbins [49] have estimated the first quantum corrections for H_2 using a different approach.

Powles and Richayzen [29] obtained expression for the first order quantum correction in terms of $\langle F^2 \rangle$ and $\langle \tau^2 \rangle$. From eq. (5.27), the expression for the Helmholtz free energy for the rigid linear molecules can be written as

$$(A - A^c)/(N\hbar^2/24m\sigma^2) = (1/T^{*2}) \times [\langle F^{*2} \rangle + \langle \tau^{*2} \rangle / I^*] - 4/I^*, \quad (7.1)$$

where $F^{*2} = F^2/(\epsilon/\sigma)^2$, $\tau^{*2} = \tau^2/\epsilon^2$ and $I^* = I/m\sigma^2$.

Eq. (7.1) can be rewritten in the form

$$\beta f - \beta f^c = (A^*)^2 (f_{\text{tr}}^I)^* + (\delta^*)^2 (f_{\text{rot}}^I)^* - (\delta^*)^2 / (24\pi^2 T^*), \quad (7.2)$$

where $f^c = A^c/N$ is the free energy per particle of the classical molecular fluid, and $(f_{\text{tr}}^I)^*$ and $(f_{\text{rot}}^I)^*$ are the first order quantum correction to the free energy due to the translational and rotational contribution, respectively. They are given as

$$(f_{\text{tr}}^I)^* \equiv (A_{\text{tr}}^I)^* / N = (\rho^* / 96\pi^2 T^{*2}) \int \langle g^c(\mathbf{r}^* \omega_1 \omega_2) \times \nabla_{\omega_1}^2 u^*(\mathbf{r}^* \omega_1 \omega_2) \rangle_{\omega_1, \omega_2} d\mathbf{r}^*, \quad (7.3)$$

$$(f_{\text{rot}}^I)^* \equiv (A_{\text{rot}}^I)^* / N = (\rho^* / 96\pi^2 T^{*2}) \int \langle g^c(\mathbf{r}^* \omega_1 \omega_2) \times \nabla_{\omega_1}^2 u^*(\mathbf{r}^* \omega_1 \omega_2) \rangle_{\omega_1, \omega_2} d\mathbf{r}^*. \quad (7.4)$$

Here, $\rho^* = \rho\sigma^3$, $T^* = kT/\epsilon$ and $u^* = u/\epsilon$.

7.1. Classical molecular fluids :

In order to calculate the properties of classical molecular fluid, we employ the perturbation theory, where the central LJ(12-6) potential u_0 is treated as the reference and the angle dependent potential u_a as the perturbation.

Using the perturbation theory, the PDF $g^c(x_1, x_2)$ of the classical molecular fluid can be expanded as

$$g^c(x_1, x_2) = g_0^c(r_{12}) + g_1^c(x_1, x_2), \quad (7.5)$$

where $g_0^c(r_{12})$ is the PDF of the classical reference fluid and $g_1^c(x_1, x_2)$ is the first order correction to it. Thus [6]

$$g_1^c(x_1, x_2) = -\beta u_a(x_1, x_2) g_0^2(r_{12}) - \beta \rho \langle u_a(x_1, x_3) + u_a(x_2, x_3) \rangle_{\omega_3} g_0^c(r_1 r_2 r_3), \quad (7.6)$$

where $g_0^c(r_1, r_2, r_3)$ is the three body distribution function for the classical reference system. For multipole-like potential, $\langle u_a(x_1, x_3) \rangle_{\omega_3} = \langle u_a(x_2, x_3) \rangle_{\omega_3} = 0$ and eq. (7.5) can be simplified as [6]

$$g^c(x_1, x_2) = g_0^c(r_{12}) [1 - \beta u_a(x_1, x_2)]. \quad (7.7)$$

The corresponding perturbation expansion for the free energy per particle of the classical molecular fluid is given by

$$f^c = f_0^c + f_a^c, \quad (7.8)$$

where f_0^c is the free energy per particle of the classical LJ(12-6) reference fluid and f_a^c is the free energy per particle due to the angle dependent potential. Thus,

$$f_a^c = f_1^c + f_2^c + f_3^c, \quad (7.9)$$

where f_n^c is the n -th order perturbation correction to the free energy. When eq. (2.6) is used, we have the explicit expressions for f_n^c

$$f_1^c = f_1^c(\text{in}), \quad (7.10)$$

$$f_2^c = f_2^c(\text{perm}) + f_2^c(\text{anis-dis}) + f_2^c(\text{shape}) + f_2^c(\text{perm-dis}) + f_2^c(\text{dis-in}) + f_2^c(\text{shape-in}) + f_2^c(\text{shape-dis}) \quad (7.11)$$

$$f_3^c = f_3^c(\text{perm}) = f_{32}^c(\text{perm}) + f_{33}^c(\text{perm}) \quad (7.12)$$

where

$$\beta f_1^c(\text{in}) = -(2\pi\rho^* \alpha^* / T^*) [2\mu^{*2} I_6 + 3Q^{*2} I_8] \quad (7.13)$$

$$\beta f_2^c(\text{perm}) = -(2\pi/3)(\rho^* / T^{*2}) [(\mu^{*2}) I_6 + 3\mu^{*2} Q^{*2} I_8 + (21/5)(Q^{*2})^2 I_{10}] \quad (7.14a)$$

$$\beta f_2^i(\text{anis-dis}) = -(32\pi/5)(\rho^*/T^{*2}) K^2(1+1.9K^2)I_{12}, \quad (7.14b)$$

$$\beta f_2^i(\text{shape}) = -(128\pi/5)(\rho^*D^2/T^{*2})I_{24}, \quad (7.14c)$$

$$\beta f_2^i(\text{perm-dis}) = (288\pi/5)(\rho^*K^2Q^{*2}/T^{*2})I_{11}, \quad (7.14d)$$

$$\beta f_2^i(\text{dis-in}) = -(4\pi/5)(\rho^*\alpha^{*2}/T^{*2}) \times [\mu^{*2}(5-9K^2)I_{12} + (48/7)Q^{*2}K I_{14}], \quad (7.14e)$$

$$\beta f_2^i(\text{shape-in}) = (32\pi/5)(\rho^*\alpha^*D/T^{*2}) \times [\mu^{*2}I_{18} + (12/7)Q^{*2}I_{20}], \quad (7.14f)$$

$$\beta f_2^i(\text{shape-dis}) = (128\pi/5)(\rho^*KD/T^{*2})I_{18}, \quad (7.14g)$$

$$f_3^i(\text{perm}) = (8\pi/5)(\rho^*/T^{*3})[(\mu^{*2})^2 Q^{*2}I_{11} + \mu^*(Q^{*2})^2 I_{13} + (18/49)(Q^{*2})^3 I_{15}], \quad (7.15)$$

$$f_3^i(\text{perm}) = (4\pi^2/3)(\rho^{*2}/T^{*3})[(\mu^{*2})^3 L_{\mu\mu\mu} + 3(\mu^{*2})^2(3Q^{*2}/4)L_{\mu\mu Q} + 3(\mu^{*2})(3Q^{*2}/4)^2 L_{\mu Q Q} + (3Q^{*2}/4)^3 L_{Q Q Q}], \quad (7.16)$$

$$\text{where } I_n(\rho^*, T^*) = \int g_0^i(r^*)(r^*)^{-n+2} dr^*, \quad (7.17)$$

$$L_{mnp} = \iiint M_{mnp} g_0^i(r_{12}^*, r_{23}^*, r_{13}^*)(r_{12}^*)^{-n+1} \times (r_{23}^*)^{m+1} (r_{13}^*)^{-n+1} r_{12}^*, r_{23}^*, r_{13}^* \quad (7.18)$$

$$\text{with } M_{mnp} = (4\pi)^{-3} \int \Phi_n(\omega_1\omega_2)\Phi_m(\omega_2\omega_3) \times \Phi_p(\omega_1\omega_3) d\omega_1 d\omega_2 d\omega_3. \quad (7.19)$$

Here, Λ denotes integration over $r_{12}^* = r_{12}/\sigma$, $r_{23}^* = r_{23}/\sigma$ and $r_{13}^* = r_{13}/\sigma$ forming a triangle, and n, m, p denote μ and Q . In the above expressions, we have used the reduced variable defined as

$$\alpha^* = \alpha\sigma^3, \mu^{*2} = \mu^2/\epsilon\sigma^3 \text{ and } Q^{*2} = Q^2/\epsilon\sigma^5.$$

The contribution of the permanent moment interaction to the free energy beyond f_3^c (perm) is calculated using the Padé approximant [41]

$$\beta f_3^i(\text{perm}) = \beta f_2^i(\text{Perm}) \times [1 - \beta f_3^i(\text{perm})/\beta f_2^i(\text{perm})]^{-1}. \quad (7.20)$$

The integral I_n at density ρ^* and temperature T^* can be evaluated following the empirical equation of Ananth [50]

$$\ln I_n(\rho^*, T^*) = A_n \rho^{*2} \ln T^* + B_n \rho^{*2} + C_n \rho^* \ln T^* + D_n \rho^* + E_n \ln T^* + F_n \quad (7.21)$$

The coefficient $A_n - F_n$ appearing in eq. (7.21) are reported by Gray and Gubbins [51]. In order to evaluate eq. (7.18), we use the superposition approximation for $g_0^i(r_{12}^*, r_{23}^*, r_{13}^*)$ i.e. [52]

$$g_0^i(r_{12}^*, r_{23}^*, r_{13}^*) = g_0^i(r_{12}^*)g_0^i(r_{23}^*)g_0^i(r_{13}^*) \quad (7.22)$$

and replace LJ(12-6) $g_0^i(r_{ij}^*)$ by hard sphere $g_{\text{HS}}^i(r_{ij}^*)$ with properly chosen hard sphere diameter. The numerical integration of L in general is time consuming except for the $\mu-\mu-\mu$ and $Q-Q-Q$ interactions. Boublik [53] has obtained the values of L by Monte-Carlo (MC) integration, which is fitted to formula

$$L_{\mu\mu\mu} = 0.0236(1 + 2\eta + 2\eta^2)/K^{1.063}, \quad (7.23)$$

$$L_{QQQ} = 0.0155 \exp(4.3158\eta)/K^{2.63265}. \quad (7.24)$$

Theoretical developments for classical molecular fluids are given by Gubbins *et al* [54], Shing and Gubbins [55], Ananth *et al* [56], Shukla *et al* [57] and Watanabe *et al* [58]. Shukla *et al* have discussed the problem in presence of three-body interactions. The three-body interaction is not taken into consideration in the present article.

The thermodynamic properties of the classical LJ(12-6) system can be calculated using the Verlet-Weis (VW) [59] version of the Weeks-Chandler-Andersen (WCA) [60] perturbation theory. According to the WCA scheme, the free energy per particle of the reference system is given by

$$f_0^i = f_r^i + f_1^i, \quad (7.25)$$

where f_r^i is the free energy per particle of the classical reference system and f_1^i is the first order perturbation correction. Thus [59],

$$\beta f_r^i = \eta(4-3\eta)/(1-\eta)^2 + 12\delta\eta^2 \times (1+1.759\eta-5.249\eta^3)/(1-\mu)^3, \quad (7.26)$$

where $\eta = (\pi/6)\rho^*(d^*)^3$,

$$\rho^* = \rho\sigma^3, \quad (7.27)$$

$$d^* = d/\sigma.$$

Here, d is the diameter of a hard sphere and is given by [59]

$$d = d_H[1 + A\delta], \quad (7.28)$$

where

$$d_H = \sigma[1.068 + 0.3887T^*]/[1 + 0.4293T^*], \quad (7.29)$$

$$A = (1 - 4.25\eta_\omega + 1.363\eta_\omega^2 - 0.8751\eta_\omega^3)/(1 - \eta_\omega)^2, \quad (7.30)$$

$$\delta = [210.31 + 404.67T^*]^{-1}, \quad (7.31)$$

$$\eta_\omega = \eta - (1/16)\eta^2. \quad (7.32)$$

The second term of eq. (7.25) is given by

$$\beta f_1^i = 2\pi\rho \int_0^\infty w(r)g_{\text{HS}}^i(r)r^2 dr, \quad (7.33)$$

where $g_{\text{HS}}^i(r)$ is the PDF of the classical hard-sphere fluid of diameter d and $w(r)$ is defined as

$$w(r) = -\epsilon, \quad r < 2^{1/6}\sigma, \\ = u_0(r), \quad r > 2^{1/6}\sigma. \quad (7.34)$$

Using the standard relations, we can calculate the other thermodynamic properties from the free energy of the classical LJ(12-6) fluid.

7.2. Quantum corrections to thermodynamic properties :

Substituting eqs. (2.5), (2.6) and (7.7) in eq. (7.2), the first order quantum correction to the free energy per particle due to the translational contribution is given by

$$\begin{aligned} (f_{tr}^I)^* &= [f_{tr}^I(LJ)]^* + [f_{tr}^I(in)]^* + [f_{tr}^I(perm)]^* \\ &+ [f_{tr}^I(anis-dis)]^* + [f_{tr}^I(shape)]^* \\ &+ [f_{tr}^I(perm-dis)]^* + [f_{tr}^I(dis-in)]^* \\ &+ [f_{tr}^I(shape-in)]^* + [f_{tr}^I(shape-dis)]^*, \end{aligned} \quad (7.35)$$

where

$$[f_{tr}^I(LJ)]^* = (1/\pi)(\rho^*/T^{*2})[22I_{14} - 5I_8], \quad (7.36a)$$

$$\begin{aligned} [f_{tr}^I(in)]^* &= (1/\pi)(\rho^*\alpha^*/T^{*2}) \\ &\times [(\mu^{*2})(5/2)I_8 - (2/T^*)(22I_{20} - 5I_{14}) \\ &+ (Q^*)^2(7I_{10} - (3/T^*)(22I_{22} - 5I_{16}))], \end{aligned} \quad (7.36b)$$

$$\begin{aligned} [f_{tr}^I(perm)]^* &= -(1/6\pi)(\rho^*/T^{*3})[(\mu^*)^4 I_8 \\ &+ 6(\mu^*Q^*)^2 I_{10} + 14(Q^*)^4 I_{12}], \end{aligned} \quad (7.36c)$$

$$[f_{tr}^I(anis-dis)]^* = -(8/\pi)(\rho^*/T^{*3})K^2(1 + 1.9K^2)I_{14}, \quad (7.36d)$$

$$[f_{tr}^I(shape)]^* = -(704/5\pi)(\rho^*D^2/T^{*3})I_{26}, \quad (7.36e)$$

$$[f_{tr}^I(perm-dis)]^* = (12/\pi)(\rho^*KQ^2/T^{*3})I_{13}, \quad (7.36f)$$

$$\begin{aligned} [f_{tr}^I(dis-in)]^* &= -(4/5\pi)(\rho^*\alpha^*/T^{*3})[(1/4)\mu^{*2} \\ &\times (5 - 9K^2)I_{14} + (86/7)Q^{*2}KI_{16}], \end{aligned} \quad (7.36g)$$

$$\begin{aligned} [f_{tr}^I(shape-in)]^* &= (4/5\pi)(\rho^*\alpha^*D/T^{*3}) \\ &\times [27\mu^{*2}I_{20} + (376/7)Q^{*2}I_{22}], \end{aligned} \quad (7.36h)$$

$$[f_{tr}^I(shape-dis)]^* = (432/5\pi)(\rho^*KD/T^{*3})I_{20}. \quad (7.36i)$$

Similarly, the first order quantum correction to the free energy per particle due to the rotational contribution is given by

$$\begin{aligned} (f_{rot}^I)^* &= [f_{rot}^I(perm)]^* + [f_{rot}^I(in)]^* + [f_{rot}^I(anis-dis)]^* \\ &+ [f_{rot}^I(shape)]^* + [f_{rot}^I(perm-dis)]^* \\ &+ [f_{rot}^I(perm-shape)]^* + [f_{rot}^I(dis-in)]^* \\ &+ [f_{rot}^I(shape-in)]^* + [f_{rot}^I(shape-dis)]^*, \end{aligned} \quad (7.37)$$

where

$$\begin{aligned} [f_{rot}^I(perm)]^* &= (1/6\pi)(\rho^*/T^{*3})[(1/3)(\mu^*)^4 I_6 + (1/20) \\ &\times (\mu^*Q^*)^2 I_8 + (106/27)(Q^*)^4 I_{10}], \end{aligned} \quad (7.38a)$$

$$\begin{aligned} [f_{rot}^I(in)]^* &= (1/20\pi)(\rho^*\alpha^*/T^{*3}) \\ &\times [(\mu^*)^4 I_{12} + 6(Q^*)^2 I_{16}], \end{aligned} \quad (7.38b)$$

$$\begin{aligned} [f_{rot}^I(anis-dis)]^* &= (4/5\pi)(\rho^*/T^{*3})K^2 \\ &\times (1 + 3.8K^2)I_{12}, \end{aligned} \quad (7.38c)$$

$$[f_{rot}^I(shape)]^* = (16/5\pi)(\rho^*D^2/T^{*3})I_{24}, \quad (7.38d)$$

$$[f_{rot}^I(perm-in)]^* = -(183/1680\pi)(\rho^*\alpha^*Q^{*4}/T^{*3})I_{13}, \quad (7.38e)$$

$$[f_{rot}^I(perm-shape)]^* = (143/80\pi)(\rho^*Q^{*2}D/T^{*3})I_{17}, \quad (7.38f)$$

$$[f_{rot}^I(dis-in)]^* = (12/35\pi)(\rho^*\alpha^*Q^{*2}K/T^{*3})I_{14}, \quad (7.38g)$$

$$[f_{rot}^I(shape-in)]^* = (48/35\pi)(\alpha^*Q^{*2}D/T^{*3})I_{20}, \quad (7.38h)$$

$$[f_{rot}^I(shape-dis)]^* = -(8/5\pi)(\rho^*DK/T^{*3})I_{18}. \quad (7.38i)$$

Other thermodynamic properties can be obtained from eq. (7.4). Thus, the equation of state is given by

$$(\beta P/\rho) - (\beta P^c/\rho) = (\Lambda^*)^2 (P_{tr}^I)^* + (\delta^*)^2 (P_{rot}^I)^*, \quad (7.39)$$

$$\text{where } (P_{tr}^I)^* = \rho^* \left[\partial (f_{tr}^I)^* / \partial \rho^* \right], \quad (7.40a)$$

$$(P_{rot}^I)^* = \rho^* \left[\partial (f_{rot}^I)^* / \partial \rho^* \right]. \quad (7.40b)$$

The coefficients $(P_{tr}^I)^*$ and $(P_{rot}^I)^*$ are the first order quantum correction to the pressure due to the translational and rotational contribution, respectively.

The entropy S and internal energy U , correct to the first order quantum correction, are given by

$$(S/Nk) - (S^c/Nk) = (\Lambda^*)^2 (S_{tr}^I)^* + (\delta^*)^2 (S_{rot}^I)^*, \quad (7.41)$$

$$\text{where } (S_{tr}^I)^* = -(\partial/\partial T^*) \left[T^* \partial (f_{tr}^I)^* / \partial T^* \right], \quad (7.42a)$$

$$(S_{rot}^I)^* = -(\partial/\partial T^*) \left[T^* \partial (f_{rot}^I)^* / \partial T^* \right], \quad (7.42b)$$

$$\text{and } (U/NkT) - (U^c/NkT) = (\Lambda^*)^2 (U_{tr}^I)^* + (\delta^*)^2 (U_{rot}^I)^*, \quad (7.43)$$

$$\text{where } (U_{tr}^I)^* = -T^* \left[\partial (U_{tr}^I)^* / \partial T^* \right], \quad (7.44a)$$

$$(U_{rot}^I)^* = -T^* \left[\partial (U_{rot}^I)^* / \partial T^* \right]. \quad (7.44b)$$

Here, P^c , S^c and U^c are the pressure, entropy and internal energy of the classical molecular fluids.

Singh and Sinha [27,28] and Dey and Sinha [26] have obtained eqs. (7.35) and (7.37) for the first order quantum correction terms for the linear molecular fluids.

7.3 Applications :

The theory has been applied to calculate the quantum correction to the thermodynamic properties of simple molecular fluids. Powles and Rickayzen [29] estimated the quantum corrections to the free energy of the molecular fluids with the dipole-dipole ($\mu\mu$) and quadrupole-quadrupole (QQ) interactions, based on the Monte-Carlo (MC) values [61,62] of $\langle F^{*2} \rangle$ and $\langle \tau^{*2} \rangle$. Dey and Sinha [26] have estimated the quantum correction terms numerically. The value of $(A - A^c)$ for these fluids at density $\rho r^* = 0.80$ at temperature $T^* = 0.719$ are compared in Figs. 1 and 2, respectively for $I^* = 0.07$ and 0.001. The agreement is good for low values of μ^{*2} or Q^{*2} . The discrepancy increases

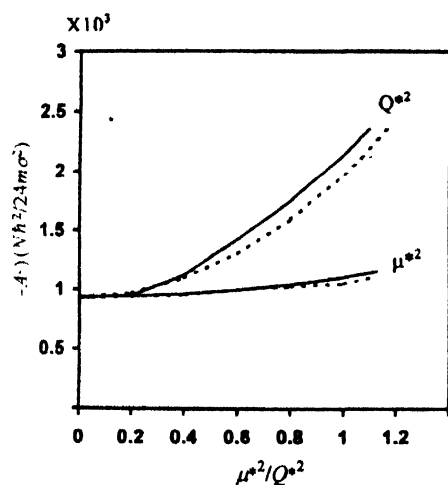


Figure 1. Quantum correction to the free energy $(A - A^c)/(N\hbar^2/24m\sigma^2)$ for a diatomic fluid with pair potential $u_{LJ} + u_a$, where u_a is the dipole-dipole or quadrupole-quadrupole potential, at $\rho^* = 0.80$, $T^* = 0.719$ for $I^* = 0.07$. Solid and dashed curves represent theoretical and Monte Carlo values (taken from Ref. [26]).

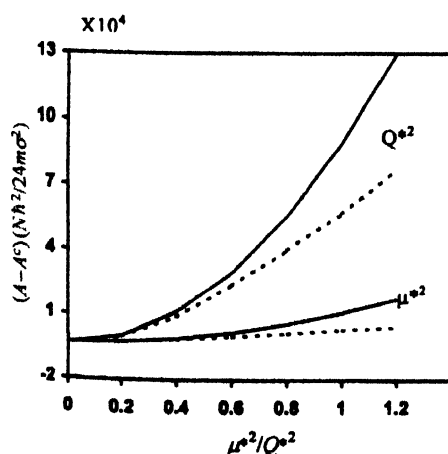


Figure 2. Same as Figure 1 for $I^* = 0.001$ (taken from Ref. [26]).

with increase of μ^{*2}/Q^{*2} and/or decrease of I^* . This discrepancy is mainly due to approximation (7.7) for g^c used in calculating $(f_{tr}^c)^*$ and $(f_{rot}^c)^*$.

Eqs. (7.36) and (7.38) are used to estimate the contribution of various branches of pair interactions to the first order quantum corrections to the free energy. The contributions of these terms are found to be small but not negligible [26,27].

Dey and Sinha (DS) [26] have also applied the theory to evaluate the quantum effects on the thermodynamic properties of HCl. Table 6 demonstrates the percentage of the quantum correction to the free energy per particle of HCl. This shows that the quantum effect for HCl is small but not negligible particularly at high density or low temperature. Powles and Rickayzen [29] also estimated roughly the quantum corrections to the configurational energy and pressure for several liquids like N_2 , F_2 and HCl, where the quantum effects are found to be small but not negligible at low temperature.

Table 6. Quantum correction to free energy per particle of HCl (taken from [26]).

| ρr^* | T^* | $[(f - f^c)/f^c] \times 100$ |
|------------|-------|------------------------------|
| 0.45 | 1.552 | -0.94 |
| | 1.710 | -0.75 |
| 0.65 | 0.900 | -2.83 |
| | 1.584 | -1.47 |
| 0.85 | 0.658 | -5.64 |
| | 1.127 | -3.07 |

For hydrogen isotopes like H_2 , D_2 , the quantum effects are appreciable. Therefore, the truncation of the WK series after the first order quantum correction term is justified for them at moderately high temperatures. Clancy and Gubbins [49] calculated the quantum correction to the equation of state of H_2 using the pair potential model

$$u = u_{LJ} + u_{QQ} + u_{dis} + u_{sh} \quad (7.45)$$

and found that the $0(\hbar^2)$ correction significantly improves the results for the temperatures range 100–200 K. However they have not taken u_m into their calculations.

Singh and Sinha (SS) [28] have estimated the influence of quantum effects on the configurational internal energy, entropy and pressure for fluid H_2 with u_a given by eq. (2.6) as shown in Table 7. From the table we find that the quantum effects increase with the increase of density and/or decrease of temperature. The calculated values of the pressure $\beta P/\rho$ and entropy S/Nk are compared with the experimental data [62] in Table 8. The agreement is found to be good at high

temperature and decreases when temperature decreases. For low temperature, the results can be improved by considering the second order quantum correction term.

Table 7. Quantum correction to the configuration internal energy, entropy and pressure for fluid H₂ (taken from Ref [28])

| $T(K)$ | ρ (mol ⁻¹) | $((U - U^*)/U^*)$ $\times 100$ | $((S - S^*)/S^*)$ $\times 100$ | $((P - P^*)/P^*)$ $\times 100$ |
|--------|--------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| 100 | 9.47 | -25.29 | 1.51 | 8.55 |
| | 14.97 | -23.37 | 2.47 | 14.45 |
| | 30.32 | -22.10 | 6.70 | 33.57 |
| 80 | 9.47 | -42.32 | 2.86 | 15.35 |
| | 14.97 | 38.52 | 4.73 | 25.89 |
| | 30.32 | -33.90 | 12.46 | 64.29 |

Table 8. Pressure and entropy of fluid H₂.

| $T(K)$ | ρ (mol ⁻¹) | $\beta P/\rho$ | | S/NK | |
|--------|--------------------------------|----------------|--------|--------|-------|
| | | Theory | Expt | Theory | Expt |
| 120 | 9.468 | 1.0743 | 1.0726 | 7.9689 | 7.996 |
| 100 | 11.540 | 1.0665 | 1.0560 | 7.3240 | 7.400 |
| 80 | 14.973 | 1.0484 | 1.0174 | 6.3342 | 6.642 |
| 60 | 21.619 | 1.0430 | 0.9395 | 5.3521 | 5.557 |

7.4. Concluding remarks :

In this section, we have discussed the method to evaluate the PDF and thermodynamic properties of molecular fluids using the WK expansion method, in which the expansion of properties is made in terms of the distribution functions of the classical molecular fluid. The PDF and thermodynamic properties of the classical molecular fluid are calculated by using a second perturbation expansion, where the LJ(12-6) potential is taken as a reference and the angle-dependent potential as a perturbation. Thus the quantum correction terms are expressed in terms of the distribution functions of the LJ(12-6) fluid. In spite of these approximations the theory is able to predict qualitative, and frequently quantitative, account of the influence of quantum effects on the thermodynamic properties of molecular fluids. In particular, the quantum corrections for H₂ are appreciable and does not fall within the errors introduced in theory due to these approximations. Even with these approximations, the theory predicts good results when compared with experiments in some cases. This shows the usefulness of the theory.

The $O(\hbar^2)$ expansion is suitable when the quantum effects are small. For H₂ the quantum corrections are particularly large at low temperature, so that the first order correction term alone is not sufficient at low temperature and full quantum treatment becomes necessary [64].

For heavier fluids (e.g. HCl, N₂, N₂), the quantum effects are considerably smaller. They can be safely considered as classical molecular fluids except at very low temperatures.

From the results quoted above, we find that the quantum effects increase with increase of density and/or decrease of temperature. At liquid densities, one has to consider higher order quantum correction terms, which involve higher order distribution functions of the classical molecular fluids. All these suggest that the expansion method is not suitable to treat the properties of the condensed state.

8. Effective pair potential method

8.1. Introduction :

Effective pair potential method has proven to be useful and general for discussing the equilibrium properties of fluids. The quantum features (excluding those due to the exchange effects) can be included in the calculation of the equilibrium properties of atomic fluids through the effective pair potential [65-69]. The effective pair potential is not unique-different properties lead to different effective potential [70]. When the bare LJ(12-6) potential is used, the effective pair potential is expressed in the 'modified' LJ(12-6) potential form by simply replacing σ by $\tilde{\sigma}(T^*, \Lambda^*)$ and ϵ by $\tilde{\epsilon}(T^*, \Lambda^*)$ in eq.(2.4) [71,72]. This approach has been extended for molecular fluids.

The 'preaveraged' potential method originally developed by Cook and Rowlinson [73] and generalised and extended by other [74,75] is the starting point for most of our understanding of thermodynamic properties of molecular fluids. In this method the orientation-dependent contribution to the pair potential may be averaged to give an 'effective' temperature dependent (preaveraged) potential, which is independent of orientations. This is thermodynamically equivalent to the orientation-dependent pair interaction. In its original form, it is employed to calculate the properties of classical polar gases. This method was extended to calculate the thermodynamic properties of classical molecular fluid [41,76], considering all branches of anisotropic pair interactions. The 'preaveraged' pair potential may be termed as the effective pair potential in the sense that it is a function of intermolecular separation only.

Using the 'preaveraged' pair potential, obtained by Shukla *et al* [76], recently Karki *et al* [77] have derived an effective potential in the LJ(12-6) potential form for the classical molecular fluid. This was further extended to include the quantum effects by Dey and Sinha [78] and Karki and Sinha [79].

8.2 Effective pair potential for semiclassical molecular fluids :

Substituting eq. (4.24) in eq (3.15) and integrating by parts, we get

$$Z_N = \int \dots \int \exp[\beta\Phi] \left[1 - \left\{ (\hbar^2\beta^2/24m) \times \sum (\nabla_{\eta}^2 \Phi) + (\hbar^2\beta^2/24I) \sum \nabla_{\omega_i}^2 \Phi \right\} 0(\hbar^2) \right] \prod_{i=1}^N dx_i, \quad (8.1)$$

Assuming the total interaction potential to be pair-wise additive, eq. (8.1) can be written as

$$Z_N = \int \dots \int \exp \left[-\beta \sum_{i<j} U(x_i, x_j) \right] \prod_{i=1}^N dx_i, \quad (8.2)$$

$$\text{where } U(x_i, x_j) = u(x_i, x_j) + (\hbar^2\beta^2/12m) \nabla_{\eta}^2 u(x_i, x_j) + (\hbar^2\beta^2/12I) \nabla_{\omega_i}^2 u(x_i, x_j) + 0(\hbar^4). \quad (8.3)$$

Using eq. (2.5), eq. (8.3) can be written as

$$U(x_i, x_j) = U_0(r_{ij}) + U_a(x_i, x_j), \quad (8.4)$$

where $U_0(r_{ij}) = u_0(r_{ij}) + (\hbar^2\beta^2/12m) \nabla_{\eta}^2 u_0(r_{ij})$,

$$U_a(x_i, x_j) = u_a(x_i, x_j) + (\hbar^2\beta^2/12m) \nabla_{\eta}^2 u_a(x_i, x_j) + (\hbar^2\beta^2/12I) \nabla_{\omega_i}^2 u_a(x_i, x_j). \quad (8.5)$$

Here, U_0 is the effective central potential and U_a the effective angle-dependent potential. Thus the quantum effects are included in the effective potential.

Substituting eq. (8.3) in eq. (8.2) and after angle-integrations, Karki and Sinha [79] have expressed the configurational integral in the form

$$Z_N = \int \dots \int \exp \left[-\beta \sum_{i<j} \Psi_e(r_{ij}) \right] \prod_{i=1}^N dr_i, \quad (8.6)$$

where $\Psi_e(r_{ij})$ is the orientation-independent effective 'preaveraged' pair potential of the semiclassical molecular fluid and expressed as

$$\Psi_e(r) = \Psi(r) + \Lambda^2 [\Psi_{tr}^1(r)] + \delta^2 [\Psi_{rot}^1(r)], \quad (8.7)$$

where $\Psi(r)$ is the 'preaveraged' pair potential for classical molecular fluid, and $[\Psi_{tr}^1(r)]$ and $[\Psi_{rot}^1(r)]$ are the first order quantum corrections arising from the translational and rotational contribution, respectively. They are expressed as

$$[\Psi_{tr}^1(r)] = (\sigma^2\beta^2/48\pi^2) \left[\left\langle \nabla_{\eta}^2 u(r\omega_1\omega_2) \right\rangle_{\omega_1\omega_2} - \beta \left\langle u_a(r\omega_1\omega_2) \nabla_{\eta}^2 u(r\omega_1\omega_2) \right\rangle_{\omega_1\omega_2} + \dots \right], \quad (8.8)$$

$$[\Psi_{rot}^1(r)] = (\beta^2/48\pi^2) \left[\left\langle \nabla_{\omega_i}^2 u_a(r\omega_1\omega_2) \right\rangle_{\omega_1\omega_2} - \beta \left\langle u_a(r\omega_1\omega_2) \nabla_{\omega_i}^2 u_a(r\omega_1\omega_2) \right\rangle_{\omega_1\omega_2} + \dots \right]. \quad (8.9)$$

Shukla *et al* [76] obtained expression of $\Psi(r)$ for the classical molecular fluid with u_a given by eq. (2.6), and Karki and Sinha [79] have obtained expressions for $[\Psi_{tr}^1(r)]$ and $[\Psi_{rot}^1(r)]$. Finally, eq. (8.7) can be written in the form

$$\Psi_e(r) = 4 \epsilon \left[(A_{11}(\sigma/r)^{11} + A_{12}(\sigma/r)^{12} + A_{13}(\sigma/r)^{13} + (L_{14} + A_{14})(\sigma/r)^{14} + A_{15}(\sigma/r)^{15} + A_{16}(\sigma/r)^{16} + A_{17}(\sigma/r)^{17} + A_{18}(\sigma/r)^{18} + A_{19}(\sigma/r)^{19} + A_{20}(\sigma/r)^{20} + A_{21}(\sigma/r)^{21} + A_{22}(\sigma/r)^{22} + A_{23}(\sigma/r)^{23} + A_{24}(\sigma/r)^{24} + A_{25}(\sigma/r)^{25} + A_{26}(\sigma/r)^{26} \right] - [A_5(\sigma/r)^5 + A_6(\sigma/r)^6 + (L_8 + A_8)(\sigma/r)^8 + A_{10}(\sigma/r)^{10}], \quad (8.10)$$

where the coefficient L_m associated with the LJ(12-6) potential are expressed as

$$L_8 = (5/8\pi^2 T^*) \Lambda^{*2}, \\ L_{14} = (11/4\pi^2 T^*) \Lambda^{*2}, \quad (8.11)$$

whereas the coefficient A_m are given in Ref. [79].

Eq. (8.10) can be expressed in the LJ(12-6) potential form by simply replacing $\sigma \rightarrow \sigma_T(T^*, \Lambda^*, \delta^*)$ and $\epsilon \rightarrow \epsilon_T(T^*, \Lambda^*, \delta^*)$ in eq. (2.4). In order to obtain expressions for σ_T and ϵ_T , we approximate $r/\sigma = 1$ in L_m , as the quantum effects are largely determined from the hard-core [80] and approximate $r/\sigma \approx r_{min}/\sigma \approx 2^{1/6}$ in A_m [81]. Then eq. (8.10) can be written as

$$\Psi_e(r) = 4 \epsilon [X(\sigma/r)^{12} - Y(\sigma/r)^6], \quad (8.12)$$

where X and Y are expressed in compact form

$$X = a + (b/T^*) + (c/T^{*2}), \quad (8.13)$$

$$Y = 1 + (d/T^*) + (e/T^{*2}) + (f/T^{*3}). \quad (8.14)$$

The coefficients a, b, \dots are given by

$$a = 1 + (1/2)\alpha^* \mu^{*2} + (3/4)(2^{1/3})\alpha^* Q^{*2}, \quad (8.15a)$$

$$b = \left[(1/12)(\mu^{*2})^2 + (1/4)(2^{1/3})\mu^{*2} Q^{*2} + (7/20)(2^{2/3})(Q^{*2})^2 \right] + (\Lambda^{*2}/8\pi^2) \\ \times \left[5 + (5/2)(2^{1/3})\alpha^* \mu^{*2} + (7/(2^{2/3}))\alpha^* Q^{*2} \right] \\ - (\delta^{*2}/8\pi^2) \left[(2^{1/6}/120) Q^{*2} \right], \quad (8.15b)$$

$$c = (\Lambda^2/8\pi^2) \left[(1/6(2^{1/3}))(\mu^2)^2 + (1/(2^{2/3}))\mu^2 Q^2 \right] + (\delta^2/8\pi^2) \left[(1/18)(\mu^2)^2 + (1/120(2^{1/3}))\mu^2 Q^2 + (53/405(2^{2/3}))(Q^2)^2 \right], \quad (8.15c)$$

$$d = [-(4/5)K^2(1+1.9K^2) - (4/5)D^2 + (8/5)DK + (2/5)\alpha^* \mu^2 D + (24/35(2^{1/3}))\alpha^* Q^2 (D-K)] + (11/4\pi^2) \Lambda^2, \quad (8.16a)$$

$$e = \left[(2^{1/6}/5)(\mu^2)^2 Q^2 + (6/35(2^{1/6}))\mu^2 (Q^2)^2 + (18/245(2^{1/2}))(Q^2)^3 \right] + (\Lambda^2/\pi^2) \times \left[-(7/24)(Q^2)^2 - (2^{-1/3})K^2(1+1.9K^2) + (22/5(2^{1/3}))D^2 + (27/5(2^{1/3}))DK \right] + (\delta^2/\pi^2) \left[(1/10)K^2(1+3.8K^2) + (1/10)D^2 + (1/10)DK + (3/70(2^{1/3}))\alpha^* Q^2 K + (3/35(2^{1/3}))\alpha^* Q^2 D \right], \quad (8.16b)$$

$$f = (7/1800)(\mu^2)^4. \quad (8.16c)$$

Eq. (8.12) can be expressed in the LJ(12-6) form

$$\psi_e(r) = 4 \epsilon_T \left[(\sigma_T/r)^{12} - (\sigma_T/r)^6 \right], \quad (8.17)$$

$$\text{where } \hat{\sigma} \equiv \sigma_T/\sigma = F^{-1/6}, \quad (8.18a)$$

$$\hat{\epsilon} \equiv \epsilon_T/\epsilon = XF^2, \\ = \left[1 + (d/T^*) + (e/T^{*2}) + (f/T^{*3}) \right] F^2 \quad (8.18b)$$

$$\text{and } F = Y/X = \left[a + (b/T^*) + (c/T^{*2}) \right] / \left[1 + (d/T^*) + (e/T^{*2}) + (f/T^{*3}) \right]. \quad (8.19)$$

Thus, the quantum effects and angle-dependent part of potential modify the values of σ and ϵ . The salient feature of this approach is that once the effective pair potential is expressed in the LJ(12-6) potential form, the system can be treated as the classical LJ(12-6) system. The effective potential $\psi_e(r)$ depends on temperature and so is not a true potential. However use of such effective potential simplifies the calculations by using the simple and accurate theories developed for classical atomic fluids. For the angle dependent parts Karki and Sinha [79] have considered multipole moments, induced multipole moments, dispersion and overlap shape interactions. They obtained the effective potential parameters σ_T and ϵ_T for semiclassical molecular fluid and applied to the fluids of hydrogen isotopes, namely H₂, HD and D₂, where the quantum effects are appreciable.

8.2.1. Classical molecular fluids :

In the classical limit $\Lambda^* = \delta^* = 0$ in eqs. (8.15) and (8.16). Karki *et al* [77] have not taken the overlap shape interaction into consideration and obtained expressions for a, b, \dots, f as

$$a = 1 + (1/2)\alpha^* \mu^2 + (3/4(2^{1/3}))\alpha^* Q^2 \quad (8.20a)$$

$$b = (1/12)(\mu^2)^2 + (1/4(2^{1/3}))\mu^2 Q^2 + (7/20(2^{2/3}))(Q^2)^2 \quad (8.20b)$$

$$c = 0 \quad (8.20c)$$

$$d = -(4/5)K^2(1+1.9K^2) - (24/35(2^{1/3})) \times \alpha^* Q^2 K \quad (8.21a)$$

$$e = (2^{1/6}/5)(\mu^2)^2 Q^2 + (6/35(2^{1/6}))\mu^2 (Q^2)^2 + (18/245(2^{1/2}))(Q^2)^3 \quad (8.21b)$$

$$f = (7/1800)(\mu^2)^4 \quad (8.21c)$$

Karki *et al* [77] have neglected the term 'e' as its contribution is found to be very small for the fluids like N₂, O₂ considered there.

8.2.2. Classical polar fluids :

For classical polar fluids, where the LJ(12-6) potential is taken as a central potential and for the angle dependent part of potential, dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interactions are taken into consideration, $a = c = d = 0$ and only b, e and f of eqs. (8.20) and (8.21) contribute to derive σ_T and ϵ_T . Recently, Karki and Sinha [82] have employed this theory to study the phase equilibria of polar Lennard Jones (PLJ) fluid.

Thus, we come to the conclusion that when the effective pair potential is expressed in the LJ(12-6) form, the molecular system can be treated as the classical LJ(12-6) system.

In the following sections, we apply this theory to discuss different thermodynamic properties of the molecular fluids.

8.3. Thermodynamic properties of molecular fluids :

This theory may be applied to estimate the thermodynamic properties of (semiclassical) molecular fluids. In this approach, we consider the reduced density $\rho^* = \rho\sigma^3$ and reduced temperature $T^* = kT/\epsilon$ and replace ρ^* by $\rho_T^* = \rho^* \hat{\sigma}^3$ and T^* by $T_T^* = T^*/\hat{\epsilon}$. Then the free energy and pressure of the semiclassical molecular fluid can be given by

$$A(\rho^*, T^*, \Lambda^*, \delta^*) = A_{LJ}(\rho_T^*, T_T^*), \quad (8.22)$$

$$P(\rho^*, T^*, \Lambda^*, \delta^*) = P_{LJ}(\rho_T^*, T_T^*), \quad (8.23)$$

where $A_{LJ}(\rho_T^*, T_T^*)$ and $P_{LJ}(\rho_T^*, T_T^*)$ are, respectively, free energy and pressure of the classical LJ(12-6) fluid at the

reduced density ρ_T^* and reduced temperature T_T^* . In case of the classical molecular fluid A and P are not functions of A^* and δ^* .

8.3.1 Virial equation of state for dilute molecular fluids :

At low densities we may express the pressure of the fluid in the virial form

$$\beta P/\rho = A + B/V + C/V^2 + \dots, \quad (8.24)$$

where $A = 1$, B and C are, the second and third virial coefficients, which are given by

$$B = b_0 \hat{\sigma}^3 B_{LJ}^*(T_T^*), \quad (8.25)$$

$$C = (b_0 \hat{\sigma}^3)^2 C_{LJ}^*(T_T^*), \quad (8.26)$$

$$\text{where } b_0 = 2\pi N\sigma^3/3, \quad (8.27)$$

Table 9. Second and third virial coefficients for H₂ and D₂ (taken from Ref [79])

| T(K) | B(cm ³ -mol ⁻¹) | | C(cm ⁶ -mol ⁻²) | |
|----------------|--|-------|--|-------|
| | Theory | Expt | Theory | Expt |
| H ₂ | | | | |
| 173 | 8.43 | 9.16 | 356.2 | 369.4 |
| 223 | 11.54 | 12.10 | 336.3 | 350.0 |
| 323 | 14.82 | 15.17 | 310.8 | 323.0 |
| 473 | 15.59 | 15.71 | 301.3 | 290.0 |
| D ₂ | | | | |
| 173 | 9.67 | 8.39 | 876.8 | 439.0 |
| 223 | 10.78 | 11.51 | 361.5 | 410.0 |
| 323 | 14.17 | 14.45 | 311.2 | 30.0 |
| 473 | 15.39 | 15.55 | 303.2 | 335.0 |

Here, $B_{LJ}^*(T_T^*)$ and $C_{LJ}^*(T_T^*)$ are the reduced second and third virial coefficients for the classical LJ(12-6) fluid at the reduced temperature T_T^* . They can be evaluated numerically and are available [15].

Karki and Sinha (KS) [79] have calculated the second and third virial coefficients for H₂ and D₂ where the quantum effects are appreciable and treated semiclassically. The results are compared with the exact [38] and experimental [38] data in Table 9. The agreement of B is good at high temperature. For C , the agreement is moderately good. When compared with the values of Singh *et al* [24] for H₂ reported in Table 4, we find them in close agreement.

8.3.2. Thermodynamics for dense molecular fluids :

Thermodynamic properties of the dense semiclassical molecular fluids can be calculated using the Verlet-Weiss (VW) method [59] discussed in Section 7.1, where $u_0(r)$ is replaced by $\Psi_2(r)$ given in eq. (8.17). Karki and Sinha (KS) [79] have applied this theory to calculate the equation of state, $\beta P/\rho$ for fluid H₂ at different densities and temperature.

They are compared with experimental data [63] and results of Singh and Sinha (SS) [28] in Table 10. The agreement is good. The table shows that the KS theory underestimates while the SS theory overestimates the values.

Table 10. Equation of state $\beta P/\rho$ for fluid H₂ (taken from Ref [79])

| T(K) | ρ (mol/l) | KS | SS | Expt. |
|------|----------------|--------|--------|--------|
| 120 | 9.468 | 1.0583 | 1.0743 | 1.0736 |
| 100 | 11.540 | 1.0381 | 1.0665 | 1.0560 |
| 80 | 14.973 | 0.9809 | 1.0484 | 1.0174 |
| 60 | 21.619 | 0.9273 | 1.0430 | 0.9395 |
| 40 | 16.342 | 0.8949 | 0.9940 | 0.9391 |

Sometimes it is interesting to calculate the thermodynamic properties such as Gibb's free energy G , enthalpy H and molar volume V at zero pressure (*i.e.* $P = 0$). These properties at zero pressure can be calculated using the expressions given by Grundke *et al* [83]. Thus,

$$\beta A/N = \beta G/N = -4.50151 - 2.23463X - 0.00255[8X^2(X^2 - 1) + 1], \quad (8.28)$$

$$U/N \epsilon_T = H/N \epsilon_T = -5.47348 - 1.03040X + 0.22235(2X^2 - 1) - 0.06177X(4X^2 - 3) + 0.01857[8X^2(X^2 - 1) + 1], \quad (8.29)$$

$$N\sigma_T^3/V = 0.782792 + 0.138646X - 0.030534(2X^2 - 1) + 0.009398X(4X^2 - 3) + 0.002908[8X^2(X^2 - 1) + 1], \quad (8.30)$$

where $X = (2.5/T_T^*) - 3.25$,

$$T_T^* = kT/\epsilon_T = T^*/\hat{\epsilon}.$$

Table 11. Gibbs free energy G , enthalpy H and molar volume V of fluids at $P = 0$ at $T = 83.82^\circ\text{K}$ (taken from Ref [77])

| System | | $-G(\text{J mol}^{-1})$ | $-H(\text{J mol}^{-1})$ | $V(\text{cm}^3 \text{mol}^{-1})$ |
|----------------|--------|-------------------------|-------------------------|----------------------------------|
| N ₂ | Theory | 2873.50 | 4844.89 | 35.91 |
| | MD | | 4980.00 | 36.12 |
| O ₂ | Theory | 3994.25 | 6467.29 | 25.10 |
| | MD | | 6443.00 | 27.24 |
| Ar | Theory | 3560.40 | 5852.72 | 28.41 |
| | MD | | 6066.00 | 28.21 |

Karki *et al* [77] have calculated G , H and V of fluids N₂, O₂ and Ar (treating classically) at $P = 0$ and $T = 83.82^\circ\text{K}$. The results are compared with the molecular dynamic (MD) values [84] in Table 11. The agreement is found to be good.

8.4. Concluding remarks :

In this section we have discussed the method of calculating the thermodynamic properties of the semiclassical molecular

fluids, using the effective LJ(12-6) potential. This potential is obtained simply by replacing $\sigma \rightarrow \sigma_T(T^*, \Lambda^*, \delta^*)$ and $\epsilon \rightarrow \epsilon_T(T^*, \Lambda^*, \delta^*)$ in the bare LJ(12-6) potential. The influence of the quantum effects and the angle dependent potential, which are usually of opposite nature, are incorporated through the expressions of σ_T and ϵ_T . Then the system can be treated as the classical LJ(12-6) system. For the classical molecular fluids, σ_T and ϵ_T are not the functions of Λ^* and δ^* .

This approach is simple and provides method of predicting the thermodynamics with reasonable accuracy over a wide range of temperature and density.

9. Theory of corresponding state for semiclassical molecular fluids

The effective LJ(12-6) potential can be employed to obtain the theory of corresponding state for the semiclassical molecular fluid. For the classical LJ(12-6), the law of corresponding state is written as

$$P^* = P^*(\rho^*, T^*), \quad (9.1)$$

where $P^* = P\sigma^3/\epsilon$, $\rho^* = \rho\sigma^3$ and $T^* = kT/\epsilon$. This gives the reduced pressure as a universal function of reduced density and temperature.

In order to study the theory of corresponding state for the semiclassical molecular fluids, we replace $\sigma \rightarrow \sigma_T$ and $\epsilon \rightarrow \epsilon_T$ and write the equation of state as

$$\tilde{P}^* = \tilde{P}^*(\rho_T^*, T_T^*), \quad (9.2)$$

where $\tilde{P}^* = P\sigma_T^3/\epsilon_T$, $\rho_T^* = \rho\sigma_T^3$ and $T_T^* = kT/\epsilon_T$. Here, $P_{LJ}(\rho_T^*, T_T^*)$ is the pressure of the classical LJ(12-6) fluid at the reduced density ρ_T^* and reduced temperature T_T^* . Eq. (9.2) is the statement of the theory of corresponding state for the semiclassical molecular fluids. It is possible to calculate properties of the semiclassical molecular fluids from this theory of corresponding states.

9.1. Critical point location :

We apply this theory to study the critical temperature T_c , critical volume V_c and critical pressure P_c for molecular fluids. For the classical LJ(12-6) fluid, they are given by

$$T_c^* = kT_c/\epsilon = 1.26, \quad (9.2a)$$

$$V_c^* = V_c/N\sigma^3 = 3.16, \quad (9.2b)$$

$$P_c^* = P_c\epsilon/\sigma^3 = 0.117. \quad (9.2c)$$

In order to study the critical constants of the semiclassical fluids, we replace $\epsilon \rightarrow \epsilon_T$ and $\sigma \rightarrow \sigma_T$ in eq. (9.2). Thus, we get

$$T_c^* = 1.26 \hat{\epsilon}, \quad (9.3a)$$

$$V_c^* = 3.1 \hat{\sigma}^3, \quad (9.3b)$$

$$P_c^* = 0.117 \hat{\epsilon}/\hat{\sigma}^3. \quad (9.3c)$$

Eq. (9.3a) may be solved by the 'iterative' process. After knowing T_c^* , one may estimate V_c^* and P_c^* . Karki and Sinha [72,79] have used eq. (9.3) to calculate the T_c , V_c and P_c of semiclassical molecular fluids of H₂, HD and D₂ molecules with and without u_d . These results are compared with the experimental data [67,85] in Table 12. The agreement is found to be good.

Table 12. Critical constants for fluids of hydrogen isotopes.

| System | method | T_c^* | V_c^* | $10P_c^*$ | V_c^*/P_c^* |
|----------------|------------|---------|---------|-----------|---------------|
| H ₂ | KS [79] | 0.90 | 4.12 | 0.642 | 0.288 |
| | KS [72] | 0.92 | 3.90 | 0.680 | 0.288 |
| | Expt [67] | 0.90 | 4.42 | 0.646 | 0.318 |
| HD | KS [79] | 1.00 | 3.68 | 0.804 | 0.288 |
| | KS [72] | 1.02 | 3.68 | 0.813 | 0.288 |
| | Expt [67] | 1.03 | 4.10 | 0.730 | 0.310 |
| D ₂ | KS [79] | 1.09 | 3.59 | 0.877 | 0.288 |
| | KS [72] | 1.08 | 3.50 | 0.891 | 0.288 |
| | Expt. [67] | 1.10 | 3.90 | 0.860 | 0.305 |

9.2. Surface tension :

As an application of this theory to the thermodynamic properties below T_c , we consider the surface tension (ST) of the semiclassical molecular fluids along the liquid-vapour phase boundary. The ST of the classical LJ(12-6) fluid is given by

$$\gamma^* = \gamma\sigma^2/\epsilon = 2.666(1 - T^*/T_c^*)^{1.27} \quad (9.4)$$

where $T_c^* = 1.26$. In order to obtain expression of the ST of the semiclassical molecular fluid, we replace $\epsilon \rightarrow \epsilon_T$ and $\sigma \rightarrow \sigma_T$ in eq. (9.4). Then the ST of the semiclassical molecular fluid is expressed as

$$\tilde{\gamma}^* = \tilde{\gamma}\sigma_T^2/\epsilon = (\hat{\epsilon}/\hat{\sigma}^2) 2.666(1 - T_T^*/1.26)^{1.27}, \quad (9.5)$$

where $T_T^* = kT/\hat{\epsilon}$. In this approach, the amplitude is modified but the exponent remains a constant with a value of 1.27. Eq. (9.5) is applicable to a semiclassical molecular fluid over a wide ranges of temperatures. Recently, eq. (9.5) was employed to calculate the ST $\tilde{\gamma}^*$ for H₂ and D₂ [79]. They are compared with the experimental data [85] in Table 13. The values of γ^* decreases with rise of temperature T^* . It is found that the agreement is good.

Table 13. Surface tension γ^* of H₂ and D₂ fluids.

| System | T^* | γ^* Theory [79] | γ^* Expt [85] |
|----------------|-------|------------------------|----------------------|
| H ₂ | 0.40 | 0.369 | 0.468 |
| | 0.53 | 0.281 | 0.320 |
| | 0.66 | 0.178 | 0.190 |
| | 0.80 | 0.061 | 0.046 |

Table 13. (Cont'd.).

| System | T^* | γ^* Theory [79] | γ^* Expt. [85] |
|--------|-------|------------------------|-----------------------|
| D_2 | 0.50 | 0.681 | 0.675 |
| | 0.55 | 0.632 | 0.625 |
| | 0.60 | 0.572 | 0.575 |
| | 0.65 | 0.509 | 0.515 |

9.3 Liquid-vapour coexistence curve :

Next we apply this theory to study the behaviour of the liquid-vapour coexistence curve of the semiclassical molecular fluid. The behaviour of the classical LJ(12-6) fluid may be described by the equations [86]

$$V_c^*/V_l^* = 1 + (3/4)(1 - T^*/T_c^*) + (7/4)(1 - T^*/T_c^*)^{1/3} \quad (9.6)$$

$$V_c^*/V_v^* = 1 + (3/4)(1 - T^*/T_c^*) - (7/4)(1 - T^*/T_c^*)^{1/3} \quad (9.7)$$

where V_l^* , V_v^* and V_c^* are the reduced liquid, vapour and critical molar volume. Here $T_c^* = 1.26$ and $V_c^* = 3.16$. These equations represent the behaviour of V_c^*/V^* for $T^* \leq T_c^*$.

A quantity of particular significance for our study is the rectilinear diameter

$$d = (1/2)(V_c^*/V_l^* + V_c^*/V_v^*) = 1 + (3/4)(1 - T^*/T_c^*) \quad (9.8)$$

Replacing $\epsilon \rightarrow \epsilon_T$ and $\sigma \rightarrow \sigma_T$ in eqs. (9.6)–(9.8), the behaviour of the semiclassical molecular fluid can be described by

$$V_c^*/V_l^* = (\hat{\sigma}_c/\hat{\sigma})^3 \left[1 + (3/4)(1 - T_T^*/1.26) + (7/4)(1 - T_T^*/1.26)^{1/3} \right] \quad (9.9)$$

$$V_c^*/V_v^* = (\hat{\sigma}_c/\hat{\sigma})^3 \left[1 + (3/4)(1 - T_T^*/1.26) - (7/4)(1 - T_T^*/1.26)^{1/3} \right] \quad (9.10)$$

$$\text{and } d = (\hat{\sigma}_c/\hat{\sigma})^3 \left[1 + (3/4)(1 - T_T^*/1.26) \right] \quad (9.11)$$

where $\hat{\sigma}_c$ is the value of $\hat{\sigma}$ at $T^* = T_c^*$.

Karki and Sinha [79] have applied this theory to estimate V_c^*/V^* for fluid H_2 with and without u_a . These values are shown in Figure 3 along with the experimental data [67,85]. Figure shows that the angle dependent potential u_a lowers the values of V_c^*/V_l^* and the experimental data lie between these values.

9.4. Conclusions :

Using the effective LJ(12-6) potential, we obtain computationally convenient approximations to study the thermodynamic properties of the semiclassical molecular fluids. The quantum features (excluding those due to the exchange effects) and influence of the angle-dependent part of potential can be included in an essentially simple classical

description if the LJ(12-6) potential is replaced by the effective LJ(12-6) potential.

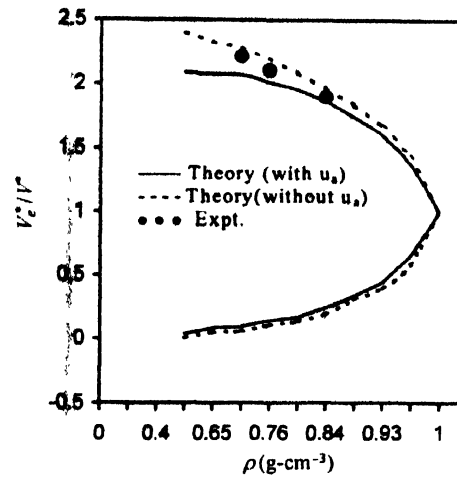


Figure 3. Values of V_c^*/V_l^* as a function of T^*/T_c^* along the liquid-vapour coexistence curve of H_2

We have also found that the effective pair potential method, described in Section 8, is quite simple and general in the sense that it can be applied to any molecular fluid under the scheme of any theory of the classical LJ(12-6) fluid, provided the effective pair potential is expressed in the LJ(12-6) form.

10. Some concluding remarks

There is much interest in the properties of quantum fluids in recent years. However this is confined to the simple atomic fluids, as it requires the solution of N -body problem in quantum mechanics, which is a difficult task.

The semiclassical fluid is quantum fluid at high temperature, where the quantum effects are small. In the present work, we have discussed methods of estimating the quantum corrections to the properties of semiclassical fluids, such as H_2 , D_2 , etc, where the quantum effects are appreciable. When the quantum effects are large, the first order quantum correction term alone is not sufficient at low temperature and a full quantum treatment becomes necessary [64]. Apart from direct application of such studies to real system, they may help in framing a theory for quantum fluids. Thus, the theoretical methods developed to describe the properties of molecular fluids in the semiclassical limit are of general interest and can be of use in other area of physics.

The Feynman path integral approach [87] makes possible to compute large quantum corrections. In this formulation, one begins with the quantum mechanical partition function

$$Q(\beta, V) = \int dx_1 \int_{x_1}^{x_2} Dx(\tau) \exp(-S[x(\tau)]), \quad (10.1)$$

$$\text{where } S[x(\tau)] = \int_0^{\beta\hbar} d\tau H(x(\tau)) \quad (10.2)$$

is the Euclidian action corresponding to the path $x(\tau)$ in Euclidian time τ and $Dx(\tau)$ implies that paths are constrained to begin and end at x_1 . In the discrete path representation, the Euclidian time τ is discretized in units $\epsilon = \beta\hbar/P$, where P is an integer and the continuous path $x(\tau)$ is assumed to be straight line path between neighbouring times. Then eq. (10.1) can be expressed as

$$Q_P = (mP/2\pi\hbar^2\beta) \int \dots \int dx_1 \dots dx_P \times \exp[-\beta\Phi_P(x_1 \dots x_P, \beta)], \quad (10.3)$$

where $x_i = x(i\beta\hbar/P)$, $x_{P+1} = x_1$ and

$$\Phi_P(x_1 \dots x_P, \beta) = (mP/2\beta^2\hbar^2) \sum_{i=1}^P (x_i - x_{i+1})^2 + \sum_{i=1}^P u(x_i). \quad (10.4)$$

Eq. (10.4) is equivalent to the classical configurational partition function of P classical particle with potential Φ_P and the quantum system is said to be isomorphic [88–91] to a classic P particle cyclic chain polymer.

In path integral simulation, we empirically determine and use that P beyond which the thermodynamic properties do not effectively change. The isomorphic classical system can be simulated by Monte Carlo (MC) [92] or molecular dynamics (MD) [93] to evaluate path integrals. These simulation methods are called path integral Monte Carlo (PIMC) and path integral Molecular Dynamic (PIMD). Equilibrium properties of the quantum system can be obtained by solving the equivalent classical problem by using PIMC and PIMD techniques [94]. The path integral methods have been used to study the interesting and difficult problems of quantum systems [94]. No attempts have, however, been made so far to apply these methods in simulation of the equilibrium properties of quantum fluids.

One major advantage of path integral simulations of quantum system is that they can be made as accurate as one wishes by increasing the number of points used to approximate the continuous paths. For a strong quantum system, however, the convergence to the correct result, $P \rightarrow \infty$, can be very slow, which poses a serious computational problem [89].

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