

## Semiclassical theory for thermodynamics of molecular fluid mixtures

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Received 8 May 2003, accepted 1 September 2004

**Abstract** : An effective pair potential for the semiclassical molecular fluid mixture is expressed in the effective Lennard-Jones (12-6) potential form, which includes the influence of the angle-dependent potential and quantum effects through the expressions of the effective diameter  $\tilde{\sigma}_{ab}$  and well depth  $\tilde{\epsilon}_{ab}$ . We employ the theory to estimate the thermodynamic properties of equimolar binary mixtures at zero pressures. Agreement with experiment for the excess properties such as excess Gibb's function, excess enthalpy and excess molar volume for  $N_2 + Ar$ ,  $O_2 + Ar$ ,  $H_2 + Ne$ ,  $D_2 + Ne$  and  $H_2 + D_2$  are found to be good.

**Keywords** : Semiclassical molecular fluid mixture, effective pair potential, thermodynamic properties.

**PACS Nos.** : 03.65.Sq, 82.60.Lf, 31.15.Gy

### 1. Introduction

Aim of the present paper is to estimate the thermodynamic properties of molecular fluid mixture in the semiclassical limit. One of the theoretical method for calculating the thermodynamic properties of classical molecular fluid is the 'preaveraged' potential method [1,2]. Using this method, Karki *et al* [3] have derived an effective Lennard-Jones (ELJ) (12-6) potential for classical molecular fluid. This was extended to include the quantum effects [4,5]. This method can be extended to study the thermodynamic properties of molecular fluid mixtures in the semiclassical limit.

In the present work, we obtain an effective pair potential to evaluate the equilibrium properties of molecular fluid mixtures in the semiclassical limit. We assume that the total interaction potential is pair-wise additive, *i.e.*

$$\Phi(X_1, X_2, \dots, X_N) = \sum_{a,b} \sum_{i < j} u_{ab}(X_i, X_j), \quad (1)$$

where  $u_{ab}(X_i, X_j)$  is the pair interaction potential between molecule  $i$  of species  $a$  and molecule  $j$  of species  $b$ , and the vector  $X_i \equiv (r_i, \omega_i)$  represents both the position of the centre of mass and orientation of the molecule  $i$  of species  $a$ . The pair interaction potential is usually assumed to be expressed as

$$u_{ab}(X_i, X_j) = u_{ab}^o(r_i, r_j) + u_{ab}^a(X_i, X_j), \quad (2)$$

where  $u_{ab}^o$  is the spherically symmetric potential and  $u_{ab}^a$  is the angle-dependent part of pair potential.

In Section 2, we describe the basic theory for a molecular fluid mixture in the semiclassical limit. Section 3 is devoted to derive effective pair potential of the semiclassical fluid mixture, which is further expressed in a Lennard-Jones (LJ) (12-6) potential form. Section 4 is concerned with the effective pair potential for the semiclassical binary mixture. The thermodynamic properties of binary mixture is discussed in Section 5. The results and discussion are given in Section 6. The summary is given in Section 7.

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## 2. Theoretical basis

We consider a molecular fluid mixture of rigid linear molecules, which are permanently in their ground electronic and ground vibrational states. In quantum statistical mechanics, the canonical partition function for a fluid mixture containing  $s$  components is defined as [6]

$$Q_N = Z_N / \prod_a^s (N_a! \lambda_a^{3N_a} q_a^{-N_a}), \quad (3)$$

where

$$\lambda_a = (2\pi\hbar^2\beta/m_a)^{1/2}, \quad (4a)$$

$$q_a = \sum_{J_a} (2J_a + 1)^2 \exp(-\beta J_a(J_a + 1)\hbar^2/2I_a), \quad (4b)$$

( $m_a$  is mass and  $I_a$  is the moment of inertia of a molecule of species  $a$  and  $\beta = (kT)^{-1}$ ). Here,  $\lambda_a$  is the thermal wave length and  $q_a$  is the single-molecule rotational partition function of species  $a$ .  $N_a$  is the number of molecules of species  $a$  such that the total number of molecules is  $N = \sum_a N_a$ .

In eq. (3),  $Z_N$  is the configurational integral which is defined in this case as

$$Z_N = \int \dots \int W_N(X_1, X_2, \dots, X_N) \prod_{i=1}^N dX_i, \quad (5)$$

where

$$dX_i = (4\pi)^{-1} dr_i d\omega_i,$$

and  $W_N$  is the Slater sum.

In the semiclassical limit, where the quantum effects are small,  $q_a$  for linear molecule is given by [7]

$$q_a = (\beta \hbar^2/I_a) [1 + (1/6) (\beta \hbar^2/I_a)], \quad (6)$$

where the first term is the classical value for the single-molecule rotational partition function. The Slater sum of the fluid mixture in the semiclassical limit can be expanded in powers of  $\hbar^2$  as [8]

$$W_N(X_1, X_2, \dots, X_N) = \exp(-\beta\Phi) \left[ 1 - \left\{ \sum (\hbar^2\beta^2/12m_a) \right. \right.$$

$$\times \sum_{i=1}^N \left[ \nabla_i^2 \Phi - (1/2)\beta(\nabla_i^2 \Phi)^2 \right] +$$

$$\left. \sum (\hbar^2\beta^2/12I_a) \right\}$$

$$\left. \times \sum_{i=1}^N \left[ \nabla_{\omega_i}^2 \Phi - (1/2)\beta(\nabla_{\omega_i}^2 \Phi)^2 \right] + O(\hbar^4) \right] \quad (7)$$

Substituting eq. (7) in eq. (5) and integrating by parts, we get

$$Z_N = \int \dots \int \exp[-\beta\Phi] \left[ 1 - \left\{ \sum_a (\hbar^2\beta^2/24m_a) \sum_i (\nabla_i^2 \Phi) \right. \right. \\ \left. \left. + \sum (\hbar^2\beta^2/24I_a) \sum \nabla_{\omega_i}^2 \Phi \right\} + O(\hbar^4) \right] \prod_{i=1}^N dX_i \quad (8)$$

Assuming the total interaction potential to be pair-wise additive and extending our method for one-component system [5], we can express the configurational integral in the form

$$Z_N = \int \dots \int \exp[-\beta \sum_{a,b} \sum_{i < j} \Psi_{ab}^e(r_{ij})] \prod_{i=1}^N dr_i, \quad (9)$$

where  $\Psi_{ab}^e(r_{ij})$  is the orientation-independent effective 'preaveraged' pair potential of the semiclassical molecular fluid mixture (acting between molecule  $i$  of species  $a$  and molecules  $j$  of species  $b$ ). This is written as

$$\Psi_{ab}^e(r) = \Psi_{ab}(r) \Lambda_{ab}^{*2} [\Psi_{tr}^1(r)]_{ab} + \delta_{ab}^{*2} [\Psi_{rot}^1(r)]_{ab}, \quad (10)$$

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

$$[\Psi_{tr}^1(r)]_{ab} = \left( \sigma_{ab}^2 \beta^2 / 48\pi^2 \right) \left[ \langle \Delta_r^2 u_{ab}(r\omega_1\omega_2) \rangle_{\omega_1\omega_2} \right. \\ \left. - \beta \langle u_{ab}^a(r\omega_1\omega_2) \nabla_r^2 u_{ab}(r\omega_1\omega_2) \rangle_{\omega_1\omega_2} + \dots \right] \quad (11)$$

$$[\Psi_{rot}^1(r)]_{ab} = \left( \beta / 48\pi^2 \right) \left[ \langle \Delta_{\omega_1}^2 u_{ab}^a(r\omega_1\omega_2) \rangle_{\omega_1\omega_2} \right. \\ \left. - \beta \langle u_{ab}^a(r\omega_1\omega_2) \nabla_{\omega_1}^2 u_{ab}^a(r\omega_1\omega_2) \rangle_{\omega_1\omega_2} + \dots \right] \quad (12)$$

In eq. (10), we use the following quantum parameters

$$\Lambda_{ab}^{*2} = h/\sigma_{ab}(m_{ab}\epsilon)^{1/2},$$

$$\delta_{ab}^{*2} = h/\sigma_{ab}(I_{ab}\epsilon)^{1/2}. \quad (13)$$

Here,  $m_{ab} = 2m_a m_b / (m_a + m_b)$  and  $I_{ab} = 2I_a I_b / (I_a + I_b)$ .

### 3. Effective pair potential for semiclassical molecular fluid mixture

For a molecular fluid mixture of nearly spherical molecules, the pair potential is given by eq. (2), where  $u_{ab}^a$  is the central potential and  $u_{ab}^a$  is the angle-dependent part of pair potential. For central potential, we consider the Lennard-Jones (LJ) (12-6) potential

$$u_{ab}^o(r) = 4\epsilon_{ab} [(\sigma_{ab}/r)^{12} - (\sigma_{ab}/r)^6], \quad (14)$$

where  $\epsilon_{ab}$  and  $\sigma_{ab}$  are, respectively, the well-depth and molecular diameter of species  $a$  and  $b$ . For angle dependent interaction, we take [7,8]

$$u_{ab}^a = u_{ab}^{\text{perm}} + u_{ab}^{\text{in}} + u_{ab}^{\text{dis}} + u_{ab}^{\text{shape}}, \quad (15)$$

where  $u_{ab}^{\text{perm}}$  is the interaction between permanent multipole moment of molecules of species  $a$  and  $b$ ,  $u_{ab}^{\text{in}}$  is the interaction of the induced multipole moment in one molecule with the permanent moment in the other molecule,  $u_{ab}^{\text{dis}}$  is the interaction between anisotropic dispersion forces of molecules and  $u_{ab}^{\text{shape}}$  is the anisotropy of the short-range overlap forces of molecules. For numerical calculation, these interaction potentials are expressed in the explicit angle-dependent form [7,8]. There  $\mu_a$  and  $Q_a$  are, respectively, the dipole and quadrupole moments,  $\alpha_a$  is the average polarizability,  $K_a$  is the anisotropy in the polarizability of the molecule of species  $a$ .  $D_{ab}$  is the dimensionless shape parameter for molecules of species  $a$  and  $b$ .

One can evaluate eq. (10) by employing the method discussed previously for one-component system [5] and evaluating the angle-integrals, we can obtain expressions for  $Y_{ab}(r)$ ,  $[\Psi_{tr}^I(r)]_{ab}$  and  $[\Psi_{rot}^I(r)]_{ab}$ . Finally eq. (10) can be written in the form

$$\begin{aligned} \Psi_{ab}^e(r) = 4\epsilon_{ab} & \left( [A_{ab}^{11}(\sigma_{ab}/r)^{11} + A_{ab}^{12}(\sigma_{ab}/r)^{12} + \right. \\ & A_{ab}^{13}(\sigma_{ab}/r)^{13} + (L_{ab}^{14} + A_{ab}^{14})(\sigma_{ab}/r)^{14} + \\ & \left. A_{ab}^{15}(\sigma_{ab}/r)^{15} + A_{ab}^{16}(\sigma_{ab}/r)^{16} + \right. \end{aligned}$$

$$A_{ab}^{18}(\sigma_{ab}/r)^{18} + A_{ab}^{20}(\sigma_{ab}/r)^{20}$$

$$A_{ab}^{22}(\sigma_{ab}/r)^{22} + A_{ab}^{24}(\sigma_{ab}/r)^{24} +$$

$$A_{ab}^{26}(\sigma_{ab}/r)^{26} \left] - [A_{ab}^5(\sigma_{ab}/r)^5 +$$

$$A_{ab}^6(\sigma_{ab}/r)^6 - (L_{ab}^8 + A_{ab}^8)(\sigma_{ab}/r)^8$$

$$A_{ab}^{10}(\sigma_{ab}/r)^{10} \left. \right], \quad (16)$$

where the coefficient  $L_{ab}^m$  and  $A_{ab}^m$  correspond to the LJ (12-6) potential and the angle-dependent potentials, respectively. The coefficients  $L_{ab}^m$  are expressed as

$$L_{ab}^8 = (5/8\pi^2 T_{ab}^*) \Lambda_{ab}^{*2}, \quad (17)$$

$$L_{ab}^4 = (11/4\pi^2 T_{ab}^*) \Lambda_{ab}^{*2},$$

and the coefficients  $A_{ab}^m$  are given in Appendix A, where  $T_{ab}^* = kT/\epsilon_{ab}$  ( $T$  being the absolute temperature).

The effective pair potential  $\Psi_{ab}^e(r)$  for such a model can be expressed in the LJ (12-6) form by simply replacing  $\sigma_{ab} \rightarrow \sigma_{ab}^T(T_{ab}^*, \Lambda_{ab}^*, \delta_{ab}^*)$  and  $\epsilon_{ab} \rightarrow \epsilon_{ab}^T(T_{ab}^*, \Lambda_{ab}^*, \delta_{ab}^*)$  in eq. (14), where  $T_{ab}^* = kT/\epsilon_{ab}$  is the reduced temperature, and  $\Lambda_{ab}^*$  and  $\delta_{ab}^*$  are the quantum parameters, which are introduced to measure the deviation from the classical behaviour. In order to obtain expressions for  $\sigma_{ab}^T$  and  $\epsilon_{ab}^T$ , we approximate  $r/\sigma_{ab} \approx 1$  in  $L_{ab}^m$ , as the quantum effects are largely determined from the hard core [9] and further approximate  $r/\sigma_{ab} \approx r_m/\sigma_{ab} \approx 2^{1/6}$  in  $A_{ab}^m$  [10]. Then eq. (16) can be written as

$$\Psi_{ab}^e(r) = 4\epsilon_{ab} [X_{ab}(\sigma_{ab}/r)^{1/2} - Y_{ab}(\sigma_{ab}/r)^6], \quad (18)$$

where using the values of the coefficients  $L_{ab}^m$  and  $A_{ab}^m$  we obtain expression for  $X_{ab}$  and  $Y_{ab}$  in compact form

$$Y_{ab} = a_{ab} + b_{ab}/T_{ab}^* + c_{ab}/T_{ab}^{*2}, \quad (19)$$

$$X_{ab} = 1 + b_{ab}/T_{ab}^* + e_{ab}/T_{ab}^{*2} + f_{ab}/T_{ab}^{*3}. \quad (20)$$

The expressions of  $a_{ab}, \dots, f_{ab}$  are reported in Appendix B. In classical limit,  $\Lambda_{ab}^* = \delta_{ab}^* = 0$  in the expression of  $a_{ab}, \dots, f_{ab}$ .

Eq. (18) can be used to determine  $\sigma_{ab}^T$  and  $\epsilon_{ab}^T$ .  $\sigma_{ab}^T$  is the value of  $r$  at which  $\Psi_{ab}^e(r)$  is zero i.e.  $\Psi_{ab}^e(\sigma_{ab}^T) = 0$ . Then, the position of the minimum of  $\Psi_{ab}^e(r)$  shifts from  $2^{1/6}\sigma_{ab}$  to  $2^{1/6}\sigma_{ab}^T$ , where the effective

pair potential is  $-\epsilon_{ab}^T$ . Eq. (18) can then be expressed in the LJ (12-6) :

$$\Psi_{ab}^e(r) = 4\epsilon_{ab}^T \left[ \left( \sigma_{ab}^T / r \right)^{12} - \left( \sigma_{ab}^T / r \right)^6 \right], \quad (21)$$

where

$$\sigma_{ab} = \sigma_{ab}^T / \sigma_{ab} = F_{ab}^{1/6}, \quad (22a)$$

$$\epsilon_{ab} = \epsilon_{ab}^T / \epsilon_{ab} = X_{ab}^e / F_{ab}^2, \quad (22b)$$

with

$$F_{ab} = X_{ab} / Y_{ab}, \quad (23)$$

$$X_{ab}^e = X_{ab} - \alpha_{ab} (10F_{ab} - 22) (1 - (2F_{ab})^{-1/3}), \quad (24)$$

and

$$\alpha_{ab} = \Lambda_{ab}^{*2} / 8\pi^2 T_{ab}^*. \quad (25)$$

When the quantum effect is small,  $\alpha_{ab}$  is small and  $X_{ab}^e$  is approximated as

$$X_{ab}^e = X_{ab}$$

giving

$$\epsilon_{ab} = X_{ab} / F_{ab}^2, \quad (26)$$

as given for one component fluid [5].

Thus, the effective pair potential is expressed as the 'modified' LJ (12-6) form by simply replacing

$$\sigma_{ab} \rightarrow \sigma_{ab}^T(T_{ab}^*, \Lambda_{ab}^*, \delta_{ab}^*),$$

$$\epsilon_{ab} \rightarrow \epsilon_{ab}^T(T_{ab}^*, \Lambda_{ab}^*, \delta_{ab}^*).$$

The advantage of this approach is that once the effects of angle-dependent potential and/or quantum effects are incorporated in  $\sigma_{ab}^T$  and  $\epsilon_{ab}^T$ , the system can be treated as the classical LJ (12-6) fluid mixture.

#### 4. Thermodynamic properties of semiclassical fluid mixture

In this section, we apply our theory to calculate the thermodynamic properties of semiclassical molecular binary mixtures like  $H_2 + D_2$ ,  $H_2 + Ne$ ,  $D_2 + Ne$ ,  $N_2 + Ar$ ,  $O_2 + Ar$  and  $N_2 + O_2$ . In our approach, we consider the reduced density and reduced temperature for the LJ (12-6) fluid to be given by

$$\rho_{ab}^* = \rho \sigma_{ab}^3,$$

$$: kT / \epsilon_{ab},$$

and replace  $\rho_{ab}^*$  and  $T_{ab}^*$ , respectively, by

$$\rho_{ab}^{T*} = \rho \sigma_{ab}^{T3} = \rho_{ab}^* \delta_{ab}^3,$$

$$T_{ab}^{T*} = kT / \epsilon_{ab}^T = T_{ab}^* / \hat{\epsilon}_{ab}.$$

Then the free energy and pressure of the semiclassical molecular fluid mixture can be given by

$$A(\rho_{ab}^*, T_{ab}^*, \delta_{ab}^*) = A_{LJ}(\rho_{ab}^*, T_{ab}^*) - \sum_a x_a (d_{aa}^{*2} / 24\pi^2 T_{ab}^*), \quad (27)$$

$$P(\rho_{ab}^*, T_{ab}^*, \Lambda_{ab}^*, \delta_{ab}^*) = P_{LJ}(\rho_{ab}^{T*}, T_{ab}^{T*}), \quad (28)$$

where  $A_{LJ}$  and  $P_{LJ}$  are, respectively, the free energy and pressure of the classical LJ (12-6) fluid mixture at the reduced density  $\rho_{ab}^{T*}$  and reduced temperature  $T_{ab}^{T*}$ . Here  $x_a = N_a / N$  is the concentration of species  $a$ .

Eqs. (27) and (28) are the general expressions for a molecular fluid mixture.

#### 5. Binary mixtures

We apply this theory to binary mixtures such as (i)  $N_2 + Ar$ ,  $O_2 + Ar$  and  $N_2 + O_2$  and (ii)  $H_2 + Ne$ ,  $D_2 + Ne$  and  $H_2 + D_2$ . In the first case, the quantum effects are small but negligible. In the second case, the quantum effects are appreciable and play an important role in estimating the thermodynamic properties of the systems. The force and quantum parameters for these systems are those used previously [8,11].

The unlike force parameters  $\sigma_{12}$ ,  $\epsilon_{12}$  and  $D_{12}$  of the species 1 and 2 are given by the following combination rules

$$\sigma_{12} = (\sigma_{11} + \sigma_{22})/2, \quad (29a)$$

$$\epsilon_{12} = \xi_{12} (\epsilon_{11} \epsilon_{22})^{1/2}, \quad (29b)$$

$$D_{12} = (D_{11} + D_{22})/2, \quad (29c)$$

where  $\xi_{12}$  is an adjustable parameter, which is less than unity. We have used the value of  $\xi_{12}$  obtained from the measurement of second virial coefficient [12]. The quantum parameters  $\Lambda_{ab}^*$  and  $\delta_{ab}^*$  of molecules of unlike species are obtained by the following combination rule [8]

$$\epsilon_{12} \sigma_{12}^2 = [\epsilon_{11} \sigma_{11}^2 \Lambda_{11}^{*2} \epsilon_{22} + \sigma_{22}^2 \Lambda_{22}^{*2}] / 2, \quad (30a)$$

$$\epsilon_{12} \delta_{12}^{*2} = [\epsilon_{11} \delta_{11}^{*2} + \epsilon_{22} \delta_{22}^{*2}] / 2. \quad (30b)$$

We adopt the van der Waals one (vdW1) fluid theory of mixture [13] to calculate the thermodynamic properties of the effective LJ (12-6) fluid mixture. This theory approximates the properties of a mixture by those of a fictitious pure fluid with the interaction parameters

$$\sigma_x^{T^3} = \sum_{a,b} x_a x_b \sigma_{ab}^{T^3}, \quad (31)$$

$$\epsilon_x^T \sigma_x^{T^3} = \sum_{a,b} x_a x_b \epsilon_{ab}^T \sigma_{ab}^{T^3}, \quad (32)$$

where  $\sigma_{ab}^T$  and  $\epsilon_{ab}^T$  are the force parameters of the effective LJ (12-6) potential of binary mixture of species  $a$  and  $b$ .

In the vdW1 fluid theory of mixture, the free energy, enthalpy and pressure of the effective LJ fluid mixture are given by

$$A_{LJ} = A_x + NkT \sum_a x_a \ln x_a + \text{second order term}, \quad (33)$$

$$H_{LJ} = H_x + \text{second order term}, \quad (34)$$

$$P_{LJ} = P_x + \text{second order term}, \quad (35)$$

where  $A_x$ ,  $H_x$  and  $P_x$  are the values of the free energy, enthalpy and pressure for the pure fluid containing  $N$  molecules in volume  $V$  and temperature  $T$ , whose molecules interact *via* the effective LJ (12-6) potential with the parameters  $\sigma_x^T$  and  $\epsilon_x^T$ .

In this work, we are interested to calculate the thermodynamic properties at zero pressure, for which simple expressions are available. We calculate  $A_x$ ,  $H_x$  and  $V_x$  at zero pressure using the relations given by Grundke *et al* [14].

## 6. Results and discussion

We employ the theory developed in the previous sections to calculate the thermodynamic properties of binary mixtures such as  $N_2 + Ar$ ,  $O_2 + Ar$  and  $N_2 + O_2$  at zero pressure (*i.e.*  $P = 0$ ), where the quantum effects are small but not negligible. We first calculate the effective parameters  $\sigma^T$  and  $\epsilon^T$ , which include the quantum effects as well as the effect of the angle-dependent part of potential. We use these parameters to calculate the thermodynamic properties of the effective LJ (12-6) mixture at zero pressure both in classical (CI) and semiclassical (SCI) limits.

The calculated CI and SCI values of Gibb's function, enthalpy and molar volume are reported in Table 1 for

**Table 1.** Gibb's free energy, enthalpy and molar volume of the binary mixture at  $P = 0$  and  $x_1 = x_2 = 0.5$

Mixture	$T(K)$	$G/(J\text{-mol}^{-1})$	$H/(J\text{-mol}^{-1})$	$V/(\text{cm}^3\text{-mol}^{-1})$	
$N_2 + Ar$	83.82	CI	-3171.76	-5291.10	31.81
		SCI	-3123.55	-5220.25	32.14
	Singh-Sinha [8]		-3106.44	-5180.51	32.50
		MD [15]		-5455.00	31.99
$O_2 + Ar$	83.82	CI	-3702.76	-6055.62	27.57
		SCI	-3652.40	-5983.64	28.82
	Singh-Sinha [8]		-3590.63	-5903.23	28.21
		MD [15]		-6304.00	27.61
$N_2 + O_2$	83.82	CI	-3265.16	-5427.43	31.26
		SCI	-3204.19	-5338.53	31.65
	Singh-Sinha [8]		-3178.00	-5298.98	32.16

$N_2 + Ar$ ,  $O_2 + Ar$  and  $N_2 + O_2$  at  $T = 83.82$  K for  $P = 0$  and  $x_1 = x_2 = 0.5$ . Singh and Sinha [8] have studied the properties of these mixtures by treating them semiclassically and using the perturbation theory. These values are also shown in the table. The molecular dynamic (MD) values of  $N_2 + Ar$  and  $O_2 + Ar$ , obtained by Gupta and Coon [15] are demonstrated in the table for comparison. The agreement is found to be good. Further comparing the classical and semiclassical values, we find that the quantum effects increase the thermodynamic properties.

In Table 2, we have reported the excess Gibb's function  $G^E$ , excess enthalpy  $H^E$  and excess molar volume  $V^E$  at zero pressure for  $N_2 + Ar$  and  $O_2 + Ar$  at  $T = 83.82$  K and  $x_1 = x_2 = 0.5$  along with the experimental [8,16] values. The results obtained by Singh and Sinha [8] are

**Table 2.** Excess thermodynamic properties of binary mixtures at  $P = 0$  and  $x_1 = x_2 = 0.5$ .

System	$T(K)$	$G^E/(J\text{-mol}^{-1})$	$H^E/(J\text{-mol}^{-1})$	$V^E/(\text{cm}^3\text{-mol}^{-1})$	
$N_2 + Ar$	83.82	Present work	35.80	41.30	-0.20
		Singh-Sinha [8]	32.79	37.97	-0.26
		Expt. [8,16]	34.00	51.00	-0.18
$O_2 + Ar$	83.82	Present work	32.04	45.42	0.11
		Singh-Sinha [8]	52.60	75.74	0.10
		Expt. [8,16]	37.00	60.00	0.14

also shown in the table. We find that the agreement with the experimental results is good.

We next apply the theory to calculate the thermodynamic properties of the binary mixtures such as  $H_2 + Ne$  and  $D_2 + Ne$  at zero pressure (*i.e.*  $P = 0$ ), where the quantum effects are appreciable. The quantum effects for  $H_2$  and  $D_2$  are large. For better results, the parameters  $\sigma^T$  and  $\epsilon^T$  for  $H_2$ ,  $D_2$  and  $D_2 + Ne$  are calculated without the shape parameter  $D$  and those for  $H_2 + Ne$  with parameter  $D$ . We calculate the excess Gibb's function  $G^E$  and excess enthalpy  $H^E$  for  $H_2 + Ne$  at  $T = 30$  °K and for  $D_2 + Ne$  at  $27$ °K at  $P = 0$  and  $X_1 = X_2 = 0.5$ . We calculate these properties with and without shape parameter  $D$ . These results are reported in Table 3, where the experimental results [17] are also shown for comparison. The agreement with the experimental values is good.

**Table 3.** Excess thermodynamic properties of binary mixtures at  $P = 0$  and  $x_1 = x_2 = 0.5$ .

System	$T(K)$	$G^E(J\text{-mol}^{-1})$	$H^E(J\text{-mol}^{-1})$
$H_2 + Ne$	30.0 Present work	121.33	205.32
	Expt. [17]	121	208
$D_2 + Ne$	27.0 Present work	101.65	159.74
	Expt. [17]	104	165

Next, we apply the theory for the binary mixture  $H_2 + D_2$  where the quantum effects are large. In order to test the theory, we calculate the properties whose experimental results are available for comparison. We have calculated the thermodynamic properties of  $H_2$  and  $D_2$  [5] for a range of temperatures where the agreement is good. Here, we calculate the molar volume  $V$  of  $H_2$  and  $D_2$  at  $T = 20.4$  K for  $P = 0$ , with and without the shape parameter  $D$ . These results are compared with the experimental data [18] in Table 4. The results with  $D$  are better. We

**Table 4.** Molar volume  $V(\text{cm}^3\text{mol}^{-1})$  of  $H_2$  and  $D_2$  for  $P = 0$ .

System	$T(K)$	Theory		Expt [18]
		Without $D$	With $D$	
$H_2$	20.4	22.56	25.10	28.40
$D_2$	20.4	19.51	20.36	23.63

calculate the excess molar volume  $V^E$  for  $H_2 + D_2$  mixture at  $T = 20.4$  K for  $P = 0$  for  $x_1 = x_{H_2} = 0.264, 0.434$  and  $0.698$  with and without  $D$ . They are compared with experimental data [18] in Table 5. The agreement is relatively good where  $D$  is taken into account.

**Table 5.** Excess molar volume  $V^E(\text{cm}^3\text{mol}^{-1})$  of binary mixture  $H_2 - D_2$  for  $P = 0$ .

System	$T(K)$	$x_{H_2}$	Theory		Expt [18]
			Without $D$	With $D$	
$H_2 + D_2$	20.4	0.264	-0.022	0.021	-0.109
		0.434	-0.002	-0.064	-0.147
		0.698	0.029	-0.091	-0.109

## 7. Summary

We have extended the theory developed previously [4,5,19] for one-component molecular fluid in the semiclassical limit, to the molecular fluid mixtures. We have obtained the effective pair potential in the LJ (12-6) potential form by simply replacing  $\sigma_{ab} \rightarrow \sigma_{ab}^T(T_{ab}^*, \Lambda_{ab}^*, \delta_{ab}^*)$  and  $\epsilon_{ab} \rightarrow \epsilon_{ab}^T(T_{ab}^*, \Lambda_{ab}^*, \delta_{ab}^*)$ , where  $T_{ab}^*$  is the reduced temperature, and  $\Lambda_{ab}^*$  and  $\delta_{ab}^*$  are the quantum parameters. Thus, the quantum effects and effects of angle-dependent interactions are incorporated through the expressions of the effective diameter  $\sigma_{ab}^T$  and well depth  $\epsilon_{ab}^T$ . In this process the problem is simplified and the semiclassical molecular fluid mixtures becomes equivalent to the classical LJ (12-6) fluid mixture.

In this development, we have considered the first order quantum corrections to define the effective LJ (12-6) potential. So the effective LJ (12-6) potential, thus defined, is suitable in general, when the quantum effects are small. However, the theory provides good results for the binary mixture like  $H_2 + Ne$ ,  $D_2 + Ne$  and  $H_2 + D_2$ , where the quantum effects are large. This is probably due to the facts that the influence of quantum effects and angle-dependent interactions are opposite in nature [5,19]. So with the proper selection of the angle-dependent interactions, one can employ this theory for the systems of appreciable quantum effects at low temperature.

One can improve the theory by considering the higher order quantum correction terms to define the effective pair potential. The second order correction term of  $O(\hbar^4)$  is of opposite sign [20]. When this is taken into account to define the effective pair potential, its effect is opposite in nature in comparison to the first order term *i.e.* it decreases the effective diameter and increases the well-depth. Hence one can improve the results by considering the second order term in defining the effective pair potential. However no such attempt has been made in this paper. This method can be employed to  $H_2 + He$  mixture at high temperature, where the quantum effects are small. However this method is not suitable for this system at

low temperature, where the quantum effects are large. He molecules interact via the central potential only. 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 [21].

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Appendix-A

In this Appendix, expressions for the coefficients  $A_{ab}^m$  appearing in the right hand side of eq. (10) are given as

$$A_{ab}^5 = -(1/960\pi^2 T_{ab}^*) (Q_a Q_b / \epsilon_{ab} \sigma_{ab}^5) \delta_{ab}^{*2}, \quad (A.1)$$

$$A_{ab}^6 = \left[ 1 + (1/4) \left( (\alpha_a \mu_b^2 + \alpha_b \mu_a^2) / \epsilon_{ab} \sigma_{ab}^6 \right) + (1/12 T_{ab}^*) (\mu_a^2 \mu_b^2 / \epsilon_{ab}^2 \sigma_{ab}^6) \right]$$

$$+ (1/144\pi^2 T_{ab}^*) (\mu_a^2 \mu_b^2 / \epsilon_{ab}^2 \sigma_{ab}^6) \delta_{ab}^{*2}, \quad (A.2)$$

$$A_{ab}^8 = \left[ (3/8) \left( (\alpha_a Q_b^2 + \alpha_b Q_a^2) / \epsilon_{ab} \sigma_{ab}^8 \right) + (1/8 T_{ab}^*) \left( (\mu_a^2 Q_b^2 + \mu_b^2 Q_a^2) / \epsilon_{ab}^2 \sigma_{ab}^8 \right) \right] + (1/8\pi^2 T_{ab}^*) \left[ (5/4) \left( (\alpha_a \mu_b^2 + \alpha_b \mu_a^2) / \epsilon_{ab} \sigma_{ab}^6 \right) + (1/6 T_{ab}^*) (\mu_a^2 \mu_b^2 / \epsilon_{ab}^2 \sigma_{ab}^2) \right] \Lambda^{*2} + (1/1920\pi^2 T_{ab}^{*2}) \left( (\mu_a^2 Q_b^2 + \mu_b^2 Q_a^2) / \epsilon_{ab}^2 \sigma_{ab}^8 \right) \delta_{ab}^2, \quad (A.3)$$

$$A_{ab}^{10} = (7/20 T_{ab}^{*2}) (Q_a^2 Q_b^2 / \epsilon_{ab}^2 \sigma_{ab}^{10}) + (1/8\pi^2 T_{ab}^*) \left[ (7/2) \left( (\alpha_a Q_b^2 + \alpha_b Q_a^2) / \epsilon_{ab} \sigma_{ab}^8 \right) + (1/2 T_{ab}^*) \left( (\mu_a^2 Q_b^2 + \mu_b^2 Q_a^2) / \epsilon_{ab}^2 \sigma_{ab}^8 \right) \right] \Lambda^{*2} + (53/3240\pi^2 T_{ab}^*) (Q_a^2 Q_b^2 / \epsilon_{ab}^2 \sigma_{ab}^{10}) \delta_{ab}^{*2}, \quad (A.4)$$

$$A_{ab}^{11} = (1/5 T_{ab}^*) (Q_a Q_b / \epsilon_{ab} \sigma_{ab}^5) \left[ (36/5) K_a K_b + (1/T_{ab}^*) (\mu_a^2 \mu_b^2 / \epsilon_{ab}^2 \sigma_{ab}^6) \right] \quad (A.5)$$

$$A_{ab}^{12} = \left[ - (2/5 T_{ab}^*) \left\{ (K_a^2 + K_b^2 + (19/5) K_a^2 K_b^2) + (1/2) (\alpha_a K_a \mu_b^2 + \alpha_b K_b \mu_a^2) / \epsilon_{ab} \sigma_{ab}^6 \right\} \left( 1 + (1/2) (K_a + K_b) + 3.8 K_a K_b \right) \right] + (7/1800 T_{ab}^{*3}) (\mu_a^4 \mu_b^4 / \epsilon_{ab}^4 \sigma_{ab}^{12}) - (7/24\pi^2 T_{ab}^{*2}) (Q_a^2 Q_b^2 / \epsilon_{ab}^2 \sigma_{ab}^{10}) \Lambda_{ab}^{*2} + (1/20\pi^2 T_{ab}^{*2}) \left[ (K_a^2 + K_b^2 + (38/5) K_a^2 + K_b^2) \right] \delta_{ab}^{*2}, \quad (A.6)$$

$$A_{ab}^{13} = - (1 - T_{ab}^{*2}) (6/35) (\mu_a \mu_b Q_a^2 Q_b^2 / \epsilon_{ab}^3 \sigma_{ab}^{13}) + (3/4\pi^2) (Q_a Q_b / \epsilon_{ab} \sigma_{ab}^5) (K_a + K_b) \Lambda_{ab}^{*2}, \quad (A.7)$$

$$A_{ab}^{14} = - (24/35 T_{ab}^*) (\alpha_a K_a Q_a^2 + \alpha_b K_b Q_b^2) / \epsilon_{ab} \sigma_{ab}^8$$

$$\begin{aligned}
 & - (1/4\pi^2 T_{ab}^{*2}) \left[ 2(K_a^2 + K_b^2 + (19/5)K_a^2 K_b^2) \right. \\
 & \left. - (1/20) \left( (\alpha_a K_a \mu_b^2 + \alpha_b K_b \mu_a^2) / \epsilon_{ab} \sigma_{ab}^6 \right) \right] \\
 & \Lambda_{ab}^{*2} + (3/140\pi^2 T_{ab}^{*2}) (\alpha_a K_a Q_b^2 \\
 & + \alpha_b K_b Q_a^2) / \epsilon_{ab} \sigma_{ab}^8 \delta_{ab}^{*2}, \tag{A.8}
 \end{aligned}$$

$$A_{ab}^{15} = (18/245 T_{ab}^{*2}) (Q_a^3 Q_b^3 / \epsilon_{ab}^3 \sigma_{ab}^{15}) \tag{A.9}$$

$$A_{ab}^{16} = - (43/50\pi^2 T_{ab}^{*2}) \left[ (\alpha_a K_a Q_b^2 \alpha_b K_b Q_b^2) / \epsilon_{ab} \sigma_{ab}^8 \right] \Lambda_{ab}^{*2}, \tag{A.10}$$

$$\begin{aligned}
 A_{ab}^{18} &= (2/5 T_{ab}^{*2}) D_{ab} \left[ 4(K_a + K_b) + (\alpha_a \mu_b^2 + \alpha_b \mu_a^2) \right. \\
 & \left. \epsilon_{ab} \sigma_{ab}^6 \right] + (1/10\pi^2 T_{ab}^{*2}) D_{ab} (K_a + K_b) \delta_{ab}^{*2}, \tag{A.11}
 \end{aligned}$$

$$\begin{aligned}
 A_{ab}^{20} &= (24/35 T_{ab}^{*2}) \left( (\alpha_a Q_b^2 + \alpha_b Q_a^2) / \epsilon_{ab} \sigma_{ab}^8 \right) D_{ab} \\
 & + (27/20\pi^2 T_{ab}^{*2}) D_{ab} \left[ 4(K_a + K_b) + (\alpha_a \mu_b^2 + \alpha_b \mu_a^2) \right. \\
 & \left. \epsilon_{ab} \sigma_{ab}^6 \right] \Lambda_{ab}^{*2} + (3/35\pi^2 T_{ab}^{*2}) \left[ (\alpha_a Q_b^2 - \alpha_b Q_a^2) / \right. \\
 & \left. \epsilon_{ab} \sigma_{ab}^8 \right] D_{ab} \delta_{ab}^{*2}, \tag{A.12}
 \end{aligned}$$

$$\begin{aligned}
 A_{ab}^{22} &= (94/35\pi^2 T_{ab}^{*2}) \left[ (\alpha_a Q_b^2 + \alpha_b Q_a^2) / \epsilon_{ab} \sigma_{ab}^8 \right] D_{ab} \\
 & \Lambda_{ab}^{*2}, \tag{A.13}
 \end{aligned}$$

$$A_{ab}^{24} = - (16/5 T_{ab}^{*2}) D_{ab}^2 + (2/5\pi^2 T_{ab}^{*2}) D_{ab}^2 \delta_{ab}^{*2}, \tag{A.14}$$

$$A_{ab}^{26} = - (88/5\pi^2 T_{ab}^{*2}) D_{ab}^2 \Lambda_{ab}^{*2}. \tag{A.15}$$

**Appendix-B**

In this Appendix, we give expressions for coefficients  $a_{ab}$  ...  $f_{ab}$ , appearing in the right hand side of eqs. (19) and (20). Thus,

$$\begin{aligned}
 a_{ab} &= 1 + (1/4) \left( (\alpha_a \mu_b^2 + \alpha_b \mu_a^2) / \epsilon_{ab} \sigma_{ab}^6 \right) + (3/8(2^{1/3})) \\
 & \left( (\alpha_a Q_b^2 + \alpha_b Q_a^2) / \epsilon_{ab} \sigma_{ab}^8 \right), \tag{B.1}
 \end{aligned}$$

$$b_{ab} = \left[ (1/12) (\mu_a^2 \mu_b^2 / \epsilon_{ab}^2 \sigma_{ab}^6) + (1/8(2^{1/3})) (\mu_a^2 Q_b^2 \right.$$

$$\begin{aligned}
 & \left. + \mu_b^2 Q_a^2) / \epsilon_{ab}^2 \sigma_{ab}^8 \right] + (7/20(2^{2/3})) (Q_a^2 Q_b^2 / \\
 & \epsilon_{ab}^2 \sigma_{ab}^{10}) + (\Lambda_{ab}^{*2} / 8\pi^2) \left[ 5 + (5/2^{7/3}) \left( (\alpha_a \mu_b^2 \right. \right. \\
 & \left. \left. + \alpha_b \mu_a^2) / \epsilon_{ab} \sigma_{ab}^6 \right) + (7/2^{5/3}) \left( (\alpha_a Q_b^2 + \alpha_b Q_a^2) / \right. \right. \\
 & \left. \left. \epsilon_{ab} \sigma_{ab}^8 \right) \right] + (\delta_{ab}^{*2} / 8\pi^2) \left[ - (2^{1/6} / 120) \right. \\
 & \left. (Q_a Q_b / \epsilon_{ab} \sigma_{ab}^5) \right], \tag{B.2}
 \end{aligned}$$

$$\begin{aligned}
 c_{ab} &= (\Lambda_{ab}^{*2} / 8\pi^2) \left[ (1/6(2^{1/2})) (\mu_a^2 \mu_b^2 / \epsilon_{ab}^2 \sigma_{ab}^2) \right. \\
 & \left. + (1/2^{5/3}) \left( (\mu_a^2 Q_b^2 + \mu_b^2 Q_a^2) / \epsilon_{ab}^2 \sigma_{ab}^8 \right) \right] \\
 & + (\delta_{ab}^{*2} / 8\pi^2) \left[ (1/18) (\mu_a^2 \mu_b^2 / \epsilon_{ab}^2 \sigma_{ab}^6) \right. \\
 & \left. + (1/240(2^{1/3})) (\mu_a^2 Q_b^2 + \mu_b^2 Q_a^2) / \epsilon_{ab}^2 \sigma_{ab}^8 \right) \\
 & \left. + (53/405(2^{2/3})) (Q_a^2 Q_b^2 / \epsilon_{ab}^2 \sigma_{ab}^{10}) \right], \tag{B.3}
 \end{aligned}$$

$$\begin{aligned}
 d_{ab} &= \left[ - (2/5) (K_a^2 + K_b^2 + (19/5)K_a^2 K_b^2) - (4/5) D_{ab}^2 \right. \\
 & \left. + (4/5) D_{ab} (K_a + K_b) + (1/5) \right. \\
 & \left. \times (\alpha_a \mu_b^2 + \alpha_b \mu_a^2) / \epsilon_{ab} \sigma_{ab}^6 \right] D_{ab} \\
 & + (12/35(2^{1/3})) \left( (\alpha_a Q_b^2 + \alpha_b Q_a^2) / \epsilon_{ab} \sigma_{ab}^8 \right) D_{ab} \\
 & - (1/5) \left( (\alpha_a K_a \mu_b^2 + \alpha_b K_b \mu_a^2) / \epsilon_{ab} \sigma_{ab}^6 \right) \\
 & \times \left( 1 + (1/2)(K_a + K_b) + 3.8K_a K_b \right), \\
 & - (12/35(2^{1/2})) \left( (\alpha_a K_a Q_b^2 + \alpha_b K_b Q_a^2) / \right. \\
 & \left. \epsilon_{ab} \sigma_{ab}^8 \right) + (36(2^{1/2}) / 25) (Q_a Q_b / \epsilon_{ab} \sigma_{ab}^5) K_a K_b \\
 & \left. + (1/4\pi^2) \Lambda_{ab}^{*2}, \tag{B.4}
 \end{aligned}$$

$$\begin{aligned}
 e_{ab} &= \left[ 2^{1/6} / 5 \right] (\mu_a^2 \mu_b^2 Q_a Q_b / \epsilon_{ab}^3 \sigma_{ab}^{11}) \\
 & + (6/35(2^{1/6})) \left( (\mu_a^2 \mu_b^2 Q_a^2 Q_b^2 / \epsilon_{ab}^3 \sigma_{ab}^{13}) \right. \\
 & \left. + (18/245(2^{1/2})) (Q_a^3 Q_b^3 / \epsilon_{ab}^3 \sigma_{ab}^{15}) \right]
 \end{aligned}$$



$$\begin{aligned}
 & + (\Lambda_{ab}^{*2} / \pi^2) \left[ - (7/24) (Q_a^2 Q_b^2 / \epsilon_{ab}^2 \sigma_{ab}^{10}) \right. \\
 & - (1/2^{4/3}) (K_a^2 + K_b^2 + (19/5) K_a^2 K_b^2) \\
 & - (22/5 (2^{1/3})) D_{ab}^2 + (27/10 (2^{1/3})) D_{ab} (K_a + K_b) \\
 & - (1/80 (2^{1/3})) (\alpha_a K_a \mu_b^2 + \alpha_b K_b \mu_a^2) / (\epsilon_{ab} \sigma_{ab}^6) \\
 & \left. - (43/50 (2^{2/3})) (\alpha_a K_a \mu_b^2 + \alpha_b K_b \mu_a^2) / (\epsilon_{ab} \sigma_{ab}^8) \right] \\
 & + (3/32 (2^{1/6})) (Q_a Q_b / \epsilon_{ab} \sigma_{ab}^5) K_a K_b \\
 & + (\delta_{ab}^{*2} / \pi^2) \left[ (1/20) (K_a^2 + K_b^2 + (38/5) K_a^2 K_b^2) \right. \\
 & + (1/10) D_{ab}^2 + (1/20) D_{ab} (K_a + K_b) \\
 & + (3/(140 (2^{1/3})) (\alpha_a K_a Q_b^2 + \alpha_b K_b Q_a^2) / \epsilon_{ab} \sigma_{ab}^8) \\
 & \left. + (3/70 (2^{1/3})) (\alpha_a Q_b^2 + \alpha_b Q_a^2) / \epsilon_{ab} \sigma_{ab}^8) D_{ab} \right], \quad (B.5)
 \end{aligned}$$

$$f_{ab} = (7/800) (\mu_a^4 \mu_{ab}^4 \sigma_{ab}^{12}). \quad (B.6)$$