Equilibrium and transport properties of semiclassical Lennard-Jones fluids

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Abstract : We compute the quantum effects on the equilibrium and transport properties of the Lennard-Jones (LJ) (12-6) system. We develop an effective LJ (12-6) potential, which includes the quantum effects through the expressions of the effective diameter $\sigma\sim$ and well depth $c\sim$ We employ this theory to calculate the quantum effects on some equilibrium and transport properties of the fluids In all these cases the agreement· is found to be qualitatively and sometime quantitatively good.

1. Introduction

In the present paper, we investigate the efluence of quantum effects on the equilibrium and transport properties of nearly classical fluids, whose molecules interact via a Lennard Jones (LJ) (12-6) potential. The quantum features (excluding those due to the exchange effects) may be included in an effective pair potential [1,2] which may be functions of temperature T and thermal wavelength λ This effective pair potential can be expressed in the LJ (12-6) form [3-5] Young [3] derived an effective LJ (12-6) potential. However, his approach is not based on the well-defined mathematical procedure. Singh and Sinha [4], using the Wigner-Kirkwood expansion approach [1], obtained the effective LJ (12-6) potential.

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In the present work, we employ the effective LJ (12-6) potential given by Singh and Sinha [4] to calculate the quantum correction to the equilibrium and transport properties of fluids.

2. Basic theory

We consider a fluid, whose molecules interact via the LJ (12-6) potential

$$u(r) = 4\epsilon [(\sigma/r)^{12} - (\sigma/r)^6] \tag{1}$$

where ϵ represents the well-depth and σ the diameter of the molecules. For such a model, the effective pair potential $u\sim(r)$ can be expressed in the LJ (12-6) form by simply replacing $\sigma \rightarrow \sigma\sim (T^*,\Lambda^*)$ and $\epsilon \rightarrow \epsilon\sim (T^*,\Lambda^*)$ in Eq (1), where $T^* = kT/\epsilon$ is the reduced temperature and $\Lambda^* = h/\sigma(m\epsilon)^{1/2}$ is a quantum parameter (where m is the mass of a molecule). Λ^* is a measure of a ratio of the de Broglie wavelength of the relative kinetic energy ϵ, to the diameter σ of the molecule. It is introduced to measure the deviation from the classical behavior. Explicit expressions for $\sigma\sim$ and $\epsilon\sim$ are given by [4,5].

$$\sigma^\Lambda \equiv \sigma\sim/\sigma = [1 + X]^{1/6} \tag{2}$$

$$\epsilon^\Lambda \equiv \epsilon\sim/\epsilon = [1 + 2X - 0.56026X (1+X)^{-1/3}] (1+X)^{-2} \tag{3}$$

where $X = 17 \Lambda^{*2} / 8 \pi^2 T^*$.

This shows that $\sigma\sim$ and $\epsilon\sim$, which depends on X, are function of the reduced temperature T^* and quantum parameter Λ^*. Thus, the effective pair potential can be expressed as the 'modified' LJ (12-6) form in terms of $\sigma\sim$ and $\epsilon\sim$. Then the system may be treated as classical

3. Critical point location

In this section, we consider the influence of the quantum effects on the critical temperature T_c, critical volume V_c and critical pressure P_c For a purely classical system interacting via the LJ (12-6) potential, they are given by

$$T_c^* = kT_c/\epsilon = 1.26 \tag{4a}$$

$$V_c^* = V_c/N \sigma^3 = 3.1 \tag{4b}$$

$$P_c^* = P_c\sigma^3/\epsilon = 0.117 \tag{4c}$$

The quantum effects on the critical constants may be taken into account by replacing $\epsilon \to \epsilon\sim$ and $\sigma \to \sigma\sim$ in Eq.(4). Thus

$$T_c^* = 1.26 \, \epsilon^\wedge \tag{5a}$$

$$V_c^* = 3.1 \, \sigma^{\wedge 3} \tag{5b}$$

$$P_c^* = 0.117 \, \epsilon^\wedge / \sigma^{\wedge 3} \tag{5c}$$

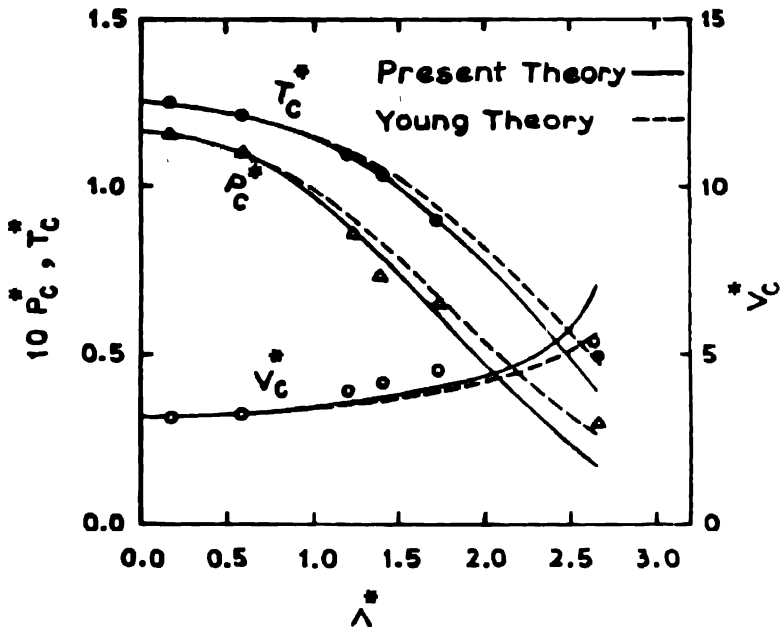Eq.(5a) may be solved by the interative process. Knowing T_c^*, one may obtain V_c^* and P_c^*

Fig.1. The reduced critical constants T_c^*, V_c^* and P_c^* as a function of the quantum parameter Λ^*. The points (O T_c^*, Δ P_c^* and O V_c^*) represents the experimental values.

In order to test the accuracy of our theory, we compare the results in Fig.1 with experimental data as well as those of Young [3], who calculated the results using his expressions for $\sigma\sim$ and $\epsilon\sim$. The agreement is good for $\Lambda^* \leq 1$ better than those of Young. The agreement decreases with the increase of Λ^*.

4. Liquid-gas coexistence curve

In this section, we apply our theory to estimate the quantum effects on the behaviour of the liquid-gas coexistence curve. The behaviour of a classical liquid may be described by the following equations [6].

$$V_c^* / V_l^* = 1 + (3/4)(1 - T^*/T_c^*) + (7/4)(1 - T^*/T_c^*)^{1/3} \qquad (6)$$

$$V_c^* / V_g^* = 1 + (3/4)(1 - T^*/T_c^*) - (7/4)(1 - T^*/T_c^*)^{1/3} \qquad (7)$$

where V_l^*, V_g^* and V_c^* are the reduced liquid, gas and critical molar volume These equations show the behaviour of V_c^* / V_l^* and V_c^* / V_g^* for $T^*/T_c^* \leq 1$. These equations represents the behaviour of purely classical fluid, where $T_c^* = 1 \, 26$ and $V_r^* = 3.1$

When the quantum effects are introduced, Eq.(6) and (7) take the form [3]

$$V_c^* / V_l^* = (\sigma_c^\wedge / \sigma^\wedge)^3 [1 + (3/4)(1 - T^{\sim*}/1.26) + (7/4)(1 - T^{\sim*}/1.26)^{1/3}] \qquad (8)$$

$$V_c^* / V_g^* = (\sigma_c^\wedge / \sigma^\wedge)^3 [1 + (3/4)(1 - T^{\sim*}/1.26) - (7/4)(1 - T^{\sim*}/1.26)^{1/3}] \qquad (9)$$

where $\sigma_c^\wedge$ is the value of $\sigma^\wedge$ at $T^* = T_c^*$ and $T^{\sim*} = T^*/\epsilon^\wedge$.
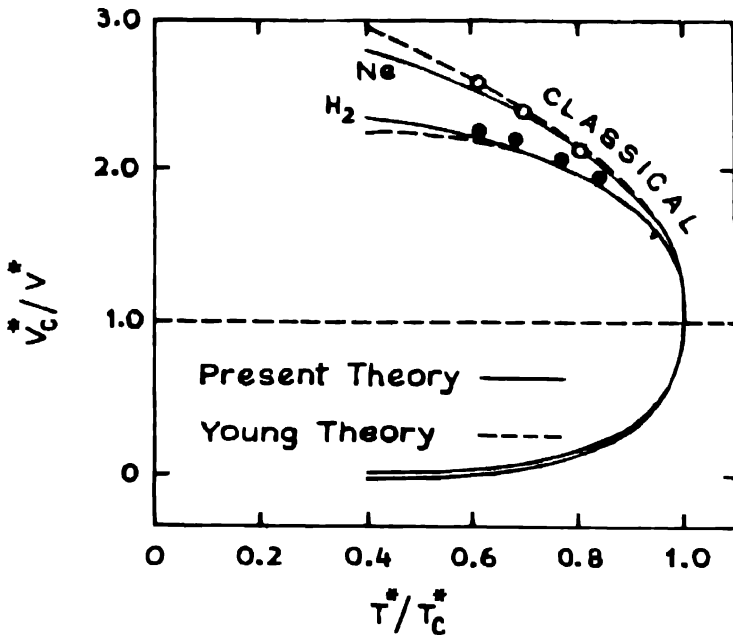

Fig.2. The values of V_c^* / V^* as a function of T^*/T_c^* along the Liquid-gas coexistence curves. Experimental points are for Ne (O) and H_2(O).

The values of V_c^*/N^* for Ar (classical), Ne and H_2 are demonstrated in Fig.2 along with Young's the experimental data for Ne and H_2. The qualitative and somtime quantitative agreement is good. For Ne, our results are not distinguishable from those of Young in figure. For H_2, it is better than Young.

5. Trabsport properties

In this section, we apply our theory to study the quantum effects on the transport properties (TP's) such as shear viscosity μ and thermal conductivity λ of the fluids. The basic ideal of the present approach is that the structure of a dense fluid is very similar to that of a hard sphere (HS) fluid of properly chosen effective hard sphere diameter d. We employ the revised Enskog theory (RET) of Beijener and Ernst [7] to estimate μ and Λ of the HS fluid In terms of the packing fraction n, they are given by

$$\mu = [g_{HS}(d)]^{-1} [1 + (4/5) L + 0.7615 L^2] \mu_0 \qquad (10)$$

$$\lambda = [g_{HS}(d)]^{-1} [1 + (6/5) L + 0.7575 L^2] \lambda_0 \qquad (11)$$

where $L = 4 n g_{HS}(d)$, $\mu_0 = (5/16 \pi d^2) (\pi m k T)^{1/2}$ and $\lambda_0 = (75 k / 64 \pi d^2) (\pi k T/m)^{1/2}$. Here $n = \pi \rho d^3/6$ and $g_{HS}(d)$ is the radial distribution function (RDF) of the HS fluid at the contact.

The hard sphere diameter d and RDF $g_{HS}(d)$ may be obtained from the experimental values of the second virial coefficient and equation of state, respectively [8]. In the present case the diameter d is determined by the Verlet-Weis method [9] and equilibrium RDF $g_{HS}(d)$ is given by [10]

$$g_{HS}(d) = (1 - n/2) (1 - n)^{-3} \qquad (12)$$

This approach has been found to provide good results of μ and λ for classical molecular fluids [11].

No experimental results are available for dense semiclassical fluids. In order to test the accuracy of our theory, we employ it to calculate the shear viscosity μ and thermal conductivity λ of dilute Ne gas and compare with

the experimental data [12] in Table 1. The agreement is good at high temperature and decreases with decrease of temperature.

Table: Shear viscosity μ and thermal conductivity λ for Ne.

$\mu \times 10^7$ (g.cm^{-1}.sec^{-1}) $\lambda \times 10^7$ (cal.cm^{-1}.sec^{-1}.deg^{-1})

T(k)	Theory	Expt.	T(k)	Theory	Expt.
80	1366	1198	90.2	562	489
120	1803	1646	194.7	908	876
160	2108	2026	273.2	1102	1092
					1110
200	2425	2376	373.2	1341	1357
240	2739	2708			
280	3002	3021			
300	3145	3173			

7. Concluding remarks

The effective LJ (12-6) potential, where the quantum effects are incorporated through the effective diameter $\sigma\sim$ and well depth $\epsilon\sim$, is employed to study the quantum effects on the thermodynamic and transport properties of some systems. In all these cases, the agreement with the experimental data is good, particularly when the quantum effects are small.

A detailed study, particularly of TP's will be considered in future publication.

Acknowledgements

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