

Semi classical theory for thermodynamic and transport properties of simple fluids

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Abstract An effective pair potential is expressed in a modified Lennard Jones (12-6) form by simply replacing the diameter of a molecule σ by $\sigma^-(T^*, \Lambda^*)$ and the well-depth ϵ by $\epsilon^-(T^*, \Lambda^*)$, where T^* is the reduced temperature and Λ^* the quantum parameter. This theory is employed to calculate the quantum corrections to thermodynamic and transport properties of simple systems. In all these cases the agreement with experimental results is fairly good.

Keywords . Semiclassical fluids, quantum corrections, thermodynamic and transport properties

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1. Introduction

The purpose of the present work is to describe a theory for calculating the quantum corrections to the thermodynamic and transport properties of semiclassical fluids, whose molecules interact via a Lennard-Jones (LJ) (12-6) potential. In a theoretical approach, the quantum features (excluding those due to the exchange effects) may be included by replacing the bare pair potential with an effective pair (EP) potential [1], which may be a function of temperature and thermal wavelength. The EP potential is not unique, different properties lead to different EP potential [1, 2]. However, using the bare LJ (12-6) potential, it can be expressed in the 'modified' LJ (12-6) potential form [3,4]. The effective LJ (12-6) potential derived by Young [3] is not based on the well-defined mathematical procedure, whereas Singh and Sinha [4] has used the Wigner-Kirkwood expansion approach [1] to derive the effective potential. The effective LJ (12-6) potential derived by Singh and Sinha [4] was employed to calculate the thermodynamic and

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transport properties [4, 5]. However, this theory provides good results when the quantum effects are small.

In the present work, we improve the effective LJ (12-6) potential and then apply it to estimate the quantum corrections to the thermodynamic and transport properties of simple fluids in the semiclassical limit.

In Section 2, we describe the basic theory and obtain an effective pair potential. Our theory is applied to calculate the second virial coefficient, critical point location and surface tension in Sections 3, 4 and 5 respectively. Section 6 is devoted to estimate the quantum effects on the thermodynamic behaviour of the liquid-gas coexistence curve. Section 7 is concerned with the evaluation of the quantum effects on the melting curve. In Section 8, we apply our theory to estimate the quantum correction to the transport properties of the simple system. Concluding remarks are given in Section 9.

2. Basic theory

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

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

where ϵ represents the well-depth and σ the diameter of a molecule. In presence of quantum effects, the effective pair potential $u^-(r)$ for such a model can be expressed in the LJ (12-6) form by simply replacing σ by $\tilde{\sigma}(T^*, \Lambda^*)$ and $\epsilon \rightarrow \tilde{\epsilon}(T^*, \Lambda^*)$ in eq. (1), where $T^* \equiv kT / \epsilon$ is the reduced temperature and $\Lambda^* \equiv h / \sigma (m \epsilon)^{1/2}$ is a quantum parameter, which is introduced to measure the deviation from the classical behaviour.

In order to determine $\tilde{\sigma}$ and $\tilde{\epsilon}$, we start with the effective pair potential expressed as [1, 4]

$$u^-(r) = u(r) + (\hbar^2 \beta / 12m) \nabla^2 u(r) + O(\hbar^4). \quad (2)$$

Here $\beta = (\lambda T)^{-1}$, m is the mass of the molecule and $\hbar = h / 2\pi$.

Eq. (2) is correct to the first order quantum correction. It is valid at a temperature, where the contribution of second and higher order correction terms are negligible.

Substituting eq. (1) in eq. (2) and using $\nabla^2 = r^{-2}(\partial / \partial r)(r^2(\partial / \partial r))$ for three dimensional space, we get

$$\tilde{u}(r) = 4 \epsilon \{ [(\sigma / r)^{12} - (\sigma / r)^6] + (\hbar^2 \beta / 2m \sigma^2) [22(\sigma / r)^{14} - 5(\sigma / r)^8] \}$$

which can be written as

$$\tilde{u}(r) = 4 \epsilon \{ [(\sigma / r)^{12} - (\sigma / r)^6] + \alpha [22(\sigma / r)^{14} - 5(\sigma / r)^8] \} \quad (3)$$

where

$$\alpha = \hbar^2 \beta / 2m \sigma^2 = \Lambda^{*2} / 8\pi^2 T^*. \quad (4)$$

Eq. (3) can be used to determine $\tilde{\sigma}$ and $\tilde{\epsilon}$. $\tilde{\sigma}$ is the value of r at which $\tilde{u}(r)$ is zero *i.e.* $\tilde{u}(\tilde{\sigma}) = 0$.

Then the position of the minimum of $\tilde{u}(r)$ shifts from $2^{1/6} \sigma$ to $2^{1/6} \tilde{\sigma}$, where the effective pair potential is $-\tilde{\epsilon}$. Thus the expressions for $\tilde{\sigma}$ and $\tilde{\epsilon}$ are given by

$$\hat{\sigma} \equiv \tilde{\sigma} / \sigma = F^{1/6}, \quad (5)$$

$$\hat{\epsilon} \equiv \tilde{\epsilon} / \epsilon = [2F - 1 - 12\alpha(2F)^{-1/3}] / F^2, \quad (6)$$

$$F = (1 + 22\alpha) / (1 + 5\alpha). \quad (7)$$

They may be called Karki-Sinha's expressions for $\tilde{\sigma}$ and $\tilde{\epsilon}$ and are derived in Appendix. When α is small $F \approx 1 + X$, where $X = 17\alpha$ and eqs. (5) and (6) reduce to

$$\hat{\sigma} = [1 + X]^{1/6}, \quad (8)$$

$$\hat{\epsilon} = [1 + 2X - 0.560X(1 + X)^{-1/3}] (1 + X)^{-2}, \quad (9)$$

as given by Singh and Sinha [4]. This is discussed in Appendix.

Thus, the effective pair potential is expressed as the 'modified' *LJ* (12-6) form, where the quantum effects are incorporated in $\tilde{\sigma}(T^*, \Lambda^*)$ and $\tilde{\epsilon}(T^*, \Lambda^*)$. 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 classically. The Singh-Sinha (SS) expressions for $\tilde{\sigma}$ and $\tilde{\epsilon}$ are suitable when the quantum effects are small. The Karki-Sinha (KS) expressions for $\tilde{\sigma}$ and $\tilde{\epsilon}$ are the improvement over the SS expressions and can be safely employed even when the quantum effects are moderately high. These expressions for $\tilde{\sigma}$ and $\tilde{\epsilon}$ may be used to calculate the thermodynamic and transport properties of the system. However, for the correlation functions, one has different expressions for $\tilde{\sigma}$ and $\tilde{\epsilon}$, which is not considered in the present paper. The quantum parameter Λ^* , used in the present calculation, is reported in Ref. 1.

In the following sections, we employ this theory to estimate the thermodynamic and transport properties of the semiclassical fluids. The quantum effects are incorporated in these properties through the expressions of $\tilde{\sigma}$ and $\tilde{\epsilon}$.

3. Thermodynamic properties

We apply our theory to calculate the thermodynamic properties of a semiclassical fluid. In our approach, the classical values of the thermodynamic properties at the reduced density $\tilde{\rho}^* \equiv \rho \tilde{\sigma}^3$ and reduced temperature $\tilde{T}^* \equiv kT / \tilde{\epsilon}$ will be the thermodynamic properties of the semiclassical fluid at the reduced density $\rho^* \equiv \rho \sigma^3$ and reduced temperature $T^* \equiv kT / \epsilon$. Thus the pressure of the semi classical fluid can be given by

$$P(\rho^*, T^*, \Lambda^*) = \tilde{P}(\tilde{\rho}^*, \tilde{T}^*), \quad (10)$$

where $\tilde{P}(\tilde{\rho}^*, \tilde{T}^*)$ is the pressure of the classical fluid at $\tilde{\rho}^*$ and \tilde{T}^* .

In the low density limit, the pressure of the fluid can be expanded in the virial form

$$\beta P / \rho = 1 + \sum_{n=2}^{\infty} B_n(T^*, \Lambda^*) / V, \quad (11a)$$

where B_n is the nth virial coefficient, which is given by

$$\begin{aligned} B_n(T^*, \Lambda^*) &= (2\pi N \sigma^3 / 3)^{n-1} B_n^*(T^*, \Lambda^*), \\ &= (2\pi N \tilde{\sigma}^3 / 3)^{n-1} \tilde{B}_n^*(\tilde{T}^*), \end{aligned} \quad (11b)$$

where $\tilde{B}_n^*(\tilde{T}^*)$ is the reduced nth virial coefficient of the classical fluid at the reduced temperature \tilde{T}^* .

For example, the values of the reduced second virial coefficient \tilde{B}_2^* for Ne and ^4He are reported in Figure 1 as a function of \tilde{T}^* . We find a good agreement with the experimental results [6]. The values of $\tilde{B}_2^*(\tilde{T}^*)$ for noble gases are identical with those of the classical LJ(12-6) gas. This predicts that $\tilde{B}_2^*(\tilde{T}^*)$ is a universal function of \tilde{T}^* and placed on a universal curve. However, $B_n^*(T^*, \Lambda^*)$ is not a universal function of T^* .

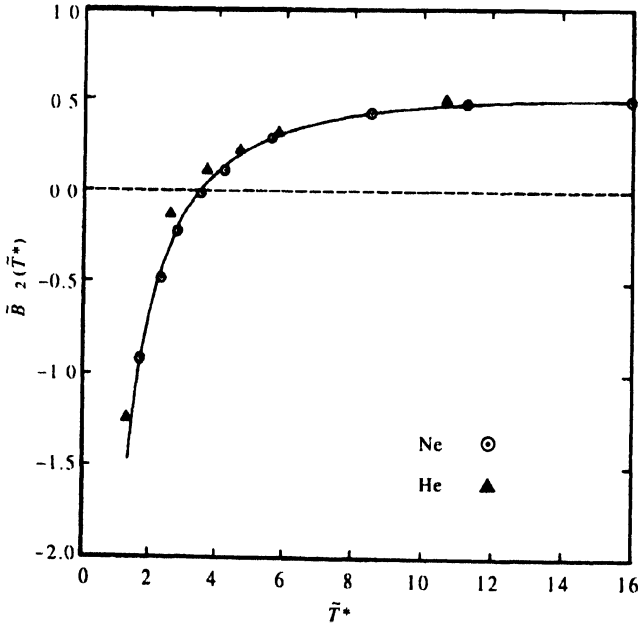


Figure 1 The reduced second virial coefficient $\tilde{B}_2^*(\tilde{T}^*)$ as function of the reduced temperature \tilde{T}^* .

4. Critical point location

In this section, we employ the theory to estimate the quantum effects on the critical temperature

T_c^* , critical volume V_c^* and critical pressure P_c^* . For a classical system interacting via the LJ(12-6) potential, they are given by

$$T_c^* \equiv kT_c / \epsilon = 1.26, \tag{12a}$$

$$V_c^* \equiv V_c / N\sigma^3 = 3.1, \tag{12b}$$

$$P_c^* \equiv P_c \sigma^3 / \epsilon = 0.117. \tag{12c}$$

In order to take the quantum effects into account, we replace $\epsilon \rightarrow \tilde{\epsilon}(T^*, \Lambda^*)$ and $\sigma \rightarrow \tilde{\sigma}(T^*, \Lambda^*)$ in eq. (12). Thus

$$T^* = 1.26 \hat{\epsilon} \tag{13a}$$

$$V_c^* = 3.1 \hat{\sigma}^3 \tag{13b}$$

$$P_c^* = 0.117 \hat{\epsilon} / \hat{\sigma}^3 \tag{13c}$$

Eq. (13a) may be solved by the interactive process or graphically [3]. Once T_c^* is known, we may obtain V_c^* and P_c^* .

The results obtained by Karki-Sinha (KS), Singh-Sinha (SS) and Young (Y) theories are reported in Figure 2 as a function of quantum parameter Λ^* and compared with the experimental data [3]. The KS theory provides better results in comparison to the y-theory for lower value of Λ^* ($\Lambda^* \leq 2.0$). However for $\Lambda^* > 2.0$, the y-theory gives relatively better agreement. The SS theory is an approximation of the KS theory for $\Lambda^* \leq 1.223$. So the SS theory is not employed further in the paper.

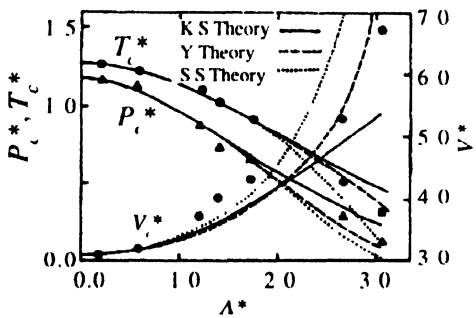


Figure 2.

Figure 2. The reduced critical temperature T_c^* , critical volume V_c^* and critical pressure P_c^* as a function of the quantum parameter Λ^* . The points (●) T_c^* , (▲) P_c^* and (○) V_c^* represent the experimental values.

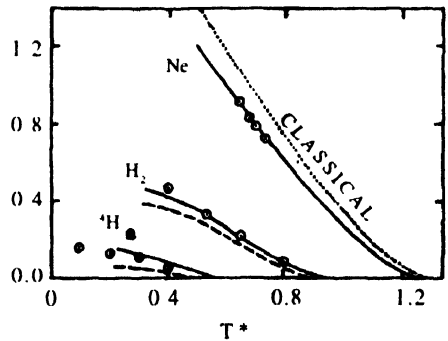


Figure 3.

Figure 3. The reduced surface tension γ^* as function of T^* . The points (○) represent the experimental values, the thickline KS theory, dashed line Y-theory and dotted line classical value.

5. Surface tension

We consider the quantum correction (QC) to the surface tension (ST) along the liquid-gas phase boundary. The ST of the classical LJ (12-6) fluid is given by

$$\gamma^* = \gamma \sigma^2 / \epsilon = 2.666 (1 - T^*/T_c^*)^{1.27} \tag{14}$$

For classical fluid $T_c^* = 1.26$. Replacing $\epsilon \rightarrow \tilde{\epsilon}$ and $\sigma \rightarrow \tilde{\sigma}$, the ST of the semiclassical fluid is expressed as

$$\tilde{\gamma}^* \equiv \tilde{\gamma} \sigma^2 / \epsilon = 2.666 (\hat{\epsilon} / \hat{\sigma}^2) (1 - \tilde{T}^*/1.26)^{1.27} \tag{15}$$

where $\tilde{T}^* = kT / \hat{\epsilon} = T^* / \hat{\epsilon}$. Eq. (15) is applicable to both classical and quantum fluid over a wide temperature range. In this approach, the amplitude is modified but the exponent remains a constant with a value of 1.27. Thus, the quantum mechanical variation of the exponent [7] is ignored here.

The surface tension $\tilde{\gamma}^*$ for classical fluid, Ne, H₂ and ⁴He is shown in Figure 3 as a function of T^* along with the experimental data. The agreement is fairly good. The results obtained by the KS theory is better than those of the y-theory. For ⁴He, the KS theory overestimates the surface tension while the Y theory underestimates it. This shows the usefulness of eqs. (5) and (6).

6. Liquid gas coexistence curve

In this section we apply the theory to estimate the quantum effects on the behaviour of the liquid-gas coexistence curve. The behaviour of a classical fluid may be described by the relations [3, 8]

$$V_c^*/V_l^* = 1 + (3/4)(1 - T^*/T_c^*) + (7/4)(1 - T^*/T_c^*)^{1/3} \tag{16}$$

$$V_c^*/V_g^* = 1 + (3/4)(1 - T^*/T_c^*) - (7/4)(1 - T^*/T_c^*)^{1/3} \tag{17}$$

where V_l^* , V_g^* and V_c^* are the reduced liquid, gas and critical molar volume. Here $T_c^* = 1.26$ and $V_c^* = 3.1$. These equations represent the behaviour of V_c^*/V^* for $T^*/T_c^* \leq 1$.

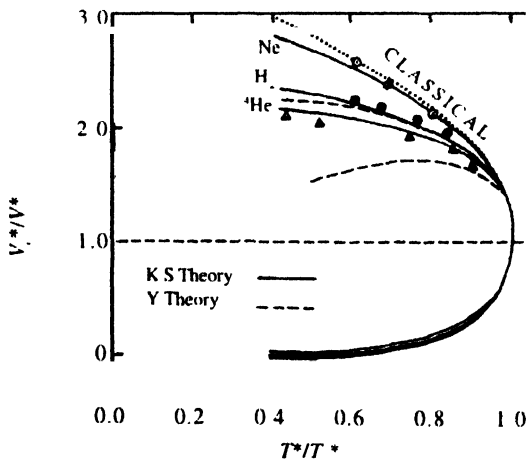


Figure 4. Values of V_c^*/V^* as a function of T^*/T_c^* along the liquid gas coexistence curve. The experimental points are for Ne (○), H₂(●) and ⁴He(Δ). Other keys are same as in Figure. 3.

For the semiclassical fluid, where ϵ is replaced by $\tilde{\epsilon}$ and σ by $\tilde{\sigma}$, we find

$$V_c^*/V^* \rightarrow (V_c^*/V^*)(\hat{\sigma}/\hat{\sigma}_c)^3,$$

$$T^*/T_c^* \rightarrow \tilde{T}^*/1.26,$$

where $\hat{\sigma}_c$ is the value of $\hat{\sigma}$ at $T^* = T_c^*$. Then eqs. (16) and (17) can be expressed as

$$V_c^*/V_1^* = (\hat{\sigma}_c/\hat{\sigma})^3 [1 + (3/4)(1 - \tilde{T}^*/1.26) + (7/4)(1 - \tilde{T}^*/1.26)^{1/3}], \quad (18)$$

$$V_c^*/V_k^* = (\hat{\sigma}_c/\hat{\sigma})^3 [1 + (3/4)(1 - \tilde{T}^*/1.26) - (7/4)(1 - \tilde{T}^*/1.26)^{1/3}]. \quad (19)$$

The values of V_c/V^* for classical fluid, Ne, H₂ and ⁴He are demonstrated in Figure 4 along with the experimental data [8, 9]. From the figure, it is clear that the KS theory predicts better results than those of the Y theory.

7. Melting curve

In this section, we apply our theory to estimate the quantum effects on the melting curves of simple systems. The melting equations for the classical LJ (12-6) system are expressed in a very simple form [10]

$$T^{*L(S)} \equiv kT^{L(S)}/\epsilon = 4 \left[(\rho^{*L(S)}/a_{12}^{L(S)})^4 - (\rho^{*L(S)}/a_6^{L(S)})^2 \right], \quad (20)$$

$$P^{*L(S)} \equiv P^{L(S)}/\epsilon = 4 \left[\pi_{12}^{L(S)} (\rho^{*L(S)})^5 - \pi_6^{L(S)} (\rho^{*L(S)})^3 \right], \quad (21)$$

where

$$\rho^{*L(S)} = \rho^{L(S)} \sigma^3; \quad \pi_n^{L(S)} = P_n / (a_n^{L(S)})^{1+n/3}$$

The melting constants of the inverse power potentials are reported elsewhere [10]. $T^{L(S)}$ and $P^{L(S)}$ are the temperature and pressure, respectively, along the liquidus (L) and solidus (S).

Replacing $\sigma \rightarrow \tilde{\sigma}$ and $\epsilon \rightarrow \tilde{\epsilon}$ in eqs. (20) and (21), the quantum corrected melting equations for the LJ (12-6) system can be given by

$$T^{*L(S)} = 4 \hat{\epsilon} \left[(\rho^{*L(S)} \hat{\sigma}^3 / a_{12}^{L(S)})^4 - (\rho^{*L(S)} \hat{\sigma}^3 / a_6^{L(S)})^2 \right], \quad (22)$$

$$P^{*L(S)} = (4 \hat{\epsilon} / \hat{\sigma}^3) \left[\pi_{12}^{L(S)} (\rho^{*L(S)} \hat{\sigma}^3)^5 - \pi_6^{L(S)} (\rho^{*L(S)} \hat{\sigma}^3)^3 \right]. \quad (23)$$

For a given melting temperature, the melting pressure $P(T)$ is given by

$$P(T) = [P^L(T) + P^S(T)]/2. \quad (24)$$

Then the triple point is obtained from the equation $P(T_{triple}) = 0$.

For example, we calculate the melting temperature and melting pressure for ⁴He using eqs. (22) and (23). They are given in Figure 5, where they are compared with the experimental results as well as those obtained by Rosenfeld-Thieberger (RT) theory [9]. The present KS theory provides results better than those due to the RT theory. This provides additional

evidence that $\hat{\sigma}$ and $\hat{\epsilon}$ are of real physical significance and eqs. (5) and (6) can be employed to estimate the properties of the semiclassical fluids.

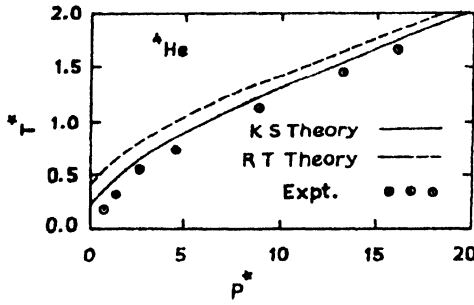


Figure 5.

Figure 5. Melting pressure against melting temperature for ^4He

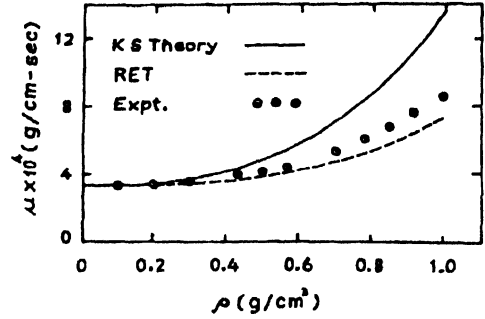


Figure 6.

Figure 6. The shear viscosity μ of Ar as a function of ρ at $T = 348^\circ\text{K}$

8. Transport properties

Lastly, we apply our theory to estimate the quantum correction to the transport properties (TP's) such as shear viscosity μ and thermal conductivity λ of simple fluids. We assume that the structure of a dense classical fluid is similar to that of a hard sphere (HS) fluid of properly chosen hard sphere diameter d . The TP's of the classical LJ (12-6) fluid may be evaluated through the evaluation of the TP's of the HS fluid. We employ the revised Enskog theory (RET) of Beijener and Ernst [11] to estimate μ and λ of the HS fluid. In terms of the packing fraction η , (defined as $\eta = \pi\rho d^3/6$; where ρ is the number density) they are given by

$$\mu = [g_{HS}(d)]^{-1} [1 + (4/5)(4\eta g_{HS}(d)) + 0.7615(4\eta g_{HS}(d))^2] \mu_0, \quad (25)$$

$$\lambda = [g_{HS}(d)]^{-1} [1 + (6/5)(4\eta g_{HS}(d)) + 0.7575(4\eta g_{HS}(d))^2] \lambda_0, \quad (26)$$

where

$$\mu_0 = (5/16 \pi d^2) (\pi m k T)^{1/2}, \quad (27)$$

$$\lambda_0 = (75k / 64 \pi d^2) (\pi k T / m)^{1/2}. \quad (28)$$

Here, $g_{HS}(d)$ is the equilibrium RDF of the HS fluid at the contact, m is the mass of a molecule, k the Boltzman constant and T the absolute temperature. We assume that the molecules of the system interact *via* the LJ (12-6) potential with force parameters σ and ϵ .

For the semiclassical fluid, where the quantum effects are incorporated by replacing $\sigma \rightarrow \tilde{\sigma}(T^*, \Lambda^*)$ and $\epsilon \rightarrow \tilde{\epsilon}(T^*, \Lambda^*)$, the shear viscosity μ and thermal conductivity λ can be expressed as

$$\mu = [g_{HS}(\tilde{d})]^{-1} [1 + (4/5)(4\tilde{\eta} g_{HS}(\tilde{d})) + 0.7615(4\tilde{\eta} g_{HS}(\tilde{d}))^2] \tilde{\mu}_0, \quad (29)$$

$$\lambda = [g_{HS}(\tilde{d})]^{-1} [1 + (6/5)(4\tilde{\eta} g_{HS}(\tilde{d})) + 0.7575(4\tilde{\eta} g_{HS}(\tilde{d}))^2] \tilde{\lambda}_0, \quad (30)$$

where $\tilde{\mu}_0$ and $\tilde{\lambda}_0$ are the values of μ_0 and λ_0 , respectively, where d is replaced by \tilde{d} . Here $g_{HS}(\tilde{d})$ is the equilibrium RDF of the HS fluid at the contact and $\tilde{\eta} = \pi\rho\tilde{d}^3 / 6$.

The hard sphere diameter \tilde{d} and the RDF $g_{HS}(d)$ may be determined from the experimental data of the second virial coefficient $B(T)$ and Equation of state PV/NkT , respectively [12]. However, in the present case the diameter \tilde{d} is determined from the Verlet-Weis method [13] with the effective LJ (12-6) potential and the equilibrium RDF $g_{HS}(\tilde{d})$ is given by

$$g_{HS}(\tilde{d}) = (1 - \tilde{\eta}/2)(1 - \tilde{\eta})^{-3}. \tag{31}$$

In order to test the theory for TP's, we first employ our theory to calculate the shear viscosity μ of Ar (treating classically) at $T = 348^\circ\text{K}$, at which the experimental results are available [12]. The values of μ as a function of ρ are compared with the RET and experimental results in Figure 6. We find good agreement at low density. At high density the present theory overestimates while the RET underestimates it.

This theory can be applied to estimate the quantum effects on the TP's of the semiclassical fluids. However, the simulation or experimental results are not available for these systems. So no definite conclusion can be drawn. Figures 7 and 8 demonstrate, respectively, μ and λ for Ne as a function of ρ at $T = 120^\circ\text{K}$. We find that the quantum effects enhance the values of μ and λ and increase with increase of density.

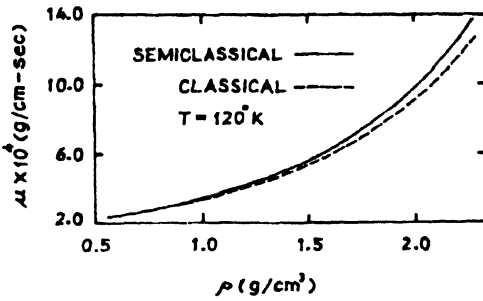


Figure 7.

Figure 7. The shear viscosity μ of Ne as a function of ρ at $T = 120^\circ\text{K}$

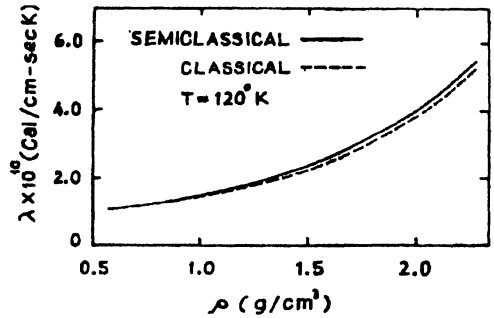


Figure 8.

Figure 8. The thermal conductivity λ of Ne as a function of ρ at $T = 120^\circ\text{K}$

9. Concluding remarks

The effective pair potential is expressed in the 'modified' LJ (12-6) form by simply replacing $\sigma \rightarrow \tilde{\sigma}(T^*, \Lambda^*)$ and $\epsilon \rightarrow \tilde{\epsilon}(T^*, \Lambda^*)$. The expressions are given for the functions $\tilde{\sigma}$ and $\tilde{\epsilon}$ which are functions of T^* and Λ^* . Then the systems can be treated classically. The modified LJ (12-6) potential is employed to estimate the quantum correction to the thermodynamic and transport properties of some simple systems over a wide range of density and temperature. In all these cases, the agreement with experimental data (where available) is good.

We have used the first order quantum correction to the pair potential to obtain the expressions for $\tilde{\sigma}$ and $\tilde{\epsilon}$. By taking into consideration the higher order correction terms, one

can improve the expressions for $\tilde{\sigma}$ and $\tilde{\epsilon}$ for better results. However, it is not attempted in the present work.

Acknowledgments

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Appendix

(i) Derivation of $\tilde{\sigma}$

When $\tilde{u}(r) = 0$ eq. (3) can be written as

$$4 \in ([(\sigma/r)^{12} - (\sigma/r)^6] + \alpha [22 (\sigma/r)^{14} - 5 (\sigma/r)^8]) = 0$$

or

$$(r/\sigma)^6 = [1 + 22\alpha(\sigma/r)^2] / [1 + 5\alpha(\sigma/r)^2]. \quad (\text{A1})$$

As the quantum effects are largely determined from the hard-core [14], we approximate $r/\sigma \approx 1$ and write eq. (A1) as

$$\tilde{\sigma}/\sigma = F^{1/6}, \quad (\text{A2})$$

where

$$F = (1 + 22\alpha) / (1 + 5\alpha). \quad (\text{A3})$$

(ii) **Derivation of $\tilde{\epsilon}$**

To determine ϵ , we put $r = 2^{1/6} \tilde{\sigma}$ in eq. (3). Thus

$$\begin{aligned} \tilde{u}(2^{1/6} \tilde{\sigma}) &= 4 \epsilon \{ [(1/4F^2) - (1/2F)] + \alpha[(22/4F^2)^2 - (5/2F)] / (2F)^{1/3} \} \\ &= -\epsilon [2F - 1 + \alpha(10F - 22 / (2F)^{1/3})] / F^2. \end{aligned} \quad (A4)$$

At $r = 2^{1/6} \tilde{\epsilon}$, the effective pair potential is $-\tilde{\epsilon}$. Thus the expression for $\tilde{\epsilon}$ is obtained from (A4) as

$$\begin{aligned} \tilde{\epsilon} &= \epsilon [2F - 1 + \alpha(10F - 22)(2F)^{-1/3}] F^{-2} \\ &= \epsilon [2F - 1 - 12\alpha(1 - (5/6)(F - 1))(2F)^{-1/3}] F^{-2} \\ &\approx \epsilon [2F - 1 - 12\alpha(2F)^{-1/3}] F^{-2}. \end{aligned} \quad (A5)$$

(iii) **Approximation**

When the quantum effects are small *i.e.* either Λ^* is small or/and T^* is high, α is small, we can approximate F as

$$\begin{aligned} F &\approx (1 + 22\alpha)(1 - 5\alpha) \\ &\approx 1 + X, \end{aligned} \quad (A6)$$

where $X = 17\alpha$.

Using eq. (A6) in eqs. (A2) and (A5), we get Singh-Sinha (SS) [4] expressions for $\tilde{\sigma}$ and $\tilde{\epsilon}$

$$\tilde{\sigma} / \sigma = (1 + X)^{1/6}, \quad (A7)$$

$$\tilde{\epsilon} / \epsilon = [1 + 2X - (6(2)^{2/3} / 17)(1 + X)^{-1/3}] (1 + X)^{-2}. \quad (A8)$$