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Quantum correction for transport properties of simple fluids

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Abstract

The effective diameter hard sphere theory is employed to estimate the transport properties (TP's) of classical and semiclassical fluids. The TP's of the fluids are expressed in terms of a classical hard sphere (HS) fluid of properly chosen hard sphere diameter. The explicit expressions for the shear viscosity and thermal conductivity for the HS fluid are given. The theory is applied to estimate the TP's of fluids Ar, Ne and H₂. The agreement is found to be fairly good at low density.

Introduction

The aim of the present paper is to develop a theory for estimating the transport properties (TP's) of dense classical and semiclassical fluids, whose molecules interact via the Lennard – Jones (LJ) (12-6) potential. In the semiclassical limit (i.e. at high temperature) the quantum effects are small and treated as a correction to the classical values. One of the theoretical method to deal with the problem is the effective pair potential method^[1], where the effective pair potential is expressed in the LJ(12-6) potential form. The TP's of the LJ (12-6) fluid may be estimated through the evaluation of the TP's of the classical hard sphere (HS) fluid with the properly chosen hard sphere diameter. The basic ideas of this approach is responsible for much progress achieved in the equilibrium theory of dense fluid^[2]. This idea can be used even in framing the non-equilibrium theory of dense fluids.

The effective diameter hard sphere theory (EDHST)^[3] is an important method for studying the TP's of dense real fluids in terms of the classical HS fluid with state-dependent effective hard sphere diameter. The HS fluid can be handled with the revised Enskog theory (RET) of van Beijeren and Ernst^[4]. Karki and Sinha^[1] have employed the EDHST for estimating the TP's of the LJ(12-6) fluid.

In the present paper, we extend this approach to estimate the TP's of the semiclassical fluids.

Basic Theory: Effective Pair Potential

The quantity of central importance in the quantum theory of fluids is the Slater sum defined as^[5]

$$W_N(1,2,\dots,N) = N! \lambda^{3N} \langle 1,2,\dots,N | \exp[-\beta \hat{H}_N] | 1,2,\dots,N \rangle, \quad [1]$$

where

$$\lambda = (2\pi\hbar^2\beta/m)^{1/2}$$

is the thermal wavelength and \hat{H}_N is the Hamiltonian operator of a system of N identical particles, each of mass m, in volume V. One can write the Hamiltonian operator as

$$\hat{H}_N = (\hbar^2/2m) \sum_{i=1}^N \nabla_i^2 + \sum_{i<j} u(r_{ij}), \quad [2]$$

where $u(r_{ij})$ is the pair potential between particles i and j separated by a distance $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. Here $\beta = (kT)^{-1}$ and $\hbar = h/2\pi$ (k being Boltzmann constant, h the Planck constant and T the absolute temperature).

In the semiclassical limit (i.e. at high temperature), where the quantum effects are small, the Slater sum can be expanded to give [5]

$$W_N = \exp [-\beta U] \left(1 + (\hbar^2 \beta^2 / 24m) \sum_i [\beta (\nabla_i U)^2 - 2 \nabla_i^2 U] + O(\hbar^4) \right), \tag{3}$$

where the first term of the right hand side of Eq.(3) is the Boltzmann factor and the second term is the first order quantum correction to it. Here U is the total interaction potential, which is assumed to be pairwise additive.

In terms of the Slater sum, the canonical partition function can be written as

$$Q_N = (N! \lambda^{3N})^{-1} \int \dots \int W_N(1,2,\dots,N) \prod_{i=1}^N d\mathbf{r}_i. \tag{4}$$

Integrating by parts, Eq.(4) can be written as [1,5]

$$Q_N = (N! \lambda^{3N})^{-1} \int \dots \int \exp[-\beta \sum_{i<j} \tilde{u}(r_{ij})] \prod_{i=1}^N d\mathbf{r}_i, \tag{5}$$

where

$$\tilde{u}(r_{ij}) = u(r_{ij}) + (\hbar^2 \beta / 12m) \nabla_{r_{ij}}^2 u(r_{ij}) + O(\hbar^4) \tag{6}$$

is the effective pair potential, which is a function of both T and λ .

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

$$u(r) = 4 \epsilon [(\sigma/r)^{12} - (\sigma/r)^6], \tag{7}$$

where ϵ represents the well depth and σ the molecular diameter of a molecule. The effective pair potential $\tilde{u}(r)$ for such a model can be expressed in the LJ(12-6) form by simply replacing σ by $\tilde{\sigma}(T^*, \Lambda^*)$ and ϵ by $\tilde{\epsilon}(T^*, \Lambda^*)$ in Eq.(7). Thus the effective pair potential is expressed in the form [1]

$$\tilde{u}(r) = 4 \tilde{\epsilon} [(\tilde{\sigma}/r)^{12} - (\tilde{\sigma}/r)^6], \tag{8}$$

where

$$\hat{\sigma} = \tilde{\sigma}(T^*, \Lambda^*) / \sigma = F^{1/6} \tag{9}$$

$$\hat{\epsilon} = \tilde{\epsilon}(T^*, \Lambda^*) / \epsilon = [2F - 1 - 12\alpha(2F)^{-1/3}] F^{-2} \tag{10}$$

and

$$F(T^*, \Lambda^*) = 1 + 22\alpha / [1 + 5\alpha] \tag{11}$$

with

$$\alpha = (\hbar^2 / 2kTm \sigma^2) = (\Lambda^{*2} / 8^2 T^*) \tag{12}$$

Here $T^* = kT/\epsilon$ is the reduced temperature and $\Lambda^* = h/\sigma(m\epsilon)^{1/2}$ is the quantum parameter, which is introduced to measure the deviation from the classical behaviour. The value of $\hat{\sigma}$ and $\hat{\epsilon}$ for neon (Ne) (with $\Lambda^* = 0.593$) and Hydrogen (H_2) (with $\Lambda^* = 1.729$) are reported in Table 1 for $T^* = 0.75$ and 1.0 . $\hat{\sigma}$ increases with decrease of T^* and increase of Λ^* , while $\hat{\epsilon}$ decreases when T^* decreases and Λ^* increases. Thus we find that the quantum effects make the effective pair potential, both shallower and longer-ranged.

Table 1 : Values of $\hat{\sigma}$ and $\hat{\epsilon}$ for Ne ($\Lambda^* = 0.593$) and H_2 ($\Lambda^* = 1.729$)

System	T^*	$\hat{\sigma}$	$\hat{\epsilon}$
Ne	0.75	1.01571	0.94656
	1.00	1.01198	0.95934
H_2	0.75	1.07476	0.74526
	1.00	1.07476	0.74526

Thus the semiclassical fluid is treated as the classical LJ (12-6) fluid. The quantum effects are incorporated through the expressions of $\bar{\sigma}$ and $\bar{\epsilon}$. Karki and Sinha^[1] have employed this theory to calculate the thermodynamic and transport properties of simple fluids. In this paper we extend this theory to estimate the TP's of the semiclassical fluids.

Perturbation Expansion: Determination of Effective Hard Sphere Diameter

We divide the effective pair potential $\bar{u}(r)$ according to the Weeks-Chandler-Andersen (WCA) scheme [2] and follow the method of Verlet and Weis (VW) [6] to obtain an expression for the effective diameter \bar{d} as

$$\bar{d} = \bar{d}_B [1 + z\bar{\delta}], \tag{13}$$

where

$$\bar{d}_B = \bar{\sigma} [1.068 + 0.3837 \bar{T}^*] / [1 + 0.4293 \bar{T}^*] \tag{14}$$

$$\bar{\delta} = [210.31 + 404.6 / \bar{T}^*]^{-1} \tag{15}$$

with $\bar{T} = kT / \bar{\epsilon} = T^* / \bar{\epsilon}$ and $\bar{\epsilon}$ is a function of density $\bar{\rho}^* = \rho \bar{\sigma}^3 = \rho^* \bar{\sigma}^{*3}$ and temperature \bar{T}^* .

Using the semiempirical expression for $Y_{HS}(r)$, Verlet and Weis [6,12-14] derived expression for z

$$z = [1 - 4.25\eta_\omega + 1.363\eta_\omega^2 - 0.8757\eta_\omega^3] / (1 - \eta_\omega)^2, \tag{16}$$

where

$$\eta_\omega = \eta - \eta^2 / 16$$

$$\eta = (\pi/6) \rho \bar{d}^3 = (\pi/6) \rho^* (\bar{\sigma} d^*)^3,$$

Here $d^* = \bar{d} / \bar{\sigma}$ and η is the packing fraction.

Recently Dey – Karki – Sinha (DKS) [7] have used the ‘modified’ Born-Green-Yvon (BGYM) integral equation for $Y_{HS}(r)$ and obtained expression for z

$$z = (1 - 5.5\eta + 4.25\eta^2 - \eta^3) (1 - \eta)^{-3} \tag{17}$$

Knowing the packing fraction η , the RDF of the HS fluid at contact, $g_{HS}(\bar{d})$ is given by [6,7]

$$g_{HS}(\bar{d}) = (1 - \eta/2) / (1 - \eta)^3, \tag{18}$$

Using the DKS [7] and VW [6] methods we evaluate the effective hard sphere diameter d/σ and hard sphere RDF $g_{HS}(d)$ for the classical LJ(12-6) fluid at $T^* = 2.90$. They are reported in Table 2. The DKS values of d^* and $g_{HS}(d)$ are less than those of the VW values. Further d^* decreases with the increase of density $\rho^* = \rho \sigma^3$.

Table 2 : The effective hard sphere diameter $d^* = d / \sigma$ and equilibrium hard sphere RDF $g_{HS}(d)$ for the fluid at $T^* = 2.90$.

ρ^*	d^*		$g_{HS}(d)$	
	DKS	VW	DKS	VW
0.119	0.97326	0.97446	1.160	1.161
0.179	0.97312	0.97423	1.254	2.55
0.238	0.97296	0.97398	1.359	1.360
0.298	0.97277	0.97369	1.477	1.478
0.358	0.97255	0.97337	1.610	1.612
0.417	0.97229	0.97301	1.761	1.763
0.477	0.97198	0.97259	1.932	1.935
0.537	0.97163	0.97212	2.127	2.130
0.596	0.97120	0.97158	2.350	2.253
0.656	0.97071	0.97096	2.607	2.609
0.715	0.97011	0.97024	2.903	2.905

We also evaluate the effective diameter $\tilde{d}^* = \tilde{d}/\tilde{\sigma}$ and hard sphere RDF $g_{HS}(\tilde{d})$ for the semiclassical fluids such as Ne (with $\Lambda^* = 0.593$) and H_2 (with $\Lambda^* = 1.729$) at $T^* = 0.75$ using the VW method. They are compared with the classical values in Table 3. The quantum effects decrease the diameter \tilde{d}^* and increases the RDF $g_{HS}(\tilde{d})$.

Table 3 : The effective hard sphere diameter $\tilde{d}^* = \tilde{d}/\tilde{\sigma}$ and equilibrium hard sphere RDF $g_{HS}(\tilde{d})$ for the fluid at $T^* = 0.75$.

ρ^*	\tilde{d}^*			$g_{HS}(\tilde{d})$		
	Classical	Ne	H_2	Classical	Ne	H_2
0.1	1.02674	1.02499	1.01412	1.158	1.165	1.203
0.2	1.02650	1.02473	1.01371	1.353	1.372	1.469
0.3	1.02620	1.02439	1.01315	1.599	1.635	1.827
0.4	1.02582	1.02396	1.01240	1.913	1.975	2.322
0.5	1.02533	1.02340	1.01135	2.322	2.424	3.023
0.6	1.02469	1.02266	1.00987	2.864	3.029	4.049
0.7	1.02384	1.02168	1.00775	3.598	3.864	5.602
0.8	1.02271	1.02034	1.00469	4.615	5.044	8.026

Transport Properties of Dense Fluid

We assume that the structure of a dense fluid is similar to that of a HS fluid. The TP’s of the semiclassical LJ(12-6) fluid may be estimated through the evaluation of the TP’s of the classical HS fluid with property chosen hard sphere diameter ‘ \tilde{d} ’. We employ the RET of van Beijeren and Ernst [4] to estimate the shear viscosity μ and thermal conductivity λ of the HS fluid. In terms of the packing fraction η , they are given by

$$\mu = [g_{HS}(\tilde{d})]^{-1} [1 + (4/5)(4\eta g_{HS}(\tilde{d})) + 0.7615(4\eta g_{HS}(\tilde{d}))^2] \mu_0 \tag{19}$$

$$\lambda = [g_{HS}(\tilde{d})]^{-1} [1 + (6/5)(4\eta g_{HS}(\tilde{d})) + 0.7575(4\eta g_{HS}(\tilde{d}))^2] \lambda_0, \tag{20}$$

where

$$\mu_0 = (5/16\pi\tilde{d}^2)(\mu m k T)^{1/2} \tag{21}$$

$$\lambda_0 = (75k/64\pi\tilde{d}^2)(\mu k T / m)^{1/2} \tag{22}$$

and $g_{HS}(\tilde{d})$ is the equilibrium RDF of the HS fluid at the contact and given by Eq. (8). The effective hard sphere diameter \tilde{d}^* and RDF $g_{HS}(\tilde{d})$ may be obtained from the experimental values of the second virial coefficient B(T) and equation of state PV/NkT, respectively[3]. Recently Karki and Sinha [1,9-11] have used the VW method to determine the diameter \tilde{d} . However, in the present case, the diameter \tilde{d} is determined by Eq. (13) using either the DKS or VW method and the equilibrium RDF $g_{HS}(\tilde{d})$ is given by eq. (18). For the classical LJ(12-6) fluid, $\tilde{\sigma} = \tilde{\sigma}/\sigma = 1.0$ and $\tilde{\epsilon} = \tilde{\epsilon}/\epsilon = 1.0$.

Results and Discussion

We first apply our theory to calculate the shear viscosity μ of Ar treating classically as the quantum effect for Ar is negligible. We use the DKS and VW methods to calculate d^* and RDF $g_{HS}(d)$. Using these values, we calculate the shear viscosity μ for Ar at $T = 348K$. They are compared with the experimental data [3,15] in Fig.1 The results obtained by DKS and VW values of d^* and $g_{HS}(d)$ are in good agreement through the density range. When compared with experimental data we find a good agreement at low density.

In order to study the quantum effects on the TP's of the semiclassical fluids, we calculate the shear viscosity μ and thermal conductivity λ for Ne and H₂ at $T^* = 0.75$, where the, quantum effects are assumed to be appreciable. The values of $\lambda^* = \lambda\sigma^2/k(\epsilon/m)^{1/2}$ and $\mu^* = \mu\sigma^2/(m\epsilon)^{1/2}$ for Ne and H₂ at $T = 0.75$ are compared with the classical values in Fig.3 and 4, respectively. The semiclassical values are lower than the classical values at low densities ($\mu^* \leq 0.2$) and greater at high ($\lambda^* > 0.2$). The deviation increase with increase of the quantum parameter Λ^* and increase of density λ^* . However for lower density $\mu^* \leq 0.2$, the deviation increase with the decrease of density. Thus we find that the quantum effects on the TP's depends on the density as well as the quantum parameter.

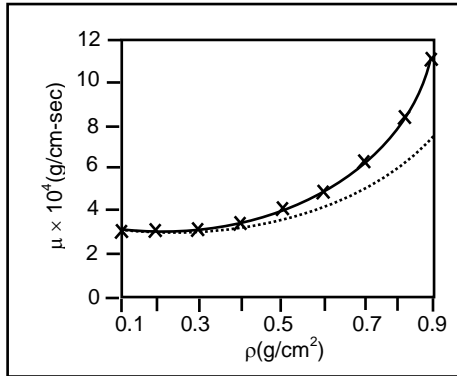


Fig. 1 : The shear viscosity $\mu \times 10^4$ g/cm-sec of Ar at $T = 348K$. — DKS, XXX VW and ... Expt.

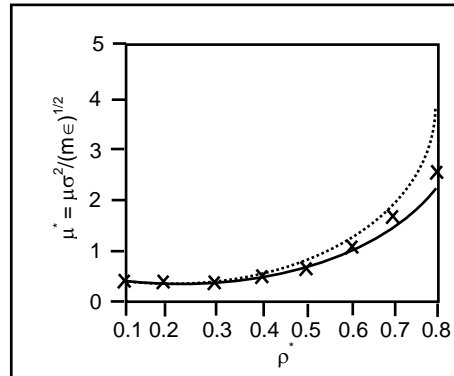


Fig. 2 : Values of $\mu^* = \mu\sigma^2/(m\epsilon)^{1/2}$ for simple fluids as a function of ρ^* at $T^* = 0.75$. — Classical, XXX Ne and ... H₂

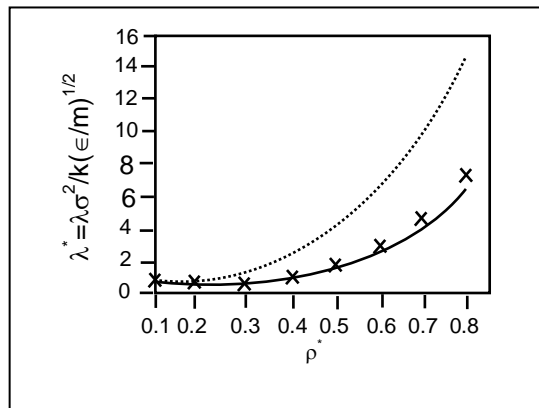


Fig. 3 : Values of $\lambda^* = \lambda\sigma^2/k(\epsilon/m)^{1/2}$ for simple fluids as a function of ρ^* at $T^* = 0.75$, Key same as Fig. 2

Conclusions

We have developed a theory for estimating the quantum corrections to the transport properties of simple fluid whose molecules interact via the LJ(12-6) potential. The effective pair potential is expressed in the LJ(12-6) potential form by simply replacing $\sigma \rightarrow \bar{\sigma}(T^*, \Lambda^*)$ and $\epsilon \rightarrow \bar{\epsilon}(T^*, \Lambda^*)$. The TP's of the semiclassical fluid is expressed in terms of the classical HS fluid of the properly chosen hard sphere diameter. The theory is applied for Ar, and H₂ and Ne, giving good results at low density.

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