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Shear viscosity of square – well fluid

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Abstract A formula for the shear viscosity of the square well fluids is proposed through the modified pair correlation function in hard sphere system The results are compared with the expressions of the viscosity and diffusion coefficients derived by Nigra and Evans for square-well fluid, the diffusion coefficient is changed into viscosity coefficient by employing Stokes- Einstein relation The numerical results of the viscosity obtained by employing Stokes – Einstein relation The numerical results of the viscosity obtained by employing Stokes – Einstein relation are found poor at low temperatures

Keywords Diffusion coefficient, viscosity coefficient, Stokes – Einstein relation

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1. Introduction

The study of viscosity of fluid is of great interest in various research areas both applied and fundamental. The parameters such as composition, mass, density and temperature are required for the understanding of fundamentals and microscopic behaviors of fluid and fluid mixtures. Thus in the recent past considerable interest has been shown in obtaining accurate and reliable values of transport properties for a variety of fluids and fluid mixtures.

During the last few years, there has been a growing appreciation of the role of the nearly harmonic molecular motions in dense fluids [1-5] Tang and Evans [6] derived a damped harmonic oscillator equation of motion for the velocity time correlation function. In that work, the VTC function term arose from Enskog theory [7] describing uncorrelated binary collisions and the memory term describing oscillatory frequency arose from correlated back scattering. In an other paper, Tang and Evans [8] investigated the wave vector and frequency dependence of the time correlation function (tcfs) at $K = 0$. This theory describes the Enskog theory for the HS system, which can be used for normal fluids. In the present

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work, we have employed the Evans's expression of the shear viscosity of hard sphere for wave number $K \to 0$ to describe the shear viscosity of the square-well fluid. The second motivation for this study is to investigate the validity of the Stokes-Einstein relation at low temperatures.

2. Theory

Thermodynamic transport properties, such as shear viscosity, can provide evidence fo coherent phenomenon. The coherence takes the form of free translation interrupted by collisions and this effect is reflected in the wave vector dependence of the Shear Viscosity. Thus, Tang and Evans [8] treated the shear viscosity as consisting of an Enskog part plus a harmonic mode contribution. They described a wavenumber and frequency dependent Enskog theory for a very dense fluid. This theory $\eta(K, Z)$ reduced to the improved Enskog results *i.e.* $\eta(K \to 0, Z)$ which will be applicable to normal fluids. The Shear Viscosity is defined by them as (see equation (38) of reference [8])

$$\eta(K \to 0, Z) = m\rho\sigma^2 \left(\frac{f_E}{10} + \frac{1}{m\rho\sigma^2\left(Z + \frac{6}{5} f_E\right)} \times \left[1 + \frac{4\pi}{15}\sigma^3 \rho g(\sigma)\right]^2 \right) \tag{1}$$

where f_E is the Enskog friction arising from uncorrelated binary collisions and is given by

$$f_E = \frac{16}{\sqrt{\pi}} \rho^* g(\sigma)\, \omega \tag{2}$$

and $\beta = 1/(K_B T)$, Z is the collision frequency per particle $(Z = 3/2\, f_E)$, $\omega = \sqrt{K_B T / m\sigma^2}$;

$\rho^* = \pi/6\, \rho\sigma^3$ is the packing fraction. On Solving, we get the shear viscosity of dense fluid with two body correlation function in the hard sphere system [8,4]

$$\eta_{HS} = m\rho\sigma^2\omega \left\{ \frac{5\sqrt{\pi}}{96\,\rho^* g(\sigma)} \left(1 + \frac{8\rho^* g(\sigma)}{5}\right)^2 + \frac{8\rho^* g(\sigma)}{5\sqrt{\pi}} \right\}. \tag{3}$$

Where $g(\sigma)$ is the pair correlation at contact for hard sphere system $\left(g(\sigma) = (1 - \rho'/2)/(1 - \rho^*)^3\right)$ and $\rho^* = (\pi/6)\, \rho\sigma^3 = (\pi/6)\, \rho_x$. For a square well fluid the pair correlation function can be defined by using the Chapman-Enskog method of solution or by Longuest-Higgins and Valleau solution of velocity auto correlation function [details see in reference 9] as

$$g^{SQ}(\sigma) = \left\lfloor g^{SW}(\sigma) + \lambda^2 E g^{SW}(\lambda\sigma) \right\rfloor. \tag{4}$$

Where $g^{SW}(\lambda\sigma)$ is the radial distribution function of square-well fluid evaluated at $\lambda\sigma$. The expression of E and $g^{SW}(\lambda\sigma)$ are defined by Yu *et al* [9].

Thus the shear viscosity in square well system becomes

$$\eta_{SW} = m\rho\sigma^2\sqrt{\frac{KT}{m\sigma^2}}\left\{\frac{5\sqrt{\pi}}{96\,\rho^* g^{SQ}(\sigma)}\left(1+\frac{8\rho^* g^{SQ}(\sigma)}{5}\right)^2+\frac{8\rho^* g^{SQ}(\sigma)}{5\sqrt{\pi}}\right\}. \quad (5)$$

In the present work, the value $g^{SW}(\sigma)$ is determined in high temperature approximation (HTA) [10]. Hence

$$g^{SW}(\sigma) = \left(g(\sigma) + \frac{1}{4T^*}\frac{\partial a_1^{SW}}{\partial\eta} + \frac{\lambda^3 g(\lambda\sigma)}{T^*}\right) \quad (6)$$

where $g(\sigma)$ is the radial distribution function of hard sphere at contact and a_1 is the mean attractive energy as given below [10].

$$a_1^{SW} = \left(-4\rho^*\varepsilon\left(\lambda^3-1\right)\left\{\frac{\left(1-\rho^*_{eff}/2\right)}{\left(1-\rho^*_{eff}\right)^3}\right\}\right) \quad (7)$$

$$\rho^*_{eff} = \left(c_1\rho^* + c_2\rho^{*2} + c_3\rho^{*3}\right)$$

c_1, c_2, c_3 are the matrices and are given in reference [10]. Throughout the paper, we have defined the reduced viscosity as

$$\eta^* = \eta\Big/\left\{(mKT)^{1/2}\rho^{2/3}\right\}.$$

Thus the expression for the reduce shear viscosity η^* can be written as

$$\eta^*_{SW} = \rho_x^{1/3}\left\{\frac{5\sqrt{\pi}}{96\rho^* g^{SQ}(\sigma)}\left(1+\frac{8\rho^* g^{SQ}(\sigma)}{5}\right)^2+\frac{8\rho^* g^{SQ}(\sigma)}{5\sqrt{\pi}}\right\}. \quad (8)$$

Another (second) way to compute Shear Viscosity is the time evaluation of the dynamical variable described by a Smoluchowski equation. Nigra and Evans [11] considered a classical fluid subject to an effective two-body intermolecular force, derived from a square-well fluid, undergoing dynamics as described by a Smoluchowski equation for pair diffusion. Specifically, they represented the time correlation functions (tcf's) of intermolecular forces appropriate for D and η as the sum of two independent parts : that arising from repulsion and that from attraction. Inclusion of attractive part is the main theme of Nigra and Evans work [11]. The Shear viscosity is the time integral of the stress tcf [11].

$$\eta = \frac{\beta}{VZ_N} \int dr_1 ... dr_N \int dt\, e^{\beta u} J^{xy} e^{iLt} J^{xy} \tag{9}$$

With Z_N the N-particle configurational integral iL the system N-particle Liouville operator and J^{xy} the xy component of the potential part of the stress tensor. The equation (9) is solved (see equation (64) of reference [11] as

$$\eta_{SW} = \eta_{HS} + \frac{4f^2 \pi (\lambda\sigma)^5\, KT\, \rho^2 g_1(\lambda\sigma) n}{15\, D_0} \tag{10}$$

Where η_{HS}, D_{HS}, D_0, f, $g_1(\lambda\sigma)$ and n are defined as

$$\eta_{HS} = \frac{KT}{2\pi\sigma\, D_{HS}} \tag{11}$$

and

$$D_{HS} = \frac{D_0}{g^{HS}(\sigma)} \tag{12}$$

$$D_0 = \frac{3}{8\rho\sigma^2} \left(\frac{KT}{\pi m} \right)^{1/2}, \tag{13}$$

$$f = 1 - e^{-\varepsilon/KT} = 1 - e^{-1/T^*} \qquad \left(T^* = KT/\varepsilon \right), \tag{14}$$

$$g_1(\lambda\sigma) = e^{\varepsilon/KT} = e^{1/T^*}, \tag{15}$$

$$n = \frac{11\lambda^5 + 4}{11(10-f)\,\lambda^5 - 24f}, \tag{16}$$

We can solve the equation (10) as

$$\dot{\eta}_{SW} = \frac{8\rho_x^{1/3}\sqrt{\pi}}{} \left\{ \frac{g^{HS}(\sigma)}{2\pi} + \frac{4f^2 \pi \lambda^5 \rho_S^{*2}\, g_1(\lambda\sigma)\, n}{15} \right\}. \tag{17}$$

Further (third method), shear viscosity of the square-well fluid can be determined from self-diffusion coefficient of square-well fluid by employing Stokes-Einstein relation. In the Stokes-Einstein (SE) relation, the self diffusion coefficient D of a particle in a classical fluid and the shear viscosity η of the fluid are connected by

$$D = \frac{KT}{2\pi\eta\sigma}$$

with KT the thermal energy and σ the diameter of the reference spherical particle which interact with the surrounding fluid in accord with hydrodynamic slip boundary conditions. Thus, we need as expression of diffusion coefficient under the same condition in which shear viscosity is determined.

The self-diffusion coefficient for square-well potential is defined by Nigra and Evans as [11].

$$D_{SW} = \frac{D_{HS}}{1 + 8\rho^* \lambda^3 g_1(\lambda\sigma)\, f^2 F} \tag{18}$$

where

$$F = \frac{7\lambda^3 + 2}{\left(42\lambda^3 - 7f\lambda^3 - 8f\right)}.$$

The Stokes-Einstein relation is written as

$$\frac{2\pi\sigma\eta_{SW} D_{SW}}{KT} = 1. \tag{19}$$

Hence
$$\eta_{SW} = \frac{Kt}{2\pi\sigma D_{HS}} \left(1 + 8\rho^* \lambda^3 g_1(\lambda\sigma) f^2 F\right) \tag{20}$$

and
$$\eta^*_{SW} = \frac{\eta_{SW}}{(mKT)^{1/2}\, \rho^{2/3}}$$

$$= \frac{4}{3\sqrt{\pi}} \rho_x^{1/3} g^{HS}(\sigma) \left(1 + \frac{4}{3}\pi\rho_x \lambda^3 g_1(\lambda\sigma)\, f^2 F\right). \tag{21}$$

3. Results and discussion

In the present work, as expression of the shear viscosity for the square-well fluid is derived from the hard sphere system. It has been shown that the equilibrium radial distribution function $g^{SW}(\sigma)$ and $g^{SW}(\lambda\sigma)$ of square-well fluid can predict the shear viscosity for a square-well fluid The present results are compared with the results of the expression of the shear viscosity proposed by Nigra and Evans [11] for a square-well

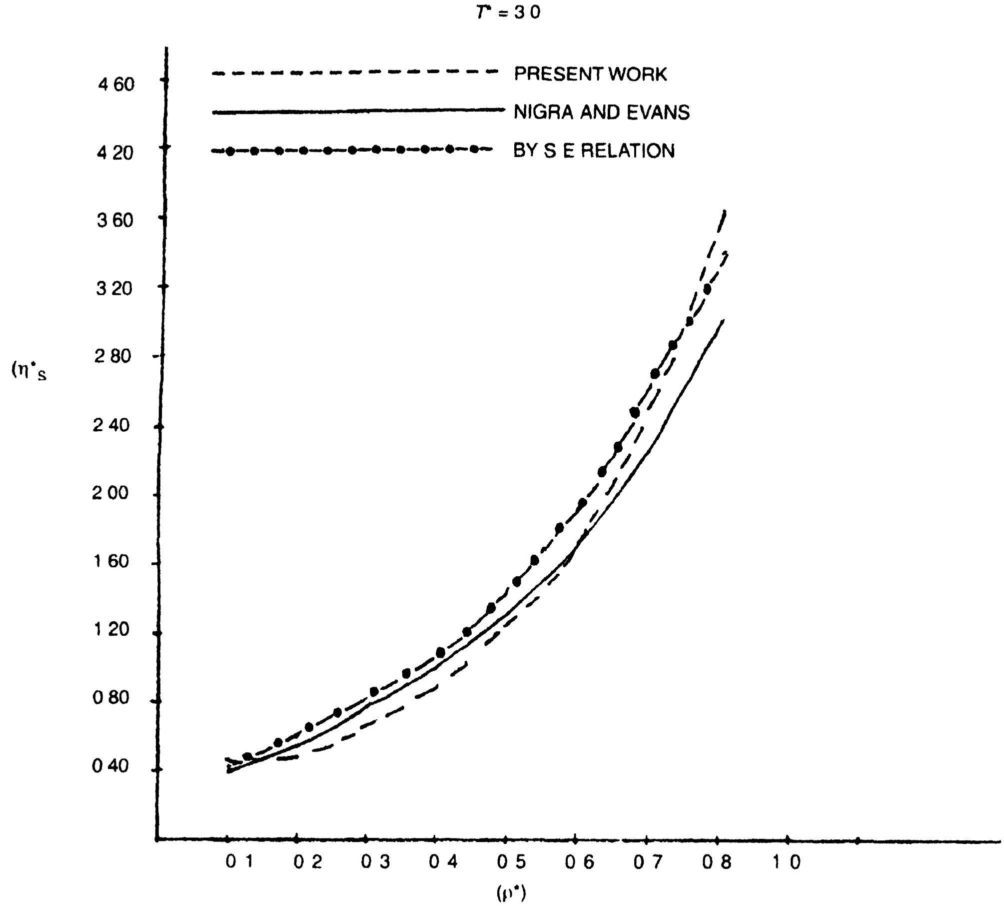

Figure 1. Plot of the reduced Shear viscosity η^* *vs* reduced density ρ^* at $T^* = 3.0$ Present results (---------), Nigra and Evans (————) and results of the reduced viscosity employing Stokes-Einestein relation (– • – • – • –)

fluid. They have calculated the shear viscosity by employing time correlation function with the contribution of delta function, hard sphere forces and from soft forces of square well fluid. The equation derived by Nigra and Evans are presented here by equation (10) It has been further modified to reduced units and presented by equation (17) We find a good agreement in-between present results and with those obtained by equation (17) proposed by Nigra and Evans [11] at all temperatures. Further, we have also calculated the shear viscosity obtained from diffusion coefficient by employing Stokes-Einstein relation *i.e.* equation (21). Figures 1 to 3 show the reduced shear viscosity coefficient as a function of the reduced density at various reduced temperature. $T^* = 3.0$, 2.0 and 1.5. It can be seen that at $T^* = 3.0$ both the equations (8) and (21) predict good agreement with equation

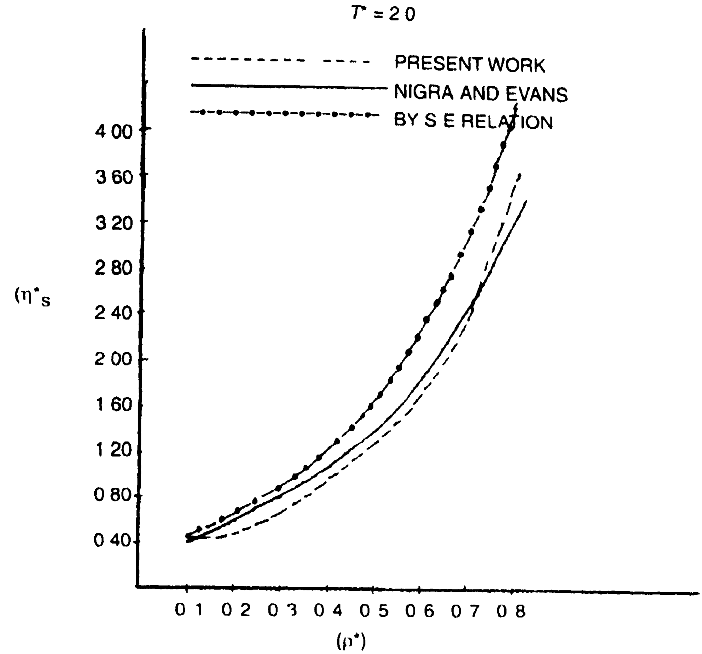

Figure 2. Plot of the reduced Shear viscosity η^* *vs* reduced density ρ^* at $T^* = 2\,0$ Present results (---------), Nigra and Evans (————) and results of the reduced viscosity employing Stokes-Einestein relation (– • – • – • –)

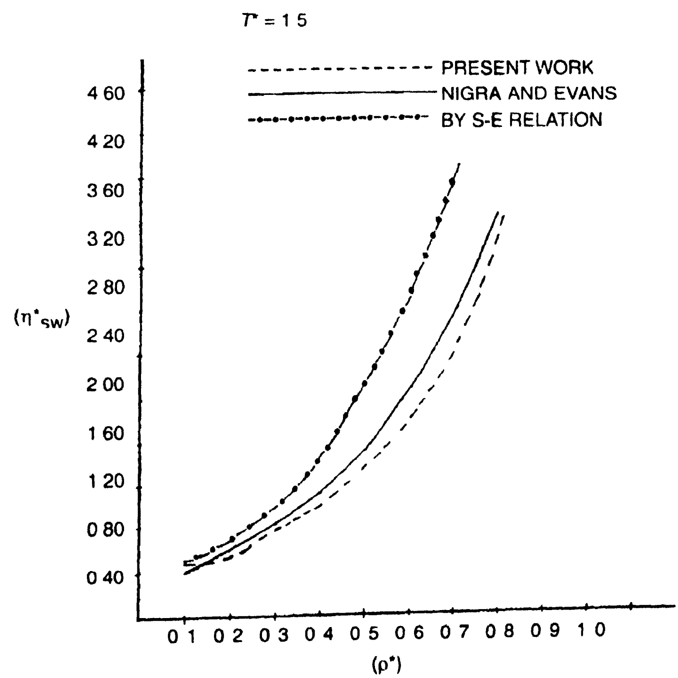

Figure 3. Plot of the reduced Shear viscosity η^* *vs* reduced density ρ^* at $T^* = 1\,5$ Present results (---------), Nigra and E.ans (————) and results of the reduced viscosity employing Stokes-Einestein relation (– • – • – • –)

(17) *i.e.* with the equation proposed by Nigra and Evans. As the temperature decreases *i.e.* $T^* = 2.0$ and $T^* = 1.5$ the equation obtained by employing Stokes-Einstein relation shows the deviation from the equation (17) predicted by Nigra and Evans. Nigra and Evans also pointed out the severe failure of Stokes-Einstein relation at low temperatures close to the glass transition temperature. Molecular dynamics simulation of high-density hard sphere fluid (super cooled liquid)clearly show a breakdown of the Stokes-Einstein equation [12]. These results [11, 12] support the present work that Stokes-Einstein relation cannot be used for square-well fluid at low temperatures.

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