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The Characteristics of Square-Well Fluid Transport Coefficients

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Abstract

The transport coefficients of the hard sphere system were computed by Alder A generalized Langevin equation was derived by Evans. The addition of an attractive square-well potential in place of hard sphere leads to a substantial on characteristics transport coefficients find breakdown of the stokes-Einstein relation is at minimum densities for square-well.

Keywords: Liquids, Behaviour, Measurements, Hypotheses, Potential.

Introduction

The transport coefficients of liquids have been the subject of extensive study in recent years. The Chapman-Enskog theory has provided a comprehensive explanation for the transport properties of low-density gases [1], but the features of thick, stiff fluids have been mainly ignored. It is only very lately that kinetic and mode-coupling theories have provided an understanding of dense hard spheres with enough features for different many-body systems [2-4]. These hypotheses are supported by neutron scattering measurements [6] and computer models of hard-sphere-like fluids [5], which show that important collision events associated with inter-atomic potentials are key.

The velocity-time correlation function (tcf) displays oscillating behavior for fluids with densities near the solid-liquid boundary, according to Alder et al. [7]'s investigation of hard-sphere fluids. Both Tang and Evans [9] and Kirkpatrick [8] found harmonic behavior in hard particles, and both studies determined the harmonic mode's frequency. While Tang and Evans discover that connected static and dynamic three-body correlations contribute to the oscillation frequency, Kirkpatrick attributes it to the fluid's static structural features. Consequently, there are a number of approaches that deal with correlated and uncorrelated collisions [10–15].

For non-spherical molecules, the spin dynamics can be influenced by both correlated and uncorrelated collisions, according to Evans's [14] investigation of the translational and rotational dynamics of ordinary fluids. For a rigid spherical system, Evans [15] calculated the correlation functions for self-diffusion, shear viscosity, and velocity-time assuming that friction is induced by both correlated backscattering (caging) collisions and uncorrelated binary collisions. We shall stick to this method for the present undertaking.

According to [15], the hard sphere concept does not account for attractive intermolecular interactions. We examine the square-well fluid, where the velocity-time correlation function (tcf) of intermolecular interactions is affected by attracting and repulsive forces, to ensure consistency.

Theory

Knowing the velocity-time correlation function (tcf) allows one to compute the transport coefficients, which in turn characterize the mass, momentum, and energy of a system. Applying the Green-Kubo relations [16] in reference systems like the hard sphere becomes challenging due to the singularity in the temporal correlation function. Their application in determining the integral of a limited time correlation function and its transport coefficient remains ineffective in resolving the issue. This leads us to consider alternate methods, such as using the memory function instead of the velocity autocorrelation function.

The transport coefficients of the hard sphere system were computed by Alder et al. [7] using the mean-square displacement method. A generalized Langevin equation was derived by Evans [15] by using Equation [17].

$$\left(\frac{\mathrm{d}}{\mathrm{d}t}\right) C_{\mathrm{v}}(t) = -f_{\mathrm{E}} C_{\mathrm{v}}(t) + \int_0^t \mathrm{d}\tau R(t-\tau) C_{\mathrm{v}}(\tau) \qquad ....(1)$$

where $Cv(t)$ is the velocity tcf:

$$C_{\mathrm{v}}(t) = \frac{m}{3k_{\mathrm{B}}T} < v.v(t) > \qquad ....(2)$$

and m the mass of the particle, which is the $k_{\mathrm{B}}T$ is the thermal energy, f_{E} provides a representation of the Enskog friction drag that is produced by binary collisions that are not correlated, while R(t) provides a representation of the memory function that is produced by events that are correlated. A formula may be found for the Enskog friction fE, which is:

$$f_{\mathrm{E}} = \frac{2}{3}\pi\sigma^2 g^{\mathrm{HS}}(\sigma) V_{\mathrm{F}} = \frac{2}{3} Z = \frac{16}{\sqrt{\pi}} \eta g^{\mathrm{HS}}(\sigma)\omega$$

$$V_{\mathrm{F}} = \sqrt{\frac{16k_{\mathrm{B}}T}{\pi m}} \quad \text{and} \quad \omega = \sqrt{\frac{k_{\mathrm{B}}T}{m\sigma^2}} \qquad ....(3)$$

In this equation, Z represents the collision frequency per particle, vF represents the relative thermal velocity, and $\eta = (\pi/6)\rho\sigma 3$ the proportion of the packing and $g^{\mathrm{HS}}(\sigma)$ this rigid spherical fluid's contact pair correlation function, which may be approximated using the following form of the Carnahan and Starling equation:

$$g^{\mathrm{HS}}(\sigma) = (1 - 0.5\eta)/(1 - \eta)^3. \qquad (3.a)$$

is the Enskog friction drag as a result of binary collisions that are not correlated, and R(t) means the memory function the result of correlated events. The Enskog friction, denoted as fE, may be expressed as follows:

$$C_1(t) = < \delta(r - \sigma) P_1(\hat{r}\hat{r}(t)) \delta(r(t) - \sigma) > \qquad \ldots\ldots\ldots\ldots.(4)$$

According to the frequency-dependent memory function, in order to

$$\breve{R}(s) = \int_0^\infty \mathrm{d}t \exp(-st) R(t) = -\Omega^2 \breve{C}_1(s) \qquad \ldots\ldots\ldots\ldots.(5)$$

It is sufficient to just enter t = 0 into the tcf in order to obtain an infinite. Tang and Evans [9] discovered that the memory function may be obtained from its zero time value by using the following formula:

$$R(t = 0^+) = -\Omega^2, \quad \Omega = \left(\frac{1}{4}\right) f_{\mathrm{E}} \qquad (5.a)$$

assumed to have been significant dynamical events involving three bodies. The potential expression for the velocity correlation function thereafter is [15].

$$C_{\mathrm{V}}(s) = \left(s + f_{\mathrm{E}} + \frac{\Omega^2}{\omega} \breve{h}_1(s)\right)^{-1} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots.(6)$$

where

$$\breve{h}_1(s) = \frac{1}{1 + x + (1 + x)^{-1}}$$

with

$$x = \sqrt{\frac{s^2 \sigma^2}{2D(s)}}$$

where *D*(*s*) relates to the frequency-dependent diffusion coefficient. Following is a new way to define the diffusion coefficient::

$$D = \frac{k_{\mathrm{B}} T}{m} \breve{C}_{\mathrm{v}}(s = 0) \qquad (7)$$

$$\widehat{C}_{\mathrm{v}}(s=0) = \left(0+\frac{16}{\sqrt{\pi}}\eta g^{\mathrm{HS}}(\sigma)\omega+\frac{16\eta^2[g^{\mathrm{HS}}(\sigma)]^2\omega\widehat{h}_1(s{=}0)}{\pi}\right)^{-1} \qquad \text{..........................} \quad (8)$$

On solving:

$$\widehat{h}_1(s=0) = \left(\frac{1}{2}\right) \qquad (9)$$

As a result, the diffusion coefficient may be solved mathematically as

$$D = \left(\frac{k_{\mathrm{B}}T}{m\sigma^2}\right)^{(1/2)}\sigma^2\left(\frac{16}{\sqrt{\pi}}\eta g^{\mathrm{HS}}(\sigma)+\frac{8\eta^2 g^{2\mathrm{HS}}(\sigma)}{\pi}\right)^{-1} \qquad \text{..........................}(10)$$

In addition, the reduced diffusion coefficient's final formula can be expressed in the same way as shown below.

$$D^{HS}{*} = \frac{D}{(k_B T/m\sigma^2)^{(1/2)}\sigma^2} = \left(\frac{16\,\eta\,g^{HS}(\sigma)}{\sqrt{\pi}}+\frac{8\,\eta^2 g^{2HS}(\sigma)}{\pi}\right)^{-1} \qquad (11)$$

here $g^{\mathrm{HS}}(\sigma)$ The hard sphere system's pair correlation function is represented by this equation. The Chapman-Enskog technique of solution [18,19] may be used to estimate the self-diffusion coefficient of a fluid contained in a square well, for instance, by inserting the pair correlation function $g^{\mathrm{HS}}(\sigma)$ in Eq. (11) by $g^{\mathrm{SQ}}(\sigma)$ as

$$g^{\mathrm{SQ}}(\sigma) = g^{\mathrm{SW}}(\sigma)+\lambda^2 g^{\mathrm{SW}}(\lambda\sigma)E \qquad (11.a)$$

Equation (11.a) was similarly obtained by Longuet-Higgins and Valleau [20] by supposing that a particle's velocity autocorrelation function decays exponentially with time. Their research was carried out with this assumption. In order to obtain the achieved values, several actions were essential. Thus, in the case of self-diffusion, the results obtained using the Chapman-Enskog approach, the Longuet-Higgins method, and the Valleau method are identical. Applying the pair correlation function to fluids with square wells is the standard procedure $g\mathrm{SW}(\sigma)$ in a way that, using the high temperature approximation (HTA) [21], might be stated as

$$g^{\mathrm{SW}}(\sigma) = g^{\mathrm{HS}}(\sigma)+\frac{1}{4T*}\frac{\partial a_1^{\mathrm{SW}}}{\partial\eta}+\frac{\lambda^3}{T*}g^{\mathrm{HS}}(\lambda\sigma) \qquad (12)$$

where $a^{SW}{}_1$ is the first-order disturbance term linked to attractive energy, denoted as εφ in the table below [22]:

$$a_1^{\mathrm{SW}} = -4\eta(\lambda^3 - 1)\left\{\frac{1-(\eta_{\mathrm{eff}}/2)}{(1-\eta_{\mathrm{eff}})^3}\right\} \tag{13}$$

and

$$\eta_{\mathrm{eff}} = C_1\eta + C_2\eta^2 + C_3\eta^3 \tag{14}$$

Matrices C1,C2, and C3 are provided in Ref. [22]. The functions $gsw(\sigma)$ and $gsw(\sigma)$ are the radial distribution functions that may be defined as indicated in [23], and they are evaluated at the specified sites σ and λ σ, respectively.

$$g^{\mathrm{SW}}(\lambda\sigma) = g^{\mathrm{HS}}(\lambda\sigma)\exp\left(\frac{\alpha}{T*} + \frac{\beta}{T*^2}\right) \tag{15}$$

where $T^* = k_{\mathrm{B}}T/\varepsilon$. After a thorough analysis, it was found that α was -0.4317 and β was -0.1177. The hard sphere system's pair correlation function is represented by this equation. The self-diffusion coefficient of a fluid in a square well can be found, for instance, by using the Chapman-Enskog technique of solution [18,19] to the pair correlation function.

$$g^{\mathrm{HS}}(\lambda\sigma) = 0.99948 + 0.82404\eta - 3.46976\eta^2 \quad .... (16)$$

It is possible to define the term E in Equation (11A) as

$$E = \exp\left(\frac{\varepsilon}{kT}\right) - \left(\frac{\varepsilon}{2kT}\right) - 2J$$

where J represents the function that is dependent on temperature as [22]

$$J = \frac{0.5 + 0.28304/T*}{1 + 0.15360/T*}$$

A Stokes–Einstein relation is used to establish a connection between the shear viscosity and the diffusion coefficient $(2\pi\_\mathrm{F}D\sigma/k\mathrm{B}T = 1)$.

This SE connection that Evans presented was utilized by us [25]

$(2\pi\eta^{\mathrm{SW}}{}_{\mathrm{F}}\ D^{\mathrm{SW}}\sigma/k_{\mathrm{B}}T = 1)$. Also, we followed this SE link that Evans had supplied us. Yeah, that's right; it's [15]. Nonetheless, the outcomes predicted by the two assertions are identical. [15]

The shear viscosity must be determined in this case. $\eta^{\mathrm{SW}}{}_{\mathrm{F}}$,Using Evans's suggested Stokes-Einstein relation, we have as

$$\frac{2\pi D^{\mathrm{SW}}[\eta_{\mathrm{F}}^{\mathrm{SW}}-\eta_{\mathrm{E}}]\sigma}{k_{\mathrm{B}}T}=\frac{4\eta f_{\mathrm{E}}}{25\omega(1+S)} \tag{17}$$

where

$$\frac{[\eta_{\mathrm{F}}^{\mathrm{SW}}-\eta_{\mathrm{E}}]}{m\rho}=\frac{256\sigma^{2}(\eta g^{\mathrm{SQ}}(\sigma))^{2}\omega}{75\pi} \tag{18}$$

and

$$\frac{\eta_{\mathrm{E}}}{m\rho}=\sigma^{2}\omega Y \tag{19}$$

where

$$Y=\left\{\frac{5\sqrt{\pi}}{96\eta g^{\mathrm{SQ}}(\sigma)}\left(1+\frac{8\eta g^{\mathrm{SQ}}(\sigma)}{5}\right)^{2}+\frac{8\eta g^{\mathrm{SQ}}(\sigma)}{5\sqrt{\pi}}\right\} \tag{20}$$

The lower shear viscosity is the result of solving the problem $\eta^{*\mathrm{SW}}{}_{\mathrm{F}}$ as

$$2\pi D{*}^{\mathrm{SW}}\eta_{\mathrm{F}}^{*\mathrm{SW}}=\frac{4\eta f_{\mathrm{E}}}{25\omega(1+S)}+12D{*}^{\mathrm{SW}}\eta Y \tag{21}$$

where

$$\eta_{\mathrm{F}}^{*\mathrm{SW}}=\frac{\eta_{\mathrm{F}}^{\mathrm{SW}}}{(k_{\mathrm{B}}T/m\sigma^{2})^{1/2}m/\sigma} \tag{22}$$

and

$$S=\frac{f_{\mathrm{E}}}{32\omega}=\frac{\eta g^{\mathrm{SQ}}(\sigma)}{2\sqrt{\pi}} \tag{23}$$

We make a comparison between our findings and the concept that Nigra and Evans [25] initially proposed in order to prove the reliability of our findings. It is possible that the value that Nigra and Evans [25] offered for the diffusion coefficient (in reduced units) has a solution is something that can be determined.

$$D{*}_{\mathrm{Evans}}^{\mathrm{SW}}=\frac{3}{8\rho*\sqrt{\pi}}\frac{1}{g^{\mathrm{HS}}(\sigma)[1+8\eta\lambda^{3}g_{1}(\lambda\sigma)f^{2}F]} \tag{24}$$

where $F=(7\lambda^{3}+2)/(42\lambda^{3}-7f\lambda^{3}-8f),$,

$f=1-\mathrm{e}^{-\varepsilon/kT}=1-\mathrm{e}^{-1/T^{*}},\ g_{1}(\lambda\sigma)=\mathrm{e}^{\varepsilon/kT}=\mathrm{e}^{1/T^{*}}.$

The shear viscosity that Nigra and Evans [25] proposed can be expressed as being able to be expressed in reduced units.

$$\eta *_{\text{Evans}}^{\text{SW}} = \frac{8\rho * \sqrt{\pi}}{3}\left(\frac{g^{\text{HS}}(\sigma)}{2\pi} + \frac{4f^2\pi\lambda^5\rho *^2 g_1(\lambda\sigma)\bar{n}}{15}\right) \tag{25}$$

where

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

$$\rho^* = \rho\sigma^3.$$

Through the utilization of the SE relation, it is possible to get the shear viscosity (in reduced units) from Equation (24).

$$\eta *_{\text{SE}}^{\text{SW}} = \frac{4\rho * g^{\text{HS}}(\sigma)}{3\sqrt{\pi}}(1 + 8\eta\lambda^3 g_1(\lambda\sigma)f^2F) \tag{26}$$

Discussion & Results

Due to the fact that it is one of the most straightforward fluid models, the square-well fluid is able to accurately depict the fundamental behavior of interactions between hard spheres. As a result, it is an appropriate model for modeling liquids. The square-well model was initially utilized by Longuet-Higgins and Valleau [20] in order to provide a description of the self-diffusion coefficients of thick fluids. The DRS hypothesis, which is analogous to the Enskog hard sphere (EHS) theory, was created by Davis and colleagues [18] with the intention of gaining better understanding of the transport coefficients of square-well fluids. In addition, Wilbertz et al. (WMBL) [26] developed a kinetic theory in order to ascertain the self-diffusion coefficients of square-well fluids. The outcomes of their theoretical predictions were validated through the use of computer simulations. In spite of this, the WMBL hypothesis argues that reliable forecasts are restricted to concentrations that are about moderate.

When it comes to accounting for the intricacy of multi-body interactions and the short period of collisions, the kinetic theory of transport mechanisms has encountered a number of obstacles. In spite of this, a great number of novel models [9–15] have been created in order to offer formulations of the self-diffusion coefficient for hard-sphere systems that are more precise. An example of such a theory is offered by Evans [15], which computes the velocity time correlation function for a system that is rigid and spherical. After that, the self-diffusion coefficient and the shear viscosity of a fluid that is contained within a square well may be calculated with the help of this function.

The radial distribution function at contact, which indicates where the centers of two molecules meet during collision, is a defining feature of the square-well fluid under Chapman-Enskog theory. This feature largely accounts for the attractive properties of the square-well fluid. In this study, we examine this distinct characteristic by estimating the pair correlation function at contact using the high-temperature approximation [21,22]. The factor η_{eff}, used to calculate the mean attractive energy, plays a crucial role in determining the transport properties. Based on the molecular dynamic calculations of Michels and Trappeniers [27,28], the numerical results presented in this study are expressed in reduced units.

Figure 1 displays case-specific molecular dynamics results and the reduced self-diffusion coefficients obtained from equations (11) and (11.a). The values of T (reduced temperature) are 2, 3, and 5, while λ (well width)is set at 1.5. Using $g_{\text{HS}}(\sigma)$ and Eq. (11), we deriveD^{HS}x as shown in Figure 1. Additionally, we calculate the self-diffusion coefficient Dusing the Smoluchowski equations for pair diffusion with an effective two-body intermolecular force, based on the square-well potential formula by Nigra and Evans [25]. For $\lambda = 1.5$ and $T^* = 2, 3,$ and 5, the results of this study are compared to molecular dynamics (MD) data in Figures 2-4. The proposed method yields results that are in strong agreement with Nigra and Evans' [25] expression at medium and high densities, though a slight discrepancy is noted at low densities. This disparity may arise because the present formula is tailored for dense fluids.

Figure 5 illustrates the experimentally measured relationship between density, well depth, and the square-well fluid's reduced shear viscosity, with $\lambda = 2.5$. Shear viscosity increases with density, while diffusivity decreases, regardless of whether the well depth $(T^* - 1)$ is increasing or decreasing. Discrepancies between low-density diffusivity and molecular dynamics results may stem from the focus on dense fluids in the theoretical transport coefficient formulation [15]. For highly viscous fluids, it is assumed that the memory function remains constant over time [29].

Figure 1 shows the diffusivity of a system using dotted lines to represent hard spheres. At low and intermediate densities, adding a square-well to hard spheres reduces diffusion, while at high densities, it has no impact. This can be explained by the square-well increasing the cross-section of the particles, causing more scattering and reducing diffusivity. If a well potential disrupts the negative temporal correlation at high densities, diffusivity may increase, aligning with Michels and Trappeniers' findings [27,28]. Figures 1 and 5 also show that, unlike in previous harmonic models [8,9], shear viscosity is finite, and the diffusion coefficient remains present.

Lastly, Figure 6 validates the Stokes-Einstein relation for a square-well fluid, demonstrating its temperature dependence at low densities. However, the relation approaches unity at high densities, behaving like a hard-sphere system at medium and high densities due to its temperature dependence.

Additionally, it is observed that when the product is at lower densities, $\eta^{*\text{SW}}{}_{\text{F}}\, D^{*\text{SW}}$ with increasing well depth, has a tendency to vary to much lower values ε^* (i.e., T^{*-1}). As will become clear in the next paragraphs, molecular dynamics data [27,28] corroborate this. Michels and Trappeniers [27] claim that, under identical conditions, the diffusion coefficient for hard spheres is greater than that for square-well systems. Furthermore, as the hole depth increases, the diffusion coefficient drops for materials with low densities. This happens as the depth of the well is raised. Furthermore, it has been shown that the diffusion coefficient variation is more significant than the shear viscosity fluctuation [25]. The purpose of this experiment was to test the viability of the Stokes-Einstein connection at low temperature applications. Because they are both derived from the same set of parameters, Nigra and Evans [25] are able to generate both the shear viscosity (Eq. (6.1.25)) and the diffusion coefficient (Eq. (6.1.24)) formulations. The results of comparing two separate outcomes are shown in Figure 6.1.7. given that λ is 1.5 and T* is 3, 2, and 1.5. Figure 6.1.7 shows this.

$\varepsilon^* = 0.5$ or $T^* = 2.0$

ρ^* $\lambda = 1.4$ $\lambda = 1.5$ $\lambda = 1.6$

Continued work by MD Continued work by MD Continued work by MD

0.2 0.526 0.664 0.518 0.628 0.503 0.598

0.4 0.232 0.265 0.225 0.247 0.213 0.236

0.6 0.116 0.114 0.109 0.106 0.100 0.102

0.8 0.050 0.039 0.045 0.039 0.042 –

0.86 0.037 0.025 0.033 0.026 0.031 –

0.90 0.029 0.002 0.027 0.020 0.025 –

MD results are from Ref. [26].

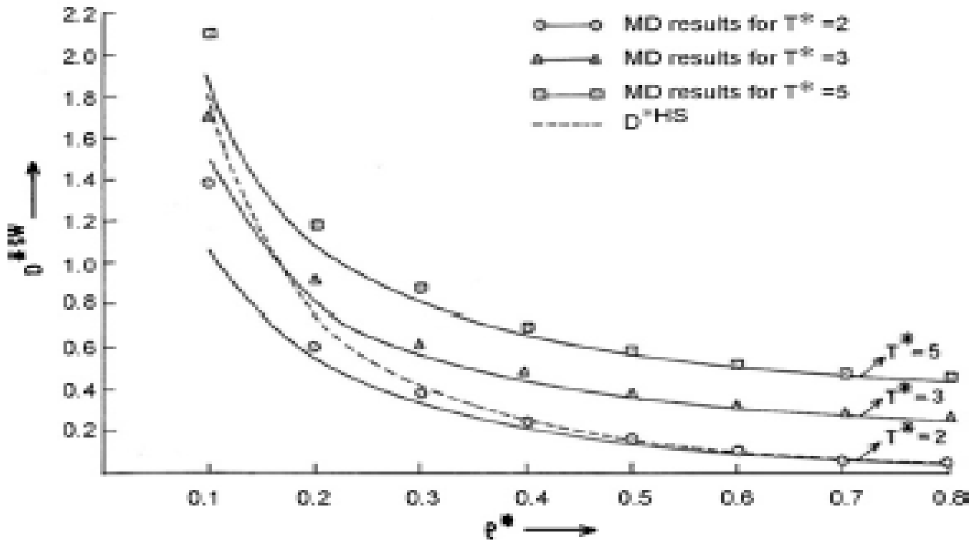

Figure 1 demonstrates the lowered self-diffusion coefficients of a square-well fluid as a function of the reduced density of the fluid under consideration. $(\rho\sigma^3 = \rho^*)$ at reduced temperatures $T^* = 2, 3,$ and 5. For clarity, the Y-axis has been shifted by +0.2 units for $T^* = 3$ and by +0.4

units for $T^* = 5$. he dotted line represents the reduced diffusion coefficient for a hard sphere fluid. Molecular dynamics (MD) simulation results are indicated by symbols for each temperature: for $T^* = 2$, $\diamond$ for $T^* = 3$, and $\triangle$ for $T^* = 5$.

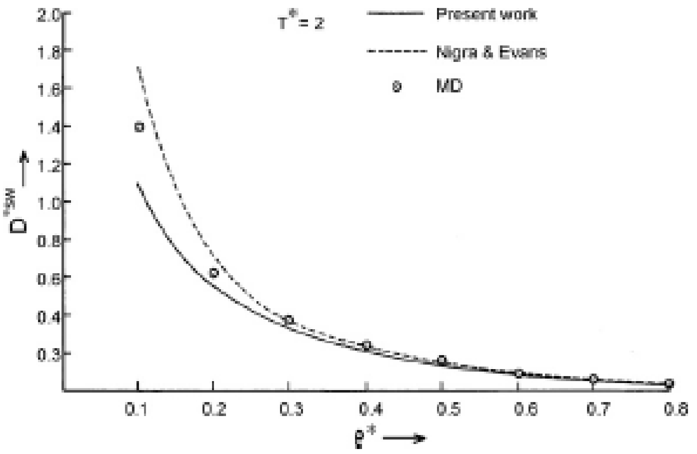

Figure 2 compares the present model to the one created by Nigra and Evans [25], drawing attention to the parallels and variations in how the two models anticipate the self-diffusion coefficients of a square-well fluid at a lowered temperature of $T^* = 2$. The two models are compared with respect to the patterns of decreasing self-diffusion coefficients, highlighting their commonalities and differences.

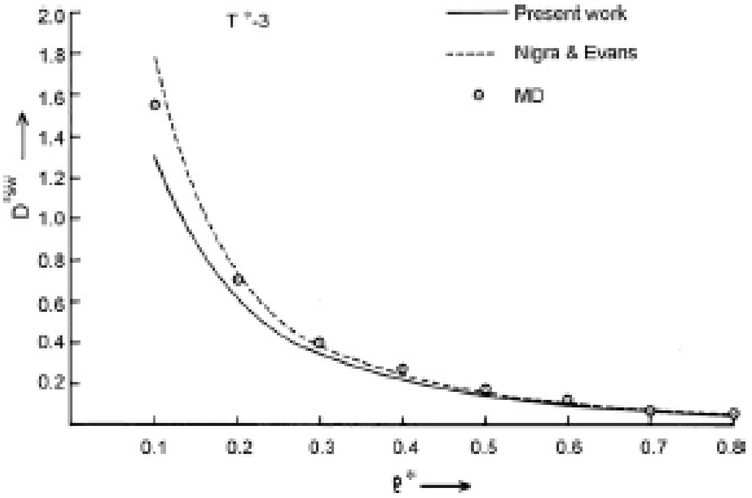

Figure 3 shows a comparison between the current model and the model proposed by Nigra and Evans [25] for finding the square-well fluid's lowered self-diffusion coefficients at a reduced temperature of $T^* = 3$ To find out how well either model predicts the fluid's self-diffusion behavior under these circumstances, we're comparing the two.

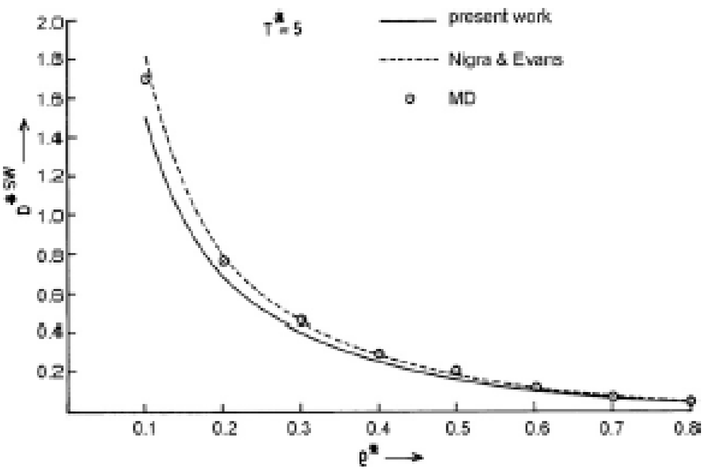

Figure4 draws comparisons between the current model and the one developed by Nigra and Evans [25] with the purpose of predicting the reduced self-diffusion coefficients of a square-well fluid at a reduced temperature of $T^* = 5.$ contrasts and compares the present model with that of Nigra and Evans [25] in order to forecast the lowered self-diffusion coefficients of a square-well fluid at a reduced temperature of

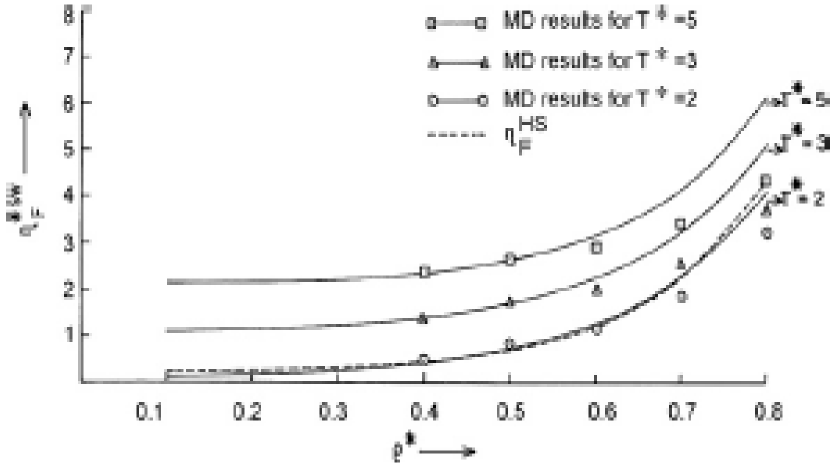

Figure 5 illustrates the decreasing shear viscosity of a square-well fluid as a function of reduced density $(\rho\sigma^3 = \rho^*)$ for reduced temperatures $T^* = 2, 3,$ and $5.$ To enhance clarity, the Y-axis has been offset by +1 unit for $T^* = 3$ and by +2 units for $T^* = 5.$ The decreased shear viscosity for a hard spherical fluid is seen by the dotted line. Results of molecular dynamics (MD) simulations are shown using several symbols: for $T^* = 2$, ◇ for $T^* = 3$, and △ for $T^* = 5$.

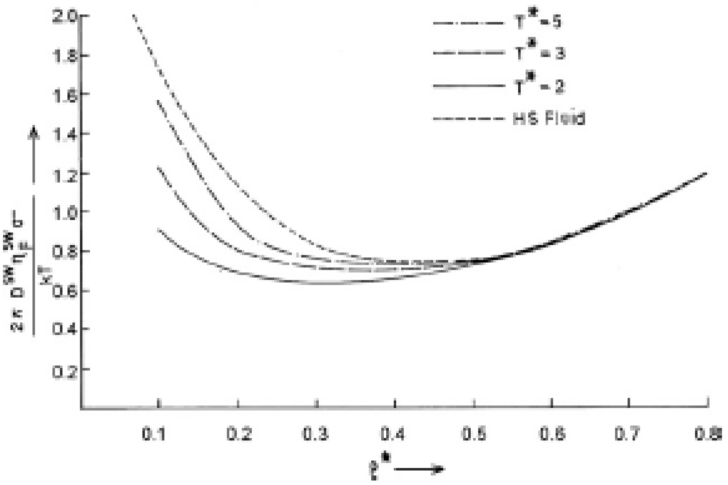

Figure 6 uses a square-well fluid to investigate the Stokes-Einstein connection. The solid line depicts to show this relation for a rigid spherical system $T^* = 2$, the large dashed line represents $T^* = 3$, and the dash-dotted line represents $T^* = 5$. There is a little dashed line that represents the Stokes-Einstein (SE) connection.

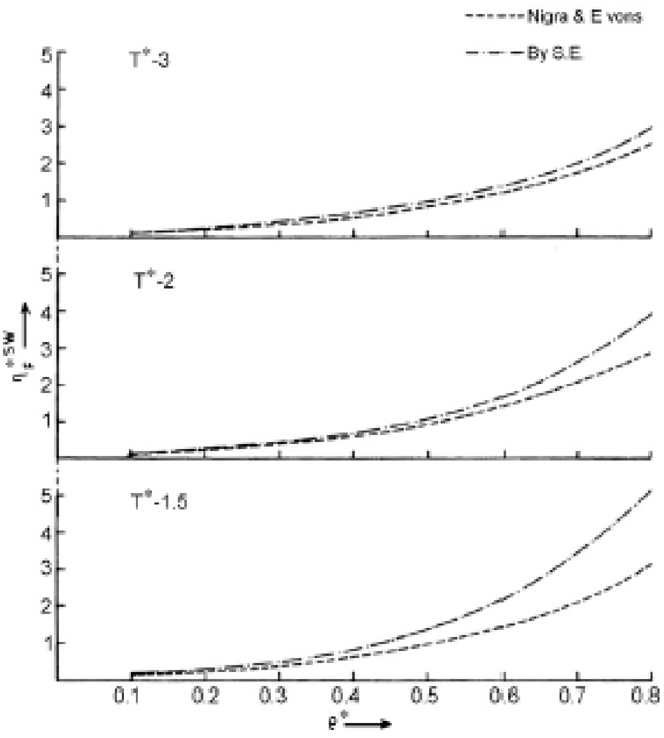

Figure 7 evaluates the square-well fluid's decreased shear viscosity by comparing it to the shear viscosity computed using the Stokes-Einstein relation, which is based on the Nigra and Evans model. At lower temperatures, the comparison is made. $T^* = 3, 2,$ and $1.5.$

Conclusion

This model, which was provided by Evans [15], will function well regardless of whether the fluid is square-well or hard spherical. In addition, it functions very well with fluids that are square-well. However, more modifications to its memory function are required, and these modifications have the potential to provide outcomes which conform to the findings that Nigra and Evans [25] articulated for square-well fluids in your article.

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