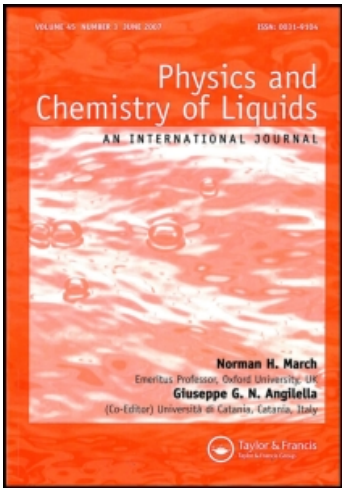


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# Transport coefficients for hard-chain fluid

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# Transport coefficients for hard-chain fluid

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Diffusion coefficient and shear viscosity are calculated for fluids containing molecules modelled as chains of tangent hard spheres. A formula for the Stokes–Einstein relation is proposed for hard chain fluids to calculate the shear viscosity from the diffusion coefficient. The numerical results show a good agreement between theoretical values and molecular dynamics results

**Keywords:** Stokes–Einstein relation; diffusion coefficient; shear viscosity



## 1. Introduction

The study of transport coefficients is very important in the development of our standing of molecular motions and interactions in the dense fluids [1]. For monoatomic fluids the Enskog kinetic theory of a hard sphere fluid has been used with reasonable success [2]. In this theory, the transport properties are calculated through the use of simple equations relating the particle mass, temperature, density, particle size and radial distribution function at contact diameter. Several empirical methods [3–5] have been developed to calculate diffusion coefficients for normal real fluids based on smooth and rough–hard sphere systems. For chain molecules, Yu and Gao [6] developed equation to estimate self–diffusion coefficients of Lennard-Jones chain (LJC model). Smith *et al*. [7]. have presented the molecular dynamics study of transport coefficients for chains of tangent hard spheres. Most of the work is limited to diffusion coefficients and no theoretical study has been done to study the viscosity coefficient of chain molecules. In this article, we propose a modified Stokes–Einstein relation for hard chain molecules. Thus, the present work describes the results for self diffusion coefficients and shear viscosity of hard chain fluid with chain lengths 2, 4, 8 and 16.

## 2. Theory

The Enskog equation for the hard sphere fluid given by

$$D_E = \frac{D_0}{g(\sigma)} = \frac{3}{8\rho\sigma^2}\left(\frac{k_B T}{\pi m}\right)^{1/2}\frac{1}{g(\sigma)}, \tag{1}$$

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where $g(\sigma)$ is the radial distribution function at contact is [8],

$$g(\sigma) = \frac{1 - 0.5\eta}{(1-\eta)^3}, \tag{2}$$

where $\eta$ is packing fraction, $\eta = (\pi/6)\ \rho\sigma\ [3] = (\pi/6)\ \rho^*$.

A correction factor is proposed by Ruckenstein and Liu [9], employing molecular dynamics simulation data to describe diffusion coefficient at high densities as,

$$D_{\mathrm{HS}} = D_{\mathrm{E}} f(\rho^*) = \frac{D_o f(\rho^*)}{g(\sigma)}, \tag{3}$$

where $f(\rho^*) = 1 + 0.94605\ \rho^{*1.5} + 1.4022\ \rho^{*3} - 5.8698\rho^{*5} + 2.6626\ \rho^{*7}$.

For the chain molecule $D_{\mathrm{o}}$ in Equation (1) can be described as

$$D_{\mathrm{oc}} = \frac{3}{8\rho\sigma'^2}\left(\frac{k_{\mathrm{B}}T}{\pi \mathrm{m}'}\right)^{1/2}, \tag{4}$$

where $\sigma'$ and $m'$ are expressed as

$$\sigma'^3 = N\sigma^3;\ m' = Nm. \tag{5}$$

On solving Equation (4) we get

$$D_{\mathrm{oc}} = \frac{3\sigma}{8\rho^* N^{1/6}}\left(\frac{k_{\mathrm{B}}T}{\pi m}\right)^{1/2}, \tag{6}$$

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

Hence, the self–diffusion coefficient of hard-chain fluid can be expressed as

$$D_{\mathrm{HSC}} = \frac{D_{\mathrm{oc}} F(N, \rho^*)}{g(\sigma)}, \tag{7}$$

where $F(N,\rho^*)$ is correction factor for the hard chain length

$$F(N, \rho^*) = f(\rho^*) \exp\left\{-0.06356(N-1) - 0.05212\left[\frac{N-1}{N}\right]\rho^* - 1.9709\left[\frac{N-1}{N}\right]^2 \rho^*\right\}, \tag{8}$$

where $N$ represents chain length.

The reduced diffusion coefficient can be defined as

$$D^*_{\mathrm{HSC}} = \frac{D_{\mathrm{HSC}}}{(k_{\mathrm{B}}T/m\sigma^2)^{1/2}\sigma^2} = \frac{3F(N, \rho^*)}{8\sqrt{\pi N^{1/6}}\rho^* g(\sigma)}. \tag{9}$$

To determine the shear viscosity, we propose a Stokes–Einstein relation for chain molecules as

$$\frac{2\pi\sigma' N^{1/3}\eta_{\mathrm{shear}} D}{k_{\mathrm{B}}T} = 1, \tag{10}$$

where $\sigma'$ is assumed as single hard-sphere diameter for chain molecules [6]. Thus we get shear viscosity as

$$\eta_{\text{shear}} = \frac{4(k_B Tm)^{1/2}\rho^* g(\sigma)}{3\sqrt{\pi}\sigma^2 N^{1/2} F(N,\rho^*)}, \tag{11}$$

and reduced shear viscosity as

$$\eta^*_{\text{shear}} = \frac{\eta_{\text{shear}}}{(k_B Tm)^{1/2}/\sigma^2} = \frac{4\rho^* g(\sigma)}{3\sqrt{\pi}N^{1/2} F(N,\rho^*)}. \tag{12}$$

## 3. Results and discussion

In this article, we report the self-diffusion coefficient and shear viscosity of hard-chain fluids with lengths 2, 4, 8 and 16 at different volume fractions. The general trend is that the self-diffusion coefficient decreases with increasing volume fraction and also with increasing chain length, while the shear viscosity increases with increasing volume fraction and also with increasing chain length. Self-diffusion coefficient decreases with chain length is due to stronger connectivity constraints that impede motion. Our proposed formula of Stokes–Einstein relation predicts good agreement between theoretical and molecular dynamics results of shear viscosity. However, the deviation increases with increasing chain length at high densities. The results are shown in Table 1. The most notable feature of the



Table 1. Comparison of present results for reduced transport coefficients of hard chain fluids with simulation results.

| $\eta$ | $D^*_{\text{HSC}}$ Equation (9) | $D^*_{\text{HSC}}$ MD [7] | $\eta^*_{\text{shear}}$ Equation (12) | $\eta_{\text{shear}}$ MD [7] |
|---|---|---|---|---|
| | | $N=2$ | | |
| 0.1 | 0.699 | 0.680 | 0.143 | 0.152 |
| 0.2 | 0.271 | 0.266 | 0.368 | 0.313 |
| 0.3 | 0.127 | 0.121 | 0.786 | 0.733 |
| 0.4 | 0.049 | 0.047 | 2.018 | 2.208 |
| 0.5 | 0.009 | 0.009 | 10.37 | 10.68 |
| | | $N=4$ | | |
| 0.1 | 0.486 | 0.479 | 0.129 | 0.125 |
| 0.2 | 0.167 | 0.175 | 0.376 | 0.330 |
| 0.3 | 0.069 | 0.070 | 0.905 | 0.896 |
| 0.4 | 0.024 | 0.025 | 2.621 | 3.24 |
| 0.5 | 0.004 | 0.004 | | |
| | | $N=8$ | | |
| 0.1 | 0.311 | 0.307 | 0.127 | 0.114 |
| 0.2 | 0.099 | 0.101 | 0.400 | 0.411 |
| 0.3 | 0.038 | 0.036 | 1.040 | 1.399 |
| 0.4 | 0.012 | 0.012 | 3.26 | 4.66 |
| 0.5 | 0.001 | 0.001 | | |
| | | $N=16$ | | |
| 0.1 | 0.159 | 0.175 | 0.156 | 0.150 |
| 0.2 | 0.048 | 0.050 | 0.574 | 0.663 |
| 0.3 | 0.017 | 0.016 | 1.396 | 2.200 |

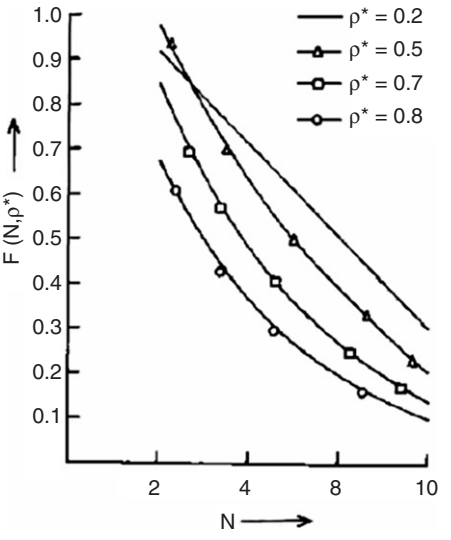


Figure 1. Friction coefficient *versus* chain length at various densities.



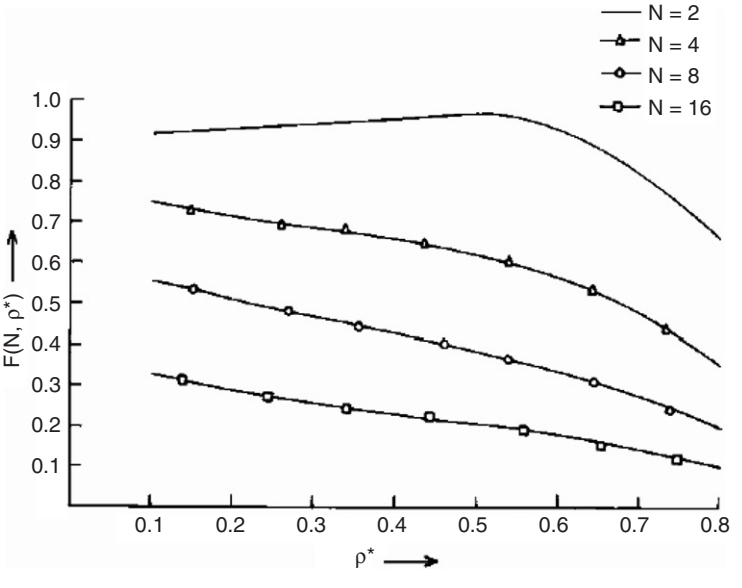


Figure 2. Friction coefficient *versus* densities at various chain length.

results is the non-monotonous behaviour of the friction coefficient of the chain molecules, i.e. $F(N, \rho^*)$. This is observed with increasing density for a particular chain length as well as with increasing chain length at a particular value of density. The non-linearity is found to be maximum with increasing chain length at high density $\rho^* = 0.8$. Thus, the friction coefficient plays an important role in describing the transport coefficients. The results are shown in Figures 1 and 2.

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