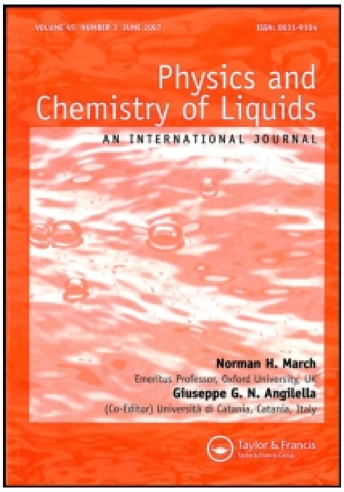

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J. Amorós[a]; J. R. Solana[a]; E. Villar[a]
[a] Department of Fundamental Physics, University of Santander, Santander, Spain

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Behaviour of the Coefficients of Viscosity and Selfdiffusion of a Hard Spheres Dense Fluid Using the Significant Structures Theory

J. AMORÓS, J. R. SOLANA and E. VILLAR

Department of Fundamental Physics, University of Santander, Santander, Spain.

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The coefficient of viscosity and the Stokes relation between this and the coefficient of self-diffusion for a hard spheres dense fluid obtained from the Significant Structures Theory, have been compared with the corresponding Molecular Dynamics data obtained from the bibliography on this subject. In both cases, a satisfactory level of agreement was achieved.

INTRODUCTION

The Significant Structures Theory (SST) establishes two different approaches with respect to the coefficient of viscosity of liquids.[1] A simple relationship has also been suggested between the coefficients of viscosity and selfdiffusion for a rigid sphere dense fluid. It is these equations that we examine in comparison with the Molecular Dynamics results. In order to obtain equations independent on the nature of the fluid, they are usually divided by the equations provided by Enskog's theory. In this way, simple equations are obtained that depend only on the V/V_0 ratio, where V_0 is the close packed volume and on the characteristic equation of state, introduced through the compressibility factor Z.

COEFFICIENT OF VISCOSITY

In accordance with the SST,[1] the viscosity of a hard sphere dense fluid may be expressed in the following way:

$$\eta = (\pi mkT)^{1/2} N \frac{(\sqrt{2}V_s/N)^{1/3} - d}{V - V_s} + \frac{V - V_s}{V}\eta_g \tag{1}$$

where V_s is the volume of the solid at the melting point, d is the diameter assigned to the rigid spheres, m is the mass of a single molecule, k the Boltzmann's constant and η_g the viscosity of the diluite gas.

Now, if a molecular dynamics method is used,[2] a phase transition is found for a hard sphere dense fluid to a volume of $1.5V_0$, where V_0 is the close packed volume of the rigid spheres. If we accept this result, and assuming the viscosity of a dilute hard sphere system to be valid for the gas-like contribution, we may then express Eq. (1) in the following form:

$$\eta = (\pi mkT)^{1/2} N \frac{(1.5\sqrt{2}V_0/N)^{1/3} - d}{V - 1.5V_0} + \frac{V - 1.5V_0}{V}\frac{5}{16d^2}(mkT/\pi)^{1/2} \tag{2}$$

On the other hand, we shall suppose that the viscosity of a hard sphere dense fluid can be expressed in accordance with Enskog's equation, as follows[3]:

$$\eta_E = \frac{1}{Y_E(n)}\left[1 + \frac{2}{5}nb_E Y_E(n)\right]^2 \eta_B + \frac{3\tilde{\omega}}{5} \tag{3}$$

where η_B is Boltzmann's viscosity for hard spheres:

$$\eta_B = (5/16d^2)(mkT/\pi)^{1/2} \tag{4}$$

and $Y_E(n)$ is supplied by the equation:

$$Y_E(n) = \frac{Z - 1}{nb_E} \tag{5}$$

$Z = P/nkT$, being the characteristic equation of state for a hard spheres system, in which:

$$b_E = \frac{2\pi d^3}{3} \tag{6}$$

Finally:

$$\tilde{\omega} = n^2 b_E^2\, Y_E(n)\frac{(mkT)^{1/2}}{d^2\pi^{3/2}} \tag{7}$$

Therefore, we can finally state:

$$\eta_E = \frac{Nb_E}{Vd^2}\left(\frac{mkT}{\pi}\right)^{1/2}\left\{\frac{1}{Z-1}\left[1+\frac{2}{5}(Z-1)^2\right]^2\frac{5}{16}+\frac{3}{5}\frac{Z-1}{\pi}\right\} \tag{8}$$

In present work we will use the Molecular Dynamics results for the equation of state of the rigid sphere system. If we wish to discover the $\eta_{\mathrm{SST}}/\eta_E$ ratio between the coefficient of viscosity supplied by both theories, after making some transformations, we obtain:

$$\frac{\eta_{SST}}{\eta_E} = \frac{9\pi}{2.9619}\,\frac{0.2051/q - 1.5 + (1-1.5/q)\,0.0994}{1/Z - 1\,\{[1+2/5\,(Z-1)]^2 5/16 + 3/5\,Z - 1/\pi\}} \tag{9}$$

where $q = V/V_0$. This equation depends only on V/V_0 and Z, as we stated above.

Figure 1 shows the values for this expression, together with the corresponding values obtained using simulation methods.[4] The agreement is most satisfactory, although at lower values of V/V_0 the SST overestimates the solid-like contribution.

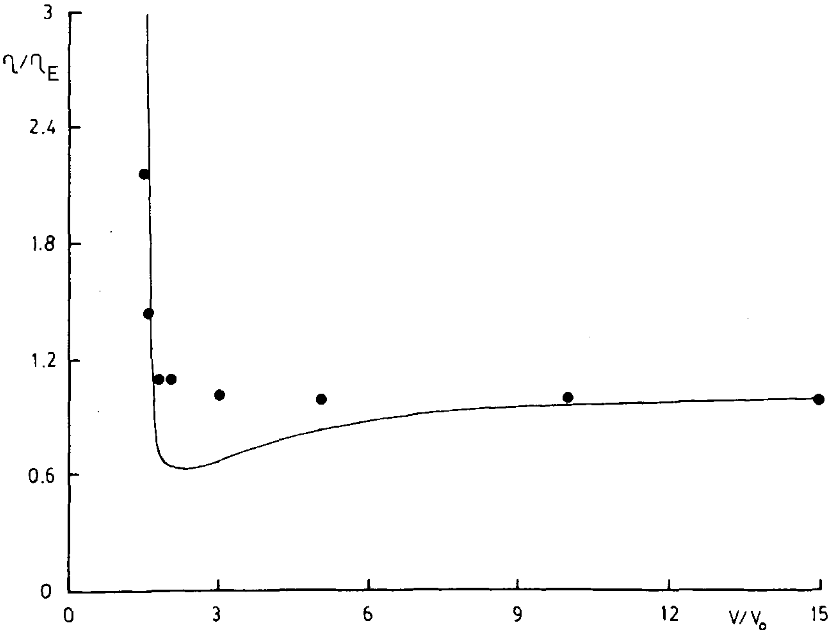

FIGURE 1 Graph showing the ratio between viscosity and Enskog's viscosity for hard spheres as a function of V/V_0. Continuous line: theoretical results. Points: M. D. calculations of Ref. 4.

STOKES RELATION

According to the SST,[1] the relationship between the coefficients of self-diffusion and viscosity for a rigid sphere system may be expressed as follows:

$$D = \frac{kT}{\eta \xi \lambda_2 \lambda_3 / \lambda_1} \tag{10}$$

where $\xi = 6$ for hexagonal packing and

$$\lambda_2 \lambda_3 = \frac{\sqrt{3} a^2}{2}; \qquad \lambda_1 = \frac{\sqrt{3}}{2}; \qquad a^3 = \frac{\sqrt{2} V_s}{N} \tag{11}$$

The Stokes relation, on the other hand, takes the following form:

$$\frac{D \eta d}{kT} = \frac{\pi}{3} \tag{12}$$

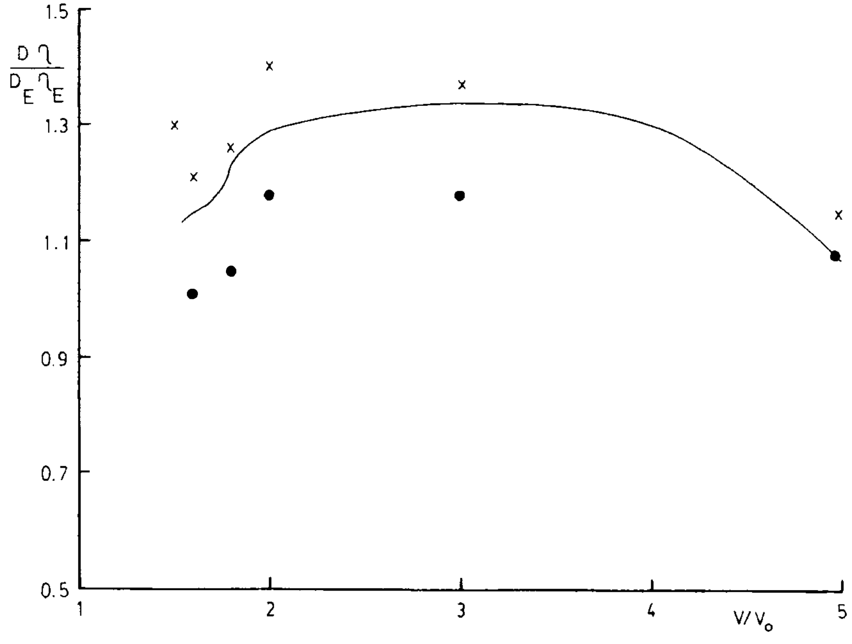

FIGURE 2 Graph of the Stokes relation ratio to that obtained from the Enskog theory for hard spheres. Continuous line: theoretical results. Points: M D. results for a 108 particles system (×) and for an infinite system (●).

where D is the selfdiffusion coefficient which, on the basis of the Enskog's theory, may be expressed either as:

$$D_E = \frac{3}{8\pi d^2 Y_E(n)} \left(\frac{kT}{\pi m}\right)^{1/2} \tag{13}$$

or as:

$$D_E = \frac{d}{4(Z-1)} \left(\frac{kT}{\pi m}\right)^{1/2} \tag{14}$$

In a similar way to what we have seen for the coefficient of viscosity, the $D_{\mathrm{SST}}\eta_{\mathrm{SST}}/D_{\mathrm{E}}\eta_{\mathrm{E}}$ ratio, may be expressed by a simple equation that depends only on q and Z, viz:

$$\frac{D_{\mathrm{SST}}\eta_{\mathrm{SST}}}{D_{\mathrm{E}}\eta_{\mathrm{E}}} = \frac{0.1966q}{[1/(Z-1)^2 + 4/25 + 4/5\ 1/Z - 1]\ 5/16 + 3/5\pi} \tag{15}$$

Figure 2 shows this ratio, together with the corresponding values obtained using molecular dynamics methods.[4]

DISCUSSION AND CONCLUSIONS

We have therfore found that the SST, with a hard sphere potential, satisfactorily reproduces simulation results for the coefficient of viscosity and the Stokes relation. On the other hand, as we can see in Figure 1, the SST overestimates the solid-like contribution to the viscosity of a hard sphere system in the neighbourhood of $V/V_0 = 2.5$, probably due to the fact that the choice of $V_s = 1.5V_0$ is a little arbitrary.[5]

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