

V.21.7 TRANSPORT PROPERTIES

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To evaluate numerically the transport properties such as diffusion coefficient and shear viscosity for dispersed systems, we have two ways – direct and indirect simulations. In the former way, we simulate the experimental situation on the computer and measure the quantity directly, while in the latter way, we calculate time-correlation functions in the equilibrium state and interpret them into the transport properties by the Green-Kubo formula, which is widely used for simple liquids [1]. The main difference between simple liquids and dispersed systems such as colloidal suspensions is the existence of hydrodynamic interaction by the fluid surrounding the particles [2]. Here we focus on the contribution of the hydrodynamic interaction[3]. Other contributions such as interparticle forces and Brownian motion are briefly commented later.

Diffusion Coefficients

The self-diffusion coefficient is defined by the mean-square displacement of a tracer particle as

$$D^s = \frac{1}{6} \frac{d\langle |\mathbf{x}(t) - \mathbf{x}(0)|^2 \rangle}{dt}, \quad (1)$$

where $\mathbf{x}(t)$ is the position of the tracer particle at time t . The bracket $\langle \rangle$ denotes the average on many time sequences. It has two asymptotes: short- and long-time diffusion coefficients. The splitting timescale is a^2/D_0 where a is the particle radius and D_0 is the Stokes-Einstein diffusion coefficient of a single isolated particle in the fluid defined by

$$D_0 = \frac{k_B T}{6\pi\eta a}. \quad (2)$$

Here k_B is the Boltzmann constant, T is the temperature, and η is the viscosity of the fluid. The long-time self-diffusion coefficient is also written as

$$D_\infty^s = \lim_{t \rightarrow \infty} \frac{\langle |\mathbf{x}(t) - \mathbf{x}(0)|^2 \rangle}{6t} = \frac{1}{3} \int_0^\infty dt \langle \mathbf{U}(0) \cdot \mathbf{U}(t) \rangle, \quad (3)$$

where \mathbf{U} is the velocity of the tracer particle. The last form with the time-correlation function of the velocity is called Green-Kubo formula. By (1) or

(3), the self-diffusion coefficients are calculated from many series of dynamical simulations: This is the indirect way.

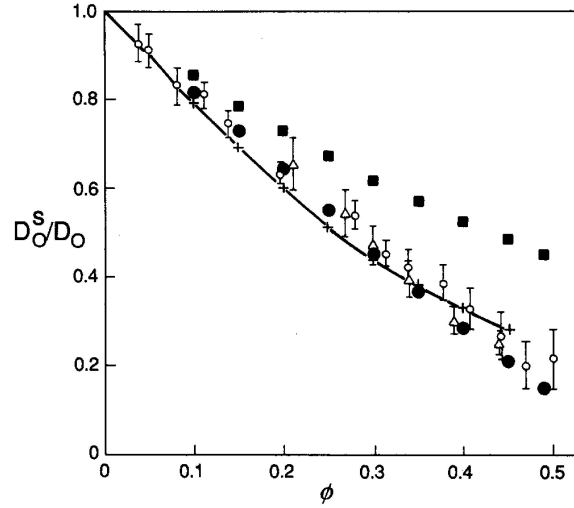


Figure 1: Short-time self-diffusion coefficients obtained by Stokesian Dynamics methods (solid symbols), a theoretical calculation (solid line), and experimental results (open symbols). (From Ref. 3.)

The direct way for diffusion coefficients is to calculate the mobility of the tracer particle. The factor $1/6\pi\eta a$ in (2) is the mobility of the single isolated particle. For dispersed systems, on the other hand, the mobility is not just $1/6\pi\eta a$ because of the hydrodynamic interaction among particles. Under the Stokes approximation, the hydrodynamic interaction is expressed by the resistance equation

$$\begin{pmatrix} \mathbf{F} \\ \mathbf{S} \end{pmatrix} = \begin{pmatrix} \mathbf{R}_{FU} & \mathbf{R}_{FE} \\ \mathbf{R}_{SU} & \mathbf{R}_{SE} \end{pmatrix} \cdot \begin{pmatrix} \mathbf{U} - \mathbf{u}^\infty \\ -\mathbf{E}^\infty \end{pmatrix}, \quad (4)$$

where \mathbf{F} is the force and torque vector with $6N$ components, \mathbf{S} is the stresslet, $\mathbf{U} - \mathbf{u}^\infty$ is the translational and rotational velocities relative to the imposed flow, and \mathbf{E}^∞ is the strain imposed to the system, for N particles in the system. The whole resistance matrix with $11N \times 11N$ elements depends only on the configuration of the particles and is calculated by Stokesian Dynamics method [4]. From (4), the particle velocity \mathbf{U} under no external flow is given by

$$\mathbf{U} = \mathbf{R}_{FU}^{-1} \cdot \mathbf{F}. \quad (5)$$

Then, the Stokes-Einstein relation is extended for dispersed systems as

$$D_0^s = k_B T \langle (\mathbf{R}_{FU}^{-1})_{\alpha\alpha} \rangle, \quad (6)$$

where D_0^s is a matrix with 6×6 elements and $(\mathbf{R}_{FU}^{-1})_{\alpha\alpha}$ denotes the self part of the inverse of the resistance matrix with 6×6 elements. The diagonal elements of the translational part of D_0^s is the short-time self-diffusion coefficients D_0^s . Figure 1 shows the numerical results of D_0^s/D_0 with experimental results[3].

Shear Viscosity

The shear viscosity is usually calculated by the direct way rather than indirect way: The reason is that the interparticle force of hydrodynamic interaction needed for the Green-Kubo formula of the shear viscosity is complicated.

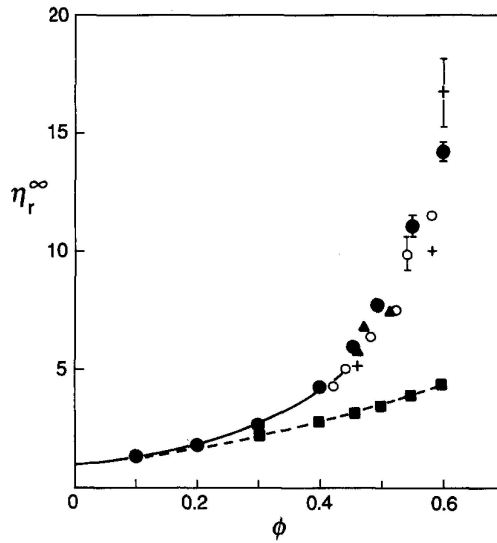


Figure 2: Shear viscosities obtained by Stokesian Dynamics methods (solid symbols), theoretical calculations (lines), and experimental results (open symbols). (From Ref. 3.)

In the direct way, the bulk stress Σ is calculated under the shear flow. Neglecting Brownian motion and interparticle forces, the bulk stress is given

by

$$\langle \boldsymbol{\Sigma} \rangle = -\langle p \rangle \mathbf{I} + 2\eta \langle \mathbf{E}^\infty \rangle - n \langle \mathbf{S} \rangle, \quad (7)$$

where p is the pressure and n is the number density of particles [5]. From (4), the stresslet for force-free particles is given by

$$\mathbf{S} = (\mathbf{R}_{SU} \cdot \mathbf{R}_{FU}^{-1} \cdot \mathbf{R}_{FE} - \mathbf{R}_{SE}) \cdot \mathbf{E}^\infty. \quad (8)$$

After taking the average of the stresslet \mathbf{S} , the shear viscosity of dispersed system η_r scaled by the fluid viscosity η is obtained as

$$-n \langle \mathbf{S} \rangle = 2\eta (\eta_r(\phi) - 1) \langle \mathbf{E}^\infty \rangle, \quad (9)$$

where ϕ is the volume fraction of particles. Note that in the dilute limit, we have the Einstein’s result

$$\eta_r = 1 + \frac{5}{2}\phi. \quad (10)$$

Figure 2 shows the numerical results of η_r with experimental results[3].

Remarks

Using the Stokesian Dynamics method, we can calculate micro structures of dispersed systems in (4) under arbitrary circumstances and evaluate any quantities like sedimentation velocity and normal stresses as well, by the direct way. To do this, however, we need to know the quantity to calculate, as shown in (7). The Brownian contributions are shown for the diffusion coefficient[6] and the bulk stress[7]. General form of the bulk stress is shown[8] and thorough numerical analysis on the Péclet number dependence of diffusion coefficients and shear viscosity is shown[9].

Acknowledgments

The author would like to acknowledge the support by DOE grant FG02-99ER14966.

Notation

a	Particle radius (m)
D_0	Diffusion coefficient of an isolated particle (m^2/s)
D^s	Self-diffusion coefficient (m^2/s)
D_∞^s	Long-time self-diffusion coefficient (m^2/s)
D_0^s	Short-time self-diffusion coefficient (m^2/s)
D_0^s	Short-time self-diffusion matrix
E^∞	Rate-of-strain tensor imposed to the system (1/s)
\mathbf{F}	Force and torque vector of particles
k_B	Boltzmann constant (J/K)
n	Number density of particles ($1/\text{m}^3$)
p	Pressure (Pa)
\mathbf{R}	Resistance matrix
\mathbf{S}	Stresslet of particles (N m)
t	Time (s)
T	Temperature (K)
$\mathbf{U}(t)$	Velocity of particle at time t (m/s)
$\mathbf{U} - \mathbf{u}^\infty$	Translational and rotational velocities relative to the imposed flow of particles
$\mathbf{x}(t)$	Position of particle at time t (m)
η	Viscosity of a fluid (Pa s)
η_r	Effective viscosity of the dispersed system
ϕ	Volume fraction of particles
Σ	Bulk stress (N m)

References

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[Rev 1.5 2003/07/03 for “Powder Technology Handbook” 3rd Ed.]

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