

Velocity Autocorrelation Function of Fluctuating Particles in Incompressible Fluids

— Toward Direct Numerical Simulation of Particle Dispersions —

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Motions of fluctuating Brownian particles in an incompressible viscous fluid have been studied by coupled simulations of Brownian particles and host fluid. We calculated the velocity autocorrelation functions of Brownian particles and compared them with the theoretical results. Extensive discussions have been made on the time scales for which our numerical model is valid.

§1. Introduction

The motions of small fluctuating particles in viscous fluids have been studied for a long time. Although theoretical or numerical analysis based on the coupled motions of the particles and the host fluid are very complicated, it becomes rather simple if one considers only the particles' motions by assuming that the host fluid degree of freedom can be safely projected out from the entire degree of freedom of the dispersions. One of such models is the well-known generalized Langevin equation (GLE) for Brownian particles, i.e.,

$$M_i \frac{d\mathbf{V}_i}{dt} = \int_{-\infty}^t ds \sum_j \Gamma_{ij}(t-s) \mathbf{V}_j(s) + \mathbf{G}_i(t), \quad (1.1)$$

$$\langle \mathbf{G}_i(t) \cdot \mathbf{G}_j(0) \rangle = 3k_B T \Gamma_{ij}(t), \quad (1.2)$$

where M_i and \mathbf{V}_i denote the mass and the translational velocity of the i -th particle, respectively. $\Gamma_{ij}(t)$ is a friction tensor, which represents the effect of hydrodynamic interactions (HI) between i -th and j -th particles. \mathbf{G}_i is the random force acting on the i -th particle induced by thermal fluctuations of the solvent, k_B is Boltzmann constant, and T is the temperature of Brownian particles.

For a single spherical particle ($i = 1$) immersed in a infinitely large host fluid, the analytic form of the time-dependent friction¹⁾ is known as

$$\int dt \Gamma_{11}(t) \exp(-i\omega t) = \hat{\Gamma}_{11}(-i\omega) = 6\pi\eta a(1 + a\sqrt{-i\omega/\nu} - i\omega a^2/9\nu), \quad (1.3)$$

where $\hat{\Gamma}_{11}(-i\omega)$ is the Fourier transform of $\Gamma_{11}(t)$ and ω is the angular frequency. The first term corresponds to the normal Stokes friction for a spherical particle of radius a in a Newtonian fluid whose viscosity is η . The second term represents the memory

effect, which is related to the momentum diffusion in a viscous medium. Here the kinematic viscosity is defined as $\nu = \eta/\rho_f$ with ρ_f being the density of the fluid. The third term corresponds to the effect of the acceleration of the host fluid surrounding the tagged particle when the particle is accelerated through the host fluid. Using Eq. (1.3), the hydrodynamic GLE can be solved analytically. The translational velocity autocorrelation function (VACF) $\langle \mathbf{V}_i(t) \cdot \mathbf{V}_i(0) \rangle/3$ then obtained is known to exhibit the characteristic power-law relaxation for long-time region, which is widely known as the ‘‘hydrodynamic long-time tail’’.²⁾⁻⁵⁾

For dispersions composed of many particles interacting via HI, the situation is still not straightforward because we do not know the true analytic expression for the hydrodynamic friction tensor $\Gamma_{ij}(t)$. Some approximated expressions, such as Oseen or Rotne-Prager-Yamakawa (RPY) tensor, can be obtained by introducing the Stokes approximation. However, those expressions completely neglect the memory effect that corresponds to the second term of Eq. (1.3). This means that the hydrodynamic long-time tail cannot be reproduced correctly with Oseen or RPY tensor.

In the present study, we developed a numerical method to take into account the effects of hydrodynamics directly by simultaneously solving the Navier-Stokes equation for the host fluid with the Brownian motions of the particles. We first examined the VACF for a single Brownian particle and compared it with the analytical form mentioned above. Secondly, we examined the rotational motions of a single Brownian particle. We furthermore examined the motions of Brownian particles in harmonic potentials to check the validity of our method.

§2. Simulation method

Here we briefly explain the basic equations of our numerical model since those are explained in detail elsewhere.⁶⁾ A smooth profile function $0 \leq \phi(x, t) \leq 1$ is introduced to define fluid ($\phi = 0$) and particle ($\phi = 1$) domains on a regular Cartesian grid. Those two domains are separated by thin interface regions whose thickness is ξ . The position of the i -th particle is \mathbf{R}_i , the translational velocity is \mathbf{V}_i , and the rotational velocity is $\boldsymbol{\Omega}_i$. The motion of i -th particle with mass M_i and the moment of inertia \mathbf{I}_i is governed by the following Langevin-type equations,

$$M_i \frac{d\mathbf{V}_i}{dt} = \mathbf{F}_i^H + \mathbf{F}_i^C + \mathbf{F}_i^{ex} + \mathbf{G}_i^V, \quad \frac{d\mathbf{R}_i}{dt} = \mathbf{V}_i, \quad (2.1)$$

$$\mathbf{I}_i \cdot \frac{d\boldsymbol{\Omega}_i}{dt} = \mathbf{N}_i^H + \mathbf{G}_i^\Omega, \quad (2.2)$$

where \mathbf{F}_i^H and \mathbf{N}_i^H are the hydrodynamic forces and torques acting on the i -th particle due to HI, respectively. \mathbf{F}_i^C and \mathbf{F}_i^{ex} denote the direct particle-particle interaction and external force. \mathbf{G}_i^V and \mathbf{G}_i^Ω are the random force and torque due to thermal fluctuations defined stochastically as

$$\langle \mathbf{G}_i^V \rangle = \langle \mathbf{G}_i^\Omega \rangle = \mathbf{0}, \quad (2.3)$$

$$\langle \mathbf{G}_i^V(t) \cdot \mathbf{G}_j^V(0) \rangle = 3k_B T \alpha^V \delta(t) \delta_{ij}, \quad (2.4)$$

$$\langle \mathbf{G}_i^\Omega(t) \cdot \mathbf{G}_j^\Omega(0) \rangle = 3k_B T \alpha^\Omega \delta(t) \delta_{ij}, \quad (2.5)$$

where α^V and α^Ω are parameters to control the temperature T .

The motions of the host fluid are governed by the Navier-Stokes equation

$$\rho_f(\partial_t \mathbf{v} + \mathbf{v} \cdot \nabla \mathbf{v}) = -\nabla p + \eta \nabla^2 \mathbf{v} + \rho_f \phi \mathbf{f}_p \quad (2.6)$$

with the incompressible condition $\nabla \cdot \mathbf{v} = 0$, where \mathbf{v} and p are the velocity and the pressure fields of the host fluid, respectively, and $\phi \mathbf{f}_p$ is the body force defined so that the rigidity of the particles is automatically satisfied. Note that \mathbf{F}_i^H and \mathbf{N}_i^H are determined from the body force $\phi \mathbf{f}_p$.^{7),8)}

§3. Results and discussion

A single spherical particle fluctuating in a Newtonian fluid was simulated in the absence of external forces $\mathbf{F}_i^{ex} = 0$ as depicted in Fig. 1. We take the mesh size Δ and $\tau = \Delta^2 \rho_f / \eta$ as the units of space and time. Simulations have been performed with $\eta = 1$, $a = 5$, and $\xi = 2$ in a three-dimensional cubic box composed of $64 \times 64 \times 64$ grid points. The particle and fluid densities are identically set to be unity, $\rho_p = \rho_f = 1$.

Figure 2 shows our simulation results (Δ) of VACF for a single Brownian particle fluctuating in a Newtonian host fluid at $k_B T = 0.83$. The temperature T was determined by comparing the long-time diffusion coefficient D_{sim} obtained from simulations with $D^V = k_B T / 6\pi\eta a K(\Phi)$, where $K(\Phi)$ takes into account the effects of finite volume fraction⁹⁾ and Φ denotes the volume fraction. The volume fraction of a single particle is $\Phi = 0.002$. One finds that the VACF approaches asymptotically to the power-law line with the exponent $-3/2$, and the long-time behavior of our simulation agrees well with the analytical solution⁵⁾ of the hydrodynamic GLE rather than the Markovian VACF which neglects memory effects. This behavior indicates

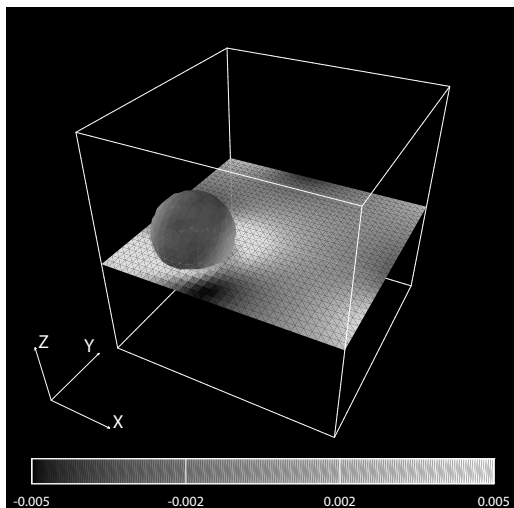


Fig. 1. A snapshot of a single Brownian particle immersed in a Newtonian fluid. The one eighth of the entire system is graphically displayed. The color map on the horizontal plane shows the value of the local fluid velocity in the x -direction.

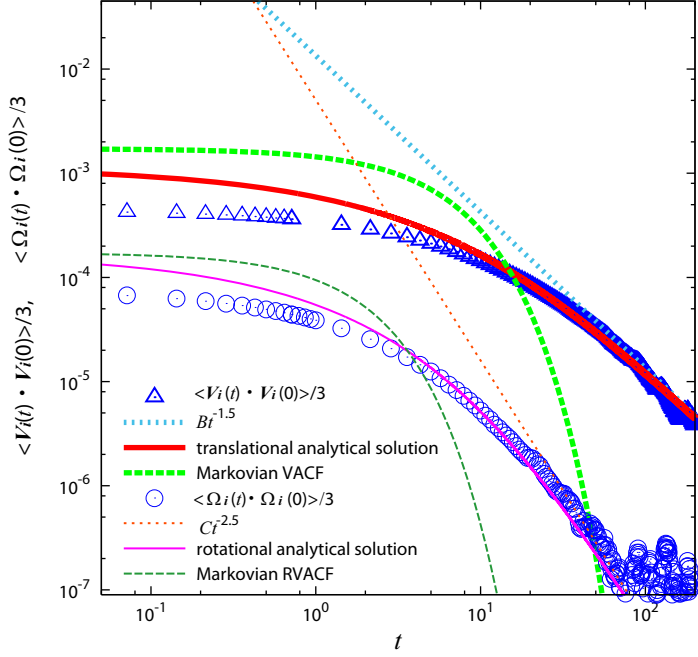


Fig. 2. The translational velocity autocorrelation function $\langle \mathbf{V}_i(t) \cdot \mathbf{V}_i(0) \rangle / 3$ (triangle) and the rotational velocity autocorrelation function $\langle \boldsymbol{\Omega}_i(t) \cdot \boldsymbol{\Omega}_i(0) \rangle / 3$ (circle) for a single Brownian particle fluctuating in a Newtonian fluid. The simulation data was taken at $k_B T = 0.83$. The solid lines indicate the analytic results for the translational⁵⁾ and the rotational motions. The dotted lines show power-laws, $Bt^{-3/2}$ with $B = k_B T / 12\rho_f(\pi\nu)^3$ for the translational motions and $Ct^{-5/2}$ with $C = \pi k_B T / 32\rho_f(\pi\nu)^{5/2}$ for the rotational motions. The dashed lines indicate the Markovian VACF and RVACF, which decay exponentially as $\exp(-t/\tau_B)$ and $\exp(-t/\tau_r)$, respectively.

that the memory effects are accurately taken into account. Similar to the translational motions, we have studied the rotational motions of the Brownian particle in the host fluid. The GLE of the rotational motions for a single spherical particle can be written as

$$I_i \dot{\boldsymbol{\Omega}}_i = - \int_{-\infty}^t ds \mu(t-s) \boldsymbol{\Omega}_i(s) + \mathbf{G}_i(t), \quad (3.1)$$

$$\langle \mathbf{G}_i \rangle = 0, \quad \langle \mathbf{G}_i(t) \cdot \mathbf{G}_i(0) \rangle = 3k_B T \mu(t), \quad (3.2)$$

where the time-dependent friction $\mu(t)$ has the form $\hat{\mu}(-i\omega) = 8\pi\eta a^3 [1 - i\omega/3\nu(1 + a\sqrt{-i\omega/\nu})]$ ¹⁰⁾ in Fourier space. The first term in $\hat{\mu}$ is the Stokes friction and the second term represents the memory effect due to the kinematic viscosity of the fluid. The GLE can be solved analytically, and the analytical solution of the rotational velocity autocorrelation function (RVACF) is obtained in the following form:

$$\begin{aligned} & \langle \boldsymbol{\Omega}_i(t) \cdot \boldsymbol{\Omega}_i(0) \rangle \\ &= - \frac{3k_B T \nu}{8\pi\eta a^5} \int_0^\infty \frac{dy}{3\pi} \exp(-yt/\tau_\nu) \left[\frac{y^{3/2}}{[1 - (\frac{\tau_r}{\tau_\nu} + \frac{1}{3})y]^2 + y(1 - \frac{\tau_r}{\tau_\nu}y)^2} \right], \quad (3.3) \end{aligned}$$

where $\tau_\nu = a^2/\nu$ and $\tau_r = I_i/8\pi\eta a^3$. In Fig. 2, simulation results (\circ) of RVACF are also plotted. The RVACF clearly shows the asymptotic approach to the hydrodynamic long-time tail with the exponent $-5/2$ which agrees well with the analytical solution (3.3) rather than a simple Markovian RVACF. By comparing the present simulation results with the corresponding analytical solutions more in detail, one may notice that some discrepancies become notable for $t < \tau_B$ or $t < \tau_r$, where $\tau_B = M_i/6\pi\eta a = 2a^2\rho_p/9\eta \simeq 5$ is the Brownian relaxation time and $\tau_r = I_i/8\pi\eta a^3 = 3\tau_B/10 \simeq 1.5$ is the Brownian rotational relaxation time. For opposite cases $t > \tau_B$ or $t > \tau_r$, however, the agreements between the numerical results and the analytical solutions are excellent. This is because we neglected memory effects in thermal noises \mathbf{G}_i^V and \mathbf{G}_i^Ω . We however believe that the long-time behavior of our numerical model is valid for $t > \tau_B$ since τ_B is much longer than the memory times of the thermal noises.

There exist many other characteristic time-scales in particle dispersions. Important ones are the kinematic time-scale $\tau_\nu = a^2\rho_f/\eta = 25$ which measures the momentum diffusion over the particle size and the diffusion time-scale $\tau_D = a^2/D \simeq 3 \times 10^3$ which measures the particle diffusion over the particle size. As one can see in Fig. 2, the present model works quite well for the time-scales comparable to τ_ν and τ_D , while it becomes inaccurate for $t < \tau_B$.

In order to test the validity of our method for the long-time behavior of Brownian particles, we next applied the present model to simulate Brownian particles fluctuating in external harmonic potentials. The potentials are introduced with the form

$$\mathbf{F}_i^{ex} = -k(\mathbf{R}_i - \mathbf{R}_i^{eq}) = -k\Delta\mathbf{R}_i, \quad (3.4)$$

where \mathbf{R}_i^{eq} is the i -th particle's equilibrium position and k is the spring constant.

Figure 3 shows the positional autocorrelation function $\langle \Delta\mathbf{R}_i(t) \cdot \Delta\mathbf{R}_i(0) \rangle / 3$ of two Brownian particles in harmonic potentials whose minimum positions are separated by a fixed distance of $5a$. The pair of particles are interacting only hydrodynamically, and there exists no direct interactions between them. The spring constant is set to $k = 10$, and the temperature is $k_B T \simeq 0.0066$, which was determined by the average potential energy $k_B T = k \langle \Delta\mathbf{R}_i^2 \rangle / 3$. The simulation results (\circ) agree well with the hydrodynamic analytical solution⁵⁾ in harmonic potentials which account for the effects of finite volume fraction. The analytical solution was derived by solving the GLE of a single Brownian particle in a harmonic potential which includes the modified Stokes friction $\zeta = 6\pi\eta a K(\Phi)$. The correlation functions decay much slower than the Markovian relaxation functions. We also confirmed that the validity of our method is excellent for $t \geq \tau_\nu$.

§4. Conclusion

We proposed a numerical model to simulate Brownian particles fluctuating in Newtonian host fluids. To test the validity of the model, the translational velocity autocorrelation function (VACF), the rotational velocity autocorrelation function

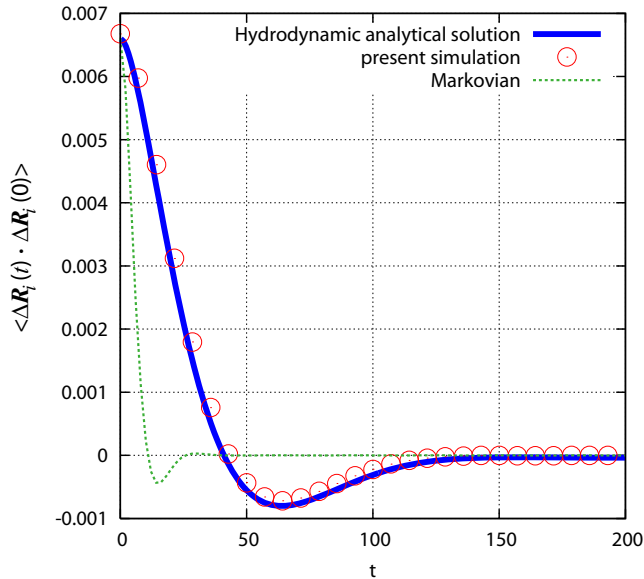


Fig. 3. The positional autocorrelation function $\langle \Delta \mathbf{R}_i(t) \cdot \Delta \mathbf{R}_i(0) \rangle / 3$ (circle) for a system composed of two Brownian particles in harmonic potentials $-k(\mathbf{R}_i - \mathbf{R}_i^{eq})$. The distance between their equilibrium positions is $|\mathbf{R}_1^{eq} - \mathbf{R}_2^{eq}| = 5a$. The solid line shows the analytical solution.⁵⁾ The dotted line shows the Markovian functions, i.e. the solution of $M_i \dot{\mathbf{V}}_i = -6\pi\eta a \mathbf{V}_i - k\mathbf{R}_i + \mathbf{G}_i$.

(RVACF), and the positional autocorrelation function of fluctuating Brownian particles were calculated in some simple situations for which analytical solutions were obtained. We compared our numerical results with the analytical solutions and found excellent agreements between them specially for long-time regions $t > \tau_B$ while some discrepancies were found for short time regions $t < \tau_B$. This is because our model is designed to simulate correct long-time behaviors of Brownian particles in host fluids. Applications of the present method for more complicated situations are in progress.

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