



# Effects of interactions between particles on dynamics in microrheology



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## ABSTRACT

We have studied the effects of interactions between particles on the dynamics in a colloidal dispersion system using the time-dependent density functional theory. We consider a hard-sphere probe particle fixed at the origin and hard-sphere colloidal particles suspended in a solvent that flows at a constant velocity against the probe particle. We calculated the density fields of colloidal particles, forces acting on the probe particle, and friction coefficients for small volume fractions of colloidal particles. The results show that hard-sphere interactions between colloidal particles decrease the forces and friction coefficients. The effect of the interactions is more significant for small colloidal particles than for large particles. The effect also becomes weak with increasing velocity of the solvent.

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## 1. Introduction

Microrheology is the study of complex fluids (e.g. colloidal suspensions, polymer solutions, and gels) using microsize probe particles [1–5]. When probe particles are embedded in a complex fluid, their motion reflects the mechanical properties of the fluid. Therefore, the mechanical properties of complex fluids can be investigated by observing the motion of probe particles. In addition, we can also investigate the mechanical properties by moving probe particles at a constant velocity against a complex fluid [5]. Thus, to estimate the mechanical properties, we should measure forces exerted by the complex fluid on the probe particles.

The motion of probe particles is affected by interactions between particles constituting complex fluids (e.g. colloidal particles). The motion depends on the density distribution of the constituent particles around the probe particles. A high density around the probe particles can hinder the motion of the probe particles. The density distribution is governed by the interactions between constituent particles as well as between the probe and constituent particles. Therefore, when analyzing the motion of probe particles, it is necessary to study the effects of interactions between constituent particles.

However, the effects of interactions between constituent particles on the dynamics in microrheology are not yet well understood. Although Brady and coworkers theoretically studied the dynamics of a probe particle in a colloidal dispersion system, they ignored interactions between colloidal particles [6–8]. Carpen and Brady studied the effects of the interactions through Brownian dynamics simulations [9]. However, their study was restricted to a small variety of volume fractions of

colloidal particles and, in particular, lacked results for small volume fractions. To study such a problem theoretically, a colloidal dispersion system has often been employed because of its simplicity.

Time-dependent density functional theory (TDDFT) is a powerful tool for studying the effects of interactions between particles [10–30]. This theory has been successful in describing the dynamics of atomic and molecular liquids [10–25]. It has been employed for the system with a velocity field [31] and various densities of liquids [23,32,33]. In particular, using this theory, the dynamics of solvent particles has been extensively studied in the case of solvent particles distributed around solvated solutes [10–18]. Since TDDFT can be applied regardless of the size of particles constituting a system, the theory can be applied to particles constituting complex fluids [26–30].

In the present study, by performing numerical calculations based on TDDFT, we investigate the effects of interactions between colloidal particles on the dynamics in microrheology. We consider a spherical probe particle pulled at a constant velocity  $\mathbf{U}$  [6–8]. By calculating the density distribution of colloidal particles around the probe particle, we obtain the force  $\mathbf{F}$  exerted by the colloidal particles on the probe particle. The force  $\mathbf{F}$  is calculated in two systems comprising colloidal particles with and without hard-sphere interactions between each other. For these systems, when the volume fraction of colloidal particles  $\phi$  is small, we calculate the dependences of  $\mathbf{F}$  on  $\phi$  and the velocity  $\mathbf{U}$ .

## 2. Model and methods

We consider a probe particle fixed at the origin and colloidal particles suspended in a solvent that flows at a constant velocity  $\mathbf{U}$  against the probe particle. The system is equivalent to that of a probe particle pulled at a constant velocity  $-\mathbf{U}$  in a stationary colloidal suspension. We assume that the interactions between the probe and colloidal particles can be

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modeled as those of hard spheres. For the interactions between colloidal particles, we consider two cases: hard-sphere interactions and no interactions. In addition, we ignore the hydrodynamic interactions mediated by the solvent.

In this system, to calculate the time development of the density field of colloidal particles  $\rho(\mathbf{r}, t)$ , we apply TDDFT [10] using the basic equation

$$\frac{\partial \rho(\mathbf{r}, t)}{\partial t} = D \nabla^2 \rho(\mathbf{r}, t) - \mathbf{U} \cdot \nabla \rho(\mathbf{r}, t) - D \nabla \cdot \left[ \rho(\mathbf{r}, t) \nabla \int c_2(\mathbf{r} - \mathbf{r}') \Delta \rho(\mathbf{r}', t) d\mathbf{r}' \right], \quad (1)$$

where

$$\Delta \rho(\mathbf{r}, t) \equiv \rho(\mathbf{r}, t) - \rho_0. \quad (2)$$

Here,  $D$  is the diffusion coefficient and  $c_2(\mathbf{r})$  is the direct correlation function between two colloidal particles. The homogeneous density  $\rho_0$  is defined at an infinite distance from the probe particle. Eq. (1) is valid even if the size of a colloidal particle is comparable to that of the probe particle [10]. To calculate the force  $\mathbf{F}$  acting on the probe particle, we solve Eq. (1) and obtain a steady-state density field  $\rho(\mathbf{r}, t \rightarrow \infty)$ .

For numerical calculation of Eq. (1), we approximate this equation by

$$\frac{\partial \rho(\mathbf{r}, t)}{\partial t} = D \nabla^2 \rho(\mathbf{r}, t) - \mathbf{U} \cdot \nabla \rho(\mathbf{r}, t) - D \nabla \cdot \left[ \rho(\mathbf{r}, t) \nabla \int c_2(\mathbf{r} - \mathbf{r}') \Delta \rho_{id}(\mathbf{r}', \infty) d\mathbf{r}' \right], \quad (3)$$

where

$$\Delta \rho_{id}(\mathbf{r}, \infty) \equiv \rho_{id}(\mathbf{r}, \infty) - \rho_0. \quad (4)$$

Here,  $\rho_{id}(\mathbf{r}, t)$  is the density field in the case that colloidal particles do not interact with each other but have hard-sphere interactions with the probe particle. The steady-state density field  $\rho_{id}(\mathbf{r}, \infty)$  can be obtained by solving the following equation [6–8]:

$$\frac{\partial \rho_{id}(\mathbf{r}, t)}{\partial t} = D \nabla^2 \rho_{id}(\mathbf{r}, t) - \mathbf{U} \cdot \nabla \rho_{id}(\mathbf{r}, t). \quad (5)$$

The present approximation is valid when the volume fraction of colloidal particles  $\phi$  is small. To show this, we divide  $\rho(\mathbf{r}, t)$  into two parts:

$$\rho(\mathbf{r}, t) = \rho_{id}(\mathbf{r}, t) + \rho_{ex}(\mathbf{r}, t), \quad (6)$$

where we assume that  $\rho_{id}(\mathbf{r}, t)$  includes the effects of the first order of  $\phi$ . To obtain Eq. (3), we ignore  $\rho_{ex}(\mathbf{r}', t)$  in  $\Delta \rho(\mathbf{r}', t)$  in Eq. (1). The ignored excess part  $\rho_{ex}(\mathbf{r}', t)$  includes the effects of the second order of  $\phi$  and above. Thus, we ignore terms in the second order of  $\phi$  and above in  $\Delta \rho(\mathbf{r}', t)$ , or in the third order of  $\phi$  and above in  $\rho(\mathbf{r}, t) \Delta \rho(\mathbf{r}', t)$  on the right-hand side of Eq. (1). Therefore, this approximation ensures accuracy to the second order of  $\phi$ .

Using the steady-state density field  $\rho(\mathbf{r}, \infty)$  obtained from Eq. (3), we calculate the force  $\mathbf{F}$  exerted by colloidal particles on the probe particle. When the interactions between the probe and colloidal particles are modeled as those of hard spheres, the force is obtained by [6]

$$\mathbf{F} = -k_B T \int_S \rho(\mathbf{r}, \infty) \mathbf{n} dS. \quad (7)$$

Here,  $S$  is the surface of the depletion zone around the probe particle and  $\mathbf{n}$  is a normal vector of this surface. The depletion zone is the region where colloidal particles cannot enter because of its overlap with the probe particle. Eq. (7) shows that the force  $\mathbf{F}$  is generated by the inhomogeneity of the density field around the probe particle.

To solve Eqs. (3) and (5), we impose two boundary conditions. One is that the inflow and outflow of colloidal particles are zero across the surface of the depletion zone  $S$ . This condition is described by

$$\mathbf{n} \cdot \mathbf{j}(\mathbf{r}, t)|_{\mathbf{r}=\mathbf{r}_S} = 0, \quad (8)$$

$$\mathbf{n} \cdot \mathbf{j}_{id}(\mathbf{r}, t)|_{\mathbf{r}=\mathbf{r}_S} = 0, \quad (9)$$

where  $\mathbf{j}(\mathbf{r}, t)$  is the flow of colloidal particles for Eq. (3),  $\mathbf{j}_{id}(\mathbf{r}, t)$  is the flow for Eq. (5), and  $\mathbf{r}_S$  is the position of the surface  $S$ . The definitions of the flow  $\mathbf{j}(\mathbf{r}, t)$  and  $\mathbf{j}_{id}(\mathbf{r}, t)$  are given by

$$\mathbf{j}(\mathbf{r}, t) \equiv D \nabla \rho(\mathbf{r}, t) - \mathbf{U} \rho(\mathbf{r}, t) - D \rho(\mathbf{r}, t) \nabla \int c_2(\mathbf{r} - \mathbf{r}') \Delta \rho_{id}(\mathbf{r}', \infty) d\mathbf{r}', \quad (10)$$

$$\mathbf{j}_{id}(\mathbf{r}, t) \equiv D \nabla \rho_{id}(\mathbf{r}, t) - \mathbf{U} \rho_{id}(\mathbf{r}, t). \quad (11)$$

The other condition is that  $\rho(\mathbf{r}, t)$  and  $\rho_{id}(\mathbf{r}, t)$  are equal to  $\rho_0$  at a position sufficiently far from the probe particle. In numerical calculation, this position corresponds to the edge of the calculation region.

We solve Eqs. (3) and (5) through the finite difference method. The spatial difference is  $(a + b)/100$ , where  $a$  and  $b$  are the radii of the probe and colloidal particles, respectively. We calculate the force  $\mathbf{F}$  by using the solution of Eq. (3) for various values of the velocity  $\mathbf{U}$  and the volume fraction  $\phi$ , the size ratio between the probe and colloidal particles  $b/(a + b)$ . Here, the volume fraction  $\phi$  alters the direct correlation function  $c_2(\mathbf{r})$  which is obtained by the Percus–Yevick approximation [34]. The size ratio  $b/(a + b)$  affects the boundary condition at the surface of the depletion zone  $S$ . Thus, the volume fraction and size ratio are incorporated to the calculation via the direct correlation function and boundary conditions, respectively.

### 3. Results

To study the effect of interactions between colloidal particles, we calculate the dependence of the force  $\mathbf{F}$  on the volume fraction of colloidal particles  $\phi$ . Then, the force is scaled by

$$\tilde{F} \equiv \frac{b^3}{(a + b)^2 k_B T} |\mathbf{F}|, \quad (12)$$

and the volume fraction is defined by

$$\phi \equiv \frac{4}{3} \pi b^3 \rho_0. \quad (13)$$

The dependence of  $\tilde{F}$  on  $\phi$  is plotted for  $\tilde{U} = 0.1$  (Fig. 1) and  $\tilde{U} = 1.0$  (Fig. 2), where  $\tilde{U}$  is defined by

$$\tilde{U} \equiv \frac{a + b}{D} |\mathbf{U}|. \quad (14)$$

In these figures, the symbols and solid line represent the values of  $\tilde{F}$  obtained by integrating  $\rho(\mathbf{r}, \infty)$  and  $\rho_{id}(\mathbf{r}, \infty)$ , respectively. The four types of symbols represent the results obtained for the different sizes of colloidal particles.

Fig. 1 shows that the force exerted by colloidal particles on the probe particle is decreased by the effect of the interactions between the colloidal particles. Although the solid line and symbols are in agreement at small values of  $\phi$ , the symbols at large values of  $\phi$  lie below the solid line. The deviations of the symbols from the solid line is caused by the effect of the hard-sphere interactions between the colloidal particles. These deviations increase as the size of the colloidal particles decreases. This

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