KAPSEL: Kyoto Advanced Particle Simulator for ELectrohydrodynamics
—Toward Direct Numerical Simulations of Colloidal Dispersions—[†]

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Abstract

We have released a colloid simulator named KAPSEL implemented the "Smoothed Profile (SP) method" which has been developed by ourselves for direct numerical simulations of particulate flow providing a way to couple continuum fluid dynamics with rigid-body dynamics through smoothed profile of colloidal particle. KAPSEL enebles us to simulate multi-component fluids, such systems as charged colloids in electrolyte solutions. Dynamics of colloidal dispersions is solved as much computational cost as required for solving non-particulate flows. KAPSEL computes the fluid velocity and the electrostatics potential by solving both Navier–Stokes and Poisson equations directly. The time evolutions of the colloidal particles and the density of counter ions are then determined by solving Newton's equation of motion and advection-diffusion equation, respectively, in a consistent manner so that the electro-hydrodynamic coupling can be fully taken into account. The electrophoretic mobility of spherical colloidal particles is calculated in several situations including those in concentrated dispersions. The comparisons with theories show excellent quantitative agreements.

Keywords: Colloidal dispersion, Simulation, Rheology, Electrophoresis, Hydrodynamics, Sedimentation

1. Introduction

Interparticle interactions in colloidal dispersions mainly consist of thermodynamic potential interaction and hydrodynamic interactions 2). Whereas the former works in both static and dynamic situations, the latter works solely in dynamic situation. Although the thermodynamic interactions in static situations have been studied extensively and summarized as a concept of effective interactions, the nature of dynamic interactions are poorly understood. Since the hydrodynamic interaction is essentially long-ranged, many-body, it is extremely difficult to study its role by means of analytical way alone. Numerical simulations can aid to investigate fundamental role of the hydrodynamic interaction in colloidal dynamics.

Between November 2002 and March 2006, the "Development of Hybrid Molecular Dynamics Simulation Project,"[4] sponsored by the Japan Science and Technology Agency,[5] was carried out initially at the Department of Physics and Astrophysics,[6] Graduate School of Science, Kyoto University and later at the Department of Chemical Engineering,[7] Graduate School of Engineering, Kyoto University. As the ma-

jor objective of this project, we developed a reliable and efficient numerical method, called smoothed profile (SP) method 5) 6) 10) and 11), to resolve the hydrodynamic interactions acting on solid particles immersed in complex host fluids. In the SP method, the original sharp boundaries between colloids and host fluids are replaced with diffuse interfaces with finite thickness ξ. This simple modification greatly improve the performance of numerical computations since it enables us to use the fixed Cartesian grid even for problems with moving boundary conditions.

In 2006, we have released a program package named KAPSEL, the Kyoto Advanced Particle Simulator for Electrohydrodynamics, which is based on the SP method and applicable to several electrohydrodynamic phenomena such as electrophoresis of charged colloidal particles. The entire KAPSEL source code is viewable on the web[8] and anyone agreeing to the "OCTA Free Software License Agreement"[9] can download it freely for use. This document outlines the basic principles of the SP method and tutorials describing how to install and execute KAPSEL using a few sample test cases. The latest information will be appearing online, so the reader is recommended to refer to the web if the instructions described in this paper return unsuccessful results.

2. Installation

2.1 Installation of OCTA

KAPSEL is designed to be used as an add-on engine of "OCTA[10]," an integrated simulation system for soft materials developed by the joint project of industry and academia funded by Ministry of Economy, Trade and Industry (METI), Japan. To use KAPSEL, one needs a graphical user interface called "Gourmet" distributed within the "OCTA" program package, whose newset version[11] can be obtained from the web. One must install "OCTA" properly by following the installation procedure of "OCAT" on each machine.

Because KAPSEL needs library called "libplatform," whose source codes are attached to "Gourmet" to implement data input/output through UDF files, one must follow the instructions below to build "libplatform" on each machine in advance of compilation of KAPSEL.

Linux: For Linux machines, follow the instruction below to build "libplatform."

```
% cd /usr/local/OCTA2006/GOURMET_2006
% tar xvfpz gourmet*_src.tar.gz
```

```
% cd src
% make
% make install
```

Windows: For Windows machines, first install the free software Cygwin[12] that emulates UNIX on the Windows. In doing so, be sure to include "gcc," "gcc-mingw," and "make." Subsequently, start up the Cygwin shell and build "libplatform" as follows.

```
% ln -s /cygdrive/c/OCTA2006/ /usr/local/.
% cd /cygdrive/c/OCTA2006/GOURMET_2006
% ./GOURMET2006_SRC.EXE
% cd src
% make -f Makefile.cygmingw
% make -f Makefile.cygmingw install
% cd ../lib/cygwin
% ln -s ../win32/libplatform.a .
```

Mac: For MacOS X machines, follow the instruction below to build "libplatform." Here we assume "OCTA2006" is installed in "/Application/OCTA/" and two environment variables, "PATH" and "PF_FILES" , are set properly.

```
% cd /Application/OCTA/GOURMET_2006/src
% make
% make install
```

2.2 Installation of KAPSEL

The complete source codes of the latest version of KAPSEL can be obtained from the web as a "gzipped-tar" archive file under the name of "kapsel.tar.gz." The file can be decompressed into the "./kapsel/" using the following command.

```
% tar xvfpz kapsel.tar.gz
```

Linux and Windows: The compilation of KAPSEL can be made as follows using the supplied "Makefile" without any changes.

```
% cd kapsel
% make
```

Mac: For MacOS X machines, put the following in the "Makefile," and then perform "make."

```
ARCH=macosx
CC=gcc
CXX=g++
```

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8   http://www-tph.cheme.kyoto-u.ac.jp/kapsel/
9   http://octa01.t.u-tokyo.ac.jp/OCTA/license_eng.html
10 http://octa.jp/
11 At this moment, the newest version is "OCTA2006." We further assume "OCTA2006" is properly installed.
12 http://cygwin.com/

CCOPT=-DMACOSX -03 -fno-inline
LINKS=-lm -lplatform

2.3 User support

The BBS of the OCTA home page http://octa.jp contains the bulletin board of KAPSEL. Enter questions or bug reports about KAPSEL in the bulletin board.

3. Rheology of Colloidal Dispersions

Although the rheology of suspensions is important in terms of practical application, its theoretical generalization is too complex a process. (For example, refer to Ref. 2) In the low concentration limit of colloidal particles, the theoretical result shows that the apparent viscosity of a suspension η_{eff} increases as given in equation (1) (see 2), for example.),

$$\frac{\eta_{eff}}{\eta} = 1 + \frac{5}{2}\varphi, \tag{1}$$

where η denotes the viscosity of the solvent and φ the volume fraction of the colloidal particles. This is Einstein's well-known viscosity equation, although it only holds for the range with the volume fraction $\varphi \ll 0.1$. As the particle concentration increases, the effect of particle interactions becomes visible with changes in particle structures resulting from the interaction, vitrification and crystallization occurring. This makes it difficult to predict the rheology of a suspension theoretically on the basis of the basic laws. Although affected by the aforementioned difficulties, the importance of the subject means a number of experimental studies have been performed, with several empirical or semi-empirical formulas for the apparent viscosity having been proposed to summarize such studies. (See the Doughherty-Krieger equation 3), Refs. 4), and references therein.)

As the particle concentration increases, the involvement of diverse effects other than the colloid volume fraction in the phenomena necessitates analysis of an individual phenomenon rather than the formation of a cohesive theory. The Smoothed Profile (SP) method provides a simulation method allowing solvent-induced many-body interactions between colloidal particles to be calculated directly; it also allows the rheology of various kinds of suspensions to be analyzed. KAPSEL so far allows simulation and rheology measurement in a simple shear flow condition to be performed for a monodisperse system in a Newtonian fluid.

3.1 Basic Equations
3.1.1 Equation of Motion of Colloidal Particles

Let us consider the motion of N spherical particles in a Newtonian fluid. The position, velocity, and angular velocity $\{R_i, V_i, \Omega_i\}$ of the ith colloidal particle having mass M_p evolve over time according to the equations of motion:

$$\dot{R}_i = V_i, \tag{2}$$
$$M_p\dot{V}_i = F_i^H + F_i^{other}, \tag{3}$$
$$I_p \cdot \dot{\Omega}_i = N_i^H, \tag{4}$$

$I_p = (2/5) M_p a^2 I$ denotes the moment of inertia of the colloidal particle, with I denoting the unit tensor. In the above equations, F_i^H and N_i^H respectively denote the force and torque received by the colloidal particle from the fluid, expressing the momentum balance. For the implementation of this calculation, see Refs. 5, 6). F_i^{other} denotes direct interaction between colloidal particles and buoyancy.

3.1.2 Solvent Motion: Navier-Stokes Equation in Shear Flow

Solvent motion is in the form of incompressible flow ($\nabla \cdot v = 0$). The velocity field v of the entire system of the solvent and the colloidal particles follows the Navier-Stokes equation:

$$(\partial_t + v \cdot \nabla)v = -\frac{1}{\rho}\nabla p + \nu \nabla^2 v + \phi f_p + f^{shear}, \tag{5}$$

ρ, $\eta = \rho\nu$, and p denote the density, viscosity, and pressure of the solvent, respectively. The body force ϕf_p takes into account the solid/non-slip boundary condition on surfaces of colloidal particles. For the detailed implementation, see Ref. 5, 6).

3.2 Rheology Measurement

The external force f^{shear} controls v_x so that it is kept at the profile of a simple shear flow given by

$$v_x = S\left(\frac{L_y}{2} - y\right). \tag{6}$$

In equation (6), S denotes the shear rate. This driving method is the product of the application of the Schumacher and Eckhardt method 9), devised for uniform flow, to the Smoothed Profile (SP) method[13]. In this driving method, periodic boundary conditions are applied in the flow direction (x-) and span direc-

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[13] To solve a simple shear flow problem, we can use a method involving giving the velocity/force at the boundary wall as the boundary conditions, Rogallo's moving grid method 8, 9), analogous to the Lees-Edwards boundary condition in molecular dynamics simulation, and another method; however, we used the aforementioned calculation method, in which grids do not distort and no boundary problems occur.

tion (z-), while a free-slip boundary condition $(\partial_y v_{x,z}(y=0, L_y)=0)$ is imposed on the upper and lower walls. The upper and lower walls are non-transparent, that is, condition $v_y(y=0, L_y)=0$ holds. In the SP method, f^{shear} is applied as feedback during each step of calculation after the advection of colloidal particles and fluid is completed.

The apparent viscosity of a suspension is defined by

$$\eta_{eff}=\frac{\sigma_{xy}^{eff}}{S}, \tag{7}$$

where S (denoting the shear rate) is a control parameter, and the macroscopic shear stress σ_{xy}^{eff} is evaluated on the basis of the calculation data. Let us derive a stress calculation method for a suspension. To facilitate the explanation, the case of a uniform fluid is initially considered. Subsequently, the case of a colloidal dispersion (SP method) is described.

3.2.1 Uniform fluids

Let us write the equations of motion for the shear flow of uniform fluid as follows:

$$\nabla \cdot v=0, \tag{8}$$
$$\rho\dot{v}= \nabla \cdot \sigma+\rho f^{shear}. \tag{9}$$

In equation (9), f^{shear} denotes the external force field per unit mass that exerts shear on the system. This gives the definition of macroscopic stress in the following form:

$$\sigma^{eff}=\frac{1}{V}\int dx\sigma. \tag{7}$$

This can be calculated through the volume integral of local stresses σ.

Let us consider evaluating σ^{eff} by using external force ρf^{shear}. Using an identity of second order

$$\sigma=[\nabla \cdot (\sigma x)]^T-x \nabla \cdot \sigma, \tag{11}$$

the following equations are obtained:

$$\int dx\sigma=\int dx\left[[\nabla\cdot(\sigma x)]^T-x \nabla\cdot\sigma\right] \tag{12}$$

$$=\int dx[-x\nabla\cdot\sigma] \tag{13}$$

$$=\int dx\left[x \left(\rho f^{shear}-\rho\dot{v}\right) \right] \tag{14}$$

$$=\int dxx\rho f^{shear}-\frac{d}{dt}\int dx\rho v. \tag{15}$$

Here, we drop the surface term and use the incompressible condition ($\nabla\cdot v=0$). In the steady state, since the change in the total momentum is zero, we ultimately obtain

$$\sigma^{eff}=\frac{1}{V}\int dxx\rho f^{shear}. \tag{16}$$

3.2.2 SP Method for Particle Dispersion

Let us formally write the equation of the momentum of suspension in shear flow as follows:

$$\frac{d}{dt}(\rho_t v)= \nabla \cdot \sigma^{suspension} +\rho_t f^{shear}, \tag{17}$$

$$\rho_t=(1- \phi)\rho_f+ \phi \rho_p. \tag{18}$$

In equation (17), $\sigma^{suspension}$ denotes the stress of the suspension. Since this $\sigma^{suspension}$ cannot be calculated directly, the formula to be obtained through the integration of stress (10) cannot be implemented.

On the other hand, the SP-method-based equation for the velocity field of a suspension under a shear flow condition is given by

$$\dot{v}=\frac{1}{\rho} \nabla \cdot \sigma + \phi f_p+f^{shear}. \tag{19}$$

Comparing this with equation (17), we obtain

$$\frac{1}{\rho_t} \nabla \cdot \sigma^{suspension} =\frac{1}{\rho} \nabla \cdot \sigma + \phi f_p, \tag{20}$$

From this, we obtain

$$\sigma^{eff}=\frac{1}{V} \int dxx\rho_t f^{shear} \tag{21}$$

as an expression of the stress of the suspension. Although this contains the position vector explicitly, the macroscopic shear stress to be measured is free from how the origin of the system of coordinates is defined. This is compatible with the fact that the translational motion of the entire system is not driven by f^{shear}. This fact will be confirmed in the following. When the origin of coordinates is shifted to a position expressed by $x=x'+x_0$, we obtain

$$\int dx(x'+x_0)\rho_t f^{shear}=\int dxx'\rho_t f^{shear}+ x_0\int dx\rho_t f^{shear}. \tag{22}$$

Since the external force f^{shear} is controlled such as to produce a shear flow, rather than a translational motion of the entire system, $\int dx\rho_t f^{shear}=0$. The SP method uses equation (21) to evaluate macroscopic stress.

3.3 UDF Description
3.3.1 Input Parameters

Selecting "Shear_Navier_Stokes" for "constitutive_eq" makes it possible to simulate the motion of colloidal particles in a Newtonian fluid under shear flow[14]. In the following, the variables to be specified in an input

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14 Simulation can be performed similarly when other alternatives for "constitutive_eq" are selected: for example, "Navier_Stokes" for the motion of colloidal particles in a Newtonian fluid, such as gravitational sedimentation of particles, and "Electrolyte" for the motion of charged colloids, electrophoresis in an external electric field, and similar.

UDF file are described.

The section "constitutive_eq.Shear_Navier_Stokes" specifies the characteristics of the solvent:

- constitutive eq.Shear Navier Stokes.DX...Grid width Δ as the unit quantity for length.
- constitutive eq.Shear Navier Stokes.RHO... Density of the solvent.
- constitutive eq.Shear Navier Stokes.ETA... Viscosity of the solvent.
- constitutive eq.Shear Navier Stokes.Shear rate... Shear rate.

The section "particle_spec[]," specifies the characteristics concerning the particle:

- particle spec[].Particle number... Number of particles.
- particle spec[].MASS RATIO... Ratio of the density of the particles to that of the fluid.

The pieces of information on the particle radius and boundary thickness are entered as follows:

- A_XI...Boundary thickness ξ. When "Shear_Navier_Stokes" is selected, at least $\xi \geq 1$ must be selected.
- A··· Particle radius.

The section "gravity," enter the pieces of information on gravity:

- gravity.G... Gravitational acceleration.
- gravity.direction... Select the direction in which to apply gravity.

Specify the type of Lennard-Jones potential for interparticle force.

- EPSILON... the energy unit for the Lennard-Jones potential.
- LJ powers... the power exponent of the Lennard-Jones potential.

The section "mesh," specifies the simulation size (The current version is only compatible with a periodic boundary condition in a rectangular parallelepiped cell.):

- mesh.NPX... The size in the x-direction is $L_x = 2^{NPX}$.
- mesh.NPY... The size in the y-direction is $L_y = 2^{NPY}$.
- mesh.NPZ... The size in the z-direction is $L_z = 2^{NPZ}$.

The section "time_increment," specifies the time increment:

- time_increment... When you select "auto," specify the time increment upper limit $T_{dump} = \rho / \eta k_{max}^2$, where k_{max} is the wave number determined by the grid width DX. When you select "manual," specify the value manually.
- time_increment.auto.factor... The time increment is specified as $\Delta t = T_{dump} \times factor$.
- time_increment.manual.delta_t··· Enter Δt manually.

The section "switch," specifies the simulation condition:

- switch.ROTATION... Select "ON" to solve an equation of motion for particle rotation.
- switch.HYDRO_int... Select "Correct" to solve a Navier-Stokes equation for a fluid; for "Shear_Navier_Stokes," however, the "Correct" switch is the only one implemented.
- switch.Stokes... Select "with advection" to take the inertia term into consideration when solving a Navier-Stokes equation. Select "w/o advection" to perform Stokes approximation not taking the inertia term into consideration; for "Shear_Navier_Stokes," however, the option "w/o advection" is not implemented yet.
- swithch.LJ truncate... When handling force between particles arising from the Lennard-Jones potential, select "OFF" for a normal form containing the attractive force term, "ON" for repulsive force, not containing the attractive force term, or "NONE" when no force is applied at all.
- switch.INIT_distribution... With this switch, select the initial configuration of particles from "uniform_random" (random), "random_walk" (shifted from a square lattice randomly), "FCC" (on an FCC lattice), "BCC" (on a BCC lattice), and "user_specify" (the coordinates and velocity are user-specified.). When you select "user_specify," enter the initial particle position and velocity into "user_specify.Particles[].R" and "user_specify. Particles[].v," respectively. If the number of lists to be entered is smaller than that specified in "Particle_number," increase "user_specify.Particles[]" by implementing the "Edit → Add an array Element" operation on "Gourmet" or edit the UDF file directly.
- switch.FIX_CELL... Set the direct current component of the full velocity at zero, $v_{k=0}=0$. To introduce gravitational acceleration to measure the settling velocity, set this to "ON."

The section "output," specifies the pieces of information on the data output:

- output.GTS... Number of data output interval steps.
- output.Num_snap...Frequency of data output; in other words, the total number of steps is specified by GTS × Num_snap.
- output.AVS... Select "ON" to carry out data output in the AVS format.
- output.AVS.ON.Out_dir... Insert the directory for outputting AVS format data. For example, when "data" is specified, it is necessary to create the "./data" and "./data/avs/" directories in advance. The AVS field file is outputted to the "./data/" direc-

tory under the filename of "data.fld"; the data file is outputted to the "./data/avs/" directory under the filename of "data_∗.dat." The number of steps is entered in the asterisk ∗.

- output.AVS.ON.FileType... Select between "Binary" and "ASCII" for formatting the AVS data file.
- output.UDF... Select "ON" for output UDF.

As many pieces of record data of the coordinates and velocities of particles as specified in "output.Num_snap" are stored after "Particles[]" of the output UDF.

In the section "resume," select from the following options to resume an interrupted calculation for the resume UDF:

- resume.caclucation... Select "NEW" to start a new calculation. Select "CONTINUE" to restart calculation after reading the pieces of information concerning the number of calculation steps, particle coordinates, velocity, angular velocity, solvent velocity field, and ion density field obtained at the end of the previous calculation. The data is saved in a location below "resume.CONTINUE.Saved_Data" of the restart UDF file. In this case, calculation is resumed with the restart UDF created at the end of the previous calculation being used as the input UDF. How to use this input UDF will be described in detail in Section 5.5.

3.3.2 Units of Space and Time

The grid width Δ is used as the unit of length.

The following points should be noted concerning the unit of time:

- A system of units is adopted that makes the relation $\rho = \eta = \Delta = 1$ hold in the Navier-Stokes equation.
- When the entries RHO=A, ETA=B, and DX=C are made in the input udf file, the maximum wave number k_{max} is given using C, with the upper limit of the time increment given as $T_{dump} = (A/B)/k_{max}^2$ on the basis of the diffusion time of the momentum. The time increment Δt is adjusted by $T_{dump} \times$ factor. However, the unit for time itself is the same as in the case of $\rho = \eta = \Delta = 1$.

4. Electrophoresis of Charged Colloids

When colloidal particles are dispersed in a solvent with very large permittivity such as water, ions are emitted from leaving groups on colloid surfaces, with the particle surfaces becoming charged. The emitted ions are electrostatically attracted to particle surfaces, and at the same time, are diffused by thermal fluctuation and form a cloud-like ionic atmosphere called

an electric double layer around the colloidal particles. The properties of a colloidal disperse system in equilibrium are described by a Poisson-Boltzmann equation. The Debye-Hückel approximation, obtained by linearizing the Poisson-Boltzmann equation, allows an unobstructed understanding to be obtained. In contrast, in so-called electrokinetic phenomena, such as electrophoresis, the behavior of particles and ionic distribution is determined by competition between hydrodynamic and electrostatic interactions. As a result of the competition, the ionic distribution becomes incapable of following the motion of particles, with electric double layers distorted out of spherical symmetry, resulting in a non-equilibrium state. The only means to analyze such a complex state is to introduce a theoretically simple approximation. In addition, even computer-based simulation has seldom yielded a correct reproduction.

To overcome this situation, this project involved developing a new simulation method called the Smoothed Profile (SP) method 5, 10, 6, and 11). In the SP method, colloids are handled as particle pictures. In contrast, the solvent and ions are presented as a coarse-grained density field in the state of a continuum. In a continuum picture, the interface between a colloidal particle and a solvent, usually expressed through a step function, is expressed safely on a fixed orthogonal grid, using an interface function to overcome difficulties in numerical calculation. Accordingly, the SP method uses both particle and continuum pictures to describe their degrees of freedom and the interaction between them with physical correctness. This is an outstanding feature of the SP method that allows multi-scaled complex phenomena to be analyzed. In addition, the SP method solves hydrodynamic interactions by carrying out direct numerical calculations of a Navier-Stokes equation 5, 6). To implement these calculations, we constructed a formalism to consistently solve the three degrees of freedom, namely, colloidal particles (the Newton's equation of motion), ion distribution (an advection-diffusion equation), and a solvent velocity field (the Navier-Stokes equation), based on the assumption of a smooth interface function. Using this, we firstly succeeded in simulating electrophoresis quantitatively 11). In the following section, the basic equations taken into consideration in KAPSEL are described, with a brief mention of the underlying theory.

4.1 Basic Equations

As described in the Refs. 6, 11), let us take a general view of the basic electrohydrodynamics equa-

tions necessary for simulation. N colloidal particles with a radius of a, dispersed in an electrolytic solvent, are considered. The permittivity of the solvent ϵ is assumed to be spatially uniform. The SP method expresses the interface between a particle and solvent in the form of a smooth function $\phi(r) \in [0,1]$ of finite thickness ξ. On a fixed orthogonal grid, the particle domain is expressed by $\phi = 1$, the solvent domain by $\phi = 0$, and the interface domain by $0 < \phi < 1$. Other methods using $\phi(r)$ on an orthogonal grid are proposed by Tanaka-Araki [12] and Kajishima et al. [13]. Introducing an interface function allows remarkably improved calculation efficiency in comparison with the finite element method using nonstructural lattices. The surface of a colloidal particle is assumed to be charged uniformly and the quantity of charge per particle to be Ze. In an ordinary continuum picture, the particle surface charge distribution is expressed using a delta function. Consequently, a suitable boundary-compatible lattice is used in the finite element method; which significantly encumbers the calculation efficiency. In contrast, the SP method also uses a smooth distribution for this particle surface charge distribution $eq(r)$. For example, when we use the differential of the first order of the interface function ϕ, $eq(r)$ is expressed as

$$eq(r) = \frac{Ze|\nabla\phi(r)|}{4\pi a^2}. \tag{23}$$

Just as the interface function $\phi(r)$ is structured such as to be reduced to a step function with $\xi \to 0$, $q(r)$ is structured such as to be reduced to a delta function with $\xi \to 0$.

4.1.1 Advection-diffusion Equation

Let us define the density distribution C_α of α type ions with a valence of Z_α in the entire calculation domain as shown below:

$$C_\alpha(r, t) = (1 - \phi(r, t))C_\alpha^*(r, t). \tag{24}$$

The domain where ions exist is expressed by $(1 - \phi)$. $C_\alpha^*(r, t)$ is the auxiliary variable for calculation, being defined as smooth throughout the entire calculation domain. C_α^* in the colloid domain $(\phi = 1)$ has no physical meaning. The total charge distribution, including the particle surface charge distribution, is given by

$$\rho_e(r) = e\sum_\alpha Z_\alpha C_\alpha(r) + eq(r). \tag{25}$$

In the equation, the initial distribution is constructed such as to meet the electrical neutrality condition $\int \rho_e dr = 0$.

The time evolution of the auxiliary ion density C_α^* is assumed to follow the advection-diffusion equation

$$\partial_t C_\alpha^* = -\nabla \cdot C_\alpha^* v + \Gamma_\alpha \nabla \cdot (C_\alpha^* \nabla \mu_\alpha). \tag{26}$$

This equation consists of two terms, one expressing the advection, due to the solvent velocity field v, and the other expressing the diffusion due to the gradient of the chemical potential μ_α. Since C_α^* follows the advection-diffusion equation, $\int dr C_\alpha^*$ is conservative.

The absence of ion permeation into colloidal particles is considered to be the condition for the component normal to the interface of the ion diffusion flow rate to become zero. In other words, it is expressed by $n \cdot \nabla\mu_\alpha = 0$ [6, 11]. In this equation, n denotes the (outward) normal vector on the particle surface. Using the interface function, n can be expressed in the form of $n = -\nabla\varphi/|\nabla\varphi|$. Γ_α is the Onsager transport coefficient of an α-type ion, being related to the friction and diffusion coefficients of the ion as $f_\alpha = 1/\Gamma_\alpha$, $D_\alpha = k_B T \Gamma_\alpha$. The chemical potential of the ion is assumed to be expressed in the form [16]:

$$\mu_\alpha = k_B T \ln C_\alpha^* + Z_\alpha e(\Psi - E \cdot r). \tag{27}$$

In the equation, E denotes the external electric field, and the electrostatic potential $\Psi(r)$ is obtained by solving the Poisson equation

$$\epsilon \nabla^2 \Psi = -\rho_e. \tag{28}$$

This chemical potential assume a Poisson-Boltzmann distribution in equilibrium.

4.1.2 Navier-Stokes Equation

Solvent flow is incompressible ($\nabla \cdot v = 0$). The velocity field v of a solvent follows the Navier-Stokes equation

$$\rho(\partial_t + v \cdot \nabla)v = -\nabla p + \eta \nabla^2 v - \rho_e(\nabla\Psi - E) + \phi f_p. \tag{29}$$

In the equation, ρ, η, and p denote the density, the viscosity of a solvent, and pressure, respectively. Note here that electrostatic force $-\rho_e(\nabla\Psi - E)$ acts on the fluid. The external force term ϕf_p ensures the rigidity of a particle. In other words, ϕf_p takes the non-slip boundary conditions of the particle surface into consideration. The details are defined in Refs. 5, 6).

4.1.3 Equation of Motion of Colloidal Particles

The position, velocity, and angular velocity of the ith colloidal particle having mass M_p evolve over time according to the equations of motion

$$\dot{R}_i = V_i, \tag{30}$$
$$M_p \dot{V}_i = F_i^H + F_i^{other}, \quad I_p \cdot \dot{\Omega}_i = N_i^H. \tag{31}$$

In equation (31), F_i^H denotes the force acting on the particle induced by the fluid, expressing the momentum balance between the solid and fluid [6]; F_i^{other} denotes the force due to the potential between particles, such as the Lennard-Jones potential. The rotational motion of the particles is also taken into consider-

ation, though not described here 6). The above are the equations necessary for the simulation.

4.2 Electric Double Layer
4.2.1 Poisson-Boltzmann Equation

The basis for quantitative treatment of the structure of an electric double layer is the Poisson-Boltzmann equation. Let us determine the equilibrium distribution of ions under equation (27) for the case where the external electric field does not exist (E=0). When the chemical potential has become uniform, that is, μ_α=constant, we obtain

$$C_\alpha^*(r)=\bar{C}_\alpha\exp\left(-\frac{Z_\alpha e\Psi(r)}{k_BT}\right) \tag{32}$$

as the equilibrium ion distribution. This is a Boltzmann distribution under the electrostatic potential Ψ. Combined this with equation (28), called the Poisson-Boltzmann equation.

4.2.2 Debye-Hückel Approximation and Debye Screening Length

Let us consider a spherical colloidal particle in a z:z-symmetry electrolytic solvent. The Poisson-Boltzmann equation for this condition is given by 2)

$$\nabla^2\Psi(r)=\frac{2ze\bar{C}}{\epsilon}\sinh\left(\frac{ze\Psi(r)}{k_BT}\right). \tag{33}$$

The boundary conditions at a point at infinity are $\Psi|_{r=\infty}=0$ and $C^*|_{r=\infty}=\bar{C}$. The boundary condition on the surface of the particle is given by

$$\nabla\Psi|_{\text{surface}}=-\frac{\sigma e}{\epsilon}, \tag{34}$$

where the surface charge density is given by $\sigma e=Ze/4\pi a^2$. In other words, a boundary condition of constant surface charge is considered. A method of approximation, in which $ze\Psi/k_BT\ll1$ is assumed and equation (33) is linearized, is called the Debye-Hückel approximation.
It gives

$$\nabla^2\Psi(r)=\frac{2z^2e^2\bar{C}}{k_BT\epsilon}\Psi=\kappa^2\Psi. \tag{35}$$

In connection with this equation, the constant having a length dimension

$$\kappa^{-1}=\frac{1}{\sqrt{8\pi\lambda_Bz^2\bar{C}}} \tag{36}$$

is called the Debye screening length. In equation (36), $\lambda_B=e^2/4\pi k_BT\epsilon$ is called the Bjerrum length. In an ordinary electrolyte,

$$\kappa^{-1}=\frac{1}{\sqrt{4\pi\lambda_B\Sigma_\alpha Z_\alpha^2\bar{C}_\alpha}} \tag{37}$$

holds. Since the system is spherically symmetric, it is sufficient to consider the radius $r=|r|$ only, then we obtain

$$\frac{d^2\Psi}{dr^2}+\frac{2}{r}\frac{d\Psi}{dr}=\kappa^2\Psi. \tag{38}$$

The general solution of this equation is given by a Yukawa-type potential

$$\Psi(r)=\Psi_0\frac{a}{r}\exp[-\kappa(r-a)]. \tag{39}$$

The electrostatic force arising from colloidal charge is screened to the extent of κ^{-1}. the Debye screening length κ^{-1} can be considered the distance at which a balance is struck between the effect of the Coulomb force, via which a surface charge attracts an ion of the opposite sign, and the thermal diffusion tending to scratch out the local presence of an ion. For this reason, κ^{-1} can be regarded as the thickness of an electric double layer. When the temperature is high and hence the thermal energy k_BT is large, κ^{-1} becomes large. In addition, as the ionic strength ($\Sigma_\alpha Z_\alpha^2\bar{C}_\alpha/2$) increases, the screening effect increases and κ^{-1} decreases. For example, let us consider the bulk salt concentration $\bar{C}$ throughout a z:z-symmetric electrolytic solvent. With the medium assumed to be water with a temperature of 25℃, the Bjerrum length is given by λ_B=0.72nm; substituting the actual value into equation (36), we obtain

$$\kappa^{-1}=\frac{0.3}{z\sqrt{\bar{C}}}(\text{nm}). \tag{40}$$

When z=1 and $\bar{C}$=0.1M, κ^{-1}=1nm; and when z=1 and $\bar{C}$= 0.001M, κ^{-1}=10nm.

The surface potential $\Psi(r=a)=\Psi_0$ is determined on the basis of the boundary condition $d\Psi/dr(r=a)=-\sigma e/\epsilon$. Ψ and the surface charge density σe are related by

$$\sigma e=\epsilon\kappa\Psi_0(1+(\kappa a)^{-1}). \tag{41}$$

In other words, as the surface charge increases, the surface potential increases linearly. The Debye-Hückel approximation cannot be applied to locations where the surface potential is high. In reality, as the surface charge increases, the increase in the surface potential becomes more difficult. The relation for this situation can be obtained by solving the nonlinear Poisson-Boltzmann equation. Approximate solutions for a 1:1 electrolyte solvent are proposed by Loeb-Overbeaak-Wiersema 2) and Oshima-Healy-White 15).

4.3 Backgrounds of Electrophoresis

When an electric field E is applied from outside, a colloidal particle charged to Ze is subjected to the electrostatic force ZeE, and starts moving. Although the particle is accelerated by the electrostatic force, it is subject to viscous resistance from the fluid;

and reaches the steady velocity V when a balance is struck between the electrostatic force and the viscous resistance. Assuming the viscous resistance to be Stokes resistance, $6\pi\eta aV$, this allows the balance between forces to be written in the form of

$$ZeE = 6\pi\eta aV. \qquad (42)$$

From this, the electrophoresis mobility

$$\frac{V}{E} = \frac{Ze}{6\pi\eta a} \qquad (43)$$

is derived. However, this is unsuitable, and the actual electrophoresis mobility is smaller than this value. This is due to the lack of consideration of the motion of the ion atmosphere and electrostatic force, despite the electrostatic force acting on the ion atmosphere around the colloid. Accompanied by the motion of the ion atmosphere, colloid migration exhibits a much slower migration velocity. In addition, if the electric double layer distorts out of spherical symmetry, the resulting force must be taken into consideration. This will make theoretical consideration extremely complicated. For this reason, several analyses of electrophoresis have been made on simplified models 2).

4.3.1 Smoluchowski Theory

In the case of $\kappa a \gg 1$, where the radius of a particle a considerably exceeds the thickness of an electric double layer κ^{-1}, Smoluchowski's equation is applicable. Since the thickness of an electric double layer is infinitely small in this case, the particle surface can be regarded as a plane with the curvature of the particle surface neglected. An external electric field Ex, parallel to the plane (assumed to be in the x-direction), is assumed to be applicable. When the motion of the fluid is observed from above the particle, in a coordinate system fixed to the latter, the fluid, apart from the particle, should have a velocity of $-V$. Considering the balance between the viscous resistance and the electrostatic force, we obtain

$$\eta \frac{\partial^2 v_x}{\partial y^2} = \sum_\alpha e C_\alpha E_x = 0. \qquad (44)$$

Since the ion distribution is related to the second order differentiation of the electrostatic potential through the Poisson equation, the following relation holds:

$$\eta \frac{\partial^2 v_x}{\partial y^2} = \epsilon \frac{\partial^2 \Psi}{\partial y^2} E_x. \qquad (45)$$

Performing integration under the boundary conditions whereby the velocity gradient, potential gradient, and potential are all equal to zero for $y \rightarrow \infty$, this yields

$$\eta [v_x(y) + V] - \epsilon E \Psi(y) = 0. \qquad (46)$$

Subsequently, we obtain Smoluchowski's equation

$$\frac{V}{E} = \frac{\epsilon \zeta}{\eta} \qquad (47)$$

because the velocity is zero at the particle surface ($y = 0$). In equation (47), the zeta potential ζ is originally defined as the potential at the slip plane, but it is replaced by the potential at the particle surface $\Psi(0)$.

4.3.2 Hückel Theory

Let us consider a limit opposite to the condition represented by Smoluchowski, $\kappa a \ll 1$, at which the particle is extremely small compared with the thickness of the electric double layer. In other words, when Ze is a limit of a point charge, Hückel's equation is applicable. When the potential on the particle surface is replaced by the Coulomb potential

$$\zeta = \frac{Ze}{4\pi\epsilon a}, \qquad (48)$$

Hückel's equation

$$\frac{V}{E} = \frac{2}{3} \frac{\epsilon \zeta}{\eta} \qquad (49)$$

is obtained.

4.3.3 Henry and O'Brien-White Theories

For an ordinary κa value, Henry's equation

$$\frac{V}{E} = f(\kappa a) \frac{\epsilon \zeta}{\eta} \qquad (50)$$

is known as a coupler of equations (47) and (49). $f(\kappa a)$ is called Henry's coefficient, being defined as follows:
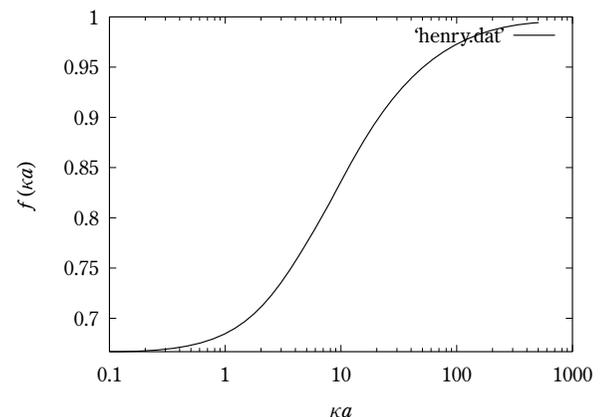

Fig. 1 Henry's coefficient $f(\kappa a)$.

$$f(\kappa a)=1-5\exp(\kappa a)E_7(\kappa a)+2\exp(\kappa a)E_5(\kappa a) \qquad (51)$$

$$=\frac{2}{3}+\frac{(\kappa a)^2}{24}-\frac{5(\kappa a)^3}{72}-\frac{(\kappa a)^4}{144}+\frac{(\kappa a)^5}{144}$$

$$+\left[\frac{(\kappa a)^4}{12}-\frac{(\kappa a)^6}{144}\right]\exp(\kappa a)E_1(\kappa a). \qquad (52)$$

In equation (51), $E_n(\kappa a)$ is an exponential-integral function of the nth order. Smoluchowski's equation corresponds to $f=1(\kappa a\rightarrow\infty)$ and Hückel's equation to $f=2/3$ ($\kappa a\rightarrow0$). (**Fig. 1**)

Henry's equation (50) is a linear relation to the zeta potential, applicable only when the zeta potential is low. As the zeta potential increases, consideration of the deformation effect of the electric double layer (called the relaxation effect) becomes necessary. Using numerical analysis, O'Brien and White have proposed, for ordinary κa and ζ values, the relationship between the electrophoretic mobility and the zeta potential 16). Subsequently, Ohshima, Healy, and White have proposed an analytical equation for the range of $\kappa a \geq 10$ 17).

4.4 UDF Description
4.4.1 Input Parameters

Selecting "Electrolyte" as "constitutive_eq" allows the simulation of motion of charges colloids and an electrophoretic phenomenon under an external electric field[15]. In the following, the variables to be specified in an input UDF file are described.

Enter pieces of information on the solvent and ion distribution in the section "constitutive_eq.Electrolyte":
- constitutive_eq.Electrolyte.DX... Grid width Δ as the unit quantity for length
- constitutive_eq.Electrolyte.RHO... Solvent density.
- constitutive_eq.Electrolyte.ETA... Solvent viscosity.
- constitutive_eq.Electrolyte.kBT... Thermal energy at the temperature T.
- constitutive_eq.Electrolyte.Dielectric cst... Solvent permittivity.
- constitutive_eq.Electrolyte.Init_profile... Choose between "Uniform" and "Poisson_Boltzmann." When you choose "Boltzmann," note that considerable

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time may be needed in induction periods of simulations to handle a multi-particle problem, in particular.
- constitutive_eq.Electrolyte.Add_salt... When you use "saltfree," consider a single component of ion having the sign opposite to that of the particle surface. If you use "salt," consider two types of ions, positive and negative.
- constitutive_eq.Electrolyte.Add_salt.saltfree. Valency_counterion... Valency of a counterion.
- constitutive_eq.Electrolyte.Add_salt.saltfree.Onsager_coeff_counterion... Onsager transport coefficient of a counterion.
- constitutive_eq.Electrolyte.Add_salt.salt.Valency_positive_ion... Valency of a positive ion.
- constitutive_eq.Electrolyte.Add_salt.salt.Valency_negative ion... Valency of a negative ion.
- constitutive_eq.Electrolyte.Add_salt.salt.Onsager_coeff_positive_ion... Onsager transport coefficient of a positive ion.
- constitutive_eq.Electrolyte.Add_salt.salt.Onsager_coeff_negative_ion... Onsager transport coefficient of a negative ion.
- constitutive_eq.Electrolyte.Add_salt.salt.Debye_length... Specifying the Debye screening length causes the corresponding salt concentration to be specified.
- constitutive_eq.Electrolyte.Electric_field... Choose between "ON" and "OFF" of the external electric field.
- constitutive_eq.Electrolyte.Electric_field.ON... Choose between DC (direct current electric field) and AC (alternating current electric field).
- constitutive_eq.Electrolyte.Electric_field.ON.DC. Ex... Intensity of the x-direction electric field; the same applies in the case of an alternating current electric field.
- constitutive_eq.Electrolyte.Electric_field.ON.DC. Ey... Intensity of the y-direction electric field; the same applies in the case of an alternating current electric field.
- constitutive_eq.Electrolyte.Electric_field.ON.DC. Ez... Intensity of the z-direction electric field; the same applies in the case of an alternating current electric field.
- constitutive_eq.Electrolyte.Electric_field.ON.AC. Frequency... Frequency of an alternating current electric field.

The section "particle_spec[]," specifies pieces of information on the particle type:
- particle_spec[].Particle_number... Number of particles.

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[15] Simulations can be performed also when alternatives to the above parameters are selected for "constitutive_eq" : for example, "Navier_Stokes" for the motion of colloidal particles in a Newtonian fluid, such as gravitational sedimentation of particles and "Shear_Navier_Stokes" for the motion of colloidal particles in a Newtonian fluid under a shear flow condition, rheology of a dispersion system, and similar.

- particle_spec[].MASS_RATIO... Specific weight of a particle relative to the fluid.
- particle_spec[].Surface_charge... Total amount of particle surface charges.

Enter the pieces of information on the particle radius and interface thickness into the following locations:

- A_XI... Interface thickness ξ. When "Electrolyte" is selected, the differential of the first order of the interface function $\nabla\phi$ is used; consequently, the thickness of the smallest interface is $\xi=2$.
- A... Particle radius.

The section "gravity," specifies the pieces of information on gravity:

- gravity.G... Gravitational acceleration.
- gravity.direction... Select the direction in which gravity is applied.

Determine the type of the Lennard-Jones potential for interparticle force.

- "EPSILON"... Specify the unit for the energy of the Lennard-Jones potential.
- "LJ_powers"... Specify the power exponent of the Lennard-Jones potential.

The section "mesh," specifies the simulation size (The current version is compatible only with a periodic boundary condition in a rectangular parallelepiped cell.):

- mesh.NPX... The size in the x-direction is $Lx=2^{NPX}$.
- mesh.NPY... The size in the y-direction is $Ly=2^{NPY}$.
- mesh.NPZ... The size in the z-direction is $Lz=2^{NPZ}$.

The section "time_increment," specifies the time increment:

- time_increment... When you select "auto," specify the time increment upper limit $T_{dump}=\min(\rho/\eta k_{max}^2, 1/k_B T \Gamma_\alpha k_{max}^2)$, where k_{max} is the maximum wave number determined by the grid width DX. When you select "manual," specify the value manually.
- time_increment.auto.factor⋯ The time increment is specified as $\Delta t=T_{dump} \times$ factor using "factor," the value to be entered.
- time_increment.manual.delta_t⋯ Enter the Δt value manually.

The section "switch," specifies the simulation conditions:

- switch.ROTATION... Select "ON" to solve an equation of motion for particle rotation.
- switch.HYDRO int... Select "Correct" to solve a Navier-Stokes equation for a fluid; for "Electrolyte," however, the "Correct" switch is the only one imple-

mented.

- switch.Stokes... Select "with advection" to take the inertia term into consideration when solving a Navier-Stokes equation. Select "w/o advection" to perform a Stokes approximation not taking the inertia term into consideration; for "Shear_Navier_Stokes," however, the option "w/o advection" is not implementedyet.
- swithch.LJ_truncate... When handling force between particles arising from the Lennard-Jones potential, select "OFF" for a normal form containing the attractive force term, "ON" for repulsive force not containing the attractive force term, or "NONE" when no force is applied at all.
- switch.INIT_distribution... With this switch, select the initial configuration of particles from "uniform_random" (random), "random_walk" (shifted from a square lattice randomly), "FCC" (on an FCC lattice), "BCC" (on a BCC lattice), and "user_specify" (the coordinates and velocity are user-specified.). When you select "user_specify," enter the initial particle position and velocity into "user_specify.Particles[].R" and "user_specify. Particles[].v," respectively. If the number of lists to be entered is smaller than that specified in "Particle_number," increase "user_specify.Particles[]" by carrying out the "Edit → Add an array Element" operation on "Gourmet" or edit the UDF file directly.
- switch.FIX_CELL... Set the direct current component of the full velocity at zero, that is, $v_{k=0}=0$. To introduce gravitational acceleration to measure the settling velocity, set this to "ON."

The section "output," specifies the pieces of information on the data output:

- output.GTS... Number of data output interval steps
- output.Num snap... Number of times of data output; in other words, the number of total steps is specified by "GTS × Num_snap."
- output.AVS... Select "ON" to carry out data output in the AVS format.
- output.AVS.ON.Out_dir... Insert the directory for outputting AVS format data. For example, when "data" is specified, the "./data" and "./data/avs/" directories must be created in advance. The AVS field file is outputted to the "./data/" directory under the filename of "data.fld"; and the data file is outputted to the "./data/avs/" under the filename of "data_*.dat." The number of steps is entered in the asterisk*.
- output.AVS.ON.FileType... Select between "Binary"

and "ASCII" for formatting the AVS data file.
- output.UDF... Select "ON" for output UDF.

The number of pieces of record data of coordinates and velocities of particles specified in "output. Num_snap" is stored after "Particle[]" of the output UDF.

In the section "resume," select from the following options to resume an interrupted calculation for the resume UDF:
- resume.caclucation... Select "NEW" to start a new calculation. Select "CONTINUE" to restart calculation after reading the pieces of information on the number of calculation steps, particle coordinates, velocity, angular velocity, solvent velocity field, and ion density field obtained at the end of the previous calculation. The data is saved in a location below "resume.CONTINUE.Saved_Data" of the restart UDF file. In this case, calculation is resumed with the restart UDF created at the end of the previous calculation being used as the input UDF. How to use this input UDF will be described in detail in Section 5.5.

4.4.2 Units of Space and Time
The grid width Δ is used as the unit of length.
The following points should be noted for the unit of time:

- A system of units is adopted that makes the relation $\rho = \eta = \Delta = 1$ hold in the Navier-Stokes equation.
- If the entries RHO=A, ETA=B, and DX=C are made in the input UDF file, the maximum wave number k_{max} is given using C, with the upper limit of the time increment given as $T_{dump} = (A/B)/k_{max}^2$ on the basis of the diffusion time of the momentum. The time increment Δt is adjusted by $T_{dump} \times$ factor. However, the unit for time itself is the same as in the case of $\rho = \eta = \Delta = 1$.
- In the case of "Electrolyte," use either $(A/B)/k_{max}^2$ or $(1/k_B T \Gamma_a)/k_{max}^2$ as T_{dump}, whichever is smaller. Use a unit for time so that $\rho = \eta = \Delta = 1$ holds.

5 Tutorial

5.1 How to Run KAPSEL
KAPSEL is executed as follows:
    % kapsel -Iinput.udf -Ooutput.udf -Ddefine.udf -Rrestart.udf
KAPSEL is executed by using -I to designate the input UDF, -O to designate the output UDF, -D to
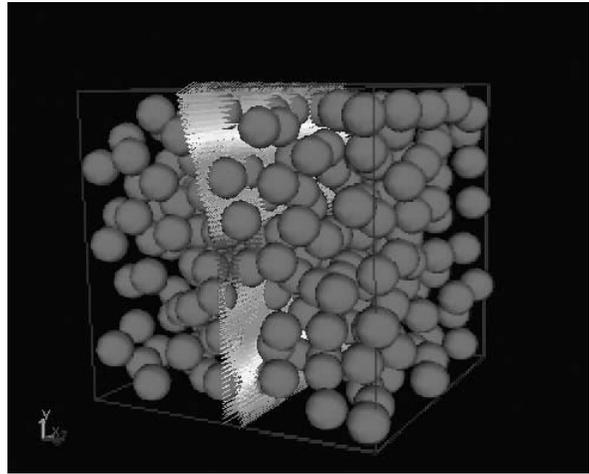

Fig. 2 Flow of a suspension under shear; arrows indicate the velocity field on a plane normal to the flow.

designate the definition UDF, and -D to designate the restart UDF. Note that no option can be omitted. The restart UDF will be described in Section 5.5.

5.2 Sample Simulations
5.2.1 Particle Dispersion under Shear
"shear.udf" can be used as a sample input UDF file; to be more specific, initially ensure that "./data" and "./data/avs/" have been created, and then execute the following:
    % kapsel -Ishear.udf -Ooutput.udf -Ddefine.udf -Rrestart.udf
In this example (shown in **Fig. 2**), calculation is carried out on the assumption that the mesh size is $64 \times 64 \times 64$, the shear rate $S=0.01$, the particle radius $a=4$, the interface thickness $\xi=1$, and the number of particles is 288. Under this condition, the particle volume fraction φ is 0.29.

With "Shear_Navier_Stokes" selected as "constitutive_eq," the data as shown below is outputted in the standard error output:

#1:dev_sigma_yx 2:shear_rate_obs 3:shear_rate ...
0.00647023 -0.00449194 0.01 ...
.
.
.

The data in the second and the eighth columns show the temporal shear rate and the temporal shear stress, respectively. Since the data in the 17th column represents the shear strain multiplied by L_y, one may draw the stress-strain curve by plotting "−$8" versus "−$17/L_y," where "$n" denotes the data in the nth column. The data in each column is accumulated over
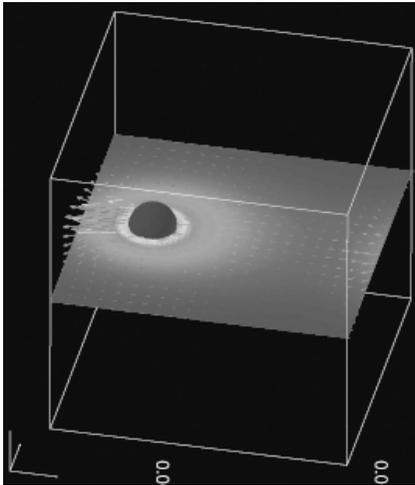
Fig. 3 A colloidal particle (colored blue) in electrophoretic motion under an external electric field applied in the +x direction; in the figure, light and shade represent the electric charge density distribution and the arrows the solvent velocity fields.

Fig. 4 Evolution of the migration velocity of a colloidal particle over time.

Fig. 5 A colloidal particle (colored blue) in electrophoretic motion under an external electric field applied in the +x direction.

Fig. 6 Positively charged colloidal particles (colored red) and negatively charged colloidal particles (colored blue) in electrophoretic motion under an external electric field applied in the +x direction; positive-signed colloids migrate in the +x direction and negative-signed ones in the -x direction.

simulation time excluding the initial one fourth of the total duration, and the averaged value is printed in the last line.

5.2.2 Electrophoresis: a single particle

To obtain an example of calculation for the simulation of single-particle electrophoresis, use "sample1. udf" as a sample input UDF file; to be more specific, first make sure that "./data" and "./data/avs/" have been created, and then execute the following:

> % kapsel -Isample1.udf -Ooutput.udf -Ddefine.udf -Rrestart.udf

In this example, a 1:1 electrolytic solvent is considered in a mesh size of $64 \times 64 \times 64$, and the calculation is carried out on the assumption that the radius a=5, the interface thickness ξ=2, the colloidal charge Z=−100, the electric field E_x=0.1, and the Debye screening length κ^{-1}=10. **Fig. 4** shows the evolution of the migration velocity over time. The figure shows that a steady velocity is realized at the point of equilibrium between the electrostatic force and the fluid resistance.

5.2.3 Electrophoresis: many particles

The simulation of electrophoresis with the number of particles assumed to be 32 can be calculated with "sample2.udf." Other parameters are identical to those in the previons case where the number of particles is one.

5.2.4 Electrophoresis: +/- binary particles

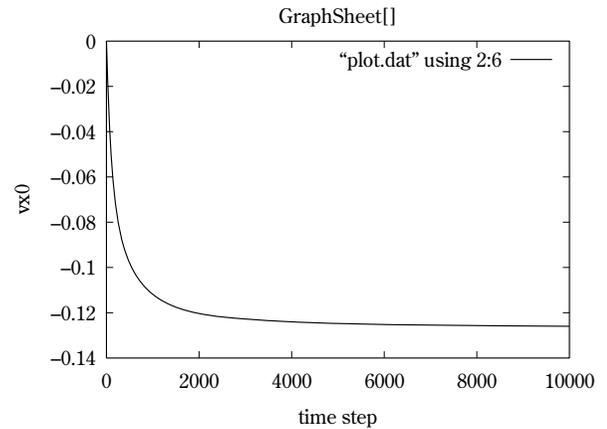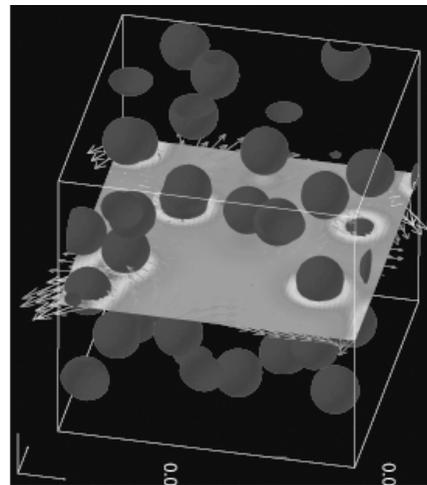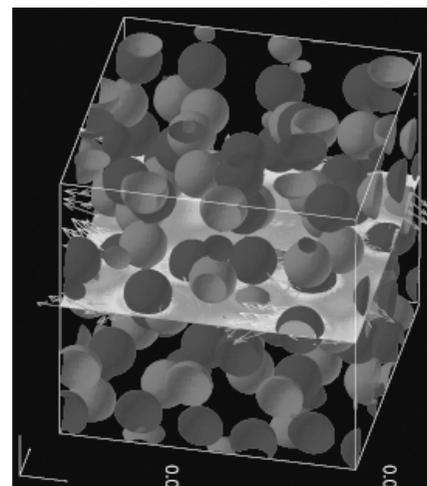The electrophoresis of a mixed system, in which 64 positively charged colloidal particles and as many

negatively charged particles exist, can be calculated with "sample3.udf." Other parameters are identical to those in the previous cases.

5.3 Visualization
5.3.1 Using AVS/Express

With "output.AVS" set at "ON," an AVS-format file is outputted. Using AVS/Express[16] to read the "avs_charge.v" file and designating the field file "data.fld" as the "Read_field" module allows the particles, solvent velocity field, and charge distribution to be visualized respectively. The particles are displayed in colors according to the surface charge value Ze. The visualization shown in **Figs. 3, 5**, and **6** is obtained by using AVS/Express with "avs_charge.v."

5.3.2 Using "Gourmet"

When one starts up "Gourmet" to read "output.udf," loads a Python script "show_field.py" supplied with KAPSEL on the Python panel of "Gourmet," and executes "Run," the graphic window opens to visualize the particles, solvent velocity field, and charge density distribution[17]. And clicking on the playback button at the bottom of the graphic window causes animation to start. Since particles are visualized on the basis of the particle coordinate data outputted to the output UDF as record data, setting "output.UDF" at "ON" is necessary. Since the solvent velocity field and the charge density distribution have read "Binary" files outputted in the AVS format, it is necessary to set "output.AVS" at "ON" and "output.AVS.ON.FileType" at "Binary."

5.4 Plotting Data: gnuplot

Using "gnuplot[18]," it is possible to plot the time series of the position and velocity of a particle in graph form on the basis of the record data outputted to UDF 1).

When one starts up "Gourmet" to read "output.udf," loads a Python script "plot.py" supplied with KAPSEL on the Python panel of "Gourmet," and executes "Run," one can create a graph sheet on the basis of the record data storing the positions and velocities of particles. To plot those data, change the

---

[16] http://www.avs.com/
[17] Versions earlier than "Gourmet_2003" have some glitches and it has been shown that this script does not work normally. In such cases, use the supplied Python script "particleshow.py" for visualization. The solvent velocity field and the charge density distribution are not displayed; only particles are displayed.
[18] http://www.gnuplot.info/

check mark placed on "Tree" in the "View" box to "Table," select "GraphSheet" in the list of variables, and browse the "GraphSheet" data. Subsequently, executing the "Make" operation on the "Plot" panel of "Gourmet" and executing the "Plot" operation allows the graph shown in **Fig. 4** to be drawn. If an excessive number of line types hinders an easy view of a graph, one may delete unnecessary portions from the "plot" command created in the editor of the "Plot" panel. How to call "gnuplot" from "Gourmet" is described in detail in Chapter 3 of the document 1).

5.5 Restart UDF

Select "NEW" in "resume.Calculation" in the input UDF and end the calculation in the sequence

> % kapsel -Iinput.udf -Ooutput.udf -Ddefine.udf -Rrestart.udf

and the pieces of information concerning the number of steps, particles, solvent velocity field, and ion distribution at the end of the calculation will be outputted to "restart.udf." To restart calculation using these pieces of data, follow the steps below:

1. Copy "restart.udf" to "input.udf."
2. Open "input.udf" on "Gourmet" and select "CONTINUE" in "resume.Calculation."
3. Specify and store the number of steps to be calculated as a single unit after increasing "output.Num_step."
4. If the sequence

> % kapsel -Iinput.udf -Ooutput.udf -Ddefine.udf -Rrestart.udf

is followed again, the data is read from "input.udf" to restart calculation.
5. For both the AVS data and "output.udf," the output data of the resumed calculation can be added with the previously calculated data as it is.
6. The data at the completion of calculation is stored in "restart.udf" again; therefore, repeating the steps above allows calculation to be continued.

5.6 Known Problems

1. When "Electrolyte" is selected for "constitutive_eq," a segmentation error or abortion may occur at the time of ending a program run (at the time of manipulating the restart UDF file) depending on the machine used. However, the result of the execution itself seems to pose no problems.
2. "show_field.py" seems not to work normally on "Gourmet_2003."
3. KAPSEL that has been built in the Windows Cygwin + MinGW environment seems to end due to errors during execution. When "MinGW" is not used,

no problems occur.

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