Mesoscopic Dispersion of Colloidal Agglomerate in a Complex Fluid Modelled by a Hybrid Fluid–Particle Model

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The dispersion of the agglomerating fluid process involving colloids has been investigated at the mesoscale level by a discrete particle approach—the hybrid fluid–particle model (FPM). Dynamical processes occurring in the granulation of colloidal agglomerate in solvents are severely influenced by coupling between the dispersed microstructures and the global flow. On the mesoscale this coupling is further exacerbated by thermal fluctuations, particle–particle interactions between colloidal beds, and hydrodynamic interactions between colloidal beds and the solvent. Using the method of FPM, we have tackled the problem of dispersion of a colloidal slab being accelerated in a long box filled with a fluid. Our results show that the average size of the agglomerated fragments decreases with increasing shearing rate $\Gamma$, according to the power law $A \cdot \Gamma^k$, where $k$ is around 2. For larger values of $\Gamma$, the mean size of the agglomerate $S_{\text{avg}}$ increases slowly with $\Gamma$ from the collisions between the aggregates and the longitudinal stretching induced by the flow. The proportionality constant $A$ increases exponentially with the scaling factor of the attractive forces acting between the colloidal particles. The value of $A$ shows a rather weak dependence on the solvent viscosity. But $A$ increases proportionally with the scaling factor of the colloidal–solvent dissipative interactions. Similar type of dependence can be found for the mixing induced by Rayleigh–Taylor instabilities involving the colloidal agglomerate and the solvent. Three types of fragmentation structures can be identified, which are called rupture, erosion, and shatter. They generate very complex structures with multiresolution character. The aggregation of colloidal beds is formed by the collisions between aggregates, which are influenced by the flow or by the cohesive forces for small dispersion energies. These results may be applied to enhance our understanding concerning the nonlinear complex interaction occurring in mesoscopic flows such as blood flow in small vessels.

Key Words: hybrid fluid–particle model; mesoscopic flow; colloidal agglomerates; fragmentation; agglomeration.

1. INTRODUCTION

Mesoscopic flows are important to understand because they hold the key to the interaction between the macroscopic flow and the microstructures. This is especially true in colloidal flows, which involve colloidal mixtures, thermal fluctuations, and particle–particle interactions. In many technological and physical processes, such as emulsification, formation of nanojets (1), water desalination, food production, gel filtration, and transport processes in sedimentary rocks (2) or in tiny blood vessels, the microscopic or microstructural effects may even dominate over the hydrodynamical processes and these phenomena take place in the realm of mesoscopic flows. For example, blood is a system rich in rheological properties, exhibiting shear-thinning, viscoelastic, and sedimenting behavior. But still, only qualitative correlations have ever been made between the observed microstructure and the reported rheology. Central to understanding these correlations is the determination of the intrinsic link between the rheology and the microstructure.

There exists a large body of knowledge on theoretical, experimental, and numerical models of various aspects of flow of powdered solids in liquid (3). However, colloidal beds cannot be treated as dry powders. In a general sense, colloids comprise two types of particles, large and small ions, which are suspended in a solvent. Colloidal agglomerates consist of large ions due to complex ion–ion and ion–solvent interactions, which are of entropic and electrostatic origin (4). The classical models of powder granulation in liquids assume that the Péclet number is much greater than unity and the agglomerate size is much larger than the interaction range of cohesion forces (3). This means that thermal fluctuations, diffusion effects in liquid, and microscopic interactions are neglected. For these assumptions fragmentation microstructures such as rupture, erosion, shatter, and aggregation processes can be considered separately. In the mesoscale, with the presence of diffusion, thermal fluctuations, and long-range interactions between colloidal particles, fragmentation and aggregation microstructures usually occur simultaneously or overlap.

Since blood can be regarded as a colloid (5), we will use it as an example to explain the rationale of our modeling. The axisymmetric pulsatile flows and flows subject to acceleration in blood vessels have been investigated both experimentally and numerically for a long time (see, e.g., (6–9)). These investigations...
were focused on the influence of material damping on the wall vessels, of the viscoelastic properties (10) of blood on the flow of, deformation properties of blood vessels from the shear stresses exerted on the wall, and of the mass transfer and fluid dynamics of blood flow. All of these phenomena can be simulated using Navier–Stokes equations with proper substitution of the blood rheological properties. However, there are medical circumstances in which the Navier–Stokes equations with simple rheology may not work: rapid heart attack or a rapid stroke developed by sudden clotting in small blood vessels. These are critical phenomena in which a transition has taken place in the microscale and propagates over to the mesoscale and macroscale. In this mesoscale regime, blood’s rheology has changed and it should be treated as a complex fluid with various kinds of microstructures, which have suddenly been developed. A review of the relevant concepts in block of microcirculation in blood vessels was first given by Fung and Zwiefach (11). Until now not much progress has been made in the field in these aspects concerning the flow interactions between the microstructural dynamics and the larger-scale flow. The modeling of the dispersion of drugs and thrombus along tiny blood vessels needs a completely different approach, which is still undetermined. In this paper we will model the colloidal interactions between these recently formed microstructures with the complex types of flows by means of a discrete particle model.

Microscopic techniques employing discrete particles such as molecular dynamics (MD) and Monte Carlo (MC) are very useful in studying interactions between primary particles, which form molecules and microstructures. For example, the large-scale MD simulations were employed for investigating microscopic flows (1, 12, 13) and microstructures in solid materials such as impurities in crystals and cracks (14). However, MD becomes too demanding for simulating larger particle ensembles. At the present time particle systems of size about 1 µm can be simulated by using $10^9$ atoms over tens of nanoseconds on the largest parallel computers (14). Most of the computations spend time producing information on microscopic fluctuations, which are not necessary for scales in the ordering of complex fluids.

In recent years, new numerical methods have been developed for modeling physical and chemical phenomena occurring in the mesoscale. The most popular are lattice Boltzmann gas (LBG) (15–17), diffusion-limited aggregation (18), direct numerical simulations (DNS) (19, 20), or other particle methods such as stochastic rotational dynamics (SRD) (21), fluid particle dynamics (FPD) (22), dissipative particle dynamics (DPD) (23), and fluid particle model (FPM) (24). In Fig. 1 we depict the principal features of some of discrete particle models employed for simulation of complex fluids in the mesoscale. We note that molecular dynamics (MD) forms the centerpiece from which the other techniques, such as dissipative particle dynamics (DPD)

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**FIG. 1.** The principal differences between selected discrete particle models: dissipative particle dynamics (DPD), fluid particle model (FPM), lattice Boltzmann gas (LBG), stochastic rotational dynamics (RSD), and molecular dynamics (MD).
and fluid particle model (FPM), are derived and are applicable over a longer length scale.

Dissipative particle dynamics (DPD) is one of the mesoscopic techniques, which allows one to model hydrodynamic behavior with thermal fluctuations. This particle-based off-lattice algorithm was inspired by ideas coupling the advantages of the molecular dynamics and lattice-gas methods. A strong background drawn from statistical mechanics has been provided to DPD (25) from which explicit formulas for transport coefficients in terms of the particle interactions can be derived. Since then the DPD model has attracted a great deal of attention from the chemical community (see, e.g., (26–28)).

As shown in (29, 30), DPD can be used for studying various types of phase separation processes in binary or multicomponent fluids. By employing two-level models for which colloidal beds are modeled by MD particles and solvent by DPD fluid particles, one can simulate micellar solutions (31) and large colloidal aggregates, which can use as many as 20 million particles (32). Dissipative particle dynamics can also be employed for simulating hydrodynamical instabilities such as thin-film falling down the inclined plane (33), the breakup of droplets and mixing in complex fluids (26, 34–36).

For simulating mixing of colloidal agglomerates, over the mesoscale, we have implemented generalized version of dissipative particle dynamics devised by Español (24)—the fluid–particle model (FPM)—which is hybridized within the framework of a classical MD code. We first describe the model. We then present the results from the FPM simulations. Finally we summarize our findings and discuss the prospects of employing the discrete particle method in modeling dynamics of complex colloidal fluid in the mesoscale.

2. DESCRIPTION OF THE FLUID PARTICLE MODEL (FPM)

We begin our discussion by first going over some rudiments of the dissipative particle dynamics (DPD) method (23). The DPD technique portrays the mesoscopic portions of a real fluid. They can be viewed as “droplets” of liquid molecules with an internal structure and with some internal degrees of freedom. As shown in (24, 25), the interactions between these particles are postulated from simplicity and symmetry principles. These principles ensure their correct hydrodynamic behavior. The advantage of DPD over other methods, such as lattice-gas or lattice-Boltzmann, lies in the possibility of matching the scale of discrete-particle simulation to the dominant spatiotemporal scales of the entire system (24).

One of the serious drawbacks of DPD is the absence of a drag force between the central particle and the second particle orbiting about the first. This relative motion may produce a net drag, which is hybridized within the framework of a classical MD code. We first describe the model. We then present the results from the FPM simulations. Finally we summarize our findings and discuss the prospects of employing the discrete particle method in modeling dynamics of complex colloidal fluid in the mesoscale.

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For the dissipative particle dynamics (DPD) method $A(r) = 0$; consequently $\tilde{A}(r) = B(r) = 0$, and $V'(r) \propto B(r)$, which means that all the DPD forces are central.

The noncentral force in FPM, which is proportional to the difference between particle velocities, introduces an additional drag lacking in the DPD model. The noncentral force results also in additional rotational friction given by Eq. [4].

The temporal evolution of the particle ensemble obeys the Newtonian laws of motion,

$$v_i = \frac{1}{m} \sum_{j \neq i} F_{ij}$$  \hspace{1cm} [8]$$

$$r_i = v_i$$  \hspace{1cm} [9]$$

$$\omega_i = \frac{1}{l} \sum_{j \neq i} N_{ij},$$  \hspace{1cm} [10]$$

where the torques in Eq. [11] are given by

$$N_{ij} = -\frac{1}{2} r_{ij} \times F_{ij}.$$  \hspace{1cm} [11]$$

The FPM can predict precisely the transport properties of the fluid, thus allowing one to adjust the model parameters according to the formulas of kinetic theory. Unlike in the macroscopic particle-based method—smoothed particle dynamics SPH (37)—the angular momentum is conserved exactly in FPM. In short, the FPM model can be physically interpreted as a Lagrangian discretization of the nonlinear fluctuating hydrodynamic equations.

3. NUMERICAL MODEL

We have employed a two-dimensional model of a simulation clearly involving a three-dimensional process. However, the simplified 2-D models are less time-consuming than 3-D models and we can certainly glean some useful basic information before venturing into the 3-D arena. It is a matter of more computer time to carry out 3-D simulations with the FPM.

This is a two-level approach and we will consider two types of particles: solvent droplets and colloidal beds. We assume that the concentration of electrolyte in the solvent is low, which is appropriate for the blood. In this case we can neglect the long-range interactions and focus just on the short-range forces. Therefore, the electrolyte-solvent particles can be represented by FPM fluid particles.

We assume that the weight functions (Eqs. [6], [7]) satisfy the conditions imposed. Due to the degree of freedom allowed by the model in selecting the weight functions we may assume that

$$\tilde{A}(r) = 0, \hspace{0.5cm} A(r) = B(r) = \left(1 - \frac{r}{r_{cut}}\right)^2, \hspace{1cm} [12]$$

where $r_{cut}$ is a cut-off radius, which defines the range of particle–particle interactions. For $r_{ij} > r_{cut}$, $F_{ij} = 0$. The first assumption is recommended in (24). We postulate the rest of the weight functions the same as in DPD (22, 24). Due to additional drag between particles caused by the noncentral interactions we can reduce the computational load assuming that the interaction range is shorter than for DPD fluid.

The colloidal agglomerates consist of primary particles—the colloidal beds. They can represent large charged ions, which are a few times larger than electrolyte-solvent droplets. We assume that the agglomerates are “wet”; i.e., colloidal beds are covered by electrolyte binder. This assumption allows us to use the in the model mean forces similar to those obtained for charged macroions in realistic colloidal mixtures.

Interactions among colloidal particles have been studied for more than 50 years. Colloids can be regarded as a complex many-body systems described by highly approximate treatments drawn from classical statistical physics. As follows from the conventional Derjaguin–Landau–Verwey–Overbeek (DLVO) theory the long-range electrostatic interaction between colloidal spheres can be modeled by a screened Coulomb repulsion (38). Additional interactions come from hydrodynamic (39) and depletion forces (40). Some experimental findings (39, 41) show that like-charged macroions have been attracted to one another by short-ranged forces. This fact cannot be explained by the conventional theories. The recent simulation results (4) show that the fluctuation of the charge distribution by the small ions results in the attraction between microions. The mean force is a combination of hard-sphere and electrostatic force. As an approximation $V'(r_{ij})$ (see Eq. [2]) of the mean force between colloidal beds, we use the sum of the Lennard–Jones (L–J) force and a very steep force with a soft core. In Fig. 2 we depict that the approximation is very close to the mean force obtained from large-scale Monte Carlo calculations performed for a real colloidal mixture (4). The force well is proportional to $\varepsilon$—the minimum L–J potential—which is called here the cohesion factor. Unlike in our previous papers exploiting the two-level model (31, 32, 35), we introduce additional dissipative force between colloidal beds. This force is responsible for dissipation of energy due to bed collisions. The colloidal particles are larger and heavier than FPM “droplets” and their interactions are singular. Therefore, thermal fluctuations are transferred from the bulk of fluid and are partly dissipated inside the colloidal agglomerates ($F_{ij} = 0$, if $i$ and $j$ are colloidal particles). There is also no central drag between colloidal beds ($B(r_{ij}) = 0$) because the binder layer covering colloidal beds is assumed to be very thin.

The bed–“droplet” interactions are simulated by employing FPM forces. This is justifiable on the following grounds:

1. The bed–“droplet” forces cannot be singular.
2. Nonzero Brownian component ($F_{ij} \neq 0$) comes from the fluid “droplet.”
3. Viscous drag ($B(r_{ij}) \neq 0$) comes from the fluid “droplet” and the electrolyte binder.
4. The electrolyte concentration in electrolyte–solvent mixture surrounding the agglomerate is low, thus electrostatic bed–“droplet” interactions are negligibly small.

Because the colloidal bed contains a hard core, we have modified the repulsive part of the conservative \( F^C \) bed–“droplet” forces, thus making it steeper than for “droplet”–“droplet” interactions.

The FPM model is based on concepts drawn from statistical physics. In contrast to DPD and two-level models used in our earlier simulations, it is a more general and self-consistent particle method. Simulation of multiphase flow consists of appropriate definition of conservative forces between particles representing different phases and setting some interactions to zero. Thermodynamic properties of the model and the detailed balance condition are always preserved according to the rigorous theoretical basis set out in (24).

The forces are computed by using O(M) order (M-number of particles) link-list scheme combined with neighbor tables (42). Multiple link-lists are used because the sizes of particles and ranges of interactions \( r_{\text{cut}} \) are different; that is, larger Hockney cells (42) are used for longer-range interactions.

In the integration of the equations of motion, which are, in fact, stochastic differential equations (SDE), we have employed at first the leap-frog numerical scheme as it is in (23, 29). Because the scheme is only an approximation of stochastic integrator it generates artifacts leading to unphysical correlations and monotonically increasing (or decreasing) temperature drift. Due to large instabilities observed by using leap-frog, we have used the following higher-order temporal O(\( \Delta t^4 \)) scheme for \( \omega \),

\[
\omega^{n+1/2} = 2\omega^{n-1/2} - \omega^{n-2/3} + (N^n - N^{n-1}),
\]

while the values of \( \gamma^{n+1} \) and \( \omega^{n+1} \) are predicted by using the O(\( \Delta t^2 \)) Adams–Bashforth procedure as in (30). As shown in (35), both the hydrodynamic temperature and hydrodynamic pressures do not exhibit noticeable drift for 1 million time steps. However, the hydrodynamic temperature is 2% higher than the assumed temperature. This is due to the non-energy-conserving character of the scheme applied. However, the detailed balance condition appeared to be only slightly violated (35). For simulations requiring more accurate conservation of thermodynamical quantities, another integrator, which uses a thermostat, should be considered.

The parameters associated with the fluid dynamical interactions of FPM have been matched to the fluid transport coefficients by using the equations in the continuum limit and the detailed balance condition (24),

\[
P_{k\neq l} = \frac{n\Pi_{k\neq l}(r)}{2D}
\]

\[
v_b = \gamma n \left[ \frac{A_2}{2D} + \frac{D + 2}{2D} B_2 \right] + c^2 \frac{1}{\gamma D n(A_0 + B_0)}
\]

\[
v_S = \frac{1}{2} \gamma n \left[ \frac{A_2}{2} + B_2 \right] + c^2 \frac{1}{2\gamma n(A_0 + B_0)}
\]

\[
v_R = \frac{\gamma n A_2}{2}
\]

\[
A_0 = \int d\mathbf{r} A(r), \quad B_0 = \frac{1}{D} \int d\mathbf{r} B(r),
\]

\[
A_2 = \frac{1}{D} \int d\mathbf{r} \mathbf{r}^2 A(r), \quad B_2 = \frac{1}{D(D + 2)} \int d\mathbf{r} \mathbf{r}^2 B(r)
\]

\[
\gamma = \frac{\sigma^2 m}{2k_B T}
\]

where \( P \) is a partial pressure, \( T_0 \) is the temperature of the particle system, \( v_b, v_S, v_R \) are bulk, shear, and rotational kinematic viscosities, respectively, and \( D = 2, c^2 = k_BT/m, \) and \( \Pi, \sigma, \gamma \) are scaling factors of conservative, Brownian, and dissipative forces, respectively.

The results of our test runs show that our FPM model satisfies the basic physical constraints:

1. Total angular and translational momenta are preserved.
2. The actual thermodynamical pressure computed from the virial theorem is constant. Its average is 5–10% larger than \( P \) assumed (for \( M = 50,000 \) particles).
3. The actual thermodynamical temperature computed from the average kinetic energy of the particle system is constant and deviates no more than 2–5% from the value of \( T \).
4. The rotational kinetic energy is about one-third of the total kinetic energy.

Since the compressibility of the fluid is low (for a large value of $\Pi$), there are some quantitative differences between the theory and the simulation. The kinetic theory formulas have been developed in the limit where no conservative forces are present. The actual transport coefficients computed from generalized Einstein and Green–Kubo formulas (43) are larger than those predicted from the classical kinetic theory (44). Therefore, the transport coefficients computed from the theory can be used only as the first coarse approximation. The most precise matching can be done by using a new generic formulation of DPD model, which is a natural generalization of both the DPD and FPM (47).

We have solved the problem for finding clusters of very sophisticated shapes created during granulation by employing an efficient $O(M)$ clustering procedure. It is based on the mutual nearest neighboring (mnn) distance concept. This procedure is outlined in (32).

In Table 1 we have collected dimensionless units used in the model. To define the transport properties of liquid, we introduce dimensionless dissipation factor $\Omega$ as it is in (45),

$$\Omega = \gamma r_c / D c,$$

where $D$ is the dimensionality of the system. For the two-phase solvent–colloid system we have defined three $\Omega$ values: $\Omega_{1-1}$ for colloid-colloid, $\Omega_{1-2}$ for colloid-solvent, and $\Omega_{2-2}$ for solvent-solvent interactions. The value of $\Omega_{2-2}$ represents the magnitude of the viscous forces in the solvent assuming that the conservative forces between fluid particles are small or negligible. For the colloidal system, the value of $\Omega_{1-1}$ characterizes only the dissipative component of colloid–colloid interactions. Because the viscous forces depend also on the long-range correlations resulting from conservative interactions between colloidal beds, the shear viscosity in the colloidal system cannot be computed directly from Eq. [15b]. The actual transport coefficients can be obtained from the Green–Kubo formula employing averaged autocorrelation functions from direct simulation. For the sake of simplicity we use instead of viscosity the dissipative factors $\Omega$ representing the magnitude of the viscous forces resulting from only dissipative component of interparticle forces. The scaling factor for dissipative component of DPD force, defined by the dimensionless $\Omega$ parameter, is set between 10 and 100 (45). For $\Omega$ value greater than 100 the integration scheme becomes numerically unstable but $\Omega = 10$–90 yields reasonably fast relaxation for medium temperatures corresponding to the [1–4] interval in $\epsilon_{unit}$ units (see Table 1).

Table 2 comprises the principal dimensionless parameters used in 2D simulations. Since the droplets represent clusters of molecules, we can estimate that a colloidal bed is a few orders of magnitude larger than a molecule, which would put it around 0.1 to 1 $\mu$m. The problems with simulating an ensemble

<table>
<thead>
<tr>
<th>Value Unit</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length $\lambda$</td>
<td>The average distance between the neighboring fluid particles</td>
</tr>
<tr>
<td>Mass $m$</td>
<td>Dimensionless, mass of the lightest fluid particle $m = 1$</td>
</tr>
<tr>
<td>Time $t$</td>
<td>In $t = \lambda / c$ where $c^2 = k_B T / m \lambda$, unit of length</td>
</tr>
<tr>
<td>Energy $\epsilon_{unit}$</td>
<td>In $3k_B T$ (average kinetic energy for Maxwell distribution)</td>
</tr>
<tr>
<td>Dissipation factor $\Omega$</td>
<td>$\Omega = \gamma r_c / 2c$ where $\gamma$ is the scaling factor of dissipative forces</td>
</tr>
</tbody>
</table>

### Table 2

**Principal Physical and Numerical Parameters**

<table>
<thead>
<tr>
<th>General parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$</td>
<td>1</td>
</tr>
<tr>
<td>$\rho$</td>
<td>0.00001 $\lambda / \Delta t^2$</td>
</tr>
<tr>
<td>$\Delta t$</td>
<td>0.008</td>
</tr>
<tr>
<td>Types of interactions →</td>
<td>Liquid particle–liquid particle</td>
</tr>
<tr>
<td>Average distance between neighboring particles $\lambda$</td>
<td>1</td>
</tr>
<tr>
<td>Number density</td>
<td>3.2 (particles in sphere of radius $\lambda$)</td>
</tr>
<tr>
<td>Cut-off radius (in $\lambda$)</td>
<td>1.5</td>
</tr>
<tr>
<td>Particle mass $m_1 = 1$</td>
<td>$m_{1,2} = 2m_1 m_2 / (m_1 + m_2)$</td>
</tr>
<tr>
<td>Sound velocity $\sqrt{T / \rho}$ (in c)</td>
<td>7.4</td>
</tr>
<tr>
<td>Dissipation factor $\Omega$</td>
<td>25</td>
</tr>
<tr>
<td>Cohesion factor $\epsilon$</td>
<td>—</td>
</tr>
<tr>
<td>Number of particles $1 \times 10^6$</td>
<td>—</td>
</tr>
<tr>
<td>(for large-scale R-T simulations) $(1 \times 10^6)$</td>
<td>—</td>
</tr>
</tbody>
</table>
consisting of particles with such different sizes result from the
different time scales in which the both types of particles evolve.
By approximating the solvent using FPM particles of size similar
to that of the colloidal particles, we have met the requirements
of both scales. The mass variation can be simulated by using
different masses of solvent and colloid particles and/or different
particle sizes for the solvent and colloid. We assume that

1. spacing between colloidal beds is 50% greater than for
liquid “droplets” (thus the colloidal beds are bigger);
2. the density of the colloidal system is 10 times greater than
the density of the liquid (for such a contrast in density and differ-
ence in size of particles, the mass of a colloidal particle should be
more than 20 times greater than the mass of a solvent particle).

The value of $\Pi$—the scaling factor for conservative FPM forces,
which is responsible for the compressibility of the fluid (repre-
sented by the velocity of sound in Table 2)—is chosen so that
the particle system exhibits liquid ordering in the mesoscale; i.e.,
its RDF (the radial distribution function) is characteristic of the
liquid phase. As it is suggested in (30), the value of $\Pi$ was
computed assuming that the FPM fluid has the compressibility
characteristic of water. The energy unit ($\varepsilon_{\text{unit}}$) is set arbitrarily
as a reference point for scaling the colloid–colloid interactions.
It is measured in $3k_B T$ (average kinetic energy for Maxwell dis-
tribution) dimensionless units. The cohesion factor is given in
$\varepsilon_{\text{unit}}$ and is equal to the $\varepsilon$ parameter of the Lennard–Jones force.

The existence of the noncentral force in the FPM allows for
employing a shorter cut-off radius for forces calculation than in
DPD simulations, thus saving computational time. A typical cut-
off radius used in DPD simulation is $2.5\lambda$ (23, 29). The number
density from Table 2 is also representative for MD and DPD
simulations of liquids in 2D.

The system size depends on the total number of particles $M$.
Due to the multiresolution patterns created during flow we use
medium-sized particle ensembles ranging from $10^5$ to $10^6$ par-
ticles simulated for $10^4–10^5$ time steps.

We study two types of flow. At first we consider a colloidal slab
accelerated in a periodic box. Similar types of flows were studied
for solid–liquid mixing by assuming a constant shear rate (3).
By using an accelerated flow we can investigate the granulation
of colloidal agglomerate over a broad range of kinetic energies
in the flow with a single simulation. The particles are confined
within the rectangular box with periodic boundary conditions
in $y$ and reflecting walls in $x$ direction. The aspect ratios of the
slab to the box dimensions are 1 : 5 and 1 : 10 along the $x$ and $y$
axes, respectively. As shown in Fig. 3, the V-shaped profile of
velocity field stabilizes after about 15,000 time steps. Over the
whole periodic box along both the $x$ and $y$ directions we can
observe strong correlations along the horizontal direction. The
vertical correlations are weaker due to greater aspect ratio and
vanishing velocity gradients in the $y$ direction. In the following
section we report the simulation results of granulation for this
type of flow.

4. DISPERSION OF COLLOIDAL SLAB IN A PERIODIC BOX

In Figs. 4 and 5 we present the snapshots from 2-D FPM
simulations of dispersion of colloidal agglomerate accelerated
in a periodic box. We recognize several stages of granulation,
which usually occur with some degree of overlap:

![Fig 4](image-url)
1. **Imbibition**—consisting of spreading the liquid solvent into the colloidal cluster and reducing the cohesive forces between the colloidal beds. This process corresponds to the wetting of a dry, porous solid by the liquid.

2. **Fragmentation**—consisting of shatter, producing a large number of smaller fragments in a single event; rupture, breakup of a cluster into several fragments of comparable size; and erosion, gradual shearing off of small fragments of comparable size (3).

3. **Aggregation**—the reverse of dispersion. Two traditional mechanisms can be recognized: nucleation, defined as the gluing together of primary particles due to the attractive forces, and coalescence, the process by which two larger agglomerates combine to form a granule.

Imbibition is the principal mechanism responsible for initiating fragmentation. As shown in Fig. 4, fluid particles penetrate the permeable agglomerate. The repulsive forces between colloidal and fluid particles (see Eq. [12]) reduce the attractive interactions between colloidal beds. In the case where there is a lack of cohesive forces between the primary particles and $\varepsilon = 0$, the fluid particles create longitudinal paths parallel to the streamlines (see Fig. 4). Simulation results from Fig. 5 ($\varepsilon = 0$) show that for longer simulation times ($T = 5000–7500$) the slab brakes up (shatters) along these paths. For larger values of $\varepsilon$ (see Figs. 4 and 5), fluid particles concentrate in the center of agglomerate. Unlike the case without any cohesive forces ($\varepsilon = 0$), the presence of cohesive force allows one to observe the crosswise fragmentation of the colloidal slab.

Fragmentation may be caused by a few mechanisms. Rupture or shatter of the slab from Fig. 5 for $T = 5000–7500$ is the consequence of cracks formed at the initial stages of simulation. The formation of cracks is due to direct compressive loads and particle–particle impacts than to the hydrodynamic forces. The relevance of hydrodynamic forces in fragmentation shows up at greater kinetic energies of the flow.

The dimensionless number which characterizes fragmentation, the fragmentation number $Fa$, is defined as

$$Fa = \frac{\mu \Gamma}{T},$$

where $\mu$ is dynamic viscosity, $T$ denotes the cohesive strength, $\Gamma$ is shearing rate,

$$\Gamma = \frac{V}{\delta s},$$

$V$ is a characteristic velocity, and $\delta s$ is a characteristic length scale for the Stokes flow. The agglomerate strength $T$ is not an intrinsic material property, like the surface tension, but depends on many factors, including the internal structure, compaction, and many other physical parameters.

When the fluid dynamical stresses exceed a critical value $F_{a_{\text{crit}}}$, that is, $Fa > F_{a_{\text{crit}}}$, the agglomerates rupture in shear flow. As shown in (3), for fragmenting polystyrene lattices the value of $F_{a_{\text{crit}}}$ is the reciprocal of the mean agglomerate size $S_{\text{avg}}$. Ionic effects at high electrolyte concentrations are well accounted for by assuming $T$ to be proportional to the force between two primary particles, i.e., $T \approx g(\varepsilon)$ where $\varepsilon$ is here a maximum cohesion strength, the cohesion factor. Thus, the value of $T$ is independent on the agglomerate size and the shear rate. From Eqs. [19] and [20] we obtain

$$S_{\text{avg}} \approx \frac{g(\varepsilon)}{\mu \Gamma},$$

where $g(\varepsilon)$ is a monotonically increasing function of $\varepsilon$ determined empirically (3). A similar relationship between the mean cluster size and the shear rate $\Gamma$ is also found in the case of converging flow and in the granulation of wet agglomerate in powder due to the shear flow (22).
Mixing and segregation of granular materials can be simulated also employing the discrete particle model rooted in molecular dynamics simulations. The rapid granular flow simulation (RGFS) employs actual expressions for the magnitude of the forces for describing the interactions between the finite-sized particles (22). Interactions between particles in RGFS are restricted to frictional effects and elastic and plastic deformations of the surface, which limits the applicability of these models to dry powder flows. The agglomeration of fine particles in wet granulation can be achieved by introducing an intermediary viscous binder fluid into a shearing mass of powder (22). Viscous interactions between solid particles covered by the binder allow the particles to adhere together or bounce off one another. The wet agglomerates break up in a shear flow. The wet agglomerates rupture when the Stokes number $St$—determined by the ratio of the initial kinetic energy in the shearing mass and the energy resisting deformation—exceeds a critical value.

According to (22), the stable cluster size at the point of equilibrium before deformation and break-up is given by the formula

$$S_{\text{avg}} \approx \left( \frac{\mu}{\Gamma} \right)^\alpha,$$

where $\mu$ is dynamic viscosity of fluid binder and $\alpha = 1$ for $T = \text{const}$. Since cohesive strength $T$ will depend on shear rate and/or the size of granule, the value of $\alpha$ is greater than 1. The results from RGFS simulations show that, for a small capillary number ($Ca$), $\alpha = 2$ (for $Ca > 10$, $\alpha = 5$).

In both cases, i.e., powder-in-liquid and mud-in-powder flows, the microscopic effects such as the thermal fluctuations can be neglected and shear rate is constant. In the FPM model, thermal fluctuations in the solvent are simulated by the Brownian component of particle–particle forces. The fluctuations are transferred to the agglomerate particles.

The shear rate $\Gamma$ changes in time and is defined as

$$\Gamma = \sqrt{v_{\text{diff}}^2 v_{\text{diff}}^2 / \lambda},$$

where $v_{\text{diff}} = \langle U_{\text{Bed}} \rangle - \langle U_{\text{fluid}} \rangle$,

and the average distance between the neighboring beds, $\lambda$ is the average distance between the neighboring beds, and $\langle U_{\text{Bed}} \rangle$ and $\langle U_{\text{fluid}} \rangle$ are the average translational velocities in y direction for the agglomerate beds and fluid particles, respectively.

From Fig. 6a one can discern that in the beginning the average kinetic energy $E_K$ of the accelerated slab increases with time linearly. After incipient rupture, the value of $E_K$ decreases (compare $N_{\text{clus}}$ time dependence from Fig. 6b with the plot from Fig. 6a). This drop in kinetic energy is due to larger dissipation caused by an increase of the frictional surface and the potential energy of the colloidal particle system after rupture. As shown in Fig. 6a, the second mechanism dominates at stronger cohesions. In the course of the simulation, the V-shaped velocity field (Fig. 3) causes the colloidal beds to concentrate in the center of the box where the velocity is the highest. This mechanism dominates over the previous two after 10,000–13,000 time steps. The kinetic energy of the colloidal beds increases. Together with an increase of kinetic energy, the agglomerate deforms by creating elongated structures, which then rupture and are eroded.

As shown in Figs. 6b and 7, in this power law regime the mean cluster size is

$$S_{\text{avg}} = \frac{A(\varepsilon, \Omega, T_0, \ldots)}{\Gamma^\alpha},$$

where $\alpha \approx 2$ and $A(\cdot)$ is a function of material properties and

![FIG. 6.](image_url) (a) The average kinetic energy of the colloidal agglomerate with time for various cohesion factors $\varepsilon$. (b) Mean cluster size ($S_{\text{avg}}$, gray) with shear rate $\Gamma$ and number of clusters ($N_{\text{clus}}$, black) with number of time steps for the colloidal slab accelerated in a periodic box. The value of $\varepsilon = 1.5$. The scales of shear rate $\Gamma$ and number of time steps do not correlate exactly.
physical conditions of the particle system such as temperature, viscosity, and partial pressure. The value of $\alpha$ obtained from a linear regression for the different simulation parameters is found to locate within the interval $[1.82, 2.12]$. This result is surprisingly similar to that obtained from RGFS (rapid granular flow simulations) (22) of mud-in-powder shearing flow. The value of $\alpha$ is greater than 1 (as it is in Eq. [21]) because the cohesive strength depends on the shear rate and the size of granule. For an increasing shear rate,

**FIG. 7.** Mean cluster size with time for a few different cohesion factors.

**FIG. 8.** The zoomed-in snapshots from FPM simulations of dispersion of the colloidal slab from Fig. 5 for different viscous forces $\Omega_{1-1}$ for a time step corresponding to the power law regime.

**FIG. 9.** The zoomed-in snapshots from FPM simulations of dispersion of the colloidal slab from Fig. 5 for different cohesion factor $\epsilon$, for a time step corresponding to the power law regime.
the temperature of a colloidal granule increases because the energy from friction cannot be dissipated away. Thus, there is a positive feedback, since the cohesive strength decreases sharply.

In Fig. 8 we present two snapshots from FPM simulations for different $\Omega_{1-1}$, which stands for dissipative factor in the colloidal system. For smaller values of $\Omega_{1-1}$ dissipation is lower and the temperature of the colloidal agglomerate becomes higher. The
cohesion decreases with temperature; thus, the mean cluster size is smaller. As in (21), one can roughly estimate that

\[ A(\varepsilon, \Omega, T_0, \ldots) \propto f(\Omega_{1-1}), \tag{25} \]

where \( f(\Omega_{1-1}) \) is a monotonically increasing function of \( \Omega_{1-1} \).

As was depicted in Figs. 5, 7, and 9, the parameter \( A(\varepsilon, \Omega, T_0, \ldots) \) is also a function of cohesion factor \( \varepsilon \). In the case of \( \varepsilon = 0 \) the cohesion strength comes from viscous forces or it is of entropic origin (e.g., depletion forces). The agglomerate clusters create long threads (see Figs. 5, 9), which are parallel to the streamlines even for a low shear rate. These threads are very fragile and can easily be torn, for example, by the horizontal fluctuations caused by the reflecting walls. By simulating ensembles with many more particles, we can discern the act of creating very complex multiresolution structures (Fig. 10). For greater \( \varepsilon \), we can observe that the structures become more rigid and compact and that the mean agglomerate size \( S_{\text{Avg}} \) increases.

Let us now assume that the cohesive factor \( \varepsilon \) increases by \( d\varepsilon \). The change in energy \( d(E_B) \) supplied from the bulk of fluid to the agglomerate of mean size \( S_{\text{Avg}} \) must be compensated by the change in potential energy \( d(E_S) \) on the agglomerate surface \( L \) (boundary in 2-D). This comes from an assumption that the energy supplied is dissipated entirely in the agglomerate interior. Because \( (E_B) \) should be proportional to the agglomerate surface and \( d(E_S) = L d\varepsilon \), hence,

\[ b_1 L d\varepsilon = d(b_2 L). \tag{26} \]
where the border of the agglomerate with a mean size $S_{\text{Avg}}$ in 2-D is given by

$$\begin{align*}
L &= b_3 S_{\text{Avg}}^{\beta},
\end{align*}$$

[27]

where $\beta = 1/2$ for a circle and 1 for a rod of a given width.

From Eqs. [26] and [27] we can obtain that

$$A(\varepsilon, \Omega, T_0, \ldots) = S_{\text{Avg}}^{\Gamma = \text{const}} = b_5 e^{b_6 \varepsilon},$$

[28]

where $b_1, b_2, b_3, b_4$, and $b_5$ are proportionality constants.

In Fig. 11 we present the plot showing $A(\varepsilon, \Omega, T_0, \ldots)$ increases exponentially with $\varepsilon$. We show also that the mean agglomerate size in the power law regime does not depend on the

FIG. 16. Particle positions (above) and momenta (below) for selected snapshots from the simulation of mixing caused by Rayleigh–Taylor instability ($\varepsilon = 3.5$, $\Omega_{12.2-2} = 25$, $M_{\text{TOT}} = 1 \times 10^5$, $M_{\text{COL}} = 5 \times 10^3$, acceleration = $g$).

FIG. 17. The results from the mixing due to R-T instability. (a) Mean cluster size with the average kinetic energy of the system. (b) Kinetic energy of colloidal beds and liquid in time.
solvent viscous forces represented by the dimensionless factor $\Omega_{2-2}$. We have checked that this relationship is also true for fluid with $\Omega_{2-2} \in [1, 90]$. This fact stands in contradiction to the Eq. [21] obtained for empirical data from rupture of the fractal agglomerate in a shear flow. Instead, we can observe in Fig. 12 that $S_{\text{Avg}}$ decreases with the reciprocal of $\Omega_{1-2}$, which represents direct dissipative interactions between colloidal beds and fluid particles. The effect of these interactions can be discerned in Fig. 13. A greater value of $\Omega_{1-2}$ results in greater degree of fragmentation and smaller value of $S_{\text{Avg}}$.

Finally, we can summarize that in the power law regime, the mean agglomerate size decreases with shear rate $\Gamma$ as

$$S_{\text{Avg}} = b_5 f(\Omega_{1-1}) \frac{e^{bet}}{\Omega_{1-2} \Gamma^2}.$$  \hspace{1cm} [29]$$

As shown in Fig. 6b, the linear regime is perturbed for larger values of $\Gamma$. The colloidal beds concentrate in the center of the box where the velocity is the highest. We display in Fig. 14 that for a longer simulation time the fragments of colloidal slab

FIG. 18. The snapshots from the simulation of mixing of colloidal beds in liquid caused by Rayleigh–Taylor instability. More than a million particles were simulated by including $M_{\text{COL}} = 5 \times 10^4$ colloidal beds. The acceleration is equal to $0.2 \times g$ (see Table 2). The simulation time is $T = 20,000$, $40,000$, and $60,000$ time steps, respectively.
create long threads. The threads break up and agglomerate due to the convergent flow. The number of clusters \(N_{cl}\) fluctuates in this regime (Fig. 6a).

Dissipative forces damp out the thermal fluctuations and fluctuations generated by the boundary conditions, which are responsible for rupture. For larger value of the solvent viscosity represented by \(\Omega_{2.2}\) the process of agglomeration is getting faster and the resulting structures are smoother than for a lower viscosity. The effect can be observed by comparing Fig. 9 \((\Omega_{2.2} = 15)\) and Fig. 15 \((\Omega_{2.2} = 45)\). The direct influence of the fragmentation and agglomeration on flow can also be discerned for more complex types of flows.

5. DISPERSION PRODUCED BY MIXING INDUCED BY RAYLEIGH–TAYLOR INSTABILITY

In (35, 36), we have employed the dissipative particle dynamics approach to tackle the problem of mixing induced by Rayleigh–Taylor instability at the mesoscale. We show that the interactions between DPD particles and thermal fluctuations in dissipative fluids influence strongly the speed of mixing. The flow changes from rising mushrooms to bubble dynamics induced by the transformation to microscopic morphology, the breaking-up of spikes, and the coalescence of the droplets.

We have simulated a Rayleigh–Taylor type of flow but for a liquid–solid system. The discrete particles are confined to move about within the confines of a rectangular box with a height \(h\) and a length \(L_{xy}\). Periodic boundary conditions are imposed along the \(x\) direction. Initially, the thin upper part of the box is filled with heavy colloidal beds and the lower part filled with lighter fluid particles. The Atwood number, representing the ratio of the density jump, is 0.82. An external gravity acceleration \(g\) pointing downward is present. Unlike the liquid–liquid situation in which mixing starts spontaneously, the liquid–solid system does not mix so easily. Fragmentation occurs only when the colloidal system becomes permeable from oversaturation and undergoes an excessive wetting process.

In Fig. 16 we display particle positions (above) and momenta (below) for selected snapshots from the simulation of mixing caused by the Rayleigh–Taylor instability. The microstructures arising during mixing are completely different than bubbles and spikes detected in classical R–T instability. Instead, one can observe multiscale structures consisting of large fishbone clusters made of long threads or more oblate agglomerates. Comparing position and momenta of the particle systems one can conclude from Fig. 16 that the fishbone fragmentation of large clusters is caused by flow. The threads go along with streamlines of this flow while the oblate aggregates are located in the places of the slowest flow. We show in Fig. 17a that after vigorous fragmentation, the energy of flow damps out and the threads shrink and agglomerate. As depicted in Fig. 17b, the maximum of kinetic energy of the lighter fluid correlates very well with the minimum of the mean agglomerate size. From Fig. 15a it is apparent that the agglomeration takes place much slower than the fragmentation.

**FIG. 19.** Similar to Fig. 18 but for gravitational acceleration \(0.6 \times g\). Unlike in Fig. 18, the aggregation is observed at the mixing front.
6. CONCLUDING REMARKS

In this work we have presented results taken from 2-D fluid particle modeling in which we have simulated two types of accelerated solid–fluid flows on the mesoscale. These flows portray the flow of a colloidal slab along a long periodic box and the mixing induced by the solid–liquid type of Rayleigh–Taylor instability.

The first type of flow may be applied to blood flow or transport processes in sedimentary rocks (2). In both types of solid–liquid flows we can easily recognize the characteristic dispersion caused by the microstructural dynamics and they include phenomena such as rupture, erosion, shatter, and agglomeration, all of which would be very difficult to model with conventional continuum methods. We have studied rather thoroughly the process of fragmentation in the power law regime (3). In solid–liquid systems, such as the fractal agglomerate in solvent and wet granulation in powder under shear, the mean cluster size $S_{avg}$ varies with the shear rate $\Gamma$ as $1/\Gamma^\alpha$. This very important relationship can also be detected in mesoscopic solid–liquid systems in which thermal fluctuations play a definite role. In Table 3 we categorize the various types of fragmentation with the mean cluster size.

1. For wet granulation in powder and mesoscopic solid–liquid fragmentation the mean agglomerate size depends inversely on the square of the shear rate. For both cases the cohesive strength $T$ depends on shear rate and/or the size of a granule.

2. For shear flow with a constant rate and a constant cohesive strength $T$ in fractal agglomerate-in-liquid, the average mean size of the granule varies as $1/\Gamma^\alpha$.

3. The attractive forces arising from the binder fluid covering the colloidal beds are found to correspond to the dissipative forces in the mesoscopic colloidal agglomerate.

4. The hydrodynamic forces developed in fractal agglomerate/liquid system would correspond to the dissipative colloidal-bed/fluid–particle interactions on the mesoscale.

5. The exponential dependence of $S_{avg}$ on the cohesive factor $\epsilon$ is derived from collective mesoscopic effects, such as short-ranged, attractive ion–ion forces and thermal fluctuations.

Another aspect concerning complexity is revealed by the strong heterogeneity in the flow structure. With the fluid–particle

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<td>Mean cluster size, $S_{avg}$</td>
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<tr>
<td>$S_{avg} \approx \frac{g(\epsilon)}{\mu T}$</td>
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<td>$S_{avg} \approx \left(\frac{\mu}{T}\right)^2$</td>
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<tr>
<td>$S_{avg} \approx \frac{b_0 f(\Omega_1)}{\Omega_1^{-2} T^2}$</td>
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model one can discern properly the multiscale character of the solid–fluid system. As shown in Fig. 18, multiresolution structures prevail in a solid–fluid system. These multiscale structures are complicated due to the inflexibility of the description level with varying scale of observation. Unlike in (46), where different numerical methods were employed for describing the particle, the cluster, and the entire system, the FPM model is the sole numerical paradigm in our simulations. From a computational standpoint, we do not observe any methodological disparity of solid–fluid interaction mechanisms in totally different regimes in which either fluids or particles may dominate.

Even though the fluid–particle model is superior to the older mesoscopic scheme—dissipative particle dynamics—it does not solve the serious conceptual problem of the method of DPD. The thermodynamic behavior of the fluid particle model is determined by the conservative forces, which are soft in comparison with the singular MD interactions. Hence, there does not exist a well-defined procedure to relate the shape and amplitude of the conservative forces with a prescribed thermodynamic behavior. Furthermore, it is not clear what physical time and length scales the model actually describes. The presence of thermal noise suggests a fuzzy area belonging to the mesoscopic realm. In (30) we show, for example, that the DPD and FPM fluid structures resemble short-chain polymers. In (47) it is proved that the spatiotemporal scale for DPD can be precisely defined by introducing the volume of a fluid particle as a new variable. The model is interesting from a theoretical point of view but it is very hard for implementing efficiently in simulating multicomponent fluids. Moreover, it is less efficient involving a larger cut-off radius than FPM and DPD. This price paid for being more strict with matching the spatiotemporal scale may appear currently too demanding, especially for 3-D simulations (48). There is a thin border between the applicability of a numerical model and the theory.

With the FPM we can extend further the capabilities of the discrete particle method to the mesoscopic regime and show that they are competitive to standard simulation techniques with continuum equations. These methods establish a foundation for cross-scale computations ranging from nanoscales to microns and can provide a framework to study the interaction of microstructures and large-scale flow, which may be of value in blood flow and other applications in polymeric dynamics.

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