A Stochastic Rotation Dynamics Model for Dilute Spheroidal Colloid Suspensions

Takehiro YAMAMOTO*,†, Shinpei HIROTA**, and Takuya FUJIWARA*

*Division of Mechanical Engineering, Graduate School of Engineering, Osaka University
2-1 Yamadaoka, Suita, Osaka 5650871, Japan
**Department of Mechanical Engineering, School of Engineering, Osaka University
(Received : November 11, 2015)

In multi-particle collision dynamics (MPCD), a solvent is modeled as a large number of point-like particles with a given mass, and particle collisions are expressed in terms of a redistribution of momentum among them. The present study proposes a computational model for dilute spheroidal colloid particle suspensions using an MPCD method called stochastic rotation dynamics (SRD). The present model describes the effect of the colloidal particle volume fraction on the shear viscosity of suspensions by modeling the colloidal particles as SRD particles in a similar manner to solvent particles.

Key Words: Stochastic rotation dynamics / Multi-particle collision dynamics / Colloid suspensions / Computational models

1. INTRODUCTION

Multi-particle collision dynamics (MPCD) is a computational method that can model both hydrodynamic interactions and Brownian motion at relatively low computational costs.1,2 A solvent is modeled as a large number of point-like particles with a given mass, and particle collisions are expressed in terms of a redistribution of momentum among them. Stochastic rotation dynamics (SRD) is one form of MPCD, and has been applied to simulations of complex fluids such as polymer solutions.3 However, when simulating particle suspensions using MPCD, the colloid particles cannot be considered to be point-like, and collisions between colloid and solvent particles must be computed based on interactions at the surfaces of the colloid particles. This leads to a high computational cost, and diminishes the advantage of MPCD in treating particle collisions using low-cost momentum redistribution procedures. In the present study, we propose a computational model for dilute spheroidal colloid particle suspensions within the framework of SRD, in which particle collisions are described by a momentum redistribution. The effectiveness of the proposed model is examined for the case of simple two-dimensional shear flows.

2. STOCHASTIC ROTATION DYNAMICS

Simulations of the behavior of solvents based on MPCD involve streaming and collision steps.1,2 The positions of the solvent particles are updated in the streaming steps, and their velocities are computed in the collision steps by considering particle collisions.

In a streaming step, the position \( \mathbf{r}_i(t) \) of a solvent particle at time \( t \) is updated using:
\[
\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \Delta \mathbf{v}_i(t),
\]
where \( \mathbf{v}_i(t) \) is the velocity vector for the particle and \( \Delta t \) is the time increment. In MPCD, particle collisions are described in terms of a redistribution of momentum among the solvent particles. The computational region is divided into sub-grids referred to as collision cells, and particle collisions are computed within each of these cells. Several schemes for expressing the momentum redistribution in collision steps have been proposed.1,2 In the present study, we employed SRD, in which a collision is expressed in terms of a random rotation of the relative velocity vector \( \mathbf{v}_i - \mathbf{u} \), where \( \mathbf{u} \) is the mean velocity of the particles in a collision cell. The velocity vector \( \mathbf{v}_i \) is updated using the following equations:
\[
\mathbf{v}'_i(t + \Delta t) = \mathbf{u}(t) + R(\omega) \cdot (\mathbf{v}_i(t) - \mathbf{u}(t)),
\]
\[
\mathbf{u}(t) = \frac{\sum m_i \mathbf{v}_i(t)}{\sum m_i},
\]

*E-mail: take@mech.eng.osaka-u.ac.jp
where \( m_i \) is the mass of particle \( i \), and \( \mathbf{R}(\alpha) \) is a random rotation tensor of a rotation angle \( \alpha \). For two-dimensional cases, \( \mathbf{R}(\alpha) \) corresponds to a rotation of an angel \( \pm \alpha \) about the axis perpendicular to the two-dimensional computational region, where the sign is randomly chosen. The summation in Eq. (3) is performed over all particles \( i \) belonging to the collision cell considered.

For a two-dimensional shear flow, the solvent viscosity \( \eta_s \) is expressed in SRD as\(^1,2\)

\[
\eta_s = \eta_{sw} + \eta_{cel} = \frac{n k_B T \Delta t}{2 \alpha^2 (n - 1 + e^{-\alpha}) (1 - \cos \alpha)}
+ \frac{m}{12 \Delta t} (n - 1 + e^{-\alpha}) (1 - \cos \alpha),
\]

where \( n \) is the average number of solvent particles in a square collision cell with sides \( \alpha \), \( k_B \) is the Boltzmann constant, \( T \) is the absolute temperature, and \( m \) is the mass of a solvent particle. The first and the second terms in Eq. (4) represent the contributions of streaming (\( \eta_{sw} \)) and collisions (\( \eta_{cel} \)) to the viscosity, respectively.

3. SRD MODEL FOR SPHEROIDAL COLLOID SUSPENSIONS

In typical simulations of colloidal particle suspensions using SRD, collisions between colloid and solvent particles are computed based on interactions on the colloid particle surface. However, this approach incurs a high computational cost, which diminishes the advantages of SRD (or MPCD). In the present study, we propose a computational model for dilute colloidal suspensions within the framework of SRD, in which colloid particles are also treated as point particles.

The shear viscosity of colloidal particle suspensions depends on the volume fraction of the particles. However, the volume of particles cannot be expressed if colloidal particles are modeled as SRD point particles. Therefore, we consider an alternative method for representing the effect of the volume fraction on the shear viscosity while staying within the framework of SRD. If \( n_p \) solvent particles in a collision cell are replaced by the same number of SRD colloidal particles with a mass \( m_p \), and with the same rotation angle \( \alpha \) as the solvent particles, this corresponds to an increase in the number of solvent particles from \( n \) to \( n' = n + (m_p/m - 1)n_p \) where \( m \) is the mass of a solvent particle. Furthermore, when \( \Delta t \) is small enough, the streaming contribution is negligible compared to the collisional distribution. Consequently, the viscosity ratio, \( \eta/\eta_s \), where \( \eta \) is the suspension viscosity and \( \eta_s \) is the solvent viscosity, is approximately given by

\[
\frac{\eta}{\eta_s} = \frac{n' - 1 + e^{-\alpha}}{n - 1 + e^{-\alpha}} = C,
\]

This equation indicates that the viscosity of suspensions can be adjusted by changing the mass ratio \( m_p/m \) and/or \( n_p \). On the other hand, the shear viscosity \( \eta \) of a dilute suspension of hard spheres can be predicted using a modified Einstein equation:\(^3,4\)

\[
\frac{\eta}{\eta_s} = 1 + 2.5 \phi + 6.2 \phi^2,
\]

where \( \phi \) is the volume fraction of colloid particles. This formula is usually applied when \( \phi \leq 0.1 \). Comparing Eqs. (5) and (6), one obtains Eq. (7):

\[
6.2 \phi^2 + 2.5 \phi + 1 - C = 0.
\]

The quadratic equation (7) can be solved to evaluate the equivalent volume fraction \( \phi_{eq} \), which is the volume fraction when \( \eta = C \eta_s \), if the values of \( m, m_p, n, \) and \( n_p \) are given.

The shear viscosity can also be evaluated from the results of SRD simulations for simple shear flows. In the present simulation, we considered two-dimensional shear flows with \( \mathbf{v}_f = \mathbf{y} \) and \( \mathbf{v}_c = 0 \), where \( \mathbf{v}_f \) is the flow velocity in the \( \alpha \)-direction (\( x \) is the flow direction and \( y \) is the direction of the velocity gradient) and \( \mathbf{v}_c \) is the shear rate. The stress tensor \( \sigma = (\sigma_{\alpha\beta}) \) is computed using Eq. (8) and the shear viscosity \( \eta \) is evaluated using Eq. (9).\(^5\)

\[
\sigma_{\alpha\beta} = -\frac{1}{V} \left\{ \sum_{i=1}^{N_p} \left( m_i \mathbf{v}_{i,\alpha} - \mathbf{v}_c \right) \left( \mathbf{v}_{i,\beta} - \mathbf{v}_c \right) \right\}
+ \sum_{i=1}^{N_p} \left( \mathbf{v}_{i,\alpha} - \mathbf{v}_c \right) \left( \mathbf{v}_{i,\beta} - \mathbf{v}_c \right)
- \frac{1}{V \Delta t} \left\{ \sum_{i=1}^{N_p} \left( \mathbf{D}_{i,\alpha} r_{i,\beta} \right) + \sum_{i=1}^{N_p} \left( \mathbf{D}_{i,\beta} r_{i,\alpha} \right) \right\}
= \sigma_{\alpha\beta}^{sw} + \sigma_{\alpha\beta}^{cel},
\]

\[
\eta = \frac{\sigma_{\alpha\beta}}{\gamma} = \frac{\sigma_{\alpha\beta}^{sw} + \sigma_{\alpha\beta}^{cel}}{\gamma} = \eta_{sw} + \eta_{cel}.
\]

Here, \( i \) denotes the \( i \)th particle and the subscripts \( \alpha \) and \( \beta \) (both with and without a comma) indicate the \( \alpha \) and the \( \beta \) components (\( \alpha, \beta \in \{ x, y \} \)), respectively. The angle brackets, \( \langle \cdots \rangle \), denote the time average. \( V, \mathbf{v}_c, \mathbf{D}_{i,\alpha}, \mathbf{D}_{i,\beta}, \) and \( r \) are the volume of a collision cell, the \( \alpha \)-component of the velocity vector \( \mathbf{v}_c \), the change in momentum \( m_i \mathbf{v}_c \), the change in momentum \( m_p \mathbf{v}_c \), and the position vector for particle \( i \) relative to the center of mass of the particles in the cell, respectively. The physical quantities can be scaled as follows: \( \varepsilon = \sqrt{\frac{k_B T}{m \sigma}} \), \( \eta = \eta \sqrt{m \sigma^2 / \varepsilon^2} \), \( \gamma = \gamma \sqrt{m \sigma^2 / \varepsilon^2} \). In the remainder of this paper, the...
superscript * indicating dimensionless variables is omitted.

The computational domain used in the present simulation consists of $64a \times 64a$ square cells. Simulations of simple shear flows were performed using the Lees-Edwards moving periodic boundary conditions.\(^5\) We fixed both $n$ and $n_p$ and varied $m_p/m$ to compare the predicted shear viscosities with those obtained from Eq. (6) with $\phi = \phi_{eq}$ estimated by Eq. (7).

4. RESULTS

The values for the model parameters are summarized in Table I. The numerical results described below are averages over time $\bar{t}$ until 120 of shear strain ($\gamma \bar{t}$) is imposed on the system after it reaches an almost steady state. In the present simulations, the values of $\alpha$, $m$, $n$, $n_p$, and $\dot{\gamma}$ were fixed.

Figure 1 compares the solvent viscosities computed by SRD simulations with theoretical predictions using Eq. (4). There is seen to be good agreement between the two sets of results, thus confirming the effectiveness of the SRD code.

Figure 2 shows the shear viscosity as a function of the equivalent volume fraction $\phi_{eq}$. In this simulation, $m_p$ was varied and $\phi_{eq}$ was evaluated using Eq. (7). The results for $m_p=1$ correspond to those for the solvent. The computational results show good agreement with the predictions using the modified Einstein model for $\phi_{eq}$ below around 0.1, which suggests that the proposed model for dilute colloidal suspensions using SRD is suitable for describing the effect of the particle volume fraction on the shear viscosity at relatively low volume fractions. The deviation from the theoretical predictions is greater for larger $\Delta t$ because the contribution of streaming becomes non-negligible.

Table I. Values for model parameters.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>1</td>
</tr>
<tr>
<td>$m$</td>
<td>1</td>
</tr>
<tr>
<td>$k_B T$</td>
<td>1</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>133°</td>
</tr>
<tr>
<td>$\dot{\gamma}$</td>
<td>0.015</td>
</tr>
<tr>
<td>$n$</td>
<td>20</td>
</tr>
<tr>
<td>$n_p$</td>
<td>2</td>
</tr>
<tr>
<td>$m_p$</td>
<td>1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5</td>
</tr>
</tbody>
</table>

Fig. 1. Comparison of solvent viscosities computed using SRD simulations and those predicted theoretically. Plotted points and dashed lines indicate numerical results and theoretical predictions, respectively.

Fig. 2. Viscosity ratio, $\eta/\eta_s$, as function of equivalent volume fraction, $\phi_{eq}$. Open circles: numerical results for $\Delta t = 0.2$. Filled circles: numerical results for $\Delta t = 0.4$. Dashed line: theoretical prediction using modified Einstein model Eq. (6).
5. CONCLUSION

We proposed a computational model for dilute colloidal suspensions within an MPCD framework. In this model, colloidal particles were described as SRD particles, whose mass was used to represent the volume fraction of the colloidal particles. By varying the particle mass, the dependence of the shear viscosity on the equivalent volume fraction was successfully determined. It is straightforward to extend this approach to three-dimensional cases. We believe that the present method is useful for modeling dilute colloidal suspensions without diminishing the cost advantages of SRD, and that it can be effectively adopted to describe the behavior of suspended components whose size changes while flowing, e.g. suspensions of microalgae. Furthermore, we think that this approach can be extended to model semi-dilute to concentrated colloidal systems by introducing excluded-volume effects using a repulsive potential function to represent the force between particles. These topics will be considered in future research.

ACKNOWLEDGEMENT

This work was supported by JSPS KAKENHI Grant Number 25289032.

REFERENCES