Collective behavior of Suspended Janus Particles via an Integral Equation Method

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Abstract

INTRODUCTION

GOVERNING EQUATIONS

Screened Laplace Mobility Problem

The mathematical formulation is a nonlinear system for the dynamics of a collection of particles. The interactions come from a system of partial differential equations (PDEs) that comprise hydrodynamic interactions and hydrophobic interactions. The hydrodynamic interactions come from the mobility problem for rigid particles immersed in a viscous solvent. We then use a second-order Adams-Bashforth method to update the particle configuration. Assuming inertial terms are negligible, the particle motion is goverened by the Stokes equations

$$-\mu\Delta\mathbf{u} + \nabla p = \mathbf{0}, \qquad \mathbf{x} \in \Omega, \tag{1}$$

$$\nabla \cdot \mathbf{u} = 0, \qquad \mathbf{x} \in \Omega, \tag{2}$$

$$\mathbf{u} - \mathbf{u}_\infty \to \mathbf{0}, \qquad |\mathbf{x}| \to \infty, \tag{3}$$

where $\mathbf{u}$ is the velocity and p is the pressure of the solvent, $\mathbf{u}_\infty$ is the background flow, and μ is the constant solvent viscosity. The domain $\Omega = \Omega(t)$ is the fluid region surrounding the particles and changes shape as the particles move. Since the particles are rigid, the solvent velocity satisfies a no-slip boundary condition for a rigid body motion on the particle boundary Γ_i with translational velocity $\mathbf{v}_i$ and angular velocity ω_i. Given imposed forces acting on each particle, the *mobility problem* consists of finding translational and angular velocities so that viscous fluid forces balance the imposed forces.

The hydrophobic interactions come from the tendency of particles to minimize the free energy of the structure of the surrounding water molecules. The free energy functional takes the form

$$F[u] = C \int_\Omega \left(\rho |\nabla u|^2 + \rho^{-1} f(u) \right) \, d\mathbf{x}, \tag{4}$$

where u is an order parameter for the structure of water, ρ is a decay length, C is a constant, and $f(u)$ is a potential. Hydrogen-bond persistence times are on the order of picoseconds which is much smaller than characteristic time for particle motion.Thus we assume u minimizes $F[u]$ for all times. Assuming appropriate conditions on $f(u)$,u is bounded and satisfies the Euler-Lagrange equation

$$-\rho^2 \Delta u + \tfrac{1}{2} f'(u) = 0 \text{ in } \Omega, \quad u = g, \text{ on } \partial\Omega. \tag{5}$$

The boundary condition g is a material label that is transported with the particle (Figure 1).

The particles lower the free energy $F[u]$ of the surrounding water by moving. We calculate the rate of change of $F[u]$ using *variation of the domain*Carrying out this variation yields a stress

$$\mathbf{T} = C\left[\rho^{-1} f(u)\mathbf{I} + \rho\left(|\nabla u|^2 \mathbf{I} - 2\nabla u \nabla u^T\right)\right]. \tag{6}$$

The imposed forces and torques come from the integration of $\mathbf{T}$ along the particle boundary. These forces and torques couple the Stokes equations (1), to semilinear elliptic equation (5). Solving for the translational and rotational velocities gives the particle evolution.

$$\mathbf{u}(\mathbf{x}) = \mathbf{u}_\infty(\mathbf{x}) + \mathcal{D}[\boldsymbol{\eta}](\mathbf{x}) + \sum_{i=1}^{N_b} \left(\mathbf{S}(\mathbf{x}, \mathbf{a}_i) \cdot \mathbf{F}_i + \mathbf{R}(\mathbf{x}, \mathbf{a}_i) T_i\right), \quad \mathbf{x} \in \Omega. \tag{7}$$

$$\begin{aligned} \mathbf{v}_i + \omega_i (\mathbf{x} - \mathbf{a}_i)^\perp = \mathbf{u}_\infty(\mathbf{x}) - \frac{1}{2}\boldsymbol{\eta}(\mathbf{x}) + \mathcal{D}[\boldsymbol{\eta}](\mathbf{x}) \\ + \sum_{j=1}^{N_b} \left(\mathbf{S}(\mathbf{x}, \mathbf{a}_j) \cdot \mathbf{F}_j + \mathbf{R}(\mathbf{x}, \mathbf{a}_j) T_j\right), \quad \mathbf{x} \in \Gamma_i,\ i = 1, \ldots, N_b, \end{aligned} \tag{8}$$

$$\int_{\Gamma_i} \boldsymbol{\eta} \, \mathrm{d}s = \mathbf{F}_i, \qquad i = 1, \ldots, N_b, \tag{9}$$

$$\int_{\Gamma_i} \boldsymbol{\eta} \cdot (\mathbf{x} - \mathbf{a}_i)^\perp \, \mathrm{d}s = T_i, \qquad i = 1, \ldots, N_b. \tag{10}$$

Energy Calculation via Singularity Subtraction

Suppose we split the solution to the screened Laplace boundary value problem (1) into smooth portion w_i and singular portion u_i. That is, $u = w_i + u_i$. Consider the case when $f(u) = u^2$ in (4), we can rewrite the free energy functional as

$$E[u(\mathbf{x})] = C\rho \sum_{i=1}^{N_b} \int_{\Gamma_i} u \frac{\partial u}{\partial \boldsymbol{\nu}} \, \mathrm{d}s = C\rho \sum_{i=1}^{N_b} \int_{\Gamma_i} g \left(\frac{\partial w_i}{\partial \boldsymbol{\nu}} + \frac{\partial u_i}{\partial \boldsymbol{\nu}} \right) \mathrm{d}s, \quad \mathbf{x} \in \Gamma_i. \tag{11}$$

Follow the divergence theorem on the last term in the equation above and denote $g_i(x)$ as the boundary data on Γ_i, we obtain

$$E[u(\mathbf{x})] = C\rho \sum_{i=1}^{N_b} \left(\int_{\Gamma_i} g \frac{\partial w_i}{\partial \boldsymbol{\nu}} \, \mathrm{d}s + \int_{U_i} \nabla g_i \nabla u_i + g_i (u_i + \frac{1}{2}\sigma) \, \mathrm{d}\mathbf{x} \right) \tag{12}$$

$$= C\rho \sum_{i=1}^{N_b} \left(\int_{\Gamma_i} g_i \frac{\partial w_i}{\partial \boldsymbol{\nu}} + u_i \frac{\partial g_i}{\partial \boldsymbol{\nu}} \, \mathrm{d}s - \int_{U_i} \Delta g_i u_i - g_i (u_i + \frac{1}{2}\sigma) \, \mathrm{d}\mathbf{x} \right) \tag{13}$$

$$= C\rho \sum_{i=1}^{N_b} \int_{\Gamma_i} g \frac{\partial w_i}{\partial \boldsymbol{\nu}} + (u_i + \frac{1}{2}\sigma) \frac{\partial g_i}{\partial \boldsymbol{\nu}} \, \mathrm{d}s, \quad \mathbf{x} \in \Gamma_i. \tag{14}$$

σ satisfies the second-kind integral equation

$$g(\mathbf{x}) = \frac{1}{2}\sigma(\mathbf{x}) + \frac{1}{2\pi} \int_{\partial\Omega} \left(\frac{\partial}{\partial \boldsymbol{\nu}_{\mathbf{y}}} K_0 \left(\frac{|\mathbf{x} - \mathbf{y}|}{\rho} \right) \right) \sigma(\mathbf{y}) \, \mathrm{d}s_{\mathbf{y}}, \quad \mathbf{x} \in \partial\Omega, \tag{15}$$

NUMERICAL RESULTS

Self-Assembled Janus Particle with Specific Boundary Conditions

Distinct morphologies can be obtained from the HAP model by shifting the boundary condition $g(\mathbf{x})$. Consider the linear case where $f(u) = u^2$. This choice makes (5) a boundary value problem for the screened-Laplace equation and the solutions have a boundary layer structure that decays to 0 in the bulk with the decay length ρ. We consider three kinds of boundary conditions on particle Γ_i:

(a)	(b)	(c)
$g(\mathbf{x}) = \dfrac{1 + \cos(\theta_i(\mathbf{x}))}{\sqrt{3\pi r}}$	$g(\mathbf{x}) = \dfrac{2 + \cos(\theta_i(\mathbf{x}))}{\sqrt{9\pi r}}$	$g(\mathbf{x}) = \dfrac{\cos(\theta_i(\mathbf{x}))}{\sqrt{\pi r}}$

(16)

The number $\theta_i(\mathbf{x})$ is the angle formed by the position $\mathbf{x}$, the particle center $\mathbf{a}_i$, and the particle director $\mathbf{d}_i$.The normalizations e.g., $(\pi r)^{-1/2}$, provide a uniform surface energy $\int_{\Gamma_i} g^2 \, ds = 1$ for circular particles of radius r. The cases (b) and (c) are obtained by applying a vertical shift and scaling to case (a), see Figure 1. Using this setup, we simulate the dynamics of 100 particles with random initial position and orientation.

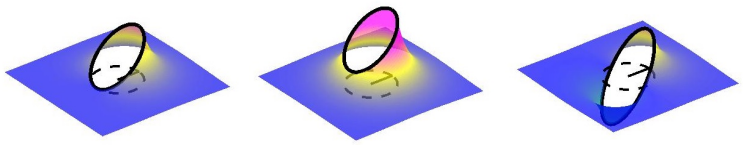

FIG. 1. Boundary conditions characterize the water structure at the particle interface: an amphiphilic particle (left), a hydrophobic particle with anisotropic intensity (middle), a water structure with positive/negative charge (right). The dashed curve is the boundary of the disk and the arrow is its director for each particle.

Case (a) models amphiphilic particles. Amphiphilic particles have a hydrophobic tail and a hydrophilic head and these are accounted for as follows. The hydrophilic side takes the value $u = 0$. This mimicks the apolar head of a lipid, for example, which does not alter the structure of adjacent waters. The hydrophobic side represents hydrocarbons and takes the value $u > 0$. The interaction between particles is attractive, and particles will collectively orient their tails toward one another.

Multilamelar bilayers arise when both sides of the particle are hydrophobic. The boundary condition (16)(b) gives a particle with a hydrophobic intensity that is greater on the $\theta_i = 0$ side than on the $\theta_i = \pi$ side. The initial self-assembly is similar to that in case (a). The difference arises in the long-time dynamics where the bilayers no longer remain well-separated. Rather, the bilayers form layers as a consequence of the interfacial tension of exposed particle heads.

Finally, boundary condition (16)(c) models a particle whose head surface repels the tail surface as proposed in [**?** **?**]. The particles initially form chains with their directors perpendicular to the length of the chain. The equilibrium structure resembles a checkerboard pattern where each particle coordinates its head with the head of three other particles and its tail with the tail of three other particles.

Collective Janus Particles Suspended in a Shear Flow

CONCLUSIONS

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