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Constraint Dissipative Hydrodynamics (HydroRattle) Algorithm for Aggregate Dynamics

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A constraint hydrodynamics algorithm for non-Brownian spherical particles in aqueous systems is developed by applying the RATTLE algorithm to Stokesian dynamics. Hydrodynamic interactions were calculated using far-field grand mobility tensors, and the holonomic translational forces were determined using the time-dependent Lagrange multiplier. The proposed constraint algorithm successfully describes the dynamic motion of a colloidal chain with an initial helical structure under the influences of unidirectional fluid flow and gravitational force.

In numerous applications of chemical, environmental, and biomedical engineering disciplines, dynamics of individual and aggregated particles are ubiquitous in nano- and mesoscale phenomena. An aggregate can be considered as a structural collection of individual particles with geometrical constraints, e.g., paired particles (dimers), setting flocs, and colloidal chains and rings. To simulate the true dynamic motion of the connected molecules/particles of various sizes, a constraint mechanism must be applied to molecular dynamics (MD) or Brownian dynamics (BD). The basic task in constraint dynamics is to dynamically determine constraint forces, to maintain the (center-to-center) distance invariant (i.e., holonomic constraints) between two stuck particles. As an alternative to a constraint mechanism, the Hookean potential can be applied between two paired particles, but this is computationally much more expensive because of the short time scale of intermolecular vibrations.

Constraint forces are calculated as negative derivatives of the constraint potential to maintain holonomic constraints using Lagrange's multipliers.[1,2] At each time step, the Lagrange multipliers are iteratively updated in a cyclic manner until all the holonomic (bond-length) constraints are satisfied. This numerical technique, called SHAKE algorithm,[2] is efficient when a large number of molecules are involved, and it can be easily combined into the Verlet algorithm for MD, for time evolution.[3–5] When the constraint forces are combined in the velocity Verlet algorithm,[6] it is termed RATTLE,[7] as analogous to SHAKE. These are two mainstream algorithms for constraint molecular dynamics (CMD) that provide simulation methods for conceptual generality and programming convenience. Further development of CMD includes methods using a penalty function,[8] damping correction,[9] noniterative algorithm,[10,11] and projection matrix.[12]

The above-mentioned algorithms are for translational constraints as applied to MD, which treats ions/particles as volumeless masses. These constraint algorithms may be easily applied to BD,[13–16] which originates from MD. For nanoparticles and colloidal particles, whose sizes are at least one or two orders of magnitude larger than those of molecules and ions, mesoscale hydrodynamic interactions play an important role in particle motion. Stokesian dynamics (SD) rigorously updates drag and stochastic forces exerted on the spherical particles. The SHAKE algorithm was applied to SD (and termed HydroSHAKE (HSHAKE)) to study the sedimentation of aggregates and nonspherical particles,[4,5] in which (net) torques were assumed to be zero.[17,18] SHAKE-based dynamics requires inverting a Jacobian matrix to iteratively update Lagrange's multipliers. Although the Jacobian is a universal approach, it is often reduced to a tri-diagonal (or sparsely banded) matrix for constraints of a colloidal chain(s) and ring(s). Each particle of a chain has at most two holonomic constraints in terms of distances to the associated neighbors. In this case, the combination of RATTLE with SD must be convenient and as accurate as HSHAKE. We develop a HydroRATTLE (HRATTLE) algorithm for the dynamics of a colloidal chain consisting of polydisperse rigid spheres in general.

A general law governing the motion of an N particle system is the least principle, $\delta S = \delta \int_{t_1}^{t_2} L(\mathbf{q}, \dot{\mathbf{q}}, t)\mathrm{d}t = 0$, where S is the *action* and $L = T - V$ is the Lagrangian, i.e., the difference between the kinetic energy (T) and the potential energy (V), as a function of the generalized coordinates $\boldsymbol{q}$ and velocities $\dot{\mathbf{q}} = \mathrm{d}\mathbf{q}/\mathrm{d}t$. Lagrange's equation results in $\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L(\mathbf{q},\dot{\mathbf{q}},t)}{\partial \dot{q}_i}\right) - \frac{\partial L(\mathbf{q},\dot{\mathbf{q}},t)}{\partial q_i} = \mathbf{Q}^{\mathrm{np}}$, where $\mathbf{Q}^{\mathrm{np}}$ are nonpotential forces such as dissipative drag or random fluctuation. L can include C holonomic constraints such as $L(\mathbf{q}, \dot{\mathbf{q}}, t) = T - V + \Psi^C$, and the constraint potential and force are defined as $\Psi^C = \frac{1}{2}\sum_{k=1}^{C} \lambda_k(t)\sigma_k(\mathbf{q}, t)$ and $\mathbf{F}_i^C = -\nabla_i \Psi^C$, where σ_k and λ_k are the k^{th} constraint equation and time-dependent Lagrange's multiplier, respectively. In Lagrange's equation, $\boldsymbol{\lambda}$ is included in the general coordinate ($\mathbf{q}$), but C constraints are satisfied at any time t so that the net degree of freedom is reduced to $6N - C$.

When a rigid chain consisting of N non-Brownian spherical particles is in a unidirectional fluid flow $\mathbf{V}_\infty$, the coupled N-body Langevin equation describes the three-dimensional motion of particle i of mass m_i and moment of inertia I_i undergoing external, constraint, and hydrodynamic forces/torques, i.e., $\mathbf{F}_i^{\mathrm{Ex}}/\mathbf{T}_i^{\mathrm{Ex}}$, $\mathbf{F}_i^{\mathrm{C}}/\mathbf{T}_i^{\mathrm{C}}$, and $\mathbf{F}_i^{\mathrm{H}}/\mathbf{T}_i^{\mathrm{H}}$, respectively:

$$\begin{bmatrix} m_i\mathbf{a}_i \\ I_i\boldsymbol{\alpha}_i \end{bmatrix} = \begin{bmatrix} \mathbf{F}_i^{\mathrm{Ex}} \\ \mathbf{T}_i^{\mathrm{Ex}} \end{bmatrix} + \begin{bmatrix} \mathbf{F}_i^{\mathrm{C}} \\ \mathbf{T}_i^{\mathrm{C}} \end{bmatrix} + \begin{bmatrix} \mathbf{F}_i^{\mathrm{H}} \\ \mathbf{T}_i^{\mathrm{H}} \end{bmatrix} \quad (1)$$

$$\begin{bmatrix} \mathbf{F}_i^{\mathrm{H}} \\ \mathbf{T}_i^{\mathrm{H}} \end{bmatrix} = -\begin{bmatrix} \mathbf{A}_{ij} & \tilde{\mathbf{B}}_{ij} \\ \mathbf{B}_{ij} & \mathbf{D}_{ij} \end{bmatrix} \begin{bmatrix} \Delta\mathbf{v}_j \\ \Delta\boldsymbol{\omega}_j \end{bmatrix} \quad (2)$$

where $\mathbf{a}_i/\alpha_i$ are the translational/angular accelerations, the matrix in eq 2 is the grand resistance, and $\Delta\mathbf{v}_j$ ($= \mathbf{v}_j - \mathbf{V}_\infty$) and $\Delta\omega_j$ ($= \omega_j - \boldsymbol{\Omega}_\infty$) are the translational and angular velocities of particle j with respect to the unidirectional flow $\mathbf{V}_\infty$ and ambient vortice $\boldsymbol{\Omega}_\infty$, respectively. The external forces and torques can be oriented by many physical, chemical, and biological sources. These include soft- and hard-sphere inter-

actions, van der Waals attraction and electrostatic repulsion (DLVO interactions), depletion forces, divalent ion binding between colloids, and polymer bridging. These conservative interactions can be readily included in $\mathbf{F}_i^{\mathrm{Ex}}/\mathbf{T}_i^{\mathrm{Ex}}$, and their quantitative evaluation is not computationally expensive or difficult. In this manuscript, the focus is the constraint hydrodynamics of chains consiting of unequal-sized spheres so that only the gravitational force is included, as an external force.

A chain consisting of N spheres has $N-1$ sequential pairs of contacts with fixed translational distances. This holonomic constraint function can be expressed as $\sigma_k(t) = [\mathbf{r}_k(t) - \mathbf{r}_{k+1}(t)]^2 - d_{k,k+1}^2 = 0$ for $1 \le k < N$, where $d_{ij} = a_i + a_j + h$ is the center-to-center distance between particle i and j, i.e., the sum of radius a_i and a_j and their surface-to-surface distance h. The constraint force exerted on particle i is calculated as $\mathbf{F}_i^{\mathrm{C}} = \lambda_{i-1}(\mathbf{r}_{i-1} - \mathbf{r}_i) - \lambda_i(\mathbf{r}_i - \mathbf{r}_{i+1})$, where $\lambda_0 = \lambda_N = 0$, because the first and last particles in the chain have only one constraint each.

With the known initial conditions of $\mathbf{r}_i(t)$ and $\mathbf{v}_i(t)$ at time t with $\sigma_k = 0$ for all k, the unconstrained position $\mathbf{r}_i^*(t')$ at the next time step $t' = t + \delta t$ is calculated as $\mathbf{r}_i^*(t') = \mathbf{r}_i(t) + \mathbf{v}_i(t)\delta t + \frac{1}{2}\mathbf{a}_i^{\dagger}(t)\delta t^2$, where $\mathbf{a}_i^{\dagger}$ is the unconstrained acceleration due to external and hydrodynamic forces/torques. Note that the grand resistance matrix consists of functions depending on the relative position of particles i to j: $\mathbf{r}_i - \mathbf{r}_j$. After the unconstrained evolution under external/hydrodynamic influences, the holonomic constraints are instantaneously broken so that constraint forces/torques must react to external forces/torques. The constrained evolution is $\mathbf{r}_i(t') = \mathbf{r}_i^*(t') + \frac{1}{2}\mathbf{a}_i^{\mathrm{C}}(t)\delta t^2$, where $\mathbf{a}_i^{\mathrm{C}} = m_i^{-1}\mathbf{F}_i^{\mathrm{C}}$. We assume that in a quiescent flow, the particle rotation does not provide any significant impact.

The relative displacement of particles i to $i+1$ should satisfy the same holonomic constraint at time t as well as t', $d_{i,i+1}^2 = |\mathbf{r}_i(t) - \mathbf{r}_{i+1}(t)|^2 = |\mathbf{r}_i(t') - \mathbf{r}_{i+1}(t')|^2$, which provides an approximate representation of

$$\lambda_i \delta t^2 = -\frac{d_{i,i+1}^2 - [\Delta \mathbf{r}_{i,i+1}^*(t')]^2}{2m_{i,i+1}^{-1}\Delta \mathbf{r}_{i,i+1}^*(t') \cdot \Delta \mathbf{r}_{i,i+1}(t)} \tag{3}$$

where $m_{i,i+1} = 1/(m_i^{-1} + m_{i+1}^{-1})$ is one-half of the harmonic mean of the masses of particles i and j, and the displacement changes are $\Delta \mathbf{r}_{i,i+1}^*(t') = \mathbf{r}_i^*(t') - \mathbf{r}_{i+1}^*(t')$ and $\Delta \mathbf{r}_{i,i+1}(t) = \mathbf{r}_i(t) - \mathbf{r}_{i+1}(t)$.

Because d_{ij} is time-invariant, its time derivative vanishes: $\frac{\mathrm{d}}{\mathrm{d}t} d_{ij}^2 = 0$, which gives an orthogonal relationship $[\mathbf{r}_i(t') - \mathbf{r}_{i+1}(t')] \cdot [\mathbf{v}_i(t') - \mathbf{v}_{i+1}(t')] = 0$. We represent the translational velocity of particle i at time $t + \delta t$ as $\mathbf{v}_i(t') = \mathbf{v}_i^*(t) + \frac{1}{2}\mathbf{a}_i^{\mathrm{C}}(t')\delta t$, where $\mathbf{v}_i^*(t') = \mathbf{v}_i(t) + \mathbf{a}_i^{\dagger}(t)\delta t + \frac{1}{2}\mathbf{a}_i^{\mathrm{C}}(t)\delta t^2$ is the semi-constraint evolution influenced by unconstrained and half-weighted constrained forces at time t.[7] Note that $\mathbf{a}_i^{\mathrm{C}}(t) = m_i^{-1}\mathbf{F}_i^{\mathrm{C}}$ is already known to satisfy $\boldsymbol{\sigma}(t) = 0$. The constraint acceleration at time t' is $\mathbf{a}_i^{\mathrm{C}}(t') = m_i^{-1}\kappa_{i-1}\mathbf{r}_{i-1,i}(t') - m_i^{-1}\kappa_i \mathbf{r}_{i,i+1}(t')$, where κ_i is a new Lagrange's multiplier to satisfy the velocity-position orthogonality. Now, one calculates

$$\kappa_i \delta t = \frac{[\mathbf{r}_i(t') - \mathbf{r}_{i+1}(t')] \cdot [\mathbf{v}_i^*(t') - \mathbf{v}_{i+1}^*(t')]}{m_{i,i+1}^{-1} d_{i,i+1}^2} \tag{4}$$

which is sequentially updated for i from 1 to $N-1$. This iterative procedure continues until all the particles satisfy the orthogonal relationships within an acceptable tolerance error.

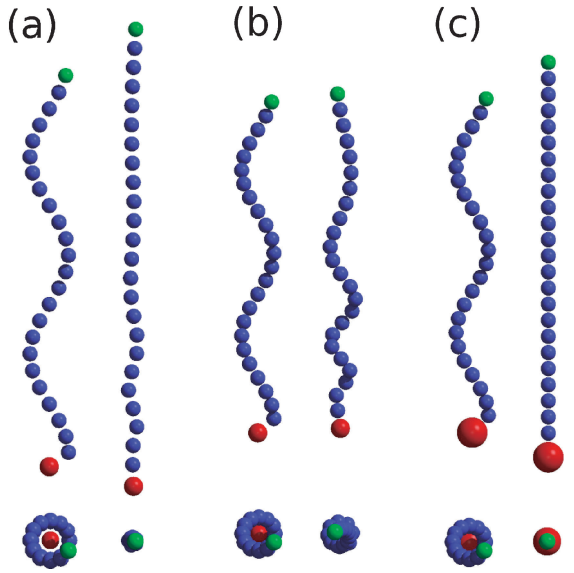

Figure 1. Dynamic configurations of helical colloidal chain (upper row: side view of initial (left) and later (right) states, and lower row: top view of initial (left) and later (right) states): (a) long ($\hat{D} = 1.50$) and (b) short ($\hat{D} = 1.05$) chains with normal head ($\hat{a} = \sqrt[3]{2}$) and (c) short chain with a big head ($\hat{a} = 2$). Red, blue, and green colors indicate head, tail, and the last tail particles.

We selected a colloidal chain consisting of one head and 24 (smaller) tail particles with equal densities and set the initial helix configuration as shown in Figure 1a (left). The initial helix was chosen because it is geometrically elegant and mathematically complex enough to test our constraint algorithm. The dimensionless interparticle distance, $\hat{D} \equiv d_{i,i+1}/(a_i + a_{i+1})$, was chosen as 1.50 and 1.05 for long and short chains, respectively. The head-to-tail size ratio ($\hat{a} = a_{\mathrm{head}}/a_{\mathrm{tail}}$) was chosen as $\sqrt[3]{2}$ and 2 for normal and big heads, respectively. Therefore, the normal head has twice the tail volume, and the big head has twice the tail diameter (i.e., eight times the volume).

Figure 1 shows the effects of chain length and head size on the dynamic settling behavior of the colloidal chain with the initial helical structure. In the three subfigures (a), (b), and (c), the left-hand columns indicate the initial configurations based on preset bond lengths and head particle sizes. The bottom row shows the locations of head particles surrounded by projected rings consisting of 24 tails.

Figure 1a shows the time evolution of a long chain under the gravitational force. Initially, the long chain has a helical structure, and the head is circularly surrounded by tails from the top view. During the settling process, hydrodynamic drag forces are applied to each tail particle without generating strong inter-relevant particle motion. In other words, the long chain underwent reptile-like group-angular motion and eventually stretched like a chopstick in the vertical direction. This stretching was dominant when interdistances were long so that the fluid flow could penetrate the local spaces between adjacent particles.

In Figure 1b, we reduced the intertail distance $\hat{D}$ from 1.50 to 1.05, keeping the head size invariant. In this case, the initial dynamics of the short colloidal chain was similar to that of case (a), but in the later state, everlasting twisting was observed

instead of linear stretching. This continuous twisting is caused by the complex tensorwise hydrodynamic forces as responses to the downward gravitational force. Because of the short interparticle distance, particles of the short chain cannot immediately find energetically nested locations; therefore, twisting must be a better way to minimize action S (instead of stretching).

To investigate the effects of head size on the twisting phenomena, we increased the head-to-tail size ratio $\hat{a}$ from $\sqrt[3]{2}$ to 2 so that the head is 8 times bigger and heavier, as shown in Figure 1c. Although the chain length is identical to that in case (b), the big head leads to much faster settling motion in comparison to that in case (a) and (b). Tail particles are strongly forced down to follow the big head so that the twisting motion (dominant in case (b)) was observed for a short period in the initial stage of case (c), and later, the chain primarily underwent full stretching. Tail particles near the big head lost the initial twisting motion first, and this local stretching propagated from the head to the end of the chain (marked in green). At the end, a small degree of lateral motion of a few tail particles near the chain-end followed the full stretching of the entire chain.

In this study, we found that the final chain configuration in the quasi-steady state significantly depends on the intertail distance and the size and mass ratio between heads and tails. In summary, the constraint force influences the hydrodynamic reactions to minimize the action S, resulting in stretching or twisting phenomena depending on the geometrical conditions of the chain: size, mass, and interdistance ratios.

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References

1 J.-P. Ryckaert, A. Bellemans, *Chem. Phys. Lett.* **1975**, *30*, 123.
2 J.-P. Ryckaert, G. Ciccotti, H. J. C. Berendsen, *J. Comput. Phys.* **1977**, *23*, 327.
3 L. Verlet, *Phys. Rev.* **1967**, *159*, 98.
4 J. P. Ryckaert, *Mol. Phys.* **1985**, *55*, 549.
5 G. Ciccotti, J. P. Ryckaert, *Comput. Phys. Rep.* **1986**, *4*, 346.
6 W. C. Swope, H. C. Andersen, P. H. Berens, K. R. Wilson, *J. Chem. Phys.* **1982**, *76*, 637.
7 H. C. Andersen, *J. Comput. Phys.* **1983**, *52*, 24.
8 R. Edberg, D. J. Evans, G. P. Morriss, *J. Chem. Phys.* **1986**, *84*, 6933.
9 A. Baranyai, D. J. Evans, *Mol. Phys.* **1990**, *70*, 53.
10 M. Yoneya, H. J. C. Berendsen, K. Hirasawa, *Mol. Simul.* **1994**, *13*, 395.
11 J. T. Slusher, P. T. Cummings, *Mol. Simul.* **1996**, *18*, 213.
12 B. Hess, H. Bekker, H. J. C. Berendsen, J. G. E. M. Fraaije, *J. Comput. Chem.* **1997**, *18*, 1463.
13 M. Fixman, *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 3050.
14 M. Fixman, *J. Chem. Phys.* **1978**, *69*, 1527.
15 E. J. Hinch, *J. Fluid Mech.* **1994**, *271*, 219.
16 P. Grassia, E. J. Hinch, *J. Fluid Mech.* **1996**, *308*, 255.
17 R. Kutteh, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.* **2004**, *69*, 011406.
18 R. Kutteh, *J. Chem. Phys.* **2010**, *132*, 174107.

