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Flocculation Efficiencies Under Shear

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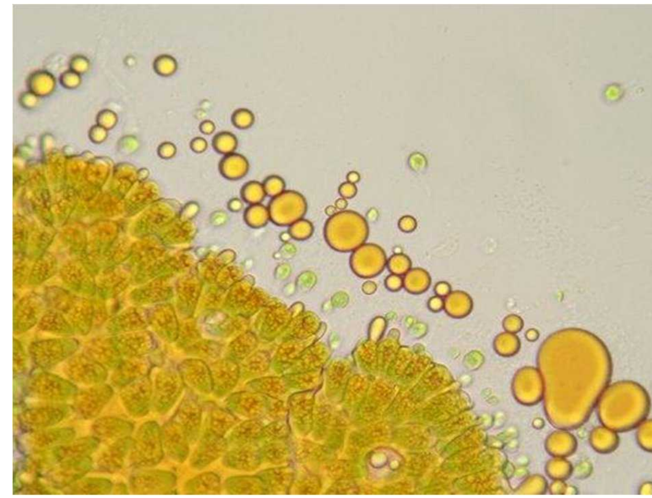
Outline

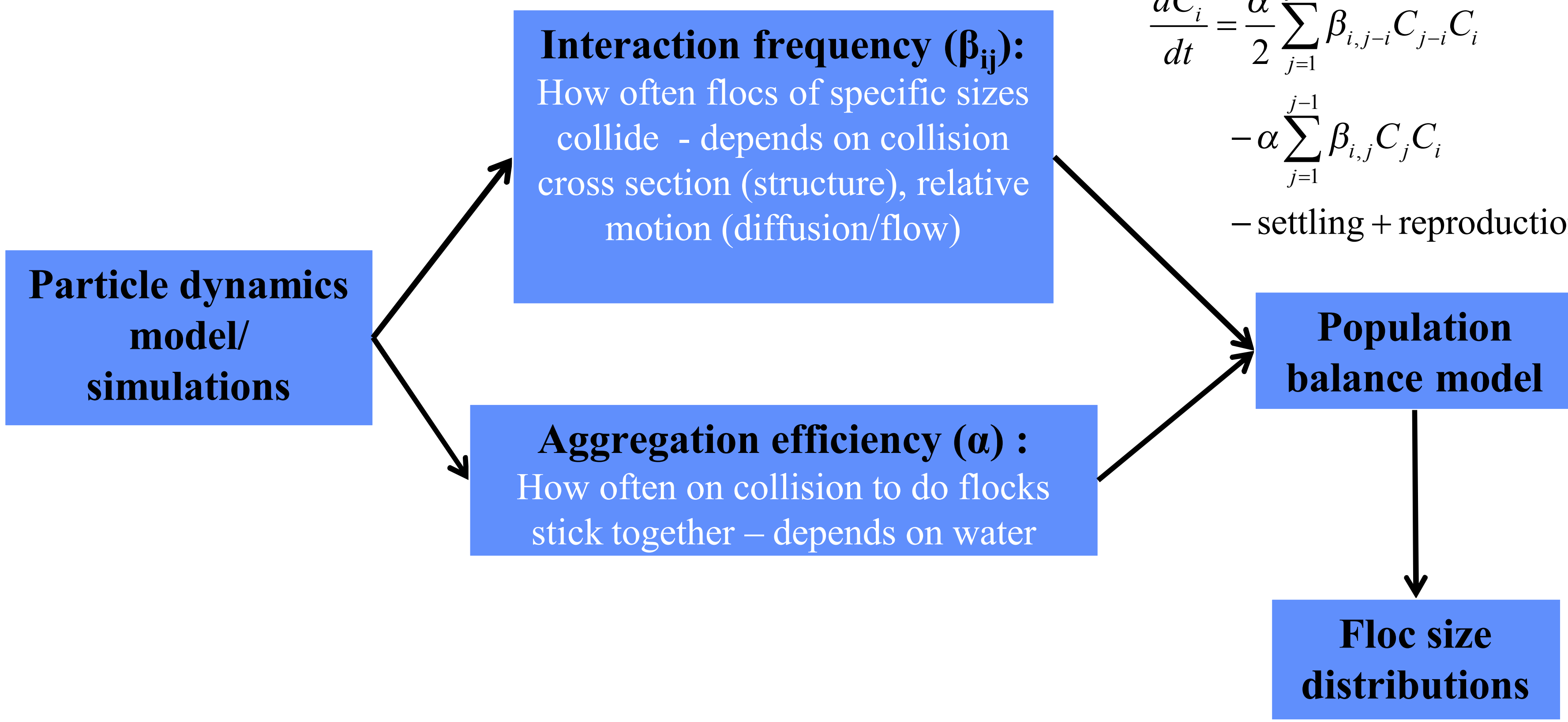
- Motivation
- System and Simulation Details
- Results and Analysis
- Important Considerations
- Goals
- Current and Future Developments
- Acknowledgements

Motivation

- Algae produce lipids in sufficient quantities to be a viable source of ***biofuels***
- Physical separation techniques like microbubble flotation, forced-flow filtration, centrifugation or high temp/pressure processing are inherently ***cost prohibitive***, requiring large energy inputs for separation of biological materials
- Algae are known to form ***flocs*** under various environmental conditions
- Flocculation is a possibly ***efficient route to concentrate*** algae for lipid extraction



Research Components



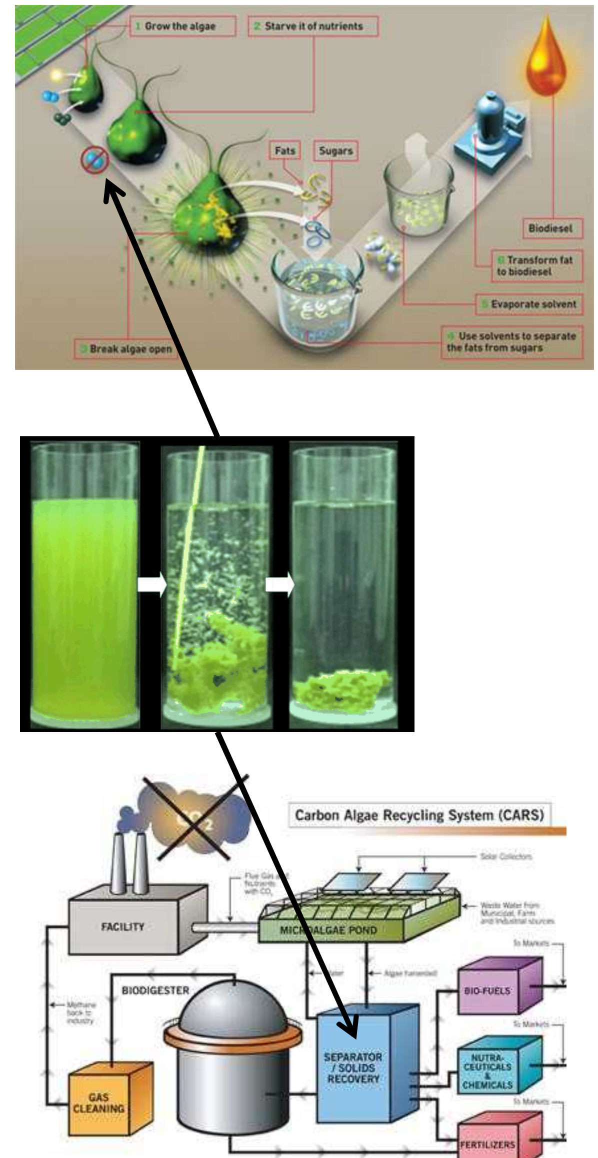
$$\frac{dC_i}{dt} = \frac{\alpha}{2}\sum_{j=1}^{j-1}\beta_{i,j-i}C_{j-i}C_i - \alpha\sum_{j=1}^{j-1}\beta_{i,j}C_jC_i - \text{settling} + \text{reproduction}$$

- Results of particle level simulations including floc structure and dynamics are fed into larger Population Balance Models to determine Floc Size Distributions as a function of shear rate, oscillatory frequency, and total time sheared

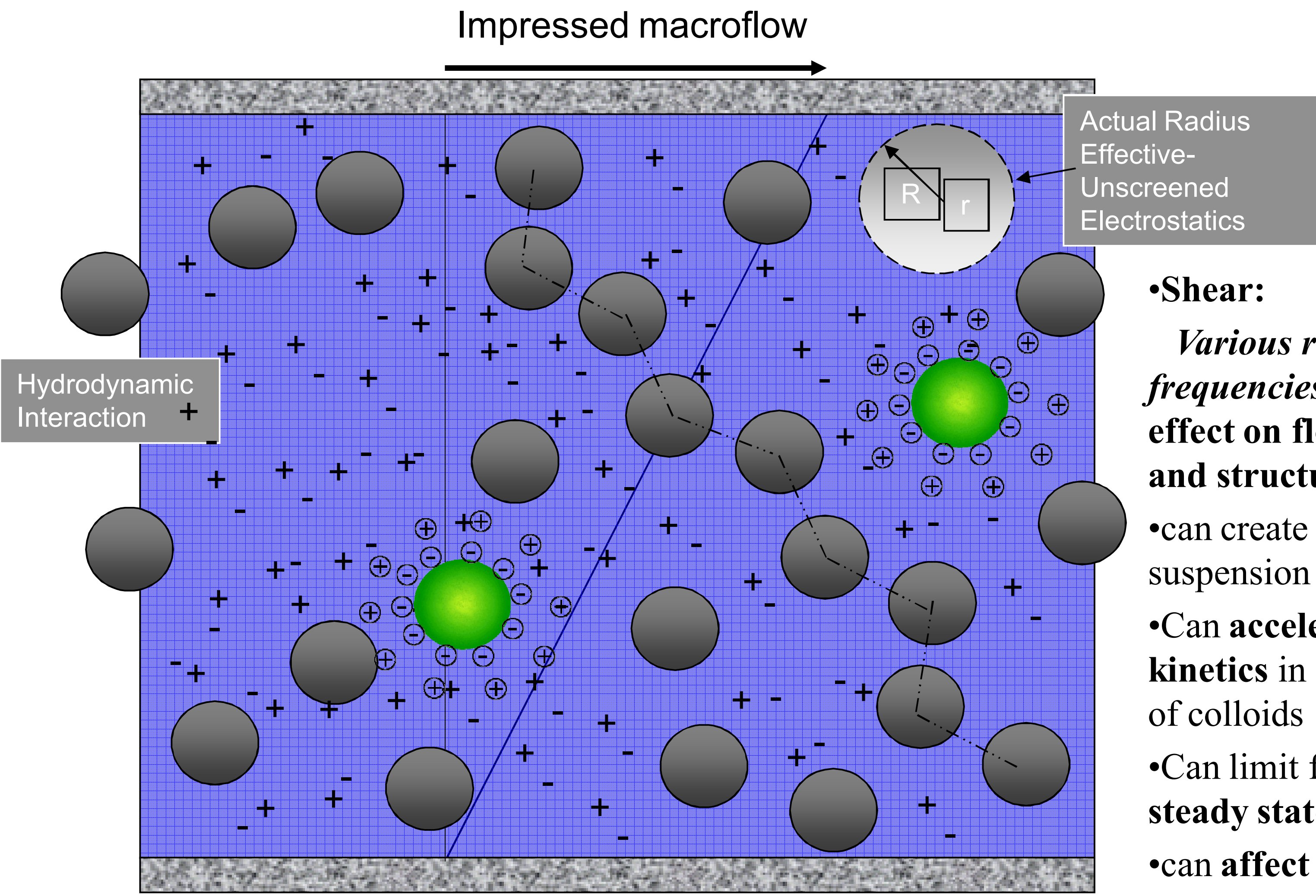
Simulation Method

- **Molecular dynamics simulations** are used to study the flocculation of model algae particles under **steady and oscillatory shear.**

- **Experimentally determined** parameters characterizing the chemical environment of the medium and algae surface properties are incorporated into the models.
  - Optical trap measurements of algae interaction and pull-off force
  - Steady state size distribution of algae flocs under shear
- Determine evolving **aggregation/ fragmentation kernels** as well as the steady-state behavior as a function of **shear rates, total shear** and **algae interaction parameters**.

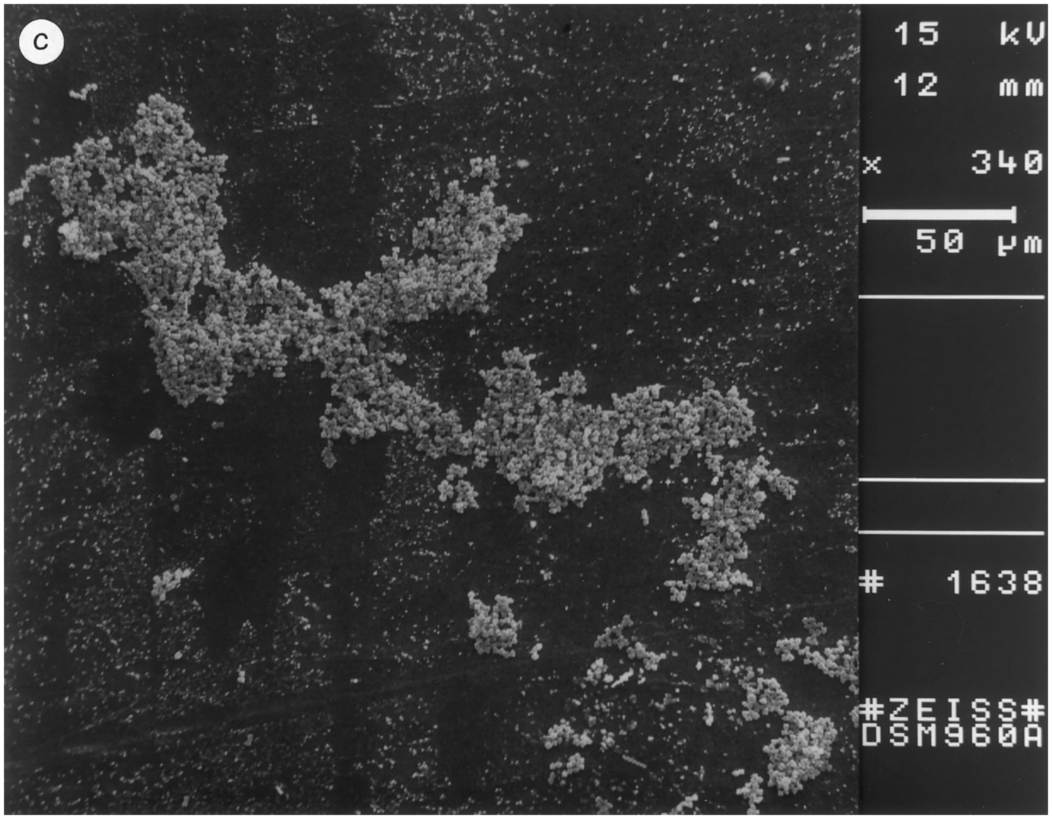


Simulation Details (cont.)

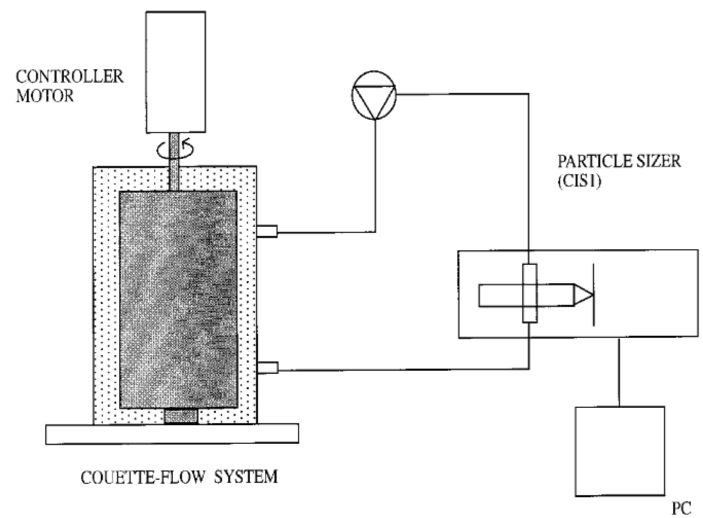


- **Shear:**
  ***Various rates (and oscillatory frequencies)* to determine effect on flocculation kinetics and structure**
- can create **ordering** in colloidal suspension
- Can **accelerate aggregation kinetics** in aggregating systems of colloids
- Can limit flocs to specific **steady state size**
- can **affect microstructure**

Current Validation



- Aggregation of PS Spheres in Couette Cell as model system to test simulation methodology on aggregating systems



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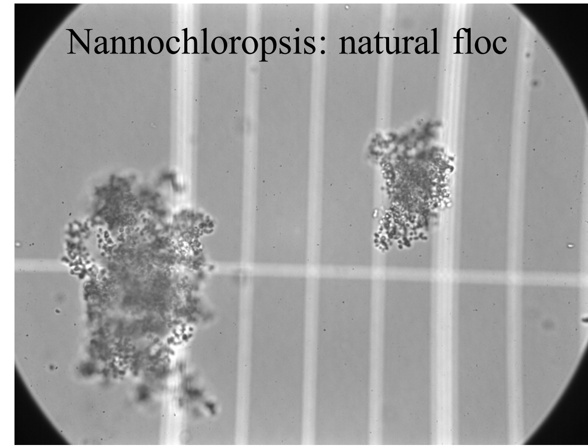
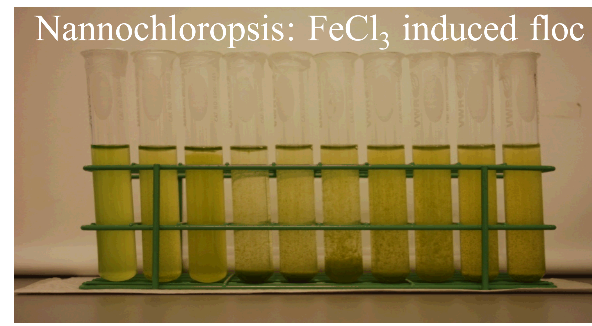
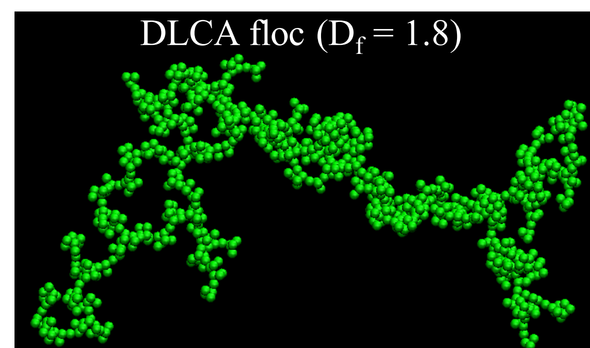
Considerations – Verification

- Algae, like other μm colloidal particles tend to form ***fractal flocs*** via aggregation on contact between cells.
- Diffusion limited aggregates (DLCA) have ***fractal dimensions*** (D_f) in the range 1.8-1.9, where the mass scales with the size as D_f :

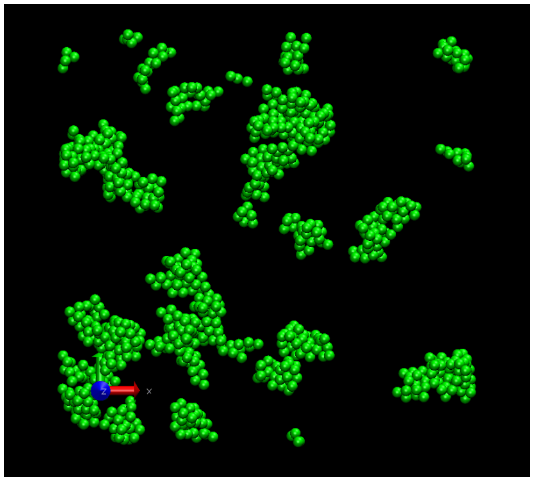
  $M \sim R^{Df}$
- Particle pair ***central-force potentials*** like DLVO are ***unable to produce persistent fractal structure***. Surface diffusion of particles inevitably leads to collapse and formation of close-packed flocs with sufficient time.
- A more sophisticated model should include hindrances to ***normal, twisting, rolling, and shearing modes*** at contact between cells. This is consistent with other particulate systems like soot aggregates.



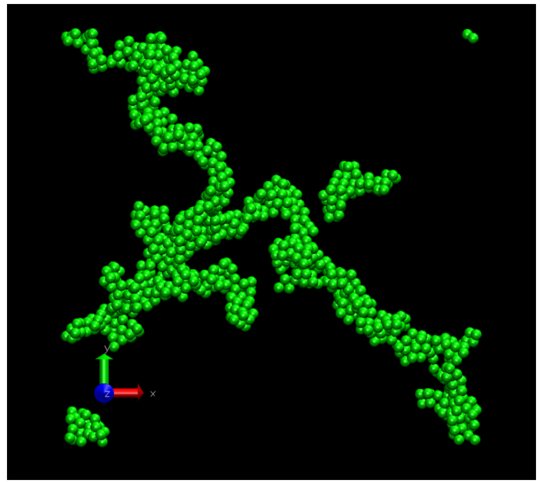




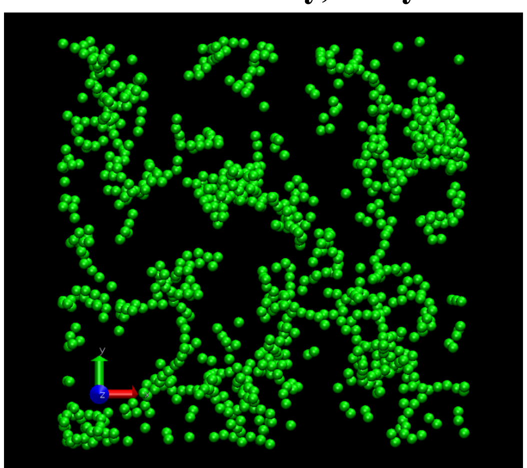
Flocculation with Adhesion



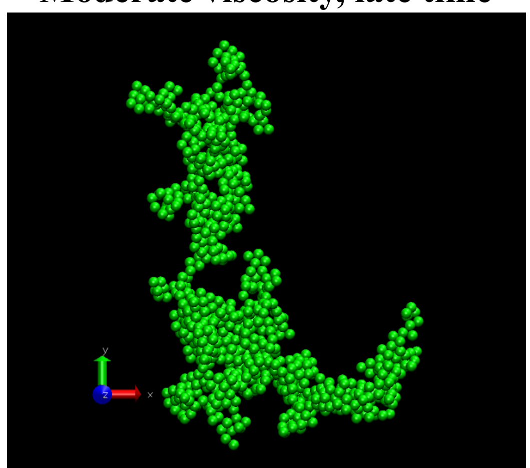
•Moderate viscosity, early time



•Moderate viscosity, late time



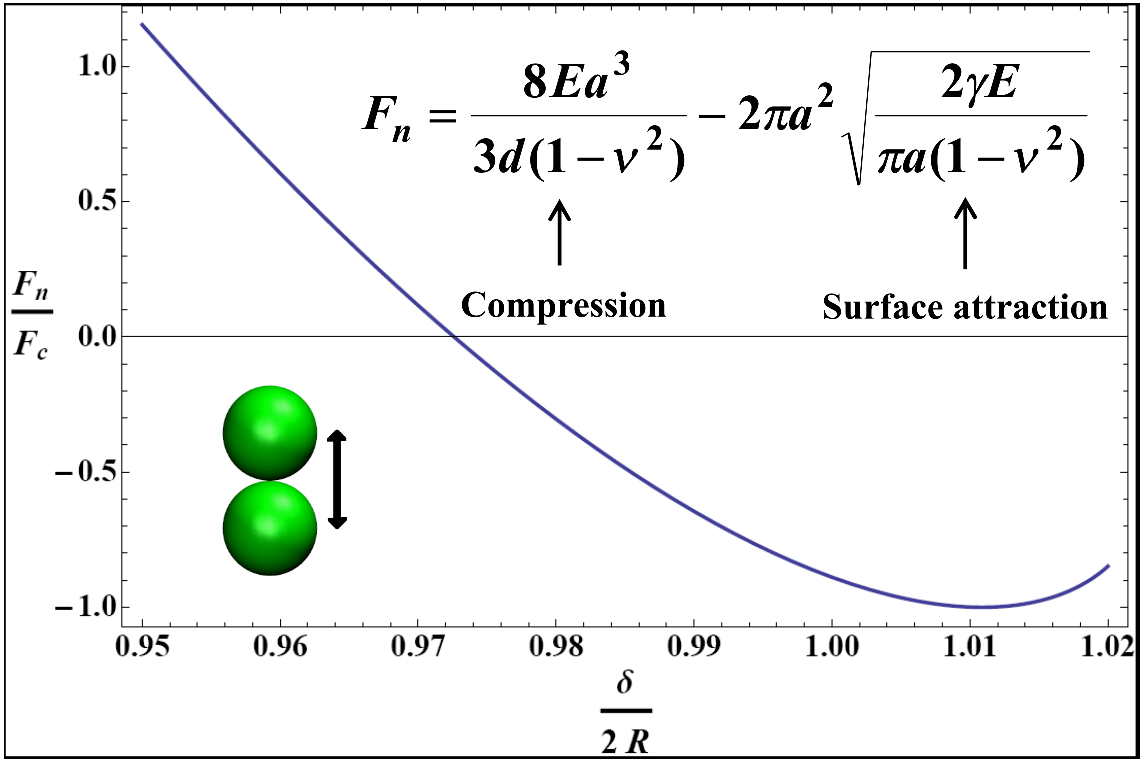
•Low viscosity, early time



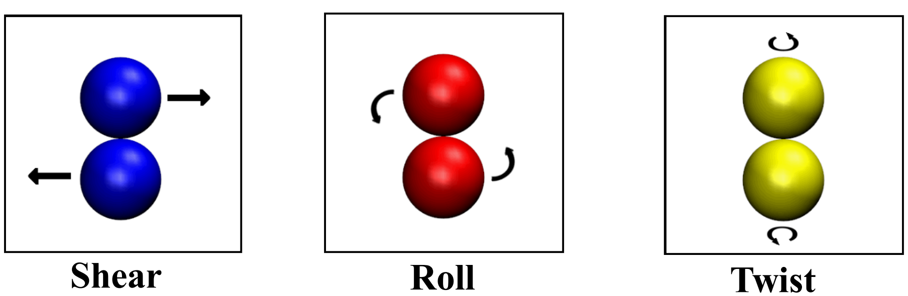
•Low viscosity, late time

- Inclusion of normal, shear, roll, twist modes/ constraints → extended, fractal flocs
- Structure depends on system parameters: temperature, solvent viscosity, binding energy at cell contact, surface potentials, shear rate, etc.
- JKR granular model circumvents problem of unrealistic collapse/ restructuring

Toward a Realistic Flocculation Model



Normal component



- We have developed a sophisticated general purpose granular model (akin to JKR) that incorporates normal, twisting, rolling, and shearing modes (reference Marshall) with associated hindrances and frictional terms.
- Model can incorporate experimentally determined surface energies of aggregated cells in addition to details of previous model

Simulation Details

- All system parameters are in idealized units for easier investigation of parameter space
- System Size: 10^3-10^5 particles
- Surface Energies: $\gamma = 1$
- Temperature: $kT = 10^{-3}$
- Thermal Adhesive Number (Adhesive/thermal):
  - $A_{therm} = \pi d^2\gamma/kT = 3140$
- Elastic modulus: $E = 100$
- Viscosity: $\eta = 5.6\times10^{-3}$
- Volume fraction: $\Phi=10^{-3}$
- Shear: $Pe = \tau_D \cdot \gamma' = 3\pi\eta d^3/kT \cdot \gamma' = 0, 10^{-3}, 10^{-2}, 10^{-1}, 1$
- Shear Adhesive Number (Shear/adhesive):
  - $A_{shear} = Pe/A_{therm}$
- Can include hydrodynamic solver for inclusion of short range lubrication forces and effect of particle concentration on isotropic drag (work proceeding to be able to resolve this in aggregating systems)

Aggregation Metrics

- **Kinetics:** how fast do the flocs grow with time
- **Floc Structure:**

  What fractal dimension characterizes the flocs?

  Do the flocs fragment or restructure due to shear?

  How does the coordination number evolve with time?
- **Cluster Size Distributions**:

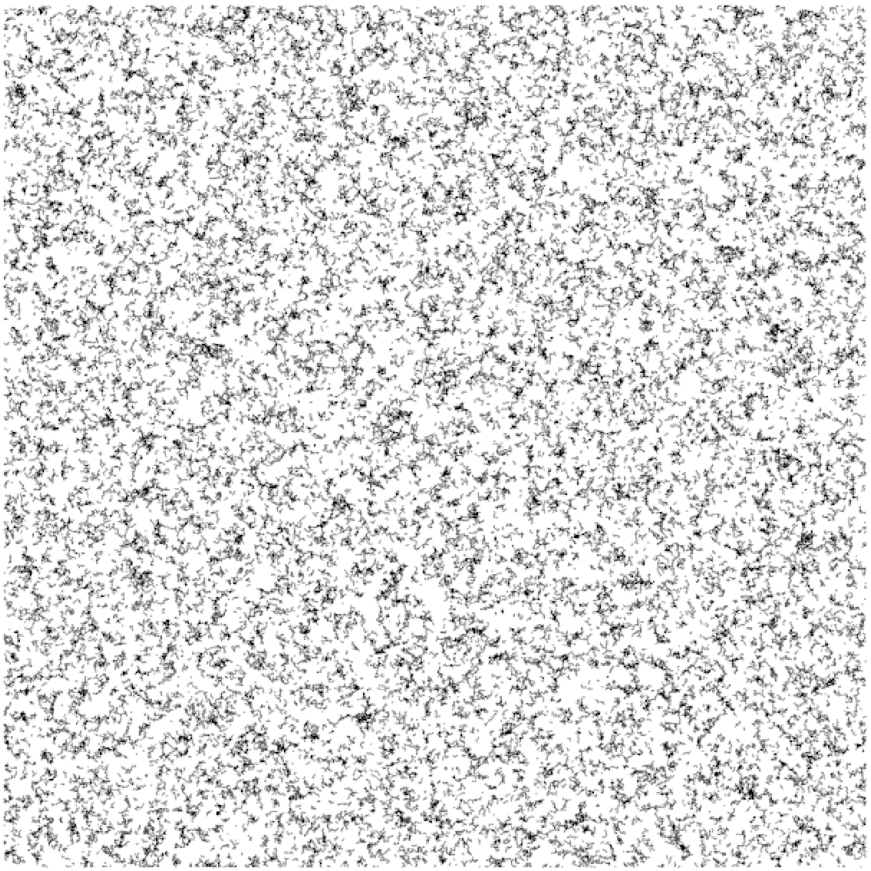
  How is the total mass distributed among clusters of various size?

  Is system more monodisperse or polydisperse – can affect harvesting efficiencies?
- **Other considerations:**

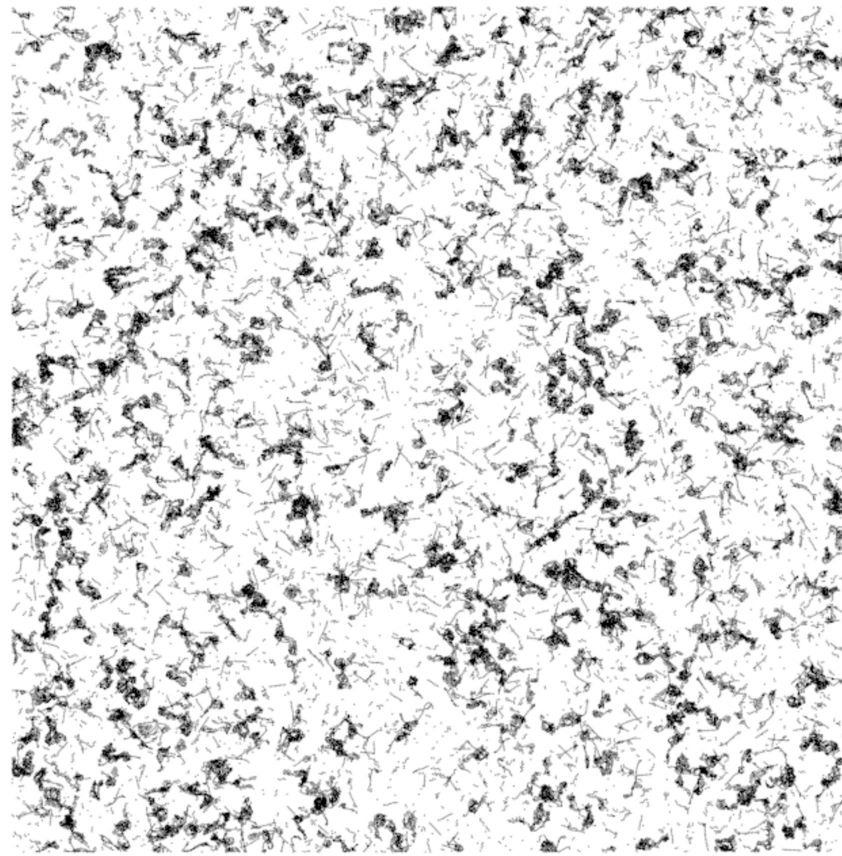
  Time dependent response of floc structure to stress imposed by shear

  Alignment of flocs into shear planes

Flocculated Systems

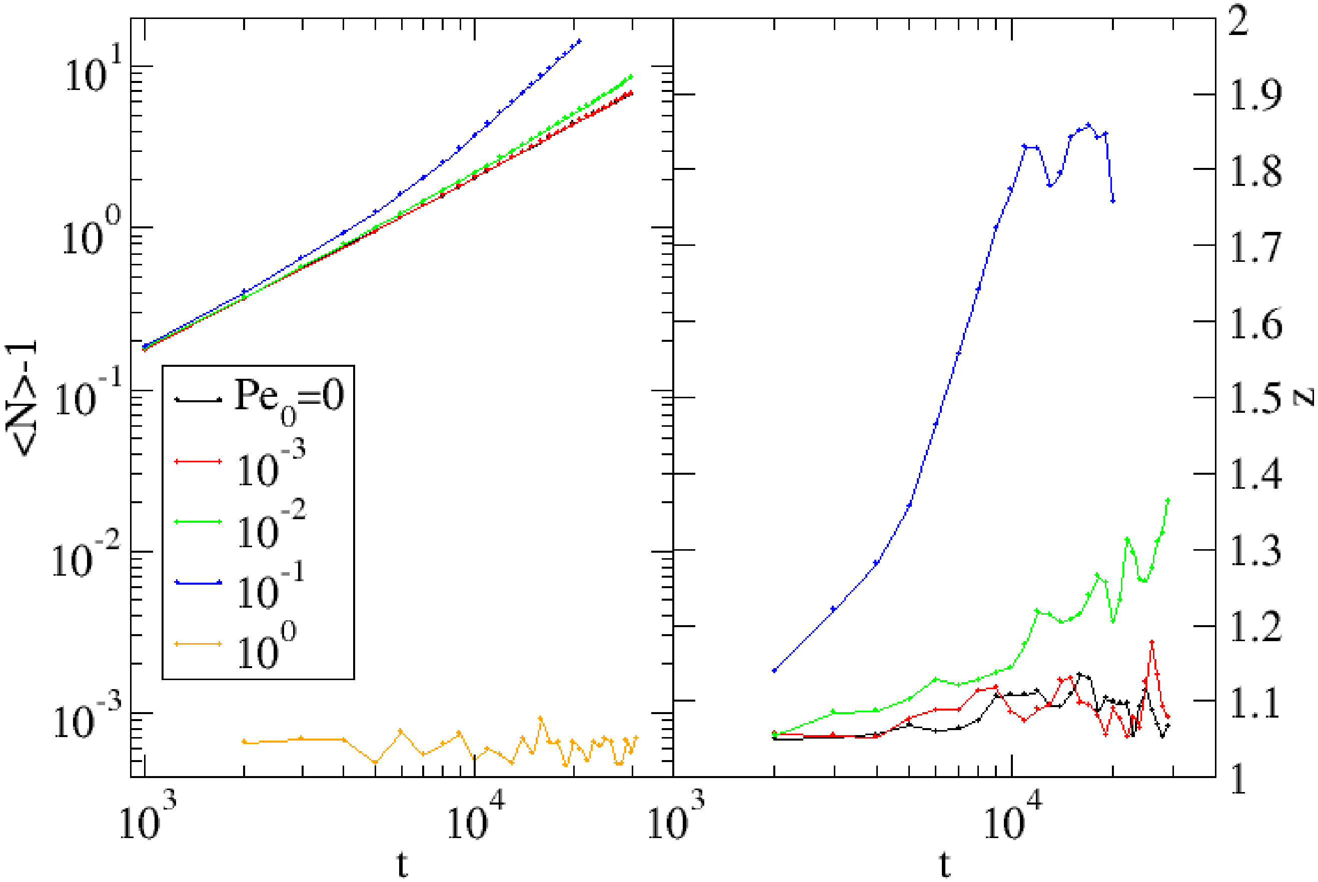


- Diffusive



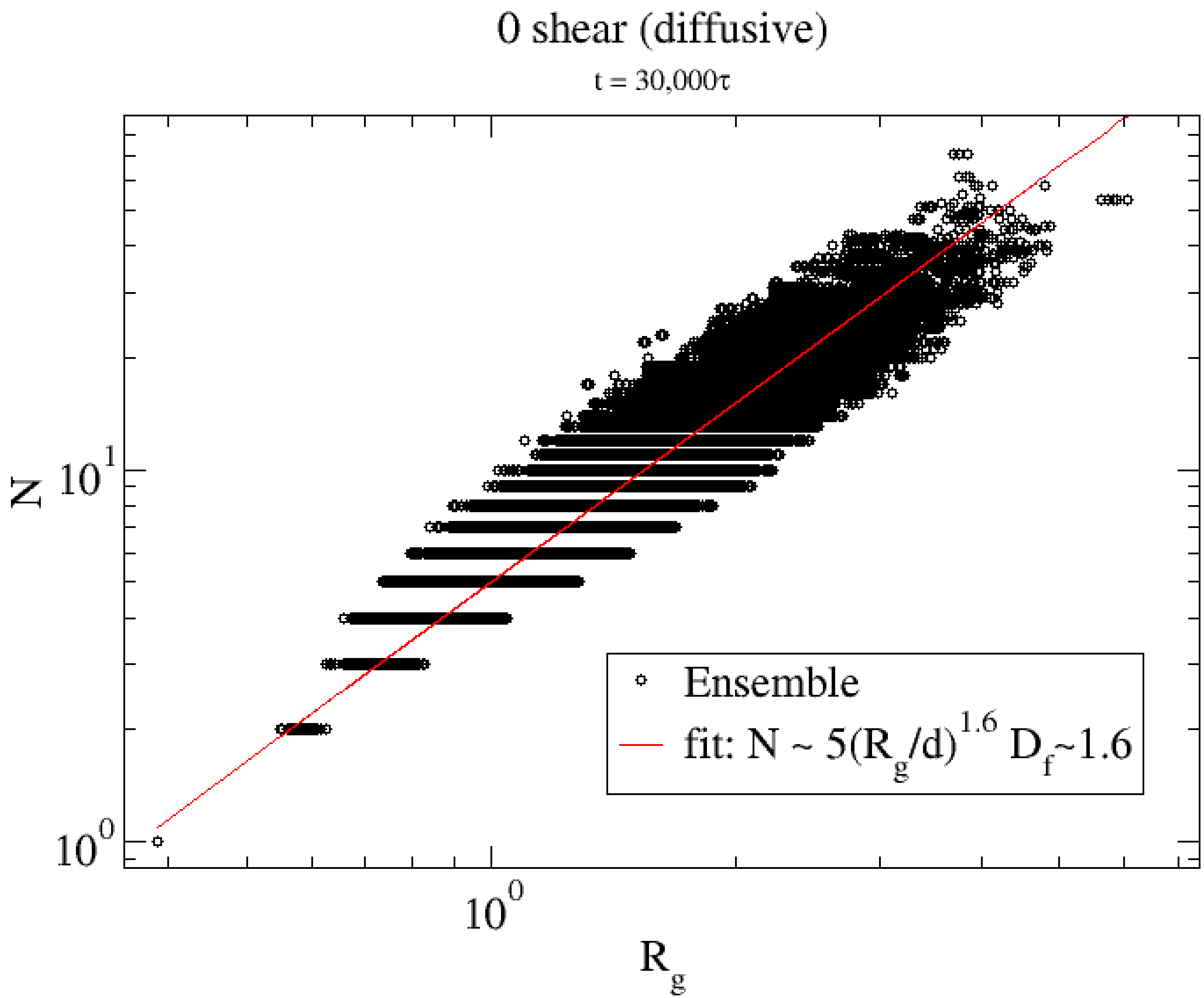
- Sheared

Kinetics



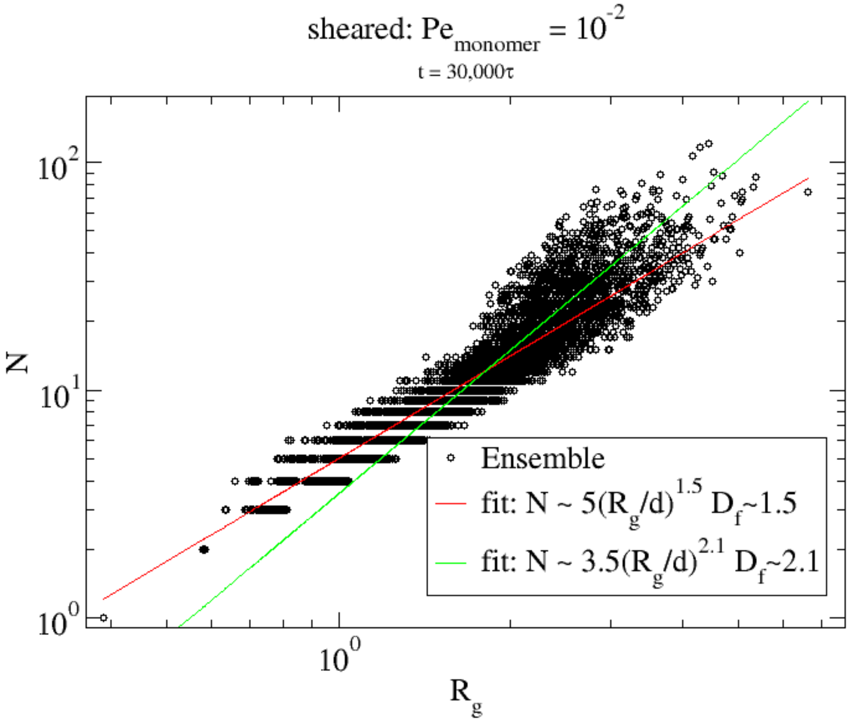
- Kinetic exponent z characterizes growth: $\langle N \rangle \sim t^z$
- low shear rates: linear growth with time ($z \approx 1$) - DLCA
- higher shear rates: z increases from 1 at early times to near 2 (quadratic growth) at late times
- Highest shear rates: clusters torn apart completely
- NO exponential growth – predicted for monodisperse growth of coalescing drops under steady shear

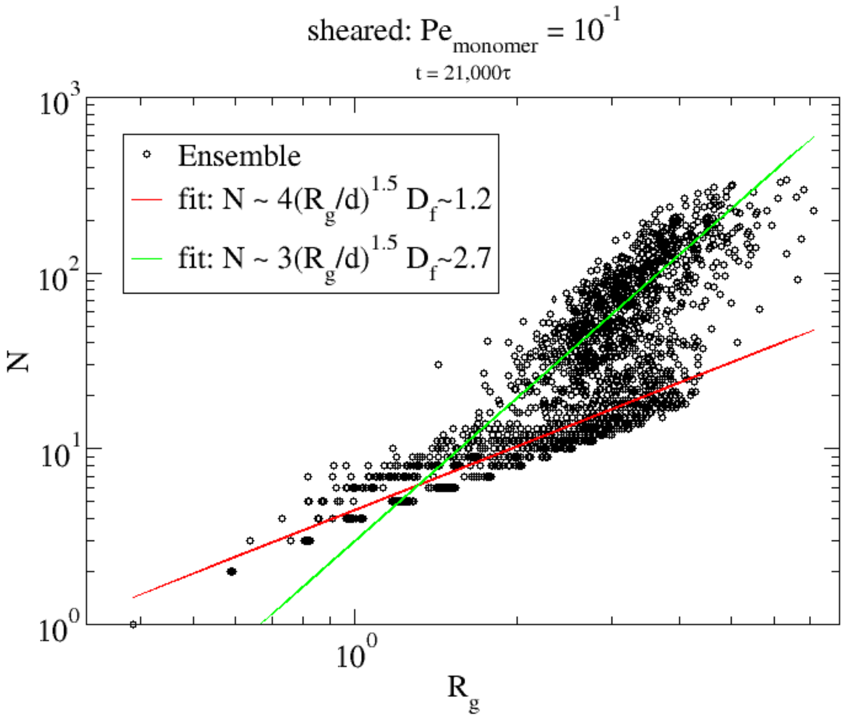
Floc Structure: Diffusive



- For no shear (diffusive aggregation – DLCA), floc structure is characterized by a fractal dimension of D_f = 1.6, somewhat lower than the value of 1.8 expected from previous Monte Carlo simulations of DLCA

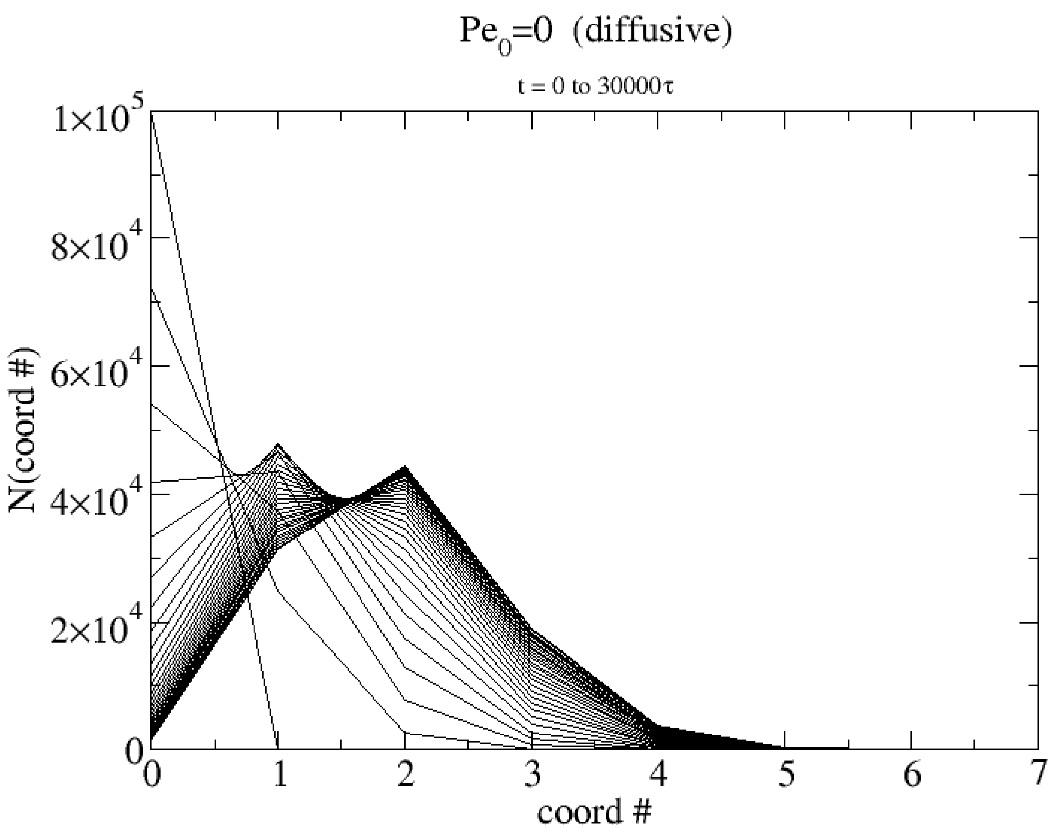
Floc structure: Higher Shear





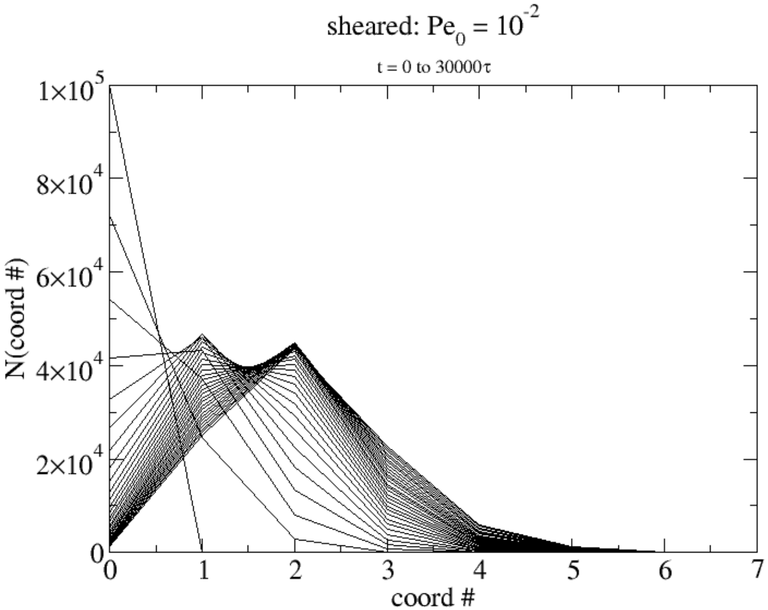
- For increased shear rates, fractal dimension at small length scales is decreased due to Jeffrey's orbits (shear plane alignment) and fast rotation in shear planes, while D_f at large length scales increases as long clusters collapse under shear stresses – both effects increases with shear rate
- At the highest shear rates, a bifurcation in the fractal dimension is observed due to restructuring and collisional timescales approaching the same order - two clusters can collide at various stages of restructuring

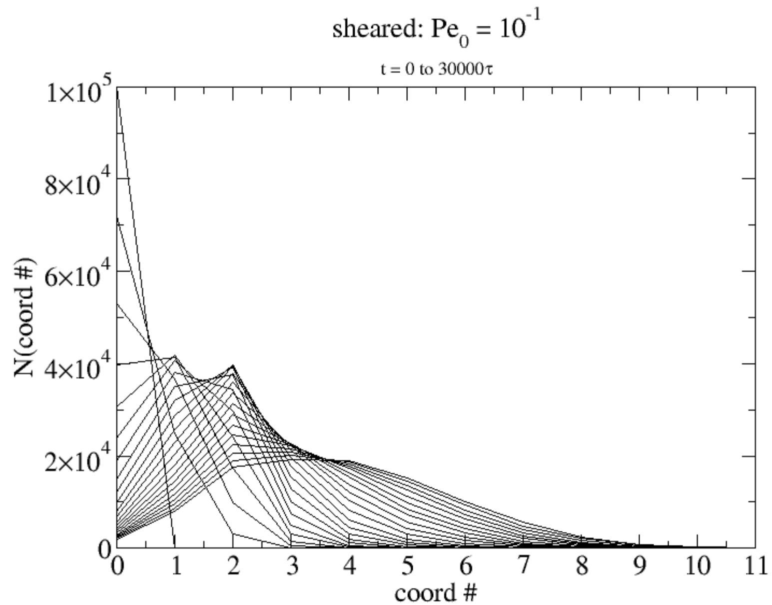
Coordination Numbers



- Floc structure evolution can also be observed through the time evolution of the distribution of coordination numbers (average number of particle-particle contacts)
- For diffusive simulations, the average coordination number grows from 0 (monomers) to 1 (dimers) to 2 (larger flocs) and stays peaked a 2
- flocs grow as open extended structures and are not collapsing or significantly restructuring

Coordination Numbers (Cont.)





- At higher shear rates, the number of particles with coordination number >2 is increasing significantly with time
- At very high shear rates, the average coordination number begins evolving away from 2 to higher and higher values due to significant restructuring

Cluster Size Distributions (Diffusive)

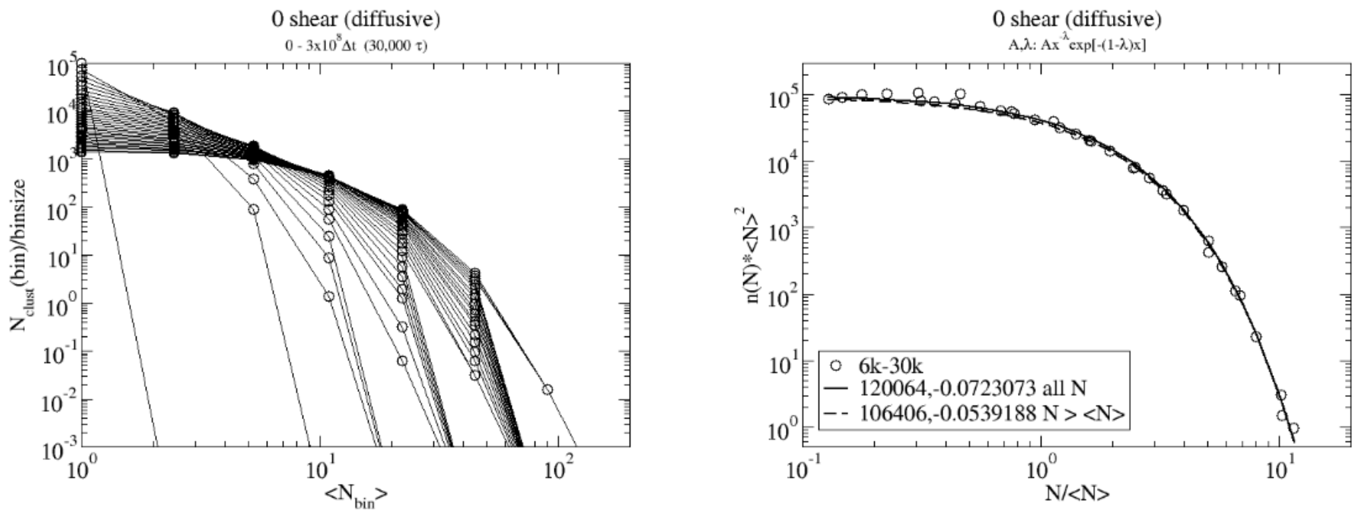
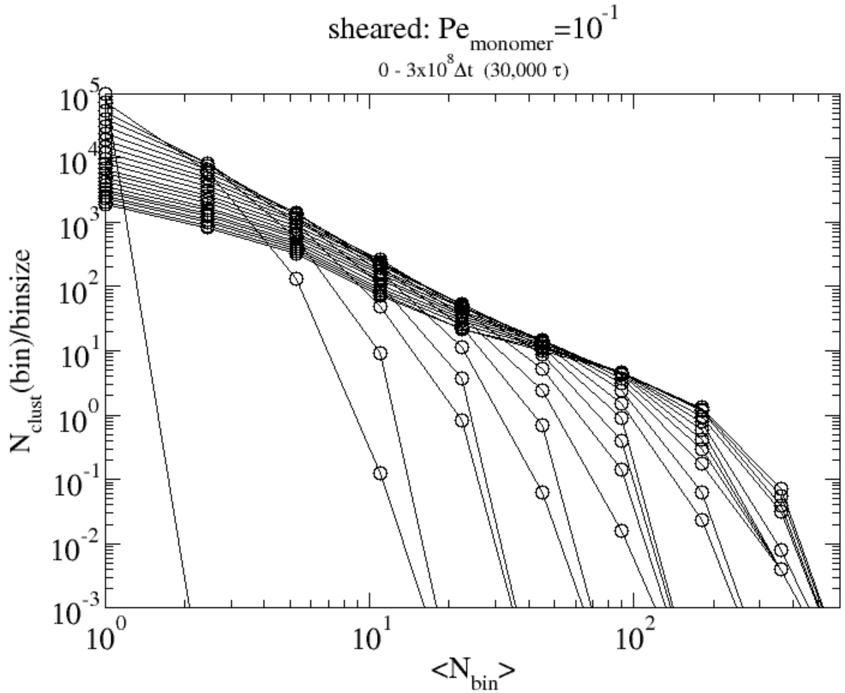
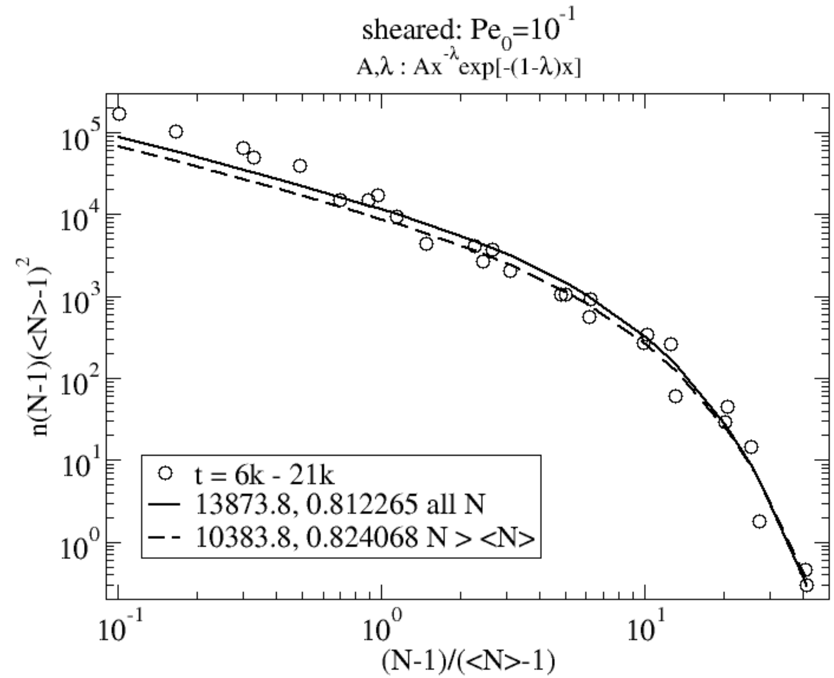


FIG. 3: a) (left) Evolution of cluster size distributions for diffusive system $Pe_0 = 0$ from $t = 0$ to $t = 30,000\tau$ b) (right) cluster size distributions with size N normalized by average size, $\langle N \rangle$, and number of clusters of size N, $n(N)$, multiplied by $\langle N \rangle^2$. Collapse onto master curve is apparent. Fits to scaling form with prefactor, A, and homogeneity, λ, are also displayed.

- CSD for diffusive systems are consistent with kinetics results
- Homogeneity λ connected to kinetic exponent z by z=1/(1-λ) with λ≈0
- Scaling distribution – collapse of distribution at all times onto master curve

Cluster Size Distributions (Sheared)





- CSD for highly sheared systems shows power law decay
- Homogeneity λ not connected to kinetic exponent z by $z = 1/(1-\lambda)$
  - At late times $z \approx 2$, $1/(1-\lambda) = 1/(1-0.81) \approx 5$
  - Result of CSD not being well described by quasi-monodisperse assumption
- Scaling distribution – works well for late times when <N> → <N> -1

Shear Effects on Floc Structure: A closer look

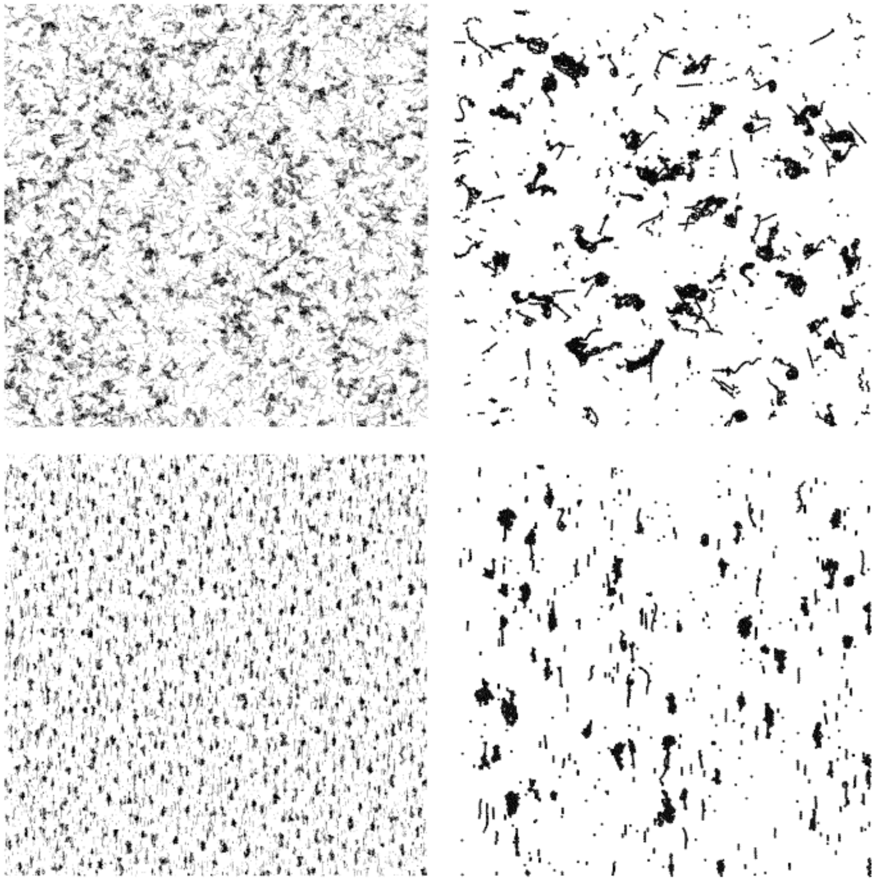


FIG. 7: a) (upper-left) Snapshot of sheared system with $Pe_0 = 10^{-1}$ at $t = 21,000\tau$ looking down on x-y plane. Shear velocities are along x, increasing in y b) (upper-right) 150x150x150 d^3 section of system showing individual cluster morphologies also in x-y. a) (lower-left) Snapshot of same system now looking down at y-z plane b) (lower-right) 150x150x150 d^3 section of system showing individual clusters, looking down at y-z plane.

- For highly sheared systems, flocs first form as dimers and take on Jeffrey's orbits, aligning into shear planes, where rotation in the shear flow favors growth near the floc edges, forming quasi-linear flocs
- As flocs grow, they cannot support the shear stress and begin to collapse, forming more compact structures
- Floc structure is anisotropic – flocs and entire system look different when viewed along shear direction or normal to it

Summary

- A physically motivated adhesive particle dynamics model has been developed that includes all relevant interparticle modes of motion
- This model allows for prediction of **flocculation dynamics** and **structure**
- Model accurately reproduces known DLCA kinetics and size distribution results
- Shear is found to accelerate aggregation significantly – but can result is complicated dynamical processes where restructuring timescales encroach on collisional timescales – bifurcation of ensemble floc structure
- Shear can initiate confinement of aggregates into shear planes, which can modify growth kinetics – Jeffreys orbits
- Unlike previous models, restructuring/fragmentation of flocs is dealt with in a realistic manner – both directly results from particle-particle, particle-solvent interactions

Future work

- Work with Experimentalists to define parameters for systems of interest

- Currently – Steady→ unsteady Taylor-couette

- Turbulent shear

- Settling

Acknowledgements

- Algae Flocculation LDRD team, Sandia
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