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Discrete Particle Dynamics Simulations of Adhesive Systems with Thermostatting

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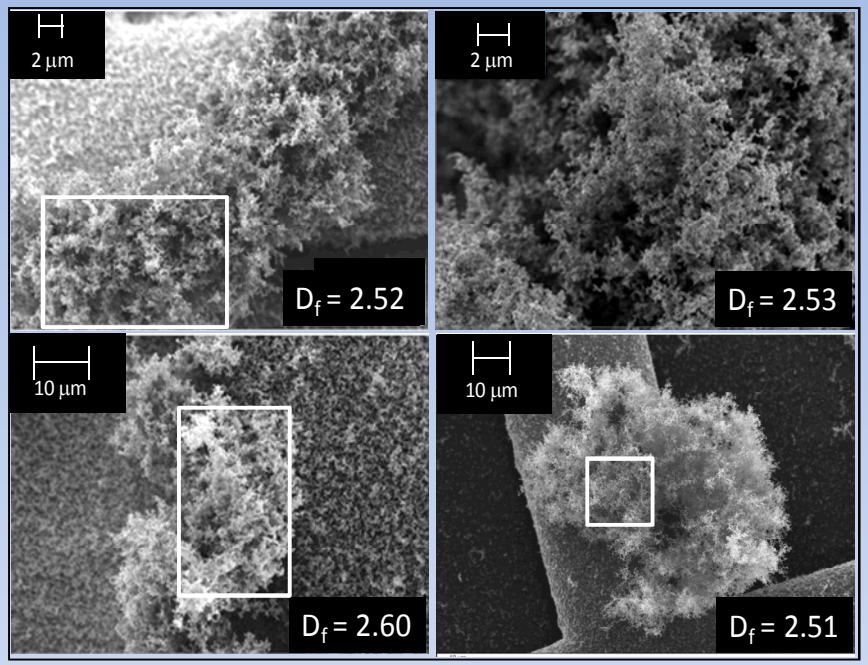
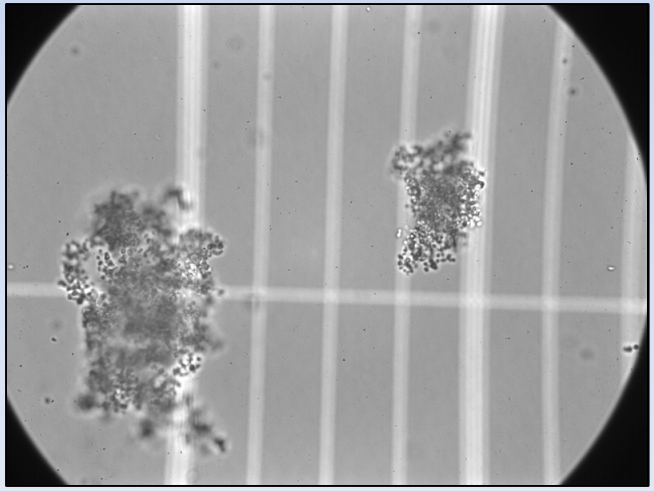
LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

Particle Adhesion - Ubiquitous

Soot: Graphitic Carbon Aggregates



Algae: Nanno-chloropsis floc

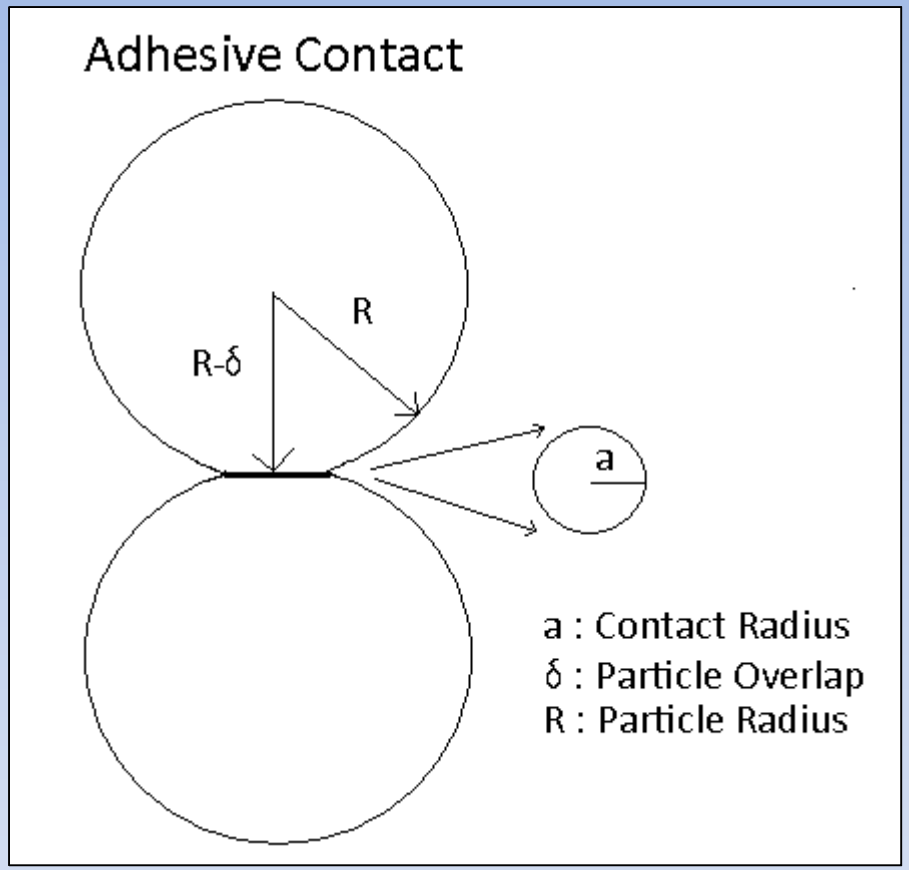


- *Carbonaceous soot* - pool fires containing toluene produce fractal aggregates as a result of random (brownian/turbulent) collisions leading to adhesive particle/particle contacts – particle/surface adhesion is also observed
- *Algae cells* - flocculate with fractal structures governed by intercellular adhesive contacts which result from complex fluid mixing mechanisms (steady/turbulent shear, etc.)
- MANY other systems

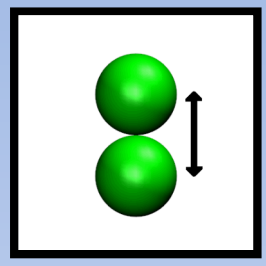
Motivation

- *Diverse particulate systems* - aerosols to aqueous dispersions need an adhesive description that resolves all binary contact modes of relative particle motion
- *Restructuring dynamics* in particle agglomerates or flocs requires realistic physics-based models
  - Central potentials cannot inhibit restructuring
  - multiple system length and time and scales (eg: restructuring, particle aggregation)
- *Thermal considerations*: Binary contact modes have dissipation – should we couple with fluctuation? – a "mode" should contain ½ kT of thermal energy by Fluctuation-Dissipation
- This study looks at restructuring dynamics and morphological forms that result from realistic thermal treatment of isolated clusters of adhesive particles

Particle Dynamics Adhesion Model



Normal Mode

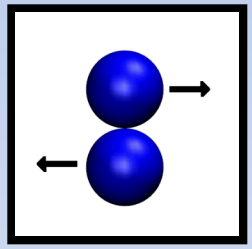


$$F_n = 4F_c\left[(a/a_0)^3 - (a/a_0)^{3/2}\right]$$

$$F_c = 3\pi\gamma R$$ Critical (Pulloff) Force

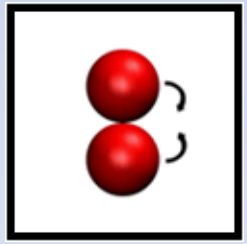
$$a_0 = \left(\frac{9\pi\gamma R^2}{E}\right)^{1/3}$$ Equilibrium contact radius

Shearing Mode



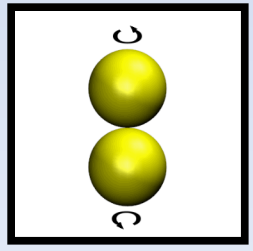
$$F_s = -k_s R_s \hat{v}_s$$

Rolling Mode



$$\tau_r = -k_r R_r$$

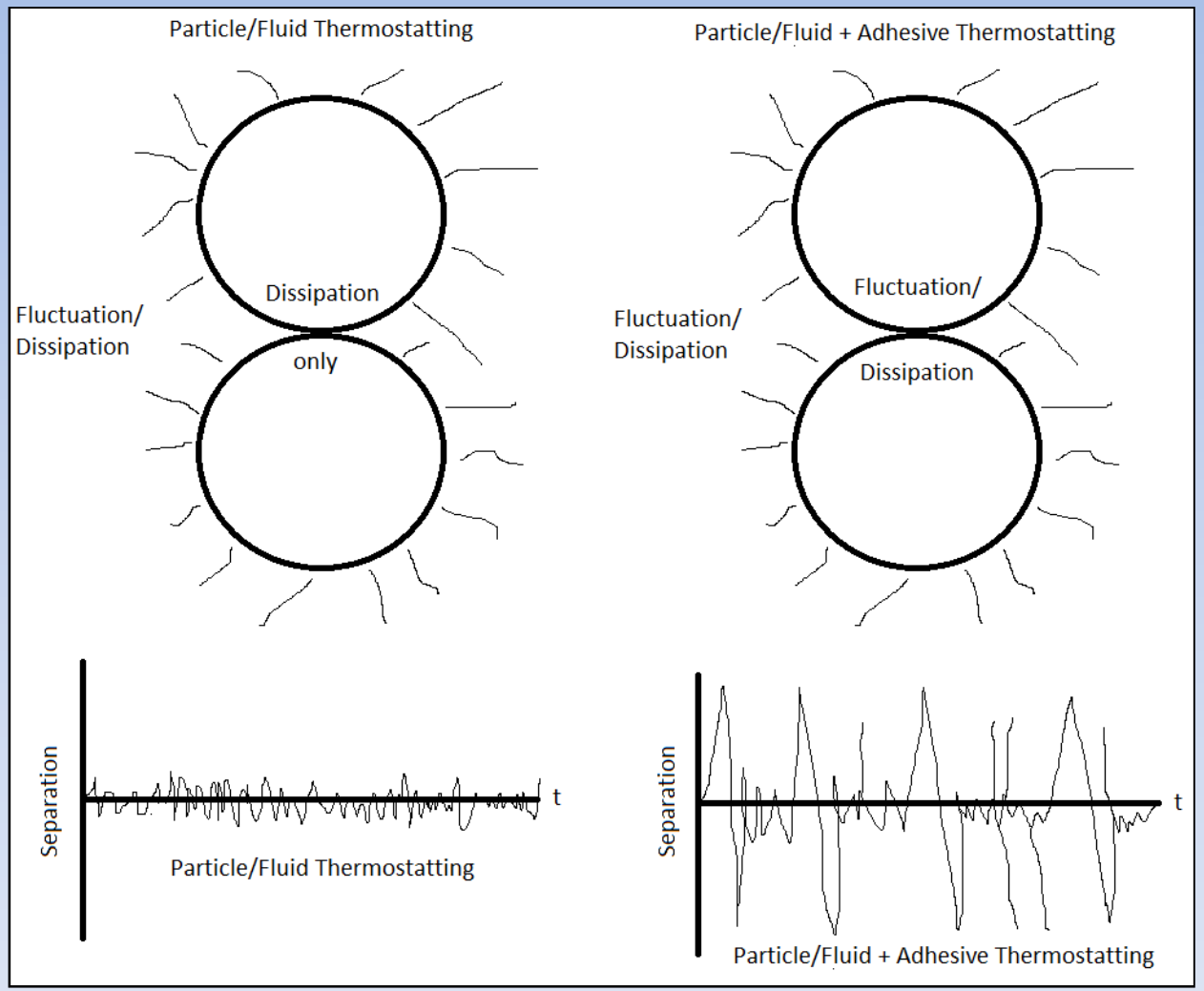
Twisting Mode



$$\tau_t = -k_t \theta_t$$

- Granular adhesive model (akin to JKR) including normal, twisting, rolling, and shearing modes with associated hindrances and frictional terms (not shown). (Marshall 2008, 2009)
- Can incorporate experimentally determined surface energies, critical displacements in each mode

Thermostatting Methods



- **Method 1**: *P/F* (Particle/Fluid) thermostatting only
  Dissipation *P/F* and *P/P* (particle/particle)
  Fluctuation *P/F*
  - T appears low as seen from rms particle velocities (**v**, **ω**) (< ½ kT per mode)
- **Method 2**: *P/P* and *P/F* thermostatting
  Dissipation *P/P, P/F*
  Fluctuation *P/P, P/F*
  - v, ω consistent with T (½ kT per mode)

Particle Motion

- Langevin Equation:

  normal, shear modes: $m d\mathbf{v}/dt = \mathbf{F}_{adhesive} + \mathbf{F}_{hydro} + \mathbf{F}_{stoch}$

  roll, twist modes: $I d\boldsymbol{\omega}/dt = \boldsymbol{\tau}_{adhesive} + \boldsymbol{\tau}_{hydro} + \boldsymbol{\tau}_{stoch}$

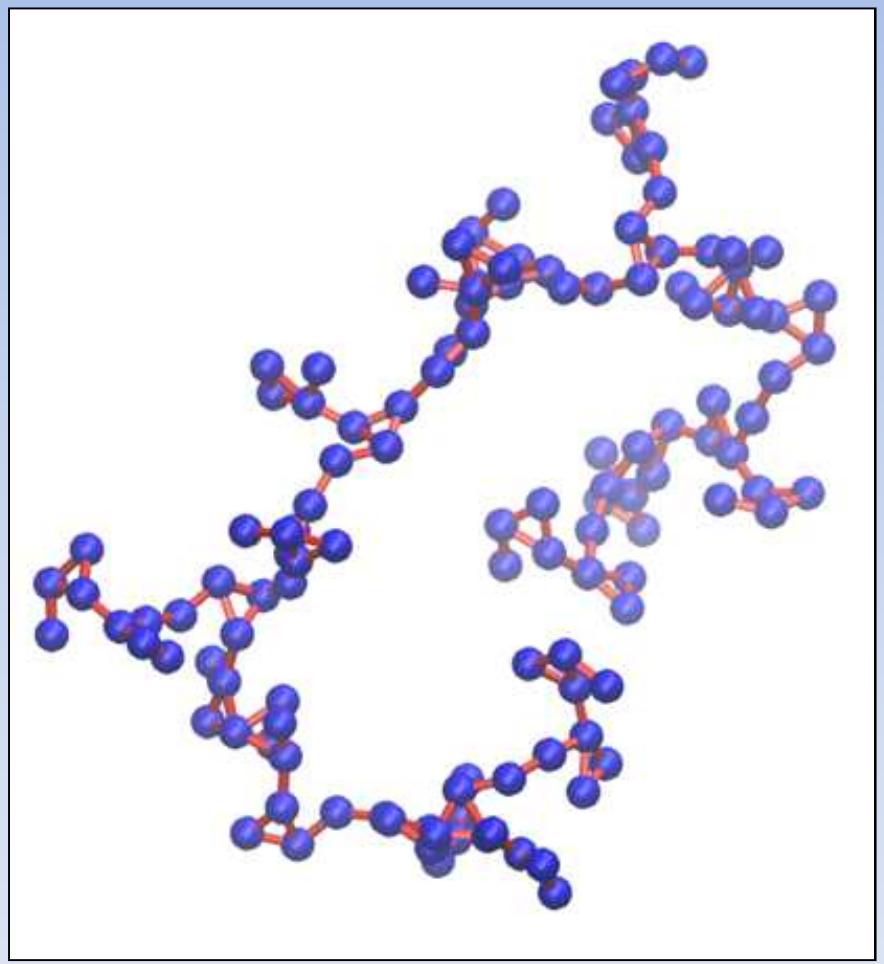
  - shear also has angular term for conservation of **L**

- solvent viscosity η, temperature T, particle size d, volume fraction ϕ
- $\mathbf{F}, \boldsymbol{\tau}_{adhesive}$ = adhesive particle forces, torques
- $\mathbf{F}, \boldsymbol{\tau}_{hydro} = R\mathbf{v}$ (hydrodynamic forces)
  - full resistance tensor *R* characterizes dissipative forces: $R\mathbf{v}=\mathbf{F}_{iso\text{-}drag}+\mathbf{F}_{lub}$
  - $\mathbf{F}_{iso\text{-}drag} = 3\pi\eta d v f(\phi)$
    - f(ϕ) is a function of the volume fraction of the system – Higdon et al. determined this for monodisperse system
  - $\mathbf{F}_{lub} = 6\pi\eta R/4h_{ij}\ \mathbf{v}_{ij,normal}$
    - Depends on relative normal particle velocities $\mathbf{v}_{ij}$, surface separation h_{ij}
    - *For the purpose of this study we ignore lubrication forces*
- $\mathbf{F}, \boldsymbol{\tau}_{stoch}$ (stochastic thermal forces)
    - coupled to dissipative forces through fluctuation/dissipation theorem

Simulation Details

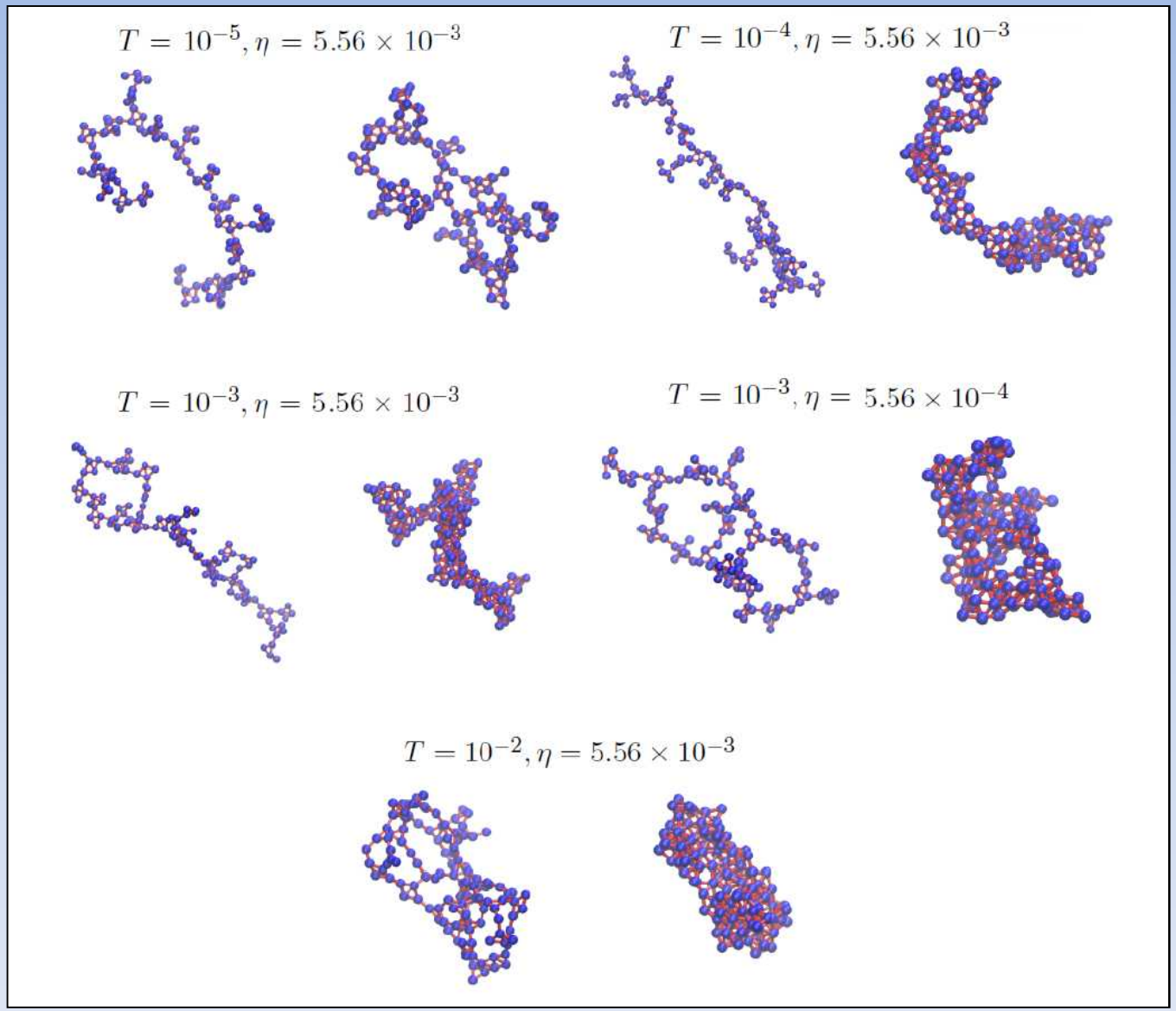
- DEM (Discrete Element Modeling) in LAMMPS
- Initial structure: 128 particle *fractal agglomerate*
- "stiff" adhesive parameters
  - don't want structure to collapse too easily
  - If too stiff, timestep will be small – not enough sim time
- Temperatures: $T = 10^{-5}$ to 10^{-2}
  - 10 different random seeds for statistical averaging
- Viscosities: $\eta = 5.56 \times 10^{-3}, 5.56 \times 10^{-4}$
- Total time ~ 10^{8} timesteps - allow nearly convergeds restructuring of initial structure

Starting Structure



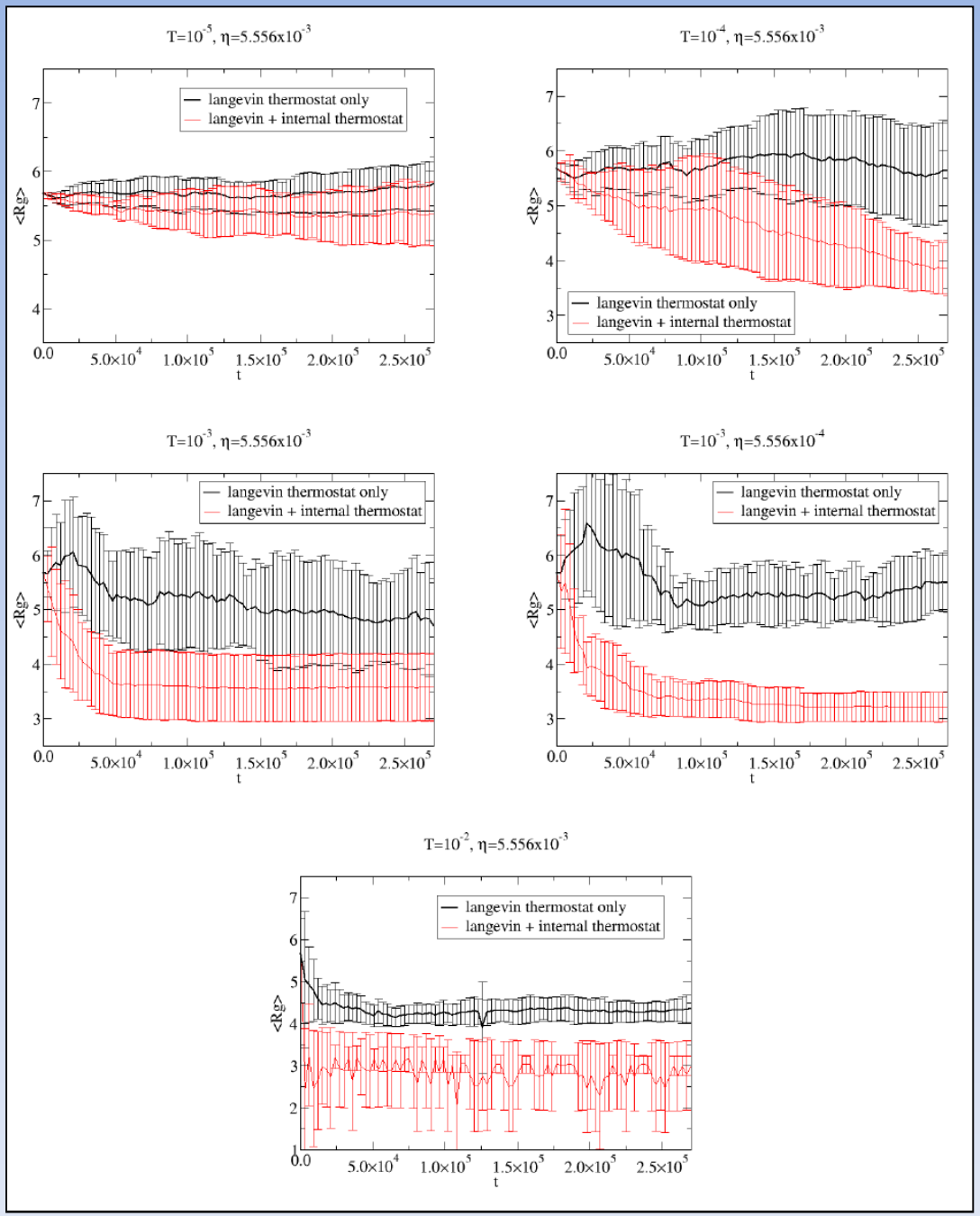
- DLCA (Diffusion Limited Cluster Aggregation) fractal structure
- $N = k(R_g/a)^{Df}$
  - N = 128
  - k = 1.3
  - D_f = 1.8
- Statistical Averaging: 1 starting structure, 10 random noise seeds for each set of simulation parameters

Restructured Aggregates



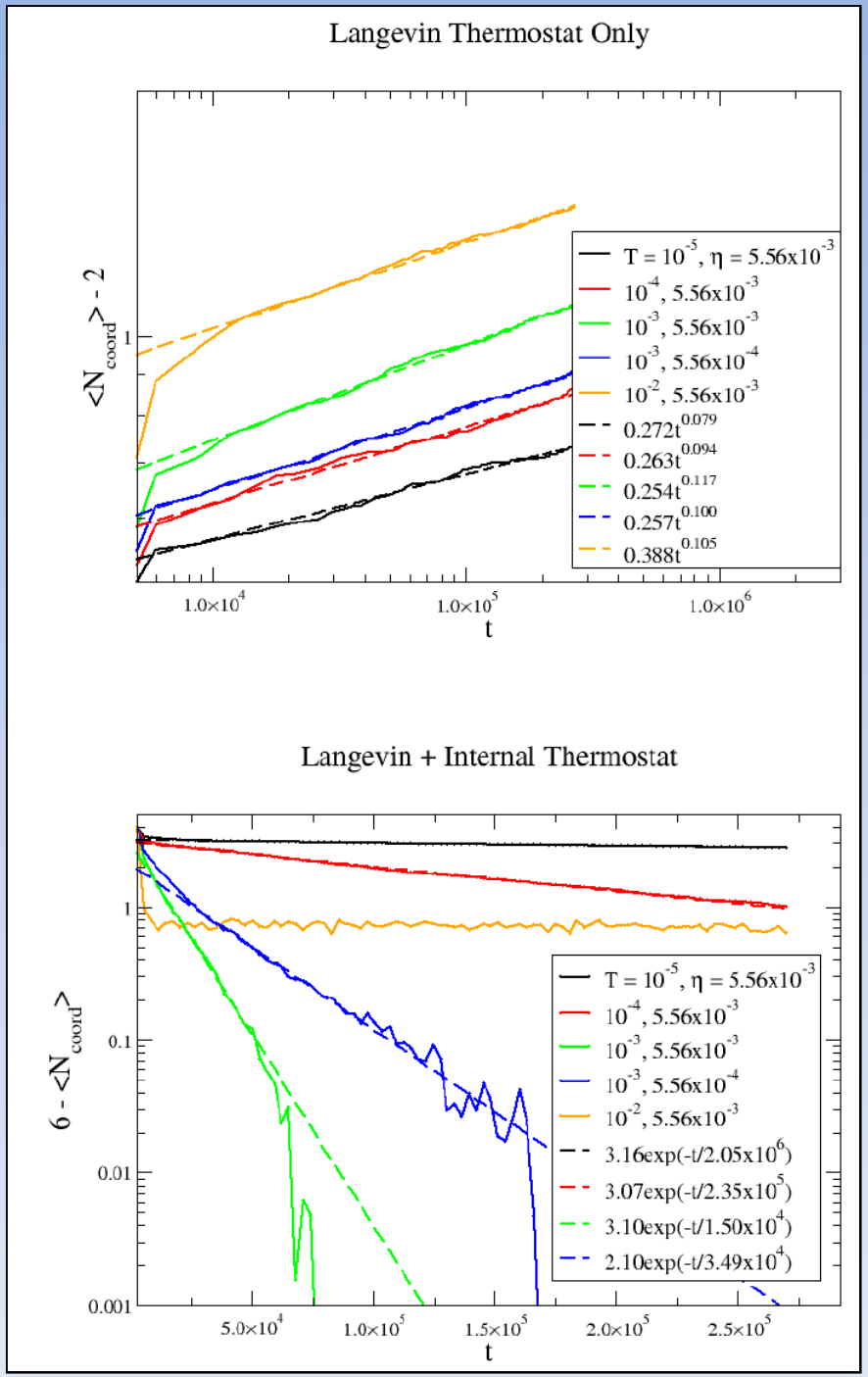
- Fluid-particle thermostatting only (*left*) and including adhesion thermostatting (*right*)
- 1 of 10 realizations for each parameter set
- T ↑ enhances restructuring
  - Lower T: Formation of stress-bearing closed loops
  - Higher T: Multiple particle contacts – thicker branches
- Adhesive Thermostatting enhances restructuring

Evolution of Aggregate Size (R_g)



- Average over 10 realizations - error bars are standard deviation
- Including Adhesion thermostatting reduces R_g and better convergence compared to fluid/particle thermostatting alone
- Higher T leads to smaller final R_g

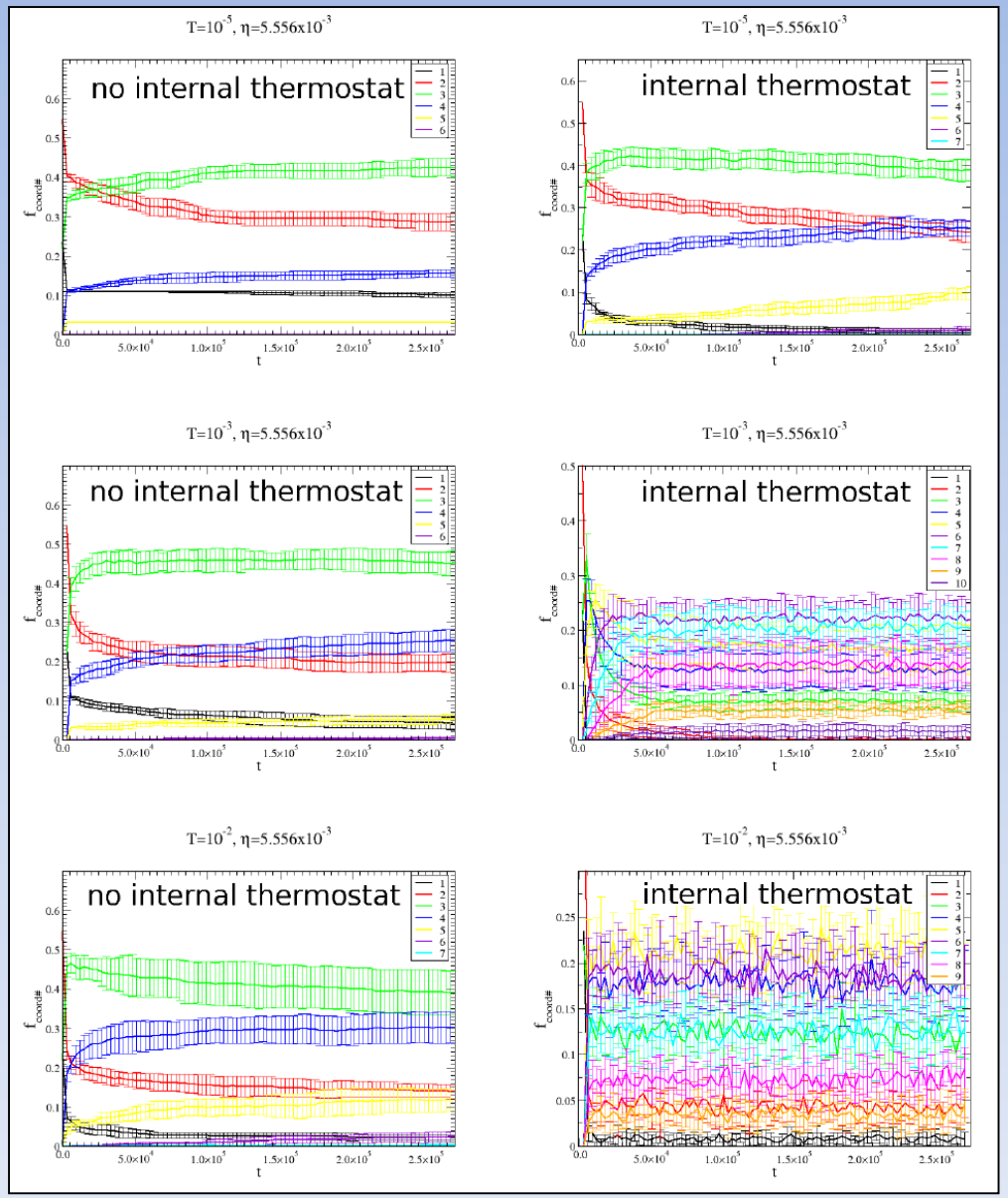
Evolution of Average Coodination Number $\langle N_c \rangle$



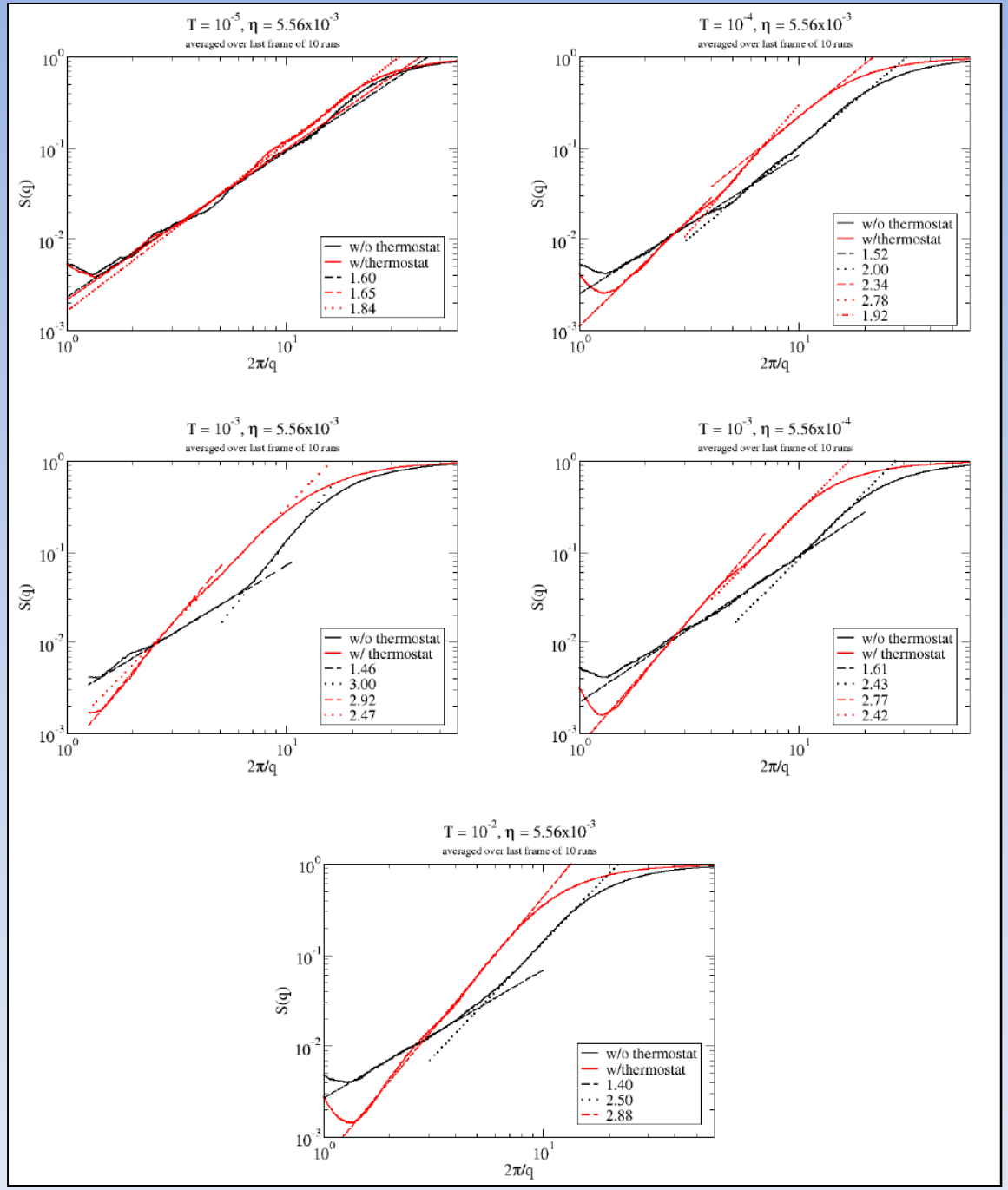
- *Particle/fluid thermostatting only*: **power law** with time from initial value of 2
- *Adhesive thermostatting included*: **exponential** approach to 6 (kinetically frustrated/ glassy configuration)

  - at highest T, steady state $\langle N_c \rangle \rightarrow \sim 5$: thermal energy can break some contacts

Evolution of Specific Coordination Numbers



- Without adhesive thermostat – slow restructuring - T dependent distribution of coordination numbers (few above 6 even at T = 10^{-2})
- With adhesive thermostat – rapid restructuring, especially at high T with broad distribution of coordination numbers (as high as 10)



Restructuring Length Scales

- Lowest T: Little restructuring for either thermostatting method
- Increasing T – w/o adhesive thermostat: restructuring influences large scale structure (increased Df), with smaller length scales less affected (Df has slight decrease)
- Increasing T – w/ adhesive thermostat: Df is increased on all length scales, driving toward percolation fractal dimension (~2.6) or higher at highest temperatures

Conclusions

- Restructuring in adhesive systems is a dynamical process with highly sensitivity to the treatment of thermal energy (thermostatting) – resulting structures can relax to form stress-bearing closed loop structures or multiple particle contacts leading to thicker branches
- With adhesive thermostatting, restructuring occurs at all length scales , an effect that increases with T, resulting in larger average coordination numbers and a wide distribution of coordination number values
- Without adhesive thermostatting, restructuring occurs mostly at larger length scales with a narrower distribution of particle coordination numbers and a smaller average value