Hydrodynamic Simulations of Colloidal Suspensions with Short-Range Attraction and Long-Range Repulsion

Michael Bybee

Department of Chemical and Biomolecular Engineering
University of Illinois at Urbana-Champaign

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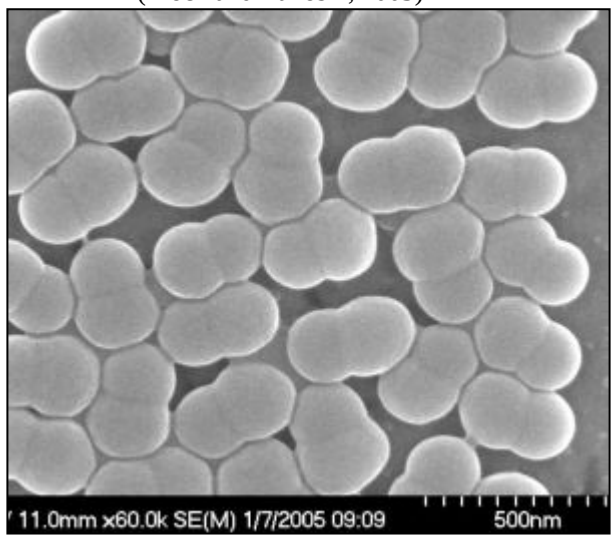
Colloidal Suspensions

- Nanometers to microns
- Spheres, platelets, ...
- Complex rheology and phase behavior
- Applications
  - Paints, inks, coatings
  - Pharmaceuticals
  - Foodstuffs
  - Personal care products
  - Ceramic processing
- Novel Materials
  - Direct writing
  - Photonic band-gap crystals
  - Chemical and biological sensors

Interparticle Interactions → Microstructure & Dynamics → Macroscopic Properties & Behavior

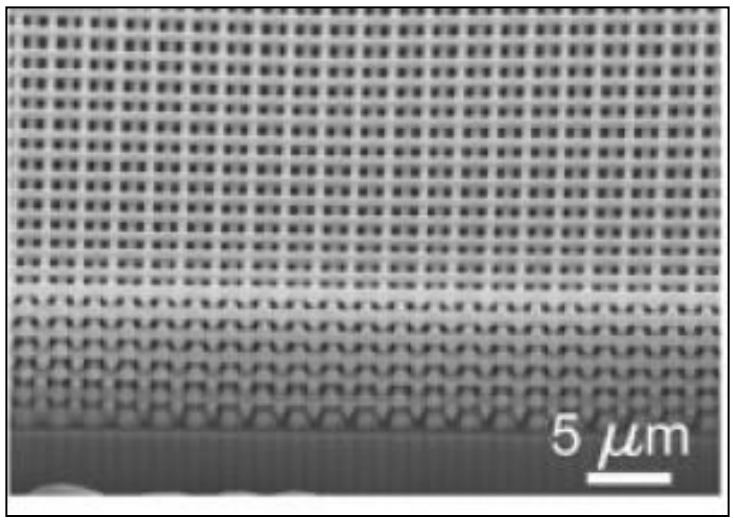
Anisotropic Particles

(Mock and Zukoski, 2005)



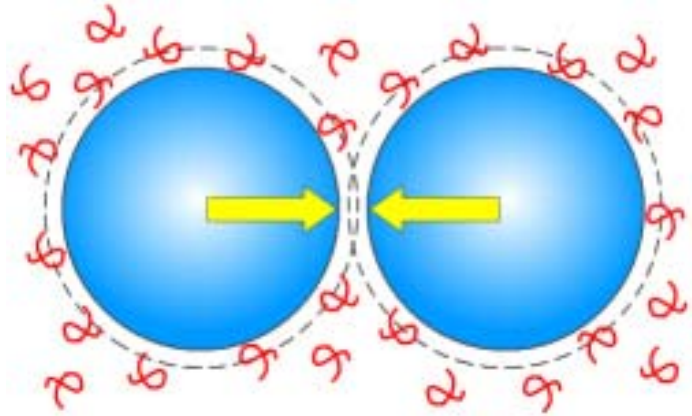
Direct-Writing of Photonic Band-Gap Crystal

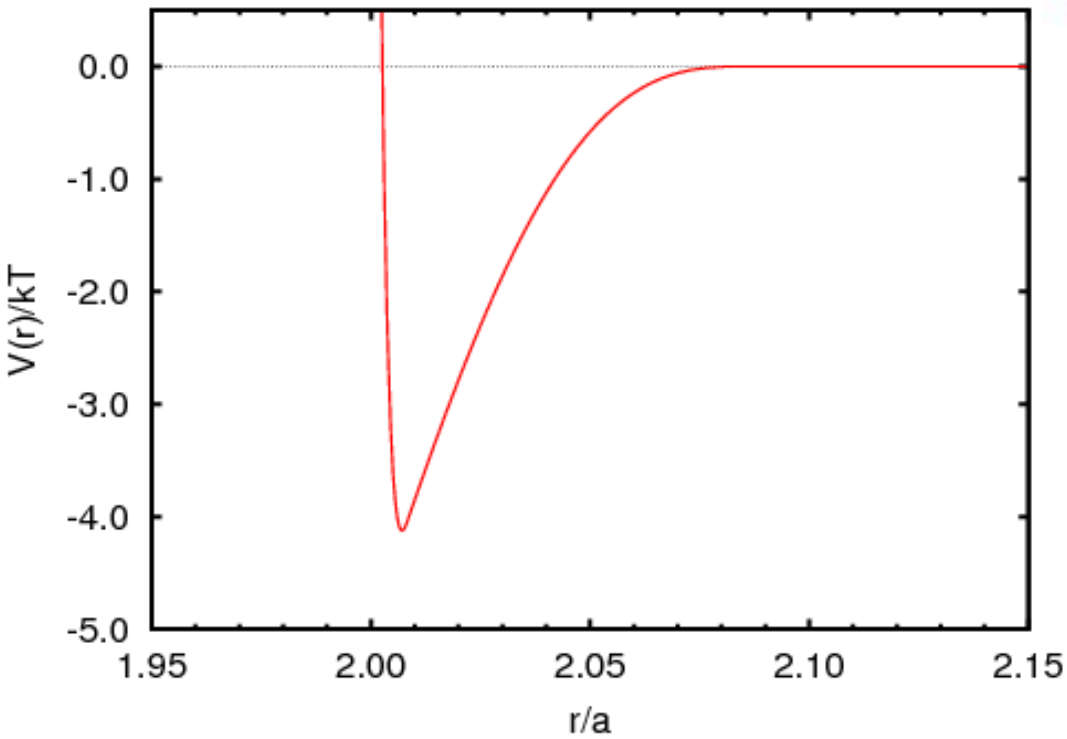
(Lewis, 2007)



Depletion Attraction: Colloid-Polymer Mixtures

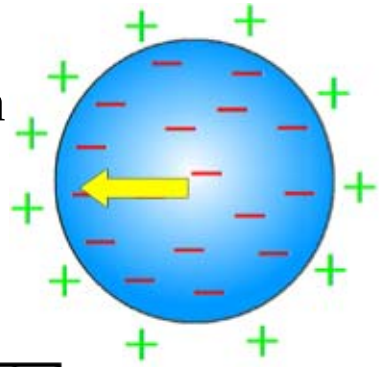
- Strength (ε_A) ~ concentration of polymer
- Range (δ_A) ~ size of polymer

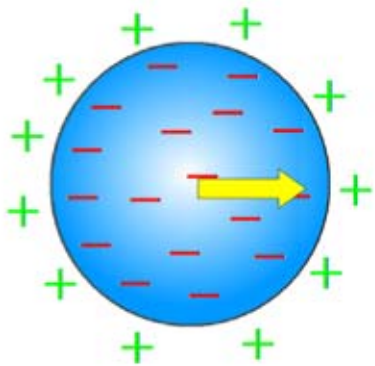


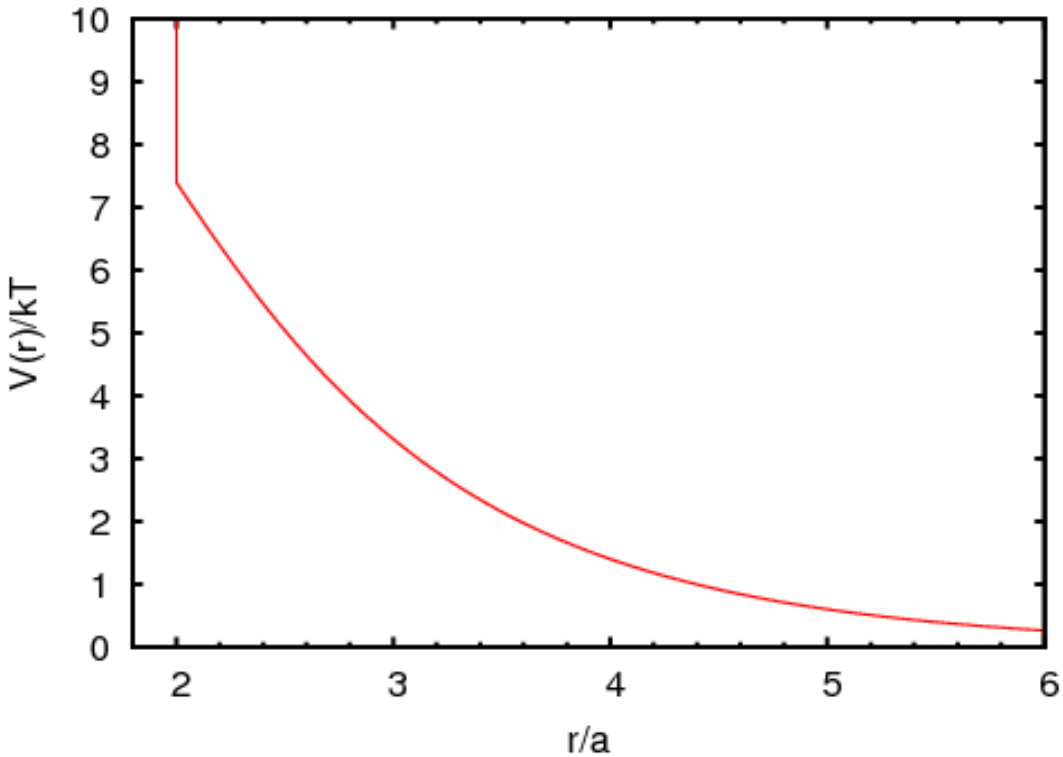


Electrostatic Repulsion: Charged Colloids

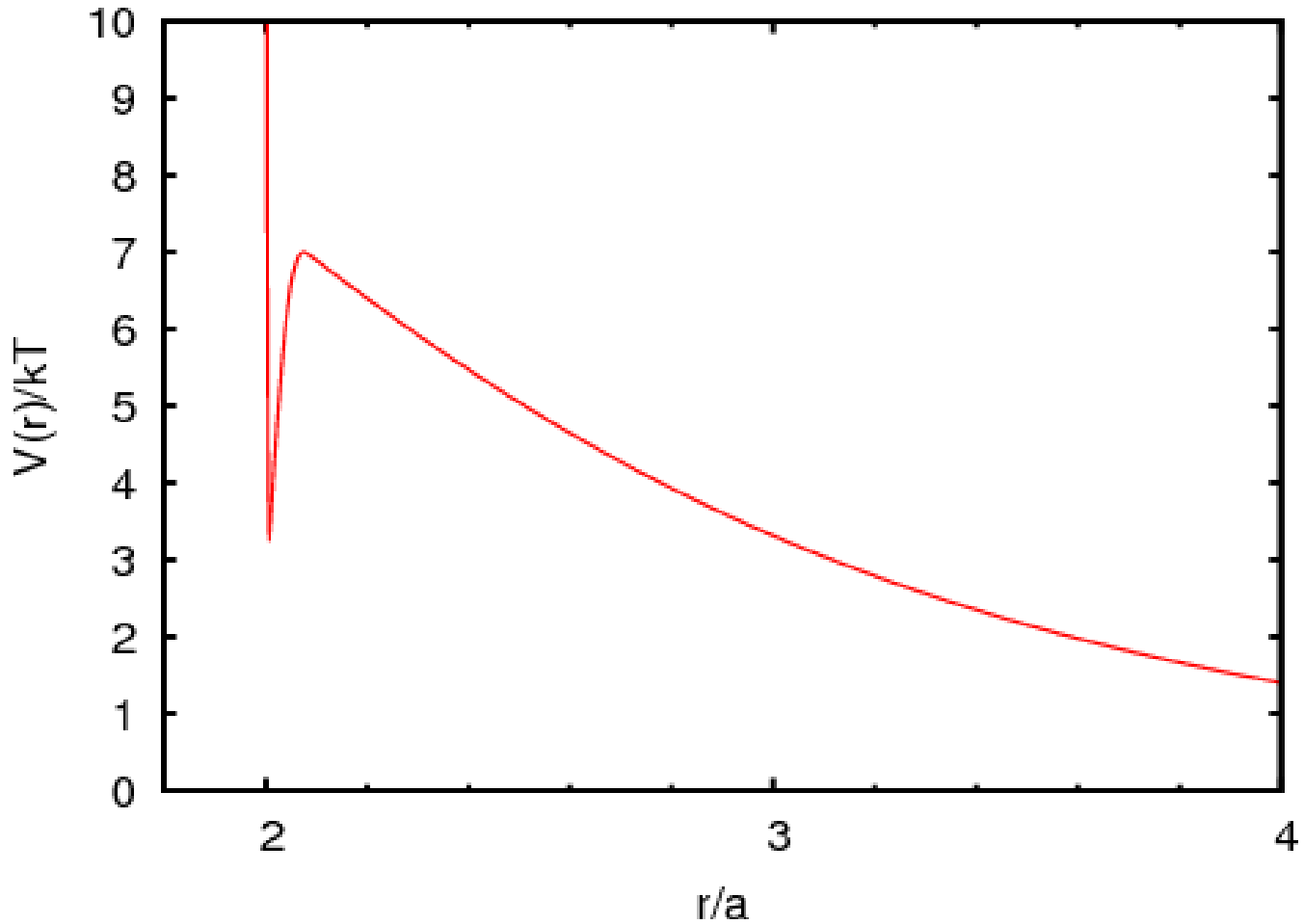
- Strength (ε_R) ~ surface charge
- Screening length (κ^{-1}) ~ ionic concentration







Total Interparticle Potential



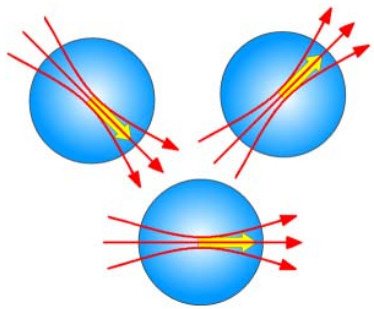
Dynamics

Langevin Equation

$$m\frac{d\boldsymbol{U}}{dt} = \boldsymbol{F}^{\mathrm{H}} + \boldsymbol{F}^{\mathrm{B}} + \boldsymbol{F}^{\mathrm{P}}$$

Hydrodynamic Force

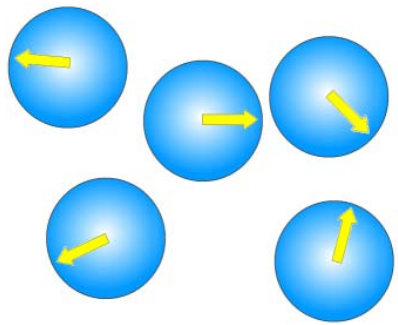
$$\begin{pmatrix} \boldsymbol{F}^{\mathrm{H}} \\ \boldsymbol{S}^{\mathrm{H}} \end{pmatrix} = \boldsymbol{R} \cdot \begin{pmatrix} \boldsymbol{U}^{\infty} - \boldsymbol{U} \\ \boldsymbol{E}^{\infty} \end{pmatrix}$$



Brownian Force

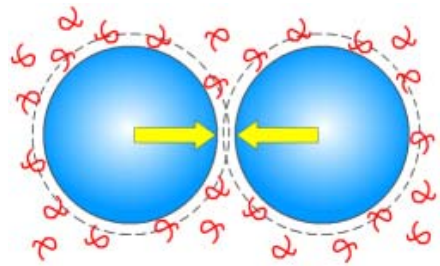
$$\left\langle \boldsymbol{F}^{\mathrm{B}}(t) \right\rangle = \boldsymbol{0}$$

$$\left\langle \boldsymbol{F}^{\mathrm{B}}(t)\boldsymbol{F}^{\mathrm{B}}(t+\Delta t) \right\rangle = 2kT\delta_{\mathrm{D}}(\Delta t)\boldsymbol{R}_{\mathrm{FU}}$$



Interparticle Force

$$\boldsymbol{F}_i^{\mathrm{P}} = -\sum_{j \neq i} \frac{dV(r_{ij})}{dr}\hat{\boldsymbol{r}}_{ij}$$



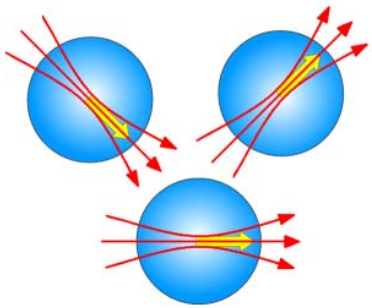
Overdamped Limit

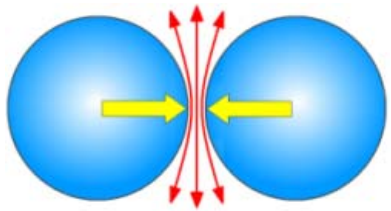
$$m\frac{d\boldsymbol{U}}{dt} = \boldsymbol{0} \qquad \boldsymbol{U} = \boldsymbol{U}^{\infty} + \boldsymbol{R}_{\mathrm{FU}}^{-1} \cdot \left(\boldsymbol{R}_{\mathrm{FE}} : \boldsymbol{E}^{\infty} + \boldsymbol{F}^{\mathrm{B}} + \boldsymbol{F}^{\mathrm{P}} \right)$$

Stokesian Dynamics

- Approximation to resistance tensor (Brady and Bossis 1988)

$$\boldsymbol{R} = \underbrace{(\boldsymbol{I} - \boldsymbol{\mathcal{R}})^{-1} \cdot \boldsymbol{R}_{\mathrm{1B}}}_{\text{Far Field}} + \underbrace{\boldsymbol{R}_{\mathrm{LUB}}}_{\text{Near Field: Lubrication}}$$





- Original Stokesian Dynamics, Cost ~ $O(N_P^3)$
- Particle-Mesh-Ewald (PME) (Guckel 1999, Viera 2002)
- Preconditioned GMRES
- Brownian – iterative square root
- PME Stokesian Dynamics, Total Cost ~ $O(N_P \log N_P)$

Fast Lubrication Dynamics

- Approximation to resistance tensor

$$\boldsymbol{R} = R_0 \boldsymbol{I} + \boldsymbol{R}_{\mathrm{LUB}}$$

Far Field

Isotropic Constant R_0

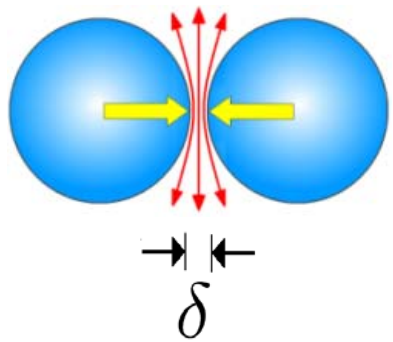
Match short-time self-diffusivity

$$D_s^s = \frac{kT}{3N_{\mathrm{P}}} \left\langle \mathrm{tr}\left(\boldsymbol{R}^{-1}\right) \right\rangle$$

Near Field: Lubrication

Squeeze mode only

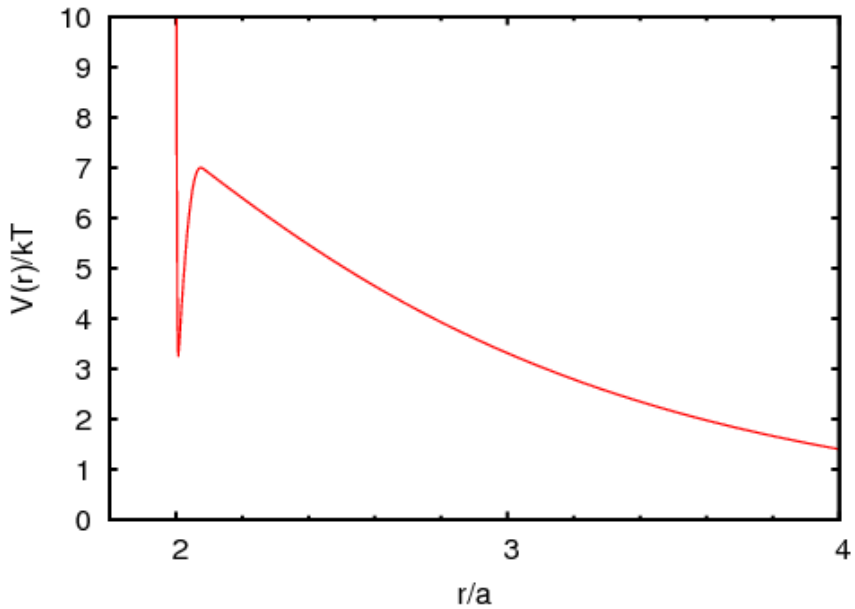
$$\boldsymbol{R}_{\mathrm{LUB}} \sim \frac{1}{\delta}$$



- MINRES
- Brownian – analytical square root
- Total cost ~ $O(N_{\mathrm{P}})$
- ~200 times faster than PME Stokesian Dynamics (N_{P}=1000)

System Parameters

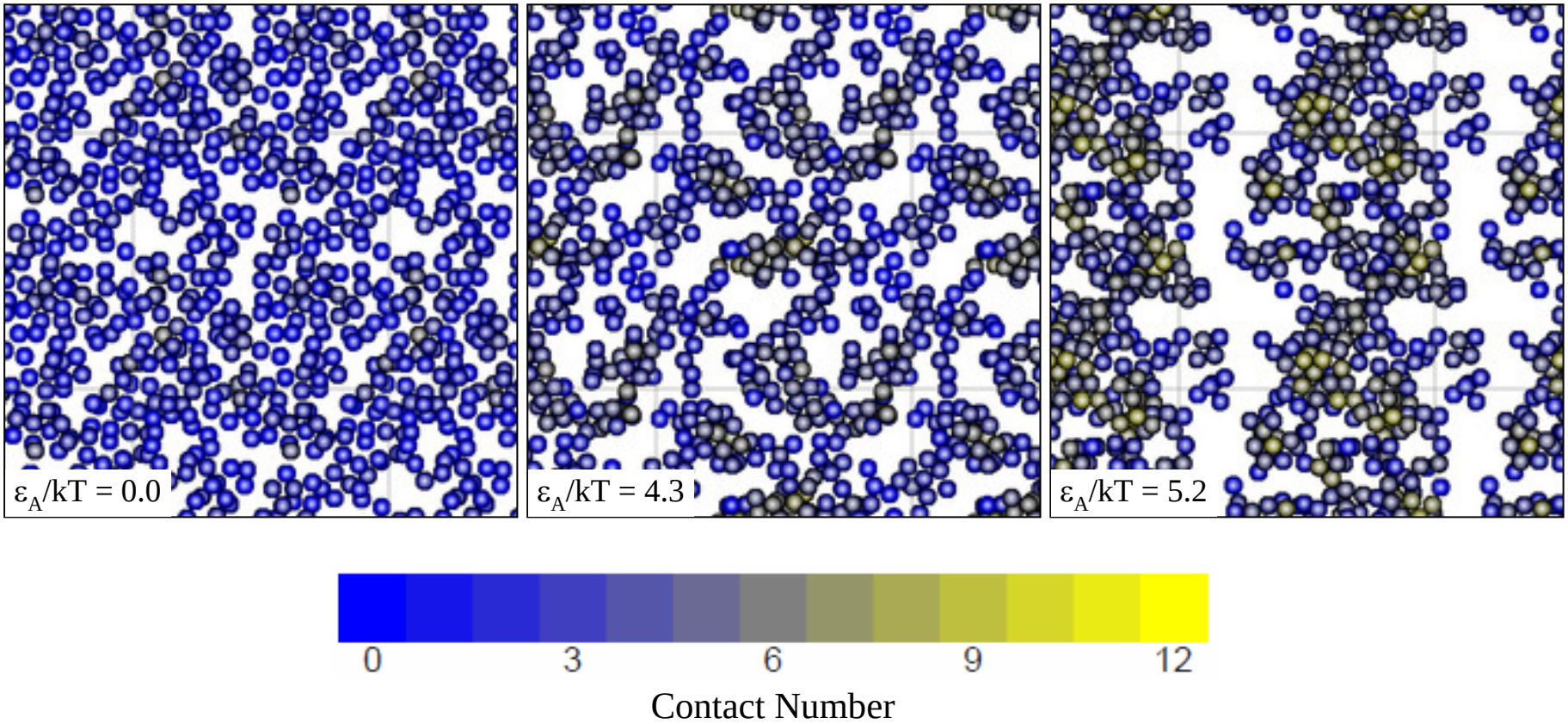
- Volume fraction, $\phi = 0.20$
- Short-range attraction
  - $\delta_A/a = 0.086$
  - $\varepsilon_A/kT = 0 - 71.1$
- Long-range repulsion
  - $(\kappa a)^{-1} = 1.55$
  - $\varepsilon_R/\varepsilon_{ref} = 0 - 1$ $\quad (\varepsilon_{ref}/kT = 37.0)$
- Dynamic simulations
  - 1000 particles
  - 3D periodic boundaries
  - Hard-sphere initial configuration
  - No ambient flow
  - Duration, $1600t_B$ $\quad (t_B = 6\pi\mu a^3/kT = 8.2$ s)



A: Microstructure

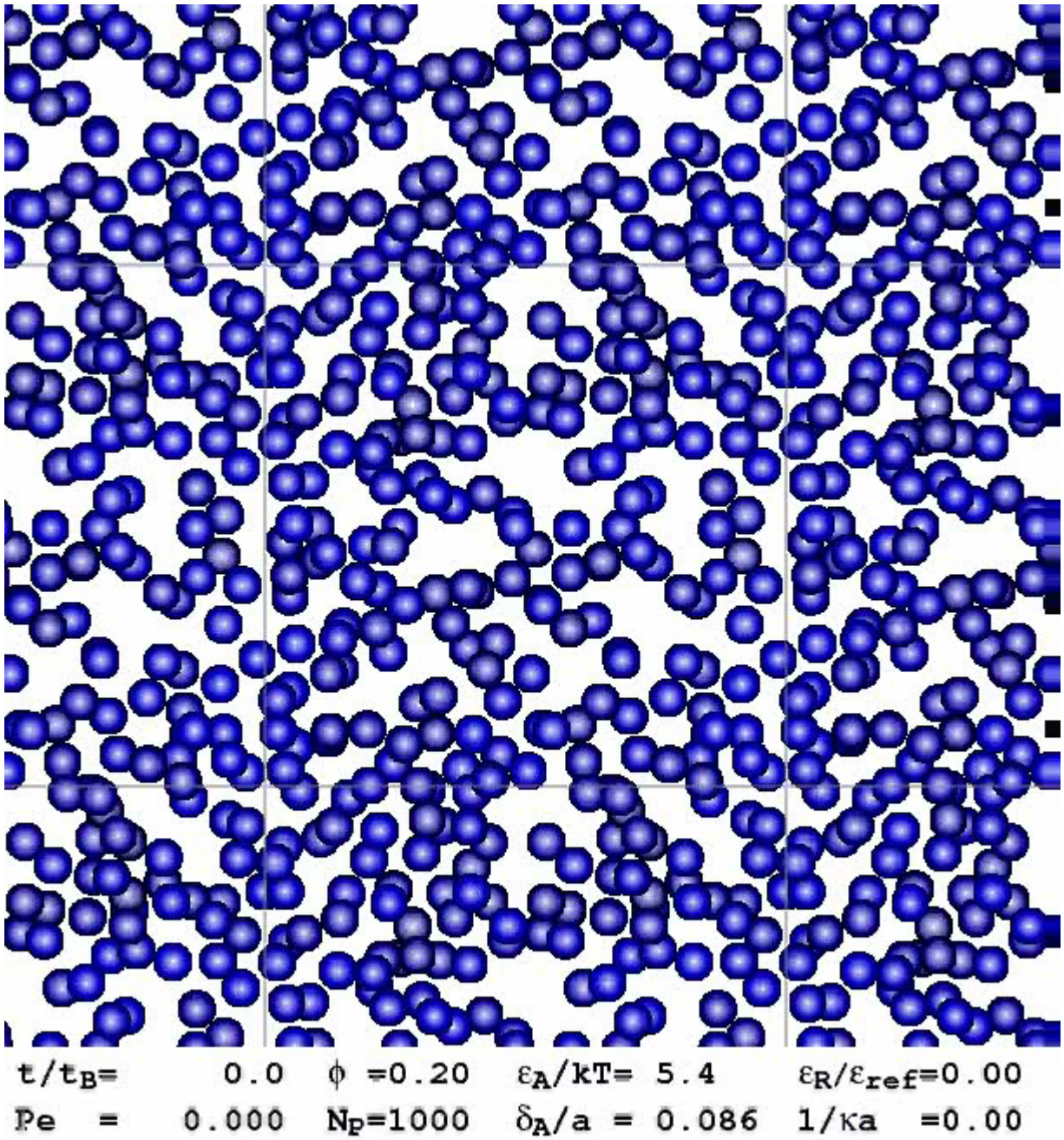
$\varepsilon_R/\varepsilon_{ref}$ = 0.0, t/t_B = 1500

Fluid



Diffusive Fluid

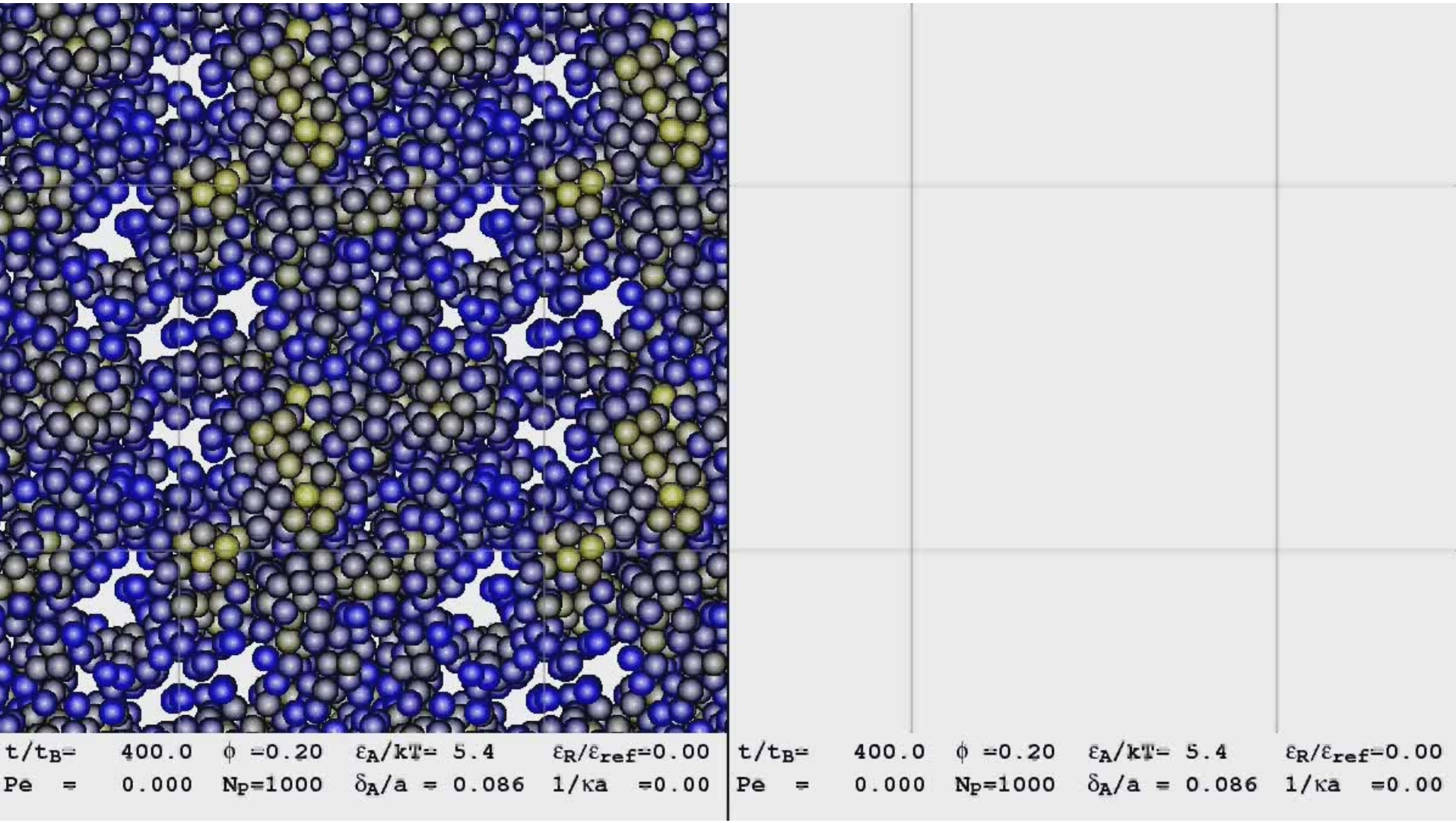
$\varepsilon_R/\varepsilon_{ref}$ = 0.0, ε_A/kT= 5.2



Fluid-Crystal Phase Separation

$\varepsilon_R/\varepsilon_{ref}$ = 0.0, ε_A/kT= 5.4

(all particles) (particles with contact number=12)



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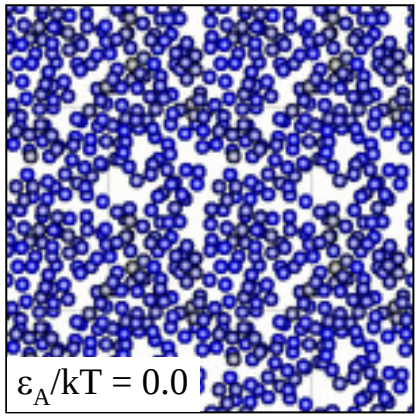
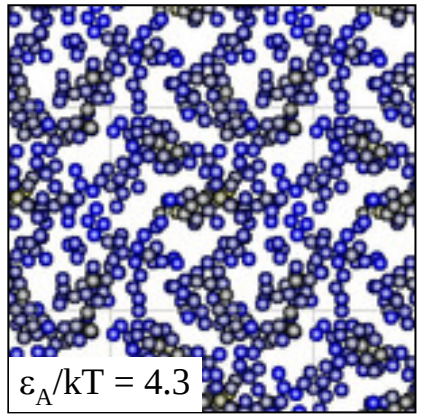
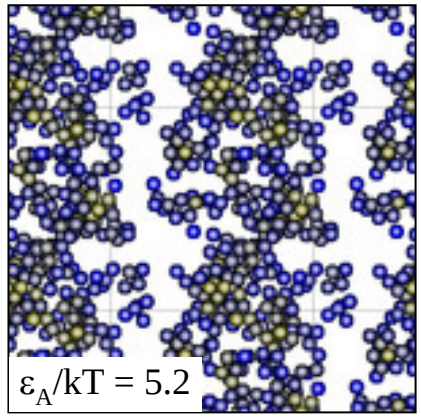
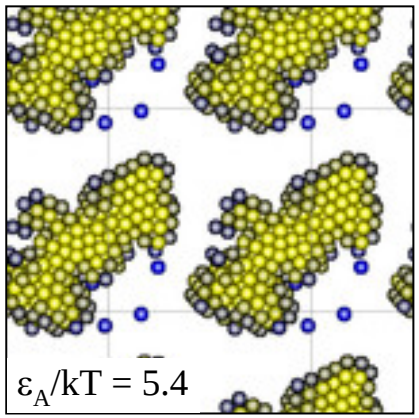
Fluid

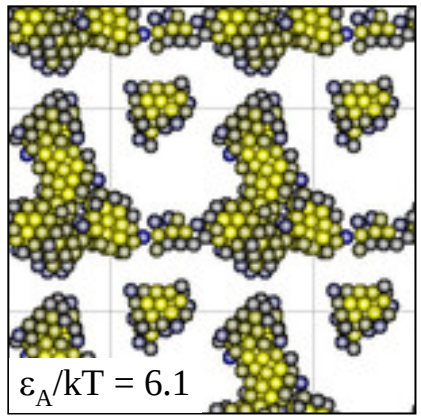


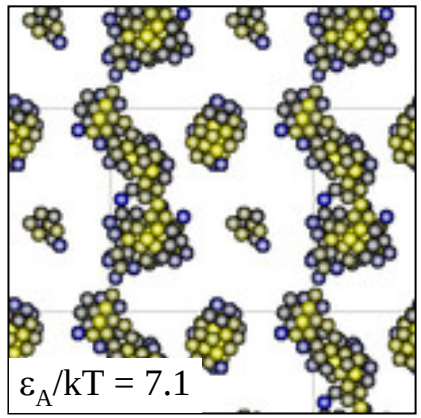




Fluid-Crystal

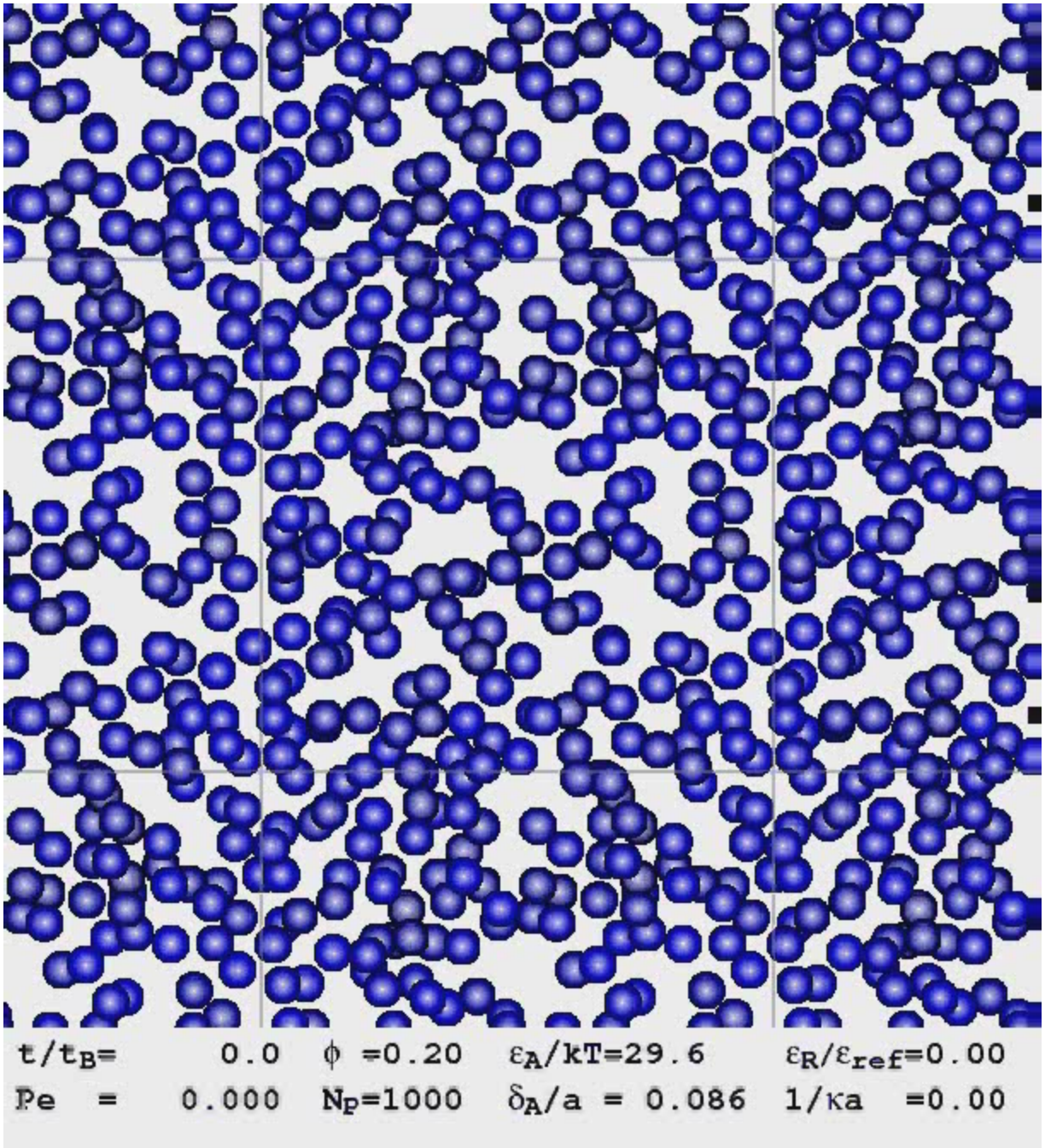






Dynamic Arrest and Gelation

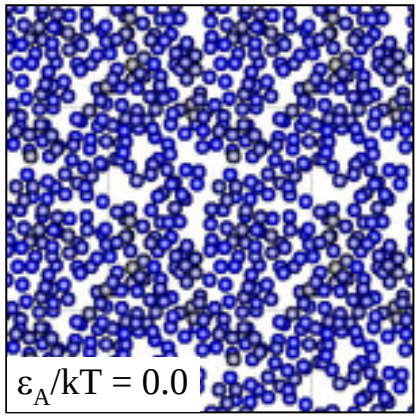
$\varepsilon_R/\varepsilon_{ref}$ = 0.0, ε_A/kT= 29.6

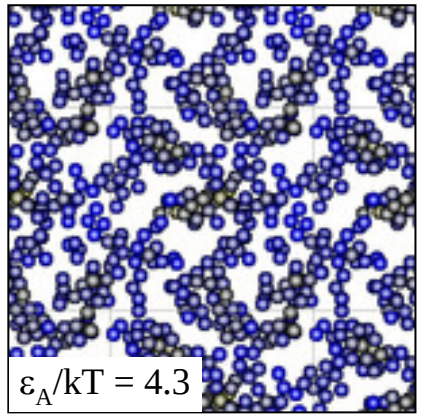


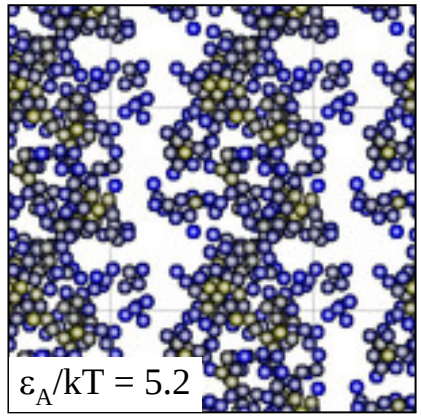
A: Microstructure

$\varepsilon_R/\varepsilon_{ref}$ = 0.0, t/t_B = 1500

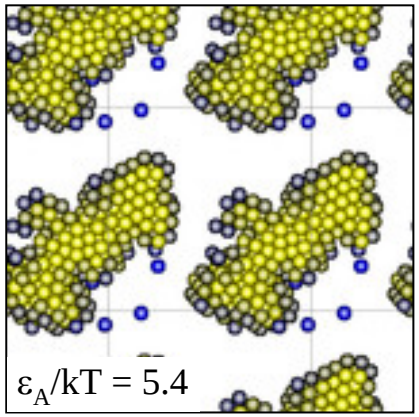
Fluid

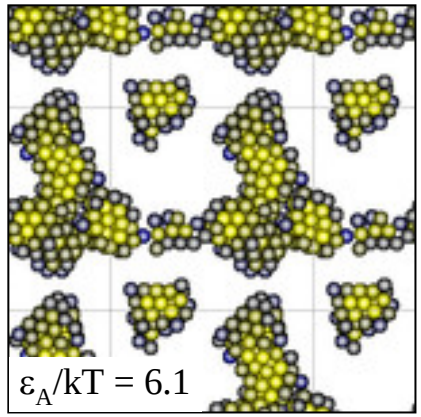


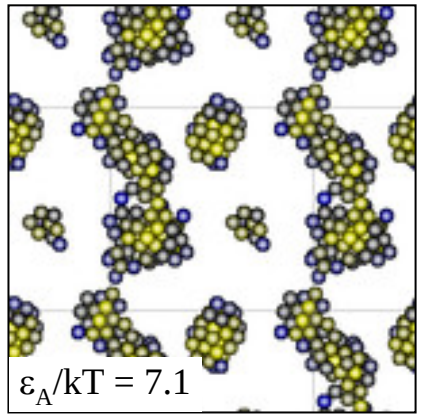




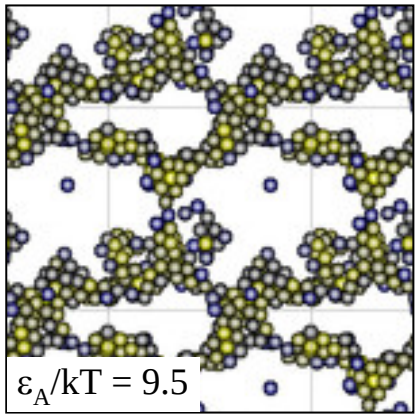
Fluid-Crystal

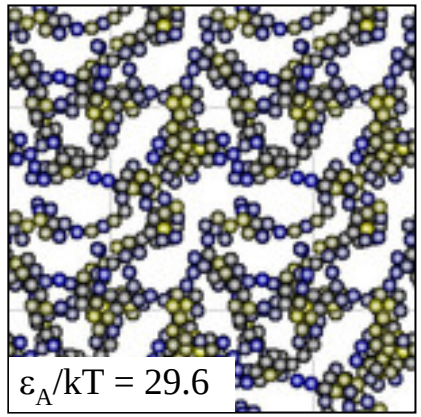


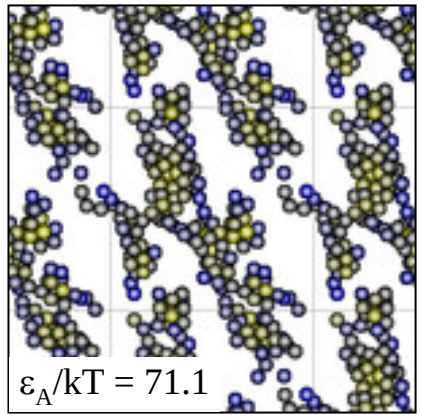




Gel





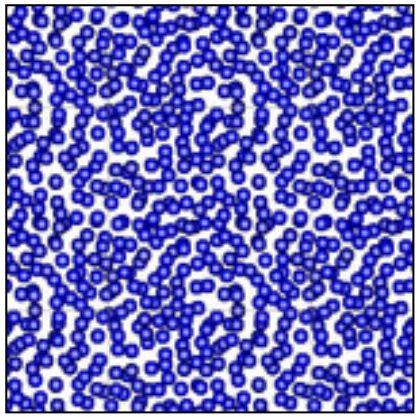
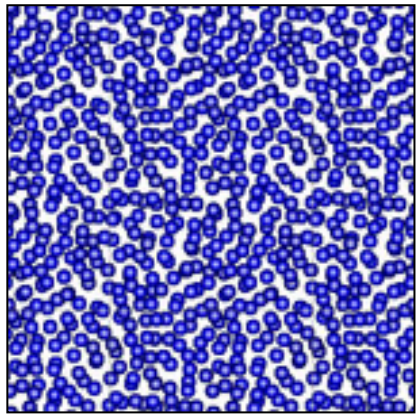
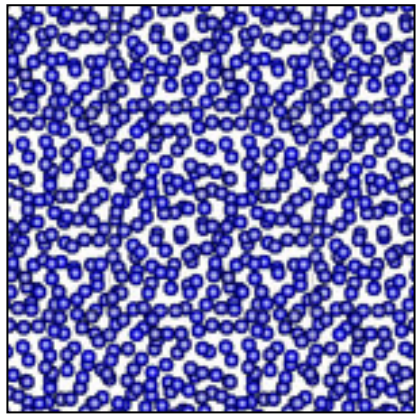
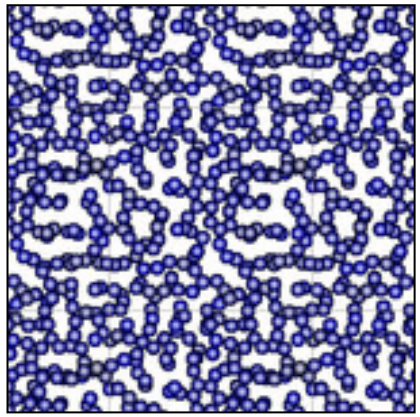
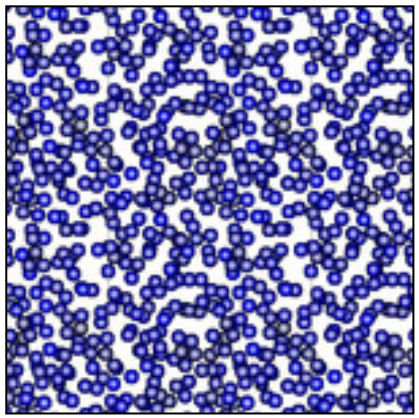
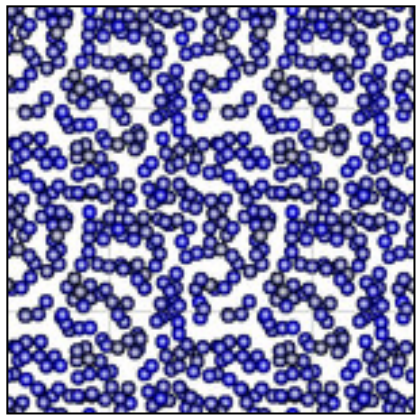
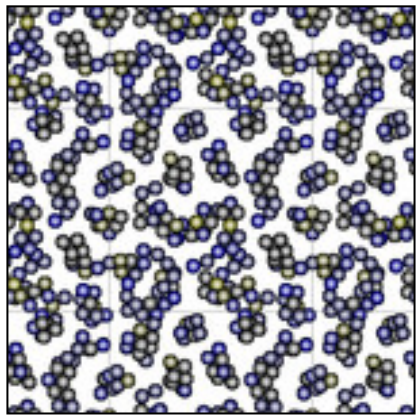
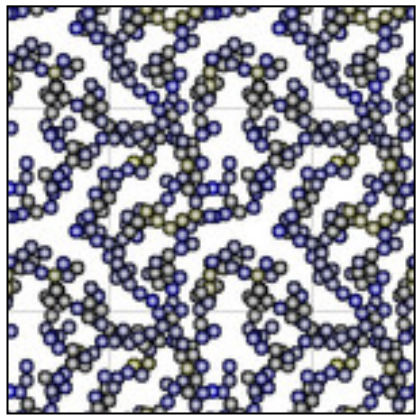
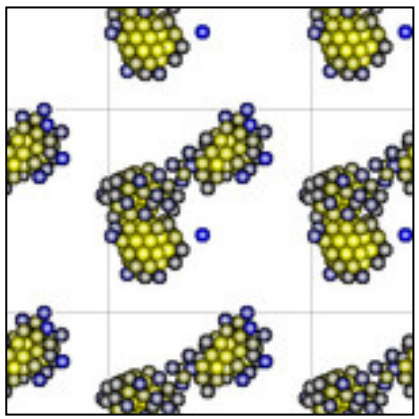
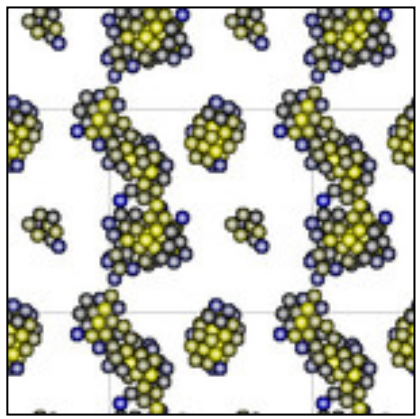
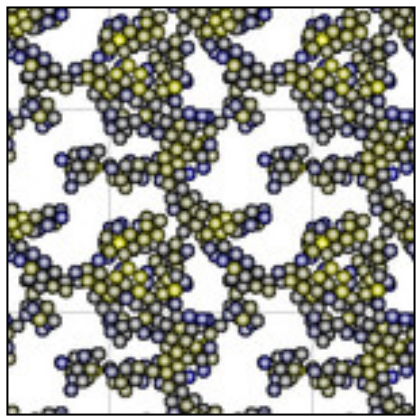
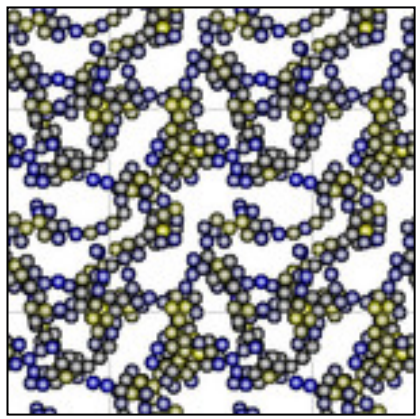


A+R: Microstructure

Attraction →

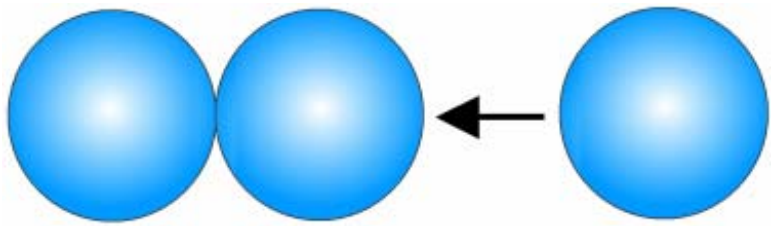
$t/t_B = 1500$

Repulsion ↑

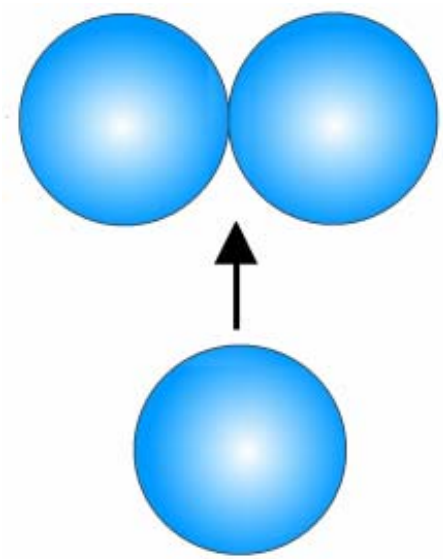
	$\varepsilon_A/kT = 5.9$	$\varepsilon_A/kT = 7.1$	$\varepsilon_A/kT = 11.8$	$\varepsilon_A/kT = 29.6$
$\varepsilon_R/\varepsilon_{ref} = 1.0$				
$\varepsilon_R/\varepsilon_{ref} = 0.1$				
$\varepsilon_R/\varepsilon_{ref} = 0.0$				

A+R: Bond Formation and Cluster Growth

I.



II.

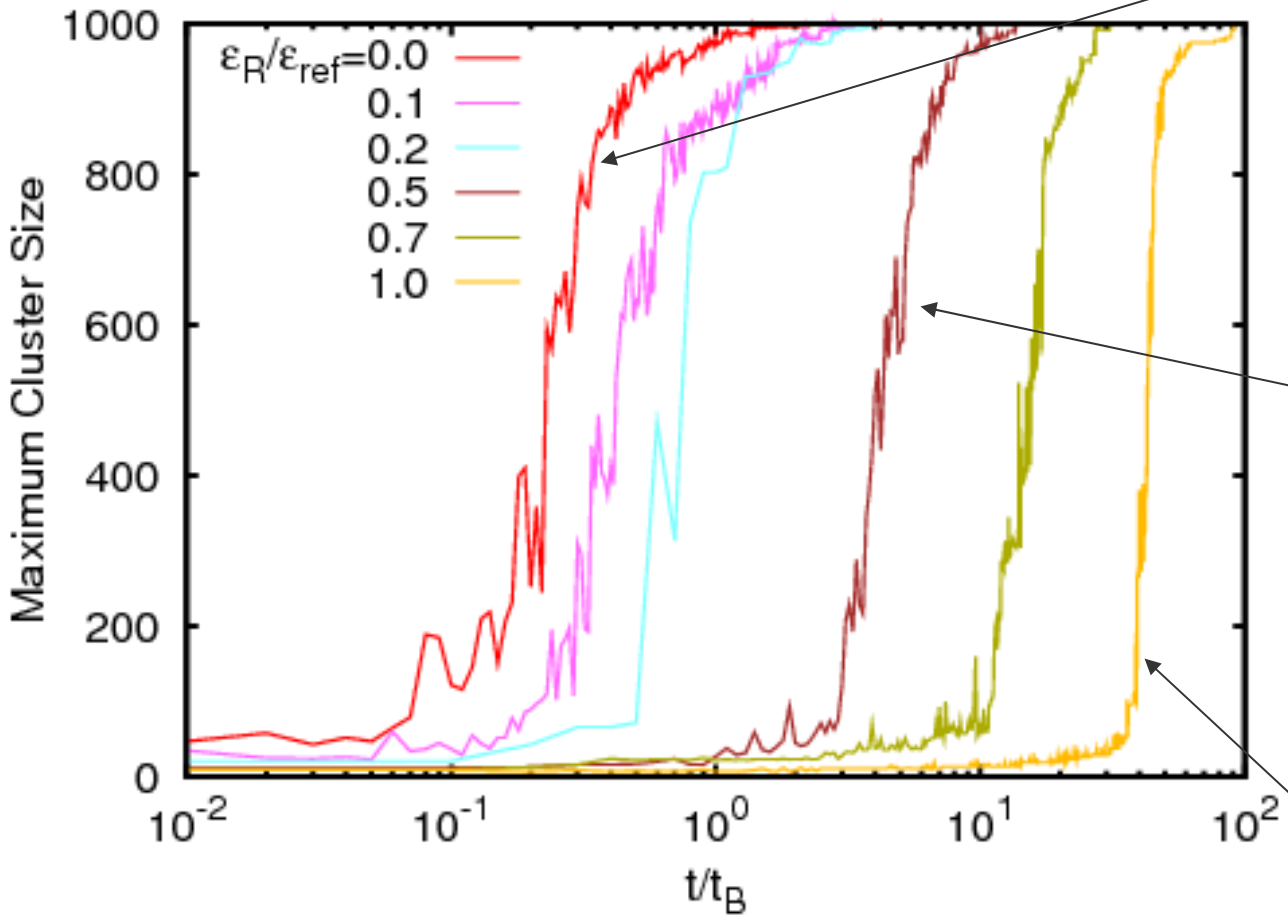


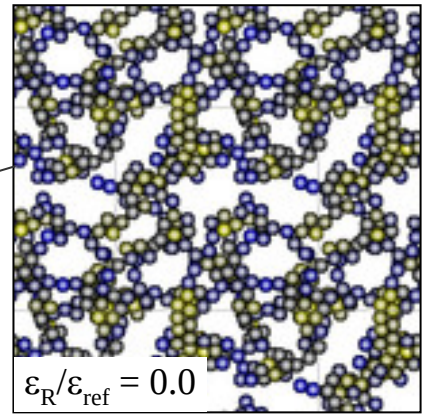
Time scale for bond formation $\sim t_{\mathrm{B}} \exp\left(\frac{\epsilon_R}{kT}\right)$

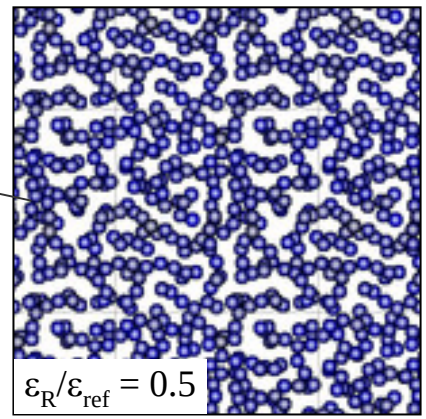
Time scale for bond breakup $\sim t_{\mathrm{B}} \exp\left(\frac{\epsilon_A}{kT}\right)$

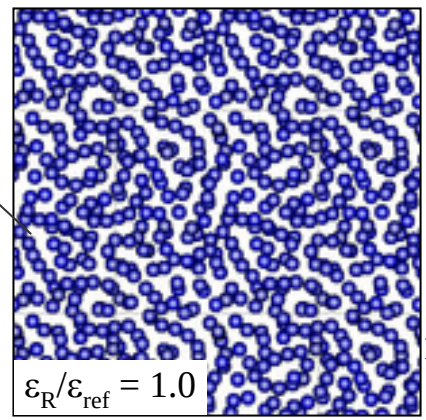
A+R: Maximum Cluster Size

$\varepsilon_A/kT = 29.6$



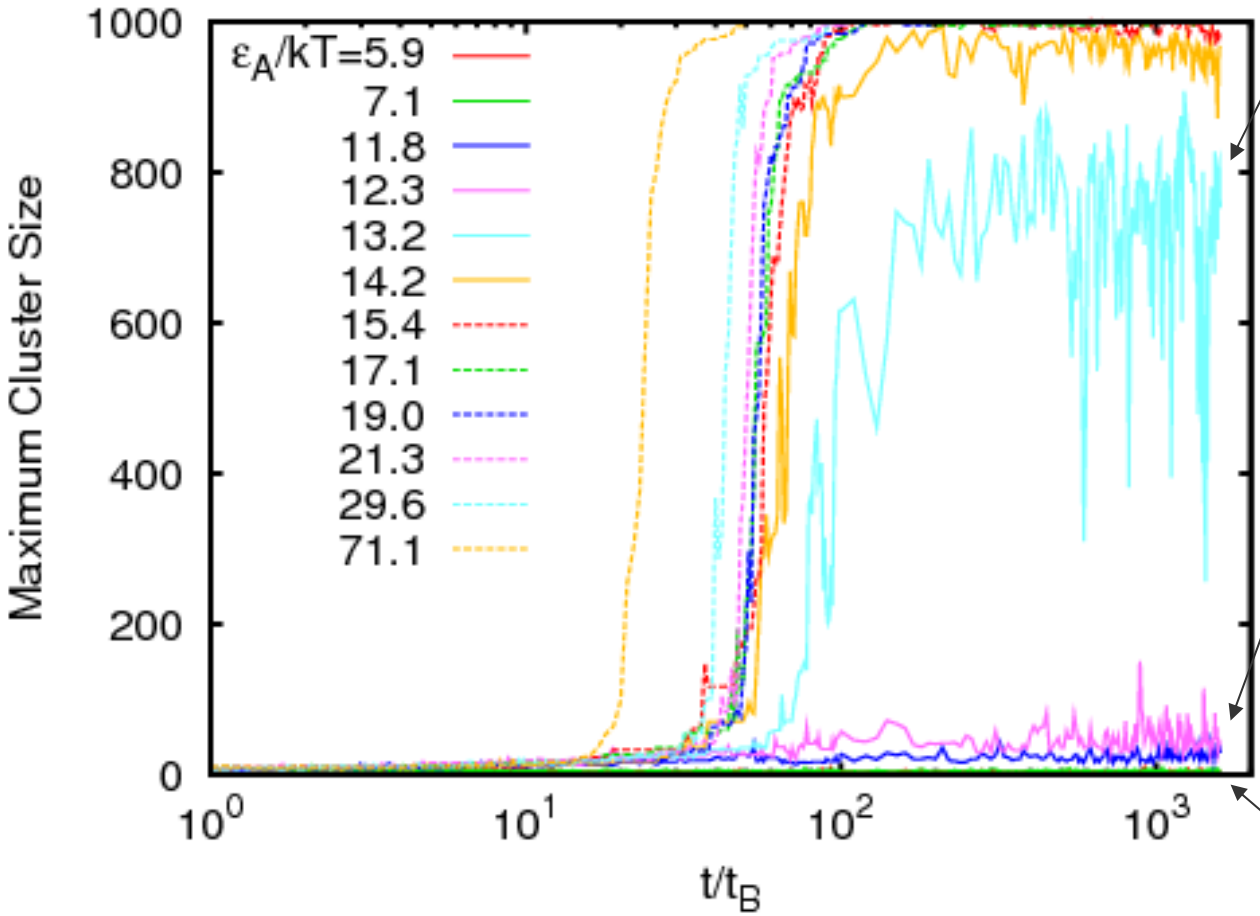


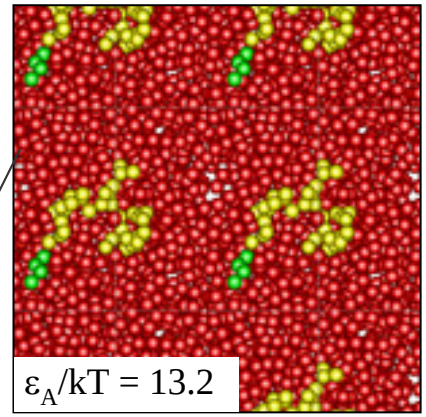


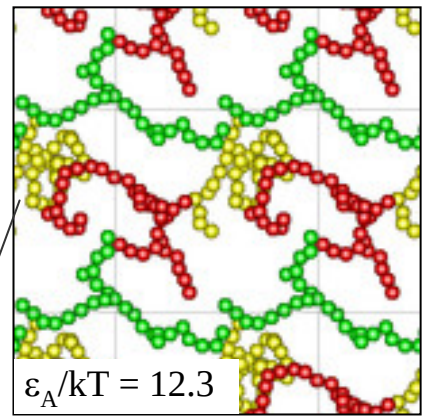


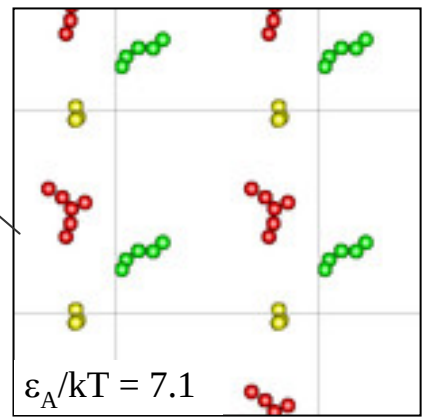
A+R: Maximum Cluster Size

$\varepsilon_R/\varepsilon_{ref} = 1.0$



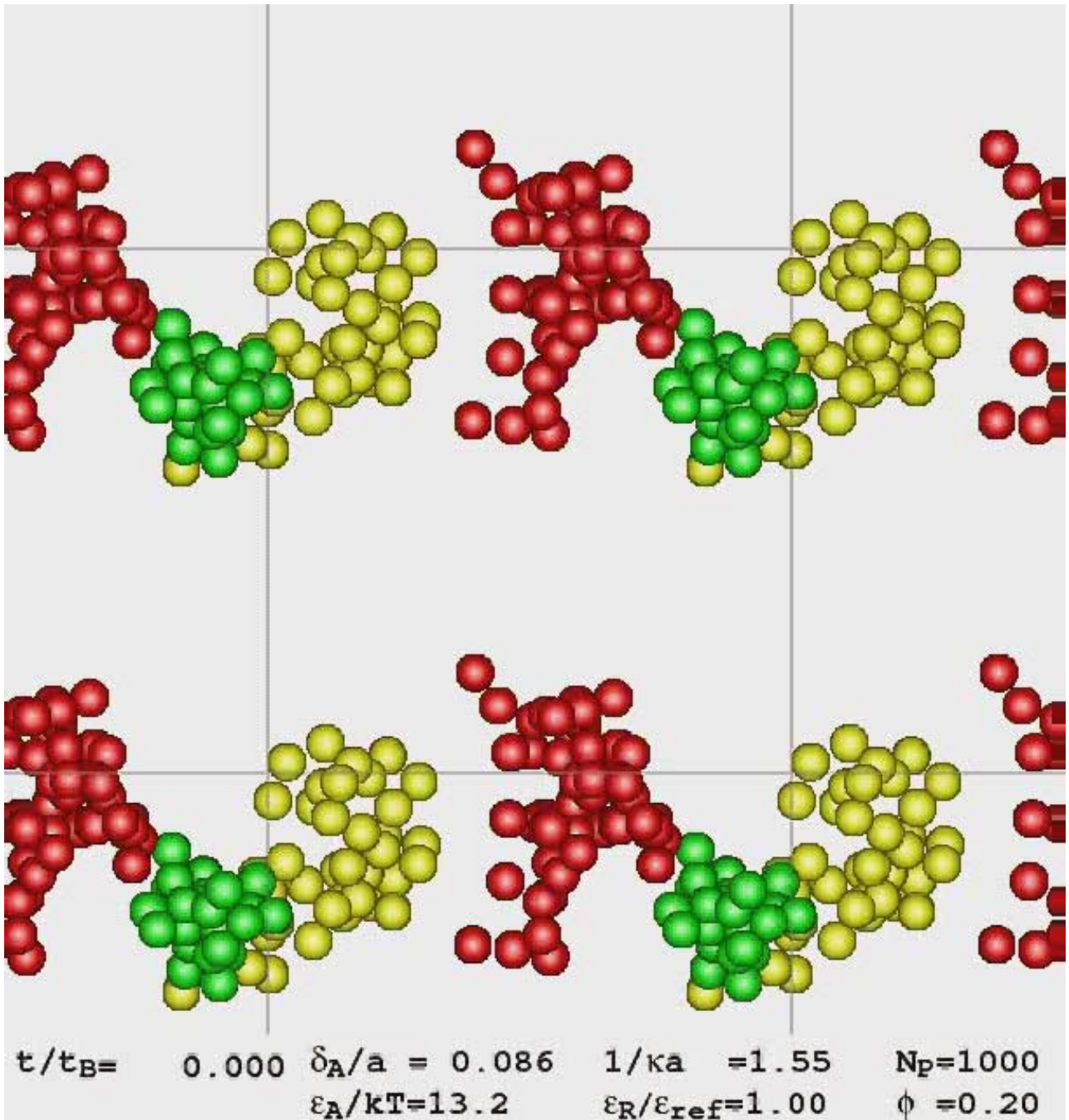






Cluster Growth

$\varepsilon_R/\varepsilon_{ref}$ = 1.0, ε_A/kT= 13.2



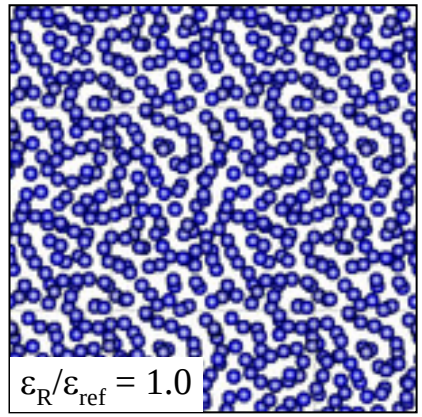
Conclusion

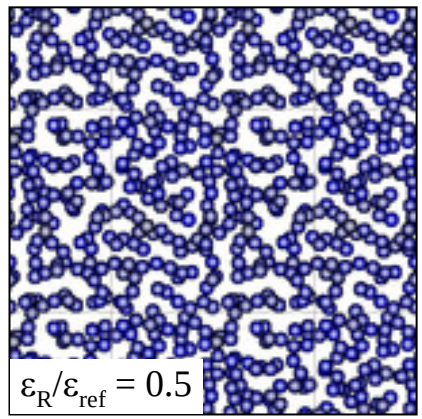
- Summary
  - Fluids, crystals, clusters, gels
  - Wide range of microstructures and dynamics
  - Increasing $\varepsilon_R \rightarrow$ thinner structures, longer time scales

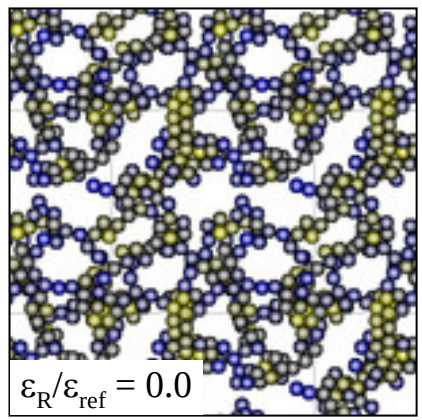
Interparticle Interactions → Microstructure & Dynamics → Macroscopic Properties & Behavior

- Future Work
  - Explore gel rheology (elastic modulus, viscosity, response to and relaxation from shear)
  - Interleave Stokesian Dynamics for rheological calculations
  - Importance of hydrodynamic interactions

    (Stokesian vs. Fast Lubrication vs. Brownian Dynamics)







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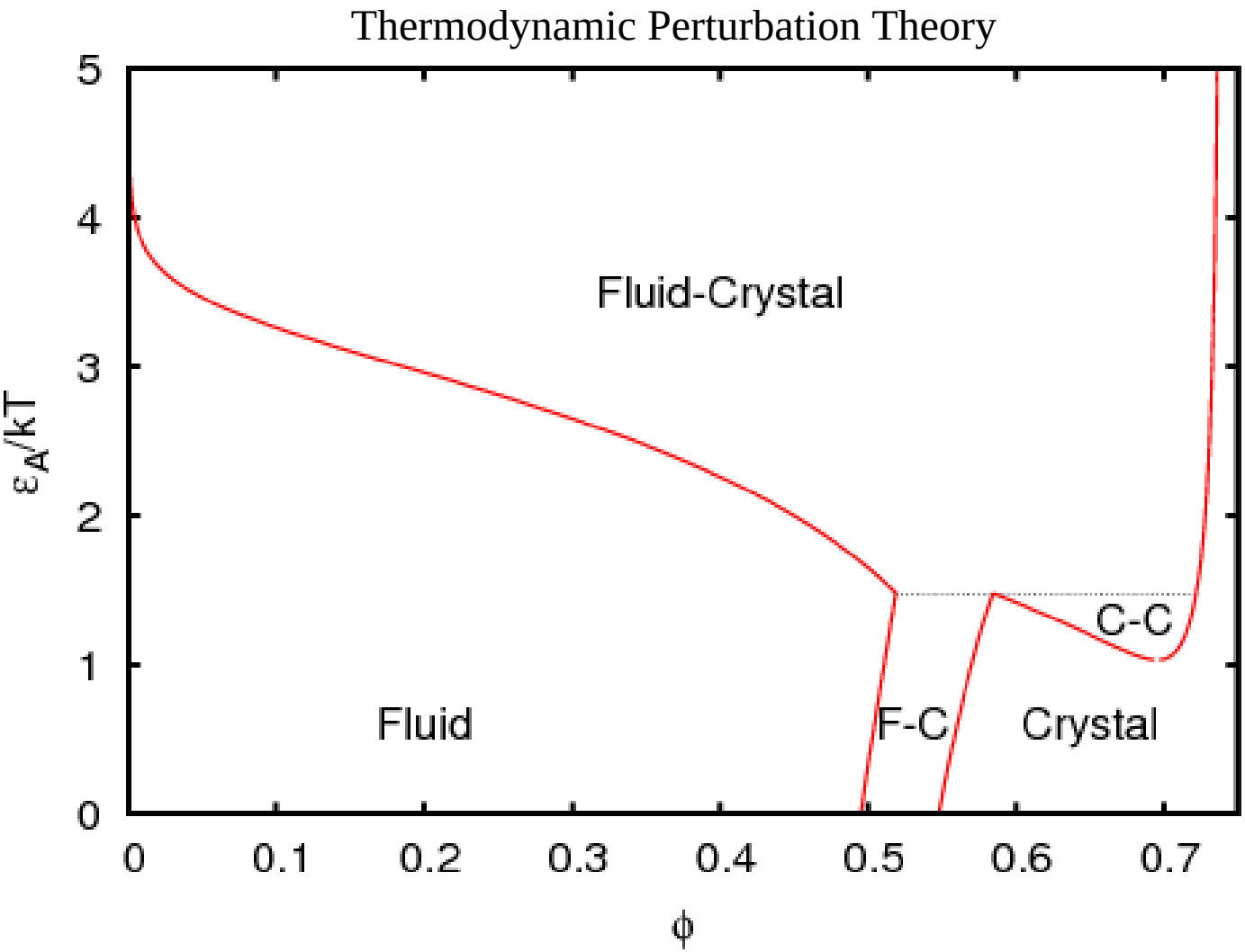
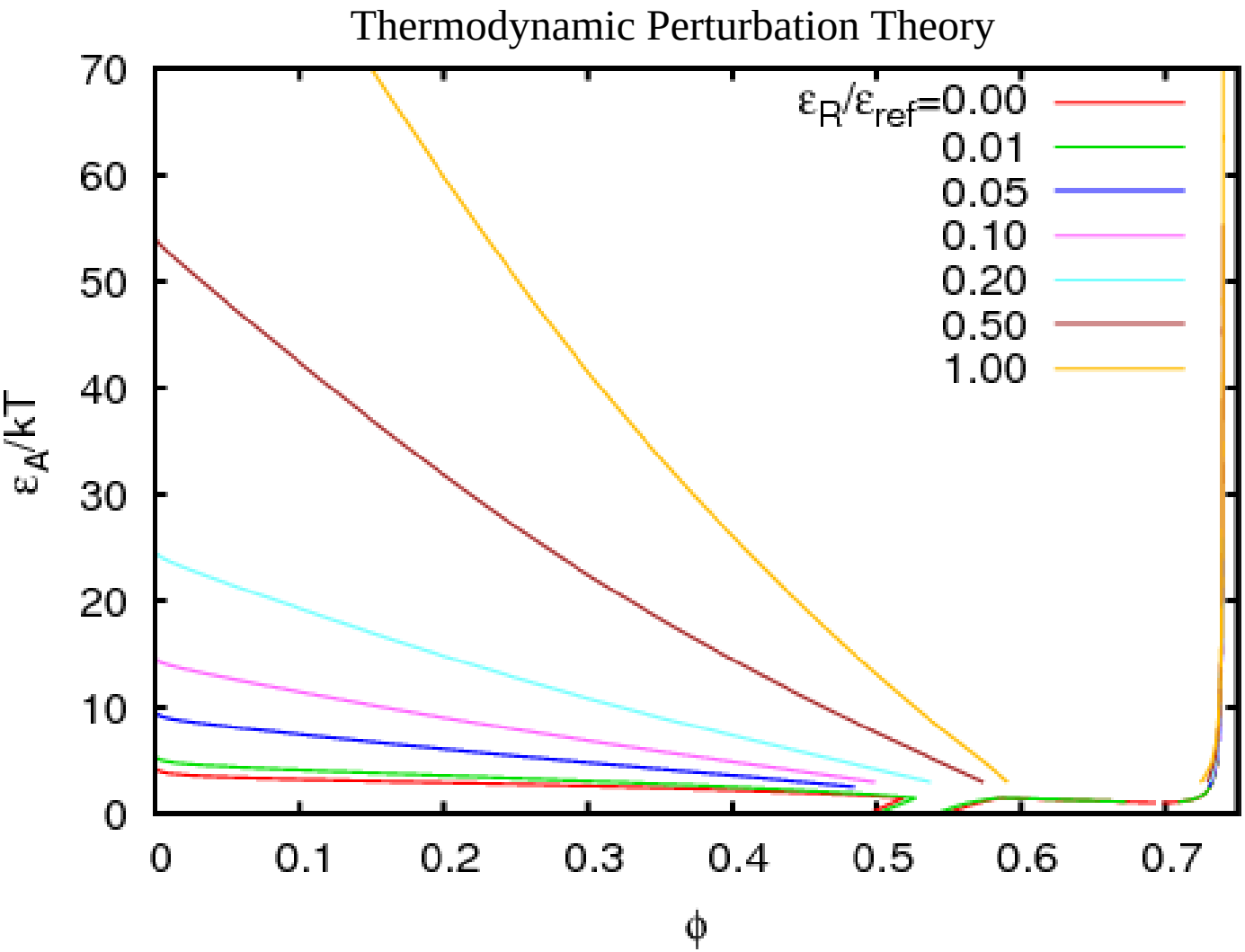
A: Equilibrium Phase Diagram

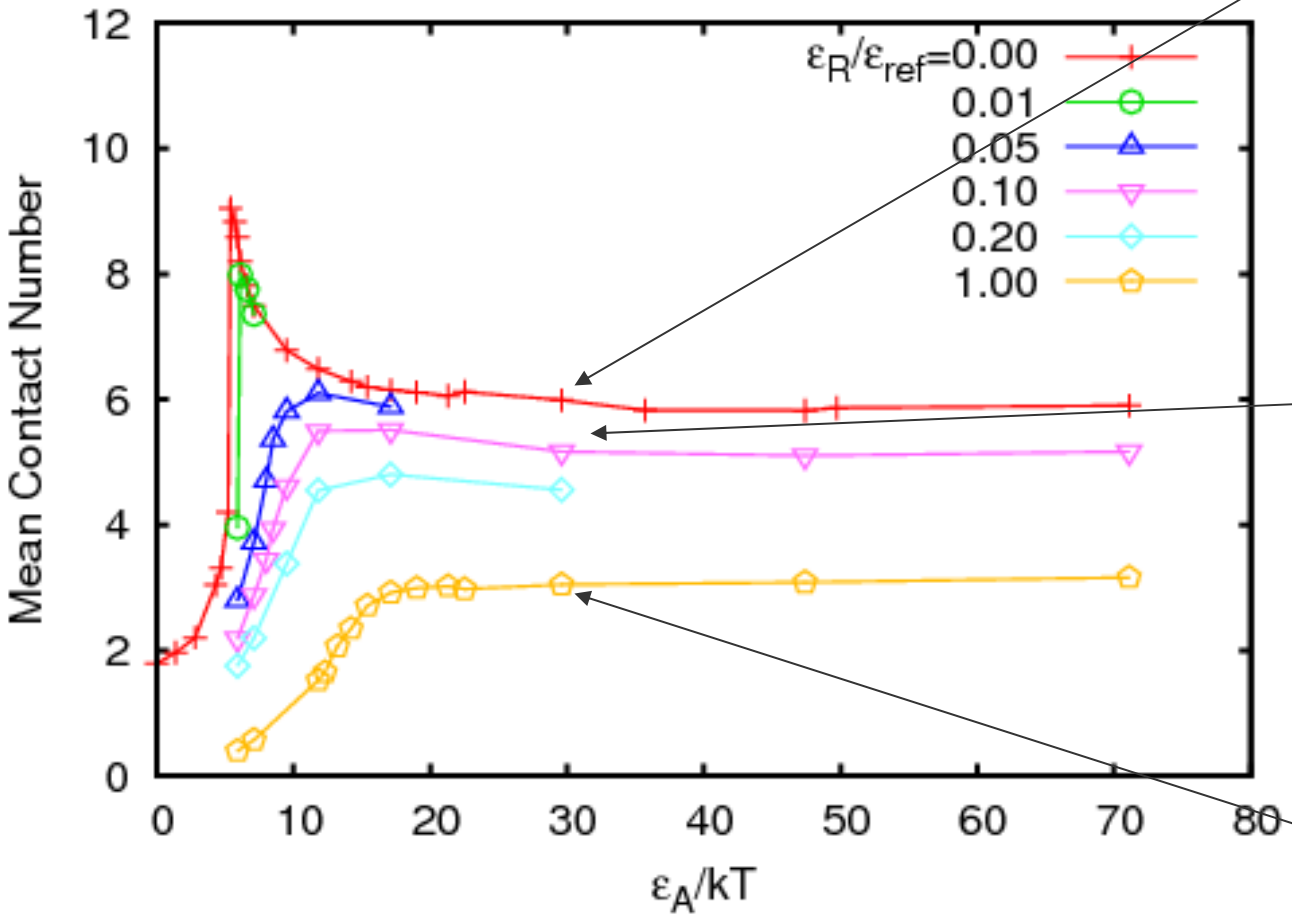


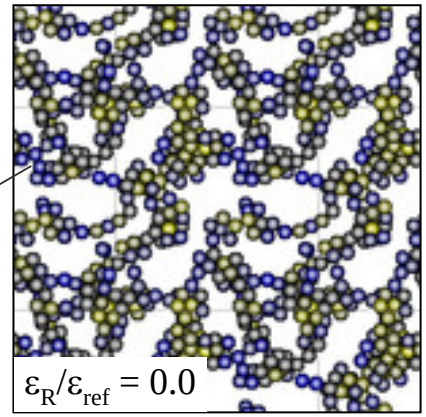
A+R: Equilibrium Phase Diagram

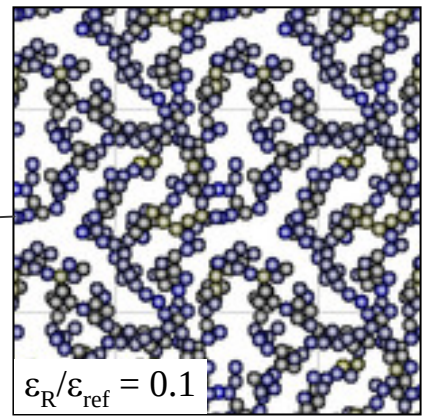


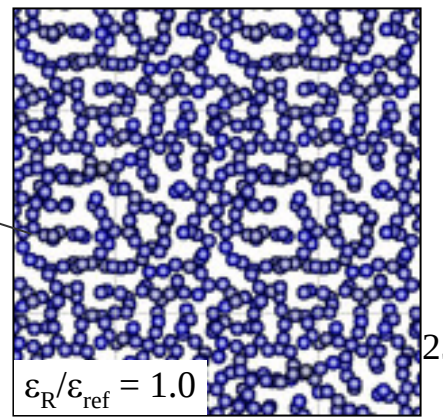
A+R: Mean Contact Number

t/t_B = 1500



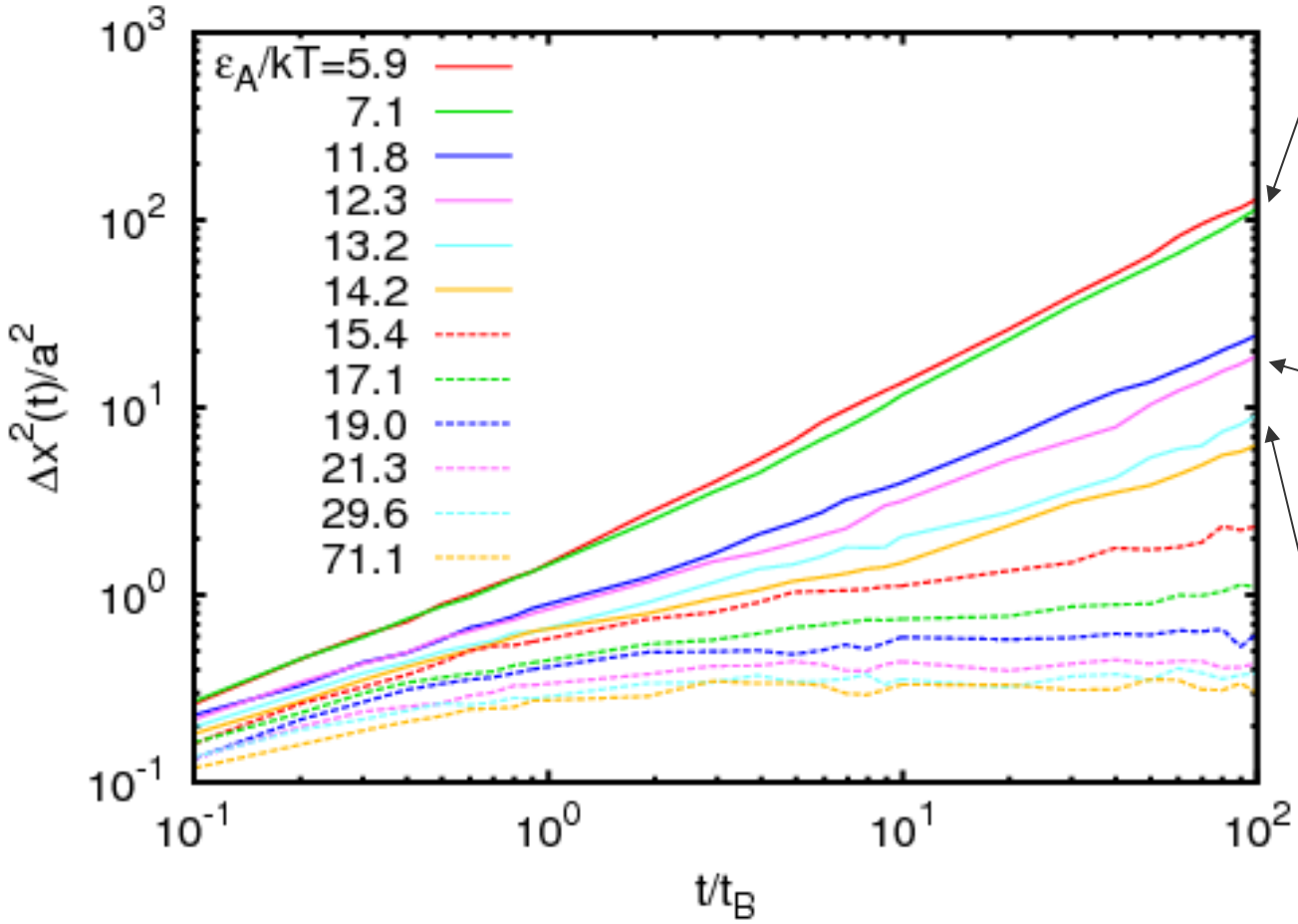


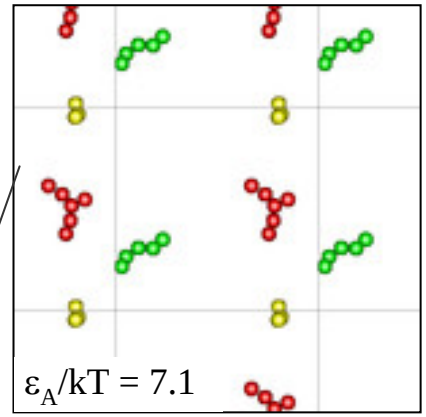


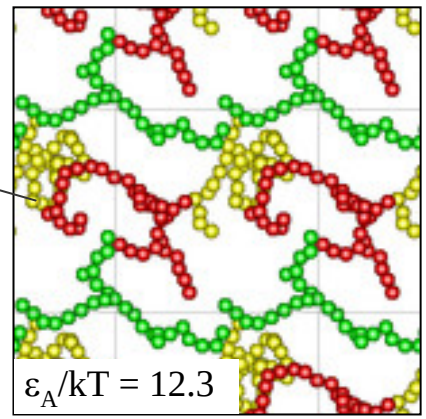


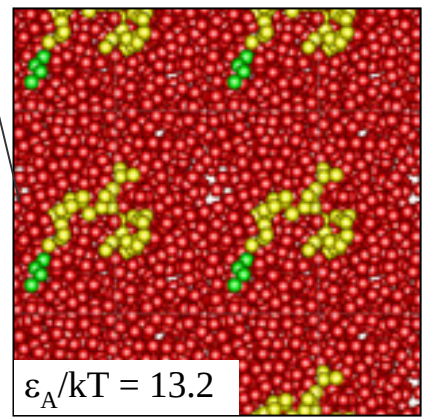
A+R: Mean Square Displacement

$\varepsilon_R/\varepsilon_{ref}$ = 1.0









A+R: Localization Length

$t/t_B = 1500$