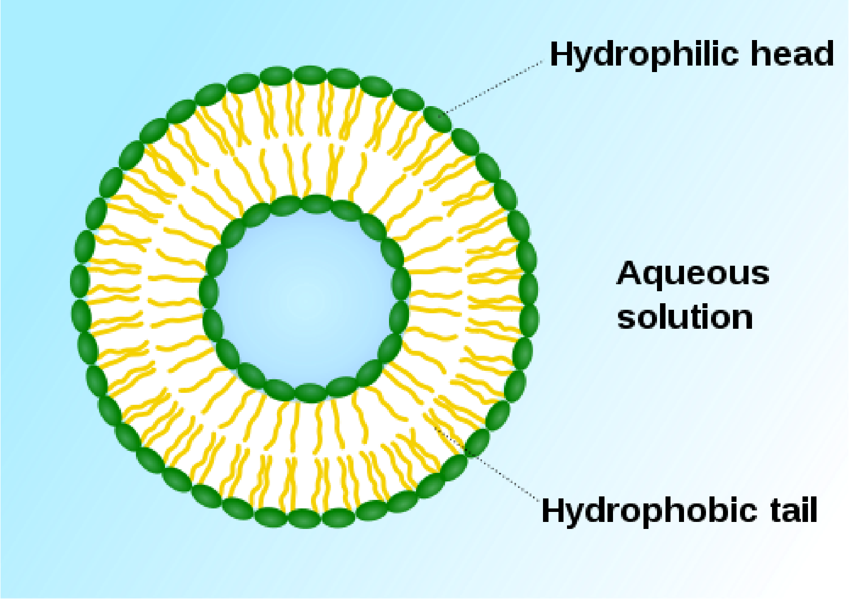
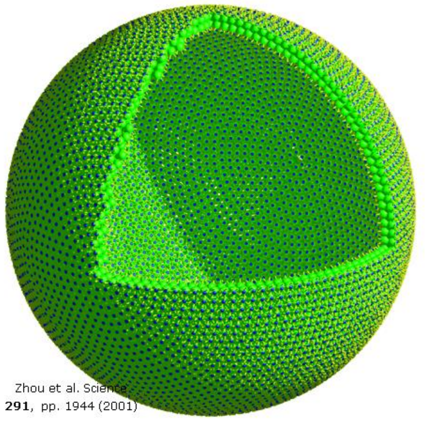
Modeling the Free Energy Landscape for Janus Particle Self-Assembly in the Gas Phase

Andy Long
Kridsanaphong Limtragool

Motivation

- We want to study the spontaneous formation of micelles and vesicles
- Applications in drug delivery and biological self-assembly





Past work

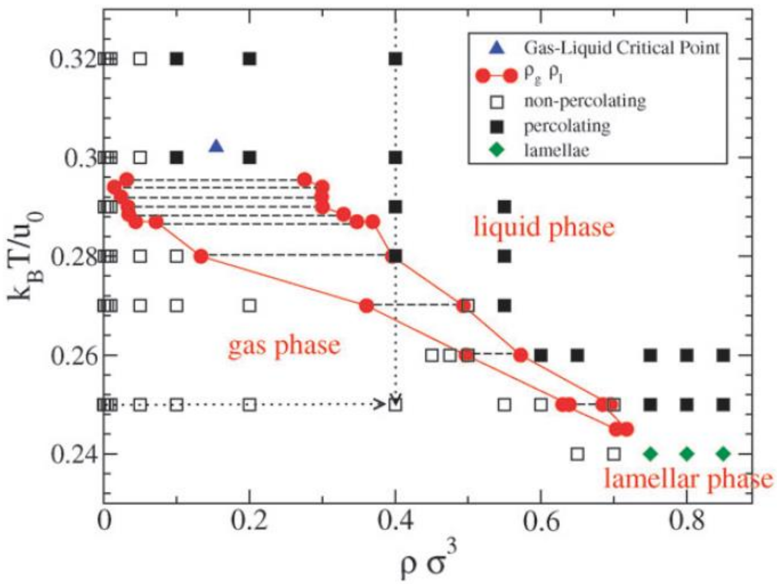
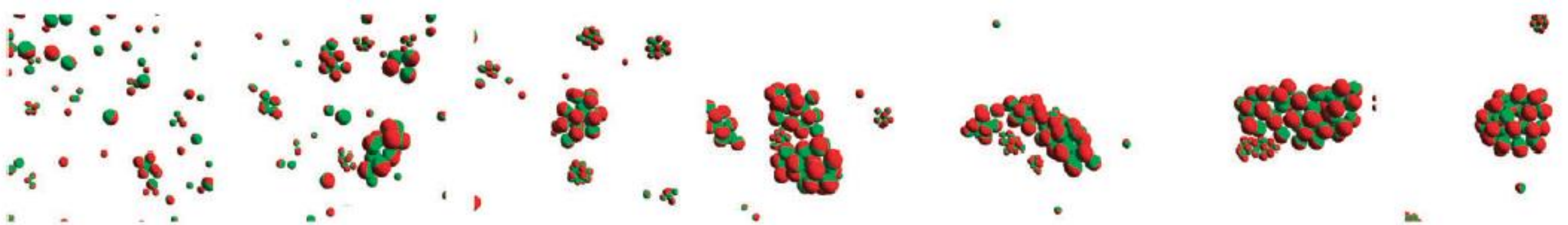


Fig. 4 Phase diagram of the Janus particles. Filled (red) circles indicate the gas–liquid coexistence lines with the (blue) triangle denoting the critical point. The filled and open squares indicate the percolating and non-percolating state points, respectively, whereas (green) diamonds indicate the simulations that show a lamellar phase. Dashed lines connect coexisting state points whereas the two dotted lines refer to the two paths followed in the calculation of the structure factor of Fig. 8.



(a)25.000 (b)125.000 (c)500.000 (d)750.000 (e)825.000 (f)950.000 (g)1.000.000

Fig. 10 Snapshot from a simulation at $\rho = 0.005$ and $T = 0.25$ for several MC steps, indicated in the labels. The initial configuration, composed by isolated monomers, quickly evolves to form small micelles (a–c). The final vesicle (g) arises from a collision between three distinct micelles (d–e) which form an elongated transient tubular cluster (f). Each picture has a side length of 9σ.

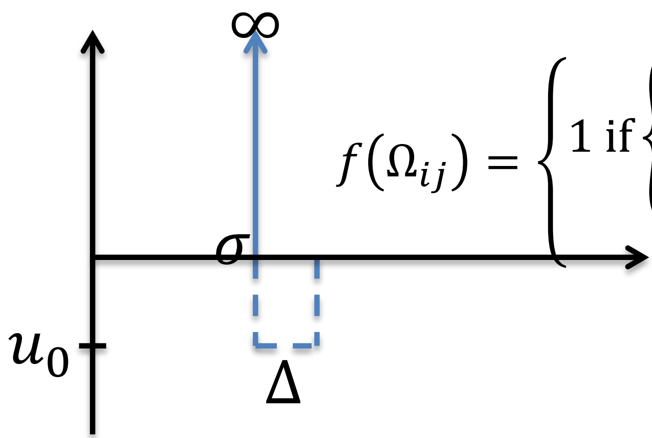
Outline of the project

- Use canonical ensemble MC to simulate system of Janus particles with umbrella sampling
- Use weighted histogram analysis method (WHAM) to reconstruct a free energy surface
- Investigate assembly landscapes for different temperature/density systems

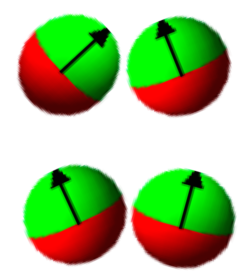
Janus Particle System

- Kern-Frenkel Janus Particle
- Hard sphere on one side and hard sphere with a square-well attraction on the other side

$$U(\vec{r}_{ij}) = u(\vec{r}_{ij}) f(\Omega_{ij})$$



$$f(\Omega_{ij}) = \begin{cases} 1 \text{ if } \begin{cases} \vec{r}_{ij} \cdot \vec{n}_i > 0 \\ \text{and} \\ \vec{r}_{ji} \cdot \vec{n}_j > 0 \end{cases} \\ 0 \quad \text{else} \end{cases}$$



Free energy calculation

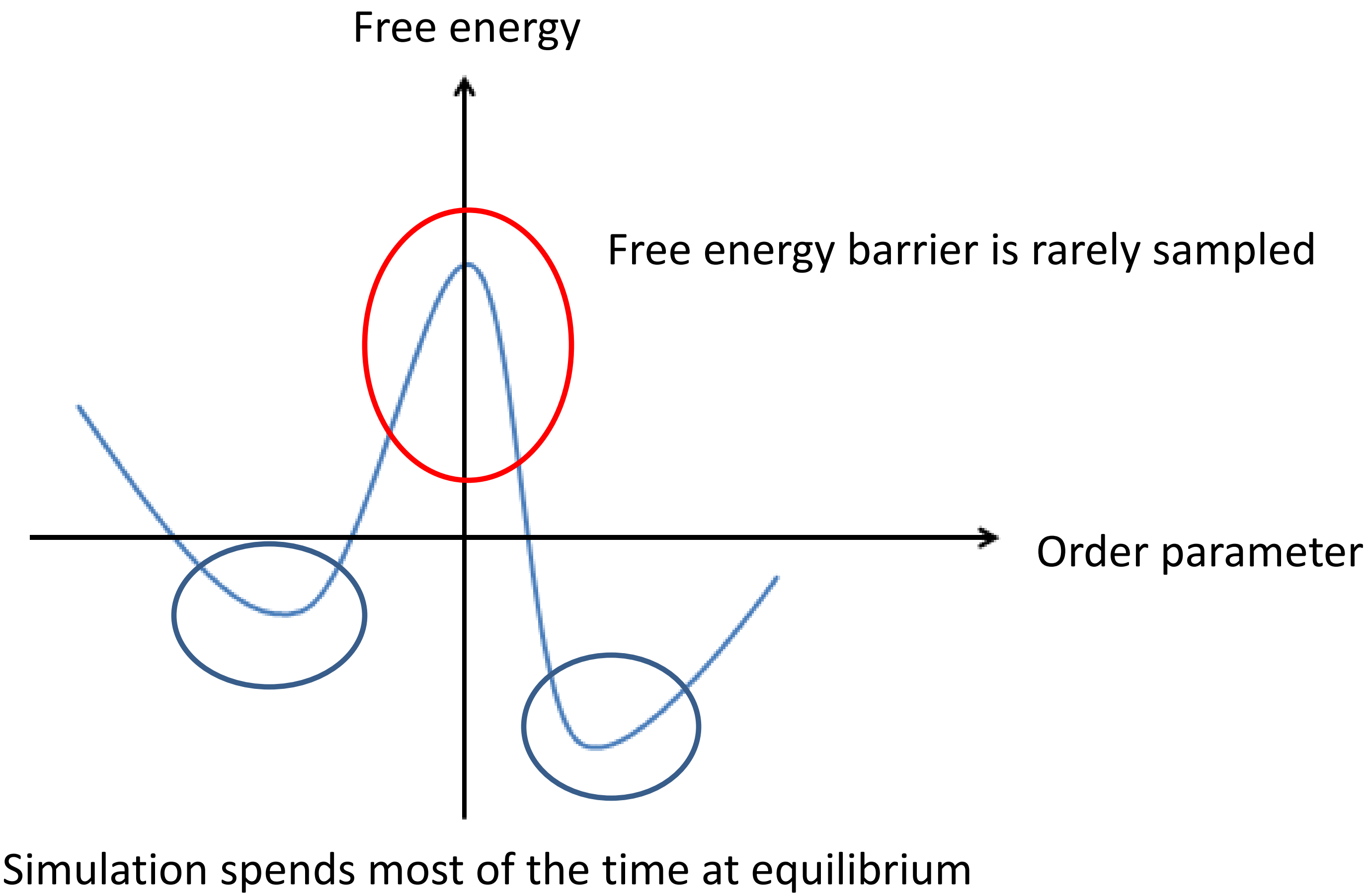
- Want to calculate the free energy along the reaction coordinate/order parameter ξ

$$A(\xi) = -\frac{1}{\beta}\ln Q(\xi)$$

where $$Q(\xi) = \frac{\int \delta(\xi(r) - \xi)\exp(-\beta E)\, d^N r}{\int \exp(-\beta E)\, d^N r}$$

- $Q(\xi)$ can be obtained from the probability distribution of ξ
- Can use MC/MD to find $Q(\xi)$ directly

Problem with direct sampling



Umbrella sampling

- Bias the sampling toward a fixed order parameter by a harmonic potential

$$\alpha(\xi) = k_B T \frac{\kappa}{2} (\xi - \xi_0)^2$$

- Construct histograms for the distribution of ξ at various fixed points along the chosen order parameter

Reaction Coordinate/Order Parameter

- Use the order 4th rotationally invariant spherical harmonics : Q_4
- Used in umbrella sampling of nucleation of Lennard Jones clusters to drive from liquid to aggregate structures

$$\bar{Q}_{lm} \equiv \frac{1}{N_b} \sum_{r_{ij}} Y_{lm}\left(\theta(r_{ij}), \phi(r_{ij})\right)$$

$$Q_l \equiv \left[\frac{4\pi}{2l+1} \sum_{m=-l}^{l} |\bar{Q}_{lm}|^2\right]^{\frac{1}{2}}$$

Canonical Ensemble MC

- Possible particles moves
  - translation
  - rotation of a patch vector
- Add harmonic potential term to total energy for umbrella sampling

$$acc(s_i \rightarrow s_i') = \min\left\{1, e^{-\beta \Delta V} e^{-\beta \Delta \alpha}\right\}$$

- Construct histograms of Q_4 for set of fixed Q_4 windows

Reconstruct free energy surface

- Use WHAM to reconstruct the free energy surface
- Need to convert the biased distributions of Q_4 to become unbiased
- Tries to find weights for each window that maximize the expected likelihood of the data from our unbiased distribution

How to use WHAM

- Self-consistently solve the system of equations

$$P^{\mathrm{u}}(\xi) = \sum_{i}^{\text{windows}} p_i(\xi) P_i^{\mathrm{u}}(\xi)$$

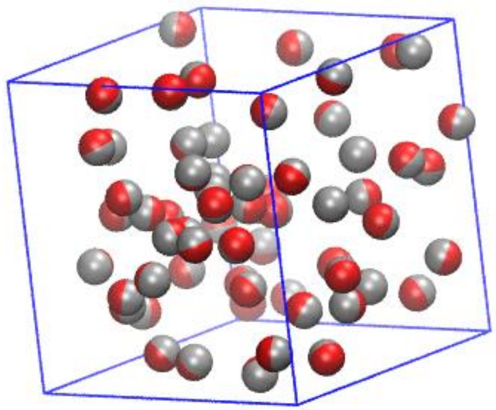
$$p_i = \frac{a_i}{\sum_j a_j},\ a_i(\xi) = N_i \exp[-\beta\,\omega_i(\xi) + \beta F_i]$$

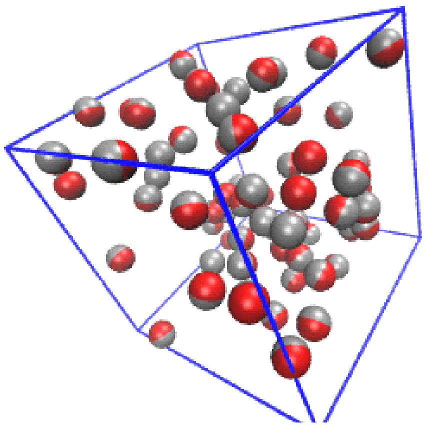
$$\exp(-\beta F_i) = \int P^{\mathrm{u}}(\xi) \exp[-\beta w_i(\xi)]\, d\xi$$

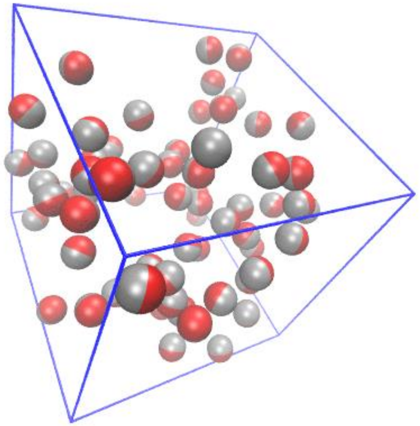
- Calculate A(ξ) from P(ξ)

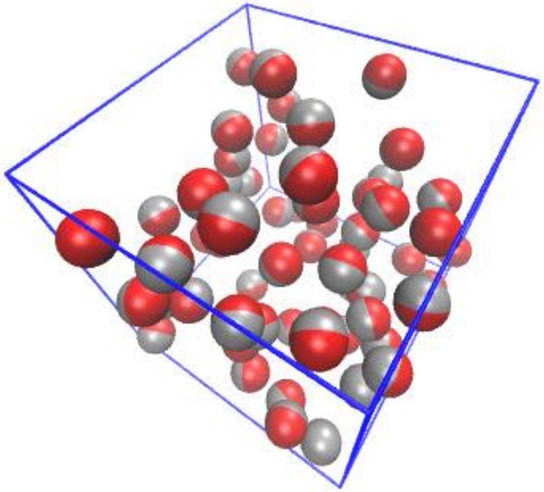
$$A(\xi) = -\frac{1}{\beta} \ln P^u(\xi)$$

Different Assembly Phenomena



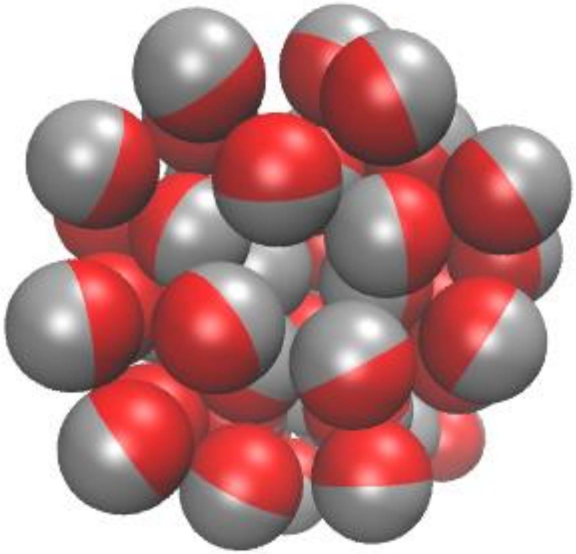




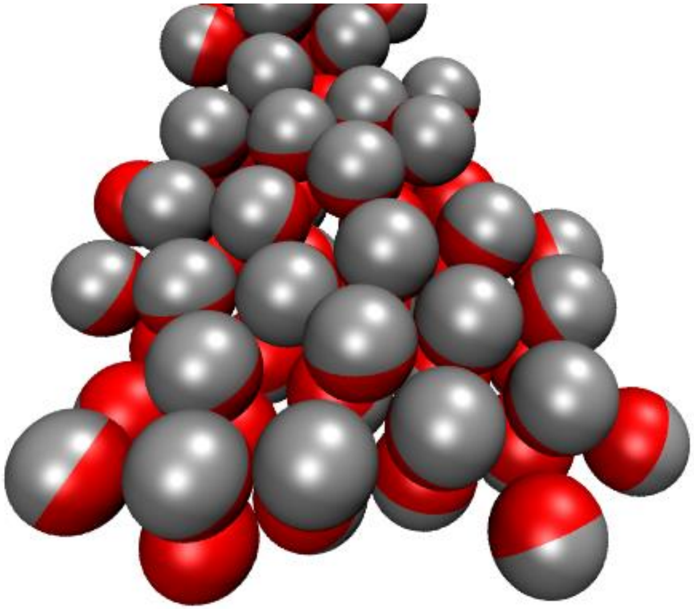


Structures

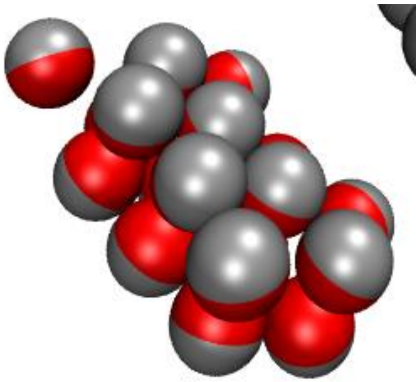
Vesicle



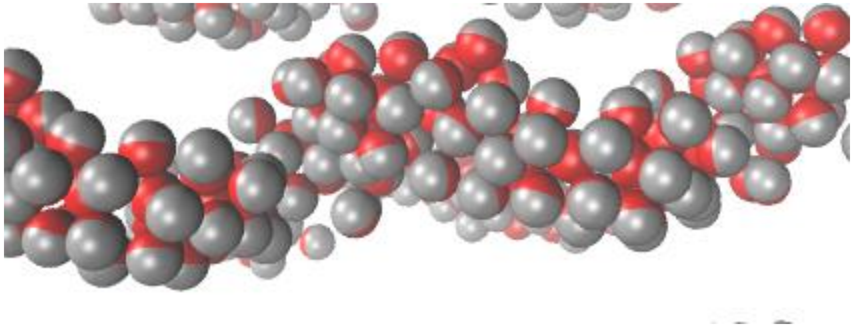
Sheet



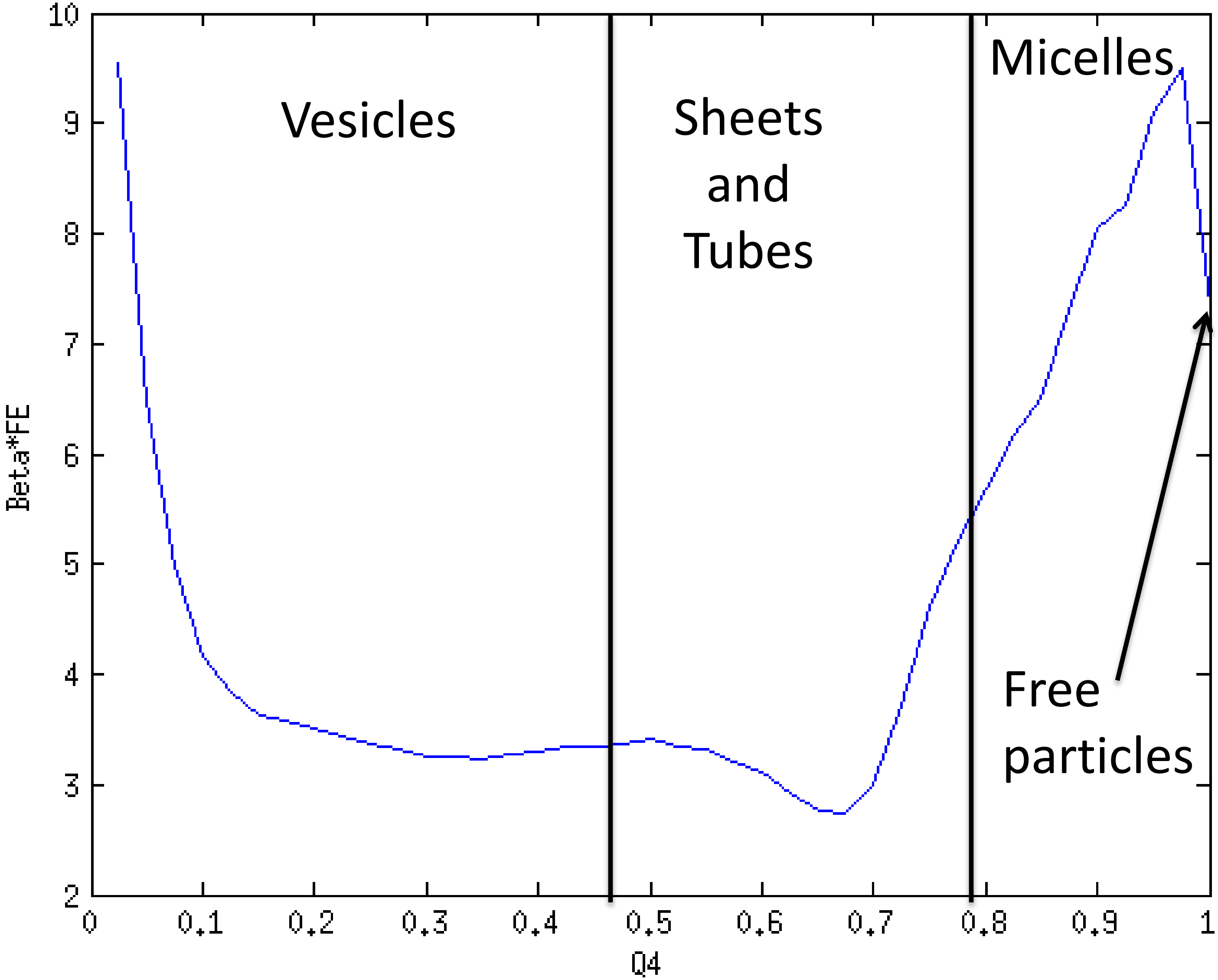
Micelle



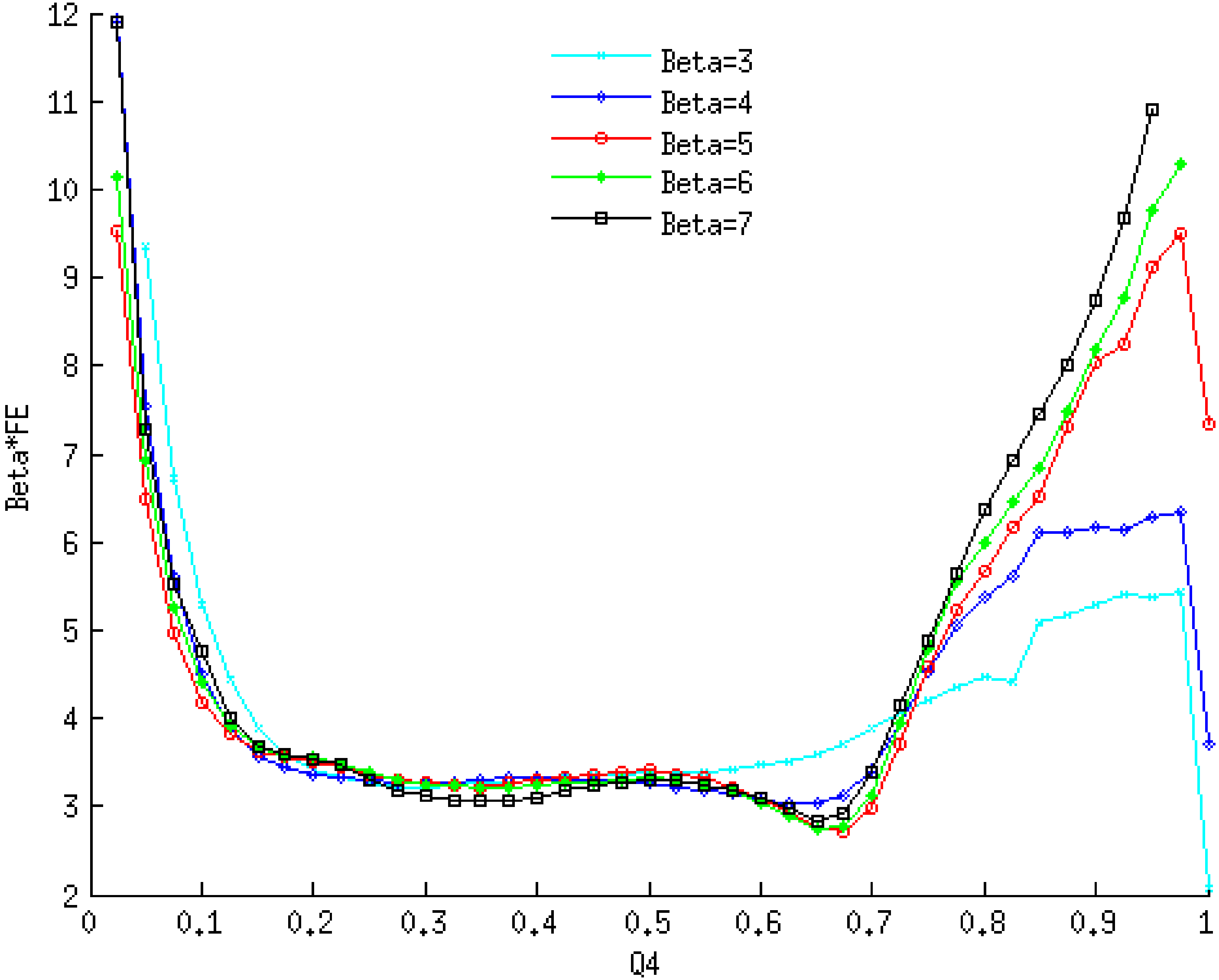
Tube



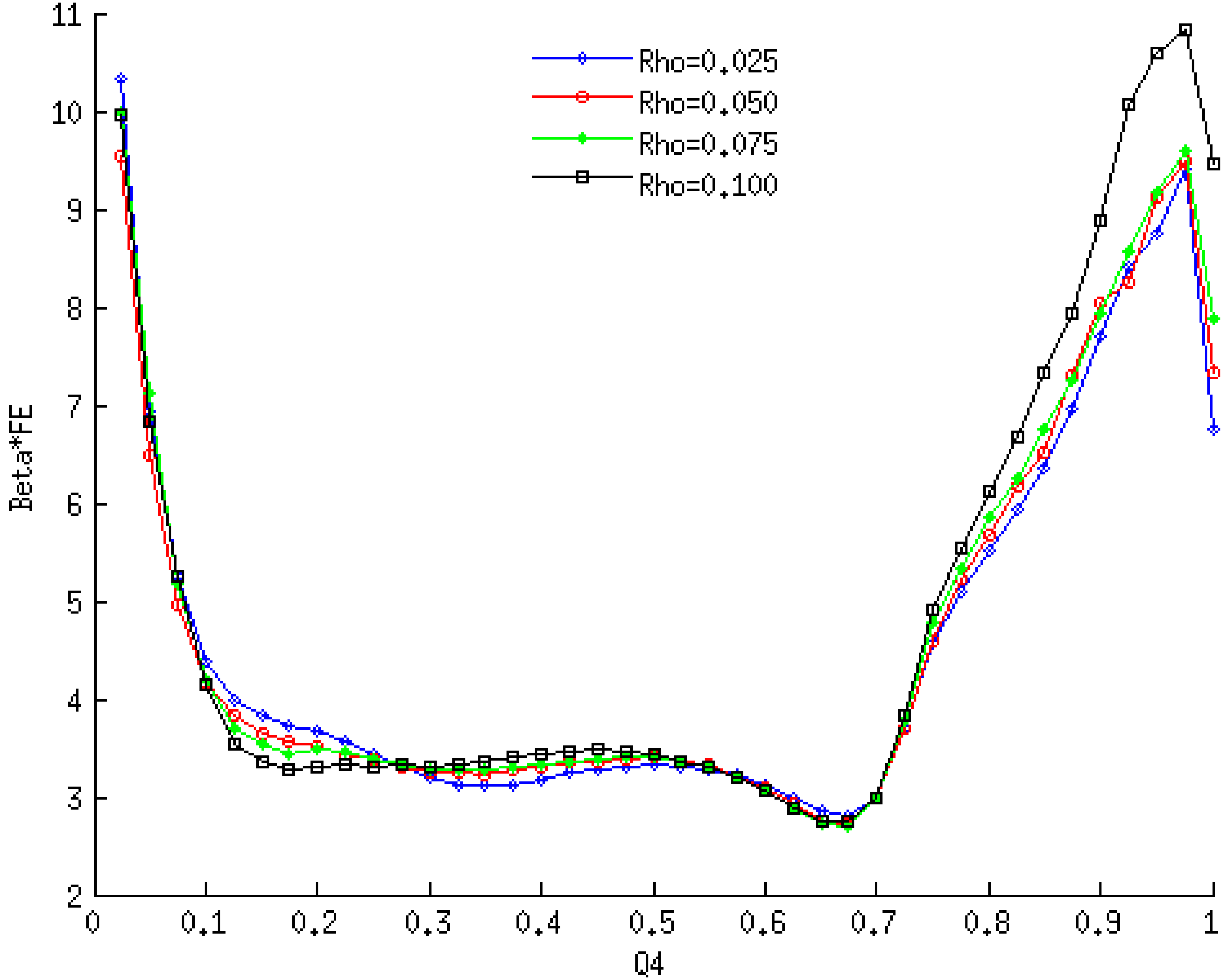
Mapping Structure to FE Landscape



Constant Density ($\rho\sigma^3 = 0.05$)



Constant Temperature ($\beta = 5$)



Conclusions

- Umbrella sampling able to bias simulations to different assembled structures
- Able to effectively capture the assembly landscape for Janus particles based on local particle symmetry using the WHAM algorithm
- Issues with chosen reaction coordinate

Proposed Future Work

- Bias based on a cluster order parameter, not particle order parameter
- Incorporate Grand/Gibbs Canonical moves to allow for easier fluctuations in structure as cell volume and number of particles change
- Utilize generalized geometric cluster algorithm to allow for cluster moves

References

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[6] http://www.engr.ucsb.edu/~shell/che210d/Biased_sampling.pdf