Electronic Supplementary Material (ESI) for Soft Matter.

Electronic Supplementary Information for: Thermodynamic signatures and cluster properties of self-assembly in systems with competing interactions

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I. RADIAL DISTRIBUTION FUNCTIONS

Radial distribution functions were calculated to provide insight into how the key entities of the self-assembled systems, free oligomer-sized and large clusters, interact. The radial distribution functions for oligomer-oligomer and oligomer-cluster, plotted in Fig. 1, show little difference between different temperatures and ε values. Oligomer-oligomer radial distributions show that as the temperature increases oligomers are able to approach closer to each other. Similarly, the oligomer-cluster radial distribution functions show that oligomers are able to approach clusters closer at higher temperatures. Attractions and repulsions between oligomers and clusters are also slightly stronger and longer-ranged at lower temperatures. For the cluster-cluster radial distribution functions (Fig. 2), the amplitude fades more drastically with temperature. The $\varepsilon = 1.0$ radial distribution functions are shifted to lower values than for $\varepsilon = 1.6$; the insert of Fig. 2 shows that this shift is due to the different sizes of clusters. Importantly, the radial distribution functions show that there are no qualitative differences in the interactions between different cluster sizes as a function of temperature for the different attraction strengths, and cannot, therefore, explain the repulsion-dominated pressure behavior.

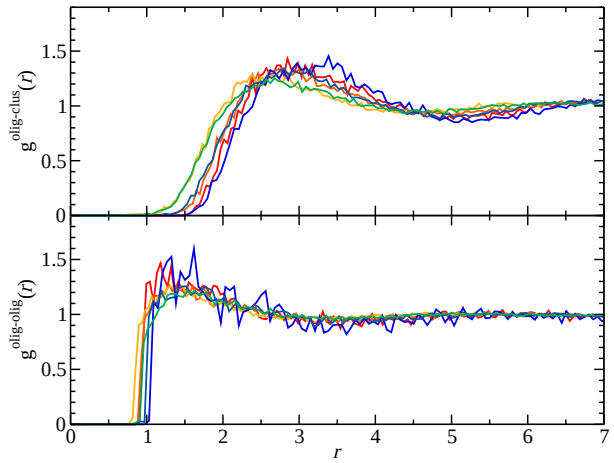

FIG. 1: Oligomer-oligomer ($g^{\text{olig-olig}}(r)$, bottom) and oligomer-cluster ($g^{\text{olig-clus}}(r)$, top) radial distribution functions. Calculated using center-of-mass positions of all oligomer-sized clusters of size $M \leq M_{\text{olig}}$ and large clusters of size $M > M_{\text{olig}}$. All data are from MD simulations with $L = 30\sigma$, at $\rho = 0.63$. The color code is the same as in the pressure figure in the main text.

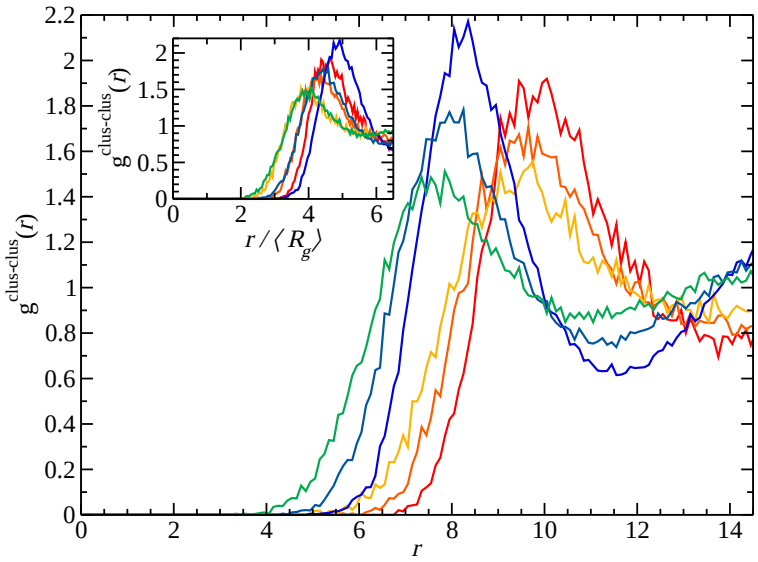

FIG. 2: Cluster-cluster ($g^{\text{clus-clus}}(r)$) radial distribution functions. Calculated using center-of-mass positions of large clusters of size $M > M_{\text{olig}}$. The insert shows the x-axis normalized by the average radius of gyration of the preferred cluster size. All data are from MD simulations with $L = 30\sigma$ and $\rho = 0.63$. The color code is the same as in the pressure figure in the main text.

II. RADIUS OF GYRATION

The principal radii of gyration for different cluster sizes at the higher temperature of interest are plotted in Fig. 3. Similar to model surfactants[1, 2], as clusters grow, their shape changes from more spherical to rod-like. This is distinct from the sphere-to-oblate behavior observed in the moment of inertia figures with respect to temperature. Similar behavior of $\langle R_g \rangle (M)$ is observed at lower temperatures. The rod-like clusters that form, are best described as aspherical, as opposed to well defined rods. However, the $\langle R_g \rangle (M)$ trend is another example of surfactant-like behavior. For surfactants, it is argued that this is due to a decrease in head-to-tail ratio[3], and the limit of the distance of the tail-length anchoring to the center. For SALR systems, the effective range of attraction seems to anchor the particles; it seems that it is preferable to transition into one single, as opposed to two, elongated axes.

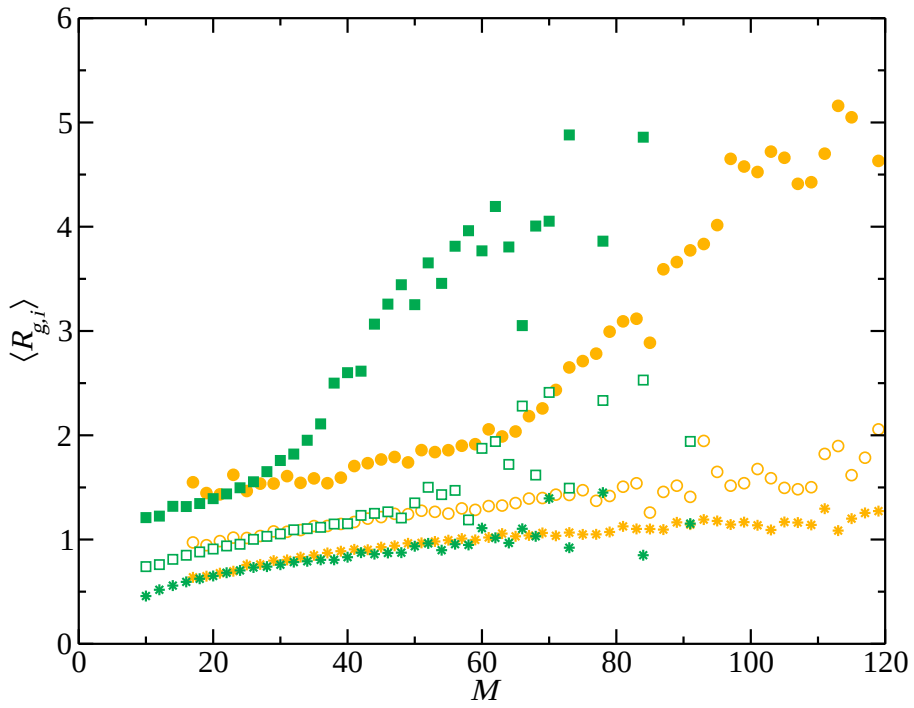

FIG. 3: Average radius of gyration of clusters with M particles along the principal (closed symbols), secondary (open symbols) and tertiary (stars) axes for $\varepsilon = 1.0, k_B T = 0.374$ (green squares) and $\varepsilon = 1.6, k_B T = 0.725$ (orange circles). All data are from MD simulations with $L = 30\sigma$ and $\rho = 0.63$.

III. CONFIGURATION SNAPSHOTS

The configurations at additional temperatures (Fig. 4) show that there is not a drastic change between the two ε values, as temperature increases. It is apparent that at lower temperatures: more particles are in clusters (due to the lower ρ_{ccd}), that the clusters are more spherical (in agreement with the ratios of the moments of inertia) and are more dense (in agreement with the density profiles).

[1] A. D. Mackie, A. Z. Panagiotopoulos and I. Szleifer, *Langmuir*, 1997, **13**, 5022–5031.

[2] A. G. Daful, J. B. Avalos and A. D. Mackie, *Langmuir*, 2012, **28**, 3730–43.

[3] J. N. Israelachvili, D. J. Mitchell and W. Ninham, *J. Chem. Soc. Farad. T. 2*, 1975, **60**, 1525–1568.

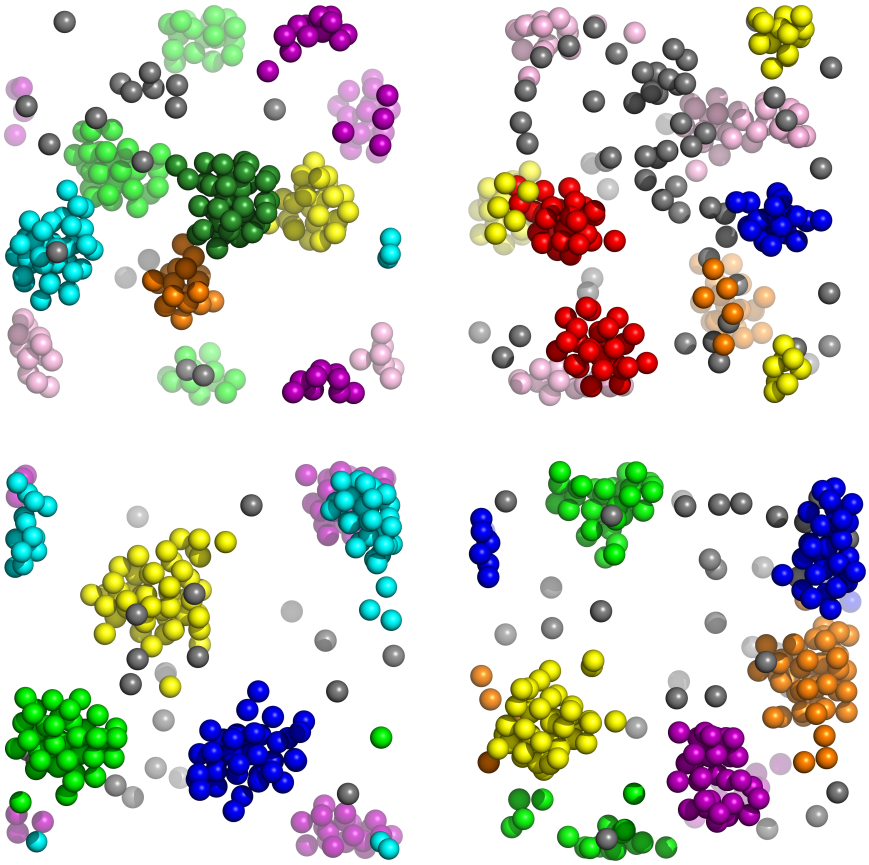

FIG. 4: Snapshots of configurations for $\varepsilon = 1.0$, $k_BT = 0.291$ (top left panel) and $k_BT = 0.333$ (top right panel), and $\varepsilon = 1.6$, $k_BT = 0.607$ (bottom left panel) and $k_BT = 0.674$ (bottom right panel). In both cases $\rho = 0.053$ and $L = 17\sigma$. Particles colored gray are part of different small, free aggregates; otherwise particles of matching colors are part of the same larger cluster.