

The cluster vapor to cluster **solid** transition

Martin B. Sweatman*

*Institute of Materials and Processes, School of Engineering,
University of Edinburgh, Edinburgh EH9 3JL, UK.*

Leo Lue

*Department of Chemical and Process Engineering, University of Strathclyde,
James Weir Building, 75 Montrose Street, Glasgow G1 1XJ, UK*

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Until now, depletion induced transitions have been the hallmark of multicomponent systems only. Monte Carlo simulations reveal a depletion-induced phase transition from cluster vapor to cluster solid in a one-component fluid with competing short range and long range interactions. This confirms a prediction made by earlier theoretical work. Analysis of renormalized cluster-cluster and cluster-vapor interactions suggest that a cluster liquid is also expected within a very narrow range of model parameters. These insights could help identify the mechanisms of clustering in experiments and assist the design of colloidal structures through engineered self-assembly.

The formation of solute aggregates in solution is important in many areas of science and engineering, from neurodegenerative diseases such as Alzheimer’s [1] to bioinspired nanomaterial production [2] and pharmaceutical manufacture [3]. A classic example is the formation of micellar aggregates and ordered mesophases in solutions of amphiphilic molecules [4]. Aggregate formation and organization can be driven by many other mechanisms, typically through the interplay of two or more competing interactions [5]. Particles with a short-range attractive and long-range repulsive (SALR) interactions are generally thought to be relevant to clustering of large solute molecules and molecular assemblies, such as colloids [6] and proteins [7], that become charged in solution through, for example, proton exchange with the solvent. The attractive interactions can arise through a variety of mechanisms, such as hydrophobicity, hydrogen bonding or specific binding interactions, or a depletion interaction induced by solvated polymer for example. Experimental observations of anomalously large clusters in small-molecule solutions, such as glycine [8], urea [9], and many others suggest this SALR-controlled mechanism might be more universal, but there is considerable debate in this area and many experimental uncertainties need to be resolved. In particular, the composition of anomalously-large clusters in small-molecule solutions appears to be difficult to establish.

The prototypical SALR system is comprised of spherical particles interacting through a hard core of diameter d plus a pair of Yukawa potentials. When the particles are separated by more than the distance d , the interaction potential ϕ is given by

$$\beta\phi(r) = -\frac{A_a}{r}e^{-z_a(r-1)} + \frac{A_r}{r}e^{-z_r(r-1)} \quad (1)$$

where r is the separation between the particles, scaled by d , and $\beta = 1/(k_B T)$. The parameters A_a and A_r (both

positive) determine the strength of short range attractive and long range repulsive interactions, respectively, relative to $k_B T$, while z_a and z_r (with $z_a > z_r > 0$) determine the inverse decay length of these interactions. Together with the overall fluid density ρ_b , the phase behavior exists in a five-dimensional space.

Each SALR particle normally represents a single solute particle (e.g., molecule or colloid), where the solvent has been “integrated-out” with long-range repulsions normally representing a screened Coulomb interaction. Despite a growing volume of work in recent years using a variety of theoretical methods, from molecular dynamics simulations [10] to density functional theory [11–13] and integral equations theory [14, 15], the behavior of this model is still not fully mapped or understood. This is partly because of the high dimensionality of the state space, but also because of difficulties encountered in modelling this system due to the disparity of length and time scales. Even the equilibrium behavior of this model is not completely established. Nevertheless, its behavior is often seen to be similar to that of amphiphilic solutions: within certain ranges of parameters a fluid of clusters exists (cluster fluid), and, at higher densities, a series of modulated phases are observed. The cluster size depends on the balance between the attractive and repulsive interactions, and can be fine-tuned from relatively small clusters to arbitrarily large ones. An approximate formula for cluster size of the SALR cluster fluid is provided in Ref. [16]. Large clusters are typically relatively monodisperse, provided the system can easily equilibrate, which occurs when the interactions are relatively weak. As the attraction is strengthened, the clusters grow in size and become denser, but less concentrated. The dynamics of the system can also slow down, leading to kinetic arrest and gelation if either the attractive or repulsive interactions are sufficiently strong [17–19]. Indeed, the underlying equilibrium behavior is often masked for this reason in experimental systems, e.g. in many colloidal systems.

The thermodynamic model in Ref. [16] was developed to understand the low density equilibrium behavior of

* martin.sweatman@ed.ac.uk

FIG. 1. Low density portion of the phase diagram of the SALR system as predicted by the DFT-micelle model [16]. Above the critical cluster concentration (CCC) the concentration of large clusters grows almost linearly with system density ρ_b . Below the CCC the cluster concentration decays exponentially with reducing ρ_b . The blue line is an estimate, based on considering the packing fraction of clusters, for the transition to a cluster solid. The red lines describe the predicted binodal of the first order cluster vapor to cluster liquid transition. Adapted from M.B. Sweatman et.al., J. Chem. Phys. 140, 124508 (2014), with permission from AIP publishing.

such SALR systems. **The model can be considered a novel kind of density functional theory for cluster formation, similar in some respects to theories of micellization** [4]. In addition to predicting the existence of a cluster fluid (consisting of large spherical clusters of particles diffusing freely within, and in equilibrium with, a background vapor composed of individual particles), this thermodynamic model also predicts a first order cluster vapor to cluster liquid transition might exist for a very narrow range of parameters. A typical phase diagram is presented in Fig. 1; the transition under discussion is the one bounded by red lines at smaller values of A_a . It was argued that this transition was driven by a depletion interaction mediated by the vapor between clusters, and therefore only occurred once the clusters were sufficiently large and the system pressure was sufficiently high. Essentially, the theory predicts that depletion-induced phase separation can occur in a one-component system. This is an interesting feature, because previously such depletion interactions have been the hallmark of particular binary mixtures, such as colloid-polymer mixtures or size-asymmetric hard sphere mixtures. **However, direct simulation evidence for a transition from a cluster vapour to another cluster phase (e.g., cluster liquid or cluster solid) has been lacking, until now.**

The unusual feature of this phase transition is that it is driven by a self-mediated depletion interaction in a one-component system. For sufficiently large values of A_a (keeping other parameters fixed), the transition is expected to be absent (i.e. if we move far enough to the right in Fig. 1) because the system pressure is too low. In this case, as one increases the overall system density from a very low initial value, one would expect to see a vapor, followed by an increasing concentration of large clusters once the CCC is exceeded. This cluster fluid is expected to eventually transform to a cluster solid at sufficiently high density, driven by repulsive cluster-cluster interactions. Systems that interact through purely repulsive, soft potentials can organize to form a wide variety of organized mesophases, driven primarily through entropy [20]. This freezing mechanism is different to that observed here. Instead, in this work, the transition is from a low density cluster vapor to a **cluster solid**, where

aggregation is driven by an attractive depletion interaction between clusters. That this can occur in a one-component system is the truly remarkable aspect of this work.

We investigate the potential for a first order cluster vapor to cluster solid phase transition within the SALR phase diagram. Using Monte Carlo simulations, the transition is demonstrated to exist for one particular combination of model parameters. Analysis of renormalized cluster-cluster and cluster-particle interactions indicates that the original explanation for this transition is correct, i.e. it is driven by a depletion potential mediated by the vapor between clusters, and that a cluster vapor to cluster liquid (as opposed to solid) transition is likely to exist within a very narrow range of parameters. In effect, this work shows that depletion-induced first order phase transitions can exist in a one component system, and it supports the existence of another disordered cluster phase — the **cluster liquid**. It also provides support for the utility of such “DFT-micelle” theories [16].

Canonical ensemble (NVT) Monte Carlo simulations are used to observe equilibrium behavior for this system. These simulations are of a **standard type** [21, 22], except that (i) translational moves are allowed with two different step sizes to ensure faster equilibration of vapor-like and liquid-like regions and (ii) cluster moves are used to ensure efficient sampling of cluster positions. The cluster moves are of a particularly simple form. Essentially, a particle is chosen at random, and an attempt is made to translate all particles within a given range (chosen to reflect the structure of the fluid) of that particle by the same vector. The attempt is rejected, to satisfy microscopic reversibility, if the reverse operation would result in an attempt to move more particles, and the attempt is accepted with the usual Boltzmann condition involving a change in potential energy ΔU . To approach the equilibrium state, simulations are started from two very different microstates; one similar to a vapor and the other similar to a compressed liquid slab sandwiched by vacuum. All length scales are reduced with respect to d . In this work, we use $A_a = 1.75$, $A_r = 0.5$, $z_a = 1.0$, $z_r = 0.25$ and $\rho_b = 0.0463$.

Each simulation box has dimensions $90 \times 30 \times 30$ and contains 3750 particles, with a cut-off of 15 used in all simulations. The monomer and cluster density profiles (ρ_m and ρ_c , respectively) are measured to observe the phase transition. The latter is simply the particle density of particles belonging to clusters of two particles or more, where a cluster is defined whenever two particles are within a separation of $2^{1/2}$. The former is the density of all other particles.

Snapshots of the initial and final configurations of both simulations are shown in Fig. 2. It can **be clearly seen** that in both simulations the system has separated into cluster vapor and cluster solid phases, separated by two interfaces. Figure 3 shows the evolution of a convenient order parameter, $\rho_c - \rho_m$, for each simulation. When starting with a compressed slab-like configuration

FIG. 2. Snapshots from the Monte Carlo simulations showing the configurations shortly after initialisation (left), and at the end of each simulation (right). Regardless of the initial configuration (upper — slab, lower — vapor), each simulation develops a slab of cluster crystal interfacing with a cluster vapor by the end of the simulation. **The cluster crystals have adopted a different orientation with respect to the fixed simulation box axes in each simulation.**

FIG. 3. Variation of the order parameter with distance along the simulation box: (a) initialised with a slab, (b) initialized with vapor. An average is taken over 200 cycles for each plot: immediately after initialization (dotted line), after 49900 cycles (dashed line), and after 99800 cycles (full bold line).

the system quickly evolves towards a state consisting of a portion of cluster solid sandwiched between vapor phases. Once formed, this state appears to be stable; only changes involving translation of the entire system in the direction normal to the cluster solid interface appear to take place after formation of the solid. Similarly, when starting from a random vapor-like initial configuration we see that clusters form quickly, and then more slowly aggregate. At longer times the same cluster solid, sandwiched by vapor, is formed as for the first simulation, i.e. freezing of the cluster solid is observed directly. The crystal structure observed in the snapshots of Fig. 2 appears as an oscillating density in Fig. 3.

We can understand the nature of this transition by analyzing the effective cluster-cluster and cluster-particle interactions. We treat each cluster as a spherical and uniform liquid-like droplet of radius R_c ; the particle density profile within a single cluster centered at position \mathbf{R} is

$$P_c(\mathbf{r} - \mathbf{R}) = \rho_l \Theta(R_c - |\mathbf{r} - \mathbf{R}|), \quad (2)$$

where ρ_l is the particle number density within a cluster, and Θ is the Heaviside step-function. These clusters are dispersed within a background monomer vapor (the capillary model). The effective cluster-cluster and cluster-particle interactions are computed in k -space as

$$\begin{aligned} \hat{\phi}_{cc}(k) &= [\hat{P}_c(k)]^2 \hat{\phi}(k) \\ \hat{\phi}_{pc}(k) &= \hat{P}_c(k) \hat{\phi}(k), \end{aligned} \quad (3)$$

respectively, where the caret ($\hat{}$) denotes the 3-dimensional Fourier transform. The depletion potential experienced by two isolated clusters at separation r is given by the change in the grand potential of the background fluid for this two-cluster system relative to the case where the cluster separation $r \rightarrow \infty$, assuming the clusters themselves are insensitive to r (i.e. they are not deformed by their mutual proximity). By assum-

FIG. 4. (a) Total interaction between clusters with diameter $d_c = 10$ and body-density $\rho_l = 0.9$ for several background vapor pressures p , from $\beta p = 0.005$ (top) to 0.015 (bottom). (b) Total interaction between clusters with background vapor pressure $\beta p = 0.01$ and body-density $\rho_l = 0.9$ for several cluster diameters, from $d_c = 5$ (left) to 15 (right).

ing the background fluid is an ideal gas with local density depending on the total interaction with both clusters (i.e. $\rho(\mathbf{r}) = \rho_v e^{-\beta\phi_{pc}(|\mathbf{r}-\mathbf{R}_1|) - \beta\phi_{pc}(|\mathbf{r}-\mathbf{R}_2|)}$, where ρ_v is the number density of the background monomer vapor, and \mathbf{R}_1 and \mathbf{R}_2 denote the positions of the clusters), we obtain the background fluid grand potential, and hence the depletion potential, as

$$\beta\Delta\Omega = -\rho_v [\hat{f}(k)]^2 \quad (4)$$

where

$$f(r) = e^{-\beta\phi_{pc}(r)} - 1 \quad (5)$$

is the effective particle-cluster Mayer function. While the ideal gas approximation is reasonable for low density vapors, Eq. (4) can be improved by substituting $\rho_v = \beta p$, where p is the system pressure.

By summing this depletion potential, $\beta\Delta\Omega(k)$, and the direct cluster-cluster effective interaction ϕ_{cc} , we obtain the total interaction ϕ_{tot} between an isolated pair of clusters. This is plotted in Fig. 4a for several system pressures for $R_c = 5$ and $\rho_l = 0.9$, and in Fig. 4b for several cluster sizes for $\beta p = 0.01$ and $\rho_l = 0.9$. A deep potential well develops for sufficiently large clusters and high pressures. We can therefore expect to see phase separation of clusters from the background vapor for systems where the depletion interaction is sufficiently strong to overcome the direct cluster-cluster repulsion. It follows that for very strong cluster depletion interactions, we should expect to observe a cluster solid separating from a cluster vapor, while for depletion interactions within a narrow range of moderate well depths we should expect to observe a cluster liquid separating from a cluster vapor provided the depletion interaction is not too short-ranged.

Figures 4a and 4b also indicate that the strength of the depletion interaction is very sensitive to pressure and cluster size, respectively. Therefore, the cluster vapor to cluster liquid transition is likely to be very rare compared to the cluster vapor to cluster solid transition. **With regard to Fig. 1**, these results indicate that the blue cluster solid transition line is likely to meet the red cluster liquid transition line much earlier than suggested, and the cluster liquid region will be very small.

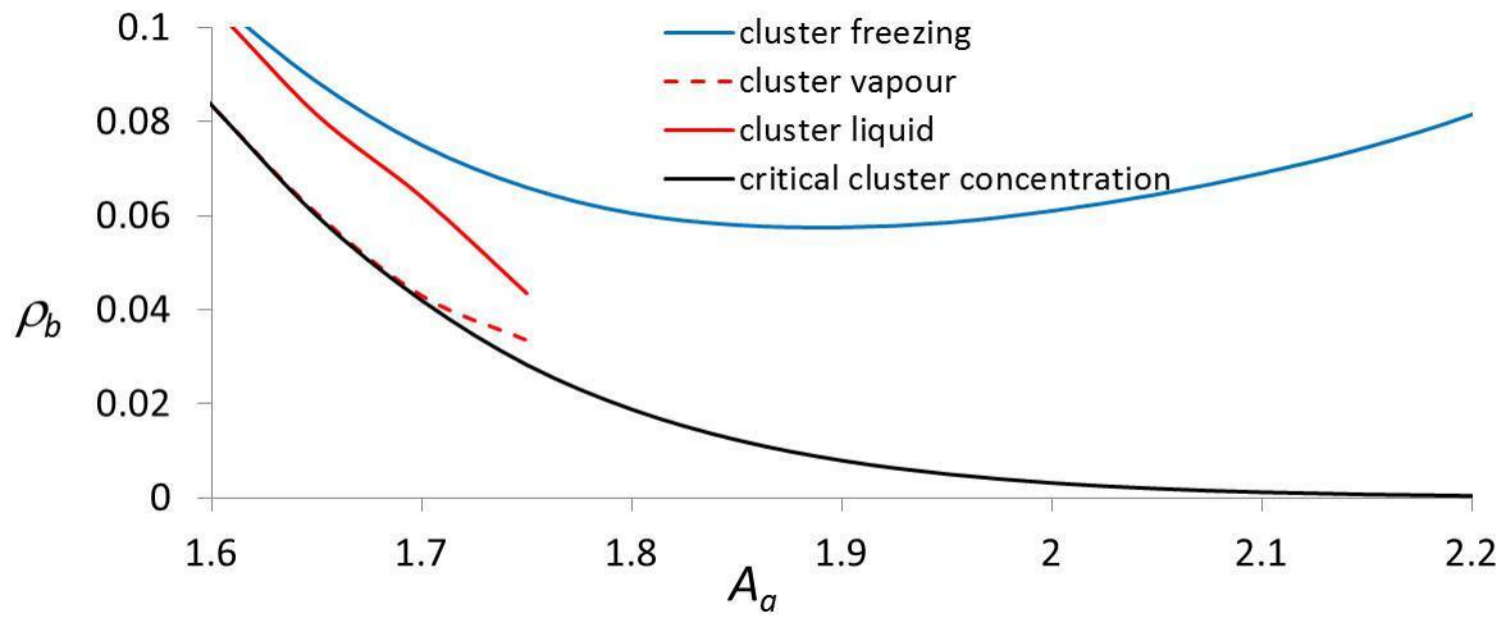
In summary, an analysis of effective (renormalized) interactions support predictions by our earlier theory that the SALR can exhibit first order cluster vapor-cluster solid and cluster vapor to cluster liquid phase transitions. In this work, Monte Carlo simulations clearly demonstrate the cluster vapor to cluster solid transition.

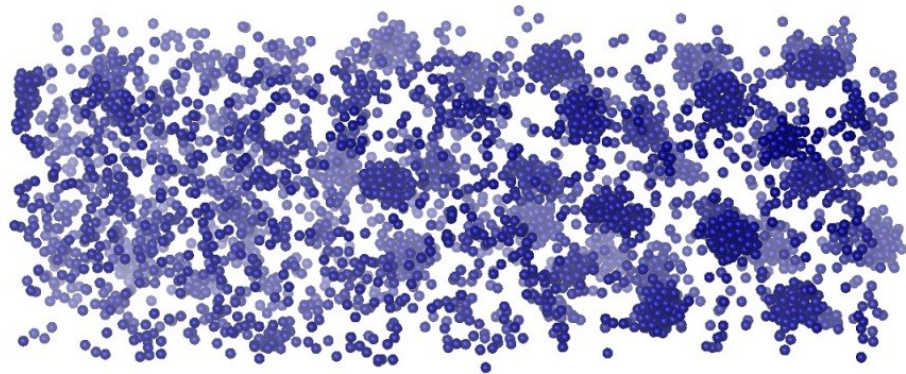
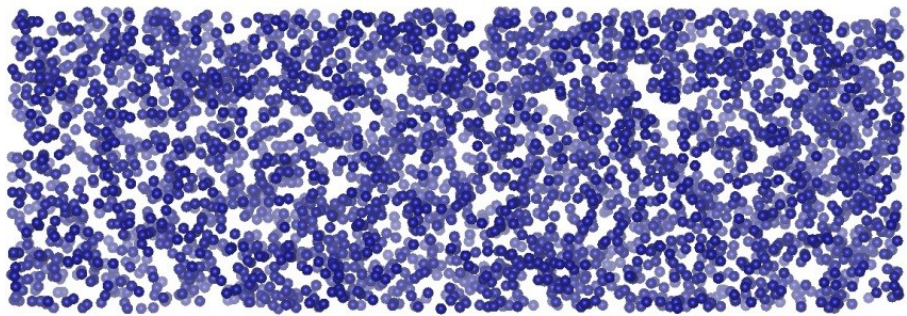
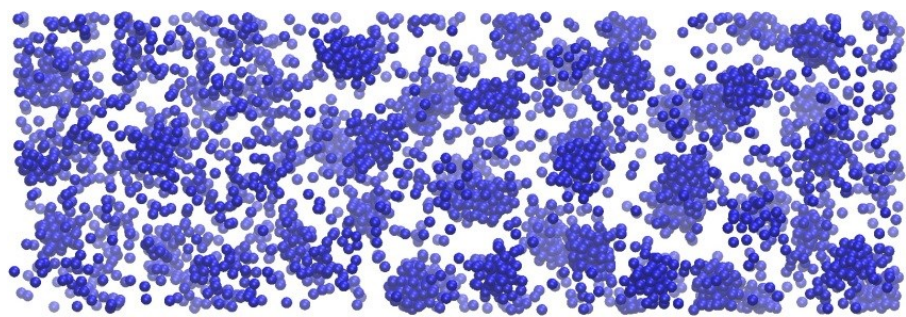
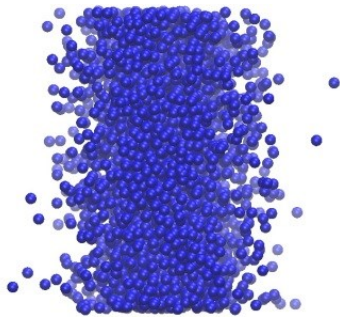
These transitions should be observable in experiments where the solute particles interact through an appropriate form of effective SALR potential, where interactions are not so strong that they cause kinetic arrest. By careful tuning of solute-solute interactions (for example, by

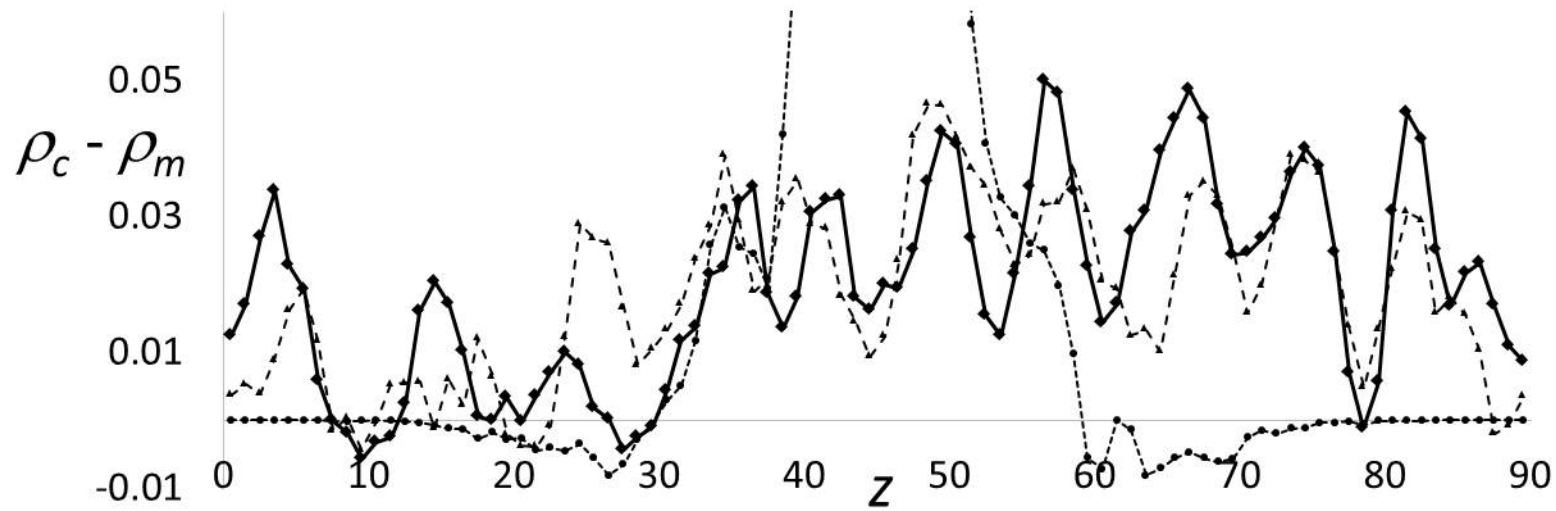
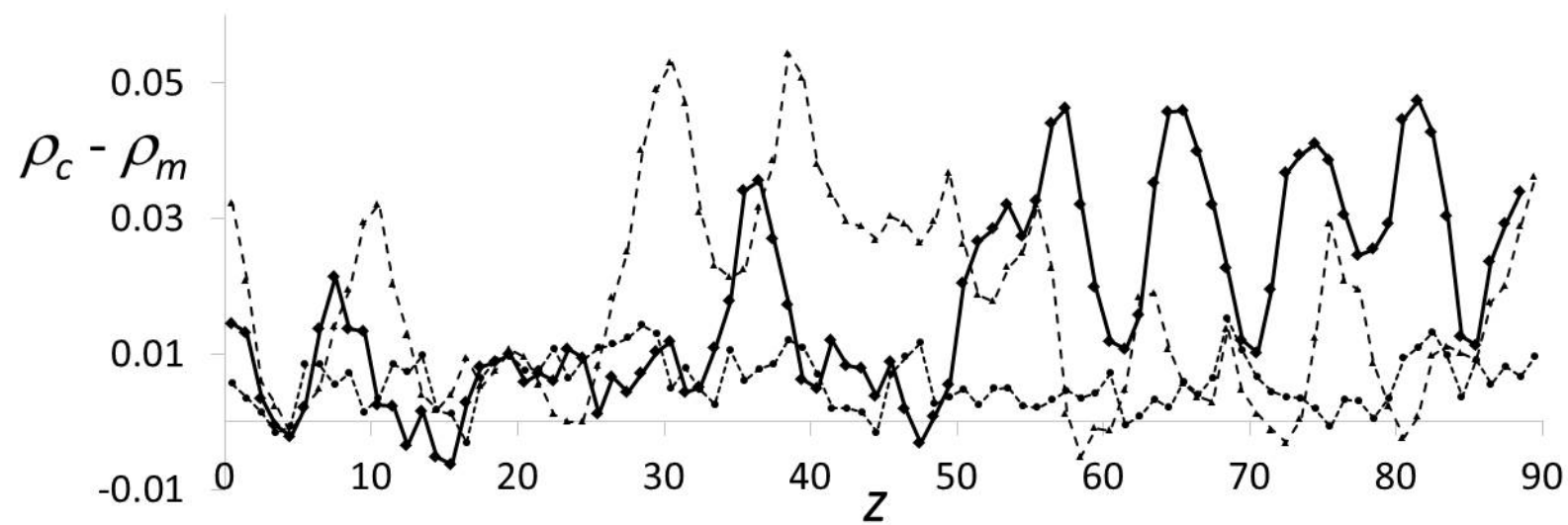
adding a depletant or changing temperature or solvent), it should be possible to create ordered cluster solids and cluster liquids in solution with tunable cluster sizes and separations, which might have technological applications.

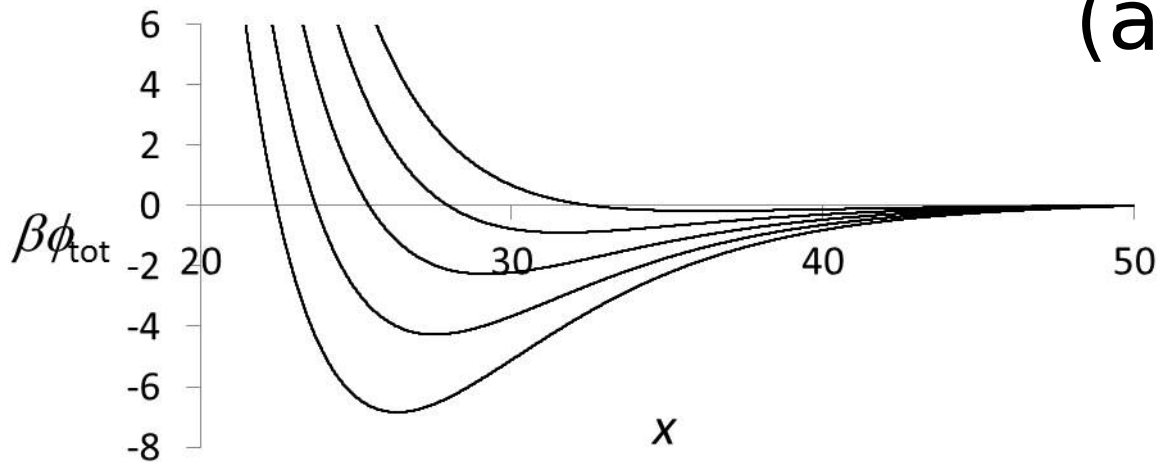
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