FLUIDS ON A SPHERE

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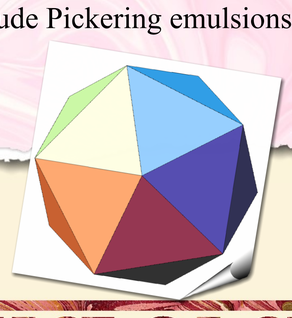
OBJECTIVES + MOTIVATION

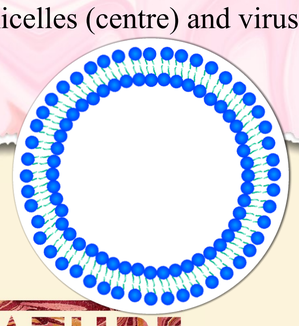
The phase transitions of attractive colloids confined to the surface of a sphere are strongly influenced by both the curvature and finite extent of the surface. These influences include the frustration of crystal structures and the modification of the perimeter-area relationship of isotropic patches.[1,2]

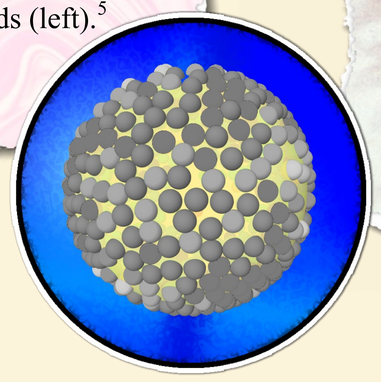
Here, we investigate the gas-liquid transition of a system of Lennard-Jones particles by Monte Carlo simulation in the grand canonical ensemble.[3] We measure the gas-liquid coexistence curve as well as the free energy profile for liquid nucleation in the gas phase, with the objective of observing the influence of the confining surface.

We demonstrate that it is possible to construct modifications to classical nucleation theory (CNT) which capture the finite size of the system and the curvature dependent geometry of a cluster.[2,4]

In nature, colloidal systems are often found at the surfaces of spheres. Examples include Pickering emulsions (right), micelles (centre) and virus capsids (left).[5]







EFFECT OF CURVATURE

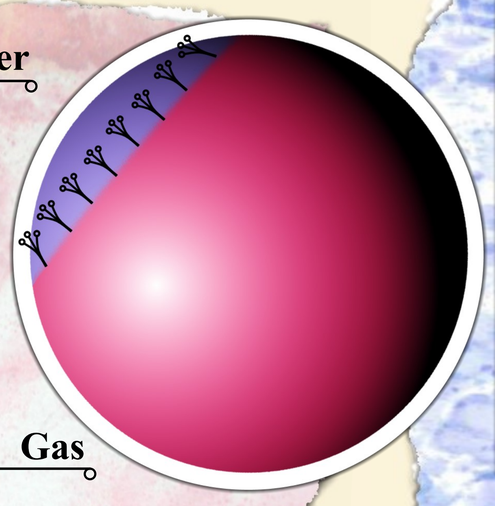
Finite size
When the cluster covers the whole sphere particles may still be added, which increases the density.

Liquid cluster

Line tension
Similar to CNT, the line tension acts to constrict the cluster.

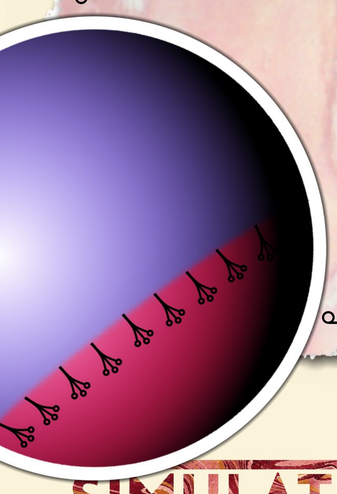
Liquid cluster

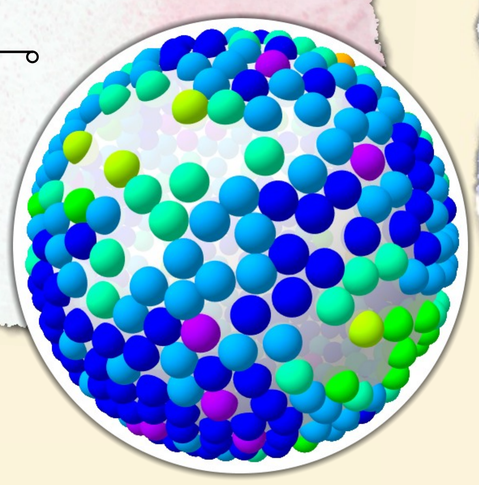
Gas



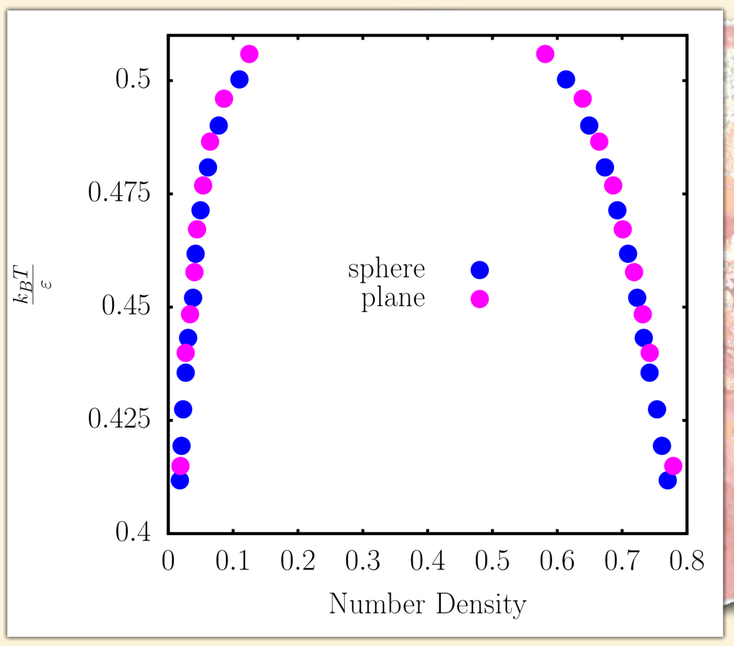
Line tension
Unlike CNT, the line tension acts to stretch the cluster.

Gas





SIMULATION



The system described above was simulated using the grand canonical Monte Carlo technique. These simulations allowed for the construction of the gas-liquid coexistence curve (left). This curve is very similar to the planar case.

Umbrella sampling was used to measure the free energy profiles of nucleation.[6]

MODEL + FITTING

The Helmholtz free energy of a spherical cap shaped liquid nucleus of area A containing N particle, confined to a sphere of area A_0.

$$\Delta F = -Nk_B T \ln\frac{A - aN}{N} + c'N - \frac{(a - B2)N^2}{A} - g'A + \sigma'\sqrt{A - A^2/A_0}$$

The density dependent entropy of the liquid patch, as predicted by the van de Waals equation of state.[7]

Constants including the temperature and de Broglie wavelength.

The interaction between particles in the liquid, as predicted by the van de Waals equation of state.[7]
B2 is the second virial coefficient for the Lennard-Jones potential on a sphere.

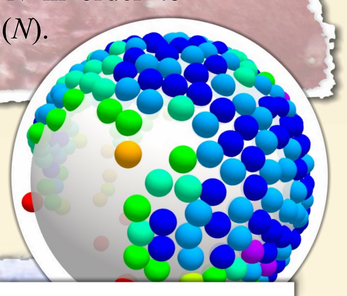
The chemical potential difference between the gas and liquid phase.

The line tension term increases up to $A = A_0/2$ and then falls to zero when the whole sphere is covered.

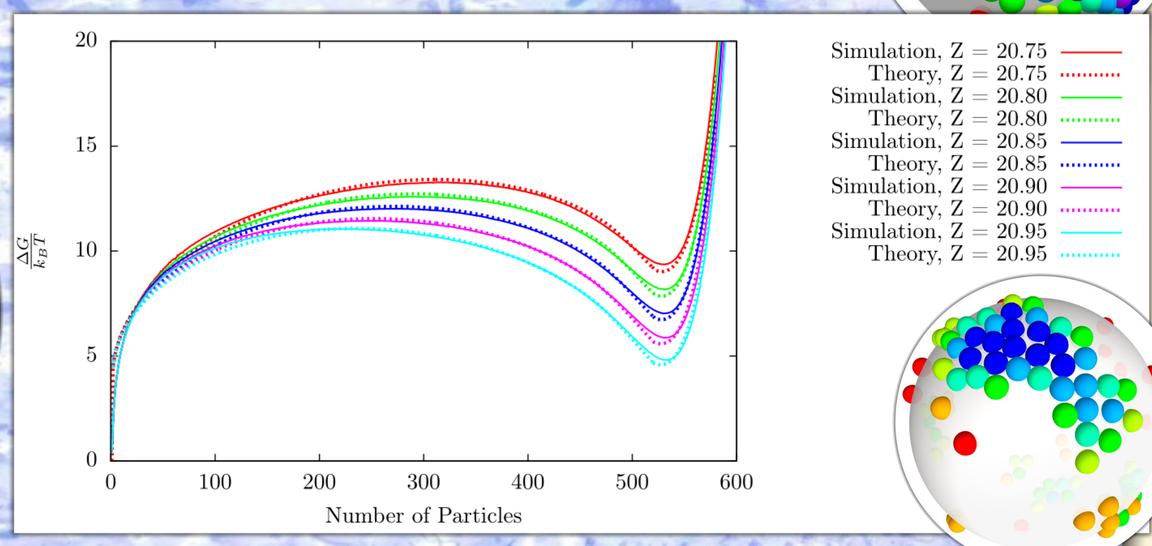
Guess σ, a , c and g.

$\Delta F(A,N)$ is fitted to the simulation curve by *via* σ, g, b and c.

$\Delta F(A,N)$ is minimised for A at each N in order to obtain A (N).



RESULTS



The free energy of formation of a liquid cluster of a given size on the surface of a sphere in the gas phase is plotted for a range of applied chemical potentials. The temperature and surface geometry is constant for all experiments. The solid lines represent data obtained from simulations and the dashed lines are fits to the model presented above. These curves were fitted simultaneously, with the constraint that all the fitting parameters are equal across each experiment, except for g', which we predict is the only fitting parameter to depend on the chemical potential. It can be seen that the fits are very good, despite this constraint. This suggests that the model accurately captures the physics of the system of interest. Also shown are snapshots of the system containing clusters of various sizes.

FUTURE WORK

We are also working on understanding the nucleation process on a sphere in the canonical ensemble. We are also comparing the nucleation barriers of systems confined to spheres of different radii.

In the future we plan to explore the nucleation barrier to crystallisation of these systems on the sphere. It would also be possible to explore nucleation pathways using molecular dynamics simulations.

LITERATURE CITED

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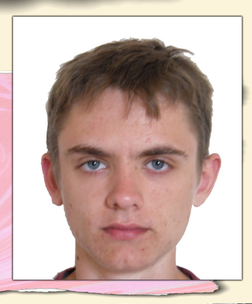

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