Equilibrium and transient behaviour of modulated binary colloid

Suravi Pal

Senior Research Fellow

Under the supervision of

Prof. Jaydeb Chakrabarti

Department of Physics of Complex Systems,
Satyendra Nath Bose National Centre for Basic Sciences,

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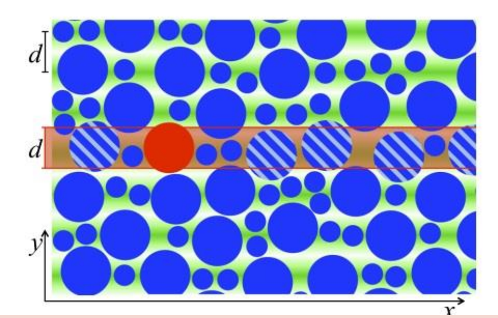
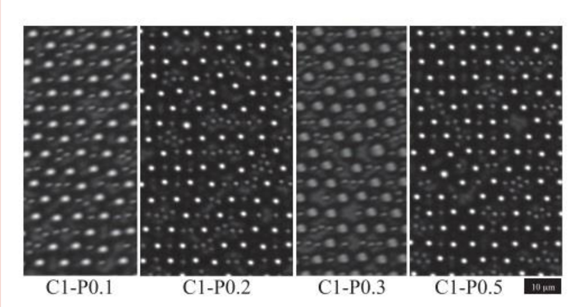
Binary colloids under modulation

- A system of binary colloids consisting of polysterene beads → subjected to an external sinusoidal laser beam along x-direction.





S. U. Egelhaalf *et al. J. chem. Phys.* 2018 **148** 114903

- Alignments of bigger particles.

- The smaller particles form triangular arrangements within the cages of bigger particles.

- They tune strength of laser beam and packing fraction to observe the particles arrangement. themselves along and away from minima.

➢ Objective:

- Phase behaviour of binary modulated system.
- Dynamics of structural changes.

System and Model (MC simulation)

- The particles interact via repulsive potential of the form of :

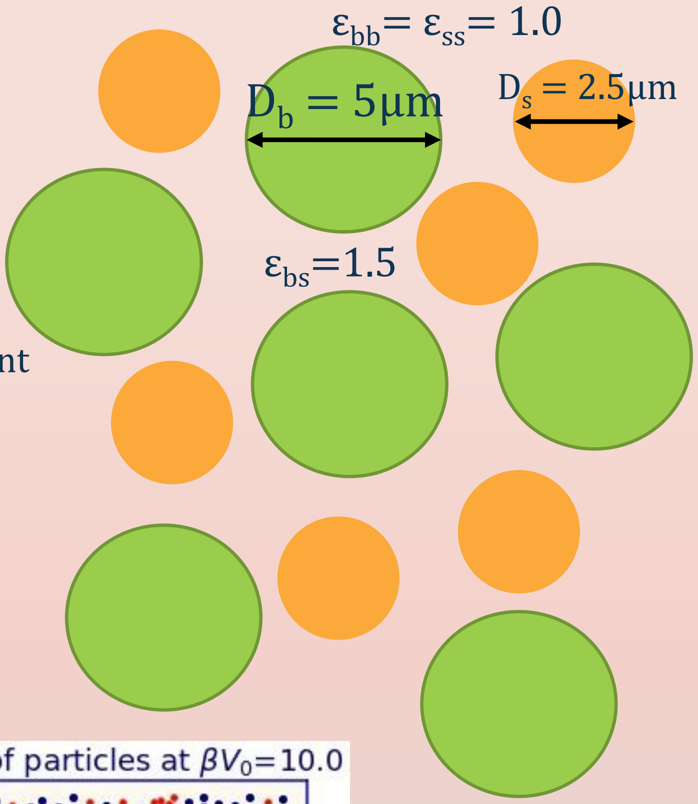
$$V_{ij}^{(\alpha\beta)}(r) = 4\epsilon_{\alpha\beta}\left(\frac{\sigma_{\alpha\beta}}{r_{ij}}\right)^{12}$$

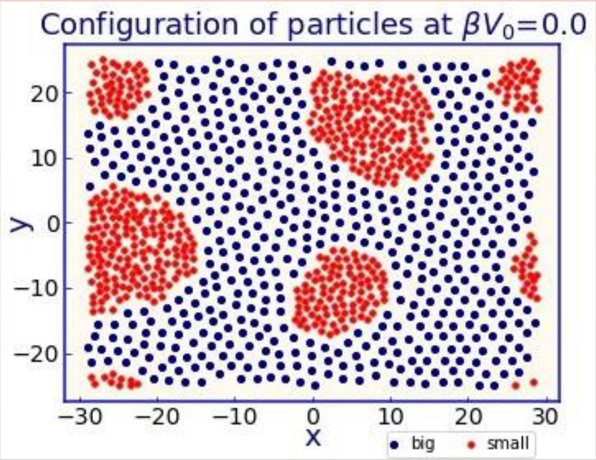
- subject the system to an external spatially periodic potential of the form of :

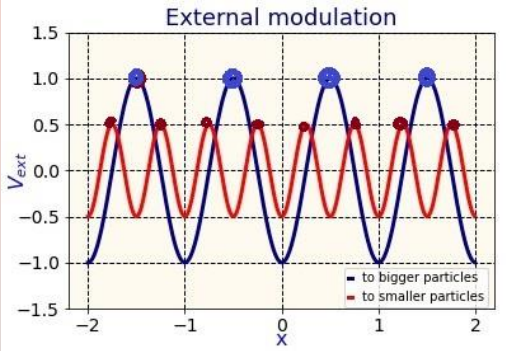
$$V_{ext}(x_i) = -fV_0\cos\left(\frac{2\pi x_i}{\lambda}\right)$$

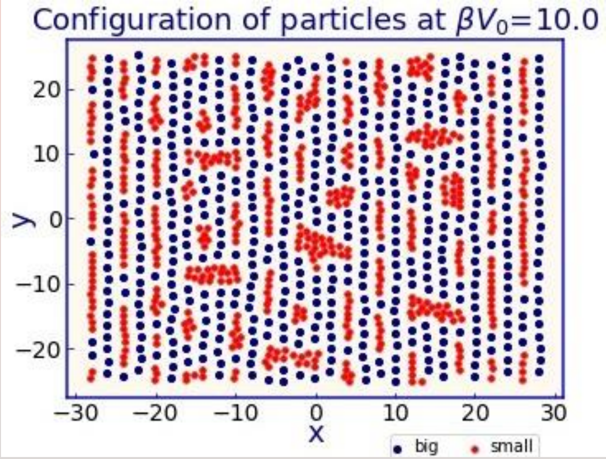
- Packing fraction $\eta\left(=\frac{N_b\pi R_b^2+N_s\pi R_s^2}{A}\right)$=0.7201.

- $\alpha=\beta$ => particles of the same species,
- $\alpha\neq\beta$ => particles of the different species.
- D_b/D_s=2.0, $N_b=N_s$
- $\lambda= D_b$
- f=1 => bigger particles,
- f=0.5 => smaller particles.









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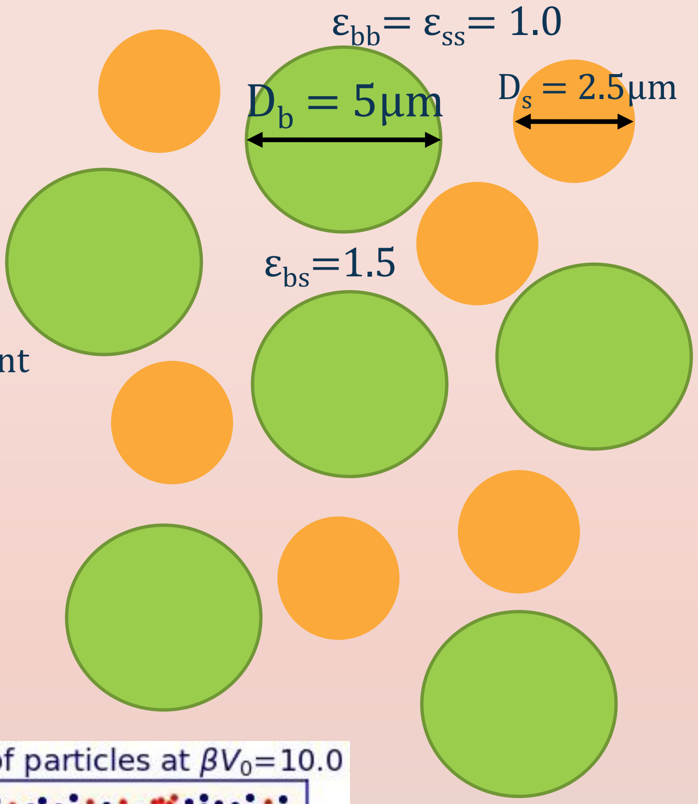

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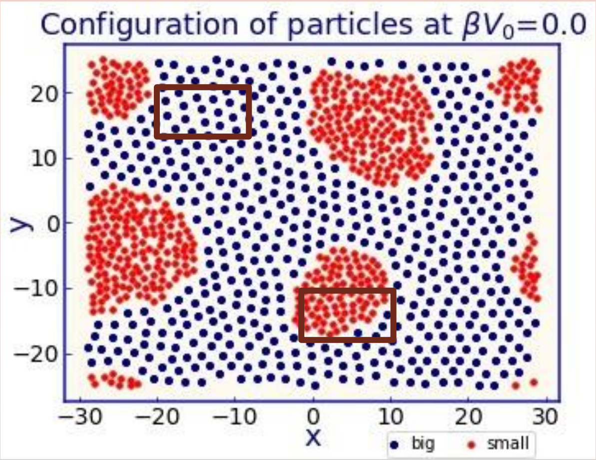
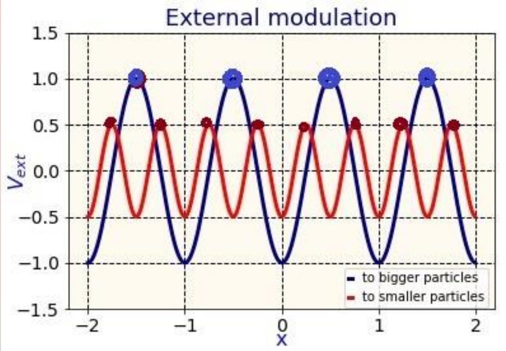
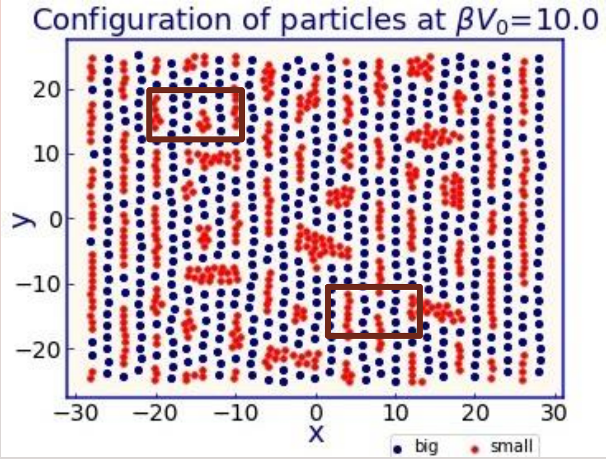


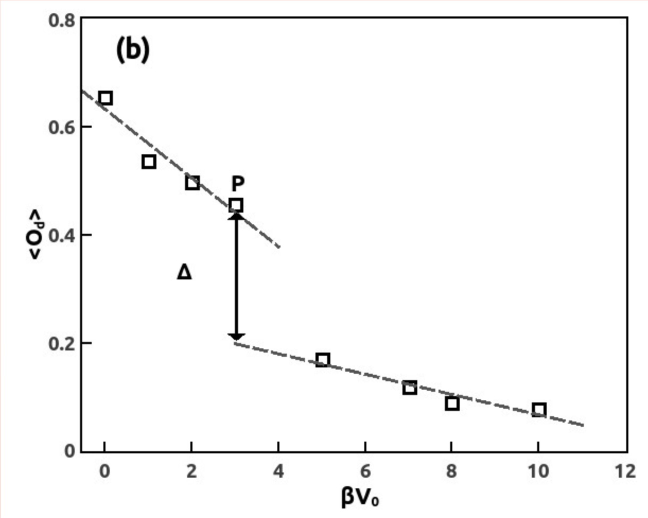




Demixing order parameter and specific heat

- Order parameter :

$$O = < \frac{1}{N} \sum_{i=1}^{M} |n_{ib} - n_{is}| >$$

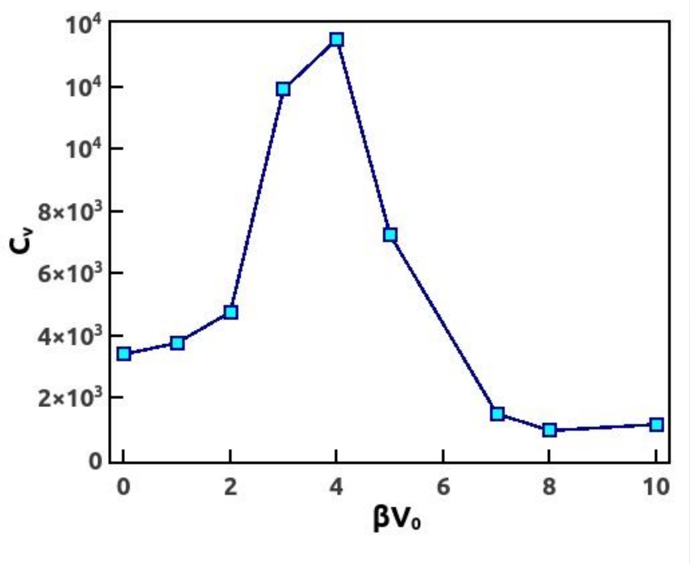


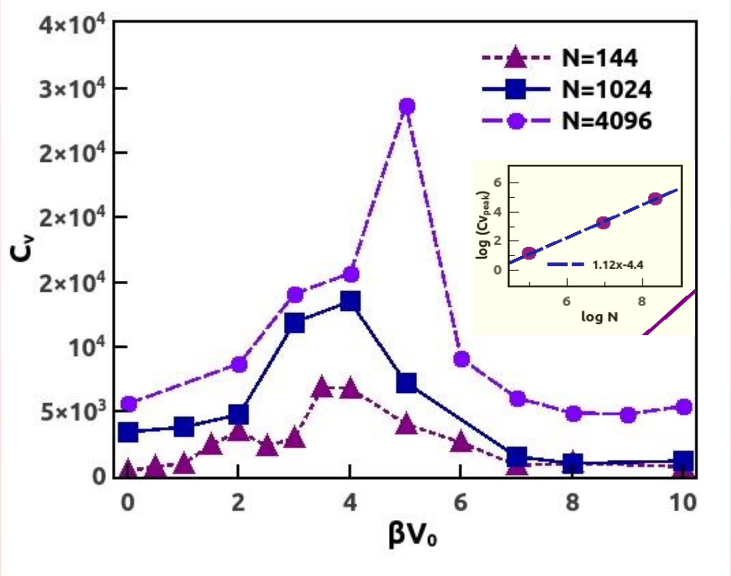
Order parameter decreases as field strength increases

→ enhanced tendency of mixing

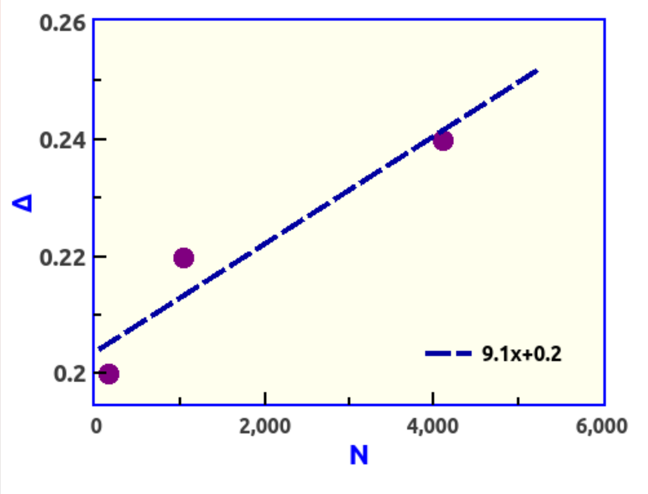
- Specific heat :

$$C_v = \frac{< \sum (E - \bar{E})^2 >}{K_B T^2}$$





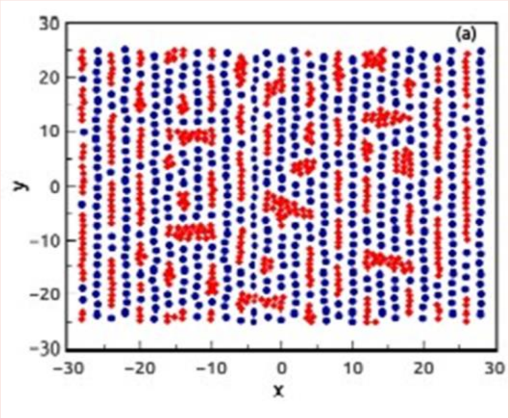
Jump in order parameter increases with system size → First order phase transition



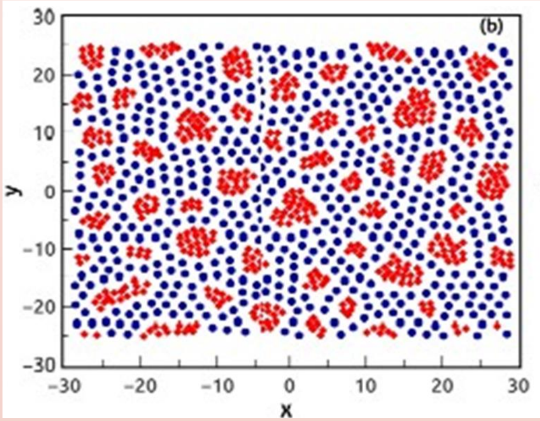
- The peaks in C_v shift to higher βV_0 values with increment of N.
- The peak value (heat capacity max) increases in the order of N;
- The exponent comes out to be ~ 1 which is in agreement with the case of first order phase transition.

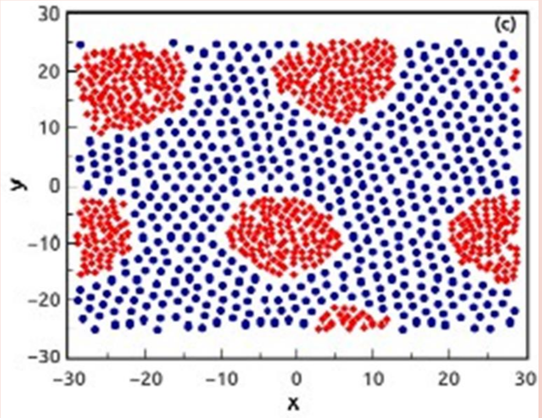
KINETICS (BD SIMULATION)

- The kinetics and dynamics of modulated binary colloidal system, i.e. dynamics of growth of clusters, is yet to be explored in details.
- Switching off the field → accumulation of similar species.



Potential turned off →

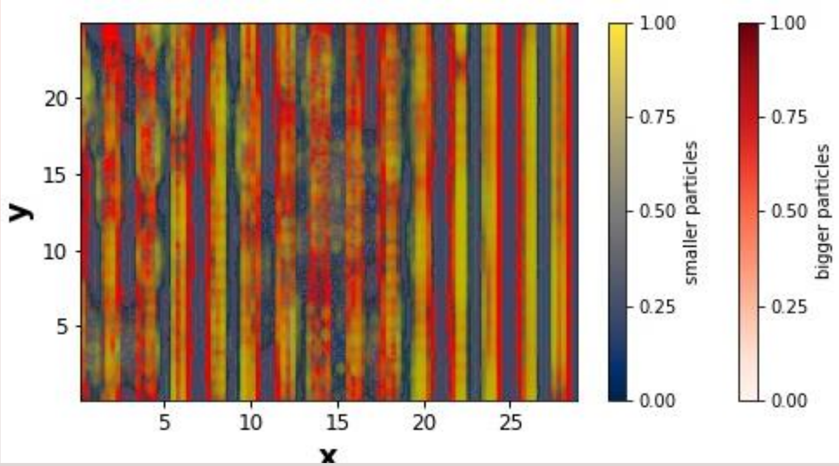




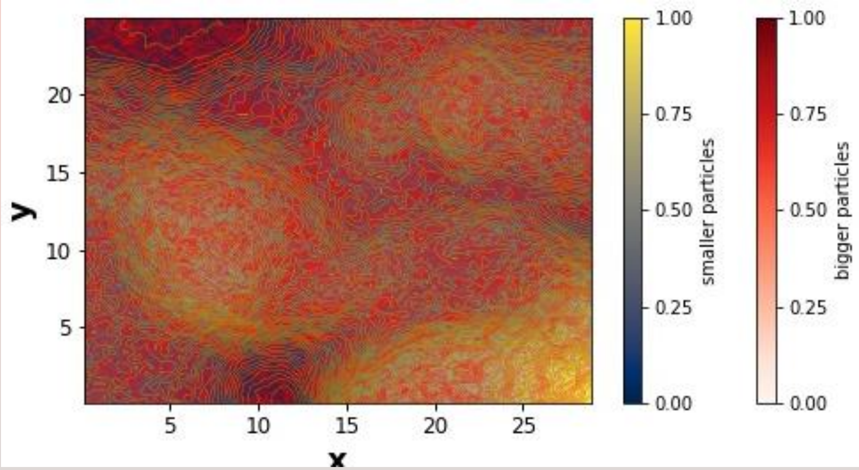
Initial time

intermediate time

final time



Density contour plot



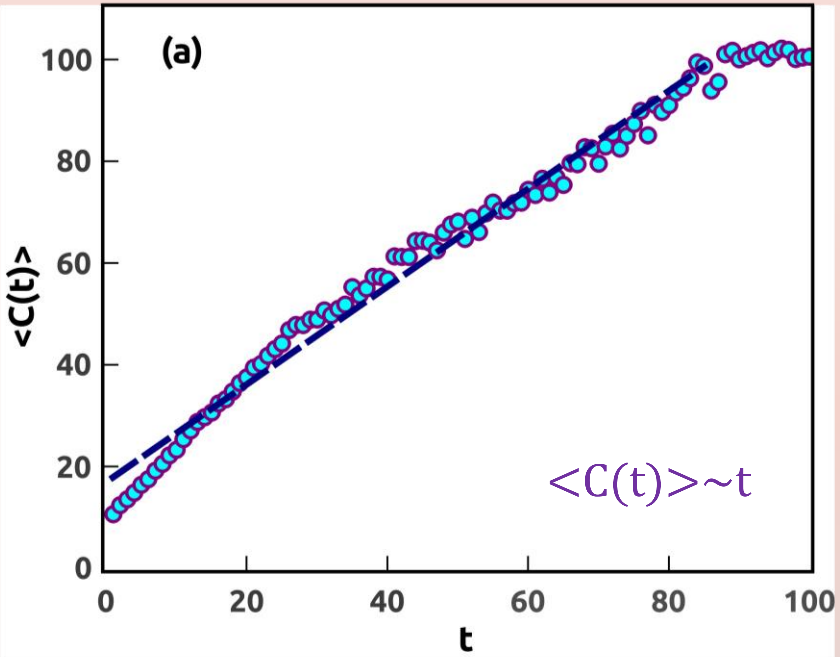
Mixed modulated binary liquid

Phase separated binary liquid

STRUCTUAL EVOLUTION

- **Average cluster size :**

- We compute the average cluster size :
  - ➢ Two particles are in a cluster if their relative center to center distance → ≤ x_{cl} and y_{cl}
  - ➢ Gradual growth in size and then saturates.
  - ➢ Growth follows linear time dependence with exponent 0.92.



- Transient time : The time until the mean cluster size becomes 50% of the equilibrium size (T_s=40).

RADIUS OF GYRATION : SHAPE OF THE CLUSTERS

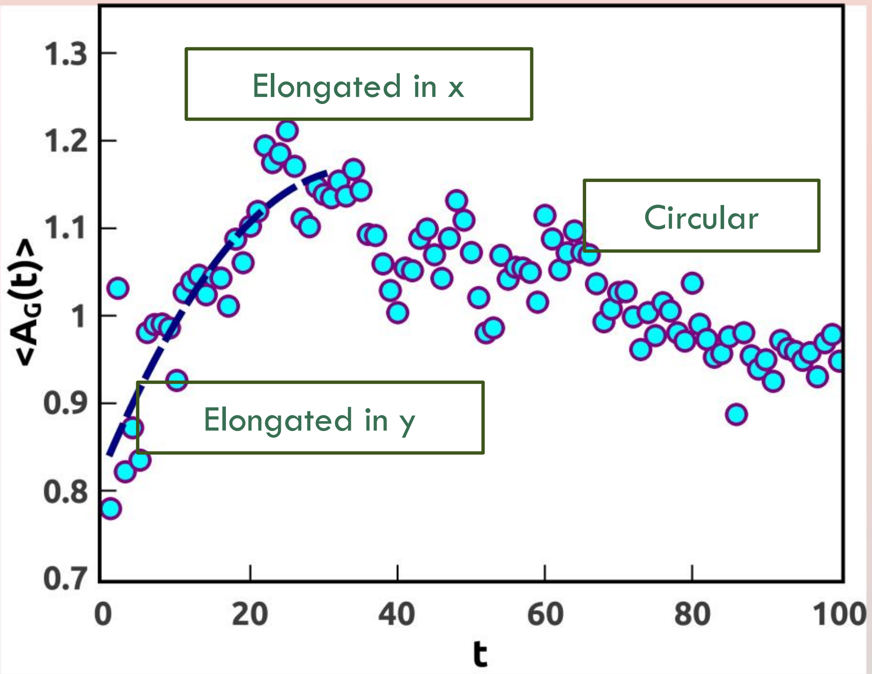
$$x(t)_G^2 = \frac{1}{N}\sum_{i=1}^{N} |x_i(t) - x_{CM}(t)|^2, \qquad y(t)_G^2 = \frac{1}{N}\sum_{i=1}^{N} |y_i(t) - y_{CM}(t)|^2,$$

and $< A_G(t) >= \frac{<x_G(t)>}{<Y_G(t)>}$

- Shape changes from elongated small clusters to big circular compact type ones;

- Ratio of radii of gyration in x and y direction is plotted.

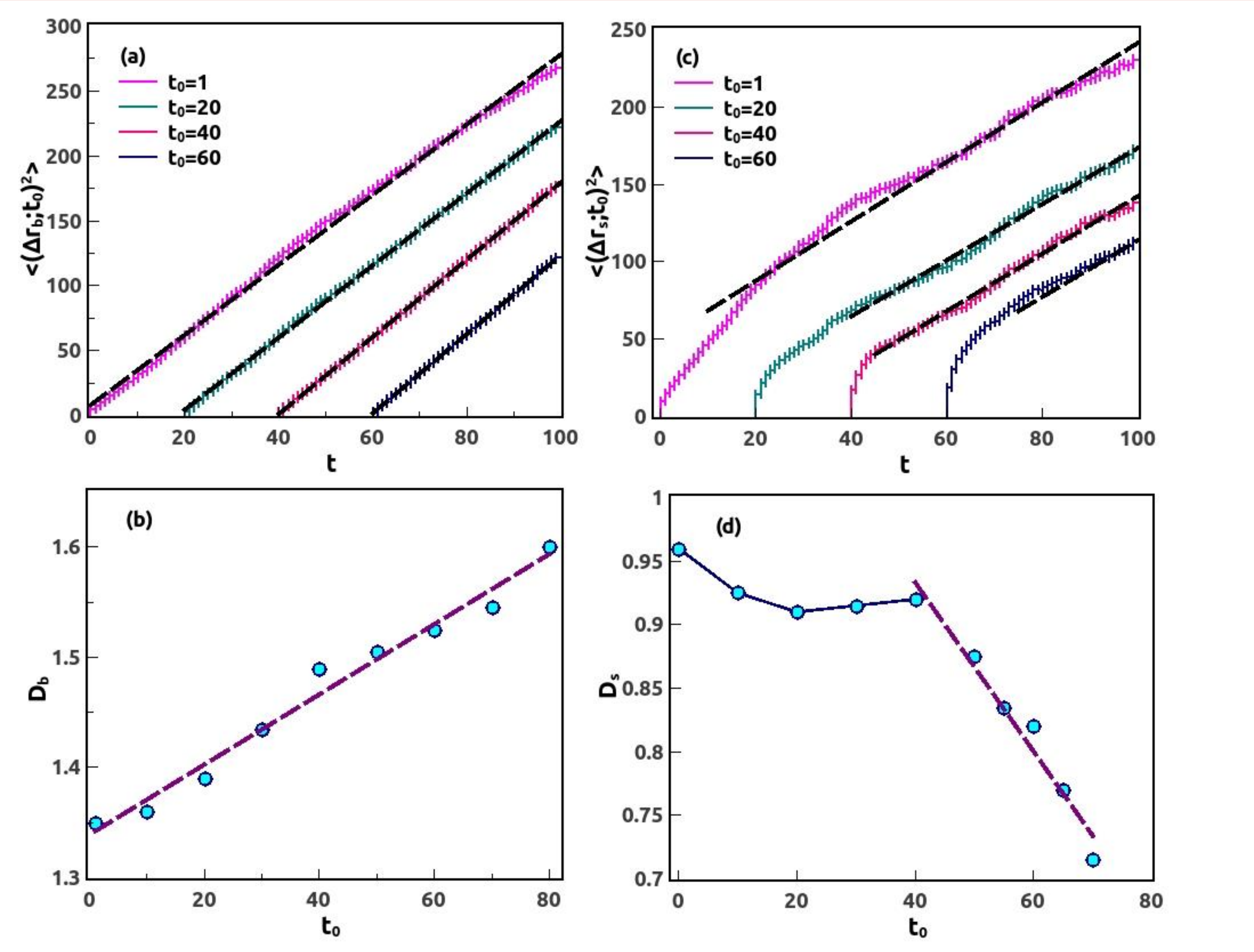
- Ratio reaches unity as the system reaches equilibrium.



Mean Square displacement (ONLY AVERAGED OVER DIFFERENT BD TRAJECTORIES.)

$$< (\Delta r; t_0)_b^2 > = < \frac{1}{N} \sum_i \left[(x_{ib}(t) - x_{ib}(t_0))^2 + (y_{ib}(t) - y_{ib}(t_0))^2 \right] >$$ And

$$< (\Delta r; t_0)_s^2 > = < \frac{1}{N} \sum_i \left[(x_{is}(t) - x_{is}(t_0))^2 + (y_{is}(t) - y_{is}(t_0))^2 \right] >$$



- Both D_b and D_s plotted against $t_0 < T_s$
- Linear MSD for all t0's for bigger particles
- Linear MSD at long time limit for smaller particles
- Faster diffusion for bigger particles and slower for smaller particles.

a) and c) → bigger particles,
b) and d) → smaller particles

Conclusion

- In, summary, we study, using MC and BD simulations, phase behaviour and dynamics of a two dimensional binary colloidal film subjected to one dimensional periodic modulation.
- The density modulation ensures modulated liquid phase.
- Big clusters of small particles are broken into smaller clusters.
- Transition from de-mixed to mixed state occurs with increment of field strength, through a first order phase transition.
- The clusters of smaller particles grow over time until they saturate in size as the system reaches new equilibrium.
- The smaller particles forms slower moving clusters in a background of faster moving bigger particles.

Thank you !

Acknowledgements

- My supervisors.
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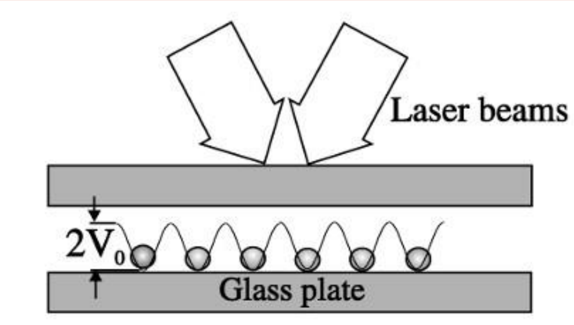
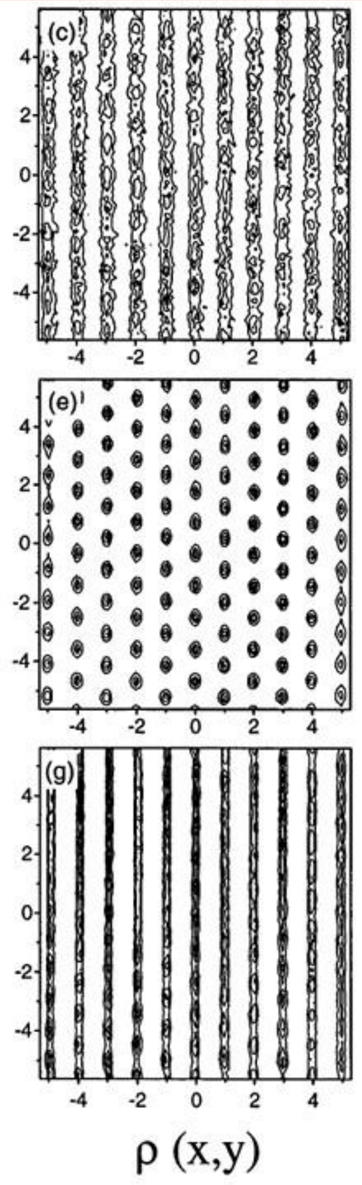
- DST for funding the research.
- My past and present lab members.

Laser induced freezing: modulated colloids



- Experiments and simulation of a colloidal liquid system, subjected to a one dimensional stationary laser modulation to find modulated liquid phase (Laser Induced Freezing).
- The dynamics of such system had not been explored in details in past years.



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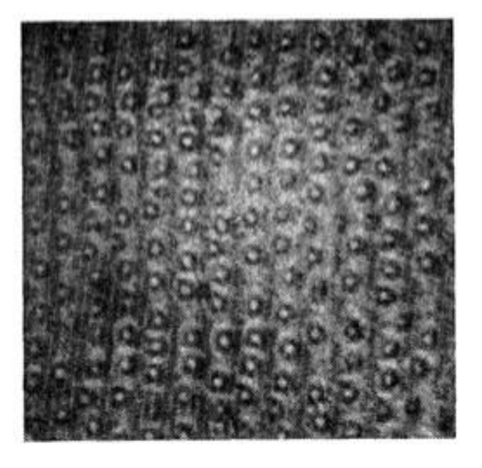

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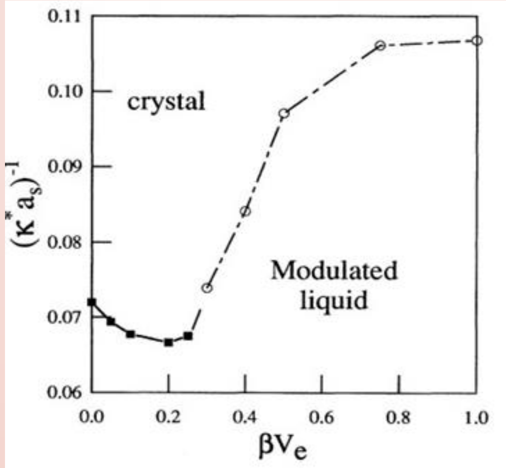

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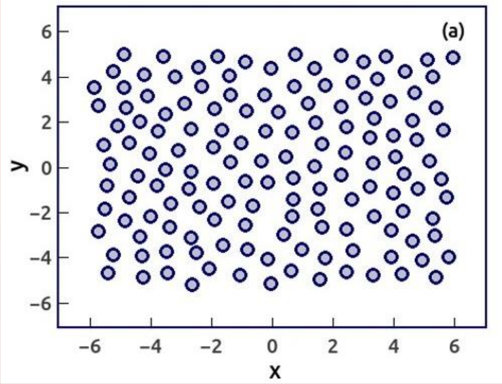
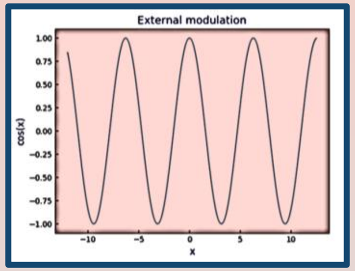
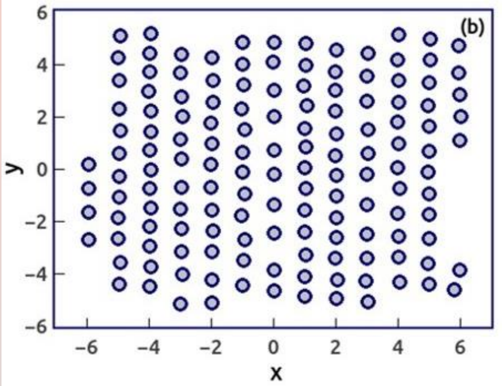


Homogeneous liquid

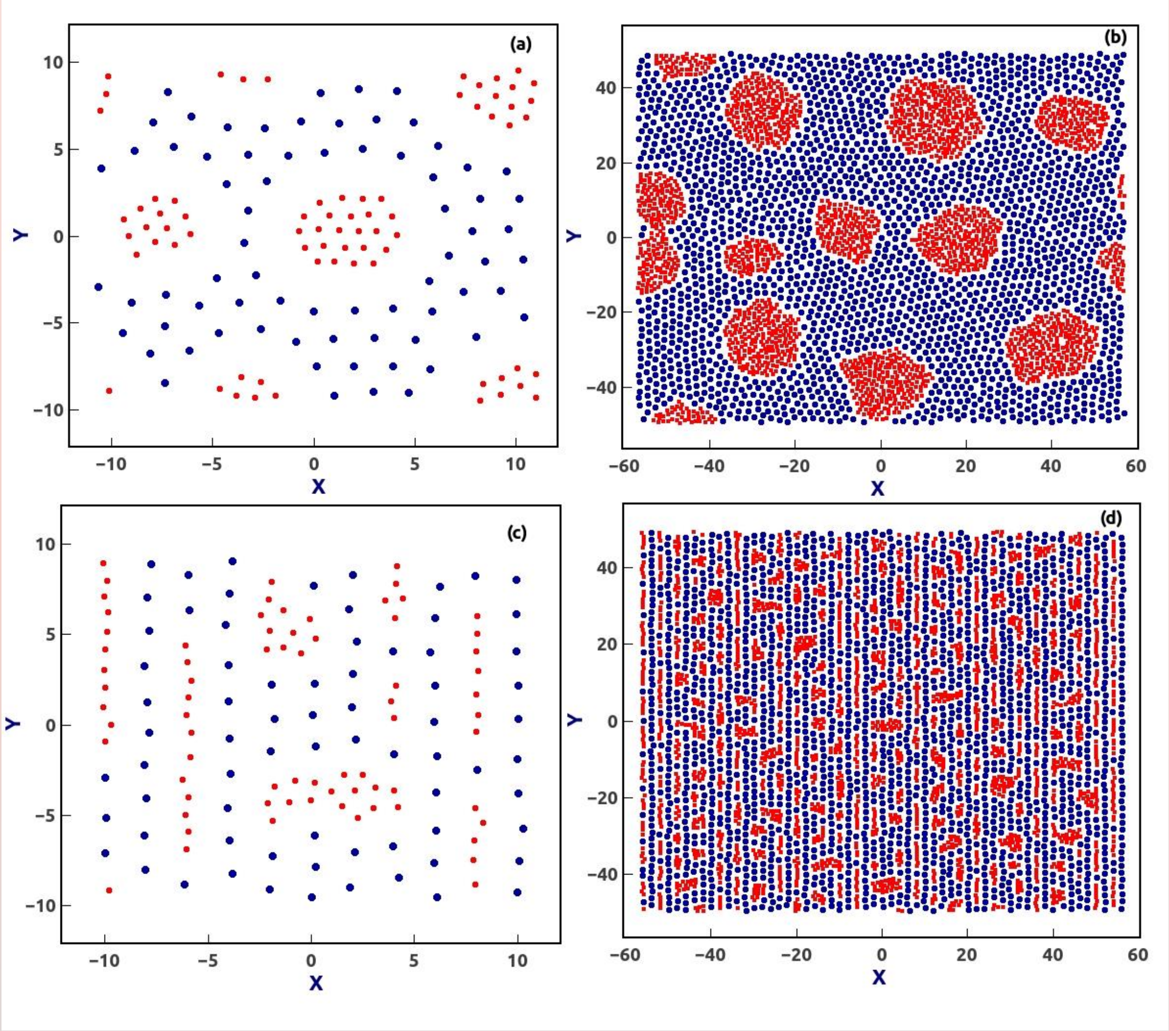




Modulated liquid

S. Pal and J. Chakrabarti, J. Phys.: Condens. Matter 32, 124001 (2020)

Other system sizes



a) and c) → N=144,
b) and d) → N=4096