

# Colloidal Crystal: emergence of long range order from colloidal fluid

Lanfang Li

December 19, 2008

## **Abstract**

Although emergence, or spontaneous symmetry breaking, has been a topic of discussion in physics for decades, they have not entered the set of terminologies for materials scientists, although many phenomena in materials science are of the nature of emergence, especially soft materials. In a typical soft material, colloidal suspension system, a long range order can emerge due to the interaction of a large number of particles. This essay will first introduce interparticle interactions in colloidal systems, and then proceed to discuss the emergence of order, colloidal crystals, and finally provide an example of applications of colloidal crystals in light of conventional molecular crystals.

# 1 Background and Introduction

Although emergence, or spontaneous symmetry breaking, and the resultant collective behavior of the systems constituents, have manifested in many systems, such as superconductivity, superfluidity, ferromagnetism, etc, and are well accepted, maybe even trivial crystallinity. All of these phenonema, though they may look very different, share the same fundamental signature: that the property of the system can not be predicted from the microscopic rules but are, “in a real sense, independent of them. [1] Besides these emergent phenonema in hard condensed matter physics, in which the interaction is at atomic level, interactions at mesoscale, soft will also lead to emergent phenemena. Colloidal systems is such a mesoscale and soft system. This size scale is especially interesting: it is close to biological system so it is extremely informative for understanding life related phenomena, where emergence is origin of life itself; it is within visible light wavelength, so that it provides a model system for atomic system with similar physics but probable by optical microscope.

Colloids are defined as particles with at least one dimension in the size range  $1 \text{ nm} - 1 \mu\text{m}$ , usually in liquid medium. Solvent mediated interaction has reduced strength compared to solid state, and better increased diffusion facilitates homogeneity. In comparison to atom, the interactions between colloids are almost always classical. Quantum effect can manifest at each individual particle level, but the range of the interaction force and the size of the particles themselves determined the equation of motion governing these particles in the classical regime. Interactions in colloidal system mainly include the following:

## 1.1 van der Waals force.

The quantum fluctuations at the atomic level within each colloid show up as a fluctuating dipole that will induce dipoles in other parts of the material, and interact with the induced dipole. This fluctuation dipole-induced dipole interaction accounts for the most important interaction, called Landon disperson force, in colloidal interactions. Others include permanent dipole induced dipole interactions, free ion dipole interactions etc. The fluctuation induced dipole interaction is featured with  $1/r^6$  law and is commonly called van der Waals force. The Van der Waals force is long range and ubiquitous and is always attractive. For spherical particles of equal size,  $V_{vdW}$  is given by the Hamaker expression:

$$V_{vdW} = \frac{A}{6} \left( \frac{2}{s^2 - 4} + \frac{2}{s^2} + \ln \frac{s^2 - 4}{s^2} \right) \quad (1)$$

where  $s$  is

$$s = \frac{2a + h}{a} \quad (2)$$

where  $h$  is the minimum separation between the particle surfaces,  $a$  is the particle radius, and  $A$  the Hamaker constant [2] which is material dependent. Dielectric constant and refractive index differences contribute to the Hamaker constant, so it is possible to engineer the system

so that the solvent and the colloids have matching refractive index. The resultant “index matched” colloidal system is effectively attraction free.

The attractive van der Waals force must be balanced by other repulsive forces to keep the suspension stable, otherwise instead of having dispersed colloids undergoing Brownian motion, the system will evolve into consolidated particle blobs and lose all the interesting features.

## 1.2 Electrostatic force

For charged colloid particles, an electro-double layer will form from the ions in solution around the surface of the particles. The potential of the charged particle is

$$V_{elect} = 2\pi\epsilon_r\epsilon_0a\Psi_0^2\ln[1 + \exp(-\kappa h)] \quad (3)$$

Where  $a$  is still the particle radius,  $\Psi$  is the surface charge density,  $h$  is distance away from surface of particle, and  $\kappa$  is the Debye Huckle screening length

$$\kappa = \left( \frac{F^2 \sum_i N_i z_i^2}{\epsilon_r \epsilon_0 kT} \right)^{1/2} \quad (4)$$

With  $N_i$  and  $z_i$  the number density and valence of the counter-ions of type  $i$  and  $F$  is the faraday constant [2].

Particles of the same kind possess the same surface charge and thus the interaction between the particles due to electrostatic force is repulsive in most cases. This is one of the most often used mechanisms to counter balance van der Waals attraction.

## 1.3 Steric forces

Adsorption of organic molecules, often mediate chain polymer, can be utilized to provide steric repulsion. Basically the polymer acts as a cushion to prevent particles from coming close enough for the van der Waals interaction to pull the particles together. The adsorbed layer should have sufficient thickness to overcome the van der Waals force, yet can not be too long as to prevent bridging between particles. The interaction between adsorbed polymer and solvent determines the morphology and effectiveness of steric stabilization. If the solvent is a good solvent for the polymer, and adsorption density is high enough, steric stabilization is optimized. Surface coverage as a function of adsorption density can be estimated by deGennes brush model.

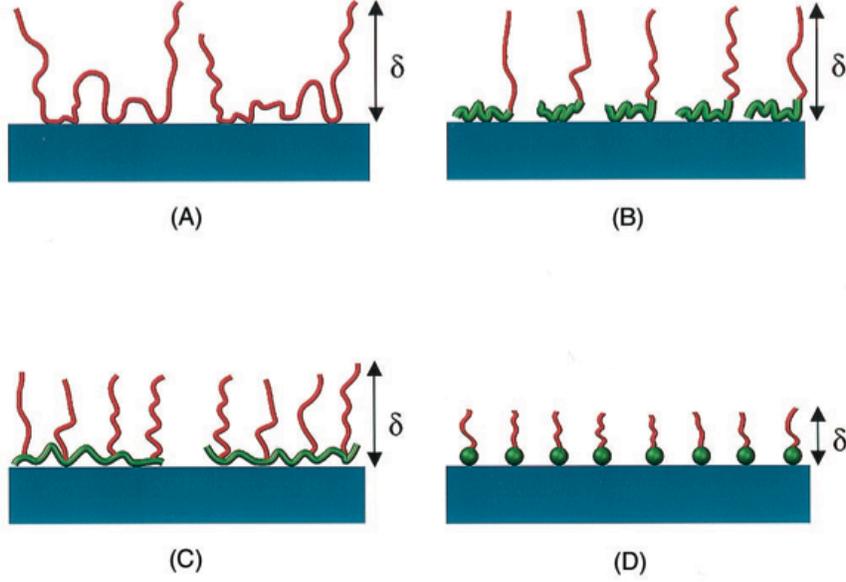


Figure 1: Schematic of surface adsorbed polymer induced steric repulsion: (A) homopolymer, consisting of tails, loops, and train configuration; (B) diblock copolymer, consisting of short anchor block and extended chain block; (C) comblike copolymer, consisting of extended segments attached to anchored backbone; and (D) functional, short-chain dispersant, consisting of anchoring head group and extended tail [2].

When the adsorbed polymer is charged, the solution ionic strength and pH will play a roll in the stabilization. Charged polymers will provide electrostatic repulsion in addition to steric repulsion. Both of these effects are sensitive to ionic strength and pH of solution. The mechanism based on the combination of electrostatic and steric forces are called electrosteric stabilization

## 1.4 Depletion forces

If the suspension contains colloidal particles of size 10-1000 nm, and a smaller species, such as polymer, smaller particles, or polyelectrolytes, the smaller species will exert osmotic pressure on the bigger colloidal particles. This interaction can be repulsive or attractive, depending on the concentration of the depletant. The interaction strength for uncharged depletant is

$$V_{dep}(\lambda) = \begin{cases} 0 & h > 2a_{dep} \\ \frac{a\phi_{dep}^2 kT}{10a_{dep}} (12 - 45\lambda + 60\lambda^2 - 30\lambda^3 + 3\lambda^5) & 4a_{dep} > h \geq 2a_{dep} \\ -\frac{3a\phi_{dep} kT}{2a_{dep}} + \frac{a\phi_{dep}^2 kT}{10a_{dep}} (12 - 45\lambda - 60\lambda^2) & h < 2a_{dep} \end{cases} \quad (5)$$

Where  $\phi_{dep}$  is the depletant volume fraction and  $l = (h - 2 * a_{dep})/2a_{dep}$ , when we consider depletant as rigid uniform spheres [2].

The sum of all these interactions gives the interaction potential for colloidal particles. While this interaction can be complicated, there are a couple models that are simplified yet still capture the most important character of the system. These models include: hard sphere potential, which is a zero potential at  $r > a$  and infinity at  $r \leq a$ ; DLVO potential [3], which is the  $r^{-6}$  van der Waals potential plus the electrostatic potential.

Such a system is similar to a normal molecular liquid, with a long range attractive force and a short range repulsion force, and stabilized by the two at a energy minimized distance. No long range order but on the short scale a short range order due to excluded volume interaction exists and pair correlation function show decaying peaks at  $2a$ ,  $3a$ ,  $4a$  and then the correlation function goes to 1. However, just like molecular crystals, colloidal systems are also observed to exhibit an emergent crystalline order with periodic structure and non-zero shear modulus [3,4]. Shear stress can melt the crystal when it exceeds a critical value.

Besides interaction potential, for concentrated system, the degree of freedom can be frustrated, and thus ergodicity symmetry breaking is shown in some systems, especially, crowded ones. Free energy landscape is used to theoretically describe such situations, where system falls into a local energy minimized state, and have very slow or even frozen freedom to transition into lower energy equilibrium state.

Phase behavior of colloidal suspensions therefore became an important question, when some systems have demonstrated the transition between colloidal liquid, to colloidal crystal others have not. It is instructional to systematically study the phase behavior of concentrated colloidal suspension. Also, since colloidal crystallization share similarities as molecular crystal crystallization yet with a size scale that is easier to probe and with slower dynamics shifting the time scale to readily observable range. Even the shape of colloid particles can be controlled to have different symmetries. In this way colloidal systems can be used as a model system to study crystallization in molecular systems.

## 2 Method and Results

Due to the complicated nature of the inter-particle interactions, it is informative to be able to construct a system with simple potential. Hard sphere potential being the first choice.

Pusey and Megan [5] carried out the phase digram study on such a simple model potential. Their system is engineered to be a nearly hard sphere system, with zero potential at inter-particle distance greater than diameter of particles and an infinite potential for distances equal to or less than diameter of particles.

The particles are 300 nm PMMA particles with 5% polydispersity, which is very important for crystallization. Bigger polydispersity will frustrate the system by having too much lattice strain when particles try to crystallize. The PMMA particles were coated with a layer of

10-20 nm thick poly-12-hydroxystearic acid to provide steric stabilization, and suspended in 2.66:1 decalin and carbon disulphide mixture. The solvent is selected to be index matched with the colloidal particles so that van der Waals interaction is diminished. Crystallization was carried out by gravitational sedimentation after randomizing the sample by extensive tumbling. Sedimentation occurred slowly and undisturbed, analogous to crystallization of a molecular crystal. The result are shown in Fig 2.

It is shown that there exists a critical volume fraction below which crystallization does not occur. Samples with higher concentration crystallized, as demonstrated by the iridescent color from Bragg reflection from the poly crystals. Coexistence of a colloidal liquid with a colloidal crystal shows that the concentration in this situation is playing the role of temperature in molecular crystals. At very high volume fraction of particles, crystallization was not observed, rather a glassy state formed due to the very slow dynamics of the system and frustrated rearrangement of particles to energy minimized states.

The phase diagram shows that below a critical effective volume fraction  $\phi_c = 0.494$  [6], (the number from extrapolation of experiment data)no crystallization occurred. Considering the polymer layer on surface of particles, the critical core volume fraction is 0.407. It is also shown that for samples with a volume fraction above 64%, the theoretical packing upper limit for monodisperse particles, a glassy state occurred instead of crystallization. Which agrees well with theory. The only invalidity of the experiment would be how close is this system to an ideal “hard sphere potential system. The answer is very close, but not exactly the same. The polymer coating is still soft. Which should be account for the discrepancy between the exact phase transition volume fraction from simulation and experimental results.

The convenient size scale of colloidal particles and the similar but slowed down kinetics enabled in-depth studies of crystallization phenomena also applicable to molecular crystals but that are much harder to probe on molecular size and time scales. Zhang and Liu carried out a real time direct imaging and quantitative measurements of the pre and post nucleation processes of colloidal spheres and the kinetics of nucleation driven by an alternative electric field. This work presented a well-defined thermodynamic driving force in 2-D which could be translated to molecular crystal systems of low dimension [7].

The nucleation process is governed by the competition between volume free energy gain by decreasing chemical potential and surface energy cost. The experiment apparatus is shown in Fig. 4.

An alternating electric field is applied across the slab of colloidal suspension The coupling between the electric field induced fluid flow and the colloidal particles, allows the particles to be transported by the flow to the electrode area and change the local concentration. Where  $\Delta G_{crit}$ , cost of total free energy to form a critical circular nucleus with radius  $r_c$  in a supersaturated solution with the crystal-liquid interfacial energy  $\gamma$ , and  $\Omega$  is the area per structural unit,  $\sigma$  the supersaturation can be directly controlled by electric field which plays the same role here as temperature.



Figure 2: (a), nearly-hard-sphere suspensions, 4 days after tubling, illuminated obliquely from behind by white light. From left to right from the readers perspective, samples are numbered 2 10. all the samples appeared featureless, reflecting randomization of the particle positions. (b), close-up of samples 7-9 at same condition.

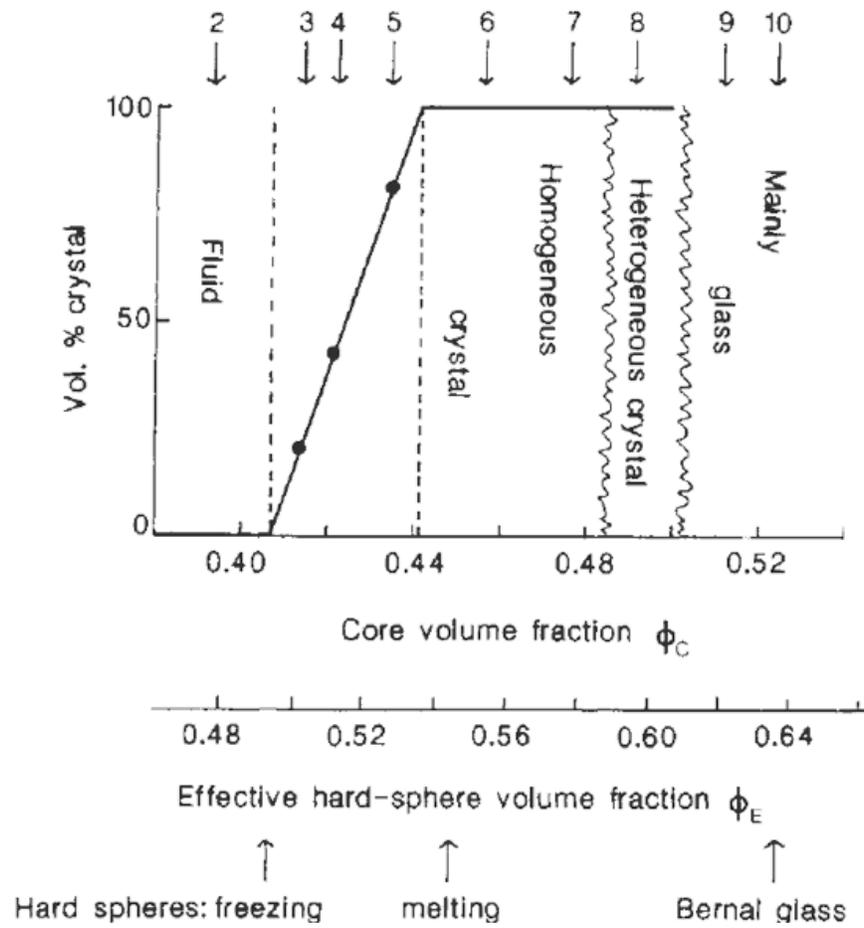


Figure 3: Phase diagram of the samples. Arrows at the top indicate the sample concentrations. The two horizontal axes indicate the measured volume fraction of PMMA cores and the effective hard-sphere volume fraction.

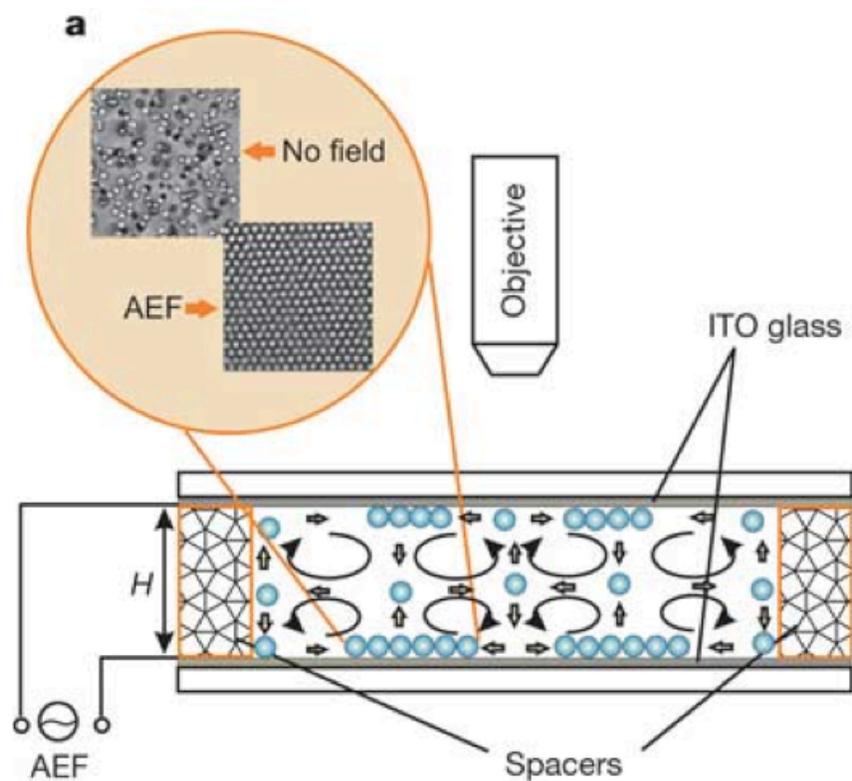


Figure 4: Experimental apparatus

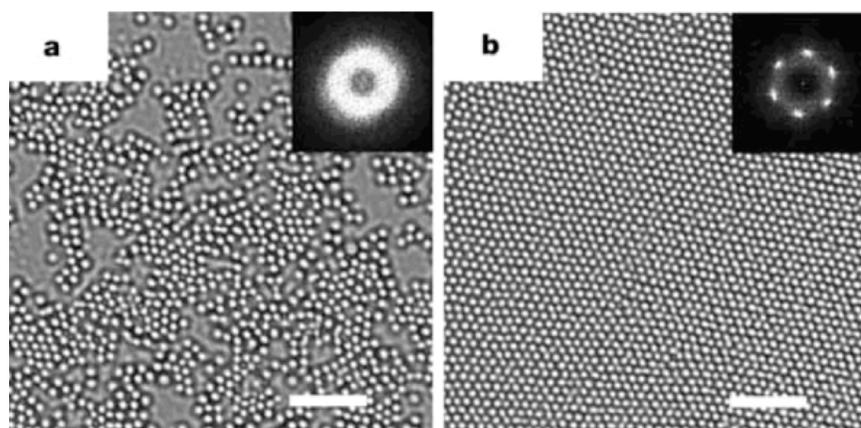


Figure 5: Comparison of the colloidal assemblies obtained under constant electric field and under an AEF. a, Constant electric field at 3.2 V. The fast Fourier transform (FFT) in the inset at upper right shows the diffraction ring. b, AEF at 2.4 V, 600 Hz. The FFT in the inset at upper right shows the uninterrupted six-fold symmetry of the hexatic phase. Scale bars, 10  $\mu$ m.

A large single crystal with low nucleation rate was achieved, and indicated the optimal condition informative to molecular crystal system.

### 3 Summary

Colloidal particle interactions are reviewed, colloidal crystallization as an emergent behavior from a colloidal suspension provides new understanding of the connection between atomic/molecular level phase transition kinetics and also the possibility of fabricating optically interesting materials.

### 4 References

1. Laughlin, R. B.; Pines, D.; Schmalian, J.; Stojkovic, B. P.; Wolynes, P., The middle way. *Proceedings Of The National Academy Of Sciences Of The United States Of America* 2000, 97, (1), 32-37.
2. Lewis, J. A., Colloidal Processing of Ceramics. *J. Am. Ceram. Soc.* 2000, 83, (10), 2341.
3. Vanmegen, W.; Snook, I., Equilibrium Properties Of Suspensions. *Advances In Colloid And Interface Science* 1984, 21, (1-2), 119-194.
4. Lindsay, H. M.; Chaikin, P. M., Elastic Properties Of Colloidal Crystals And Glasses. *Journal Of Chemical Physics* 1982, 76, (7), 3774-3781.
5. Pusey, P. N.; Vanmegen, W., Phase-Behavior Of Concentrated Suspensions Of Nearly Hard Colloidal Spheres. *Nature* 1986, 320, (6060), 340-342.
6. Leutheusser, E., Dynamical Model Of The Liquid-Glass Transition. *Physical Review A* 1984, 29, (5), 2765-2773.
7. Zhang, K. Q.; Liu, X. Y., In situ observation of colloidal monolayer nucleation driven by an alternating electric field. *Nature* 2004, 429, (6993), 739-743.