Bond-orientational ordering and shear rigidity in modulated colloidal liquids

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Abstract

From Landau-Alexander-McTague theory and Monte-Carlo simulation results we show that the *modulated liquid* obtained by subjecting a colloidal system to a periodic laser modulation has long range bond-orientational order and non-zero shear rigidity. From *infinite field* simulation results we show that in the *modulated liquid* phase, the translational order parameter correlation function decays to zero exponentially while the correlation function for the bond-orientational order saturates to a finite value at large distances.

Key words: Laser induced freezing; Bond-orientational order; modulated liquid

1 Introduction

Consider a 2-d charge stabilized colloidal system subject to a one-dimensionally modulated stationary laser field (obtained by superposing two beams). Chowdhury, Ackerson and Clark [1] found that when the wave-vector of the laser modulation is tuned to be half the wave-vector q_0 at which the structure factor of the colloidal liquid shows its first peak, above a certain laser field intensity, the system freezes into a 2-D triangular crystal. This phenomena of laser induced freezing (LIF) has been studied subsequently by experiments [2-4], simulations[5-7] and density functional calculations [8-10]. For field strengths below the value at which the system undergoes freezing, the laser field induces a density modulation with wave-vector q_0 in the liquid, and this phase has been called *modulated liquid* in the literature. In this paper we show that the modulated liquid has rather interesting properties. Specifically the induced translational order generates a field conjugate to the bond-orientational order parameter. Hence the *"modulated liquid"* has a non-zero value of bond-orientational order parameter, and consequently a finite rigidity (shear modulus). We first present a qualitative picture in terms of a generalized Landau-

Alexander-McTague [11] theory and substantiate the picture with results from a detailed Monte-Carlo simulation.

2 Mean-field treatment

From general symmetry grounds the coarse-grained free energy functional in two dimensions in the presence of an external field V_e, coupled to one of the six density Fourier modes $(\rho_{\vec{G}_1})$ characterizing a 2-D crystal has the form [12]:

$$
\begin{aligned}
F = &-2V_e\rho_{\vec{G}_1} + \frac{1}{2}r_T\sum_{\vec{G}}|\rho_{\vec{G}}|^2 \\
&+w_T\sum_{\vec{G}+\vec{G}'+\vec{G}''=0}\rho_{\vec{G}}\rho_{\vec{G}'}\rho_{\vec{G}''} + u_T(\sum_{\vec{G}}|\rho_{\vec{G}}|^2)^2 + u_T'\sum_{\vec{G}}|\rho_{\vec{G}}|^4 + ... \\
&+\frac{1}{2}r_6|\psi_6|^2 + u_6|\psi_6|^4 + ... \\
&+\gamma\sum_{\vec{G}}|\rho_{\vec{G}}|^2[\psi_6(G_x - iG_y)^6 + \psi_6^*(G_x + iG_y)^6];
\end{aligned}
\tag{1}
$$

where the summations run over all the wave-vectors forming the first shell of the reciprocal lattice vector of the triangular lattice into which the colloid freezes and ψ_6 is the bond-orientational order parameter.
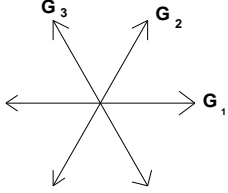
Notations:
$\rho_1 \equiv \rho_{\vec{G}_1} \equiv \rho_{-\vec{G}_1}$
$\rho_2 \equiv \rho_{\vec{G}_2} \equiv \rho_{\vec{G}_3} \equiv \rho_{-\vec{G}_2} \equiv \rho_{-\vec{G}_3}$

Fig. 1. Density Fourier modes for 2-D triangular crystal.

In the absence of external field, for large positive values of r_T and r_6, the free energy is minimum when all order parameters are zero (ie. for the liquid phase). If, as a consequence of a change in temperature, screening length or some other parameter, r_T decreases much faster than r_6, then because of the cubic term in equation (1) one gets a first order freezing transition into a crystalline phase. On the other hand, if r_6 decreases much faster than r_T, one gets a continuous transition to an orientationally ordered hexatic phase, characterized by nonzero values of ψ_6 and zero values of $\rho_{\vec{G}}$.

The external field induces a non-zero $\rho_{\vec{G}_1}$ even in the liquid phase. The non-zero value of $\rho_{\vec{G}_1}$ leads to an effective field conjugate to the bond-orientational order through the coupling γ in eqn. 1. So ψ_6 is also turned on as the external field is applied. Since the external field modulation fixes the directions

in which the order develops, we can treat the order parameters as real number to get the equilibrium phase diagram (the phase in the order parameters will be important in determining the elastic coefficients but not in determining the stable equilibrium phase). The experimental systems and the earlier simulations referred to above [1-7] corresponded to volume fraction and salt concentration values such that the zero field freezing transition was first order; hence they presumably correspond to $r_T \leq r_6$. Even if r_6 is much smaller than r_T, such that the freezing mechanism at zero external field is a two stage transition with the first (continuous) transition being to the hexatic phase, the external field will immediately destroy the intervening hexatic phase.
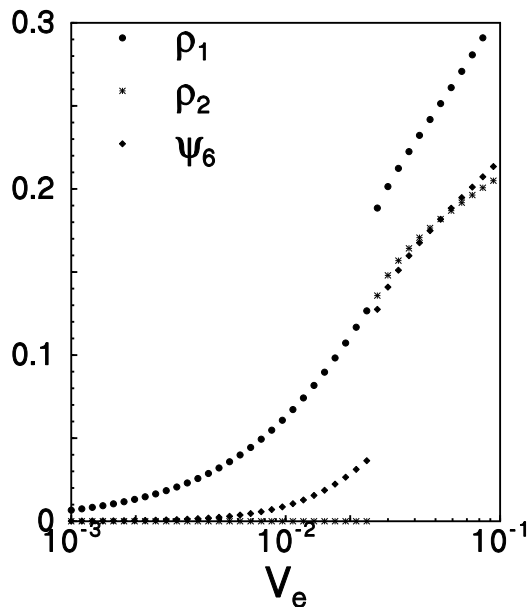

Fig. 2. Values of the translational and orientational order parameters as a function of external field in Landau-Alexander-McTague theory

Choosing the coefficients $r_T = r_6 = 0.30$, $w_T = -1/3$, $u_T = u_6 = 1.5$, $u'_T = 0.5$ and $\gamma = -0.7$ numerical minimization of eqn. 1 gives the order parameter profile as a function of external field shown in Fig. 2. ψ_6 and $\rho_{\vec{G}_1}$ becomes nonzero as soon as V_e is turned on, and at $V_e = 0.0239$ all the order parameters jump simultaneously signifying a first order transition to a crystalline structure.

One can define a rigidity modulus in analogy to the helicity modulus in superfluids [13]:

$$Y = \lim_{q \to 0} \frac{1}{q^2} \frac{\partial^2 F}{\partial^2 \vec{q}}, \tag{2}$$

where we consider an field coupled to the orientational order parameter as $\psi_6(\vec{r}) \longrightarrow \psi_6(\vec{r})e^{i\vec{q}.\vec{r}}$. The free-energy cost for such a field will depend on the gradient term in ψ_6 (not included in eqn. 1). To leading order such a term would predict $Y \sim V_e^4$ as $|q| \to 0$.

3 Monte-Carlo Simulations

3.1 Simulation details

Since the parameters in eqn. 1 are phenomenological and there is no direct way to fix them to characterize the experimental system, we have performed Monte-Carlo simulations to study the *modulated liquid phase*. We have considered a 2-D system of charge stabilized colloidal particles (with diameter $2R = 1.07 \mu m$) confined in a rectangular box of size $\frac{\sqrt{3}}{2} a_s L \times a_s L$ with periodic boundary conditions and subjected to an external potential of the form $U(\vec{r}) = -V_e cos(q_0 x)$, with $q_0 = 2\pi/(\frac{\sqrt{3}}{2} a_s)$, where a_s is the mean inter-particle separation. The inter-particle interaction is modeled by the DLVO potential:

$$U_{ij}(r) = \frac{(Ze)^2}{\epsilon} (\frac{exp(\kappa R)}{1 + \kappa R})^2 \frac{exp(-\kappa r_{ij})}{|r_{ij}|} \tag{3}$$

Here Ze ($Z = 7800$) is the effective surface charge, ϵ (=78) is the dielectric constant of the solvent and κ is the inverse of the Debye screening length due to the small ions (counterions and impurity ions) in the solvent. The parameters are the same as in earlier simulation studies and similar to the experiments [1].

To study the effect of very large external field (*infinite field*), in some of the simulations we had fixed the particles in parallel lines defined by the potential minima. Though the particles move freely only along the lines, they interact in full two dimensional space. The resulting simplification allows us to simulate systems with L as large as 100, which allows us to compute correlation functions at large distances.

The translational order parameters are defined by:

$$\rho_{\vec{G}} = < \frac{1}{N} \sum_i e^{i\vec{G}.\vec{r_i}} > . \tag{4}$$

G_1 refers to the direction parallel to the modulation wave-vector $[\frac{2\pi}{\sqrt{3}/2a_s}(1,0)]$, while G_2 refers to the other independent wave-vector $[\frac{2\pi}{\sqrt{3}/2a_s}(\frac{1}{2}, \frac{\sqrt{3}}{2})]$ forming the first shell of wave-vectors of the triangular lattice. Value of $\rho_{\vec{G}}$ as defined in eqn.(4) depends on the coordinate origin. So we measure the translational order parameter as $\rho_{\vec{G}} = < \frac{1}{N}\sqrt{[\sum_i cos(\vec{G}.\vec{r_i})]^2 + [\sum_i sin(\vec{G}.\vec{r_i})]^2} >$ [14]. This quantity is of order unity in crystalline state, while in liquid this goes to zero as $\frac{1}{\sqrt{N}}$ for a system of N particles.

We define the bond-orientational order parameter as:

$$\Psi_6 = < \frac{1}{N} \sum_m \frac{1}{z_m} \sum_n e^{6i\theta_{m,n}} >, \tag{5}$$

where $\theta_{m,n}$ is the angle made by the line joining the position of particle m to the neighboring particle n, measured with respect to some fixed direction. z_m is the number of neighbors corresponding to the Voronoi cell of particle m.

To calculate order parameter correlation functions we define local order parameters $\rho_{\vec{G}}(\vec{r_m}) = \frac{1}{z_m+1}[e^{i\vec{G}.\vec{r_m}} + \sum_n e^{i\vec{G}.\vec{r_n}}]$ and $\psi_6(\vec{r_m}) = \frac{1}{z_m} \sum_n e^{6i\theta_{m,n}}$, where the order parameters are defined at the position of a particle m, and n denotes the particles forming the Voronoi cell of particle m. The order parameter correlation functions are defined as,

$$G_T(\vec{r}) = < \rho_{\vec{G}}^*(\vec{r})\rho_{\vec{G}}(0) >, \tag{6}$$
$$G_6(\vec{r}) = < \psi_6^*(\vec{r})\psi_6(\vec{0}) > . \tag{7}$$

To measure the helicity modulus Y, we have applied "anti-periodic" boundary condition along the x direction. In case of the standard periodic boundary condition, one repeats the simulation cell throughout space for calculating the inter-particle potential and to put back the particle inside the simulation box once it moves out in the course of the simulation. In case of the "anti-periodic" boundary condition, in the x direction for example, successive imaginary repeat boxes are shifted by half the lattice spacing in the y-direction. Equivalently, while folding back a particle that exits from the simulation box in the $\pm x$ direction, a displacement $\pm\frac{1}{2}a_s\hat{y}$ is applied. The change in energy between periodic and "anti-periodic" boundary conditions gives a measure of Y.

3.2   results

The specific heat in figure 3 (a) shows a peak as function of βV_e signifying a phase transition at $\beta V_e = 0.25$. In figure 3(b) we present order parameters for $L = 20$ and $\kappa a_s = 15.5$ (where the system is liquid for zero external field) as a function of βV_e. The translational order parameters ρ_1 and ρ_2 are non-zero even in the liquid phase because of the finite system size. Also they seem to grow continuously. But a finite-size scaling analysis shows that the results are consistent with first order transition scenario with small discontinuity in energy [7]. In addition to ρ_1, Ψ_6 also shows non-zero value as soon as the external field is switched on as expected from the coarse-grained free energy.

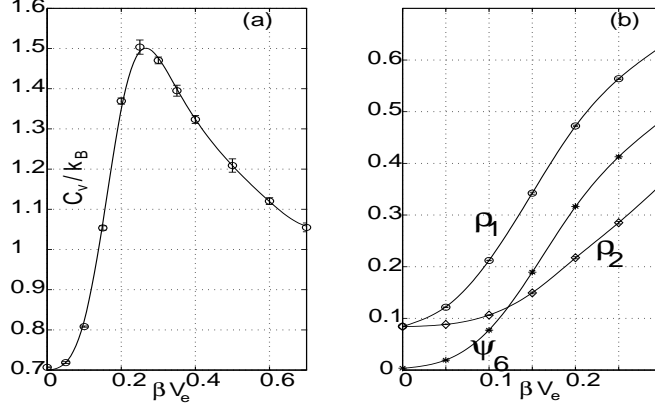In figure 4, we plot ρ_2 and Ψ_6 for infinite field and 10^4 particle system ($L =$

Fig. 3. (a) Specific heat, and (b) Order parameters, obtained from Monte-Carlo simulations of a 400 particle system as a function of βV_e. κa_s was chosen to be 15.5 for these simulations, such that the system is in liquid state in absence of external field
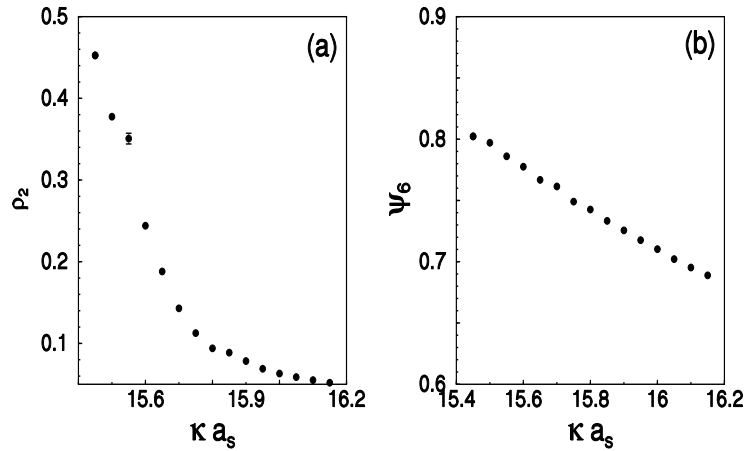

Fig. 4. $\rho_{\vec{G}_2}$ and Ψ_6 across the melting transition for infinite field and 10000 particles

100) as a function of κa_s. While the translational order parameter shows a sharp fall at the melting transition ($\kappa a_s = 15.6$), the bond-orientational order parameter remains large and finite.

In figure 5 we plot the order parameter correlation functions in the crystalline region(5.a) and in the liquid region (5.b). In crystalline region $G_T(y)$ decays as a power law, while $G_6(y)$ saturates to a constant value. In the liquid region, while $G_T(y)$ decays to zero exponentially at large distances, $G_6(y)$ still remain finite.

In figure 6 we have shown the difference in energy in units of $k_B T$ per particle for anti-periodic and periodic boundary conditions. We have considered a system with $L = 10$ in order to have a measurable enegy difference because of the large shear. The system freezes around $\beta V_e = 0.2$. From figure 6 we
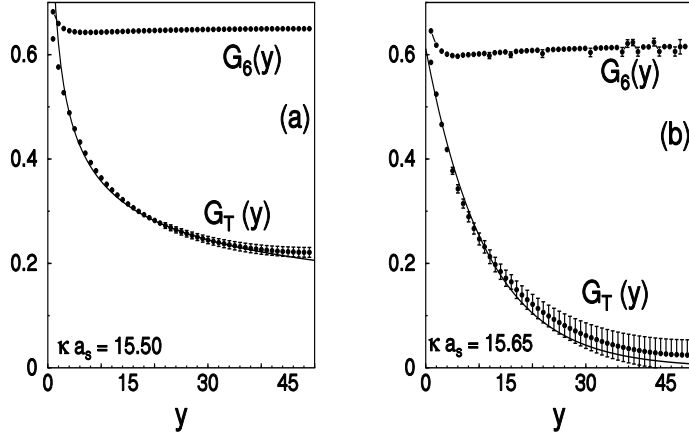
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Fig. 5. Translational and bond-orientational correlation functions along the external field minima (y axis) from simulation of 10000 particles and infinite field
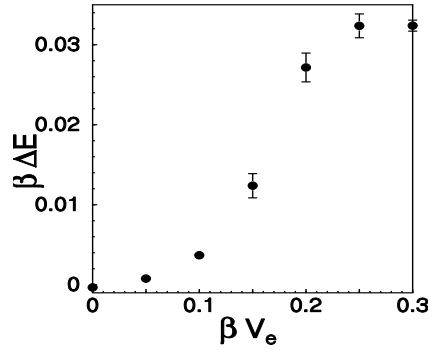

Fig. 6. Energy difference between anti-periodic and periodic boundary conditions

find that there is a non-zero elastic energy cost and hence a non-zero shear modulus even before the system freezes to crystalline structure. At $\beta V_e = 0.2$, there is a sharp change in ΔE, which then saturates.

4   Conclusion

We have shown that the *modulated liquid* phase obtained by inducing density modulation in a colloidal liquid by subjecting it to external laser modulations has properties intermediate between crystal and liquid; specifically partial translational order, finite bond-orientational order, and non-zero rigidity modulus. In two dimensional freezing, a large part of the loss of entropy upon freezing is due to the bond-orientational ordering. In LIF, the fact that the freezing transition occurs from a partially bond-orientationally ordered phase to a crystalline phase, helps one to understand why the transition becomes more weakly first order as the external field strength is increased.

Acknowledgments

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