

Melting of lamellar phases in temperature sensitive colloid-polymer suspensions

A. M. Alsayed, Z. Dogic, and A. G. Yodh

Department of Physics and Astronomy, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6396

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We investigate the behavior of a novel suspension composed of rod-like fd virus and thermo-sensitive polymer Poly(N-isopropylacrylamide) whose phase diagram is temperature and concentration dependent. The system exhibits a rich variety of stable and metastable phases, and, more importantly, provides a unique opportunity to directly observe melting of lamellar phases and single lamellae. Typically lamellar phases swell with increasing temperature before melting into the nematic phase. The highly swollen lamellae can even be superheated as a result of topological nucleation barriers that slow formation of nematic phases. Using optical forces we prepare metastable nematic and multilayer structures starting from a single colloidal membrane, and then observe the system evolve back into a single membrane.

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Melting of three-dimensional (3D) crystals is among the most ubiquitous phase transition in nature [1]. In contrast to freezing, melting of 3D crystals has no associated energy barrier. Bulk melting is initiated at a pre-melted surface, which then acts as a heterogeneous nucleation site and eliminates the nucleation barrier for the phase transition [2–4]. In this paper we investigate pathways for melting of lamellar phases. In contrast to 3D crystals, lamellar phases have one-dimensional (1D) quasi-long-range order [5–7]. Additionally while 3D crystals have only one surface between coexisting media the lamellar phase is a microphase separated state in which the entire bulk is spanned by interfaces between immiscible phases. These phases are frequently built from amphiphilic molecules such as surfactants and block copolymers in solution. Although lamellar phases are very common, melting transitions of lamellar into nematic phases are rarely observed. Here we create a novel system that exhibits lamellar-nematic melting, and we show melting of a lamellar phase is fundamentally different from melting of 3D crystalline solids.

We have developed a temperature sensitive aqueous colloidal suspension in order to carry out these studies. The suspension is composed of lyotropic monodisperse rods of fd virus [8, 9], and thermosensitive Poly(N-isopropylacrylamide) (NIPA) polymer. The thermotropic character of the fd /NIPA mixture stems from the temperature dependent solubility of NIPA polymer in water [10]. Below its Θ -temperature of 31°C , water is a good solvent and NIPA polymer assumes a swollen coil form. Above the Θ -temperature water is a poor solvent and NIPA has a collapsed globule form [11]. The resultant mixture forms isotropic, lamellar and nematic phases depending on temperature and constituent concentration. The lamellar phases resemble those of fd with hard spheres, in which layers of spheres are intercalated between layers of rods [12]. Our temperature sensitive aqueous suspension, however, enables us to directly study transitions from one phase to another with optical microscopy.

These fd /NIPA solutions are unusual new materials

whose lamellar phases differ from those of amphiphilic molecules. The lamellae can swell considerably and melt into a nematic phase, a transition almost never observed in block-copolymer lamellar systems. The different phase behaviors arise primarily because of the rod-like character of the fd component, and also because of the absence of covalent cross-links between fd and NIPA polymer. The kinetic pathways exhibited by these fd /NIPA mixtures are also more complex than those found in temperature-dependent (thermotropic) molecular liquid crystals and concentration-dependent (lyotropic) amphiphilic systems [13, 14]. For example the lamellar phases of fd /NIPA mixtures can be swollen to the point where isolated layers (lamellae) of rods are observed. These isolated membrane-like structures of non-amphiphilic mesogens are stable against mechanical perturbations, melt into nematic droplets, and raise questions about the simplest interacting mesogens capable of assembling into two-dimensional (2D) membranes. Most of the assembly into 2D membranes is driven by hydrophobic-hydrophilic interactions [15–17], while our work indicates that a much simpler system of rods with uniform attractions is capable of assembling into membranes under specific conditions.

Finally, our temperature sensitive fd /NIPA solutions offer a powerful new model system for studies of melting. Lyotropic suspensions such as colloids have proven to be ideal for real-time studies of freezing [18–20]. Melting transitions, however, are much more difficult to investigate with lyotropic colloids. Once a stable ordered phase is obtained, microscopic observation and concurrent concentration variation are required to monitor melting, a challenging experimental task. The advantage of our weakly “thermotropic” fd /NIPA polymer based suspension is that simple changes in temperature enable us to prepare the “lyotropic” colloidal system in a metastable ordered state, and then study its melting transition *in situ*. Generally a small increase of temperature increases monomer-monomer attractions and thus decreases the osmotic pressure of the semi-dilute NIPA polymer solution. As a result, water from polymer-rich

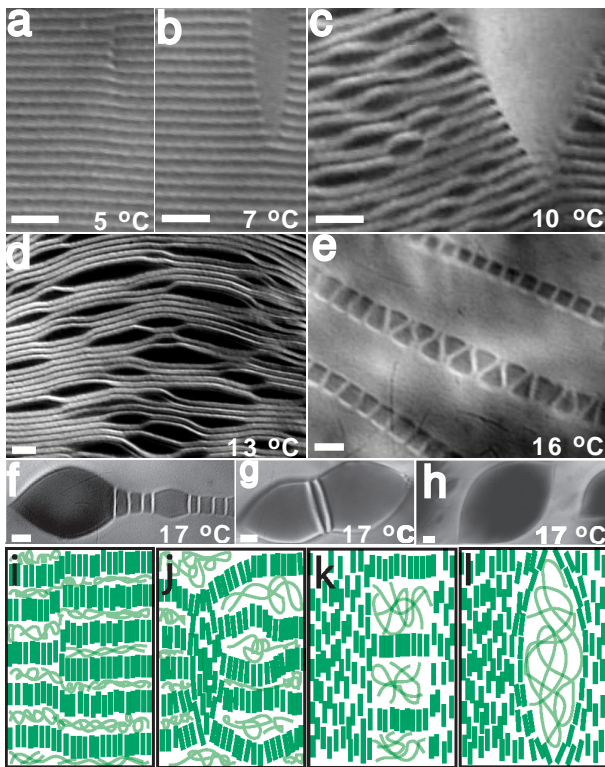


FIG. 1: Melting behavior of sample S1 (50 mg/ml *fd* and 7.5 mg/ml NIPA). (a) Lamellar phase at low temperature exhibits visible dislocation defects (b) At 7 °C the dislocation defects act as a site for nucleation of the nematic phase. (c) Nematic domains grow, expelling NIPA polymer into lamellar phase, which leads to swelling of lamellar layers. (d) Swollen lamellar phase (e) Coexistence between nematic phase and highly swollen lamellar phase. Lamellar phase has the shape of an elongated stripe while the nematic phase fills the rest of the space. (f-g) Isolated monolayer-deformed isotropic tactoid. (h) Isotropic-nematic coexistence observed at high temperature. (i-l) Illustration of the proposed melting processes of the lamellar rod/polymer mixture. Scale bars are 5 μm .

layers flows into rod-rich layers until osmotic equilibrium is re-established. This phenomena dilutes the rod concentration locally, which in turn can lead to melting of the lamellar phase.

NIPA polymer was synthesized at 22°C by polymerization of N-isopropylacrylamide (7 gm) dissolved in 100 ml of 20mM (pH=8.15) tris buffer. Ammonium persulfate (61 mg) and tetramethylethylenediamine (TEMED) (280 μl) were added as initiator and accelerator [10]. Bacteriophage *fd* is a negatively charged semi-flexible rod with diameter of 6.6 nm, contour length of 880 nm and persistence length between 1000 nm and 2200 nm [9, 21]. It forms isotropic, cholesteric(nematic) and smectic phases with increasing concentration [8]. A standard protocol was used to grow *fd* virus [9]. The *fd*/NIPA mixtures were suspended in a buffer (pH=8.15, 20 mM tris) and were placed between the coverglass and coverslip and then sealed. All observations were made with an inverted

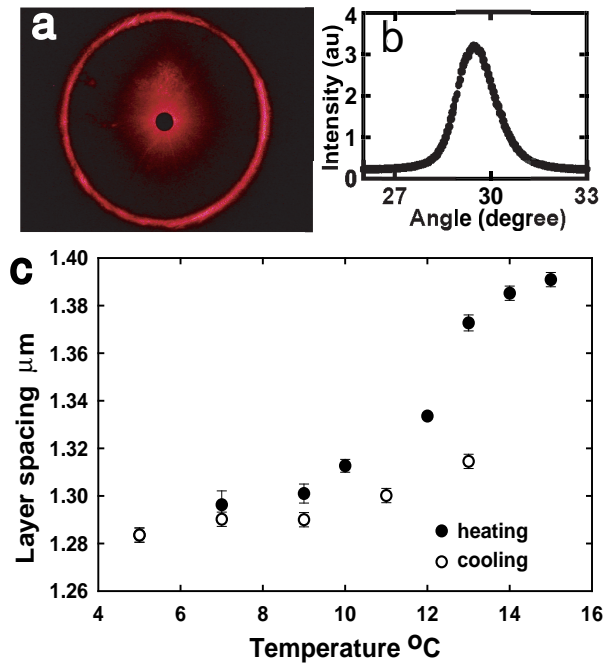


FIG. 2: Melting of the lamellar sample S1 studied by small angle light scattering. The real space images of the melting behavior are shown in Fig. 1. (a) Small angle light scattering pattern of an orientationally disordered lamellar phase at 5 °C (b) Angularly averaged intensity profile at 5 °C and 13 °C. (c) Lamellar periodicity for a sample during heating (filled circles) and cooling (open circles). There is a large hysteresis of layer spacing between heating and cooling cycles.

microscope (Leica DM IRB) equipped with DIC optics using an oil immersion lens (100X, N.A. 1.4). The temperature of the sample and the objective was controlled with a water circulator. Images were captured by a CCD camera and digitized using NIH-image software. The optical trap for the melting experiments was created with IR light ($\lambda = 1054 \text{ nm}$) as described elsewhere [22].

The melting behavior of a *fd*/NIPA mixture with high rod concentration is illustrated in Fig. 1. Hereafter we refer to this sample as S1. At low temperature (5 °C), the mixture forms a lamellar phase where layers of rods are intercalated with layers of polymers; the polymers are in the semidilute regime (Fig. 1a). The measured layer periodicity (1.2 μm) is much larger than the periodicity of the smectic phase (0.9 μm) in isolated *fd* suspensions. Dislocations and grain boundaries are observed at low temperature (Fig. 1a and i); with increasing temperature they act as nucleation sites for formation of nematic tactoids (Fig. 1b). The shape of the nematic tactoid in the smectic background is very similar to the shape of the nematic tactoid in the isotropic background [23].

Although polymer is macroscopically miscible with rods in the lamellar phase, it is highly immiscible with rods in nematic phases [24]. Therefore as the nematic tactoids grow, they expel polymer into coexisting lamellar phase which in turn leads to swelling of the lamellar

layers (Fig. 1c and j). In a swollen lamellar phase there are regions where individual layers are tightly bound and regions where they are well separated (Fig. 1d). Above 15 °C most of the sample is melted into a nematic phase which coexists with a highly swollen lamellar phase. The lamellar phase assumes a form of elongated stripes (Fig. 1e and k). Upon increasing the temperature further, the lamellar stripes transform into polymer rich isotropic tactoids which are frequently deformed by a few isolated lamellar layers (Fig. 1f-h). Finally, above 17 °C isolated layers melt, and the isotropic tactoids in the nematic background assume their characteristic shape (Fig. 1h and l) [23].

Lamellar periodicity is also obtained from the diffraction pattern of lamellar phases (Fig. 2a). With increasing temperature the peak simultaneously broadens and shifts to lower angles (Fig. 2b and c) indicating swelling of the lamellar phase. Above 15 °C most of the sample has melted into the nematic: in this case only large forward scattering is observed. At this temperature we still observe highly swollen lamellar stripes with an optical microscope (Fig. 1e). When the sample is cooled from the high temperature nematic phase, the lamellar phase forms at 13 °C. Taken together, the observation of coexistence and hysteresis in the heating/cooling cycle suggest lamellar melting into the nematic phase is a first order phase transition with significant nucleation barriers. Moreover the structure of the lamellar phase depends on sample history. The lamellar spacing of samples prepared at high temperature and subsequently cooled is smaller than the lamellar spacing of samples prepared at low temperatures and subsequently heated. In order for the polymer to form an isotropic droplet the lamellar layers must melt. In the next part of the paper we show there is a kinetic barrier for melting of isolated lamellae into a nematic. Therefore with increasing temperature, the sample forms a metastable highly swollen lamellar phase until the individual lamellae overcome a nucleation barrier for melting.

In the experiments with sample S1, we observed swelling of the lamellar phase. The concentration of lamellar layers in these samples was high, and thus swelling was limited by steric interactions. In order to determine the maximum swelling of the lamellar system, we repeated the melting experiments at much lower *fd* concentration (Fig. 3). Hereafter we refer to this sample as S2. At low temperatures most of the sample is an isotropic polymer solution. At temperatures between 21-25 °C we observe coexistence between lamellar droplets (Fig. 3a) and isolated lamellae (colloidal membranes) (Fig. 3c). The spacing of the layered droplets is 1.2 μm , indicating a lamellar phase similar to S1. The colloidal membranes we observe are composed of a single liquid-like layer of highly aligned rods; similar membranes have been observed in athermal rod/polymer mixtures and perhaps in aqueous solutions of β -FeOOH rods [9, 19, 25]. Over time isolated lamellae grow from the interface of the isotropic-lamellar droplet into the isotropic phase; this

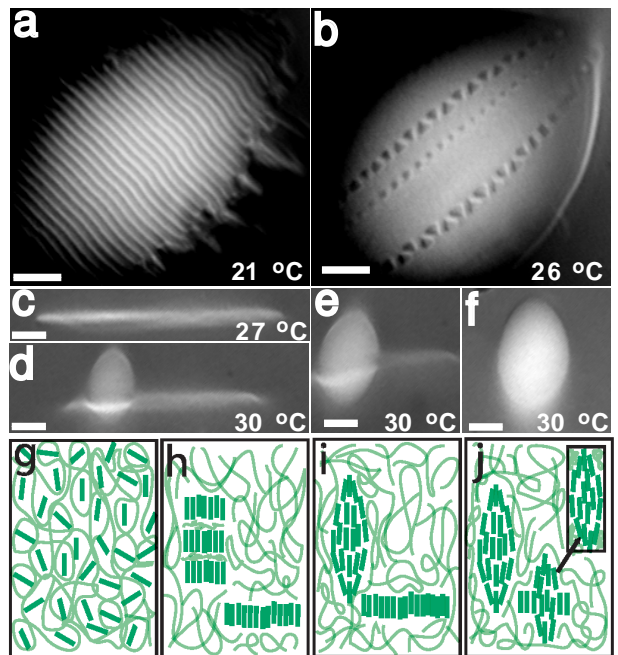


FIG. 3: Melting behavior of sample S2 (7.5 mg/ml *fd* and 37 mg/ml NIPA). (a) At 24 °C lamellar droplets form in a background isotropic phase. Simultaneously, the formation of isolated layers (shown in image c) is observed. (b) At higher temperature, lamellar droplets melt into a nematic phase by the mechanism described in Fig. 1. (c) An isolated membrane is stable for a temperatures from 22-27 °C. (d-f) Sequence of images showing nucleation and growth of a 3D nematic nematic tactoid from an isolated superheated 2D membrane. (g-j) Illustration showing the above described melting processes. At temperatures below 10 °C, the sample forms a miscible isotropic phase. The reason for this is not understood. Scale bars are 5 μm .

indicates that single membranes are more stable than lamellar droplets.

The coexistence of isolated membranes and lamellar droplets with well defined spacing implies another first order transition, this time from bound to unbound layers. Related binding-unbinding transitions have been studied theoretically in the context of lipid bilayers; the order of these transitions was found to be sensitive to the range of the intermolecular interactions [26, 27]. It is also notable that the suspension of *fd* rods usually contain a low volume fraction of dimers. The dimers can affect the swelling kinetics of smectic layers and probably increase the stability of the multilayer structure since they dissolve more easily in a bilayer than in a monolayer.

We have investigated melting and layer reducing dynamics associated with isolated membranes (sample S3). At temperatures above 25 °C lamellar droplets melt into a nematic phase. The mechanism for this melting is similar to melting of the bulk lamellar phase (Fig. 3b). The isolated colloidal membranes, however, remain stable at temperatures well above the melting temperature of the multi-layer lamellar droplets. Only upon rais-

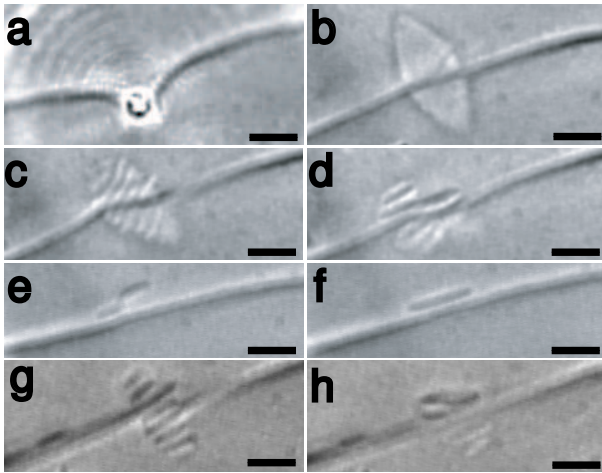


FIG. 4: Layer reducing transition of a colloidal membrane observed in sample S3 (12 mg/ml fd, 31 mg/ml NIPA). The sample temperature is 28 °C, below the melting of the bulk lamellar phase (29 °C). (a) A membrane is repeatedly punctured by a 2.1 μm silica sphere trapped with laser tweezers. (b) A metastable nematic droplet forms due to shear melting. (c) Upon removal of the laser beam the nematic droplet freezes into a multilayer smectic structure. (d-f) The structure undergoes a sequence of layer reducing transitions. (g-h) In a separate experiment a formation of a dislocation in the main membranes is visible. The dislocation subsequently disappears as layers slide over each other which reducing the number of layers by one.

ing the temperature to almost 30 °C is nucleation of a three-dimensional nematic tactoid observed in the two-dimensional membrane (Fig. 3d-f). Once a nematic tactoid is nucleated it quickly grows until the whole membrane melts. If the sample is subsequently cooled, the formation of single layer smectic will be observed only at temperatures below 27 °C. These observations suggest colloidal membranes are metastable superheated structures between 27-30 °C. Nucleation of a 3D nematic tactoid from a 2D membrane requires a large collective fluctuation in which many rods protrude into the third dimension. Our experiments indicate the topological barrier for nucleation of a nematic tactoid is very large. In this sense the melting behavior of lamellae are very different from melting of 3D solids.

Finally we explored the stability of isolated colloidal membranes against external mechanical perturbations (Fig. 4). These experiments were done at temperatures below the bulk lamellar melting transition so that the

membranes were stable. A silica bead was trapped with an optical tweezer and the colloidal membrane repeatedly punctured (Fig. 4a). This mechanical perturbation produced local shear melting of the membrane into a nematic droplet (Fig. 4b). We were only able to shear melt membranes at temperatures close to bulk lamellar-nematic phase transition. At lower temperatures the punctured membrane rapidly returned to its equilibrium shape. After the membrane melted, the laser beam is kept in close vicinity of the nematic droplet, locally heating the sample. When the laser beam is on, the nematic droplet coexists with the membrane. The temperature is reduced when the laser beam is turned off, and the nematic droplet quickly freezes into a multilayer smectic structure (Fig. 4c). This multilayer smectic structure is unstable and undergoes a sequence of layer reducing transitions until the initial equilibrium membrane configuration is obtained. This experiment provides additional evidence that colloidal membranes are equilibrium structures in this temperature range. By directly visualizing the smectic layers we can discern the mechanism by which a layer reducing transition takes place. The number of layers can be reduced when individual layers slide over each other (Fig 4e-f) or by spontaneous formation of dislocations in the main membrane and their subsequent annihilation (Fig. 4g-h). These transitions are relevant to layer reducing transitions in superheated smectic films of thermotropic liquid crystals [28].

To conclude, we have created a novel *fd*/NIPA lamellar phase which can simultaneously melt into a nematic phase and swell into individual lamellae. The interplay between these two processes creates multiple melting pathways of unexpected complexity. The lamellar phase differs from a conventional 3D crystal in that interfaces between microphase separated layers of aligned rods and polymers in isotropic phase span the entire sample. As a result, melting of these interfaces corresponds to melting of the entire bulk sample and it is possible to superheat the lamellar structure. Another unique feature of our experiment is the ability to control the phase behavior of a “lyotropic suspension” by temperature, which in turn controls the solvent quality of the polymer phase. This strategy can be used in the future to study phase transitions of other systems in soft condensed matter.

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