

Melting of Lamellar Phases in Temperature Sensitive Colloid-Polymer Suspensions

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(Received 10 March 2004; published 29 July 2004)

We prepare a novel suspension composed of rodlike *fd* virus and thermosensitive polymer poly(*N*-isopropylacrylamide) whose phase diagram is temperature and concentration dependent. The system exhibits a rich variety of stable and metastable phases, and 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 be superheated as a result of topological nucleation barriers that slow the formation of the nematic phase.

DOI: 10.1103/PhysRevLett.93.057801

PACS numbers: 64.70.Md, 61.30.-v, 64.60.My

Melting of three-dimensional (3D) crystals is among the most ubiquitous phase transitions in nature [1]. In contrast to freezing, melting of 3D crystals usually has no associated energy barrier. Bulk melting is initiated at a premelted surface, which then acts as a heterogeneous nucleation site and eliminates the nucleation barrier for the phase transition [2]. In this Letter, we investigate pathways for melting of lamellar phases. In contrast to crystals which have 3D order, lamellar phases have one-dimensional (1D) quasi-long-range order [3]. Additionally, while 3D crystals have only one surface with coexisting gas or liquid, the lamellar phase is a micro-phase separated state in which the entire bulk is spanned by interfaces between immiscible materials. Lamellar structures are typically built from amphiphilic molecules such as surfactants, lipids, and block copolymers, and their phase transformations provide insight about membrane biophysics. Although lamellar phases are frequently studied, melting transitions of lamellar into nematic phases are rarely observed. Here we create a novel system that exhibits such melting, and show that this process is fundamentally different from melting of 3D crystalline solids.

We have developed a temperature sensitive colloidal suspension to carry out these studies. The suspension is composed of lyotropic monodisperse rods of *fd* virus [4], 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. Below its temperature of 31 °C, water is a good solvent and NIPA polymer assumes a swollen coil form. Above the temperature, water is a poor solvent and NIPA has a collapsed globule form [5]. 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 [6]. However, using our temperature dependent system we are able to study previously inaccessible phase transition kinetics between

lamellar phases and coexisting isotropic or nematic phases.

The *fd*/NIPA solutions are unusual new materials whose lamellar phases differ from those of amphiphilic molecules. The lamellar phase can swell considerably and melt into a nematic phase, a transition almost never observed in block-copolymer lamellar systems. This unique behavior arises primarily because of the rodlike 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 more complex than those found in either temperature-dependent (thermotropic) molecular liquid crystals or concentration-dependent (lyotropic) amphiphilic systems [7,8]. For example, lamellar phases of *fd*/NIPA mixtures can be swollen to the point where isolated layers (lamellae) of rods are observed. These isolated membranelike structures of nonamphiphilic 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. Assembly of typical 2D membranes is driven by hydrophobic-hydrophilic interactions [9]. Our work indicates that a much simpler system of rods with uniform attractions is capable of assembling into membranes.

Finally, our temperature sensitive *fd*/NIPA solutions offer a powerful new model system for studies of melting. Lyotropic suspensions such as colloids are ideal for real-time studies of freezing [10–12]. 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 changes in temperature enable us to prepare the “lyotropic” colloidal system in a metastable ordered state, and then study its melting transition *in situ*. Similar ideas have been suggested with NIPA-based particles

[13]. A small increase of temperature increases monomer-monomer attractions and thus decreases the osmotic pressure of the semidilute NIPA polymer solution. As a result, water from polymer-rich layers flows into rod-rich layers until osmotic equilibrium is reestablished. This phenomenon dilutes the rod concentration locally, which in turn can lead to melting of the lamellar phase.

NIPA polymer was synthesized at 22 °C starting from an aqueous monomer solution (70 mg/ml in 20 mM tris buffer) as described elsewhere [5]. Bacteriophage *fd* is a negatively charged semiflexible rod with a diameter of 6.6 nm and a contour length of 880 nm [4]. With increasing concentration, *fd* forms a disordered isotropic phase, a nematic phase in which rods are aligned along one direction, and smectic phases with 1D positional order. Bulk *fd* forms a cholesteric phase. However, when confined within small tactoids the boundary effects dominate, and in this Letter we observe only nematic phases [14]. Usually the lamellar phase refers to a smectic phase that has been swollen due to the presence of another isotropic component. Because both smectic and lamellar phases have the same symmetry, hereafter we refer to *all* layered structures as 1D positionally ordered lamellar phases. A standard protocol was used to grow the *fd* virus [4]. The *fd*/NIPA mixtures were suspended in a buffer ($pH = 8.15$, 20 mM tris). All observations were made with an inverted microscope (Leica DM IRB) equipped with DIC optics. The temperature of the sample, objective (100 \times 1.4 NA), and oil immersion condenser was controlled with the same water circulator to within 0.1 °C. Images were captured by a video rate charge-coupled device camera and digitized using NIH software. The optical trap was created with a Nd-YVO laser ($\lambda = 1054$ nm) as described elsewhere [15].

The melting behavior of *fd*/NIPA mixtures (sample S1) with high rod concentration is illustrated in Fig. 1. At low temperature (5 °C), the mixture forms a lamellar phase where layers of rods are intercalated with layers of polymer; the polymer is in the semidilute regime [Fig. 1(a)]. The measured layer periodicity (1.2 μ m) is larger than the periodicity of the ordered phase (0.9 μ m) in pure *fd* suspensions. Dislocations and grain boundaries are observed at low temperature [Figs. 1(a) and 1(i)]; with increasing temperature they act as nucleation sites for formation of nematic tactoids [Fig. 1(b)]. The shape of nematic tactoids in the lamellar background is similar to tactoids observed at the I-N transition [16].

Although polymer is macroscopically miscible with rods in the lamellar phase, it is immiscible with rods in nematic phases [17]. Therefore, as the nematic tactoids grow, they expel polymer into the coexisting lamellar phase which in turn leads to swelling of the lamellar layers [Figs. 1(c) and 1(j)]. In a swollen lamellar phase, there are regions where individual layers are tightly bound and regions where they are well separated [Fig. 1(d)]. Above 15 °C, most of the sample is melted into a nematic phase which coexists with a highly swollen

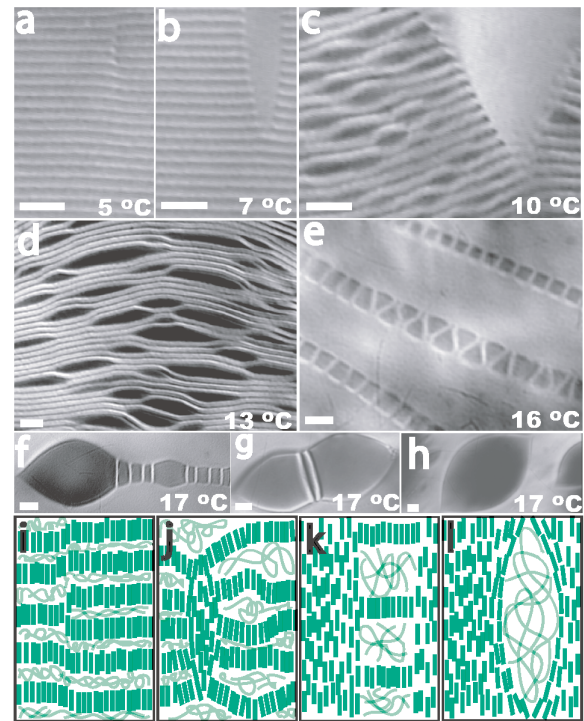


FIG. 1 (color online). Melting behavior of sample S1 (50 mg/ml *fd* and 7.5 mg/ml NIPA). (a) Lamellar phase at low temperature exhibits visible dislocation defects. (b) At 7 °C, the dislocation defects act as a site for nucleation of the nematic phase. (c) Nematic domains grow, expelling NIPA polymer into the lamellar phase, which leads to swelling of lamellar layers. (d) Swollen lamellar phase. (e) Coexistence between nematic phase and highly swollen lamellar phase. The 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 μ m.

lamellar phase. The lamellar phase assumes a form of elongated stripes [Figs. 1(e) and 1(k)]. Upon increasing temperature further, the lamellar stripes transform into polymer-rich isotropic tactoids which are frequently deformed by a few isolated lamellae [Figs. 1(f)–1(h)]. Finally, above 17 °C isolated layers melt, and isotropic tactoids in the nematic background assume their characteristic nonspherical shape [Figs. 1(h) and 1(l)] [16].

Lamellar periodicity is also obtained from the diffraction pattern of lamellar phases (Fig. 2). With increasing temperature, the peak simultaneously broadens and shifts to lower angles 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. 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

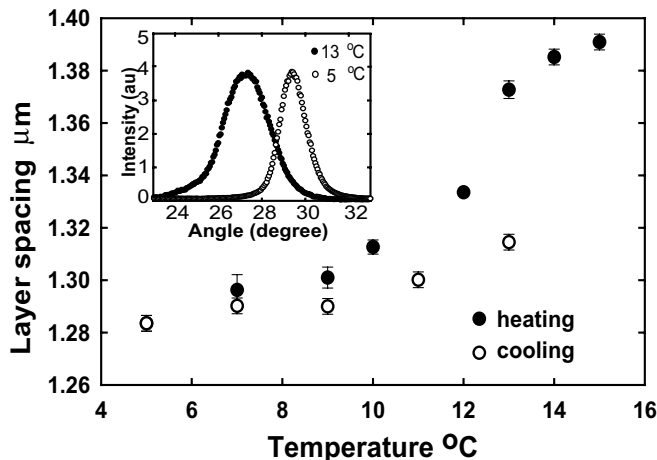


FIG. 2. Melting of the lamellar sample S1 studied by small angle light scattering. Lamellar periodicity for a sample during heating (filled circles) and cooling (open circles). There is hysteresis of layer spacing between heating and cooling cycles. The inset shows angularly averaged intensity profile of the diffraction rings at 5 °C and 13 °C (intensity rescaled).

transition with significant nucleation barriers. In the next part of the Letter, 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.

The concentration of lamellar layers in sample S1 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 (sample S2, Fig. 3). 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. 3(a)] and isolated lamellae (colloidal membranes) [Fig. 3(c)]. The spacing in the layered droplets is 1.2 μm , indicating a lamellar phase similar to S1. The lamellae we observe are composed of a single liquid layer of highly aligned rods; similar structures have been observed in athermal rod/polymer mixtures and perhaps in aqueous solutions of α -FeOOH rods [11,18]. Over time isolated lamellae grow from the interface of the isotropic-lamellar droplet into the isotropic phase; this indicates that single membranes are more stable than lamellar droplets. The coexistence of isolated membranes and lamellar droplets with well-defined spacing suggests another first order transition, this time from bound to unbound layers. This might be related to the binding-unbinding transition in lipid bilayers that is due to van der Waals induced attraction [19]; in our case the binding might be due to effective depletion forces. It is also notable that fd rods contain a low volume fraction of dimers which increase the stability of the multilayer structure since dimers dissolve more easily in a bilayer than in a monolayer.

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 [Figs. 3(a) and 3(b)]. The isolated colloidal membranes, however, remain stable at temperatures well above the melting temperature of the multilayer lamellar droplets. Only upon raising the temperature to almost 30 °C is nucleation of a three-dimensional nematic tactoid observed in the two-dimensional membrane [Figs. 3(d)–3(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 lamellae 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. The fact that multilayer structures melt before isolated lamellae explains the hysteresis observed in Fig. 2. With increasing temperature, the metastable lamellar phase swells which in turn increases the nucleation barrier for the nematic melting. These observations indicate the melting behavior of lamellar systems is very different from melting of conventional 3D solids.

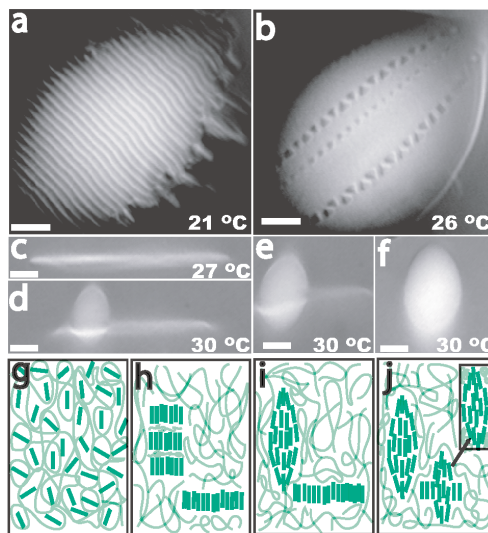


FIG. 3 (color online). Melting behavior of sample S2 (7.5 mg/ml fd and 37 mg/ml NIPA). (a) At 24 °C, lamellar droplets form in a background isotropic phase. Simultaneously, the formation of isolated layers [shown in image (c)] is observed. (b) At higher temperature, lamellar droplets melt into a nematic phase by the mechanism described in Fig. 1. (c) An isolated lamella is stable for a temperatures from 22–27 °C. (d)–(f) Sequence of images showing nucleation and growth of a 3D 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 .

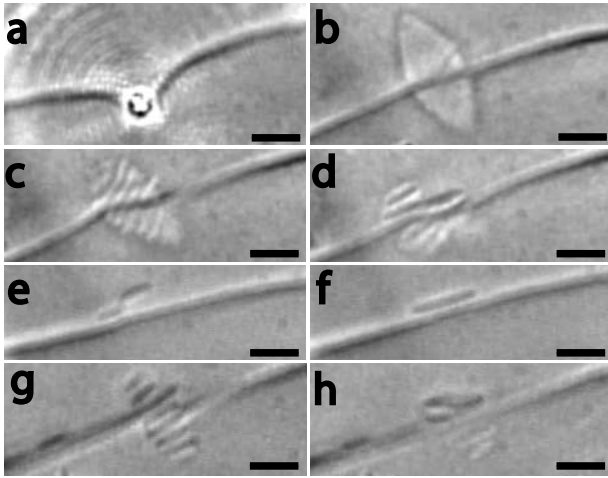


FIG. 4. Layer reducing transition of a colloidal membrane observed in sample S3 (12 mg/ml *fd*, 31 mg/ml NIPA). The sample temperature (28 °C) is below bulk lamellar phase (29 °C), so that the membranes are stable. (a) A membrane is repeatedly punctured by a 2.1 μm silica sphere trapped with laser tweezers.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

Finally, we explored the stability of isolated colloidal membranes against mechanical perturbations (Fig. 4). A silica bead was trapped with an optical tweezer and the colloidal membrane was repeatedly punctured [Fig. 4(a)]. This mechanical perturbation produced local shear melting of the membrane into a nematic droplet [Fig. 4(b)]. We were 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 the 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 lamellar structure [Fig. 4(c)]. This 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. By directly visualizing lamellar layers, we can discern the mechanism by which a layer reducing transition takes place. The number of layers is reduced when individual layers slide over each other [Figs. 4(e) and 4(f)] or by spontaneous formation of dislocations in the main membrane and their subsequent annihilation [Fig. 4(g) and 4(h)]. These transitions are relevant to layer reducing transitions in superheated smectic films of thermotropic liquid crystals [20].

In conclusion, 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. In the lamellar phase the interfaces between microphase separated layers of aligned rods and polymers in the isotropic phase span the entire bulk 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. The colloidal suspension we have studied is a two component system. An important open question is if the melting pathways described in this Letter are also relevant to other one-component systems that exhibit lamellar phases. 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.

We thank T. Lubensky, D. Discher, P. Janmey, and R. Kamien for useful discussions. This work was supported by the NSF through Grants No. DMR-0203378 and No. DMR-079909 (MRSEC) and by NASA (NAG8-2172).

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