The origin of network formation in colloid–liquid crystal composites

LETTER TO THE EDITOR

The origin of network formation in colloid–liquid crystal composites

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Abstract

With a variety of experimental techniques we studied the formation of particle networks when a suspension of colloids in nematic liquid crystal is cooled through the isotropic–nematic transition. Rheological data suggest that, contrary to previous expectation, network formation is possible with particles over a broad range of sizes. Only little dependence on particle size is observed. NMR data indicate the presence of a significant fraction of isotropic material down to 10 K below the bulk nematic transition of the liquid crystal. On the basis of calorimetric findings we suggest that small amounts of alkane impurities, carried originally by the dispersed particles, are present. These molecules act as a second solvent. They play a crucial role in 'tuning' the kinetics of phase separation to allow network formation by (i) opening up a biphasic region and (ii) wetting the particles with a layer of isotropic material.

Besides their technological relevance, liquid crystals and colloids are both of fundamental interest. Liquid crystals are model systems for anisotropic fluids with adjustable properties [1, 2]. Colloids can be used to model hard spheres without [3] or with [4] a tunable attraction. Due to an interplay of free energies of different origins but similar magnitudes, both types of systems show rich phase behaviour.

When liquid crystals are mixed with colloids, the particles disturb the long-range orientational order the liquid crystal molecules can adopt [5–7]. Consequently, the orientational elasticity of the nematic liquid crystals expels the colloids, so typically the suspension phase separates macroscopically into an almost pure liquid crystalline phase coexisting with a phase rich in colloids [7, 8]. However, long-lived non-macrophase-separated morphologies have also been observed, as follows.

(i) In mixtures of liquid crystals and micrometre sized emulsion or silica droplets, chains of droplets can be formed embedded in a nematic matrix [9, 10, 7, 11].

(ii) Mixtures of liquid crystals and micelles can remain stable for temperatures almost one degree below the isotropic-to-nematic phase transition temperature, T_{IN} [12].

(iii) Mixtures of liquid crystals and colloid can give rise to particle network formation when the liquid crystal is cooled to below T_{IN} [13–15].

In this letter we focus on network formation. Investigation of the phenomenon by laser scanning confocal fluorescence microscopy supports the following scenario [16]. Homogeneously distributed particles undergo Brownian motion in the isotropic phase. At and below T_{IN}, essentially particle-free nematic droplets grow. The particles are pushed by the moving nematic–isotropic interfaces [17] into the borders between droplets, forming a network. It has been suggested that the dense packing of particles in the network is held together by a nematic–isotropic pressure between nematic domains and residual amounts of isotropic phase associated with the particles [18].

Although the qualitative features of this scenario are well established, it is not clear under which conditions one can expect a network to form. Two key questions arise for a more detailed interpretation. (i) What is the influence of the particle size? (ii) Is the liquid crystal within the domain walls in a nematic or isotropic state?

Below we investigate these questions by comparing detailed rheological, nuclear magnetic resonance (NMR) and calorimetric measurements. Our results challenge aspects of the data and theoretical explanations in the current literature, and reveal a crucial role played by alkane impurities.

The system. We studied suspensions of 4-*n*-pentyl-4′-cyanobiphenyl (5CB; Merck, used as supplied) and polymethylmethacrylate particles (PMMA) with nominal radii of 120, 370 and 780 nm, sterically stabilized by chemically grafted poly-12-hydroxy stearic acid of ≈15 nm thickness [19]. The radii were determined either from diffusion coefficients or lattice parameters in the crystal phase of colloids. The former measurements also gave a polydispersity of <0.1 (except for the 780 nm sized particles, where it was not measured). The particles, initially dispersed in heptane or hexane, were dried in a vacuum oven (≈10^{-2} mbar) at 45 °C for up to one week and then dispersed in liquid crystal and homogenized in the isotropic phase for up to four weeks. The suspension was continuously stirred until just before use. Calorimetry gave $T_{IN} = 35.2$ °C for bulk 5CB.

Rheology. Homogenized samples were loaded into a rheometer (CSL^{2}100, TA Instrument) set up in the cone-and-plate geometry operated in the oscillatory mode, taking care that the sample remained isotropic during loading. Samples were cooled *in situ* at rates from −3 to −6 K h^{-1}. Figure 1 shows the temperature dependence of the loss $G''(T)$ and storage $G'(T)$ moduli for three different particles sizes, ranged between 100 and 800 nm, and all at a particle concentration of 10 wt%.

In the isotropic phase the loss modulus $G'' \sim 0.3$ Pa. At $T \approx 33.5$ °C, $G''(T)$ starts to increase until it takes values of $(3 \pm 2) \times 10^5$ Pa close to 20 °C. In comparison, $G''(T)$ for pure 5CB depends only weakly on temperature [23]. The storage moduli of our samples in the isotropic phase, where one expects liquid-like behaviour, should be close to zero. $G'(T)$ starts to increase strongly at $T \approx 33.5$ °C, taking values of $(5 \pm 4) \times 10^5$ Pa at 20 °C.

The temperature-induced increase of G' by several orders of magnitude suggests that stress-bearing particle networks are formed under our experimental conditions for particles with $R \sim 0.1$–0.8 μm. Moreover, these data show that the mechanical properties of the resulting soft solids are independent of particle size to well within an order of magnitude.
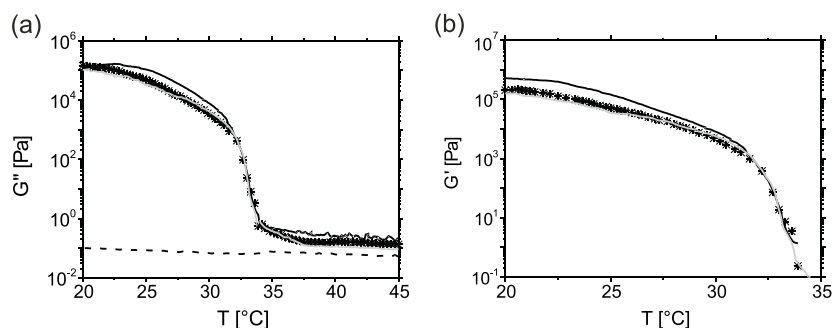
Figure 1. The temperature dependence of (a) the loss G'' and (b) the storage G' modulus for suspensions of 10 wt% sterically stabilized PMMA particles dispersed in 5 CB. ($*$) $R = 120$ nm, (grey line) $R = 370$ nm and (black line) $R = 780$ nm. The dashed line shows the temperature dependence of 5CB for comparison. Within experimental error no dependence was observed for cooling rates between -3 and -6 K h^{-1}. For moduli above $\approx 5 \times 10^5$ Pa and below 1 Pa there are systematic errors caused by the resolution of the rheometer, which cannot be quantified.

This is particularly surprising for the large particles, since network formation was previously attributed to a suppression of the formation of nematic phase in the swollen walls caused by particle-induced confinement [18]. For micrometre sized particles, however, this is unlikely since the nematic correlation length of 5CB is about 10 nm [14]. Our data also contrast with the experimental findings of [18]. (i) Petrov *et al* proposed a particle size dependence $G'(R_1)/G'(R_2) \sim (R_2/R_1)^2$. For our $R_1 = 120$ nm and $R_2 = 780$ nm this predicts $G'(R_1)/G'(R_2) \approx 40$, which is incompatible with our findings shown in figure 1. (ii) They found the storage moduli for suspensions with $R = 100$ nm particles to be three to four orders of magnitude *lower* than those for larger particles. Hence, they suggested that perhaps 'normal' network formation was suppressed.

NMR. To investigate the possible presence of isotropic material below the bulk nematic transition, we measured the temperature-dependent orientational order of the liquid crystal by means of ^{1}H nuclear magnetic resonance (NMR) at the Larmor frequency 90 MHz [24]. A narrow, liquid-like peak in the NMR spectrum is characteristic of the isotropic phase. In the nematic phase, orientational order leads to non-vanishing dipolar interaction, which is seen as a broad spectrum. The solid echo spectra were recorded with different delay times to ensure proper weighting of the isotropic and nematic contributions. A typical ^{1}H spectrum is given in figure 2(a) for a suspension of 15% PMMA particles ($R = 430$ nm) dispersed in 5CB. The spectrum is a superposition of a narrow and a broader peak, reflecting the coexistence of isotropic and nematic regions. The colloids also contribute a broad component to the spectra which, however, is masked by the dominant nematic feature from 5CB. The spectra were analysed quantitatively to obtain the volume fraction of isotropic phase; figure 2(b).

Surprisingly, the transition is far from sharp, figure 2(b). In fact, a transition region of significant width is recorded at all three particle radii. This is particularly noticeable for the smallest particles ($R = 120$ nm), where at 30 °C the isotropic fraction is 40%. However, even 10 K below T_{IN} the isotropic fraction amounts to >10%. If all of the liquid crystal in the pores between the particles forming the network is isotropic [18], we can expect an isotropic fraction of $\phi(1 - \phi_{net})/\phi_{net}$, where ϕ_{net} is the packing fraction of particles in the network. Taking $\phi_{net} \sim 0.6$ [16], this gives an isotropic fraction of 10% at $\phi = 0.15$, suggesting that colloids can indeed be situated in an isotropic matrix, and that only at about 10° below T_{IN} do the particles in the domain walls approach close packing.
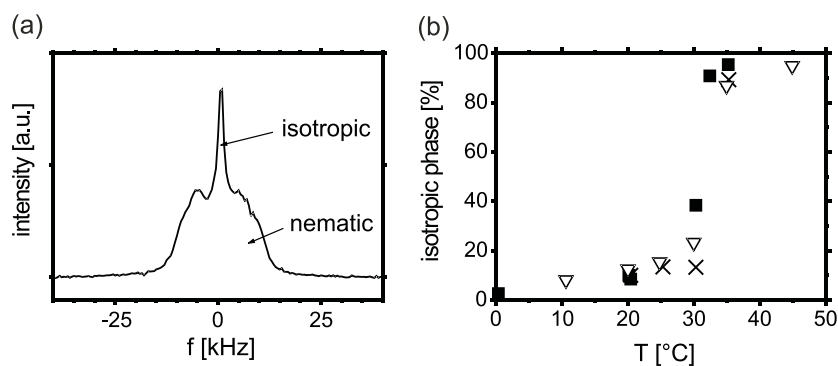
Figure 2. (a) A ^{1}H NMR solid echo spectrum, taken at 30 °C (particle size: $R = 430$ nm).
(b) The temperature dependence of the fraction of the isotropic phase for different particle sizes.
■: $R = 120$ nm; ▽: $R = 430$ nm; ×: $R = 780$ nm. Weight fraction of colloids: 15%.

While supporting the earlier views on the nature of the walls of the network, this finding raises a question about the origin of the substantial amount of isotropic material. We suggest that the broadening of the transition region is due to the presence of residual solvent on the dried particles before they were dispersed in the liquid crystal. The 'hairs' on the surface and possibly even the core of our PMMA particles act as 'traps' for molecules of the alkanes in which the particles were dispersed before drying [20]. These solvent molecules are subsequently liberated when the particles are dispersed in 5CB. The presence of short-chain alkanes lowers T_{IN} and introduces a biphasic region in the phase diagram in which isotropic (alkane-rich) and nematic (alkane-poor) phases coexist over a range of temperatures [21, 22], even in the absence of colloids. The presence of a colloidal network may widen this range further, by allowing alkane to condense in particle-rich regions, stabilized by capillary forces (a wetting effect). This view is supported by optical microscopy [25]. Clusters of particles are surrounded by a thick layer of isotropic material, embedded in a nematic matrix. In contrast, the ability for colloids in a pure nematogen to stabilize such a high volume fraction of isotropic material, several degrees below T_{IN}, is much more questionable, even if a strong anchoring condition [13–15] is assumed.

Calorimetry. The width of the biphasic region can conveniently be determined by calorimetric measurements (VP-DSC, MicroCal Inc.), where it is reflected in the width of the peak of the specific heat induced by the transition. In figure 3(a) the temperature dependence of the specific heat $C_v(T)$ (the 'thermogram') is given for (i) pure 5CB, ((ii)–(iv)) suspensions of 10% PMMA and 5CB and (v) a mixture of 5CB and 0.9% hexane.

The thermogram of a sample of 5CB with 0.9 wt% hexane (v) strikingly resembles that of the particle–5CB suspension (iv). On the other hand, particles dried at ≈60 °C and ≈10^{-5} mbar, more severe than our normal protocol, mixed with 5CB and homogenized for one week gave a thermogram (ii) with peak width and position more similar to those of pure 5CB (i) (but still somewhat wider and occurring at slightly lower temperature). Moreover, even for the most intensively dried particles a decrease of T_{IN} is observed after stirring the samples for another six weeks (iii), suggesting a slow liberation of the alkane molecules. This supports the notion that hexane molecules are not only trapped in the hairs but also in the core of the particles. It should be noted that the drying procedure is reflected in the strength of the network. The intensively dried samples remained liquid like after homogenizing for one week. The storage modulus of the intensively dried particles could not be determined with the present set-up.

These findings constitute a strong indication for the importance of alkane in the composition. To quantitatively underpin this view we have measured T_{IN} (onset of the
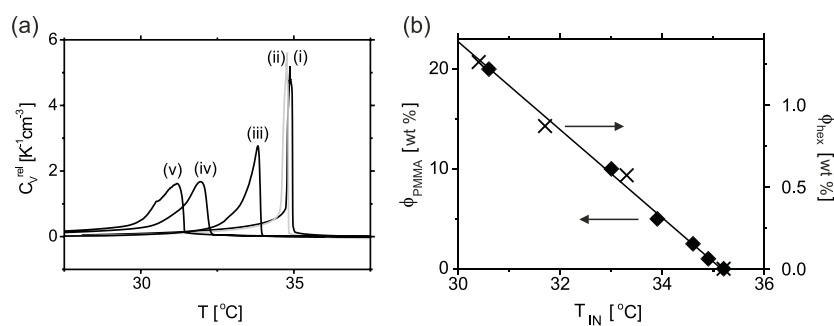
Figure 3. (a) The dependence of the specific heat C_v on temperature (cooling rate: ≈ -4 K h^{-1}): (i): pure 5CB; (ii): 10 wt% of intensively dried PMMA in 5CB, measured after stirring the sample for one week, $R = 430$ nm; (iii): 10 wt% of intensively dried PMMA in 5CB, measured after stirring for seven weeks, $R = 430$ nm; (iv): 10 wt% PMMA in 5CB, measured after stirring for about six weeks, $R = 430$ nm; (v) 0.9 wt% hexane in 5CB, no particles. (b) The dependence of the phase transition temperature T_{IN} on the weight fraction of PMMA particles ϕ_{PMMA}, $R = 240$ nm ($\blacksquare$, left axis), and the weight fraction of hexane ϕ_{hex} ($\times$, right axis).

thermogram peak) for several weight fractions of PMMA (figure 3(b), left axis) and different amounts of hexane (figure 3(b), right axis) in 5CB. A linear decrease of T_{IN} with either variable is observed [21]. Some 3×10^7 alkane molecules on each particle ($R = 240$ nm) are needed for the two data sets in figure 3(b) to agree. Using estimated densities of hairs on PMMA particles [20], it can easily be shown that this already can be achieved with a layer of hexane molecules (taking the length of a hexane molecule to be 8 Å) filling the space between $\sim$15 nm hairs.

As far as the width of the peaks is concerned we note that typically the peaks (cf (iv)) show a long tail towards lower temperatures (hardly visible in figure 3). In the case of the composites this may be more than 10 K in width. This may be due to capillary condensation of the alkane-rich phase in the region occupied by particles, effectively causing a local reduction in the transition temperature, in line with figure 2.

Previously, the reduction of T_{IN} was attributed to the elastic energy around the particles [14]. Calorimetric measurements performed by Petrov *et al* [18] gave two peaks in $C_v(T)$ in 5CB with dispersed PMMA particles. This was taken as evidence of a two-staged transition. We always observed a single peak in the thermogram for freshly prepared samples; figure 3(a). Taking the sample through a number of heating/cooling cycles led to the emergence of two peaks. Visual observation shows [26] that upon taking a sample a number of times through a cooling/heating cycle the network hardly breaks up, even after resting in the isotropic phase for several hours. Possibly, the two peaks are due to slightly different hexane concentrations in the coexisting particle-rich domains compared to the particle-free domains.

Origin of network formation. It is widely believed that network formation in suspensions of liquid crystal and sterically stabilized colloids is a kinetic effect [13–15, 18]. Time-resolved confocal microscopy [16] shows that particles are swept up by moving isotropic–nematic (IN) interfaces. West *et al* have recently derived the conditions that must be satisfied for this to happen, by considering the balance of hydrodynamic, elastic and surface tension forces of a particle situated at an IN interface [17]. They concluded that within a large range of particle sizes ($\sim$10 nm–1 μm), the IN interface must move slower than $v_{crit} \approx 1$ mm s^{-1}. The IN interfaces in pure thermotropic liquid crystals are expected to move at a speed of the order of cm s^{-1} [27], while the interfaces in our system typically move with speeds below 1 μm s^{-1} before getting stuck [16]. This explains why network formation is possible in our system, but

raises the question of why the interfacial speeds are so much slower than in pure 5CB.

A possible explanation lies with the opening up of a biphasic region in the phase diagram due to the presence of alkane molecules. In the liquid crystal 5CB the impurity level is quite low and the biphasic region is narrow, i.e., the whole of the system wants to become nematic at $T < T_{IN}$. In that case, the undercooling itself, $\tau = T_{IN} - T$, rather than the quench rate, $d\tau/dt$, controls the speed of the interface between growing nematic droplets and the surrounding (shrinking) isotropic material [27]. Even a very small degree of undercooling will give velocities exceeding v_{crit} for interface-driven particle transport.

On the other hand, our system with alkane present remains in a biphasic region throughout the temperature range in which the network morphology is undergoing formation. At any one temperature within this interval, the state of the system is a fixed amount of nematic droplets coexisting with isotropic phase. The nematic fraction grows with the undercooling, $T_{IN} - T$. If the temperature is fixed the IN interfaces will come to rest and the domain walls then hardly move. The interfacial speed is now controlled mainly by the cooling rate which can be very low. This, we suggest, is the mechanism whereby the existence of an alkane-induced biphasic region slows down the movement of IN interfaces. A question remaining is the meaning of the interaction between the grafted polymer and the liquid crystal—i.e. wetting of the particles— on the rheological properties of the network. Therefore we have investigated silica particles ($R = 340$ nm) coated with stearyl chains. Visual observation does not support wetting of the particles by isotropic liquid crystal. Instead of network formation, clustering or chaining of particles is observed for all hexane concentrations and cooling rates investigated so far [25].

In the presence of alkane, i.e. a second solvent, the mechanism of particle transport by an IN interface [17] provides a generic mechanism for network formation for particles wetted by isotropic material. According to our rheological data, network formation takes place for a broad range of particle size and density. Rather than particle size, the sample preparation plays a crucial role in as much as it has a strong influence on the amount of alkane released by the particles into the liquid crystal.

Conclusions. Our experimental results from NMR and calorimetry suggest that the presence of alkane is a key factor for network formation in colloid–liquid crystal suspensions. Rheological data show that network formation is possible for a wide range of particle sizes and hardly depends on particle radii.

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