Progr Colloid Polym Sci (2004) 129: 1–6
DOI 10.1007/b100306

D. Vollmer
A. B. Schofield
G. Hinze

Network formation in suspensions of colloids and liquid crystal: reversibility – memory effects

D. Vollmer (✉)
MPI for Polymer Research,
Ackermannweg 10, 55128 Mainz, Germany
e-mail: vollmerd@mpip-mainz.mpg.de
Tel.: +49-6131-379-208
Fax: +49-6131-379-100

A. B. Schofield
School of Physics,
The University of Edinburgh, JCMB,
Kings Buildings, Mayfield Road,
Edinburgh EH9 3JZ, UK
e-mail: abs@ph.ed.ac.uk

G. Hinze
Institut for Physical Chemistry,
Jakob-Welderweg 11, 55099 Mainz,
Germany
e-mail: hinze@chemie.uni-mainz.de

Extra address:
D. Vollmer
School of Physics,
The University of Edinburgh, JCMB,
Kings Buildings, Mayfield Road,
Edinburgh EH9 3JZ, UK

Abstract Suspensions of colloids, thermotropic low molecular weight liquid crystal, and small amounts of alkane are investigated by laser scanning confocal microscopy and calorimetry. While cooling the suspension through the isotropic-nematic phase transition the colloidal particles are expelled by the liquid crystal, causing the formation of a three-dimensional particle network. Upon reheating back into the isotropic phase the network may break up. However, taking the sample a number of times through the cooling/heating cycle leads to annealing of the network, accompanied by an increase of the loss modulus of the system by several orders of magnitude. Eventually it hardly breaks up, even after resting in the isotropic phase for several hours. When this happens calorimetric studies reveal that the temperature dependent heat capacity of the system contains two peaks.

Keywords Liquid crystals · Colloids · Network formation · Confocal microscopy · Calorimetry

Introduction

Liquid crystals [1] and colloids [2] are interesting model systems for fundamental research. Its macroscopic properties can be tuned by systematically changing the interactions between the particles [3]. The phase behaviour of both systems has been studied experimentally [3–6], theoretically [7, 8] and by computer simulations [9]. When combining liquid crystals with colloids, typically, the mixture phase separates macroscopically, since the colloids disturb the long range orientational order of the liquid crystal molecules [6, 10]. However, a few examples are encountered, where long-term stability is observed. In mixtures of colloidal rod-like and sphere-like particles short-range repulsive interactions appear to be the driving force causing a microphase separation into a variety of morphologies [6, 11]. In these lyotropic system, transition between different morphologies can be induced by varying the sphere volume fraction.

Recently, long-term stable phases have also been observed when mixing thermotropic low-molecular weight liquid crystals with colloids or droplets [10, 12–18]. Inverted nematic emulsions may form droplet chains [12, 13]. This self-organization is caused by a long-range two-particle interaction, resulting from an elastic distortion of the director field due to the anchoring of the molecules at the surface of the particles [10]. Networks,

2	8	8	2	2	9	1	0	B	Dispatch: 21.9.2004	Journal: Progress in Colloid and Polymer Science	No. of pages: 6
Journal number			Manuscript number						Author's disk received ☑ Used ☑	Corrupted ☐	Mismatch ☐ Keyed ☐

that remain stable for years, have also been observed after cooling a mixture containing a thermotropic low molecular weight liquid crystal, a small fraction of alkane and colloids below the isotropicnematic phase transition of the liquid crystal T_{IN} (onset of biphasic region) [16–20].

The alkane [21], acting as a second solvent, leads to a depression of the nematic-isotropic transition temperature and a formation of a two-phase region, i.e. a temperature interval where isotropic and nematic liquid crystal coexist [22, 23]. Passing T_{IN}, growing nematic liquid crystalline droplets expel the particles. The particles are swept up by the moving nematic-isotropic interfaces [24] into the borders between the liquid crystalline droplets, forming a three dimensional particle network of unusually large storage modulus [16]. At, and below, T_{IN} essentially particle-free nematic droplets grow. Due to the presence of alkane, the suspension remains in a region, where isotropic and nematic liquid crystal coexist, throughout the temperature range of network formation [19].

In this paper we focus on the phase transition kinetics, and the reversibility of this network formation. The reversibility of network formation has already been investigated by Petrov et al. [25]. They observed a double peak in the specific heat capacity of their system as the temperature was varied, which became more pronounced with increasing number of heating and cooling cycles. Their interpretation of the double peak is based on the assumption of a two-stage phase transition, in which firstly, particle-rich domains assemble, and these later collapse to form a self-supporting network. Network formation has also been visualized using laser scanning confocal microscopy, LSCM. In early work [20, 26] 100 μm thick capillaries, loaded with homogenized sample in the isotropic phase, were examined. Since the thickness of the capillary was in the same range as the size of the network domains, wall artefacts were encountered. After repeated heating and cooling almost all particles sedimented to the lower wall. However, these observations prompted a more detailed investigation into the importance of sedimentation, reversibility and memory in samples that have been taken a number of times through a cooling/heating cycle. To minimize wall artefacts in LSCM a different set-up was used, permitting thicker samples to be studied.

Experimental

We studied suspensions of 4-*n*-pentyl-4-cyanobiphenyl (5CB; Merck, used as supplied) and micrometer sized polymethylmethacrylate particles (PMMA) sterically stabilized by chemically-grafted poly-12-hydroxy stearic acid of ≈15 nm thickness [27, 28]. The particles used for LSCM were labelled with the florescent monomer NBD-MAEM (7-nitrobenzo-2-oxa-1,3-diazol methyl methacrylate-) [29] which was chemically attached to the PMMA. The particles, initially dispersed in hexane, were dried in a vacuum oven ($\approx 10^{-2}$ mbar) at 45 °C for about one week to remove remnants of solvent, and then dispersed in liquid crystal and homogenized in the isotropic phase for several weeks. It should be noted that even after this drying procedure hexane is left within the stabilizing polymer on the particle surface and possibly also in their cores. The alkane slowly diffuses into the suspension after re-dispersing the particles in liquid crystal. The amount of alkane dissolved in bulk liquid crystal can be determined from the reduction of T_{IN} [19] compared to pure liquid crystal. It is found

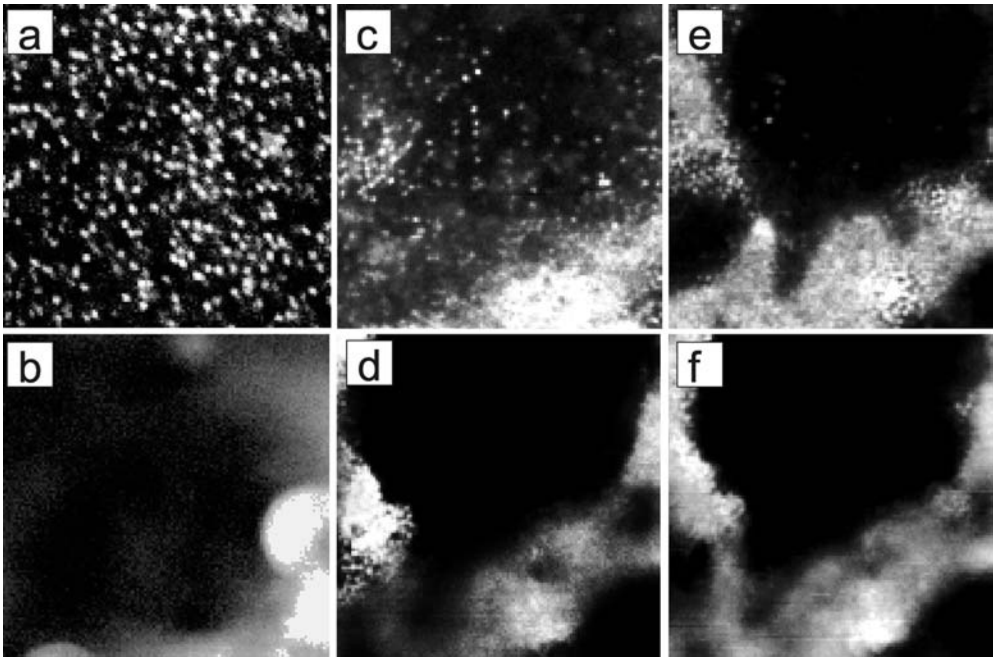


Fig. 1a–f Images of a sample containing 10 wt% fluorescent labelled PMMA particles (R = 500 nm) dispersed in a mixture of 5CB and about 0.7 wt% hexane. The sample was taken three times through a cooling/heating cycle: **a,c,e** images the sample in the isotropic (T = 318 K) phase; **b,d,f** the nematic (T = 296 K) phase. Cooling rate: –6 K/h; heating rate: 6 K/h. Confocal area: 80 × 80 μm^2. Images were taken 10 μm above the microscope slide

that this increases linearly with particle concentration and can be as much as a few percent [19]. Instead of waiting for the alkane required for rigid network formation to diffuse from the particles into the liquid crystal it is also possible to add it separately.

Laser scanning confocal microscopy

The conformation of the colloids in the suspension was studied by time-resolved LSCM. About 0.05 ml suspension was loaded into a homemade sample holder, which essentially consisted of a heated metal vessel sealed with a microscope slide. Due to the high sensitivity of the detector (single-photon avalanche photodiode), a laser ($\lambda = 488$ nm) power of 2 nW was sufficient to resolve the fluorescent labelled particles.

This low laser power reduces photo bleaching of the dye molecules, permitting particle tracing for several days.

The temperature dependent morphology of a suspension of 10% PMMA particles (R = 500 nm) dispersed in a mixture of 5CB and 0.7% hexane is depicted in Fig. 1. The colloids are shown as light-grey dots, while the liquid crystal appears as black regions. Figure 1a–f shows the influence of the temperature and of successive cooling and heating cycles on the morphology. The suspension was cooled with a constant rate of −6 K/h from 12 K above the phase transition of bulk liquid crystal and hexane $T_{\mathrm{IN}} = 306$ K down to 296 K, and left over night. The next day, the suspension was reheated to 318 K with a constant rate of 6 K/h. The sample was taken through this cooling/heating cycle twice more.

In agreement with previous results [17, 20, 26] after loading in the isotropic phase we found a homogenous arrangement of the particles without large aggregates, Fig. 1a. Entering the biphasic region led to the emergence of nematic nuclei. Growing nematic droplets pushed along the colloids. This led to the coexistence of nematic particle-free droplets with particle-rich domains embedded in isotropic liquid crystal. Closely below T_{IN} the morphology changed rapidly due to growth and coarsening of the nematic droplets. Only a few degrees below T_{IN}, the domain structure became fixed and the motion of the particles within the domain walls ceased. In Fig. 1b a section of the particle-rich domain wall, outlining a nematic liquid crystalline droplet, is depicted. Holding at 296 K for 15 h, and even during reheating up to T_{IN}, its morphology hardly changed. Above T_{IN} particles and particle clusters slowly broke off the network. However, even 2 h after passing T_{IN} significant parts of the particle walls still existed (see Fig. 1c), although particle-free domains were no longer visible. After the start of a second cooling cycle the breaking up of the network slowly proceeded as long as $T > T_{\mathrm{IN}}$. However, after passing T_{IN}, the network formed very rapidly and little rearrangement occurred below T_{IN}, see Fig. 1d. These observations point towards a significant memory of the pre-existing structure even after the system was tempered far above T_{IN} in the isotropic phase for 4 h. During the second re-heating hardly any particles dissolved from the walls and as shown in Fig. 1e they were fairly intact, even after 2 h in the isotropic phase at 318 K. The slight enhancement of the contrast in Fig. 1e compared to Fig. 1d is caused by less scattering of the laser beam in the isotropic phase compared to the nematic phase. A third cooling down to 296 K did not lead to significant changes in network architecture, Fig. 1f. The reduction of particle movement point towards a stronger binding of the particles in the walls. Note, that the images are taken 10 μm above the lower glass plate. Even here, close to the bottom of the sample no signs of sedimentation are detectable.

Next we wanted to check the reversibility of the mechanical properties of the system when repeatedly cooling and heating a sample through the isotropic-nematic transition of the liquid crystal without homogenizing the sample between successive scans. A preheated, homogenized samples was loaded into a preheated rheometer (CSL^{2}100, TA Instrument) set up in the cone-and-plate geometry and operated in the oscillatory mode. The samples were cooled in situ at a rate of −10 K/h and heated at a rate of 15 K/h. Figure 2 shows the temperature dependence of the storage modulus G'' for 120 nm sized particles at a particle

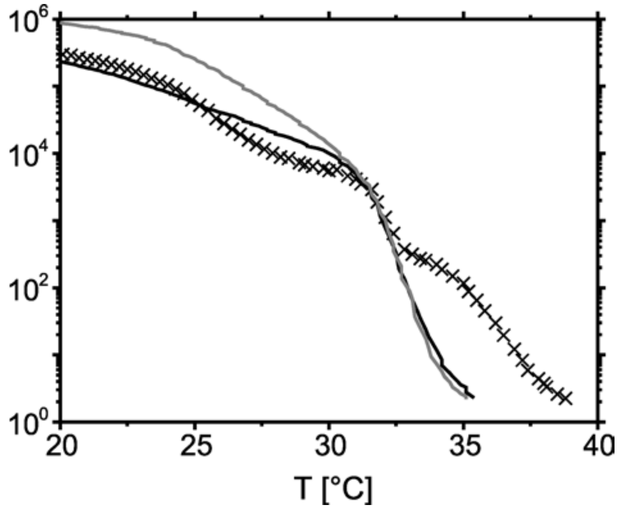


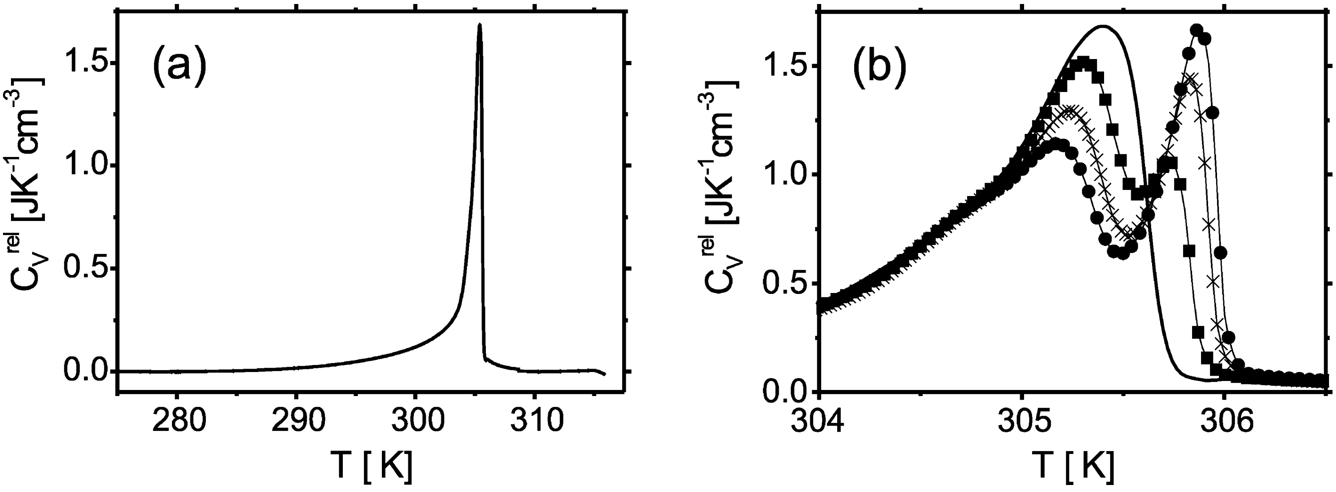
Fig. 2 Temperature dependence of the storage modulus G'' for a suspension containing 15 wt% of 120 nm sized PMMA particles dispersed in 5CB. The sample was taken twice through a cooling/heating cycle, with the upper and lower temperature limits at 45 °C and 15 °C, respectively. *Black solid line*: first cooling; grey line: heating; x: second cooling. Typically the time lag between successive scans was in the order of several minutes. Cooling rate: –10 K/h; heating rate: 15 K/h. The measurements are performed at a constant strain of 1% and frequency of 1 Hz. The sample was only pre-sheared before the first runs and not subsequently

concentration of 15 wt%. The sample was taken twice through a cooling/heating cycle. The sample was not homogenized between successive scans. Passing the isotropicto-nematic transition is accompanied by an increase of the storage modulus G'' by several orders of magnitude. Reheating the sample back into the isotropic phase causes a decrease of the storage modulus. The sample shows a pronounced hysteresis, causing the delayed decrease of G'' for $T > T_{IN}$. Cooling the sample a second time gave rise to even higher values for the storage modulus. The increase of G'' by about a factor of 4 suggests a significant strengthening of the network.

Calorimetry

To investigate the correlation of particle network formation and memory effects, with temperature dependent changes of the specific heat, C^{rel}_{v} (T), a differential scanning micro-calorimeter (VP-DSC, MicroCal Inc.) was used. The specific heat was measured relative to a reference solution (a mixture of water and octane) which does not show temperature-induced reactions or transitions in the temperature interval considered. The preheated sample-cell was loaded with the homogenized suspension at a temperature well within the isotropic phase. In Fig. 3a C^{rel}_{v} (T) (the 'thermogram') is given for a suspension of 10% PMMA and 5CB. The phase transition of bulk liquid crystal gives rise to a peak in C^{rel}_{v} (T). The reduction of T_{IN} compared to pure liquid crystal ($T^{5CB}_{IN} = 308.4$ K) is due to the presence of hexane [22, 23] which linearly decreases T_{IN} with increasing concentration as defined by the equation $T_{IN} = (308.4–4\phi^{hex})$K, where ϕ^{hex} denoted the weight percent of hexane in 5CB [19]. In this case T_{IN} is reduced by 2.6 K compared to pure 5CB, which implies that about 0.65 wt% hexane is dissolved in bulk liquid crystal. The width of the biphasic region of isotropic and nematic liquid crystal is reflected in the width of the peak of the specific heat. After passing a sharp maximum, C^{rel}_{v} (T) slowly levels off, suggesting that even several degrees below T_{IN} part of the liquid is still isotropic. This is in agreement with previous NMR measurements [19] where the temperature dependent fraction of isotropic material has been determined quantitatively. In contrast, binary mixtures of colloids and 5CB show only a biphasic region of up to about four degrees, depending on the purity of the liquid crystal, for the investigated compositions.

Fig. 3 Dependence of the specific heat C^{rel}_{v} on temperature for a mixture of 10 wt% PMMA particle (R = 430 nm) dispersed in a mixture of 5CB and about 0.65 wt% hexane. The sample was taken through four cooling (cooling rate = −4.5 K/h) and heating (heating rate = 4.8 K/h) cycles, where the upper temperature was chosen to be 318 K and the lower temperature to be 274 K. Both, the maximum temperature of 318 K and the minimum temperature of 274 K were held for five minutes before starting the next temperature run: **a** first cooling; **b** 1st cooling (*solid line*), 2nd cooling (*filled squares*), 3rd cooling (*crosses*), 4th cooling (*filled circles*)



During the first cooling C^{rel}_{v} (T) showed a single peak, see Fig. 3a, replotted on an enhanced scale in Fig. 3(b, solid line). With further cooling/heating cycles this peak splits into two with the first peak showing a decrease in the values of C^{rel}_{v} (T) and temperature as more cycles are completed and the second an increase in both; see Fig. 3(b). This dithering behaviour of the height of the peaks is consistent with the invariance of total heat of the phase transition. Given that a peak in the specific heat corresponds to a phase transition, a splitting of the peak suggests the coexistence of two well-separated regions, where the liquid crystal passes its isotropic-nematic phase transition.

Discussion and conclusions

The question raised by this result is what are these regions and why could they cause a splitting of the peak?

To gain insight into these questions we will bring together the microscopic, rheological and calorimetric data. In the experiment, colloidal particles are initially distributed homogeneously throughout the suspension, Fig. 1a, causing a single peak of the specific heat when passing through the isotropic to nematic phase transition, Fig. 3a. The formation of nematic domains results in compaction of particles, giving rise to an increase of the storage modulus by several orders of magnitude, Fig. 2. The elastic modulus of pure nematic liquid crystal is below experimental resolution. The increase of G'' towards values $>10^5$ Pa underpins the formation of a three dimensional network. This particle-rich network coexists with particle-free regions of up to micrometer sized liquid crystalline domains (see Fig. 1b).

During re-heating above T_{IN} the outermost particles become free, Fig. 1c but the particle network does not disintegrate completely while resting for several hours far above T_{IN}. However, only after the connectivity of the network is lost does the elastic modulus decrease towards values below experimental resolution. Cooling below T_{IN} for a second time results in a reformation of the network, Fig. 1d. This is accompanied by an increase of G'' by a factor of 4, Fig. 2. This supports a strengthening of the network, likely due to a compactions of particles in the walls. In distinction to the first cooling, the second is accompanied by a splitting and a broadening of the calorimetric peak (Fig. 3b).

Morphological changes are further depressed and the separation of the peaks in the specific heat become enhanced after repetitive cooling and heating. Due to annealing of the morphology, breaking up and reorganization of the network slows down after taking the sample through further heating/cooling cycles. As a consequence the separation between the particle-rich network and particle-poor liquid crystalline domains become more distinct and remains even in the isotropic phase. At the same time the separation of both peaks in the specific heat is further enhanced.

Petrov et al. [25] observed a calorimetric double-peak in mixtures of 5CB with dispersed PMMA particles. Since the reduction of T_{IN} was attributed to the elastic energy around the particles [17, 21], this data was considered as evidence for a two-stage phase transition in which firstly, particle-rich domains assemble, and these later collapse to form a self-supporting network. On the contrary, our data do not support this theory as in our experiments splitting of the calorimetric peak only occurred after repetitive cooling/heating cycles, whereas for fresh samples a single peak was always observed. Our time-resolved LSCM data showed that after repeated cooling/heating the breaking up of the network is slowed down, probably due to an annealing of the structure. This could give rise to severe steric constrains and enhanced Van-der-Waals attraction between particles, which is sensitive to the average distance between them. Both, however, do not explain the emergence of a second peak in the specific heat. Moreover, within the accuracy of the present experiments no dependence of the splitting of the peak on particle size could be resolved (data not shown).

A plausible explanation takes position dependent differences of the alkane concentration into account. After preparation of the mixture, alkane diffuses into the liquid crystal. This is consistent with the experience that long equilibration of the sample is required for rigid network formation (several weeks in the present case). Possibly, particles are wetted by alkane-rich liquid crystal, due to higher affinity of alkane to the polymer coating the particle surface. In that case, capillary condensation of the hexane-rich phase in the particle network would further increase the hexane concentration in the particle-rich domains, and conversely, decrease the alkane concentration in the particle-free domains. After re-entering the isotropic phase possibly a spatial inhomogeneous distribution of hexane persists as long as the network hasn't broken up. Calculated from the increase of the phase transition temperature between the first and fourth cooling, the average hexane concentration in the liquid crystalline domains decreases from 0.65 wt% towards 0.55 wt%. Previous quantitative nuclear magnetic resonance spectroscopy revealed tiny amounts of isotropic material almost down to 273 K [19], corresponding to a maximum of 8% hexane in the particle network.

In summary we have shown that taking a sample through a number of heating/cooling cycles led to an annealing of the morphology, going in line with a compactions of particles in the walls. Significant memory of the pre-existing structure could be established. Sedimentation is negligible, even if the sample rested in the isotropic phase for hours. The two peaks in the specific heat, emerging after repeated heating and cooling cycles, reflect the coexistence of particle-rich domains enclosing particle-free domains, which even persist in the isotropic phase. Most likely, the two peaks are due to slightly different hexane concentration in the particle-rich compared to the particle-free domains.

Acknowledgements The authors thank Wilson Poon for bringing the topic to their attention. We have benefited form discussions with Günter Auernhammer, Mike Cates, Julie Cleaver, Harald Pleiner, Sara Romer and Jürgen Vollmer. The authors are grateful to Beate Ullrich for detailed comments on the manuscript. D. V. acknowledges funding by the European Commission under the Marie Curie program. A.B.S. is supported by the NASA Microgravity Sciences Program.

References

1. de Gennes PG, Prost J (1993) Physics of liquid crystals. Clarendon, Oxford
2. Pusey PN (1991) Colloidal suspensions. In: Hansen JP, Levesque D, Zinn-Justin J (eds) Liquids, freezing and the glass transition. Nato Advanced Study Institute at Les Houches, Session LI, 3–28 July 1989, North Holland, Amsterdam, pp 763–942
3. Anderson VJ, Lekkerkerker NW (2002) Nature 416:811
4. Pusey PN, van Megen W (1986) Nature 320:340
5. Fraden S (1995) In: Baus M, Rull LF, Ryckaert JP (eds) Observation, prediction, and simulation of phase transitions in complex fluids. Kluwer Academic, Dordrecht, pp 113–164
6. Adams M, Dogic Z, Keller SL, Fraden S (1998) Nature 393:349
7. Onsager L (1949) Ann NY Acad Sci 51:627
8. Hosino M, Nakano H, Kimura H (1979) J Phys Soc Jpn 46:1709
9. Frenkel D (1991) In: Hansen JP, Levesque D, Zinn-Justin J (eds) Liquids, freezing and the glass transition. Elsevier Science, Amsterdam, chap 9, pp 689–762
10. Stark H (2001) Phys Rep 351:387
11. Lekkerkerker NW, Stroobants A (1998) Nature 393:305
12. Poulin P, Stark H, Lubensky TC, Weitz DA (1997) Science 275:1770
13. Poulin P, Weitz DA (1998) Phys Rev E 57:626
14. Zapotocky M, Ramos L, Poulin P, Lubensky TC, Weitz DA (1999) Science 283:209
15. Yamamoto J, Tanaka H (2001) Nature 409:321
16. Meeker SP, Poon WCK, Crain J, Terentjev EM (2000) Phys Rev E 61:R6083
17. Anderson VJ, Terentjev EM, Meeker SP, Crain J, Poon WCK (2001) Eur Phys J E 4:11
18. Anderson VJ, Terentjev EM (2001) Eur Phys J E 4:21
19. Vollmer D, Hinze G, Poon WCK, Cleaver J, Cates ME (in preparation)
20. Cleaver J, Vollmer D, Crain J, Poon WCK (2004) Mol Cryst and Liq Cryst (in press)
21. Since the particles investigated in [16–18, 25] were prepared and handled according to the same procedure, all samples contained a small amount of alkane, acting as a second solvent [19]
22. Oweimreen GA, Martire DE (1980) J Chem Phys 72:2500
23. Heuer H, Kneppe H, Schneider F (1989) Ber Bunsenges Phys Chem Chem Phys 93:923
24. West JL, Glushchenko A, Liao G, Reznikov Y, Andrienko D, Allen MP (2002) Phys Rev E66:012702
25. Petrov PG, Terentjev EM (2001) Langmuir 17:2942
26. Cleaver J, Poon WCK J Phys Condens Matter (to be published)
27. Antl L, Goodwin JW, Hill RD, Ottewill RH, Owens SM, Papworth S, Waters JA (1986) Colloid Surf 17:67
28. Bosma G, Pathmamanoharan C, de Hoog EHA, Kegel WK, van Blaaderen A, Lekkerkerker HNW (2002) J Colloid Interface Sci 245:292
29. Jardine RS PhD Thesis, Bristol; Jardine RS, Bartlett P (2002) Colloids Surf A Physiochem Eng Aspects 211:127