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Abstract
We study the influence of nanoparticles (NPs) on liquid crystal (LC) ordering. As regards the structural ordering we consider NPs as a source of a quenched random field. Roughly such a situation is encountered in mixtures of LCs and aerosil NPs (aerosil NPs are spherular ones). Using the semi-microscopic lattice model and Brownian molecular simulation we show that after a quench from the isotropic phase a quasi-stable domain pattern forms. The characteristic size of an average domain is inversely proportional to the concentration of NPs, and domain patterns exhibit memory effects. In the study of the phase behaviour we limit consideration to NPs resembling LC molecules. A Landau-type free energy expression is derived for the mixture, originating from the Maier–Saupe molecular approach. We show that the resulting phase behaviour exhibits the *slave–master* behaviour as the temperature or pressure is varied.

1. Introduction

The past decade has witnessed an increased interest in the study of two-component mixtures [1, 2], A + B, where B represents nanoparticles (NPs) in a host material, A. A characteristic feature of a NP is that at least one of its dimensions is limited to being between 1 and 100 nm. The focus of current research worldwide is on finding an appropriate combination A +B yielding quantitatively dramatically enhanced or qualitatively new features that the individual components do not exhibit on their own. Such systems are expected to play important roles in the emerging field of nanotechnology and also for composites with extraordinary material properties.

We consider cases where the component A exhibits a continuous symmetry breaking phase transition on varying a control parameter. The latter is either the pressure or temperature. In the continuum picture the degree of ordering of the lower symmetry phase is given by the so called *order parameter field*, and its structure by the *gauge field* [3]. These fields can be scalars, vectors or tensors. The *gauge field* exhibits a Goldstone fluctuation mode, 'trying' to recover the lost symmetry in the symmetry broken phase. In the case of imposed contradictory constraints this field typically exhibits spatial variations on the geometrically imposed length scale ξ_g (i.e., in the absence of external fields this length does not depend on material properties) [4, 5]. On the other hand the *order parameter field* responds to local perturbations on the length scale given by the order parameter correlation length ξ [4, 5], which attains the maximal value at the phase transition. As the B component we consider noncritical and chemically inert nanoparticles which act like a local field on the component A. This field can have either ordering or disordering tendencies.

If a component A suffers a sudden quench into the lower symmetry phase, then unavoidably a domain pattern forms. The basic ingredients of this ordering are simple: (i) continuous symmetry breaking and (ii) causality (i.e., a finite speed with which information spreads in a system). The generality of these principles gives rise to a broad universality of the phenomenon. The basic features of domain pattern dynamics in a pure bulk system A can be well described by the Kibble–Zurek mechanism [6, 7], which was originally introduced to explain the formation of topological defects in the early universe following the big bang, and are the

following. If A is quenched into the lower symmetry phase, then a randomly chosen configuration of the symmetry breaking gauge field is established in causally disconnected parts. This choice is based on local fluctuation mediated preferences. Consequently a domain structure appears, which is well characterized by a single domain length $\xi_d(t)$ [6, 7]. With time t the domain growth gradually enters the dynamic scaling regime, where the power law $\xi_d(t) \propto t^\gamma$ is obeyed [8]. The universal scaling coefficient γ depends on whether a conservation law for the order parameter exists or not. The *gauge field* evolution across a domain wall obeys the geodesic rule, i.e., it follows the shortest possible path in the continuum field space.

In the case where B imposes a kind of disorder on A, then in general the domain pattern becomes stabilized after a long enough time. The resulting domain structure reflects the balance between the ordering and disordering tendencies in the system. The pioneering work on the resulting domain structure has been done by Imry and Ma [9] on static grounds. They studied the influence of non-correlated quenched disorder on systems with a continuously broken symmetry and an interaction energy density proportional to the square of the gradient of the relevant order parameter. The Imry–Ma argument claims that an arbitrary weak random field with onefold symmetry (i.e., the field is linearly coupled to the conjugated order parameter) breaks the system into a stable domain-like pattern provided the spatial dimension d is less than 4. Consequently, the (quasi-)long-range order of the system is replaced by a short-range order. The characteristic domain size ξ_d is predicted to scale as $\xi_d \propto w^{-2/(4-d)}$, where w is a measure of the disorder strength. However, the applicability of this argument for various condensed matter systems is still disputable [10–12].

We next consider the phase behaviour of the component A in the presence of NPs in homogeneous mixtures. In this respect several universal features (i.e., valid for a variety of condensed matter systems) have been studied in liquid crystal (LC) phases. It has been reported that A can exhibit dramatically enhanced [13] or new material properties [14–18] for even moderate concentrations c of NPs. For example, a small concentration of ferroelectric colloids can significantly amplify the nematic LC ordering [13]. The isotropic–nematic transition temperature T_{IN} can be dramatically increased (temperature shifts up to 40 K); however, the qualitative LC behaviour remains unchanged. On the other hand, LC–aerosil NP mixtures (aerosil NPs are spherular ones [14]) typically show a decreased T_{IN} and increasingly changed qualitative LC behaviour on increasing the concentration of NPs [14–17].

We henceforth use for demonstration purposes the nematic LC phase [4] as the component A. On lowering the temperature or increasing the pressure it is reached from the isotropic (ordinary liquid) phase via the weakly first-order phase transition in which the continuous orientational symmetry is broken. In the nematic phase the molecules tend to be oriented locally parallel. Consequently in bulk samples (in which the influence of confining boundaries is negligible) the molecules are on average aligned homogeneously along a single symmetry breaking direction in the thermodynamically

stable state. Note that the LC phases (and different structures within them) are often chosen [7, 19] as testing grounds of basic mechanisms in physics for the following main reasons. They are typical representatives of soft matter systems [4], i.e., a relatively weak local perturbation can trigger responses on experimentally easily accessible scales of length and time. Samples with different LC structures can be readily shaped by confining surfaces or external fields due to their liquid and soft characteristics. LC phases are transparent to light and have anisotropic electro-optic properties. They can be studied using visible light, or they can be used to manipulate light. Furthermore, there exist a large variety of different LC phases and structures within them (e.g. induced by different confining cavities, immersed particles, or external ordering fields) exhibiting a rich gallery of universal physical phenomena. The chemistry of LCs is relatively well developed, so a desirable behaviour can also be tailored by chemists.

In the paper we analyse the influence of nanoparticles (the component B) on the (i) domain structure and (ii) phase behaviour of the nematic LC phase (the component A). We show that the resulting domain pattern depends on the history of the samples. We introduce the *slave–master* mechanism, which reveals conditions when quantitative or qualitative changes in phase behaviour of A are expected. The plan of the paper is as follows. In section 2 we introduce the semi-microscopic model and Brownian molecular dynamics, with which we study the domain patterns. In section 3 we derive a Landau form of the free energy for a simple bicomponent mixture originating from the Maier–Saupe mean field approach. We introduce the universal *slave–master* mechanism. In the last section we draw conclusions.

2. Structural behaviour

We first consider the structural behaviour in the nematic LC phase in the presence of nanoparticles, which act as a kind of disorder. For real samples such a case roughly corresponds to mixtures of LC molecules and aerosil particles [14]. The aerosils form a fractal-like network, which introduces to LC molecules orientational frustration.

2.1. Semi-microscopic lattice model

To study the domain patterns in the nematic LC phase as a function of the concentration c of nanoparticles and the history of the samples we use the three-dimensional (3D) lattice model. The lattice sites are occupied by rod-like molecules. The orientation of the ith LC molecule is described by the unit vector $\vec{m}_i$. The interaction between the neighbouring LC molecules is given by the modified Lebwohl–Lasher potential

$$f_{ij} = -\frac{J}{r^6}\left(\vec{m}_i \cdot \vec{m}_j - \frac{3\eta}{r^2}\left(\vec{m}_i \cdot \vec{r}_{ij}\right)\left(\vec{m}_j \cdot \vec{r}_{ij}\right)\right)^2. \quad (1)$$

Here $r = |\vec{r}_{ij}| = |\vec{r}_i - \vec{r}_j|$ denotes the separation between the ith and jth molecules, J is a positive interaction constant and the parameter η describes the degree of orientational anisotropy. The potential exhibits the so called head-to-tail invariance of a typical nematic LC structure, i.e., the

orientations $\pm \vec{m}_i$ are physically equivalent. The case $\eta = 0$ is equivalent to the Lebwohl–Lasher (LL) model [21], also referred to as the Maier–Saupe lattice model, which corresponds in the continuum limit to the approximation of equal Frank nematic elastic constants [4]. For $\eta = 1$ one gets the induced-dipole–induced-dipole-type potential. However, the interaction f_{ij} yields nematic-like properties only for $\eta < 0.3$ [20]. Despite its simplicity, the LL model mimics well the main static and dynamic properties of a typical isotropic–nematic (I–N) phase transition. By studying cases with $\eta > 0$ we probe the impact of elastic anisotropies on the system properties.

The system is enclosed within a cube of volume $N a_0^3$, where N is the number of molecules in the system. The unit cell is the simple cubic one with the lattice constant a_0. At the systems' boundary, periodic boundary conditions are imposed. We further distribute nanoparticles of concentration c to randomly chosen lattice sites $\vec{r}_i^{(0)}$ of the system. The ith nanoparticle enforces the orientation $\vec{e}_i$ on the jth neighbouring LC molecule via the short-range potential

$$f_{ij} = -\frac{J_w}{r^6}\left(\vec{e}_i \cdot \vec{m}_j - \frac{3\eta}{r^2}\left(\vec{e}_i \cdot \vec{r}_{ij}\right)\left(\vec{m}_j \cdot \vec{r}_{ij}\right)\right)^2. \quad (2)$$

The orientations of unit vectors $\vec{e}_i$ are randomly distributed in 3D, and J_w stands for the orientational anchoring constant.

The interaction energy W_{int} of the whole sample is given as a sum over all pair interactions. In calculations we limit the interactions to the neighbours within a sphere of radius $2a_0$. Furthermore, we assume that W_{int} roughly equals the free energy of the system.

The positions $\vec{r}_i$ of molecules are allowed to fluctuate about the lattice points $\vec{r}_i^{(0)}$ of the three-dimensional lattice. In this way we get rid of the lattice induced ordering anisotropy which is known to appear on choosing the unit cubic cell. The random departures $\Delta r = |\vec{r}_i - \vec{r}_i^{(0)}|$ obey the Gaussian statistics centred at $\Delta r = 0$, the width of which depends on the temperature T.

The orientation of the ith molecule is parametrized in the laboratory frame as

$$\vec{m}_i = (\sin \vartheta_i \cos \varphi_i, \sin \vartheta_i \sin \varphi_i, \cos \vartheta_i), \quad (3)$$

where $\vartheta_i = \vartheta(\vec{r}_i, t)$ and $\varphi_i = \varphi(\vec{r}_i, t)$ represent dynamic variables of the model. The rotational dynamics of the system is driven by the Brownian molecular dynamics. At each time interval Δt (one sweep) the molecular orientation at the ith site is updated in the local frame $\vec{r}' = (x', y', z')$ obeying the equations [22]

$$\vartheta_i^{(x')} = -\frac{\Delta t D}{k_B T}\sum_{j\neq i}\frac{\partial f_{ij}}{\partial \vartheta_j^{(x')}} + \vartheta_{i,r}^{(x')}, \quad (4a)$$

$$\vartheta_i^{(y')} = -\frac{\Delta t D}{k_B T}\sum_{j\neq i}\frac{\partial f_{ij}}{\partial \vartheta_j^{(y')}} + \vartheta_{i,r}^{(y')}, \quad (4b)$$

in which the orientational diffusion tensor is diagonal. Its eigenvalues are assumed to be degenerate, equal to D, and k_B is the Boltzmann constant. The z'-axis of the local frame is oriented along the long axis of a LC molecule. The angles $\vartheta_i^{(x')}$ and $\vartheta_i^{(y')}$ describe small rotations of the ith molecule about the x' and y' axes, respectively. The gradient of the potential for these two rotations is calculated numerically. The quantities $\vartheta_{i,r}^{(x')}$ and $\vartheta_{i,r}^{(y')}$ are stochastic variables obeying the Gaussian probability distribution centred at $\vartheta_{i,r}^{(x')} = \vartheta_{i,r}^{(y')} = 0$, where the distribution widths $\Delta \vartheta_r^{(x')} = \Delta \vartheta_r^{(y')}$ are proportional to $\sqrt{T}$ [22]. The corresponding multiplicative constant is chosen so as to yield a correct equilibrium value of the nematic uniaxial order parameter S in the continuum picture. The shortest time interval Δt of the model in the simulation is set by $\Delta t D = 0.01$. For a typical nematic LC [4] this ranges within the interval $\Delta t \approx 0.1 \, \mu s$ to $\Delta t \approx 0.001 \, \mu s$ depending on the size of a molecule (i.e., in our model a molecule in fact corresponds to a cluster of real molecules).

In order to link this semi-microscopic level with the continuum mesoscopic level, we define the tensor order parameter

$$\underline{q} = \langle \vec{m}_i \otimes \vec{m}_i - \underline{I}/3 \rangle_i, \quad (5)$$

where $\langle \cdots \rangle_i$ stands for the time averaging over relatively fast molecular fluctuations and over the first neighbours of the ith LC molecule, and $\underline{I}$ is the unit tensor. This definition roughly matches with the definition of the Landau–de Gennes tensor order parameter $\underline{Q}$ in the mesoscopic approach [4]. For uniaxial nematic states one commonly expresses it as

$$\underline{Q} = s\left(\vec{n} \otimes \vec{n} - \underline{I}/3\right), \quad (6)$$

where $\vec{n}_i$ is the so called nematic director field, and $s \approx \frac{1}{2}\langle 3(\vec{n} \cdot \vec{m}_i)^2 - 1 \rangle_i$ is the uniaxial order parameter. The unit vector $\vec{n}$ points along the local uniaxial axis of an average LC molecule. The isotropic (i.e. normal fluid) phase is characterized by $s = 0$. Rigidly homogeneously aligned nematic structure along $\vec{n}$ corresponds to $s = 1$. Note that $\vec{n}$ and s play the roles of *gauge* and *order parameter fields*, respectively, which are described in section 1. In calculations we estimate a value of s by diagonalizing $\underline{q}$, where its maximal eigenvalue corresponds to s. The average order parameter S of the sample is given by $S = \frac{1}{N}\sum_i s(\vec{r}_i)$.
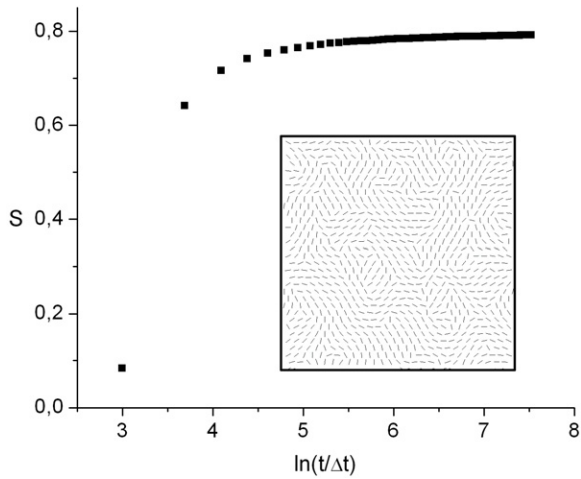
In the simulations we monitor in addition to S also the average domain size. We estimate a typical linear size ξ_d of an average domain of textures as follows. We calculate an average volume V_d in which relatively small changes occur in the orientational ordering. As the criterion of being in a domain we choose $|\vec{m}_i \cdot \vec{m}_j| = 1 - \Delta$, where the ith and jth molecules are adjacent. We set $\Delta = 0.2$, corresponding to the amplitude of thermal fluctuations at approximately double width of the Gaussian distribution. The domain size is estimated via $\xi_d = \left(\frac{6V_d}{\pi}\right)^{1/3}$.

2.2. Stable domain patterns

In figure 1 we show the time evolution of the domain coarsening in the pure bulk LC sample (i.e., $c = 0$) following a sudden isotropic–nematic phase transition. Soon after the quench the scaling regime is entered, where $\xi_d(t) \propto t^{0.49}$. The corresponding average order parameter evolution $S(t)$ is shown in figure 2. In the inset of the figure a typical
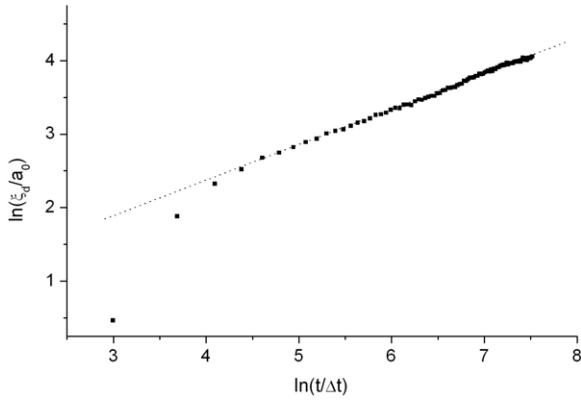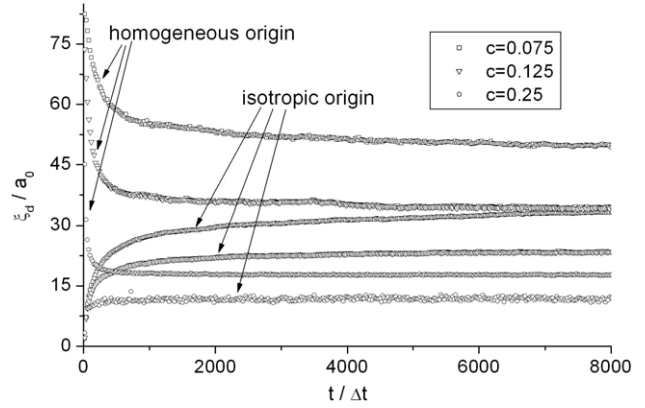
Figure 1. The time evolution of characteristic domain length in a bulk sample following the sudden quench from the isotropic phase. Soon after the quench the scaling law $\xi_d \propto t^{0.49}$ is obeyed, which is plotted with the dotted line. In simulations we set periodic boundary conditions: $N = 70^3$, $\eta = 0$.

Figure 3. Domain growth for different concentrations of nanoparticles after sudden quenches from the isotropic phase or homogeneously aligned structure. $N = 70^3$, $\eta = 0$.
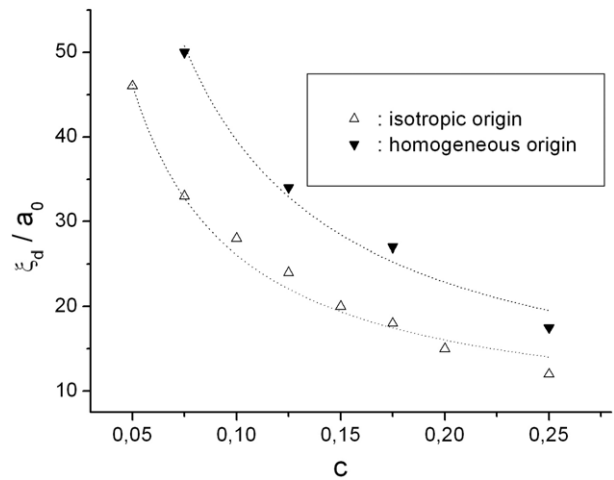

Figure 2. Time dependence of the average order parameter of the system. The domains, which are shown in the inset, become apparent when the value of the order parameter is strong enough.

Figure 4. Saturated average domain length values as a function of c and history of the samples. $N = 70^3$, $\eta = 0$.

domain structure is presented. Note that it is sensible to define domains only after the so called Zurek time [7], at which the degree of orientational order is strong enough, i.e. $S(t) \approx S$. Here $S \approx 0.8$ stands for the saturated value of the order parameter. Within each domain a rather uniform configuration of the *gauge field* is established. Contradicting orientational tendencies at domain walls can give rise to topological line and point defects. The annihilation of these topological defects of opposite winding number enables the domain growth. There is growing numerical evidence that understanding of the annihilation process of a pair of isolated topological defects gives essential information on domain coarsening dynamics (i.e. from the velocity of the defect pair annihilation one can estimate well the domain coarsening dynamics). A detailed study of such an annihilation process for the case of point defects is given in [23]. Our simulations show negligible influence on η.

We next study the influence of spatially quenched impurities on the domain pattern. For this purpose we introduce a concentration c of randomly distributed impurities imposing random directions in the space. The strength of coupling of impurities with LC molecules is equal to the LC molecule–LC molecule coupling (i.e., $J = J_W$; see equations (1) and (2)). Our main goal is to find the characteristic saturated domain length value ξ_d as a function of c for different histories of the samples. For this purpose we follow the domain length time evolution $\xi_d(t)$ for different concentrations c, where we quench the system starting (i) from the isotropic phase, and (ii) from a perfectly homogeneously aligned sample. The latter case corresponds to a sudden switch-off of a strong external magnetic or electric ordering field.

In figure 3 we show the $\xi_d(t)$ dependences for different concentrations of NPs for the cases (i) and (ii). For these cases the $\xi_d(t)$ values monotonically increase and decrease with time, respectively. Soon after the quenches the domain patterns stabilize. The saturated values ξ_d, shown in figure 4, exceed the average distance between impurities. The patterns originating from isotropic configurations have shorter values of ξ_d in comparison to the structures reached from homogeneously

aligned samples. In all cases the scaling $\xi_d \propto 1/c$ is well obeyed.

3. Phase behaviour

We next consider the phase behaviour in a simple homogeneous LC + NP mixture, where LC molecules and nanoparticles are comparable. In particular, we show that such systems often display the *slave–master* type of behaviour.

3.1. Binary nematic mixture

Our aim is to obtain a free energy expression in a conventional Landau-type phenomenological picture. To obtain an insight into the structure and origin of phenomenological parameters we start from the mean field Maier–Saupe approach on the molecular level. We assume that the two components are similar in size and shape (i.e., rod-like). Consequently, we can treat them as a simple mesomorphic binary nematic mixture. Starting from the molecular level we derive the expression for the corresponding Landau free energy of the mixture in terms of dominant order parameters.

We henceforth label the quantities referred to the ith molecular component with the index i. The concentration of the first component is $c_1 = 1 - c$, and the second one $c_2 = c$. We set that the molecules are cylindrically symmetric. The symmetry axis of a molecule points along the unit vector $\vec{m}_i(\Omega)$, where the solid angle Ω, is defined by the two Euler angles ϑ and φ. The state of the ith component is defined by the orientational distribution function $p_i(\Omega)$. The states with orientational ordering are distinguished by an axis of symmetry, the director $\vec{n}$, and an infinite set of order parameters [24]

$$\overline{P}_{2n}^{(i)} = \int P_{2n}(\cos\vartheta)\, p_i(\Omega)\, d\Omega, \tag{7}$$

where $n > 0$ is an integer and P_{2n} are the Legendre polynomials. Among these order parameters the dominant role is played by $S_1 = \overline{P}_2^{(1)}$ and $S_2 = \overline{P}_2^{(2)}$, and we henceforth neglect the remaining order parameters. In the isotropic phase all molecular orientations are equivalent; therefore $P_i(\Omega) = \frac{1}{4\pi}$, $S_1 = S_2 = 0$.

In an ordered state some orientations are preferred. The corresponding entropy change $\Delta\Sigma$ is given by [24]

$$\Delta\Sigma = -k_B \left(c_1 \int p_1(\Omega) \ln(4\pi p_1(\Omega))\, d\Omega \right. \\ \left. + c_2 \int p_2(\Omega) \ln(4\pi p_2(\Omega))\, d\Omega \right). \tag{8}$$

In the framework of the Maier–Saupe theory, the anisotropic contribution to the internal energy $\Delta\Phi$ is equal to [24]

$$\Delta\Phi = -\frac{1}{2} \left(\varepsilon_{11} c_1^2 S_1^2 + 2\varepsilon_{12} c_1 c_2 S_1 S_2 + \varepsilon_{22} c_2^2 S_2^2 \right), \tag{9}$$

where $\varepsilon_{ii} > 0$ is the intermolecular orientational interaction of the neighbouring molecules of type i, while $\varepsilon_{ij} > 0$ is the orientational interaction between different types of neighbouring molecules. Therefore, we assume that the

molecules have the tendency to align parallel. One typically assumes that the temperature dependences of the interaction terms in equation (9) are negligible.

In this mean field approximation the free energy difference Δf between the ordered and disordered phase can be written as

$$\Delta f = k_B T \left(c_1 \int p_1(\Omega) \ln(4\pi p_1(\Omega))\, d\Omega \right. \\ + c_2 \int p_2(\Omega) \ln(4\pi p_2(\Omega))\, d\Omega \\ \left. - \frac{1}{2} \left(\varepsilon_{11} c_1^2 S_1^2 + 2\varepsilon_{12} c_1 c_2 S_1 S_2 + \varepsilon_{22} c_2^2 S_2^2 \right) \right). \tag{10}$$

We further expand p_i in terms of Legendre polynomials:

$$p_i = \frac{1}{4\pi} \sum_{n=0}^{\infty} \frac{\overline{P}_{2n}^{(i)}}{4n+1} P_{2n}(\cos\vartheta) \approx \frac{1}{4\pi} \left(1 + \frac{S_i P_2(\cos\vartheta)}{5} \right) \tag{11}$$

and expand Δf in terms of S_1 and S_2. It follows that

$$\Delta f \approx c_1 \left(\frac{k_B}{250} \left(T - c_1 T_*^{(1)} \right) S_1^2 - \frac{k_B T}{13\,125} S_1^3 + \frac{k_B T}{87\,500} S_1^4 \right) \\ + c_2 \left(\frac{k_B}{250} \left(T - c_2 T_*^{(2)} \right) S_2^2 - \frac{k_B T}{13\,125} S_2^3 + \frac{k_B T}{87\,500} S_2^4 \right) \\ - \varepsilon_{12} c_1 c_2 S_1 S_2, \tag{12}$$

where $T_*^{(i)} = \frac{125\varepsilon_{ii}}{k_B}$. With this in mind we obtain the conventional Landau–de Gennes expression for the free energy density f:

$$f \approx f_0 + c_1 \left(\frac{a}{2} \left(T - (1 - c_2) T_*^{(1)} \right) S_1^2 - \frac{B}{3} S_1^3 + \frac{C}{4} S_1^4 \right) \\ + c_2 \left(\frac{a}{2} \left(T - (1 - c_1) T_*^{(2)} \right) S_2^2 - \frac{B}{3} S_2^3 + \frac{C}{4} S_2^4 \right) \\ - \varepsilon_{12} c_1 c_2 S_1 S_2, \tag{13}$$

where f_0 is the free energy density of the isotropic phase, and a, B, C are positive material constants. In the spirit of the conventional Landau-type approach we henceforth assume that the temperature variation of these constants is negligible in the temperature regime of interest to us.

For $c_i = 1$ this form of the free energy describes a weakly first-order nematic–isotropic phase transition of the ith component at the transition temperature $T_{IN}^{(i)} = T_*^{(i)} + \frac{2B^2}{9aC}$. At $T = T_{IN}^{(i)}$ the two phases (the nematic one with $S_i(T_{IN}^{(i)}) = S_0 \equiv \frac{2B}{3C}$, and the isotropic one with $S_i = 0$) coexist in equilibrium. $T_*^{(i)}$ is the supercooling limit temperature of the isotropic phase. For typical nematic liquid crystals $T_{IN}^{(i)} - T_*^{(i)} \approx 1$ K and $S_0 \approx 0.4$. We further introduce non-dimensional quantities. The order parameter is normalized with respect to its value at the pure bulk phase transition, i.e., $\tilde{S}_i = S_i/S_0$, $r_i = \frac{T - T_*^{(i)}}{T_{IN}^{(i)} - T_*^{(i)}}$ is the reduced temperature, $\Delta\tilde{f} = (f - f_0)/F_0$ is the dimensionless excess free energy density, where $F_0 = \frac{4B^4}{81C^3}$. Omitting the tildes, the non-dimensional excess free energy density becomes

$$\Delta f = c_1((r_1 + \lambda c_2) S_1^2 - 2 S_1^3 + S_1^4) + c_2((r_2 + \lambda c_1) S_2^2 \\ - 2 S_2^3 + S_2^4) - w c_1 c_2 S_1 S_2, \tag{14}$$

where w measures the coupling strength, and λ measures the transition temperature shifts due the presence of the other

molecular component. The term $c_1 c_2 (\lambda (S_1^2 + S_2^2) - w S_1 S_2) \equiv \chi_{\text{eff}} c_1 c_2$ is the driving force toward fractionation through phase separation. Here $\chi_{\text{eff}} = \lambda (S_1^2 + S_2^2) - w S_1 S_2$ is an effective Flory–Huggins interaction parameter [25], which is expected to trigger the phase separation above its critical value $\chi_c = 2$. We henceforth assume that the mixtures are homogeneous.

3.2. Slave–master mechanism

The derivation above gives a rough insight into the expected coupling term and into the structure of material constants entering a free energy of a simple bicomponent mixture. Next, we generalize the expression (14) into a more general form:

$$\Delta f = f_c^{(1)} + \kappa f_c^{(2)}, \tag{15a}$$

$$f_c^{(i)} = \tau_i S_i^2 - 2 S_i^3 + S_i^4, \tag{15b}$$

$$f_{\text{int}} = -w S_1^{n_1} S_2^{n_2}. \tag{15c}$$

Here $f_c^{(i)}$ stands for the condensation term of the ith component, κ measures the relative weight of the condensation terms in Δf and f_{int} represents the direct coupling between the components. The generalized reduced temperatures τ_1 and τ_2 trigger the first-order phase transition (the condensation) in components at $\tau_i = 1$ for $f_{\text{int}} = 0$ (i.e., $S_i(\tau_i = 1) = 1$, $S_i(\tau_1 > 1) = 0$). They can be controlled by the temperature (as derived in equation (14)) or by pressure. For demonstration purposes we express them for the temperature driven transitions as

$$\tau_i = \frac{T - T_*^{(i)}}{T_c^{(i)} - T_*^{(i)}} \tag{16}$$

where $T_c^{(i)}$ and $T_*^{(i)}$ stand for the phase transition and supercooling temperature of the ith component for $f_{\text{int}} = 0$, respectively (for brevity we set $\lambda = 0$ in equation (14)). The strength of the coupling term is measured by the interaction constant $w > 0$. In order to generalize the potential to an even broader class of different mixtures LC + NP, we set the integers n_1 and n_2 in equation (15c) to either 1 or 2. For example, the choice $n_1 = n_2 = 1$ corresponds to the derived interaction potential in equation (14), while the choice $n_1 = n_2 = 2$ roughly mimics the mixture of ferroelectric particles and nematic LC molecules, as derived in [13].

In the following we consider the phase behaviour of the system for the case $T_c^{(1)} < T_c^{(2)}$ and sufficiently weak coupling strengths w (i.e., for stronger enough coupling strength the components behave as one component). We first focus on the phase behaviour of the first component in the temperature interval $T_c^{(1)} < T < T_c^{(2)}$. In this temperature interval the second component is ordered, i.e. $S_2 > 0$. If the S_2 temperature dependence is relatively weak, then the behaviour of $S_1(T)$ is approximately governed by the effective excess free energy

$$\Delta f_{\text{eff}} = \tau_1 S_1^2 - 2 S_1^3 + S_1^4 - w_{\text{eff}} S_1^{n_1}, \tag{17}$$

where $w_{\text{eff}} = w S_2^{n_2} > 0$.

For $n_1 = 1$ the first component exhibits quantitative changes in behaviour, which are discussed in detail in [5]. For
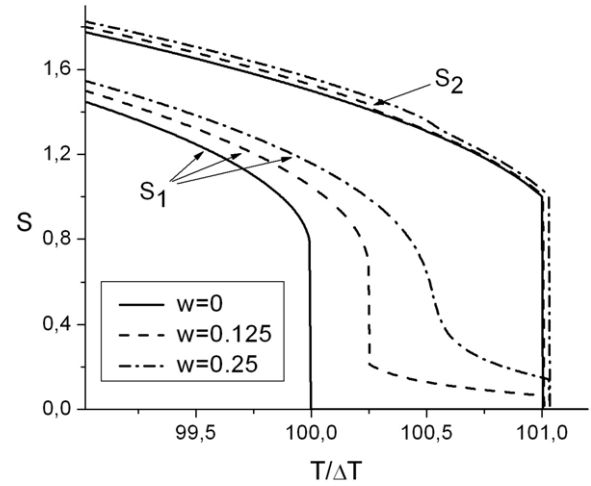
Figure 5. Illustration of the *slave–master mechanism* for $n_1 = n_2 = 1$. On increasing w the $S_1(T)$ (the *slave*) dependence exhibits relatively large changes in comparison to $S_2(T)$ (the *master*). In simulations we set $\Delta T = T_c^{(1)} - T_*^{(1)} = T_c^{(2)} - T_*^{(2)} = 1$ K, $T_c^{(1)} = 100$ K and $T_c^{(1)} = 101$ K, $\kappa = 1$.

$0 < w_{\text{eff}} < 0.5$ the phase transition temperature $T_{c,w}^{(1)}$ is shifted to

$$T_{c,w}^{(1)} = T_c^{(1)} + \left(T_c^{(1)} - T_*^{(1)} \right) w_{\text{eff}} \tag{18}$$

and in the regime $T_c^{(2)} > T > T_{c,w}^{(1)}$ it displays pretransitional behaviour. For $w_{\text{eff}} \geqslant 0.5$ the temperature evolution of S_1 is gradual below $T_c^{(2)}$.

For $n_1 = 2$ the $S_1(T)$ dependence exhibits only a quantitative change in behaviour for weak enough positive values of w_{eff}. The phase transition temperature is increased and given by equation (18), with no pretransitional effects above $T_{c,w}^{(1)}$.

We next consider the behaviour of the second component, which is only slightly quantitatively changed. For temperatures $T < T_c^{(2)}$ the $S_2(T)$ dependence exhibits only a slight increase in ordering for $w > 0$. For $T > T_c^{(2)}$ both free energy condensation terms in equation (14) favour $S_i = 0$. Consequently the components are decoupled and the $S_2(T)$ dependence is governed solely by $f_c^{(2)}$.

In such a behaviour we refer to the components 1 and 2 as the *slave* and *master*, respectively. The *slave* is characterized by a weaker intermolecular potential, i.e., lower value of the phase transition temperature, in comparison to the *master* for the pure components. The phase behaviour of the *slave* is strongly affected by the presence of the *master*, while the reverse influence is negligible if the coupling is not too strong. A numerical analysis of this behaviour is shown in figure 5 for $n_1 = n_2 = 1$.

4. Conclusions

We study theoretically the phase and structural behaviour of a liquid crystal (LC) in a mixture of a liquid crystal and nanoparticles (NPs) of concentration $c \ll 1$. The behaviour is analysed across the isotropic–nematic (I–N) phase transition, which can be crossed either by changing temperature or

pressure. Focus is on universal features that are of interest also for other condensed matter systems.

We first consider the structural behaviour in the nematic phase. To monitor the domain structure we use the semi-microscopic lattice model and Brownian molecular dynamics. The LC is quenched from the isotropic phase in the presence of NPs, which influence the LC orientational degree of ordering like a quenched random anisotropy field. Examples of such systems are mixtures of LCs and aerosil particles. For $c \geqslant 0.01$ the aerosil NPs form a fractal-like network, which is adaptive for $c < 0.1$ and rigid for $c > 0.1$ [15–17]. Therefore, in such systems partially annealed or quenched disorder is present depending on the concentration of NPs. In simulations we studied quasi-equilibrium domain structures, that are stabilized by the presence of randomly distributed NPs. The domain structure is well characterized by a single length $\xi_d \propto 1/c$, in accordance with experimental results on aerosil–LC mixtures [26]. This length is larger than the average separation between particles and reflects the history of the sample. To demonstrate memory effects we quench systems either from the isotropic or from homogeneously aligned structure, which resulted in different ξ_d values. The results obtained are qualitatively valid for any system which suffers a sudden symmetry breaking phase transition.

We further analyse the phase behaviour of a bicomponent nematic mixture. In this case we assume that NPs are rod-like and similar to LC molecules, and exhibit mesomorphic behaviour. We derive the Landau-type free energy expressed in terms of the dominant order parameters S_1 and S_2 starting from the Maier–Saupe approach on the molecular level. This study gives us insight into the structure of different terms that enter the phenomenological free energy expression. We demonstrate that the resulting coupling term gives rise to the *slave–master* behaviour for weak enough coupling constants w. The role of the *master* is played by the component with stronger intermolecular interaction, which reflects in the higher phase transition temperature. We show that the phase behaviour of the *slave* is strongly affected by the *master*, while the reverse influence is negligible. Depending on the character of the coupling term, the *master* can influence the *slave* qualitatively or quantitatively. For stronger couplings the components become strongly coupled and behave like a single-component system. Detailed understanding of this mechanism is in our opinion of great importance. It suggests how one can control phase behaviour of a *slave* by adding an adequate concentration of a *master*, where the coupling between the systems is appropriate. An experimental illustration of such a mechanism is the recent observation of a mixture of ferroelectric particles and LC [13]. The free energy coupling term structure is approximately of type $-wS_1^2S_2^2$ and triggers only quantitative changes in the LC behaviour (i.e., the *slave* experiences $f_{int} = -w_{eff}S_1^2$). Another example represents the coupling between the nematic orientational S and the smectic translational order parameter ψ in n CB liquid crystals. Note that in this case we

have a single-component structure, where $S_1 = \psi$ and $S_2 = S$. On increasing the so called de Gennes coupling strength w [3] (in the coupling term of the form $f_{int} = -wS\psi^2$), which can be realized by increasing n of for n CB molecules, the smectic A phase exhibits qualitative change in behaviour. On the other hand the I–N behaviour remains essentially the same for weak enough values of w. In this case the *slave* (i.e., the smectic degree of ordering) experiences the effective coupling $f_{int} = -w_{eff}\psi^2$. Therefore, the proposed *slave–master mechanism* is valid for general systems with coupled order parameter, that exhibit critical phase behaviour.

In our future study we will analyse in detail the applicability of the Imry–Ma theorem for the LC + NP mixtures. The scaling relation between ξ_d and the disorder strength for different concentrations of NPs and the range of ordering will be systematically analysed. We will study the behaviour above and below the NP percolation threshold. Our preliminary investigations suggest that the Imry–Ma scaling is not always obeyed. Furthermore, the structures obtained via quenching from the (i) isotropic and (ii) homogeneously aligned structure seemed to be qualitatively different.

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