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Stationary statistical size distribution of nematic droplets in the course of the isotropic liquid–nematic phase transition

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The statistical size distribution of nematic droplets in the course of the phase transition isotropic liquid–nematic has been analysed using polarizing optical microscopy and described by the model of reversible aggregation. The materials under investigation are low molecular mass nematics, polymeric nematics and polymer dispersed liquid crystals observed at their clearing temperatures in the stationary time regime.

1. Introduction

In isotropic liquids, the nematic phase is known to appear at the clearing point in the form of spherical droplets [1]. The temperature interval of the biphasic region varies from 1° to 2° for low molecular mass nematics to some tens of degrees for liquid crystal (LC) polymers. Polymer dispersed liquid crystals (PDLCs) present a special kind of LC system. They are important materials especially for optical applications [2, 3]. In these systems, the phase separation occurs in the course of polymerization of a mixture consisting of a monomer and a nematic LC. PDLC films consist usually of nematic LCs dispersed in the form of micron-sized droplets within a solid polymer matrix.

The morphology of LC droplets including their size, shape, spatial distribution and number density is known strongly to influence the electro-optical properties of LC films [2, 3]. The phase-ordering kinetics of the growth of an ordered LC phase originating from a disordered isotropic melt has already been carefully investigated by Dierking [4, 5] under isothermal conditions after a temperature quench. The growth of the LC droplet diameter L, with time t, was reported to follow a universal growth law $L(t) \approx t^n$, where n varies from 0.5 to 1. Yet the momentary experimental statistical size distribution of nematic droplets at the phase transition/separation has not been investigated and its analytical description is still not known.

To fill this gap, the model of reversible aggregation proposed by Kilian *et al.* [6, 7] has been adopted and applied to a description of the stationary size distribution of nematic droplets. The universality of the model had already been put in evidence by its application to statistical ensembles of carbon-black particles [7], compartments in poly(methylmethacrylate) [6, 7], microdomains at the surface of polyamic acids in the course of their transformation into polyimides [8], defects at the surface of loaded metals [7], and bacteria and yeast in the course of their growth [7]. This has given us hope of describing successfully the stationary size distribution of nematic droplets in the course of either, phase transition in low molecular mass nematics and nematic polymers, or phase separation in PDLC formation, using the model of reversible aggregation.

2. Experimental

The materials under investigation were:

(**1**) the low molecular mass nematic 4-n-decyloxycinnamic acid, observed at 166°C (about 0.1° lower than its isotropisation temperature) [1];
(**2**) the nematic polymer, poly-1,9-trimethylene-4,4,6,6-tetramethyl-4,6-disila-5-oxanonamethylene terephthaloylamide (polysiloxaneterephthaloylamide), observed at 260°C (about 10° lower than its isotropization temperature) [9];
(**3**) an ultraviolet polymerized blend of a commercial LC mixture (50:50) E7 (Merck Ltd, Poole, UK) and 2-ethylhexyl acrylate, observed at 21°C [10].

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For observation of the textural patterns investigated, samples were placed in the gap (approximately 3–6 μm) between two glass plates. The nematic droplets were identified in the polarized light photographs at ×100 magnification; their shape was nearly spherical. The diameters of droplets were measured visually with an error $\leqslant 5\%$; the number of droplets under analysis varied from 200 to 800 in each photograph.

3. Model

According to the model of reversible aggregation [6, 7], stationary microstructures with a disordered internal structure should be built up by linkage of identical units in metastable clusters called aggregates. In the liquid state they are linked in a percolation pattern with a definite life time (this is a condition of their reversibility). The configuration of the aggregate ensembles permanently fluctuates and a momentary photograph ('quasi-frozen' state) demonstrates only one of many possible configurations. Collective structural fluctuations within the ensemble are the mechanism for optimization of the properties of the stationary ensembles. The stationary size distribution in an aggregate is assumed to be easily achieved (within some seconds). The condition for optimization of the properties is given by the production of the maximum entropy.

In the model, the statistical size distribution $n(y)$ reads as follows:

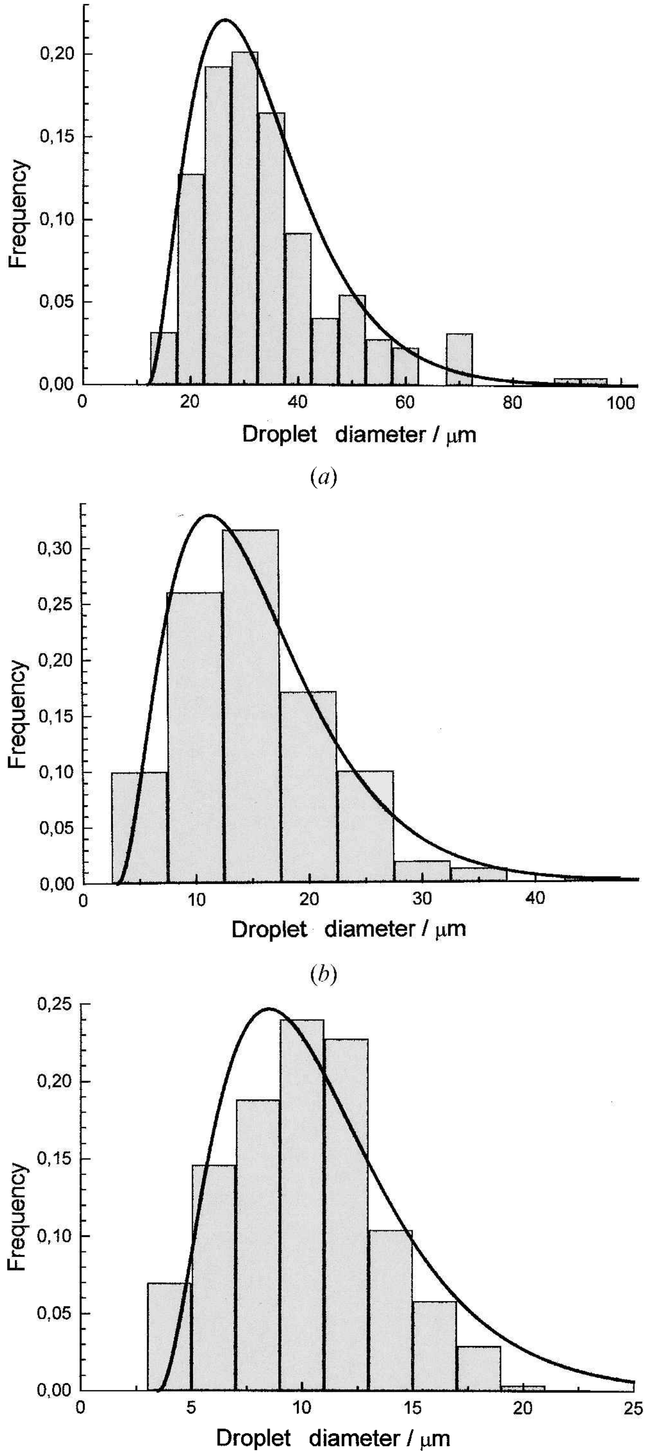
$$n(y) = n_0 y^{p-1} \exp(-\beta U) \tag{1}$$

where n_0 is a normalizing factor, y is the size of the units comprised, p is a parameter determined by extra-components of the ensemble entropy (it seems to be related to the dimension of space in which the aggregation occurs [11]), $\beta \equiv 1/k_B T$ (k_B is the Boltzmann constant, T is the absolute temperature) and U is the aggregation energy.

If $p = 0$, the distribution coincides with the 'entropy-maximum' distribution, i.e. the Boltzmann distribution. With respect to the entropy, this distribution corresponds to a gas-like behaviour [12]. The decisive role of the entropy in optimizing the meta-stable structural patterns of dissipative systems like the aggregate ensemble is thus clearly indicated by this type of distribution.

In so far as the aggregation energy depends on the size of the comprised units, the standard aggregation energy, $\Delta U_0 = U/y$, should be introduced. In the final form at $p = 3$† equation (1) gives

$$n(y) = n_0 y^2 \exp(-\beta y \Delta U_0). \tag{2}$$



(*a*)

(*b*)

(*c*)

Figure. Statistical size distribution of the diameters of nematic droplets at the phase transition isotropic liquid–nematic for (*a*) 4-n-decyloxycinnamic acid at 166°C, (*b*) polysiloxane-terephthaloylamide at 260°C and (*c*) a UV-polymerized PDLC from a commercial LC mixture E7 with the monomer 2-EHA (composition 50:50) at 21°C.

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† Essentially no crossover from three-dimensional to two-dimensional growth has been observed as the nucleus diameter reaches the dimension of the experimental cell gap and the growth of nucli saturates after about 1 min [4, 5].

Table. Parameters of equations (3) and (4) for the systems investigated.

System	$T/^\circ\mathrm{C}$	n_0	$\beta\Delta U_0/\mu\mathrm{m}^{-1}$	$\Delta U_0/\mathrm{kJ\ mol}^{-1}\ \mu\mathrm{m}^{-1}$	$y_0/\mu\mathrm{m}$	$\langle y\rangle/\mu\mathrm{m}$
1	166	0.080	0.14	0.51	12.0	33.4
2	260	0.035	0.24	1.06	3.0	15.5
3	21	0.073	0.40	0.98	3.5	10.5

Taking into consideration the minimum droplet diameter y_0, obtained from experimental data, equation (2) yields

$$n(y-y_0)=n_0(y-y_0)^2\exp[-\beta(y-y_0)\Delta U_0]. \quad (3)$$

4. Results and discussion

Systems **1** and **2** (see §2) have been investigated in the stationary time regime, maintaining them for about 1 min after the temperature quench, whereas system **3** has been investigated just after complete droplet formation. The results of the statistical treatment of the photographs under investigation are given in the figure. The statistical distributions of the nematic droplet diameters for all the systems are evidently asymmetrical and could be described by neither a Gaussian nor a log-normal distribution. Results of computation using equation (3) are presented in the figure in the form of solid lines. The y_0, n_0 and U_0 parameters have been accepted as free and are collected in the table. The figure shows that equation (3) describes the experimental data quite fairly.

In addition, the mean diameter of the droplets, $\langle y\rangle$, has been evaluated as the reduced mathematical expectation. For the distribution described by equation (3) it is given by

$$\langle y\rangle - y_0=\frac{\int_0^\infty (y-y_0)n(y-y_0)\,\mathrm{d}y}{\int_0^\infty n(y-y_0)\,\mathrm{d}y}=\frac{3}{\beta\Delta U_0}. \quad (4)$$

The $\langle y\rangle$ values are collected in the table. The highest $\langle y\rangle$ value (33.4 μm) corresponds to the low molecular mass nematic (system **1**), whereas the lowest $\langle y\rangle$ value (10.5 μm) corresponds to the PDLC (system **3**). For all the systems investigated, the $\beta\Delta U_0$ parameter is less than 1 per length size unit (1 μm). This confirms the supposition that the creation and reorganization of ensembles of nematic droplets are governed by thermal fluctuations having the energy kT.

In so far as equation (4) describes the experimental data quite fairly, the condition of optimization of the properties of the nematic droplets in the ensemble is fulfilled, i.e. the entropy of the system is maximized at the formation of the statistical ensemble [4].

The table shows that the mean diameter of the droplets in the polymer systems **2** and **3** is lower compared with that for the low molecular mass nematic **1**. Simultaneously the ΔU_0 parameter (having been evaluated within a 10% error) for systems **2** and **3** is approximately double that for low molecular mass system **1**. Therefore one may suppose that the creation of the droplet ensemble is hindered in polymer systems (perhaps because of their high viscosity) compared with a low molecular mass system.

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