Electronic Supplementary Material (ESI) for Soft Matter. This journal is © The Royal Society of Chemistry 2023

-Supplementary Information-Long term phase separation dynamics in liquid crystal-enriched microdroplets obtained from binary fluid mixtures

Mehzabin Patel,^a Seishi Shimizu,^b Martin A. Bates,^b Alberto Fernandez-Nieves,^{c,d,e} Stefan Guldin^{*a}

 $[^]a$ Department of Chemical Engineering, University College London, Torrington Place,London, WC1E 7JE, U.K.; E-mail: s.guldin@ucl.ac.uk b Department of Chemistry, University of York, Heslington, York YO10 5DD, United Kingdom c Department of Condensed Matter Physics, University of Barcelona, 08028 Barcelona, Spain d ICREA-Institució Catalana de Recerca i Estudis Avançats, 08010 Barcelona, Spain e Institute for Complex Systems (UBICS), University of Barcelona, 08028 Barcelona, Spain

1 Experimental Results



Supplementary Figure S1: Evolution of 5CB-rich droplets after isotropic-tonematic transition. The sample cell was kept constant at -5° C, with image captures under bright-field (t = 00:00:00) and subsequently cross-polarised light. The time after the initial isotropic-to-nematic transition is displayed on the top right corner in the format hour:min:sec. Scale bar: 20 μ m.



Supplementary Figure S2: Thermal imaging of sample microscope stage over time. (a) Thermographic camera images (FLIR) measured on a glass substrate that was placed on top of a Peltier-controlled temperature stage (Linkam, LTS120) set to $-5^{\circ}C$, (b) Schematic of points (1-5) on the stage wherein the grey area represents the cut-out aperture for transmission investigations. (c) Corresponding temperature - time graph for the various measured points.

2 Theory

Our objective is to show that the nematic-isotropic phase boundary for a droplet deviates from the one for the bulk. We consider a mixture of methanol (denoted as the subscript m) and 5CB (denoted as the subscript 5) at the temperature (T), pressure (P), and the mole fraction of methanol (x_m) . Below UCST, the mixture separates into two phases: the methanol-rich phase (denoted as the superscript (m)) and the 5CB-rich phase. The 5CB-rich phase can either be in the nematic phase (denoted as the superscript (n)) or the isotropic phase ((i)).

We focus on the nematic-isotropic phase boundary and how this boundary deviates from the bulk one when a droplet is formed. At the nematic-isotropic phase transition boundary, the stability of the nematic phase is equal to the stability of the isotropic phase. Thereafter, with an increase in temperature or methanol, the isotropic phase becomes more stable.

As explained in Discussion, considering nematic-isotropic stability difference of a droplet immersed within the bulk isotropic phase requires more degrees of freedom than allowed from the conventional Gibbs phase rule. Such additional degrees of freedom come from "the number of independent length scales influencing the free energy" ¹ characterizing the difference between the nematic and isotropic phases, as well as from the small size of the droplet. ² Indeed, interfacial effects cannot be ignored for a droplet. Consequently, the surface free energy, γ is an additional variable affecting the chemical potentials in the droplet of 5CB and methanol in the nematic and isotropic phases, in line with the thermodynamics of small systems.² Due to its small size, the pressure in the droplet P' is different from that of the surroundings (P) bulk methanol-rich phase, influenced by the droplet size R. The pressure, surface free energy, and droplet size are interlinked (a special case for a spherical droplet is the Young-Laplace equation). Moreover, surface free energy is also dependent on composition and droplet size. Consequently, we adopt the droplet size R and composition x_m as the additional variables, and consider the chemical potentials in the droplet as expressed as $\mu_5^{(i)}(T, x_m, R^{-1}), \ \mu_m^{(i)}(T, x_m, R^{-1}), \ \mu_5^{(n)}(T, x_m, R^{-1}), \ and \ \mu_m^{(n)}(T, x_m, R^{-1})$ for 5CB and methanol in isotropic and nematic phases, respectively. Adopting R^{-1} instead of R as a variable is convenient to consider deviations from the bulk phase, corresponding to $R^{-1} = 0$.

With the above setup, we consider the nematic-isotropic phase boundary for droplets. To do so, we consider the nematic-isotropic phase equilibrium for 5CB (where $\alpha = 5$ in the following equation) and methanol (where $\alpha = m$ in the following equation), $\Delta \mu_{\alpha} \equiv \mu_{\alpha}^{(n)} - \mu_{\alpha}^{(i)} = 0$ with respect to the changes in x_m , T, and R^{-1} , expressed as δx_m , δT , and δR^{-1} , respectively, as

$$\delta \Delta \mu_{\alpha} = \left(\frac{\partial \Delta \mu_{\alpha}}{\partial x_{m}}\right)_{T,R^{-1}} \delta x_{m} + \left(\frac{\partial \Delta \mu_{\alpha}}{\partial T}\right)_{R^{-1},x_{m}} \delta T + \left(\frac{\partial \Delta \mu_{\alpha}}{\partial R^{-1}}\right)_{T,x_{m}} \delta R^{-1} = 0$$

$$(1)$$

(Note that the gradient of the nematic-isotropic phase boundary for the macroscopic system can be recovered under the equilibrium condition ($\delta\Delta\mu_{\alpha} = 0$) when $R^{-1} = 0$ is not a variable.)

Keeping the droplet size constant, we obtain the following relationship for the phase boundary for the droplet.

$$\frac{\delta T_t}{\delta x_m} = \frac{\left(\frac{\partial \Delta \mu_\alpha}{\partial x_m}\right)_{T,R^{-1}}}{\frac{\Delta h_\alpha}{T_t}} \tag{2}$$

where T_t and $\Delta h_{\alpha} = T_t \Delta s_{\alpha} = -T_t \left(\frac{\partial \Delta \mu_{\alpha}}{\partial T}\right)_{R^{-1}, x_m}$ are the transition temperature and the partial molar enthalpy of species α , respectively. Keeping the temperature constant, we obtain the following relationship for the effect of droplet size on the nematic-isotropic boundary \mathbf{x}_m :

$$\frac{\delta x_m}{\delta R^{-1}} = -\frac{\left(\frac{\partial \Delta \mu_\alpha}{\partial R^{-1}}\right)_{T,x_m}}{\left(\frac{\partial \Delta \mu_\alpha}{\partial x_m}\right)_{T,R^{-1}}}$$
(3)

Before considering the isotropic-nematic transition in droplets, we analyse how methanol interacts differently with the bulk isotropic and nematic phases. According to the phase diagram reported by Serrano et al.,³ the nematic-isotropic

transition temperature decreases with increasing methanol concentration, i.e., $\frac{\delta T_t}{\delta x_m} < 0$. At constant T, the increase of x_m across the phase boundary leads to the stabilization of the isotropic phase, which means $\left(\frac{\partial \Delta \mu_5}{\partial x_m}\right)_{T,R^{-1}=0} > 0$, since $\Delta \mu_5$ is defined as nematic minus isotropic. Consequently, $\Delta h_5 < 0$ from Eq. 3 (and $\Delta s_5 < 0$ from the equilibrium condition), meaning that both the molar enthalpy and entropy of 5CB are lower in the nematic phase than in the isotropic phase, which is a plausible result.

Because of the Gibbs-Duhem equation, the chemical potential changes of 5CB and methanol have the opposite signs in the bulk nematic and isotropic phases, considering the equilibrium with the surrounding bulk methanol-rich phase at a given temperature and pressure. Consequently, we expect $\left(\frac{\partial \Delta \mu_m}{\partial x_m}\right)_{T,R^{-1}=0} < 0$ for methanol. This sign can also be justified from the less favourable methanol-nematic interaction energy compared to the isotropic, $\Delta h_m > 0$, in combination with Eq. 2. These signs are used in the Discussion to infer how the droplet size affects nematic-isotropic transition.

3 Simulations: Model and phase diagram

To simulate the formation and motion of defects in LC droplet systems, we require a model that is computationally tractable rather than chemically detailed, so that we can investigate both the large system sizes necessary to represent a droplet with an ordered interior and also to allow for simulations long enough such that the defects that may form within the droplet interior can move in a physical way. We have therefore used a simple soft core repulsive model based on spheres of diameter σ with an embedded short-ranged attraction to represent a small volume that is either LC rich or solvent (MeOH) rich. There are certain physical features of the phase diagram and droplet behaviour that allow us to parameterise the interactions between the two types of fluid volumes. The two types should be predominantly (but not totally) immiscible at lower temperatures but partially miscible at higher temperatures, the attractions for the LC model must be anisotropic to ensure the possibility of an aligned phase at low enough temperature and similarly the LC-solvent interactions must allow for tangential ordering at the interface between the LC-rich minority nematic phase and the solvent-rich majority isotropic phase. We define our model for the solvent-solvent interactions as:

$$U_{SS}(\boldsymbol{r}_{ij}) = \frac{\epsilon'_{SS}}{\sigma^2} (\sigma - r_{ij})^2 - \epsilon_{SS} f(r_{ij})$$
(4)

for $r_{ij} < \sigma$, in which r_{ij} and r_{ij} are the vector and the distance between a pair of particles *i* and *j*. The first term is a soft repulsive sphere, typical of

the form used in many dissipative particle dynamics simulations ^{4,5}; the second term is a weak short-range attraction chosen with a form such that it does not overwhelm the repulsion at low r_{ij} . ϵ'_{SS} and ϵ_{SS} govern the strengths of the solvent-solvent repulsive and attractive interactions respectively, and $f(r_{ij})$ is a Gaussian function centred towards the outer edge of the particle at 0.75σ that decays essentially to zero within $r_{ij} < \sigma$:

$$f(r_{ij}) = \exp\left(-\frac{1}{2}\frac{(r_{ij} - 0.75\sigma)^2}{(0.075\sigma)^2}\right).$$
(5)

We can similarly define the LC-LC interactions using an anisotropic modification to the attraction part of the potential:

$$U_{LL}(\boldsymbol{r}_{ij}, \hat{\boldsymbol{u}}_i, \hat{\boldsymbol{u}}_j) = \frac{\epsilon'_{LL}}{\sigma^2} (\sigma - r_{ij})^2 - \epsilon_{LL} (\hat{\boldsymbol{u}}_i \cdot \hat{\boldsymbol{u}}_j)^2 f(r_{ij})$$
(6)

where \hat{u}_i is a unit vector describing the orientation of particle *i*. Finally, interactions between unlike particles are defined as:

$$U_{LS}(\boldsymbol{r}_{ij}, \hat{\boldsymbol{u}}_i) = \frac{\epsilon'_{LS}}{\sigma^2} (\sigma - r_{ij})^2 - \epsilon_{LS} (\hat{\boldsymbol{u}}_i \cdot \hat{\boldsymbol{r}}_{ij})^2 f(r_{ij})$$
(7)

where the anisotropic term tends to assist tangential alignment at the interface between a LC-rich nematic and a solvent-rich isotropic phase. To ensure similar compressibilities for the LC and solvent phases, we set $\epsilon'_{LL} = \epsilon'_{SS}$ to ensure the compressibility of the solvent is similar to that of the mesogen and to ensure (partial) immiscibility, $\epsilon'_{LS} > \epsilon'_{SS}$. Varying ϵ_{LL} with respect to ϵ_{SS} varies the strength of the LC-LC attractions and so the nematic–isotropic transition temperature in a pure system can be controlled via this parameter. Similarly, the values of ϵ_{LS} and ϵ'_{LS} can be varied to adjust the anchoring at interfaces and the miscibility of the components and hence the coexistence compositions, as well as the critical point in the phase diagram. The potential energy plots for the parameter set $\epsilon'_{LL} = 20\epsilon$, $\epsilon'_{LS} = 25\epsilon$, $\epsilon'_{sS} = 20\epsilon$, $\epsilon_{LL} = 2\epsilon$, $\epsilon_{LS} = 2\epsilon$ and $\epsilon_{SS} = \epsilon$ where ϵ is an energy parameter are shown in Fig. S3 and the resulting phase diagram in Fig. S4.

We note that the form of the interactions that could lead to the required phase behaviour and properties is not unique. For example, phase separation between two (isotropic) species can be achieved through purely repulsive interactions, so long as the mixed interaction is more repulsive than the like interactions. Liquid crystallinity can then be introduced by have the repulsive interaction between orthogonally aligned particles to be larger than for parallel aligned particles. However, this implies that the compressibility of the nematic phase that such a parametrisation forms would be less than that of the isotropic phase which is less satisfactory. Similarly, the model would need to account for anchoring at the surface and again varying this through a single repulsive parameter would mean lowering the overall repulsive interaction for a solvent region approaching a nematic region end-on compared to side on. We therefore use the attractive regions confined to the periphery of the soft spheres



Supplementary Figure S3: Potential energy curves with parameters $\epsilon'_{LL} = 20$, $\epsilon'_{LS} = 25\epsilon$, $\epsilon'_{sS} = 20\epsilon$, $\epsilon_{LL} = 2\epsilon$, $\epsilon_{LS} = 2\epsilon$ and $\epsilon_{SS} = \epsilon$. Thin lines - solid: LC-LC ($\hat{\boldsymbol{u}}_i \cdot \hat{\boldsymbol{u}}_j = 1$), dashed: LC-LC ($\hat{\boldsymbol{u}}_i \cdot \hat{\boldsymbol{u}}_j = 0$), dotted: S-S. Thick lines - solid: LC-S ($\hat{\boldsymbol{u}}_i \cdot \hat{\boldsymbol{r}}_{ij} = 1$), dashed: LC-S ($\hat{\boldsymbol{u}}_i \cdot \hat{\boldsymbol{r}}_{ij} = 0$).

while retaining similar repulsive interactions for all orientations for significantly overlapped particles.

The phase diagram was obtained using semi-grand canonical Monte Carlo simulations of 12288 soft-core particles in a simulation box of size $(16\sigma)^3$, giving an overall particle density of $\rho^* = \rho\sigma^3 = N\sigma^3/V = 3$, similar to the densities used in dissipative particle dynamics with similar soft sphere potentials^{4,5}. A series of simulations were run at constant temperature in which the fugacity fraction of the LC species was varied so that the identities of the particles, and hence the overall composition, can change⁶. Identifying the discontinuities in the equation of state generated at each temperature allows us to determine the coexistence densities of the two phases at equilibrium as a function of temperature.

In order to parametrise the model, the repulsive parameters ϵ'_{LL} , ϵ'_{SS} and ϵ'_{LS} were fixed while ϵ_{LL} and ϵ_{LS} were varied to ensure that we observe both isotropic–isotropic and nematic–isotropic phase coexistence in a binary system as a function of temperature and that the critical point for I1-I2 coexistence was not significantly higher than the NI transition. If the immiscibility is high leading to strong phase separation, the two phases are essentially immiscible and there is no difference in the coexistence compositions for I1-I2 a little above and N-I2 a little below the triple point; the phase diagram is essentially pure mesogen on the left hand side and pure solvent on the right. The partial miscibility is



Supplementary Figure S 4: Phase diagram of the model system showing isotropic–isotropic I_1 - I_2 coexistence at higher temperatures and nematic– isotropic N- I_2 coexistence at lower temperatures. Here, ρ^* is the solvent density. Since the total particle density is 3, this can be divided by 3 to give the solvent composition(s) at the boundaries. T^* is a reduced temperature, defined in terms of the energy parameter ϵ as $T^* = kT/\epsilon$.

clearly a key factor of this system, different to other oil in water type droplets.

Simulations of a planar slab were also run to ensure that the choice of ϵ_{LL} and ϵ_{LS} led to homeotropic (tangential) alignment at the interface.

With the phase diagram determined and found to be comparable with experimental results³, we construct a LC-rich isotropic droplet in an solvent-rich majority phase at $T^* = kT/\epsilon = 1.375$, just above the triple point in the bulk phase diagram, with the appropriate compositions for the droplet and exterior read off from the phase diagram. 862488 particles were placed at random positions inside a box of dimensions $(66\sigma)^3$ and any particles within 29σ of the centre of the box are determined to be inside the droplet and assigned their identity with a probability such that the overall composition of the droplet is equal to that of the minority phase I_1 at this temperature. Those particles outside the droplet are assigned their identity such that the external composition is that of the majority phase I_2 . Canonical Monte Carlo simulations were then run at $T^* = 1.375$ to equilibrate the isotropic droplet. Once equilibrated, the temper ature was reduced below the triple point to $T^{\ast}=1.275$ such that the droplet enters the region of the phase diagram exhibiting a minority nematic phase in coexistence with a majority solvent-rich phase. Note, similar simulation runs at other temperatures were performed but gave a similar series of results. The director structure and any defects formed were monitored using parameters based on Westin matrices^{7,8}. Although Monte Carlo is strictly a stochastic rather than a time-dependent simulation method, the pathway followed should be similar to that in a time-dependent simulations as only localised movements are allowed; more drastic trials that are non-physical, such as the swapping of identities of particles that are far away from each other or the transfer of particles deep in the middle of the droplet into the majority phase, are not used as these would deviate from the expected pathway. Indeed, the pathways for disclination lines in simulations of lattice models for liquid crystal droplets have been shown to be similar to those of real LC droplets⁹.

4 Simulations: Defect formation and motion

In Fig. S5, the defect configuration at the end of a higher temperature run $(T^* = 1.325)$ is shown a short time after the inner droplet has been expelled and the simulation droplet has transformed into the axial configuration.



Supplementary Figure S5: The axial director field some time after the inner droplet was expelled, run at $T^* = 1.325$.

References

- V. F. Peters, M. Vis, G. García, H. H. Wensink and R. Tuinier, *Phys. Rev. Lett.*, 2020, **125**, 127803.
- [2] T. L. Hill, Nano Lett., 2001, 1, 273–275.
- [3] L. A. Serrano, M. J. Fornerod, Y. Yang, F. Stellacci and S. Guldin, *Soft Matter*, 2018, 14, 4615–4620.
- [4] P. Espanol and P. Warren, EPL (Europhysics Letters), 1995, 30, 191.
- [5] P. Espanol and P. B. Warren, The Journal of chemical physics, 2017, 146, 150901.
- [6] D. Frenkel and B. Smit, Understanding molecular simulation: from algorithms to applications, Elsevier, 2001, vol. 1.
- [7] A. C. Callan-Jones, R. A. Pelcovits, V. A. Slavin, S. Zhang, D. H. Laidlaw and G. B. Loriot, *Phys. Rev. E*, 2006, **74**, 061701.
- [8] M. A. Bates, G. Skačej and C. Zannoni, Soft Matter, 2010, 6, 655–663.
- [9] T. Lopez-Leon, M. A. Bates and A. Fernandez-Nieves, *Phys. Rev. E*, 2012, 86, 030702.