EUROPHYSICS LETTERS 1 December 1995

Europhys. Lett., 32 (7), pp. 607-612 (1995)

Stability of Liquid Crystalline Macroemulsions.

E. M. TERENTJEV

Cavendish Laboratory, University of Cambridge
Madingley Road, Cambridge, CB3 0HE, UK

(received 19 July 1995; accepted in final form 16 October 1995)

PACS. 82.70-y – Disperse systems.
PACS. 68.10-m – Fluid surfaces and fluid-fluid interfaces.
PACS. 61.30Jf – Defects in liquid crystals.

Abstract. – The topological stability of emulsions of liquid crystal in water (glycerol) matrices is demonstrated for a wide range of materials and concentrations. Coalescence is prevented by an energy barrier for a topological ring defect formation in a neck between the two merging droplets. There is a characteristic size of emulsion droplets, typically tens of micrometres or more, controlled by the balance of elastic and anchoring energies of the liquid crystal. On removal of liquid crystallinity (by raising the temperature above $T_{\rm ni}$ in thermotropic nematic materials, for example) the energy barriers for coalescence disappear and emulsion droplets can merge quickly, controlled only by the traditional kinetic effects. Practical applications of this effect, as well as some wider theoretical implications are discussed in the end.

Physics and chemistry of colloids and emulsions are rapidly becoming, from an empirical domain of paint design and food technology, an important area of fundamental research. The reason for this is the recognition of the possibilities and benefits of new applications generated from fundamental studies and, on the other hand, more clear, challenging and wide-ranging problems are seen in this area (a good example being, for instance, the physics of membranes, which made an impressive progress in the recent years [1]).

When two immiscible fluids are thoroughly blended together, an emulsion is formed (or a colloid suspension, when the characteristic viscosities of the fluids differ significantly). The best known examples are, of course, oil-in-water or water-in-oil emulsions. There is an understanding, quite general for colloids and emulsions, that their structural stability is a kinetic concept and not a thermodynamic one [2]. Some emulsions have only a short lifetime before complete phase separation, whereas others remain kinetically stable for years. In order to prepare a stable emulsion there must be a surface active material present to protect the newly formed droplets from immediate recoalescence. Such surfactant molecules, typically, have two distinct parts—hydrophobic and hydrophilic for oil-water interfaces. By aggregating on such interfaces they reduce the surface tension and, when such a reduction is complete, a microemulsion, *i.e.* the solution of microscopic micelles is formed. That represents a truly thermodynamically stable phase, as opposed to the kinetic stability of macroscopic droplets. The argument is simple: if the local energy of the interface covered with surfactant is very small («zero» for practical purposes), the entropy preference of having many small particles in favour of the few big ones makes the molecular micelles a ground state of the total free energy. If, on the other hand, the local interface energy is considerable, the configurational entropy is irrelevant and the minimal surface area of the completely separated phases is the ground state—which the system may take some time to reach, however. It is not easy to give a reference to such a broad and well-studied area, but an interested reader, new to the field, could find useful information in [3,4].

The situation may change if an additional physical field comes into the problem, bringing along its own energy and entropy contributions. The simple example studied in this work is the orientational order when one of the two emulsified fluids is a liquid crystal. This question has been recently examined theoretically, when a nematic liquid crystal is the majority phase with surfactant-covered fluctuating interfaces inducing bulk curvature deformations of the director [5]. Here I shall address the opposite end of the problem, when the isotropic majority phase (water, for instance) has small droplets of nematic liquid crystal dispersed in it. Surfactant is needed, as usual, to reduce the interface energy and also to impose strong anchoring boundary conditions for the nematic director. The basic result of this work is that there is an additional contribution, the elastic energy of topological defects in the confined nematic, in the analysis of emulsion stability. This energy creates a significant barrier for the droplet coalescence and leads to a new effect—topological stability of macroemulsions.

Droplets of nematic liquid crystal in an isotropic fluid and the related topological defect structures have been extensively studied before [6]. Since the development of polymer-dispersed liquid crystals has been formulated [7], much more work has been done in this area [8]. However, in all cases the properties and effects of individual droplets have been addressed, with authors looking at the structure, and field and temperature-driven transitions [9]. Interesting physical effects here stem from the topological constraint, imposed on the director field in a closed volume by the anchoring condition on its surface, leading to topological defects of total point charge $(+1)$ for nematic and more complex structures in other phases.

In this paper I study the question of cooperative effects for such droplets in a (dense) emulsion, focusing on the mechanism of their coalescence, which one would expect to happen by analogy with isotropic macroemulsions. First I explain the experimental procedure of forming such an emulsion (certainly well understood by the authors of quoted papers) and the facts about the coalescence kinetics. After that I propose a model structure of the «neck» between the two merging droplets and calculate the related energy barrier, which explains the observations. In the end I shall briefly discuss practical implications of this effect and also its relation to the wider theoretical problem of the effect of topological defects on phase ordering in various field theories.

Experiment. – Since we are modelling oil-in-water emulsions, with the oil phase being a liquid crystal, the following general rule for the choice of materials should apply. If the majority isotropic phase is water (or glycerol, similar in properties, or their mixture), that is a fluid with large molecular dipoles, then the «oil» liquid crystal should be chosen with the least possible dipole. In this way the surfactant molecules will have a clear preference for positioning their hydrophilic and hydrophobic parts on the interface. With the above choice of non-polar rod-like mesogenic molecules, the best surfactant type would be an ionic one, with one long aliphatic hydrophobic tail similar to the typical end group of a nematic molecule. Along these guidelines the weakly polar mesogenic MBBA (methoxybenzylidene-butilaniline, supplied by Aldrich) must be given preference to with respect to, for instance, cyanobiphenils (another typical nematic material, but with significant molecular dipole in the C-N group) (1).

---

(1) In fact, MBBA also has a disadvantage, since it is weakly miscible with water, which causes the eventual loss of its mesogenic power. However, in a good surfactant-mediated emulsion this mixing takes a very long time, sufficient to allow unambiguous observations.

A simplest choice of surfactant leads to CTAB (cetyltrimethylammonium bromide, supplied by Aldrich), which has a strongly polar hydrophilic head and a single hydrophobic tail with 14-16 CH_2 groups. One expects this tail to align itself along the rod-like mesogenic molecule and, in fact, CTAB is one of the best materials used to treat liquid crystal cells for homeotropic anchoring.

The preparation of an emulsion is fairly standard. One dissolves a small amount of CTAB in water, 3–5 weight %, taking care to avoid the surfactant aggregation into various lyotropic phases above the CMC (critical micelle concentration). Then a small amount (also ~ 5 weight %) of MBBA is added and the resulting mixture is thoroughly blended in an ultrasonic bath. As will be clear below, it is important to keep the «oil» all the time in the nematic phase, below the clearing temperature T_{ni}. As a result, a very small sub-micrometre size emulsion of MBBA in water, with CTAB aggregated on the interfaces, is formed. Due to the initial small size of droplets the material scatters light and appears turbid. After some time these droplets recombine into much bigger ones (~ 30–100 μm) and then the dynamics stops: samples then stayed unchanged for many months. The time of initial recombination can vary between minutes and hours depending on conditions and concentrations, but the physics and the resulting structure are fairly robust. For instance, since the density of MBBA is slightly higher than that of water ($d = 1.027$), the droplets eventually sink to the bottom of the container. In order to improve their buoyancy one may choose to mix water with glycerol ($d = 1.26$) to equilibrate the density with MBBA. One also may significantly alter the concentration of CTAB in the mixture, or blend again at some moderate ultrasonic energy input. None of these factors appear to qualitatively influence the resulting stable macroemulsion.

In order to test the «strength» of macroscopic droplets in the stable emulsion, one can use pure water with its low viscosity and density in comparison with the MBBA liquid crystal. (There is no need to prepare a new sample, one can, at will, add or remove water and surfactant from the clear regions of the established emulsion, without any effect on droplet distribution.) All droplets quickly sink to the bottom, but can be disturbed by shaking the container. In the stationary state the droplets are so tightly compressed together in the pile by gravity, that their shape no longer remains spherical, see fig. 1. And yet, in spite of the physical force pushing droplets together, no coalescence takes place over the observation time of several months. This fact is a surprise, considering what we know about isotropic

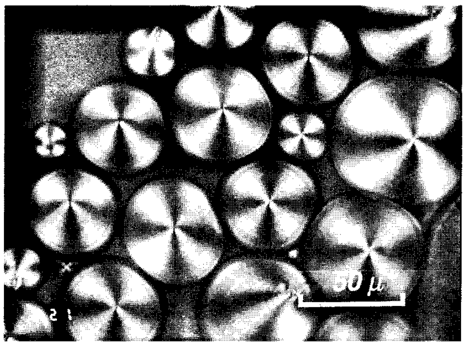

Fig. 1. – A group of tightly squeezed nematic droplets in water/glycerol/CTAB matrix, viewed between crossed polarizers to reveal the radial director distribution. The bar represents the 50 μm length scale. Note the squeezed droplets in the bottom-left corner of the picture.

oil-in-water emulsions. To test this comparison, the obvious thing to do is to raise the temperature of the thermotropic liquid crystal above its clearing point, after which the system must behave like a «normal» o-w emulsion without an additional elastic energy of the nematic. On doing so a remarkable thing happens: all droplets that were in direct contact (like those shown in fig. 1) coalesce immediately, within a few seconds after T_{ni} is exceeded! This observation clearly proves that the nematic curvature elastic energy holds the macro-emulsion stable.

Theory. – How can we rationalize these observations? We have the following facts: in the initial stage very small droplets recombine quickly to form a stable macroemulsion with characteristic size $\sim 50\ \mu\mathrm{m}$ (broadly distributed within this order of magnitude); this size and droplet lifetime appears to be independent of the character of the isotropic majority phase (as long as it supports the CTAB placement on the interface); the application of significant force pushing droplets against each other is not sufficient to make them merge and, finally, the coalescence and complete phase separation take place very rapidly after the liquid crystallinity is removed from the picture.

All following arguments will be based on the assumption that hydrophobic tails of densely packed surfactant (CTAB in this case) are extended perpendicular to the interface and impose a strong homeotropic anchoring on the nematic director. (We certainly know this is the case with CTAB-treated glass surfaces.) The deviation $\delta\boldsymbol{n}$ of the director from this perpendicular orientation is penalized by the anchoring energy $\sim W|\delta\boldsymbol{n}|^2$ per unit area, while the curvature deformations in the bulk give rise to the Frank energy density $(1/2)K(\nabla\delta\boldsymbol{n})^2$. Big droplets with radius $R^* \geqslant K/W$ form a radial hedgehog point defect in the middle due to the topological constraint at non-zero W (or, possibly, a small ring of disclination [10], which would be indistinguishable from the monopole at large length scales); this is what we see in fig. 1 and in either droplet of fig. 2.

Let us consider the act of two-droplet coalescence in some more detail, see fig. 2. As separate bounded volumes before collision, each of them contains a topological point charge of $(+1)$ (regarding the director as pointing outwards from the monopole). After the merging process is completed we are left with one simply connected piece of bounded nematic volume, which must have just one $(+1)$ point defect. Hence, in between, another defect with point charge (-1) was born and then annihilated one of the two initial monopoles. This defect is, as one can see from fig. 2, a ring of the wedge disclination with the *linear* charge $(-1/2)$ on the tip of the neck connecting the two droplets. The late-stage scenario can be different: one possibility is that the ring detaches itself from the surface, when the curvature of the neck decreases, and transforms into a hyperbolic monopole structure with point charge (-1) which then drifts into the volume towards one of the radial monopoles; the other is that the $(-1/2)$ ring remains as a surface disclination [6] and one of the point defects is, being

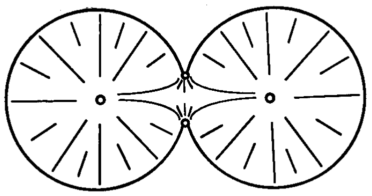

Fig. 2. – A scheme of the neck formation in the coalescing spherical droplets (the picture represents a cross-section of a cylindrically symmetric dumb-bell object). The resulting topological ring defect, situated on the neck tip, is required to conserve the total topological charge of the merged system.

attracted to it, moves towards and disappears on the surface. This choice is curious but is of little relevance to the practical phenomena; what is important is that in order to form the initial neck the system must create an accompanying total (-1) point charge not as a *pair* (a fluctuational birth of small (± 1) pairs should be a normal event in a vector-field system), but in isolation, at a distance $\sim R$ from other defects. This costs a macroscopic elastic energy $\sim KR$, while the gain due to the surface tension is minimal as the total area of the «dumb-bell» is the same as that of the two separate droplets.

Now we can trace the evolution of the nematic emulsion. Initial droplets, broken to very small sizes by ultrasonic energy, prefer to violate the surface anchoring energy of the director (at a cost $\sim WR^2$) but have a uniform director field inside. No topological-defect arguments apply in this situation and small droplets recombine without an energy barrier. At a critical size $R^* = K/W$ the surface energy cost becomes too high and droplets form a radial director distribution with a monopole in the middle, with bulk elastic energy $\sim KR$. From now on each individual pair of droplets, in order to merge, would have to overcome the topological energy barrier $\Delta E \sim KR \sim K^2/W$. We can now understand why the conditions *outside* the droplet do not affect the emulsion stability, as long as the strong anchoring constraint imposed by the ordered surfactant is preserved. Near the nematic-isotropic transition the Frank elastic constant K and the anchoring energy W depend on the order parameter Q, as $K \sim Q^2$ and $W \sim Q$ and, therefore, the energy barrier to coalescence $\Delta E \sim Q^3$ rapidly disappears near the transition. This is why the complete phase separation takes place so rapidly above T_{ni}.

The same estimate, $\Delta E \sim K^2/W$, controls the parameter of another test on the emulsion stability. We saw already that the weak force of gravity, compressing the droplets together, is not sufficient to overcome this barrier. However, if we place the established emulsion in a high-energy ultrasonic field, the droplets may again break into very small sizes. Note, however, that in order to break the droplet in two parts the same topological analysis demands the formation of a disclination ring on the surface, preferably in the breaking-neck region, in order to provide *two* point singularities after the break. The energy estimate is the same, $\Delta E \sim KR$, and dictates the threshold value for the ultrasonic energy input of a blender (shaking by hand is certainly not enough to provide this energy per droplet). For a typical nematic liquid crystal the Frank constant is of the order $K \sim 10^{-11}$ N and «strong» surface anchoring usually means $W \sim 10^{-5}$–10^{-6} J/m^2. From this we obtain the correct characteristic stable droplet size $R^* \sim 10$–$100\ \mu\mathrm{m}$ and the energy barrier per particle $\Delta E \sim 10^{-16}$ J (compare with room temperature thermal energy $k_{\mathrm{B}} T \sim 5 \cdot 10^{-21}$ J). Note that at weak anchoring the characteristic size R^* would increase and the spherical droplets may transform into large flexible vesicles (in practice this happens at $R \sim 1$–10 mm), after which the energy barrier ΔE will decrease again. Thus, when the director anchoring on surfactant-treated interfaces is weak, no stable emulsion should be expected.

Conclusions. – Besides the possibility of topological stability of macroemulsions, the main practical implication of this work is the ability to have a fine temperature control over the morphology of emulsions. Also of interest is the control over the equilibrium droplet size R^* through the choice of surfactant (affecting W) and nematic material. One can imagine, among many other possibilities, an application of such emulsions, carrying a liquid crystalline chemical inhibitor, temperature-tuned in such a way that emulsion becomes isotropic, rapidly coalesces and releases the chemical to stop an overheating reactor. Another possible application could use the polymerization of surfactant to form a percolating sponge with mesh size controlled by K/W.

Another, more fundamental aspect of this work is related to the general problem of phase ordering of a non-scalar field. Such a problem arises in various areas of physics, from cosmology to soft condensed matter, where a first-order phase transition takes place.

Currently general opinion is in favour of the so-called Kibble mechanism, when *uniform* nucleating domains merge and form topological defects in the ordered phase due to their random orientation [11]. There are various opinions on why point defects (monopoles) are never observed after such quenching. However, there seems to be no good reason to disregard the additional symmetry breaking due to the order parameter gradient on the nuclei surface and corresponding surface energy (equivalent to our W). Then, if the characteristic size R^* were to be reached, the domains would be topologically non-trivial and their coalescence will follow the route shown in fig. 2, completely altering the predictions about the broken-symmetry phase properties after the quench.

* * *

I gratefully acknowledge many useful and enlightening discussions with J. A. McDonald, R. Peck, O. D. Lavrentovich, P. Palffy-Muhoray, M. Warner and P. D. Olmsted. This research has been initiated and supported by Unilever PLC.

REFERENCES

[1] Helfrich W., *J. Phys. (Paris)*, **46** (1985) 1263; Lipowsky R. and Leibler S., *Phys. Rev. Lett.* **56** (1986) 2541; Roux D., *Physica A*, **172** (1991) 242.

[2] Bibette J., Morse D. C., Witten T. A. and Weitz D. A., *Phys. Rev. Lett.*, **69** (1992) 2439.

[3] Clint J. H., *Surfactant Aggregation* (Blackie, Glasgow, London) 1992.

[4] Dickinson E., *An Introduction to Food Colloids* (Oxford University Press) 1992.

[5] Olmsted P. D. and Terentjev E. M., to be published in *J. Phys. II*.

[6] Volovik G. E. and Lavrentovich O. D., *Sov. Phys. JETP*, **58** (1983) 1159.

[7] Zumer S., Golemme A. and Doanne J. W., *J. Opt. Soc. A*, **6** (1989) 403.

[8] Xu F., Kitzerow H. S. and Crooker P. P., *Phys. Rev. A*, **46** (1992) 6535; Drzaic P. S. and Muller A., *Liq. Cryst.*, **5** (1989) 1467.

[9] Lavrentovich O. D. and Terentjev E. M., *Sov. Phys. JETP*, **64** (1986) 1237; Koehler A. E., *Z. Phys. Chem.*, **269** (1988) 196; Kralj S. and Zumer S., *Phys. Rev. A*, **45** (1992) 2461.

[10] Mori H. and Nakanishi H., *J. Phys. Soc. Jpn.*, **57** (1988) 1281.

[11] Hindmarsh M. B. and Kibble T. W. B., *Rep. Prog. Phys.*, **58** (1995) 477; Bray A. J., *Physica A* **194** (1993) 41.