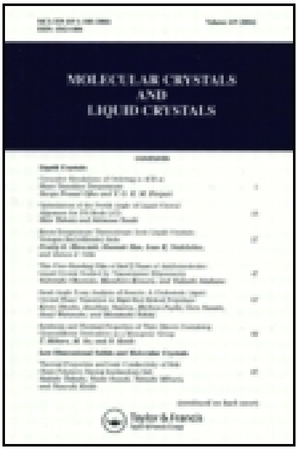

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Nematic-Wetted Colloids in the Isotropic Phase

P. Galatola [a] & J.-B. Fournier [b]

[a] Dipartimento di Fisica and Unità INFM, Politecnico di Torino, Corso Duca degli Abruzzi 24, I-10129, Torino, Italy

[b] Laboratoire de Physico-Chimie Théorique, ESA CNRS 7083, ESPCI, 10 rue Vauquelin, F-75231, Paris, France

Version of record first published: 24 Sep 2006

To cite this article: P. Galatola & J.-B. Fournier (1999): Nematic-Wetted Colloids in the Isotropic Phase, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 330:1, 535-539

To link to this article: http://dx.doi.org/10.1080/10587259908025631

Mol. Cryst. Liq. Cryst., 1999, Vol. 330, pp. 535-539
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Nematic-Wetted Colloids in the Isotropic Phase

P. GALATOLA[a] and J.-B. FOURNIER[b]

[a]*Dipartimento di Fisica and Unità INFM, Politecnico di Torino, Corso Duca degli Abruzzi 24, I-10129 Torino, Italy and* [b]*Laboratoire de Physico-Chimie Théorique, ESA CNRS 7083, ESPCI, 10 rue Vauquelin, F-75231 Paris, France*

We study the interaction and phase behavior of spherical particles immersed in the isotropic phase of a nematogenic liquid crystal. We find that colloidal stabilization can be achieved by a surface nematic wetting.

Keywords: colloid; interaction; wetting; nematic; defect

INTRODUCTION

The possibility of inducing a nematic ordering at the boundary of a solid substrate in the isotropic phase of a nematogenic compound was theoretically proposed by Ping Sheng[1]. The existence of such a nematic boundary layer was experimentally verified by Miyano[2]. Recently, Borštnik and Žumer have analyzed the interaction between two nematic-wetted parallel plates immersed in the isotropic phase[3]. In the absence of nematic distortions, an attractive interaction develops since the volume of the surface-induced nematic is reduced when the boundary layers overlap.

The effect of a competing nematic distortion has not yet been studied. This problem naturally arises in the case of curved surfaces with strong, e.g., homeotropic, anchoring. Moreover, if the surfaces are mobile, one might expect interesting many-body interactions. This suggests to study how colloidal particles wetted by the nematic phase would interact through their nematic halos. The somewhat related problem of the interaction of water droplets in a nematic emulsion has been recently studied by Poulin *et al.*[4]: long-range anisotropic forces were evidenced, mediated by the nematic matrix. In our case, the matrix is overall isotropic; however, short-range anisotropic forces may develop in the vicinity of the particles. In the following, we will show that nematic boundary layers can effectively stabilize colloidal suspensions, in a way similar to the more classical polymer and ionic double-layer coatings[5].

MODEL

The Landau-de Gennes free-energy density of the isotropic phase of a nematogenic compound can be written as[6]

$$f = \frac{1}{2}aS^2 + \frac{1}{2}L_1\, Q_{ij,k}Q_{ij,k} + \frac{1}{2}L_2\, Q_{ij,j}Q_{ik,k} + \frac{1}{2}L_3\, Q_{ij,k}Q_{ik,j}\,, \tag{1}$$

to second order in $Q_{ij} = S(n_i n_j - \delta_{ij}/3)$, the quadrupolar nematic order-parameter, which collectively describes the degree of ordering S and the nematic director $\mathbf{n}$. Normalizing the lengths with respect to the nematic coherence length

$$\xi = \sqrt{\frac{2L_1 + L_2 + L_3}{3a}}\,, \tag{2}$$

and the energies by $a\xi^3$, for fixed boundary conditions and no twist deformations, f becomes

$$\begin{aligned} \bar{f} &= \frac{1}{2}S^2 + \frac{1}{2}\left[(1-2\eta)(\nabla S)^2 + 3\eta\,(\mathbf{n}\cdot\nabla S)^2\right] \\ &+ \frac{3}{2}S^2\left[(\nabla\cdot\mathbf{n})^2 + (\mathbf{n}\times\nabla\times n)^2\right] - 3\eta\, S\,\nabla S\cdot\mathbf{n}\times\nabla\times\mathbf{n}\,. \end{aligned} \tag{3}$$

The coefficient $-1 < \eta < 1/3$ measures the anisotropy of the elastic constants. In the following, we concentrate on the case $\eta = 0$. No new qualitative effect appears for $\eta \neq 0$. The energy scale $a\xi^3$, for typical thermotropic compounds, is of the order of $3 \div 30\, k_\mathrm{B}T$, depending on the distance to the nematic transition.

We consider two spheres of radius R (in units of ξ) imposing a fixed surface order-parameter S_0 and a strong homeotropic nematic anchoring. Minimizing the total free energy

$$F = \int \bar{f}\, d\mathbf{r} \tag{4}$$

yields a set of two coupled non-linear partial differential equations for $\mathbf{n}$ and S that cannot be solved analytically. We solved them numerically.

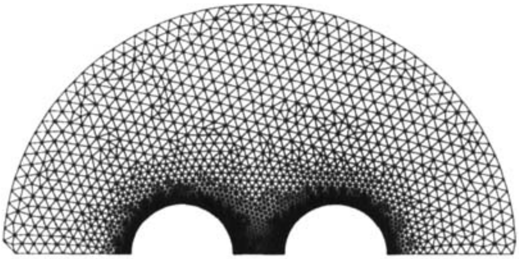

FIGURE 1 Typical Delaunay triangulation of the revolution section of the space between two spheres with reduced radius $R = 2$.

RESULTS

We developed an adaptative Delaunay triangulation with a Bowyer-Watson algorithm[7] to mesh the space between the two spheres (Fig. 1). Inside each triangle, the free-energy F is computed by linearly interpolating S and $\mathbf{n}$. Because of the large number of degrees of freedom $\simeq 3 \times 10^4$, F is minimized by a simulated annealing algorithm.

A typical nematic texture around the two spheres is shown in Fig. 2. A "Saturn" disclination ring of strength $-\frac{1}{2}$ spontaneously develops, although it is not topologically required. It lives however in a region of space where the order-parameter is rather small.

For the interaction energy, we find that small spheres with $R \lesssim 4$ repel each other: when the nematic halos begin to overlap, the elastic energy dominates because of the small curvature radius. On the other hand, large spheres feel an attraction on approaching up to a distance $\simeq 0.5\xi$, and a repulsion close to contact.

Colloidal stability

The existence of an energy barrier has important consequences for the stability of a colloidal suspension. In fact, all materials also experience van der Waals attractions. The corresponding energy for two spheres is given by[8]

$$F_w = \frac{2A}{3}\left[\frac{2-\rho^2}{\rho^4-4\rho^2} - \frac{1}{4}\ln\left(1-\frac{4}{\rho^2}\right)\right], \qquad (5)$$

where $\rho = d/R$ is the ratio between the center-to-center distance and the radius of the particles, and $A \simeq k_B T$ is the Hamaker constant. Adding

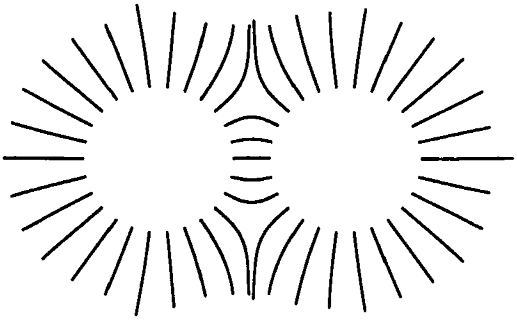

FIGURE 2 Director lines of the nematic field between two spheres of reduced radius $R = 2$ separated by a center-to-center distance $d = 5$. The lines are terminated when $S < 10^{-2} S_0$.

together F and F_w yields, depending on the values of S_0 and ξ, either an overall attraction, or a more or less pronounced energy barrier giving rise to a metastable state in which the particles are not aggregated.

We have calculated the coagulation time of our colloidal suspension[9]. For typical thermotropic material parameters, we find that an effective stabilization can be achieved close to the nematic transition for a surface order-parameter $S_0 \simeq 0.5$. The corresponding metastable phase is either a gas or a crystal, depending on the size of the particles with respect to the nematic coherence length. Precisely, for $R \lesssim 3$, the particles form a gas phase, while for $R \gtrsim 4$ they are arranged in a crystal. This allows to induce a reversible gas-crystal transition upon heating the system.

Many-body effects

The interaction between more than two spheres is a non-trivial problem because of the topological constraints that develop in between the particles, where the nematic order is strong. To get a feeling of the possible effects, we have analyzed the interaction of three particles in a two-dimensional ($2D$) geometry. When they are arranged in a triangular fashion, the nematic develops a point-like defect of strength $-\frac{1}{2}$ in between the spheres. Such a defect strongly depresses the nematic order close to the spheres (Fig. 3).

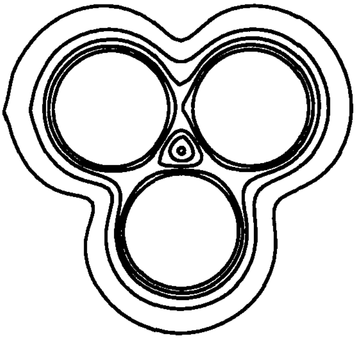

FIGURE 3 Contour lines of the nematic scalar order-parameter S around three interacting $2D$ "spheres".

References

[1] Ping Sheng, *Phys. Rev. Lett.*, **37**, 1059 (1976).
[2] K. Miyano, *Phys. Rev. Lett.*, **43**, 51 (1979).
[3] A. Borštnik and S. Zumer, *Phys. Rev. E*, **56**, 3021 (1997).
[4] P. Poulin, H. Stark, T.C. Lubensky and D.A. Weitz, *Science*, **275**, 1770 (1997).
[5] J.N. Israelachvili, *Intermolecular and Surface forces* (Academic Press, London, 1992).
[6] P.G. de Gennes and J. Prost, *The physics of Liquid Crystals* (Clarendon Press, Oxford, 1993).
[7] S. Rebay, *J. Comp. Phys.*, **106**, 125 (1993).
[8] R.J. Hunter, *Foundations of Colloid Science*, (Clarendon Press, Oxford, 1991).
[9] Benjamin Chu, *Molecular Forces. Based on the Baker lectures* of *Peter J.W.* Debye (John Wiley & sons, New York, 1967).