Dynamics in Reentrant Nematics

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1. Introduction

Liquid crystals have attracted enormous interest because of the variety of their phases and richness of their application. The interplay of general physical symmetries and specific molecular features generates countless different phenomena. A surprising behavior of liquid crystals is the reentrancy of phases as temperature, pressure or concentration are varied.

Recently, some computer simulations of a system confined to nanoscopic scales have found new dynamical features of the reentrant nematic phase. Using a combination of isothermal-isobaric Monte Carlo and microcanonical molecular dynamics we investigate the relation between structure and self-diffusion in various phases of a model liquid crystal using the Gay-Berne-Kihara potential. These molecules are confined to a mesoscopic slit-pore with atomically smooth substrate surfaces. As reported recently [see M.G. Mazza *et al.*, Phys. Rev. Lett. **105**, 227802 (2010)], a reentrant nematic (RN) phase may form at sufficiently high pressures/densities (see Fig. 1). This phase is characterized by a high degree of nematic order and a substantially enhanced self-diffusivity in the direction of the director **n** which exceeds that of the lower-density nematic and an intermittent smectic A phase by about an order of magnitude.

Fig.1: Snapshots of characteristic configurations at T=4.0; (a) P=1.6 (N), (b) P=2.1 (smA), (c) P=2.9 (RN). Flat surfaces on top and bottom in dark represent the solid substrates.

2. Dynamics

A suitable measure of mass transport is the mean square displacement (MSD) of molecules. It measures the on-average net distance a molecule's center of mass is able to travel in a given amount of time. Because of the large degree of nematic order characteristic of the RN phase it seems sensible to introduce a *specialized* MSD by considering displacements of molecules in the direction of their long axes.
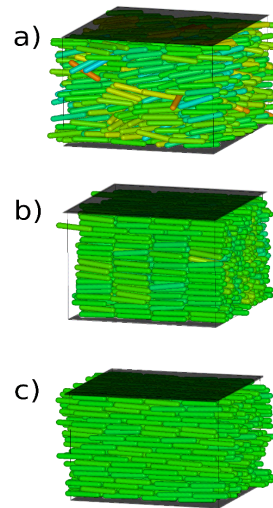
Specifically, we define the MSD for the displacement of molecules in the direction of their long axes

$$\left\langle \Delta r_\parallel^2 (\tau) \right\rangle_t \equiv \frac{1}{N} \left\langle \sum_{i=1}^{N} \left[r_i^\parallel (t+\tau) - r_i^\parallel (t) \right]^2 \right\rangle_t$$

As a quantitative measure of mass transport in the diffusive regime it is convenient to introduce the parallel self-diffusion coefficient via the expression

$$D_\parallel = \lim_{\tau \to \infty} \frac{1}{2\tau} \left\langle \Delta r_\parallel^2 (\tau) \right\rangle_t$$

Figure 2 shows a dramatic increase of $D_\parallel$ as one enters the RN phase whereas lower-pressure (I, N, or smA) phases exhibit rather small self-diffusivity.

3. Conclusion

Under conditions of confinement a sequence of mesophases is observed. These involve the more conventional I and N phases and, under suitable thermodynamic conditions, a smA phase. At higher pressures (densities) the more exotic RN phase may form which is a nematic phase with surprisingly large nematic order and enhanced self-diffusivity in the direction of the nematic director. Quantitatively, we express the extent of mass transport in terms of the self-diffusion constant $D_\parallel$.

In the reentrant nematic phase $D_\parallel$ may exceed that characteristic of the I, N, and smA phases by up to an order of magnitude.
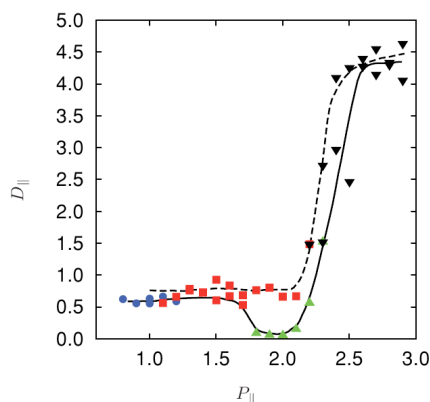

Fig.2: Parallel self-diffusion coefficient $D_\parallel$ as a function of transverse pressure. Results on the solid line are for T=4.0, and on the dashed line for T=6.0. Lines are guides for the eye. Different phases are denoted with different symbols: I (circles), N (squares), smA (triangles up), RN (triangles down).

References

[1] M. G. Mazza, M. Greschek, R. Valiullin, J. Kärger, M. Schoen, Phys. Rev. Lett. 105, 227802 (2010).

[2] M. G. Mazza, M. Greschek, R. Valiullin, M. Schoen, Phys. Rev. E **83**, 051704 (2011).