

Constant-pressure simulations of Gay-Berne liquid-crystalline phases in cylindrical nanocavities: Electronic supplementary information

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1 Calculating order parameters

Order parameters were calculated for each simulation snapshot and then averaged over all snapshots. The calculations of each parameter in individual snapshots are explained below.

For an N particle system, the orientational order parameter P_2 is calculated as the largest eigenvalue of the orientational ordering tensor Q :¹

$$Q_{\alpha\beta} = \frac{1}{2N} \left(3 \sum_{j=1}^N u_{j\alpha} u_{j\beta} - \delta_{\alpha\beta} \right); \quad \alpha, \beta = x, y, z. \quad (1)$$

Here $u_{j\alpha}$ is the α cartesian component of the unit vector along the long axis of particle j . The eigenvector corresponding to the largest eigenvalue is the LC director \vec{n} .

The translational order parameter τ_1 is calculated as

$$\tau_1 = \max \left| \sum_{j=1}^N \exp(2\pi i r_{j\parallel} / d) \right| \quad (2)$$

Here $r_{j\parallel} = \vec{r}_j \cdot \vec{n}$ and \vec{r}_j is the position vector of particle j , and \vec{n} is the unit vector corresponding to the LC director. Maximizing is done by varying d , the distance between layers in the interval $d^* \in [1.7, 6.1]$. This was done using Brent's method.² Again, we calculate the order parameter for each configuration written on the disk during the simulation and average over these configurations.

Bond-order parameter ψ_6 is calculated as

$$\psi_6 = \left| \frac{1}{N} \sum_{j=1}^N \psi_6(\vec{r}_j) \right|, \quad (3)$$

$$\psi_6(\vec{r}_j) = \frac{\sum_k w(r_{jk}) \exp(6i\theta_{jk})}{\sum_k w(r_{jk})}, \quad (4)$$

$$w(r_{jk}^*) = \begin{cases} 1, & r_{jk}^* < 1.4 \\ 0, & r_{jk}^* > 1.8 \\ \frac{-(r_{jk}^* - 1.4)}{1.8 - 1.4} + 1, & 1.4 \leq r_{jk}^* \leq 1.8, \end{cases} \quad (5)$$

where r_{jk} is distance between molecules j and k . θ_{jk} is the angle of the "bond" calculated with respect to some reference direction in the plane that is perpendicular to the LC director.

2 Thermalization at low temperatures

As noted in the main text, the hexagonal short-range order and the development of the crystal/smectic- B phase at low temperatures behaved inconsistently between the different cavity sizes. We suspect that this is due to insufficient equilibration, although this can not be directly verified from the data. The large fluctuations of the ψ_6 parameter mask any possible trends that would reveal that equilibration is not complete. In the bulk simulations no such problems in equilibration appear even at low temperatures.

We selected the smallest system with $R^* = 7$ and number of GB particles $N = 1560$ to study the equilibration process and the formation of the low-temperature phases. Our starting point was a well-equilibrated nematic configuration at $T^* = 1.5$. Initially, 60 temperatures were assigned in the range $T^* = 0.8 \dots 1.5$ for the PT replicas. In this temperature interval, the bulk LC phases range from crystal to smectic- A . This thermalization setup is denoted here as CrSm. Also, two thermalization processes with stepwise cooling were carried out. In these processes 10k or 100k MC sweeps of equilibration were run with four PT replicas at adjacent temperatures $T_i \dots T_{i+3}$. Then the temperatures of the replicas were set to $T_{i-1} \dots T_{i+2}$ and another equilibration of 10k or 100k MC sweeps followed. This was repeated until the temperature of the first replica reached the lowest temperature in the CrSm temperature sequence, $T^* = 0.78$. The final configurations at each temperature were used as the starting points for PT simulation with 60 replicas. We refer to these simulations and thermalization procedures as 10k and 100k. Finally, we also tested starting a PT simulation from an equilibrated SmA configuration at $T^* = 1.3$ from the CrSm simulation mentioned above and continued from there to a 44-replica PT simulation at temperature range $T^* = 0.8 \dots 1.3$. In this range the bulk system appears in the crystal phase, hence the abbreviation Cr is used for this simulation.

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CrSm is the procedure that has been used in all the confinement simulations in this paper. It is in principle the fastest method measured in wall clock time since all the thermalization can be done in parallel, by relying on the PT algorithm. There is, however, doubt that this potentially leads to metastable configurations at low temperatures if the PT trials can not mix the temperatures of the replicas. The rest of the thermalization procedures, 10k, 100k and Cr are meant to ease the path of the LC to a stable low-temperature configuration. With the Cr procedure we wanted to test if starting from a well-defined layer structure would help increasing the translational order further with in-layer short-range hexagonal order. The 10k and 100k procedures resemble most the traditional cooling sequences used in many simulation works before. 100k demands the most wall-clock time of the procedures compared here but should also be the one to give the most time for the LC to reach equilibrium, before the temperature is changed to a lower one.

The results for the translational order parameters are shown in Figure 1 for the four different thermalization procedures described above. No difference between the methods can be seen for the SmA-N transition near $T^* = 1.44$. Arriving at $T^* = 1.21(1)$, the τ_1 parameter of the CrSm simulation jumps from 0.7 to 0.78 and also a very faint change in ψ_6 can be observed in the same simulation. The same kind of changes follow in the Cr simulation at $T^* = 1.14$ and for the more slowly cooled 10k and 100k simulations at $T^* = 1.10$. Consequently, it appears that the temperature at which the hexagonal order appears is very sensitive to the thermalization procedure. At still lower temperatures in the range $T^* = 0.8...1.1$, the differences in the short-range hexagonal order between different thermalization procedures are large. ψ_6 for the 10k simulation never exceeds 0.2. For the CrSm simulation ψ_6 goes up to about 0.5 but suddenly drops below 0.2 at $T^* < 0.86$. The highest values of ψ_6 for the Cr simulation are about 0.4.

Looking at the thermodynamics in Figure 2 it appears that rapid decrease in temperature can cause supercooling of the system. The fastest thermalization procedure, CrSm, is the first one to display hexagonal order at around $T^* = 1.21(1)$ (Figure 1). At the same temperature the number density N/V^* in the uppermost panel of Figure 2 jumps up (towards lower temperatures) for this simulation, whereas the enthalpy and energy per particle decrease. The Cr simulation follows at about $T^* = 1.14$. The simulations 10k and 100k, both with slower thermalization than the previous simulations, take the jump at the still lower temperature of $T^* = 1.10$. These results are consistent with the observations made for order parameters.

At lower temperatures the situation is a bit different. Here, the number density in Figure 2 for the 10k thermalization is the first to jump up towards a new phase at $T^* = 0.96(1)$. Enthalpy and energy also drop at the same temperature.

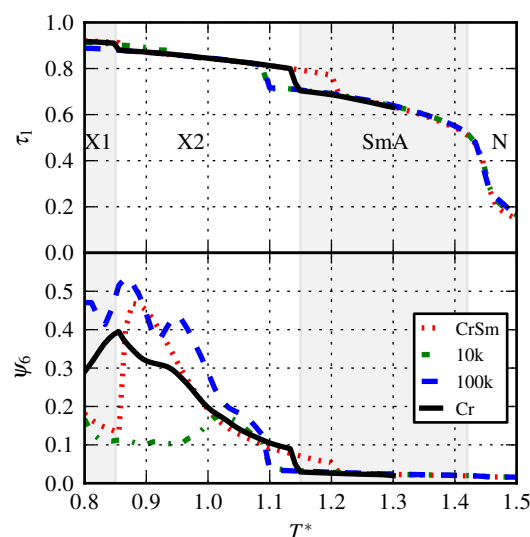


Fig. 1 Simulated translational (τ_1) and bond-orientational order (ψ_6) parameters for a Gay-Berne liquid crystal confined to a cylindrical cavity of radius $R^* = 7$. Curves illustrate the results for simulations after four different thermalization procedures. 10k and 100k are slowly stepwise-cooled simulations starting from a well-equilibrated nematic configuration at $T^* = 1.5$. CrSm and Cr are parallel tempering thermalizations starting from a well-equilibrated nematic and smectic-A configurations, at temperatures $T^* = 1.5$ and $T^* = 1.3$, respectively.

CrSm and Cr simulations follow at a lower temperature $T^* = 0.86(1)$. The slowest thermalization process (100k) does not show this abrupt change in the thermodynamic parameters at all. It can also be seen from Figure 1, that it is the only simulation where $\psi_6 > 0.4$ at the lowest temperatures close to $T^* = 0.8$.

The slowest thermalization procedure 100k produces the most ordered states. As this procedure was already 6 million MC sweeps long we did not pursue it in further simulations. We may conclude that sufficient equilibration of confined LC to the bulk Cr/SmB phases at the low-temperature range is a tedious task. It is also hard to tell whether it is a crystal or a smectic B phase that appears in the confined LCs simulated here. Although PT has the potential to prevent the system from getting stuck in non-equilibrium or metastable configurations at low temperatures, it only works if the temperatures have been selected well and the exchange period is longer than the energy autocorrelation time.³⁻⁶ It is possible that our selection of temperatures was suboptimal in the low-temperature range.

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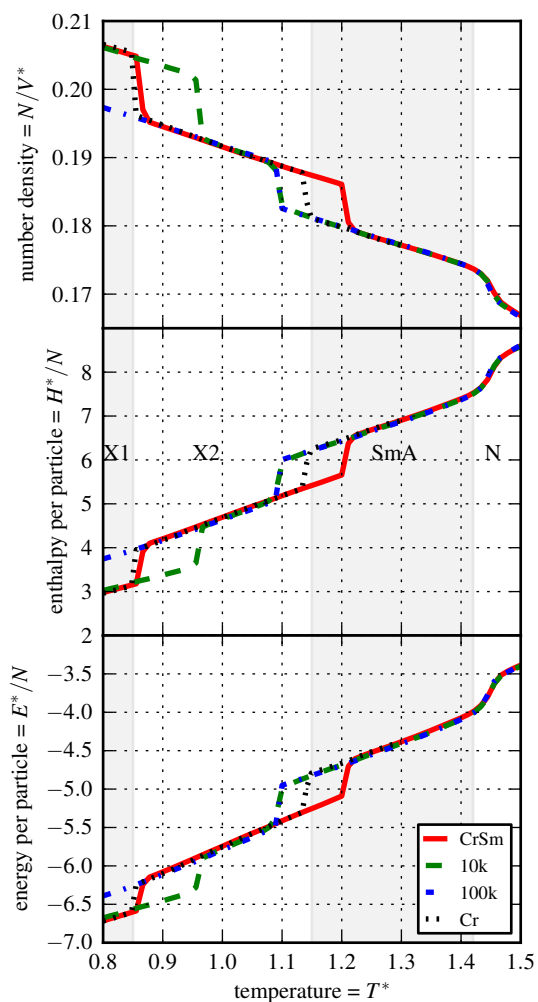


Fig. 2 Simulated thermodynamic parameters for a Gay-Berne liquid crystal confined to a cylindrical cavity of radius $R^* = 7$. Curves illustrate the results of simulations after four different thermalization procedures as described in Fig 1.

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