

# Supporting Information:

## Direct Liquid to Crystal Transition in a Quasi-Two-Dimensional Colloidal Membrane

Thomas Gibaud<sup>†</sup> and Doru Constantin<sup>\*,‡</sup>

<sup>†</sup>*Univ Lyon, Ens de Lyon, Univ Claude Bernard, CNRS, Laboratoire de Physique, F-69342  
Lyon, France*

<sup>‡</sup>*Laboratoire de Physique des Solides, CNRS, Univ. Paris-Sud, Université Paris-Saclay,  
91405 Orsay Cedex, France*

E-mail: doru.constantin@u-psud.fr

### Data uncertainty and fitting

The uncertainties  $\sigma_i(q_i)$  (where index  $i$  labels the experimental values of the scattering vector  $q$ ) are obtained as the standard error of the mean (SEM) over the integrated raw signal given by  $N = 10$  consecutive frames (denoted by the upper index  $k$ ):

$$\langle I_i(q_i) \rangle = \frac{1}{N} \sum_{k=1}^N I_i^k(q_i)$$
$$\sigma_i(q_i) = \frac{1}{\sqrt{N}} \sqrt{\frac{1}{N} \sum_{k=1}^N (I_i^k(q_i) - \langle I_i(q_i) \rangle)^2}$$

where the  $1/\sqrt{N}$  prefactor in the last equation converts the standard deviation to the standard error of the mean (we make the usual assumption that the errors are independent and

identically distributed.)

This uncertainty is then propagated according to standard statistical formulas through the background subtraction and normalization steps.

The goodness-of-fit function is calculated as:

$$\chi^2 = \sum_i \left( \frac{\langle I_i \rangle - f(q_i)}{\sigma_i} \right)^2$$

and minimized using the Levenberg-Marquardt algorithm implemented in Igor Pro 7.0 (called by invoking the FuncFit command.)

## Measuring the form factor

We measured the scattering signal of dilute virus solutions (without Dextran), shown in Figure S1 as lines of various colors. We model it as the (azimuthally averaged) form factor of a hollow cylinder (open dots).

The intensity measured in the membrane solutions was divided by this theoretical form factor to yield the structure factors analyzed in the main text.

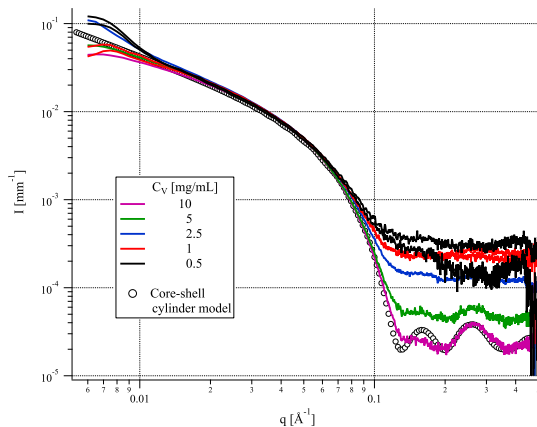


Figure S1: The scattered intensity  $I(q)$  for several dilute virus solutions (lines; the concentration is indicated alongside the curves) and fit with a core-shell cylinder model (open dots). The experimental data was rescaled to a concentration of 1 mg/mL.

# Osmotic pressure

In the isotropic phase, we obtain the pressure in the membrane as  $P_{\text{exp}} = \Pi_{2\text{D}}/L$ . This parameter is shown in Figure S2, alongside the bulk osmotic pressure imposed by the same concentration of Dextran, estimated from the data of Parsegian et al. ( S1, Fig. 3.) and Livney et al. ( S2, Fig. 3.) The latter dataset was extrapolated to our working concentrations using a power law dependence.

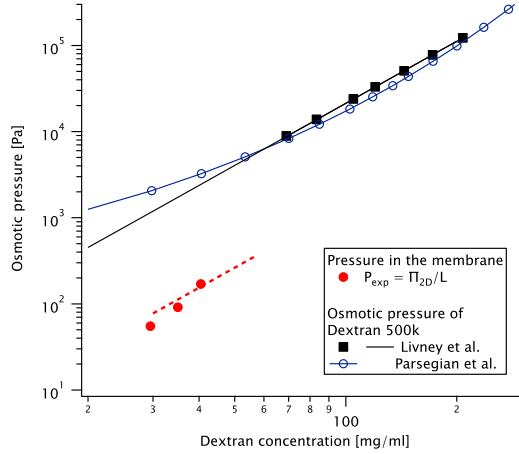


Figure S2: Pressure within the membrane  $P_{\text{exp}}$  (solid red dots) and osmotic pressure imposed by Dextran solutions of the corresponding concentration, according to Parsegian et al. ( S1, Fig. 3, open blue dots and line) and Livney et al. ( S2, Fig. 3, solid black squares, with power law extrapolation shown as solid black line.)

The measured pressure  $P_{\text{exp}}$  is much lower than the one imposed by the polymer solution. One possible explanation for this discrepancy is that Dextran is not completely excluded from the membranes, unlike the situation in bulk phases.<sup>S3</sup>

Assuming that  $P_{\text{exp}}/P_D$  does not change with  $c_D$ , we can extrapolate  $P_{\text{exp}}$  to the crystalline phase (red dashed line in Fig S2.) Using the definition of the compressibility:

$$\kappa = -\frac{1}{V} \frac{\partial V}{\partial P_{\text{exp}}} = \frac{1}{n_{2\text{D}}} \frac{\partial n_{2\text{D}}}{\partial P_{\text{exp}}} \quad (1)$$

and combining the data in Figure 2 of the main text and Figure S2 above yields the bulk

modulus:

$$B = \mu + \lambda = \kappa^{-1}L = 6.5 \cdot 10^{-3} \text{ Pa m} \quad (2)$$

## Effect of the line tension

The edge structure of the membranes engenders an effective line tension  $\gamma_{\text{eff}}$ .<sup>S4</sup> In this subsection, we compare its effect to the pressure within the membrane,  $P_{\text{exp}}$ .

We estimate  $\gamma_{\text{eff}} \sim 10 - 100 k_{\text{B}}T/\mu\text{m}$ <sup>S5</sup> and would like to find the equivalent “pressure due to tension”  $P_T$  via the energy cost of a variation in membrane radius from  $R$  to  $R + dR$ . The associated infinitesimal changes in contour length and area are  $dC = 2\pi dR$  and  $dA = 2\pi R dR$ , respectively. The work of the line tension  $\gamma_{\text{eff}}$  and of the pressure  $P_t$  are respectively:

$$W_T = \gamma_{\text{eff}} dC$$

$$W_P = P_T L 2\pi R dR$$

and equating them yields:  $W_T = W_P \implies P_T = \frac{\gamma_{\text{eff}}}{LR} \leq 1 \text{ Pa}$ , with  $R \sim 10 \mu\text{m}$ . Thus, even in the liquid phase  $P_T \ll P_{\text{exp}}$ : although the line tension does influence the size and shape of the membrane (at the micron scale) it is negligible with respect to the pressure in the membrane, which results from the interaction between objects at the nanometer scale.

## Comparison of the structure factor for dilute and concentrated membrane systems

High-quality data is crucial for a quantitative analysis; to this end, we increased the concentration of our solutions by mild centrifugation. We checked that the structure factors were very similar for the dilute and the concentrated samples, as shown in Figure S3 for three Dextran concentrations, two in the crystal and one in the liquid phase. No systematic difference can be detected between the two types of curves.

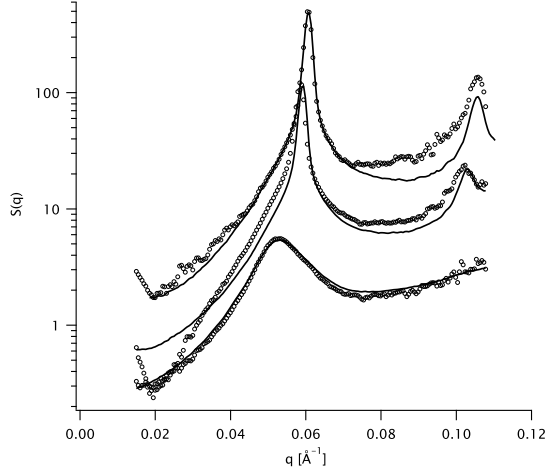


Figure S3: Structure factors measured in dilute (open dots) and concentrated (solid lines) membrane systems at Dextran concentrations of 58.5, 50.2 and 35.1 mg/mL.

## Detail of the Dutta & Sinha model

We perform an azimuthal average:

$$S(q) = \frac{3C}{\pi} \int_{-\pi/6}^{\pi/6} S(\mathbf{q}) d\phi + \alpha(q - q_1) + \beta \quad (3)$$

over the analytical expression of the structure factor of a harmonic model given by Dutta and Sinha:<sup>S7</sup>

$$S(\mathbf{q}) = {}_1F_1 \left( 1 - \frac{\eta}{2}, 1; -\frac{\delta q^2 L_{DS}^2}{4\pi} \right) \quad (4)$$

with  $\mathbf{q}_1 = (q_1, 0)$  the first peak of the crystalline phase,  $\phi = \widehat{(\mathbf{q}, \mathbf{q}_1)}$  the angle between this vector and the current vector  $\mathbf{q}$  and  $\delta q = |\mathbf{q} - \mathbf{q}_1|$ .  ${}_1F_1(a, b; z)$  is a confluent hypergeometric function (also known as the Kummer function  $M$ ).

The fit parameters are the exponent  $\eta$  (related to the elasticity of the lattice), the “domain size”  $L_{DS}$ , the peak position  $q_1$ , the amplitude  $C$ , the background value  $\beta$  (at the peak position) and the slope of the background  $\alpha$ .

It is difficult to extract relevant information from parameter  $L_{DS}$ , which is influenced by details of the experimental setup, such as beam divergence and coherence length. At any

rate, its value is much lower than the typical membrane size (microns to tens of microns) so we conclude that this latter parameter does not affect the peak profile.

## Implementation of the Kummer function

For moderate values of  $|z|$  we compute  ${}_1F_1(a, b; z)$  using the implementation of the function available in Igor Pro, but for  $z < -20$  we use the (much faster) asymptotic form<sup>S9</sup> restricted to real  $z$ . Since  $z < 0$ , we make use of  ${}_1F_1(a, b; z) = e^z {}_1F_1(b - a, b; -z)$  to get:

$${}_1F_1(a, b; z) = \frac{\Gamma(b)}{\Gamma(b-a)} (-z)^{-a} \sum_{j=0}^{\infty} \frac{(a)_j (1+a-b)_j}{j!} (-z)^j \quad (5)$$

where  $(\cdot)_j$  denotes the Pochhammer symbol.

## References

- (S1) Parsegian, V.; Rand, R.; Fuller, N.; Rau, D. *Methods in Enzymology*; Elsevier, 1986; Vol. 127; pp 400–416.
- (S2) Livney, Y. D.; Ramon, O.; Kesselman, E.; Cogan, U.; Mizrahi, S.; Cohen, Y. Swelling of dextran gel and osmotic pressure of soluble dextran in the presence of salts. *Journal of Polymer Science Part B: Polymer Physics* **2001**, *39*, 2740–2750.
- (S3) Dogic, Z.; Purdy, K. R.; Grelet, E.; Adams, M.; Fraden, S. Isotropic-nematic phase transition in suspensions of filamentous virus and the neutral polymer Dextran. *Physical Review E* **2004**, *69*, 051702.
- (S4) Gibaud, T.; Barry, E.; Zakhary, M. J.; Henglin, M.; Ward, A.; Yang, Y.; Berciu, C.; Oldenbourg, R.; Hagan, M. F.; Nicastro, D.; Meyer, R. B.; Dogic, Z. Reconfigurable self-assembly through chiral control of interfacial tension. *Nature* **2012**, *481*, 348–351.

- (S5) Ref. S4, Fig. 2c.
- (S6) Dutta, P.; Sinha, S. K. Analytic form for the static structure factor for a finite two-dimensional harmonic lattice. *Physical Review Letters* **1981**, *47*, 50–53.
- (S7) Ref. S6, Eq. (5).
- (S8) Pearson, J. W.; Olver, S.; Porter, M. A. Numerical Methods for the Computation of the Confluent and Gauss Hypergeometric Functions. *arXiv:1407.7786 [math-ph, physics:physics]* **2014**, arXiv: 1407.7786.
- (S9) Ref. S8, Eq. (3.8).