Electronic supplementary information for
Xenon NMR of liquid crystals confined to cylindrical nanocavities:
A simulation study

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1 Parallel tempering

Parallel tempering (PT) is a variant of the more general replica exchange algorithm. 1 In PT, several replicas
of the same system are simulated at different temperatures simultaneously. Periodically, a swap of temper-
atures between two replicas is attempted. 1 In the NPT ensemble, the swaps are accepted with probability
\[
W(\beta_i \leftrightarrow \beta_j) = \min \{1, \exp \left[ (\beta_i - \beta_j) (H_i - H_j) \right]\},
\]
where the two replicas \(i\) and \(j\) share the same pressure. 2 Here, \(\beta_i = 1/(k_BT_i)\), \(H_i\), \(E_i\) and \(V_i\) are the inverse
temperature, enthalpy, energy and volume of the replica \(i\), respectively. We used parallel tempering to
simulate the high temperature range \(T = 1.3 \ldots 2.0\) and the low temperature range \(T = 0.9 \ldots 1.6\) with a
variable number of replicas, depending on the system (see Table 1 in the main text).

The motivation for using parallel tempering is to enable the simulated system to cross high energy
(enthalpy) barriers and thus to accelerate the sampling of the phase space. With the temperature of a
replica now being a dynamical variable, the system can reach a new low energy (enthalpy) configuration
by making a round-trip via higher temperatures. However the selection of temperatures and/or update
frequencies is crucial to the efficiency of the method. 3–8 The two replicas on which the temperature swap is
attempted, must have a small enthalpy difference for the swap to be probable. If the temperatures of the two
systems are, however, too close to each other, the significance of the swap becomes small. We guaranteed a
sufficient probability of swaps by checking for temperature regions of low swap frequency (< 20% swaps
accepted between adjacent temperatures) and placing additional replicas to those regions of temperature.
This procedure was first performed after equilibration of \(10^5\) sweeps, and repeated after \(3 \times 10^5\) sweeps.
Trapping of replicas to temperatures that are very close to each other was circumvented by selecting the
two replicas for swapping randomly from all replicas and performing (number of replicas) \(^3\) trial swaps in a
sequence. 9

2 Gay-Berne potential

The Gay-Berne potential 10 pictures the interacting pair of LC molecules as ellipsoids of revolution with a
dispersion-type attraction and a repulsive term. The potential has a Lennard-Jones (LJ) -like 12-6 form,
\[
U_{GB} = 4\epsilon \left( \hat{u}_i \cdot \hat{u}_j \right) \left( R_{GB}^{-12} - R_{GB}^{-6} \right)
\]
\[
R_{GB} = \left[ r - \varsigma \left( \hat{u}_i \cdot \hat{u}_j \cdot \hat{r}_{ij} \right) + \varsigma_0 \right]/\varsigma_0,
\]

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with anisotropic well-depth and distance terms $\epsilon(\hat{u}_i, \hat{u}_j, \hat{r}_{ij})$ and $\varsigma(\hat{u}_i, \hat{u}_j, \hat{r}_{ij})$, respectively, depending on the unit orientation vectors of the two molecules $\hat{u}_i$, $\hat{u}_j$ and the unit vector of the internuclear axis, $\hat{r}_{ij}$. $\varsigma_0$ defines the distance where the potential crosses zero when two GB molecules are side-by-side in a cross configuration and $r$ is the distance between the centers of the two molecules.

The generic form of the Gay-Berne potential omits many of the details present in real LC molecules. The relative featurelessness of the model gives generality to our results and aids in interpreting them. The downside of this simplicity is, of course, that we may be lacking an essential property for some specific LC. Another important aspect of the coarse-grained GB potential is that it is computationally less expensive than a fully atomic description.

3 Xe-LC potential

The pair interaction potential between the GB particle and the Xe atom is\textsuperscript{11,12}

$$U_{GB-Xe} = 4\epsilon(\hat{u}_i, \hat{r}_{ij}) \left[ \left( \frac{\varsigma_0}{R_{GB-Xe}} \right)^{12} - \left( \frac{\varsigma_0}{R_{GB-Xe}} \right)^6 \right],$$

where $\hat{u}_i$ is the unit orientation vector of the long axis of the GB molecule and $\hat{r}_{ij}$ is the unit vector along the interparticle axis between the Xe atom and the GB molecule. Fig. 2 a) in the main text presents the potential energy curves for the "side" and "end" configurations of the GB-Xe pair, as well as the potential energy curve for the Xe dimer. The parameter $\varsigma_0^{GB-Xe}$ defines the distance at which the potential crosses zero when the Xe atom is on the side of the GB molecule, as depicted in Fig. 2 a). For the GB-Xe potential, the anisotropic distance $R_{GB-Xe}$ and range $\varsigma(\hat{u}_i, \hat{r}_{ij})$ are defined as

$$R_{GB-Xe} = r - \varsigma(\hat{u}_i, \hat{r}_{ij}) + \varsigma_0^{GB-Xe}$$

$$\varsigma(\hat{u}_i, \hat{r}_{ij}) = \varsigma_0^{GB-Xe} \left[ 1 - \chi^{GB-Xe} (\hat{u}_i \cdot \hat{r}_{ij})^2 \right]^{1/2}$$

$$\chi^{GB-Xe} = 1 - \left( \frac{\varsigma_e^{GB-Xe}}{\varsigma_s^{GB-Xe}} \right)^{-2}$$

Here, $r$ is the distance between the centres of the two particles. The expression $(\varsigma_e^{GB-Xe}/\varsigma_s^{GB-Xe})$ refers to the distances where the potential crosses zero when the Xe atom is at the end of the GB molecule (subscript e) and on the side (subscript s). The insets of Fig. 2 a) in the main text illustrate the end and side configurations of the GB-Xe pair. The well depth is

$$\epsilon(\hat{u}_i, \hat{r}_{ij}) = \epsilon_0^{GB-Xe} \left[ 1 - \chi^{GB-Xe} (\hat{u}_i \cdot \hat{r}_{ij})^2 \right]^{\mu^{GB-Xe}}$$

$$\chi^{GB-Xe} = 1 - \left( \frac{\epsilon_e^{GB-Xe}}{\epsilon_s^{GB-Xe}} \right)^{1/\mu^{GB-Xe}}$$

where $\epsilon_0^{GB-Xe}$ defines the well depth of the potential when the Xe atom is on the side of the GB molecule. $\epsilon_e^{GB-Xe}/\epsilon_s^{GB-Xe}$ defines the potential well-depth at the end configuration in relation to the side configuration. The parameter $\mu^{GB-Xe}$ can be used to further adjust the anisotropy of the potential.

The strength of the GB-Xe interaction in relation to the GB-GB interaction was tested with three different settings for the well-depth parameter; $\epsilon_0^{GB-Xe} = 1.55$ represents the result of the QC parameterisation\textsuperscript{13} (relative to the present choice of $\epsilon_0$ mentioned earlier) and the other two represent $\pm 20\%$ deviations from
this value. We monitored the changes between these choices through the LC order parameters $P_2$ and $\tau_1$ (defined in Sec. 4 of the ESI) as a function of temperature (see Fig. 1 in ESI), as well as the GB-Xe pair distribution functions resulting from the three parameterisations. This was done to see whether our model is sensitive to the choice of the details of the GB-Xe potential and if this parameter affects the LC phase structure and/or the distribution of Xe atoms among the LC molecules. The resulting LC order parameters (in Fig. 1 of the ESI) show no notable differences between the parameterisations at the temperatures studied here. The Xe-GB radial distribution functions, shown in Fig. 2 a), imply that the larger the value of $\epsilon_{0}^{\text{GB-Xe}}$ is, the higher the first peak of the distribution function. This is a natural result of increasing the attraction between the Xe atom and the GB molecule. Otherwise the features of the distribution functions for the different choices of the $\epsilon_{0}^{\text{GB-Xe}}$ parameter bear a strong resemblance to each other.

Figure 1: Orientational and translational order parameters from simulations of Xe dissolved in bulk liquid crystal, with three different well-depth parameters $\epsilon_{0}^{\text{GB-Xe}}$ for the Xe-GB interaction.

To gain another view to the distribution of the Xe atoms in the LC solvent, especially in relation to the
smectic layers, we computed the director-projected pair distribution functions for GB-GB and GB-Xe pairs,

\[ g_{\text{GB-GB}}(r_{||}) = \frac{V}{N_{\text{GB}}(N_{\text{GB}} - 1)V_{\text{slice}}} \left\langle \sum_{i,j=1}^{N_{\text{GB}}} \delta(|\mathbf{r}_{ij} \cdot \hat{d}| - r_{||}) w(\mathbf{r}_{ij}) \right\rangle \]

\[ g_{\text{GB-Xe}}(r_{||}) = \frac{V}{N_{\text{Xe}}N_{\text{GB}}V_{\text{slice}}} \left\langle \sum_{i=1}^{N_{\text{Xe}}} \sum_{j=1}^{N_{\text{GB}}} \delta(|\mathbf{r}_{ij} \cdot \hat{d}| - r_{||}) w(\mathbf{r}_{ij}) \right\rangle \]
Here, $r_\parallel$ measures the projection of the internuclear distance to the LC director, $\hat{d}$. The slice thickness (which defines the resolution of the distribution function) was set to $s = 0.1$. A cutoff radius perpendicular to the director, $r_{c,\perp} = 2.0$ was employed via the function $w$. By employing the cutoff we get a practically uniform slice volume $V_{\text{slice}} = \pi s r_{c,\perp}^2$ regardless of the length of $r_{ij}$ and the director orientation in the simulation cell. $N_{\text{GB}}$, $N_{\text{Xe}}$ and $V$ are the number of GB particles, the number of Xe atoms and the system volume, respectively. The $g_{\text{GB-Xe}}(r_\parallel)$ distribution shows where the Xe atoms are positioned with respect to the smectic layers at low temperatures. With the $g_{\text{GB-GB}}(r_\parallel)$ distribution we gain insight in the structure of the layers and compare it to the positions of the Xe atoms.

The director-projected pair distribution functions are presented in Fig. 2 b) for the three values of $\epsilon_{0}^{\text{GB-Xe}}$. At $T = 1.36$ the maxima at $r_\parallel \approx 2.0, 6.0, \ldots$ in the Xe-GB distributions are aligned with the minima in the GB-GB distribution, which indicates that the Xe atoms slightly prefer the interlayer region in the SmA phase. The preference grows stronger the weaker the attraction between the Xe atom and the GB molecule is. Still, compared to the respective GB-GB distribution, the difference between the maxima and the minima is small even for the weakest attraction, with $\epsilon_{0}^{\text{GB-Xe}} = 1.24$. For $\epsilon_{0}^{\text{GB-Xe}} = 1.86$, the number of the Xe atoms inside the layers and in the interlayer region is almost equal. Analysis of experimental data has suggested that the Xe atoms dissolved in a smectic LC would only slightly prefer the interlayer regions and the distribution of the Xe atoms would deviate less than 10% from uniform.\(^\text{14,15}\) Our chosen parameterisation ($\epsilon_{0}^{\text{GB-Xe}} = 1.55$) reproduces better the experimental Xe distribution in the SmA phase, as compared to the value used in Ref. 13, $\epsilon_{0}^{\text{GB-Xe}} = 0.67$.

### 4 Calculating liquid crystal order parameters

Order parameters were calculated for each simulation snapshot and then averaged over all the 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 $Q$:\(^\text{16}\)

$$Q_{\alpha\beta} = \frac{1}{2N} \left( 3 \sum_{j=1}^{N} u_{j\alpha} u_{j\beta} - \delta_{\alpha\beta} \right); \quad \alpha, \beta = x, y, z. \tag{10}$$

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

The translational order parameter $\tau_1$ is calculated as

$$\tau_1 = \max \left| \frac{1}{N} \sum_{j=1}^{N} \exp \left[ 2\pi i (r_j \cdot \hat{n}) / d \right] \right|. \tag{11}$$

Here $r_j$ is the position vector of particle $j$, and $\hat{n}$ is the unit vector of the reference direction perpendicular to the smectic layers. To detect the smectic-$A$ phase we use the instantaneous LC director as the reference direction: $\hat{n} = \hat{d}$. Maximizing is done by varying $d$, the distance between layers. The process yields both
the value of $\tau_1$ and the average spacing $d$ of the smectic layering. Here, we used the Gay-Berne potential parameterisation, where the contact distance for the end-to-end configuration of two molecules is 4.4 in reduced units. We chose to maximise $\tau_1$ around this distance, using the interval $d \in [1.7, 6.1]$ which allows the layers of molecules to be partly interlaced or separated. The maximisation was done using Brent’s method.\textsuperscript{17}

5 Interactions of the Xe atoms with the cavity wall

The interaction between the Xe atoms and the cavity wall is based on the Eq. 1 in the main text, describing the interaction energy between a LJ particle and a smooth cylindrical LJ wall. The choice of parameters for the Xe-wall interaction was made empirically based on the aim of maintaining the strength of this interaction as well as its contact distance comparable with the GB-Xe interaction and the GB-wall interaction. So, as the GB-GB and GB-wall contact distance parameters are equal, the GB-Xe and Xe-wall contact distance parameters should be equal to each other as well, and this gives $\varsigma_{\text{Xe}} = \varsigma_{\text{w}}^{\text{GB-Xe}} = 0.8$. The maximum GB-wall interaction is twice as strong as the maximum GB-GB interaction ($\epsilon_0^{\delta} = \max[\epsilon(\mathbf{u}_i, \mathbf{u}_j, \mathbf{r}_{ij})] = 157.58$ meV in our current parameterisation for the side-by-side configuration), so the maximum Xe-wall interaction strength should be equal to twice the Xe-GB interaction. This gives us

$$\epsilon_{\text{w}}^{\text{Xe}} = 2\epsilon_{\text{GB-Xe}}^{\delta} = 1.33989. \quad (12)$$

One should note, however, that the range-defining contact distance parameter for the Xe-wall interaction is smaller than for the LJ centres in the GB particle, $\varsigma_{\text{w}}^{\text{Xe}} < \varsigma_{\text{w}}$. Hence, the Xe atom "feels" a less dense wall and the actual Xe-wall interaction is of about the same strength as the Xe-GB interaction. In the previously used parameterisation scheme\textsuperscript{18} we now get the combined effect

$$K_{\text{Xe}}^{\text{w}} = 8\epsilon_{\text{w}}^{\text{Xe}} \rho_{\text{w}} (\varsigma_{\text{w}}^{\text{Xe}})^3 = 5.48819. \quad (13)$$

Fig. 2 a) in the main text presents the potential curve $U_{\text{w,Xe}}$ for the interaction of the Xe atom with the wall of the cavity with radius $R = 9$.

As with the GB-Xe interaction strength, we investigated whether the distribution of Xe atoms in the system is sensitive to the chosen parameterisation for the Xe-wall interaction. The interaction was tested with three different settings for the strength parameter $K_{\text{w}}^{\text{Xe}} = 3.57, 5.48819$ and $10.72$. Fig. 3 presents the simulated Xe and GB density profiles with these parameters in the SmA, N and PN phases in the cavity with radius $R = 9$. The first peak of the Xe density profile shows that, with the strongest parameter for the attraction, $K_{\text{w}}^{\text{Xe}} = 10.72$, an excess of Xe atoms gathers close to the wall. For the two weaker parameters, $K_{\text{w}}^{\text{Xe}} = 3.57$ and $5.48819$, the Xe density profiles are nearly indistinguishable. The GB density profiles are indifferent to the choice of the Xe-wall interaction strength. Hence, we use $K_{\text{w}}^{\text{Xe}} = 5.48819$ in the production runs.

6 Xe nuclear shielding tensors for Xe-LC and Xe-Xe interactions

Fig. 4 a) presents the local coordinate system in which the Xe-GB shielding tensor is defined. The nuclear site symmetry of the Xe-GB system is $C_s$ for a general location of the Xe atom with respect to the GB
Figure 3: Simulation results for Xe atoms dissolved in model liquid crystal, confined to a cylindrical cavity with radius $R = 9$. Number density profiles for a) Xe atoms and b) GB particles with three different Xe-wall interaction strength parameters $K_{Xe}^w$, in three different LC phases. To help the viewer there is an offset of 0.005 between the Xe density profiles and an offset of 0.5 between the GB density profiles.

particle (higher symmetry in end and side configurations), so the nuclear shielding tensor can be expressed as

$$\sigma_{GB-Xe} = \begin{pmatrix} \sigma_{xx} & 0 & \sigma_{xz} \\ 0 & \sigma_{yy} & 0 \\ \sigma_{zx} & 0 & \sigma_{zz} \end{pmatrix}. \quad (14)$$

Owing to the $C_s$ symmetry of the system, the components of the tensor can be written using the spherical coordinates as

$$\sigma_{xx} = \sigma_{xx}^s(R_{GB-Xe}) \sin^2 \theta + \sigma_{xx}^e(R_{GB-Xe}) \cos^2 \theta,$$

$$\sigma_{yy} = \sigma_{yy}^e(R_{GB-Xe}),$$

$$\sigma_{zz} = \sigma_{zz}^s(R_{GB-Xe}) \sin^2 \theta,$$

$$\sigma_{xz} = \sigma_{xz}^s(R_{GB-Xe}) \sin \theta \cos \theta,$$

$$\sigma_{zx} = \sigma_{zx}^e(R_{GB-Xe}) \sin \theta \cos \theta. \quad (15)$$

This presentation contains five quantum-chemically parameterised functions $\sigma_{xx}^s(R_{GB-Xe})$, $\sigma_{yy}^e(R_{GB-Xe})$, $\sigma_{zz}^s(R_{GB-Xe})$, $\sigma_{xz}^s(R_{GB-Xe})$ and $\sigma_{zx}^e(R_{GB-Xe})$. The superscripts e and s refer to the end ($\theta = 0^\circ$) and side ($\theta = 90^\circ$) con-
figurations. The subscripts \( \perp \) and \( \parallel \) denote directions perpendicular to (in the \( e \) configuration) and parallel with the long axis of the GB particle. \( R_{\text{GB-Xe}} \) is adopted from the Xe-GB potential energy function, and is presented in Eq. 4. \( \theta \) is the angle between the interparticle vector from GB to Xe and the orientation vector of the GB molecule, as shown in Fig. 4 a). The parameterisation of the tensor representation, Eq. 14 was done in Ref. 13 via computing the Xe shielding tensor quantum-chemically for different arrangements of a system of a model LC molecule and Xe atom. These functions can be found in the original work by Lintuvuori et al.

![Figure 4: Schematic showing the local coordinate systems in which the a) GB-Xe and b) Xe-Xe NMR interactions have been defined.](image)

The contribution of the Xe-Xe interactions to the NMR shielding are parameterised using the local coordinate system displayed in Fig. 4 b). Here, the \( z \)-axis coincides with the internuclear axis and the shielding tensor is cylindrically symmetric, having only the diagonal components \( (\sigma_\perp, \sigma_\perp, \sigma_\parallel) \). The tensor elements are then given by the relations

\[
\sigma_\perp = \sigma(r) - \frac{1}{3} \Delta \sigma(r) \tag{16}
\]

\[
\sigma_\parallel = \sigma(r) + \frac{2}{3} \Delta \sigma(r), \tag{17}
\]

where \( r \) is the internuclear distance between the two Xe atoms. The quantum-chemically pre-parameterised isotropic shielding \( \sigma(r) \) and the anisotropy of shielding (with respect to the \( z \)-axis), \( \Delta \sigma(r) \), can be split into components as

\[
\sigma = \frac{1}{3} (\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) = \frac{1}{3} (2\sigma_\perp + \sigma_\parallel) \tag{18}
\]

\[
\Delta \sigma = \sigma_{zz} - \frac{1}{2} (\sigma_{xx} + \sigma_{yy}) = \sigma_\parallel - \sigma_\perp. \tag{19}
\]

The numerical parameterisation of this interaction is presented in the original work of Ref. 19.

### 7 Formulation of the wall interaction contribution to the \(^{129}\text{Xe}\) nuclear shielding

#### 7.1 Parameterisation of the Xe-wall element interaction contribution to shielding

Similarly to the interaction potential of Sec. 5 of the main text, the model of the Xe-wall interaction contributions to the \(^{129}\text{Xe}\) nuclear shielding is based on describing the cavity wall as infinitely thick and consisting
of smoothly and evenly distributed Lennard-Jones particles. The appropriate strength and range of the wall contribution to the shielding are obtained by scaling the Xe-Xe interaction contribution analogously to the parameterisation of the LJ potential. For this purpose and to simplify the integration over the wall, we represent the quantum-chemically computed isotropic shielding and shielding anisotropy of a Xe dimer with inverse power series

\[
\sigma(r) = \sum_n \sigma_n r^{-n} ; \quad \Delta\sigma(r) = \sum_n \Delta\sigma_n r^{-n}.
\]  

(20)

These were fitted to the quantum-chemically parameterised functions and the fit coefficients are shown in Table 1. The strength and range scaling are applied with the well-depth and range parameters \((\varsigma_w, \epsilon_Xe)\) and \((\varsigma_0^{Xe-Xe}, \epsilon_0^{Xe-Xe})\) of the Xe-wall and Xe-Xe interaction potentials, respectively, as follows:

\[
\sigma(r) = \frac{\epsilon_{Xe}}{\epsilon_0^{Xe-Xe}} \sum_n \sigma_n \left( \frac{\varsigma_0^{Xe-Xe}}{\varsigma_w} r \right)^n \rightarrow \frac{\epsilon_{Xe}}{\epsilon_0^{Xe-Xe}} \sum_n \sigma_n \left( \frac{\varsigma_0^{Xe-Xe}}{\varsigma_0^{Xe-Xe}} r \right)^n
\]

\[
\Delta\sigma(r) = \frac{\epsilon_{Xe}}{\epsilon_0^{Xe-Xe}} \sum_n \Delta\sigma_n \left( \frac{\varsigma_0^{Xe-Xe}}{\varsigma_w} r \right)^n \rightarrow \frac{\epsilon_{Xe}}{\epsilon_0^{Xe-Xe}} \sum_n \Delta\sigma_n \left( \frac{\varsigma_0^{Xe-Xe}}{\varsigma_0^{Xe-Xe}} r \right)^n.
\]  

(21)

Now we are ready to use these series in a term-wise integration over the wall volume, similarly to the particle-wall interaction potentials.

Table 1: The results of refitting the quantum-chemically computed isotropic shielding \(\sigma(r')\) and shielding anisotropy \(\Delta\sigma(r')\) of the Xe dimer to the functional forms \(\sum_n \sigma_n/r^n\) and \(\sum_n \Delta\sigma_n/r^n\), respectively. Only odd \(n = 11, 13, \ldots, 35\) were used to simplify the integrals of Sec. 7.2. This choice made the functions easier to implement robustly in the analysis program but had no effect on the goodness of the fit.

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7.2 Integrals of the Xe shielding tensor components over the cylindrical wall

The contribution of the wall to the shielding of the Xe atom is defined analogously to the Xe-wall interaction potential in Sec. 5 of the main text. The wall of an infinitely long cylindrical cavity is infinitely thick and consists of smoothly and evenly distributed Xe atoms. The total shielding due to the interaction between a
confined Xe atom and the wall is calculated as an integral of the Xe-Xe nuclear shielding function over the wall volume. To begin with the integration process, we repeat the notion of Sec. 6 that the Xe-Xe shielding tensor is cylindrically symmetric. Thus, it can be expressed in arbitrary coordinates as

\[ \sigma_{Xe-Xe}^{\alpha\beta}(r') = \sigma(r')\delta_{\alpha\beta} + \frac{2}{3}\Delta\sigma(r')s_{\alpha\beta}, \]

where \( s_{\alpha\beta} \) is the orientation tensor of the internuclear axis \( r' \):

\[ s_{\alpha\beta} = \frac{1}{2}(3\hat{r}'_{\alpha}\hat{r}'_{\beta} - \delta_{\alpha\beta}). \]

The Xe-wall system has \( C_{2v} \) nuclear site symmetry and we place the coordinate axis as in Fig. 5. We sum up the contributions of the wall elements by integrating the tensor \( \sigma_{Xe-Xe}^{\alpha\beta} \) over the wall volume. For the integration we move to cylindrical coordinates \( (r, \phi, z) \), \( x = r\cos\phi, \ y = r\sin\phi, \ z = z \) as illustrated in Fig. 5. The distance between the Xe atom and a wall element is \( r' = \sqrt{r'^2 + z'^2} \). The diagonal components of the orientation tensor in these coordinates are

\[ s_{xx} = \frac{3}{2}\frac{r'^2}{r'^2 + z'^2}\cos^2\phi - \frac{1}{2}, \]
\[ s_{yy} = \frac{3}{2}\frac{r'^2}{r'^2 + z'^2}\sin^2\phi - \frac{1}{2}, \]
\[ s_{zz} = \frac{3}{2}\frac{z'^2}{r'^2 + z'^2} - \frac{1}{2}, \]

and the Xe-wall shielding tensor components become

\[ \sigma_{wall}^{xx} = \rho_w \int_{wall} \left[ (\sigma(r') - \frac{\Delta\sigma(r')}{3}) + \frac{r'^2}{r'^2 + z'^2}\Delta\sigma(r') \right] r'dr'd\phi'dz \]
\[ \sigma_{wall}^{yy} = \rho_w \int_{wall} \left[ (\sigma(r') - \frac{\Delta\sigma(r')}{3}) + \frac{r'^2}{r'^2 + z'^2}\Delta\sigma(r') - \frac{r'^2}{r'^2 + z'^2}\Delta\sigma(r') \right] r'dr'd\phi'dz \]
\[ \sigma_{wall}^{zz} = \rho_w \int_{wall} \left[ (\sigma(r') - \frac{\Delta\sigma(r')}{3}) + \frac{z'^2}{r'^2 + z'^2}\Delta\sigma(r') \right] r'dr'd\phi'dz, \]

where \( \rho_w \) is the density of the wall.

To proceed, we use the inverse power series representation of the isotropic shielding and shielding anisotropy formulated in the previous section. With these we arrive at

\[ \sigma_{wall}^{XX} = \rho_w \frac{\epsilon_{w}^{Xe}}{\epsilon_{0}^{Xe-Xe}} \sum_{n} \left( \frac{\epsilon_{w}^{Xe}}{\epsilon_{0}^{Xe-Xe}} \right)^n \left[ \left( \sigma_n - \frac{\Delta\sigma_n}{3} \right) J_{1,n} + \Delta\sigma_n J_{2,n} \right] \]
\[ \sigma_{wall}^{YY} = \rho_w \frac{\epsilon_{w}^{Xe}}{\epsilon_{0}^{Xe-Xe}} \sum_{n} \left( \frac{\epsilon_{w}^{Xe}}{\epsilon_{0}^{Xe-Xe}} \right)^n \left[ \left( \sigma_n - \frac{\Delta\sigma_n}{3} \right) J_{1,n} + \Delta\sigma_n J_{3,n} - \Delta\sigma_n J_{2,n} \right] \]
\[ \sigma_{wall}^{ZZ} = \rho_w \frac{\epsilon_{w}^{Xe}}{\epsilon_{0}^{Xe-Xe}} \sum_{n} \left( \frac{\epsilon_{w}^{Xe}}{\epsilon_{0}^{Xe-Xe}} \right)^n \left[ \left( \sigma_n - \frac{\Delta\sigma_n}{3} \right) J_{1,n} + \Delta\sigma_n J_{4,n} \right], \]
where the integrals to be computed can now be written as

\[
\begin{align*}
J_{1,n} &= \int_{\text{wall}} \frac{r}{(r^2 + z^2)^{n/2}} \, dr \, d\phi \, dz \\
J_{2,n} &= \int_{\text{wall}} \frac{r^3 \cos^2 \phi}{(r^2 + z^2)^{n/2+1}} \, dr \, d\phi \, dz \\
J_{3,n} &= \int_{\text{wall}} \frac{r^3}{(r^2 + z^2)^{n/2+1}} \, dr \, d\phi \, dz \\
J_{4,n} &= \int_{\text{wall}} \frac{z^2 r}{(r^2 + z^2)^{n/2+1}} \, dr \, d\phi \, dz.
\end{align*}
\] (27)

The volume to integrate over is the volume of the infinitely thick wall of the infinitely long cylindrical cavity. The outline of the integration procedure used here follows the one presented in Ref. 20. Fig. 5 presents the variables used when integrating in the plane perpendicular to the axis of the cavity (z-direction). Integrating
first over the \( z \)-direction from \(-\infty \) to \( \infty \) and then over \( r \) yields
\[ J_{1,n} = \frac{\sqrt{\pi} \Gamma \left( \frac{n-1}{2} \right)}{\Gamma \left( \frac{n}{2} \right)} \int_0^{2\pi} \int_0^\infty r^{2-n} dr d\phi = \frac{\sqrt{\pi} \Gamma \left( \frac{n-1}{2} \right)}{\Gamma \left( \frac{n}{2} \right) (n-3)} \int_0^{2\pi} r^{3-n} dr d\phi \]
\[ J_{2,n} = \frac{\sqrt{\pi} (n-1) \Gamma \left( \frac{n-1}{2} \right)}{n \Gamma \left( \frac{n}{2} \right)} \int_0^{2\pi} \int_0^\infty r^{2-n} \cos^2 \phi dr d\phi = \frac{\sqrt{\pi} (n-1) \Gamma \left( \frac{n-1}{2} \right)}{n \Gamma \left( \frac{n}{2} \right) (n-3)} \int_0^{2\pi} r^{3-n} \cos^2 \phi dr d\phi \]
\[ J_{3,n} = \frac{n-1}{n} J_{1,n} \]
\[ J_{4,n} = \frac{1}{n} J_{1,n} \]. \tag{28} \]
\( \Gamma(n) \) denotes the gamma function (see, e.g., Ref. 21 for a definition). \( r_\phi \) is obtained from Fig. 5 by the law of cosines:
\[ R^2 = r_\phi^2 - 2r_\phi(R - r_w) \cos(\pi - \phi) + (R - r_w)^2 \]
\[ \Rightarrow r_\phi/R = -k \cos \phi + \sqrt{1 - k^2 \sin^2 \phi} = \frac{1 - k^2}{k \cos \phi + \sqrt{1 - k^2 \sin^2 \phi}}, \tag{29} \]
where \( k = 1 - r_w/R \). After substituting \( r_\phi \) into \( J_{1,n} \) and \( J_{2,n} \) we have
\[ J_{1,n} = \frac{2 \sqrt{\pi} \Gamma \left( \frac{n-1}{2} \right)}{\Gamma \left( \frac{n}{2} \right) (n-3) R^{n-3} (1 - k^2)^{n-3}} \tilde{I}_{n-3}^{(0)}(k) \]
\[ J_{2,n} = \frac{2 \sqrt{\pi} (n-1) \Gamma \left( \frac{n-1}{2} \right)}{n \Gamma \left( \frac{n}{2} \right) (n-3) R^{n-3} (1 - k^2)^{n-3}} \tilde{I}_{n-3}^{(2)}(k) \]
\[ \tilde{I}_{n-3}^{(m')} (k) = \int_0^\pi \cos^{m'} \phi \left( \sqrt{1 - k^2 \sin^2 \phi} + k \cos \phi \right)^{n-3} d\phi. \tag{30} \]
The integral above is divided to two intervals, \([0,\pi/2]\) and \([\pi/2, \pi]\), followed by a substitution \( \phi = \pi - \gamma \) in the latter interval. After this we write the binomial powers as a sum resulting in
\[ \tilde{I}_{n-3}^{(m')} (k) = \sum_{l=0}^{n-3} \binom{n-3}{l} k^l [1 + (-1)^l] \int_0^{\pi/2} \cos^{m'+l} \phi \left( \sqrt{1 - k^2 \sin^2 \phi} \right)^{n-3-l} d\phi. \tag{31} \]
With the substitution \( \sin^2 \phi \to t \) we arrive at
\[ \tilde{I}_{n-3}^{(m')} (k) = \frac{1}{2} \sum_{l=0}^{n-3} \binom{n-3}{l} k^l [1 + (-1)^l] \int_0^1 \! t^{-1/2} (1 - t)^{\frac{1}{2}(l + m' - 1)} (1 - k^2 t)^{\frac{1}{2}(n-3-l)} \, dt. \tag{32} \]
Using the formula (15.3.1) in Ref. 21 we can write the integral as
\[ \tilde{I}_{n-3}^{(m')} (k) = \frac{1}{2} \sum_{l=0}^{n-3} \binom{n-3}{l} k^l [1 + (-1)^l] \frac{\Gamma \left( \frac{1}{2} \right) \Gamma \left[ \frac{1}{2}(l + m' + 1) \right]}{\Gamma \left[ \frac{1}{2}(l + m' + 2) \right]} _2F_1 \left[ \begin{array}{c} \! -\frac{1}{2}(n-3-l), \frac{1}{2} \! ; \frac{1}{2}(l + m' + 2) ; k^2 \! \end{array} \! \right]. \tag{33} \]
where \(_2F_1\) is the hypergeometric function, as defined in Eq. 15.1.1 of Ref. 21. The terms with odd \(l\) will vanish from the sum. With the above equation, Eq. 28 and Eq. 30, the tensor components in Eq. 26 can be written as

\[
\sigma_{xx}^{\text{wall}}(k, R) = \rho_w \frac{\epsilon_{Xe}}{\epsilon_0} \sum_n \left( \frac{\epsilon_{Xe}}{\sigma_0} \right)^n P_n(k, R) \left[ \left( \sigma_n - \frac{\Delta \sigma_n}{3} \right) \tilde{I}_{n-3}^{(0)}(k) + \frac{n - 1}{n} \Delta \sigma_n \tilde{I}_{n-3}^{(2)}(k) \right]
\]

\[
\sigma_{yy}^{\text{wall}}(k, R) = \rho_w \frac{\epsilon_{Xe}}{\epsilon_0} \sum_n \left( \frac{\epsilon_{Xe}}{\sigma_0} \right)^n P_n(k, R) \left[ \left( \sigma_n - \frac{\Delta \sigma_n}{3} + \frac{n - 1}{n} \Delta \sigma_n \right) \tilde{I}_{n-3}^{(0)}(k) - \frac{n - 1}{n} \Delta \sigma_n \tilde{I}_{n-3}^{(2)}(k) \right]
\]

\[
\sigma_{zz}^{\text{wall}}(k, R) = \rho_w \frac{\epsilon_{Xe}}{\epsilon_0} \sum_n \left( \frac{\epsilon_{Xe}}{\sigma_0} \right)^n P_n(k, R) \left( \sigma_n - \frac{\Delta \sigma_n}{3} + \frac{1}{n} \Delta \sigma_n \right) \tilde{I}_{n-3}^{(0)}(k), \tag{34}
\]

where

\[
P_n(k, R) = \frac{2 \sqrt{\pi} \Gamma \left[ \frac{1}{2} (n - 1) \right]}{\Gamma \left( \frac{n}{2} \right) (n - 3) R^{n-3} (1 - k^2)^{n-3}}. \tag{35}
\]

Furthermore, if we restrict ourselves to odd values of \(n\), with \(n > 3\), the first argument of the hypergeometric function in Eq. (33) is a non-positive integer and we can use Eq. (15.4.1) of Ref. 21 to write the hypergeometric function as a finite polynomial in \(k\):

\[
\tilde{I}_{n-3}^{(m')} (k) = \frac{\pi}{2} \sum_{l=0}^{\frac{n-3}{2}} \binom{n-3}{l} k^l [1 + (-1)^l] \frac{(l + m')!}{2^{l+m'} \left\{ \frac{1}{2} (l + m')! \right\}^2} \sum_{n'=0}^{\frac{1}{2}(n-3-l)} \frac{[-\frac{1}{2} (n - 3 - l)]_{n'} \left( \frac{1}{2} \right)_{n'} k^{2n'} }{\left[ \frac{1}{2} (l + m' + 2) \right]_{n'} n!}. \tag{36}
\]

The Pochhammer symbols \(()_n\) represent rising factorials \((x)_n = x(x + 1) \cdots (x + n - 1).\) The formula (6.1.12) from Ref. 21 can be used to write out the gamma functions in a more implementation-friendly form. Applying the same restrictions for \(n\) as above, we can write

\[
P_n(k, R) = \frac{\left[ (\frac{n-3}{2})! \right]^2 2^{n-1}}{(n - 2)! (n - 3) R^{n-3} (1 - k^2)^{n-3}}. \tag{37}
\]

### 8 Translational order profiles \(g_1\)

We want to see how the layer structure of the LC changes as a function of distance from the cavity wall. The regular translational order parameter \(\tau_1\) of Eq. 11 is not readily separable to contributions from different parts of the cavity. Averaging and maximising in Eq. 11, using only particles residing in a cylindrical shell of thickness \(b\) will yield problems when the number of particles in the shell is small. Also, it would not give the contribution of those particles to the total translational order of the system. Instead, we look at the square

\[
\tau_1^2 = \left[ \bar{\tau}_1(d_0) \right]^2 \tilde{\tau}_1(d_0). \tag{38}
\]

Here,

\[
\bar{\tau}_1(d_0) = \frac{1}{N} \sum_{j=1}^{N} \exp \left[ 2\pi i (\mathbf{r}_j \cdot \mathbf{n})/d_0 \right] = \frac{1}{N} \sum_{j=1}^{N} \exp (iqr_{\parallel,j}), \tag{39}
\]
where \( q = 2\pi/d_0 \) and \( r_{||,j} = r_j \cdot \hat{n} \). \( d_0 \) is the layer separation value resulting from the maximisation of the global \( \tau_1 \). In the cavities we use \( \hat{n} = \hat{z} \), the direction parallel to the cavity axis. We can write the above as a sum over particles in \( K \) non-overlapping cylindrical shells,

\[
\tilde{\tau}_1(q) = \frac{1}{N} \sum_{k=1}^{K} \sum_{j=1}^{N_k} \exp(iqr_{||,k,j}) = \frac{1}{N} \sum_{k=1}^{K} N_k \tilde{\tau}_{1,k}(q)
\tag{40}
\]

where \( N_k \) is the number of particles in \( k \):th shell. The square of the translational order parameter is

\[
\tau_1^2 = \sum_{k=1}^{K} \frac{N_k}{N} [\tilde{\tau}_{1,k}(q)]^* \tilde{\tau}_1(q) = \sum_{k=1}^{K} \frac{N_k}{N} g_{1,k}(q).
\tag{41}
\]

We identify the above as a sum over the contributions of each shell to the total square of the translational order parameter, where \( N_k/N \) is the weight of each shell and the measure

\[
g_{1,k}(q) = \Re \left\{ [\tilde{\tau}_{1,k}(q)]^* \tilde{\tau}_1(q) \right\}.
\tag{42}
\]

gives the contribution of shell \( k \) to the total translational order parameter.

![Figure 6: Translational order profiles \( g_1 \) and the average number of Xe atoms \( N_{Xe} \) in each cylindrical shell, in the two cavities with radii \( R = 9 \) (left) and \( R = 18 \) (right) at four different temperatures and LC phases.](image)

The \( g_1 \) profiles in the two cavities R9 and R18 have been plotted in Fig. 6 a) and c) together with the respective profiles for the number of Xe atoms in panels b) and d). The figure shows that the degree of smectic layering is lower near the cavity wall and that there is a relatively high number of Xe atoms in this region.
References