Electronic Supplementary Material (ESI) for Soft Matter.

Density Functional Theory of nematic elasticity: softening from polar order

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APPENDIX

Small χ expansion of $d^j_{l,r}(\chi)$ and irreducible spherical representation of tensors

From the expression of $d^j_{l,r}(\chi)$ [1], the following approximated form is obtained in the limit $\chi \to 0$:

$$\begin{aligned} d^j_{l,r}(\chi) \sim \quad & \delta_{l,r} + \frac{\chi}{2}\left\{\delta_{l,r-1}\sqrt{(j+l+1)(j-l)} - \delta_{l,r+1}\sqrt{(j-l+1)(j+l)}\right\} \\ & \frac{\chi^2}{8}\left\{-\delta_{l,r}2(j+j^2-l^2) + \delta_{l,r-2}\sqrt{(j+l+2)(j+l+1)(j-l)(j-l-1)}\right. \\ & \left. + \delta_{l,r+2}\sqrt{(j+l)(j+l-1)(j-l+2)(j-l+1)}\right\}. \end{aligned} \tag{1}$$

Using eq. (8) in the main text, expressions of $d^j_{l,r}(\chi)$ in terms of the deformation wavenumber, q, and the Cartesian components of the inter-particle vector $\mathbf{R}_{AB}$ in the LAB frame, suitable for the three basic deformation in the long-wavelength limit, are obtained.

To calculate the contributions to the excluded volume integrals (see below), it is convenient to express the components of the $\mathbf{R}_{AB}$ vector in the LAB frame in terms of those in the $\mathbf{A}$-frame, using the rotation defined by the Euler angles $\mathbf{\Omega}_A$, as follows [1]:

$$\begin{aligned} X_{AB} &= \frac{1}{\sqrt{2}}\sum_{p=-1}^{1}\left[\mathcal{D}^{1\ *}_{-1,p}(\Omega_A) - \mathcal{D}^{1\ *}_{1,p}(\Omega_A)\right]T^{1,p} \\ Y_{AB} &= \frac{i}{\sqrt{2}}\sum_{p=-1}^{1}\left[\mathcal{D}^{1\ *}_{-1,p}(\Omega_A) + \mathcal{D}^{1\ *}_{1,p}(\Omega_A)\right]T^{1,p} \\ Z_{AB} &= \sum_{p=-1}^{1}\mathcal{D}^{1\ *}_{0,p}(\Omega_A)T^{1,p} \end{aligned} \tag{2}$$

Analogously, for the components of $\mathbf{R}_{AB} \otimes \mathbf{R}_{AB}$ we can write:

$$\begin{aligned} X^2_{AB} &= -\frac{1}{\sqrt{3}}T^{0,0} + \sum_{p=-2}^{2}\left[-\frac{1}{\sqrt{6}}\mathcal{D}^{2\ *}_{0,p}(\Omega_A) + \frac{1}{2}\mathcal{D}^{2\ *}_{-2,p}(\Omega_A) + \frac{1}{2}\mathcal{D}^{2\ *}_{2,p}(\Omega_A\right]T^{2,p} \\ Y^2_{AB} &= -\frac{1}{\sqrt{3}}T^{0,0} + \sum_{p=-2}^{2}\left[-\frac{1}{\sqrt{6}}\mathcal{D}^{2\ *}_{0,p}(\Omega_A) - \frac{1}{2}\mathcal{D}^{2\ *}_{-2,p}(\Omega_A) - \frac{1}{2}\mathcal{D}^{2\ *}_{2,p}(\Omega_A\right]T^{2,p} \\ Z^2_{AB} &= -\frac{1}{\sqrt{3}}T^{0,0} + \sum_{p=-2}^{2}\sqrt{\frac{2}{3}}\mathcal{D}^{2\ *}_{0,p}(\Omega_A)T^{2,p} \\ X_{AB}Z_{AB} &= \frac{1}{2}\sum_{p=-2}^{2}\left[\mathcal{D}^{2\ *}_{-1,p}(\Omega_A) - \mathcal{D}^{2\ *}_{1,p}(\Omega_A)\right]T^{2,p} \end{aligned} \tag{3}$$

In eqs. (2)-(3), $T^{j,p}$ are irreducible spherical components of $\mathbf{R}_{AB}$ and $\mathbf{R}_{AB} \otimes \mathbf{R}_{AB}$, expressed in the **A**-frame:

$$\begin{aligned}
T^{0,0} &= -\frac{1}{\sqrt{3}} R_{AB}^2 \\
T^{1,0} &= Z_{AB}^{(A)} \\
T^{1,\pm 1} &= \mp \frac{1}{\sqrt{2}} \left[X_{AB}^{(A)} \pm \imath\, Y_{AB}^{(A)} \right] \\
T^{2,0} &= \frac{1}{\sqrt{6}} \left[3 (Z_{AB}^{(A)})^2 - 1 \right] \\
T^{2,\pm 1} &= \mp Z_{AB}^{(A)} \left[X_{AB}^{(A)} \pm \imath\, Y_{AB}^{(A)} \right] \\
T^{2,\pm 2} &= \frac{1}{2} \left[(X_{AB}^{(A)})^2 - (Y_{AB}^{(A)})^2 \right] \pm \imath\, X_{AB}^{(A)} Y_{AB}^{(A)}
\end{aligned} \tag{4}$$

Explicit form of the average excluded volume

Using the small χ expansion of $d_{l,r}^{j}(\chi)$ eq. (1) and the properties of Wigner rotation matrices [1], the average excluded volume can be expressed as:

$$\overline{v^{excl}}|_{\langle\rangle} = \overline{v_0^{excl}}|_{\langle\rangle} + q \overline{v_1^{excl}}|_{\langle\rangle} + \frac{1}{2} q^2 \overline{v_2^{excl}}|_{\langle\rangle} \tag{5}$$

where the symbol $|_{\langle\rangle}$ is introduced to stress that the explicit q dependence refers to given order parameters. It is important to remark that within the present theory the equilibrium order parameters will in general depend on the type and wavenumber of the deformation, so $\overline{v_1^{excl}}|_{\langle\rangle}$ and $\overline{v_2^{excl}}|_{\langle\rangle}$ bear themselves an implicit q dependence.

The first term in eq. (5) is given by:

$$\begin{aligned}
\overline{v_0^{excl}}|_{\langle\rangle} = -\frac{1}{8\pi^2} \sum_{j_A=0}^{\infty} (2j_A+1) \sum_{r_A=-j_A}^{j_A} \sum_{n_A=-j_A}^{j_A} \sum_{n_B=-j_B}^{j_B} (-1)^{r_A+n_A} \langle \mathcal{D}_{r_A,n_A}^{j_A\,*} \rangle \langle \mathcal{D}_{-r_A,n_B}^{j_A\,*} \rangle \times \\
\int d\Omega_{AB}\, \mathcal{D}_{-n_A,n_B}^{j_A}(\Omega_{AB}) \int d\mathbf{R}_{AB}\, e_{AB}(\Omega_{AB}, \mathbf{R}_{AB})
\end{aligned} \tag{6}$$

where Ω_{AB} are Euler angle describing the rotation from the **A** to the **B**-frame. This is the form of the average free volume in the absence of deformation ($q = 0$). The other terms in eq. (5) arise in the presence of deformation and have a different form for each distinct mode. Henceforth, the index S will be used for splay, T for twist and B for bend.

For $\overline{v_1^{excl}}$ the following forms are obtained:

$$\begin{aligned}
\overline{v_{1,S}^{excl}} = &-\frac{1}{6\sqrt{2}} \frac{1}{8\pi^2} \sum_{j_A=0}^{\infty} (2j_A+1) \sum_{r_A=-j_A}^{j_A} \sum_{n_A=-j_A}^{j_A} \langle \mathcal{D}_{r_A,n_A}^{j_A\,*} \rangle \sum_{j_B=0}^{\infty} (2j_B+1) \sum_{n_B=-j_B}^{j_B} \\
&\Big\{ C(j_A, j_B, 1; r_A, -r_A-1, -1) \left[\langle \mathcal{D}_{-r_A,n_B}^{j_B\,*} \rangle \sqrt{(j_B+r_A+1)(j_B-r_A)} - \langle \mathcal{D}_{-r_A-2,n_B}^{j_B\,*} \rangle \sqrt{(j_B-r_A-1)(j_B+r_A+2)} \right] \\
&+ C(j_A, j_B, 1; r_A, -r_A+1, 1) \left[-\langle \mathcal{D}_{-r_A+2,n_B}^{j_B\,*} \rangle \sqrt{(j_B+r_A-1)(j_B-r_A+2)} + \langle \mathcal{D}_{-r_A,n_B}^{j_B\,*} \rangle \sqrt{(j_B-r_A+1)(j_B+r_A)} \right] \Big\} \\
&\times \sum_{m=-j_B}^{j_B} \sum_{p=-1}^{1} C(j_A, j_B, 1; n_A, m, p) \int d\Omega_{AB}\, \mathcal{D}_{m,n_B}^{j_B}(\Omega_{AB}) \int d\mathbf{R}_{AB}\, e_{AB}(\Omega_{AB}, \mathbf{R}_{AB}) T^{1,p}
\end{aligned} \tag{7}$$

$$\overline{v_{1,T}^{excl}} = -\frac{i}{6\sqrt{2}}\frac{1}{8\pi^2}\sum_{j_A=0}^{\infty}(2j_A+1)\sum_{r_A=-j_A}^{j_A}\sum_{n_A=-j_A}^{j_A}\langle\mathcal{D}_{r_A,n_A}^{j_A\ *}\rangle\sum_{j_B=0}^{\infty}(2j_B+1)\sum_{n_B=-j_B}^{j_B}$$
$$\Big\{C(j_A,j_B,1;r_A,-r_A-1,-1)\Big[\langle\mathcal{D}_{-r_A,n_B}^{j_B\ *}\rangle\sqrt{(j_B+r_A+1)(j_B-r_A)}-\langle\mathcal{D}_{-r_A-2,n_B}^{j_B\ *}\rangle\sqrt{(j_B-r_A-1)(j_B+r_A+2)}\Big]$$
$$+C(j_A,j_B,1;r_A,-r_A+1,1)\Big[\langle\mathcal{D}_{-r_A+2,n_B}^{j_B\ *}\rangle\sqrt{(j_B+r_A-1)(j_B-r_A+2)}-\langle\mathcal{D}_{-r_A,n_B}^{j_B\ *}\rangle\sqrt{(j_B-r_A+1)(j_B+r_A)}\Big]\Big\}$$
$$\times\sum_{m=-j_B}^{j_B}\sum_{p=-1}^{1}C(j_A,j_B,1;n_A,m,p)\int d\Omega_{AB}\ \mathcal{D}_{m,n_B}^{j_B}(\Omega_{AB})\int d\mathbf{R}_{AB}\ e_{AB}(\Omega_{AB},\mathbf{R}_{AB})T^{1,p} \tag{8}$$

$$\overline{v_{1,B}^{excl}} = -\frac{1}{6}\frac{1}{8\pi^2}\sum_{j_A=0}^{\infty}(2j_A+1)\sum_{r_A=-j_A}^{j_A}\sum_{n_A=-j_A}^{j_A}\langle\mathcal{D}_{r_A,n_A}^{j_A\ *}\rangle\sum_{j_B=0}^{\infty}(2j_B+1)\sum_{n_B=-j_B}^{j_B}$$
$$C(j_A,j_B,1;r_A,-r_A,0)\Big[\langle\mathcal{D}_{-r_A+1,n_B}^{j_B\ *}\rangle\sqrt{(j_B+r_A)(j_B-r_A+1)}-\langle\mathcal{D}_{-r_A-1,n_B}^{j_B\ *}\rangle\sqrt{(j_B-r_A)(j_B+r_A+1)}\Big]$$
$$\times\sum_{m=-j_B}^{j_B}\sum_{p=-1}^{1}C(j_A,j_B,1;n_A,m,p)\int d\Omega_{AB}\ \mathcal{D}_{m,n_B}^{j_B}(\Omega_{AB})\int d\mathbf{R}_{AB}\ e_{AB}(\Omega_{AB},\mathbf{R}_{AB})T^{1,p} \tag{9}$$

It can be easily verified that the lowest rank contribution to $\overline{v_{1,S}^{excl}}$ and $\overline{v_{1,B}^{excl}}$ depends on polar order parameters, whereas this polar contribution vanishes for $\overline{v_{1,T}^{excl}}$.

The third term on the rhs of eq. (5) is conveniently decomposed as follows:

$$\overline{v_{2,S}^{excl}} = \overline{v_{2,I}^{excl}}+\overline{v_{2,II}^{excl}}-\overline{v_{2,III}^{excl}}+\overline{v_{2,IV}^{excl}} \tag{10}$$
$$\overline{v_{2,T}^{excl}} = \overline{v_{2,II}^{excl}}-\overline{v_{2,III}^{excl}}-\overline{v_{2,IV}^{excl}} \tag{11}$$
$$\overline{v_{2,B}^{excl}} = -\overline{v_{2,I}^{excl}}+\overline{v_{2,II}^{excl}}+2\overline{v_{2,III}^{excl}} \tag{12}$$

where the various contributions are defined as:

$$\overline{v_{2,I}^{excl}} = \frac{1}{10}\frac{1}{8\pi^2}\sum_{j_A=0}^{\infty}(2j_A+1)\sum_{r_A=-j_A}^{j_A}\sum_{n_A=-j_A}^{j_A}\langle\mathcal{D}_{r_A,n_A}^{j_A\ *}\rangle\sum_{j_B=0}^{\infty}(2j_B+1)\sum_{n_B=-j_B}^{j_B}$$
$$\Big\{C(j_A,j_B,2;r_A,-r_A-1,-1)\Big[\langle\mathcal{D}_{-r_A,n_B}^{j_B\ *}\rangle\sqrt{(j_B+r_A+1)(j_B-r_A)}-\langle\mathcal{D}_{-r_A-2,n_B}^{j_B\ *}\rangle\sqrt{(j_B-r_A-1)(j_B+r_A+2)}\Big]$$
$$-C(j_A,j_B,2;r_A,-r_A+1,1)\Big[\langle\mathcal{D}_{-r_A+2,n_B}^{j_B\ *}\rangle\sqrt{(j_B+r_A-1)(j_B-r_A+2)}-\langle\mathcal{D}_{-r_A,n_B}^{j_B\ *}\rangle\sqrt{(j_B-r_A+1)(j_B+r_A)}\Big]\Big\}$$
$$\times\sum_{m=-j_B}^{j_B}\sum_{p=-2}^{2}C(j_A,j_B,2;n_A,m,p)\int d\Omega_{AB}\ \mathcal{D}_{m,n_B}^{j_B}(\Omega_{AB})\int d\mathbf{R}_{AB}\ e_{AB}(\Omega_{AB},\mathbf{R}_{AB})T^{2,p} \tag{13}$$

$$\overline{v_{2,II}^{excl}} = \frac{1}{4\sqrt{3}}\frac{1}{8\pi^2}\sum_{j_A=0}^{\infty}(2j_A+1)\sum_{r_A=-j_A}^{j_A}(-)^{r_A+n_A}\sum_{n_A=-j_A}^{j_A}\langle\mathcal{D}_{r_A,n_A}^{j_A\ *}\rangle\sum_{n_B=-j_B}^{j_B}$$
$$\Big\{-2\langle\mathcal{D}_{-r_A,n_B}^{j_A\ *}\rangle(j_A+j_A^2-r_A^2)$$
$$+\langle\mathcal{D}_{-r_A+2,n_B}^{j_A\ *}\rangle\sqrt{(j_A-r_A+2)(j_A-r_A+1)(j_A+r_A)(j_A+r_A-1)}$$
$$+\langle\mathcal{D}_{-r_A-2,n_B}^{j_A\ *}\rangle\sqrt{(j_A-r_A)(j_A-r_A-1)(j_A+r_A+2)(j_A+r_A+1)}\Big]\Big\}$$
$$\times\int d\Omega_{AB}\ \mathcal{D}_{-r_A,n_B}^{j_B}(\Omega_{AB})\int d\mathbf{R}_{AB}\ e_{AB}(\Omega_{AB},\mathbf{R}_{AB})T^{0,0} \tag{14}$$

$$\overline{v_{2,III}^{excl}} = -\frac{1}{20\sqrt{6}}\frac{1}{8\pi^2}\sum_{j_A=0}^{\infty}(2j_A+1)\sum_{r_A=-j_A}^{j_A}\sum_{n_A=-j_A}^{j_A}\langle\mathcal{D}^{j_A\,*}_{r_A,n_A}\rangle\sum_{j_B=0}^{\infty}(2j_B+1)\sum_{n_B=-j_B}^{j_B}C(j_A,j_B,2;r_A,-r_A,0)$$
$$\Big[-2\langle\mathcal{D}^{j_B\,*}_{-r_A,n_B}\rangle(j_B+j_B^2-r_A^2)$$
$$+\langle\mathcal{D}^{j_B\,*}_{-r_A+2,n_B}\rangle\sqrt{(j_B-r_A+2)(j_B-r_A+1)(j_B+r_A)(j_B+r_A-1)}$$
$$+\langle\mathcal{D}^{j_B\,*}_{-r_A-2,n_B}\rangle\sqrt{(j_B-r_A)(j_B-r_A-1)(j_B+r_A+2)(j_B+r_A+1)}\Big]$$
$$\times\sum_{m=-j_B}^{j_B}\sum_{p=-2}^{2}C(j_A,j_B,2;n_A,m,p)\int d\Omega_{AB}\ \mathcal{D}^{j_B}_{m,n_B}(\Omega_{AB})\int d\mathbf{R}_{AB}\ e_{AB}(\Omega_{AB},\mathbf{R}_{AB})T^{2,p} \qquad (15)$$

$$\overline{v_{2,IV}^{excl}} = -\frac{1}{40}\frac{1}{8\pi^2}\sum_{j_A=0}^{\infty}(2j_A+1)\sum_{r_A=-j_A}^{j_A}\sum_{n_A=-j_A}^{j_A}\langle\mathcal{D}^{j_A\,*}_{r_A,n_A}\rangle\sum_{j_B=0}^{\infty}(2j_B+1)\sum_{n_B=-j_B}^{j_B}$$
$$\Big\{C(j_A,j_B,2;r_A,-r_A-2,-2)\Big[-2\langle\mathcal{D}^{j_B\,*}_{-r_A-2,n_B}\rangle(j_B+j_B^2-(r_A-2)^2)$$
$$+\langle\mathcal{D}^{j_B\,*}_{-r_A,n_B}\rangle\sqrt{(j_B-r_A)(j_B-r_A-1)(j_B+r_A+2)(j_B+r_A+1)}$$
$$+\langle\mathcal{D}^{j_B\,*}_{-r_A-4,n_B}\rangle\sqrt{(j_B-r_A-2)(j_B-r_A-3)(j_B+r_A+4)(j_B+r_A+3)}\Big]$$
$$+C(j_A,j_B,2;r_A,-r_A+2,2)\Big[-2\langle\mathcal{D}^{j_B\,*}_{-r_A+2,n_B}\rangle(j_B+j_B^2-(r_A+2)^2)$$
$$+\langle\mathcal{D}^{j_B\,*}_{-r_A+4,n_B}\rangle\sqrt{(j_B-r_A+4)(j_B-r_A+3)(j_B+r_A-2)(j_B+r_A-3)}$$
$$+\langle\mathcal{D}^{j_B\,*}_{-r_A,n_B}\rangle\sqrt{(j_B-r_A+2)(j_B-r_A+1)(j_B+r_A)(j_B+r_A-1)}\Big]\Big\}$$
$$\times\sum_{m=-j_B}^{j_B}\sum_{p=-2}^{2}C(j_A,j_B,2;n_A,m,p)\int d\Omega_{AB}\ \mathcal{D}^{j_B}_{m,n_B}(\Omega_{AB})\int d\mathbf{R}_{AB}\ e_{AB}(\Omega_{AB},\mathbf{R}_{AB})T^{2,p} \qquad (16)$$

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[1] R. N. Zare, *Angular Momentum*, Wiley, New York, 1988.