Density – nematic coupling in isotropic linear polymers

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• new macroscopic equation for linear polymers
• important role of simulations
• numerical experiment on a model system, substitutes scattering on a real material
**Isotropic linear polymer**

\[
\partial_j \left[ \rho \left( Q_{ij} + \frac{1}{2} \delta_{ij} \right) \right] = \frac{3}{2} \frac{1}{\ell_0} g_i + \frac{3}{2} \rho k_i
\]

- **Continuity equation with sources.** Key: the sources can be made small.
- **Coupled density and orientational order, even in isotropic phases.**
- **Totally generic.**

**Physics:** osmotic optical birefringence in a static polymeric liquid. (any observation?)

Valid for linear polymers: DNA, common synthetic polymers like polyethylene, polyvinyls, polyamides, polyesters, polystyrene, polycarbonates …
"Tensorial" conservation law

\[
\partial_j \left[ \rho \left( Q_{ij} + \frac{1}{2} \delta_{ij} \right) \right] = \frac{3}{2} \frac{1}{\ell_0} g_i + \frac{3}{2} \rho \delta k_i
\]

Enables full Q-tensor description of nematic polymers (important for defects).

Properly includes chain backfolding (hairpins) – characteristic for nematic symmetry.

But there is more: relevant also for isotropic systems! Therefore, extremely general.

\[
\rho_0 \partial_j \delta Q_{ij} + \frac{1}{2} \partial_i \delta \rho = \frac{3}{2} \frac{1}{\ell_0} \delta g_i + \frac{3}{2} \rho_0 \delta k_i
\]

Fluctuations of density and orientational order are coupled!

On the other hand, no coupling with polar orientational order.

Hence, it should be interesting to study coupled fluctuations in an isotropic system. There, nematic fluctuations are inherently tensorial and require the tensorial framework.

\[
\nabla \cdot (\rho_0 \delta \mathbf{a}) = \delta \rho^\pm
\]

as opposed to the "old" vectorial continuity
But …!

Facing sporadic questions, where this equation comes from ;)

microscopic *length density* (length per unit volume)

\[ \rho_{\text{mic}}(x) = \int_{x(s)} ds \delta(x - x(s)) \]

microscopic quadrupole moment

\[ J_{ij\text{mic}}(x) = \int_{x(s)} ds \delta(x - x(s)) \frac{3}{2} \left[ t_i(s)t_j(s) - \frac{1}{3} \delta_{ij} \right] \]

\[ \partial_j \left( J_{ij\text{mic}} + \frac{1}{2} \delta_{ij} \rho_{\text{mic}} \right) = \frac{3}{2} \int_{x(s)} ds \frac{dx_i(s)}{ds} \frac{dx_j(s)}{ds} \frac{\partial}{\partial x_j} \delta(x - x(s)) \]

using \[ \frac{dx_i(s)}{ds} \frac{\partial}{\partial x_j} \delta(x - x(s)) = -\frac{dx_j(s)}{ds} \frac{\partial}{\partial x_j} \delta(x - x(s)) = -\frac{d}{ds} \delta(x - x(s)) \] and integrating by parts, we get

\[ \partial_j \left( J_{ij\text{mic}} + \frac{1}{2} \delta_{ij} \rho_{\text{mic}} \right) = \frac{3}{2} \left[ t_i(0) \delta(x - x(0)) - t_i(L) \delta(x - x(L)) \right] + \frac{3}{2} \int_{x(s)} ds \frac{d^2x_i(s)}{ds^2} \delta(x - x(s)) \]

1x per partes – a rather straightforward microscopic identity.

The true value pops out after coarse-graining.

The physics is in the sources!
Coarse-graining

\[ \mathbf{F}^{\text{mic}}(\mathbf{x}) = \int_{x(s)} ds \, \delta(\mathbf{x} - \mathbf{x}(s)) \, f(\mathbf{x}(s)) \]

\[ \mathbf{F}(\mathbf{x}) = \mathbf{F}^{\text{mic}}(\mathbf{x}) = \frac{1}{V} \int_{V(\mathbf{x})} d^3x' \, \mathbf{F}^{\text{mic}}(\mathbf{x}') = \frac{1}{V} \int_{x(s) \in V(\mathbf{x})} ds \, f(\mathbf{x}(s)) = \frac{L(\mathbf{x})}{V} \left( \frac{1}{L(\mathbf{x})} \int_{x(s) \in V(\mathbf{x})} ds \, f(\mathbf{x}(s)) \right) \]

\[ \rho(\mathbf{x}) = \frac{N(\mathbf{x})}{V} \]

\[ \bar{f}(\mathbf{x}) = \frac{1}{L(\mathbf{x})} \int_{x(s) \in V(\mathbf{x})} ds \, f(\mathbf{x}(s)) \]

for example:

\[ Q_{ij} = \frac{1}{L(\mathbf{x})} \int_{x(s) \in V(\mathbf{x})} ds \, \frac{3}{2} \left[ t_i(\mathbf{x}(s)) t_j(\mathbf{x}(s)) - \frac{1}{3} \delta_{ij} \right] = \frac{3}{2} \left( \langle d_i^\alpha d_j^\alpha \rangle - \frac{1}{3} \delta_{ij} \right) \]

Apply the c.-g. to our microscopic identity: (commutes with spatial derivative)

\[ \partial_j \left( J_{ij}^{\text{mic}} + \frac{1}{2} \delta_{ij} \rho^{\text{mic}} \right) = \frac{3}{2} \left[ t_i(0) \delta(\mathbf{x} - \mathbf{x}(0)) - t_i(L) \delta(\mathbf{x} - \mathbf{x}(L)) \right] + \frac{3}{2} \int_{x(s)} ds \, \frac{d^2x_i(s)}{ds^2} \delta(\mathbf{x} - \mathbf{x}(s)) \]

\[ \partial_j \left[ \rho \ell_0 Q_{ij} + \frac{1}{2} \rho \ell_0 \delta_{ij} \right] = \frac{3}{2} g_i + \frac{3}{2} \rho \ell_0 k_i \]

density of chain end tangents (inward-pointing)

average local chain curvature vector
Some analogies of form (and physics)

geometric line constraints (polymers) vs. stationary continuity equations for fluids

Vectorial constraint for polar order fully analogous to continuity equation for mass.

\[ \nabla \cdot (\rho \ell_0 \mathbf{a}) = \rho^\pm \quad \text{and} \quad \nabla \cdot (\rho \mathbf{v}) = q \]

Tensorial constraint for nematic order a bit more complicated, but still analogous to … ? some patience needed …
**Some analogies of form (and physics)**

geometric line constraints (polymers) vs. stationary continuity equations for fluids

Tensorial constraint for **nematic** order ... ... **linear momentum conservation!**

\[
\partial_j \tilde{J}_{ij} = \frac{3}{2} g_i + \frac{3}{2} \rho \ell_0 k_i \\
\tilde{J}_{ij} = \frac{3}{2} \frac{\ell_0}{V} \sum_n t^n_i t^n_j
\]

\[
\partial_j \Pi_{ij} = f_i \\
\Pi_{ij} = \rho v_i^* v_j^* + p \delta_{ij}
\]

In the geometric case, Galilean invariance has no meaning \(\rightarrow\) no decomposition into \(v^n = v^* + v^{0n}\)

\[
\Pi_{ij} = \frac{1}{V} \sum_n m_n v_i^n v_j^n
\]

\[
p = \frac{1}{3V} \sum_n m_n (v^{0n})^2
\]

These constraints are not affected by a possible polar order, i.e., \(\langle t \rangle \neq 0\), \(v^* \neq 0\).

No additional geometrical constraint for polar order, while Newton's law for motion of CoM.
Fluctuations in the isotropic phase

Strategy:

- MC simulations of „soft“ worm-like chains („soft model“, K. Daoulas, MPIP Mainz)
- vary length and flexibility
- extract density and nematic fluctuations
- compare with fluctuations calculated from a macroscopic model that includes the tensorial constraint
Fluctuations in the isotropic phase

\[ f = \frac{1}{2} B \left( \frac{\delta \rho}{\rho_0} \right)^2 + \frac{1}{2} B' \left( \frac{\partial_i \delta \rho}{\rho_0} \right)^2 \]
\[ + \frac{1}{2} A (\delta Q_{ij})^2 + \frac{1}{2} L (\partial_k \delta Q_{ij})^2 \]
\[ + \frac{1}{2} G \left( \frac{2}{3} \rho_0 l_0 \right)^2 \left[ \partial_j \delta Q_{ij} + \frac{1}{3} \partial_i \left( \frac{\delta \rho}{\rho_0} \right) \right]^2 \]

\[ q = q \hat{e}_z \]

constraint: penalty potential

\[ f(q) = \frac{1}{2} (A + L q^2) \left( 2|\delta Q_{xy}|^2 + |\delta Q_{xx} - \delta Q_{yy}|^2 \right) \]
\[ + \left[ A + (L + \frac{1}{2} G) q^2 \right] \left( |\delta Q_{xz}|^2 + |\delta Q_{yz}|^2 \right) \]
\[ + \frac{\lambda^+}{v_+^2} |a_+ \delta \tilde{\rho} + \delta Q_{zz}|^2 + \frac{\lambda^-}{v_-^2} |a_- \delta \tilde{\rho} + \delta Q_{zz}|^2 \]

\[ \langle |\delta Q_{xy}|^2 \rangle \quad \langle |\delta Q_{zz}|^2 \rangle \quad \langle |\delta Q_{xz}|^2 \rangle \quad \langle |\delta Q_{yz}|^2 \rangle \]

FIG. 2. Nematic ($\delta Q_{ij}$) fluctuations of stiffer ($\epsilon = 4.926 k_B T$, left) and more flexible ($\epsilon = 1.642 k_B T$, right) chains with $N_s = 128$ (top) and $N_s = 4$ (bottom) segments, fitted with Eqs. (6) and (7) to extract the values of the parameters $A$, $L$ and $G$. The $\langle |\delta Q_{zz}|^2 \rangle$ curves are not fitted but are direct plots of the theoretical result Eq. (8).
Cross-correlation (density–nematic coupling)

Parameters from the fluctuations.
No direct fit.

As anticipated, the coupling gets stronger with chain stiffness and length.

This was measured (from the simulation). Can we predict the coupling strength?

Free energy of sources

\[ \rho_0 \partial_j \delta Q_{ij} + \frac{1}{2} \partial_i \delta \rho = \frac{3}{2} \frac{\delta g_i}{l_0} + \frac{3}{2} \rho_0 \delta k_i \]

Chain-end tangents: orientational entropy of independent vectors

\[ F(p_1) = -T S(p_1) = k_B T \int d\Omega \rho(\Omega) \ln \rho(\Omega) \]
\[ p(\Omega) = p_0 + \rho_1 \sqrt{\frac{3}{2} P_1(\cos \theta)} \]
\[ g = \rho_0^\pm \langle \cos \theta \rangle = \rho_0^\pm \sqrt{\frac{2}{3} p_1} \]

\[ \Delta f = \frac{1}{2} 2 \rho_0^\pm k_B T p_1^2 = \frac{1}{2} \frac{1}{\rho_0^\pm} g^2 \]

Chain curvature: curvature energy of independent joints as elements of curvature

\[ \Delta F_i = \frac{1}{2} \epsilon l_0^2 |k|^2 \]
\[ k^i = (u^{i+1} - u^i)/l_0 \]

\[ \Delta f(k) = \frac{1}{2} \frac{3 \epsilon l_0^2}{2 \rho_0} (\rho_0 k)^2 \]
Combined sources

To predict the strength of the coupling, $G$ …

… if we enforce the constraint by the penalty potential, rather than by introducing both source fields as new system variables.

\[
\Delta f(g, k) = \Delta f(g) + \Delta f(k) = \frac{1}{2} \left[ \frac{3k_B T}{\rho_0^{\pm}} g^2 + \frac{3}{2} \frac{\epsilon l_0^2}{\rho_0} (\rho_0 k)^2 \right]
\]

\[
\text{goal} \quad h = g + \rho_0 l_0 k \quad \Delta f(h) = \frac{1}{2} G h^2
\]

We average the free energy over all possible $g$ and $k$ that give a total source $h$.

\[
Z = \int \int d^3g \, d^3k \mathcal{P}(g)\mathcal{P}(k) \delta(g + \rho_0 l_0 k - h)
\]

\[
\text{partition function,} \quad \Delta f(h) = -(1/V_1) \frac{d}{d\beta} (\ln Z)
\]

\[
\Delta \bar{f}(h) = \frac{3k_B T}{2} \left( \frac{1}{V_1} + \frac{h^2}{\rho_0^{\pm} + 2k_B T \rho_0/\epsilon} \right)
\]

\[
G = \frac{3k_B T}{\rho_0^{\pm} + 2k_B T \rho_0/\epsilon}
\]
**Induced orientational order**

Coupled density – nematic fluctuations: efficient way to determine the parameters of realistic, polymer-specific macroscopic models!

Once known, the response to a given concentration field is known: induced orientational order.

\[
f = \frac{1}{2} B \left( \frac{\delta \rho}{\rho_0} \right)^2 + \frac{1}{2} B' \left( \frac{\partial_i \delta \rho}{\rho_0} \right)^2 + \frac{1}{2} A (\delta Q_{ij})^2 + \frac{1}{2} L (\partial_k \delta Q_{ij})^2 + \frac{1}{2} G \left( \frac{2}{3} \rho_0 l_0 \right)^2 \left[ \partial_j \delta Q_{ij} + \frac{1}{2} \partial_i \left( \frac{\delta \rho}{\rho_0} \right) \right]^2
\]

Leads e.g. to osmotic-stress-induced optical birefringence.

\[
\partial_z^2 Q_{zz} \approx -\frac{1}{2} \frac{G' \rho}{L + G' \rho^2} \partial_z^2 \delta \rho
\]

\[
G' = G \left( \frac{2}{3} l_0 \right)^2
\]

e.g., solution for diffusive field around a bubble:

\[
\delta Q_{rr}(r) \approx -\frac{G' \rho_0}{6L + G' \rho_0^2} \frac{\Phi}{4\pi Dr}
\]

\[
\varepsilon_{ij} = \varepsilon \delta_{ij} + \frac{2}{3} \varepsilon_\alpha \delta Q_{ij}
\]

Resembles *photoelasticity* (stress-optic law) in dielectric solids, *flow-induced birefringence* in polymeric fluids, but takes place in a **static polymeric liquid**.
Density--nematic coupling in isotropic linear polymers

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Linear polymers and other connected "line liquids" exhibit a coupling on a macroscopic level that gives rise to a Meyer-de Gennes vectorial conservation law. Melts/solutions exhibit fluctuations of the density and of the nematic order parameter in linear polymer liquids, leading to a tensorial conservation law. Fluctuations couple density and nematic order, already in the orientational phase transition. This coupling implies that a spatial variation of the nematic order and thereby an acoustic or osmotic optical birefringence validates the theoretical conceptions by performing detailed Monte Carlo simulations with variable length and flexibility, and comparing the numerically determined results with the macroscopic theory. The methodology drawn sets forth a means of simulations to yield realistic collection models of realistic polymers.

\[
\partial_j \left[ \rho \left( Q_{ij} + \frac{1}{2} \delta_{ij} \right) \right] = \frac{3}{2} \frac{1}{\ell_0} g_i + \frac{3}{2} \rho k_i
\]

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