Viscosities of Smectic-A Phases ...and molecular rotation, possibly

Michael P Allen

H H Wills Physics Laboratory, Royal Fort, Tyndall Avenue, Bristol and Department of Physics, University of Warwick, Coventry

Brunel, 17 January 2020

Collaboration





Anja Humpert Warwick

Junju Mu Manchester





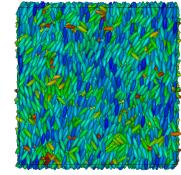
Daniel Corbett Andrew Masters Manchester Manchester

Introduction

Smectic-A viscosity

Rotational long-time tails

Nematic liquid crystals Orientational order



n

Liquid-like:

- positional order,
- short-ranged.

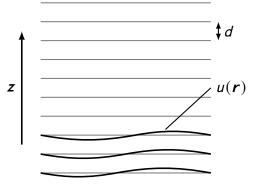
Crystal-like:

- orientational order,
- long-ranged,
- director n,
- order parameter *S*.
- Ordering is second-rank, so $n \equiv -n$.
- Global rotation of *n* costs zero free energy (but is slow).
- Director fluctuations $n(r) = n_0 + \delta n(r)$ are elastic.
- They cost free energy \propto squared gradient(s) of n(r).
- Thermal fluctuations, Fourier modes $\langle |\tilde{n}(\mathbf{k})|^2 \rangle \propto k^{-2}$.

Smectic-A liquid crystals

Positional and orientational order

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- Long-ranged positional order in z: layers.
- Short-ranged positional order in *x*, *y*: liquid-like.
- Long-ranged orientational order, perpendicular to layers.
- Symmetry: $z \equiv -z$.

Smectic-A elasticity

Free energy involves compression elasticity and curvature

$$\mathcal{F} = \frac{1}{2} \int d^3 \boldsymbol{r} B \big[\partial_z u(\boldsymbol{r}) \big]^2 + K_1 \big[\nabla_{\perp}^2 u(\boldsymbol{r}) \big]^2,$$

where $\nabla_{\perp}^2 = \partial_x^2 + \partial_y^2$. Setting $k_{\perp}^2 = k_x^2 + k_y^2$

$$\mathcal{F} = \frac{1}{2} \int \frac{\mathrm{d}^3 \mathbf{k}}{8\pi^3} \left(Bk_z^2 + K_1 k_\perp^4 \right) |\tilde{u}(\mathbf{k})|^2$$
$$\langle |\tilde{u}(\mathbf{k})|^2 \rangle = \frac{k_\mathrm{B}T}{Bk_z^2 + K_1 k_\perp^4}.$$

Director *n* relaxes towards layer normal on microscopic timescale

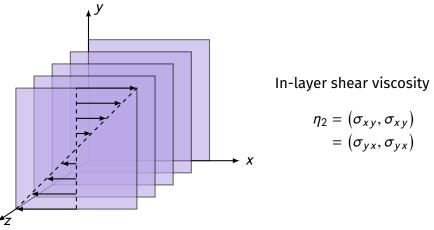
$$\boldsymbol{n} = \boldsymbol{z} + \delta \boldsymbol{n}(\boldsymbol{r}), \qquad \delta \boldsymbol{n}(\boldsymbol{r}) \propto \boldsymbol{\nabla}_{\perp} \boldsymbol{u}(\boldsymbol{r}),$$
$$\langle |\tilde{\boldsymbol{n}}(\boldsymbol{k})|^2 \rangle \propto \frac{k_{\rm B} T k_{\perp}^2}{B k_z^2 + K_1 k_{\perp}^4} = \frac{k_{\rm B} T}{B (k_z / k_{\perp})^2 + K_1 k_{\perp}^2}.$$

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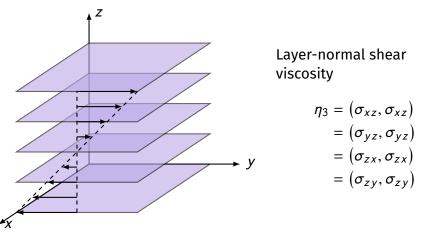
Smectic-A viscosity



We adopt a shorthand for the Green-Kubo integral

$$(\sigma,\sigma) = \frac{V}{k_{\rm B}T} \int_0^\infty {\rm d}t \langle \sigma(0)\sigma(t) \rangle$$

Smectic-A viscosity



Flows in the *z* direction would quickly leave the linear regime, and cause layer disruption.

In-layer bulk viscosity

$$\eta_4 = (\sigma_{xx}, \sigma_{xx}) = (\sigma_{yy}, \sigma_{yy})$$

Layer-normal bulk viscosity

$$2\eta_1 + \eta_2 = (\sigma_{zz} - \sigma_{xx}, \sigma_{zz} - \sigma_{xx}) = (\sigma_{zz} - \sigma_{yy}, \sigma_{zz} - \sigma_{yy})$$

In-layer-layer-normal cross term viscosity

$$\eta_5 = (\sigma_{zz}, \sigma_{xx}) = (\sigma_{zz}, \sigma_{yy})$$

All the diagonal elements have a pressure term subtracted, that is $\sigma_{\alpha\alpha}$ is short for $\sigma_{\alpha\alpha} - \langle \sigma_{\alpha\alpha} \rangle$.

Nonlinear coupling — elasticity & dynamics

Applying a tension in the *z*-direction can induce undulations (as an alternative to uniform increase of the layer spacing). The free energy is modified to account for this:

$$\mathcal{F} = \frac{1}{2} \int d^3 \boldsymbol{r} B \left[\partial_z u(\boldsymbol{r}) - \frac{1}{2} |\boldsymbol{\nabla}_{\perp} u|^2 \right]^2 + K_1 \left[\boldsymbol{\nabla}_{\perp}^2 u(\boldsymbol{r}) \right]^2$$

and in particular there is a cross-term $\propto B(\partial_z u) |\nabla_{\perp} u|^2$.

- This generates a nonlinear stress-strain relation.
- Can be approximated as a renormalization $B \rightarrow B^{\text{eff}}(k)$.
- ▶ $B^{\text{eff}} \rightarrow 0$ as $k \rightarrow 0$. Dramatic consequences!

 K_1 is also renormalized, but is predicted to increase.

PG de Gennes, J Prost, The physics of liquid crystals (Oxford, 1993) Chap. 8.

- This also affects the hydrodynamics.
- Physically, the free energy cost of the undulation mode becomes very small at long wavelengths.

The result is a renormalization of the viscosity coefficients.

Do the viscosities exist?

Oh no they don't!

GF Mazenko, S Ramaswamy, J Toner. Phys. Rev. Lett., **49,** 51 (1982).

GF Mazenko, S Ramaswamy, J Toner. Phys. Rev. A, **28**, 1618 (1983). For $k_z \equiv 0$,

• η_1, η_4, η_5 , and also η_2 , are predicted to diverge as ω^{-1} .

• η_3 (layer-normal shear) is predicted to diverge as $\ln \omega$. For $\omega \equiv 0$, divergence as k_z^{-1} is also predicted. η_2 and η_3 predicted to show non-Newtonian behaviour.

Oh yes they do!

ST Milner, PC Martin. *Phys. Rev. Lett.*, **56**, 77 (1986). This paper contends that cancellations of terms invalidate all the previous results, and that the viscosities do not diverge.

Simulated system

Gay–Berne potential, elongation $\kappa = 4.4$. Known to have a stable smectic-A phase.

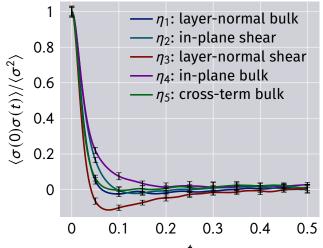
JG Gay, BJ Berne. J. Chem. Phys., **74,** 3316 (1981).

- E de Miguel et al. J. Chem. Phys., **121,** 11183 (2004).
- T = 1.4, ρ = 0.19.
- Order parameter S = 0.84.
- $N = 405\,000, \Delta t = 0.001.$
- 10^7 steps equilibration $NP_{\parallel}P_{\perp}T$.
- 10^6 steps production *NVT* or *NVE*.

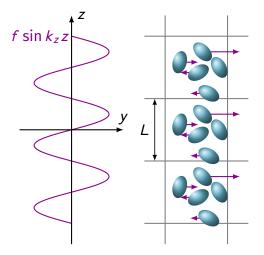
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Green-Kubo stress correlations

Results averaged over five independent runs



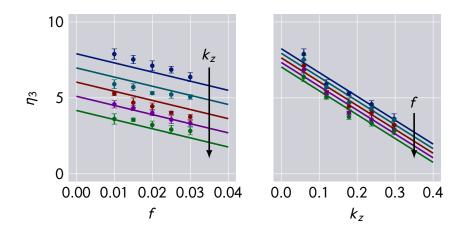
Non-equilibrium simulations



We have calculated η_3 by applying a steady force, sinusoidally varying in z, to each particle, and measuring the induced velocity profile.

$$f_{iy}^{\text{ext}} = f \sin(2\pi n z_i/L)$$
$$= f \sin k_z z_i$$
$$\overline{v_y(z)} \approx \frac{\rho}{k_z^2 \eta_3(k_z)} f \sin k_z z$$

Non-equilibrium simulations



Five values of k_z were combined with five amplitudes f, and the measured viscosity seems to depend (roughly) linearly on both quantities. There is no sign of a divergence.

- Although the equilibrium Green–Kubo correlation functions are limited by noise at long times, we see no evidence of a divergence in their integrals, i.e. for k = 0 as ω → 0.
- The nonequilibrium simulations conducted so far also have provided no evidence of divergence for $\omega = 0$ as $k \rightarrow 0$.
- Continuing equilibrium and nonequilibrium simulations will probe the (k, ω) dependence.
- E.g. SLLOD simulations, steady and time-dependent.
- Constant- σ_{xy} simulations might reveal Bingham plasticity. This is work in progress, so the conclusions may yet change.

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Orientational correlation functions

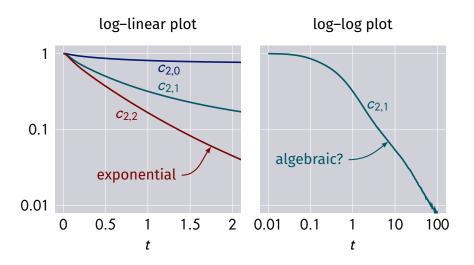
$$c_{\ell,m}(t) \propto \left\langle Y_{-m}^{\ell}(0) Y_{m}^{\ell}(t) \right\rangle$$

$$Y_m^\ell(t)=Y_m^\ell\big(\theta(t),\phi(t)\big)$$

- θ , ϕ are polar angles of a single molecule;
- $Y_m^{\ell}(\theta, \phi)$ is a spherical harmonic function;
- we average over all (equivalent) molecules.

Some $c_{\ell,m}$ components are affected by coupling to the director.

Nematic phase simulations



Nematic phase

AJ Masters, Mol. Phys., **95,** 251 (1998).

Simplified version of the theory. $c_{2,1}(t)$ is the correlation function of a second-rank orientational tensor component $Q_{xz}(u)$ for an individual 'tagged' molecule. If $\tilde{n}_x(\mathbf{k})$ is the director fluctuation

$$Q_{xz} \propto \sum_{\boldsymbol{k}} \tilde{n}_{x}(\boldsymbol{k}) \tilde{\rho}(-\boldsymbol{k})$$

where $\tilde{\rho}(\mathbf{k})$ is the Fourier transform of the tagged particle density. Making the Gaussian (factorization) approximation

$$\langle Q_{xz}(0)Q_{xz}(t)\rangle \propto \sum_{k} \langle \tilde{n}_{x}(-k,0)\tilde{n}_{x}(k,t)\rangle \langle \tilde{\rho}(-k,0)\tilde{\rho}(k,t)\rangle$$

 $\tilde{n}_{x}(-k,0)\tilde{n}_{x}(k,t)\rangle \propto k^{-2} \exp(-\lambda k^{2}t), \text{ for nematic phase,}$

where λ is a combination of hydrodynamic transport coefficients.

Nematic director coupling

$$c_{2,1}(t) \propto \int_0^\infty 4\pi k^2 \mathrm{d}k \ k^{-2} \mathrm{e}^{-\lambda k^2 t} \propto \int_0^\infty \mathrm{d}k \ \mathrm{e}^{-\lambda k^2 t} \propto t^{-1/2}.$$

In periodic boundaries $k_{\min} = 2\pi/L$, not zero, and we define

$$t_{\max} = \frac{1}{\lambda k_{\min}^2} \propto L^2.$$

Expect a finite size cutoff of the tail, for $t > t_{max}$. Various versions of the Gay–Berne potential, elongation $\kappa = 3$.

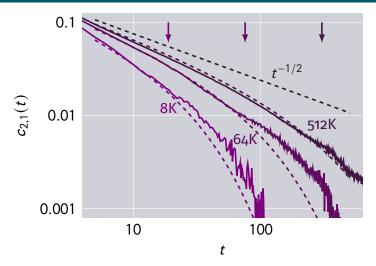
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$$10^6$$
 steps of $\Delta t = 0.002$,

▶ *N* = 8 000, 64 000, 512 000,

 $\blacktriangleright L \rightarrow 2L \rightarrow 4L.$

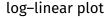
Finite system size effects

Gay–Berne potential, nematic phase, N = 8K, 64K, 512K

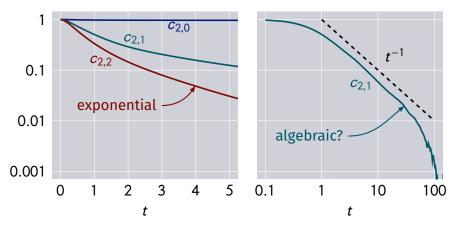


A Humpert, AJ Masters, MP Allen. Orientational dynamics in nematic liquid crystals. *Europhys. J. Spec. Topics*, **225**, 1723 (2016).

Gay-Berne potential, smectic phase, N = 405K



log-log plot



Smectic phase

A Poniewierski et al. Phys. Rev. E, **58,** 2027 (1998).

$$\langle \tilde{u}(-\boldsymbol{k},0)\tilde{u}(\boldsymbol{k},t)\rangle \propto \frac{k_{\rm B}T}{Bk_z^2 + K_1k_{\perp}^4} \exp[-t/\tau(\boldsymbol{k})]$$

$$c_n(\boldsymbol{k},t) = \langle \tilde{n}_x(-\boldsymbol{k},0)\tilde{n}_x(\boldsymbol{k},t)\rangle \propto \frac{k_{\rm B}Tk_{\perp}^2}{Bk_z^2 + K_1k_{\perp}^4} \exp[-t/\tau(\boldsymbol{k})],$$

$$\tau(\boldsymbol{k}) = \frac{\eta_3 k_{\perp}^2}{Bk_z^2 + K_1k_{\perp}^4}.$$

If we just pay attention to *d* and *L* in the *z*-direction,

$$c_{2,1}(t) \propto \int_{2\pi/L}^{2\pi/d} \mathrm{d}k_z \int_0^\infty 2\pi k_\perp \mathrm{d}k_\perp c_n(\boldsymbol{k}, t).$$

The integral over k_{\perp} may be evaluated (Daniel Corbett) giving a modified Bessel function of the second kind

$$c_{2,1}(t) \propto t^{-1} \int_{k_{\min}\lambda t}^{k_{\max}\lambda t} dz \,\mathcal{K}_{0}(2z) \quad \text{where} \begin{cases} k_{\min} &= 2\pi/L \\ k_{\max} &= 2\pi/d \\ \lambda &= \sqrt{BK_{1}}/\eta_{3} \end{cases}$$
$$\propto t^{-1} \quad \text{when } k_{\min} \to 0, \, k_{\max} \to \infty$$

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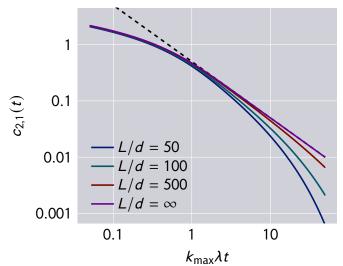
If we take account of d and L, we shall find t^{-1} behaviour for

$$\frac{1}{k_{\max}\lambda} \ll t \ll \frac{1}{k_{\min}\lambda}$$
 or $\frac{d}{2\pi\lambda} \ll t \ll \frac{L}{2\pi\lambda}$.

The remaining integral can actually be done analytically.

Smectic phase

Predicted behaviour: fix layer spacing d and vary system size L.



Conclusions

- Good evidence for algebraic long-time tails $\propto t^{-1/2}$ in some molecular rotational correlation functions in nematics.
- Due to coupling with director fluctuations.
- We see the expected finite-size effects.
- A Humpert, AJ Masters, MP Allen. Orientational dynamics in nematic liquid crystals. *Europhys. J. Spec. Topics*, **225**, 1723 (2016).
- Some evidence of algebraic long-time tails ∝ t⁻¹ in some molecular rotational correlation functions in smectics.
- Due to coupling with layer undulations.
- We have not carried out studies at different system sizes.
- Theoretical analysis for $L/d \approx 50$ does not exactly agree with extent of algebraic tail.

This is work in progress, so the conclusions may yet change.