Viscosities of Smectic-A Phases

...and molecular rotation, possibly

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Collaboration

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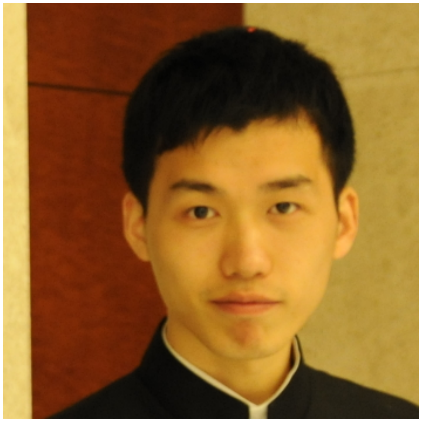

Junju Mu
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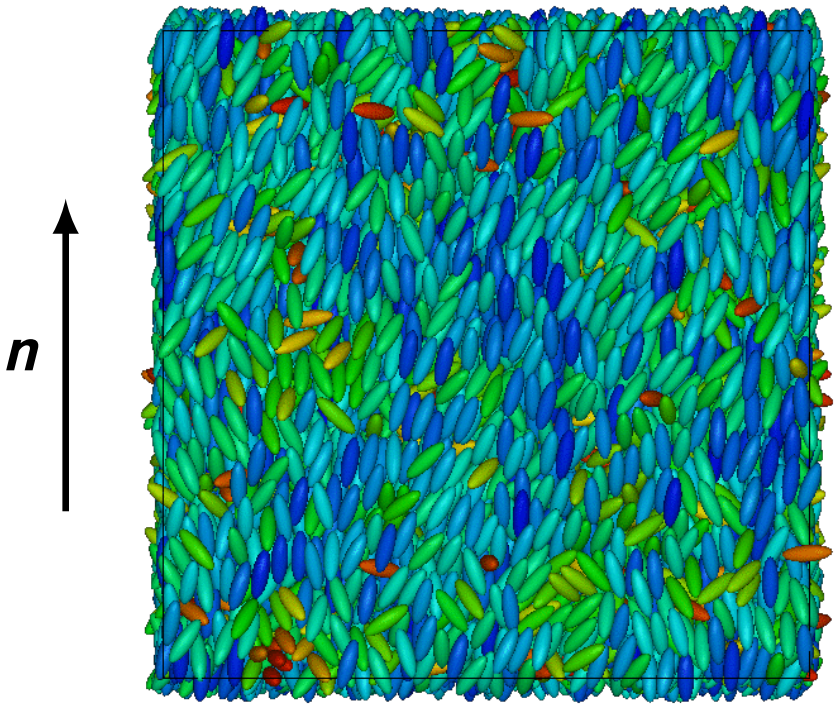
Outline

Nematic liquid crystals

Orientational order



Liquid-like:

- positional order,
- short-ranged.

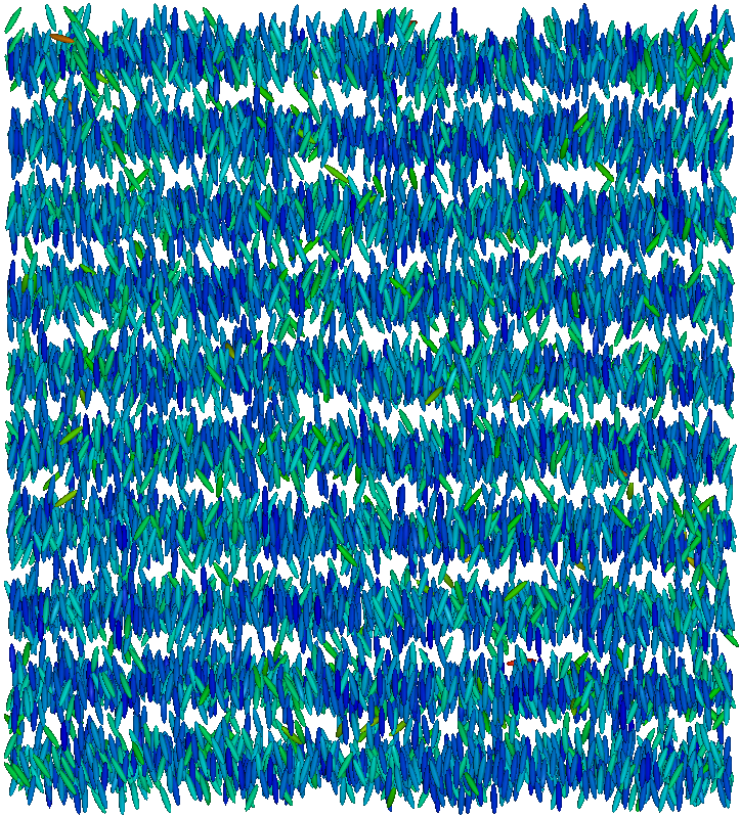
Crystal-like:

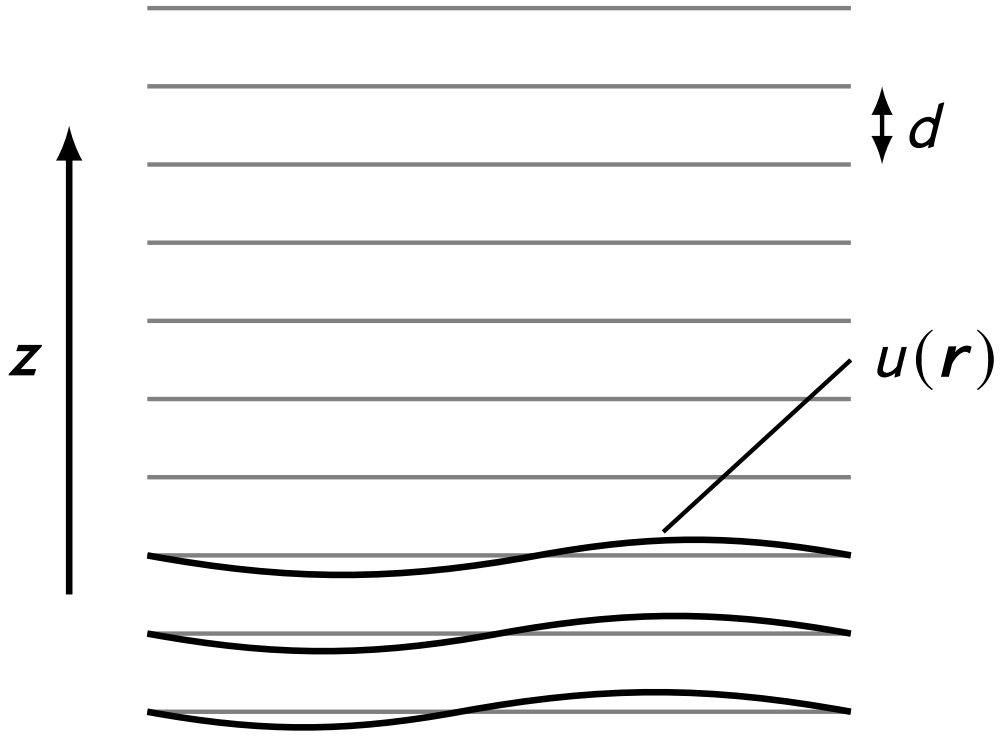
- orientational order,
- long-ranged,
- director $\boldsymbol{n}$,
- order parameter S.

- Ordering is second-rank, so $\boldsymbol{n} \equiv -\boldsymbol{n}$.
- Global rotation of $\boldsymbol{n}$ costs zero free energy (but is slow).
- Director fluctuations $\boldsymbol{n}(\boldsymbol{r}) = \boldsymbol{n}_0 + \delta\boldsymbol{n}(\boldsymbol{r})$ are elastic.
- They cost free energy $\propto$ squared gradient(s) of $\boldsymbol{n}(\boldsymbol{r})$.
- Thermal fluctuations, Fourier modes $\left\langle \left| \tilde{n}(\boldsymbol{k}) \right|^2 \right\rangle \propto k^{-2}$.

Smectic-A liquid crystals

Positional and orientational order





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

Smectic-A elasticity

Free energy involves compression elasticity and curvature

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

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

$$\mathcal{F} = \tfrac{1}{2} \int \frac{\mathrm{d}^3\boldsymbol{k}}{8\pi^3}\left(Bk_z^2 + K_1 k_\perp^4\right)|\tilde{u}(\boldsymbol{k})|^2$$

$$\langle|\tilde{u}(\boldsymbol{k})|^2\rangle = \frac{k_\mathrm{B}T}{Bk_z^2 + K_1 k_\perp^4}.$$

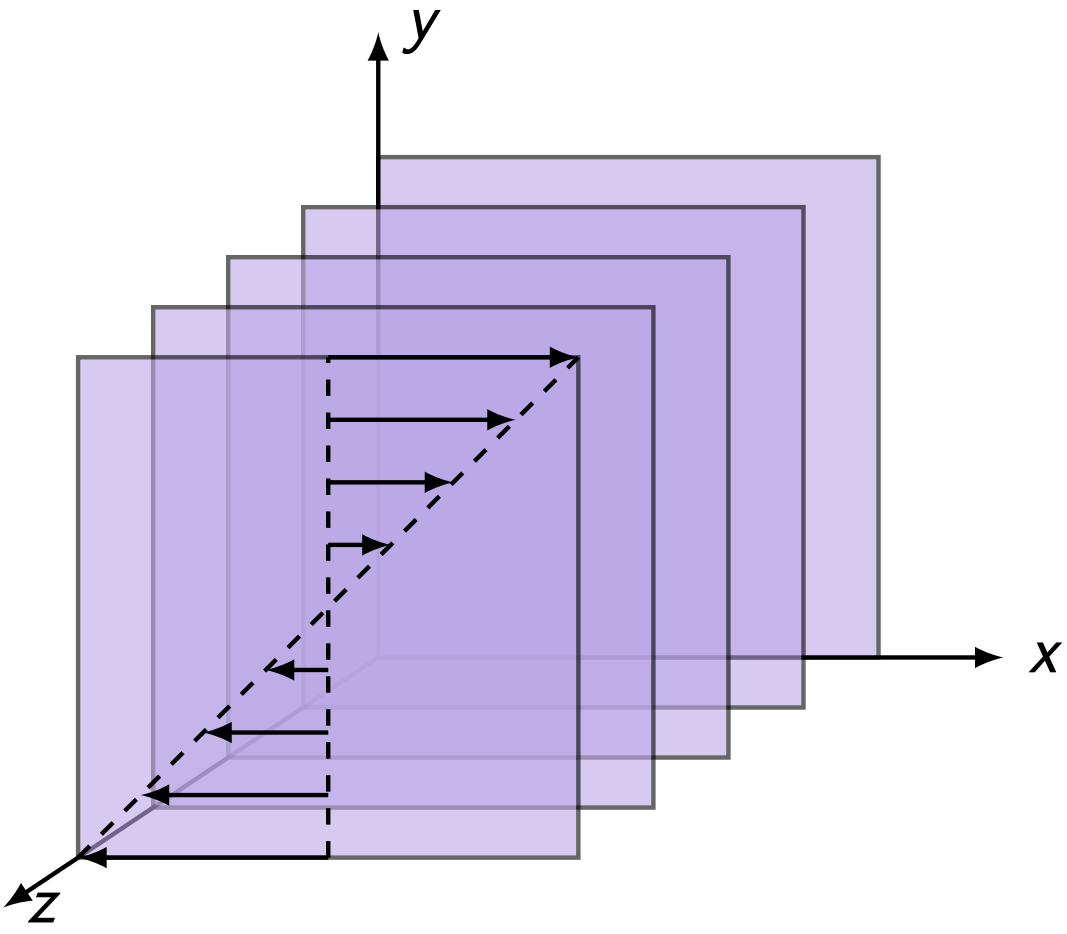
Director $\boldsymbol{n}$ relaxes towards layer normal on microscopic timescale

$$\boldsymbol{n} = \boldsymbol{z} + \delta\boldsymbol{n}(\boldsymbol{r}), \qquad \delta\boldsymbol{n}(\boldsymbol{r}) \propto \boldsymbol{\nabla}_\perp u(\boldsymbol{r}),$$

$$\langle|\tilde{\boldsymbol{n}}(\boldsymbol{k})|^2\rangle \propto \frac{k_\mathrm{B}T k_\perp^2}{Bk_z^2 + K_1 k_\perp^4} = \frac{k_\mathrm{B}T}{B(k_z/k_\perp)^2 + K_1 k_\perp^2}.$$

Outline

Smectic-A viscosity



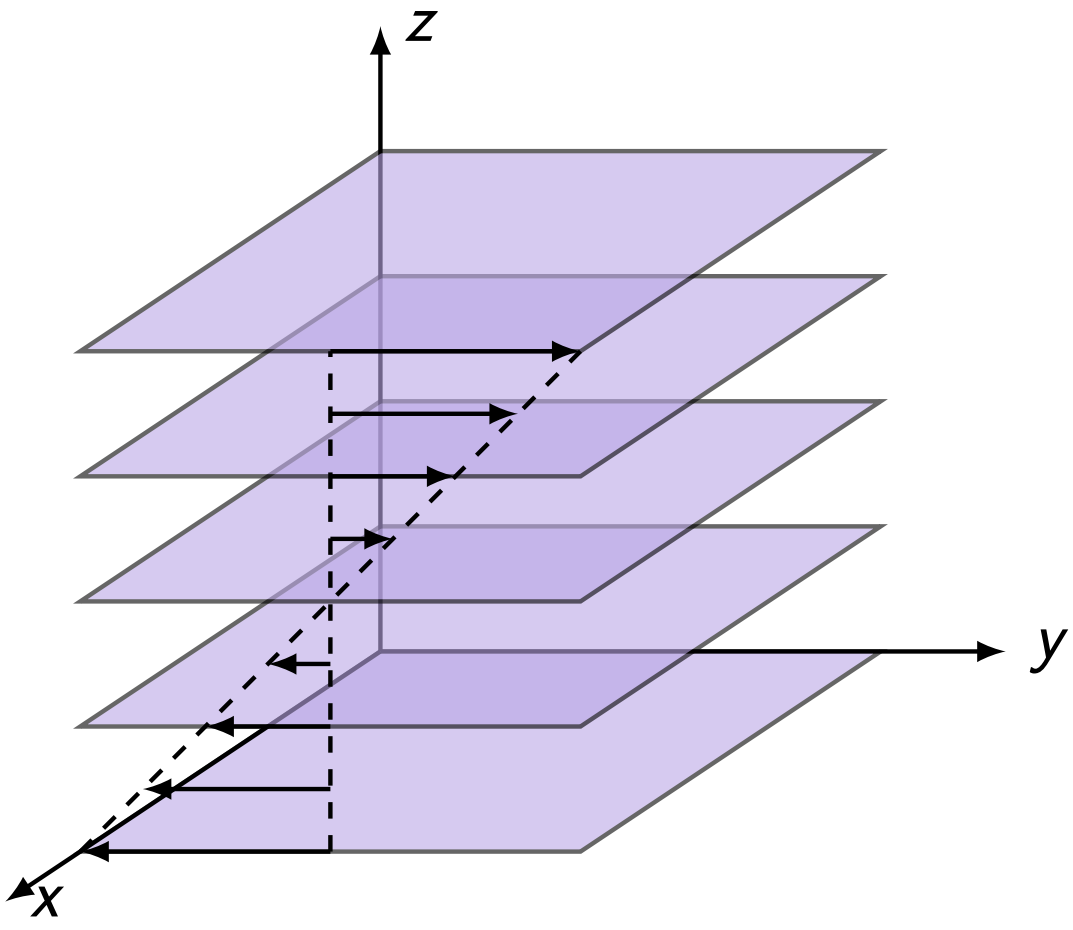
In-layer shear viscosity

$$\eta_2 = (\sigma_{xy}, \sigma_{xy}) = (\sigma_{yx}, \sigma_{yx})$$

We adopt a shorthand for the Green–Kubo integral

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

Smectic-A viscosity



Layer-normal shear viscosity

$$\begin{aligned}\eta_3 &= (\sigma_{xz}, \sigma_{xz}) \\ &= (\sigma_{yz}, \sigma_{yz}) \\ &= (\sigma_{zx}, \sigma_{zx}) \\ &= (\sigma_{zy}, \sigma_{zy})\end{aligned}$$

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

Smectic-A viscosity

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:

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

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

- This generates a nonlinear stress–strain relation.
- Can be approximated as a renormalization $B \longrightarrow B^{\mathrm{eff}}(k)$.
- $B^{\mathrm{eff}} \longrightarrow 0$ as $k \longrightarrow 0$. 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.

The key question

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.

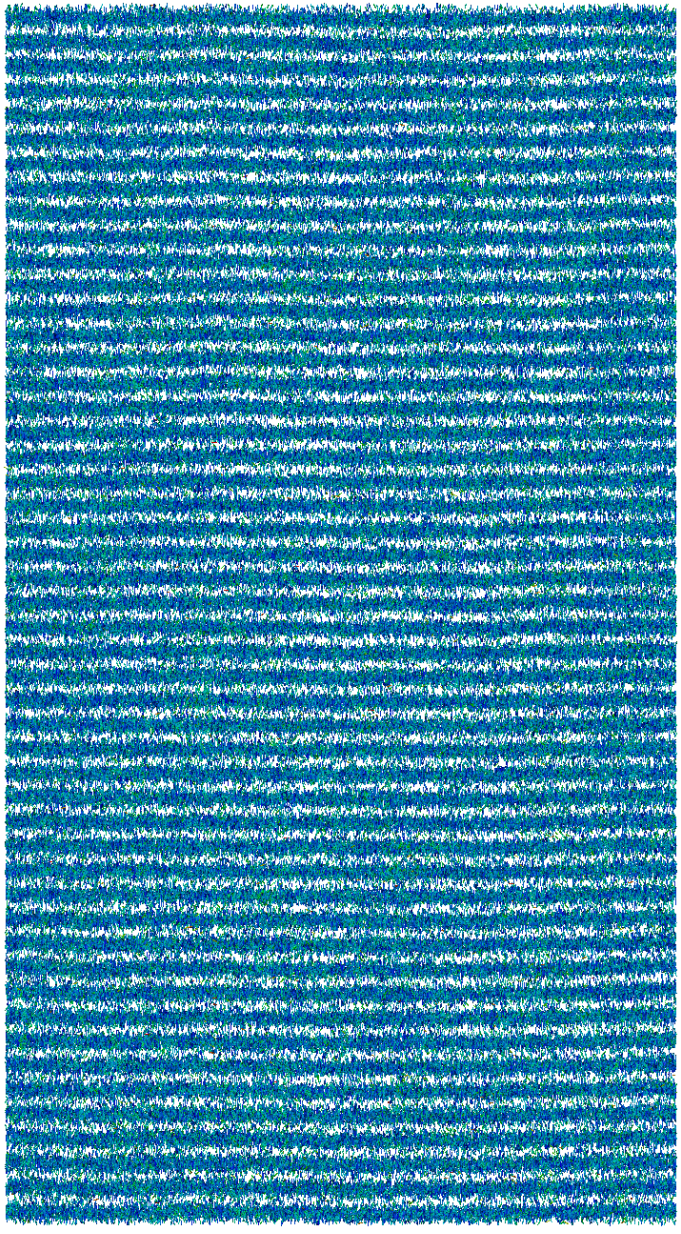
Simulated system

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).

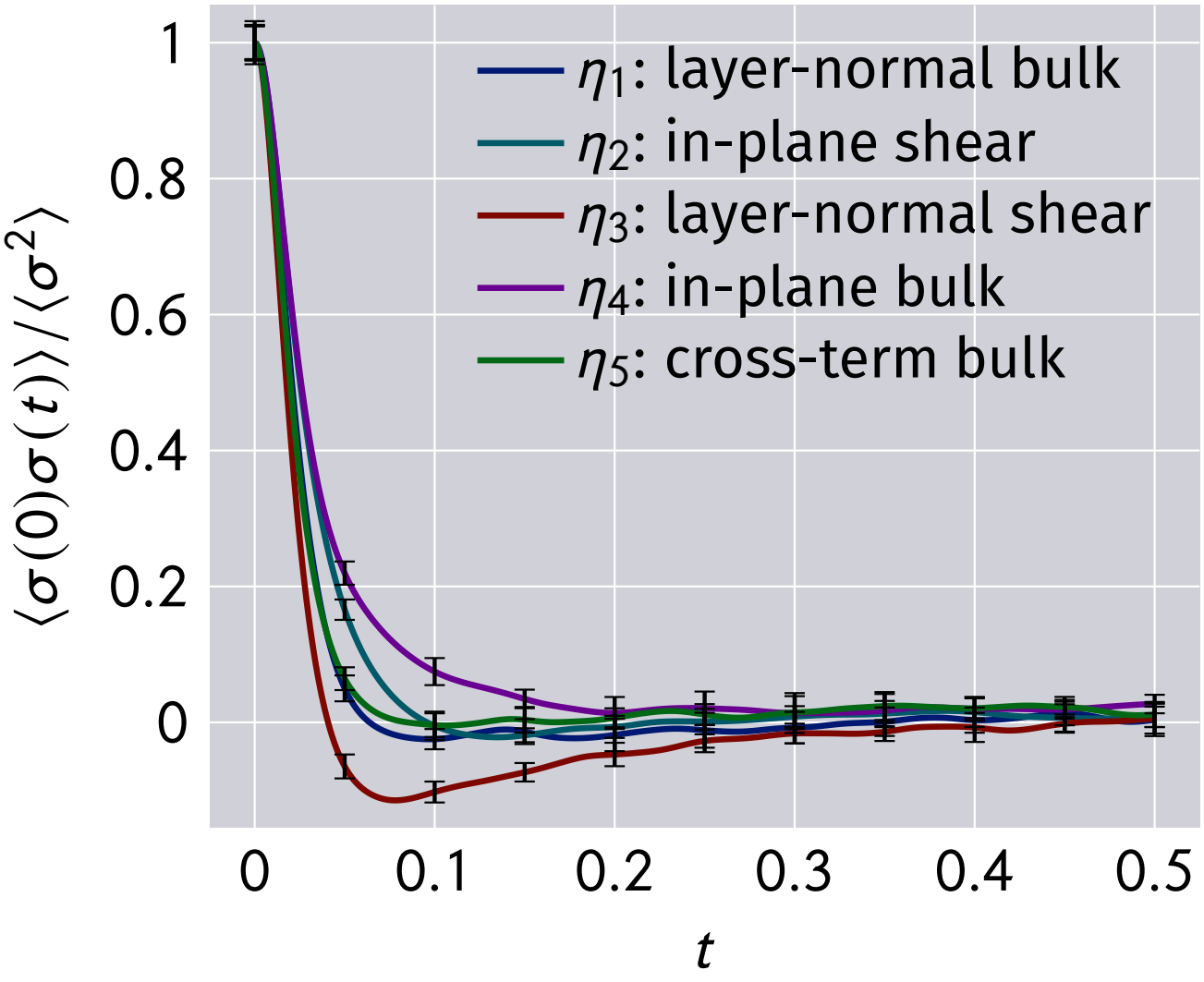

E de Miguel et al.
J. Chem. Phys., **121,** 11183 (2004).

- $T = 1.4, \rho = 0.19$.
- 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.

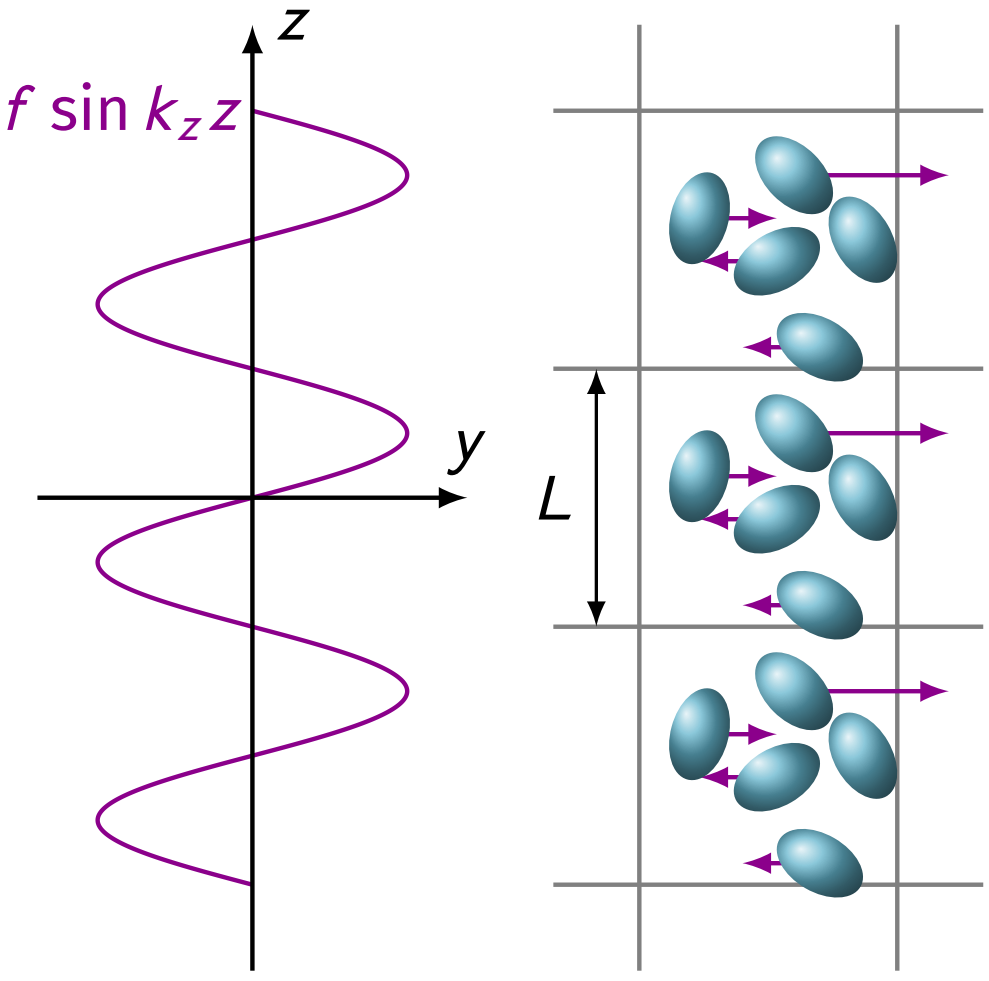


Green–Kubo stress correlations

Results averaged over five independent runs



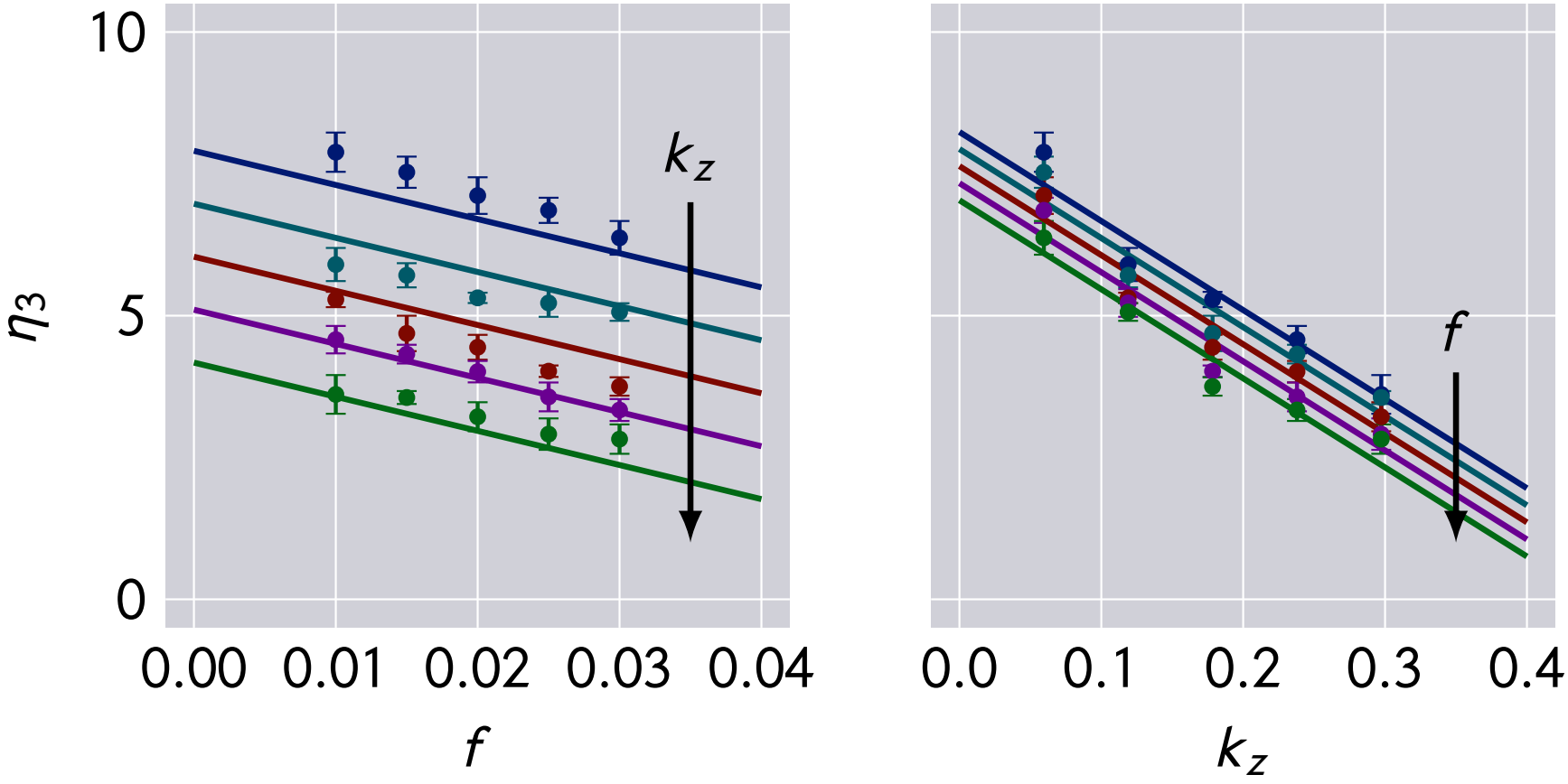
Non-equilibrium simulations



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.

Conclusions

- 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 $\omega \longrightarrow 0$.
- The nonequilibrium simulations conducted so far also have provided no evidence of divergence for $\omega = 0$ as $k \longrightarrow 0$.
- 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.

Outline

Rotational dynamics

Single-particle motion

Orientational correlation functions

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

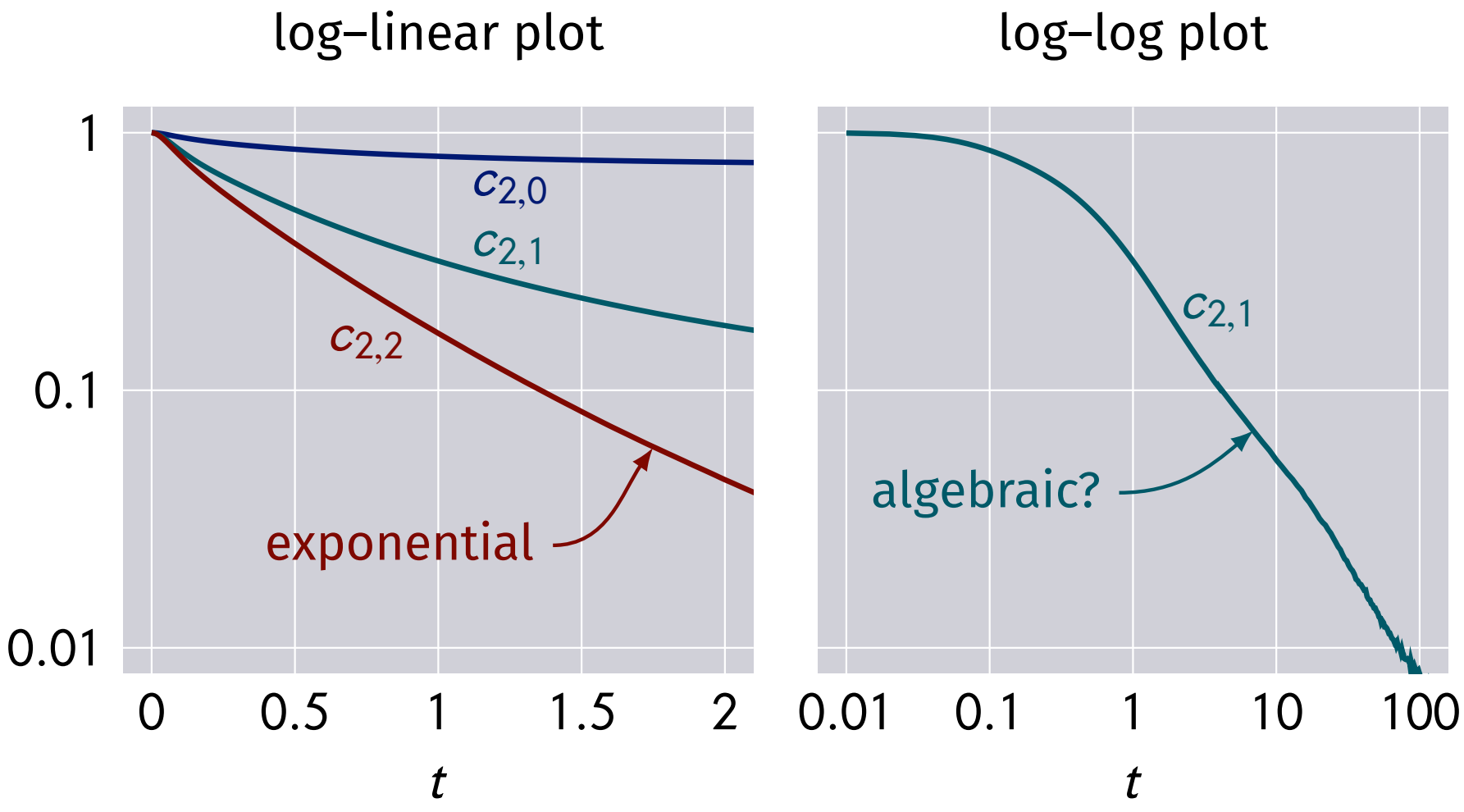
$$Y^{\ell}_{m}(t) = Y^{\ell}_{m}\big(\theta(t), \phi(t)\big)$$

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

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

Rotational dynamics

Nematic phase simulations



Rotational dynamics

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 $Q_{xz}(\boldsymbol{u})$ for an individual 'tagged' molecule. If $\tilde{n}_x(\boldsymbol{k})$ is the director fluctuation

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

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

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

$$\langle \tilde{n}_x(-\boldsymbol{k},0)\tilde{n}_x(\boldsymbol{k},t)\rangle \propto k^{-2}\exp(-\lambda k^2 t), \quad \text{for nematic phase,}$$

where λ is a combination of hydrodynamic transport coefficients.

Rotational dynamics

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

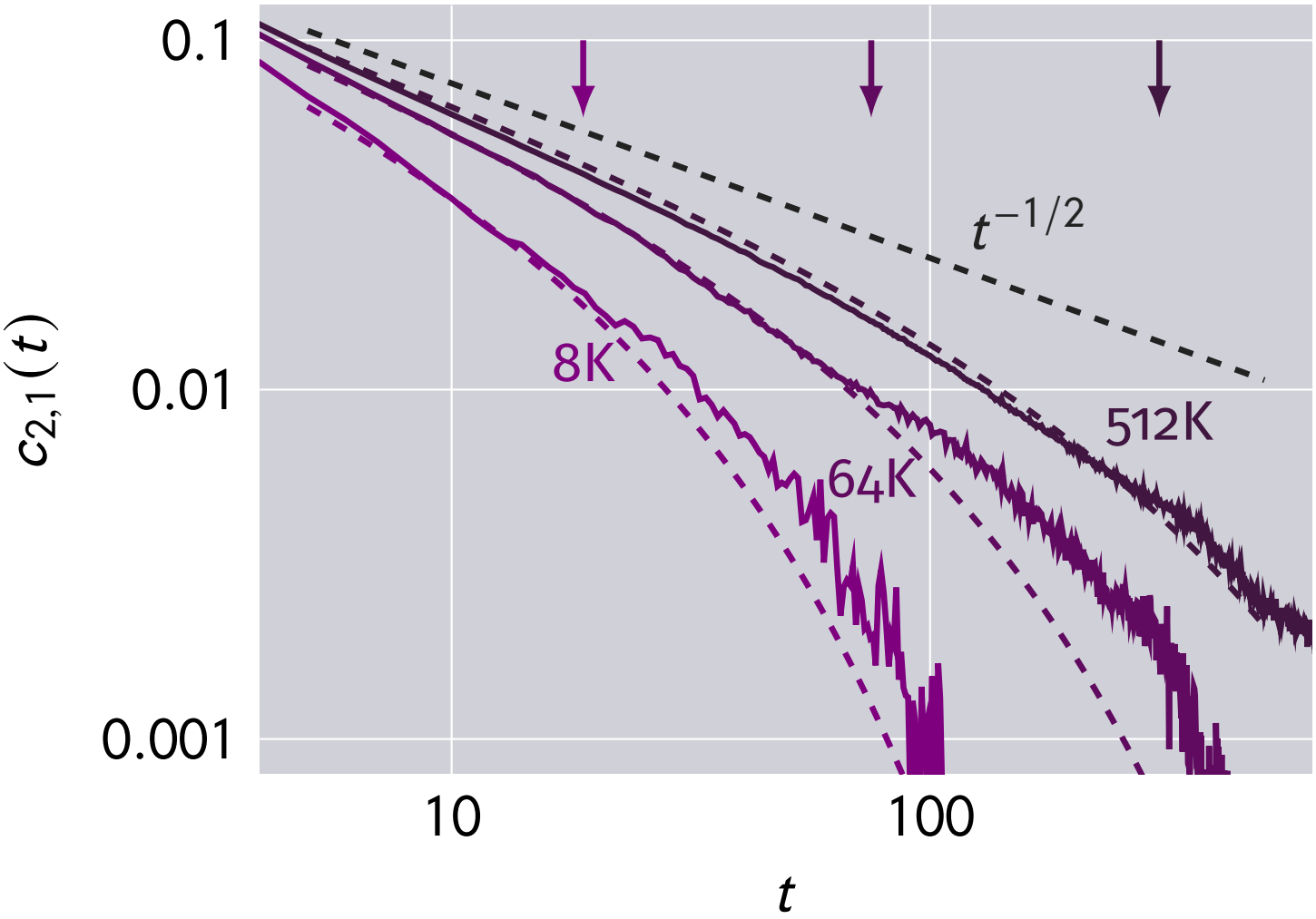
$$t_{\mathrm{max}} = \frac{1}{\lambda k_{\mathrm{min}}^2} \propto L^2.$$

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

- 10^6 steps of $\Delta t = 0.002$,
- $N = 8\,000, 64\,000, 512\,000$,
- $L \to 2L \to 4L$.

Finite system size effects

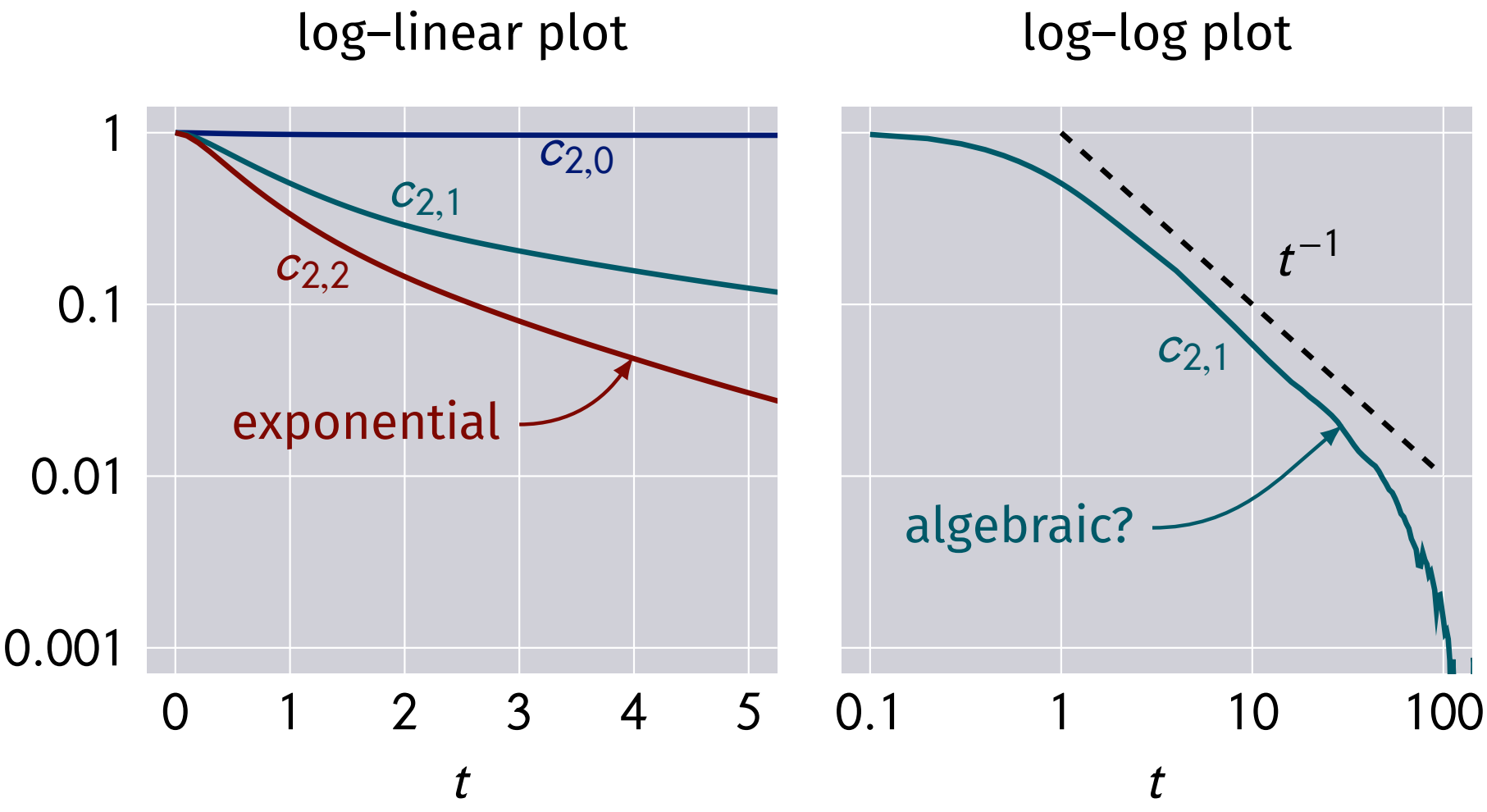
Gay–Berne potential, nematic phase, N = 8K, 64K, 512K



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

Rotational dynamics

Gay–Berne potential, smectic phase, $N = 405$K



Rotational dynamics

Smectic phase

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

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

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

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

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

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

Rotational dynamics

Smectic phase

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

$$c_{2,1}(t) \propto t^{-1} \int_{k_{\min}\lambda t}^{k_{\max}\lambda t} \mathrm{d}z\, \mathcal{K}_0(2z) \quad \text{where} \begin{cases} k_{\min} & = 2\pi/L \\ k_{\max} & = 2\pi/d \\ \lambda & = \sqrt{BK_1}/\eta_3 \end{cases}$$

$$\propto t^{-1} \quad \text{when } k_{\min} \to 0,\ k_{\max} \to \infty$$

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

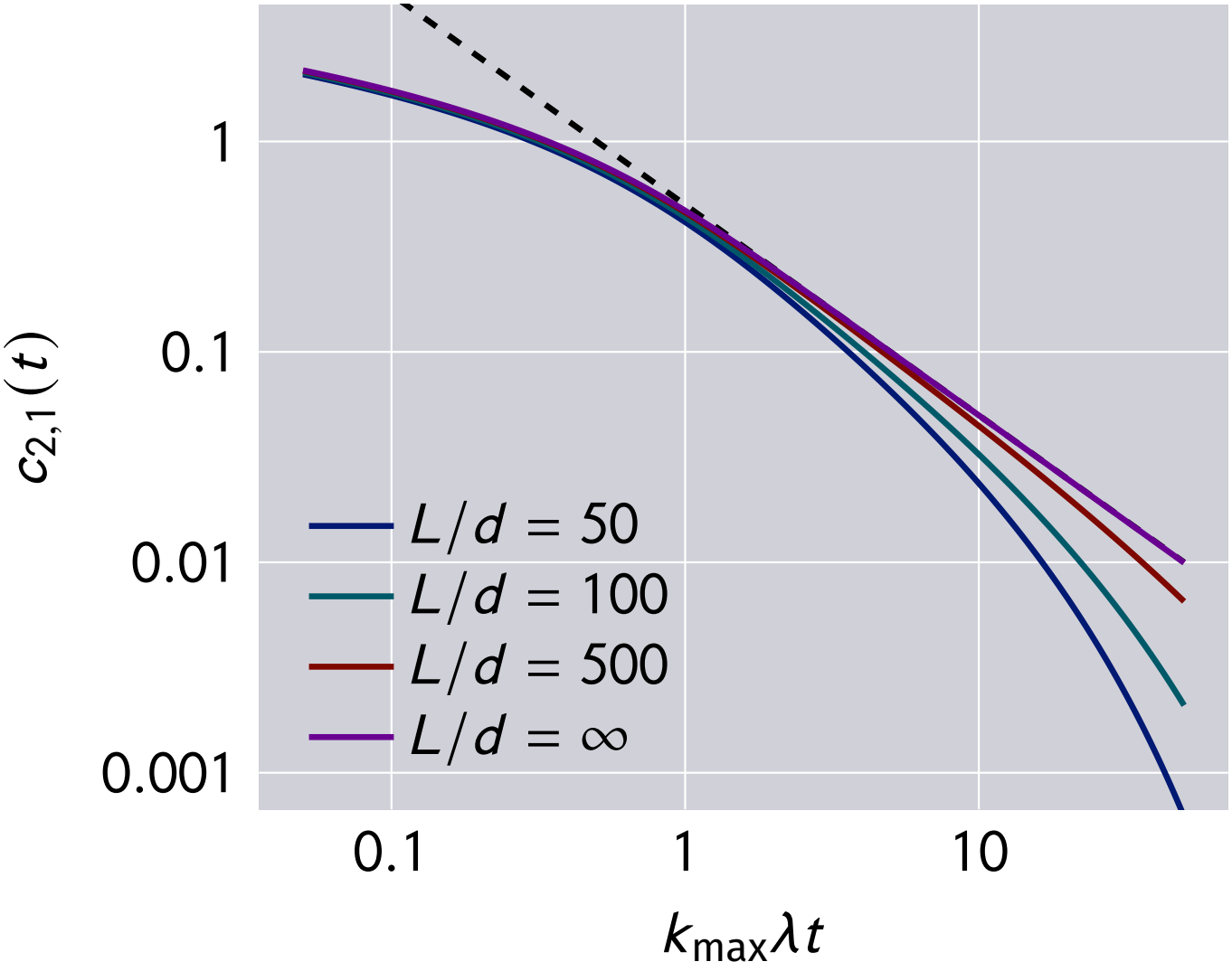
$$\frac{1}{k_{\max}\lambda} \ll t \ll \frac{1}{k_{\min}\lambda} \qquad \text{or} \qquad \frac{d}{2\pi\lambda} \ll t \ll \frac{L}{2\pi\lambda}.$$

The remaining integral can actually be done analytically.

Rotational dynamics

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 $\propto t^{-1}$ 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.