A Nematic Theory For Non Spherical Rarefied Gas

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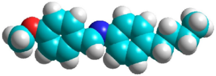
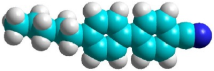
The Molecules

Our ultimate goal is to understand properties of special molecules such as MBBA and 5CB, which are well known to establish a liquid crystal mesophase under appropriate conditions.

- Molecules can be regarded as **slender bodies**.
- Molecules are **achiral**, i.e. they can be superimposed with their mirror images.
- Molecules are **neutrally charged**.



MBBA

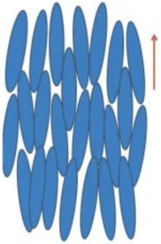


5CB

The nematic ordering

Onsager first relate the ability of certain colloidal particles to have a partial ordering before they freeze (hence retaining liquids ability to flow) to the particle gemetry. The greater the elongation of the molecule the more likely the colloidal will form a nematic ordering.

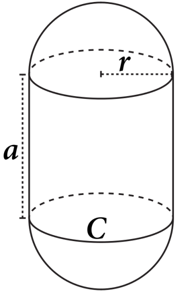
- There is an **enthalpic drive**, i.e. the van der Waals forces favor alignement.
- There is an **entropic drive**, i.e. aligned elongated molecules are more loosely packed, i.e. we have less constraint on the velocity and position.



Curtiss collision operator

In his seminal paper, Curtiss [Cur56] proposed a kinetic theory for spherocylindrical molecules as an idealisation of a polyatomic gas.

- He considered a larger configuration space made by **position**, **velocity**, the **Euler angles** for describing the orientation of each molecule, and the **angular velocity** with respect to a fixed coordinate system.
- Molecules would interact by **excluded volume**, which give rise to **short range interactions**, hence the **nematic ordering**.



This led Curtiss to formulate the following **Boltzmann** type equation,

$$\partial_t f + \nabla_{\boldsymbol{r}} \cdot (\boldsymbol{v} f) + \nabla_{\boldsymbol{\alpha}} \cdot (\dot{\boldsymbol{\alpha}} f) = C[f,f] \tag{1}$$

where $f(\boldsymbol{r}, \boldsymbol{v}, \boldsymbol{\alpha}, \varsigma)$ is the usual first reduced distribution function and $C[f,f]$ is the collision operator defined as

$$C[f,f] = -\iiiint (f_1' f' - f_1 f)(\boldsymbol{k} \cdot \boldsymbol{g}) S(\boldsymbol{k}) d\boldsymbol{k} d\boldsymbol{v}_1 d\boldsymbol{\alpha}_1 d\varsigma_1$$

with $S(\boldsymbol{k})d\boldsymbol{k}$ being the surface element of the excluded volume and $\boldsymbol{g} = \boldsymbol{v} - \boldsymbol{v}_1$. Here without loss of generality the equation is stated in **absence of external force** and **torque**.

Collision invariants

It is possible to prove that the following quantities are **collision invariants** for $C[f,f]$, i.e.

$$\iiint \psi^{(i)} C[f,f] d\boldsymbol{v}_1 d\boldsymbol{\omega}_1 d\boldsymbol{\alpha}_1 = 0.$$

- $\psi^{(1)} = 1$, the **number of particles** in the system;
- $\psi^{(2)} = m\boldsymbol{v}$, the **linear momentum**;
- $\psi^{(3)} = \mathbb{I}^1 \cdot \omega + \boldsymbol{r} \times m\boldsymbol{v}$, the **angular momentum**;
- $\psi^{(4)} = \frac{1}{2} m\boldsymbol{v} \cdot \boldsymbol{v} + \frac{1}{2} \boldsymbol{\omega} \cdot \mathbb{I} \cdot \boldsymbol{\omega}$, the **kinetic energy of the system**.

[1] The inertia tensor for the spherocylinder we are considering.

The hydrodynamic equations – notation

We first introduce the **number density**, i.e.

$$n(\boldsymbol{r}) = \iiint f(\boldsymbol{r}, \boldsymbol{v}, \alpha, \boldsymbol{\omega}) d\boldsymbol{v} d\alpha d\boldsymbol{\omega}.$$

Then we can give a meaning to the following *chevrons*, i.e.

$$\langle\!\langle \cdot \rangle\!\rangle(\boldsymbol{r}) := \frac{1}{n(\boldsymbol{r})} \iiint \cdot\, f(\boldsymbol{r}, \boldsymbol{v}, \alpha, \boldsymbol{\omega}) d\boldsymbol{v} d\alpha d\boldsymbol{\omega}.$$

Using this notation we can define **macroscopic stream velocity** and **macroscopic stream angular velocity** respectively as:

$$\boldsymbol{v}_0 := \langle\!\langle \boldsymbol{v} \rangle\!\rangle, \qquad \boldsymbol{\omega}_0 := \langle\!\langle \boldsymbol{\omega} \rangle\!\rangle.$$

The Hydrodynamic Equations – Curtiss Balance Laws

Testing (1) against the first two **collision invariants** and integrating, Curtiss obtained the following **balance laws**:

$$\partial_t \rho + \nabla_{\boldsymbol{r}} \cdot (\rho \boldsymbol{v}_0) = 0,$$

$$\rho \Big[\partial_t \boldsymbol{v}_0 + (\nabla_{\boldsymbol{r}} \boldsymbol{v}_0) \boldsymbol{v}_0 \Big] + \nabla_{\boldsymbol{r}} \cdot (\rho \mathbb{P}) = 0,$$

where ρ is the **density** defined as $\rho(\boldsymbol{r}) = mn(\boldsymbol{r})$ and $\mathbb{P}$ is the **pressure tensor** defined as $\mathbb{P} := \langle\!\langle \boldsymbol{V} \otimes \boldsymbol{V} \rangle\!\rangle$, with V being the **peculiar velocity** $\boldsymbol{V} := \boldsymbol{v} - \boldsymbol{v}_0$.

The hydrodynamic equations – surprise balance laws

For the third collision invariant we took a different route than Curtiss, which led to the following balance law

$$\rho\Big[\partial_t \boldsymbol{\eta} + (\nabla_{\boldsymbol{r}}\boldsymbol{\eta})\boldsymbol{v}_0\Big] + \nabla_{\boldsymbol{r}} \cdot (\rho\mathbb{N}) = \boldsymbol{\xi}, \tag{2}$$

where $\boldsymbol{\eta}$ is the **macroscopic intrinsic angular momentum** defined as $\boldsymbol{\eta}(\boldsymbol{r}) := \langle\!\langle \mathbb{I}\cdot\omega \rangle\!\rangle$ and $\mathbb{N}$ is the **couple tensor** defined as $\mathbb{N} := \langle\!\langle \boldsymbol{V} \otimes (\mathbb{I}\boldsymbol{\omega}) \rangle\!\rangle$. Here ξ_l is defined in tensor notation as $\langle\!\langle mn(\varepsilon_{lki}v_i v_k)\boldsymbol{e}_l \rangle\!\rangle$ and we proved that $\boldsymbol{\xi}$ vanishes (as stated by Curtiss in [Cur56]) in this particular setting.

Maxwell–Boltzmann distribution

In [Cur56] Curtiss gives an expression for the Maxwell–Boltzmann distribution, i.e. the distribution $f^{(0)}$ such that $C[f^{(0)}, f^{(0)}]$ vanishes:

$$f^{(0)}(\boldsymbol{v}, \boldsymbol{\omega}) = \frac{n \sin(\alpha_2) Q}{\int Q \sin(\alpha_2) d\boldsymbol{\alpha}} \frac{m^{\frac{3}{2}}}{(2\pi \langle\langle \theta \rangle\rangle)^3} (\Gamma)^{\frac{1}{2}} \exp\left[-m \frac{|\boldsymbol{V}|}{2\langle\langle \theta \rangle\rangle} - \frac{\boldsymbol{\Omega} \cdot \mathbb{I} \cdot \boldsymbol{\Omega}}{2\langle\langle \theta \rangle\rangle}\right],$$

where the **peculiar angular velocity** defined as $\boldsymbol{\Omega} := \boldsymbol{\omega} - \boldsymbol{\omega}_0$, $\Gamma = \prod_{i=1}^{3} \Gamma_i$, Γ_i are the moments of inertia of the spherocylinder we are considering and $Q := \exp\left[\frac{\boldsymbol{\omega}_0 \cdot \mathbb{I} \cdot \boldsymbol{\omega}_0}{2\theta}\right]$.

Notice in particular that we assumed $\boldsymbol{\omega}_0$ and the **peculiar kinetic energy** $\theta = \frac{m}{2} \boldsymbol{V} \cdot \boldsymbol{V} + \frac{1}{2} \boldsymbol{\Omega} \cdot \mathbb{I} \cdot \boldsymbol{\Omega}$ are fixed.

Equipartition of energy theorem

We have defined the **peculiar kinetic energy** as

$$\theta = \frac{m}{2}\boldsymbol{V} \cdot \boldsymbol{V} + \frac{1}{2}\boldsymbol{\Omega} \cdot \mathbb{I} \cdot \boldsymbol{\Omega}$$

We can relate to the **kinetic temperature** T making use of the Boltzmann constant,

$$\theta = 3k_B T.$$

Such a relation comes from the **equipartition of energy theorem** since we have six degree of freedom in the kinetic energy each of which appears with a quadratic dependence. From this relation it follows that the **heat capacity** of a polyatomic gas constituted by N particles is $3NK_B$.

Momentum closure around the equilibrium

Now we can use the Maxwell–Boltzmann distribution to compute an approximation of the **pressure tensor** near the equilibrium, i.e.

$$\mathbb{P}^{(0)} = \frac{\Gamma}{3m}\theta \boldsymbol{Id}.$$

We can define the **pressure** as $p = \frac{\Gamma}{3m}\rho\theta$ and rewrite,

$$\left[\partial_t \boldsymbol{v}_0 + (\nabla_{\boldsymbol{r}} \boldsymbol{v}_0)\boldsymbol{v}_0\right] = -\frac{1}{\rho}\nabla p,$$

Unfortunately the same procedure results in a **vanishing** $\mathbb{N}^{(0)}$.

Noether's Theorem and Momentum Coupling

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Let us consider the equation for the angular momentum under, and observe that under the assumption $\mathbb{N}^{(0)} = 0$ it reads

$$\dot{\boldsymbol{\eta}} = \boldsymbol{\xi} = 0.$$

In particular, this is a consequence of Noether's theorem since when $\mathbb{N}^{(0)} = 0$ we have a **rotationally invariant** Lagrangian.

Near the thermal equilibrium is the fluid isotropic ? No !

Balance laws for kinetic temperature

We need another way to formulate the **constitutive relation** for the **couple tensor**. We begin by observing that from $\psi^{(4)}$ we get the following balance law:

$$\dot{\psi}_0 + \nabla_{\boldsymbol{r}} \boldsymbol{v}_0 : (\rho\mathbb{P}) + \nabla_{\boldsymbol{r}} \boldsymbol{\omega}_0 : (\rho\mathbb{N}) - \nabla \cdot \left[\mathbb{P}^T \boldsymbol{v}_0 + \mathbb{N}^T \boldsymbol{\omega}_0\right] + \nabla_{\boldsymbol{r}} \cdot Q = 0$$

where $\psi_0 = \langle\langle\theta\rangle\rangle$ and $Q = \frac{1}{2}\langle\langle \boldsymbol{V}(m|\boldsymbol{V}|^2 + \boldsymbol{\Omega} \cdot \mathbb{I}\boldsymbol{\Omega})\rangle\rangle$.
Without loss of generality we assume that the fluids motion is purely exothermic and drop the exact divergence to obtain the following inequality

$$\dot{\psi}_0 + \nabla_{\boldsymbol{r}} \boldsymbol{v}_0 : \mathbb{P} + \nabla_{\boldsymbol{r}} \boldsymbol{\omega}_0 : \mathbb{N} \geq 0. \tag{3}$$

The nematic ordering and the inertia tensor

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We know that for a **slender body** the inertia tensor can be decomposed as,

$$\mathbb{I} = \lambda_1(I - \boldsymbol{\nu} \otimes \boldsymbol{\nu}) + \mathcal{O}(\varepsilon)$$

where $\varepsilon = (\frac{r}{H})^2$. Furthermore, the macroscopic kinetic energy can be computed as

$$m\frac{1}{2}|\boldsymbol{v}_0|^2 + \frac{1}{2}\boldsymbol{\omega}_0 \cdot \mathbb{I}\boldsymbol{\omega}_0 = \frac{1}{2}m|\boldsymbol{v}_0|^2 + \frac{\lambda_1}{2}|\boldsymbol{\nu}|^2 + \mathcal{O}(\varepsilon),$$

as $\varepsilon \to 0$ we retrieve the same energy that is the starting point for **Ericksen theory of anisotropic fluids**.

Leslie-Ericksen rate of work hypothesis

Starting from the law for the kinetic temperature and the previous decomposition of the inertia tensor in terms of the nematic director we can obtain the following expression,

$$\int_{\Omega} \frac{d}{dt}(\psi - \frac{1}{2}m|\boldsymbol{v}_0|^2) + \nabla_{\boldsymbol{r}}\boldsymbol{v}_0 : \mathbb{P} + \nabla_{\boldsymbol{r}}\boldsymbol{\omega}_0 : \mathbb{N} \geq 0, \qquad (4)$$

where $\psi = \frac{1}{2}m|\boldsymbol{v}|^2 + \frac{1}{2}\boldsymbol{\Omega}\cdot\mathbb{I}\boldsymbol{\Omega}$ can be interpreted as the stored energy.

This is a **kinetic derivation** of **Leslie rate of work hypothesis**.

The Oseen-Frank stored energy

"Whenever possible, substitute constructions out of known entities for inferences to unknown entities." – B. Russell

Making use of the fact that $\dot{\boldsymbol{\nu}} = \boldsymbol{\omega}_0 \times \boldsymbol{\nu} = (\nabla\boldsymbol{\nu})\boldsymbol{v}_0$ we can rewrite part of the stored energy as

$$\psi_{OF}(\boldsymbol{\nu}, \nabla\boldsymbol{\nu}) = \frac{1}{2}\boldsymbol{\Omega}\cdot\mathbb{I}\boldsymbol{\Omega} = \frac{\lambda}{2} tr\Big[\nabla\boldsymbol{\nu}^T\mathbb{P}\nabla\boldsymbol{\nu}\Big].$$

Using $\mathbb{P}^{(0)}$ we get a **stored energy functional** very similar to the **Oseen-Frank** energy

$$\psi_{OF} = p\frac{\lambda_1}{2} tr\Big[\nabla\boldsymbol{\nu}^T\nabla\boldsymbol{\nu}\Big].$$

Noll–Coleman procedure

Since we are happy with our **pressure tensor** so far we make the following **ansatz**

$$\psi = \psi(\nu, \nabla\nu)$$

where ν is the **nematic director**. Expanding the total derivative and using the Ericksen identity we get the following expression in tensor notation

$$\dot{\psi} = \varepsilon_{iqp}\Big[(\nu_q \frac{\partial\psi}{\partial(\nu_p)} + \partial_k(\nu_q)\frac{\partial\psi}{\partial(\partial_k\nu_p)})\omega_i^0 + \nu_q \frac{\partial\psi}{\partial(\partial_k\nu_p)}\partial_k\omega_i^0\Big] - \frac{\partial\psi}{\partial(\partial_k\nu_p)}\partial_q(\nu_p)\partial(v_q^0)$$

Noll–Coleman procedure

Substituting this expression into (4) and considering thermodynamic processes for which the exact divergences disappear, we get:

$$\left[\mathbb{P}_{ij} + \frac{\partial\psi}{\partial(\partial_j\nu_p)}\partial_i(\nu_p)\right]\partial_j(\nu_i) + \left[N_{ij} - \varepsilon_{iqp}\nu_q\frac{\partial\psi}{\partial(\partial_j\nu_p)}\right]\partial_j(\omega_i^0)$$

$$\left[P_{pq} - \frac{\partial\psi}{\partial(\partial_p\nu_k)\partial_q(\nu_k)}\right]\varepsilon_{iqp}\omega_i^0 \geq 0.$$

Since the above expression must hold for all thermodynamic processes for which the exact divergences disappear, we get the following **constitutive relations**:

$$\mathbb{P} = \nabla\boldsymbol{\nu}^T\frac{\partial\psi}{\partial(\nabla\boldsymbol{\nu})} + \mathbb{P}^{(0)}, \qquad N_{ij} = \varepsilon_{iqp}\nu_q\frac{\partial\psi}{\partial(\partial_j\nu_p)} = \boldsymbol{\nu}\times\frac{\partial\psi}{\partial(\nabla\boldsymbol{\nu})}.$$

Nematic law of angular momentum

Thanks to the new expression of the **couple stress tensor** it is possible to rewrite the law of angular momentum for a static nematic field as:

$$\frac{\partial \psi}{\partial \boldsymbol{\nu}} - \nabla \cdot \frac{\partial \psi}{\partial \nabla \boldsymbol{\nu}} = \lambda(\boldsymbol{x})\boldsymbol{\nu}.$$

Substituting inside ψ_{OF} we get the following partial differential equation,

$$\nabla \cdot \Big[p \nabla \boldsymbol{\nu} \Big] + p |\nabla \boldsymbol{\nu}|^2 \boldsymbol{\nu} = 0.$$

The solutions are not harmonic maps on a sphere.

Experiments on acoustic propagation

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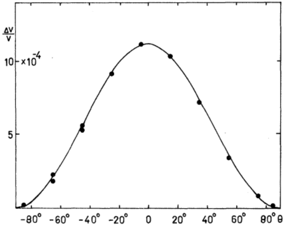

FIG. 2. Angular dependence of sound velocity. $T = 21°C$, $\nu = 10$ MHz, and $H = 5$ kOe. θ is the angle between the field direction and propagation direction. Solid line is $12.5 \times 10^{-4} \cos^2\theta$.

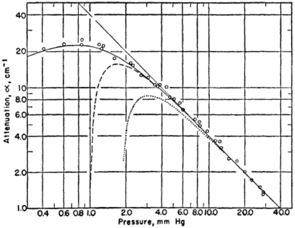

FIG. 1. Attenuation of sound at 1 Mc/sec. in helium. Circles—experimental results. Heavy full line—exact hydrodynamic. Light full line—first approximation, hydrodynamic and Burnett. Dashed line—second approximation, hydrodynamic. Dotted line—second approximation, Burnett.

Acoustic waves travel in NLC faster in the direction parallel to the nematic director [MLS72].

First order theory better fits experimental data on acoustic attenuation at low pressure [Gre49].

Anisotropic waves

It can be shown that steady spherical solutions of (2) verify $\nabla\boldsymbol{\nu}^T\nabla\boldsymbol{\nu} \approx \boldsymbol{Id} + \boldsymbol{\nu}\otimes\boldsymbol{\nu}$. Therefore for this particular case we have the following choice of **pressure tensor**:

$$\mathbb{P} = \mathbb{P}^{(0)} + p\boldsymbol{Id} + p\boldsymbol{\nu}\otimes\boldsymbol{\nu}.$$

If we linearise the **Euler equation** with this choice of **pressure tensor** we get the wave equation:

$$\frac{1}{c^2}\partial_t^2 p_\delta - \nabla\cdot\Big[(2I + \boldsymbol{\nu}\otimes\boldsymbol{\nu})\nabla p_\delta + p_\delta\nabla\cdot(\boldsymbol{\nu}\otimes\boldsymbol{\nu})\Big] = 0.$$

Assuming $p_\delta \ll 1$ we can ignore the last term inside the divergence.

Anisotropic waves

It is well known that a planar wave solution of the above partial differential equation

$$p(\boldsymbol{r}, t) = A\cos(\boldsymbol{k} \cdot \boldsymbol{r} - \omega t)$$

travelling in a transversely isotropic medium has phase speed

$$\boxed{c_s = \frac{\partial p}{\partial \rho}(\rho_0) + \frac{\partial p}{\partial \rho}(\rho_0)\frac{(\boldsymbol{k} \cdot \boldsymbol{\nu})^2}{|k|^2}}$$

so we have an anisotropic speed of sound. A similar reasoning was presented in [BDT14], where a theory for anisotropic waves propagation across **dense liquid** crystals is developed.

Conclusions

- Is the naive relation between the temperature and the peculiar energy obtained from equipartition of energy theorem correct ?
- Using a Noll–Coleman argument for the closure of the momentum hierarchy allows us to capture the anisotropy of acoustic waves in rarefied liquid crystals.
- We hope to use the relations that arise from the closure procedure presented today to compute Frank constants from $\mathbb{I}$, the inertia tensor of the spherocylinder we are considering.

Thank you for the attention !

References

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