

# Notes on Diffusion in Liquid Crystals

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## 1 Translational Diffusion

One convenient expression for the translational diffusion constant in the isotropic phase is a Green-Kubo relation:

$$D = \frac{1}{3N} \sum_{i=1}^N \int_0^{\infty} \langle \vec{v}_i(0) \cdot \vec{v}_i(t) \rangle dt$$

Using this formula, we can just numerically integrate the velocity autocorrelation function to get the diffusion coefficient.

In the nematic phase, where there is a preferred direction of alignment, we have a diffusion tensor which, when diagonalized, has two distinct components. These components, parallel and perpendicular to the director of the phase, are also given by Green-Kubo expressions:

$$D^{\parallel} = \frac{1}{3N} \sum_{i=1}^N \int_0^{\infty} \langle \vec{v}_i(0) \cdot \hat{n}\hat{n} \cdot \vec{v}_i(t) \rangle dt$$
$$D^{\perp} = \frac{1}{3N} \sum_{i=1}^N \int_0^{\infty} \langle \vec{v}_i(0) \cdot (\mathbf{1} - \hat{n}\hat{n}) \cdot \vec{v}_i(t) \rangle dt$$

Here,  $\hat{n}\hat{n}$  is the director dyad and  $\mathbf{1}$  is the unit tensor. For a nematic phase with  $T^* \approx 1.00$ ,  $\rho^* = 0.34$ , I calculated:

$$D^{*\parallel} \approx 0.0333$$

$$D^{*\perp} \approx 0.0180$$

So, Gay-Berne molecules seem to be able to diffuse farther parallel to the director than perpendicular to the director.

## 2 Rotational Diffusion

One commonly used model for understanding rotational diffusion is the Debye model. In this model, a unit vector, describing the orientation of a molecule, diffuses on the surface of a sphere. The vector is assumed to take a random walk with small steps. We can write down a diffusion equation for this situation:

$$\nabla^2 P(\psi, t) = D_R \frac{\partial P(\psi, t)}{\partial t}$$

Here,  $P(\psi, t)$  is the probability of diffusing an angle  $\psi$  away from the initial orientation in a time  $t$ , and  $D_R$  is the rotational diffusion coefficient. Solving this equation, subject to the condition that the unit vector is constrained to move on the surface of a sphere, yields the following expression for  $P(\psi, t)$ :

$$P(\psi, t) = \sum_{l=0}^{\infty} \left( \frac{2l+1}{2} \right) P_l(\cos \psi) e^{-l(l+1)D_R t}$$

Where  $P_l(\cos \psi)$  is the (unassociated)  $l$ th order Legendre polynomial in  $\cos \psi$ . Now, to find  $D_R$ , we consider the  $l$ th order reorientational time correlation function:

$$C^l(t) = \frac{1}{N} \sum_{i=1}^N \langle P_l(\hat{\Omega}_i(0) \cdot \hat{\Omega}_i(t)) \rangle$$

Where we can identify  $\hat{\Omega}_i(0) \cdot \hat{\Omega}_i(t) = \cos \psi_i$ . In the Debye approximation, this function assumes a simple form:

$$C^l(t) = e^{-l(l+1)D_R t}$$

We can then define a correlation time:

$$\tau_l = \int_0^{\infty} C^l(t) dt$$

From which we can obtain the rotational diffusion coefficient:

$$D_R = \frac{1}{l(l+1)\tau_l}$$

Unfortunately, we cannot assume that the orientation vectors of molecules in the nematic phase are performing a random walk with short steps. The orientation vectors have a preferred direction of alignment (the director), and

so will spend most of their time near the director. Large deviations from alignment with the director will likely require large-angle “jumps.” Thus, we cannot use the Debye approximation to calculate rotational diffusion coefficients in the nematic phase. An alternative is to calculate the rotational diffusion coefficient using mean-squared angular displacements:

$$D_R^\alpha = \lim_{t \rightarrow \infty} \frac{1}{2tN} \sum_{i=1}^N \langle [\Delta\varphi_i^\alpha(t)]^2 \rangle$$

$$\Delta\varphi_i^\alpha(t) = \varphi_i^\alpha(t) - \varphi_i^\alpha(0) = \int_0^t \omega_i^{\alpha,b} dt$$

Where  $D_R^\alpha$  is the rotational diffusion coefficient in the  $\alpha$ th direction (relative to the molecules), and  $\omega_i^{\alpha,b}$  is the  $\alpha$ th component of the angular velocity of the  $i$ th molecule, expressed in the body-fixed ( $b$ ) frame. By substituting the definition of  $\Delta\varphi_i^\alpha(t)$  into the expression for  $D_R$  (and performing a few manipulations), we arrive at a Green-Kubo expression for  $D_R^\alpha$ :

$$D_R^\alpha = \frac{1}{N} \sum_{i=1}^N \int_0^\infty \langle \omega_i^{\alpha,b}(t) \omega_i^{\alpha,b}(0) \rangle dt$$

In the nematic phase,  $T^* \approx 1.00$ ,  $\rho^* = 0.34$ , I obtained:

$$D_R^x \approx 0.0129$$

$$D_R^y \approx 0.0151$$

These values are close, but not quite the same. I intend to determine whether this is due to numerical integration error, or whether it is actually a feature of the nematic phase.