Novel algorithmic framework for DLS data analysis of highly anisotropic CNCs

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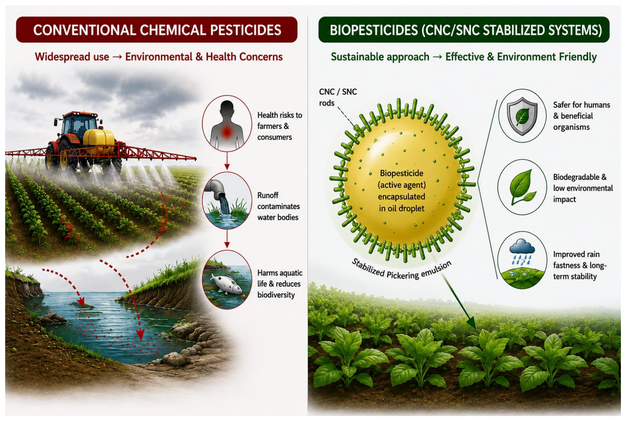
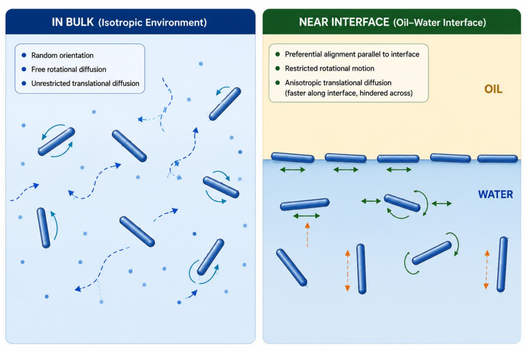
Overview

- The excessive use of chemical pesticides for agricultural purposes is a cause of concern.
- These pesticides poison millions of agricultural workers every year and pollute water bodies.
- The BIOMAC-BP consortium is part of the Marie Sklodowska Curie Actions (MSCA) network and is sponsored by the EU to develop novel biopesticide formulations.
- It brings together various institutes in Europe with a total of 14 Doctoral Candidates working in collaboration to realize the goals of this project.



Introduction

- Cellulose nanocrystals (CNCs) are ingot-shaped colloidal particles with inherently broad size distributions.
- These can be used as stabilizers in Pickering emulsions.
- The aim of this project is to analyse the dynamics of CNCs in interfaces using light scattering techniques.



Conventional Methodology

- We used Atomic Force Microscopy (AFM) and Dynamic Light Scattering (DLS) (stretched exponential fits) to obtain the diffusion coefficients for sulphated cotton CNCs.
- The values of the rotational diffusion coefficient obtained from the two techniques are very different.
- We have developed a new framework for analysing the DLS data in order to resolve this crisis.

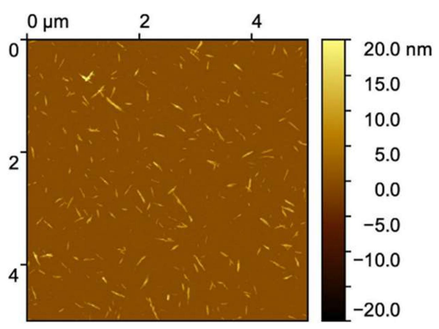


Figure 1. AFM image of sulfated-carboxylated cotton CNCs showing rod-like morphology

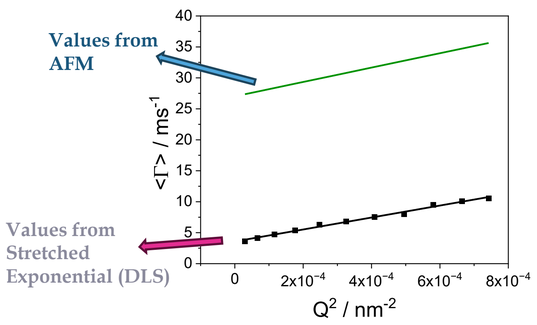


Figure 2. Plot of the relaxation rates vs square of the wavevector

New Methods

- CNCs modelled as anisotropic rods.
- Rayleigh-Gans-Debye scattering assumed.
- Size polydispersity (variance in lengths and diameters) and optical anisotropy included.
- The diffusion coefficient corresponding to the rotation about the long axis is also taken into account.
- Monte-Carlo Integration for efficient evaluation.

Siegert relation (DDLS)

$$g_2(t, \boldsymbol{Q}, \boldsymbol{L}, d) = 1 + A\left[g_1(t, \boldsymbol{Q}, \boldsymbol{L}, d)\right]^2 + B_L$$

t – time delay | Q – scattering vector | L – particle length | d – particle diameter
A – optical intercept (coherence factor) | B_L – baseline (long-time residual)

Field autocorrelation function model

$$g_1(t, \boldsymbol{Q}, \boldsymbol{L}, d) = \left[\underbrace{A_2\, e^{-(6D_r^{\perp} + 4(D_r^{\parallel} - D_r^{\perp}))t}}_{\text{2nd-order rotational mode } (m = \pm 2)} + \underbrace{A_0\, e^{-6D_r^{\perp} t}}_{\text{0th-order rotational mode } (m = 0)}\right] \underbrace{e^{-6D_t Q^2 t}}_{\text{translational diffusion}}$$

$D_r^{\perp}$ – rotational diffusion coefficient (perpendicular) | D_t – translational diffusion coefficient | m – rotational mode number $(0, \pm 2)$
$D_r^{\parallel}$ – rotational diffusion coefficient (parallel) | A_2, A_0 – mode amplitudes

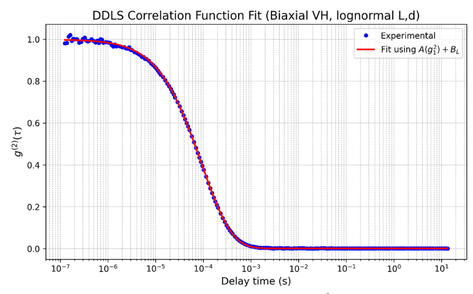


Figure 3. DDLS fit for 90^0 scattering angle using the new model

Results

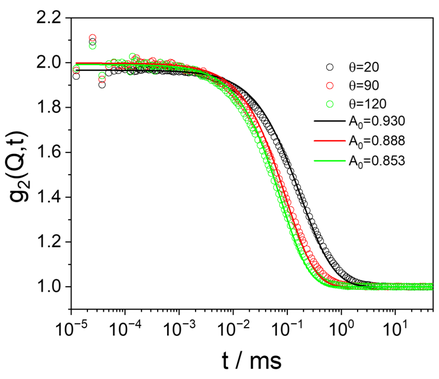
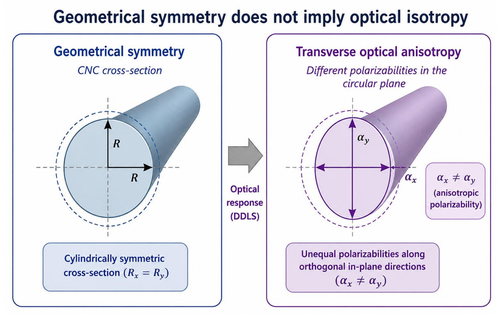


Figure 4. Multi-angle DDLS fits with AFM values as global parameters and optical anisotropy as local parameter



- Multi-angle DDLS fits are accurately reproduced using AFM-derived dimensions and a floating optical anisotropy parameter.
- The analysis reveals that cylindrical geometrical symmetry does not preclude transverse optical anisotropy in CNCs.

Future Plans

- Study the dynamics of rod-like and platelet-like particles near solid interfaces using Evanescent Wave Dynamic Light Scattering (EWDLS).
- Setting up a Differential Dynamic Microscopy (DDM) apparatus for investigating the dynamics of entrapped CNCs and SNCs in fluid interfaces.

References

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Acknowledgments

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