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# Anisotropic Diffusion and Phase Behavior of Cellulose Nanocrystal Suspensions

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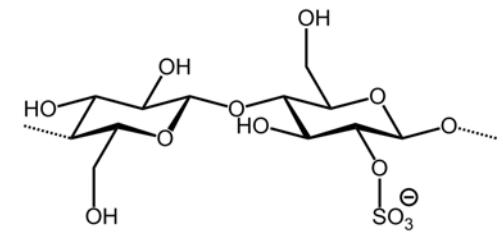
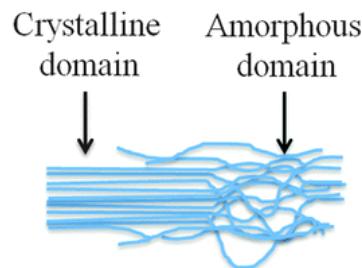


# Contents

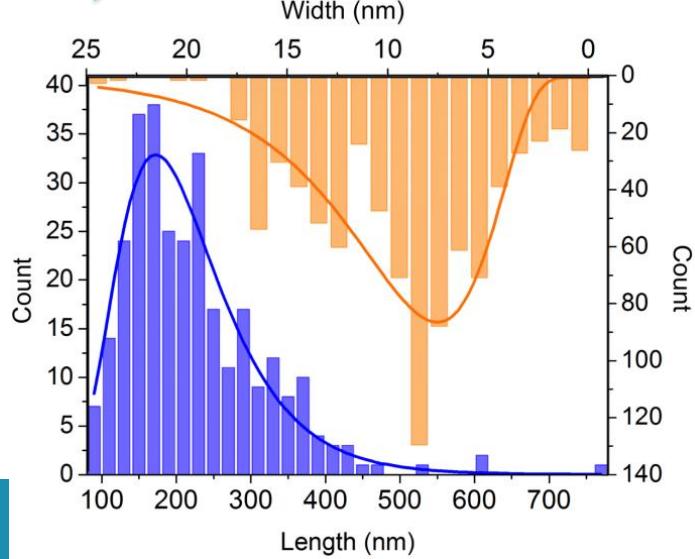
- Introduction
- (Depolarized) dynamic light scattering
- Results
- Summary and conclusion

# Cellulose nanocrystals (CNCs)

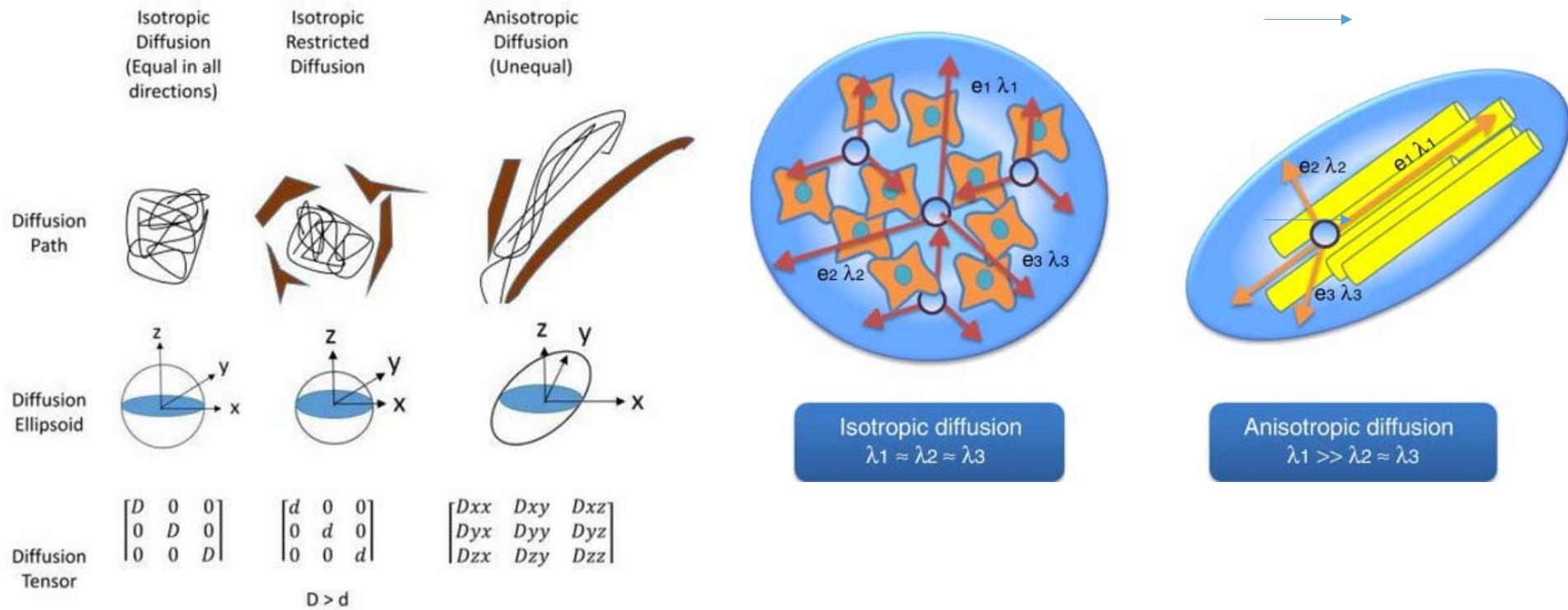
- Sulfuric acid hydrolysis of cotton wool



- L: ~225 nm, W: ~9 nm
- Sulfate groups: 0.26 mmol/g CNC
- 1-5 wt% aqueous CNC suspensions

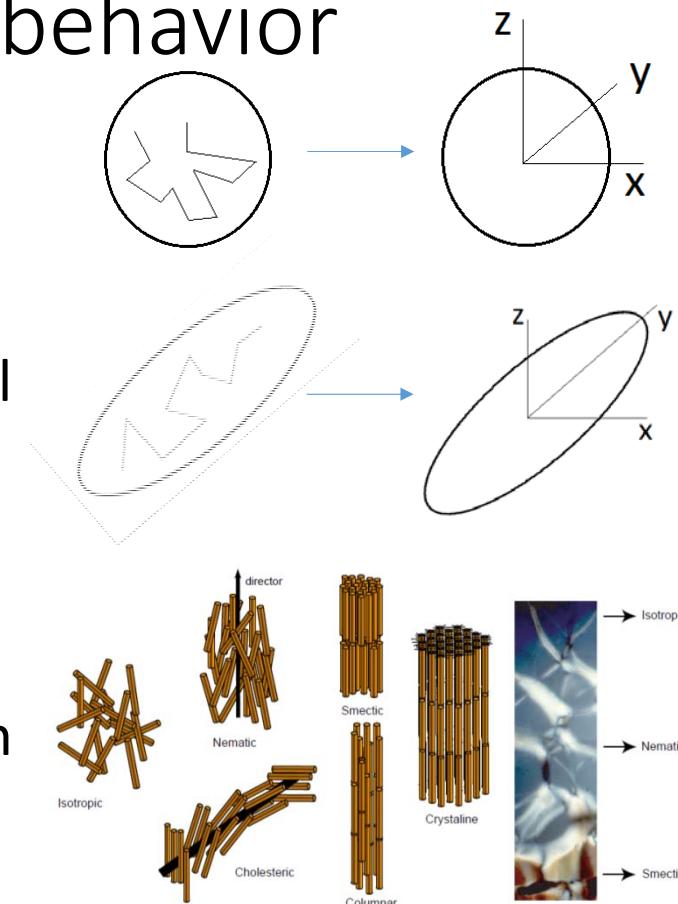


# Anisotropic diffusion and phase behavior

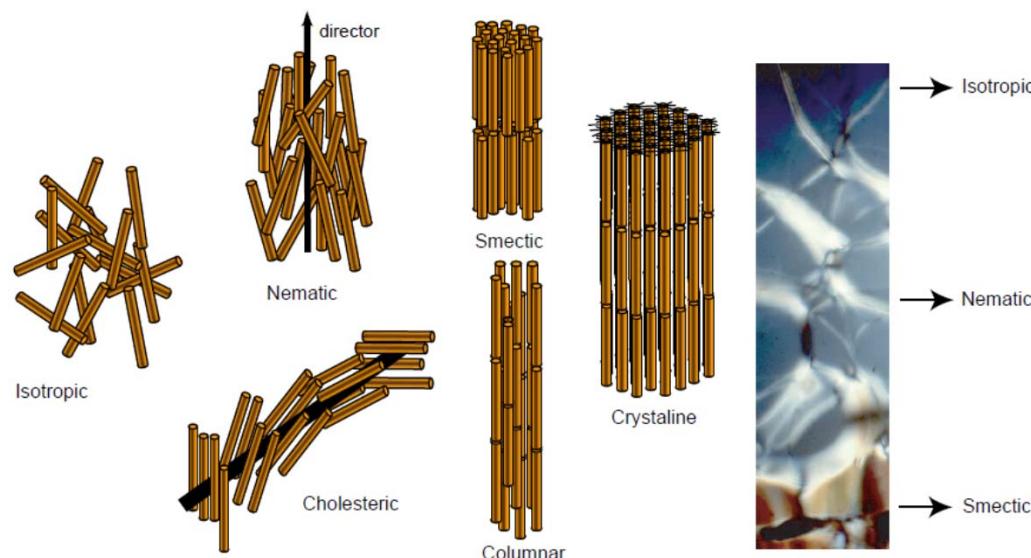


# Anisotropic diffusion and phase behavior

- Direction dependent
- Diffusion tensor to describe directionality
- Biological tissues, structured materials in general
- Fast and slow diffusional translation and rotation
- $\parallel$  and  $\perp$  to main axis



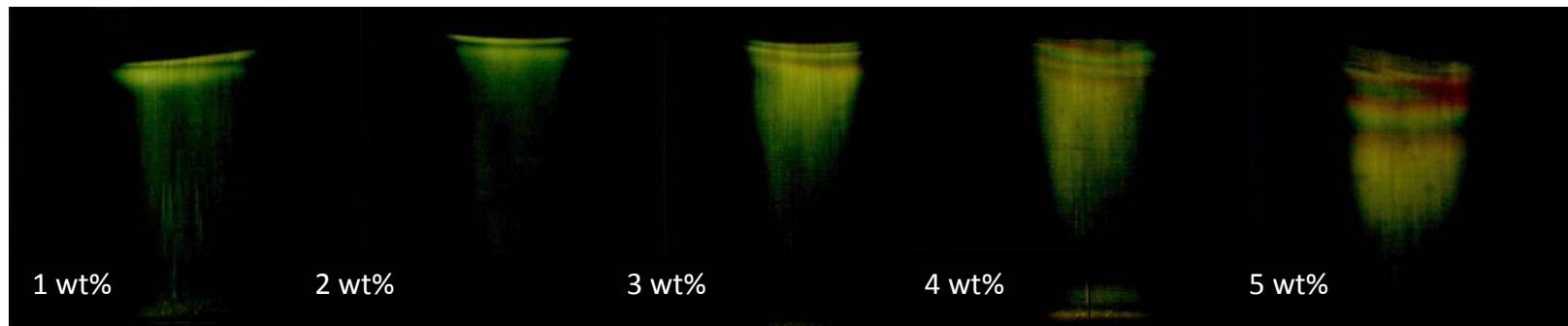
# Phase behavior



- Fast and slow diffusional translation and rotation
- $\parallel$  and  $\perp$  to main axis

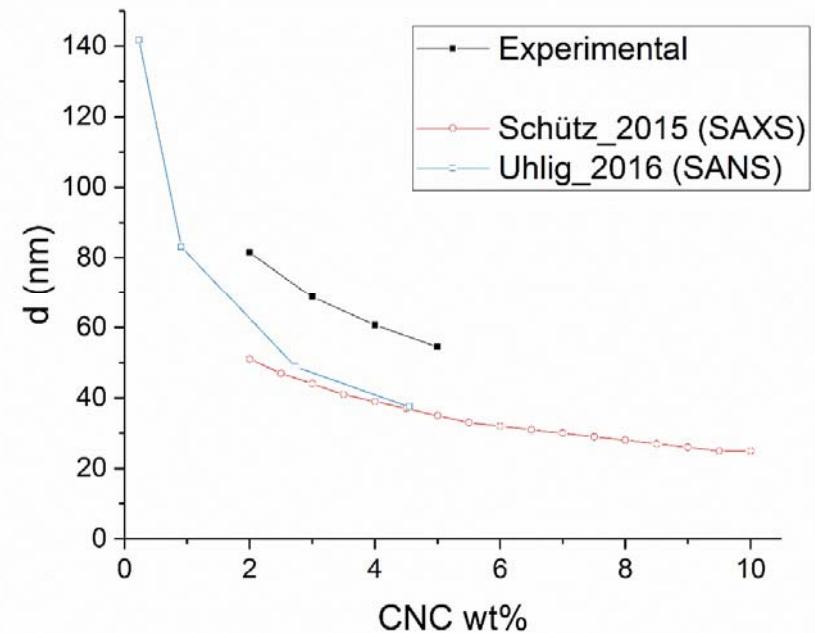
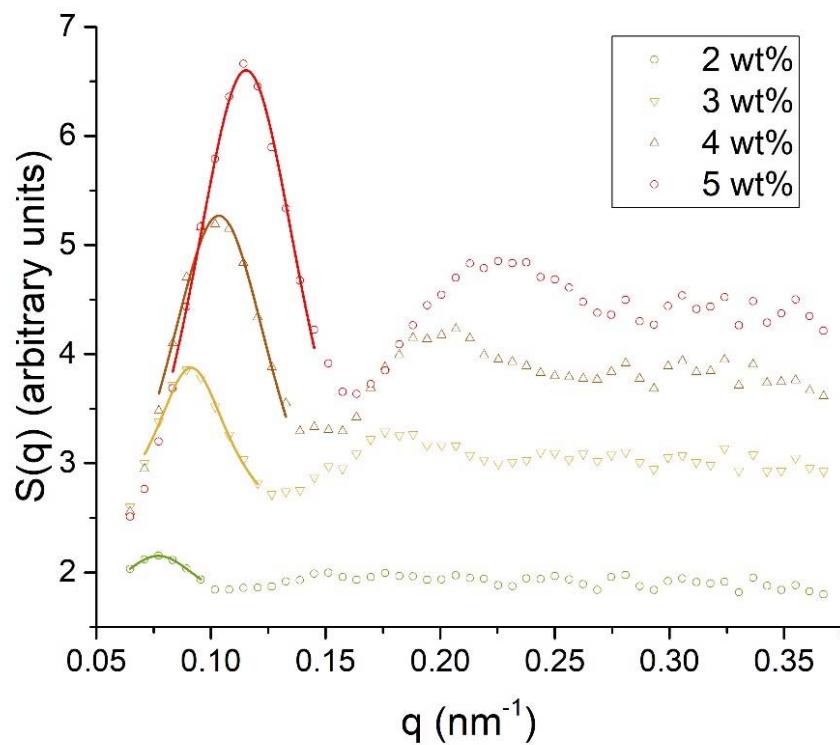
# Anisotropic diffusion of cellulose nanocrystals

- Behavior in aqueous suspensions
- Relation of diffusion to liquid crystalline behaviour



- Towards predicting and controlling kinetics and self-assembly

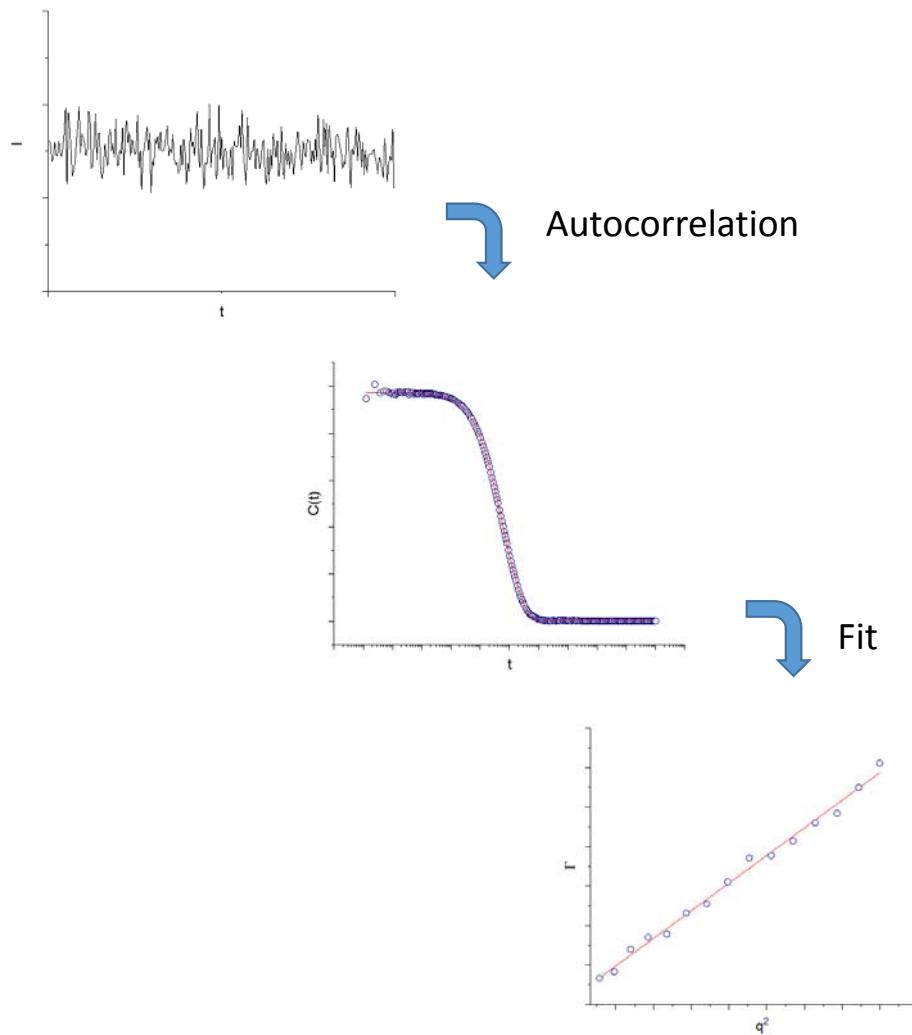
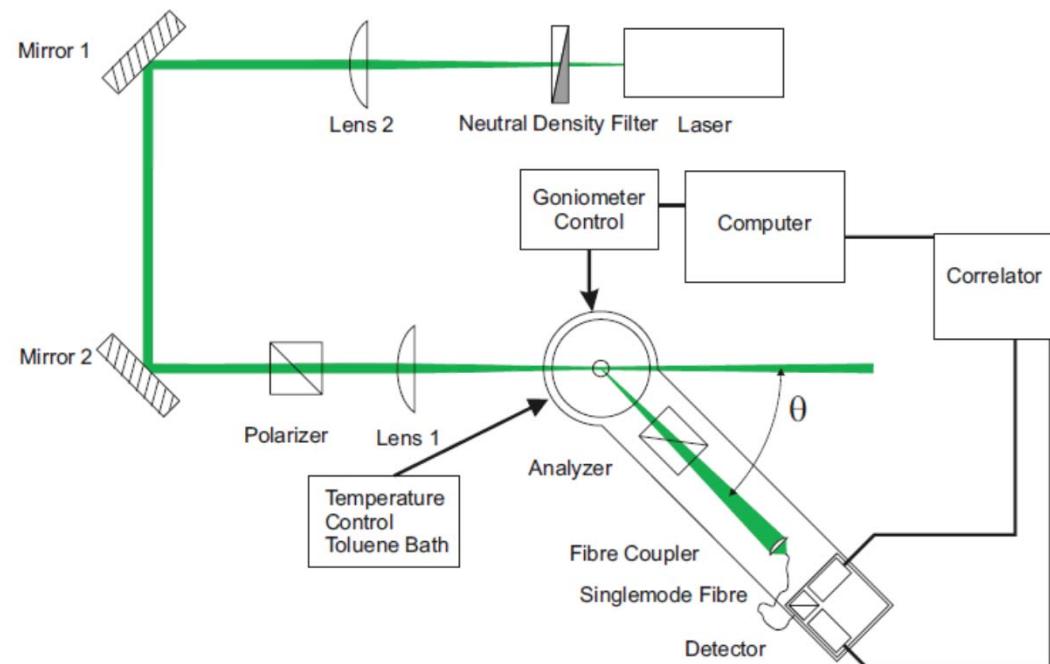
# Structure formation before isotropic-chiral nematic phase separation



Schütz, C., et al. *ACS Syst. Chem. Eng.* **2018**, 6, 8317–8324

Uhlig, M. et al. *Langmuir* **2016**, 32 (2), 442–450  
Schütz, C., et al. *Langmuir* **2015**, 31, 6507–6513

# Dynamic light scattering



# Dynamic light scattering of CNCs

- Dilute CNC suspensions ( $\leq 0.3$  wt%)
- Effect of particle dimensions
- $D_{\text{rot}}$  :concentration independent in range 0.1-0.27 wt% (De Souza Lima *et.al.* 2002)
- Polydispersity
- Interparticle interactions
- Restricted systems

# (Depolarized) dynamic light scattering

- VV (DLS) vs. VH (DDLS):  $\parallel$  vs.  $\perp$  positioning of polarizer and analyser
- Rotational and translational coupling
- $\hat{g}_{E,VV}(q, t) = \exp\{-q^2 t [C(qL)\Delta D + D_t]\} [S_0(qL) + S_2(qL) \exp(-6D_r t) + S_4(qL) \exp(-20D_r t) + S_6(qL) \exp(-42D_r t) + \dots]$
- $\hat{g}_{E,VV}(q, t) = \exp\{-q^2 D_t t\}$  for  $qL < 5$
- $\hat{g}_{E,VH}(q, t) \propto \exp[-(q^2 D_t + 6D_r)t]$

# Autocorrelation functions

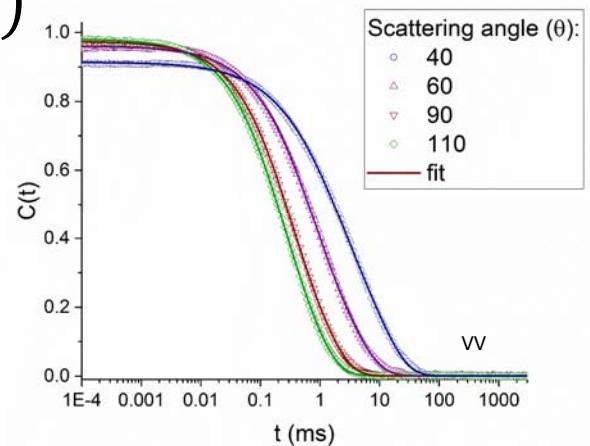
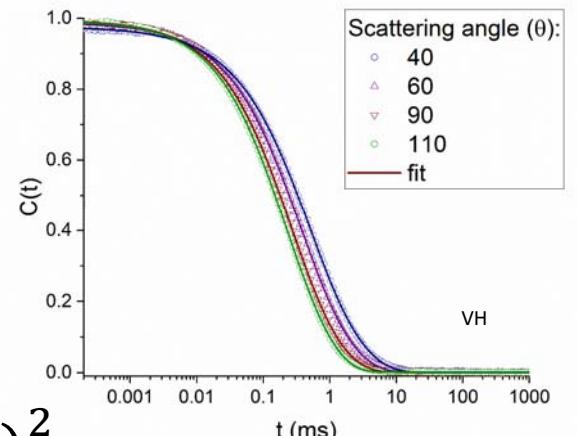
- Normalized autocorrelation functions
- Introducing polydispersity via stretched exponentials

$$\text{Fit: } g_E(t) = \left( A_1 \exp\{-(\Gamma_1 t)\} + A_2 \exp\{-(\Gamma_2 t)^\beta\} + B \right)^2$$

$$\Gamma_{VV} = q^2 D_t$$

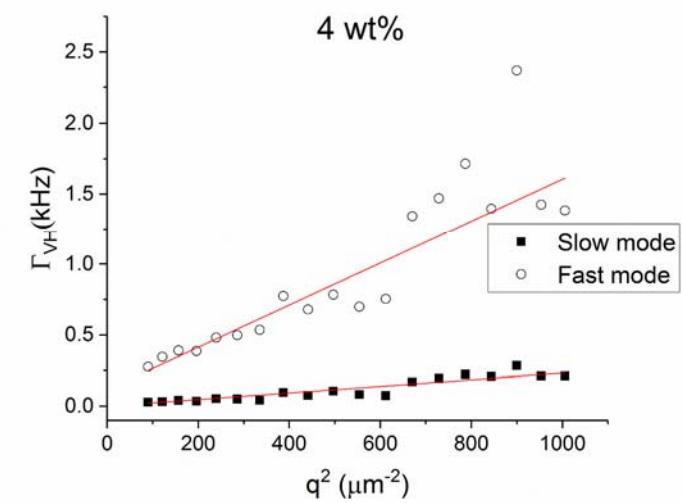
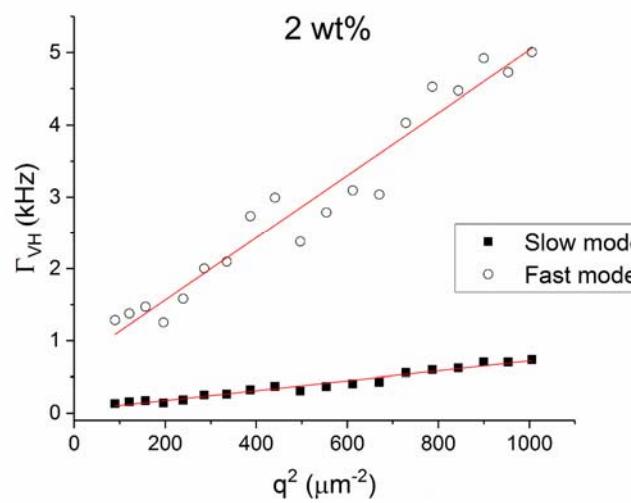
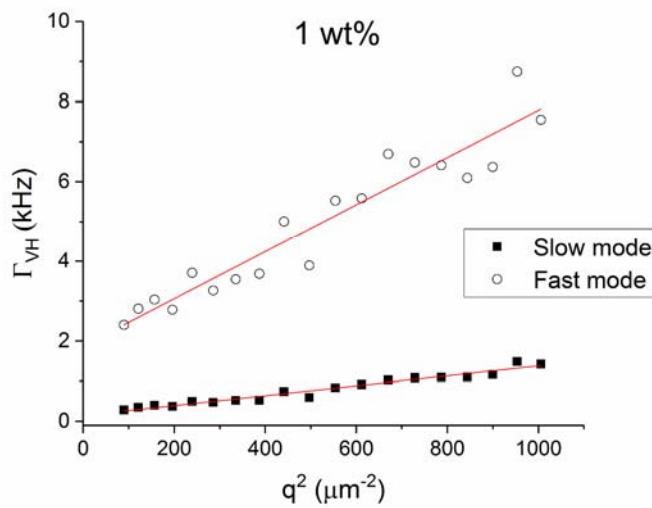
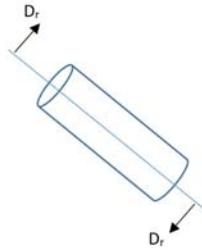
$$\Gamma_{VH} = q^2 D_t + 6D_r$$

$$q = \frac{4\pi n}{\lambda} \sin \frac{\theta}{2}$$



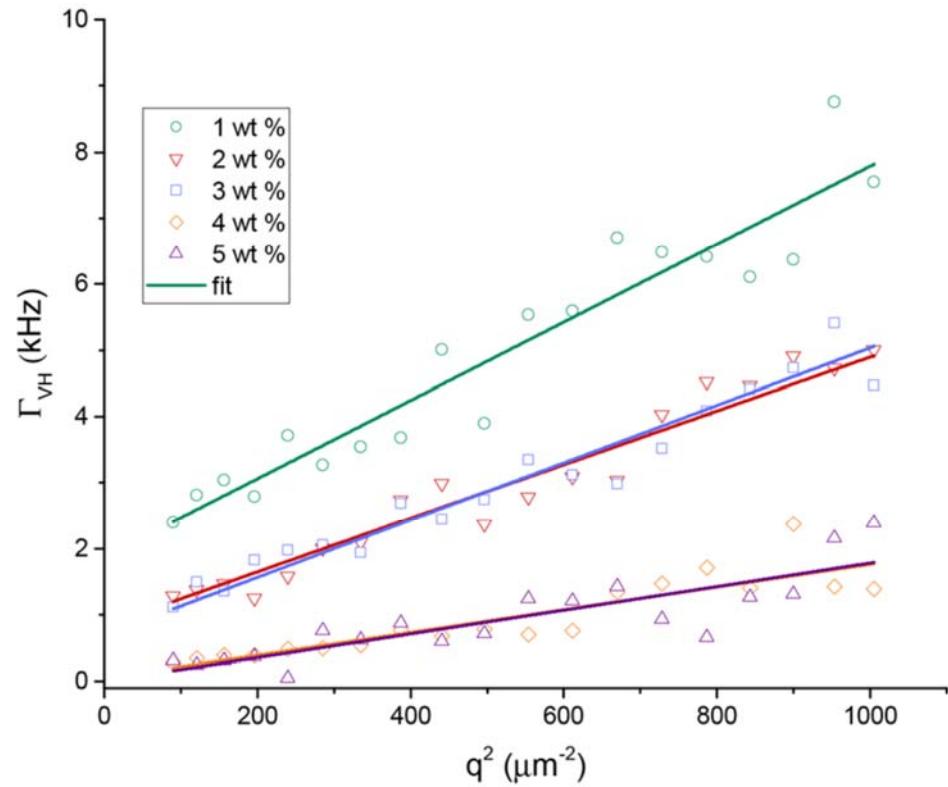
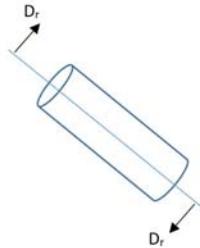
# Rotational diffusion

$$\Gamma_{VH} = q^2 D_t + 6D_r$$



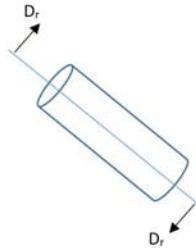
# Rotational diffusion

$$\Gamma_{VH} = q^2 D_t + 6D_r$$



Inter-particle interactions hindering rotational motion

# Rotational diffusion



CNC wt%	Apparent ( $\pm$ )	$D_r (s^{-1})$	
		Theoretical	
		Cyl. model <sup>†</sup>	Debye <sup>‡</sup>
Infinite dilution	-	17000	-
1	<b>310</b> (13)	8500	1700
2	<b>130</b> (10)	5300	1500
3	<b>140</b> (19)	4200	1400
4	<b>20</b> (7)	3000	1100
5	<b>0</b> (7)	2000	800

$$D_r = \frac{k_B T p^2}{A_0 \pi \eta L^3 (1 + \delta)}$$

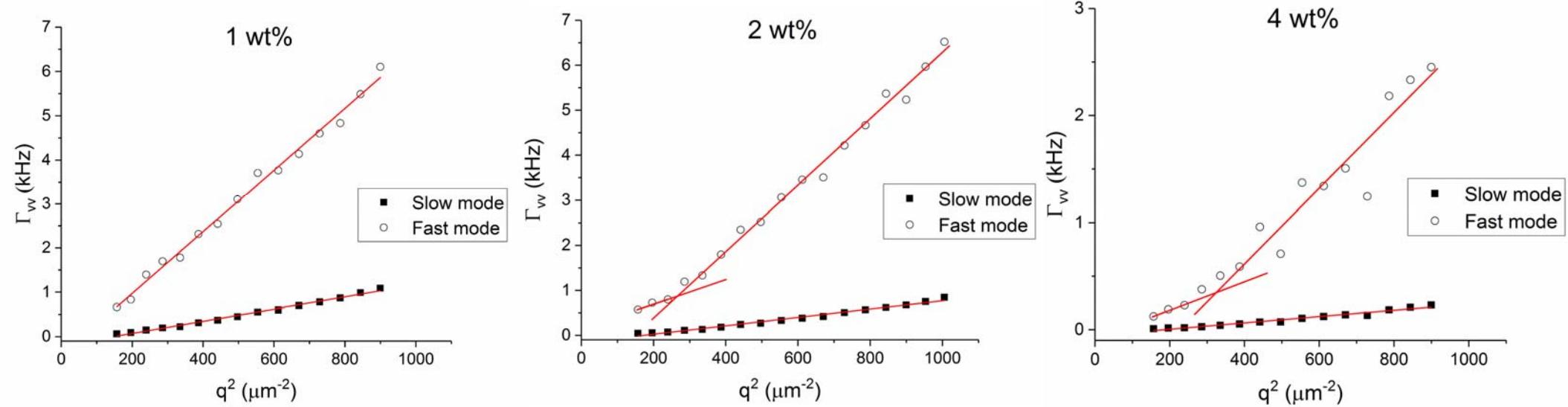
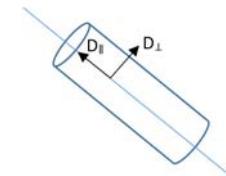
- Towards rotational arrest

<sup>†</sup>Tirado & García de la Torre, 1979, 1980 and Broersma, 1960.

<sup>‡</sup>Using Debye length in stead of the average length determined by AFM.

# Translational diffusion

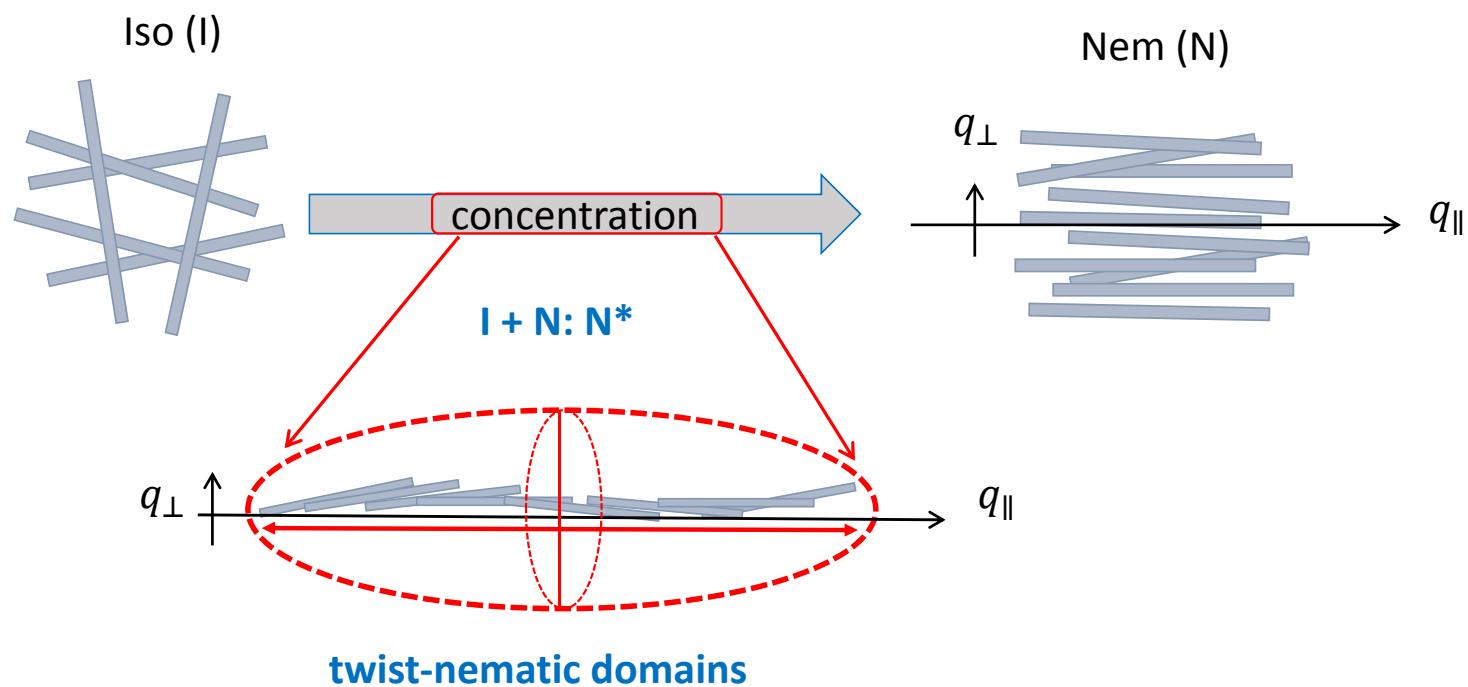
$$\Gamma_{VV} = q^2 D_t$$

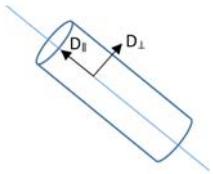


Non-linear dependence of  $\Gamma_{VV}$  on  $q^2$  in fast mode (parallel diffusion)

→ Particle structuring starts around 2 wt%

# Long-range twist coupling in transition





# Translational diffusion

CNC wt%	$D_t^\perp (\mu\text{m}^2/\text{s})$			$D_t^{\parallel} (\mu\text{m}^2/\text{s})$		
	Theoretical		App. ( $\pm$ )	Theoretical		App. ( $\pm$ )
	Cyl. model <sup>†</sup>	Debye <sup>‡</sup>		Cyl. model <sup>†</sup>	Debye <sup>‡</sup>	
Infinite dilution	-	5.8	-	-	8.7	-
1	<b>1.3</b> (0.1)	2.9	2.3	<b>6.5</b> (0.5)	4.4	3.2
2	<b>0.7</b> (0.2)	1.8	1.5	<b>5.2</b> (0.3)	2.7	2.2
3	<b>0.7</b> (0.1)	1.4	1.2	<b>5.7</b> (0.5)	2.1	1.8
4	<b>0.3</b> (0.1)	1	0.9	<b>1.9</b> (0.4)	1.6	1.3
5	<b>0.2</b> (0.1)	0.7	0.6	<b>1.8</b> (0.2)	1	0.9

- Translational and rotational coupling in nematic phase
- Long range twist fluctuations

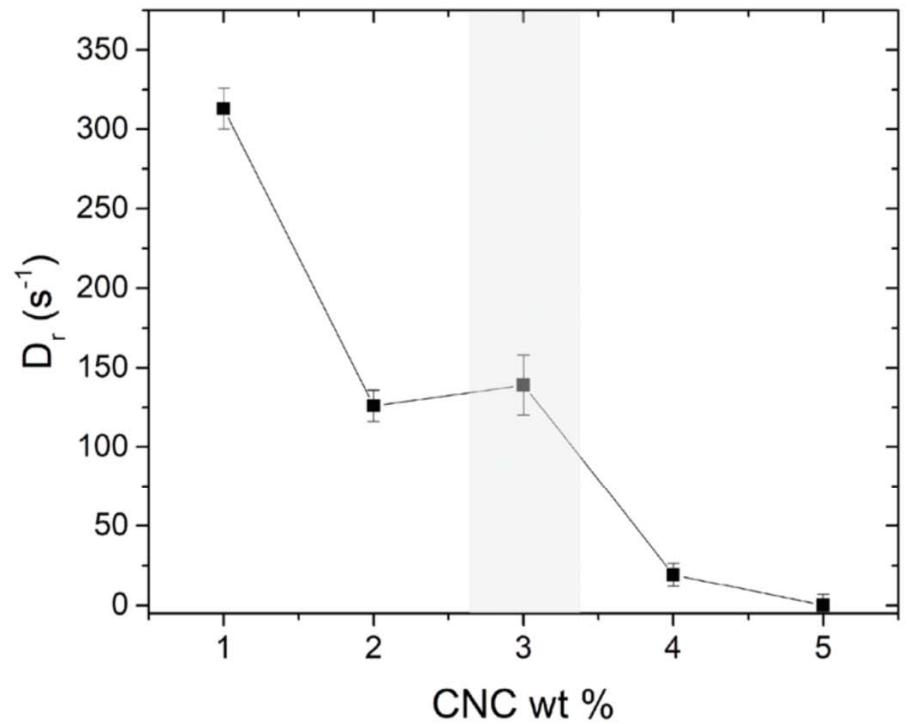
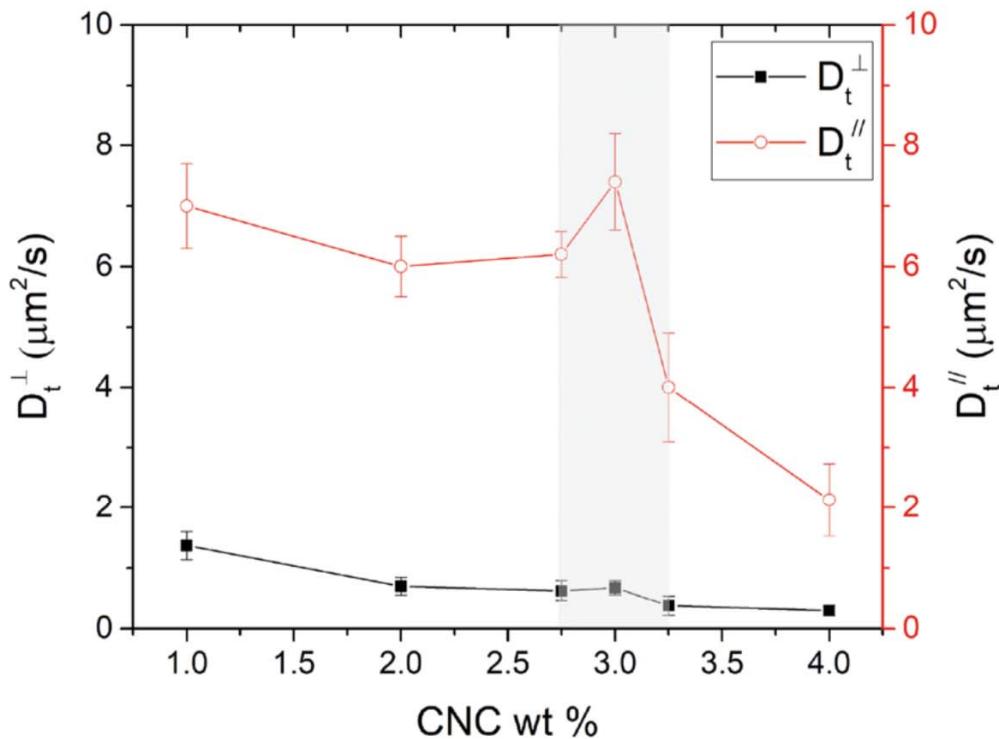
$$D_t^{\parallel} = \frac{1}{2} \frac{k_B T (\ln p + \gamma_{\parallel})}{\pi \eta L}$$

$$D_t^{\perp} = \frac{1}{4} \frac{k_B T (\ln p + \gamma_{\perp})}{\pi \eta L}$$

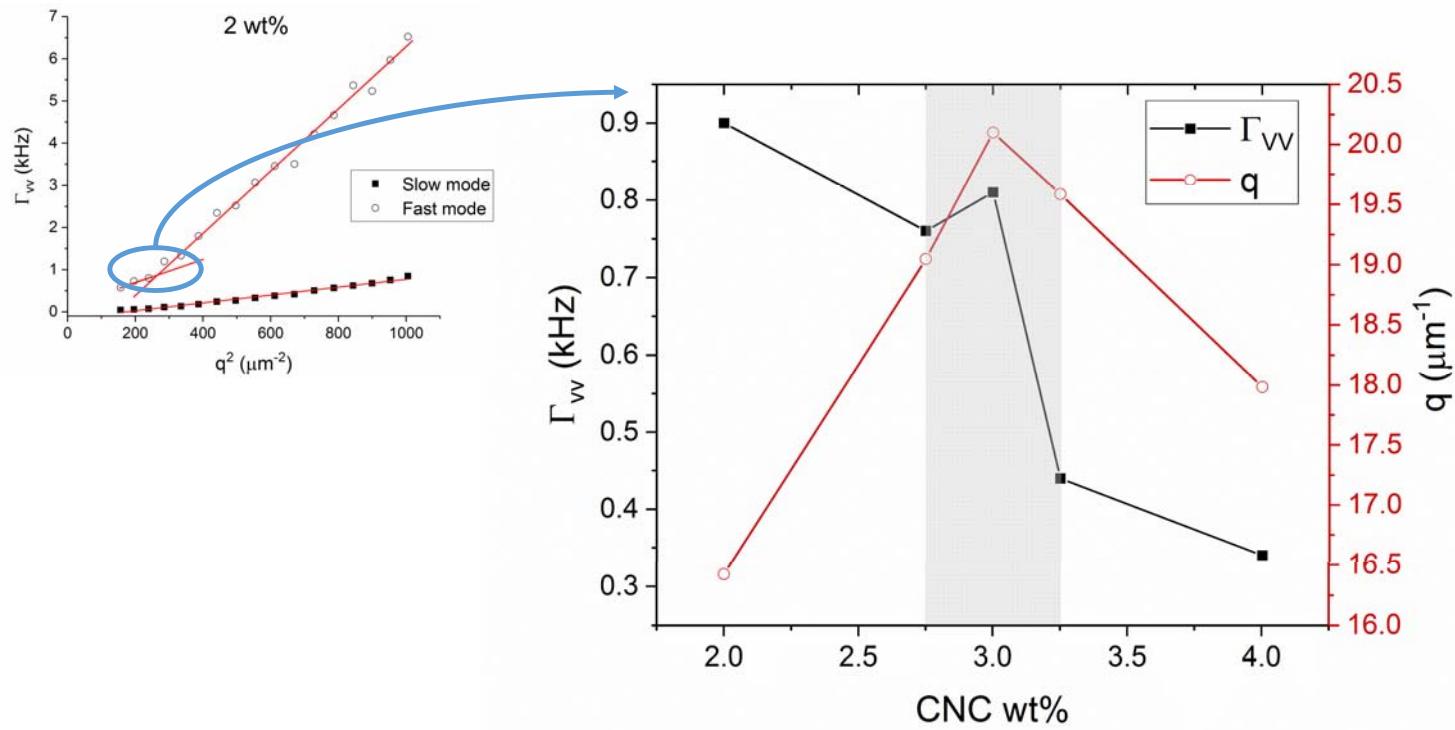
<sup>†</sup>Tirado & García de la Torre, 1979, 1980 and Broersma, 1960.

<sup>‡</sup>Using Debye length in stead of the average length determined by AFM.

# Diffusion coefficients



# Translational diffusion



# Conclusions and outlook

- Particle alignment starts in the isotropic phase (for our samples around 2 wt%)
- Formation of jointly-diffusing domains in isotropic phase
- Nematic domain formation accompanied by:
  - Increased translational entropy
  - Loss of rotational freedom
- Expand to higher concentrations
- Kinetic parameters to be used to understand self-assembly during water evaporation

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## Anisotropic Diffusion and Phase Behavior of Cellulose Nanocrystal Suspensions

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# Thank you

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