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'RoadMaP' X-PressMatter Lab: Soft Matter, Food & Glasses under Pressure
Anniversary Symposium „Unipress 50"

Liquid Crystals based nanocolloids new phenomena, emerging applications

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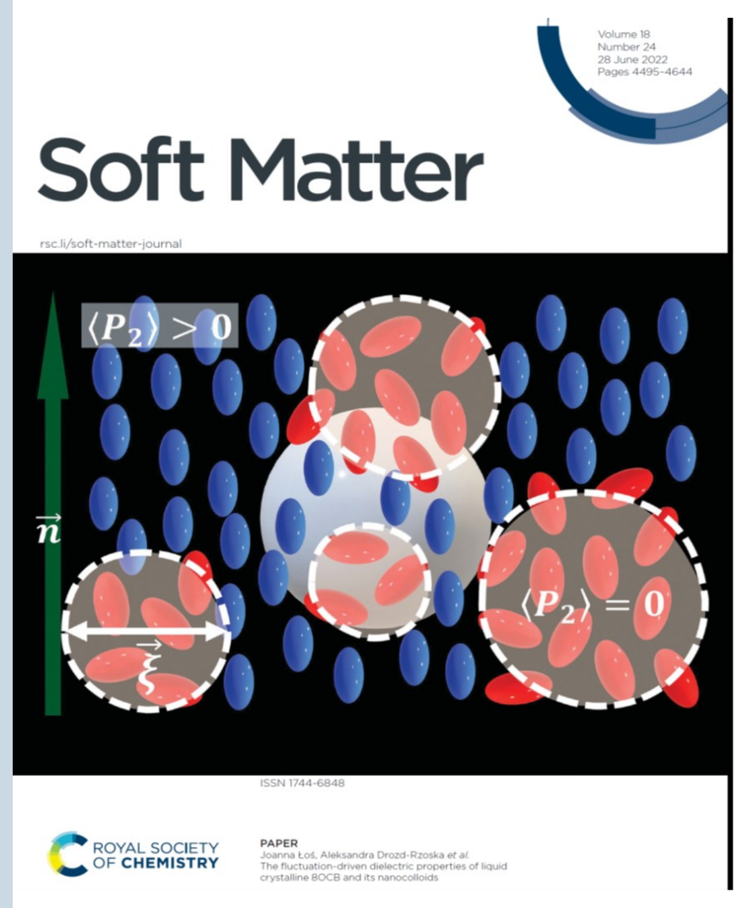
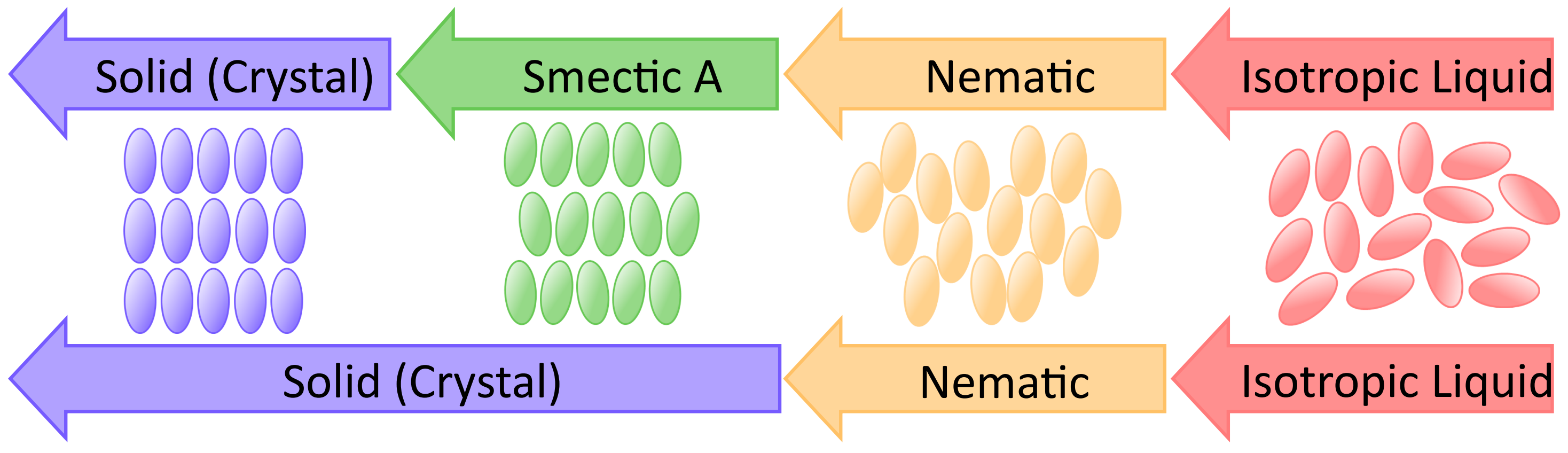


The presented below results of 8OCB and its nanocolloids measurements, were published in Soft Matter [1]. The paper was awarded an invitation to prepare the front cover.

Liquid crystals

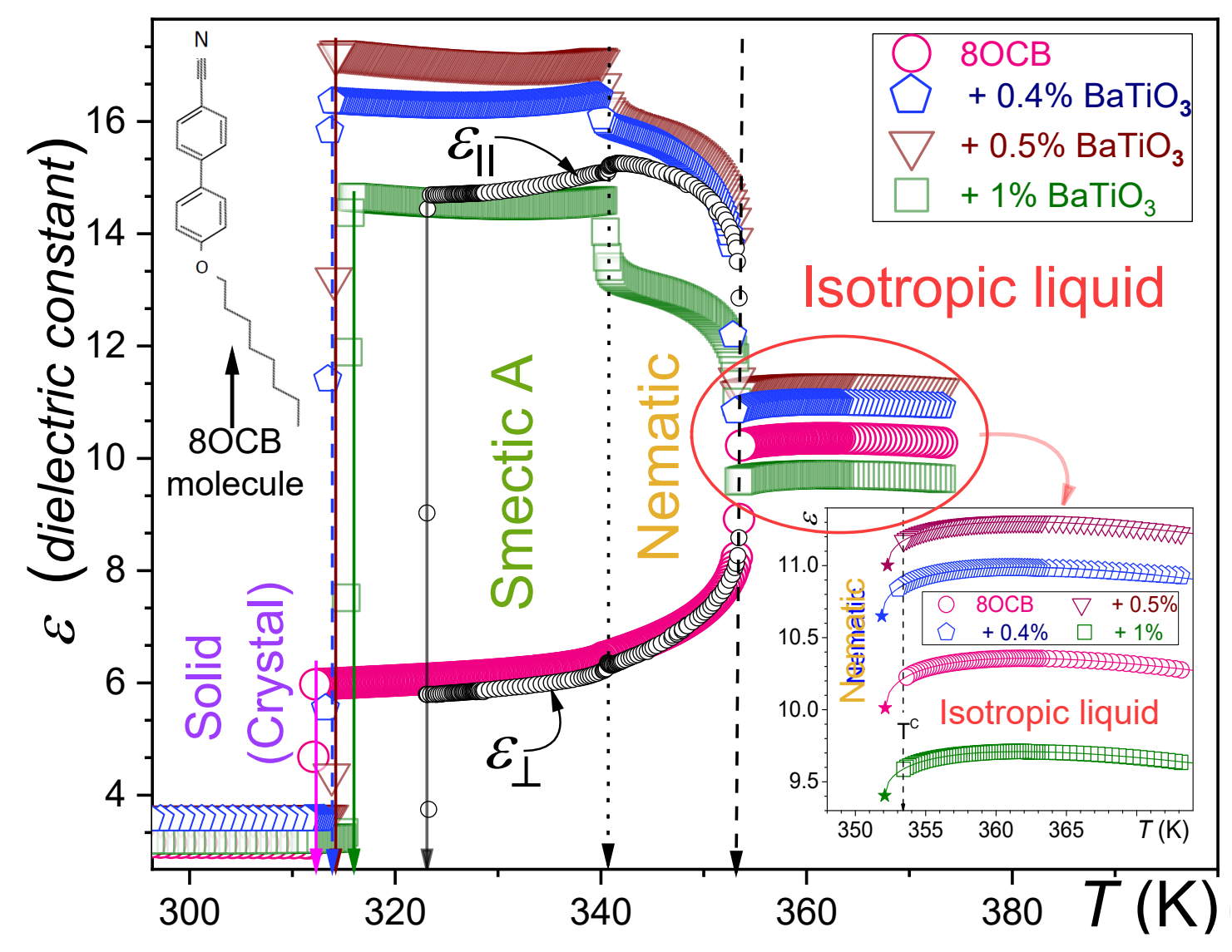
Liquid crystalline (LC) materials are a model example of soft matter, i.e., systems strongly susceptible to external disturbations, rich in phase transitions and complex dynamics. Properties of liquid crystals are dominated by multimolecular fluctuations, due to the weakly discontinuous character of subsequent phase transitions.

Basic mesomorphism:


Solid (Crystal) ← Smectic A ← Nematic ← Isotropic Liquid

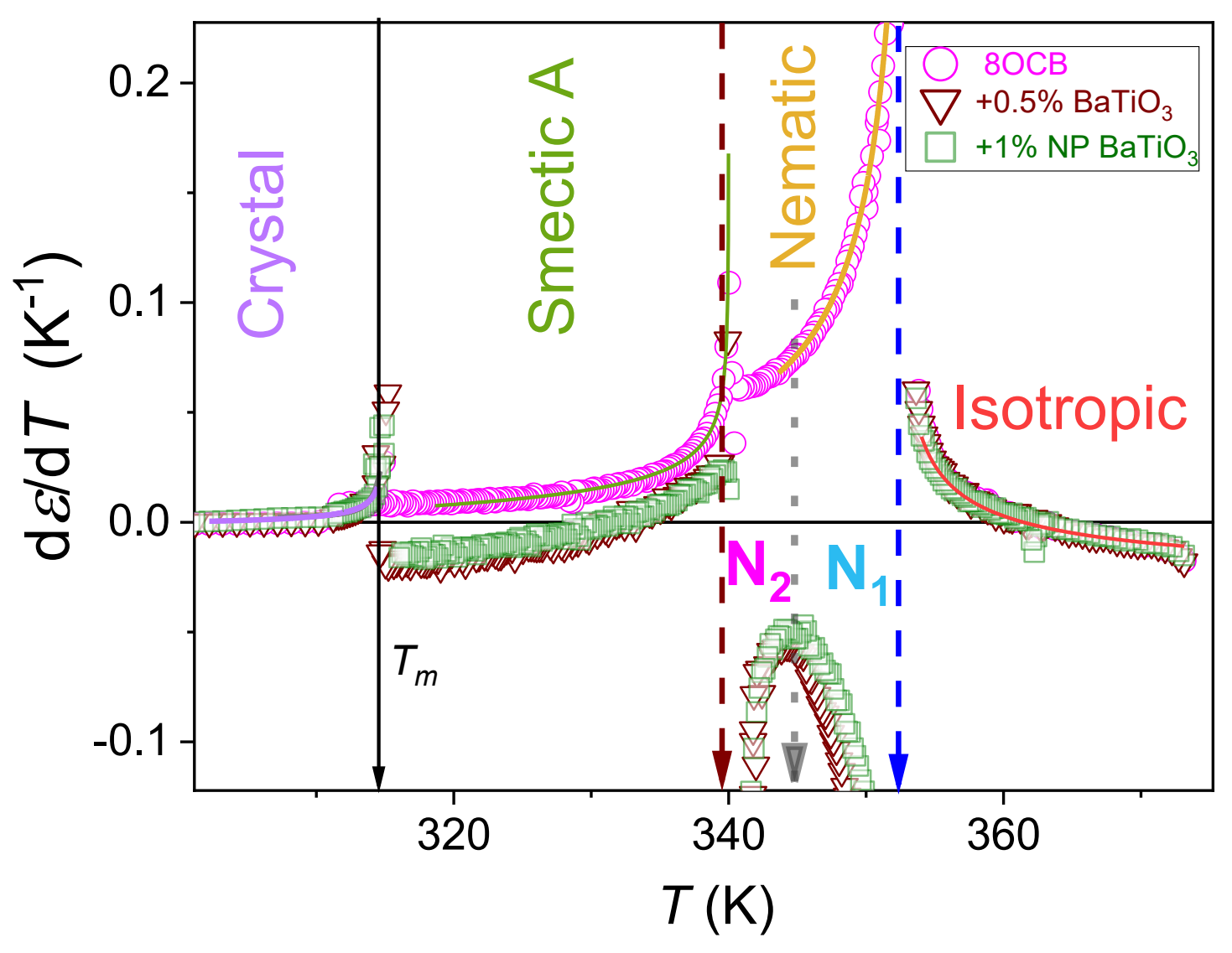
Solid (Crystal) ← Nematic ← Isotropic Liquid

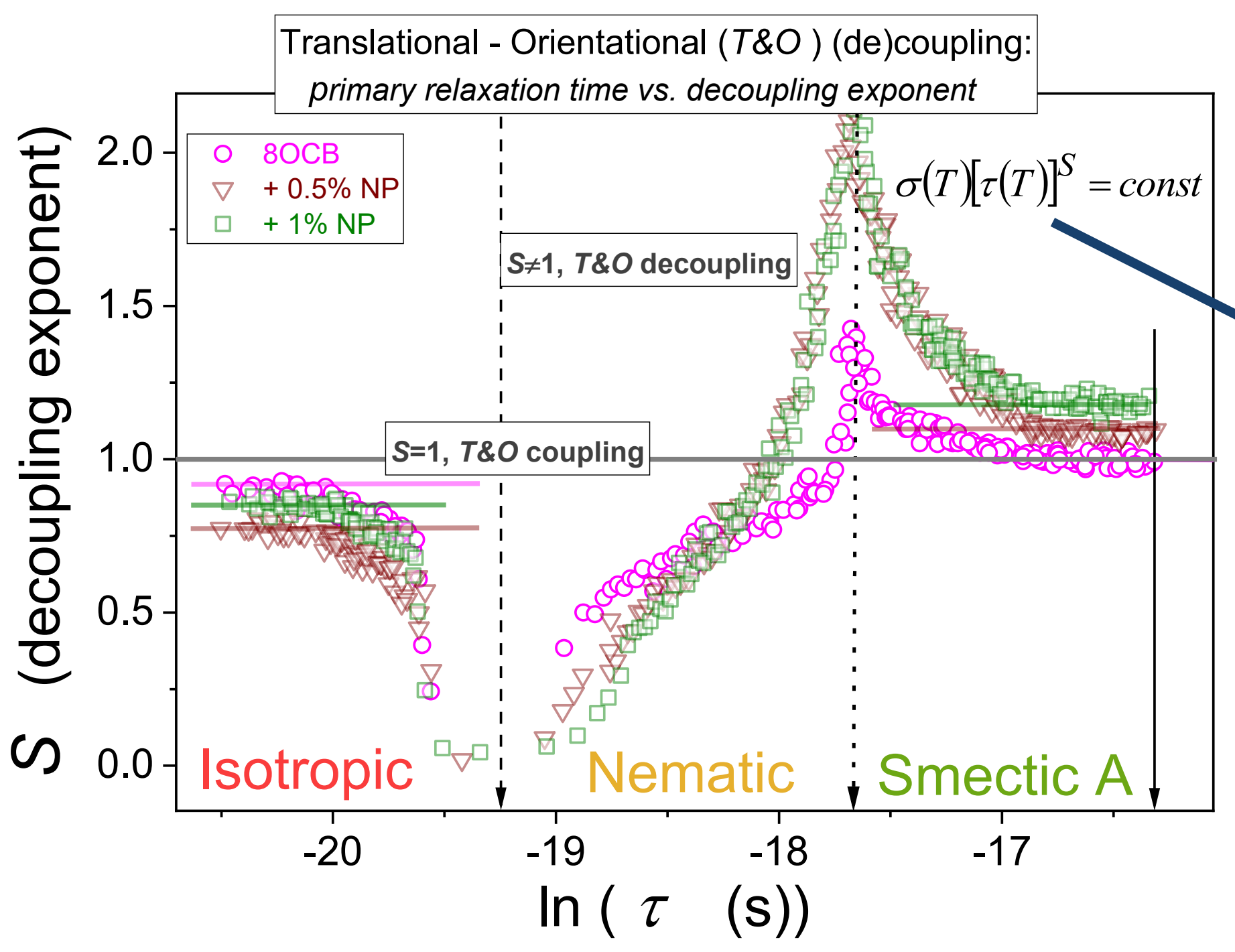
8OCB and its nanocolloids

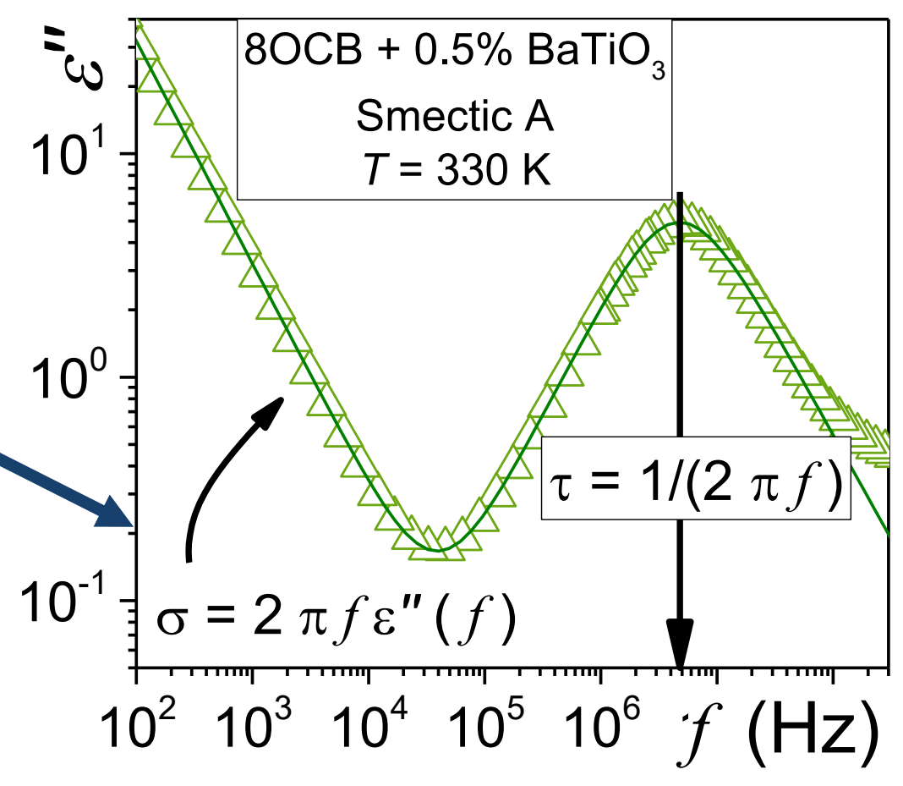


Nanoparticles (NPs), here paraelectric $BaTiO_3$ (with diameter 2r = 50 nm), **can yield a permanent 'parallel' arrangement of LC molecules – even more prominent than the one forced by a strong magnetic field** (black circles). It is the extreme 'endogenic' orientation that substitutes the classic exogenic one – induced by external magnetic or electric fields.

The derivative-based analysis of the temperature changes of dielectric constant reveals strong pretransitional effects in all phases. In composite samples **there is no homogeneous nematic phase but 2 nematic regions** dominated by pre-isotropic and pre-SmA fluctuations **In the solid phase, the premelting effect occurs.**





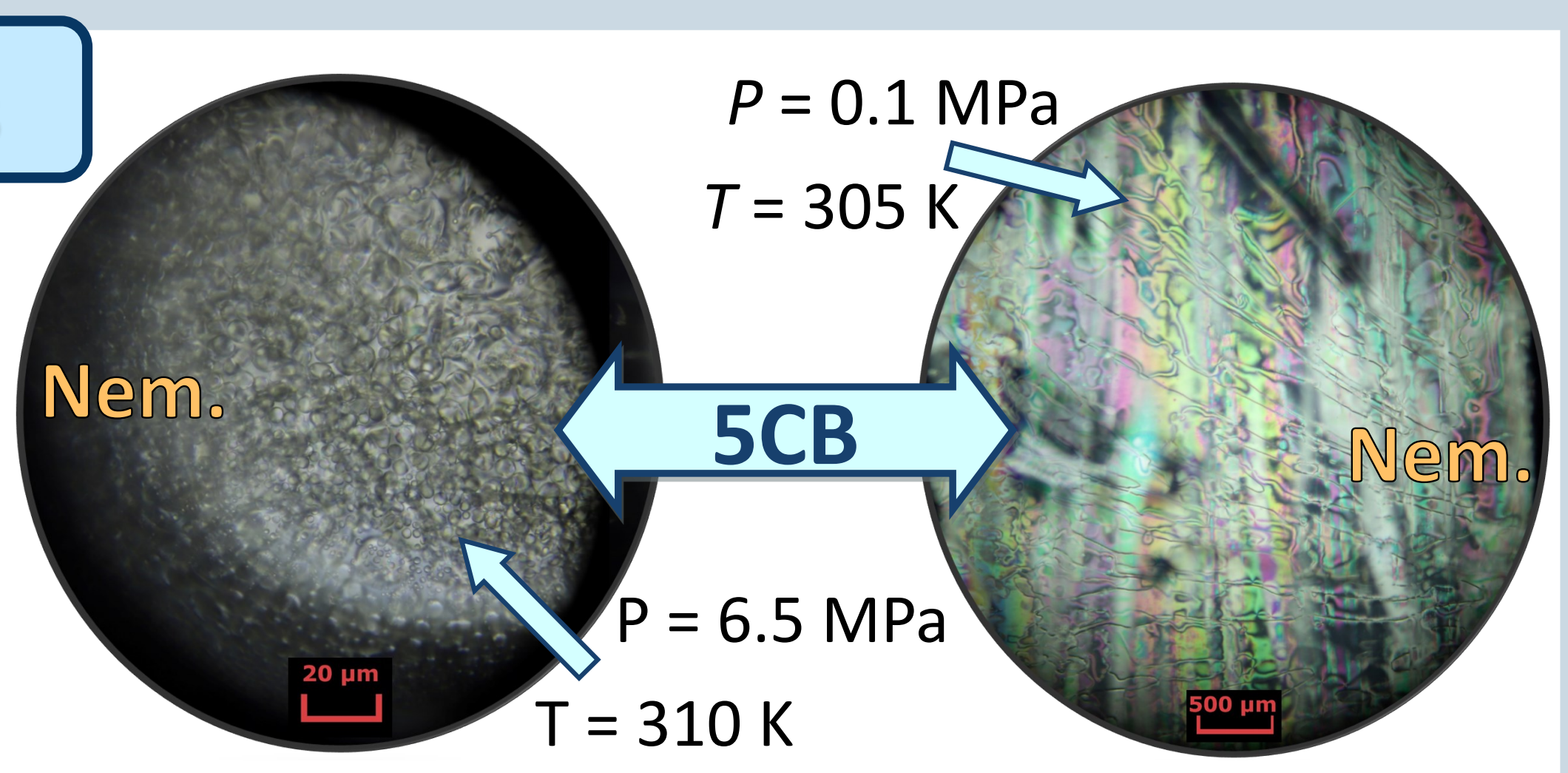


An exemplary dielectric loss curve ($\varepsilon''(f)$). DC conductivity (σ) and relaxation time (τ) are marked.

Changes of **the decoupling exponent**: $S = -d\ln\sigma(T)/d\ln\tau(T)$. So far, values in the range $0.5 < S \leq 1$ were reported, in glass-forming, supercooled liquids. Here we present evidence for ***S* values from ~0 to ~2.5.**

Microscopic observations

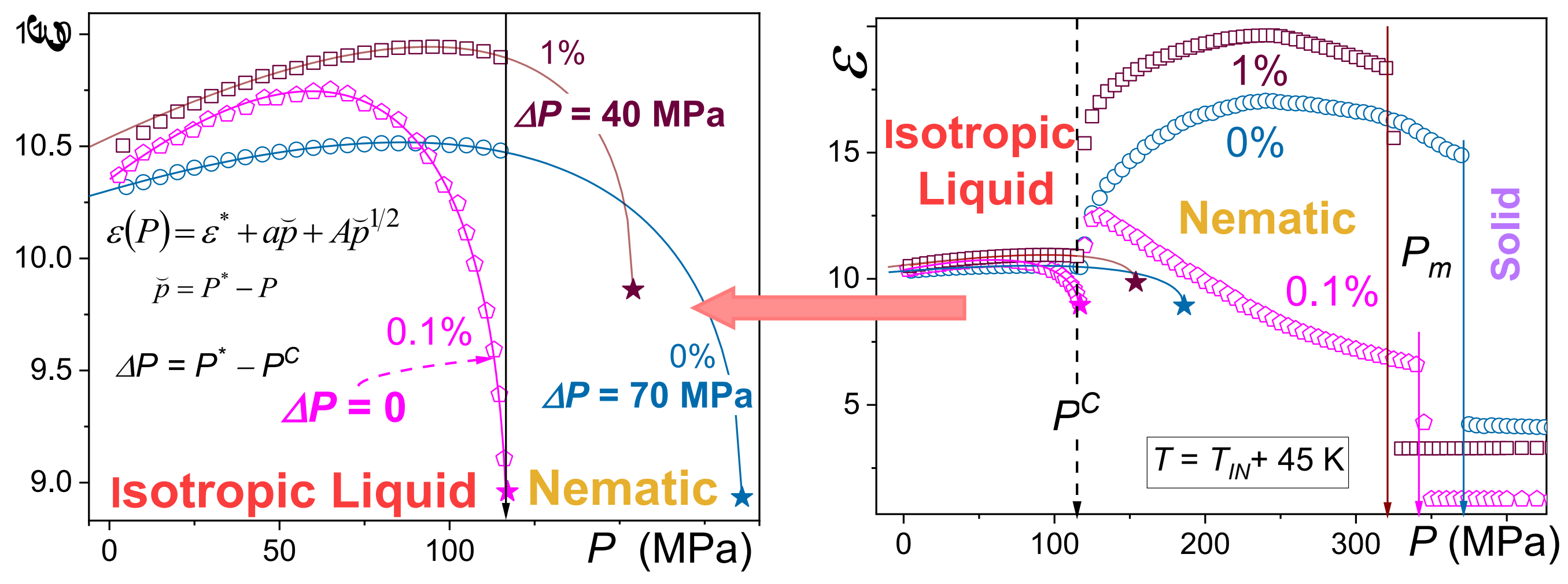
Microscopic studies of LCs and nanocolloids allow the direct observation of topological defects, and their evolution as a function of time, temperature, and (only in X-PressMatter) compression.

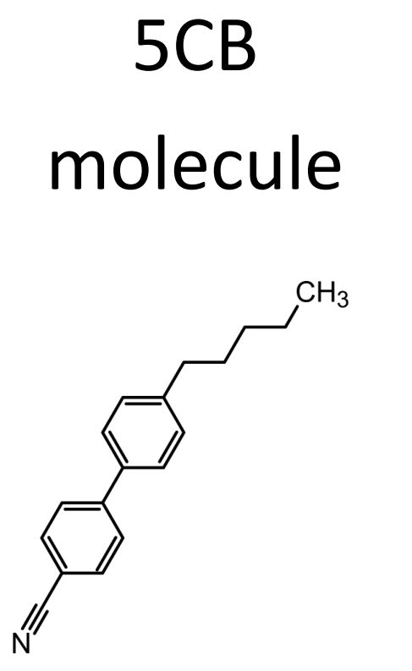


References

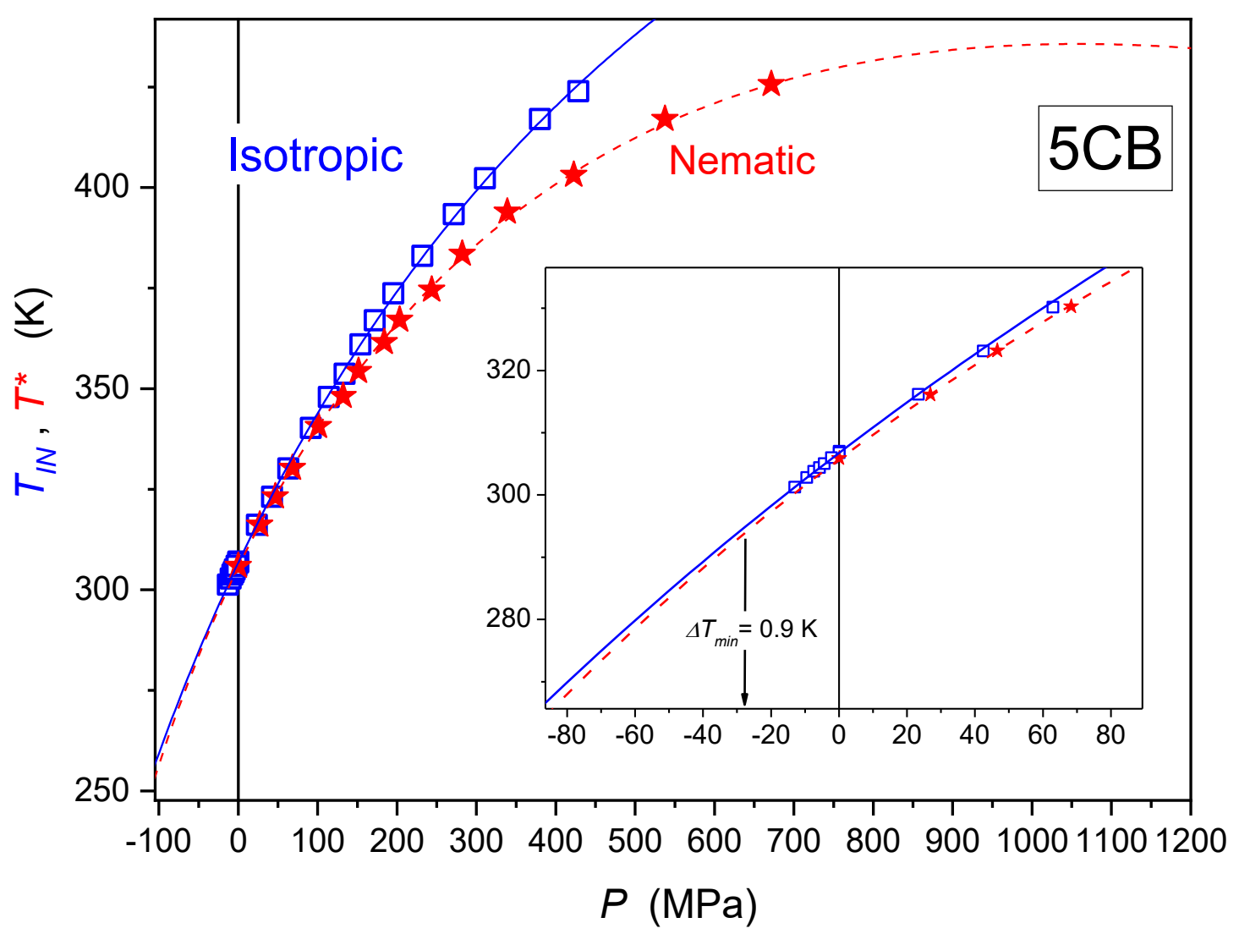
1. J. Łoś, A. Drozd-Rzoska, S. J. Rzoska, S. Starzonek, K. Czupryński. The *fluctuation-driven dielectric properties of liquid crystalline 8OCB and its nanocolloids*. Soft Matter. 18: 4502-4512 (2022).
2. P. Lloveras , A. Aznar, M. Barrio, et al. *Colossal barocaloric effects near room temperature in plastic crystals of neopentylglycol*. Nat. Comm. 10, 1803 (2019).
3. B. Li, Y. Kawakita, S. Ohira-Kawamura, et al. *Colossal barocaloric effects in plastic crystals*, Nature 567: 506-510 (2019).

5CB and its nanocolloids




5CB molecule

Changes in dielectric constant in 5CB and its nanocolloids (with paraelectric $BaTiO_3$ NPs) on compressing. The pretransitional effect portrayal is shown (solid curves). The Isotropic → Nematic phase transition discontinuities ΔP are given. For the 0.1% concentration of NPs, the discontinuity of the transition disappears. This means that **in compressed LC-based nanocolloids the Isotropic Liquid – Nematic transition can become continuous**. Note that there are clear theoretical indications, given by de Gennes (Nobel Prize 1991), that the I-N transition has to be (weakly) dis-



Changes of the Isotropic Liquid – Nematic transition temperature on compressing. Stars show the 'hidden' continuous phase transition. The distance between curves is the metric of the discontinuity of the transition. **The discontinuity reaches the minimal value in the negative-pressures domain,** where also the SmA phase emerges.

The Colossal Barocaloric Effect in LCs

The barocaloric effect is characterized as thermal responses in a material resulting from compression. 2 years ago, for the first time, the metric of the phenomenon (the entropy change related to the transition ΔS) obtained in a plastic crystal was similar to the one occurring in the classic vapor process [2,3].The discontinuous melting transition in pure LC materials exhibits even higher values of ΔS than plastic crystals. LC materials are also much more sensitive to pressure changes. Values of ΔS might be optimized by selecting proper LC material and nanoparticles. **Due to the colossal barocaloric effect, LCs have a great potential to become a new generation of refrigerants**.

Material	Entropy change ΔS ($J\,K^{-1}\,kg^{-1}$)
Plastic Crystal Neopentylglycol (NPG) [2,3]	380 (0.1 MPa) 445 (250 MPa) 500 (500 MPa)
LC: 8OCB+NPs ($BaTiO_3$) (first estimations)	8OCB - 330, composite: 420 (0.1 MPa) 450 (100 MPa) 600 (300 MPa)
LC: 11CB+NPs ($BaTiO_3$) (first estimations)	11 CB - 340, composite 370 (0.1 MPa) 450 (100 MPa) 500 (200 MPa)
For comparison: Agent R114a — Classic 'vapor' technology	380 - 450

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