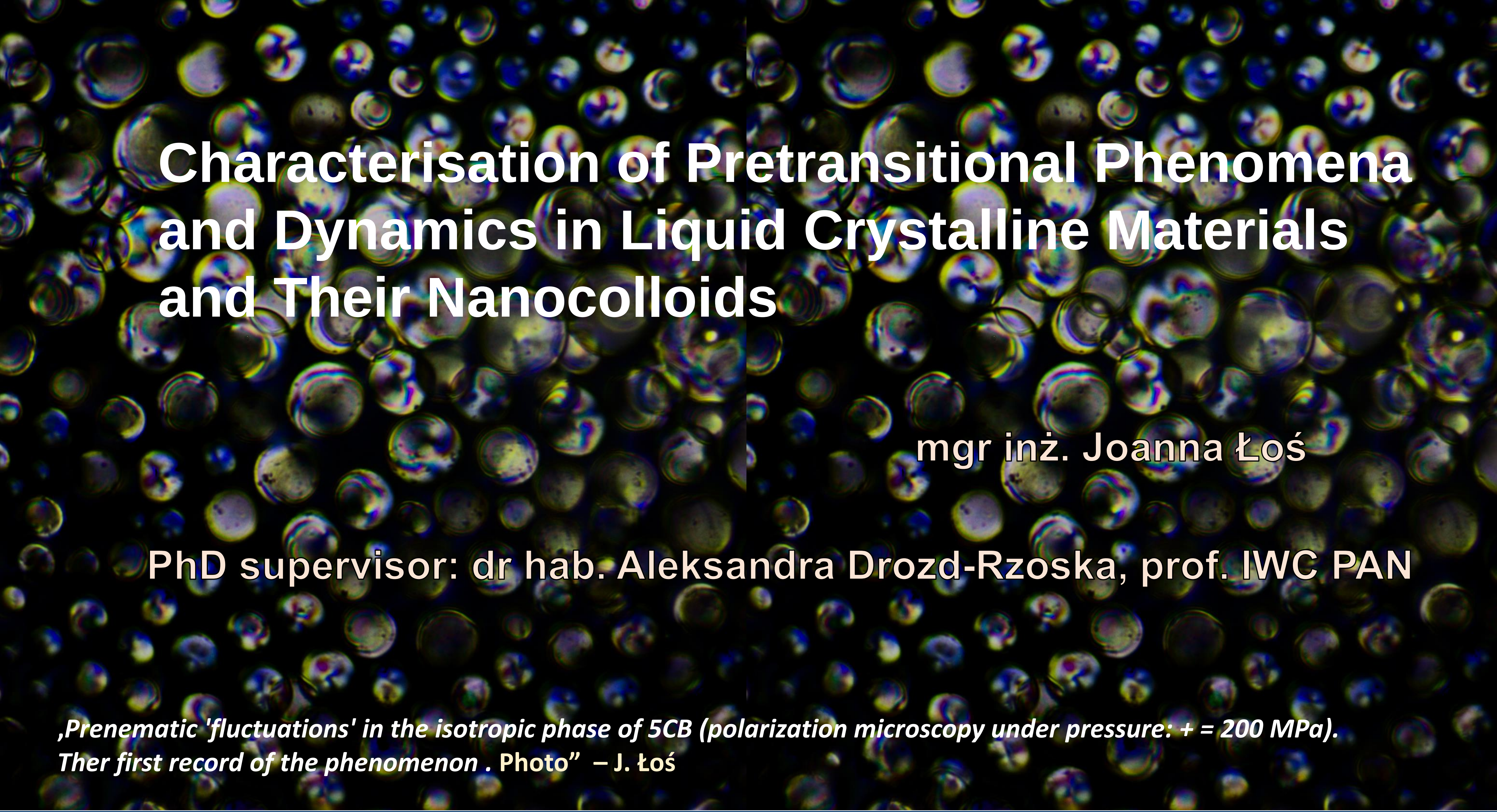


Characterisation of Pretransitional Phenomena and Dynamics in Liquid Crystalline Materials and Their Nanocolloids

mgr inż. Joanna Łoś

PhD supervisor: dr hab. Aleksandra Drozd-Rzoska, prof. IWC PAN

‚Prenematic 'fluctuations' in the isotropic phase of 5CB (polarization microscopy under pressure: + = 200 MPa).
Ther first record of the phenomenon . Photo” – J. Łoś

List of publications on which the dissertation is based

[P1] J. Łoś, A. Drozd-Rzoska, S.J. Rzoska, S. Starzonek, K. Czupryński, *„Fluctuations-driven dielectric properties of liquid crystalline octyloxycyanobiphenyl and its nanocolloids"*, Soft Matter**, 2022**, vol. 18, pp. 4502-4512.

https://doi.org/10.1039/D2SM00105E **IF = 2.9, pkt. MEiN = 140 pkt**

[P2] J. Łoś, A. Drozd-Rzoska, S.J. Rzoska, K. Czupryński, *„The impact of ionic contribution to dielectric permittivity in 11CB liquid crystal and its colloids with* $BaTiO_3$ *nanoparticles"*, European Physical Journal E, **2022**, vol. 45, p. 74.

https://doi.org/10.1140/epje/s10189-022-00228-9 **IF = 1.8, pkt. MEiN = 40 pkt**

[P3] J. Łoś, A. Drozd-Rzoska, S.J. Rzoska, *„Critical-like behavior of low-frequency dielectric properties in compressed liquid crystalline octyloxycyanobiphenyl (8OCB) and its nanocolloid with paraelectric* $BaTiO_3$*"*, Journal of Molecular Liquids, **2023**, vol. 377, p. 121555.

https://doi.org/10.1016/j.molliq.2023.121555 **IF = 5.3, pkt. MNiSW = 100 pkt**

[P4] J. Łoś, A. Drozd-Rzoska, S.J. Rzoska, S. Starzonek, K. Czupryński, P. Mukherjee, *„Near-continuous isotropic – nematic transition in compressed rod-like liquid crystal based nanocolloid"*, Journal of Molecular Liquids, **2023**, vol. 382, p. 121844.

https://doi.org/10.1016/j.molliq.2023.121844 **IF = 5.3, pkt. MNiSW = 100 pkt**

[P5] A. Drozd-Rzoska, J. Łoś, S.J. Rzoska, *„The Dominance of Pretransitional Effects in Liquid Crystal-Based Nanocolloids: Nematogenic 4-methoxybenzylidene-4'–butylaniline with Transverse Permanent Dipole Moment and* $BaTiO_3$ *Nanoparticles"*, Nanomaterials, **2024**, vol.14, p.655.

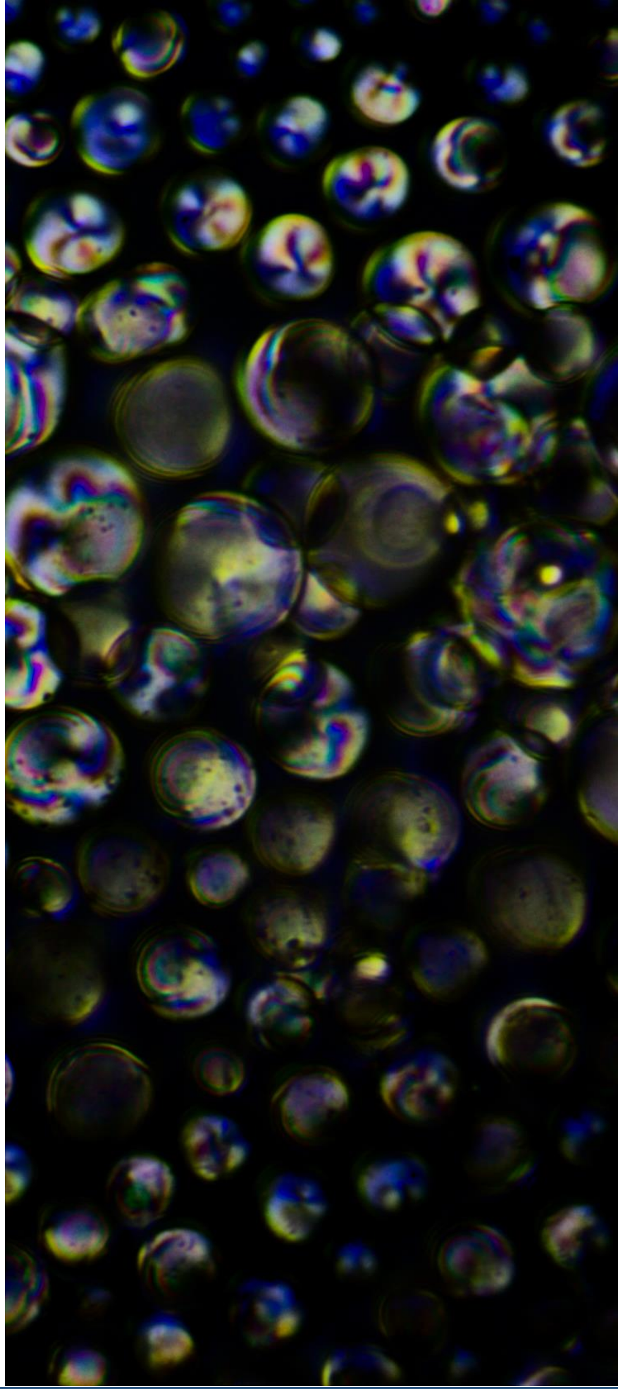
https://doi.org/10.3390/nano14080655 **IF = 4.4 pkt. MNiSW = 100 pkt**

Motivation - Nobel Prizes related to the scope of work: phase transitions, critical phenomena, critical/pre-transition fluctuations and the influence of exo- and endogenous factors

- Lev D. Landau **(1962)** – pointed out the role of symmetry and the order parameter for continuous phase transitions
- Kenneth G. Wilson **(1982)** – award for “the theory of critical phenomena in phase transitions, in particular showing the role of critical exponents with values depending only on the dimensions of space and the order parameter. This is the informal beginning of the physics of critical phenomena
- Pierre G. de Gennes **(1991)** – for “the discovery that the methods developed in the study of order phenomena in simple systems can be generalized to more complex forms of matter, such as liquid crystals and polymers”; de Gennes introduced a new category of materials : Soft Matter
- David J. Thouless, Duncan Haldane, John M. Kosterlitz **(2016)** – award for “theoretical discoveries in the field of topological phase transitions and topological phases of matter”
- Giorgio Parisi **(2021)** – for the discovery of interactions between disorder and fluctuations in complex systems, in physical systems from the atomic to planetary scale
- Moungi Bawendi, Louise Brus i Alexei Ekimov **(2023)** –The Nobel Prize in Chemistry for “fundamental discovery in the field of nanotechnology ... for the study of so-called quantum dots, or nanoparticles so small that their size determines their properties”

Motivation – research gap

- The *Physics of Liquid Crystals* (LCs) is of grand interest both in theoretical research and because of its applications in technology (displays, photonics). The addition of nanoparticles (NPs) to LCs leads to qualitatively new properties.
- **In 2000, 127** papers were published on the subject of LCs+NPs. In **2010**, there were **851** publications and **in 2024: 3020 papers**. Nanocolloids based on liquid crystals have become a new branch of *Physics of Liquid Crystals* and *Soft Matter Physics*. Notwithstanding, records on the impact of critical fluctuations in LCs+NPs nanocolloids have been almost absent, although their fundamental impact on 'pure' LC materials is proven.
- The *Physics of Critical Phenomena* is the Grand Universalistic success of Physics in recent decades. The influence of pressure (exogenic factor) and nanoparticles (endogenic factor) on critical fluctuations is still an area with alimited experimental evidence.
- The discontinuous Liquid-Crystal (Liquid-Solid) phase transition remains a cognitive gaps. The main reference are still more than a century old works by Clapeyron & Clausius and Lindemann. The evidence for the LC mesophase - crystal transition was particularly poor. For LCs+NPs nanocolloids, it was absent.

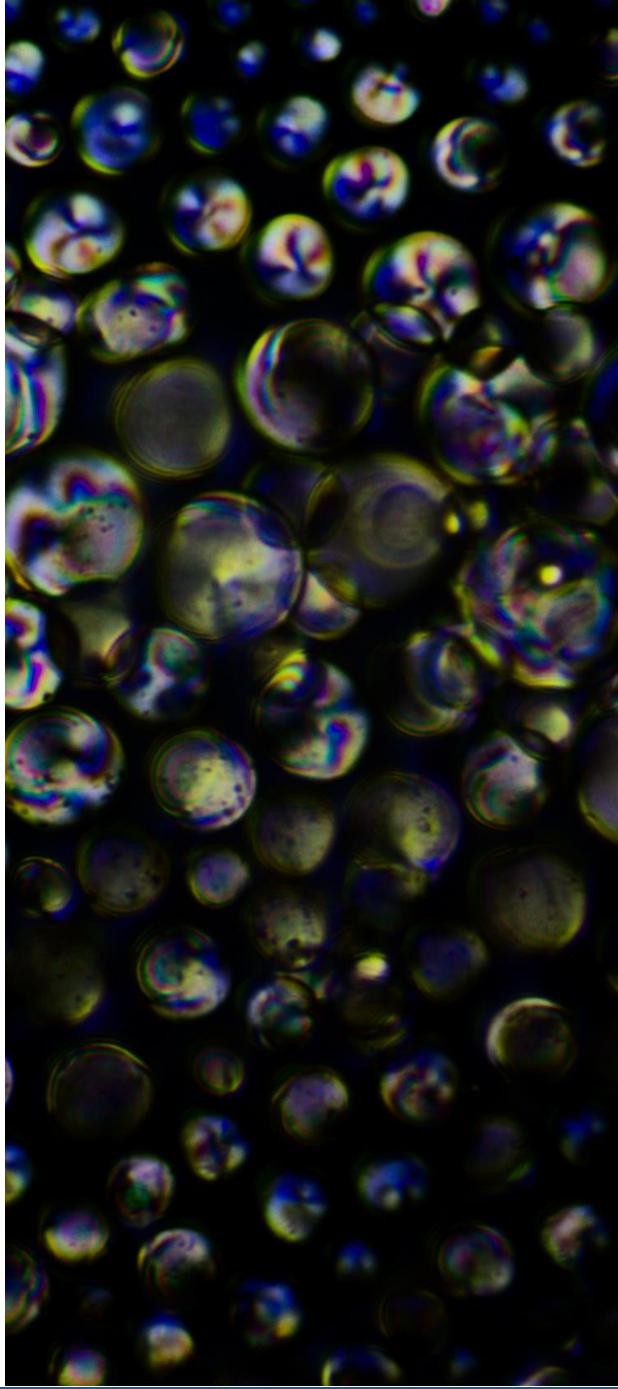


AIM

The aim of this dissertation is to determine the influence of pre-transition fluctuations on the properties of liquid crystals and liquid crystal nanocolloids and to verify whether the observed phase transitions in liquid crystal nanocolloids are described by critical exponents analogous to those for phase transitions in pure liquid crystalline material

Studies were conducted in rod-like liquid crystalline materials with parallel permanent dipole moment (5CB, 11CB, 8OCB) & perpendicular dipole moment (MBBA) and their nanocolloids with $BaTiO_3$ nanoparticles (d ~ 50 nm, ~spherical, paraelectric).

Main research method: broadband dielectric spectroscopy (BDS).



CONCLUSIONS AND MAIN ACHIEVEMENTS OF THE DISSERTATION **[P1 - P5]**

- The critical changes in the dielectric constant ***ε***, indicating the arrangement of dipole moments, in 8OCB, 5CB, 11CB, MBBA and their nanocolloids with $BaTiO_3$ nanoparticles:

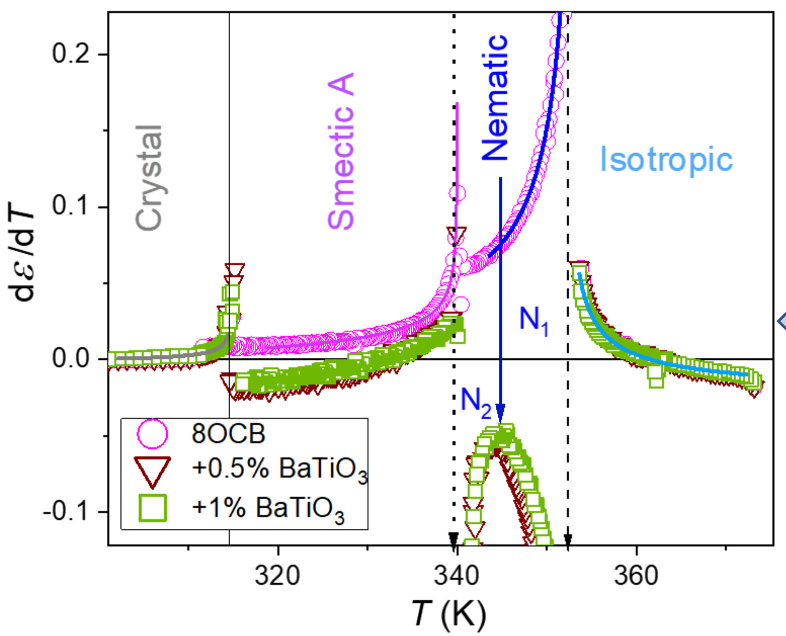
$$\varepsilon(T) = \varepsilon^* + a|T - T^*| + A|T - T^*|^{1-\alpha}$$

$$\frac{d\varepsilon}{dT} = a + A(1-\alpha)|T - T^*|^{-\alpha}$$

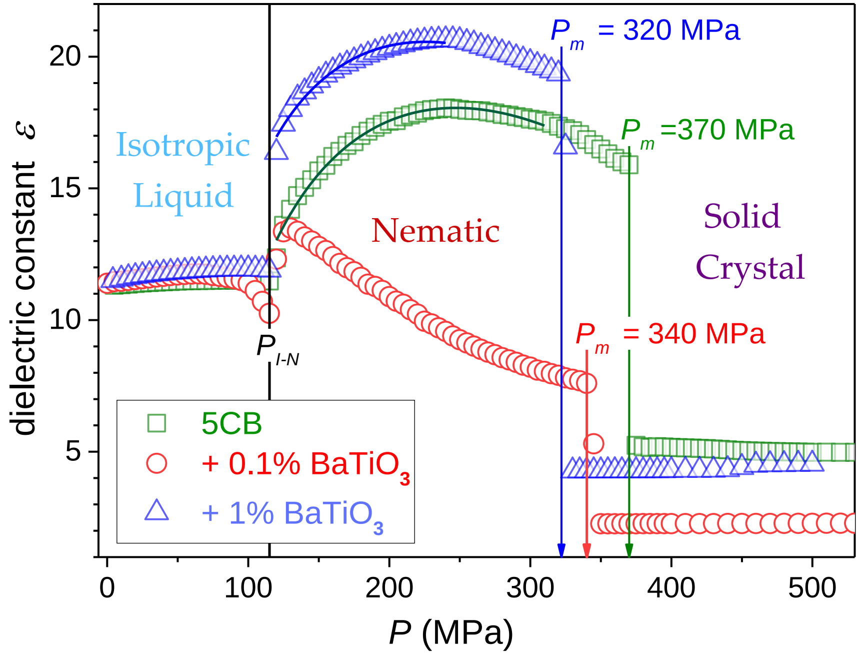
[P1, P2, P5]

$$\varepsilon(P) = \varepsilon_T^* + b|P^* - P| + B|P^* - P|^{1-\alpha}$$

[P3, P4]



Temperature and pressure changes are analogous:
Isomorphism of Critical Phenomena



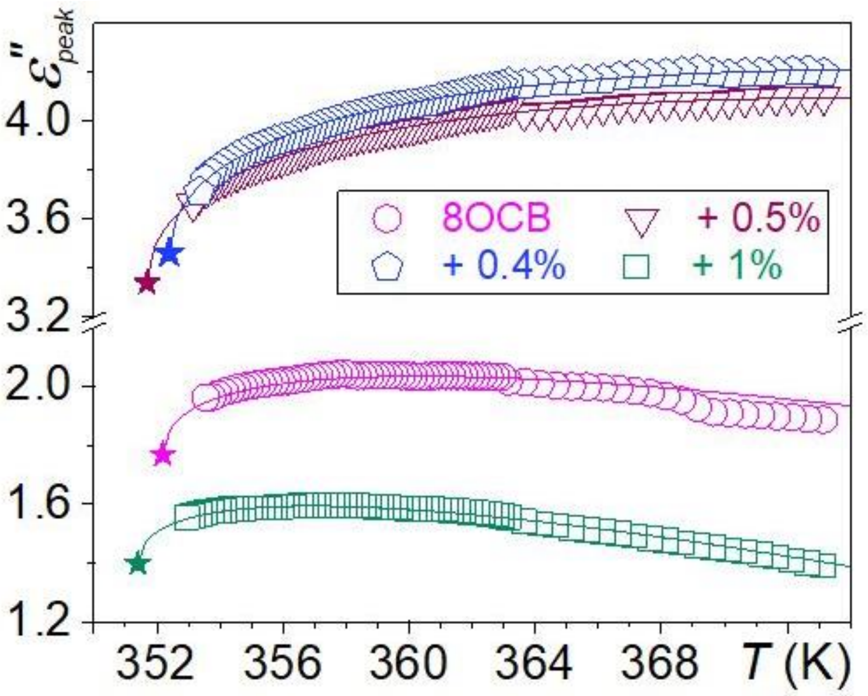
Pretransitional / precritical effects are the manifestation of critical fluctuations

Nanoparticles (endogenic factor) yield the permanent orientation of LC molecules in the mesophase. <u>The (exogenic) strong magnetic field, used so far for orientation, is not needed</u>.

CONCLUSIONS AND MAIN ACHIEVEMENTS OF THE DISSERTATION **[P1]**

Loss curve maximum ε''_{peak} **is described in the same way as** $\varepsilon\,(f)$

$$\varepsilon''_{max}(T) = \varepsilon^{**} + a^{**}|T - T^{**}| + A^{**}|T - T^{**}|^{1-\alpha} \Rightarrow \frac{d\varepsilon''_{max}}{dT} = a^{**} + A^{**}(1-\alpha)|T - T^{**}|^{-\alpha}$$

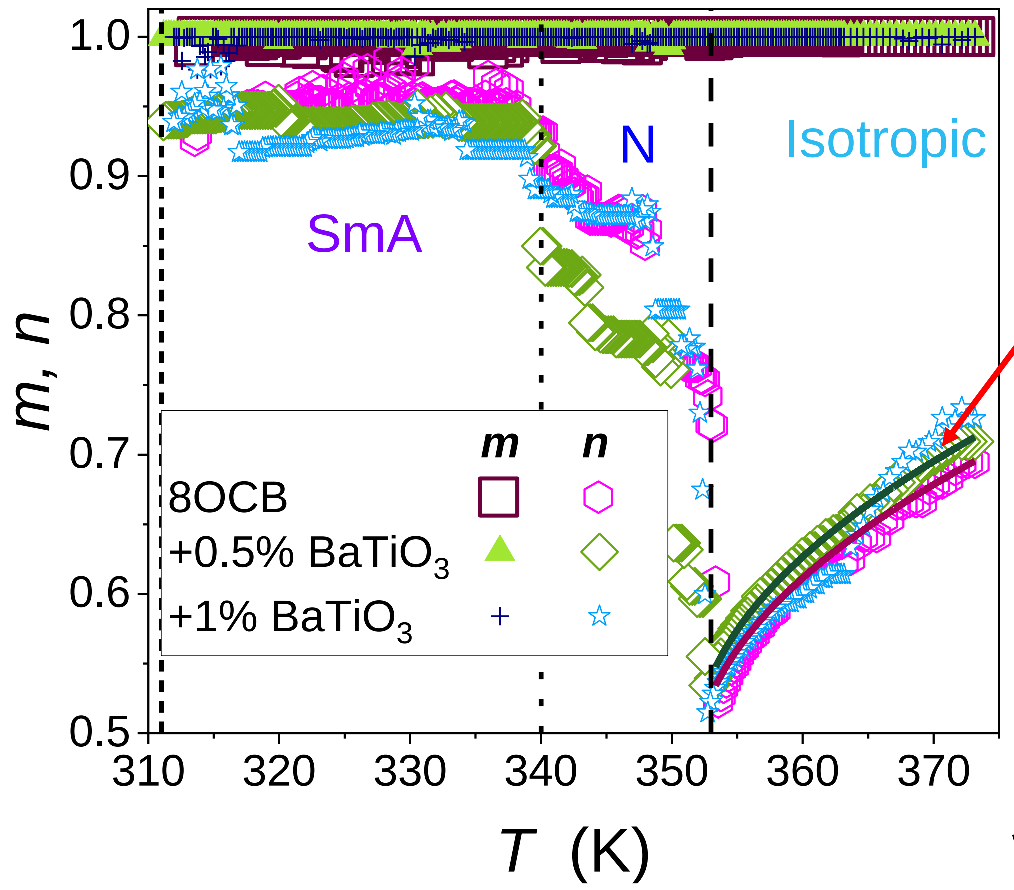


Isotropic phase, *Isotropic – Nematic* (I-N) phase transition

- Changes in dielectric constant $\varepsilon = \varepsilon'(f_{static})$ are related to the uniaxial arrangement of dipole moments within the pretransitional / precritical fluctuations
- Loss curve maximum ε''_{peak} defines the energy associated with the arrangement of dipole moments within the fluctuations
- Pretransitional effects show the same pattern for $\varepsilon(T)$ and $\varepsilon''_{peak}(T)$ in the isotropic phase ($I \rightarrow N$) and smectic A phase (SmA→N)
- Nanoparticles do not affect the value of the critical exponent α, related to specific heat (internal energy) changes

CONCLUSIONS AND MAIN ACHIEVEMENTS OF THE DISSERTATION [P1]

For the first time, the critical behavior of parameter describing distribution of relaxation times (*n*(T)) was shown :



$$n = 0.48 + (\mathrm{T} - \mathrm{T}^*)^{0.5}$$

Loss curve related to $\varepsilon''(f)$ spectrum provides basic information about relaxation dynamics. Its peak defines the values: $\tau = 1/2\pi f_{peak}$ (relaxation time) and ε''_{peak} (energy associated with the reorientation). The slopes of the curve reprezent the distribution of relaxation times, described by the famous Jonsher scaling:

$$\varepsilon''(f < f_{peak}) \propto f^{m} \text{ oraz } \varepsilon''(f > f_{peak}) \propto f^{-n}$$

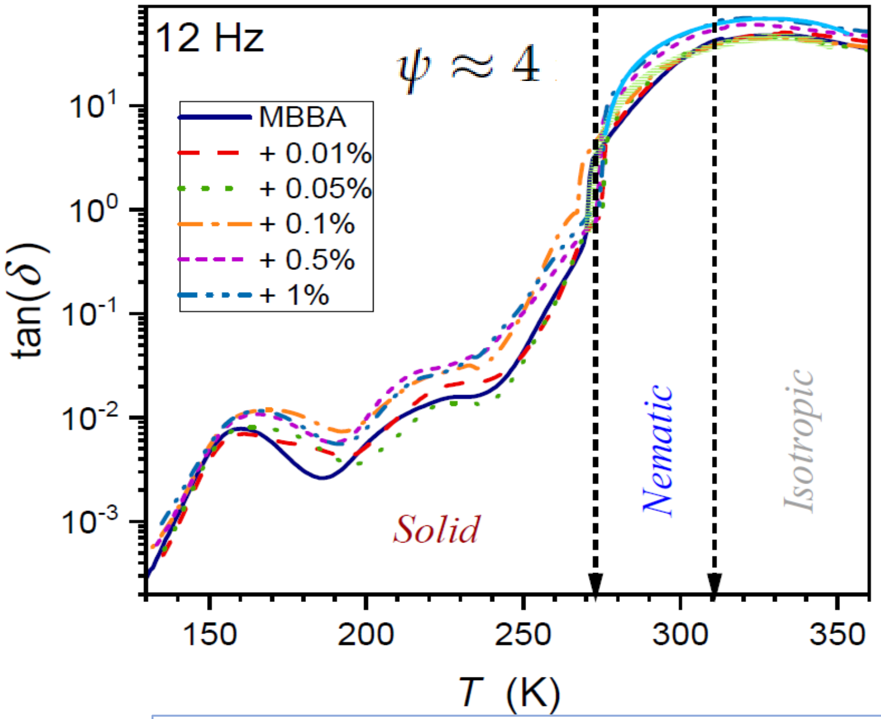
where $m, n \leq 1$ -- disribution parameters.

For the simple Debye relaxation with only one relaxation time: *m*, n = 1

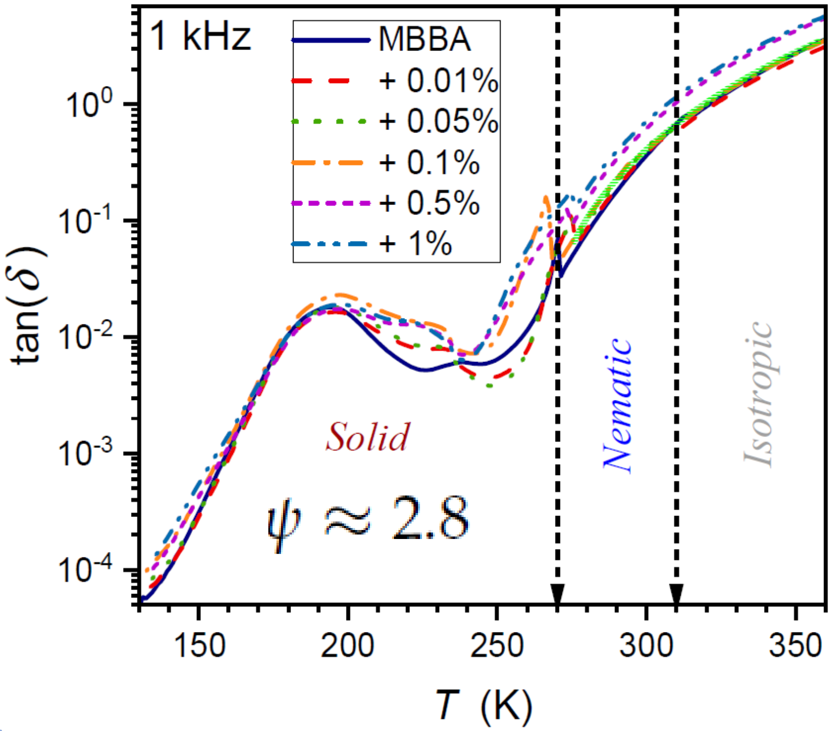
CONCLUSIONS AND MAIN ACHIEVEMENTS OF THE DISSERTATION **[P5]**

- **'Critical' changes in the electric loss tangent and the surprising smooth evolution through subsequent phase transitions:**

$$D(T) = \tan\delta(T) = \tan\delta^{*} + d(T - T_{\delta}) + D(T - T_{\delta})^{\Psi}$$



The electric loss tangent $D = \tan\delta = \varepsilon''/\varepsilon'$ is a measure of the power loss that can be converted into heat.



$D = \tan\delta$ is an important quantity in engineering work but - so far – it has been (completely) neglected in the *Physics of Liquid Crystals*

CONCLUSIONS AND MAIN ACHIEVEMENTS OF THE DISSERTATION **[P3]**

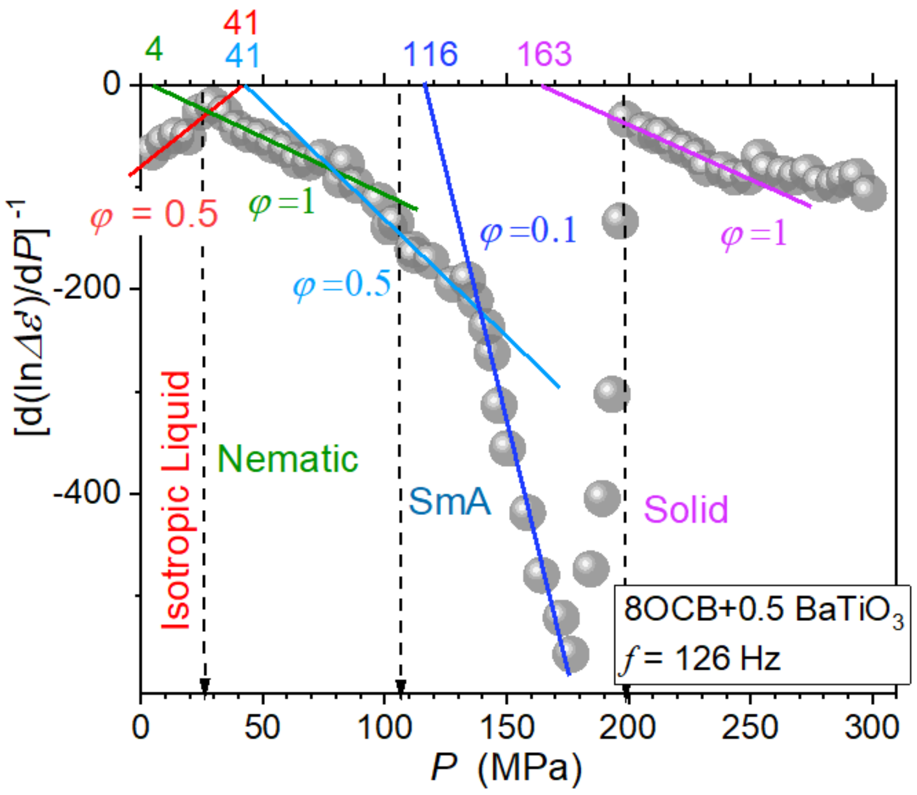
The low-frequency region (LF: for f <1 kHz) is significant for technology applications, but in fundamental research, it is a '*tabula rasa*'. The analysis of the exclusively LF part of the spectrum of the real part of the dielectric permittivity was carried out. Critical changes in the LF region were discovered.

$$\Delta\varepsilon'(f,\mathrm{P}) = \mathrm{A}(\mathrm{P}^{+} - \mathrm{P})^{-\varphi}$$

$$ln\,\Delta\varepsilon'(f,P) = lnA - \varphi ln(P^{+} - P)$$

$$\frac{dln\Delta\varepsilon'(f,P)}{dP} = \frac{-\varphi}{P^{+} - P}$$

$$\frac{P^{+}}{\varphi} + \frac{1}{\varphi} P = a + b\,P$$



The research was conducted as a function of temperature and pressure

CONCLUSIONS AND MAIN ACHIEVEMENTS OF THE DISSERTATION **[P1, P5]**

It was shown that changes in relaxation time τ and DC conductivity σ in tested LC nanocolloids follow patterns described by relations introduced by A. Drozd-Rzoska in 2019* for vitrifying liquids:

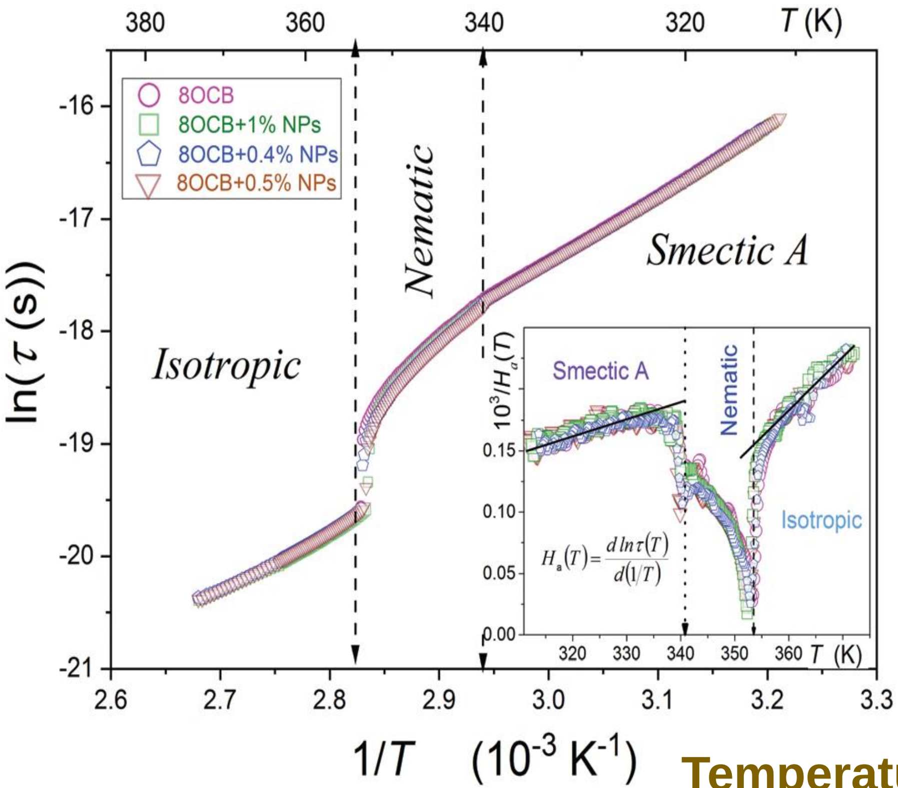
- Critical and activated:

$$\tau(T) = C_\Gamma \left(\frac{T - T_g^*}{T}\right)^{-\Gamma} \left[exp\left(\frac{T - T_g^*}{T}\right)\right]^{\Gamma}$$

- Critical changes in the apparent enthalpy value

$$H_a'(T) = \frac{dln(T)}{d(1/T)} \sim \frac{1}{T - T_g^*}$$

$$\frac{1}{H_a'(T)} = a\left(T - T_g^*\right)$$



Temperature path

Before, the analysis (limited to 5-10 temperature points) indicated the Arrhenius or Super-Arrhenius (VFT) relations, for pure LC.

*A. Drozd-Rzoska, „*Universal behavior of the apparent fragility in ultraslow glass forming systems*", Sci. Rep., vol. 9 (**2019**).

CONCLUSIONS AND MAIN ACHIEVEMENTS OF THE DISSERTATION **[P3]**

It was shown that changes in relaxation time τ and DC conductivity σ in the investigated LC nanocolloids follow patterns described by relations introduced by A. Drozd-Rzoska in 2019* for vitrifying liquids:

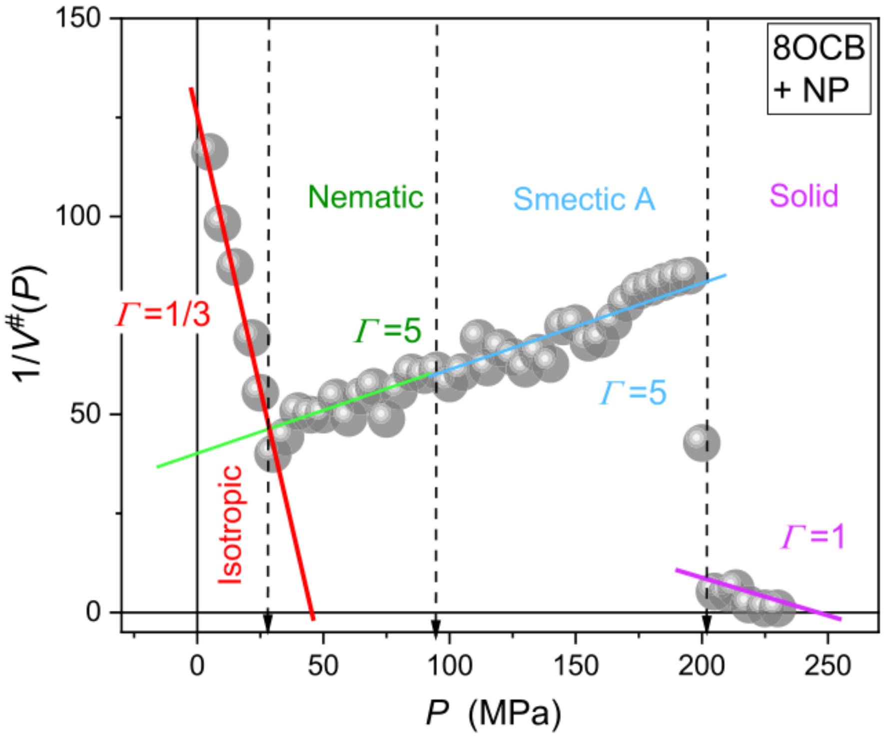
- Critical relation:

$$\tau(P) = \tau_o(P - P^*)^{-\Gamma}$$

$$V^{\#}(P) = \frac{d\ln\sigma^{-1}(P)}{dP}$$

- Critical changes in activation volume value

$$V^{\#}(P) \propto \frac{1}{|P - P^{+}|}$$



Pressure path

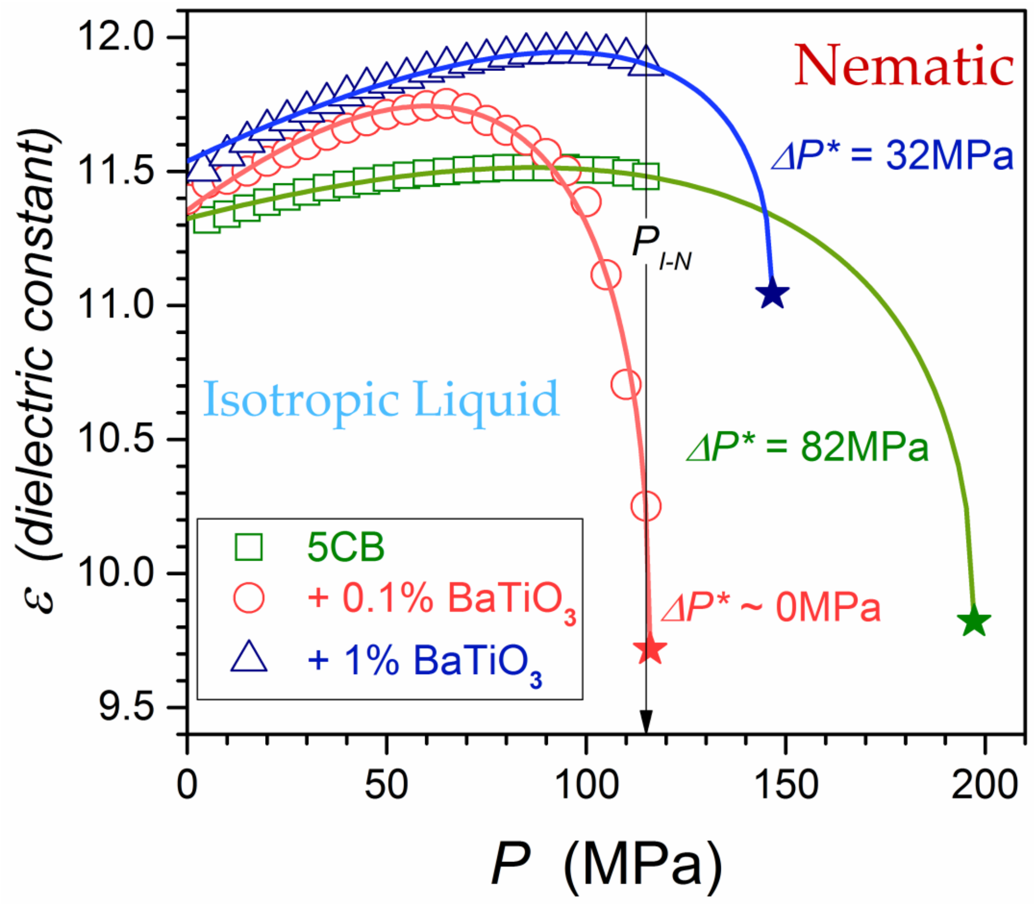
Before, based on limited data analysis (a few pressure-points), Barus or Super-Barusus relations were suggested - only for ‚pure' LCs.

*A. Drozd-Rzoska, „*Activation volume in superpressed glass-formers*", Scientific Reports, **2019**, vol. 9.

*A. Drozd-Rzoska, *Pressure-related universal previtreous behavior of the structural relaxation time and apparent fragility*. Frontiers in in Materials **2019**, vol.6.

CONCLUSIONS AND MAIN ACHIEVEMENTS OF THE DISSERTATION [P4]

The addition of an extremely small amount of nanoparticles and compressing can yield a near-continuous *Isotropic – Nematic* phase transition



Isothermal, pressure pretransitional changes in the dielectric constant are described by the relation:

$$\varepsilon(P) = \varepsilon_T^* + b|P^* - P| + B|P^* - P|^{1-\alpha}$$

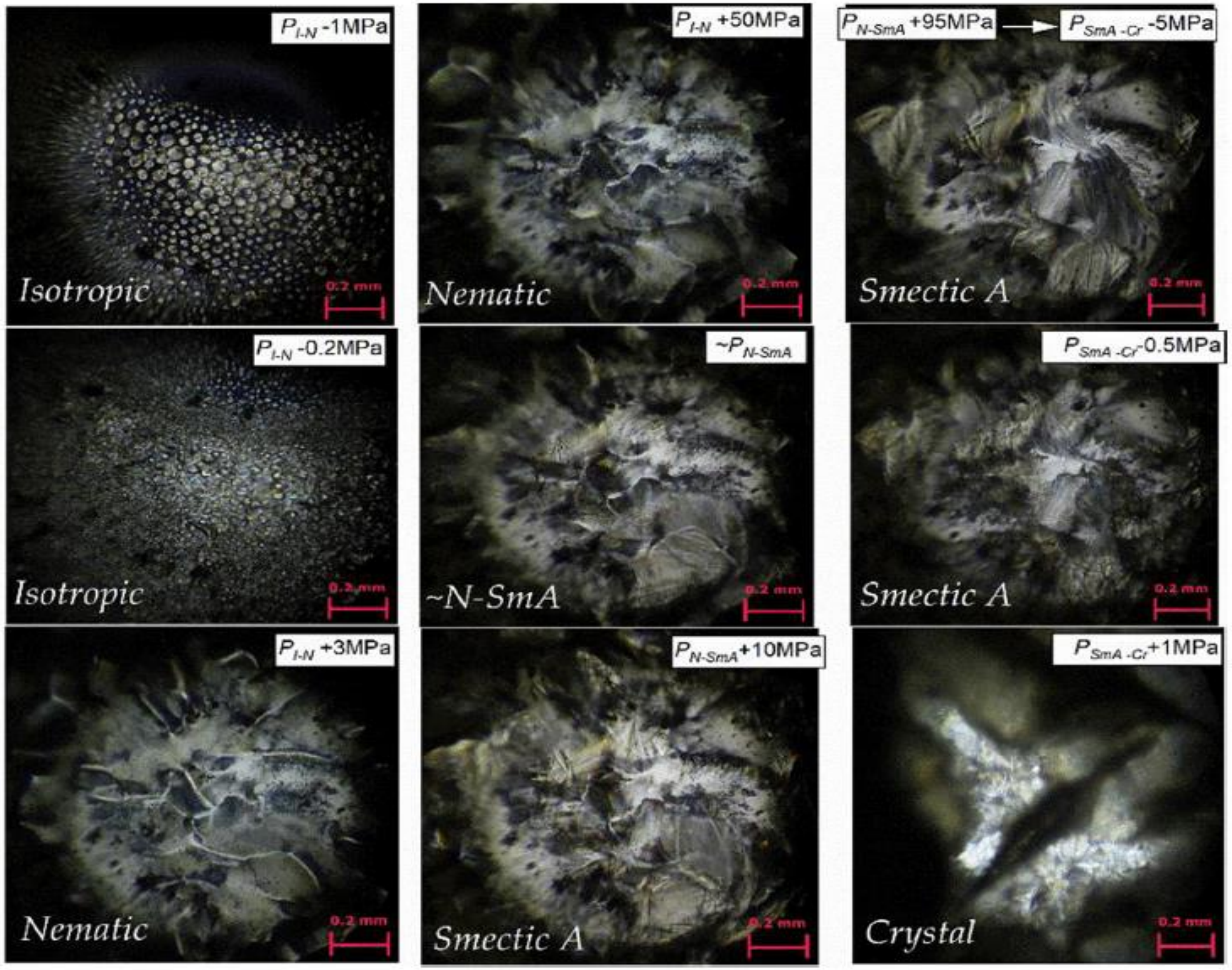
The measure of the discontinuity of the phase transition is: $\Delta P = P^* - P_{I-N}$, where P^* is the hypothetical, extrapolated pressure point of the continuous phase transition.

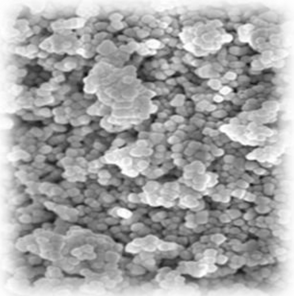
For NPs concentration c_p = 0.1%: $\Delta P \to 0$

In 1936 Lev. D. Landau demonstrated that it is impossible for the liquid-crystal phase transition (melting/freezing) to be continuous (critical) type.
In 1974, Pierre G. de Gennes pointed out that this also applies to the uniwur case of 'melting', associated with the isotropic Liquid-Nematic phase transition.

Ref.[P4] shows that continuous I-N transision can be possible, under the simultaneous exogenic impact of pressure and endogenic of nanoparticles.

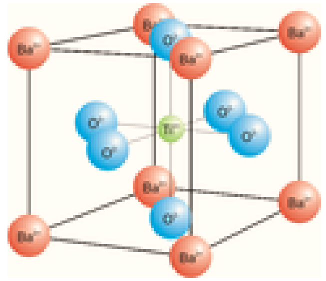
CONCLUSIONS & MAIN ACHIEVEMENTS OF THE DISSERTATION [P3, P4]





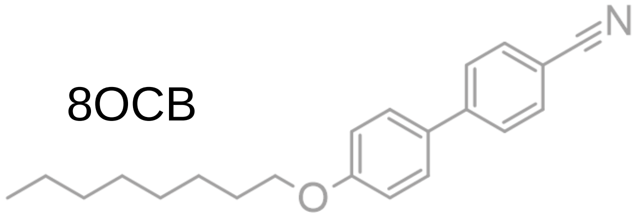
https://www.us-nano.com/

$BaTiO_3$



https://pl.wikipedia.org/wiki/Tytanian_baru

8OCB



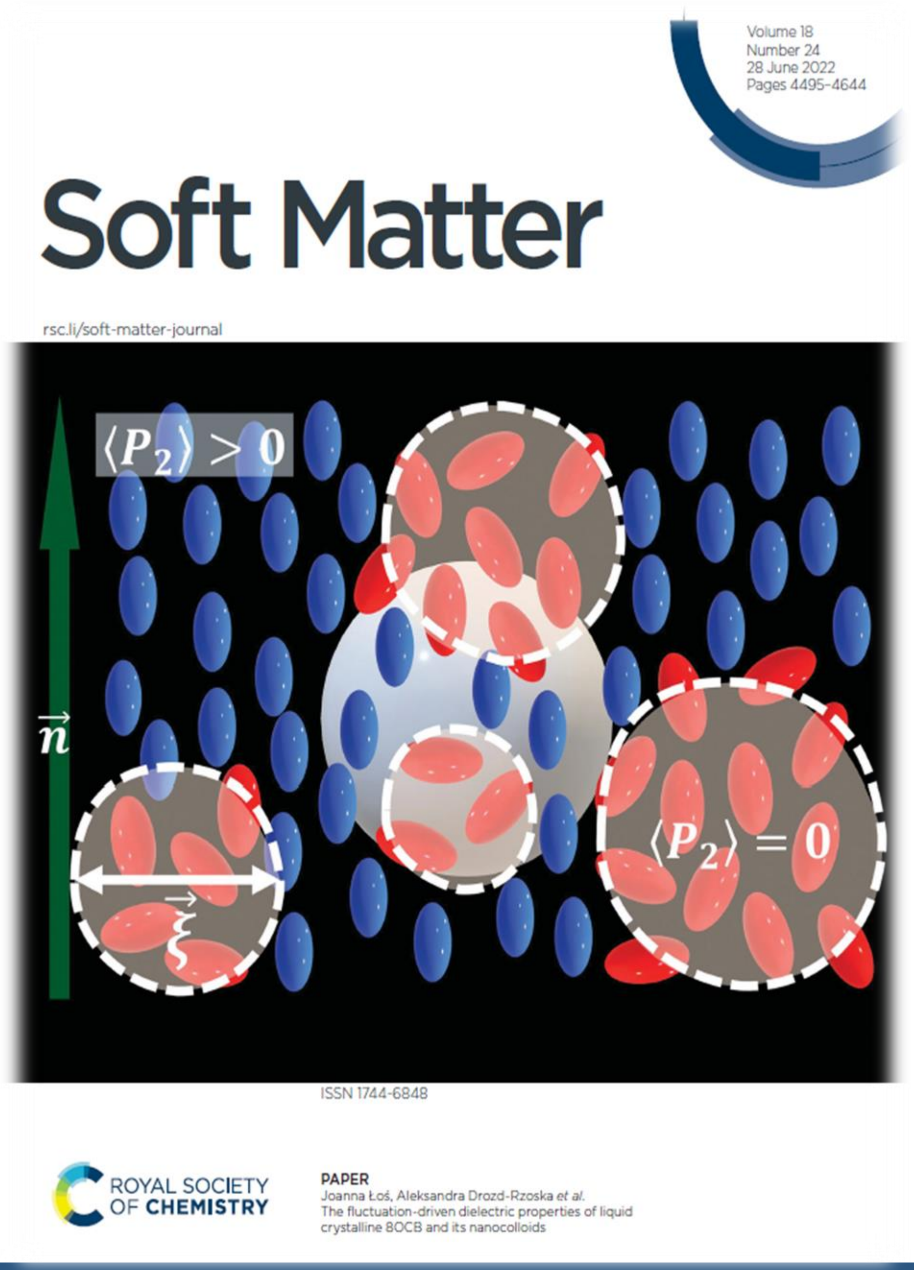
First images of the morphology of a liquid crystal (and its nanocolloids) under high pressure - the polarization microscopy.
The picture shows morfology of 8OCB+$BaTiO_3$ nanocolloids, under *P* = 200 MPa pressure.

Article:

[P1] J. Łoś, A. Drozd-Rzoska, S.J. Rzoska, S. Starzonek, K. Czupryński, *„Fluctuations-driven dielectric properties of liquid crystalline octyloxycyanobiphenyl and its nanocolloids"*, Soft Matter, **2022**, vol. 18, pp. 4502-4512.

was featured on the front cover of

SOFT MATTER journal



Thank You for the Attention

Prenematic 'nuclei-fluctuations' in the isotropic phase of 5CB (pressure polarizing microscopy *: P = 200 MPa)*

– Photo: J. Łoś.

The first experimental evidence