Article

Melting Temperature Hidden Behind Liquid−Liquid Phase Transition in Glycerol

Szymon Starzonek,* Jakub Kalabiński, Aleksandra Drozd-Rzoska, Sylwester J. Rzoska, and Aleš Iglič

Cite This: https://doi.org/10.1021/acs.jpcb.4c04552

Read Online

ACCESS | 📊 Metrics & More | 📰 Article Recommendations

ABSTRACT: Liquid−liquid phase transitions play a pivotal role in various scientific disciplines and technological applications, ranging from biology to materials science and geophysics. Understanding the behavior of materials undergoing these transitions provides valuable insights into complex systems and their dynamic properties. This review explores the implications of liquid−liquid phase transitions, particularly focusing on the transition between low-density liquid (LDL) and high-density liquid (HDL) phases. We investigate the thermodynamic, structural, and mechanistic aspects of these transitions, emphasizing their relevance in diverse fields. The creation of dynamic heterogeneities and critical fluctuations during liquid−liquid phase transitions is discussed, highlighting their role in shaping the phase behavior and dynamics of complex fluids. Experimental observations, including the use of dielectric spectroscopy and nonlinear methods, shed light on the intricate nature of these transitions. Our findings suggest a connection between liquid−liquid phase transitions and critical phenomena, with implications for understanding the supercooled state and phase behavior of hydrogen-bonded liquids such as glycerol. Overall, this review underscores the importance of interdisciplinary approaches in unraveling the complexities of liquid−liquid phase behavior and addressing fundamental questions.
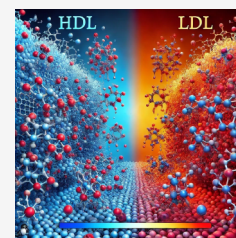
INTRODUCTION

Liquid−liquid (LL) phase transitions have implications across various scientific disciplines and technological applications.[1−5] In biology, for example, understanding the behavior of intracellular water can provide insights into cellular processes and biomolecular interactions. In materials science, the design of new functional materials often relies on controlling phase transitions to achieve desired properties.[5,6] Furthermore, the study of LL phase transitions in geophysical systems, such as Earth's mantle, has implications for understanding planetary dynamics and evolution.[7,8]

Melting is a first-order transition from a solid to a liquid phase, taking place at a characteristic temperature T_m. According to phenomenological thermodynamics, this process is characterized by the reduction of the Gibbs free energy (ΔG) to zero and nonzero changes in enthalpy (ΔH) and entropy (ΔS).[9] Another important criterion of melting is that the Gibbs free energy of the liquid is lower than that of the solid.[10] On the other hand, glass-forming liquids and melted metals exhibit a lambda-like transition between the liquid and supercooled states.[3,11] Refs 12 and 13 indicate that such behavior can also be found in water and its metastable state.

Liquid−liquid phase transitions have attracted significant attention due to their relevance in understanding the behavior of diverse materials ranging from simple liquids to complex biological systems. Of particular interest are transitions between low-density liquid (LDL) and high-density liquid (HDL) phases, which have been observed in various substances, including water, silicon, and silica.[4,9,11−13] These LL phase transitions occur under specific conditions of temperature, pressure, and composition, and elucidating their underlying mechanisms is crucial for understanding the properties of materials in different states.

LL phase transitions are intimately connected to the creation of dynamic heterogeneities and critical fluctuations, which are crucial phenomena in understanding the behavior of complex fluids.[14−17] These phenomena arise due to the inherent structural and dynamical complexities present in systems undergoing LL phase transitions.

Several mechanisms have been proposed to explain the driving forces behind LL phase transitions.[1,2,4,9,12,13,17] Among these are changes in hydrogen bonding, structural rearrangements, and percolation phenomena. In water,[1,17−19] for instance, the competition between hydrogen bonding networks leads to the formation of LDL and HDL phases under specific conditions. In other systems, such as colloidal suspensions,[20,21] changes in particle interactions and crowding effects play a significant role in driving phase transitions.

Barrat[22] and Glotzer et al.[23] introduced a critical-like description for nonlinear susceptibility (χ_4) related to a four-point correlation density function in hard-sphere liquids. They showed that, based on the mean-field approach, the critical

exponent describing the nonlinear susceptibility is $\gamma = 1/2$ upon approaching from below and above the critical temperature T_c. During LL phase transitions, regions of differing densities and local structures emerge as the system traverses the coexistence region between the LDL and HDL phases. These heterogeneous regions, referred to as domains, exhibit distinct dynamic behaviors, including variations in diffusion rates, viscosity, and molecular arrangements.[22,23] Near the critical point, the correlation length diverges, leading to the emergence of large-scale density fluctuations. These fluctuations manifest as regions of enhanced density or compositional fluctuations, giving rise to heterogeneous structures within the fluid. In the context of LL phase transitions, critical fluctuations play a crucial role in promoting the formation of dynamic heterogeneities by driving the system toward criticality, where fluctuations become long-ranged and exhibit scale invariance.[17,24,25]

Furthermore, the presence of dynamic heterogeneities and critical fluctuations influences the kinetics of phase separation, affecting the dynamics of the nucleation, growth, and coarsening processes. Nonequilibrium effects, such as spinodal decomposition and droplet coalescence, are governed by the spatial and temporal correlations arising from dynamic heterogeneities and critical fluctuations. Understanding the role of these phenomena in controlling phase transitions is essential for predicting and manipulating the phase behavior of complex fluids under different thermodynamic conditions.

■ EXPERIMENTAL SECTION

In soft matter systems, like liquid crystals, supercooled liquids, etc., the broadband dielectric spectroscopy is very helpful and commonly used.[25−32] It is based on the electrical measurements of complex dielectric permittivity, $\varepsilon^*(f) = \varepsilon'(f) + i\varepsilon''(f)$, as a function of temperature and pressure.[33] By taking a value of the real part $\varepsilon'(f)$ at a plateau region in the spectrum, which for soft matter systems occurs for $f \in (1, 100)$ kHz, one may define the dielectric constant, $\varepsilon(f = 100 \text{ kHz}) \equiv \varepsilon_s$.[27,28] The temperature (or pressure) change of the value of $\varepsilon_s(T, p)$ describes the orientation of dipole moments of molecules, which is commonly used to study phase transitions.[27−32] Since broadband dielectric spectroscopy is based on a two-point correlation function,[26,34] which gives only a macroscopic portrayal, other sophisticated methods are the nonlinear dielectric effect (NDE) and third-harmonics analysis.[26−28,31,34] These approaches allow the separation of dielectric response of molecules enclosed in a cluster from the background.[26−32] Rzoska et al.[28,29] proposed a critical-like description of the temperature dependency of the nonlinear dielectric effect ε_{NDE} for complex liquids. Comparing the above with[22,23] it leads to the following relation:

$$\chi_4 \equiv \frac{d\varepsilon_{NDE}(T)}{dT} = \frac{A}{(T - T_c)^\gamma} + B, \quad \text{for } T > T_c \tag{1}$$

$$\chi_4' \equiv \frac{d\varepsilon_{NDE}(T)}{dT} = \frac{A'}{(T - T_c)^{\gamma'}} + B', \quad \text{for } T < T_c \tag{2}$$

where T_c denotes the critical temperature, γ is the critical exponent for the three-dimensional Ising ($d = 3$, $n = 1$) universality class,[23,27] and A and B are the constants.

The pure glycerol (99.9%) was purchased from Sigma-Aldrich and was heated under vacuum to remove the rest of the bonded water. The concentration of water after heating was less than 0.05% (Karl Fischer titration and DSC). The capacitor, with a diameter of $2r = 20$ mm and a gap $d = 0.2$ mm, was filled with glycerol at a high temperature (above 373 K) and cooled to room temperature. Experiments were carried out by the use of Novocontrol Alpha-A Impedance Analyzer with wide ranges of frequency ($10^7 - 10^{-2}$ Hz) and temperature (305−280 K) with a step $\Delta T = 0.2$ K and a stability better than $\Delta \dot{T} = 0.02$ K. Nonlinear parameters such as third harmonics $\varepsilon_3'(T)$ and nonlinear dielectric effect (ε_{NDE}) were measured using the Novocontrol HV/Trek Amplifier setup. The obtained data were analyzed by the use of derivative methods described here.[28−31,33−35]

To calculate the DC conductivity (σ_{DC}) from dielectric spectra, one may use the frequency-dependent complex conductivity ($\sigma^*(f)$), which is related to the complex permittivity: $\sigma^*(f) = \sigma'(f) + i\sigma''(f) = i2\pi f\varepsilon_0\varepsilon^*(f)$. In the dielectric spectrum, ($\sigma'(f)$) typically shows a plateau at low frequencies corresponding to σ_{DC}. Therefore, the value of ($\sigma'(f)$) in this low-frequency plateau is the DC conductivity. Alternatively, if the dielectric loss $\varepsilon''(f)$ is dominated by conductive contributions at low frequencies, one may estimate σ_{DC} using $\sigma_{DC} = 2\pi f\varepsilon_0\varepsilon''(f)$.

■ RESULTS AND DISCUSSION

Figure 1 presents the temperature changes of the dielectric constant ε_s (A) and DC conductivity σ_{DC} (B) in glycerol and its supercooled state. The insets in part (A) show the real part of the complex dielectric permittivity spectra $\varepsilon'(f)$ for all studied temperatures and the first-order derivative of the dielectric constant as a function of temperature $d\varepsilon_s/dT$, where a minimum refers to the melting temperature T_m. The values of the dielectric constant were taken from the static region, also marked in the data plot. It is worth noting that a characteristic and strong change in the slope of the temperature dependence of the dielectric constant may be observed. Such behavior occurs near the melting point T_m, which is purely apparent for $d\varepsilon_s/dT$. Another interesting result was obtained from the DC conductivity analysis. Part (B) in Figure 1 shows an anomaly of σ_{DC} around T_m. Derivative-based analysis $d\ln \sigma_{DC}/dT$ showed a strong discontinuity at the melting point. Such behaviors were previously reported for liquid−liquid phase transition.[1,11−13]

This unusual result led us to study nonlinear effects like the nonlinear dielectric effect (NDE) and third-harmonics analysis, which are very useful for analyzing hidden or high-order phase transitions. Moreover, nonlinear methods are very sensitive to critical fluctuations occurring in the vicinity of phase transitions[28−32] and may be used to define dynamic heterogeneities.[14−19,22,32,33]
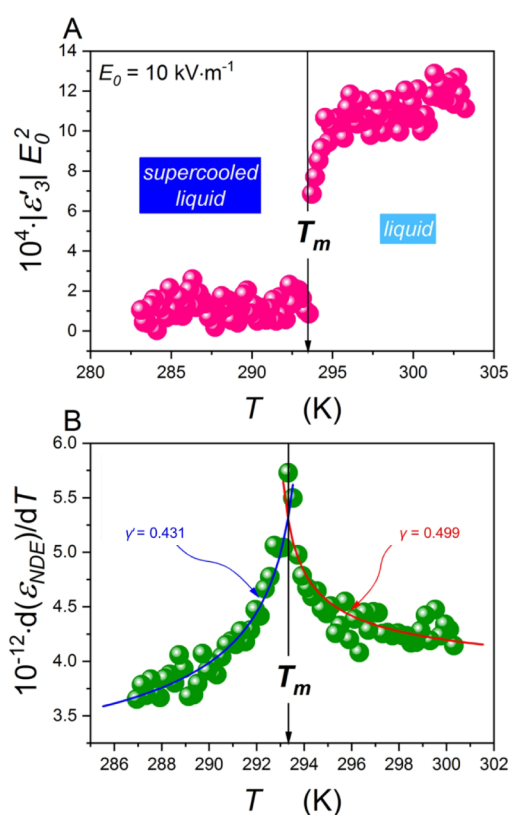
Figure 2A shows third-harmonic behavior in the vicinity of the melting temperature with a strong discontinuity at T_m, which corresponds to the liquid−liquid phase transition. On the other hand, Figure 2B presents the first-order derivative of the nonlinear dielectric effect in the same temperature regime. The equivalent of the dielectric constant in strong electric fields is the nonlinear dielectric effect (NDE). It is directly sensitive to the appearance of multimolecular heterogeneities/aggregates/fluctuations. The dielectric constant records their average impact on the entire system.
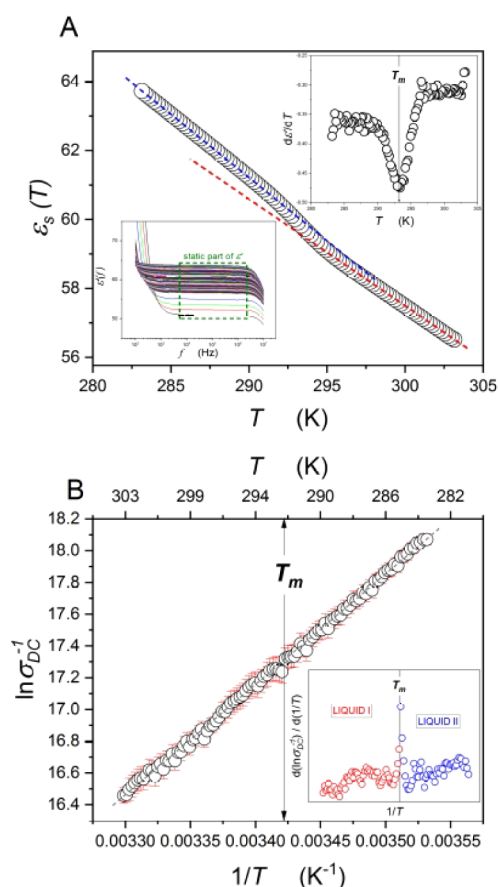
Figure 1. (A) Temperature evolution of the dielectric constant for supercooled glycerol. The left inset presents the frequency-dependent real part of the complex electric permittivity with the marked static region. The right inset shows derivative-based analysis of the dielectric constant ε_s. Characteristic minimum at melting temperature can be found. (B) Reciprocal DC conductivity behavior in vicinity of the temperature T_m. Error bars are marked in red. The inset portrays derivation with strong discontinuity at T_m. The gray straight dashed line presents the typical dependence of DC conductivity in glycerol.

Figure 2. (A) Third harmonic temperature dependence under a weak electric field $E_0 = 10$ kV m^{-1}. Discontinuity can be found at T_m. (B) Derivative analysis of the nonlinear dielectric effect (χ_4) with critical-like description (eqs 1 and 2) may be found. Blue and red frames contain function parameters. Notably, critical exponents $\gamma = 0.499$ and $\gamma' = 0.431$ for $T > T_m$ and $T < T_m$, respectively.

Notably, for T_m, strong critical-like behavior may be observed with characteristic critical exponents: $\gamma = 0.499$ for $T > T_m$ and $\gamma' = 0.431$ for $T < T_m$. More details calculated from eqs 1 and 2 are given in Figure 2B. Such behavior may be connected to the λ-transition, which also can describe liquid–liquid phase transition I metallic glasses.[35] Based on the above results, we propose to define a liquid above as liquid I, whereas below as liquid II.

According to previous studies,[9,12,13,25] liquid I corresponds to low-density liquid (LDL), whereas liquid II refers to the high-density one (HDL). It also suggests a type of dynamic behavior, i.e., Arrhenius and non-Arrhenius for LDL and HDL, respectively. Such a consideration is in good agreement with experimental evidence.[9,25,33,34] The molecular understanding of the observed behavior might be explained by the use of Fischer's clusters theory[36,37] also called heterogeneities. For non-aqueous liquids, like "dry" glycerol, molecules can interact by hydrogen bonds, which may produce clusters of molecules. Approaching the melting point T_m, the correlation length of clusters ξ_{cl} increases, forming denser "islands" in a low-density "sea". The isotropic–nematic, nematic–smectic A, or plastic phase behavior can be used for such a description.[26–28,30,38,39] High-density "islands" are referred to mostly as heterogeneities

or critical fluctuations.[9,12,13,15,30,39–42] Crossing the critical point, the correlation length becomes large enough to create high-density liquid (HDL) in a supercooled state, which is extremely stable and can be transformed into glassy state.[9,22,23,26–28,30,31] There is a lack of experimental data taking into account the crystallization process in bulk glycerol. Several results showed such a possibility only in nanopores[40] or after a very long time of slow cooling.[9,13,17,22]

Liquid–liquid phase transitions between low- and high-density phases represent intriguing phenomena with implications across multiple scientific disciplines. By elucidating the thermodynamic, structural, and mechanistic aspects of these transitions, researchers can advance our understanding of the fundamental properties of materials and pave the way for innovative applications in fields ranging from biology to materials science. Continued interdisciplinary efforts are essential for unraveling the complexities of liquid–liquid phase behavior and addressing outstanding questions in this fascinating area of research. Liquid–liquid phase transitions are intricately linked to the creation of dynamic heterogeneities and critical fluctuations, which arise from the inherent complexity of the system near the critical point. These phenomena play a pivotal role in shaping the phase behavior and dynamics of fluids undergoing phase transitions, highlighting their importance in diverse fields, ranging from soft matter physics to materials science and beyond.

CONCLUSIONS

This report demonstrates that in glycerol, as it approaches T_m, although maintaining liquidity and the absence of a clear liquid−solid transition, changes can be detected through certain physical properties. The report highlights that alterations in the configurations of permanent dipole moments, as evidenced by the dielectric constant and the nonlinear dielectric effect, which is directly responsive to the emergence of multimolecular fluctuations or "heterogeneities" in less ordered or dense environments, can be observed. The findings suggest that the region of supercooled liquids within glass-forming liquids may deviate from the realm of the equilibrium liquid observed above T_m. Notably, there appears to be a discernible indication of a weakly discontinuous liquid−liquid phase transition, closely associated with multiparticle fluctuations.

In summary, our results showed for the first time the shadow of the melting temperature T_m during the cooling process in glycerol. Analysis of dielectric constant results, as well as comparing them with nonlinear methods, allowed us to define a liquid−liquid phase transition occurring at and covering the first-order phase transition−melting. The presented results also suggest that for $T > T_m$, low-density liquid (LDL) occurs. However, while cooling, strong hydrogen-bonded clusters increased their correlation length, ξ_{cl}, which produced high-density liquid (HDL). The supercooled state of glycerol is caused by a liquid−liquid phase transition between LDL and HDL, which can be described using critical phenomena. Based on critical-like description, the obtained data suggest a possible λ-type of LL transition with characteristic critical exponents found previously in metallic glasses.[35] This result may imply that to obtain the supercooled state in H-bonded liquids, the liquid−liquid phase transition is required. Such a statement finds confirmation in many previous considerations.[9,11−13,15,19,21,22] Understanding the causes and characteristics of liquid−liquid phase transitions continues to pose a challenge, despite mounting evidence of their significance across various systems. This study reveals that such transitions can also occur during the transition to the supercooled liquid state en route to the glass transition temperature. Additionally, it sheds light on novel attributes and underscores the significance of the melting temperature in elucidating the enigma of canonical discontinuous melting/freezing phase transitions.

AUTHOR INFORMATION

Corresponding Author

Szymon Starzonek − *Institute of Theoretical Physics and Mark Kac Center for Complex Systems Research, Jagiellonian University, Kraków 30-348, Poland;* orcid.org/0000-0003-2793-7971; Email: szymon.starzonek@uj.edu.pl

Authors

Jakub Kalabiński − *Institute of High Pressure Physics of the Polish Academy of Sciences, Warsaw 01-142, Poland*

Aleksandra Drozd-Rzoska − *Institute of High Pressure Physics of the Polish Academy of Sciences, Warsaw 01-142, Poland;* orcid.org/0000-0001-8510-2388

Sylwester J. Rzoska − *Institute of High Pressure Physics of the Polish Academy of Sciences, Warsaw 01-142, Poland;* orcid.org/0000-0002-2736-2891

Aleš Iglič − *Laboratory of Physics, Faculty of Electrical Engineering, University of Ljubljana, Ljubljana 1000, Slovenia*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.jpcb.4c04552

Notes
The authors declare no competing financial interest.

REFERENCES

(1) Tanaka, H. General view of a liquid-liquid phase transition. *Phys. Rev. E* **2000**, *62* (5), 6968.

(2) Harrington, S.; Zhang, R.; Poole, P. H.; Sciortino, F.; Stanley, H. E. Liquid-liquid phase transition: Evidence from simulations. *Phys. Rev. Lett.* **1997**, *78* (12), 2409.

(3) Franzese, G.; Malescio, G.; Skibinsky, A.; Buldyrev, S. V.; Stanley, H. E. Generic mechanism for generating a liquid−liquid phase transition. *Nature* **2001**, *409* (6821), 692−695.

(4) Sastry, S.; Austen Angell, C. Liquid−liquid phase transition in supercooled silicon. *Nat. Mater.* **2003**, *2* (11), 739−743.

(5) Falahati, H.; Haji-Akbari, A. Thermodynamically driven assemblies and liquid−liquid phase separations in biology. *Soft Matter* **2019**, *15* (6), 1135−1154.

(6) Peng, P.-H.; Hsu, K.-W.; Wu, K. J. Liquid-liquid phase separation (LLPS) in cellular physiology and tumor biology. *Am. J. Cancer Res.*, **2021**, *11*, 8, 3766, 3776.

(7) Willatt, M. J.; Ceriotti, M.; Althorpe, S. C. Approximating Matsubara dynamics using the planetary model: Tests on liquid water and ice. *J. Chem. Phys.* **2018**, *148* (10), 102336.

(8) McMillan, P. F.; Dubessy, J.; Hemley, R. Applications in Earth, planetary and environmental sciences In *Raman Microscopy*; Academic Press, 1996, pp. 289−365.

(9) Debenedetti, P. G. *Metastable liquids: Concepts and principles*; Princeton University Press, 1996.

(10) Pedersen, U. R.; Costigliola, L.; Bailey, N. P.; Schrøder, T. B.; Dyre, J. C. Thermodynamics of freezing and melting. *Nat. Commun.* **2016**, *7* (1), 12386.

(11) Lucas, P.; Wei, S.; Angell, C. A. Liquid-liquid phase transitions in glass-forming systems and their implications for memory technology. *Int. J. Appl. Glass Sci.* **2020**, *11* (2), 236−244.

(12) Buldyrev, S. V.; Franzese, G.; Giovambattista, N.; Malescio, G.; Sadr-Lahijany, M. R.; Scala, A.; Skibinsky, A.; Stanley, H. E. Models for a liquid−liquid phase transition. *Phys. A* **2002**, *304* (1−2), 23−42.

(13) Corradini, D.; Gallo, P.; Buldyrev, S. V.; Stanley, H. E. Fragile-to-strong crossover coupled to the liquid-liquid transition in hydrophobic solutions. *Phys. Rev. E* **2012**, *85* (5), 051503.

(14) Duan, Y. R.; Li, T.; Wu, W. K.; Li, J.; Zhou, X. Y.; Liu, S. D.; Li, H. Spatial heterogeneity in liquid−liquid phase transition. *Chin. Phys. B* **2017**, *26* (3), 036401.

(15) Khoshtariya, D. E.; Zahl, A.; Dolidze, T. D.; Neubrand, A.; van Eldik, R. Local dense structural heterogeneities in liquid water from ambient to 300 MPa pressure: evidence for multiple liquid−liquid transitions. *ChemPhysChem* **2004**, *5* (9), 1398−1404.

(16) Rosinski, J.; Kopcewicz, B.; Sandoval, N. Heterogeneous nucleation of ice at the liquid-liquid interface. *J. Aerosol Sci.* **1990**, *21* (1), 87−96.

(17) Stanley, H. E.; Buldyrev, S. V.; Giovambattista, N. Static heterogeneities in liquid water. *Phys. A* **2004**, *342* (1−2), 40−47.

(18) Yamada, M.; Mossa, S.; Stanley, H. E.; Sciortino, F. Interplay between time-temperature transformation and the liquid-liquid phase transition in water. *Phys. Rev. Lett.* **2002**, *88* (19), 195701.

(19) Bellissent-Funel, M. C. Is there a liquid-liquid phase transition in supercooled water? *Europhys. Lett.* **1998**, *42* (2), 161.

(20) Van der Kooij, F. M.; Kassapidou, K.; Lekkerkerker, H. N. Liquid crystal phase transitions in suspensions of polydisperse plate-like particles. *Nature* **2000**, *406* (6798), 868−871.

(21) Levin, Y.; Trizac, E.; Bocquet, L. On the fluid−fluid phase separation in charged-stabilized colloidal suspensions. *J. Phys.: Condens. Matter* **2003**, *15* (48), S3523.

(22) Barrat, A. The p-spin spherical spin glass model. *arXiv*, **1997**.

(23) Donati, C.; Franz, S.; Glotzer, S. C.; Parisi, G. Theory of non-linear susceptibility and correlation length in glasses and liquids. *J. Non-Cryst. Solids* **2002**, *307*, 215−224.

(24) *Dynamical heterogeneities in glasses, colloids, and granular media*; Berthier, L.; Biroli, G.; Bouchaud, J.-P.; Cipelletti, L.; van Saarloos, W. Eds.; OUP, Oxford, 2011; Vol. 150.

(25) Vollmayr-Lee, K.; Kob, W.; Binder, K.; Zippelius, A. Dynamical heterogeneities below the glass transition. *J. Chem. Phys.* **2002**, *116* (12), 5158−5166.

(26) Stanley, H. E. *Phase transitions and critical phenomena*; Clarendon Press, Oxford, 1971, Vol. 7.

(27) Stanley, H. E. Scaling, universality, and renormalization: Three pillars of modern critical phenomena. *Rev. Mod. Phys.* **1999**, *71* (2), S358.

(28) Rzoska, S. J.; Chrapeć, J.; Zioło, J. Nonlinear dielectric effect in the vicinity of the critical point of binary and doped critical solutions. *Phys. A* **1986**, *139* (2−3), 569−584.

(29) Drozd-Rzoska, A.; Rzoska, S. J.; Zioło, J. Critical behavior of dielectric permittivity in the isotropic phase of nematogens. *Phys. Rev. E* **1996**, *54* (6), 6452.

(30) Rzoska, S. J.; Zioło, J. Dynamics of glassy clusters appearing by nonlinear dielectric effect studies. *Phys. Rev. E* **1999**, *59* (2), 2460.

(31) Starzonek, S.; Rzoska, S. J.; Drozd-Rzoska, A.; Pawlus, S.; Biała, E.; Martinez-Garcia, J. C.; Kistersky, L. Fractional Debye−Stokes−Einstein behaviour in an ultraviscous nanocolloid: glycerol and silver nanoparticles. *Soft Matter* **2015**, *11* (27), 5554−5562.

(32) Rzoska, S. J.; Drozd-Rzoska, A.; Starzonek, S. Nonlinear dielectric effect in critical liquids. In *Nonlinear Dielectric Spectroscopy* Springer International Publishing, Cham, 2018, pp. 187−217

(33) Starzonek, S.; Drozd-Rzoska, A.; Rzoska, S. J. Long-range static and dynamic previtreous effects in supercooled squalene—impact of strong electric field. *Molecules* **2021**, *26* (19), 5811.

(34) Drozd-Rzoska, A.; Rzoska, S. J.; Szpakiewicz-Szatan, A.; Starzonek, S.; Łoś, J.; Orzechowski, K. Supercritical anomalies in liquid ODIC-forming cyclooctanol under the strong electric field. *J. Mol. Liq.* **2022**, *345*, 117849.

(35) Drozd-Rzoska, A.; Rzoska, S. J.; Starzonek, S. New scaling paradigm for dynamics in glass-forming systems. *Prog. Mater. Sci.* **2023**, *134*, 101074.

(36) *Broadband dielectric spectroscopy*, Kremer, F.; Schönhals, A., Eds.; Springer Science Business Media, 2003.

(37) Wei, S.; Yang, F.; Bednarcik, J.; Kaban, I.; Shuleshova, O.; Meyer, A.; Busch, R. Liquid−liquid transition in a strong bulk metallic glass-forming liquid. *Nat. Commun.* **2013**, *4* (1), 2083.

(38) Rasmussen, D. H.; MacKenzie, A. P. Clustering in supercooled water. *J. Chem. Phys.* **1973**, *59* (9), 5003−5013.

(39) Stevenson, J. D.; Wolynes, P. G. The ultimate fate of supercooled liquids. *J. Phys. Chem. A* **2011**, *115* (16), 3713−3719.

(40) Łó, J.; Drozd-Rzoska, A.; Rzoska, S. J.; Starzonek, S.; Czupryński, K.; Mukherjee, P. Near-continuous isotropic−nematic transition in compressed rod-like liquid crystal based nanocolloid. *J. Mol. Liq.* **2023**, *382*, 121844.

(41) Drozd-Rzoska, A.; Starzonek, S.; Rzoska, S. J.; Kralj, S. Nanoparticle-controlled glassy dynamics in nematogen-based nano-colloids. *Phys. Rev. E* **2019**, *99* (5), 052703.

(42) Busselez, R.; Lefort, R.; Ji, Q.; Affouard, F.; Morineau, D. Molecular dynamics simulation of nanoconfined glycerol. *Phys. Chem. Chem. Phys.* **2009**, *11* (47), 11127−11133.