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Thermodynamics of Fluids with Interconversion of Molecular States

PI: M. A. Anisimov
Department of Chemical & Biomolecular Engineering and Institute for Physical Science & Technology, University of Maryland, College Park

This research addresses fundamental issues in macroscopic and mesoscopic thermodynamics of fluid systems containing interconverting molecular or supramolecular states. Such systems include protein and polymer solutions where macromolecules could exhibit equilibrium conformations and interconversion between alternative states: folded/unfolded (proteins) or collapsed/expanded (polymers). Another example is a polyamorphic fluid, such as highly debatable polyamorphic supercooled water in which polyamorphism can be explained and described by interconversion between alternative configurations of hydrogen-bond network. The current research contains experimental and theoretical/computational parts. Theoretical part includes thermodynamic modeling of interconversion of molecular or supramolecular states in supercooled water and protein solutions and its application to experimentally observable properties. Experimental part is a study of conformation of polymer macromolecules near the critical temperature of liquid-liquid separation and a study of aggregation of proteins induced by interconversion between folding/unfolding.

The results of the first year:

During the first year, we have applied thermodynamic theory of molecular interconversion to explain the pattern of extrema property lines in three atomistic supercooled-water models. We found a generic correlation between this pattern and stability limit of the liquid state with respect to vapor. The work has been published in Journal of Chemical Physics [1]. We have also apply the same approach to revisit the supercooled water equation of state by including new experimental data at negative pressures and below the temperature of homogeneous ice nucleation. The work has been published in Journal of Chemical Physics and presented at the Congress on Water at Roma Tre in June 2019. We experimentally discovered a new kind of conformation of a polymer chain near the critical point of demixing of a binary solution. We attribute this effect to the critical Casimir forces that act in the confined polymer chain. The results have been published in Physical Review Letters [3] and presented at the AIChE Annual Meeting in November 2018. In solutions of lysozyme, we have found that purely folded lysozyme molecules do not favor aggregation. We proved that impurities or/and partially unfolded molecules of lysozyme might cause the aggregation. The results have ben published in Colloid Journal [4] and presented by Shakiba Nikfarjam (a student supported by the PRF Award) at the Gordon Research Conference on Chemistry and Physics of Liquids in August 2019.

Publications supported by the PRF Award:

1. Betul Uralcan, Folarin Latinwo, Pablo G. Debenedetti, and Mikhail A. Anisimov, “Pattern of property extrema in supercooled and stretched water models and a new correlation for predicting the stability limit of the liquid state”, J. Chem. Phys. **150**, 064503 (2019).
2. Frédéric Caupin and Mikhail A. Anisimov, “Thermodynamics of supercooled and stretched water: Unifying two-structure description and liquid-vapor spinodal”, J. Chem. Phys. **151**, 034503 (2019).
3. Xiong Zheng, Mikhail A. Anisimov, Jan V. Sengers, and Maogang He, “Unusual Transformation of Polymer Coils in a Mixed Solvent Close to the Critical Point”, Phys. Rev. Lett. **121**, 207802 (2019).
4. S. Nikfarjam, M. Ghorbania, S. Adhikaria, A. J. Karlssona, E. V. Jouravleva, T. J. Woehl, and M. A. Anisimov, “Irreversible Nature of Mesoscopic Aggregates in Lysozyme Solutions”, Colloid Journal, **81**, 546–554 (2019).