Structure, Dynamics, and Thermodynamics of an Anomalous Fluid Between Attractive and Repulsive Walls: Templating, Molding, Superdiffusion, and Liquid-Liquid Phase Transition

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Confinement can modify the structure, dynamics, and thermodynamics of anomalous liquids, such as water, globular proteins, colloids, or liquid metals [1-3]. We study via molecular-dynamics simulations an anomalous fluid confined in a slit pore with one wall structured and attractive and another unstructured and repulsive [4]. We find that at low temperatures, the structured wall induces heterogeneous crystal nucleation, determining a long-range influence thanks to a sequence of templating, molding, templating effects in the first, second, and further layers, respectively. We show that the walls also have an influence on the dynamics of the liquid, with a stronger effect near the attractive wall. In particular, we observe that the dynamics is largely heterogeneous (i) among the layers, as a consequence of the sequence of structures caused by the walls' presence, and (ii) within the same layer, due to superdiffusive liquid veins within a frozen matrix of particles near the walls at low temperature and high density. Hence, the partial freezing of the first layer does not correspond necessarily to an effective reduction of the channel's section in terms of transport properties, as concluded by other authors [5]. Furthermore, we find that the phase diagram of the homogeneous part of the confined fluid is shifted to higher temperatures, densities, and pressures with respect to the bulk, but it can be rescaled on the bulk case [6]. We calculate a moderate increase of mobility of the homogeneous confined fluid that we interpret as a consequence of the layering due to confinement and the collective modes due to long-range correlations. We show that, as in bulk, the confined fluid has structural, diffusion, and density anomalies that order in the water-like hierarchy, and a liquid-liquid critical point (LLCP) that displaces to higher temperature compared to bulk. Motivated by experiments [7], we calculate also the phase diagram not just for the homogeneous part of the confined fluid but for the entire fluid in the pore, and we show that it is shifted toward higher pressures but preserves the thermodynamics, including the LLCP. Because our model has water-like properties, we argue that in experiments with supercooled water confined in slit pores with a width of >3 nm if hydrophilic and of >1.5 nm if hydrophobic, the existence of the LLCP could be easier to test than in bulk, where it is not directly accessible [6,8].

References:

[1] P. Vilaseca and G. Franzese, Softness dependence of the anomalies for the continuous shouldered well potential, J. Chem. Phys. 133, 084507 (2010).
[2] P. Vilaseca and G. Franzese, Isotropic soft-core potentials with two characteristic length scales and anomalous behaviour, J. Non-Cryst. Sol. 357, 419 (2011).
[3] P. Vilaseca, K. A. Dawson and G. Franzese, Understanding and modulating the competitive surface-adsorption of proteins through coarse-grained molecular dynamics simulations, Soft Matter, 9, 6978 (2013).
[4] F. Leoni and G. Franzese, Structural behavior and dynamics of an anomalous fluid between attractive and repulsive walls: Templating, molding, and superdiffusion, J. Chem. Phys. 141, 174501 (2014).
[5] E. G. Solveyra, E. d. l. Llave, V. Molinero, G. J. A. A. Soler-Illia, and D. A. Scherlis, Structure, Dynamics, and Phase Behavior of Water in TiO2 Nanopores, J. Phys. Chem. C 117, 3330 (2013).
[6] F. Leoni and G. Franzese, Effects of confinement between attractive and repulsive walls on the thermodynamics of an anomalous fluid, Phys. Rev. E 94, 062604 (2016).
[7] J. M. Zanotti, M. C. Bellissent-Funel, and S. H. Chen, Experimental evidence of a liquid-liquid transition in interfacial water, Europhys. Lett. 71, 91 (2005).
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