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The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Entropy Scaling, Structure, and Dynamics of Confined Fluids

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1. Introduction

Fluids trapped in small spaces feature prominently in science and technology, and understanding their properties is critical to progress in fields that range from cell biology to the engineering of nanoscale devices. Such confined fluids often behave differently than bulk samples that have the same chemical potential or average density. Properties affected by confinement include (i) how the particles pack, (ii) how the fluid responds to quasi-static heating or squeezing [i.e., the equation of state], and (iii) how rapidly the fluid relaxes, diffuses, conducts heat, or flows. Quantitatively accurate theories exist for the first two types of properties, but even qualitative rules of thumb for estimating the third type have proven elusive.

2. Results and Discussion

In this talk, we explain how accurate predictions of transport coefficients from first principles are still possible for a wide variety of confined fluid systems, even in the absence of an explicit theory, once one recognizes that certain relationships between static and dynamic properties are insensitive to confinement [1-4]. These relationships not only provide insights into what aspects of structure “matter” for dynamics of inhomogeneous fluids, but also provide a guide for how to passively tune the transport properties of these systems. For example, we discuss how one can leverage predictions of classical density functional theory – together with knowledge of bulk fluid behaviour – to estimate how the dynamics of confined fluids will respond to changes in experimental parameters such as confining geometry, fluid-boundary interactions, bulk pressure, etc. As we discuss in [5], diffusivity and viscosity of a confined equilibrium fluid with a fixed average density can be tuned upward or downward, spanning an order of magnitude in total change, by modifying how the fluid interacts with its confining substrate (i.e., the structure of the density profile). Some of these results appear counterintuitive at first glance, e.g., mobility can be *increased* by enhancing the structure of the density profile [3-6]. However, as we explain, they can be readily understood by considering the balance between singlet and multi-particle correlations in the system [5,6]. Based on the results of these studies, more pronounced effects are expected to be possible for deeply supercooled confined liquids [4,5].

3. Conclusion

In summary, we explore recent theoretical results on the connection between static structure and dynamics of confined fluids, and we discuss implications for complex fluid properties of both fundamental and technological interest.

References

[1] J. Mittal, J. R. Errington, and T. M. Truskett, “Relationships between self-diffusivity, packing fraction, and excess entropy in simple bulk and confined fluids,” *J. Phys. Chem. B*, vol. 111, pp. 10054–10063, 2007.

[2] J. Mittal, J. R. Errington, and T. M. Truskett, “Thermodynamics predicts how confinement modifies the dynamics of the equilibrium hard-sphere fluid,” *Phys. Rev. Lett.*, vol. 96, art. no. 177804, 2006.

[3] J. Mittal, J. R. Errington, and T. M. Truskett, “Does confining the hard-sphere fluid between hard walls change its average properties?,” *J. Chem. Phys*., vol. 126, art. no. 244708, 2007.

[4] G. Goel, W. P. Krekelberg, M. J. Pond, J. Mittal, V. K. Shen, J. R. Errington, and T. M. Truskett, “Available states and available space: Static properties that predict self-diffusivity of confined fluids,” *J. Stat. Mech.: Theory and Experiment*, art. no. P04006, 2009.

[5] G. Goel, W. P. Krekelberg, J. R. Errington, and T. M. Truskett, “Tuning density profiles and mobility of inhomogeneous fluids,” *Phys. Rev. Lett*., vol. 100, art. no. 106001, 2008.

[6] J. Mittal, T. M. Truskett, J. R. Errington, and G. Hummer, “Layering and position-dependent diffusive dynamics of confined fluids,” *Phys. Rev. Lett*., vol. 100, art. no. 145901, 2008.