

Relationship between thermodynamics and dynamics of supercooled liquids

Jeetain Mittal^{a)}

Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas 78712-0231

Jeffrey R. Errington^{b)}

Department of Chemical and Biological Engineering, University at Buffalo, The State University of New York, Buffalo, New York 14260-4200

Thomas M. Truskett^{c)}

Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas 78712-0231 and Institute for Theoretical Chemistry, The University of Texas at Austin, Austin, Texas 78712-0231

(Received 15 May 2006; accepted 20 July 2006; published online 18 August 2006)

[DOI: 10.1063/1.2336197]

Diffusivity, a measure for how rapidly a fluid self-mixes, shows an intimate, but seemingly fragmented, connection to thermodynamics. On one hand, the “configurational” contribution to entropy (related to the number of mechanically stable configurations that fluid molecules can adopt)¹ has long been considered key for predicting supercooled liquid dynamics near the glass transition.² On the other hand, the excess entropy (relative to ideal gas) provides a robust scaling for the diffusivity of fluids above the freezing point.^{3–6} Here we provide, to our knowledge, the first evidence that excess entropy also captures how supercooling a fluid modifies its diffusivity, suggesting that dynamics, from ideal gas to glass, is related to a single, standard thermodynamic quantity.

Several theories of the glass transition are based upon the idea that supercooled liquids vitrify when their configurational entropy vanishes.^{1,7–9} Moreover, experiments^{10,11} and computer simulations^{12–14} reveal a quantitative link between dynamics and configurational entropy in supercooled liquids, a prediction of Adam-Gibbs theory of structural relaxation.² However, the configurational entropy loses relevance at high temperature, and it does not generally correlate with dynamics far above the freezing transition. As a result, it cannot provide a comprehensive description of liquid-state diffusivity. On the other hand, the excess entropy, a fundamental thermodynamic quantity that captures the correlations between particles due to their finite volumes and mutual interactions, does capture the diffusivity of equilibrium fluids.^{3–6} If excess entropy also turns out to describe supercooled liquid dynamics, which is the issue we investigate here via computer simulations, then the relationship between thermodynamics and dynamics will be much simpler than previously anticipated.

We first examine the behavior of a “core-softened” fluid¹⁵ that belongs to a larger class of model potentials known to reproduce many of liquid water’s distinctive properties.^{15,16} In particular, we perform simulations for a broad range of thermodynamic conditions where the model displays pronounced increases in self-diffusivity D upon isothermal compression, a well-known experimental signature

of supercooled liquid water’s dynamics.¹⁶ Figures 1(a) and 1(b) show that the excess entropy s^{ex} and diffusivity D of this fluid have strikingly similar dependencies on density ρ for a wide range of temperatures T . In fact, when plotted along curves of constant ρ [Fig. 1(c)], we find $D \propto \exp[A(\rho)s^{\text{ex}}]$, where $A(\rho)$ is a T -independent parameter. Figure 2 shows that this robust scaling is also exhibited by a model binary alloy¹² for conditions where it displays many of the experimental characteristics of fragile supercooled liquids.^{12,17,18} This is a stringent test since this alloy has become one of the most well-characterized model glass formers.

Adam-Gibbs theory predicts a different form of exponential relationship between D and configurational entropy

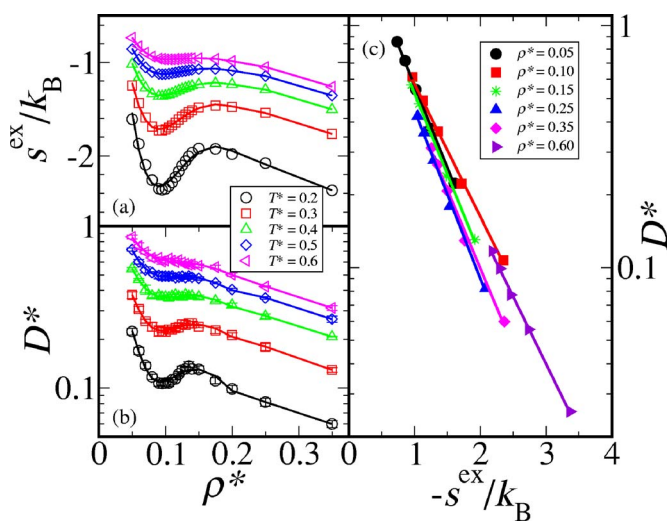


FIG. 1. [(a) and (b)] Excess entropy and diffusivity vs density obtained from molecular dynamics simulations of 1000 particles interacting via a “core-softened” potential (i.e., a Lennard-Jones potential plus a Gaussian repulsion; for details, see Ref. 15). Symbols are simulation data, and curves are guides to the eyes. The quantities are reported in reduced units of $T^* = k_B T/\epsilon$, $\rho^* = \rho\sigma^3$, and $D^* = D(M/\epsilon\sigma^2)^{1/2}$, where k_B is the Boltzmann constant, T is the temperature, ϵ is the energy scale of the potential, ρ is the number density, σ is the particle diameter, and M is the particle mass. The excess entropy s^{ex} has been calculated using transition-matrix Monte Carlo simulations (Refs. 6 and 21). (c) Diffusivity vs excess entropy for the data shown in (a) and (b) along paths of constant ρ (symbols). Symbols are simulation data, and lines reflect the form $D \propto \exp[A(\rho)s^{\text{ex}}]$.

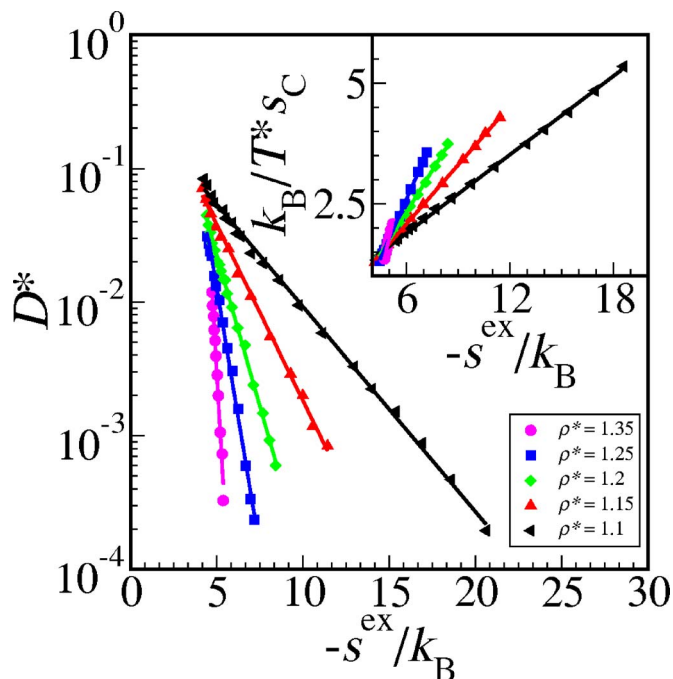


FIG. 2. Diffusivity vs excess entropy for different density states of a binary Lennard-Jones alloy (Refs. 12 and 18). Excess entropy has been obtained from the semiempirical free energy expression reported in Ref. 18, and diffusivity has been extracted from Fig. 3 in Ref. 18. The lines reflect the form $D \propto \exp[A(\rho)s^{\text{ex}}]$. The inset shows the linear dependence between excess entropy and the inverse product of temperature and configurational entropy, $1/Ts_C$, the latter extracted from Fig. 2 in Ref. 12. The quantities are reported in the same reduced units as in Fig. 1.

s_C , $D \propto \exp[-B(\rho)/(Ts_C)]$, where $B(\rho)$ is a T -independent parameter. Since Adam-Gibbs relationship can adequately describe the diffusivity for many liquids near the glass transition, it is natural to ask whether s^{ex} and $-(Ts_C)^{-1}$ contain the same thermodynamic information about the supercooled fluid. Indeed, the inset of Fig. 2 demonstrates that these quantities are linearly related (at constant ρ) for the binary alloy^{12,18} over all conditions for which data are available.

The results presented here represent, to our knowledge, the first evidence that s^{ex} , which provides a scaling for the diffusivity of simple equilibrium fluids,³⁻⁶ also captures supercooled liquid dynamics. Moreover, since s^{ex} is a standard thermodynamic quantity that can be approximated based on structural data from, e.g., scattering experiments,¹⁹ it also

promises to provide the elusive link between structure and dynamics²⁰ of the liquid state.

The authors thank Srikanth Sastry, Pablo Debenedetti, and Frank Stillinger for their useful comments on an earlier version of the paper. Two of the authors (T.M.T. and J.R.E.) acknowledge the financial support of the National Science Foundation Grants No. CTS-0448721 and CTS-028772, respectively, and the Donors of the American Chemical Society Petroleum Research Fund Grants Nos. 41432-G5 and 43452-AC5, respectively. One of the authors (T.M.T.) also acknowledges the support of the David and Lucile Packard and the Alfred P. Sloan Foundations. The Texas Advanced Computing Center (TACC) and the University at Buffalo Center for Computational Research provided computational resources for this study.

^aElectronic mail: jeetain@che.utexas.edu

^bElectronic mail: jerring@buffalo.edu

^cAuthor to whom correspondence should be addressed. Electronic mail: truskett@che.utexas.edu

¹P. G. Debenedetti and F. H. Stillinger, *Nature (London)* **410**, 259 (2001).

²G. Adam and J. H. Gibbs, *J. Chem. Phys.* **43**, 139 (1965).

³Y. Rosenfeld, *Phys. Rev. A* **15**, 2545 (1977).

⁴Y. Rosenfeld, *J. Phys.: Condens. Matter* **11**, 5415 (1999).

⁵M. Dzugotov, *Nature (London)* **381**, 137 (1996).

⁶J. Mittal, J. R. Errington, and T. M. Truskett, *Phys. Rev. Lett.* **96**, 177804 (2006).

⁷J. H. Gibbs and E. A. di Marzio, *J. Chem. Phys.* **28**, 373 (1958).

⁸X. Xia and P. G. Wolynes, *Proc. Natl. Acad. Sci. U.S.A.* **97**, 2990 (2000).

⁹M. Mezard and G. Parisi, *Phys. Rev. Lett.* **82**, 747 (1999).

¹⁰L.-M. Martinez and C. A. Angell, *Nature (London)* **410**, 663 (2001).

¹¹R. A. Richert and C. A. Angell, *J. Chem. Phys.* **108**, 9016 (1998).

¹²S. Sastry, *Nature (London)* **409**, 164 (2001).

¹³A. Scala, F. W. Starr, E. La Nave, F. Sciortino, and H. E. Stanley, *Nature (London)* **406**, 166 (2000).

¹⁴I. Saika-Voivod, P. H. Poole, and F. Sciortino, *Nature (London)* **412**, 514 (2001).

¹⁵A. B. de Oliveira, P. A. Netz, T. Colla, and M. C. Barbosa, *J. Chem. Phys.* **124**, 084505 (2006).

¹⁶G. Franzese, G. Malescio, A. Skibinsky, S. V. Buldyrev, and H. E. Stanley, *Nature (London)* **409**, 692 (2001); Z. Yan, S. V. Buldyrev, N. Giovambattista, and H. E. Stanley, *Phys. Rev. Lett.* **95**, 130604 (2005).

¹⁷W. Kob and H. C. Anderson, *Phys. Rev. E* **51**, 4626 (1995).

¹⁸S. Sastry, *Phys. Rev. Lett.* **85**, 590 (2000).

¹⁹R. E. Nettleton and M. S. Green, *J. Chem. Phys.* **29**, 1365 (1958); H. J. Raveché, *ibid.* **55**, 2242 (1971); A. Baranyai and D. J. Evans, *Phys. Rev. A* **40**, 3817 (1989).

²⁰J. Mittal, J. R. Errington, and T. M. Truskett (unpublished).

²¹J. R. Errington, *J. Chem. Phys.* **118**, 9915 (2003).