Relationship between Structure, Entropy, and Diffusivity in Water and Water-Like Liquids

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Anomalous behavior of the excess entropy (S_e) and the associated scaling relationship with diffusivity are compared in liquids with very different underlying interactions but similar water-like anomalies: water (SPC/E and TIP3P models), tetrahedral ionic melts (SiO_2 and BeF_2), and a fluid with core-softened, two-scale ramp (2SRP) interactions. We demonstrate the presence of an excess entropy anomaly in the two water models. Using length and energy scales appropriate for onset of anomalous behavior, we show the density range of the excess entropy anomaly to be much narrower in water than in ionic melts or the 2SRP fluid. While the reduced diffusivities (D^*) conform to the excess entropy scaling relation, $D^* = A \exp(\alpha S_e)$ for all the systems (Rosenfeld, Y. *Phys. Rev. A* **1977**, *15*, 2545), the exponential scaling parameter, α, shows a small isochore dependence in the case of water. Replacing S_e by pair correlation based approximants accentuates the isochore dependence of the diffusivity scaling. Isochores with similar diffusivity-scaling parameters are shown to have the temperature dependence of the corresponding entropic contribution. The relationship between diffusivity, excess entropy, and pair correlation approximants to the excess entropy are very similar in all the tetrahedral liquids.

1. Introduction

Water displays a number of thermodynamic and kinetic anomalies when compared to simple liquids.[1–3] The density anomaly, corresponding to a negative isobaric thermal expansion coefficient (α_P), is the best known of these unusual properties of water and is observed for state points lying within an approximately parabolic boundary defined by the locus of temperatures of maximum density (TMD) for which $\alpha_P = 0$. The density anomaly implies the presence of other thermodynamic anomalies, such as those associated with the isobaric heat capacity (C_P) and the isothermal compressibility (κ_T). The kinetic anomalies of water are associated with an increase in molecular mobility on isothermal compression, measured in terms of diffusivity, orientational relaxation times, or viscosity. A number of network-forming inorganic melts with local tetrahedral order have been shown to possess water-like anomalies, most notably, AB$_2$ ionic melts such as SiO_2 and BeF_2 and the liquid phase of elements such as silicon and germanium.[4–7] More recently, water-like anomalies have been demonstrated in mesoscopic liquids with isotropic, core-softened effective interactions or anisotropic patchy interactions.[8–18] Despite a very diverse set of underlying interactions, liquids with water-like anomalies are found to have essentially conformal liquid-state "phase diagrams" with a nested structure of anomalous regimes of density, diffusivity, and structural order.

The similarity in the phase diagrams of water-like liquids reflects similar structure–entropy–diffusivity relationships that can be conveniently analyzed in terms of the excess entropy, S_e, defined as the difference between the total thermodynamic entropy (S) and the corresponding ideal gas entropy (S_{id}) at the same temperature and density. A necessary condition for a fluid to show water-like thermodynamic and transport anomalies is the existence of an excess entropy anomaly, corresponding to a rise in excess entropy, S_e, on isothermal compression ($(\partial S_e/\partial \rho)_T > 0$).[8,15,19–22] Liquids with water-like anomalies display distinct forms of local order or length scales in the low- and high-density regimes; competition between the two types of local order results in a rise in excess entropy at intermediate densities. Most liquids, including anomalous ones, obey semiquantitative excess-entropy-scaling relationships for transport properties of the form $X^* = A \exp(\alpha S_e)$ where X^* are reduced transport coefficients and A and α are scaling parameters that are very similar for systems with conformal potentials.[23–33] Consequently, the existence of an excess entropy anomaly is reflected in mobility anomalies. To make a more precise connection between thermodynamic and mobility anomalies, it is necessary to understand the assumptions underlying the scaling rule. Rosenfeld scaling assumes that diffusion in liquids takes place through a combination of binary collisions and cage relaxation. The binary collision contribution is approximately factored out by using macroscopic reduction parameters based on elementary kinetic theory. For example, reduced diffusivities are defined as $D^* = D\rho^{1/3}(m/k_BT)^{1/2}$. The frequency of cage relaxations is assumed to be proportional to the number of accessible configurations, $\exp(S_e)$, since configuration space connectivity is high in the stable liquid phase. For the scaling relationship to be state point independent, it is necessary that the exponential parameter α controlling the number of accessible configurations is determined by the interaction potential and is otherwise state point independent.

This paper develops a basis for quantitative comparison of structure–entropy–diffusivity relationships in liquids with very different underlying interactions but similar water-like anomalies. We focus on three different categories of liquids: (i) molecular fluids (H_2O), (ii) tetrahedral ionic melts (BeF_2 and

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