THE JOURNAL OF CHEMICAL PHYSICS 125, 204501 (2006)

Entropy, diffusivity, and structural order in liquids with waterlike anomalies

Ruchi Sharma, Somendra Nath Chakraborty, and Charusita Chakravarty[a]
Department of Chemistry, Indian Institute of Technology Delhi, Hauz Khas,
New Delhi 110016, India

(Received 20 September 2006; accepted 17 October 2006; published online 22 November 2006)

The excess entropy, defined as the difference between the entropies of the liquid and the ideal gas under identical density and temperature conditions, is studied as a function of density and temperature for liquid silica and a two-scale ramp potential, both of which are known to possess waterlike liquid state anomalies. The excess entropy for both systems is evaluated using a fairly accurate pair correlation approximation. The connection between the excess entropy and the density and diffusional anomalies is demonstrated. Using the pair correlation approximation to the excess entropy, it can be shown that if the energetically favorable local geometries in the low and high density limits have different symmetries, then a structurally anomalous regime can be defined in terms of orientational and translational order parameters, as in the case of silica and the two-scale ramp system but not for the one-scale ramp liquid. Within the category of liquids with waterlike anomalies, we show that the relationship between the macroscopic entropy and internal energy is sufficient to distinguish between those with local anisotropy and consequent open packings at low densities and those with isotropic interactions but multiple length scales. Since it is straightforward to evaluate the pair correlation entropy and internal energy from simulations or experimental data, such plots should provide a convenient means to diagnose the existence as well as type of anomalous behavior in a range of liquids including ionic and intermetallic melts and complex fluids with ultrasoft repulsions. © 2006 *American Institute of Physics*. [DOI: 10.1063/1.2390710]

I. INTRODUCTION

Water displays a number of anomalous thermodynamic and kinetic properties, when compared to simple liquids, due to the fluctuating three-dimensional locally tetrahedral hydrogen bonded network.[1,2] For example, over certain ranges of temperature and pressure, the density of water increases with temperature under isobaric conditions (density anomaly) while the self diffusivity increases with density under isothermal conditions (diffusional anomaly). Waterlike anomalies are seen in other tetrahedral network forming liquids, such as silica, as well as in model liquids with isotropic core softened or two-scale pair potentials.[3–10]

In the case of liquids such as water and silica, a quantitative connection between the structure of the tetrahedral network and the macroscopic density or temperature variables can be made by introducing order metrics to gauge the type as well as the extent of structural order.[5,6] The local tetrahedral order parameter, q_{tet}, associated with an atom i is defined as

$$q_{tet} = 1 - \frac{3}{8}\sum_{j=1}^{3}\sum_{k=j+1}^{4}(\cos\psi_{jk} + 1/3)^2, \tag{1}$$

where ψ_{jk} is the angle between the bond vectors $\mathbf{r}_{ij}$ and $\mathbf{r}_{ik}$ where j and k label the four nearest neighbor atoms of the same type.[5] The translational order parameter, τ, measures the extent of pair correlations present in the system and is defined as

$$\tau = (1/\xi_c)\int_0^{\xi_c}|g(\xi) - 1|d\xi, \tag{2}$$

where $\xi = r\rho^{1/3}$, r is the pair separation, and ξ_c is a suitably chosen cutoff distance.[5,6,11] Since τ increases as the random close packing limit is approached, it can be regarded as measuring the degree of density ordering. At a given temperature, q_{tet} will show a maximum and τ will show a minimum as a function of density; the loci of these extrema in the order define a structurally anomalous region in the density-temperature (ρT) plane within which q_{tet} and τ are strongly correlated. The region of the density anomaly, where $(\partial\rho/\partial T)_P > 0$, is bound by the structurally anomalous region. The diffusionally anomalous region $[(\partial D/\partial\rho)_T > 0]$ closely follows the boundaries of the structurally anomalous regime especially at low temperatures. In water, the structurally anomalous region encloses the region of anomalous diffusivity while this is reversed in silica.

The pattern of nested anomalies seen in tetrahedral liquids can be reproduced by a model liquid with an isotropic two-scale ramp (2SRP) pair potential with the crucial difference that q_{tet} must be replaced by a local orientational order parameter, q_l, which is defined for a particle i as[12]

$$q_l = \left[\frac{4\pi}{2l+1}\sum_{m=-l}^{l}|\bar{Y}_{lm}|^2\right]^{1/2}, \tag{3}$$

where $\bar{Y}_{lm}(\theta,\phi)$ denotes the spherical harmonics of order l,m averaged over bonds connecting particle i with its 12 nearest neighbors. The 2SRP potential has two length scales, the hard-core and soft-core diameters, σ_0 and σ_1, respec-

---

[a] Electronic mail: charus@chemistry.iitd.ernet.in

Copy attested

Ruchi Sharma

THE JOURNAL OF CHEMICAL PHYSICS 127, 164502 (2007)

Ionic melts with waterlike anomalies: Thermodynamic properties of liquid BeF_2

Manish Agarwal, Ruchi Sharma, and Charusita Chakravarty[a]
Department of Chemistry, Indian Institute of Technology-Delhi, New Delhi 110016, India

(Received 27 April 2007; accepted 12 September 2007; published online 23 October 2007)

Thermodynamic properties of liquid beryllium difluoride (BeF_2) are studied using canonical ensemble molecular dynamics simulations of the transferable rigid ion model potential. The negative slope of the locus of points of maximum density in the temperature-pressure plane is mapped out. The excess entropy, computed within the pair correlation approximation, is found to show an anomalous increase with isothermal compression at low temperatures which will lead to diffusional as well as structural anomalies resembling those in water. The anomalous behavior of the entropy is largely connected with the behavior of the Be–F pair correlation function. The internal energy shows a $T^{3/5}$ temperature dependence. The pair correlation entropy shows a $T^{-2/5}$ temperature dependence only at high densities and temperatures. The correlation plots between internal energy and the pair correlation entropy for isothermal compression show the characteristic features expected of network-forming liquids with waterlike anomalies. The tagged particle potential energy distributions are shown to have a multimodal form at low temperatures and densities similar to those seen in other liquids with three-dimensional tetrahedral networks, such as water and silica. © 2007 *American Institute of Physics*. [DOI: 10.1063/1.2794766]

I. INTRODUCTION

Many network-forming liquids are characterized by strongly anisotropic short-range interactions which impose a preference for local tetrahedral symmetry, distinct from the random close-packing arrangements seen in simple liquids.[1] Examples of such systems include water, silicon, germanium, bismuth, and a number of ionic melts, such as SiO_2,[2–10] BeF_2,[11–13] $ZnCl_2$,[14] and GeO_2.[15,16] The presence of a random, three-dimensional, tetrahedral liquid-state network is associated in a number of these systems with waterlike thermodynamic and kinetic anomalies.[16–21] The most obvious signature of the thermodynamic anomalies is the existence of a regime of anomalous density behavior where the thermal expansion coefficient $\alpha=(1/V_m)(\partial V_m/\partial T)_P$ is negative, implying that the molar volume V_m decreases with increasing temperature T along an isobar at pressure P. This region of anomalous density must be bounded by temperatures of maximum and minimum densities for which $\alpha=0$. While the temperature of maximum density (TMD) is well known experimentally for many systems (4 °C for H_2O), the temperature of minimum density has been observed only in simulations. The other thermodynamic waterlike anomalies are related to the behavior of the compressibility (κ_T) and the constant pressure heat capacity (C_P), both of which increase with decreasing temperature along an isobar in anomalous fluids. On thermodynamic grounds, it can be shown that a negatively sloped locus of TMD points on the TP plane should lead to such anomalous behavior of the compressibility.[22–27] Given that only C_P, and not the constant volume heat capacity (C_V), shows the anomalous behavior, one can surmise that the heat capacity anomaly must be connected to anomalies in α and κ_T. Thus, the presence of the density anomaly signals the presence of a set of connected thermodynamic anomalies. The waterlike kinetic anomalies are associated with an increase in various measures of molecular mobility with increasing density. For example, the diffusional anomaly corresponds to a regime in which the diffusivity increases as a function of density, in contrast to simple liquids where diffusivity decreases with density due to increasing steric hindrance. Qualitatively, this anomalous behavior of the mobility can be understood in terms of the disruption of the tetrahedral network by increasing pressure or density which facilitates translational motion. There is also increasing evidence that tetrahedral liquids can show polyamorphism, i.e., the existence of low- and high-density distinct liquid or glassy phases.[28–30]

A quantitative connection between the structure of the tetrahedral network and the thermodynamic and diffusional anomalies can be made by introducing two order metrics: (i) a local tetrahedral order parameter q_{tet} and (ii) a translational or pair correlation order parameter τ.[5,29] At a given temperature, q_{tet} will show a maximum and τ will show a minimum as a function of density; the loci of these extrema in order define a structurally anomalous region in the density-temperature (ρT) plane within which q_{tet} and τ are strongly correlated. The region of the density anomaly, where $(\partial\rho/\partial T)_P>0$, is bounded by the structurally anomalous region. The diffusionally anomalous region $((\partial D/\partial\rho)_T>0)$ closely follows the boundaries of the structurally anomalous region, specially at low temperatures. The connection between these structural, diffusional, and density anomalies can be understood in terms of the behavior of the excess entropy.

---

[a] Author to whom correspondence should be addressed. Tel.: +91-11-2659-1503. FAX: +91-11-2686-2122. Electronic mail: charus@chemistry.iitd.ernet.in

0021-9606/2007/127(16)/164502/10/$23.00

Copy attested

Ruchi Sharma

J. Phys. Chem. B **2008**, *112*, 9071–9078

Multiple Time Scale Behaviors and Network Dynamics in Liquid Methanol

Ruchi Sharma,[†] **Charusita Chakravarty,**[*,†] **and Eduardo Milotti**[‡]

Department of Chemistry, Indian Institute of Technology-Delhi, New Delhi 110016, India, and Dipartimento di Fisica, Università di Trieste and INFN - Sezione di Trieste, Via Valerio 2, I-34127 Trieste, Italy

Received: March 16, 2008; Revised Manuscript Received: May 12, 2008

Canonical ensemble molecular dynamics simulations of liquid methanol, modeled using a rigid-body, pair-additive potential, are used to compute static distributions and temporal correlations of tagged molecule potential energies as a means of characterizing the liquid state dynamics. The static distribution of tagged molecule potential energies shows a clear multimodal structure with three distinct peaks, similar to those observed previously in water and liquid silica. The multimodality is shown to originate from electrostatic effects but not from local, hydrogen bond interactions. An interesting outcome of this study is the remarkable similarity in the tagged potential energy power spectra of methanol, water, and silica, despite the differences in the underlying interactions and the dimensionality of the network. All three liquids show a distinct multiple time scale (MTS) regime with a $1/f^{\alpha}$ dependence with a clear positive correlation between the scaling exponent α and the diffusivity. The low frequency limit of the MTS regime is determined by the frequency of crossover to white noise behavior which occurs at approximately 0.1 cm^{-1} in the case of methanol under standard temperature and pressure conditions. The power spectral regime above 200 cm^{-1} in all three systems is dominated by resonances due to localized vibrations, such as librations. The correlation between α and the diffusivity in all three liquids appears to be related to the strength of the coupling between the localized motions and the larger length/time scale network reorganizations. Thus, the time scales associated with network reorganization dynamics appear to be qualitatively similar in these systems, despite the fact that water and silica both display diffusional anomalies but methanol does not.

1. Introduction

Considerable experimental as well as theoretical attention has been devoted to characterizing the structure and dynamics of hydrogen-bonded liquids.[1-10] The motivation for these studies is primarily due to the importance of water as a solvent for biological and chemical processes. A comparison of the behavior of water with other second-row hydrides, such as HF, NH$_3$, and CH$_3$OH, is essential for understanding the nature of hydrogen bonded dynamics and the extent to which the behavior of water is unique. Methanol, in particular, is of interest because it is the simplest molecule which can exhibit both hydrogen bonding and nonpolar interactions.

While interactions in simple liquids are dominated by steep short-range repulsions and long-range isotropic attractions, hydrogen bonded liquids have strong, local anisotropic interactions. In the case of water, each molecule can form at most four hydrogen bonds, leading to a three-dimensional, open, locally tetrahedral network structure. The strength of hydrogen bonds is estimated to be between 5 and 10k_BT at melting[11] which is strong enough that a substantial fraction of hydrogen bonds will be intact at room temperature. Thermal fluctuations will, however, be large enough, in comparison to the bond strength, to ensure that such bonds will have a finite lifetime of the order of picoseconds. As a result, the dynamics of the liquid will be dominated by the behavior of the three dimensional, hydrogen-bonded network, parts of which are constantly broken and reformed. In the case of methanol, hydrogen bond strengths are similar to those in water,[12] but each methanol molecule can form at most three hydrogen bonds, of which only one can be as a proton donor. In liquid methanol, however, simulations as well as neutron scattering experiments show that the typical number of hydrogen bonds per molecule is two.[13-15] Consequently, linear chains with very rare branch points are seen, rather than the three dimensional network characteristic of water.

Hydrogen-bonded liquids can be thought of as a subset of network forming liquids, other examples being ionic melts such as ZnCl$_2$, SiO$_2$, and BeF$_2$.[16] The strong local coupling of individual atomic or molecular units leads to the existence of multiple length and time scales corresponding to cooperative rearrangements of the network involving different numbers of molecules. To characterize the dynamical behavior of network-forming liquids, it is convenient to use the power spectral density of a mechanical quantity that is sensitive to motion on a number of different length scales. The power spectral density of an observable $A(t)$ as a function of time t over a time interval T is defined as[17]

$$S(f) = \lim_{T\to\infty} \frac{1}{T}\left|\int_{-T/2}^{T/2} A(t)\, e^{-2\pi i f t}\, dt\right|^2 \qquad (1)$$

where $S(f)$ is the spectral power associated with frequency f. In a recent set of studies, we have shown that the power spectrum associated with the tagged particle potential energy can be used to characterize the dynamics of tetrahedral, network-forming liquids such as water[18-21] and SiO$_2$.[22] Simple liquids show a white noise power spectrum where $S(f)$ is independent of frequency. Network forming liquids, however, have a characteristic multiple time scale regime with $1/f^{\alpha}$ dependence on frequency f with α lying between 1 and 1.8.[20] The three liquids that we have studied all show a region of anomalous diffusivity

---

[*] Corresponding author. Tel: +11 91 11 2659 1510. Fax: +11 91 11 [illegible]. E-mail: charus@chemistry.iitd.ernet.in.

[†] Indian Institute of Technology-Delhi.

[‡] Università di Trieste and INFN.

10.1021/jp801508x CCC: $40.75

Copy attested

Ruchi Sharma

J. Phys. Chem. B 2010, 114, 6995–7001

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

Manish Agarwal,[†] **Murari Singh,**[†‡] **Ruchi Sharma,**[†] **Mohammad Parvez Alam,**[‡] **and Charusita Chakravarty***[†]

Department of Chemistry, Indian Institute of Technology–Delhi, New Delhi 110016, India, and School of Physical Sciences, Jawaharlal Nehru University, New Delhi 110067, India

Received: March 4, 2010; Revised Manuscript Received: April 15, 2010

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 ($(\partial S_e/\partial \ln \rho)_T > 0$). 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. 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, $\exp(\alpha S_e)$, 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

---

[*] Corresponding author. Tel.: +91-11-2659 1510. Fax: +91-11-2658 [illegible]. E-mail: charus@chemistry.iitd.ac.in.

[†] Indian Institute of Technology.

[‡] Jawaharlal Nehru University.

10.1021/jp101956u © 2010 American Chemical Society

Copy attested

Ruchi Sharma