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Entropy, Diffusivity and Structural Order in Liquids with Water-like Anomalies

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Abstract

The excess entropy, S_e , defined as the difference between the entropies of the liquid and the ideal gas under identical density and temperature conditions, is shown to be the critical quantity connecting the structural, diffusional and density anomalies in water-like liquids. Based on simulations of silica and the two-scale ramp liquids, water-like density and diffusional anomalies can be seen as consequences of a characteristic non-monotonic density dependence of S_e . The relationship between excess entropy, the order metrics and the structural anomaly can be understood using a pair correlation approximation to S_e .

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The behaviour of water is anomalous when compared to simple liquids for which the structure and dynamics is dominated by strong, essentially isotropic, short-range repulsions [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). Experiments as well as simulations suggest that the anomalous thermodynamic and kinetic properties of water are due to the fluctuating, three-dimensional, locally tetrahedral hydrogen-bonded network. Water-like 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, 4, 5, 6, 7, 8, 9, 10, 11].

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 [6, 7]. The local tetrahedral order parameter, q_{tet} , associated with an atom i (e.g. Si atom in SiO_2) is defined as

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

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 neighbour atoms of the same type [6]. The translational order parameter, τ , measures the extent of pair correlations present in the system and is defined as

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

where $\xi = r\rho^{1/3}$, r is the pair separation and ξ_c is a suitably chosen cut-off distance[12]. 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 this structurally anomalous region, the tetrahedral and translational order parameters are found to be strongly correlated. The region of the density anomaly, where $(\partial\rho/\partial T)_P > 0$, is bounded by the structurally anomalous region. The diffusional anomaly region ($(\partial D/\partial\rho)_T > 0$) closely follows the boundaries of the structurally anomalous region, specially 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 an icosahedral order parameter, q_{ico} , which is defined for a particle i as [13]

$$q_{ico} = \left[\frac{4\pi}{2l+1} \sum_{m=-l}^{m=l} |\bar{Y}_{lm}|^2 \right]^{1/2} \quad (3)$$

where $\bar{Y}_{lm}(\theta, \phi)$ denotes the spherical harmonics of order $l = 6$ averaged over bonds connecting particle i with its 12 nearest neighbours. The 2SRP potential has two length scales: the hard-core and soft-core diameters, σ_0 and σ_1 respectively with $\sigma_0/\sigma_1 = 0.568$. A linear repulsive ramp potential, $u(r) = (U_1/\sigma_1)(\sigma_1 - r)$ acts when the interparticle distance r lies between σ_0 and σ_1 . At low temperatures, the 2SRP liquid shows a maximum in q_{ico} and a minimum in τ as a function of ρ , resulting in a well-defined structurally anomalous region.

Based on simulations of silica and the two-scale ramp(2SRP) liquid, here we show that the excess entropy, S_e , is the critical quantity connecting the structural, diffusional and density anomalies in water-like liquids where S_e is the difference between the entropy of the liquid and that of the ideal gas under identical density and temperature conditions.

Molecular dynamics (MD) simulations in the canonical (NVT) ensemble have been performed for the liquid phase of the BKS model of silica [5, 14] for which computational details are given in [ref.\[15\]](#). NVT-MD simulations for the Lennard-Jones (LJ) and NVT Monte Carlo simulations for the 2SRP liquid were performed using a 256-particle cubic simulation cell. Excess entropy for these systems was estimated to better than 90% accuracy using the pair correlation contribution, S_2 [16, 17, 18, 19]. For a one-component liquids with isotropic pair interactions, $S_2/Nk_B = -2\pi\rho \int [g(r) \ln g(r) - g(r) + 1] r^2 dr$ where $g(r)$ is the pair correlation function[17]. For a binary liquid mixture of two species A and B interacting via isotropic potentials, this expression can be suitably generalised [18] and applied to BKS silica to give a total entropy, $S = S_{id} + S_2$ which is consistently $6.5 \pm 0.3\%$ higher than the values in [ref.\[5\]](#) for the 3.0 g cm^{-3} isochore.

We first consider the connection between S_2 and the density anomaly. Figure 1 shows the behaviour of the excess entropy, S_2 , and the configurational energy, $\langle U \rangle$, as a function of density for silica and for the two-scale ramp liquid. The $S_2(\rho)$ curves of the two systems are qualitatively the same even though the dependence of $\langle U \rangle$ on ρ is completely different. The non-monotonic behaviour of S_2 with a well-defined maximum and minimum results in

extrema in the total entropy, $S = S_{id} + S_e$, since S_{id} is a monotonic function of density along an isotherm. At these extrema, $(\partial S / \partial \rho)_T = V^2(\alpha / \kappa)$ where α is the isobaric expansion coefficient and κ is the isothermal compressibility. Provided the liquid is mechanically stable ($\kappa > 0$), maxima and minima in S must correspond to state points which lie at the boundaries of the region of the density anomaly where α equals zero.

A relationship between S_e and a suitably scaled diffusivity, D^* , is expected on the basis of corresponding states relationships of the form $D = A \exp(\alpha S_e)$ for dense liquids [20, 21, 22, 23]. We have scaled diffusivity for the binary SiO_2 system using an Enskog-type scaling [22] and the resulting $D^*(\rho)$ curves have maxima and minima whose locations coincide with those of $S_2(\rho)$ (cf. Figs. 1(a) and 2(a)). The 2SRP system, for which $D(\rho)$ data is given in refs.[10, 11], reveals the same correlation between S_2 and D . Figure 2(b) shows the strong linear dependence of $\ln D^*$ on S_2 with a slope of 1.5 for liquid silica. Consequently, the non-monotonic behaviour of S_2 as a function of ρ at low temperatures should give rise to a region of anomalous diffusivity in the ρT -plane, even if the underlying diffusional mechanisms in simple and tetrahedral liquids are widely different [24, 25].

In the case of supercooled water, the configurational entropy (S_{conf}), defined as the number of inherent structure basins accessible to the system, has been shown to mirror the variation in diffusivity ($\ln D$) with temperature in an analogous manner to the S_e variation discussed above [26]. S_e is a more convenient quantity to deal with it since it can be readily obtained from calorimetric data or simulations and is well approximated by a structural measure such as S_2 . While S_e can be defined for any system, S_{conf} can be unambiguously defined only for supercooled liquids where there is a clear separation of time-scales between interbasin and intrabasin motions.

From the definitions of S_2 and τ , both of which depend on deviations of $g(r)$ from unity, it is to be expected that variations in S_2 and τ are anticorrelated (cf. Figs. 1(c) and 3(a)). Thus, the existence of a maximum in $S_2(\rho)$ at high densities implies a minimum in τ as a function of density and the locus of such minima in the ρT -plane is sufficient to determine the high-temperature boundary of the structurally anomalous region. It is interesting to consider the structural changes that give rise to qualitatively similar behaviour in $\tau(\rho)$ (or $S_2(\rho)$) curves in systems as dissimilar as silica and the 2SRP liquids. In the low ρ and low T regime for silica and other tetrahedral liquids, increasing ρ tends to destroy local tetrahedral order thereby reducing q_{tet} and destructure $g(r)$ thereby reducing τ and enhancing S_2 . Since

the system is very far from the close-packing limit, density-induced ordering is negligible. Only after reaching a critical density when excluded volume effects dominate over local tetrahedral order, does further increase in density promote pair correlations and lead to a decrease in S_2 with increasing ρ . In the case of the 2SRP liquid, there is a single length scale at very low densities, corresponding to the soft wall diameter, $\sigma_1 = 1$, as shown by the $g(r)$ curve at $\rho = 1.0$ in Figure 3(b). As density increases the second length scale σ_0 emerges. This leads to a peak at $r = 0.568$ and the greater structure in $g(r)$ tends to decrease S_2 . Simultaneously, the introduction of additional distances for second and higher-order neighbours implies that the $g(r)$ function becomes less structured and plateau-like at intermediate distances. The net effect is a maximum in τ at $\rho = 1.3$, followed by a decrease until a minimum value is reached at $\rho = 1.9$. Further increase in ρ leads to a more structured $g(r)$ as the second short length scale (σ_0) becomes dominant and τ begins to increase.

We now consider the chain of arguments that relates S_2 and local orientational order, q . S_2 and τ contain the same structural information; therefore it is sufficient to consider the relationship between τ and q_{tet} or q_{ico} . The characteristic feature of the water-like liquids studied here is that the correlation between τ and q breaks down with density because the energetically favourable local structures have very different symmetries in the low density and high density limits. Systems, such as LJ, characterized by strong, short-range isotropic repulsions have local icosahedral order in the liquid phase and hcp or fcc packing in the solid phase. Increasing density enhances particle correlations and local structure leading to a strong correlation between τ and q_{ico} [12]. In contrast, the stable crystalline forms of the 2SRP system at low and high densities are fcc and rhombohedral respectively [9] suggesting that the low density liquid will have local, icosahedral order which will be attenuated with increasing density; consequently the correlation between q_{ico} and τ will break down with density. In the case of tetrahedral liquids, the local geometry at low and high densities is tetrahedral and icosahedral respectively and therefore there is a density-driven breakdown of the correlation between q_{tet} and τ . Figure 4 illustrates how S_2 shifts from being negatively correlated with q_{tet}/q_{ico} in the anomalous regime to positively correlated in the normal regime along various isotherms as a consequence of the changing relationship between translational and orientational order.

It is useful to apply the above arguments to the one-scale ramp (1SRP) liquid with $\sigma_0 = 0$ which displays density and diffusional anomalies but not the structural anomaly

since $q_{ico}(\rho)$ does not have a maximum [10]. The 2SRP and 1SRP liquids show the same qualitative behaviour in τ and S_2 with an effective second length scale originating from a peak in $g(r)$ close to zero at intermediate and high densities. However, there is no density-induced shift in symmetry of local order since the low and high density crystalline structures are fcc and hcp respectively, both of which are compatible with icosahedral local order in the liquid. Consequently, 1SRP does not display a well-defined structural anomaly.

We now consider the relationship between the positional or configurational contribution to the entropy (S_e) and internal energy ($\langle U \rangle$). Figure 5 shows the striking contrast between the S_e versus $\langle U \rangle$ plots for silica, 2SRP and Lennard-Jones (LJ) liquids, generated by varying density along different isotherms. The LJ system shows a strong positive correlation between S_2 and $\langle U \rangle$. In the case of the 2SRP liquid, the positive correlation between S_2 and $\langle U \rangle$ in the anomalous regime shifts to a negative correlation at high densities. The S_2 versus $\langle U \rangle$ curves for the tetrahedral liquid show distinct low-density and high-density segments. In the anomalous regime, the entropy of the high density segment always lies above that of the low-density one, while in the normal regime this order is reversed; the two segments coincide for the crossover temperature. Since it is straightforward to evaluate S_2 and $\langle U \rangle$ from simulations or experimental data, such plots should provide a convenient means to diagnose anomalous behaviour in a range of liquids, including ionic and intermetallic melts and complex fluids with ultra-soft repulsions.

Our results demonstrate that if the excess entropy, S_e , of a liquid shows a well-defined minimum followed by a maximum as a function of density, then the system will have nested diffusional and density anomalies. Since S_e is well approximated by the pair correlation entropy, S_2 , a connection with the order metrics can be readily formulated to show that if the energetically favourable local geometries in the low and high density limits have different symmetries, then a structurally anomalous regime can be defined in terms of an orientational local order parameter and a translational or pair-correlation order parameter. Such anomalous liquids will show a characteristic fingerprint when excess entropy is plotted as a function of configurational energy. The relationship between the excess entropy and the diffusional and density anomalies will be valid even if the pair correlation approximation is substituted by more accurate experimental or computational estimates. Provided pair correlations play a dominant role in liquid state structure and dynamics, as is likely in most systems of interest, the close correspondence between S_e and the translational order parameter will remain

and our conclusions regarding the structural anomaly will also be valid.

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Figure Captions

1. Dependence of pair correlation entropy, S_2 , and configurational energy, $\langle U \rangle$, on density, ρ . Results for silica are shown in the left panel with isotherms corresponding from top to bottom to $T = 6000\text{K}$, 5500K , 5000K , 4500K and 4000K . The units of ρ , S_2 and $\langle U \rangle$ are g cm^{-3} , $\text{J K}^{-1} \text{mol}^{-1}$ and 10^3kJ mol^{-1} . Results for 2SRP liquid are shown in the right panel with isotherms corresponding from top to bottom to $T = 0.2$, 0.109 , 0.082 , 0.063 , 0.045 , 0.036 and 0.027 . Reduced units of ρ , S_2 and $\langle U \rangle$ are σ_1^{-3} , k_B and U_1 .
2. Scaled diffusivity, D^* , of liquid BKS silica: (a) Dependence of D^* , on ρ at different T and (b) Correlation plot of D^* and S_2 . The scaled diffusivity, D^* equals $(D_{Si}/\chi_{Si})^{x_{Si}}(D_O/\chi_O)^{x_O}$, where D_a , x_a and χ_a are the self-diffusivity, mole fraction and scaling parameter respectively of component a in the mixture [22]. The straight line in part(b) corresponds to $D = 0.16 \exp(1.5S_2)$; the three lowest density state points at 4000K have been excluded from the fit.
3. (a) Dependence of translational order parameter, τ , on ρ for 2SRP liquids along isotherms at T values given in Figure 1. (b) Pair correlation function, $g(r)$, at different densities along the $T=0.027$ isotherm.
4. Correlation between the excess entropy, S_2 and (a) the tetrahedral order parameter, q_{tet} , for silica and (b) the icosahedral order parameter, q_{ico} , for 2SRP liquid. Isotherms are shown in order of increasing T from left to right at T values given in Figure 1.

5. Correlation plot of excess entropy, S_2 and configurational energy, $\langle U \rangle$ for (a) silica (b) 2SRP and (c) Lennard-Jones (LJ) along different isotherms. The highest and lowest density state points for each isotherm are marked by horizontal and vertical arrows. Isotherms for 2SRP liquid labelled as in Figure 1.

