

Connecting diffusion and entropy of bulk water at the single particle level[†]

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Abstract. The relation between the dynamic (e.g., diffusion) and thermodynamic (e.g., entropy) properties of water and water-like liquids has been an active area of research for a long time. Although several studies have investigated the diffusivity and entropy for different systems, these studies have probed either the configurational entropy or the excess entropy of the overall system. In this study, we focus on the entropy of water at a single molecule level at different temperatures. We have used a method developed in our group to calculate the translational and rotational entropy of individual water molecules at various temperatures. We find that the single water translational and rotational entropy exhibit a transition at around 240 K. The translational entropy of individual water molecules shows a consistent variation with change in temperature whereas the variation in the case of rotational entropy is much smaller at different temperatures. We have also calculated diffusion coefficients of water molecules at these temperatures. We find that diffusion also shows the well-known fragile to strong crossover transition at around the same temperature where transition in entropy values has been seen. We have calculated both kinetic and thermodynamic fragilities and crossover points using diffusion and single water translational entropy values. Finally, we correlate the diffusion and translational entropy of individual water molecules using an analog of the Adam-Gibbs relation.

Keywords. Single water entropy; Diffusion coefficient; Fragility.

1. Introduction

The properties of a liquid can be characterised by its dynamical quantities such as diffusion coefficient and relaxation times, or by its thermodynamic and structural properties such as entropy and structure factor. At equilibrium, the dynamic and thermodynamic quantities must be related. For example, the diffusivity of a liquid gets modified on the basis of the thermodynamic condition of the system. At low temperatures, the rearrangement of molecules responsible for the diffusion is dominated by jumps across different local energy minima,¹ and these energy minima for a liquid correspond to the different accessible configurations at the corresponding thermodynamic state.² Thus, the configurational entropy and diffusivity for the molecules in liquid systems are connected. However, the translational diffusion of the molecules is likely to influence the translational entropy of the system and the variation of these two quantities can be correlated.

Over the years, different approaches have been adopted to connect the entropy with diffusion. A number of studies in this context have discussed the relation between diffusion and the excess entropy of the system, S_{ex} . The excess entropy denotes the difference between the actual entropy of the system and the system's entropy if it behaves as an ideal gas at the same condition. An empirical relation between diffusion and this excess entropy was given by Rosenfeld as,^{3,4}

$$D = a \exp\left(\frac{bS_{\text{ex}}}{k_{\text{B}}}\right), \quad (1)$$

where k_{B} is the Boltzmann constant and, a and b are empirical constants. Several studies have used the excess entropy to connect the thermodynamics with the dynamics of the systems for different models of water and water-like liquids.^{5–14} Thermodynamic states of various liquid models that mimic real systems were varied to investigate the correlation between diffusion and entropy. The excess entropy used in these studies can be expanded into a n -body contributions.¹⁵ S_{ex} has often been approximated to a two-body excess entropy S_2 that depends on the radial distribution function $g(r)$ as,

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[†]Dedicated to the memory of the late Professor Charusita Chakravarty.

$$S_2 = -2\pi \rho k_B \int \{g(r) \ln [g(r)] - [g(r) - 1]\} r^2 dr. \quad (2)$$

A universal relation between the S_2 and diffusion coefficient was given by Dzugutov¹⁶ which was tested for several systems.¹⁶ Recently, Seki and Bagchi provided a statistical mechanical derivation of the Rosenfeld relation and showed that this equation remains valid for any dimension.¹⁷ The other popular approach to connect diffusion with entropy comes from the relation between the configurational entropy S_C with the diffusion coefficient. The quantitative relation between these two was given by Adam and Gibbs (AG) in the following form.¹⁸

$$D^{-1}(T) = D^{-1}(T_0) \exp \{A_{AG} / (T S_{Conf})\}, \quad (3)$$

Where $D(T_0)$ is the diffusion at a higher temperature T_0 . A_{AG} is a constant known as Adam-Gibbs parameter. In different studies, the S_{Conf} has been calculated by subtracting the vibrational entropy from the total entropy as, $S_{Conf}(T) = S_{Total}(T) - S_{vib}(T)$.

Thermodynamic integration has been widely used in determining the total entropy of the system with water and water-like liquids.^{19–22} The vibrational entropy is calculated by making harmonic approximation to the local potential energy minimum. The constant A_{AG} in the AG relation has been associated with the high temperature activation energy,²⁰ and it has been found to depend strongly on the density of the system.^{22,23} Most of the studies devoted to the relation between diffusion and entropy focused on the thermodynamic and dynamic properties of the whole system. However, an understanding of the behaviour of individual water molecules in terms of thermodynamics and dynamics is missing.

Despite the numerous studies, the behaviour of water at low temperatures remains an area of active research due to its uniqueness compared to other liquids. One such distinct property is the existence of a singular temperature close to which various thermodynamic properties such as compressibility and thermal expansion coefficient diverge.²⁴ The study of the glass transition (GT) of water poses various challenges due to the dramatic slowdown of macroscopic properties such as viscosity or self-diffusion coefficient as well as the microscopic property such as translational correlation time. These changes ought to govern the thermodynamic properties of the water molecules. Hence, a correlation between the thermodynamic properties with the dynamics of the system can provide a general pattern to predict the thermodynamic behaviour of liquids from the knowledge of the dynamic quantities. The crystallization of water makes different experimental techniques inadequate to study the super-cooled region of liquid

water. Hence, the dynamics of the super-cooled water has been measured by confining water in nano-sized pores.^{25–27} Computer simulations have been very effective in exploring both the dynamic and thermodynamic properties of super-cooled water.

In this study, we have used molecular dynamics (MD) simulation and have adopted a different approach to establish a connection between the thermodynamic and dynamic properties of individual water molecules. We have calculated the translational and rotational entropy of individual water molecules at various temperatures using a method developed recently in our group.²⁸ Single molecule translational entropy was also calculated by Siebert *et al.*,²⁹ where they used free volume to calculate the effect of translational entropy in binding processes. Our method, however, is based on the volume accessed by a single molecule during the dynamics. We have found a systematic change for translational entropy with temperature whereas the rotational entropy faces a sharp change at a particular temperature. The calculations of self-diffusion coefficient (D) shed light on this phenomenon where we find a transition in the dynamics at around the same temperature where a dip is observed in entropy values indicating a fragile-to-strong crossover (FSC) transition in water. Thus, from the entropy and diffusion data, we have discussed kinetic and thermodynamic fragilities^{30,31} and the associated dynamical temperatures for water. We have obtained the temperature at which the translational entropy contribution originating from the movement of individual water oxygen becomes zero. Finally, to relate the single water translational entropy with D , we propose the generalization of the Adam-Gibbs relation which connects the configurational entropy with the translational relaxation time.

2. Computational methods

2.1 System set-up and simulation details

All-atom molecular dynamics simulations were carried out to obtain the entropy and diffusion coefficients of water molecules. We have used the TIP5P/E water model³² for this study which has been proven to exhibit correct density trend with the variation of temperature. Our system contains 1000 water molecules. The entropies have been calculated from simulations at temperatures 220, 230, 240, 250, 260, 273, 285, 300, 315, and 330 K. Diffusion coefficients were calculated for two additional temperatures 200 and 210 K in addition to the above temperatures. Since the fragile-to-strong crossover was observed at 240 K, obtaining converged value for entropy below this temperature becomes computationally expensive.

We have used GROMACS³³ molecular dynamics program for carrying out the simulations. The bulk water system was

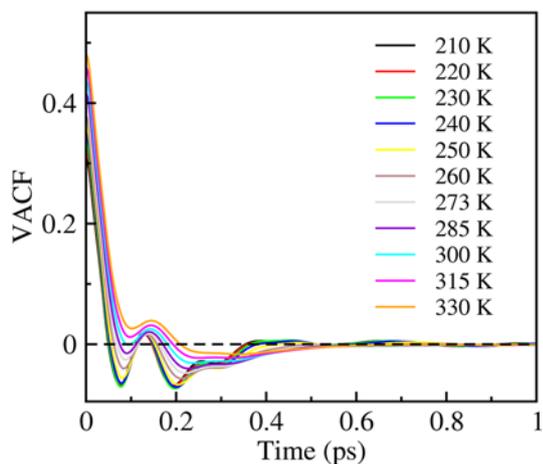


Figure 1. Time dependence of the velocity auto correlation function (VACF) of water at different temperatures.

first energy minimized using the steepest descent method,³⁴ followed by heating up to the temperature required in each case using Berendsen thermostat³⁵ with a coupling constant of 0.2 ps. Each system was equilibrated for 10 ns at constant temperature and pressure of 1 bar using Nosé-Hoover thermostat^{36,37} and Parrinello-Rahman barostat,³⁸ respectively, where the coupling constants were kept at 0.2 ps for both. Long equilibration allowed the system to attain their natural density at atmospheric pressure. No constraint was applied in controlling the density of the systems. PME electrostatics³⁹ were used for treating the electrostatic interactions. Cut-off distance of 10 Å was used for both electrostatic and van der Waals interactions. The density pattern was then compared to the experimental values shown by Mallamace *et al.*,⁴⁰ to verify the accuracy of the simulations. The simulations were continued further for 200 ns for systems at temperatures 250 K and below to obtain converged entropy values under same NPT condition. For temperatures above this, only 100 ns simulations were enough to obtain converged entropy values. For calculating the diffusion coefficients, the equilibrated systems were subjected to short, 500 ps, simulations with the frames saved at every 4 fs to enable an accurate estimation of the velocity auto correlation function (VACF). Diffusion coefficients were calculated from VACF using the following Green-Kubo relation,⁴¹

$$D = \frac{1}{d} \int_0^{\infty} dt \langle \vec{V}(0) \cdot \vec{V}(t) \rangle, \quad (4)$$

where d is the dimensionality and \vec{V} is the velocity vector. The VACF profiles for water at different temperatures are shown in Figure 1.

2.2 Method for translational and rotational entropy for individual water

Due to the diffusive nature of water molecules, standard method used for biomolecular entropy calculation⁴² cannot

be used to estimate the entropy of water. Hence, in our calculations, the method known as permutation reduction (PR)^{43,44} developed by Grubmuller and co-workers have been used that considers the water to be indistinguishable and obtain an effect localized configuration space of a water molecule close to a particular region. More details can be found elsewhere.²⁸ Each of the localized permuted water molecules was subjected to quasi-harmonic analyses to estimate the translational entropy individually. For that, we obtain the covariance matrix of translational fluctuation of the permuted water molecule along X, Y, and Z direction giving rise to a 3×3 matrix. Diagonalization of this matrix provides three eigenvalues ($\lambda_i, i = 1, 2, 3$) and consequently three frequencies $\omega_i = (\kappa_B T / \lambda_i)^{1/2}, i = 1, 2, 3$. With these frequencies, the translational entropy was calculated using the expression for entropy of solid state quantum harmonic oscillator shown in the following.⁴⁵

$$S_{\text{tr}}^{\text{QH}} = \kappa_B \sum_{i=1}^3 \frac{\hbar \omega_i / \kappa_B T}{e^{\hbar \omega_i / \kappa_B T} - 1} - \ln \left(1 - e^{-\hbar \omega_i / \kappa_B T} \right), \quad (5)$$

where, $\hbar = \frac{h}{2\pi}$, h is the Planck's constant, T denotes the temperature, and κ_B is the Boltzmann constant. Considering the classical limit at high temperature ($\hbar \omega_i / \kappa_B T < 1$), the above formula can be written in the following form.

$$S_{\text{tr}}^{\text{QH}} = \kappa_B \sum_{i=1}^3 1 - \ln (1 - \hbar \omega_i / \kappa_B T) = C(T) + \kappa_B \ln V, \quad (6)$$

where, $C = (3 - \ln(\frac{4\pi}{3})) - \frac{3}{2} \ln \left(\frac{\hbar^2}{\kappa_B T} \right)$ and $V = 4\pi/3 \left(\frac{1}{2\sqrt{2}} \right) (\lambda_1 \lambda_2 \lambda_3)^{\frac{1}{2}}$. Here, $(\lambda_i)^{1/2}, i = 1, 2, 3$ represents the length of the principal axes of the ellipsoidal volume that a permuted water molecule occupies. The permuted water molecules were also used for calculating the rotational entropy of individual water molecules, as mentioned in detail elsewhere.²⁸ We have shown recently that the calculated entropy values correlate well (correlation coefficient of 0.97) with the reported experimental values of entropy in the solvation shell of ions.⁴⁶ The good correlation found between the calculated and experimental entropy established the reliability of our method. Since we discuss the entropy of individual water molecules for bulk water system, the permutation of water molecules has been done by keeping one water molecule at the center of the box followed by ordering other water molecules around the central one. Since the central water molecule remains static in calculation, the entropy of water molecules immediately next to it does not represent the bulk water; rather, it represents the first solvation shell water around another water molecule. Hence, we consider the entropy of water molecules away from the central water molecule. The average entropy values of 40 such water molecules were considered as the single water entropy at that particular temperature. The convergence of translational entropy values for a few water molecules are shown in Figure 2 for some temperatures. Similar convergence was found for rotational entropy as well (figure not shown).

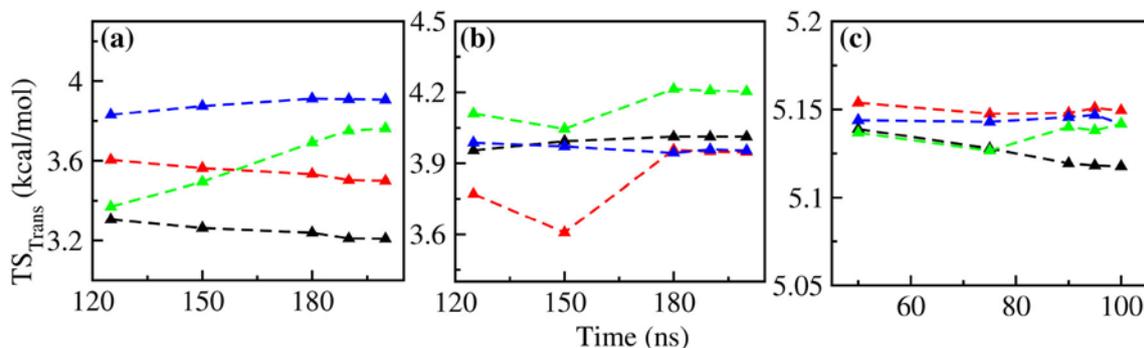


Figure 2. The convergence of translational entropy values for simulation at (a) 220 K, (b) 230 K, and (c) 273 K for four different water molecules. The black, red, blue, and green colours indicate the 40th, 50th, 60th, and 70th water molecule with respect to distance from the central water molecule.

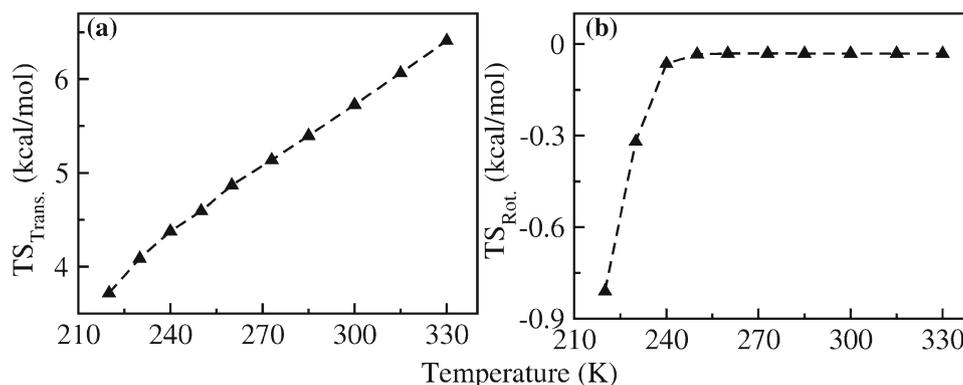


Figure 3. (a) The translational entropy and (b) the rotational entropy of individual water molecules with respect to temperature. The dashed lines here are only to guide the eyes.

2.3 Fragility

Here, we discuss a quantity called fragility,^{30,31} which quantifies the rate at which any dynamic quantity such as relaxation time, inverse diffusivity, or viscosity grows with temperature. In this study, the kinetic fragility is obtained by studying the temperature dependence of the dynamic quantity, diffusion coefficients above 250 K only due to the divergence of the diffusivity at the low temperature region. We plot the inverse of the diffusion coefficient against temperature using the Vogel-Fulcher-Tammann (VFT) equation of the following form:¹⁹

$$D^{-1}(T) = D_0^{-1} \exp \left[\frac{1}{K_{\text{VFT}} \left(\frac{T}{T_{\text{VFT}}} - 1 \right)} \right], \quad (7)$$

where, K_{VFT} is the kinetic fragility marker and T_{VFT} is the temperature at which the diffusivity diverges. D_0 is the high temperature diffusivity.

In general, the thermodynamic fragility is studied by evaluating the temperature dependence of configurational entropy. The temperature dependence of S_{Conf} is given as,²²

$$TS_{\text{Conf.}} = K_{\text{T}} \left(\frac{T}{T_{\text{K}}} - 1 \right), \quad (8)$$

where, K_{T} is the thermodynamic fragility marker and T_{K} is the Kauzmann temperature.¹⁸ At T_{K} , the entropy contribution from configurations become zero and the entropy reaches the crystalline entropy. The AG relation (Eq. 3) connects between dynamics and thermodynamics, while Eq. 8 provides a thermodynamic relation and Eq. 7 gives a dynamic relation. *Here, we study the thermodynamic fragility by using the translational entropy variation with temperature.* The extrapolation of the values provides the temperature at which the contribution to translational entropy originating from the movements of water oxygen atoms becomes zero.

3. Results and Discussion

3.1 Single water entropy variation with temperature

In this section, we discuss the variation of entropy of individual water molecules at different temperatures. Hence, in Figure 3, we show the variation of TS_{Trans} and TS_{Rot} for individual water molecules at different temperatures. As can be seen from the figure, there is a deviation from linear behaviour in the translational entropy values at 240 K. The deviation is more prominent in the

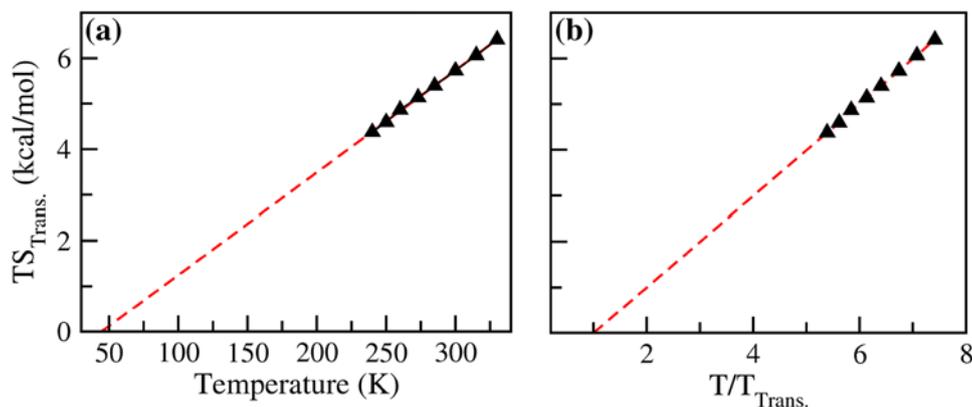


Figure 4. (a) Extrapolation of $TS_{\text{Trans.}}$ values to the temperature where the translational entropy value reaches zero. This temperature is denoted as $T_{\text{Trans.}}$ here. (b) The variation of $TS_{\text{Trans.}}$ with $T/T_{\text{Trans.}}$. The slope of this line gives the analog of thermodynamic fragility value, $K_{\text{Trans.}}$ which is found to be 0.02 from translational entropy values of individual water molecules.

case of rotational entropy. It is previously known that water undergoes a fragile-to-strong crossover transition at temperature close to 225 K.^{47,48} This transition is clearly indicated in the entropy values as the system is expected to get stuck in local minima at that temperature. The time scale required to go from one energy basin to another will be much longer at these temperatures and could be inaccessible through molecular dynamics simulation. However, the molecules at these low temperatures will still have vibrations around their mean positions which will be expected to contribute to the translational entropy values in our calculations. Hence, the translational entropy observed at lower temperatures can be expected to be close to the crystalline entropy values. The values obtained here for translational entropies are found to be slightly higher than the reported absolute translational entropy values by Lin *et al.*,⁴⁹ using two-phase thermodynamic model (2PT) method for several water models. However, the water model and also the approach used here is very different from the 2PT method. The rotational entropy values obtained here show much less variation compared to the translational entropy with the variation of temperature. Also, minor change in the values at different temperatures for TS_{Rot} is insignificant to be observed in Figure 3 (b).

Extrapolation of the translational entropy values above 240 K provides the temperature where translational entropy goes to zero. However, this is different from the Kauzmann temperature, T_{K} , which is obtained by extrapolating the configurational entropy values to zero. The Kauzmann temperature for SPC/E water has been reported to be ~ 150 K. The temperature at which the extrapolated translational entropy goes to zero is denoted here as $T_{\text{Trans.}}$. It is found to be 44.51 K for

a single bulk water molecule. At this temperature, the water oxygen atoms will likely be static. This is shown in Figure 4(a). The slope of TS_{Conf} vs T/T_{K} gives the thermodynamic fragility of the system. Hence, we obtain an analog of this thermodynamic fragility, denoted here by $K_{\text{Trans.}}$, by obtaining the slope of the plot for $TS_{\text{Trans.}}$ vs $T/T_{\text{Trans.}}$. This is shown in Figure 4(b). The value for $K_{\text{Trans.}}$ is found to be 0.02.

3.2 Diffusion coefficients (D) at different temperatures

To obtain an insight on the dynamics of water molecules at different temperatures, we have calculated the self-diffusion coefficient of water. To get the temperature dependence of D , we have plotted the logarithm of the inverse of D with respect to temperature. This is shown in Figure 5. As seen from the figure, a non-Arrhenius behaviour appears for the D values at around 250 K. A similar transition was observed by the quasi-elastic neutron scattering (QENS) experiment for the dynamics of water around the similar temperature range.^{47,48} However, in these studies, the transition at ambient pressure takes place at a slightly lower temperature compared to ours (around 225 K compared to 250 K in our case).

From the D , we can obtain the dynamic fragility of the system by fitting the non-Arrhenius segment using VFT equation given as Eq. 7. This is shown in Figure 5 by the solid line. Here we find that the K_{VFT} , known as the dynamic fragility marker to be 0.8 and T_{VFT} , the temperature at which glass transition takes place to be 204.8 K. These values are somewhat close to the ones reported by Chen *et al.*,²⁷ where the T_{VFT} was found to be 187 K and K_{VFT} is 0.56.

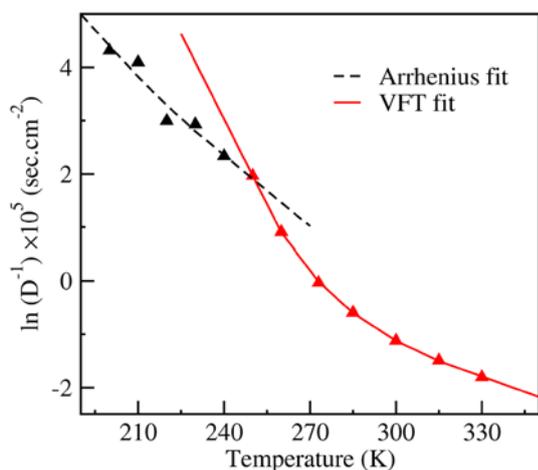


Figure 5. The logarithm of inverse diffusion coefficient with respect to temperature. The red solid line shows the VFT fit, while the black dashed line shows the Arrhenius fit.

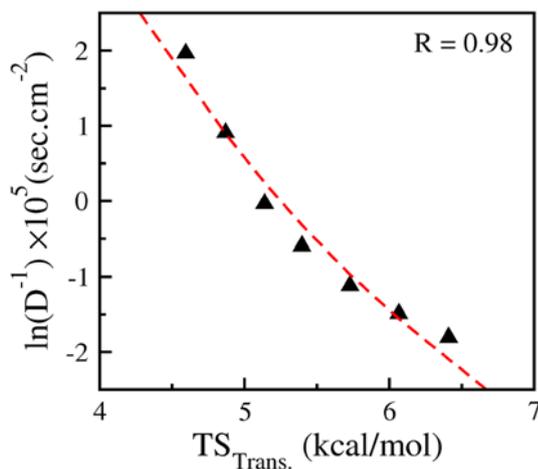


Figure 6. $\ln(D^{-1})$ is shown against TS_{Trans} for single water molecules. The red dashed line shows the fit with an analog of AG relation. R is the Pearson's correlation coefficient.

3.3 Connecting the translational entropy with dynamics

An analog of Adam-Gibbs (AG) relation has been used here to connect the entropy and diffusion coefficient. While the AG relation connects the configurational entropy with diffusion, we use the same form for connecting the translational entropy and diffusion by replacing the TS_{Conf} term in Eq. 3 by TS_{Trans} . A similar approach has been used for connecting the tetrahedral entropy and tetrahedral relaxation time by Kumar *et al.*⁵⁰ The fit is shown in Figure 6. It can be seen that the fit for the translational entropy and diffusion with the AG relation is very good as indicated by the correlation coefficient. The A_{AG} parameter, which indicates

the high temperature barrier, is 60.6 kcal/mol. Thus, our study indicates a relation between the diffusion and translational entropy for a single water molecule. To our knowledge, this is the first study that connects the translational entropy with the translational diffusion of water. The good fit also indicates that a common relation could be obtained between the translational entropy and diffusion so that from the knowledge of dynamics only (which is computationally cheap), the information on the thermodynamics (computationally costly and challenging) can be obtained. However to obtain a general behavior, the method will be needed to be applied on different systems.

4. Conclusions

In this study, we have calculated the translational and rotational entropy of single water molecules in the bulk at different temperatures. The values obtained here show the transition at a particular temperature. At the same temperature, diffusion coefficients show fragile-to-strong transition. While kinetic fragility has been obtained from the diffusion coefficient, we used this translational entropy to calculate an equivalent description of thermodynamic fragility. Therefore, we have estimated the temperature at which the contribution of entropy originating from the translation of water vanishes. The thermodynamic and dynamic information follow an Adam-Gibbs type of relation. Therefore, this study shows that the present method can be used to obtain the computationally expensive and challenging quantity, entropy, from a faster and cheaper dynamical quantity, diffusion coefficient. Also, the new thermodynamic and kinetic fragility parameters provide new structural and dynamical information of a single water molecule in bulk water. Therefore, this method can be extended to study the dynamics and thermodynamics of water molecules in more complicated environments.

Acknowledgements

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