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Assessing Thermodynamic-Dynamic Relationships for Water-Like Liquids

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Here we investigate a family of isotropic water-like glass-forming liquids, in which each thermodynamic state point corresponds to a different potential energy surface which is prescribed to reproduce the $g_{OO}(r; T,\rho)$ of the reference TIP4P-Ew water model potential. Although each isotropic potential is simulated separately, together the family of isotropic potentials displays anomalous dynamics with density and fragile diffusivity with temperature. By removing a common energy landscape, and therefore expected thermodynamic trends with temperature within a single potential, we can more rigorously evaluate whether various entropic measures used in popular phenomenological thermodynamic theories can quantitatively predict the diffusivity or viscosity. We find that the Adam-Gibbs relation between diffusion (or viscosity) and the temperature scaled configurational entropy, S_c, is a poor predictor of fragility trends and density anomalies when necessary anharmonic corrections are added. By contrast the Dzugutov scaling relationship that uses the pair correlation approximation to $S_{excess} \sim S_2$ provides excellent agreement for diffusion anomalies and for fragile dynamics for weakly supercooled states for the family of isotropic potentials, within a single isotropic potential, and for the TIP4P-Ew model, but deviates strongly in all three cases at more deeply supercooled temperatures. By studying the microscopic dynamics at these low temperatures, we find an increased heterogeneity in the mobility of particle populations reflected in a highly non-Gaussian distribution of particle displacements, even at very long time scales. We conclude that after the onset of dynamical heterogeneity, new consideration of higher structural correlations and/or more complex connectivity paths between basins through barriers appear to be critical for the formulation of a predictive theory for dynamics.

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INTRODUCTION

Although the diffusion constant and relaxation times of a fluid can be measured via equilibrium simulations, much like thermodynamic and structural properties, these dynamical constants cannot be formulated in terms of a partition function. Therefore whether dynamical properties should be predictable from thermodynamic or structural features of the liquid is an interesting question, but not an obvious one. If a formal theory relating dynamics to a particular structural or thermodynamic property existed, there would be no the need for time-evolved configurations to characterize actual barrier transitions between accessible configurations in predicting diffusion trends with density or temperature. Here we evaluate whether different entropy definitions that provide different estimates of accessible configurations at each state point are all that is needed to predict diffusivity, without ever needing to consider the transitions between the available configurations.

The phenomenological Adam-Gibbs relation[1] provides an explicit connection between the temperature dependence of the diffusion, D_t (or viscosity, η) and the configurational entropy, S_c, through the relation

$$D_t = D_0 \, exp\left(\frac{A}{TS_c}\right) \tag{1}$$

where D_0 and A are assumed to be temperature-independent constants. Numerical application of Adam-Gibbs theory and its formulation in terms of basins on the potential energy landscape (PEL) has shown a strong correlation between a fragile dynamical temperature trend and the S_c ansatz, for both simulation studies[2-4] and experimental studies[5,6]. However, if S_c can be empirically related to observed trends of heat capacity and temperature[7]

$$S_c \approx \int_{T_0}^{T} \frac{\Delta C_p}{T'} dT' \approx \int_{T_0}^{T} \frac{A'}{T'^2} dT' = A'\left(\frac{1}{T_0} - \frac{1}{T}\right) \tag{2}$$

then by substituting Eq. (2) into Eq. (1) we recover the Volger-Tamman-Fulcher (VFT) function,

$$D_t(T) = D_0 \exp\left(\frac{B}{T - T_0}\right) \tag{3}$$

where T_0 is an estimate of the glass transition temperature, and $\kappa = T_0/B$ is the fragility index[5]. Since Eq. (3) is known to fit experimental or simulated transport properties very well over a large temperature range, a linear correlation between lnD_t and $1/TS_c$ is expected from observed trends of these two quantities with temperature. Therefore it is not strictly proven that the configuration count contained in S_c can yield predictive diffusion trends with temperature. Thus without

independent confirmation of the expected slope of the linear relationship (the *A* parameter in Eq. (1)) it is not possible to assert any actual cause and effect relationship between decreasing configurational entropy and decreasing diffusivity.

An alternative empirical relationship between a liquid's macroscopic thermodynamic and dynamic quantities, originally proposed by Rosenfeld[8], suggests a correlation between a scaled (dimensionless) diffusion constant, D^*, and a liquid's excess entropy, S_{excess} (relative to the ideal gas), such that

$$D^* = D_0^* \exp(\alpha S_{excess}).$$ (4)

where S_{excess} is scaled by (Nk_B), and D_0^* and α are dimensionless constants. The scaling factor for the diffusion constant used in this study was introduced by Dzugutov[9], where $D^* = D\Gamma_E^{-1}\sigma^{-2}$, where $\Gamma_E = 4\sigma^2 g(\sigma)\rho\sqrt{\pi k_B T/m}$ is the Enskog collision frequency, σ is taken as the location of the first peak in the g(r), g(σ) is the value of the g(r) at this separation, ρ is the density, k_B is Boltzmann's constant, T is temperature and m is the mass. This scaling factor is distinct from the choice made in the initial paper by Rosenfeld[8] who scaled with the macroscopic quantities ρ, T, and m (see ref [10] for a full comparison of different scaling factors). By definition S_{excess} provides a different configuration count relative to S_c, which is further modified when S_{excess} in Eq. (4) is replaced with the pair correlation approximation[11,12]

$$S_{excess} \approx S_2 = -2\pi\rho \int_0^\infty \{g(r) \ln g(r) - [g(r) - 1]\} r^2 dr$$ (5)

in which accessible configurations are now completely determined by the corresponding changes in structural correlations as a function of temperature and density. Because the entropy scaling relation is based on data fitting[8] of S_{excess} vs. scaled diffusivity, it provides no guidance as to any physical meaning of the α parameter (although the possibility of a more rigorous derivation has been suggested[10]). Despite the ambiguity in the molecular origin of the α and D_0^* fit parameters, Dzugutov found these parameters to be nearly 'universal' for the liquids he studied, yielding values $\alpha\sim1$ and $D_0^*\sim0.049$[9], although subsequent studies have observed significant variation from these values[13-15] It has been suggested that long range interactions in the potential[15], or the existence of strong orientational correlations[16] may be the origin for why certain fluids show values of $\alpha\neq1$. Here we propose additional insight into a possible dependence of the α parameter on the form of the interaction potential.

Both the Adam-Gibbs relation[2,3,17,18] and the excess entropy scaling relations[13,14,16,18] have been tested through simulation and shown to produce linear correlations over limited temperature ranges. While the Adam-Gibbs relation is understood to fail at higher temperatures[6,19] because the assumption that particle motion is cooperative and non-Arrhenius is incorrect, the excess entropy correlation for dense liquids deviates at very low temperatures with a corresponding breakdown in the Einstein-Stokes relation[13]. Due to the empirical nature of the excess entropy scaling relation, it is difficult to predict whether the scaling functional form may change with extremes of density or temperature, although some arguments have been made to justify observed changes in behavior for dilute gases[10].

Here we study a family of isotropic potential energy functions[20] in which each member exactly reproduces the oxygen-oxygen radial distribution function, $g_{OO}(r)$, of the TIP4P-Ew water model[21] at a given temperature and density, thereby preserving the translational structural order of the original full potential across the phase diagram[22,23] (Figure 1). The family of isotropic potentials can provide a more stringent test of thermodynamic relationships for predicting diffusion trends, by removing a common PEL so we may examine whether the values of D_t and a given entropy quantity, simulated in their own state point phase space, are quantitatively connected rather than just both having appropriate temperature dependence as implied by Eqs. (2) and (3). Investigation of thermodynamic-dynamic relationships *across* the family of isotropic potentials will answer whether enforcing translational structural order is a sufficient constraint on allowed potential energy landscapes[24] that may accurately predict diffusion trends using these thermodynamic relationships. We also analyze the correlations *within* the potentials (i.e. within their own phase diagram) to examine how the fitting parameters used in Eqs. (1) and (4) may be estimated from the interaction potential, the PEL, and/or structural order.

METHODS

Simulation Protocol

The isotropic potentials were derived[20,25] for each new state point (examples shown in Figure 1) to reproduce the density and temperature dependent $g_{OO}(r)$ of the TIP4P-Ew four-site water model.[21] Simulations were run in NVT with 1728 particles of mass=18.01528g/mol. Equations of motion were integrated with the velocity-verlet algorithm. Temperature was controlled via Nose-Hoover thermostats[26] with a timescale of 1.5ps. Simulations were

equilibrated for 900ps and statistics collected for 600ps for T>250K, and equilibrated for 1.2ns below 250K with 1ns of statistics. For each temperature 5 additional independent trajectories of 600ps each were run to collect diffusion statistics, with the thermostat timescale changed to 10ps. A time step of 3fs was used for temperatures between 100K and 500K and 2fs for T>500K.

For the simulations run below 100K for a single isotropic potential across its own phase diagram, the timestep was increased to 4fs. We collected statistics for 100ns at 100K and 900ns for 80K due to the extremely slow relaxation times. We were not able to converge the viscosity calculations for these low temperatures, and hence did not evaluate a potential breakdown of the Einstein-Stokes relation at cold temperatures.

For the data points evaluated across the family of isotropic potentials, the densities corresponded to the P=1atm isobar of the TIP4P-Ew simulations (dense liquids). For data collected within one isotropic potential, the same constant density was maintained across temperature.

For the TIP4P-Ew simulations[20], 1728 water molecules were simulated at the temperatures 373K, 348K, 310.5K, 298K, 285.5K, 273K, 260.5K, 248K, 235.5K, 225K, 215K, 200K and 190K. The densities for each temperature corresponded to the P=1atm isobar, where values from ref. [21] were used. For the lower temperature points, simulations were first run in NPT[27] to calculate the density for the P=1 atm state points. For evaluating dynamic properties, NVT calculations were run with a Nose-Hoover[26] thermostat lightly coupled to the system (timescale of 10ps) to minimize perturbations from the heat bath. For T>200K, a timestep of 1fs was used and for 200K and 190K a timestep of 2fs was used. For T>200K, five independent trajectories were additionally run at each temperature to collect diffusion statistics. For 200K and 190K statistics were collected from two independent trajectories of ~130ns each (200K) and 200ns each (190K).

Free Energy Calculation

We calculate the Helmholtz free energy, $A(\rho,T)$, via thermodynamic integration[28,29], starting at the state point of interest, and decreasing the density in increments of 0.03g/cm^3 to a final point of $\rho_{low}=0.01\text{g/cm}^3$. We then hold the system at constant volume and increasing the temperature in increments of 20-50K (depending on current temperature) to a final temperature of $T_{high}=1000K$, to reach the ideal gas state reference; any excess free energy at this state was

calculated using the virial expansion. This procedure (simulating across the phase diagram to the ideal gas reference state) was carried out for *each* potential. Explicitly, we calculate

$$A_{tot}(\rho,T) = A_{ideal}(\rho,T) + A_{ex}(\rho,T) \tag{6}$$

where

$$A_{ideal}(\rho,T) = k_B T N[3\ln(\lambda) + \ln(\rho) - 1] \tag{7}$$

and $\lambda = \sqrt{h^2/(2\pi k_b T m)}$. $A_{ex}(\rho,T)$ is calculated via:

$$\beta A_{ex}(\rho,T) = \beta A_{ex}(\rho_{low},T) + \int_{\rho_{low}}^{\rho} d\rho' \frac{N}{\rho'^2}[\beta P(\rho') - \rho'] \tag{8}$$

and

$$\beta A_{ex}(\rho_{low},T) = \beta_{highT} A_{ex}(\rho_{low},T_{high}) + \int_{\beta_{highT}}^{\beta} d\beta V(\beta) \tag{9}$$

where $\beta=1/(k_bT)$, P is the pressure, and V is the potential energy. Using the virial expansion, any excess free energy at our low density, high temperature reference state is calculated as:

$$\beta_{highT} A_{ex}(\rho_{low},T_{high}) = N\rho_{low} B_2(T_{high}) \tag{10}$$

where $B_2(T) = -2\pi \int_0^{\infty} r^2 dr[\exp(-\beta v(r)) - 1]$. This correction was very small as expected, <0.5% of the total excess free energy for all state points. For the integration, both $P(\rho)$ and $V(\beta)$ were fit with cubic splines to avoid any errors arising due to deviations from polynomial fits.

The total entropy is calculated from

$$S_{tot}(T,\rho) = \frac{1}{T}(U - A), \tag{11}$$

where U is the internal energy, and the excess entropy is calculated from

$$S_{ex} = \frac{1}{T}(\langle V \rangle - A_{ex}), \tag{12}$$

where $<V>$ is the average potential energy. To evaluate the configurational entropy, we subtract off the vibrational entropy, $S_{vib}(T,\rho)$ from $S_{tot}(T,\rho)$. For the vibrational entropy calculation, 500-2000 decorrelated equilibrium configurations were quenched into their local minima, using the Broyden-Fletcher-Goldfarb-Shanno quasi-second order Newton method[30]. We then can evaluate the quenched energy V_0 and eigenvalues, $\lambda_i = m\omega_i^2$, of the Hessian matrix. Within the

harmonic approximation to the basin shape, $V(\{q\}) = \frac{1}{2}\sum_{i=3}^{3N}\lambda_i q_i^2$, where q_i is the displacement

along mode i, S_{vib} is exactly given by:

$$S_{vib}^{harm} = k_B \sum_{i=3}^{3N}\left[1 - ln\left(\frac{h\omega_i}{2\pi k_B T}\right)\right]. \tag{13}$$

Deviations from the harmonic approximation to the energy

$$U(T,\rho) = V_0 + U_{harm} + \Delta V, \tag{14}$$

where

$$U_{harm} = (3N-3)k_b T \tag{15}$$

and ΔV is the correction to the potential energy due to anharmonicity, were typically found to be

between 10-25% for all state points. By assuming $\Delta V = aT^2$, and using the relation $\frac{dU}{dT} = T\frac{dS}{dT}$,

we calculate the anharmonic correction, $S_{vib}^{anharm}(T,\rho) = 2aT$ where $a = \Delta V/T^2$. Similarly, the

anharmonic correction to the basin free energy (needed for Eq. (17) below) is $A_{vib}^{anharm} = -\Delta V$.

We show in the Appendix that this anharmonic addition to the entropy, $S^{anh} = 2\langle \Delta V\rangle/T$ is

exactly what is given by thermodynamic perturbation theory with second order cubic corrections,

and first order quartic corrections (the standard expansion). For each state point, a sharply

peaked distribution of S_{vib} values is calculated. The variance in these values is used as an estimate

of the error in the ultimate S_c value. By characterizing the changes in potential energy as we

displaced along the modes, we found noticeable coupling between modes, which are assumed to

be uncoupled in the harmonic approximation, and which gives rise to our deviations which we

describe in the Appendix.

We also calculate S_c from statistics of the PEL basins[31] as in previous studies[2,17,32] using

$$S_c(T) = \int S_c(\Phi)P(\Phi,T)d\Phi \tag{16}$$

where $S_c(\Phi) = kln\Omega(\Phi)$ counts the number of basins with energy depth Φ, and $P(\Phi,T)$ is the

probability of observing an inherent structure (IS) basin of energy Φ at temperature T.

$$P(\Phi,T) = \Omega(\Phi)\exp[-\beta(\Phi + A_{vib}(\Phi,T))]/Q(\rho,T) \tag{17}$$

The partition function, $Q(\rho,T)$, is determined via the relation $\beta A_{total} = -\ln(Q)$. We again include

an anharmonic correction to the basin free energy consistent with the method above such that

$A_{vib}^{anharm} = -\Delta V$ (see Appendix).

Dynamic Observables

We evaluate the diffusion constant, D_t, using the Einstein relation,

$$D_t = \frac{1}{6} \lim_{t \to \infty} \frac{d}{dt} \left\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \right\rangle \tag{18}$$

where the value of D_t is averaged over 5 independent simulations. We verify the mean square displacement has converged to the linear diffusive regime by calculating the slope over multiple time windows. We also calculate viscosity using the Green-Kubo relation[29]

$$\eta = \frac{1}{Vk_BT} \int_0^\infty dt \left\langle \sigma^{xy}(t)\sigma^{xy}(0) \right\rangle \tag{19}$$

where

$$\sigma^{xy} = \sum_{i=1}^{N} m_i v_i^x v_i^y + \frac{1}{2} \sum_{j \neq i} x_{ij} F_y(r_{ij}). \tag{20}$$

Due to the difficulty in converging the shear autocorrelation function, additional simulations were run for 30ns, with the shear matrix elements σ^{xy}, σ^{yz}, σ^{xz} calculated and saved at each time step for maximum statistics. Figure 2 shows the convergence profile of such a simulation. The van Hove self correlation function[33] was calculated from:

$$G_s(\mathbf{r}, t) = \left\langle \frac{1}{N} \sum_{i=1}^{N} \delta[\mathbf{r} - \mathbf{r}_i(t) + \mathbf{r}_i(0)] \right\rangle \tag{21}$$

In Figures 9 and 10 we plot the probability (modulo a constant 4π), $r^2 G_s(r,t)$, of finding the particles displaced by a magnitude r after a time t.

RESULTS

We have previously reported that the family of isotropic potentials shows evidence of a structurally anomalous region in which structural order collapses under applied pressure[20]. Figure 3a shows that the family of isotropic potentials traces out similar dynamical trends with temperature and density to the TIP4P-Ew model shown in Figure 3b. Despite the diffusion data being collected across a changing set of interaction potentials, we nevertheless observe surprisingly similar dynamical trends to those observed in the reference water model.

Adam-Gibbs Relationship. Figure 4a displays lnD_t vs. $1/TS_c$ across the family of isotropic potentials in which the configurational entropy is calculated using thermodynamic

integration as well as from basin topography measures of the PEL[2,17,32] using Eqs. (16) and (17). The vibrational free energy, $\underline{A}_{vib}(\Phi,T)$, is calculated with anharmonic corrections since the anharmonicity of the basins were found to be both significant (10-25% of the harmonic energy) and dependent on temperature. Figure 4a shows a pronounced non-linear relationship in the plot of lnD_t vs. $1/TS_c$. A calculation of the percentage of error between the calculated diffusion data and the best fit line (over the *full* temperature range) gave an average error of 18% for the Adam-Gibbs relationship, with deviations occuring for both high and low temperature. Furthermore, although the translational diffusion values for the family of isotropic potentials vary only over one decade in timescales (a result of coarse-graining that differs from the diffusion values of the parent potential which varies over 3-4 decades over the same temperature range), the non-linearity of the Adam-Gibbs relationship would be even more severe over a larger temperature range.

In Figure 4b we analyze the Adam-Gibbs equation between lnD_t and $1/TS_c$ *within* each potential, i.e. by simulating each of their own phase diagrams at constant density but over a limited temperature range. Similar to other studies[2,18], we see reasonable linear correlation within one potential over our 4-5 data points, but emphasize that this is not a rigorous test of the Adam-Gibbs theory because of the smaller temperature variation than that used in Figure 4a. We can clearly see that the parameters A and D_0 of Eq. (1) change noticeably with the changing interaction potential (reflected in the changing slope and intercept, respectively; see Table 1). There is a general trend towards increasing barrier parameter A with decreasing temperature, consistent with noticeable changes of increasing potential energy barriers between the first two major wells of the interaction potentials (see Figure 1), but we were unable to extract something close to a average value of these parameters from our model one-component potential family. This outcome highlights the limitations of the Adam-Gibbs relation and the landscape paradigm in making quantitative predictions about dynamic behavior, given the lack of theoretical basis for the temperature independent fitting parameter A in Eq. (1).

Excess entropy scaling. We next consider the Dzugutov scaling relationship between D_t* and using either S_{excess} or S_2. Figure 5a shows that the two different entropies yield different D_0* but have highly similar α parameters; while the two parameters are not the same as that found for metals[9], supercooled liquids[15,34], and silica[16], (and thus Eq. (4) is not universal and therefore predictive), the correlation between diffusivity and S_{excess} or S_2 is excellent over the temperature range of 348K down to 200K. We note that there is very little difference in the

Dzugutov scaling correlation whether using scaled or unscaled diffusion constants (data not shown). A calculation of the percentage of error between the calculated diffusion data and the best fit line (over the *full* temperature range) gave an average error of 2.5% for the S_{excess} correlation, and 5% for the S_2 correlation. Given the very good –agreement using S_2, apparently three-body and higher terms in the expansion of S_{excess} are only weakly dependent on temperature as has been seen before[12]. However, we note that the largest deviation for Dzugutov scaling relationship becomes evident at 190K.

In Figure 5b we analyze the Dzugutov scaling relationship between diffusion and S_{excess} and S_2 correlations *within* each isotropic potential, again by simulating each of their own phase diagrams at constant density but over a limited temperature range. In contrast to the Adam-Gibbs result (Figure 4b), the parameter trends are very similar for each new potential, giving rise to similar fitting parameters reported in Table 1, with average values of $\alpha \sim 1.6$ and $D_0 \sim 0.16$. Although our fit parameters are distinct from the values of Dzugutov[9] and the values reported for other liquid types[13,15] they are nevertheless very closely related to one another, and to the values found across the family of isotropic potentials. Examination of the interaction potential (Figure 1) shows that the relative lengthscales of the two potential energy minima remains relatively constant (reflected in the location of the first two peaks in the *gOO(r)*), and we speculate that perhaps the constancy of these relative lengthscales in a spherically symmetric liquid controls the Dzugutov scaling fitting parameters used in Eq. (4). We note that the largest deviation in the parameters becomes evident at 190K when there is an appearance of two new shallow minima at lengthscales of ~5.75Å and ~8.0Å, and this supports our proposal that the number or ratio of lengthscales within the system may largely determine the magnitude of the α parameter.

Diffusion trends with density. Previous work has shown that the anomalous density dependent diffusion trends correlate with both S_{excess} and S_c[3,4,14,34]. More specifically, it has been shown that in regions where the diffusivity increases anomalously with increasing compression, both S_{excess} and S_2 also increase anomalously with compression (although not necessarily the reverse)[4]. We consider this comparison of the Adam-Gibbs and Dzugutov scaling relations vs. diffusion *across* the family of isotropic potentials, in which we examine the diffusion anomaly at T=235K, where both the TIP4P-EW reference model and the family of isotropic potentials have the same diffusion maximum with respect to density.

Figure 6 shows that for S_c, the density dependent trends show a poor correlation with the diffusion constant. We also observe for the first time in our family of isotropic potentials that the

trends in S_{excess} and S_2 are not equivalent, and S_{excess} does not increase anomalously to encompass the region of the diffusion anomaly (regardless of whether we consider unscaled D or the Dzugutov scaling $D*$), while only S_2 is able to demonstrate good agreement with the density dependent diffusion trends. While there is certainly nothing in the development of the excess entropy relations that supports S_{excess} over S_2, or vice versa, we note that other studies *within* a single potential find that S_{excess} is more accurate than S_2 in determining the onset of diffusion anomalies[4] when scaled as per the Rosenfeld prescription[8], and that the thermodynamic-dynamic relation can be sensitive to the choice of scaling[35]. By contrast, our results are the same whether using the Dzugutov scaling for diffusion, or no scaling at all!

The success of S_2 over such a large temperature and density range suggests that the entropic information encoded by the static pair structural correlations (in which the density anomaly is shown by Yan and co-workers to originate from the second peak in the pair correlation function[36]), regardless of changes in the underlying interaction potential or scaling prescriptions, is a central factor in determining dynamic trends without ever needing to consider the transitions or pathways of transitions between the available configurations, at least down to lightly supercooled states. Because our isotropic models have the same values of S_2 at the same state points as the TIP4P-Ew water model by construction, it therefore is also the entropy quantity that correlates with the diffusion anomaly of the full potential.

Excess entropy scaling for TIP4P-Ew. Since our isotropic models have the same values of S_2 at the same state points as the TIP4P-Ew water model by construction, we can also ask how well Eq. (5) using S_2 predicts the fragility trends of the TIP4P-Ew water model. Figure 7 shows D_t* vs. S_2 for the complete TIP4P-Ew water model for values of D_t* that vary by four orders of magnitude over the temperature range of 373K to 190K. While the Dzugutov relationship[9] between S_2 and the scaled diffusion constant provides quantitative agreement for fragile dynamics down to 215K, it deviates strongly for the two lowest temperatures of 200K and 190K. The inset of Figure 7 shows that the result is the same whether we use the Dzugutv scaling, or no scaling at all. Apparently the pair density correlations folded into the S_2 entropic metric are no longer sufficient to capture the diffusion trends, predicting that the dynamics should actually be faster than the actual observed diffusion.

The failure of these phenomenological thermodynamic-dynamic relationships at low temperatures has been noted in other studies as well[13,19], and in one case correlates with a breakdown in the Einstein-Stokes relation[13]. In order to elucidate any possible change in the

mechanism of structural relaxation (similar to characterizing a possible breakdown in the Einstein-Stokes relation[37]) we calculate the van Hove self correlation function (Eq. 21), which will approach a Gaussian distribution of particle displacements at long time-scales for a system whose diffusion conforms to Fick's law. In Figure 7b we see that for the TIP4P-Ew model at T=215K (at which diffusivity still correlates with S_2) the distributions appear to approach a Gaussian distribution of particle displacements as time progresses. As we lower the temperature, however, we see a notably non-Gaussian distribution of displacements, as has been previously observed in a cold binary LJ system[2]. This change reflects a growing separation in populations of particles that remain trapped near their original location (small r), versus relatively mobile particles (advancing beyond their nearest neighbor shells). With different populations relaxing on different time scales, the change to more heterogeneous dynamics has been closely linked to a breakdown in the Einstein-Stokes relation[38,39].

Failure of excess entropy trends for translational diffusion. It appears that the Dzugutov scaling relation using S_2 gets fragility trends right down to lightly supercooled temperatures for TIP4P-Ew because diffusion is controlled by density correlations over two short-ranged lengthscales. However the pair correlation approximation to S_{excess} used in the relation fails for deeply supercooled states of the TIP4P-Ew model, when the slow down in diffusivity is accompanied by a change in the underlying mechanism for particle dynamics, such that the displacements of particles are no longer evenly distributed around some mean value. It is accepted that as the system approaches a glassy state, cooperative motion between particles is necessary to allow for relaxation[38], and the Einstein-Stokes breakdown indicates a decoupling between single particle diffusion and this long-range structural relaxation. Since we determine that the pair structure cannot capture macroscopic diffusion trends when the underlying microscopic dynamics is heterogeneous for the TIP4P-Ew model, it suggests that average pair separation of particles can't describe the long-range structural relaxation. This is evident in the isotropic family since the same low temperature states cause almost imperceptible changes in the pair structure and resulting isotropic potentials (Figure 8a), and hence we see no change in dynamical mechanism as evidenced by the lack of dynamical heterogeneity, as shown in Figure 8b. We speculate that because our coarse-graining procedure neglects explicit many body correlations that exist within the reference model, these many body effects are important for long-range structural relaxation that contribute to the observed change in the dynamics for TIP4P-Ew at low temperatures, and its expected breakdown of the Einstein-Stokes relation.

As we noted above, the pair structure changes very little for TIP4P-Ew at these low temperatures, and as a result, our coarse grained potential also changes very little. At this point looking across a family of isotropic potentials is no different than looking within a single isotropic potential, which is now controlled by usual thermodynamic and dynamical trends arising from temperature and density variations. Therefore we examine the Dzugutov scaling scaling relationships for one single isotropic potential that is derived from the 235.5K state point of the TIP4P-Ew model. We see in Figure 9a that diffusion trends are well-predicted using either S_2 or S_{excess} in Eq. (4), remaining very linear for several orders of magnitude in diffusion values, before failing at temperatures below ~100K. In Figure 9b we see that while the van Hove correlation function distributions approaches a Gaussian distribution of particle displacements as time progresses at 100K, the displacement distributions become distinctly non-Gaussian at 90K and 80K. The many body correlations that may be important for decoupling of short-range diffusion and longer-ranged relaxation emerges at a much lower temperature for the isotropic potentials than the full reference model, because that information is poorly encoded in the pair correlation function and core-softened potentials. Rather, more sophisticated theoretical models are needed that can account for these many body correlations and their connections to the changing microscopic dynamics (emergence of heterogeneity), if thermodynamic-dynamic relationships apply as the glass transition is approached. It is of course also possible that the thermodynamic-dynamic breakdown reflects that the glassy state is purely a kinetic phenomena, independent of any thermodynamic origin.

DISCUSSION AND CONCLUSION

In summary, the various entropy measures and/or their associated thermodynamic theories are not equivalent in their estimates of the accessible configurations at each state point, and hence vary in their predictive quality for quantifying dynamical trends with density and temperature. A significant weakness of these thermodynamic-dynamic relations is the ill-defined fitting parameters, A and D_0 for Adam-Gibbs, and α and D_0* for Dzugutov scaling. Since these parameters can only be extracted once one has collected both the entropic data and the diffusion data of interest, these theories lack any genuine predictive power. We find that the Adam-Gibbs relationship fails completely in regards to prediction of dynamical anomalies and fragility trends across the family of isotropic potentials, because the barrier parameter A is sensitive to the form of the interaction potential that varies with temperature and density. We conclude that only basin

enumeration of the PEL (via S_c) does not fully address the complexity of diffusion trends without complementary analysis of barriers. By contrast, the Dzugutov scaling relation accurately predicts both the temperature-dependent dynamics down to lightly supercooled states, which may be because the α parameter is nearly constant across the family because the two lengthscales are maintained across each core-softened potential with temperature changes. The increase in the α parameter at the lowest temperatures may then be due to the emergence of new longer lengthscales in the potentials (Figure 1).

We previously showed that our coarse-graining method of translocating the reference water model's pair structure into a family of isotropic potentials disrupted thermodynamic stability criteria involving the virial pressure[20], and as a result our family of isotropic potentials did not generate any water-like density anomaly. Despite the loss of these thermodynamic trends, the diffusion trends in the isotropic family were remarkably similar to those of the reference water model. It suggests that S_2 as used in the Dzugutov scaling relation captures the dynamical trends for both the isotropic and TIP4P-Ew model because diffusion is controlled by density fluctuations captured in the pair distribution function. However, the Dzugutov scaling thermodynamic-dynamic relation fails for deeply supercooled temperatures because density correlations vary minimally with lowering temperature, while the diffusivity decreases rapidly and the mechanism for relaxation appears to change[40]. We believe that many body correlations may be important for representing longer-ranged relaxation, which is poorly represented in the pair correlation function and core-softened potentials. Thermodynamic stability trends are much more sensitive to these longer range correlations at higher temperatures, but they are not operative for dynamics until a very different region of the phase diagram is reached.

It is intriguing that idealized mode coupling theory (MCT) also utilizes only the pair correlation function in its prediction of the intermediate scattering function, successfully predicting the diffusion trends for many liquids down to lightly supercooled temperatures. However, MCT is not able to predict dynamics at low temperatures, where dynamic heterogeneity sets in and the mean-field like approximations used in MCT no longer applies[41]. Although we did not explicitly test the predictions of MCT, we expect it to fail at the temperature where the Dzugutov scaling relation fails, that is, at the onset of heterogeneous dynamics. The inability of both the Dzugutov scaling relation and MCT to apply at low temperatures emphasizes that the radial packing of the particles (even when considered within the more rigorous framework of MCT) is simply not detailed enough to describe the motion of particles at

lower temperatures, where cooperative motion and heterogeneous dynamics[37,42] emphasizes relaxation over multiple lengthscales.

It is also interesting how the Dzugutov scaling thermodynamic relation using S_2, idealized MCT dynamical theory[43], and MCT and its connection to the PEL[44], invoke very different assumptions about the relevance of available configurations, available pathways between basins, and basin properties. What appears more relevant is that theories that account for the density fluctuations captured in the pair correlations and their trends with temperature can predict the fragile diffusivity over a large temperature (and density) range, with no direct reliance on the potential energy surface or pathways. But because phenomenological theories eventually fail at the coldest temperatures, we conclude that a predictive theory for dynamics will be difficult to achieve without more explicit information about many-body correlations or connectivity paths between basins through barriers[45].

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APPENDIX

Here we use thermodynamic perturbation theory to derive the anharmonic corrections to the Helmholtz free energy of a reference quadratic potential specifically for a liquid, rather than a crystal[46,47]. We similarly include cubic terms to 2nd order, and quartic terms to 1st order. The Taylor expansion of a potential V in normal modes q about its minimum gives:

$$V(\{q\}) = \frac{1}{2}\sum\nolimits_{i=3}^{3N}\lambda_i q_i^2 + \frac{1}{6}\sum\nolimits_{i=3,j=3,k=3}^{3N}\kappa_{ijk}q_i q_j q_k + \frac{1}{24}\sum\nolimits_{i,j,k,l}^{3N}\gamma_{ijkl}q_i q_j q_k q_l + ... \qquad (A.1)$$

where the second, third, and fourth derivatives of the potential are given by λ_i, κ_{ijk}, and γ_{ijkl} respectively. As usual[46,47], we treat the quadratic term as the reference potential, such that

$$V_0 = \frac{1}{2}\sum\nolimits_{i=3}^{3N}\lambda_i q_i^2, \qquad \text{and} \qquad \text{the} \qquad \text{perturbation} \qquad \text{is}$$

$$V_3 = \frac{1}{6}\sum\nolimits_{i,j,k}^{3N}\kappa_{ijk}q_i q_j q_k + V_4 = \frac{1}{24}\sum\nolimits_{i,j,k,l}^{3N}\gamma_{ijkl}q_i q_j q_k q_l. \qquad \text{Hence} \qquad \text{the} \qquad \text{hamiltonian} \qquad \text{is}$$

$V = V_0 + \lambda V_3 + \lambda^2 V_4$ [46]. Upon evaluating the partition function for this potential and linearizing the exponentials for the cubic V_3 and quartic V_4 terms, we have the following expression to second order in the cubic term, and first order in the quartic term:

$$Z = \int dq^N \exp(-\beta V_0(q^N))[1 - \beta\lambda V_3(q^N) + \beta^2\lambda^2/2(V_3(q^N))^2][1 - \beta\lambda V_4(q^N)] \qquad (A.2)$$

and we keep terms to order λ^2 in (A.2)[46,48]. The linear V_3 term will vanish due to the even symmetry of the harmonic V_0 term, as will all terms that have odd powers of q. Hence we are left with the following contributions to Z, the harmonic term:

$$Z_0 = \int dq^N \exp(-\beta V_0(q^N)) = \prod_{i=3}^{3N}\left(\frac{2\pi k_B T}{\lambda_i}\right)^{1/2} \qquad (A.3)$$

The second order cubic term:

$$Z_1 = \int dq^N \exp(-\beta V_0(q^N))\frac{\beta^2}{2*36}\sum\nolimits_{ijk}^{3N}\kappa_{ijk}^2 q_i^2 q_j^2 q_k^2 = Z_0\sum\nolimits_{ijk}^{3N}\frac{\beta^{-1}}{72}\kappa_{ijk}^2\left(\frac{1}{\lambda_i\lambda_j\lambda_k}\right) \qquad (A.4)$$

and the first order quartic term:

$$Z_2 = \int dq^N \exp(-\beta V_0(q^N)) \frac{\beta}{24} \sum_{ij}^{3N} \gamma_{ij} q_i^2 q_j^2 = Z_0 \sum_{ij}^{3N} \frac{\beta^{-1}}{24} \gamma_{ij} \left(\frac{1}{\lambda_i \lambda_j} \right) \tag{A.5}$$

where in the right hand sides, the integrals have been explicitly evaluated. Based on the right hand sides of Z_1 and Z_2, we define $Z_1'=Z_1/Z_0$, and $Z_2'=Z_2/Z_0$. The free energy is given by the logarithm of the partition function, (we absorb the momentum term into Z_0 for all terms). We have[46]

$$-\beta A = \ln(Z_0) + \ln(1 + \lambda^2 (Z_1/Z_0) - \lambda^2 (Z_2/Z_0)) \tag{A.6}$$

simplified to[46,48]

$$-\beta A = -\beta A_0 + \lambda^2 [(Z_1/Z_0) - (Z_2/Z_0)] = -\beta A_0 + [Z_1' - Z_2']. \tag{A.7}$$

If we now evaluate the average internal energy, using $\langle U \rangle = \dfrac{\partial \beta A}{\partial \beta}$, with the above β dependence of Z_1' and Z_2' we find that

$$\langle U \rangle = \langle U_0 \rangle - \left[-\frac{1}{\beta}(Z_1' - Z_2') \right] \tag{A.8}$$

which implies that the anharmonic correction to internal energy, and therefore the correction to the potential energy ΔV is:

$$\langle \Delta V \rangle = \beta^{-1}[Z_1' - Z_2']. \tag{A.9}$$

Comparison with the anharmonic correction to the free energy, the RHS of (A.7) shows that

$$A = A_0 - \langle \Delta V \rangle. \tag{A.10}$$

The correction to the free energy appears in other forms [47,48], but the explicit evaluation of these equations gives the same result as that noted above.

Finally, the evaluation of the entropy $S = \dfrac{(U - A)}{T}$ has an anharmonic correction to the reference quadratic potential of

$$S^{anh} = 2\langle \Delta V \rangle / T. \tag{A.11}$$

Table 1. *Fit parameters to the Adam-Gibbs equation (Eq. (1)) and the Dzugutov scaling relation (Eq.(4)) for each isotropic potential across its own phase diagram.* The Adam-Gibbs parameters are listed in units of kcal/mol for *A*, and $10^{-4} cm^2/s$ for D_0. The Dzugutov scaling unitless parameters, α and D_0^* are from fits to the scaled diffusivity D^* vs. S_2 and S_{excess}.

Potential	A	D_0	α (S_2)	D_0^* (S_2)	α (S_{excess})	D_0^* (S_{excess})
V_{190}	3.06	1.872	-1.84	0.232	-1.84	0.579
V_{200}	3.15	2.748	-1.68	0.141	-1.67	0.320
V_{225}	2.64	3.536	-1.40	0.073	-1.41	0.150
V_{235}	2.61	3.957	-1.42	0.079	-1.40	0.153
V_{248}	2.37	3.763	-1.52	0.099	-1.44	0.175
V_{260}	2.41	4.208	-1.65	0.132	-1.53	0.230
V_{285}	2.27	4.380	-1.59	0.120	-1.46	0.201
V_{310}	1.98	3.922	-1.70	0.148	-1.47	0.211
V_{373}	1.95	4.307	-1.88	0.210	-1.49	0.223
Family	4.48	14.30	-1.70	0.151	-1.67	0.328
TIP4P-Ew	-	-	-3.95	1.400		

FIGURE CAPTIONS

Figure 1. *Isotropic potentials as a function of temperature for T=348K (solid), 285.5K (dashed), 235.5K (dot-dash), and 190K (dotted).*

Figure 2. *Plot of viscosity vs the time integrated over the shear auto-correlation function.* The integral shows excellent convergence within 5ps to the same viscosity value for all three correlation functions. XY shear (solid), XZ shear (dashed), YZ shear (dot-dash). As mentioned in the methods, this level of convergence required 30ns of simulation, with the shear matrix elements calculated and saved at every time step.

Figure 3. *Translational diffusion constants trends with temperature and density for (a) the family of isotropic potentials and (b) for the TIP4P-Ew model.* Symbols are for the simulated values. Insets show D_t as a function of density for the four isotherms T=310.5K, T=285.5K, 260.5K, and 235.5K[20]. Lines are two different fits to the VFT form (Eq. (5)) over two temperature ranges. In (a), the VFT parameters for the isotropic family over temperature data down to 200K are D_0=6.11E-4cm^2/s, κ=0.61, and T_0=145K (solid line), which gives a higher quality of fit compared to the VFT fit down to 190K with D_0=7.46E-4cm^2/s, κ=0.49, and T_0=136K (dotted line). The activation energy for the family increases from ~1.5kcal/mol at T=350K to between 4-5kcal/mol at the lowest temperatures. In (b), the VFT parameters for the TIP4P-Ew model over temperature data down to 215K are D_0=6.89E-4cm^2/s, κ=0.35, and T_0=160K (solid line), compared to the VFT parameters fit down to 190K with D_0=61.4E-4cm^2/s, κ=0.27, and T_0=151K (dotted line). For TIP4P-Ew the activation energy increases from 3.5kcal/mol at T=350K, to ~15kcal/mol at the lowest temperature.

Figure 4. *Test of the Adam-Gibbs relation across the family of isotropic potentials.* (a) ln D_t vs $1/TS_c$ (and inset lnη vs. $1/TS_c$) with S_c calculated from both thermodynamic integration (black circles) and from basin distributions via Eq. (16) (red triangles). For both methods, anharmonic corrections were included for the vibrational properties due to 10-25% deviations from the harmonic approximation. The two methods of calculating S_c give nearly identical results. It is evident that the expected linear correlation is not reproduced in our family of isotropic potentials.

Lines are the best fit expected from Eq. (1). Error bars on D_t capture the 1-3% deviation among simulated values, compared to deviations of up to 40% to the best linear fit. The mean percent error between the diffusion and the best fit is 18%. Error bars on S_c reflect a distribution of values of S_{vib}, including the anharmonic corrections. (b) Evaluation of the Adam-Gibbs relation within each isotropic potential over small temperature variations. It is clear that each new potential has its own set of barrier parameter, A, and D_0 which is not captured by the family of isotropic potentials (Table 1).

Figure 5. *Test of the Dzugutov scaling relation across the family of isotropic potentials.* (a) $\ln D_t^*$ vs. S_{excess} and S_2 evaluated as a function of temperature. We recover excellent linear correlation for both entropy metrics, except perhaps at the lowest temperature of 190K. Symbols are for the simulated values and lines are the best fit expected from Eqs. (2) and (3). The average percent error between D_t^* and the best line fit is 5% for the S_2 data, and 2.5% for the S_{excess} data. (b) Evaluation of the Dzugutov scaling relation for S_2 and S_{excess} within each isotropic potential over small temperature variations. The fitting parameters, α and D_0^*, are very similar between each potential, except at the lowest temperatures.

Figure 6. *Various entropy measurements vs. density for prediction of diffusion anomalies.* The red circles are the scaled diffusion data for the family of isotropic potentials. (the unscaled diffusion constant has the same trend). We also note that as seen in Figure 3b (inset), the TIP4P-Ew has the same diffusion trends, with the maximum located at the same density. We find the s_2 provides the best correlation of the diffusion maximum with density. In order to plot the curves over the same y-axis range, the D* values were multiplied by a factor of 1000, and both s_2 and s_{excess} were increased by a constant factor of 6 from their actual values.

Figure 7. (a) *Test of Dzugutov scaling relation in the TIP4P-Ew water model using S_2.* Symbols are for the simulated values and lines are the fits expected from Eq. (4) using the approximation based on Eq. (5). The linear correlation persists over the temperature range 373K down to 215K, but deviates noticeably at the lowest temperatures (200K and 190K). Line shows the best fit down to 215K. Inset shows the correlation using the unscaled diffusion constant (units cm^2/s). (b) *Plot of the van Hove self correlation function for TIP4P-Ew* at 215K (left), 200K (middle), and 190K (right). All three plots have 20 curves, where the first (blue) curve is the distribution of

particle displacements at t=510ps, for (a) each curve is incremented by 500ps, (final red curve is ~11ns), for (b) the increment is 2500ps (final red curve is ~50ns), and for (c) the increment is 3500ps (final red curve is ~70ns).

Figure 8. (a) *Family of isotropic potentials at the lowest temperatures*. The potentials show shallow minima at longer lengthscales, but stagnate at the coldest temperatures. *(b) Plot of the van Hove self correlation function for the family of isotropic potentials at 200K (top), and 190K (bottom).* Both plots have 12 curves, where the first (blue) curve is the distribution of particle displacements at t=39ps and each curve is incremented by 39ps.

Figure 9. (a) *Test of Dzugutov scaling relation within one isotropic potential (from the T=235.5K state point) using both S_2 and S_{excess}.* For this model, we collected data over the temperature range of T=348K down to T=80K. The linear correlation persists over the temperature range down to ~120K, but deviates noticeably at the lowest temperatures (100K and 80K). Line shows the best fit down to 120K, where the average percent error is 4.6% for S_2 and ~6% for S_{excess}. Inset shows the same correlation using the unscaled diffusion constant (units cm^2/s). Again we see very similar trends regardless of the scaling factor. (b) *Plot of the van Hove self correlation function for the single isotropic potential (at the T=235.5K state point) at 100K (left), 90K (middle), and 80K (right).* All three plots have 20 curves, for (a) the first blue curve is at 99ps, and each curve is incremented by 1200ps (final red curve is ~24ns) (b) first blue curve is 1ns, and each curve is incremented by 4ns (final red curve is 81ns), (c) first blue curve is 1ns, and each curve is incremented by 7ns (final red curve is 141ns).