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Communication: On the origin of the non-Arrhenius behavior in water reorientation dynamics

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We combine molecular dynamics simulations and analytic modeling to determine the origin of the non-Arrhenius temperature dependence of liquid water’s reorientation and hydrogen-bond dynamics between 235 K and 350 K. We present a quantitative model connecting hydrogen-bond exchange dynamics to local structural fluctuations, measured by the asphericity of Voronoi cells associated with each water molecule. For a fixed local structure the regular Arrhenius behavior is recovered, and the global anomalous temperature dependence is demonstrated to essentially result from a continuous shift in the unimodal structure distribution upon cooling. The non-Arrhenius behavior can thus be explained without invoking an equilibrium between distinct structures. In addition, the large width of the homogeneous structural distribution is shown to cause a growing dynamical heterogeneity and a non-exponential relaxation at low temperature. © 2012 American Institute of Physics.

\[ \langle \tau_{\text{jump}} \rangle = \int_0^\infty S(t) \, dt. \] (1)

At low temperature, \( S(t) \) displays a non-exponential decay similar to that of the orientation tcf (Fig. 1(c)).\textsuperscript{13} The anomalous reorientation dynamics thus essentially result from the HB jump dynamics, which we now examine.

Jumps between HB acceptors can be fruitfully described as chemical reactions whose kinetics is mostly determined by the free energy costs to elongate the initial HB (\( \Delta G_f \)) and for a new HB acceptor to approach and enter in the first hydration shell (\( \Delta G_i \)).\textsuperscript{20} Fluctuations in the local water structure may

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Both the translational and rotational dynamics of liquid water exhibit a non-Arrhenius behavior.\textsuperscript{1–5} The increase of the apparent activation energy (\( E_a \)) upon cooling is already perceptible at room temperature and becomes evident in the supercooled liquid. Many explanations have been suggested for this anomalous behavior, including, e.g., a change in the translation and reorientation mechanisms,\textsuperscript{6} the coexistence of high- and low-density liquid (HDL/LDL) structures,\textsuperscript{7, 8} the increasingly collective character of water motions at low temperature,\textsuperscript{9} and the freezing of some collective motions.\textsuperscript{10, 11} Here, we combine molecular dynamics simulations with an analytic extended jump model (EJM) to study the hydrogen-bond (HB) and reorientation dynamics in liquid water at ambient pressure from high temperatures (350 K) down to temperatures just above homogeneous nucleation (235 K).

At each investigated temperature, 40,000 water molecules described by the TIP4P/2005 potential\textsuperscript{12} are simulated during up to 5 ns in the microcanonical ensemble.\textsuperscript{13} Figure 1(a) shows that simulations quantitatively reproduce the non-Arrhenius behavior of the reorientation times measured experimentally. The computed orientation time-correlation functions (tcf) are also in excellent agreement with the available ultrafast measurements,\textsuperscript{14} and increasingly deviate from an exponential decay at low temperature (Fig. 1(b)), which suggests the presence of dynamical heterogeneities.\textsuperscript{15–17} However, in contrast with the popular mode-coupling theory description developed for glass-forming liquids,\textsuperscript{2} at long delays this decay cannot be satisfactorily fit with a stretched exponential (Fig. 1(b)).

For each of our simulations in the 235–350 K range, the average reorientation mechanism is found to be the same as at room temperature, with a dominant contribution arising from large angular jumps due to HB exchanges and a minor frame reorientation contribution due to the tumbling of an intact HB.\textsuperscript{19, 20} The non-Arrhenius behavior of the reorientation dynamics therefore does not result from a change in the reorientation mechanism at low temperature but instead from the non-Arrhenius kinetics of its two components. Through the entire temperature range, the value of the minor frame contribution is well predicted by the Debye-Stokes-Einstein (DSE) relation and follows the non-Arrhenius behavior of viscosity.\textsuperscript{13} This thus contrasts with the observed breakdown of this relation for the overall reorientation time,\textsuperscript{21} whose dominant jump contribution is non-diffusive,\textsuperscript{19} precluding application of DSE at any temperature. The jump contribution also exhibits a non-Arrhenius behavior, which accounts for most of the increase in the reorientation \( E_a \) (>80% of 8 kcal between 350 K and 235 K, cf. Fig. 1(d)). Since the average jump amplitude is found to be temperature independent, this entirely results from the temperature dependence of the (integrated) jump time \( \langle \tau_{\text{jump}} \rangle \) separating successive jumps. The latter is defined as the relaxation time of the HB survival probability \( S(t) \), i.e., the probability not to have jumped to a new HB acceptor after a delay \( t \).\textsuperscript{13, 22}
While it slightly shifts to more tetrahedral environments upon cooling, it displays no sign of the two distinct interconverting structures suggested by the LDL/HDL hypothesis \(^5,^6\) (the same behavior was found for the local density \(^7\)).

At each temperature and each local structure, the jump free energy barrier can be approximated as
\[
\Delta G^i(\eta, T) = a + \Delta G_0^i(\eta) + \Delta G_f^i(\eta, T)
\]
where \(r_1\) and \(r_2\) are the positions of the first and second shells in the rdf, \(r^i\) is the OO distance at the jump transition state, \(k_B\) is the Boltzmann constant, and \(a\) is a minor, \(\eta\)-independent free energy contribution. As previously noted \(^2\), the microscopic \(\Delta G^i\) is distinct from the phenomenological \(E_a\).

The fluctuating local structures experienced by water molecules lead to \(\Delta G^i\) values differing by as much as 4 kcal/mol, \(^3\) thus strongly affecting the jump rate constant, especially at low temperature (Fig. 2(b)). The change in \(\Delta G^i\) with \(\eta\) is found to be approximately linear and temperature independent. \(^13\) The jump rate constant for a given local structure and a given temperature can thus be expressed within a Transition State Theory description as
\[
k_{\text{jump}}(\eta, T) = \frac{k_B}{h} \exp\left(-\Delta G^i/k_B T\right)
\]
where \(\kappa\) is the transmission factor, \(\alpha\) is a constant, and \(h\) is Planck’s constant. \(f(T)\) is determined at each temperature by fitting the average jump time \(\langle \tau_{\text{jump}}(T) \rangle\) calculated directly from the simulations (Eq. (1)) with our model based on the \(\eta(t)\) time fluctuations (Eq. (3)),
\[
\langle \tau_{\text{jump}}(T) \rangle = \int_0^\infty dt' \left\langle \exp \left[ - \int_0^{t'} k_{\text{jump}}(\eta(t), T) \ dt \right] \right\rangle.
\]
Remarkably, the temperature dependence of the resulting \(k_{\text{jump}}(\eta, T)\) is found to be perfectly Arrhenius,
\[
k_{\text{jump}}(\eta, T) = k_0 \exp \left( -\frac{\alpha \eta + \Delta G_0^i}{k_B T} \right),
\]
with \(k_0 \approx 0.053\) fs\(^{-1}\), \(\alpha \approx 5.8\) kcal/mol, and \(\Delta G_0^i \approx -6.3\) kcal/mol. \(^26\) For a fixed local structure, there is thus nothing anomalous in the HB dynamics temperature behavior. The jump dynamics is determined by a free energy barrier which exhibits stochastic fluctuations due to the structural fluctuations.

The time-dependent HB survival probabilities calculated from the simulations (Eq. (1)) and from the model based on the \(\eta\) fluctuations (Eqs. (4) and (5)) are in excellent agreement over the 235–350 K range (Fig. 3(a)).

Our model thus shows that while the jump rate constant for a given local structure (Eq. (5)) is strictly Arrhenius, the jump time averaged over the structural fluctuations (Eq. (4)) captures the non-Arrhenius behavior observed in the simulations (Fig. 3(b)). We can now use this model to determine the

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**FIG. 1.** (a) Arrhenius plot of the integrated water reorientation time from our simulations (\(\langle \tau_{\text{reor}} \rangle = \int_0^\infty dt (P_2 [u|u(t)])\) where \(u\) is the OH bond direction and \(P_2\) is the 2nd Legendre polynomial), from experiments\(^8\) and from the extended jump model \(^11,^12,^13\). (b) Orientation tcf from simulations and experiments (crosses in inset, at 278 K and 343 K); \(^14\) (c) HB survival probability \(S(t)\); and (d) \(E_a = k_B \ln(\tau_{\text{reor}}) / k_B T\) for \(\tau_{\text{reor}}\) and its jump and frame contributions.\(^13\)

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**FIG. 2.** (a) Radial distribution functions \(g_{OO}(r)\) at 235 K; (b) Voronoi asphericity distributions (solid lines) and \(k_{\text{jump}}(\eta, T)\) (dashes, Eq. (5)).
The continuous shift of the homogeneous η distribution toward more tetrahedral (higher η) structures upon cooling (Fig. 2(b)), we recalculate (τjump) at each temperature with Eq. (4) after shifting the η time fluctuations by an offset which ensures that the average η value remains constant with temperature. As illustrated in Fig. 3(b) for average structures constrained to be those at high (350 K) and low (235 K) temperatures respectively, removing the progressive ordering upon cooling strongly reduces the anomalous temperature dependence (the jump contribution to the reorientation Eo change between 350 K and 235 K is reduced from +6.6 kcal/mol to +1.0 kcal/mol, see Fig. 3(e)) and a quasi-Arrenius behavior is recovered, i.e., ln⟨τjump⟩ is almost perfectly linear with 1/T.

The continuous shift of the homogeneous η distribution toward more ordered structures leads to a small increase in the apparent free energy barrier for HB exchanges (Fig. 3(d)) and to a large decrease in the jump rate constants,29 thus causing a non-Arrenius behavior (this decrease is much reduced when the structural shift is suppressed13). Changes in the local structure upon cooling were recently invoked to explain some other water anomalies.27 However, a two-state description of the water structure was employed, while its validity was challenged28 and it is not supported by our present results.13 Our results critically differ in two key aspects: a molecular quantitative connection between structure and dynamics is provided and the non-Arrhenius behavior is shown to arise from a continuous shift of a unimodal structural distribution, and not from an equilibrium between two distinct structures.

In addition to the change in the average jump rate constant with temperature,13 cooling also leads to a dramatic increase in the width of the kjump distribution. This increasing dynamical heterogeneity upon cooling explains both the residual (very minor) contribution to the non-Arrenius behavior and the increasingly non-exponential orientational relaxation at low temperature (Fig. 1(b)) (it also leads to a non-exponential distribution of jump times).13 While the width of the η distribution and thus that of the apparent free energy barrier distribution are almost temperature independent (Fig. 3(e)). HB jumps and η fluctuations are connected, since water molecules which remain hydrogen-bonded to their four closest neighbors do not experience a full η relaxation (Fig. 3(f)). Since a jump in one of the four HB formed on average by a water molecule can randomize, its average and its width.

First, to assess the consequences of the shift toward more tetrahedral (higher η) structures upon cooling (Fig. 2(b)), we recalculate (τjump) at each temperature with Eq. (4) after shifting the η time fluctuations by an offset which ensures that the average η value remains constant with temperature. As illustrated in Fig. 3(b) for average structures constrained to be those at high (350 K) and low (235 K) temperatures respectively, removing the progressive ordering upon cooling strongly reduces the anomalous temperature dependence (the jump contribution to the reorientation Eo change between 350 K and 235 K is reduced from +6.6 kcal/mol to +1.0 kcal/mol, see Fig. 3(e)) and a quasi-Arrenius behavior is recovered, i.e., ln⟨τjump⟩ is almost perfectly linear with 1/T.

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This growing discrepancy is not due to a freezing of rate fluctuations upon cooling, since τk(κ), which approximately represents the ratio between the respective timescales of structural relaxation (τk) and of jumps (1/k), is almost temperature independent (Fig. 3(e)). HB jumps and η fluctuations are connected, since water molecules which remain hydrogen-bonded to their four closest neighbors do not experience a full η relaxation (Fig. 3(f)). Since a jump in one of the four HB formed on average by a water molecule can randomize the water η value, molecular structural relaxation is approximately four times faster than HB jumps, which may explain why τk(κ) ≃ 1/4 (Fig. 3(e)).

The growing dynamical disorder upon cooling is instead due to the broadening range of kjump values,13 leading to the dramatic increase in (δk2)/k2 (Fig. 3(e)) and thus explains why τk(κ) increasingly differs from τshort.

Interestingly, our model can provide an explanation to the origin of the dynamical heterogeneities recently observed in

\[
S(t) \approx \exp \left[ -\langle k \rangle t + \int_0^t (t-s) C(s) ds \right],
\]

where \( \langle k \rangle \) is the (static) average of kjump over the η distribution and C(t) is the tcf of the kjump(t) fluctuations around the average value. At short delays, the S(t) relaxation rate is \( k_{short} \approx \langle k \rangle \), while at long delays this rate becomes \( k_{long} = \langle k \rangle (1 - \frac{\delta k^2}{k^2} \tau_k) \), where \( \delta k^2 \approx C(0) \) and \( \tau_k = \tau_0^\infty \) C(t)dt.

This qualitative picture first explains why the relaxation of S(t) at low temperature resembles a bi-exponential decay (in contrast to the commonly assumed stretched-exponential decay) (Fig. 1(b)). While at high temperature the two relaxation rates are approximately equal (leading to a single exponential decay of S(t)), upon cooling klong becomes markedly slower than kshort, due to the increase in \( \delta k^2 \tau_k/k \) term, which can be decomposed as a product of two factors \( \tau_k(k) \times \langle (\delta k^2)^2/k^2 \rangle \), which we now analyze.

This growing discrepancy is not due to a freezing of rate fluctuations upon cooling, since τk(κ), which approximately represents the ratio between the respective timescales of structural relaxation (τk) and of jumps (1/k), is almost temperature independent (Fig. 3(e)). HB jumps and η fluctuations are connected, since water molecules which remain hydrogen-bonded to their four closest neighbors do not experience a full η relaxation (Fig. 3(f)). Since a jump in one of the four HB formed on average by a water molecule can randomize the water η value, molecular structural relaxation is approximately four times faster than HB jumps, which may explain why τk(κ) ≃ 1/4 (Fig. 3(e)).

The growing dynamical disorder upon cooling is instead due to the broadening range of kjump values, leading to the dramatic increase in (δk2)/k2 (Fig. 3(e)) and thus explains why τlong increasingly differs from τshort.
liquid water at room temperature,\textsuperscript{30} the experimental 500 fs timescale measured for the relaxation of these heterogeneities is consistent with the $\tau_k$ relaxation time measured to be $\pm 600$ fs at 298 K in our simulations. These heterogeneities simply arise from structural fluctuations within a single Gaussian distribution which lead to fluctuations in the HB dynamics, but they do not imply the existence of distinct inter-converting structures.

Our simulations and our model thus show that the increase in the apparent $E_a$ of water reorientation between 350 K and 235 K (ca. $+8$ kcal/mol) is mainly due to the continuous progressive shift toward more ordered structures upon cooling (for 65%), with additional contributions coming from the increase in viscosity (20%) and from the growing dynamical disorder (15%). The HB dynamics exhibits a regular Arrhenius behavior for a fixed local structure. No change in the reorientation mechanism occurs at low temperature. While an equilibrium between distinct structures cannot be excluded, it is not found in our simulations and we show that the non-Arrhenius behavior can be explained with a homogeneous structure distribution. The anomalous temperature dependence does not imply either an increasingly collective character of some motions leading to a dynamical arrest and a glass transition upon cooling.\textsuperscript{10} Although the shift toward more ordered structures results in an increasing $E_a$, it does not lead to any divergence of water dynamics, in contrast with the popular mode-coupling approach. The absence of such a critical temperature where dynamics diverges is consistent with recent results showing the structural instability of liquid water below the homogeneous nucleation temperature,\textsuperscript{31} which indicates it is not trapped in a glassy state, as already suggested for this water model.\textsuperscript{5,12} At very low temperature, a transition to a regime where $E_a$ becomes constant, i.e., a fragile to strong transition,\textsuperscript{32} may arise within our model if the structural distribution stops shifting. The importance of the shift to more tetrahedrally ordered structures for water dynamics also echoes the recent suggestion that the increase in four-coordinated waters explains the water anomalous thermodynamics.\textsuperscript{31}

An extension of the present model is underway to describe structural fluctuations in the hydration shell of hydrophobic solutes and proteins and explain the unexpected temperature dependence of the water retardation factor in the shell relative to the bulk.\textsuperscript{33}

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\textsuperscript{13} See supplementary material at http://dx.doi.org/10.1063/1.4737390 for methodology, jump times and Voronoi asphericity.
\textsuperscript{26} In this effective description, the temperature dependence of $\kappa$ (Ref. 22) is included in $\Delta G_\kappa$. While $\Delta G_\kappa < 0$, $\alpha > \Delta G_\kappa$ is always positive for the $\eta$-range of interest.
\textsuperscript{29} While a second-order truncation is not exact for the jump rate constants which are not Gaussian, Fig. 3(a) shows that this approximation is numerically acceptable over the studied temperature range.
\textsuperscript{32} C. A. Angell, Science \textbf{319}, 582 (2008).