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Comment on "Hyperquenched Glassy Water and Hyperquenched Glassy Ethanol Probed by Single Molecule Spectroscopy"

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In a recent paper Reinot et al. reported on the rotational dynamics of the probe molecule Rhodamine 700 (Rh700) in hyperquenched water as studied by single-molecule spectroscopy (SMS).[1] The major conclusion is that water above 136 K (the usual location of the glass transition temperature T_g) is most likely a solid (i.e., a glass) until it crystallizes near 154 K or, possibly, that water has a fragility index $m < 7$.

The key assumption of ref 1 is that similar guest molecules exhibit comparable average reorientation time τ_{rot} in host liquids being even different provided with equal viscosity. On this basis, τ_{rot} values of both Rh700 in ethanol[1] and Rhodamine 6G (Rh6G) in o-terphenyl (OTP)[2] are associated to the presumed viscosity of that liquids which, in turn, is taken as the corresponding viscosity of water. In particular, the evidence of no reorientation of Rh700 in deeply supercooled water in the range $110\ K \leq T \leq 154\ K$[1] was compared to the observed reorientation of both Rh-700 in ethanol at 99 K and Rh6G in OTP at 245 K on comparable time scales[2] and it was concluded that the viscosity of water at 154 K exceeds 10^{12} P, that is, $m < 7$ if $T_g = 136$ K. This comparison relies on the following two critical assumptions:

(1) the viscosity of OTP and ethanol are well documented around T_g,

(2) the viscosity of water is $\eta \simeq 10^{13}$ P at T_g,

Here, I argue that the above assumptions are not free from considerable ambiguity.

(1) Are the viscosities of OTP and ethanol well-known around T_g? The OTP viscosity was measured by different groups over the past years. Around $T_g^{OTP} = 243$ K the most recent and careful study by Plazek and co-workers[3] (see also ref 4 for an accurate fit of the data) differs little from the results of ref 5 and considerably disagrees with ref 6, for example, it was found $\eta^{OTP}(243\ K) = 3.0 \times 10^{11}$ P,[3] 4.0×10^{11} P,[5] and 1.0×10^{13} P.[6] Note that $\eta^{OTP}(243\ K) = 10^{13}$ P was adopted by ref 1.

The viscosity of ethanol η^{Et} around $T_g^{Et} = 97$ K is not known. In similar cases the usual alternative is resorting to the Maxwell relation $\eta = G_\infty \tau$, where G_∞ and τ are the instantaneous shear modulus and the structural relaxation time, respectively. In the absence of direct information on τ, as it happens for ethanol around T_g^{Et}, τ is often approximated by the dielectric relaxation time τ_α. The subsequent relation $\eta \simeq G_\infty \tau_\alpha$, implicitly adopted in ref 1, is often useful but it is questionable in ethanol. In fact, the latter forms two different kinds of glassy state, namely a structural glass and a glassy plastic crystal both showing the same glass transition temperature.[7–9] $\tau_\alpha(T_g^{Et})$ is virtually identical for the two glasses.[8,9] Therefore, if $\eta \simeq G_\infty \tau_\alpha$ the plastic crystal

and the structural glass would have comparable viscosity at T_g (unless one speculates that the proportionality constant G_∞ is largely different for the two systems). This is clearly wrong in that the structural glass has finite viscosity at T_g, whereas the plastic crystal does not flow, that is, it has infinite viscosity. Since the dielectric susceptibility of ethanol is dominated by the reorientation of the strong permanent dipole moment situated in the OH group of the molecule,[8] Miller et al. concluded that "the rotational degrees of freedom provide the dominant contribution to structural relaxation near the glass transition, while flow processes provide a smaller contribution",[9] that is, the approximation $\tau \simeq \tau_\alpha$ works in ethanol but the Maxwell relation does not. Benkhof et al. stated that (i) "the reorientational motions of the ethanol molecules in the supercooled liquid and crystal II are essentially the same, being isotropic" and (ii) "the origin of the main relaxation peak in primary alcohols is not well understood".[8] Then, it seems fair to conclude that the relation between τ_α and η in ethanol is still an open question and it is by no means obvious how to relate reliably the reorientation of Rh700 in ethanol to the viscosity of the latter.

(2) Is the viscosity of water about 10^{13} P at T_g ? The viscosity of deeply supercooled water is not known and only theoretical predictions are reported.[10]

I now show that the absence of reliable measurements of the ethanol viscosity, the considerable spread concerning the OTP viscosity around T_g as well as the use of uncontrolled assumptions concerning the water viscosity allow only speculative estimates of the water fragility. To reach consistence between the missing evidence of reorientation of Rh700 in deeply supercooled water in the range $110\ K \leq T \leq 154\ K$[1] and the observed reorientation of rhodamine 6G in OTP at 245 K,[2] Reinot et al. conclude that the viscosity of water at 154 K must be not less than $\eta^{OTP}(245\ K)$. One finds $\eta^{OTP}(245\ K) = 8.0 \times 10^{10}$ P ($m_{max}^{H_2O} = 18$),[3] 1.1×10^{11} P ($m_{max}^{H_2O} = 17$),[5] 1.2×10^{12} P ($m_{max}^{H_2O} = 8$),[6] where $m_{max}^{H_2O} = (\log \eta^{OTP}(245\ K) - \log \eta^{H_2O}(T_g^{H_2O}))/(T_g^{H_2O}/154 - 1)$ is the upper limit of the water fragility by taking, as in ref 1, $\eta^{H_2O}(T_g) = 10^{13}$ P and $T_g^{H_2O} = 136$ K. In conclusion, given the assumptions made, the OTP viscosity data of ref 6 support the conclusion of Reinot et al. that water is an ultrastrong liquid, but the two other sets of data do not rule out the typical fragilities of strong liquids, that is, $m \simeq 20$. However, both the above analysis and the one of ref 1, rely on the provisoes $\eta^{H_2O}(T_g) = 10^{13}$ P and $T_g^{H_2O} = 136$ K which need, especially the former, further assessment.

References and Notes

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