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Specific surface area and neutron scattering analysis of water's glass transition and micropore collapse in amorphous solid water

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Physico-chemical instability is commonly associated with the amorphous state, and the understanding of instability mechanisms (e.g. the glass transition) involved is essential in designing pharmaceutical products. The glass transition of bulk water might occur at 210 K [Oguni *et al.*, *J. Phys. Chem. B* **115** (2011) 14023] but it was recently proposed that the glass transition of water could happen around 121 K [C. R. Hill *et al.*, *Phys. Rev. Lett.* **116** (2016) 215501]. Note that molecular self-inclusions in a glassy water show relaxation features that are characteristically different from those observed in thermodynamically stable, crystalline solids with inclusions. Here we point out some doubtful results and calculations in Hill *et al.*'s work [C. R. Hill *et al.*, *Phys. Rev. Lett.* **116** (2016) 215501] which was based on the small-angle neutron scattering (SANS) measurements. We also made some remarks about the possible mistakes in their previous works [C. Mitterdorfer, *Phys. Chem. Chem. Phys.* **16** (2014) 16013] considering the calculation of the specific surface area. The latter is crucial to the doubtful fixing of the glass transition temperature in Hill *et al.*'s work [C. R. Hill *et al.*, *Phys. Rev. Lett.* **116** (2016) 215501].

Keywords: Self-inclusion; glassy; inclusion complex; amorphous solid water; SANS.

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It is important to understand the role of water in the chemical reactivity of amorphous solids although the water content and its associated activity exist until the glass transition temperature decreases below the storage temperature, or for the (amorphous) material to crystallize. As a result, the majority of such (amorphous) systems can only be studied at low water activities. We noticed that amorphous states (e.g. existing in amorphous solid water (ASW)), ubiquitous in pharmaceutical products, possess higher tendency for physico-chemical degradation in comparison to crystalline materials. This physico-chemical instability might be further enhanced by (amorphous solid) water, which is present even in nominally dry systems. It has been increasingly recognized that in addition to the plasticizing effect of lowering the glass transition temperature (which should be considered as an important reference point), (amorphous solid) water can influence the physico-chemical degradation rates through medium effects (e.g. through change in solvation of the reactants and the transition state) as well as by direct participation in solid-state hydrolytic degradation processes.

Some researchers argued that previous postulated glass transition temperature of water (136 K) is not correct, and must be reassigned to a higher value.¹⁻⁴ According to McCartney and Sadtchenko's conjecture, bulk pure ASW (ASW which was also referred to as low density amorphous ice) is a glass at temperatures up to its crystallization¹ near 205 K. Moreover they proposed unperturbed ASW may remain in its glassy form at temperatures up to 228 K. Meanwhile as reported in Ref. 2 by Oguni *et al.*, the possible glass transition of the internal water might occur at a temperature around 160–165 K for pore diameters in the range 1.5–2.0 nm and around 205–210 K for diameters of 2.0 nm and 2.1 nm; thus, the glass transition temperature of water jumped from 165 K to 205 K at 2.0 nm.

In fact, using quasi-elastic neutron scattering and analyzing the data with the relaxing cage model, Faraone *et al.* observed the existence of a dynamical (fragile-to-strong liquid) transition⁴ around 225 K. As remarked in Ref. 4, a fragile-to-strong liquid transition in water has been proposed on the basis of the determination of the fragility of water near the melting and glass transition temperatures: Near the glass transition temperature water is a very strong liquid, whereas in the supercooled region it is the most fragile one.⁴ We noticed that Miyatou *et al.* recently observed the vitrification of water in micropores around 200 K via their ²H NMR measurement.⁵ The microscopic origin of the above is: The rotation of water in micropores is strongly affected by the growth of a hydrogen bond before forming low density non-crystalline ice in this temperature range.⁵ Similarly Roussanova *et al.* based on the positron annihilation lifetime spectroscopy measurements observed the glass transition temperature of water in confinement around⁶ 190 K. The latter is a little higher than that (glass transition temperature of water: 185 K) observed by Sattig *et al.*⁷ Although a glass transition temperature of (bulk supercooled) water around 160 K or above (due to the development of an energetically more stable hydrogen-bonding network of water molecules) was proposed after using the adiabatic calorimetry.⁸

We remind the readers that using data obtained for neutron diffraction from ice nucleation Seyed-Yazdi *et al.* demonstrated that several defective ice states contribute to the measured diffraction pattern for the nucleated solid phase of water in confined geometry (their results suggested that the phase relationship of ices in confined geometry is more complex than has been previously realized).⁹ Nevertheless Mancinelli *et al.* have performed small-angle neutron scattering (SANS) experiments on water confined to nanopores (of 1 micron depth) and their results casted some doubt about previous interpretation of SANS experiments on water confined in the same substrate as evidence for the existence of a point of minimum density¹⁰ at 210 K.

Note that features of molecular relaxation in amorphous or non-crystalline solids bear a remarkable resemblance to those observed for ice clathrates and other crystalline solids with molecular inclusions. Meanwhile, because of voids and pores in some cellulosic interfaces, water molecules are able to form crystalline aggregates (low-density amorphous ice formation which is temperature dependent). Beyond that, water is able to penetrate. We also noticed that there is a molecular inclusion phenomenon in a non-crystalline or amorphous microstructure with loosely packed local regions, or islands of mobility (generated on the freezing-out of density fluctuations). Within such regions, atoms or molecules undergo thermally-activated, limited, rotational-translational diffusion in a different rigid matrix formed by the same type of atoms or molecules. Due to the kinetic instability and thermodynamic metastability, which are intrinsic to the structure of a glass, molecular self-inclusions in a glass show relaxation features that are characteristically different from those observed in thermodynamically stable, crystalline solids with inclusions. In fact number of self-inclusions decreases as a glass spontaneously densifies on ageing. There is an open question whether diffusive, translational motion is involved in water's glass transition.

Recently Hill *et al.* published a study on neutron scattering analysis of water's glass transition as one new approach of measurements.¹¹ It gave much inspiration in this research area as they introduced a creative methodology to apply the Guinier–Porod model on the research of ASW's glass transition as it is originally used from the 0.5% P85/d-water sample. However, there are some weaknesses in the reasoning logic of Hill *et al.*¹¹ Hill *et al.* continued the doubtful work of Mitterdorfer *et al.*¹² further and carried experiment on 1 g D₂O-c-ASW for non-baffled flow. They heated the sample at a rate of about 0.4 K min⁻¹ from 77 K to 144 K with four isothermal “pauses”.¹¹ Hill *et al.* showed that the raw NIMROD neutron scattering data in Fig. 1 and claimed that crystallization was detected because of the appearance of Bragg peaks at 144 K of Fig. 1(d).¹¹ Early researchers analyzed the relationship between scattering intensity $I(Q)$ with scattering variable Q or scattering angle θ as the independent variable, and thus related Bragg peaks to crystallization (since the subject of the structure of amorphous solids has attracted the attention of the pharmaceutical science community).^{13–15} However, in Fig. 1(d), Hill *et al.*

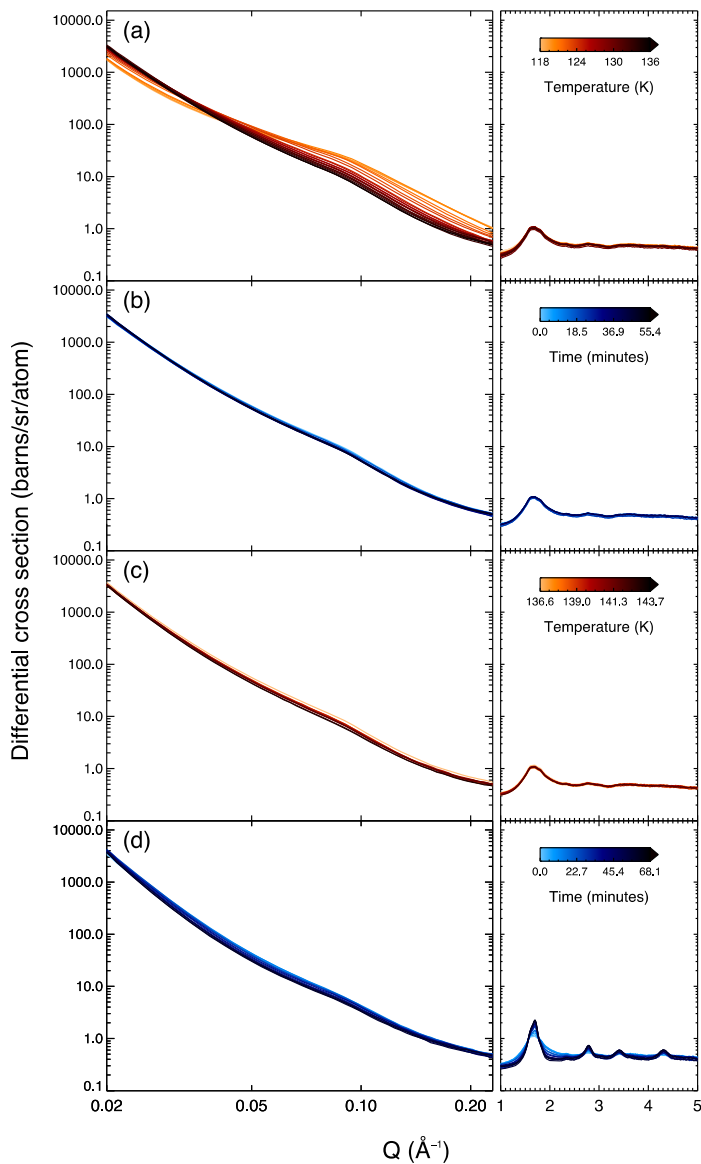


Fig. 1. (Color online)¹¹ Raw NIMROD neutron scattering data covering both the mesoscale and molecular scale scattering cross sections simultaneously. The evolution of the spectra is shown as a function of (a), (c) temperature, heating at 0.4 K min^{-1} and (b), (d) time, during an isothermal pause. The time-temperature evolution (in approximately 1 K steps or 5 min intervals) is indicated by the decreasing color scale of each plot.

analyzed differential cross-section instead of scattering intensity to claim crystallization happened.¹¹ It is not efficient to draw this conclusion, as the differential cross-section cannot be simply equated with scattering intensity.

SSA and neutron scattering analysis of water's glass transition and micropore collapse

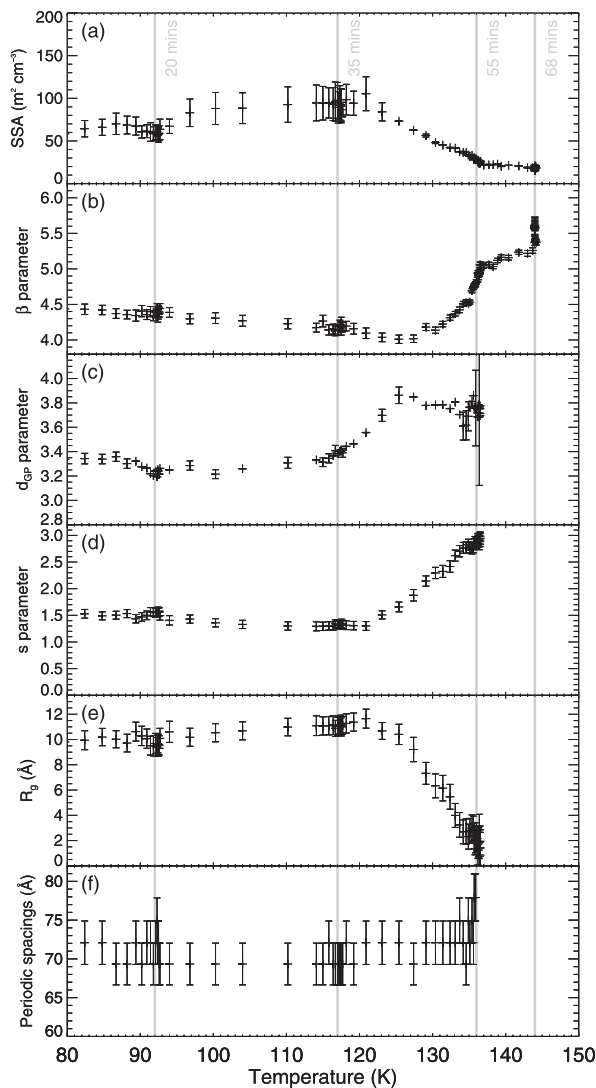


Fig. 2. (Color online)¹¹ Evolution of the key structural parameters derived from the neutron scattering differential cross section data with temperature isothermal stopping points are indicated by gray lines at 92, 117, 136, and 144 K, with the isothermal pause given alongside each line in minutes. (a) Specific surface area calculated from the plateau in $I(Q) \times Q^4$ versus Q . (b) Porod β parameter, determined from the low Q region at $Q = 0.02\text{--}0.03 \text{ \AA}^{-1}$ where $I(Q) = D \times Q^\beta$, indicating the size, shape, and surface roughness of the granular scattering material. (c) Guinier-Porod d parameter, calculated from the Guinier-Porod fits to the data between around $Q = 0.045\text{--}0.2 \text{ \AA}^{-1}$, describing the internal surface roughness of the pores, where $d = 3$ indicates a rough surface and $d = 4$ indicates that the surface is smooth, on this length scale. (d) GP s parameter, representing the geometry of the pores, where $s = 0 =$ sphere, $s = 1 =$ cylinder, $s = 2 =$ platelets, and $s \rightarrow 3$ as the pore collapses and disappears. (e) GP radius of gyration R_g and (f) periodic spacing between pores, as calculated from $I(Q) \times Q^d$ versus Q (where $d = 2.5$ or 3).

In fact, according to Fig. 2(b): Porod β parameter, Fig. 2(c): Guinier–Porod d parameter and Fig. 2(f): periodic spacing between pores; we can observe a transition temperature 127 K (either minimum or maximum) which is different from 121 K claimed in Ref. 11 using other doubtful parameters (e.g. Fig. 2(a): specific surface area (SSA), Fig. 2(d): s parameter¹¹). Moreover, the featured temperature of 127 K corresponds to other former measurements and deductions using positronium annihilation spectroscopy.^{16,17} Note that with measurements in Ref. 18, higher SSA relates to flake-like while lower SSA represents glass-like. The latter trend is not consistent with that: considering glass-transition using Fig. 2(a) SSA data in Ref. 11, where the lowest SSA corresponds to either 137 K or 144 K. It means SSA is not suitable to define the (glass) transition in Ref. 11.

The latter can also be traced in Ref. 19 where SSA of the pores in ASW water ices decreases with increasing temperatures but SSA in Ref. 11 (see e.g. Fig. 2(a)) shows wavy-like profile with two peaks (one is around 87 K and the other (almost plateau) is around 115 K) and the smallest (SSA) locates around 137 K or 144 K? In Ref. 11, to analyze the small-angle scattering data, the standard linear plots were used including Guinier and Porod plots as the traditional model-free method. It estimates the radius of gyration (R_g) as particle size, and the Porod exponent d that relates the scattering inhomogeneities. Hammouda introduced a new generalized Guinier–Porod empirical model²⁰ that describes nonspherical scattering objects.

Hammouda used the SANS data from the 0.5% P85/d-water sample at different temperatures to test the model and acknowledged that his model has limitations that it only fitted the SANS data in the Q range approximately from 0.0038 \AA^{-1} to 0.075 \AA^{-1} , can neither handle peaks in data nor “reproduce oscillations characteristics of form factors for compact mono-disperse scattering objects”.²⁰ However, Hill *et al.* did not discuss whether their analysis meets all these conditions.¹¹

Besides, Hill *et al.* analyzed three parameters:¹¹ SSA, s parameter and R_g . Then they obtained the average critical temperature being 121 K, and assigned it to the water’s glass transition temperature.¹¹ It should be noted that Hill *et al.* did not give the demonstration¹¹ and there is no clear evidence that complicated water’s glass transition relates with only these three parameters.

Moreover, it is worth noting that Hill *et al.* used the model-free approach to extract the SSA and applied direct power-law fitting to extract the Porod exponent β that related with the mass fractal dimension. They stated¹¹ in the captions of Fig. 2(b) that $I(Q) = D \times Q^\beta$. However, according to Teixeira, the exponent β relating to mass fractal is smaller than the dimension of the space that the fractal object is inside, and β should be larger than the “dimension parameter minus one”.²¹ Here regarding to the data of ASW, the “dimension parameter” is s , and $s = 0$ for three-dimensional globular objects including spheres, $s = 1$ for rods, and $s = 2$ for lamellae or platelets.²⁰ Hence, β should be in the range $(s - 1, s)$, and it is apparently contradictory with that shown in Figs. 2(b) and 2(d).²¹

Hill *et al.* also fitted the data using the Guinier–Porod model to extract parameters of pore shape (s), pore size (R_g), and nature of the interface between granules (d_{GP}).¹¹ They quoted that they used “the Guinier–Porod model”, however, instead of it, what they actually used is the generalized empirical Guinier–Porod model introduced by Hammouda.²⁰ This point should be clarified or confusion may occur. Meanwhile our observation that a possible glass transition temperature is around 127 K (either minimum or maximum) which is much higher than that of the glass transition temperature 121 K claimed in Ref. 11 agrees with previous results:²² Coalesced amorphous homopolymers exhibit higher glass-transition temperatures, than samples consolidated from their disordered solutions since this same process (coalescing amorphous homopolymers) is almost similar to that as evidenced in Ref. 11, the scenario of heating compact ASW (that was slowly heated at ≈ 0.4 K/min) as well as the relevant structural changes associated with the possible collapse of the microscopic network of micropores in the ice as it warms. Note that previous SANS results¹⁵ suggested an intriguing possibility of a thermal memory retained by the glasses even after heating above the glass transition temperature. However, details of the structural changes leading to improved physico-chemical stability are not fully understood in Ref. 11 as well as Ref. 12.

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References

1. S. A. McCartney and V. Sadtchenko, *J. Chem. Phys.* **138** (2013) 084501.
2. M. Oguni, Y. Kanke, A. Nagoe and S. Namba, *J. Phys. Chem. B* **115** (2011) 14023.
3. M. Chonde, M. Brindza and V. Sadtchenko, *J. Chem. Phys.* **125** (2006) 094501.
4. A. Faraone, L. Liu, C.-Y. Mo, C.-W. Yen and S.-H. Chen, *J. Chem. Phys.* **121** (2004) 10843.
5. T. Miyatou, R. Ohashi, T. Ida, S. Kittaka and M. Mizuno, *Phys. Chem. Chem. Phys.* **18** (2016) 18555.
6. M. Roussanova, M. A. Alam, S. Townrow, D. Kilburn, P. E. Sokol, R. Guillet-Nicolas and F. Kleitz, *New J. Phys.* **16** (2014) 103030.
7. M. Sattig, S. Reutter, F. Fujara, M. Werner, G. Buntkowsky and M. Vogel, *Phys. Chem. Chem. Phys.* **16** (2014) 19229.
8. M. Oguni, S. Maruyama, K. Wakabayashi and A. Nagoe, *Chem. Asian J.* **2** (2007) 514.
9. J. Seyed-Yazdi, H. Farman, J. C. Dore, J. B. W. Webber, G. H. Findenegg and T. Hansen, *J. Phys.: Condens. Matter* **20** (2008) 205108.
10. R. Mancinelli, F. Bruni and M. A. Ricci, *J. Phys. Chem. Lett.* **1** (2010) 1277.
11. C. R. Hill, C. Mitterdorfer, T. G. A. Youngs, D. T. Bowron, H. J. Fraser and T. Loerting, *Phys. Rev. Lett.* **116** (2016) 215501.
12. C. Mitterdorfer, M. Bauer, T. G. A. Youngs, D. T. Bowron, C. R. Hill, H. J. Fraser, J. L. Finney and T. Loerting, *Phys. Chem. Chem. Phys.* **16** (2014) 16013.

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13. A. Ramzi, M. Sutter, W. E. Hennink and W. Jiskoot, *J. Pharm. Sci.* **95**(8) (2006) 1703.
14. M. P. G. Peixoto, J. Treter, P. E. de Resende, N. P. da Silveira, G. G. Ortega, M. J. Lawrence and C. A. Dreiss, *J. Pharm. Sci.* **100** (2011) 536.
15. J.-R. Authelin, A. P. MacKenzie, D. H. Rasmussen and E. Y. Shalaev, *J. Pharm. Sci.* **103** (2014) 2663.
16. S. Townrow and P. G. Coleman, *J. Phys.: Condens. Matter* **27** (2015) 225401.
17. S. Townrow and P. G. Coleman, *J. Phys.: Condens. Matter* **27** (2015) 475007.
18. Z. Dong, A. Chatterji, H. Sandhu, D. S. Choi, H. Chokshi and N. Shah, *Int. J. Pharm.* **355** (2008) 141.
19. S. Cazaux, J.-B. Bossa, H. Linnartz and A. G. G. M. Tielens, *Astron. Astrophys.* **573** (2015) A16.
20. B. Hammouda, *J. Appl. Cryst.* **43** (2010) 716.
21. J. Teixeira, *J. Appl. Cryst.* **21** (1998) 781.
22. A. E. Tonelli, *J. Inclusion Phenom. Macrocyclic Chem.* **60**(3–4) (2008) 197.