Comment on "Pressure Dependence of Fragile-to-Strong Transition and a Possible Second Critical Point in Supercooled Confined Water"

Recently, Liu *et al.* [1] reported quasielastic neutron scattering measurements at different pressures on water confined in nanopores of a silica glass (MCM-41-S). Their Fig. 2 shows the temperature dependence of the relaxation times where the data at low temperatures are fitted by an Arrhenius equation and the high-temperature data to a Vogel-Fulchel-Tammann (VFT) equation. Based on this result, they concluded that: "This transition of VFT to Arrhenius behavior, ..., is the signature of a 'fragile-to-strong' dynamic transition predicted by Ito *et al.*"

Other authors, however, found the same kind of crossover for the confined water relaxation time in other systems [2–5]. In particular, it is also possible to observe the apparent crossover in systems such as some water mixtures. Even more, a similar crossover has been observed in polymer-polymer blends [6–8] where the mobility of the two components is very different. In such a condition, the dynamics of the faster component shows a crossover from liquidlike behavior (VFT) towards localized (Arrhenius) motions in the range of the glass transition of the blends. In all of these systems, confinement takes place and the change in the dynamic behavior (from VFT to Arrhenius) is due to the onset of finite size effects. In fact, it is well established that when a liquid is confined within a pore, its structural and dynamical properties can be strongly modified. The crossover would be associated with the fact that any presumed characteristic length of the dynamics in a supercooled liquid cannot extend further than the typical pore size. Therefore, this finite size effect leads to an increase of the relaxation time lowering temperature, which is less pronounced than the expected VFT extrapolation, once the characteristic length reached the pore size. In this way, the relaxation time at low temperature follows an Arrhenius behavior instead of VFT, and, therefore, the crossover would not be related to a fragile-to-strong transition.

Figure 1(a) shows both the relaxation time of confined water (solid circles) in a similar confinement [2] to that used in Ref. [1] and the data from Ref. [1] at ambient pressure (solid triangles). It is clear that the relaxation time for water in a different geometry follows a similar VFT behavior at high temperature that persists even at temperatures lower than the crossover (T_L in Ref. [1]). Thus, the crossover, associated in Ref. [1] with the fragile-to-strong transition, is observed at significantly lower temperatures [see Fig. 1(a)]. In addition, Figs. 1(b) and 1(c) show how the dynamics of confined water in two different mixtures is also affected in a similar way at the glass transition of the mixture ($T_{g,m}$); i.e., the dynamics of water molecules becomes restricted by the freezing-in of the system. These confinement effects on water dynamics produce the Arrhenius-like behavior. As a consequence, at low tem-
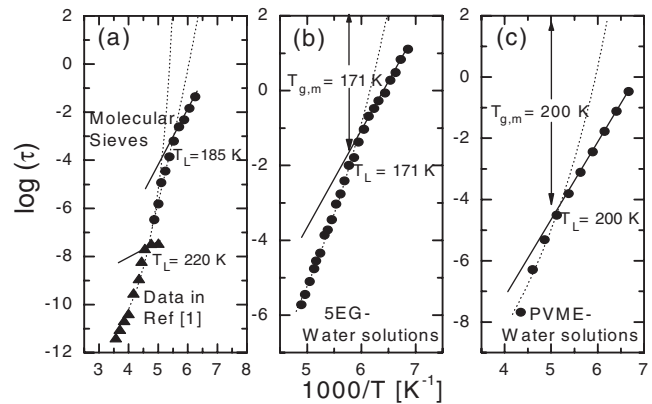

FIG. 1. Relaxation times for confined water in different systems. T_L is the presumed dynamic transition temperature, which is different for each system. (a) MCM-41-S [1] and molecular sieves (10 Å) [2]. (b),(c): 5-ethylene glycol (5EG) [4] and poly(vinyl methyl ether) (PVME) water solutions [5]. $T_{g,m}$ means the glass transition temperature of the mixtures measured by differential scanning calorimetry.

peratures ($T < T_{g,m}$) the relaxation times are smaller than expected from the high-temperature VFT extrapolation.

Thus, from the reported crossover (VFT to Arrhenius) on confined water in MCM-41-S, it is not possible to deduce that a fragile-to-strong transition occurs in water, and, therefore, it is not possible to claim that data presented in Ref. [1] are a definitive experimental verification of the existence of the liquid-liquid critical point of water [1].

We thank R. Bergman for careful reading and helpful discussion.

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