## **Supplementary Information**

# Evidence suggesting kinetic unfreezing of water mobility in two distinct processes in pressure-amorphized clathrate hydrates.

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### **Experimental method**

This section is partly copied from the SI in ref. 1. The theory of the method is reiterated here to provide the fundamentals for calculating the properties of glass transitions 1 and 2 of the study presented here.

Heat capacity per unit volume *c* (the product of density and specific heat per unit mass) and thermal conductivity  $\kappa$  were measured *in situ* by the transient hot-wire method. <sup>2,3</sup> Briefly, a 0.1 mm Ni wire, embedded in the sample, was heated by a square pulse of 1.4 s duration, which increased the wire temperature by ~3.5 K. The increase occurs in a time-dependent manner, which is determined by *c* and  $\kappa$  of the sample. The increase was measured with time as a change in the resistance between two electrical potential taps on the hot wire, which was placed in a ring of approximately constant radius within a Teflon® sample cell. The heat transfer equations for the wire and the surrounding solid or liquid are given by:

$$\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} - \frac{1}{a_w} \frac{\partial T}{\partial t} = -\frac{q}{\kappa_w \pi r_w^2}$$
(S1)
$$\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} - \frac{1}{a} \frac{\partial T}{\partial t} = 0$$

where *t* is time, *T* is temperature, *r* is the radial coordinate, *q* is the power per unit length,  $\kappa_w$  represents the thermal conductivity of the wire, and *a* and  $a_w$  represent the thermal diffusivity of the sample and wire, respectively. The exact solution of the temperature increase  $\Delta T$  of an infinitely long and infinitely conducting wire immersed in an infinitely large sample is <sup>4</sup>

$$\Delta T = \frac{2q\alpha^2}{\pi^3 \kappa} \int_0^\infty \frac{1 - \exp(-\beta u^2)}{u^3 \left\{ (u J_0(u) - \alpha J_1(u))^2 + (u Y_0(u) - \alpha Y_1(u))^2 \right\}} du,$$
(S2)

where  $\alpha = 2c/c_w$ ,  $\beta = \kappa t/(c r_w^2)$ ,  $r_w$  is the radius of the wire,  $c_w$  is the heat capacity per unit volume of the hot wire,  $J_0$  an  $J_1$  represent Bessel functions of the first kind of the zero and first orders, and  $Y_0$  and  $Y_1$  represent Bessel functions of the second kind of the zero and first orders.

#### Hot-wire results in the glass to liquid transition range.

As shown in numerous hot-wire measurements of glass-formers, <sup>5,6,7,8,9</sup> a peak in  $\kappa$  and a dip in c typically appear at glass to liquid transitions. The reason is due to the time-dependence in the heat capacity  $C_p(t)$  associated with the kinetic unfreezing of structural fluctuations in the glass to liquid (kinetically unfrozen state) transition range; this time dependence is not taken into account in the fitting of the analytical solution for the temperature rise of the hot-wire (eqn S2), instead  $\kappa$  and c are treated as adjustable, *time-independent*, parameters. As shown before,<sup>8,9</sup> and here, the consequences of the time dependent heat capacity are a peak in  $\kappa$  and a dip in c, which are superimposed on the real changes in  $\kappa$  and c caused by temperature change and devitrification. The influence of the time-dependence is most pronounced when the major part of the  $C_p(t)$  change occurs during the probing time of 1.4 s. It has been previously analyzed in detail (ref. 9) and it was found that the peak maximum in  $\kappa$  occurs at a relaxation time of about 0.3 s.

It is well known that the glass transition temperature is a function of the time scale used to analyze the heat exchange response with the sample. In the hot-wire analysis of the response to a 1.4 s heating pulse while the sample is simultaneously heated (or cooled) at a rate of less than 0.5 K min<sup>-1</sup>, the measured kinetic unfreezing occurs within a second. More specifically, the *c* rise is observed when the relaxation time of the sample becomes less than ~1 s;<sup>1</sup> the transient heating of 3.5 K in 1.4 s corresponds to an average of 150 K min<sup>-1</sup>. Thus, the slow heating of about 0.5 K min<sup>-1</sup> caused by the surroundings (external heating) does not affect the position of the sigmoidal-shaped *c* increase in the temperature plane. Because of the transient heating, the time scale of the hot-wire method is significantly shorter than those of adiabatic calorimetry and differential scanning calorimetry; these more commonly used methods provide glass transition temperatures which are typically associated with relaxation times of order  $10^2$  s or longer.

The influence of time-dependent heat capacity on the measured data can be studied using a model for the time,<sup>9</sup> or frequency dependence.<sup>10</sup> Here, we use a simple model function for the time dependence of the heat capacity per unit volume

$$c(t) = c_{\infty} + (c_0 - c_{\infty})e^{-(t/\tau)^{\beta}},$$
(S3)

where  $c_0$  and  $c_{\infty}$  are the short and long time values associated with the glass and kinetically unfrozen states, respectively,  $\tau$  represents the calorimetric relaxation time, and  $\beta$  is an exponent between 0 and 1. That is, the total increase in *c* due to the rise at the glass transition  $\Delta c$  is given by  $c_{\infty} - c_0$ . By inserting eqn (S3) in eqn (S1), the temperature increase of the wire probe can be calculated for a given relaxation time. (We assume a constant relaxation time during the heat pulse.) A subsequent fit of eqn (S2) yields the values of  $\kappa$  and *c*, which would be measured for the given relaxation time.

#### **Properties of glass transition 2.**

The 'real' values of  $c_0$ ,  $c_\infty$  and  $\kappa$  for glass transition 2 to be inserted in the calculation were chosen on the basis of experimental values for collapsed CHs at 0.4 GPa. The value for the heat capacity for the glass state was obtained by a linear interpolation from low temperature up to 159 K. This is the temperature of the maximum in  $\kappa$ , which was (somewhat arbitrary) chosen as the center temperature for the calculation. (As mentioned above and shown below, the temperature corresponds to  $\tau=0.3$  s.) The corresponding value for the kinetically unfrozen state was obtained by a linear extrapolation from above 159 K. The value for the best estimate of (real)  $\kappa$  at 159 K was obtained by a similar procedure through an interpolation between  $\kappa$ of the kinetically unfrozen state and that of the glassy state. The lines in Fig. S1 illustrate the procedures. The slight change in the temperature dependence of  $\kappa$ , shown by the solid lines in Fig. S1, is typically observed at the devitrification temperature in measurements of  $\kappa$  using static methods; this occurs when the relaxation time is in the range  $10^2-10^3$  s, which is at the low temperature side of the peak in  $\kappa$ .<sup>1</sup>



Fig. S1. Illustration of the procedure to estimate the heat capacity step  $\Delta c = c_{\infty} - c_0$  at glass transition 2, and the value for  $\kappa$  without the superimposed (unreal) peak. That is, the solid lines show the estimated (real) variation of the properties in the glass state and the kinetically unfrozen state.  $\kappa$  ('real') (filled square) at 159 K shows the value used in the calculations and the small difference from this value at other temperatures, indicated by the solid lines, was subsequently taken into account.

The estimated values for the step increase of *c* and  $\kappa$  used for the calculations (Fig. S1) were kept constant and therefore used for all values of the relaxation time. A very short relaxation time in eqn (S3) yields  $\Delta c = c_{\infty} - c_0$  ('liquid') in the measurement's time-range of 10 ms to 1.4 s, whereas a long relaxation time yields  $\Delta c = 0$  ('glass'). In both cases, the subsequent fit of eqn (S2) yields the 'real'  $\kappa$ , i.e. the value used to calculate the temperature rise of the probe. But for relaxation times near 1 s,  $\kappa$  (from the fit) comes out larger than the 'real'  $\kappa$  and  $\Delta c$  (from the fit) may be negative. (The increasing heat capacity during the heat pulse lowers the temperature rise of the wire probe, i.e. it has the same effect as an increase in a sample's  $\kappa$ .) The time evolution of  $\Delta c$  during the heat pulse depends on  $\beta$ , and here we have calculated the results for  $\beta = 1$  and  $\beta = 0.42$ ; the latter value gave the best fit to the measured peak maximum in  $\kappa$  of the normal water (H<sub>2</sub>O) samples.

The results for  $\kappa$  and *c* obtained by subsequent fitting of eqn (S2) to the calculated temperature rise of the wire are plotted against the relaxation time in Fig. S2. The results show that measurements on heating will detect a strong rise in *c* when  $\tau$  decreases from the very long times in the glass to the short times in the kinetically unfrozen state. In more detail,

the values for *c* may initially (on heating) show a slight decrease when  $\tau$  becomes of order  $10^2$  s and a subsequent minimum. This decrease is thus purely artificial and due to the neglected time dependence in *c* in the fitting process of the experimental (or calculated) data for the temperature rise of the hot-wire. On further decrease in  $\tau$ , at  $\tau \sim 0.3$  s, *c* increases 2–5% from the minimum value, which is easily detected in measured data, and finally *c* levels off at the value of *c* for the kinetically unfrozen state (liquid state) when  $\tau < 10^{-3}$  s. Concurrently with these features in *c*,  $\kappa$  shows an artificial peak. The peak size and width depends on  $\beta$ ; the onset of the peak on heating, or decreasing  $\tau$ , occurs in the  $10^1-10^2$  s  $\tau$ -range for  $\beta=1$  and at an order of magnitude longer  $\tau$  for  $\beta=0.42$ , whereas the peak maximum occurs at  $\tau \sim 0.3$  s for both  $\beta=1$  and  $\beta=0.42$ . At very long and very short values for  $\tau$ , the temperature rise of the wire probe is unaffected by the glass transition relaxation and, therefore, measurements (and calculations) yield the 'real' (estimated, see Fig. S1) value for  $\kappa$ . To account for the (real) weak changes in  $\kappa(T)$ , the results from the fits were subsequently corrected for the deviation from  $\kappa$  used in the calculations (filled square in Fig. S1).



Fig. S2. Thermal conductivity  $\kappa$  and heat capacity per unit volume *c* plotted against the relaxation time for two different cases of the exponent  $\beta$  (see eqn S3):  $\beta = 1$  (open circles) and  $\beta = 0.42$  (filled circles).

To estimate the activation energy of glass transition 2, we can transform values for  $\tau$  to temperatures and use the activation energy as a free parameter. The temperature variation of

the relaxation time is often well described by an Arrhenius function in a limited temperature range. It is given by

$$\tau = A \, e^{\frac{E_a}{RT}},\tag{S4}$$

where A and the activation energy  $E_a$  are constants, and R is the gas constant. Here A was calculated so that  $\tau=0.3$  s at 159 K and  $E_A$  was manually fitted to best retrace the temperature variation of the peak in  $\kappa$ .



Fig. S3. Thermal conductivity  $\kappa$  plotted against the relaxation time for THF CH, TDF CH and calculated data for two different cases of the exponent  $\beta$  (dashed lines):  $\beta = 1$  (magenta dashed line) and  $\beta = 0.42$  (blue dashed line). The dark yellow lines show the estimated real variation of  $\kappa(T)$ .



Fig. S4. Thermal conductivity  $\kappa$  plotted against the relaxation time for THF CD, TDF CD and calculated data for two different cases of the exponent  $\beta$  (dashed lines):  $\beta = 1$  (magenta dashed

line) and  $\beta = 0.39$  (green dashed line). The dark yellow lines show the estimated real variation of  $\kappa(T)$ . Results for THF CH are inserted for comparison.

The measured results suggest that the temperature dependence of  $\kappa(T)$  in the kinetically unfrozen state (above 151 K) is slightly negative in normal water CH samples and about constant in deuterated samples. The shape of the peak (and dip) artifacts changes slightly on deuteration of water but remain unaffected on deuteration or exchange of the guest. The calculations yield slightly lower  $\beta$  and slightly higher activation energy for deuterated water than normal water CH samples. The (apparent) activation energies,  $E_a$ , obtained through this procedure in the narrow temperature range 150–165 K (ultraviscous state) are (230±10) kJ mol<sup>-1</sup> and (240±10) kJ mol<sup>-1</sup> for amorphous CH and CD samples, respectively. We note that  $E_a$  is large compared to values reported for water at high temperatures and atmospheric pressure, e.g. 13 kJ mol<sup>-1</sup> from viscosity data at 330 K. The values for water increase strongly on cooling and  $E_a$  is 53 kJ mol<sup>-1</sup> at 240 K.<sup>11</sup>

To determine the reliability of using the artificial peak in  $\kappa$  to estimate  $E_a$ , we have made a comparison with results from other measurements using data for glycerol near  $T_g$ . The result from data for  $\kappa$  (peak) measured in the 185-210 K at 0.05 GPa<sup>5</sup> is (170±10) kJ mol<sup>-1</sup>. This is the same as we find using Birge's results of specific-heat spectroscopy (172 kJ mol<sup>-1</sup>) and somewhat larger than that obtained from Birge's results of dielectric spectroscopy (160 kJ mol<sup>-1</sup>).<sup>8</sup> Lunkenheimer et al.'s data<sup>12</sup> for the dielectric relaxation time yield 162 kJ mol<sup>-1</sup> in this narrow temperature range. Thus, the comparison shows that we can derive an estimate for the activation from the artificial peak in  $\kappa$ .

# Properties of glass transition 1 and the effect of changing heat capacity rise and activation energy

The calculations presented above for glass transition 2 were done also for glass transition 1. Glass transition 1 show no or only weak peak and dip artifacts in  $\kappa(T)$  and c(T). The reason is due to the weak and gradual increase of c(T). The results, which are depicted in Fig. S5, show that the small heat capacity rise on heating the collapsed CH at 1 GPa can generate a small and broad (artificial) peak in  $\kappa(T)$  of similar size as that observed. The behavior in  $\kappa(T)$  and c(T) are in correspondence with the small activation energy, ca. 38 kJ mol<sup>-1</sup>, derived from dielectric measurements;<sup>13</sup> the temperature of the peak feature and rise in *c* agree well with the features experimentally observed suggesting good agreement between heat capacity and dielectric relaxation times.

To show the effect of changing heat capacity step and activation energy, the calculation was also done using a much larger heat capacity step and  $E_a$ ; the result shows that the artificial features caused by the dynamic nature of the method, i.e. the peak in  $\kappa$  and dip in c, becomes much more pronounced. If the activation energy increased by a factor of 2, then the width of the artificial  $\kappa$ -peak decreased from 40 K to 22 K becoming closer to the experimental result for glass transition 2 of 10 K at 0.4 GPa.



Fig. S5. (A) Thermal conductivity plotted against temperature. Experimental data: (black circles) collapsed THF CH on heating at 1 GPa, (black triangles) collapsed DXL CH on heating at 1 GPa, (dark yellow squares) collapsed ice or VHDA on heating at 1 GPa (the data has been shifted vertically with a factor 0.77). Calculations: (red line) calculations for a *c* rise of 0.24 MJ m<sup>-3</sup> K<sup>-1</sup> and the activation energy obtained from dielectric data for collapsed THF CH, (red dashed line) corresponding data with twice as large activation energy, (blue line) calculations for a *c* rise of 1.2 MJ m<sup>-3</sup> K<sup>-1</sup> and the activation energy obtained from dielectric data for collapsed THF CH, (blue dashed line) corresponding data with twice as large activation energy. (B) Heat capacity per unit time plotted against temperature. Same labeling as in (A). (Experimental data only for collapsed THF CH.) A linear function was added to the calculated data to account for the roughly linear temperature variation of *c* and  $\kappa$  outside the glass transition range.

### Notes and references

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