

Pressure Effect on the Boson Peak in Deeply Cooled Confined Water: Evidence of a Liquid-Liquid Transition

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The boson peak in deeply cooled water confined in nanopores is studied to examine the liquid-liquid transition (LLT). Below ~ 180 K, the boson peaks at pressures P higher than ~ 3.5 kbar are evidently distinct from those at low pressures by higher mean frequencies and lower heights. Moreover, the higher- P boson peaks can be rescaled to a master curve while the lower- P boson peaks can be rescaled to a different one. These phenomena agree with the existence of two liquid phases with different densities and local structures and the associated LLT in the measured (P, T) region. In addition, the P dependence of the librational band also agrees with the above conclusion.

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Water is a continuing source of fascination to scientists because of its abnormal behavior at low temperatures T . Upon cooling, its thermodynamic properties, such as density, isobaric heat capacity, and isobaric thermal expansivity, deviate from those of simple liquids significantly [1–4]. In addition, glassy water, also called amorphous ice, exhibits polymorphism. Experiments show that two kinds of amorphous ice, low-density amorphous ice (LDA) and high-density amorphous ice (HDA), exist at very low temperatures [5–7]. These two phases can transform to each other through a first-order-like transition [7,8]. To account for these mysterious phenomena, a “liquid-liquid critical point (LLCP)” scenario, which assumes a first-order low-density liquid (LDL) to high-density liquid (HDL) phase transition in the deeply cooled region of liquid water, has been proposed [9]. Therefore, experimental tests on the existence of the LDL and the HDL and the associated liquid-liquid transition (LLT) are important for understanding water. Nevertheless, such measurements are practically difficult due to the rapid crystallization of bulk water below the homogeneous nucleation temperature (235 K at 1 atm). To overcome this barrier and enter the deeply cooled region of water, different systems, including aqueous solutions [10–14], microsized water droplets [15], and confined water systems [16–19], have been prepared and studied. Particularly, when confined in a nanoporous silica matrix, MCM-41, with a 15-Å pore diameter, water can be kept in the liquid state at least down to 130 K [20,21]. Thus, the MCM-41-confined water system provides a chance to explore the hypothetical LLT.

Recently, we observed a likely LLT in heavy water confined in MCM-41 by a density measurement. The associated phase diagram is shown in Fig. 1(a) [22]. However, the relevant measurements on the dynamic properties are still lacking. In fact, various dynamic

properties, including the structural relaxation [10,16], the stretching vibration [10,11], the mean square displacement [23], etc., have been measured to study the phase behaviors of aqueous solutions or confined water. Examinations of

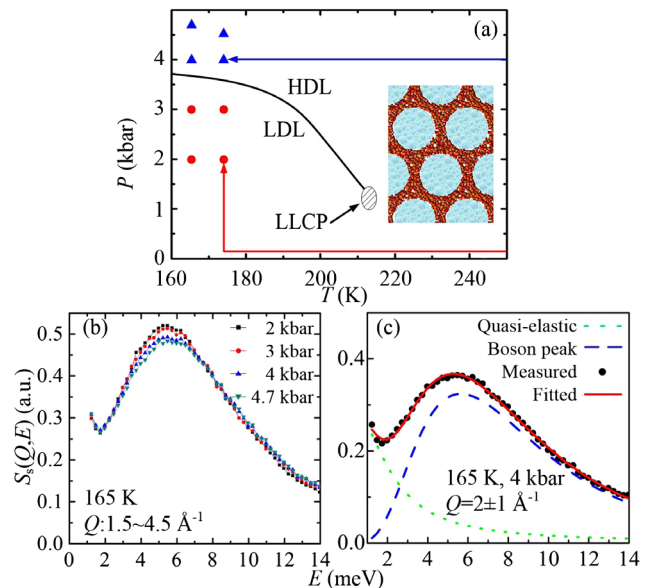


FIG. 1 (color online). (a) Phase diagram of deeply cooled confined heavy water [22]. The inset shows the two-dimensional hexagonal structure of MCM-41. The red circles denote the measured points in the LDL. These points are approached by first cooling the system to the desired temperature and then pressurizing (red arrow). The blue triangles denote the measured points in the HDL. These points are approached by cooling the system to the desired temperature at the desired pressure (blue arrow). With these approaches we avoid crossing the phase boundary directly [24]. (b) The measured INS spectra at $T = 165$ K, and $P = 2, 3, 4,$ and 4.7 kbar. (c) Model fitting of the measured $S_s(Q, E)$ with Eq. (1) at $Q = 2 \pm 1 \text{ \AA}^{-1}$, $T = 165$ K, $P = 4$ kbar.

the phase behaviors by the dynamic properties are indispensable, because they provide complementary insights into the thermodynamic and structural results.

With inelastic neutron scattering (INS), we investigate the boson peak as the dynamic property to examine the LLT in the water confined in MCM-41. The measurement was performed at the Cold Neutron Chopper Spectrometer [25] at Spallation Neutron Source (SNS) at Oak Ridge National Laboratory (ORNL). Data were reduced by DAVE [26]. The boson peak is a broad peak observed at frequencies ~ 2 –10 meV in the inelastic neutron [27–31], nuclear inelastic [32–35], and Raman [36–39] scattering spectra of disordered materials and supercooled liquids. Its origin is widely believed to be related to the transverse dynamics of the material [32–34,40,41]. Moreover, both theoretical and experimental studies assign the boson peak in glass to a phenomenon reminiscent of the van Hove singularity of the transverse phonon of the crystal counterpart [33,42,43]. It is worth mentioning that the boson peak has a dependence on the density of the material: as the density increases, the frequency of the boson peak increases and the height decreases [29–31,35,37,44]. Then, considering that the order parameter of the hypothetical LLT is just the density [9], the boson peak provides a good way to examine the existence of the LLT. In addition, a previous study shows that the emergence of the boson peak in deeply cooled confined water tracks the Widom line of the possible LLT determined by the dynamic crossover below the critical pressure P [28,45]. And the locus of the emergence of the boson peak in the (P, T) plane changes the slope at the critical pressure [28]. These observations also suggest that the behaviors of the boson peak may respond to the existence of the LLT in deeply cooled water.

Figure 1(b) shows the measured boson peak at $T = 165$ K, $P = 2, 3, 4,$ and 4.7 kbar. According to the phase diagram in Fig. 1(a), the former two points are in the LDL phase, while the latter two are in the HDL phase (We cannot obtain the phase diagram of confined H_2O with the method used in Ref. [22] due to the exceptionally large incoherent cross section of the H atom. The difference between the phase diagrams of confined H_2O and confined D_2O is expected to be several kelvin due to the isotope effect [46]. In fact, the conjectured phase diagram of deeply cooled bulk D_2O is quite similar to that of bulk H_2O [47]). The height of the boson peak decreases as pressure increases in the energy range from 3 to 8 meV. This pressure dependence reverses at higher energies. In addition, the largest difference between the spectra of adjacent pressures is found between 3 and 4 kbar. In order to quantitatively analyze the data, we use the following equation to fit the measured INS spectrum of confined water at a specific Q :

$$S_{s,m}(Q, E) = R(E) \otimes \left\{ \left[\frac{1}{\pi} \frac{A_1 \gamma_1}{E^2 + \gamma_1^2} + \frac{A_2}{\sqrt{2\pi} \sigma_{\text{BP}} E} \exp\left(-\frac{(E_{\text{BP}} - \ln E)^2}{2\sigma_{\text{BP}}^2}\right) \right] D(E) \right\}, \quad (1)$$

where $S_{s,m}(Q, E)$ is the measured self-dynamics structure factor of the confined water, and $R(E)$ is the energy resolution function. In the square brackets, the first term is a Lorentzian function, which represents the quasielastic contribution; the second term is a log-normal distribution function. σ_{BP} and E_{BP} relate to the width and position, respectively. A_1 and A_2 are the amplitudes of these two parts. $D(E)$ is the detailed balance factor and is expressed as $\exp(E/2k_B T)$ [48]. The log-normal distribution function can describe the boson peak well [49] and has been applied to confined water successfully [27]. A typical fit is shown in Fig. 1(c).

Since a probability distribution function is used to represent the boson peak, it is convenient to define the mean frequency M and the variance V of the boson peak as follows [50]:

$$M = \exp(E_{\text{BP}} + \sigma_{\text{BP}}^2/2), \quad (2)$$

$$V = [\exp(\sigma_{\text{BP}}^2) - 1] \exp(2E_{\text{BP}} + \sigma_{\text{BP}}^2). \quad (3)$$

M and V denote the position and the broadness of the boson peak in the frequency domain, respectively. In addition, we define the maximum of the log-normal distribution function in Eq. (1) as the height of the boson peak H .

Figures 2(a)–2(f) show the values of M , V , and H of the boson peaks for $Q = 2 \pm 1 \text{ \AA}^{-1}$ [51] at the measured points shown in Fig. 1(a). For both measured temperatures, as pressure increases, M and V increase, while H decreases. These dependences on pressure, or density, agree with the observations in other experimental [29–31,35,37,44] and

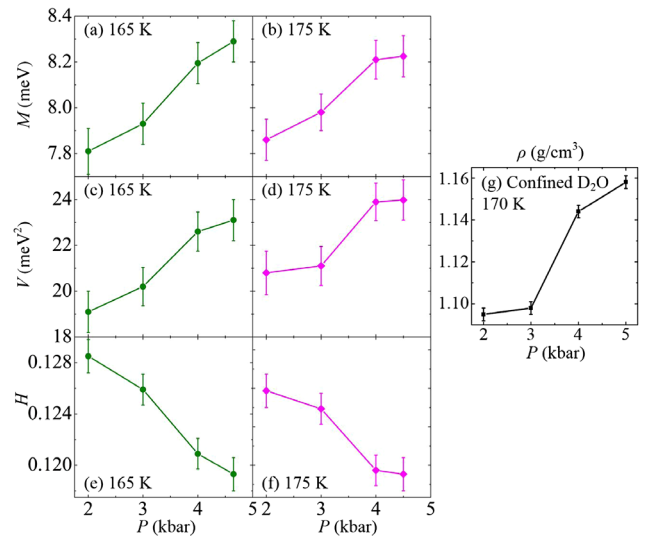


FIG. 2 (color online). Panels (a), (c), and (e) show the mean frequency (M), variance (V), and height (H) of the boson peak as a function of pressure at 165 K, respectively. Panels (b), (d), and (f) show M , V , and H of the boson peak as a function of pressure at 175 K, respectively. Panel (g) shows the average density of confined D_2O at $T = 170$ K and $P = 2, 3, 4,$ and 5 kbar.

computer simulation studies [40,41]. Particularly, as the pressure changes from 3 to 4 kbar, all of these quantities undergo larger changes. This phenomenon strongly suggests an abrupt increase in density as the pressure changes from 3 to 4 kbar, and is consistent with the observation that there is a LDL to HDL transition from 3 to 4 kbar at ~ 170 K in confined water [22]. For comparison, we show the average density of confined D_2O as a function of pressure at 170 K in Fig. 2(g) (obtained by the same method used in Ref. [22]).

The line shapes of the boson peak extracted from the fit $[S_{BP}(Q, E)]$ at $T = 165$ K, $Q = 2 \pm 1 \text{ \AA}^{-1}$, and $P = 2, 3, 4,$ and 4.7 kbar are shown in Fig. 3(a). The red curve in Fig. 3(a) shows the difference between the boson peaks at 4.7 (the HDL) and 2 kbar (the LDL). In addition, we show the reduced vibrational density of state (vDoS) $g(E) [= G(E)/E^2, G(E)$ is the vDoS] of LDA and HDA measured by INS and their difference in Fig. 3(b) [52]. Note that, in the classic limit, the self-dynamics structure factor $S_s(Q, E)$ is related to the reduced vDoS $g(E)$ as follows [53]:

$$g(E) \propto \lim_{Q \rightarrow 0} \frac{1}{Q^2} S_s(Q, E). \quad (4)$$

Thus, we can compare $g(E)$ (the effect of the Debye-Waller factor needs to be considered [54]) with $S_s(Q, E)$. It is significant that the spectral difference of the confined water shown in Fig. 3(a) resembles the one of the amorphous ices shown in Fig. 3(b). This similarity is consistent with the hypothesis that the LDL and the HDL are thermodynamic extensions of LDA and HDA to the liquid state [4]. The amplitude of the difference of the confined water is smaller than that of the amorphous ices. This is partially because (i) only the free water part in the confined water can undergo a LLT [22], and (ii) the confinement can suppress

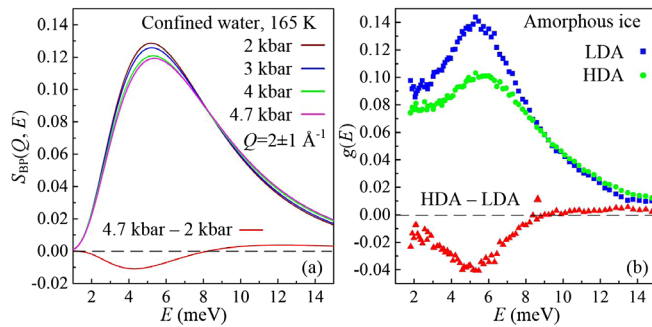


FIG. 3 (color online). (a) Line shapes of the boson peak extracted from the fit $[S_{BP}(Q, E)]$ at $T = 165$ K, $Q = 2 \pm 1 \text{ \AA}^{-1}$, and at $P = 2$ (brown), 3 (blue), 4 (green), and 4.7 (pink) kbar. The red curve shows the spectral difference between 4.7 and 2 kbar. (b) The reduced vDoS of HDA (green circles) and LDA (blue squares) [52] and their difference (red triangle). The amplitudes are rescaled for comparison with the boson peaks of the confined water.

the phase transition [55]. Generally, the INS spectrum reflects the strength of the hydrogen bonds between water molecules. Therefore, the similarity of the spectral differences between the HDL-LDL case and the HDA-LDA case suggests that the difference of the local structure between the LDL and the HDL is similar to that between LDA and HDA. In fact, Soper and Ricci [56] show that the principal difference between the local structures of the LDL and the HDL is that the first peak in the O-O structure factor $g_{OO}(r)$ is barely altered in position, while the second peak position becomes smaller from the LDL to the HDL. And a similar change in $g_{OO}(r)$ from LDA to HDA is also found [57].

A theoretical study [58] shows that the boson peaks at different conditions can be rescaled to one master curve with a characteristic energy E_c in the following way:

$$E \rightarrow \varepsilon = E/E_c, \quad g(E) \rightarrow g(\varepsilon) = E_c^2 g[E(\varepsilon)]. \quad (5)$$

We perform a similar rescaling on $S_{BP}(Q, E)$ of the confined water shown in Fig. 3(a). The fitting parameter E_{BP} in Eq. (1) is employed as the characteristic energy E_c . The result is shown in Fig. 4(a). It can be seen that, even though values of $H, M,$ and V are different, the curves obtained in the LDL region can be approximately rescaled to one master curve, and the curves in the HDL region can be rescaled to a different one. A common master curve for

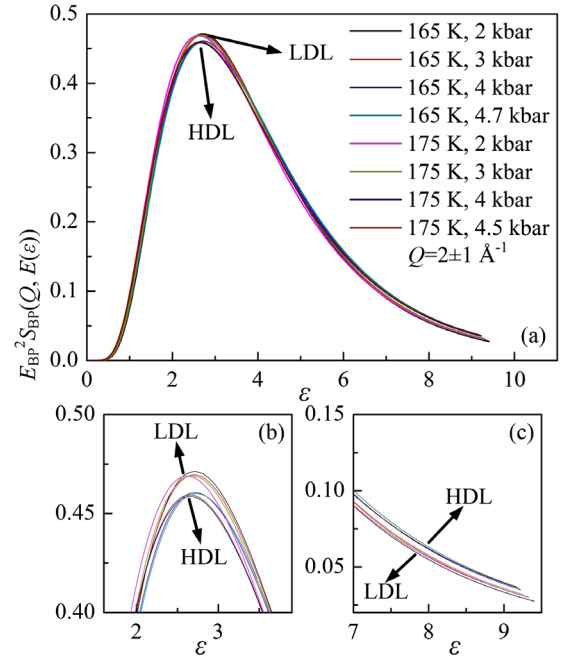


FIG. 4 (color online). (a) Rescaling of the boson peaks by $E \rightarrow \varepsilon = E/E_{BP}$, $S_{BP}(Q, E) \rightarrow E_{BP}^2 S_{BP}[Q, E(\varepsilon)]$. The $S_{BP}(Q, E)$ obtained in the LDL are rescaled to a master curve approximately, while the $S_{BP}(Q, E)$ obtained in the HDL are rescaled to a different one. Panels (b) and (c) show rescaled curves within ε ranges from 1.6 to 3.9 and from 7 to 9.5, respectively.

all measured boson peaks in the LDL (or the HDL) suggests a common mode distribution, and reflects the similarity in dynamic behavior between different measured points. The failure in rescaling the boson peaks to one master curve is attributed to the difference in the local structure [30,35]. Thus, the existence of two different master curves supports the existence of two structurally different liquid phases in confined water. Figures 4(b) and 4(c) show the rescaling quality in detail.

We also studied the librational band of the confined water at $T = 170$ K and at $P = 2, 3, 4,$ and 4.8 kbar with INS. The experiment was performed at the vibrational spectrometer (VISION) at SNS, ORNL [59]. The measured vDoSs in the librational band are shown in Fig. 5(a1) [60]. The spectral differences between adjacent measured pressures are shown in Fig. 5(a2). It can be seen that the energy of the low-energy side of the librational band measured at 4 kbar (the HDL) is lower than that measured at 3 kbar (the LDL) by a few meV. The librational band of the confined water has also been measured at ambient pressure [61,62]: on crossing ~ 225 K from the low temperature side, the change in the librational band is very similar to the spectral change from 3 kbar (the LDL) to 4 kbar (the HDL) shown in Fig. 5(a2). Mallamace *et al.* [17] show that on crossing 225 K from the low temperature side at ambient pressure, the local structure of water transforms from a predominately LDL form to a predominately HDL form. Therefore, our result is consistent with the previous measurements and suggests the existence of the LDL and the HDL. The

spectral difference observed here indicates that the hydrogen bond between the central water molecule and first shell becomes weaker from the LDL to the HDL. Previous studies on aqueous organic solutions [10,11] show that the OH-stretching mode is softer in the LDL than that in the HDL. This softening suggests that the hydrogen bond between the central water molecule and the first shell becomes weaker from the LDL to the HDL. Our result is thus consistent with the result in aqueous organic solutions. In addition, the softening of the librational band from the LDL to the HDL is also consistent with a recent quasielastic neutron scattering study, which shows that the activation energy decreases from the LDL to the HDL [63].

We show the vDoSs in the librational band of LDA and HDA in Fig. 5(b1) and their spectral difference in Fig. 5(b2) [64–66]. By comparing one can find that the low-energy side of the librational band of confined H_2O is much smoother than those of the amorphous ices and ice Ih (the spectrum of ice Ih, which is very similar to that of LDA, is not shown here). This difference suggests that the confined H_2O is in the liquid phase. The spectral change from LDA to HDA is similar to that from the LDL to the HDL (but with much larger amplitude): there are excess modes between ~ 45 and ~ 65 meV in the vDoS of HDA compared with that of LDA because of the red shift of the low-energy side of the librational band from LDA to HDA. This spectral change is assigned to a larger O-O distance [57] and a weaker hydrogen bond from LDA to HDA [65].

In summary, we measured the INS spectra of confined water at low temperatures and high pressures to examine the existence of the LLT in the confined water. The behaviors of the boson peak suggest a transition from the LDL to the HDL between 3 and 4 kbar at ~ 170 K. This result is consistent with the phase diagram found in confined heavy water by a density measurement [22]. In addition, the behaviors of the librational band also agree with the existence of the LDL and HDL phases.

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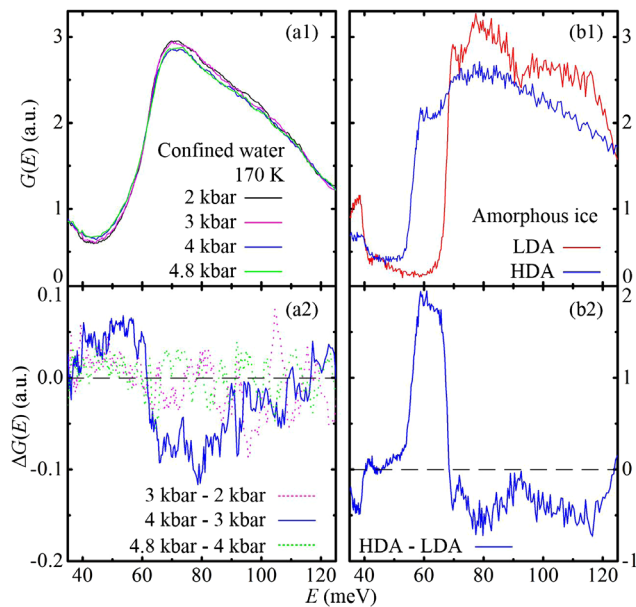


FIG. 5 (color online). (a1) Librational bands of confined water at $T = 170$ K and $P = 2, 3, 4,$ and 4.8 kbar. (a2) The spectral differences between the adjacent pressures. (b1) Librational bands of LDA and HDA. (b2) The spectral difference between HDA and LDA. The data of the amorphous ices are rescaled for comparison with the data of the confined water.

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- [1] P. G. Debenedetti, *J. Phys. Condens. Matter* **15**, R1669 (2003).
- [2] P. G. Debenedetti and H. E. Stanley, *Phys. Today* **56**, 40 (2003).
- [3] C. A. Angell, *Annu. Rev. Phys. Chem.* **34**, 593 (1983).

- [4] O. Mishima and H. E. Stanley, *Nature (London)* **396**, 329 (1998).
- [5] E. F. Burton and W. F. Oliver, *Proc. R. Soc. A* **153**, 166 (1935).
- [6] O. Mishima, L. D. Calvert, and E. Whalley, *Nature (London)* **310**, 393 (1984).
- [7] O. Mishima, L. D. Calvert, and E. Whalley, *Nature (London)* **314**, 76 (1985).
- [8] V. V. Brazhkin, E. L. Gromnitskaya, O. V. Stal'gorova, and A. G. Lyapin, *Rev. High Pres. Sci. Tech.* **7**, 1129 (1998).
- [9] P. H. Poole, F. Sciortino, U. Essmann, and H. E. Stanley, *Nature (London)* **360**, 324 (1992).
- [10] K.-I. Murata and H. Tanaka, *Nat. Mater.* **11**, 436 (2012).
- [11] K.-I. Murata and H. Tanaka, *Nat. Commun.* **4**, 2844 (2013).
- [12] O. Mishima, *J. Chem. Phys.* **123**, 154506 (2005).
- [13] O. Mishima, *J. Chem. Phys.* **126**, 244507 (2007).
- [14] Y. Suzuki and O. Mishima, *J. Chem. Phys.* **141**, 094505 (2014).
- [15] J. A. Sellberg, C. Huang, T. A. McQueen *et al.*, *Nature (London)* **510**, 381 (2014).
- [16] L. Liu, S.-H. Chen, A. Faraone, C.-W. Yen, and C.-Y. Mou, *Phys. Rev. Lett.* **95**, 117802 (2005).
- [17] F. Mallamace, M. Broccio, C. Corsaro, A. Faraone, D. Majolino, V. Venuti, L. Liu, C.-Y. Mou, and S.-H. Chen, *Proc. Natl. Acad. Sci. U.S.A.* **104**, 424 (2007).
- [18] Y. Zhang, A. Faraone, W. A. Kamitakahara, K.-H. Liu, C.-Y. Mou, J. B. Leo, S. Chang, and S.-H. Chen, *Proc. Natl. Acad. Sci. U.S.A.* **108**, 12206 (2011).
- [19] Z. Wang, K.-H. Liu, L. Harriger, J. B. Leão, and S.-H. Chen, *J. Chem. Phys.* **141**, 014501 (2014).
- [20] K.-H. Liu, Y. Zhang, J.-J. Lee, C.-C. Chen, Y.-Q. Yeh, S.-H. Chen, and C.-Y. Mou, *J. Chem. Phys.* **139**, 064502 (2013).
- [21] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevLett.115.235701> for a description of the sample and a derivation of the equations.
- [22] Z. Wang, K. Ito, J. B. Leão, L. Harriger, Y. Liu, and S.-H. Chen, *J. Phys. Chem. Lett.* **6**, 2009 (2015).
- [23] A. Cupane, M. Fomina, I. Piazza, J. Peters, and G. Schirò, *Phys. Rev. Lett.* **113**, 215701 (2014).
- [24] The liquid-liquid transition in confined water exhibits strong metastability [18,19,22]. Crossing the phase boundary does not necessarily lead to a phase transition.
- [25] G. Ehlers, A. A. Podlesnyak, J. L. Niedziela, E. B. Iverson, and P. E. Sokol, *Rev. Sci. Instrum.* **82**, 085108 (2011).
- [26] R. T. Azuah, L. R. Kneller, Y. Qiu, P. L. W. Tregenna-Piggott, C. M. Brown, J. R. D. Copley, and R. M. Dimeo, *J. Res. Natl. Inst. Stand. Technol.* **114**, 341 (2009).
- [27] A. Cupane, M. Fomina, and G. Schirò, *J. Chem. Phys.* **141**, 18C510 (2014).
- [28] Z. Wang, K.-H. Liu, P. Le, M. Li, W.-S. Chiang, J. B. Leão, J. R. D. Copley, M. Tyagi, A. Podlesnyak, A. I. Kolesnikov, C.-Y. Mou, and S.-H. Chen, *Phys. Rev. Lett.* **112**, 237802 (2014).
- [29] K. Niss, B. Begen, B. Frick, J. Ollivier, A. Beraud, A. Sokolov, V. N. Novikov, and C. Alba-Simionesco, *Phys. Rev. Lett.* **99**, 055502 (2007).
- [30] L. Orsingher, A. Fontana, E. Gilioli, G. Carini, Jr., G. Carini, G. Tripodo, T. Unruh, and U. Buchenau, *J. Chem. Phys.* **132**, 124508 (2010).
- [31] Y. Inamura, M. Arai, T. Otomo, N. Kitamura, and U. Buchenau, *Physica (Amsterdam)* **284–288B**, 1157 (2000).
- [32] A. I. Chumakov and G. Monaco, *J. Non-Cryst. Solids* **407**, 126 (2015).
- [33] A. I. Chumakov, G. Monaco, A. Monaco *et al.*, *Phys. Rev. Lett.* **106**, 225501 (2011).
- [34] A. I. Chumakov, G. Monaco, A. Fontana *et al.*, *Phys. Rev. Lett.* **112**, 025502 (2014).
- [35] A. Monaco, A. I. Chumakov, G. Monaco, W. A. Crichton, A. Meyer, L. Comez, D. Fioretto, J. Korecki, and R. Rüffer, *Phys. Rev. Lett.* **97**, 135501 (2006).
- [36] M. Zanatta, G. Baldi, S. Caponi, A. Fontana, C. Petrillo, F. Rossi, and F. Sacchetti, *J. Chem. Phys.* **135**, 174506 (2011).
- [37] M. Zanatta, G. Baldi, S. Caponi, A. Fontana, E. Gilioli, M. Krish, C. Masciovecchio, G. Monaco, L. Orsingher, F. Rossi, G. Ruocco, and R. Verbeni, *Phys. Rev. B* **81**, 212201 (2010).
- [38] E. Stavrou, C. Raptis, and K. Syassen, *Phys. Rev. B* **81**, 174202 (2010).
- [39] S. Caponi, A. Fontana, F. Rossi, G. Baldi, and E. Fabiani, *Phys. Rev. B* **76**, 092201 (2007).
- [40] H. Shintani and H. Tanaka, *Nat. Mater.* **7**, 870 (2008).
- [41] O. Pilla, S. Caponi, A. Fontana, J. R. Gonçalves, M. Montagna, F. Rossi, G. Viliani, L. Angelani, G. Ruocco, G. Monaco, and F. Sette, *J. Phys. Condens. Matter* **16**, 8519 (2004).
- [42] S. N. Taraskin, Y. L. Loh, G. Natarajan, and S. R. Elliott, *Phys. Rev. Lett.* **86**, 1255 (2001).
- [43] W. Schirmacher, G. Diezemann, and C. Ganter, *Phys. Rev. Lett.* **81**, 136 (1998).
- [44] L. Hong, B. Begen, A. Kisliuk, C. Alba-Simionesco, V. N. Novikov, and A. P. Sokolov, *Phys. Rev. B* **78**, 134201 (2008).
- [45] P. Kumar, K. T. Wikfeldt, D. Schlesinger, L. G. M. Pettersson, and H. E. Stanley, *Sci. Rep.* **3**, 1980 (2013).
- [46] D. Chandler, *Introduction to Modern Statistical Mechanics* (Oxford University Press, Oxford, England, 1987), p. 195.
- [47] O. Mishima, *Phys. Rev. Lett.* **85**, 334 (2000).
- [48] G. L. Squires, *Introduction to the Theory of Thermal Neutron Scattering* (Cambridge University Press, Cambridge, England, 1978), p. 68.
- [49] Yu. V. Denisov and A. P. Rylev, *JETP Lett.* **52**, 411 (1990).
- [50] http://en.wikipedia.org/wiki/Log-normal_distribution.
- [51] In certain Q and energy ranges, the shape of the incoherent scattering spectrum does not depend on Q ; see J. M. Carpenter and C. A. Pelizzari, *Phys. Rev. B* **12**, 2397 (1975).
- [52] M. M. Koza, *Phys. Rev. B* **78**, 064303 (2008).
- [53] S.-H. Chen, K. Toukan, C.-K. Loong, D. L. Price, and J. Teixeira, *Phys. Rev. Lett.* **53**, 1360 (1984).
- [54] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevLett.115.235701> for a detailed explanation. The data for calculating the Debye-Waller factors of LDA and HDA are from M. M. Koza, B. Geil, H. Schober, and F. Natali, *Phys. Chem. Chem. Phys.* **7**, 1423 (2005).
- [55] L. Gelb, K. Gubbins, R. Radhakrishnan, and M. Sliwinski-Bartkowiak, *Rep. Prog. Phys.* **62**, 1573 (1999).
- [56] A. K. Soper and M. A. Ricci, *Phys. Rev. Lett.* **84**, 2881 (2000).

- [57] J. L. Finney, A. Hallbrucker, I. Kohl, A. K. Soper, and D. T. Bowron, *Phys. Rev. Lett.* **88**, 225503 (2002).
- [58] T. S. Grigera, V. Martin-Mayor, G. Parisi, and P. Verrocchio, *Nature (London)* **422**, 289 (2003).
- [59] P. A. Seeger, L. L. Daemen, and J. Z. Larese, *Nucl. Instrum. Methods Phys. Res., Sect. A* **604**, 719 (2009).
- [60] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevLett.115.235701> for the full VISION spectra with the energy range from 2 to 120 meV.
- [61] S. Kittaka, S. Takahara, H. Matsumoto, Y. Wada, T. J. Satoh, and T. Yamaguchi, *J. Chem. Phys.* **138**, 204714 (2013).
- [62] L. Liu, S.-H. Chen, A. Faraone, C.-W. Yen, C.-Y. Mou, A. I. Kolesnikov, E. Mamontov, and J. Leao, *J. Phys. Condens. Matter* **18**, S2261 (2006).
- [63] Z. Wang, P. Le, K. Ito, J. B. Leão, M. Tyagi, and S.-H. Chen, *J. Chem. Phys.* **143**, 114508 (2015).
- [64] A. I. Kolesnikov, J.-C. Li, S. Dong, I. F. Bailey, R. S. Eccleston, W. Hahn, and S. F. Parker, *Phys. Rev. Lett.* **79**, 1869 (1997).
- [65] A. I. Kolesnikov, J. Li, S. F. Parker, R. S. Eccleston, and C.-K. Loong, *Phys. Rev. B* **59**, 3569 (1999).
- [66] J. Li and A. I. Kolesnikov, *J. Mol. Liq.* **100**, 1 (2002).