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Phys. Rev. Lett. **115**, 235701 — Published 3 December 2015

DOI: [10.1103/PhysRevLett.115.235701](https://doi.org/10.1103/PhysRevLett.115.235701)

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

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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 librational band also agrees with the above conclusion.

PACS numbers: 64.70.Ja, 63.50.-x, 25.40.Fq

Water is a continuing source of fascination to scientists because of its abnormal behaviors 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, the glassy water, also called amorphous ice, exhibits polyamorphism. Experiments show that two kinds of amorphous ice, the low-density amorphous ice (LDA) and the 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, the experimental tests on the existence of the LDL and 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 the bulk water below the homogeneous nucleation temperature (235 K at atm). To overcome this barrier and enter the deeply cooled region of water, different systems, including aqueous solutions [10–14], micro-sized 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 15-Å pore diameter, water can keep in 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 the heavy water confined in MCM-41 by density measurement. The associated phase diagram is shown in Fig. 1 (a) [22]. However, the relevant measurements on dynamic properties still lack. In fact, various dynamic properties, including structural relaxation [10, 16], stretching vibration [10, 11], mean square displacement [24], etc., have

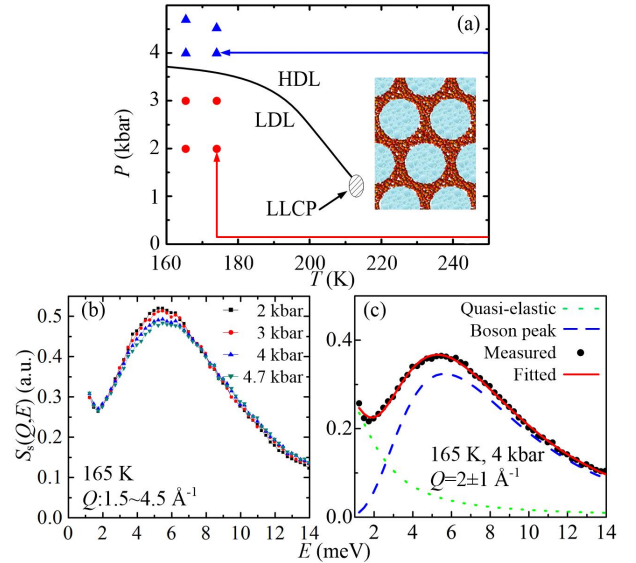


FIG. 1. (a) Phase diagram of the deeply cooled confined heavy water[22]. The inset shows the two dimensional hexagonal structure of MCM-41. The red circles denote the measured points in LDL. These points are approached by first cooling the system to desired temperature and then pressurizing (red arrow). The blue triangles denote the measured points in HDL. These points are approached by cooling the system to desired temperature at desired pressure (blue arrow). With these approaches we avoid crossing the phase boundary directly [23]. (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.

been measured to study the phase behaviors of the aqueous solutions or confined water. The examinations of the phase behaviors by the dynamic properties are indispensable, because they provide complementary insights to 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 (CNCS) [25] at Spallation Neutron Source (SNS), Oak Ridge National Laboratory (ORNL). Data were reduced by DAVE [26]. 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 to the van Hove singularity of the transverse phonon of the crystal counterpart [33, 42, 43]. It is worth mention that, boson peak has dependence on the density of the material: as 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, 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 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 boson peak may response to the existence of the LLT in the 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 the confined H_2O with the method used in Ref. [22] due to the exceptionally large incoherent cross section of H atom. The difference between the phase diagrams of confined H_2O and confined D_2O is expected to be several K due to the isotope effect [46]. In fact, the conjectured phase diagram of deeply cooled bulk D_2O is quite similar to that of the 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 the confined water at a specific Q :

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

where $S_{s,m}(Q, E)$ is the measured self dynamic structure factor of the confined water, $R(E)$ is the energy resolu-

tion function. In the square brackets, the first term is a Lorentzian function, which represents the quasi-elastic contribution; the second term is a log-normal distribution function. σ_{BP} and E_{BP} relate to 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]. Log-normal distribution function can describe the boson peak well [49] and has been applied to the confined water successfully [27]. A typical fit is shown in Fig. 1 (c).

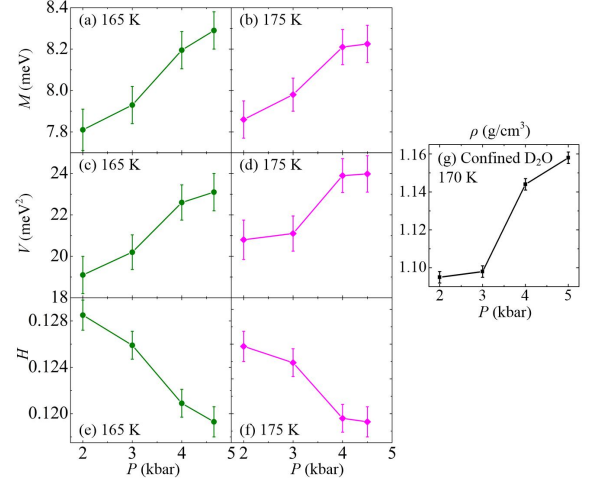


FIG. 2. Panels (a), (c) and (e) show the Mean frequency (M), variance (V) and height (H) of the boson peak as a function of pressure at 165 K, respectively. Panels (b), (d) and (f) show M , V and H of the boson peak as a function of pressure at 175 K, respectively. Panel (g) shows the average density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

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]:

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

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

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).

Figure 2 (a)-(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 computer simulation studies [40, 41]. Particularly, as the pressure changes from 3 to 4 kbar,

all 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 the confined D_2O as a function of pressure at 170 K in Fig. 2 (g) (obtained by the same method used in ref. [22]).

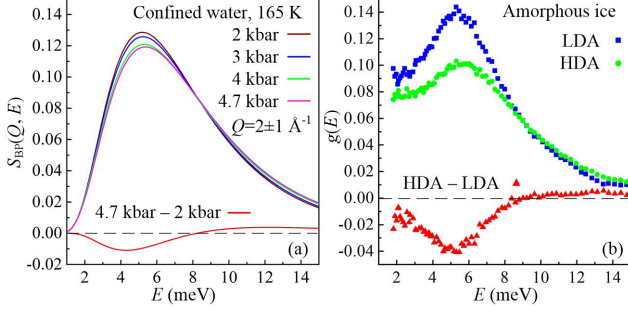


FIG. 3. (a) Line shapes of the boson peak extracted from the fit ($S_{BP}(Q, E)$) at $T=165$ K, $Q=2 \pm 1 \text{ \AA}^{-1}$ and at $P=2$ (brown), 3 (blue), 4 (green), and 4.7 (pink) kbar. The red curve shows the spectral difference between 4.7 and 2 kbar. (b) The reduced vDoS of HDA (green circles)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

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 (HDL) and 2 kbar (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 dynamic 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 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 HDL are thermodynamic extensions of LDA and HDA to 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 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 HDA-LDA case suggests that the difference of local structure between LDL and 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 LDL and 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 LDL to HDL. And a similar change in $g_{OO}(r)$ from LDA to HDA is also found [57].

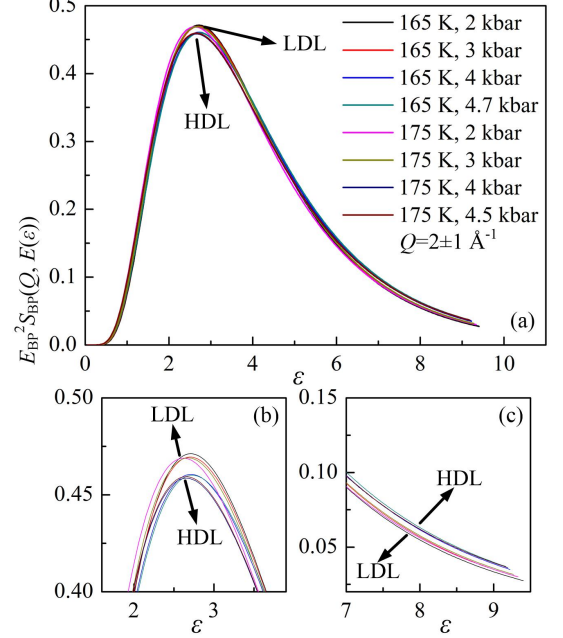


FIG. 4. (a) Rescaling of the boson peaks by $E \rightarrow \varepsilon = E/E_{BP}$, $S_{BP}(Q, E) \rightarrow E_{BP}^2 S_{BP}(Q, E(\varepsilon))$. The $S_{BP}(Q, E)$ obtained in LDL are rescaled to a master curve approximately, while the $S_{BP}(Q, E)$ obtained in HDL are rescaled to a different one.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

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 by the following way:

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

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 the values of H , M and V are different, the curves obtained in LDL region can be approximately rescaled to one master curve, and the curves in HDL region can be rescaled to a different one. A common master curve for all measured boson peaks in LDL (or 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 the confined water. Figure 4 (b) and (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 (HDL) is lower than that measured at 3 kbar (LDL) by a few meV. The librational band of the confined water has also been measured at ambient pressure [61, 62]: as crossing ~ 225 K from low temperature side, the change in librational band is very similar to the spectral change from 3 kbar (LDL) to 4 kbar (HDL) shown in Fig. 5 (a2). Mallamace et al. [17] show that as crossing 225 K from 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 HDL. The spectral difference observed here indicates that the hydrogen bond between the central water molecule and first shell becomes weaker from LDL to HDL. Previous studies on aqueous organic solutions [10, 11] show that the OH-stretching mode is softer in LDL than that in HDL. This softening suggests that the hydrogen bond between the central water molecule and the first shell becomes weaker from LDL to HDL. Our result is thus consistent with the result in the aqueous organic solutions. In addition, the softening of the librational band from LDL to HDL is also consistent with a recent quasi-elastic neutron scattering study, which shows that the activation energy decreases from LDL to HDL [63].

We show the vDoSs in 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 the ice Ih (the spectrum of ice Ih, which is very similar to that of the LDA, is not shown here). This difference suggests that the confined H_2O is in liquid phase. The spectral change from LDA to HDA is similar to that from LDL to HDL (but with much larger amplitude): there are excess modes between ~ 45 and ~ 65 meV in the vDoS of HDA comparing 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 larger O-O distance [57] and weaker hydrogen bond from LDA to HDA [65].

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

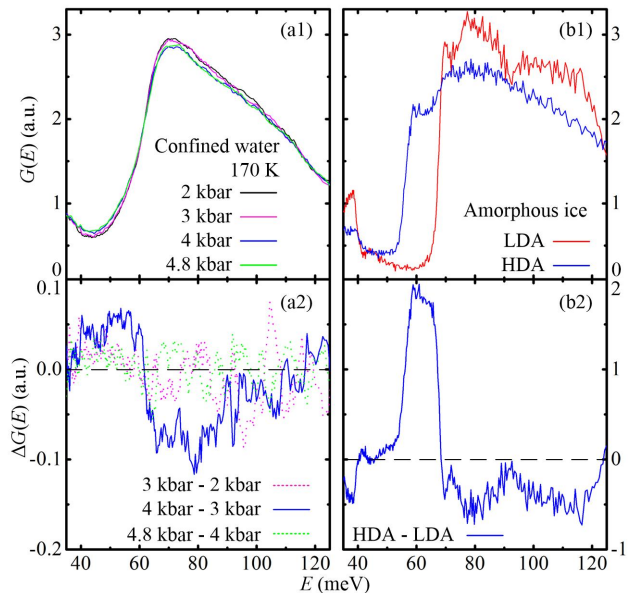


FIG. 5. (a1) Librational bands of confined water at $T=170$ K and $P=2, 3, 4$, and 4.8 kbar. (a2) The spectral differences between the adjacent pressures. (b1) Librational bands of LDA and HDA. (b2) The spectral difference between HDA and LDA. The data of amorphous ices are rescaled for comparing with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

The research at MIT was supported by DOE grant DE-FG02-90ER45429. The work at ORNL was supported by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy. WZ thanks Dr. K.-H. Liu, VISION team and sample environment team in SNS, ORNL for their helps and Dr. J.-L. Kuo for valuable discussions.

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