Boson Peak in Deeply Cooled Confined Water: A Possible Way to Explore the Existence of the Liquid-to-Liquid Transition in Water

The MIT Faculty has made this article openly available. Please share how this access benefits you. Your story matters.

<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>As Published</td>
<td><a href="http://dx.doi.org/10.1103/PhysRevLett.112.237802">http://dx.doi.org/10.1103/PhysRevLett.112.237802</a></td>
</tr>
<tr>
<td>Publisher</td>
<td>American Physical Society</td>
</tr>
<tr>
<td>Version</td>
<td>Final published version</td>
</tr>
<tr>
<td>Accessed</td>
<td>Fri Feb 16 12:40:09 EST 2018</td>
</tr>
<tr>
<td>Citable Link</td>
<td><a href="http://hdl.handle.net/1721.1/88649">http://hdl.handle.net/1721.1/88649</a></td>
</tr>
<tr>
<td>Terms of Use</td>
<td>Article is made available in accordance with the publisher's policy and may be subject to US copyright law. Please refer to the publisher's site for terms of use.</td>
</tr>
<tr>
<td>Detailed Terms</td>
<td></td>
</tr>
</tbody>
</table>
Boson Peak in Deeply Cooled Confined Water: A Possible Way to Explore the Existence of the Liquid-to-Liquid Transition in Water

Zhe Wang,1 Kao-Hsiang Liu,1,2 Peisi Le,1 Mingda Li,1 Wei-Shan Chiang,1 Juscelino B. Leão,3 John R. D. Copley,3 Madhusudan Tyagi,3,4 Andrey Podlesnyak,5 Alexander I. Kolesnikov,5 Chung-Yuan Mou,6 and Sow-Hsin Chen1,*

1Department of Nuclear Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA
2Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan, Republic of China
3NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA
4Department of Materials Science and Engineering, University of Maryland, College Park, Maryland 20742, USA
5Spallation Neutron Source, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA
6Department of Chemistry, National Taiwan University, Taipei 106, Taiwan, Republic of China

(Received 24 December 2013; published 12 June 2014)

The boson peak in deeply cooled water confined in nanopores is studied with inelastic neutron scattering. We show that in the \((P, T)\) plane, the locus of the emergence of the boson peak is nearly parallel to the Widom line below \(\sim 1600\) bar. Above \(1600\) bar, the situation is different and from this difference the end pressure of the Widom line is estimated. The frequency and width of the boson peak correlate with the density of water, which suggests a method to distinguish the hypothetical “low-density liquid” and “high-density liquid” phases in deeply cooled water.

DOI: 10.1103/PhysRevLett.112.237802 PACS numbers: 61.20.Lc, 63.50.--x

The boson peak is a broad peak observed at low frequencies (\(\sim 2\)–\(10\) meV) in the inelastic neutron, x-ray, and Raman scattering spectra of many amorphous materials and supercooled liquids [1–3]. Preliminary measurements on the boson peak in deeply cooled water confined in nanopores [4] and protein surfaces [5] under ambient pressure have been reported. The measured spectra include a boson peak at about 6 meV, which only emerges below \(\sim 230\) K. A similar result was also observed in a computer simulation study [6]. Since this temperature is close to the ambient-pressure Widom line temperature \(T_W \sim 224\) K (the Widom line is the locus of specific heat maxima [7]), the authors tentatively explained this phenomenon as due to transformation of the local structure of water from a predominantly high-density liquid (HDL) to a predominantly low-density liquid (LDL) form as \(T_W\) is crossed from above. However, this experimental result is insufficient. First, it is clear that this emergence of the boson peak in the raw spectra depends on the energy resolution of the experimental facility. Second, and more importantly, the situation at high pressures has, heretofore, remained unknown. Therefore, without quantitative analysis of the entire spectra, including quasielastic and inelastic components at high pressure, definite conclusions cannot be drawn.

In this Letter, we have measured the boson peak in deeply cooled water with a series of inelastic neutron scattering (INS) experiments in the temperature \((T)\) range from 120 to 230 K and the pressure \((P)\) range from 400 to 2400 bar employing the Disk Chopper Spectrometer (DCS) [8] at the National Institute of Standards and Technology (NIST) Center for Neutron Research and the Cold Neutron Chopper Spectrometer (CNCS) [9] at the Spallation Neutron Source of the Oak Ridge National Laboratory (ORNL). The DAVE software was used for the data reduction [10]. We find that below \(\sim 1600\) bar, the emergence of the boson peak is correlated (but does not overlap) with the Widom line and with the fragile-to-strong crossover (FSC) in deeply cooled water [11]. Above \(\sim 1600\) bar, the locus of the emergence of the boson peak in the \((P, T)\) plane has a different slope as compared with its behavior below \(\sim 1600\) bar, and the end pressure of the Widom line is estimated by determining where the slope begins to change. Moreover, the \((P, T)\) dependences of the shape of the boson peak are found to be related to the density minimum of water [12–14], and a possible way to distinguish the hypothetical LDL phase and HDL phase [15] in deeply cooled water is discussed.

In order to enter the deeply supercooled region of water, we used a nanoporous silica matrix, MCM-41-S, with 15-Å pore diameter to confine the water. When confined, water can remain in the liquid state without crystallization at temperatures much lower than the homogeneous nucleation temperature \((\sim 235\) K under \(P = 1\) bar) [14,16].

The measured energy \((E)\) spectrum at a fixed value of \(Q\) (the magnitude of the momentum transfer of the incident neutron) \(S_m(Q, E)\) was analyzed using the following equation:

\[
S_m(Q, E) = I_{hP}(Q, E) + I_E(Q)R(Q, E) + R(Q, E) \otimes \left[ (I_{Q}(Q)S_Q(Q, E) + I_I(Q, E)S_I(Q, E))D(E) \right].
\]

(1)
where $I_{pq}(Q, E)$ is the background signal from the MCM-41-S matrix, $R(Q, E)$ is the energy resolution function, $I_{E}(Q)R(Q, E)$ represents the elastic scattering component, $S_0(Q, E)$ is the quasielastic incoherent dynamic structure factor, $S_l(Q, E)$ is the inelastic incoherent dynamic structure factor, and $D(E)$ is the detailed balance factor \([17]\). $I_{Q}$ and $I_{l}$ are the intensities of the quasielastic and inelastic components, respectively. $S_0(Q, E)$ represents the diffusive, nonvibrational motions of water molecules and can be modeled using the relaxing cage model (RCM) \([18]\). In this Letter, the parameters of the RCM are known from previous quasielastic neutron scattering measurements \([11,19]\). $S_l(Q, E)$ describes the vibrational behavior of water, i.e., the boson peak. Here we use the damped harmonic oscillator (DHO) \([20]\) model to represent $S_l(Q, E)$. The DHO has been used to model various kinds of vibrations, from the self-motion of a single classical damped oscillator to collective excitations in different amorphous materials \([20–22]\). Using the DHO model, both the frequency and the width of the boson peak can be extracted. Detailed descriptions of the sample, instrument, models, and data analysis can be found in the Supplemental Material \([23]\). In the following paragraphs, we will present our results and their implications.

The left set of panels in Fig. 1 shows INS spectra $S_n(Q, E)$ measured with the DCS at $Q = 2 \text{ Å}^{-1}$ and corresponding fitted curves under different temperatures and pressures. The right set of panels shows the theoretical incoherent dynamic structure factors extracted from the fit: $S_{th}(Q, E) = n_0S_0(Q, E) + n_lS_l(Q, E)$ and $n_l = 1 - n_0$ are the fractional quasielastic and inelastic contributions, respectively. In order to study the relation between the emergence of the boson peak and Widom line crossing in deeply cooled confined water, we first define the emergence of the boson peak as follows: if there is a maximum in the $S_{th}(Q, E)$ curve between ~2 and 10 meV, we state that the boson peak is visible or that the boson peak emerges \([e.g., the 200 K case in Fig. 1(b2)]; on the other hand, if the $S_{th}(Q, E)$ curve does not have a maximum, decreasing monotonically in this $E$ range, we state that the boson peak is not visible \([e.g., the 225 K case in Fig. 1(b2)]\). This definition can be illustrated better if one considers the derivative of $S_{th}(Q, E)$ with respect to $E$, $\partial_ES_{th}(Q, E)$. A boson peak is observed if $\partial_ES_{th}(Q, E)$ has two roots with $E > 0$ \([e.g., the 200 K case in Fig. 2(a1)]; similarly, no peak is observed if $\partial_ES_{th}(Q, E)$ has no roots at $E > 0$ \([e.g., the 225 K case in Fig. 2(a1)]. The intermediate condition that $\partial_ES_{th}(Q, E)$ has just one root with $E > 0$, or equivalently, that the maximum value of $\partial_ES_{th}(Q, E)$ just equals 0, corresponds to the critical case that the boson peak just emerges. From the above discussions, it can be found that the emergence or disappearance of the boson peak in the full spectrum is due to the $(P, T)$ dependences of the dynamics of the confined water system, including the slow dynamics [$S_0(Q, E)$] and the subpicosecond dynamics [$S_l(Q, E)$]. We denote the temperature at which the boson peak just emerges as $T_B$. In the right column of Fig. 1, we mark the $S_{th}(Q, E)$ curve whose temperature is closest to $T_B$ for each pressure. One
may estimate the value of $T_B$ better with a linear interpolation method. Take the 1200 bar case, for example; from Fig. 2(a2), it is found that the value of $\max \left[ \frac{\partial E S_{th}}{ \partial E} \right]_{Q,E}$ changes smoothly and monotonically as $T$ changes; therefore, one can perform a linear interpolation with respect to $\max \left[ \frac{\partial E S_{th}}{ \partial E} \right]_{Q,E}$ and $T$ to find out the approximate value of $T_B$ at which $\max \left[ \frac{\partial E S_{th}}{ \partial E} \right]_{Q,E}$ vanishes. With this method, we obtain $T_B = 219.8/3 K$ under 1200 bar, as shown in Fig. 2(a2). Another example is provided by Fig. 2(b2) where $T_B$ is estimated to be 211.2 $\pm$ 1.2 K under 2000 bar.

The values of $T_B$ obtained using the method just described are denoted by squares in Fig. 3. The FSC temperatures $T_X$ at different pressures are also shown (as triangles) [11,19]. One can find that below $\sim$1600 bar, the solid curve, which represents the behavior of $T_B(P)$, is nearly parallel to the blue dashed curve that represents the profile of $T_X(P)$. Computer simulation studies suggest that for water models displaying a liquid-liquid critical point (LLCP [15]), the FSC coincides with the Widom line [7]. Thus, we conclude that below $\sim$1600 bar, the emergence of the boson peak has similar $P$ dependence as the Widom line in the sense of the LLCP hypothesis, even though they do not overlap.

Figure 4 shows the extracted frequency ($\Omega$) and full width at half maximum height ($\Gamma$) of $S_I(Q,E)$, i.e., the boson peak, as a function of $T$ and $P$ at $Q = 2 \ A^{-1}$. Below $\sim$1600 bar, crossing the Widom line, both $\Omega$ and $\Gamma$ change slightly and smoothly. The inset shows that such smooth changes make the boson peak less sharp as $T$ increases. In addition, the quasielastic peak broadens, and its wing is strengthened with increasing $T$ due to a decrease in the translational relaxation time of water molecules $\langle \tau_T \rangle$. Both of these phenomena contribute to the invisibility of the boson peak in the entire spectrum as $T$ increases. Notice that, when crossing the Widom line temperature $T_W$ from...
Figure 4(a) shows that the frequency of the boson peak $\Omega$ slightly increases as $T$ increases within 200 K $< T < 230$ K. However, from Fig. 5, one can find that within 120 K $< T < 180$ K, $\Omega$ decreases as $T$ increases. (Since we do not have the RCM parameters for confined water in this $T$ range, we cannot perform a quantitative analysis. However, in this $T$ range, the quasielastic peak in the spectrum is very narrow and will not affect the shape of the inelastic spectrum too much.) This result suggests that a frequency minimum exists between about 180 and 200 K. Notice that the density of water also exhibits a minimum in the same region [14]. In addition, $\Omega$ tends to increase as the pressure increases. These facts suggest that $\Omega$ and the density of the deeply cooled water are positively correlated. The width of the boson peak ($\Gamma$) also exhibits such a behavior. In fact, similar phenomena were also observed in other amorphous materials [25]. This result is of particular importance to water. In the LLCP hypothesis, the order parameter to distinguish the LDL and HDL phases is just the density. With this in mind, and considering that a change in the local structure can also shift the boson peak [25], one may distinguish the hypothetical LDL and HDL phases in deeply cooled water by looking at the shape of the boson peak. In other words, the frequency or the width of the boson peak may exhibit abrupt change as the water transforms between LDL and HDL, due to significant differences in density and local structure of the different sides of the hypothetical first order transition line between LDL and HDL [15,26].

The research at MIT was supported by DOE Grant No. DE-FG02-90ER45429. K. H. L. is sponsored by the National Science Council of Taiwan, “New Partnership Program for the Connection to the Top Labs in the World.” The work at NIST was supported in part by the National Science Foundation under Agreement No. DMR-0944772. The work at ORNL was supported in part by the Scientific User Facilities Division, Office of Basic Energy Sciences, and U.S. Department of Energy. We thank Professor Li Liu for providing the RCM parameters.

*Corresponding author.
sowhsin@mit.edu


See the Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.112.237802 for descriptions of the sample, instrument, model, and data analysis used in this study.

A full DHO curve contains two asymmetric peaks that reside in the Stokes and anti-Stokes sides of the spectrum. They overlap each other so that the position of the maximum of the curve is not equal to the frequency of the DHO model.
