【Title】

Origin of sperific heat anomaly in ambient liquid water was experimenally identified for the first time -"Fluctuation" that existed over a wide range of temperature and pressure regions -

[Key points of this research result]

1: Liquid water has an unusually large specific heat near its melting point, but its origin and mechanism are not well understood.

2: A new experimental concept was devised to measure the strength of "fluctuation" (*1) in liquids and this fluctuation measurement was conducted on liquid water. The measured fluctuation-strength was linked to the change in specific heat near room temperature and pressure, and this fluctuation was identified as the origin of the specific heat anomaly in water.

3: The measured fluctuations can be judged to be critical fluctuation associated with the liquid-liquid phase transition (*2), which is believed to exist in the supercooled region. It has been thought that the effect is limited only in the supercooled region, but it is now clear that it exists over a very wide range of temperatures and pressures.

[Summary]

Assistant Professor Yukio Kajihara of Hiroshima University, in collaboration with Professor Masanori Inui of Hiroshima University, Professor Kazuhiro Matsuda of Kumamoto University, Senior Scientist Satoshi Tsutsui of Japan Synchrotron Radiation Research Institute (JASRI), RIKEN SPring-8 Center/JASRI Researcher Daisuke Ishikawa, and Group Director Alfred Baron, devised a new experimental concept to measure the strength of "fluctuation" of liquids using the sound waves (Fig. 1), and actually conducted fluctuation measurement of liquid water at synchrotron radiation facility SPring-8 (*3). As a result, it was revealed for the first time that fluctuation in liquid water exists over a wide temperature and pressure ranges. The strength of this fluctuation is also linked to change in specific heat, and this fluctuation has been experimentally identified as the origin of the famous specific heat anomaly near its melting point for the first time. The fluctuation measured in this study are considered to be critical fluctuation corresponding to the liquid-liquid phase transition (LLT) (*2), which is believed to exist in the supercooled region, and the experimental results strongly support the LLT scenario to explain liquid water's anomalies [1,2].

It goes without saying that the specific heat of water, the most universal liquid, is important for both fundamental and applied purposes, and the fact that its origin has been identified is of great value. Moreover, by using this fluctuation measurement, we can expect new developments in the study of liquids other than water in the future.

[Article information]

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Article title: Experimental observation of mesoscopic fluctuations to identify origin of thermodynamic anomalies of ambient liquid water

Authors: Yukio Kajihara, Masanori Inui, Kazuhiro Matsuda, Daisuke Ishikawa, Satoshi Tsutsui, A.Q.R. Baron

[Background]

Water is the most familiar and ordinary liquid. However, from a research perspective, it is a unique liquid with thermodynamic properties that differ greatly from those of other liquids: ice floats on water (solid is lighter than liquid), its specific heat is unusually high, and its density and sound velocity show maxima at 4 C and 80 C, respectively, in response to temperature changes. The LLT scenario is currently the most promising hypothesis to explain such water anomalies. It is believed that LLT exists in the supercooled region and that the associated critical fluctuation affect thermodynamic properties near ambient temperature and pressure. Recently, the existence of density fluctuation, which is thought to originate from the LLT, has been clarified by experiments [3], but the problem is that the effect is seen only in the supercooled region. Under these circumstances, we focused our attention on another type of "fluctuation" that can be detected by sound waves. By combining two sound velocity measurement methods with very different frequencies, inelastic x-ray scattering (IXS) and ultrasonic (US), we devised an experimental concept to measure the strength of fluctuation present in liquids (Fig. 1). We decided to perform IXS measurements of liquid water in a wide range of temperature and pressure regions at SPring-8, aiming to deepen the discussion of water anomalies in terms of fluctuation that can be detected by sound waves as well as density fluctuation.

[Research results]

IXS measurements of water were performed at BL35XU at SPring-8 in the temperature and pressure range from near ambient temperature and pressure to 500 C and 600 bar (Fig. 2). By comparing the high-frequency sound velocity obtained from this experiment with the low-frequency sound velocity value (literature value) obtained from the US measurement, the strenght of fluctuation Sf can be extracted (Fig. 3). Sf shows two remarkable increases, indicating the existence of two origins of "fluctuations”. That in the high temperature range (above 300 C) show maxima at the liquid-gas transition (LGT) critical isochore line (~420 C), indicating that this is LGT critical fluctuation. The change in Sf is also linked to the change in the isochoric specific heat, Cv, and it is verified that the origin of the increase in specific heat in this region is the LGT critical fluctuation. The fact that LGT critical fluctuation increases specific heat is a fundamental concept described in statistical mechanics textbooks. On the other hand, the change in Sf in the low temperature range (below 300 C) is also linked to the change in Cv, and the origin of the unusually large specific heat near the melting point was identified as the "fluctuation" measured in this study. It can be concluded that this fluctuation originates from the LLT, which is believed to exist in the supercooled region. Based on density fluctuation measurement and other data, it has been previously thought that the effects of LLT critical fluctuation is limited to the supercooled region, but it is now clear for the first time that this extends to the high-temperature region around 300 C. In fact, it turns out that the density fluctuation associated with LLT is so small that it is not a good parameter for understanding the effects of LLT critical fluctuation.

[Future Expectations]
The identification of the origin of specific heat will greatly advance the understanding of liquid water, which has remained poorly understood until now. In addition, by focusing on such fluctuations, we can expect new developments in the thermodynamic study of liquids in the future.

[Support]
Grants: JSPS KAKENHI No.20244061 and No. 20K03789.
Experiment: JASRI Proposal No. 2008B1108.

[Explanation of keyword]
(*1) “Fluctuation”
The state in which some physical quantity varies in time and space is called "fluctuation”. Generally, when a phase transition exists, "critical fluctuation" at the mesoscopic level (time-space size larger than atoms and molecules) are said to occur in the temperature and pressure region in the vicinity of the phase transition. For example, in the region near the liquid-gas phase transition, density fluctuation = spatial inhomogeneity of particles is known to be very large, which can be measured by small-angle scattering. However, this is "static fluctuation," and "dynamic fluctuation," which is how such particles are moving collectively, is also important. This time, we devised an experimental concept to measure this strength using sound waves.

(*2) Liquid-Liquid phase transition (LLT)
The concept that one liquid-structured phase undergoes a phase transition to another liquid-structured phase, just as a liquid changes to a gas = phase transition. Although the concept itself has existed for a long time, it has attracted attention because of its use in the 1990s in a hypothesis to explain water anomalies and the experimental demonstration in the early 2000s that discontinuous LLT occur in liquid phosphorus. In the case of liquid water, discontinuous LLT have not been observed experimentally and the hypothesis has not been proven.

(*3) Synchrotron radiation facility SPring-8
A third-generation synchrotron radiation facility that generates powerful X-rays, located in Hyogo Prefecture. It starts from 1997. IXS is the experimental technique made possible by such a third-generation synchrotron radiation facility.

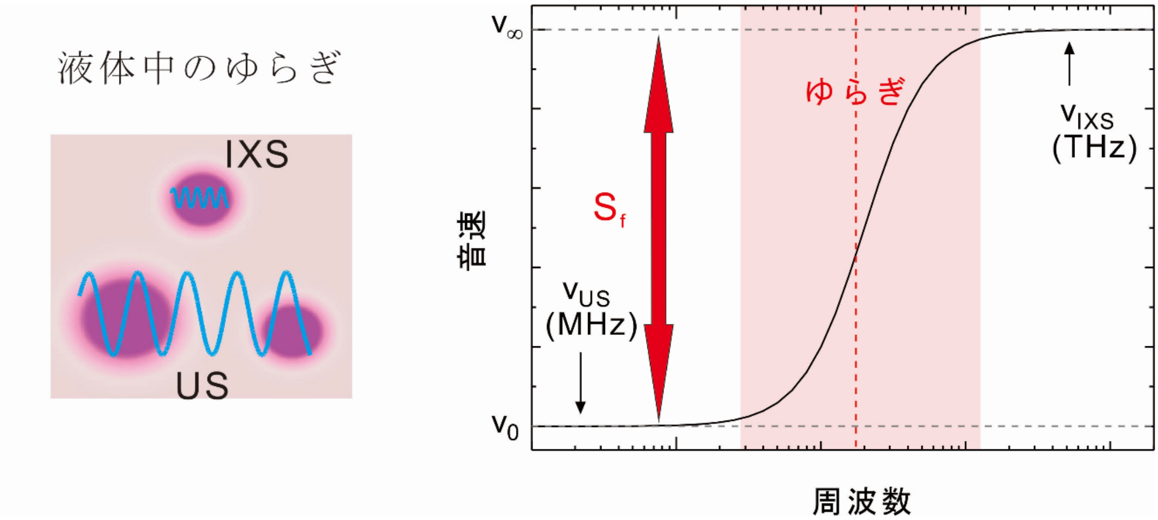
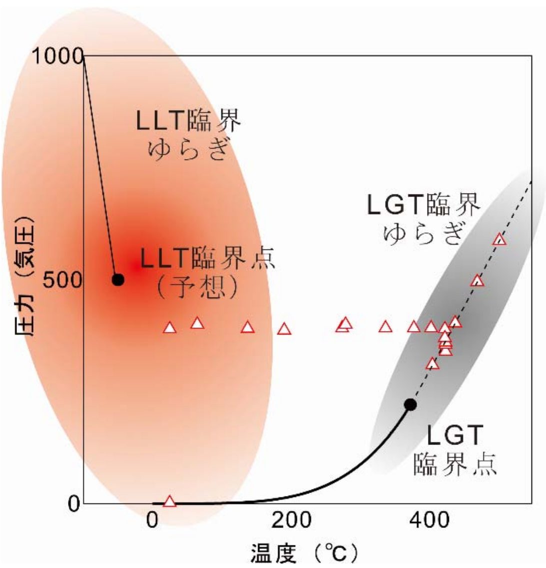


Figure 1: Scematic illustration of the "Fluctuation" strength measurement method. A frequency slow enough like ultrasound (US) combined with a frequency high enough like IXS is used to extract the fluctuation strength Sf.



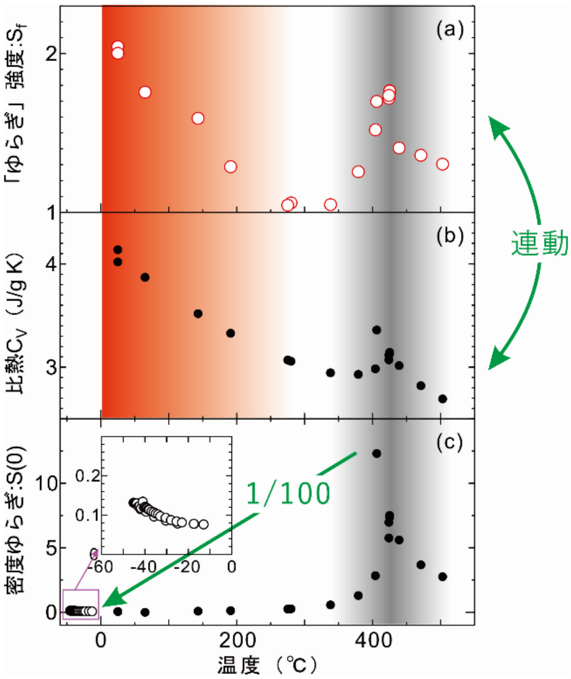


Figure 2 (left): State points of fluctuation (IXS) measurement and schematic illustration of the spread of LGT and LLT critical fluctuations.

Figure 3 (right): Temperature variation of (a) the strength of fluctuation Sf measured in this study, (b) the specific heat Cv and (c) the sterngth of density fluctuation S(0) calculated from the literature. In the high temperature range (>300 C), Sf, Cv, and S(0) all show maxima due to LGT critical fluctuation. On the other hand, in the low temperature range (<300 C), Sf and Cv increase in tandem due to the LLT critical fluctuation. However, the effect of LLT on S(0) is small, only about 1/100th that of the LGT region.