A New Perspective for Understanding the Thermodynamics of Liquids: Mesoscopic Fluctuation

Yukio Kajihara[1]

[1] *Graduate School of Advanced Science and Engineering, Hiroshima University, Higashi-Hiroshima, Hiroshima 739-8521, Japan*
E-mail: kajihara@hiroshima-u.ac.jp

Liquid water near ambient conditions is known to exhibit various thermodynamic anomalies, and the liquid-liquid phase transition (LLT) scenario has been proposed as a model to explain these anomalies [1]: Water has two phases, and these phases undergo a discontinuous phase transition in the supercooled region; Water near ambient conditions is located in the supercritical region of this LLT, and is affected by the associated mesoscopic-level LLT critical fluctuation, resulting in anomalous thermodynamics. This scenario is being verified by recent experiments: X-ray emission spectroscopy measurements have shown that two types of electronic states coexist in liquid water [2,3]; Small-angle scattering measurements using an X-ray free electron laser have revealed that liquid water is inhomogeneous density state at the mesoscopic-level due to LLT critical fluctuation [4].

To investigate such mesoscopic-level fluctuation state in more detail, we have developed a new dynamic fluctuation measurement method. This method combines two sound-velocity measurement methods, inelastic x-ray scattering and ultrasonic method, to detect fluctuation in liquids using the relaxation phenomenon of sound waves. Depending on the target sample, this method is expected to be much more sensitive than the small-angle scattering method, which detects static density fluctuation. When actually applied to liquid water, this LLT critical fluctuation was successfully detected over a wider temperature and pressure ranges. It was also revealed for the first time that the changes of dynamic fluctuation strength and isochoric specific heat capacity are linked over a wide temperature and pressure ranges, establishing that such mesoscopic-level dynamic fluctuation is in fact the origin of the well-known specific heat anomaly of ambient liquid water [5].

Dynamic-fluctuation measurements were also performed for water-alcohol mixtures, which is also known to exhibit various thermodynamic anomalies [6], and details will be presented.

References

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