High-resolution adiabatic calorimetry of supercooled water

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Abstract. Liquid water exhibits anomalous behavior in the supercooled region. A popular hypothesis to explain supercooled water’s anomalies is the existence of a metastable liquid-liquid transition terminating at a critical point. The hypothesized phase transition is not directly accessible in a bulk experiment because it is expected to occur in “no-man’s” below the kinetic stability limit of the liquid phase at about 233 K, the temperature of homogeneous ice formation. Therefore, verifications of this hypothesis are usually based on extrapolations from the experimentally accessible region. In this work, we present the results of high-resolution adiabatic calorimetry measurements of cold and supercooled liquid water in the range from 294 to 244 K, the lowest temperature of water’s supercooling achieved so far in a bulk adiabatic-calorimetry experiment. The resolution of the measurements is also record-high, with the average statistical (random) error of about 0.1%. The data are consistent with adiabatic-calorimetry measurements of supercooled water earlier reported by Tombari et al (1999 Chem. Phys. Lett. 300 749) but significantly deviate from differential-scanning calorimetry measurements in emulsified water reported by Angell et al (1982 J. Phys. Chem. 86 998) and by Archer and Carter (2000 J. Phys. Chem. 104 8563) Consequences of the new heat-capacity data in interpretation of the nature of water’s anomalies are discussed.

1. Introduction

Liquid water exhibits anomalous behavior in the supercooled region, as manifested by the growth of the isothermal compressibility and isobaric heat capacity [1]. A popular hypothesis to explain supercooled water’s anomalies is the existence of a metastable liquid-liquid transition terminating at a critical point [2–5]. The hypothesized phase transition is not directly accessible in a bulk experiment because it is presumably located a few degrees below the kinetic stability limit of the liquid phase at about 233 K, the temperature of homogeneous ice formation [6, 7]. Inevitably, verifications of this hypothesis are usually based on extrapolations of the anomalies observed in the experimentally accessible region [8–11].

The liquid-liquid coexistence, terminated at a critical point, has been reported for some atomistic water models (see review [5]), most notably in molecular simulations of the ST2 model of water [12–14], but also in TIP4P/2005 model [15–17]. However, in simulation of some other models of water, such as mW [18] no liquid-liquid transition was found. The situation in real supercooled water is much less certain. While the hypothesis of the metastable liquid-liquid separation has been proved useful for building an equation of state and accurate
describing the thermodynamic anomalies in the experimentally accessible region, these results cannot unambiguously confirm or reject the underlying hypothesis. Thus, only further, more comprehensive and accurate experiments on deeply supercooled water could provide more robust and reliable information on the nature of water’s anomalies and the existence of a metastable critical point.

One of the most informative thermodynamic property is the isobaric heat capacity, $C_P$. An anomaly of $C_P$ is an indication of growing fluctuations of entropy, $\delta S$, since $\langle (\delta S)^2 \rangle = k_B C_P$ (where $k_B$ is Boltzmann’s constant). The first adiabatic heat-capacity measurements in supercooled water were reported by Anisimov et al. in 1972 [19]. The degree of supercooling was very modest, $\sim 7$ K, however, the data clearly demonstrated the growth of the heat capacity in metastable liquid water upon supercooling. A year later, in a breakthrough experiment, Angell et al. [20] (further improved and summarized in ref. [21]) were able to supercool water, emulsified in heptane, down to 239 K. Using a differential scanning calorimeter (DSC), they discovered a spectacular growth of the heat capacity of metastable water upon supercooling. Some limited DSC data for supercooled water were also reported by Bertolini et al. in 1985 [22]. In 2000, Archer and Carter [23], also using a DSC and emulsified water, qualitatively confirmed the results of Angell and co-workers, however, the discrepancy between the two sets of data were not insignificant.

While a DSC method has certain advantages, being fast and sensitive [24], in investigations of phase transitions and critical phenomena, unlike adiabatic calorimetry [25–27], it may not be sufficiently accurate because of long thermal equilibration. In 1999, Tombari et al. [28] measured the isobaric heat capacity of bulk supercooled water (down to 244.8 K) in 10 ml glass ampules with an adiabatic calorimeter. The reported data significantly deviate from those obtained by a DSC method.

In this work, we revisit this problem and present the results of high-resolution adiabatic calorimetry measurements of cold and supercooled liquid water in the range from 294 to 244 K, the lowest temperature of water’s supercooling achieved so far in a bulk adiabatic-calorimetry experiment (0.8 K below the temperature achieved by Tombari et al. [28]). While the results are basically consistent with the data reported by Tombari et al., the resolution of our measurements is record-high, with the statistical (random) error of about 0.1%. Remarkably, the results of the both adiabatic calorimetry measurements significantly deviate from differential-scanning calorimetry measurements in water (emulsified in heptane) reported by Angell et al. [21] and, even more significantly, from the data reported by Archer and Carter [23]. Consequences of the new heat-capacity data in interpretation of the nature of water’s anomalies are discussed.

2. Experimental technique and measurement procedure
The isobaric heat-capacity measurements of cold and supercooled water were performed with a high-resolution slow-scanning adiabatic calorimeter. This calorimeter was previously used for studies of phase transitions and critical phenomena in liquid crystals [29], polymers [30], fluids and fluid mixtures [31], gas hydrates [32] and in porous media [33,34]. The adiabatic calorimeter enables one to measure the heat capacity, heats of phase transitions, and estimate a relaxation time of achieving thermal equilibrium. The measurements can be carried out upon heating or cooling, in a temperature-step regime or in a slow-scanning regime [25]. All the results reported in this work were obtained in the scanning regime. The chosen temperature rate was determined on required adiabatic conditions.

The measurements were performed under saturated vapor pressure in the range 0.05-0.7 kPa in sealed glass ampules containing 1 ml dust-free, air-free water for medical injections (Microgen, Irkutsk, Russia). In this range of saturated vapor pressure a correction to the isobaric heat capacity of water is negligible [27]. The samples were stored in a freezer for a week. Only in a small fraction of the stored ampules (further used for the measurements) water remained liquid
at \( \approx 245 \, \text{K} \) (\( \approx -28^\circ \text{C} \)).

A custom-made calorimetric cell (a cylinder, 12 mm diameter) was made of a 0.1 mm copper film (0.1 mm thickness). The ampules and cell are shown in figure 1. The temperature was measured with a platinum-film (100 \( \Omega \) resistance) thermometer HEL-705-T-1-12, placed on the external surface of the cell. After completing the measurements, used ampules were broken and dried, then the mass and heat capacity of an empty ampule were measured in order to obtain the mass and specific heat capacity of studied water.

The heat-capacity measurements of supercooled water started to be carried out in the regime of slow heating from the initial temperature 243.25 K, at which the calorimeter was set for a few hours to establish thermal equilibrium, while avoiding crystallization. We note that the thermal equilibrium should not be confused with global thermodynamic equilibrium because the supercooled water is thermodynamically metastable.

We divided the temperature range of the measurements in 5 narrow intervals, as illustrated in figure 2, for accurately estimating the heat losses to be compensated to establish adiabatic conditions. Within each interval the estimated heat loss was linearized. The temperature scan for each interval started at a “star” point at a thermally nonequilibrium condition. The equilibrium heat-capacity data were collected upon heating from a low temperature after the system reached a stationary quasi-adiabatic regime. If the stationary adiabatic runs obtained in different intervals were overlapping, the data were considered as reliable.

3. Results and discussion
The results of our measurements, together with the data reported earlier, are shown in figure 3. All the data demonstrate that the isobaric heat capacity of supercooled water exhibits a striking anomaly with an apparent tendency to a “divergence” or to a sharp maximum at a temperature beyond the kinetic stability limit of liquid water. However, a closer look reveals significant deviations between the results obtained by DSC and adiabatic-calorimeter measurements. The DSC data, especially those obtained by Archer and Carter [23], are systematically lower than the data obtained with slow-scanning adiabatic calorimeters. Contrarily, the adiabatic measurements are mutually consistent. However, the average statistical error (standard deviation) in our measurements over the studied range of temperatures is lower and the achieved supercooling is deeper. An empirical approximation of the heat capacity anomaly, suggested by the International Association for the Properties of Water and Steam (IAPWS-95), is also shown in figure 4 (solid curve). This approximation is, in fact, a fit to the data of Angell et al. [21]. A comprehensive description of supercooled water’s anomalies, suggested by Holten et al. [11] and

![Figure 1. Calorimetric cell with an ampule.](image-url)
Figure 2. Establishing stationary quasi-adiabatic regimes in slow-scanning adiabatic calorimetry measurements. The stationary adiabatic data obtained in different runs are overlapping.

in 2015 recommended by IAPWS as a guideline for supercooled water (see ref. [35]), predicts a heat-capacity divergence at 228.2 K, while the \( C_p \) curve in the experimentally accessible region closely follows the shape of IAPWS-95.

On the other hand, the results of our adiabatic measurements and the data of Tombari et al. [28]; significantly deviate from the DSC data and from approximations based on these data.

To clarify the shape of the observed anomaly, we approximated all available adiabatic calorimetry data obtained for cold and supercooled water. The fitting results are demonstrated in figure 4. We tried an empirical power-law divergence at a temperature \( T^* \) (located below the kinetic stability limit of liquid water):

\[
C_p/R = A \left( (T - T^*)/T^* \right)^{-n} + B \left( T/T^* \right) + C,
\]

where \( R \) is the universal gas constant. We obtain a surprisingly good fit (\( \chi^2/\text{DoF} \approx 0.03 \)) with \( A \approx 0.16, B \approx 1.68, C \approx 6.37, \) and \( n \approx 0.89 (\pm 0.19) \). The extrapolated temperature of the apparent divergence of the heat capacity, \( T^* \approx 233.31 (\pm 1.20) \) K appears to be close to upper bound of “no-man’s” region, and higher than the temperature of the heat-capacity maximum at about 228 K, predicted by a two-structure equation of state, which estimates the hypothesized liquid-liquid critical point at an elevated pressure [10] or a divergence at 228.2 K if the critical point is at zero pressure [11]. However, this apparent “divergence” in no way can be regarded as an evidence of the existence of a liquid-liquid transition and hypothesized criticality in supercooled water because the extrapolation is made from the region too far away from a possible heat-capacity divergence or maximum. The analysis of supercooled water’s anomalies made with scaling [8,9] and two-structure models [10,11] show that an effective power low as a reasonable approximation only in a narrow range of temperatures. A more reliable temperature of the heat-capacity divergence (if the measurements are assumed to be performed along the critical isobar) or a temperature of the heat-capacity maximum (if the isobar is assumed to be not critical) could be obtained only from a comprehensive and thermodynamically consistent analysis of all water’s anomalies at much deeper supercooling.
Figure 3. Isobaric heat capacity (per mole) of cold and supercooled water. Shown together with new data: Anisimov et al. [19], Angell et al. [21], Archer and Carter [23], Tombari et al. [28] and Bertolini et al. [22]. Solid curve is IAPWS-95 (see ref. [9]).

Figure 4. Approximation of the adiabatic heat-capacity measurements in supercooled water by an empirical power law (1). Deviations of experimental data from the fit are shown as the insert.

4. Conclusion
Adiabatic-calorimetry measurements under much deeper supercooling are needed to unambiguously establish the shape of the heat-capacity anomaly in supercooled water. To achieve this goal, one may need to significantly reduce (down to milligrams) the amount of...
waters samples. A collection of microcapillary samples or long-lived emulsified water could be considered as promising candidates. Upon further progress in calorimetric measurements, the new data may require a reconsideration of the thermodynamic description of supercooled waters anomalies, in particular, if the concept of a hypothesized metastable liquid-liquid transition is used for the construction of an equation of state.

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