Temperature independence of the heat capacity of liquid water at atmospheric pressure

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Abstract. Debye temperature and Frenkel temperature of liquid water at atmospheric pressure are estimated from the modified phonon-polariton model. Moreover, the decrease in the Debye temperature and the increase in the Frenkel temperature as rising temperature are pointed out. The heat capacity of liquid water is given by the phonon theory reported in 2012, covering both classical to quantum regimes for both the motion of phonon polariton and the diffusion motion of particles. Because the ratio between temperature and the Debye temperature varies from 0.8 to 1.5, leading to the temperature independence of the heat capacity of liquid water at atmospheric pressure, in agreement with experimental work.

1. Introduction
Heat capacity of liquid water is considered to be an important parameter because it could reveal information about water microdynamics such as molecular motion, hydrogen bonding, and the interaction between particles. Although research into anomalous features of liquid water attracts a great attention with significant accomplishments, the micro-thermodynamic mechanism in relation to the temperature independence of the heat capacity of liquid water at atmospheric pressure has not been clearly understood [1–3].

The interaction between water molecules in liquid phase is a bit strong due to the hydrogen bonding. Therefore, it is impossible to apply theories of gases for liquid water. In fact, there are the collective density oscillations of particles as well as the diffusion motion in the system. It is necessary to interest in the vibration around the equilibrium sites of the water molecules as well as their interaction, i.e., the collective dynamics.

The phonon theory covering both the classical and quantum regimes for the phonon motion and the diffusion to calculate the heat capacity for liquids was built in the work of D. Bolmatov et.al. [1]. However, the term "Debye temperature" of liquid water at atmospheric pressure was not still known before 2015 [4]. Therefore, the authors could not interpret the temperature independence of the heat capacity of liquid water at that time.

According to the literature, the structure of liquid water is quite close to that in the glass phase with chains of tetrahedral shapes [5]. Moreover, its collective dynamics on the energy scale from 0 to 30 meV has just been clarified by phonon-polariton theory [6]. Information about the Debye temperature of liquid water under atmospheric pressure can be revealed by this model. Thus, the temperature independence of the heat capacity of liquid water under air conditions could be illuminated.
In this work, the Debye and the Frenkel temperatures of liquid water at atmospheric pressure are estimated from the modified phonon-polariton model. The changes in the values of both the temperatures are also considered carefully. In addition, the phonon theory reported in Ref. [1] is used to determine the heat capacity of liquid water. According to the change in the Debye temperature and the Frenkel temperature given from the phonon-polariton theory, the thermodynamic mechanism in relation to the temperature independence of the heat capacity of liquid water at atmospheric pressure is pointed out.

2. Phonon polaritons of liquid water at atmospheric pressure

It is widely acceptable that phonon is supported in solid state. Due to the special structure very close to the hydrogen bonding network of glassy phase, phonons could be appeared and propagate in the liquid water at high enough frequencies $\Omega > \omega_F$ \cite{5} ($\omega_F$ - Frenkel frequency). Indeed, the dynamics of liquid water at high frequencies seem to be related to the process of structural relaxation, where the forming and the breaking of the hydrogen bonds with a characteristic time $\tau = 1/\omega_F \approx 1 \text{ ps}$ \cite{7,8} occur. The collective oscillation whose frequency satisfies the condition $\Omega \tau < 1$ could be sensible with the rearrangement of the hydrogen bonding network arisen from the reorientation as well as the self-diffusion of each molecule. Liquid water system is regarded as in the hydrodynamic regime. As a result, only longitudinal vibration is supported. Inversely, as $\Omega \tau \geq 1$, neither the orientation nor the self-diffusion could happen. Therefore, the system seems to be in the glass-like regime. In this situation, both the longitudinal and the horizontal collective vibrations could travel on the hydrogen bonding network \cite{5}. It means that the shear phonons could be supported in liquid water as $\Omega \geq \omega_F$.

Figure 1. Dispersion of the collective vibrations in liquid water in the modified phonon polariton model against wave vector $Q$: the upper solid curve for the fast sound mode and the lower one for the common sound wave. The dot-dashed line exhibits the dispersion of the transverse phonons with energy $\hbar \omega_T$. The diamond symbols display the data of IXS in Ref. \cite{12}, the full circle symbols correspond to the data from INS in Ref. \cite{11}, and open triangles are data in Ref. \cite{7}.

When excitations in high enough energies such as photons of X-ray or neutrons with high velocity are brought into interaction with the liquid water, shear phonons will appear, propagating on the hydrogen bonding network. Note that the water molecule is a polar one. It is reasonable to consider that liquid water is a plasma. Plasmon frequency of liquid water has ever estimated, about $10^{12}$ Hz \cite{9}. The vibration of dipoles arisen from the propagation of collective density oscillations could radiate a local electromagnetic field with frequency in the THz scale whose wavelength is approximate $10 \mu$m and it is much larger than the inter-molecular distance (about 2.8 Å \cite{9}). The interaction between the traverse sound wave and the local electromagnetic
field could happen, leading to the presence of the high-energy mode (fast sound mode or strong
dispersion mode) and the low-energy one (dispersionless mode or common sound mode) traveling
in liquid water that have been widely recognized in both empirical and theoretical works [10–13],
in similar to that taking place in semiconductor materials. According to the phonon-polariton
theory, the dispersion relations of both the collective density oscillation modes \( \Omega_{\pm}(Q) \), \( \Omega_{+}(Q) \)
for high energy mode and \( \Omega_{+}(Q) \) for low-energy mode, against the wave vector \( Q \) for liquid
water [6] take the forms

\[
\Omega_{\pm}^2(Q) = \frac{1}{2} \left( \frac{c^2}{\varepsilon_{\infty}} \right) Q^2 + \omega_L^2 \pm \sqrt{\left( \frac{c^2}{\varepsilon_{\infty}} \right) Q^2 + \omega_L^2} \pm \left[ \left( \frac{c^2}{\varepsilon_{\infty}} \right) Q^2 + \omega_L^2 \right]^2 - 4 \left( \frac{c^2}{\varepsilon_{\infty}} \right) Q^2 \omega_L^2 \right]^{1/2},
\]

where \( \varepsilon_{\infty} \) is the dielectric response of liquid water at high frequency, \( c \) is the speed of photons in
vacuum, \( \omega_L \) and \( \omega_T \) are the longitudinal and the transverse resonance frequencies of collective
density vibrations in liquid water, respectively.

According to expression [1], in the low-\( Q \) limit, the upper branch \( \Omega_{+}(Q) \) reaches to \( \omega_L \) while
the lower branch exhibits the linear regime,

\[
\Omega_{-}(Q) = v_s Q,
\]

where \( v_s \) is the speed of the ordinary sound wave. As \( Q \to \infty \) the lower branch \( \Omega_{-}(Q) \) tends to
\( \omega_T \) whereas the other is a linear function of the wave vector

\[
\Omega_{+}(Q) = v_f Q,
\]

in which \( v_f \) is the speed of the fast sound. Combining expression [1] with the experimental data
of IXS [12] and INS [7,11] of water at atmospheric pressure and at room temperature where
\( \omega_L = 6.8 \) meV, \( \omega_T = 5.6 \) meV, and \( h v_f = 20 \) meV/Å\(^{-1} \) (\( v_f \approx 3050 \) m/s and \( h \) is the Plank
constant), a quite good agreement between theory and experiment was given. Moreover, the
ratio of \( v_f/v_s \approx 2 \) was automatically obtained, in similarity with the result in previous works. A
correlation between electrodynamics and collective density oscillation phenomenon is exhibited
in liquid water: a pressure wave could produce an alternating electric field and vice-versa.

3. Debye temperature of liquid water at atmospheric pressure

Phonon polaritons could travel in the continuous medium as the wavelength of the photon is
much larger than the lattice constant of the sample. Therefore, there is a maximum frequency
of the phonon polaritons called Debye frequency. According to the Debye theory [14], the Debye
frequency combines with the Debye temperature \( \Phi_D \) by

\[
\Phi_D = \frac{\hbar \omega_D}{k_B},
\]

where \( k_B \) is Boltzmann constant. It was accepted that the Debye temperature of ice depends
on temperature, increasing from about 222K to 300K [15,16] as rising temperature from
approximately zero to about 100K. However, the Debye temperature of liquid water at
atmospheric pressure [3] is still not known.

In the glass-like regime (\( \Omega \geq \omega_F \)), besides the propagation of the longitudinal collective
vibration, both the common and the fast sound modes could travel on the hydrogen bonding
network. The propagation length \( d \) of the collective density mode with speed \( v_f \) given by
equation \( d = v_f/\Omega_{+}(q) \) [6]. Both the collective modes could travel in the system with the
propagation length \( d \) larger than the intermolecular spacing \( a \). When \( d \approx a \), \( \Omega_{+}(Q) = \omega_D \),
corresponding to the Debye wave vector \( Q_D \). According to experimental works [7,11,12], the
wave vector $Q_D$ is about $1.2 \, \text{Å}^{-1}$ that is almost independent of the temperature. The Debye frequency of liquid water is given from the dispersion relation of the high-energy mode (3)

$$\omega_D = v_f Q_D.$$  

(5)

Due to the decrease in the speed of fast sound versus temperature ($Q_D$ holds constant), the Debye frequency will decrease as temperature increases. In more detail, $\omega_D \approx 24.00 \, \text{meV}$ at 293K but $\omega_D \approx 21.48 \, \text{meV}$ at 333K [17]. As a consequence, the Debye temperature of liquid water at atmospheric pressure reduces with the increase in temperature. For example, $\Phi_D \approx 278 \, \text{K}$ at 293K and $\Phi_D \approx 249 \, \text{K}$ at 333K.

The decrease in the Debye temperature originates from the decrease in the shear module $M$ of liquid water at high frequency as temperature increases. Indeed, $v_f = \sqrt{M/\rho}$, where $\rho$ is the water density. The increase in temperature makes the strength of the hydrogen bonding between water molecules weaker while the density of the water mostly holds constant. Therefore, under the action of the sound pressure, the transverse displacement $\Delta x$ of water molecules increases. Because $M$ is proportional to $1/\Delta x$, the shear module $M$ reduces as rising temperature, resulting in the decrease in the speed of fast sound.

4. Temperature independence of the heat capacity of liquid water at atmospheric pressure

As mentioned above, the collective dynamics of liquid water consists of a single longitudinal branch and two transverse modes. The two shear modes could travel on the hydrogen bonding network with the spectrum range from $\omega_F$ to $\omega_D$ whereas the spectrum of the longitudinal mode is from zero up to $\omega_D$. The heat capacity of liquid water at atmospheric pressure can be estimated by the phonon theory that covers both the classical and quantum regimes for the phonon motion and the diffusion of the particles of liquids reported in Ref. [1].

Indeed, the inner energy of water is given by

$$E = E_l + E_s,$$

(6)

in which $E_l$ and $E_s$ are the energies of the longitudinal mode and the shear modes, respectively. Although there is the diffusion of water particles, the phonon polaritons’ motion is still dominated in the system. Thus, the energy in relation to the diffusion motion could be neglected.

The energy of longitudinal collective mode is defined by the expression

$$E_l = \int_0^{\omega_D} d\omega g_l(\omega)n(\hbar \omega)\hbar \omega$$

(7)

where $g_l(\omega) = 3N\omega^2/\omega_D^3$ ($N$ - the water molecule number) is the density of state and $n(\omega)$ is the number of phonons with energy $\hbar \omega$. Because phonon polaritons are boson particles, they obey Bose–Einstein statistical function. The energy of the longitudinal mode for liquid water is totally determined by Eq. (7)

$$E_l = NT (\frac{\hbar \omega_D}{T}),$$

(8)

in which $D(\hbar \omega/T)$ is the third Debye function.

Analogously, the energy of both the shear modes is also given

$$E_s = 2NT \{D(\frac{\hbar \omega_D}{T}) - (\frac{\omega_F}{\omega_D})^3 D(\frac{\hbar \omega_F}{T})\},$$

(9)
Figure 2. The heat capacity of liquid water at atmospheric pressure against temperature is presented by the solid line, in agreement with experimental data (open circles) [18]. Below 273.15 K (on the left side of the dotted vertical line), the heat capacity of ice increases versus temperature: square symbols - data [20] and the dashed line - fitting result.

where the density of state $g_s(\omega) = 6N\omega^2/\omega^2_D$ with $2N$ for the normalization of the number of shear modes.

Because $C_v = \frac{dT}{dT}$, it is easy to give the heat capacity of liquid water

$$C_v = 9Nk_B \left( \frac{T}{\Phi_D} \right)^3 \int_0^{\Phi_D/T} \frac{e^{x^4}x^4}{(e^x - 1)^2} dx - 6Nk_B \left( \frac{\omega_F}{\omega_D} \right)^3 \left( \frac{T}{\Phi_F} \right)^3 \int_{\Phi_F/T}^{\Phi_D/T} \frac{e^{x^4}x^4}{(e^x - 1)^2} dx,$$

(10)

where $\Phi_F = \hbar \omega_F/k_B$ is the Frenkel temperature.

The heat capacity of liquid water depends on both the ratios of $T/\Phi_D$ and $T/\Phi_F$. According to the information about the Debye temperature extracted from the modified phonon polariton theory, the temperature independence of the heat capacity of liquid water at atmospheric pressure can be interpreted. At atmospheric pressure, despite of the fact that the Debye temperature decreases with the increase in temperature, the ratio of $T/\Phi_D$ varies from 0.8 to 1.5. Therefore, the value of the first term holds mostly constant versus temperature form 273.15 K to 373.15 K.

According to the experimental data, the Frenkel frequency, at which the splitting of the shear modes from the longitudinal mode happens, changes a little versus temperature and it is significantly smaller than the Debye frequency. Rising temperature leads to the decrease in the relaxation time [7,8] resulting in the increase in the Frenkel frequency $\omega_F$. However, the Frenkel frequency $\omega_F$ is about meV [12,13] and $\omega_F < \omega_D$. Moreover, the ratio of $T/\Phi_F$ is always larger than 1. Thus, the value of the second term in Eq. (10) is extremely small in comparison to the first term. It also holds constant with the variation of temperature. As a consequence, the heat capacity of liquid water is almost independent of the temperature (Fig. 2), in accordance with experimental observation [19].

It was shown that the heat capacity of ice increases as temperature increases [20] and it is always smaller than the heat capacity in liquid phase (representing on the left side of the dotted line in Fig. 2) at atmospheric pressure. Indeed, although the Debye temperature of ice increases with rising temperature, the ratio of $T/\Phi_D$ always increases and it is significantly smaller than 1. As a result, increasing temperature makes the heat capacity of ice increase. Inversely, the ratio of $T/\Phi_D$ of liquid water is about 1 or larger, resulting in the constant value of heat capacity. It is well-known that ice is less dense than liquid water, i.e., the intermolecular spacing $a$ of liquid water is smaller than that in ice. Therefore, the Debye temperature of liquid water could be significantly higher than the Debye temperature of ice, leading to the difference between the
heat capacity characteristic of liquid water and that of ice. Moreover, the heat capacity of liquid water at high pressure decreases as temperature increases [1], differing from its temperature independence at atmospheric pressure. It is possible that the strong decrease of the ratio $T/\Phi_D$ versus temperature makes the heat capacity of liquid water at high pressure reduce.

5. Conclusions

According to the modified phonon polariton model that describes the dispersion of collective density oscillations in liquid water, the Debye temperature for liquid water at atmospheric pressure is estimated, decreasing as rising temperature. The heat capacity of liquid water is therefore given by the phonon theory reported in Ref. [1] for both the motion of phonon polariton and the diffusion motion. Because the ratio between the temperature of liquid water and Debye temperature changes from 0.8 to 1.5, the heat capacity of liquid water is almost independent of the temperature.

Recently, the collective density oscillations in the hydration water of biomolecules have been observed via the coherent neutron scattering [21], in similarity to that of pure liquid water. It means that the thermodynamic mechanism responsible for the temperature independence of the heat capacity of hydration water in living systems could be understood as that reported in this research.

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