Thermodynamic Behavior of Water from Soft-Cell Theory

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Abstract

A soft-cell concept is introduced into cell theory to describe the deformable nature of water. The intermolecular vibration energy of water derived from soft-cell theory is applied to a simple energy model to explore hydrogen-bonding and associated thermodynamic properties. This study is able to accurately predict the temperature and pressure dependences of hydrogen-bonding in water and explains the distinctive thermodynamic behaviors of water in relation to hydrogen-bonding energy and intermolecular vibration energy.

Keywords: Soft-cell theory; cell theory; hydrogen bond; intermolecular vibration; specific heat; entropy; water.

1. Introduction

Water is well known as one of the most important materials on earth, as it functions as a solvent in biological systems as well as in industries. Water is also a prominent factor in affecting the global climate since the transitions of its three primary phases take place actively and over 70 % of the earth's surface is covered with water. It is also commonly recognized that water is hydrogen-bonded and, because of its hydrogen-bonds, water has a number of distinctive physical properties, such as its large specific heat and heat of vaporization.

Throughout the years, water science has drawn much attention from scientists and engineers. Theoretical approaches such as kinetic theory (Frenkel, 1955), molecular dynamics (Luzar & Chandler, 1996; Yagasaki & Saito, 2008), Monte-Carlo simulation (Kalinichev & Bass, 1997), quasichemical analysis (Asthagiri, Pratt & Kress, 2003), density functional theory (Nygård et al., 2006) and cell theory (Eads, 2002; Hemchman, 2007; Klefas-Stennett & Henchman, 2008; Truskett & Dill, 2002), as well as experimental techniques such as IR spectroscopy (Luck 1967), Raman spectroscopy (Bergmann et al., 2007; Carey & Korenowski, 1998; Castner, Chang, Chu & Walrafen, 1995; Walrafen, Fisher, Hokmabadi & Yang, 1986; Wernet et al., 2004), X-ray absorption spectroscopy (Wernet et al., 2004; Smith et al., 2006), and Kerr effect (Castner et al.,1995; Palese, Schilling, Miller, Staver & Lotshaw, 1994) are employed to investigate the local structure of water, its dynamic behaviors, thermodynamic properties, optical properties, and so on. Among these studies, cell theory interprets the molecular motion of each water molecule as an oscillator vibrating in a restricted space, or "cell", without interference by other molecules. Some of the advantages of this model are that it gives a physically comprehensive picture for the dynamical behaviors of water and it qualitatively explains water's physical phenomena. Most often, cell theory also offers analytical expressions for thermodynamic functions in a simple and meaningful way. On the other hand, since cell theory places a simplified picture on water structure, it has to sacrifice microscopic resolution by introducing effective potentials and it is somewhat unrealistic because water in liquid-state is deformable. In view of the deficiency of the lattice assumption for liquids in cell theory, a variable cell description of water's structure is presented to account for the structural complexity of water arising from water's hydrogen-bond network. For example, Truskett & Dill (2002) adapted a variable-structure cell approach with three allowable cell types to develop a 2-D statistical model of water, classifying each cell as one of the three types at a given instant. In this way, and with properly chosen potentials, cell theory is able to generate reasonable predictions for thermodynamic properties. Being a useful tool in condensed-matter physics, cell theory usually cooperates with other models for complex-liquids research. Eads (2002) developed a lattice fluid model for water introducing a quasichemical approximation to estimate the ratio of the number of intacting hydrogen-bonds to broken bonds. Thermodynamic functions and the volumetric behavior of water are successfully predicted by this quasichemical lattice fluid model.

To account for the fact that water is deformable or "soft" at liquid-state, this study modifies the cell (*i.e.* lattice frame) assumption in the cell theory. Since this study is intended as an improvement to cell theory by considering the "soft" nature of liquids, the proposed model is called soft-cell theory. The fundamental concept of soft-cell theory is similar to the traditional cell theory, which regards molecules at liquid-state as oscillators in the wall-spring-mass system, except that the "wall" of the oscillation system in soft-cell theory is no longer fixed but instead vibrates correspondingly with respect to the vibrating molecule in the cell. As a first approach based on soft-cell model, this study emphasizes the research of liquid-water from the viewpoint of intermolecular vibration dynamics.

In this study, the intermolecular vibration energy of water is formulated analytically via soft-cell theory and then expressed empirically based on the numerical results of the model to utilize its application in various areas. The unusually large specific heat of water is attributed to two kinds of energetic components in water: intermolecular vibration energy and hydrogen-bonding energy. Interesting findings on water hydrogen-bonding and heat of vaporization are discussed in this study. A simple but meaningful expression for water entropy is presented.

2. Theoretical Basis

Cell theory for liquids typically assumes that molecules are confined in rigid cells and the motions of molecules in different cells are mutually independent. Since liquids are not as "structured" as solids, the present model accommodates the deformable feature of water by introducing a moving-wall concept into the wall-spring-mass system of cell theory. To say that the wall in the wall-spring-mass system is moving is equivalent to saying that the oscillations between molecules are constrained, or "softened", by intermolecular interactions with neighbor molecules, which are oscillating simultaneously. Similar to cell theory, water molecules within cells are assumed to be harmonic oscillators resembling the classical wall-spring-mass system, while intermolecular interactions arising from higher order terms of derivatives of potential energy are modeled by moving-walls, as shown in Figure 1 (a).
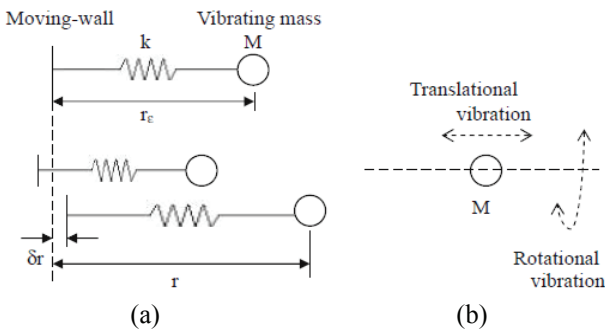

Figure 1. (a) The moving-wall-spring-mass system for soft-cell model; (b) a schematic of two kinds of intermolecular vibrations.

Basic assumptions for soft-cell theory are as follows. First of all, the adiabatic approximation for electronic structure is assumed, *i.e.* electrons remain at ground state. Secondly, water molecules are assumed to be internally unexcited in vibration, so that the contributions from intra-molecular vibrations are neglected. Thirdly, the intermolecular vibration energy of the system can be decomposed into six effective potentials for six degrees of freedom: three for intermolecular translational vibrations and three for intermolecular rotational vibrations. Finally, the cell walls are assumed to vibrate correspondingly and elastically with respect to the molecular motions within each cell and are effectively described by elastically vibrating walls in each degree of freedom for the wall-spring-mass system. Following the assumption of intermolecular vibrations in six independent degrees of freedom, the effective characteristic frequencies are independent of one another, and so are the spring constants in the moving-wall-spring-mass system. The term translational or rotational "vibration" denotes that the motion of molecules, in the condensed state, is of two kinds of hindered (restricted) vibration: hindered translational vibration and hindered rotational vibration, as shown in Figure 1 (b). To better understand the dynamics of water molecules subject to intermolecular forces, it is beneficial to begin with water molecules at gaseous state. For example, at 373.15 K and 1 atm, a water molecule in gaseous-state at thermal equilibrium possesses translation energy and rotational energy, while the intra-molecular vibration mode mostly stays unexcited and the intermolecular potential energy is nearly absent. In this case, the motion of a water molecule can be considered to be free, *i.e.* unhindered, motion and the translational/rotational mode of molecular motion does not exhibit "vibration-like" behavior. When the water molecule becomes confined in liquid-water, however, the translational/rotational mode of molecule motion is no longer unhindered. Instead, the translational mode as well as rotational mode of molecular motion in the presence of intermolecular potentials in liquid-water appear as hindered translational vibrations and hindered rotational vibrations. A brief review of studies on hindered vibrations of condensed-state water can be found in an intermolecular vibration study of lattice ice by Wang & Brewster (2010).

Following similar procedures performed in the wall-spring-mass system for the traditional cell theory, the displacement x_i of a water molecule in each dimension becomes

$$x_i = \left(r - \delta r - r_\varepsilon\right)_i, \qquad (1)$$

where i=1~3 are for intermolecular translational vibrations, i=4~6 for intermolecular rotational vibrations, δr the displacement of the moving-wall, and r_ε the location of water molecule at mechanical equilibrium. The elastic moving-wall statement immediately correlates δr with x: $\delta r = bx$, where b is a positive constant while the sign of δr alternates as the molecule moves back and forth. The idea of the elastic-vibration assumption is to make each cell restore to its initial states after a vibration cycle under thermodynamic equilibrium conditions, so that the microscopically deformable liquid water maintains its bulk state macroscopically. For each cell, in the view of the wall-spring-mass system, the interactions from other cell units are effectively included in the intermolecular potential that acts on the mass through the vibrating-wall and spring, and the thermodynamic characteristics of water are represented in a cell. With the soft-cell effect, or b effect, the characteristic frequency for a degree of freedom is represented as

$$\left(\nu_s\right)_i = \left(\frac{\nu}{\sqrt{1+b}}\right)_i, \qquad (2)$$

where ν and ν_s are the characteristic frequencies in the wall-spring-mass system and moving-wall-spring-mass system, respectively, and the subscript s indicates soft-cell model. For translational vibrations, each ν is subject to the corresponding force constant k_M and mass M; while for rotational vibrations, each ν is subject to the corresponding torque constant k_I and moment of inertia I (Henchman, 2007),

$$\nu_{i=1\sim3} = \left(\frac{1}{2\pi}\sqrt{\frac{k_M}{M}}\right)_{i=1\sim3} ; \quad \nu_{i=4\sim6} = \left(\frac{1}{2\pi}\sqrt{\frac{k_I}{I}}\right)_{i=4\sim6} . \qquad (3)$$

Since the characteristic frequencies of intermolecular vibrations of water molecules are associated with the force/torque constants, these frequencies contain the information of intermolecular interactions arising from intermolecular forces, such as the Coulomb forces and the van der Walls attraction. In the literature, the intermolecular vibration frequencies for water are found to be smaller than those of ice (Bertie, Labbe & Whalley, 1968, 1969; Bertie & Whalley, 1964, 1967; Carey &

Korenowski, 1998; Castner et al., 1995; Palese et al., 1994; Prask, Boutin & Yip, 1968; Walrafen et al., 1986). This is described in the present model by the b effect. The characteristic vibration frequency ν_s from soft-cell theory is reduced by a factor of $1/(1+b)^{1/2}$ as compared to the frequency in cell theory. The averaged kinetic energy (KE) of the system is obtained through the integration of kinetic energy over a complete vibration cycle inside a cell, giving

$$\left\langle KE_s \right\rangle_i = \left(\frac{1+b}{2+b} \right)_i (E_s)_i . \qquad (4)$$

Since the soft-cell theory does not explicitly contain hydrogen-bonding information at this point, the expression for the potential energy of the system is to be further formulated in a simple water energy mode in the next section.

Letting $h_s = \dfrac{h}{\sqrt{1+b}}$, the eigen energy in the Schrödinger equation for each vibration mode i then appears in the same form as that in the wall-spring-mass system,

$$\left(E_{s_v} \right)_i = \left[h_s \nu_s \left(v + \frac{1}{2} \right) \right]_i , \ v = 0,\ 1,\ 2,\ 3\ ... \qquad (5)$$

Therefore, one may regard that the Planck constant is effectively reduced by the b effect. The total intermolecular vibration energy (Sonntag & Van Wylen, 1966), composed of intermolecular translational and rotational vibration energies, is

$$E_s = \sum_{i=1}^{6} (E_s)_i = \sum_{i=1}^{6} \left(\frac{1}{2} h_s \nu_s + \frac{h_s \nu_s}{e^{h_s \nu_s /kT} - 1} \right)_i . \qquad (6)$$

The b's for each intermolecular vibration mode can be calculated by

$$(b)_i = \left(\frac{\nu}{\nu_s} \right)_i^2 - 1 . \qquad (7)$$

Water Energy Model

To investigate hydrogen-bonding information and the related thermodynamic properties, a simple energy model for water is presented as

$$H = (KE) + (PE) + (Pv), \qquad (8)$$

showing that the enthalpy H is comprised of kinetic energy, potential energy, and (Pv) work. Water molecules at gaseous-state are treated as ideal gas so that (PE) is dropped. Furthermore, it is assumed that the translational and rotational kinetic energies are fully exited while intra-molecular vibration mode remains unexcited as the temperature range in this study is below critical and extreme pressure conditions are not considered. The total energy for gaseous H_2O is

$$H_g = 3RT + (Pv)_g , \qquad (9)$$

where R is the universal gas constant and the subscript g refers to gaseous-state.

For liquid H_2O, the hydrogen-bond enthalpy H_{HB} is introduced to account for (PE) and the b effect is applied to formulate (KE), which includes intermolecular translational and rotational vibration energies. It is a rather difficult task to separate hydrogen-bonding energy from other types of intermolecular vibration energy because the intermolecular vibrations of liquid-water molecules are under the influence of the potential field by hydrogen-bonds. The hydrogen-bonding energy, however, does not explicitly manifest itself unless the hydrogen-bonds are broken such that it is released in other forms, like latent heat of vaporization, for instance. In other words, the soft-cell model alone is not sufficient in obtaining the information of hydrogen-bonds in liquid-water, although hydrogen-bonds surely contribute to intermolecular potentials. As a result, two steps are taken to formulate the hydrogen-bonding information. First, the averaged kinetic energy for intermolecular vibrations is obtained based on *spectroscopic* data for intermolecular vibration bands of liquid-water. Secondly, the information of hydrogen-bonding is introduced into the model through a simple energy model for water and the averaged number of hydrogen-bonds in liquid-water is calculated based on *steam table* data. Efforts are made here to distinguish hydrogen-bonding energy from the averaged kinetic energy. This makes it possible to include the information of the "soft" nature of liquid-water in the averaged kinetic energy term and contain the information of hydrogen-bonding in the potential energy term. Similar to the gaseous H_2O case, the contribution of intra-molecular vibration energy is not taken into account. The same value of H_{HB} is used for each hydrogen-bond throughout this study. Liquid H_2O energy is then described as

$$H_l = \sum_{i=1}^{6} \left[\left(\frac{1+b}{2+b} \right)_i (E_s)_i \right] + \frac{N_{HB}}{2} H_{HB} + (Pv)_l , \qquad (10)$$

where the subscript l signifies liquid-state and $(KE)_l$ from soft-cell theory appears in the first term on the right hand side. N_{HB} is the average number of hydrogen-bonds per water molecule and is divided by 2 because each water molecule shares hydrogen-bonds with the hydrogen-bonded neighbor molecules. An H_2O molecule has 4 hydrogen-bonds if it is fully hydrogen-bonded, including 2 hydrogen-bonds on the donor side (2 H atoms) and 2 hydrogen-bonds on the acceptor side (1 O atom). $(Pv)_l$ is usually negligible except at extreme temperature and pressure conditions. It is possible to express $(KE)_l$ in terms of a much simpler form analogous to gas kinetic energy by using a term mRT with variable m,

$$H_l = mRT + \frac{N_{HB}}{2} H_{HB} + (Pv)_l . \qquad (11)$$

It is found that m is well approximated by a constant value of *4* for liquid H_2O at ambient conditions, as shown in Results and Discussion section.

Hydrogen-Bond Enthalpy, H_{HB}

Hydrogen-bond enthalpy of liquid H_2O is evaluated by considering the saturated-solid to saturated-vapor phase change process, *i.e.* sublimation, at 273.15 K. For water at solid-state, each term in the water energy model is applied

to ice. With $b = 0$ and $N_{HB} = 4$ for saturated-solid H_2O, the hydrogen-bond enthalpy H_{HB} is

$$H_{HB} = \frac{1}{2}\left[(3-m)RT + P_{sat}v_{sg} - H_{sg} \right]. \tag{12}$$

where P_{sat}, v_{sg} and H_{sg} are, respectively, the saturation pressure, the specific volume change and enthalpy change, during the sublimation process. The subscript s here refers to solid-state. The intermolecular vibration energy term, including translational vibrational and rotational vibration energies, is represented by mRT.

Number of Hydrogen-bonds, N_{HB}

Applying the energy formula of liquid H_2O, Eq. (11), to saturated-liquid or compressed-liquid H_2O, the number of hydrogen-bonds in H_2O can be linked to liquid H_2O enthalpy for saturated or compressed H_2O, $H_{f,c}$,

$$N_{HB} = \frac{2}{H_{HB}}\left[H_{f,c} - mRT - (Pv)_{f,c} \right]. \tag{13}$$

where the subscript f denotes saturated-liquid and c compressed-liquid. In order to make the reference states of enthalpy in steam tables consistent with the corresponding enthalpy in the present water energy model, the reference state in steam tables is shifted by the difference of gaseous-state enthalpies in steam tables and the present water energy model, $(H_{g,steam\ tables} - H_{g,Eq.(9)})$. Eq. (13) shows that the formation of hydrogen-bonds depends on both temperature and pressure. If water is not under very high pressure conditions, the (Pv) term can usually be ignored and the number of hydrogen-bonds is mainly governed by temperature. The above equation can also be written in terms of internal energy, which combines enthalpy and (Pv) together. However, in order to stress the pressure effect on N_{HB}, the (Pv) term is expressed explicitly.

Heat of Vaporization, H_{fg}

The heat of vaporization H_{fg} for water is obtained by subtracting H_l from H_g at saturation conditions, assuming $(P_{sat}v_g - P_{sat}v_f) \approx RT$,

$$H_{fg} \approx (4-m)RT - \frac{N_{HB}}{2}H_{HB}. \tag{14}$$

It is shown in Results and Discussion that a constant value of 4 is a fairly good approximation for m. In this case, the kinetic energy of water vapor, $3RT$, the change of (Pv) between water vapor and liquid-water, RT, and the intermolecular vibrational kinetic energy, mRT, cancel out in Eq. (14). Henceforth, the heat of vaporization for water turns out to be essentially governed by the hydrogen-bonding effect.

Specific Heat, C_p

The isobaric specific heat of water C_p can be derived by differentiating liquid-water enthalpy H_l with respect to T, noting that $P(dv_l/dT) \sim 0$ and the temperature derivative of H_{HB} term is assumed to be negligible as compared to the temperature derivative of N_{HB} term,

$$C_p \approx \frac{H_{HB}}{2}\frac{dN_{HB}}{dT} + mR. \tag{15}$$

As shown in Eq. (15), C_p is dominated by two kinds of energy storage mechanisms in water: the hydrogen-bonding energy and intermolecular vibration energy.

Entropy, S

The entropy of water can be evaluated from the fundamental thermodynamic relation for entropy as a function of enthalpy and pressure. Employing Eq. (11) for water enthalpy and assuming the volume change of water under normal conditions is negligible, it can be shown that

$$dS \approx mR\frac{dT}{T} + \frac{H_{HB}}{2}\frac{dN_{HB}}{T}. \tag{16}$$

Similar to the specific heat case, entropy is primarily governed by two factors: hydrogen-bonding contribution and intermolecular vibration contribution. The integral form of S is available since N_{HB} can be expressed in terms of temperature by a curve-fit in the following section.

3. Discussion

The first parameter to be determined in soft-cell theory is b. It is reasonable to assume that b depends on both the vibration mode and temperature as water molecules tend to be thermally more active at higher temperatures. However, it is not feasible to tabulate b values with respect to temperature because only very limited experimental data of intermolecular vibration frequencies for water are available. From the previous solid H_2O study (Wang & Brewster, 2010), the three translational vibration frequencies and three effective rotational vibration frequencies of ice Ih are, consecutively, (65 cm^{-1}, 229 cm^{-1}, 229 cm^{-1}, 560 cm^{-1}, 560 cm^{-1}, 560 cm^{-1}). Following Eq. (7), the b's of water for intermolecular vibration frequencies (60 cm^{-1}, 175 cm^{-1}, 175 cm^{-1}, 440 cm^{-1}, 440 cm^{-1}, 440 cm^{-1}) (Carey & Korenowski, 1998; Castner et al., 1995; Palese et al., 1994; Walrafen et al., 1986) are therefore (0.17, 0.71, 0.71, 0.62, 0.62, 0.62), respectively.

Table 1. The values of m defined in Eq. (11) for different tested effective frequencies of liquid-water intermolecular rotational vibrations at various temperatures.

T [K]	m		
	$v_{rot} = 440$ cm^{-1}	$v_{rot} = 400$ cm^{-1}	$v_{rot} = 360$ cm^{-1}
273.15	4.20	4.21	4.24
323.15	4.05	4.09	4.15
373.15	3.95	4.02	4.09
423.15	3.89	3.97	4.06
473.15	3.84	3.93	4.03
523.15	3.81	3.91	4.01
573.15	3.79	3.89	4.00
623.15	3.77	3.87	3.99

With the 6 b's for 6 intermolecular vibration modes, m is obtained for $(KE)_l$ in Eq. (11). Table I shows that the numerical values of m varies from 4.2 to 3.8 at temperatures from 273.15 K to 623.15 K for the tested rotational vibration frequencies ranging from 360 cm^{-1} to 440 cm^{-1}. Effective characteristic frequencies below 440 cm^{-1} are also tested because water tends to be "softer" (the b's tend to be bigger) at higher temperatures, which in turn yields smaller characteristic frequencies. The translational vibration frequencies, which do not change as fast with temperature as rotational modes, are kept constant during the calculation (Carey & Korenowski, 1998; Walrafen et

al., 1986). The *m* values shall be updated to reflect the temperature dependence of kinetic energy when more experimental data are available for intermolecular vibration frequencies. As a first approximation, $m= 4$ is adopted throughout this study over the whole temperature range.
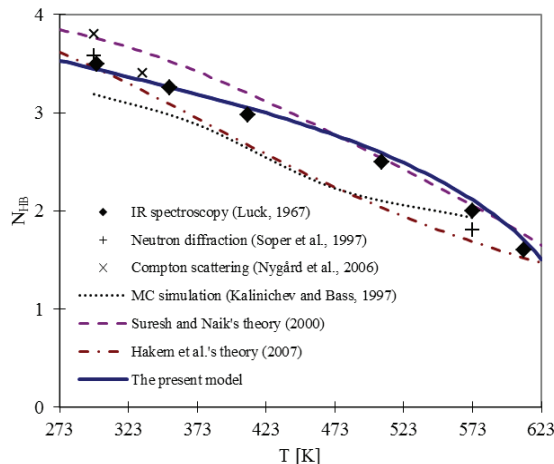

Figure 2. The average number of hydrogen-bonds N_{HB} in water with respect to temperature. Experimental data are shown in symbols. The solid line is the prediction from the present model at saturation pressures. Other theoretical results are plotted with broken curves.

Using Eq. (13) with $m= 4$, the calculated hydrogen-bond enthalpy $H_{HB}= -25.5$ kJ/mol-water is in good agreement with literature values (Carey & Korenowski, 1998; Suresh & Naik, 2000). Substituting steam table data for H_{fg}, P_{sat}, v_f, and v_g, the average number of hydrogen-bonds N_{HB} for water with respect to temperature at saturation pressures is plotted in Figure 2. The predicted N_{HB} of liquid H_2O at saturation conditions agrees with the experimental data well for T= 273.16K to 623.15 K, indicating that $m= 4$ is a good approximation for kinetic energy in Eq. (11).

Overall, in Figure 2, all experimental and theoretical studies produce a downward trend of N_{HB} with respect to temperature, *i.e.* negative temperature dependence of N_{HB}. As temperature goes higher, N_{HB} decreases faster. At lower temperatures, the slope of N_{HB} curve becomes nearly constant, resulting in a somewhat unusual phenomenon in nature: nearly constant specific heat, as indicated by Eq. (15). Hakem, Boussaid, Benchouk-Taleb & Bockstaller's model (2007), which explores the temperature dependence of hydrogen-bond formation at low pressure limit, and MC simulation by Kalinichev and Bass (1997) both yield less hydrogen-bonds than the results from IR experiments. N_{HB} by Suresh and Naik's theory (2000) is overestimated below 430 K but gives good predictions at higher temperatures. According to their theory, N_{HB} is determined by temperature and liquid density. However, as far as compressed-liquid is concerned, experiments as well as MC simulations show that N_{HB} changes not only with temperature but also pressure, as also indicated in Eq. (13) (Kalinichev & Bass, 1997; Soper, Bruni & Ricci, 1997). A curve-fit of N_{HB} in Figure 2 is obtained with $R^2 > 0.99$:

$$N_{HB} = aT^2 + bT + c \; ; \tag{17}$$

273.15 K < T≤ 520 K,
  a= -6.06E-6, b= 7.56E-4, c= 3.76;

520 K < T< 623.16 K,
  a= -4.19E-5, b= 3.84E-2, c= -6.15.

In addition to the temperature effect on hydrogen-bonding, this model is also able to demonstrate the pressure dependence of N_{HB} in compressed-liquid water, as presented in Figure 3. It is seen that high pressure environments are in favor of the formation of hydrogen-bonds. The same conclusion is also obtained in MC simulations (Kalinichev & Bass, 1997). Neutron diffraction experiment by Soper et al. (1997) also shows that water at 2,800 bar and 573 K is more hydrogen-bonded ($N_{HB}= 3.06$) than that at 95 bar and 573 K ($N_{HB}= 1.80$). In contrast, the lattice model by Hakem et al. (2007) produces debatable outcomes of pressure dependence for the fraction of hydrogen-bonds in water. Their theory suggests a negative dependence of hydrogen-bond formation on pressure. Following their conclusion, as compressed-liquid at constant temperature is de-pressurized, the number of hydrogen-bonds increases. However, if pressure continues to drop below saturation pressure, liquid-water turns to vapor and the hydrogen-bonding vanishes, which does not agree with their theory of negative pressure dependence for hydrogen-bond formation.
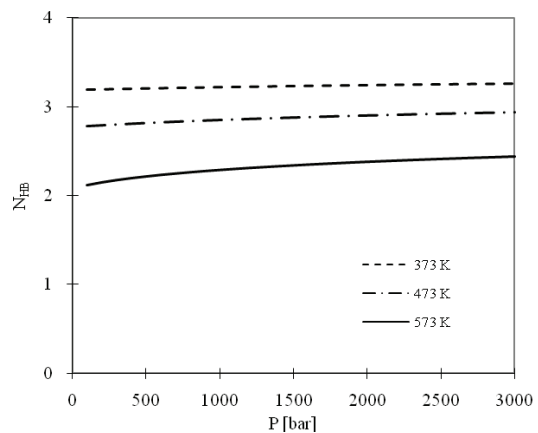

Figure 3. The average number of hydrogen-bonds of compressed-water with respect to pressure at different temperatures.

The numerical results show that if the ambient pressures do not exceed the saturation pressures by 100 bars for the three tested temperatures in Figure 3, the change of N_{HB} due to pressure elevation is smaller than 1.5 %. In other words, as long as the pressure is not significantly large, N_{HB} is almost independent on pressure. It is also seen that pressure effect on N_{HB} at moderate temperatures, such as 373 K, is not as important as that at higher temperatures, such as 573 K. For liquid H_2O at T= 273.16 K to 373.15 K and P= 1,000 bars, e.g. ocean water at 10 km deep below the sea level (without the presence of volcano), pressure effect is still negligible and N_{HB} is about the same as that at saturation pressure (less than 1 % change in N_{HB}). However, if water on the ocean floor is subject to high-temperature environment due to eruptions of submarine volcano, thermodynamic properties may change as a result of the pressure effect on N_{HB}.
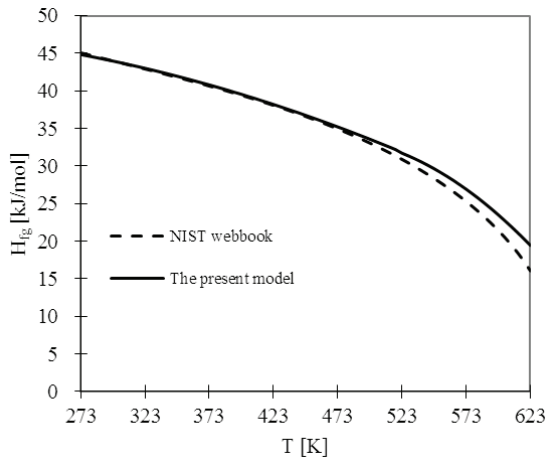
Figure 4. Heat of vaporization H_{fg} of water. H_{fg} from the present model with the curve-fit N_{HB} from Eq. (17) is compared with the steam table data from NIST Webbook.
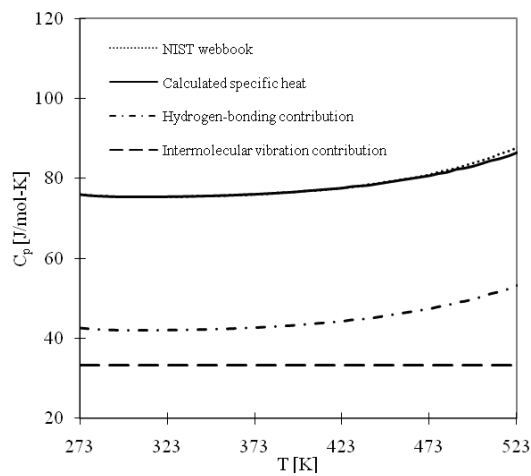

Figure 5. Specific heat C_p of water with respect to temperature. The two contributions of specific heat are obtained following Eq. (15).

Heat of vaporization is evaluated using Eq. (14), in which the (RT) term cancels out and hydrogen-bonding energy is the only contribution to H_{fg},

$$H_{fg} \approx -\frac{N_{HB}}{2}H_{HB}. \qquad (14a)$$

The calculated results from Eq. (14a) are plotted in Figure 4. The predicted values of H_{fg} agree well with steam table data for T= 273.16 K to 523.16 K. Higher temperatures tend to produce larger discrepancies due to the approximation of ($P_{sat}v_{fg}$) by (RT). Nevertheless, at T= 523.16 K, the discrepancy is still smaller than 3 %. If ($P_{sat}v_{fg}$) is obtained from steam table instead of using (RT) approximation, the derived H_{fg} curve will overlap with the steam table data. It is interesting to see from Eq. (14a) and Figure 4 how heat of vaporization is closely related to and dominated by hydrogen-bonding energy. Since water is hydrogen-bonded, a considerable amount of heat from the sun is absorbed in water vaporization process to break down the hydrogen-bonds. In this way, the radiative heating from the sun serves as the energy supply to vaporize a large amount of ground water and at the same time the weather is regulated. Without the hydrogen-bonding in water, the weather would likely be less stable,

because the phase change process of water would take place more abruptly.

Water specific heat and its two components from Eq. (15) are plotted in Figure 5. The specific heat analysis performed here does not intend to predict the specific heat itself, since Eq. (15) is derived directly from water enthalpy H_l and the calculated specific heat does not contain new thermodynamic information. It is to show that the heat storage mechanism in water has two components: hydrogen-bonding energy and intermolecular vibration energy. As a consequence of these two contributions, water has relatively large specific heat. At T= 273.16 K to 373.15 K, not only does the specific heat due to intermolecular vibration stay about the same, but also the contribution from the temperature derivative of N_{HB} term remains nearly unchanged. However, as temperature gets higher, N_{HB} drops faster, resulting in the growing C_p at higher temperatures.
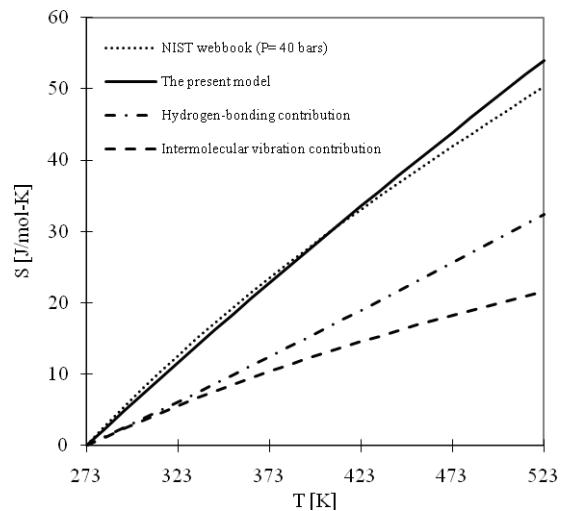

Figure 6. Water entropy with respect to temperature. The entropy calculated from the present model is compared to the NIST Webbook data. The two major contributions of entropy are directly obtained from Eq. (18).

Taking advantage of the fact that N_{HB} is nearly independent of pressure under normal ambient conditions, the entropy of water is conveniently expressed using Eq. (17) for N_{HB} as a function of temperature,

$$S \approx mR\ln T + \frac{H_{HB}}{2}(2aT + b\ln T). \qquad (18)$$

The calculated water entropy is compared with the entropy data from NIST Webbook in Figure 6. For calculation simplicity, the pressure is set to 40 bars for the whole temperature range such that water is in liquid state. The reference state of entropy is $S= 0$ at 273.16 K for saturated water.

For temperature lower than 420 K, the present model gives acceptable results for entropy. As the temperature gets higher, the discrepancies between the model predictions and steam table data become more appreciable. This is because the pressure becomes more influential on N_{HB} at higher temperatures. It has been clearly seen from Figure 3 that higher temperatures result in higher pressure dependence of N_{HB}, while the curve-fit N_{HB} is obtained for saturation conditions. Nevertheless, our simple approximation of water entropy in Eq. (18) is quite useful

for water at T< 420K.   In addition to the comparison on entropy, Figure 6 also shows that the contribution of entropy from hydrogen-bonding is more important than that from intermolecular vibration, especially at higher temperatures.   The formation or breaking of hydrogen-bonds in liquid-water appears to be an important factor in terms of water entropy.

4. Conclusion

The deformable nature of water is taken into account to model the intermolecular vibrations of water molecules. The new model is called soft-cell theory, with which the total intermolecular vibration energy of the system is found to be able to be empirically represented by an energy form resembling the kinetic energy form for ideal gas.   Along with a simple energy model for water, soft-cell theory successfully brings out hydrogen-bonding information and the related thermodynamic properties.   The findings of this study are summarized below:

(1) The lattice view in the traditional cell theory is modified to bring forth a soft-cell model to better describe the physics of water.
(2) The average number of hydrogen-bonds in water has a much stronger temperature-dependence than pressure; the average number of hydrogen-bonds can be treated to be independent on pressure if the ambient pressure is not extremely large (less than 1,000 bars).
(3) Water under ultra high temperature and pressure environments may exhibit unusual thermodynamic behaviors as the hydrogen-bonding of water is influenced by extreme ambient conditions.
(4) The heat of vaporization of water is primarily governed by hydrogen-bonding energy.
(5) The uncommonly large specific heat of water is a consequence of two types of energy storage mechanism in water: intermolecular vibration energy and hydrogen-bonding energy.
(6) The specific heat of water appears nearly constant at normal ambient conditions because the contributions to specific heat from both the change of hydrogen-bonds and the intermolecular vibration energy remain approximately the same.
(7) The water entropy is dominated by two factors: hydrogen-bonding contribution and intermolecular vibration contribution.

Nomenclature

Roman characters

b	Soft-cell effect parameter
C_p	Isobaric specific heat
E	Total intermolecular vibration energy
h	Planck's constant
H	Enthalpy
H_{HB}	Hydrogen-bond enthalpy
I	Moment of inertia
k	Boltzmann's constant
k_M	Force constant
k_I	Torque constant
m	Empirical parameter for intermolecular vibration energy
M	Mass
N_{HB}	Average number of hydrogen-bonds per water molecule
$P\mathrm{v}$	($P\mathrm{v}$) work, pressure times volume

r	Location of mass
R	Universal gas constant
S	Entropy
T	Temperature
x	Displacement of mass

Greek symbols

ε	Mechanical equilibrium
ν	Characteristic frequency

Subscripts

c	Compressed-liquid
f	Saturated-liquid
g	Gaseous-state
i	Intermolecular vibration mode
l	Liquid-state
rot	Rotational vibration mode
s	Soft-cell; solid-state
sat	Saturated-state
v	Intermolecular vibration quantum number

Abbreviations

HB	Hydrogen-bond
KE	Kinetic energy
PE	Potential Energy

References:

Asthagiri, D., Pratt, L. R., & Kress, J. D. (2003). Free Energy of Liquid Water on the Basis of Quasichemical Theory and ab initio Molecular Dynamics. *Phys. Rev. E, vol 68*, 041505

Bergmann, U., Nordlund, D., Wernet, Ph., Odelius, M., Pettersson, L. G. M., & Nilsson, A. (2007). Isotope Effects in Liquid Water Probed by X-ray Raman Spectroscopy. *Phys. Rev. B., vol 76*, 024202.

Bertie, J. E., Labbe, H. J., & Whalley, E. (1968). Far-infrared Spectra of Ice II, V, and IX. *J. Chem. Phys., 49*(2), 775-780.

Bertie, J. E., Labbe, H. J. & Whalley, E. (1969). Absorptivity of Ice I in the Range 4000-30cm^{-1}. *J. Chem. Phys., 50*(10), 4501-4520.

Bertie, J. E., & Whalley, E. (1964). Infrared Spectra of Ices II, III and V in the Range 4000 to 350 cm^{-1}. *Chem. Phys., 40*(6), 1646-1659.

Bertie, J. E., & Whalley, E. (1967). Optical Spectra of Orientationally Disordered Crystals. II. Infrared Spectrum of Ice Ih and Ice Ic from 360 to 50 cm^{-1}. *J. Chem. Phys., 46*(4), 1271-1284.

Carey, D. M., & Korenowski, G. M. (1998). Measurement of the Raman Spectrum of Liquid Water. *J. Chem. Phys., 108*(7), 2669-2675.

Castner, E. W., Jr., Chang, Y. J., Chu, Y. C., & Walrafen, G. E. (1995). The Intermolecular Dynamics of Liquid Water. *J. Chem. Phys., 102*(2), 653-659.

Eads, C. D. (2002). Quasichemical Lattice Fluid Model for Water and Hydrophobic Solvation. *J. Phys. Chem. B, vol 106*, 12282-12290.

Frenkel, J. (1955). *Kinetic Theory of Liquid.* New York, Dover Publication Inc..

Hakem, I. F., Boussaid, A., Benchouk-Taleb, H., & Bockstaller, M. R. (2007). Temperature, Pressure, and Isotope Effects on the Structure and Properties of Liquid Water: A Lattice Approach. *J. Chem. Phys., vol 127*, 224106.

Henchman, R. H. (2007). Free Energy of Liquid Water From a Computer Simulation via Cell Theory. *J. Chem. Phys., vol 126*, 064504.

Kalinichev, A. G., & Bass, J. D. (1997). Hydrogen Bonding in Supercritical Water. 2. Computer Simulations. *J. Phys. Chem. A, vol 101*, 9720-9727.

Klefas-Stennett, M., & Henchman, R. H. (2008). Classical and Quantum Gibbs Free Energies and Phase Behavior of Water Using Simulation and Cell Theory. *J. Phys. Chem. B, vol 112*, 9769-9776.

Luck, W. A. P. (1967). Spectroscopic Studies Concerning the Structure and the Thermodynamic Behaviour of H_2O, CH_3OH and C_2H_5OH. *Discussions of the Faraday Society, no 43*, 115-127.

Luzar, A., & Chandler, D. (1996). Effect of Environment on Hydrogen Bond Dynamics in Liquid Water. *Phys. Rev. Letters, 76*(6), 928-931.

Nygård, K., Hakala, M., Manninen, S., Andrejczuk, A., Itou, M., Sakurai, Y., Pettersson, L. G. M., et al. (2006). Compton Scattering Study of Water Versus Ice Ih: Intra- and Intermolecular Structure. *Phys. Rev. E., vol 74*, 031503.

Palese, S., Schilling, L., Miller, R. J. D., Staver, P. R., & Lotshaw, W. T. (1994). Femtosecond Optical Kerr Effect Studies of Water. *J. Phys. Chem., 98*(25), 6308-6316.

Prask, H., Boutin, H., & Yip, S. (1968). Frequency Spectrum of Hydrogenous Molecular Solids by Inelastic Neutron Scattering. Hexagonal H_2O Ice. *J. Chem. Phys., 48*(8), 3367-3376.

Smith, J. D., Cappa, C. D., Messer, B. M., Drisdell, W. S., Cohen, R. C., & Saykally, R. J. (2006). Probing the Local Structure of Liquid Water by X-ray Absorption Spectroscopy. *J. Phys., Chem. B, vol 110*, 20038-20045.

Sonntag, R. E., & Van Wylen, G. J. (1966). *Fundamentals of Statistical Thermodynamics*. John Wiley & Sons, Inc., 137-141.

Soper, A. K., Bruni, F., & Ricci, M. A. (1997). Site-site Pair Correlation Functions of Water From 25 to 400 °C: Revised Analysis of New and Old Diffraction Data. *J. Chem. Phys., 106*(1), 247-254.

Suresh, S. J., & Naik, V. M. (2000). Hydrogen Bond Thermodynamic Properties of Water from Dielectric Constant Data. *J. Chem. Phys., 113*(21), 9727-9732.

Truskett, T. M., & Dill, K. A. (2002). A Simple Statistical Mechanical Model of Water. *J. Phys. Chem. B, vol 106*, 11829-11842.

Yagasaki, T., & Saito, S. (2008). Ultrafast Intermolecular Dynamics of Liquid Water: A Theoretical Study on Two-dimensional Infrared Spectroscopy. *J. Chem. Phys., vol 128*, 154521.

Walrafen, G. E., Fisher, M. R., Hokmabadi, M. S., & Yang, W.-H. (1986). Temperature Dependence of the Low- and High-frequency Raman Scattering From Liquid Water. *J. Chem. Phys., 85*(12), 6970-6982.

Wang, K. T., & Brewster, M. Q. (2010). An Intermolecular Vibration Model for Lattice Ice. *Int. J. Thermodynamics, 13*(2), 51-57.

Wernet, Ph., Nordlund, D., Bergmann, U., Cavalleri, M., Odelius, M., Ogasawara, H., Näslund, L. Å., et al. (2004). The Structure of the First Coordination Shell in Liquid Water. *Science, vol 304*, 995-999.

Appendices:

(1) Derivation of Eq. (2)
Based on the elastically moving-wall assumption, $\delta r = bx$, the following relation between x and r is immediately obtained after Eq. (1), dropping the sub-index i,

$$r = (1+b)x + r_\varepsilon . \qquad (A1)$$

Since the intermolecular vibrations in six degrees of freedom in the soft-cell model (cell theory, too) have similar mathematical representations for equations of motion, the translational vibration mode is considered here to illustrate the reduction of characteristic frequency due to the b effect, which, mathematically, is also a result of transformation of coordinates from r to x. Replacing r by x in the equation of motion for the mass M in the moving-wall-spring-mass system,

$$M \frac{d^2 r}{dt^2} = -kx \Rightarrow (1+b)M \frac{d^2 x}{dt^2} = -kx , \qquad (A2)$$

the characteristic frequency of the moving-wall-spring-mass system, ν_s, can be written in terms of the characteristic frequency of the wall-spring-mass system, ν, and the soft-cell effect parameter, b,

$$\nu_s = \frac{\nu}{\sqrt{1+b}} , \qquad (A3)$$

where ν is defined in Eq. (3) for different intermolecular vibration modes.

(2) Derivation of Eq. (4)
Given the initial condition, $x=0$ at $t=0$, which is somewhat arbitrary, the solution of Eq. (A2) is

$$x = A\sin(\omega_s t), \qquad (A4)$$

where A is the amplitude of vibration and the characteristic angular frequency ω_s is $2\pi\nu_s$. The averaged kinetic energy is obtained through the integration of kinetic energy over a complete vibration cycle inside a cell,

$$\langle KE_s \rangle = \frac{1}{2\pi} \int_0^{2\pi} \frac{1}{2} M\dot{r}^2 d(\omega_s t) . \qquad (A5)$$

Again, employing Eq. (A1) and Eq.(A4) to respectively transform r to x and x to $(\omega_s t)$, and noting that $\omega_s^2 = k/[M(1+b)]$, the averaged kinetic energy for intermolecular vibrations finally becomes

$$\langle KE_s \rangle = \frac{1}{2}\left(\frac{1}{2}kA^2\right)(1+b) . \qquad (A6)$$

Likewise, the averaged potential energy arising from intermolecular vibrations (not due to H-bonding) is

$$\langle PE_s \rangle = \frac{1}{2\pi}\int_0^{2\pi}\frac{1}{2}kx^2 d(\omega_s t) = \frac{1}{2}\left(\frac{1}{2}kA^2\right). \tag{A7}$$

As a result, the total intermolecular vibration energy E_s is

$$\left(E_s\right) = \langle KE_s \rangle + \langle PE_s \rangle = \left(\frac{2+b}{1+b}\right)\langle KE_s \rangle. \tag{A8}$$

(3) Derivation of Eq. (5):
To investigate the form of quantized energy in the moving-wall-spring-mass system, information of the external potential on mass has to be known prior to solving the Schrödinger's equation. Given the spring constant k, the external potential on M as a function of x is

$$\phi(x) = -\int_0^x (-kx)dx = \frac{1}{2}kx^2. \tag{A9}$$

Substituting Eq. (A9) into the Schrödinger's equation, the equation can be written as a function of x,

$$\frac{d^2\psi_s}{dr^2} + \frac{8\pi^2 M}{h^2}(E_s - \frac{1}{2}kx^2)\psi_s = 0$$

$$\Rightarrow \frac{1}{\left(1+b\right)^2}\frac{d^2\psi_s}{dx^2} + \frac{8\pi^2 M}{h^2}(E_s - \frac{1}{2}kx^2)\psi_s = 0. \tag{A10}$$

The resulting quantized energy is

$$E_{s_v} = \frac{h}{(1+b)}\nu\left(v+\frac{1}{2}\right) = \frac{h}{\sqrt{(1+b)}}\nu_s\left(v+\frac{1}{2}\right), \tag{A11}$$

where the intermolecular vibration quantum number $v=0, 1, 2, 3, \dots$ Letting $h_s = \dfrac{h}{\sqrt{1+b}}$, the eigen energy in the Schrödinger equation then appears in the same form as that in the wall-spring-mass system

$$\left(E_{s_v}\right) = h_s \nu_s\left(v+\frac{1}{2}\right), \; v= 0, 1, 2, 3 \dots \tag{A12}$$

(4) Derivation of Eq. (7):
Following Eq. (A3), the soft-cell effect parameter b can be calculated:

$$\nu_s = \frac{\nu}{\sqrt{1+b}} \Rightarrow b = \left(\frac{\nu}{\nu_s}\right)^2 - 1, \tag{A13}$$

where ν and ν_s are the characteristic frequencies of intermolecular vibration respectively for ice and liquid-water in the present study.