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TITLE: An Intermolecular Vibration Model for Lattice Ice

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PAGES: 51-57

ORIGINAL PDF URL: <https://dergipark.org.tr/tr/download/article-file/65781>

## An Intermolecular Vibration Model for Lattice Ice

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### Abstract

Lattice ice with tetrahedral arrangement is studied using a modified Einstein's model that incorporates the hindered translational and rotational vibration bands into a harmonic oscillation system. The fundamental frequencies for hindered translational and rotational vibrations are assigned based on the intermolecular vibration bands as well as thermodynamic properties from existing experimental data. Analytical forms for thermodynamic properties are available for the modified model, with three hindered translational bands at (65, 229, 229)  $\text{cm}^{-1}$  and three effective hindered rotational bands at 560  $\text{cm}^{-1}$ . The derived results are good for temperatures higher than 30 K. To improve the model below 30 K, Lorentzian broadening correction is added. This simple model helps unveil the physical picture of ice lattice vibration behavior.

**Keywords:** *Hindered translation, hindered rotation, intermolecular vibration, heat capacity, entropy, ice.*

### 1. Introduction

Understanding the lattice vibration behavior in crystalline solids is one of the most fundamental subjects in condensed matter physics. As early as 1907, the molecular vibrations in monatomic solids were firstly described by a simple harmonic oscillation model proposed by Einstein (Sonntag and Van Wylen, 1966; Pohl, 1987), whose work led to a generally good prediction of heat capacity except at ultra low temperatures. The deficiency of Einstein's model at very low temperature is a result of the over simplified assumption that all the oscillators have the same fundamental vibration frequency. An improvement to Einstein's model was brought about by Debye in 1912 to deal with the low temperature discrepancy in Einstein's model by spreading intermolecular vibration frequencies with the Debye distribution function (Sonntag and Van Wylen, 1966). Since Debye's model produces excellent results for heat capacity over a wide temperature range for monatomic solids, not much effort has been made throughout the years to refine the Debye model for lattice vibrations, even though Debye's model is theoretically unrealistic due to the existence of singularities in the density of states (Patterson and Bailey, 2007).

Despite the success of Debye's model for monatomic solids, the model itself is mathematically inconvenient because of the integration work related to the Debye temperature, which also leads to no simple forms for thermodynamic properties. Moreover, as Debye's model is applied to polyatomic solids, such as ice, the Debye temperature is no longer a constant but has to be a function of temperature in order to fit the experimental data (Patterson and Bailey, 2007; Flubacher et al., 1960). It is this issue of Debye's model in complex solids that calls for a re-modeling of the lattice vibration system. In view of the simplicity and applicability of Einstein's original model in monatomic solids, even though not good at low temperature but at least applicable from moderate to higher temperatures, a modification of

Einstein's model is made in this work to portray the vibration behavior of water molecules in solid state.

The molecular vibration behavior of ice has been studied extensively over the years. In the 1930s, Raman studies of ice (Cross et al., 1937; Hibben, 1937) noticed the low frequency vibration bands below 1020  $\text{cm}^{-1}$  and referred to them as "hindered" translational and rotational bands. Whether a vibration frequency is classified as hindered translation or hindered rotation is determined by a simple argument: a hindered translation vibration frequency is proportional to the reciprocal of the square root of mass, while a hindered rotational vibration frequency is inversely proportional to the square root of moment of inertia based on the assumption of harmonic oscillators for ice molecules. The vibration frequency ratios of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  were found close to  $(20/18)^{0.5} = (\text{mass ratios of } \text{D}_2\text{O} \text{ to } \text{H}_2\text{O})^{0.5}$  below 320  $\text{cm}^{-1}$  and close to  $(2/1)^{0.5} \sim (\text{moment of inertia ratios of } \text{D}_2\text{O} \text{ to } \text{H}_2\text{O})^{0.5}$  for 320-1,020  $\text{cm}^{-1}$ , and these two spectral ranges were consequently assigned as the locations for hindered translation and hindered rotation, respectively (Cross et al., 1937; Hibben, 1937; Bjerrum, 1951; Bertie and Whalley, 1967; Prask et al., 1968; Bertie et al., 1969; Palese et al., 1994; Yagasaki and Saito, 2008). In the 1950's, the concept of hindered translational and rotational vibrations was applied to the ice heat capacity calculation through Debye's model and the general trend was able to be produced (Bjerrum, 1951). In the 1960s, infrared spectroscopy experiments (Bertie and Whalley, 1964, 1967; Bertie et al., 1968, 1969) as well as inelastic neutron scattering (Prask et al., 1968) were conducted and the understanding of the hindered translation and rotation bands was further advanced. Meanwhile, attempts to predict ice heat capacity always accompanied intermolecular vibration studies. However, the ice heat capacity models either deviated from experimental results (Prask et al., 1968) or accommodated semi-empirical functions for Debye's model in order to fit the data (Flubacher et al., 1960). Efforts were also made to apply Einstein's model on

other materials but the predicted heat capacity again deviated from experimental results over some temperature range (Johari, 2003). Both kinds of restricted motions stated above are essentially vibration-like (Bertie and Whalley, 1967; Bertie et al., 1969; Johari, 2003; Carey and Korenowski, 1998), usually termed by “hindered translation” and “hindered rotation” (or libration) (Cross et al., 1937; Hibben, 1937; Bjerrum, 1951; Palese et al., 1994; Yagasaki and Saito, 2008; Castner, 1995; Lawrence and Skinner, 2002, 2003; Henchman, 2007).

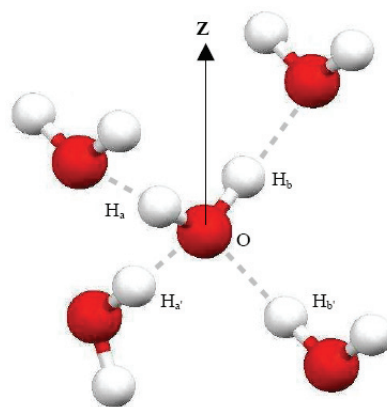
As for the water intramolecular vibrations, which are hardly excited unless the temperature reaches  $\sim 400$  K, at which temperature the bending mode vibration is 10% excited in terms of heat capacity, the contributions from these high-frequency vibration bands are henceforth neglected for ice study. The assumption of rigid water molecules for the solid phases of water is also adopted in many water potential models, such as SPC (Berendsen et al., 1981), SPC/E (Berendsen et al., 1987), TIP5P (Mahoney and Jorgensen, 2000), TIP4P (Jorgensen et al., 1983), TIP4P/Ice (Abascal et al., 2005), and TIP4P/2005 (Abascal and Vega, 2005). In these models, the intermolecular interactions are typically described by a Lennard-Jones potential between oxygen atoms and a Coulomb potential between charged sites. However, different potential models have different assignments for negative charge locations as well as experimentally determined potential parameters. A brief comparison of these models can be found in (Aragones et al., 2007). Among these empirical models, the TIP4P model is able to qualitatively predict the phase diagram of water. The TIP4P/Ice and TIP4P/2005 are two popular reparameterized versions of the the TIP4P model in order to improve the quantitative representations. In addition to classical simulations, quantum effects have been recently introduced to reparameterize the TIP4P/2005 model, yielding a new empirical model called the TIP4PQ/2005 model (McBride et al., 2009). Computer simulations, such as molecular dynamics and Monte Carlo methods, are required for these water potential models.

In contrast to the study of ice properties by computer simulation, we propose an analytical model to study the thermodynamic properties of ice. In this study, the single-frequency harmonic oscillator in Einstein’s model is firstly extended to six degrees of freedom with six fundamental frequencies: three for hindered translations and three for hindered rotations. The fundamental frequencies used in this study are based on ice Ih spectroscopic absorption bands. In other words, these frequencies are the characteristic frequencies for intermolecular vibrations. This approach is quite different from the conventional treatments in Einstein’s model, in which the value of the Einstein temperature is obtained in order to match the experimental heat capacity. Ice Ih is adopted as a representative of lattice ice because ice Ih is the natural form of ice on the earth (Schulson, 1999). To deal with the low-temperature discrepancies in the original Einstein model, the intermolecular interactions, which include the interactions of the Coulomb forces, the van der Waals attraction, and the Pauli repulsion, are taken into account and modeled by Lorentzian broadening. The purpose of including the broadening effect is to more closely approach the true lattice vibration behavior and thus

hopefully the modified model may reflect more real features of the complex vibration system and subsequently provide better predictions of thermodynamic properties. With the modified Einstein model for ice, the intermolecular vibration magnitudes are examined and thermodynamic properties are evaluated to compare with experimental data. All the calculations performed in this study are based on the intermolecular vibration frequencies of ice Ih.

## 2. Theoretical Basis

In crystalline solid water, each water molecule is assumed to possess intermolecular vibrations in six degrees of freedom, comprising three hindered translational vibrations and three hindered rotational vibrations, and confined in a local “cell” (cage) by intermolecular potentials. The confinement assumption of molecular motions within a cell without interference by other molecular motions from other cells is usually called cell theory and commonly used for liquid-state vibration study (Henchman, 2007). The vibration motions of each molecule in a cell are formulated by harmonic oscillators, which can be considered as a composition of mass-spring systems with different force constants. It has to be noted that the application of harmonic oscillators on the vibrating system is acceptable only when most of the molecules stay at low energy levels where the molecular vibrations can be approximated by harmonic oscillations. This assumption is valid for the majority of ice molecules that do not get excited to high enough energy states where anharmonic effects are appreciable. In this study, the tetrahedral arrangement is adopted for lattice ice structure (Bjerrum, 1951; Salzmann et al., 2006), as shown in Figure 1. A typical example of tetrahedrally hydrogen bounded ice is ice Ih.



*Figure 1. Tetrahedral ice structure. Each  $H_2O$  molecule is surrounded by 4  $H_2O$  molecules. The dashed lines denote hydrogen bonding between oxygen atoms and hydrogen atoms.*

In a harmonic oscillating mass-spring system, which is analogous to the hindered translational vibration in lattice ice, the fundamental vibration frequency is determined by the mass of the vibrating object and the force constant acting on the mass. As for hindered rotational vibrations, similar formulations for fundamental frequencies can be obtained by replacing mass with moment of inertia and force constant with “torque” constant in the “mass-spring” system. The mathematical forms for both types of fundamental frequencies can be found in (Sonntag and Van Wylen, 1966; Henchman, 2007). By invoking the harmonic

oscillator assumption, however, the force/torque constants do not necessarily need to be directly involved in specifying the vibration bands, for this will require foreknowledge of intermolecular potentials. Rather, the fundamental frequencies can be obtained from IR absorption spectroscopic data as shown in Figure 2, in which the dotted points are absorption coefficients and the solid curve is the combination of two Lorentzian line shapes with fundamental frequencies at 65 and 229 cm<sup>-1</sup> with hwhm's (half width at half maximum) of 5 and 15 cm<sup>-1</sup>, respectively (Bertie and Whalley, 1967; Prask et al., 1968; Bertie et al., 1969; Eisenberg and Kauzmann, 1969). The magnitudes of the line shapes are scaled to fit the experimental data near the line centers. The reason the Lorentzian line shape is used here is because it is a consequence of intermolecular interactions (or "collisions") which alter the energy levels of ice molecules and bring about dispersed absorption bands around vibration line centers (Brewster, 1992). Moreover, we shall assume that the molecule population follows the Lorentzian distribution function, since the Lorentzian distribution is used to describe the spectral absorption coefficient, which is supposed proportional to the molecular population at the corresponding vibration frequency. This assumption is later used to derive the thermodynamic properties for ice as the "collision" effect is accounted for. Also in the same figure, the shoulder at ~160 cm<sup>-1</sup> is not considered as a fundamental frequency because it cannot produce agreeable results for ice heat capacity. It may be interpreted as a combination of the overtones of the low frequency band and the far wings of other vibration bands.

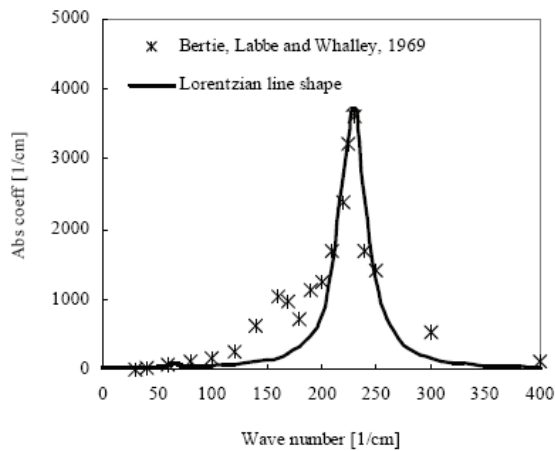


Figure 2. Absorption coefficient of ice Ih at 100 K.

For the modified Einstein model with six fundamental frequencies, the resulting quantized energy  $\varepsilon$  for each degree of freedom is

$$\varepsilon_i = h\nu_i \left( v + \frac{1}{2} \right), \quad v = 0, 1, 2, \dots, \quad (1)$$

where  $h$  is the Planck's constant,  $\nu_i$  the fundamental frequency of the  $i$ -th intermolecular vibration band,  $v$  the intermolecular vibration quantum number. The partition function  $Z$  and thermodynamic properties for the  $i$ -th band are shown in Eqs. (2)-(5):

Partition function

$$Z_i = \sum e^{-\varepsilon_i/kT} = e^{-\theta_i/2T} + \frac{1}{1 - e^{-\theta_i/T}} \quad (2)$$

Internal energy (= Enthalpy)

$$u_i = R\theta_i/2 + \frac{R\theta_i}{e^{\theta_i/T} - 1} \quad (3)$$

Heat capacity

$$C_i = \left( \frac{\theta_i}{T} \right)^2 \frac{e^{-\theta_i/T}}{(1 - e^{-\theta_i/T})^2} R \quad (4)$$

Entropy

$$S_i = R \left[ -\ln(1 - e^{-\theta_i/T}) + \frac{\theta_i/T}{e^{\theta_i/T} - 1} \right] \quad (5)$$

where  $k$  is the Boltzmann constant,  $1.38 \times 10^{-23}$  J/K,  $T$  the temperature,  $\theta_i = h\nu_i/k$  the characteristic temperature, and  $R$  the universal gas constant for H<sub>2</sub>O, 0.462 kJ/kg-K. Summing up each  $i$ -th mode thermodynamic property gives the total property.

In addition to the simple harmonic oscillation approximation for lattice ice, the collision effect is also considered by adding a linear damping term into the mass-spring system and the resulting vibration frequencies are no longer discrete but broadened by the Lorentzian line shapes. The details for the collision effect derivation can be found in (Brewster, 1992). The Lorentzian profile with respect to wave number  $1/\lambda$  (commonly used in spectroscopy) is assumed proportional to the population distribution at different energy levels for the aforementioned reasons, giving

$$N_{1/\lambda} = \frac{dN}{d(1/\lambda)} = A \frac{(1/\lambda_a)^2}{(1/\lambda - 1/\lambda_0)^2 + (1/\lambda_a)^2}, \quad (6)$$

$$A = \frac{N}{(1/\lambda_a) \left[ \frac{\pi}{2} + \tan^{-1} \left( \frac{1/\lambda_0}{1/\lambda_a} \right) \right]} \quad (7)$$

where  $1/\lambda_0$  = line center,  $1/\lambda_a$  = hwhm, and  $N_{1/\lambda}$  is the population at  $1/\lambda$ . The coefficient  $A$  is obtained from normalization conditions for  $N$  particles. Replacing  $R$  by  $k$  and  $\nu$  by  $c/\lambda$  in Eq. (2), the total energy for the  $i$ -th mode subject to collision effect becomes

$$u_{i,c} = \int \left( \frac{hc}{2\lambda} + \frac{hc/\lambda}{e^{hc/\lambda kT} - 1} \right) (N_{1/\lambda})_i d(1/\lambda)_i, \quad (8)$$

the heat capacity and entropy,

$$C_{i,c} = \int \left[ \left( \frac{hc}{\lambda kT} \right)^2 \frac{e^{-hc/\lambda kT}}{(1 - e^{-hc/\lambda kT})^2} k \right] (N_{1/\lambda})_i d(1/\lambda)_i, \quad (9)$$

$$S_{i,c} = \int \frac{C_{i,c}}{T} dT. \quad (10)$$

Integrated forms are obtained for thermodynamic properties when the collision effect is taken into account.



### 3. Discussion

For hindered translational vibrations, it has been recognized (Bertie and Whalley, 1967; Prask et al., 1968; Bertie et al., 1969; Eisenberg and Kauzmann, 1969) that the intermolecular vibration bands are located at about 65 and 229 cm<sup>-1</sup>. Therefore, these two frequencies are employed as two fundamental frequencies for hindered translations. The assignment of the third fundamental frequency basically relies on the ice structure as well as the experimental data. In the tetrahedral model shown in Figure 1, the molecular motion of H<sub>2</sub>H<sub>2</sub>O along the H<sub>a</sub>-H<sub>b</sub> direction in the H<sub>a</sub>-H<sub>b</sub>-O plane has similar restoring forces as that along the H<sub>a</sub>-H<sub>b</sub> direction in the H<sub>a</sub>-H<sub>b</sub>-O plane. However, the motion along the Z-direction experiences quite different restoring forces from the other two. Consequently, two degrees of freedom are assumed to have similar fundamental frequencies near either 229 or 65 cm<sup>-1</sup>. The third hindered translational band is eventually assigned at 229 cm<sup>-1</sup> for it gives a much better agreement with experimental data than 65 cm<sup>-1</sup> does. This assignment is also mechanistically logical as motion along the Z-direction involves primarily bending of the four hydrogen bonds and would have the lower frequency compared to the other two motions, which involve stretch/compression of two hydrogen bonds.

Unlike the hindered translational bands, the band features for hindered rotations are somewhat indistinguishable, for the bands spread over a very wide spectral range. Instead of assigning three distinctive frequencies for this broad band region, a single fundamental frequency 560 cm<sup>-1</sup>, which is a shoulder in the hindered rotational band (Bertie et al., 1969), is used to effectively represent the three degree of freedoms for the hindered rotational vibrations by optimizing the derived data, as what has been done for the assignment of the third hindered translational band.

With the assigned fundamental frequencies, the vibration amplitudes of ice molecules are calculated by letting the vibration energy equal the maximum potential energy at zero kinetic energy position and then averaging by population (in the same way as the average energy calculation in statistical mechanics) for three fundamental frequencies for hindered translation 65, 229, and 229 cm<sup>-1</sup> at different temperatures. Finally, the root-mean-square (rms) vibration amplitude ( $\Delta x$ ) is obtained from the three averaged amplitudes. To ensure the oscillations fall within the allowable hydrogen bond region, *i.e.* without breaking the hydrogen bond structure, the maximum rms amplitude for hindered translation,  $\Delta x_{max}$ , is calculated at 273 K and the maximum torsion amplitude for hindered rotation,  $\Delta \theta_{max}$ , is checked for the effective 560 cm<sup>-1</sup> band using the smallest moment of inertia 1.022×10<sup>-40</sup> g-cm<sup>2</sup> at 273 K (Sonntag and Van Wylen, 1966). The results are compared with experimental data (<sup>1</sup>Springer, 1961; <sup>2</sup>Kuhs and Lehmann, 1983; <sup>3</sup>Peterson and Levy, 1957; <sup>4</sup>Goto et al., 1990; <sup>5</sup>Bjerrum, 1951; <sup>6</sup>Luzar and Chandler, 1996; <sup>7</sup>Pauling, 1935; <sup>8</sup>Pitzer and Polissar, 1956) in Table I.

It is clear that the three assigned hindered translational frequencies capture the lattice vibration characteristics well over a wide temperature range. This also shows that the thermal motion of lattice ice to a certain extent follows a harmonic oscillator behavior, as pointed out by Kuhs and Lehmann (1983).

Table 1. Root-mean-square Amplitudes of Ice for Hindered Intermolecular Vibrations and Comparison with the Hydrogen-bond Limit.

T [K]	$\Delta x$ [Å]	
	Theoretical <sup>a</sup>	Experimental <sup>b</sup>
4	0.106	0.090 <sup>1</sup>
60	0.119	0.118 <sup>2</sup>
123	0.146	0.138 <sup>3</sup> 0.153 <sup>2</sup>
223	0.185	0.173 <sup>3</sup> 0.208 <sup>2</sup>
243	0.192	0.216 <sup>4</sup>

H-bond limit:  $\Delta x = 0.74$  Å,  $\Delta \theta = 30^{\circ}$ <sup>5-8</sup>

$\Delta x_{max} = 0.20$  Å < 0.74 Å

$\Delta \theta_{max} = 19^{\circ}$  < 30°

<sup>a</sup>Einstein model,

$\lambda_0^{-1} = (65, 229, 229, 560, 560, 560)$  cm<sup>-1</sup>

<sup>b</sup>rms displacements of oxygen atoms

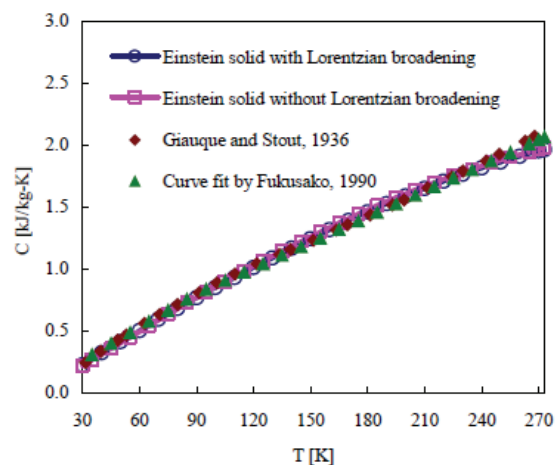


Figure 3. Heat capacity of ice, 30-273 K. The curve with open circles is the prediction of the modified Einstein model with fundamental frequencies (65, 229, 229, 560, 560, 560) cm<sup>-1</sup> and Lorentzian broadening for hindered translations with hwhm 5 cm<sup>-1</sup> for 65 cm<sup>-1</sup> and 15 cm<sup>-1</sup> for 229 cm<sup>-1</sup>. The curve with open squares is from the modified Einstein model with the same fundamental frequencies but no Lorentzian broadening. The solid diamonds are from Giauque and Stout's experiments (1936). The solid triangles are curve-fits of experimental data by Fukusako (1990).

Figure 3 shows the ice heat capacity predicted by the modified Einstein model and the experimental (Giauque and Stout, 1936) and curve-fit data (Fukusako, 1990). The intermolecular interaction effect is modeled by Lorentzian broadening lineshape for hindered translational vibration bands, with 5 cm<sup>-1</sup> hwhm for 65 cm<sup>-1</sup> band and 15 cm<sup>-1</sup> hwhm for 229 cm<sup>-1</sup> double bands. The fundamental frequencies used in the modified Einstein model for both solid curves are (65, 229, 229, 560, 560, 560) cm<sup>-1</sup>, corresponding to the characteristic temperatures (94, 330, 330, 806, 806, 806) K, respectively. The effective hindered rotational frequency of 560 cm<sup>-1</sup> is chosen to match the experimental data by Giauque and Stout (1936). The broadening effect is not applied to the effective bands at

560  $\text{cm}^{-1}$ . Fukusako's curve-fit heat capacity (1990) is also plotted for comparison. It is found that, for temperatures lower than 110 K, the heat capacity is nearly independent of the hindered rotational bands according to the modified Einstein model. This is mainly because the hindered rotational bands have a high characteristic temperature 806 K for 560  $\text{cm}^{-1}$ , and remain unexcited as temperature is not high enough. The predictions with and without Lorentzian broadening yield similar results and both match the experimental data well except near the melting point where the "cell" assumption for ice lattice may break down.

These results convey an important finding that the modified Einstein model with properly chosen fundamental frequencies is a powerful tool for exploring the intermolecular vibration behavior as well as energy levels in crystalline solids at moderate temperatures even without Lorentzian broadening correction. This is also why the Lorentzian broadening is not included in the effective hindered rotational bands. Then what does the Lorentzian broadening do to the modified Einstein model? As mentioned in (Sonntag and Van Wylen, 1966), the Einstein model is over-simplified such that its predicted heat capacity decays too fast at low temperature. The Lorentzian broadening consideration is basically a correction to Einstein's model which does not have broadening feature around the vibration line center. In the original Einstein model, all the molecules are assumed to have the same fundamental frequency regardless of whether intermolecular interactions are strong or negligible. This causes the single fundamental-frequency model to be insufficient to describe the physical system, especially when the population distribution is sensitive to low-energy thermal excitations. As the energy levels are altered, the population distribution changes and so do the thermodynamic properties. At low temperature, most molecules are at ground states, so the thermal excitations of low-energy molecules are very sensitive to the energy levels which actually fluctuate due to intermolecular interactions. When the temperature is moderately high, higher energy levels can be occupied by thermally excited molecules, resulting in less sensitivity on the energy level change due to intermolecular interactions. Other factors like lifetime broadening due to spontaneous emission, anharmonic oscillator effect, or nonlinearity of the damping term may also be taken into account to better represent the real physical system. For instance, a rigorous study that accounts for anharmonic effects arising from higher order terms of intermolecular potential in a complex ice system should serve as a better approximation of the real system than the harmonic oscillation model. In fact, better knowledge about the potential will also improve the damped oscillator model. However, such treatments usually yield expensive computation costs, and, due to the complexity of ice structure, it is nearly impossible to obtain the exact form of intermolecular potential.

The low-temperature heat capacity data are plotted in Figure 4. The line centers and hwhm's for hindered translation vibrations are the same as stated before. The modified Einstein model with Lorentzian broadening correction is able to predict the low-temperature heat capacity better than the uncorrected model and thus is expected to be a better representation of the real system. A further refinement of the present model can be carried

out by introducing temperature-dependent fundamental frequencies and Lorentzian widths when relevant spectroscopic data are available. By manipulating the hindered translational frequencies, it is possible to achieve better data fit for the modified Einstein model without Lorentzian broadening effect, but the calculated heat capacity at very low temperature (a few degrees K) always drops too fast as is commonly seen in monatomic solids (Sonntag and Van Wylen, 1966). Nevertheless, the modified Einstein model without Lorentzian broadening correction has its value, because it is a convenient and easy to use tool for lattice study as long as fundamental frequencies are properly assigned and the temperature is not too low.

Finally, the entropy of ice at 273.10 K is examined. For the modified Einstein model without broadening, entropy for each vibration mode is calculated using Eq. (5). As broadening effect is considered, integration of heat capacity with respect to temperature, Eq. (10), has to be carried out for entropy evaluation. At 273.10 K, the predicted entropies for ice with and without Lorentzian broadening correction are 2.078 and 2.064 kJ/kg-K, respectively. The entropy obtained from ice calorimetric data by Giauque and Stout (1936) is 2.114 kJ/kg-K. Since the calorimetric entropy of ice is obtained by graphical integration of the measured heat capacities, the discrepancies in entropy prediction directly reflect the discrepancies in the predicted heat capacities. The discrepancy with Lorentzian broadening correction is 1.7 %, which is slightly better than that without Lorentzian broadening correction, 2.4 %, because both methods only have minor differences for heat capacity at very low temperatures. It has to be mentioned that these entropy calculations do not include the residual entropy at 0 K, 0.19 kJ/kg-K (Giauque and Stout, 1936). Including the residual entropy, the entropy evolution with temperature by the present model is shown in Figure 5. The predicted entropy values near the melting point are in agreement with the entropy data at 273.16 K, 2.291 kJ/kg-K, and 273.10 K, 2.304 kJ/kg-K, respectively by Haida et al. (1974) and Giauque and Stout (1936).

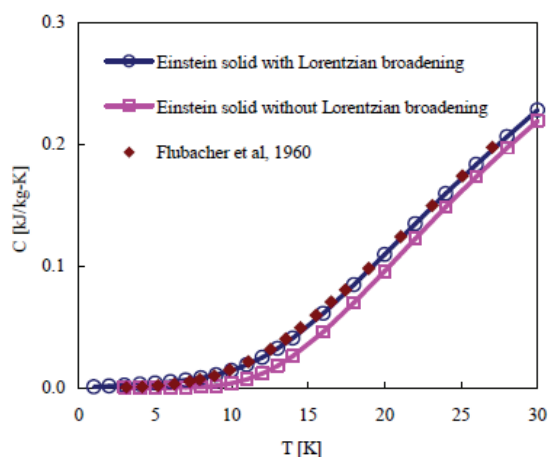


Figure 4. Heat capacity of ice below 30 K. The curves with open circles and open squares are from the modified Einstein model with same frequency parameters as in Figure 3. The diamonds are from Flubacher's experiments (1960).

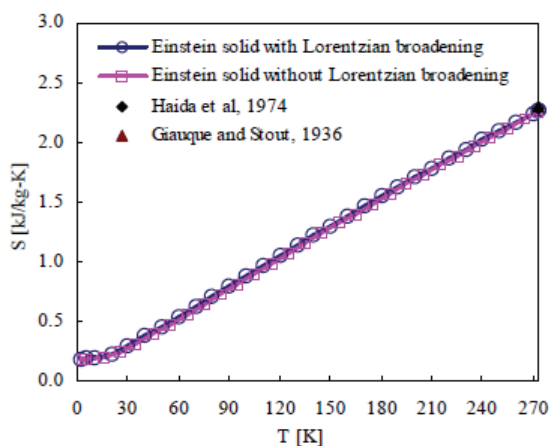


Figure 5. Entropy of ice. The curves with open circles and open squares are from the modified Einstein model with same frequency parameters as in Figure 3. Entropy data by Haida et al. (1974) and Giauque and Stout (1936) are obtained by graphical integration of ice heat capacities at 273.16 K and 273.10 K, respectively. The residual entropy at 0 K, 0.19 kJ/kg-K, is included in all the calculations.

#### 4. Conclusion

The Einstein model for monatomic solids is extended and modified for polyatomic solids in this work and is applied to lattice ice. Six fundamental frequencies taken from ice spectroscopic data are assigned to characterize the hindered translational and rotational vibrations. The intermolecular vibration amplitudes of water molecules and the heat capacity are examined and good agreement between theoretical and experimental results is obtained. This in turn suggests that the six fundamental vibration bands and the harmonic oscillator model convey the major physical information of crystalline solid water. As an analytical, intermolecular vibration model for lattice ice, the modified Einstein's model does not require the information of intermolecular potentials.

In summary, we show that the lattice vibrations in crystalline solid water can be approximated by harmonic oscillations in six degrees of freedom; the fundamental frequencies for hindered translational and rotational vibrations are (65 cm<sup>-1</sup>, 229 cm<sup>-1</sup>, 229 cm<sup>-1</sup>) and (560 cm<sup>-1</sup>, 560 cm<sup>-1</sup>, 560 cm<sup>-1</sup>), respectively. At low temperatures, the thermodynamic behavior of ice is very sensitive to low-frequency vibrations and the thermal excitations of low energy molecules are markedly influenced by intermolecular interactions. A Lorentzian broadening correction for hindered translational vibrations is able to improve the low temperature heat capacity deviations that appear in the Einstein model. On the other hand, the modified Einstein model without Lorentzian broadening is mathematically convenient and is capable of expressing the thermodynamic information of lattice ice over a fairly wide temperature range from 30 K to sub-melting point.

#### Acknowledgments:

Partial support from the H. G. Soo professorship is gratefully acknowledged.

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