Chapter 2: A modified Statistical Thermodynamic Model of Liquid Water

In this chapter we introduce a modified physical model of liquid water, which combines the ideas from the mixture models and the continuum models. According to this model, liquid water's structure is described in terms of big patches of highly organized ice-like regions. The model-parameters are determined by statistical thermodynamic calculations, based on the previous work of Nemethy and Scheraga (Nemethy and Scheraga 1962).

In the course of the statistical thermodynamic treatment, one has to first find a criterion to make a distinction between different water species in partitioning the thermal energy. In liquid water the key properties of water species are mainly determined by the number of H-bonds they form. Therefore it is adequate to choose the H-bonding state of the water molecules as a criterion to partition the thermal energy. At this point, we get use of the physical model to find relative amounts of different H-bonded species.

2.1 The Description of the Physical Model

We describe the structure of supercooled liquid water in terms of big patches of ice-like structure. These patches consist of several thousands of water molecules. Among these molecules there are four hydrogen bonded species constituting the regular ice structure, and many bulk defect molecules, which can be 1-, 2-, 3- bonded or non-bonded. The bulk defects cause local disorders and prohibit the crystallization in the patches before a nucleation event occurs. On the other hand, we assume that defect-free agglomerations of four-bonded water molecules lead to ice embryos of various sizes, in the patches. If the size of an agglomerate reaches a critical value, the ice phase can grow very rapidly, and the liquid-to-solid phase transition takes place. The patches are isolated from each other by the presence of an interphase, which contains mostly the non-bonded water molecules.

For describing the time and space averaged structure of the patches and of the interphase between the patches, we use a "hypothetical phase", which contains only all the lattice defects. The nature of the defects in the hypothetical phase may vary substantially from each other. For instance, one that is formed during the H-bond exchange process can lead to bifurcated-bonds(Ludwig 2007); other one that result from the cooperative concerted motions of disoriented water molecules can lead to Bjerrum defects (Rehtanz 1999) [or equivalently known as flip-flop H-bonds (Saenger, Betzel et al. 1982)]; and another one that couples to the diffusion of water molecules can lead to occupancy of interstitial sites (Rehtanz 1999). Indeed, liquid water has a dynamic structure, where the coordinates of any particular molecule is a function of space and time. We consider the time-average spatial coordinates of water molecules, whenever we refer to our physical model and to the distribution of defects.

The hypothetical phase of defects forms a microheterogeneous mixture with the ice-like phase in liquid water at variable mixing ratios. This ratio changes locally. As a result, there occur different compositions of the patches, which lead to LDL and HDL structures.

The proposed structure of supercooled liquid water is shown in Figure 2.1. In the figure there are two kinds of patches. The ones that are filled with light blue colour symbolize the LDL modification, and the other ones that are filled with dark blue colour symbolize the HDL modification. The main difference between LDL and HDL patches is related to the concentration of hypothetical phase, which contains "fifth water molecules". The surface of an isolated patch (coloured in yellow) is defined by the oxygen atoms of water molecules, which are connected to the bulk of the patch by 2 or 3 hydrogen bonds.

Between the two patches there exists an interphase, which is coloured in green in Figure 2.1. This interphase contains generally the non-bonded water molecules of the hypothetical defect phase. These molecules are adherent on the surface of the patches, highly mobile and have no structural order.
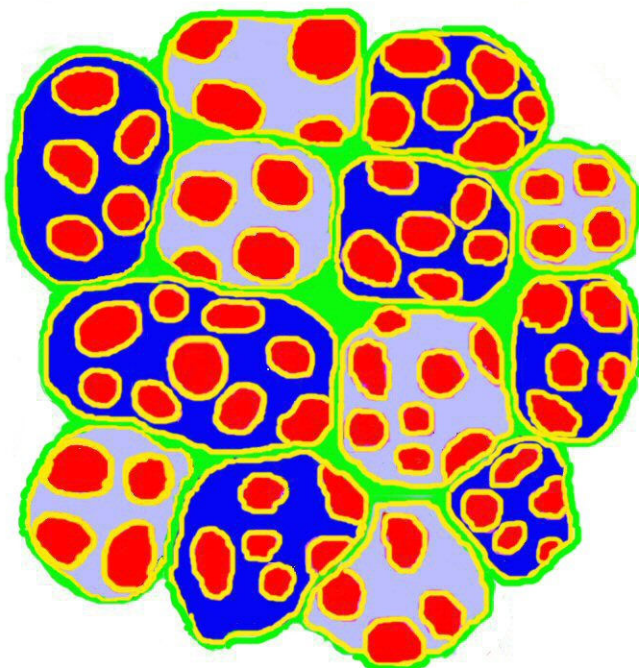
Figure 2.1: Proposed structure of supercooled liquid water in relation to the modified physical model.

The red coloured regions in Figure 2.1 symbolize the 4-bonded agglomerates, which are defect free and have ice-structure. These agglomerates can be found in the bulk of the patches; in the interiors or near to the patch surfaces. When we talk about the agglomerates, we mean four-bonded clusters of water molecules bigger than a certain size. As the sizes of the agglomerates get bigger they start to have more or less spherical shapes (see also Figure 2.2). There can also be 4-bonded molecules of smaller size in the patches. These molecules generally form chains.

The surfaces of the **agglomerates** may not have a smooth and regular structure. The surfaces can rather be fractal and diffuse, which are composed of more than one layer of thickness.

In the progression of the new water model, the non-bonded; 1-, 2-, and 3- bonded water molecules, which belong to the hypothetical phase of defects, are assumed to have binomial distribution. In this manner, we use the likely concept of "hydrogen-bond formation probability" that was introduced by Stanley et al(Stanley and Teixeira 1980; Blumberg, Stanley et al. 1984):

"p" denotes the H-bond formation probability in the hypothetical phase of defects. Bond formation probability p = 1 specifies only the 4-bonded water molecules. The lattice defect molecules of the hypothetical phase have hydrogen bond formation probability *p* less than 1 as a result of broken H-bonds. A binomial distribution given by equation (2-1) is used to relate the fraction of water molecules with *j* intact H-bonds to the to the bond formation probability *p*:

$$f_j = \binom{z}{j} p^j (1-p)^{z-j} \tag{2-1}$$

In equation (2-1), z is defined as the functionality of a water molecule. Given that, water could form a maximum of 4 intact hydrogen bonds with its first coordination shell molecules in a tetrahedral geometry; z equals to 4. *j* changes between zero and four.

With this physical model, we identify the different water species, which is necessary to partition the energy, as being 1-, 2-, 3- , 4- hydrogen bonded and non-bonded. Therefore we fulfil one of the two essential considerations that are required to perform statistical thermodynamical calculations. As a second step we need to quantify the variation in the ratio of different H-bonded species. This can be achieved by relating the concentrations to the structural parameters of the physical model. These parameters are the average size of patches, the mole fraction of the molecules that belong to the hypothetical defect phase and the bond formation probability in the defect phase. The details of the calculations in determining the ratio of different H-bonded species will be given in section 2.2. Prior to these calculations, it is deserving of praise to clarify what we expect from our modified physical model of liquid water, in conjunction to the statistical thermodynamical calculations.
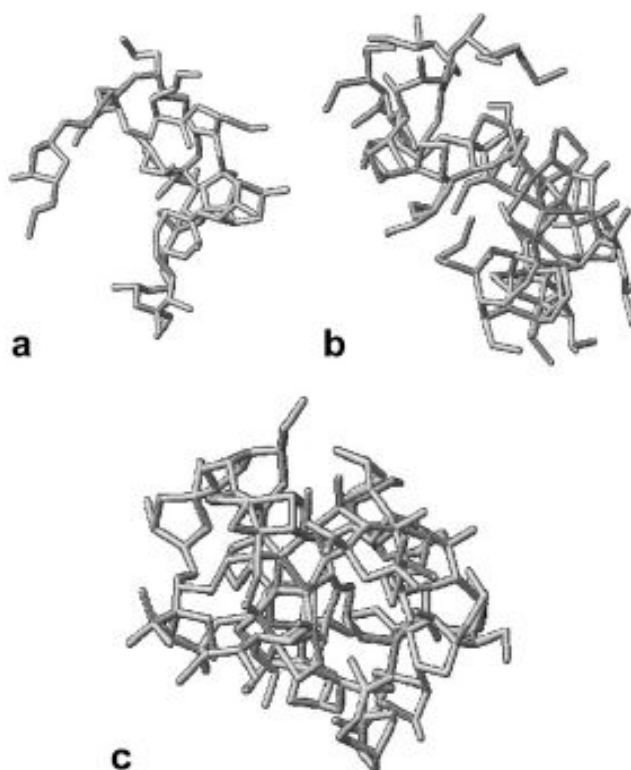
Figure 2.2: Four bonded agglomerates of 'ice-like' structure in supercooled liquid water obtained from a molecular dynamics simulation at 200 K. (a) 100 molecules, (b) 167 molecules, and (c) 250 molecules are shown. After Zasetsky et al (Zasetky, Remorov et al. 2007).

2.1.1 Why do we need a modified physical model?

It is mentioned earlier that neither the continuum models nor the mixture models alone, could give a complete and fully accurate description of entire structural properties of liquid water. A satisfactory explanation of experimental results requires the combination of ideas from the continuum and the mixture models.

The modified physical model of liquid water that is described here has similarities with the mixture models in the sense that water consists of distinguishable species. Most mixture models assume liquid water consists of low density and high density regions as the result of local density fluctuations. The low density regions dominate the well-ordered ice-like structure. For the high density regions considerable amounts of "fifth" water molecule exists.

Proposing big patches with very large number of water molecules differs from the common point of view of the mixture models. We propose that water is a microheterogeneous mixture of an ice-like phase and a hypothetical defect phase. These phases mix with each other at variable mixing ratios. Depending on the ratio of mixing LDL and HDL modifications of the patches are obtained.

This model also incorporates the idea of bond formation probability from the percolation model of liquid water, in order to identify the distribution of the number of H-bonds among the molecules that belong to the hypothetical phase of lattice defect. However, we do not assume a continuous medium of gel-like liquid as in the case of percolation model. Instead, we do assume isolated patches. The presence of patches is used to encapsulate the dynamics of water in their interiors in connection with the lattice defects.

The H-bond formation probability "p" is assumed to be independent of the nature of lattice-defects. Whatever their natures are, they contribute to either one of 1-, 2-, 3- or non-bonded water molecules. Distorted and bifurcated bonds are counted as broken. The rest is evaluated as regular water (or ice-like water). The separation of water species into two main classes and the encapsulation of the minor differences in the subclasses allow us to simplify the mathematical evaluation of our model.

2.2 Mathematical Evaluation of the Physical Model

2.2.1 Determining the Ratio of Different H-bonded Species

There are three parameters that are used to determine the ratio of different H-bonded species for the physical model of liquid water developed here. These are:

1. The total number of 4-bonded water molecules in the bulk of an ice-like patch, plus the 2- and 3- hydrogen bonded molecules on its surface. This number is denoted by the symbol "*g*".
2. The fraction of ice-like molecules in 1 mole of liquid water X_i.

3. The H-bond formation probability of the defect molecules p, which belong to the hypothetical lattice defect phase.

The size parameter "g" refers to the size of an ice-like patch with its surface, excluding the hypothetical phase of defects, in the initial stages of mathematical evaluation. Given a size g of a patch, the relations given by Eadie (1971)(Eadie 1971) can be used to find the number of four-bonded molecules (g4) in the interior of the patch and the number of two- (g2) and three- (g3) bonded molecules on its surface:

$$g2 = 2.621 * g^{(1/3)} \tag{2-2}$$
$$g3 = 3.434 * g^{(2/3)} - 5.241 * g^{(1/3)}$$
$$g4 = g - g3 - g2$$

At this point we do not consider the defects in the bulk. We consider ice-like patches, which are free of defects. In this manner, the sum of four-bonded molecules in the interior of a patch, and the 2- and 3-bonded molecules on the surface layer are counted as ice-like molecules.

As a next step, we introduce the hypothetical phase of lattice defect molecules and an average bond formation probability p for a molecule belonging to this phase. The distribution of hydrogen bonds for these molecules is obtained by the use of equation (2-1). As a result, the open expressions for the mole fractions of non-bonded (b_0), 1- bonded (b_1), 2-bonded (b_2), 3-bonded (b_3), and 4-bonded (b_4) molecules of hypothetical defect phase have the form:

$$b_0 = (1-p)^4 \tag{2-3}$$
$$b_1 = 4 \cdot p \cdot (1-p)^3$$
$$b_2 = 6 \cdot p^2 \cdot (1-p)^2$$
$$b_3 = 4 \cdot p^3 \cdot (1-p)$$
$$b_4 = p^4$$

We now consider the interface between adjacent patches. We mentioned earlier that the molecules in the interface are mostly non-bonded and higly mobile. However, in reality there is a certain possibility that some of the mobile molecules in the interface become connected to the

surface molecules of the patches. Therefore the net result for the long-time average of the surface molecules is an increase in the H-bonding states of them. We can use the following expressions to reflect these changes:

$$g_{3\rightarrow4} = \mathbf{p} \cdot g_3 \tag{2-4}$$
$$g_{2\rightarrow3} = 2 \cdot \mathbf{p} \cdot (1\text{-}\mathbf{p}) \cdot g_2$$
$$g_{2\rightarrow4} = \mathbf{p}^2 \cdot g_2$$

Here $g_{3\rightarrow4}$ indicates the number of 3-bonded molecules becoming four bonded with the attachment of a non-bonded molecule from the interphase. Similarly $g_{2\rightarrow3}$ indicates the number 2-bonded molecules that become 3-bonded, and $g_{2\rightarrow4}$, the number of 2-bonded molecules that become 4-bonded, on the surface of the patches.

Above expressions are based on the assumption that the broken H-bonds of the surface molecules become bonded with the same hydrogen-bond formation probability $\mathbf{p}$ of the hypothetical lattice defect phase. With these corrections the number of 2-, 3- and 4-bonded molecules contributing to the ice-like fraction of patches are given by:

$$G_2 = g_2 - g_{23} - g_{24} \tag{2-5}$$
$$G_3 = g_3 - g_{34} + g_{23}$$
$$G_4 = g_4 + g_{24} + g_{34}$$

If G_2, G_3, and G_4 contribute to the fraction of ice-like molecules $\mathbf{X_i}$ in 1 mole of liquid water, the mole fraction of water molecules that belongs to the hypothetical lattice defect phase would be $\mathbf{(1\text{-}X_i)}$. With this in mind, the mole fractions of all the 0-, 1-, 2-, 3-, and 4- H-bonded species are found by the equations given in (2-6):

$$\mathbf{h_0} = (1\text{-}X_i) \cdot b_0 \tag{2-6}$$
$$\mathbf{h_1} = (1\text{-}X_i) \cdot b_1$$
$$\mathbf{h_2} = (1\text{-}X_i) \cdot b_2 + X_i \cdot (G_2/g)$$
$$\mathbf{h_3} = (1\text{-}X_i) \cdot b_3 + X_i \cdot (G_3/g)$$

$\mathbf{h_4} = (1-X_i) \cdot b_4 + X_i \cdot (G_4/g)$

Here $\boldsymbol{h_0}$, $\boldsymbol{h_1}$, $\boldsymbol{h_2}$, $\boldsymbol{h_3}$, $\boldsymbol{h_4}$, represents the fractions of non-bonded, 1-, 2-, 3- and 4-bonded molecules in a 1 mole of liquid water. The smallest unit for which these mole fractions of different H-bonded species could be obtained is an LDL or an HDL patch plus the adherent interface on its surface. The total size of an LDL or an HDL patch is denoted by the symbol "S_T".

2.2.2 Statistical Thermodynamic Treatment

The expressions for the mole fractions of five different H-bonded species have already been given in (2-6). As a next step the canonical partition function for the liquid water should be constructed. This is done in the same way that is explained by Nemethy and Scheraga (Nemethy and Scheraga 1962). Therefore, the partition function has the same form that is introduced by these authors:

$$Z = \sum_y g(y) \prod_{i=0}^{4} \left[f_i e^{-E_i/RT} \right]^{N_i} \tag{2-7}$$

In equation (2-7), g(y) is the combinatorial factor, which provides the number of all possible configurations for a given state of y with certain mole fractions of H-bonded species ($\boldsymbol{h_0}$, $\boldsymbol{h_1}$, $\boldsymbol{h_2}$, $\boldsymbol{h_3}$, $\boldsymbol{h_4}$):

$$g(y) = \frac{N_A}{N_4! \cdot N_3! \cdot N_2! \cdot N_1! \cdot N_0!} \tag{2-8}$$

Here N_A is the Avogadro's number and $N_i = N_A \cdot \boldsymbol{h_i}$.

Discrete energy levels and equal spacing between each energy level are assumed for the hydrogen bonding interaction in water. The four-bonded water molecules is assigned the ground state, i.e. $E_4 = 0$. The energies assigned to the other H-bonded species are given as $\boldsymbol{E_i} = (i/2) \cdot \boldsymbol{E_H}$, where

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E_H is the apparent hydrogen-bond energy in liquid water, and "i" denotes the number H-bonds a water molecule shares with other water molecules. Since there exists "i/2" moles of H-bonds in a 1 mole of "i-H-bonded molecules", we divide the number of H-bonds "i" by 2 in calculating the contribution of H-bond energy of i-bonded molecules to the system of 1 mole of liquid water.

Nemethy and Scheraga obtained a best-fitting value of E_H = *1.32 kcal/mole* from their calculations for the various thermodynamic properties of liquid water. This value for the H-bond energy in liquid water is also confirmed independently by Smith et al (Smith, Cappa et al. 2004) in an X-Ray absorption study of liquid water.

The factors denoted by f_i in the partition function Z in (2-7), are the molecular partition functions for i-bonded H_2O molecules, which describe their vibrational, rotational and translational freedoms. These assignments are not accounted for the distorted or bifurcated H-bonds. Furthermore it is assumed that the H-bonded species have only vibrational degrees of freedom, whereas the non-bonded species can also have rotational and translational degrees of freedom:

$$f_i = f_v \quad \text{for i= 1,2,3,4} \tag{2-9}$$

$$f_0 = f_t \cdot f_r \cdot f_v$$

f_v, f_t and f_r are given by :

$$f_v = \prod_{j=1}^{s} [1 - \exp(-h\nu_{ij}/kT)]^{-1} \tag{2-10}$$

and

$$f_t = (2\pi m k T / h^2)^{\frac{3}{2}} V_f \tag{2-11}$$

$$f_r = (2\pi/\sigma)(2\pi I k T / h^2)^{\frac{3}{2}} \tag{2-12}$$

The subscripts t, r, and v refer to translation, rotation and vibration respectively. "s" is the number of assigned frequencies for an H-bonded molecule based on the comparison of the infrared and Raman spectra of water and ice (s = 6 for i = 1,2,3,4 and s = 2 for i = 0). These assignments are given in detail in Table 2.1. "σ" is the symmetry number (for water, σ = 2), "m" is the mass of a

water molecule (m = 2.99E-23 g), and I is the moment of inertia along the z-axis (I_z = 1.92E-40

g·cm^2). V_f represents a "free volume" for the translation of an non-bonded molecule, and it is

given by Nemethy and Scheraga as V_f = 4.4E-25 cm^3/molecule as a fitting parameter to their

calculations. The other parameters in the equations given above have their usual meanings; k

being the Boltzmann constant, T is the temperature in Kelvin and h is Planck's constant.

The partition function in (2-7) is evaluated by setting Z to the maximum term in the right-hand

side. Algebraically, the values of the characteristic parameters (**g**, **p** and **X$_i$**) corresponding to the

maximum term can be found by setting W = lnZ (*) and solving the three simultaneous equations

$\partial W/\partial g = 0$, $\partial W/\partial p = 0$, $\partial W/\partial x_i = 0$. However, we used a numerical method for the solution since

it offers an easier way for determining the necessary parameters.

A computer code is written in Fortran programming language in order to perform the numerical

solution. The code implements a heuristic approach, i.e. it scans all the possible combinations of

values for the characteristic parameters in a given range ($13 < g < 8000$, $0.01 < p < 100$, and 0.01

$< X_i < 100$), and finds the maximum of **ln Z**. This code is added to the Appendices (Appendix A).

Once ln Z is optimized the thermodynamic functions are obtained as:

A = -k·T lnZ (2-13)

U = kT^2 $(\partial lnZ / \partial T)_v$ (2-14)

where A is the Helmholtz free energy, and U̲ is the internal energy . By definition

A = U – TS   (2-15)

so that the entropy S is:

S = (U-A) /T   (2-16)

The Gibbs free energy can also be obtained in the same manner:

G = (U + pV – TS) = (A+ pV)   (2-17)

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* For very large values the factorials in ln Z is approximated by Stirling's approximation: ln (x!) = x · (ln x -1)

Table 2.1: Intermolecular vibrational frequency assignments for different H-bonded species in liquid water:

v_1 is attributed to a rotational band, which is assumed to correspond to the bending of the single hydrogen bond. v_2 and v_6 are the bands occurring in the liquid only; they correspond to rotational motions for axes perpendicular to the dipole axis. v_3, v_4, and v_5 are the bands occurring in the spectra of both the solid and the liquid. They are assigned to translational modes. Similarly, v_7, v_8, and v_9 occur in the spectra of both the solid and the liquid, and assigned to translational modes. v_{10} is assigned to a librational mode for 2-bonded molecule. v_{11}, v_{12}, and v_{13} are the bands that occur in the spectra of both liquid and solid, and they are assigned to rotational motions. This table is adopted from Nemethy and Scheraga (Nemethy and Scheraga 1962); refer to the references given there for more information on the frequency assignments.

i (species with i H-bonds)	v1 60 cm-1	v2 145 cm-1	v3, v4, v5 160 cm-1	v6 175 cm-1	v7, v8, v9 210 cm-1	v10 450 cm-1	v11 500 cm-1	v12 650 cm-1	v13 800 cm-1
0	-	assigned	-	assigned	-	-	-	-	-
1	assigned	assigned	assigned	assigned	-	-	-	-	-
2	-	assigned	assigned	assigned	-	assigned	-	-	-
3	-	-	-	-	assigned	-	assigned	assigned	assigned
4	-	-	-	-	assigned	-	assigned	assigned	assigned

For liquid water at 1 atm pressure the pV is relatively small (pV = 0.44 cal) and can be ignored(Nemethy and Scheraga 1962). Hence, G ≈ A. The chemical potential μ equals to the molar Gibbs energy. As a result, Equation (2-13) gives the chemical potential of liquid water when ln Z is optimized for 1 mole of water.

The results of statistical thermodynamical calculations can also be interpreted to obtain the critical size of the ice germ and the size distributions of ice embryos, i.e. the size distribution of agglomerates of four-bonded molecules, at a given temperature. These procedures will be described in summarizing the results, in the following section.

2.3 Results of the Statistical Thermodynamic Calculations

The Eadie's patch-size (*g*), the H-bond formation probability (*p*) of water molecules in the hypothetical phase of lattice defects and the fraction of ice-like molecules (X_i) in a patch are obtained from the statistical thermodynamic calculations as the characteristic parameters. The total size of the patch.

The characteristic parameters define a state of liquid water corresponding to a maximum of ***ln Z*** at a given temperature, with a specific distribution of hydrogen-bonded molecules (as mole fractions h_0, h_1, h_2, h_3, h_4). At each temperature point, these parameters are re-calculated by running the FORTRAN code with the given temperature value. The results are summarized in Tables 2.2 and 2.3.

The size of a patch *(g)*, in analogy to Eadie's definition, is given as the sum of the surface molecules which are having 2- and 3- hydrogen bonds, and the four hydrogen bonded molecules in the interior of a patch. This assignment is made according to the expressions given in (2-5):

$$(g) = (G_4) + (G_2) + (G_3) \qquad\qquad (2\text{-}18)$$

Consequently the fraction of ice–like molecules X_i is defined as the ratio of the sum ($G2 + G_3 + G_4$) to the total number of molecules S_T in a patch:

$$X_i = \frac{G_2 + G_3 + G_4 \ (in \ 1 \ mole)}{S_T} \qquad (2\text{-}19a)$$

Equivalently:

$$S_T = \mathbf{g} / X_i \qquad (2\text{-}19b)$$

The total number of defect molecules belonging to the hypothetical defect phase is then:

$$n_d = S_T - \mathbf{g} \qquad (2\text{-}20)$$

and their mole fraction is

$$\mathbf{v_d} = 1 - X_i \qquad (2\text{-}21)$$

Table 2.2: The patch size (g) in analogy to Eadie's definition, the bond-formation probability (p) of a water molecule that belongs to the hypothetical defect phase, and the fraction of ice-like molecules (X_i), which are obtained as characteristic parameters from the statistical thermodynamic calculations, and other derived parameters. Refer to the text for the nomenclature.

T / °C	g	p	X_i	n_d	S_T	ν_d
0.0	1644	0.24	0.47	1854	3498	0.53
-10.0	1752	0.25	0.52	1617	3369	0.47
-20.0	1838	0.26	0.57	1387	3225	0.43
-30.0	2066	0.28	0.62	1266	3228	0.39
-35.0	2200	0.29	0.64	1238	3338	0.37
-36.0	2171	0.29	0.65	1169	3340	0.35
-37.0	2225	0.29	0.65	1198	3423	0.35
-40.0	2220	0.30	0.67	1093	3313	0.33

Table 2.3: Mole fractions of H-bonded and non-bonded water molecules at a given temperature, obtained from statistical thermodynamical calculations; and the corresponding ln Z values.

T / °C	ln Z	h0	h1	h2	h3	h4
0.0	1.392E+24	0.177	0.223	0.110	0.116	0.379
-10.0	1.283E+24	0.152	0.203	0.107	0.123	0.416
-20.0	1.179E+24	0.129	0.181	0.101	0.130	0.459
-30.0	1.075E+24	0.102	0.159	0.098	0.134	0.507
-35.0	1.025E+24	0.091	0.149	0.097	0.135	0.528
-36.0	1.015E+24	0.089	0.145	0.094	0.136	0.535
-37.0	1.006E+24	0.089	0.145	0.094	0.136	0.536
-40.0	9.783E+23	0.079	0.136	0.092	0.138	0.534

2.3.1 Evaluation of the Thermodynamic Properties

A-) Probability of Defect Formation

The results given in Table 2.2 show that the total size of the patches (S_T) do not change considerably with the effect of decreasing temperature (see also Figure 2.3). However Eadie's patch-size (*g*) increases and the number of defect molecules per patch decreases. Therefore the probability of a defect formation decreases with decreasing temperature.

The mole fraction of hypothetical lattice defect phase $\mathbf{v_d}$ equals to the defect formation probability in a mole of liquid water. The inverse temperature dependence of this probability is plotted in Figure 2.4. As it is seen from the figure the defect formation probability $\mathbf{v_d}$ decreases with the effect of decreasing temperature.

The decrease in the probability of formation of defects tells us that the order in the patches increases. As well, this trend can be followed from the temperature dependence of the mole fractions of H-bonded species in Table 2.3. There it is seen that the mole fraction of four H-bonded water species increases whereas the mole fraction of non-bonded water species decreases as the temperature decreases.

The metastability of a supercooled system is a question of order, which is described by the entropy. The increase of order in a metastable system will bring itself closer to the more stable phase, which is ice in this case. Therefore the results given above indicate that the patches in liquid water become more ice-like as the degree of supercooling increases.
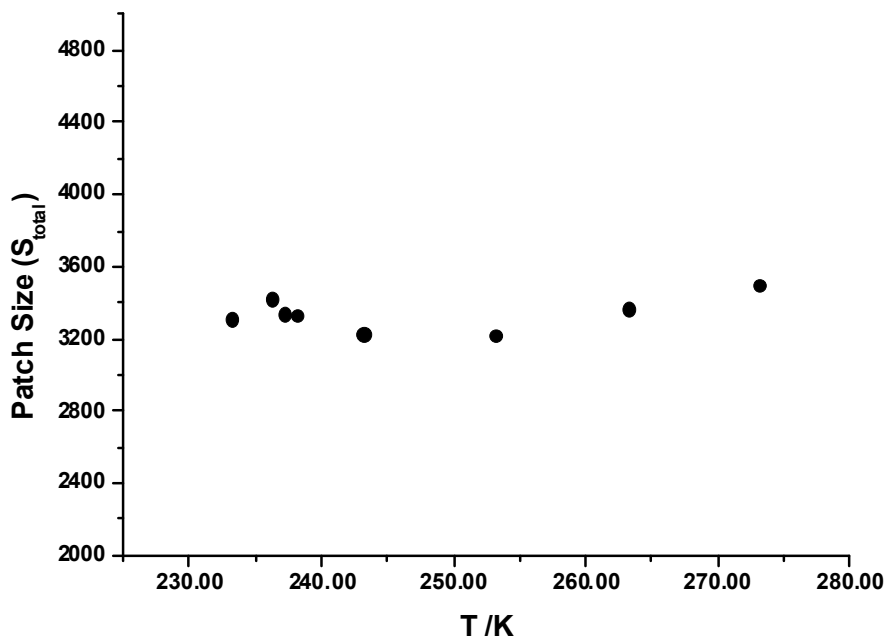
**Figure 2.3: The average total size of the patches (S_T) plotted against temperature. As the figure shows, the
total number of molecules included in a patch is almost independent of temperature.**
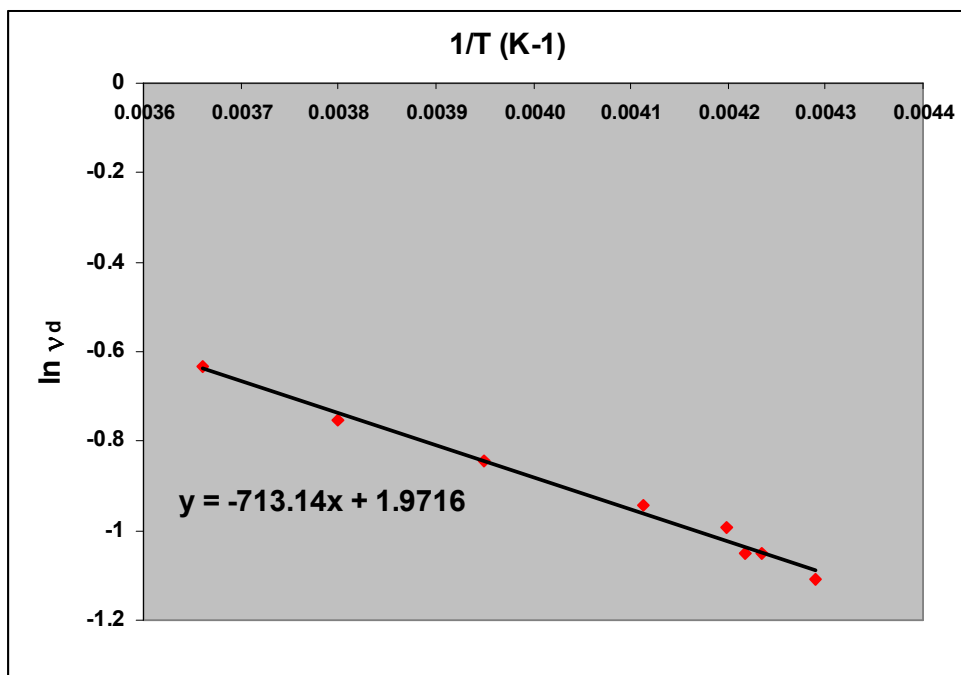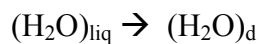

Figure 2.4: The inverse temperature dependence of defect formation probability in liquid water.

Finally we can evaluate the average activation energy for the formation of defects assuming first order kinetics with a rate R:

$(H_2O)_{liq}$ → $(H_2O)_d$

$$R = k[(H_2O)_{liq}] = d[(H_2O)_d]/dt \qquad (2\text{-}22)$$

In the case of steady state above expression can be written as:

$$k[(H_2O)_{liq}] = [(H_2O)_{b\text{-}d}] \qquad (2\text{-}23)$$

Rearranging Equation (2-26) and taking the natural logarithm of both sides, we have:

$$\ln k = \ln k_0 - E_A/RT = [(H_2O)_{b\text{-}d}]/ [(H_2O)_{liq}] \qquad (2\text{-}24)$$

Following Equation (2-24), the average activation energy for the formation of a bulk-defect molecule is obtained from the slope of the linear-fit in Figure 2.4. This energy is calculated as E_A = 1.42 kcal/mole, which is slightly larger than the hydrogen bond energy in liquid water (E_H = 1.32 kcal/mole).

B-) Interpretation of the Density Fluctuations

Although the nature of defects may vary in the hypothetical defect phase, we assume that the majority of them are interstitial water in order to be in line with the experimental temperature dependence of density. Interstitial water molecules lead to an increased coordination, thus an increased local density.

As a first approximation, we can assign an average density for the hypothetical defect phase. In addition, we assign the density of ice to the ice-like phase. As a result, we express the temperature dependence of density in supercooled liquid water with the following equation:

$$\rho_T(\text{liq}) = X_i \cdot \rho_T(\text{ice}) + (1 - X_i) \cdot \rho_T(d) \qquad\qquad (2\text{-}25)$$

Here $\rho_T(\text{liq})$, $\rho_T(\text{ice})$, $\rho_T(d)$ are the temperature dependent molar densities of liquid water, ice and hypothetical defect phase. From these density values, $\rho_T(\text{liq.})$ is available down to -35 °C from the experimental results of Hare and Sorensen (1987) (Hare and Sorensen 1987). A fitting polynomial expression is also given in the same reference. On the other hand there are several references to obtain the temperature dependence of the density of ice (Lonsdale 1958; Eisenberg and Kauzmann 1969; Feistel, Wagner et al. 2005). From these references we refer to the equations of state approach developed by Feistel et al (2005) (Feistel, Wagner et al. 2005) to calculate the density of ice.

Feistel et al provide a Fortran code for the computation of the Gibbs function of ice and its partial derivatives. The density of ice can also be calculated by getting use of this code. Therefore, we integrate their code to our main Fortran program in order to calculate the density of ice at a given temperature.

The only unknown being $\rho_T(d)$ in Equation (2-25), can be found by substituting the values of $\rho_T(\text{liq})$, $\rho_T(\text{ice})$ and X_i to this equation, at a given temperature T. The values of $\boldsymbol{\rho_T(d)}$ calculated in this manner are given in Table 2.4. For comparison purposes the density of supercooled liquid water and the density of ice are also given. These results of the density calculations show that the hypothetical phase of defect water molecules has a density maximum at about -30 °C. This finding indicates that the nature of the defects is changing below -30 °C. Most probable explanation is that the contribution of the interstitial molecules to the hypothetical defect phase decreases and the contribution from vacancies increases as the temperature fall below -30 °C.

Table 2.4: The temperature dependence of the densities of ice, hypothetical-defect phase and supercooled liquid water. The density values are given in g/ml.

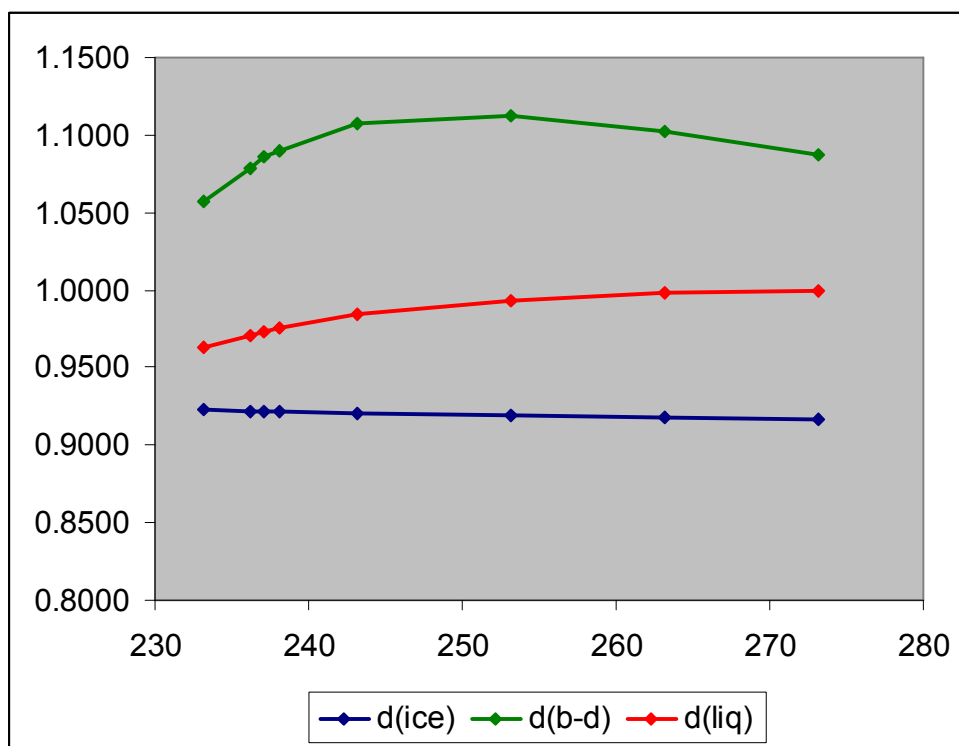| T / °C	ρ_T(ice)	ρ_T(d)	ρ_T(liq)
0.0	0.9168	1.0872	0.9997
-10.0	0.9182	1.1018	0.9981
-20.0	0.9196	1.1120	0.9937
-30.0	0.9210	1.1073	0.9839
-35.0	0.9215	1.0892	0.9754
-36.0	0.9215	1.0866	0.9733
-37.0	0.9220	1.0781	0.9712
-40.0	0.9224	1.0572	0.9629

Figure 2.5: The temperature dependence of the densities plotted for ice, liquid water and the hypothetical defect phase.

C-) Calculation of the Chemical Potentials

We calculate the chemical potentials, i.e. the molar Gibbs free energies of supercooled liquid water, ice, and the hypothetical defect phase in the following way: The chemical potential of liquid water (μ_{liq}) is obtained directly from the statistical thermodynamic calculations by using Equations (2-13) and (2-17). To evaluate the chemical potential of ice (μ_{ice}) we get use of the equilibrium vapor pressures of supercooled liquid water and ice, provided that the difference of the chemical potentials of ice and supercooled liquid water at a given temperature is the function of the ratio of their vapour pressures:

$$\Delta\mu = \mu_{ice} - \mu_{liq} = k \cdot T \, ln(P_{ice}/P_{liq}) \tag{2-26}$$

In this manner Koop et al (Koop, Luo et al. 2000) have obtained an expression that gives $\Delta\mu$ as a function of temperature:

$$\Delta\mu_{ice\text{-}liq} = (1/\,N_A) \cdot (\,210368 + 131.438T - 3.32373 \times 10^6 /T - 41729.1 \, lnT) \tag{2-27}$$

Here $\Delta\mu$ is expressed in SI units of Joule/mole.

In calculating the chemical potential of the defect phase μ_d, we applied the following method: We first find the mole fractions of i-bonded water molecules in a 1 mole of hypothetical bulk-defect phase by using the equations in (2-3), and by substituting the value of p as the bond-formation probability of a water molecule, which has been obtained from statistical thermodynamic calculations of liquid water. Finally, putting these values into the partition function in Equation (2-7) and taking the natural logarithm of the resulting expression, we arrive at the chemical potential of hypothetical phase liquid water, which is composed only of lattice defects:

$$\mu_d = k \cdot T \, lnZ(d) \tag{2-28}$$

The chemical potential values for μ_{liq}, μ_d, and μ_{ice} are given in Table 2.5. The values given for μ_{ice} in the fourth column are calculated by adding the values of μ_{liq} obtained from statistical

thermodynamic calculations, to the values of $\Delta\mu_{\text{ice-liq}}$ obtained through the expression given by Koop et al.

The trends in the chemical potentials of liquid, solid and defect phases show that the least stable phase is the hypothetical defect phase, as expected. Moreover its instability in comparison to supercooled liquid water and ice increases with decreasing temperature. This means the occurrence of a defect molecule in supercooled liquid water becomes less favorable as the temperature decreases, and the probability of defect formation decreases with decreasing temperature.

Table 2.5: Calculated values for the chemical potentials of supercooled liquid water μ_{liq}, the hypothetical defect phase of water μ_d and ice μ_{ice} ; the values are given in kJ/mole.

T / °C	μ_{liq}	μ_d	μ_{ice}
0.0	-5.247	-4.031	-5.246
-10.0	-4.659	-3.311	-4.879
-20.0	-4.118	-2.626	-4.534
-30.0	-3.609	-1.979	-4.195
-35.0	-3.369	-1.671	-4.035
-36.0	-3.323	-1.604	-4.003
-37.0	-3.277	-1.536	-3.972
-40.0	-3.146	-1.374	-3.883

2.3.2 Evaluation of the Size of Critical Ice Nucleus

According to the physical model introduced here, it is expected that the ice nucleation occurs inside a patch from the agglomerates of four-bonded molecules. These agglomerates are defect free in nature, contain four bonded molecules whose number is larger than roughly a hundred or more, and have a certain size distribution above this size. They may not be spherical given that their boundaries are determined by the portion of defect-molecules around them selves. However, it is convenient to concern spherical geometry for the simplicity of the calculations. In this manner an ice embryo is defined as the spherical agglomerates of four-bonded molecules, plus the defect molecules surrounding the agglomerate on the surface.

In the classical nucleation theory (CNT), it is supposed that a surface tension arises on the surface of an ice embryo due to mismatch of the lattice arrangement of ice molecules and the liquid water molecules. CNT assumes a monolayer of surface for the ice-liquid water interface. Here, we assume that the surfaces of the agglomerates consist of the molecules of hypothetical defect phase of one or more molecular layer thickness. Consequently, the free energy of the formation of ice-embryos is calculated as:

$$\Delta G_n = (n_4 \cdot \mu_{ice}) + (n_d \cdot \mu_d) - (n_4 + n_d) \cdot \mu_{liq} \tag{2-29}$$

Here n_d, i.e. the number of defect molecules the on the diffuse surface layer of an ice embryo. The expression that gives the relation between n_d and the surface thickness dr, in the case of a spherical embryos is:

$$n_d = V_{surf} / V_d = \frac{4 \cdot \pi \left[(R_{agg} + dr)^3 - R^3 \right]}{3 \cdot V_d} \tag{2-30}$$

V_{surf}: The volume of the surface layer of a thickness dr for spherical agglomerate.

R_{agg}: The radius of the four bonded agglomerate that belongs to the inner shell only.

dr: the thickness of the surface layer on the outer shell.

V_d: packing volume of a defect molecule of hypothetical defect phase.

V_d can be found as given below:

$$V_d = V_m(d) / N_A \tag{2-31}$$

Here $V_m(d)$ is the molar volume of the hypothetical bulk-defect phase, and can be obtained from the density values given in Table 2.4. Similarly the packing volume of an ice molecule is calculated as:

$$V_{ice} = V_m(ice) / N_A \tag{2-32}$$

The number of molecules that are contained in the agglomerates, excluding the surface layer is given by:

$$n_4 = V_{aggl.} / \mathbf{V(ice)} = (4/3)\cdot\pi\cdot R^3 / \mathbf{v(ice)} \tag{2-33}$$

The size of the critical nucleus is found in the usual manner, i.e. by determining the maximum of ΔG_n. The temperature dependence of the critical nucleus size is given in Table 2.6 for different surface thicknesses. As seen from the table, the size of critical nucleus is strongly dependent on the thickness of the outer surface layer of agglomerates, which consist of hypothetical defect phase molecules. As will be further evaluated in Chapter 3, the surface thickness near the homogenous nucleation temperature of ice is about 1.8 – 2.0 Å, which corresponds to a critical size of $n^* \approx 330$.

Table 2.6: The temperature dependence of the size of a critical ice nucleus at different surface thicknesses, in supercooled liquid water: n_4 is the number of 4-bonded water molecules in the inner shell of an ice-embryo, n_d is the number of defect molecules on the surface layer at a given surface thickness, and n_T (=n_4 + n_d) is the total number of molecules in an ice embryo.

T / °C	n_4	n_d	n_T
At a surface thickness of 1.37 Å			
0		Infinite	
-10	1150	290	1440
-20	250	110	360
-30	120	69	189
-36	90	57	147
-40	70	48	118

T / °C	n_4	n_d	n_T
At a surface thickness of 2.055 Å			
0		Infinite	
-10	3900	982	4882
-20	850	374	1224
-30	400	232	632
-36	290	187	477
-40	240	162	402

T / °C	n_4	n_d	n_T
At a surface thickness of 2.4 Å			
0		Infinite	
-10	6200	1562	7762
-20	1350	595	1945
-30	650	375	1025
-36	450	293	743
-40	380	257	637

2.3.3 The Size Distribution of Agglomerates

The size distribution of agglomerates corresponds to the steady state distribution of ice embryos, in CNT. Here, we assume that this size distribution is characterized by a Boltzmann distribution:

$$\frac{N_i}{N} = \frac{g_i e^{-E_i/k_B T}}{Z(T)}$$

$$Z(T) = \sum_i g_i e^{-E_i/k_B T}$$

(2-34)

In the above equation N_i is the number four-bonded agglomerates that is composed of "i" water molecules, and N is the total number of water molecules in the system. Similarly the term g_i .exp(-$E_i/k_B T$) defines the characteristic partition function Z(i) that belongs to the system of interest, which consists only of 4-bonded agglomerates of size "i" including their surface layers. On the other hand the term Z(T) is the canonical partition of liquid water, which includes all the possible states available to different configurations of water molecules.

A direct analysis of the size distribution of agglomerates according to (2-34) lead to too low values of N_i/N since Z(T) is much larger than Z(i). Indeed this result has already been expected referring bak to the evaluation of Z(T) in Section 2.2.2. There, it is stated that the maximum term in Z(T), is much larger than all the other contributions, and can be represented for the whole system including all other possible configurations. Therefore, it is not possible to get reasonable values for the distribution of i-bonded agglomerates, by taking the ratio of P(i) = Z(i) / Z(T). However, one can obtain the relative distribution of sizes of 4-bonded agglomerates with size i. For this purpose , the procedure given below is followed:

- In the first step the characteristic partition functions for a given systems of 4-bonded agllomerates plus the hypothetical phase of the defect molecules contributing the suface of agglomerates is evaluated. A system that is composed only of agglomerates with size "n" including the surface molecules of hypothetical defect phase would have a definite distribution of different H-bonded species. The caharacteristic partition function Z(n)

- could be obtained by putting the mole fractions of different H-bonded species into Equation (2-7).

- ▪ The maximumof $Z(n)$ obtained in this manner will correspond to the characteristic partition function for average size of the agglomerates: $Z(avg)$.

- ▪ The relative ratio of concentration of other agglomerates composed of n water molecules could be obtained by comparing $Z(n)$ to $Z(avg)$:

$$P_{rel.}(n) = Z(n) / Z(avg) \tag{2-35}$$

Finally, we assume that the isolated patches in liquid water behave as independent identitites. Therefore the probability of formation of an ice embryo with size "i" is independent of the condition of other patches. This also means that the total number of molecules in a system equals to the total size of the patches S_T, in evaluating the partition functions in Equation (2-35).

Representative examples of size distributions for 4-bonded agglomerates at different temperatures are shown in Figure 2.6. The given size distribution are obtained for a fixed value of surface thickness ≈ 2 Å. The changes of average size and the size of the critical nucleus are plotted in Figure 2.7, again at a fixed surface thickness of 2 Å. These figures show that the average size of ice-embryos increases with decreasing temperature. On the other hand the size of the critical germ decreases at colder temperatures. At -40 ° C the average size of the ice-embryos become comparable to the size of the critical ice-germ. This might be one of the reasons that we observe an asymptotic increase in the nucleation rates below -35 °C.
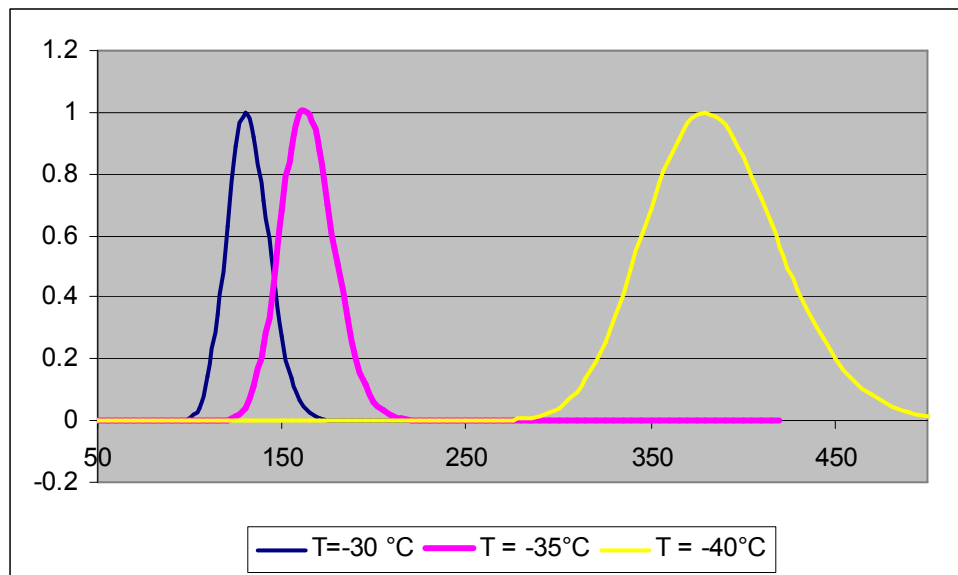
Figure 2.6: Relative size distributions of the 4-bonded agglomerates, according to the results of statistical thermodynamical calculations. With the effect of decreasing temperature the average size shifts to higher values and the distribution broadens.
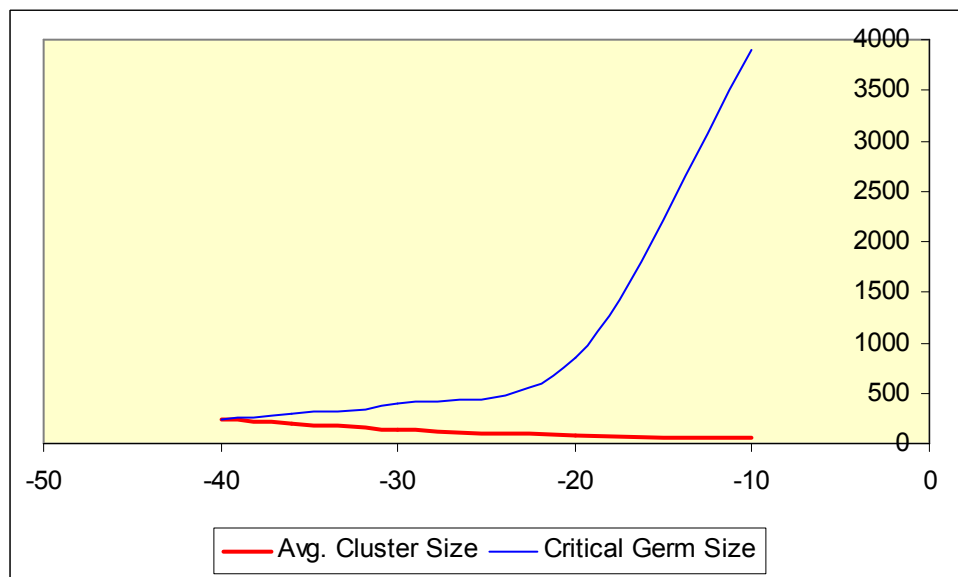

Figure 2.7: Variation of average cluster size and the critical germ size with the effect of decreasing temperature.

2.4 Summary

To describe the structure of liquid water, we have introduced a hypothetical phase of lattice defects and an ice–like phase. There is a microheterogenity in liquid water for which the ice-like phase and the hypothetical defect phase mix at variable mixing ratio. The patches in liquid water are the smallest units, which reveal the properties of liquid water. One may distinguish two kinds of patches: Those which contain only little lattice defects are called LDL patches, and those which contain a considerable number of "interstitial water molecules" are called HDL patches.

The size of the patches depends hardly on the temperature. It decreases only by ~ 5% between 0°C and -40°C. On the other hand the ratio of defect phase to ice-like phase has strong temperature dependence. With the decrease of temperature, this ratio decreases and the ice-likeliness of the patches increases.

There occur defect free agglomerations of 4-bonded molecules inside the patches. These agglomerates bear a resemblance to ice embryos of different sizes. The average size of the 4-bonded agglomerates increases with the decrease of temperature.

During homogenous nucleation of ice in supercooled liquid water, the critical nucleus grows from the 4-bonded agglomerates. As will be discussed in more detail in the following chapters, these agglomerates can grow more easily if they occur at the surface of the patches. This is because the mostly non-bonded more mobile water molecules from the interface in between the patches can catalyse a faster growth on the surface.

If there are solutes added to liquid water, they are mostly concentrated in the interface in between the patches. By this way they can inhibit nucleation more effectively by sticking on the growing sites of agglomerates near the patch surface.

Table 2.7: Nomenclature of the structural parameters related to the physical model of supercooled liquid water.

g	Defines the number of 4-bonded water molecules in the bulk of a patch plus the number of 2- and 3- bonded molecules on the surface of a patch. In line with this definition, g describes the size of an ice-like patch, free from lattice defect molecules.
S_T	Total number of 4-bonded molecules and the molecules with less than 4-Hydrogen bonds which constitutes a patch and its adherent interface.
n_d	It is the number of water molecules in the hypothetical phase of defects. It can be mixed with ice-like patches forming LDL and HDL patches. The interphase on the surface of the patches contains mostly the non-bonded water molecules, which also belong to the hypothetical defect phase.
p	H-bond formation probability in the hypothetical phase of defects. p=1 means only 4-bonded water molecules.
v_d	Mole fraction of the hypothetical defect phase.
X_i	The mole fraction of the ice like phase. $1-X_i$ is the mole fraction of hypothetical phase v_d