Chapter 3: Homogenous Nucleation of Ice in Supercooled Liquid Water

Until now, several experimental studies were conducted to investigate the homogeneous nucleation of ice in supercooled liquid water (Hagen, Anderson et al. 1981; Angell 1983; Taborek 1985; Sassen and Dodd 1988; Huang and Bartell 1995; Kramer, Hübner et al. 1999; Duft and Leisner 2004; Stöckel, Weidinger et al. 2005). In addition, the growth of the critical nucleus was simulated in molecular dynamics (MD) studies (Matsumoto, Saito et al. 2002; Radhakrishnan and Trout 2003; Vrbka and Jungwirth 2006). While the experiments provided nucleation rate data to check the validity of theoretical calculations, the molecular dynamics simulations revealed promising results in understanding the mechanism of critical-nucleus formation.

Although, these studies contributed much to the understanding of the nucleation phenomenon in supercooled liquid water, a complete picture of the dynamics of ice nucleation has not been readily drawn. At first, the comparison of experimental results and the early theoretical calculations had shown that there is a discrepancy between the experimentally obtained results and the theoretical estimations. It was found that the theory overestimates the nucleation rates at warmer temperatures and underestimates at colder temperatures (Pruppacher and Klett 1997). Secondly, the present molecular dynamics simulations are performed at most with a few hundreds of molecules, for very small time intervals. Therefore, the results of MD simulations should be evaluated cautiously in making analogies to the macroscopic evaluation of a critical ice nucleus at the homogenous nucleation temperature.

The unusual behaviour of metastable liquid water in relation to its structure adds more complexity to the problem. Since water molecules strongly associate through hydrogen bonding, and there exists large number of possibilities for their network configurations, there also exists large number of possibilities in defining a path, connecting the metastable phase of supercooled liquid water into stable solid phase (Matsumoto, Saito et al. 2002). In this respect, MD simulations may only partially describe the dynamics of critical nucleus formation.

The first theoretical calculations that deviated from the experimental results were based on the classical theory of homogeneous nucleation (CNT). The nucleation rate equation obtained from the classical theory contains both thermodynamical and kinetic parameters. The thermodynamic parameters are related to the energy of nucleus formation, and the kinetic parameters to the flux of molecules on the surface of the nuclei, that affords the growth. To match the theoretical estimations to the experimental results, several authors have modified the nucleation rate equation of CNT. Those, of whom mainly focused on the kinetic term {Hagen et al (1981)(Hagen, Anderson et al. 1981) , Pruppacher and Klett (1995) (Pruppacher and Klett 1997), Huang and Bartel (1995) (Huang and Bartell 1995)}, modified the prefactor in the nucleation rate equation. The thermodynamical term, which is the energy of germ formation, was also studied by several other authors (Eadie 1971). They mainly focused on the precise calculation of the interfacial free energy and the chemical potential differences of the mother and daughter phases.

As a result of different approaches in modifying the nucleation rate equation in CNT, different expressions had appeared. They differ in the parameterisation of the kinetic or thermodynamic terms. However, the basic mechanism assumed for the kinetics of nucleation growth stays the same, i.e the ice nucleus grows by the addition of molecules (or molecular aggregates) from the mother phase, by a particle flux.

In Chapter 2, we have introduced a modified physical model of supercooled liquid water. The most prevailing assessment of this model is the presence of big patches, which behave as independent identities, and which are the smallest units that can characterizes the thermodynamic properties of liquid water. In this model, the ice-embryos grow from the ice-like agglomerates that are found inside the patches. These agglomerates are separated from each other by diffuse surface layer of defect molecules. This model lends a new insight into the dynamics of homogeneous ice nucleation.

We propose that the agglomerates near the surface of the patches can grow faster than the agglomerates in the interior of the patches. This is because; near a patch surface the agglomerates grow by the addition of non-bonded water molecules from the interphase in between the patches. The non-bonded molecules can diffuse faster on the surface of the agglomerates, in comparison to the molecules inside the patches.

We wish to formulate this new insight to describe the kinetics of ice nucleation. At first step, we find it useful to give a review of the classical nucleation theory to familiarize the reader with the concepts and formulations of the nucleation rate equation. This is done in Section 3.1.We will also point out to other alternative approaches; in Section 3.2. Our new approach to the kinetics of ice nucleation is formulated in Section 3.3.

3.1 The Review of the Classical Nucleation Theory

The nucleation of ice in nature is mostly heterogeneous, i.e. foreign particles or surfaces take part in the formation of ice embryos. In the absence of foreign particles and surfaces, a critical nucleus of the ice phase has to be formed from the molecules of the mother phase before a phase transition occurs. It is then called homogeneous nucleation.

The growth of ice germs is described by the nucleation rate in supercooled water. The homogeneous nucleation rate is calculated in two steps: The first step involves finding out the size distribution of embryos at a given temperature from the energetic of embryo formation. A steady-state distribution of embryos is assumed. Critical size for the nucleus that would spontaneously grow into the crystal of new phase is calculated from the maximum energy of embryo formation. The second step then consists of finding out the net flux of molecules that attach on the surface of the critical cluster.

This approach, which is known as classical nucleation theory (CNT) has been first introduced by Volmer and Weber(Volmer and Weber 1926) for the droplet condensation from supercooled water vapour. Subsequent developments are followed (Becker and Döring 1935; Zeldovich 1942). It is adapted to homogeneous nucleation in supercooled liquids by Turnbull and Fischer (Turnbull and Fisher 1949).

The basic kinetic mechanism assumed in the classical nucleation theory is that the small clusters grow and decay by the absorption or emission of single molecules:

$(H_2O)_n + H_2O \leftrightarrow (H_2O)_{n+1}$
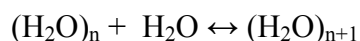
In droplet condensation from supercooled water vapour, $(H_2O)_n$ represents the liquid phase clusters containing n water molecules. In ice nucleation, these are the ice embryos embedded in the mother phase of liquid water.

The steady state nucleation rate, which is the number of embryos formed per unit volume per second, is given by:

$$J = c_g \cdot f \cdot \Omega_g \qquad (3\text{-}1)$$

Here c_g is the concentration of critical ice germs per unit volume, Ω_g is the surface area of the critical germ, and f is the net flux of water molecules on the surface of the critical germ. In this theory, the critical germ is assumed to be spherical. By convention, the nucleation rate is given in "number of ice germs per cubic centimetre per second":

$$J \,(mol \cdot cm^{-3} \cdot s^{-1}) = c_g \,(mol \cdot cm^{-3}) \times f \,(mol \cdot cm^{-2} \cdot s^{-1}) \times \Omega_g \,(cm^2 \cdot mol^{-1})$$

The detailed description and derivation of the parameters that takes part in Equation (3-1) will be given in the following sections. By substituting the equivalent expressions derived for these terms, we arrive at the nucleation rate equation given below:

$$J = N \cdot N_c \cdot Z \cdot \Omega_g \cdot \left(\frac{kT}{h}\right) \exp\left(\frac{-(\Delta G_{n*} + \Delta g^*)}{kT}\right) \qquad (3\text{-}2)$$

N: Total number of the water molecules in the system.

N_c: Number of monomers of water in contact with the unit area of the ice surface.

Z: The Zeldovitch factor.

ΔG_{n*}: The free energy of critical-nucleus formation.

Δg^*: Free energy of activation for the diffusion of water molecules across the ice-water interface.

The quantity $N_c \cdot Z \cdot \Omega_g$ is usually on the order of unity in most nucleating systems. By equating it to unity the Equation (3-2) simplifies to (3-3):

$$J = \frac{NkT}{h} \exp\left(\frac{-(\Delta G_{n*} + \Delta g^*)}{kT}\right)$$

(3-3)

Equation (3-3) does not require the knowledge of the number of molecules in contact with the surface of an ice-embryo (N_c), in evaluating the homogeneous nucleation rates.

3.1.1 The Free Energy of Critical Nucleus Formation

The energetic of embryo formation is evaluated by getting use of macroscopic quantities in the classical approach, assuming that the embryos have bulk properties. This is referred to as the capillary approximation(Debenedetti 1996). These quantities are the surface tension of the ice-water interface ($\sigma_{i/w}$) and the difference of the bulk free energies ($\Delta\mu = \mu_i - \mu_w$) of liquid and solid phases. The free energy of ice-germ formation from n water molecules is given by Equation. (3-4):

$$\Delta G_n = \sigma_{i/w} A_n + n\Delta\mu$$

(3-4)

$\sigma_{i/w}$: Surface tension of ice-water interface.

A_n: Surface area of the ice-germ composed of n molecules of the new phase.

$\Delta\mu$: The difference of chemical potential per molecule in ice and liquid water.

n: The number of water molecules.

The surface area of the germ composed of n molecules is described as:

$$A_n = \gamma \cdot n^{2/3}$$

(3-5)

Here γ is a geometric factor, which is assumed to be independent of n.

For the critical cluster, ΔG_n passes through an absolute maximum, thus the number of molecules n* in the critical cluster is found by equating ($\partial G_n/\partial n$) to zero:

$$n^* = (-2 \cdot \gamma \cdot \sigma_{i/w} / 3 \cdot \Delta\mu)^3$$

(3-6)

In a spherical nucleus $\gamma = 4\pi(r)^2$, where **r** is the Van der Waals radius of the water molecule in ice. "**r**" can be approximated by dividing the molar volume of ice to Avagadro's number N_A, for a hard-sphere of water molecule:

$$(4/3) \cdot \pi \cdot r^3 = V_M / N.A. \tag{3-7}$$

In Eq. (3-7), V_M is the temperature-dependent molar volume, which equals to M.W. / ρ_i (T) . It then follows from (3-7):

$$r(T) = \sqrt[3]{\frac{3}{4} \cdot \frac{1}{\pi} \cdot \frac{M.W.}{N_A} \cdot \frac{1}{\rho_i(T)}} \tag{3-8}$$

and

$$\gamma(T) = 4 \cdot \pi \cdot \left[\frac{3}{4} \cdot \frac{1}{\pi} \cdot \frac{M.W.}{N_A} \cdot \frac{1}{\rho_i(T)} \right]^{2/3} \tag{3-9}$$

By substituting Equation (3-9) into (3-6), we get the expression for finding the number of water molecules involved in the critical nucleus in terms of bulk values of free energy differences and ice-water surface tension:

$$n* = -\frac{32\pi}{3} \cdot \left(\frac{M.W.}{N_A \cdot \rho_i(T)} \right)^2 \cdot \left(\frac{\sigma_{i/w}}{\Delta\mu} \right)^3 \tag{3-10}$$

This expression is very similar to that is given by Huang and Bartell (1995) (Huang and Bartell 1995)[2]. The corresponding free energy of critical nucleus formation following from Equation (3-4), (3-5) and (3-10) is:

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[2] The change in the total volume of outer phase due to forming of nucleus with different density inside would be quite small and is not involved in the calculations.

$$\Delta G_{n*} = -\frac{16\pi}{3} \cdot \left(\frac{M.W.}{N_A \cdot} \frac{1}{\rho_i(T)} \right)^2 \cdot \frac{(\sigma_{i/w})^3}{(\Delta\mu)^2} \tag{3-11}$$

The energy barrier for ice-germ formation at a given temperature can be calculated if the values for ρ_i (density of ice), $\sigma_{i/w}$, and $\Delta\mu$ are known.

According to the theory of reaction rates, the probability of forming a cluster with n molecule is is related to its free energy of formation, and proportional to exp $(-\Delta F_n/kT)$. Therefore the probability of forming a critical germ in a system composed of N molecules is given by:

$$P(n*) = N \cdot \exp(-\Delta G_{n*}/kT) \tag{3-12}$$

Similarly a size distribution of various cluster sizes **n** can be calculated by using (3-12). In the metastable state of equilibrium, this distribution would lead to finite probabilities also for clusters being larger than the critical cluster. Furthermore the system would be more populated by larger clusters owing to monotonic decrease in the distribution function after the critical size, which is in conflict with the theory. To solve this conflict it is assumed that $n > n*$ is an unstable condition, and the critical cluster grows very rapidly to the solid phase. The cluster size distribution near the critical size is corrected by the use of Zeldovitch- Factor, and the distribution for larger sizes is neglected. Accordingly, the critical size is taken as point of no return, in the calculation of nucleation rates.

3.1.2 Calculation of the Molecular Flux on the Surface of the Critical Germ

In the classical theory of nucleation, it is assumed that the embryos of daughter phase grow by the addition of single molecules from the mother phase. In the droplet condensation from supercooled water vapour, the molecules in the gas phase are assumed to behave like ideal gas, i.e. they do not interact with each other. They also freely diffuse to the surface of the critical nucleus. However, in ice nucleation from supercooled liquid water, the diffusion of water molecules across the ice-water interface is subject to an activation energy barrier(Pruppacher and Klett 1997). For this process water to water H-bonds are broken, and the molecules diffuse across the interface under a force field that is created by the surrounding water molecules. Therefore the growth of critical nucleus includes the activation energy barrier (Δg^*) for the diffusion of molecules across the ice-water interface.

The probability that a molecule will diffuse out the liquid structure near the interface in a unit time is given by (3-13):

$$P_{diff.} = (kT/h) \exp(-\Delta g^*/kT) \tag{3-13}$$

Consequently the molecular flux is calculated as:

$$f = P_{diff.} \cdot N_c \tag{3-14}$$

where N_c is the number of molecules in contact with the unit surface of the ice germ.

It is discussed by Eadie (Eadie 1971) that several rate processes such as viscous flow, self diffusion, and dielectric relaxation (dipole orientation) are supposed to have essentially the same activation mechanism in liquid water. The experimentally obtained values for the activation energies of these processes are in close agreement with each other, which supports this assumption. Therefore, Δg^* can be calculated from diffusion, viscosity or dielectric relaxation data for supercooled liquid water. This has been shown by Eadie as given below:

The self diffusion coefficient of liquid water is formulated as:

$$D = \lambda^2 (kT/h) \exp(-\Delta g^{\neq} / kT) \tag{3-15}$$

and

$$\ln D = \ln(\lambda^2 k / h) + \ln T - \Delta g^{\neq} / kT \tag{3-16}$$

Here $\Delta g^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$. In condensed phases we can approximate $\Delta g^{\neq} \approx \Delta H^{\neq}$. It follows from Equation (3-16) that:

$$d(\ln D) / d(1/T) = -T - \Delta g^{\neq} / k = -(\Delta g^{\neq} + kT) / k \tag{3-17}$$

By introducing the term effective activation energy as $\Delta g^* = \Delta g^{\neq} + kT$ and rearranging Eq. (3-17), we get:

$$\Delta g^* = -k [d(\ln D) / d(1/T)] \tag{3-18}$$

Experimentally, Δg^* is obtained from the slope of Arrhenius diagram for the temperature dependence of self-diffusion constant of liquid water.

3.1.3 Shortcomings of the Classical Model

The values necessary to calculate the nucleation rates of ice in supercooled liquid water according to Equation (3-3) are the free energy of activation for the diffusion of water molecules across the ice water interface (Δg^*), and the free energy of critical-germ formation (ΔG_{n*}). From these values Δg^* is equated to the activation energy of self-diffusion for water molecules as explained above. For calculating ΔG_{n*}, the difference in the chemical potentials of ice and liquid water $\Delta \mu_{ice-liq}$, and the ice-water interface energy $\sigma_{i/w}$ at supercooled temperatures are required.

The data for the self-diffusion constant of supercooled liquid water is experimentally attainable from the measurements of Gillen et al(1972)(Gillen, Douglass et al. 1972) and Price et al (1999)

(Price, Ide et al. 1999). From these data, Δg^* can be computed. On the other hand the chemical potential difference of bulk liquid and solid phases for supercooled liquid water is obtained from their equilibrium vapour pressures. The equilibrium vapour pressures of liquid water at supercooled temperatures and ice are available from Mason (Mason 1971). More recently Koop et al (Koop, Luo et al. 2000) provided an expression that gives $\Delta\mu$ as a function of temperature.

Finally, the ice-water interface energy ($\sigma_{i/w}$) is required. Method independent experimental values could only be obtained at the melting temperature of ice or at supercooled temperatures that lie close to the melting point. For such a case, the bulk value (or the thermodynamical value) of $\sigma_{i/w}$ at 273 K is reported by Huang and Bartell (Huang and Bartell 1995), which is computed from equilibrium contact angles between water and two crystals of hexagonal ice sharing a grain boundary.

It is difficult to obtain experimentally the values for $\sigma_{i/w}$ in supercooled liquid water, since water freezes rapidly. Therefore, $\sigma_{i/w}$ is either estimated by various theoretical approaches (Eadie 1971) or calculated as a "kinetic parameter" adjusted to the experimentally obtained nucleation rates of ice in supercooled water (Pruppacher 1995). However, the theoretical estimations led to considerable scatters, and the experimentally obtained "kinetic values" strongly depend on the kinetic model used (Huang and Bartell 1995). one of the limitations of the classical model is the absence of reliable and independent experimental values for the specific surface free energy of the ice-water interface.

Another critic that is directed to the classical theory is the use of macroscopic quantities for the microscopic ice-embryos. This means that the bulk chemical potential applied to the ice embryos might fail, and there might not necessarily be a macroscopically distinguished surface for a growing ice-embryo. In reality, the geometry of the ice embryo and configuration of the water molecules in the ice water boundary determines the key features of the surface layer. The ice embryos can have non-spherical and fractal surfaces instead of having smooth and spherical shapes. The surface might be diffuse instead of being a monolayer. Under these conditions, the free energy of forming an ice-germ depends on its geometry as well as its size.

3.2 Various Approaches to Evaluate the Nucleation Rates

The classical theory of nucleation has been continuously improved since it has been first developed by Volmer and Weber. Different approaches to formulate the nucleation rates have been emerged in this manner. Among them the statistical thermodynamical approach of Eadie (1971) (Eadie 1971), Pruppacher's treatment of activation energy for the transfer of water molecules across the ice-water interface (Pruppacher and Klett 1997), equations of states approaches of Jeffery and Austin (1997) (Jeffery and Austin 1997) and of Kiselev (Kiselev and Ely 2002; Kiselev and Ely 2003), and purely kinetic treatment of Ruckenstein and Nowakovski (1990) (Ruckenstein and Nowakovski 1990), deserves particular attention to be examined in detail. Besides, the non-steady state calculations of the nucleation rates; the density functional theory applied to free energy of embryo formation (in vapour to liquid nucleation) (Debenedetti 1996); and the Monte Carlo generated cluster free energy differences (in vapour to liquid nucleation) (Dimattio 1999) to scale the surface tensions and nucleation rates can be given as other specific improvements.

3.2.1 The Statistical Thermodynamic Approach of Eadie

Eadie (1971), attempted to obtain consistent theoretical values for the surface free energies of ice embryos based on a statistical thermodynamic approach. He formulated the free energy of an ice embryo composed of g molecules as:

$$\Delta G(g) / kT = -\ln Q(g) + g \ln q_w \tag{3-19}$$

Here g_w is the average molecular partition function of supercooled liquid water, and $Q(g)$ is the canonical partition function for an ice embryo of size g. Eadie determined g_w in a similar way, which was followed by Nemethy and Scheraga (Nemethy and Scheraga 1962).

In determining Q (g), Eadie brought up mathematical expressions to calculate the number of 2-, 3- and 4- H-bonded molecules for a regular type of compact clusters having an ice-like structure. He assigned the average molecular partition function for ice to the 4- bonded molecules For the 2- and 3- bonded molecules, he assigned molecular partition functions of 2- and 3- bonded water molecules in liquid water. By this way Eadie was able to obtain the free energy of ice-germ formation from supercooled liquid water and the surface contribution to this process.

Although the ice nucleation rates predicted by Eadie were in good agreement with the experimental nucleation rates, it was criticised later on by Pruppacher(Pruppacher 1995; Pruppacher and Klett 1997) that the activation energy for the diffusion of water molecules Δg^*, used by Eadie were significantly lower than the generally cited values. Besides, the ice-water interface energy were significantly overestimated at lower temperatures, which compensates the low Δg^* values in the calculations.

3.2.2 Pruppacher's Treatment of Activation Energy for the Diffusion of Particles across the Ice-Water Interface

More recently, Pruppacher had claimed that the activation energy for the diffusion of particles across the ice water interface decreases with increasing supercooling (Pruppacher 1995; Pruppacher and Klett 1997). At first sight, the claim of Pruppacher contradicts with the fact that the activation energy of self diffusion increases with decreasing temperature in liquid water. However, Pruppacher lends support to his claim from the proposal of Hagen et al (1981) (Hagen, Anderson et al. 1981) that below certain degree of supercooling the ice-embryos grow on their surfaces with the transfer of increasingly large clusters of water molecules.

To give a quantitative basis to his treatment, Pruppacher first analyzed several experimental data and theoretical estimations for the physical and thermodynamical properties of supercooled water. As a result he obtained polynomial expressions to estimate the temperature dependence of $\sigma_{i/w}$ in supercooled liquid water, which is the "principal unknown". This polynomial is the best fit to all experimental and theoretical estimations of $\sigma_{i/w}$ and has the following form:

$\sigma_{i/w} = 28.0 + 0.25T;$ $-36 \leq T \leq 0 \, °C$

$\sigma_{i/w} = a_1 + a_2T + a_3T^2 + a_4T^3;$ $-44 \leq T \leq -36 \, °C$ (3-20)

with $\sigma_{i/w}$ in $erg \cdot cm^{-2}$, T in °C and $a_1 = 189.081$, $a_2 = 13.1625$, $a_3 = 0.3469$, $a_4 = 3.125 \, E\text{-}3$.

Consequently he formulated the nucleation rate J as:

$$J = 2N_c \, (\rho_w kT/\rho_i h) \, (\sigma_{i/w}/kT)^{1/2} \exp\left[-(\Delta G_{n*}/kT - \Delta g^*/RT)\right]$$ (3-21)

Here N_c is the number of monomers in contact with the unit surface area of the ice surface, ρ_w and ρ_i are the densities of liquid water and ice, Δg^* is the activation energy for the diffusion of water molecules across the ice water interface and ΔG_{n*} is the free energy of critical nucleus formation. "k", T and h have their usual meanings as being Boltzman's constant, temperature and Planck's constant.

The treatment of Pruppacher can be criticized from different points. One critic is directed to the nucleation rate equation where he uses the number of monomers instead of number of clusters which contradicts to his hypothesis and leads to a considerable increase in the particle flux on the surface of ice germs. Secondly the Δg^* value approaches zero as the temperature approaches the singularity temperature of -45°C. This requires a correlated change in ΔG_{n*} value in order not to neglect the contribution of Δg^* in the exponential factor. Although ΔG_{n*} decreases with increasing supercooling, it becomes much larger in comparison to Δg^* around -45°. Near -45 °C, the contribution of Δg^* is so small at that it becomes meaningless as a kinetic factor, and the nucleation rates are mainly determined by the free energy of germ formation. This is meaningful if only it can be supported by independent experimental values of $\sigma_{i/w}$, Δg^* and ΔG_{n*}, which suggests near the singularity temperature the nucleation rate is purely determined by thermodynamical parameters. However at this stage the values for Δg^* and and ΔG_{n*} are strongly dependent on the value of $\sigma_{i/w}$ which is extracted from a polynomial expression as a best fit to several experimental values that significantly scatter from each other. It is also noted by Pruppacher that the polynomial expression for the value of $\sigma_{i/w}$ does not discriminate between the basal and prism faces of the ice-crystal lattice.

3.2.3 Kiselev's Crossover Model

The equations of states are commonly used to estimate the physical and thermodynamical properties of ice and liquid water over a wide range of pressure and temperature; especially when there is not enough experimental data. In this manner most equation of states (EOS) are an improvement to the van der Waals equation of state, to give better approximations to the behaviour of real systems. The applicability of various equations of states to nucleation theory can be found elsewhere (Obeidat 2003). In this work there is also a critic stated for the crossover equation of Kiselev:

Most EOS generally fail to reproduce the singular behaviour observed at the critical point. In this manner, Kiselev and Ely (2002) (Kiselev and Ely 2002) developed a new equation of state to be able to describe both the "classical mean filed behaviour far away from the critical region" and "smoothly crossover to the singular behaviour near the critical point". They termed it as crossover equation of state (CREOS). Since the concept behind the crossover EOS is to get the right behavior near a critical point, to make this equation work at low temperatures, the scenario of a second critical point at low temperature was *exploited* by Kiselev and Ely.

Although Kiselev based his approach on the two-critical point scenario, he also assumed that liquid water has a kinetic spinodal, below which the second critical point CP_2 of low density water (LDW) – high density water (HDW) lies. Therefore, CP_2 is found in a "nonthermodynamic habitat".

The CREOS-01 (Kiselev and Ely 2002), CREOS-02 (Kiselev and Ely 2003) are used to predict the thermodynamic properties and the kinetic spinodal of supercooled liquid water and heavy water. They in turn can be used to describe homogenous nucleation behavior of water by the fluctuation theory of homogenous nucleation, near the kinetic spinodal.

In the fluctuation theory of homogeneous nucleation, the homogenous nucleation limit (T_H) arises due to the mechanical instability of the metastable phase along the kinetic spinodal line. The physical boundary of the metastable state is determined by the lifetime of metastable phase (t_M)

being on the order of the relaxation time (t_R) of a homogeneous state. The line where $t_M \approx t_R$ is treated as the kinetic spinodal. On the other hand, the thermodynamic spinodal corresponds to t_M $<< t_R$. Therefore it is experimentally unattainable.

The equation of motion in the fluctuation theory of homogeneous nucleation is given by Kiselev and it is the same as that of a system near a second order phase transition. Solving the equation of motion is used one obtains the lifetime of metastable state given by Equation (3-22):

$$t_M = t_R \cdot (4\pi\gamma/\lambda_0) \cdot \exp(\gamma W_{min}/k_B T). \tag{3-22}$$

Here t_M is the lifetime of the metastable state, which corresponds to the homogenous nucleation times near the kinetic spinodal. The full parameterization of the crossover equation can be obtained from one of the references given above.

In summary Kiselev's result indicate that the ice nucleation in liquid water at homogeneous nucleation T_H is facilitated by a kinetic spinodal, which lies near to T_H and determines the physical boundary of metastable states. If the surface tension is known the physical boundary imposed on a system by a kinetic spinodal can be determined by crossover EOS.

3.2.4 Ruckenstein's Kinetic Theory of Nucleation in Liquids

Ruckenstein and Nowakovski (1989) (Ruckenstein and Nowakovski 1990) developed a kinetic theory of nucleation in liquids, based on the analysis of mean passage times of the adsorbing and escaping molecules on the surface of a spherical cluster. The problem they studied was the precipitation of a solute from a supersaturated solution.

They supposed that the molecule escaping from the surface of a cluster performs Brownian motion under a force field applied on it by the molecules belonging to the cluster. The diffusion equation under these conditions (and having a spherical symmetry) is given by backward Smoluchowski equation:

$$\frac{\partial p(r,t \mid r_0)}{\partial t} = D \cdot r^{-2} e^{-\Phi(r)} \times \frac{\partial}{\partial r_0}\left(r^2 e^{-\Phi(r)} \frac{\partial}{\partial r_0} p(r,t \mid r_0)\right) \tag{3-23}$$

Here D is the diffusion coefficient and $\Phi = \phi/kT$ is the pair wise additive interaction potential in between a molecule and a cluster. The solution to the above partial differential equation is the Green's function P(r,t|r₀). It defines the transition probability that a molecule initially at the distance r_0 will be located after time t at the point **r**.

If the Green's function is known, the mean passage time **τ** of the escape, which is the average time for a particle that it is needed for it to disappear from the vicinity of the spherical cluster can be mathematically evaluated:

$$\tau(r_0) = -\int_0^\infty t \frac{\partial Q(t \mid r_0)}{\partial t} dt = \int_0^\infty Q(t \mid r_0) dt \tag{3-24}$$

where

$$Q(t \mid r_0) = \int_R^{R+\eta} r^2 p(r,t \mid r_0) dr \tag{3-24b}$$

is the survival probability, which defines the probability that a molecule initially at point **r₀** within the surface layer will remain in this region after time **t**.

Ruckenstein and Nowakovski calculated the average mean passage time $< \tau >$ by imposing a reflecting inner wall of the surface layer and a perfect absorption for the molecules that reach the outer layer, as boundary conditions. Therefore the dissociation rate is obtained as

$$\alpha = N_s / < \tau > \tag{3-25}$$

via the kinetic law of first-order reactions. Here N_s is the number of molecules that lie within the surface layer. The rate of condensation β is also calculated in the similar way by means of a stationary solution of the diffusion equation in an external field.

The analysis of mean passage times makes it available to estimate critical cluster size solely in terms of kinetic parameters. Tthe critical cluster size is obtained by the condition of "unstable" equilibrium, for which the rates of condensation and dissociation are balanced.

3.3 A New Approach to the Kinetics of Homogeneous Ice Nucleation in Supercooled Liquid Water

As it is seen by the discussions built up to now, the principal unknown in calculating the homogeneous nucleation rates is the free energy of surface formation in between the growing embryo of the ice phase and the liquid water molecules that surrounds the embryo $\sigma_{i/w}$ .The surface energy should be explicitly defined to calculate the nucleation rates, either by theoretical estimations or by the extrapolation of available experimental data.

In this section we present a new approach which differs at two points from the other approaches of calculating homogenous ice nucleation rates:

1. Ice nuclei preferably grow at the surface of big patches in liquid water.
2. An implicit formulation of the free energy of germ formation from the chemical potential differences of the hypothetical phase of lattice defects and the liquid water phase is introduced, which circumvents the explicit use of the surface tension.

According to the physical model of liquid water, which is introduced in Chapter 2, we have the 4-bonded agglomerates embedded in the big patches of LDL and HDL structures. The ice nuclei grow from these 4-bonded agglomerates. However the rates of the growth of these agglomerates are not the same at every place. Their growth is proposed to be much faster at the surface of a patch due to the more mobile molecules that are found in the interface in between the patches. These molecules can reorganize in a faster way on the growing sites. If a similarity is made to heterogeneous nucleation of ice, an agglomerate standing at the surface of a patch acts like a proper ice-nucleating surface which catalyses the reordering of the disordered and highly mobile interphase molecules.

In the interior of the patches, the ice-like structure dominates. Therefore, the self-diffusion constant of water molecules inside the patches can be approximated to the self diffusion constant of ice. Due to highly immobilized water molecules, the growth of an agglomerate that is placed inside a patch is too slow. On the other hand, most of the non-bonded molecules find their places in the interphase in between the patches. These molecules are more mobile than the ones in the

patches, and their self diffusion constants can be approximated to the self diffusion constant of liquid water.

In view of the fact that an agglomerate placed near the surface of a patch can grow much faster by the addition of mobile water molecules from the interface, the nucleation rate of ice is governed by the growth of the agglomerates, which are found near the surface of the patches. Referring back to the nucleation rate equation given by (3-1), the concentration of ice-germs is changed by an effective concentration in our approach:

$$J = c_{eff} \cdot \Omega \cdot f \qquad \qquad (3\text{-}26)$$

Here c_{eff} is the actual concentration of critical ice nucleus multiplied by the ratio of the number of 4-bonded agglomerates placed at the surface of a patch to the total number of agglomerates present in the patch:

$$c_{eff} = c_g \cdot (N_{Agg.\text{-}S} / N_{Agg.\text{-}T}) \qquad \qquad (3\text{-}27)$$

It is also necessary to correct for the surface area "Ω", since only some parts of the agglomerates sees the interface, and the rest looks into the bulk of the patch. This is illustrated in Figure 3.1 for various arrangements of agglomerates at the patch surface.   In reality there is a statistical distribution of these arrangements, which can occur in infinitely many ways. In the calculations, we assign an effective surface area "Ω_{eff}", which substitutes for an average value of all kinds of arrangements of the agglomerates at the patch surface. In this assignment, we get use of the results of statistical thermodynamic considerations developed in Chapter 2:

$$W_{eff} = X_i \cdot W_{patch} \qquad \qquad (3\text{-}28)$$

Here "W_{patch}" is the total surface area for the inner-shell of a patch just below its adherent interface. To find the contribution of 4-bonded ice-like agglomerates to the total surface area, we multiply the value of W_{patch} with "X_i" , the mole fraction of ice-like phase in a given patch, which is first introduced in Chapter 2. As a result, we obtain "W_{eff}" as the contribution from the surface of 4-bonded agglomerates to the total surface area of a patch.
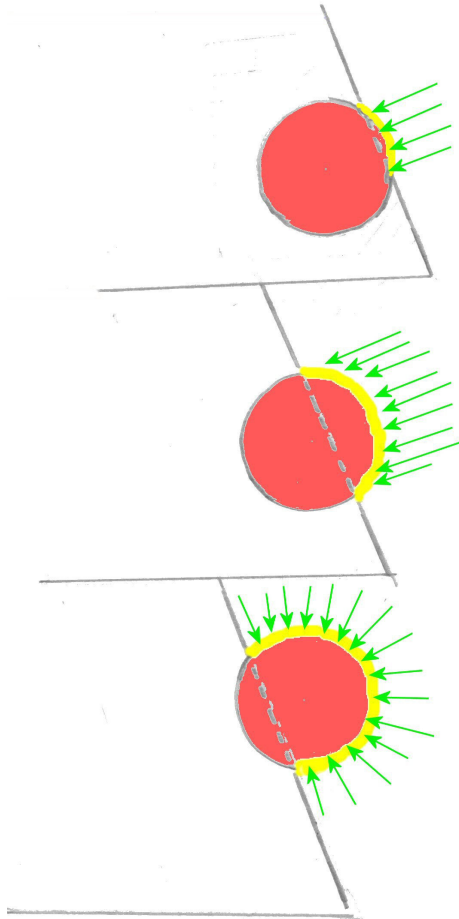
Figure 3.1: Various arrangements of agglomerates at the surface of a patch.

W_{eff} describes a total effective surface area for the growth of ice nuclei at the patch surface. To find **"Ω_{eff}",** i.e. the effective surface area per agglomerate, we must divide "W_{eff}" to the number of agglomerates that are found near the surface "$N_{Agg.-S}$":

$$\Omega_{eff} = W_{eff} / N_{Agg.-S} \tag{3-29}$$

To carry out the calculation given in Equation 3-28 and 3-29, we assume a spherical shape for a given patch. The total volume of the patch is then, calculated to be:

$$V_{patch} = (V_M(liq.H_2O) / 6.022E+23) \times S_T \tag{3-30}$$

Here $V_M(liq.H_2O)$ is the molar volume of the liquid water at a given temperature, and S_T is the total number of molecules in a patch including the ones in the adherent interface. For a spherical object the volume of the patch can also be expressed as:

$$V_{patch} = (4/3) \cdot \pi \cdot r^3 \tag{3-31}$$

where r is the radius of the sphere. Therefore the radius of a patch having a spherical shape and composed of n water molecules is obtained to be:

$$r_{patch} = \sqrt[3]{\frac{3}{4\pi} \cdot \frac{V_{M-liq.H_2O}}{6.022E+23} \cdot S_T} \tag{3-32}$$

For the radius of the inner shell we consider the thickness of adherent interface to be on the order 1.4 Å, which corresponds to the hard-sphere radius of a water molecule. Therefore the radius and the corresponding surface area of the inner shell are found to be:

$r_{inner\text{-}shell} = r_{patch} - 1.4 \text{ (in Å units)}$ (3-33)

$W_{patch} = 4\pi \, (r_{inner\text{-}shell})^2$

Until now, we defined an effective concentration and surface area of agglomerates in growing the ice nucleus. Finally, to find the nucleation rates, we have to formulate the flux of water molecules on the effective surface area of the growing agglomerates. In doing this we assume that the interface consists only of non-bonded water molecules, and the presence of a non-bonded molecule in the bulk of the patch is highly improbable. Therefore, we can calculate the number of water molecules that is found in the incremental volume of the interface adherent to the patch surface, by getting use of the mole fraction of nonbonded water molecules, which is calculated in Chapter 2:

$n_{interface} = S_T \text{ x } h_0$ (3-34)

Here $n_{interface}$ is the number of water molecules that are found in the interface, n_{patch} is the total number of molecules in a patch and h_0 is the mole fraction of non-bonded water molecules. As a result the number of molecules per unit area of the patch surface is:

$n_s = (n_{interface} \, / \, W_{patch})$ (3-35)

From these molecules we calculate the monomer flux on the unit area of growing sites by using the equations (3-13) and (3-14):

$f = N_{eff} \cdot P_{diff}$ (3-36)

$P_{diff.} = (kT/h) \exp (-\Delta g^*/kT)$

Here P_{diff} is the probability of the diffusion of water molecules adjacent on the surface of an agglomerate at a given temperature, which is defined by the frequency of thermal excitations (kT/h) and the activation energy of self diffusion for water molecules (Δg^*).

Combining the equations (3-27), (3-29) and (3-36), we obtain the homogenous nucleation rate of ice at a given temperature as:

$$J = c_{act} \cdot (N_{Agg.-S} / N_{Agg.-T}) \times (W_{eff} / N_{Agg.-S}) \times (n_{interface} / W_{patch}) \times (kT/h) \exp(-\Delta g^*/kT) \qquad (3\text{-}37)$$

In the above equation, the terms $N_{Agg.-S}$ cancel out , leading to the result:

$$J = (n_{interface} / N_{Agg-T}) \times (W_{eff}/W_{patch}) \times (kT/h) \exp(-\Delta g^*/kT) \qquad (3\text{-}38)$$

Equation (3-38) implies that we do not have to explicitly calculate the fraction of 4-bonded agglomerates on the surface of a patch. On the other hand, the total number of agglomerates in a patch is calculated by dividing the total number of 4-bonded molecules in a patch to the average size of 4-bonded agglomerates.

$$N_{Agg-T} : (S_T * h_4 / n_{avg-Agg}) \qquad (3\text{-}39)$$

The average size of the 4-bonded agglomerates in terms of the number of water molecules "$n_{avg-Agg}$" is obtained from the size distribution of agglomerates at a given temperature. The details of obtaining the size distributions are previously provided in Chapter 2.

The actual concentration in equation (3-37) corresponds to the concentration of the critical nucleus in a patch. This is because we calculate the steady-state nucleation rate, which is defined to be the net flux on the surface of the critical nucleus at stationary conditions. Therefore we could express the actual concentration as:

$$c_{act} = n_{patch} \cdot \exp(-\Delta G_{n*} /kT) \qquad (3\text{-}40)$$

Here ΔG_{n*} is the Gibbs free energy of the formation of a critical ice nucleus. In the classical approache, $\Delta G_{n*} = \sigma_{i/w} A_n + n\Delta\mu$, where the surface tension is explicitly defined. Here we circumvent this parameter in the chemical potential difference of the hypothetical lattice defect phase, which contributes to the surface of the 4-bonded agglomerates to form the critical nucleus.

As developed in Section 2.3.2 of Chapter 2 we express the free energy of critical nucleus formation with the below given equation:

ΔG (ice-embryo) = ($n_4 \cdot \mu_{ice}$) + ($n_d \cdot \mu_d$) − ($n_4 + n_d$) $\cdot \mu_{liq}$

Before ending this section of mathematical evaluation, we finally consider on the activation energy of self diffusion of water molecules. The self-diffusion data is obtained from Price et al (Price, Ide et al. 1999). Fitting expressions for the experimental data are also provided there. These expressions are Vogan Tamman Fulcher equation (VTF) and the Fractional Power Law (FPL) equations. It is mentioned by Price et al that FPL gives a better fit to experimental values. It also implies singularity behaviour at 220 K. Therefore we use the FPL equation to obtain the self-diffusion constants:

$$D = D_0 \cdot T^{1/2} \cdot (T/T_s - 1)^{\gamma}$$

(3-41)

The necessary parameters are given to be :

		Err +/-
D-0 =	7.66E-10	2.40E-11
T-s / K =	219.2	2.6
Gamma =	1.74	0.1

 The activation energy for the self diffusion of water molecules is obtained by taking the derivatives of the above equation with respect to temperature.

3.3.1 Results

The calculated results for the homogeneous nucleation rates of ice are summarized in Table 3.1 including the stepwise calculations, at four different temperature points.

Table 3.1: Stepwise calculation of the homogenous nucleation rates of ice in supercooled liquid water according to the new kinetic approach

T	°C	-33	-35	-36	-40
h	J·s	6.63E-34	6.63E-34	6.63E-34	6.63E-34
k	JK-1	1.38E-23	1.38E-23	1.38E-23	1.38E-23
Molar volume of liq. Water V_m(liq)	cm^3	18.40	18.47	18.51	18.71
Total Patch size (S_T)	-	3384	3438	3340	3313
Volume of a spherical shaped patch	cm^3	1.03E-19	1.05E-19	1.03E-19	1.03E-19
Volume of spherical shaped patch	A^3	1.03E+05	1.05E+05	1.03E+05	1.03E+05
Radius of a patch (r_{patch})	A	29.12	29.31	29.05	29.07
Radius of the inner-shell in A	A	27.22	27.41	27.15	27.17
Surf Area (inner-shell) (W_{patch})	A^2	9308.4	9439.6	9261.2	9278.6
Xi	-	0.63	0.64	0.65	0.67
Effective surface area (W_{eff})	A^2	5864.3	6041.3	6019.8	6216.7
Fraction of nonbonded molecules (h_0)		0.099	0.091	0.089	0.08
Number nonbonded molecules in the interface	-	335.016	313	297	262
Number of surface molecules per unit area	A^{-2}	3.60E-02	3.31E-02	3.21E-02	2.82E-02
Act. Energy of diffusion according to FPL	J/molecule	6.78E-20	7.35E-20	7.69E-20	9.52E-20
Total flux on the effective surface area	A^{-2}s^{-1}	1.46E+08	4.00E+07	1.86E+07	3.12E+05
Average size of the 4-bonded agglomerates	-	271	292	200	235
Number of agglomerates with average size in a patch		13	12	17	14
Probability for the formation of an average-sized agglomerate in a patch		2.70E-27	9.87E-22	7.79E-20	6.81E-12
Number of patches in 1cm^3 of liquid water		1.78E+20	1.75E+20	1.80E+20	1.82E+20
J (Germs per cm3 per s)		**5.60E+00**	**5.87E+05**	**1.57E+07**	**2.74E+13**
Corresponding thickness of the diffuse surface layer for the ice nucleus	A	2.08	1.98	1.93	1.73

The nucleation rates are first calculated for a constant interface thickness of ~2 Å by using the activation energy for the self diffusion of water molecules.   It is seen that there is a poor match between the theoretical calculations and the experimental results in that case. Therefore we change the thickness of the surface layer of critical nucleus as a fitting parameter and we obtain the results given in Table 3.1.

These results show that the surface thickness of the agglomerates is reduced with decreasing temperatures. The surfaces of the agglomerates separate them from other agglomerates in a patch. As the temperature is decreased, the ratio of ice-like phase in the patches increases. This also means, the number of the four-bonded molecules, which form the agglomerates increases, and the number of defect molecules, which form the surface of agglomerates decreases. Therefore, it is reasonable to obtain the result that the thickness of the surface of agglomerates decreases with decreasing temperature.

The surface thickness must be even shorter to have a good match at temperatures lower than -40 °C. However, the free energy of germ formation would be less than the activation energy of self diffusion at some point, if the surface thickness continues to decrease. This might be explained by a kinetic spinodal that is discussed by Kiselev(Kiselev and Ely 2003).

As will be seen in the following sections, addition of solutes can stabilize the surfaces of embryos, bypassing the kinetic spinodal. On the other hand the solution may then experience large density fluctuations when it approaches to the hypothetical second critical point, which might be the reason of freezing anomalies observed for example in water-glycol mixtures. Therefore our results indicate both a kinetic spinodal and a second critical point.