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Nucleation

Wan Nur Athirah Mazli, Mohd Afnan Ahmad
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Abstract

Nucleation is one of the processes that involves at the beginning of the certain process like freezing, melting, boiling, condensation and crystallization. This process normally occurs in the industry, where it is involving the thermodynamic phase that involves work, energy and temperature. The nuclei growth happens when the initial phase changes to the other phase. Unfortunately, the detail for the theory of nucleation is not well-known around the people who are working in the industry, even though there are many reports or writings available. Thus, few types of nucleation like homogeneous and heterogeneous nucleation and the other theory of nucleation have been summarized in this chapter.

Keywords: homogeneous, heterogeneous, ice crystal

1. Introduction

Crystallization is the process where the molecules or tiny ice crystal are attached to each other to produce bigger formation of molecule or ice layer. Large cluster is stable compared to the smaller cluster as most of the molecules are far from the surface of the solution. It starts to form at the center of the cluster and slowly spread to the outward part of the cluster [1].

Besides, crystallization happens when there is phase change from the liquid to solid or crystalline form. This process happens when concentration of the solute already exceeds the equilibrium concentration or known as the supersaturated solution. The solution provides the driving force for the process and develops the growth of the particle but it not always develops the crystallization process because the supersaturated solution might be in metastable state. The process will happen when the limit of metastable has reached the limit and it depends on the kinetics system [2].

Nucleation is the process that happens in the crystallization process and it can be divided into few categories [2]. Ice nuclei appear at the solid surface when the fusion of heat is transferred by the conduction toward the cooled surface. By this time, the thin film starts to grow thicker until the ice crystal layer is formed. Most of the nuclei are developed in the high supersaturation and it attaches to form the ice crystal [3].

Activated process is known as nucleation because there is a barrier that the growing nucleus needs to be defeated [4]. The nucleation phenomenon is widely known in most aspects of science. Besides, it normally occurs at the beginning of the form of the ice crystal, snow, volcanic and the rainfall [5]. The nucleation process can be divided into a few parts as a different process has different conditions.

Other than that, it is important to understand more detail about the formation of ice for the nucleation and the supercooling condition in a science and technology field [6].

2. Primary nucleation

The supersaturated state achieved is the first step considered in the crystallization process. For supersaturation condition itself are not sufficient for a system to crystallize. The crystal needs to grow where new crystallization centers must exist in the solution. This formation of one phase in another, under conditions where a free energy barrier exists, is known as nucleation [1].

Nucleation is a random process which in two same situations or system nucleation will happen at a different time [4, 7]. Generally, the theory introduces in describing this phenomenon include its nature and behavior of the new thermodynamic phase is called classical nucleation theory (CNT). On the other hand, the experimental result of vapor to liquid nucleation cannot be described using CNT include the Argon by a few orders of magnitude for model substances [8].

For the formation of ice in the water below 0°C, if the system not changing with time and the nucleation occurs in one step. Thus, the probability of nucleation happens is denied through exponential decay as seen in radioactive decay. This scenario can be seen in the nucleation of ice in supercooled [9]. Another example is the self-organization process that forms like amyloid assembly associated with Alzheimer's diseases which the self-assemble system by the energy consumed such as microtubules in cells are referred to the nucleation and growth [10].

There are two types of nucleation namely the homogeneous or spontaneous nucleation and heterogeneous nucleation. This phenomenon happens when nuclei are formed perfectly in a clean solution where there are no any foreign particles. In any practical situation the presence of foreign particles includes impurity molecules, dust particles or ions refer to the heterogeneous nucleation. Both the nucleation process classified as primary nucleation [11].

Besides, primary nucleation refers to the early formation of a crystal in absence of any other crystal or it will not affect or influence the process if there any presence of crystal in a system that will happen in two conditions as stated above. In homogenous nucleation, the nucleation is not affected by solids and this include walls of crystallizer vessel and particles of any substance [12]. While the second one is the heterogeneous nucleation caused by the increasing rate of nucleation by the presence of other substance of solid particles would otherwise not be seen without the existence of these foreign particles [13].

For homogeneous nucleation, it is rarely happening because higher energy is needed to start the nucleation with the absence of solid particles. Primary nucleation has been modeled with the following power-law expression.

$$B = \frac{dN}{dt} = k_n (c - c^*)^n \tag{1}$$

Eq. (1) shows that the nucleation requires the rate constant, the instantaneous solute concentration, the concentration at the saturation phase and the empirical exponent which is generally ranges between 3 and 4.

Basically, primary nucleation theories can be used to study the metastable zone width (MSZW) data and kinetic of nucleation for the crystallization process. MSZW is explained as the gap of supersaturation between the supersolubility curve

and solubility curve. The kinetics of primary nucleation of $NaNO_3$ for fractional crystallization process of high saline wastewater had been studied by Bian et al. MSZW of $NaNO_3$ was analyzed based on different stirring rate, present of seed crystals and cooling rate by using ultrasonic velocity sensor [14].

3. Secondary nucleation

The development of nuclei which refer to the influential of microscopic crystals in the magma is the phenomenon of secondary nucleation [15]. This nucleation happens when the crystal growth is introduced with a contact of other existing crystal or "seeds" [16]. For example, under a certain condition fluid shear forces are sufficient to produce secondary nuclei from an existing crystal surface [17]. Fluid shear nucleation happens when the fluid passes through the crystal with higher speed, sweep away the nuclei that would otherwise be incorporated into a crystal. The scenario led to the formation of a new crystal by the "swept away" nuclei. This contact nucleation proves to be the most effective and common method in nucleation.

In addition, this secondary nucleation depends on supersaturation. As stated Strickland-Constable that arises since the starting size distribution of potential secondary nuclei is depend on supersaturation. However, the particle produces at critical size ranged. This secondary nucleation has been performed in the agitated system that many been found in industrial crystallizers [18]. Sometimes, for needle breeding appear at high supersaturation where the dendrites may be expanding, or the needle is growing from existing crystal. As a result, when the crystal breaks the new centers for crystal growth are formed and this also refers to collision nucleation where arises from contact between two growing crystals or between a crystal with another solid surface [19].

The second nucleation gives many advantages includes lower kinetic order and rate-proportional to supersaturation which allows easy control without unstable operation, the nucleation occurs at low supersaturation which the growth rate is optimal for good quality, lower energy needed where the crystal strike avoids the breaking existing crystal to form new crystal, and the quantitative fundamental have already been isolated and are being incorporated into practical [20]. The following model, although somewhat simplified, is often used to model secondary nucleation.

$$B = \frac{dN}{dt} = k_1 M_T^j (c - c^*)^b \qquad (2)$$

where k_1 is a rate constant, MT is the suspension density, j is an empirical exponent that can range up to 1.5, and b is an empirical exponent that can range up to 5.

Xue et al. stated that secondary nucleation is one of the main steps in the crystallization industrial. Most of the researchers are focused on the mechanism and the kinetics of the secondary nucleation of the aluminum hydroxide crystallization. Besides, it is related to the growth of the crystal process through the surface nucleation mechanism. Other than that, secondary nucleation is known as the removal-limited and chemical reaction controlled [21].

4. Homogeneous nucleation

Homogeneous nucleation is known when the nucleation is occurring without any favorable nucleation sites. Normally, the nucleation process happens randomly

as well as spontaneously. It requires supercooling or superheating for the medium and it happens in the inner of the uniform substance with more difficulty. There will be the formation of an interface at the boundaries of a new phase when the nucleus is formed. To start the nucleation process, the supercooled phase is needed where the liquids need to be cooled down to below the melting temperature which is the maximum temperature of homogeneous nucleation but in the same time, the liquid need to make sure that it above the freezing temperature (homogeneous nucleation temperature) [22].

With the absence of external insoluble substance, supercooled water starts to nucleate homogeneously due to the variation temperature, density and pressure. This happens because of the endless formation of the ice cluster [23]. For homogeneous nucleation, after certain period of time when the nucleation begins, the crystals or bubbles are growing and become bigger and at the same time new crystal or bubble starts to nucleate. This can be shown through **Figure 1**.

According to the Abyzov et al., they approach new way to predict the homogeneous nucleation rates of silicate glass by estimate the nucleation rates. This is because the temperature of glass transition is closed to the maximum homogeneous rate. By using this approach, they can avoid some serious problem but in the same time they could not solved the difference between the experimental nucleation rate and the Classical Nucleation Theory, CNT [24].

Besides, Gibbs free energy is needed to determine the critical radius for homogeneous nucleation and it can be shown in Eq. (3). To find out the critical radius and the critical free energy, the formula of the Gibbs free energy need to differentiate [25]. Eqs. (4) and (5) show the critical radius and critical free energy.

$$\Delta G_{homo} = -\frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \gamma_{SL} \tag{3}$$

$$r^* = \frac{2\gamma_{SL}}{\Delta G_V} = \left(\frac{2\gamma_{SL} T_m}{L_V}\right)\frac{1}{\Delta T} \tag{4}$$

$$\Delta G^* = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2} = \left(\frac{16\pi\gamma_{SL}^3 T_m^2}{3L_V^2}\right)\frac{1}{(\Delta T)^2} \tag{5}$$

The system can lower the free energy by the dissolution of the solid when the value of r is less than by r^*. Embryos are the unstable solid particle while nuclei are the stable solid particles with the value r is more than the value of r^* Besides, the nucleation rate for homogeneous nucleation also important as it will determine the time for nuclei to transfer into the nucleus. To calculate the nucleation rate, the population of critical embryos is needed and it can be shown in Eqs. (6) and (7) shows the formula of the nucleation rate for homogeneous nucleation. ΔG_r is the
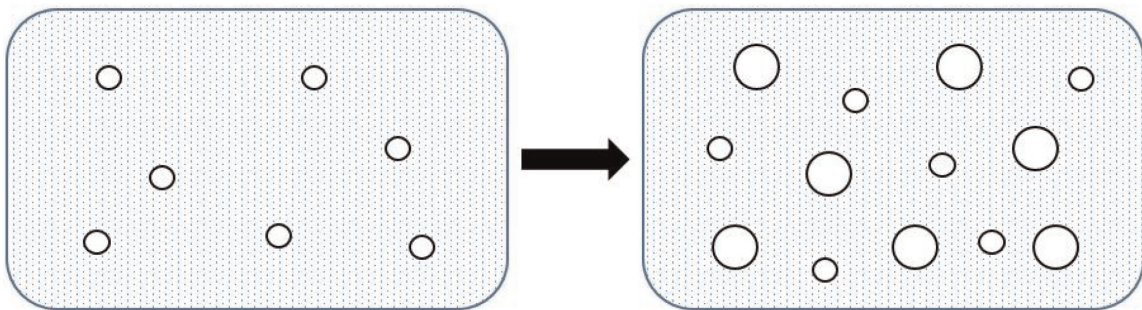
Figure 1.
Schematic diagram for transformation of homogeneous nucleation.

excess of free energy, k is the Boltzmann factor and n_0 is the total number of atoms in the system [25].

$$n_r = -\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma_{SL} \qquad (6)$$

$$N_{homo} = f_0 C_0 e^{\frac{\Delta G^*_{homo}}{kT}} \qquad (7)$$

5. Heterogeneous nucleation

Heterogeneous nucleation happens more often compared to the homogeneous nucleation. It is applicable for the phase transformation between the two-phase like bubble formation, solidification and the condensation of the gas. Normally, this process happens at a favorable site such as surfaces of the container, impurities and phase boundaries. At these sites, the effectiveness of the surface energy is lower; therefore, it can ease the nucleation process and reduce the free energy barrier.

The example of the heterogeneous nucleation is when the person is putting the finger into the carbonated water and the bubble is formed, this is because the surface of the finger is rougher compared to the surface of the container [26]. Besides, it happens when the ice nuclei at the lower temperature of supercooling [23]. For heterogeneous nucleation, after certain time when the nucleation starts to begin, the crystals or bubble only growing and become bigger and no new nucleation happens. **Figure 2** shows the transformation for heterogeneous nucleation.

As stated by Fujinaga and Shibuta, athermal heterogeneous nucleation is the process where the onset of the free growth of the phase is controlling the grain initiation of the inoculated particles. The onset of free growth is dependent on the particle sizes and undercooling temperature. In molecular dynamic simulation MD, additional condition should be chosen carefully in order to fix the heterogeneous [27].

For the heterogeneous nucleation process, the wetting will encourage the nucleation at the surfaces, thus the free energy is the same with the product of free energy for homogeneous and the contact angle (θ). Eq. (8) shows the free energy of the heterogeneous nucleation. It also has the critical radius and critical free energy and both of it can be shown through Eqs. (9) and (10).

$$\Delta G_{hete} = \Delta G_{homo} S(\theta) \qquad (8)$$

$$r^* = \frac{2\gamma_{SL}}{\Delta G_V} \qquad (9)$$

$$\Delta G^* = \frac{16\pi \gamma_{SL}^3}{3\Delta G_V^2} S(\theta) \qquad (10)$$
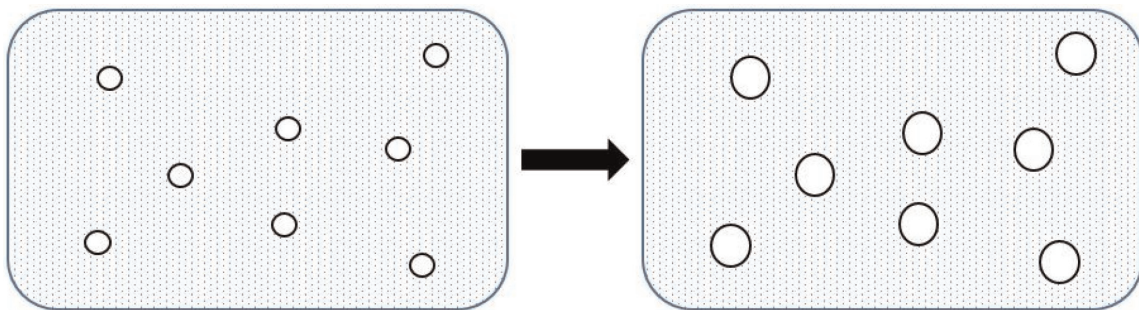
Figure 2.
Schematic diagram for transformation of heterogeneous nucleation.

To calculate the heterogeneous nucleation rate, it requires several atoms that contact with the surface of the nucleating agent surface. Eqs. (11) and (12) show the formula for the number of atoms and nucleation rates for heterogeneous nucleation. With minor undercooling situation, the nucleation process is happening in the cracks. To ensure that the cracks are effective, the opening of the crack should be large enough as it needs to let the solid to grow out freely without bothering the radius of the solid is smaller than the critical radius [25].

$$n^* = n_1 e^{-\frac{\Delta G_{hete}}{kT}} \tag{11}$$

$$N_{hete} = f_1 C_1 e^{-\frac{\Delta G^*_{hete}}{kT}} \tag{12}$$

6. Ice growth

The crystallization process for super-cooled water will start when the ice cluster solid has been formed by the nucleation. The ice starts to grow when the nucleation process has happened. Apart from it, the initial nucleus interrupts the second ice layer to growth when the latent heat is released [23].

Water forms the ices by undergoing the freezing process and this phase transition happens widely in nature. It is hard to redo the freezing process to transform water into solid with the specific crystalline structure [28]. The study of the growth of the ice layer on the subcooled surface started early in the field of geography. According to the Neumann problem, the phase change of water supposed to be uniform in the early process at the subcooled surface like ice crystal start to appear as a thin film around the surface. The ice starts thicken in the perpendicular direction uniformly. Primary nucleation will not happen simultaneously at the surface during the onset of the freezing on the subcooled surface [29].

The reaction of the ice particles in stratospheric clouds will change the halogen chemistry and at the same time, it helps to deplete the ozone layer. For the reactivity of the ice surface, it depends on its mobility or density as it is important to control the degree of the crystallinity and the structure of the ice film itself. To face this issue, ice film need to be grown well on the solid surfaces and use it as a tool to find out the reactions of the atmospheric. The structure of the ice film on the different hexagonal metal surface is sensitive to attach the energy to the metal and different structures of different transition metal surfaces [30].

For the phase change, heat and mass transfer is an important part of the onset like freezing on the subcooled surface. It is because it can be a good opportunity for the engineering application [29] such as ice formation on the cryogenic surface [31] and the ice production using scraped-surface heat exchanger [32]. For a certain process, the mass flow rate of the injected vapor is used to calculate the ice layer growth rate which is forms on the plate. Normally, the ice layer grows until it reaches the critical thickness is considered as the outcome of the process. Film-wise condensation starts to occur on the surface of the ice layer when it reaches the critical thickness [31].

The heat transfer coefficient in the scraped-surface heat exchanger without the phase change (ice growth) is three to five times smaller compared to the phase change. The torque for handle the scraper is increasing when the onset of ice growth is happening until the scrapper becomes frozen. Ice started to growth at stage II and stage III, where the ice particle from the nucleation takes place. The ice particle continuously freezes until it transforms into the ice crystal and the concentration of the mother liquor is increasing [33].

7. Kinetics of nucleation

As reviewed, the part of kinetics from the rate of nucleation gives a number of the water molecule which has a potential incorporated into the ice crystal [34]. The flux of water molecule that happens be incorporated with the ice crystal must be counted for nucleation rate estimation. The flux can be written as diffusive flux (Φ) and known as the Boltzmann distribution. The equation is expressed as below.

$$\Phi = \frac{K_B T}{h} . e^{\frac{\Delta g^{\#}}{K_B T}} \tag{13}$$

whereas h refers to the Planck's constant and $\Delta g^{\#}$ is the activation energy for the transfer of a water molecule across the water-ice boundary. The Φ can also be introduced as the frequency at water molecules overcome at the activation energy [34], as for the collisions rate or the probability in breaking the bond and reassemble of molecular.

Besides, the second pre-factor stated as the Zeldovich factor (Z) is for the depletion of the cluster population caused by crystal production. This factor includes the non-equilibrium of the kinetics process which the value is between 10^{-2} and 1, where the value 1 considers as assumed equilibrium. As a result, in describing the expression for the Φ and the pre-factor Z the rate (K) for water molecule is transformed into ice crystal can be expressed as equation below;

$$K = n_s . 4\pi r_{crystal}^2 . Z . \Phi \tag{14}$$

whereas n_s refer to the number of molecules in jumping the crystal surface of the neighboring crystal and the $4\pi r_{crystal}^2$ is the surface are of the critical ice crystal.

8. Conclusion

Most of the basic theories of the nucleation have been summarized in this chapter. The objective of this chapter is to introduce more about the primary, secondary, homogeneous, heterogeneous, ice growth and the kinetics of the nucleation. Even though the homogeneous and heterogeneous nucleation can be called as part of the primary nucleation, both of it has different characteristic as both processes happen at different situation and time. Basically, homogeneous always nucleate new crystals while heterogeneous only focus on the growth of the crystals. Both nucleations can be analyzed through the kinetics of the nucleation and the ice growth of the crystals or bubbles.

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Conflict of interest

The authors declare no conflict of interest.

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