

# Molecular Simulations of Crystal Nucleation

## 1 Introduction to the Research Problem and Objectives

*References [1-45] refer to my CCV, and references [46-59] are given at the end of Section 2.*

The general objective of the projects described in this proposal is to understand crystal nucleation processes at the molecular level. The specific topics that will be considered are heterogeneous ice nucleation in supercooled water, and crystal nucleation from solution. These systems and processes are of much current interest from a fundamental science perspective, and are of obvious practical importance, since they occur widely in our physical environment. [46] For example, ice nucleation by small particles suspended in the atmosphere (aerosols) is an important, but poorly understood, process that influences climate, and is a significant parameter in climate models. We employ realistic molecular models together with molecular dynamics (MD) simulation methods to attack these problems. These simulations can be viewed as “experiments” on model systems that allow us to elucidate physical behaviour on short time and length scales that are not directly accessible experimentally. Moreover, by considering different models, and/or systematically varying model parameters at the molecular level (clearly not possible in real experiments) one can learn which molecular properties strongly influence the physical behaviour of interest. The ability to alter and interrogate physical systems at a molecular level is a very powerful and unique feature of computer simulations.

Heterogeneous ice nucleation occurs in many situations, ranging from biological systems to the atmosphere. [46–48] Pure water can be supercooled to about  $-35^{\circ}\text{C}$ , thus, practically all ice nucleation occurring on earth or in the atmosphere involves a heterogeneous nucleation process. The fundamental question here is: Why do some “foreign bodies” nucleate ice, while others do not? To answer this question requires a detailed understanding of the microscopic mechanisms of ice nucleation. The small size and fast time scales involved pose challenges for molecular-level, experimental investigation, but recently computing power has reached the point where ice nucleation can be explored by molecular simulation. [49] Two projects on this topic are proposed. One will focus on modelling ice-nucleating atmospheric aerosols (e.g. kaolinite, feldspar, gibbsite), as realistically as possible. Comparison will be made with recent experimental results. [50] In a second project, we will consider ice nucleation in a general context, using “generic” models with parameters (e.g. surface geometry, electric fields,  $-OH$  groups) that can be systematically varied. The **short-term objective** is to understand the ice nucleation mechanism for particular ice nuclei, selected because of their importance in the physical environment. The **long-term objective** is to develop a more complete picture by identifying general features which do or do not favour ice nucleation.

Crystal nucleation and growth in supersaturated solutions are important phenomena in many physical systems, and again simulations offer a microscopic view of crystal birth. [49] We plan to examine nucleation processes of ionic and molecular crystals. The **long-term objective** is to elucidate the mechanisms of crystal nucleation and growth, and determine which properties of the crystal and/or solution are important in these processes. Our **short-term objective** is to model and understand the nucleation of alkali halide salts. Our recent work [3,6,9] suggests that even these simple salts can

have interestingly different nucleation mechanisms.

## 2 Research Justification

**Heterogeneous Ice Nucleation:** Ice nucleation is a subject of intense experimental research, [46–48] but, despite recent progress, [50] most experiments probe only at the macroscopic level. MD simulations, which follow nucleation events on molecular length and time scales, provide powerful tools with which to investigate ice nucleation. Ref. [48] gives an overview of current and future research into ice nucleation, including the important role expected of molecular simulations. Our proposed investigations of ice nucleation follow two connected, but distinct, directions. One project will focus on particular atmospheric aerosols, while the other will take a more general approach.

**Project 1, Atmospheric Aerosols:** Here we seek to model atmospherically relevant ice nuclei as realistically as possible. Based on our experience with AgI [10,15] and kaolinite (a common clay), [11] we are now in a position to explore other mineral aerosols. Two nuclei we will examine are gibbsite and feldspar. In many respects, the structure of gibbsite is similar to kaolinite, but it is a less effective ice nucleus. Understanding why this is the case will enhance our knowledge. Feldspar particles are important atmospheric ice nuclei, and the mechanism of ice nucleation by feldspar is a focus of current research. Recent experiments with K-feldspar have identified an “active site” associated with ice nucleation. [50] This is a significant advance, but ice nucleation and growth on feldspar has not been achieved by simulation, and we are vigorously pursuing this question. Our specific objective is to clearly identify the mechanism of ice nucleation on feldspar, and why the nucleation rate varies with feldspar composition.

We will also investigate the influence of common salts on heterogeneous ice nucleation. In interesting experiments using AgI and other ice nuclei, Koop *et al.* [47] found that salt reduced the ice nucleation temperature. This is perhaps an expected result, but Koop *et al.* also found that when plotted as a function of the water activity, for particular ice nuclei, the results all collapsed onto a common curve. This is surprising because one would expect specific effects, with different ions “binding” differently to sites on the ice nucleus, and indeed specific ion effects have been reported. [51] We will carry out simulation investigations of the influence of different salts on ice nucleation by AgI and kaolinite. The objective is to discover exactly how salts influence ice nucleation. Dr. Allan Bertram’s environmental research group at UBC will carry out experiments to determine the influence of salt on kaolinite nucleation, providing for direct comparison with experiment.

MD simulations require the selection of appropriate force fields. For mineral particles we will employ the CLAYFF force field, [52] and for water we will use the TIP4P/Ice [53] and six-site [54] water models, as in our earlier work. [11] For alkali halide salts we will use the Joung-Cheatham parameter sets, [55] which are the best currently available for both solid and solution phases.

The simulation method(s) used will be largely dictated by the problems we encounter. Nucleations are rare events, which occur over a wide range of system-dependant time scales. For AgI [10,15] and kaolinite, [11] models ice nucleation occurs rapidly, such that direct (brute-force) MD (employing GROMACS codes [56]) can be used. An advantage of direct MD is that there is no input “bias” and, apart from the somewhat artificial nature of thermostats and barostats, one is simulating nucleation as it would occur in a real system. Therefore, whenever possible, we will use direct MD simulations.

For systems with time scales that are too long for direct MD, we will employ a method designed to sample rare events. [49] A potential issue with most such methods is that one must define an order parameter, which is used to “drive” the system towards ice, and it is not always possible to be sure that the order parameter chosen is consistent with the actual physics of the nucleation process. However, the forward flux sampling (FFS) method has been used in simulations of ice nucleation, [57] and, if necessary we will employ this approach.

**Project 2, General Approaches to Ice Nucleation:** Earlier MD simulations [58] have shown that electric fields induce rapid freezing in bulk water, and we have more recently found that local fields acting very near a surface are very effective ice nuclei. [16,26,27,32] However, an important issue remains to be addressed. The fields necessary to induce ice nucleation on direct MD time scales ( $\sim 10^9$  V/m) are at least two orders of magnitude larger than those obtainable in experiment. Thus, meaningful comparisons between simulations and experiment have not been possible. We plan to use FFS or other enhanced sampling methods to examine nucleation at lower fields. This will allow comparison with experiment, and enable a better assessment of the influence of local electric fields as ice nucleating agents in real physical systems.

Hydroxyl ( $-OH$ ) groups occur on ice nucleating surfaces, ranging from kaolinite to alcohol monolayers, and proteins. Therefore, it is useful to explore how  $-OH$  groups influence ice nucleation. Flexibility is a feature of  $-OH$  surfaces. For example, kaolinite  $-OH$  groups can change their orientations, and in alcohol monolayers both the positions and orientations of  $-OH$  groups are variable. For kaolinite, we found [11] that  $-OH$  reorientation is necessary for ice nucleation, but allowing too much flexibility slows the process, and nucleation is not observed on direct MD time scales. For kaolinite, we also found that once ice nucleation has been achieved, if the ice-compatible surface is held rigid, nucleation rapidly occurs.

We expect flexibility to severely limit direct MD simulations for most ice nuclei where  $-OH$  groups play a key role. Implementation of methods such as FFS also appears problematic because an appropriate order parameter would likely need to take account of surface structure, as well as that of ice. Therefore, to gain some insight, we propose a new route suggested by our observations for kaolinite. Our idea is a reverse engineering approach. We propose a simulation cell with the  $-OH$  layer of interest (e.g. alcohol monolayer) at one end, and an ice nucleus at the other, such that ice grows to fill the simulation cell. We expect the forming ice to organize the  $-OH$  surface into a favourable configuration for ice nucleation. This can be checked by running simulations with the ice-conditioned  $-OH$  surface held rigid. This is an indirect method of investigating ice-nucleating  $-OH$  surfaces, and identifying “active” configurations.

**Project 3, Crystal Nucleation and Growth from Solution:** Classical nucleation theory (CNT) is widely applied to many types of homogeneous and heterogeneous crystal nucleation. CNT assumes that a potential nucleus is structurally a smaller version of the bulk crystal, and that crystal nucleation occurs in a single step. Further, it assumes that the free energy barrier to nucleation depends on competition between two terms, a bulk term which favours nucleation, and a surface term which does not. At some critical size, the bulk term overwhelms the surface penalty, and the crystal grows irreversibly. Currently, the basic assumptions of CNT are being seriously challenged. Experiments and simulations [49,59] have shown that for some systems crystal nucleation does not occur in a single step as assumed by CNT. For example, for some proteins crystallization is preceded by the formation of a liquid protein “droplet”, such that nucleation occurs in a two-step mechanism. [59]

Our recent simulations of LiF crystal nucleation show that loss of water from the ion coordination shells poses a high activation barrier, which determines the rate of crystal growth. [3] This raises an interesting question for LiF nucleation. Based on our NaCl simulations, [22,25] we expect a two-step nucleation mechanism, specifically, the formation of a disordered ion “cluster”, followed by spatial ordering. For NaCl the second step is rate determining. Our preliminary simulations for LiF suggest a similar mechanism, but in this case there is a good possibility that the first step is rate determining. We will carry out simulations to determine the rates of both steps in the nucleation process. We expect these to be challenging simulations. At high temperatures, our preliminary simulations suggest that direct MD will suffice, but at ambient temperatures, FFS, or perhaps a free energy based approach such as metadynamics, [49] will be necessary. Nevertheless, the possibility of discovering a nucleation mechanism where the rate determining step is totally unrelated to CNT, makes this project well worthwhile. Additionally, we would expect the results obtained to apply to other salts, where one has small, strongly solvated ions (e.g.  $\text{CaF}_2$ ). In the longer term, we will consider other interesting salts such as LiBr, which crystallizes as a hydrate, and molecular solids, such as urea.

## References

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