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On the Probability of Nucleation at the Surface of Freezing Drops

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Recent publications have proposed that nucleation in the freezing of supercooled drops occurs at the drop surface, an idea supported by statistical thermodynamic arguments by Cahn [*J. Chem. Phys*. **1977**, *66*, 3667] coupled with thermodynamic arguments by Tabazadeh et al. [*Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 15873]. Whether this phenomenon is general is examined by molecular dynamics simulations of the freezing of deeply supercooled liquid clusters of SeF_6. It is found for this model system that while nucleation occurs not infrequently at the surface, it more often takes place in the interior. The probability for surface nucleation increases with the depth of supercooling. How this relates to theories of Cahn and Tabazadeh et al. is discussed briefly.

Introduction

In the past few years Tabazadeh and her collaborators have published several papers[1−3] suggesting that, in the freezing of liquid drops in clouds, nucleation takes place at the surface rather than throughout the volume. In their initial paper, the authors cited as prior evidence two experimental papers of two decades ago[4,5] and several computer simulations originating in this laboratory.[6−12] Even though the idea of preferential surface nucleation is plausible, the experimental papers referred to appear to provide little evidence for the idea. The first paper cited,[4] on the freezing of water drops in emulsions, fails to support the authors' suggestion for it explicitly states that, for the data associated with homogeneous nucleation, the results scaled with the *volume*, not the *surface area*. It was in the experiments with a surfactant judged to produce heterogeneous nucleation that freezing occurred at the interface with the surfactant catalyst. In the second experimental paper[5] cited, we are unable to recognize any claim that nucleation occurred at the surface. On the other hand, in our computer simulations, in which freezing could be studied in molecular detail, there was no doubt about where nucleation took place. The present paper offers new results to clarify the situation.

To support their contention that freezing occurs preferentially at the surface, Tabazadeh et al. examined a variety of publications on the freezing of droplets in atmospheric investigations and concluded that results could be interpreted more simply in terms of surface nucleation. These authors also demonstrated by a capillary model that the work of generating nuclei was lower for surface nucleation than for bulk nucleation, provided the solid formed was not wetted by its melt.[2] To corroborate their point, the authors cited a conclusion by Cahn[13] to the effect that crystalline surfaces are not expected to be wetted by their melt. Arguments undercutting the generality of this conclusion, however, were advanced by Dietrich.[14] Also, in a review of nucleation in the freezing of aqueous solutions, Koop[15] concluded that neither a volume-dependent nor a surface-dependent nucleation process "is convincingly supported." Inasmuch as prior simulations of small nickel clusters had found the melt to wet the solid[16] and our simulations had encountered surface nucleation in similar clusters,[6,11] it seemed that more was involved in surface nucleation than nonwetting. Therefore, we undertook a more detailed study of wetting and site of nucleation.

It was clear in our simulations of the freezing of large clusters of molten NaCl that the melt did not wet the solid, and therefore it was not surprising that nucleation was initiated at the surface of molten droplets.[9,17] On the other hand, work is still in progress in the case of our most intensively studied system, drops of SeF_6, to find out whether the melt wets the solid surface. One obstacle impeding the resolution of this question is the surprisingly sharp melting point of clusters of this material, making it extremely difficult to generate a configuration at a temperature at which solid and liquid coexist in equilibrium.[18] At higher or lower temperatures, one of the phases disappeared and no equilibrium contact angle could be determined. Of course, our systems are far below their equilibrium melting point in simulations of nucleation, and Cahn's theory predicts that the degree of nonwetting increases (i.e., the contact angle increases) as the temperature drops.[13] This would presumably increase the tendency for nuclei to form at the surface. Nevertheless, preliminary evidence provides no indication of nonwetting for clusters of SeF_6, yet surface nucleation is often observed. Just how preferred the surface site is, is the subject of this paper.

Experimental Procedures

Independent sets of 100 clusters of SeF_6 with 725 molecules/cluster were generated as described in detail in prior publications.[19,20] Because of the appreciable evaporation suffered by many of the clusters, they were trimmed to quasispherical entities containing 540−560 molecules, to bring all to a nearly common size, and then quenched from 200 K to each of five final temperatures, 170, 150, 130, 110, and 90 K. Clusters were maintained at the foregoing temperatures by rescaling velocities every 10 time steps. Each time step was 7 fs. Runs were continued until the clusters froze. Coordinates and velocities were saved every 200 time steps. Bulklike solid aggregates in each cluster were identified by the Q_6 criterion of Steinhard et al.[21] as described in detail in refs 7 and 22. At the deep supercooling to which our clusters are subjected, the population of aggregates identified as solidlike (by analyses of Voronoi polyhedra or by the Q_6 criterion) differed substantially in

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TABLE 1: Analysis of Positions of Nucleation Site for Clusters with a Radius of 22 Å, as a Function of Quench Temperature[a]

	90 K		110 K		130 K		150 K		170 K	
	D[b]	% surf[c]	*D*[b]	% surf[c]	*D*[b]	% surf[c]	*D*[d]	% surf[b]	*D*[b]	% surf[c]
average	16.9	49.4	15.8	39.8	13.1	24.8	11.2	19.1	11.7	19.9
standard dev	2.8	20.7	3.5	23.7	4.0	22.8	4.5	22.0	4.3	22.3

[a] Results are for 100 runs at each temperature. Average number of bulklike solid molecules in the defined nucleating region was 15, with a standard deviation of **7**. [b] Distance between the center of mass of the nucleating region from the center of mass of the cluster, in angstroms. [c] Percentage of bulklike solid molecules in the nucleating region present on the surface. It should be noted that about 45% of all the molecules in the clusters examined in this study are on the surface. [d] The actual average cluster radius is about 24 Å, so that the radius corresponding to the center of a surface molecule is about 21.5 Å. Of more interest may be the average distance from the cluster center of the center of a nucleus of 15 molecules, which is about 17 Å.

character from populations found at more modest supercooling. A large fraction of the solidlike regions encountered at deep supercooling are very thin filaments or sheets whose presence does not correlate well with nucleation. That is, the inclusion of all such solidlike regions does not yield a well-defined time of onset of nucleation. This anomalously large concentration of such slender structural fluctuations at deep supercooling may well be associated with the breakdown of the Stokes−Einstein relationship found in deeply supercooled liquids.[23] In an attempt to bypass this complication, we introduced the criterion that true nuclei must be “bulklike solid” regions (or contain “bulklike solid” molecules) defined as follows. Nuclei must contain at least one molecule surrounded by 12 neighboring solidlike molecules for nuclei in the interior or seven for surface nuclei.[20] The introduction of this test for aggregates to be considered bona fide nuclei led to very clear-cut first-order nucleation kinetics.

The site of nucleation in each cluster was determined, starting at the end of a simulation, by examining coordinates of saved configurations sequentially, in reverse order, to trace the bulklike solid region as it decreased in size. In each step the continuity between the solid region in the current step and that in the previous step was analyzed. If a bulklike region in the prior step was not contiguous with the current bulklike region, then such a region was ignored and the current region was considered to be the product of growth of the initial nucleating region. The step before the bulklike solid region disappeared was considered to locate the initial nucleating region. Once the initial nucleating region had been determined, the center of mass of that region was calculated. Its distance from the center of mass of the entire cluster was taken to be a measure of how far the nucleation site was from the cluster surface.

Results

What we took to be the initial nucleation region, according to our search procedure of stepping backward in time, was the small aggregate of bulklike solid molecules at the step just before the bulklike solid aggregate disappeared. If molecules in such aggregates happened to be on the surface, then that aggregate could contain as few as eight molecules by our criterion for identifying bulklike solid molecules.[20] If the nucleating region occurred closer to the center of the cluster, then at least 13 molecules would be needed by our criterion for us to consider the region as a bona fide nucleus. Typically, the region found by our procedure of tracing back contained about 15 molecules if it were in the interior of the cluster, a value not greatly different from the rather more than 20 molecules found to correspond to the size of critical nuclei at 130 K.[20] Occasionally, however, the starting regions found by our procedure based on steps separated by a finite time difference could be as large as 58 molecules. Of course, due to our method of tracking back and identifying as the “starting” nucleus the smallest size of a bulklike region before it disappeared, we could go below the true size of critical nuclei. Obviously, the coarse intervals between saved time steps could also lead to “starting aggregates” much larger than critical nuclei.

The shape of the start region was not investigated in detail. Our subjective impression from looking at a number of simulations is that the start regions tend to be quasispherical when they are close to the cluster center and may be either roughly hemispherical when they are close to the surface or cone-shaped with the vertex of the cone pointing toward the cluster center. As surrounding molecules in the liquid begin to attach themselves to a growing nucleus, the nucleus becomes more irregular. In movies we made of nucleation in clusters of hexafluorides undergoing the solid-state transition from the bcc phase to monoclinic, the nuclei tended to look rather ramified from the beginning.[24] This difference may be partly because of the different type of phase change. It may also be due to the different technique for recognizing nuclei. The Q_6 method was used in the present work whereas Voronoi polyhedra were used in the movies of solid-state transitions.

How strong the tendency is for nucleation to occur at the surface is summarized in Table 1. It is apparent that nucleation at or close to the surface is not uncommon, but the surface is certainly not the exclusive site in the case of our model SeF_6 system. A wide distribution of distances from the surface was found. However, there is a clear trend overall for nucleation to occur closer to the surface with deeper supercooling. The small reverse trend in the comparison of results at 150 and 170 K is not statistically significant.

Discussion

Tabazadeh et al.[2] showed by a capillary model that if a nucleus in contact with its surroundings possesses the interfacial free energies σ_{ij} per unit area, where i and j may represent solid, liquid, or vapor, surface nucleation is to be expected if the work of forming a nucleus at the surface is lower than the work of forming a nucleus in the interior, or

$$\sigma_{\mathrm{vs}} - \sigma_{\mathrm{vl}} < \sigma_{\mathrm{ls}} \qquad (1)$$

That is also the criterion for nonwetting, that is, the condition for a contact angle greater than 0.

Our observed increased tendency for surface nucleation to be enhanced by deeper supercooling is consistent with Cahn’s theory together with a simple extension of the criterion of Tabazadeh et al [2]. Cahn concluded that the lower the temperature, the lower the completeness of wetting (the higher the contact angle),[13] and from the criterion of Tabazadeh et al,[2] we might suppose that the greater the reluctance of the liquid to wet the solid, the greater the tendency for surface nucleation. What the physical picture behind this tendency is, is not entirely clear, in view of the limitation of Tabazedeh’s capillary model when interfacial thicknesses are on the order of magnitude of the size of the critical nucleus.

Where a nucleus first forms depends on the location with the highest nucleation rate. The nucleation rate J can be expressed as

$$J = Ae^{-W^*/kT} \tag{2}$$

Clearly, the greater mobility of surface molecules enhances the prefactor A for surface molecules, while the tendency for surfaces to be disordered suggests that the surface is not the most congenial site for an ordered solid. Since a small change in the work W^* of forming a nucleus has a much stronger effect on nucleation rate than a modest change in the prefactor, it is natural to suppose that W^* holds the key to the problem. This is exactly the argument of Tabazadeh et al.,[2] which compares the work of forming a nucleus at the surface with the work in the interior and attributes bulklike quantities to nuclei containing only a few molecules. In the case of the freezing of salt, where the melt clearly avoids wetting the solid, the expected surface nucleation does take place. In cases such as small clusters of metals and SeF_6, where surface wetting seems to occur, the situation is not so clear. Why, in such cases, is there a bias toward surface nucleation, at least at low temperatures? As mentioned above, the Cahn argument coupled with that of Tabazadeh et al. provides at least a rationale. Another possible influence on nucleation site is the existence of capillary waves. Capillary waves impose momentary shears (velocity gradients) upon surface regions[25] and thereby might tend to align molecules in small pockets. Whether capillary waves have a significant effect on the generation of ordered nuclei is unknown.

Whatever the mechanism, it is clear that nucleation does not invariably occur at the surface. Nevertheless, it occurs to some extent even in cases where the thermodynamic argument of Tabazadeh et al. no longer applies. Since water is said not to wet clean ice,[26] surface nucleation in clouds may have important consequences in atmospheric processes. The subject of the site of homogeneous nucleation in freezing may also have significant implications in technology. It remains poorly understood and warrants further investigation.

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