Idiosyncrasies Of Nucleation In Large, Deeply Supercooled Liquid Clusters

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Abstract. Characteristic differences between the nucleation of solids in bulk liquids and in liquid clusters are identified in computer simulations, and the reasons for these differences are discussed.

INTRODUCTION

What is idiosyncratic about the nucleation in deeply supercooled clusters? To answer the question we first have to consider what is considered normal nucleation. Until quite recently, a picture of what happens on a molecular scale during a phase change appeared only in the imagination of the theorist. Experiments were blind to the details, and theories of the complex process had to be simplified in order to make progress. The classical theory of homogeneous nucleation (CNT) was based upon the idea proposed by Gibbs according to which a (nominally spherical) particle of the new phase appears in the old phase by structural fluctuations at the cost of the free energy to produce the interface between the old and new phases. Direct measurements of the interfacial free energy between the two condensed phases could only be performed at the equilibrium temperature of the phase change[1], and nucleation experiments were feasible only at modest degrees of supercooling where critical nuclei were large and presumably bulk-like in properties. In our investigation the nucleation process is studied by carrying out computer experiments using the molecular dynamics (MD) technique based on realistic intermolecular interaction potential functions[2]. In the computer simulations, molecules in liquid clusters can be watched as their unbiased trajectories carry the system into whatever regions of phase space are decided by chance. Phase changes take place spontaneously at different times for different members in a set of supercooled clusters. Deviations from what might be considered to be conventional nucleation behavior can come from two sources. (a) Clusters in this study are minuscule in comparison with the droplets in conventional experiments and this, alone, can lead to altered physical properties of the system. (b) The supercooling is enormously deeper, leading to considerably smaller critical nuclei. Some of the consequences are sketched below.

SIMULATIONS

The clusters whose behavior we report typically contain 100 to 2000 molecules. We first elected to chose clusters with free boundaries in order to avoid the possible interferences that can occur when periodic boundary conditions are imposed as in simulations of the bulk. Later, clusters proved to be worthy subjects in their own right.

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Their typical supercoolings are in the vicinity of half the melting temperature. Rates of spontaneous transitions at much shallower supercooling would be too slow to observe within reasonable CPU times. Although it has been proposed that such deep supercooling as we examine can be expected to lead to spinodal decomposition instead of nucleation[3], we have seen no evidence of such decomposition in our simulations. The kinetics of transformation of an ensemble of clusters has always been first-order, to within the limits of our ability to determine order, and the nuclei initiating the transition can be watched as they form and grow. Moreover, their kinetics of growth is in good agreement with the kinetics expected from a modified form of the Kolmogorov-Johnson-Mehl-Avrami equations[4] based on first-order kinetics.

Some theorists protest that aggregates of matter as small as our clusters cannot be considered to exist in what can legitimately be called a thermodynamic phase. Likewise, they dispute that structural changes in such small systems can be viewed as phase changes. It turns out that there is no difficulty in recognizing the state of the clusters, as a rule. Liquids are readily discriminated from crystalline forms, both by their haphazard structure and their facile self-diffusion. Crystalline clusters can be uniquely identified with bulk crystal structures by their periodic translational and orientational orders. Sometimes, at very fast cooling rates to deep supercooling, the solid clusters formed may consist of mixtures of several different crystalline structures, and this may confuse the identification of the structure.

Although the crystalline phases encountered can be identified, they are not necessarily those obtained when the bulk material is cooled. This is because kinetics, rather than thermodynamics, controls what happens in the nanosecond time scale of the processes.

RESULTS

Differences Between Various Clusters

Clusters investigated in this report include molecular, ionic, and metallic clusters. These behave quite differently from each other when their liquid forms are deeply cooled or when their crystalline forms are melted. When molten salt clusters are cooled, however rapidly, they have an extremely strong tendency to crystallize. If the cooling is not unphysically rapid, they tend to freeze to *single* crystals. Clusters of molecular liquids are easily frozen to glasses if cooled sufficiently rapidly. They often freeze to single crystals, however, at cooling rates of ~ 10^{11} K/s, a rate not normally considered to be slow! Metals are intermediate. Generally, both molecular and ionic crystals retain their form while heated until they melt, even if they begin with metastable structures. Crystalline clusters of metals, however, may partially transform to a mixture of crystalline forms before melting.

Differences Between Clusters And Bulk Matter

When solid clusters are heated, they invariably start melting first at their surfaces. Alternatively stated, at a given temperature, molecules in surface layers of crystals tend to be more disordered and mobile, i.e., more liquid-like than interior molecules. Therefore, we had originally supposed that when a liquid cluster froze, the freezing

would begin in the interior . Surfaces seemed to be less hospitable sites for ordered arrays. Our conjecture was wrong. For all of the kinds of supercooled liquid clusters we have studied, molecular, ionic, and metallic, crystal nuclei materialize preferentially at or very near the surface. The reasons for this are not entirely clear. This is one of the idiosyncrasies seen in clusters. A consequence is that nucleation rates in clusters tend to be higher than in the bulk because clusters have a much higher surface-to-volume ratio.

Is Nucleation In Clusters Homogeneous?

A virtue of computational studies of clusters is that the subjects in the simulations are perfectly pure with no traces of the submicroscopic contaminants that are believed to initiate heterogeneous nucleation in, and thereby subvert, studies of truly homogeneous nucleation in bulk liquids. Still, can the nucleation observed in liquid clusters be considered as truly homogeneous? Since nucleation tends to occur in surface layers, it could be argued that the nucleation is heterogeneous, catalyzed by the surface. Of interest in this respect are the solid state transitions seen in some of the simulations. For example, in the case of our clusters of hexafluorides, if freezing is carried out at temperatures not too deeply supercooled, the solid phase first formed is body-centered cubic, the same as that observed in the bulk substances. Then, if the temperature is low enough, the solid transforms to monoclinic, the stable low-temperature phase for SF_6 and SeF_6. MD simulations clearly show that the bcc to monoclinic change is facilitated by grain boundaries or solid-liquid interfaces. A cluster consisting of a single bcc crystal at the same temperature is much less likely to transform in a given time than a polycrystalline cluster or one that is partially liquid. Therefore, as in prior experimental studies of solid state transformations, the nucleation can be considered heterogeneous.

Size Of Critical Nuclei In Deep Supercooling

The number of molecules, n*, in critical nuclei found in the simulations has been much larger than the value inferred from the CNT using the interfacial free energy parameter deduced from the nucleation rate via the CNT. A similar disagreement arises when Gránásy's diffuse interface theory[5] (DIT) is applied, even though, in some respects, the DIT is superior to the CNT. In deeply supercooled liquid clusters, well before the concerted growth of the new phase signals that a critical nucleus has been formed, there exist large numbers of molecules passing the Voronoi and other tests for molecules with solid-like connectivity. They number far in excess of the n* inferred via the CNT and exist in fluctuating filaments and sheets of molecules. In view of this phenomenon, which does not correspond at all closely with the picture of precritical embryos associated with the CNT model, our criterion for the onset of nucleation is not based on the number of contiguous molecules judged to have the local structure of the new phase. It has proven to be more appropriate to monitor those molecules which not only pass the Voronoi and other order parameter tests but which can also be considered to be "bulk-like solid" in nature. In transitions to a bcc phase these are molecules which are surrounded by at least 12 other "bcc" molecules within the distance to the first minimum of the pair correlation function. Molecules in the sheets

and filaments do not pass this test. When the temporal evolution of the *total* number of bcc molecules is followed, the onset of nucleation is poorly defined but when only the "bulk-like solid" molecules are monitored, the onset of nucleation is usually fairly sharp and definite. Note that the value of n* based on the CNT at our characteristic supercoolings is typically a mere half-dozen. So our number of molecules qualifying to be considered in the critical nucleus (at least 13) is already larger than the CNT n*, and the total number of contiguous molecules passing the tests of solid-like connectivity before onset considerably exceeds the CNT n*. This is another of the idiosyncrasies of deep supercooling.

Why are the critical nuclei larger than the n* of the CNT even when the sheets and filaments are disregarded? It is worth noting that a single layer of molecules surrounding a CNT critical nucleus would complete an aggregate of roughly the size of the critical nuclei we find. Now, the CNT critical nucleus is based on a theory that completely neglects any diffuse interface between the old and new phases. Therefore, it might be speculated that the discrepancy results from a disregard in the CNT of a possible difference between the equimolar surface and the surface expressing the interfacial free energy. Other reasons may be more important. In the CNT, the cost of forming a nucleus of the new phase in the old is the product of the interfacial free energy and the area of the boundary, and the driving force to lower the free energy ultimately is $N \Delta G$, where N is the number of moles in the nucleus and ΔG is the free energy of freezing per mole of the *bulk*. For very large critical nuclei formed at shallow supercooling this is probably not a bad approximation. For the extremely small nuclei formed at deep supercooling, the absolute magnitude of $N \Delta G$ is probably a substantial overestimate. It is also quite possible that our present criterion for identifying crystalline nuclei using a structural order parameter is somewhat too liberal. In any event, nucleation at deep supercooling differs appreciably from the nucleation encountered in conventional studies at shallow supercooling. Specific examples of the behavior discussed in the foregoing will be illustrated in the presentation.

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