

Crystallization of some supercooled liquids via a second liquid phase as an “Ostwald step”. Is this what temperature-induced polyamorphism is all about?

C. Austen Angell
Dept. of Chemistry and Biochemistry,
Arizona State University,
Tempe, AZ 85287-1604

It is a common observation that a glass will crystallize first to a phase of low symmetry before recrystallizing to the stable crystal phase. This is commonly understood by reference to the Ostwald “step” rule which holds that the equilibrium state of a system may be reached by a succession of steps each being a kinetically more accessible stage than the direct route to the state of lowest free energy. Here we discuss cases in which the first step is not a crystal but another liquid. The best evidence for this possibility is found in computer simulations, which will be described here before giving experimental examples of the same phenomenology. The simulations focus on the element silicon, but comparable observations could be made on Germanium and probably also tellurium. Experiments on liquid germanium that directly support the simulation findings will be described. These will be related to prior observations on ionic and molecular liquids. In each of these the second liquid is found to be very fast to crystallize relative to the liquid phase with which it co-exists. In fact it is rarely possible to obtain samples of the low temperature liquid that are not contaminated with crystalline material. This is wholly consistent with the observation of Zanotto for silicate glasses that the glasses which nucleate internally, rather than at the surface, are those for which the crystal that forms is closest in volume to that of the glass. Finally we will describe a mesoscopic analog of this phenomenology in which the macroscopic phases are replaced by complex molecules which can assume more than one low energy topological state. This deals with the relation between normal folded proteins and misfolded proteins that provide the stepping stone to the fibrils involved in a class of fatal conditions called “folding diseases”. The polyamorphic transformation to second type of folded is the critical kinetic step in the passage from normal globular protein to pathological fibril states identified in victims of “folding’ diseases.