591d Nucleation and Crystallization from Supercooled Liquids of Nitrogen and Carbon Dioxide

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Despite many experimental and theoretical studies, it still remains impossible to predict which crystalline variety or polymorph will form upon cooling a liquid or a solution. This issue is of both fundamental and technological interest. Since polymorphs may have very different physical properties (e.g. solubility in water), it is of great importance e.g. for the pharmaceutical industry to know which polymorph of a drug molecule will be obtained. In this work, we study the structural changes during nucleation and crystallization from supercooled liquids of nitrogen and of carbon dioxide. In particular, we show that the crystallization of nitrogen takes place accordingly with the empirical Ostwald's rule of stages [1]. This rule summarizes the interplay between kinetics and thermodynamics in a polymorphic system and indicates that the crystallization process starts with the appearance of the least stable form and finishes with the most stable form. Using molecular dynamics together with the umbrella sampling technique, we show that the structure of the critical nucleus is essentially that of metastable α-N2. Subsequent growth is found to occur concomitantly with a structural transition towards stable β-N2. Our simulations also shed light on the microscopic mechanisms accounting for this transition. We show that the transition results from a faster growth rate for the stable form rather than from the dissolution of the metastable form [2]. In the case of carbon dioxide, nucleation is found to proceed directly into the stable phase [3].

[1] Ostwald, W. Z. Phys. Chem. 22, 289 (1897). [2] J.-M. Leyssale, J. Delhommelle and C. Millot, J. Am. Chem. Soc. 126,12286 (2004) [3] J.-M. Leyssale, J. Delhommelle and C. Millot, J. Chem. Phys. 122, 184518 (2005)