Ultra-fast crystallization due to confinement

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In the crystallization experiments we present in this communication confinement allows the system to be both highly supersaturated and in a metastable state. As a result, the nucleation from NaCl-solutions proceeds in less than 2 s from the dense liquid phase in agreement with the two-step nucleation mechanism.

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In a previous paper we theoretically reconsidered the effect of confinement (small volume system) on nucleation and identified a clear window of parameters where nucleation occurs alone according to a thermodynamics approach[1]. Confinement where experimentally affordable, will provide a new way to study critical clusters and nucleation. In the literature confinement (at the nanometer scale) is realized by controlled-pore glasses[2,3] or other nanoporous materials [4]. Thermal behavior of materials under confinement is examined in relation with the Gibbs–Thomson equation [3], or polymorph selectivity in ultra-small pores [4,5] or in small droplets [6]. Microemulsions are also used to produce confinement in order to measure critical nucleus size via thermal behavior [7].

In order to observe the effect of confinement on the kinetics of crystallization, we developed a set-up to generate and observe micrometer droplets. This communication presents the first findings on the crystallization of NaCl by evaporation of micrometer droplets of undersaturated NaCl solutions covered by DMS oil.

All experiments were performed on a 18 mm diameter coverslip inserted in a thermostatted well under an optical microscope (Zeiss Axio Observer D1). The well is filled with approximately 5 mL of inert DMS oil (Hampton Research HR3-419, refractive index=1.390). The micrometer droplets of NaCl solution are generated on the coverslip by a microinjector (Femtojet, Eppendorf) used for the injection of liquids in the volume range from femtoliters to microliters. A home-made micromanipulator consisting of three miniature translation stages (piezo electric, MS30 mechatonics) allows displacement of the injector (capillary holder) in X, Y and Z with a displacement of 18 mm in the 3 directions by steps of 16 nm. A hydrophobic glass capillary, obtained by vapor-depositing a toluene+5%/v n-octadecyltri-chlorosilane (ODTS) mixture on the capillary, with an internal diameter of 0.5 µm (Femtotip Eppendorf), is used. The whole set-up is shown in Fig. 1.

The principle of the experiments is to let water slowly evaporate from the crystallization drops through the layer of liquid oil [8–10], which results in an increase in the concentration of NaCl, establishing supersaturation. We control the rate of evaporation because over-drying (in air for instance) often results in the formation of polycrystalline aggregates. Fig. 2 presents the complete process: evaporation, nucleation and growth. In the first
stage. 2 droplets containing NaCl 0.7 M solution are generated (Fig. 2a). Droplets slowly evaporate until supersaturation is established (Fig. 2a–c). The NaCl concentration is qualitatively monitored through the evolution of the optical contrast between the droplet and the DMS oil in Fig. 2a–c. Droplets (1) and (2) of 61 and 53 μm, respectively (Fig. 2a) completely disappear, in 128 and 82 s, respectively, indicating an adjustment of the refractive index between the two phases. At t=0, the refractive index of the 0.7 M NaCl solution is 1.340 when the solution concentrates during evaporation the refractive index increases. At these times, t=128 and 82 s, respectively, NaCl concentration is 6.7 M in the droplets. NaCl concentration is estimated from a relation between NaCl concentration and refractive index (tables 71 D-252) [11]. Using this estimation, we calculate the supersaturation in the droplets at these times (t=128 and 82 s) to be $\beta = 1.23$. Supersaturation $\beta$ is defined as the ratio of the NaCl concentration in solution versus the solubility of NaCl, 5.42 M at 20 °C in water [12].

Nucleation occurs after 196 and 150 s in droplets (1) and (2), respectively (Fig. 2d and f). In addition, supersaturation is greater than 1.3 in both droplets at the time of nucleation, since the evaporation process continues during the lapse of time between droplets disappearing and nucleation. Note (1) the same level of supersaturation was previously obtained in small droplets by Tang and Munkelwitz [13] and (2) that non-confined NaCl solutions spontaneously nucleate at $\beta > 1.03$.

Three important observations follow from the sequence in Fig. 2.

Observation (1): Confinement stabilizes the solution up to high supersaturation. This is in agreement with the theoretical prediction using a thermodynamics approach [1]: for volume smaller than the nanoliter range and below a critical supersaturation no nucleation can occur. When applied to NaCl solution and to droplets of 50 μm we found that the critical supersaturation is 1.005 (Fig. 3). Fig. 3 is derived from the slightly modified classical nucleation developed for finite-sized system [1], namely to a volume corresponds a number of molecules in a droplet and a critical supersaturation where no nucleation can occur. Here a kinetics effect (metastable zone) of the confinement is shown to stabilize highly supersaturated NaCl solutions, in droplets of 53 and 61 μm, at supersaturation greater than 1.23.

Observation (2): Both nucleation events are single, also in agreement with the prediction: “... and there is a supersaturation-window for a single nucleation event giving one single crystal per droplet of a scalable size [1].” Here again, the kinetics effect of confinement enlarges the supersaturation window in Fig. 3.

Observation (3): Nucleation and growth occur very rapidly: in less than 2 s a crystal of 15 μm having a cubic habit (Fig. 2c, d and e, f) is produced. The growth rate appears to be about 10 μm/s, several orders of magnitude faster than that expected for NaCl grown from solution [14]. We propose an interpretation based on the two-step nucleation mechanism [15–17], where a density fluctuation is followed by a structural fluctuation, the structural fluctuation being almost instantaneous. In the experiments we present in this communication, confinement allows the system to be highly supersaturated and in a metastable state; this formation of a dense liquid phase is the first step. Nucleation then proceeds in less than 2 s from the dense liquid phase. To our knowledge this is the first time that such a mechanism has been directly observed in solution.

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References


