Journal of Crystal Growth 79 (1986) 630–635
North-Holland, Amsterdam

NUCLEATION BEHAVIOUR IN SMALL LIQUID VOLUMES AT HIGH RATES OF CHANGE OF SUPERSATURATION

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An experimental device is described which permits the study of nucleation and growth of crystals from solutions in small volumes at a high rate of change of supersaturation. The information that can be obtained from the analysis of the recorded data is also discussed.

1. Introduction

It is unusual to find in the literature experimental arrangements giving information on nucleation processes in the transitional region where the nucleation rate is time-dependent or on the properties of the subsequent growth [1]. However, in spite of the more complex formal treatment required, there is interest in it because of its importance in many industrial crystallization processes as well as in mineralogenesis.

The aim of this paper is to describe a device designed to study nucleation and growth behaviour at high and variable supersaturation levels in small liquid volumes and to discuss the analysis of the data obtained. Small volumes are used for two reasons: first is that they are necessary experimentally in order to obtain the appropriate thermal shock easily, the second has a theoretical origin since nucleation behaviour in small volumes, which is very important (for instance in biomineralization), is not well-explained by classical theories [2].

2. Statement of the problem

The metastable zone width ΔC_{max} and the experimental induction time τ have been used in the explanation of the nucleation process in cooled solutions. This information is indirectly obtained from measurements of the maximum allowable supercooling ΔT_{max}. In order to obtain reliable data for τ and ΔT_{max}, the time dependence of the supersaturation must be calculated from the equation:

$$\frac{\mathrm{d}[\Delta C(t)]}{\mathrm{d}t} = -\frac{\mathrm{d}C_e(T)}{\mathrm{d}T}\frac{\mathrm{d}T}{\mathrm{d}t}. \tag{1}$$

Usually, this analysis has been applied at constant cooling rate [1], i.e., when:

$$T(t) = T_0 - K_c t, \tag{2}$$

where K_c is the constant cooling rate, which usually takes values between 0.2 and 2.0°C/h [3]. At such a low cooling rate, the metastable zone width is small and the solubility curve could be considered as linear in the measured temperature range. Thus, the supersaturation also changes linearly and the rate of change of supersaturation is constant and not time-dependent.

However, when a system is cooled quickly (for instance, by a thermal shock) between an initial temperature T_0 and a final temperature T_f, the time dependence of temperature follows an exponential form [4]:

$$\mathrm{d}T/\mathrm{d}t = -k[T(t) - T_f], \tag{3}$$

where k is an experimental constant which depends on both the heat dissipation factor of the cell and the heat capacity per unit volume. Obviously, in such a situation, the supersaturation changes in a non-linear way and the rate of change of supersaturation changes with time.

0022-0248/86/$03.50

It can be shown from (3) that the cooling rate may be increased by increasing the value of $\Delta T = T_0 - T_f$ and by decreasing the volume of the cooled solution. Therefore, in order to understand the nucleation behaviour at high rates of change of supersaturation, which is a feature of many industrial processes, laboratory systems with small volumes ($= 25\ \mu l$) and high $\Delta T (\simeq 90\ ^\circ C)$ must be used. Unfortunately, such a high cooling rate increases the width of the metastable zone and the dependence of solubility on temperature cannot be neglected in equation (1); this introduces problems in the calculation of ΔC_{max} and τ.

What follows is a description of firstly, a laboratory apparatus of small volume designed to be operated at high ΔT and ΔC and, secondly, the preliminary formal analysis for data interpretation.

3. The apparatus

A diagram of the apparatus is shown in fig. 1. For the sake of clarity, it will be described part by part.

3.1. The T_f environment

The nucleation cell (see fig. 2b) is a cylindrical reservoir (Nc) of volume 25 μl. with an optical base and head. Two oppositely positioned needles (Ne) penetrate into the cell and connect it to the injection system. The microcell is immersed in a thermally isolated box (Ib) with a system that permits a continuous circulation of ice–water mixture (Rs) connected to a thermostated bath. Thus, a limiting final temperature of 0 °C is obtained.

3.2. The T_0 environment

The injection system consist of a small thermostatted oil-bath attached to the injection syringe (Is in fig. 1) which contains a solution at T_0.

A simultaneous aspiration-injection procedure (see fig. 2a) permits a small controlled volume to be transferred to the cell at constant pressure. This procedure avoids undesirable nucleation effects induced by pressure which were observed with previous designs. Therefore, the driving force for nucleation is only affected by the change of temperature following the thermal shock. A differen-

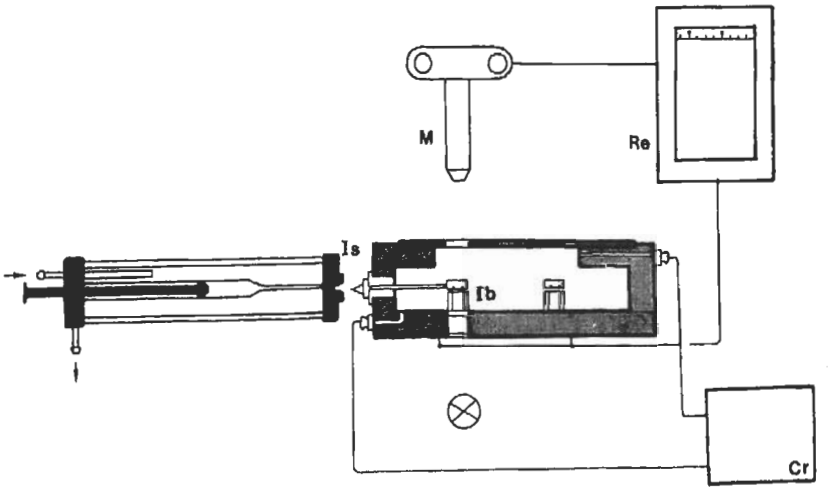

Fig. 1. A diagram of the experimental device: (Is) injection system; (M) photomicroscope; (Re) recorders; (Cr) thermostatted bath; (Ib) isolated box. (See text.)

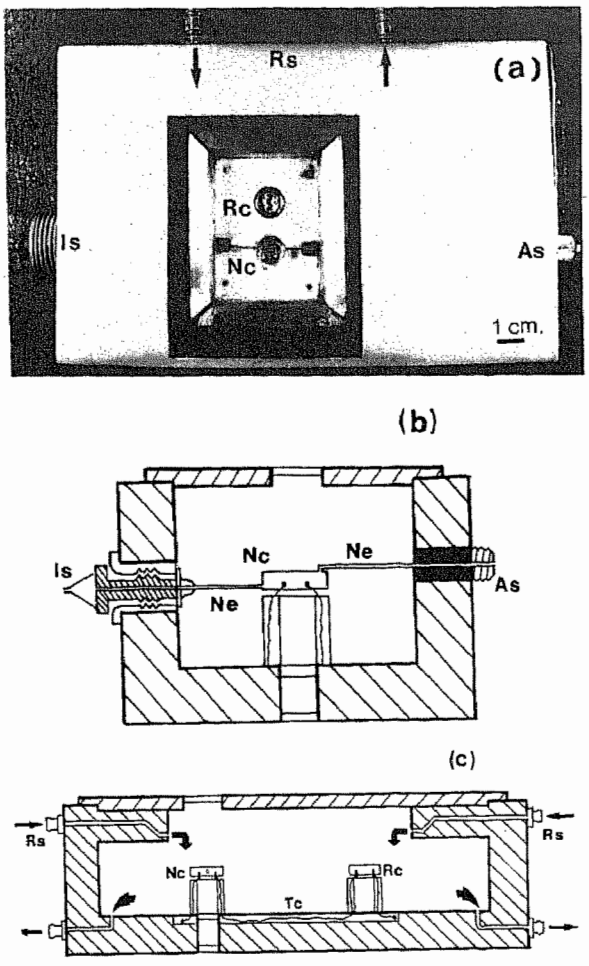

Fig. 2. A photograph (a) and a diagrammatic cross section (b) and a frontal view (c) of the crystallization cell: (Nc) nucleation cell; (Rc) reference cell; (Tc) thermocouples assembly; (Ne) injection needle; (As) aspiration system; (Is) injection system; (Rs) refrigeration system. (See text.)

tial thermocouple assembly is placed on the base of the nucleation and reference micro-cells.

3.3. The room temperature environment

The whole system is placed on a microscope stage and the use of large focal length objective makes it possible to observe the processes taking place in the cell. By using a camera attached to the microscope and connected to a time controller photographic sequences of the crystallization process can be obtained. Finally, in order to follow the change of temperature after thermal shock, the nucleation and reference cell thermocouples are connected to a μV-meter and X–t recorder or to an oscilloscope.

4. Analysis of the data

As expected, when pure water at 90°C was transferred to the micro-cell, the evolution of the temperature followed the cooling pattern of (3). Integration of (3) gives:

$$T(t) = T_f + (T_0 - T_f)\, e^{-kt}. \tag{4}$$

In our system, $T_f = 0$°C. Therefore, (4) can be rewritten as:

$$T(t) = T_0\, e^{-kt}. \tag{5}$$

Now, if an initial solution saturated at temperature $T_s (T_0 < T_s < T_f)$ is transferred to the micro-cell, its concentration C_s will be kept constant if no precipitation occurs. However, as $T = f(t)$, the equilibrium concentration C_e will change depending on both the solubility curve of the solute and the temperature change:

$$C_e(t) = C_e(T(t)). \tag{6}$$

The change of supersaturation ΔC with time can be calculated:

$$\Delta C(t) = C_s - C_e(t),$$

and the rate of change of supersaturation is given by:

$$\frac{d[\Delta C(t)]}{dt} = -\frac{dC_e(t)}{dT}\frac{dT}{dt} = \omega(T)[-k(T(t) - T_f)], \tag{7}$$

where $\omega(T)$ stands for the solubility curve of the solute. Fig. 3 displays both the supersaturation and the rate of change of supersaturation for the particular case of ammonium nitrate, NH_4NO_3.

If precipitation occurs, heat produced by the phase transition will modify the shape of Newton's Cooling Law and therefore a thermal anomaly will be recorded in the T versus t plot, as shown in fig. 4. The onset of the anomaly belongs to the end of

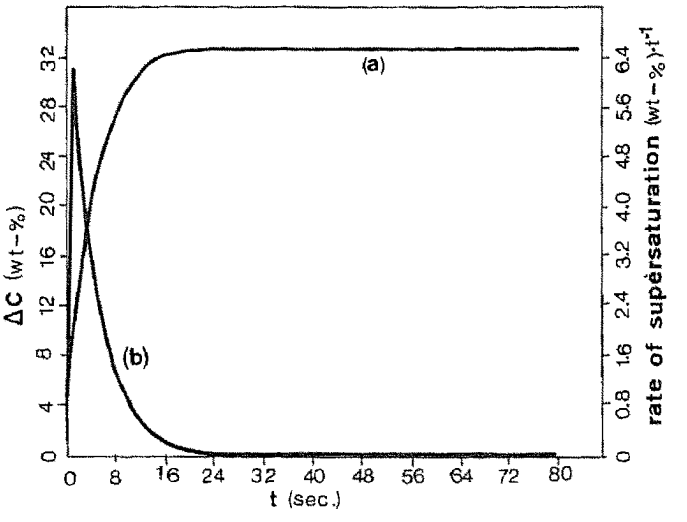

Fig. 3. Plots of supersaturation (a) and rate of change of supersaturation (b) versus time.

the nucleation period, which is given by the point P(x, y), that is, the point at which a deviation from Newton's law is first recorded. If $T_s = T_0$ then $x = \tau$, the experimental induction time, and $y = \Delta T_{max}$ is given by:

$$\Delta T_{max} = 90\ e^{-k\tau}. \quad (8)$$

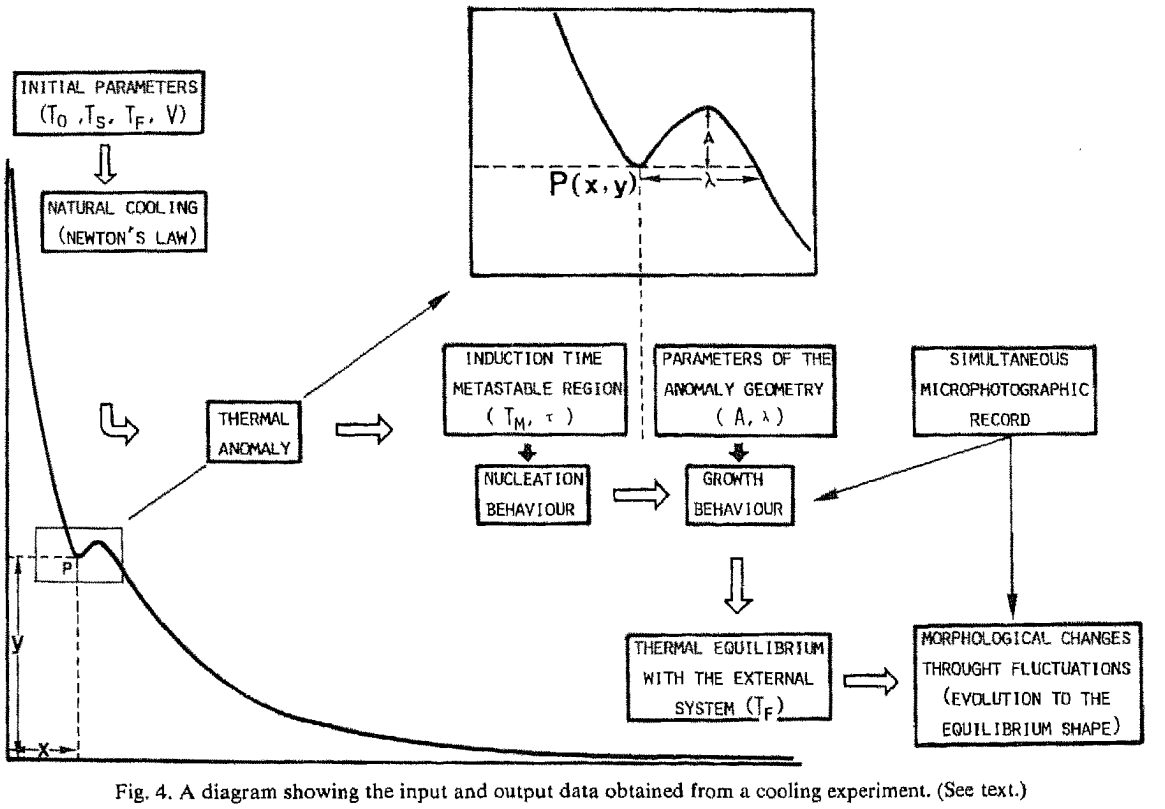

Fig. 4. A diagram showing the input and output data obtained from a cooling experiment. (See text.)

The maximum supersaturation allowable is:

$$\Delta C_{max} = C_s - C_e(\tau). \quad (9)$$

If $T_s < T_0$, the induction time is:

$$\tau = x + (1/k)\ln(T_s/T_0), \quad (10)$$

which can be substituted in (8) to obtain ΔT_{max}.

The experimental nucleation time is given by the summation of three factors:

$$\tau = \tau_r + \tau_n + \tau_g, \quad (11)$$

where τ_r is the relaxation time, τ_n the time required for the formation of critical clusters and τ_g the time consumed by crystal growth up to detectable sizes [5]. The relative contribution of each factor depends on the physical condition of the experiment and the detection system.

In this experimental arrangement, the calorimetric procedure minimizes the contribution of τ_g. If $T_{max} = T_f$ (disregarding the asymptotic nature of the cooling law), what is measured is conceptually the induction time in the so-called isothermal

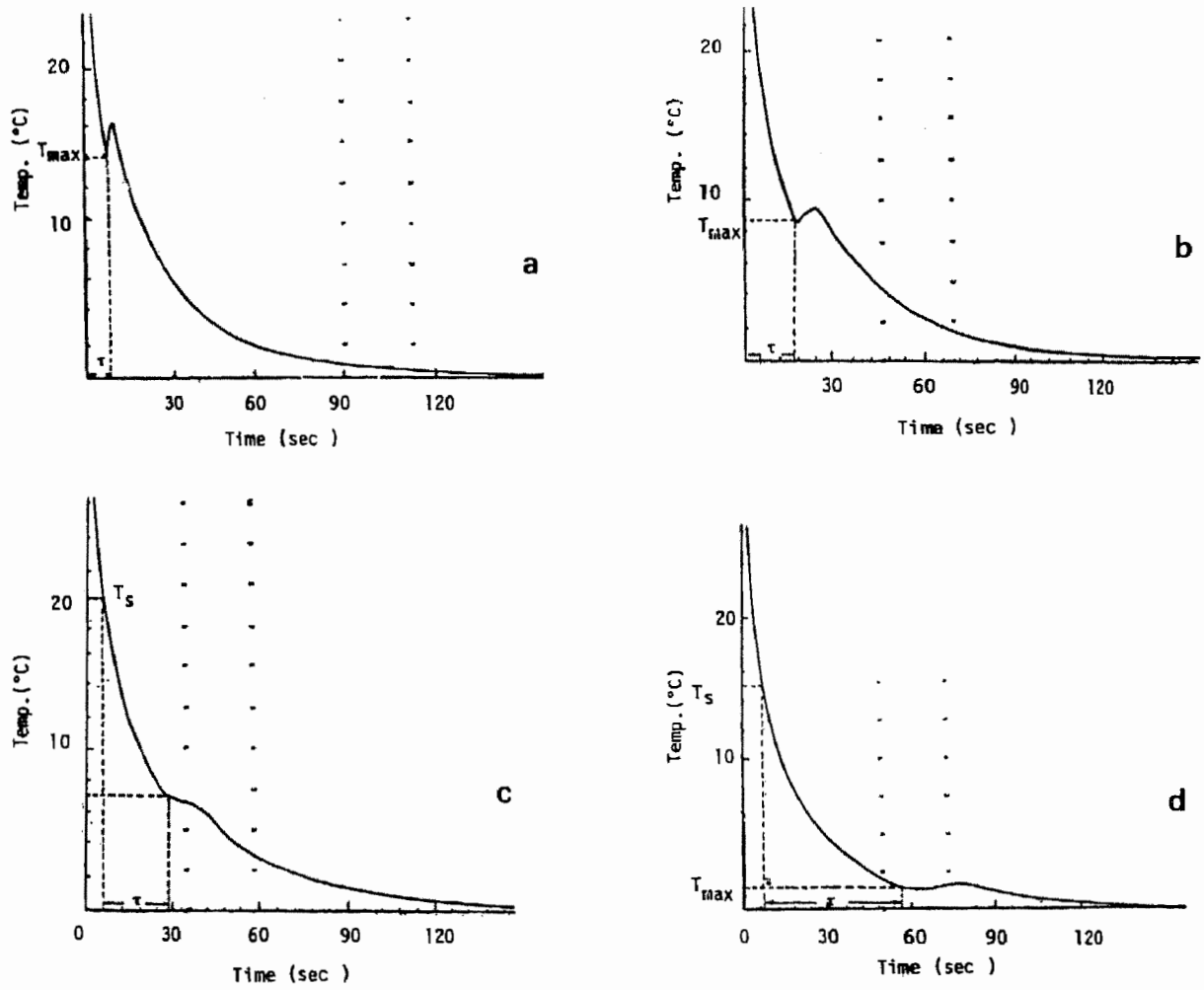

Fig. 5. Temperature versus time plots for ammonium nitrate solutions. In all cases $T_0 = 90\,°C$, $T_f = 0\,°C$. T_s values (in °C) are: (a) 60; (b) 35; (c) 20; (d) 15.

method which according to Nývlt et al. [1,3] has a cooling time contribution. If $T_{max} > T_f$, supersaturation increases continuously as seen in fig. 3 and nucleation occurs in the transitional region. Then, τ is a measure of the non-stationary induction time.

The geometric parameters of the anomaly between P and the point at which Newton's Law is again followed should be directly related to the growth behaviour by using simultaneous microphotographic records. If we call λ the time elapsed until Newton's Law is again followed, and A the maximum ΔT provoked by the anomaly as measured in fig. 4, the ratio λ/A is a measure of the precipitation rate. Thus, low λ/A values belong to dendritic morphologies and higher λ/A values to polygonal growth. In fact, we have also observed morphological changes to the equilibrium shape [6], but up to the present, we do not have a formal treatment to explain the relation between the geometry of the anomaly and photographic records.

As an example, fig. 5 shows four T versus t plots for the case of NH_4NO_3 solutions for $T_0 = 90\,^{\circ}C$ and different T_s values.

Acknowledgements

This work was supported by a grant of the SEVI. One of us (L.G.D.) wishes to thank the Ministerio de Educacion y Ciencia for a grant of PFPI.

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