SUPPORTING INFORMATION

Homogeneous Nucleation-Growth Dynamics Induced by Single Laser Pulse in Supersaturated Solutions

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Materials and Methods

Sample description and optical absorption spectra

Table S1. Samples of saturated and supersaturated solutions of KNO3 at 20 °C before the laser pulse

Weight KNO3/4 cm ³ H2O (g)	Final volume of the sample (cm ³)	Supersaturated solution concentration c ₀ (mol L ⁻¹)	Supersaturation index s = c ₀ / c _{sat}	Mean distance between dissolved KNO ₃ molecules ^b (Å)
1.2	4.4	2.7ª	1.00	8.5
1.3	4.55	2.8	1.05	8.4
1.7	4.75	3.5	1.3	7.8
2.0	4.8	4.1	1.5	7.4
2.2	5.0	4.35	1.6	7.2
2.35	5.05	4.6	1.7	7.1
2.52	5.1	4.9	1.8	7.0
2.8	5.2	5.3	2.0	6.8

a- Solubility at 20 °C or c_{sat} .

b- To be compared with the crystallographic data of KNO₃ rhomboedric crystals: 5.43 Å; 9.17 Å; 6.45 Å.

First, the optical absorption spectra of KNO₃ solutions were obtained as a reference before crystallization (Figure S1, Inset). For this purpose, the supersaturated solution, still hot, was transferred into 1 mm optical quartz cell and, after cooling to 20 °C, the absorption spectrum was recorded between 250 and 800 nm (spectrophotometer UV-visible Hewlett-Packard). The sub- or supersaturated solutions present, in addition to a UV band with an edge at 250 nm, a supplementary band with a maximum at 300 nm assigned to the absorbance by the soluble KNO₃ molecules, resulting from an electronic transition. The 300 nm band intensity depends linearly on the concentration c_0 . The molecular absorption coefficient is $\varepsilon_{300} = 5.8 \text{ mol L}^{-1} \text{ cm}^{-1}$.



Figure S1. Dependence of the Tu_f value (in cm⁻¹) of the final crystallites in the gel-like material induced by sonication on the difference between the supersaturated and saturated KNO₃ concentrations. Inset: Optical absorption spectrum of a supersaturated KNO₃ solution at s = 1.6 (black spectrum) and turbidity spectrum (in log $(I_0/I)_{1 \text{ mm}}$) after sonication for 2 seconds (red spectrum). Quartz cell, optical path: $\ell = 1 \text{ mm}$. Note that Tu_f (cm⁻¹) = 10 × Ln (10) × log $(I_0/I_f)_{1 \text{ mm}}$.

The upper limit of the set-up detection using the pulsed laser facility and the time-resolved detection is restricted to turbidity values of $Tu_t = Ln I_0/I_t = 2.7 \text{ cm}^{-1}$ through cells of 1 cm optical path, that corresponds to the early part only of the complete crystal growth. However, the measurement of the final turbidity *versus* known concentrations of crystallized molecules is required in order to evaluate the molar turbidity coefficient γ_{Tu} per crystal molecule. The final turbidity $Tu_f = \gamma_{Tu} \times (n_f \times c_{nucl} - c_{sat}) = \gamma_{Tu} \times (c_0 - c_{sat})$ was thus measured when the system has reached the equilibrium, *i.e.* when all molecules in excess with respect to saturation have crystallized ($c_0 - c_{sat}$). Because under these conditions the final turbidity reaches much higher values than in time-resolved experiments (as high as $Tu_f = 80 \text{ cm}^{-1}$), the crystallization was induced in that case in a quartz cell of 1 mm optical path only and by sonication (Elma T460, 35 kHz, peak power 240 W). The sonication is known to produce a shock-wave¹ capable to induce also a complete crystallization over a few seconds.² The power density is much less than in the single laser pulse so that the quartz cells are not broken. The final turbidity was measured using the spectrophotometer in the same configuration as in the time-resolved detection.

Similarly to the laser pulse effect, the sonication induces, at low supersaturated concentration, a few tens of crystals that, beyond reaching a certain size, sink to the cell bottom where they continue to grow into acicular and rhomboedric crystals.

Instead, in highly supersaturated solutions (s = 1.5 - 2.0), the sonication induces readily a homogeneous slurry of dispersed tiny crystallites of sub-micrometric size as by laser irradiation. The final turbidity spectra still present the 300 nm band of the supernatant saturated solution, superimposed to a new spectrum assigned to the light scattering by the crystallites. The intensity is almost independent of the wavelength in the range (350 - 800 nm) (Figure S1, Inset). The turbidity increases linearly *versus* the concentration in excess with respect to the saturation ($c_0 - c_{sat}$) (Figure S1). The slope corresponds to the molar turbidity coefficient per molecule incorporated in a crystal which is in average $\gamma_{Tu} = (30 \pm 4)$ mol L⁻¹ cm⁻¹. This value is also used to calculate the total concentration of molecules included in crystallites induced by the laser pulse. Note that the low value of γ_{Tu} imposes a limitation to the detection sensitivity, hence to the shortest observation time after the laser pulse.

Microscopies

For imaging the crystallites, they were deposited, after the pulse shock and the time-resolved turbidity signal acquisition, by quickly rolling one drop of the sample on a glass slide, so that the crystallites could be deposited without the supernatant being evaporated. For the gel samples, a very small amount was widely spread on the glass and dried. These deposits were prepared immediately after the shock in order to prevent any subsequent Ostwald maturation of the crystallites (this maturation was observed indeed to occur within hours and to replace the crystallites of the gel by long acicular crystals). Depending on the final size of the crystals at the end of the growth, the imaging was achieved using optical microscopy (Nikon 2000, \times 60, water-immersed objective) or Atomic Force Microscopy (Nanosurf, Easyscan 2).

Crystallization induced by single laser pulse

Preliminary comparative experiments were done at times shorter than 1 millisecond in water, in saturated solutions (s = 1) and in supersaturated solutions (s = 1.8) (Figure S2).

We observed that the Tu_t signal first increases rapidly within 100 μ s up to an intensity of 0.10 - 0.20 cm⁻¹ in water and saturated solutions, but not in highly supersaturated solutions. This initial phenomenon may result from the formation of micrometric bubbles like those observed at

microsecond scale in supersaturated solutions of anthracene in cyclohexane after a single-shot femtosecond laser pulse.³ To the main signal are also superimposed oscillations. This early periodical change is assigned to a shock-induced perturbation of the liquid optical properties, which lasts much longer than the 7 ns pulse. As a result of the low value of γ_{Tu} , the signal to noise ratio is too small to measure the turbidity at time shorter than the millisecond scale. No intensity of the signal, substantially higher than in water, was observed between 380 and 800 nm for even highly supersaturated solutions, meaning that the transient precursors produced early after the laser pulse are not detectable in this time scale.



Figure S2. Comparison of time-resolved signals at the millisecond scale in water, in a saturated solution (s = 1), and in a supersaturated solution (s = 1.8). The period of the oscillations of 1 millisecond is assigned to the shock wave induced by the laser pulse (1.5×10^{10} W cm⁻²). Polystyrene cell. Optical path $\ell = 1$ cm.

In the case of solutions at low supersaturation index (s = 1 - 1.30) shocked by a focused single pulse of high power density (1.5×10^{10} W cm⁻²), or at higher index (s = 1.5 - 2.0) but shocked by a pulse of half less power density (7×10^9 W cm⁻²), the corresponding signal lasts for tens of seconds and displays several steps during the crystal growth. A typical signal is shown in Figure S3.

After a short increase of the turbidity assigned to homogeneous nucleation, we observe to the naked eye that the tiny light-scattering particles, beyond reaching a certain size, are sinking to the cell bottom below the analyzing beam, so resulting in a decrease of the measured turbidity. Then, the delayed increase is due to the further growth, within tens of seconds, of some bottom seeds into thin and acicular needles in front of the beam. The delay of this second increase strongly depends on the position of the probe beam in the solution (in Figure S3, the beam probes for example the middle



Figure S3. Time-resolved turbidity signal of growing KNO₃ crystals induced by the single laser pulse at a power density of 7×10^9 W cm⁻². The supersaturated solution index is s = 1.6. Polystyrene cell, optical path $\ell = 1$ cm. Inset: Image of some acicular crystals, 80 µm long and 20 µm thick. In addition, are also observed in the same sample tens of needles, up to a few mm long.

part of the cell). Hence, the growth is not at all homogeneous throughout the solution volume and cannot be analyzed by the kinetics law. The crystal size distribution is also polydisperse.

Homogeneous nucleation in the solution volume was observed only at high supersaturation index $(s \ge 1.5)$ with a focused single laser pulse.

Calculations of c_{nucl} , k_{acc} , and final diameter d_f :

According to equation (5), the measured turbidity rate $\Delta Tu_t / \Delta t$ is proportional to the excess of concentration with respect to the saturation ($c_0 - c_{sat}$), to the molar turbidity coefficient per crystal molecule γ_{Tu} , and to the unknown nuclei concentration c_{nucl} and rate constant k_{acc} .

Since the nuclei concentration c_{nucl} remains constant and is the same as that of final crystals, we derive it from the final diameter, $d_{2.0} = (600 \pm 100)$ nm measured by AFM at s = 2.0. The final number of molecules per crystal, as calculated from the *Mw* and ρ values for a spherical particle at s = 2.0 is $n_f = (1.4 \pm 0.3) \times 10^9$, and the nuclei concentration is $c_{nucl} = (c_0 - c_{sat}) / n_f = (1.8 \pm 0.4) \times 10^{-9}$ mol L⁻¹ (Table S2). Then the rate constant is calculated from equation (5) as $k_{acc} = (3.0 \pm 0.6) \times 10^8$ mol L⁻¹ s⁻¹.

At the other supersaturation indices, we use the same value of k_{acc} as determined at s = 2.0. From $k_{\rm acc}$ and the measured values of $\Delta Tu_t / \Delta t$, the corresponding values of the nuclei concentration $c_{\rm nucl}$ are calculated by equation (5) and are then used to obtain the final crystal volume and the final mean diameter for a spherical particle under the different conditions of supersaturation s (Table S2) (Figures 4 and 5).

Table S2: Measured slopes $\Delta Tu_t / \Delta t$ and calculated nuclei concentration and final crystal diameter at various initial supersaturated KNO₃ concentrations.

S	<i>c</i> ₀ (mol L ⁻¹)	$\frac{\Delta T u_t / \Delta t}{(cm^{-1} s^{-1})}$ (meas.)	C _{nucl} (mol L ⁻¹) (calc.)	Final crystal volume (nm ³) (calc.)	Final crystal diameter d _f (nm) (calc) **
1.0	2.7	0	-	-	-
1.5	4.1	0.37 ± 0.06	$(3.0 \pm 1) \times 10^{-11}$	$(3.7 \pm 1) \times 10^9$	1920 ± 200
1.6	4.35	0.57 ± 0.1	$(4.0 \pm 1) \times 10^{-11}$	$(3.3 \pm 1) \times 10^9$	1840 ± 200
1.7	4.6	8.7 ± 1.5	$(5.3 \pm 1) \times 10^{-10}$	$(2.8 \pm 1) \times 10^8$	820 ± 100
1.8	4.9	14 ± 3	$(7.2 \pm 0.3) \times 10^{-10}$	$(2.4 \pm 0.5) \times 10^8$	780 ± 100
2.0	5.3	42 ± 9	$(1.8 \pm 0.4) \times 10^{-9}$	$(1.1 \pm 0.3) \times 10^8$	600 ± 100 [◆]

Diameter d_{2.0} = 600 nm measured by AFM.
Mean diameter with the approximation of a spherical particle.

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References

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