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LETTER TO THE EDITORS

OSCILLATORY GROWTH RATES IN SINGLE CRYSTALS GROWING UNDER DIFFUSIONAL CONTROL

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Oscillatory growth behavior in single crystals growing under diffusion control has been experimentally confirmed to be an intrinsic property of these systems.

Oscillatory behavior of precipitation in diffusing-reacting systems is a well-known phenomenon. Reduction, oxidation and double decomposition reactions give the so-called Liesegang patterns when they take place under diffusion controlled transport [1]. These oscillatory patterns are self-organized structures characteristic of far from equilibrium systems and therefore independent of the nucleation density. In fact, Liesegang patterns formed by very few crystals have been reported previously [2]. Therefore, it could be expected that for one single crystal growing under diffusion transport, its growth rate should show such an oscillatory pattern. In a preliminary work on the growth kinetics of KDP single crystals growing in silica gels by solubility reduction, some L^2 versus time plots show deviation from linearity in the form of sinusoidal patterns [3]. Therefore experiments were designed to confirm the existence of this interesting phenomenon.

The growth cell was a glass cassette with inner dimensions of $75 \times 103 \times 4.5$ mm (35 cm^3 in volume) with two syringes, one for injection and the other for air output [4]. A water solution of ADP (Panreac, puriss.) saturated at 46 °C and adjusted to pH 5 by adding the appropriate amount of NaOH was prepared under continuous stirring. After 24 h, this solution was mixed with tetramethoxysilane (Fluka, puriss.) at 5% in volume. The as-produced sol was heated some degrees and injected into the growth cell up to complete filling. Gelling time was 4 h. The glass cassette containing the gellified KDP solution was left to cool to room temperature which was 20 ± 0.5 °C and placed under an optical microphotographic device operated by a time controller. Nucleation time was about 10 h. The experiment was reproduced several times, until one ADP crystal with its (100) face parallel to the glass plates of the cassette was obtained. Sharp crystal edges were photographed with magnification $\times 13$. Once the crystal was 2 mm long, microphotographs were obtained with a time lapse of 10 min during the first 240 min and afterwards with a time lapse of 15 min. The whole microphotographic sequence endured 790 min and thus 57 pictures were obtained. The advance of the Z-axis, i.e. [001] direction, was measured in the film using an astrophotometric measurer Ascorecord (Zeiss).

Fig. 1 shows a dL/dt versus time plot, L being the semi-length of the crystal along the [001] direction. To obtain the derivative curve we have

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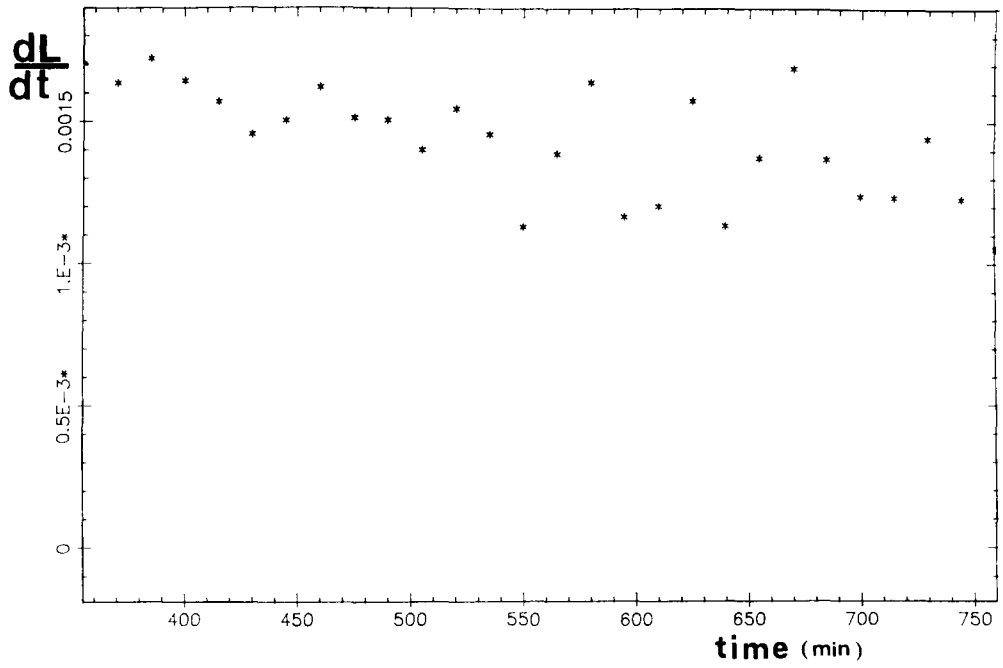

Fig. 1. Growth rate versus time plot.

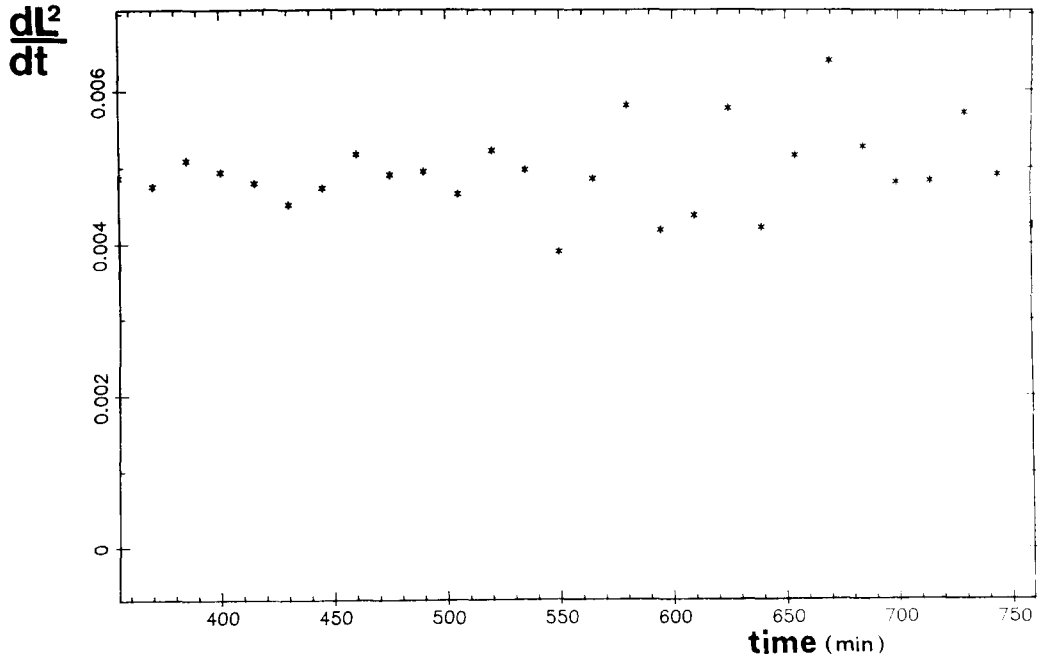

Fig. 2. Plot of the time derivative of L^2 versus time.

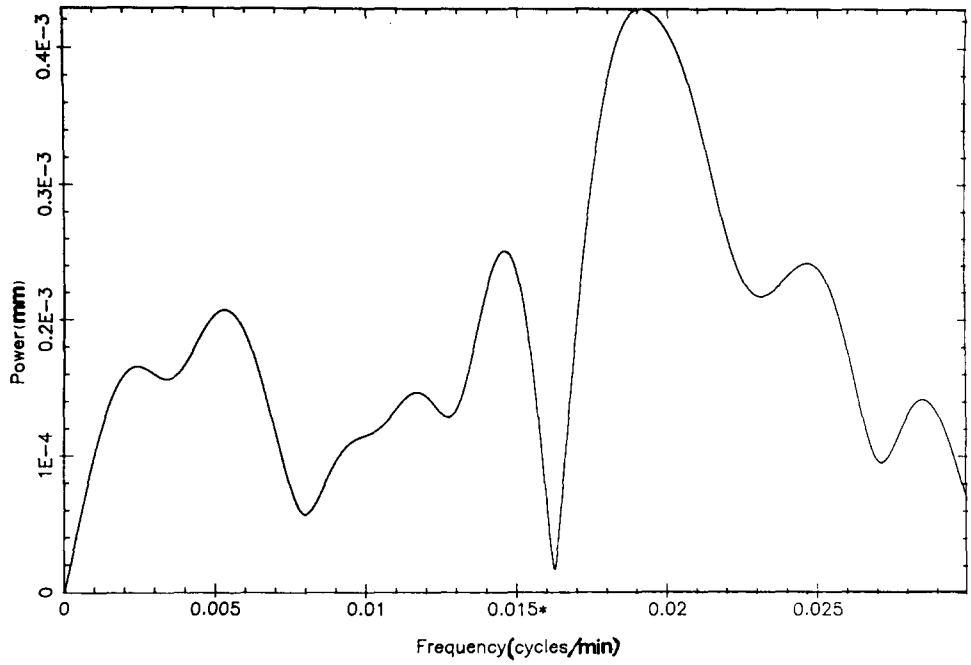

Fig. 3. Spectrogram of the data showing the main frequency.

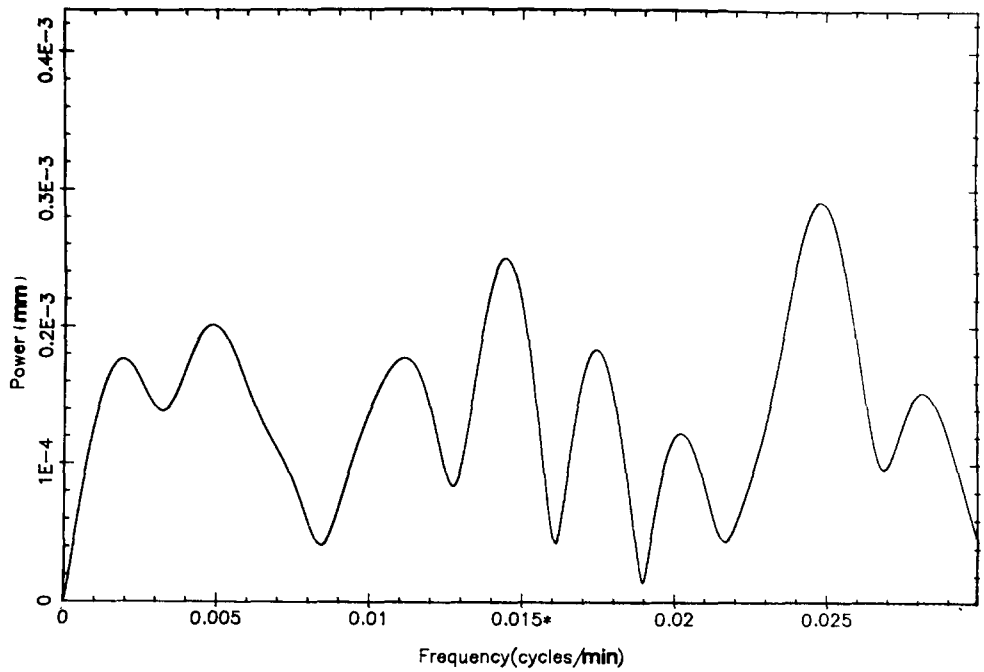

Fig. 4. Spectrogram for the same data once the main frequency in fig. 3 has been removed by least-squares technique.

used an algorithm taking data from five points around the value of each point. In this figure an oscillatory pattern can be found around a decreasent growth rate. It is well-known that crystal growth in gels is a diffusion controlled process and therefore a linear relationship between L^2 and time must be accomplished for any range of time for which the concentration far from the crystal can be assumed to be constant, i.e. as an inexhaustible mass source. Fig. 2 shows an L^2 versus t plot corresponding to the same crystal and time range of fig. 1 in which an oscillatory pattern can be also observed. In order to clarify the meaning of these departures, a simple mathematical model consisting in two principal terms was used:

$$L^2 = A + Bt + \sum_{i=1}^{n} C_i \sin(\omega_i t + \phi_i). \quad (1)$$

The linear term of (1) was fitted to the data, and the obtained residuals in the sense observational minus calculated were laser analyzed by power spectrum technique. In fig. 3 the spectrum of the analyzed data can be observed, which gives a statistically significative frequency of 0.019 cycles/min, removing 84% of the residuals not explained by the linear component. Fig. 4 shows the spectrogram obtained once the main frequency was removed. A later analysis of this spectrum does not provide any significant frequency.

From the obtained frequency values it is clear that this periodical pattern is not related to the observational frequency. As described above, the temperature was monitored and the record does not follow any oscillatory rhythm. Thus, it must be concluded that the periodical behavior recorded in single crystals growing under diffusion control is an intrinsic property of the system. A mathematical model for a quantitative explanation of this phenomenon is under progress.

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References

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