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Growth Stability in Semiopen Physical Vapour Transport

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Abstract An interface stability model is proposed for crystal growth by physical vapour transport (PVT) in semiopen (SO) systems, which is based on the constitutional supercooling criterium. The model, whose main feature is the relaxation of the local equilibrium assumption at the growing interface, proved suitable for explaining the remarkable growth stability in SO systems when applied to urea growth. A semiempirical approach for estimating the pressure inside a SO-system and the kinetic contributions to stability is also proposed, which allows for quantitative comparison of model and experimental results.

1. INTRODUCTION

Physical vapour transport (PVT) has been used for growing large-size crystals, many of which are interesting substrate materials for electronic devices [1]. Usually, PVT growth processes are carried out in closed cells (ampoules) in which a polycrystalline source is sublimated at a given temperature and made to condense (crystallize) at a lower temperature at a distance L from the source [2-3].

A modification of these closed-cell configurations makes use of semiopen (SO) cells vented to vacuum through suitable leakages[1-4].

In spite of technical complications, the SO configurations have significant advantages: 1) decrease of undesired volatile impurities, with lowering of diffusional barriers; hence purer crystals grown at a faster growth rate; 2) more flexibility, as the overall pressure (P) is now a new degree of freedom, while in closed configurations it is a fixed temperature-dependent quantity; 3) crystals grown by SO-PVT techniques usually exhibit a higher degree of interface (morphological) stability as compared to crystals grown in closed systems.

This third point, which has never been stressed in previous works, will be here analyzed and discussed with reference to urea crystals. Urea is an important non-linear optics material [5, 6] which has been grown by SO-PVT [7], obtaining crystals with high structural perfection and remarkably good morphological stability [8] at bias with what observed when growing crystals in closed configurations.

For these reasons, urea is a suitable model substance for studying the interface stability in both closed and SO-PVT systems.

In this paper, an analysis of interface stability based on the constitutional supercooling criterium, as previously developed for PVT growth in closed configurations [9-12], is extended to include SO-PVT processes. However, in order to account for the strong kinetic limitations in urea growth, the local equilibrium approximation of previous works has been relaxed.

2. ANALYSIS OF INTERFACE STABILITY CONDITIONS

Urea PVT is based on the following chemical reactions [8,13]:

in which U, A and B stand for urea (NH_2CONH_2), ammonia (NH_3) and biuret ($[\text{NH}_2\text{CO}]_2\text{NH}$) and subscripts (s) and (g) stand for “solid” and “gaseous”.

Figure 1: PVT arrangement with temperature profile $T(x)$ and actual and equilibrium partial pressure profiles $P_U(x)$ and $P_U^0(x)$ at and ahead of the growing interface; $P_U(0) - P_U^0(0)$ at $x = 0$ scales the kinetic constraints at the growing interface.

With reference to Fig.1, reaction (1) occurs at $x = 0, L$ while reaction (2) only takes place at $x = L$, where $x = 0$ and $x = L$ are the locations of the growing and subliming (flat) interfaces respectively.

In order to relax the local equilibrium assumption of previous analyses, a more general stability criterium is used, which predicts stability only when the supersaturation gradient $\nabla_x \sigma \leq 0$ at $x = 0$. As previously shown [3], this is equivalent to give the stability condition as

$$v_{U(s)} \leq \frac{D_{298}^0}{C_{U(s)} R R_0} \left(\frac{T}{298} \right)^{1.8} \frac{[\Delta H_U - RT(0)]}{T^3(0)} \left\{ \frac{P_U(0)}{P - P_U(0)} \right\} G_v \quad (3)$$

in which $v_{U(s)}$ is the average linear growth rate; D_{298}^0 is the binary diffusion coefficient of urea and ammonia at 298 K and 1 atm; $2\bar{T} = T(L) + T(0)$; $C_{U(s)}$ is the molar density of solid urea; G_v = temperature gradient at $x = 0$; R and R_0 are the gas constant in different units; ΔH_U and ΔS_U are the enthalpy and entropy changes associated to reaction (1) respectively; $T(0)$ and $P_U(0)$ are the temperature and actual pressure of urea in $x = 0$ (growing interface) respectively. As heat transport is assumed not to be rate limiting, while mass transport is, $T(0)$ is practically coinciding with the equilibrium temperature of the interface while $P_U(0)$ differs from the equilibrium value $P_U^0(0)$, as indicated in Fig. 1. As previously shown[3], $P_U(0)$ and $P_U^0(0)$ are related by

$$P_U(0) = P_U^0(0) + \left(\frac{R_0 T(0) C_{U(s)}}{k_R} \right) v_{U(s)} \quad (4)$$

in which k_R is a kinetic constant given by

$$k_R = \frac{f R_0 T(0) \alpha}{\sqrt{2\pi M_U R T(0)}} \quad (5)$$

In eq. (5), f = unit conversion factor; M_U = molecular weight of urea; α (≤ 1) = condensation (crystallization) coefficient.

Inequality (3) gives the stability condition in terms of a critical growth rate that cannot be exceeded. However, as $P_U(0)$ is also a function of $v_{U(s)}$, by replacing $P_U(0)$ in (3) with its expression (4), we obtain the new stability condition:

$$B_2[v_{U(s)}]^2 + B_1[v_{U(s)}] + B_0 \geq 0 \quad (6)$$

in which

$$B_0 = P_U^0(0)G_v \left\{ \frac{\Delta H_U - RT(0)}{RT^2(0)} \right\} \quad (7)$$

$$B_1 = R_0 C_{U(s)} \left\{ \frac{G_v [\Delta H_U - RT(0)]}{k_R RT(0)} - \frac{T(0)[P - P_U^0(0)]}{D_{298}^0 \left(\frac{T}{298} \right)^{1.8}} \right\} \quad (8)$$

$$B_2 = \frac{[C_{U(s)} R_0 T(0)]^2}{D_{298}^0 \left(\frac{T}{298} \right)^{1.8}} \quad (9)$$

From (6), we have stability only when

$$v_{U(s)} \leq v_{CRIT}, \quad v_{U(s)} \geq v'_{CRIT} \quad (10)$$

in which $v'_{CRIT} \geq v_{CRIT}$.

At constant pressure, these two critical growth rates are in relation with two different vapour compositions, the former characterized by $P_U(0) < P_A(0)$, the latter by $P_U(0) > P_A(0)$. This latter case, that can in principle be achieved in a CVD reactor, is impossible with our closed and SO-PVT urea growth processes and will no further be considered.

As to $v_{U(s)}$ in (10), it has previously been shown [3] that in the assumption of local equilibrium at $x = L$, we can write:

$$v_{U(s)} = \frac{P_U^0(L) / T(L) - P_U^0(0) / T(0)}{C_{U(s)} R_0 \left\{ \frac{1}{k_R} + \frac{L(P - P_U^0(L))}{D_{298}^0 \left(\frac{T}{298} \right)^{1.8}} \right\}} \quad (11)$$

3. STABILITY CONDITIONS AND COMPARISON WITH EXPERIMENTS

By comparing $v_{U(s)}$ with its critical values (for calculations the input data are in Table 1), it can be seen that stability increases with G_v , as in melt growth [17]. But, more specifically to vapour growth, stability is also the result of (a) low P , which explains the remarkable stability in SO-PVT growth and (b) the presence of kinetic limitations, i.e., small values of k_R and hence of α .

Table 1: The input data for calculations

$R = 1.98 \text{ cal/K} \times \text{mol}$	$\Delta H_U = 20950 \text{ cal/mol [14]}$	$C_{U(s)} = 0.022 \text{ mol/cm}^3$
$R_0 = 82.057 \text{ atm} \times \text{cm}^3/\text{K} \times \text{mol}$	$\Delta S_U = 34.59 \text{ cal / K} \times \text{mol [14]}$	$D_{298}^0 = 0.13 \text{ cm}^2/\text{sec}^{(*)}$
$f = 155.4 \text{ g}^{1/2} \text{ cal}^{1/2}/\text{cm}^2 \times \text{sec} \times \text{atm}$	$\Delta H_A = 63100 \text{ cal/mol [13]}$	$M_U = 60$
	$\Delta S_A = 160 \text{ cal / K} \times \text{mol. [13]}$	$M_A = 17$

(*) Estimated from Chapman-Enskog kinetic theory data [15, 16]

This is evident in Fig. 2. For given temperature conditions ($T(L)$, $T(0)$, G_v) and source-crystal distance (L), the instability conditions fall within a region whose boundary is approximately parabolic, which is so much the wider the greater α is, being maximum for $\alpha = 1$. Also reported for comparison is the stability limit as calculated assuming local equilibrium ($P_U(0) = P_U^0(0)$), which predicts more instability in the low- α , low- P region.

3.1. P and α in a closed system

In a closed system the overall pressure P is approximately given by

$$P = \frac{P(L)}{T(L)} \left\{ \frac{1}{L} \int_0^L T(x) dx \right\} \quad (12)$$

in which: $P(L) \sim P_U^0(L) + P_A^0(L)$; $T(x)$ is a parabolic T -profile defined by $T(L)$, $T(0)$ and G_v ; $P_A^0(L)$ is given by an Arrhenius relationship provided that ΔH_A and ΔS_A are known.

As to α , estimates can be given by comparing experimental and calculated values of $v_{U(s)}$ [13].

3.2 P and α in a semiopen system

The actual pressure within an operating SO ampoule is largely arbitrary as it depends not only on $T(x)$ and the geometry of the effusion leakage, but also on the external pressure (P_{ext}). Its estimate, as well as that of α , can be achieved semiempirically, prior to a SO-PVT growth experiment, through flux balances in the assumption of incompressible vapours and experimental measurements of crystallization and effusion fluxes.

The flux balance can be written:

$$\sum_j Q_i^j = 0 \quad i = A, U; \quad j = S, H, C \quad (13)$$

in which j stands for interface location (S = source, $x = L$; C = crystal; $x = 0$) and effusion-hole location (H); indexes i and j can apply to any other relevant quantity^(*).

The flux Q_i^j [g/sec], which is negative when entering the gaseous volume of the ampoule (Q_i^S) and positive (Q_i^C , Q_i^H) when leaving it, can be written:

$$Q_i^{j \neq H} = \pm k_i^j S^j (P X_i^j - (P_i^0)^j) \quad (14)$$

in which X_i^j is the molar fraction of the i -th component in the j -th location; S^j is the area of the solid-vapour interface in the j -th location when $j = S, C$ and the leakage area when $j = H$; in SO-ampoules it can be assumed that $S^C = S^S = \pi r^2$, r being the ampoule cross-section radius; k_i^j is a kinetic constant given by:

$$k_i^{j \neq H} = f \alpha_i^j \sqrt{\frac{M_i}{2\pi R T^j}} \quad (15)$$

The effusion flux of the i -th component is

$$Q_i^H = k^H S^H X_i^H \sqrt{M_i} (P - P_{ext}) \quad (16)$$

in which the kinetic-like constant is given by

Figure 2: Growth rate (dashed curves) and critical growth rate (solid curves) against P for different α -values; critical conditions in local-equilibrium approximation also indicated; P and experimental value of $v_{U(s)}$ for a closed configuration is also given (*, point A).

^(*) T^j , $(P_i^0)^j$ are equivalent notations of $T(x)$, $P_i^0(x)$; e.g., $T^S = T(L)$, $(P_i^0)^C = P_i^0(0)$, etc.

$$k^H = \frac{\gamma f}{\sqrt{2\pi RT^H}} \quad (17)$$

The quantity γ in (17) is related to the expect ratio (h/a) of a cylindrical effusion hole of radius a , drilled in an ampoule wall of thickness h , by[1]:

$$\gamma = \frac{1 + 0.4(h/a)}{1 + 0.95(h/a) + 0.15(h/a)^2} \quad (18)$$

The assumption of an incompressible vapour phase under steady-state effusion conditions, further requires the same overall density (ρ^j) to hold for all locations, so we write

$$\rho^S = \rho^H = \rho^C \quad (19)$$

This is obviously an approximation, as ρ^j depends on T^j , but it can be justified by the small temperature variations ($2 \div 10$ °C) and low pressure ($P < 10$ torr) involved.

Since we can also write

$$\rho^j = \sum_i \rho_i^j = \frac{P}{R_0} \sum_i \frac{X_i^j M_i}{T^j} \quad (20)$$

From (19) and (20) we obtain

$$X_U^j = \frac{M_A}{M_U - M_A} X_U^H \frac{T^j}{T^H} \left(\frac{T^j}{T^H} - 1 \right), \quad j = S, C \quad (21)$$

Now, from (13) (14) and (16) one gets:

$$\sum_{j \neq H} k_i^j S^j [(P_i^0)^j - P X_i^j] = k^H S^H X_i^H \sqrt{M_i} (P - P_{\text{ext}}), \quad i = U, A \quad (22)$$

Relations (21) and (22), taking into account the constraint

$$\sum_i X_i^j = 1, \quad i = A, U; \quad j = S, H, C \quad (23)$$

give a set of four independent equations in the eight unknowns X_U^S , X_U^H , X_U^C , P , α_U^S , α_U^C , α_A^S , α_A^C .

TABLE 2

No.	T^C (°C)	T^S (°C)	Q_{EXP}^H (mg/hr)	$[Q_U^C]_{\text{EXP}}$ (mg/hr)	a/h (mm/mm)	$P_{\text{EXT}} \times 10^3$ (mbar)	$P \times 10^3$ (mbar)	$\alpha_U^C \times 10^2$
1	90	100	0.097	25.74	0.1/1.5	10	77	2.63
2	90	97	0.079	15.13	0.1/1.5	7.5	63	2.46
3	90	94	0.068	9.08	0.1/1.5	7.5	55	2.90
4	85	90	0.070	6.62	0.1/1.5	7.5	59	2.45
5	90	100	0.171	27.00	0.15/1.5	8.0	44	2.66
6	90	97	0.150	15.70	0.15/1.5	7.5	40	2.36
7	90	94	0.130	8.18	0.15/1.5	7.0	36	2.53
8	85	90	0.100	6.9	0.15/1.5	7.0	29	2.39

(*) $T^H \cong T^C + 2.0$ °C

In the case of urea, molecular sublimation is easy, so we can write $\alpha_U^S = 1$. Further, since no biuret is formed in the growing crystal [13], we assume $\alpha_A^C = 0$ for $P_A^C < (P_A^0)^C$ and $Q_A^C = 0$ for $P_A^C > (P_A^0)^C$. Due to these simplifications, the unknowns are reduced to six. The two lacking equations can however be given when, by fixing P_{ext} , T^j and γ , we are able to measure experimentally Q_U^C and $Q^H = \sum_i Q_i^H$. We can write:

$$k_U^C S^C (P X_U^C - (P_U^0)^C) = (Q_U^C)_{\text{EXP}} \quad (24)$$

$$k^H S^H (P - P_{EXT}) \sum_i X_i^H \sqrt{M_i} = (Q^H)_{EXP} \quad (25)$$

The set of six equations (21), (22), (24), (25) in six unknowns P , α_U^C , α_A^S , X_U^S , X_U^H , X_U^C has been solved making use of the experimental data of Table 2. In the same table, the calculated values of P and $\alpha_U^C (= \alpha)$ are also reported.

3.3. Comparison with experiments

Though many PVT growth experiments with urea have been performed [7, 8, 13, 18-20], none of them was planned for a quantitative verification of the present stability model. Nevertheless all experiments points to growth instability in closed configurations and stability in SO configurations for wide ranges of experimental conditions. This stability seems however limited, for a fixed set of growth parameters, to small-size crystals [8]. As also reported for mercuric iodide [21], beyond a certain size crystals tend to destabilize through surface roughening and rounding. This last fact however cannot be explained in terms of an isotropic stability model as ours, as previously pointed out [22, 23].

Figure 3: Crystals of urea (a) grown in closed ampoules; micrograph (b) of one of these crystals, showing dendritic formation.

Here we limit ourselves to compare our calculations with a few growth experiments for which a semiquantitative estimation of growth parameters seems possible.

- A. For the set of $T(0)$, $T(L)$ and L values of Fig.2, closed-ampoule growth of urea was carried out [13, 18], and a growth rate of $v_{U(s)} = (9 \pm 2) \times 10^{-9}$ cm/sec was measured which fits with α between $0.0001 \div 0.001$ [13]. For this experiments G_V was estimated about 0.1 K/cm and the overall pressure was calculated to be about 0.01 atm. This $(v_{U(s)}, P)$ point in Fig.2 falls in an unstable region, in agreement with microscopic observations of the grown crystals (Fig.3).
- B. Urea crystals can be grown by SO-PVT techniques in which the ampoule is pulled with respect to a fixed T -profile [7, 18-20]. This means that both $T(L) - T(0)$ and G_V change with time. We can however estimate $T(L) - T(0) \sim 2 \div 5$ °C (at least in the final growth stage) and $G_V \sim 1 \div 3$ °C/cm. The external pressure (P_{EXT}) has been variously reported between 3.5×10^{-2} [18] and 1×10^{-3} torr [19] and experimental average growth rate have been measured within $(0.5 \div 7) \times 10^{-6}$ cm/sec. Since for these experiments P inside the ampoule is not known, comparisons with our model cannot be made.

We can however assume the data of Table 2 as typical of SO-PVT processes. With reference to run No.7, we have $P_{EXT} \sim 7 \times 10^{-6}$ atm, $P \sim 3.6 \times 10^{-5}$ atm, $v_{U(s)} \sim 2.2 \times 10^{-6}$ cm/sec and $\alpha \sim 0.025$. The corresponding $(P, v_{U(s)})$ point on Fig.4 (indicated by A) shows that under these growth conditions stability is to be expected.

The actual growth experiment, attempted under the above conditions, was carried out at a higher P_{EXT} (4.6×10^{-5} atm) and hence at a lower growth rate ($v_{U(s)} \sim 6 \times 10^{-7}$ cm/sec) because of a calibration error. In spite of the worsened stability conditions, a stable crystal was grown, as shown in Fig. 5. By estimating $P \sim 3P_{EXT} \sim 1.4 \times 10^{-4}$ atm, the growth conditions on Fig.4 are represented by point B which still falls in the stable region.

- C. High-quality urea crystals have also been grown with a sophisticated facility as reported in [8]. These crystals are characterized by a very high degree of morphological stability until they do not

exceed a given size. A detailed X-ray and optical characterization of these crystals was also reported [7, 8].

Though our model would predict stability for these crystals, the marked anisotropy with $v_{U(s)}$ largely changing with crystallographic orientations and the essentially three-dimensional character of the temperature profile make the present one-dimensional stability model unsuitable for quantitative considerations.

Figure 4: Calculated (dashed curves) and experimental (point A and B) growth rates for typical SO-PVT growth conditions, which fall in the stable region.

Fig.5 Crystal of urea grown by SO-PVT (see text); its growth conditions are represented by point B in Fig.4. A detailed X-ray analysis of this crystal is given in [7].

4. CONCLUDING REMARKS

The stability model presented in this paper appears suitable for predicting stable growth in SO-PVT processes, in which the pressure inside the growth system is reduced with respect to closed systems.

The relaxation of the local-equilibrium assumptions of previous analyses allows for the introduction into the model of stability effects related to kinetical constraints at the growing interfaces. It is shown that stability increases with the increase of these constraints, which are expressed in terms of the crystallization coefficient α .

A semiempirical approach to estimate P and α in SO-PVT growth experiments is further proposed, which enables a quantitative comparison between calculated and experimental growth rates and between them and the critical growth rates of the model.

It should finally be remarked that α in closed systems appears smaller than in SO systems. It can be speculated that (a) by decreasing P in SO-systems, $P_U(0)$ increases with supersaturation, which means, according to [24], that α should increase and (b) in closed system α is reduced due to a larger content of volatile impurities.

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