

Fig. 1: Principle of preferential crystallisation illustrated in ternary phase diagram.

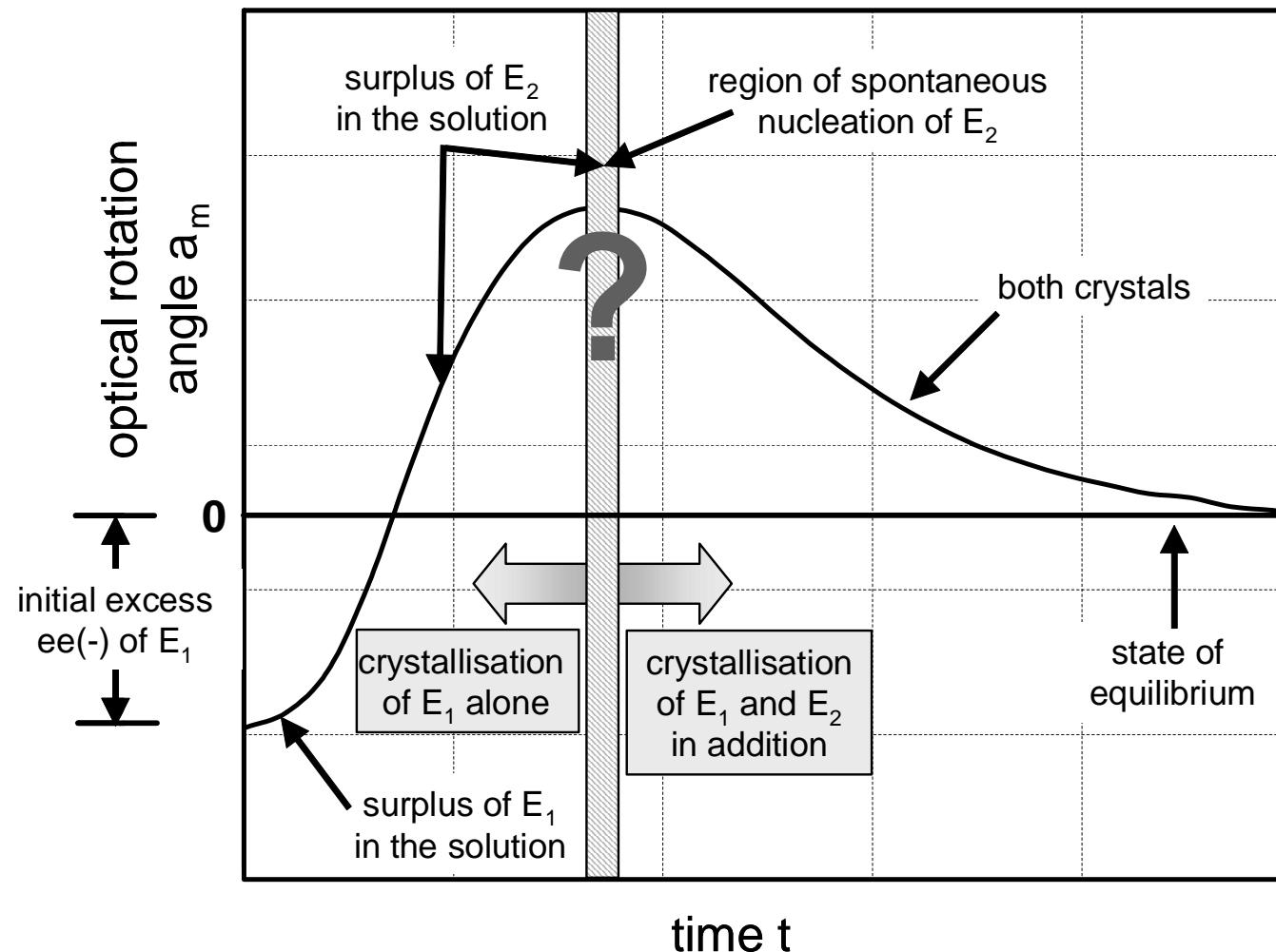


Fig. 2: Typical polarimetric signal providing qualitative information about the process of crystallisation by entrainment.

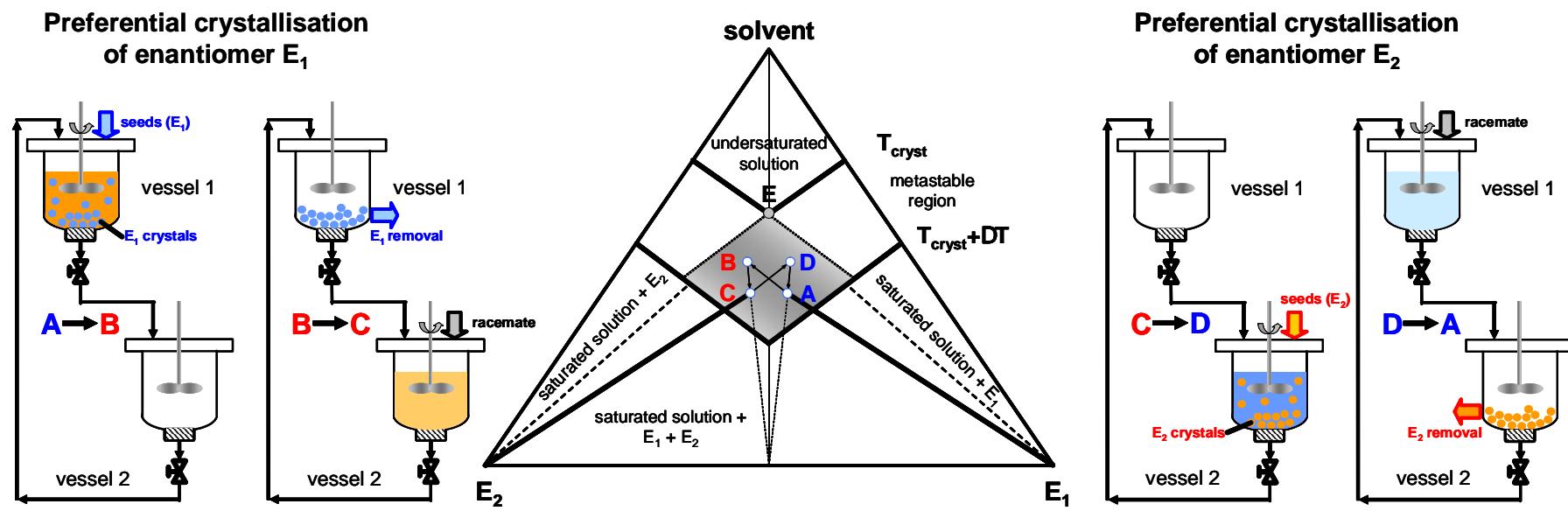


Fig. 3: Concept of the preferential crystallisation process and a possible operation mode based on two consecutive half cycles.

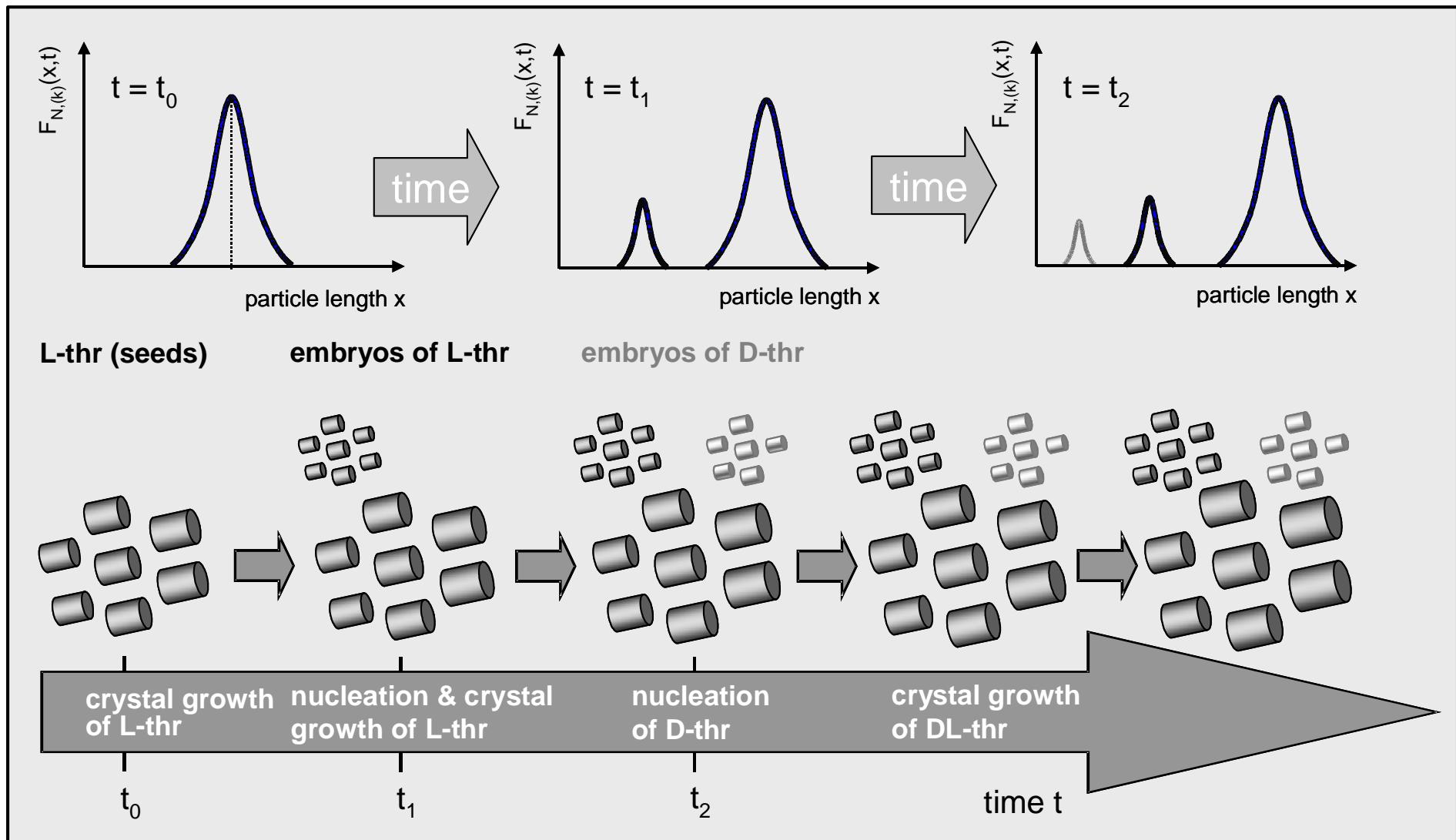


Fig. 4: Physical interpretation for the model used of the preferential crystallisation process.

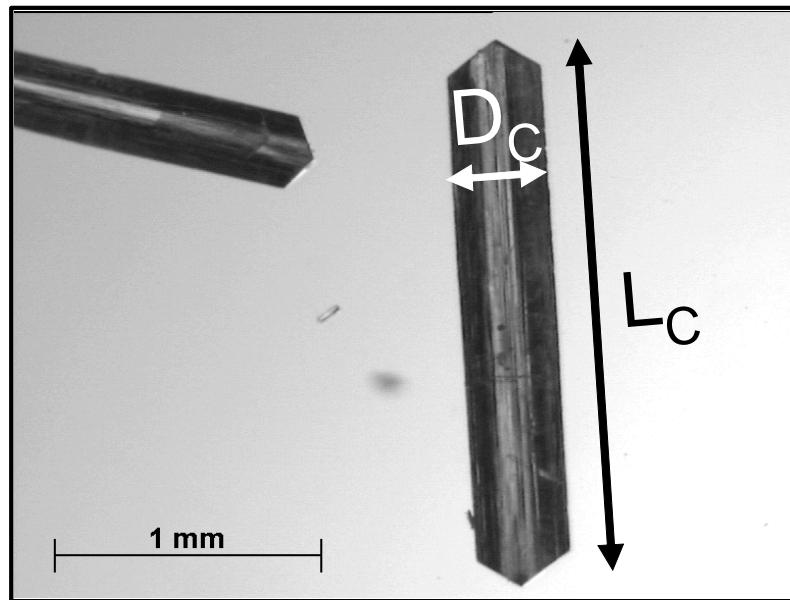


Fig. 5: Illustration of typical shapes of the investigated crystals of threonine.

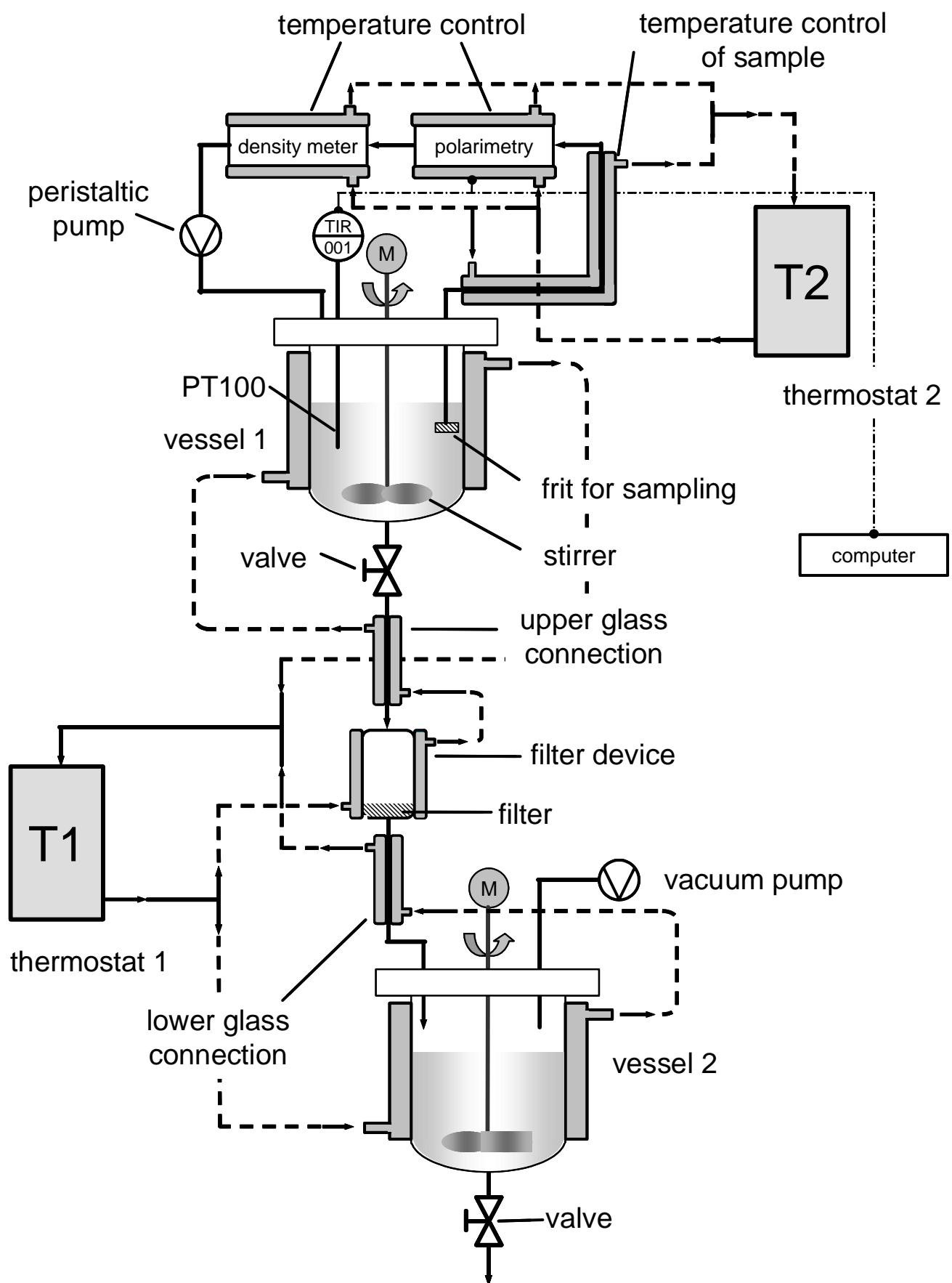


Fig. 6: Experimental set-up for the cyclic operation mode (compare Figure 3).

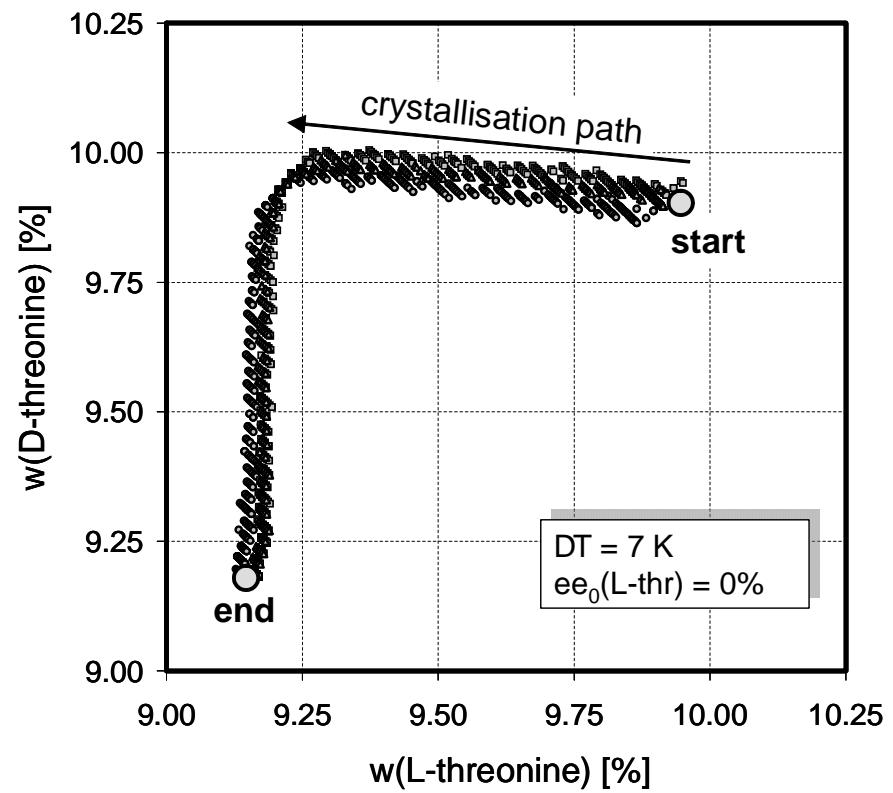
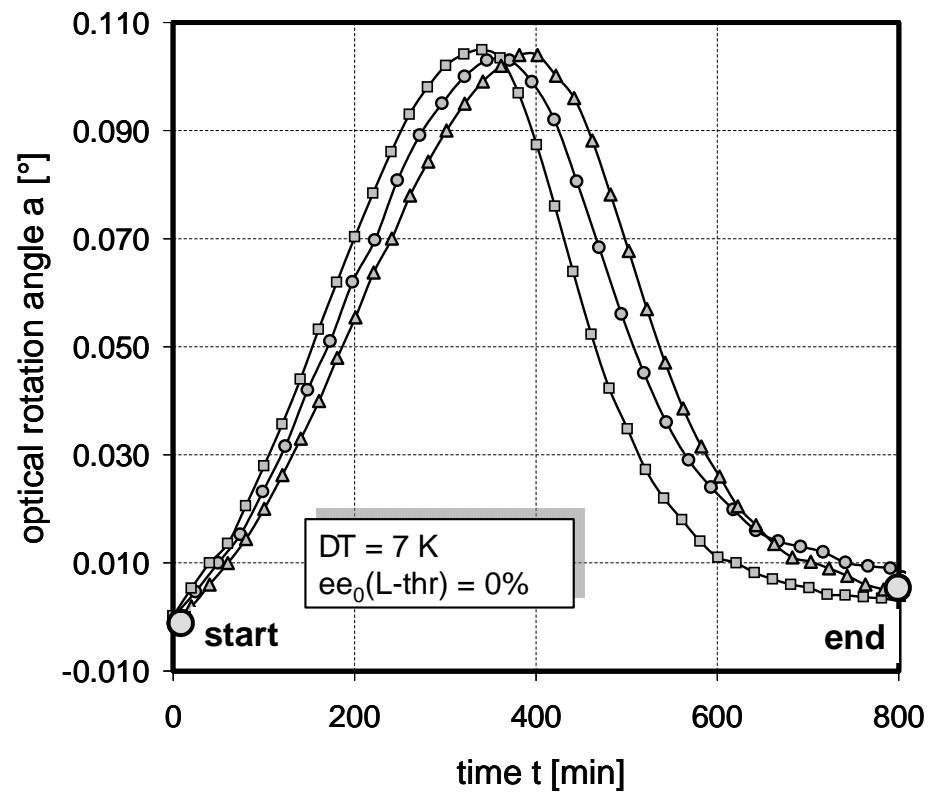


Fig. 7: Typical optical rotation angle curves (left) and trajectories (right) for reproducible, complete batch experiments until the equilibrium state is established (cf. run I, Tab. 2).

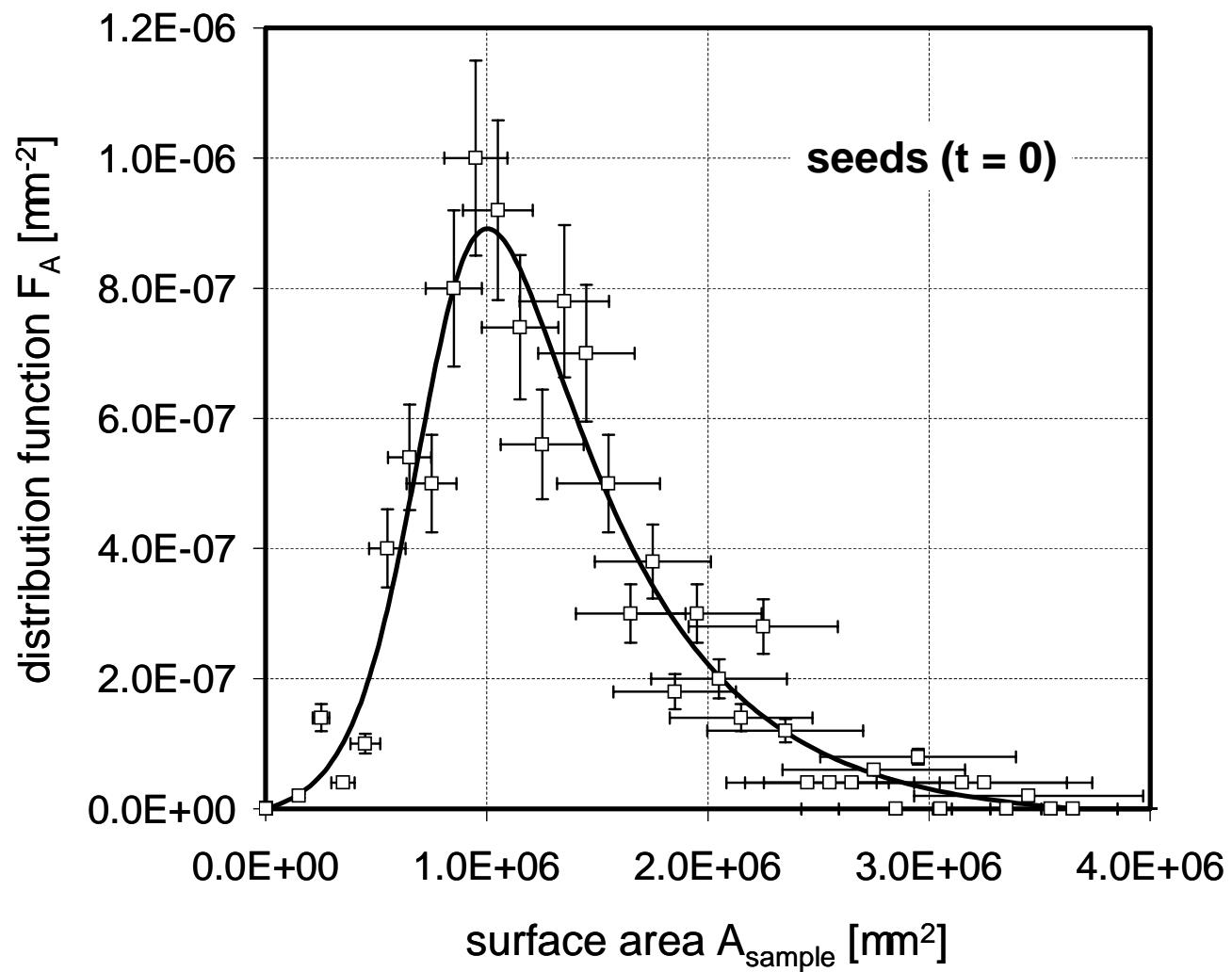


Fig. 8: Distribution of the particle surface area for an analysed basic population of $N = 500$ seeds.

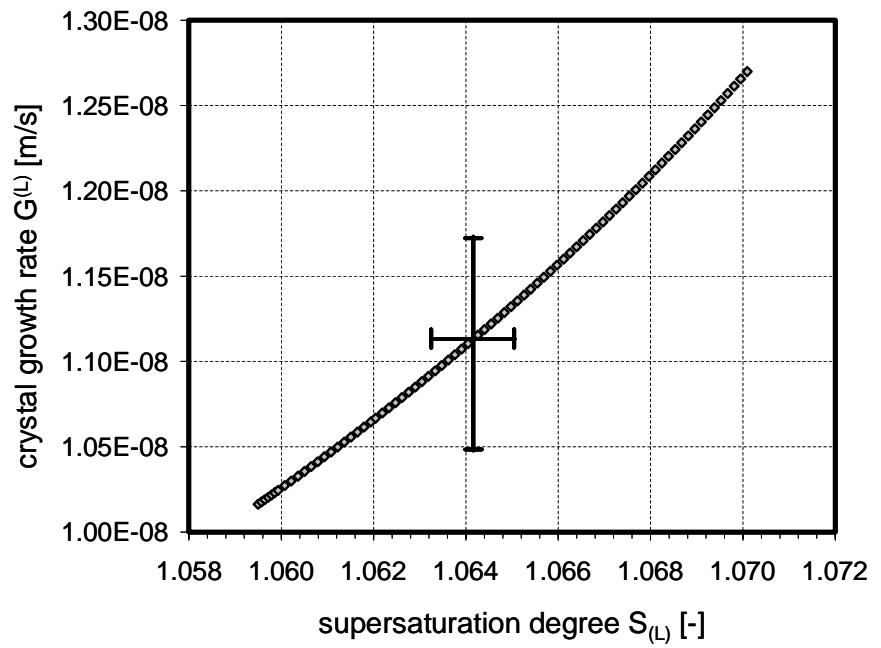
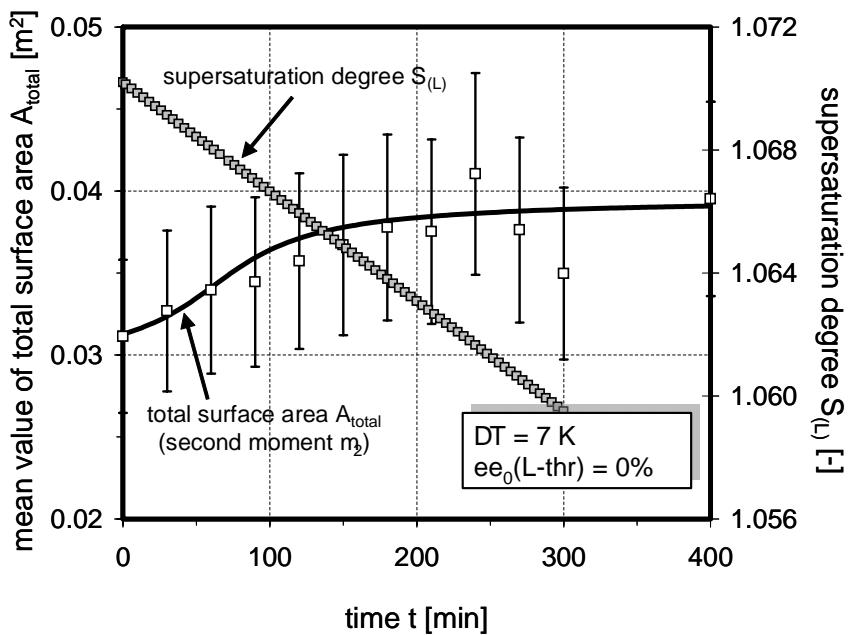


Fig. 9: The temporal increase of the total surface area and the second moment, respectively as well as a desupersaturation curve (left). The evolution of the experimentally determined total surface area was fitted with an empirical function as shown in the left diagram. Plot of crystal growth vs. supersaturation degree exemplified for one experiment (cf. run I in Tab. 2).

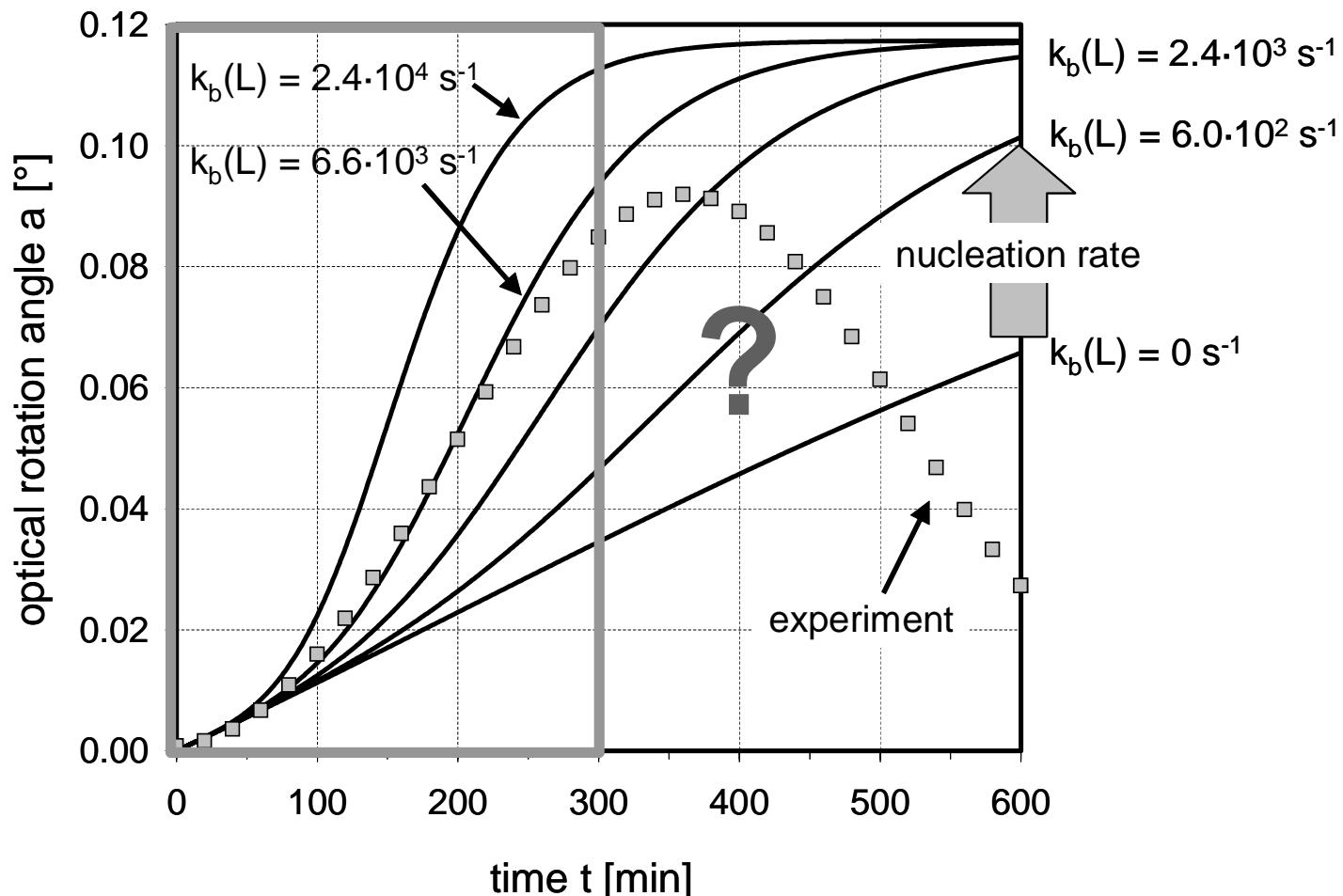


Fig. 10: Comparison of the experimental a -curve obtained by seeding with L-threonine crystals with the a -curve simulated according to the ascertained crystallisation parameters for crystal growth and different values for the nucleation rate constant k_b (indicated is the range used for parameter estimation and which is also of concern for the cyclic operation mode). Experimental conditions cf. run I, Tab. 2.

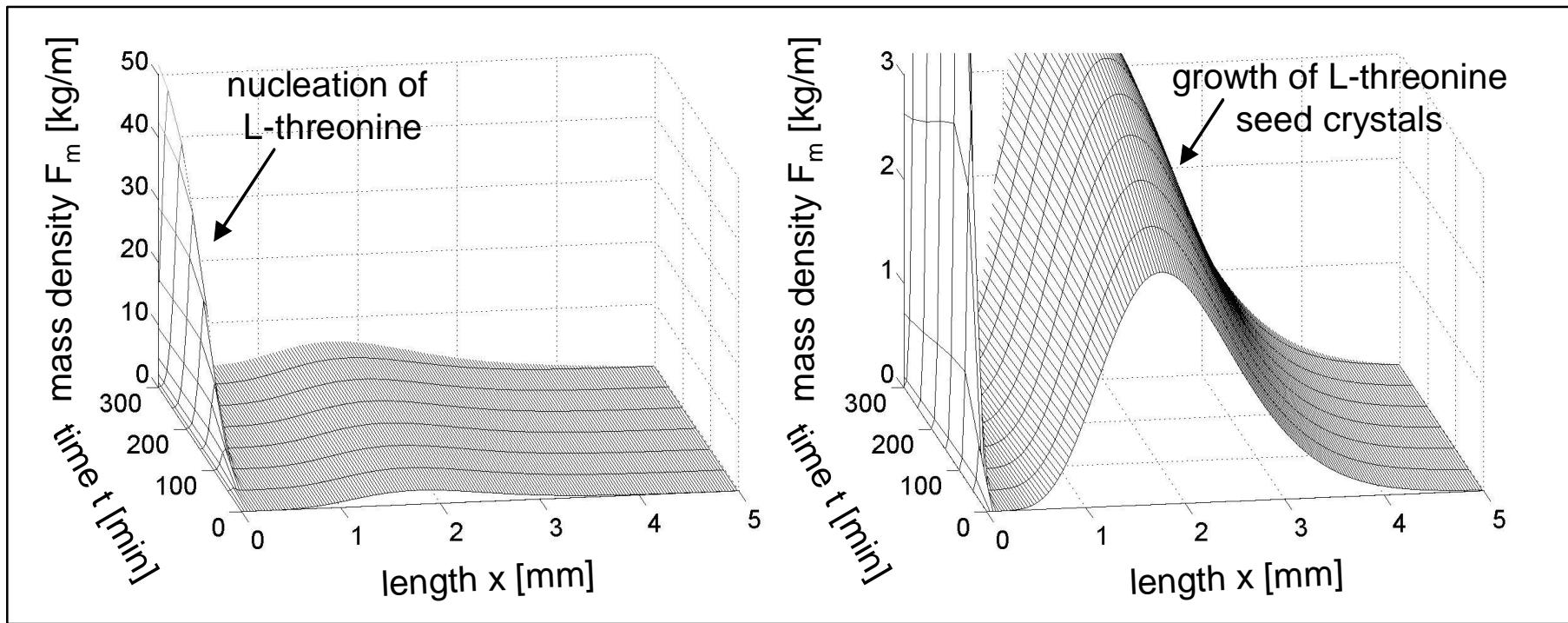


Fig. 11: Evolution of the particle size distribution under typical conditions mentioned above (compare Eqs. 1-4). For the sake of clarity the axis for the mass density function is enlarged in the right-hand diagram.

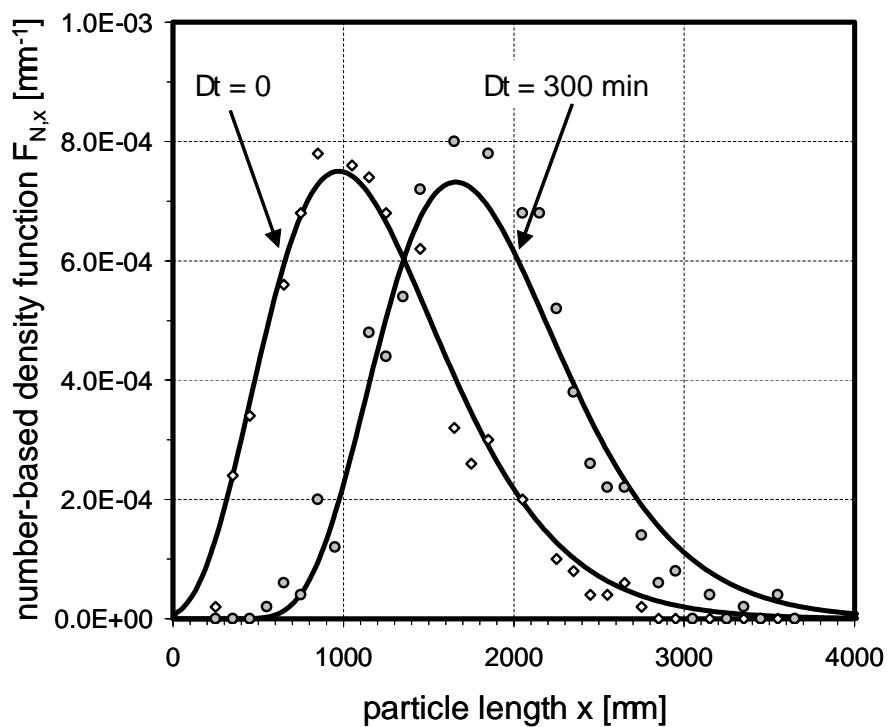
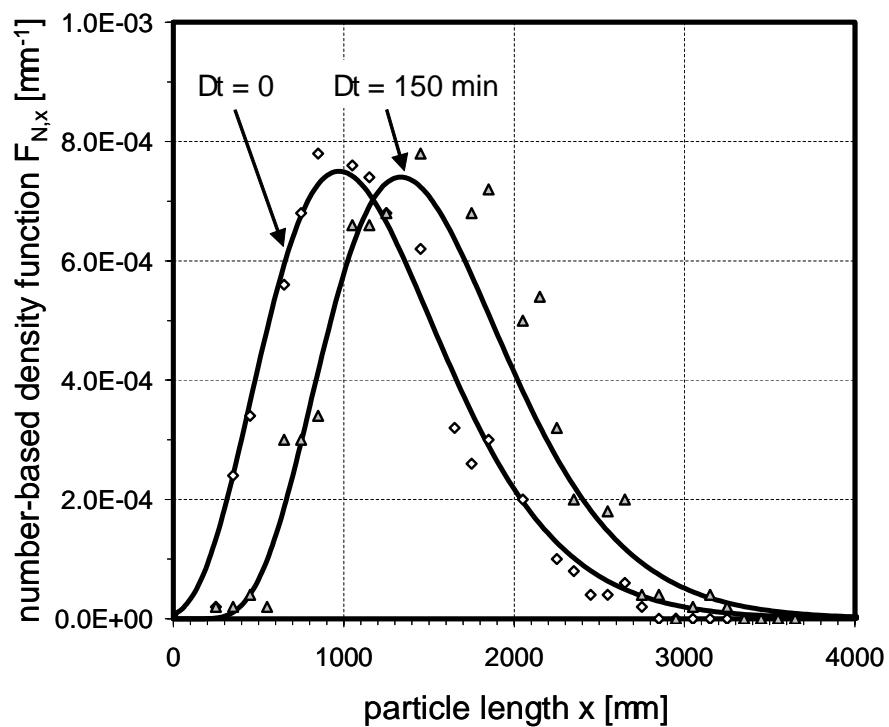


Fig. 12: Comparison between experimentally determined and theoretically predicted distribution functions for several times. Model parameters cf. Eqs. (24-25), Experimental conditions cf. run I, Tab. 2.

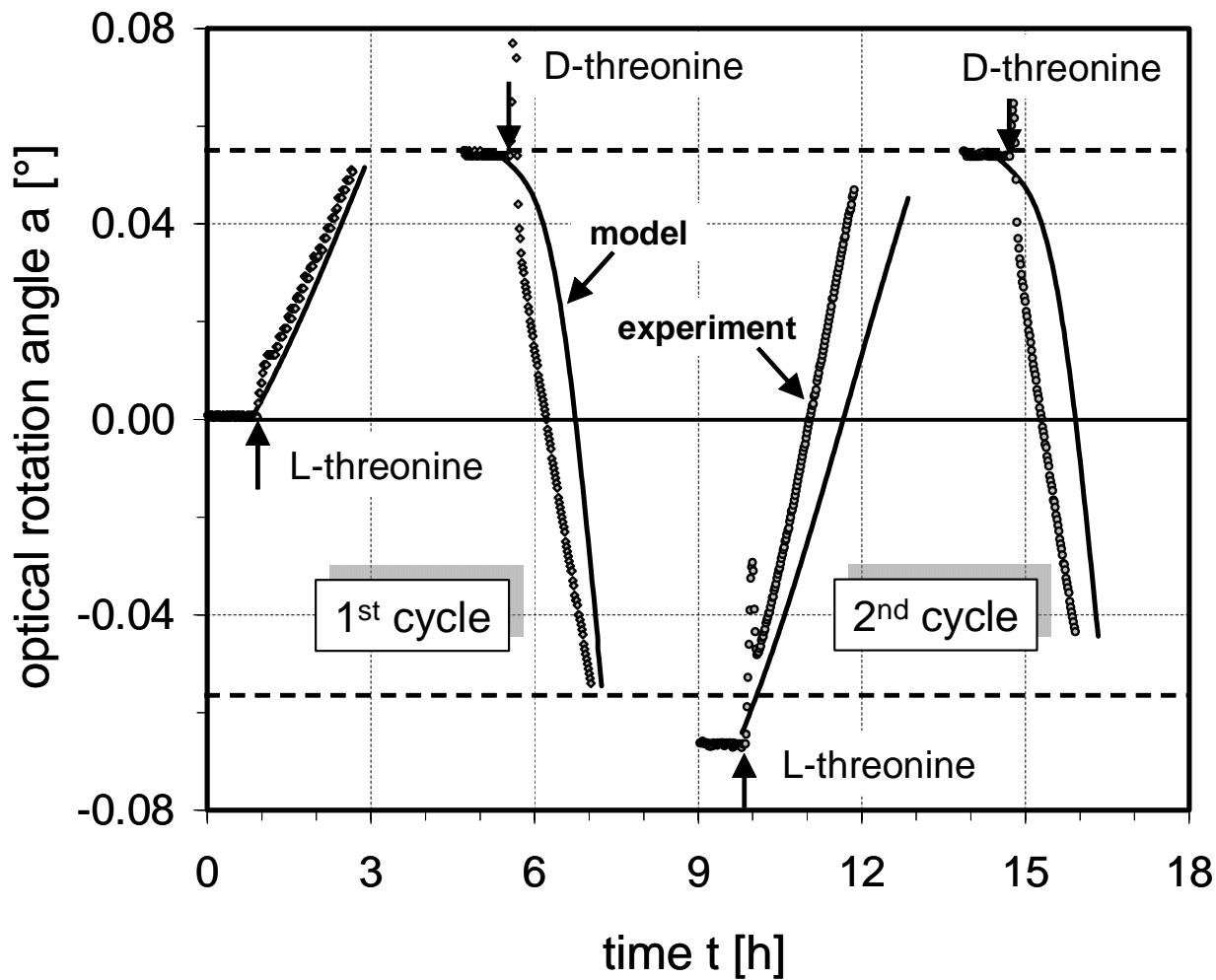


Fig. 13: Comparison of the experimental polarimetric signal for two subsequent separation cycles with the a -curves simulated according to the ascertained crystallisation parameters ($k_g = 2.5 \cdot 10^{-7} \text{ m/s}$, $k_b = 6.6 \cdot 10^3 \text{ s}^{-1}$). Seeding with L-threonine and D-threonine, respectively is marked by arrows.

Table 1: Summary of preliminary experiments performed in a batchwise set-up for preferential crystallisation in order to study effects of stirrer speed, seed amount, surface area of seeds, initial enantiomeric excess, extent of subcooling and crystallisation temperature (see also [23, 24]).

Run	T _{sat} [°C]	T _{cryst} [°C]	DT [K]	ee [%]	sieve fraction of seeds [mm]	m _{seeds} [mg]	V _{cryst} [ml]
(1)	40	33	7	2	212-300	500	250
(2)	40	36	4	2	212-300	500	250
(3)	40	30	10	2	212-300	500	250
(4)	40	24	16	2	212-300	500	250
(5)	40	33	7	2	212-300	20	250
(6)	40	33	7	2	212-300	100	250
(7)	40	33	7	2	212-300	1000	250
(8)	40	33	7	0	212-300	500	250
(9)	40	33	7	4	212-300	500	250
(10)	40	33	7	6	212-300	500	250
(11)	43	33	10	2	212-300	500	250
(12)	37	33	4	2	212-300	500	250
(13)	37	30	7	2	212-300	500	250
(14)	34	30	4	2	212-300	500	250
(15)	34	24	10	2	212-300	500	250
(16)	31	24	7	2	212-300	500	250
(17)	28	24	4	2	212-300	500	250
(18)	40	33	7	2	212-300	5000	2000
(19)	40	36	4	2	212-300	5000	2000
(20)	40	30	10	2	212-300	5000	2000
(21)	40	24	16	2	212-300	5000	2000
(22)	40	33	7	0	212-300	5000	2000
(23)	40	33	7	0	63-90	2500	1200
(24)	40	33	7	0	90-150	2500	1200
(25)	40	33	7	0	150-212	2500	1200
(26)	40	33	7	0	300-400	2500	1200

Table 2: Overview of two experiments devoted to study the growth rates and the cyclic behaviour.

Run	T _{sat} [°C]	T _{cryst} [°C]	DT [K]	ee [%]	sieve fraction of seeds [mm]	m _{seeds} [mg]	V _{cryst} [ml]
(I) ¹	40	33	7	0	212-300	2500	1200
(II) ²	40	30	10	0	212-300	2500	1200

¹ Experimental parameter set for the investigation of crystal growth kinetics examined in this work.

² “Quasi-continuous” resolution experiment in a cyclic operation mode. More details are given in the text.

Table 3: Experimentally and theoretically determined productivities for the cyclic operation mode (theoretically predicted values are in brackets).

Cycle	Steps	Product	"stop" time t* [min]	Productivity Pr _m [s ⁻¹]
1 st Cycle	A ® B	L-threonine	125	$3.5 \cdot 10^{-6}$ ($5.0 \cdot 10^{-6}$)
	C ® D	D-threonine	110	$9.8 \cdot 10^{-6}$ ($1.2 \cdot 10^{-5}$)
2 nd Cycle	A ® B	L-threonine	183	$5.8 \cdot 10^{-6}$ ($7.3 \cdot 10^{-6}$)
	C ® D	D-threonine	110	$8.9 \cdot 10^{-6}$ ($1.2 \cdot 10^{-5}$)