What is special about autocatalysis?

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1. Autocatalysis in chemistry
2. Autocatalysis in the batch reactor
3. Autocatalysis in the flow reactor
4. Autocatalysis and the logistic equation
5. Natural selection
6. Concluding remarks

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Definition of autocatalytic reactions:

Reactions that show an acceleration of the rate as a function of time.

Wilhelm Ostwald, 1890

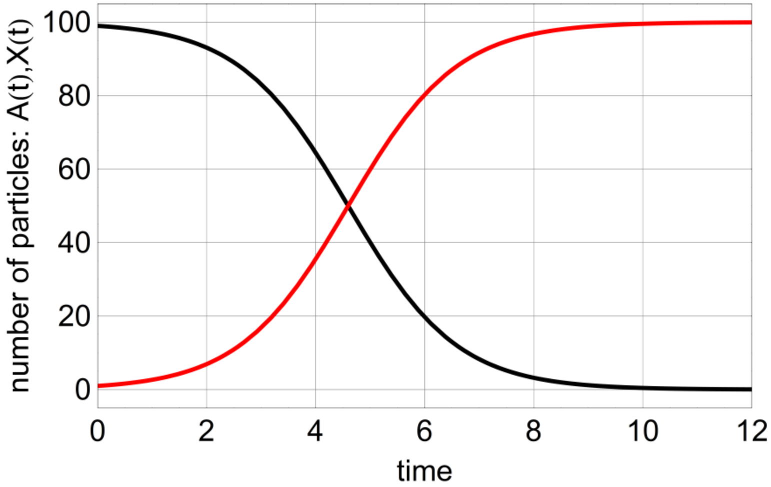
Wilhelm Ostwald, 1853 – 1932

$$\mathrm{A} + \mathrm{X} \xrightarrow{k} 2\,\mathrm{X}$$

$$\frac{dx}{dt} = k\,a\,x = k\big(a(0) + x(0) - x\big)x$$

$$x(t) = \frac{\big(a(0) + x(0)\big)x(0)}{x(0) + a(0)\,e^{-k\left(a(0)+x(0)\right)t}}$$

$$x(0) = 0 \;\Rightarrow\; x(t) = 0$$



autocatalysis

$$A \; + \; n\,X \;\; \leftrightarrow \;\; (n+1)\,X$$

first order: $n = 1$

self-enhancement
exponential growth

Darwinian selection
of the fittest

PCR-amplification

asexual reproduction of
viroids, viruses, and
bacteria

second and higher order: $n \geq 2$

(strong) self-enhancement
hyperexponential growth
nonlinear dynamics

bistability, oscillations,
chaos and spatial patterns

oscillatory chemical reactions
Turing patterns, etc.
symbioses

Exceptions: plus-minus replication, sexual reproduction

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Nonlinear chemical dynamics

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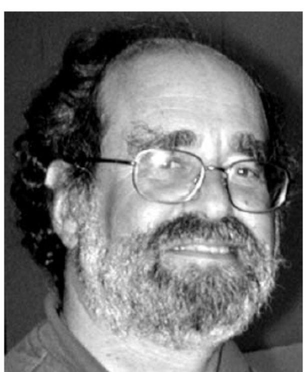

Irving R. Epstein

Irving R. Epstein received his A.B. (1966), M.A. (1968) and Ph.D. (1971) degrees from Harvard University. He was a Marshall Scholar at Balliol College, Oxford, in 1966–67, receiving a Diploma in Advanced Mathematics, and a NATO postdoctoral fellow at the Cavendish Laboratory, Cambridge in 1971, before joining Brandeis University, where he is Professor of Chemistry and has served as Dean of Arts and Sciences (1992–94) and Provost and Senior Vice President for Academic Affairs (1994–2001). He has been the recipient of Guggenheim and Humboldt Fellowships and chaired the first Gordon Research Conference on Chemical Oscillations. He serves on the Editorial Board of Chaos *and on the Board of Directors of the New England Complex Systems Institute. His current research interests include nonlinear dynamics, pattern formation and neuroscience.*

Brusselator model

$$A \leftrightarrow X$$
$$B + X \leftrightarrow Y + D$$
$$2X + Y \leftrightarrow 3X$$
$$X \leftrightarrow E$$

$$A + B = D + E$$

termolecular reaction step

Glandsdorff, Nicolis and Prigogine, 1971

Oregonator model

$$A + Y \leftrightarrow X$$
$$X + Y \leftrightarrow P$$
$$B + X \leftrightarrow 2X + Z$$
$$2X \leftrightarrow Q$$
$$Z \leftrightarrow f\,Y$$

$$f\,A + 2B = f\,P + Q$$

modeling with $f = 1$:

Field, Körös, and Noyes, 1972

Reaction	Rate Constant	Ref.
1. $Br^- + 2H^+ + BrO_3^- \rightleftharpoons HOBr + HBrO_2$	$k_1 = 2.1\ M^{-2}sec^{-1}$	6
	$k_{-1} = 1.0\times10^4\ M^{-1}sec^{-1}$	6
2. $Br^- + HBrO_2 + H^+ \rightleftharpoons 2HOBr$	$k_2 = 2.0\times10^9\ M^{-2}sec^{-1}$	6
	$k_{-2} = 5.0\times10^{-5}\ M^{-1}sec^{-1}$	6
3. $Br^- + HOBr + H^+ \rightleftharpoons Br_2 + H_2O$	$k_3 = 8.0\times10^9\ M^{-2}sec^{-1}$	6
	$k_{-3} = 110.\ sec^{-1}\ (a)$	6
4. $H^+ + CH_2(COOH)_2 \rightleftharpoons (OH)_2C{=}CHCOOH + H^+$	$k_4 = 1.3\times10^{-2}\ M^{-1}sec^{-1}$	6
	$k_{-4} = 1.3\times10^4\ M^{-1}sec^{-1}$	19
5. $Br_2 + (OH)_2C{=}CHCOOH \rightleftharpoons H^+ + Br^- + BrCH(COOH)_2$	$k_5 = 6.0\times10^6\ M^{-1}sec^{-1}$	19
	$k_{-5} = 0.$	22
6. $HOBr + (OH)_2C{=}CHCOOH \rightleftharpoons H_2O + BrCH(COOH)_2$	$k_6 = 0.$	This work
	$k_{-6} = 0.$	22
7. $HBrO_2 + BrO_3^- + H^+ \rightleftharpoons 2BrO_2\cdot + H_2O$	$k_7 = 1.0\times10^4\ M^{-2}sec^{-1}$	6
	$k_{-7} = 2.0\times10^7\ M^{-1}sec^{-1}\ (a)$	6
8. $BrO_2\cdot + Ce(III) + H^+ \rightleftharpoons Ce(IV) + HBrO_2$	$k_8 = 6.5\times10^5\ M^{-2}sec^{-1}$	This work
	$k_{-8} = 2.4\times10^7\ M^{-1}sec^{-1}$	This work
9. $Ce(IV) + BrO_2\cdot + H_2O \rightleftharpoons BrO_3^- + 2H^+ + Ce(III)$	$k_9 = 9.6\times10^4\ M^{-1}sec^{-1}\ (a,b)$	This work
	$k_{-9} = 0.$	6
10. $2HBrO_2 \rightleftharpoons HOBr + BrO_3^- + H^+$	$k_{10} = 4.0\times10^7\ M^{-1}sec^{-1}$	6
	$k_{-10} = 2.0\times10^{-10}\ M^{-2}sec^{-1}$	6
11. $Ce(IV) + CH_2(COOH)_2 \rightarrow \cdot CH(COOH)_2 + Ce(III) + H^+$	$k_{11} = 1.7\times10^{-1}\ M^{-1}sec^{-1}$ ([MA] $\ll$ 0.5 M)	6,22,25
12. $\cdot CH(COOH)_2 + Ce(IV) + H_2O \rightarrow HOCH(COOH)_2 + Ce(III) + H^+$	$k_{12} = 1.0\times10^5\ M^{-1}sec^{-1}\ (a)$	This work
13. $Ce(IV) + BrCH(COOH)_2 + H_2O \rightarrow Br^- + HO\dot{C}(COOH)_2 + Ce(III) + H^+$	$k_{13} = 8.5\times10^{-2}\ M^{-1}sec^{-1}\ (a)$ ([BrMA] $\ll$ 0.1M)	6,22,25
14. $\cdot CH(COOH)_2 + BrCH(COOH)_2 + H_2O \rightarrow HO\dot{C}(COOH)_2 + CH_2(COOH)_2 + Br^- + H^+$	$k_{14} = 1.0\times10^5\ M^{-1}sec^{-1}\ (a,b)$	This work
15. $HO\dot{C}(COOH)_2 + Ce(IV) \rightarrow O{=}C(COOH)_2 + Ce(III) + H^+$	$k_{15} = 1.0\times10^5\ M^{-1}sec^{-1}\ (b)$	This work
16. $HO\dot{C}(COOH)_2 + BrCH(COOH)_2 + H_2O \rightarrow HOCH(COOH)_2 + Br^- + HOC\ (COOH)_2 + H^+$	$k_{16} = 1.0\times10^5\ M^{-1}sec^{-1}\ (a,b)$	This work
17. $Ce(IV) + HOCH(COOH)_2 \rightarrow HO\dot{C}(COOH)_2 + Ce(III) + H^+$	$k_{17} = 1.0\times10^5\ M^{-1}sec^{-1}\ (b)$	This work
18. $Ce(IV) + O{=}C(COOH)_2 \rightarrow O{=}C(COO\cdot)(COOH) + Ce(III) + H^+$	$k_{18} = 1.0\times10^5\ M^{-1}sec^{-1}\ (b)$	This work
19. $O{=}C(COO\cdot)(COOH) + Ce(IV) + H_2O \rightarrow HCOOH + Ce(III) + H^+ + 2CO_2$	$k_{19} = 1.0\times10^5\ M^{-1}sec^{-1}\ (b)$	This work
20. $O{=}C(COO\cdot)(COOH) + BrCH(COOH) + H_2O \rightarrow HO\dot{C}(COOH)_2 + O{=}C(COOH)_2 + Br^- + H^+$	$k_{20} = 1.0\times10^5\ M^{-1}sec^{-1}\ (a,b)$	This work

D. Edelson, R.J. Field, R.M. Noyes. Mechanistic details of the Belousov-Zhabotinskii oscillations. Internat. J. Chem. Kinetics 7, 417-432 (1975)

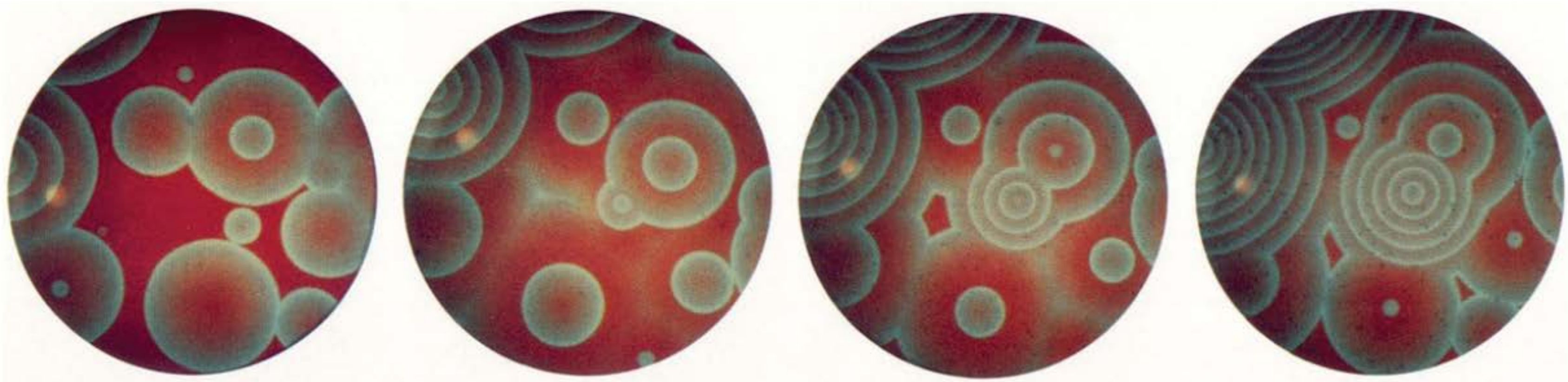

Fig. 1. Sequence of snapshots of target patterns in the aqueous Belousov-Zhabotinsky (BZ) reaction. *Patterns emerge from an initially homogeneous red solution. Catalyst/indicator is ferroin. Red areas are more reduced; blue areas are more oxidized.*

V. K. Vanag, I. R. Epstein. Internat.J.Developmental Biology 53, 673-681

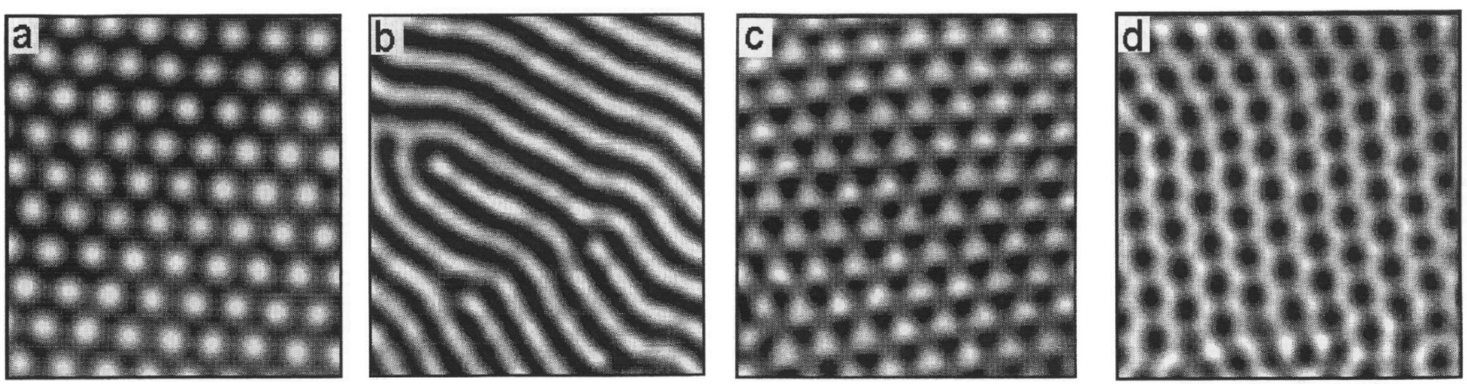

Fig. 3. Stationary planforms observed in the disc reactor. Standard patterns: (a) hexagonal array of "clear" spots from region IIa ($[KI]_B = 2.0 \times 10^{-3}$ M; $[CH_2(COOH)_2]_B = 2.25 \times 10^{-3}$ M); (b) array of parallel stripes (bands) from region IIb ($[KI]_B = 2.0 \times 10^{-3}$ M, $[CH_2(COOH)_2]_B = 2.5 \times 10^{-3}$ M). Non-standard patterns: (c) array of symmetric triangles from region IIc ($[KI]_B = 3.0 \times 10^{-3}$ M, $[CH_2(COOH)_2]_B = 3.2 \times 10^{-3}$ M); (d) array of "dark" hexa-bands from region IId ($[KI]_B = 2.5 \times 10^{-3}$ M, $[CH_2(COOH)_2]_B = 3.1 \times 10^{-3}$ M). All patterns are at the same scale: view size 1.7 × 1.7 mm.

B. Rudovics, E. Dulos, P. De Kepper. Physica Scripta T67, 43-50, 1996

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batch reactor

two basic features:

(i) homogeneous medium achieved by stirring

(ii) temperature control

facilitates modeling enormously!

$$\mathrm{A} + \mathrm{X} \underset{h}{\overset{k}{\rightleftharpoons}} 2\,\mathrm{X}$$

$$\frac{dx}{dt} = k\,a\,x - h\,x^2 = -\frac{da}{dt}$$

$$a(0) = a_0\,,\; x(0) = x_0\,,\; a(t) + x(t) = c = \mathrm{const}$$

$$x(t) = \frac{k\,c\,x_0}{(k+h)\,x_0 + (k\,a_0 - h\,x_0)\exp(-k\,c\,t)}$$

rate of reaction for a = const: $\gamma_1\, x \;-\; \gamma_2\, x^2$

stationary states: (i) state of extinction S_0: $\bar{x} = 0$ (ii) state of reproduction S_1: $\bar{x} = \dfrac{\gamma_1}{\gamma_2}$.

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$$P_M = \mathrm{Prob}\{A(t) = M\} \qquad C = A(t) + X(t)$$

$$A(t) = M\,; \quad M \in \mathbb{N}\,,\, M \in [0, C-1]$$

$$X(t) = C - M = L\,; \quad C, L \in \mathbb{N}\,,\, C - M = L \in [1, C]$$

$$\frac{\mathrm{d}P_M}{\mathrm{dt}} = k\,(M+1)\,(C-M-1)\,P_{M+1} +$$
$$+\;h\,(C-M+1)\,(C-M)\,P_{M-1} -$$
$$-\;\Big(k\,M\,(C-M) + h\,(C-M)(C-M-1)\Big)\,P_M$$

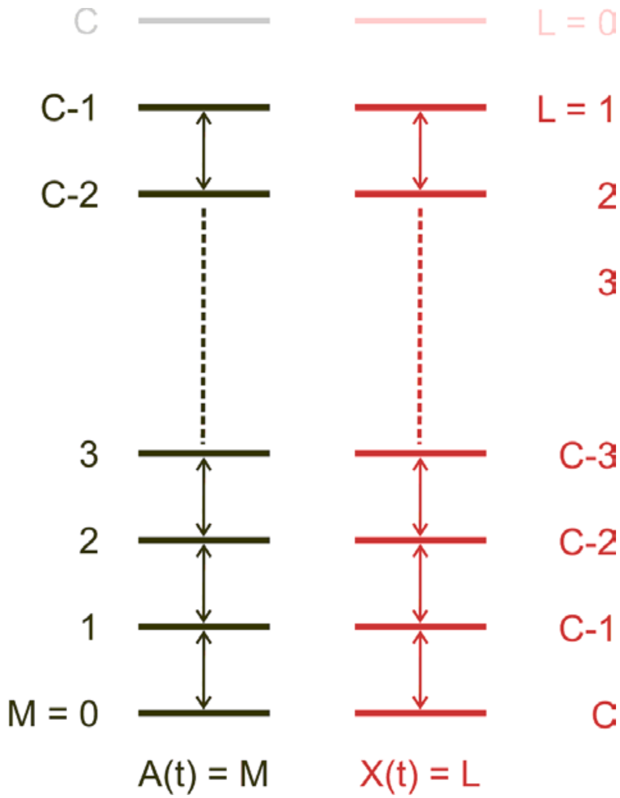
A + X ↔ 2 X

$$\frac{\mathrm{d}P_M}{\mathrm{dt}} = k\,(M+1)\,(C-M-1)\,P_{M+1} +$$
$$-\;k\,M\,(C-M)\,P_M$$

A + X → 2 X

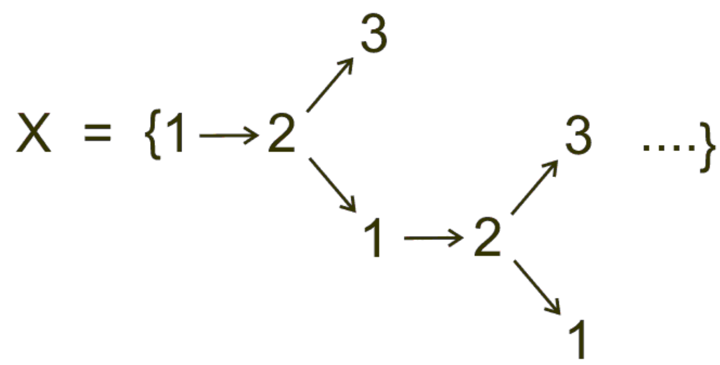
E. Arslan, I.J. Laurenzi. J.Chem.Phys.128,e015101, 2008

The master equation of the autocatalytic reaction A + X ↔ 2 X



$A(t) + X(t) = M + L = C$

$A + X \rightarrow 2\,X$ and $2\,X \rightarrow A + X$

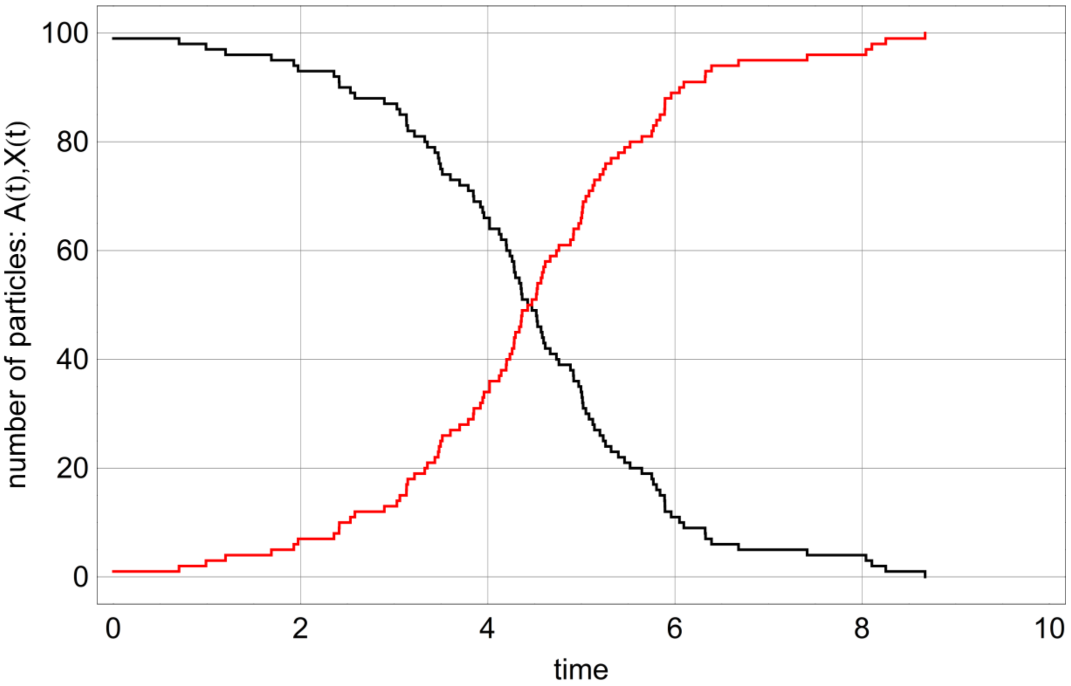


The reversible autocatalytic reaction

$A + X \leftrightarrow 2\,X$

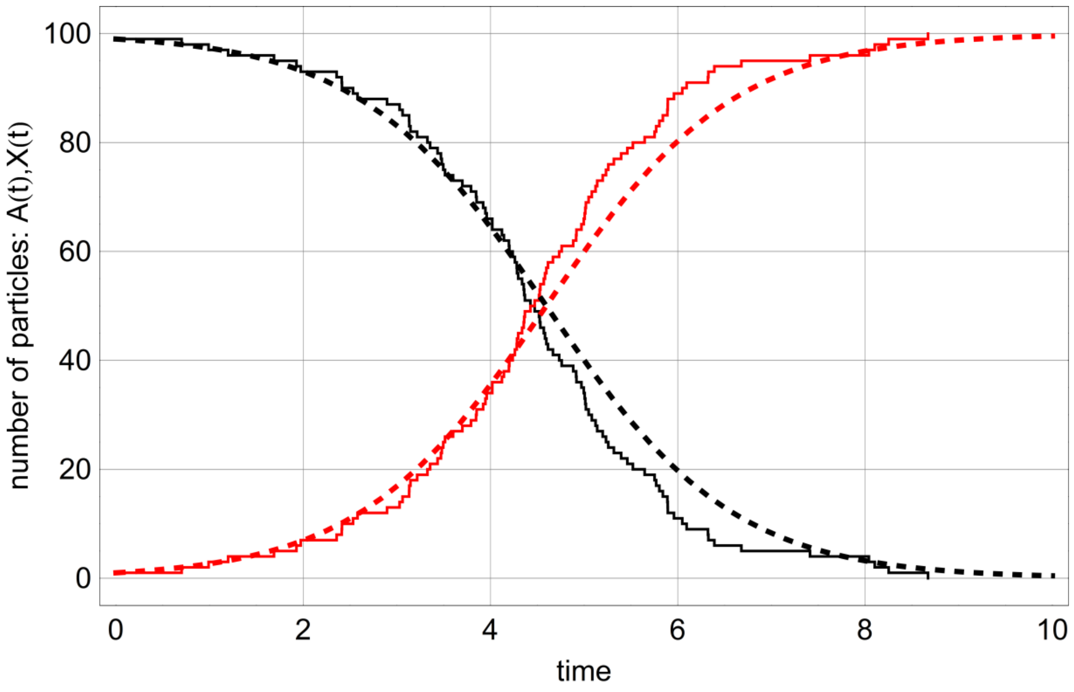
can't become extinct $\big(X(t) = 0\big)$.

The reflecting barrier of $A + X \leftrightarrow 2\,X$ at $X(t) = 1$

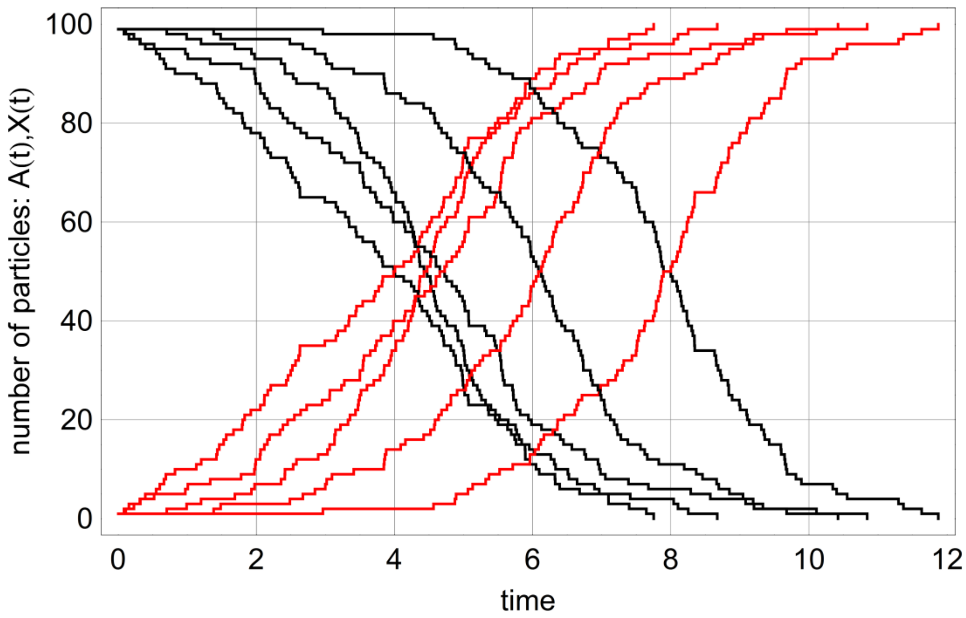


$$\{ A , X \} \to \{ A - 1 , X + 1 \}$$

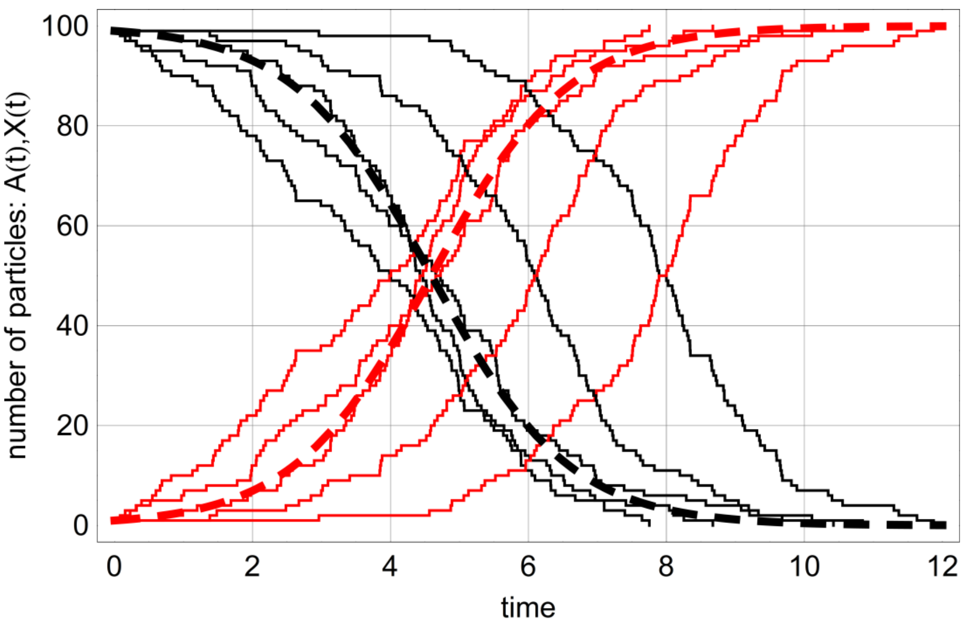
autocatalysis first order: $A + X \to 2X$, single trajectory



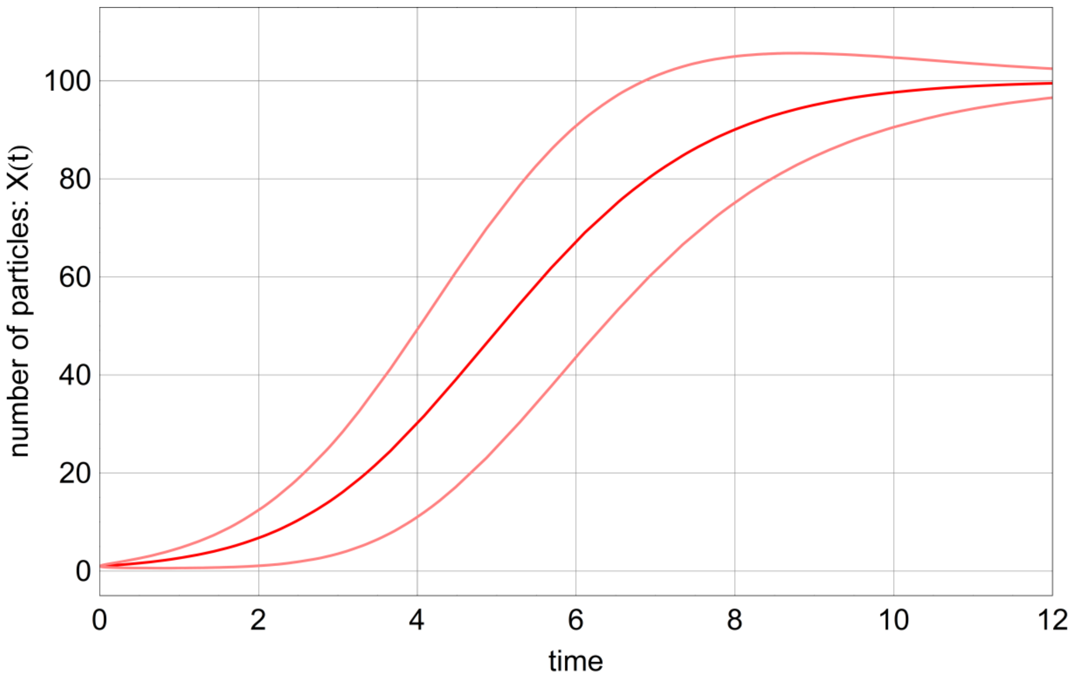
autocatalysis first order: A + X $\rightarrow$ 2 X, single trajectory and deterministic solution



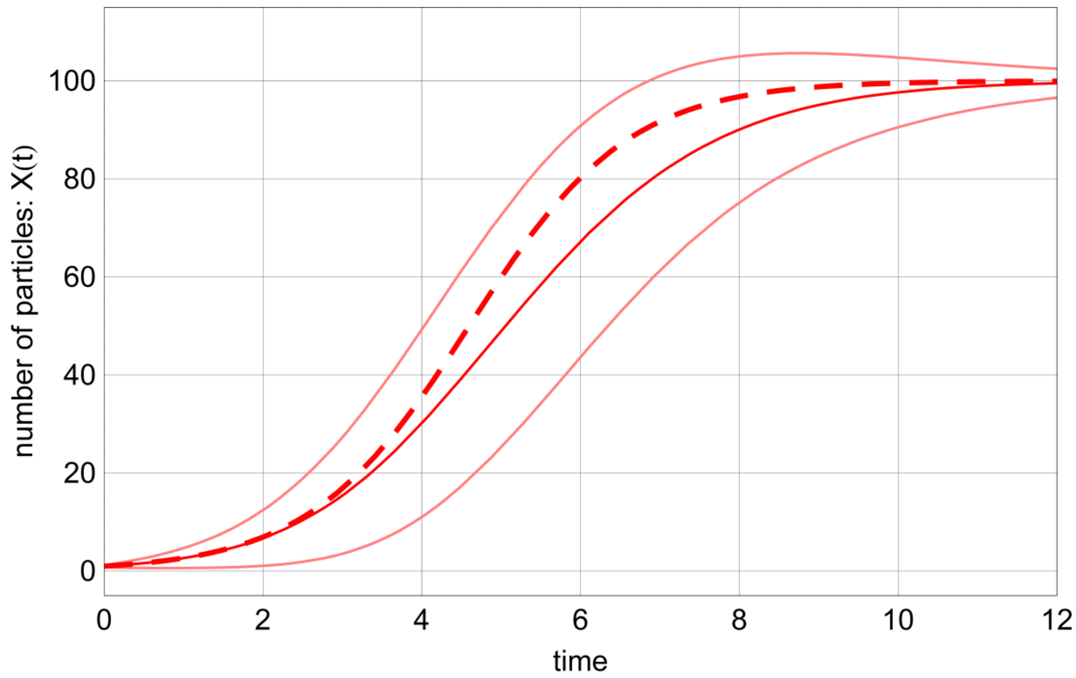
autocatalysis first order: $A + X \rightarrow 2\,X$, bundle of trajectories



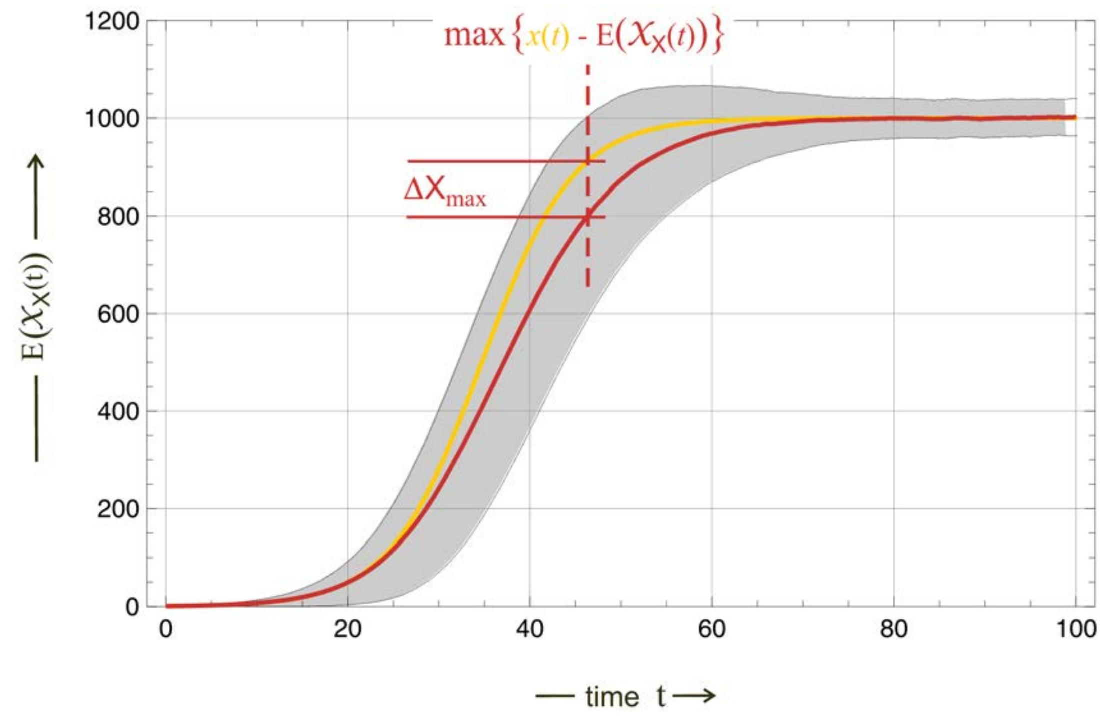
autocatalysis first order: A + X $\rightarrow$ 2 X, bundle and deterministic solution



autocatalysis first order: $A + X \rightarrow 2\,X$, expectation value and one σ error band



autocatalysis first order: A + X $\longrightarrow$ 2 X, expectation value and deterministic solution



autocatalysis first order: A + X $\rightarrow$ 2 X, measuring stochastic delay δ

N		Initial particle numbers X_0					
		1	2	3	5	7	10
100	$t(\Delta X_{max})$	6.03856	5.12539	4.75684	4.1744	3.92167	3.42010
	ΔX_{max}	13.1546	6.93289	4.57133	2.79113	1.88634	1.34232
	$\Delta X_{max} X_0 / N$	**0.1316**	**0.1387**	**0.1372**	**0.1396**	**0.1320**	**0.1342**
400	$t(\Delta X_{max})$	18.1088	15.9382	14.6904	13.2155	12.4069	11.4706
	ΔX_{max}	53.9348	27.8792	18.6441	12.0256	8.48329	5.96725
	$\Delta X_{max} X_0 / N$	**0.1348**	**0.1393**	**0.1398**	**0.1503**	**0.1485**	**0.1492**
1000	$t(\Delta X_{max})$	82.5046	73.5525	69.1473	61.5956	59.5409	55.4158
	ΔX_{max}	136.575	71.6853	47.7226	30.1260	21.6830	14.1515
	$\Delta X_{max} X_0 / N$	**0.1366**	**0.1434**	**0.1432**	**0.1506**	**0.1518**	**0.1415**

stochastic delay: $\delta = \Delta X_{max} X_0 / N$

$$A + X \xrightarrow{k} 2X$$

k = 0.01, 0.001, 0.0001; sample size: 10 000

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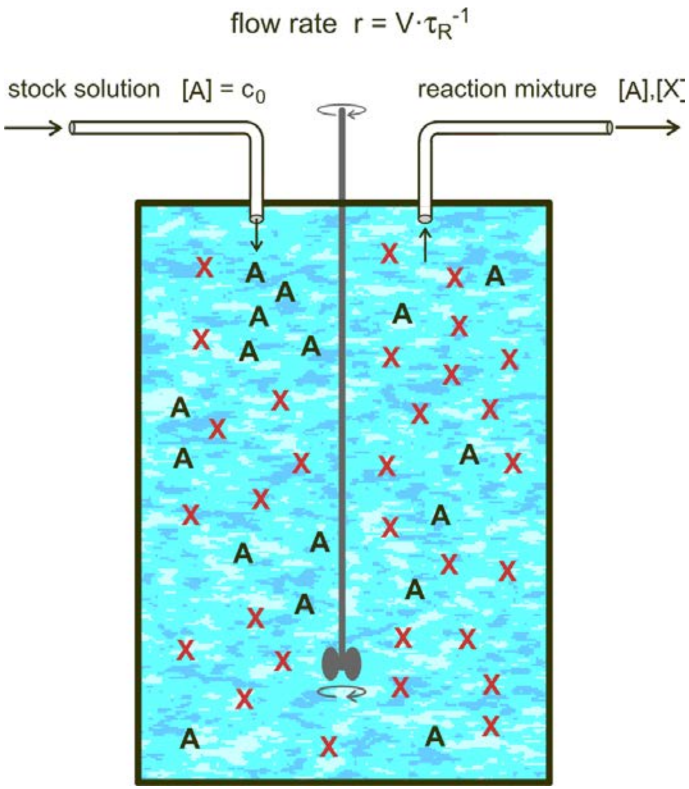


$$* \xrightarrow{r \cdot c_0} \mathrm{A}$$

$$\mathrm{A} + \mathrm{X} \underset{h}{\overset{k}{\rightleftarrows}} 2\,\mathrm{X}$$

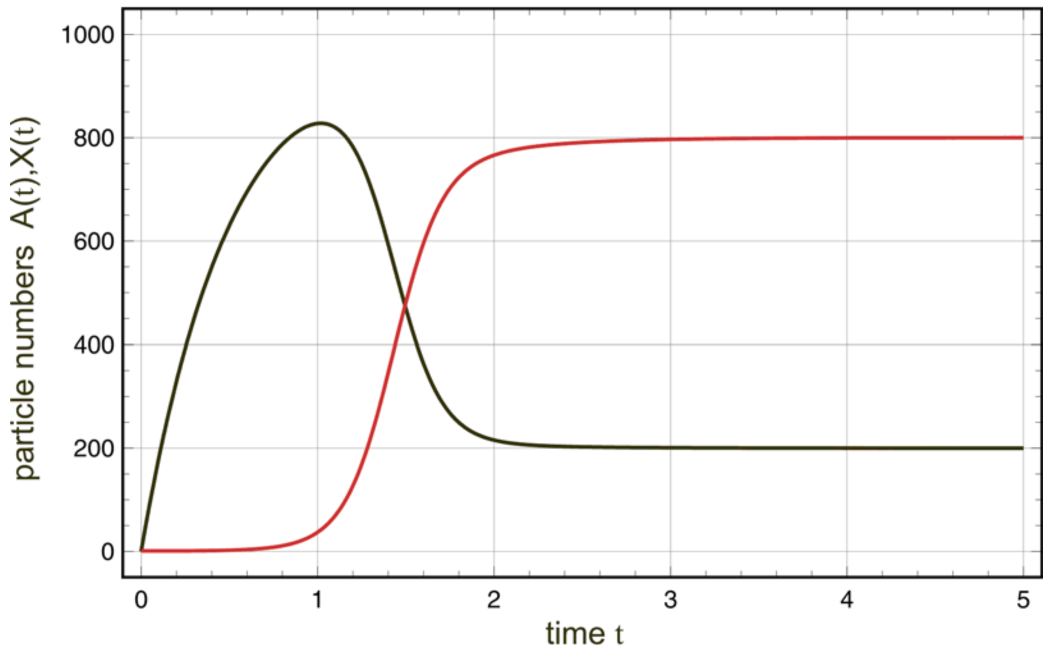
$$\mathrm{A} \xrightarrow{r} \varnothing$$

$$\mathrm{X} \xrightarrow{r} \varnothing$$

$$\frac{\mathrm{d}a}{\mathrm{dt}} = r \cdot c_0 - k\,a\,x + h\,x^2 - r\,a = -k\,a\,x + h\,x^2 + r\,(c_0 - a)$$

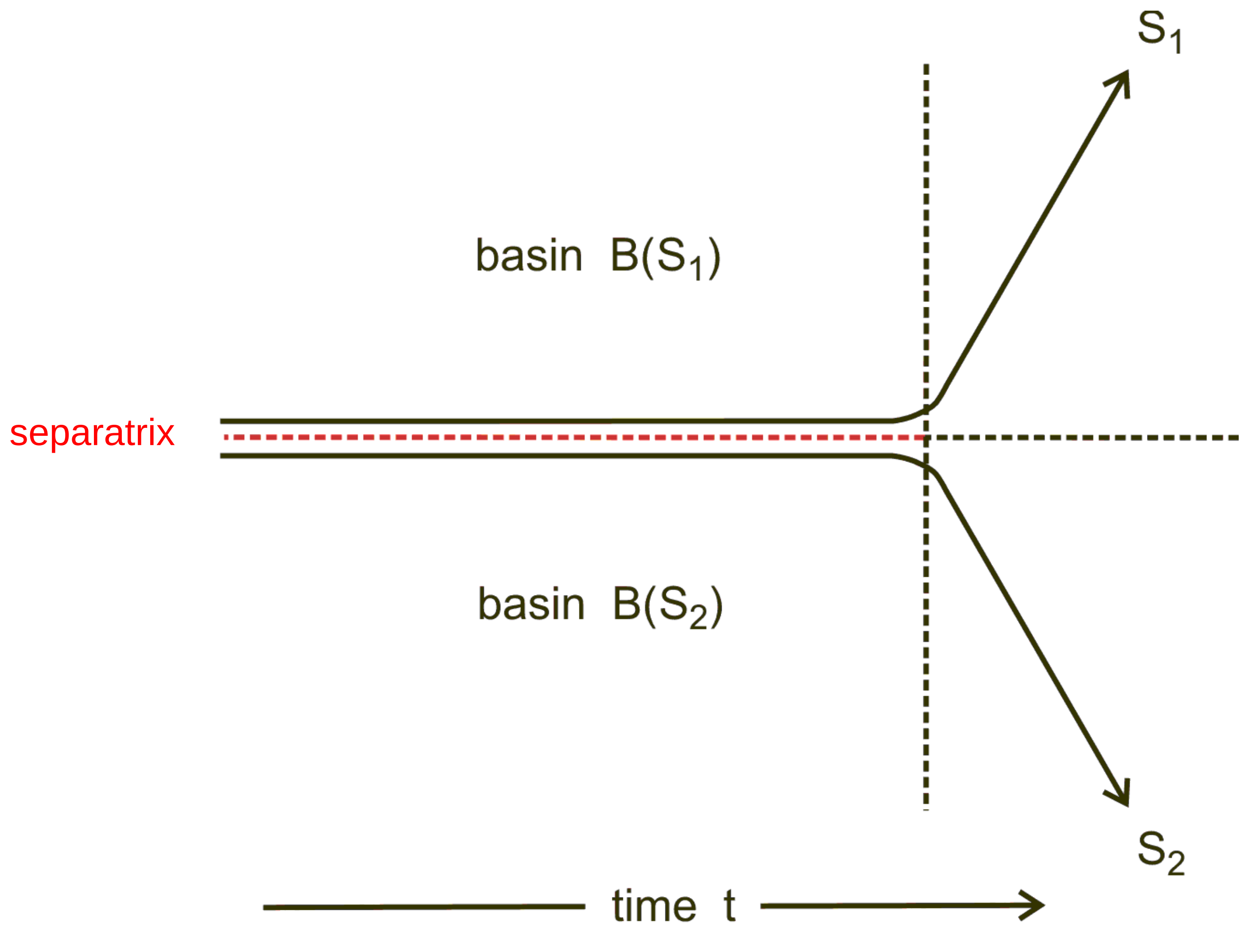
$$\frac{\mathrm{d}x}{\mathrm{dt}} = k\,a\,x - h\,x^2 - r\,x = x\,(k\,a - h\,x - r)$$

stationary states: $S_0 = (c_0\,, 0)$ and $S_1 = \big((c_0 + r)/(1+K)\,,\, K(c_0 + r)/(1+K) - r/h\big)$

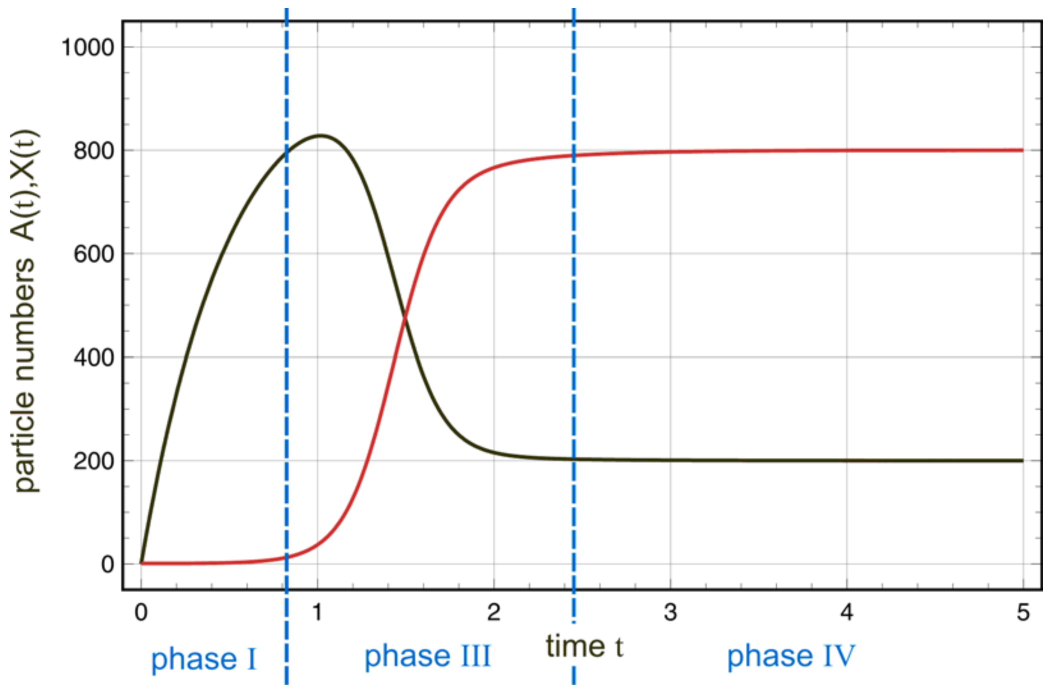


Approach of the reaction A+X→2X towards the steady state in the flow reactor

initial condition *empty reactor*: A(0) = 0, X(0) = 1,2,3,…



example of a deterministic bifurcation



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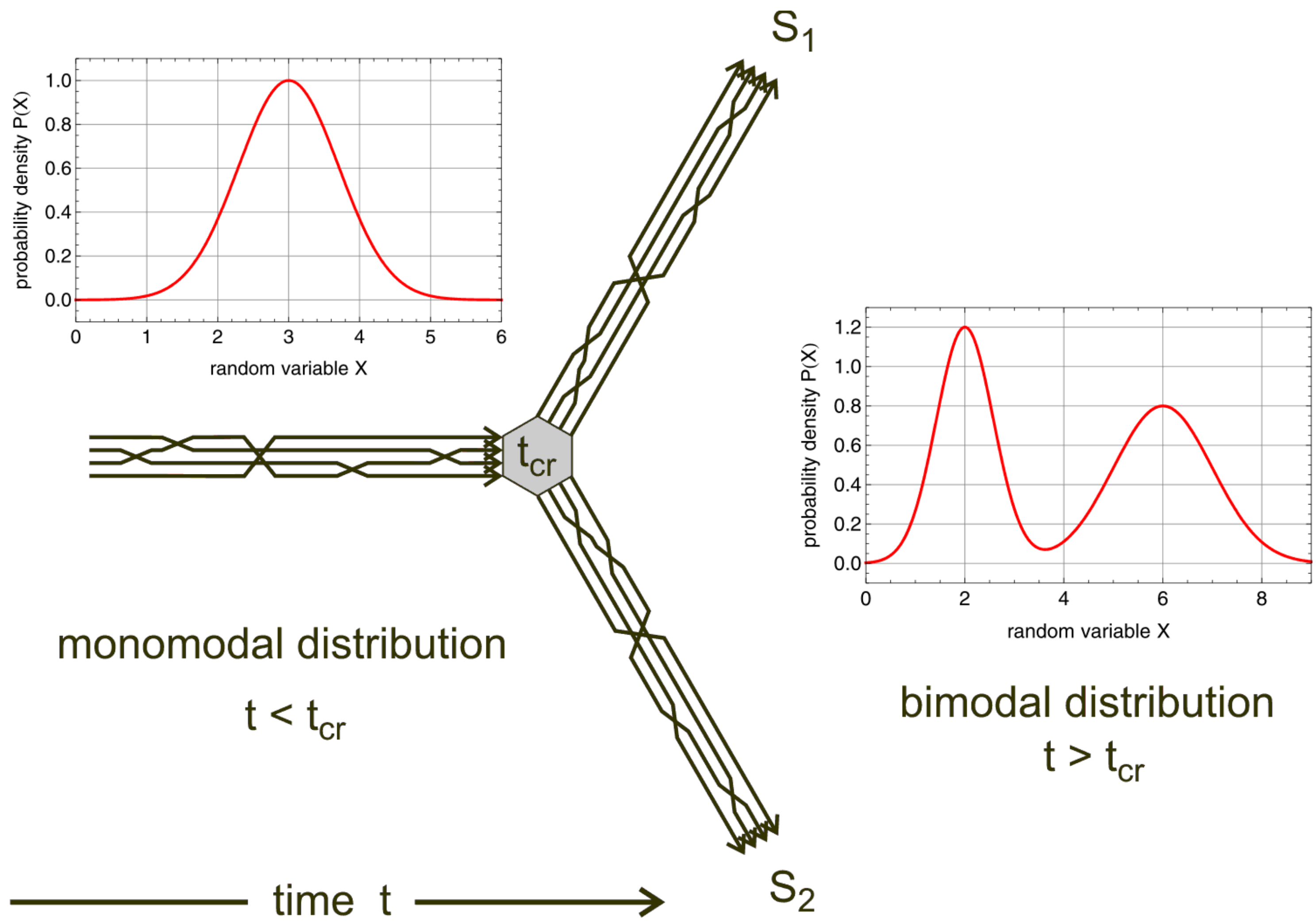
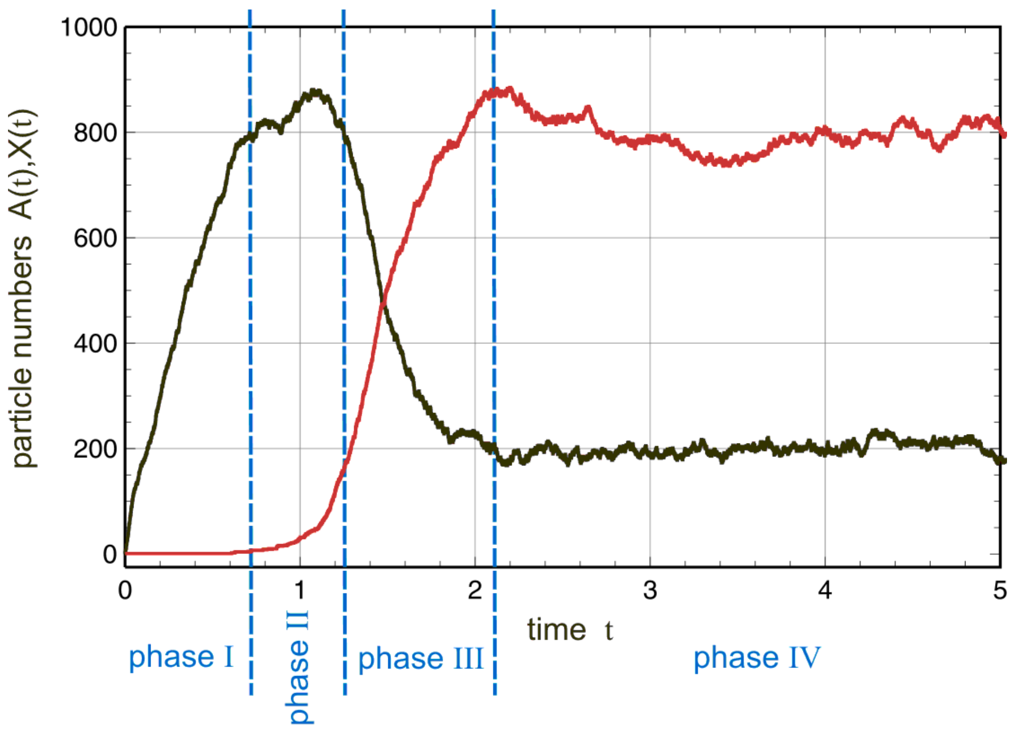


anomalous fluctuations

example of a stochastic bifurcation



Approach of the reaction A+X→2X towards the steady state in the flow reactor

initial condition *empty reactor*: A(0) = 0, X(0) = 1,2,3,…

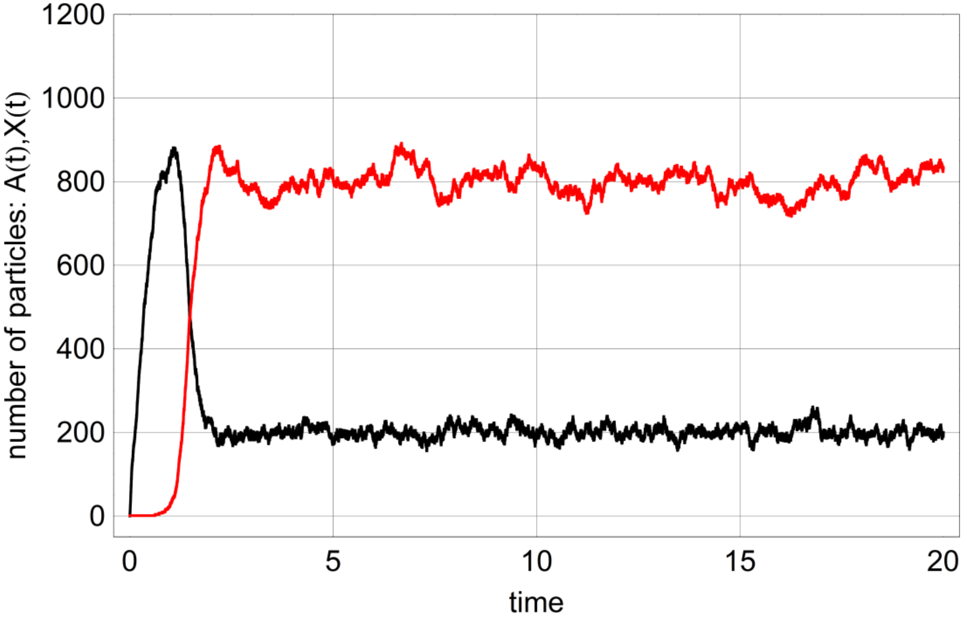
Four phases of the autocatalytic process:

(i) phase I: the empty reactor is filled with resource A,

(ii) phase II: random events select the state towards which the trajectory converges,

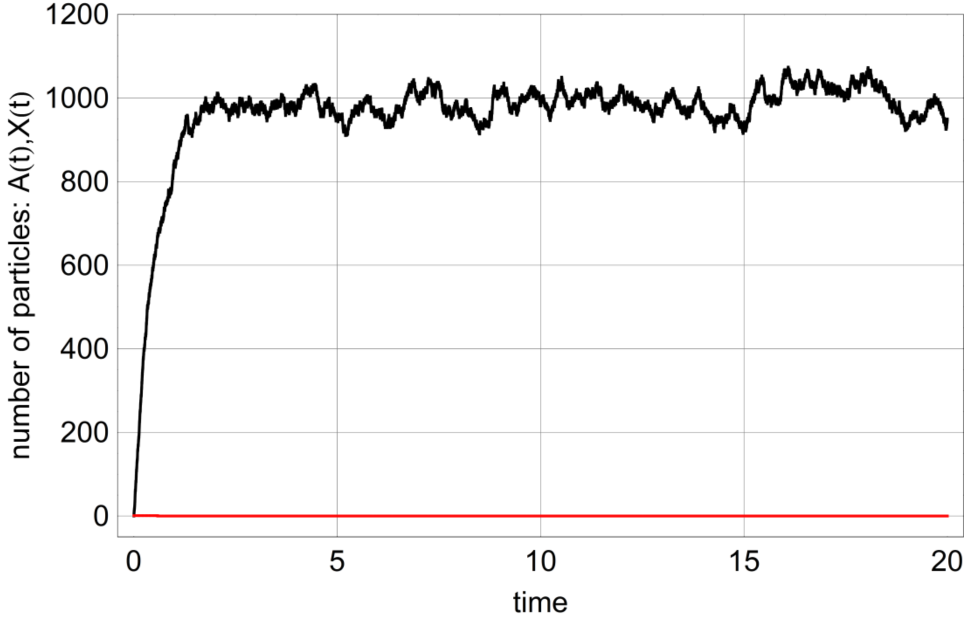
(iii) phase III: the trajectory approches the long-time state, and

(iv) phase IV: the trajectory fluctuates around the long-time state.



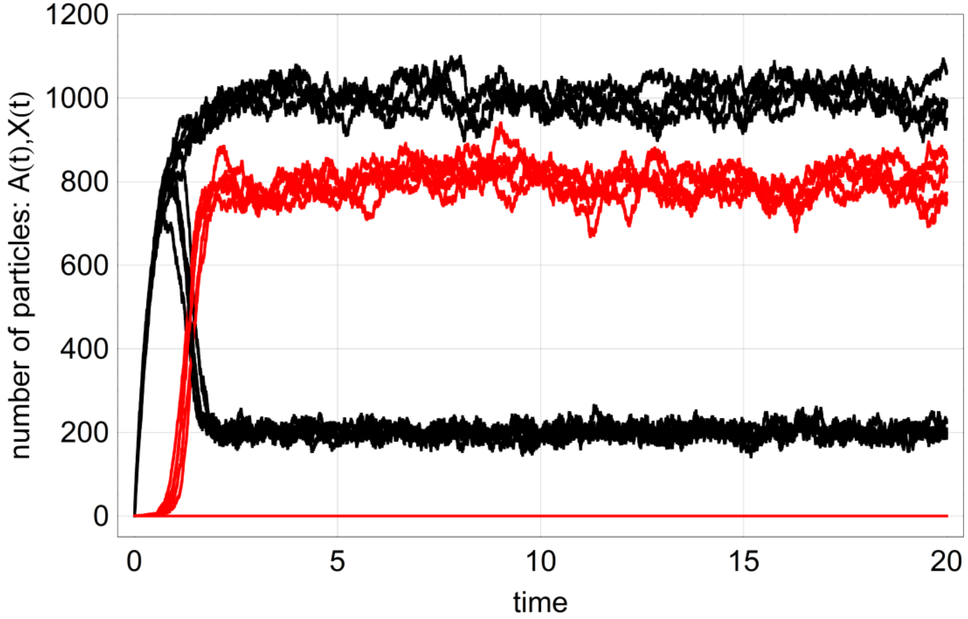
Approach of the reaction A+X$\rightarrow$2X towards the steady state in the flow reactor

initial condition *empty reactor*: A(0) = 0, X(0) = 1, convergence towards S_1



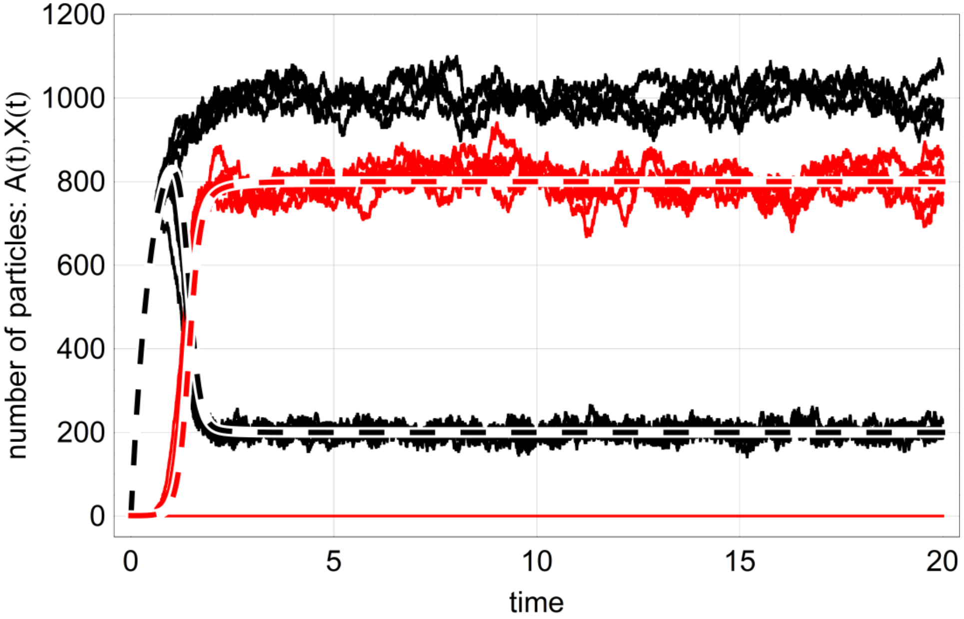
Approach of the reaction A+X$\rightarrow$2X towards the steady state in the flow reactor

initial condition *empty reactor*: A(0) = 0, X(0) = 1, convergence towards S_0



Approach of the reaction A+X→2X towards the steady states in the flow reactor

initial condition *empty reactor*: A(0) = 0, X(0) = 1

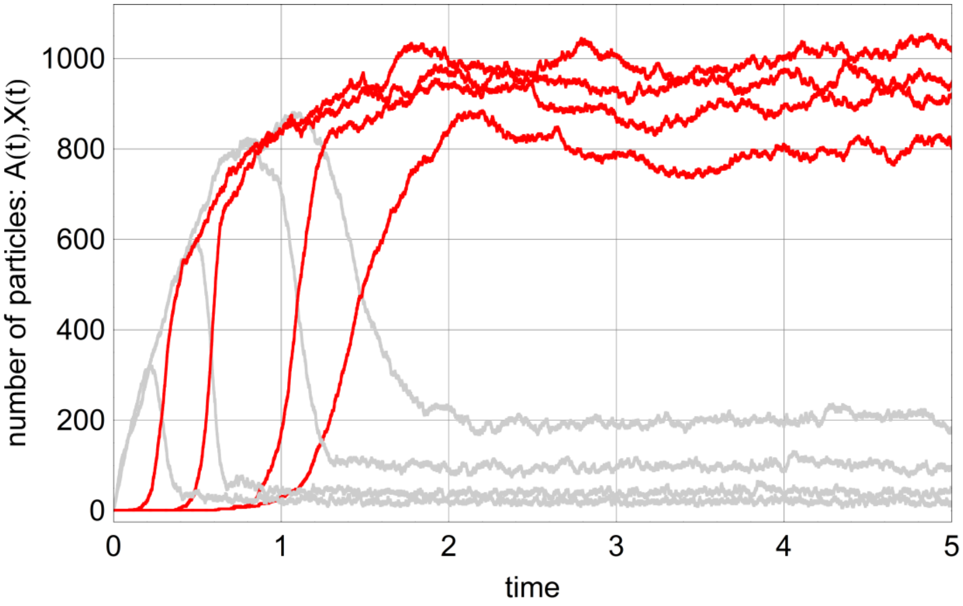


Approach of the reaction A+X→2X towards the steady states in the flow reactor

initial condition *empty reactor*: A(0) = 0, X(0) = 1; deterministic solution dashed autocatalysis, irreversible, first order, $A + X \longrightarrow 2X$: $r = 0.5$; $N = 1000$; $k = 0.01$; sample size: 10×100

	initial particle numer X(0)									
	1		2		3		4		5	
state	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
part.no.	**275**	**725**	**74**	**926**	**17**	**983**	**6**	**994**	**4**	**996**
$E \pm \sigma$	27.5 ± 3.5	72.5 ± 3.5	7.4 ± 3.2	92.6 ± 3.2	1.7 ± 1.0	98.3 ± 1.0	0.6 ± 0.7	99.4 ± 0.7	0.4 ± 0.7	99.6 ± 0.7

The stochastic trajectory approaches the steady states S_0 and S_1 with probabilities that depend strongly on the initial condition X(0).



Approach of the reaction A+X$\rightarrow$2X towards the steady state S_1 in the flow reactor

initial condition *empty reactor*: A(0) = 0, X(0) = 1; k = 0.01, 0.02, 0.05, 0.10

autocatalysis irreversible, first order, $A + X \longrightarrow 2X$: r = 2.0; seed = 491; sample size: 1000

Popul.size N	reaction rate parameter *k*					
	0.01		0.05		0.10	
	S_0	S_1	S_0	S_1	S_0	S_1
100	**1000**	**0**	**691**	**301**	**509**	**491**
400	**766**	**234**	**363**	**637**	**269**	**731**
1000	**506**	**494**	**243**	**757**	**178**	**822**

S_0: state of extinction, $A = C$, $X = 0$

S_1: state of reproduction, $A = r / k$, $X = C - r/k$

$C = A + X$

three classes of fluctuations with autocatalytic processes

(i)	thermal fluctuations	all chemical reactions	$\sigma \propto \sqrt{N}$
(ii)	stochastic delay	autocatalytic reactions	$\delta = \frac{X_0}{N} (\Delta X)_{\max} \cong \alpha = \text{const}$
(iii)	anomalous fluctuations	bistability	$\sigma = f(\Delta \overline{X}, \Delta \overline{P})$

Thermal fluctuations are universal in chemical kinetics in the sense that they occur with every reaction.

Stochastic delay is special for autocatalytic process with very small initial concentrations of the autocatalyst.

Anomalous fluctuations occur in systems with stochastic bifurcation points.
F. de Pasquale, P. Tartaglia, P. Tombesi. Lettere al Nuovo Cimento 28, 141- 145, 1980.

1. Autocatalysis in chemistry
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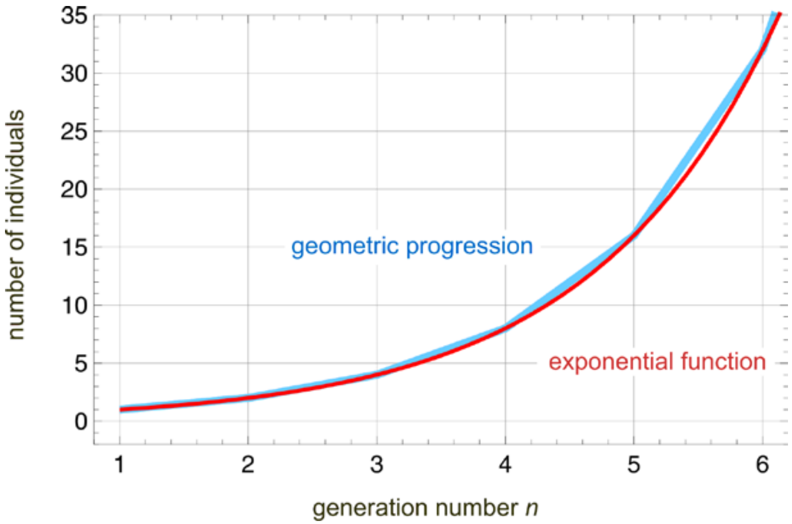
6. Concluding remarks

Thomas Robert Malthus,
1766 – 1834

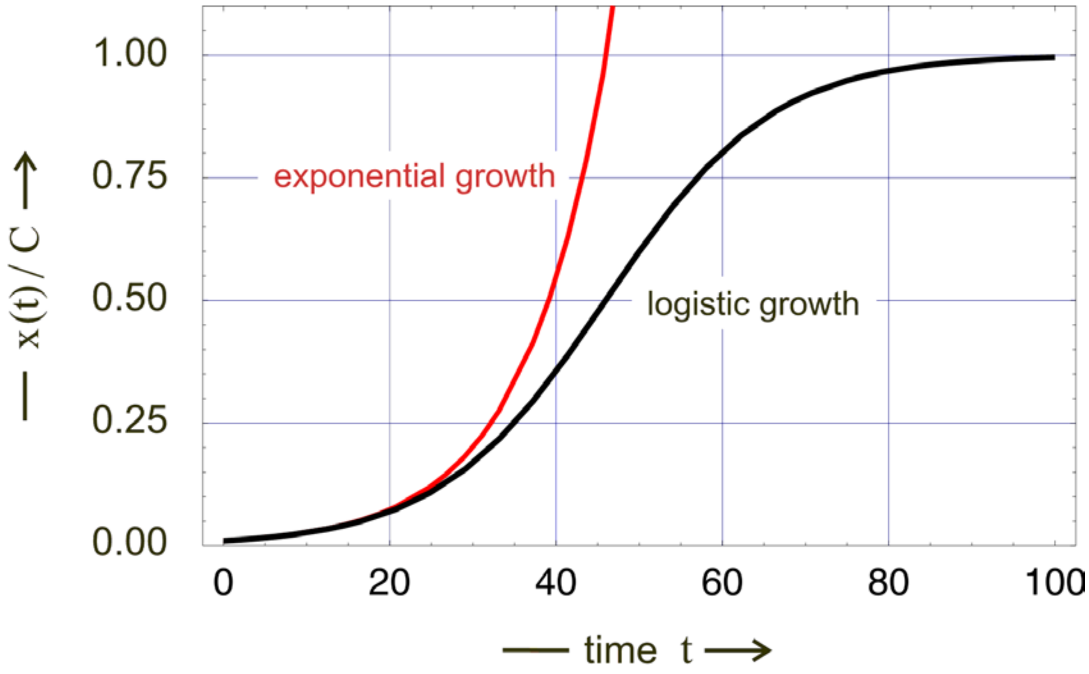
Leonhard Euler,
1717 – 1783

geometric progression

exponential function



Pierre-François Verhulst,
1804-1849



population: $\Pi = \{X\}$

the consequence of finite resources

$$\frac{dx}{dt} = f\,x\left(1 - \frac{x}{C}\right) \Rightarrow x(t) = \frac{C\,x_0}{x_0 + (C - x_0)\exp(-f\,t)}$$

the logistic equation: Verhulst 1838

Verhulst or logistic equation:

$$\frac{\mathrm{d}x}{\mathrm{d}t} \;=\; f\left(1-\frac{x}{C}\right)x \quad \text{with} \quad x(0) \;=\; x_0$$

$$x(t) \;=\; \frac{C\,x_0}{x_0 \,+\, (C-x_0)\,e^{-r\,t}}$$

basic structure of the equation:

$$\frac{\mathrm{d}x}{\mathrm{d}t} \;=\; \gamma_1\,x \;-\; \gamma_2\,x^2$$

chemical models:

$$(\mathsf{A}) + \mathsf{X} \;\underset{h}{\overset{f=k\cdot[\mathsf{A}]}{\rightleftarrows}}\; 2\,X$$

$$\frac{\mathrm{d}x}{\mathrm{d}t} \;=\; f\,x \;-\; h\,x^2$$

reversible autocatalytic reaction

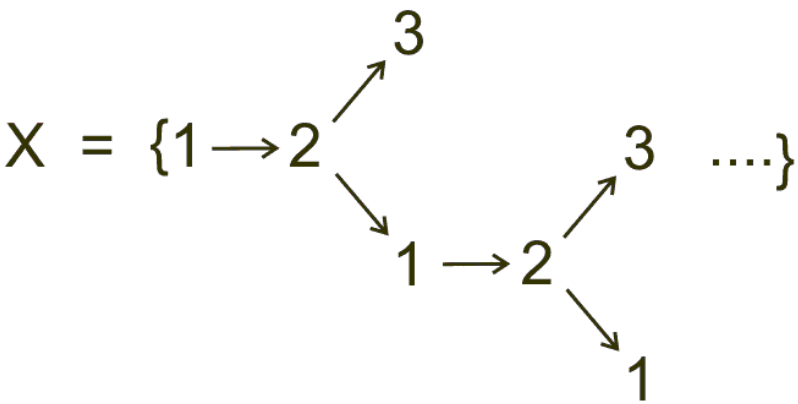
$$(\mathsf{A}) \,+\, \mathsf{X} \;\xrightarrow{f=k\cdot[\mathsf{A}]}\; 2\,\mathsf{X}\;,\;\; 2\,\mathsf{X} \;\xrightarrow{h}\; \varnothing$$

$$\frac{\mathrm{d}x}{\mathrm{d}t} \;=\; f\,x \;-\; \frac{h}{2}\,x^2$$

annihilation reaction

absorbing barrier: $X = 0 \;\rightarrow\; dx/dt = 0$

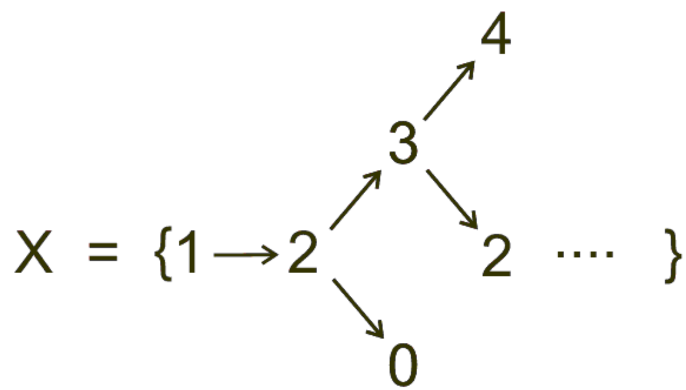
$A + X \rightarrow 2X$ and $2X \rightarrow A + X$



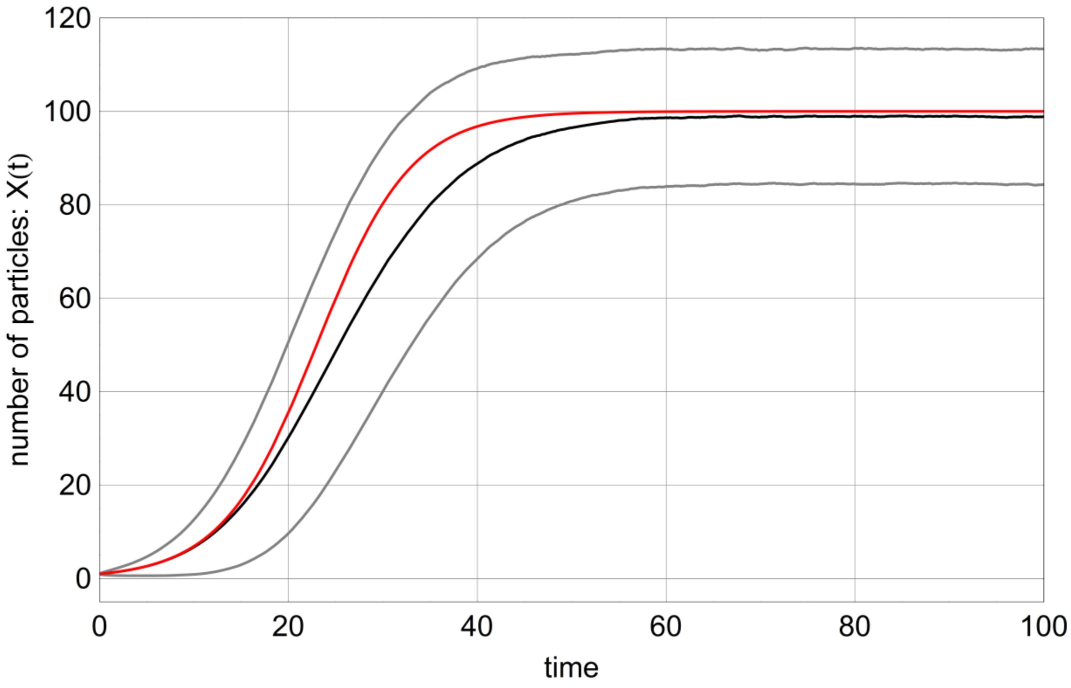
reversible autocatalytic reaction

reflecting barrier

$A + X \rightarrow 2X$ and $2X \rightarrow \varnothing$



annihilation reaction



logistic growth: A + X $\rightarrow$ 2 X, 2 X $\rightarrow \varnothing$, expectation value and deterministic solution logistic equation, f = 0.2, h = 0.001, 0.00025, 0.0001; seed: s = 491; sample size: 10 000 and 1000 for N=1000

Popul.size N		Initial particle numbers X_0					
		1	2	3	5	7	10
100	$t(\Delta X_{max})$	30.7891	26.8607	24.8953	22.3875	20.2627	18.9629
	ΔX_{max}	13.7409	7.70646	5.36579	3.22743	2.55490	1.90572
	$\mathbf{\Delta X_{max} X_0 / N}$	**0.1374**	**0.1541**	**0.1610**	**0.1614**	**0.1788**	**0.1906**
400	$t(\Delta X_{max})$	36.8968	32.7972	30.2315	27.2430	25.6571	24.0319
	ΔX_{max}	54.9010	29.7009	20.1191	12.4348	8.34684	6.44130
	$\mathbf{\Delta X_{max} X_0 / N}$	**0.1372**	**0.1485**	**0.1589**	**0.1554**	**0.1461**	**0.1610**
1000	$t(\Delta X_{max})$	82.5046	73.5525	69.1473	61.5956	59.5409	55.4158
	ΔX_{max}	136.575	71.6853	47.7226	30.1260	21.6830	14.1515
	$\mathbf{\Delta X_{max} X_0 / N}$	**0.1366**	**0.1434**	**0.1432**	**0.1506**	**0.1518**	**0.1415**

stochastic delay: $\delta = \Delta X_{max} X_0 / N$

logistic equation: $$X(t) = \frac{C X_0}{X_0 + (C - X_0) e^{-ft}}, \quad X_0 = X(0)$$

annihilation reaction: $(A) + X \rightarrow 2X,\ 2X \rightarrow \varnothing$

extinction in the logistic equation: N = 100; f = 0.2 ; h = 0.001 , sample size: 10 $\times$ 10000.

	X_0									
	1		2		3		4		5	
	X	extinct	X	extinct	X	extinct	X	extinct	X	extinct
numbers	**99443**	**557**	**99478**	**522**	**99988**	**12**	**99984**	**16**	**99999**	**1**
$E \pm \sigma$	9944.3 $\pm$ 7.5	55.7 $\pm$ 7.5	9947.8 $\pm$ 9.3	52.2 $\pm$ 9.3	9998.8 $\pm$ 1.0	1.2 $\pm$ 1.0	9998.4 $\pm$ 0.8	1.6 $\pm$ 0.8	9999.9 $\pm$ 0.3	0. 1$\pm$ 0.3

state of reproduction, S_1 and state of extinction S_0

$$\mathrm{X}: \ \lim_{t\to\infty} E\big(X(t)\big) = C \quad \text{and} \quad \text{extinct}: \ \lim_{t\to\infty} X(t) = 0$$

bistability in the logistic equation:

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$$\frac{\mathrm{d}x}{\mathrm{dt}} = f\,x\left(1 - \frac{x}{C}\right) \quad \Rightarrow \quad \frac{\mathrm{d}x}{\mathrm{dt}} = f\,x - \frac{x}{C}\,f\,x$$

$$f\,x \equiv \Phi(\mathrm{t}),\, C = 1: \quad \frac{\mathrm{d}x}{\mathrm{dt}} = x\left(f - \Phi\right)$$

$$\mathrm{X}_1, \mathrm{X}_2, \ldots, \mathrm{X}_n: \quad [\mathrm{X}_i] = x_i\,; \quad \sum_{i=1}^{n} x_i = C = 1$$

$$\boxed{\frac{\mathrm{d}x_j}{\mathrm{dt}} = x_j\left(f_j - \sum_{i=1}^{n} f_i\,x_i\right) = x_j\left(f_j - \Phi\right)}\,; \quad \Phi = \sum_{i=1}^{n} f_i\,x_i$$

Darwin

$$\boxed{\frac{\mathrm{d}\Phi}{\mathrm{dt}} = 2\left(< f^2 > - < \bar{f} >^2\right) = 2\,\mathrm{var}\{f\} \geq 0}$$

generalization of the logistic equation to *n* variables yields selection

$$\Pi = \{X_1, \dots, X_n\}$$

$$\boldsymbol{N}(t) = (N_1(t), \dots, N_n(t)) \; ; \quad C(t) = \sum_{j=1}^{n} N_j(t)$$

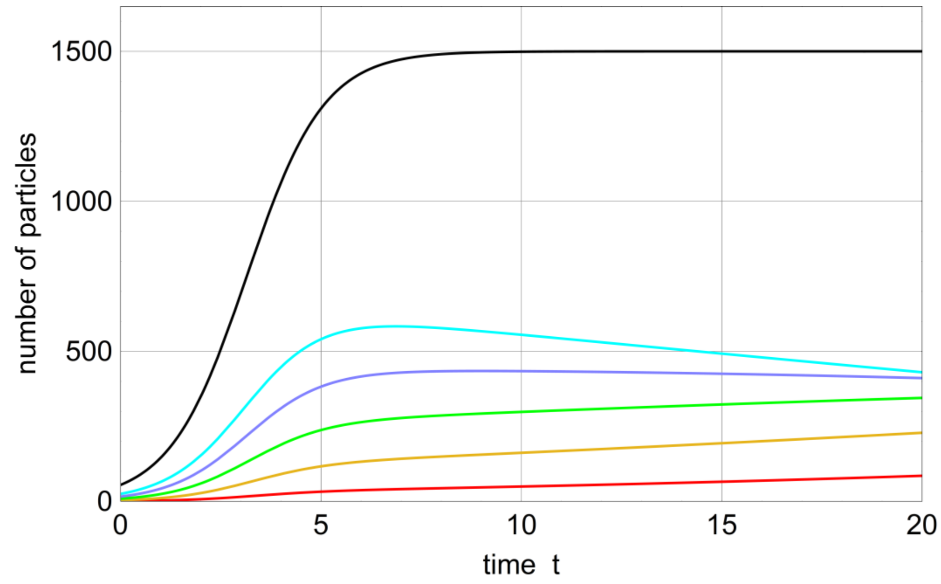
$$C(t) = \frac{C(0)\,K}{C(0) + \big(K - C(0)\big)\,e^{-\Phi}}$$

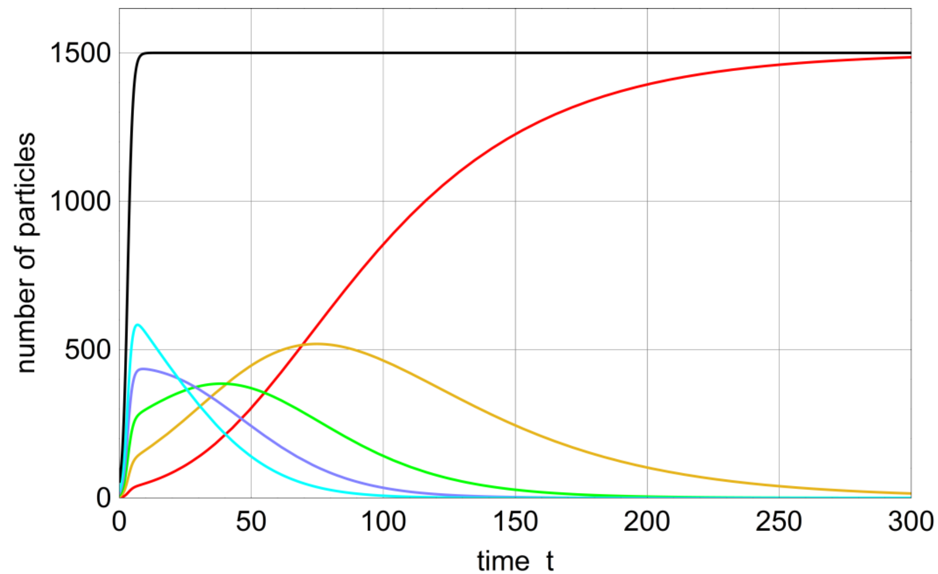
with $\Phi = \int_0^t \phi(\tau)\,d\tau$ and $\phi(t) = \frac{1}{C(t)} \sum_{i=1}^{n} f_i N_i(t)$

$$x_j(t) = \frac{N_j(t)}{C(t)} = \frac{x_j(0)\,e^{f_j t}}{\sum_{i=1}^{n} x_i(0)\,e^{f_i t}}$$

$$N(0) = (1,4,9,16,25)$$

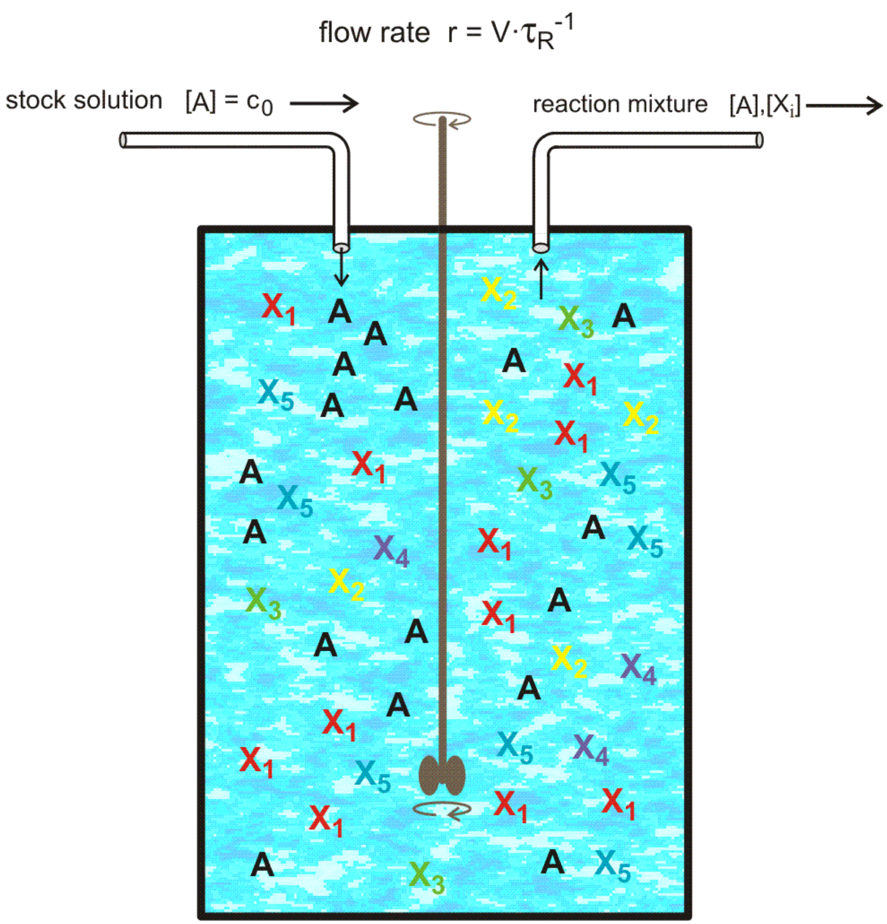
$$\boldsymbol{f} = (1.10, 1.08, 1.06, 1.04, 1.02)$$





population:

$$\Pi = \{X_1 , X_2 , X_3 , \ldots , X_n\}$$



$$* \xrightarrow{\;r\cdot c_0\;} \mathsf{A}$$

$$\mathsf{A} + \mathsf{X}_j \xrightarrow{\;f_j\;} 2\,\mathsf{X}_j\,,\ \ j = 1, 2, \ldots, n$$

$$\mathsf{A} \xrightarrow{\;r\;} \varnothing$$

$$\mathsf{X}_j \xrightarrow{\;r\;} \varnothing\,,\ \ j = 1, 2, \ldots, n$$

$$\frac{\mathrm{d}a}{\mathrm{d}t} = c_0\, r - a \left(\sum_{j=1}^{n} f_j\, x_j + r \right)$$

$$\frac{\mathrm{d}x}{\mathrm{d}t} = x\,(f_j\, a - r)\,,\ \ j = 1, 2, \ldots, n$$

selection in the flow reactor

$\Delta f / f$	t_e	Population size N = 100				Population size N = 200			
		$A(t_e)$	$X_1(t_e)$	$X_2(t_e)$	$X_3(t_e)$	$A(t_e)$	$X_1(t_e)$	$X_2(t_e)$	$X_3(t_e)$
0.0	600	**1.5** $\pm$ 1.3	**30.5** $\pm$ 3.9	**34.2** $\pm$ 4.6	**33.4** $\pm$ 4.1	**0.5** $\pm$ 0.9	**30.6** $\pm$ 4.6	**30.9** $\pm$ 5.0	**32.0** $\pm$ 4.7
0.02	600	**1.8** $\pm$ 1.4	**41.8** $\pm$ 4.8	**32.9** $\pm$ 3.8	**23.4** $\pm$ 4.0	**0.6** $\pm$ 0.8	**50.4** $\pm$ 5.7	**27.7** $\pm$ 4.9	**17.3** $\pm$ 2.6
0.04	400	**2.4** $\pm$ 2.1	**45.4** $\pm$ 5.0	**31.3** $\pm$ 4.5	**19.9** $\pm$ 2.5	**0.7** $\pm$ 0.8	**58.3** $\pm$ 4.6	**25.6** $\pm$ 4.5	**11.0** $\pm$ 2.9
0.1	400	**2.1** $\pm$ 1.7	**59.8** $\pm$ 5.5	**28.0** $\pm$ 4.1	**10.0** $\pm$ 2.9	**0.4** $\pm$ 0.5	**73.9** $\pm$ 4.1	**20.6** $\pm$ 3.5	**4.8** $\pm$ 1.9
0.2	400	**1.9** $\pm$ 1.1	**68.3** $\pm$ 4.5	**23.1** $\pm$ 3.7	**6.7** $\pm$ 2.8	**0.5** $\pm$ 0.7	**76.6** $\pm$ 4.1	**19.3** $\pm$ 2.8	**3.6** $\pm$ 1.7
0.4	400	**2.3** $\pm$ 1.8	**71.7** $\pm$ 6.0	**20.8** $\pm$ 5.2	**5.2** $\pm$ 2.4	**0.9** $\pm$ 0.6	**82.0** $\pm$ 4.2	**13.8** $\pm$ 3.8	**3.3** $\pm$ 1.7
1.0	200	**2.7** $\pm$ 2.4	**78.4** $\pm$ 4.7	**15.8** $\pm$ 3.3	**3.1** $\pm$ 1.5	**0.9** $\pm$ 0.9	**83.6** $\pm$ 4.0	**12.6** $\pm$ 3.2	**2.9** $\pm$ 1.5
1.8	200	**4.3** $\pm$ 1.1	**80.8** $\pm$ 2.9	**13.6** $\pm$ 3.1	**1.3** $\pm$ 1.2	**1.5** $\pm$ 1.3	**83.8** $\pm$ 3.3	**12.7** $\pm$ 2.5	**2.0** $\pm$ 1.7

n = 3: $\mathbf{X}_1$, $f_1 = f + \Delta f / 2f$; $\mathbf{X}_2$, $f_2 = f$; $\mathbf{X}_3$, $f_3 = f - \Delta f / 2f$; $f = 0.1$

initial particle numbers: $X_1(0) = X_2(0) = X_3(0) = 1$

probability of selection

$$
\begin{aligned}
* &\xrightarrow{d = c_0\, r} \mathsf{A}\,, \\
\mathsf{A} + \mathsf{Y} &\xrightarrow{k_1} \mathsf{X} + \mathsf{Y}\,, \\
\mathsf{A} + \mathsf{X} &\xrightarrow{k_2} \mathsf{X} + \mathsf{Y}\,, \\
\mathsf{A} &\xrightarrow{r} \varnothing\,, \\
\mathsf{X} &\xrightarrow{r} \varnothing\,, \quad \text{and} \\
\mathsf{Y} &\xrightarrow{r} \varnothing\,.
\end{aligned}
$$

$$
\begin{aligned}
\frac{\mathrm{d}a}{\mathrm{d}t} &= -\left(k_1 y + k_2 x\right) a + \left(c_0 - a\right) r\,, \\
\frac{\mathrm{d}x}{\mathrm{d}t} &= k_1\, a\, y - r\, x\,, \quad \text{and} \\
\frac{\mathrm{d}y}{\mathrm{d}t} &= k_2\, a\, x - r\, y\,,
\end{aligned}
$$

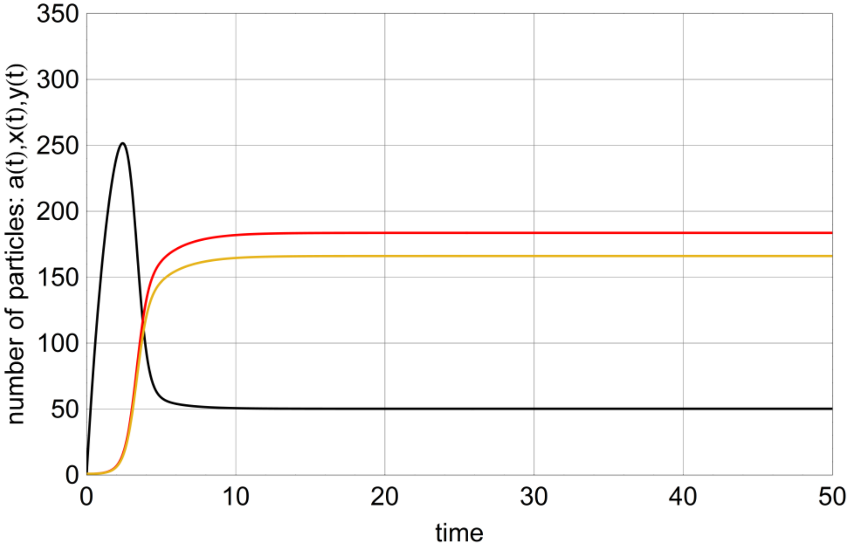
new variables: $z = x + y$

$$
\begin{aligned}
\zeta &= \sqrt{k_2}\, x - \sqrt{k_1}\, y \\
&= \kappa_2\, x - \kappa_1\, y
\end{aligned}
$$

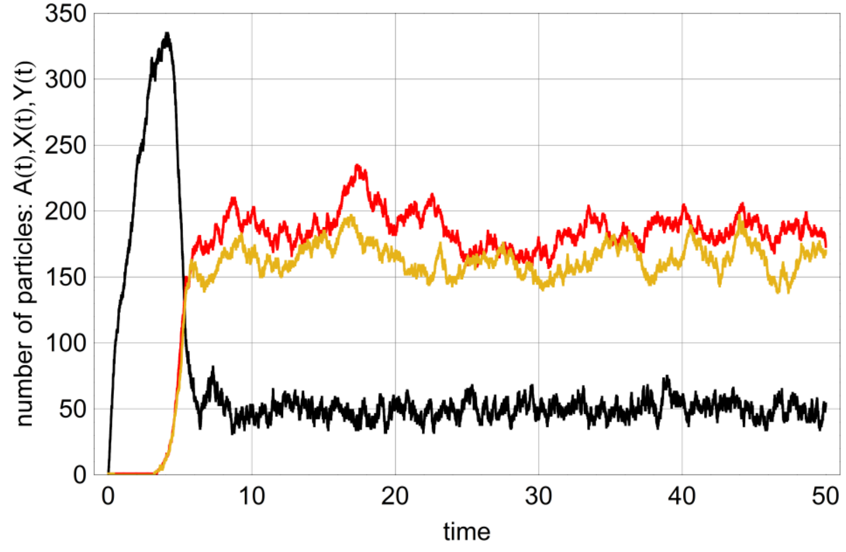
$$
\begin{aligned}
\frac{\mathrm{d}a}{\mathrm{d}t} &= -\Big(\gamma\, z - (\kappa_1 - \kappa_2)\, \zeta\Big)\, a + (c_0 - a)\, r\,, \\
\frac{\mathrm{d}z}{\mathrm{d}t} &= (\gamma\, a - r)\, z + (\kappa_2 - \kappa_1)\, a\, \zeta\,, \\
\frac{\mathrm{d}\zeta}{\mathrm{d}t} &= -(\gamma\, a + r)\, \zeta\,. \qquad \gamma = \sqrt{k_1 k_2}
\end{aligned}
$$

$$S_0 = (\overline{a}, \overline{x}, \overline{y}) = (c_0, 0, 0) \qquad S_1 = \Big(r/\gamma, (\gamma c_0 - r)/(\gamma + k_2), (\gamma c_0 - r)/(\gamma + k_1)\Big)$$

plus-minus replication



deterministic trajectory



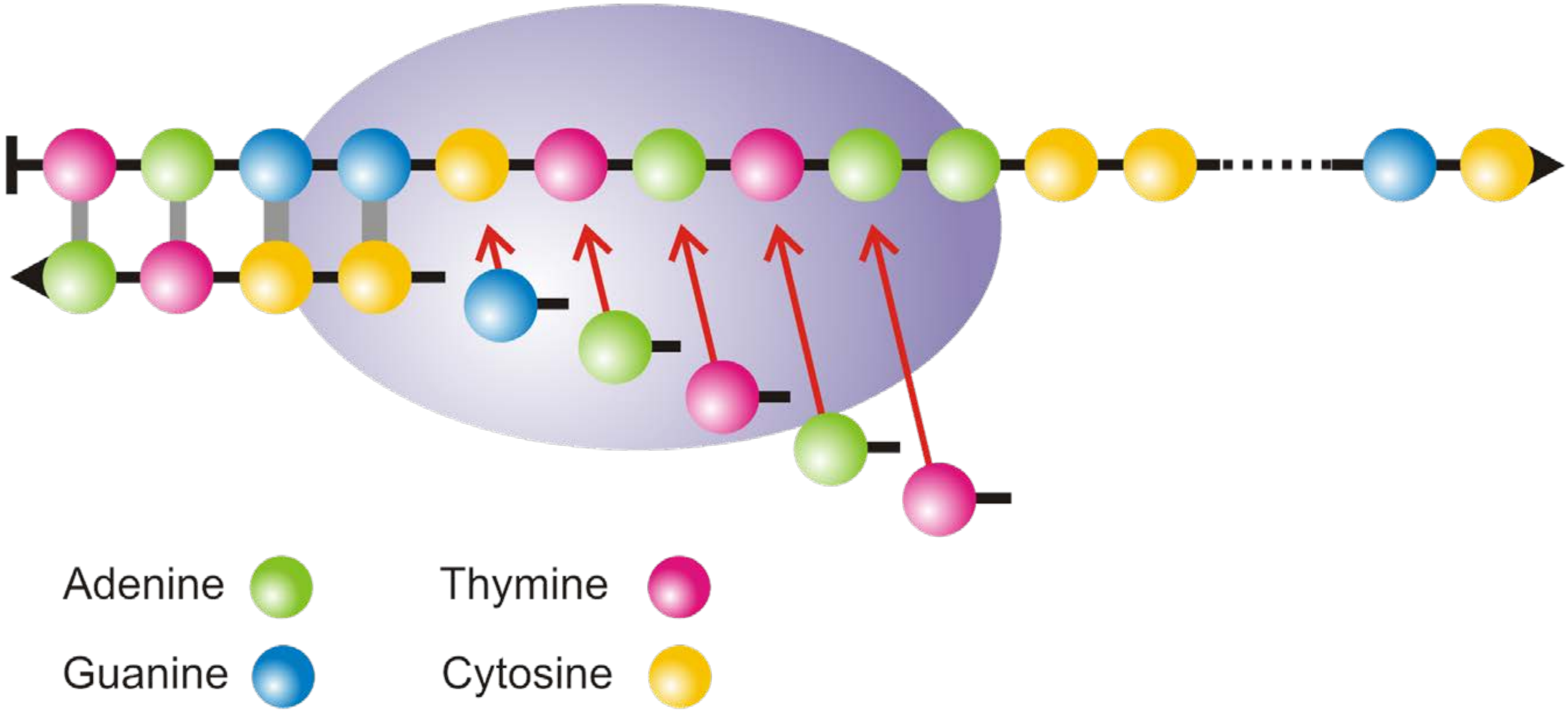
stochastic trajectory

$$* \xrightarrow{c_0\, r} \mathsf{A}\,,\ \mathsf{A} + \mathsf{X} \xrightarrow{k_1} \mathsf{X} + \mathsf{Y}\,,\ \mathsf{A} + \mathsf{Y} \xrightarrow{k_2} \mathsf{X} + \mathsf{Y}\,,$$

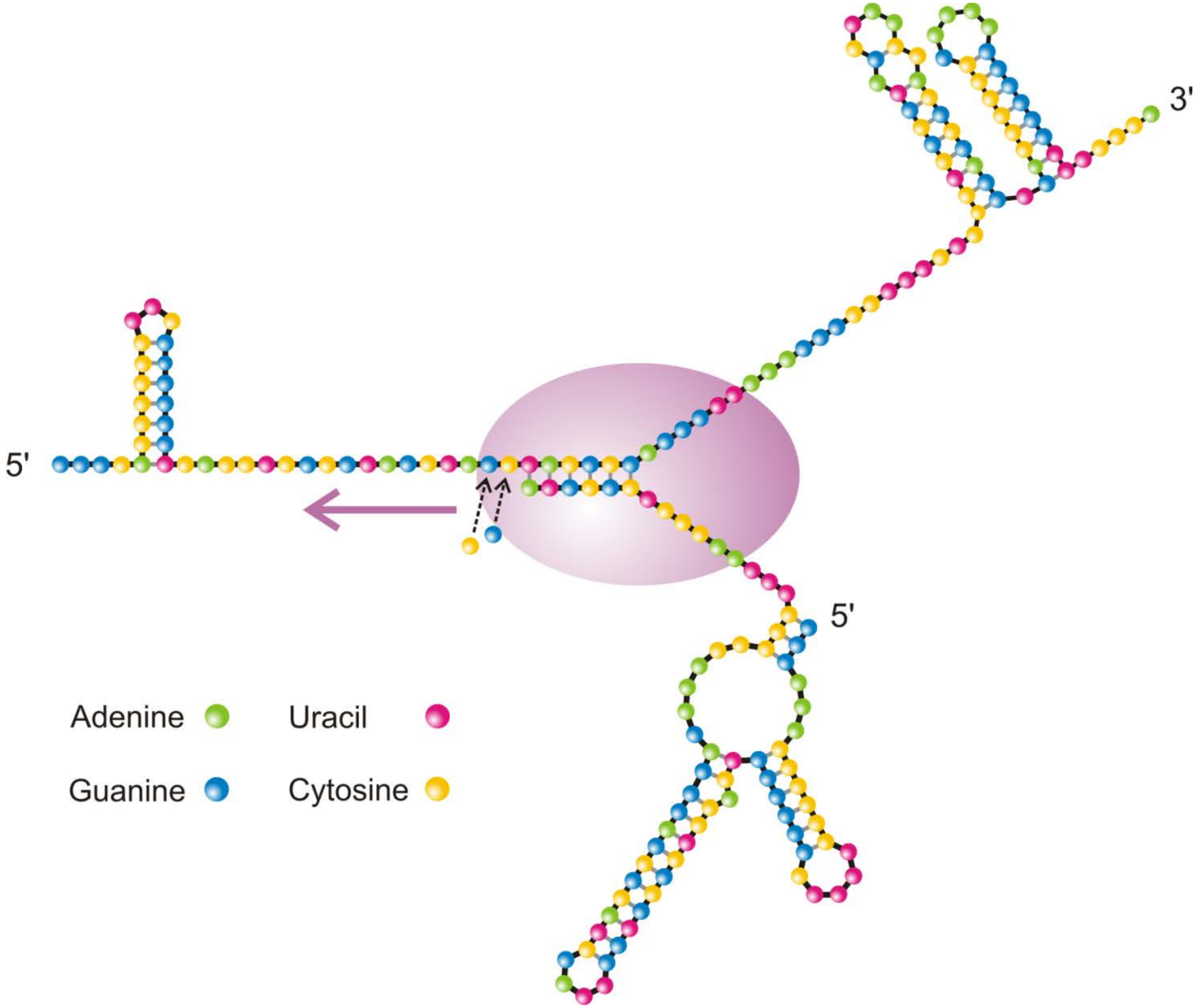
$$\mathsf{A}, \mathsf{X}, \mathsf{Y} \xrightarrow{r} 0$$

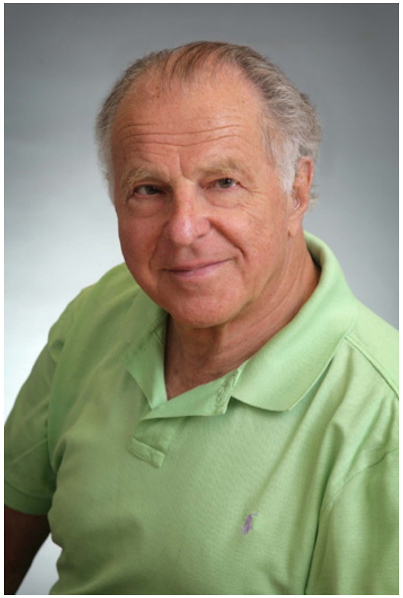
$k_1 = 0.011$, $k_2 = 0.09$, $r = 0.5$, N = 400

plus-minus replication in the flow reactor



the logic of DNA (or RNA) replication and mutation

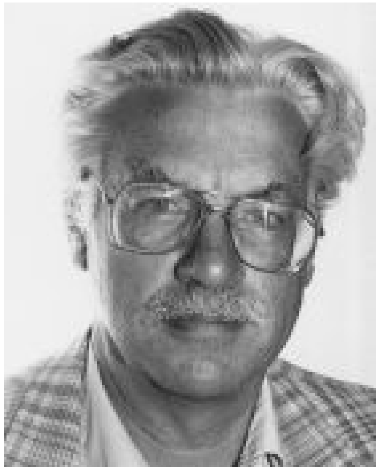




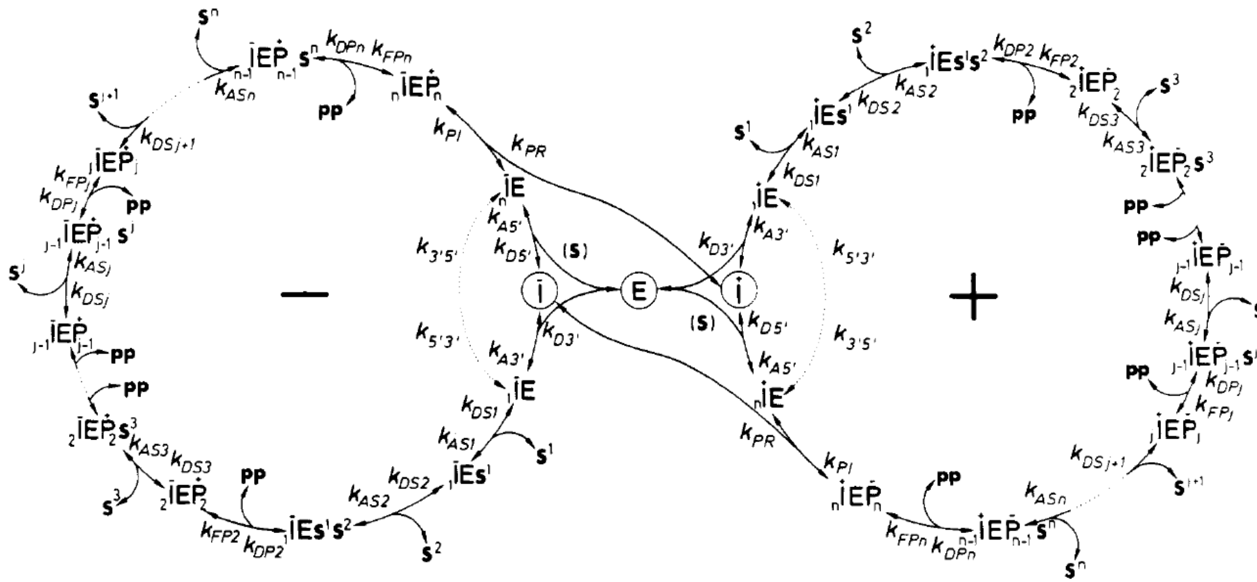
Charles Weissmann
1931-

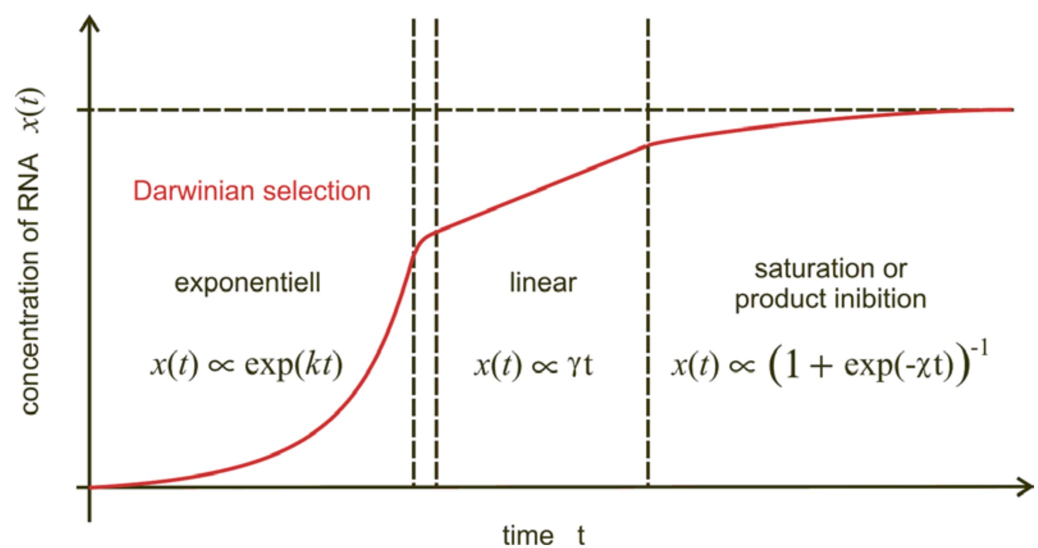
RNA replication by Qβ-replicase

C. Weissmann, ***The making of a phage***.
FEBS Letters **40** (1974), S10-S18



Christof K. Biebricher,
1941-2009





kinetics of RNA replication

C.K. Biebricher, M. Eigen, W.C. Gardiner, Jr.
Biochemistry **22**:2544-2559, 1983

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Autocatalysis is commonly not represented by a single elementary step but appears as the results of complex many-step reaction networks.

Complex autocatalytic processes in reaction networks often give rise to simple over-all kinetics under suitable conditions.

Fluctuations in autocatalytic processes consist of
(i) stochastic delay and (ii) anomalous fluctuations besides the common thermal fluctuations.

Thank you for your attention!

Web-Page for further information:

http://www.tbi.univie.ac.at/~pks