What is special about autocatalysis ?

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Institutsseminar TBI

Wien, 27.06.2018

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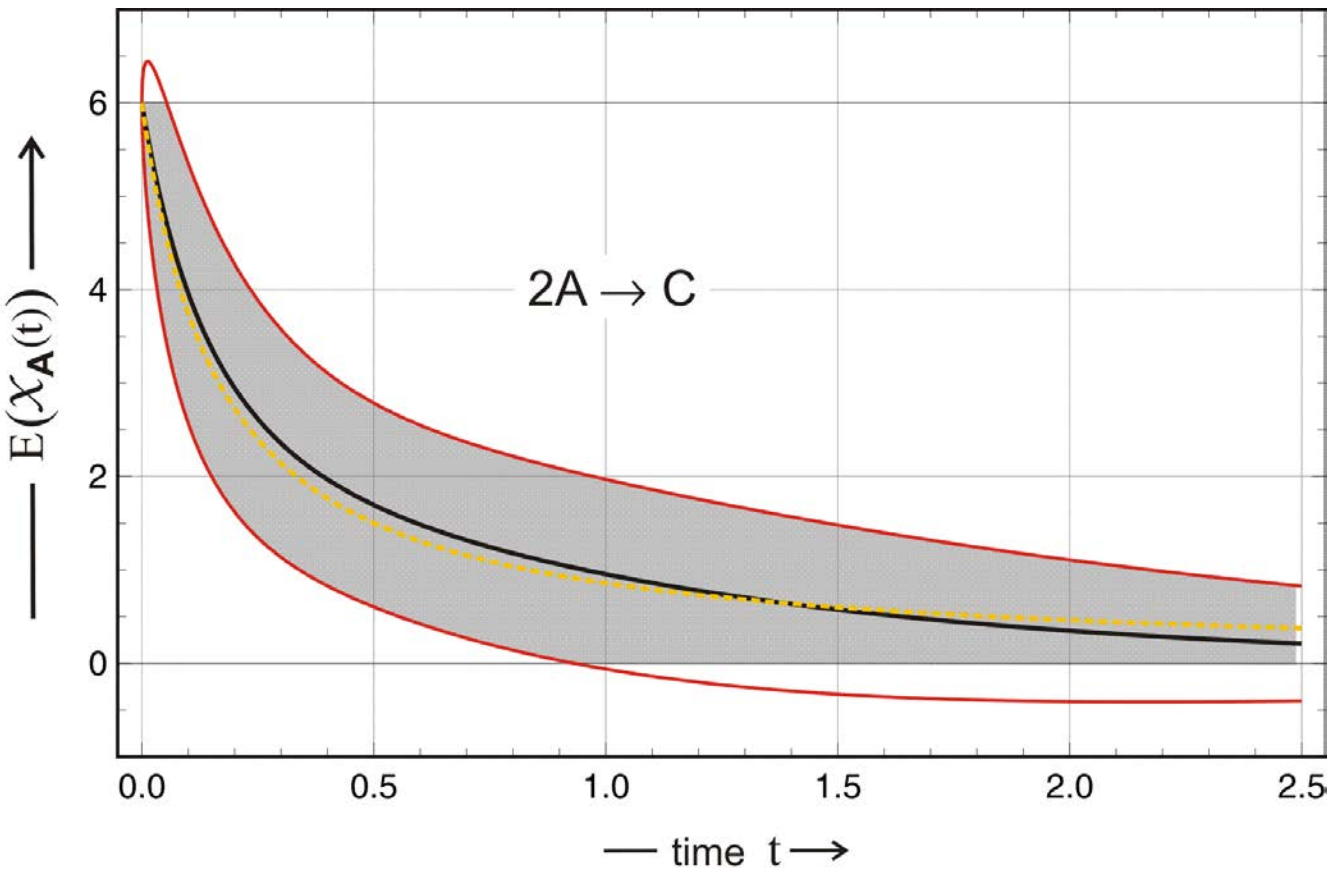
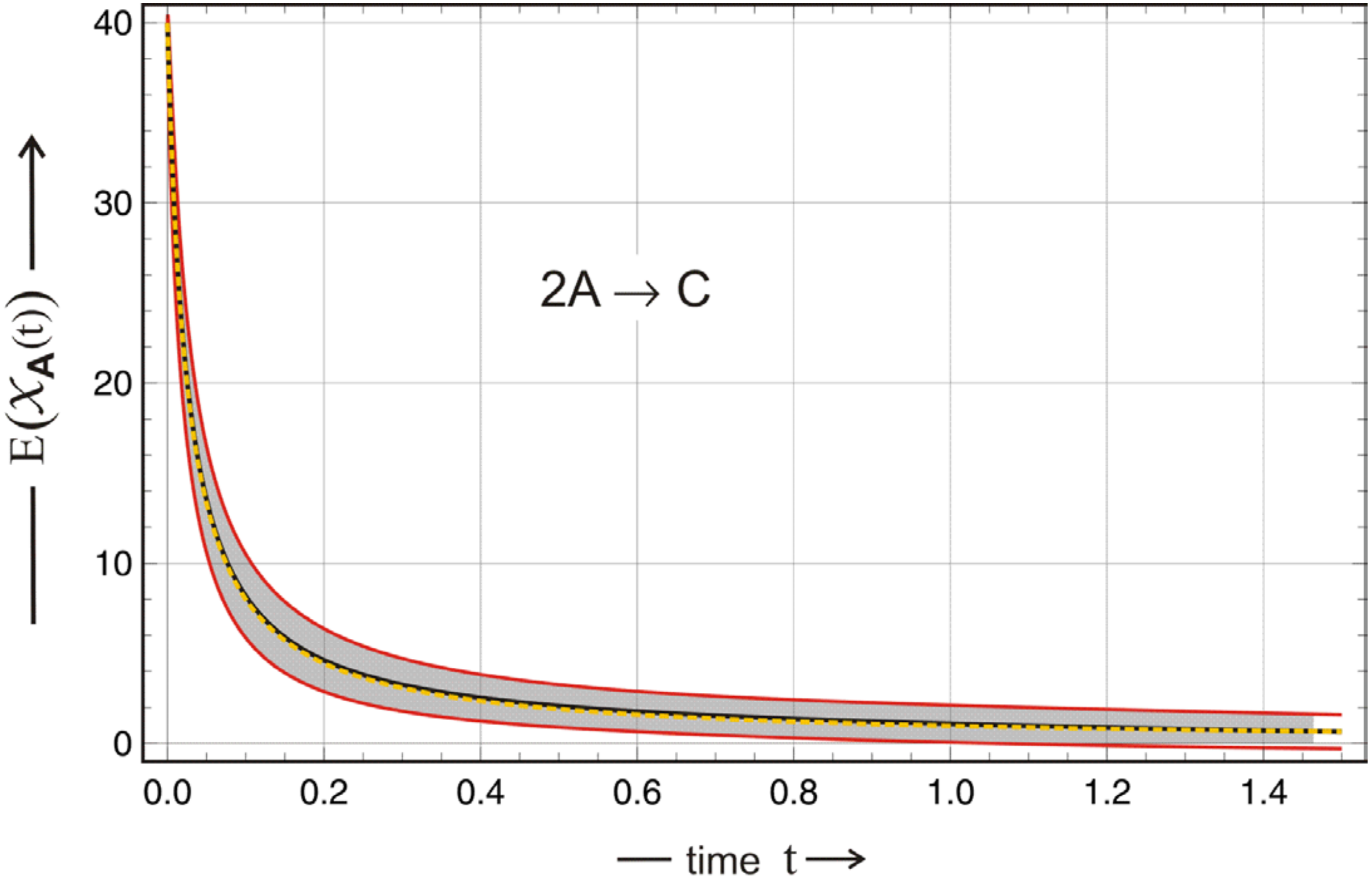


parameters: $k = 1$ [$N^{-1}t^{-1}$], $A_0 = 6$

Fluctuations in the dimerization reaction $2A \rightarrow C$



parameters: $k = 1$ [$N^{-1}t^{-1}$], $A_0 = 40$

Fluctuations in the dimerization reaction 2A → C

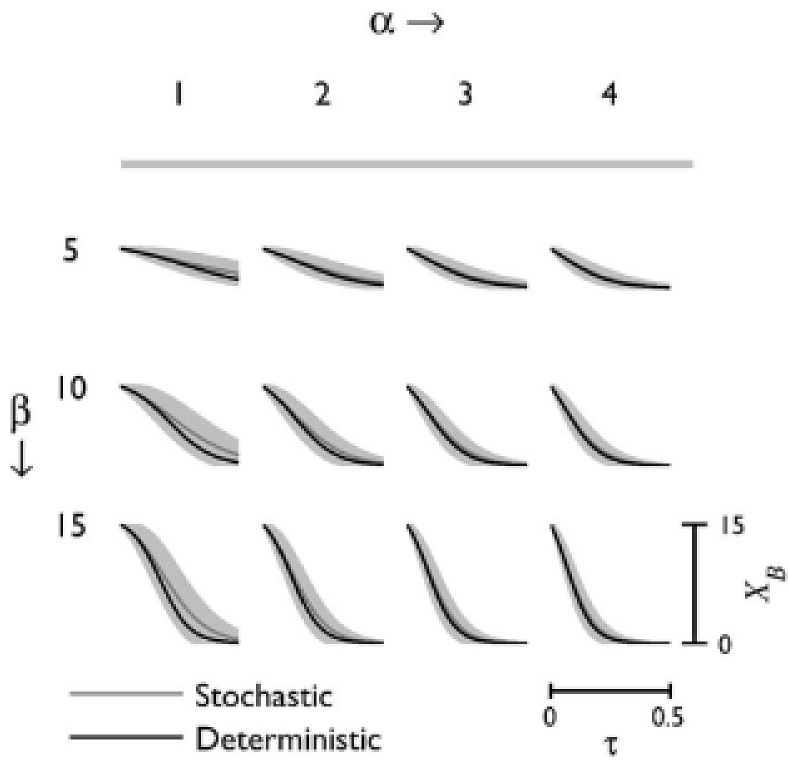
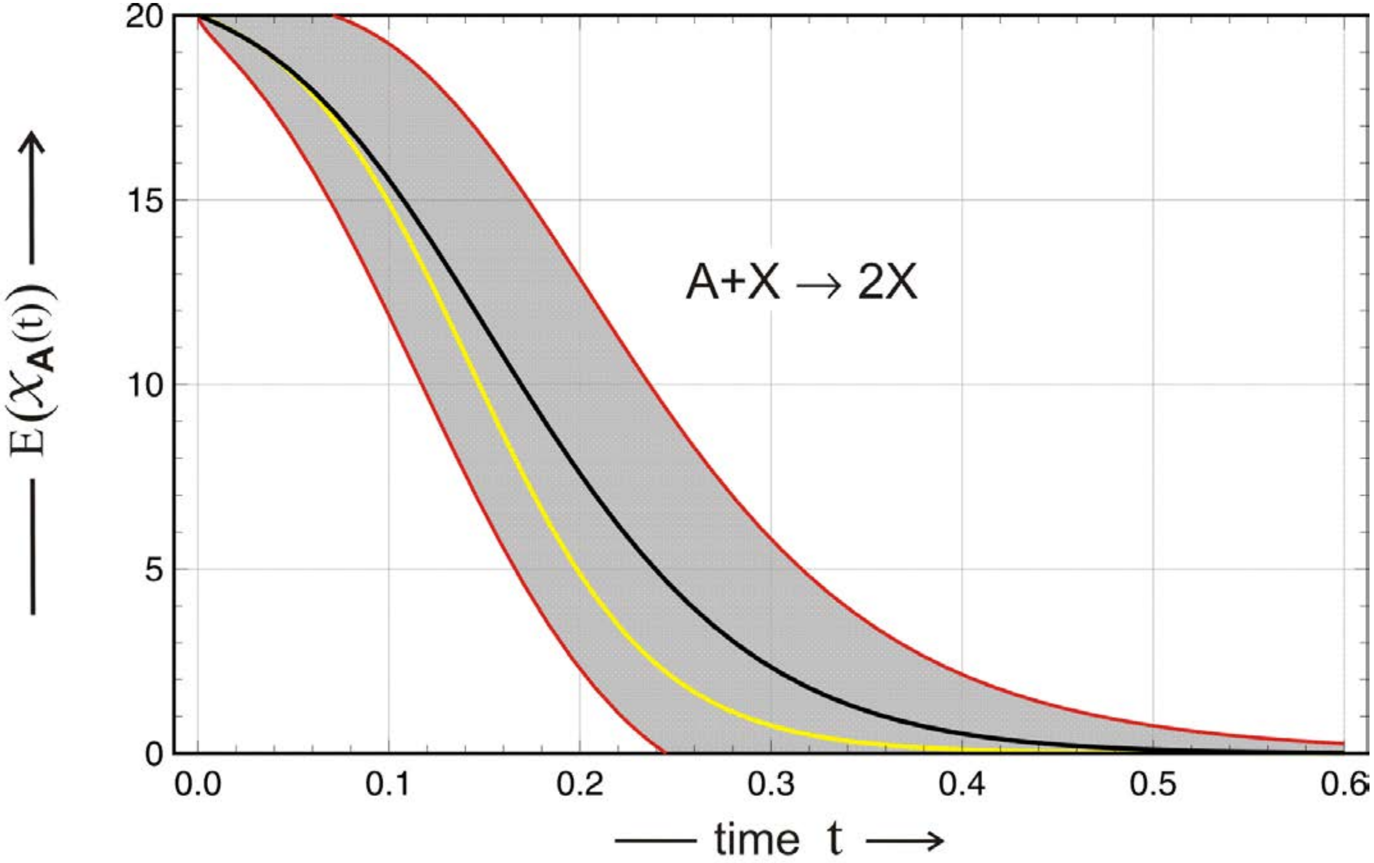


FIG. 3. Time evolution of the average number of noncatalytic (B) molecules undergoing irreversible autocatalysis. The shaded bands delineate single-standard-deviation envelopes about the mean. The average number of non-catalytic molecules decreases monotonically, but considerable fluctuations are evident for low initial populations of catalytic species (A).

E. Arslan, L.J. Laurenzi. Kinetis of autocatalysis in small systems. J.Chem.Phys. 128:e015101, 2008

Fluctuations in the autocatalytic reaction $A+X \rightarrow 2X$

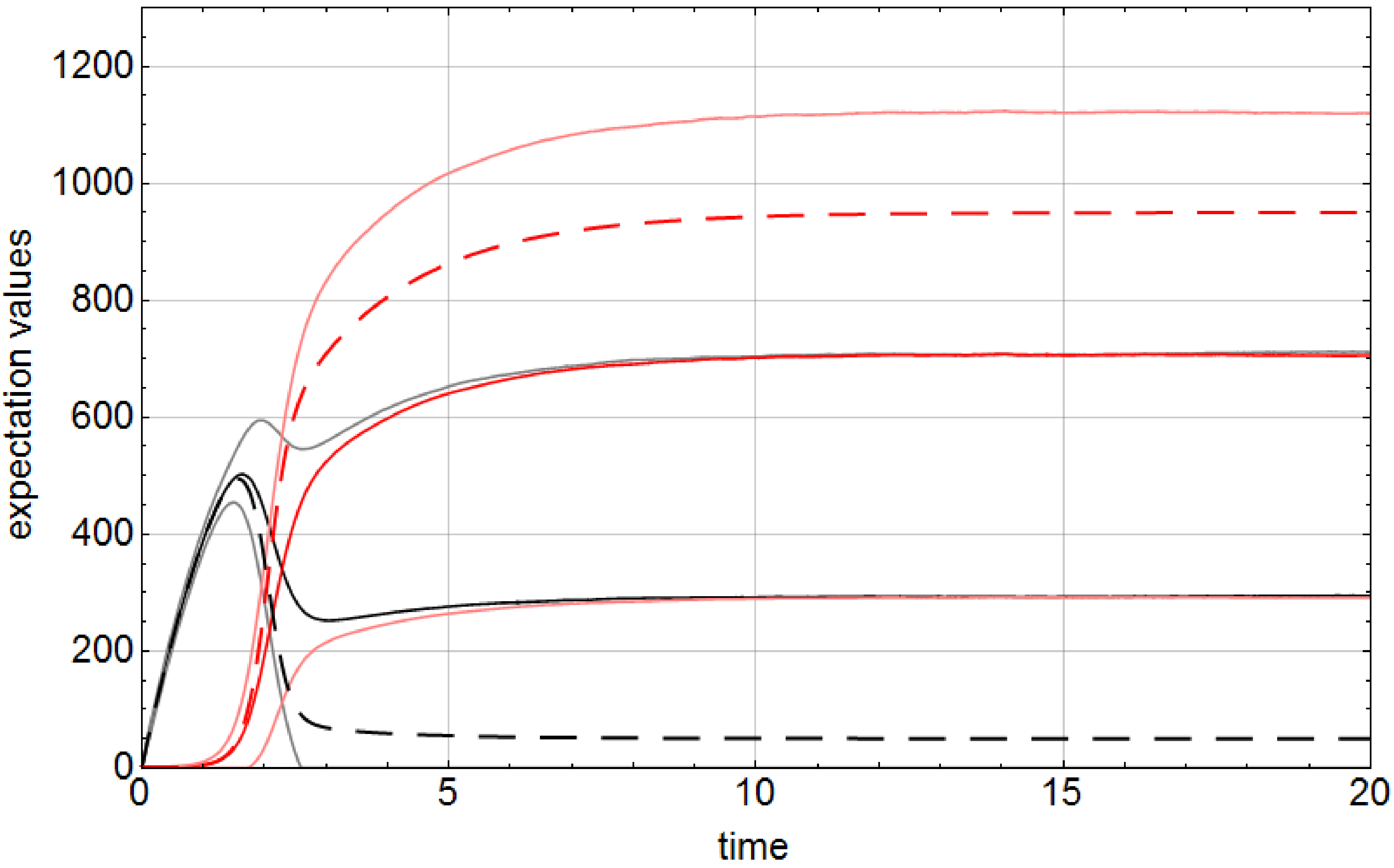


parameters: $k = 1\ [\mathrm{N}^{-1}t^{-1}]$, $A_0 = 20$, $X_0 = 1$

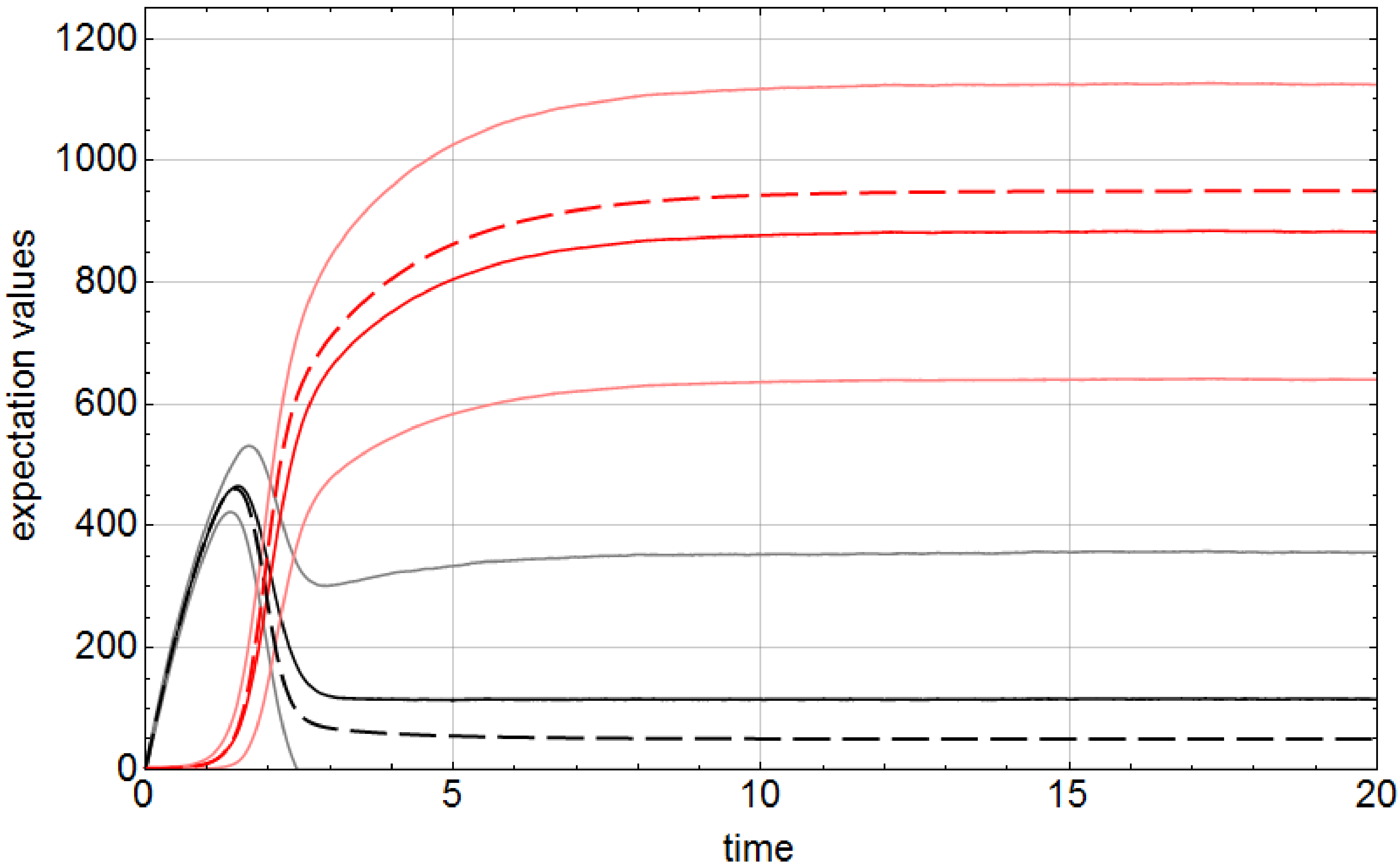
Fluctuations in the autocatalytic reaction A+X → 2X

Sources of stochasticity in autocatalytic reactions

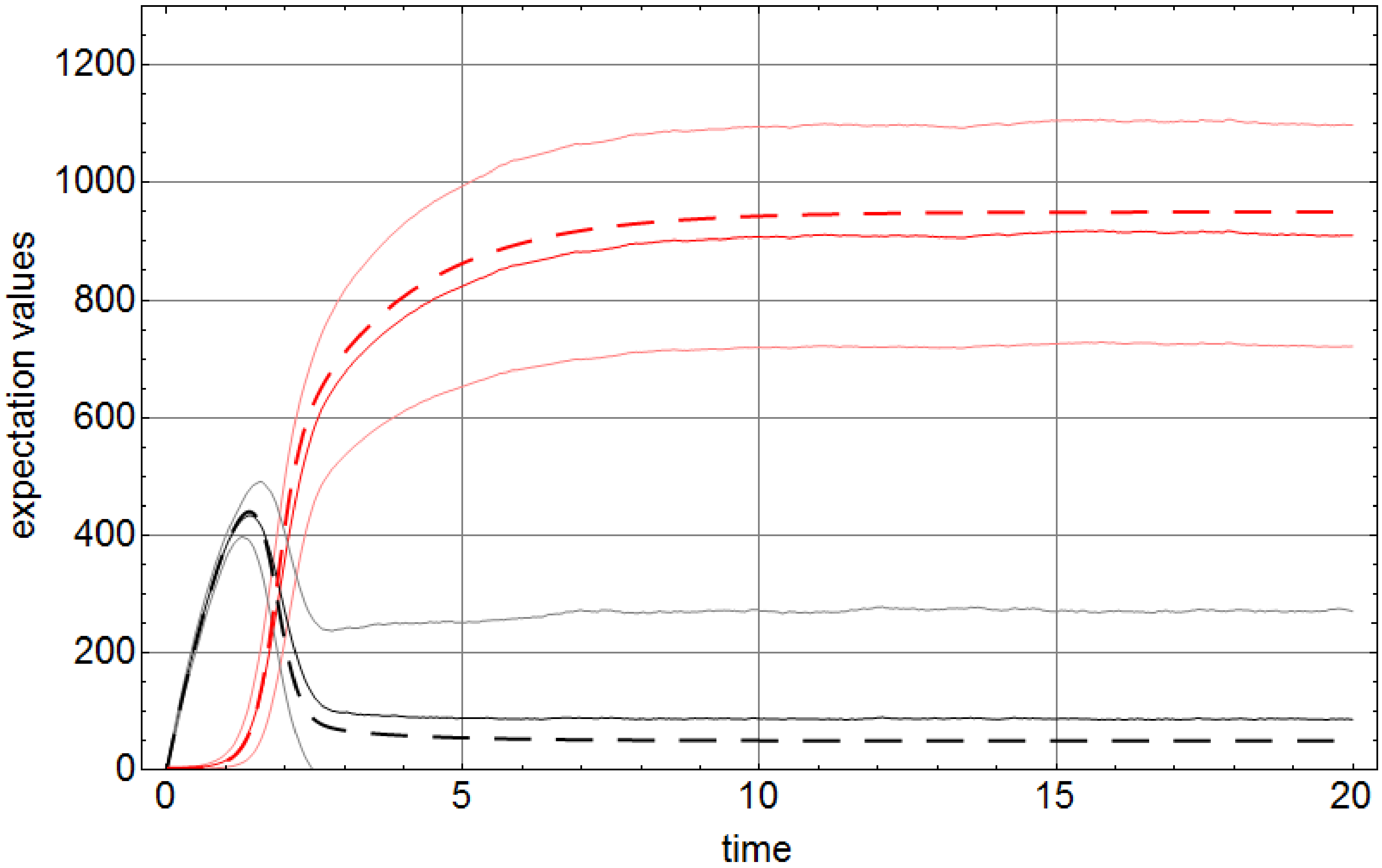
1. Thermal fluctuations
2. **Multiple (quasi)stationary states**
3. Stochastic delay



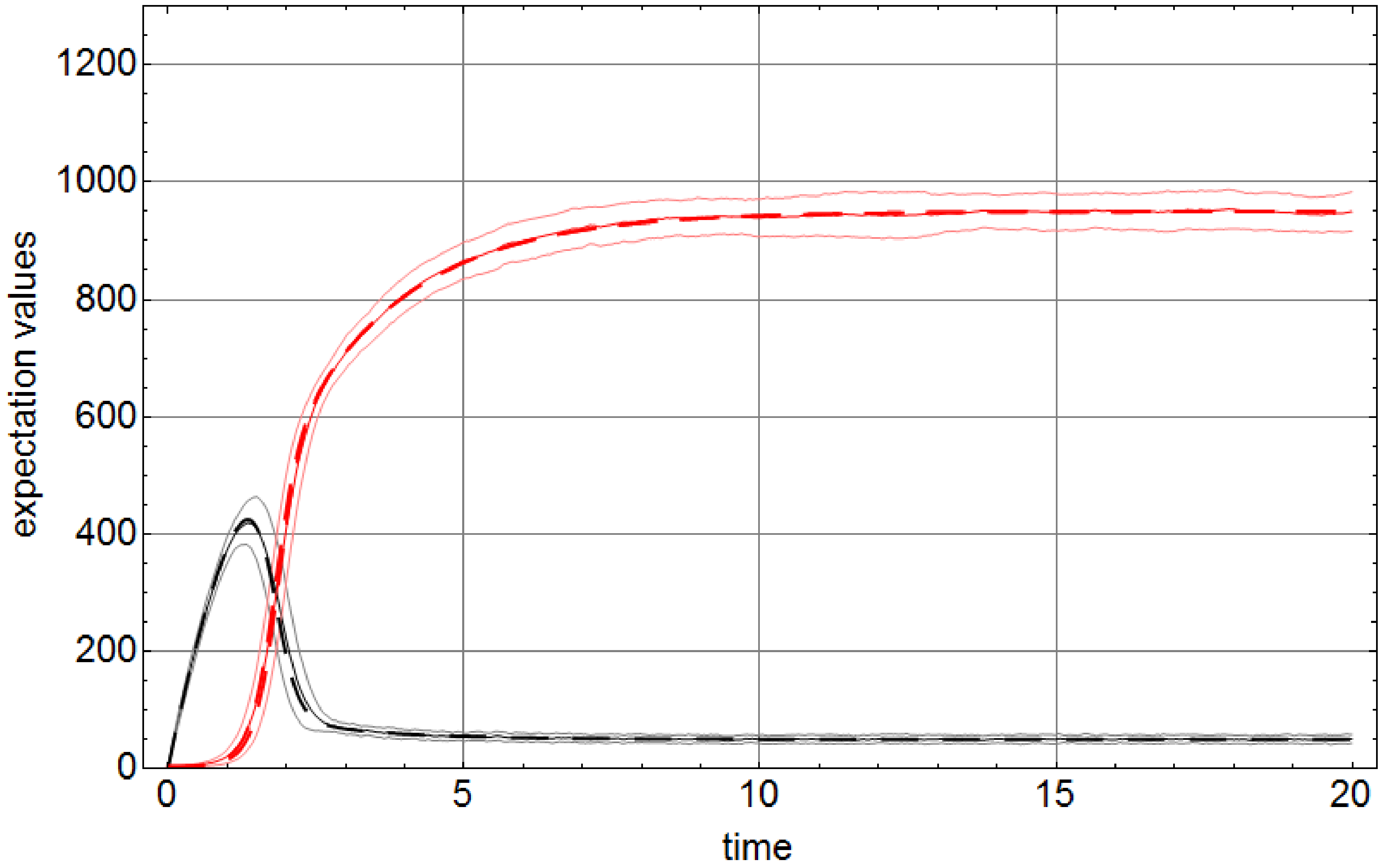
Autocatalysis A+X → 2X in the flow reactor: N=1000, X(0)=1



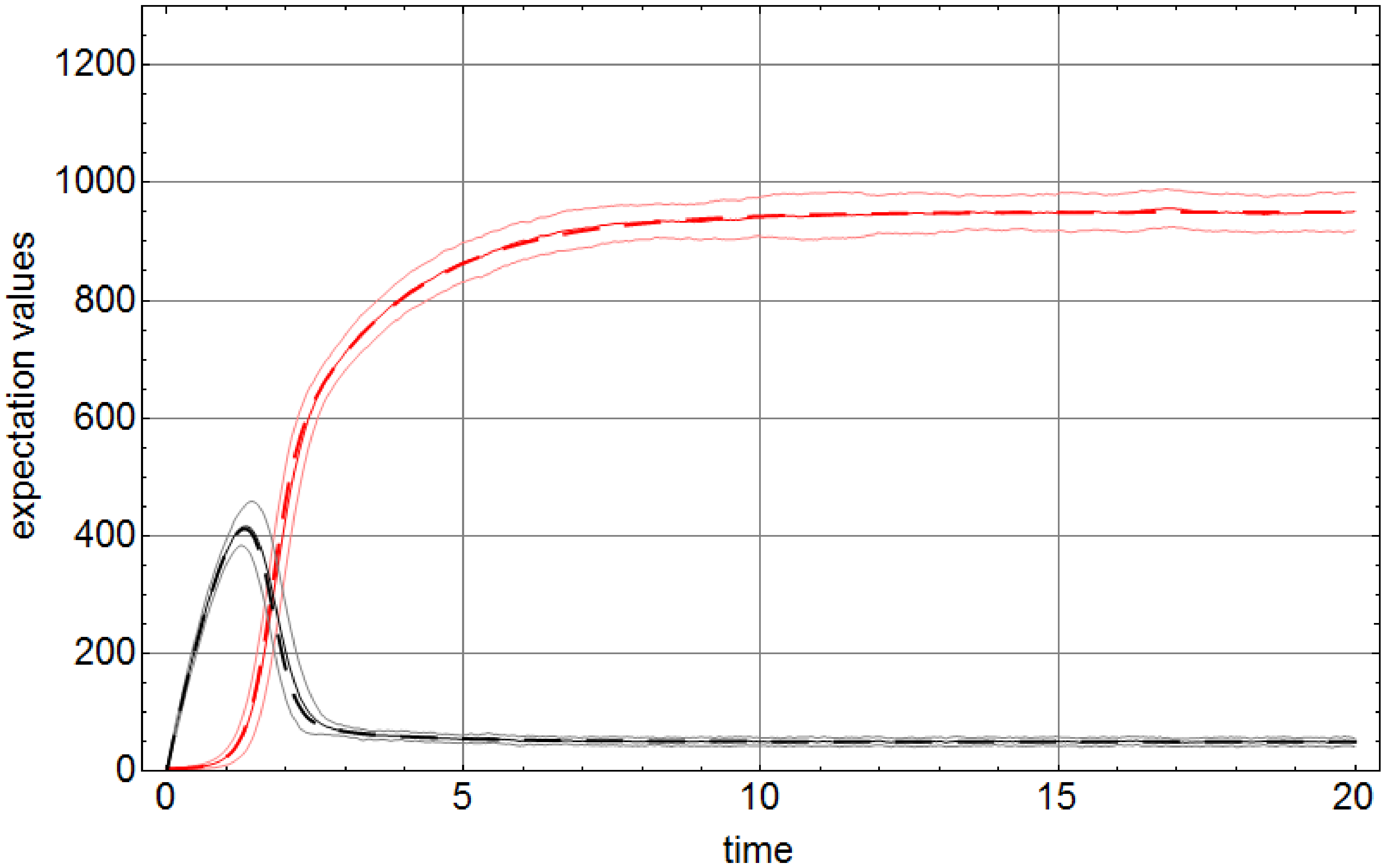
Autocatalysis A+X $\rightarrow$ 2X in the flow reactor: N=1000, X(0)=2



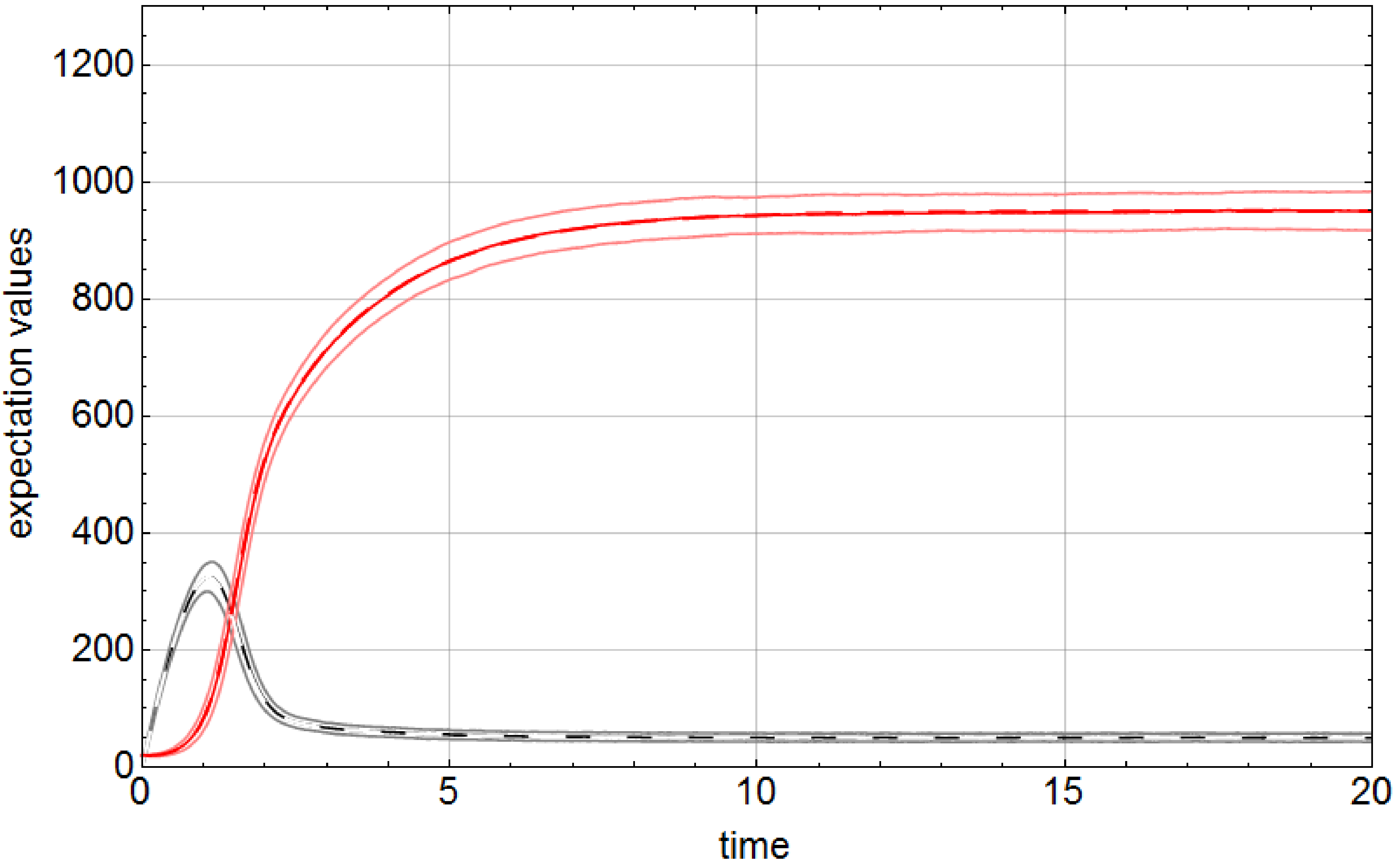
Autocatalysis A+X $\rightarrow$ 2X in the flow reactor: N=1000, X(0)=3



Autocatalysis A+X → 2X in the flow reactor: N=1000, X(0)=4



Autocatalysis A+X $\rightarrow$ 2X in the flow reactor: N=1000, X(0)=5



Autocatalysis A+X → 2X in the flow reactor: N=1000, X(0)=20

Chemical species	Initial values $X(0)$					
	1	2	3	4	5	20
A	27.5 ± 3.5	7.4 ± 3.2	1.7 ± 0.95	0.6	0.4	0
X	72.5 ± 3.5	92.6 ± 3.2	98.3 ± 0.95	99.4	99.6	100

Table 1.3 Probabilities of long-time survival of autocatalysts. The table presents numerical values for probability of survival of autocatalysts in the flow reactor. Population size: $N = 1000$; $k = 0.01\,[N^{-1}t^{-1}]$; flow rate: $d = 0.5\,[\mathrm{V}^{-1}]$.

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

Table 2: **Probability of selection of three subspecies with initial particle numbers** $X_1(0)=X_2(0)=X_3(0)=1$**.** The values are selection probabilities times 100 for the three subspecies $X_1(t_e)$, $X_2(t_e)$, and $X_3(t_e)$; $A(t_e)$ is the probability of extinction $X_1(t_e) = X_2(t_e) = X_3(t_e) = 0$. Choice of parameters: $\Delta f = f_1 - f_3, f = 0.1$ $[M^{-1} \cdot t^{-1}]$, $f_1 = f + \Delta f/2$ $[M^{-1} \cdot t^{-1}]$, $f_2 = f$ $[M^{-1} \cdot t^{-1}]$, $f_3 = f - \Delta f/2$ $[M^{-1} \cdot t^{-1}]$, and t_e is the computer time of the simulation.[l] The external parameters of the flow reactor are $d = 0.5$ $[V\ t^{-1}]$, and $a_0 = N/2$.

$X_1(0)=X_2(0)=X_3(0)$	t_e	N	**A**(t_e)	**X_1**(t_e)	**X_2**(t_e)	**X_3**(t_e)
1	400	100	**2.1** $\pm$ 1.7	**59.8** $\pm$ 5.5	**28.0** $\pm$ 4.1	**10.0** $\pm$ 2.9
2	400	100	**0.1** $\pm$ 0.3	**73.5** $\pm$ 4.2	**22.4** $\pm$ 4.4	**4.0** $\pm$ 1.4
3	400	100	**0**	**77.0** $\pm$ 4.5	**20.7** $\pm$ 4.1	**2.3** $\pm$ 1.6
4	400	100	**0**	**79.7** $\pm$ 3.1	**18.2** $\pm$ 4.1	**2.1** $\pm$ 1.3
5	600	100	**0**	**83.2** $\pm$ 4.8	**14.5** $\pm$ 4.6	**2.3** $\pm$ 1.8
10	600	100	**0**	**85.8** $\pm$ 3.8	**13.4** $\pm$ 3.7	**0.8** $\pm$ 0.8

Table 3: **Dependence of selection probabilities on initial conditions** $X_1(0)$, $X_2(0)$, and $X_3(0)$. The values are selection probabilities times 100 for the three subspecies $X_1(t_e)$, $X_2(t_e)$, and $X_3(t_e)$; $A(t_e)$ is the probability of extinction $X_1(t_e) = X_2(t_e) = X_3(t_e) = 0$. Choice of selection coefficient: $\Delta f / f = 0.1$,.and $f = 0.1$ $[M^{-1} \cdot t^{-1}]$. Further parameters see caption of table 2.

$\Delta f / f$	t_e	N	$A(t_e)$	$X_1(t_e)$	$X_2(t_e)$	$X_3(t_e)$
0.4	400	100	**2.3** ± 1.8	**71.7** ± 6.0	**20.8** ± 5.2	**5.2** ± 2.4
0.4	400	200	**0.9** ± 0.6	**82.0** ± 4.2	**13.8** ± 3.8	**3.3** ± 1.7
0.4	200	400	**0.1** ± 0.3	**86.3** ± 4.6	**12.4** ± 4.0	**1.2** ± 1.2
0.4	100	800	**0**	**90.6** ± 2.3	**8.5** ± 2.0	**0.9** ± 1.0
1.0	200	100	**2.7** ± 2.4	**78.4** ± 4.7	**15.8** ± 3.3	**3.1** ± 1.5
1.0	200	200	**0.9** ± 0.9	**83.6** ± 4.0	**12.6** ± 3.2	**2.9** ± 1.5
1.0	200	400	**0.2** ± 0.4	**88.9** ± 3.3	**9.5** ± 2.4	**1.4** ± 1.0
1.0	100	800	**0**	**91.8** ± 2.4	**7.5** ± 2.0	**0.7** ± 0.7
1.8	200	100	**4.3** ± 1.1	**80.8** ± 2.9	**13.6** ± 3.1	**1.3** ± 1.2
1.8	200	200	**1.5** ± 1.3	**83.8** ± 3.3	**12.7** ± 2.5	**2.0** ± 1.7
1.8	200	400	**0.6** ± 0.7	**88.8** ± 3.1	**9.0** ± 3.2	**1.6** ± 1.5
1.8	100	800	**0.1** ± 0.3	**93.7** ± 2.5	**5.7** ± 2.4	**0.5** ± 0.7

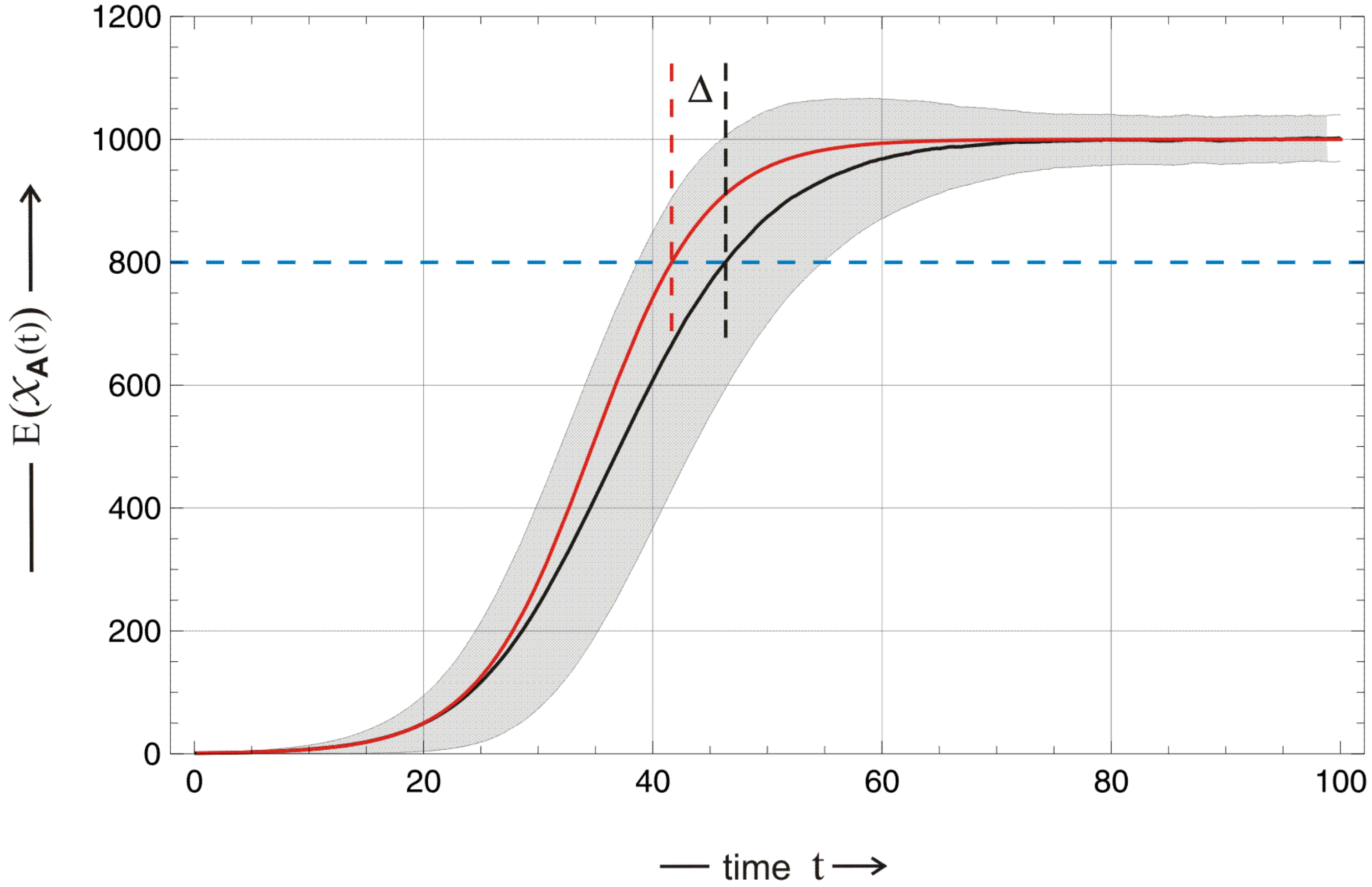
Table 4: **Dependence of selection probabilities on population size N.** The values are selection probabilities times 100 for the three subspecies $X_1(t_e)$, $X_2(t_e)$, and $X_3(t_e)$; $A(t_e)$ is the probability of extinction, which implies $X_1(t_e) = X_2(t_e) = X_3(t_e) = 0$. Initial conditions: $X_1(0) = X_2(0) = X_3(0) = 1$; mean fitness $f = 0.1$ $[M^{-1} \cdot t^{-1}]$. Further parameters see caption of table 2.

Sources of stochasticity in autocatalytic reactions

1. Thermal fluctuations

2. Multiple (quasi)stationary states

3. **Stochastic delay**



Definition of the stochastic delay Δ

Population size N	Initial values $X(0)$ 1	2	5	10	20
100	10.12	5.37	2.15	1.25	0.59
400	9.61	4.67	1.88	0.89	0.45
1000	9.30	4.52	1.69	0.95	0.43

Table 1.1 Stochastic delay. The table presents numerical values for the stochastic delay in the solutions of the logistic equation. As a measure for the stochastic delay we compute the difference in time $\Delta t = t_1 - t_2$ between the times at which the expectation value $E\big(X(t_1)\big)$ and the deterministic value $x(t_2)$ reach 80 % of the crying capacity K with the definitions $t_1 : E\big(X(t_1)\big) = 0.8 \times K$ and $t_2 : x(t_2) = 0.8 \times K$. The value "0.8" was chosen empirically since the effect is about largest at this population size.

Population size N	Initial values $X(0)$ 1	2	5	10	20	40
100	23.26	10.86	3.98	1.53*	0.56*	-0.01*
400	23.78	11.73	4.38	1.99	0.96	0.43
1000	23.54	11.66	4.29	2.12	0.99	0.54

* Values appear to be too small because of small population size N effects (see text).

Table 1.2 Stochastic delay. The table presents numerical values for the stochastic delay in the solutions of the two-step autocatalytic reaction. As a measure for the stochastic delay we compute the difference in time $\Delta t = t_1 - t_2$ between the times at which the expectation value $E\big(X(t_1)\big)$ and the deterministic value $x(t_2)$ reach 80 % of the crying capacity K with the definitions $t_1 : E\big(X(t_1)\big) = 0.8 \times K$ and $t_2 : x(t_2) = 0.8 \times K$. The value "0.8" was chosen empirically since the effect is about largest at this population size.

Thank you for your attention!

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