Supporting Information for

Sigmoidal Nucleation and Growth Curves Across Nature Fit by the Finke-Watzky Model of Slow Continuous Nucleation and Autocatalytic Growth: Explicit Formulas for the Lag and Growth Times Plus Other Key Insights

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A. <u>Derivations of the rate, acceleration, and jerk by hand: First, second and third derivatives of [B]$_t$</u>

To simplify derivations, the following constants were set:
X = k_1
Y= $k_2[A]_0$
Z = $k_1 + k_2[A]_0$

Equation (5) in the main text can then be rewritten as:

$$\boldsymbol{[B]_t = [A]_0\left(1 - \frac{k_1 + k_2[A]_0}{k_2[A]_0 + k_1\mathrm{e}^{(k_1+k_2[A]_0)t}}\right)}$$

$$[B]_t = [A]_0 - [A]_0\frac{Z}{Y + Xe^{Zt}}$$

The first derivative of [B]$_t$ leads to **Equation (6)** in the main text:

$$\frac{d[B]_t}{dt} = \frac{d\left(-[A]_0\frac{Z}{Y + Xe^{Zt}}\right)}{dt}$$

$$\frac{d[B]_t}{dt} = -[A]_0 Z\ \frac{d\left(\frac{1}{Y + Xe^{Zt}}\right)}{dt}$$

$$\frac{d[B]_t}{dt} = -[A]_0 Z\left(\frac{-1}{(Y + Xe^{Zt})^2}\right)\frac{d(Y + Xe^{Zt})}{dt}$$

$$\frac{d[B]_t}{dt} = -[A]_0 Z\left(\frac{-1}{(Y + Xe^{Zt})^2}\right)ZXe^{Zt}$$

$$\frac{d[B]_t}{dt} = X[A]_0\cdot e^{Zt}\cdot\left(\frac{Z}{Y + Xe^{Zt}}\right)^2$$

$$\boldsymbol{\frac{\mathbf{d}[B]_t}{\mathbf{d}t} = k_1[A]_0\cdot\mathrm{e}^{(k_1+k_2[A]_0)t}\cdot\left(\frac{k_1 + k_2[A]_0}{k_2[A]_0 + k_1\mathrm{e}^{(k_1+k_2[A]_0)t}}\right)^2}$$

The second derivative of [B]$_t$ leads to **Equation (7)** in the main text:

$$\frac{d^2[B]_t}{dt^2} = \frac{d\left(X[A]_0\ e^{Zt}\left(\frac{Z}{Y + Xe^{Zt}}\right)^2\right)}{dt}$$

$$\frac{d^2[B]_t}{dt^2} = X[A]_0\left[\frac{d(e^{Zt})}{dt}\left(\frac{Z}{Y + Xe^{Zt}}\right)^2 + e^{Zt}\frac{d\left(\left(\frac{Z}{Y + Xe^{Zt}}\right)^2\right)}{dt}\right]$$

$$\frac{d^2[B]_t}{dt^2} = X[A]_0\left[Ze^{Zt}\left(\frac{Z}{Y + Xe^{Zt}}\right)^2 + e^{Zt}\left(Z^2\frac{-2}{(Y + Xe^{Zt})^3}\right)\frac{d(Y + Xe^{Zt})}{dt}\right]$$

$$\frac{d^2[B]_t}{dt^2} = X[A]_0\left[Ze^{Zt}\left(\frac{Z}{Y + Xe^{Zt}}\right)^2 + e^{Zt}\left(Z^2\frac{-2}{(Y + Xe^{Zt})^3}\right)ZXe^{Zt}\right]$$

$$\frac{d^2[B]_t}{dt^2} = X[A]_0 e^{Zt}\left[\frac{Z^3}{(Y+Xe^{Zt})^2} - \frac{2\,Z^3 X e^{Zt}}{(Y+Xe^{Zt})^3}\right]$$
$$\frac{d^2[B]_t}{dt^2} = X[A]_0 e^{Zt}\left[\frac{Z^3(Y+Xe^{Zt}) - 2\,Z^3 X e^{Zt}}{(Y+Xe^{Zt})^3}\right]$$
$$\frac{d^2[B]_t}{dt^2} = X[A]_0 e^{Zt}\left[\frac{Z^3(Y+Xe^{Zt} - 2\,Xe^{Zt})}{(Y+Xe^{Zt})^3}\right]$$
$$\frac{d^2[B]_t}{dt^2} = X[A]_0 e^{Zt}.(Y - Xe^{Zt}).\left(\frac{Z}{Y+Xe^{Zt}}\right)^3$$
$$\mathbf{\frac{d^2[\boldsymbol{B}]_{\boldsymbol{t}}}{d\boldsymbol{t}^2}} = \boldsymbol{k_1[A]_0}\cdot \mathbf{e}^{(\boldsymbol{k_1+k_2[A]_0})\boldsymbol{t}}\cdot\left(\boldsymbol{k_2[A]_0 - k_1}\mathbf{e}^{(\boldsymbol{k_1+k_2[A]_0})\boldsymbol{t}}\right)\cdot\left(\frac{\boldsymbol{k_1+k_2[A]_0}}{\boldsymbol{k_2[A]_0+k_1}\mathbf{e}^{(\boldsymbol{k_1+k_2[A]_0})\boldsymbol{t}}}\right)^{\mathbf{3}}$$

The third derivative of $[B]_t$ leads to **Equation (11)** in the main text:

$$\frac{d^3[B]_t}{dt^3} = \frac{d\left(X[A]_0 e^{Zt}\,(Y - Xe^{Zt})\left(\frac{Z}{Y+Xe^{Zt}}\right)^3\right)}{dt}$$
$$\frac{d^3[B]_t}{dt^3} = \left[\frac{d(\,X[A]_0 e^{Zt})}{dt}(Y - Xe^{Zt})\left(\frac{Z}{Y+Xe^{Zt}}\right)^3\right] + \left[X[A]_0 e^{Zt}\frac{d(Y - Xe^{Zt})}{dt}\left(\frac{Z}{Y+Xe^{Zt}}\right)^3\right] + \left[X[A]_0 e^{Zt}(Y - Xe^{Zt})\frac{d\left(\frac{Z}{Y+Xe^{Zt}}\right)^3}{dt}\right]$$
$$\frac{d^3[B]_t}{dt^3} = \left[\,XZ[A]_0 e^{Zt}(Y - Xe^{Zt})\left(\frac{Z}{Y+Xe^{Zt}}\right)^3\right] + \left[X[A]_0 e^{Zt}(-XZe^{Zt})\left(\frac{Z}{Y+Xe^{Zt}}\right)^3\right] + \left[X[A]_0 e^{Zt}\,(Y - Xe^{Zt})\,\left(\frac{-3\,Z^3}{(Y+Xe^{Zt})^4}XZe^{Zt}\right)\right]$$
$$\frac{d^3[B]_t}{dt^3} = \left[\,X[A]_0 e^{Zt}(Y - Xe^{Zt})\left(\frac{Z^4(Y+Xe^{Zt})}{(Y+Xe^{Zt})^4}\right)\right] + \left[X[A]_0 e^{Zt}(-Xe^{Zt})\left(\frac{Z^4(Y+Xe^{Zt})}{(Y+Xe^{Zt})^4}\right)\right] + \left[X[A]_0 e^{Zt}(Y - Xe^{Zt})\left(\frac{Z^4(-3Xe^{Zt})}{(Y+Xe^{Zt})^4}\right)\right]$$
$$\frac{d^3[B]_t}{dt^3} = \ X[A]_0 e^{Zt}\left(\frac{Z}{Y+Xe^{Zt}}\right)^4[(Y - Xe^{Zt})(Y+Xe^{Zt}) + (-Xe^{Zt})(Y+Xe^{Zt}) + (Y - Xe^{Zt})(-3Xe^{Zt})]$$
$$\frac{d^3[B]_t}{dt^3} = \ X[A]_0 e^{Zt}\left(\frac{Z}{Y+Xe^{Zt}}\right)^4[Y^2 - (Xe^{Zt})^2 - (Xe^{Zt})^2 - XYe^{Zt} - 3XYe^{Zt} + 3(Xe^{Zt})^2]$$
$$\frac{d^3[B]_t}{dt^3} = \ X[A]_0 e^{Zt}.\left(\frac{Z}{Y+Xe^{Zt}}\right)^4.[Y^2 + (Xe^{Zt})^2 - 4XYe^{Zt}]$$
$$\mathbf{\frac{d^3[\boldsymbol{B}]_{\boldsymbol{t}}}{d\boldsymbol{t}^3}} = \boldsymbol{k_1[A]_0}\cdot \boldsymbol{e}^{(\boldsymbol{k_1+k_2[A]_0})\boldsymbol{t}}\cdot\left(\frac{\boldsymbol{k_1+k_2[A]_0}}{\boldsymbol{k_2[A]_0+k_1e}^{(\boldsymbol{k_1+k_2[A]_0})\boldsymbol{t}}}\right)^{\mathbf{4}}.\ \left(\boldsymbol{k_2^2[A]_0^2 + \ k_1^2e}^{\boldsymbol{2}(\boldsymbol{k_1+k_2[A]_0})\boldsymbol{t}} - \boldsymbol{4k_1k_2[A]_0e}^{(\boldsymbol{k_1+k_2[A]_0})\boldsymbol{t}}\right)$$

B. Application of formulas derived in the main text to Iridium(0) nanocluster formation[1] as a second example.

Here *A* represents an Ir^{I} precatalyst species, while *B* represents the growing $Ir(0)_n$ nanocluster. The values of the initial precatalyst concentration $[A]_0$, and of the rate constants k_1 and k_2 for nucleation and growth were previously reported in the literature.[1]

Figure S1 shows a plot of $[A]_t$ as a function of time for the loss of precatalyst Ir^{I} (see equation 4 in the main text).

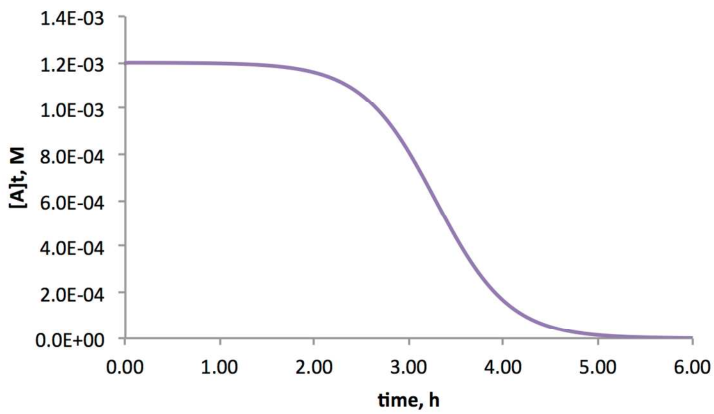

Figure S1: Concentration $[A]_t$ obtained with $[A]_0 = 1.2 \times 10^{-3}$ M, $k_1 = 5.6 \times 10^{-4}$ h^{-1}, $k_2 = 2.14 \times 10^{3}$ $M^{-1}.h^{-1}$.[1]

Figure S2 shows a plot of $[B]_t$ as a function of time for the formation of Iridium(0) nanoclusters (see equation 5 in the main text).

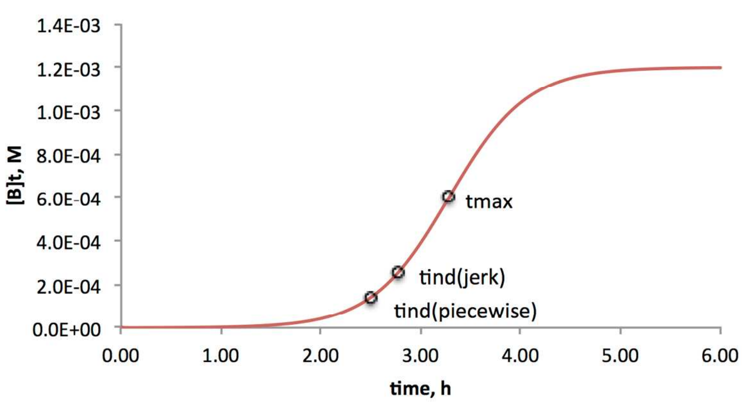

Figure S2: Concentration $[B]_t$ obtained with $[A]_0 = 1.2 \times 10^{-3}$ M, $k_1 = 5.6 \times 10^{-4}$ h^{-1}, $k_2 = 2.14 \times 10^{3}$ $M^{-1}.h^{-1}$.[1]

Figure S3 shows a plot of $d[B]_t/dt$ as a function of time for the formation of Iridium(0) nanoclusters (see equation 6 in the main text).

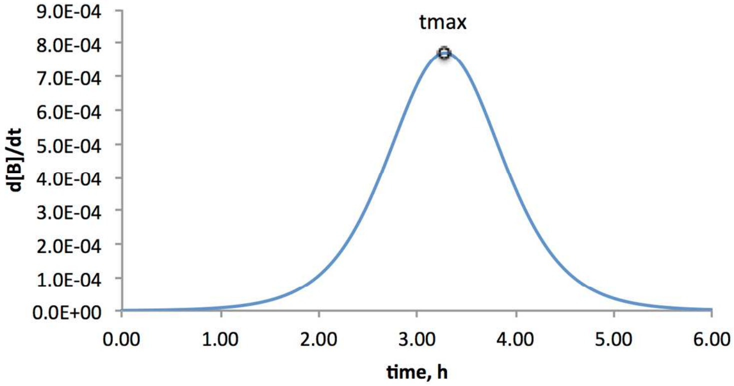

Figure S3: Rate $d[B]_t/dt$ obtained with $[A]_0 = 1.2 \times 10^{-3}$ M, $k_1 = 5.6 \times 10^{-4}$ h^{-1}, $k_2 = 2.14 \times 10^3$ $M^{-1}.h^{-1}$.[1]

Figure S4 shows a plot of $d^2[B]_t/dt^2$ as a function of time for the formation of Iridium(0) nanoclusters (see equation 7 in the main text).

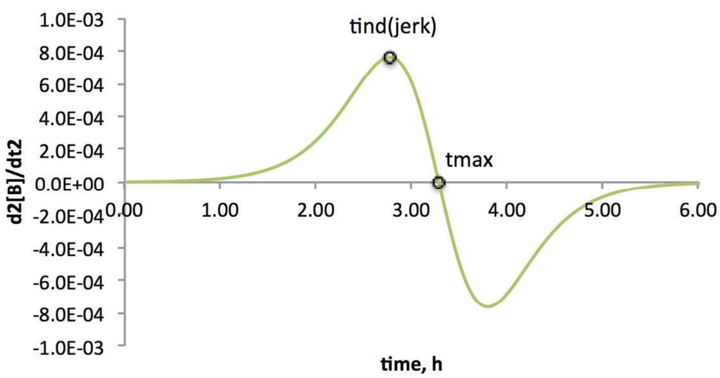

Figure S4: Acceleration $d^2[B]_t/dt^2$ obtained with $[A]_0 = 1.2 \times 10^{-3}$ M, $k_1 = 5.6 \times 10^{-4}$ h^{-1}, $k_2 = 2.14 \times 10^3$ $M^{-1}.h^{-1}$.[1]

Figure S5 shows a plot of $d^3[B]_t/dt^3$ as a function of time for the formation of Iridium(0) nanoclusters (see equation 11 in the main text).

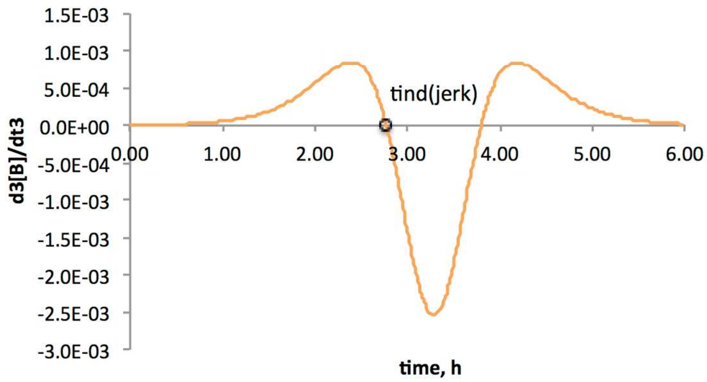

Figure S5: Jerk $d^3[B]_t/dt^3$ obtained with $[A]_0 = 1.2 \times 10^{-3}$ M, $k_1 = 5.6 \times 10^{-4}$ h^{-1}, $k_2 = 2.14 \times 10^3$ M^{-1}.h^{-1}.[1]

Table S1 gives values for parameters of interest such as the inflection point, t_{max}, the maximum rate or slope, $(d[B]_t/dt)_{max}$, the concentration at the inflection point, $[B]t_{max}$, and the induction period, $t_{induction\ (jerk)}$ or $t_{induction\ (piecewise)}$ (see Table 2 in the main text for the formulas).

Table S1. Values for parameters of interest calculated with $[A]_0 = 1.2 \times 10^{-3}$ M, $k_1 = 5.6 \times 10^{-4}$ h^{-1}, $k_2 = 2.14 \times 10^3$ M^{-1}.h^{-1}.[1]

t_{max}, inflection point	$t_{\max} = 3.28\ h$
$\left(\frac{\mathrm{d}[B]_t}{\mathrm{d}t}\right)_{\max}$, maximum rate (= slope)	$\left(\frac{\mathrm{d}[B]_t}{\mathrm{d}t}\right)_{\max} = 7.71\ \times 10^{-4}\ M.h^{-1}$
$[B]_{t_{\max}}$, concentration at the inflection point	$[B]_{t_{\max}} = 6.00\ \times 10^{-4}\ M$
$t_{induction\ (jerk)}$, induction period obtained from third derivative of $[B]_t$	$t_{induction\ (jerk)} = 2.77\ h$
$t_{induction\ (piecewise)}$, induction period obtained from piecewise linear approximation	$t_{induction\ (piecewise)} = 2.51\ h$

Table S2 gives values for the same parameters of interest as above, but approximated in the limit that $k_1 << k_2[A]_0$ (see Table 4 in the main text for the formulas).

Table S2. Values for parameters of interest approximated in the limit that $k_1 << k_2[A]_0$ and calculated with $[A]_0 = 1.2 \times 10^{-3}$ M, $k_1 = 5.6 \times 10^{-4}\ h^{-1}$, $k_2 = 2.14 \times 10^{3}\ M^{-1}.h^{-1}$.[1]

t_{max}, inflection point	$t_{\max} = 3.28\ h$
$\left(\frac{\mathrm{d}[B]_t}{\mathrm{d}t}\right)_{\max}$, maximum rate (= slope)	$\left(\frac{\mathrm{d}[B]_t}{\mathrm{d}t}\right)_{\max} = 7.70 \times 10^{-4}\ M.h^{-1}$
$[B]_{t_{\max}}$, concentration at the inflection point	$[B]_{t_{\max}} = 6.00 \times 10^{-4}\ M$
$t_{induction\ (jerk)}$, induction period obtained from third derivative of $[B]_t$	$t_{induction\ (jerk)} = 2.78\ h$
$t_{induction\ (piecewise)}$, induction period obtained from piecewise linear approximation	$t_{induction\ (piecewise)} = 2.50\ h$

1. Watzky, M. A.; Finke, R. G., Transition Metal Nanocluster Formation Kinetic and Mechanistic Studies. A New Mechanism When Hydrogen is The Reductant: Slow, Continuous Nucleation and Fast Autocatalytic Surface Growth. *J. Am. Chem. Soc.* **1997,** *119*, 10382-10400.