Nanoparticle Nucleation and Growth Model Exploration with Perturbative Analysis

Stephen T. King[1], Antonios Armaou[2,1], Themis Matsoukas[1], Griffin A. Canning[1], and Robert M. Rioux[1,3]
[1]Dept. of Chemical Engineering, The Pennsylvania State University, University Park, PA 16802, USA
[2]Dept. of Chemical Engineering, University of Patras, Patras 26504, Greece
[3]Dept. of Chemistry, The Pennsylvania State University, University Park, PA 16802, USA

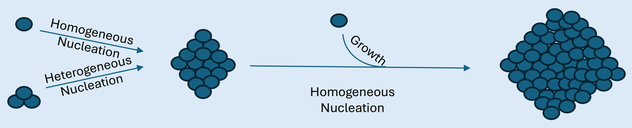
PennState College of Engineering

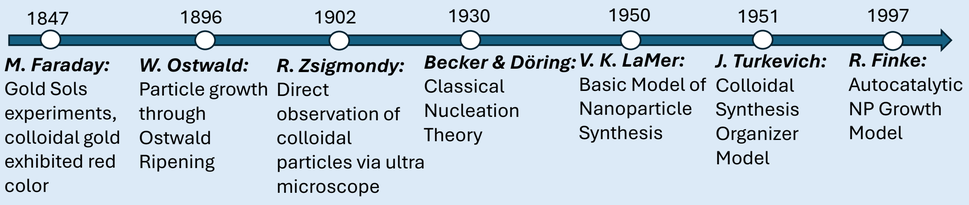
ESCAPE36 European Symposium on Computer Aided Process Engineering

Nanoparticle (NP) Nucleation and Growth History:

- 1847-1950: Classical Nucleation Theory[1]
- 1950-1997: LaMer Nucleation and Growth Model[2]
- 1997-present: Autocatalytic Model[3]

Historical Timeline of Nanoparticle (NP) Synthesis Model Development.





M. Faraday: Gold Sols experiments, colloidal gold exhibited red color

W. Ostwald: Particle growth through Ostwald Ripening

R. Zsigmondy: Direct observation of colloidal particles via ultra microscope

Becker & Döring: Classical Nucleation Theory

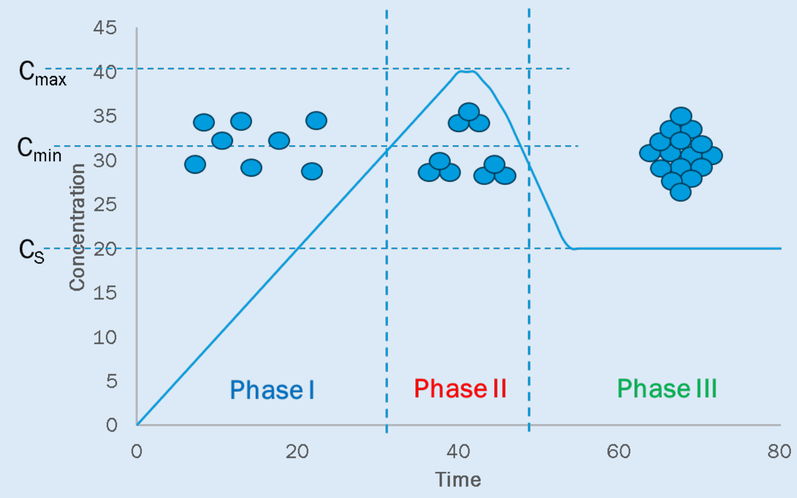
V. K. LaMer: Basic Model of Nanoparticle Synthesis

J. Turkevich: Colloidal Synthesis Organizer Model

R. Finke: Autocatalytic NP Growth Model

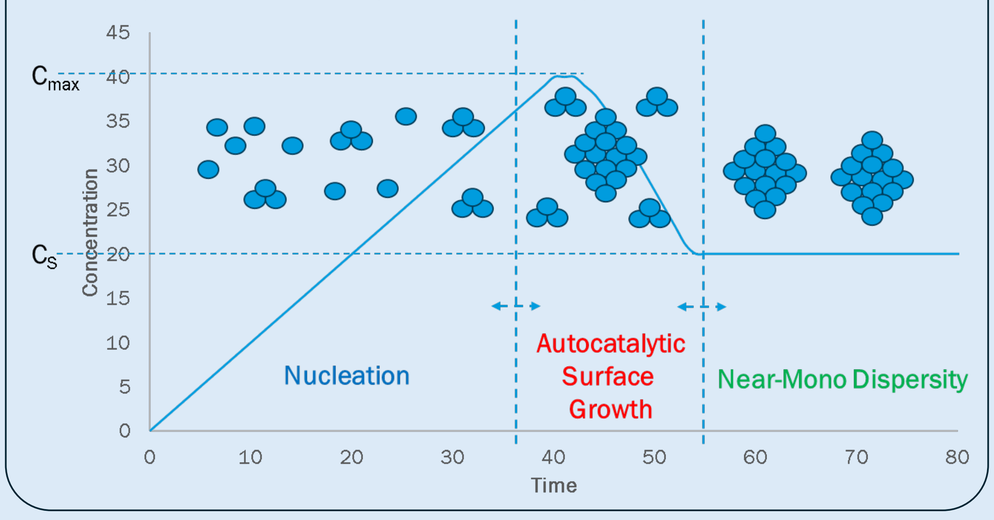
LaMer Diffusion Limited NP Model:

Supersaturation (C_S) rises to critical level needed for homogeneous nucleation C_{min}, saturation continues to increase to C_{max} causing burst nucleation. Monomer is consumed and supersaturation drops below C_{min} where NPs grow by diffusion.



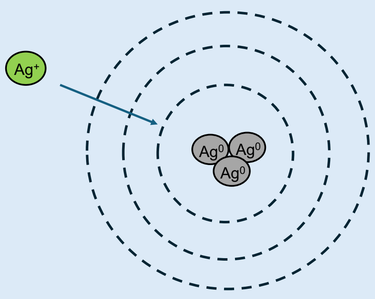
Autocatalytic NP Growth Model:

Nucleation proceeds slowly well before supersaturation. Autocatalytic surface growth is not diffusion limited. As this autocatalytic surface growth consumes monomer, supersaturation falls, nucleation ceases, and NPs size focus.



NP Model Mechanism:

Diffusion Mechanism:



Smoluchowski Equation for Diffusion:

$$R_{Di} = \frac{2}{3}\frac{k_B T}{\eta}\left(x_1^{1/y_1} + x_i^{1/y_2}\right)\left(x_1^{-1/y_1} + x_i^{-1/y_2}\right)$$

Simplified for NP Growth

- x_1 is a precursor Ag^+ value of 1
- y follows power law value of 3

Autocatalytic Mechanism:

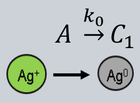
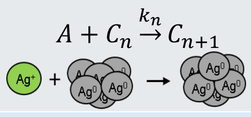
$$k_{D,n} = 4\pi D r_{Ag} n^{1/3}$$

Arrhenius-like decay - the lower surface area to volume as NP size increases

$$k_{A,n} = k_{A,1} e^{-\lambda n}$$

Combined (Diffusion + Autocatalytic) Mechanism:

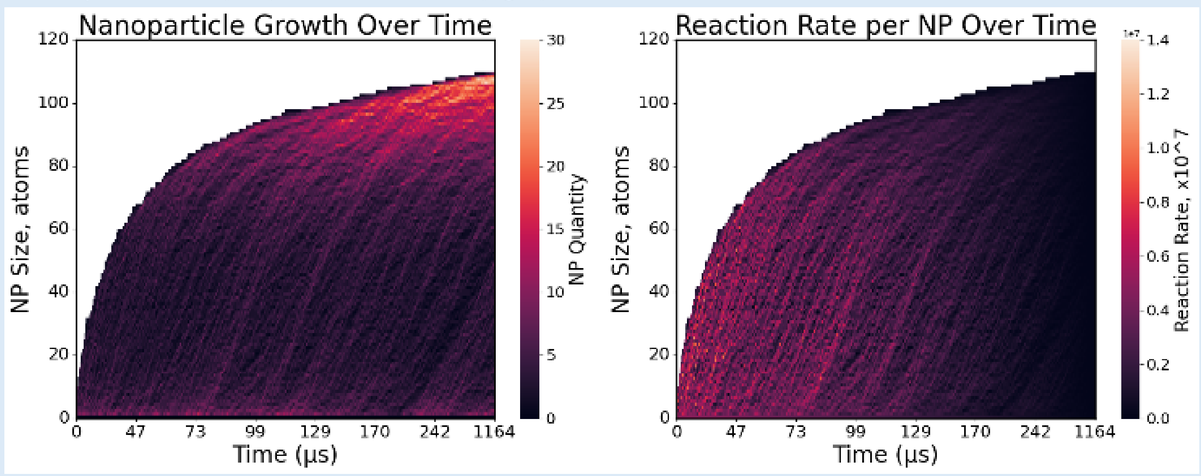
Colins-Kimball Framework: $k_{eff,n}^{-1} = k_{D,n}^{-1} + k_{A,n}^{-1}$

Step	Reaction	Rate
Nucleation	$A \xrightarrow{k_0} C_1$ 	$R_0 = \frac{d\xi_0}{dt} = k_0[A]$
Growth	$A + C_n \xrightarrow{k_n} C_{n+1}$ 	$R_n = \frac{d\xi_n}{dt} = k_n[A][C_n],$ $\forall\, n \geq 1$

Species	Rate
Precursor	$\frac{d[A]}{dt} = -k_0[A] - \sum_{n=1}^{\infty} k_n[A][C_n]$
NP Nucleate	$\frac{d[C_1]}{dt} = k_0[A] - k_1[A][C_1]$
NP	$\frac{d[C_n]}{dt} = k_{n-1}[A][C_{n-1}] - k_n[A][C_n],\ \forall n \geq 2$

Material Balanced (MB) NP Model Results:

Nanoparticle size (left) and reaction rate (right).



Assumptions: k_0=100 (s^{-1}), k_1=1,000 (s^{-1}), $D = 1.0\ \frac{l^2}{s}$, λ=0.5, Ag^+_0 = 20,000 mol.

Time calculated using the inverse sum of the reaction rates for each step.

Method of Moments (MoM) Validation:

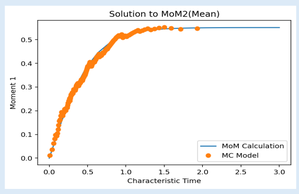
Special Case where k_i = 1, Alignment of Simulation Model with MoM

$$\frac{dc_0}{d\tau} = -k_0 c_0 - c_0 m_0$$

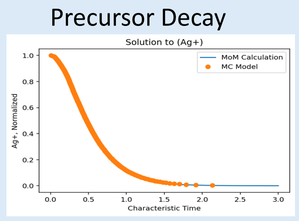
$$\frac{dm_0}{d\tau} = k_0 c_0$$

$$\frac{dm_1}{d\tau} = k_0 c_0 - c_0 m_0$$

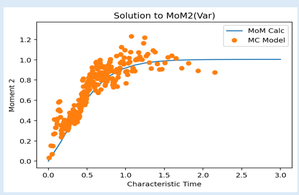
First Moment



Precursor Decay

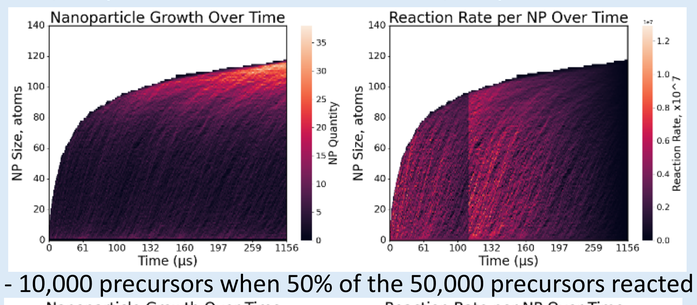


Second Moment

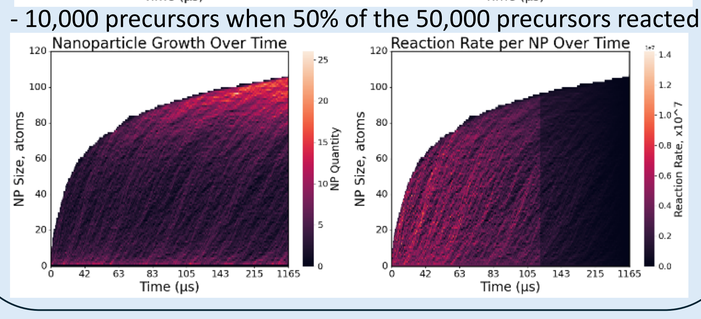


Perturbative Analysis:

+ 25,000 precursors when 50% of the 50,000 precursors reacted



- 10,000 precursors when 50% of the 50,000 precursors reacted

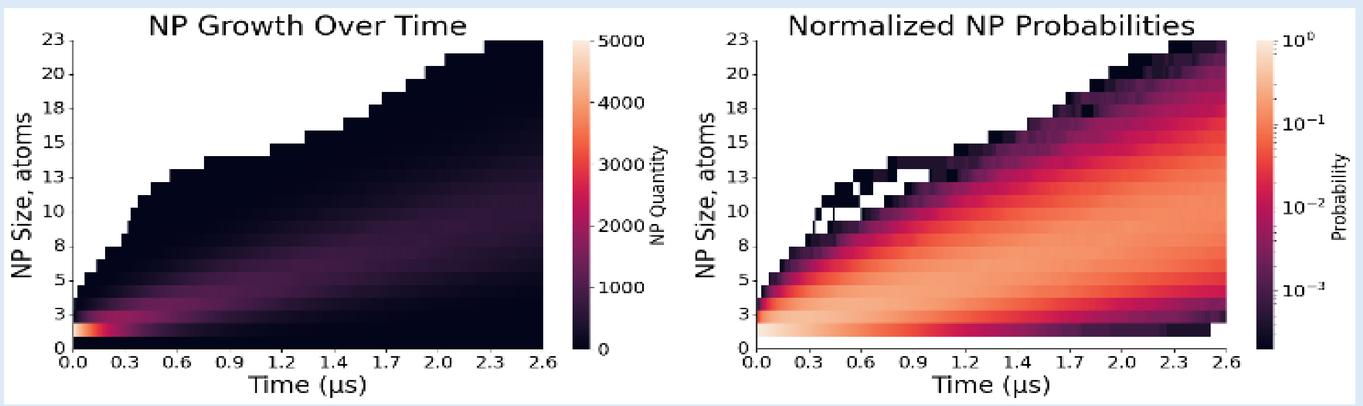


Perturbative Analysis Summary:

- Precursor perturbations strongly affect NP size evolution: additions increase the mean size and variance, while removals lower the mean and increase dispersity.
- Dispersity increases as diffusion decreases; restricted mass transport produces larger, more broadly distributed NPs.
- Diffusion effects intensify under precursor perturbations: added precursor narrows dispersity, whereas precursor removal broadens it, especially at low diffusion.
- Systems with limited diffusion are highly sensitive to precursor fluctuations. This leads to greater heterogeneity in final NP size distributions.

Diffusion Coeff	0.010	0.100	1.000
$k_{A,1}/D$	100,000	10,000	1,000
No Perturbation			
Mean NP size	104.38	90.42	73.75
Std Dev (SD)	62.46	48.19	32.96
Norm NP Size	1.00	1.00	1.00
Norm SD	0.60	0.53	0.45
Polydispersity	1.36	1.28	1.20
+25,000 Perturbation			
Mean NP size	120.58	104.89	82.33
Std Dev (SD)	63.70	49.38	34.39
Norm NP Size	1.16	1.16	1.12
Norm SD	0.61	0.55	0.47
Polydispersity	1.28	1.22	1.17
-10,000 Perturbation			
Mean NP size	91.12	81.14	67.80
Std Dev (SD)	60.46	47.30	32.50
Norm NP Size	0.87	0.90	0.92
Norm SD	0.58	0.52	0.44
Polydispersity	1.44	1.34	1.23

Constant Number Monte Carlo (cNMC) Model Results:



Diffusion Coeff	0.010	0.100	1.000
$k_{A,1}/D$	100,000	10,000	1,000
Result			
Mean NP size	5.87	9.32	10.76
Std Dev (SD)	4.47	4.53	3.09
Norm SD	0.76	0.49	0.29
Polydispersity	1.58	1.24	1.08

- Like the MB Model, NP dispersity decreases with increased diffusion. In the cNMC model, the mean size increases because continuous precursor addition expands the simulation volume.
- Faster diffusion delivers precursor to NP surfaces more efficiently, producing larger and more uniform NPs. Conversely, the MB model is supply-limited and the fixed precursor pool constrains growth as monomer depletes.
- Together, these models clarify how diffusion-limited versus supply-limited regimes govern NP growth and will be compared with TEM-derived size distributions for mechanistic assumptions.

Conclusion:

- Proposed NP growth model integrates LaMer diffusion-limited growth (Smoluchowski/Collins–Kimball) with autocatalytic Finke–Watzky kinetics using a Metropolis–Hastings MCMC framework.
- Both material-balanced and cNMC models show reduced diffusion increases dispersity.
- Removal of precursor via perturbations lowers mean NP size and increases dispersity and vice-versa.
- cNMC model shows early nucleation followed by growth, consistent with LaMer and F–W behavior; higher diffusion reduces dispersity but increases mean size due to unlimited precursor supply.
- Overall, controlled perturbations reveal how precursor availability shapes NP size and dispersity, offering mechanistic insight into size focusing and early-stage NP formation.

Acknowledgements:

Honeywell UOP

NSF

NSF# 2404221

References:

1. LaMer VK, Dinegar RH. Theory, Production, and Mechanism of Formation of Monodispersed Hydrosols. J. Am. Chem. Soc. 72:4847-4854 (1950).
2. Watzky MA, Finke RG. 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. 119:10382-10400 (1997)
3. Hastings WK. Monte Carlo sampling methods using Markov chains and their applications. Biometrika, 57:97–109 (1970)
4. Chen Z, Chang JW, Balasanthiran C, Milner ST, Rioux RM. Shape of growing silver nanoparticles is kinetically controlled by polyvinylpyrrolidone binding. J. Am. Chem. Soc. 141:4328-4337 (2019)
5. Chen Z, Balankura T, Fichthorn KA, Rioux RM. Revisiting the Polyol Synthesis of Silver Nanocubes: Role of Chlorine in Silver Nanocubes Formation. ACS Nano 13:1849-1860 (2019)Jharimune S, Chen Z, Pfukwa R, Anderson J, Klumperman B, Rioux RM. Chemical Identity of Poly(N-vinylpyrrolidone) End Groups Impact Shape Evolution during the Synthesis of Ag Nanostructures. J. Am. Chem. Soc. 143:184-195 (2021)
6. Canning G, Ogozaly S, Pekarcik M, Lieb C, Jharimune S, Pfukwa R, Klumperman B, Rioux RM. Complementary Reducing Agents are Responsible for Temporally Distinct Nucleation and Growth Phases during the Polyol Synthesis of Ag Nanocubes. *Angew Chemie* 64:e202418611 (2025)
7. Handwerk DR, Shipman PD, Whitehead CB, Ozkar S, Finke RG. Particle Size Distributions via Mechanism Enabled Population Balance Modeling. J. Phys. Chem. 124:4852-4880 (2020)
8. Collins FC, Kimball GE. Diffusion-Controlled Reaction Rates. J. Colloid Sci. 4:425–437 (1949)