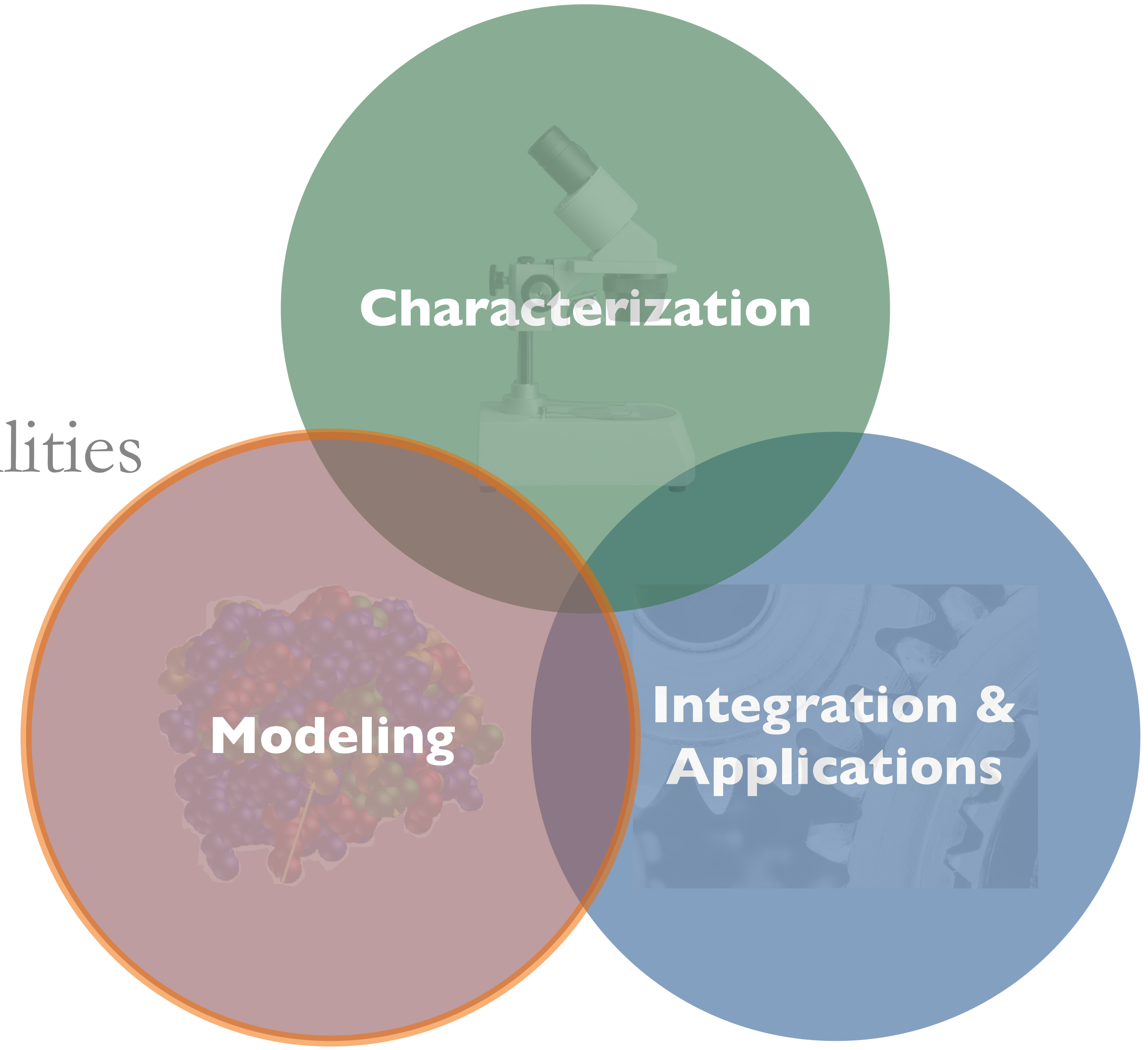
Numerical Solution of Deterministic and Stochastic Integro-differential Equations for the Synthesis of Nano-structured Materials

Sean C. Garrick
Computational Transport Phenomena Laboratory
Department of Mechanical Engineering
University of Minnesota - Twin Cities

Brandon Crook, MS
Sriswetha Modem, MS
Nelson Settumba, PhD
Kari Lehtinen, Post. Doct.
Scott Miller, MS
Guanghai Wang, PhD
Jouni Pykönnen, Post. Doct.

Outline

- Motivation
  - Industrial
  - Scientific
  - Mathematical
- Approaches, Tools & Capabilities
  - Deterministic
- Future Work
  - Stochastic



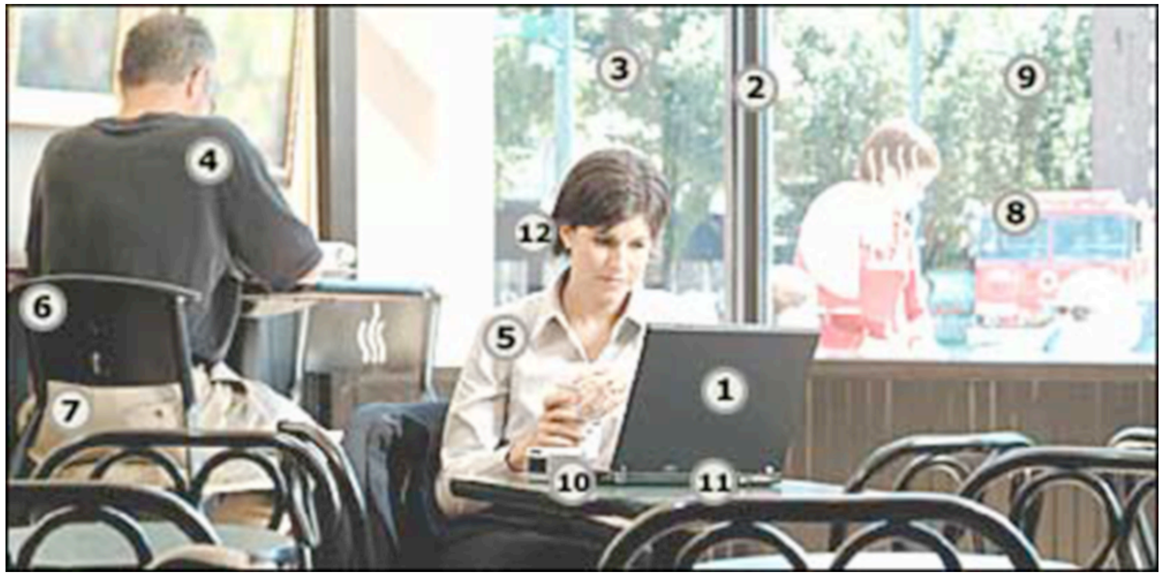
Industrial Relevance

Product	Quantity (T/yr)	Value ($)	Process	Coagulation
Carbon Black	8M	*8B*	Flame	X
Titania	2M	*4B*	Flame	X
Zinc Oxide	0.6M	*0.5B*	Evap/Oxid	X
Fumed Silica	0.2M	*2B*	Flame	X
Nickel	0.04M	*0.1B*	Decomp	X

2002 Market data for nano-structured materials

Presence of Nanoparticles

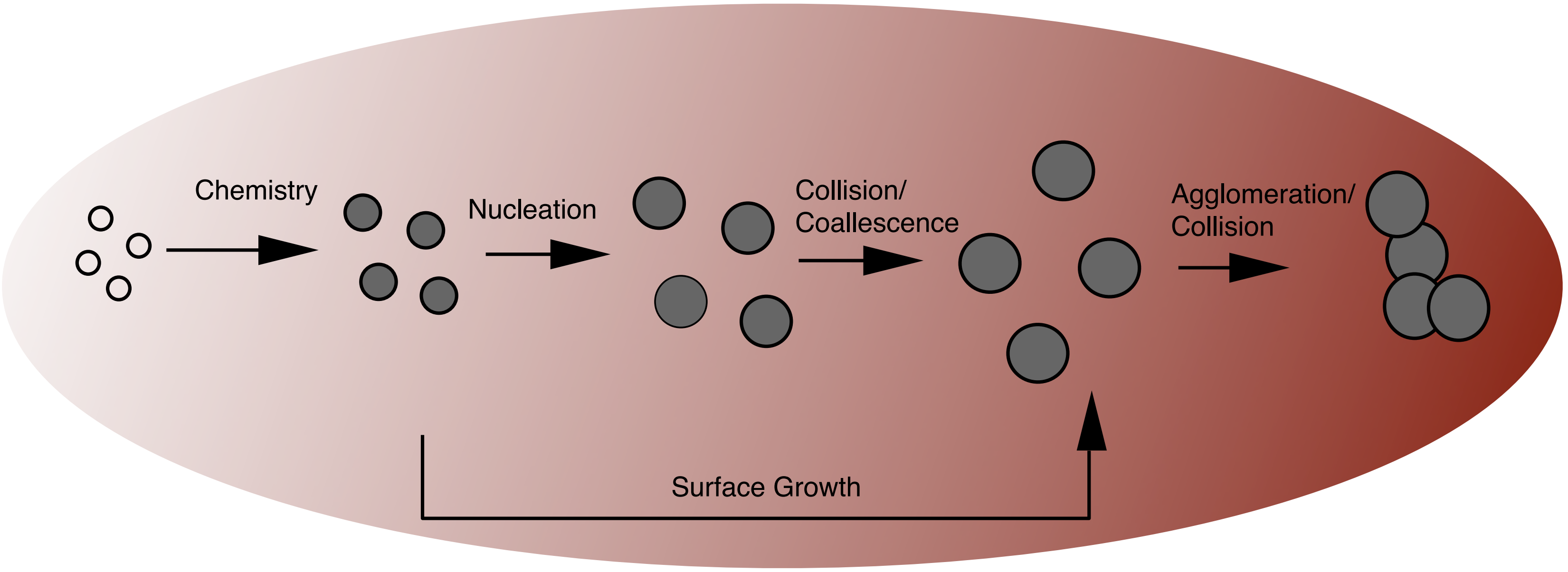
1. Organic Light Emitting Diodes (OLEDs) for displays
2. Photovoltaic film that converts light into electricity
3. Scratch-proof coated windows that clean themselves with UV
4. Fabrics coated to resist stains and control temperature
5. Intelligent clothing measures pulse and respiration
6. Bucky-tubeframe is light but very strong
7. Hip-joint made from bio-compatible materials
8. Nano-particle paint to prevent corrosion
9. Thermo-chromic glass to regulate light
10. Magnetic layers for compact data memory
11. Carbon nanotube fuel cells to power electronics and vehicles
12. Nano-engineered cochlear implant



Scientific Relevance

- **Description of nanoparticle growth processes**
  - Nucleation
  - Coagulation/coalescence
  - Condensation/evaporation & surface chemistry
- **Bridging Continuum-molecular length scales**
  - Fluid-particle interactions
  - Thermal-particle interactions
  - Chemical-particle interactions
- **New dynamics/phenomena**

Dynamics of Particle Growth



- Nucleation
- Coagulation/coalescence
- Condensation/evaporation & surface chemistry
- Other particle-particle interactions

Mathematical Relevance

- **Modeling**
  - Exploration of parameter space
  - Identify relevant features/dynamics
  - Condensation/evaporation & surface chemistry
- **Mathematical Description**
  - Captures underlying processes
  - Solvable
  - Computationally feasible/efficient
  - Robust

{Nano}Particle Formulation (1)

$$\frac{\partial \boldsymbol{n}}{\partial \boldsymbol{t}} + \nabla \cdot \boldsymbol{n}\mathbf{v} + \frac{\partial \boldsymbol{I}}{\partial \boldsymbol{v}} = \nabla \cdot \boldsymbol{D}\nabla \boldsymbol{n} + \frac{\boldsymbol{1}}{\boldsymbol{2}}\int_{\boldsymbol{0}}^{v} \beta(\tilde{\boldsymbol{v}}, \boldsymbol{v} - \tilde{\boldsymbol{v}})\boldsymbol{n}(\tilde{\boldsymbol{v}})\boldsymbol{n}(\boldsymbol{v} - \tilde{\boldsymbol{v}})\boldsymbol{d}\tilde{\boldsymbol{v}} - \int_{\boldsymbol{0}}^{\infty} \beta(\boldsymbol{v}, \tilde{\boldsymbol{v}})\boldsymbol{n}(\boldsymbol{v})\boldsymbol{n}(\tilde{\boldsymbol{v}})\boldsymbol{d}\tilde{\boldsymbol{v}} - \nabla \cdot \mathbf{c}\boldsymbol{n}$$

- Continuous distribution function
- n is the number concentration of molecular clusters of size *v*, and varies as a function of space, time, and composition *(O_2, N_2, SiO_2)*
- An impossibly-large number of equations/dimensions

{Nano}Particle Formulation (2)

$$\frac{\partial M_k}{\partial t} + \frac{\partial u_j M_k}{\partial x_j} = \frac{\partial}{\partial x_j}\left(\kappa \frac{\partial}{\partial x_j}\left(M_{k-2/3}\right)\right) + \dot{\omega}_{M_k}$$

$$\dot{\omega}_k^\star = Da \times \left(\begin{array}{c} C_M{}^{\left(-\frac{k^2}{2}\right)} \times \beta_k M_0^{\star 2} v_g^{\star k+\frac{1}{6}} \left(C_M \frac{M_0^\star M_2^\star}{M_1^{\star 2}} \right)^{\frac{k^2}{4}+\frac{k}{12}} \times \\ \left(\left(C_M \frac{M_0^\star M_2^\star}{M_1^{\star 2}} \right)^{\frac{25}{72}} + 2 \left(C_M \frac{M_0^\star M_2^\star}{M_1^{\star 2}} \right)^{\frac{5}{72}} + \left(C_M \frac{M_0^\star M_2^\star}{M_1^{\star 2}} \right)^{\frac{1}{72}} \right) \end{array} \right)$$

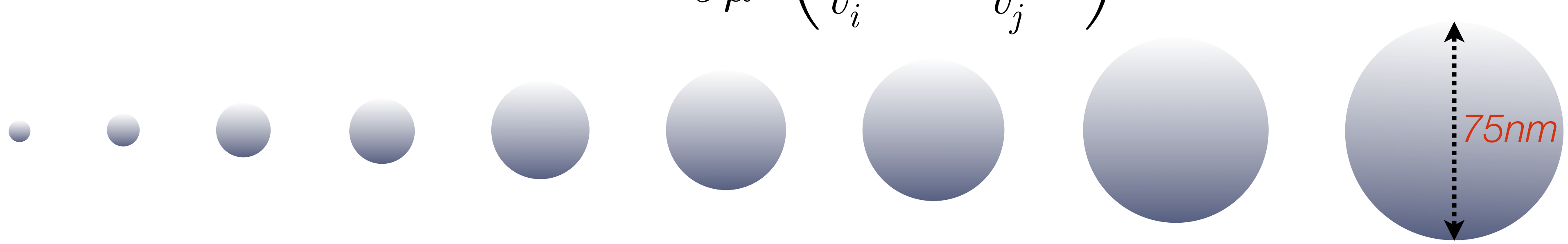
- Moment method
  - Assume a distribution for *n*
  - Solve for moments of this distribution, M_k
- Three (3) non-linear PDEs, M_0, M_1, M_2
- Physical limitations: uni-modal distributions, etc.

{Nano}Particle Formulation (3)

$$\frac{\partial \rho Q_k}{\partial t} + \frac{\partial \rho u_j Q_k}{\partial x_j} = \frac{\partial}{\partial x_j}\left(\rho D_Q \frac{\partial Q_k}{\partial x_j}\right) + \underbrace{\dot{\omega}_k^Q}_{\text{Nucleation, Condensation \& Coagulation}}$$

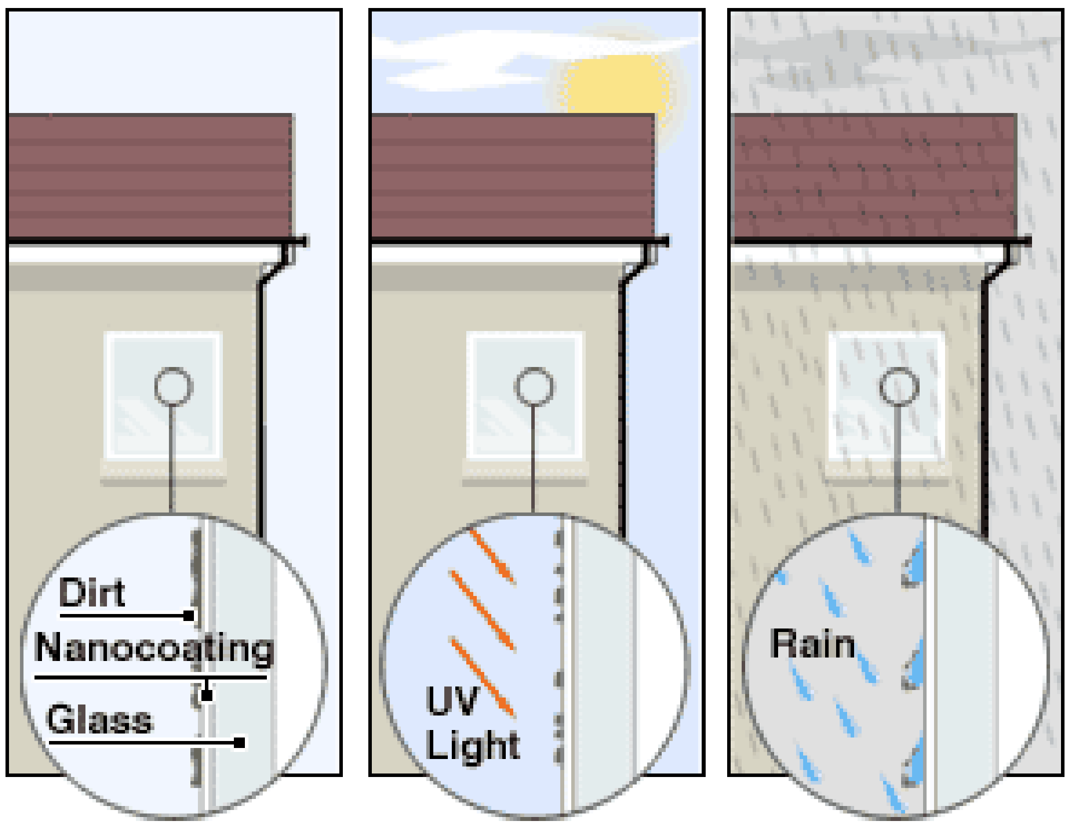
$$\dot{\omega}_k^Q = \begin{cases} J\Big|_{nucleation} - \sum_{i=1}^{N_s} \rho\beta_{i1} Q_i Q_1, & k = 1 \\ \left(\frac{1}{2}\sum_{i=1}^{N_s}\sum_{j=1}^{N_s} \rho\chi_{ijk}\beta_{ij} Q_i Q_j - \sum_{i=1}^{N_s} \rho\beta_{ik} Q_i Q_k\right), & k > 1, \end{cases}$$

collision frequency function
$$\begin{cases} \beta_{i,j} = 4\pi (R_i + R_j)^2 \left(\frac{KT}{2\pi}\right)^{\frac{1}{2}} \left(\frac{1}{m_i} + \frac{1}{m_j}\right)^{\frac{1}{2}} & \text{free-molecule regime} \\ \beta_{i,j} = \frac{2kT}{3\mu}\left(\frac{1}{v_i^{1/3}} + \frac{1}{v_j^{1/3}}\right)\left(v_i^{1/3} + v_j^{1/3}\right) & \text{continuum regime} \end{cases}$$



Titanium Dioxide (TiO_2)

- Easy clean glass
  - Aktiv Glass is coated with nano-structured TiO2.
  - Sunshine triggers chemical reaction which breaks down dirt.
  - Water spreads evenly over surface instead of forming droplets and cascades taking dirt with it.
- Chem-Bio agents, sensors, pigments, solar cells, etc.



Chemical Formulation

$$\frac{\partial \rho Y_i}{\partial t} + \frac{\partial \rho Y_i u_j}{\partial x_j} = \frac{\partial}{\partial x_j}\left(\rho D_i \frac{\partial Y_i}{\partial x_j}\right) + \dot{\omega}_i$$

Y_i concentration of species *i*
D_i diffusion coefficient of species *i*

Hydrolysis of TiCl4

$$TiCl_4 + 2H_2O \rightarrow TiO_2 + 4HCl$$

Consider infinite reaction rate

$$\omega = \triangle \rho Y_m$$
$$= C_m \times min\left(\frac{\rho Y_{TiCl_4}}{MW_{TiCl_4}}, \frac{\rho Y_{H_2O}}{2 \times MW_{H_2O}}\right) \times MW_m$$

Oxidation of TiCl4

$$TiCl_4 + O_2 \rightarrow TiO_2 + 2Cl_2$$

$$\omega = [k_f/(MW_{TiCl_4} MW_{O_2})]\, \rho^2 Y_{TiCl_4} Y_{O_2}$$

(Moody and Collins, 2003)

Methane combustion

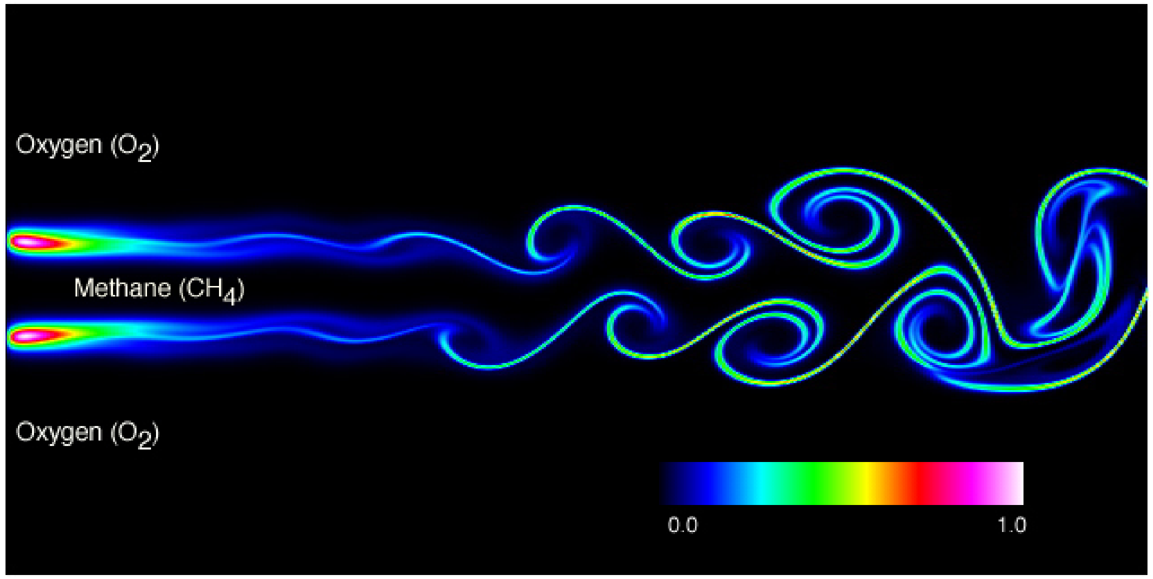
$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

$$\omega = [B/(MW_{CH_4} MW_{O_2})]\, \rho^2 Y_{CH_4} Y_{O_2} exp(-T_a/T)$$

(Bui-Pham, 1992)

Nanostructured TiO_2 Synthesis

- Two-dimensional planar jets
  - Non-premixed methane-air diffusion flame
  - Oxidation of TiCl4 (20% and 30%)
  - Particles are spherical (25 bins)
- Direct Numerical Simulation
  - Small time/spatial steps
  - Massively parallel computations
  - 400 CPU hours on Cray X1



Methane combustion

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

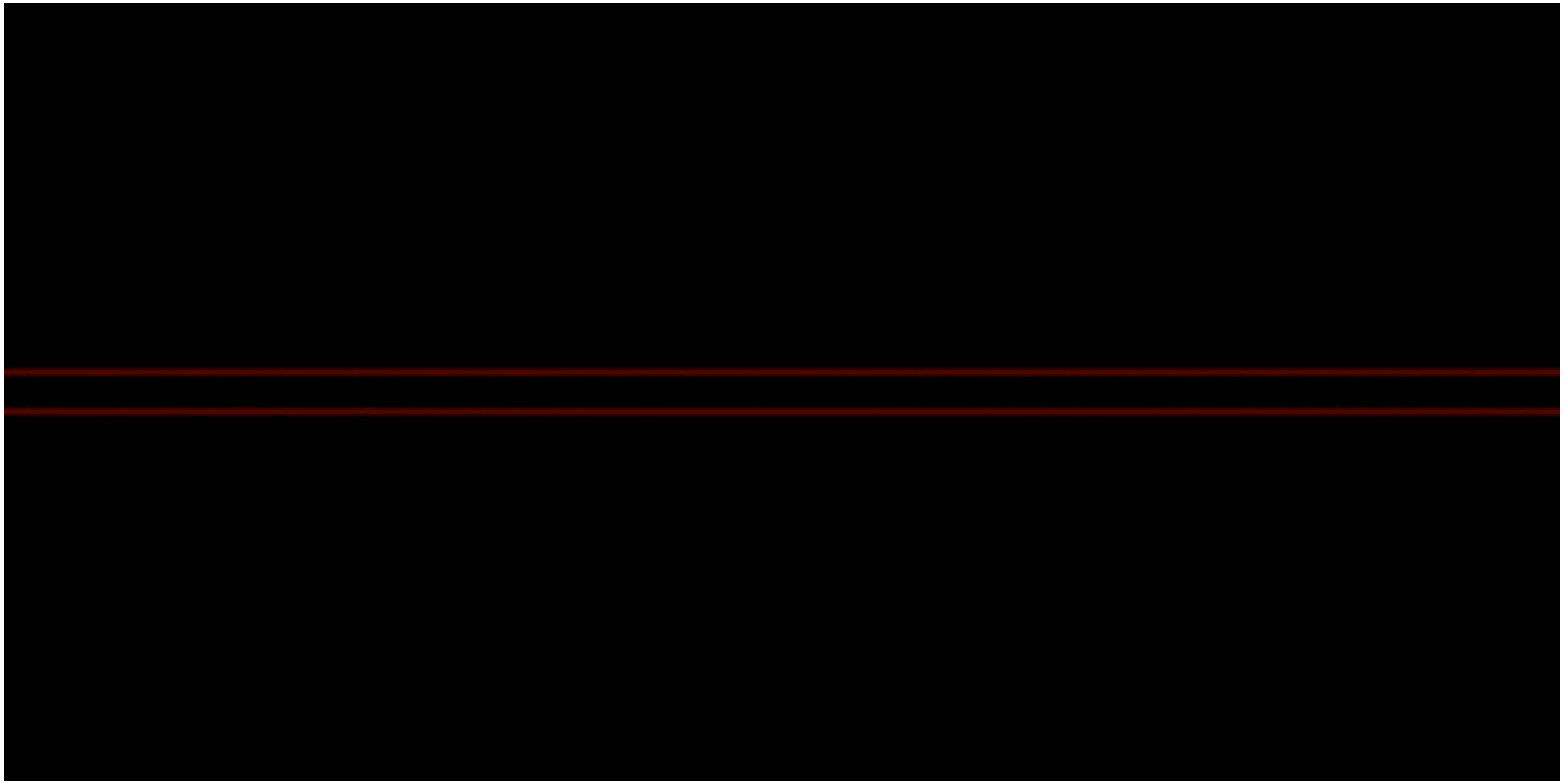
(Bui-Pham, 1992)

Oxidation of $TiCl_4$

$$TiCl_4 + O_2 \rightarrow TiO_2 + 2Cl_2$$

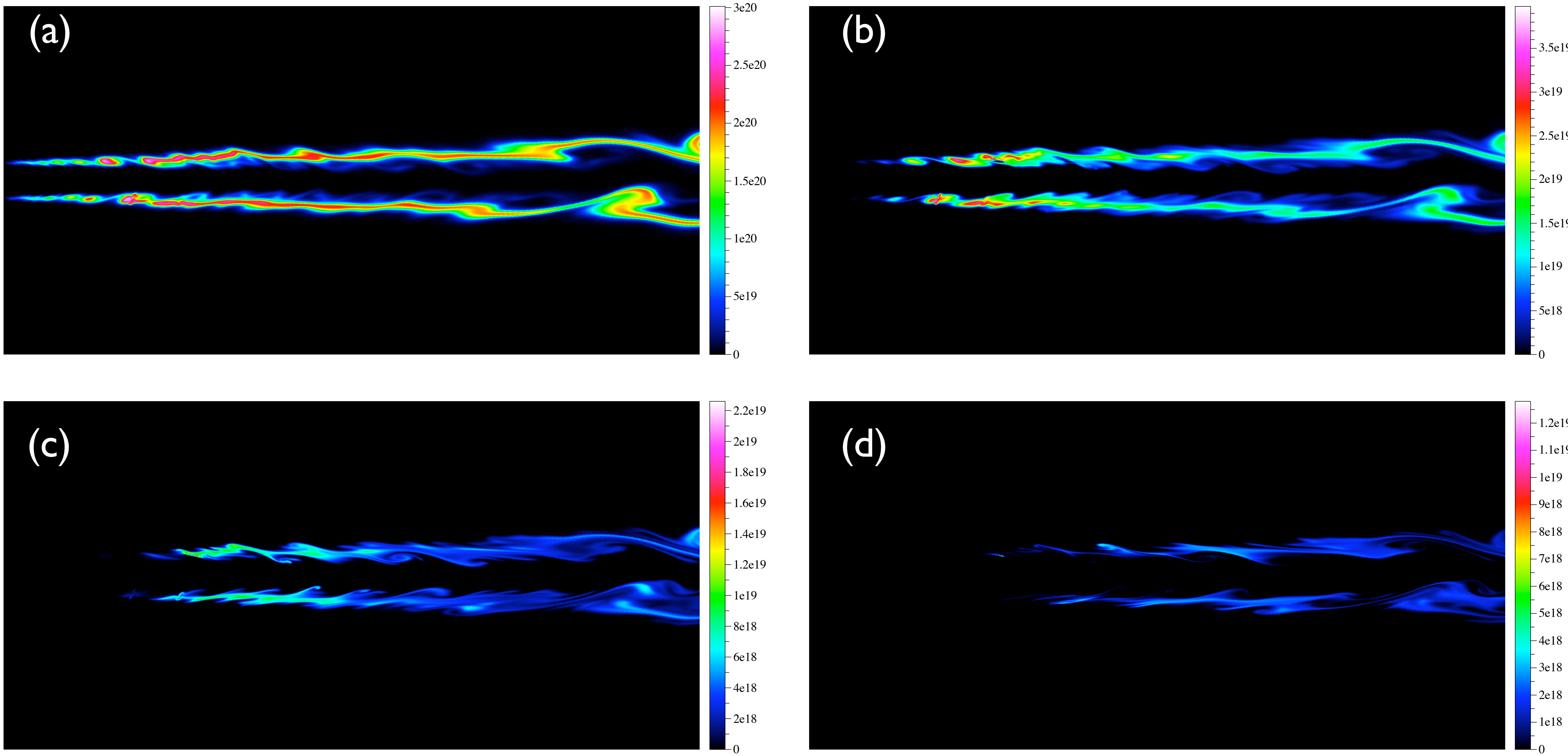
(Moody and Collins, 2003)

Flame Dynamics



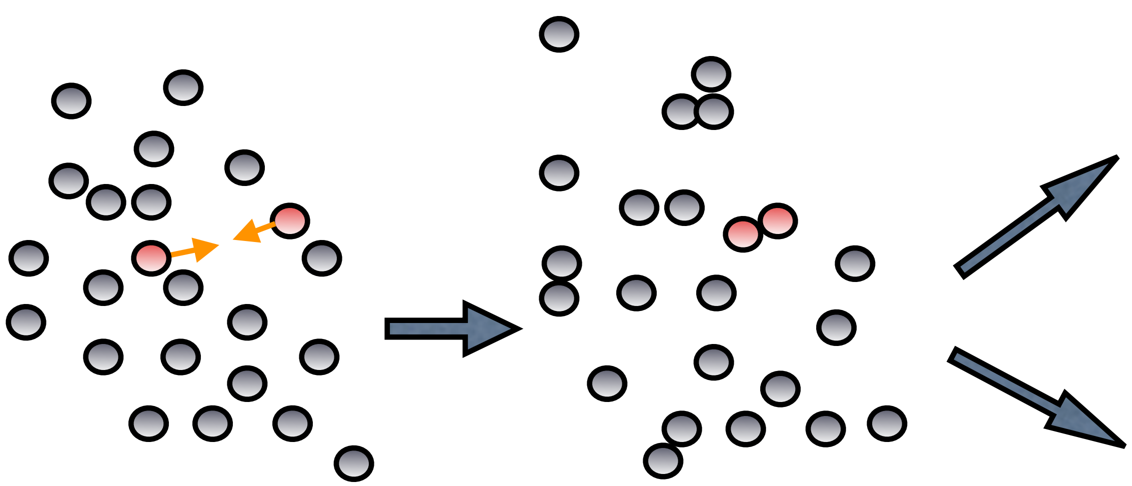
- Captures nucleation, condensation, and coagulation.
- Develop "simple" correlations for use in RANS/LES.

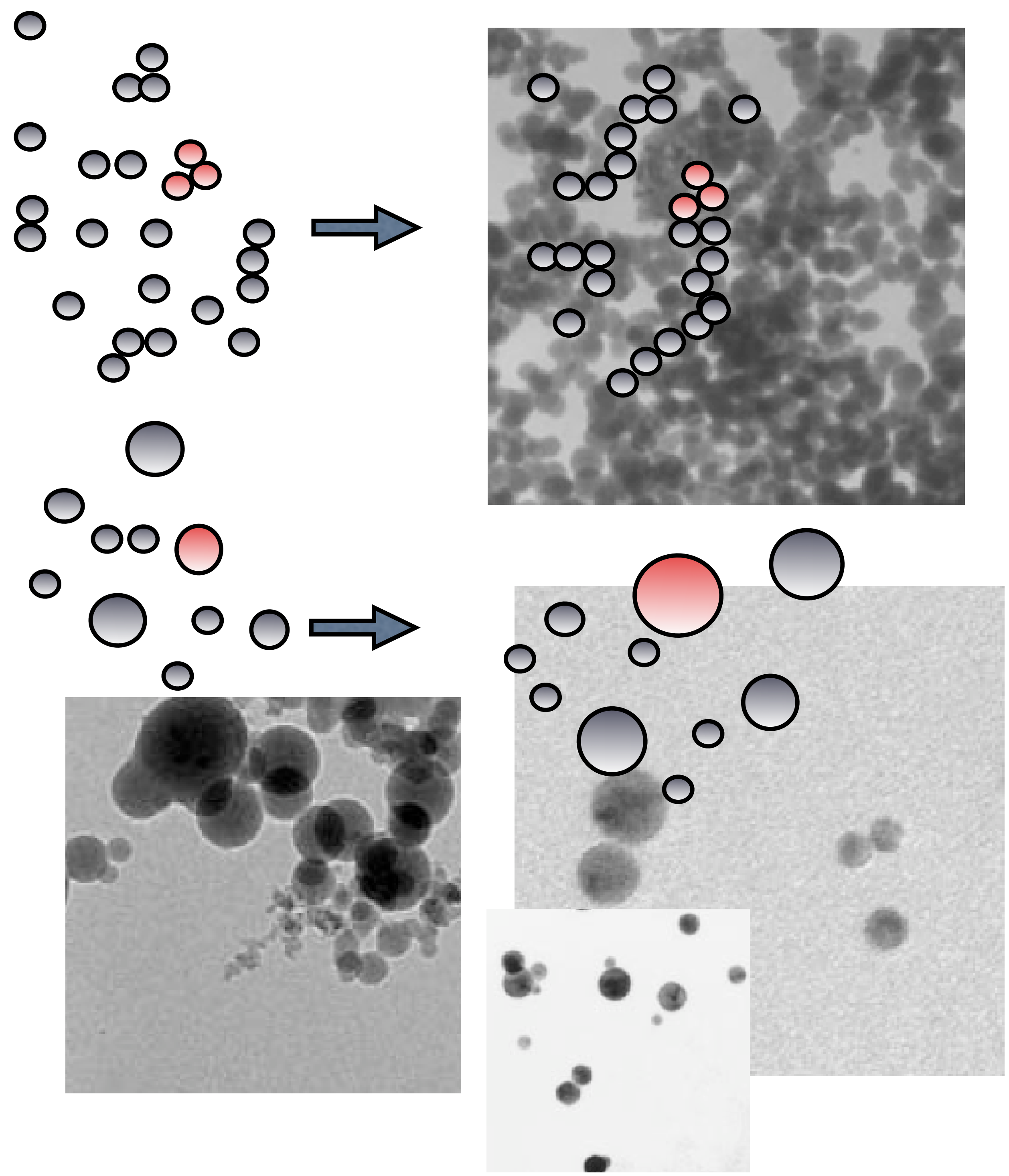
Size-selected Images (20%)



Instantaneous particle concentration contours: (a) monomers; (b) 1nm; (c) 2nm; (d) 4nm.

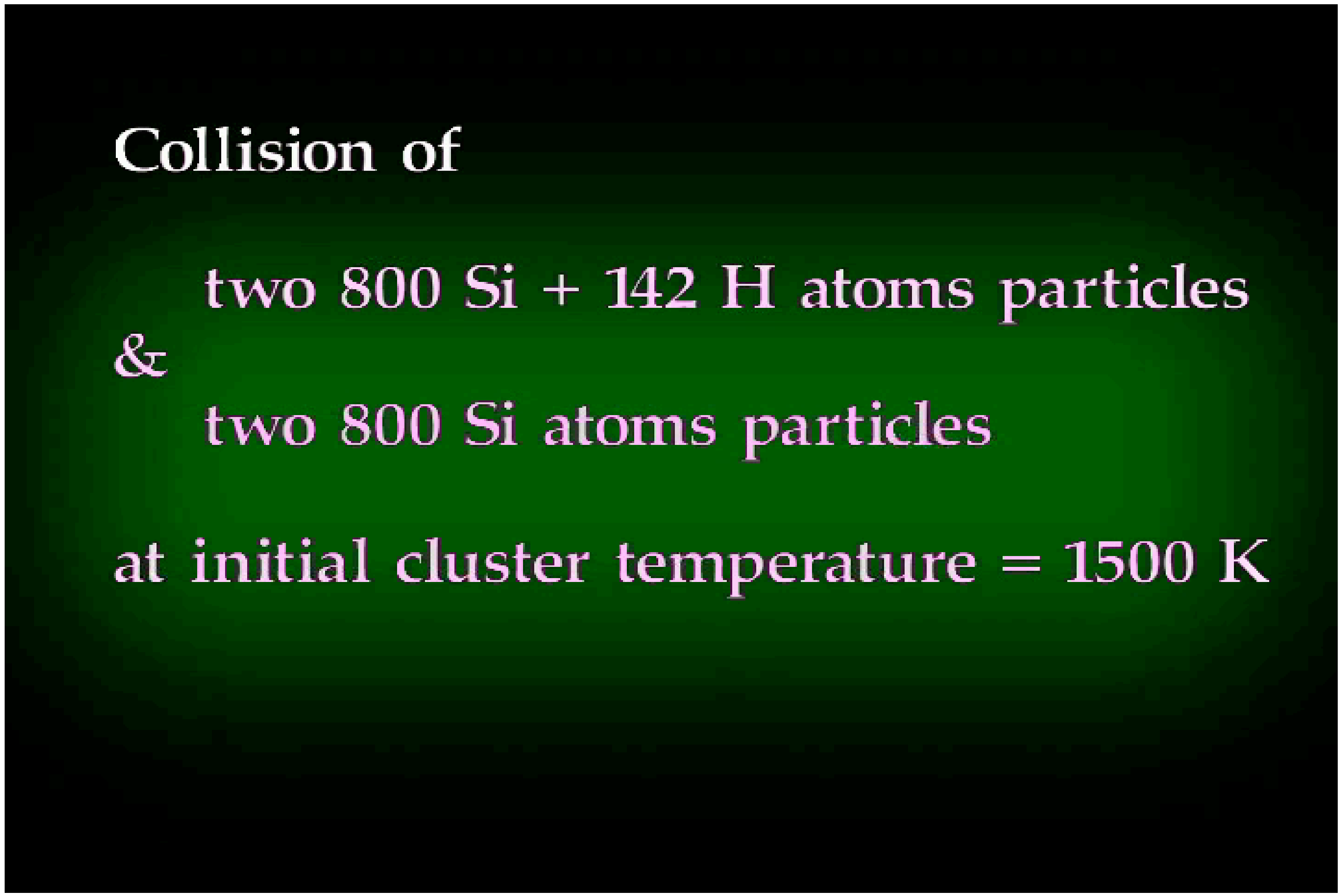
Particle Growth: Coalescence





- Nanoparticle Structure
  - Collision time-scale vs. coalescence time scale
- Sintering Rate
  - Surface tension
  - Solid-state diffusion

Particle-Particle Dynamics

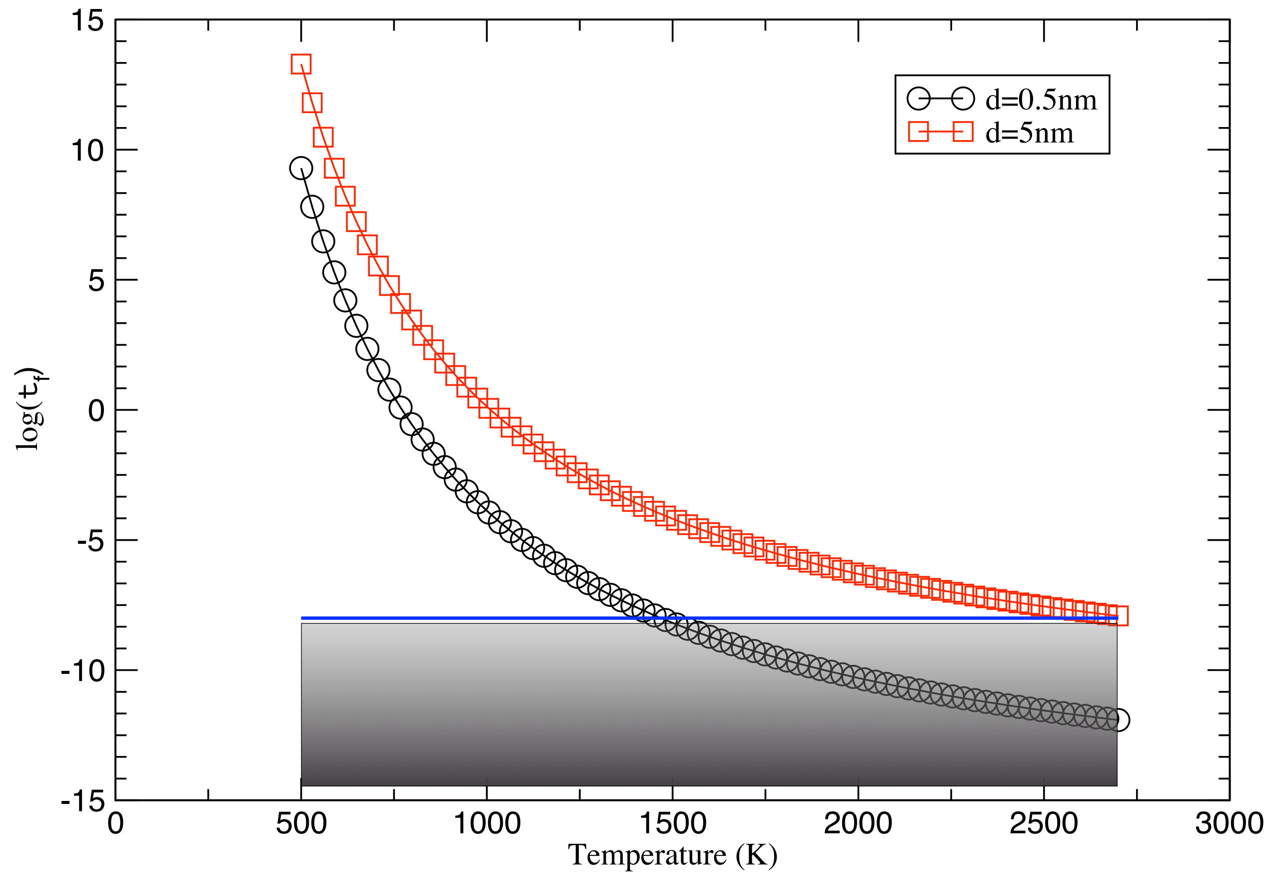


- Molecular dynamics lead to continuum-level descriptions
- Pico to nano-second time scales

Nanoparticle Coalescence

- Sintering time
  - Size
  - Material/composition
  - Temperature
- Multi-scale
  - Reaction/nucleation: very fast
  - Coalescence: fast - slow
  - Eddy turnover/mixing: medium-slow

$$\tau_f = 7.4 \times 10^8 d_p^4 exp(31000/T)$$



Simulations must resolve all time-scales or capture the effects of “faster” phenomena

Primary Particle General Dynamic Equation

$$\frac{\partial \rho Q_{p_k}}{\partial t} + \frac{\partial \rho u_j Q_{p_k}}{\partial x_j} = \frac{\partial}{\partial x_j}\left(\rho D_{Q_p} \frac{\partial Q_{p_k}}{\partial x_j}\right) + \dot{\omega}_k^{Qp} + \dot{\omega}_k\big|_{sinter},$$

convection

diffusion

nucleation+coagulation

sintering

$$\dot{\omega}_k^{Q_p} = \begin{cases} J\Big|_{nucleation} - \sum_{i=1}^{N_s} \rho\beta_{i1} Q_{p_1} Q_i, & k = 1 \\ \frac{1}{2}\sum_{i=1}^{N_s}\sum_{j=1}^{N_s} \rho\chi_{ijk}\beta_{ij}\eta_p Q_i Q_j - \sum_{i=1}^{N_s} \rho\beta_{ik} Q_i Q_{p_k}, & k > 1, \end{cases}$$

$$n_{p,i} = Q_{pi}/Q_i$$

$$\boxed{\dot{\omega}_k\big|_{sinter} = \rho\left(\frac{-3}{\tau_f}\left(n_{p,k} - n_{p,k}^{\frac{2}{3}}\right) Q_k\right)}$$

$$a_{p0,i} = \left(\frac{6(v_i/Q_{pi})}{pi}\right)^{\frac{1}{3}}$$

$$R_i = a_{p0,i}\, n_{p,i}^{1/D_f}$$

$$\beta_{i,j} = 4\pi\left(a_{p0_i} n_{p,i}^{\frac{1}{D_f}} + a_{p0_j} n_{p,j}^{\frac{1}{D_f}}\right)^2 \left(\frac{KT}{2\pi}\right)^{\frac{1}{2}} \left(\frac{1}{m_i} + \frac{1}{m_j}\right)^{\frac{1}{2}}$$

$$\Rightarrow \quad \beta_{i,j} = \frac{2kT}{3\mu}\left(\frac{1}{v_i^{1/D_f}} + \frac{1}{v_j^{1/D_f}}\right)\left(v_i^{1/D_f} + v_j^{1/D_f}\right)$$

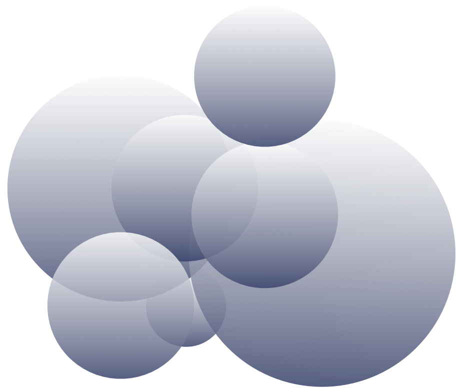
Collision Frequency Function

$$\beta_{i,j} = a_1 \left(n_{p,i}^{1/D_f} + n_{p,j}^{1/D_f} \right)^2 \left(1/n_{p,i} + 1/n_{p,j} \right)^{1/2}_{D_f > 2}$$

$$\beta_{i,j} = a \left(n_{p,i}^{1/D_f} + n_{p,j}^{1/D_f} \right)^{D_f} \left(1/n_{p,i} + 1/n_{p,j} \right)^{1/2}_{D_f < 2}$$

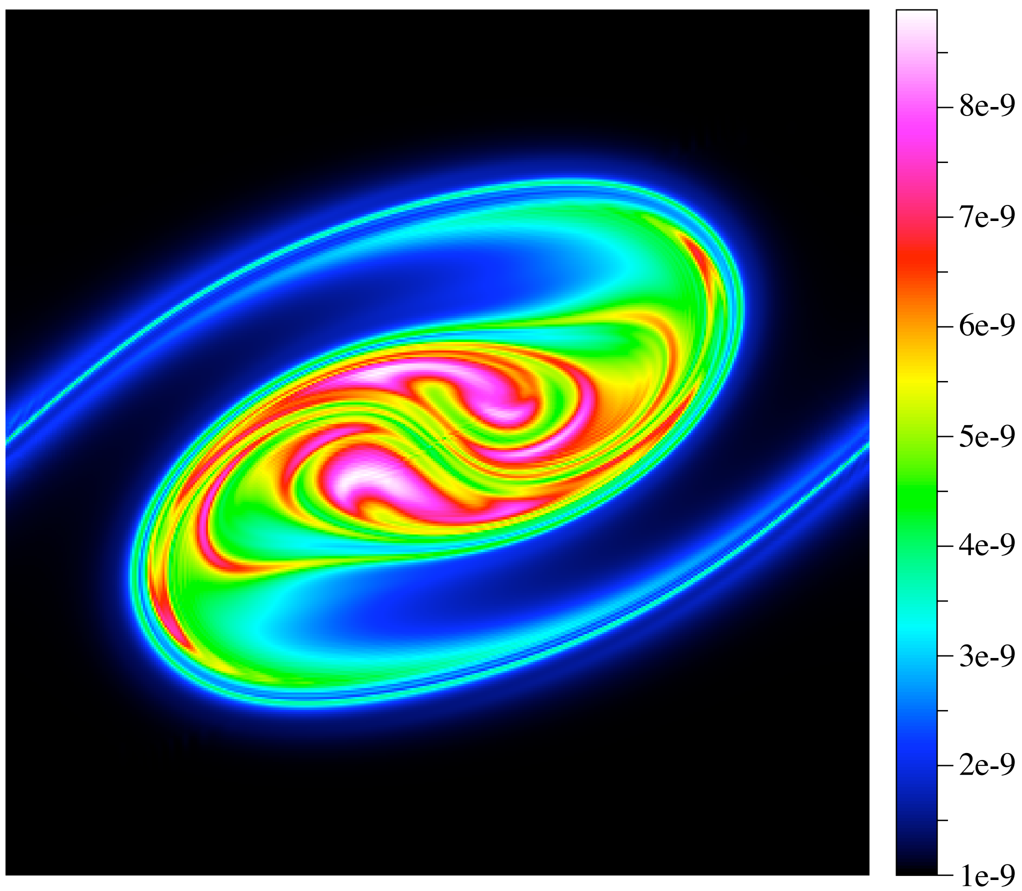
$$a_1 = \left(3v_0/4\pi\right)^{1/6} \left(6k_B T/\rho_s\right)^{1/2}$$

$$a = 2^{D_f} a_1/4.89$$

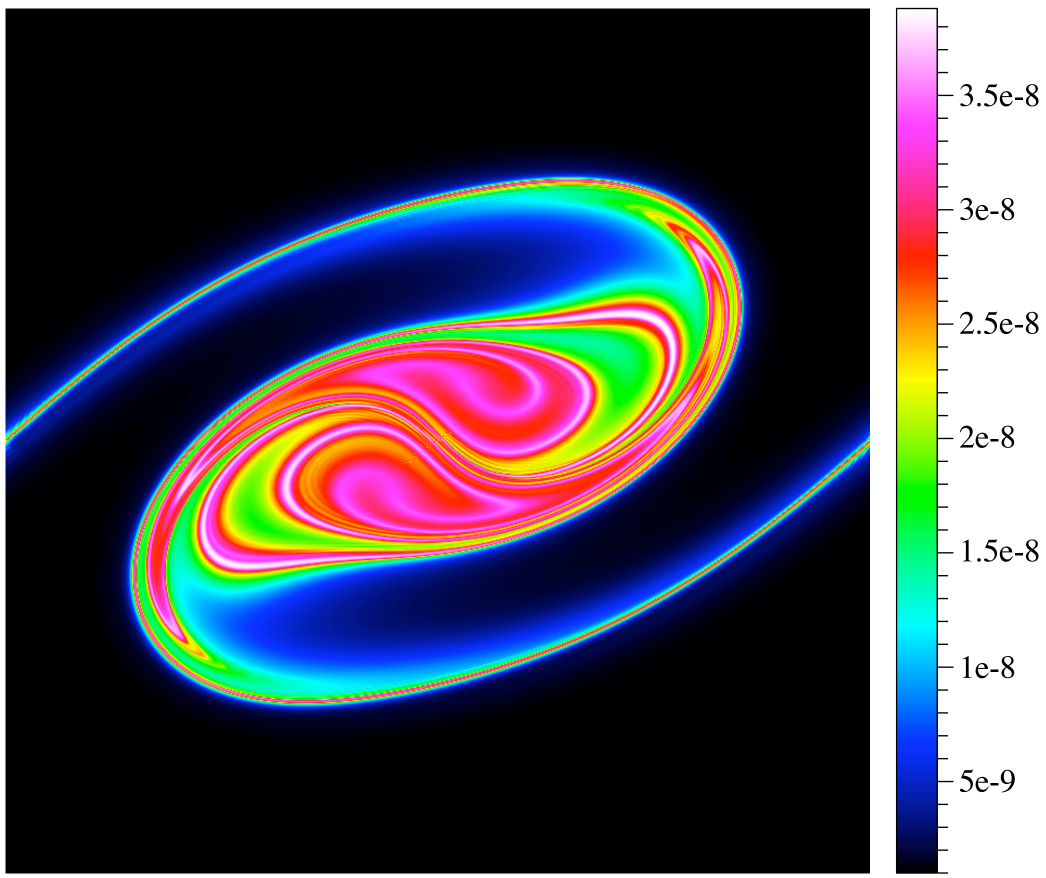


Aggregate Modeling Results

Spherical Collision Function



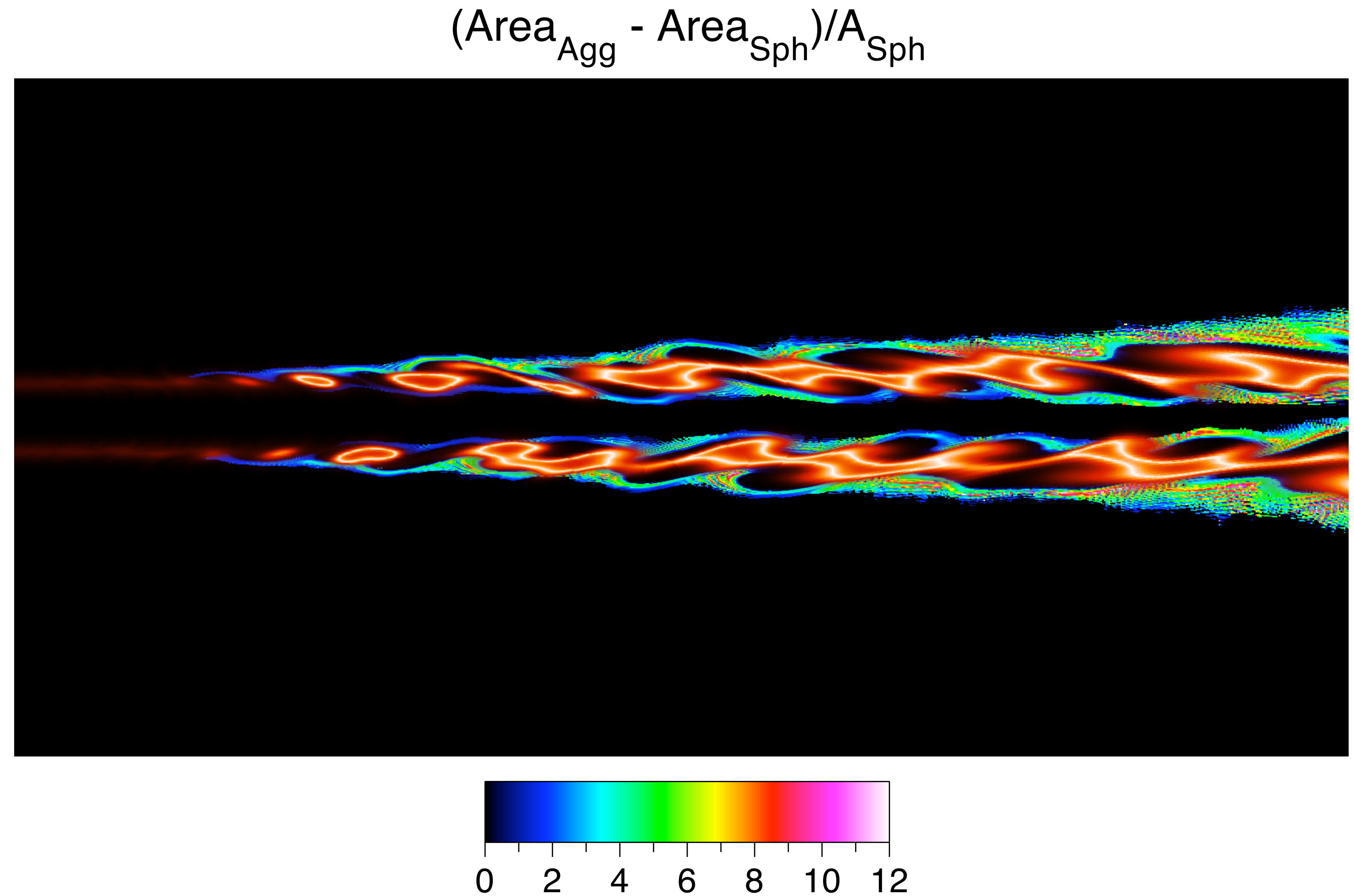
Fractal Collision Function



Instantaneous mean diameter contours of nanoparticle coagulation in temporal mixing layers

- Better prediction of growth dynamics
- Accounts for particle shape

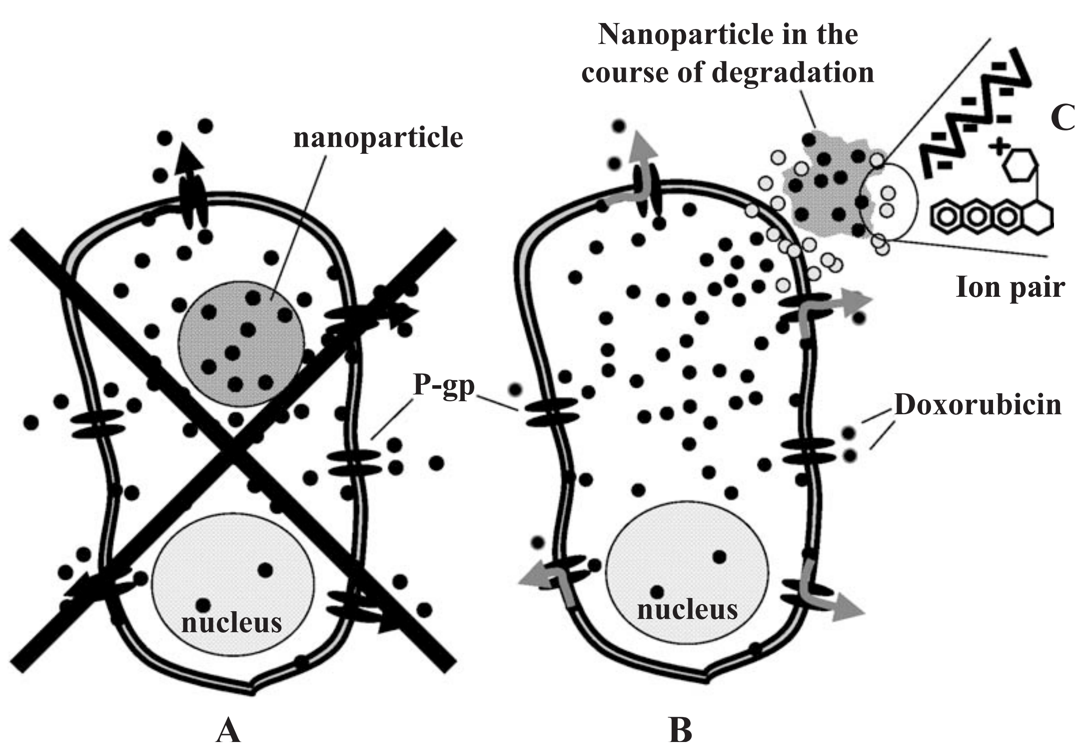
Aggregate Modeling Results

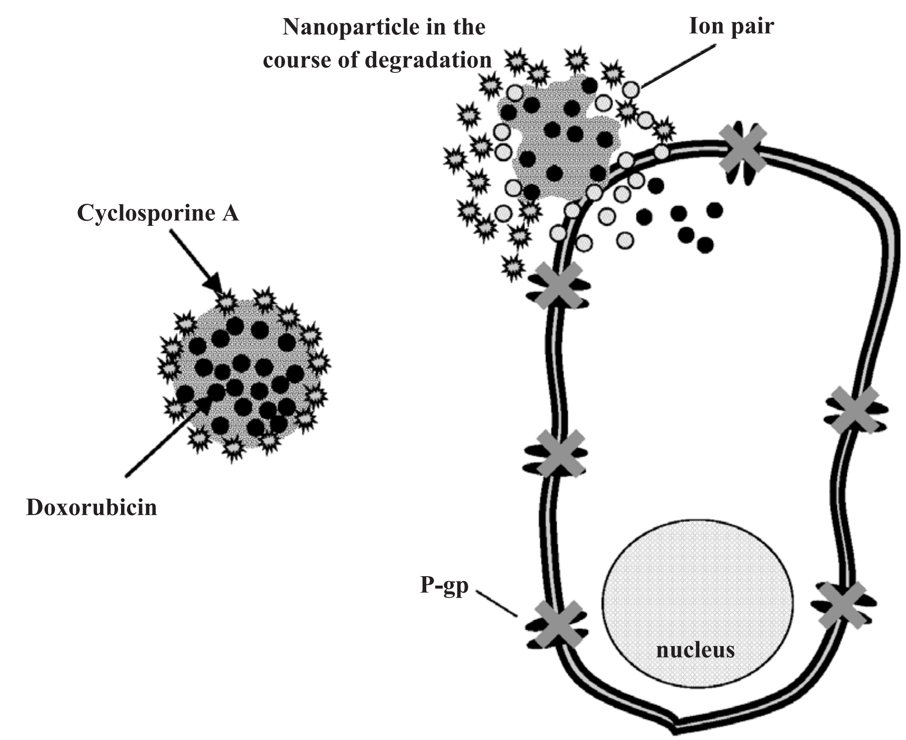


- More accurate description of nanoparticle area
  - Everything happens at the surface!

Probing the dynamics of nanoparticle growth in a flame using synchrotron radiation, Nature Materials, 3, 370-374 (2004)

Nano-bio Interaction

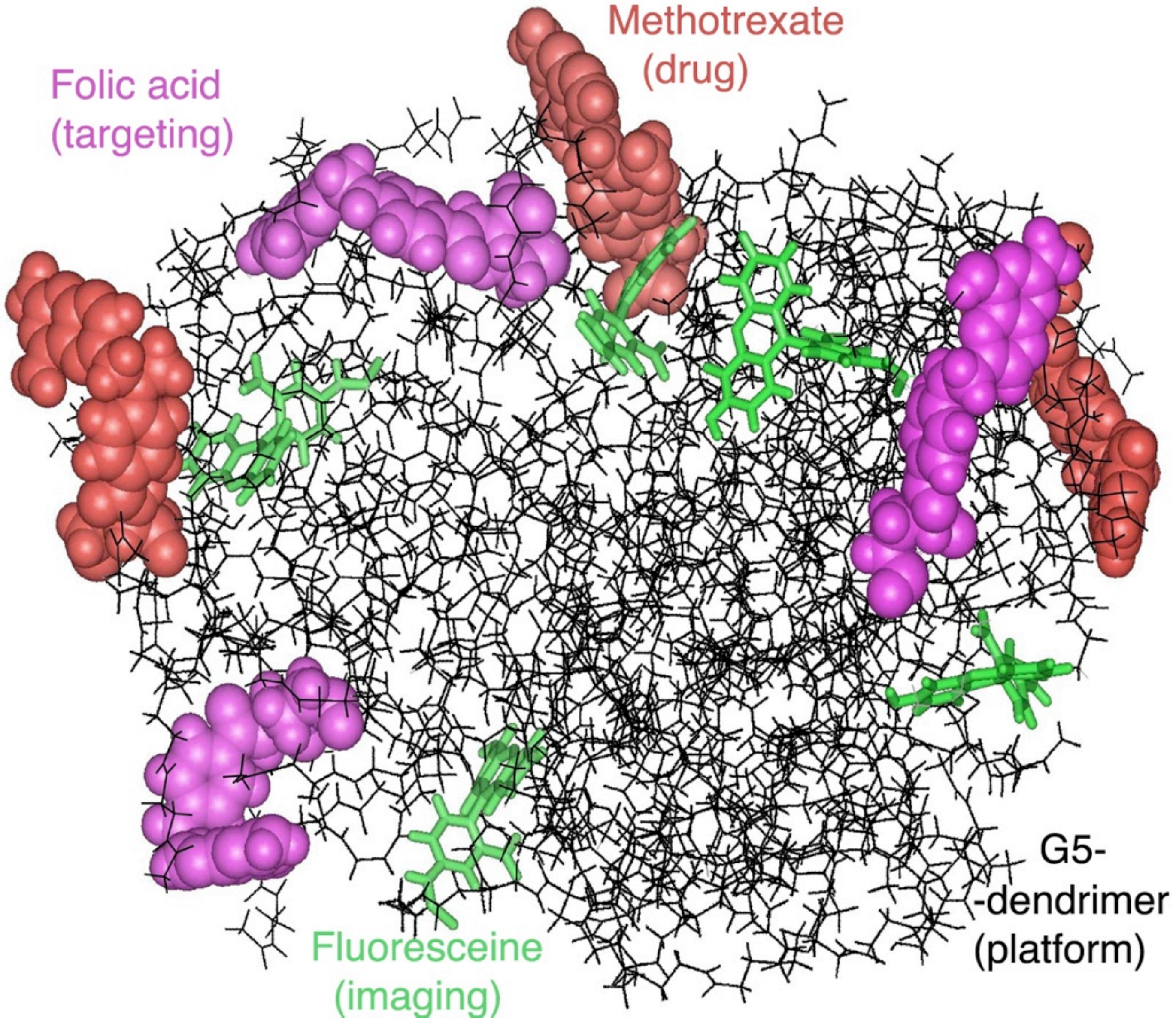




- **Nanoparticles as drug-delivery devices**
  - Chemotherapy - anticancer drugs in tumor tissue reached at expense of massive contamination
  - Multidrug Resistance - Tumor exhibit indifference to therapy
  - Create nanoparticle (drug)
  - Add coating/doping-agent

Precise control of particle morphology and composition needed!

Cancer Nano-medicine



- Prediction of crystallization is crucial
- Chemical composition
- High-rate synthesis, scalability, quality, and affordability

Nucleation Modeling

- Nodal approximation
  - Nucleation
  - Condensation
  - Coagulation
  - Full transport
- Nucleation
  - Classical (kinetics-based)
  - Correction of Girschick & Chiu
  - Many uncertainties...

$$\frac{\partial \rho Q_k}{\partial t} + \frac{\partial \rho u_j Q_k}{\partial x_j} = \frac{\partial}{\partial x_j}\left(\rho \mathcal{D}_Q \frac{\partial Q_k}{\partial x_j}\right) + \dot{\omega}_{N_k}$$

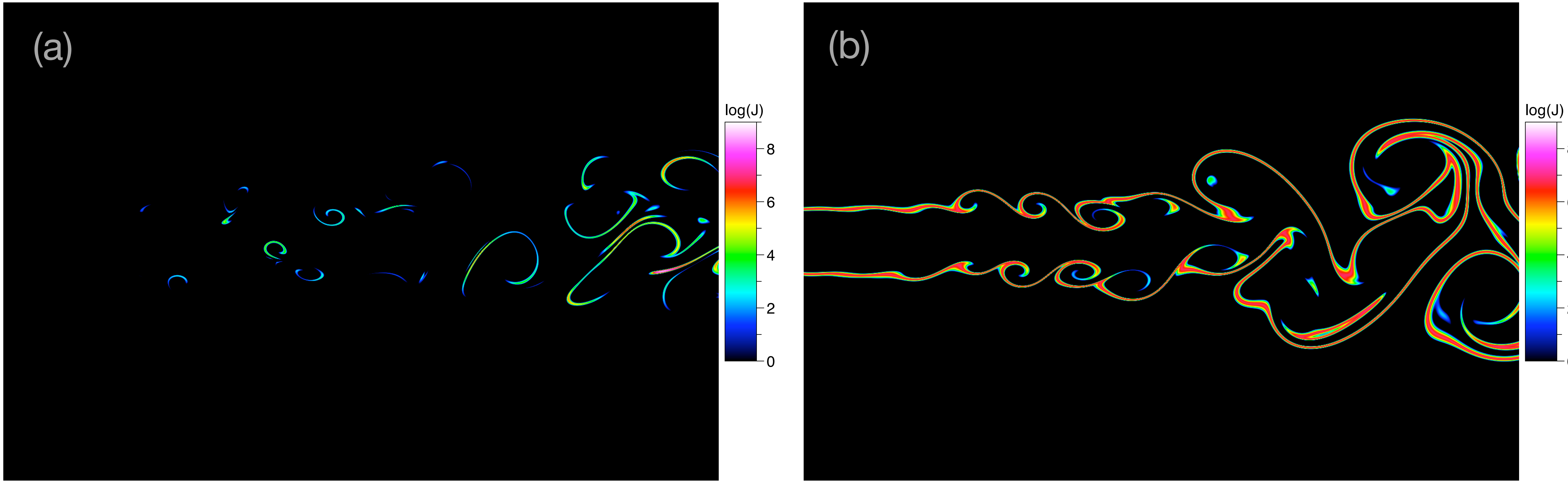
$$J_{Fr} = \frac{(\rho Y)^2}{\rho_c m_m}\sqrt{\frac{2\sigma}{\pi m_m}} exp\left(\frac{\pi\sigma {d_p^*}^2}{3kT}\right) \quad J_{Gi} = \frac{1}{S}\, exp\left(\frac{\sqrt[3]{36\pi v_m^2}\sigma}{kT}\right) J_{Fr}$$

$$d_p^* = \frac{4\sigma v_m}{k_B T\, ln(S)} \qquad \dot{\omega}_N = c_n \frac{\pi}{6}\rho_c {d_p^*}^3 J_{Gi}$$

Nanoparticle Nucleation

- Nucleation of Dibutylpthalate in a planar jet
- Nucleation occurs in regions of thermal/concentration gradients/interface(s)

Nucleation Structure



Instantaneous nucleation rate contours (log): (a) Le=~5; (b) Le=1.

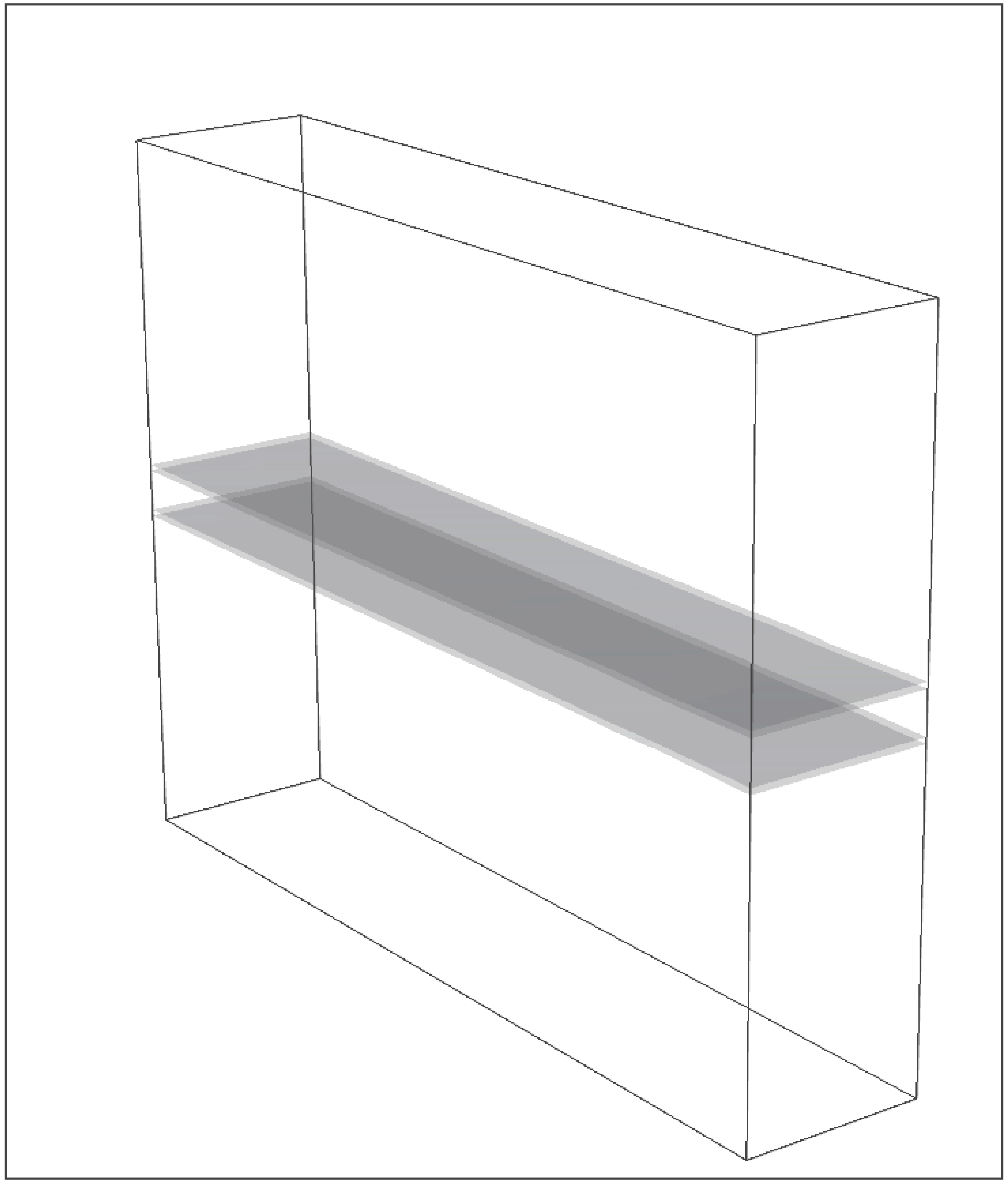
- Nucleation depends on the ratio of chemical transport to thermal transport
- Non-linear interaction between thermal & chemical mixing and molecular/crystal growth

Effects of Turbulence

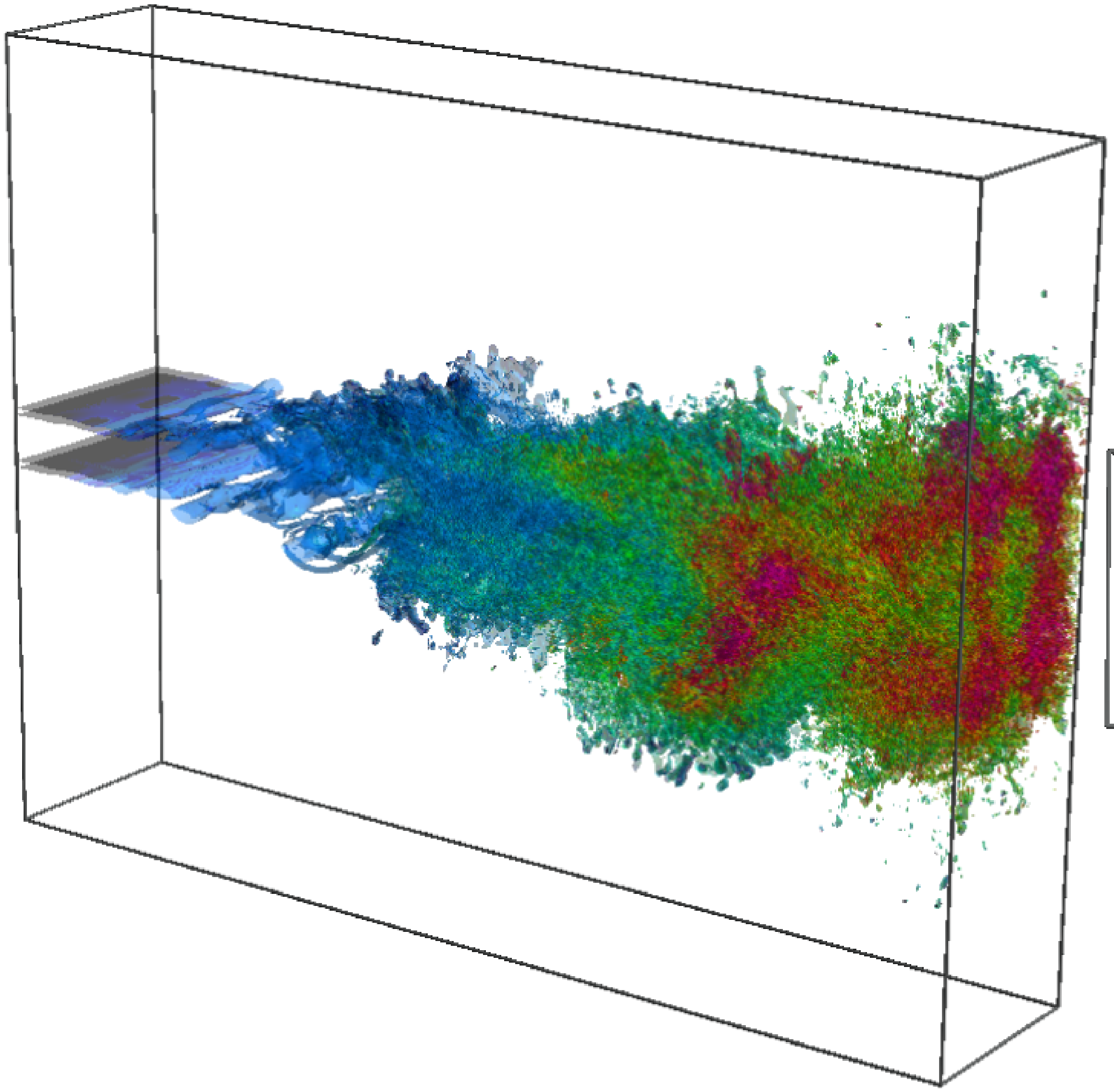
- Majority of synthesis reactors operate under turbulent flow conditions
- The effects of turbulence on nanoparticle coagulation is unknown
- Current models assume effects are negligible
- "Model-free" simulations of nanoparticle coagulation
- Decompose quantities into mean and fluctuating components
- Ascertain effects of fluctuations & provide model(s)

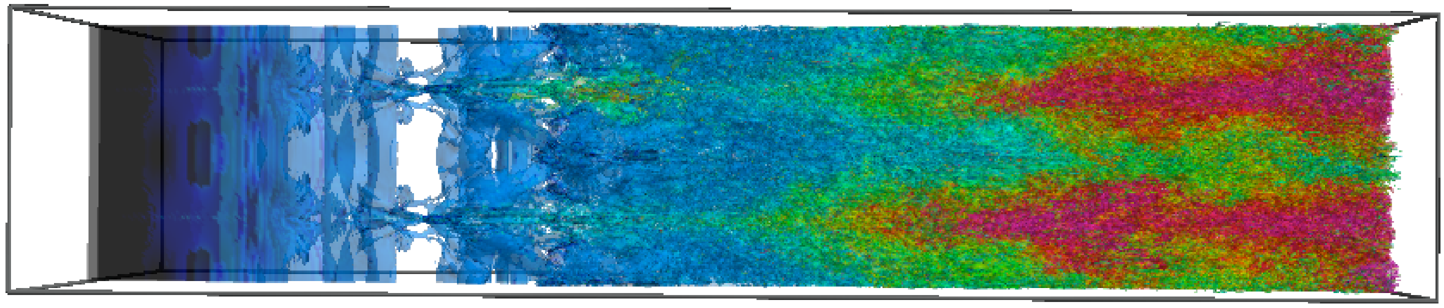
Large-Scale Mixing

- **Vorticity generation and vortex breakdown**
  - Increase entrainment of ambient/co-flowing fluid
  - Dilution of the particle-laden stream
  - Particles grow more slowly in eddy-core.



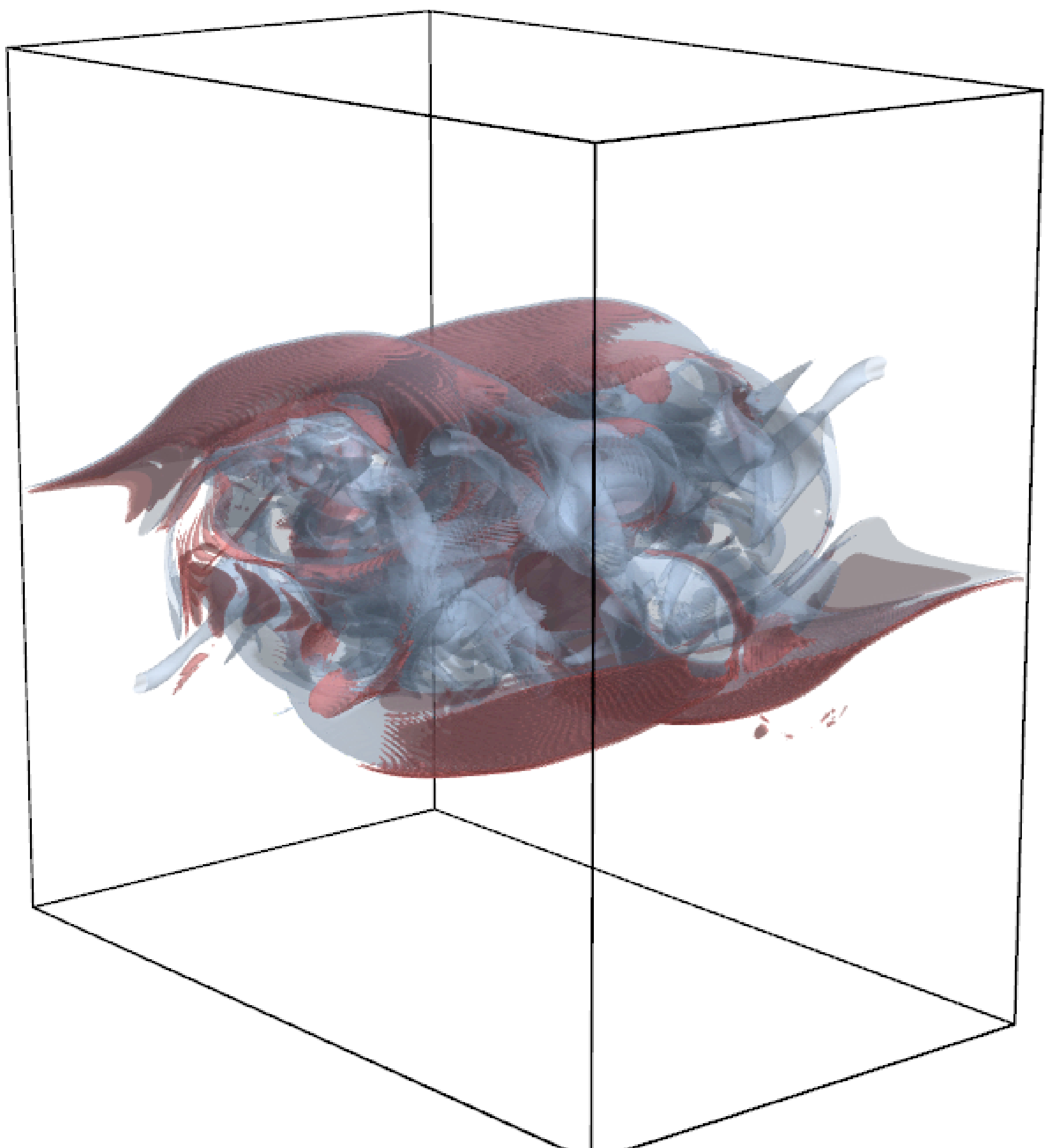
Three-Dimensional Turbulence





- 3D Computations capture dynamics present in real-world synthesis reactors
- Very expensive
  - 10,750 CPU-hours (Cray X1) 161,500 CPU-hours (Intel P4)

Nanoparticle Coagulation in Temporal Mixing Layers



a priori analysis of DNS data

$$M_i = \int Q(v) v^i dv \qquad \omega_i = \frac{\partial M_i}{\partial t}$$

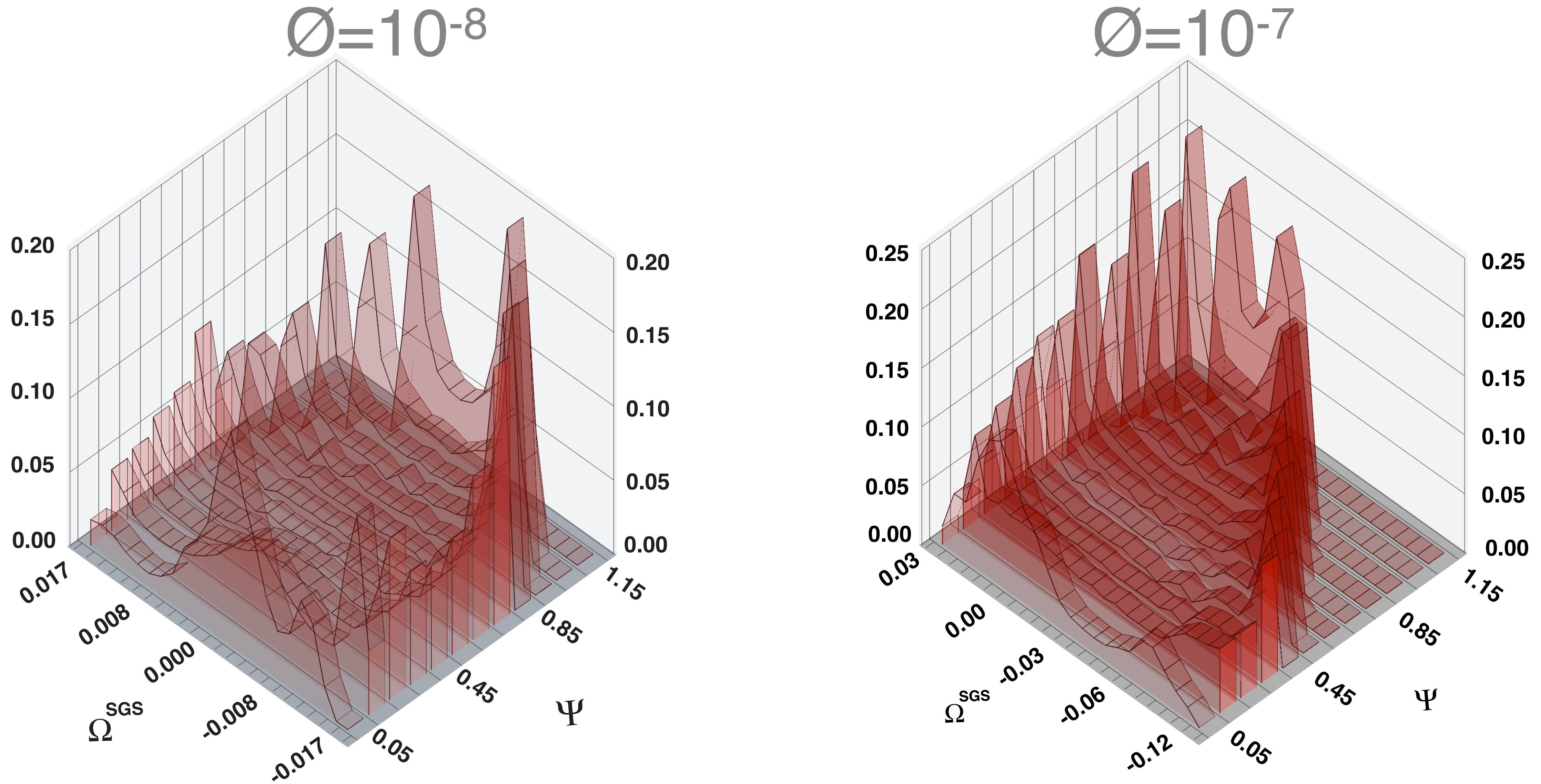
$$\Omega = \frac{\partial (d_g)}{\partial t} = \frac{1}{3}\left(\frac{6}{\pi} v_g\right)^{-2/3} \times \frac{\partial v_g}{\partial t}$$

$$\frac{\partial v_g}{\partial t} = \frac{1}{2}\left(\frac{2}{9\pi}\right)^{\frac{1}{3}} \left(\frac{M_0^{\frac{3}{2}} M_2^{\frac{1}{2}}}{M_1^4}\right)\left(\frac{-3\omega_0}{M_0} - \frac{\omega_2}{M_2}\right)$$

$$M_i = \overline{M_i} + M_i'$$

$$\Omega^M = \Omega(\overline{M_i}); \Omega^{SGS} = \Omega(M_i) - \Omega^M$$

Turbulent Coagulation



Probability density functions of Subgrid-scale coagulation conditioned on scalar dissipation.

- At low volume-fractions effects are equally distributed
- Turbulence acts to reduce nanoparticle coagulation

Future Work - SDEs

- Current approaches are impractical/unworkable
- A new/different mathematical framework must be found
- PhD dissertation

Equivalent Systems

- Two different equations can have the same solution
  - Fokker-Planck Equation (transport of a conditional PDF)

$$\frac{\partial f_L}{\partial t} + \frac{\partial[\langle u_i \rangle_L f_L]}{\partial x_i} = \frac{\partial}{\partial x_i}\left[(\Gamma + \Gamma_t)\frac{\partial f_L}{\partial x_i}\right] + \frac{\partial}{\partial \psi_\alpha}\left[\Omega_m(\psi_\alpha - \langle \phi_\alpha \rangle_L) f_L\right] - \frac{\partial[\widehat{\omega}_\alpha(\underline{\psi}) f_L]}{\partial \psi_\alpha}$$

$\psi_\alpha (\alpha = 1, N)$

N varies between 5 and 75

  - Stochastic Differential Equation

$$dX_i(t) = D_i(\underline{X}(t), t)dt + E^{1/2}(\underline{X}(t), t)dW_i(t)$$

- Must be solved in a mathematically and physically consistent manner

The large dimensionality of the Fokker-Planck equation makes it impractical

Equivalent Systems (2)

Stochastic differential is complete with specification of E and D

$$\boldsymbol{E} \equiv 2(\Gamma + \Gamma_t) \qquad \boldsymbol{D}_i \equiv \langle u_i \rangle_L + \frac{\partial(\Gamma + \Gamma_t)}{\partial x_i}$$

Numerical solution must preserve properties of the SDE

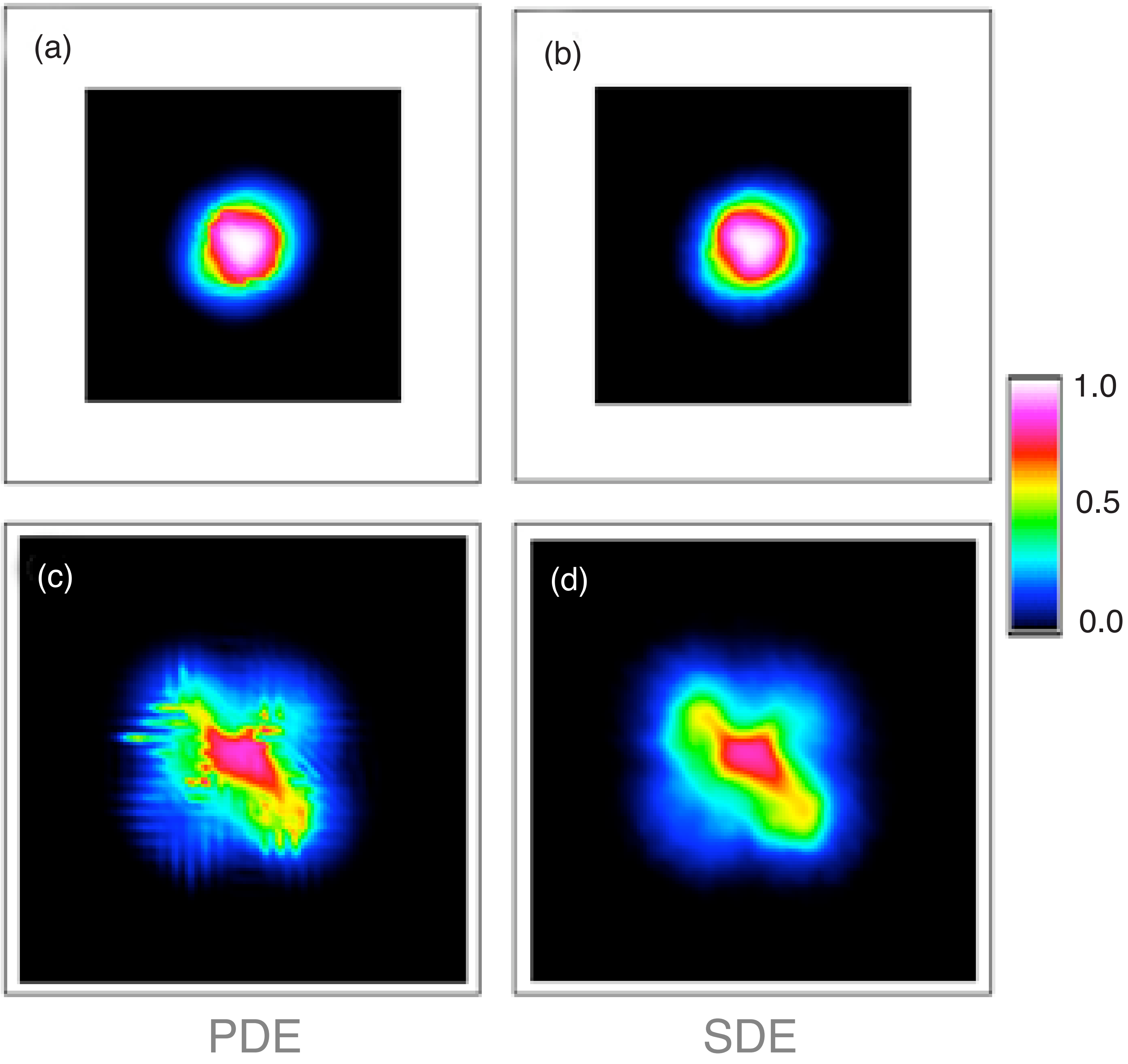
$$\boldsymbol{X}_i^{(n)}(t_{k+1}) = \boldsymbol{X}_i^{(n)}(t_k) + \boldsymbol{D}_i^{(n)}(t_k)\Delta t + \left(\boldsymbol{E}^{(n)}(t_k)\Delta t\right)^{1/2} \xi_i^{(n)}(t_k)$$

- Increased dimensionality becomes increased no. of variables
- Solution is possible.
- Run/CPU time reduced by two orders of magnitude

PDE vs SDE

Solve same problem using a set of PDEs and the equivalent SDE

- Stochastic solver produces very accurate results
- Solutions are oscillation-free



Summary

- **Applications**
  - Particle synthesis/production
  - Size control and chemical tailoring/augmentation
- **Other projects not discussed**
  - Nucleation - homogeneous vs polymerization (50+ PDEs vs 3 PDEs)
  - Stochastic solver
- **Methodology**
  - Development of mathematical models, numerical algorithms, and data-analysis tools.
- **Sponsors**
  - Army Research Office, Army Research Lab, National Science Foundation

Conclusions

- **Simulation is critical for success**
  - Appropriate mathematical modeling is crucial
- **Direct numerical simulation**
  - Very valuable as a discovery tool.
  - Provides good "data" for use in developing models .
  - Too expensive for practical work.
- **Effects of turbulence require probabilistic/ stochastic modeling**
- **Multi-disciplinary by nature**
  - Chemistry/Physics (ab initio, DFT, molecular dynamics), Chem. Eng., Mech. Eng. (experiments and computation), Mathematics,...