Maths in Industry Study Group Problem: A Model for the Reduction of Specific Surface Area of Powders with Age

Problem for the 2012 UK Maths-in-Industry Study Group, University of East Anglia.

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- Definition of Problem
- Physical processes in high surface area powders
- Review of modelling to date
- The problem and scope of the remit
- Potential strategies
- Some useful references and data

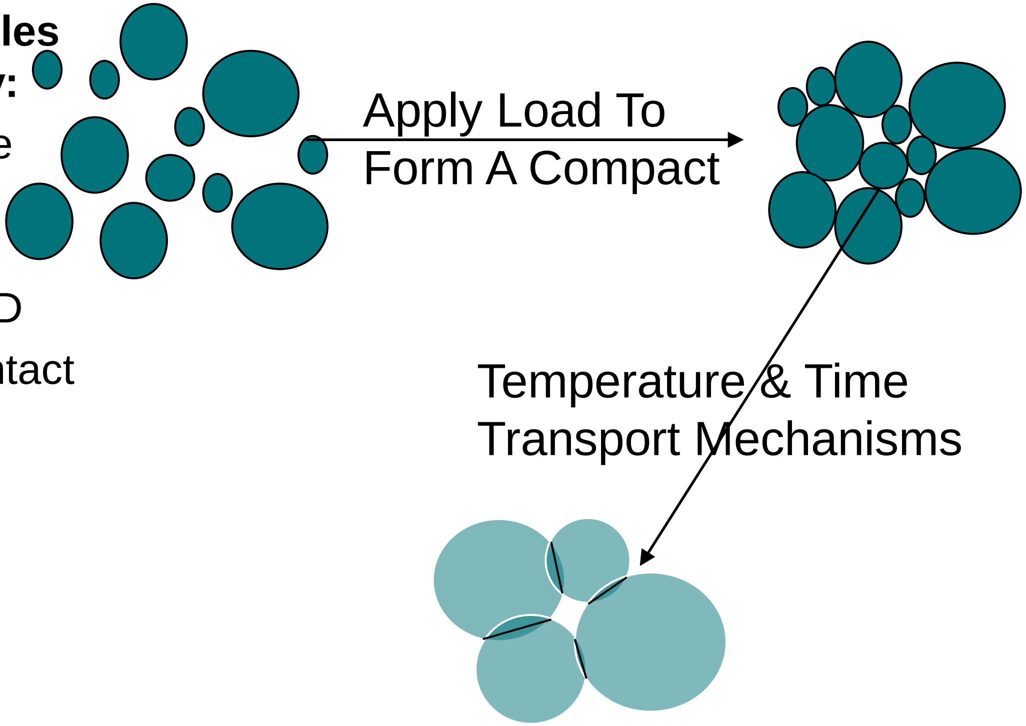
Ultimate Aim

- In an ensemble of particles large particles tend to increase in size at the expense of smaller particles
- The change in particle size is driven by complex, interacting mechanisms (*Transport Mechanisms*)
- *A model capable of describing the change in particle size distribution (PSD) and specific surface area (SSA) of a low density (50% TMD) compacted powder is required.*

Overview of Problem

Dispersed particles characterised by:

- Specific Surface Area , SSA
- Particle size distribution, PSD
- No physical contact



Apply Load To Form A Compact

Temperature & Time Transport Mechanisms

Compact:

- Particles in contact
- Reduction in effective SSA
- PSD unchanged
- Capillaries and pores size distributions determined by density and PSD

Modified Compact:

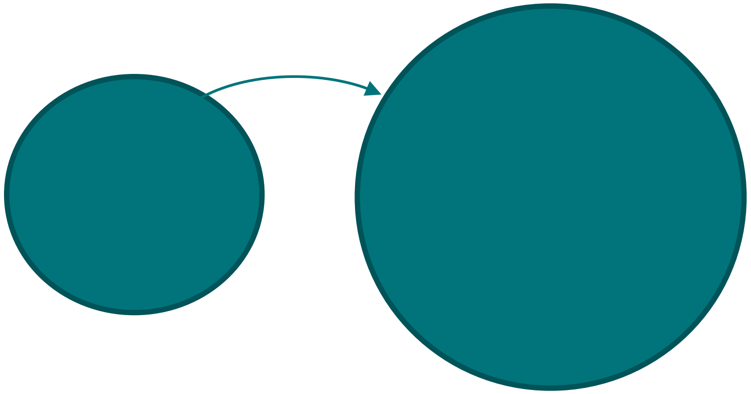
- Decrease in Specific Surface Area, SSA
- Change in Particle size distribution, PSD
- Fusing of particles
- Change in capillary and pore structure

Changes in PSD and SSA

- These changes occur as a result of Surface Transport Mechanisms, eg
    - Evaporation-Condensation
    - Surface Diffusion
- And Bulk Transport mechanisms, eg
    - Grain Boundary Diffusion
    - Plastic Flow
- Increasing the temperature drives / accelerates these processes
- *Evaporation-Condensation* and *Surface Diffusion* are considered here

Transport Mechanisms

- Evaporation-Condensation
  - Molecules detach from a particle surface, diffuse through the gas phase and condense of the surface of a different molecule
  - Driven by Gibbs Thompson effect



Gibbs - Thompson

$$kT\ln\frac{P_r}{P_\infty}=\frac{2\sigma\upsilon}{r}$$

P_r = *equilibrium pressure of particle, radius r*

P_∞ = *equilibrium pressure of bulk, radius r*

v = *volume of molecule in the solid phase*

σ = *surface energy density*

T = *temperature*

k = *Boltzmann constant*

Evaporation - Condensation

- Mass loss per unit area is given by:

$$\delta m_{-} = p_{\infty}(T)\exp\left(\frac{C}{TR}\right)\sqrt{\frac{M}{2\pi RT}}\,\delta t$$

  - C = constant which includes radius of curvature of the particle
  - M = molecular mass
  - $p_{\infty}(T)$ = vapour pressure of large particle

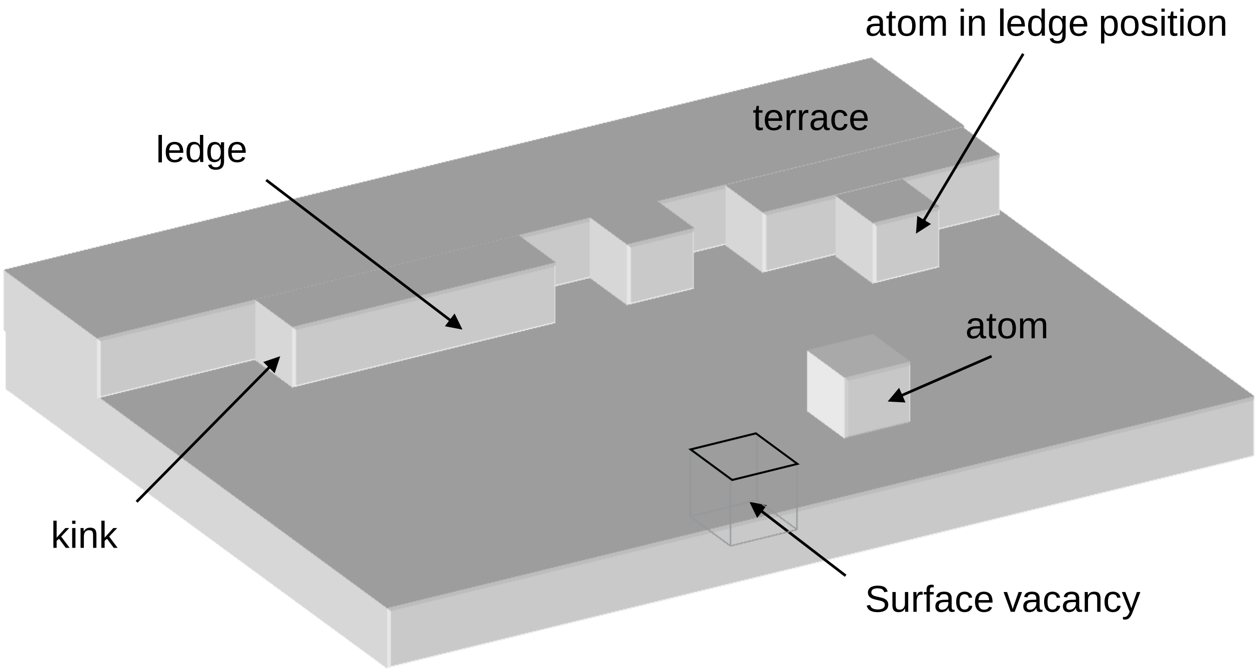
- Mass gain (no particle size dependence):

$$\delta m_{+} = p\sqrt{\frac{M}{2\pi RT}}\,\delta t$$

  - p = background partial pressure

Transport Mechanisms

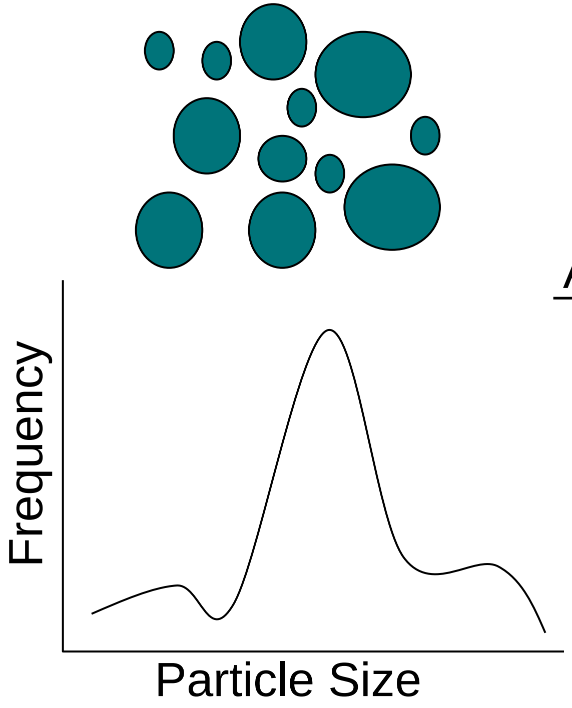
- Surface Diffusion
    - Diffusion on particle surface, without detaching to the gas phase



- Step 1 - Breaking an atom away from existing bonds, at a kink, depends on surface orientation and temperature
- Step 2 – Atom moves with a random motion across the surface (usually a fast step)
- Step 3 – the atom must re-attach at an available surface site, possibly again at a kink

Courtesy of Eun Ju Park

Compaction of a Powder



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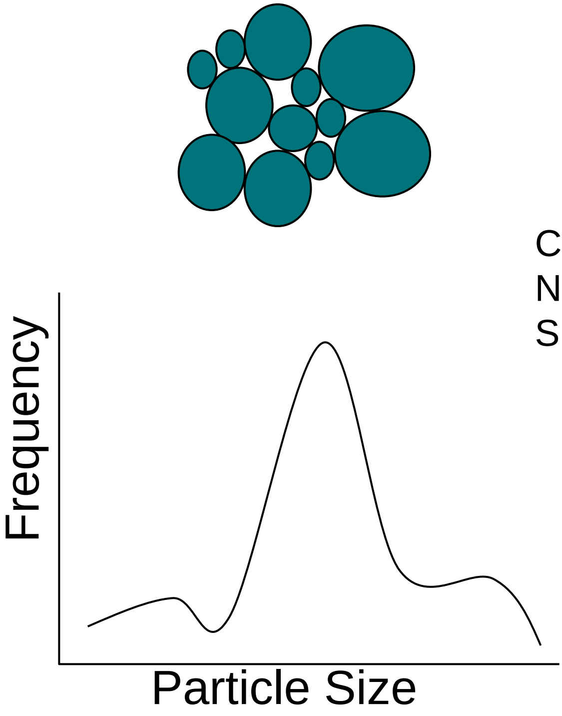
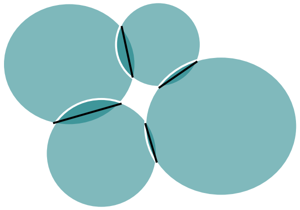


Compaction leads to:
No change to PSD
Slight decrease in SSA



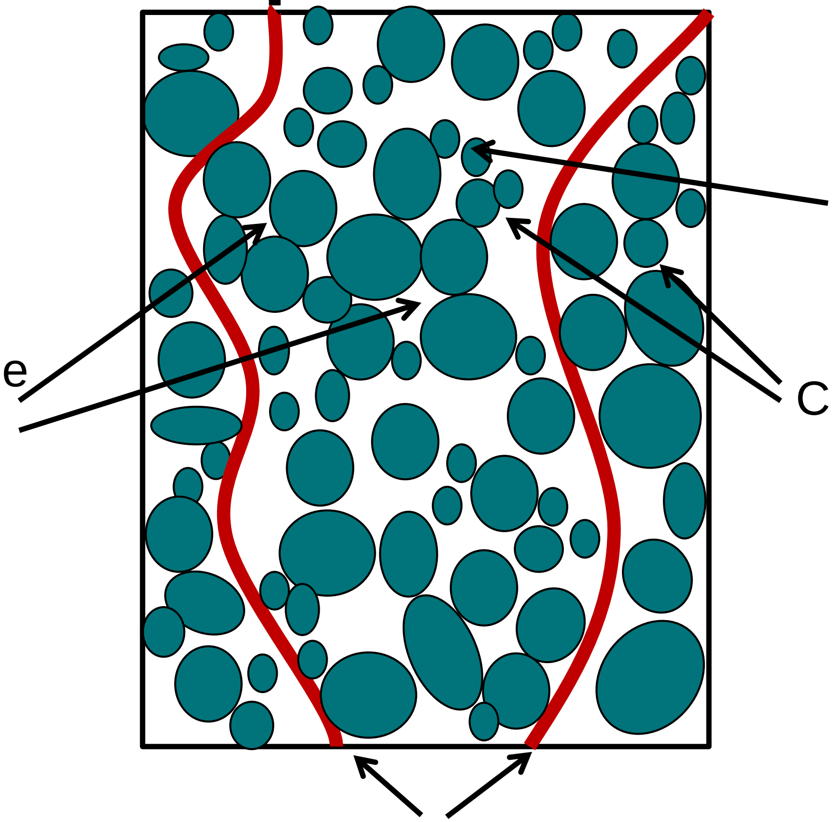
Loose Powder characterised by

- Specific Surface Area (SSA)
- Particle size distribution (PSD)

Compacted Powder characterised by

- Specific Surface Area
- Particle size distribution
- Density and porosity

Structure Of A Low Density Compacted Powder – Conceptual View



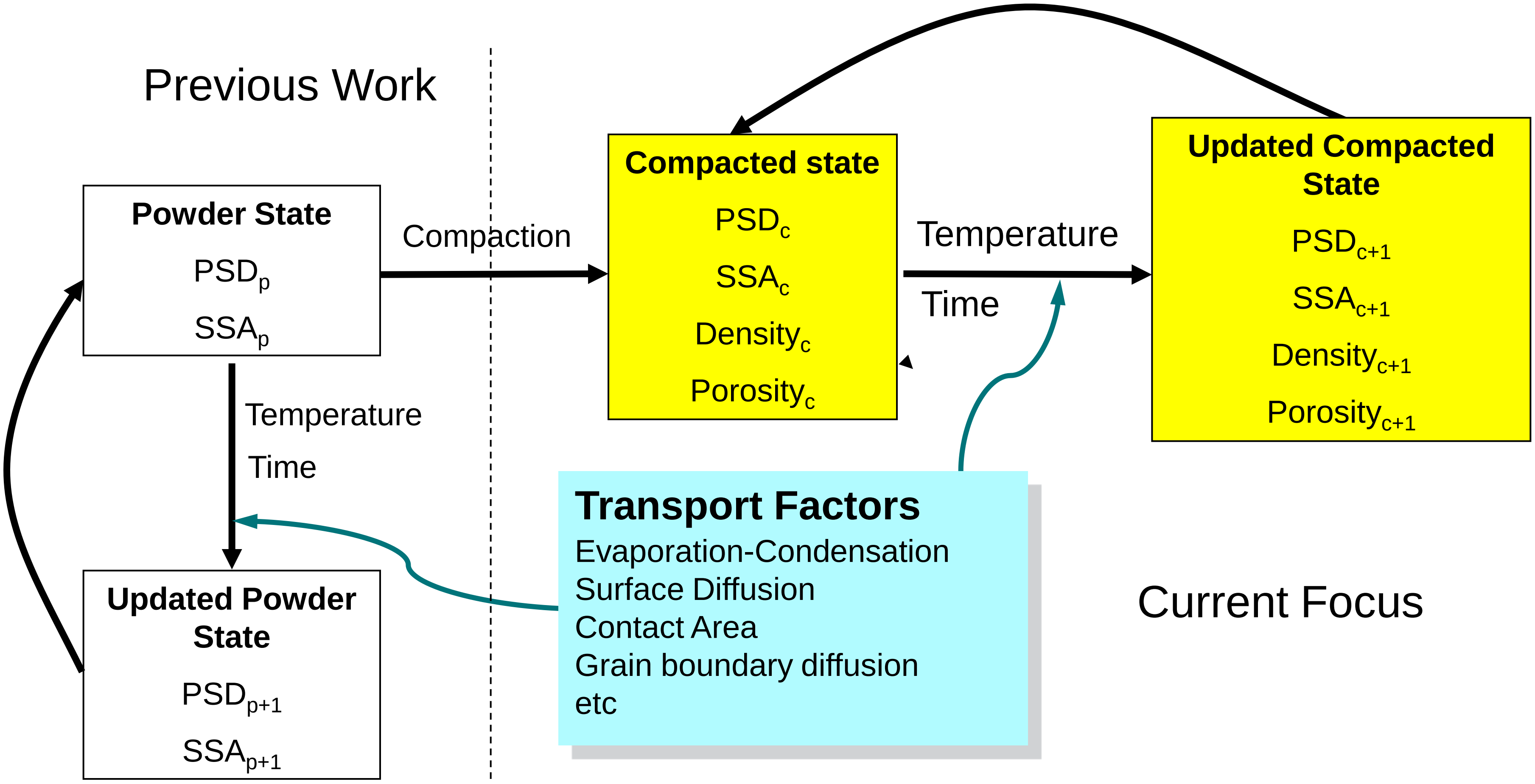
Growth could result in
a closed volume

Closed Volume
/ Pore

Contact Points/Areas –
Potential Sintering

Flow Paths
(Capillaries)

Problem Summary



Previous Work

Powder State

PSD_p

SSA_p

Compaction

Temperature

Time

Updated Powder State

PSD_{p+1}

SSA_{p+1}

Compacted state

PSD_c

SSA_c

$Density_c$

$Porosity_c$

Temperature

Time

Updated Compacted State

PSD_{c+1}

SSA_{c+1}

$Density_{c+1}$

$Porosity_{c+1}$

Transport Factors

Evaporation-Condensation
Surface Diffusion
Contact Area
Grain boundary diffusion
etc

Current Focus

Potential Strategies

Previous work

- To date the mathematical modelling of the coarsening process in explosives, sometimes referred to as ‘Ostwald Ripening’, has usually made the assumptions that:
  - the explosives comprise a collection of detached spherical particles of differing radii
  - and that mass transfer occurs via the Gibbs-Thompson effect.
- It is known that crystal growth is highly dependent on local surface curvature.
- An improved treatment of diverse shapes might improve the mathematical description of the process.
- The first highly transient phase of the coarsening process in particular is not yet well understood.

Statement of Problem and Scope - 1

- The first main aim of the proposed study is to investigate the physical modelling of the atomic-level mass-transfer processes causing coarsening of solid powders
- In particular the study should address:
    - how to relax the assumption of separate particles, instead allowing contact between them;
    - and under these circumstances how to model evaporation-condensation and surface diffusion.
- Factors to consider are likely to include particle shapes and sizes, temperature, porosity, permeability, material models, and packing issues.

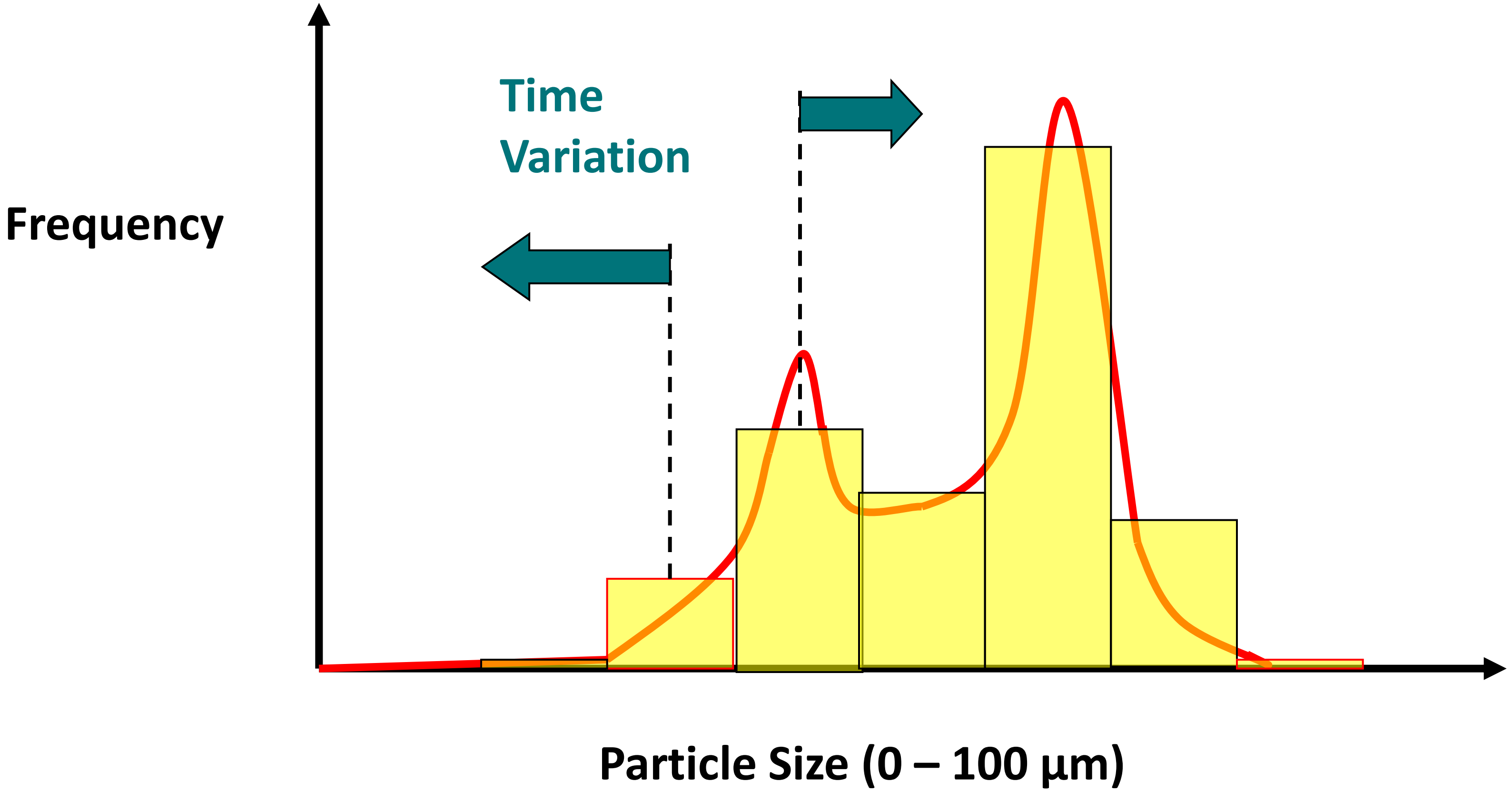
Statement of Problem and Scope - 2

- Another main aim is to model the evolution of the statistical distribution of particles.
- This could be by first assuming spherical particles and then relaxing that assumption.
- Ideally a distribution model will allow different models of the physical mechanisms to be tested.

Possible Strategy – 1: A Discrete Approach

- Start with Maiti and Gee discrete model for separate particles – simple ODE model under development
- Continue to assume spheres
- Assume rigid first – then relax this assumption to elastic particles
- Express porosity, tortuosity/permeability as functions of particle size distribution and packing?
- Adjust M&G expression for molecule addition φ(r) to reflect these functions and the contact between particles
- Further adjust same expression to represent surface diffusion, either by expressing ‘roughness factor’ s as a function or by other means (not treated in Maiti and Gee)
- Go on to allow mergers of particles, still with spherical shape assumption or perhaps allowing ellipsoids

Particle Size Distribution – Discrete Representation (like Maiti and Gee for separate particles)

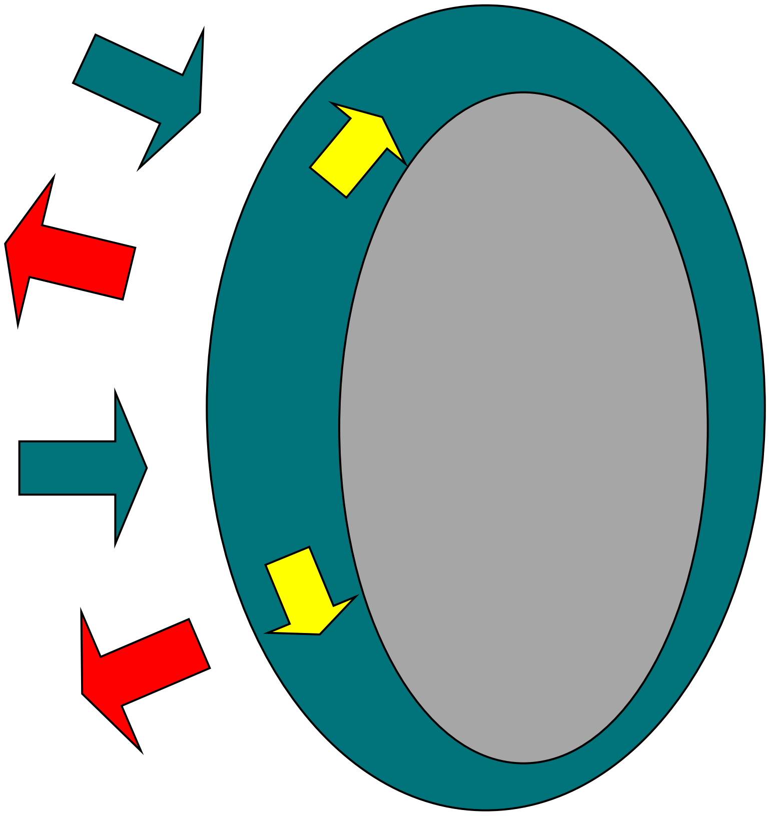


Possible Strategy – 2: Field approach

- Develop a ‘continuum’/granular flow model in which specific surface area is a field variable
- Continuous equations for evolution of particle distribution treated simultaneously
- The porosity, permeability and specific surface area are to be functions of particle size distribution and stress, strain, temperature etc.
- Possible use of random treatment of particle sizes

Possible Strategy – 3: Detailed Continuum Particle Model

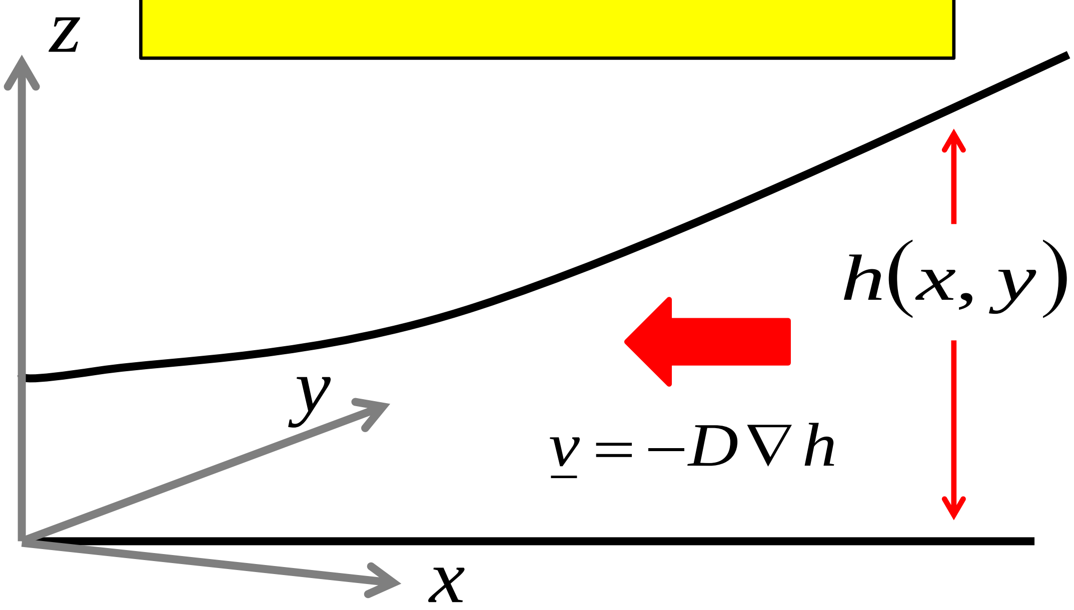
- Detailed continuum modelling of coupled evaporation / condensation / surface diffusion problem
- Plastic flow? Elastic core?
- Surface tension - like curvature dependent b.c. for Gibbs surface energy?
- Shape evolution
- Probably assuming layer thickness in which plastic flow occurs is very small



Possible Strategy – 4: Surface Diffusion
Using local co-ordinates

Fick's Law

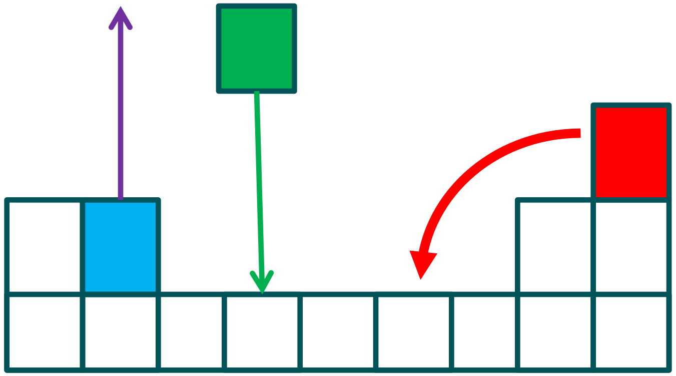
$$dA = \sqrt{\left[1+\left(\frac{\partial h}{\partial x}\right)^2\right]\left[1+\left(\frac{\partial h}{\partial y}\right)^2\right]}\,dx\,dy$$

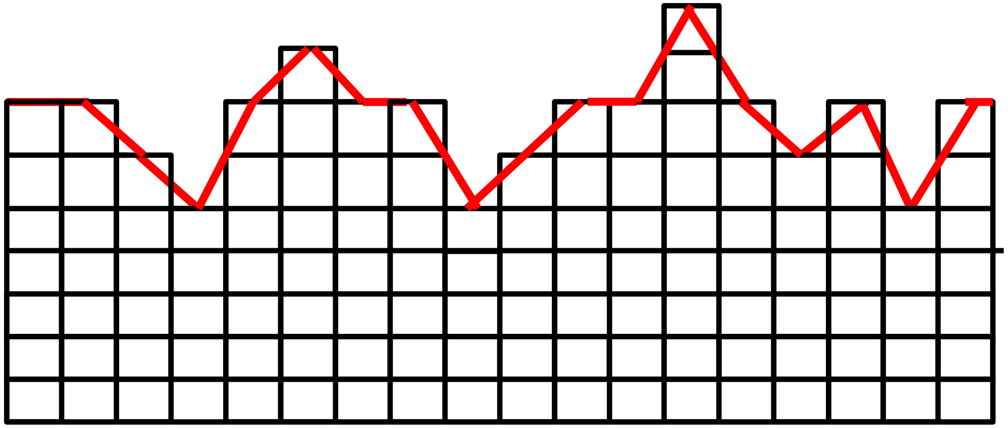


$$\underline{v} = -D\nabla h$$

Possible Strategy – 5: Detailed Discrete Probabilistic Particle Model

- Molecules as cubes
- Evaporation/condensation modelled stochastically
- Diffusion by cubes ‘jumping’ with given probability to attach elsewhere on surface
- SSA approximation from discrete profile





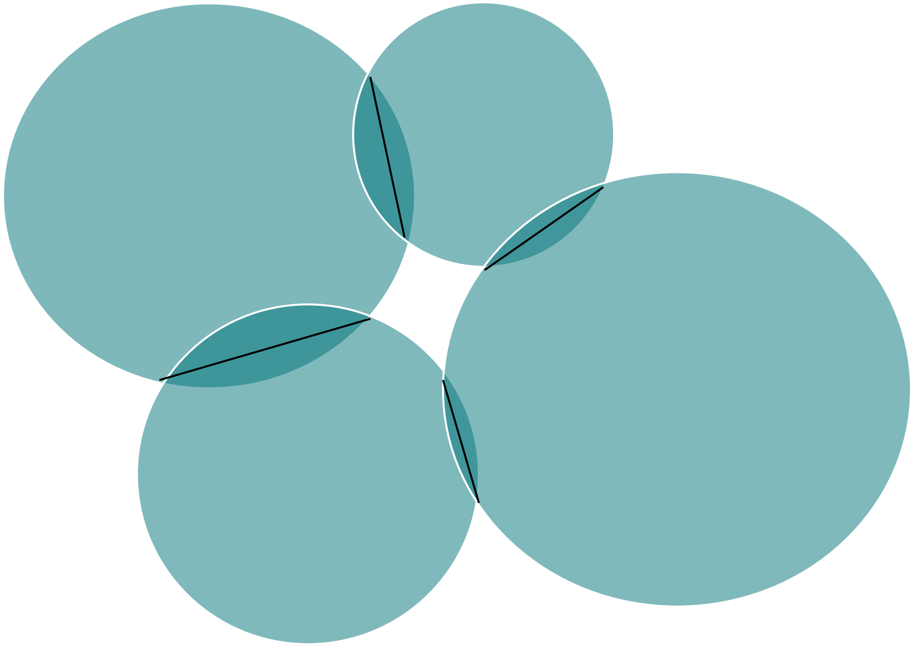
Possible Strategies – 6: PSD Evolution

- Examine methods of solution of generic continuous distribution problem
- Factors to include are:
  - particle characterisation and growth
  - particle mergers – sintering
  - vanishing of particles by evaporation
- Extend classical theory for distribution n(x,t), with x size, t time to include mergers:

$$\frac{\partial n}{\partial t}+\frac{\partial}{\partial x}\left(n\dot{x}\right)=\int_0^x v\left(x,x_1\right)dx_1-\int_x^X w\left(x,x_1\right)dx_1$$

Possible Strategies – 7: SSA From Particle Size Distribution (PSD) and Stress

- For rigid particles– no loss in Specific Surface Area (SSA)!
- Under stress, contact reduces SSA, based on Particle Size Distribution (PSA)
- Elastic deformation of spheres pressing – then ellipsoids, other crystal shapes?



References and Data – Problem Specific

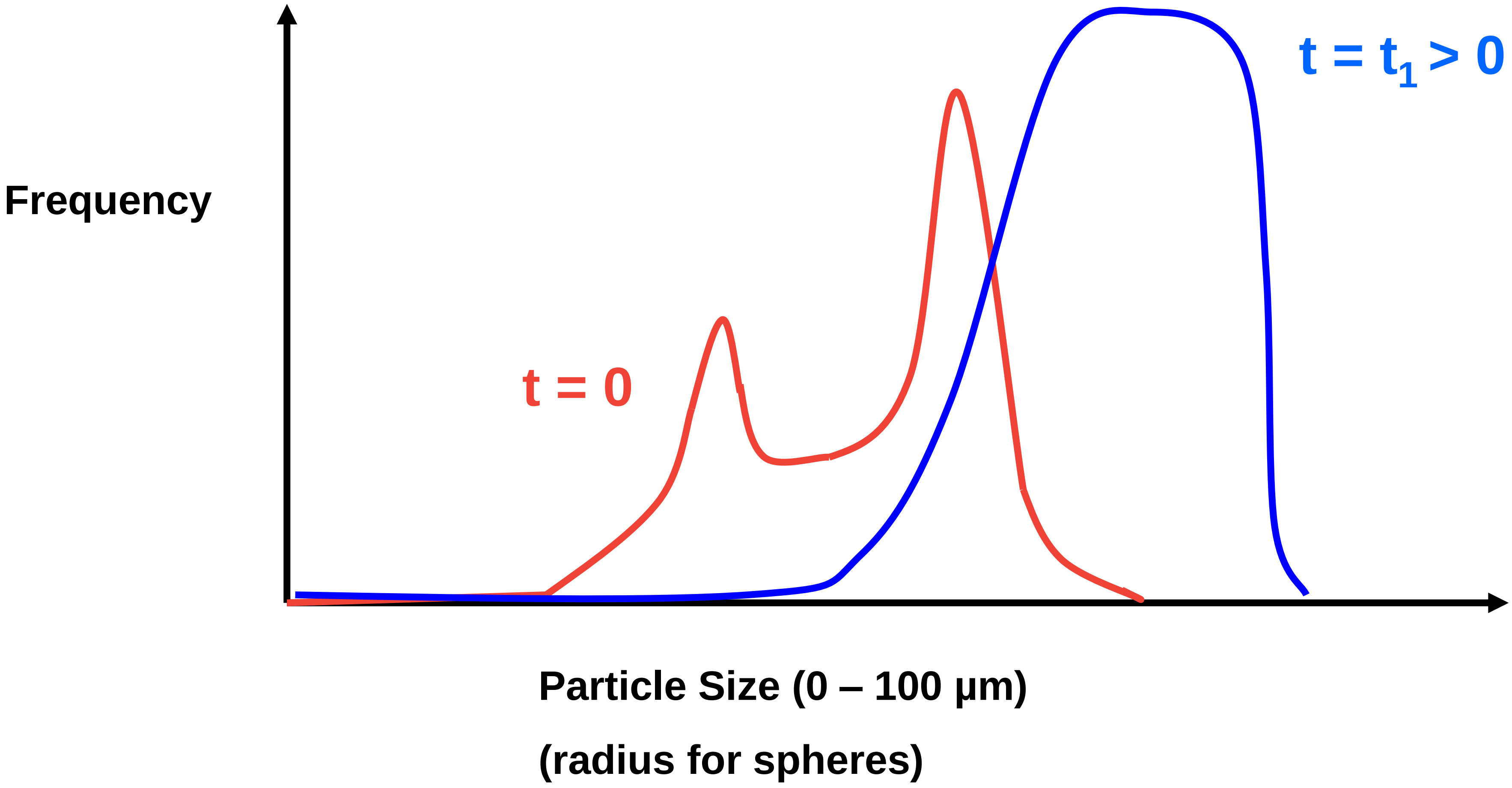
- PETN Coarsening – Predictions from Accelerated Aging Data by Maiti and Gee, PEP 2011, *36*,125-130
- Modeling Growth, Surface Kinetics and Morphology Evolution in PETN, by Maiti and Gee, PEP 2009, *34*, 489 – 497
- Thermal analysis of Pentrerythritol Tetranitrate and Development of a Powder Aging Model by Brown et al, 37th Annual Conference of the north American Thermal Analysis Society, 2009

References and Data – General Theory

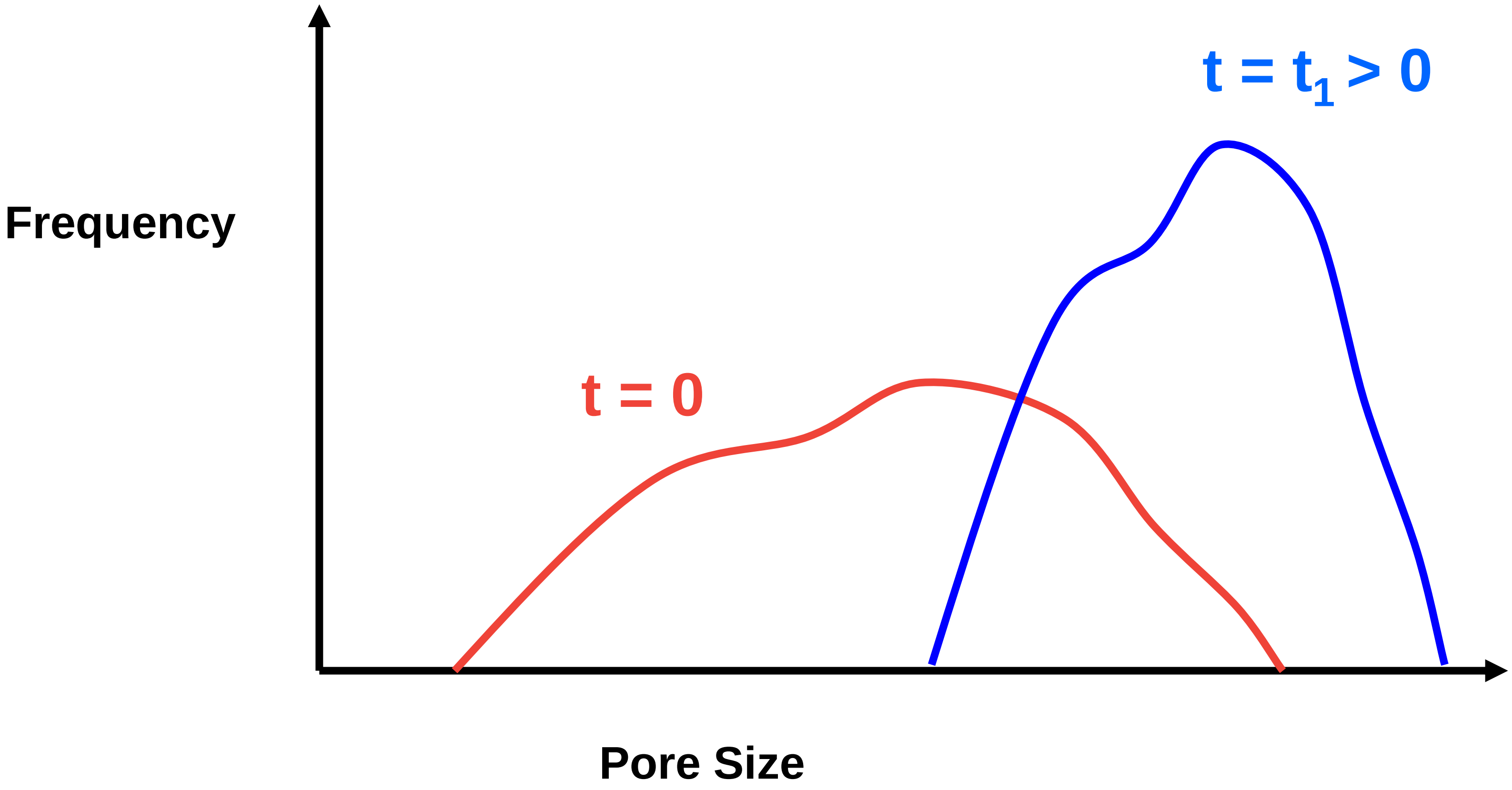
- Growth of Crystals from the Vapour (Book) by Faktor and Garrett
- Theory and simulation of Ostwald ripening by Yao et al, Physical Review B 1993, Vol 47, No 21, 110 - 125
- The Theory of Ostwald Ripening by Voorhees, J Stat. Phys. 1985, *38*, 231 – 252
- A Random Walk Approach to Ostwald Ripening by Schwind and Ågren, Acta mater. 49 (2001) 3821 – 3828
- Ostwald ripening: A stochastic approach by Ashok and Ruckenstein, J Chem. Phys. 103 (16) 7120 – 7135
- The kinetics of precipitation from supersaturated solid solutions by Lifshitz and Slyozov, J Phys. Chem. Solids, 1961, Vol 19, 35 - 50

Questions

Particle Size Distribution - Continuous



Pore Size Distribution



PETN SSA change at elevated temperature

- Pentaerythritol Tetranitrate (PETN) is an explosive commonly used in both civilian and military applications. The performance of the explosive is dependent on the properties of the packed powder bed. One of the most important properties is the specific surface area (SSA) of the crystalline powder.
- The surface of PETN crystals is highly active, and the particles will coarsen with time to minimise the surface energy, of free energy, resulting in a reduced SSA. This effects the performance of the explosive and has clear implications for ageing properties. This process is accelerated at elevated temperatures.

Powder Coarsening

- High surface area powders are required in a number of technology areas
  - For example the efficiency of catalysts depends on the surface area of the powder
- High surface area powders contain small particles which will tend to have a *high Gibbs Surface Energy*
- These powders tend to coarsen to reduce this surface energy
- Compaction of a powder complicates matters further!

Aging mechanisms

- The main mechanisms by which powders may change their surface area are believed to be:
    - evaporation-condensation, in which molecules detach from a particle surface, diffuse through the gas phase, and then condense on the surface of a different particle;
    - surface diffusion, in which the molecule undergoes long-term diffusion on (solid) particle surfaces without detaching into the gas phase.

Gibbs Free Energy

- A system will seek to achieve the minimum free energy.
- Gibbs free energy assumes the system is maintained at constant temperature and pressure

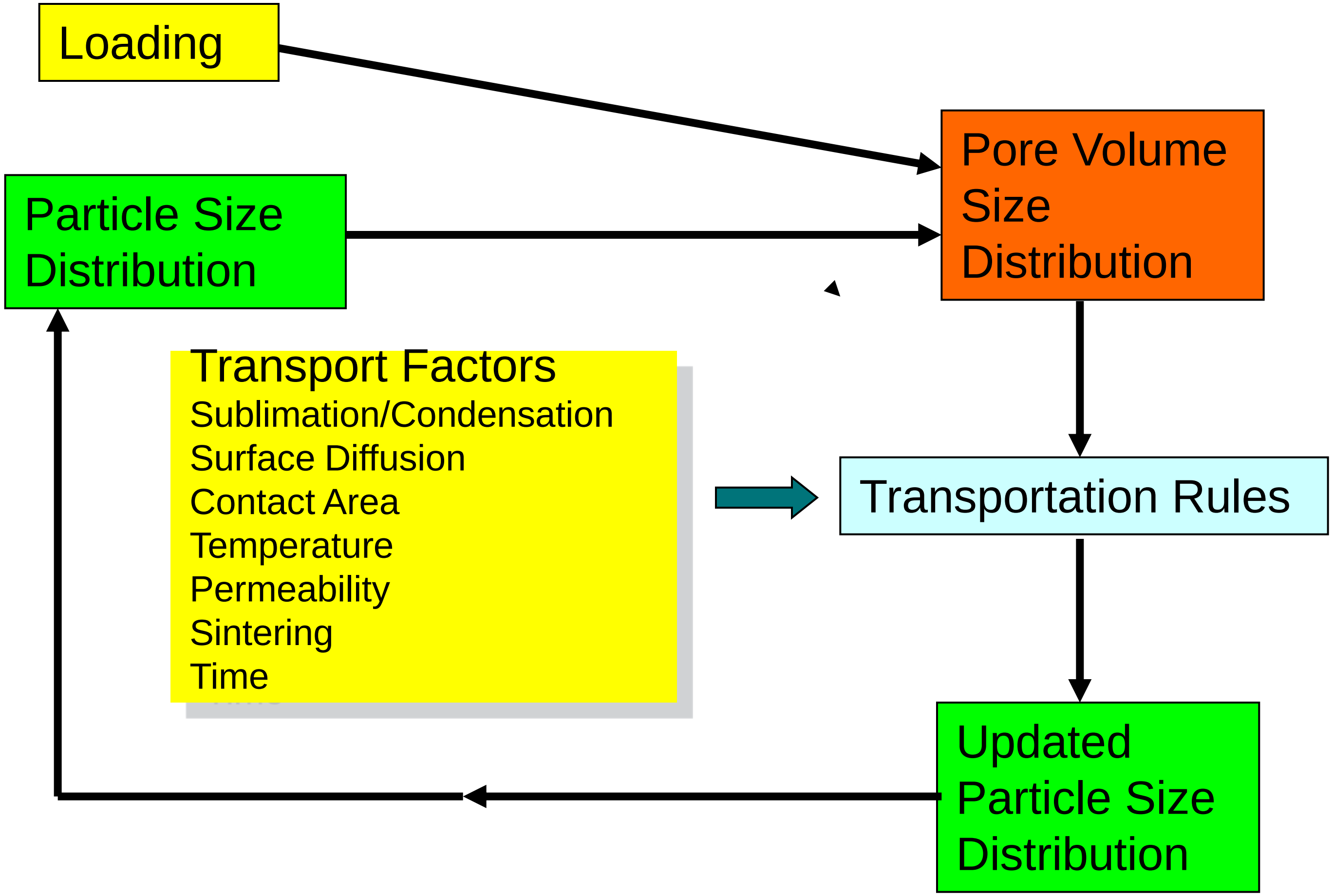
$$G = U + PV - TS$$

where

  - U is the internal energy of the system,
  - P is the pressure
  - V is the volume
  - T is the temperature
  - S is the entropy

- If $\Delta G = \Delta H - T\Delta S$

Problem Schematic



Loading

Particle Size Distribution

Pore Volume Size Distribution

Transport Factors

Sublimation/Condensation

Surface Diffusion

Contact Area

Temperature

Permeability

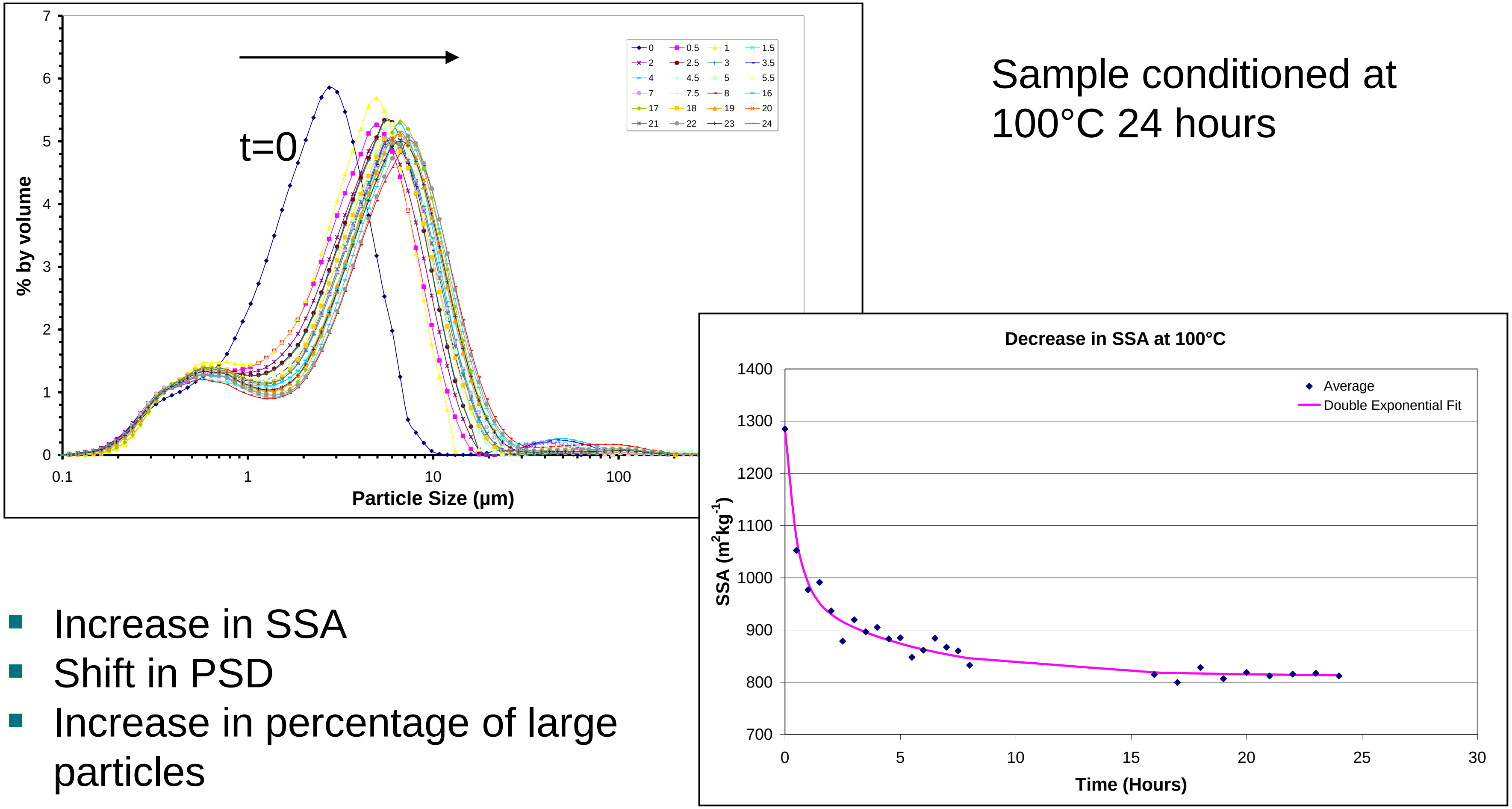
Sintering

Time

Transportation Rules

Updated Particle Size Distribution

Experimental example



Sample conditioned at 100°C 24 hours

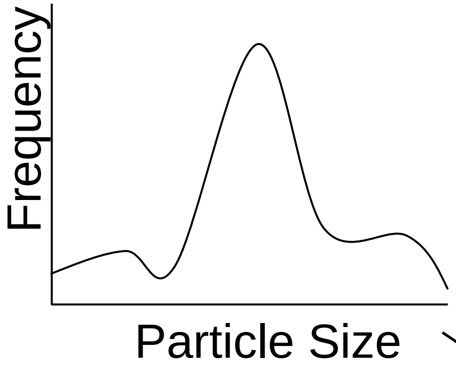
- Increase in SSA
- Shift in PSD
- Increase in percentage of large particles

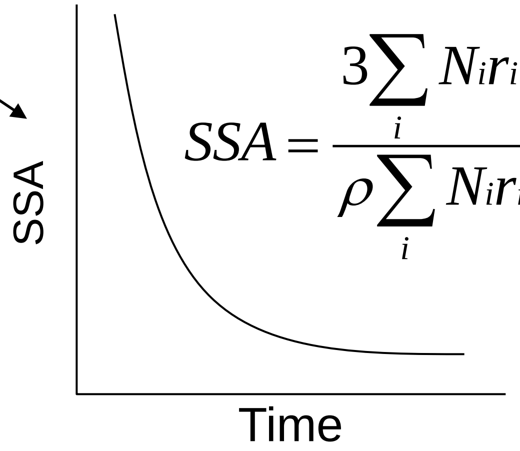
Starting assumptions

- Smooth, spherical particles
- Continuous particle size distribution
- Chemically inert species
- Sealed system

Changes in PSD and SSA

- Over time Particle Size Distribution changes:
  - Mean particle size increases
  - Specific Surface Area decreases
  - Sintering and densification may also occur





$$SSA = \frac{3\sum_i N_i r_i^2}{\rho \sum_i N_i r_i^3}$$