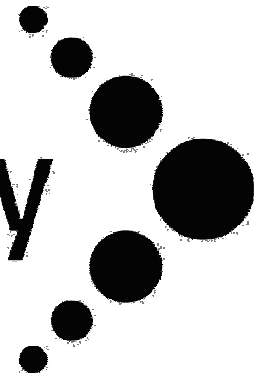


**National Nuclear Laboratory**



# Mesososcopic simulations of molten silicates using the LAMMPS code

*LAMMPS Users' Workshop, Albuquerque, New Mexico,  
9-11 August 2011*

Presented by : Dr Mark Bankhead, NNL

# Modelling at the National Nuclear Laboratory

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- **The National Nuclear Laboratory was formally established on the 1<sup>st</sup> April 2008.**
- **It was formed predominately from the R&T division of BNFL.**
- **NNL operates from 5 UK sites.**

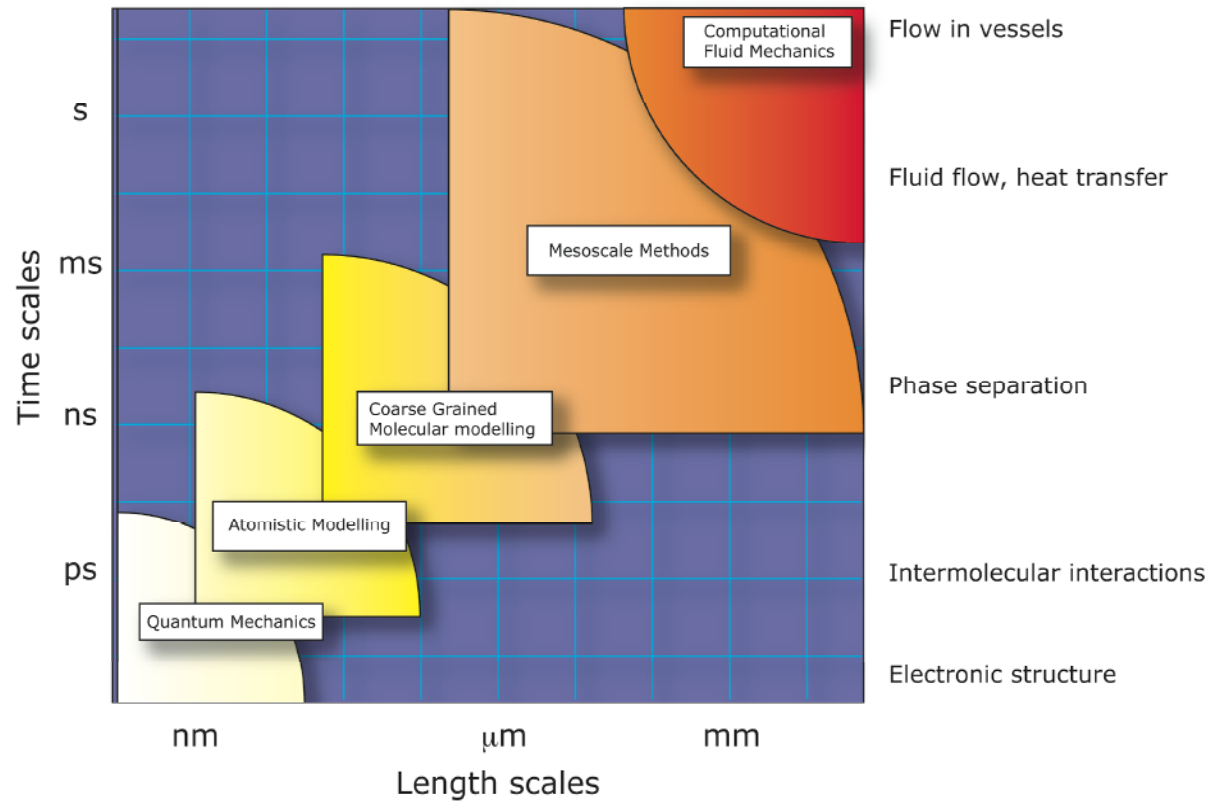
Modelling forms the cornerstone of the NNL's scientific and technical capability, underpins signature research programmes in waste management, decommissioning and new build,

- Modelling accounts for approximately 15% of direct revenue
- About 100 scientists and engineers across multiple disciplines

# Chemical and Materials Modelling

## Capabilities

## Business areas



**Plant support**

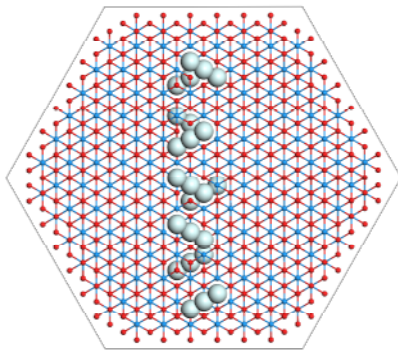
**Safety cases**

**University links**

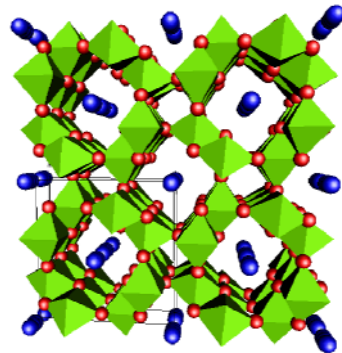
**R&D**

# Chemical and Materials modelling

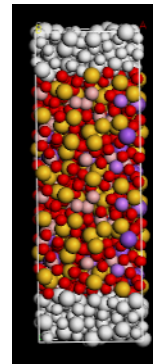
- Fundamental methods (such as MD) makes an important contribution across all the business areas.
- Customer drivers from difficult challenges and need to innovate.
- **LAMMPS has replaced commercial software for molecular dynamics simulation.**



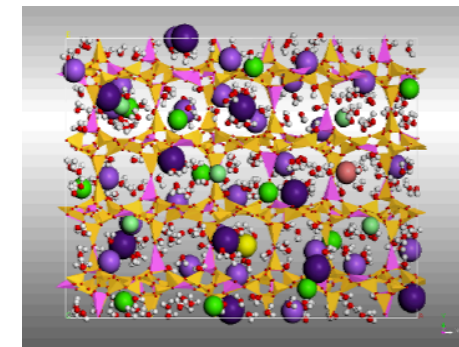
Fission gas diffusion  
in MOX fuel



'Synroc' Zirconolite  
for Pu/ immobilisation



Borosilicate glass  
physical properties



Parameters for IX  
plant kinetic models

# Challenging problems: Glass melt viscosity

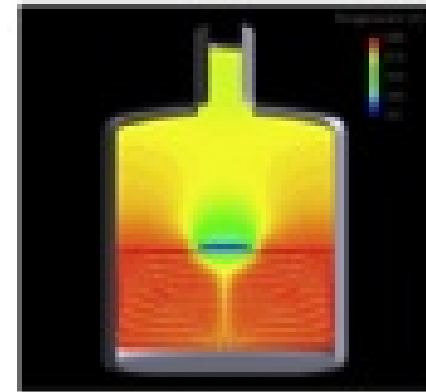
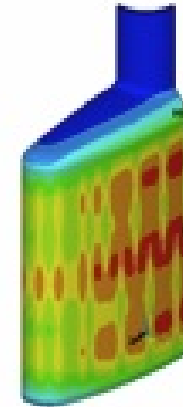
## Chemistry and fluid flow with Meso-scale methods

The operation of many nuclear plants relies on knowledge of the transport properties of chemically complex fluids and solids:

- Example problem is the convection and discharge of vitrification melter at Sellafield.
- Continuum scale modelling depends on the viscosity (depends on feed composition)

MD approaches are challenging, can mesoscale methods help meet the challenge.

LAMMPS is an ideal tool for prototyping new methods.



# An introduction to Dissipative Particle Dynamics

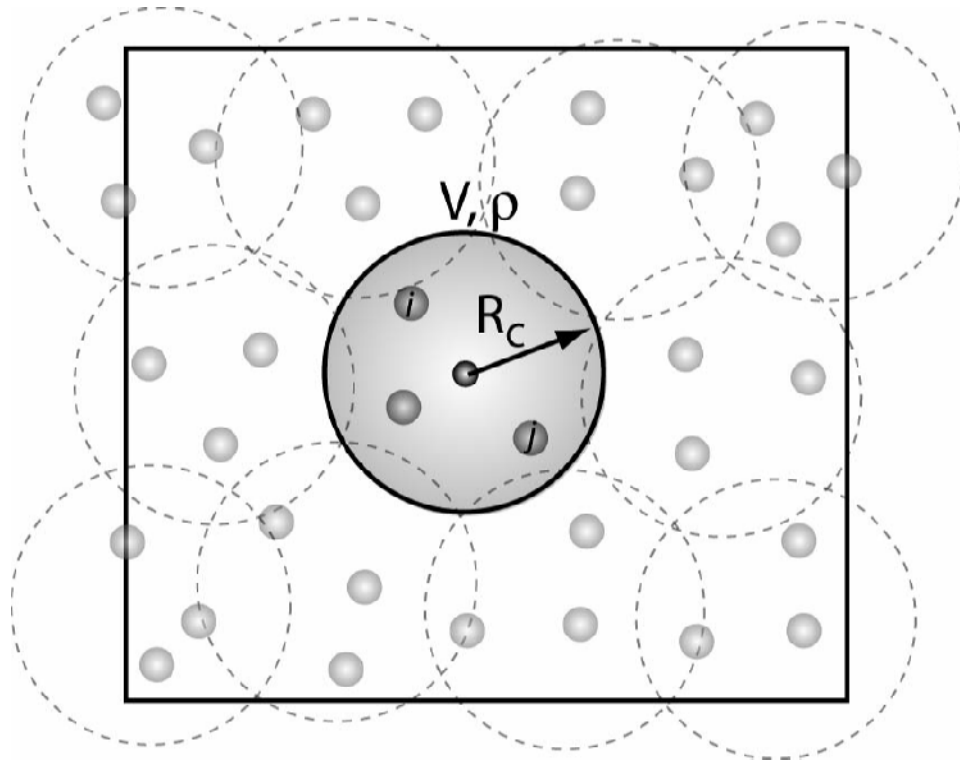
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- **Dissipative Particle Dynamics - off-lattice simulation approach for fluids derived from LGCA,**
- **Mesoscale approach to simulation of matter (analogous to Lattice Boltzmann methods in fluid mechanics),**
- **Mesoscale means it should work as well at micro and continuum scales,**

DPD has been applied to model a diverse range of systems :

- Fluid flow (pipes and porous media)
- Phase equilibria (polymer melts)
- Complex fluids (Emulsions and colloidal suspensions)
- Particle packing (concrete aggregates, liquid crystals)

# DPD Methodology



Groot-Warren method (LAMMPS):

Forces acting on beads:

$$\mathbf{F}_i = \sum_{j \neq i} (\mathbf{F}_{ij}^C + \mathbf{F}_{ij}^D + \mathbf{F}_{ij}^R)$$

- Describes condensed matter
- Internal energy is represented, but not conserved
- Momentum is conserved, preserving hydrodynamics



# Forces in the GW DPD model

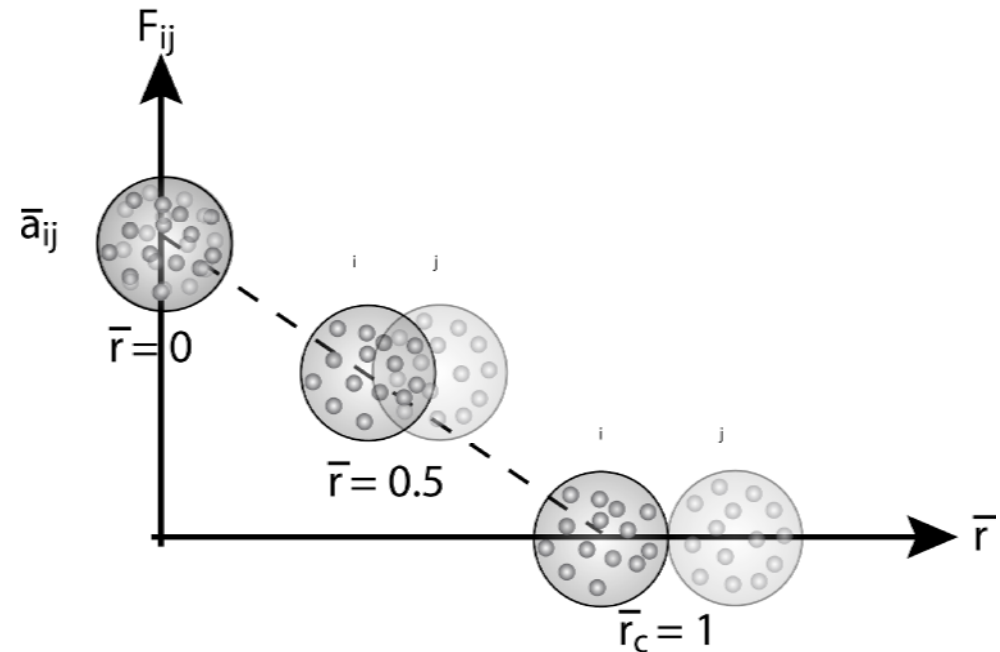
- Conservative force defines the chemical interactions within a material

$$\mathbf{F}_{ij}^C = a \omega^C \hat{\mathbf{r}}_{ij}$$

- Weight constant defines a soft interaction potential

$$\omega^C = \left( 1 - \frac{r_{ij}}{r_c} \right)$$

- 'a' determines strength of soft repulsion



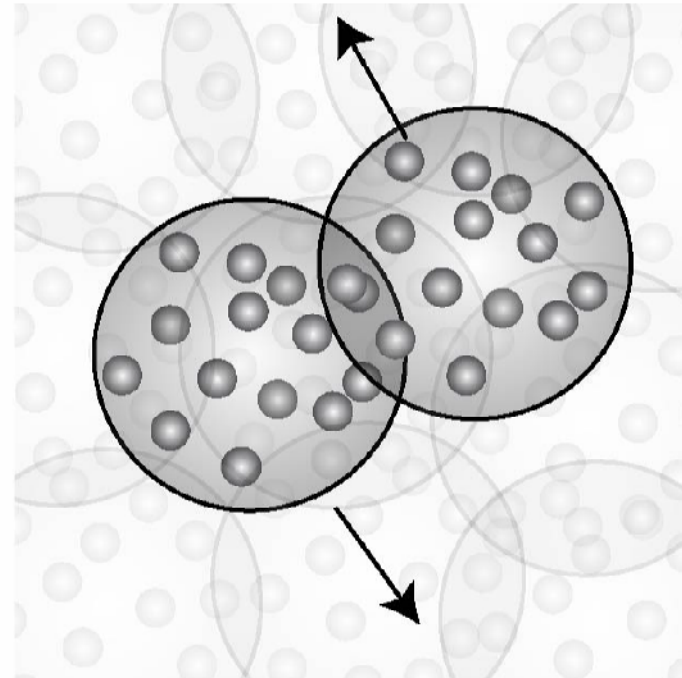
# Forces in the GW DPD model

- Fluctuations arise from the random and dissipative force terms in the model:

**Thermostat**  $\left\{ \begin{array}{l} \mathbf{F}_{ij}^D = -\zeta_{ij} \omega^D (\mathbf{v}_{ij} \cdot \hat{\mathbf{r}}_{ij}) \hat{\mathbf{r}}_{ij} \\ \text{Dissipative force (frictional drag)} \\ \mathbf{F}_{ij}^R = \sigma_{ij} \omega^R \xi \hat{\mathbf{r}}_{ij} \\ \text{Random (stochastic) force (Brownian motion)} \end{array} \right.$

- Weight constants :

$$\omega^D = (\omega^R)^2 \quad \sigma = \sqrt{2k_B T \zeta}$$



- $\zeta$  controls the strength of the dissipative force.

# Boundary conditions and unit systems

---

- Boundary conditions are can be imposed for periodicity, additional forces and solid objects:
- $r_c$  defines the length scale in DPD,  $k_B T$  is a convenient unit of energy (reduced units):

$$\bar{\rho} = \rho r_c^3 \quad \text{Particle density}$$

$$\bar{E} = E / k_B T \quad \text{Energy}$$

$$\bar{p} = p r_c^3 / k_B T \quad \text{Scalar Pressure}$$

$$\bar{a} = a r_c / k_B T \quad \text{Conservative force}$$

# How can we apply DPD?

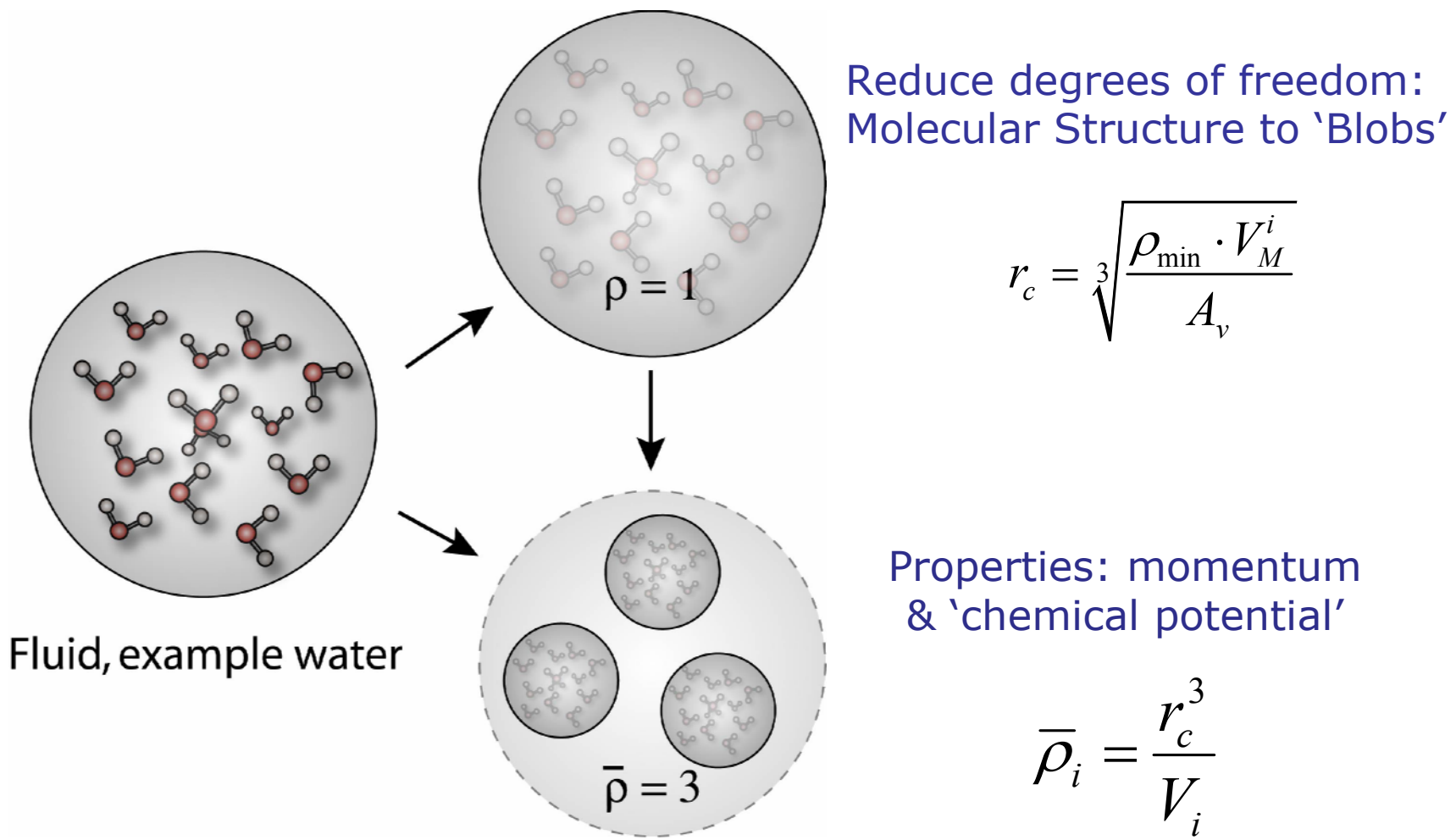
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## Simulations With DPD

DPD could be a useful technique for the nuclear industry if we can address the following (Hoover 2006):

1. A choice for the inter-particle forces, so we can model materials of interest;
2. Applying appropriate boundary conditions, so we can simulate problems of interest;
3. Finding a means of analyzing the simulations, to investigate the effect of change;

# Coarse Graining Matter in DPD



# Regular Solution Theory

---

Cohesive energy density forms the basis of the Hildebrand (*solubility*) parameter:

$$\delta = c^{1/2} = (-U / V)^{1/2} \quad \delta^2 = \left( \Delta H_{vap}^T - RT \right) \frac{Z}{V_m^T}$$

Chemical potential (driving force) and activity (degree) of mixing can be derived from the Gibb's free energy of mixing .

The excess heat of mixing of a *regular* solution ( $S^E$  (entropy of mixing) &  $V^E$  (volume of mixing)=0).

- Energy of mixing for 1 mol of solution:

$$\Delta^m U^V = (x_1 V_1 + x_2 V_2) A_{12} \phi_1 \phi_2 \equiv G_{RST}^m$$

- Change of cohesive pressure as a result of mixing:

$$A_{12} = c_1 + c_2 - 2c_{12} \quad c_{12} = \sqrt{c_1 c_2}$$

# Regular solution theory for non-regular mixtures

---

- **Non-regular mixtures**

- The method introduced by Hansen defines the  $\delta$  parameters for:
  - Dispersion  $\delta^d$
  - Polar interactions  $\delta^p$
  - Hydrogen bonds  $\delta^h$

$$G_{RST}^M = v_m \phi(1 - \phi) \left( (\delta_1^d - \delta_2^d)^2 + (\delta_1^p - \delta_2^p)^2 + (\delta_1^h - \delta_2^h)^2 \right)$$

- Note that as  $v_m$  is the volume of the mixture, which may not be a sum of the mole-fraction of the molar volumes of its components (i.e. there may be a volume change on mixing).

# DPD and solubility parameters

---

- **Correspondence between RST and DPD (Travis 2007)**

Equate the expression for the free energy of mixing from DPD to that of Regular Solution Theory:

$$(\delta_1 - \delta_2)^2 = -r_c^4 N_A^2 \alpha \left[ \frac{a_{11}}{v_1^2} - 2 \frac{a_{12}}{v_1 v_2} + \frac{a_{22}}{v_2^2} \right]$$

RST

$$\bar{\Delta} = -\alpha \left[ \bar{\rho}_1^2 \bar{a}_{11} + \bar{\rho}_2^2 \bar{a}_{22} - 2 \bar{\rho}_1 \bar{\rho}_2 \bar{a}_{12} \right]$$

DPD (reduced units)

- The expression for the  $a_{11}$  and  $a_{22}$  terms can be obtained by independently from the relationship between the internal pressure and the Virial part of the DPD free energy of mixing:

$$a_{11} = \frac{\delta_1^2}{\alpha \rho_i^2 r_c^4}$$

$$\bar{a}_i = \frac{\bar{\delta}_i^2}{\alpha \bar{\rho}_i^2} \quad \text{DPD (reduced units)}$$



# Inorganic materials: e.g. SiO<sub>2</sub>

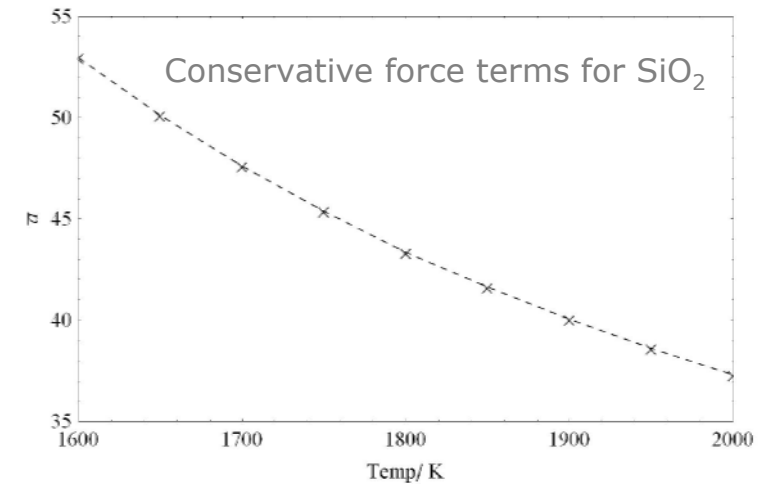
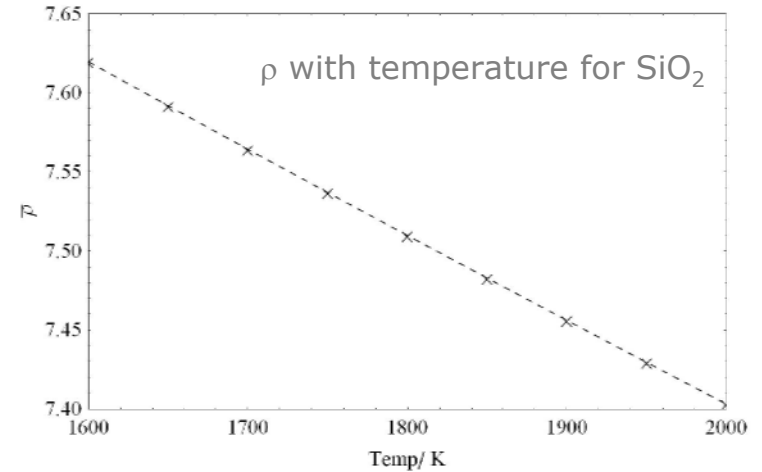
Density:  $V_i^T = V_i^{T_r} + \frac{dV_i}{dT}(T - T_r)$        $\bar{\rho}_i = \frac{r_c^3}{V_i}$

Conservative force:

$$\frac{\Delta H_{vap}^0}{T_B} = (s^0)_g - (s^0)_l$$

$$\Delta H_{vap}^T = \Delta H_{vap}^0 + (T^T - T^{BP})(Cp^T - Cp^0)$$

$$\delta^2 = \left( \Delta H_{vap} - RT \right) \frac{z}{V_m} \quad \bar{\delta}_i = \sqrt{\frac{r_c^3}{k_B T}} \delta_i$$



# Dissipative and random forces

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- **Transport Properties of materials with DPD**

DPD is very interesting as a tool to model fluid flow problems.

- Applied to generic systems, a broad spectrum of fluid behaviour is observed.

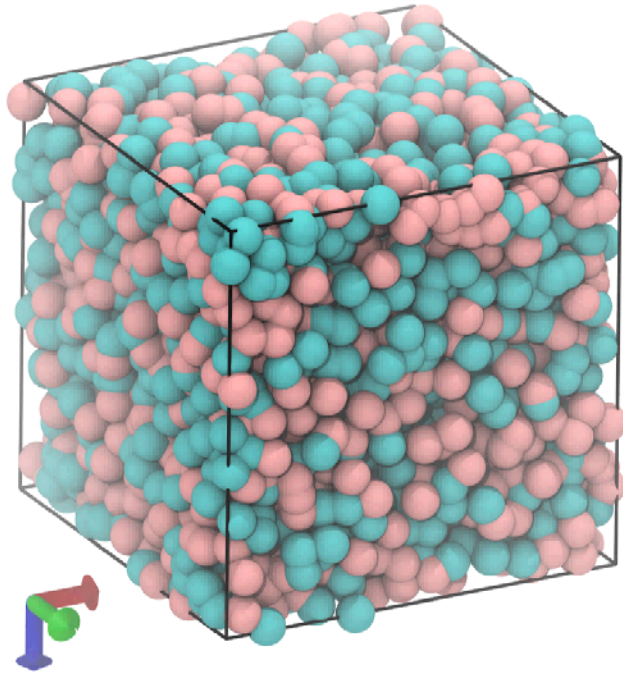
Dissipation refers to the energy loss in a material over time. The constant  $\zeta_{ij}$  (zeta) controls the strength of the dissipative force.

- A number of empirical methods have been developed towards the derivation of these forces. (Shown later)

A universal method for modelling transport properties remains beyond reach.

# Using DPD with LAMMPS

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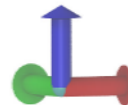
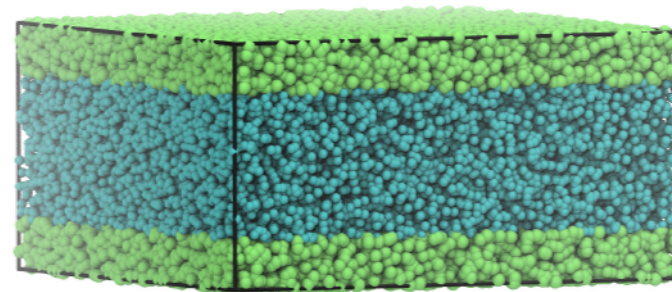
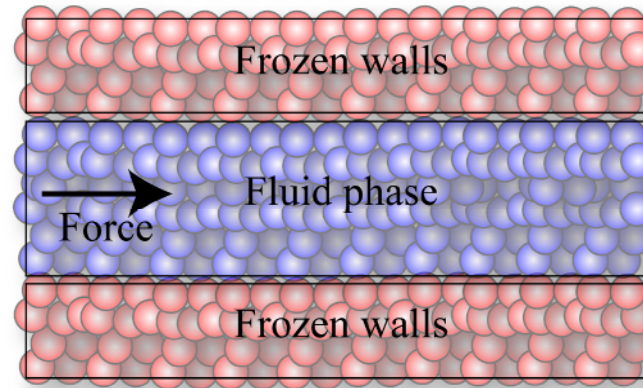


## LAMMPS is very flexible:

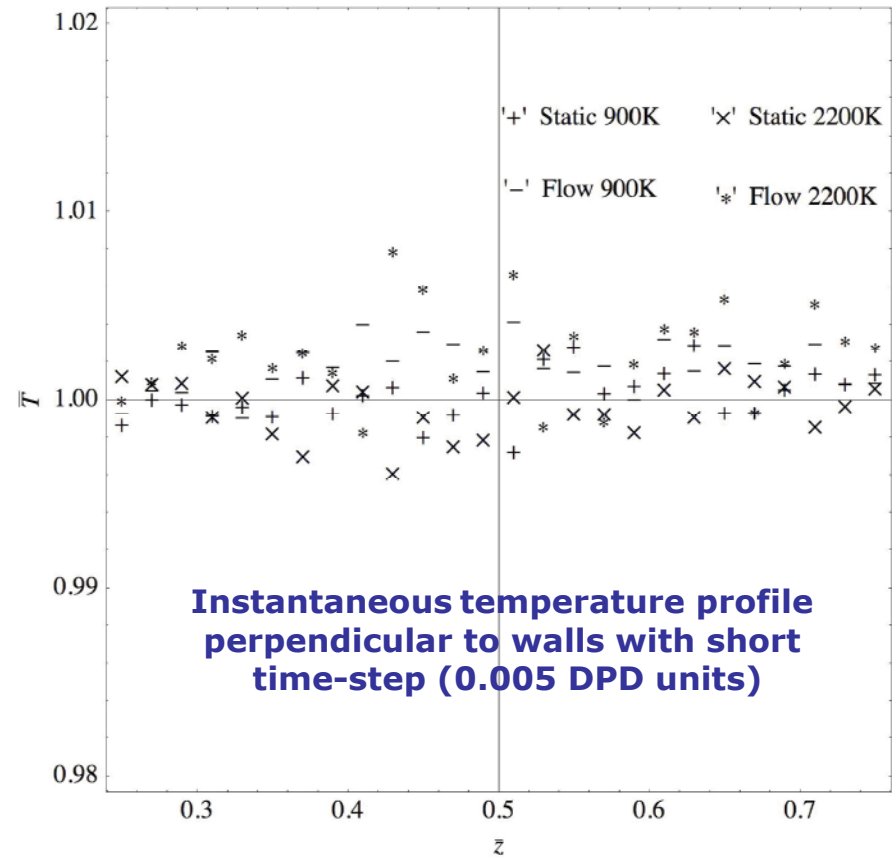
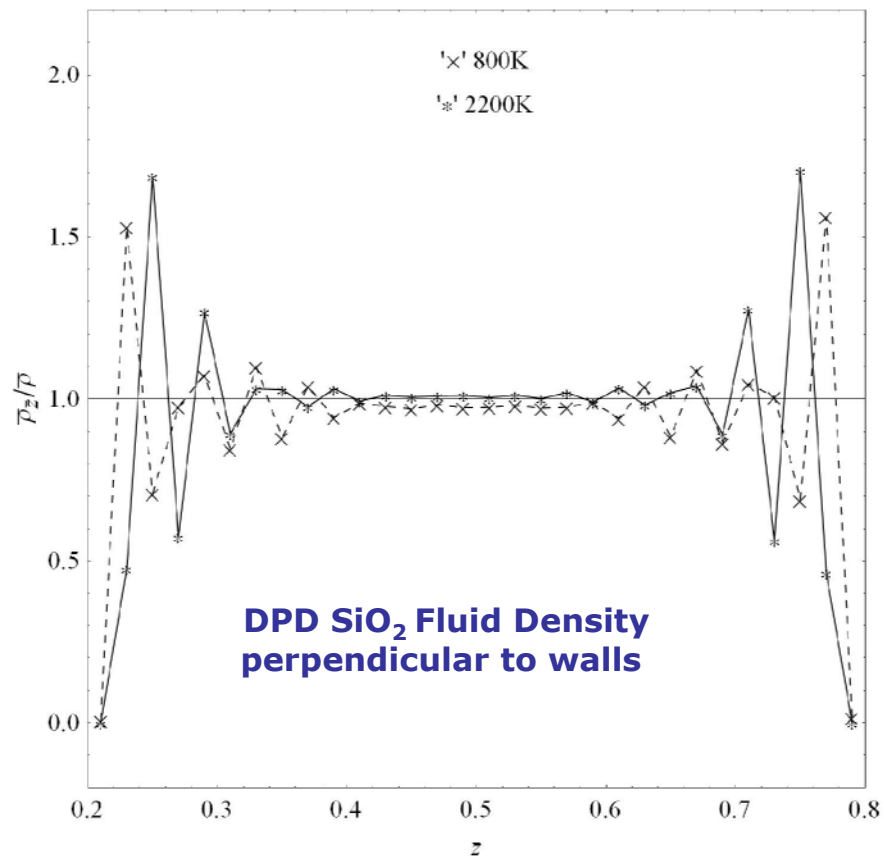
- LAMMPS scripting can be used to embed DPD parameters using polynomial functions as a function of system temperature,
- NNL have recently modified `pair_style dpd` to work with `fix_adapt`,
- Hybrid potentials possible,
- Performance is very good:  
(36 steps/ sec on 24 cores for 100K particles at NNL)

# Poiseuille flow simulations $\text{SiO}_2$ viscosity

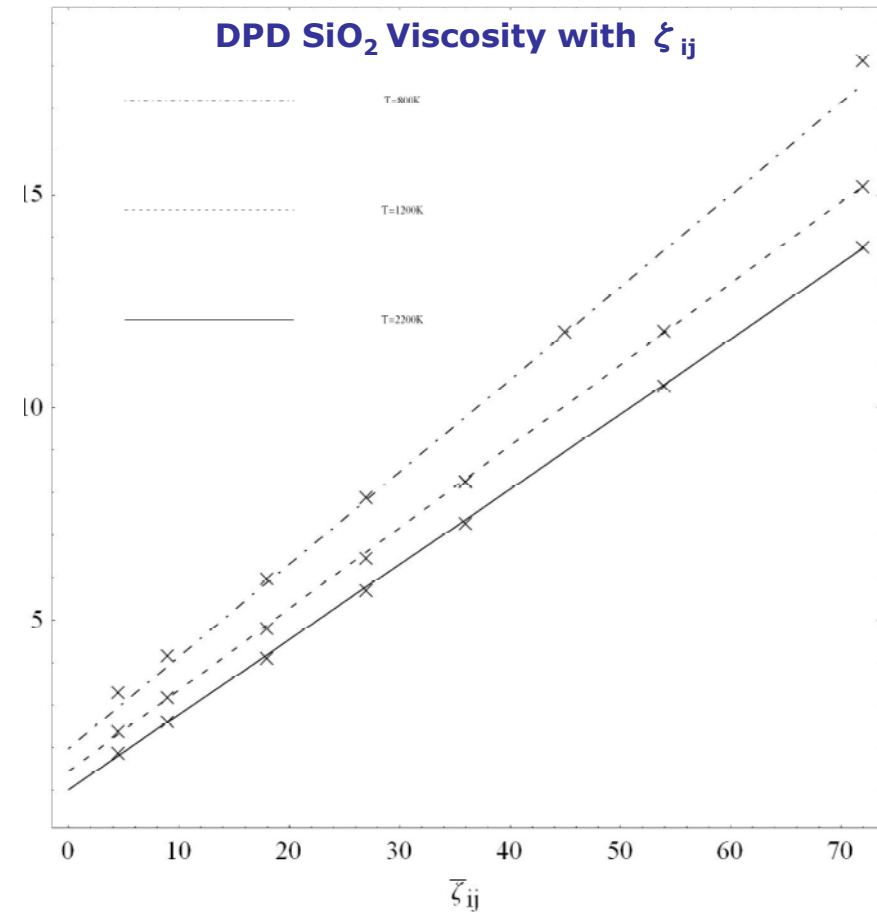
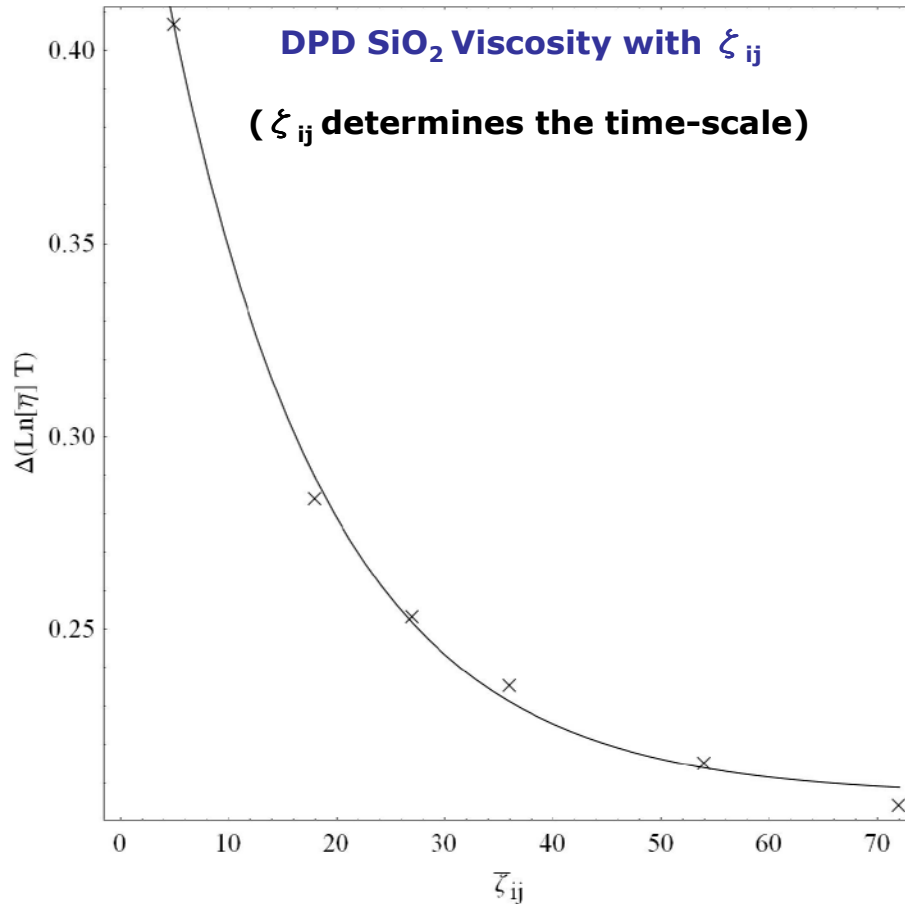
- Bead types determined via RST approach.
- 3D model of a fluid between parallel infinite plates  
(LAMMPS  $\sim 100\text{K}$  particles 4h on 24 cores)
- Non-equilibrium boundary conditions applied. Flow induced due to gravity  
(Duong-Hong, Karniadakis).



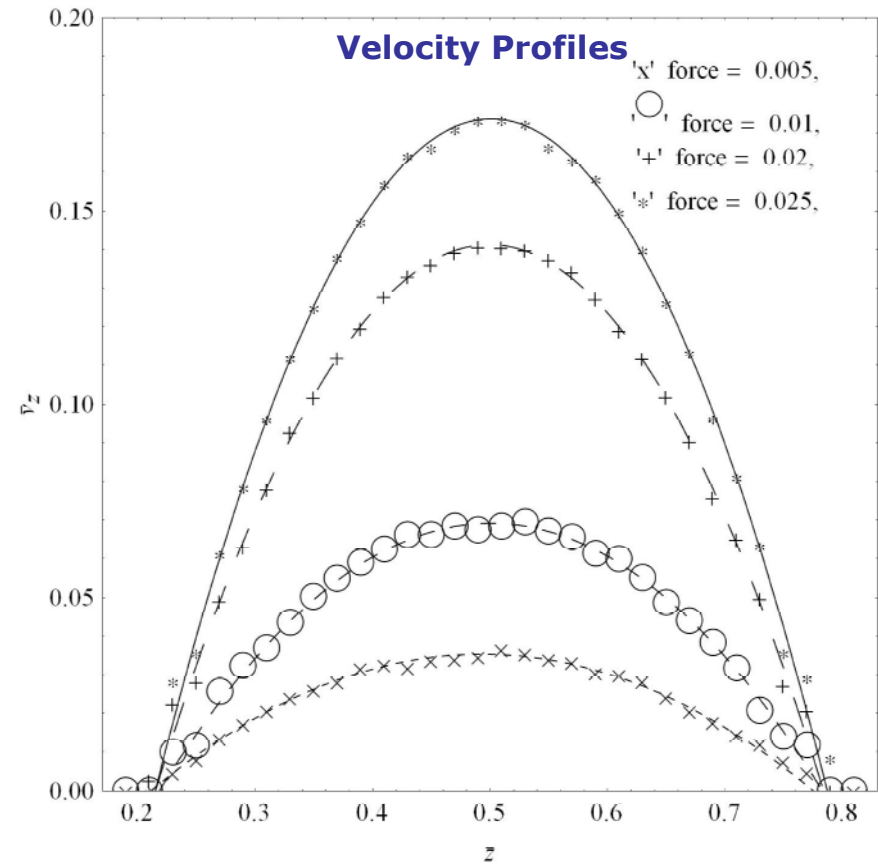
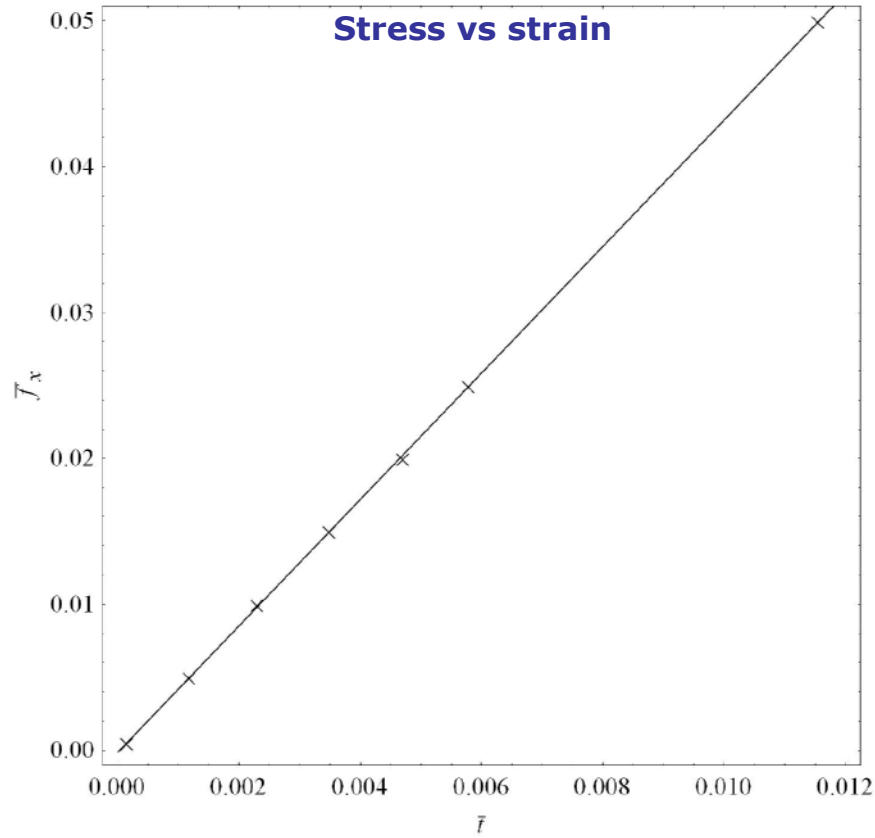
# Boundary condition validation



# Viscosity and dissipative forces



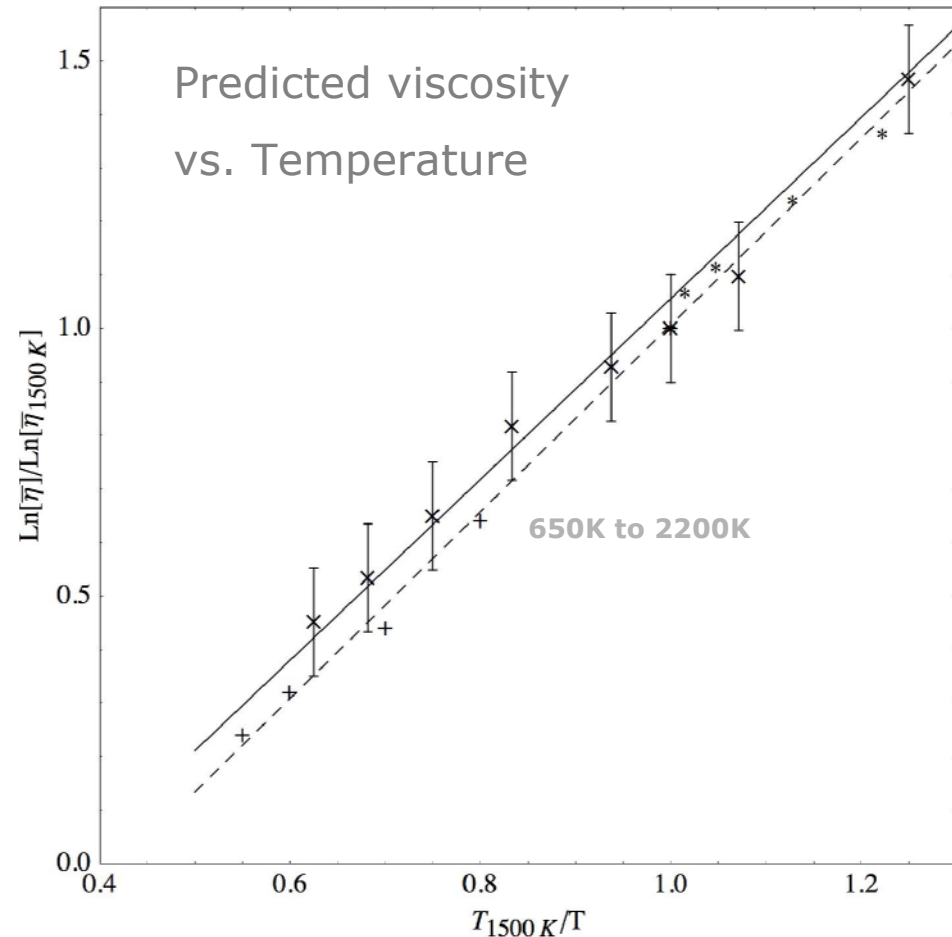
# Navier Stokes behaviour of DPD fluids



# Benchmarking the method

## Modelling $\text{SiO}_2$ rheology

- Method works for regular mixtures.
- Qualitative trends in viscosity.
- Non-regular mixtures could be modelled by using an extension of RST.





# Conclusions on the method

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- **Where do we stand with DPD?**

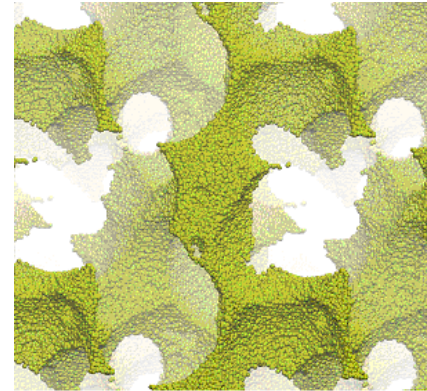
Research has delivered a robust & universal method to describe the conservative forces in a DPD simulation.

Numerical experiments can be used to establish the scope of the dissipative ( $\zeta$ ) constant.

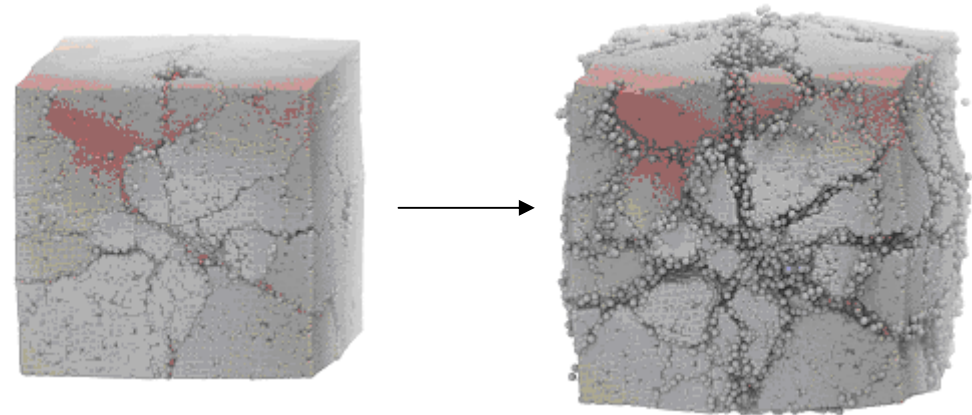
- Applying this approach means that DPD can be used to model qualitative trends in fluid behaviour, this is potentially industrially useful, if generally unsatisfactory.
- Academic challenge remains to provide a robust method to calculate these parameters so real fluids can be modelled with certainty.

# Future applications of LAMMPS

- Complex fluids and complex geometries,
- Hybrid models mixing mesoscale methods (e.g. DPD + LJ),
- Structural models
- Long-term goal to implement SPAM/SPH models in LAMMPS,



Microstructure of Sandstone used for DPD permeability simulations



PD model in LAMMPS of fracture of 'grout' due to the expansion of an internal body.

# Acknowledgements

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- **Thanks to sponsors and collaborators**

This work would not have been possible without the help and support of the following

- National Nuclear Laboratory (ex. BNFL, NSTS & Nexia Solutions),
- Sellafield Ltd.,
- Nuclear Decommissioning Authority,
- Dr S. Owens (NNL),
- Dr K. Travis (Sheffield University),

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