Molecole, Dune e Anelli di Saturno

Scale Multiple nell'Ingegneria Chimica

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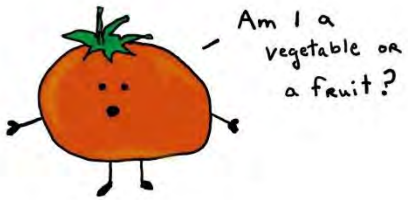

Identity crisis

Fox or Hedgehog?

"The fox knows many things; the hedgehog knows one big thing."

–Archilochus 8th Century BC

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The new engineer and the old philosopher: hedgehog or fox?

Raffaella Ocone and Corrado Ocone discuss the teaching of engineering ethics

ETHICS is taking an increasingly prominent role in engineering. Codes of conduct have always been a central aspect of the engineering profession, and professionalism implies ethical behaviour. The work on ethics undertaken by the Royal Academy of Engineering (RAE) has crystallised and unified the ethical issues in engineering, culminating in the publication of '*Engineering Ethics in Practice: a Guide for Engineers*'.

The engineering curriculum has to develop the technical capabilities of engineering students and has to prepare them for the broader challenges of professional practice, including the ethical decisions that they will have to make.

Ethics in engineering brings to mind ethical dilemmas which in turn conjures up images of bad practice and disasters: collapsing buildings, exploding reactors, and environmental pollution. This is unfortunate and based on a very limited vision of engineering ethics that might be a consequence of the way we teach (or do not teach) the subject to engineers. Indeed, key to practising engineering ethics is teaching it to students. This can be achieved either by developing a specific module on ethics or by integrating it into the curriculum. Some suggest that the latter is impractical because they believe that this would mean changing most of the existing modules.

Teaching ethics in engineering is quite different from teaching ethics in philosophy. This is because in philosophy ethics is about analysis – understanding an ethical theory and dispassionately comparing its application to an ethical problem. By contrast, ethics for engineers is about synthesis. Faced with a dilemma, the engineer has to decide on the best course of action. Hence, much like medical ethics, engineering ethics should be taught in relation to the context in which the ethical dilemma arises. It can therefore guide the engineer to make ethical decisions rather than analysing ethical theories.

But ethics in engineering goes beyond the dilemma and the application of ethical principles. Ethics in engineering implies understanding the social impact of engineering work. In this respect it is very similar to the way philosophy was seen in the classical ancient world.

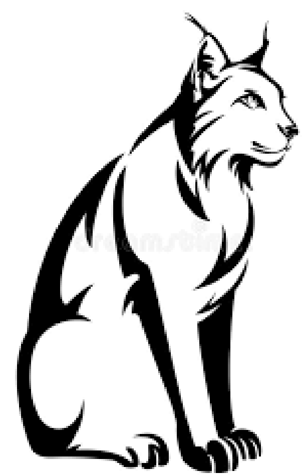
The disconnection between practice and philosophy is a fairly recent development; classical societies such as the Greeks and Romans attributed great importance to practical behaviour.

Hegel defined the ancient Greek world as the era of "involuntary" ethics where the individuals lived in immediate symbiosis and harmony with their community; only successively, with the advent of theories about individualism, did the link between individual and society weaken.

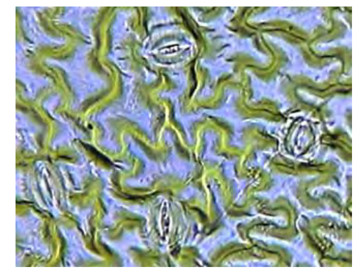
Nowadays, we tend to identify 'culture' with 'thinking'; classical philosophers did not consider philosophy as a purely intellectual activity – to them it was part and parcel of everyday life. Ethics was not just a concept, but rather an action, that is acting in and for the society. This is the lesson that we should keep in mind when teaching engineering: make the students aware of how the technology they will develop will affect people working with it, living near it, consuming its products and so on.

The engineer is a practical individual who operates within and for the society; to act professionally, they will also have to act ethically. Using disasters to introduce engineering ethics may be eye-catching but it oversimplifies matters. To be effective, engineering ethics should be taught almost in a subliminal fashion, enmeshed with practical aspects of the course. Similar to engineering mathematics, ethics should be applied and taught in view of its practical implications and not for example as a 'Ten Commandments'-style code of conduct. For example, the code of conduct may call for loyalty both to the employer and to the client: but what if those two are in conflict, and loyalty to the employer compromises loyalty to the client?

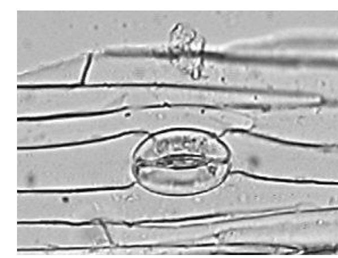
52 www.tcetoday.com july 2012



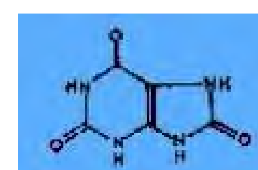
From macro to micro
(through various levels of organisation)



Scientists have been able to break down, section, analyse the matter…



The challenge:
to reassemble the various systems, to be able to explain the macro “appearance” in accordance with the micro elements



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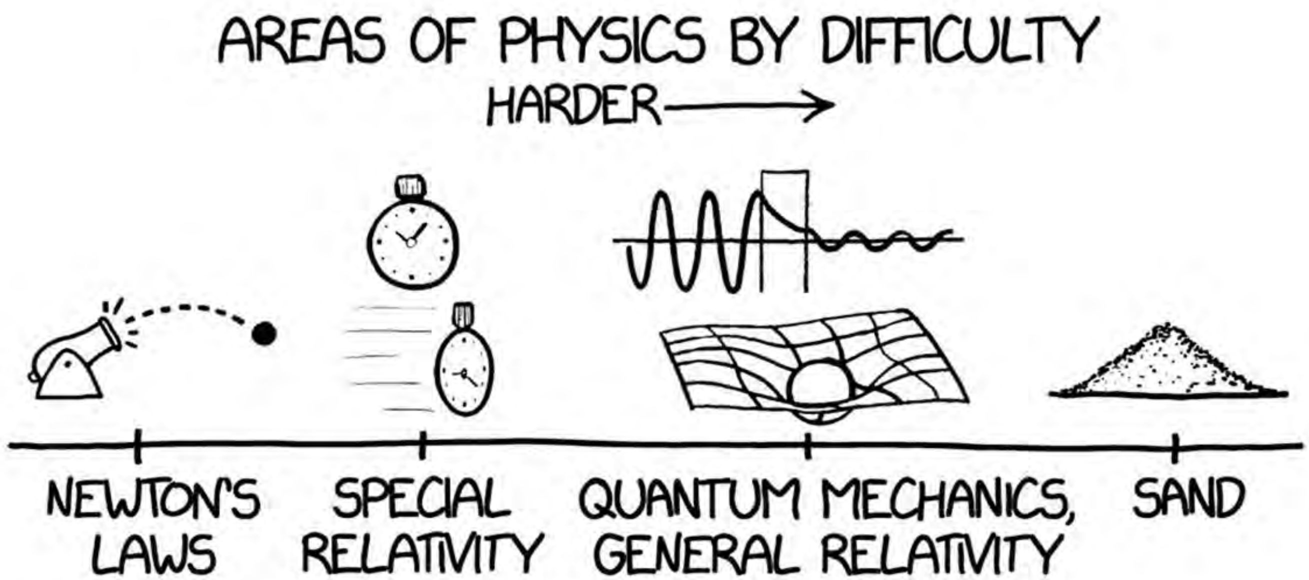
Why do we (engineers) care?

The New York Times

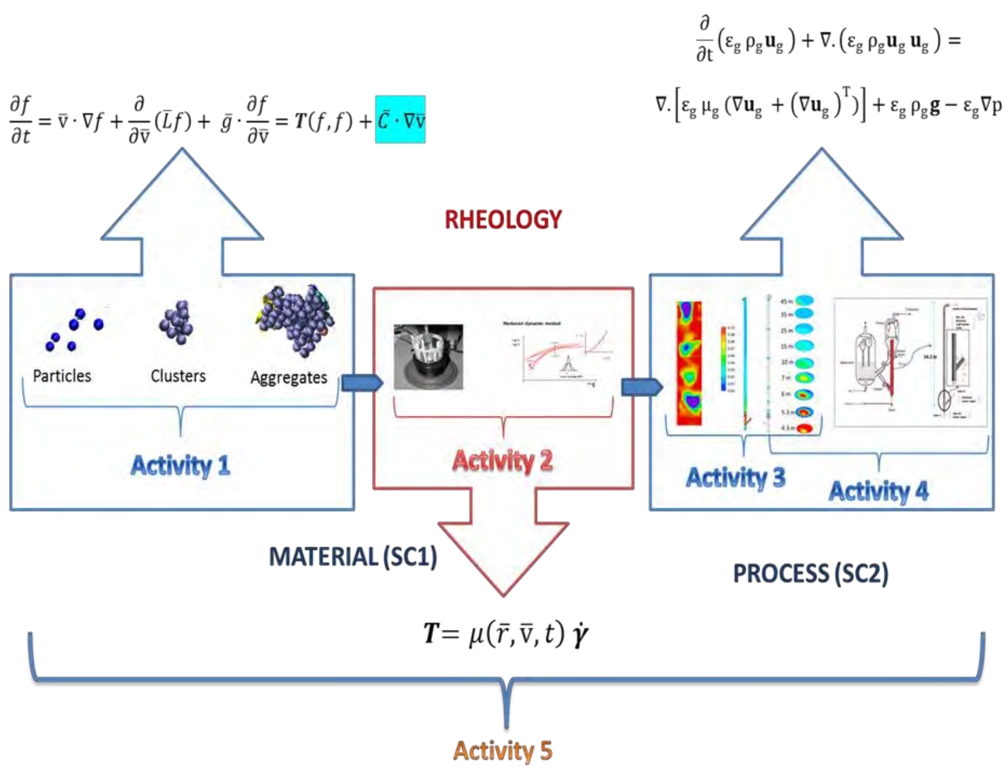
November 9, 2020

"No one understands how sand works"



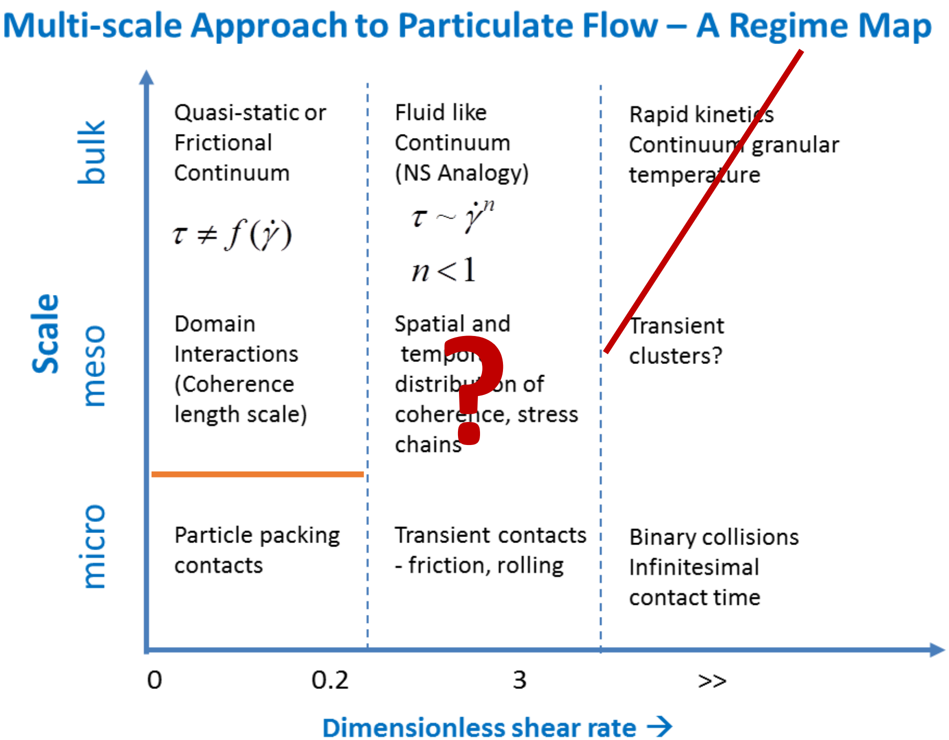
The Vision

To develop a *user-inspired* theory that help master the hydrodynamics of particulate media and improve the reliability of their industrial processing



- "Unified" theory – not a **"bolted-on"** approach
- Addressing the problem at multiple scales –"**bottom-up**" approach

The Classification of Flow Regimes Depends on the Applications



[courtesy of P Mort]

We need to understand the merge of diverse regimes

Top-down *(from macro to micro)*

The **kinetic theory** has shown to be the “correct” average procedure (developed to solve the “converse” problem)

“…by presenting the theory of gases… we already indicates ..how far we are from admitting, firmly and as a reality, that bodies are indeed everywhere composed of very small particles”

As late as 1890s there were still many chemists who did not accept the idea of existence of atoms

“…I shall demonstrate the laws of motion of an indefinite number of small, hard and perfectly elastic spheres acting on one another during impact”

Galileo was the first to observe Saturn's rings

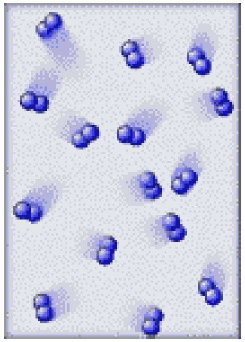
Saturn's Rings did not lead to Kinetic Theory, but quite the reverse.

'When we come to deal with collisions among bodies of unknown number, size, and shape, we can no longer trace the mathematical laws of their motion with distinctness'.

Mechanics cannot deal with collisions among many bodies flying around randomly. All Maxwell could do was gather the possible scenarios for stability and instability.

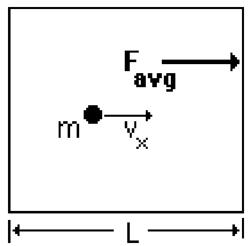
In the middle of this work on kinetic theory, **Maxwell** returned to his paper on Saturn's rings. He ran into two problems. The first one lay in restricting the molecules to motions in a thin ring held in orbit by gravitation and subject to **inelastic** collisions. If the collisions were elastic, the particles would disperse into a cloud.

E Garber, Phil. Trans. R. Soc. A (2008) 366, 1697–1705



The Kinetic Theory of Gases

Movement and collision of molecules with
the walls of the container produce a pressure



$$F_{average} = \frac{mN\overline{v_x^2}}{L}$$

and assuming random speeds in all directions

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} = 3\overline{v_x^2}.$$

Then the pressure in a container can be expressed as

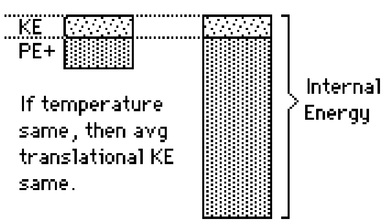
$$P = \frac{F_{avg}}{A} = \frac{mN\overline{v^2}}{3LA} = \frac{mN\overline{v^2}}{3V} = \frac{N}{3V}m\overline{v^2}.$$

Expressed in terms of average molecular kinetic energy:

$$P = \frac{2N}{3V}\left[\overline{\frac{1}{2}mv^2}\right]$$

This leads to a concept of **kinetic temperature** and to the **ideal gas law**.

Heat is a form of movement



For an ideal gas

$$\left[\frac{1}{2}mv^2\right]_{average} = \frac{3}{2}kT$$

defines the **kinetic temperature**

k = Boltzmann constant

Statistical Theories

a) Identify micro-structural elements and their local morphology

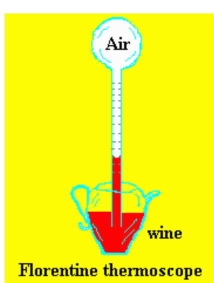
$$u = U + c$$

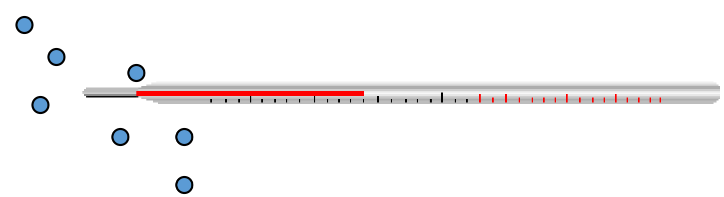
$$U = <u>$$

$$K = <U^2>/2 + <c^2>/2$$

$$<U^2>/2 + \quad T$$

The pseudo-temperature is the analogous of the “real” (thermodynamic) temperature in gases





b) Express the stress tensor in terms of morphology and kinematics

$$\tau = \left(p + \beta \frac{D \ln v}{Dt} \right) 1 - 2 \mu D^D$$

The result is a constitutive equation for a compressible, Newtonian fluid.

HOWEVER

The parameters now depend on the morphology!

c) Write differential equations for the rate of evolution of the morphology under the local kinematics and the main motion

$$\rho_p \frac{DE_{PT}}{Dt} = \mathrm{w} + q + Q - \gamma$$

d) Solve a) for the morphology and b) for the stress

Attack specific problems

e) Eliminate morphology between equations

It can **NEVER** be performed in granular flow since the pseudo-temperature can NEVER be eliminated from the governing equations

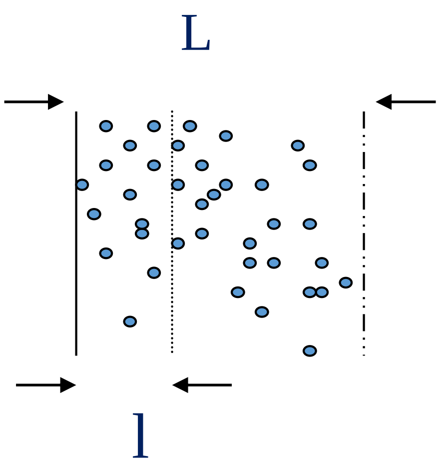
Granular Systems -Continuum Modelling

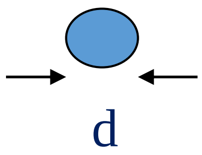
- Relying on a number of length scales and on average procedures

- Collection of particles replaced with a continuum (the “granular gas”)

- Balance equations written for the “particulate phase”

- Constitutive equations needed





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Theory used successfully to describe the hydrodynamics in a 660MW Ultra-Supercritical Fluidised Bed Boiler operated at Langfang in China

Continuum model

Solid phase:

continuity equation: $$\frac{\partial(\alpha_s\rho_s)}{\partial t}+\nabla(\alpha_s\rho_s\vec{u}_s)=0$$

momentum: $$\frac{\partial(\alpha_s\rho_s\vec{u}_s)}{\partial t}+\nabla(\alpha_s\rho_s\vec{u}_s\vec{u}_s)=-\alpha_s\nabla P-\nabla P_s+\nabla\left(\bar{\bar{\tau}}_s\right)+\beta\left(u_g-u_s\right)+F$$

Gas phase:

continuity equation: $$\frac{\partial\left(\alpha_g\rho_g\right)}{\partial t}+\nabla\left(\alpha_g\rho_g\vec{u}_g\right)=0$$

momentum: $$\frac{\partial\left(\alpha_g\rho_g\vec{u}_g\right)}{\partial t}+\nabla\left(\alpha_g\rho_g\vec{u}_g\vec{u}_g\right)=-\alpha_g\nabla P+\nabla\left(\bar{\bar{\tau}}_g\right)-\beta\left(u_g-u_s\right)+F$$

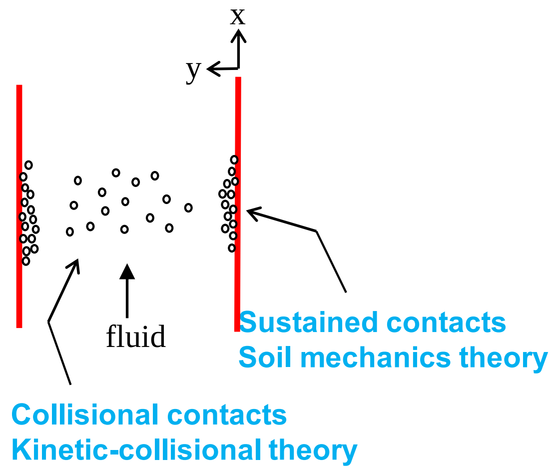
Energy equation (granular temperature):

$$\frac{3}{2}\left[\frac{\partial(\alpha_s\rho_s T)}{\partial t}+\nabla(\alpha_s\rho_s T)\vec{u}_s\right]=\left(-P_s\bar{\bar{I}}+\bar{\bar{\tau}}_s\right):\nabla\vec{u}_s-\nabla(\kappa_T\nabla T)-\gamma_T-J_T$$

Well developed KTGF (kinetic theory of granular flow)

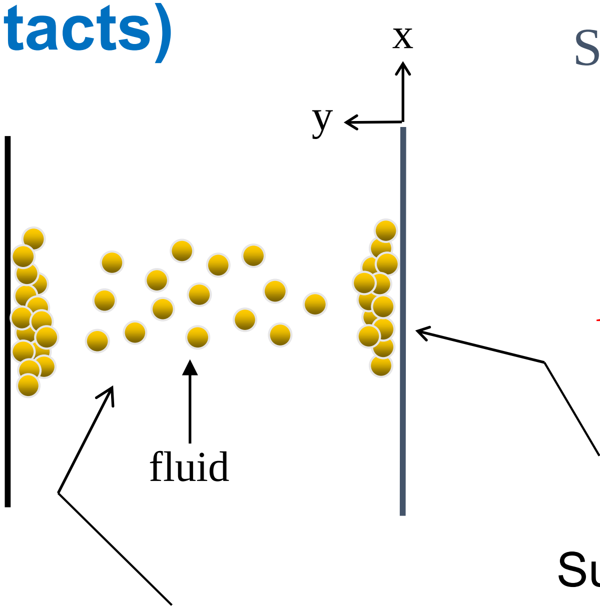
Continuum Modelling

- **Advantages:**
  - Real (industrial) systems involve more particles than direct numerical simulation can handle
  - It can model well dilute and uniformly spaced systems of particles



- **Disadvantages (Inconsistencies):**
  - Particles are inelastic
  - Distribution of particles is not uniform (and probably not Gaussian)
  - The medium is “cooling” down
  - The drag on cluster is less than on single particles

Kinetic-collisional + Frictional models (sustained contacts)



Simple addition of the two solid stress components:

$$P_s = P_k + P_f$$

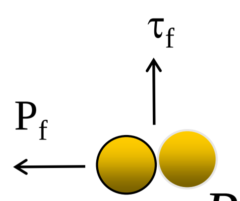
$$\tau_s = \tau_k + \tau_f$$

Assuming negligible frictional effects at $\varepsilon_s < \varepsilon_{s,critical}$

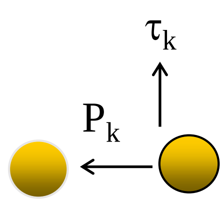
Usually taken ~ 0.5

Sustained contacts
Soil mechanics theory

Kinetic+Collisional contacts
Kinetic theory



$$P_f = C \frac{(\varepsilon_s - \varepsilon_{s,\,critical})^n}{(\varepsilon_{s,\max} - \varepsilon_{s,\,critical})^p}$$



$$P_k = \rho_s \varepsilon_s T + 2 g_o \rho_s \varepsilon_s^2 T (1 + e)$$

$$\tau_k = 2\mu \frac{dv}{dy}$$

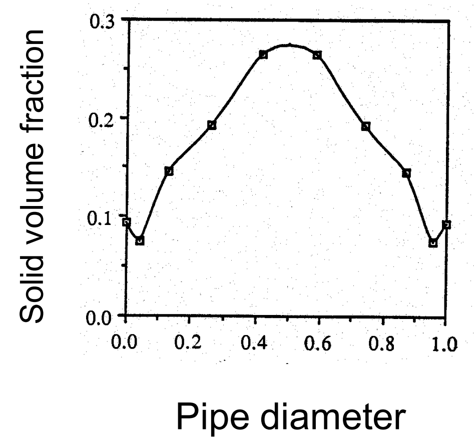
$$\tau_f = P_f \sin\phi$$

Shear Stress

$$\bar{\bar{\tau}}_s = \left(\lambda_s - \frac{2}{3}\mu_s\right)(\nabla \cdot \vec{u}_s)\bar{\bar{I}} + 2\mu_s \bar{\bar{S}}_s$$

solids shear viscosity $\mu_S = \mu_{S,col} + \mu_{S,kin} + \mu_{S,fr}$

$\mu_{S,fr} = 0$	$0 < \alpha_s < 0.5$	No friction
$\mu_{S,fr} = \dfrac{P_S \sin\phi}{2\sqrt{I_{2D}}}$	$0.5 < \alpha_s < 0.63$	Particle packing-enduring contact



The shear stress

$$\mu_S = \mu_{S,col} + \mu_{S,kin} + \mu_{S,fr} + \mu_{INT}$$

Cohesive shear stress

$\mu_{cohesive}$

Wet shear stress
(fluid shear resistance)

μ_{wet}

Current work

Y. Makkawi, P. C. Wright, R. Ocone, Powder Technology, Issue 1-2, 69-79, 2006

Proposed inter-particle “cohesive” model

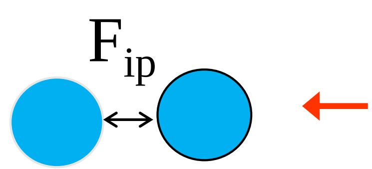
The radial component of the cohesion force

$$P_c = C_o \frac{6\sqrt{2}F_{ip}\sqrt{T}}{u_t d}\left|\nabla \varepsilon_s\right|$$

Based on experimental data on Group A/B particles, we are taking an average value of F_{ip}=0.2X10^{-8} N

The tangential cohesion force is given by a modified formula of Molerus (1982):

$$\tau_c = P_c \frac{\pi}{6(1-\varepsilon_s)}$$

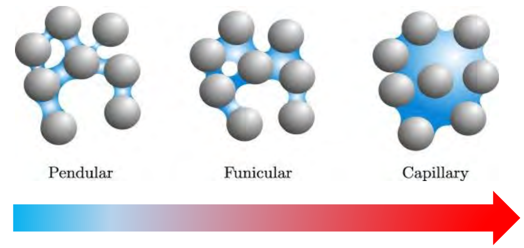


Two isolated particles in contact

Where C_o is a factor introduced due to uncertainty about the exact value of F_{ip}

F_{ip} specify any force of interaction between a couple of particle.

Liquid-bridge Stresses*

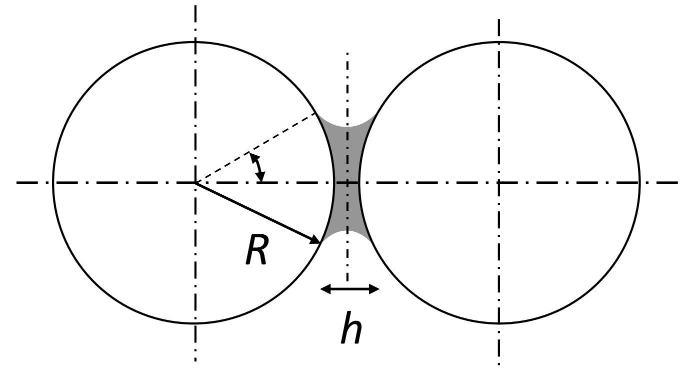


- For this, we may start from the interparticle force at single particle level:

$$\dot{F}_{liquid} = \frac{3}{8}\pi\mu_{liquid} d_p^2 \frac{\dot{u}}{h}$$

Approach velocity ($\dot{u}$)

Interparticle gap (h)



- Interparticle approach velocity can be estimated from granular temperature:

$$\dot{u}_s = \frac{3}{2}\sqrt{\pi\theta_s}$$

Normal stress

- For this, it is required to determine the force
 per unit area:

$$P_{liquid} = \frac{9}{16h}\pi\mu_{liquid}\sqrt{\pi\theta_s}\left(\frac{6\alpha_s}{\pi}\right)^{2/3}$$

Equivalent shear viscosity

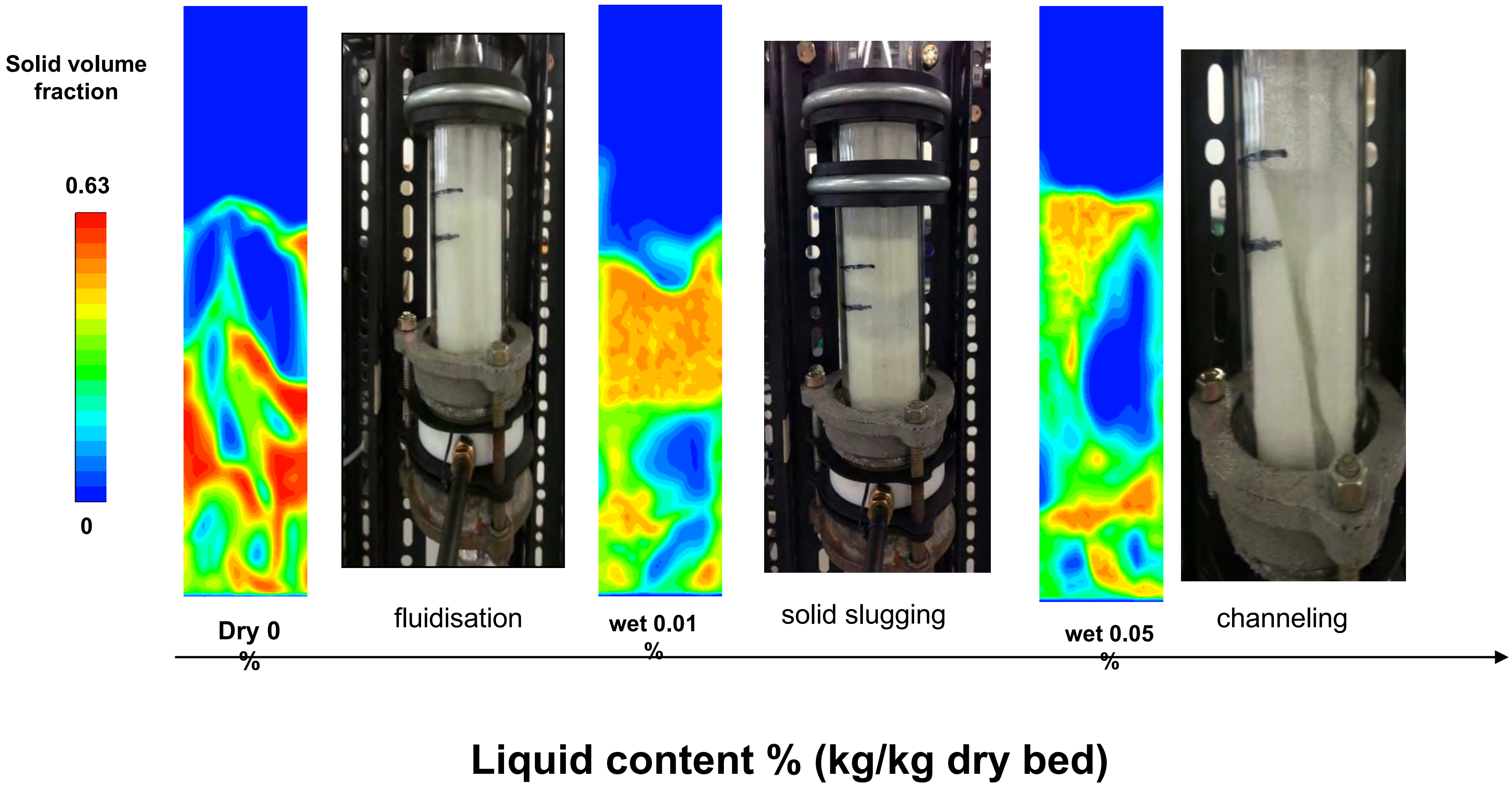
- Analogue to Coulomb friction law

$$\mu_{wet} = \frac{\sqrt{2}P_{liquid}\eta}{|\bar{\bar{S}}|}$$

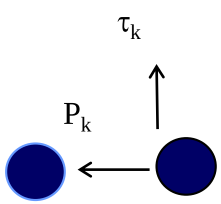
"lubrication" coefficient (η)

* In this case, F_{ip} is the inter-particles force due to the liquid bridge

Flow Patterns

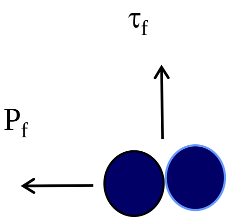


Bolted-on Approach



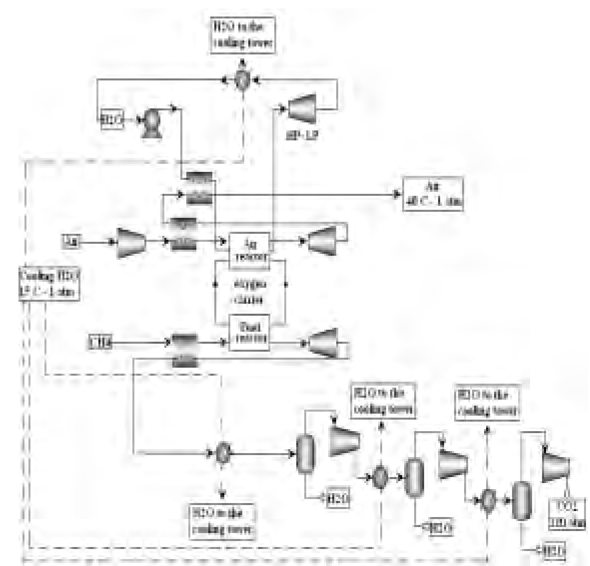
$$P_k = \rho_s \varepsilon_s \theta + 2 g_0 \rho_s \varepsilon_s (1+e)$$

$$\tau_k = 2\mu \frac{dv}{dx}$$



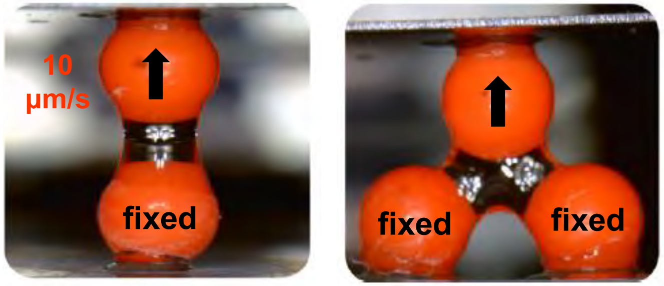
$$P_f = C \frac{(\varepsilon_s - \varepsilon_{s,\,critical})^n}{(\varepsilon_{s,\max} - \varepsilon_{s,\,critical})^p}$$

$$\tau_f = P_f \sin \phi$$



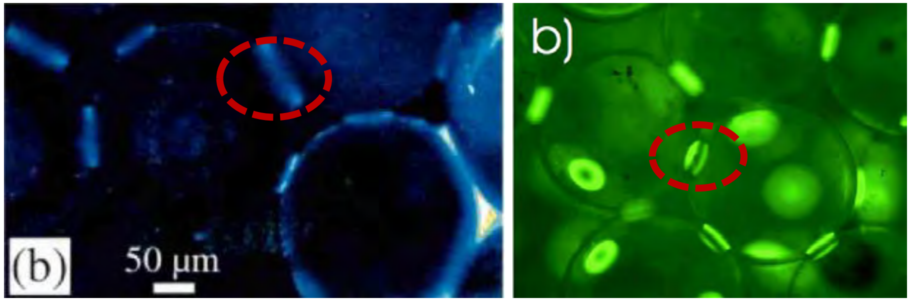
Liquid Bridge Evolution Observed in Experiments

Liquid bridges between two/three individual particles (quasi-static system)
<u>To measure force</u>



D. Lievano et al. (2017); T. G. Mason, et al., (1999)

Liquid bridges in a static particulate assembly
<u>To measure liquid bridge coordination number</u>

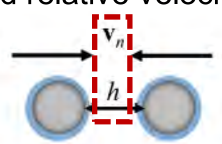


M. K. Mika, et al., (2004); D. Geromichalos, et al., (2018)

- **A stable liquid bridge is constructed to ensure measurement (i.e., not a complete lifecycle)**
- **The behavior of quasi-static/static liquid bridge might be different from that in a dynamic system, e.g. gas-fluidised bed with particle relative velocity far greater than 10 µm/s.**

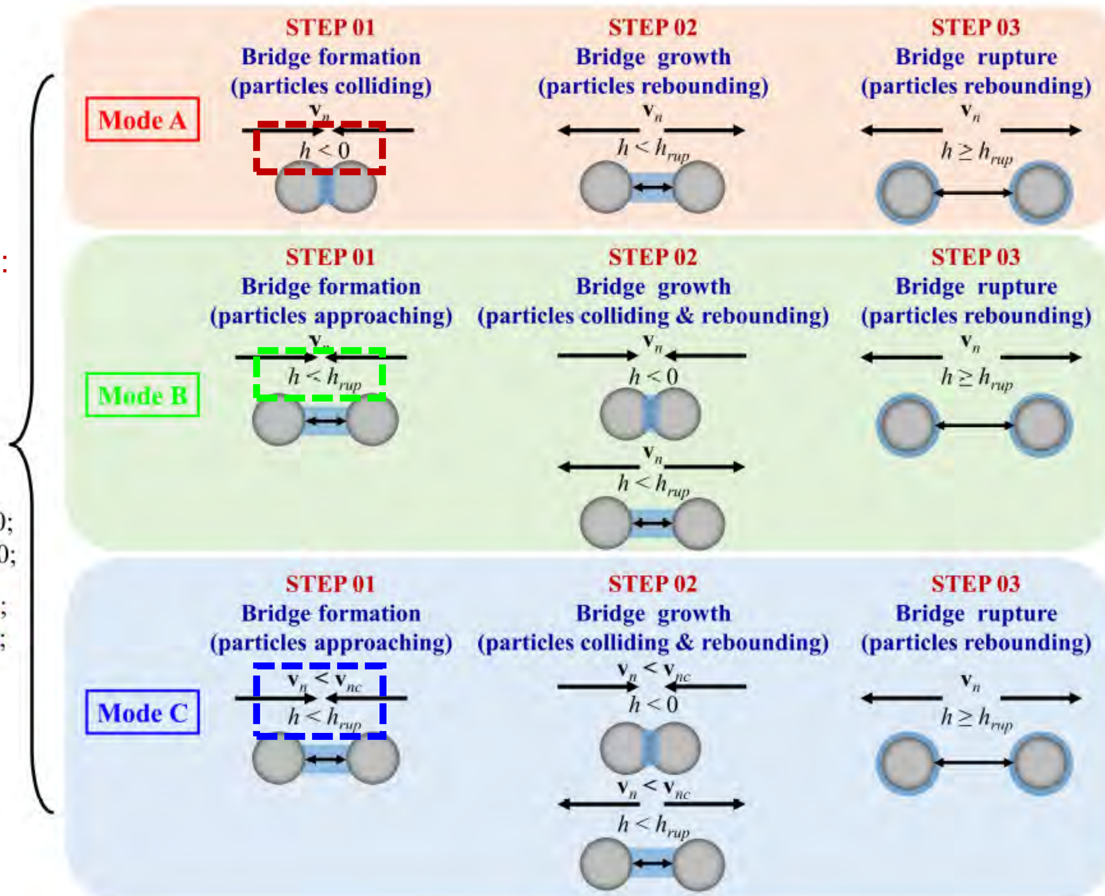
How to describe the Dynamic Bridge

There are **two** variables: separation distance h and relative velocity $\mathbf{v}_n$



If two particles approach, $\mathbf{v}_n > 0$;
If two particles rebound, $\mathbf{v}_n < 0$;

If $\mathbf{v}_{nc} = 0$, **Mode C** → **Mode A**;
If $\mathbf{v}_{nc} = \infty$, **Mode C** → **Mode B**;



Mode A:
The lifetime stage is controlled by *h*

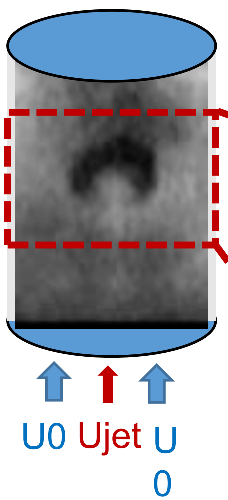
Mode B:
The lifetime stage is controlled by *h*

A new mode-Mode C:
The lifetime stage is controlled by *h* and $\mathbf{v}_n$

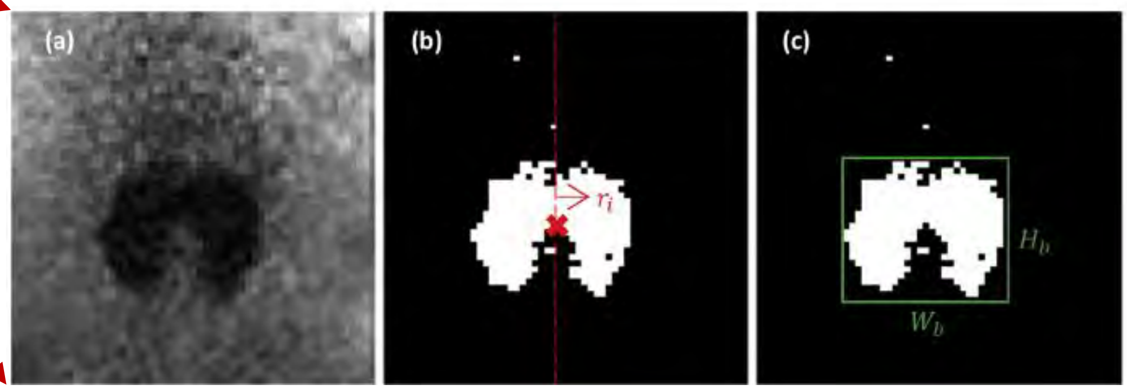
Test system: One Single Bubble in a 3D Gas-Solid Bed

- Lab-scale 3D column: I.D. 190 mm, height 300 mm, initial height 200 mm;
- Central jet: 8.95 mm diameter;
- Gas: air (0.37 L in 50 ms);
- Particles: Geldart D brown mustard seeds, ρ_s = 1080 kg/m^3, d_p = 2.11±0.09 mm;
- Liquid: silicone oil (contact angle < 30 degrees), ρ_l = 910 and 990 kg/m^3, μ_l = **5 and 100** mPas, γ = 20 mN/m;
- Liquid addition: **0.2 and 0.8 %** (weight);

2D MRI image



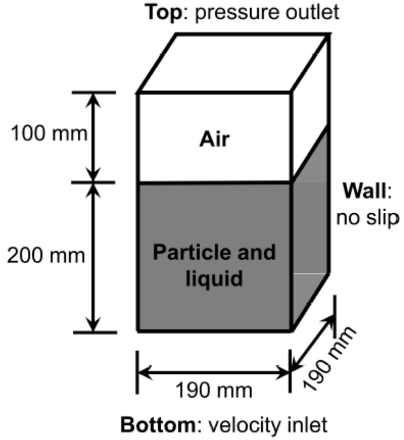
C. M. Boyce et al. (2019)



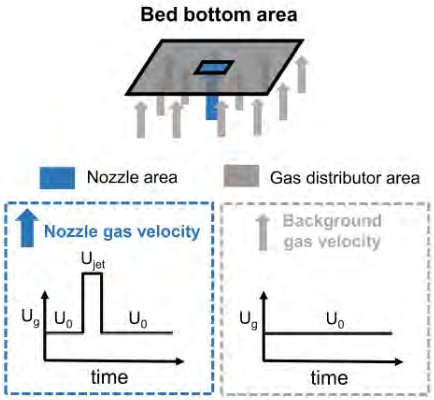
To measure the bubble properties
including bubble center, volume, and aspect ratio (W_b / H_b)

Simulation Setup in CFD-DEM

3D computational domain:



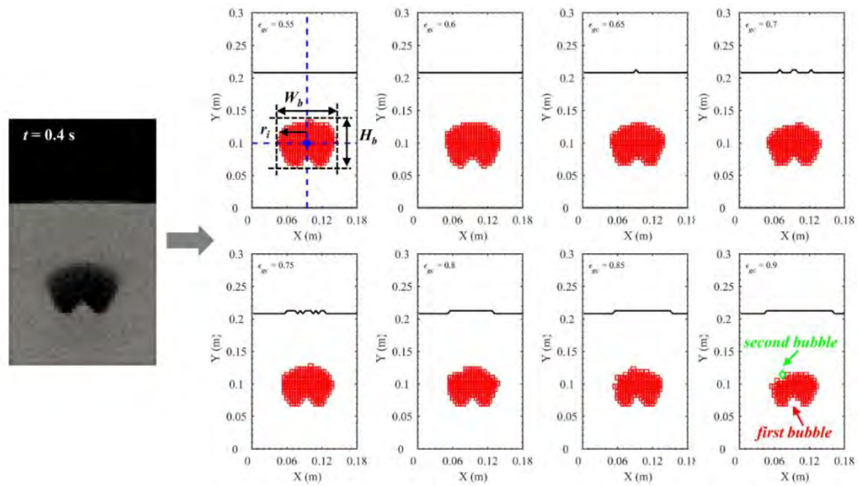
To produce one bubble:



CFD-DEM parameters:

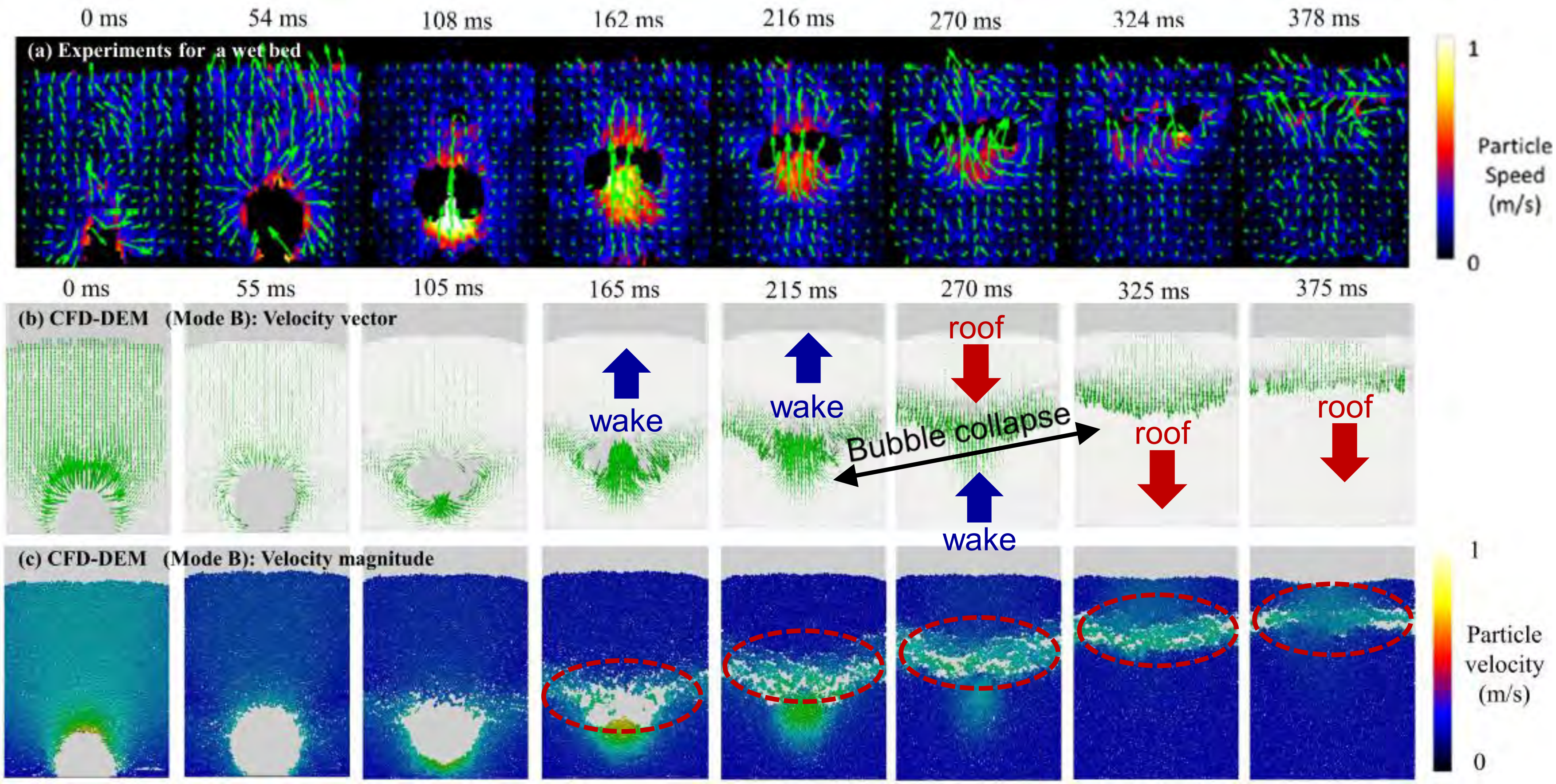
Parameter	Value
Normal spring stiffness (k_n)	1000 N/m
Tangential/normal spring stiffness (k_t/k_n)	0.4
Tangential/normal damping coefficient (η_t/η_n)	0.5
Normal coefficient of restitution (e_{ss_dry})	0.7
Coefficient of friction (μ_{s_dry})	0.55
Reduced particle stiffness scaling (Ω)	0.01
CFD time step	1.0×10^{-5} s
Grid size in x, y, and z direction	2.12 d_p
Number of particles	861,125

2D flood fill method was used to extract bubble properties:



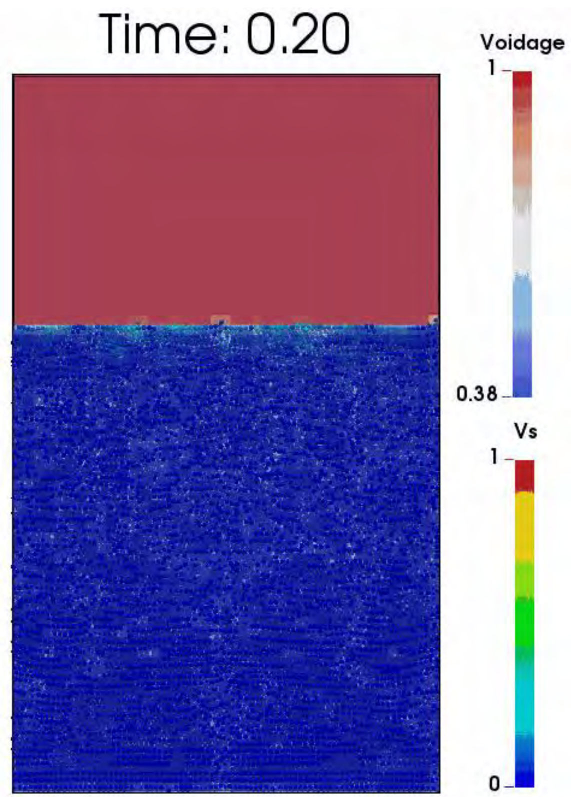
The cause of Bubble Collapse: Particle Agglomeration

The vector of particle speed at OXY plane:

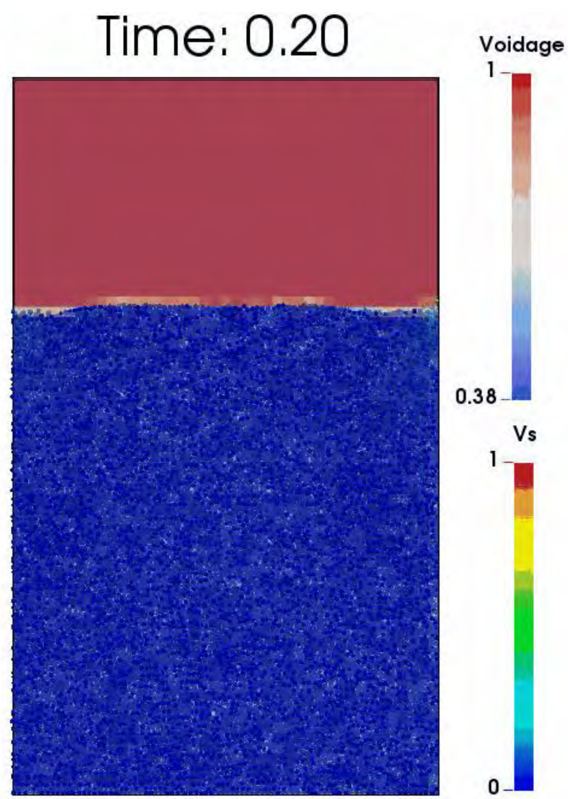


One Single Bubble in Dry and Wet Beds

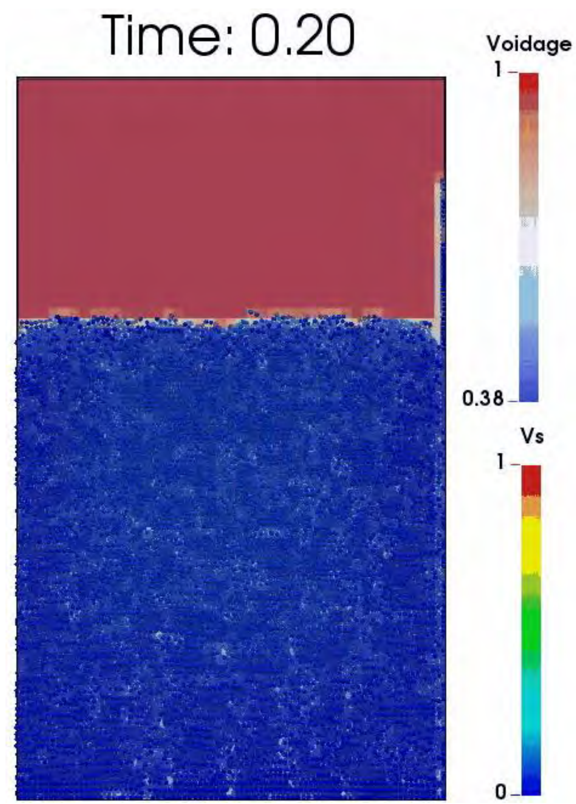
Dry bed
(no liquid)



Wet bed
liquid loading: 0.2 wt%,
liquid viscosity: 5 mPas



Wet bed
liquid loading: 0.8 wt%,
liquid viscosity: 5 mPas



The Search for a "Unified" Theory (not a "bolted-on" approach)

Dynamic Density Functional Theory*

- Cancer/tissue growth
- Microswimmers
- COVID modelling
- Protein adsorption with applications is drug delivery in the blood stream
- ….

* In collaboration with **Ben Goddard**, School of Mathematics, University of Edinburgh

Dynamic Density Functional Theory

Dynamical Density Functional Theory (DDFT)

- a statistical mechanics approach for describing the dynamics of colloids and other soft matter;
- based on Brownian/Langevin dynamics;
- derived by taking moments of the associated Smoluchowski/Kramers/Fokker-Planck equations and integrating over all but one particle;

Advantages:

- the dimension, and hence (in principle) the computational cost is independent of the number of particles, N;
- avoids the N^2 or N^3 scalings of stochastic dynamics;
- includes the full microscopic, particles-level information.

Disadvantages:

- involve some (unconstrained) approximations;
- resulting equations are non-linear, non-local partial differential equations and far from trivial to solve numerically.

Dynamic Density Functional Theory

DDFT describes the one-body density of particles, ρ, and requires the Helmholtz free energy, $\mathcal{F}$.

For high friction/overdamped dynamics typical of colloids:

$$\partial_t \rho(\mathbf{r},t) = \frac{1}{m\gamma} \boldsymbol{\nabla}_{\mathbf{r}} \cdot \left[\rho(\mathbf{r},t) \left(\boldsymbol{\nabla}_{\mathbf{r}} \frac{\delta \mathcal{F}[\rho(\mathbf{r},t)]}{\delta \rho(\mathbf{r},t)} \right) \right]$$

With inertia:

$$\partial_t \rho(\mathbf{r},t) = -\boldsymbol{\nabla}_{\mathbf{r}} \cdot \big(\rho(\mathbf{r},t) \mathbf{v}(\mathbf{r},t) \big)$$

$$\partial_t \mathbf{v}(\mathbf{r},t) + \mathbf{v}(\mathbf{r},t) \cdot \boldsymbol{\nabla}_{\mathbf{r}} \mathbf{v}(\mathbf{r},t) + \gamma \mathbf{v}(\mathbf{r},t) + \frac{1}{m} \boldsymbol{\nabla}_{\mathbf{r}} \frac{\delta \mathcal{F}[\rho(\mathbf{r},t)]}{\delta \rho(\mathbf{r},t)} = 0$$

Dynamic Density Functional Theory

What is the Helmholtz free energy $\mathcal{F}$?

- Of general form

$$\mathcal{F}[\rho] = k_B T \int d\mathbf{r} \rho(\mathbf{r}) \left[\ln \left(\Lambda^3 \rho(\mathbf{r}) \right) - 1 \right] + \mathcal{F}_{\text{exc}}[\rho] + \int d\mathbf{r} \rho(\mathbf{r}) V_1(\mathbf{r}),$$

- However $\mathcal{F}_{\text{exc}}[\rho]$ is almost always unknown.
- Ideal gas results in the diffusion equation:

$$\mathcal{F} = k_B T \int d\mathbf{r} \rho(\mathbf{r}) \left[\log \left(\Lambda^3 \rho(\mathbf{r}) \right) - 1 \right]; \quad \partial_t \rho(\mathbf{r}, t) = \frac{k_B T}{m\gamma} \nabla_{\mathbf{r}}^2 \rho(\mathbf{r}, t).$$

- Common choices for $\mathcal{F}_{\text{exc}}$ are mean field (exact for high densities of soft particles),

$$\mathcal{F}_{\text{exc}}[\rho] = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') V_2(\mathbf{r}, \mathbf{r}'),$$

or Fundamental Measure Theory (accurate for hard spheres).

Dynamic Density Functional Theory

1. Adiabatic approximation

$$\frac{N}{m}\int d\mathbf{r}^{N-1}\boldsymbol{\nabla}_{\mathbf{r}_1}V(\mathbf{r}^N,t)\rho^{(N)}(\mathbf{r}^N,t)=\frac{1}{m}\rho(\mathbf{r}_1,t)\boldsymbol{\nabla}_{\mathbf{r}_1}\frac{\delta\mathcal{F}[\rho]}{\delta\rho}-\frac{k_BT}{m}\boldsymbol{\nabla}_{\mathbf{r}_1}\rho(\mathbf{r}_1,t).$$

'Higher body interactions slaved to instantaneous density'.

This identity is *exact* at equilibrium, but in no way ensured in dynamics.

2. Local equilibrium

$$f^{(1)}(\mathbf{r},\mathbf{p},t)=\frac{\rho(\mathbf{r},t)}{(2\pi m k_BT)^{3/2}}\exp\Big(-\frac{|\mathbf{p}-m\mathbf{v}(\mathbf{r},t)|^2}{2mk_BT}\Big).$$

Easy to violate, especially in low-friction regimes such as granular media.

DDFT Extension to Granular Media

- Extend to the third moment: now have mass, velocity, and (granular) temperature;
- Include Boltzmann-type collisions;
- Requires knowledge of the pair correlation function;
- This can be obtained from microscopic dynamics, such as event-driven particle dynamics.

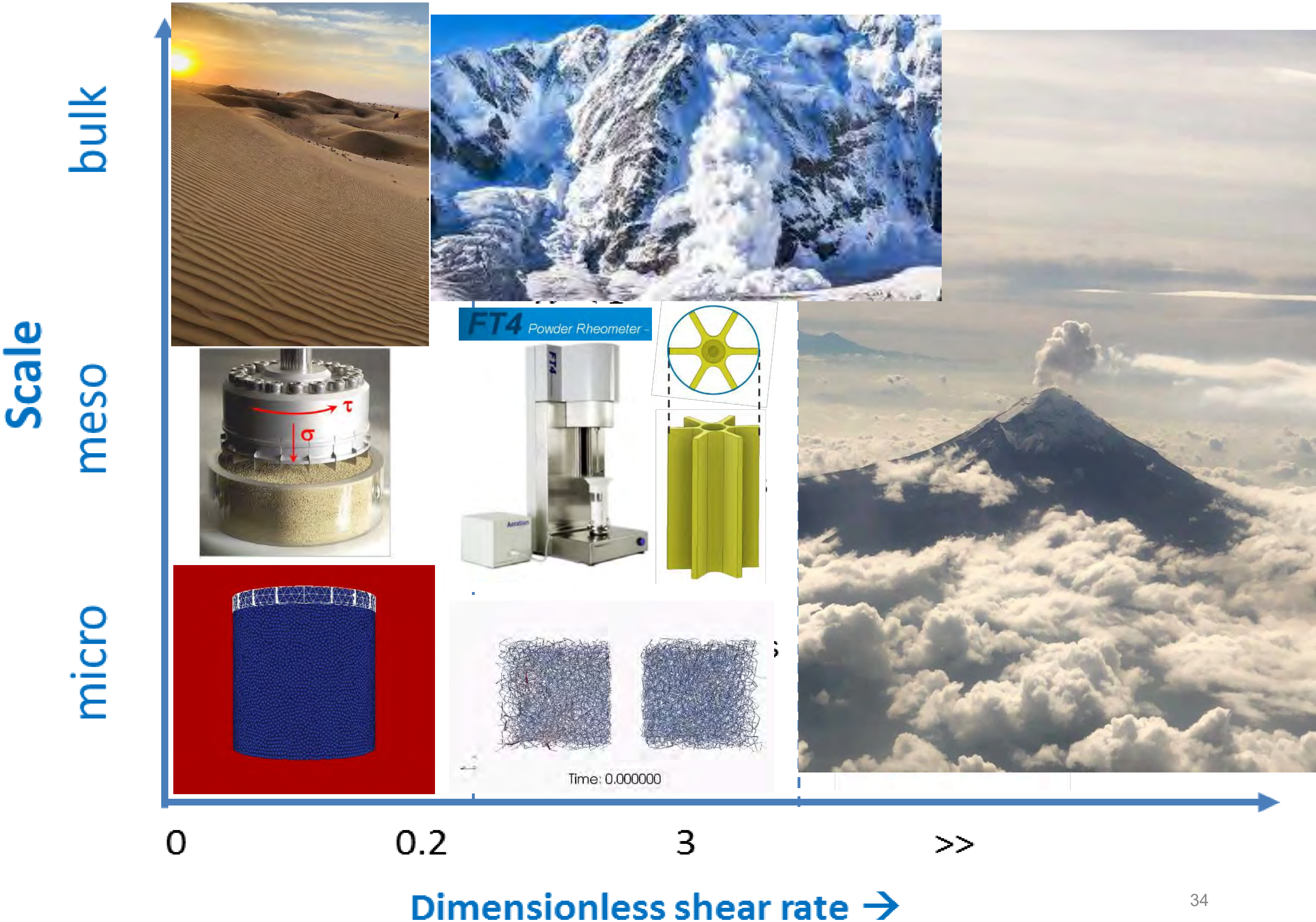
$$\frac{\partial \rho}{\partial t} = -\nabla_{\mathbf{r}} \cdot (\rho \mathbf{v}),$$

$$\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{r}} \mathbf{v} + \gamma \mathbf{v} + \frac{k_B T}{m\rho} \nabla_{\mathbf{r}} \cdot (\rho (\mathbf{E} - I)) + \frac{1}{m} \nabla_{\mathbf{r}} \frac{\delta \mathcal{F}[\rho]}{\delta \rho} - \frac{1}{m\rho} \mathcal{M}_1(\mathcal{L}_{\text{coll}}) = 0,$$

$$\partial_t \mathbf{E} + \mathbf{v} \cdot \nabla_{\mathbf{r}} \mathbf{E} + (\mathbf{E} \nabla_{\mathbf{r}} \mathbf{v}) + (\mathbf{E} \nabla \mathbf{v})^T + 2\gamma (\mathbf{E} - I) - \frac{1}{k_B T \rho} \mathcal{M}_2(\mathcal{L}_{\text{coll}}) = 0.$$

$\mathcal{M}_j(\mathcal{L}_{\text{coll}})$ are momentum moments of the collision operator.

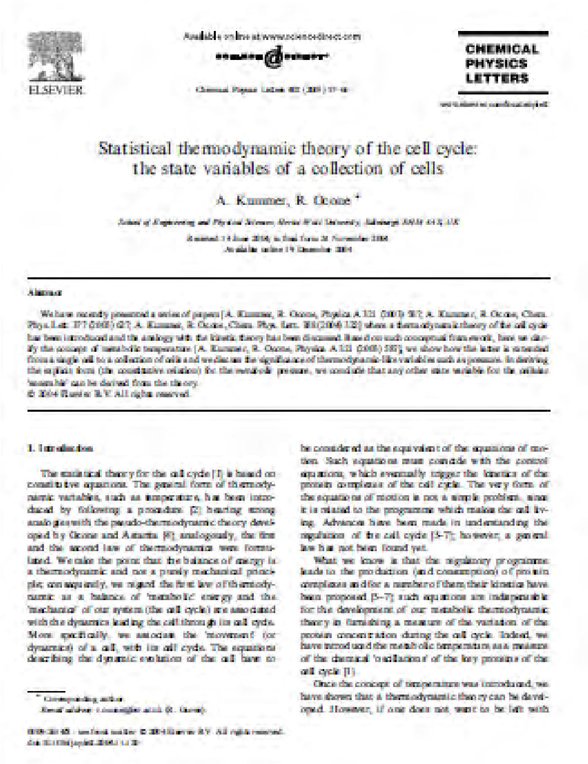
Multi-scale Approach to Particulate Flow – A Regime Map



Conclusions

- Granular materials present a number of vagaries which need sound mathematics and physics to be (possibly) solved

- Knowledge is not contained in silos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CHEMICAL PHYSICS LETTERS

Statistical thermodynamic theory of the cell cycle: the state variables of a collection of cells

A. Kummer, R. Ocone *

"Complex systems…. admit many descriptions, each of which is only partially true…" -Rosen (1979)

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Thank you for your attention

Acknowledgement:
EPSRC (grant no EP/N034066/1) is kindly acknowledged
Royal Society NAF\R1\201305-Newton Advanced Fellowships