The Statistical Physics of Athermal Particles

(The Edwards Ensemble at 25)

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Sir Sam Edwards

Physica A 157 (1989) 1080–1090
North-Holland, Amsterdam

THEORY OF POWDERS

S.F. EDWARDS and R.B.S. OAKESHOTT
Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, UK

Received 20 February 1989

> If a powder consists for example of uniform cubes of salt, and is poured into a container, falling at low density uniformly from a great height, one expects a salt powder of a certain density. Repeating the preparation reproduces the same density. A treatment such as shaking the powder by a definite routine produces a new density and the identical routine applied to another sample of the initial powder will result in the same final density. Clearly a Maxwell demon could arrange the little cubes of NaCl to make a material of different properties to that of our experiment, but if such demonics are ignored, and we restrict ourselves to extensive operations such as stirring, shaking, compressing – all actions which do not act on grains individually – then well defined states of the powder result.

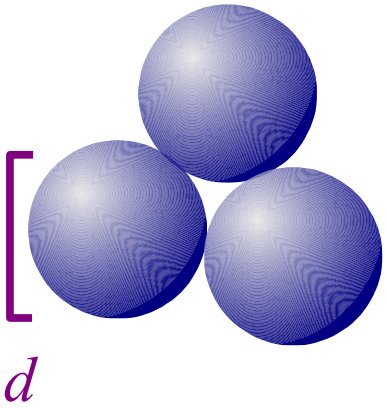
Why Consider Ensembles?

- for ordinary materials, statistical mechanics explains many phenomena
  - Example: Ideal Gas
    - microstate: list of the positions and velocities of each atom in the gas $\{r_i, v_i\}$
    - macrostate: global quantities $\{P, V, T, N, S, E\}$
    - equation of state: $PV = NkT$
  - Generally: a collection of microstates, each occurring with a probability that depends on a few macroscopic parameters

- granular materials also exhibit particle-scale probability distributions that depend on a few macroscopic quantities $\{V, P\}$
  - Can we study the ensemble of microstates? find useful macroscopic variables? equation of state?

Why Not Consider Ensembles?

- Can we study the ensemble of microstates?
- Find useful macroscopic variables?
- Write predictive equations of state?
- Or is this a crazy idea?

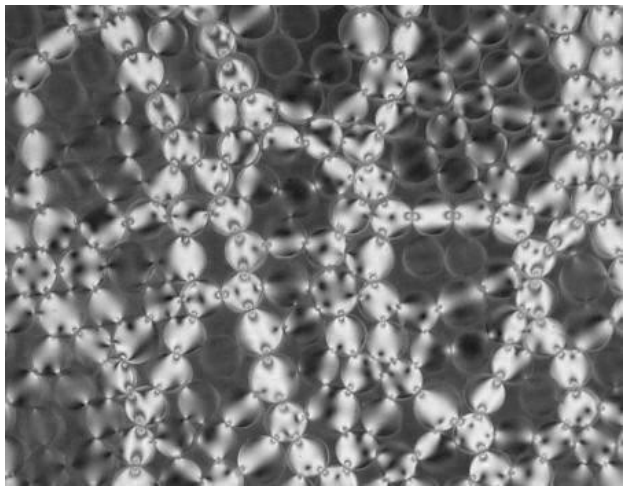


- athermal: $k_B T \sim 10^{-12}\ mgd$ (so temperature has little effect)
- dissipative (friction & collisions) → invalidates fundamental postulate of energy conservation
- poor separation of micro/macroscopic scales
- history-dependence due to frictional contacts
- without temperature, how does the system explore the ensemble?

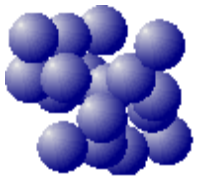
Simplify the Problem

Granular Materials
non-cohesive,
non-attractive,
macroscopic particles
which interact only
when in contact

Solid

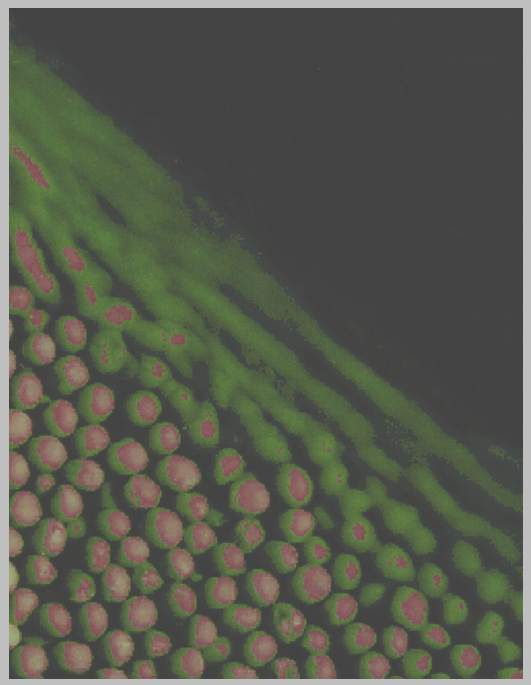


consider an ensemble of "blocked" packings (mechanically-stable, jammed)

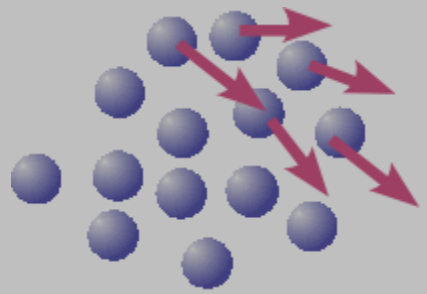


$$\Theta\left(\{\vec{r}_i\}\right) = \begin{cases} 1, \text{ blocked} \\ 0, \text{ unblocked} \end{cases}$$

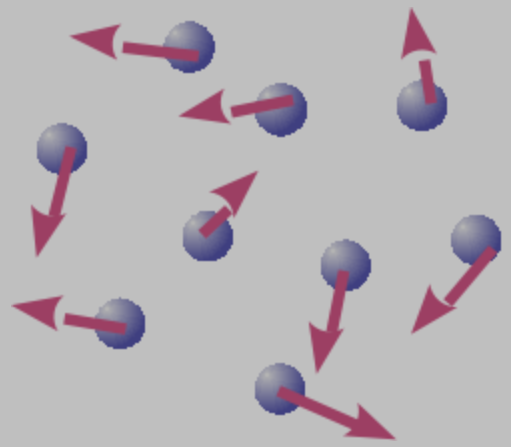
Liquid



Jaeger, Nagel, Behringer
Physics Today. (1996)



Gas



Boltzmann Refresher 1

- 1st Law → total energy E of a system in isolation is constant
- microcanonical ensemble: set of microstates (ν) with total energy $E(\{\boldsymbol{r}_i\}, \{\boldsymbol{p}_i\})$ for particles $\{i\}$
- E is a macroscopic, extensive variable
- all microstates with energy E are assumed to occur with equal probability ("flat measure")
- a physical system is characterized by its density of states: $\Omega_B(E) = \sum_\nu \delta(E - E_\nu)$

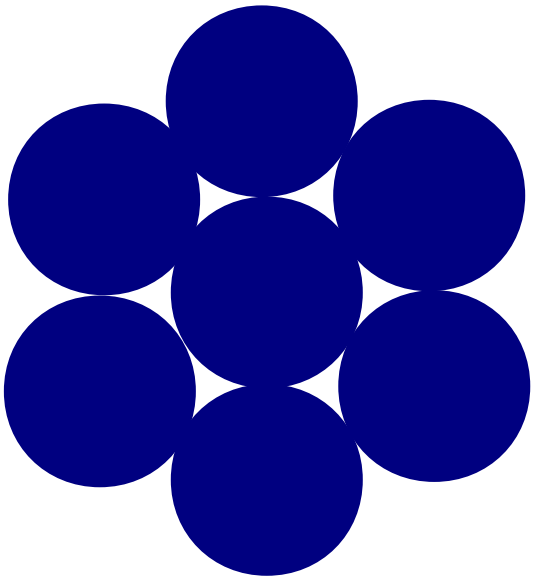
Boltzmann Refresher 2

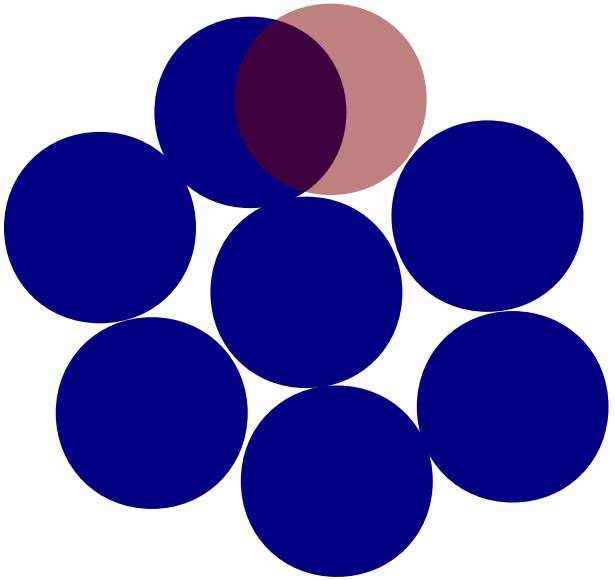
- canonical ensemble allows consideration of a subsystem (with fluctuating energy E) in contact with a large heat bath
- density of states: $\Omega = \#$ of microstates with energy E
- entropy: $S = k_B \ln \Omega(E)$
- maximization of entropy → temperature

$$\frac{1}{T} = \left(\frac{\partial S(E)}{\partial E} \right)_V$$

- temperature T is an intensive macroscopic variable, associated with the extensive variable E

Edwards' Central Idea





smallest system volume

only one valid configuration

larger volume

more valid configurations

$$S = k_E \ln \Omega(V)$$

Edwards' Granular Ensemble

- count blocked microstates at volume V
  - cannot move grains without causing a finite overlap
- density of states: $\Omega(V) = \Sigma_\nu \ \delta(V - V_\nu)$
  - sum is over blocked states: $\Theta\left(\{\vec{r}_i\}\right) = 1$
  - all blocked states are equiprobable (?)
- Edwards' entropy: $S = \cancel{\chi}^{1} \ln \Omega(V)$
- Edwards' temperature → "compactivity"

$$\frac{1}{X} = \left(\frac{\partial S(V)}{\partial V} \right)$$

Boltzmann Ensemble

Energy is conserved

Temperature equilibrates

$\Omega(E)$ counts valid states

$$e^{-\frac{E}{k_B T}}$$

$$S = k_B \ln \Omega(E)$$

$$\frac{1}{T} = \frac{\partial S}{\partial E}$$

$$C_v = \frac{d\langle E \rangle}{dT} = \frac{1}{k_B T^2} \langle dE^2 \rangle$$

Edwards Ensemble

Volume is conserved

Compactivity equilibrates

$\Omega(V)$ counts jammed states

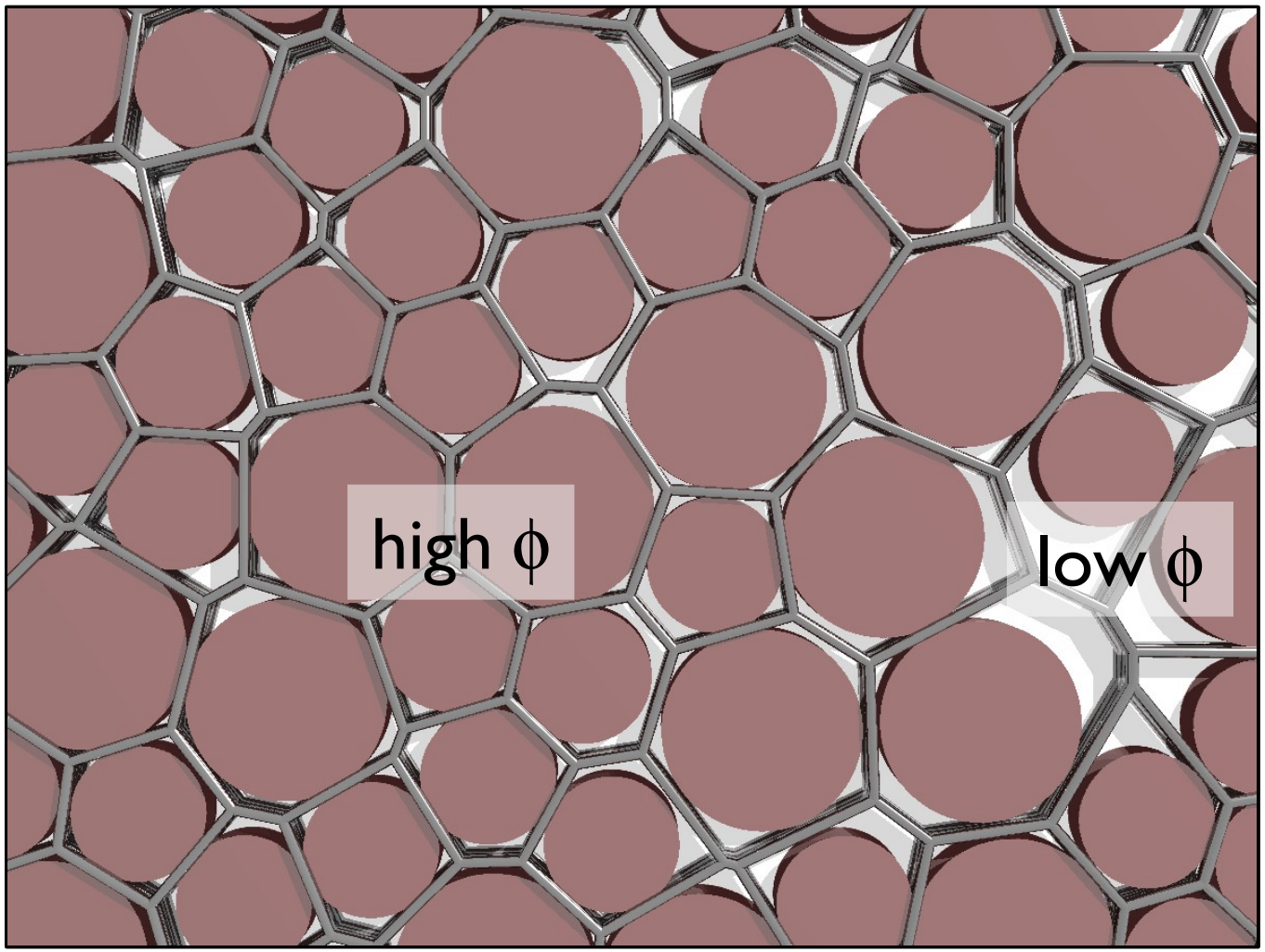
$$e^{-\frac{V}{X}}$$

$$S = k_E \ln \Omega(V)$$

$$\frac{1}{X} = \frac{\partial S}{\partial V}$$

$$\frac{d\langle V \rangle}{dX} = \frac{1}{X^2} \langle dV^2 \rangle$$

Packing Fraction, ϕ



global definition

$$\phi = \frac{N V_{particle}}{V_{system}}$$

local definition

$$\phi = \frac{V_{particle}}{V_{Voronoï}}$$

data visualization with Voro++ Rycroft et. al. *PRE* (2006) http://math.lbl.gov/voro++/

Measuring Compactivity

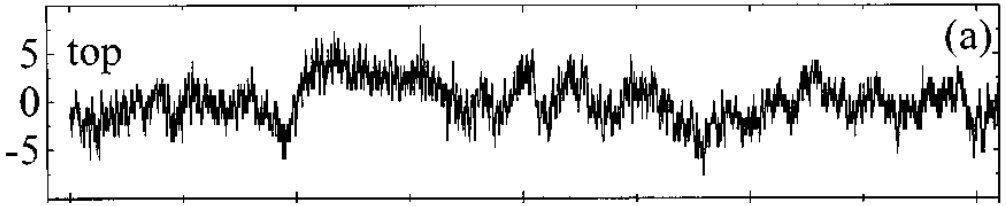
- $X \to 0$
  - random close packing: ϕ_{RCP}
  - densest packing that still has no crystalline order
  - large ϕ → little free space → can't be compacted more
- $X \to \infty$
  - random loose packing: ϕ_{RLP}
  - loosest packing that still has mechanical stability
  - small ϕ → lots of free space → high susceptibility to compaction

Method 1: "Specific Heat"

translate Boltzmann to Edwards

$$C_v = \frac{d\langle E\rangle}{dT} = \frac{1}{k_B T^2}\langle dE^2\rangle \quad \rightarrow \quad \frac{d\langle V\rangle}{dX} = \frac{1}{X^2}\langle dV^2\rangle$$

- record steady state volume fluctuations

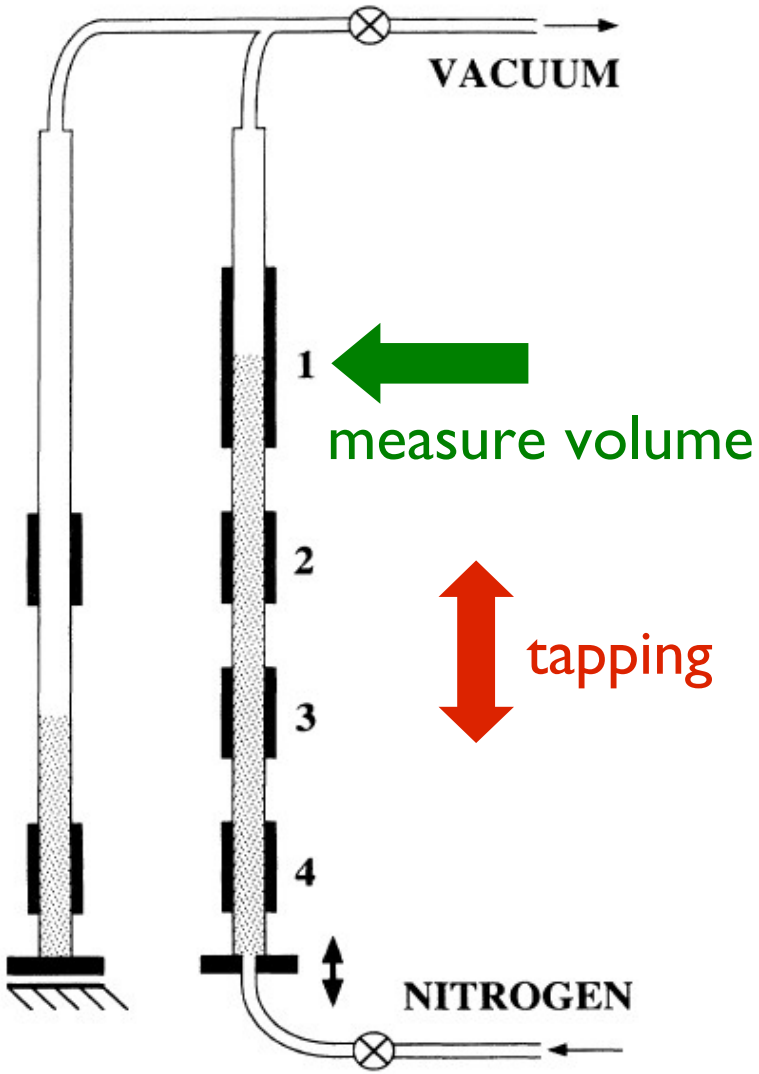


- integrate to measure changes in compactivity

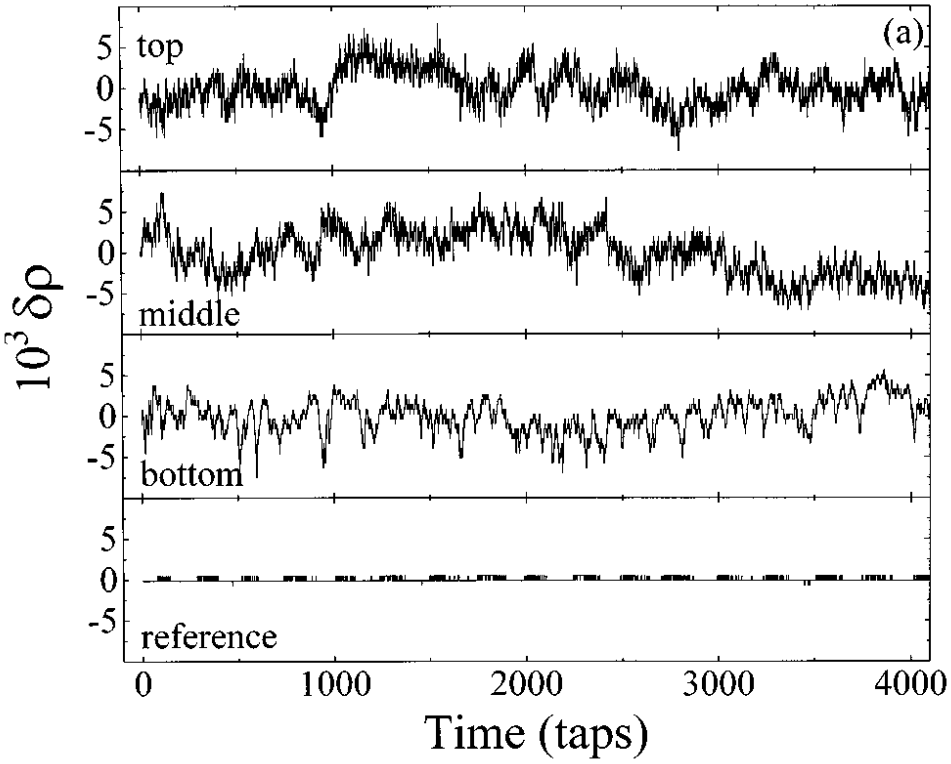
$$\int_{V_1}^{V_2} dV_{ss}/\langle (V - V_{ss})^2\rangle = \int_{X_1}^{X_2} dX/\lambda X^2$$
$$= 1/\lambda X_1 - 1/\lambda X_2$$

Nowak, Knight, Ben-Naim, Jaeger, Nagel. *PRE* (1998)

Example 1: Tapping a Granular Column



packing fraction fluctuations



Knight, Fandrich, Lau, Jaeger, Nagel. *PRE* (1995)
Nowak, Knight, Ben-Naim, Jaeger, Nagel. *PRE* (1998)

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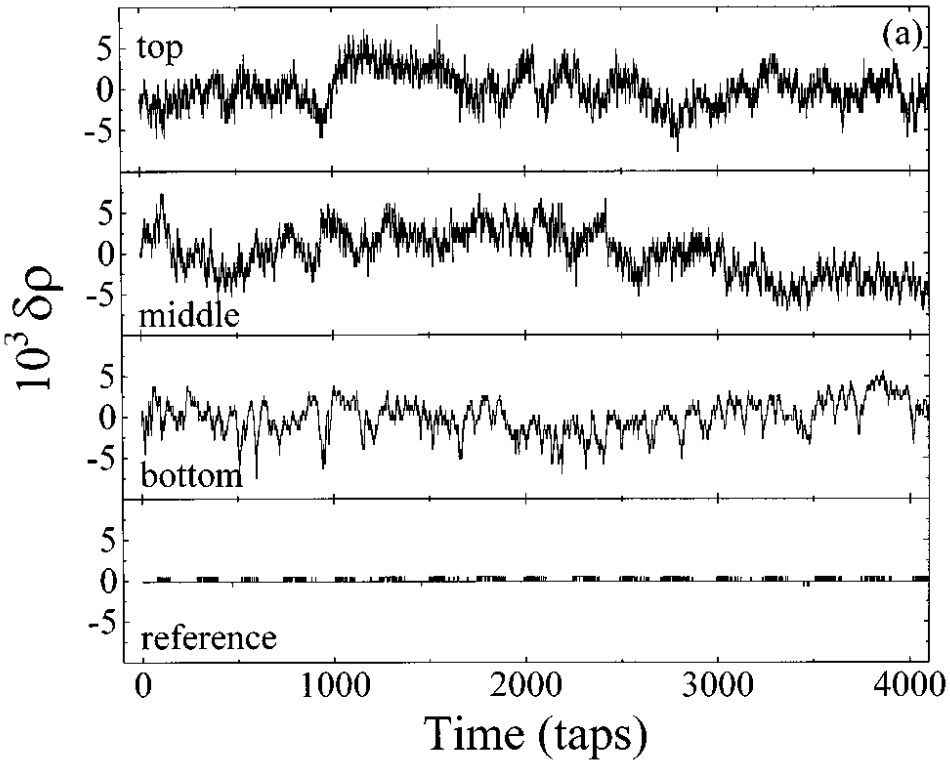
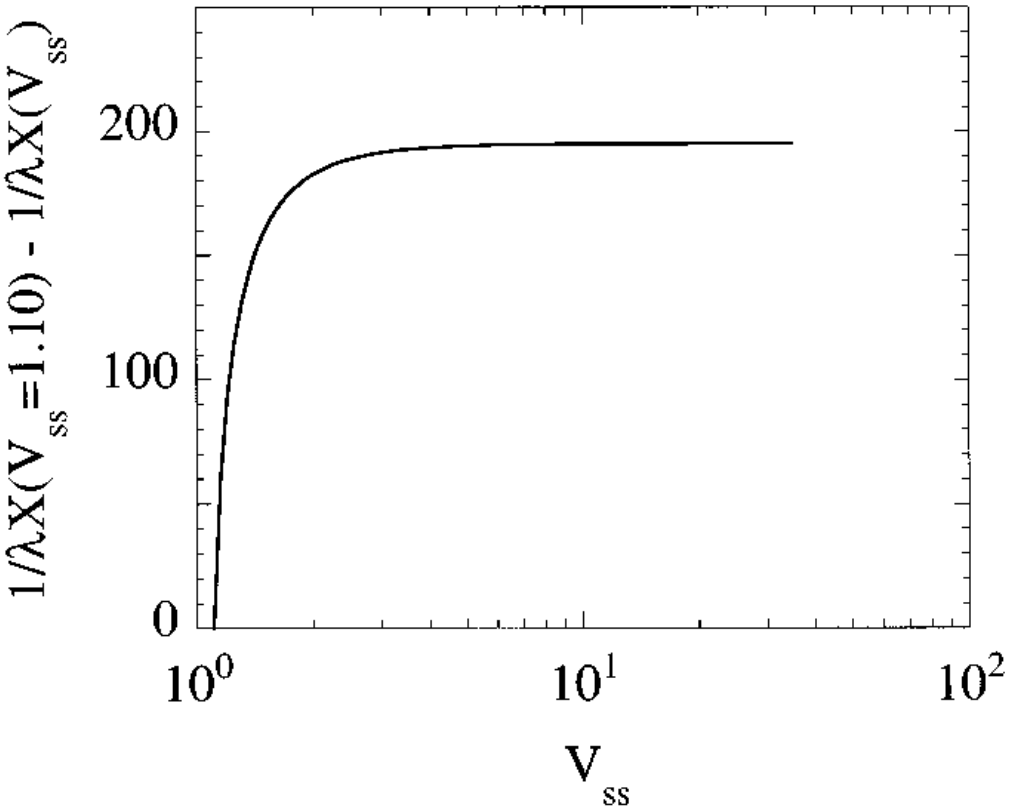


$$\int_{V_1}^{V_2} dV_{ss} / \langle (V - V_{ss})^2 \rangle = 1/\lambda X_1 - 1/\lambda X_2$$

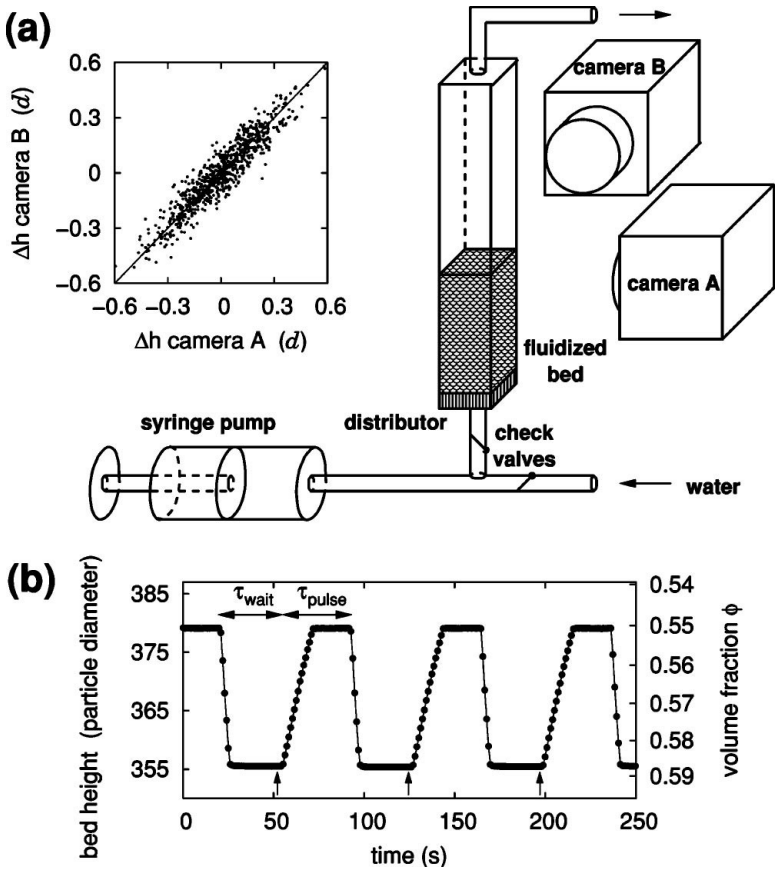
use volume fluctuations to calculate changes in compactivity

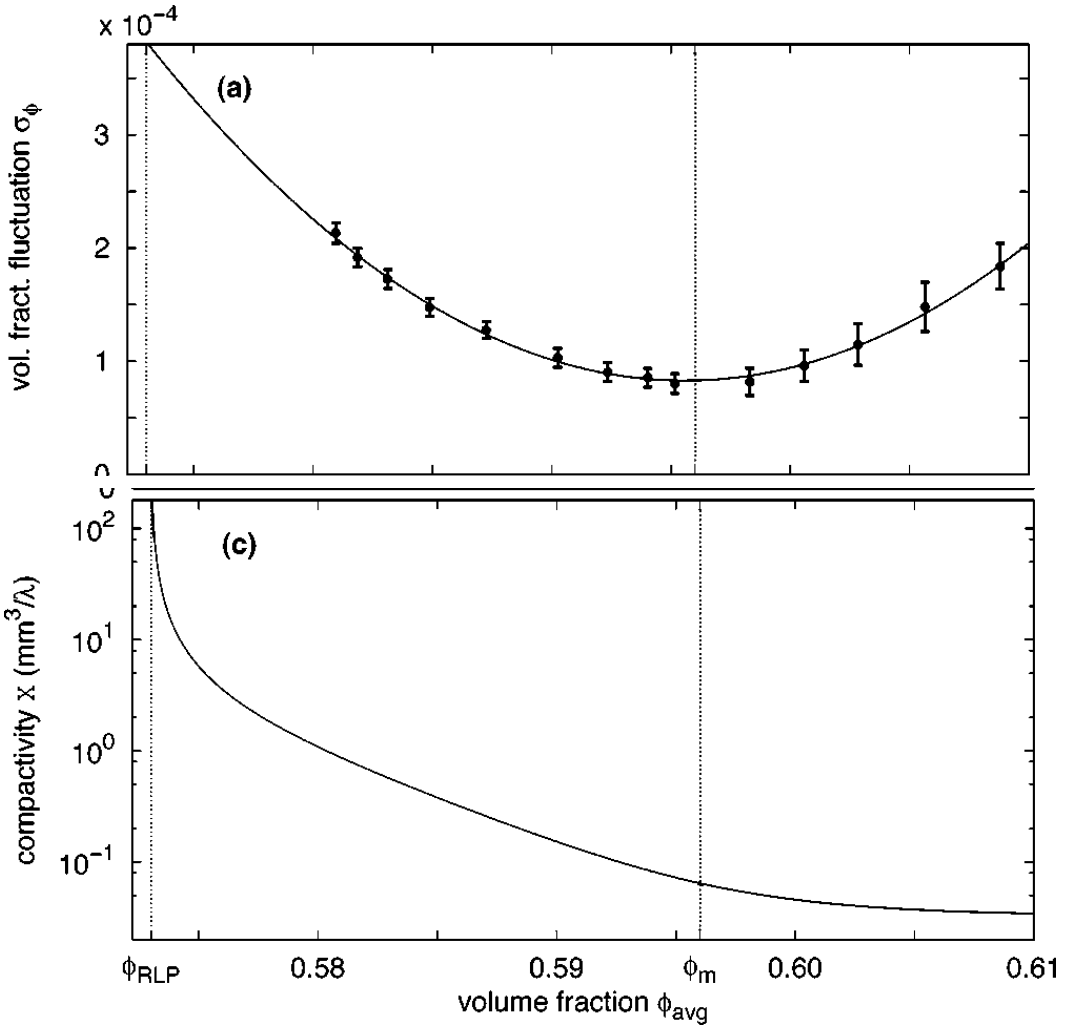


Nowak, Knight, Ben-Naim, Jaeger, Nagel. *PRE* (1998)

Example 2: Sedimentation in a Fluid

$$\int_{V_1}^{V_2} dV_{ss} / \langle (V - V_{ss})^2 \rangle = 1/\lambda X_1 - 1/\lambda X_2$$





Schröter, Goldman, Swinney. *PRE* (2005)

Method 2: "Overlapping Histograms"

- by analogy with Boltzmann, calculate the probability of observing a macroscopic volume V:

$$P(V) = \frac{\Omega(V)}{Z(X)} e^{-\frac{V}{X}}$$

- for density of states $\Omega(V)$ → generally not known, but independent of X
- partition function $Z(X)$ → generally not known

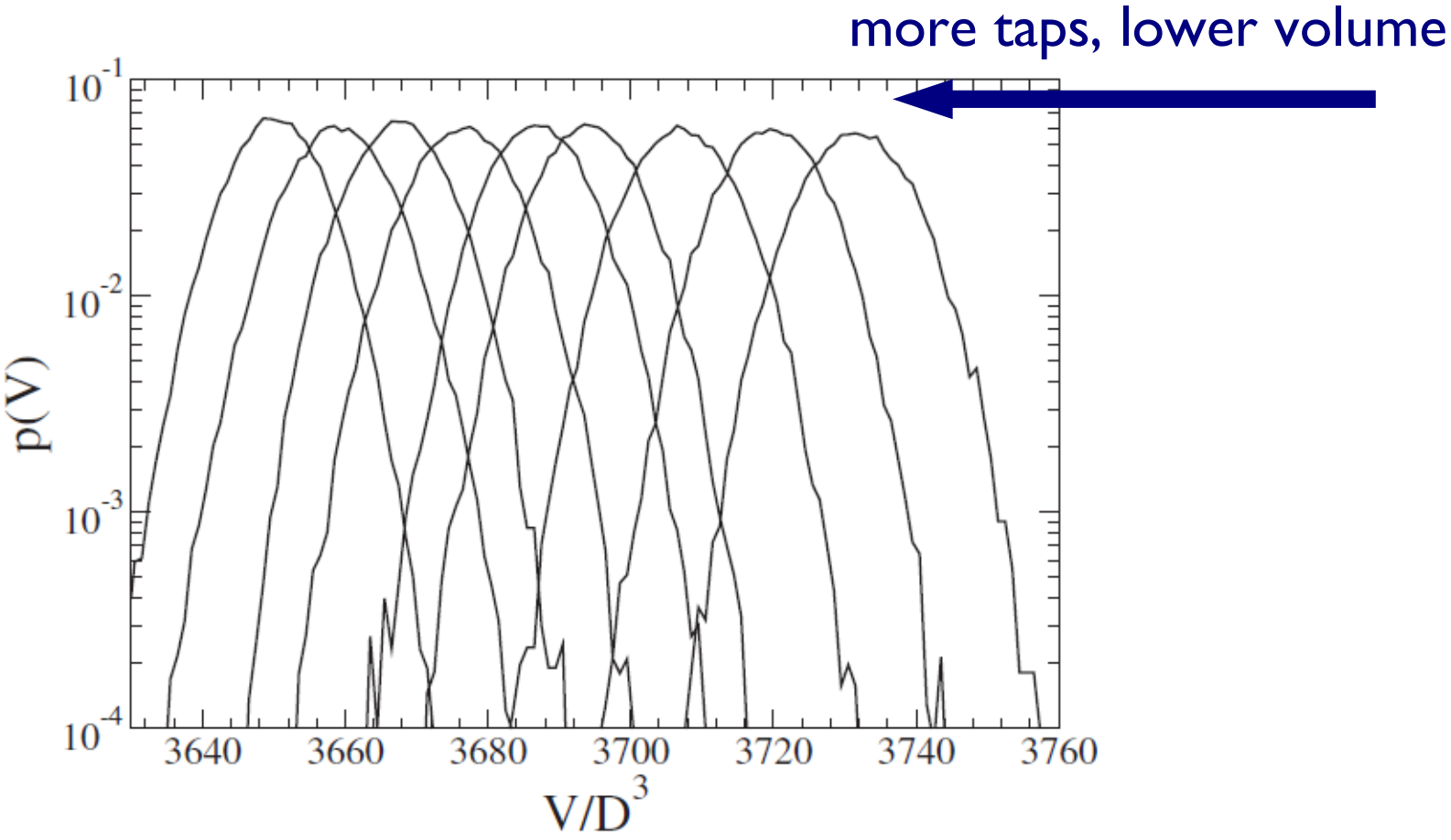
- RATIO of two measurement provides RELATIVE temperatures

$$\frac{P(V_1)}{P(V_2)} = \frac{Z(X_2)}{Z(X_1)} e^{V\left(\frac{1}{X_2} - \frac{1}{X_1}\right)}$$

Dean & Lefèvre, *PRL* (2003)
McNamara, Richard, de Richter, Le Caër, Delannay. *PRE* (2009)

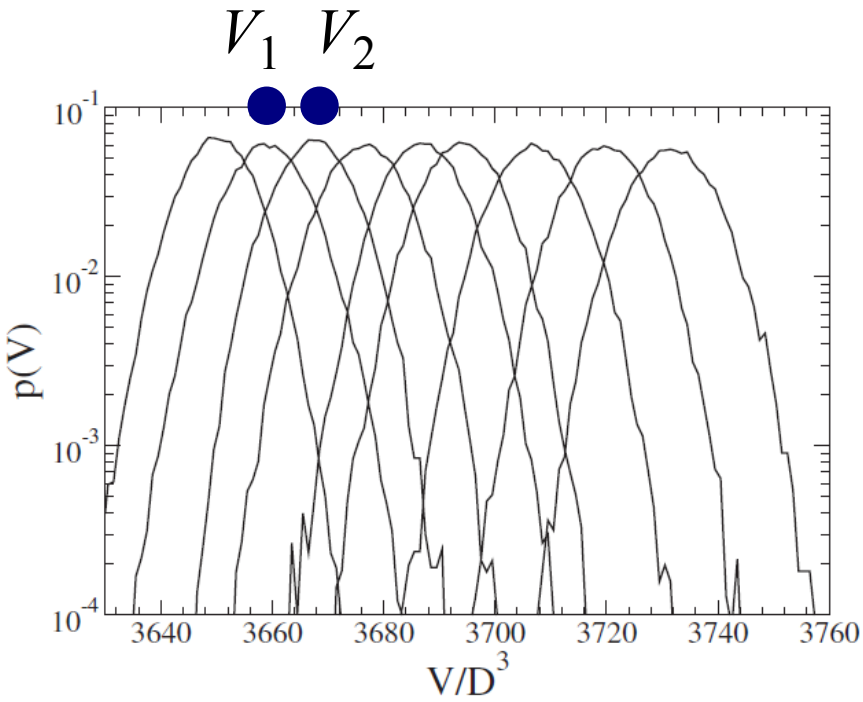
Example: Particle-Scale Volumes

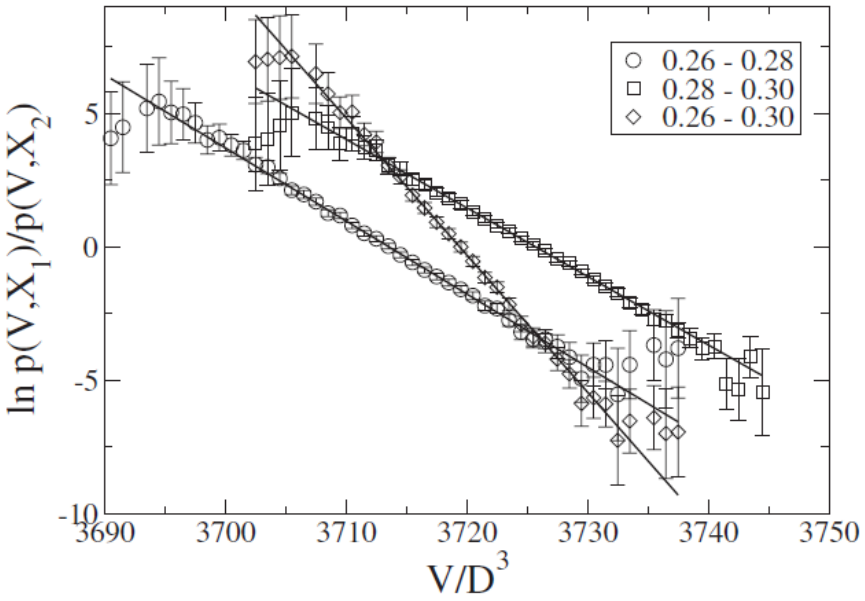
- numerical simulations, subjected to virtual "tapping"
- histogram of local (Voronoï) volumes



McNamara, Richard, de Richter, Le Caër, Delannay. *PRE* (2009)

Example: Calculate Compactivity





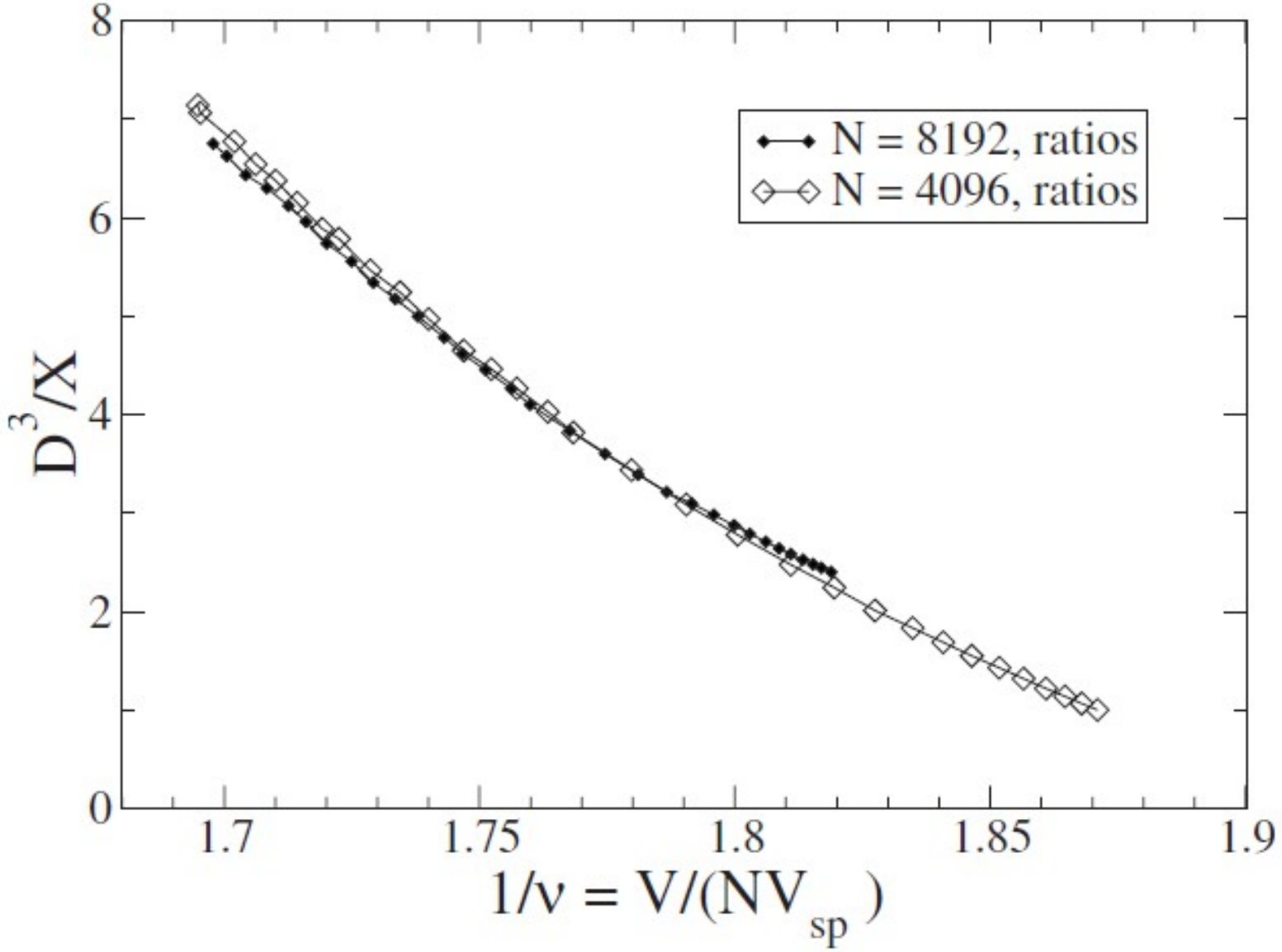
$$\frac{P(V_1)}{P(V_2)} = \frac{Z(X_2)}{Z(X_1)} e^{V\left(\frac{1}{X_2} - \frac{1}{X_1}\right)}$$

$$\log \frac{P(V_1)}{P(V_2)} = const. + V\left(\frac{1}{X_2} - \frac{1}{X_1}\right)$$

measure relative compactivities from the slope

McNamara, Richard, de Richter, Le Caër, Delannay. *PRE* (2009)

Compactivity Decreases with Taps

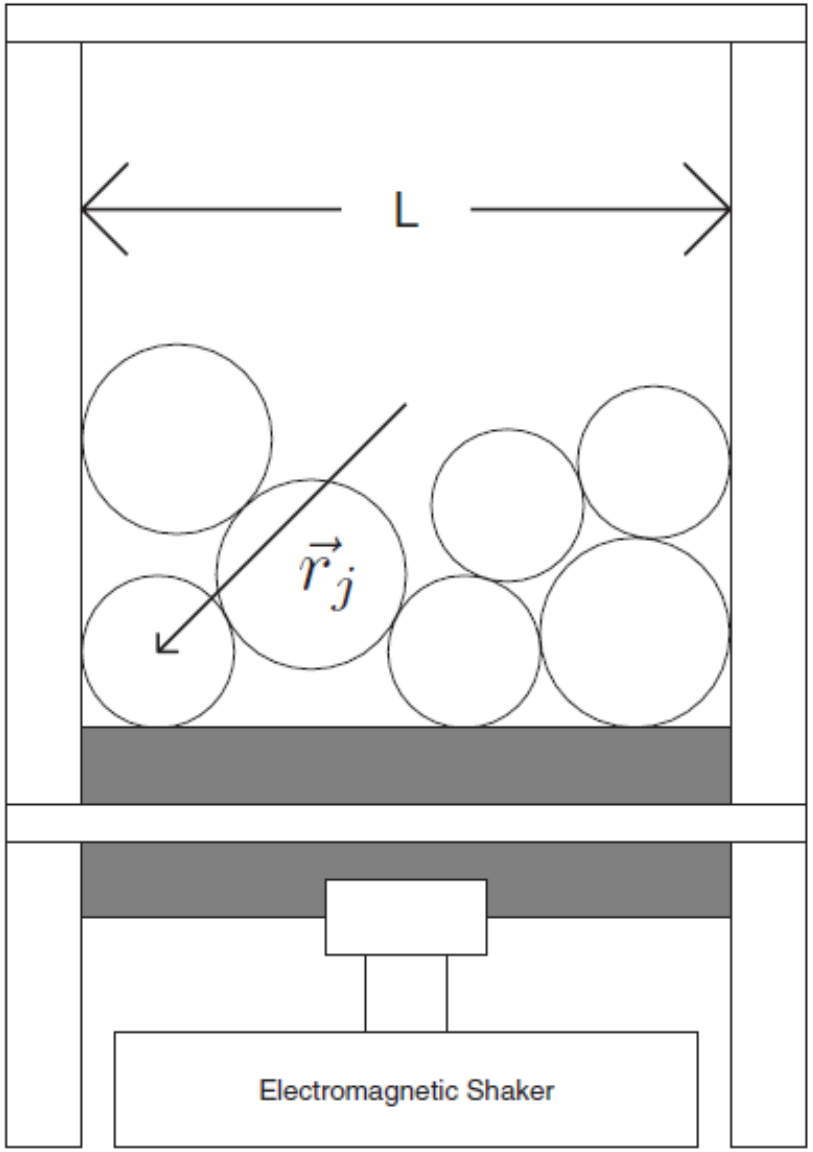


smaller compactivity

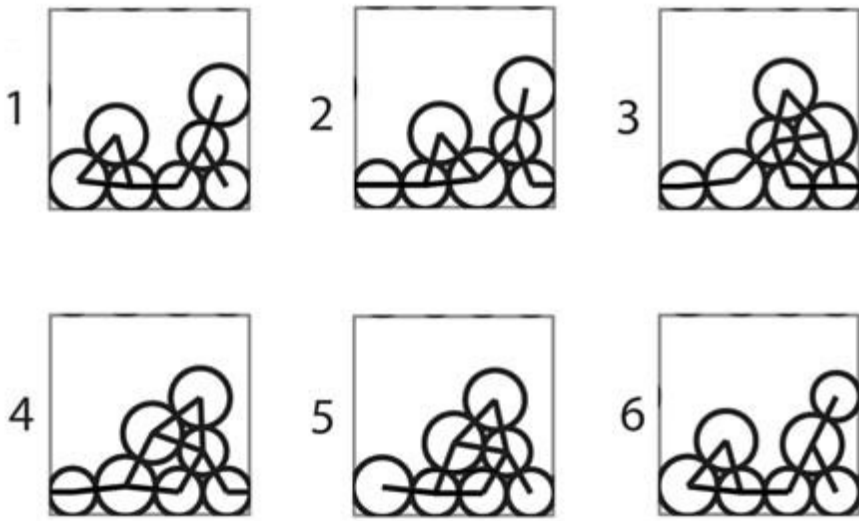
more taps = smaller volume = higher ϕ

McNamara, Richard, de Richter, Le Caër, Delannay. *PRE* (2009)

Testing Equiprobability Assumption



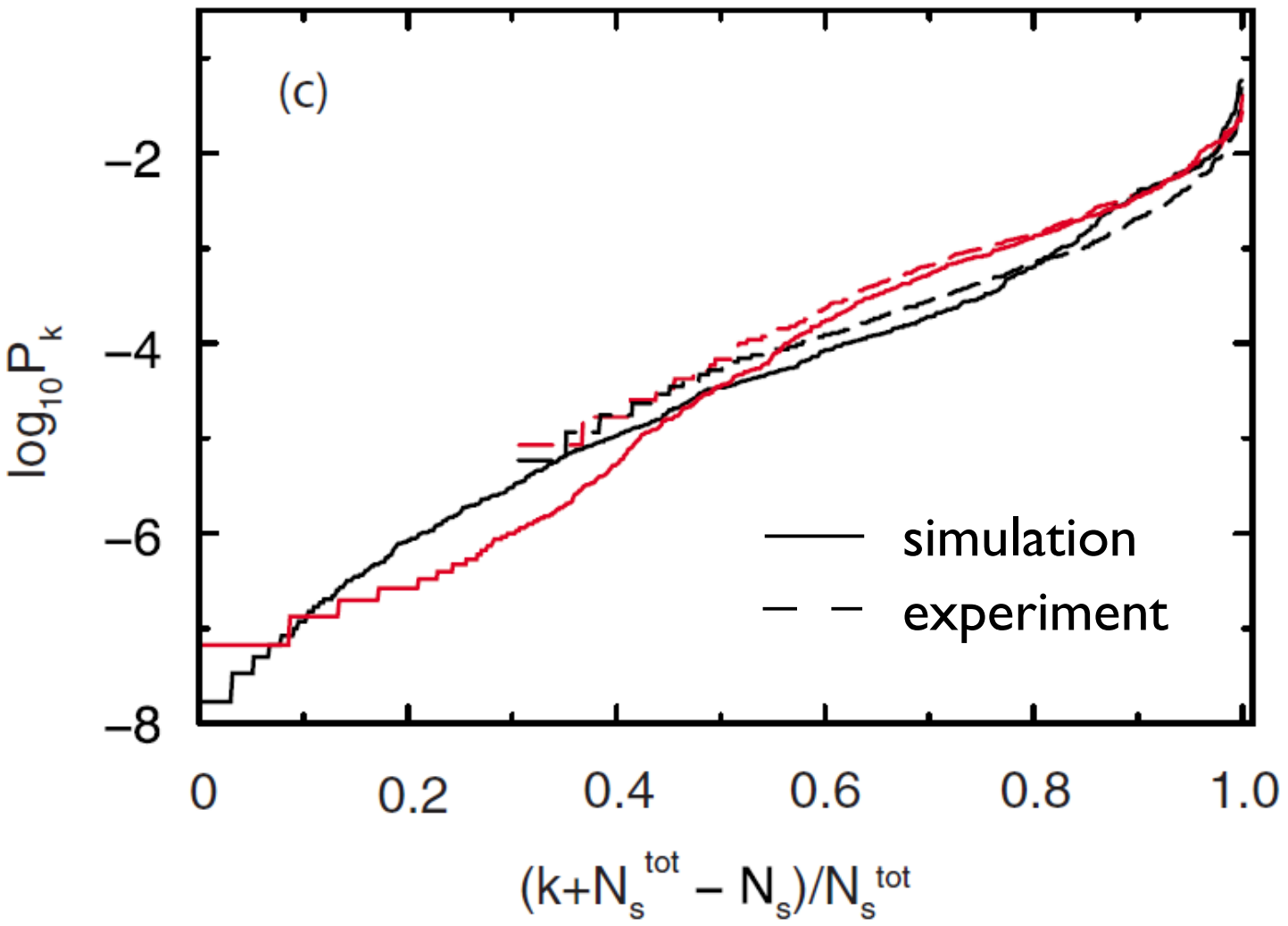
- consider 7 particles in a box
- generate millions of blocked configurations in matched simulations and experiments



- enumerate all possible configurations

Gao, Blawzdziewicz, O'Hern, Shattuck. *PRE* (2009)

Equiprobability Assumption Fails



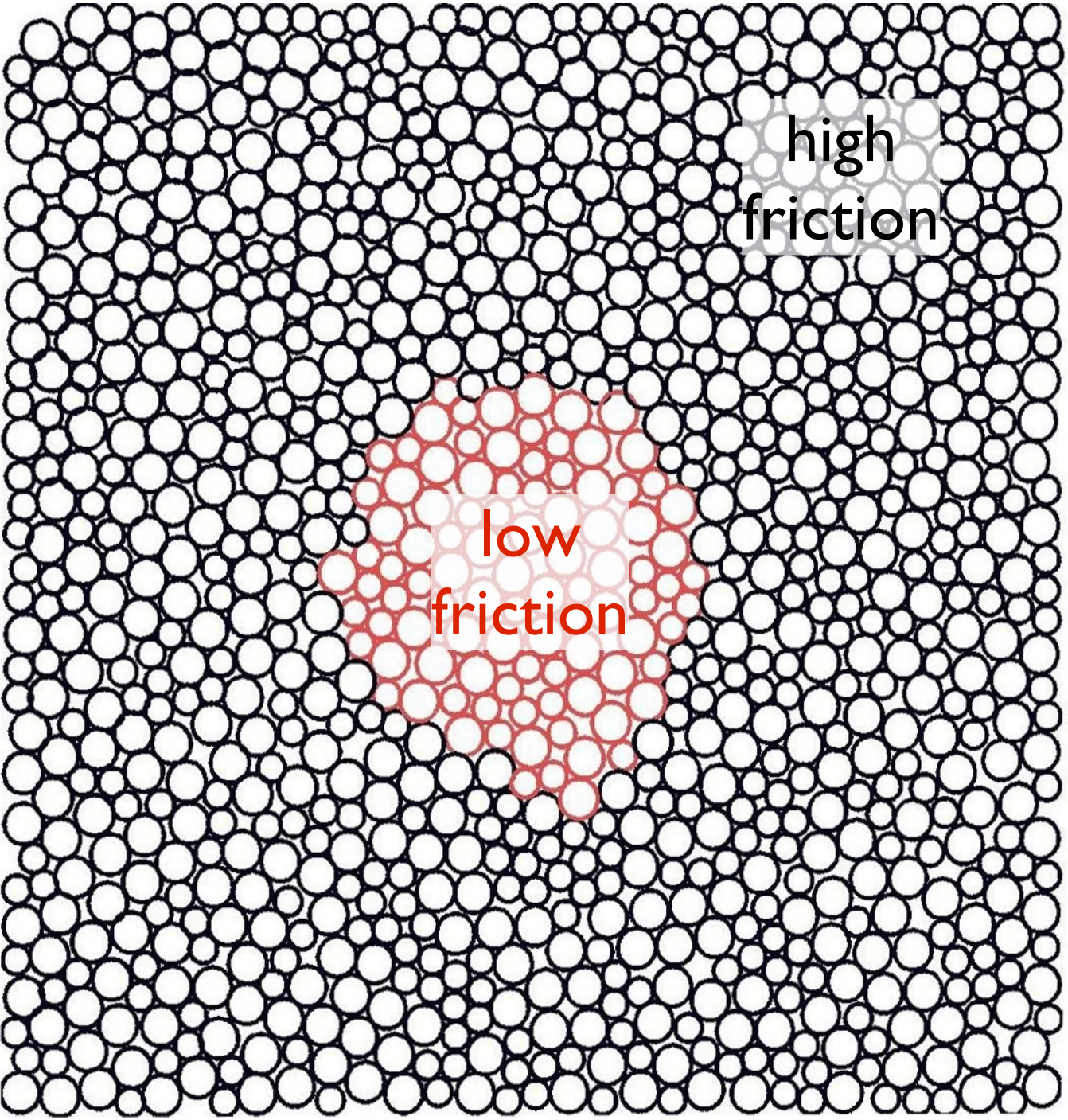
some configurations are 10^6 more likely than others → $\Omega(V)$ is non-trivial

Gao, Blawzdziewicz, O'Hern, Shattuck. *PRE* (2009)

Summary so Far

- ✔ compactivity can be measured using two methods: "specific heat" or "overlapping histograms"
- ✔ compactivity increases as packing fraction decreases
- ➔ does compactivity <u>behave</u> like a temperature?
  - ➔ equilibration?
  - ➔ useful state variable?

Test the "Zeroth Law"



Zeroth law requires temperature equilibration

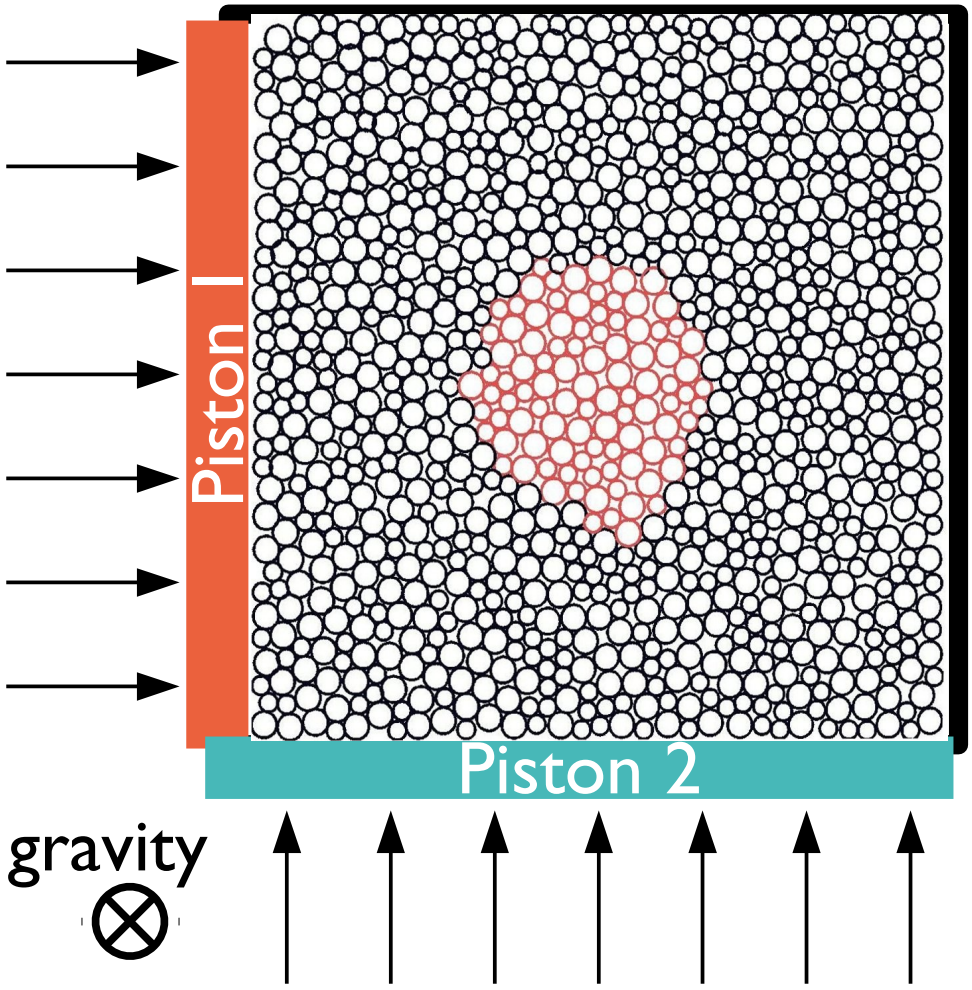
Does

$X_{bath} = X_{subsys}$

?

Puckett & Daniels. *PRL* (2013)

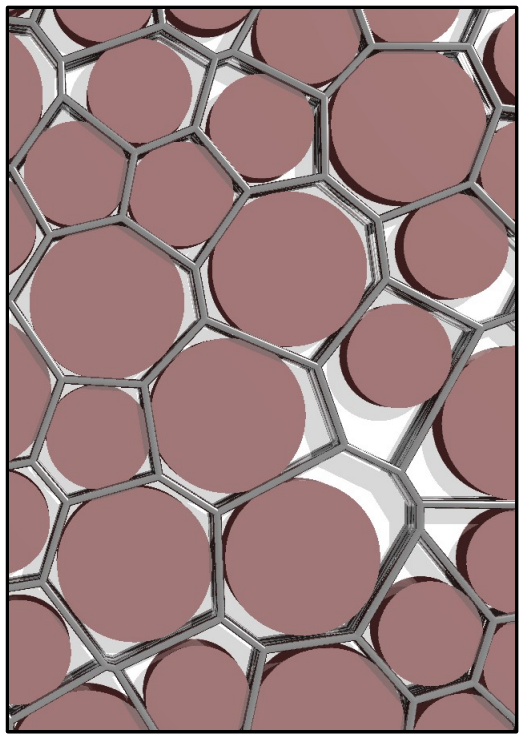
Generate Many Independent Configurations



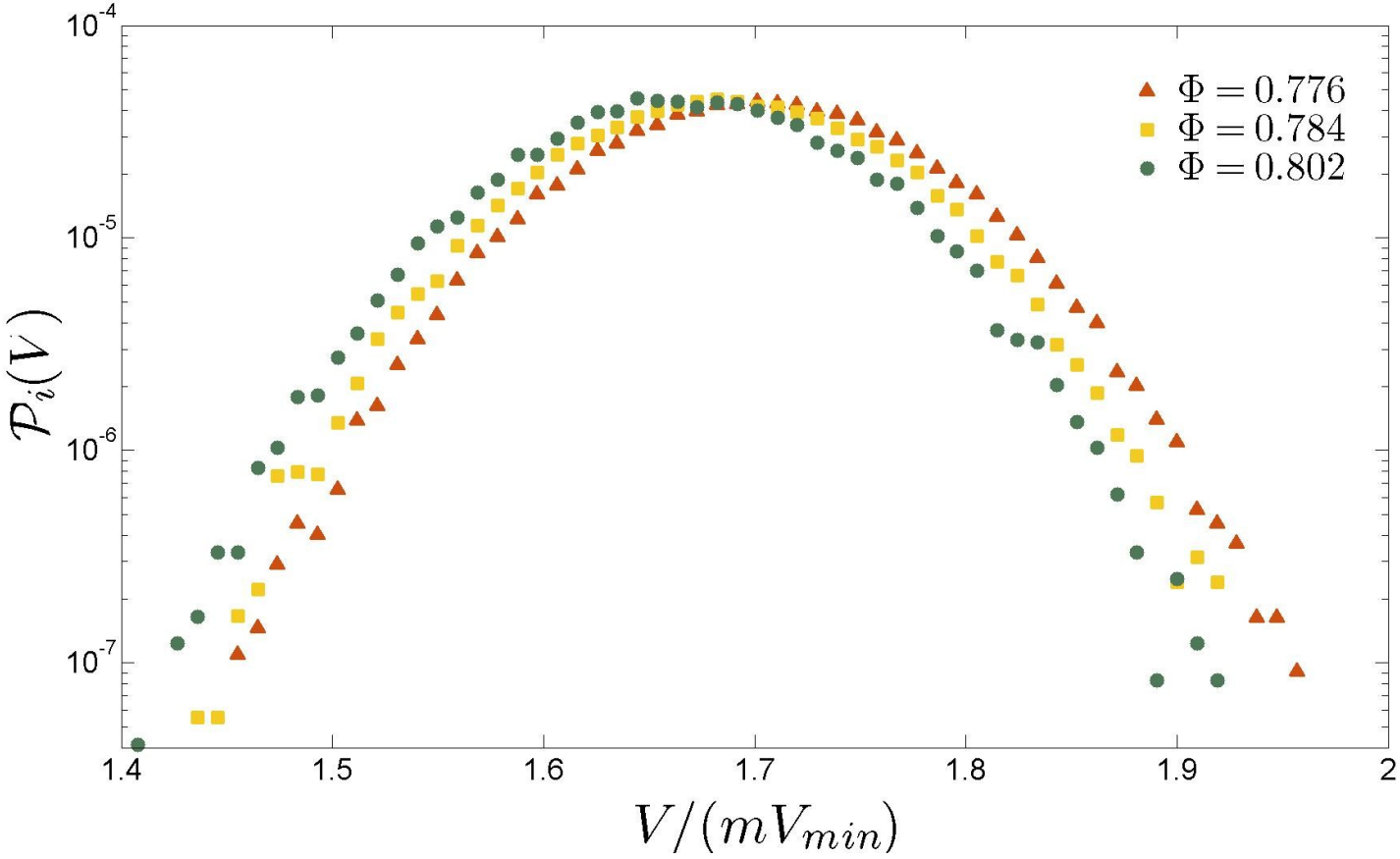
- particles float on an air table (microporous frit)
- walls alternately create loose and dense packings
- record particle positions
- analyze high and low friction regions separately

Local Voronoï Volumes

sample Voronoï tessellation



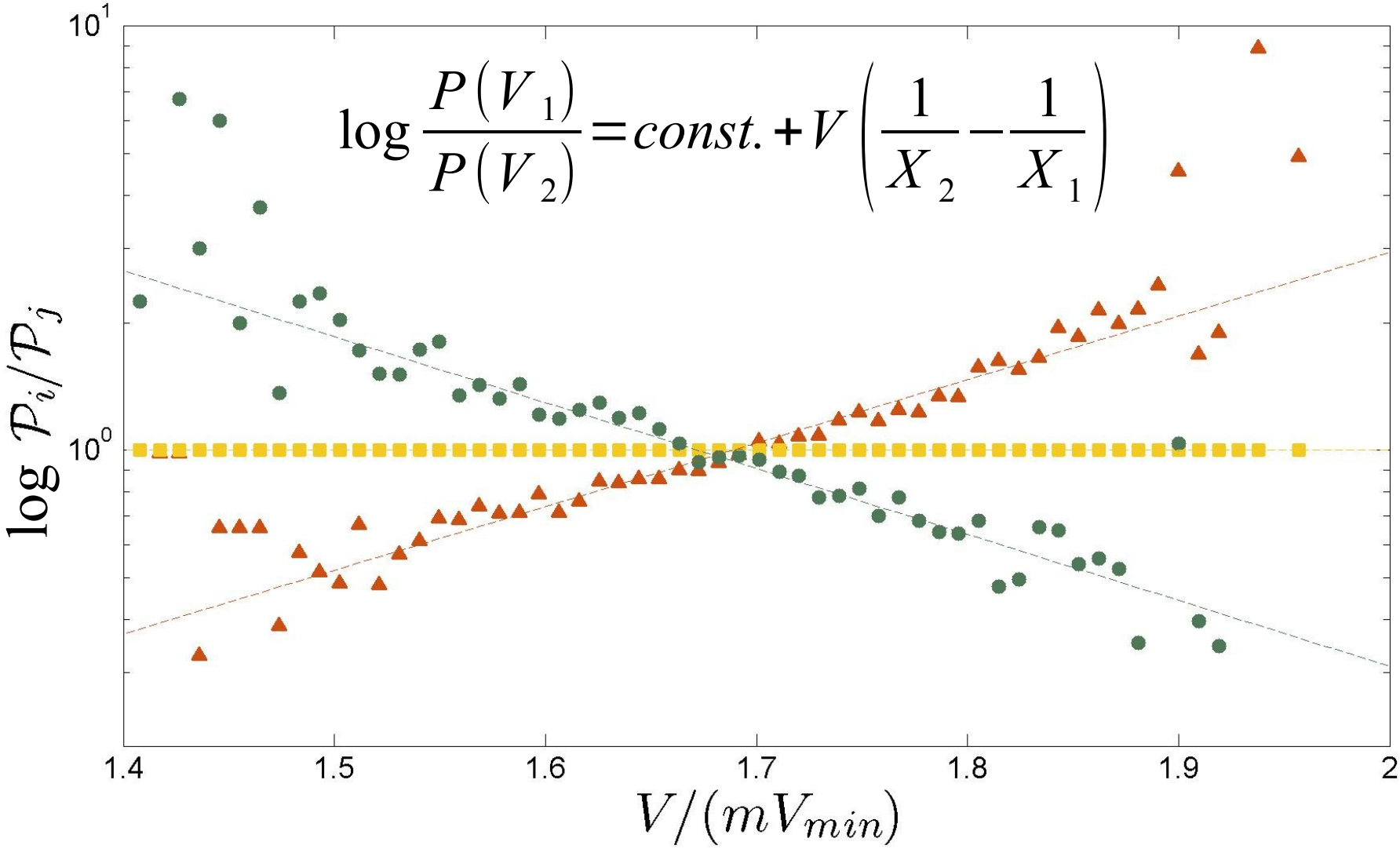
3 example histograms (for subsystem only)



Puckett & Daniels. *PRL* (2013)

Plot the Overlapping Histograms

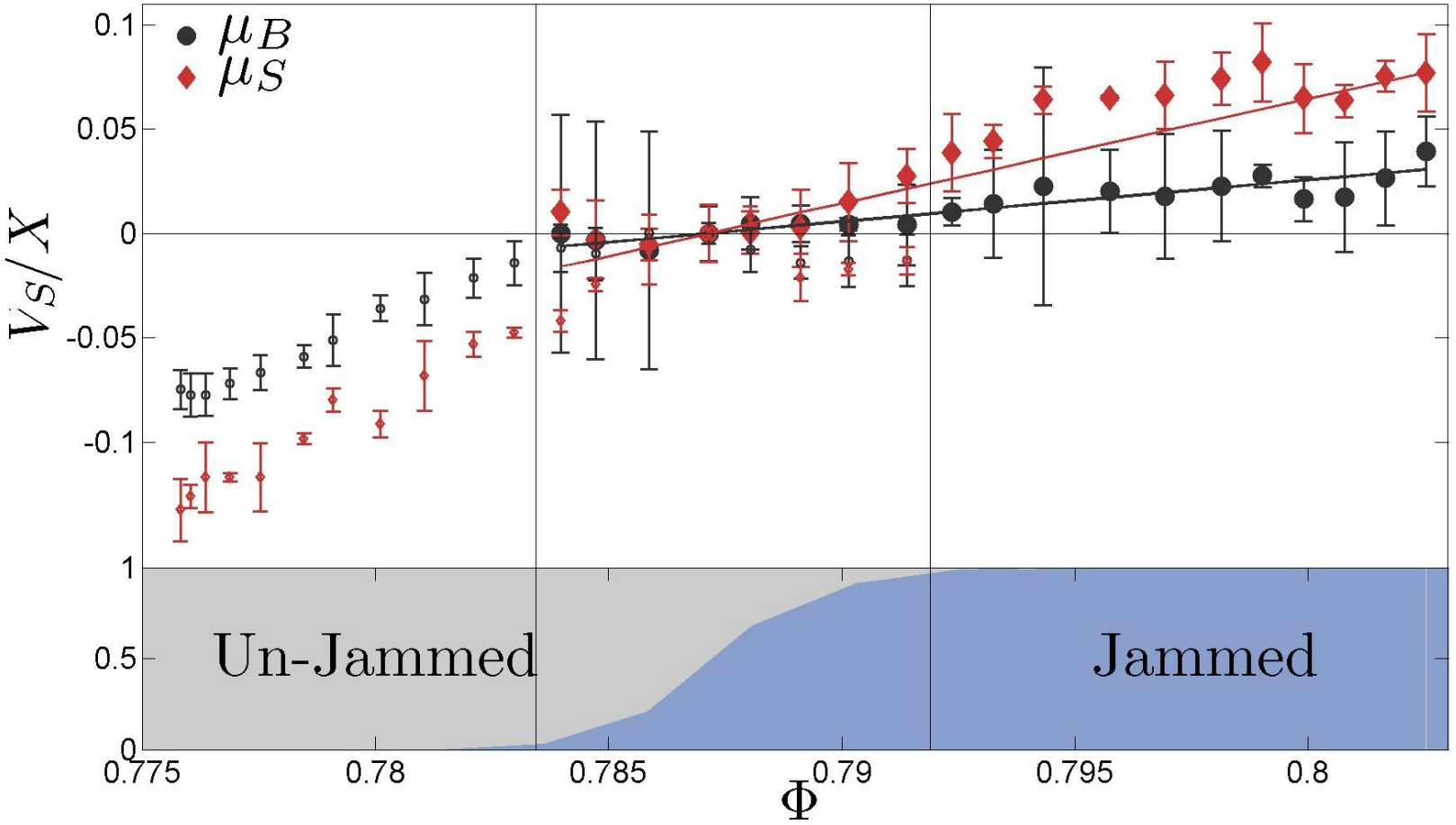
slope → difference in compactivity



Puckett & Daniels. *PRL* (2013)

Compactivity Fails to Equilibrate

red (low-friction system) and black (high-friction bath) do not have the same compactivity



Puckett & Daniels PRL 2013

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  - ✗ equilibration?
  - ➔ useful state variable?
- ➔ compactivity just considers volume: what about the pressure/stress?

Including Forces

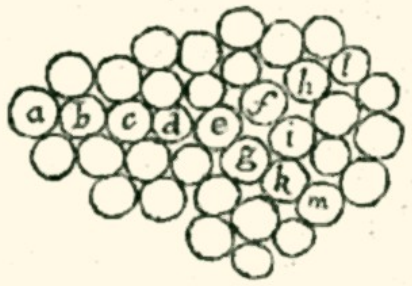
SECT. VIII.

De Motu per Fluida propagato.

Prop. XLI. Theor. XXXI.

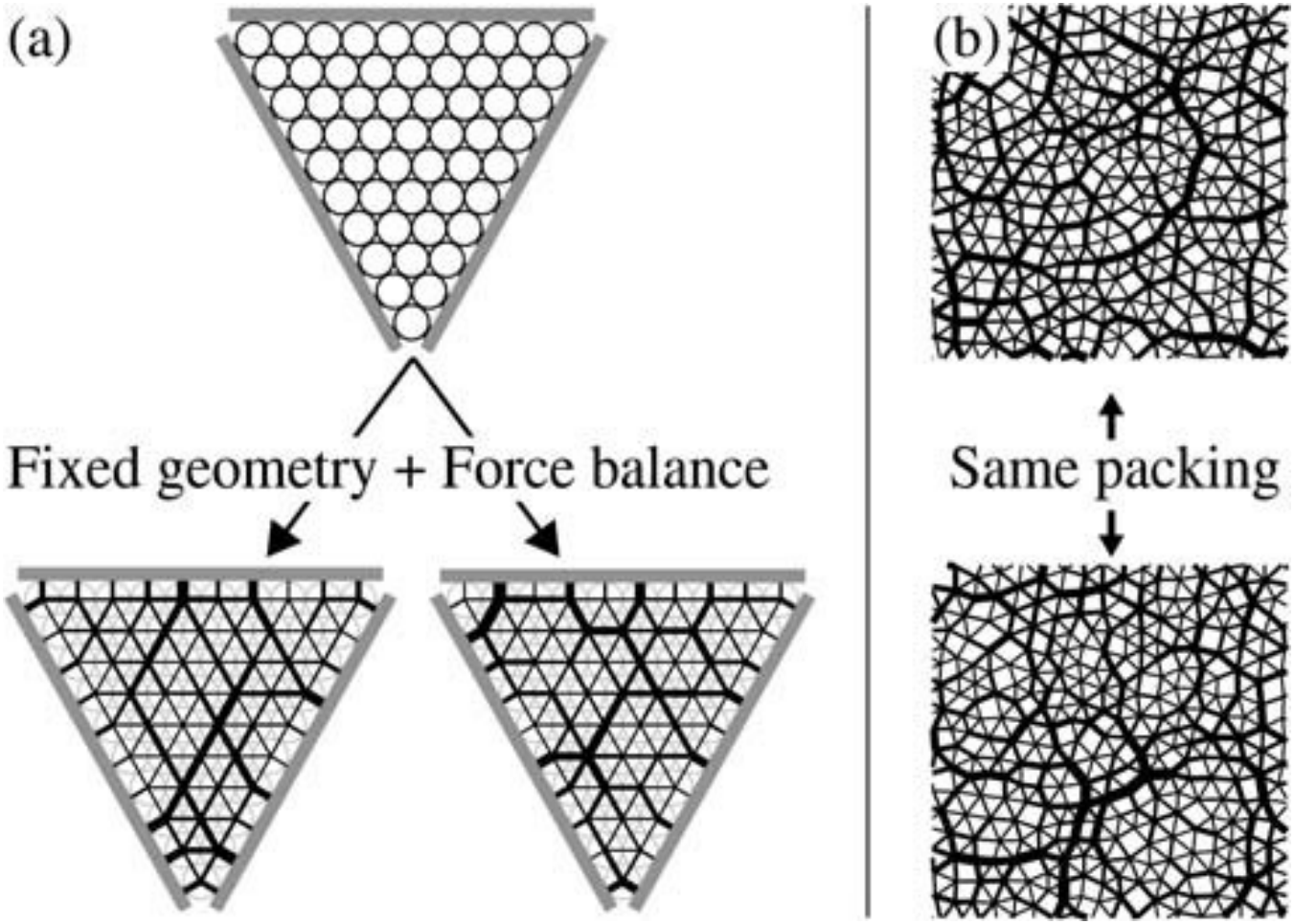
Preſſio non propagatur per Fluidum ſecundum lineas rectas, niſi ubi particulæ Fluidi in directum jacent.

Si jaceant particulæ *a*, *b*, *c*, *d*, *e* in linea recta, poteſt quidem preſſio directe propagari ab *a* ad *e*; at particula *e* urgebit particulas oblique poſitas *f* & *g* oblique, & particulæ illæ *f* & *g* non ſuſtinebunt preſſionem illatam, niſi fulciantur a particulis ulterioribus *h* & *k*; quatenus autem fulciuntur, premunt particulas fulcientes; & hæ non ſuſtinebunt preſſionem niſi fulciantur



Newton, *Principia*

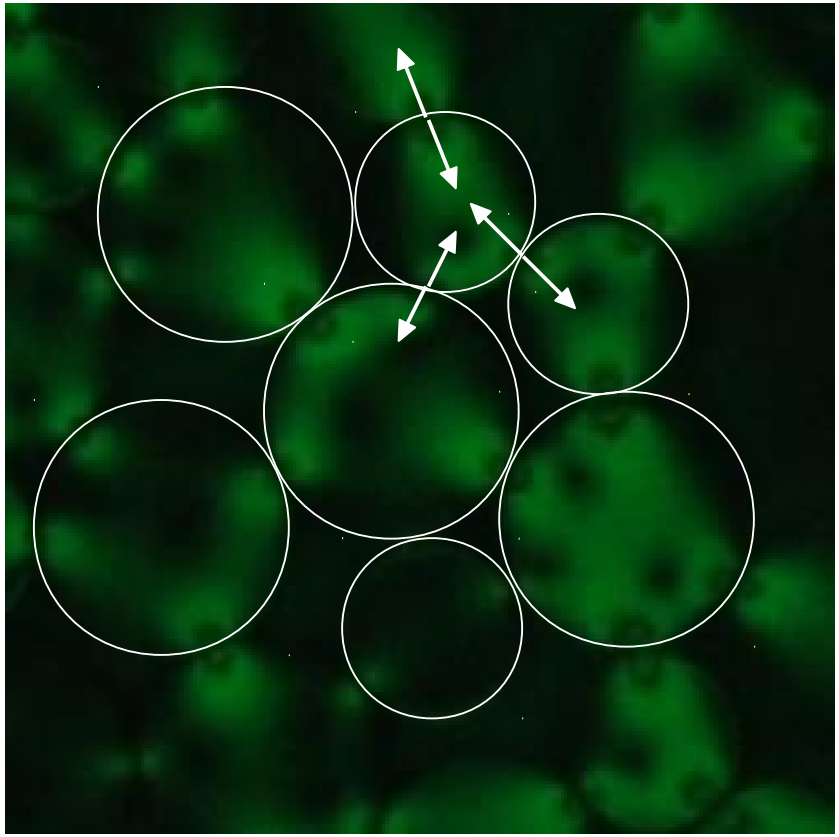
Force Network Ensemble

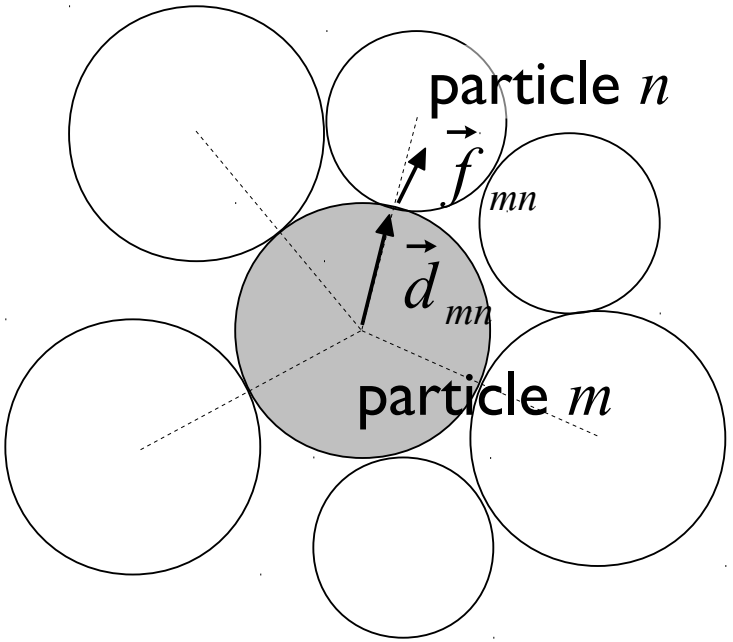


many possible arrangements of forces, for the same set of particle positions

Snoeijer, van Hecke, Somfai, van Saarloos. *PRE* (2004)
Tighe, Snoeijer, Vlugt, van Hecke. *Soft Matter* (2010)

Quantifying Interparticle Forces





force moment tensor:

$$\hat{\Sigma} = \sum_{m,n} \vec{d}_{mn} \vec{f}_{mn}$$

Angoricity α

- force moment tensor: sum over all interparticle contact positions and forces:

$$\hat{\Sigma} = \sum_{m,n} \vec{d}_{mn} \vec{f}_{mn}$$

- Σ plays the role of E in the Boltzmann ensemble (is extensive, but now also tensorial)
- its associated intensive parameter is <u>angoricity</u> (means "stress" in modern Greek)

$$\alpha_{\mu\lambda} = \left(\frac{\partial S(\hat{\Sigma}_{\mu\lambda})}{\partial \Sigma_{\mu\lambda}} \right)$$

no reciprocal!

Edwards. *Physica A.* (2005) Blumenfeld & Edwards. *J. Phys. Chem.* (2009) Metzger. *PRE* (2008)
Henkes, O'Hern, Chakraborty. *PRL* (2007) *PRE* (2009) Tighe, van Eerd, Vlugt. *PRL* (2008)

Summary

	Boltzmann	**Edwards**	**generalized Edwards**
conserved quantity	energy, E	volume, V	force moment tensor, $\hat{\Sigma}$
# of valid configurations	$\Omega_B(E)$	$\Omega(V)$	$\Omega(\hat{\Sigma})$
entropy	$S = k_B \ln \Omega_B$	$S = \lambda \ln \Omega$	$S = \lambda \ln \Omega$
equilibrating quantity	temperature	compactivity	angoricity tensor
	$\frac{1}{T} = \frac{\partial S(E)}{\partial E}$	$\frac{1}{X} = \frac{\partial S(V)}{\partial V}$	$\alpha_{\mu\lambda} = \frac{\partial S(\Sigma_{\mu\lambda})}{\partial \Sigma_{\mu\lambda}}$
distribution	$^{-\frac{E}{k_B T}}$	$e^{-\frac{V}{X}}$	$e^{-\hat{\alpha}:\hat{\Sigma}}$

Bi, Henkes, Daniels, Chakraborty. *Ann. Rev. Cond. Matt.* (2015). arXiv: 1404.1854

Angoricity a Tensor

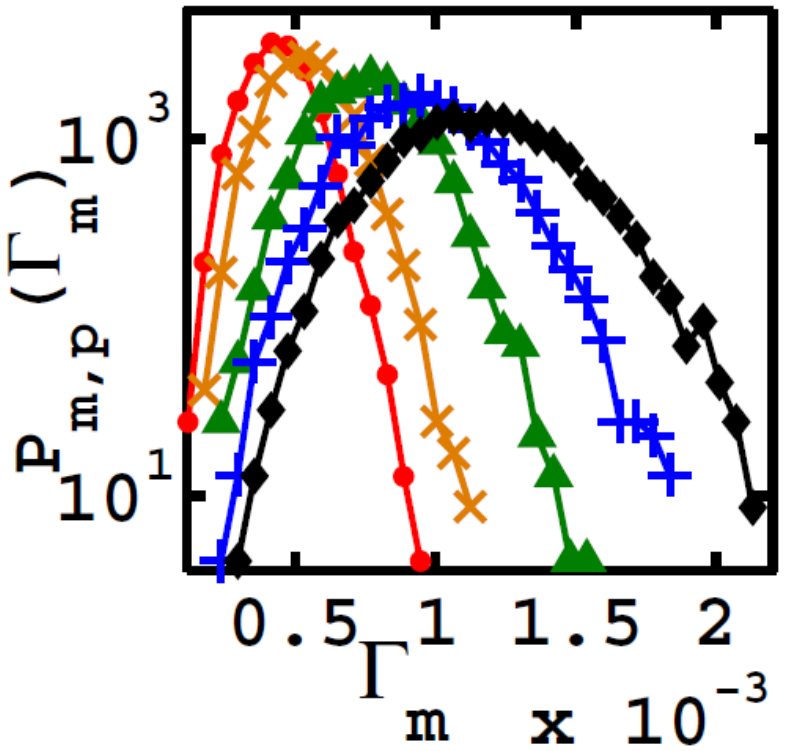
for a 2D granular system:

- force moment tensor is 2×2 matrix: $\hat{\Sigma} = \sum \vec{d}_{mn} \vec{f}_{mn}$
- has two eigenvalues: Σ_1 and Σ_2
  - pressure: $\Sigma_p = \frac{1}{2}(\Sigma_1 + \Sigma_2) = Tr\,\hat{\Sigma}$
  - shear: $\Sigma_\tau = \frac{1}{2}(\Sigma_1 - \Sigma_2)$
- each component has its own angoricity

$$\alpha_p = \frac{\partial S(\Sigma_p)}{\partial \Sigma_p} \qquad \alpha_\tau = \frac{\partial S(\Sigma_\tau)}{\partial \Sigma_\tau}$$

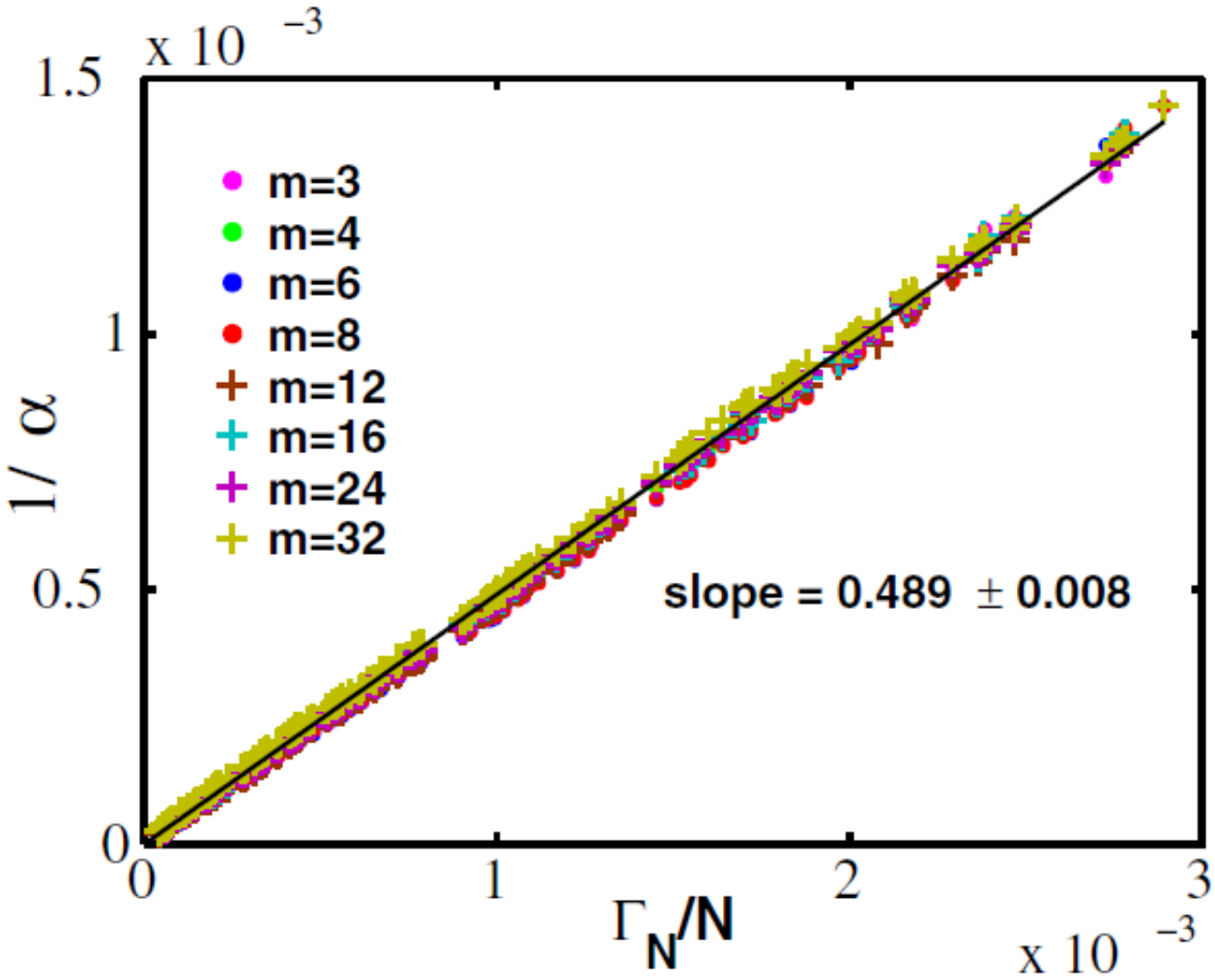
Example 1: 2D Simulations (Microcanonical)

- 2D simulations of frictionless, deformable grains
- prepare system at different pressures $\Gamma = \Sigma_p = Tr\,\hat{\Sigma}$
- no tangential forces → $\Sigma_\tau = 0$
- calculate angoricity α using overlapping histogram method



Henkes, O'Hern, Chakraborty. *PRL* (2007)

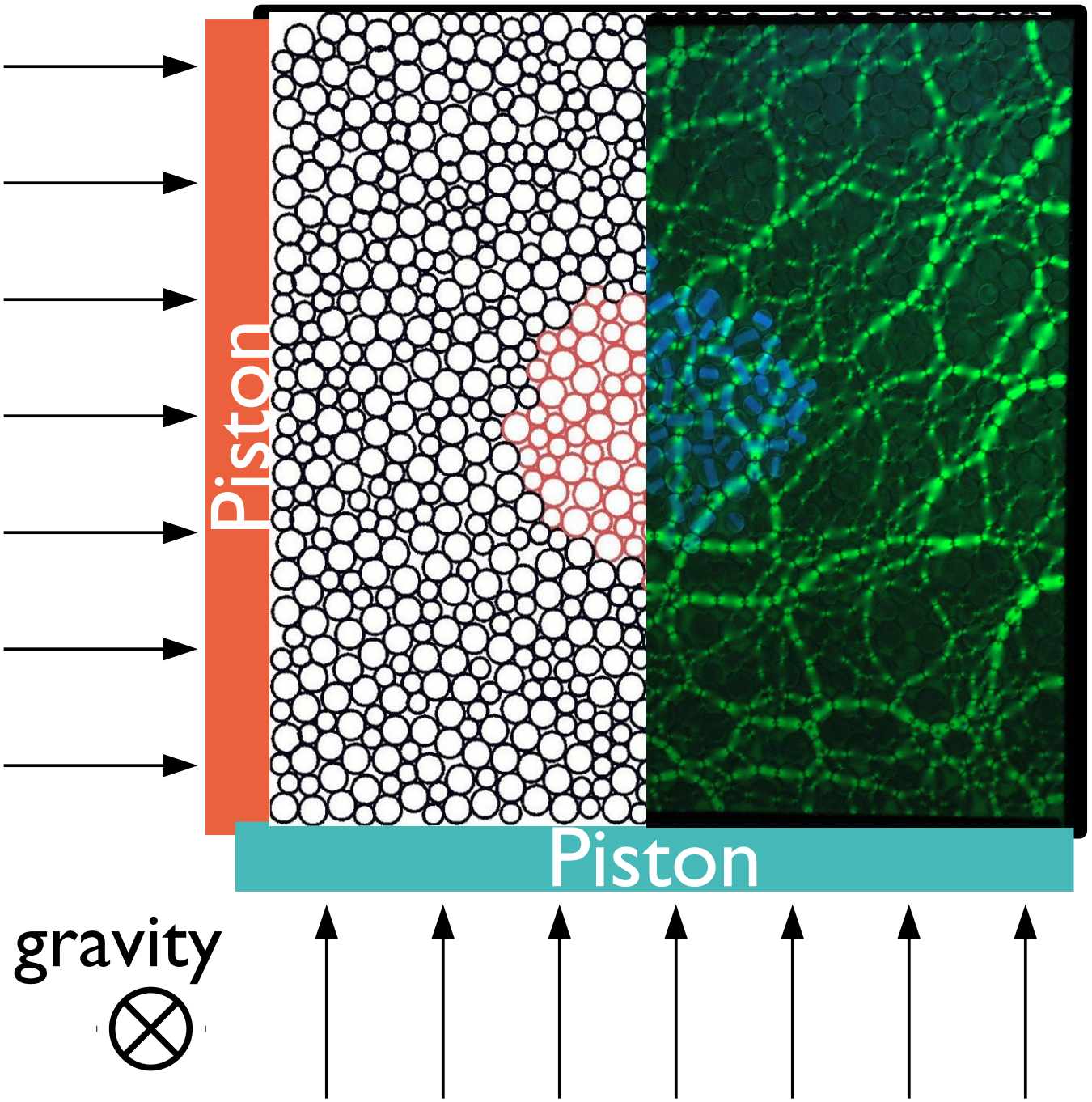
Equilibration & Equation of State



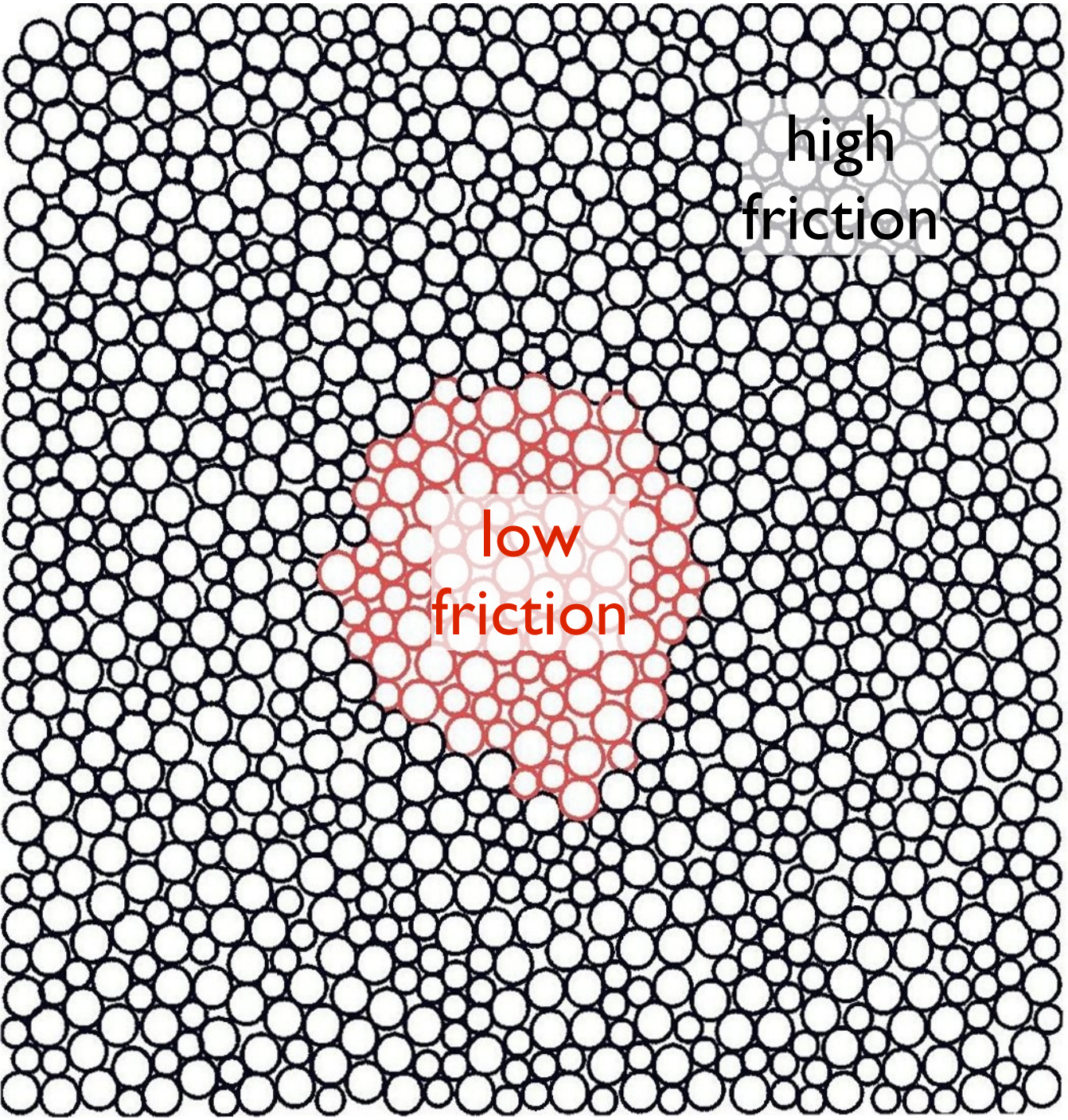
- angoricity doesn't depend on patch size (equilibration within a single system)
- equation of state: $1/\alpha = \frac{1}{2}\,\Gamma$
- a configuration entropy estimate gives slope $\sim 2/\,z_{\mathrm{iso}}$

Henkes, O'Hern, Chakraborty. *PRL* (2007)

Example 2: 2D Experiments (Canonical)



Test the "Zeroth Law"



Zeroth law requires temperature equilibration

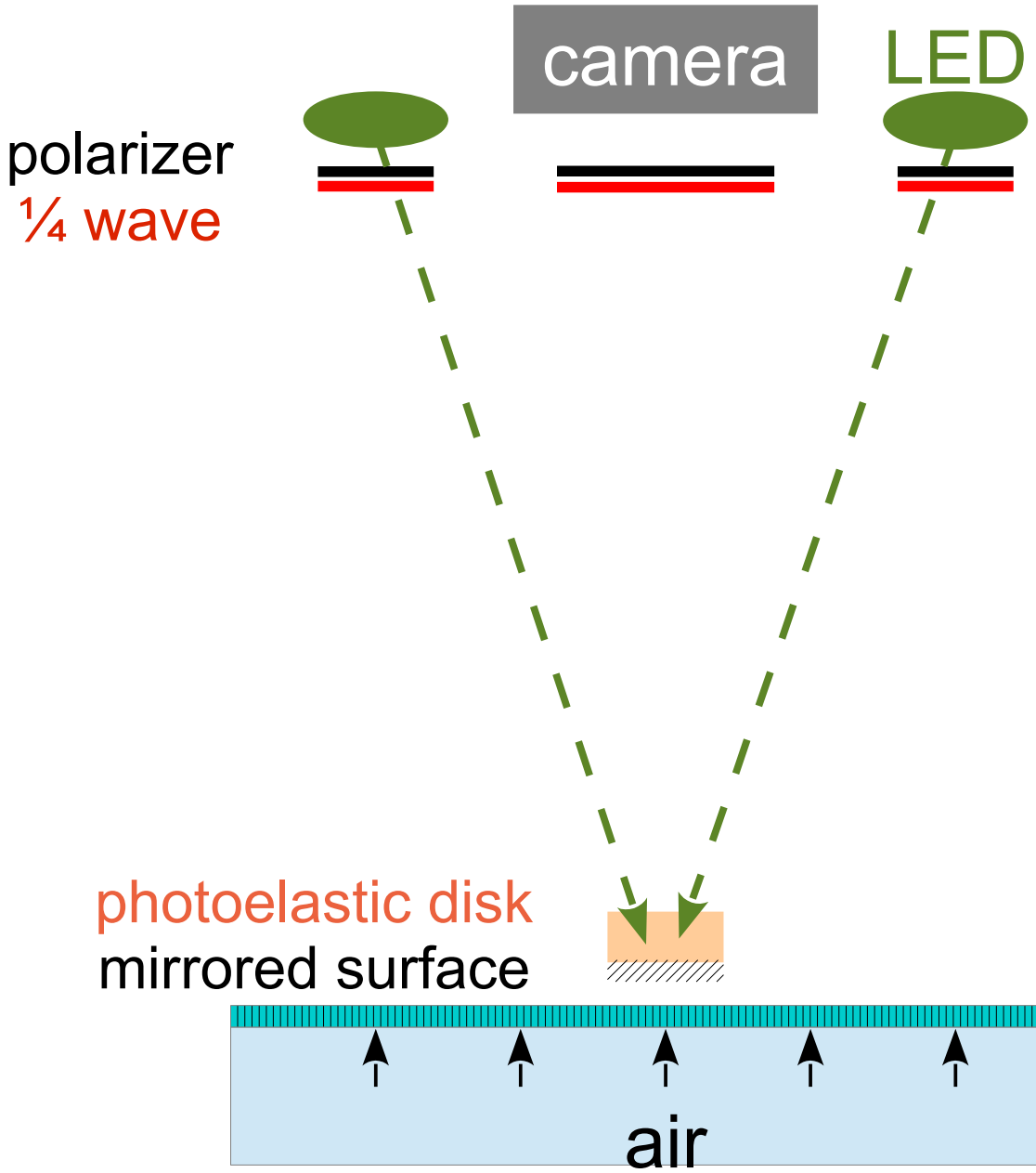
Does

~~$X_{bath} = X_{subsys}$~~

$\alpha_{bath} = \alpha_{subsys}$

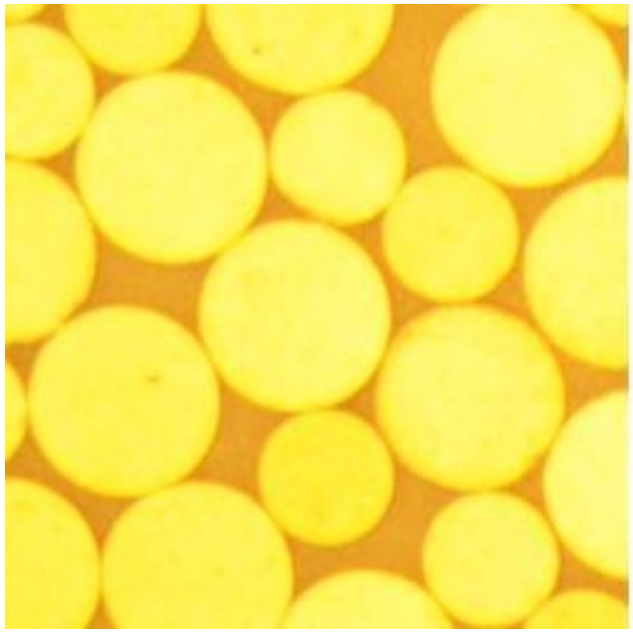
?

Puckett & Daniels. *PRL* (2013)



James Puckett

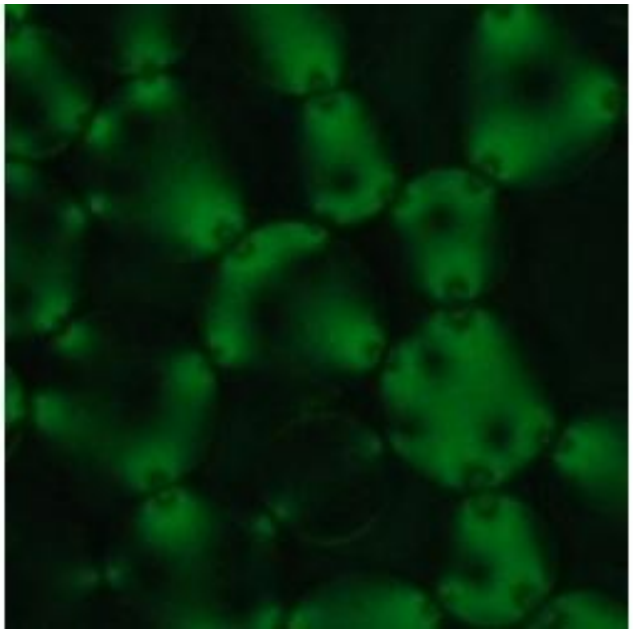
3 lighting schemes



white light

⇓

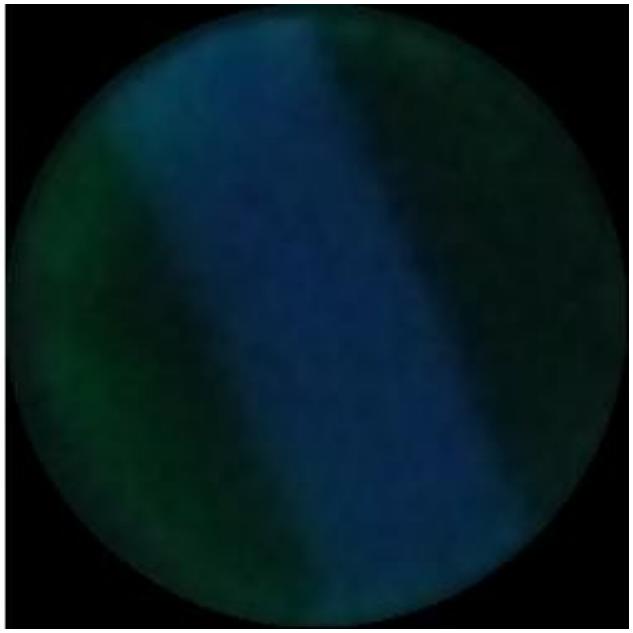
particle positions



polarized light

⇓

contact forces

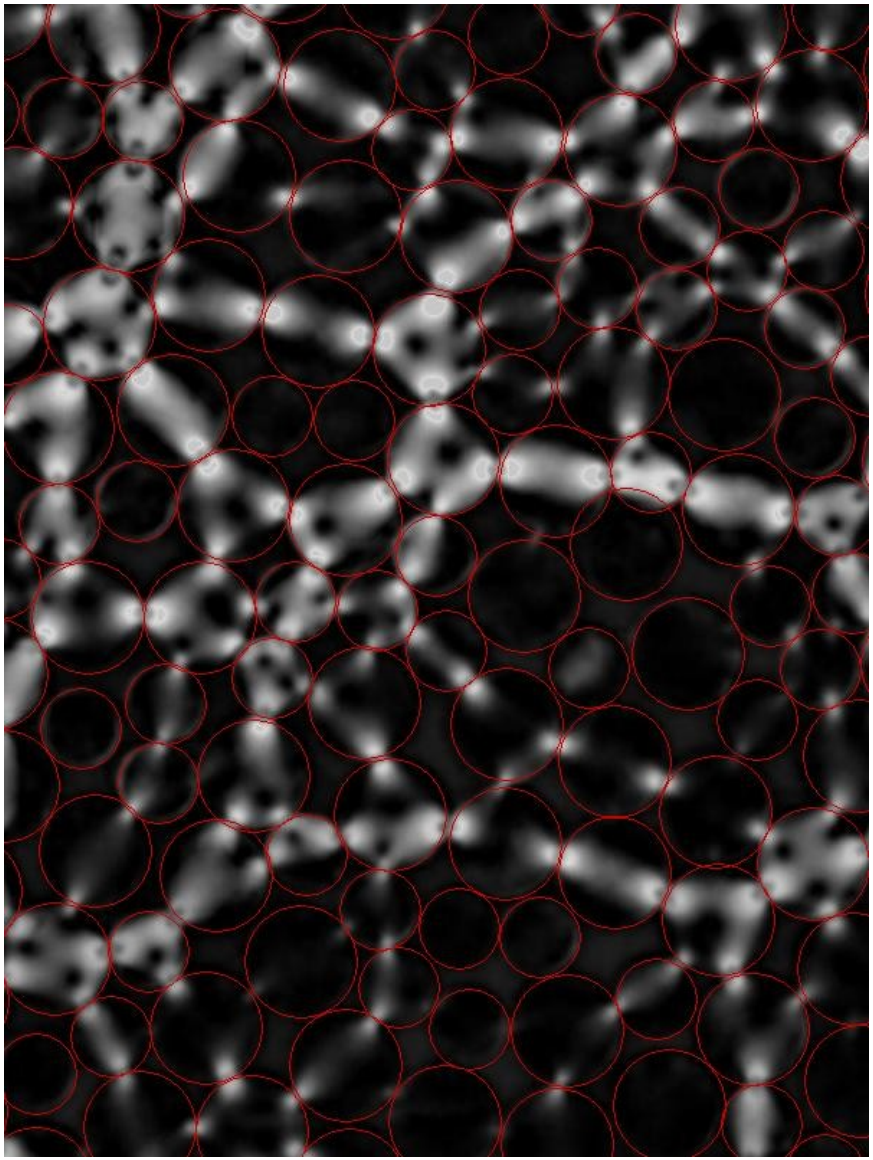


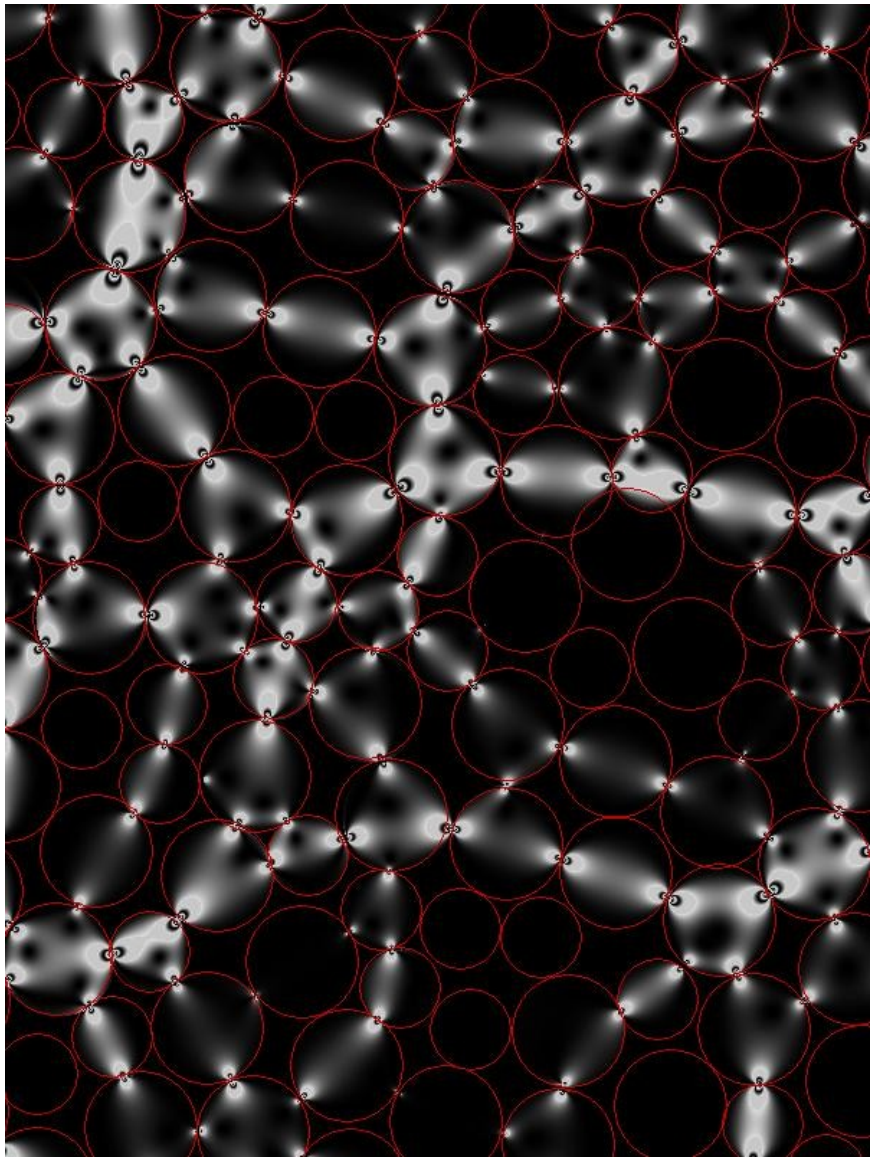
fluorescence

⇓

identify low-friction

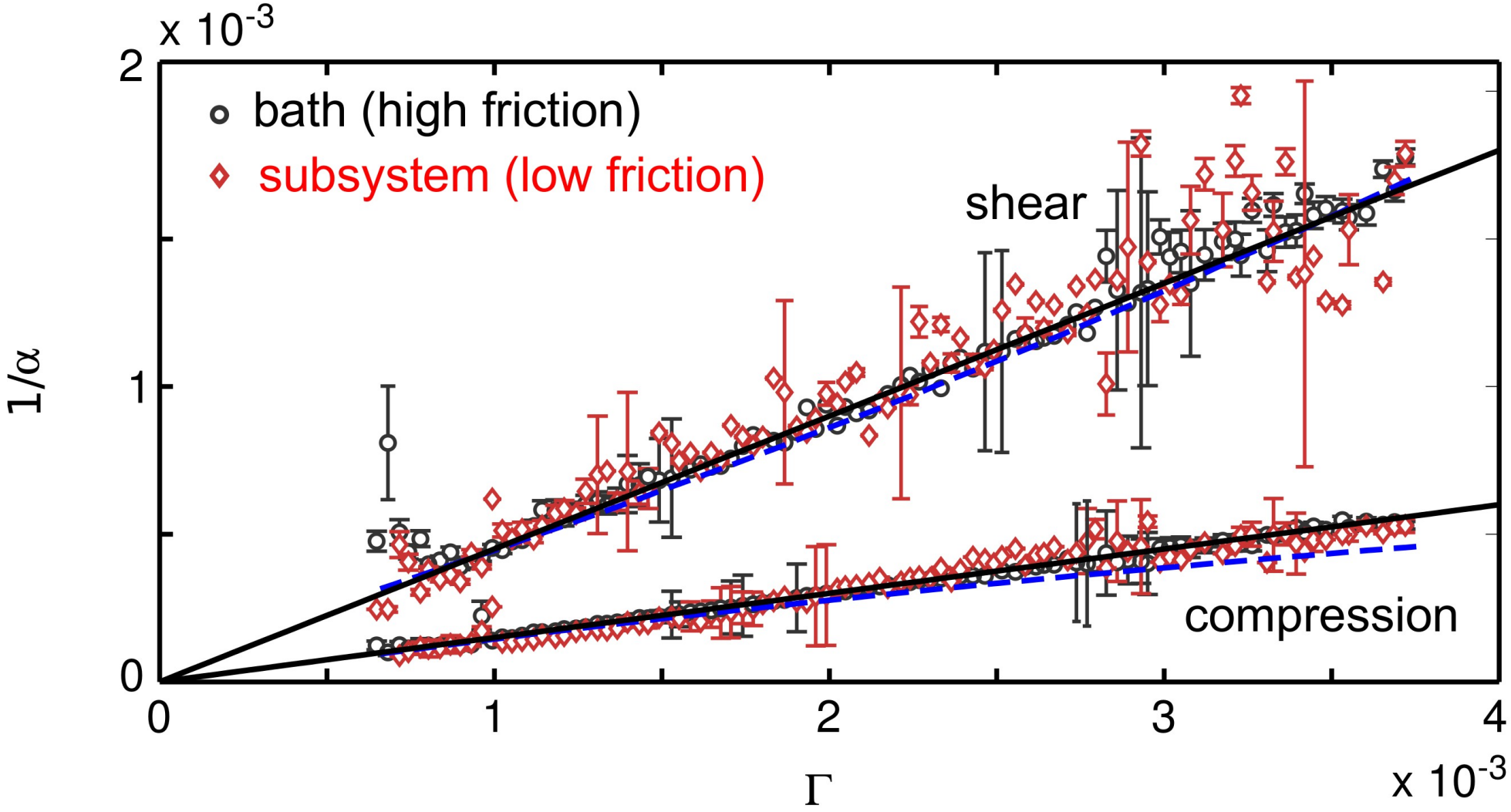
Measuring contact forces





http://nile.physics.ncsu.edu/pub/download/peDiscSolve/

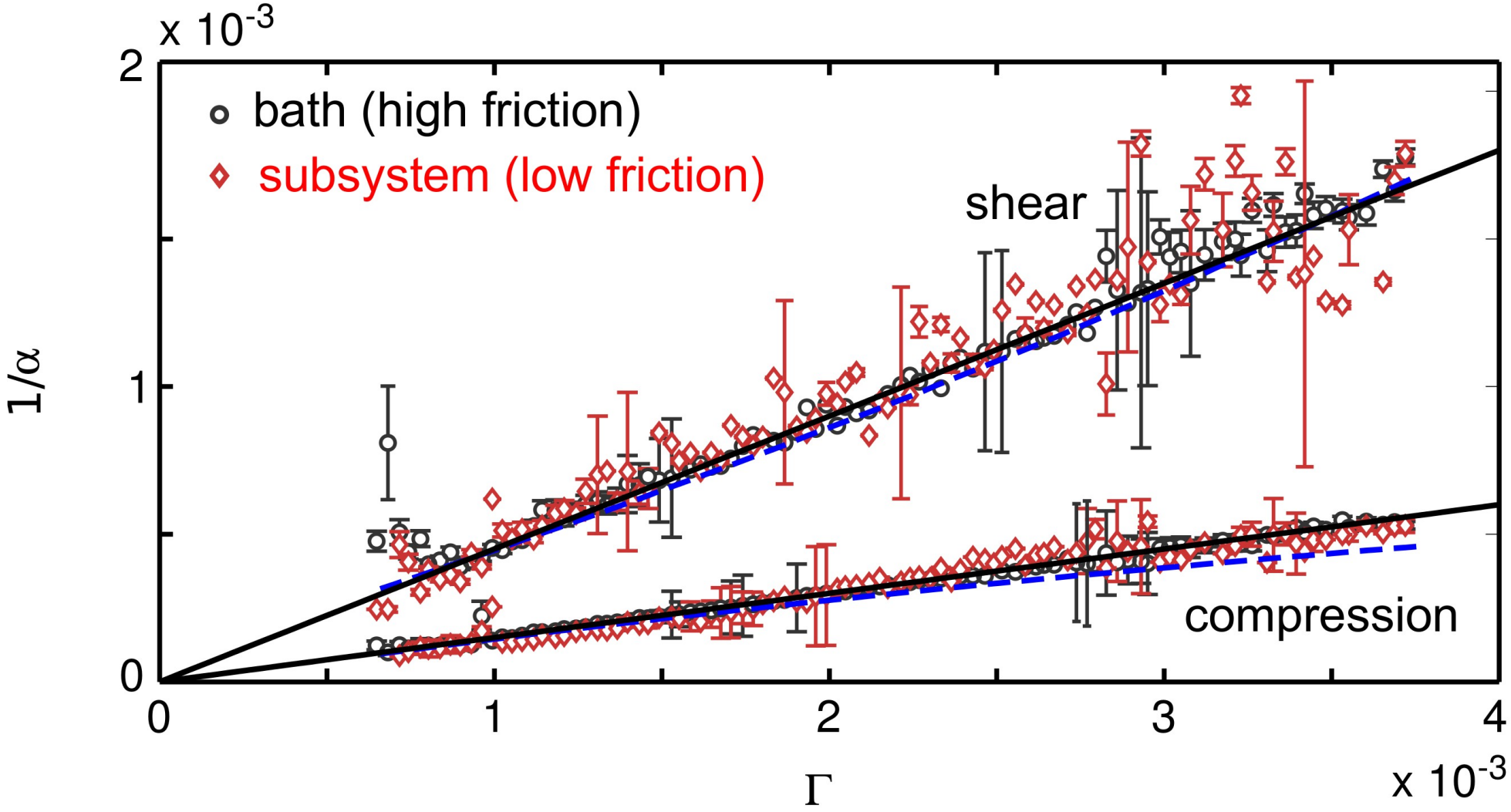
Angoricity Equilibrates!



$$\Gamma = Tr\,\hat{\Sigma}$$

Puckett & Daniels PRL 2013

"Specific Heat" vs. "Overlapping Histograms"



$$\frac{d\langle\Gamma\rangle}{d\alpha} = \frac{1}{\alpha^2}\langle d\Gamma^2\rangle$$

Puckett & Daniels PRL 2013

What's the Difference?

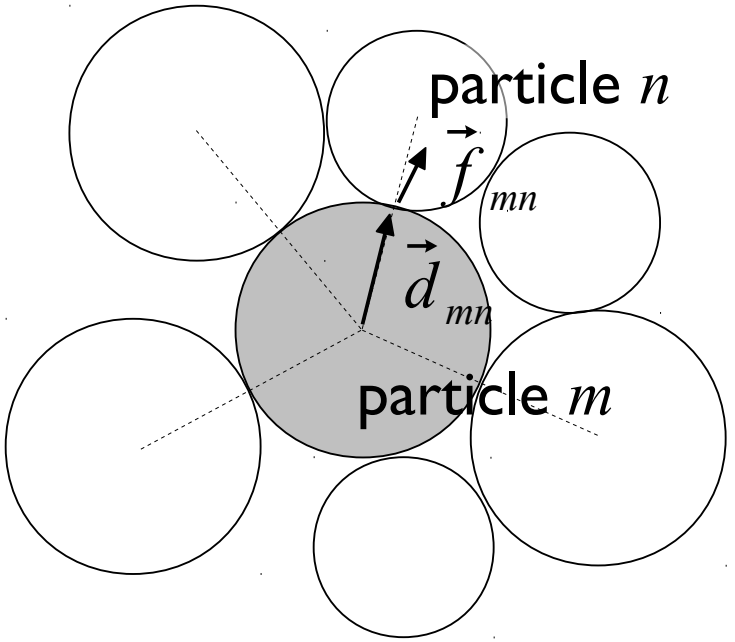
volume ensemble → compactivity X

- fails to equilibrate
- volume is only conserved globally

stress ensemble → angoricity α

- successfully equilibrates
- Newton's 3rd Law: forces and torques balance at each contact (local constraint)

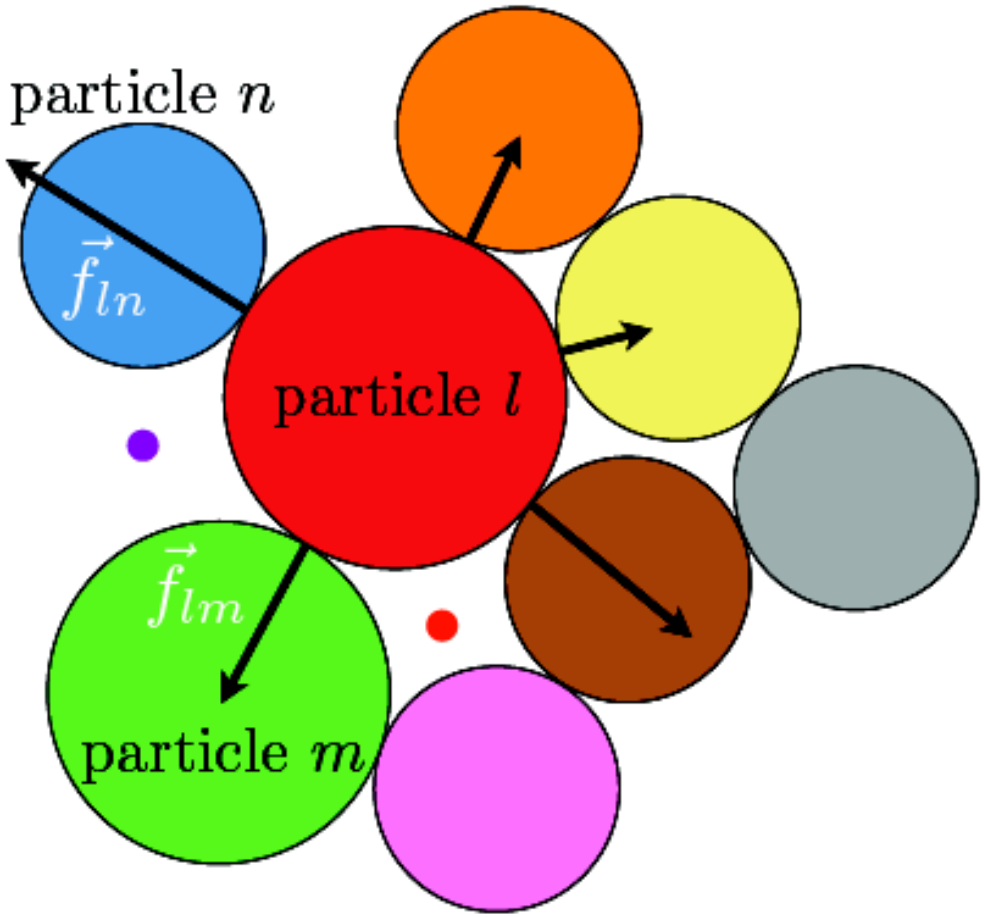
Formal Aspects of the Stress Ensemble



force moment tensor:

$$\hat{\Sigma} = \sum_{m,n} \vec{d}_{mn} \vec{f}_{mn}$$

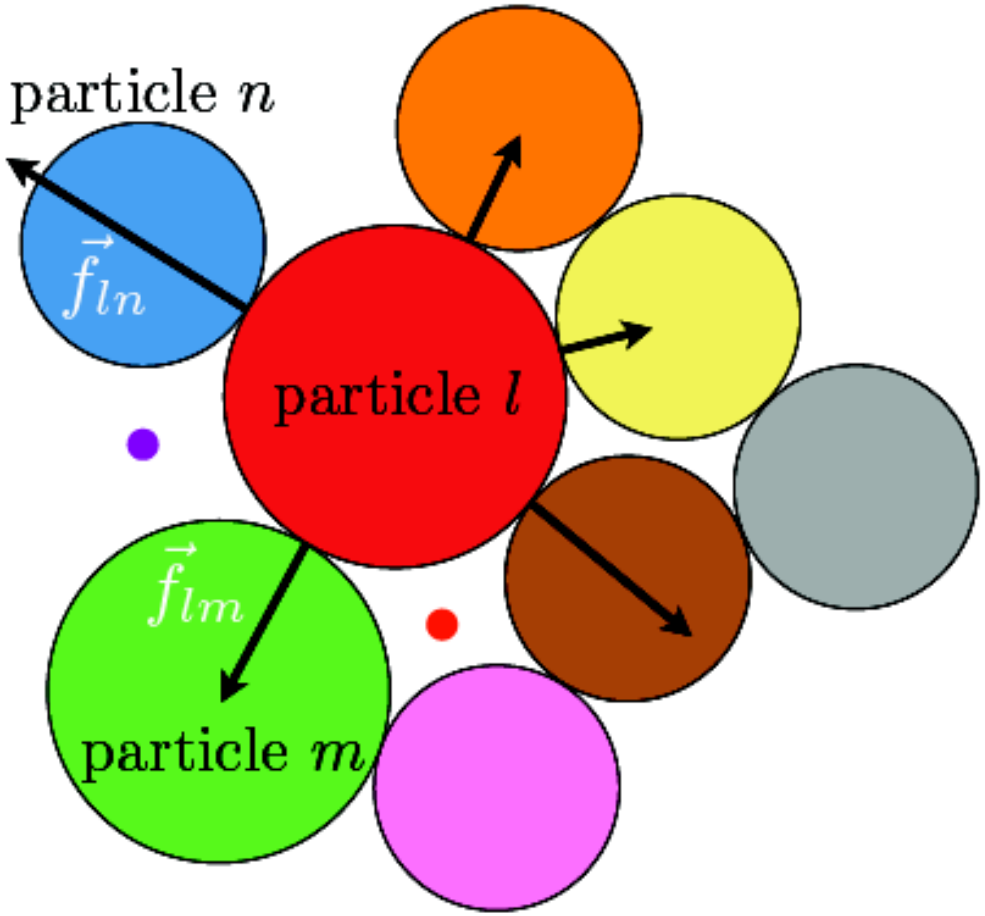
Constraints on Interparticle Forces

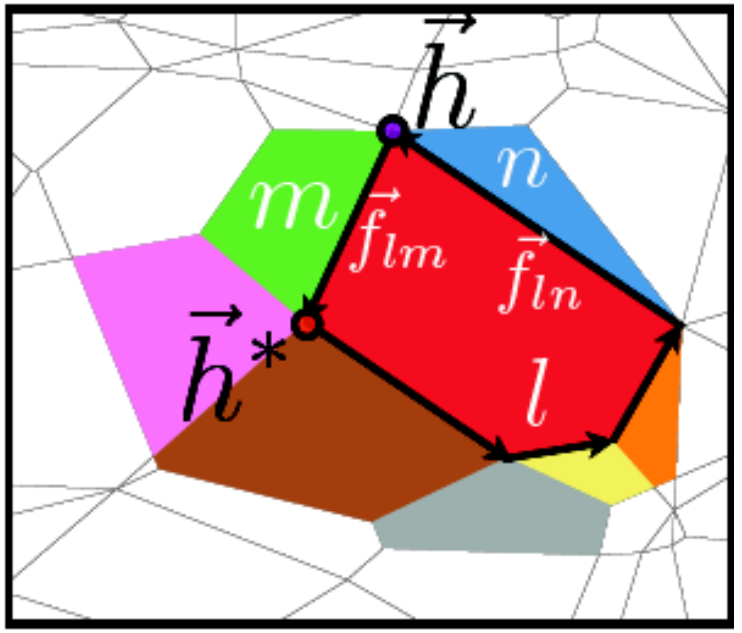


What do you know about the 5 black arrows?

Bi, Henkes, Daniels, Chakraborty. *Ann. Rev. Cond. Matt.* (2015). arXiv: 1404.1854

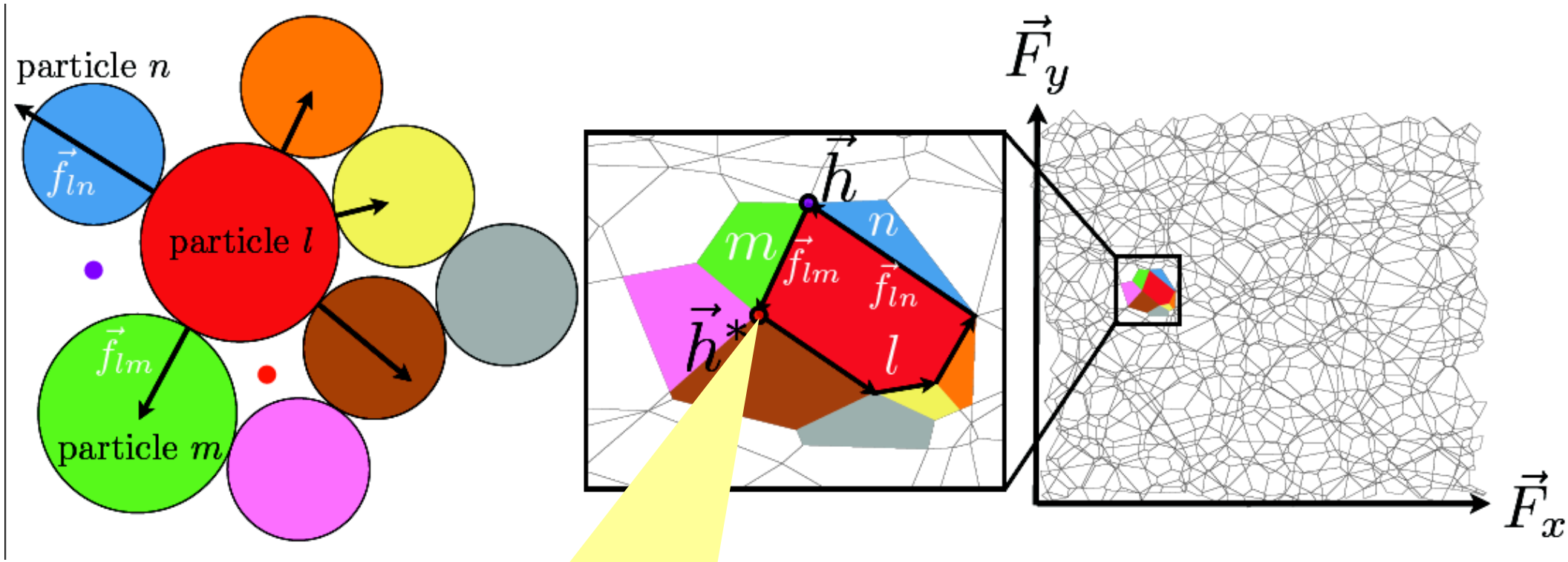
Force Balance → Tiles





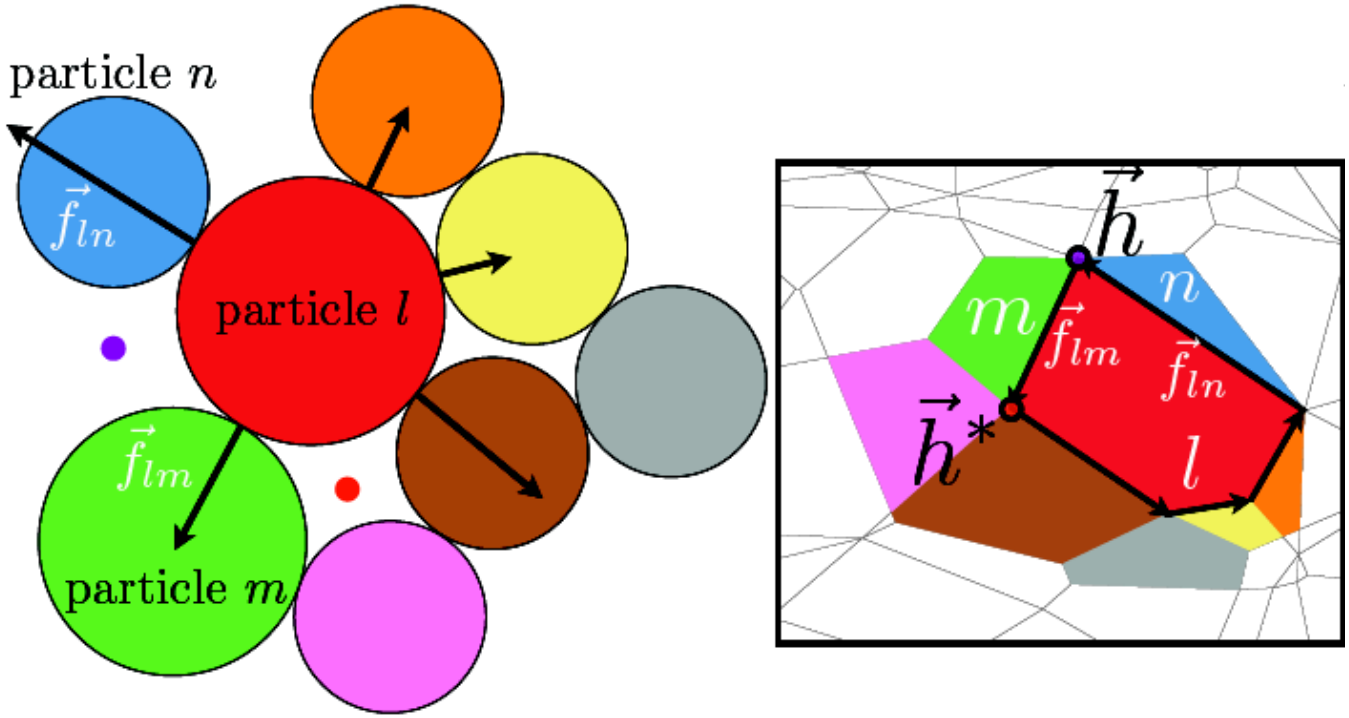
Bi, Henkes, Daniels, Chakraborty. *Ann. Rev. Cond. Matt.* (2015). arXiv: 1404.1854

Represent Whole Packing in Force Space



moving this point corresponds
to adjusting the contact forces
in a way that preserves force balance

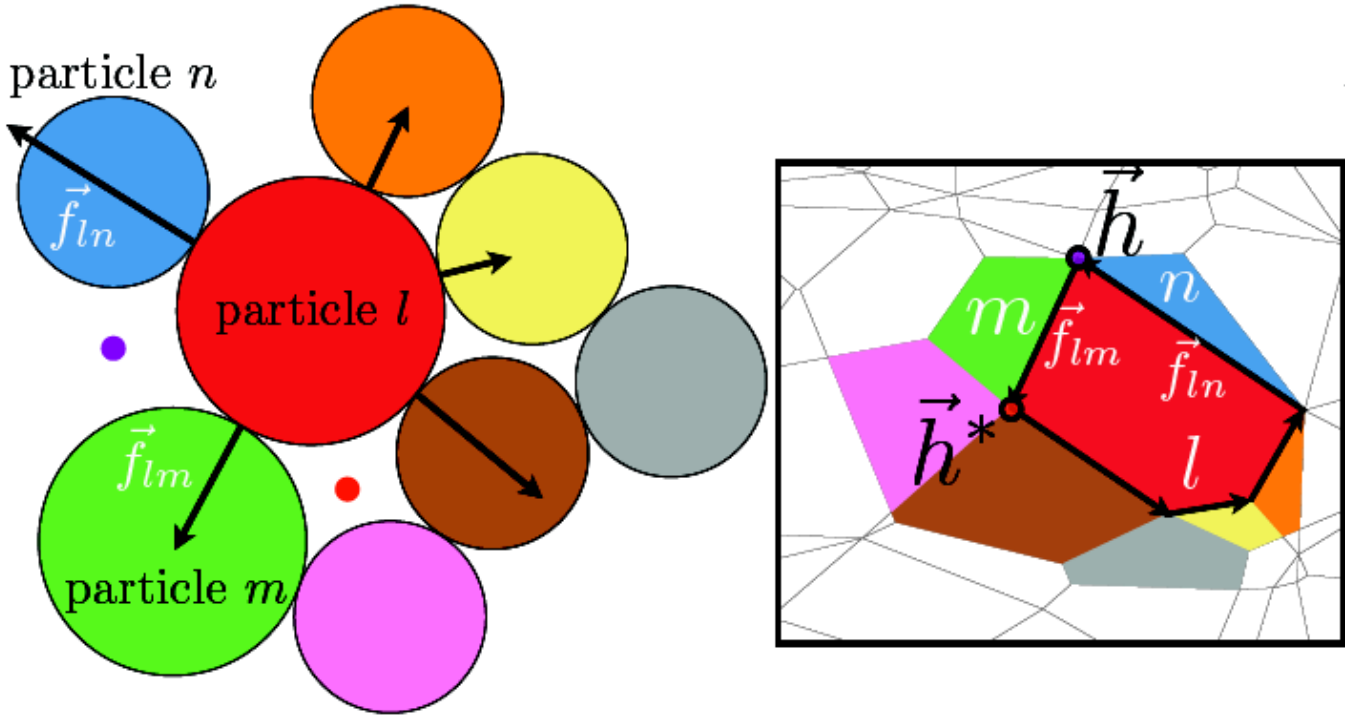
Forces → Field Theory



- define a vector gauge field $h(x, y)$ on the dual space of voids (●, ●)
- going counterclockwise around a grain, increment the height field by the contact force between the two voids: $\vec{h}^* = \vec{h} + \vec{f}_{lm}$

Ball & Blumenfeld *PRL* (2002) DeGiuli & McElwaine *PRE* (2011)
Henkes & Chakraborty *PRL* (2005) *PRE* (2009)

Relationship to Continuum Mechanics



- forces are locally balanced → $\hat{\Sigma} = V\,\hat{\sigma}$ is conserved
- Cauchy stress tensor can be calculated from the height field: $\hat{\sigma} = \vec{\nabla} \times \vec{h}$

Outstanding Questions ?

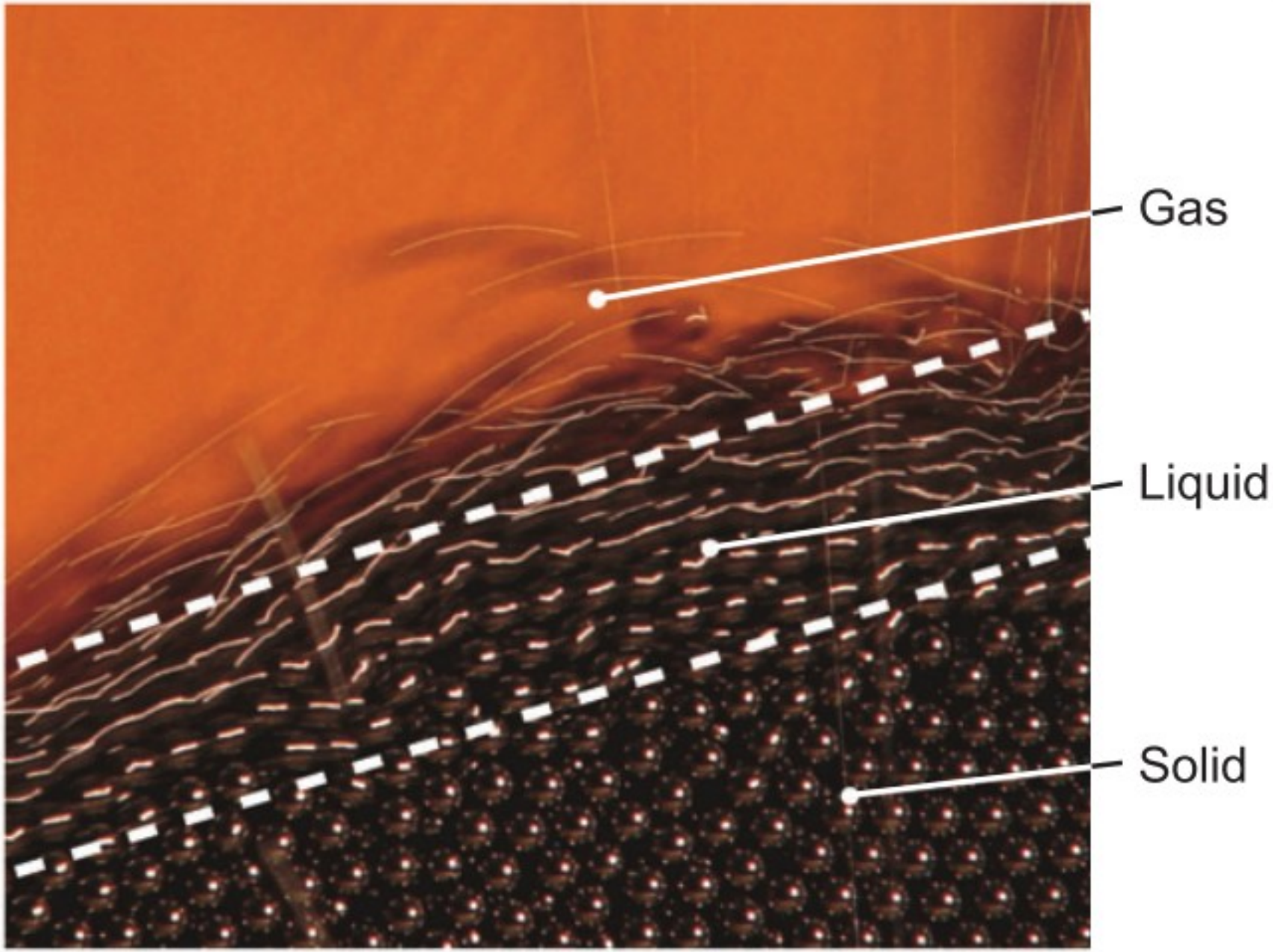
- relationship to other temperature-like variables
- the role of
  - friction
  - particle shape
  - shear vs. compression
- systems with dynamics
- segregation

What's "Temperature" in a Granular Material?

- kinetic theory $k_B T = \frac{1}{2} m \langle (v - \bar{v})^2 \rangle$
- entropy & energy $\frac{1}{T} = \frac{\partial S}{\partial E}$
- fluctuation-dissipation $C(t) = -k_B T \, R(t)$

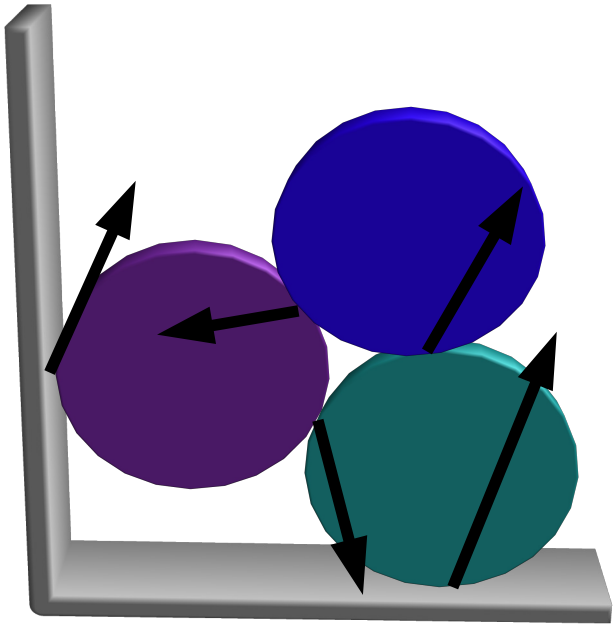
Do these "temperatures" measure the same thing?
Play a role in a useful equation of state?
Describe phase transitions?

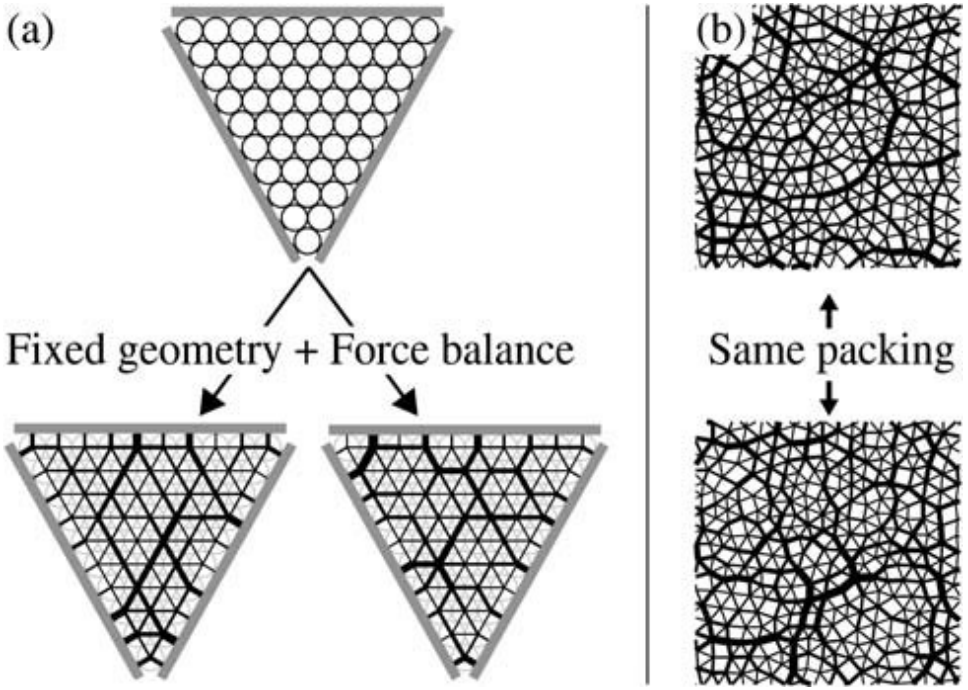
All 3 phases in coexistence



Forterre & Pouliquen *Ann. Rev. Fluid M*ech. (2008)

The Role of Friction

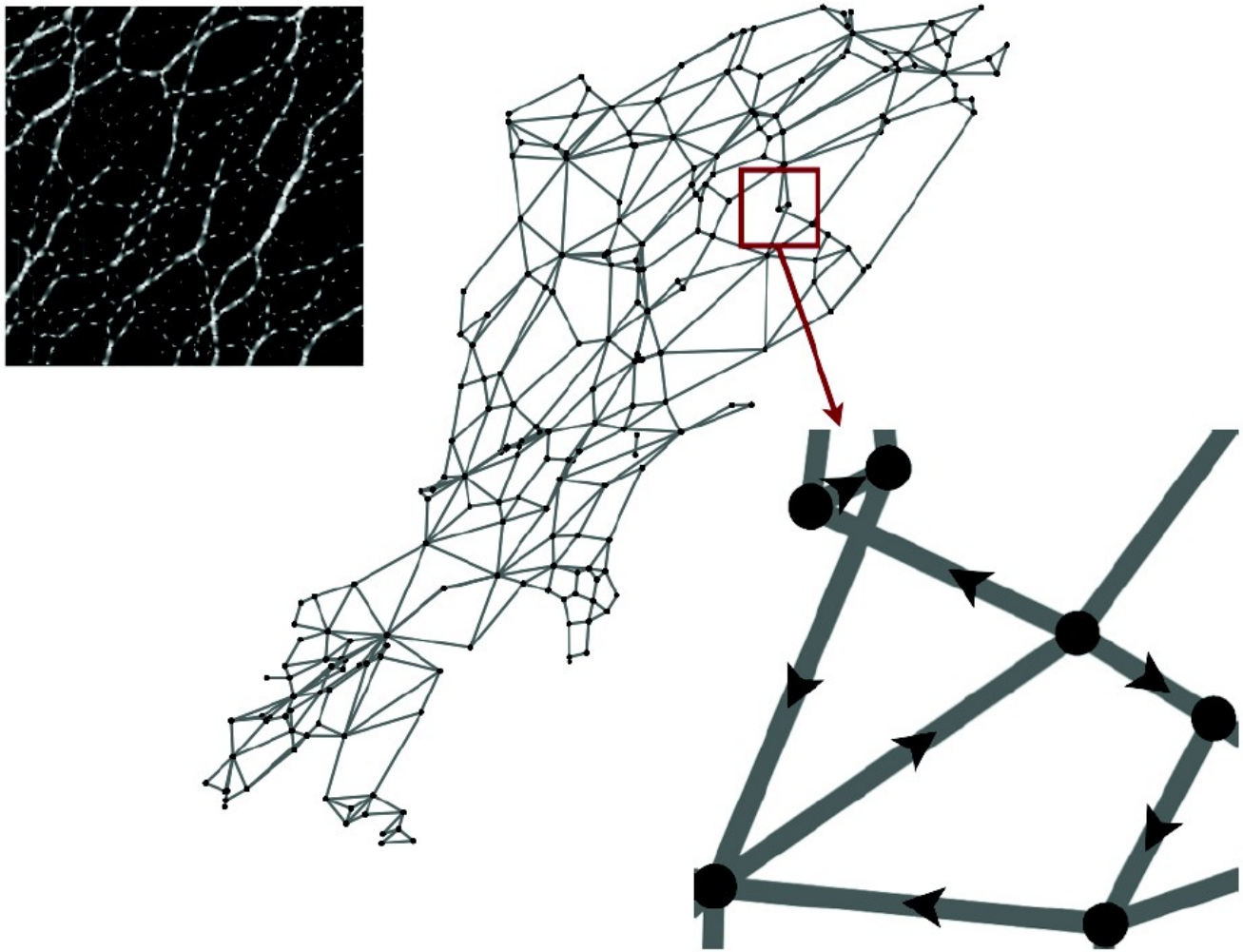




Tighe, Snoeijer, Vlugt, van Hecke.
Soft Matter (2010)

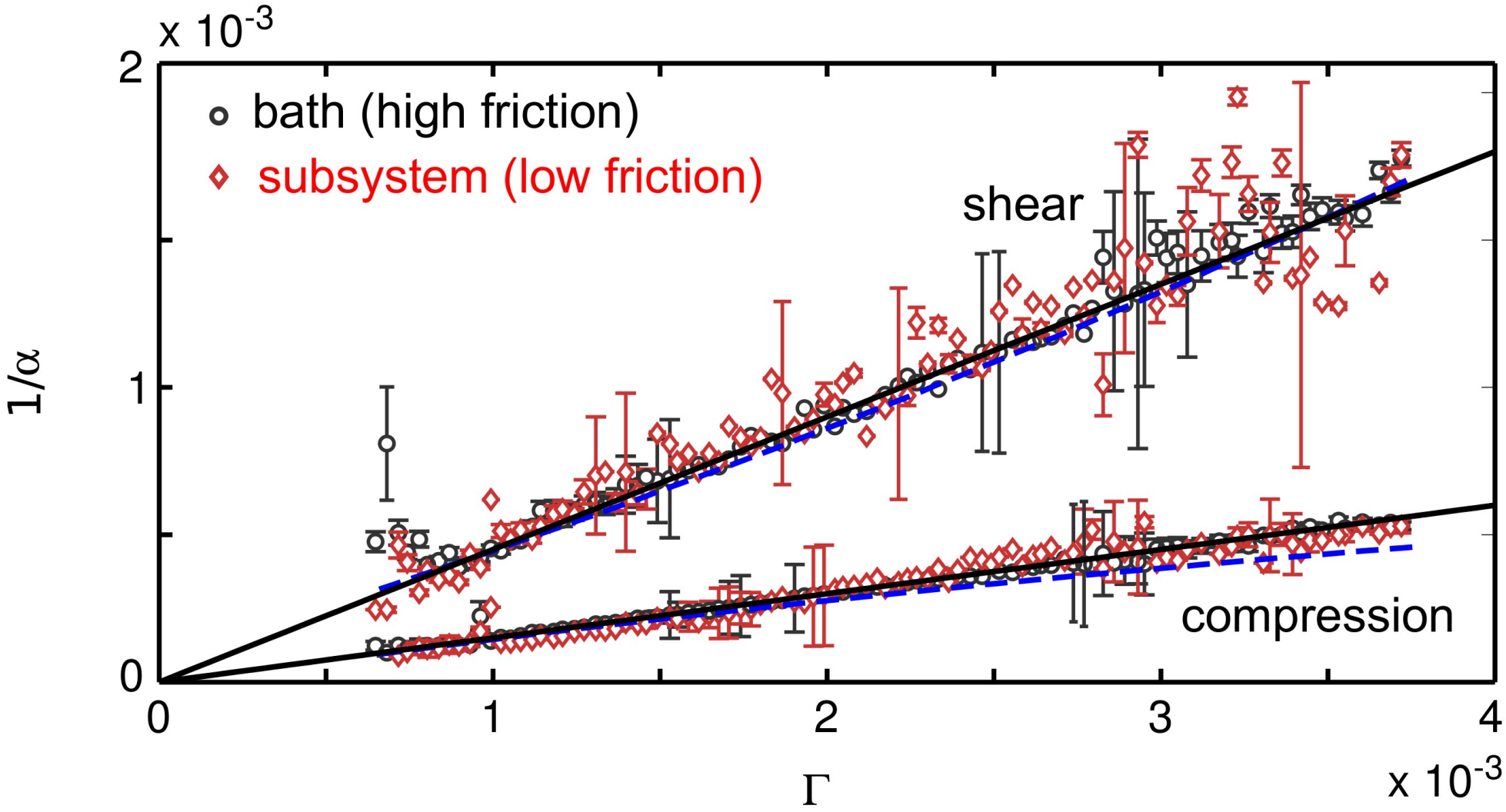
- count equations & constraints → # of degrees of freedom
- friction – provides history-dependence
  - changes the counting of valid states

Friction can cause non-convexity



Sarkar, Bi, Zhang, Behringer, Chakraborty. *PRL* (2013)
Bi, Henkes, Daniels, Chakraborty. *Ann. Rev. Cond. Matt.* (2015). arXiv: 1404.1854

Shear vs. Compression

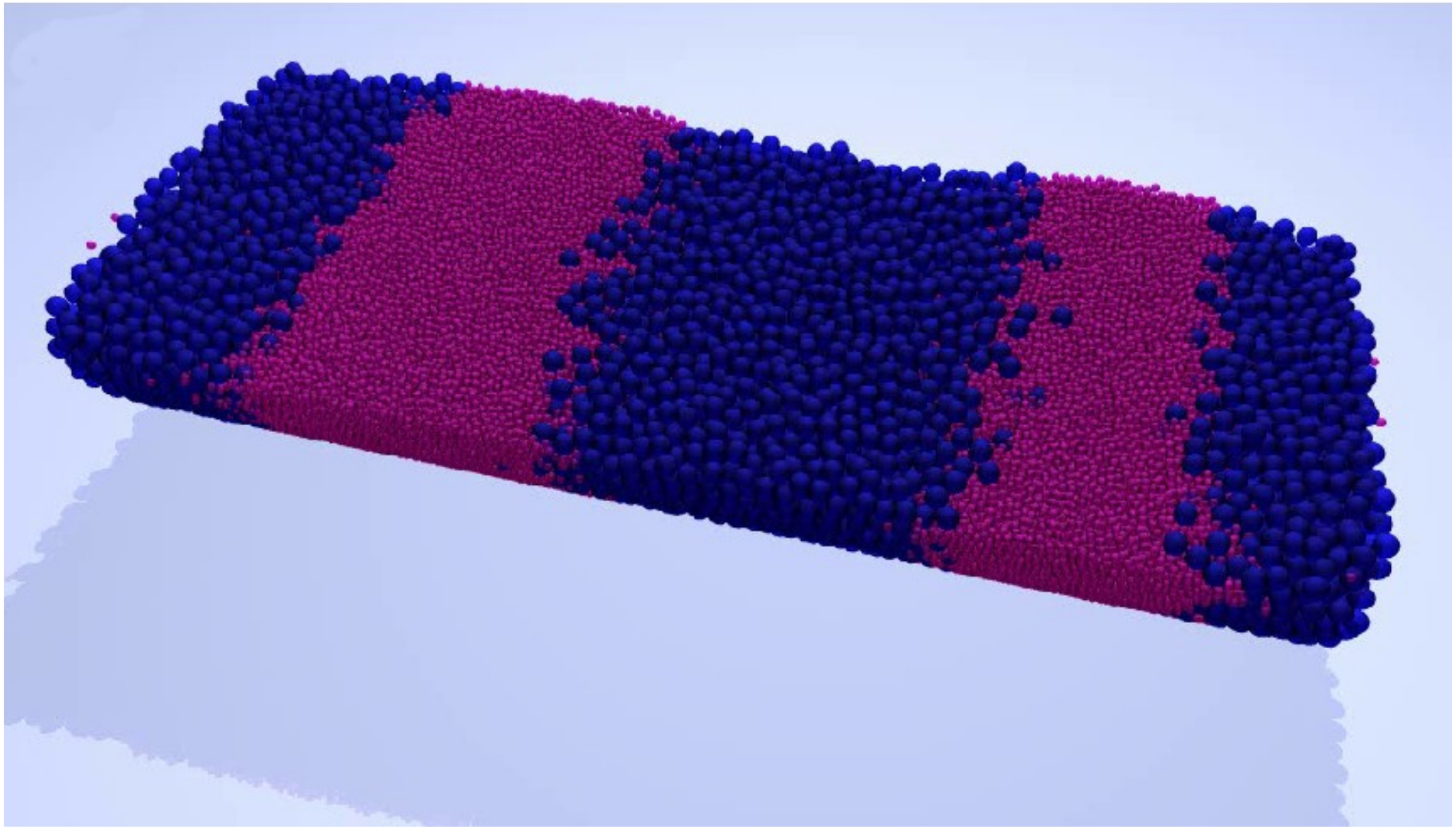


Forgotten Section: Segregation!

3. Mixtures of particles

As another example, at the simplest level, we consider a mixture of powders of type A and type B. Let us focus on the fact that when an A is next to an A there is a contribution to the volume which is different from an A next to a B and a B next to a B. Thus although the nature of coordination number matters as in the example above, we just concern ourselves with the nearest neighbour quality. This one aspect is enough to throw interesting light on the separation and miscibility of powders. Suppose the number of A type at r_i is m_A^i (=0 or 1), and similarly for B, so that

$$W = \sum_{\substack{i,j \\ \text{neighbours}}} m_A^i m_A^j v_{AA} + \cdots .$$

Edwards & Oakeshott. *Physica A* (1989)

Segregation ↔ Spinodal Decomposition?