Statistical Mechanics of Granular Solids and Dense Suspensions

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Outline

1. Statistical Ensembles
2. Jamming/Unjamming
3. Granular Materials
4. Stress Based Descriptions
5. Dense Suspensions

1. Statistical Ensembles
2. Jamming/Unjamming
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Statistical Ensembles

- The concept of **'ensembles'** plays a key role in equilibrium statistical mechanics.
- At observable timescales: **detailed balance** and **ergodicity**.
- This breaks down in several cases:
  - **Glass** forming liquids
  - Low temperature **frustrated magnets**
  - Systems composed of **macroscopic particulate matter**
  - Driven systems **out of equilibrium**
- The distinction between a liquid at thermal equilibrium and an athermal material is that in a liquid, atoms undergo **thermal motion**.

Athermal Ensembles

- In an athermal medium (in the absence of outside perturbations) the system is trapped in one of many **(very many)** local potential energy minima.
- Gibbsian statistical mechanics **cannot be used** to describe such a system.
- Athermal systems are **non-ergodic** in the extreme sense, as they stay in a single configuration unless driven externally
- In many cases exploration of configuration space is completely controlled by the **driving protocol**.

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Jamming of Hard Disks

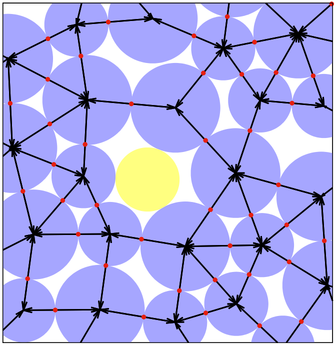
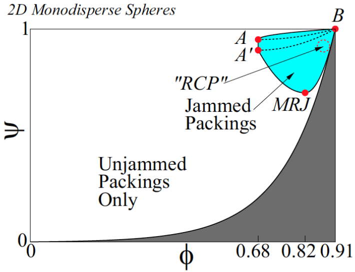


Figure: Jammed packing of hard disks along with the disordered contact network.

- System acquires **global rigidity** with external compression.
- Configurations are **inherently disordered** as the constituent particles arrange themselves into random spatial patterns.
- The jamming transition is a **critical phenomenon**, with typically irrational critical exponents.
- Occurs at a **well-defined density** ≈ 0.84 in $d = 2$ and ≈ 0.64 in $d = 3$.

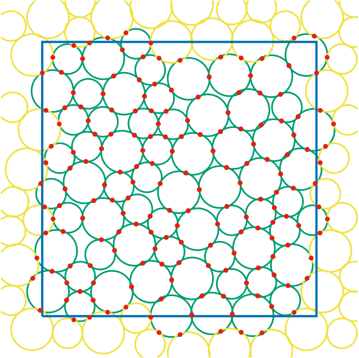
Configuration Space of Jammed Hard Disks



- Schematic order map in the densityorder $(\phi - \psi)$ plane for 2D strictly jammed, frictionless, monodisperse hard-disk packings in the infinite-system limit. The locus of points A-A' corresponds to the lowest-density jammed packings. The point B corresponds to the triangular lattice. The point MRJ represents the **maximally random jammed state**.

Source: S. Atkinson, F. H. Stillinger, S. Torquato, PNAS 111, 18436-18441 (2014).

Unjamming of Soft Disks



- Particles are allowed to overlap, based on an **energy function**.
- Collection of all **mechanically stable packings** define an ensemble. **K. Ramola**, B. Chakraborty, J. Stat. Mech. 114002 (2016).
- Critical exponents are **rational**. Can be understood from a mean-field analysis. **K. Ramola**, B. Chakraborty, Phys. Rev. Lett. 118, 138001 (2017).
- Stresses propagate through **localized channels**. **K. Ramola**, B. Chakraborty, J. Stat. Phys. 169, 1 (2017).

Global Variables approaching Unjamming

- **Pressure**: $P \to 0^+$,
- **Energy**: $E_G \to 0^+$,
- **Packing Fraction**: $\phi \to 0.84...$,
- **Coordination number**: $\Delta Z = (Z - Z_{\mathrm{iso}}) \to 0^+$,

$$Z_{\mathrm{iso}} = 2d \qquad \to \qquad \mathbf{4} \ \text{ for } \ d = 2.$$

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Granular Systems

Granular Ensembles

- Granular systems are made up of macroscopic particles and are inherrently **athermal**.
- What is the correct **statistical ensemble** for **static granular systems**?
- Edwards proposed that the collection of **all stable packings of a fixed number of particles in a fixed volume** might also play the role of an ‘ensemble’. Ref: S. F. Edwards, R. B. S. Oakeshott, Physica A 157, 180 (1991).
- A statistical-mechanics like formalism would result if one assumed that all such packings were **equally likely to be observed**, once the system had settled into a mechanically stable ‘jammed’ state.

Numerical Simulations: Energy Functions

- We use a **soft potential** around a **hard core**

$$U(r) = \begin{cases} \infty & r \leq r_{\mathrm{HS}}, \\ 4\epsilon\left[\left(\frac{\sigma(r_{\mathrm{HS}})}{r^2 - r_{\mathrm{HS}}^2}\right)^{12} - \left(\frac{\sigma(r_{\mathrm{HS}})}{r^2 - r_{\mathrm{HS}}^2}\right)^{6}\right] + \epsilon & r_{\mathrm{HS}} < r < r_{\mathrm{SS}}, \\ 0 & r \geq r_{\mathrm{SS}} \end{cases} \tag{1}$$

- For short distances $r \to r_{SS}$ this becomes a **soft linear spring repulsion** potential of the form:

$$U(r) = \begin{cases} c_0(r - r_{SS})^2 & r_{\mathrm{HS}} < r < r_{\mathrm{SS}}, \\ 0 & r \geq r_{\mathrm{SS}} \end{cases} \tag{2}$$

- We simulate **bidispersed** configurations (two different sizes of disks).

Jammed Packings: Energy Landscape

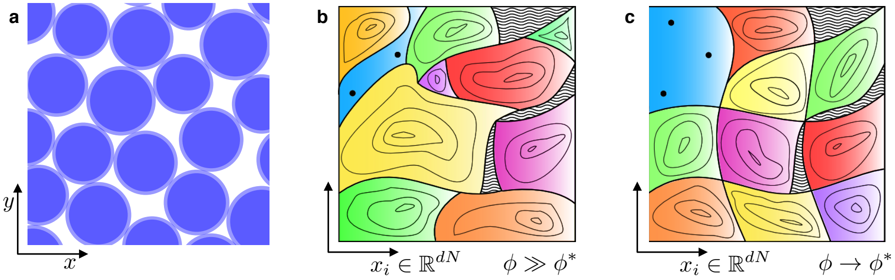

Figure: (a) Snapshot of a jammed packing of disks with a hard core (dark shaded regions) plus soft repulsive corona (light shaded regions). (b)-(c) Illustration of configurational space for jammed packings.

Testing the Edwards Conjecture

- **Direct test of the Edwards conjecture**, by numerically computing basin volumes of distinct jammed states (energy minima) of $N = 64$, frictionless disks held at a constant packing fraction ϕ.

  S. Martiniani, K. J. Schrenk, **K. Ramola**, B. Chakraborty and D. Frenkel, Nature Physics (2017).

- We computed Ω, **the number of distinct jammed states**, and the individual probabilities $p_{i\in\{1,\ldots,\Omega\}}$ of each observed packing to occur.

- The energy minimization procedure finds individual stable packings with a **probability** p_i **proportional to the volume** v_i of their basin of attraction.

- We computed v_i using a **stochastic sampling scheme**, and compute the average basin volume $\langle v\rangle(\phi)$.

Phase Space Volumes

- The **number of jammed states** is, explicitly,
$$\Omega(\phi) = V_J(\phi)/\langle v\rangle(\phi), \tag{3}$$
where $V_J(\phi)$ is the total available phase space volume at a given ϕ.
- A convenient way to check equiprobability is to **compare the Boltzmann entropy**
$$S_B = \ln\Omega - \ln N! \tag{4}$$
which counts all packings with the same weight, and
- The **Gibbs entropy**
$$S_G = -\sum_i^{\Omega} p_i \ln p_i - \ln N! \tag{5}$$
- The Gibbs entropy satisfies $S_G \leq S_B$, **saturating the bound** when all p_i are equal: $p_{i\in\{1,\ldots,\Omega\}} = 1/\Omega$.

Characterizing Basin Volume Distributions

- We analyse the statistics of v_i **along with the pressure** P_i of each packing.
- It is convenient to study $F_i \equiv -\ln v_i$ as a function of $\Lambda_i \equiv \ln P_i$.
- This yields a linear relationship Ref: S. Martiniani, K. J. Schrenk, J. D. Stevenson, D. J. Wales, D. Frenkel, Phys. Rev. E 93, 012906 (2016).

$$\begin{aligned} \langle f \rangle_{\mathcal{B}}(\phi;\Lambda) =& \lambda(\phi)\Lambda + c(\phi) \\ =& \lambda(\phi)\Delta\Lambda + \langle f \rangle_{\mathcal{B}}(\phi) \ , \end{aligned} \tag{6}$$

where $f = F/N$, and $\Delta\Lambda = \Lambda - \langle \Lambda \rangle_{\mathcal{B}}(\phi)$.

- The slope $\lambda(\phi)$ **characterizes the approach** to equiprobability.

Basin Volume Distributions

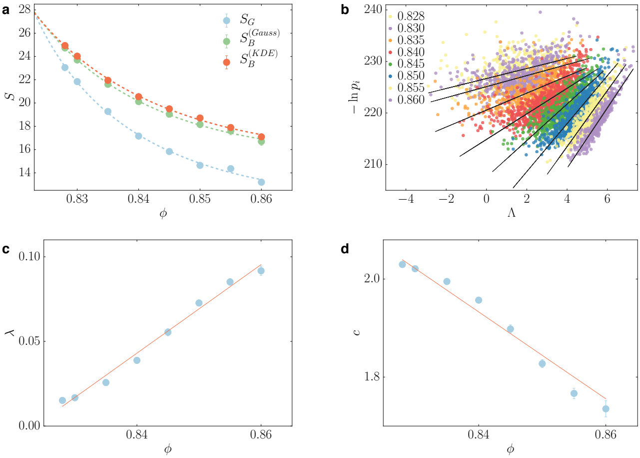

Figure: (a) Gibbs entropy S_G and Boltzmann entropy S_B. (b) Scatter plot of the negative log-probability of observing a packing, $-\ln p_i = F_i + \ln V_J(\phi)$.

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Frictional Materials

- Each packing needs to satisfy **force balance constraints**

$$\sum_c \vec{f}_{g,c} = 0,$$

where $\vec{f}_{g,c}$ represents the force acting on the grain g, through the contact c.

- The **torque balance constraint**

$$\sum_c \vec{r}_{g,c} \times \vec{f}_{g,c} = 0.$$

- Along with **Coulomb constraints**

$$|\vec{r}_{g,c} \times \vec{f}_{g,c}| \leq \mu_f |\vec{r}_{g,c} \ . \ \vec{f}_{g,c}|.$$

Solution Space of Forces

- The configuration space can be characterized by **convex regions**

  J. N. Nampoothiri, **K. Ramola**, B. Chakraborty, (in preparation).

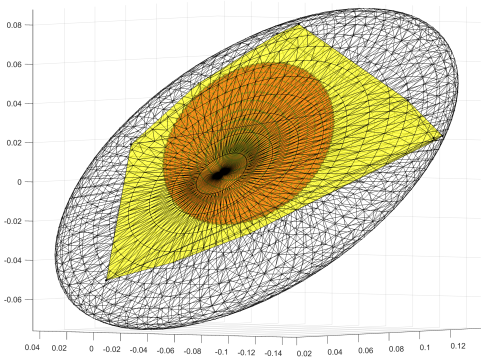

Figure: Solution space of force and torque balanced configurations of soft disks.

Statistical Mechanics for Stresses

- In the absence of an energy function, we can build a statistical mechanics **purely based on all allowed forces between particles**.

  Edwards, S. F. *Granular matter: an interdisciplinary approach* (1994).

- Introduce a volume function $\mathcal{W}(\{\mathbf{r}_i, \hat{\mathbf{t}}_i\})$, as a function of the N particles' positions $\{\mathbf{r}_i\}$ and orientations $\{\hat{\mathbf{t}}_i\}$, as a **replacement for the Hamiltonian** in equilibrium ensembles.

- The granular entropy $S(V)$ is

$$S(V) = \lambda \log \Omega(V), \tag{7}$$

$$\Omega(V) = \int \mathrm{d}\mathbf{q}\, \delta(V - \mathcal{W}(\mathbf{q}))\Theta_{\mathrm{jam}}. \tag{8}$$

- where $\mathbf{q} = \{\mathbf{r}_i, \hat{\mathbf{t}}_i\}$ and $\int \mathrm{d}\mathbf{q} = \prod_{i=1}^{N} \int \mathrm{d}\mathbf{r}_i \oint \mathrm{d}\hat{\mathbf{t}}_i$.

Statistical Mechanics for Stresses (continued)

$$
\begin{aligned}
\Theta_{\mathrm{jam}} = & \prod_{i,j=1}^{N} \theta\Big(|\mathbf{r}_i - \mathbf{r}_j| - 2R\Big) && \text{hard} - \text{core (spherical)} \\
& \times \prod_{i=1}^{N} \delta\left(\sum_{a \in \partial i} \mathbf{f}_a^i\right) && \text{force balance} \\
& \times \prod_{i=1}^{N} \delta\left(\sum_{a \in \partial i} \mathbf{r}_a^i \times \mathbf{f}_a^i\right) && \text{torque balance} \\
& \times \prod_{i=1}^{N} \prod_{a \in \partial i} \theta\left(\mu f_{a,n}^i - |\mathbf{f}_{a,\tau}^i|\right) && \text{Coulomb friction} \\
& \times \prod_{i=1}^{N} \prod_{a \in \partial i} \theta\left(-\mathbf{r}_a^i \cdot \mathbf{f}_a^i\right) && \text{repulsive forces} \\
& \times \prod_{\text{all contacts } a} \delta(\mathbf{f}_a^i + \mathbf{f}_a^j) && \text{Newton } 3^{\text{rd}} \text{ law} \; .
\end{aligned} \tag{9}
$$

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Discontinuous Shear Thickening

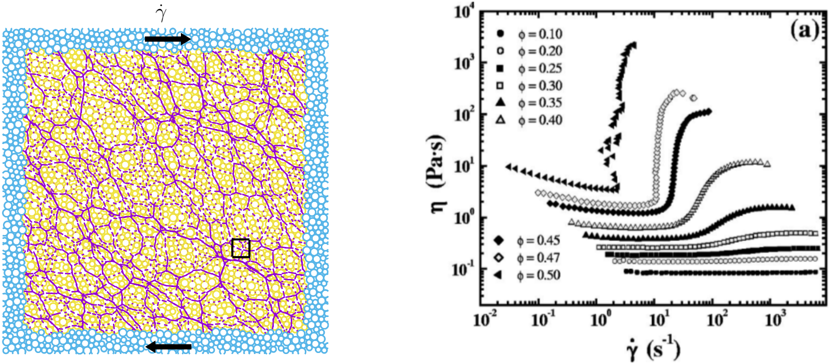
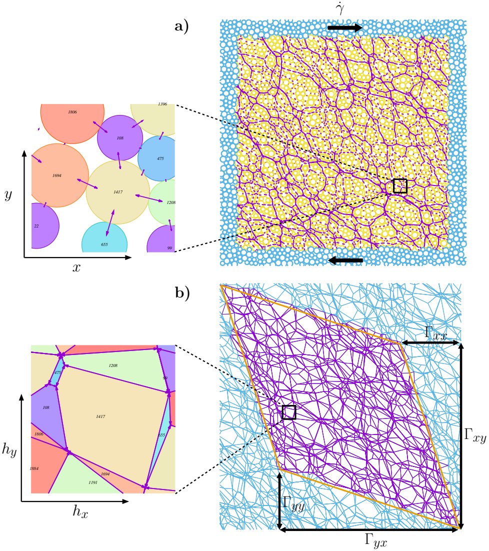


Figure: **(Left)** A snapshot of a suspension of 2000 soft frictional disks sheared at a variable rate $\dot{\gamma}$, with the shear stress $\sigma \equiv \sigma_{xy}$ held fixed. **(Right)** Viscosity vs Shear rate for 500nm calcium carbonate + polymer brush in PEG 200 R. G. Egres and Norman J. Wagner Journal of Rheology 49, 719 (2005).

Height Space Representation



Macroscopic Stress Tensor

- In the continuum, the local stress tensor is $\hat{\sigma} = \nabla \times \vec{h}$:

$$\hat{\sigma} = \begin{pmatrix} \partial_y h_x & \partial_y h_y \\ -\partial_x h_x & -\partial_x h_y \end{pmatrix}; \quad \hat{\Sigma} = \begin{pmatrix} L_y \Gamma_{yx} & L_y \Gamma_{yy} \\ -L_x \Gamma_{xx} & -L_x \Gamma_{xy} \end{pmatrix}, \tag{10}$$

  where $\hat{\Sigma}$ is the virial or the **global force moment tensor**.
- The **shear stress is held fixed** with

$$\Gamma_{\mathrm{yy}} = -\Gamma_{\mathrm{xx}} = \sigma \tag{11}$$

- The **pressure** and the **normal stress** are

$$P = \lambda_+ + \lambda_- = \Gamma_{\mathrm{yx}} - \Gamma_{\mathrm{xy}}; \quad N_1 = \Sigma_{xx} - \Sigma_{yy} = \Gamma_{\mathrm{yx}} + \Gamma_{\mathrm{xy}}. \tag{12}$$

- The **stress anisotropy** μ is

$$\mu = \frac{\tau}{P} = \frac{\sqrt{(N_1)^2 + 4\sigma^2}}{P} \approx \frac{\sigma}{P}. \tag{13}$$

Constitutive Laws: $\mu(I)$ Rheology

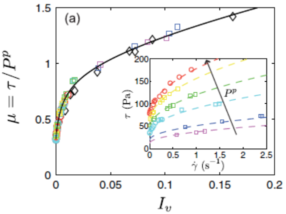


Figure: Observed $\mu = \tau/P$ from several experiments of dense suspensions. F. Boyer, E. Guazzelli, and O. Pouliquen, Physical Review Letters 107, 188301 (2011).

- μ depends on the viscous number $I_v \equiv \frac{\eta\dot{\gamma}}{P}$
- I_v depends on the packing fraction ϕ: $I_v(\phi) \propto (\phi_J - \phi)^2$.
- In the limit of small I_v is: $\mu - \mu_c \simeq I_v^{1/2}$, ($\mu_c$ depends weakly on the properties of the grains J. Dong and M. Trulsson, Physical Review Fluids 2, 081301 (2017).).

Observed Stress Anisotropy

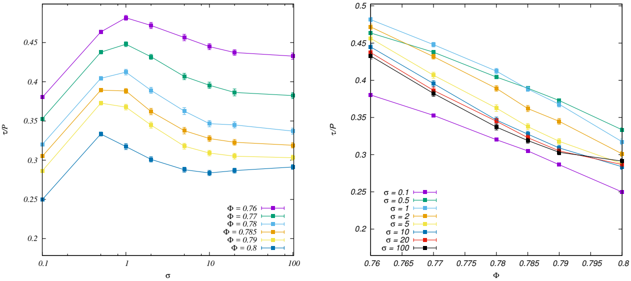


Figure: Observed $\mu = \tau/P$ from simulations of suspensions J. E. Thomas, **K. Ramola**, A. Singh, R. Mari, J. Morris, B. Chakraborty, (in preparation).

Observed Pair Correlations

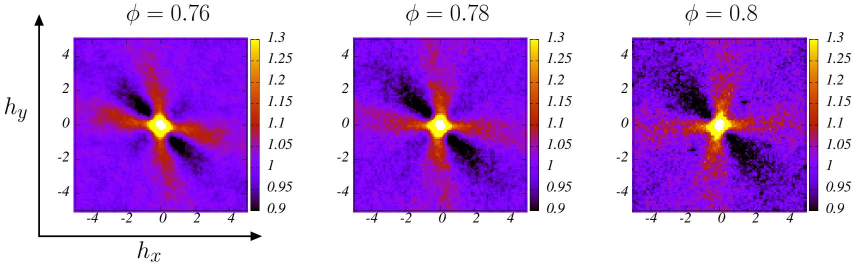


Figure: Observed pair correlation functions at $\sigma_{xy} = 2$, at packing fractions $\phi = 0.76, 0.78$ and 0.8. The forces (and consequently the heights) have been scaled by the imposed shear stress σ. The change in symmetry of $g_2(\vec{h})$ is clearly visible as the packing fraction is increased.

Constructing a Thermal Ensemble

- Using the pair correlations we can construct a **potential**

$$V_2(\vec{h}) = -\log\left(\frac{g_2(\vec{h})}{g_2(|\vec{h}|)}\right), \tag{14}$$

that induces an **anisotropy in the interactions** based on the observed correlation functions.

- The ensemble of configurations that are sampled in the non-equilibrium dynamics are assumed to obey a **statistical mechanical description**, with each configuration $\mathcal{C}$ occurring with a **probability** $p(\mathcal{C}) \propto \exp(-V(\mathcal{C}))$. J. E. Thomas, **K. Ramola**, A. Singh, R. Mari, J. Morris, B. Chakraborty, (in preparation).

Statistical Mechanics

- Shear stress sets the **pressure scale** (and Area): we control this by a **Lagrange multiplier** $f_p^*(\sigma)$.

- The **partition function** of the system is given by

$$Z_{\phi,\sigma} = \frac{1}{N_v!}\int_0^\infty dA \exp\left(-N_v f_p^* A\right) \times \underbrace{\int_A \prod_{i=1}^{N_v} d\vec{h}_i \exp\left(-\sum_{i,j} V_{\phi,\sigma}(\vec{h}_i - \vec{h}_j)\right)}_{A^{N_v}\exp(-\epsilon_{\phi,\sigma}(A,N_v))},$$
$$= \int_0^\infty dA \exp(-\mathcal{F}_{A;\phi,\sigma}). \quad (15)$$

where the positions $\vec{h}_i$ are confined to be within the box defined by $A \equiv (\vec{\Gamma}_x, \vec{\Gamma}_y)$.

Testing the Potentials

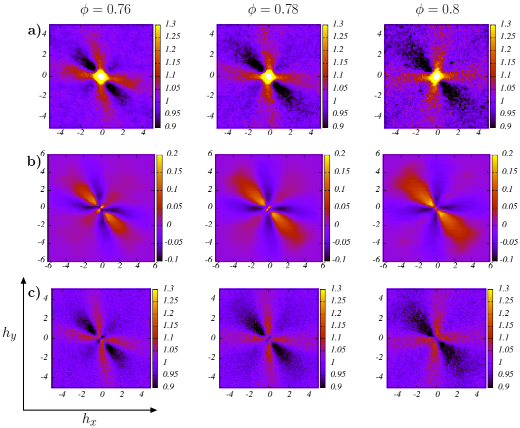


Figure: **a)** Observed pair correlation functions at $\sigma_{xy} = 2$, at packing fractions $\phi = 0.76, 0.78$ and 0.8. **b)** Potentials constructed using these pair correlation functions. **c)** A comparison with pair correlations obtained from direct Monte Carlo simulations of particles interacting via these potentials.

Sampling the Energy Function

- We perform a **Monte Carlo sampling** of the energy function

$$A^{N_v} \exp(-\mathcal{F}_{A;\phi,\sigma}) = \int_A \prod_{i=1}^{N} d\vec{h}_i \exp\left(-\sum_{i,j} V_2^{\phi}(\vec{h}_i - \vec{h}_j)\right) ; \quad A = \sigma^2 \left(\frac{1}{\mu^2} - 1\right) . (16)$$

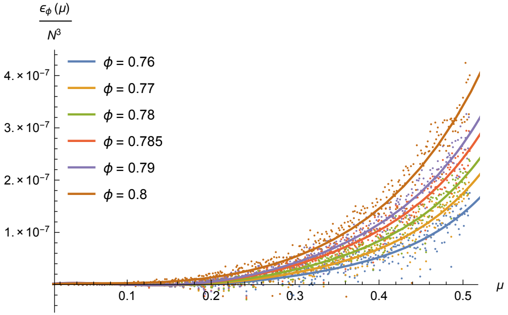


Figure: Sampled Energy Function for N = 512.

Free Energy Function

- The **free energy** of the system is then given by

$$\mathcal{F}_{\sigma,\phi} = -\log Z_{\sigma,\phi}. \tag{17}$$

- The free energy per particle is given by

$$f(\mu) = f_p^*(\sigma)\sigma^2\left(\frac{1}{\mu^2} - 1\right) - \log\left[\sigma^2\left(\frac{1}{\mu^2} - 1\right)\right] + \epsilon_\phi(\mu)/N. \tag{18}$$

Free Energy Function

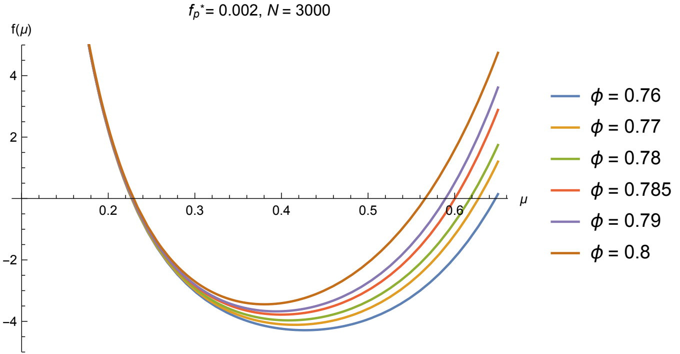


Figure: Free Energy per particle, $N = 3000$, $f_p^* = 0.002$.

Rheology from μ

- We can use μ to predict the **viscosity**

$$\eta = \frac{\mu}{(\mu - \mu_c)^2}. \tag{19}$$

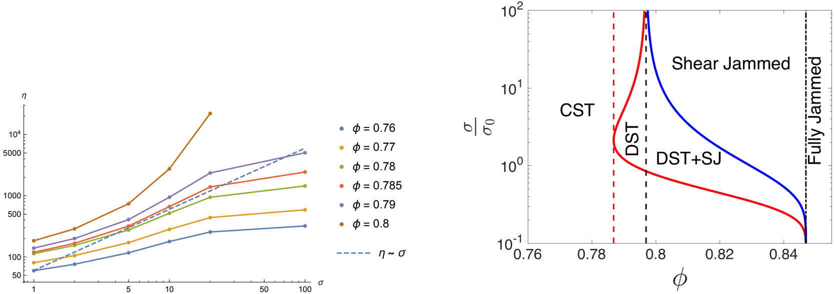


Figure: **(Left)** Predicted viscosity at different packing fractions ϕ. With $\mu_c \approx 0.385$. **(Right)** Phase diagram in the shear stress–packing fraction (σ, ϕ) plane.

Outlook

- It would be interesting to explore the analogies and differences between jamming in various **systems for which the configuration space can break up into many distinct basins**.
- Developing a **microscopic theory** for Discontinuous Shear Thickening that takes into account **both real space constraints and forces** remains an outstanding problem.
- **Constructing an Edwards-like approach for other athermal** and non-equilibrium systems where a large number of microscopic constraints 'randomize' the system is an interesting direction for future research.

Thank You.