(Unifying?) rheology of soft glasses and jammed solids

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Coworkers

- On-going work with:

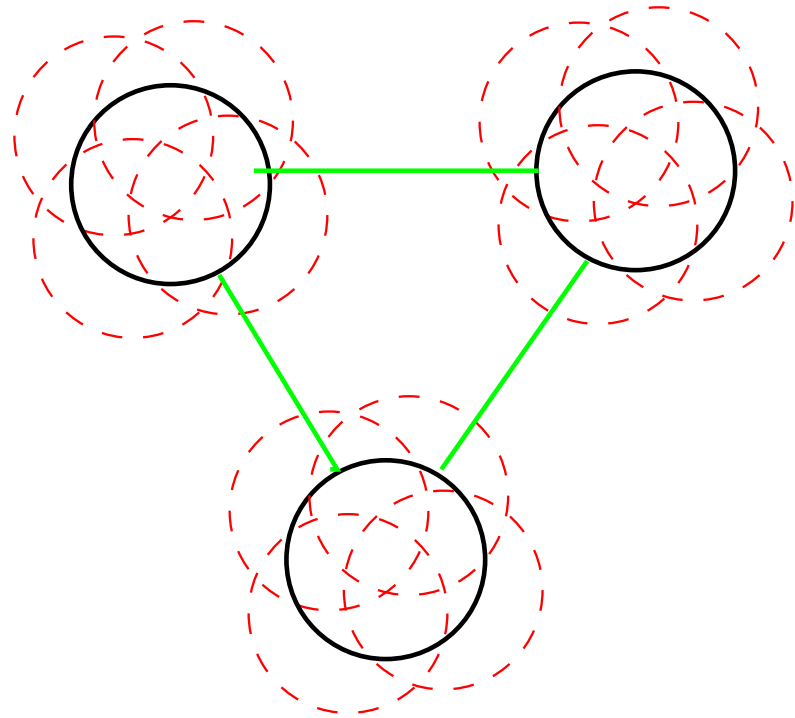A. Ikeda (Montpellier)
P. Sollich (London)

- Some previous work with:

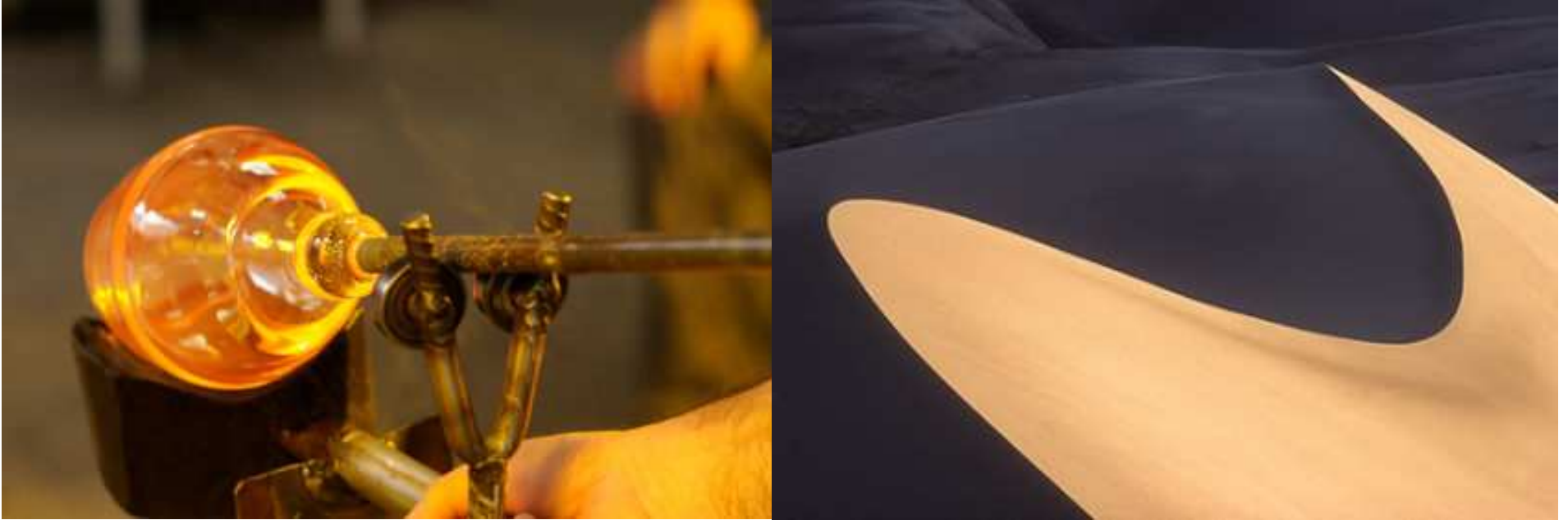P. Chaudhuri (Dusseldorf),
H. Jacquin (Paris),
S. Sastry (Bangalore),
T. Witten (Chicago),
F. Zamponi (Paris).

Disordered solid states

- Atomic glasses (window glasses, plastics) are solid materials frozen in an amorphous (non-crystalline, metastable) structure.

- Dense granular materials are disordered solids.

- Same/similar/(un-)related transitions? Similar properties in the 'fluid'? Similar mechanical response of the solid?

A geometric problem... really?

- Athermal packing of soft repulsive spheres, e.g. $V(r < \sigma) = \epsilon(1 - r/\sigma)^2$.
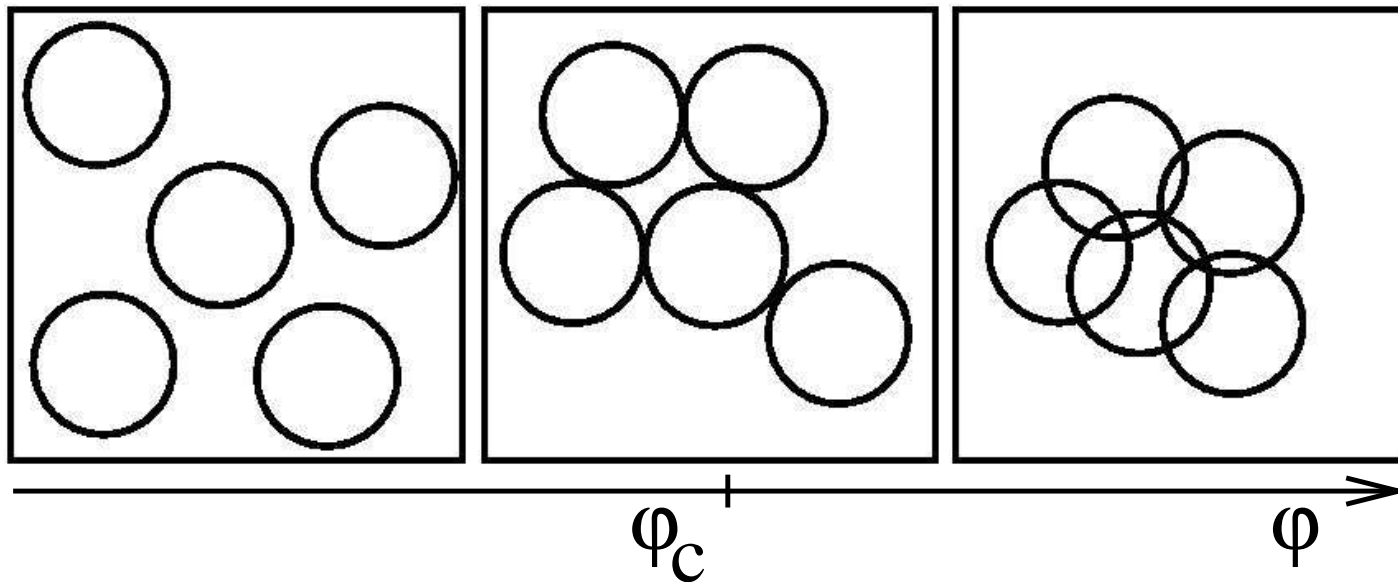
Low φ: no overlap, fluid   *Large φ: overlaps, solid*

- Useful for non-Brownian suspensions (below), grains (at), foams and emulsions (above). Many (oral) claims for glass-formers.

- Aim: equilibrium statistical mechanics approach to jamming. See if and how jamming emerges in the $T \to 0$ limit of the (T, φ, σ) phase diagram.

Numerical observations

- J-point from packing properties of soft repulsive particles at $T = 0$.

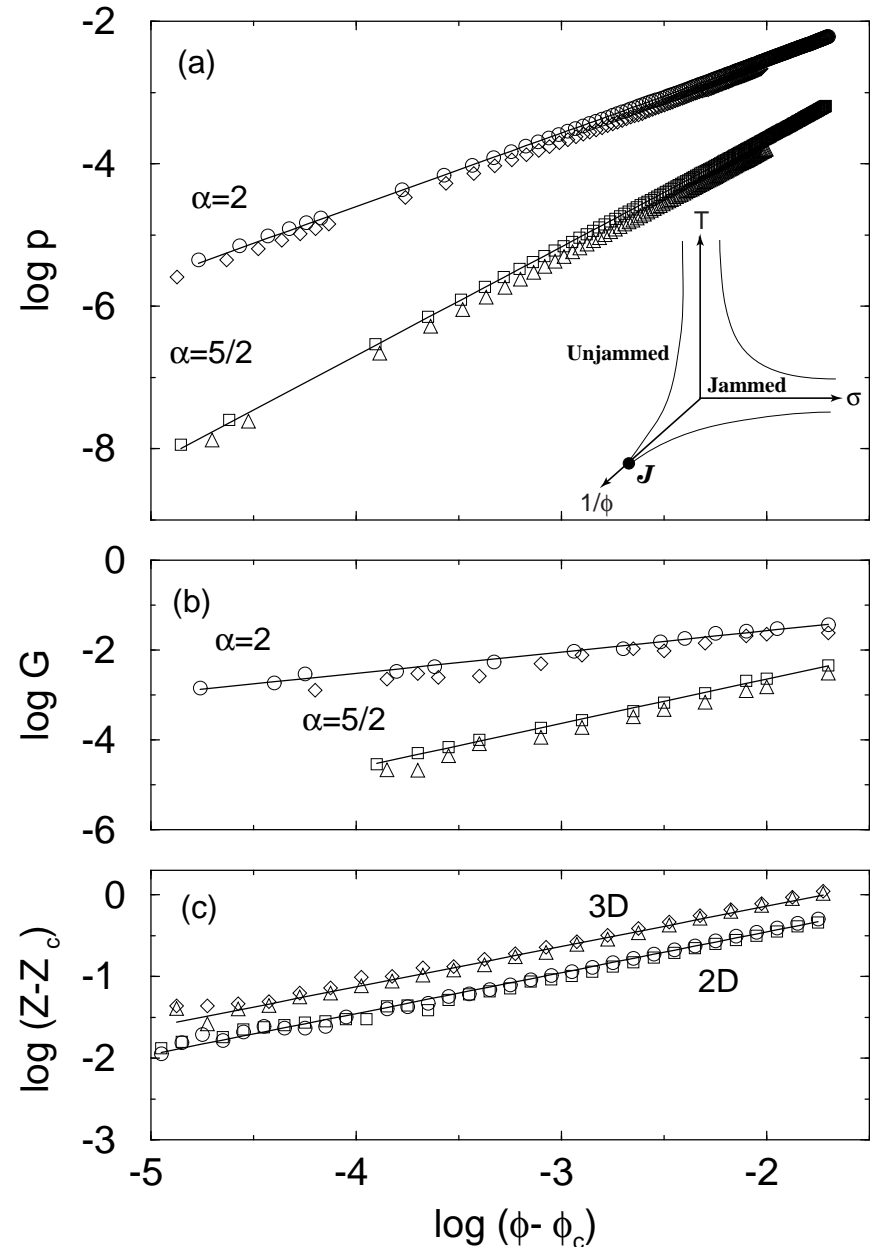 [O'Hern *et al.* PRL '02]

- Scaling laws and structure of packings near jamming [vanHecke JPCM'10]

Energy: $E = 0$ for $\varphi < \varphi_J$; $E \sim (\varphi - \varphi_J)^\alpha$ for $\varphi > \varphi_J$.
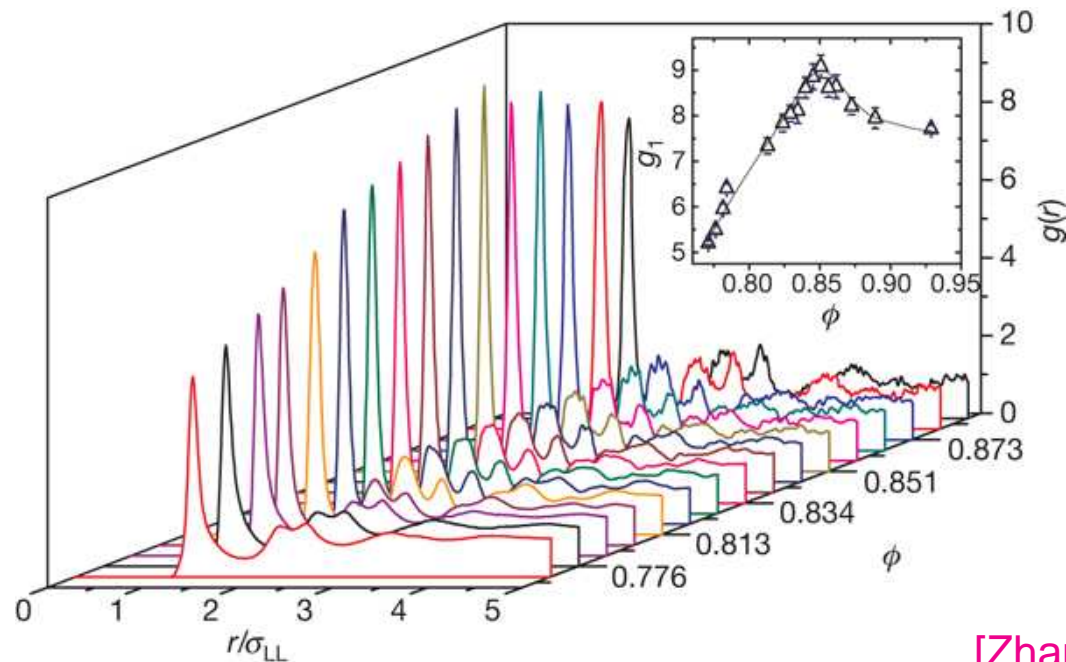
Contact number: $z = 0 \rightarrow z = z_c + a(\varphi - \varphi_J)^{1/2}$ with $z_c = 2d$ (isostaticity).

- A major numerical and experimental effort over the last decade. A new nonequilibrium phase transition.

Structure of soft colloids

- Numerous experiments performed on soft colloidal particles (microgels, emulsions) to probe the jamming transition.


[Zhang *et al.*, Nature 2009]

- Anomalous behavior of pair correlation function $g(r)$ under compression.

- Interpreted as a structural signature of the jamming transition. *"Our results conclusively demonstrate that length scales associated with the $T = 0$ jamming transition persist in thermal systems, not only in simulations but also in laboratory experiments.*

Rheology of soft particles

• Steady state rheology near jamming in overdamped (athermal) numerical simulations of harmonic spheres. Diverging viscosity, emergence of yield stress.
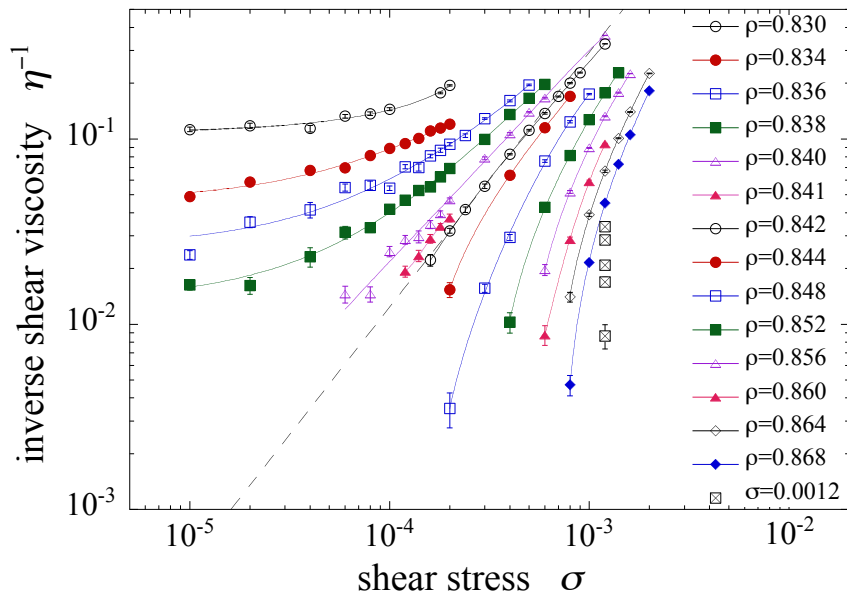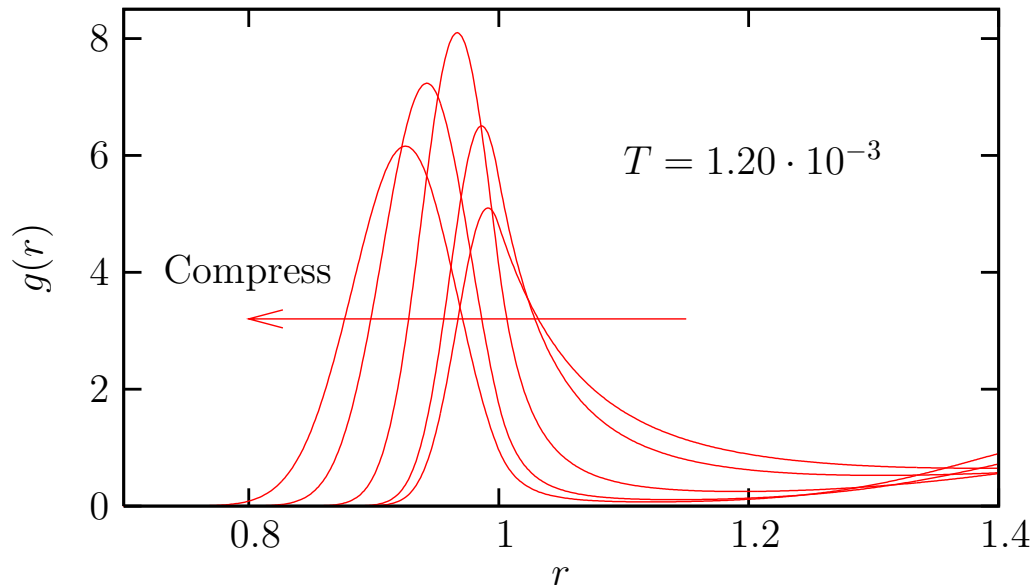

[Olson, Teitel, PRL 07]
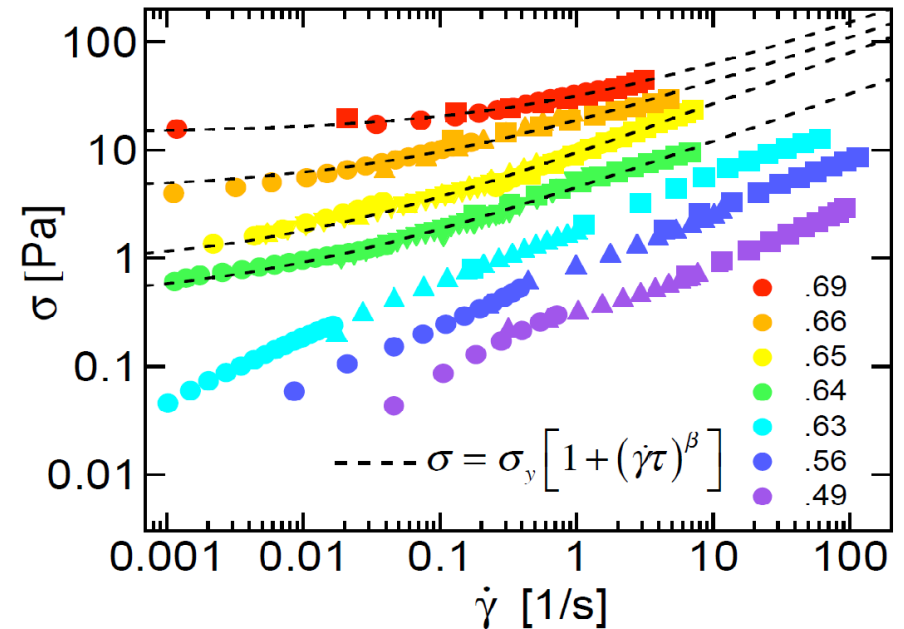
[Norstrom et al., PRL 2010]

$$\sigma = \sigma_y \left[1 + (\dot{\gamma}\tau)^{\beta} \right]$$

• "Similar" behaviour (and scaling laws) observed experimentally.
"These results support the conclusion that jamming is similar to a critical phase transition."

Equilibrium fluid

- Consider the fluid, $V(r) = (1-r)^2$, at equilibrium at $(T > 0, \varphi, \sigma = 0)$.

- Liquid state theory: solve structure, $g(r)$, thus thermodynamics using integral equations. We can use, e.g., HNC: $g(r) = e^{-\beta V(r) + g(r) - 1 - c(r)}$.

$T = 1.20 \cdot 10^{-3}$

Compress

- No glass or jamming transition is found.

- Anomalous structural evolution at all T! The system first 'orders', then 'disorders'.

- $F = E - TS$: Avoid overlap (reduce energy) at low φ. Difficult (entropically disfavoured) at larger φ. Solution: increase overlap to gain entropy.

- Softness matters (not jamming).   [Jacquin & Berthier, Soft Matter '10]

Why liquid state theory fails

- Equilibrium phase diagram of soft harmonic spheres.
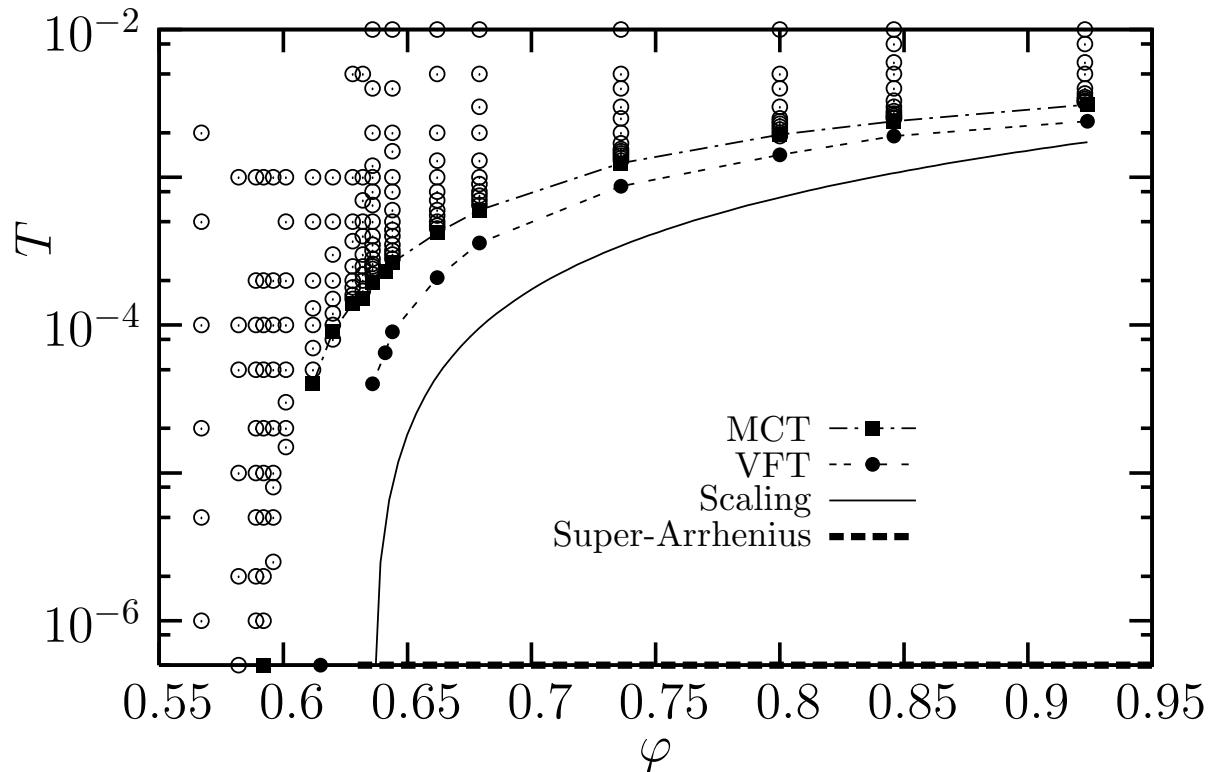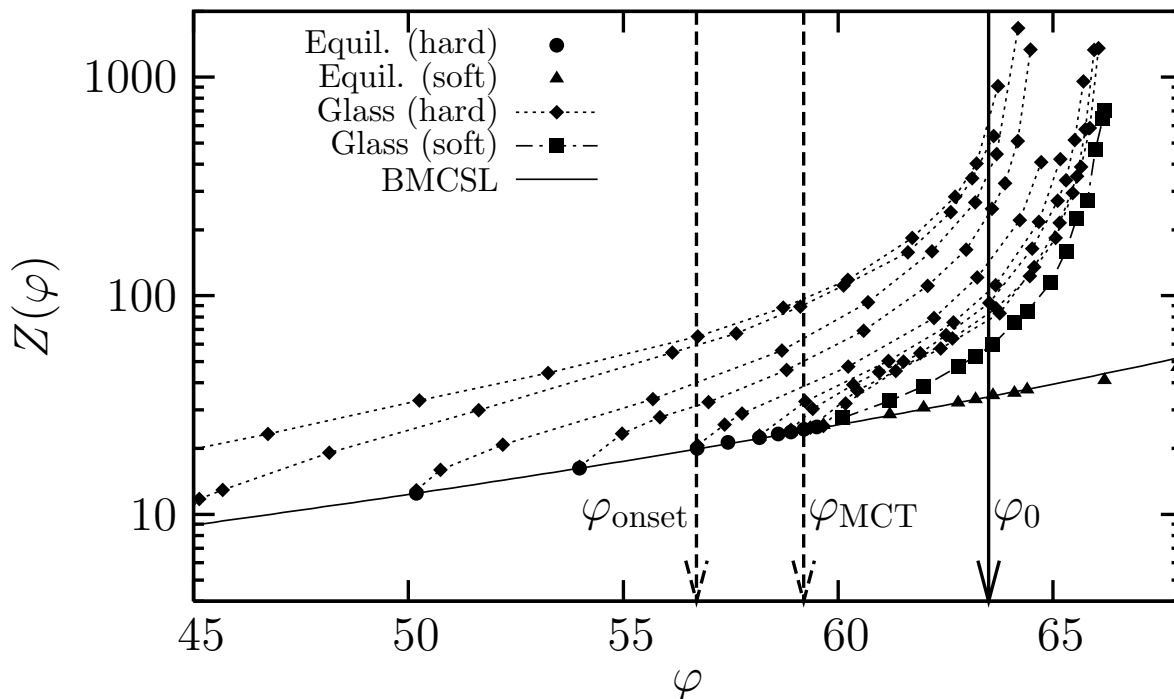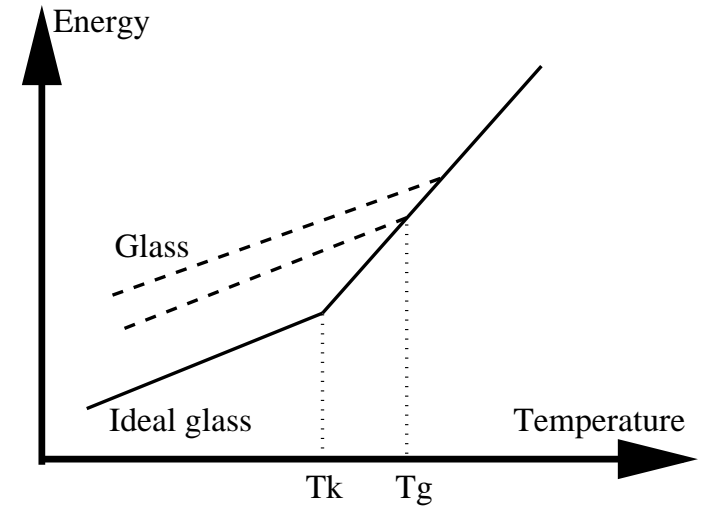
- The equilibrium fluid does not jam, but the glass structure does.

- One cannot understand the jamming transition without dealing first with the glass phase.

Metastable states & jamming

- Glasses depend on cooling history.

- Similarly, compressed fluids of hard spheres reach different glassy states.

- Jamming transition occurs along a range of densities [Chaudhuri *et al.*, PRL'10]

- Theory must handle multiplicity of metastable states.

Statistical mechanics of glasses

- Assume exponential number of metastable states exists:

$$f(T) = -\frac{T}{V} \log \int df' \exp\left[-\frac{Nf'}{T} + Ns_{\mathrm{conf}}(f', T)\right].$$

- In practice, take m replica(s) and minimize the replicated free energy
[Monasson, PRL '95, Mézard-Parisi PRL '99]

$$f(m, T) = -\frac{T}{V} \log \int df' \exp\left[-\frac{Nf'm}{T} + Ns_{\mathrm{conf}}(f', T)\right].$$

- New effective potential valid for both hard spheres ($T \to 0$ small φ) and soft glasses ($T \to 0$ large φ), to treat analytically the glass & jamming transitions of harmonic spheres.
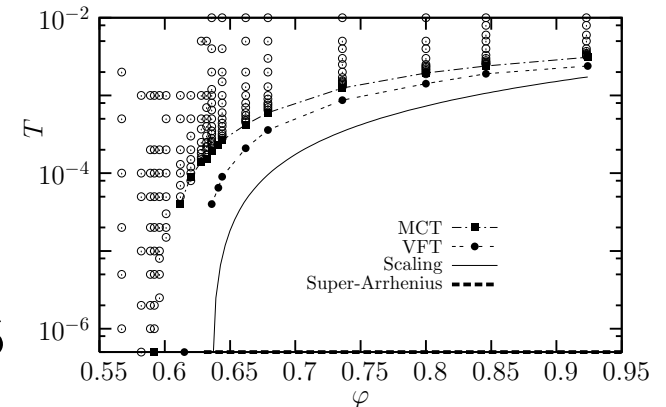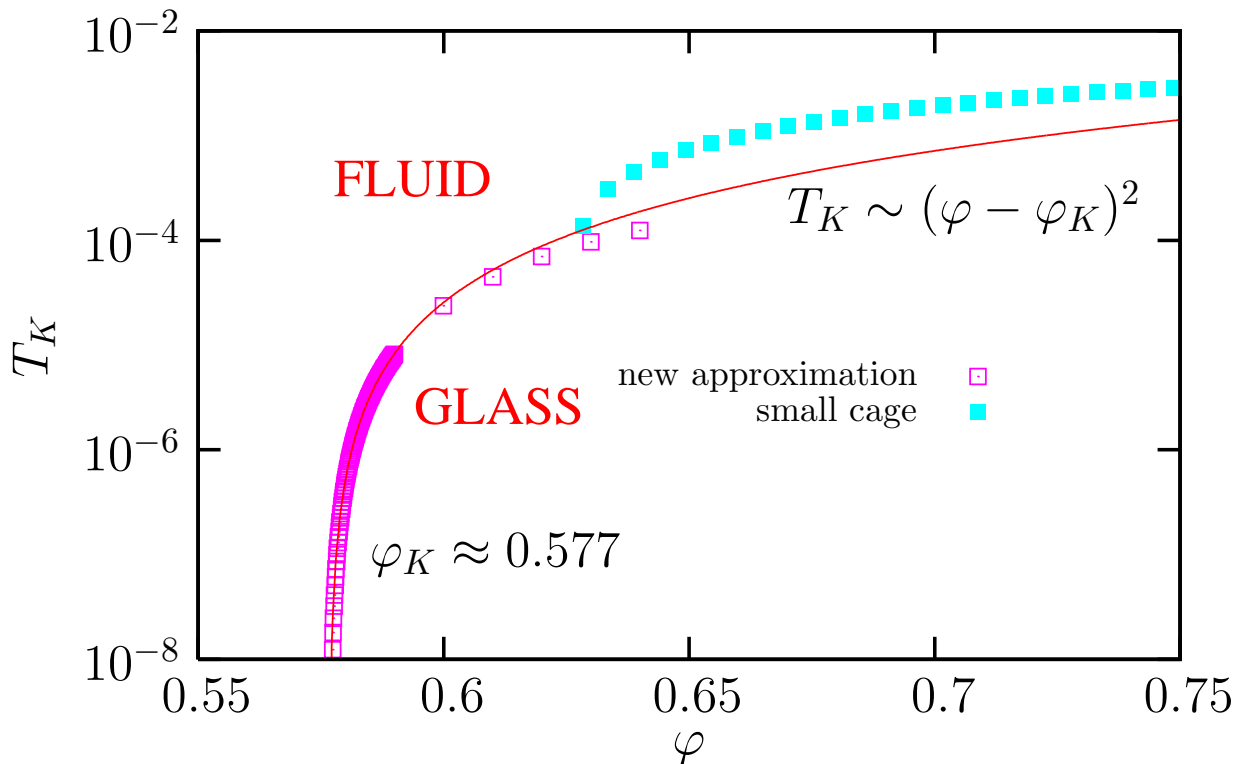
$$f(m, A, \varphi, T) =$$

$$f_{\mathrm{harm}}(m, A) + f_{\mathrm{liquid}}(\varphi, T/m) - \frac{\rho}{2} \int dr g(r)[e^{-\beta(V_{\mathrm{eff}}(r) - mV(r))} - 1]$$

[Jacquin, Berthier & Zamponi PRL '11]

The 'ideal' glass transition

- High T fluid: $m = 1$, $s_{\text{conf}}(T) > 0$ and simple liquid theory is enough.

- $s_{\text{conf}}(T)$ vanishes at $T_K(\varphi) > 0$ for $\varphi > \varphi_K \equiv$ hard sphere glass transition.

- Low-T scaling: $T_K \sim (\varphi - \varphi_K)^2$ (robust scaling) with $\varphi_K \approx 0.577$ (value depends on specific approx).
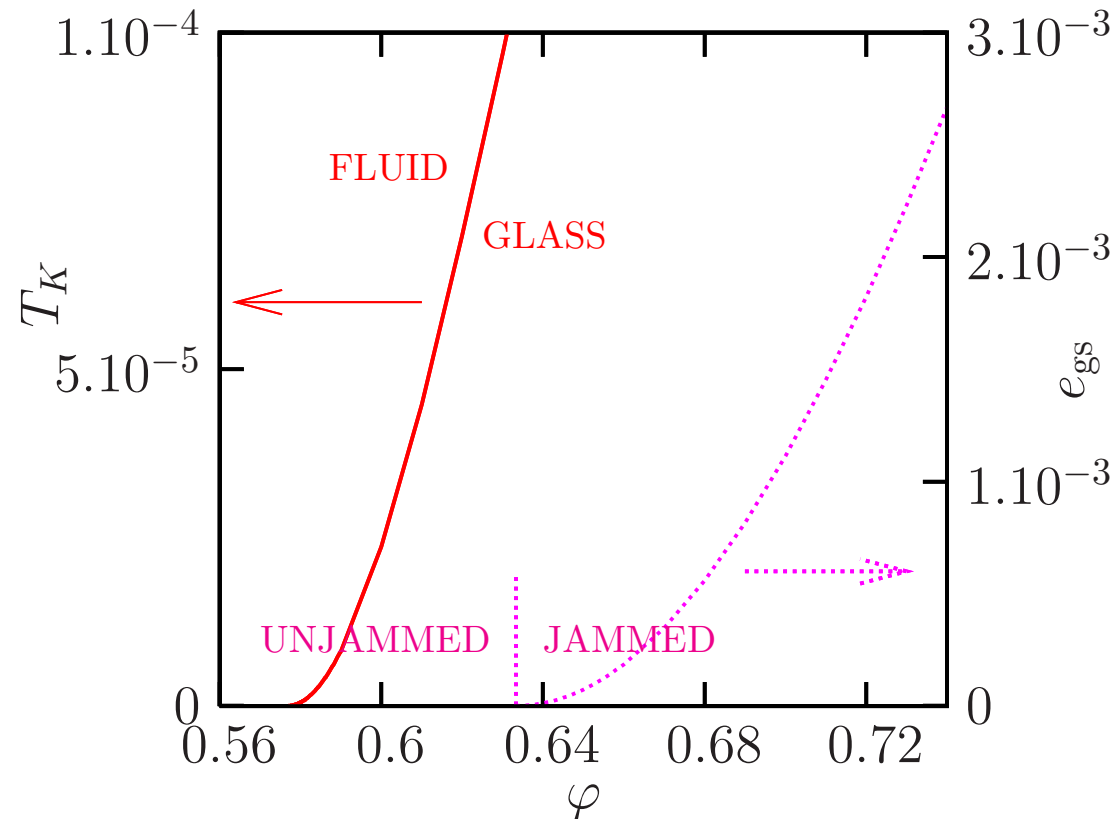
The 'ideal' jamming transition

- **Glass thermodynamics:** energy, pressure, specific heat, fragility...

- **Jamming at** $T = 0 \Leftrightarrow$ Change in ground state glass properties.

- $\varphi_{\text{GCP}} = 0.633353...$ such that:
$E_{\text{GS}} = 0$ below,
$E_{\text{GS}} \simeq a(\varphi - \varphi_{GCP})^2$ above.

- **Glass Close Packing:** densest
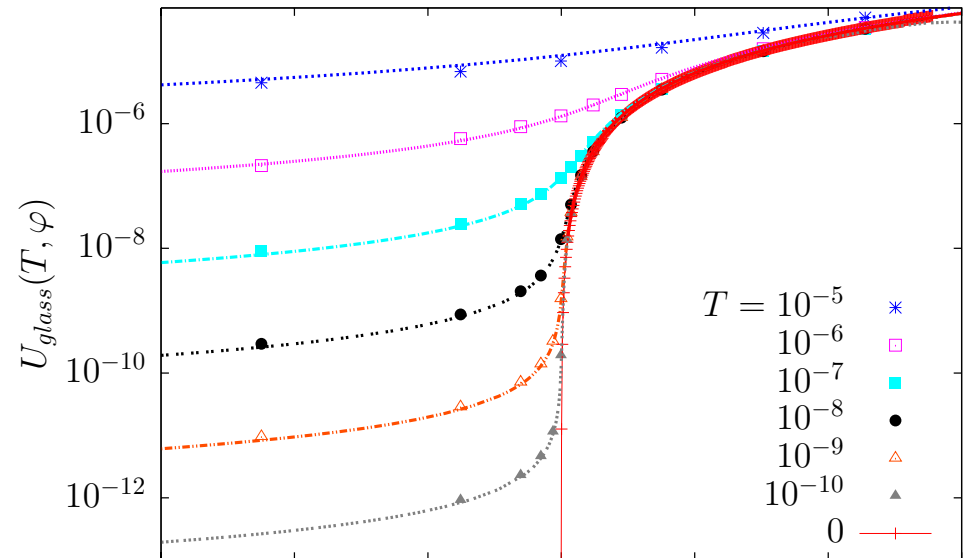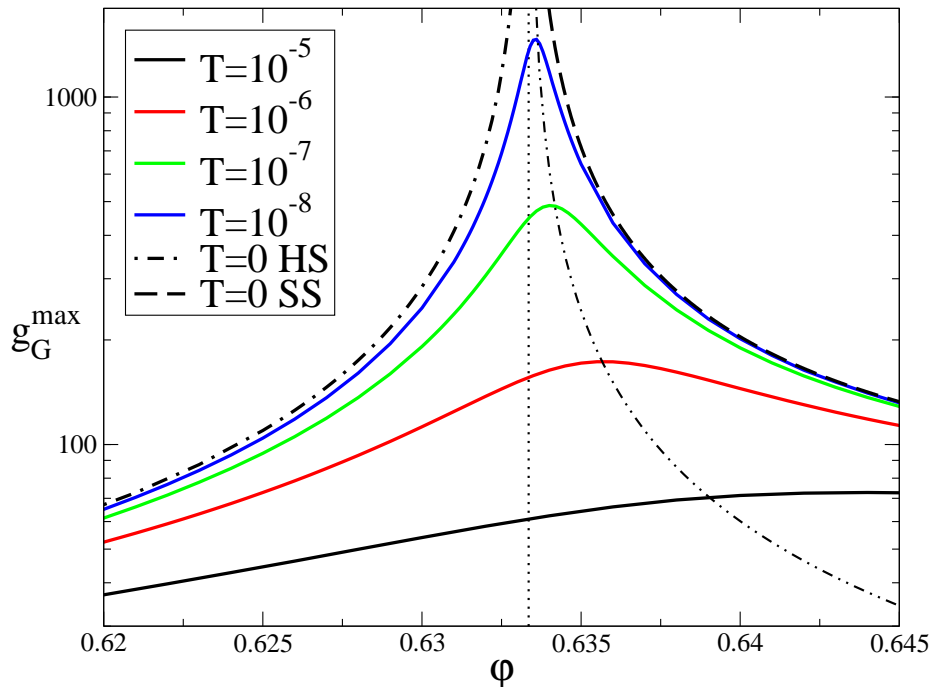$T = 0$ glass with no overlap.
[Zamponi & Parisi, RMP '10]

- $P_{\text{GS}} \sim (\varphi - \varphi_{GCP})$.

- **Existence, location(s), and scaling laws of jamming from 'first principles'.**

Structure of jammed states

- New predictions for $g(r)$ near contact at all (T, φ). Isostaticity is derived.

[Berthier, Jacquin, Zamponi, PRE '11]

- Clear emergence of jamming singularity from finite temperatures properties of glass phase–only if particles are not too soft, $T/\epsilon \ll 10^{-6}$.

- Still unconvinced G and J are different things? Rheology will do it.

Rheology at finite temperatures

• Aim: Study the harmonic sphere rheology at finite temperatures, then approach $T \to 0$.

• 'SLLOD': Newton eqs. + shear + thermostat ('SLLOD').
Problem: one cannot shear faster than thermal fluctuations, $Pe = \dot{\gamma}\tau_D < 1$.
Here $\tau_D \sim a/\sqrt{k_B T/m} \to \infty$, cannot go athermal.

• We use Langevin dynamics with shear and thermostat in $d = 3$:

$$\xi(\frac{d\mathbf{r}_i}{dt} - \dot{\gamma}y_i\mathbf{e}_x) = -\sum_j \frac{dV(|\mathbf{r}_i - \mathbf{r}_j|)}{d\mathbf{r}_i} + \eta_i,$$

with $\langle \eta_i(t)\eta_j(t')\rangle = 2k_B T\xi\mathbf{1}\delta(t - t')$.

• Two important microscopic timescales:
(i) dissipation: $\tau_0 = \xi a^2/\epsilon = 1$, our time unit.
(ii) thermal time: $\tau_D = \xi a^2/(k_B T) \to \infty$ when $T \to 0$.

• We study both finite and zero temperatures, both thermal ($Pe < 1$) and athermal ($Pe > 1$) rheologies at once.   [Ikeda, Berthier, Sollich, in preparation]

Soft glassy rheology

- Steady state rheology at $T = 10^{-4}$ and increasing φ. Diverging viscosity, emerging yield stress. Here $\tau_D^{-1} \sim 10^{-4}$.
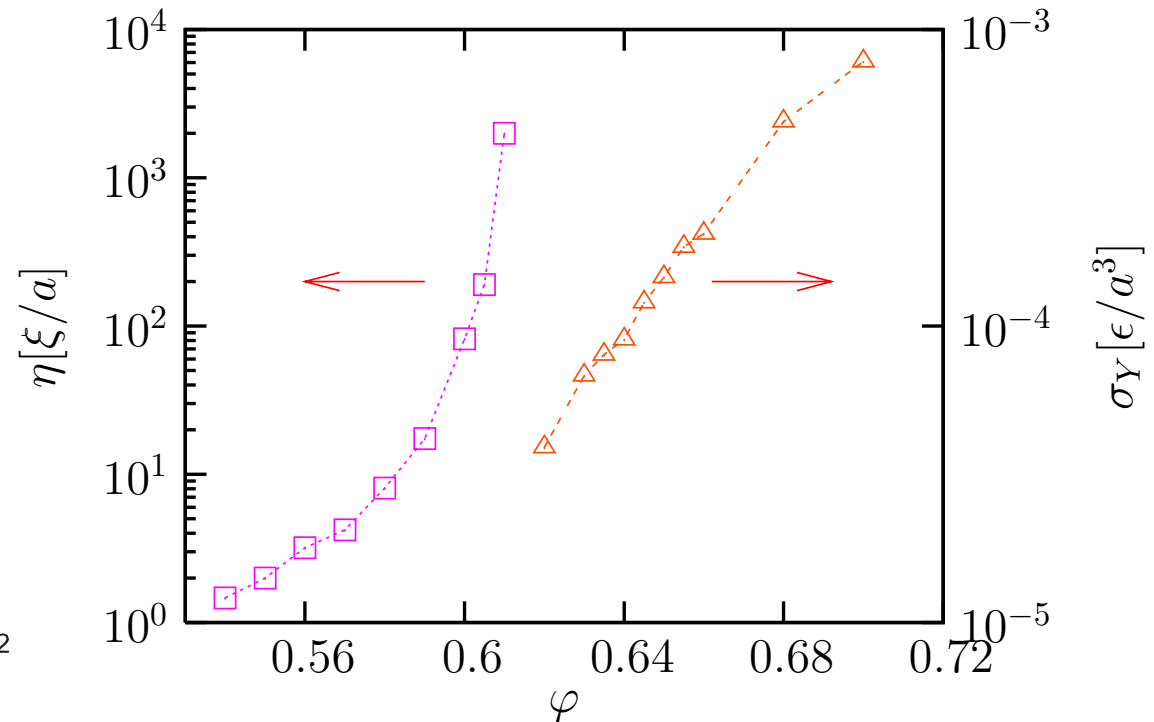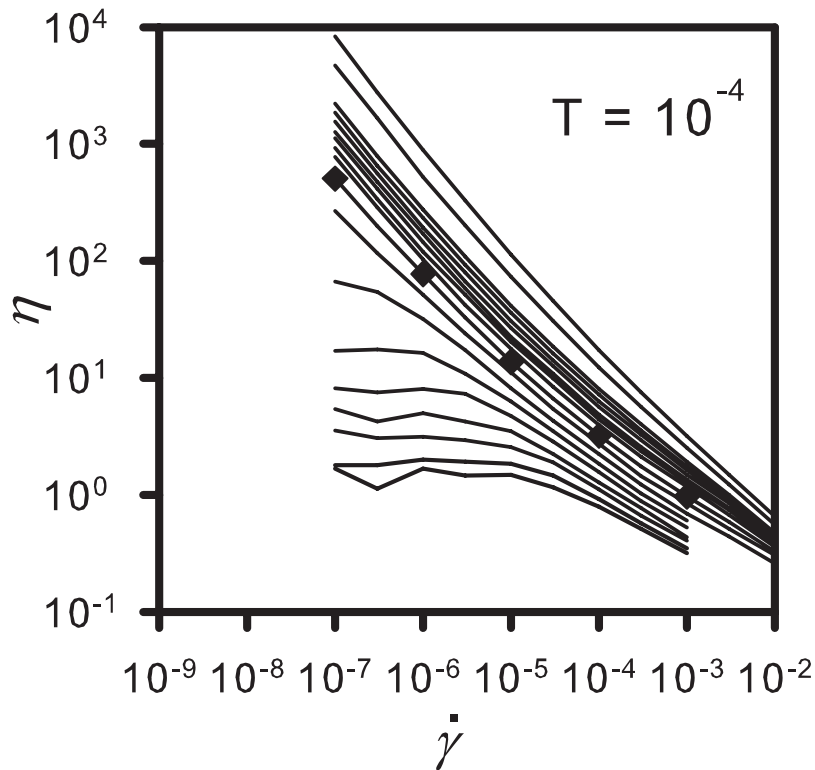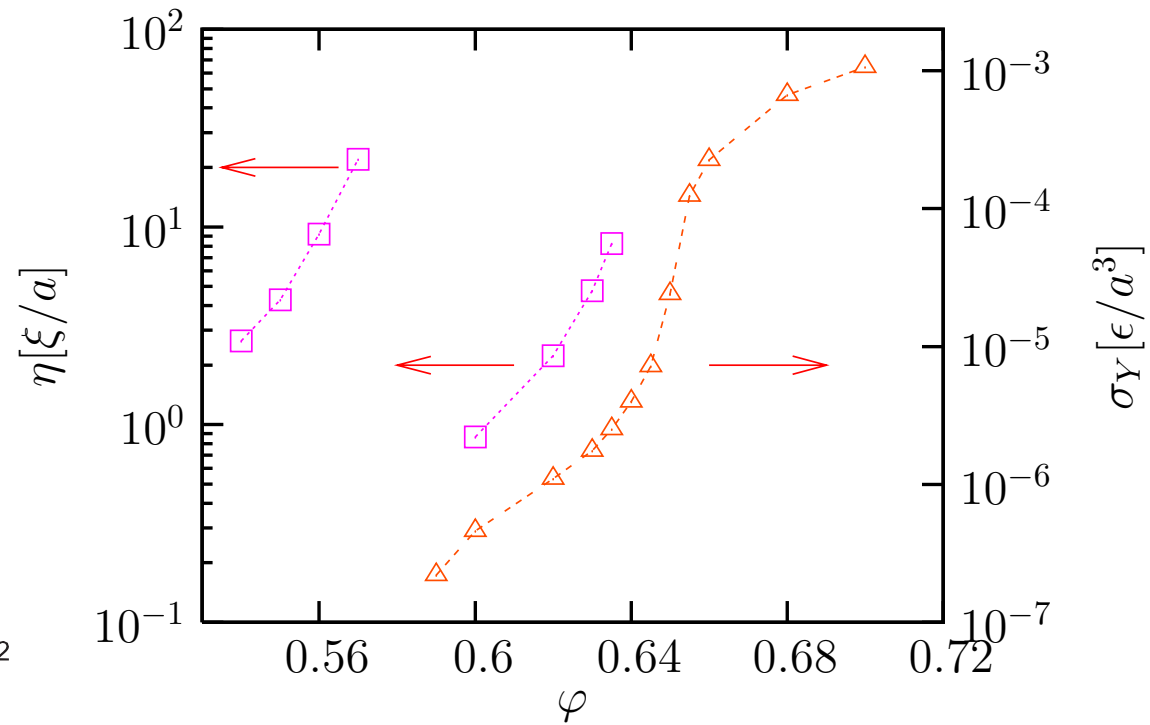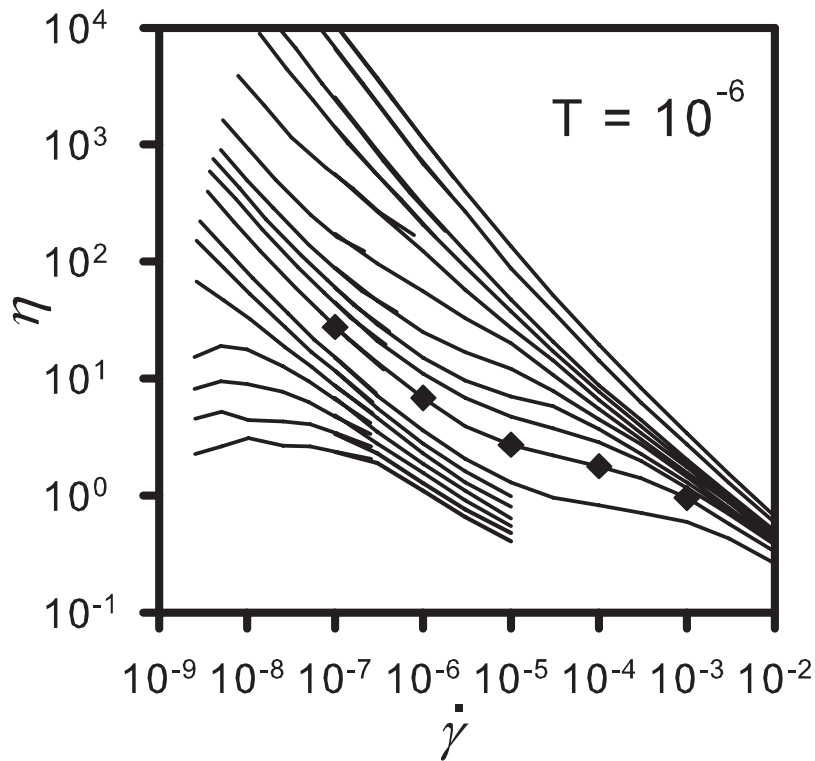

- This is a glass transition as seen in colloidal particles, star polymers, microgels, but also glassy liquids.

- Theories of driven glasses capture competition between slow glassy dynamics and shear flow.

From glass to jamming rheology
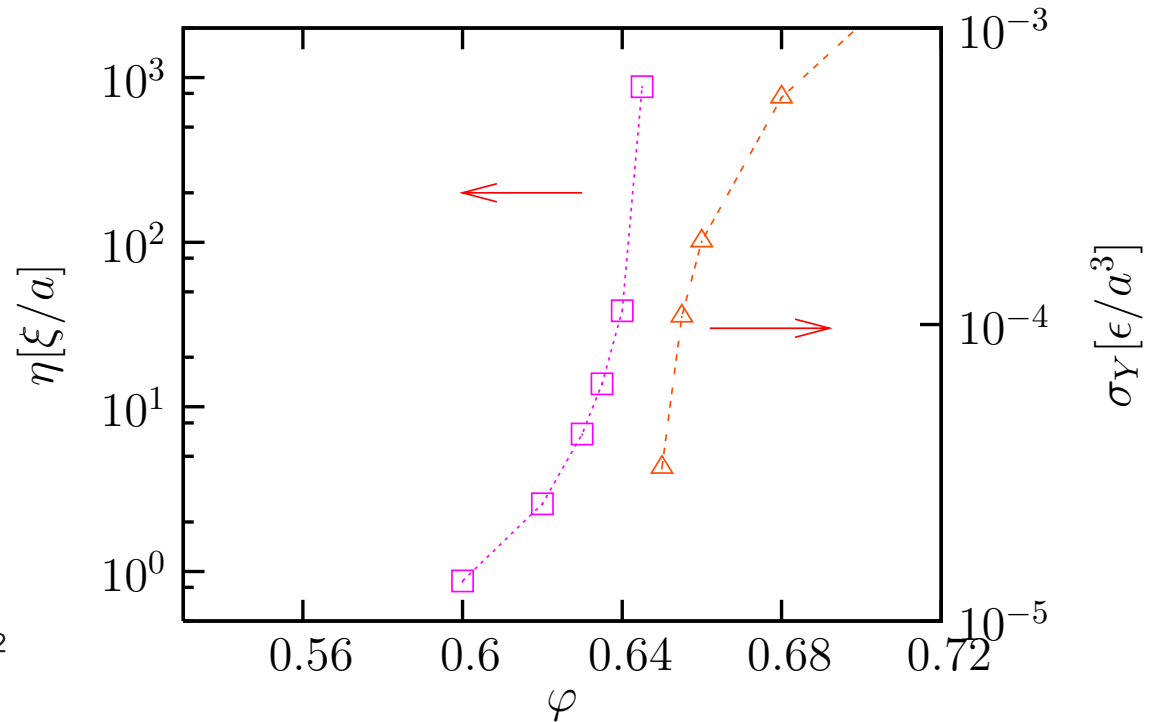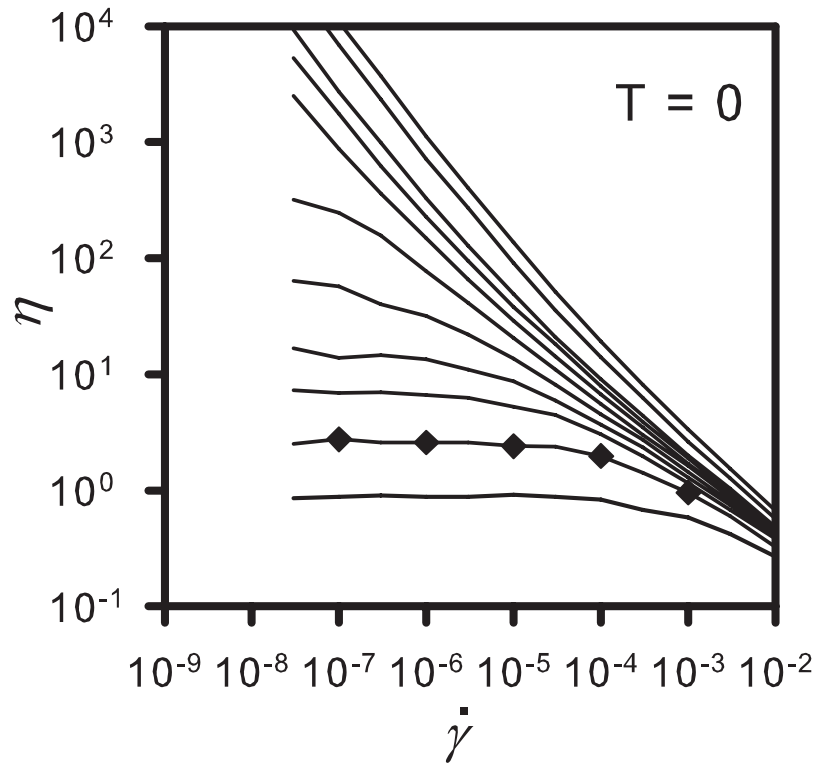
- Same at $T = 10^{-6}$, here $\tau_D^{-1} \sim 10^{-6}$. Glass physics shifts to lower shear rates: $Pe < 1 \rightarrow \dot{\gamma} < 10^{-6}$.

- The athermal jamming physics emerges when $\tau_D^{-1} \ll \dot{\gamma} \ll \tau_0^{-1}$.

- Two Newtonian regimes, two distinct viscosities, emergence of yield stress (when $\dot{\gamma} \rightarrow 0$), with funny density dependence. A real mess!
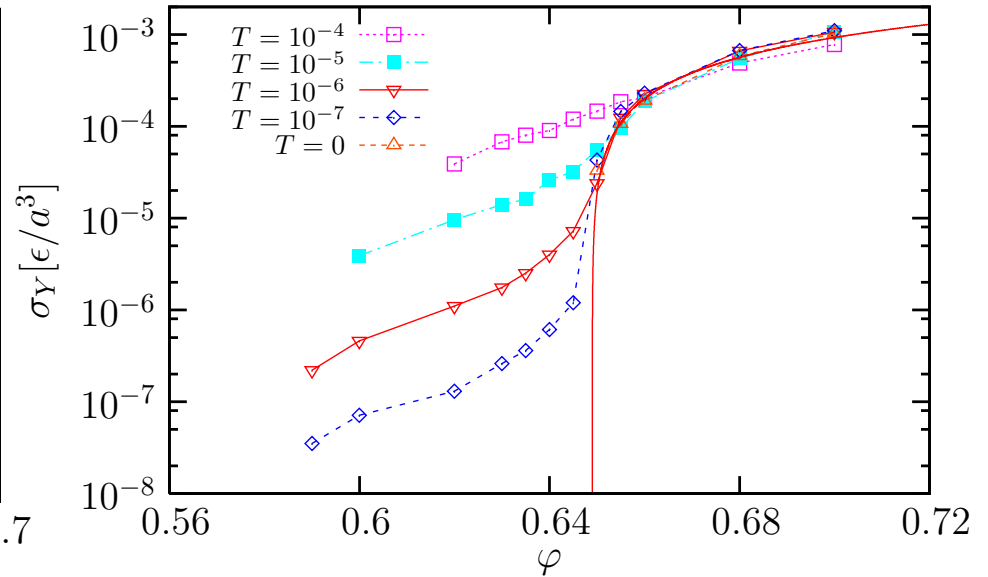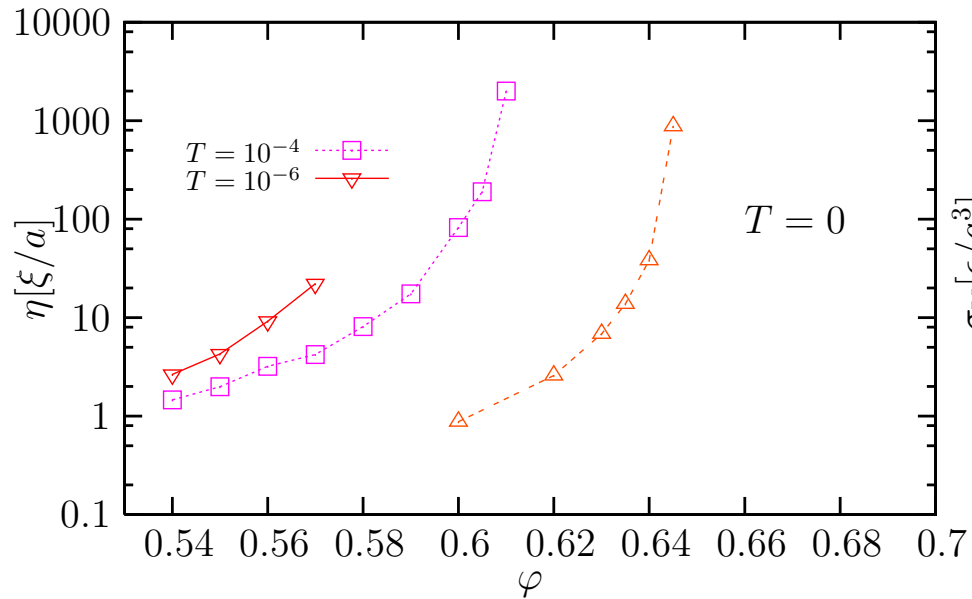
Pure jamming rheology

- Rheology at $T = 0$. Here $\tau_D^{-1} = 0$, i.e. $Pe = \infty$.

- Glass rheology has gone, $T = 0$ jamming transition remains: diverging viscosity, emergence of yield stress.

- No microscopic theory. Driven dynamics at $T = 0$ is difficult to attack from first principles (driven glass theories fail badly).

Rheology: summary

- We observed two types of Newtonian regimes, depending on the Peclet number and particle softness.

- Clearly, $\eta(T > 0)$ does not converge to $\eta(T = 0)$ when $T \to 0$. These are distinct divergences at distinct densities with distinct physics.

- Solidity emerges at the glass transition at any $T > 0$, and "transition to jammed solid" only exists at $T = 0$. cf. "Melting by freezing".

- To see jamming: $Pe \gg 1$ (kinetics) and $k_B T/a^3 \ll \epsilon/a^2$ (hardness).

Microscopic dynamics

- Widely different mean-squared displacements.
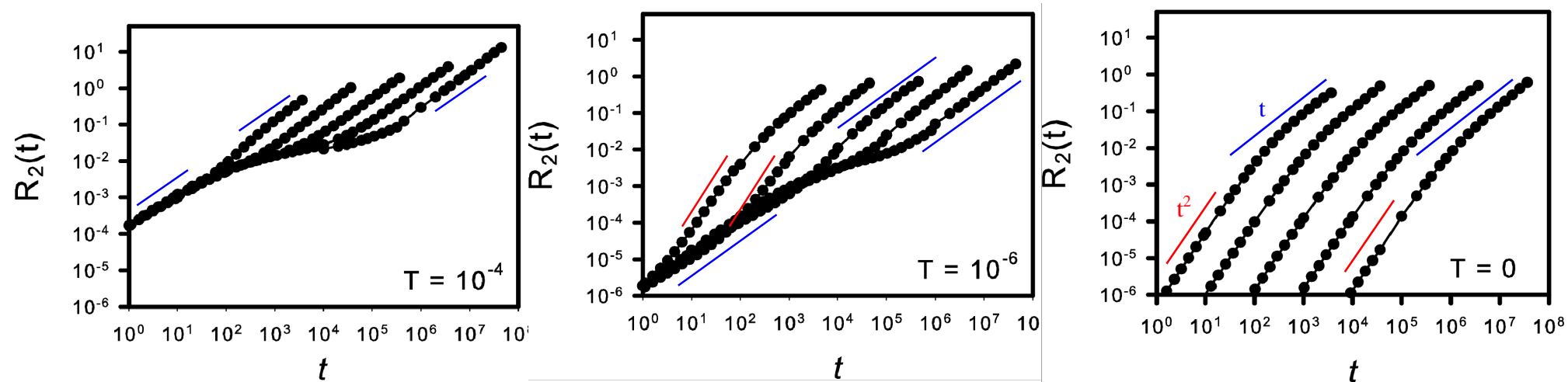
- $T = 10^{-4}$: Glass physics because particles explore their 'cage' due to thermal fluctuations.

- $T = 10^{-6}$: crossover towards athermal dynamics when thermal fluctuations do not allow sufficient exploration of the cage.

- At $T = 0$, ballistic (non-affine) short-time dynamics due to shear flow, then diffusive behaviour.
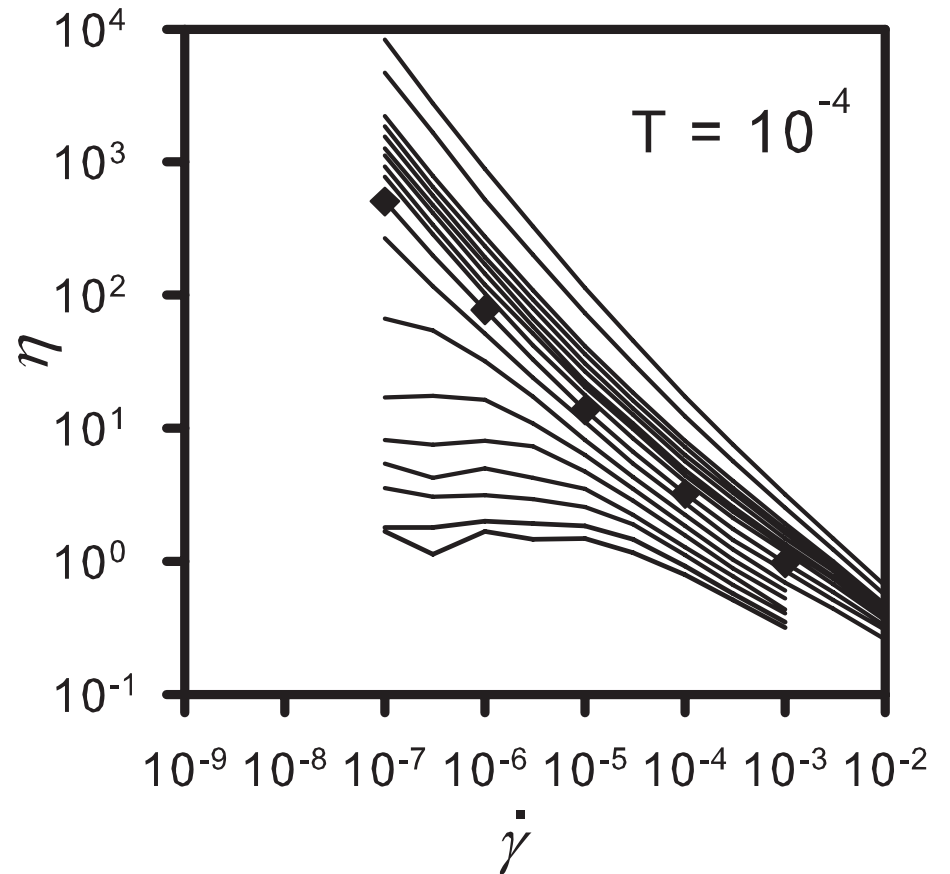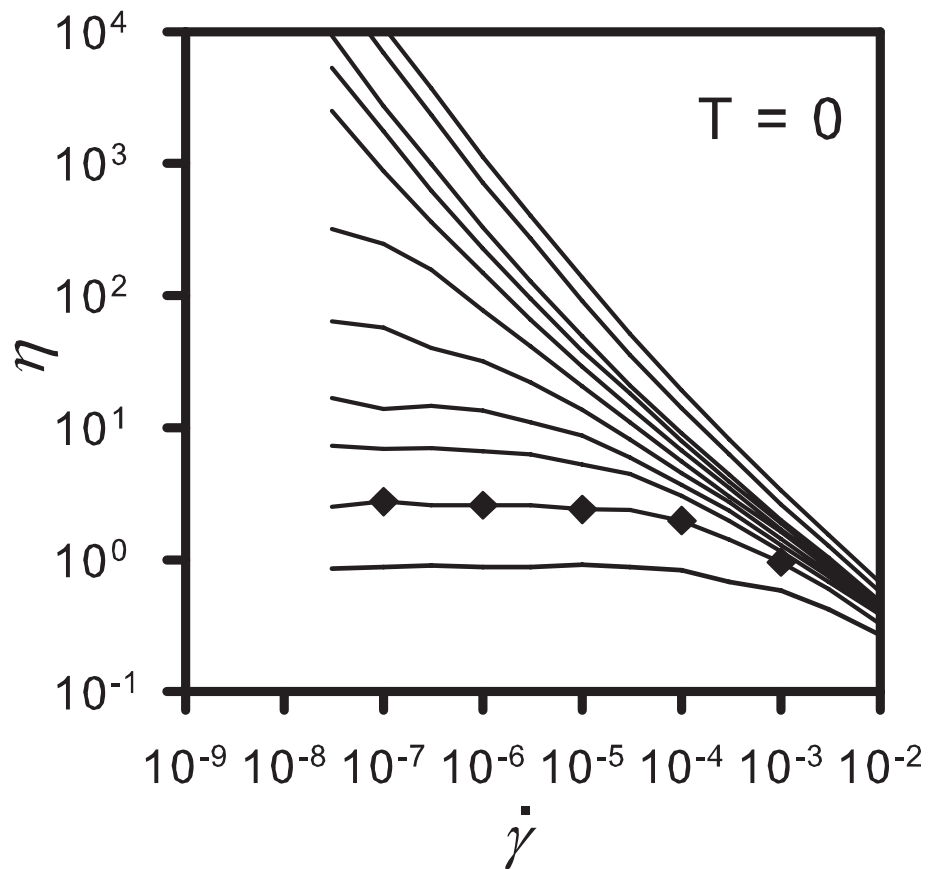
Experiments?

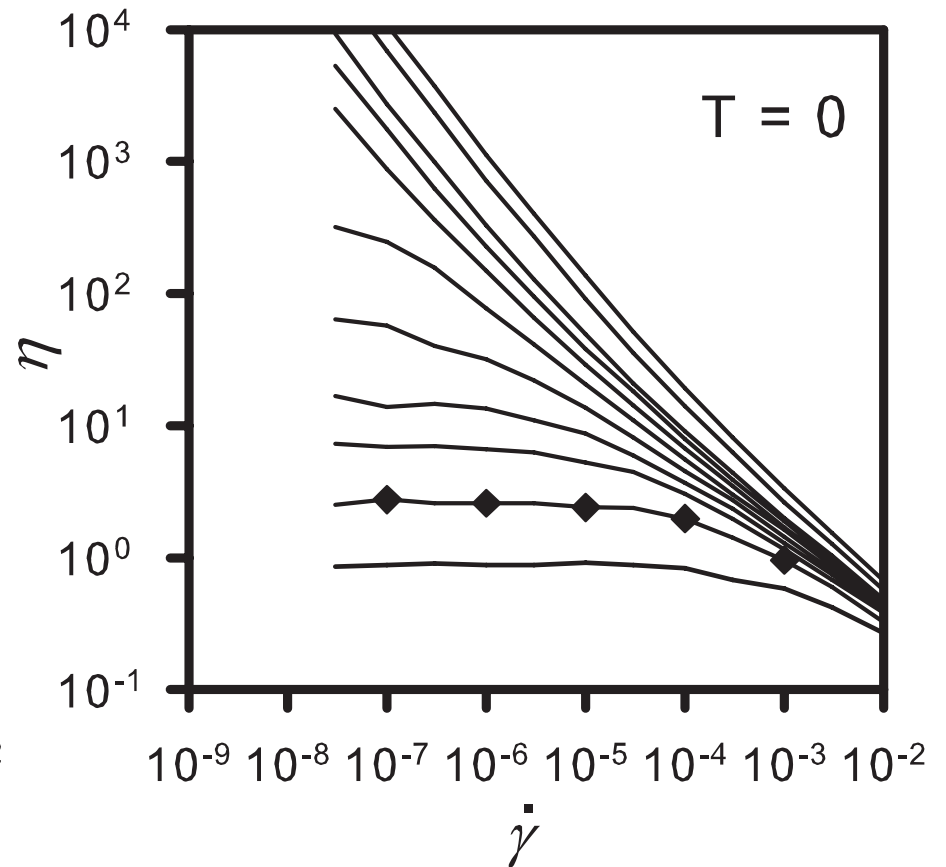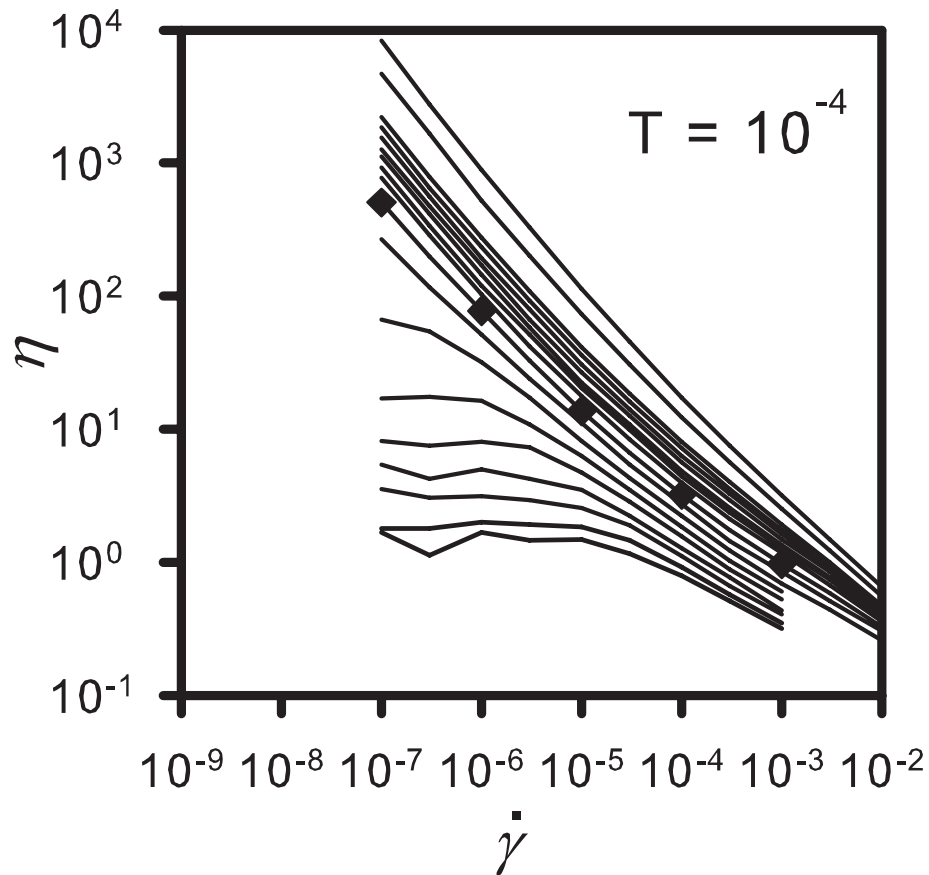● Micron-sized microemulsions seem ideal to observe the athermal/thermal crossover.
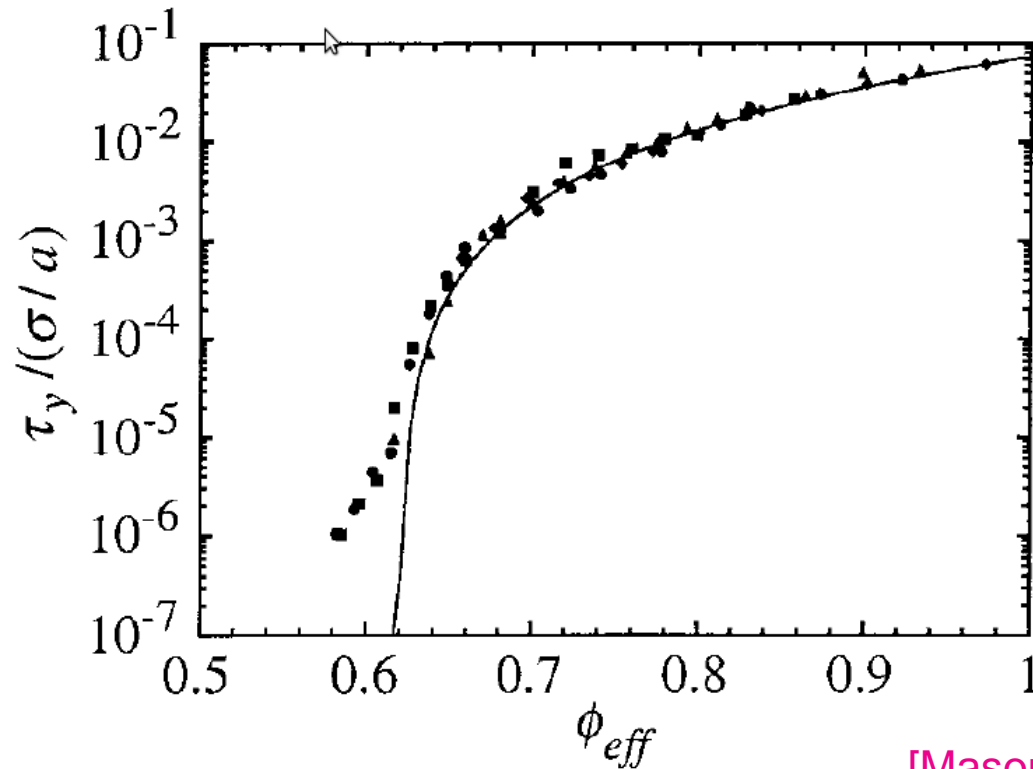
[Mason, Bibette, Weiz, 1996]

● Star polymers are too soft, grains are too large. What about microgel 'pnipam' particles? Both small (100 nm) and large (1 micron) colloids available, but quite they are also quite soft...
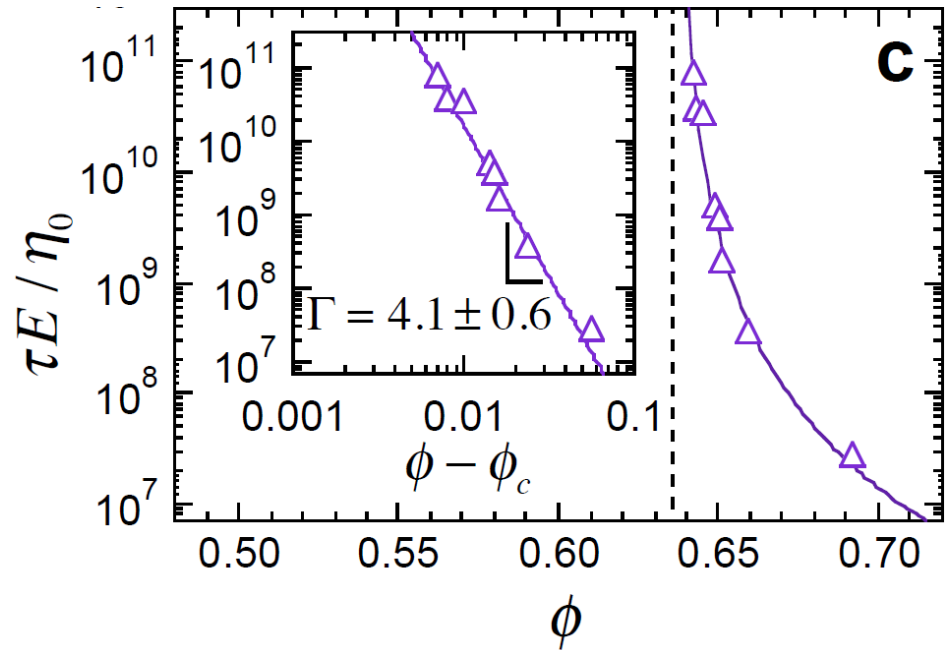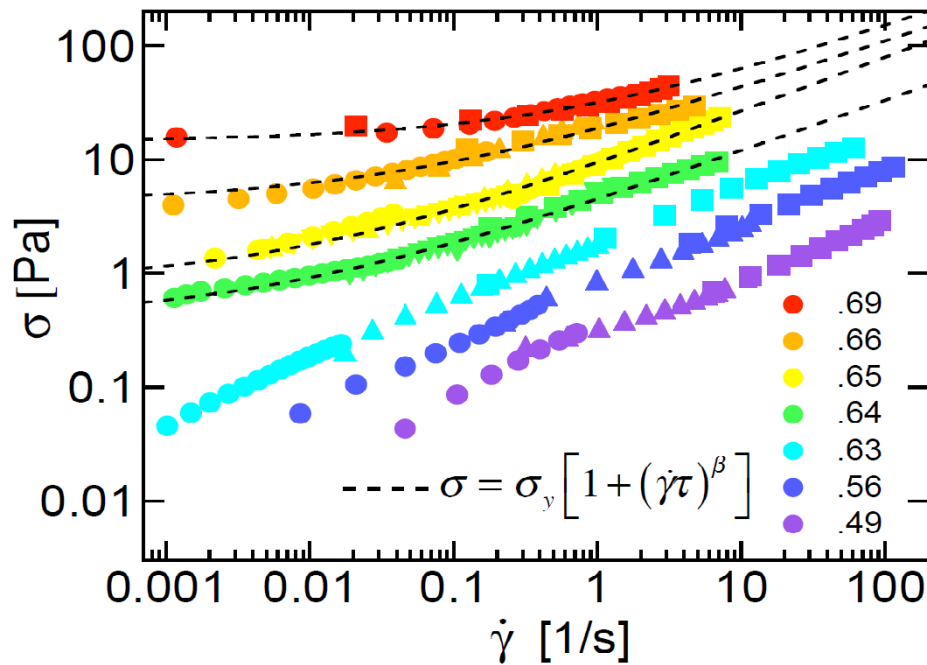
How confusing!

How confusing!

Confusion?

- Rheology of soft microgels of about 1 micron [Nordstrom et al., PRL 2010]

- Scaling analysis: $\tau/\tau_0 \sim 10^7 - 10^{11}$, $\sigma_Y/\epsilon \sim 10^{-6} - 10^{-4}$.

- Thermal units: $\dot{\gamma} = 1\text{s}^{-1} \rightarrow Pe \approx 5. \rightarrow \tau/\tau_D \sim 1 - 10^4$.

- Rheological "transition" occurs at $Pe < 1$, jamming rheology outside the shear rate window, diverging viscosity and emergence of yield stress not controlled by $T = 0$ physics.

Summary

- Why not use thermal fluctuations and statistical mechanics approaches that we know to describe the emergence of interesting physics at $T = 0$?

- Useful to understand relationship with glass transition, glass theories provide first principles approaches and new predictions for structural quantities and correlation functions.

- Also seems promising to understand steady state rheology.

- Need some theory for to study better athermal rheology, where glass theories fail.

Even more confusing