Glassy Dynamics in a Cup of Coffee: Higher-Order Glass-Transition Singularities

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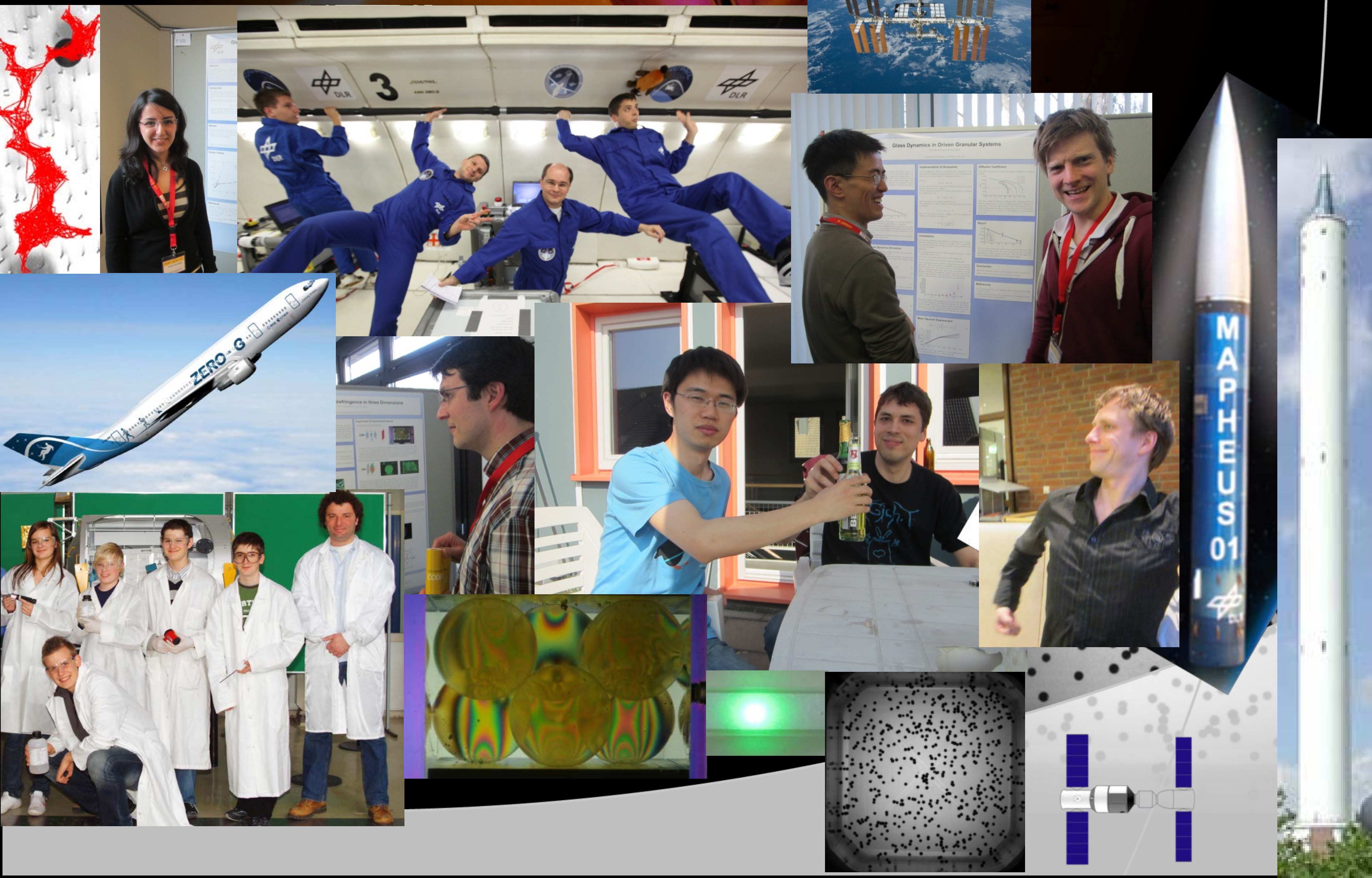
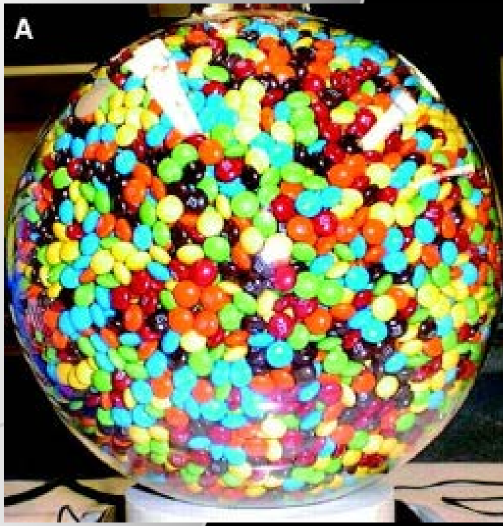
Granular Group at DLR Cologne



Prologue: Experiments in Microgravity



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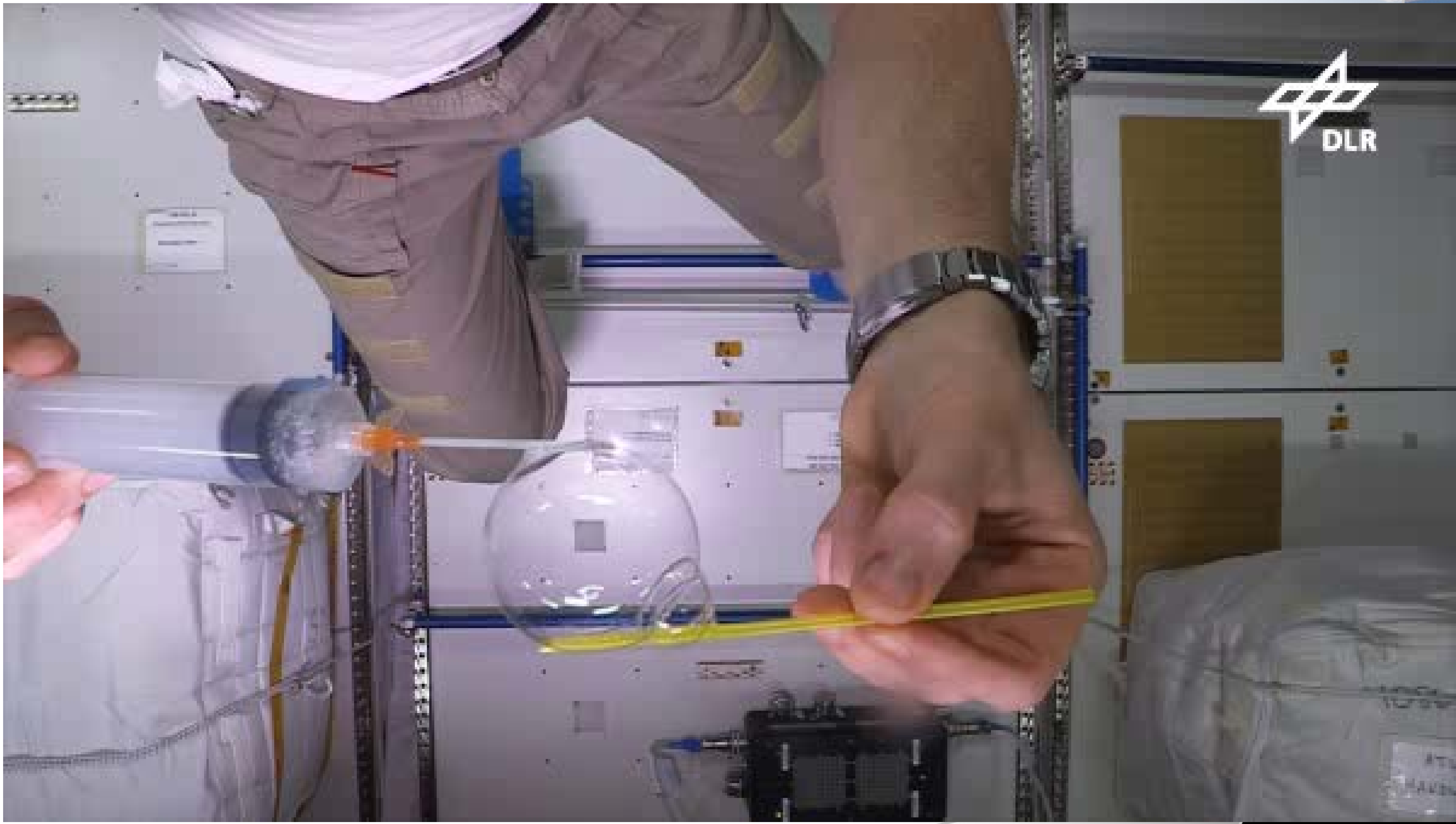

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Prologue: Experiments in Microgravity

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Outline

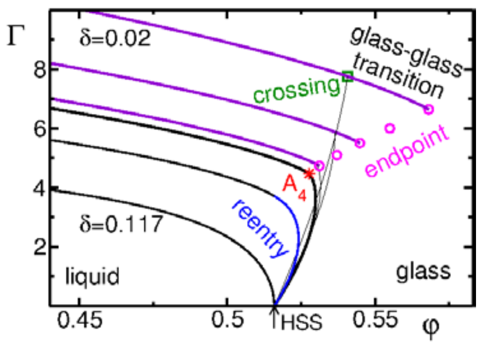
A Experimental Prologue: Experiments in Microgravity

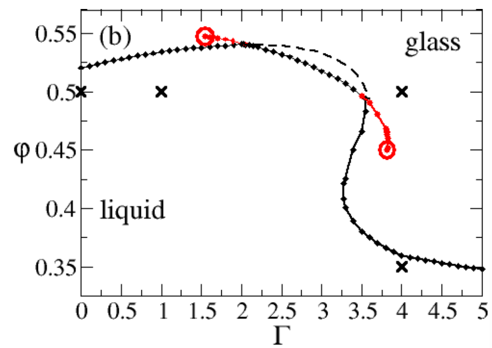
B Theory: Bifurcation Dynamics

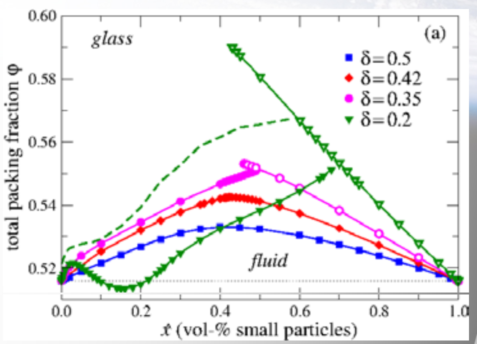
1) in Equilibrium: Glass Transition in Colloidal Liquids

2) in Non-Equilibrium: Driven Granular Fluids

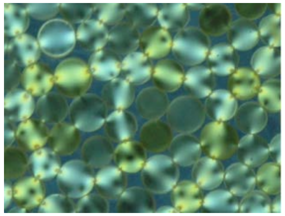
3) Higher-Order Bifurcations in Glassy Systems

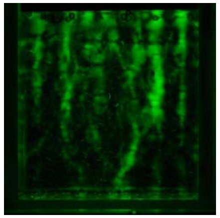






C Experimental Epilogue: disordered packing in asymmetric binary mixtures





Dense Equilibrium Fluids

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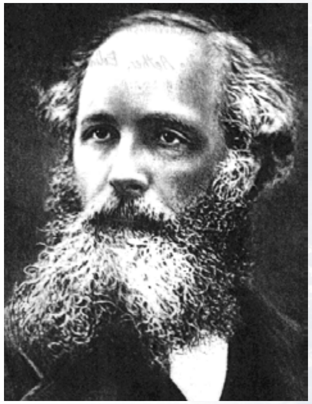
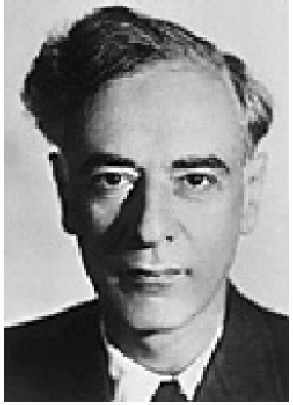
Dynamics of Dense Liquids: Theory possible?

Every viscous fluid with shear viscosity h can be considered an elastic solid if probed faster than a characteristic time scale t on which some modulus G relaxes.

Viscoelasticity: h ~ Gt



J. C. Maxwell

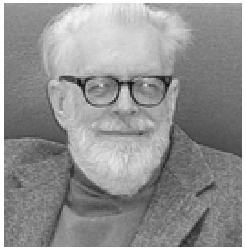


L. D. Landau

There is no theory for a conventional liquid, since there is no small parameter.

Dorfman's lemma [Zwanzig 1982] of kinetic theory:

All relevant fluxes are non-analytic functions of all relevant variables!



R. Zwanzig

R. Dorfmann

Dynamics of Dense Liquids: Liquid-Vapor Critical Point

Equation of State (1873) with fix by Maxwell (1875): critical point allows calculations in its vicinity

Density jump grows with exponent

β=0.5

J. D. van der Waals

L.P. Kadanoff (1966), K.G. Wilson (1971)

divergent correlation length **makes microscopic details irrelevant**

Iff *fluctuations* are important, exponents from mean-field theory are modified

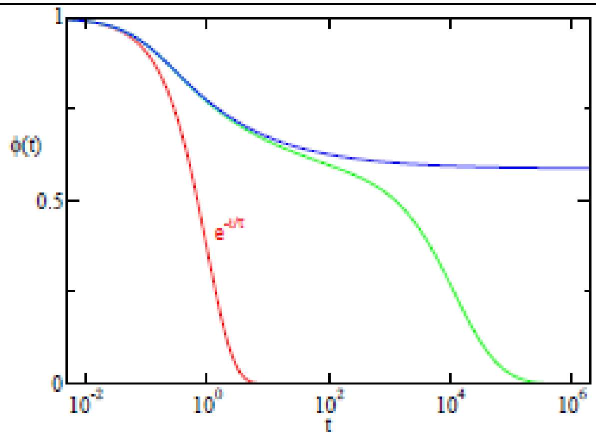
β=0.326..

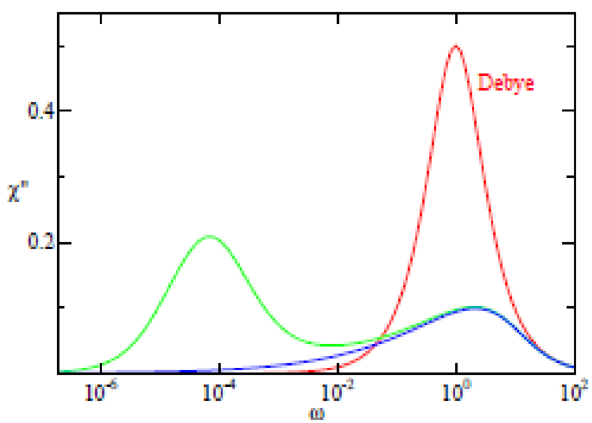
Dynamics of Dense Liquids: Correlation Functions

A System of N particles driven by a Hamiltonian $\mathcal{H}$ defines some dynamical variables, e.g., the particle density, $\rho(\vec{r},t) = \sum_i^N \delta(\vec{r} - \vec{r}_i(t))$ with the evolution $\partial_t \rho(t) = \{\mathcal{H}, \rho(t)\}_{Poisson}$. Fluctuations, $\delta\rho(t) = \rho(t) - \langle\rho\rangle$, are expressed in terms of (density-)correlation functions

$$\Phi_{\rho\rho}(q,t) = \langle \delta\rho_q(t)^* \delta\rho_q(0) \rangle$$

long-time limit $f := \phi(t \to \infty)$, $f = 0$ ergodic/fluid, $f > 0$ non-ergodic/glass





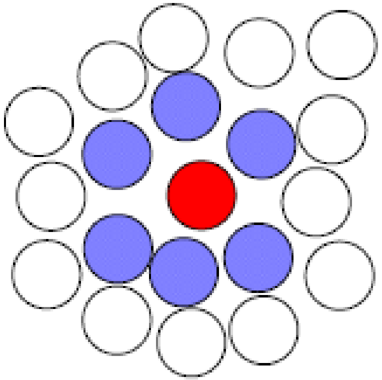
Variables that couple to the density fluctuations (should) show similar dynamics.

Dynamics of Dense Liquids: Approximation/Ansatz necessary

The Liouville equation $\partial_t \rho(t) = \{\mathcal{H}, \rho(t)\}_{Poisson}$ can be reexpressed as an exact integro-differential equation,

$$\frac{1}{\Omega_q^2}\partial_t^2\phi_q(t) + \tau_q\,\partial_t\phi_q(t) + \phi_q(t) + \int_0^t m_q(t-t')\,\partial_{t'}\phi_q(t')\,dt' = 0,\ \tau_q = \nu_q/\Omega_q^2,$$

where $m(t)$ is now hiding all the complications.



$m_q(t)$ is the correlator for fluctuating forces,
forces originate from a *cage* formed by other particles,
cage-dynamics is given by density-fluctuations,

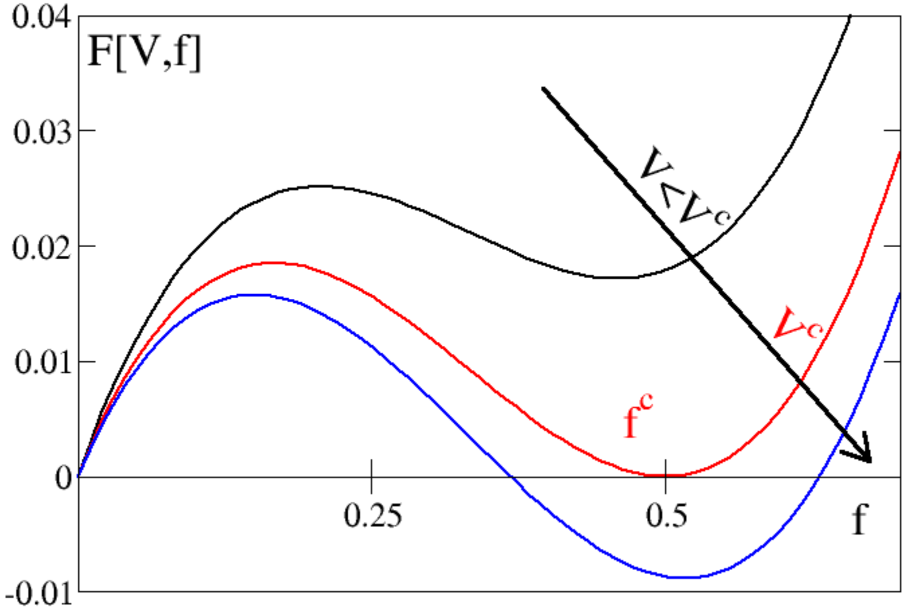
$$\boxed{m_q(t) \text{ given by } \phi_q(t), \quad m_q(t) = \mathcal{F}_q\left[V, \phi_k(t)\right]}$$

$m_q(t)$ is a polynomial in $\phi_q(t)$ with coefficients V.

$$\mathcal{F}_q[\mathrm{V}, \phi_k(t)] = \sum_{\vec{k}+\vec{p}=\vec{q}} V_{q,k\,p}\,\phi_k(t)\phi_p(t),\ V_{q,k\,p} = \rho S_q S_k S_p\{\vec{q}\cdot[\vec{k}\,c_k + \vec{p}\,c_p]\}^2/q^4,$$

Static structure, $S_q = 1/(1-\rho c_q) = S_q(\rho, T, \dots)$, depends on external control parameters and is the Fourier transform of the pair distribution function $g(r)$.

Dynamics of Dense Liquids: Glass-Transition Singularities



$$\frac{f_q}{1-f_q} = \mathcal{F}_q[\mathbf{V}, f_k]$$

Transition from f = 0 to f > 0 as natural outcome:
End of the fluid regime,
Bengtzelius, Götze, Sjölander, MCT (1984)
Singularity at transition provides small parameter
to calculate exponents and dynamics
W. Götze, Complex Dynamics of Glass-Forming Liquids:
A Mode-Coupling Theory (2009)

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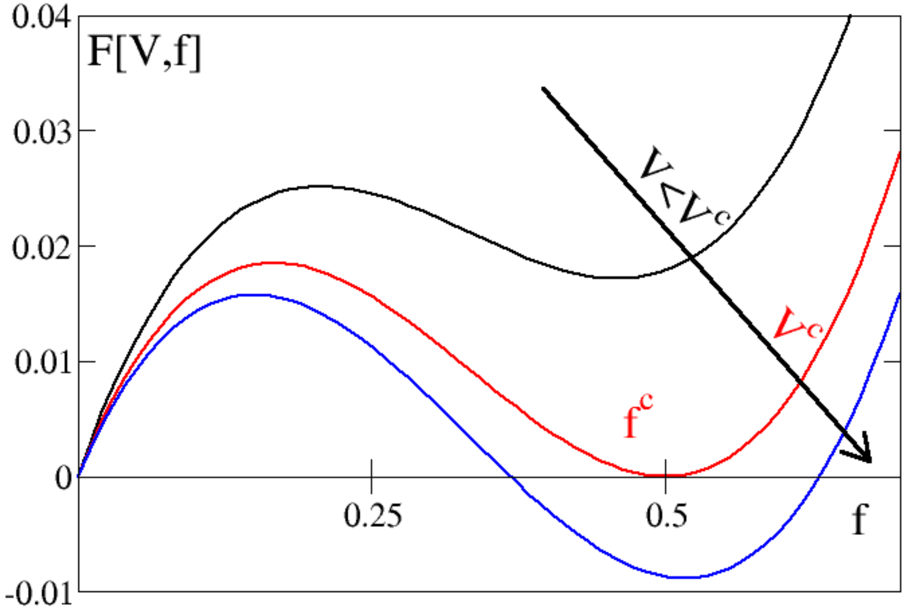

$$\frac{f_q}{1-f_q} = \mathcal{F}_q[\mathbf{V}, f_k]$$

Classification of Singularities:
Roots of simple Polynomials.
Quadratic singularity:
liquid-glass transition
Cubic singularity:
endpoint of glass-glass transition lines
Quartic singularity:
emergence of glass-glass transition lines

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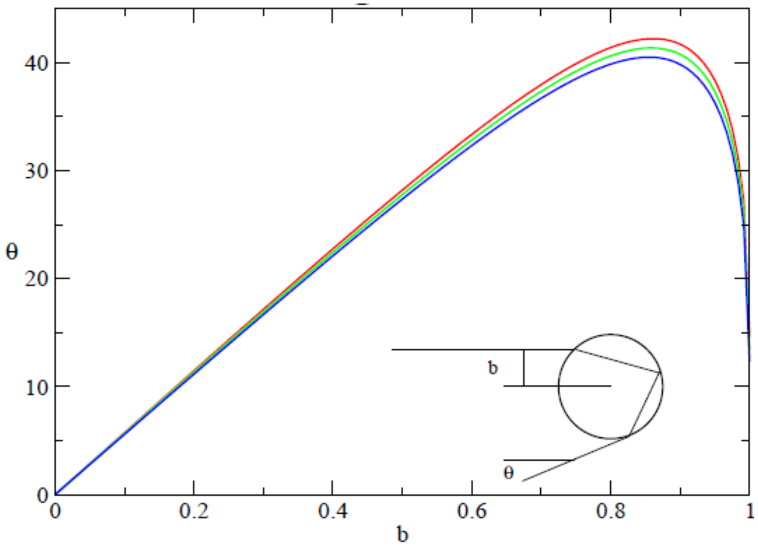
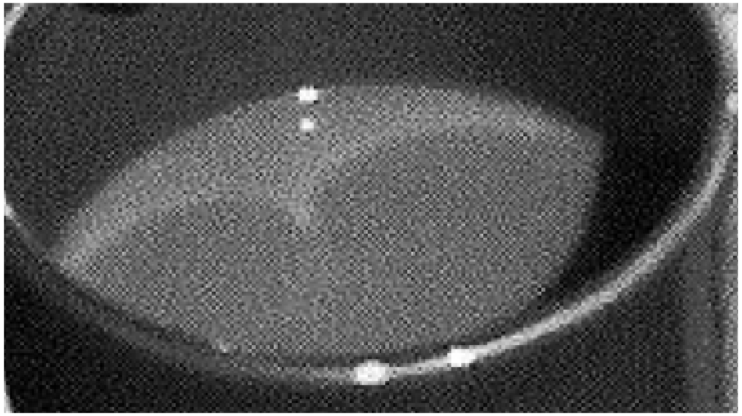
Glass-Transition Singularities in a Cup of Coffee and in Rainbows



Descartes (1638), cf Berry (1988)



Two lines of folds meet at a cusp

$$\frac{f_q}{1-f_q} = \mathcal{F}_q[\mathbf{V}, f_k]$$

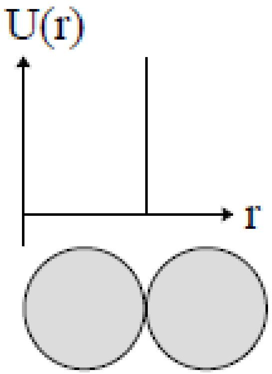
Classification of Singularities: Roots of simple Polynomials.

Quadratic singularity: liquid-glass transition

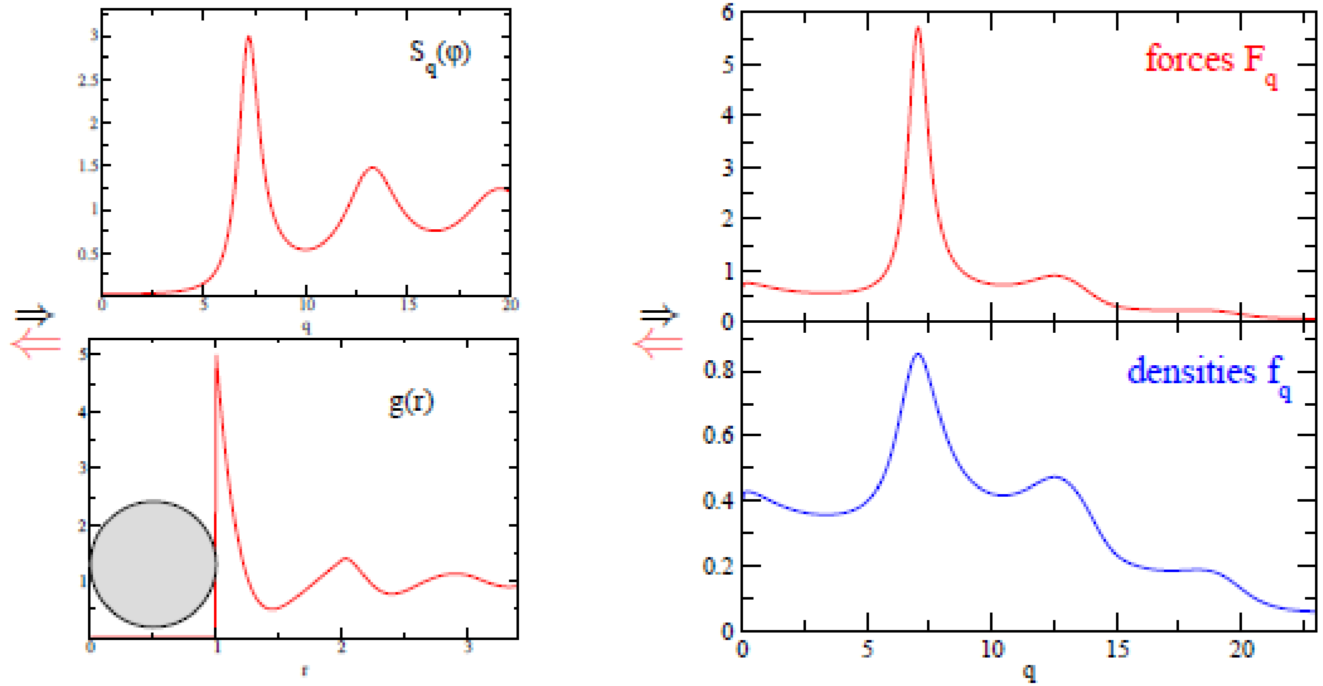
Cubic singularity: endpoint of glass-glass transition lines

Quartic singularity: emergence of glass-glass transition lines

Theoretical Picture: Glass Transition in Hard Spheres



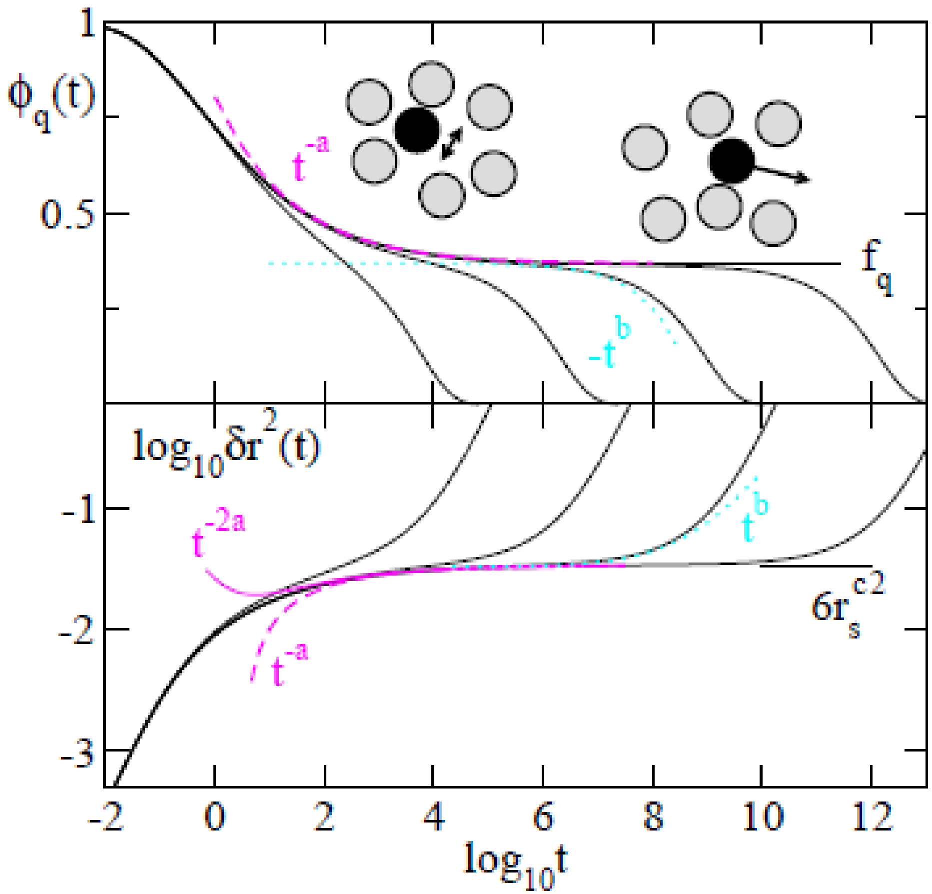
control parameter
packing fraction φ



Glass transition at $\varphi^c = 0.52$ (exp: $\varphi^c = 0.58$). Arrest of densities implies arrest of forces and is accompanied by a finite yield stress. Length scale of particle diameter dominates transition.

Geometry of arrested state encoded in glass-form factors f_q

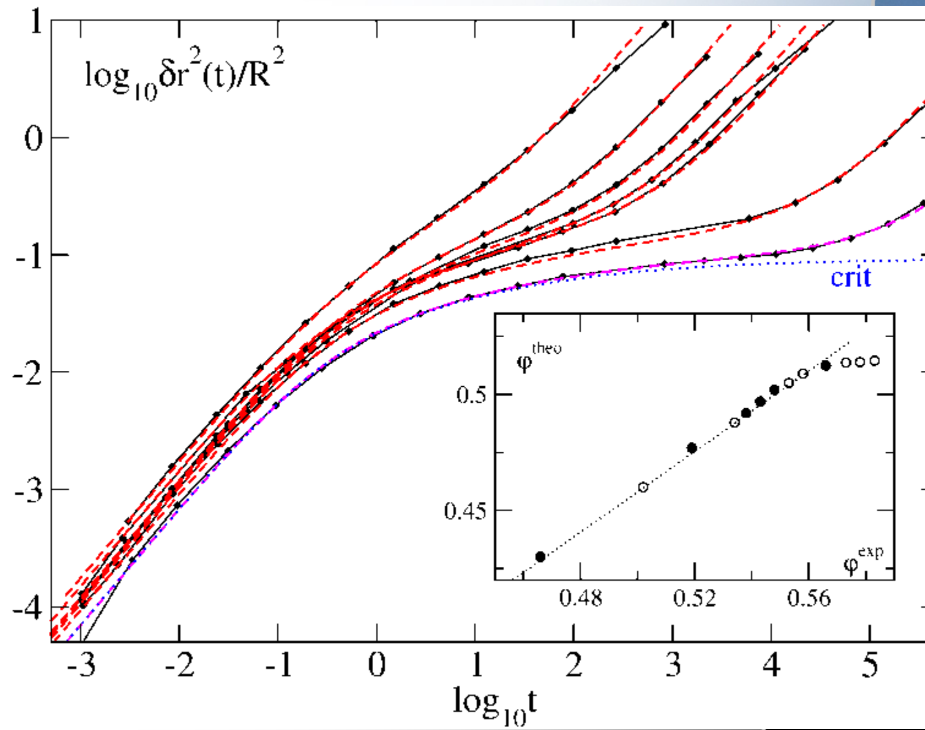
Theoretical Picture: Glassy Dynamics for Hard Spheres

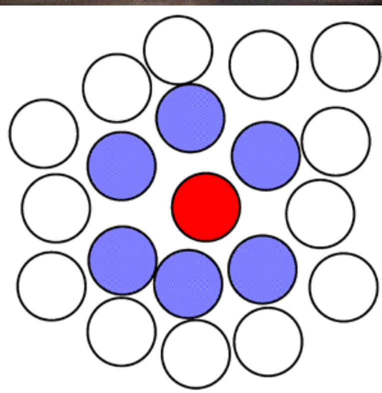


two-step process around a plateau for correlator and mean-squared displacement; finite localization length r_s^c at the transition; scaling of the solutions asymptotic power laws:
t^{-a} and t^b;

Localization with length scale close to Lindemann criterion

Glass Transition in Colloidal Hard Spheres (Equilibrium)





58% volume fraction

Mean-Squared Displacement (MSD)

van Megen et al (1998) ; M. Sperl (2005)

Glass Transition: density fluctuations persistent, diffusion vanishes

Dense Equilibrium Fluids Beyond Hard Spheres

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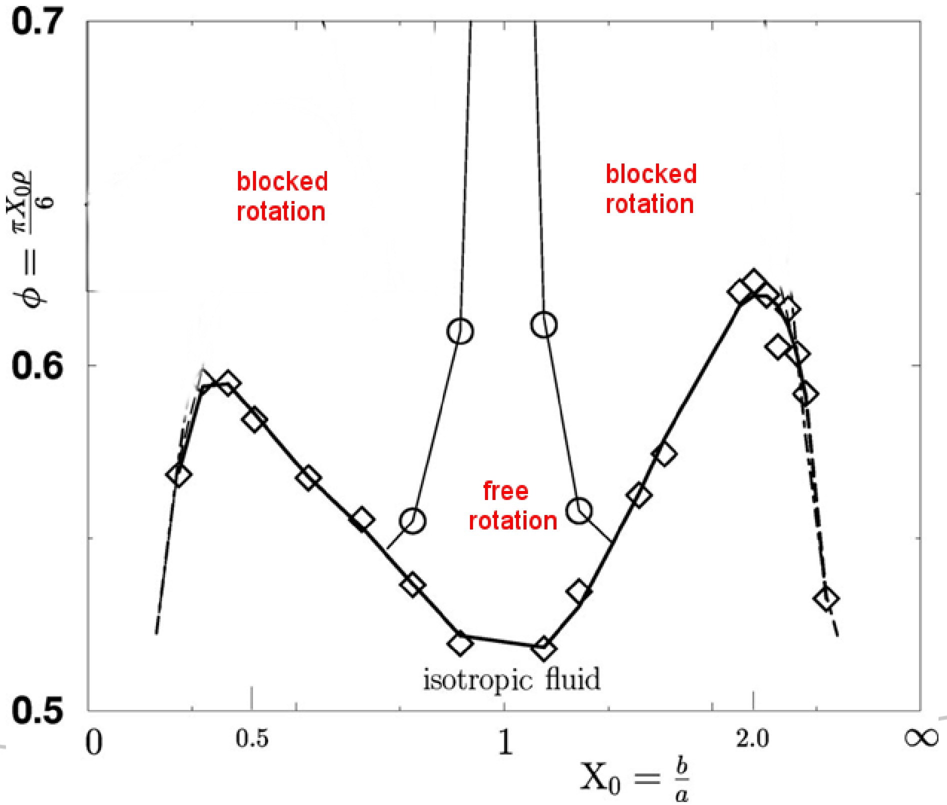
Dynamics of Dense Liquids: Beyond Hard Spheres

Extensions of microscopic calculations:

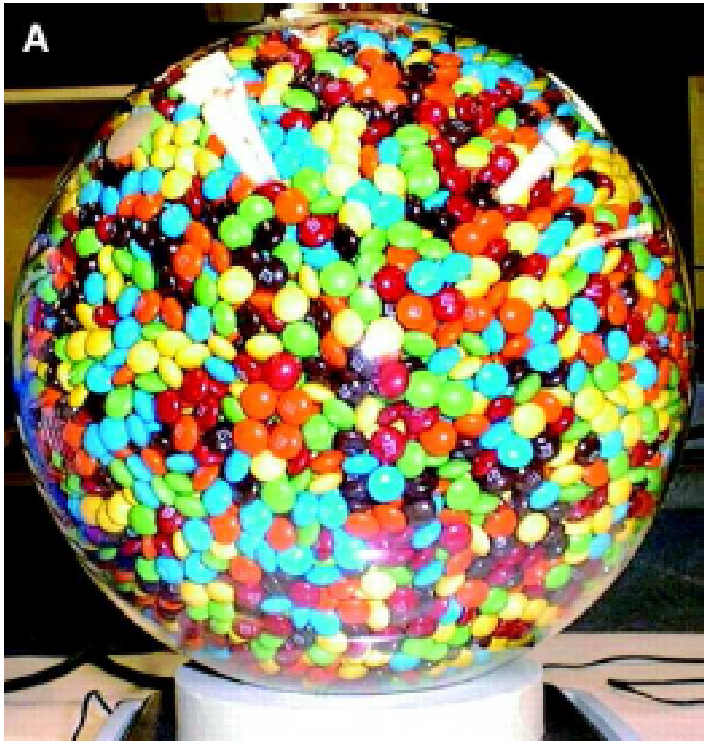
- **hard disks (2D)**
- **(binary) mixtures**
- **(short-range) attraction**
- **charged systems**
- **dumbbells and ellipsoids**



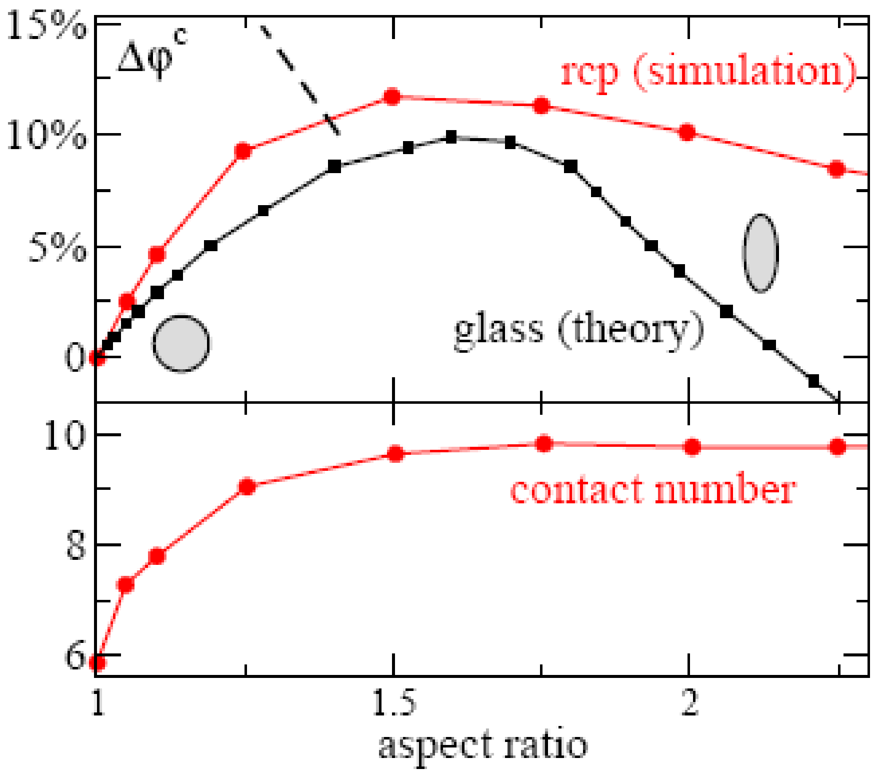
Letz/Schilling/Latz, PRE (2000)

- symmetry of transition lines around sphere case
- smooth variation from sphere
- freezing of rotation inside regime of arrested translation: continuous (type-A) transition

Beyond Hard Spheres: Ellipses, Ellipsoids, and Dumbbells



rcp: Donev et. al;
2D: Delaney et. al



MCT: Latz/Letz/Schilling,
similar: dumbbells Götze/Chong;
evolution of contacts coincides
with MCT-type-A transition

Dynamics of Dense Liquids: Beyond Hard Spheres

Extensions of microscopic calculations:

- **hard disks (2D)**
- **(binary) mixtures**
- **(short-range) attraction**
- **charged systems**
- **dumbbells and ellipsoids**
- **confinement (2D/3D crossover)**
- **shear**
- **How about granular matter?**

Dense Granular Fluids

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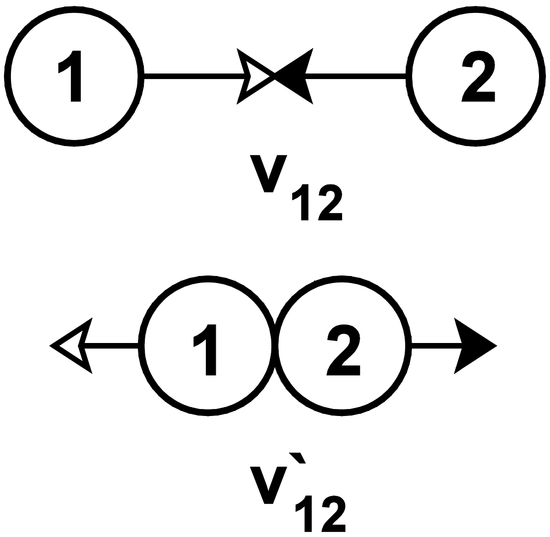
Why is granular matter a challenge?

Energy loss at collisions: coefficient of restitution



$$\hat{n} \cdot \mathbf{v}'_{12} = -\varepsilon \hat{n} \cdot \mathbf{v}_{12}$$

Challenges:

- **detailed balance violated microscopically, operator hermiticity broken**
- **reasonable thermostat with momentum conservation**
- **pseudo-Liouville operator formalism for dissipative hard spheres**

Glass Transition in Driven Granular Matter

$$\mathcal{L}_+(\varepsilon) = \mathcal{L}_0 + \mathcal{L}'_+(\varepsilon) + \mathcal{L}_{dr} \qquad \mathbf{v}'_i(t) = \mathbf{v}_i(t) + v_{dr}\xi(t)$$

yields for granular MCT:

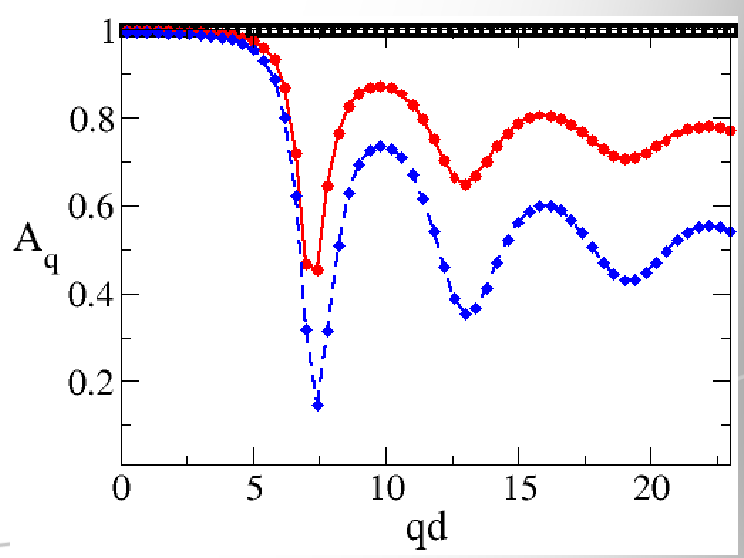
$$\left(\partial_t^2 + \nu_q \partial_t + \Omega_q^2\right)\phi_q(t) = -\int_0^t d\tau m_q(t-\tau)\partial_\tau \phi_q(\tau)$$

$$m_q[\phi](t) = [1 + \frac{1-\varepsilon}{1+\varepsilon}S_q]^{-1}\frac{nS_q}{q^2}\int d^3k\, V_{\vec{q}\vec{k}}\phi_{\vec{k}}(t)\phi_{\vec{q}-\vec{k}}(t)$$

$$\nu_q = -i\omega_E \frac{1+\varepsilon}{2}[1 - j_0(qd) + 2j_2(qd)]$$

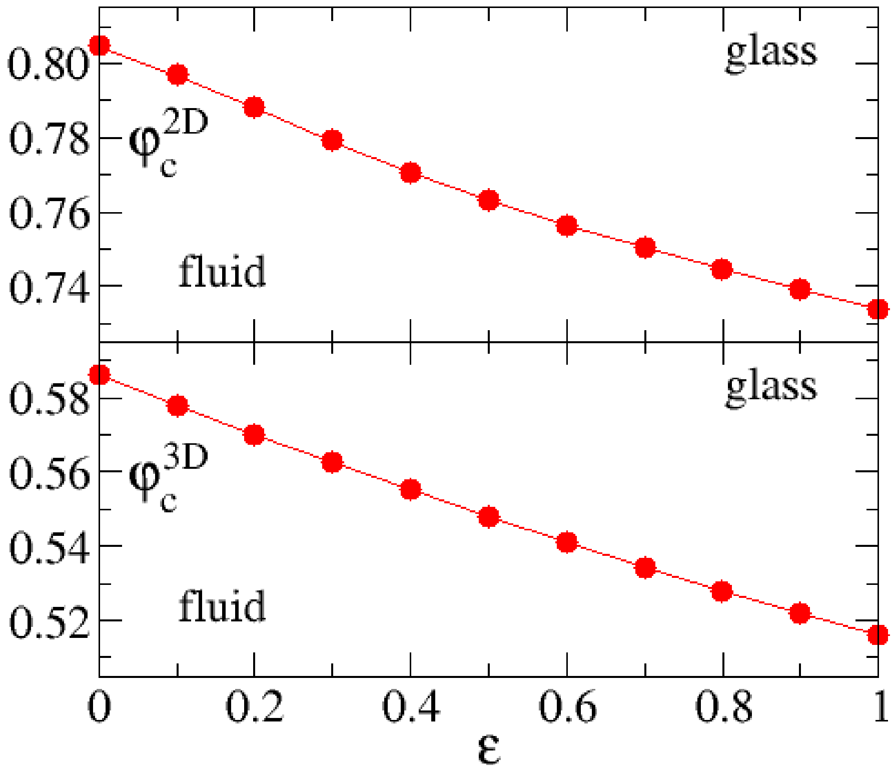
$$\Omega_q^2 = \frac{q^2 v_0^2}{S_q}\left(\frac{1+\varepsilon}{2} + \frac{1-\varepsilon}{2}S_q\right)$$

MCT equations with prefactor Aq (1.0, 0.5, 0.0) that weakens cage



Granular Glass Transition

- same glass-transition singularities exist as in equilibrium
- dissipation breaks universal glassy dynamics
- shift in glass-transition density with dissipation



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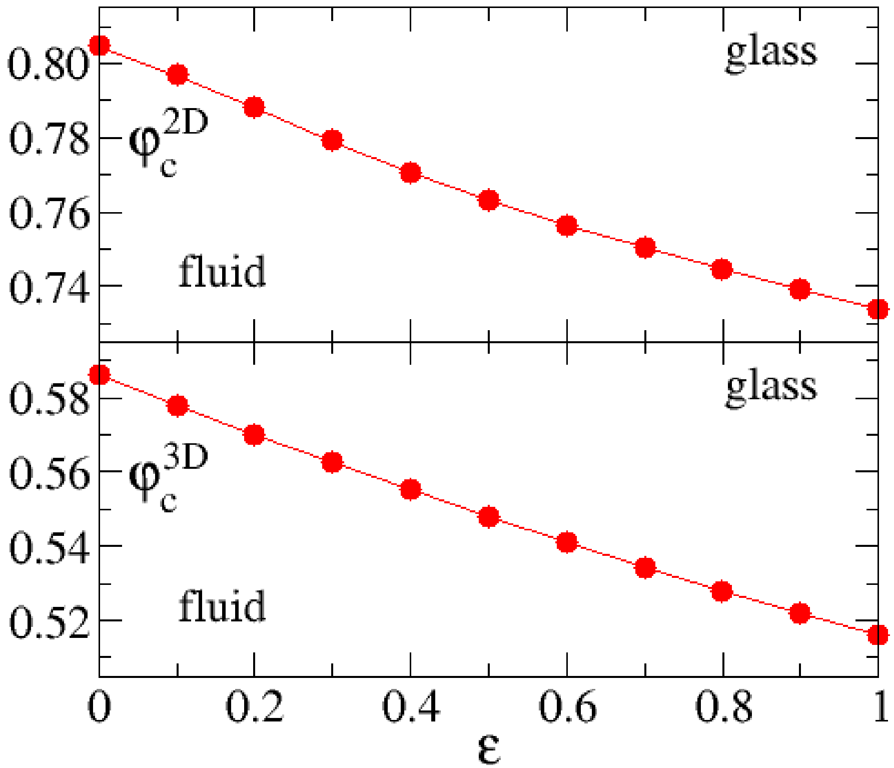


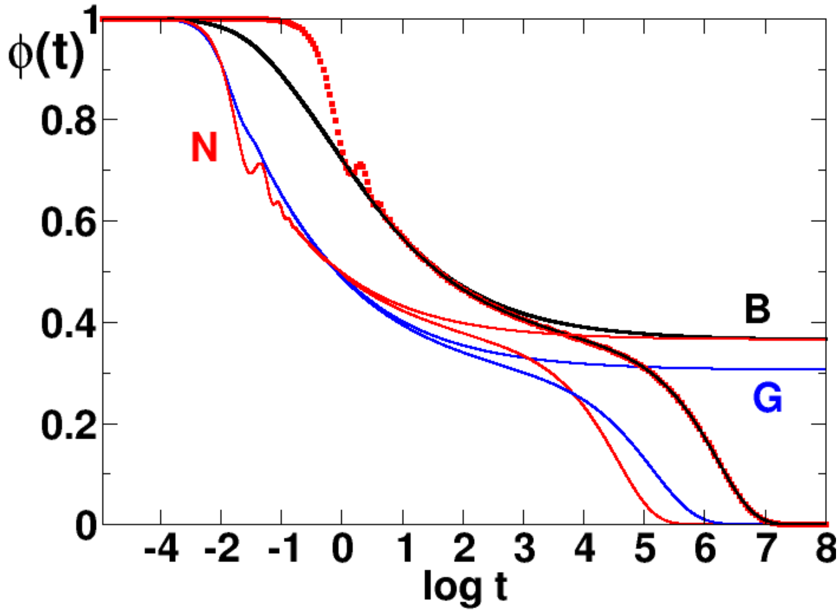
Sperl/Kranz/Zippelius:

Phys. Rev. Lett. **104**, 225701 (2010)
Europhys. Lett. **98**, 28001 (2012)
Phys. Rev. E **87**, 022207 (2013)

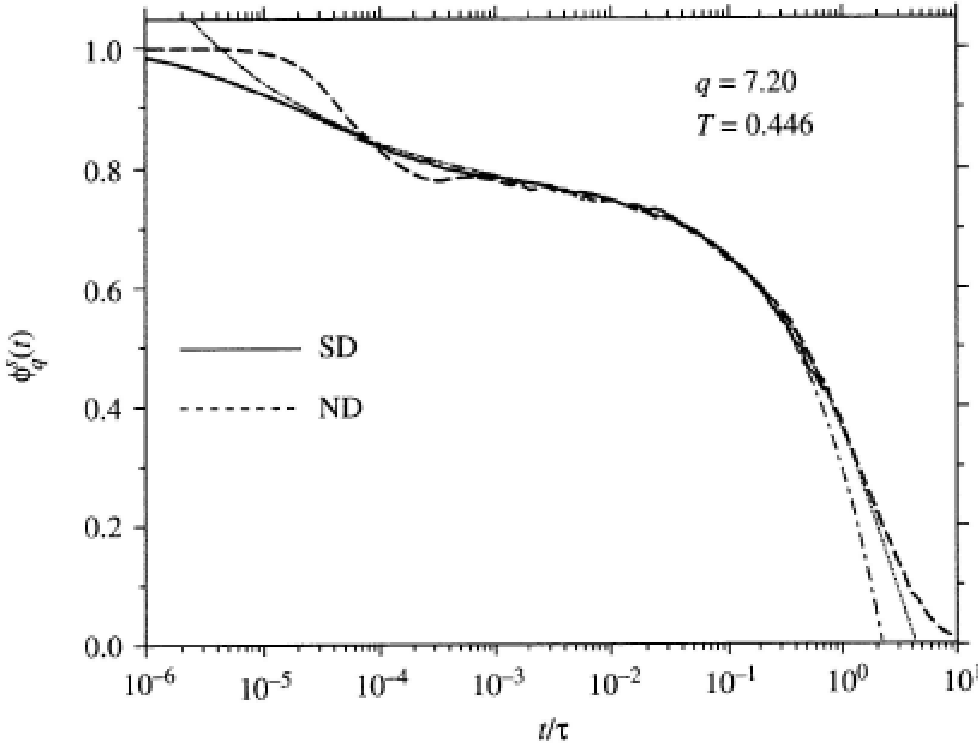
DFG-Forschergruppe 1394:
Nonlinear response to
probe vitrification

FOR1394

Granular Glass Transition: Dynamics

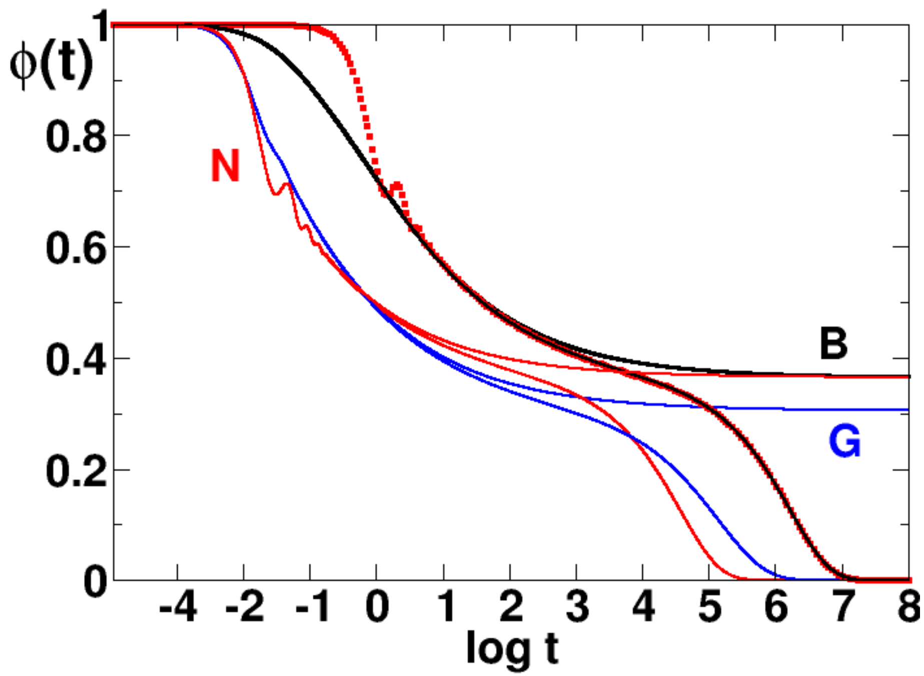


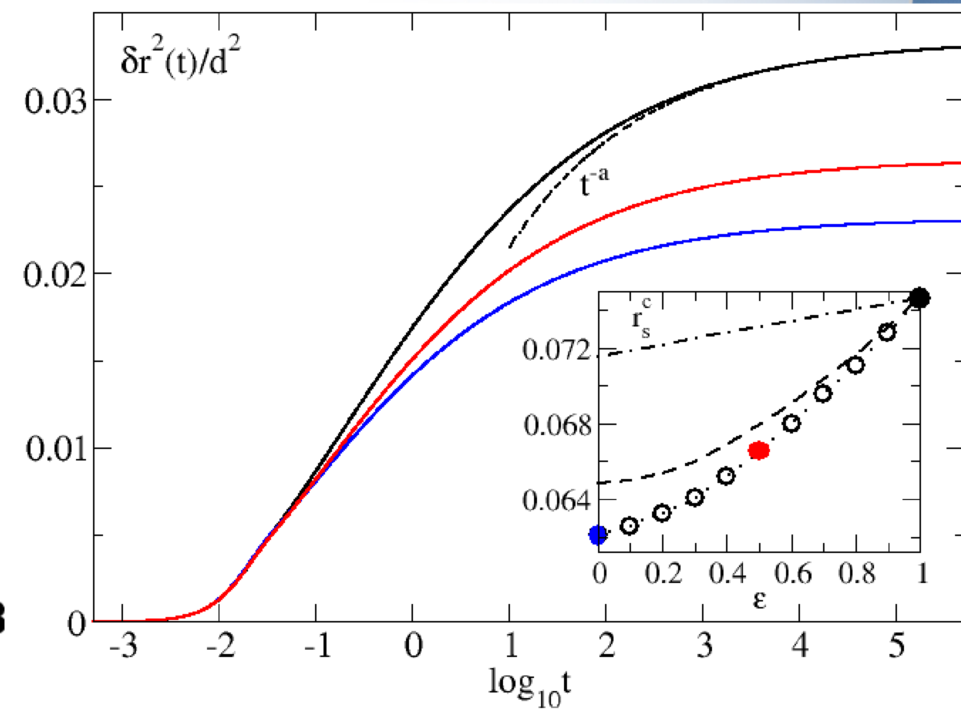
Gleim, Kob, and Binder (1998)



- glassy dynamics overall similar to Newtonian case
- not universal like Newtonian or Brownian dynamics

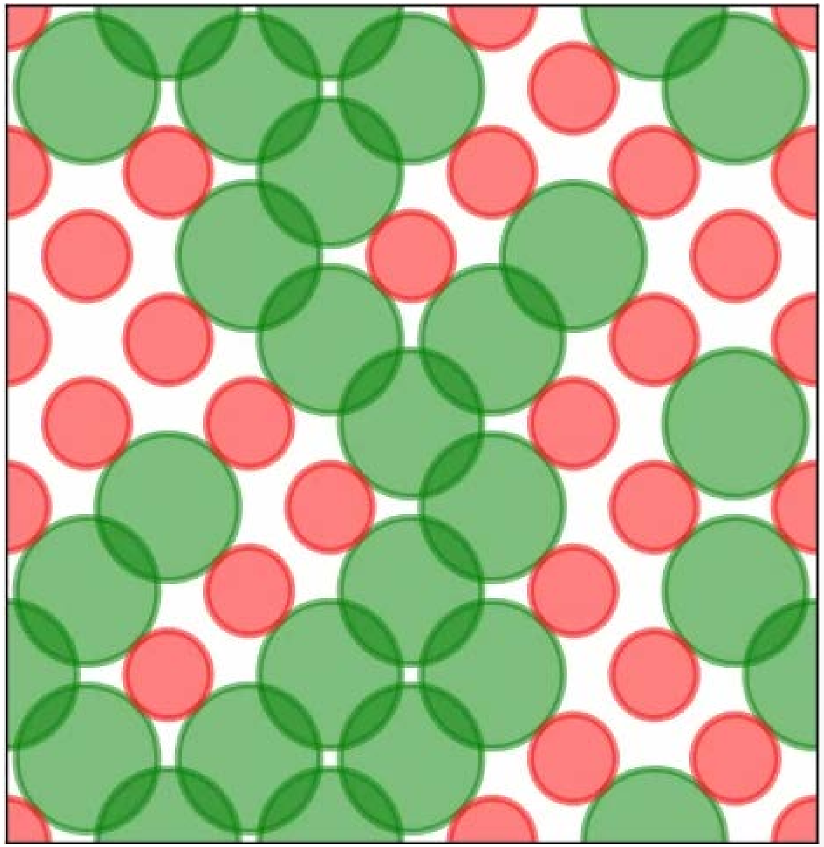
Granular Glass Transition: Dynamics





- glassy dynamics not universal like Newtonian or Brownian dynamics
- localization length decreases with increasing dissipation
- decrease in localization length more drastic than density increase alone

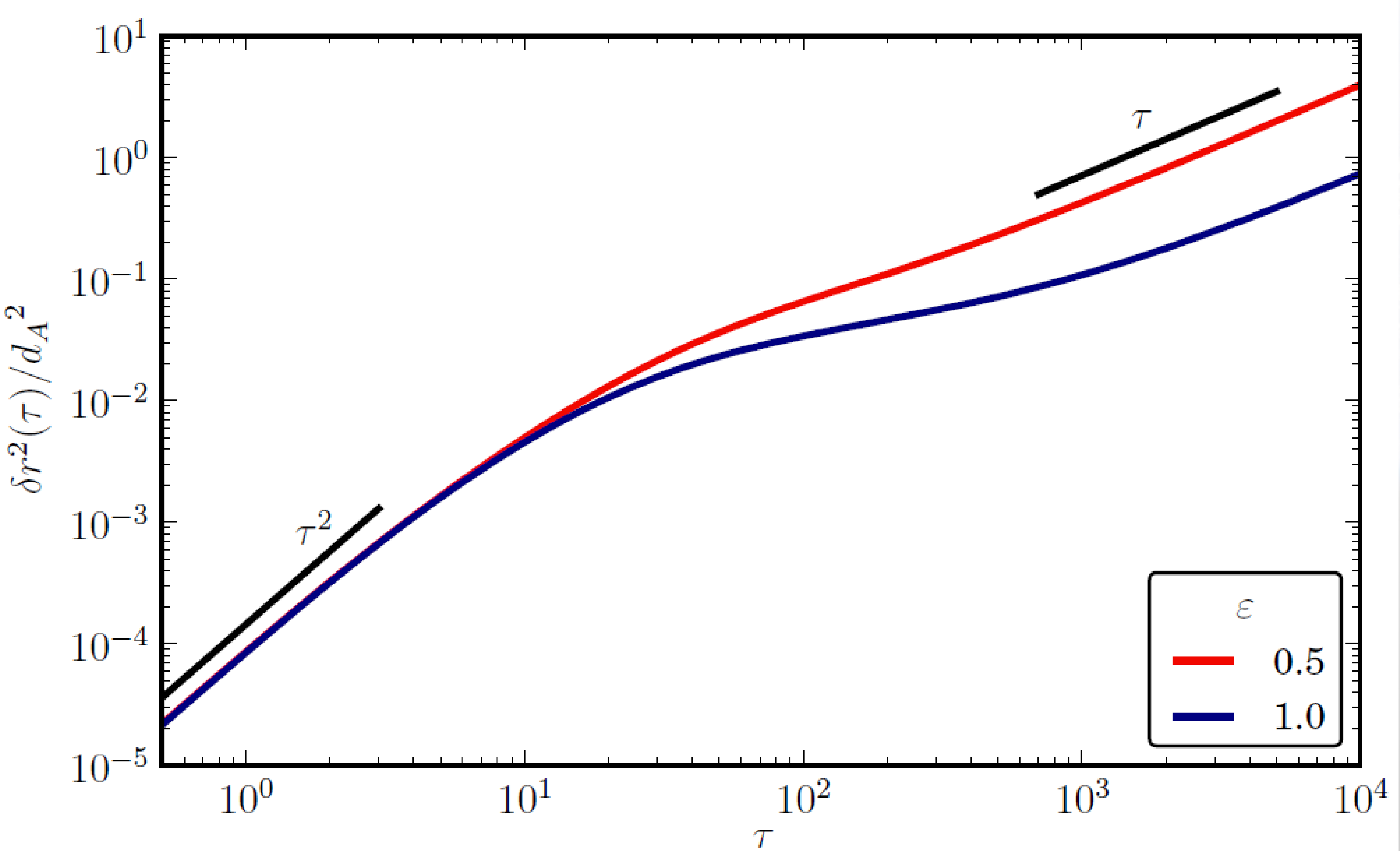
Granular Glass Transition: Simulation



Molecular Dynamics Simulation, parameters:

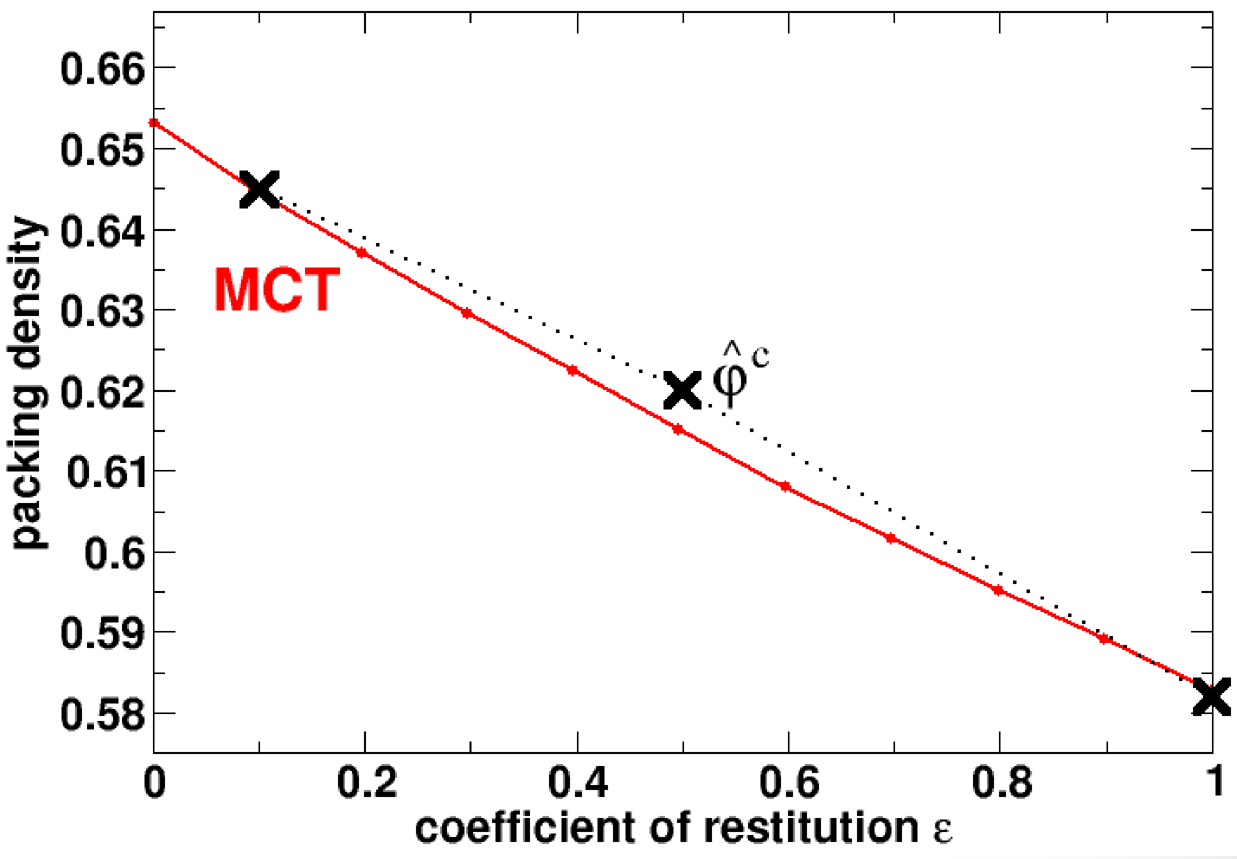
- **every 100 MD steps, 10 particle pairs are kicked in opposite directions**
- **size ratio 0.8, number concentration 0.5**
- **10000 particles**

Melting by Dissipation



- average kinetic energy set equal, identical ballistic regime
- packing fraction 0.58 for both dissipations
- diffusion 10 times faster for higher dissipation

Soft-Sphere: Glass Transition and MCT



Theory and molecular dynamics simulation agree well

Beyond Liquid-Glass

Transition Singularities

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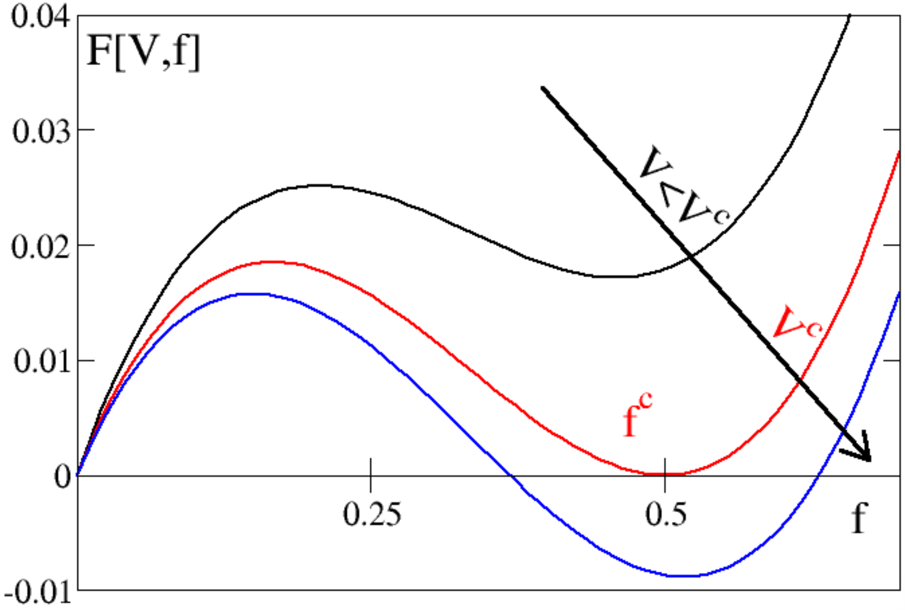
Higher-Order Singularities

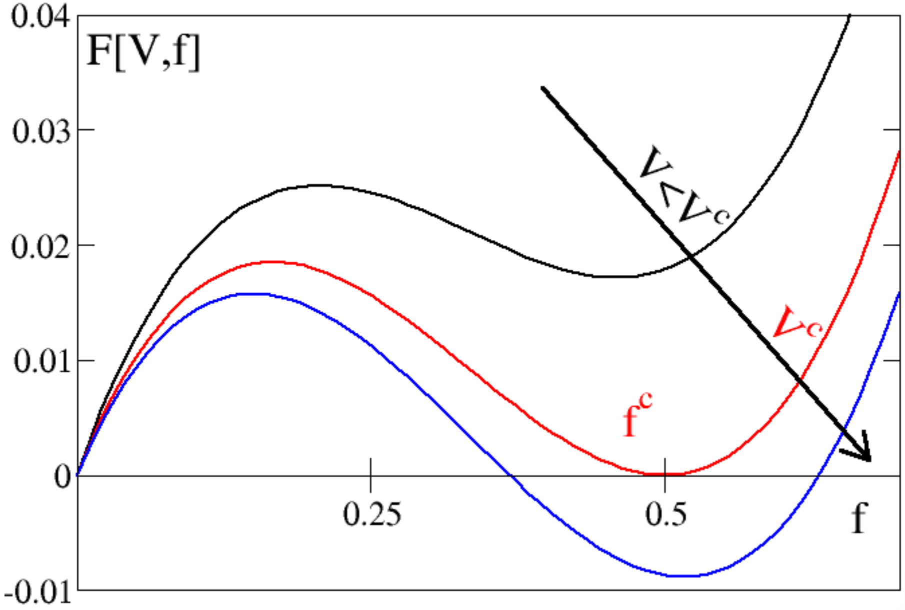
$$\frac{f_q}{1-f_q} = \mathcal{F}_q[\mathbf{V}, f_k]$$



How to get higher-order singularities?

Higher-Order Singularities

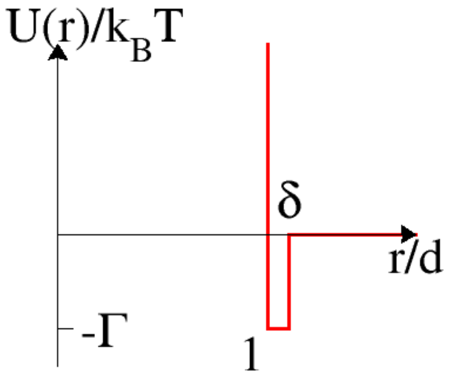
$$\frac{f_q}{1-f_q} = \mathcal{F}_q[\mathbf{V}, f_k]$$

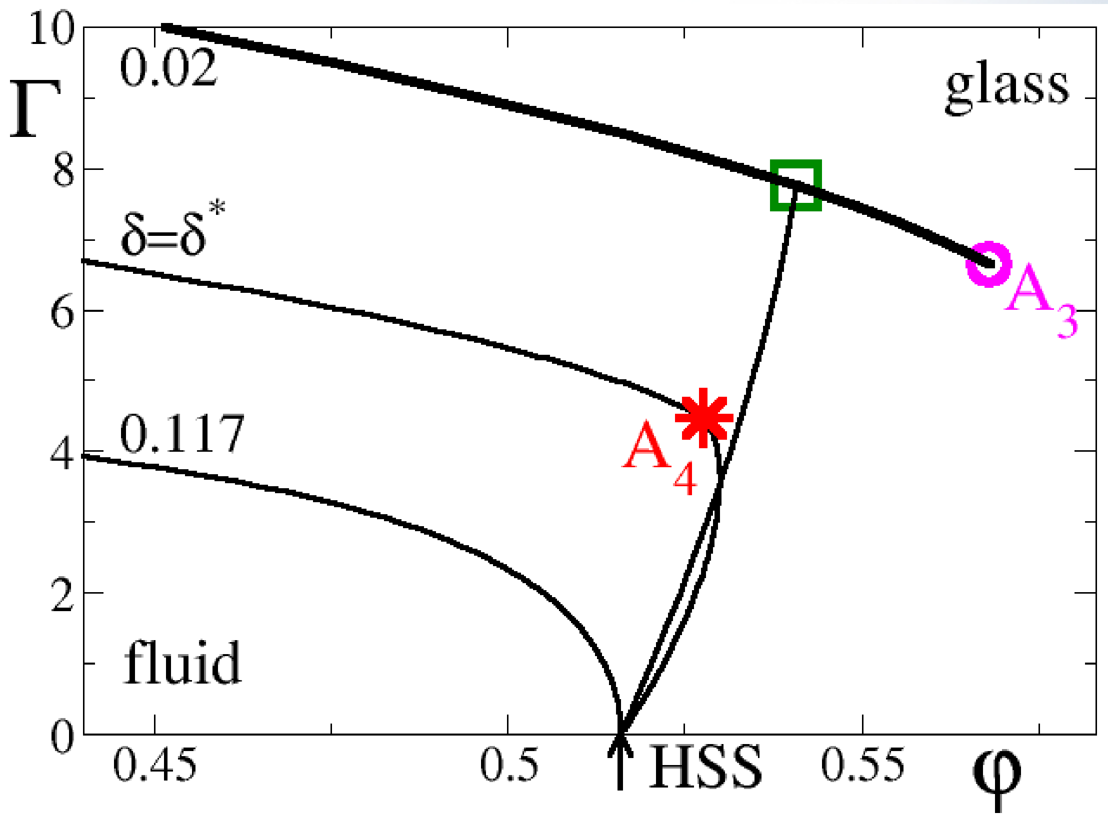


How to get higher-order singularities?

Competing mechanisms of glassy arrest

Higher-Order Singularities: Square-Well System



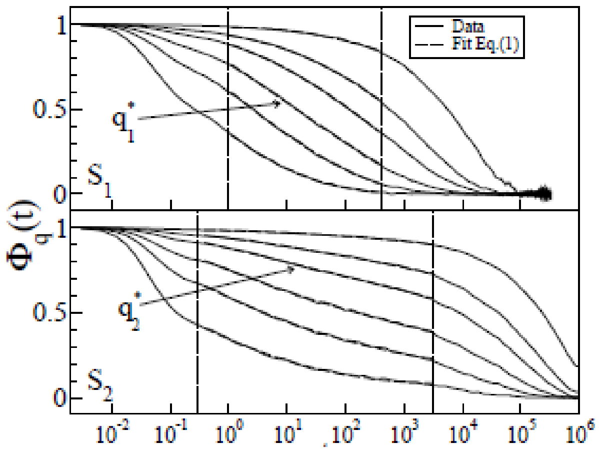


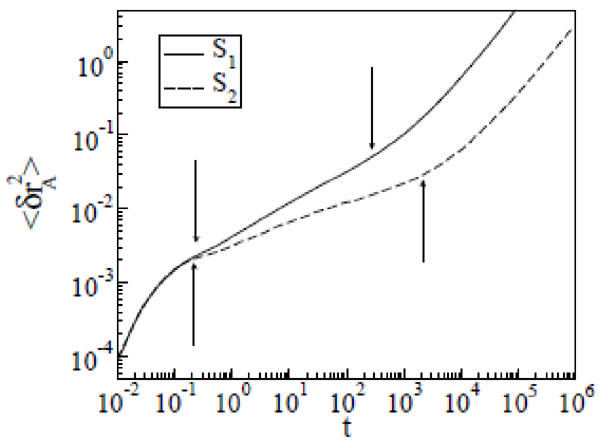
Competition between repulsion and attraction

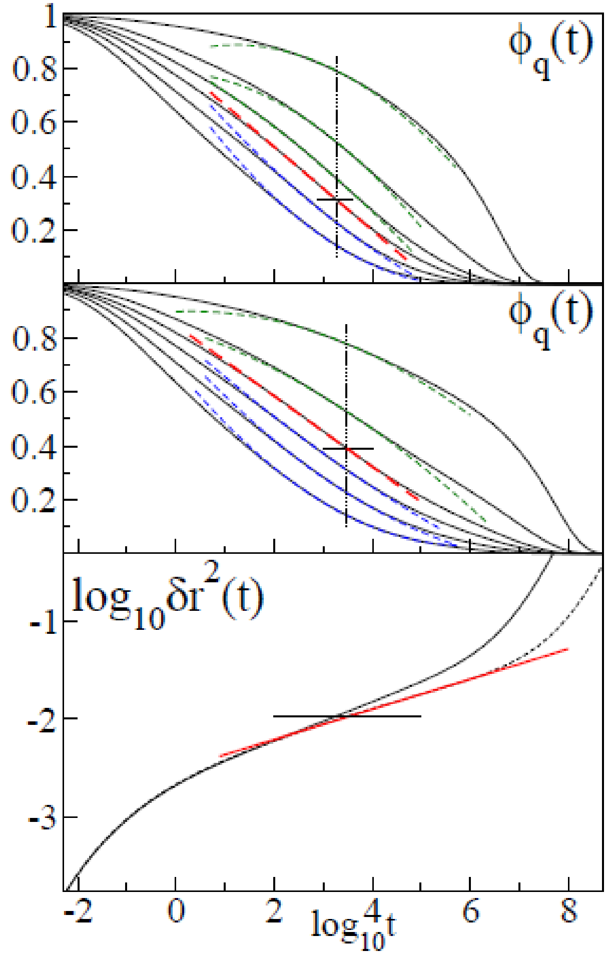
Swallowtail scenario

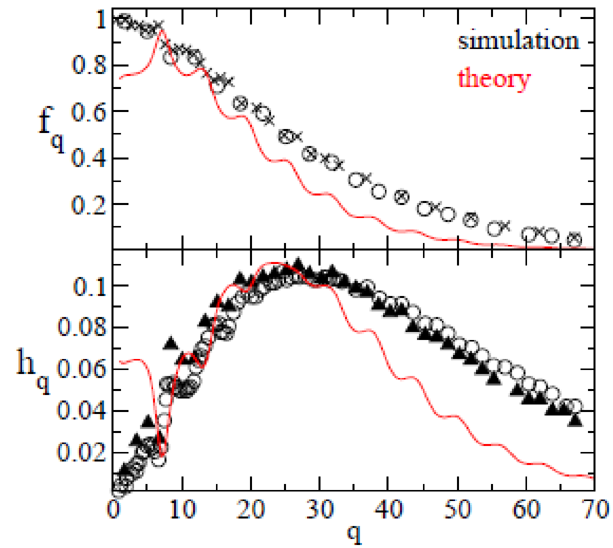
Two-step decay replaced by logarithmic relaxation

Higher-Order Singularities in SWS: MD Simulation and Theory







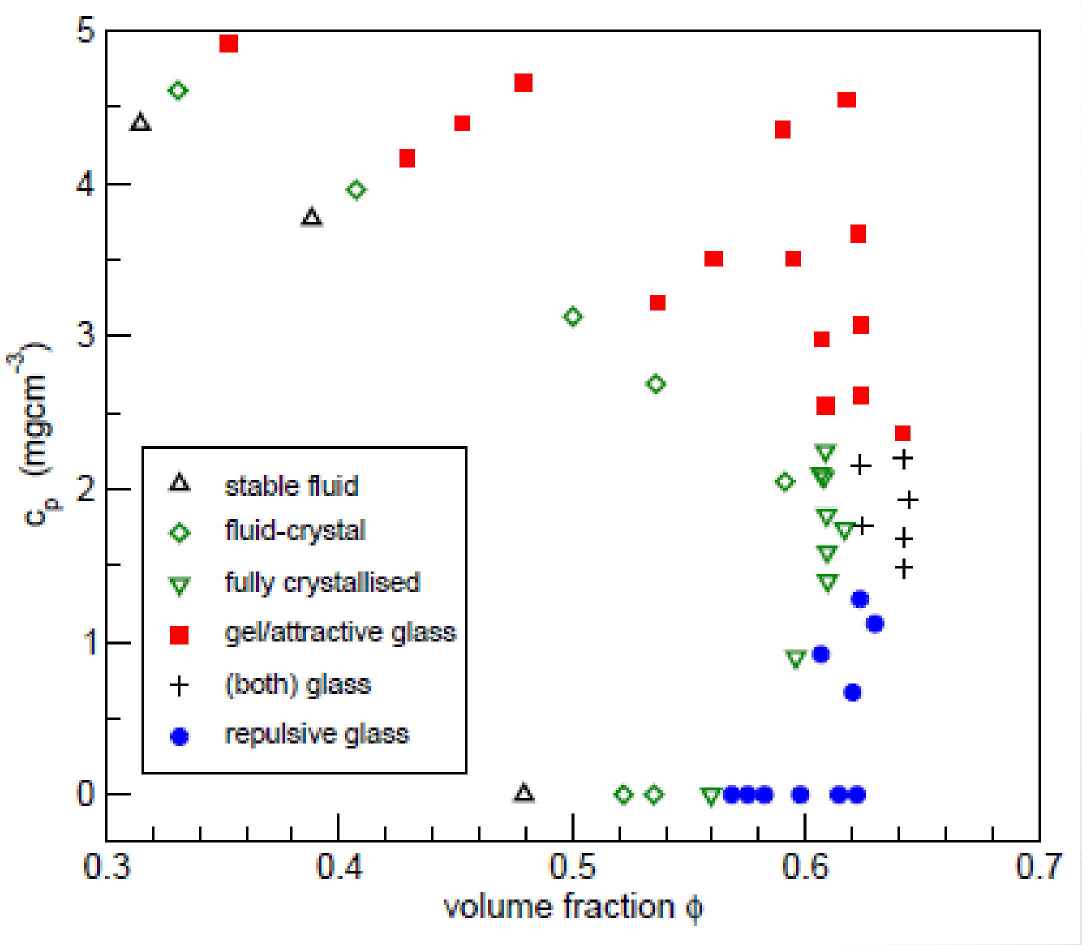


logarithmic decay for $q_1^* = 23.5$, $q_2^* = 16.8$,

deviation in f_q and h_q:
width in q: S_q input,
mixture effect for $q < 7$

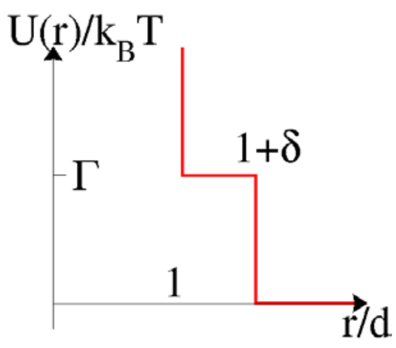
Sciortino et al (2003): simulation (left) agrees well with theory (middle)

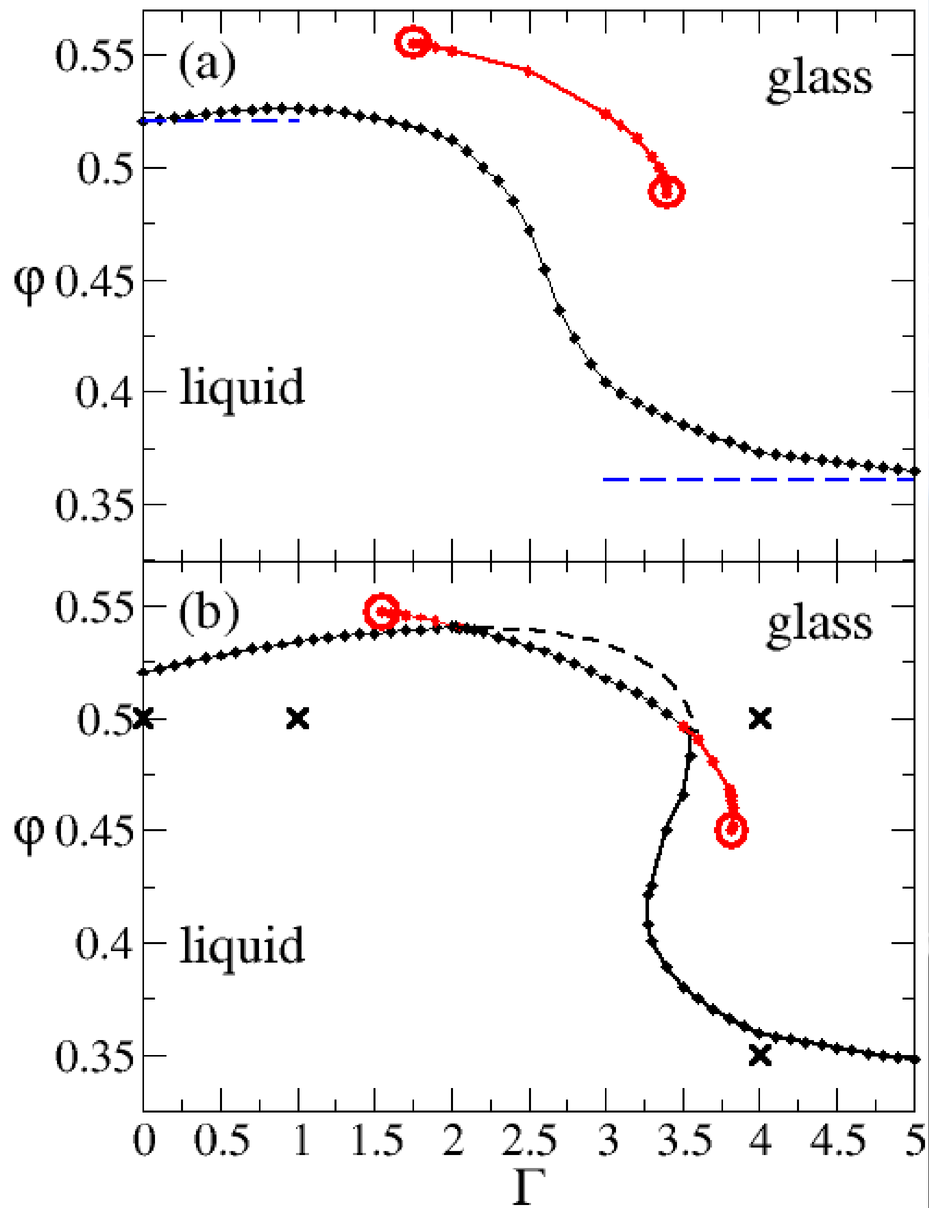
Higher-Order Singularities in SWS: Colloidal Suspension



Pham et al (2004)

Higher-Order Singularities: Square-Shoulder System

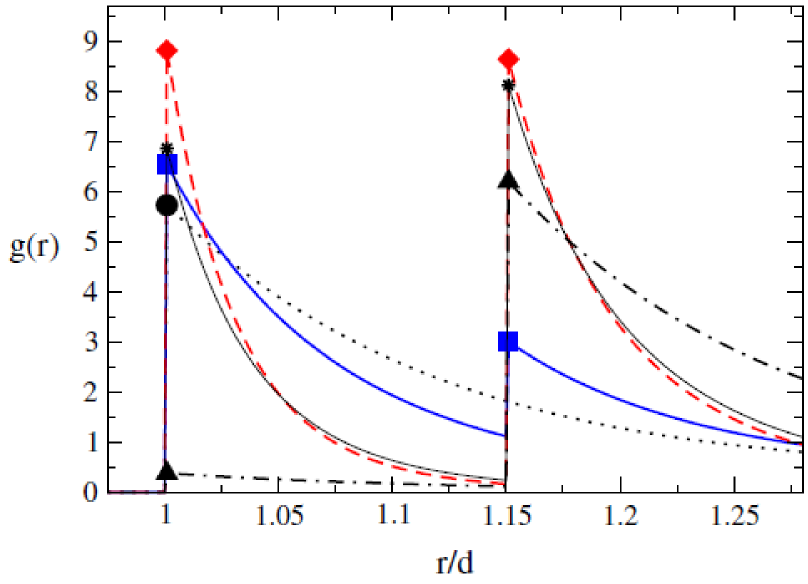




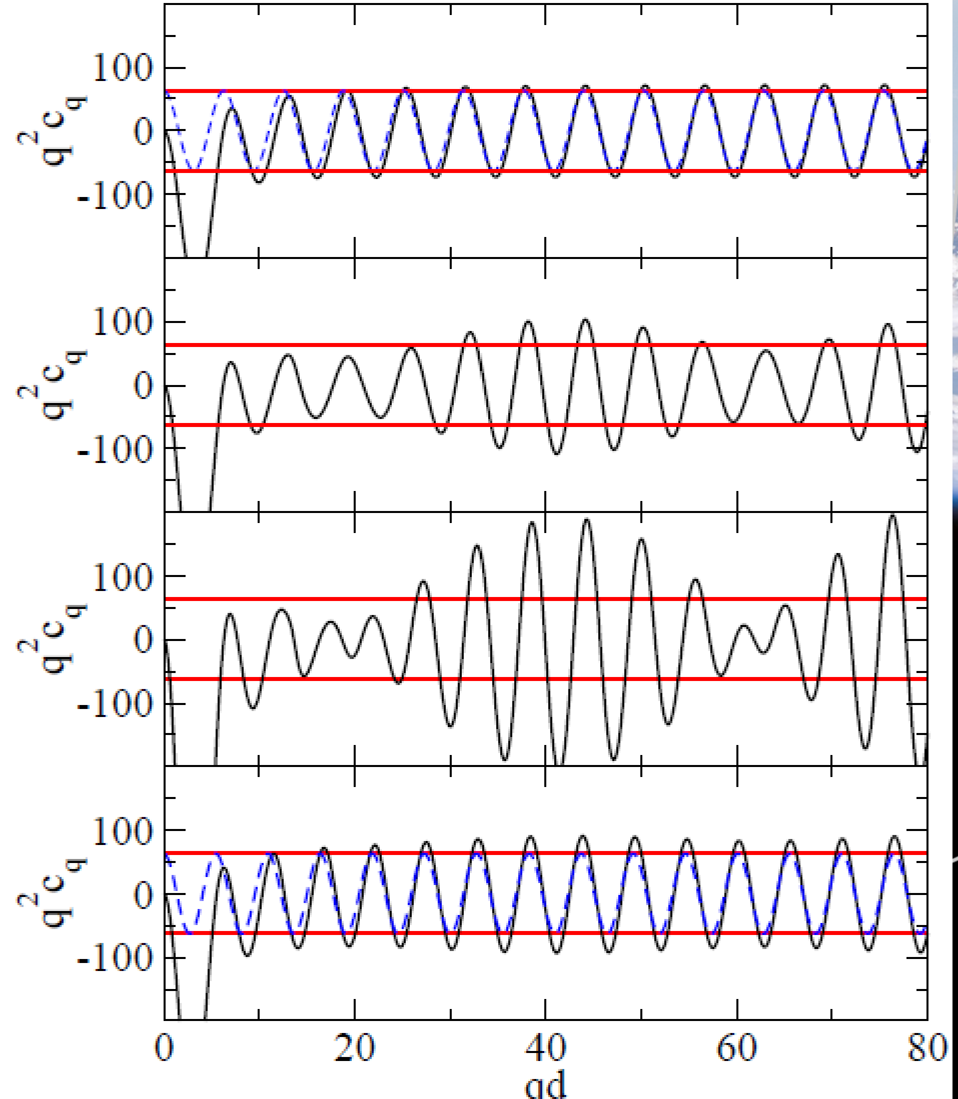
Competition between
two repulsive length scales
(a) δ = 0.13, (b) 0.15
Sperl, Zaccarelli, Sciortino, Kumar,
Stanley, PRL (2010)

Double endpoints
inside the glass regime

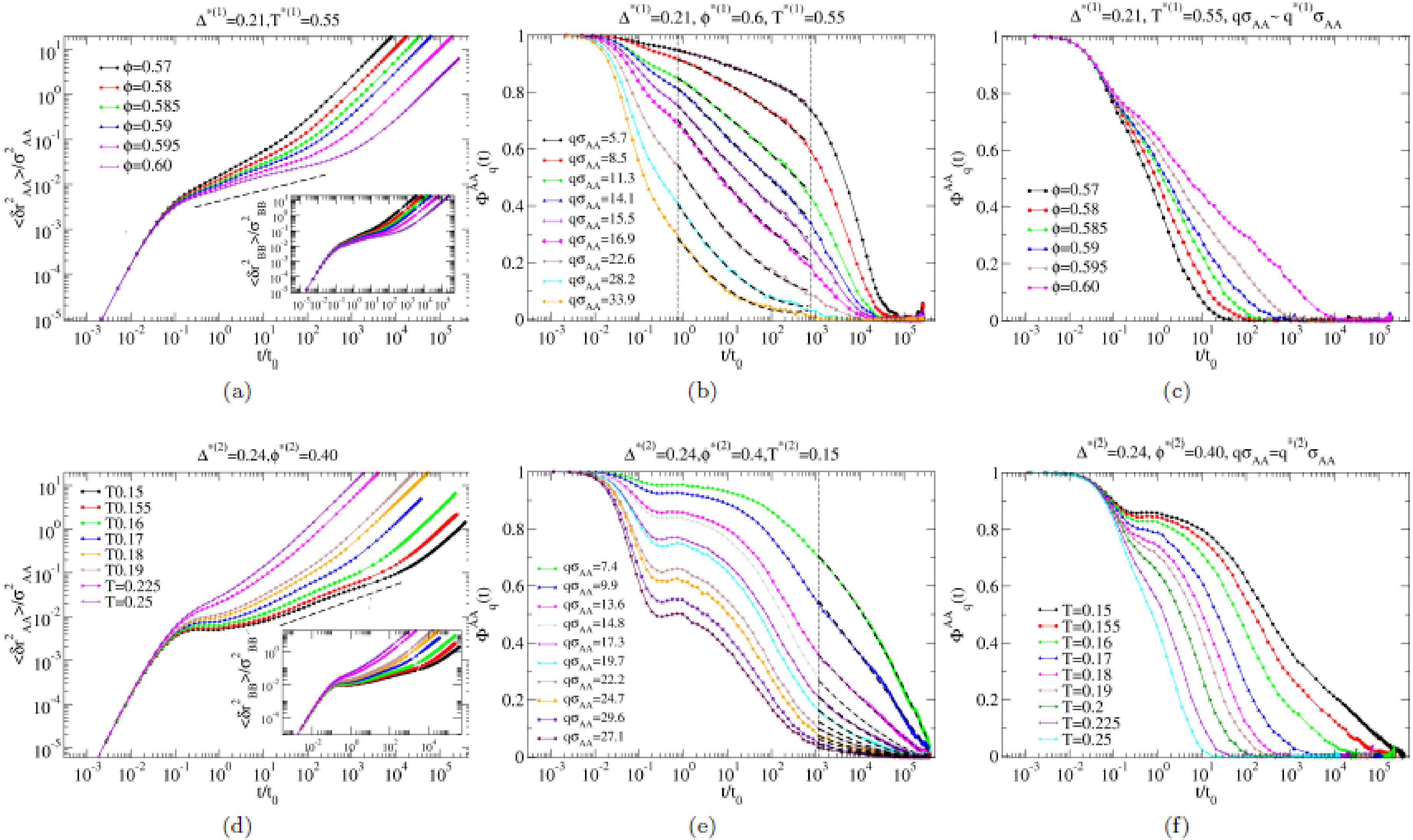
Higher-Order Singularities in the SSS: Beating in Static Structure



Two competing length scales show up as beating in the static structure factor: Only when both cores are equally important, a glass-glass transition can occur.

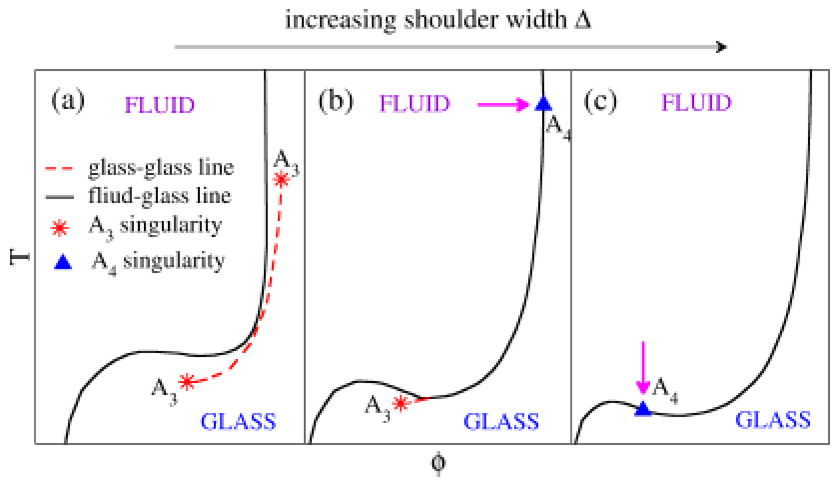


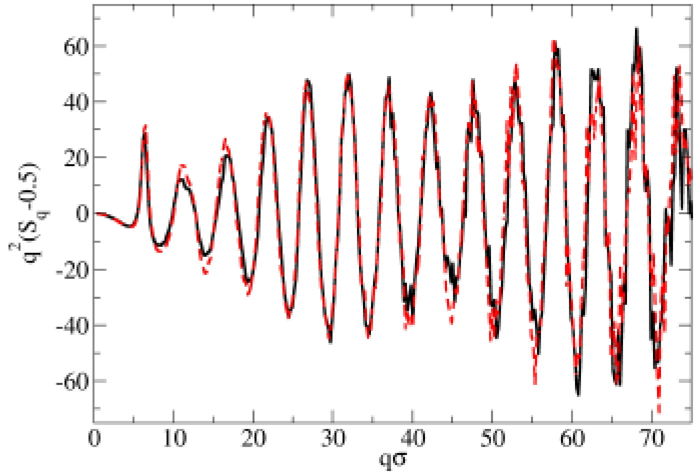
Higher-Order Singularities: Computer Simulation of SSS

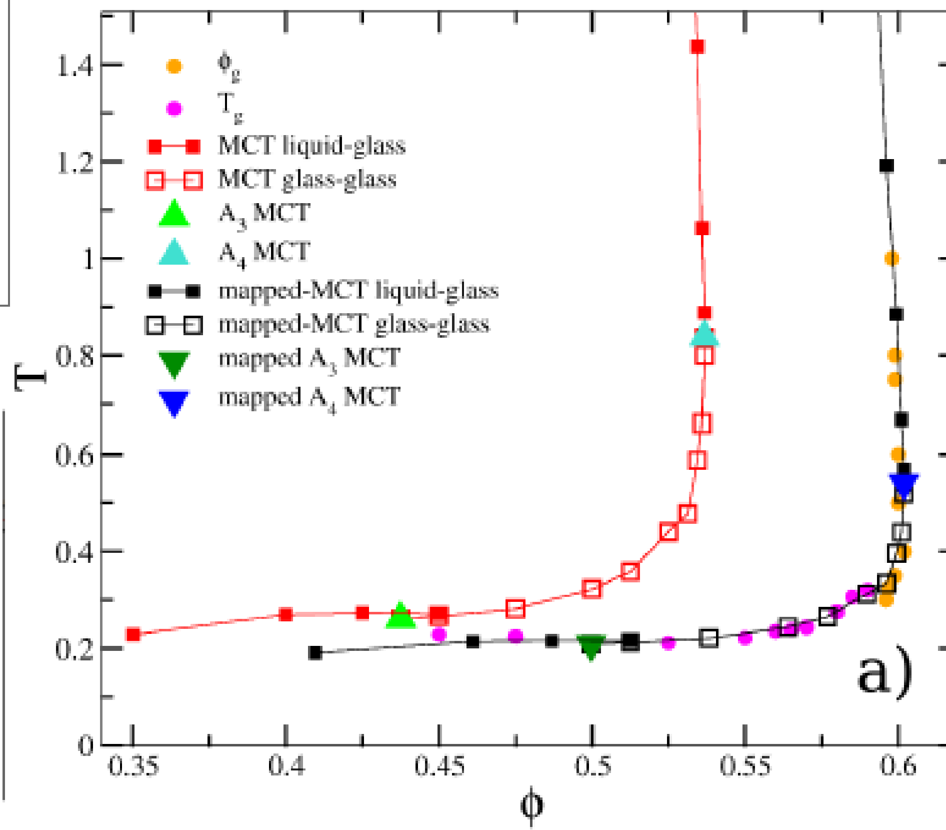


N. Gnan, G. Das, M. Sperl, F. Sciortino, E. Zaccarelli, arXiv:1407.3917

Higher-Order Singularities: Computer Simulation of SSS

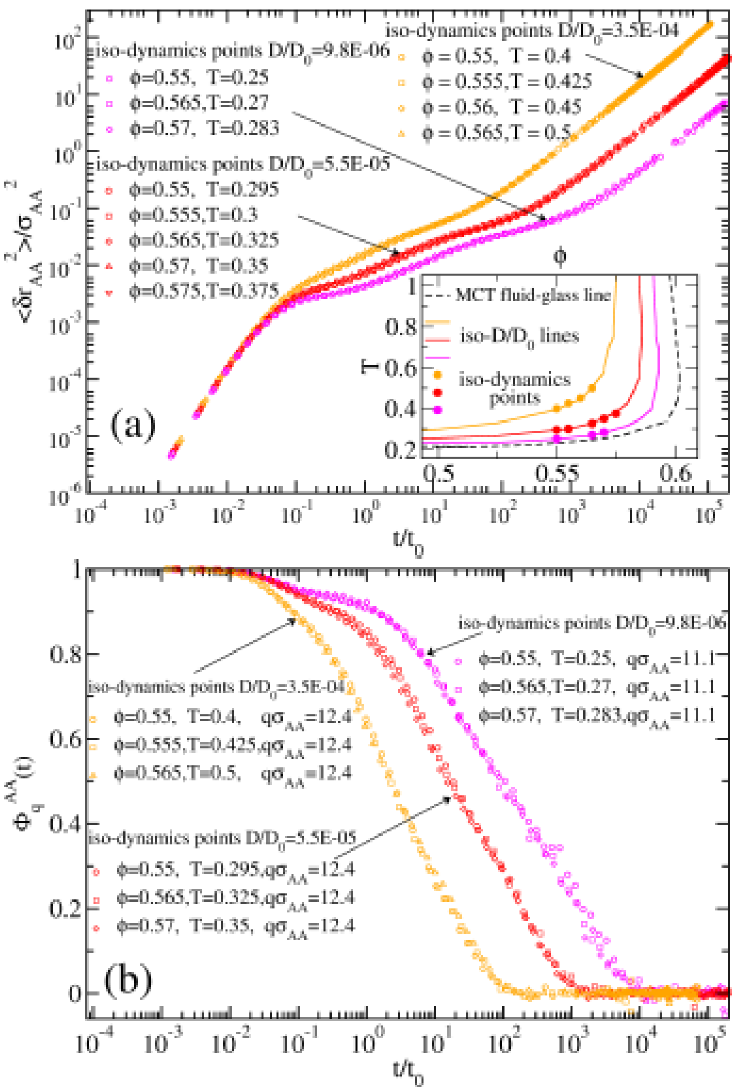


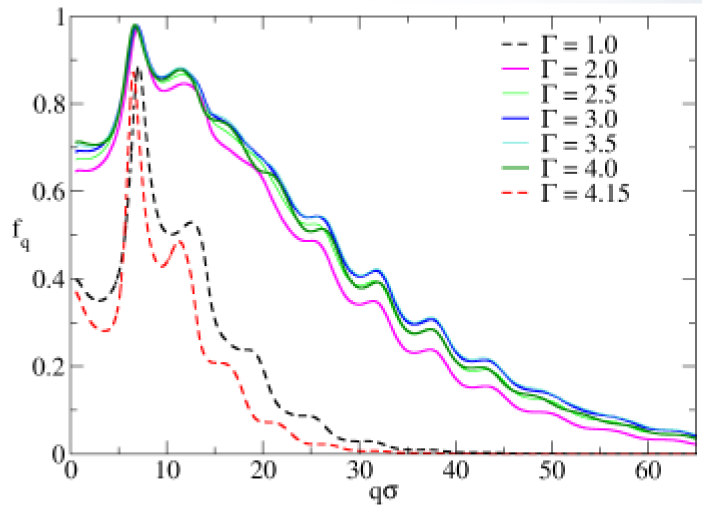


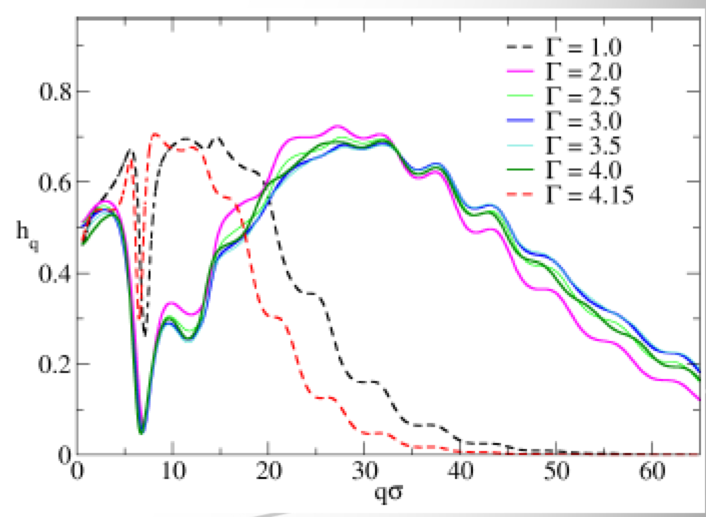


N. Gnan, G. Das, M. Sperl, F. Sciortino, E. Zaccarelli, arXiv:1407.3917

Simulation of SSS: Identical (!) Dynamics for same Diffusivity

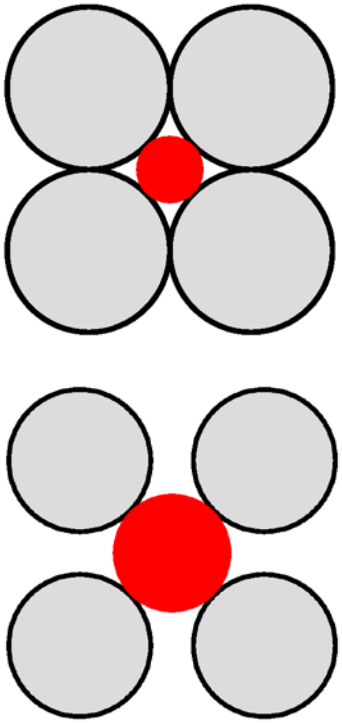


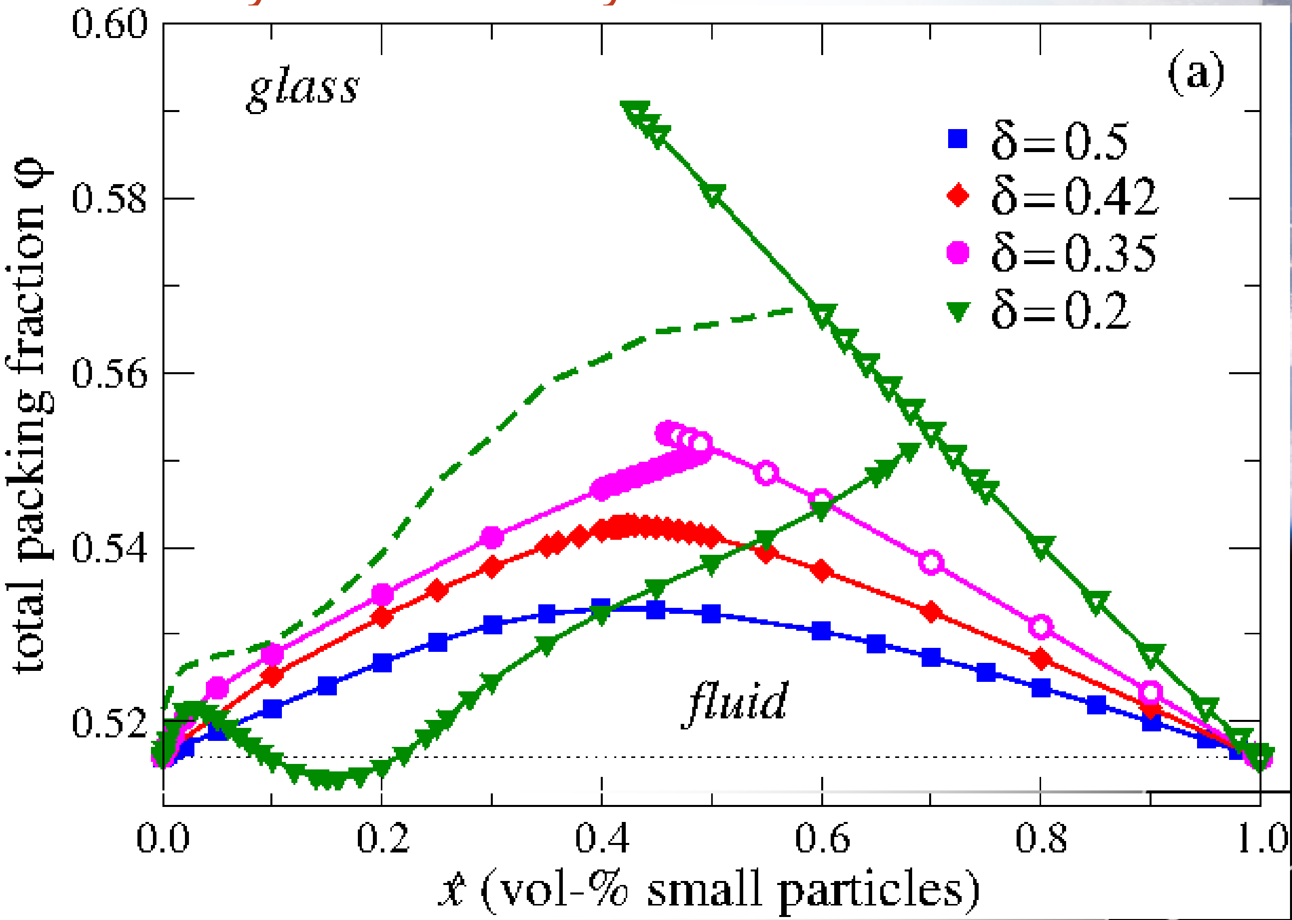




Higher-Order Singularities: Asymmetric Binary Mixtures

Competition between arrest dominated by small or large particles
Voigtmann, EPL (2011)





Epilogue:
Granular Higher-Order Singularities

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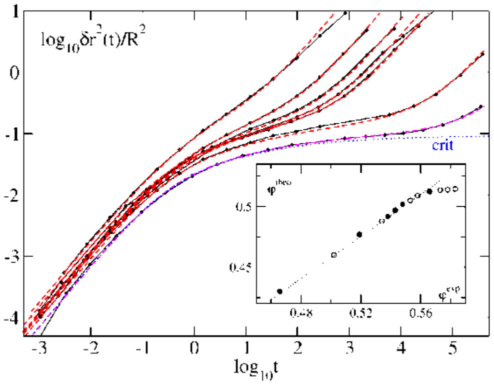
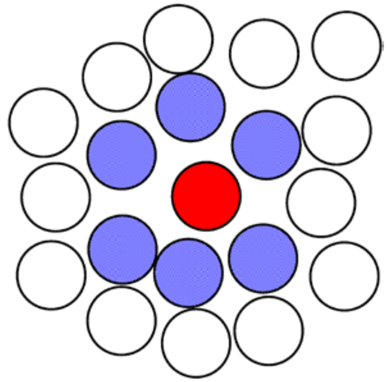
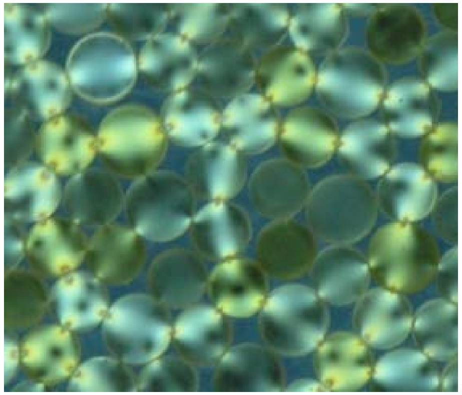
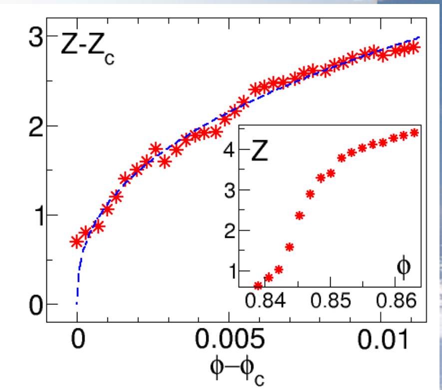
Singularities at the Glass Transition and Random-Close Packing









58% volume fraction

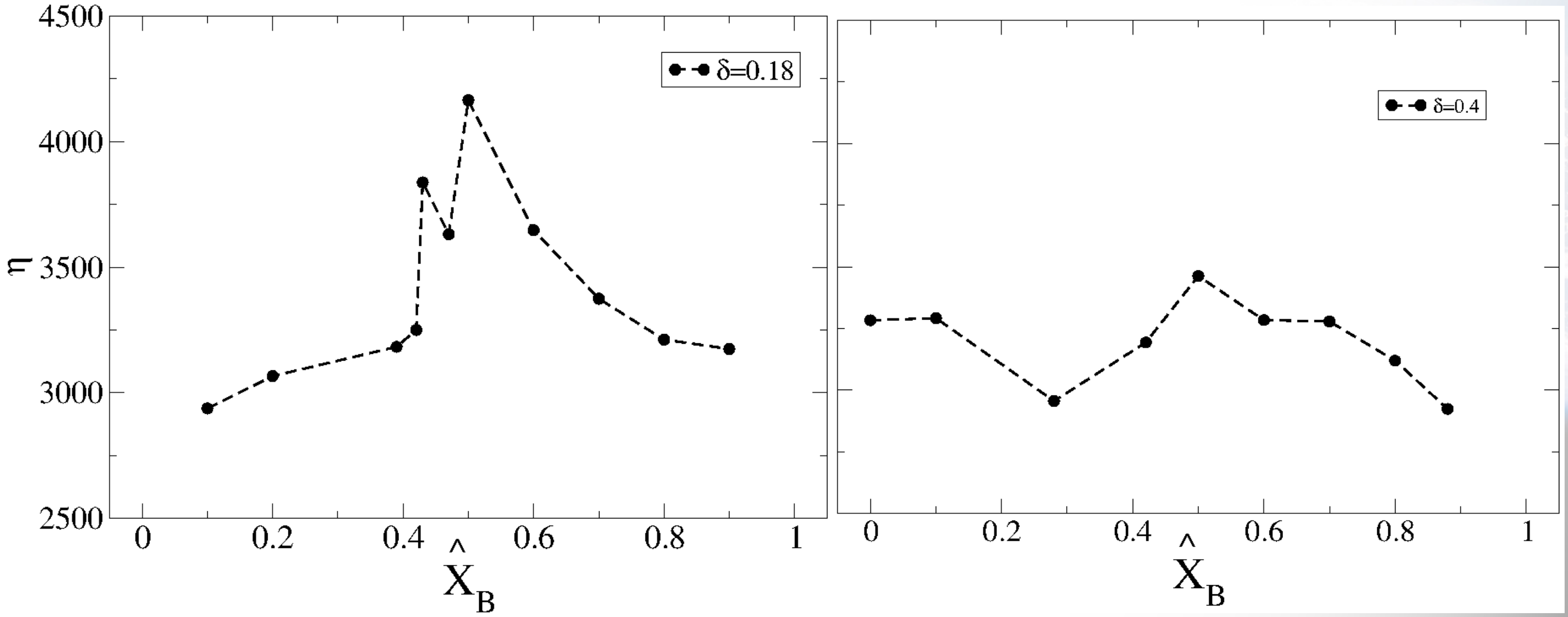
64% volume fraction

Glass Transition: density fluctuations persistent, diffusion vanishes, cage effect, glass form factor finite

Random-Close Packing: contacts permanent, force chains, contact number finite

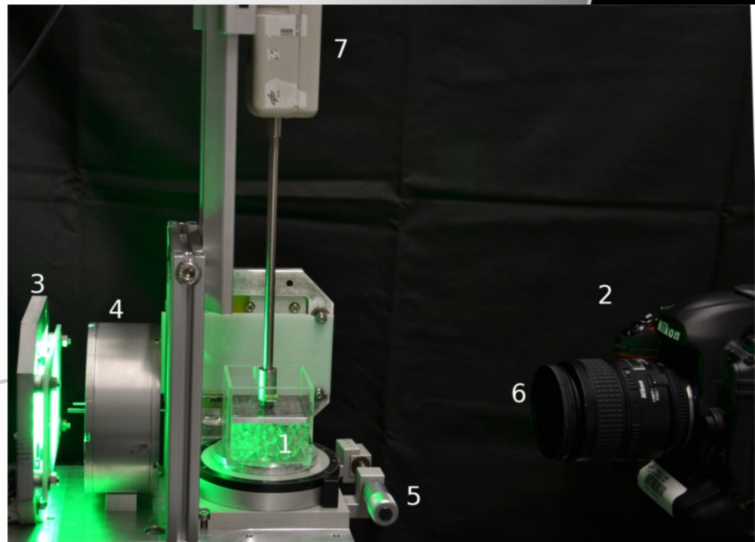
Glass-Form Factors as analogue of the Contact Number

Granular Matter: Asymmetric Binary Mixtures in 3D



Internal stress modulus η from 3D stress-birefringence:

Indication of a discontinuity around x = 0.45 for δ = 0.18, but not for for δ = 0.4. (soft spheres)



Conclusion

What are Higher-Order Glass-Transition Singularities good for?

1) **Critical Test of MCT and other Glass-Transition Theories**
2) **Possible use of new glass states**
3) **Potential similar bifurcations in disordered packings**