Technische Universität München

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# Yielding of amorphous materials

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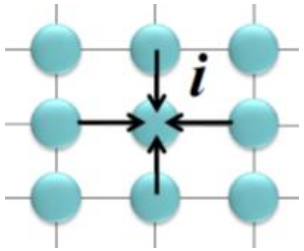
# Non-affine deformations

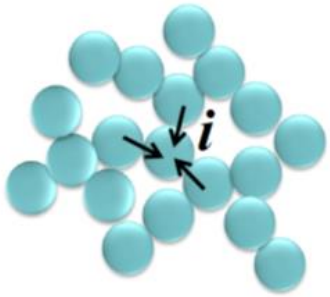
The breaking of local inversion symmetry is the cause for non-affinity. This is a key in disordered solids.

Q: But there are many non-centrosymmetric crystals: what about them?

→ In fact, it is known since Kelvin (1890) that crystals with no inversion symmetry (piezoelectrics, e.g. quartz) all have a very low shear modulus!

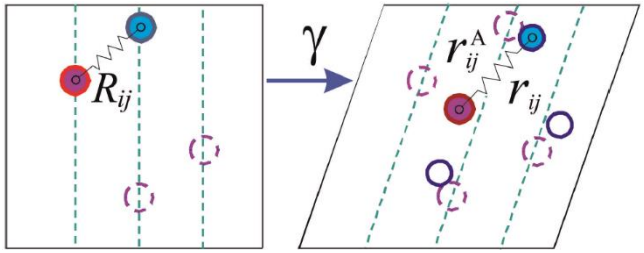



$$\sum \vec{f}_i = 0$$




The associated addition to the elastic free energy is always negative (relaxation of local forces) and can be presented as:

$$F = F_A - F_{NA} = F_A - \frac{1}{2}\left(\frac{\partial \vec{f}_i}{\partial \gamma} \cdot \frac{\partial \vec{r}_{i,NA}}{\partial \gamma}\right)\gamma^2$$



# Non-affine deformations

The non-affine reduction of shear modulus can be calculated for harmonic central forces (with spring constant $\kappa$):

$$F = F_A - F_{NA} = F_A - \frac{1}{2}\left( \frac{\partial \vec{f}_i}{\partial \gamma} \cdot \frac{\partial \vec{r}_{NA}}{\partial \gamma} \right) \gamma^2$$

Born (1940) in affine model

Non-affine softening for harmonic central forces gives a factor $z_c = 2d$

$$G \approx \frac{N}{V} \kappa r_0^2 (z - z_c)$$

Maths can be found in:

Zaccone & Scossa-Romano PRB (2011)
Zaccone, Blundell, Terentjev PRB (2011)

Q: How limiting is this? What if there are constraints: non-central forces or excluded volume?

→ In a few cases (bond-bending & excl. volume) analytical solutions are possible.

# What does the temperature do?

We now know: $G \approx \frac{N}{V} \kappa r_0^2 (z - z_c)$ ⇒ $G \approx \left( \kappa / r_0 \right) \phi \cdot (z - z_c)$

Relate ($z$-$z_c$) to the density

Relate density to temperature

The probability $g(r)$ of having two soft particles separated by a vector of length $r$ displays a divergence

$$g(r) \sim (r - r_0)^{-1/2}$$

O'Hern, Silbert, Liu, Nagel, 2003

Thermal expansion cf. of a solid

$$\alpha_T = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)$$

Replace $V$ by $f$, and integrate:

$$\ln \varphi = -\alpha_T \cdot T + \text{const}$$

The increment $\delta z = (z - z_c) \sim \int g(r) r^2 dr$

which now gives $(z - z_c) \sim \sqrt{\phi - \phi_c}$

This gives the temperature change of the shear modulus

$$(z - z_c) = \sqrt{\varphi_c [e^{\alpha_T (T_c - T)} - 1]}$$

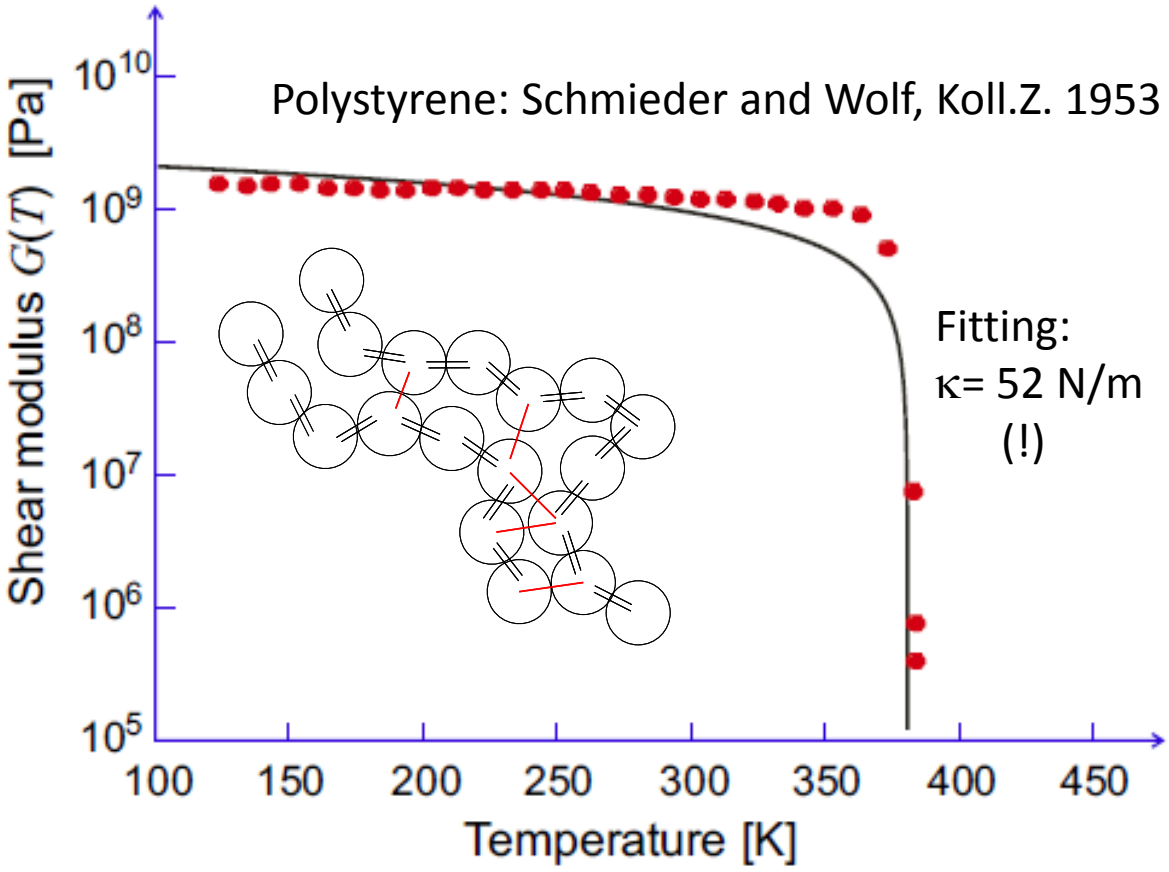
# Comparing with glassy polymer (T<Tg)

We found: $G \approx \frac{N}{V}\kappa r_0^2 (z - z_c)$ ⇒ $G \approx \frac{\kappa}{r_0}\varphi_c e^{\alpha_T (T_c - T)} \sqrt{\varphi_c [e^{\alpha_T (T_c - T)} - 1]}$

The system must be free to expand. In that case, a recent MD simulation for LJ glass has confirmed

$$(z - z_c) \sim \sqrt{\phi - \phi_c}$$

Wittmer et al., JCP 2013




Zaccone & Terentjev PRL (2013)

# Plan for today:

Two examples of fluidization:

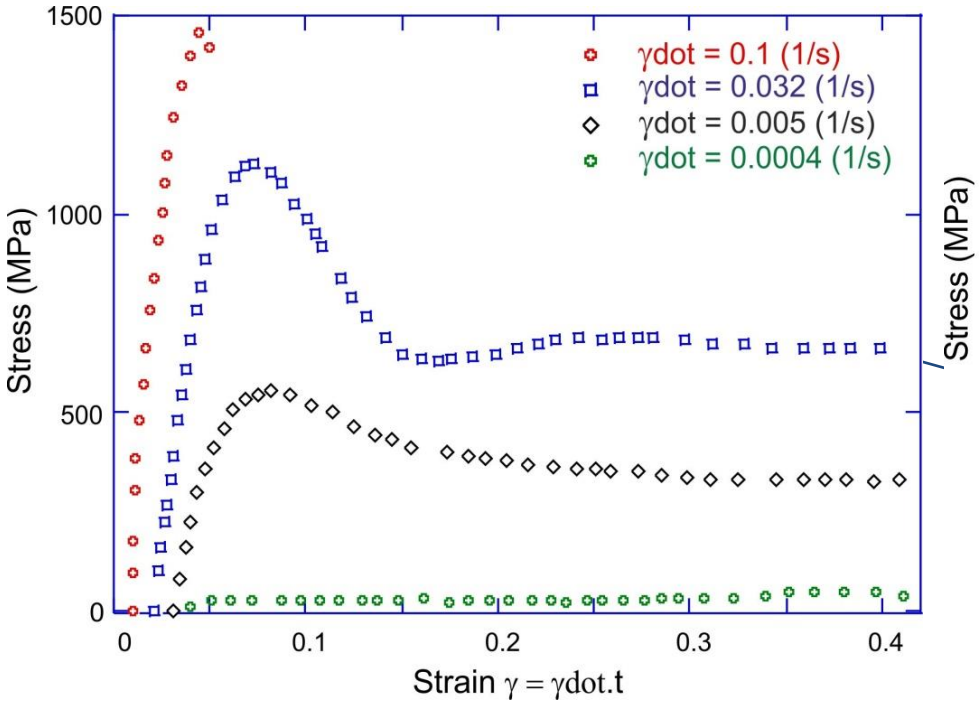
1. How a rigid disordered solid (glass) approaches a melting point ($G \to 0$) on increasing temperature. This is essentially a "glass transition" examined from below $T_g$

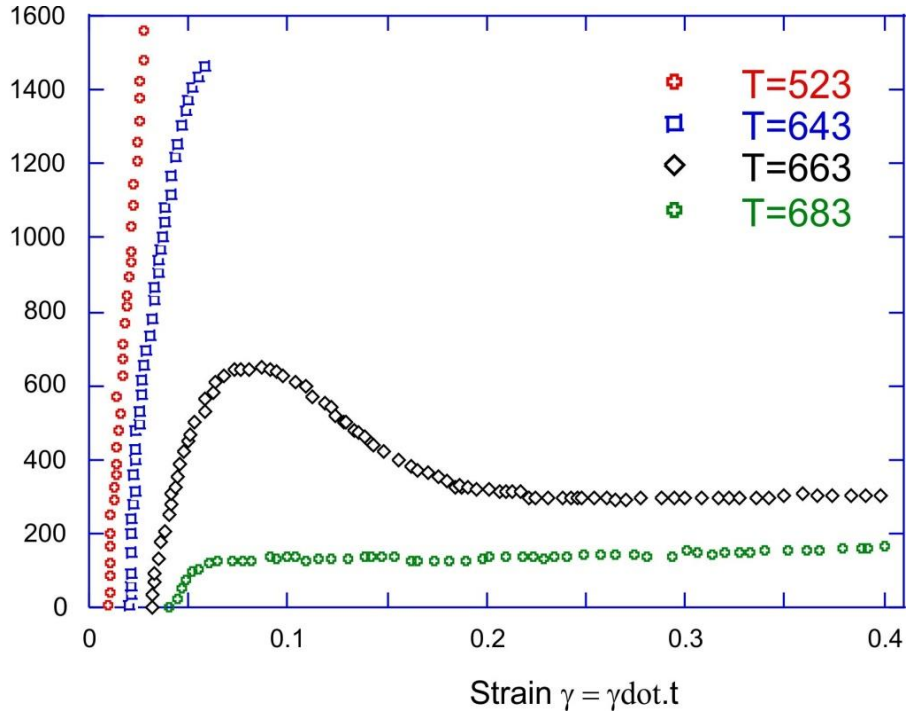
2. How a rigid disordered solid (glass) yields and starts plastic flow at finite deformation rate. Why is there a 'stress overshoot'?

# Can we fluidize the random solid by shear?

Experiment on metallic glass $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$

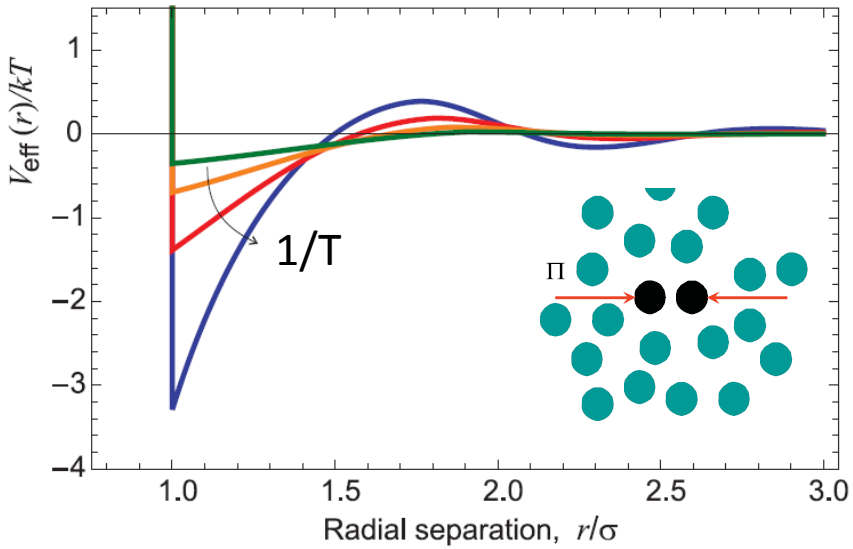
Lu, Ravichandran, Johnson, ActaMater. 2003



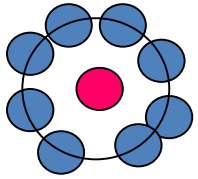




**The linear modulus**
**The overshoot**
**The plastic flow stress**

# Shear-induced cage deformation

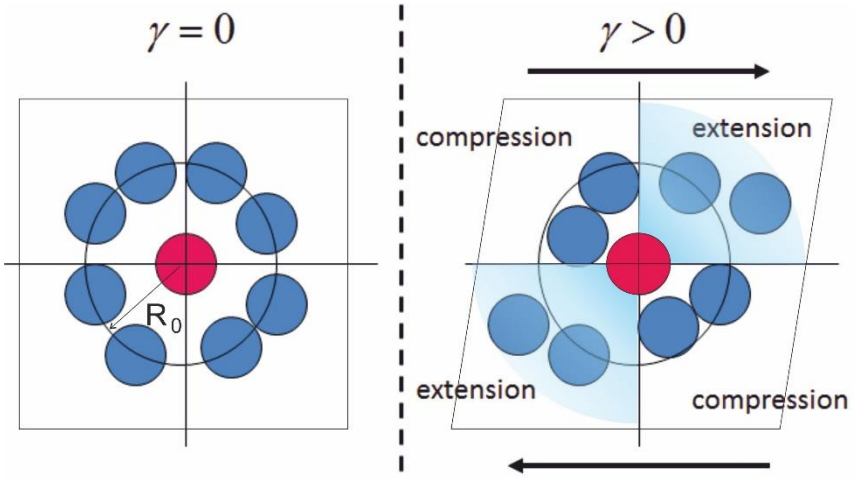



$$g(r) = \exp[-V_{\text{eff}} / kT]$$



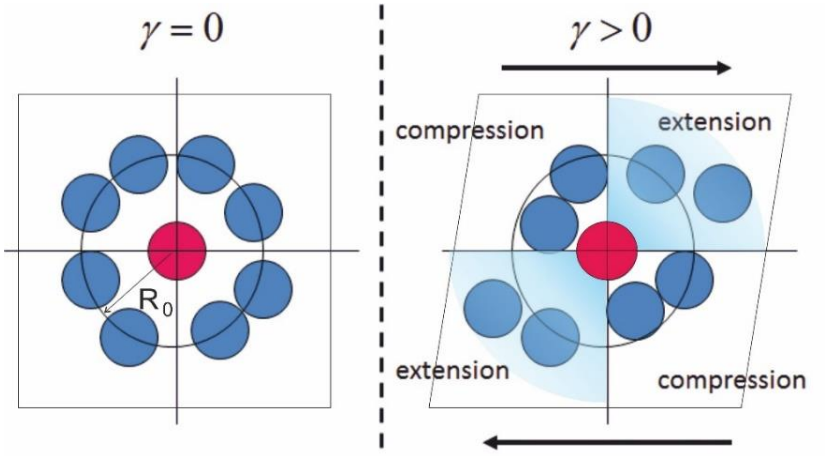
Potential of mean force, accounts also for the "cage"

$$g(\mathbf{r},\gamma) = \exp[-\mathrm{V}_{\text{eff}} / kT + h(\mathbf{r})\gamma]$$



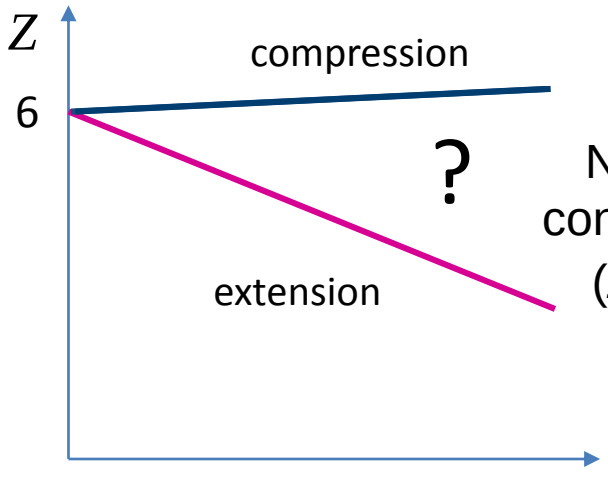

Particles escaping from the cage under shear (extensional sector) go to fill free volume spots (dilatancy is negligible)

# Av. number of contacts z decreases with γ↑




**Net decrease of 'permanent' contacts:** imbalance between extension sector (particles "pealed off") and compression sector ("crowding")

Only bonds which are '**permanent**', within the bonding minimum, contribute to elasticity: fluctuating 'fluid' contacts should be discarded




Expected trend: No. of permanent contacts *Z* vs strain (*Z* @ **γ**=0 is ~12)

Evolution of permanent Z can be measured in confocal microscopy of colloidal glasses or in simulations (in progress)

# Stress non-linearity for a strain ramp (start-up shear)

We saw it many times: $G \approx \frac{N}{V}\kappa r_0^2 (z - z_c)$ ⇒ $F_{el} = \frac{1}{2}K\left[z(\gamma) - z_c\right]\cdot\gamma^2$

*z* is calculated from g(*r*)

$$z = \int g(r)\, 4\pi r^2 dr$$

g(*r*) relaxes towards equilibrium

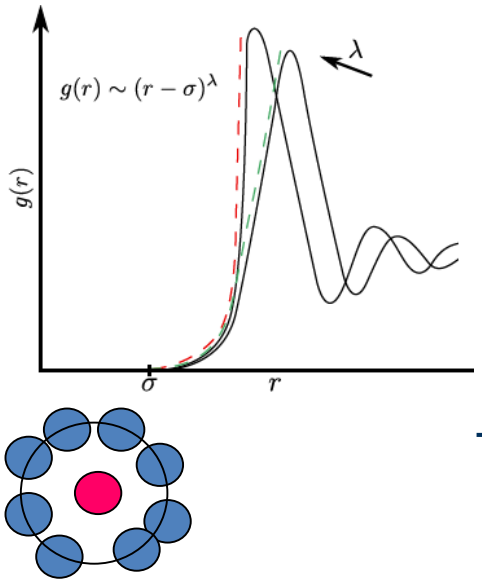
$$g(r) = \Psi_1(r)\cdot e^{-t/\tau_1}$$

lowest eigenvalue

"time is $\gamma$ "

$$t = \gamma/\dot{\gamma}$$

at constant rate




We obtain the contact number *z* as a function of shear strain $\gamma$

$$z(\gamma) = z_0 \cdot \tfrac{1}{2}(1 + e^{-t/\tau_S}) = \tfrac{1}{2} z_0 (1 + e^{-A\gamma})$$

The exponent: $A = \frac{1}{\dot{\gamma}\,\tau_S} + \frac{\Delta}{k_B T}$

half of the sectors deplete at $\gamma$ >>1

The values: $z_{MAX} = z_0 \approx 12,\ z_c = 6$

(only central forces)

# Stress non-linearity during a strain ramp (start-up shear)

We substitute $z(\gamma)$: $F_{el} = \frac{1}{2} K\left[z(\gamma) - z_c\right] \cdot \gamma^2$ and differentiate for $\sigma(\gamma)$:

➡ Elastic stress: $\sigma_{el}(\gamma) = \frac{1}{4} z_0 K e^{-A\gamma} \cdot \gamma(2 - A\gamma) + \frac{1}{2}(z_0 - 2z_c) K \cdot \gamma$

Please remember: $A = \frac{1}{\dot{\gamma}\,\tau_S} + \frac{T_g}{T}$

That's good, but we must not forget the stress relaxation (viscoelastic effect).
This produces the second part: $\sigma_{visc}(\gamma) = \int G(s) \cdot \dot{\gamma}\, ds$

Within the simplest (Zener) model: $G(t) = G + G_R e^{-t/\tau_V}$ and $\tau_V = \eta / G_R$

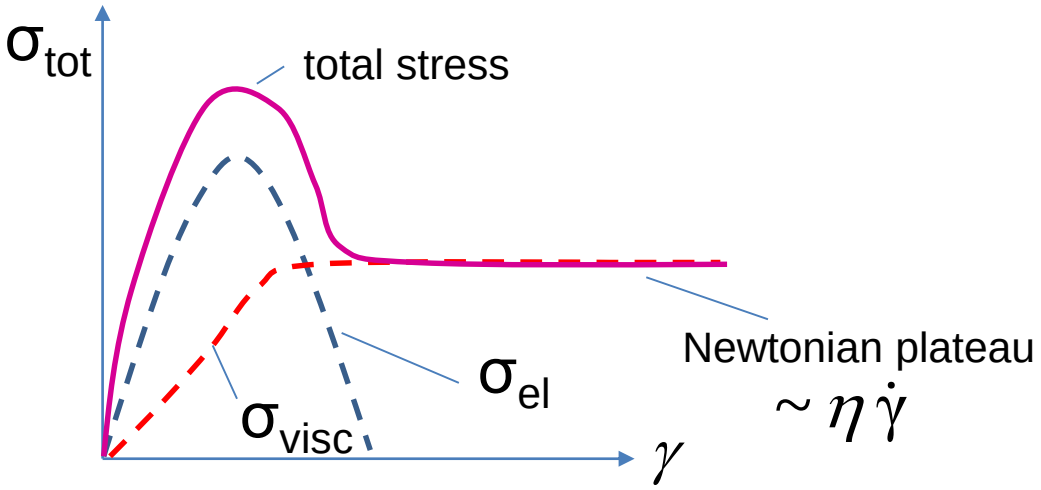
➡ Finally: $\sigma_{tot} = \sigma_{el}(\gamma) + \eta\dot{\gamma}\left(1 - e^{-\gamma/\dot{\gamma}\tau_V}\right)$

# Stress rise, overshoot and the plastic flow

Apply a constant shear ramp $\gamma = \dot{\gamma} \cdot t$

and the glassy solid responds with the stress:

$$\sigma_{\text{tot}} \approx \tfrac{1}{4} z_0 K e^{-\gamma\left(\frac{T_g}{T}+\frac{1}{\dot{\gamma}\tau_S}\right)} \gamma(2-A\gamma) + \eta\dot{\gamma}\left(1-e^{-\frac{\gamma}{\dot{\gamma}\tau_V}}\right)$$




YIELD POINT (G=0)

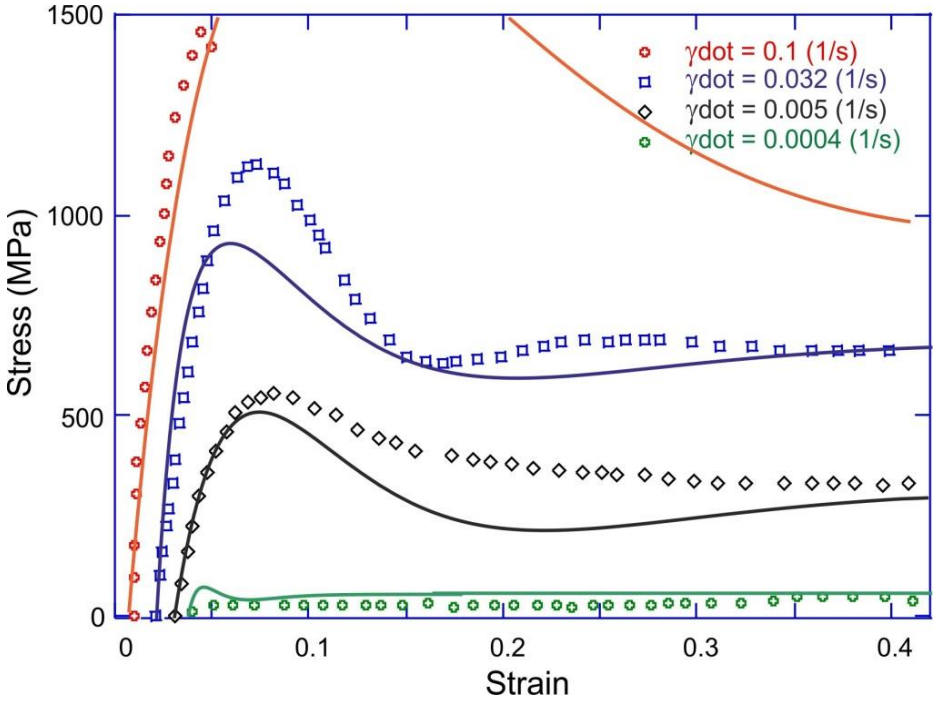
$$\gamma_{CR} \approx \frac{1}{2A} = \frac{0.5}{T_g/T + 1/\dot{\gamma}\tau_S}$$

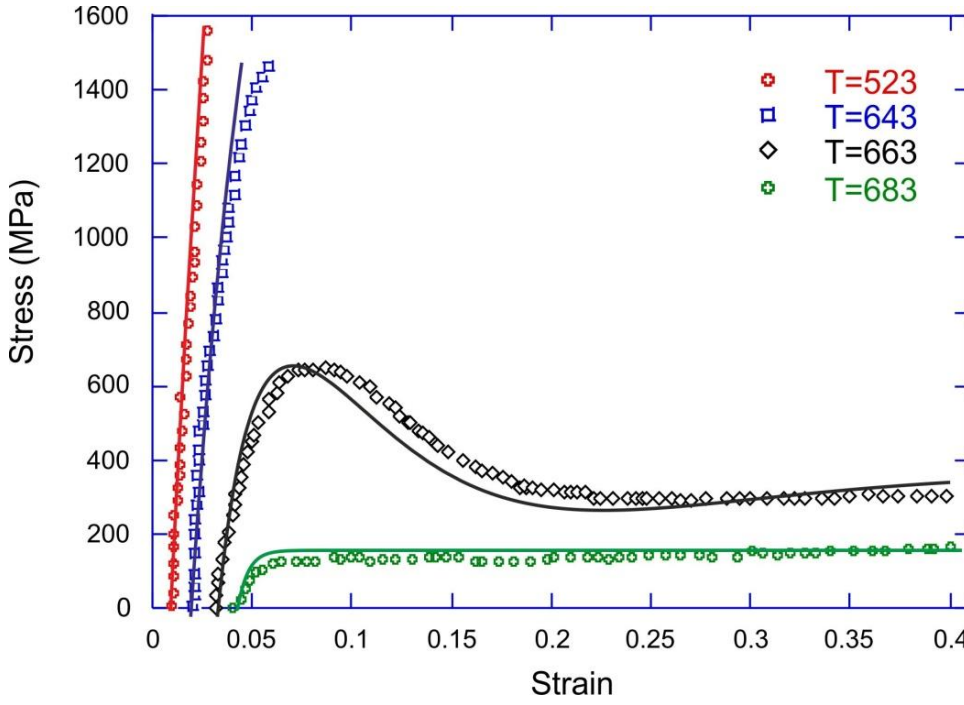
# Stress rise, overshoot and the plastic flow

Shear ramp: $\gamma = \dot{\gamma} \cdot t$

Stress: $\sigma_{\text{tot}} \approx \frac{1}{4} z_0 K e^{-\gamma\left(\frac{T_g}{T}+\frac{1}{\dot{\gamma}\tau_S}\right)} \gamma(2-A\gamma) + \eta\dot{\gamma}\left(1-e^{-\frac{\gamma}{\dot{\gamma}\tau_V}}\right)$

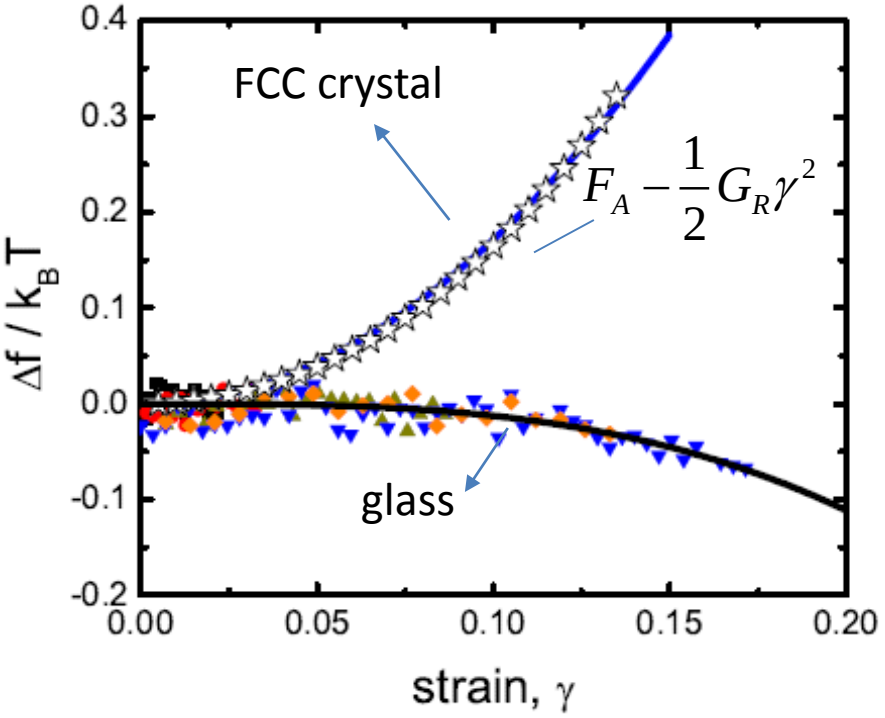
Only two t-parameters are not measured experimentally by Johnson et al.

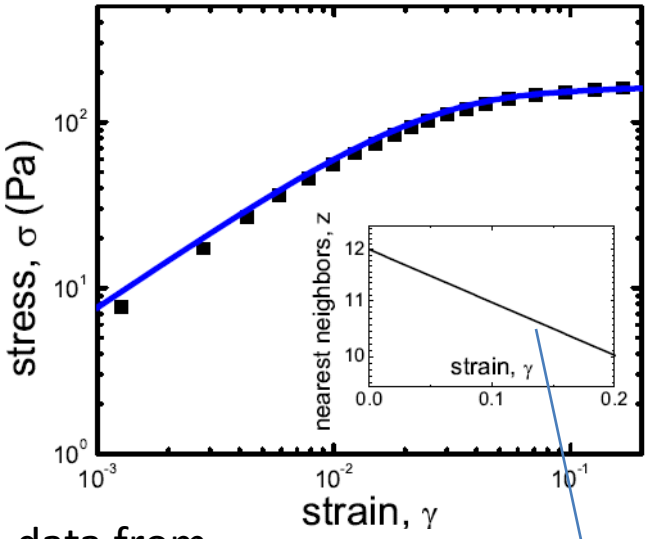


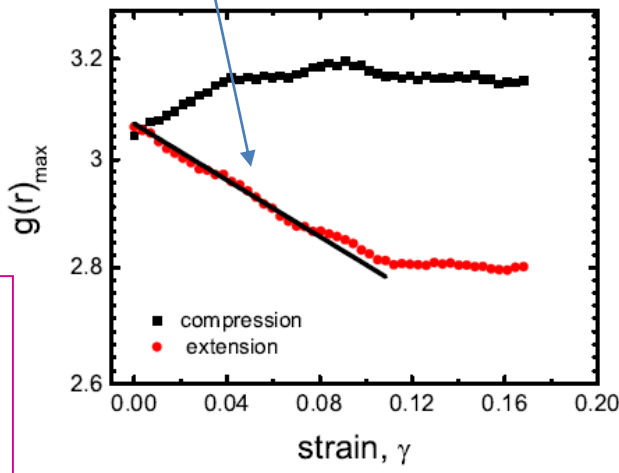

Zaccone, Schall, Terentjev PRB (2014)

# Yielding of colloidal glasses: comparing with experiments




data from
**P. Schall**'s group




free energy of deformation of colloidal glasses

$$F = F_A - F_{NA} = F_A - \frac{1}{2}\left(\frac{\partial \vec{f}_i}{\partial \gamma} \cdot \frac{\partial \vec{r}_{NA}}{\partial \gamma}\right)\gamma^2 - \frac{1}{2} G_R \gamma^2$$

Dang, Rojman, Chikkadi, Bonn, Zaccone, Schall, preprint (2015)

# Conclusion

We used the simplified model of central harmonic bonds and the linear theory of non-affine elastic deformations produces a useful form of the shear modulus, $G \sim K[z - z_c]$

Examining how the average number of contacts $z$ changes in different circumstances allows practical problems to be solved

1. Using thermal expansion ideas, and connecting $z$-$f(T)$ via $g(r)$, we produced a model of glass melting, as well as the $T_g$
2. Using the compression-extension sectors asymmetry in shear, we found $z(\gamma)$ and were able to describe the yielding of metallic glass and the of colloidal glass in agreement with several experimental data-sets

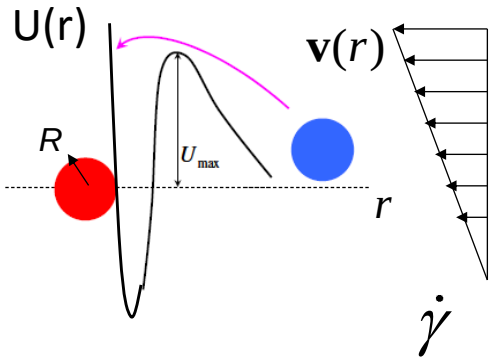
# Diffusion-advection: analytical solution

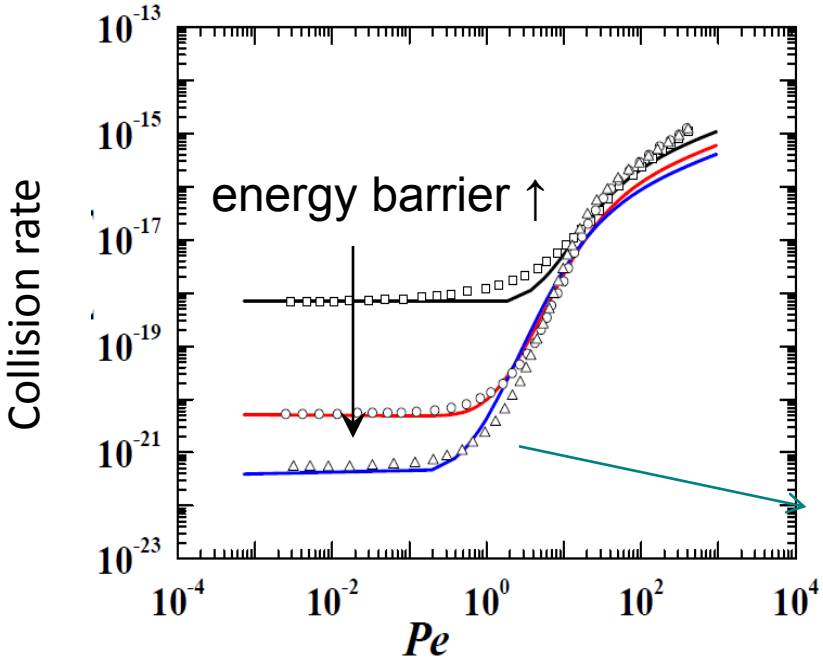
$$\frac{\partial \rho}{\partial t} = \nabla \cdot (D\nabla\rho + b\rho\nabla U - b\mathbf{v}\rho)$$

diffusion

intermolecular interactions

linear flow field




**analytical solution: Zaccone, et al. PRE (2009), PRL (2011)**

ballistic limit

$$rate \propto \dot{\gamma}\ (2R)^3$$

recovered at Pe=∞

$$rate \propto e^{-\beta U_{\max} + 2\alpha Pe}$$

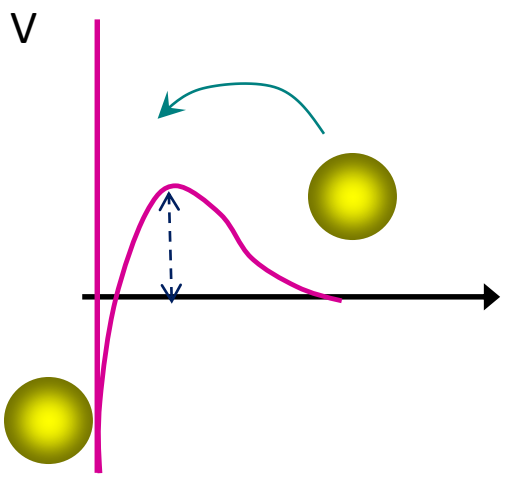
$$Pe = \frac{6\pi\mu\dot{\gamma}R^3}{kT}$$

ANALYTICAL SOLUTION: collision rate

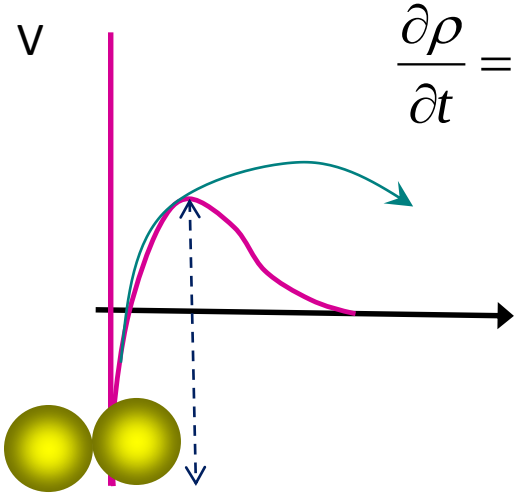
$$K_{1,1} = \frac{8\pi D_0 R c_0}{2\int_0^{\delta/R} \frac{dx}{\mathcal{G}(x)(x+2)^2} \exp \int_{\delta/R}^{x} dx \left( \beta \frac{dU}{dx} + Pe\tilde{v}_r \right)}$$

# Can we predict the cluster breakup rate?

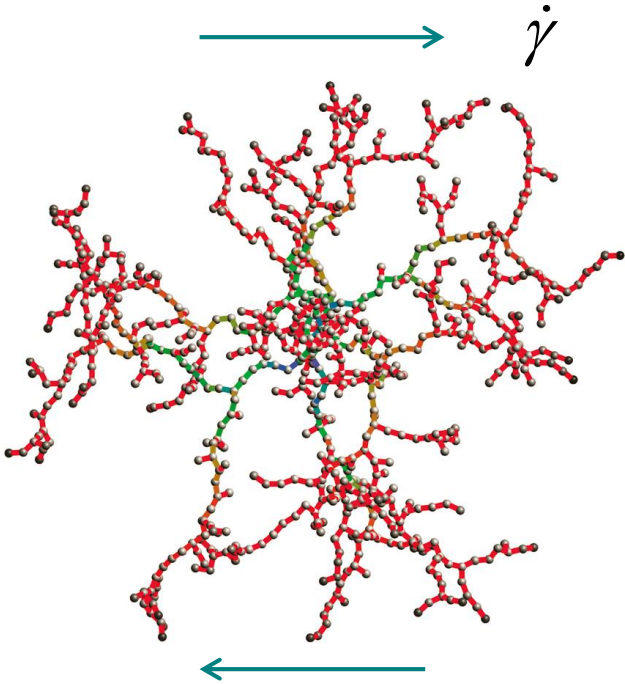
self-assembly




breakup




$$\frac{\partial \rho}{\partial t} = \nabla \cdot (D\nabla\rho + b\rho\nabla V - b\mathbf{v}\rho)$$




collective stress-transmission through the aggregate

$$\tilde{V}_{\text{eff}} = V_{\text{eff}} - \Gamma b(N/2)\int \langle v_r \rangle dr \qquad \propto \dot{\gamma}$$

$$= V - b(1+\Gamma N/2)\int \langle v_r \rangle dr - 2k_B T \ln(r/a)$$

$$\Gamma = (R_g/a)^{\alpha},$$

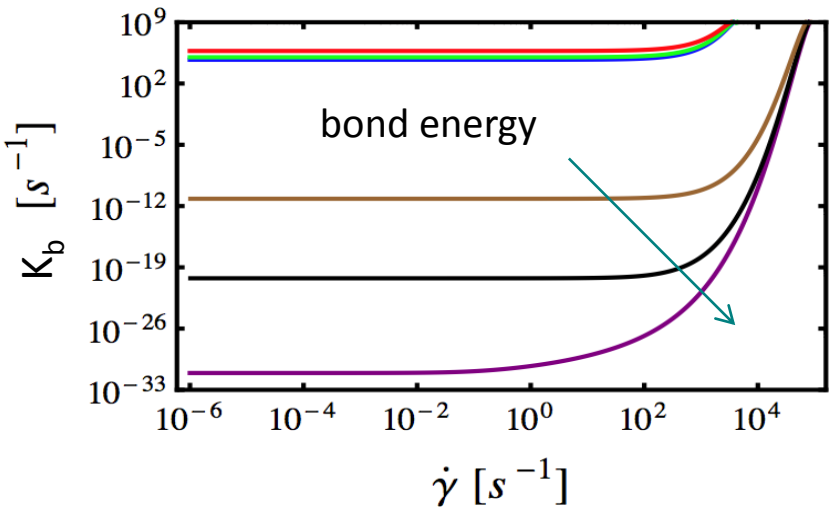
$$\alpha = -2.06491 d_f - 0.0180344/(3-d_f) + 4.98585$$

$$K_{ij}^{-} = \frac{\sqrt{-\tilde{V}''_{\text{eff}}(r_{\max})\tilde{V}''_{\text{eff}}(r_{\min})}}{2\pi b \exp[\beta\tilde{V}_{\text{eff}}(r_{\max}) - \beta\tilde{V}_{\text{eff}}(r_{\min})]}$$

first physical theory
of aggregate breakup rate

**Conchuir & Zaccone, PRE 2013**

# Successful description of several experimental data




$$K_b = \frac{\sqrt{-\tilde{V}''_{\text{eff}}(r_{\max})\tilde{V}''_{\text{eff}}(r_{\min})}}{2\pi b \exp[\beta\tilde{V}_{\text{eff}}(r_{\max}) - \beta\tilde{V}_{\text{eff}}(r_{\min})]}$$

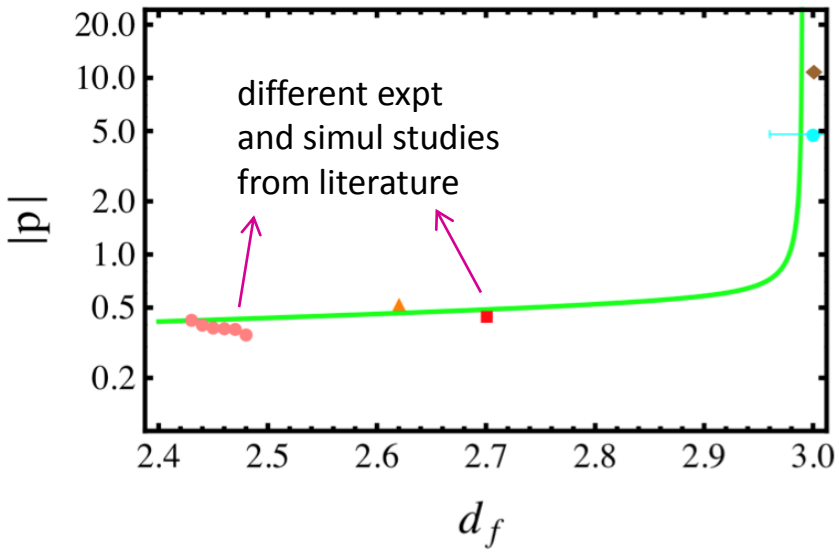
$$\beta\tilde{V}_{\text{eff}}(r_{\max}) - \beta\tilde{V}_{\text{eff}}(r_{\min}) = 0$$

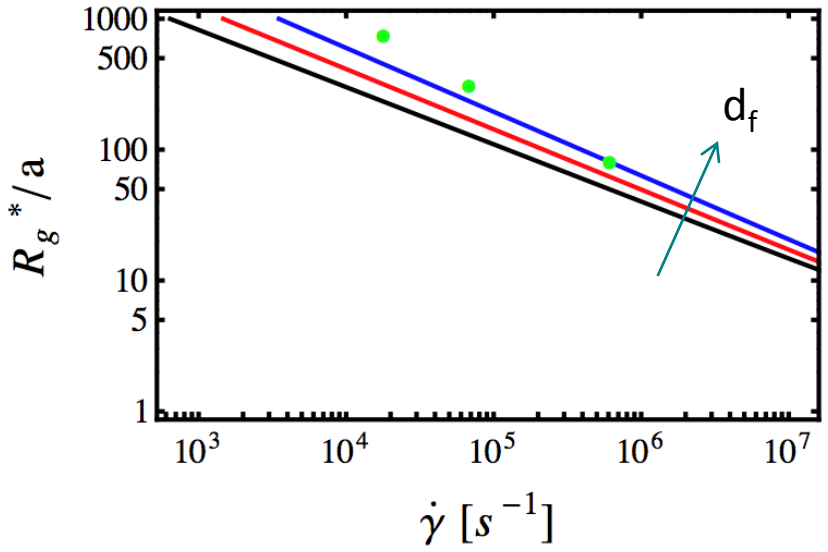
instantaneous breakup
(no activation energy)

max cluster size surviving

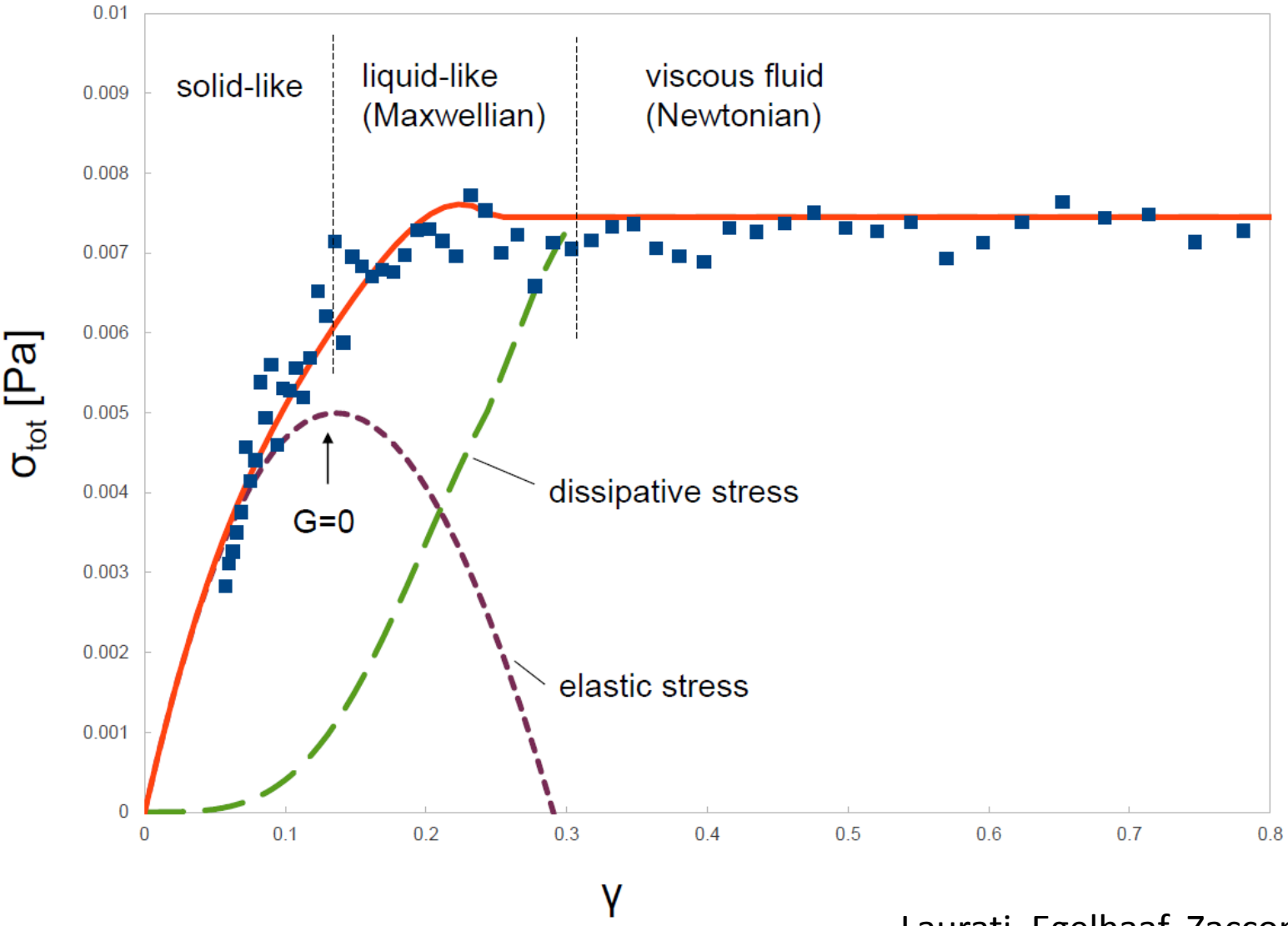
$$R_g^* \sim \dot{\gamma}^{-\frac{1}{d_f+\alpha(d_f)}} \sim \dot{\gamma}^p$$

no fitting parameters!



# Yielding of colloidal glasses: comparing with confocal microscopy (2)

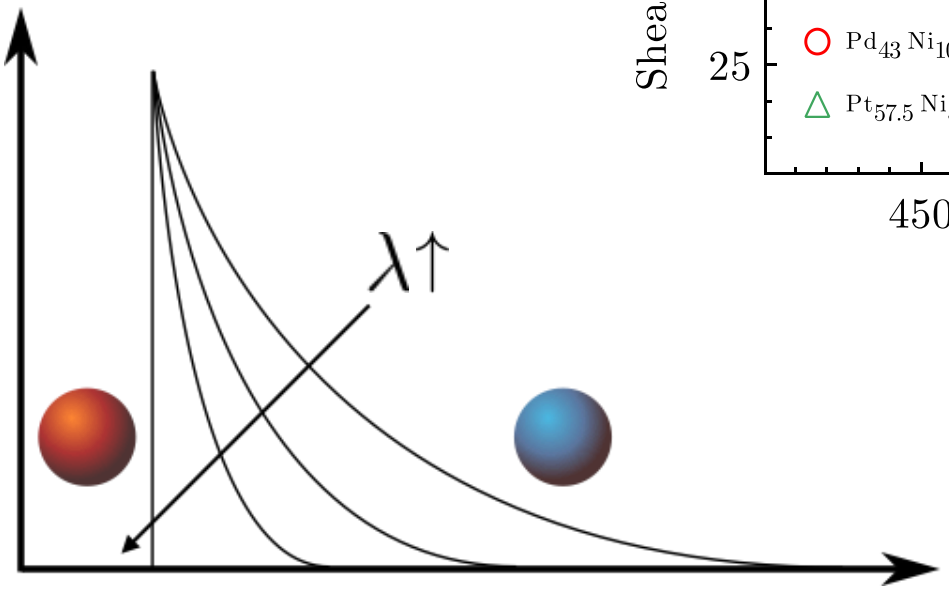


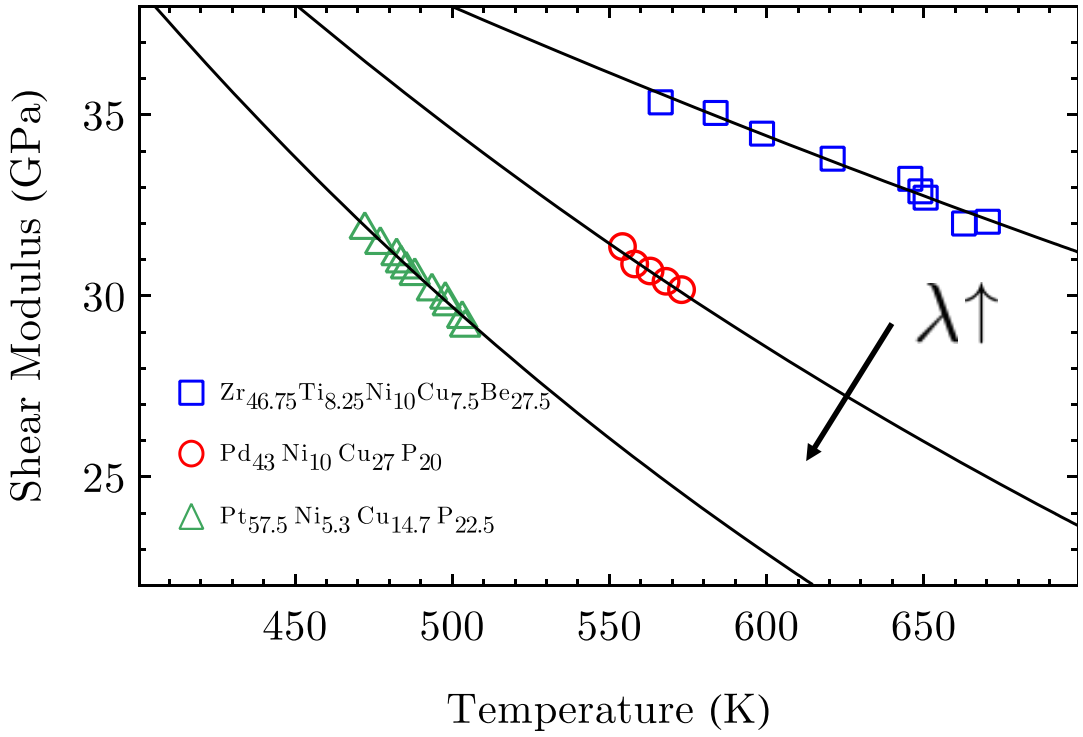

Laurati, Egelhaaf, Zaccone (2015)

# Comparison with experimental data: metallic glass (1)

Apply model to real world:

Rheological measurements for metallic glass alloys (ultra-sonic)




$\Rightarrow \lambda$ controls the **slope** of the shear modulus

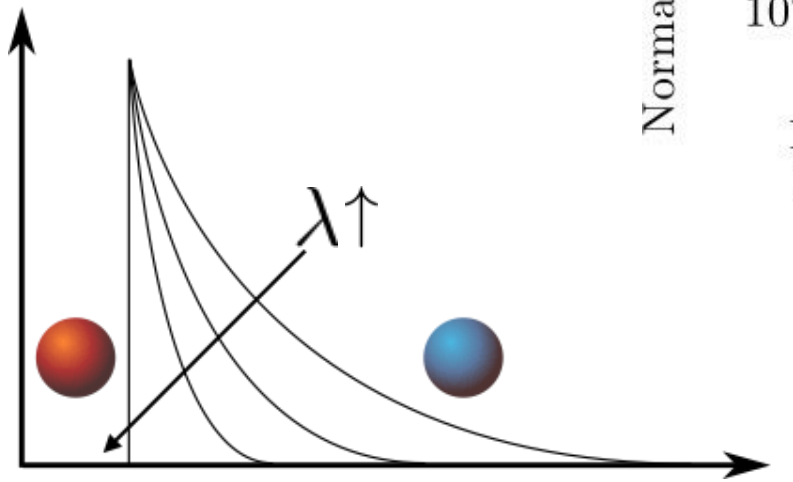
Johnson et. al, MRS Bull. (2007)

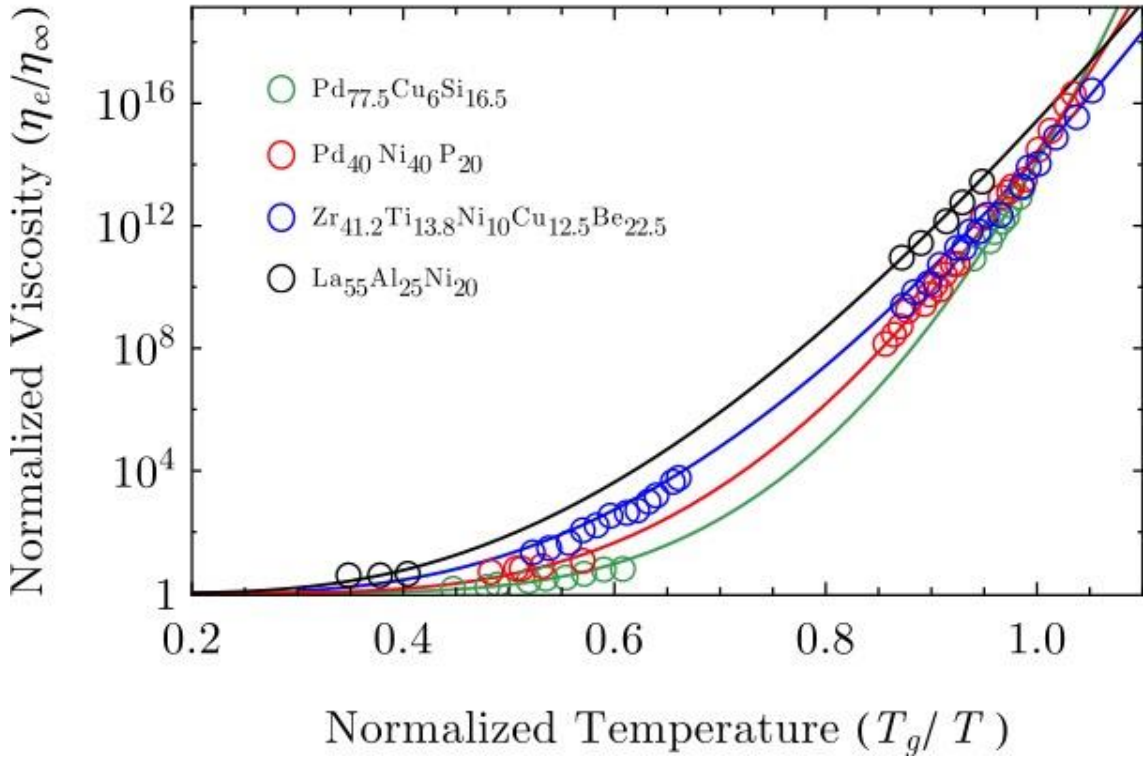
Krausser, Samwer, Zaccone, PNAS (with referees)

# Comparison with experimental data: metallic glass (2)

Definition of **fragility**:

$$m = \left. \frac{\partial \log(\eta/\eta_0)}{\partial(T_g/T)} \right|_{T=T_g}$$




$$m(\lambda) = \frac{V_c C_G}{k_B T_g} [1 + (2 + \lambda)\alpha_T T_g]$$

Johnson et. al, MRS Bull. (2007)

Krausser, Samwer, Zaccone, PNAS (with referees)

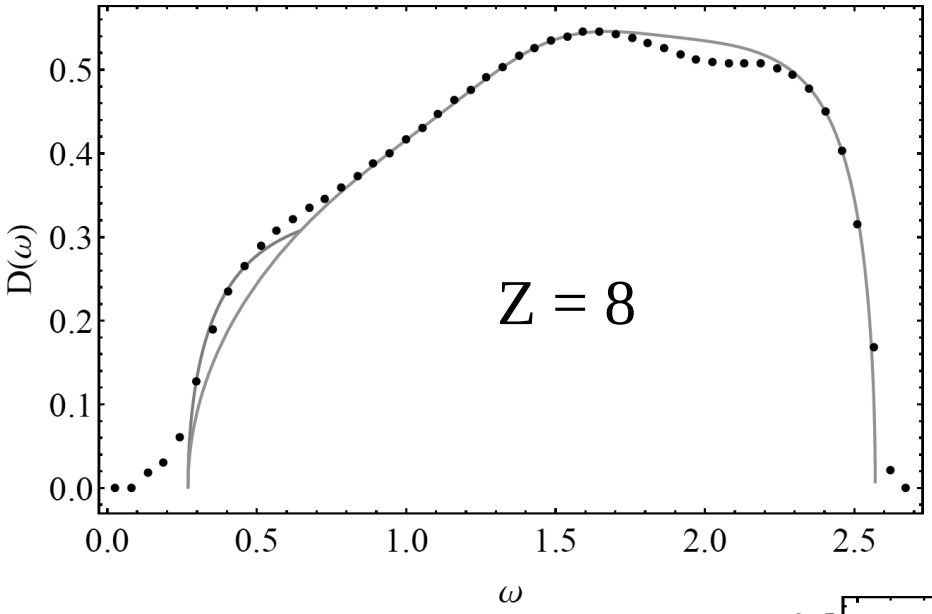
# Parameters for overshoot fitting

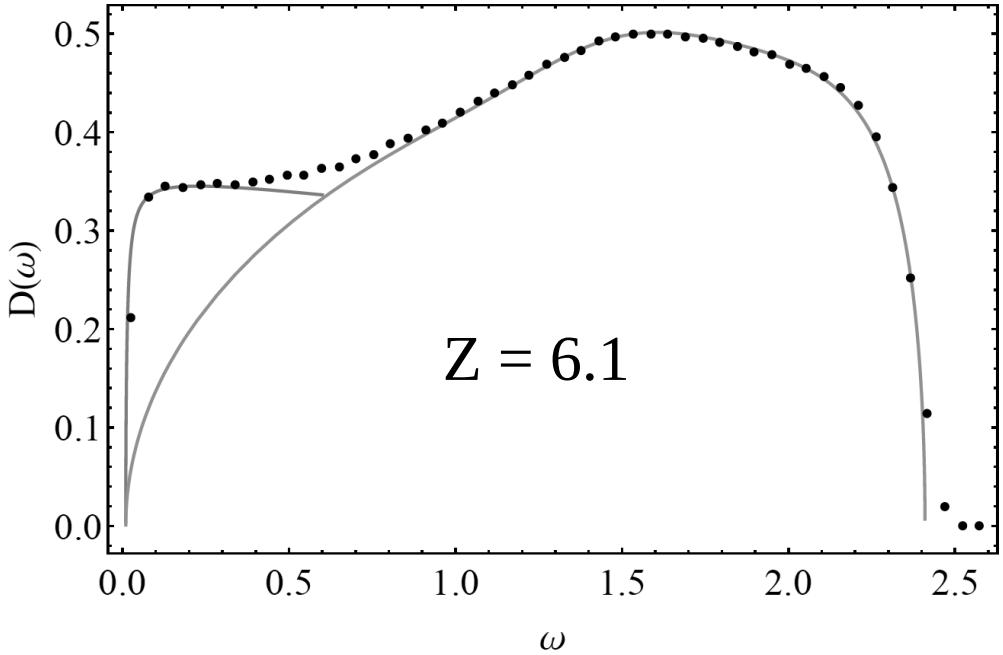
| $K$[18] (GPa) | $\eta$[18] (GPa s) | $\tau_c$ (s) | $\tau_v$ (s) | $T$[18] (K) |
|---|---|---|---|---|
| 12 | 80 | 1.6 | 2.13 | 523 |
| 3.6 | 12 | 1.6 | 0.32 | 643 |
| 1.2 | 4 | 0.6 | 0.12 | 663 |
| 0.6 | 2 | 0.01 | 0.053 | 685 |
| $K$[18] (GPa) | $\eta$[18] (GPa s) | $\tau_c$ (s) | $\tau_v$ (s) | $\dot{\gamma}$[18] ($s^{-1}$) |
| 3.6 | 80 | 12 | 9.0 | $2 \times 10^{-4}$ |
| 3.6 | 80 | 12 | 7.3 | $5 \times 10^{-3}$ |
| 3.6 | 22 | 1.8 | 0.32 | 0.032 |
| 3.6 | 12 | 1.6 | 0.12 | 0.10 |

**COMPARISON WITH ALTERNATIVE THEORIES**

- **MCT** with shear: 5-6 free parameters. Shear parameters $c_\gamma$ and $\lambda$ have no clear physical meaning (cfr. discussion in Binder & Kob's book).
- **STZ** theory: ~4 parameters (effective T not well-defined)

# Vibrational DOS from random matrix theory



# Av. number of contacts z decreases with T↑

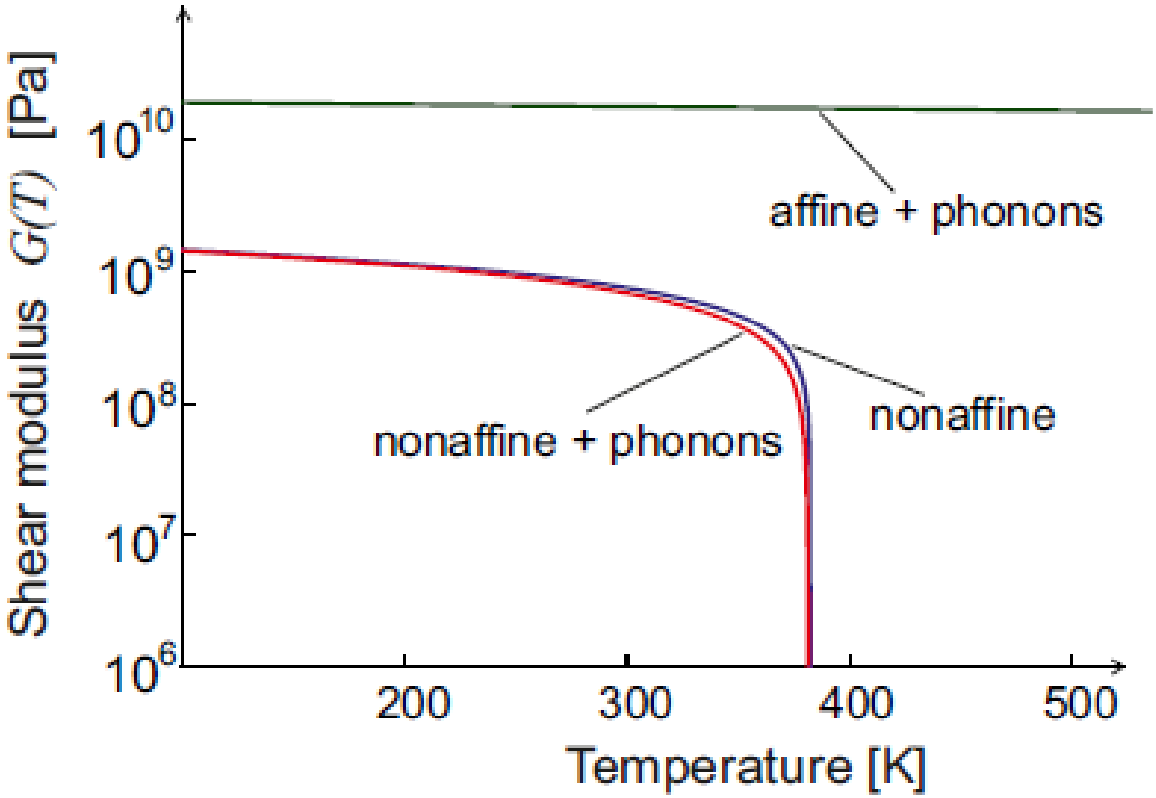
We found: $G \approx \frac{N}{V}\kappa r_0^2 (z - z_c)$ ⇒ $G \approx \frac{\kappa}{r_0}\phi_c e^{\alpha(T_c - T)}\sqrt{\phi_c[e^{\alpha(T_c - T)} - 1]}$

There is one more contribution for the $G(T)$: from **phonon modes** that shift their characteristic frequency on deformation

[J. Frenkel 1946]

$$G_{phonons} \approx -\frac{k_B T}{r_o^3} e^{-\alpha T}$$

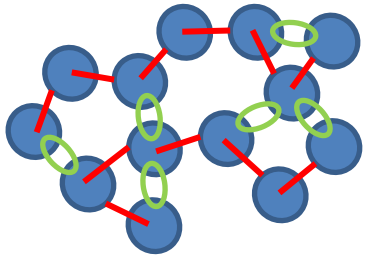
…but it turns out to be small



# May be we can find Tg from G→0 ?

We now know: $G \approx \frac{\kappa}{r_0}\phi_c e^{\alpha(T_c-T)}\sqrt{\phi_c[e^{\alpha(T_c-T)}-1]}$

because $(z-z_c) \sim \sqrt{\phi-\phi_c}$



To formulate all this in a 'normal language'

1. In order to be a rigid glass, the system has to have $z_{\mathrm{VDW}} \geq 12-5z_{\mathrm{CO}}$ additional physical LJ bonds.
2. In a long polymer chain $z_{\mathrm{CO}} \approx 2$ and so there should be at least $z_{\mathrm{VDW}} \approx 2$ of extra contacts per monomer.

The critical point $\varphi_c = e^{-\alpha_T T_g + C}$

is related to $z_{\mathrm{CO}} = 2 - 2/n$

Via $\phi_c = \phi_c^{\mathrm{O}} - \Lambda \cdot z_{\mathrm{CO}}$

~0.64

…which solves for Tg

Fox and Flory, 1950

Expanding the exponential to linear order:

$$T_g \approx \frac{1}{\alpha_T}\left(1+C-\varphi_c^{\mathrm{O}}+2\Lambda\right)-\frac{2\Lambda}{\alpha_T n}$$

$\Lambda \sim 0.1$ from experiment

$C = 0.48$ to give Tg=383K

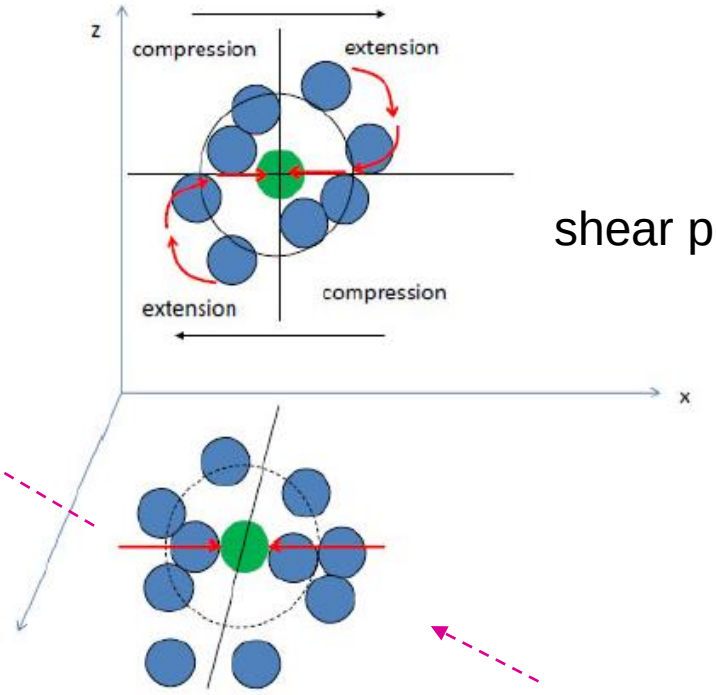
$\varphi = 0.61e^{-\alpha_T T}$

# Cage distortion and yielding of colloidal glasses

Theory predicts **p-wave** symmetry
distortion in the plane beneath shear plane
which vanishes at yielding
(fully nonaffine response after yielding)

$$\mathbf{u}(\mathbf{r}) = -\frac{p}{4\pi K}\frac{\mathbf{r}\cdot\mathbf{n}}{r^3}\mathbf{n}$$ dipole field

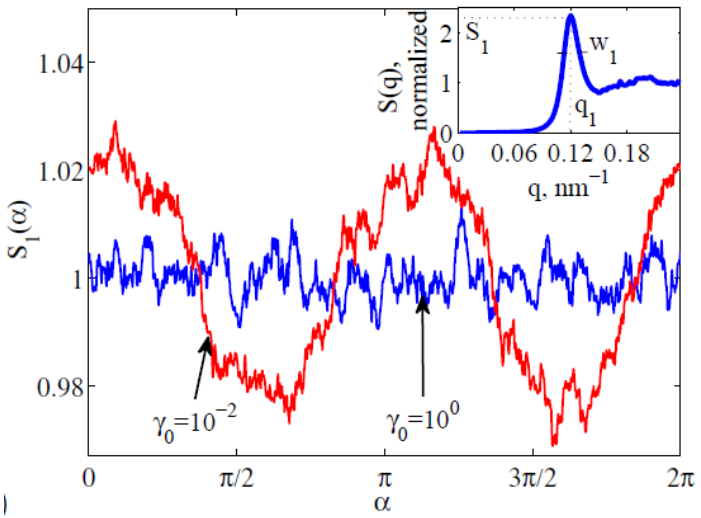
$$u(\alpha) \propto \mathbf{r}\cdot\mathbf{n} \propto \sin^2\theta\cos^2\alpha = \cos^2\alpha$$



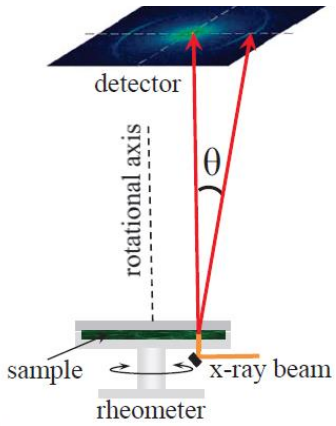

shear plane

plane where
scattering
is measured

**p-wave** symmetry in the experimental
angular correlation function (colloidal glass):



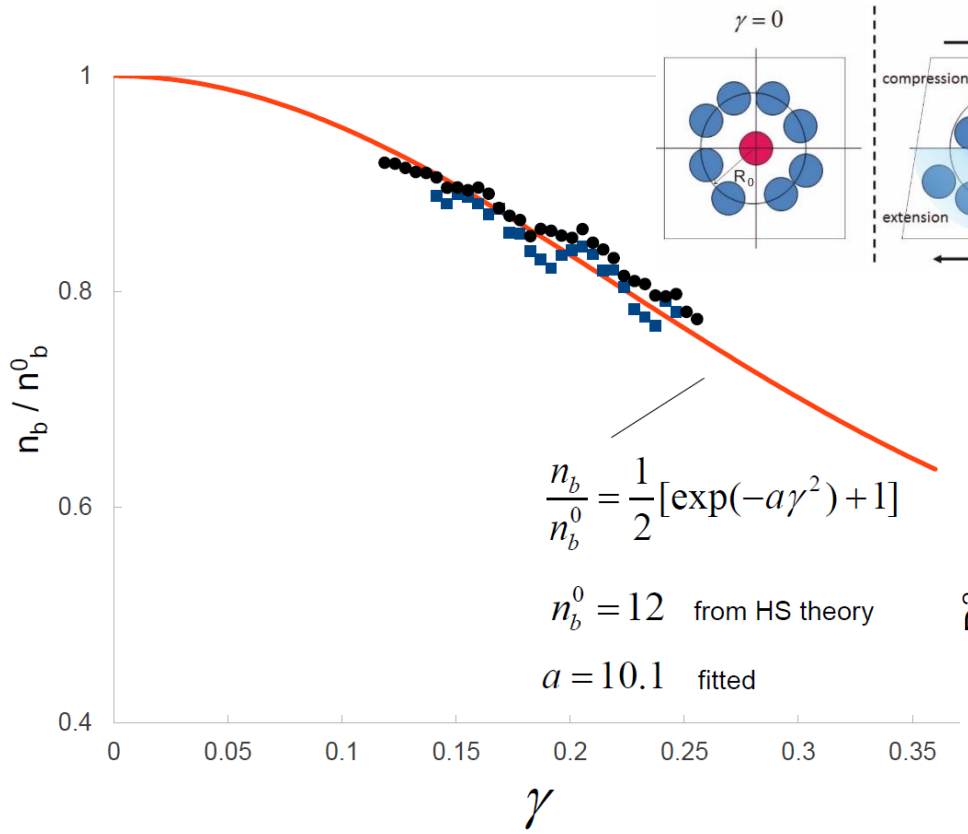

PREDICTION
VERIFIED!




angle-resolved
**rheo-SAXS**
(Desy-Hamburg)

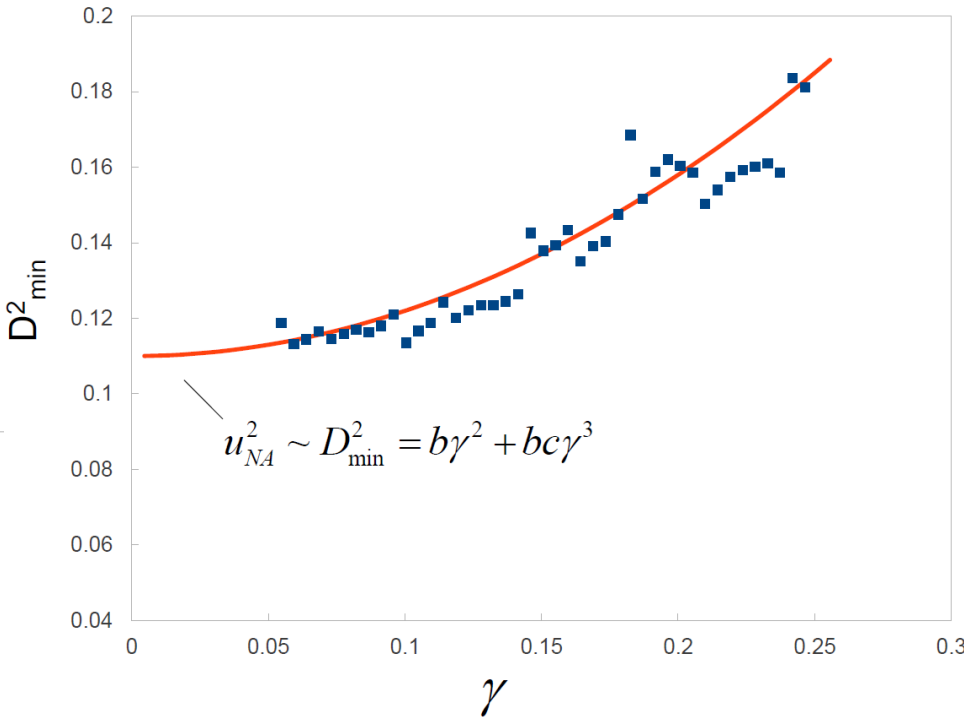
coll. with **Peter Schall (Amsterdam)**

# Yielding of colloidal glasses: Direct relation between nonaffine displacements and stress-strain relation




Strain-induced loss of **permanent** nearest-neighbours

Mean-squared nonaffine displacements

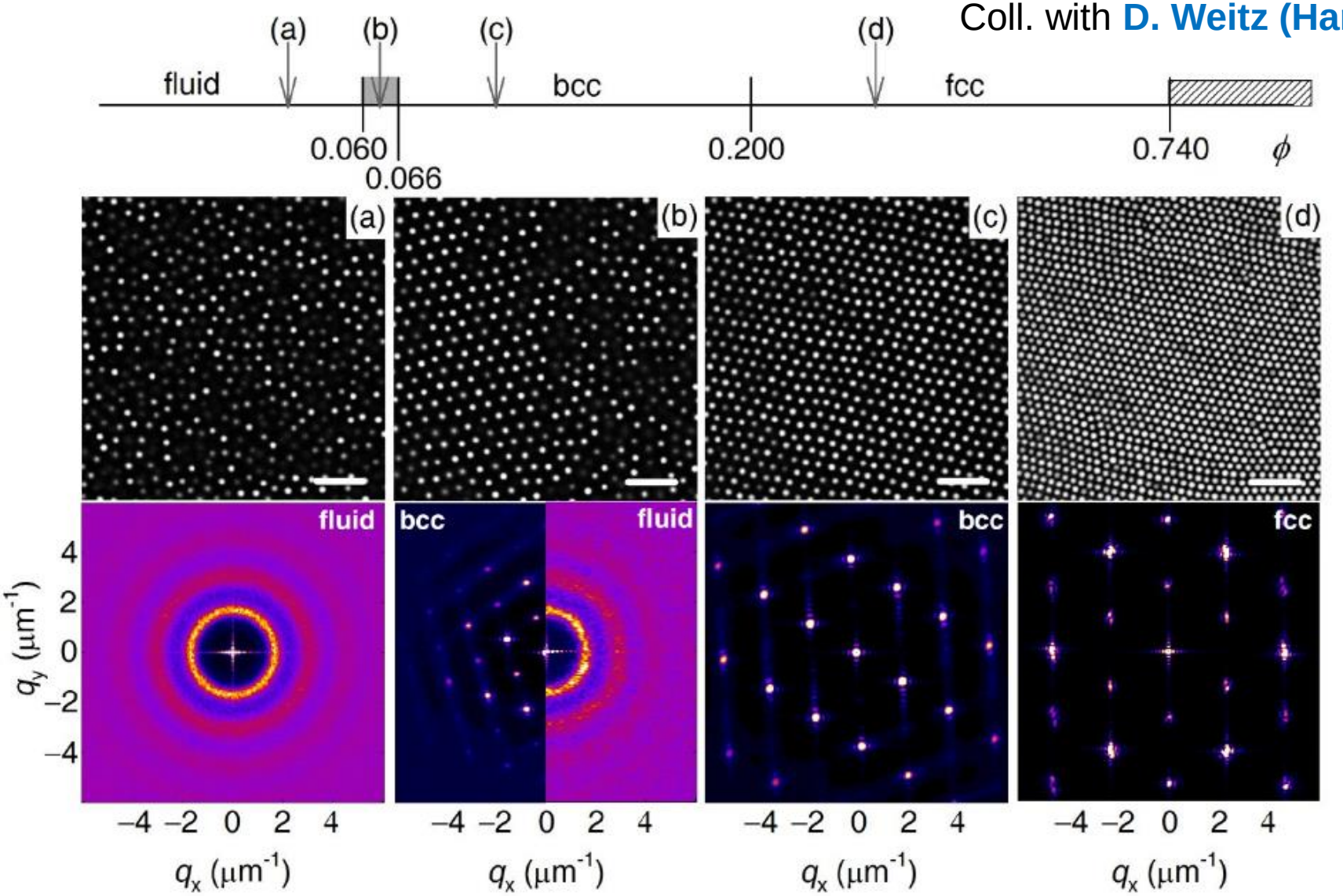



Experimental data from confocal microscopy (**S. Egelhaaf & M. Laurati**)

# Application: colloidal crystal melting in 3D

**Colloidal crystals**: the particles (~ 1 micron) and their dynamics can be followed by confocal microscopy (unlike atoms)

Coll. with **D. Weitz (Harvard)**

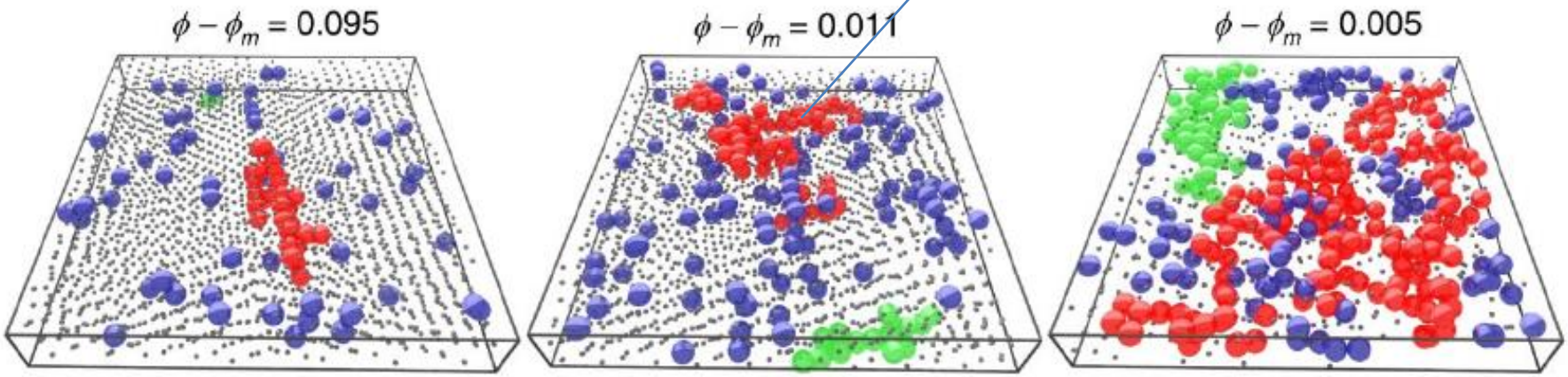


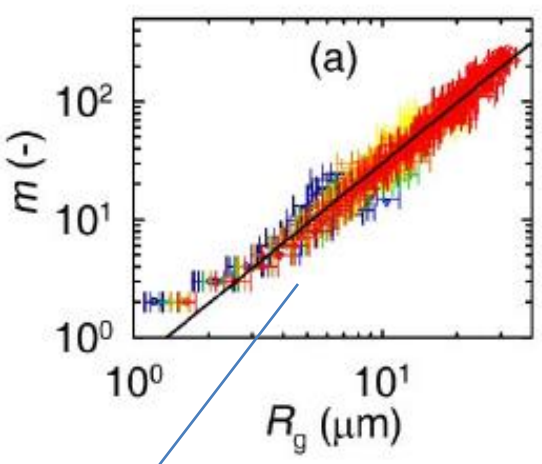
# Strong thermal disorder: fluctuations

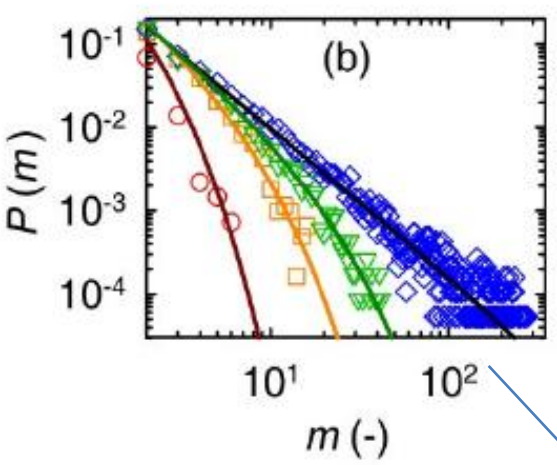
With colloids, melting is driven by the density φ. Upon approaching the melting point, the dynamics of particles becomes highly **disordered** (thermal fluctuations)

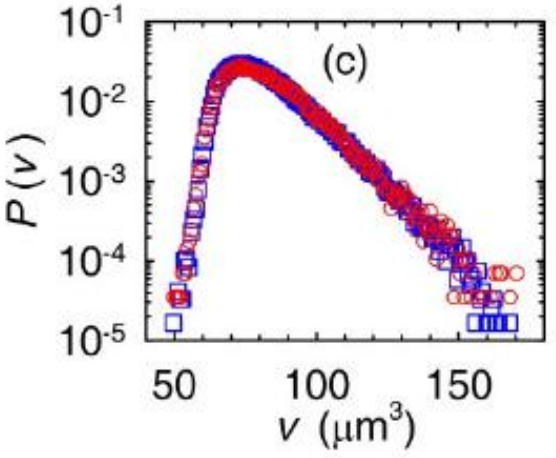
**Sprakel, Zaccone, Spaepen, Schall, Weitz, preprint 2014**

clusters of highly mobile particles



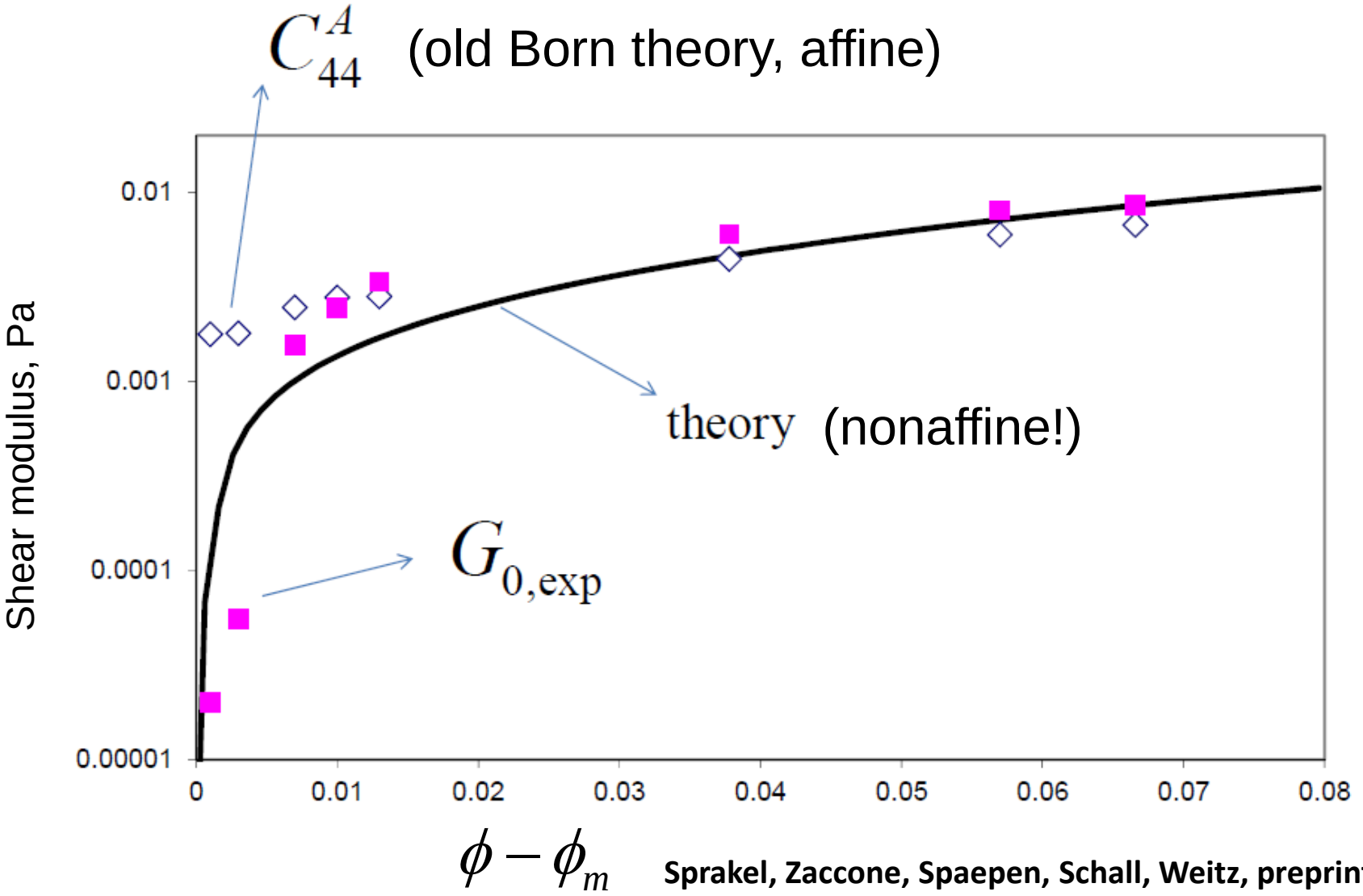




fractal dimension of the clusters ~1.75 → critical exponents

# A new melting criterion

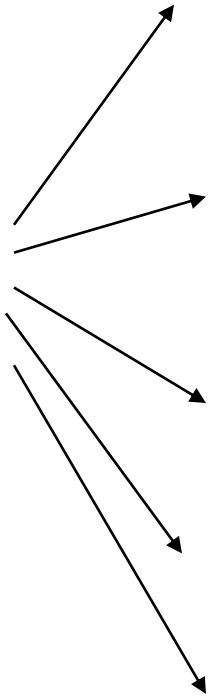
**Born** criterion (1939): crystals melt when the affine shear modulus vanishes
Our new criterion: crystals melt when the **nonaffine** shear modulus vanishes, due to thermal fluctuations!




**Sprakel, Zaccone, Spaepen, Schall, Weitz, preprint 2014**

# Overview – disordered materials

**Nonaffine theory of amorphous materials can explain and describe**



The difference in **material strength** between crystals and glasses

The **glass transition** and mechanical properties of **glassy polymers**

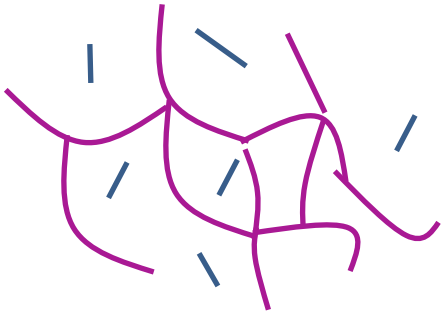
The mechanical failure of **metallic glasses** under strain

The **solid-liquid tr. of 3D crystals with no defects**

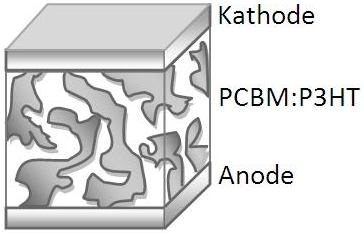
The link between **interatomic potential** and the **fragility** of **metallic glasses**

# 21st century materials: a "disordered" revolution

**SOFT** → **HARD**



hydrogels
(tissues, drug-delivery
foods, cosmetics…)

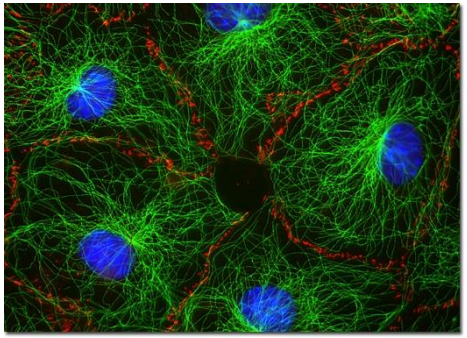



solar cells

superalloys
metallic glasses

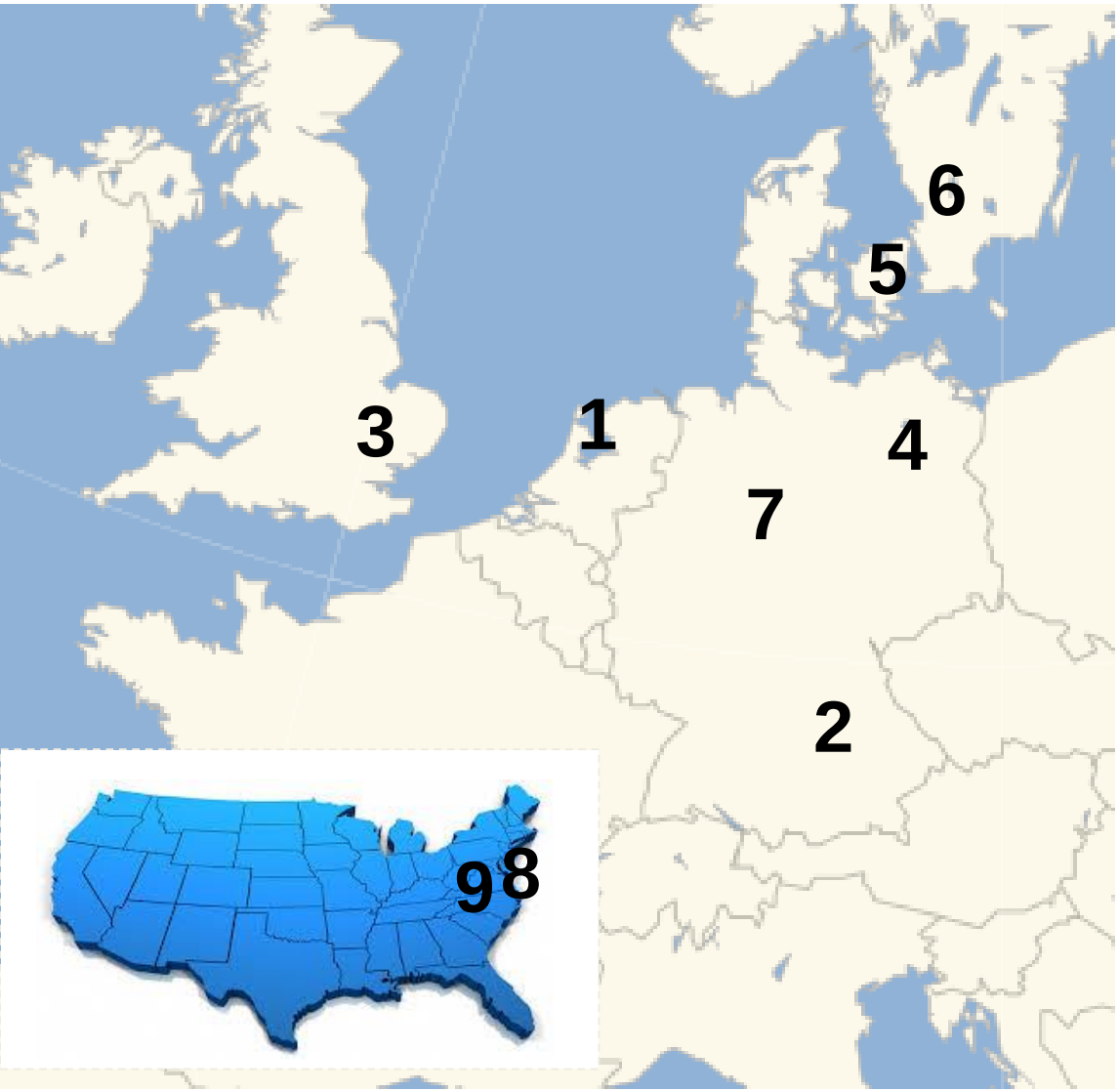
**AZ Research Group**

PhD Students:
J. Krausser
R. Milkus
Post-Docs (from 03.15):
M. Abnekar
H. Yamani



cells' cytoskeleton

# Experimental collaborators




1. **Amsterdam**
   Glasses, shear-banding
   - P. Schall, D.Bonn

2. **Munich** Bio-nanoaggregates
   - P. Muller-Buschbaum
   - A. Bausch

3. **Cambridge** Gels, proteins
   - T. Knowles
   - P. Cicuta, E. M. Terentjev

4. **Berlin** Gels, nanoparticles
   - M. Ballauff

5. **Copenhagen + 6. Lund**
   Proteins
   - B. Vestergaard
   - P. Schurtenberger

7. **Goettingen** Metals
   - K. Samwer

8. **Harvard**
   Glasses, Metallic alloys
   - D. Weitz, F. Spaepen

9. **Amherst** Gels
   - H.H. Winter

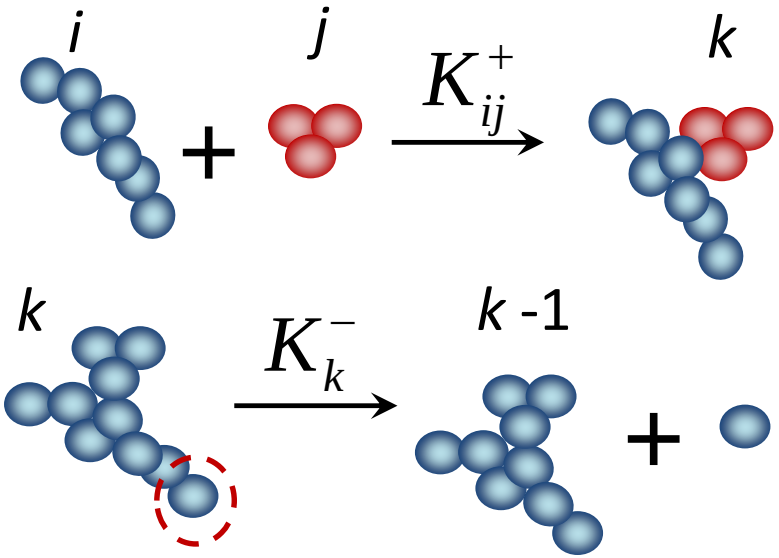
# Mathematical approach: master kinetic equation

**Until now**: **equilibrium** statistical mechanics (Flory-Stockmayer, AHS, percolation), no time-evolution, cannot link molecular level with macroscopic structure & properties

NEW APPROACH: **master kinetic equations** (**NONEQUILIBRIUM**!)

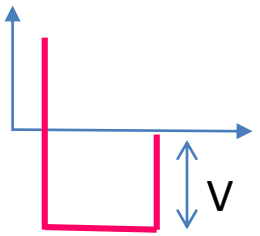
$$\frac{dc_k}{dt} = \frac{1}{2}\sum_{i,j=1}^{i+j=k} K_{ij}^{+} c_i c_j - c_k \sum_{i=1}^{\infty} K_{ik}^{+} c_i$$

$$- K_k^{-} c_k + \sum_{i=k+1}^{\infty} K_{ik}^{-} c_i$$




$K_{ij}^{+}$ **assembly** rate → diffusion-limited (Smoluchowski)

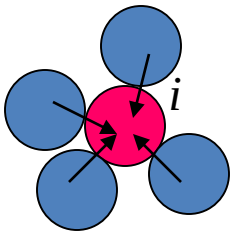
$K_k^{-}$ **disassembly** rate → Arrhenius-Kramers dependence on bond energy



# Free energy of lattice deformation with disorder

$$W = \mathcal{F}_{NA} = \int_0^{\underline{u}^{NA}} \delta \underline{f}_i \cdot \mathrm{d}\underline{x}_i = -\frac{1}{2} \underline{\underline{H}}_{ij} \underline{u}_i^{NA} \underline{u}_j^{NA}$$

$$= -\frac{1}{2} \left( \underline{\underline{\Xi}}_i \cdot \frac{\partial \mathring{\underline{r}}_i}{\partial \gamma} \right) \gamma^2$$




$$\underline{\underline{H}}_{ij} \left. \frac{\partial \mathring{\underline{r}}_j}{\partial \gamma} \right|_{\gamma \to 0} = \underline{\underline{\Xi}}_i$$

internal work done by nonaffine motions
at the expense of lattice energy of deformation

~ force acting on *i*
due to affine motions
of *j* neighbours

**Zaccone & Scossa-Romano, PRB (2011)**

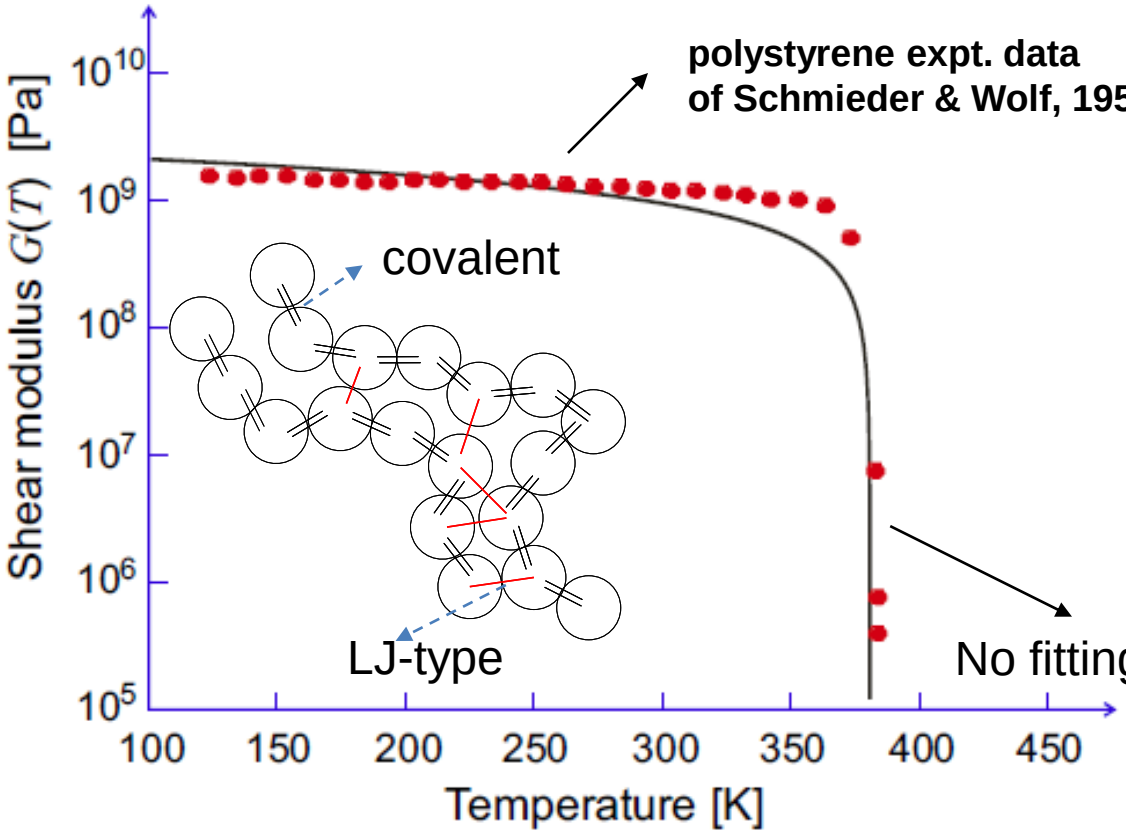
$$\mathcal{F} = \mathcal{F}_A - \mathcal{F}_{NA} = \mathcal{F}_A - \frac{1}{2} \left( \underline{\underline{\Xi}}_i \cdot \frac{\partial \mathring{\underline{r}}_i}{\partial \gamma} \right) \gamma^2$$

**affine**, “ordered”

**nonaffine**, “disordered”

# Application (1): polymer glass transition

$F = F_A - F_{NA} - F_T$ → phonons also contribute to the elastic free energy




No theories available for G at T<Tg

At T>Tg:
Doi-Edwards theory, tube theory

**Zaccone & Terentjev, PRL 2013**

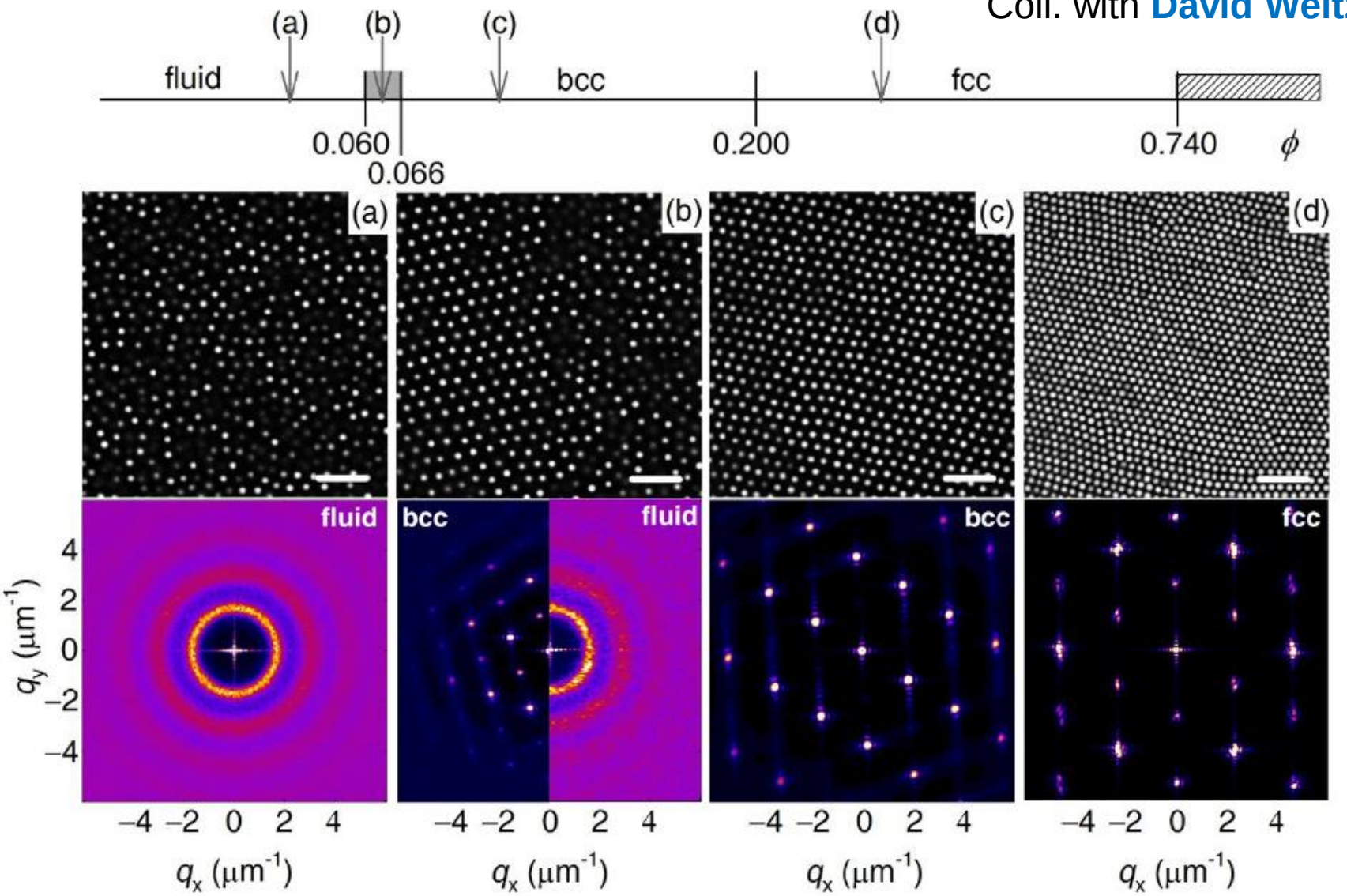
$$G = \frac{2}{5\pi}\left(\frac{\kappa}{R_0}\phi_c e^{\alpha_T(T_c-T)}\sqrt{\phi_c[e^{\alpha_T(T_c-T)}-1]}-\frac{kT}{R_0^3}e^{-\alpha_T T}\right) \sim \sqrt{T_c - T}$$

scaling confirmed by MD simulations in **J. Wittmer et al., JCP 2013**

# Application (2): crystal melting in 3D

**Colloidal crystals**: the particles (~ 1 micron) and their dynamics can be followed by confocal microscopy (unlike atoms)

Coll. with **David Weitz**

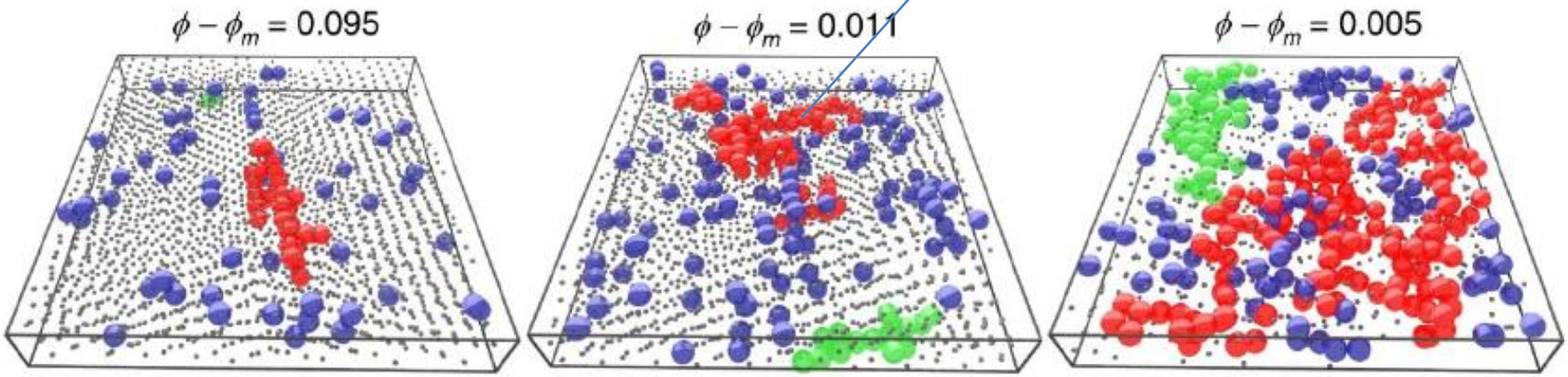


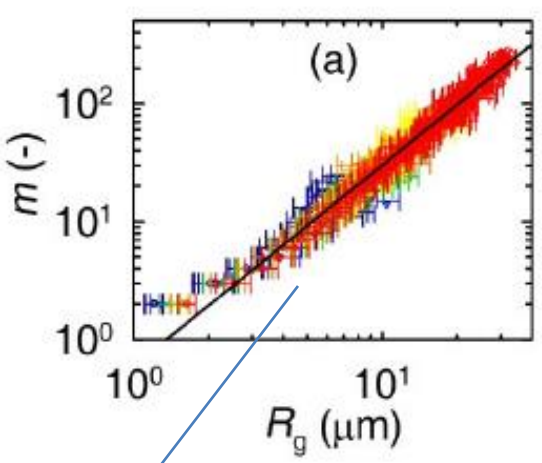
# Application (2): crystal melting in 3D

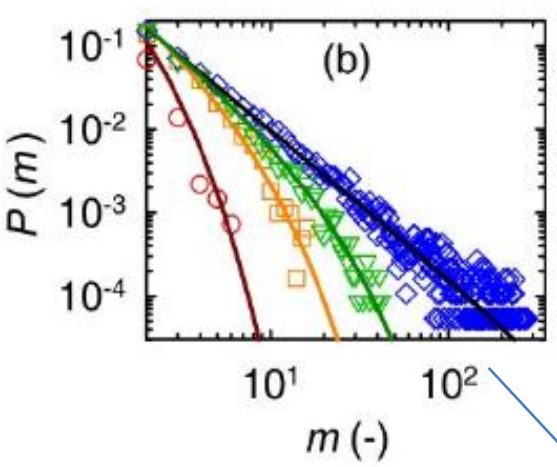
With colloids, melting is driven by the density φ. Upon approaching the melting point, the dynamics of particles becomes highly **disordered** (thermal fluctuations)

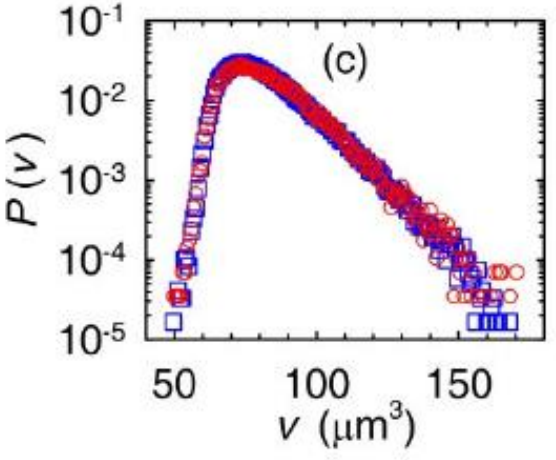
**Sprakel, Zaccone, Spaepen, Schall, Weitz, preprint 2014**

clusters of highly mobile particles



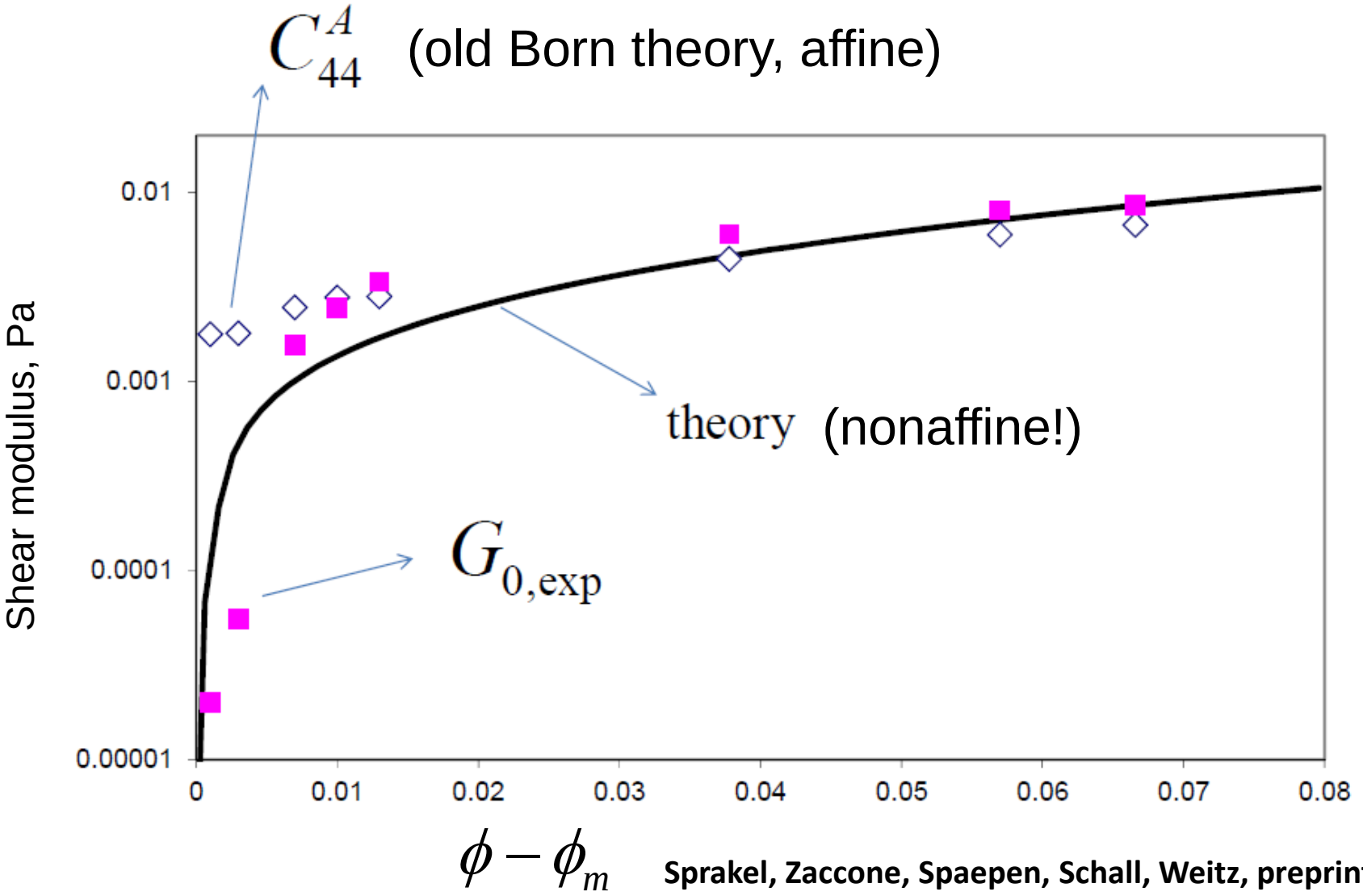




fractal dimension of the clusters ~1.75 → critical exponents

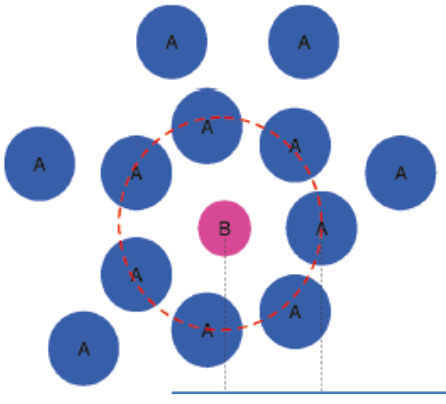
# A new melting criterion

**Born** criterion (1939): crystals melt when the affine shear modulus vanishes
Our new criterion: crystals melt when the **nonaffine** shear modulus vanishes, due to thermal fluctuations!




**Sprakel, Zaccone, Spaepen, Schall, Weitz, preprint 2014**

# Bimolecular association reactions in crowded environments

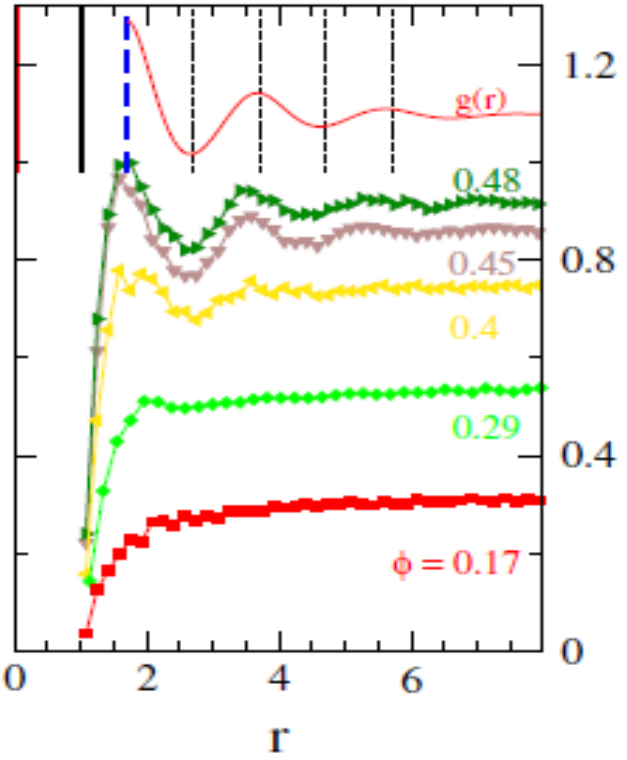



$$A + B \rightarrow B$$

- Attraction between A and B
- Hard-repulsion among A's
- Liquid-like structure

How does the association rate depend on the crowding packing fraction?

**Dorsaz et al. PRL 105, 120601 (2010)**




Governing equation (Smoluchowski diff. eq.)

$$\frac{\partial \rho}{\partial t} = D_c \nabla \cdot (\nabla \rho - \beta F \rho).$$

collective diff.

effective force-field due to crowders:

$$-\int \beta F dr = \beta \int \frac{1}{\rho} \frac{d\Pi}{dr} dr = \beta \int \frac{1}{\rho} d\Pi$$

changes with r due to g(r) !