Rigidity of materials as a consequence of configurational constraint

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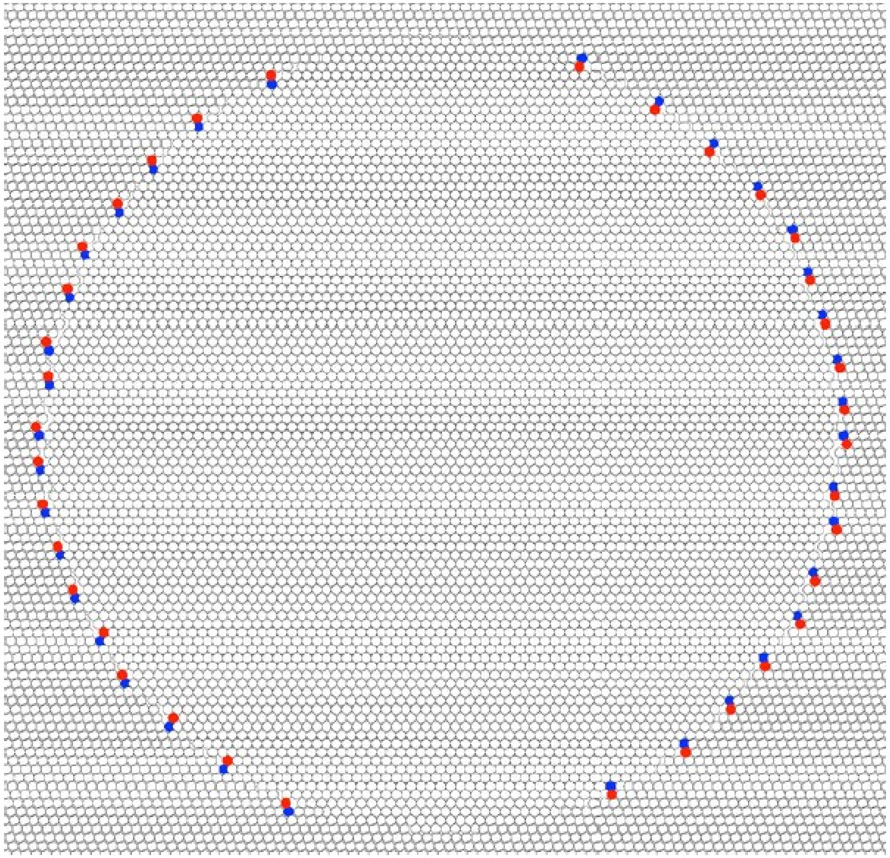
Glasses are Rigid but not Liquids

However, there is difficulty with this distinction, because, rigidity is not an equilibrium property.

Rigidity as a property of metastability



A droplet of undeformed solid is nucleated after an applied shear stress σ. This deformed state is assumed to be metastable as the energy is higher than that of the undeformed state. So, the elastic response (rigidity or shear modulus) is a metastable property.

Sausset, Biroli, Kurchan,
J. Stat. Phys. (2010)

An alternative statement of metastability: Equilibrium within a constrained configuration space

Fluctuations of Shear Stress and Shear Modulus

The zero frequency shear modulus Geq can be written in terms of fluctuation of shear stress σ

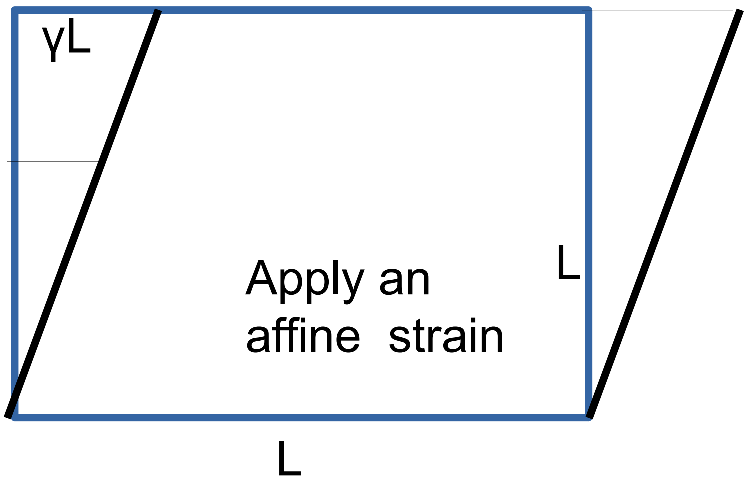
$$G_{eq} = G_{\infty} - \beta V \left[\langle \sigma^2 \rangle - \langle \sigma \rangle^2 \right]$$

Born modulus or infinite frequency modulus

Reduction in modulus due to fluctuation

Squire-Holt-Hoover, *Physica* **42**, 388 (1969).

Born modulus G_∞ at finite T



When an affine strain is applied G_∞ is determined directly as ratio of difference of stresses and applied strain.

$$G_\infty = \rho k_B T + \left\langle \frac{1}{2V} \sum_{i,j} r_{ij,x}^2 r_{ij,y}^2 \left(\frac{\phi''(r_{ij})}{r_{ij}^2} - \frac{\phi'(r_{ij})}{r_{ij}^3} \right) \right\rangle - P;$$

Fuereder and Ilg, JCP (2015).

Fluctuations of Shear Stress and Shear Modulus

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For unconstrained case, $\langle \sigma \rangle = 0$ and $G_{\infty} = \beta V \langle \sigma^2 \rangle$

Zwanzig and Mountain, JCP (1965).

⇒ $\mathbf{G_{eq} = 0}$

So, what is the meaning of 'equilibrium' non-zero shear modulus?

Take averages over a constrained configurational space

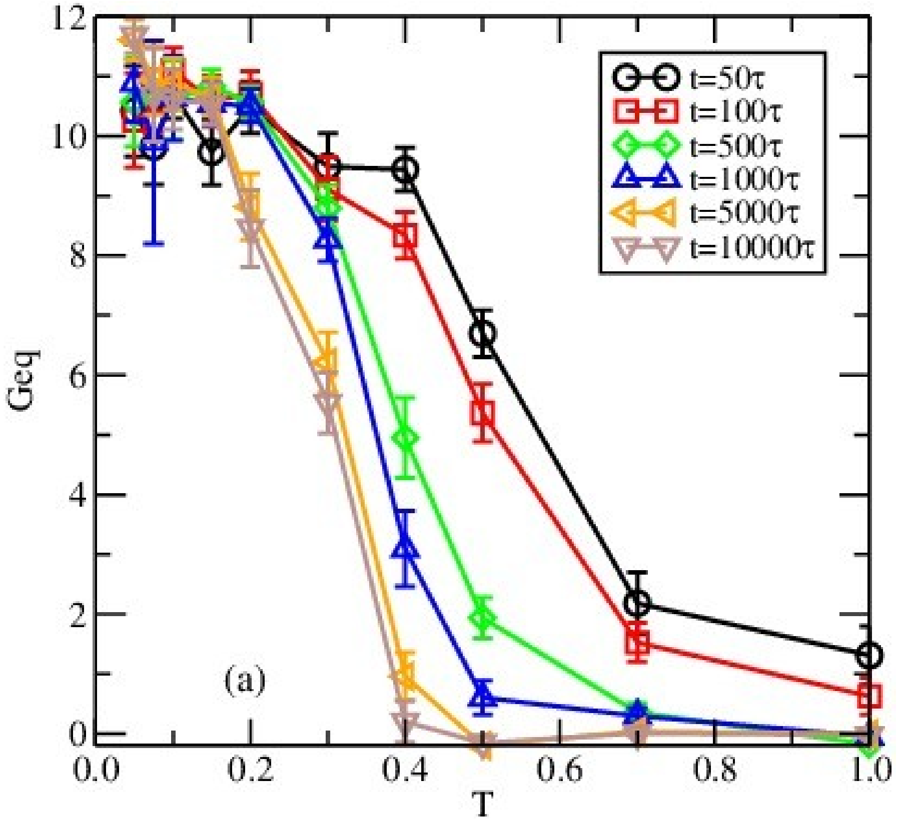
$$G_{eq} = G_{\infty} - \beta V\left(<\sigma^2>_{\alpha} - <\sigma>_{\alpha}^2\right)$$

the equilibrium averages are taken over a constrained configuration space

Williams and Evans, JCP (2009).

Temperature dependence of shear modulus of 2D amorphous solid

2D soft disk mixture $\phi_{ij}(r) = \varepsilon(\sigma_{ij}/r)^{12}$ $\sigma_{11} = 1.0$ $\sigma_{22} = 1.4$ $\sigma_{12} = 1.2$

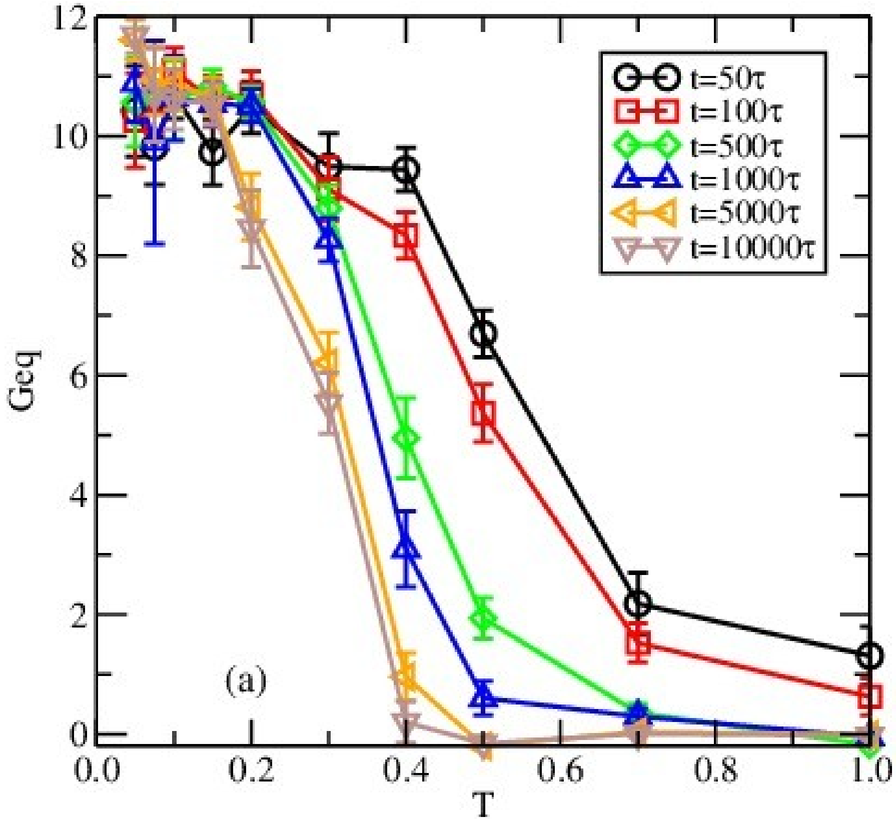


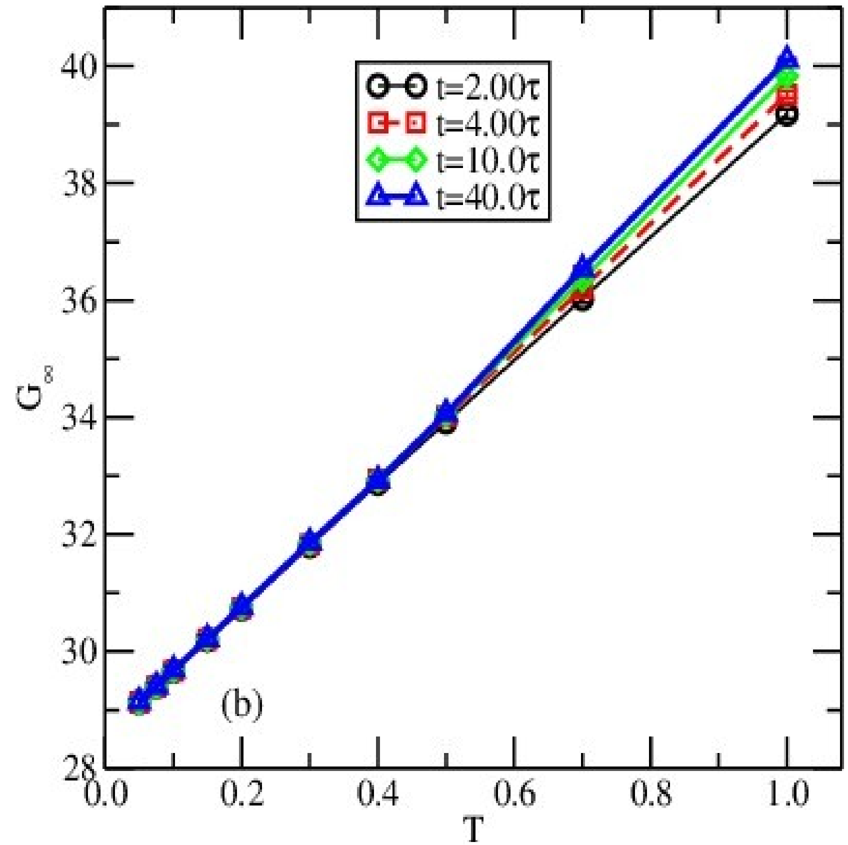
NVT simulations.

Assumption: Average of stress fluctuation over a finite time ≈ An equilibrium average over a constrained phase space

- Geq decreases with T as well as averaging times.

Dependence of shear modulus and Born modulus G_∞ on averaging times

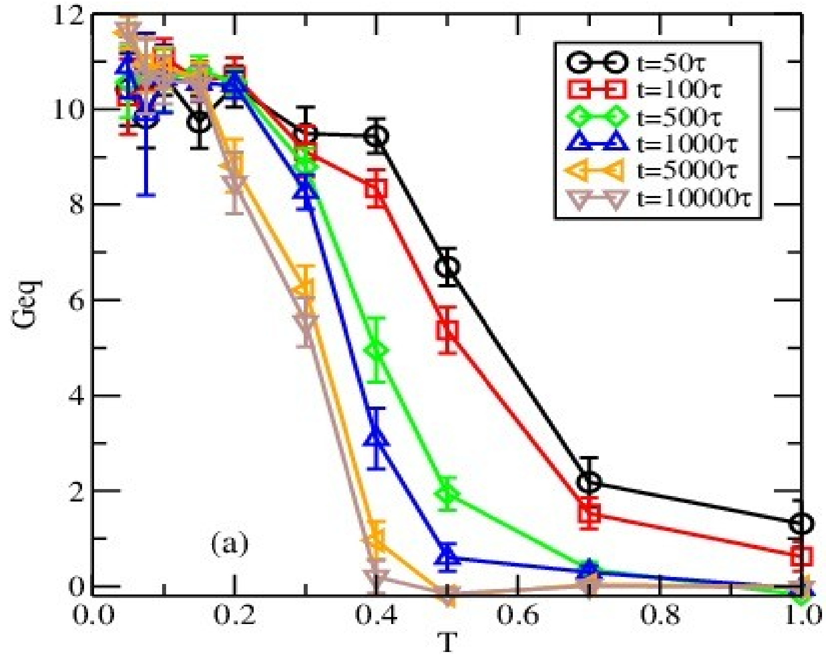


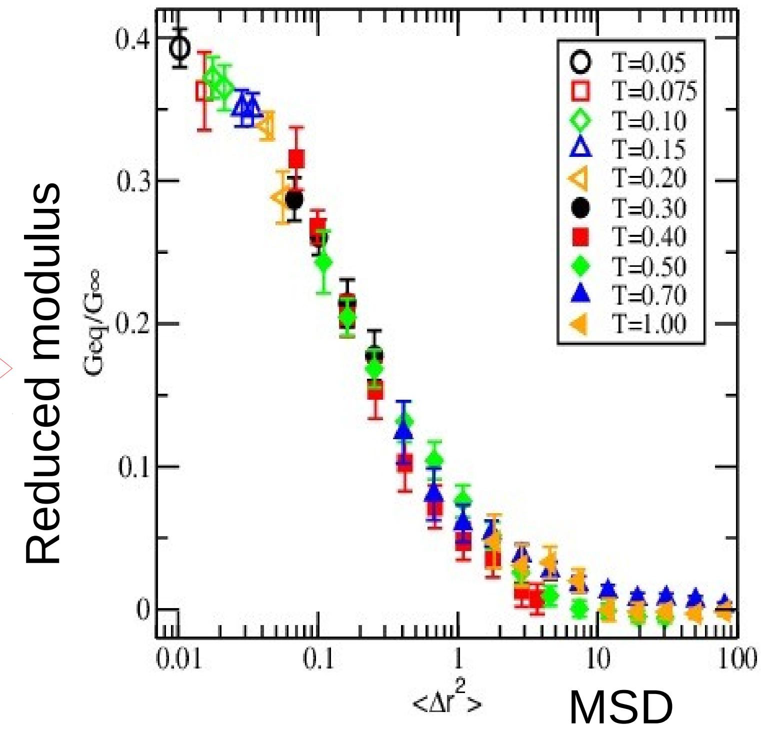


SS & PH, PRL(2016)

- G_∞ exhibits no significant dependece on the averaging times.

Dependence of shear modulus on MSD: binary glass

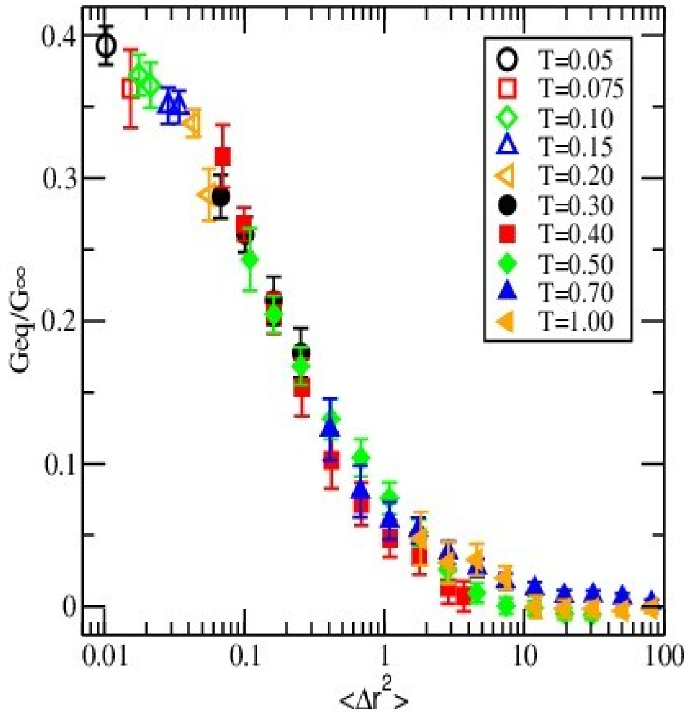


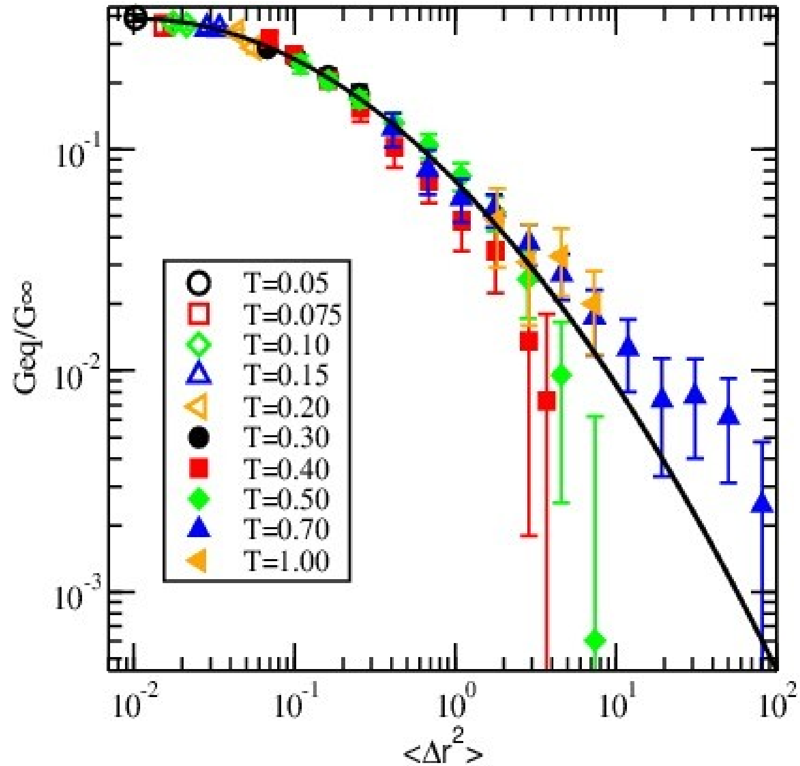


Reduced modulus (Geq/G_∞) decreases with increase of MSD (corresponding to different avearging times).

Data for all T falls on a universal curve.

Dependence of shear modulus on MSD: binary glass





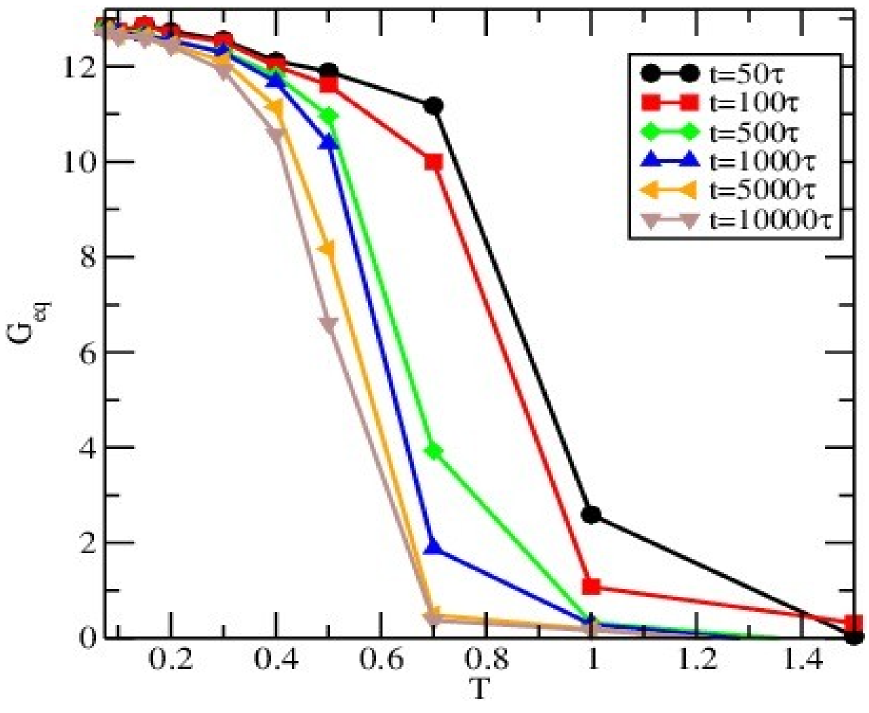
SS & PH, PRL(2016)

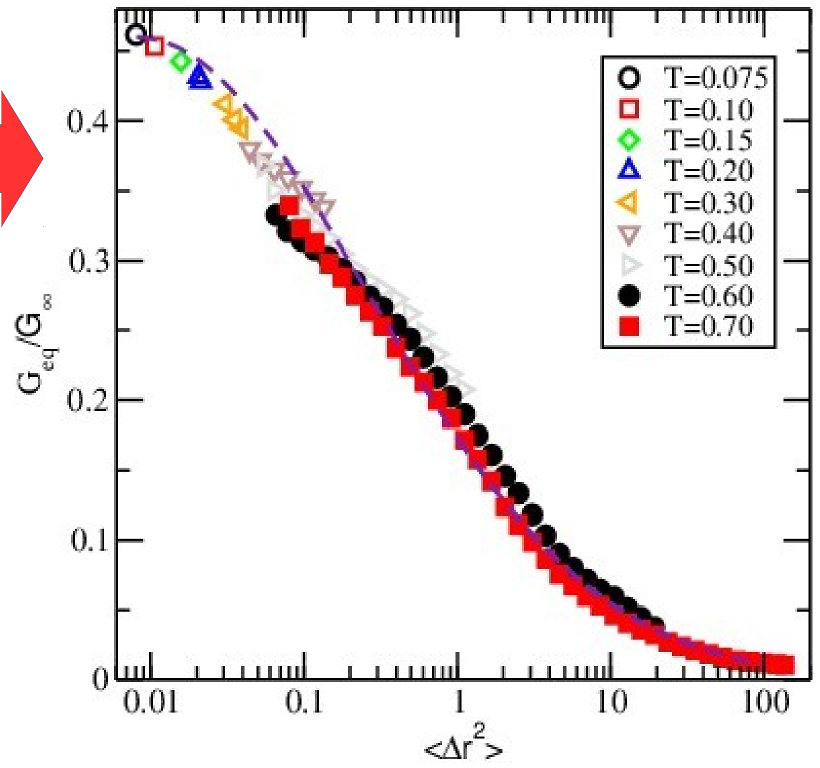
Below empirical equation describes data for whole range of values.

$$\frac{G_{eq}}{G_\infty} = \left[\frac{G_{eq}}{G_\infty}\right]_{T=0.05} \exp\left[-0.08 \ln^2\left(\frac{\Delta r^2}{\Delta r^2_{T=0.05}}\right)\right]$$

Scaling holds good in 3D systems also

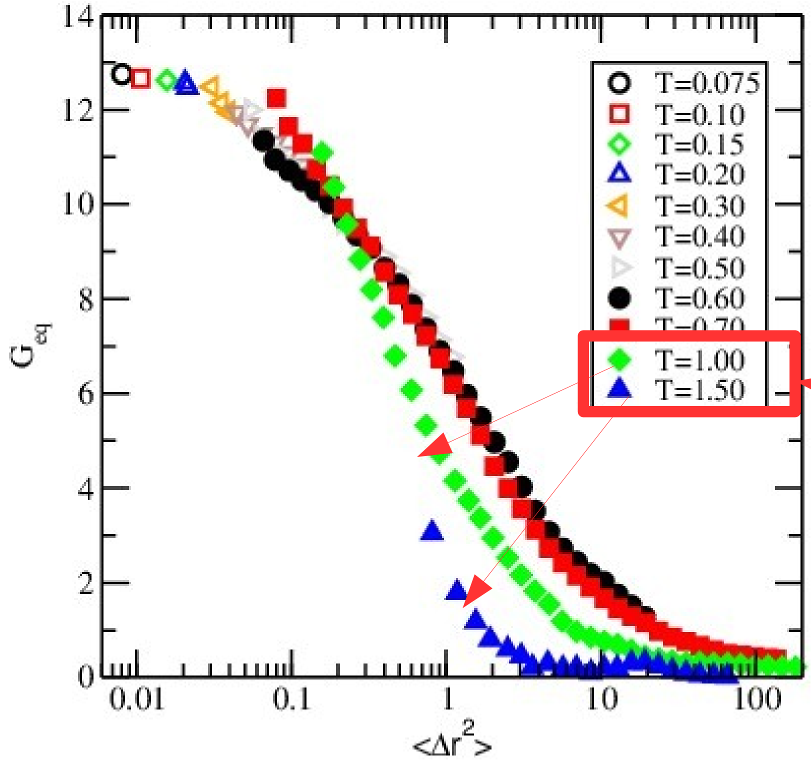
Equimolar LJ mixture with size ratio 1.2 (additive).

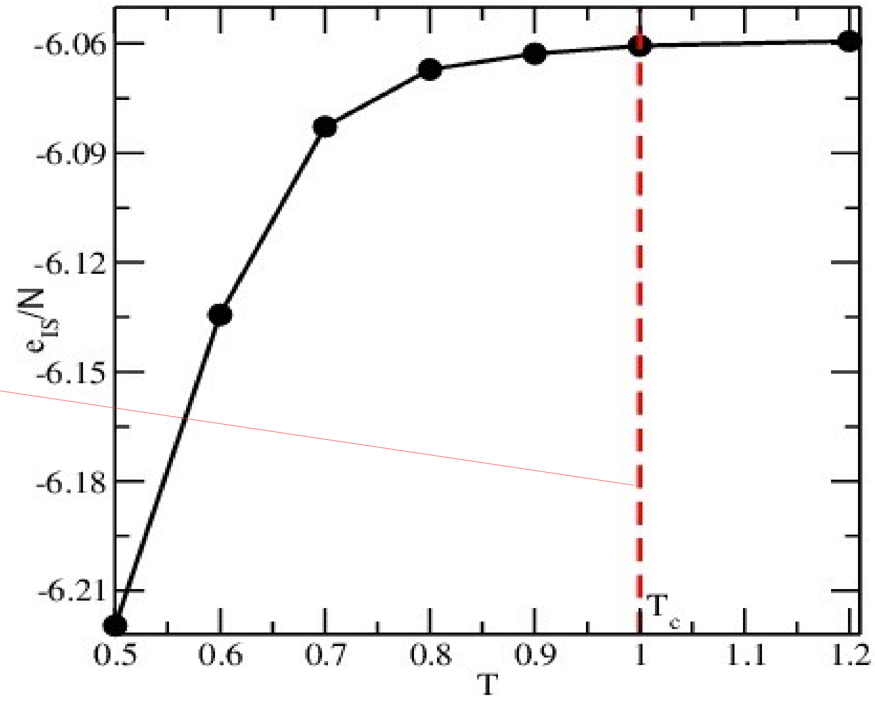




- The results of 3D systems are similar to 2D systems.
- So, rigidity of a system is due to configurational constraint and is universal.

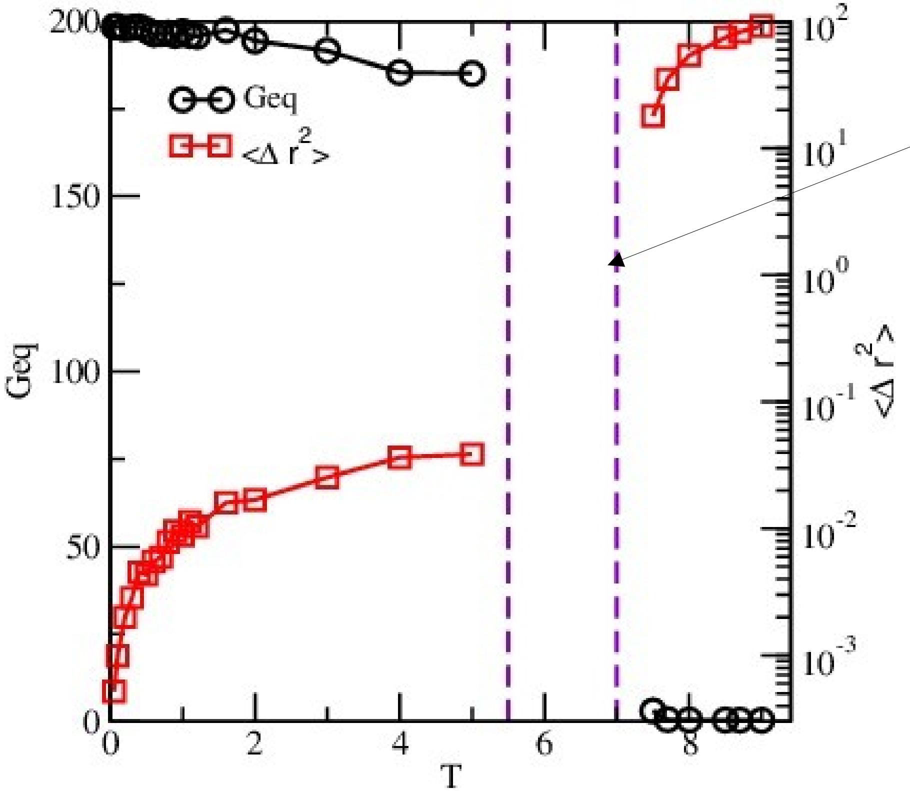
Scaling holds good only below crossover temperature





- Above crossover temperture Tc inherent structure energy is insenstitve of temperature.
- Geq/G_∞ deviates from the master curve above Tc.

Does Constraint-Rigidity Scaling also holds for crystal and their melts?

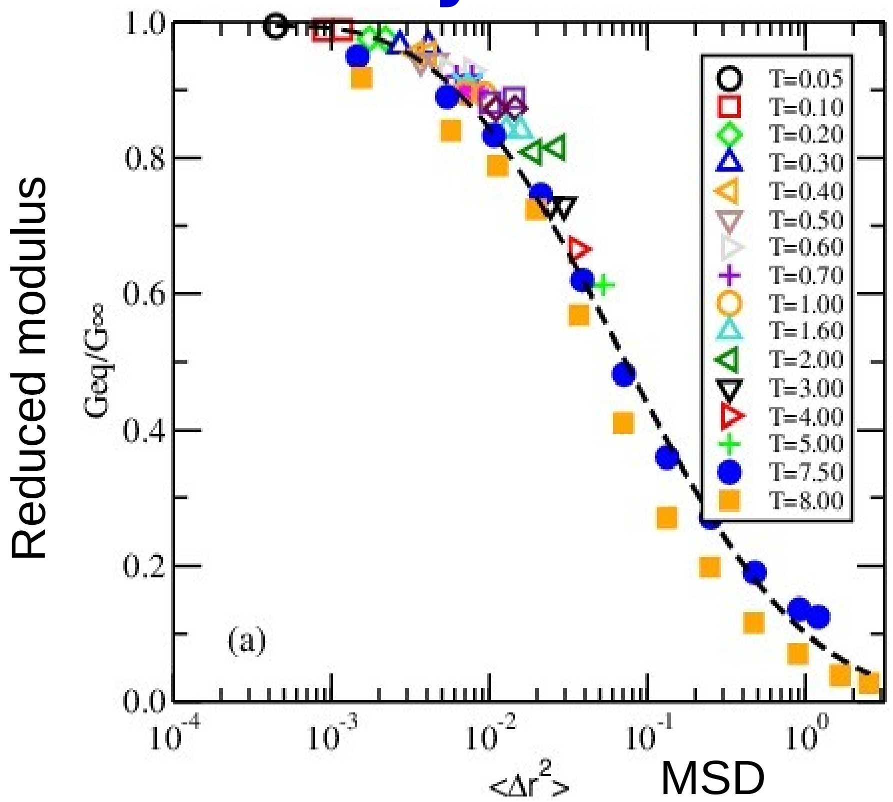


Tentative crystal+liquid coexistence line

SS & PH, PRL(2016)

- Averaging time = 199τ.
- Discontinuity in Geq as well as MSD at freezing point.
- Geq for liquids are zero.

Does Constraint-Rigidity Scaling also holds for crystal and their melts?



The reduced shear modulus falls on a common curve.

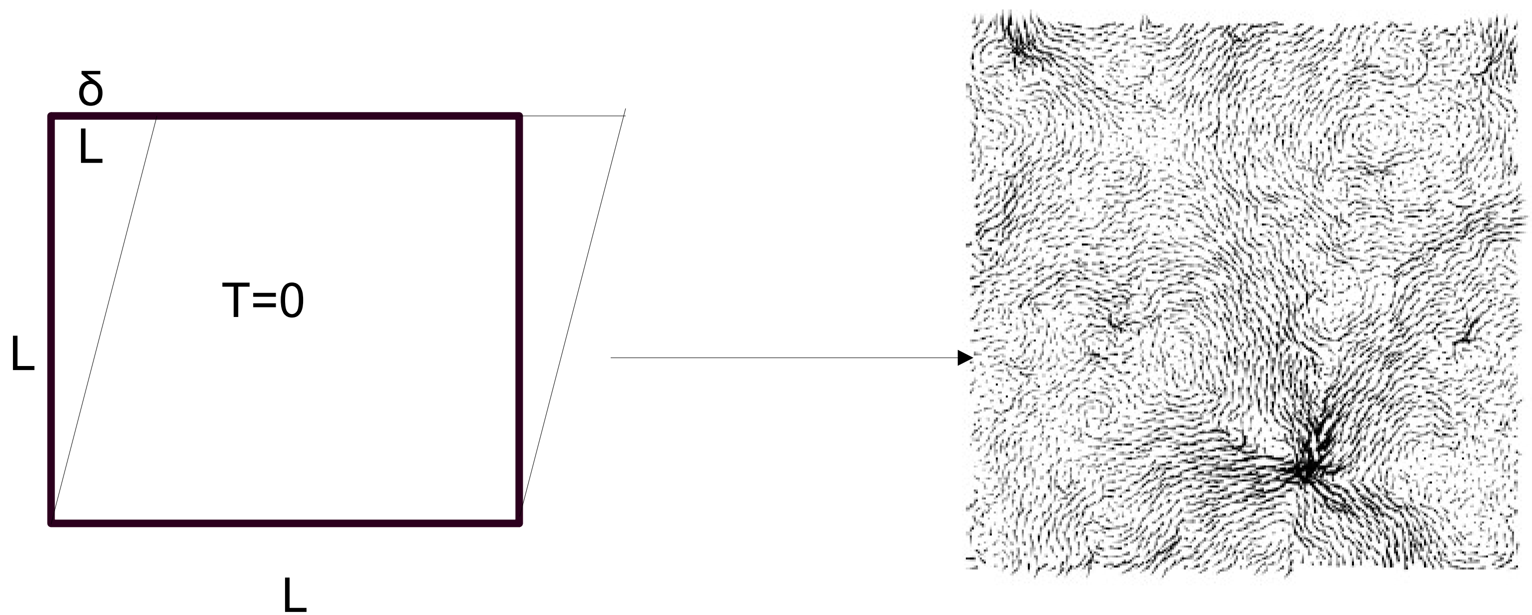
SS & PH, PRL(2016)

- Liquids have finite modulus for small MSD means large configurational constrained.
- Same emperical equation describe the data (with different parameters)

$$\frac{G_{eq}}{G_\infty}=\left[\frac{G_{eq}}{G_\infty}\right]_{T=0.05}\exp\left[-0.0061\ln^{2.9}\left(\frac{\Delta r^2}{\Delta r^2_{T=0.05}}\right)\right]$$

Another route of configurational constraint

Apply an external shear strain at T=0.



Non-affine relaxation

We measure **MSD** during this **non-affine process**.

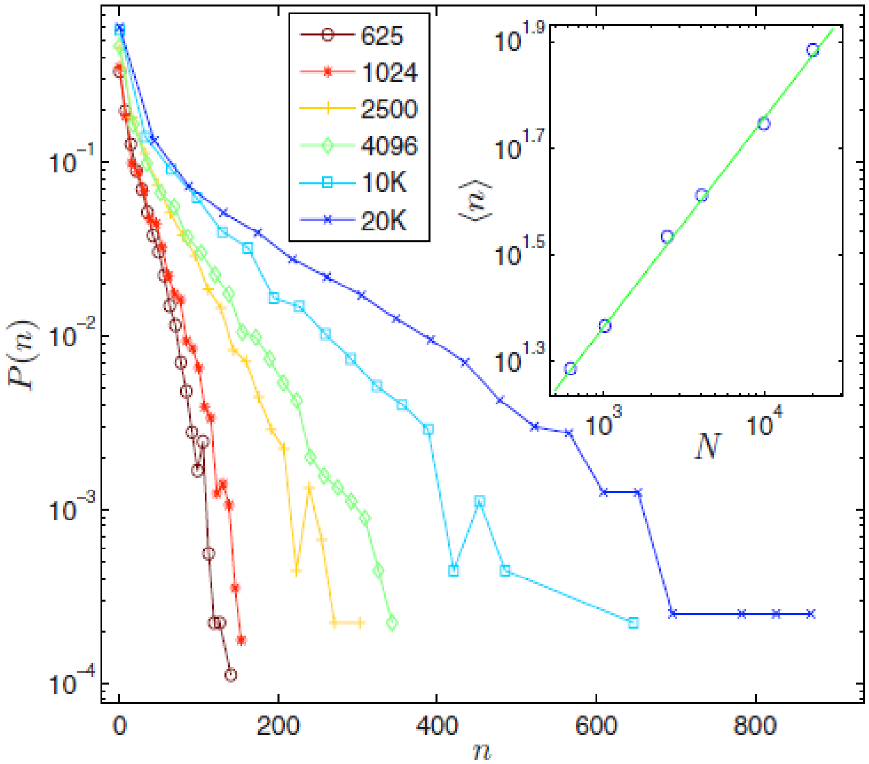
Plastic deformations

Microscopic mechanism (moleculr rearrangement under applied strain) responsible for pastic deformation are:
(1) irreversible and (2) localized

Argon, Acta Metall. (1979);
Falk and Langer, Phys. Rev. E (1998)

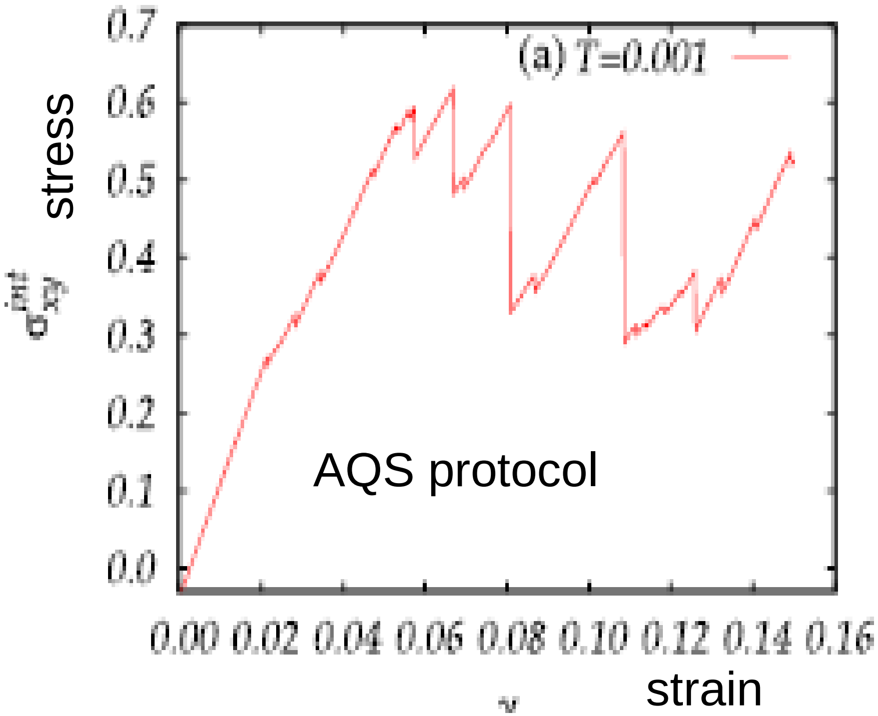
However, the locality of plastic deformations has been recenlty challanged.

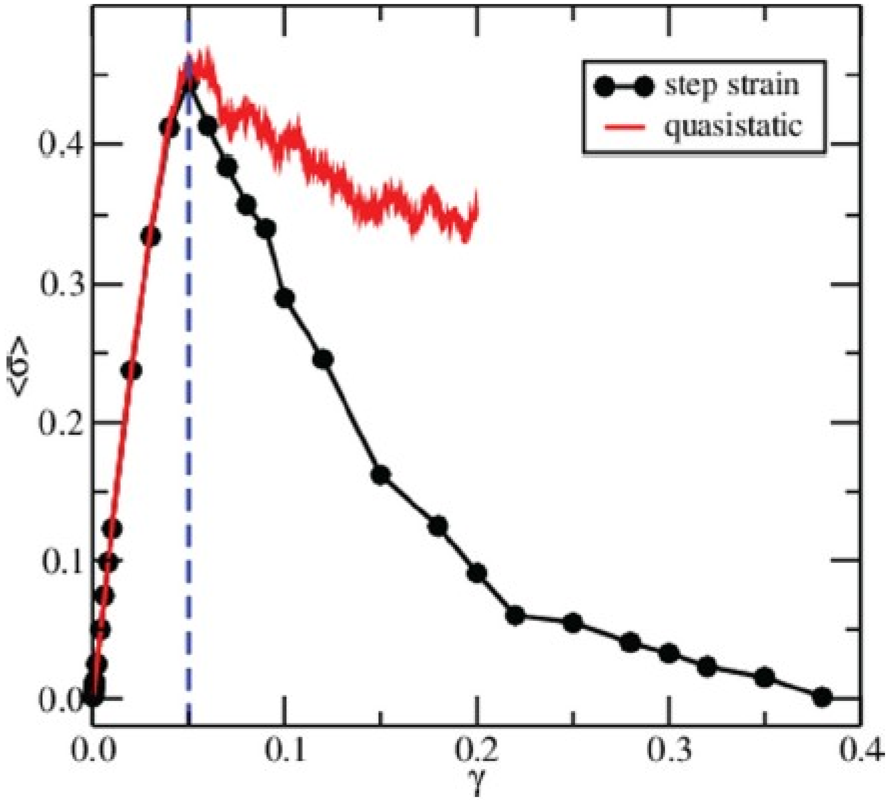
Maloney and Lemaitre, Phys. Rev. E (2006),
Lerner and Procaccia, Phys. Rev. E (2009)



Do microspcopic mechanism responsible for stress relaxation really need to be irreversible?

Same yield strain in Athermal Quasistatic (AQS) and step strain



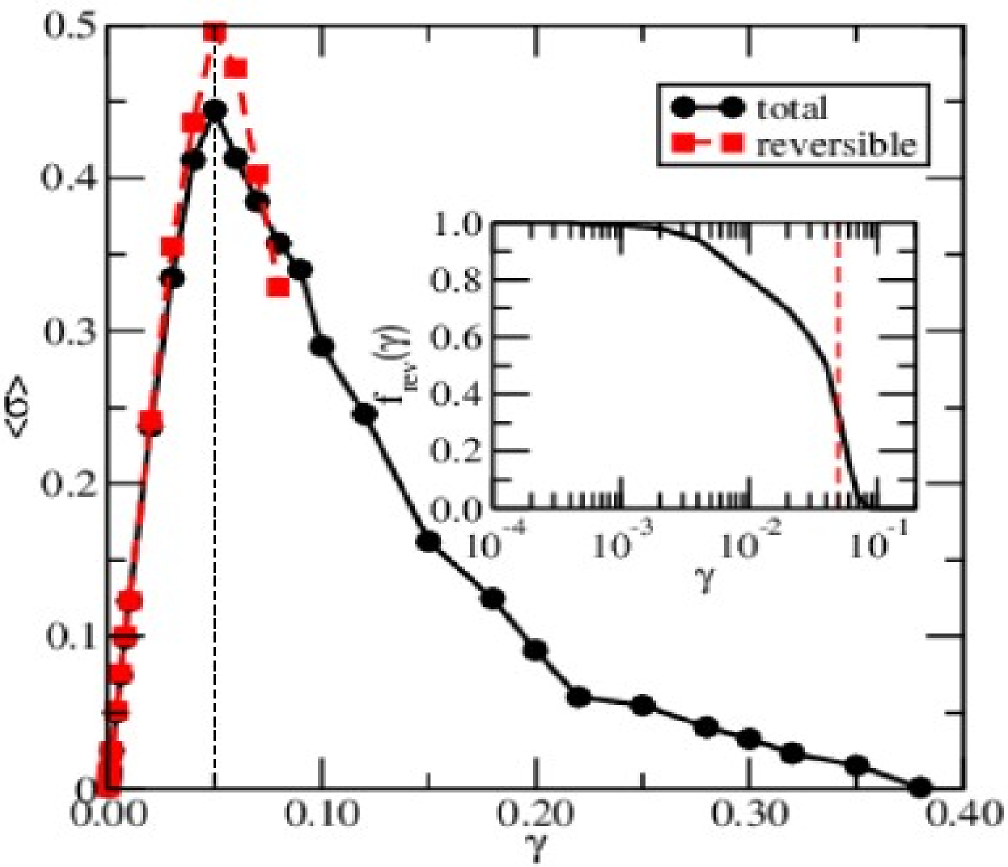


Dubey et al, PRL(2016)

SS, SA, PH, PRE(2016)

In the AQS protocol, stress is accumulated over time and then it releases as plastic events.
The yield strain is same for two protocols.

Does yield behaviour require irreversible events?



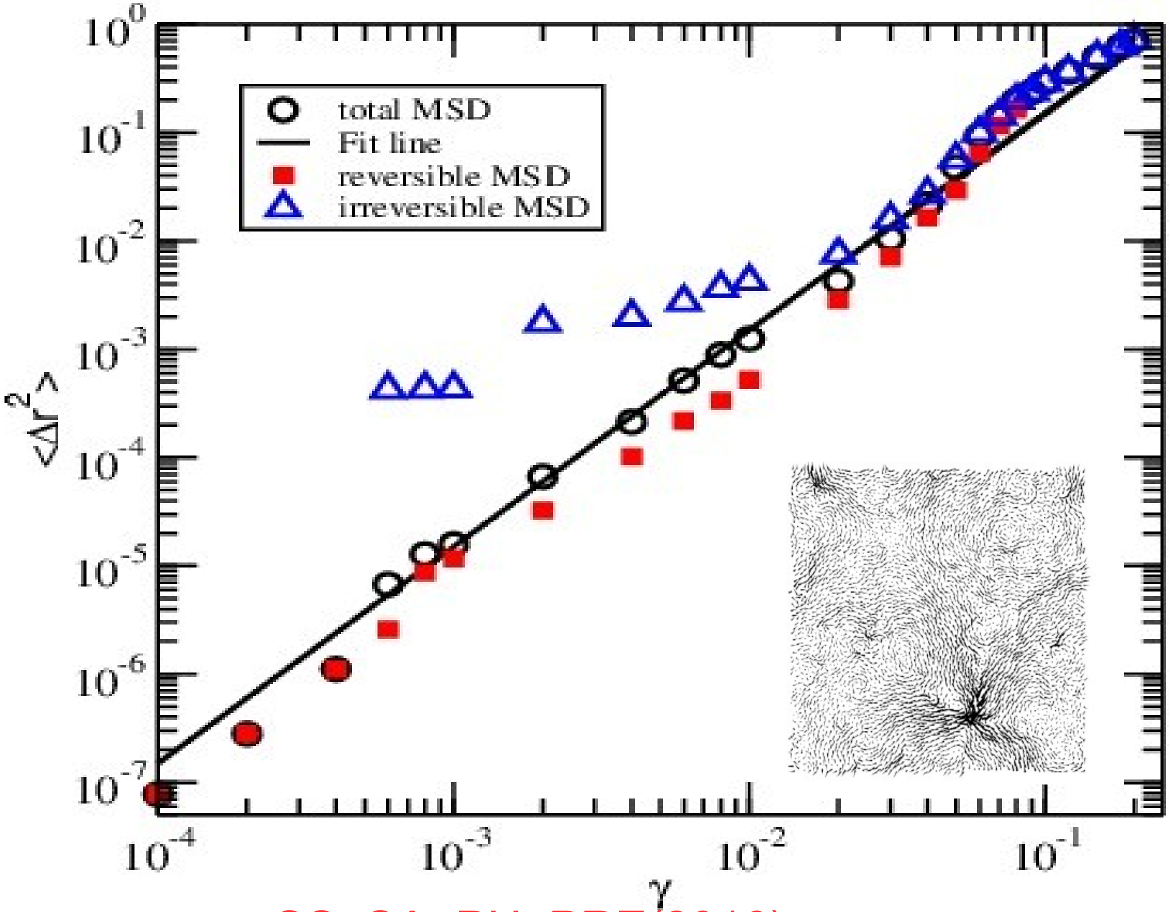
SS, SA, PH, PRE(2016)

A strain is reversible if the original configuration is recovered by reversing the strain followed by minimization.

f_v = fraction of configurations exhibiting reversible strain

Yes, irreversibility dominates at the yield strain. However, reversible strain are quite capable to show yield behaviour.

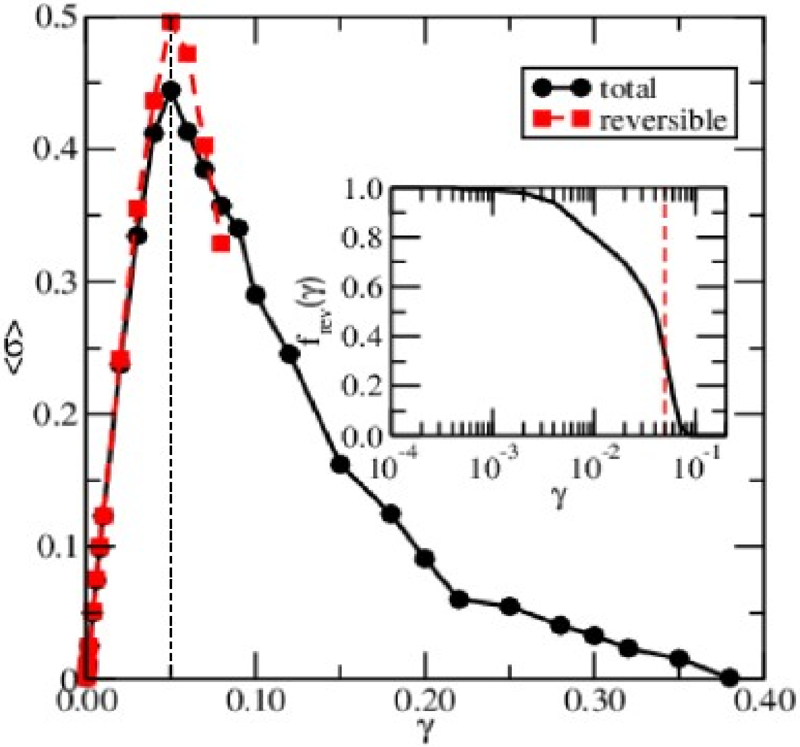
MSD for step shear strain at T=0

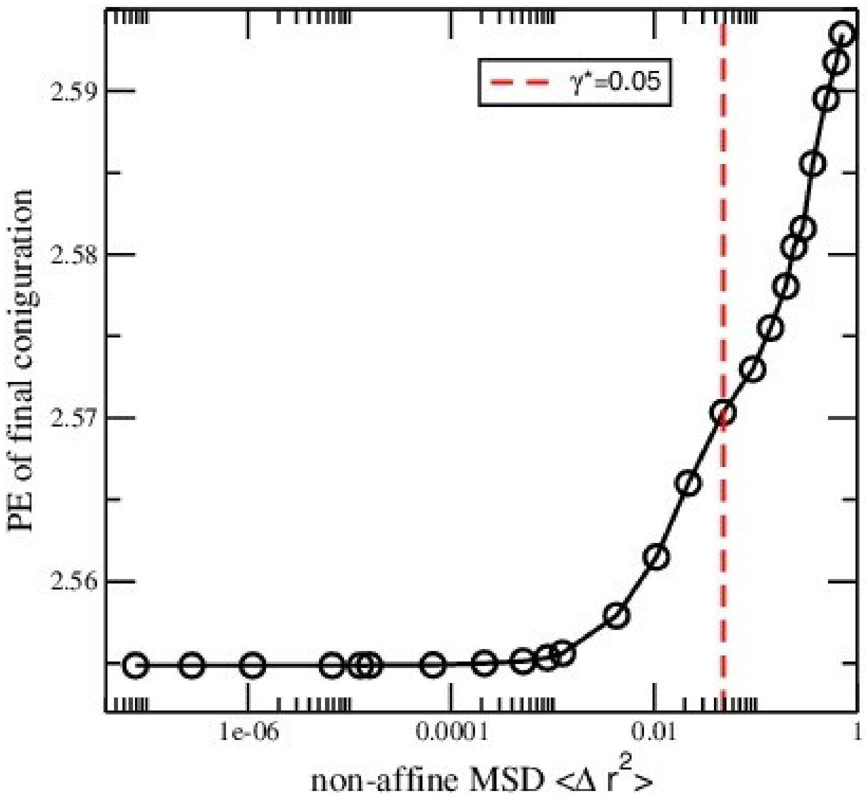


SS, SA, PH, PRE(2016)

The MSD (non-affine) increases with increasing applied strain γ.

Zero shear stress at high shear strain



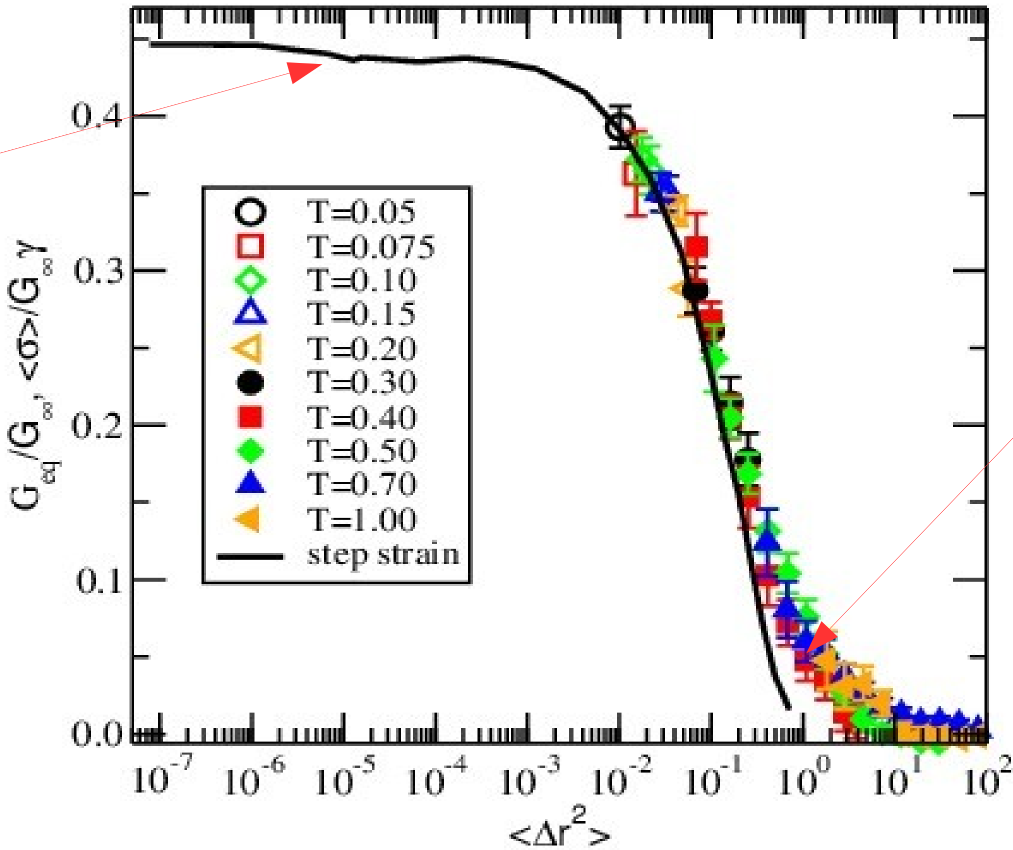


Increasing γ

The IS energy increases with the increase of the applied shear strain (non-affine MSD).

External shear strain at T=0

$\langle\sigma\rangle/G_\infty\gamma$ with shear driven displacement (T=0)

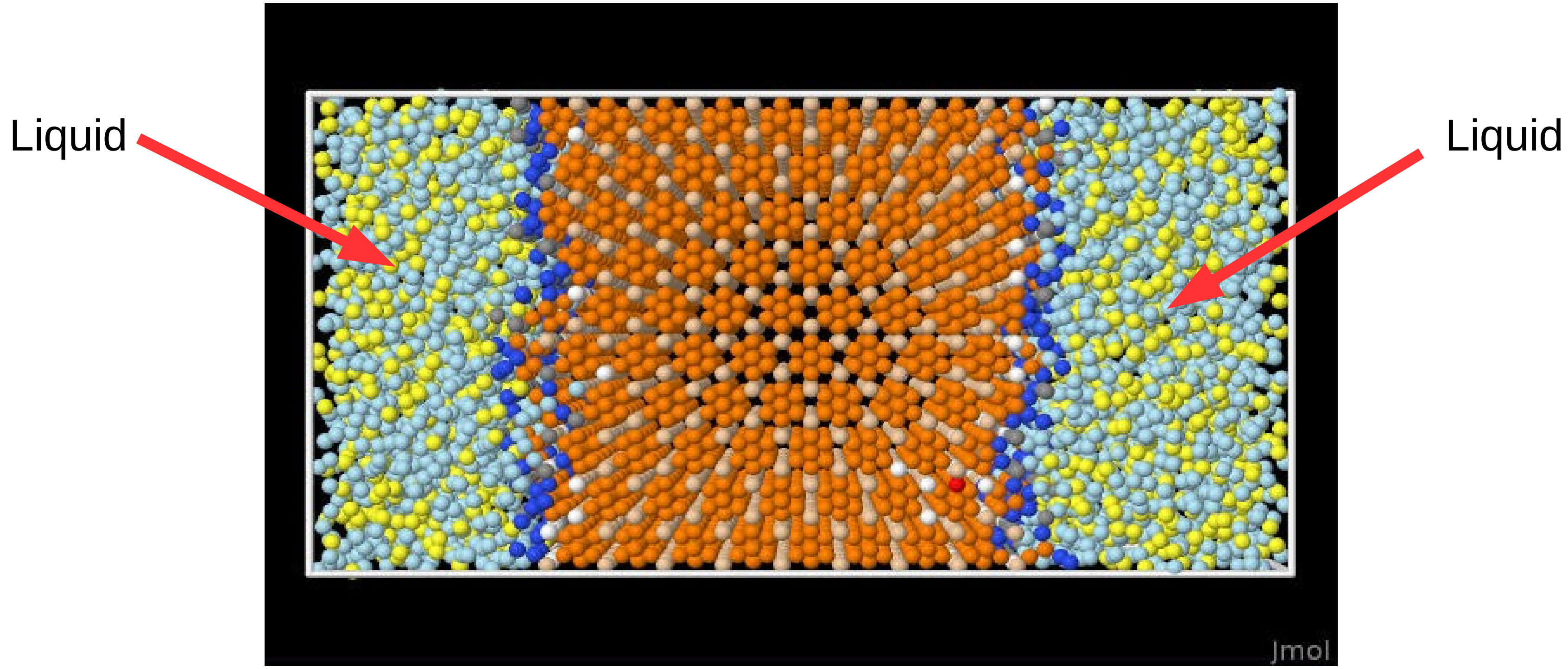


G_{eq}/G_∞ with thermal motion (T > 0)

SS, SA, PH, PRE (2016)

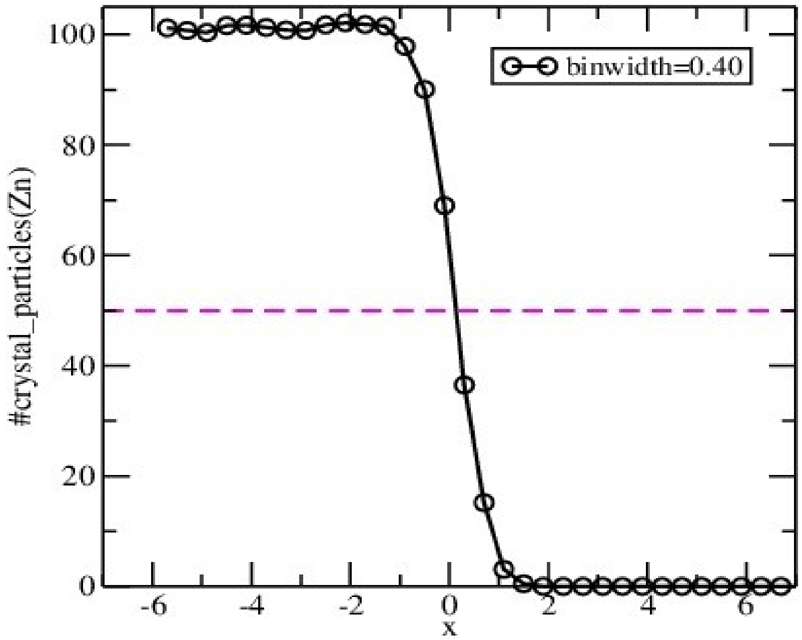
This supports the preposition that the degree of configurational constraint controls the rigidity. The manner by which this constraint is achieved is irrelevant.

Crystal-glass Interface of $MgZn_2$



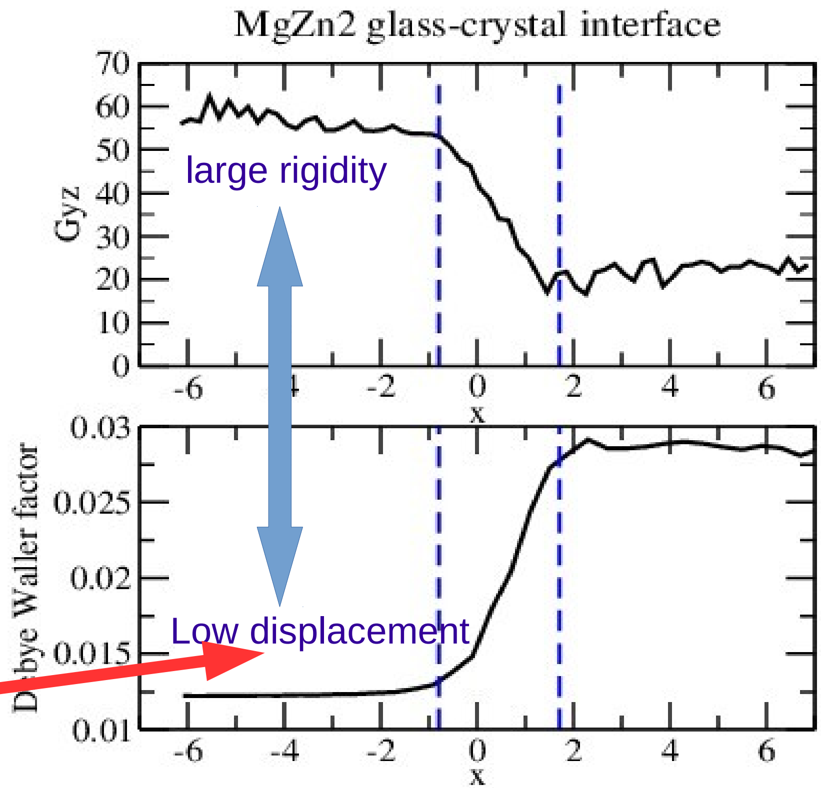
- First an equilibrated crystal and liquid configuration are obtained through molecular dynamics (MD) simulations.
- The crystal and liquids are brought together and then system is relaxed at P=0.
- Finally, this system is energetically minimized to obtain an inherent structure (minimum energy configuration) at T=0.

Structure: Variation of Zn crystal particles normal to interface



- # of crystal (Zn) particles changes smoothly at the glass-crystal interface.
- So, the glass-crystal interface is sharp (ie in yz plane).
- The structure is a local quantity and it is not affected by any change at other place.

Spatial shear modulus



Individual Debye-Waller factor is given by

$$DWi = \frac{\sum_k |e_k^i|^2}{\omega_k^2}$$

Large configurational constraint

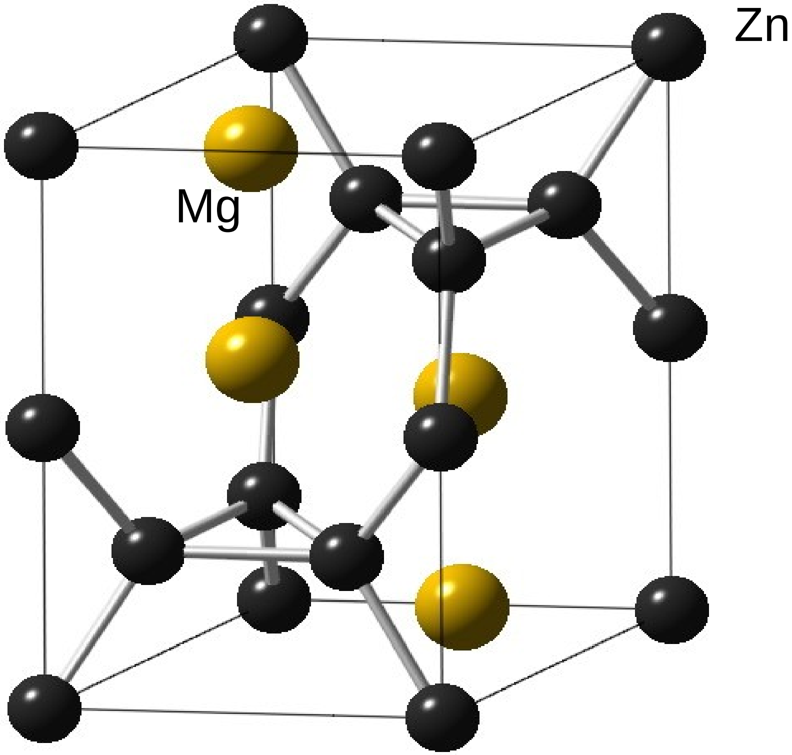
A small local dynamics means an increased configurational constrained and hence enhanced local rigidity, similar for a thermal and an athermal system under an applied strain.

Conclusions

- The degree of configurational constraint determines the magnitude of the rigidity (shear modulus) of materials.
- MSD provides a useful measure of the configurational constraint.
- This picture holds good for glasses as well as crystals which unifies the physical basis of the rigidity.
- This relationship is insensitive to the details of how the configurational constraint is achieved.
- Parameters such as low T, high frequency measurement, time and even long-range ordering add to the constraint implicitly to enhance the rigidity.
- This result holds good for both 2D and 3D systems.
- A significant fraction of solids shows yield via a reversible strain.

THANKS!

MgZn2 Crystal Structure



r_{Mg}/r_{Zn}=1.225 ➡ 71% packing fraction (largest for binary).

- Each Mg-Mg pair shares 6 Zn neighbor.

Potential for $MgZn_2$ used: Morse potential

$$\phi_{ij}(r) = \exp\left(-2\alpha\left[\frac{r}{\sigma_{ij}}-1\right]\right) - 2\exp\left(-\alpha\left[\frac{r}{\sigma_{ij}}-1\right]\right)$$

$$\varphi_{ij}^{actual}(r) = \varphi_{ij}(r) + (r^{*}-r)\varphi_{ij}'(r^{*}) - \varphi_{ij}(r^{*})$$

$\sigma_{Mg} = 1.0$

$\sigma_{Zn} = 0.815$ → $r_{Mg}/r_{Zn}=1.225$ → 71% packing fraction

$\sigma_{Mg\text{-}Zn} = (1.0+0.816)/2$

$\alpha = 6.0$

Local Born modulus: from T=0 configuration

Born modulus in yz plane=

$$C^{m}_{B\alpha\beta\gamma\delta} = \frac{1}{w_x w_y w_z}\sum_{i<j}\left(\frac{\partial^2 V_{ij}}{\partial {r_{ij}}^2} - \frac{1}{r_{ij}}\frac{\partial V_{ij}}{\partial r_{ij}}\right)\frac{r_{ij\alpha}r_{ij\beta}r_{ij\gamma}r_{ij\delta}}{{r_{ij}}^2}\frac{q_{ij}}{r_{ij}},$$

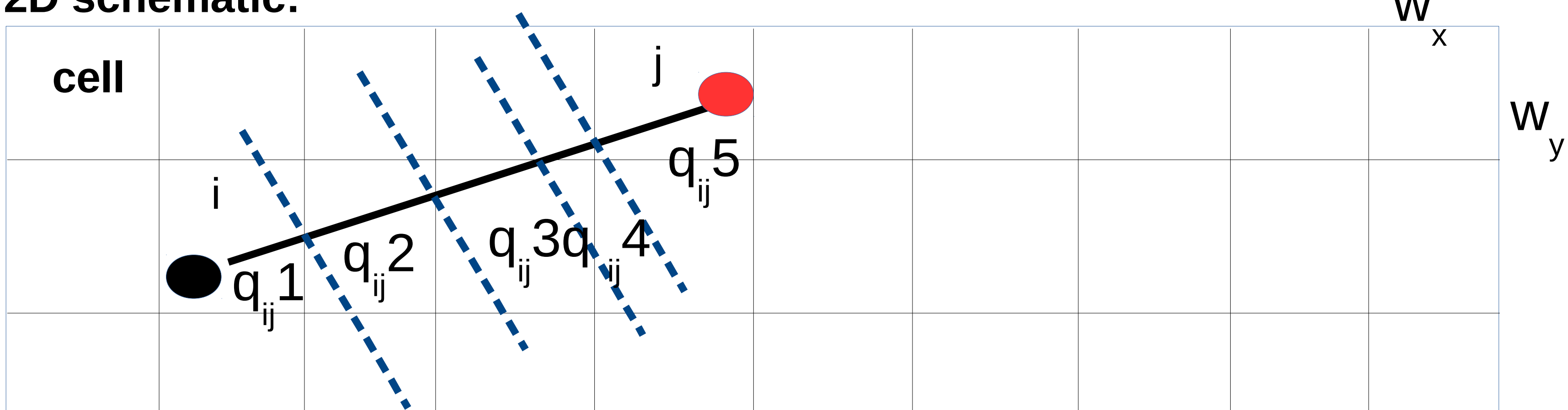
cell

+

$$C^{m}_{C\alpha\beta\gamma\delta} = -\frac{1}{2}\left(2\sigma^{m}_{\alpha\beta}\delta_{\gamma\delta} - \sigma^{m}_{\alpha\gamma}\delta_{\beta\delta} - \sigma^{m}_{\alpha\delta}\delta_{\beta\gamma} - \sigma^{m}_{\beta\gamma}\delta_{\alpha\delta} - \sigma^{m}_{\beta\delta}\delta_{\alpha\gamma}\right),$$

α=γ=y; β=δ=z

2D schematic:



Local shear modulus from normal modes

Local shear modulus in yz plane

all modes

$$C^m_{N\alpha\beta\gamma\delta} = \sum_{k=1}^{3N-3} \frac{L^3}{\omega^{k2}} \left(\sum_{i=1}^{N} \boldsymbol{e}_i^k \cdot \frac{\partial \sigma^m_{\alpha\beta}}{\partial \boldsymbol{r}_i} \right) \left(\sum_{j=1}^{N} \boldsymbol{e}_j^k \cdot \frac{\partial \sigma_{\gamma\delta}}{\partial \boldsymbol{r}_j} \right)$$

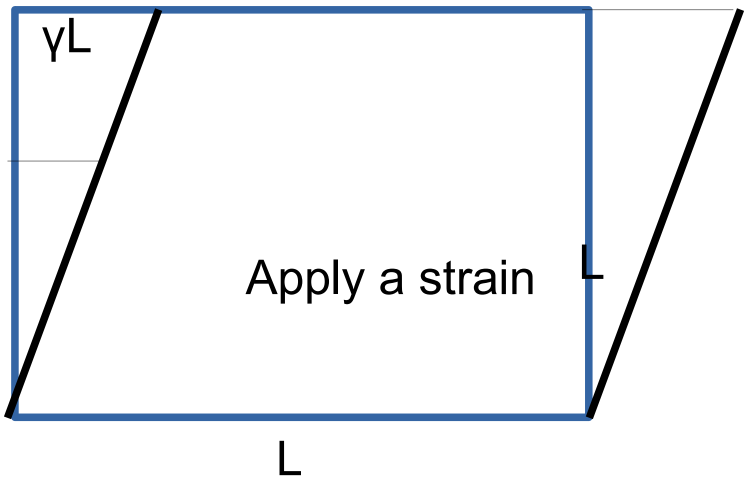
$$\sigma^m_{\alpha\beta} = -\hat{\rho}^m T \delta_{\alpha\beta} + \frac{1}{w_x w_y w_z} \sum_{i<j} \frac{\partial V_{ij}}{\partial r_{ij}} \frac{r_{ij\alpha} r_{ij\beta}}{r_{ij}} \frac{q_{ij}}{r_{ij}},$$

where ω_k is an eigen frequency and e_i^k Is an eigen vector.

Note that local shear modulus involves all modes and hence it is an extended quantitiy.

*Mizuno et al, PRL, **116**, 068302 (2016)*

Born modulus G_∞ at finite T



The potential contribution to the shear stress is

$$\sigma_{xy}V = \frac{1}{2}\sum_i\sum_{j\neq i} x_{ij}y_{ij}F_{ij} \quad \text{where } F_{ij} = -\frac{1}{r_{ij}}\frac{d\varphi}{dr_{ij}}$$

Consider a shear strain such that

$$x_{ij} \to x_{ij} + \gamma y_{ij}$$

Plus ρkBT due to temperature.

Then

$$\sigma_{xy}(\gamma)V = \frac{1}{2}\sum_i\sum_{j\neq i}(x_{ij}+\gamma y_{ij})y_{ij}F_{ij}(\gamma)$$

where

$$F_{ij}(\gamma) \approx F_{ij} + \frac{dF_{ij}}{dr_{ij}}\frac{dr_{ij}}{dx_{ij}}\gamma y_{ij} = F_{ij} + \left(\frac{1}{r_{ij}^2}\frac{d\varphi}{dr_{ij}} - \frac{1}{r_{ij}}\frac{d^2\varphi}{dr_{ij}^2}\right)\frac{\gamma x_{ij}y_{ij}}{r_{ij}}$$

When a strain is applied G_∞ is determined directly as ratio of difference of stresses and applied strain.

What about a system at finite T??

$$G_\infty = [\sigma_{xy}(\gamma) - \sigma_{xy}(0)]/\gamma = \frac{1}{2V}\sum_i\sum_{j\neq i}\left(y_{ij}^2F_{ij}\left[1-\frac{x_{ij}^2}{r_{ij}^2}\right] - \frac{d^2\varphi}{dr_{ij}^2}\frac{x_{ij}^2y_{ij}^2}{r_{ij}^2}\right)$$

Mountain and Zwanzig, *J. Chem. Phys.* 44, 2777(1966).