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SMR/1845-6

Conference on Structure and Dynamics in Soft Matter and Biomolecules: From Single Molecules to Ensembles

4 - 8 June 2007

Rigidity as a tool to understand the role of low frequency modes in glass transition and in flexible systems

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Rigidity as a tool to understand the role of low frequency modes in glass transition and in flexible systems

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Trieste, Italy, 2007

Introduction

Glass and jamming transitions
Low frequency modes “anomalies” and elastic stability.
Rigidity theory

Statistical Mechanics+Rigidity Theory

Thermodynamics and the connection with energy landscape formalism
Effects in hard-core systems, colloids, gels, etc.
Effects in the glass transition.

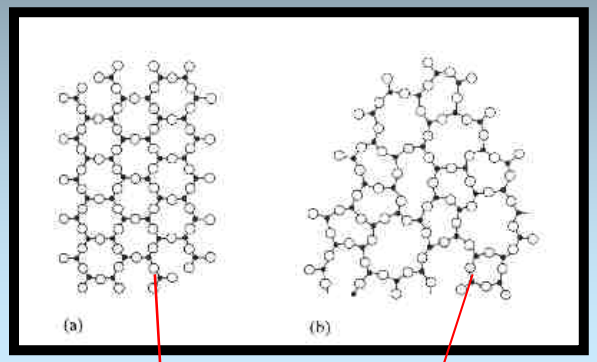
Relaxation and Rigidity

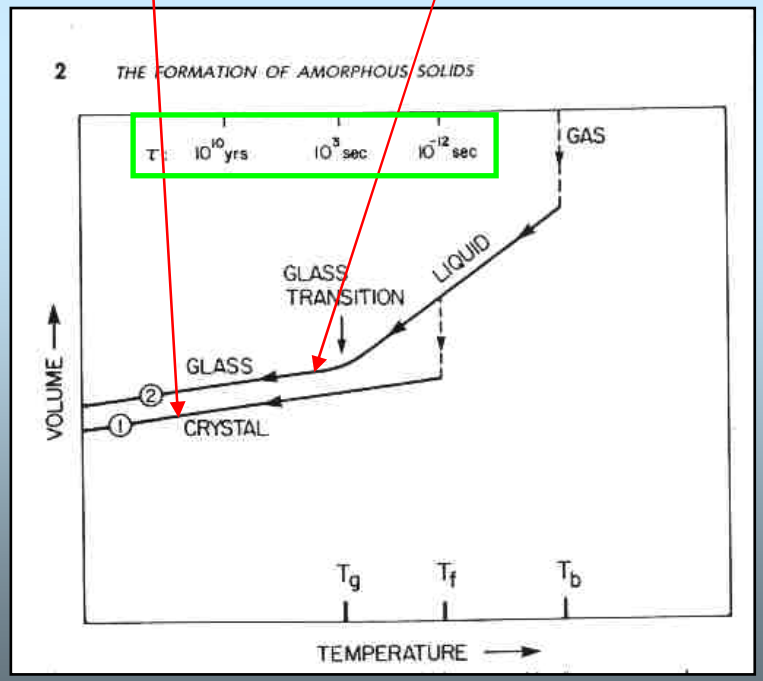
Non-linear mode coupling and relaxation
Energy cascade mechanism
Simulations

Conclusions

Glass and jamming transition

Formation of systems with disorder: glasses, dense colloids, granular matter, gels, polymers, etc.



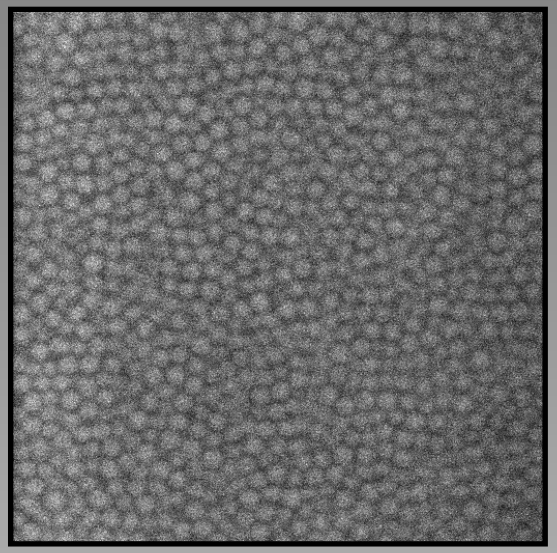


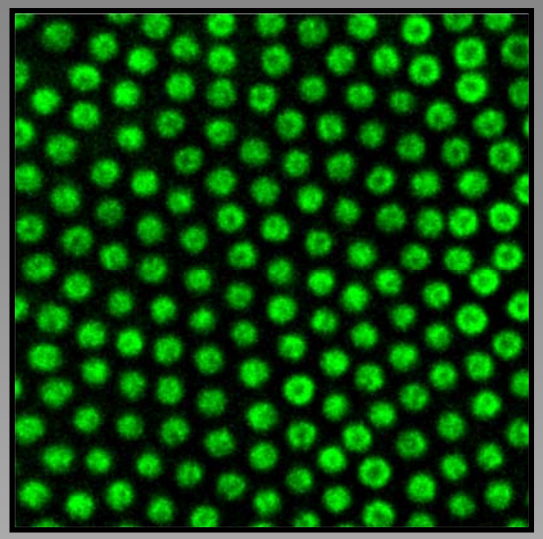
What factors determine glass transition?
Cooling speed (Dynamical process)
Chemical composition
History (ageing)
External restrictions (pressure, etc.)

Not well understood, specially the relationship with low frequency vibrational modes.

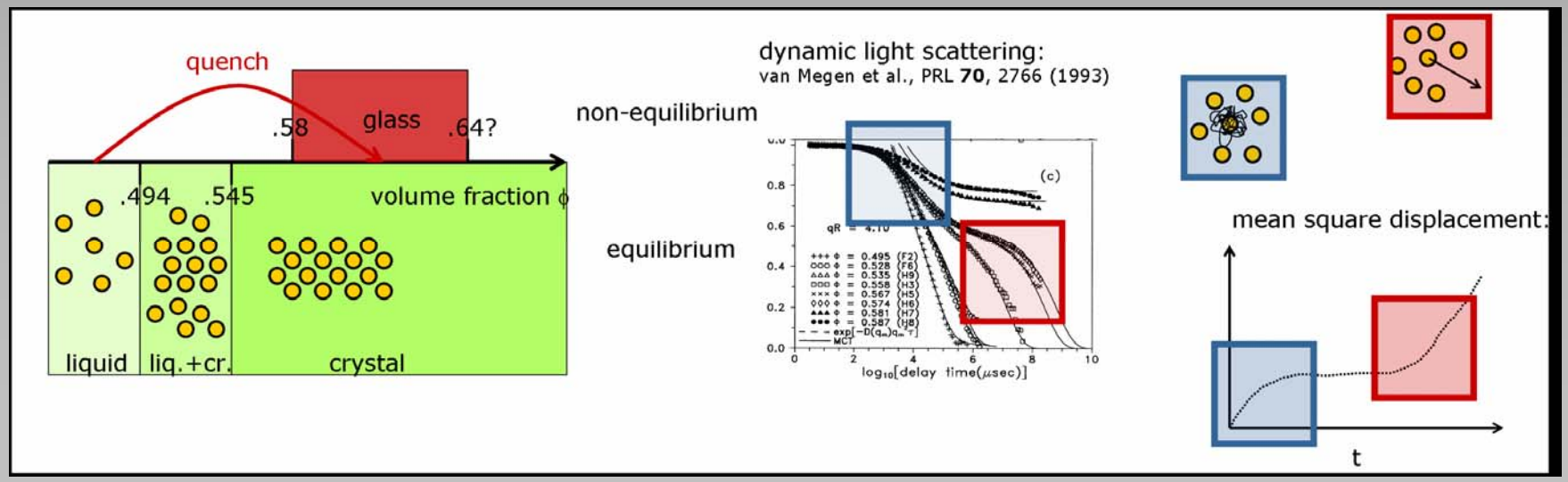
Colloids, microgels

Example: experimental results in colloids from the group of David Weitz (Harvard)
High volume fraction supercooled fluid



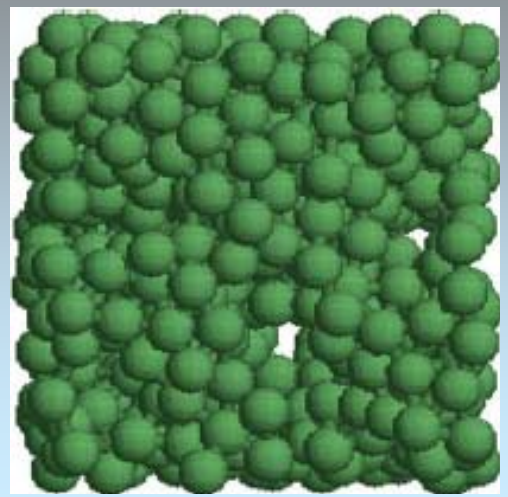


Glass: volume fraction 0.60

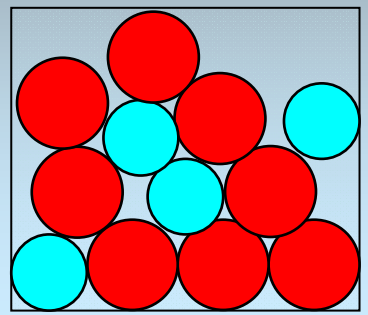


Jamming transition

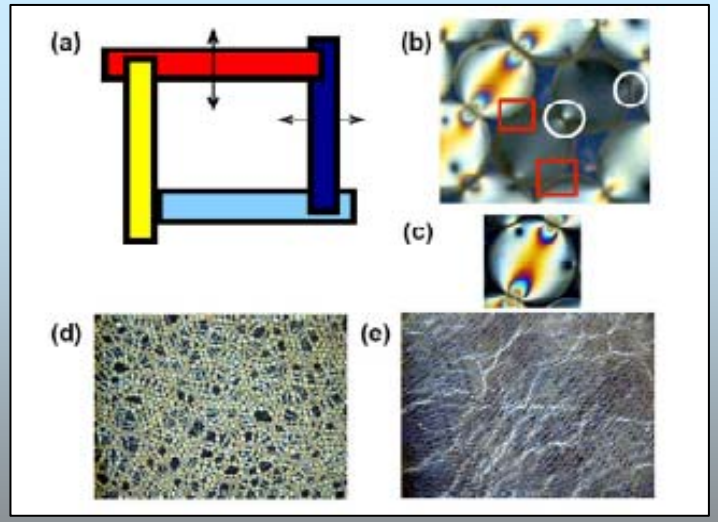
Granular media, hard-spheres, etc.



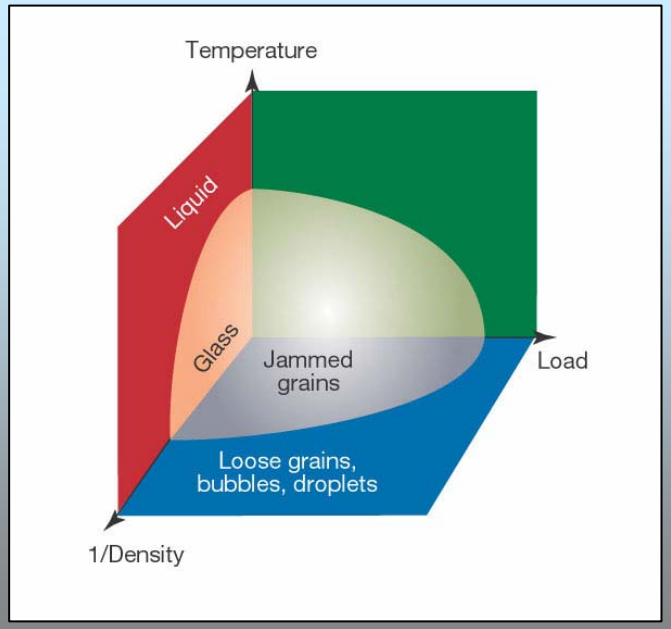
Particles are "jammed" by cages formed by neighbours.



Mechanical stability against shear and isotropic deformation

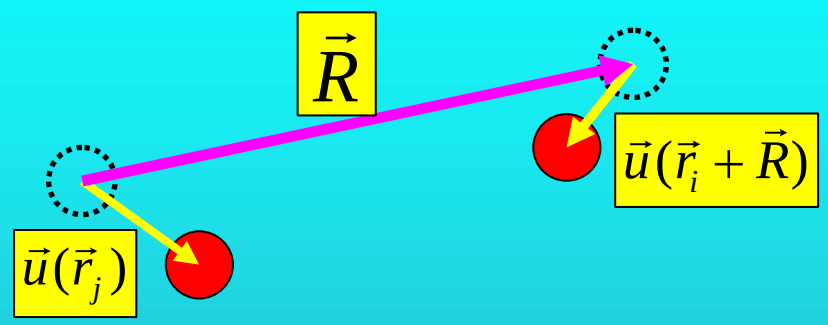


Majmudar, Sperl, Ludiny, Behringer, Phys. Rev. Lett. 98, 058001, (2007)



A.J. Liu and S.R. Nagel, Nature 396 (N6706), 21 (1998).

Mechanical stability: low frequency modes



$$\left\langle \left|\vec{u}(\vec{r}_j)-\vec{u}(\vec{r}_j+\vec{R})\right|^2 \right\rangle_T = \frac{2\hbar}{mN}\sum_{q\in 1B.Z.}\omega^{-1}(\vec{q})\left[1-\cos(\vec{q}\cdot\vec{R})\right]/\left\{exp\left[\hbar\omega(\vec{q})/k_BT\right]-1\right\}$$

The sum can be divergent due to low-frequency modes $\omega(\vec{q})=cq$

D=1 → $\left\langle \left|\vec{u}(\vec{r}_j)-\vec{u}(\vec{r}_j+\vec{R})\right|^2 \right\rangle_T \propto \frac{k_BT}{mc^2}\frac{a}{2}R,$ → ∞

D=2 → $\left\langle \left|\vec{u}(\vec{r}_j)-\vec{u}(\vec{r}_j+\vec{R})\right|^2 \right\rangle_T \propto \frac{k_BT}{mc^2}\frac{a^2}{2\pi}\ln R,$ → ∞

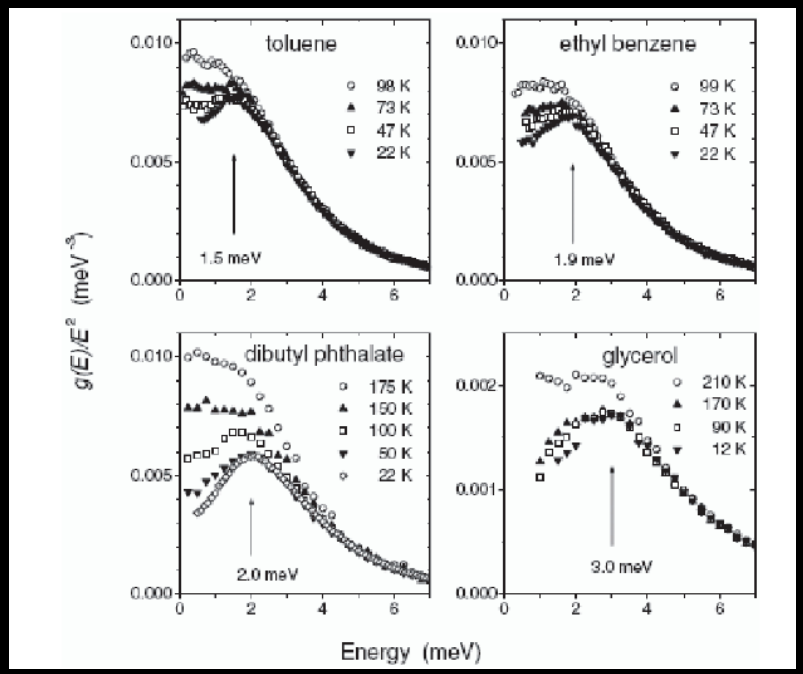
Rigidity of a solid against collective motion → contained in the DOS

Low frequency modes and glass transition

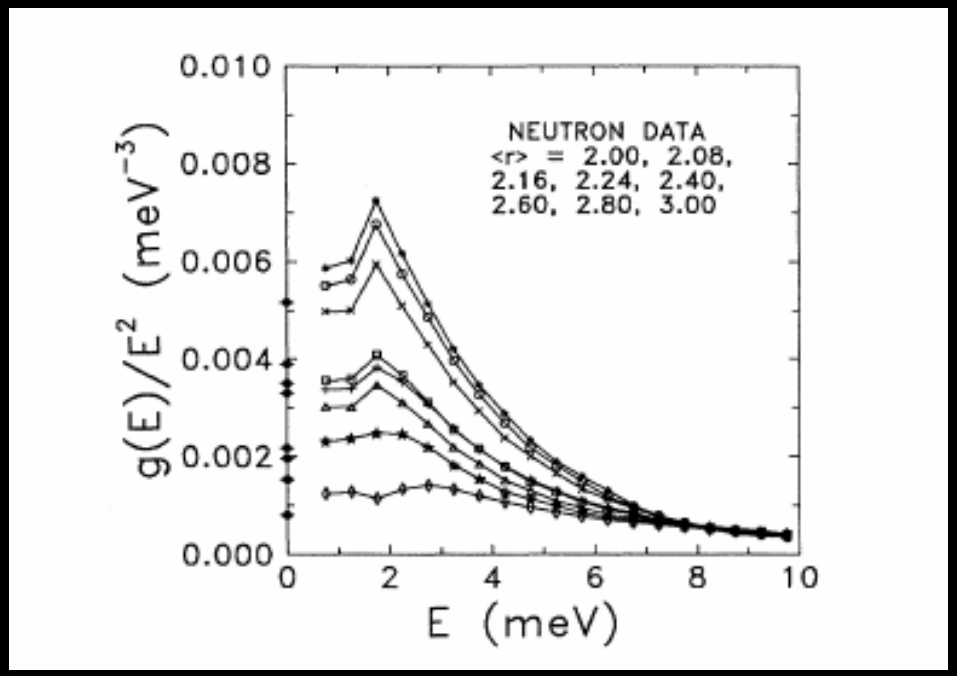
$$\rho(\omega) \sim \omega^2 \qquad g(E) \sim E^2; (E = \hbar\omega)$$

Boson peak

Floppy modes



Chumakov et. al., Phys. Rev. Lett. 92, 245508 (2004)



Kamitakahara et. al., Phys. Rev. B 44, 94 (1991)

-Rearranging cooperative regions
-Free volume
-Mode coupling

-However, in these theories, low-frequency modes anomalies do not play a "lead role", even if all glasses present such anomaly. (Maybe because some crystals present a Boson peak, but…)

Glass transition and rigidity: networks

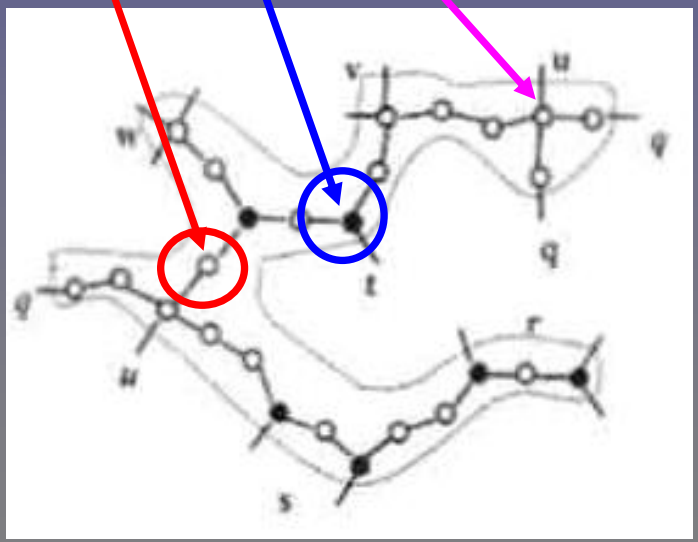
Average coordination number in glasses

(J.C. Phillips, J. Non-Cryst. Solids **34**, 153 (1979), M.F. Thorpe, J. of Non-Cryst. Solids 57, 355 (1983)

$$Se_{1-x-y}Ge_xAs_y$$

$$\langle r \rangle = (1-x-y)2 + x4 + y3$$

$$\langle r \rangle = x_A r_A + x_B r_B + x_C r_C$$



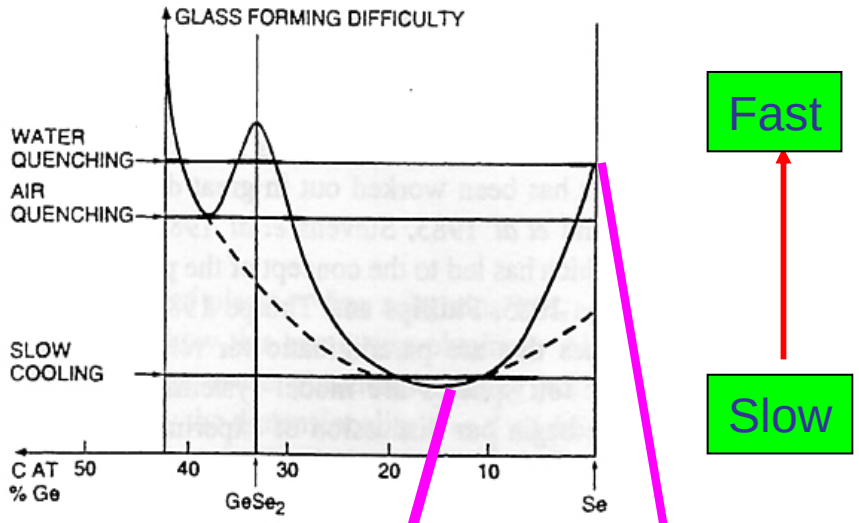


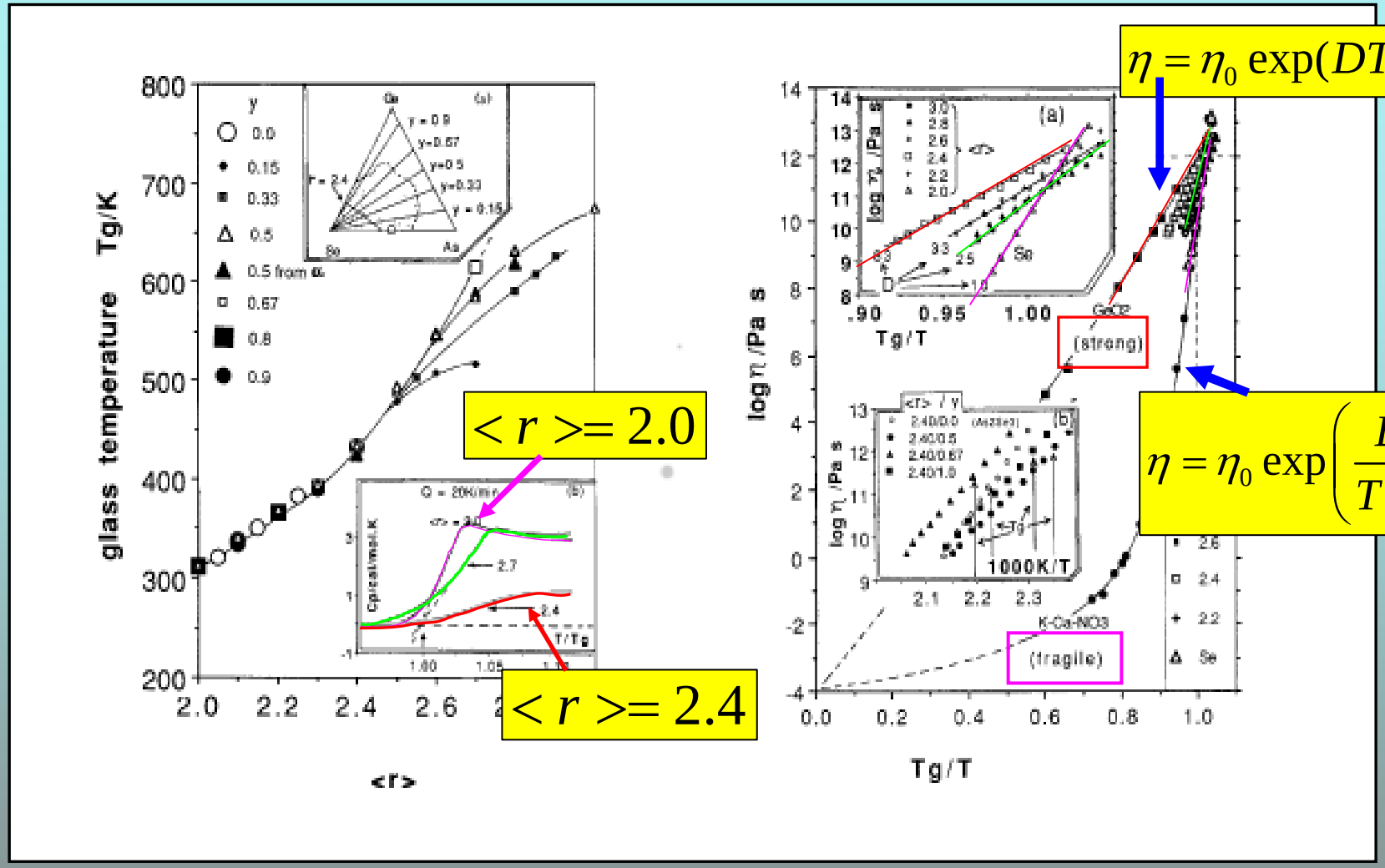
Figure 10. The glass-forming difficulty (or inverse glass-forming tendency) in Ge_xSe_{1-x} alloys (Azoulay *et al* 1975), to which we have added a broken curve which omits the effects of compound stoichiometries. The minimum of the curve falls close to $x = 0.20$.

Fast

Slow

$$\langle r \rangle = 2.4$$

$$\langle r \rangle = 2.0$$



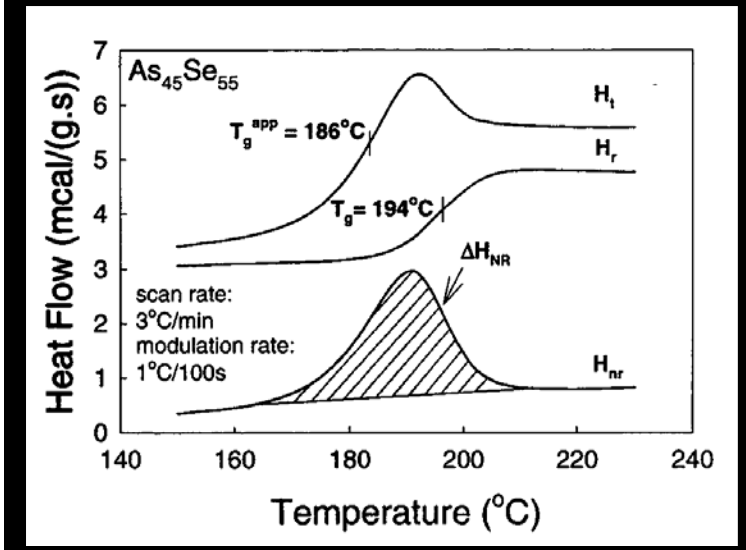
Adams-Gibbs equation:

$$\eta = \eta_0 \exp(C / TS_c) \qquad S_c = \int_{T_K}^{T} \frac{\Delta c_p(T)}{T} dT$$

Tatsumisago et. al.,Phys. Rev. Lett. **64**, 1549 (1990).

Intermediate phase

*Self-organization: Thorpe, et. al., J. Non-Cryst. Solids **266**, 859 (2000).*



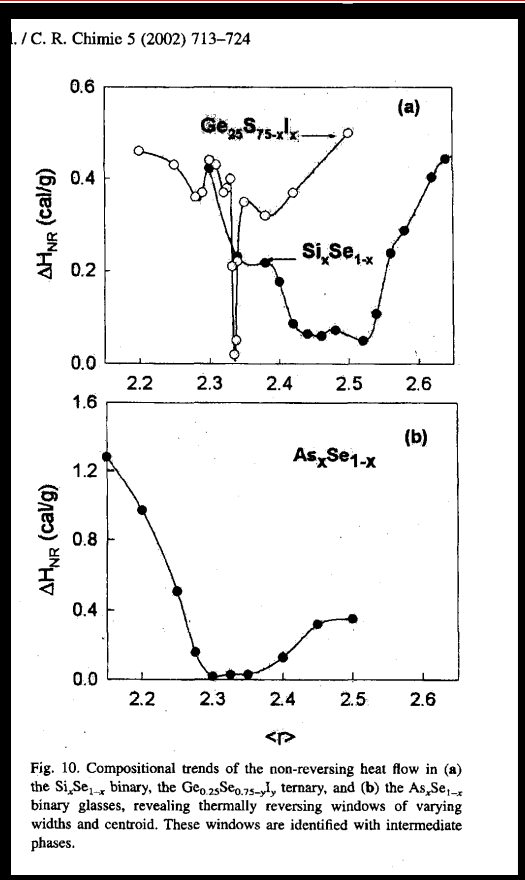
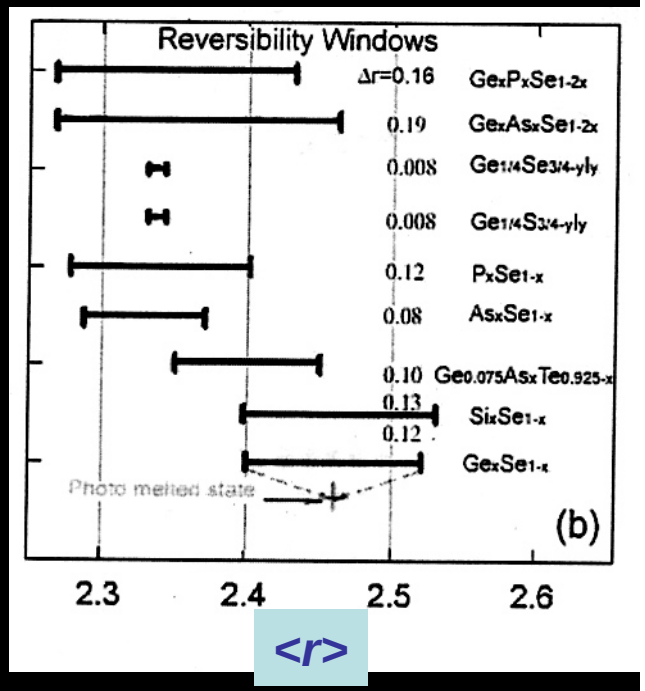


Fig. 10. Compositional trends of the non-reversing heat flow in (a) the Si_xSe_{1-x} binary, the $Ge_{0.25}Se_{0.75-y}I_y$ ternary, and (b) the As_xSe_{1-x} binary glasses, revealing thermally reversing windows of varying widths and centroid. These windows are identified with intermediate phases.



Boolchand et. al., J. of Non-Cryst. Solids **293**, 348 (2001).

P. Boolchand et. al., J. of Optoelectronics and Advanced Materials Vol. **3**, 703 (2001)).

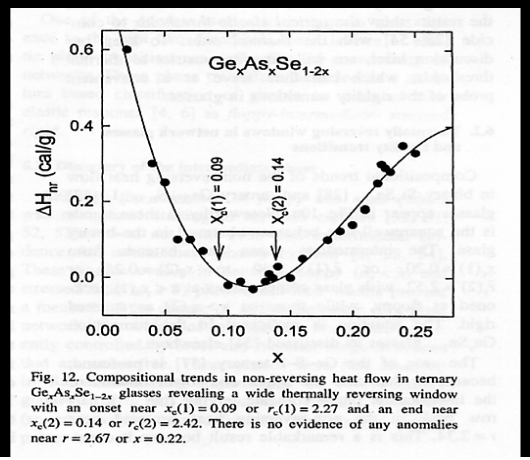
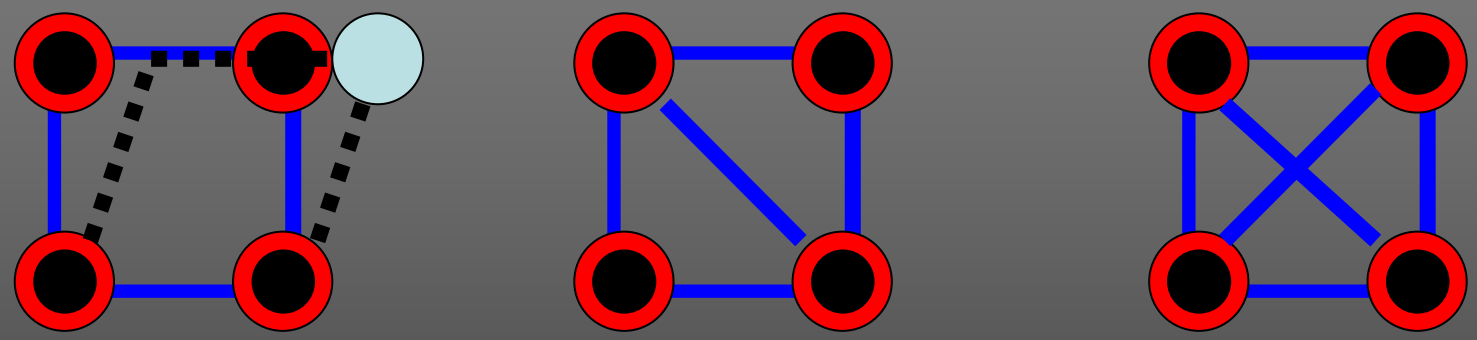


Fig. 12. Compositional trends in non-reversing heat flow in ternary $Ge_xAs_xSe_{1-2x}$ glasses revealing a wide thermally reversing window with an onset near $x_c(1) = 0.09$ or $r_c(1) = 2.27$ and an end near $x_c(2) = 0.14$ or $r_c(2) = 2.42$. There is no evidence of any anomalies near $r = 2.67$ or $x = 0.22$.

Rigidity Theory: floppy modes

With N hindges, how many bars do I need to make the system rigid?



Flexible — ***1***

Isostatic — ***0***

Rigid — ***-1***

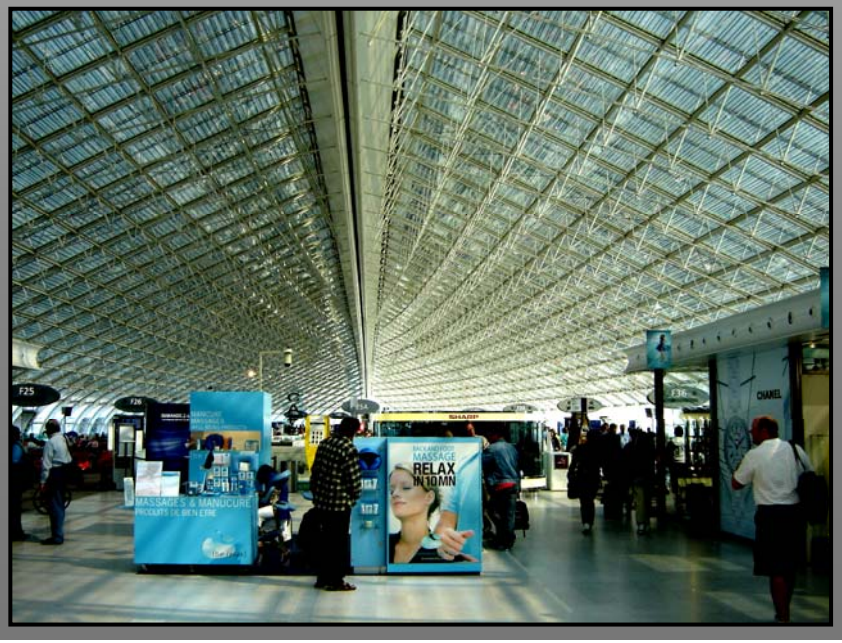
4x (2 freedom degrees)-(# constraints)=# flexible movements

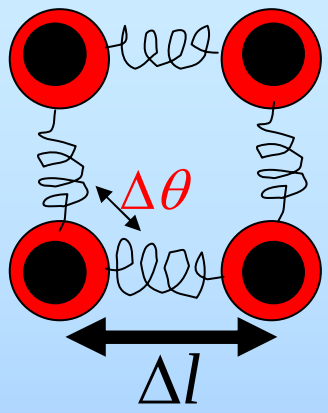
f =(3N-constraints)/3N ***Fraction of "floopy modes"***

f=# of normal modes of vibration with zero frequency/3N

$$V(x) = \frac{m\omega^2}{2} x^2$$

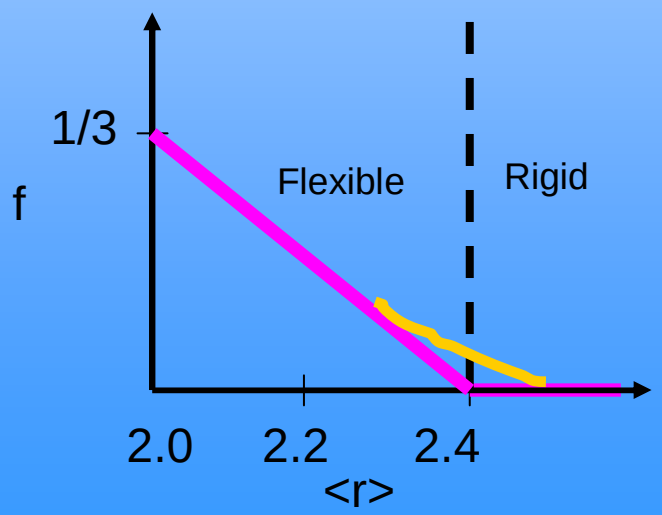
Yesterday, at terminal 2F…





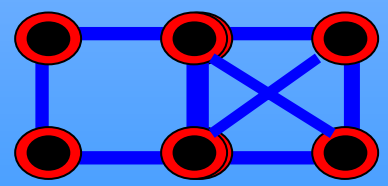
$$V = \frac{\alpha}{2}(\Delta l)^2 + \frac{\beta}{2}(\Delta\theta)^2$$

Maxwell Counting (1860)



$$f = \left[3N - \sum_r x_r \left(\frac{r}{2} + (2r-3) \right) \right] / 3N$$

$$f = 2 - \frac{5}{6} < r >$$



f=0, <r>=2.4

Floopy modes at zero frequency

Phonons in a solid are described as 3N independent oscillators

$$H(P_1,\ldots,P_{3N},Q_1,\ldots,Q_{3N}) = \sum_{i=1}^{3N} P_i^2 + \sum_{i=1}^{3N} \frac{1}{2} m\omega_i^2 Q_i^2 = E$$

When 3Nf oscillators are at zero frequency,

$$H(P_1,\ldots,P_{3N},Q_1,\ldots,Q_{3N}) = E = \sum_{i=1}^{3N} P_i^2 + \sum_{i=1}^{3N(1-f)} \frac{m}{2}\omega_i^2 Q_i^2 = E$$

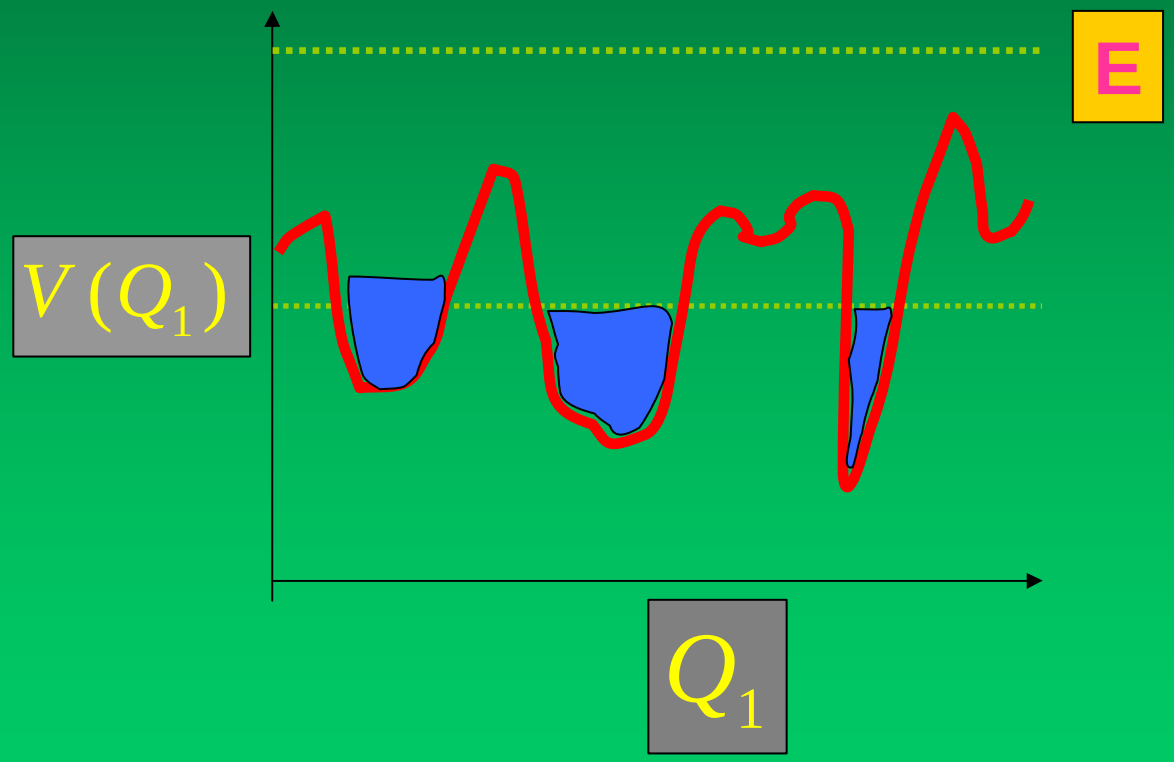
$$E = 3N(kT/2) + 3N(1-f)(kT/2) \rightarrow c_V = (1-(f/2))3Nk$$

Violation of Dulong-Petit law: not observed. ***From this simple thermodynamical argument, we observe that floppy modes are not at zero frequency.***

Experiment: there is a blueshift, with a peak around 5 meV (Kamitakahara et. al., Phys. Rev. B 44, 94 (1991)).

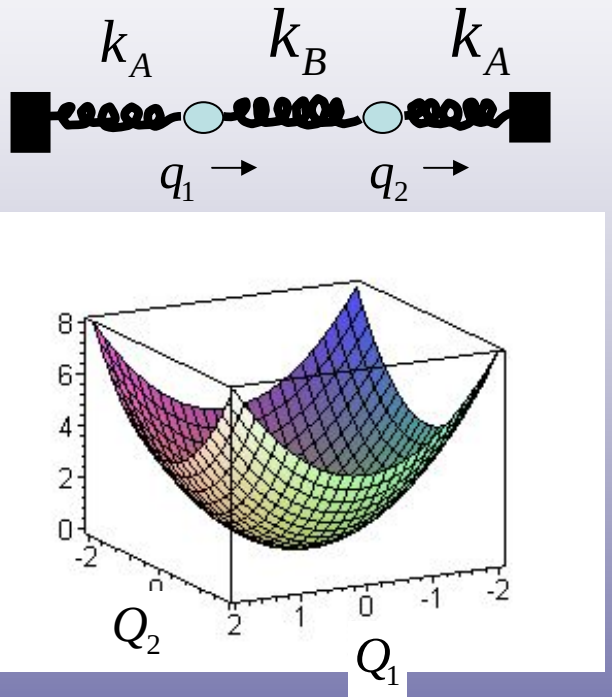
Energy Landscape

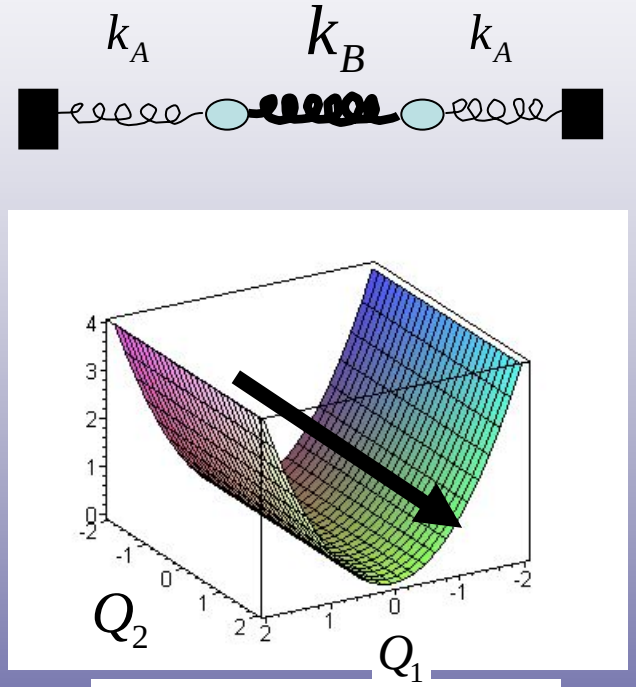
$$E = K + V(Q_1, \ldots, Q_{3N})$$



Interpretation in terms of energy landscapes

$$E - V(Q_1, \ldots, Q_{3N}) = K \geq 0$$





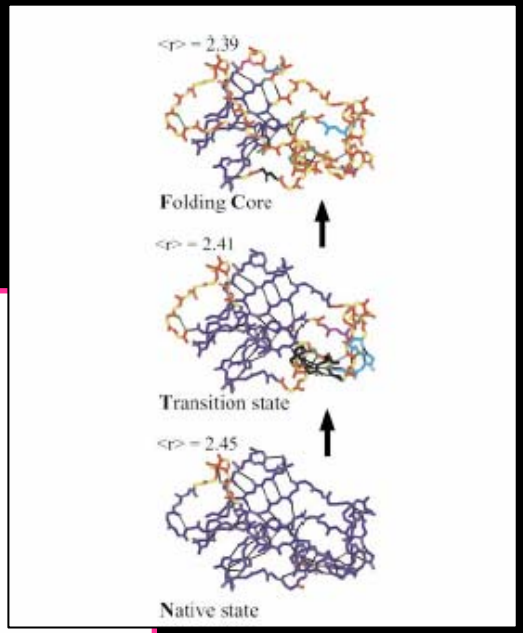
$$V(Q_1, Q_2) = \frac{m\omega_1^2}{2} Q_1^{\,2} + \frac{m\omega_2^2}{2} Q_2^{\,2}$$

$$V(Q_1, Q_2) = \frac{m\omega_1^2}{2} Q_1^{\,2}$$

$$S \approx Nf \ln(V / \lambda^3)$$

Naumis, Phys. Rev. E **71**, 026114 (2005)**.** Naumis, J. of Non-Cryst. Solids 352, 4865 (2006).

Glasses and protein folding



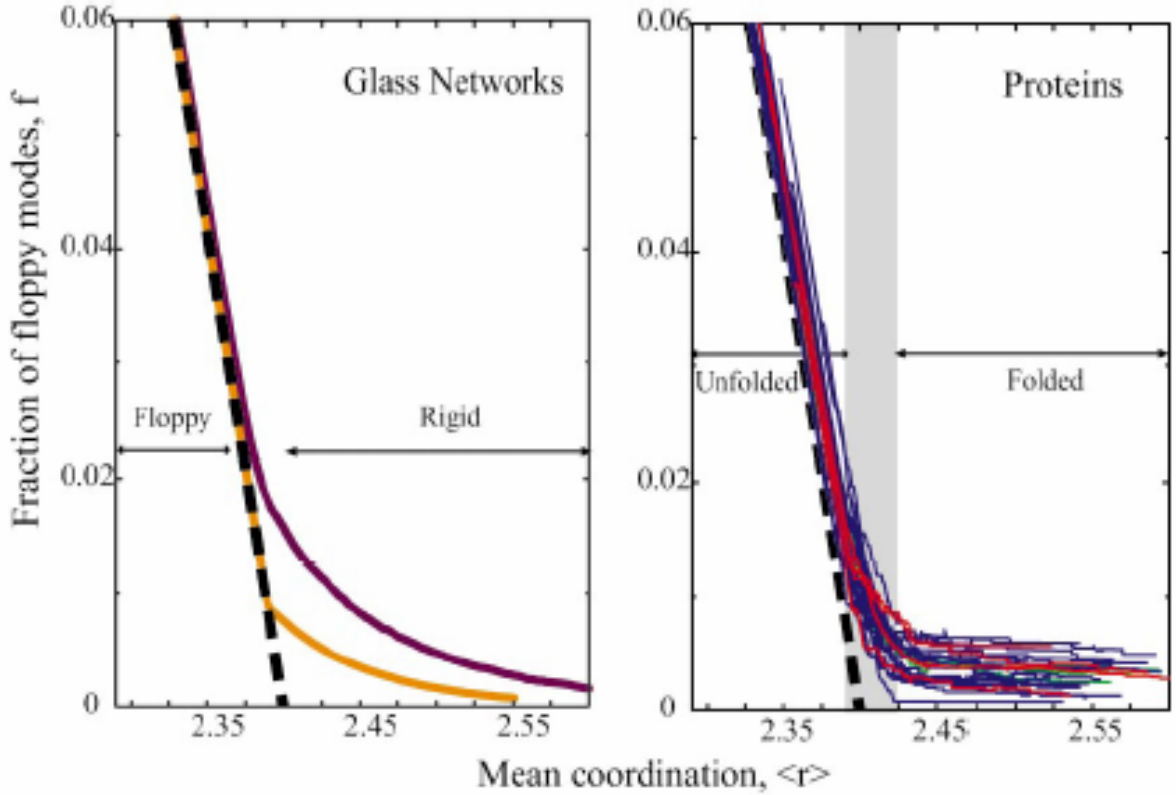
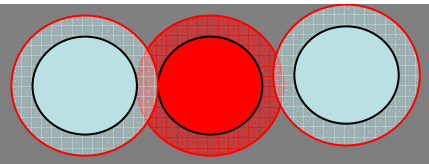
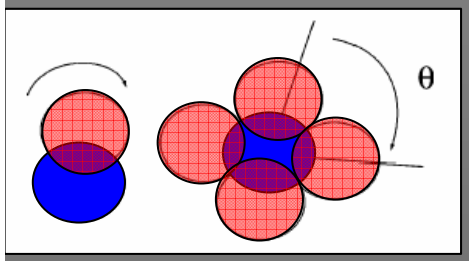


FIG. 1. The fractional number of floppy modes. $f = F/3N$ in a glass as a function of the mean coordination, $\langle r \rangle$. The Maxwell approximation (Eq. 3) is shown as a thick black dashed line. (*Left*) The results for random glass networks (purple line, where the transition is second-order; orange line, for a network with an absence of small rings where the transition is first-order; ref. 21). (*Right*) Similar results for a representative set of 26 structurally and functionally diverse proteins (blue lines, monomers; red lines, dimers; green lines, tetramers; see *Methods* for details). The gray shaded region indicates the range in which protein folding/unfolding takes place.

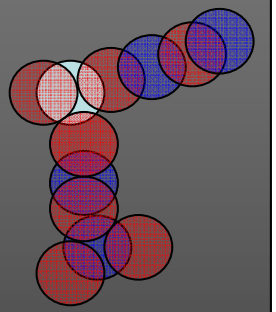
Taken from Rader, Hespenheide, Khun, Thorpe, PNAS 99, 3540 (2002)

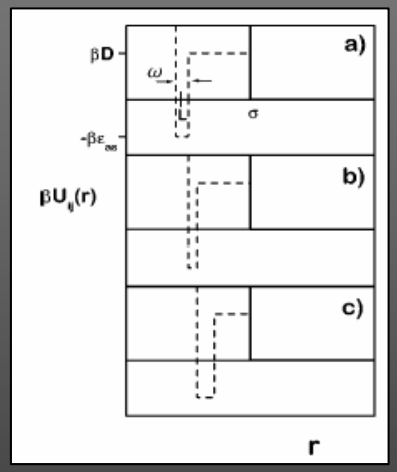


Attractive colloids (soft-disks)



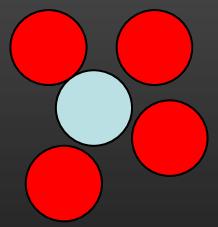
Huerta, Naumis, *J. of Chem.-Phys.* **120**, 1506 (2004)





Sticky Disks: colloids and gels

Huerta, Naumis, Phys. Rev. **B66,** 184204, (2003).

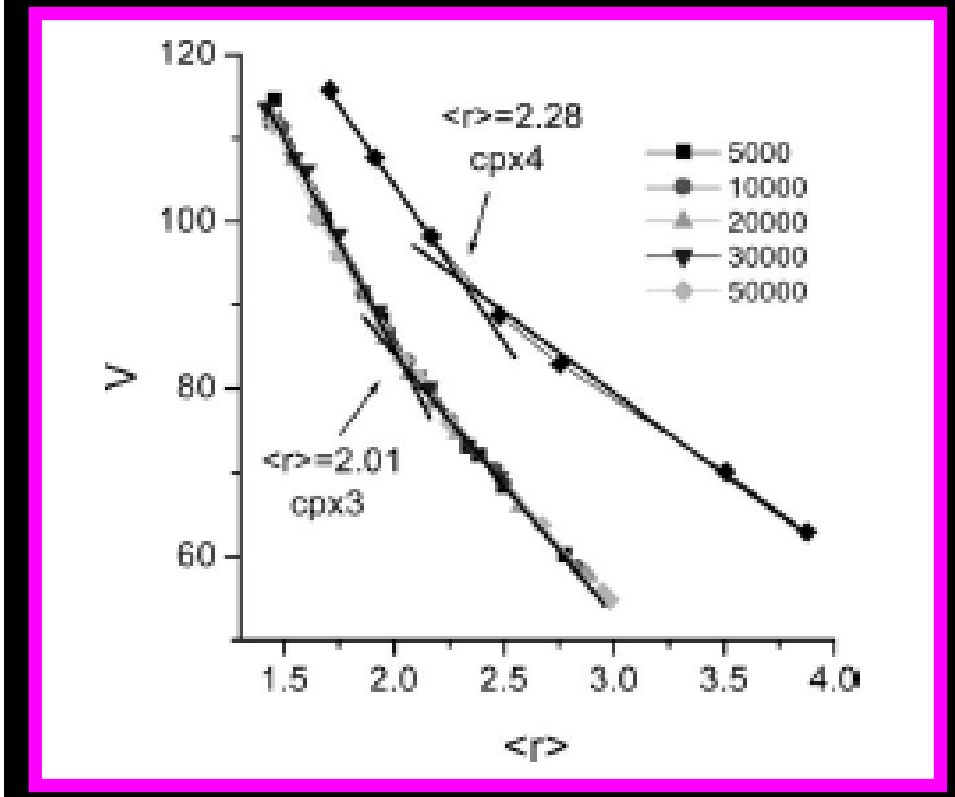


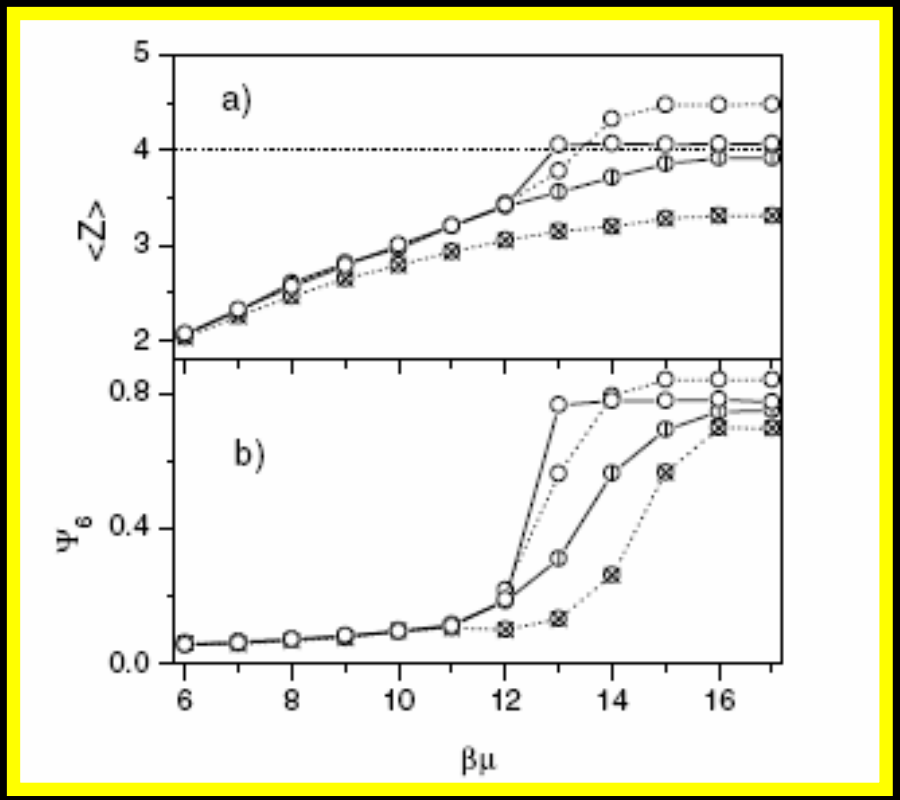
Hard-core potentials: dynamical contacts

$$\langle r \rangle \geq 2D$$

Huerta, Naumis, Phys. Rev. Lett. **90**, 145701, (2003).

In 2 Dimensions

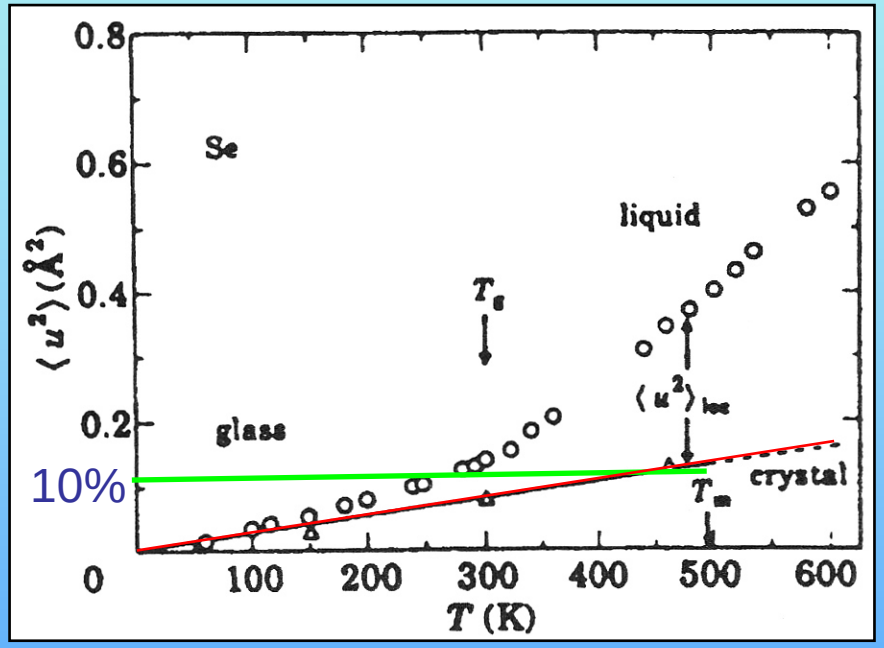




Effects on the glass transition: variation of Tg

Lindemann criteria valid for glasses:

$$< u^2 >_{T_m} \approx 0.01a^2 \approx < u^2 >_{Tg}$$



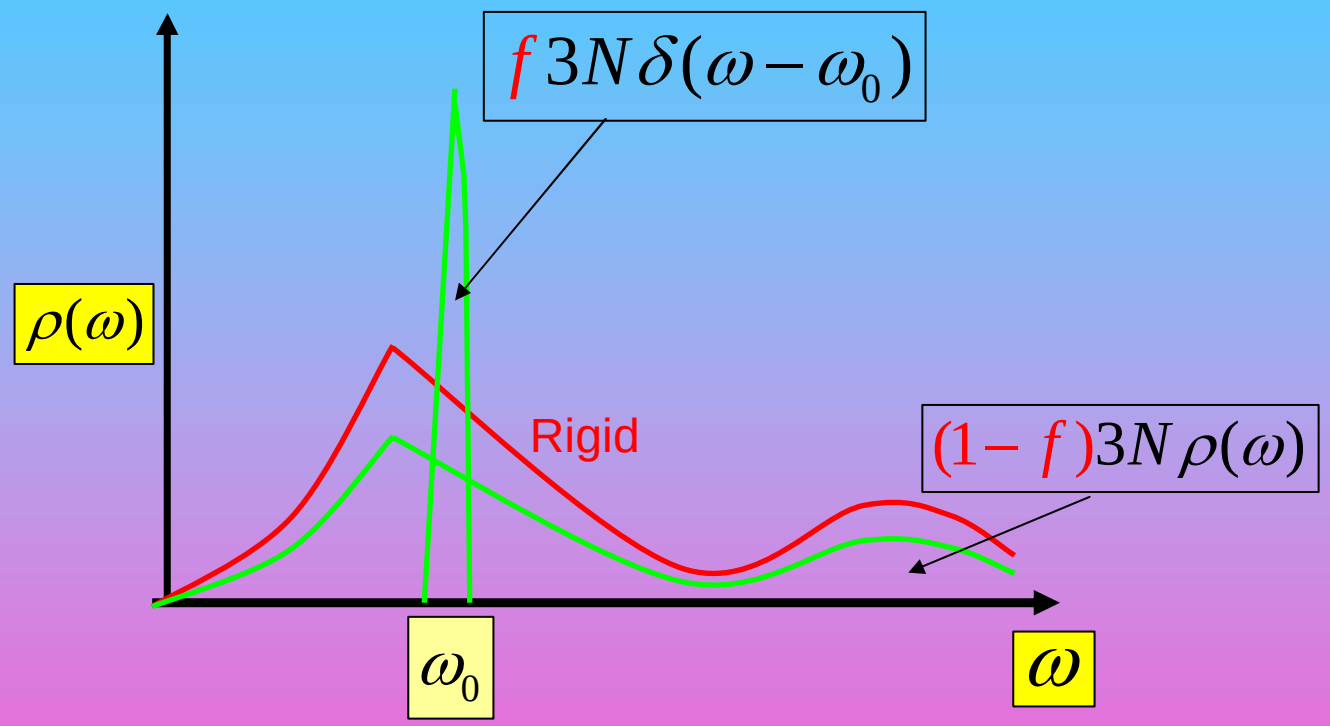
Shows the importance of floppy modes. In the harmonic approximation:

$$< u^2 >_T = \frac{3k_B T}{m} \int_0^\infty \frac{\rho(\omega)}{\omega^2} d\omega$$

U. Buchenau, Zorn, Europhys. Lett. 18, 523 (1992).

$$< u^2 >_{T_g} = \frac{3k_B T_g}{m} \int_0^\infty \frac{\rho_{glass}(\omega)}{\omega^2} d\omega \approx 0.01a^2 \approx \frac{3k_B T_m}{m} \int_0^\infty \frac{\rho_{cryst.}(\omega)}{\omega^2} d\omega = < u^2 >_{T_m}$$

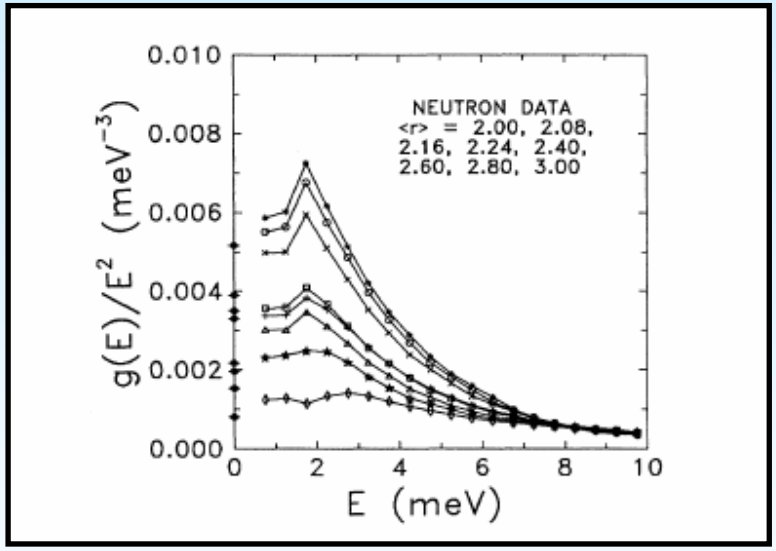
$$T_g \approx \frac{0.01ma^2}{3k_B N} \int_0^\infty \frac{\rho_{glass}(\omega)}{\omega^2} d\omega$$



$$\rho(\omega)=\begin{cases}(1-f)3N\rho_R(\omega)+f\,3N\delta(\omega-\omega_0), & if\ \ \omega\le\omega_D\\ 0\ \ if\ \ \omega\ge\omega_D\end{cases}$$

Using this model for the density of states:

$$T_g(f) \approx \frac{0.01ma^2}{3k_B N}\int_0^\infty \frac{\rho_{glass-floppy}(\omega)}{\omega^2}d\omega = \frac{0.01ma^2}{3k_B N}\int_0^\infty \frac{\left[3N(1-f)\rho_R(\omega)+3Nf\,\delta(\omega-\omega_0)\right]}{\omega^2}d\omega$$



In the Maxwell approximation:

$$f = 2 - \frac{5}{6} < r >$$

Naumis, Phys. Rev. B73, 172202 (2006).

$$T_g(<r>) = \frac{T_g(<r>=2.4)}{\left(1-\frac{5\alpha}{6}(<r>-2.4)\right)}$$

$$\alpha = \left(\omega_0^2 \left\langle \frac{1}{\omega^2} \right\rangle_R\right)^{-1} - 1$$

$$T_g(f=0) = T_g(<r>=2.4) = \frac{0.01ma^2}{3k_B \left\langle \frac{1}{\omega^2} \right\rangle_R}$$

Where:

$$\left\langle \frac{1}{\omega^2} \right\rangle_R = \int_0^\infty \frac{\rho_R(\omega)}{\omega^2} d\omega$$

This result can be transformed into the empirically modified Gibbs-DiMarzio law:

$$T_g(<r>) = \frac{T_g(<r>=2)}{1-\beta(<r>-2)}$$

$$\beta = 5\alpha/(2\alpha+6)$$

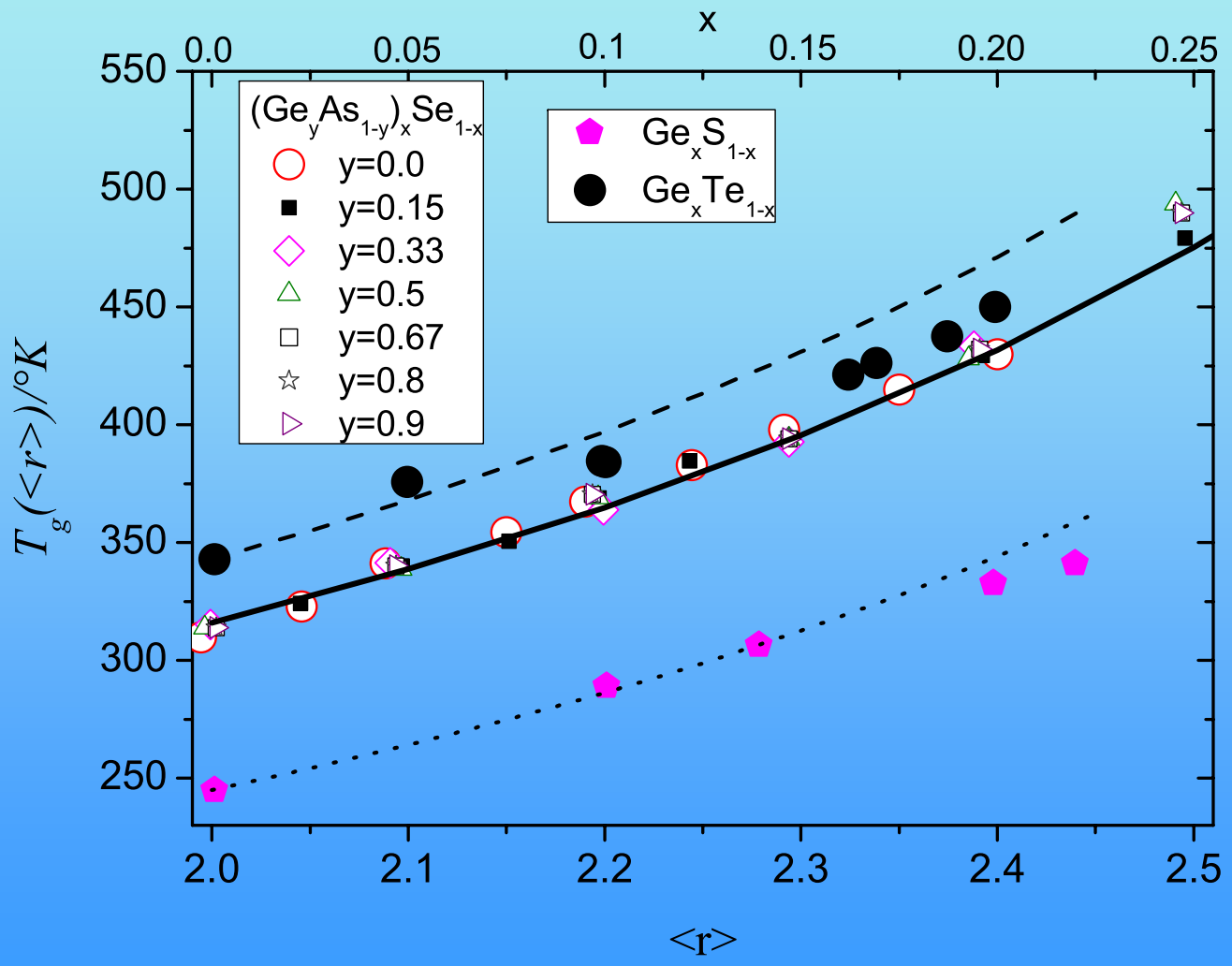
$$\beta_{neu} = 0.67 \pm 0.06; \beta_{Moss.} = 0.69 \pm 0.02; \beta_{fit.} = 0.72 \pm 0.03$$

Neutron scattering (Kamitakahara et. al., Phys. Rev. B 44, 94 (1991))
Lamb-Mössbauer factor (P. Boolchand, in Insulating and Semiconducting Glasses, Edited by P. Boolchand, World Scientific, Singapore 2000).

Modified Gibbs-DiMarzio equation:

Naumis, Phys. Rev. B73, 172202 (2006).

$$T_g(<r>) = \frac{T_g(<r>=2)}{1-\beta(<r>-2)}$$

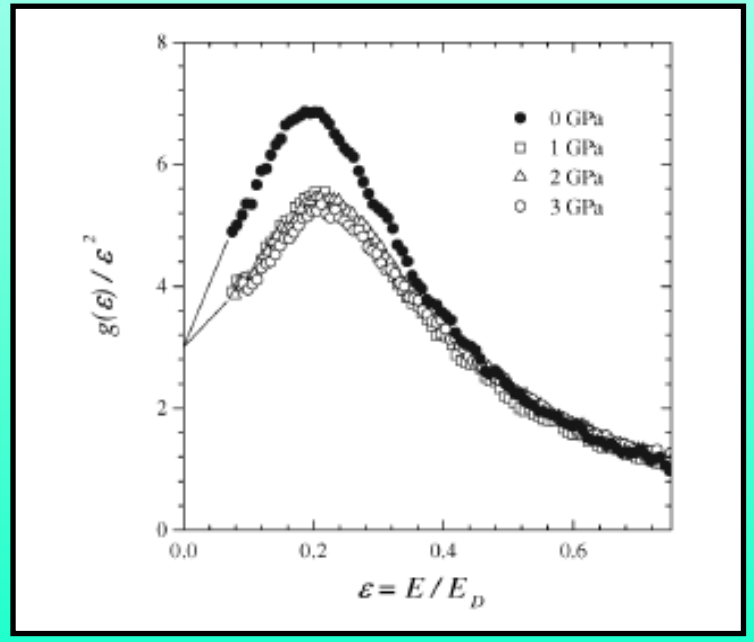


R. Kerner, M. Micoulaut, J. of Molecular Liquids 71, 175 (1997).

Pressure effects

$$T_g \approx \frac{0.01ma^2}{3k_B N}\int_0^\infty \frac{\rho_{glass}(\omega)}{\omega^2}d\omega \quad \rightarrow \quad \frac{dT_g}{dP} \approx \frac{0.01m}{3k_B N}\frac{d}{dP}a^2\int_0^\infty \frac{\rho_{glass}(\omega)}{\omega^2}d\omega$$

$$\boxed{\frac{dT_g}{dP} \approx \frac{0.01m}{3k_B N}a^2\int_0^\infty \frac{\rho_{glass}(\omega)}{\omega^2}d\omega \approx -\frac{2}{3}T_g\beta_T + \frac{0.01m}{3k_B N}a^2\int_0^\infty \frac{d\rho_{glass}(\omega)}{dP}\frac{d\omega}{\omega^2}}$$



$$\delta E = \sum_{ij}\left[V'(r_{ij}^{eq})dr_{ij} + \frac{1}{2}V''(r_{ij}^{eq})dr_{ij}^2 + \ldots\right]$$

Some other relationships…

- Empirical Tanaka law

$$\ln T_g \sim 1.6\langle r\rangle + 2.3$$

$$T_g(<r>) = \frac{T_g(<r>=2)}{1-\beta(<r>-2)} \approx T_g(<r>=2)(1+\beta(<r>-2))$$

$$\ln T_g \approx 0.7\langle r\rangle + 4.1$$

- Empirical 2/3 Law

$$T_g \approx \frac{2}{3} T_m$$

Thermal relaxation and flexibility

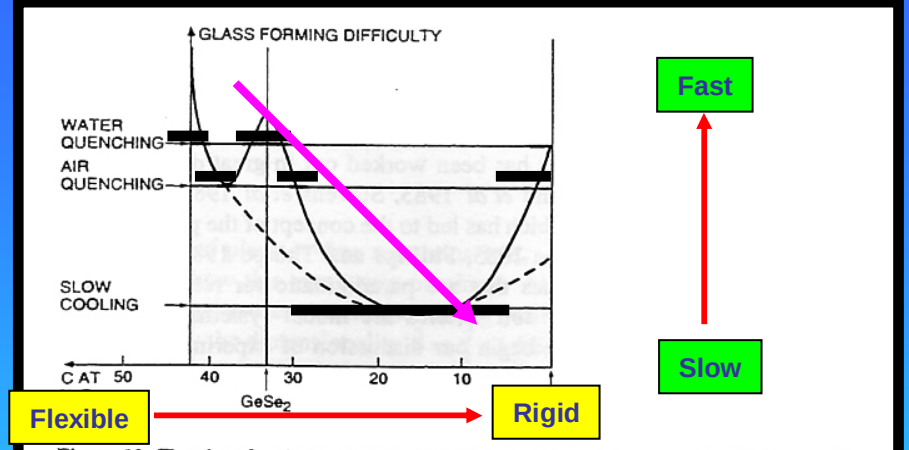


Figure 10. The glass-forming difficulty (or inverse glass-forming tendency) in Ge_xSe_{1-x} alloys (Azoulay *et al* 1975), to which we have added a broken curve which omits the effects of compound stoichiometries. The minimum of the curve falls close to $x = 0.20$.

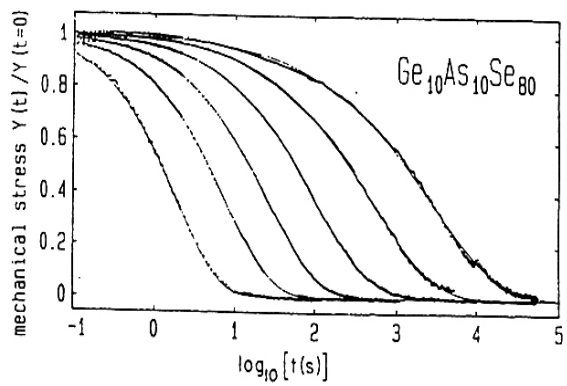


Figure 13. Tensile stress relaxation $Y(t)/Y(0)$ for the indicated ternary alloy ($T_g \sim 400$ K) at six temperatures (left to right) from 430 K to 385 K (Böhmer and Angell 1992).

(Böhmer and Angell 1992)

$$Y(t)/Y(0) = \exp(-(t/\tau)^{\beta(<r>)})$$

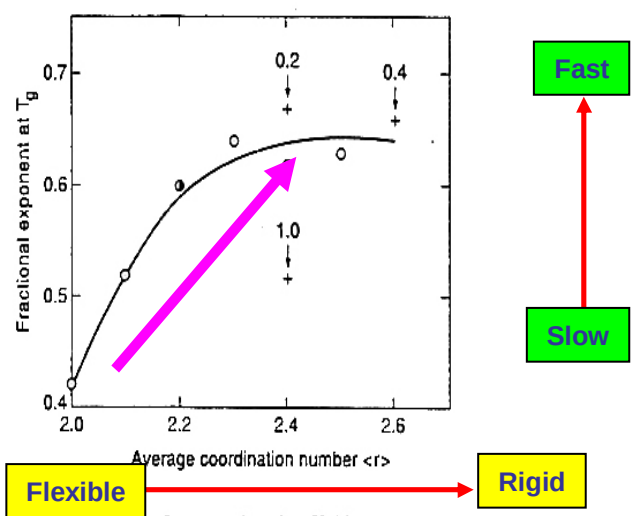
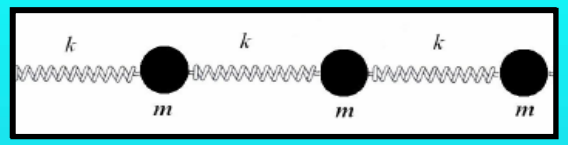


Figure 15. Plot of stress relaxation Kohlrausch exponent β against the average coordination number $\langle r \rangle$ in chalcogenide glass alloys $Ge_xAs_ySe_{1-x-y}$ with $\langle r \rangle = 2 + y + 2x$. Note that β is linear in $(\langle r \rangle - 2.0)$ initially and that it saturates near $\langle r \rangle = 2.4$. This figure (Böhmer and Angell 1992) is reproduced here for the reader's convenience.

Why are important for relaxation?

$$H(P_1,\ldots,P_{3N},Q_1,\ldots,Q_{3N}) = \sum_{i=1}^{3N} P_i^2 + \sum_{i=1}^{3N} \frac{1}{2} m\omega_i^2 Q_i^2$$

Fermi-Pasta-Ulam

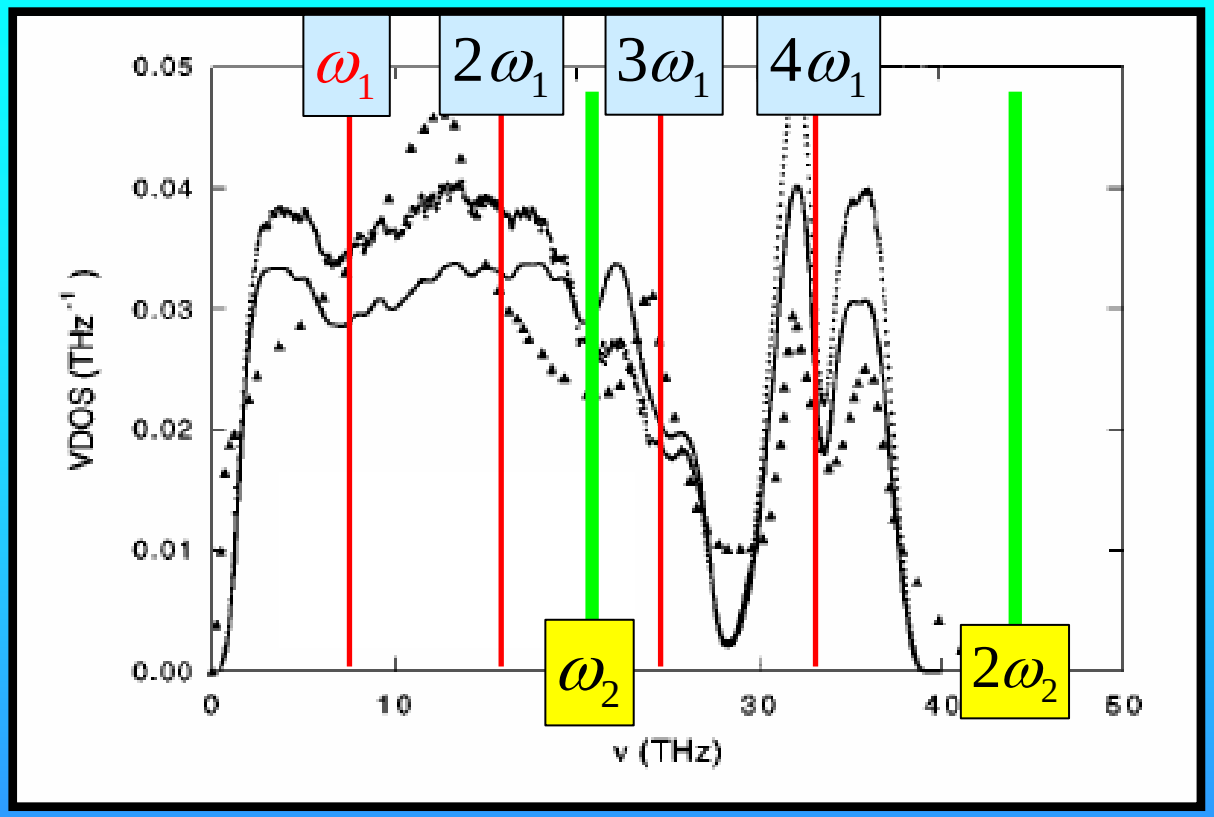


$$H(p_1,\ldots,p_N,x_1,\ldots,x_N) = \sum_{j=1}^{N} \frac{p_j^2}{2m} + \frac{k_2}{2}\sum_{j=1}^{N}(x_{j+1}-x_j)^2 + \frac{k_4}{4}\sum_{j=1}^{N}(x_{j+1}-x_j)^4$$

$$H(P_1,\ldots,P_N,Q_1,\ldots,Q_N) = \sum_{q=1}^{N} P_q^2 + \sum_{q=1}^{N} \frac{\omega^2(q)}{2} Q^2{}_q + \sum_{\alpha=1}^{N}\sum_{\beta=1}^{N}\sum_{\lambda=1}^{N}\sum_{q=1}^{N} D_{\alpha\beta}^{\lambda q} Q_\alpha Q_\beta Q_\lambda Q_q$$

Second, third , etc. harmonics are excited:

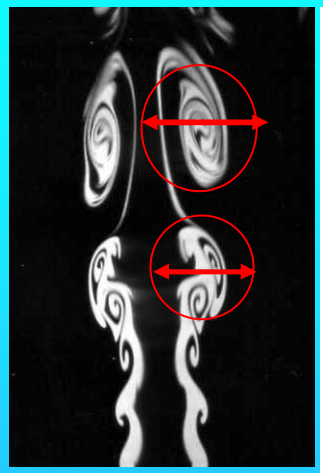
$$\omega_1 \to 2\omega_1 \to 3\omega_1 \to$$

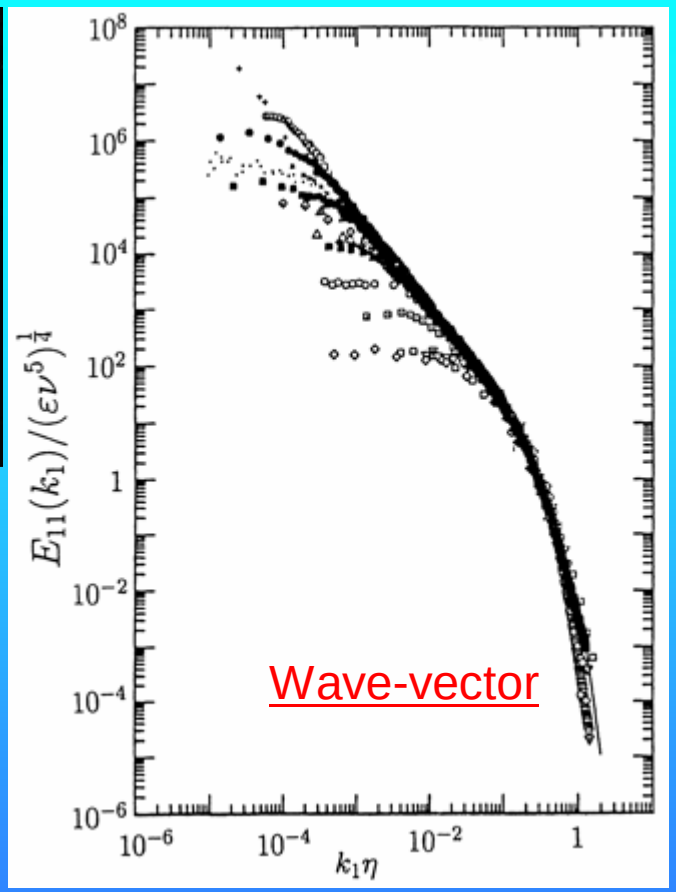


Leads to an energy cascade mechanism…

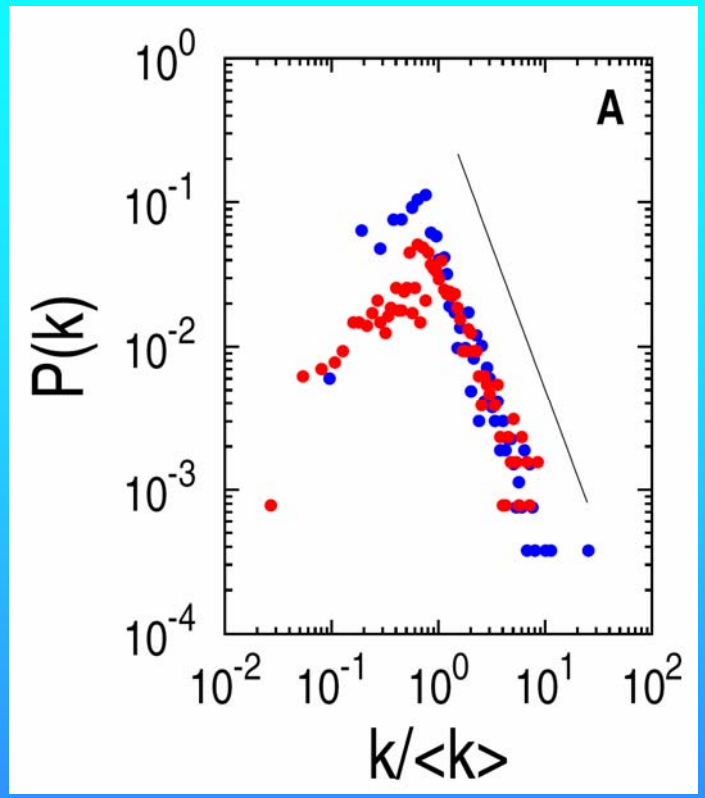
ENERGY → Low-frequency modes → Dissipation

Turbulence: -5/3 Kolmogorov law



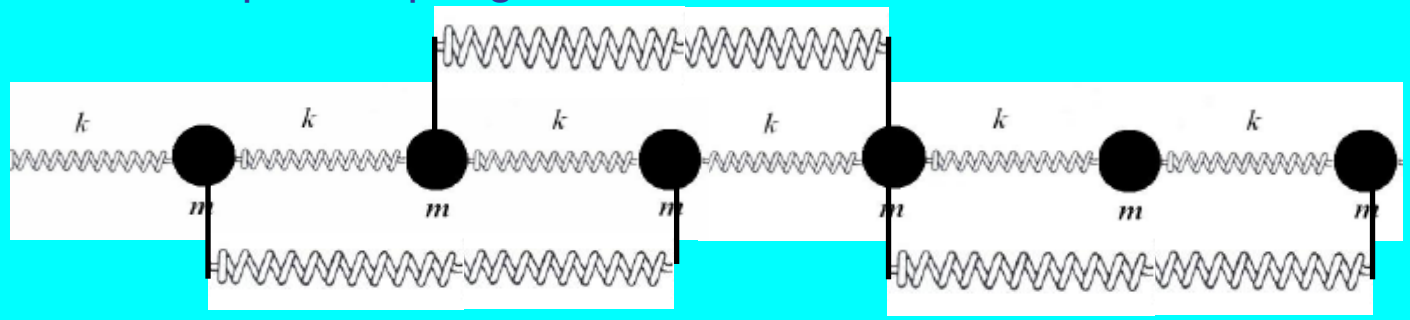


Protein folding: -5/3, -3,etc. laws

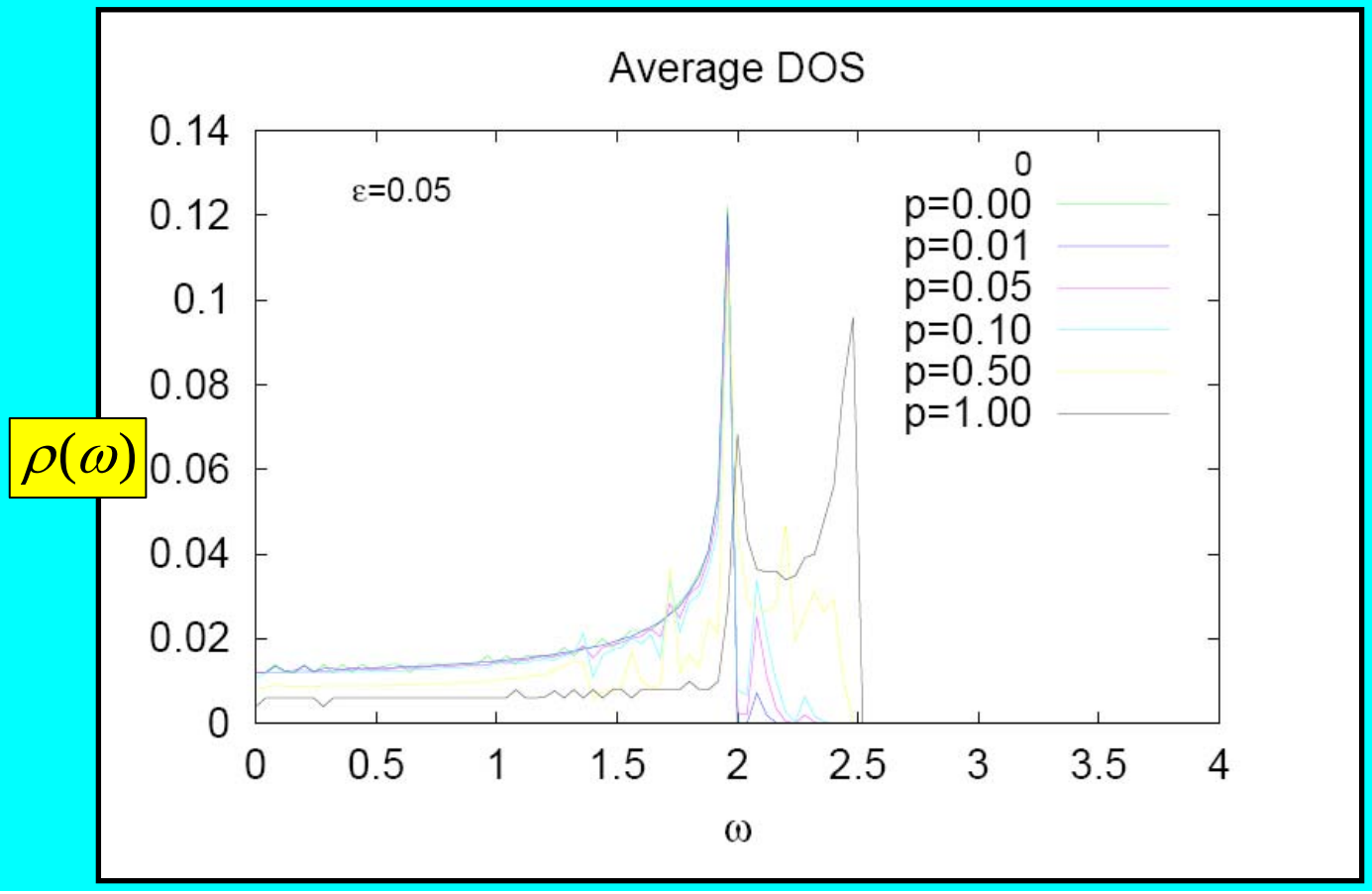


Energy transferred to shorter scales, number of degrees of freedom increases with decreasing scale.

Simple model… p new springs at random



$$V_{HARM}(x_1,\ldots,x_N)=\frac{k_2}{2}\sum_{j=1}^{N}(x_{j+1}-x_j)^2+\frac{k_2}{2}\Theta_p(j,j+2)\sum_{j=1}^{N}(x_{j+2}-x_j)^2$$



Now we include non-linear interaction

$$V(x_1,...,x_N) = V_{HARM}(x_1,...,x_N) + \frac{k_4}{4}\sum_{j=1}^{N}\left(x_{j+1}-x_j\right)^4 + \frac{k_4}{4}\Theta_p(j,j+2)\sum_{j=1}^{N}\left(x_{j+2}-x_j\right)^4.$$

The system is thermalized using a thermal bath (modelled with an stochastic force)

$$m\ddot{x}_j = -\frac{\partial}{\partial x_j}\left[V(x_1,...,x_N)\right] - \gamma_0\dot{x}_j + \eta_j(t)$$

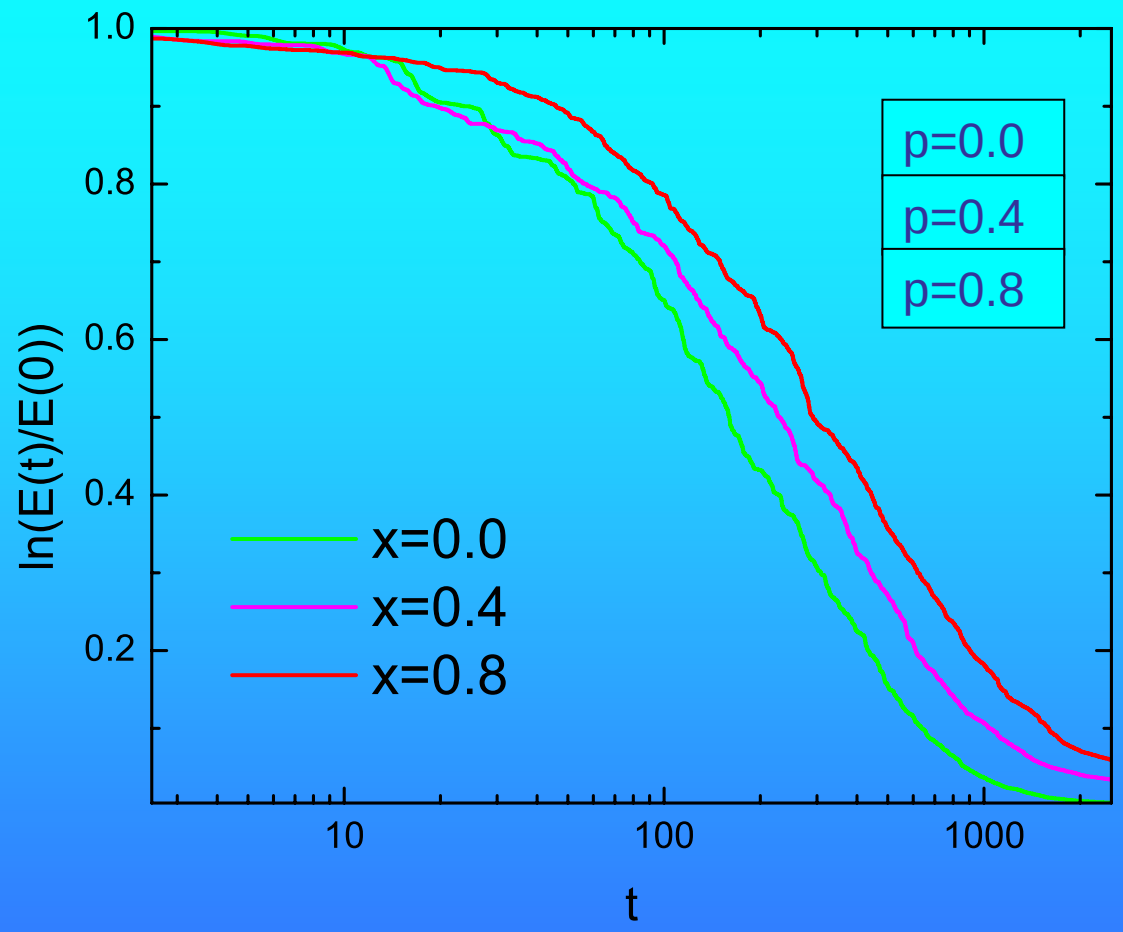
$$\left\langle \eta_j(t)\right\rangle = 0; \left\langle \eta_j(t)\eta_j(t')\right\rangle = 2\gamma_0 kT\delta(t-t')$$

Once thermalized, the bath is shut down. A damping term is add at the end of the chain

$$m\ddot{x}_{1,N} = -\frac{\partial}{\partial x_j}\left[V(x_1,...,x_N)\right] - \gamma_0\dot{x}_{1,N}$$

$$m\ddot{x} = -\frac{\partial}{\partial x_j}\left[V(x_1,...,x_N)\right]$$

Energy relaxation with different number of low-frequency modes, T=1.0



$$E(t) = E(\mathbf{0})\exp(-(t/\tau)^{\beta})$$

CONCLUSIONS

- ***Rigidity theory is a benchmark tool to understand the effects of low-frequency modes in glass transition.***
- ***The glass transition temperature changes due to the increased average quadratic displecement***
- ***Thermal Relaxation depends also in the number of floppy modes***
- ***These ideas are also useful to understand other systems likes colloids, gels, proteins, etc.***