# Three generic structural phases of network glasses

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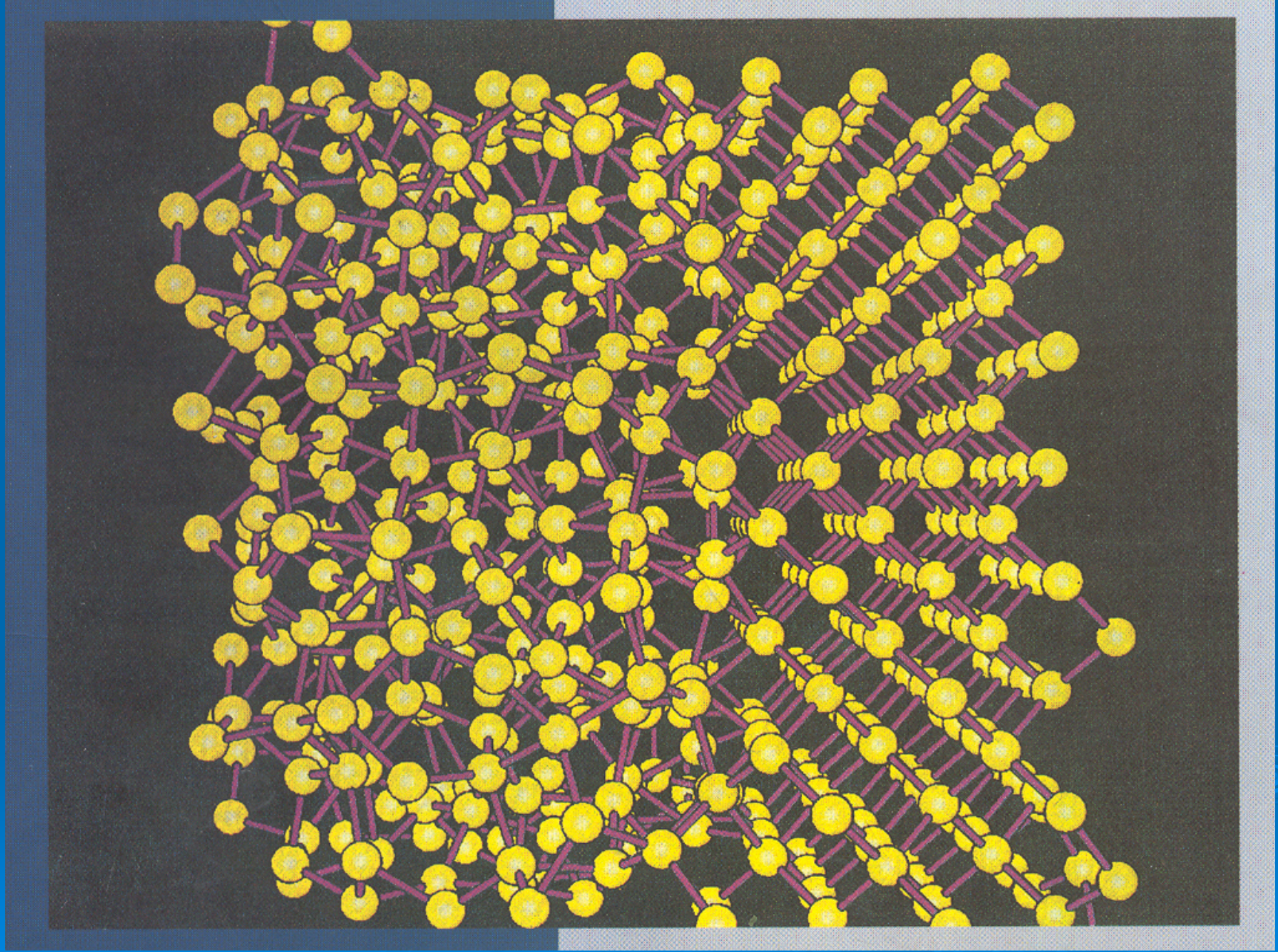


Model of an amorphous/crystalline Si interface, taken from F. Wooten, JNCS 114, 681 (1989).

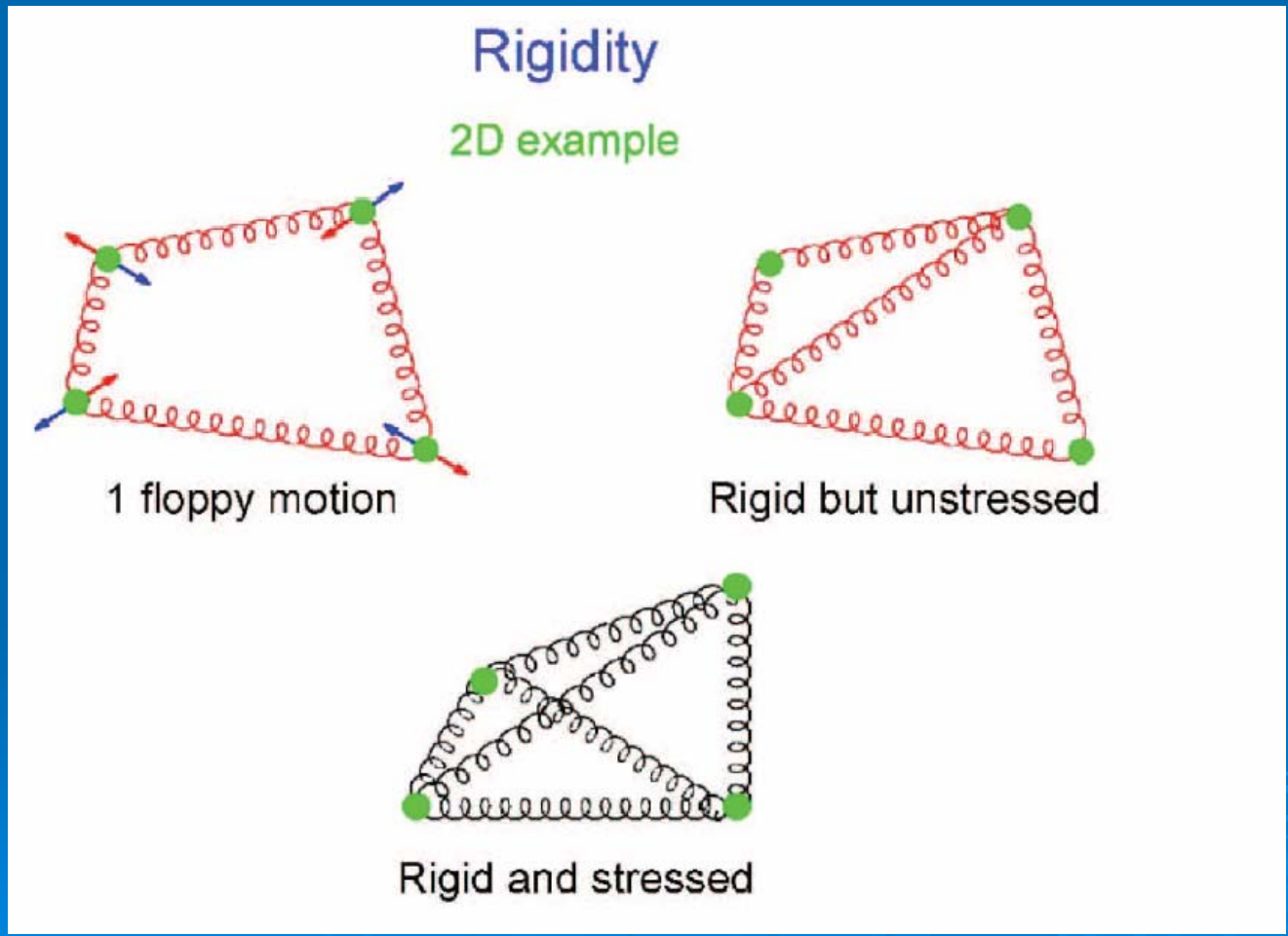
# Modern Theory of Network glasses

- MF Thorpe demonstrated that the determinative factor for metastability of network glasses lies in the *non-local internal network stress* , not in intensive free energies.

- He identified a new class of cyclical or floppy modes (unresolved in previous MDS) in simulations of realistically compacted yet fully disordered 3D mean-field models. (Expt- neutron scattering.) Network glasses are the only material in which floppy modes, and their composition dependence, have been observed.

- By establishing the count of floppy modes as a function of the number of central and non-central valence bond forces - he discovered the "Stiffness Transition"- the connectivity related flexible to stressed-rigid elastic phase transition, which has become the focus of modern theory of network glasses. (Expt.- Lamb Mossbauer factors, inelastic neutron scattering, …)

# Flexible , Isostatic and Stressed-Rigid structures in 2D networks with CFs




P.B, G Lucovsky , J C Phillips, M F Thorpe, Phil. Mag B 85, 3823 (2005).

# Maxwell Rigidity Threshold in 3D networks with central and non-central forces

Consider an atom with a CN = r,

- Bond-Stretching, $n_\alpha = r / 2$ ,
- Bond Bending, $n_\beta = 2r - 3$ ,

$$\langle n_c \rangle = 5\langle r \rangle/2 - 3$$

- Maxwell rigidity transition occurs when

$$\langle n_c \rangle = 3,$$

or $\langle r \rangle = 2.40$

- Floppy mode count $f = 3 - \langle n_c \rangle$

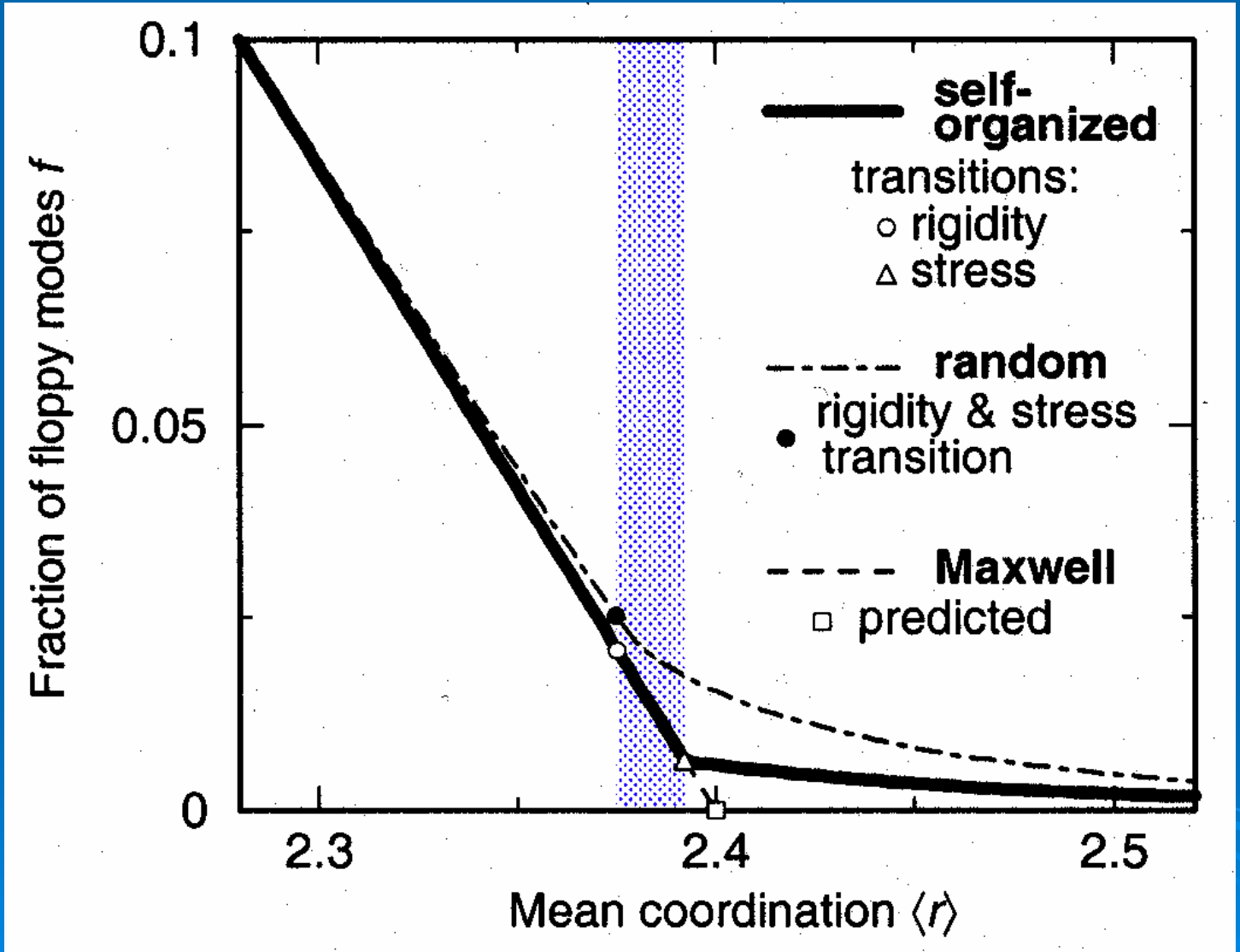
or $f = 6 - 5\langle r \rangle/2$

$f = 1$ at $\langle r \rangle = 2$ ; $f = 0$ at $r = 2.40$

# Modern Theory of network glasses-2

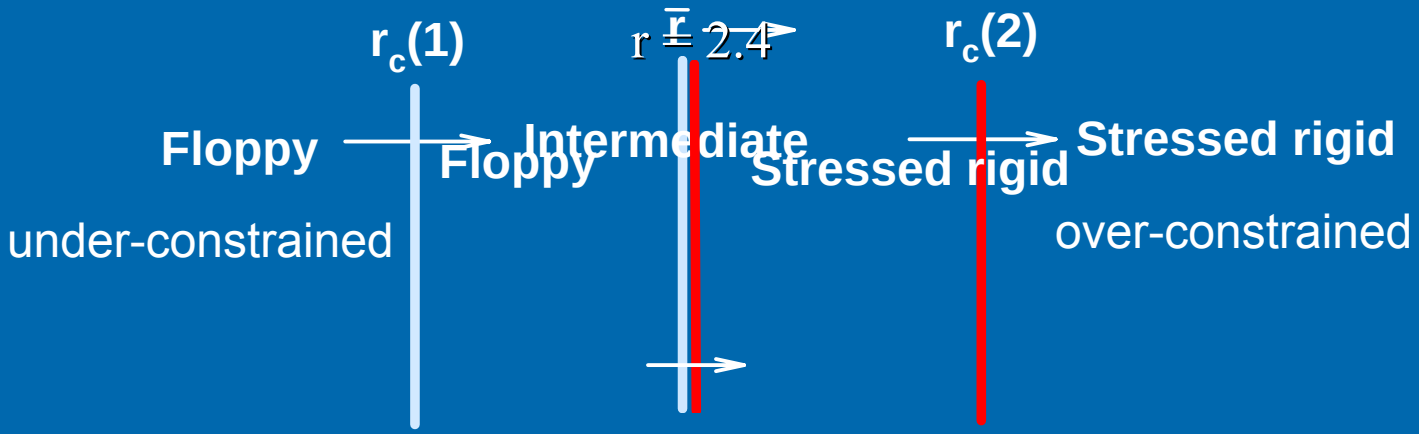
- (1995)Thorpe invented an integer algorithm (Pebble game) to map flexible and rigid regions of inorganic and biological networks, and their evolution as one approached the Stiffness transition – topologically **predicted** critical compositions and elastic power-law exponents (Many expts.). **NB:** these are one of the few phase transition compositions successfully predicted for any known phase transition.
- (2000) Thorpe found two hierarchical elastic transitions by self-organizing networks, the rigidity transition followed by the stress transition at a slightly higher connectivity. ( Raman, IR, m-DSC, Ion-conductivity) **NB:** although the rigidity transition is percolative, it is otherwise unrelated to conventional scalar or vector percolation.
- In between these two rigidity transitions there is a new elastically percolative phase of metastable matter which is rigid and stress-free – the Intermediate Phase, which is a new phase of matter (Expt.- Pressure Raman scattering, optical power-law exponents, molar volumes, on more than 600 samples synthesized in the lab.)

# Floppy mode fraction as a function of *r*




M.F. Thorpe et al. J.Non Cryst. Solids 266-269,859 (2000).

# Elastic phases in Network Glasses




optimally constrained
"isostatically rigid"
"stress-free"
**non-mean-field phase**


**Boolchand P et. al.,** ***J. Opto. Adv. Mater.*** **3 703 (2001);**
**Selvanathan D et. al.,** ***Solid State Communications,*** **111 619 (1999)**

# Broad Consequences of Theory

- Rigidity software identifies conformational hinges in proteins which explain NMR solution data and is now widely used (100 groups)

- Rigidity Theory has inspired jamming theory in soft matter (gels, granular material), which have begun to identify hidden network structures in toy models

- Although Rigidity Theory is a T = 0 K theory, recently it has been adapted by J. Mauro to describe T-dependent constraints to account for liquid viscosities (fragility) up to $10^{16}$ p, organize previously chaotic Corning data base .

# What are the ideal test glass systems?

- Covalent network glasses (mostly single bonds) (600 samples)

| | IV | V | VI | VII |
|---|---|---|---|---|
| | Si | P | S | Cl |
| | Ge | As | Se | Br |
| | Sn | Sb | Te | I |
| CN | 4 | 3 | 2 | 1 |
| | $s^2p^2$ | $s^2p^3$ | $s^2p^4$ | $s^2p^5$ |

- Modified Oxides (some oxygen double bonds) (200 samples)

  Alkali modified Silicates, Germanates, Borates, Phosphates and Tellurates

- Ag-Based Fast –Ion conducting glasses ( 50 samples)

# Floppy modes and VDOS in Chalcogenides

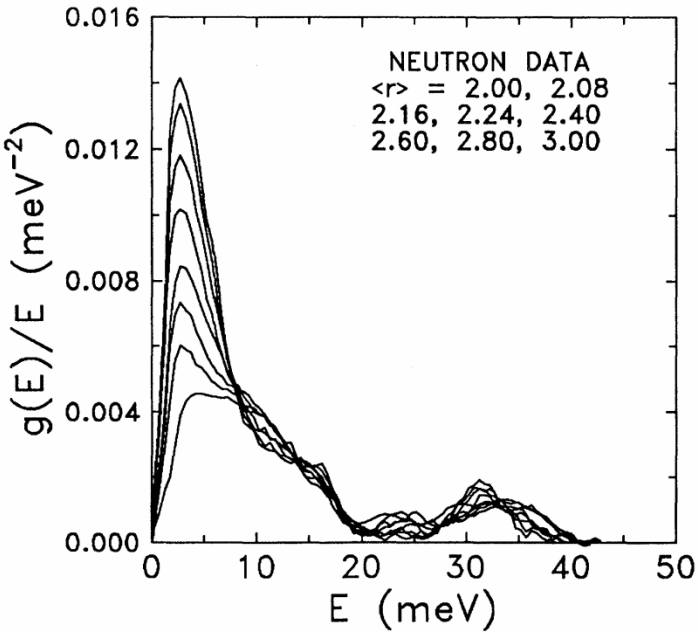
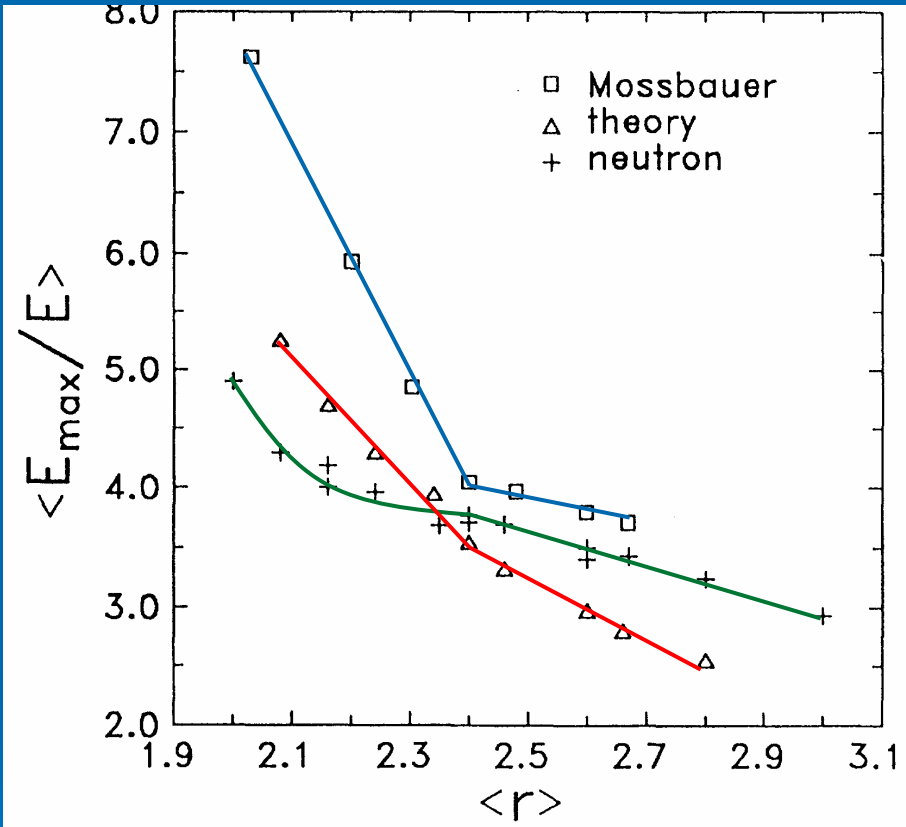



FIG. 4. VDOS measured for Se-As-Ge alloy glasses in this work plotted as $g(E)/E$ vs $E$. Top curve: $\langle r \rangle = 2.00$; bottom curve: $\langle r \rangle = 3.00$. The alloys corresponding to various $\langle r \rangle$ values are as indicated in Fig. 1.



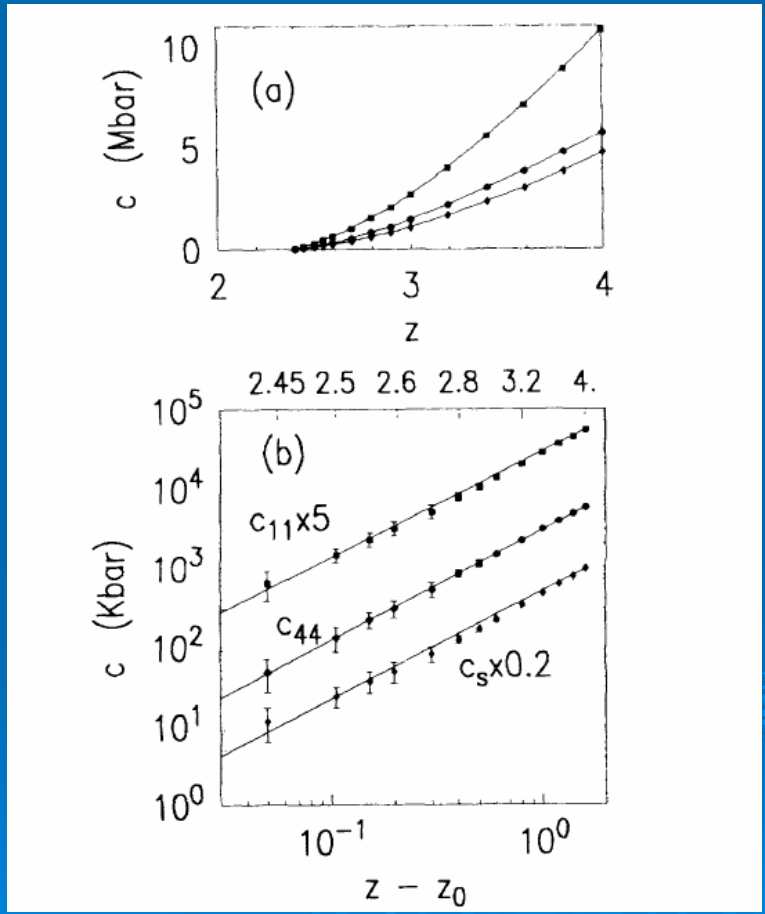

W. Kamitakahara et al. Phys. Rev. B 44, 94 (1991).

# Raman and IR reflectance as probes of elastic phases

In Stressed-Rigid and Inter-mediate Phases, characteristic optical elastic power-law in <r>

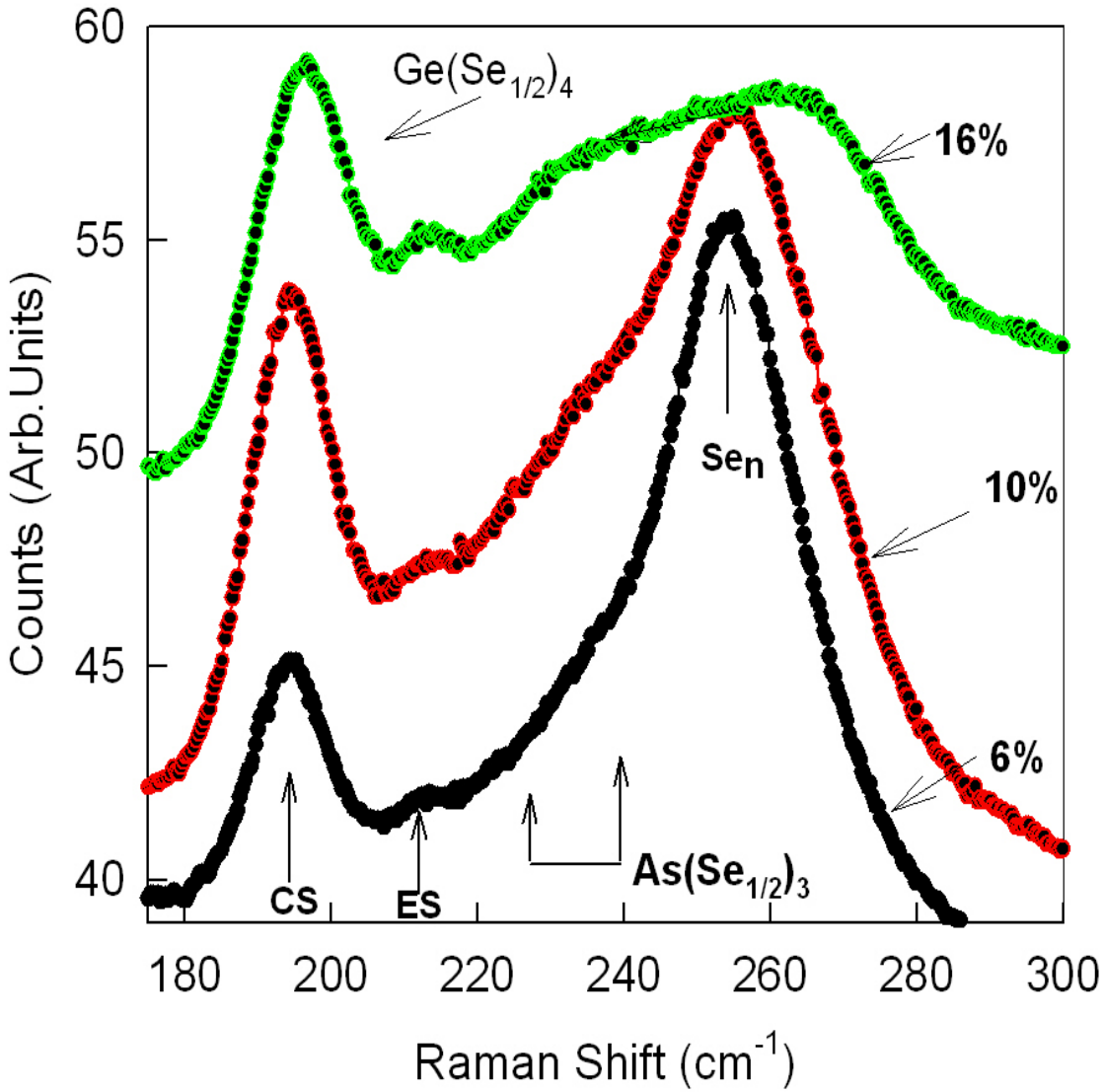
$$\nu^2 - \nu^2_c = A\,(r - r_c)^p$$

are observed from Raman Scattering. A power-law P in the 1.3 to 1.5 range is Predicted and also observed in Stressed-rigid glasses.

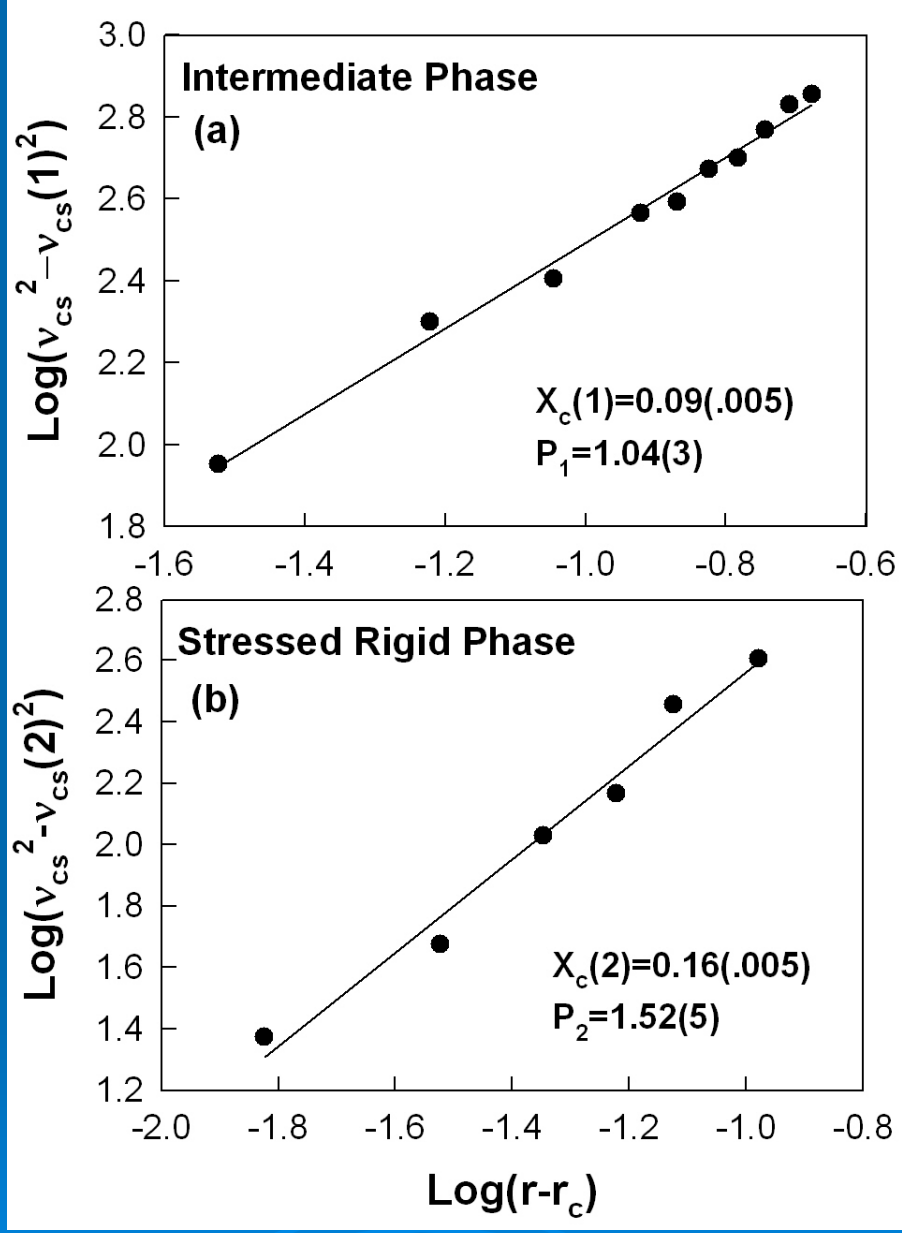



Franzblau and Tersoff PRL 68, 2172 (1992).

Raman Scattering Results of $Ge_XAs_XSe_{1-2X}$




Tao Qu, D,G,Georgiev, P.Boolchand, M.Micoulaut, Mater. Res. Soc. Symp. Proc. vol. 754, CC8.1.1 (2003).




Tao Qu, D,G,Georgiev, P.Boolchand, M.Micoulaut

Mater. Res. Soc. Symp. Proc. vol. 754, CC8.1.1 (2003).

# Nature of glass transition

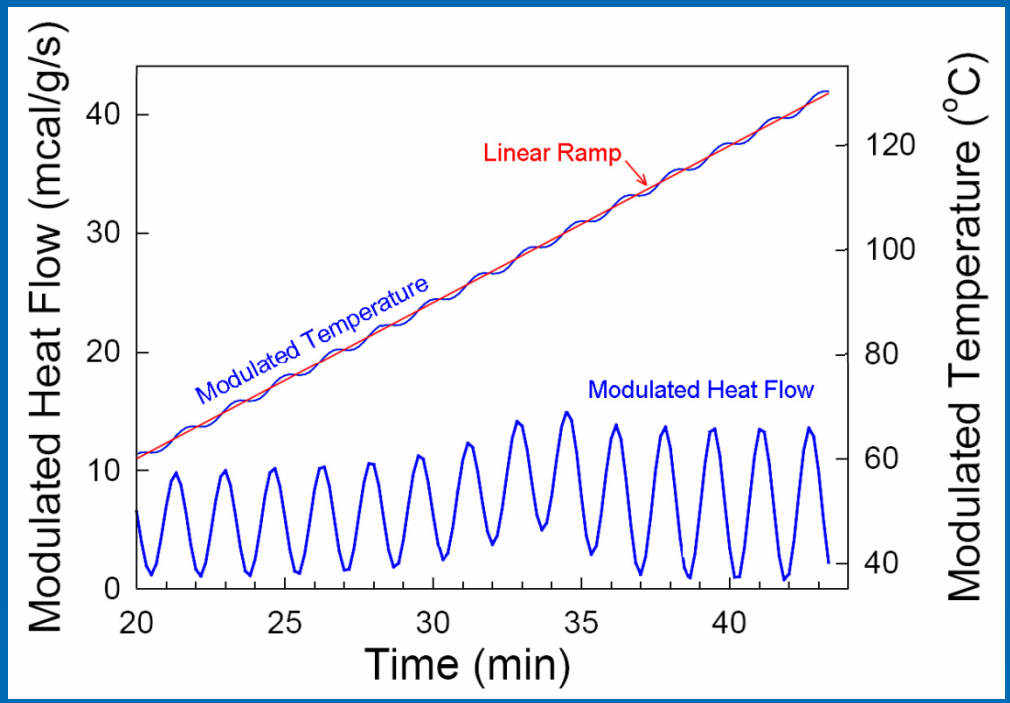
Glass transition endotherms observed in DSC have two broad features:

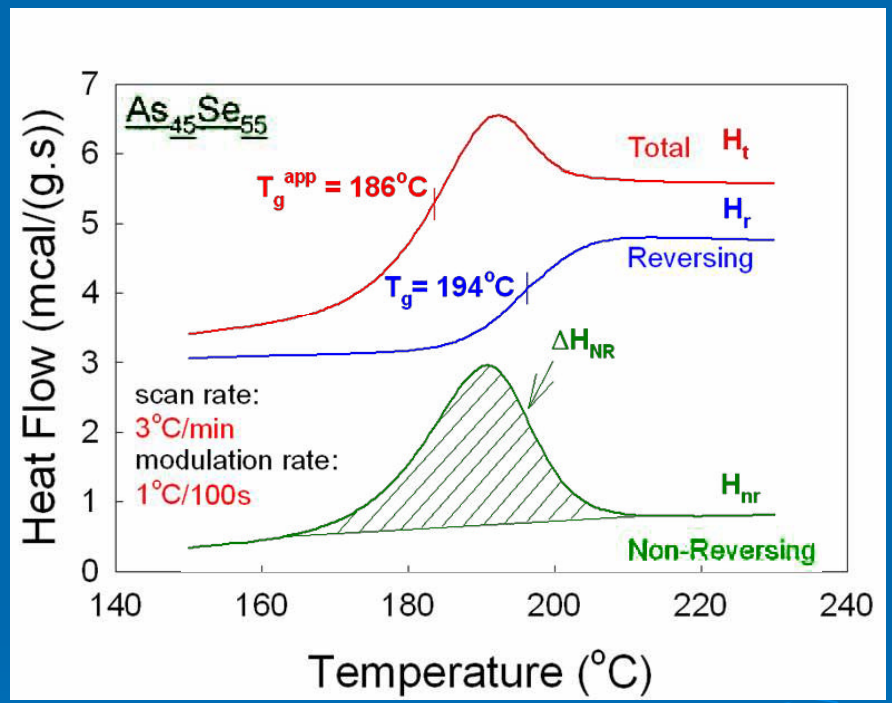
(i) a rounded step in the heat flow (or Specific heat jump) between the glassy and liquid state

(ii) an overshoot at the onset of the step.

The determinative factor in metastability of the glass transition is the overshoot feature (ii) not the step feature (i). It represents the non-ergodic, or thermally non-reversing component of heat flow related to aging, impurity content, configurational change between the glass and the liquid.

# Modulated DSC accurately measures the thermally reversing component of the heat flow at $T_g$.




D.G. Georgiev, P.Boolchand, M.Micoulaut Phys. Rev B 62, R9228 (2000).

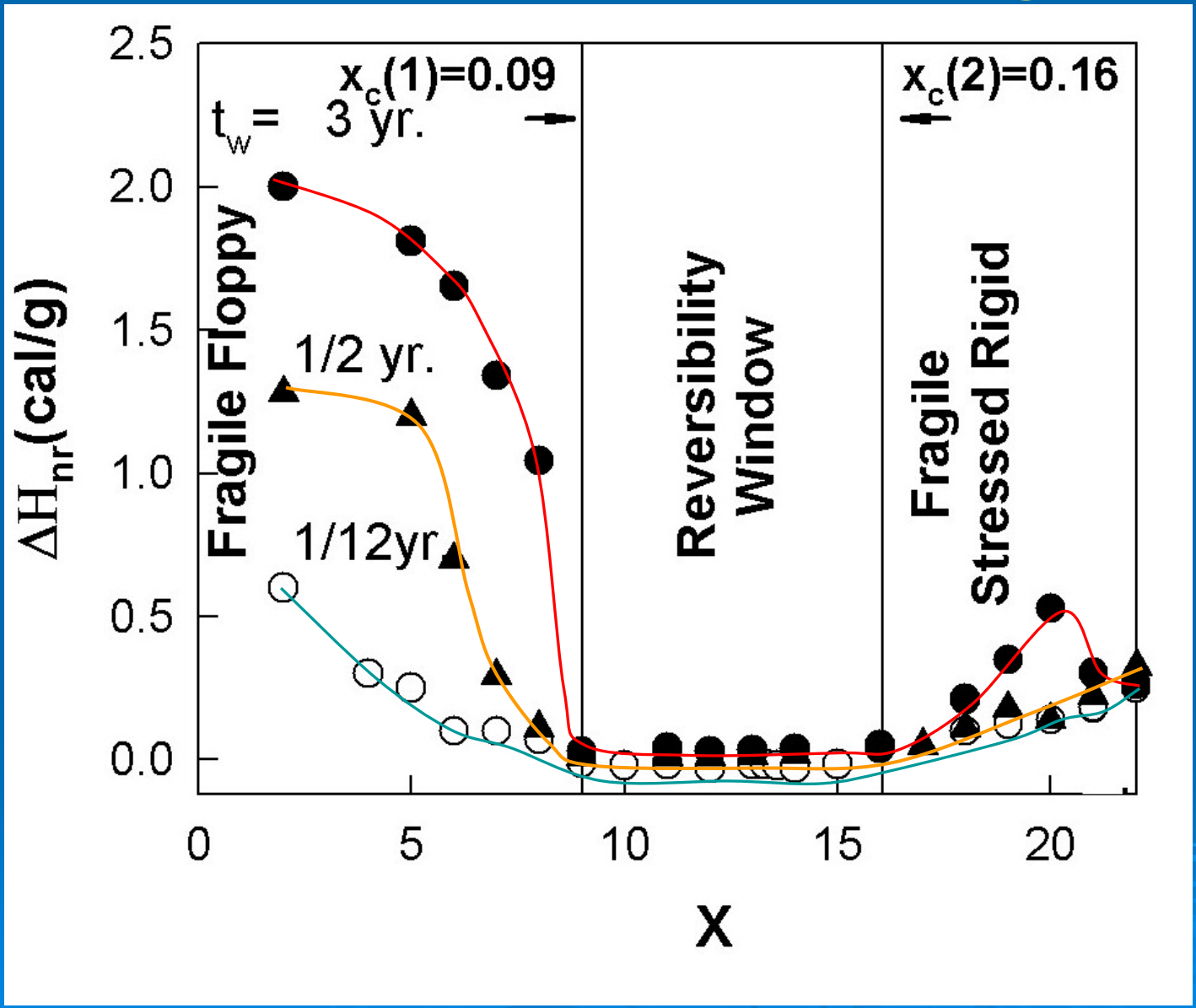
# The $\Delta H_{nr}$ Calorimetric term displays three distinct types of behavior

- Narrow and symmetric $\Delta H_{nr}$ profiles that age with waiting time: Flexible networks.

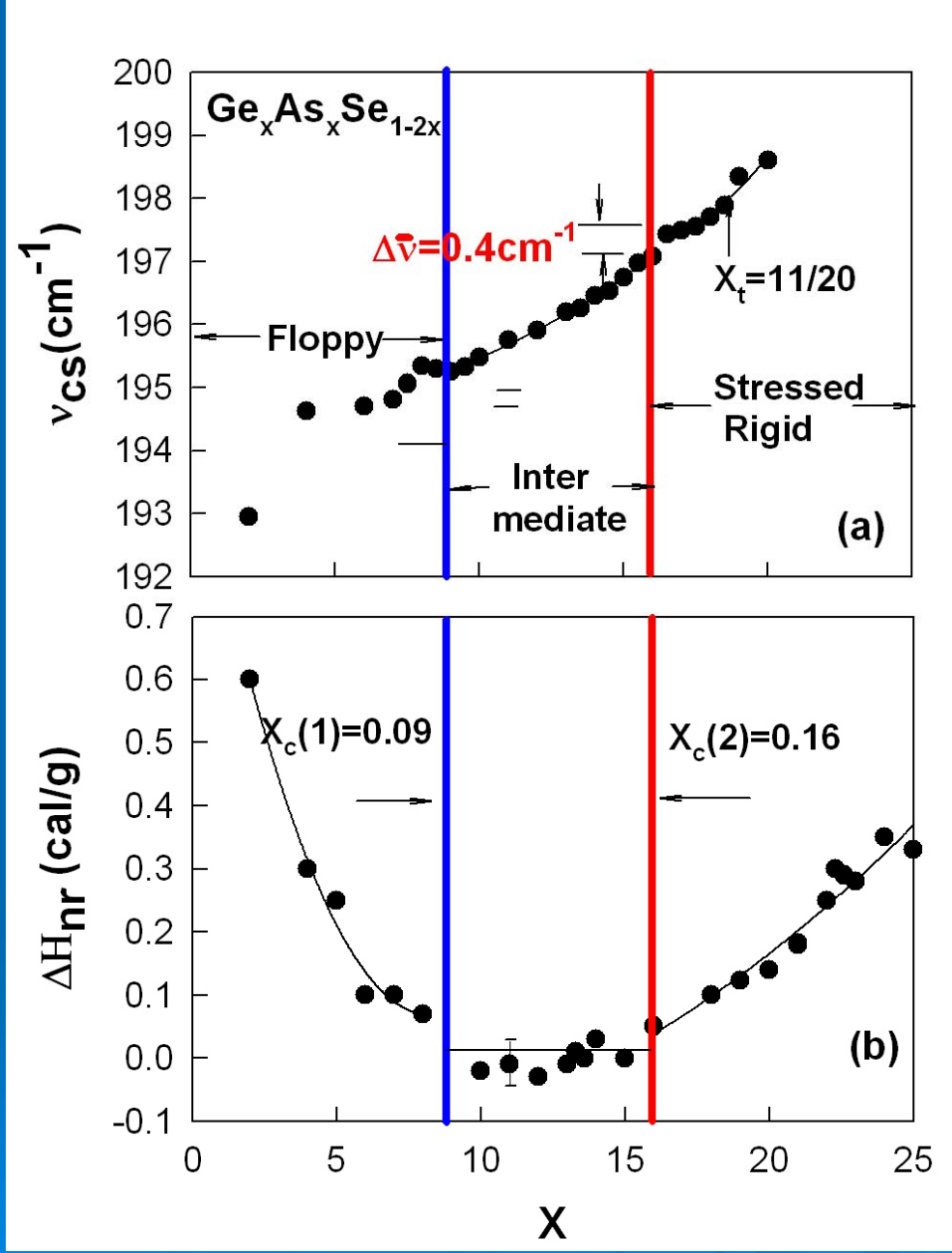
- A vanishing $\Delta H_{nr} \sim 0$ term that does not age : Rigid but stress-free networks- Intermediate.

- Wide and asymmetric $\Delta H_{nr}$ profiles that age : Stressed-rigid networks.

# Elastic Phases in $As_xGe_xSe_{1-2x}$ glasses



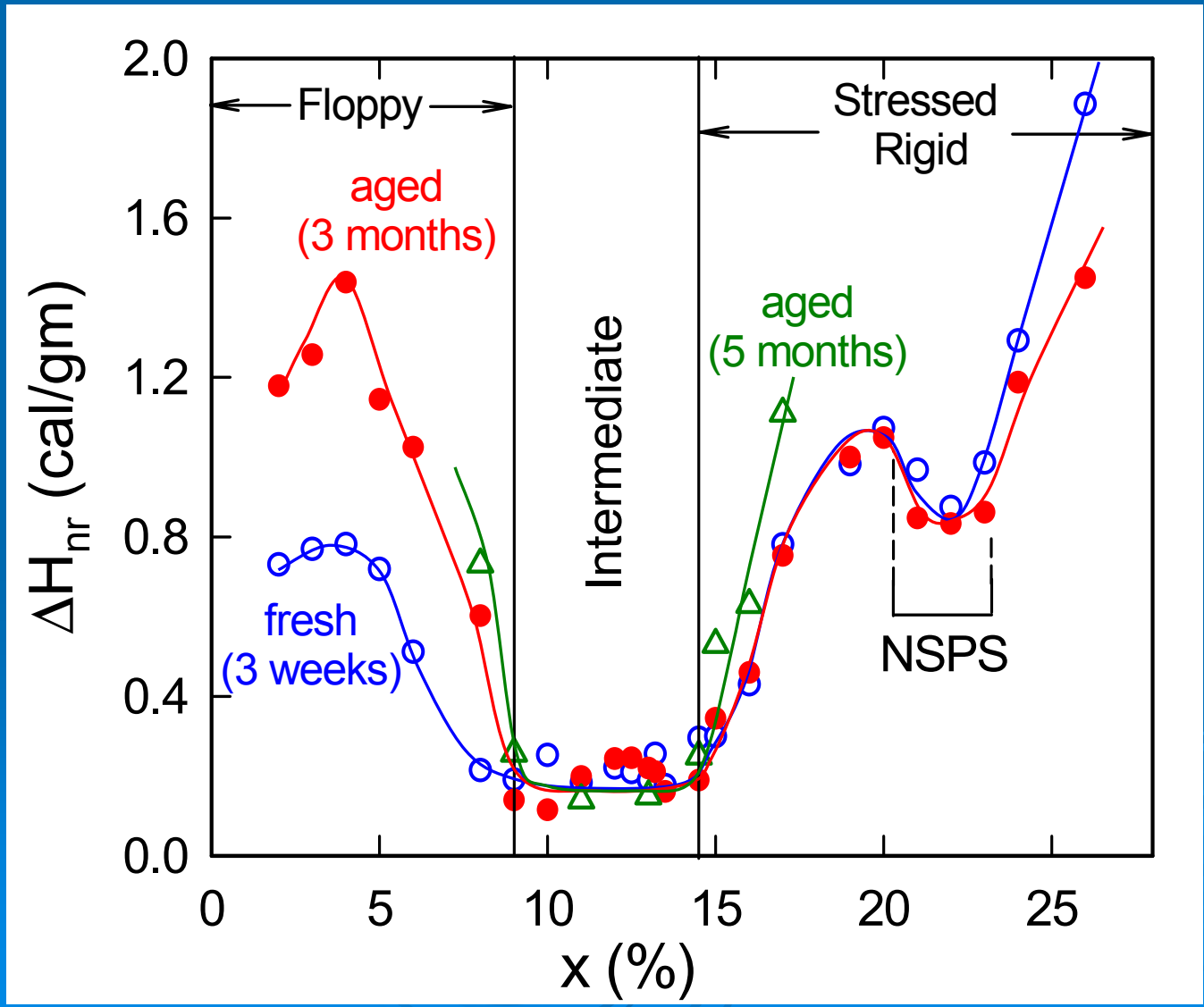

Tao Qu, D,G,Georgiev, P.Boolchand, M.Micoulaut. Mater. Res. Soc. Symp. Proc. vol. 754, CC8.1.1 (2003)

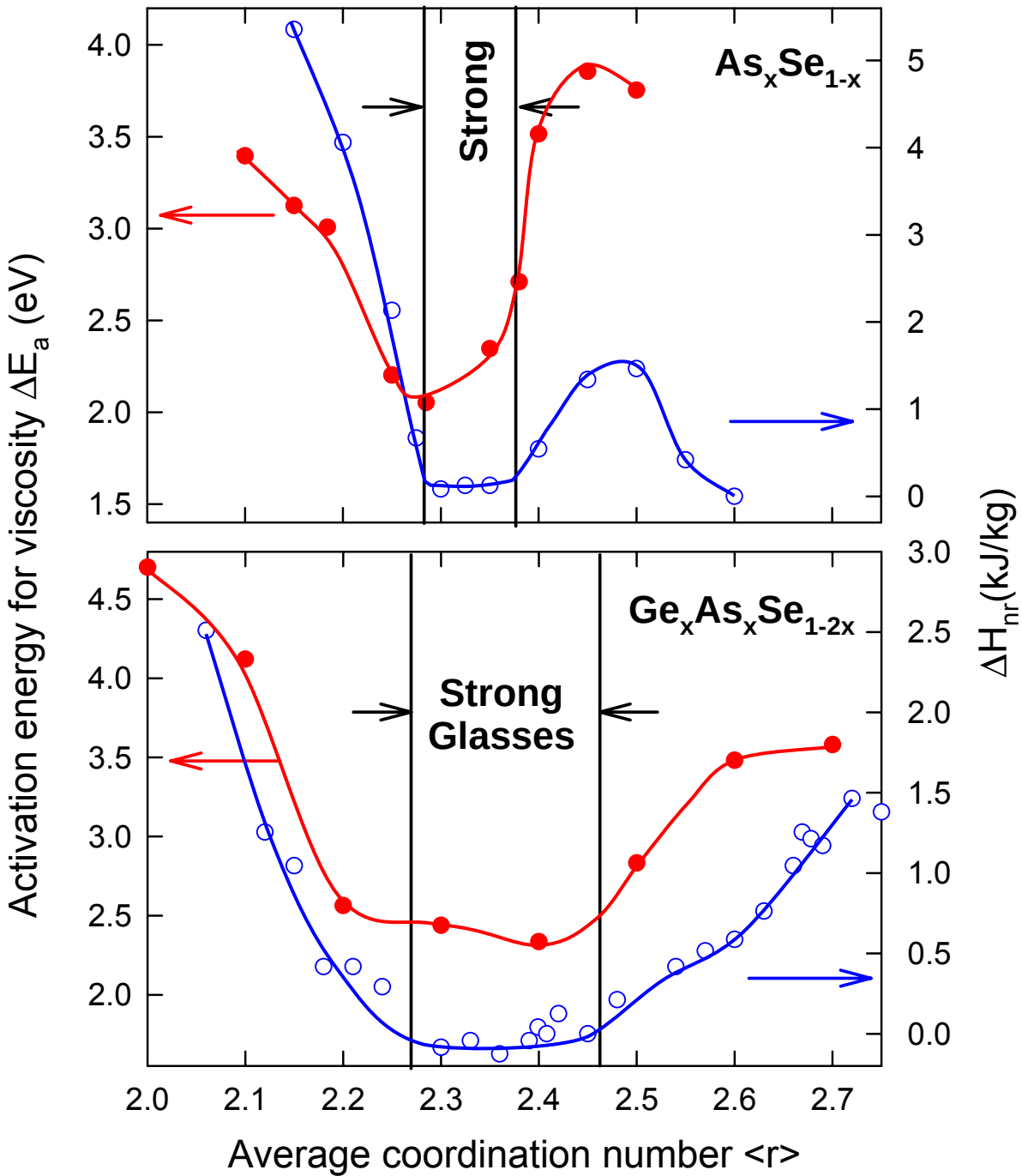



Tao Qu, D,G,Georgiev, P.Boolchand and M.Micoulaut, Mater. Res. Soc. Symp. Proc. vol. 754, CC8.1.1 (2003).

# $Ge_xP_xSe_{1-2x}$ glasses

S. Chakravarty et al. J.Phys. Cond. Matter 17,L1-L7 (2005).






Windows in $\Delta H_{nr}$ and in $\Delta E^{a}{}_{\eta}$ coincide

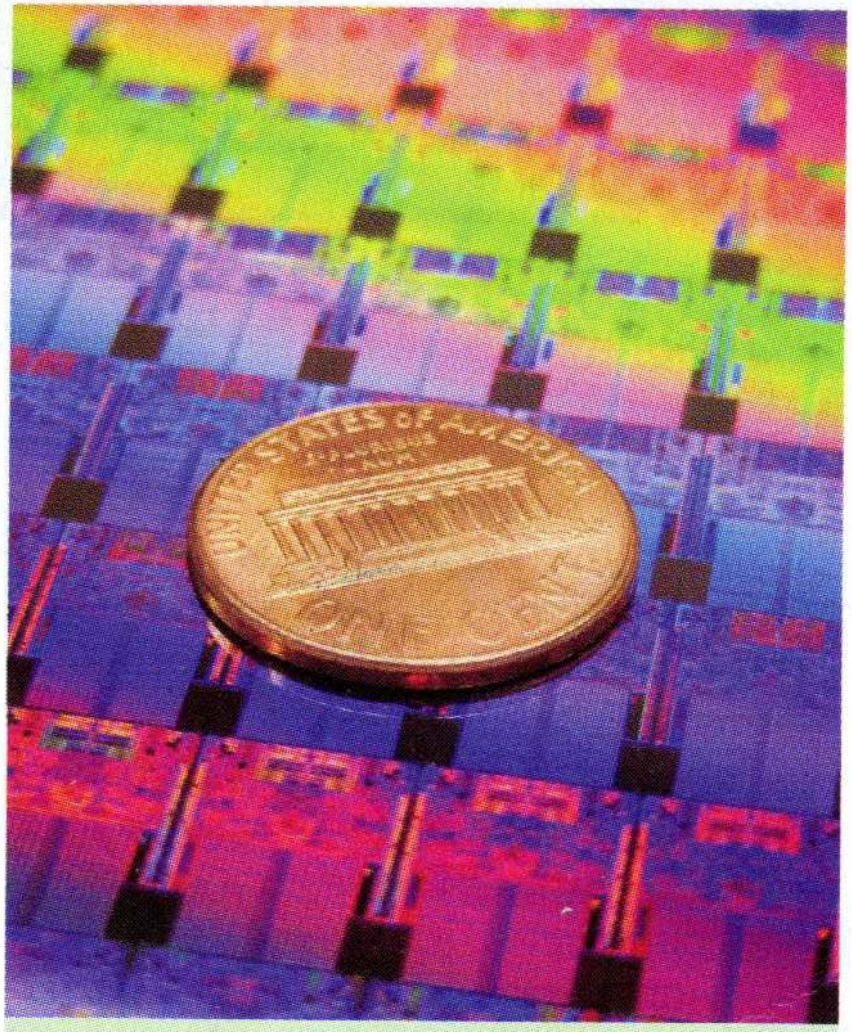
$As_xSe_{1-x}$ binary

$Ge_xAs_xSe_{1-2x}$ ternary

# $Si/SiO_2$ interface is self-organized*

- Best interface in nature; used as a gate dielectric in a standard 3-terminal device, withstands $10^9$ cycles even though the $SiO_2$ is a glass not a crystal!
- The same interface engineered with high-K dielectrics , 45 nm feature size device announced by Intel in Feb 2008. Physics Today.

* G. Lucovsky and J. C. Phillips, Interfacial strain-induced self-organization in semiconductor dielectric gate stacks. 1. Strain relief at the Si-$SiO_2$ interface, J. Vac. Sci. Technol, B22, 2087-96, 2004.



**Intel's newest 45-nm microprocessors** are now in production and incorporate, for the first time, transistors using hafnium-based insulators and metal gates. (Courtesy of Intel Corp.)

February 2008
Physics Today

# Window Glass is a Self-organized Network

$(SiO_2)_{1-x-y}(Na_2O)_x(CaO)_y$

- Ring homogeneity of alloyed network requires for every Ca atom one have 3 Na atoms, that is $2x/y = 3$

or $x = 3y/2$

- Network to be optimally constrained,

$n_c=3$

- These 2 conditions uniquely fix the chemical composition of window glass as

$(SiO_2)_{73.7}(Na_2O)_{15.8}(CaO)_{10.5}$

R.Kerner and J.C. Phillips SSC 117, 47 (2001)

# Conclusions

- Variational principle ( $n_c = 3$) through rigidity theory has proved to be most insightful in understanding the physics of glass.

- Floppy modes (in flexible) and redundant bonds (in stressed-rigid ) hold the key to non-local internal network stress in network glasses, and its absence in the Intermediate phase – the key to applications.

- These ideas have worked well in covalent, ionic-covalent, fast-ion conducting, H-bonded glass systems, and proteins with important consequences on many technologies ( Intel, Corning, Drug design).

# Rigidity Theory and Intermediate Phases in network Glasses- select references


- J.C. Phillips ,Topology of Non-crystalline Covalent Solids- Short Range Order in chalcogenide alloys, J. Non Cryst. Solids 34, 153-181 (**1979**), ibid, 43, 37-77 (1981).
- M.F. Thorpe, Continuous Deformations in random networks, J.Non-Cryst. Solids 57,355-370 (**1983**).
- H.He and M.F. Thorpe, Elastic Properties of glasses , Phys. Rev. Lett. 54, 2107-2110 (**1985**).
- D.J.Jacobs and B.Hendrickson. , An algorithm for 2D rigidity percolation: The pebble game.
- J. Comput. Phys. 137, 346-365 (**1997**).
- M.F. Thorpe, D.J. Jacobs, N.V. Chubynski , A.J. Rader Generic Rigidity of network Glasses in *Rigidity Theory and Applications*, Ed. M.F. Thorpe and P.M. Duxbury, , Kluwer Academic/Plenum Publishers, New York, p.238-278 (**1999**).
- D.Selvanathan, W. J. Bresser, P. Boolchand. *Stiffness transitions in $Si_xSe_{1-x}$ glasses from Raman scattering and temperature-modulated differential scanning calorimetry.* Phys. Rev. B 61, 22, 15061 (**2000**).
- M.F. Thorpe, D,J,Jacobs, M.V. Chubynsky, J.C. Phillips, Self-organization in network Glasses, J.Non-cryst. Solids 266-269, 859 (**2000**).
- G.G. Naumis, Contributions of floppy modes to the Heat Capacity jump and fragility in Chalcogenide glasses, Phys. Rev. B 61, R9205 (**2000**).
- M.F. Thorpe and M.V. Chubynsky, The Intermediate Phase and Self-Organization in Network Glasses in *Phase Transitions and Self-organizations in Electronic and Molecular Networks*, Ed J.C. Phillips, MF Thorpe, Kluwer Academic/Plenum Publishers **2001**, p. 43-64
- R.Kerner and J.C. Phillips, Quantitative Principles of Glass Silicate Chemistry, Sol.St.. Commun. 117, 47 (**2001**).

# Rigidity Theory and Intermediate Phases in network Glasses- select references continued


- G. Lucovsky and J. C. Phillips, Interfacial strain-induced self-organization in semiconductor dielectric gate stacks: strain relief at the Si-$SiO_2$ interface, J. Vac. Sci. Technol, B22, 2087-96, (**2004)**.
- P. Boolchand, G. Lucovsky, J.C. Phillips, M.F. Thorpe, "*Self-Organization and the Physics of Glassy Networks*", Phil. Mag. 85, 3823 (**2005**).
- G.G.Naumis, Variation of the glass transition temperature with rigidity and chemical composition, Phys. Rev.B 73, 172202 (**2006**).
- M. Micoulaut and J.C. Phillips, Rings and Rigidity in network glasses, Phys. Rev. 353, 1732 (**2007**).
- Deassy Novita, P.Boolchand, M. Malki and M. Micoulaut, "*Fast-ion Conduction and flexibility of glassy networks*", Phys. Rev. Lett**.** 98, 195501 (**2007**).
- M.A. Briere , M.V. Chubynsky, N. Mousseau, Self-organized criticality in the intermediate phase of rigidity percolation, Phys. Rev. E 75, 056108 (**2007**).
- M. Micoulaut, M. Malki, D. I. Novita, P. Boolchand, "*Fast-ion conduction and flexibility and rigidity of solid electrolyte glasses*", Physical Review B 80, 184205 (**2009**)
- M. Chubynsky, Characterizing the Intermediate Phases through Topological analysis in the Intermediate Phase of network glasses in *Rigidity and Boolchand intermediate phases in nanomaterials*, Ed. M. Micoulaut and M. Popescu, INOE, **2009**, p. 213-260
- F.Inam, G.Chen, D.N. Tafen, D.A. Drabold Intermediate Phase in Germanum Selenide glasses: A Theoretical and Experimental study, in *Rigidity and Boolchand intermediate phases in nanomaterials*, Ed. M. Micoulaut and M. Popescu, INOE, **2009,** p. 261-220.
- P. Boolchand, P.Chen, D.I. Novita, B.Goodman, New Perspectives on intermediate phases in *Rigidity and Boolchand intermediate phases in nanomaterials*, Ed. M. Micoulaut and M. Popescu, INOE, **2009,** p. 1-37.