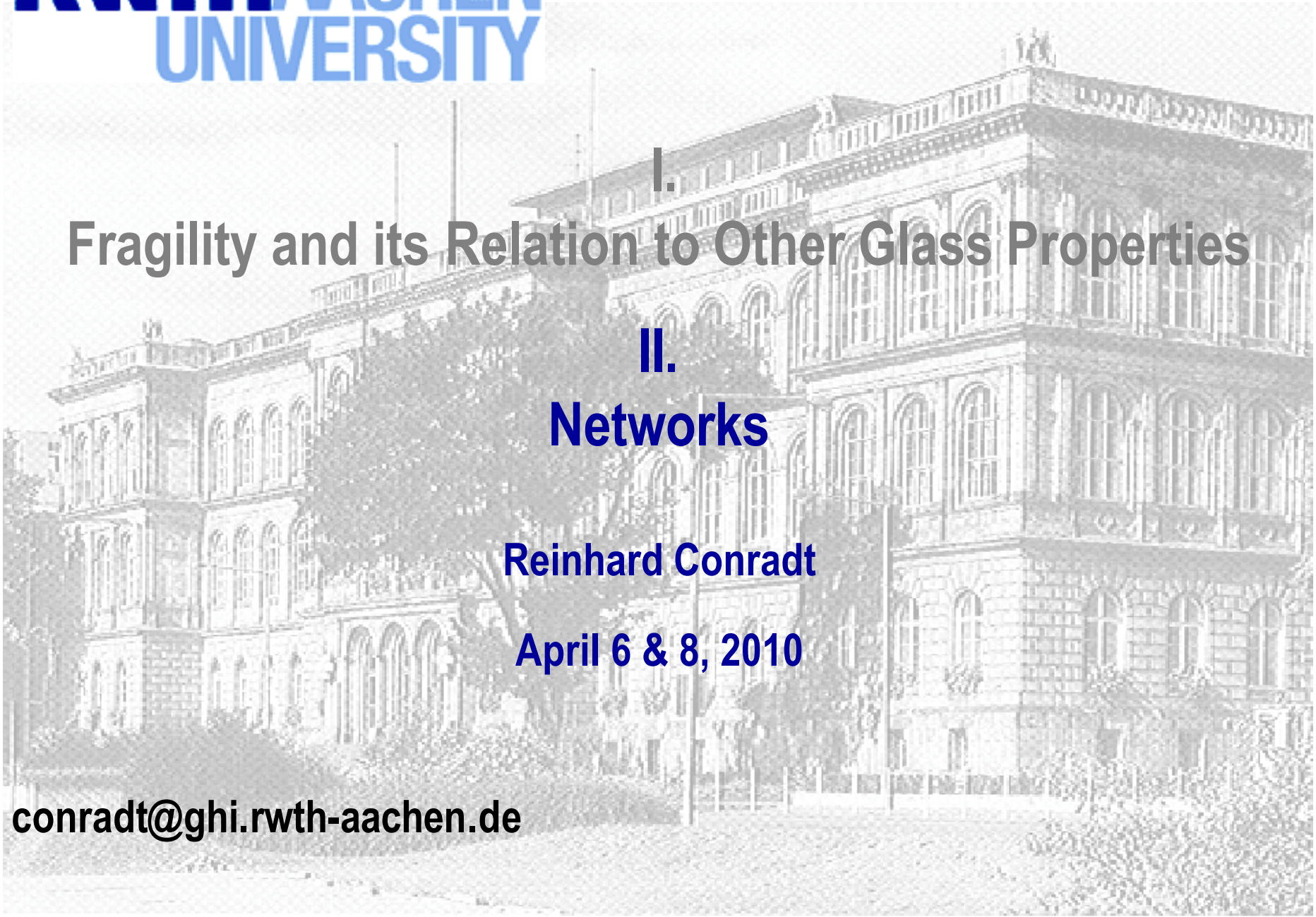

RWTH AACHEN UNIVERSITY

I.
Fragility and its Relation to Other Glass Properties

II.
Networks

Reinhard Conradt

April 6 & 8, 2010

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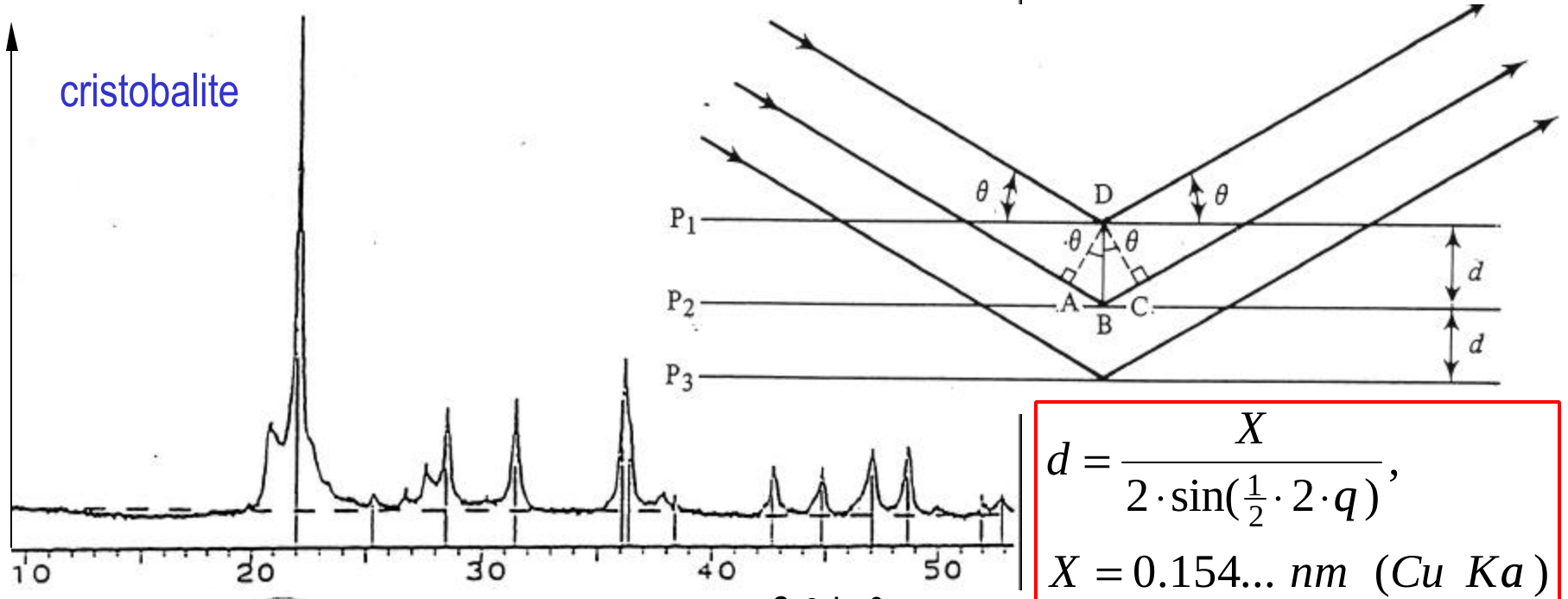
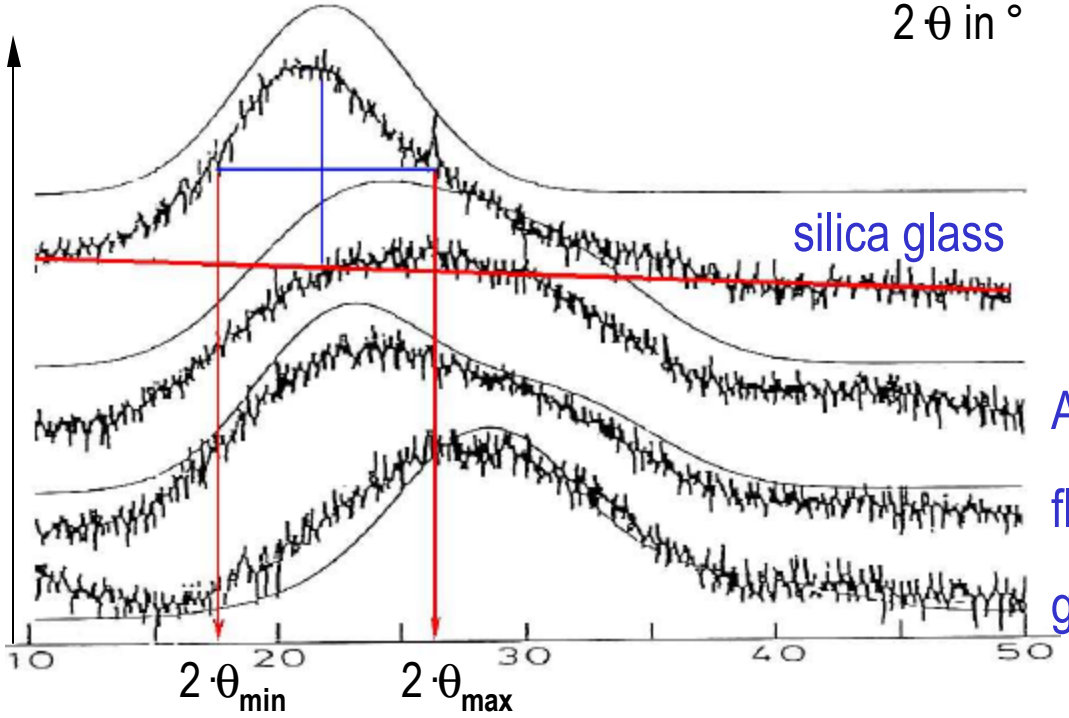
structural aspects



$$d = \frac{X}{2 \cdot \sin(\frac{1}{2} \cdot 2 \cdot q)},$$

$$X = 0.154... \; nm \;\; (Cu \;\; Ka)$$



peak broadening B

$$B = \tfrac{1}{2} \cdot (2q_{\max} - 2q_{\min}) \cdot \frac{p}{180}$$

A fibre glass

float glass

glassy basalt rock

Bragg's formula relates lattice spacing d and diffraction angle θ:

$$d = \frac{X}{2 \cdot \sin(\frac{1}{2} \cdot 2q)} \; ; \; X = 0.154\,nm \; (Cu \;\; K_a)$$

broadening B of diffraction peaks:

$$B = \frac{1}{2} \cdot (2q_{\max} - 2q_{\min}) \cdot \frac{p}{180}; \quad (22 \pm 4)^\circ \Rightarrow B = 0.0698$$

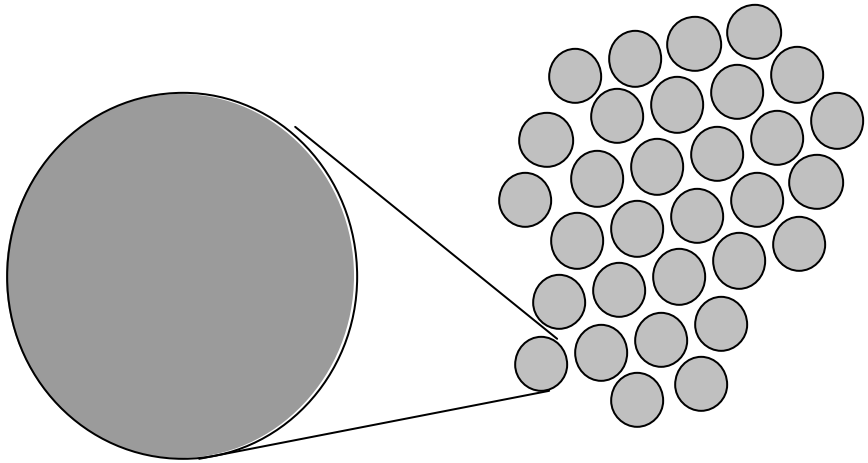
interpretation: peak broadening B ⇔ range b of translational symmetry

$$b = \frac{X}{B \cdot \cos(\frac{1}{2} \cdot 2q)} \; ; \quad (22 \pm 4)^\circ \Rightarrow b = 2\,nm$$

interpretation: peak broadening B ⇔ fluctuation$\varepsilon = \delta d/d$ of lattice spacing

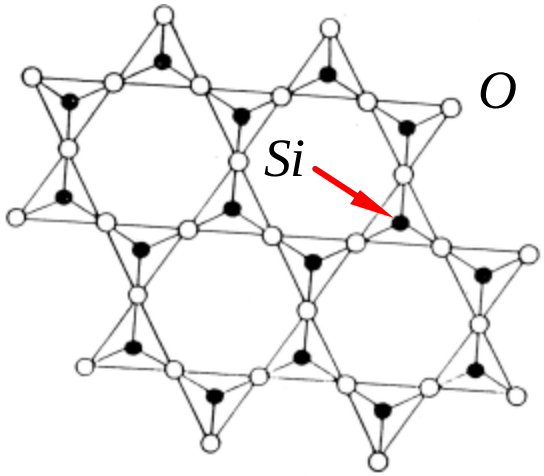
$$e = \frac{dd}{d} = \frac{B}{4 \cdot \tan\left(\frac{1}{2} \cdot 2q\right)}; \quad (22 \pm 4)^\circ \Rightarrow e = 9\ \%$$

1. *random packing of length-correlated clusters*

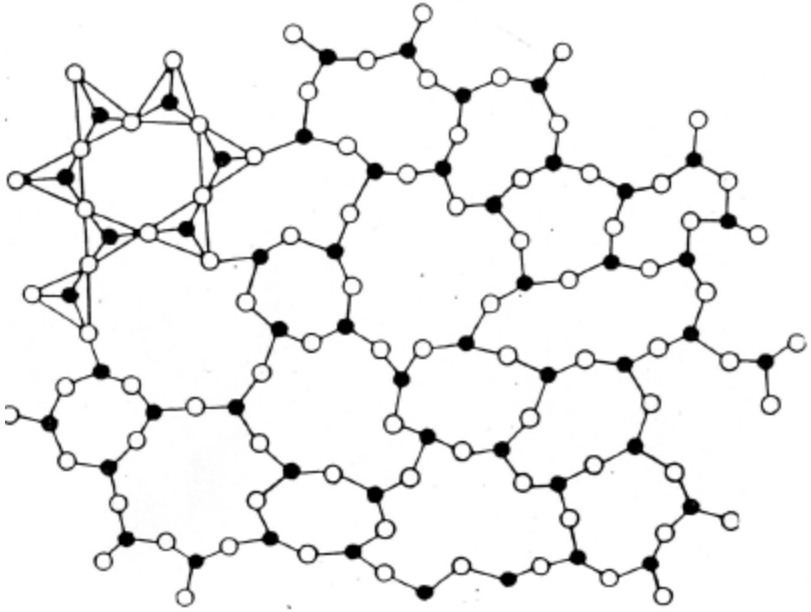


2.

crystalline silica

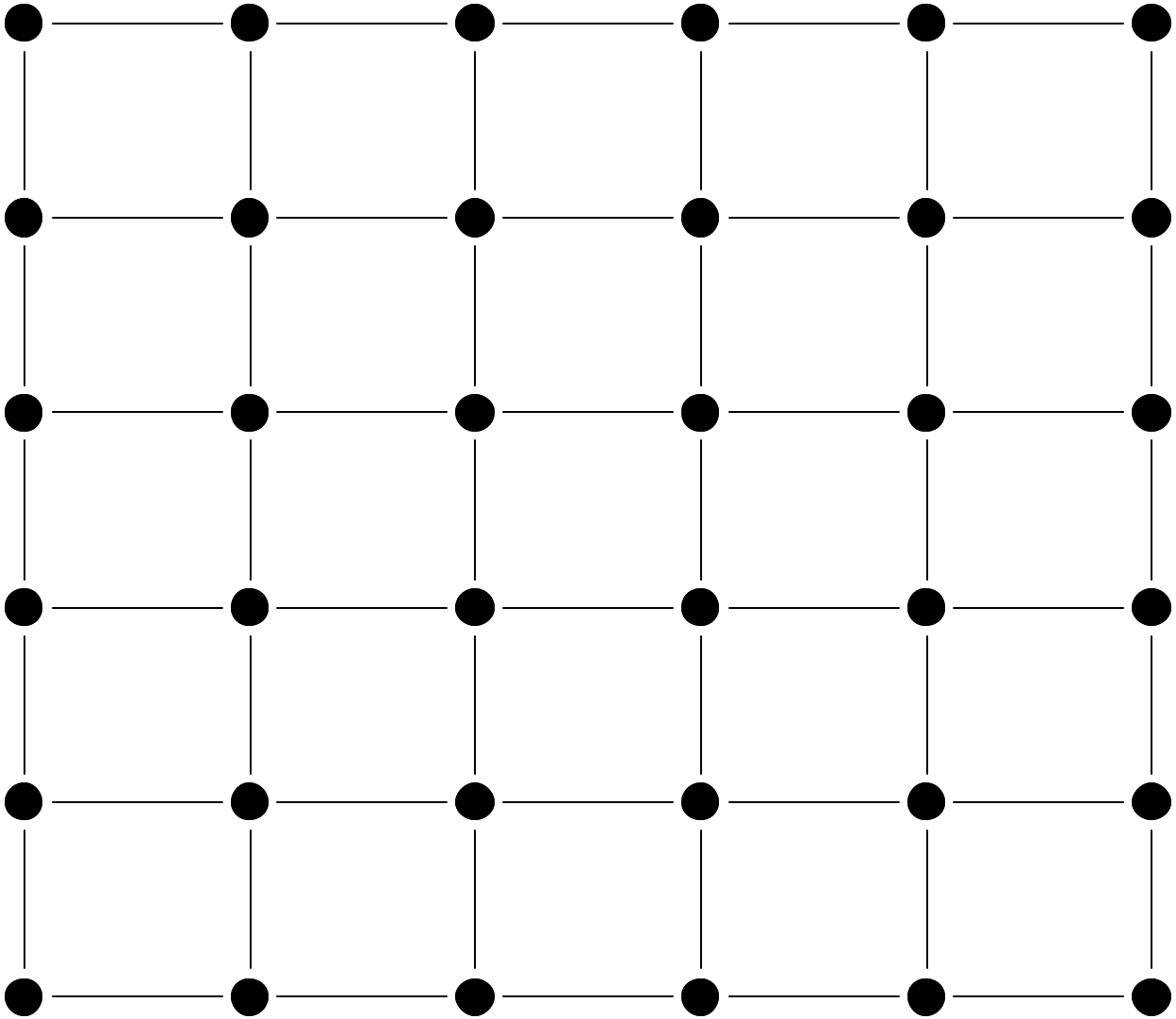


silica glass

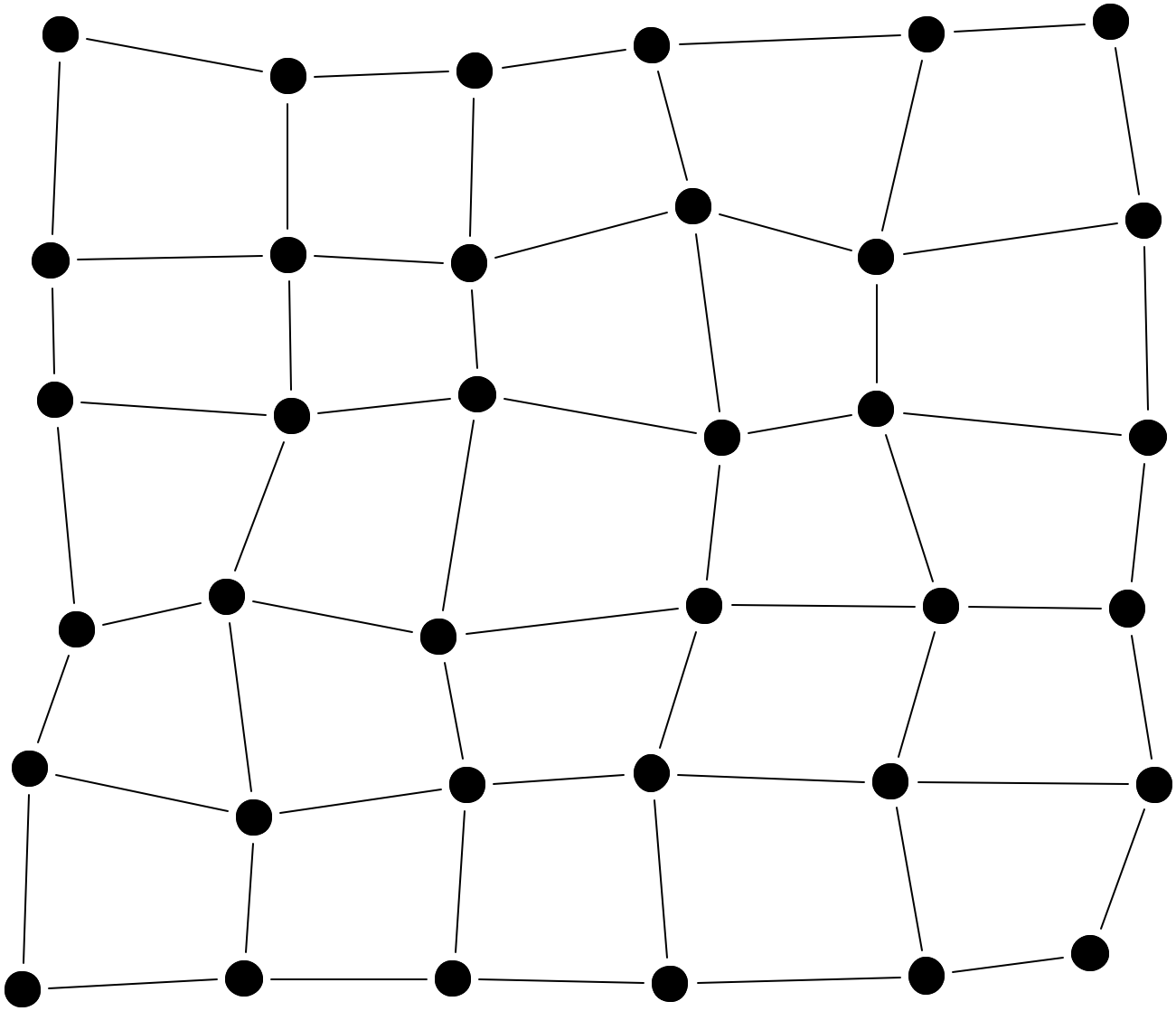


W. Zachariasen (1934)

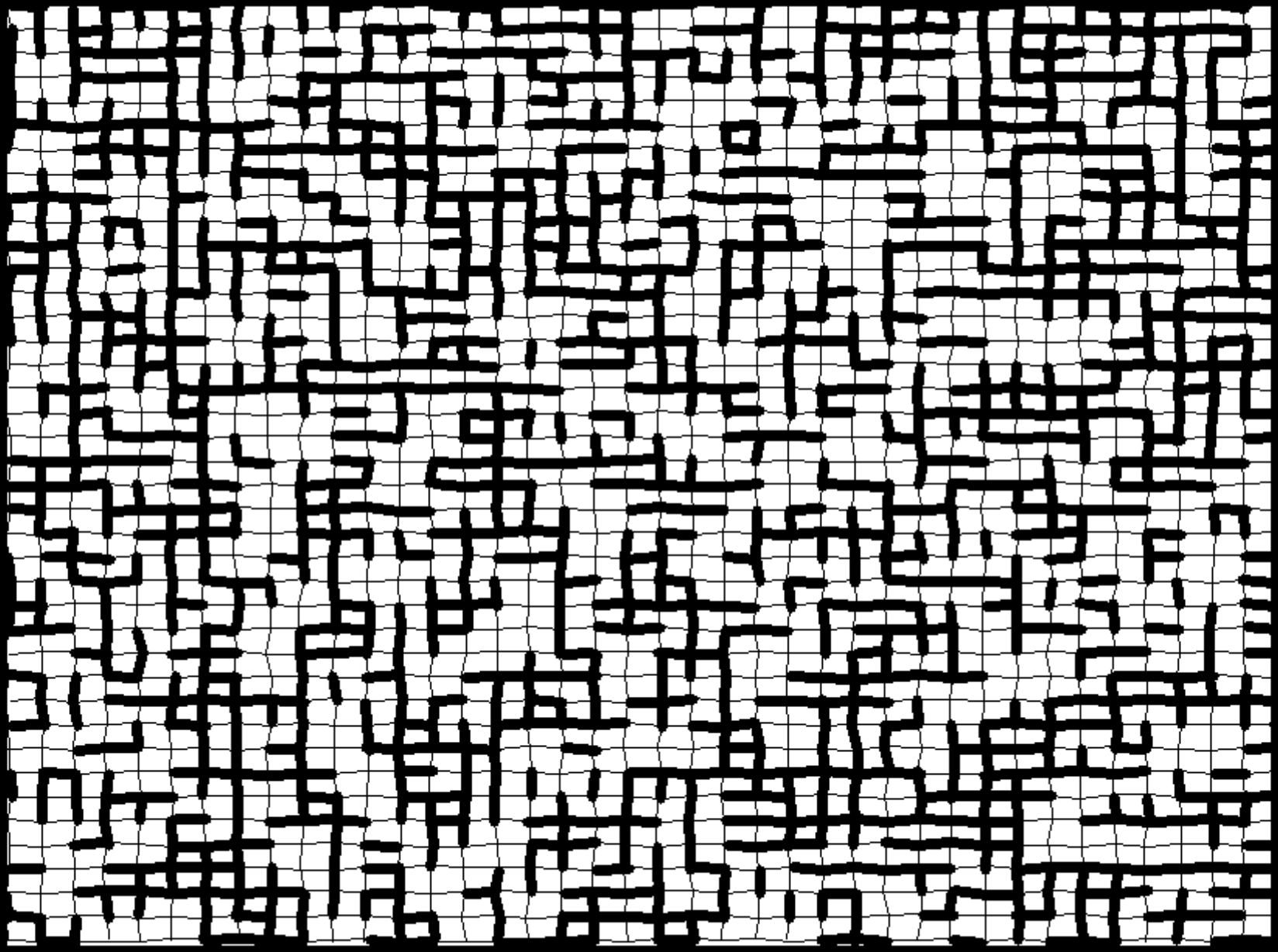
$\varepsilon = \pm 0.00$



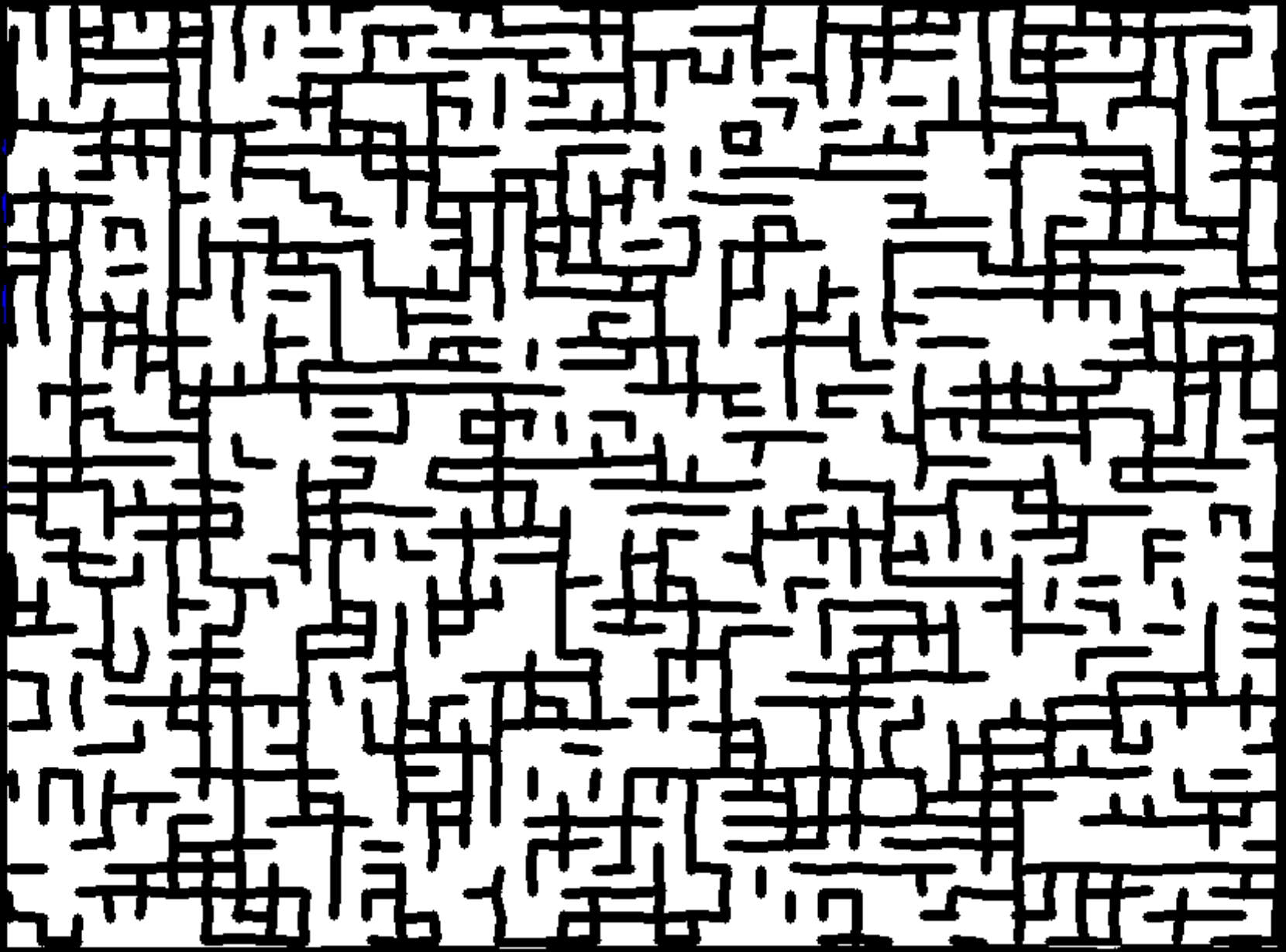
$\varepsilon = \pm 0.09$

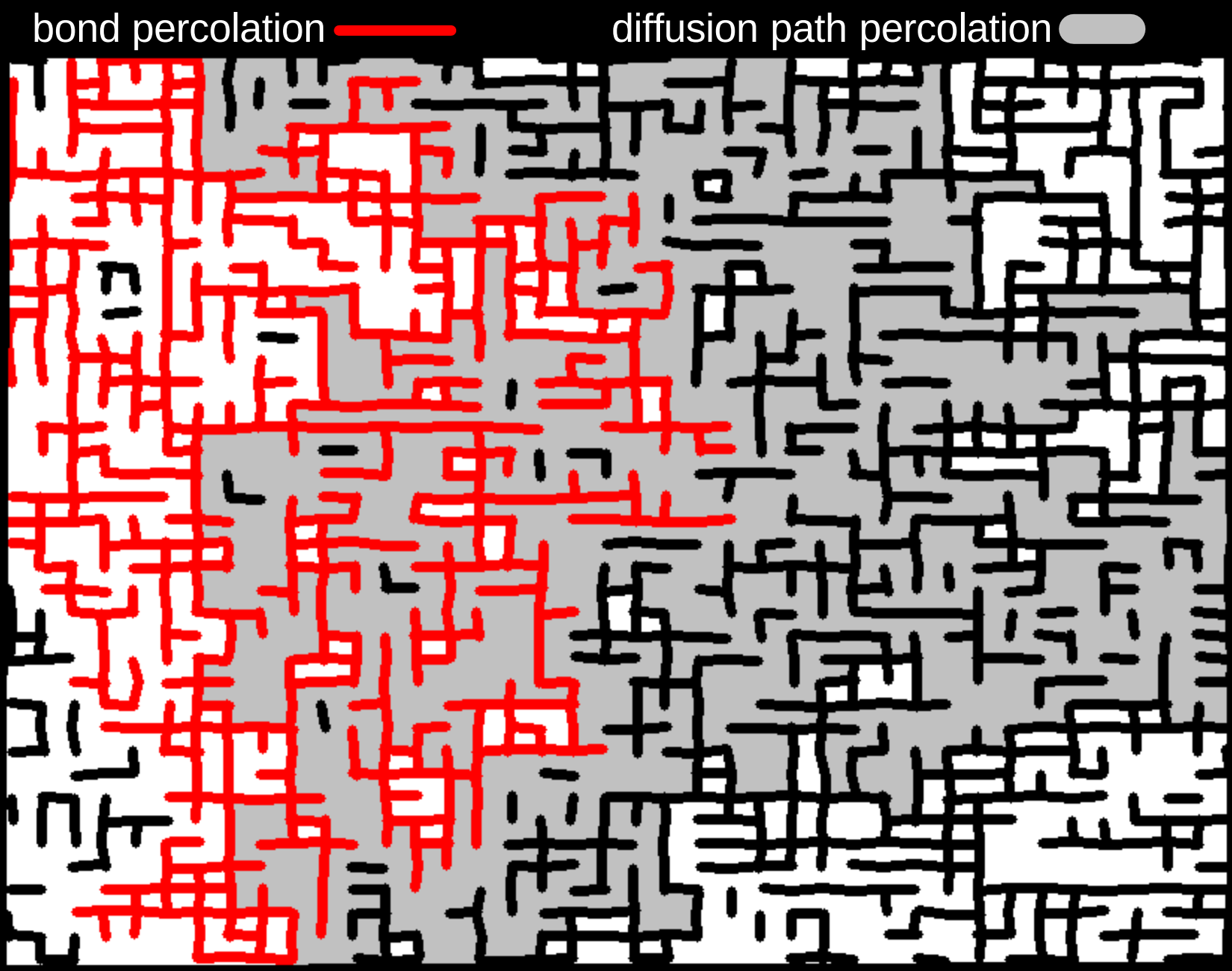


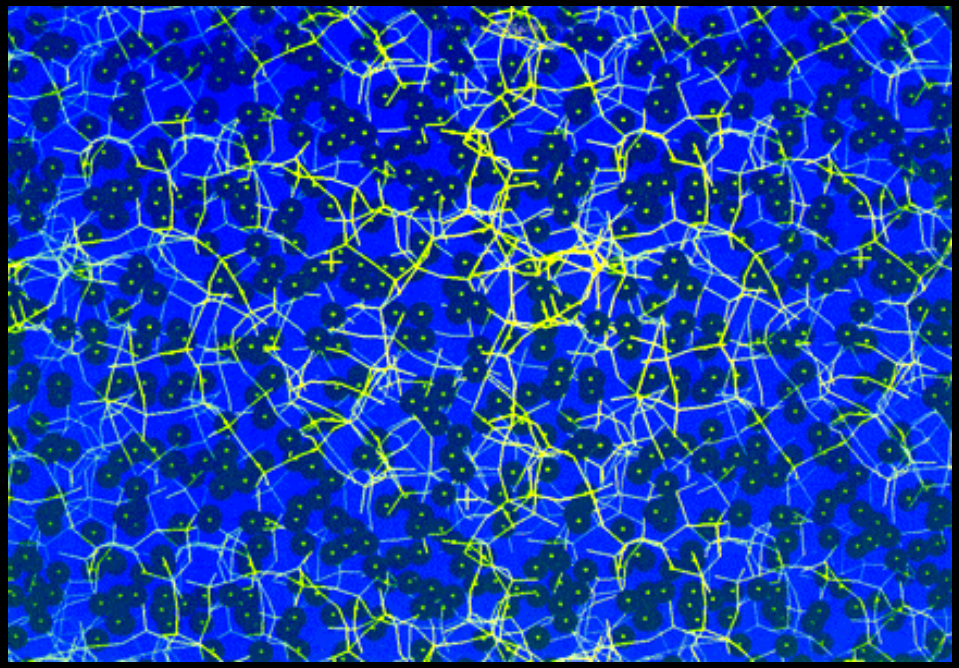
$\varepsilon = 0.09$; $d \leq \varepsilon \cdot \sqrt{2}$ is accepted as bond



$\varepsilon = 0.09$; $d \leq \varepsilon \cdot \sqrt{2}$ is accepted as bond

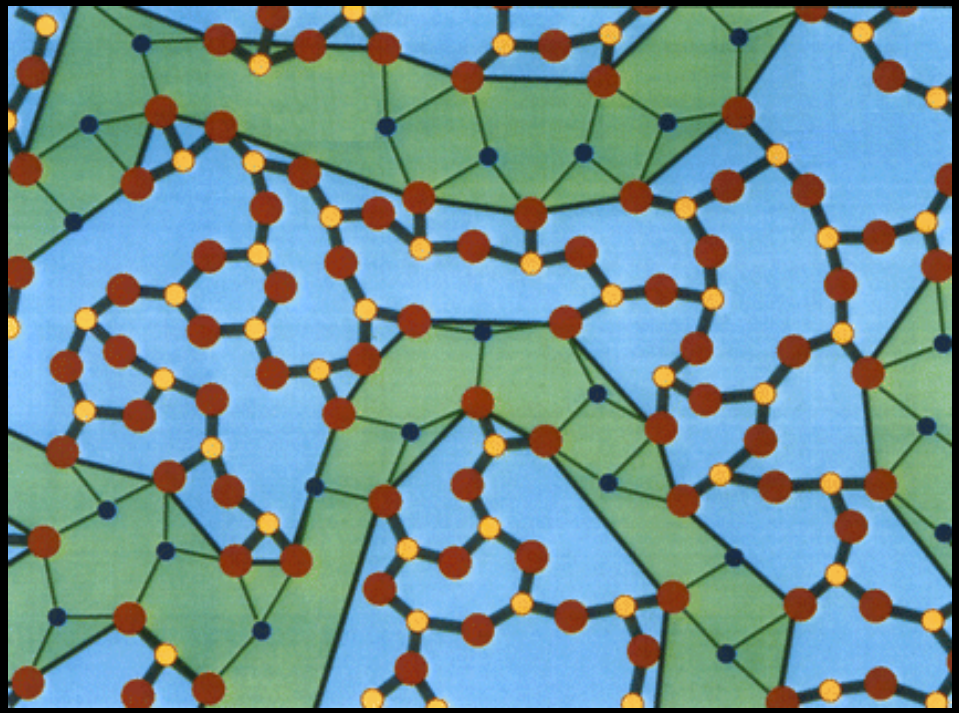



bond percolation
diffusion path percolation



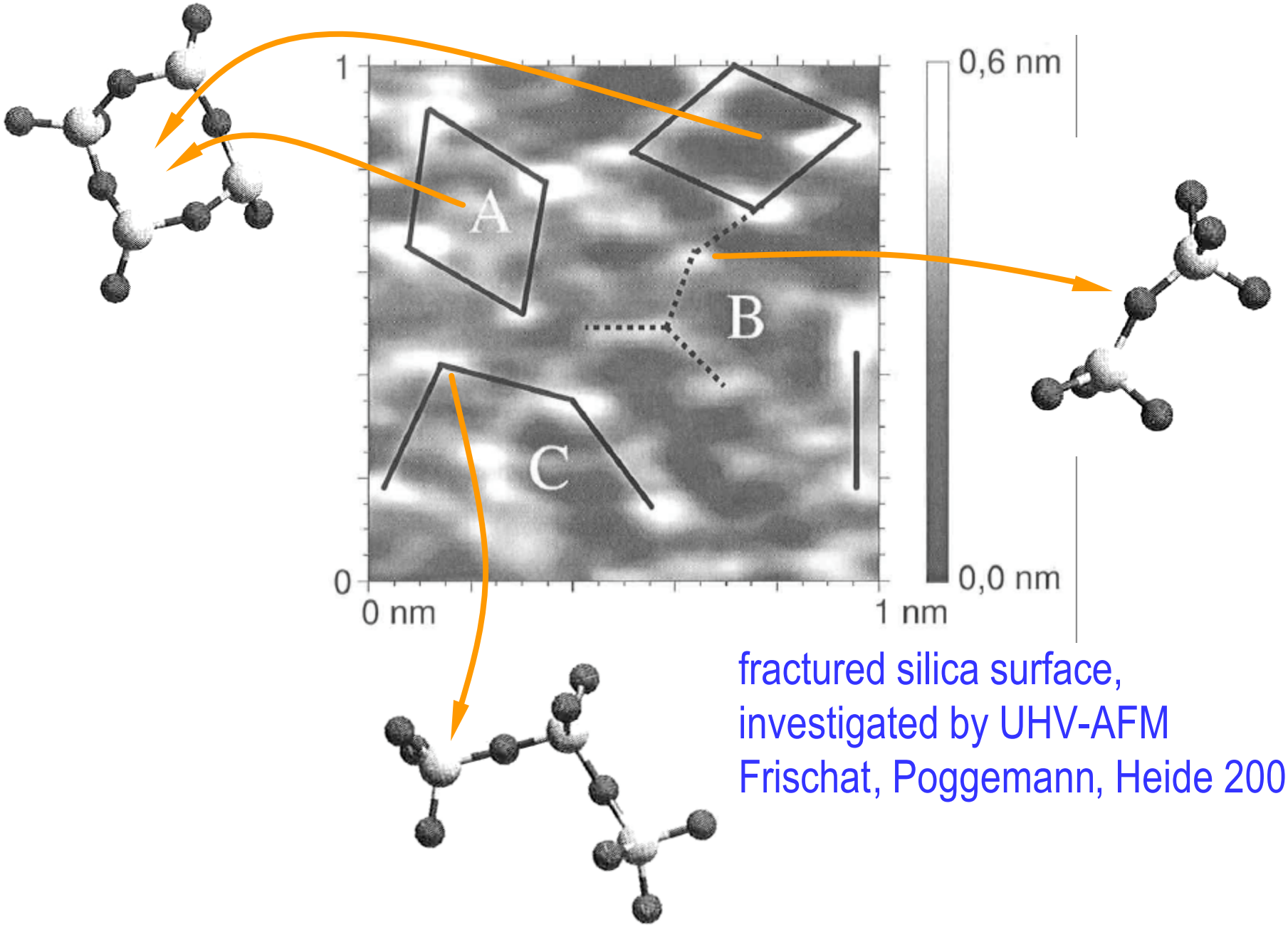
simulated 3D structure of $Na_2Si_2O_5$

Vessal et al. 1992



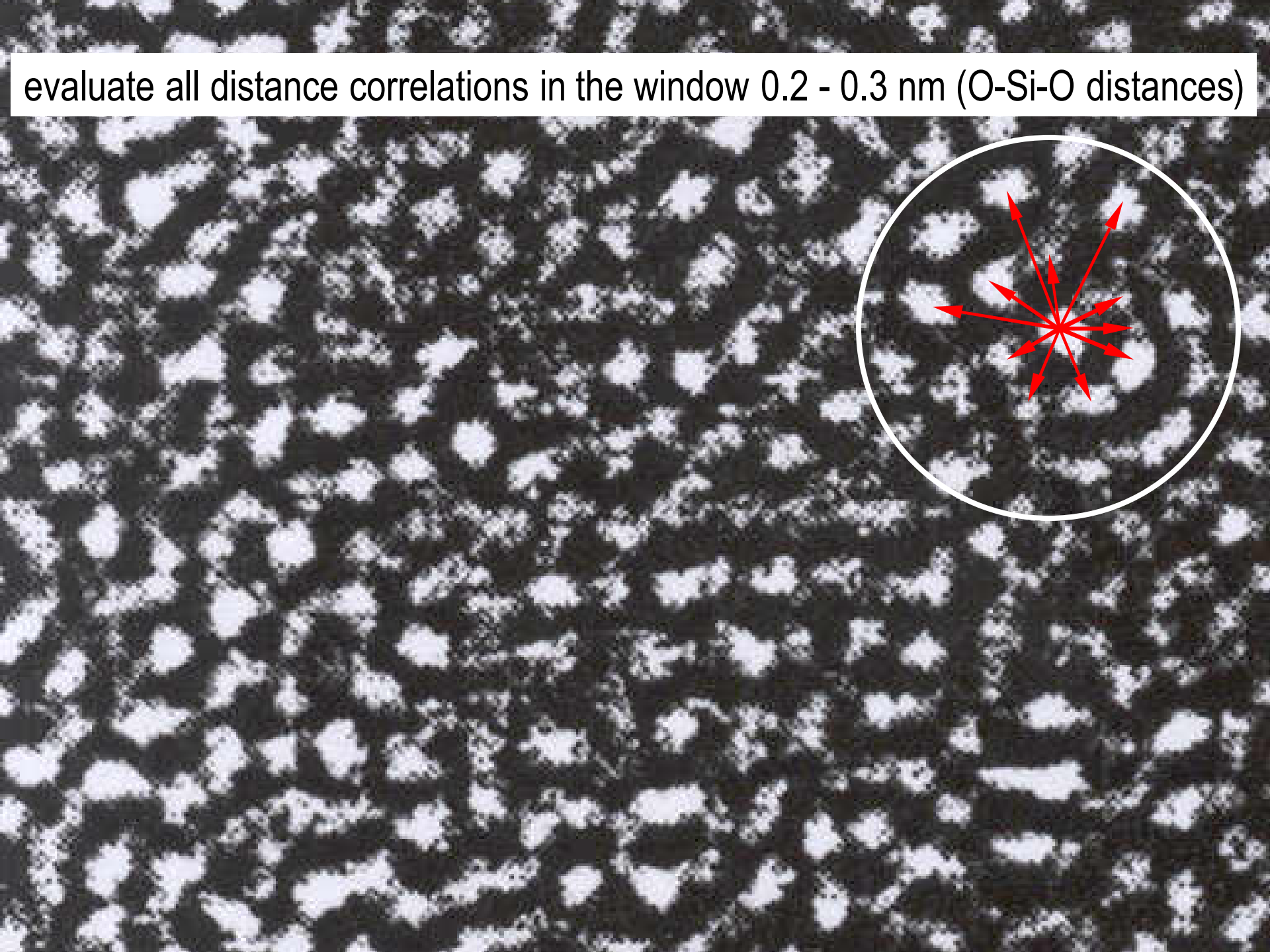
„Greaves channels“ of Na^+ transport in Na_2O-SiO_2 glasses

Greaves & Ngai 1995

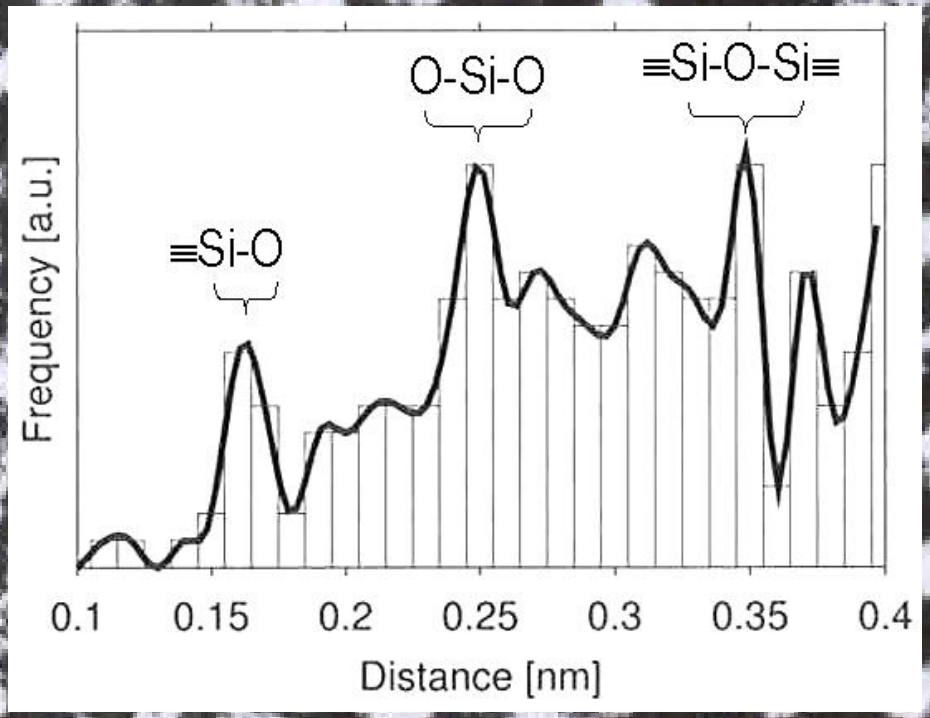


fractured silica surface,
investigated by UHV-AFM
Frischat, Poggemann, Heide 2003

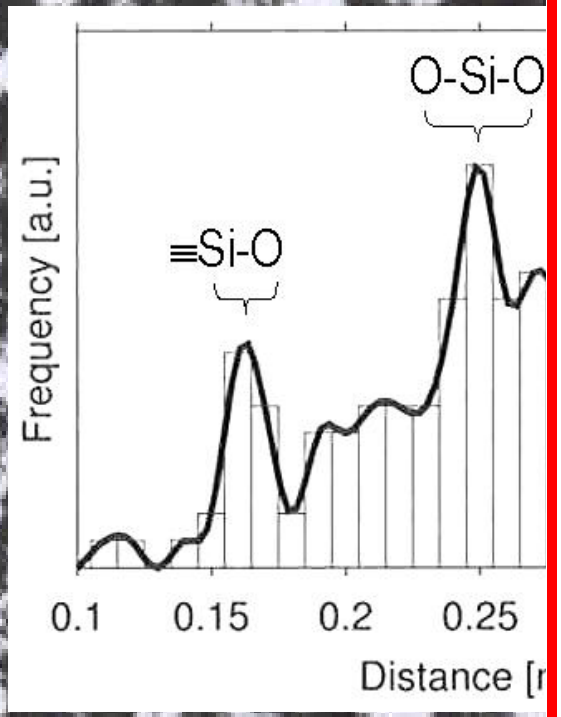
evaluate all distance correlations in the window 0.2 - 0.3 nm (O-Si-O distances)

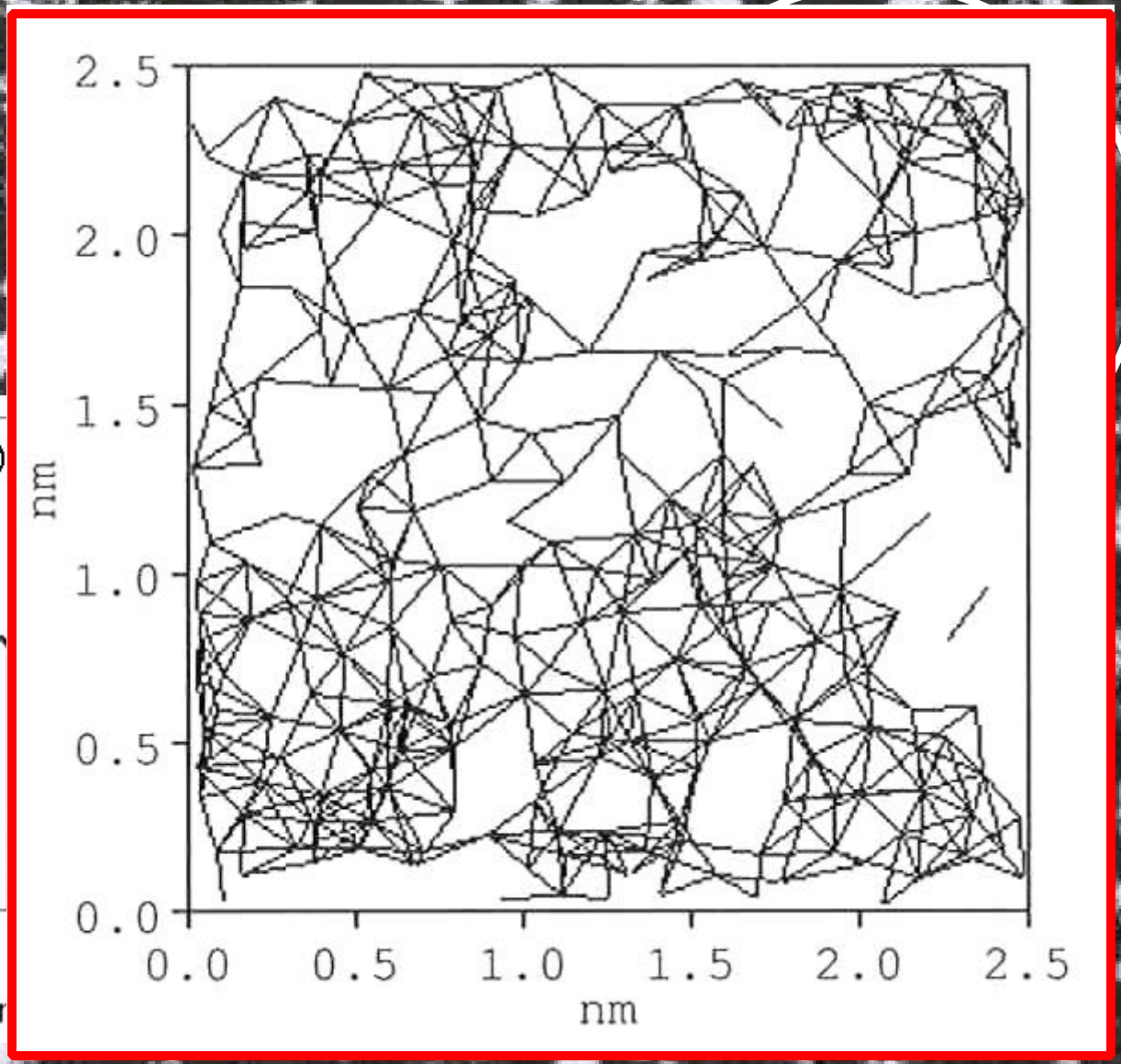


evaluate all distance correlations in the window 0.2 - 0.3 nm (O-Si-O distances)



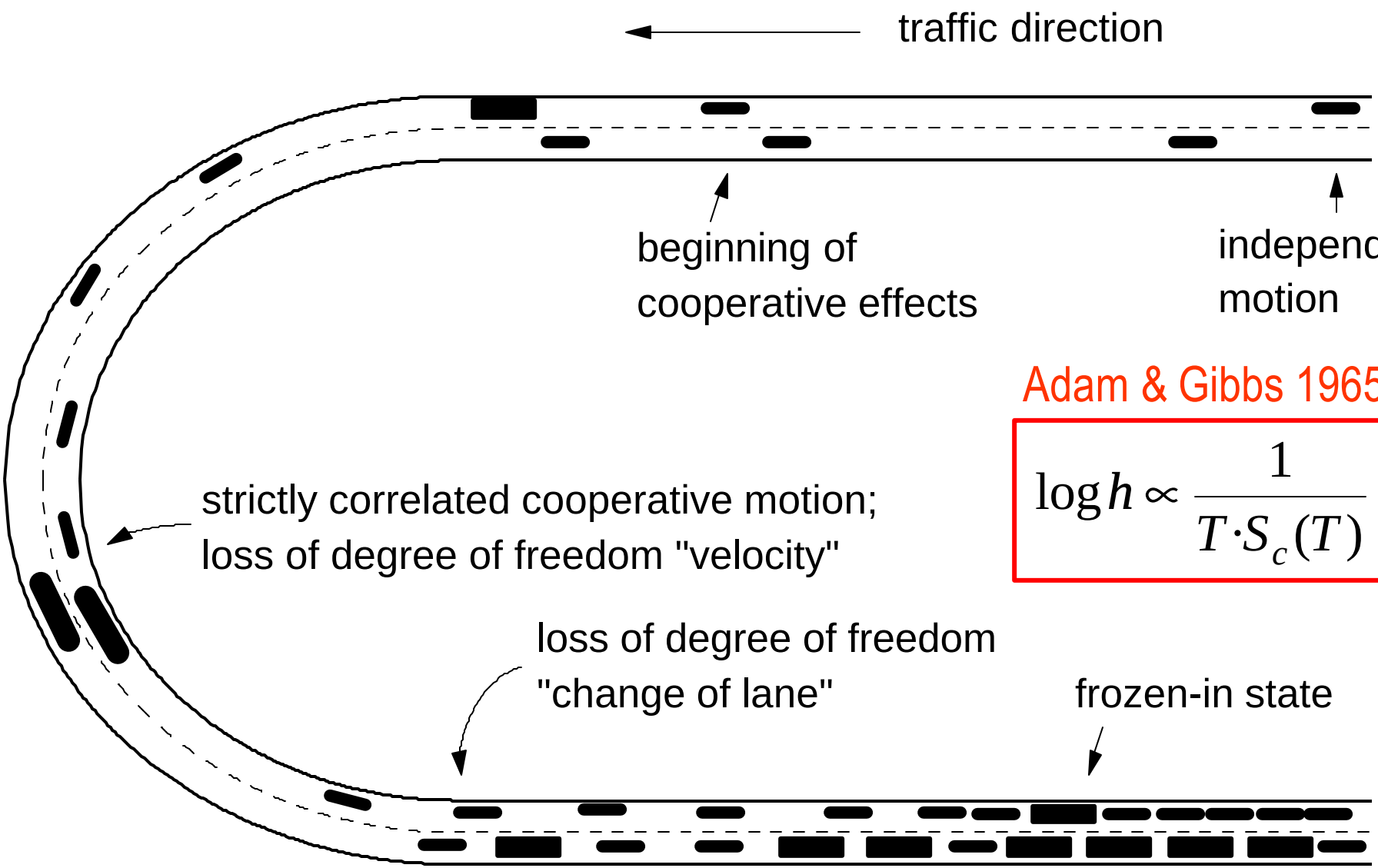
evaluate all distance correlations in the window 0.2 - 0.3 nm (O-Si-O distances)





viscosity

illustration of the concept of configurational entropy



Adam & Gibbs 1965

$$\log h \propto \frac{1}{T \cdot S_c(T)}$$

state „traffic jam“:

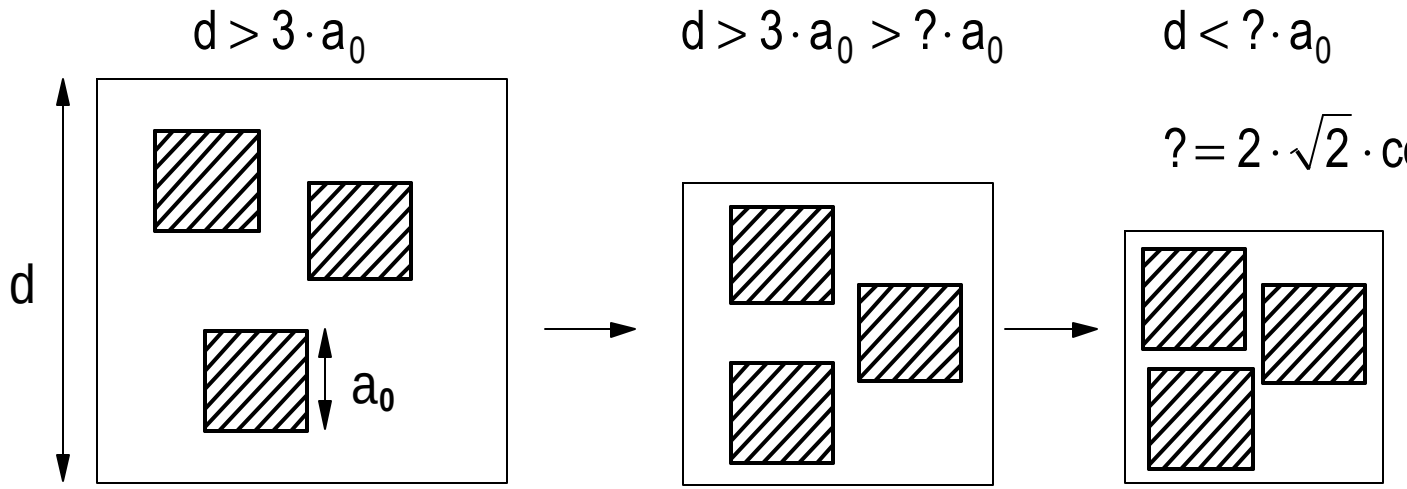
state „parking lot“:

- no flow,
- fixed mean position of all elements,
- solid state-like degrees of freedom

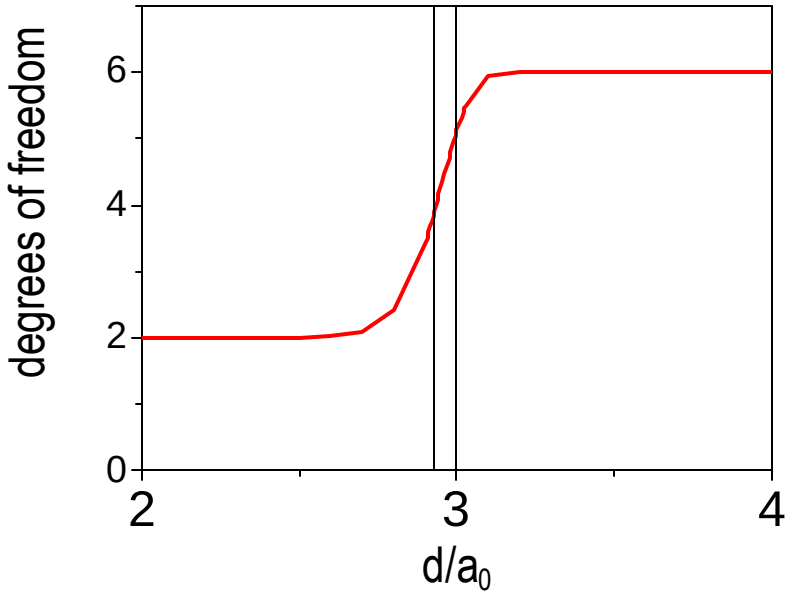
- no translational symmetry

- translational symmetry

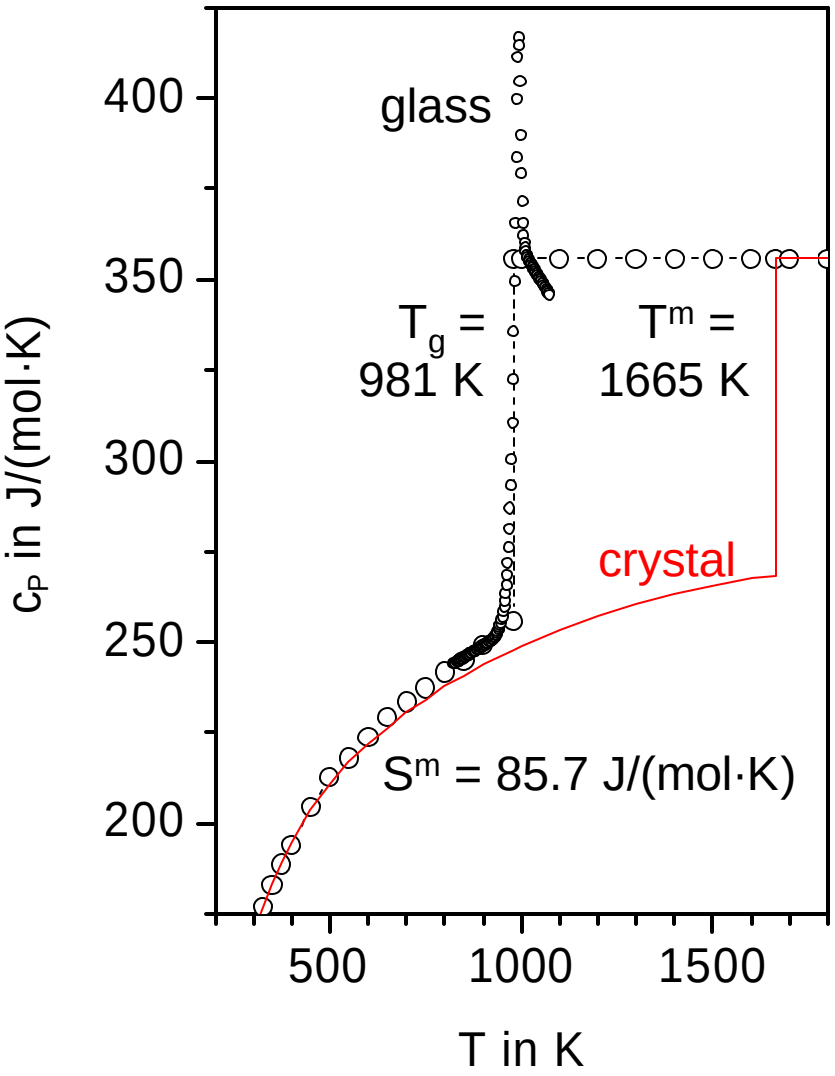
Tammann's explanation of sudden transitions due to a continuously tightened constraint



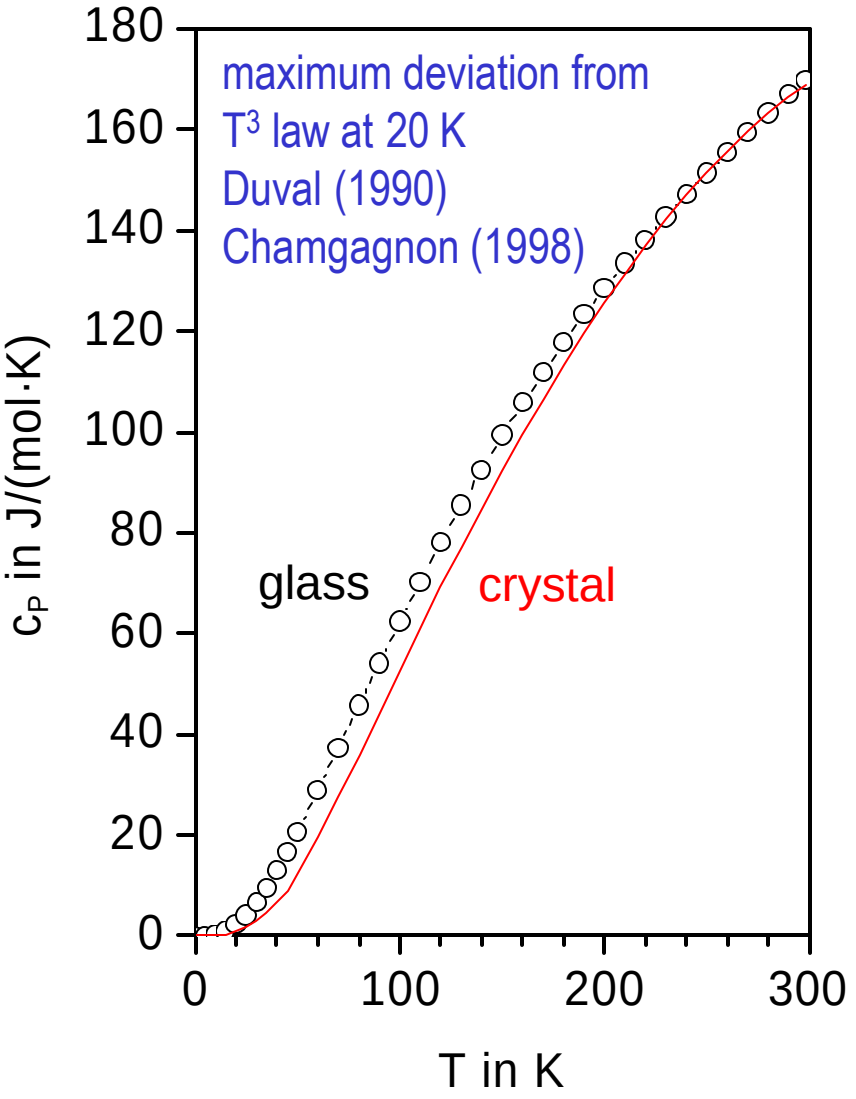
c_P = c_P(conf) + c_P(rot) + c_P(vib) c_P(rot) + c_P(vib) c_P(vib)



example: $CaO \cdot MgO \cdot 2SiO_2$ (diopside)

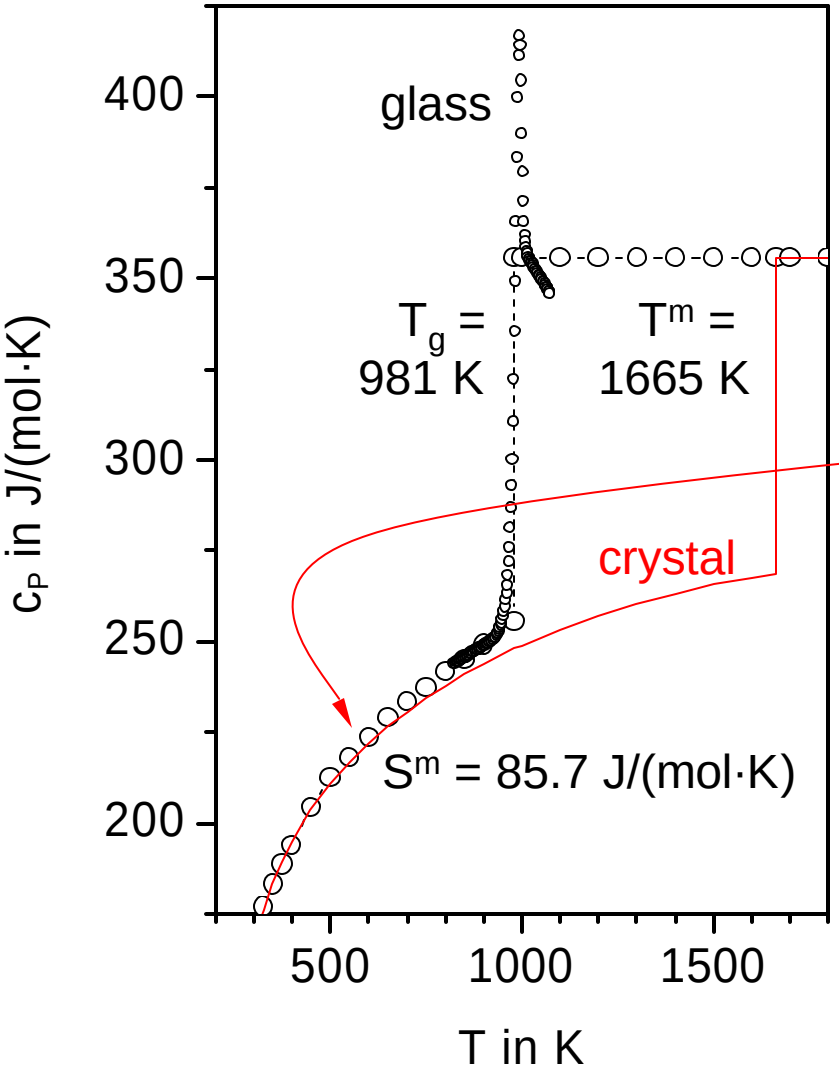


Robie et al. (1978); Martens et. al. (1987)
Richet & Bottinga (1995)



Richet, Robie, Heminway (1986)

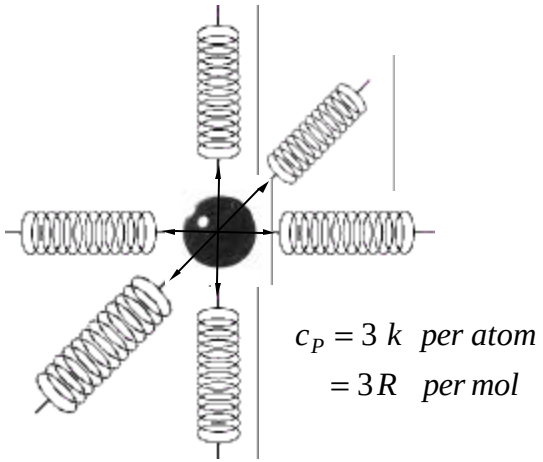
example: $CaO \cdot MgO \cdot 2SiO_2$ (diopside)



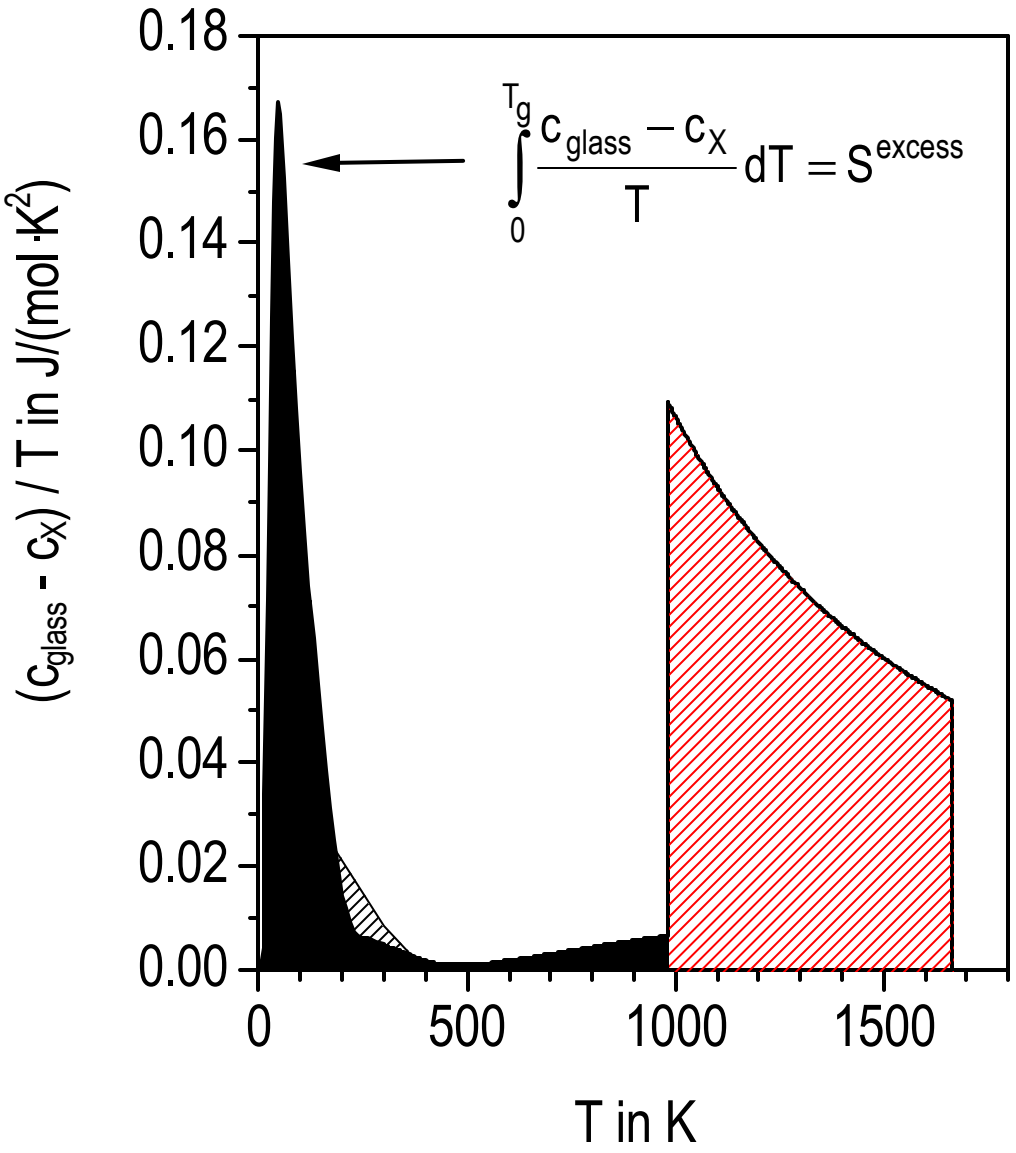
Robie et al. (1978); Martens et. al. (1987)
Richet & Bottinga (1995)

short range order S.R.O.

essentially the same as in the isochemical crystal, hence c_P(crystal) ≈ c_P(glass)

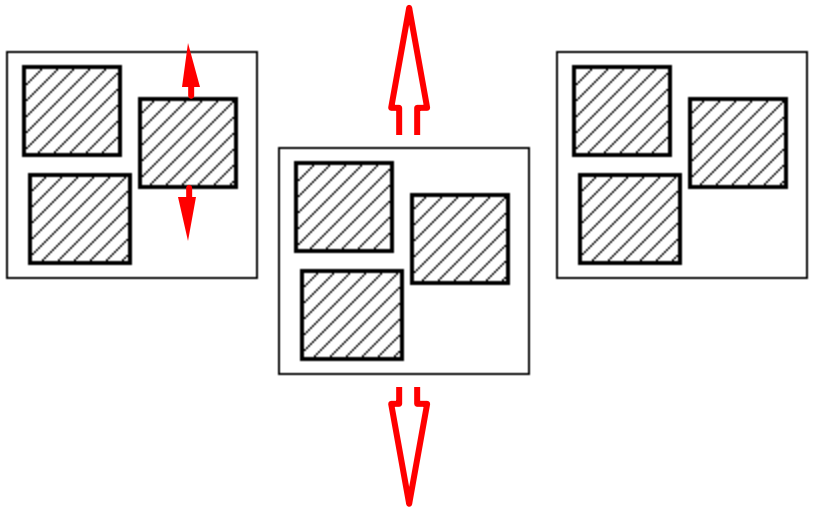


example: $CaO \cdot MgO \cdot 2SiO_2$ (diopside)



low-T vibrational excess entropy:

$$S^{excess} = \int_0^{T_g} \frac{c_{glass}(T) - c_X(T)}{T} dT$$



max. deviation from Debye's T^3 law at 20 K

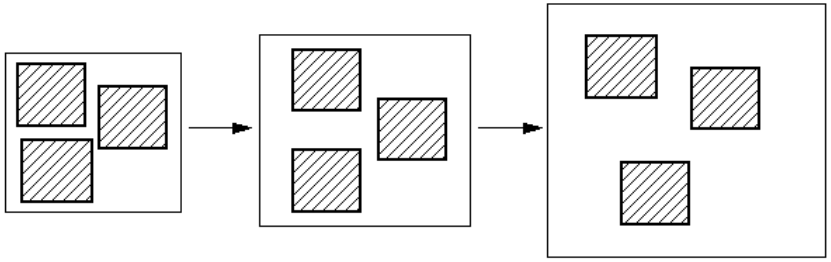
$$l_{excess} = 2 \cdot L = \frac{h \cdot u}{k \cdot T_{max}} \approx 5\,nm$$

medium range order M.R.O.

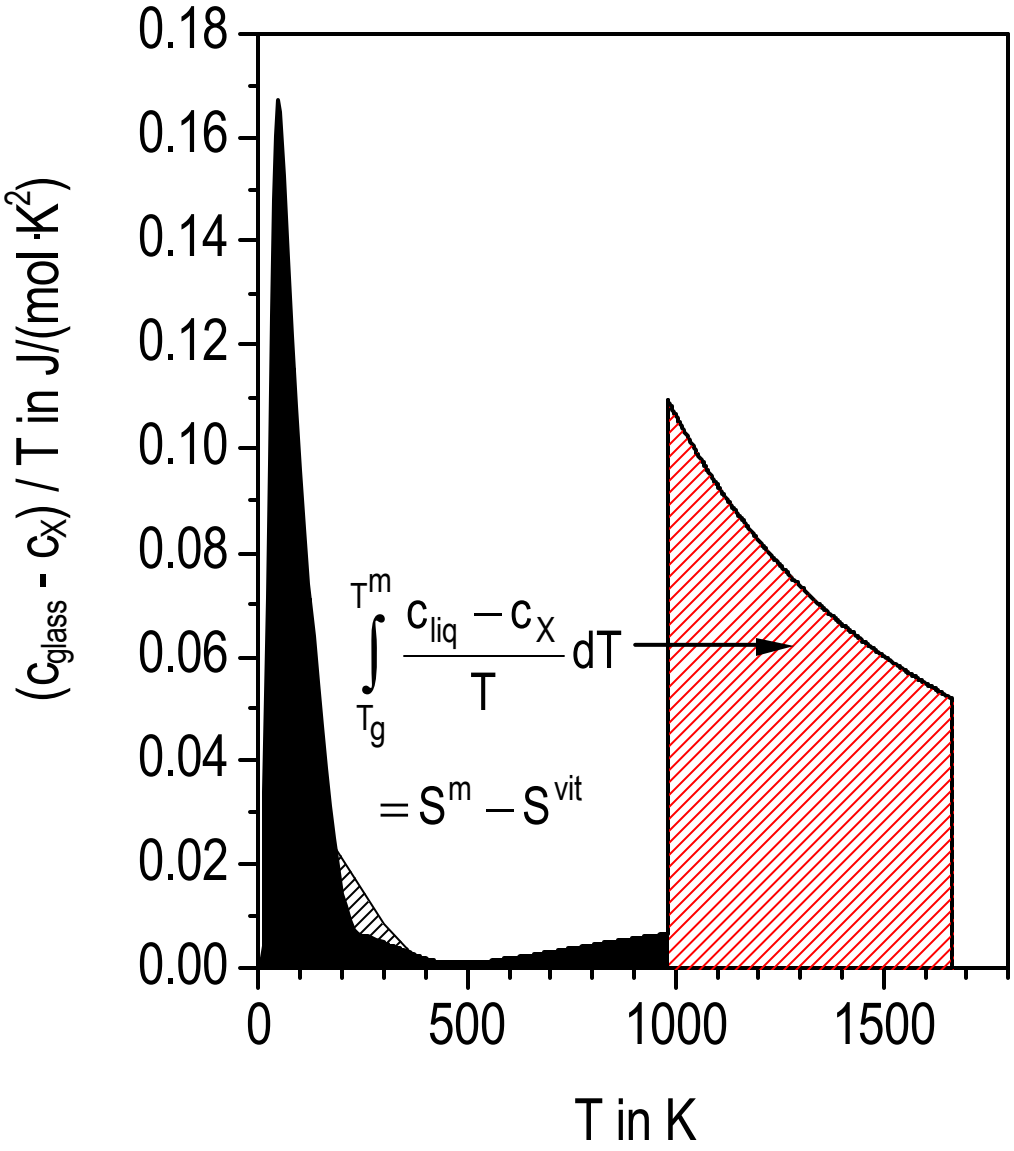
configurational entropy:

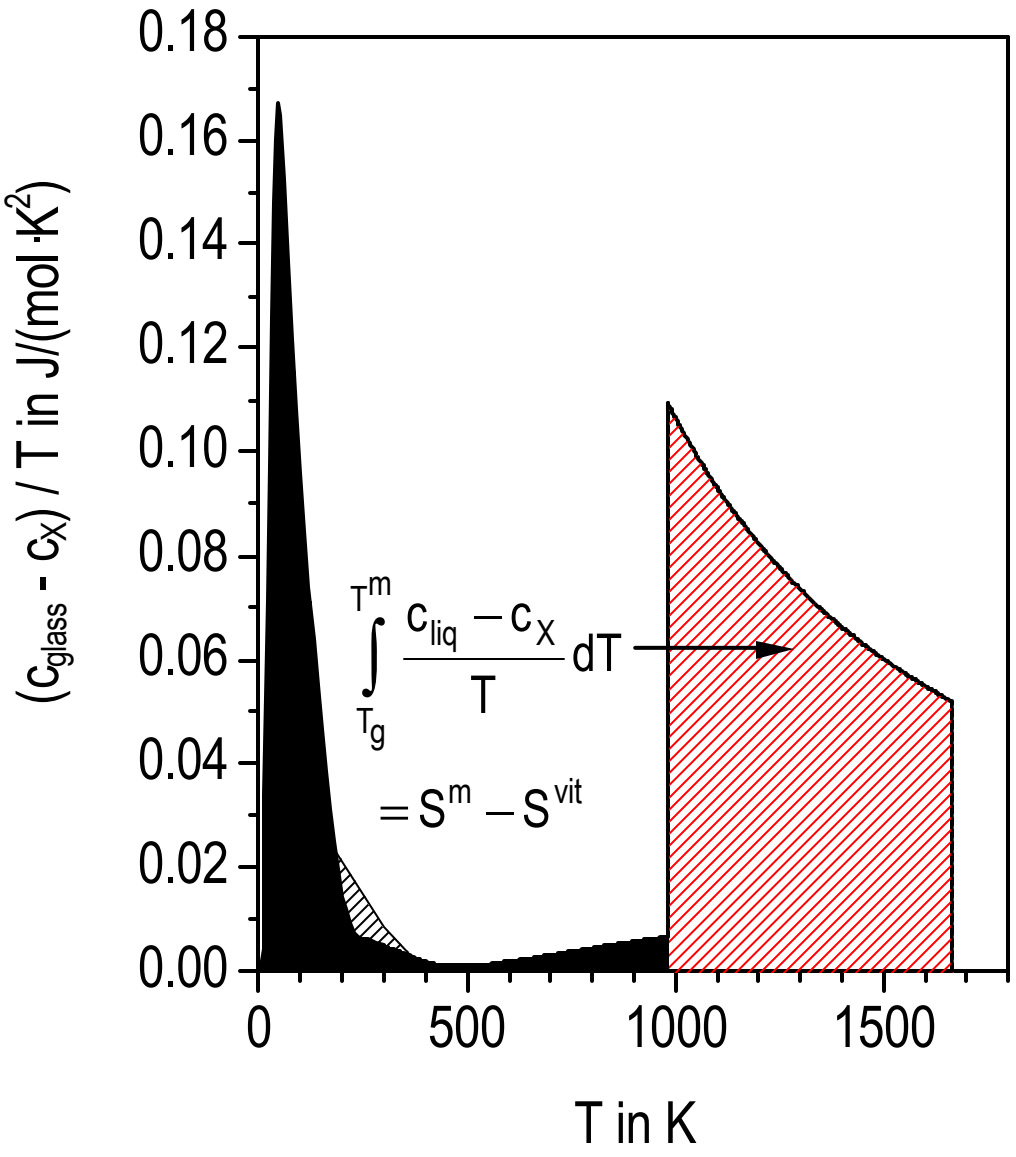
$$S_C(T) = S^{vit} + \int_{T_g}^{T} \frac{c_{liq}(T) - c_X(T)}{T}\, dT$$

$$\approx S^{vit} + \Delta c \cdot \ln \frac{T}{T_g}$$



with increasing temperature
increasingly more possibilities
to arrange the molecular units





configurational entropy:

$$S_C(T) = S^{vit} + \int_{T_g}^{T} \frac{c_{liq}(T) - c_X(T)}{T}\, dT$$

$$\approx S^{vit} + \Delta c \cdot \ln \frac{T}{T_g}$$

see, e.g., the Adam-Gibbs equation:

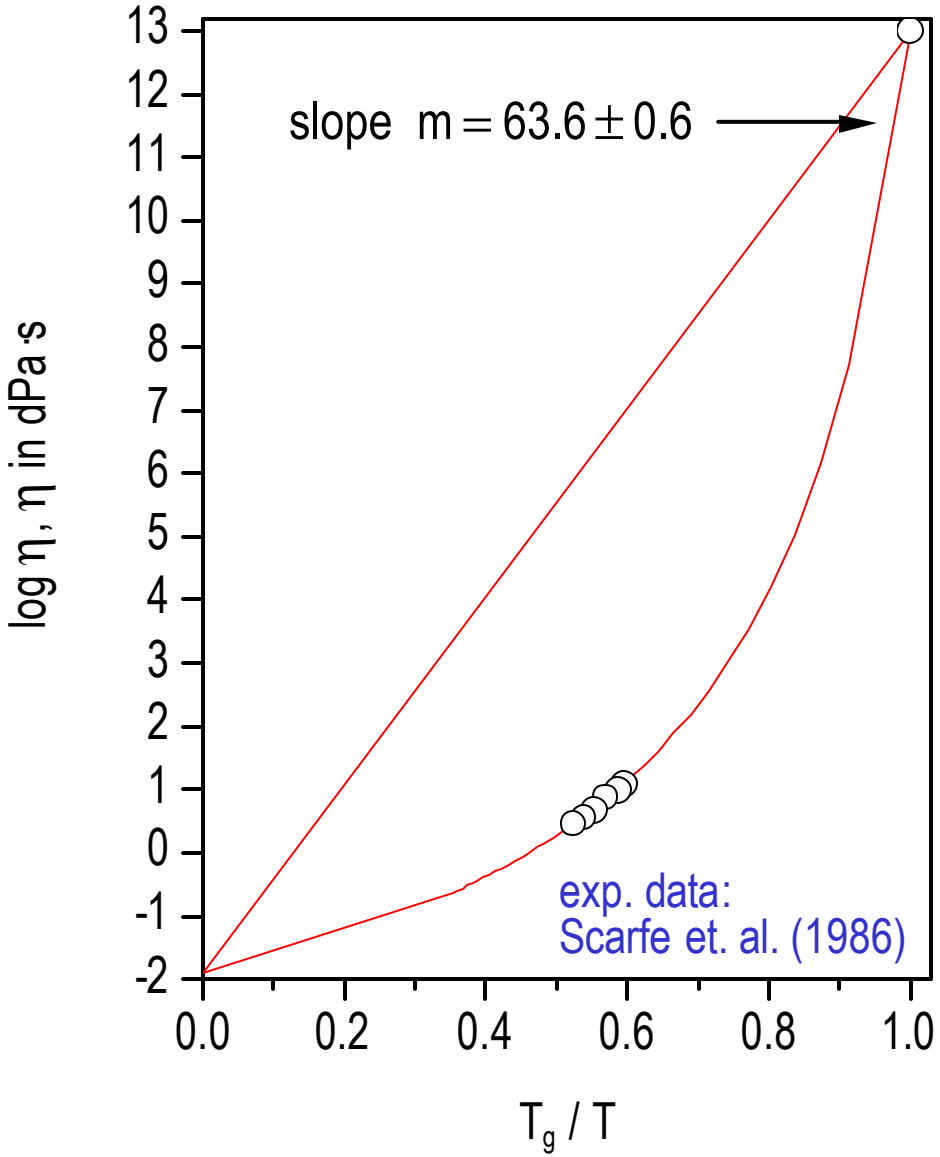
$$L = L_\infty + \frac{C}{T \cdot S_C(T)}; \quad L \equiv \log h$$

$$= L_\infty + \frac{\left(L_g - L_\infty\right) \cdot \frac{T_g}{T}}{1 + \frac{\Delta c}{S^{vit}} \cdot \ln \frac{T}{T_g}}$$

viscosity slope for $T \to T_g$:

$$\left.\frac{\partial L}{\partial (T_g / T)}\right|_{T=T_g} = \left(L_g - L_\infty\right) \cdot \left(1 + \frac{\Delta c}{S^{vit}}\right)$$

diopside $CaMg[Si_2O_6]$



$$L = \log h = A + \frac{B}{T - T_0}$$

A = -1.899 T_g = 708 °C

B = 2493.4

T_0 = 540.6

$\pm\delta \log\eta$ = 0.022

$$\left.\frac{\partial \log h}{\partial T_g / T}\right|_{T=T_g} = \frac{T_g \cdot B}{(T - T_0)^2} = m$$

$\Rightarrow$ m = 63.3 ± 0.6

$$m = \underbrace{(L_g - L_0)}_{14.9} \cdot \left(1 + \frac{\Delta c_{G,L}}{S_G(0)}\right)$$

$c_{G,L}(T_g)$ = 254.6 J/(mol·K)

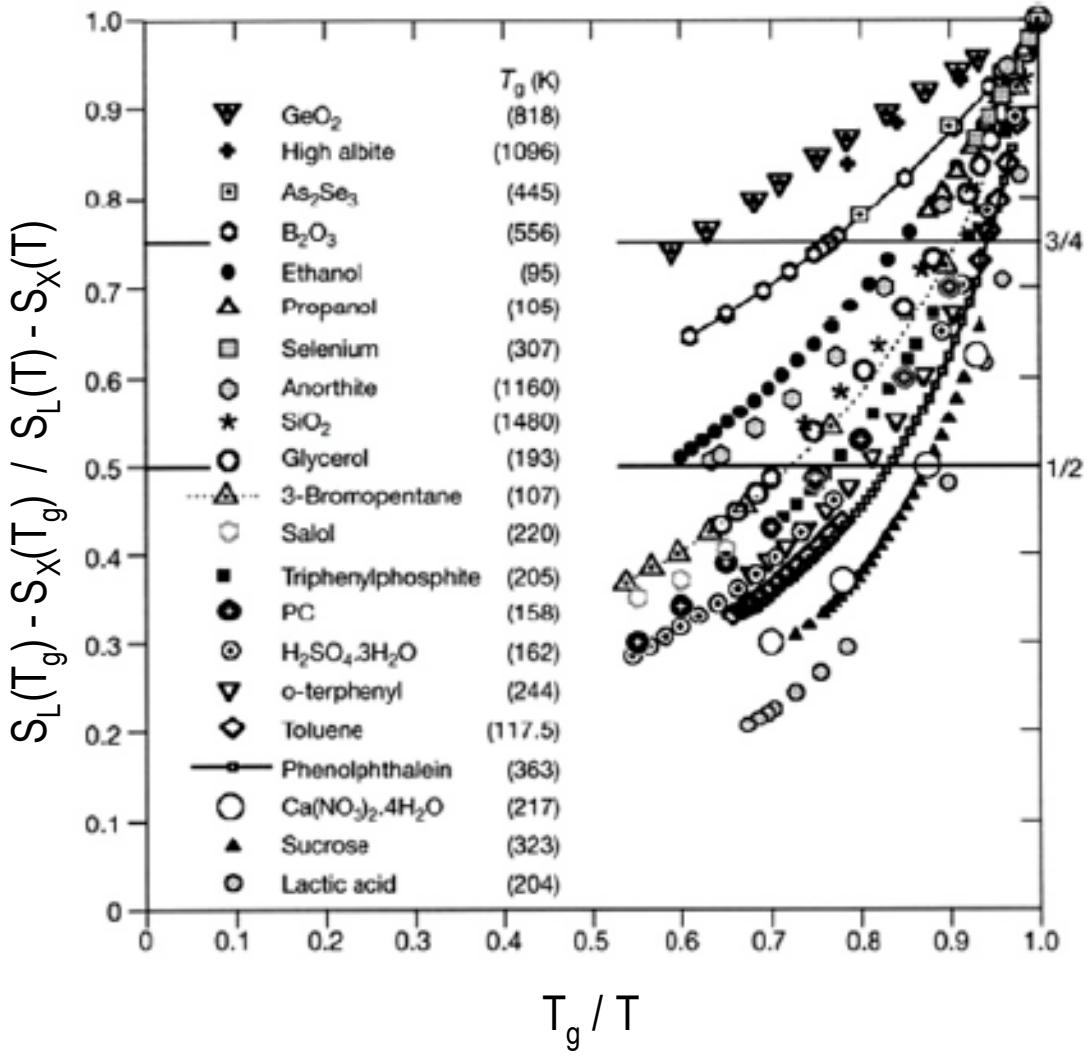
$c_X(T_g)$ = 246.5 J/(mol·K)

3·N·R = 249.0 J/(mol·K)

$\Delta c_{G,L}$ = 80.0 J/(mol·K)

$S_G(0)$ = 24.8 ± 3.0 J/(mol·K)

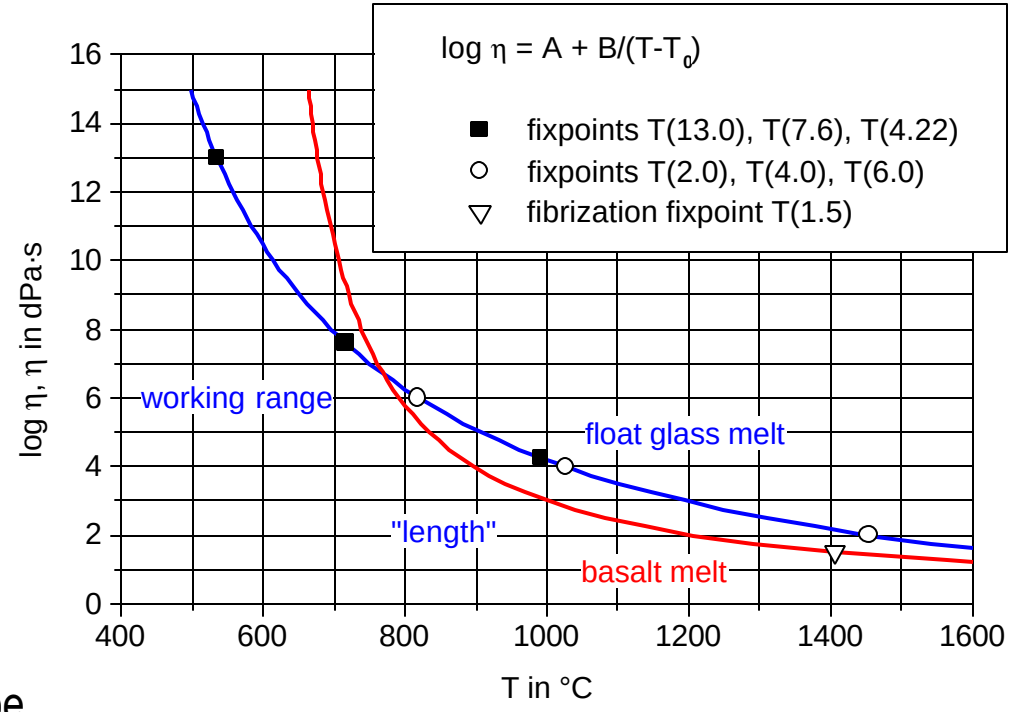
$\Rightarrow$ m = 63.7 ± 5.9

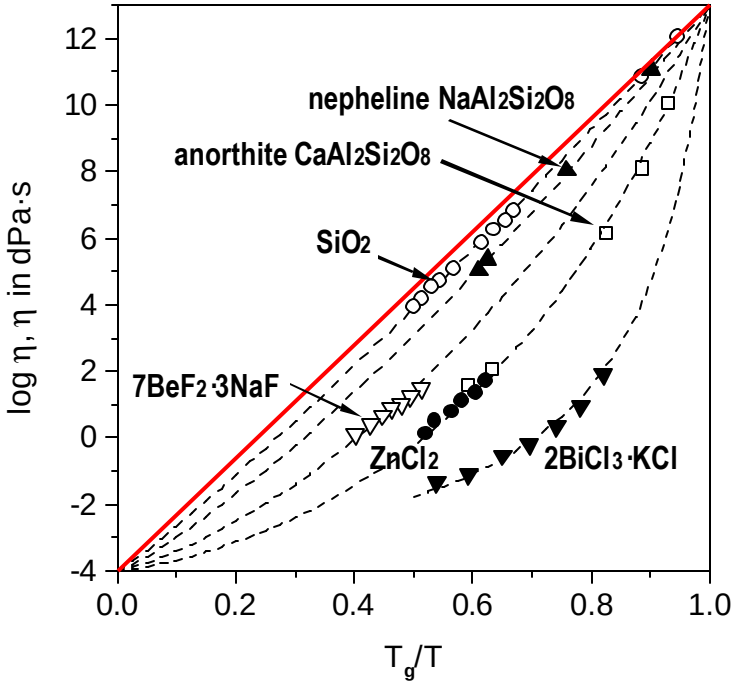


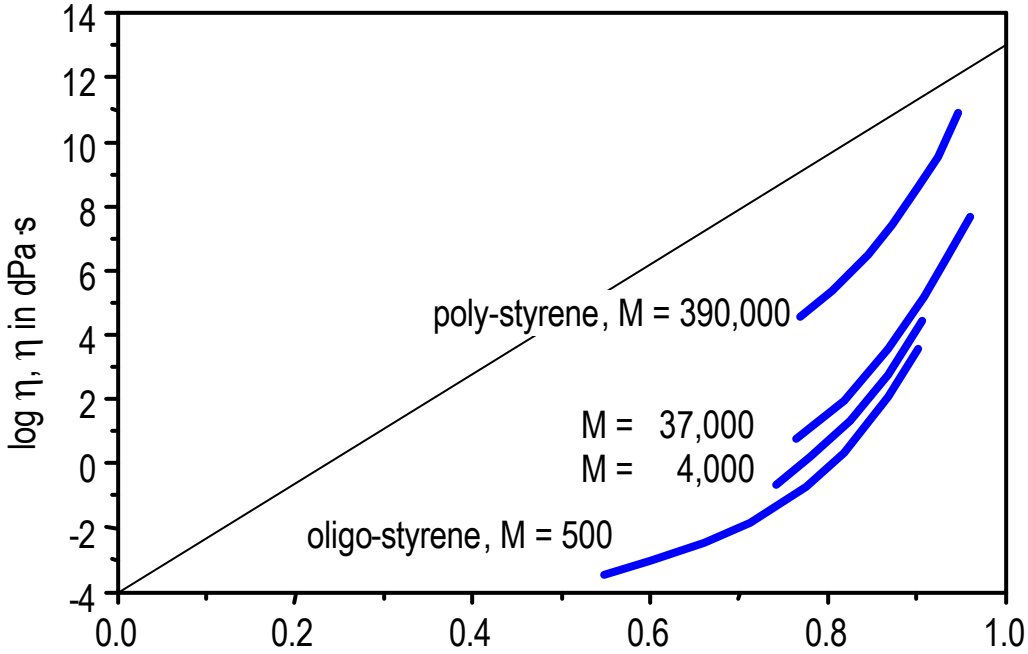
C.A. Angell (2008)

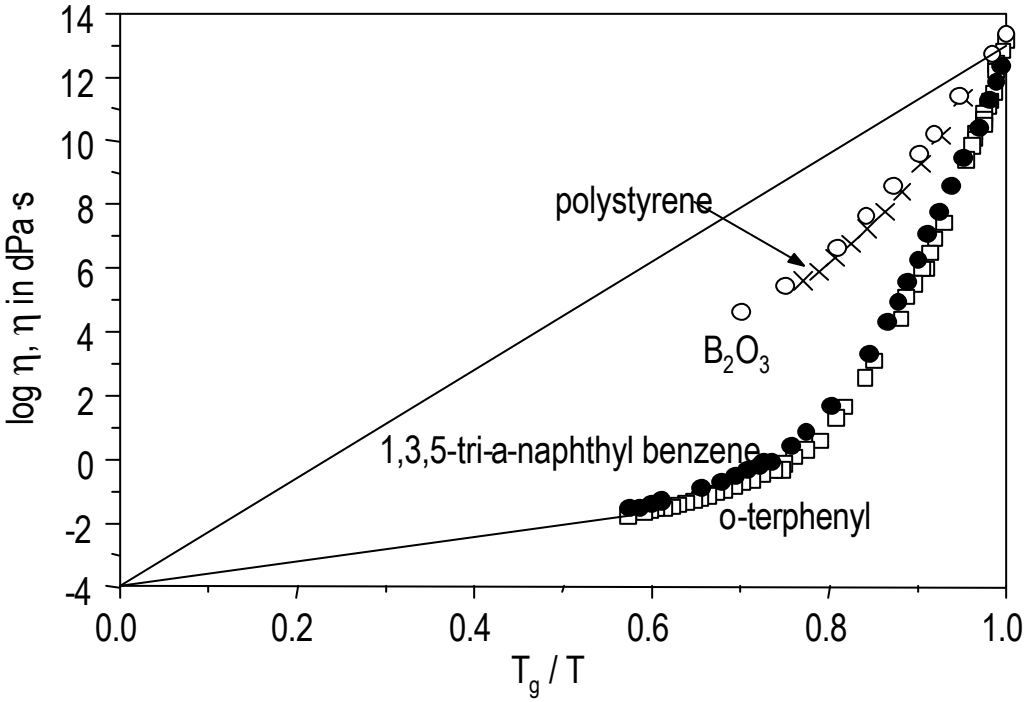
What is „fragility“?

- Technologist call it the „length“ of a glass; it determines the working range.
- Fragility is a measure of deviation from an exponential T dependence of relaxation times and transport properties (deviation from Arrhenius behavior).
- Fragility may be quantified, e.g., by the slope for $T_g / T \rightarrow 1$ in the so-called Angell plot.
- The non-exponential T dependence is commonly represented by the KWW eq. $\tau \propto \exp B \cdot (T_g/T)^n$, by the VFT eq. $\tau \propto \exp B/(T - T_0)$, etc.
- While the high-T branch reflects a universal feature of liquids, the fragility is likely to reflect the thermo-dynamics of the liquids.






log η, η in dPa·s
poly-styrene, M = 390,000
M = 37,000
M = 4,000
oligo-styrene, M = 500


log η, η in dPa·s
polystyrene
B2O3
1,3,5-tri-a-naphthyl benzene
o-terphenyl
Tg / T

„It appears that at the same point in T at which the non-Arrhenius regime is entered from above glass-forming systems develop heterogeneities in their dynamics.

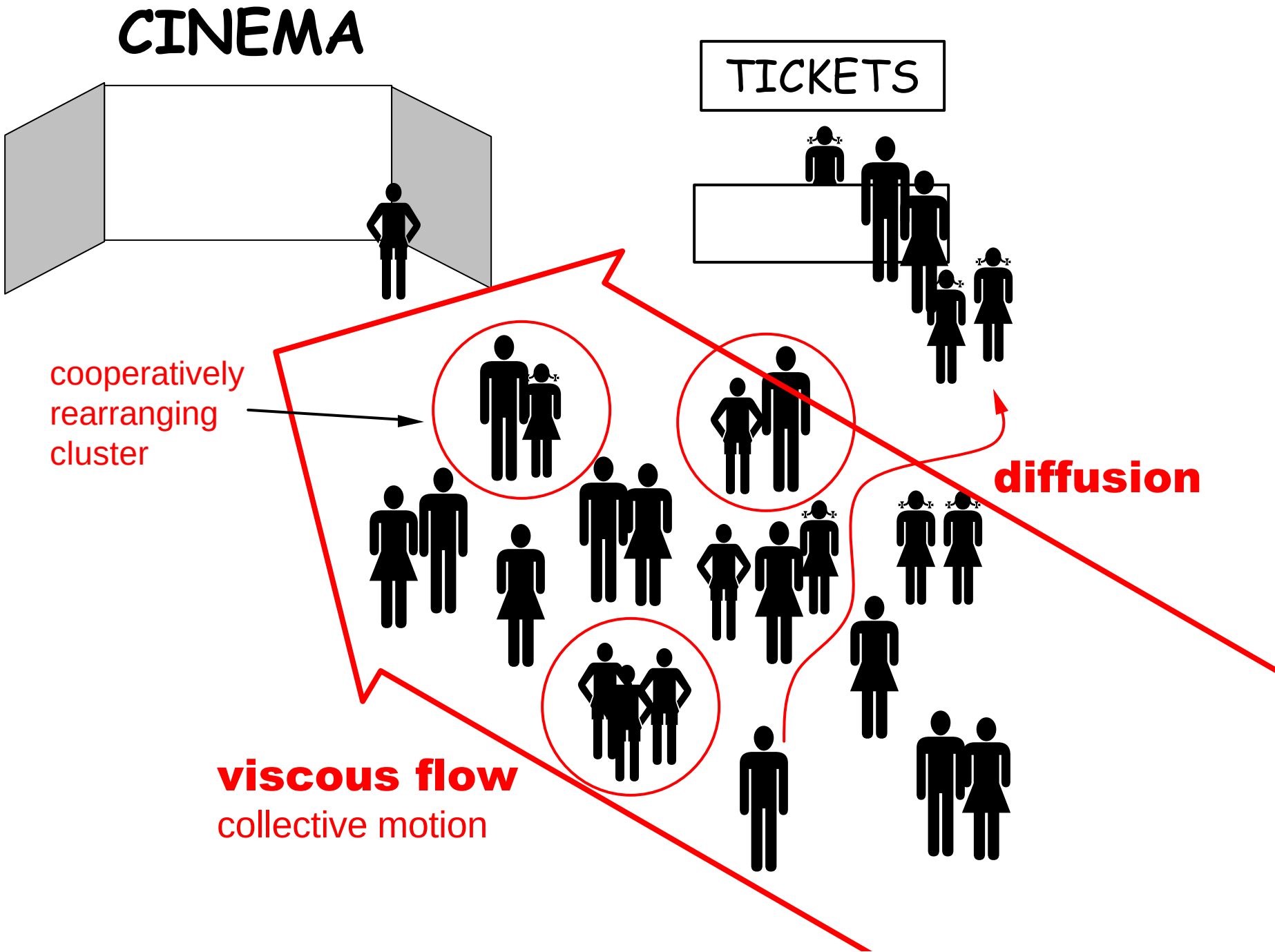
The heterogeneities are such that, for a limited period of time, one set of particles will lock together while an adjecent set will become loose will support string-like motions of the patticles, perhaps along the boundaries between nano-regions.

Within each nano-region, relaxation appears to be exponential, and it is therefore that the distribution of nano-reagions (which determines the deviation from exponentiality) is seen in the macroscopic relaxation function.

The string-like particles might lie on the Eigenvectors of the low-frequency (or Boson peak) modes of the system, by means of which relaxation occurs.“

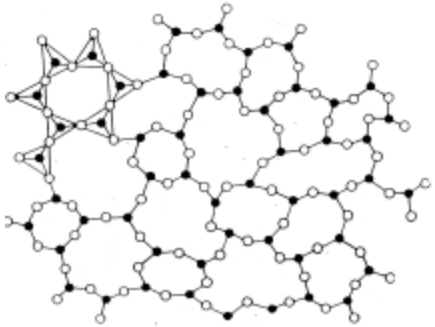
non-exponentiality
- **development of heterogeneities**
- **nano-regimes**
- **Boson peak, low c_P excess of the glass**

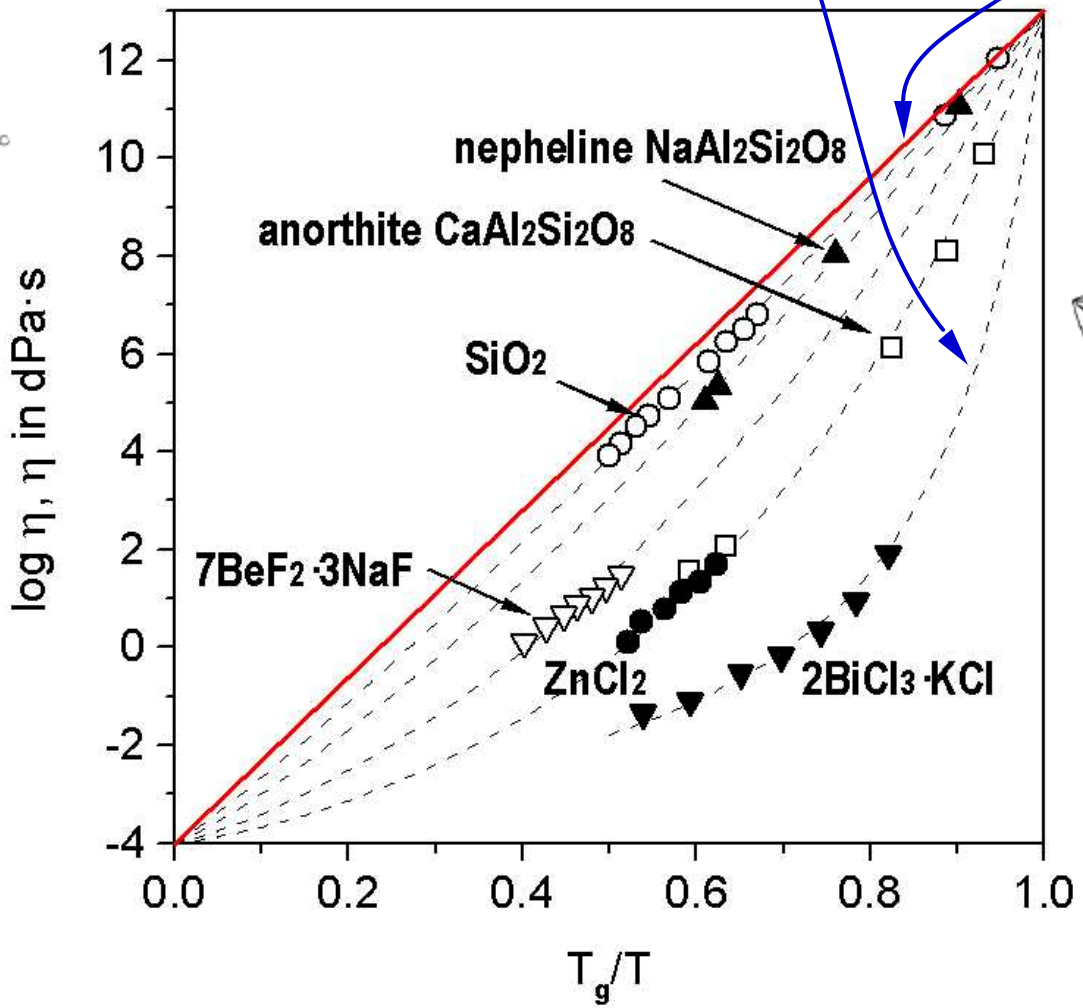
C.A. Angell (2008), using findings by Richert (2002), Kob et al. (1998), Weeks et al. (2000), Brito et al. (2007)

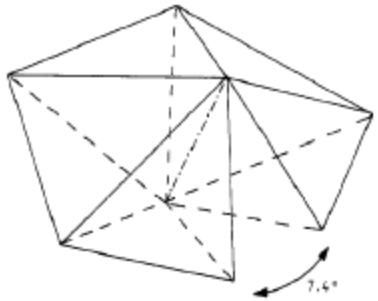

CINEMA
TICKETS
cooperatively
rearranging
cluster
diffusion
viscous flow
collective motion

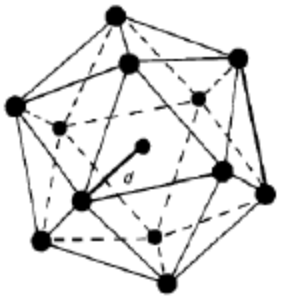
absence of translational symmetry and occurrence of M.R.O. may by caused by

- frustration (entaglement) of polymeric structures or
- by frustration of spherical packing





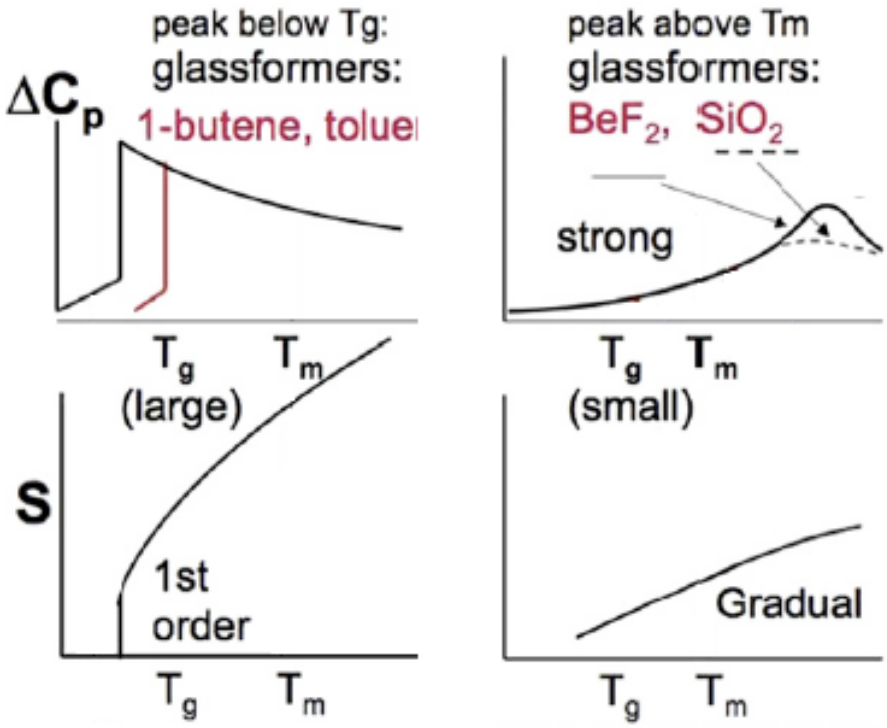


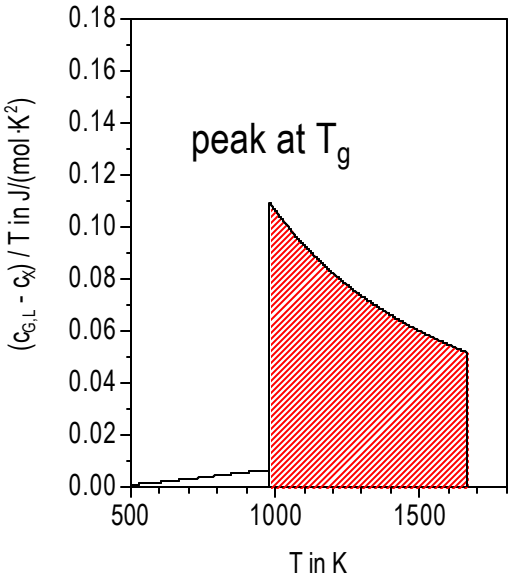


extremely fragile

very strong

our example: diopside





large Δc_P
c_P derceases above T_g

tiny Δc_P
c_P steadily inrceases above T_g
and even beyond T^m

C.A. Angell (2008)

SUMMARY OF VISCOSITY MODELS:

Arrhenius
atomic mobility

$$L = L_\infty + b/T$$

Vogel-Fulcher-Tamman (VFT)
free volume

$$L = L_\infty + \frac{B}{T - T_0}$$

Williams-Landel-Ferry (WLF)
free volume

$$L = L_g + \frac{C_1}{\ln 10} \cdot \frac{T - T_g}{C_2 + T - T_g}$$

Adam-Gibbs
configurational entropy

$$L = L_\infty + \left(L_g - L_\infty\right) \cdot \frac{T_g / T}{1 - a_0 \cdot \ln(T_g / T)}$$

Avramov
Kohlrausch relaxation

$$L = L_\infty + \left(\frac{T_g}{T}\right)^a$$

Mauro et. al
configurational entropy

$$L = L_\infty + \left(L_g - L_\infty\right) \cdot \frac{T_g}{T} \cdot \exp\left[\left(\frac{m}{L_g - L_\infty} - 1\right) \cdot \left(\frac{T_g}{T} - 1\right)\right]$$

SUMMARY OF LINEARIZED EQUATIONS:

Adam-Gibbs $$L = b_0 + b_1 \cdot \frac{x}{1 - a \cdot \ln x}$$

modified $$L = b_0 + b_1 \cdot \frac{x}{1 - a \cdot x \cdot \ln x}$$

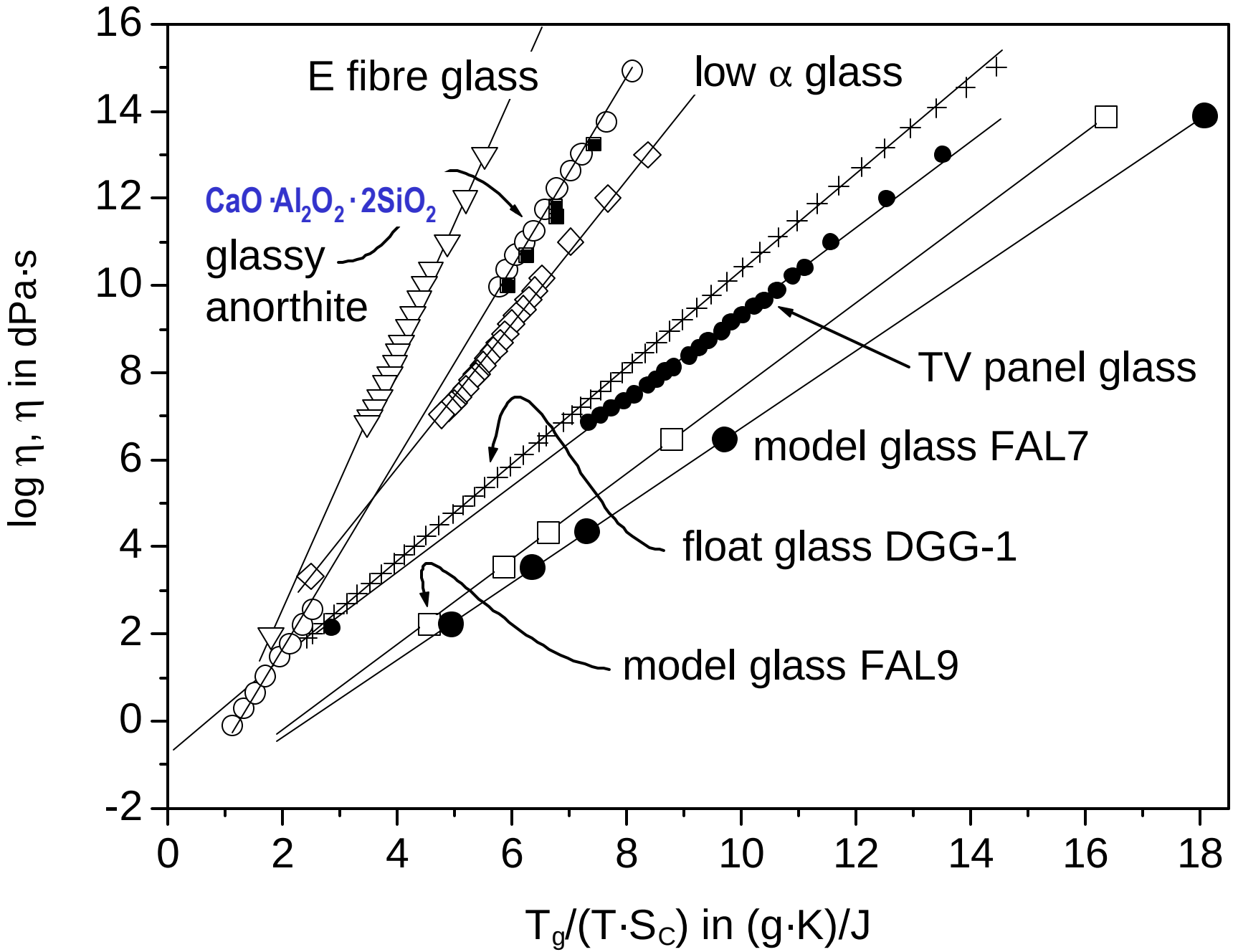
VFT; WLF $$L = b_0 + b_1 \cdot \frac{(1-a) \cdot x}{1 - a \cdot x}$$

Avramov $$L = b_0 + b_1 \cdot x^a$$

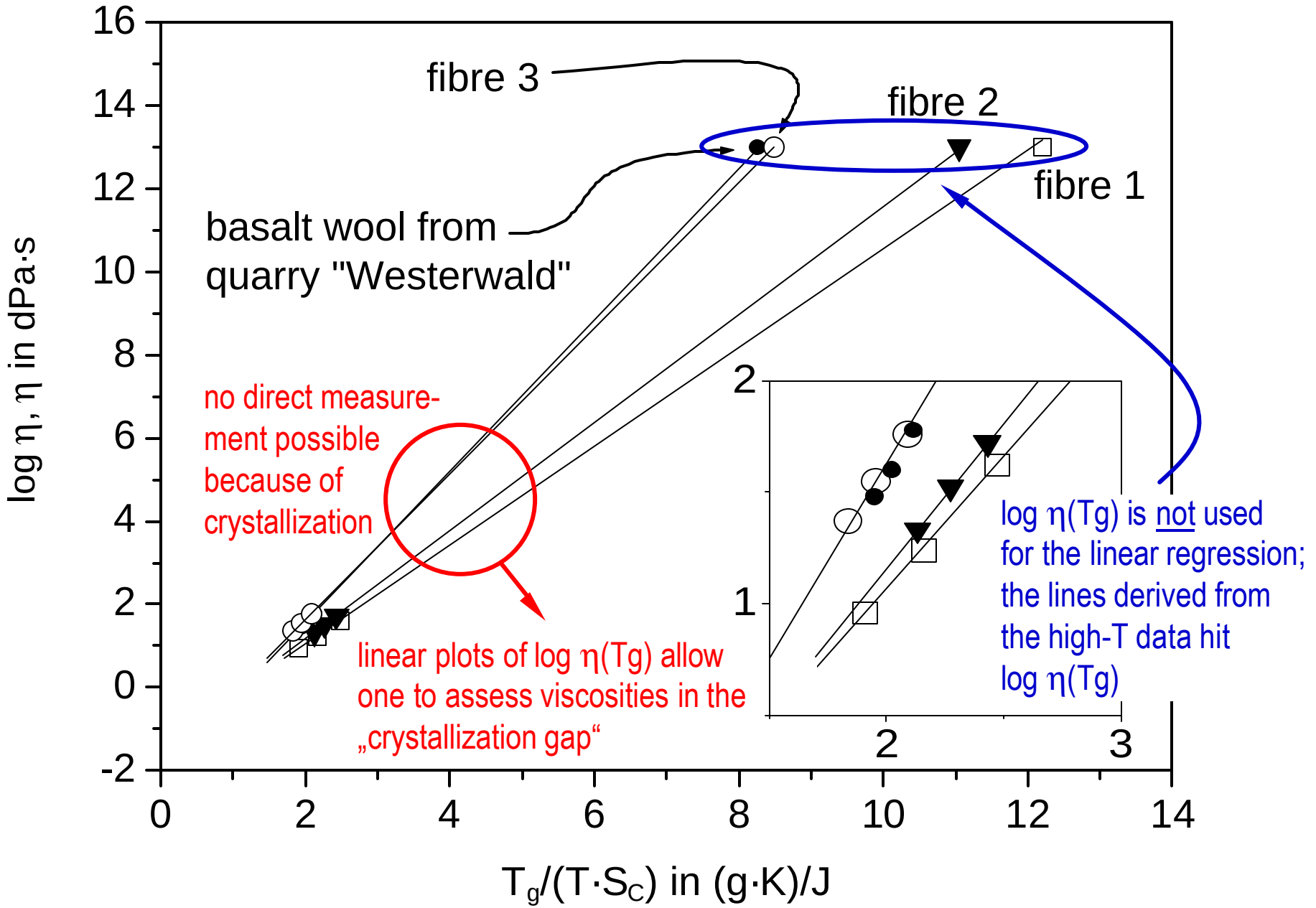
Mauro $$L = b_0 + b_1 \cdot x \cdot \exp\left(a \cdot (x-1)\right)$$

CONCLUSION:

- All established viscosity-temperature functions L = log η(T) are 3-parameter plots of x = T_g / T.
- All functions L contain a kind of „structural parameter“ ***a*** allowing to generate a linear plot.
- The high-T limits $L_\infty = \beta_0$ for x = T_g / T $\rightarrow$ 0 differ significantly.


E fibre glass
low α glass
CaO·Al2O2·2SiO2
glassy
anorthite
TV panel glass
model glass FAL7
float glass DGG-1
model glass FAL9
log η, η in dPa·s
Tg/(T·SC) in (g·K)/J
16
14
12
10
8
6
4
2
0
-2
0
2
4
6
8
10
12
14
16
18

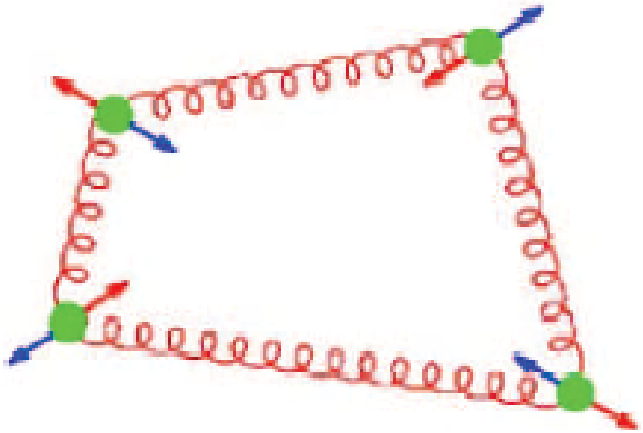
Adam-Gibbs plot, basalt melts



networks again

different states of rigidity (2D example)

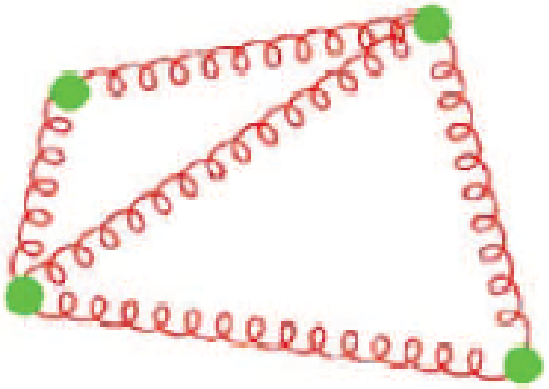
under-constrained:
one floppy motion in addition to 3 rigid body motions



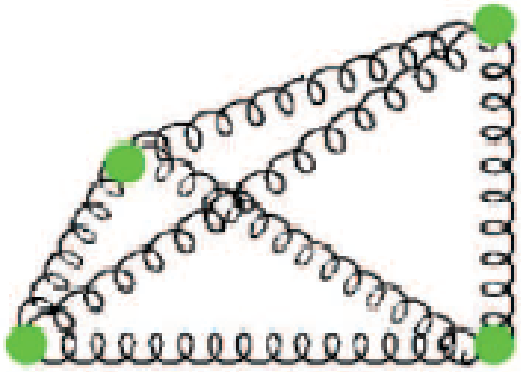
rigid and „floppy“

(a floppy motion is a motion that costs no energy)

perfectly constrained:
all bonds maintain their natural length; no floppy modes



isostatically rigid



rigid and stressed

over-constrained:
all bonds are deformed; one bond is redundant

J.C. Phillips et al
P. Boolchand et al
M.F. Thorpe et al.
R. Keding et al.

Consider a system of N atoms, classified into groups of N_r atoms with coordination number r:

$$N = \sum_r N_r$$

The mean coordination number r_m is

$$r_m = \sum_r r \cdot N_r \Big/ \sum_r N_r$$

An unconstrained atom in 3D space has 3 positional degrees of freedom; an unconstrained system of N atoms thus has

$$N_F = 3 \cdot N$$

positional degrees of freedom. Let N_C be the number of positional constraints. Then

$$N_0 = N_F - N_C$$

denotes the number of zero frequency („floppy“) modes allowing particles to change position at zero energy.

The positional constraints of distance L_{ij} between particles i and j, and of angles θ_{ijk} between bonds i-j and j-k, stem from the deviations ΔL_{ij} and $\Delta\theta_{ijk}$ from the equilibrium positions in the interparticle potential V:

$$V = \frac{a}{2} \cdot \sum_{ij} \Delta L_{ij}^2 + \frac{b}{2} \cdot \sum_{ijk} \Delta q_{ij}^2$$

It is true, V is a simple harmonic potential ($V \propto \Delta L_{ij}^2, \propto \Delta\theta_{ijk}^2$) with simple force constants α and β. But as a constraint fixes a position against very small virtual displacements δL_{ij} or $\delta\theta_{ijk}$, the actual shape of V is irrelevant.

We have two types of constraints, namely related to inter-particle distance variations ΔL, and to bond-to-bond angle variations $\Delta\theta$. In a system with N atoms, the corresponding numbers of constraints are $N_{C,\Delta L}$ and $N_{C,\Delta\theta}$, respectively:

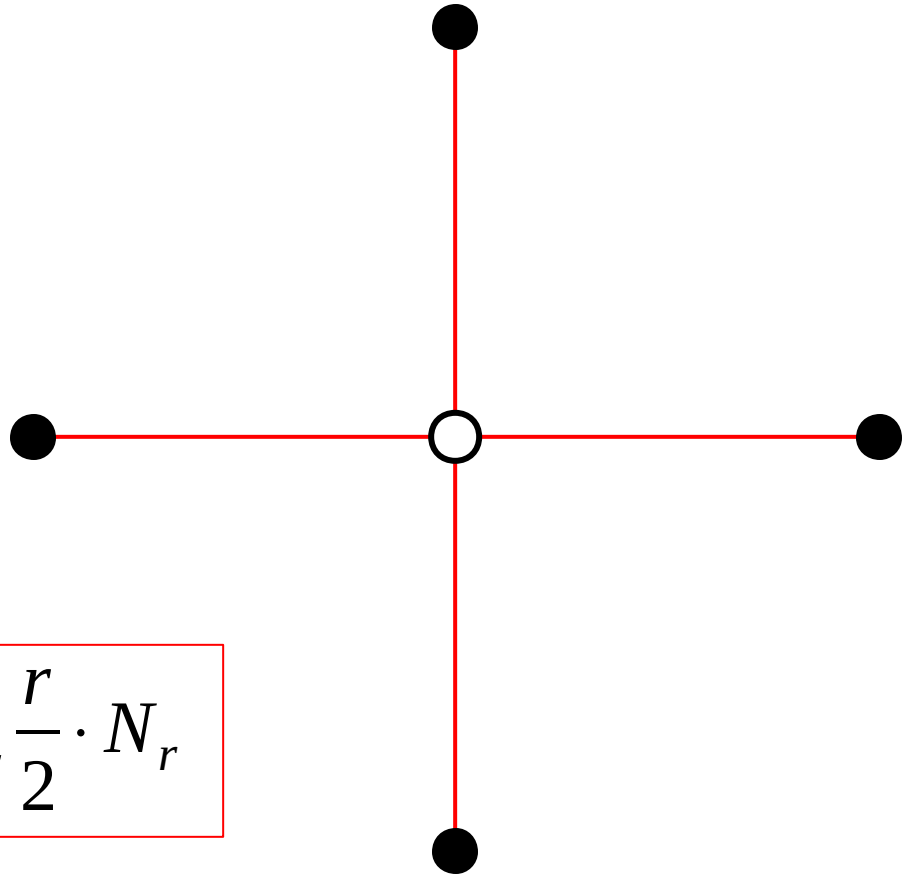
$$N_C = N_{C,\Delta L} + N_{C,\Delta q}$$

constraints related to distance variations DL:

one constraint associated with one bond
=
1/2 constraints per bond for each end member;

for an end member with coordination number r,

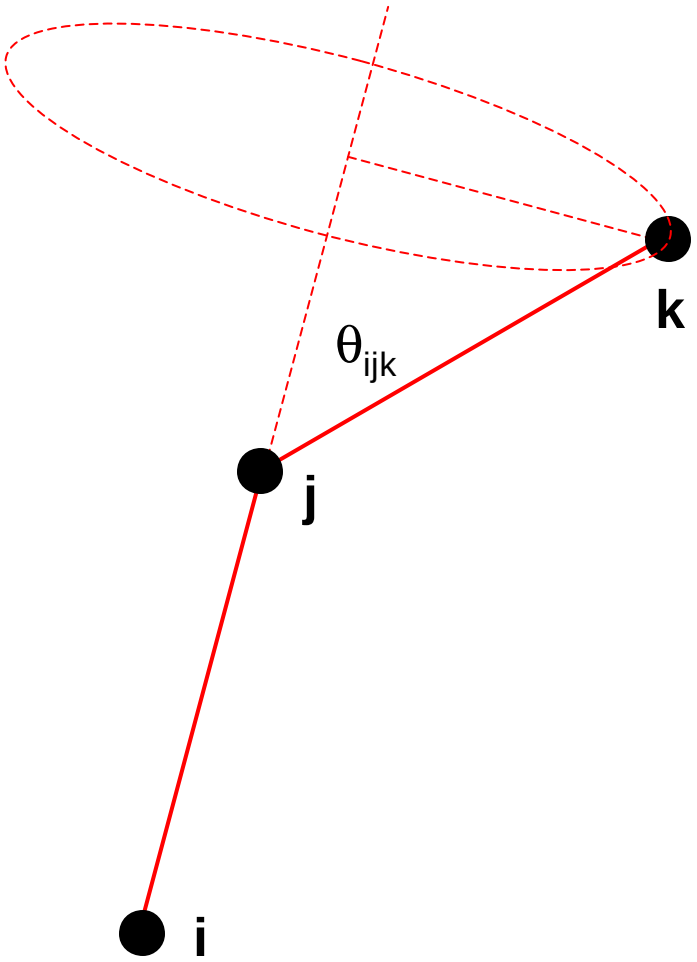
$n_{r,\Delta L} = r/2$



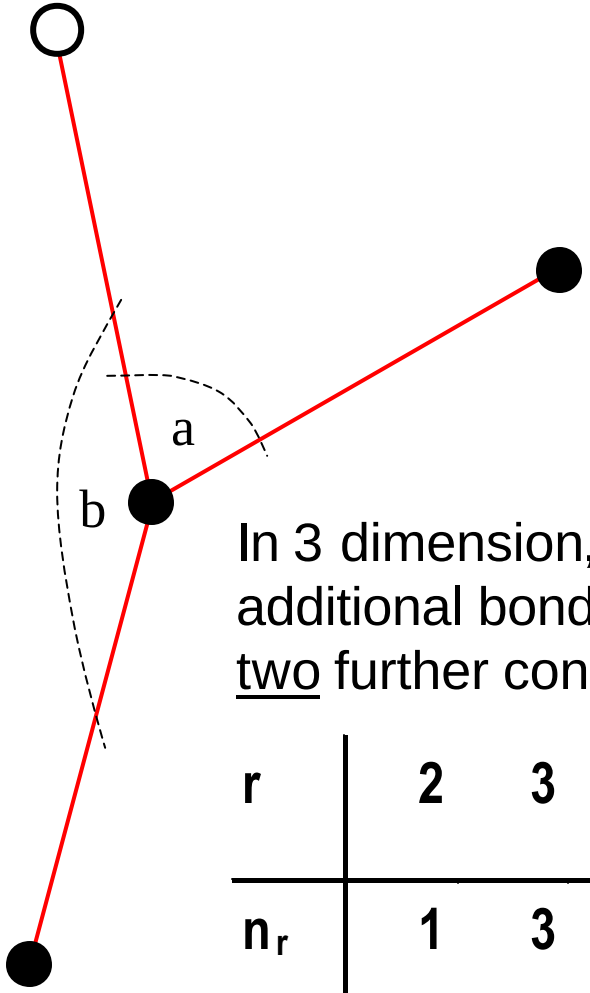
$$N_{C,\Delta L} = \sum_r n_{r,\Delta L} \cdot N_r = \sum_r \frac{r}{2} \cdot N_r$$

constraints related to angular variations Dq:

r = 2 ⇒
only one angular constraint:
$n_{r,\Delta\theta} = 1$

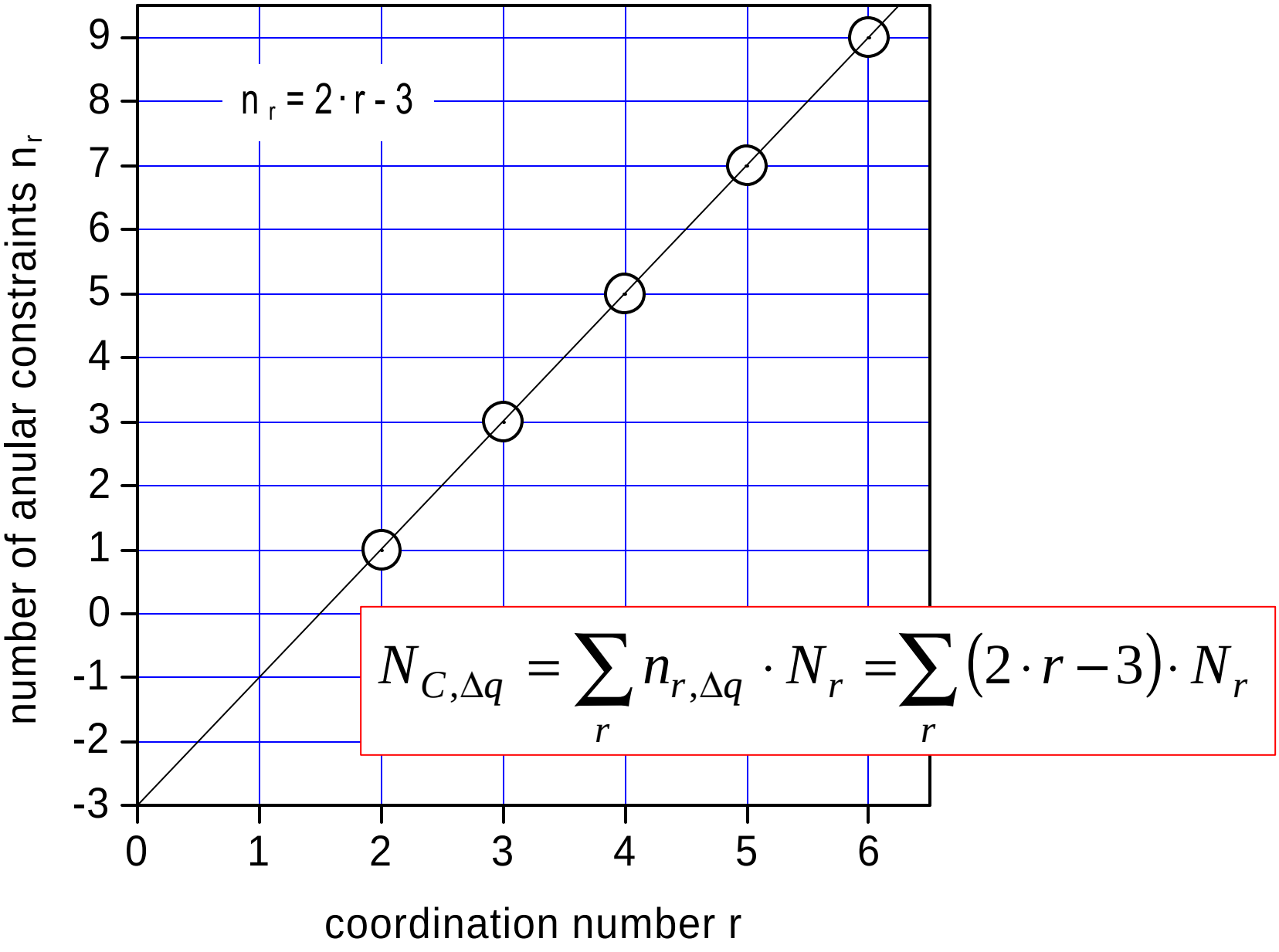


r = 3 ⇒
two additional constraints because two angles relative to two existing bonds have to be specified: $n_r = 3$



In 3 dimension, each additional bond constitutes two further constraints:

r	2	3	4	5	6
n_r	1	3	5	7	9


number of anular constraints n_r
coordination number r
$n_r = 2 \cdot r - 3$
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
0
1
2
3
4
5
6
$N_{C,\Delta q} = \sum_r n_{r,\Delta q} \cdot N_r = \sum_r (2 \cdot r - 3) \cdot N_r$

The total number of constraints thus amounts to

$$N_C = \sum_r \frac{r}{2} \cdot N_r + \sum_r (2 \cdot r - 3) \cdot N_r$$

The total number of zero frequency („floppy“) modes is

$$N_0 = N_F - N_C = 3 \cdot \sum_r N_r - \sum_r \frac{r}{2} \cdot N_r - \sum_r (2 \cdot r - 3) \cdot N_r$$

$$= \sum_r \left(6 - \frac{5}{2} r \right) \cdot N_r$$

Let us calculate the fraction $f_0 = N_0 / (3 \cdot N)$ of „floppy“ modes:

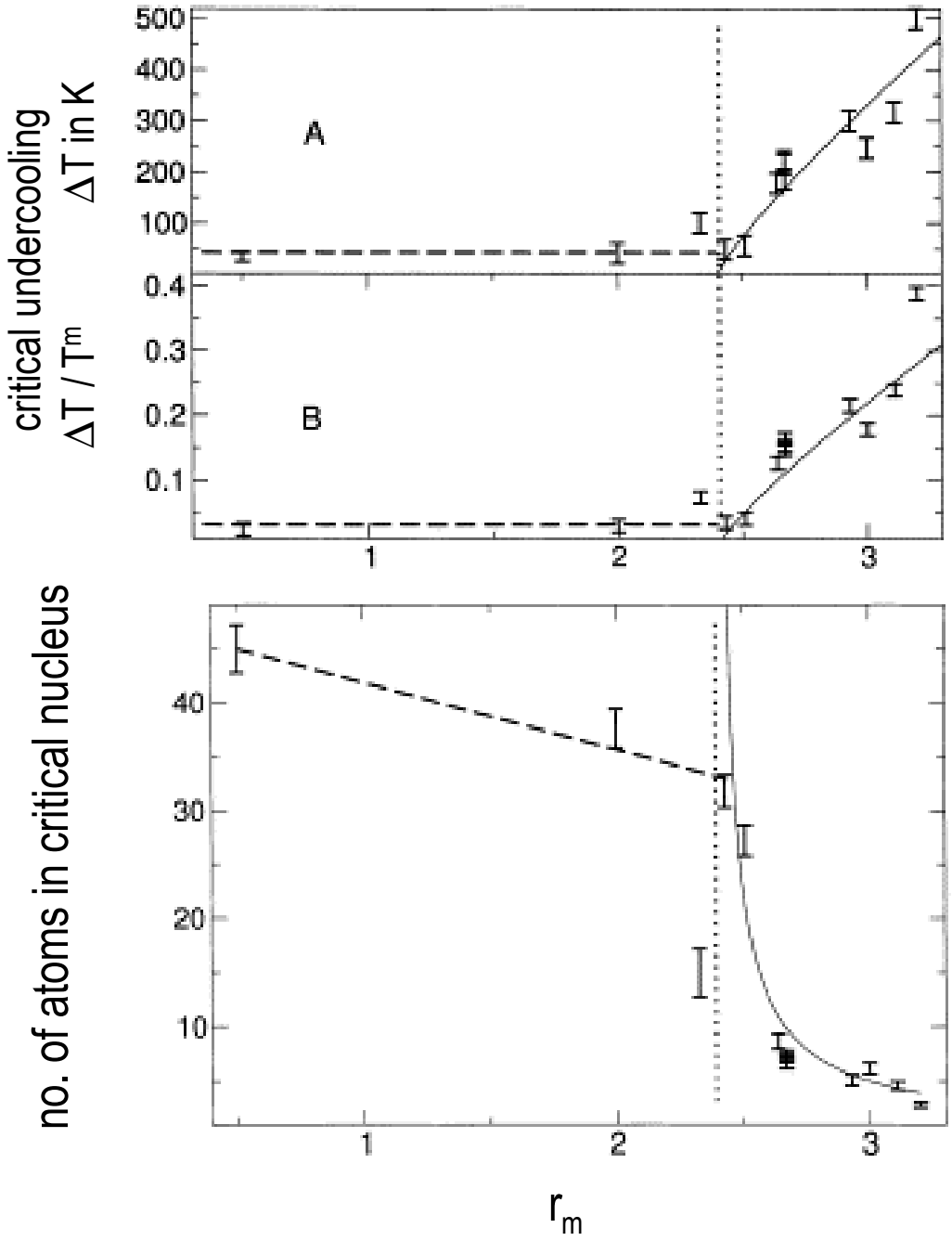
$$f_0 = \frac{N_0}{3 \cdot N} = \frac{\sum_r \left(6 - \frac{5}{2} r \right) \cdot N_r}{3 \cdot \sum_r N_r} = 2 - \frac{5}{6} r_m \to 0 \quad for \quad r_m = 2.4$$

summary: constraint counting

N = number of nodes in the network
(e.g., number of Si atoms)

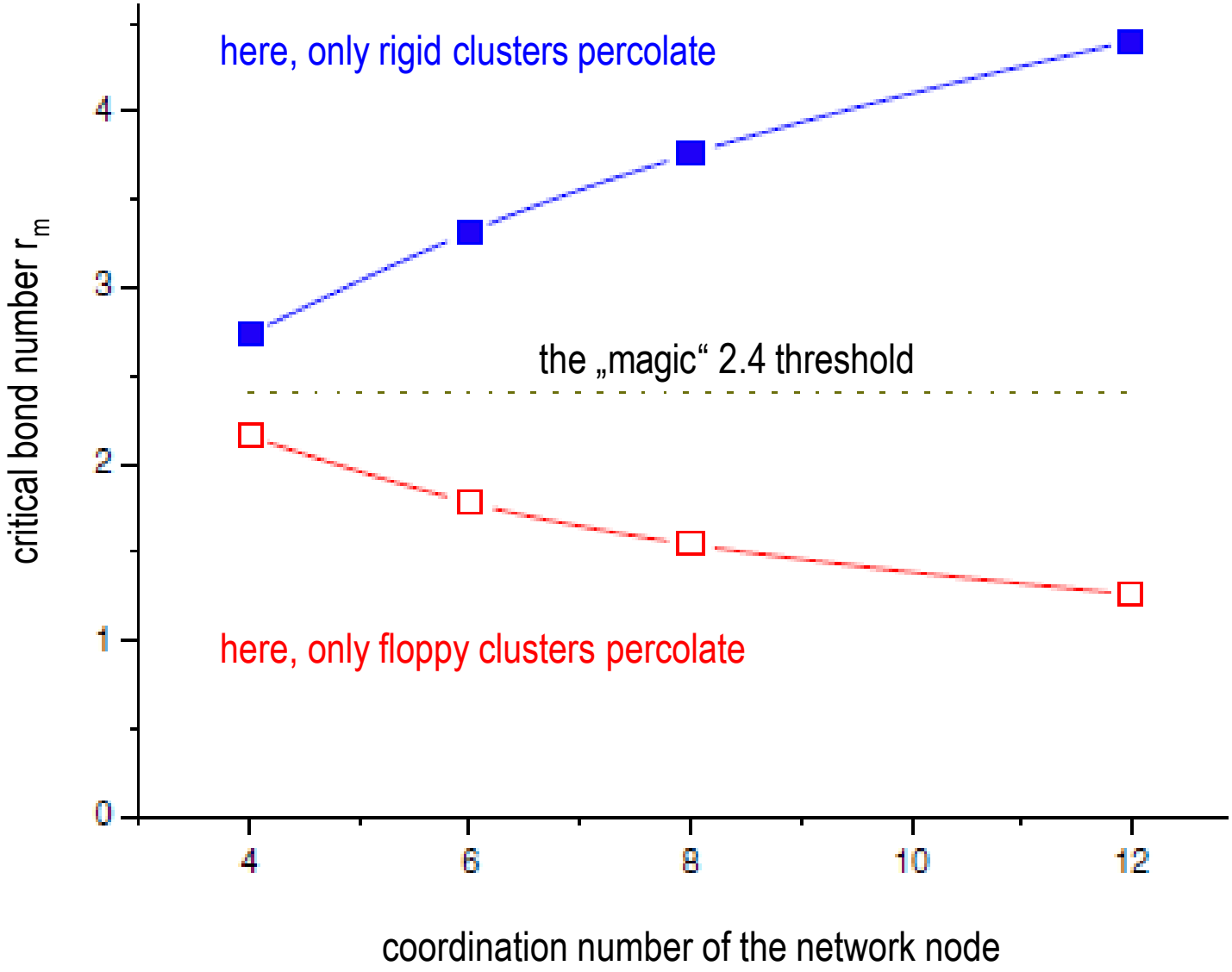
r_m = mean number of constraining bonds per node
(e.g., number of bridging oxygens per Si atom)

number of	3D network
degrees of freedom N_F	$3 \cdot N$
constraints N_C	$\left(\frac{5}{2} \cdot r_m - 3\right) \cdot N$
floppy modes $N_0 = N_F - N_C$	$\left(6 - \frac{5}{2} \cdot r_m\right) \cdot N$
$N_0 \rightarrow 0$ for	$r_m = 2.4$



$BaO \cdot TiO_2 \cdot 2SiO_2$

Avramov, Keding, Rüssel (2000)



Avramov 2009

Consider Na_2O-SiO_2 glasses:

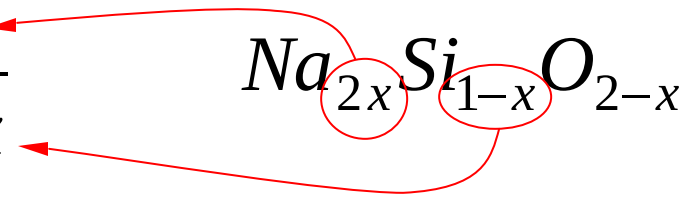
$$xNa_2O \cdot (1-x)SiO_2 \Rightarrow Na_{2x}Si_{1-x}O_{2-x}$$

- **Mean coordination number b_m per network node (each Si in one node):**

$$b_m = 4$$ **for SiO_2 as the only network former**

- **Mean number q_m of modified („broken“) bonds per network node:**

$$q_m = \frac{2x}{1-x}$$



- **Mean number r_m of constrained bonds per network node:**

$$r_m = b_m - q_m = 4 - \frac{2x}{1-x} = \frac{4-6x}{1-x}$$

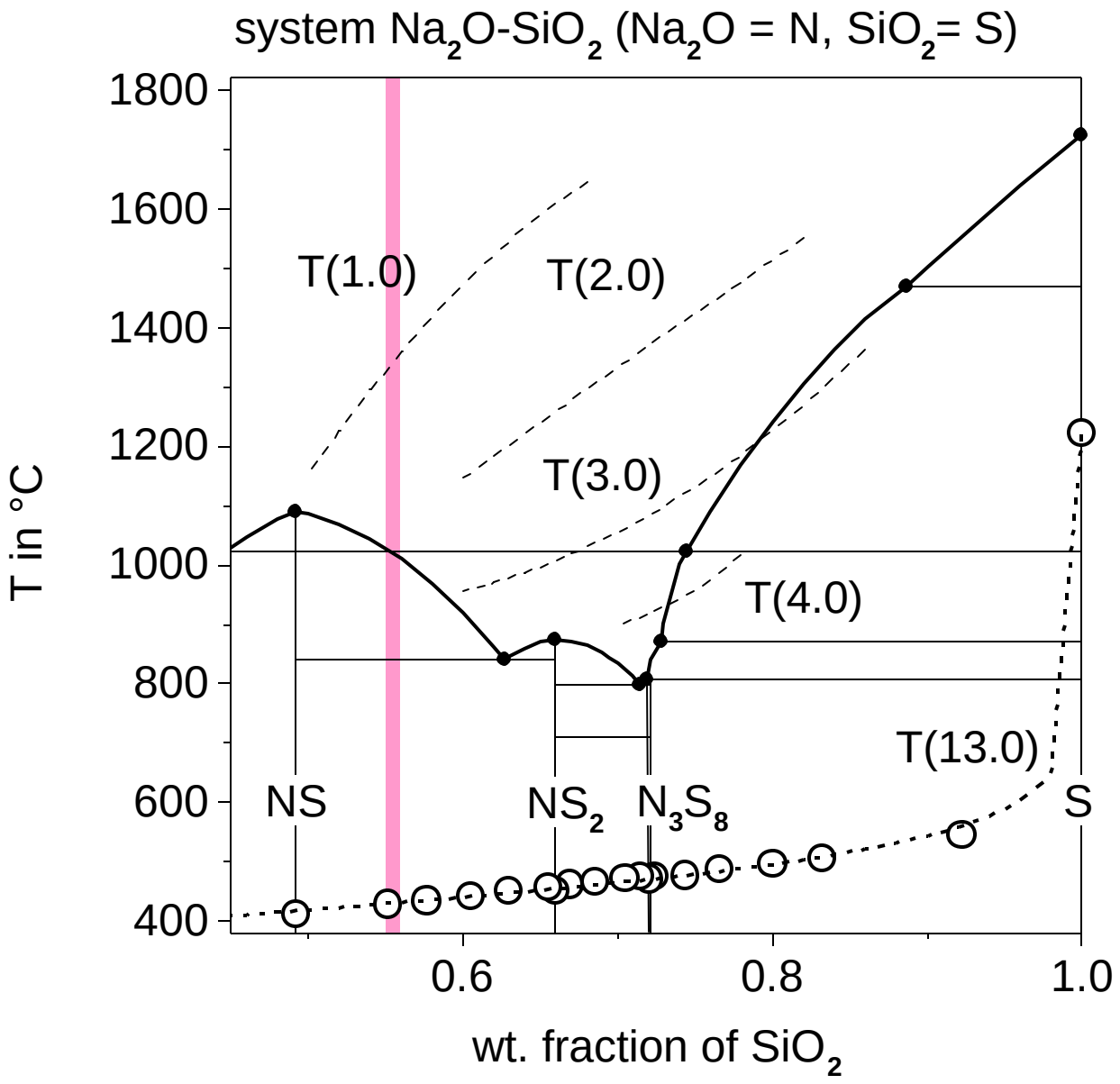
The average number of constraining bonds (or: constraints) per node is:

$$r_m = \frac{4 - 6x}{1 - x}$$

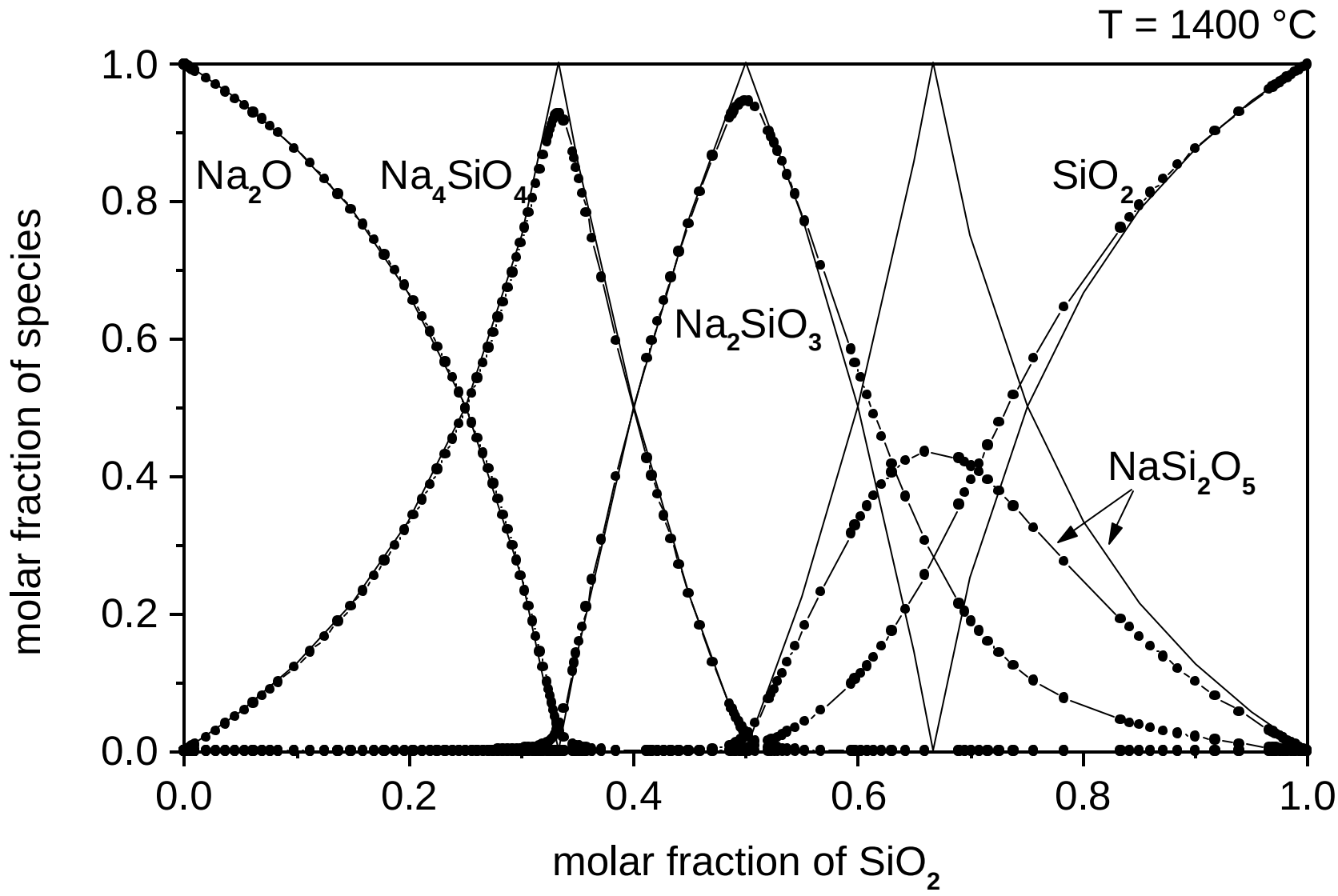
glass N-C-S (mol %)	modifier N r_m =
50.0 N + 50.0 S	2.00
44.4 N + 55.6 S	2.40
33.3 N + 66.7 S	3.00

isostatic case?

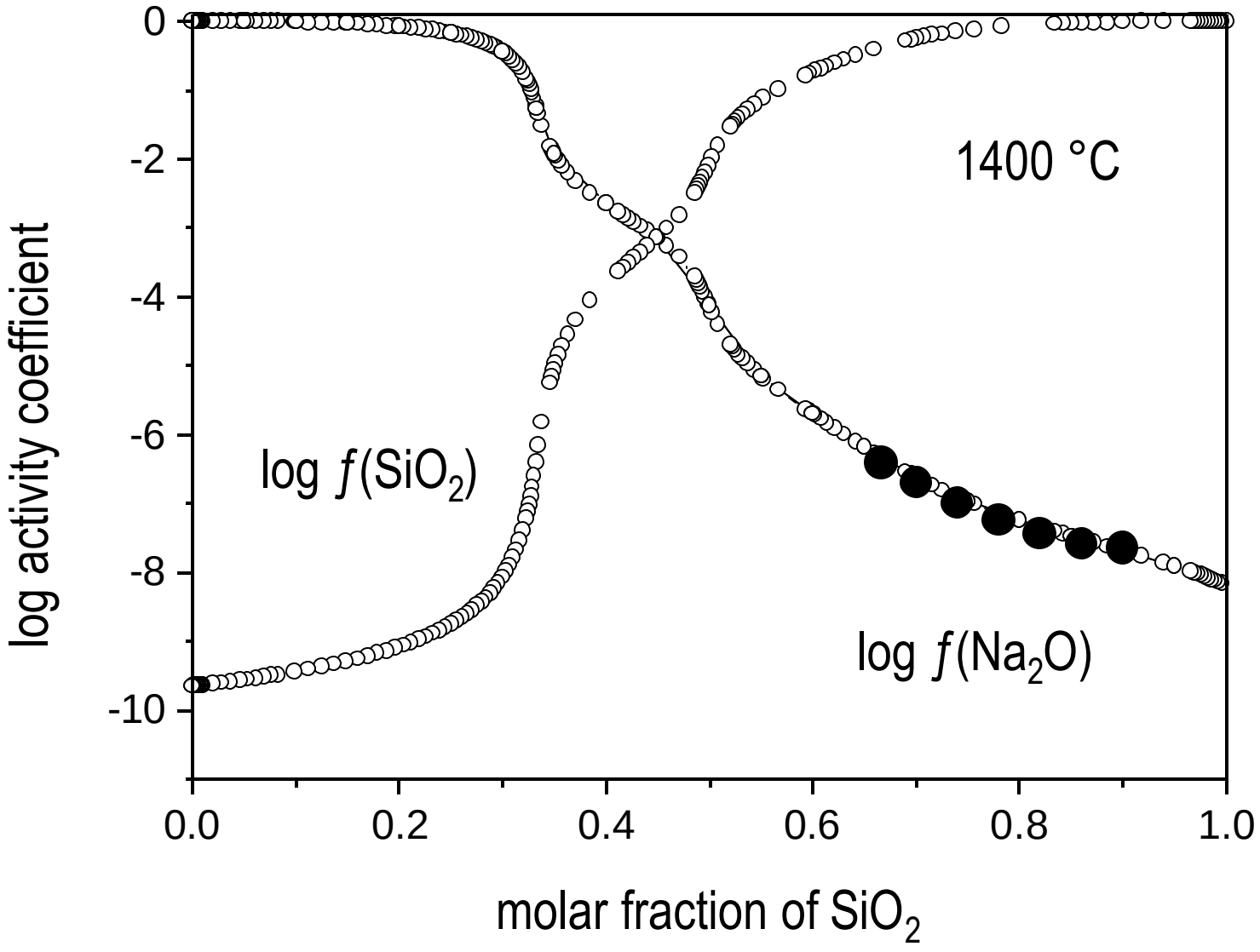
Does a glass composition with 55.6 mol-% SiO_2 stand out in any way?


system Na_2O-SiO_2 (Na_2O = N, SiO_2= S)
T in °C
1800
1600
1400
1200
1000
800
600
400
T(1.0)
T(2.0)
T(3.0)
T(4.0)
T(13.0)
NS
NS_2
N_3S_8
S
0.6
0.8
1.0
wt. fraction of SiO_2

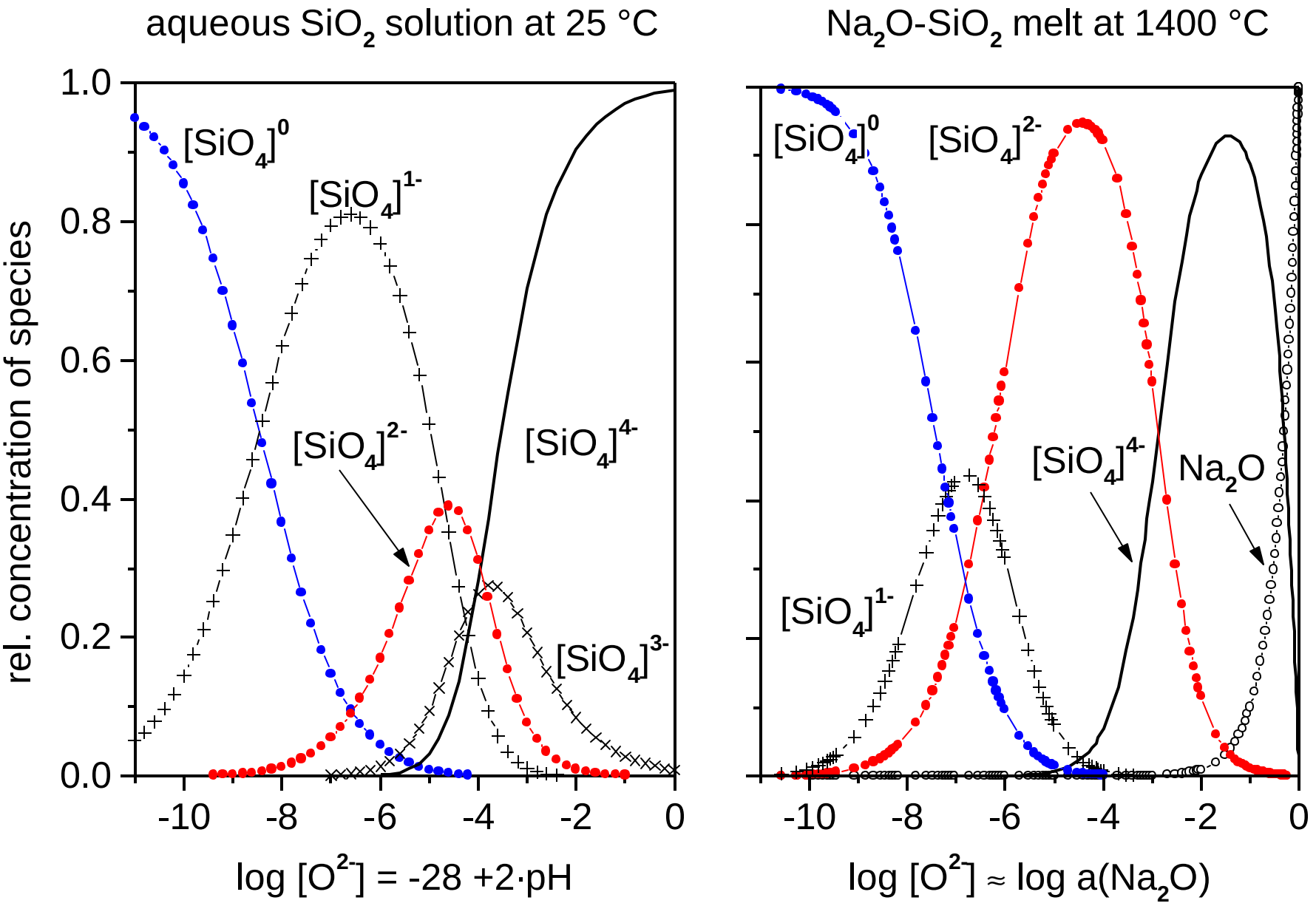
„chemical structure“ of the binary system Na_2O-SiO_2



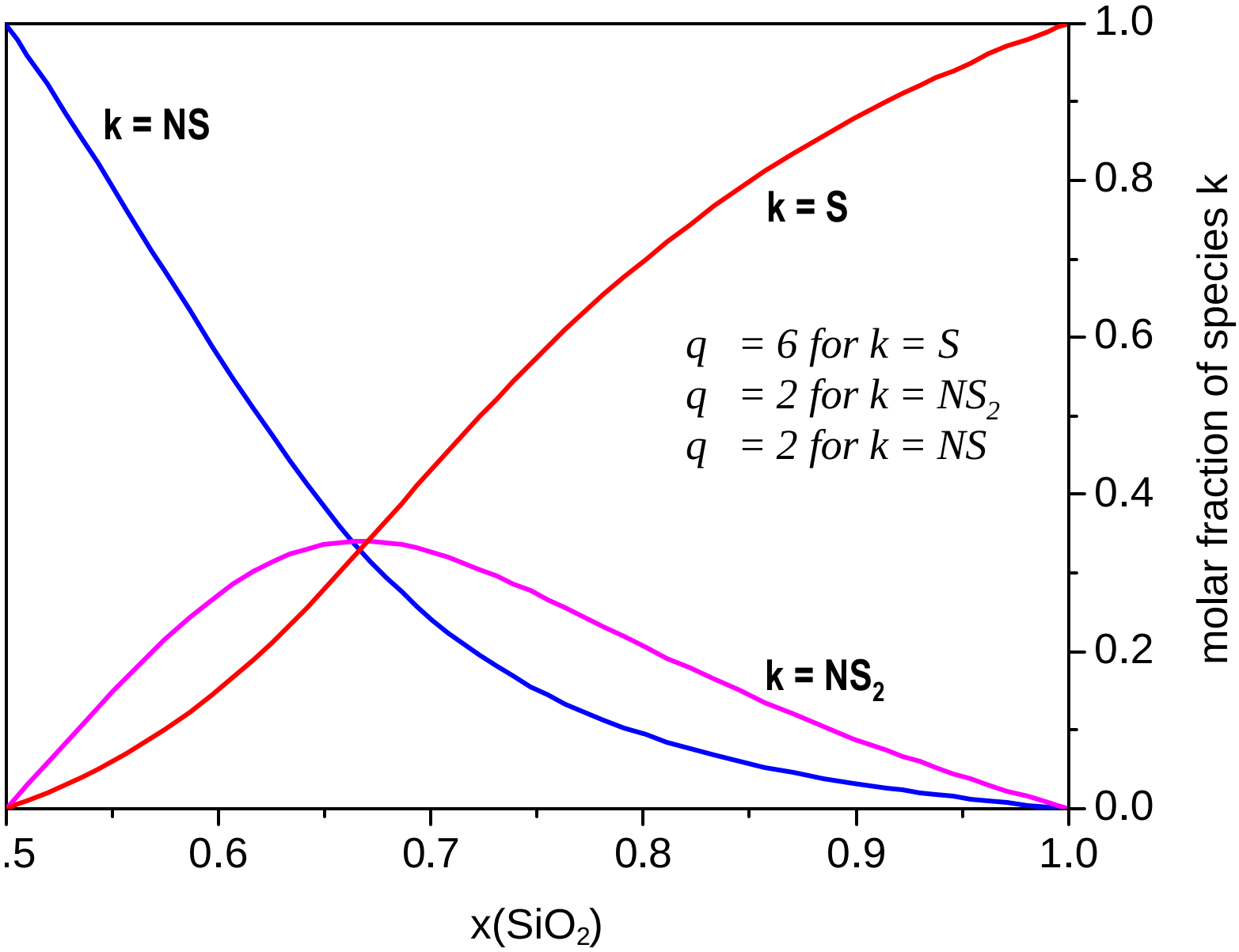
„chemical structure“ and chemical potentials are equivalent concepts both quantifying the chemical interaction of components

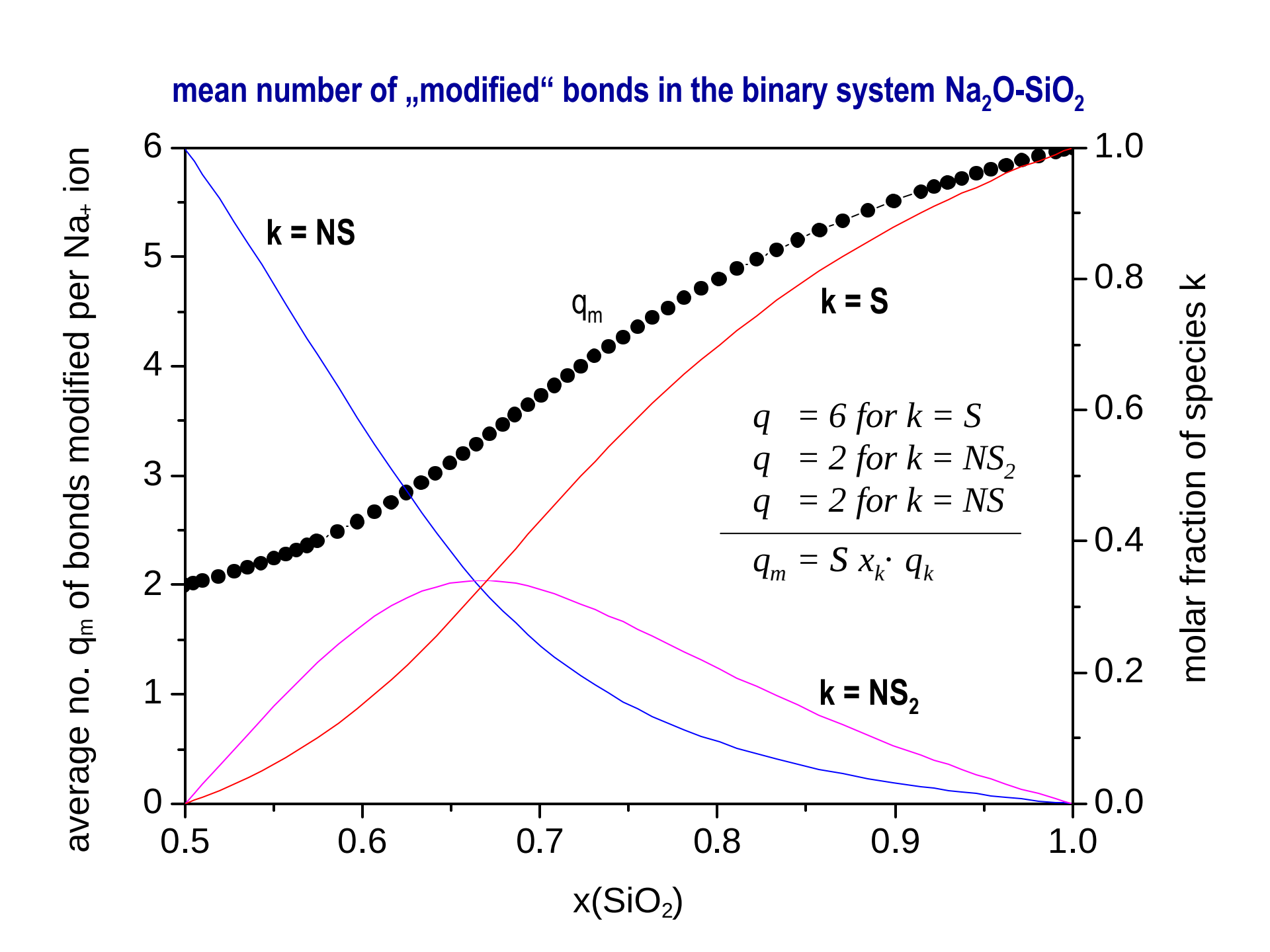


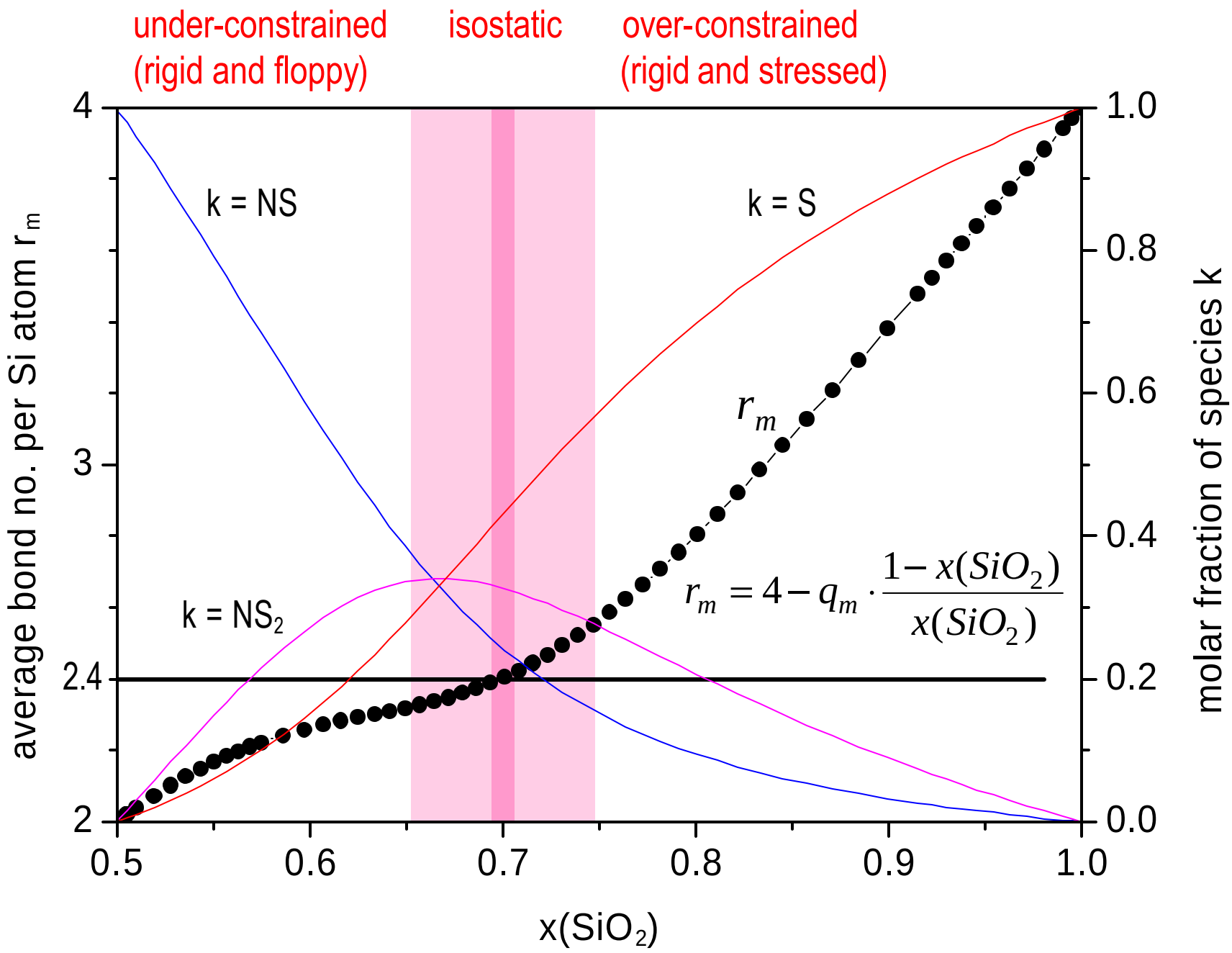
species coexistence is a feature of liquids in general Þ „chemical structure“



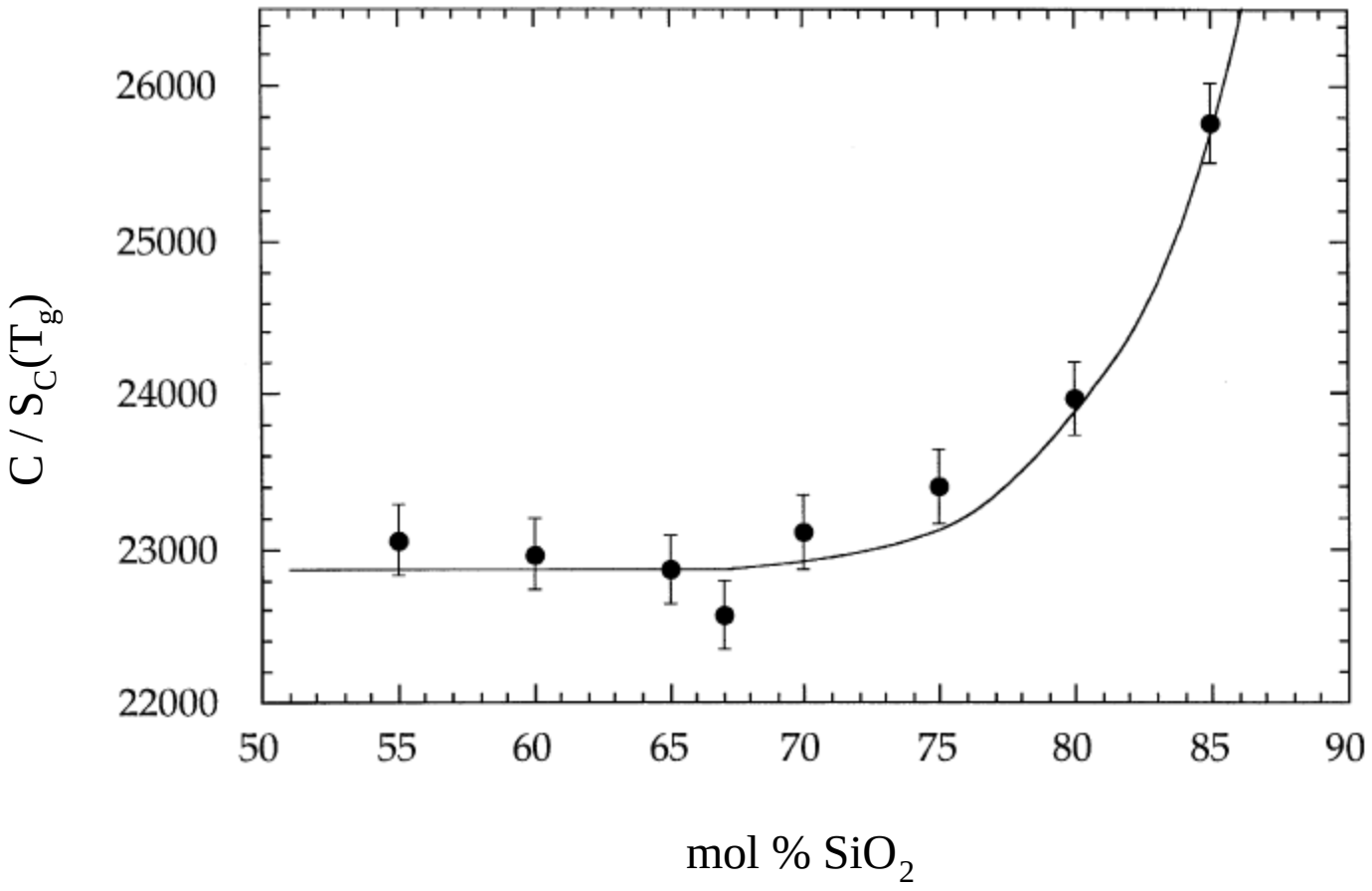
„chemical structure“ of the binary system Na_2O-SiO_2




mean number of „modified“ bonds in the binary system Na2O-SiO2
average no. qm of bonds modified per Na+ ion
molar fraction of species k
x(SiO2)
k = NS
qm
k = S
k = NS2
q = 6 for k = S
q = 2 for k = NS2
q = 2 for k = NS
qm = S xk· qk
0
1
2
3
4
5
6
0.0
0.2
0.4
0.6
0.8
1.0
0.5
0.6
0.7
0.8
0.9
1.0


under-constrained
(rigid and floppy)
isostatic
over-constrained
(rigid and stressed)
k = NS
k = S
k = NS2
r_m
$r_m = 4 - q_m \cdot \frac{1 - x(SiO_2)}{x(SiO_2)}$
average bond no. per Si atom r_m
molar fraction of species k
$x(SiO_2)$
4
3
2.4
2
1.0
0.8
0.6
0.4
0.2
0.0
0.5
0.6
0.7
0.8
0.9
1.0

$$L = L_\infty + \frac{C}{T \cdot S_C(T)}; \quad L \equiv \log h$$



M. Toplis (2001)

QUIZ

1. The fragility of a glass is a measure of
- its practical strength.
- the activation energy in an Arrhenius plot.
- the over-exponential increase of relaxation times when approaching T_g.

2. Clusters formation
- and random network formation are strictly antagonistic concepts.
- is rather supported than discouraged by random network concepts.
- is a structural feature exclusively found in metallic glasses.

3. The heat capacities of a glass and its isochemical crystal
- are essentially the same since c_P is dominated by short-range order.
- are usually quite different because the crystal is highly ordered while the glass is not.
- deviate in the low-T regime.
- None of these answers is correct.
- More than one answer is correct.

4. The c_P in the glass transition
- is of the order of 3R per g-atom.
- is approx. (3/2)R per g-atom.
- is very different for different glasses depending on their fragility.
- depends on the absolute value of T_g.

QUIZ continued

5. The viscosity of a glass-forming melt:

- The viscosity-temperature relation essentially depends on thermodynamic properties.
- The viscosity-temperature relation is a kinetic property and as such has no relation to thermodynamics.
- The viscosities of glass-forming melts at liquidus temperature are of the same order of magnitude.
- More than one answer is correct.

6. Floppy modes in a 3D random network

- occur if the average bond per network node exceeds a threshold value of approx. 2.4.
- decrease the critical undercooling of a glass melt.
- Both answers are correct.

7. The “chemical structure” of a glass

- reflects true structural entities.
- is a merely stoichiometric concept which has no real correspondence to the glass structure.
- is based on a nanocrystalline concept of the glassy state.

8. The different 3-parameter viscosity models

- although based on different scientific concepts yield – in practical terms – the same results of the viscosity-temperature function.
- agree well within limited temperature ranges, but disagree significantly at very high temperatures and at $T < T_g$.
- yield considerably different results within the entire T range.

Homework

Use the simplified form of the Adam-Gibbs relation

$$\log h = \log h_\infty + \frac{C}{T \cdot S_C(T)} = L_\infty + \frac{(L_g - L_\infty) \cdot y}{1 - a \cdot \ln y} = b_0 + b_1 \cdot f(y)$$

with abbreviations

$$\log h \equiv L; \quad \frac{\Delta c}{S^{vit}} \equiv a; \quad \frac{T_g}{T} \equiv y.$$

Use the „structural parameter“ *a* as an adjustable parameter to generate a linear fit to the following experimental viscosity data of diopside (viscosity in dPas):

T in °C	log η
708	≈13.0
1375	1.087
1400	0.992
1450	0.881
1500	0.678
1550	0.559
1600	0.465

The experimental value of Δc_P is 80.0 J/(mol·K). Derive an estimate for the conventional entropy of vitrification S^{vit}. Conclusion?

Thank you
for your attention