RWTH AACHEN UNIVERSITY

I.

Fragility and its Relation to Other Glass Properties

II.

Networks

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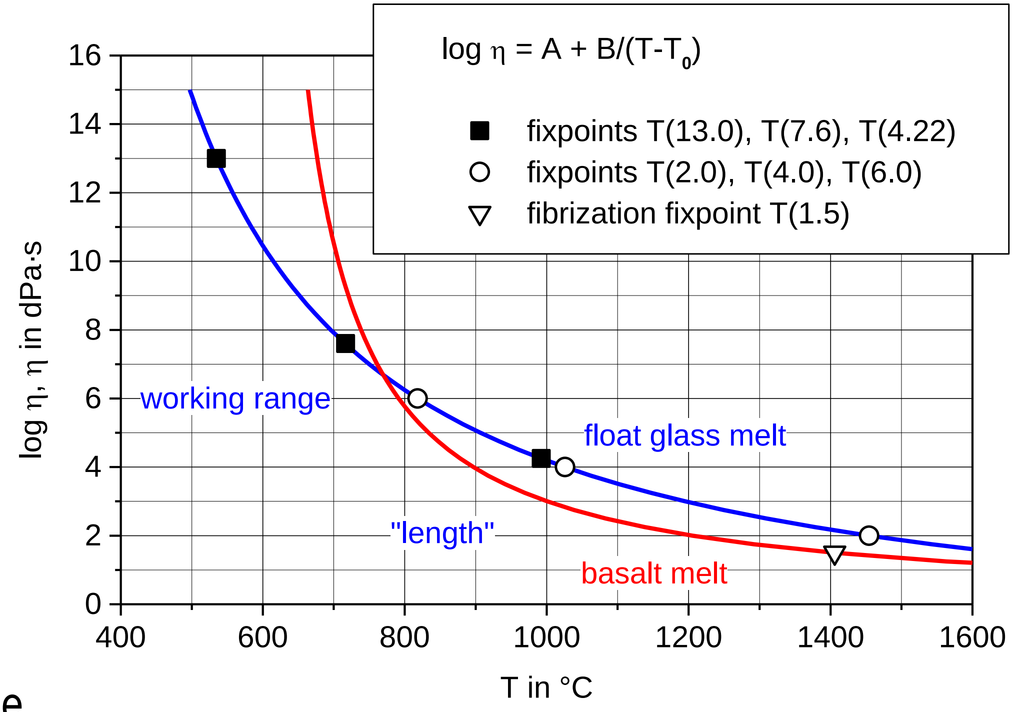
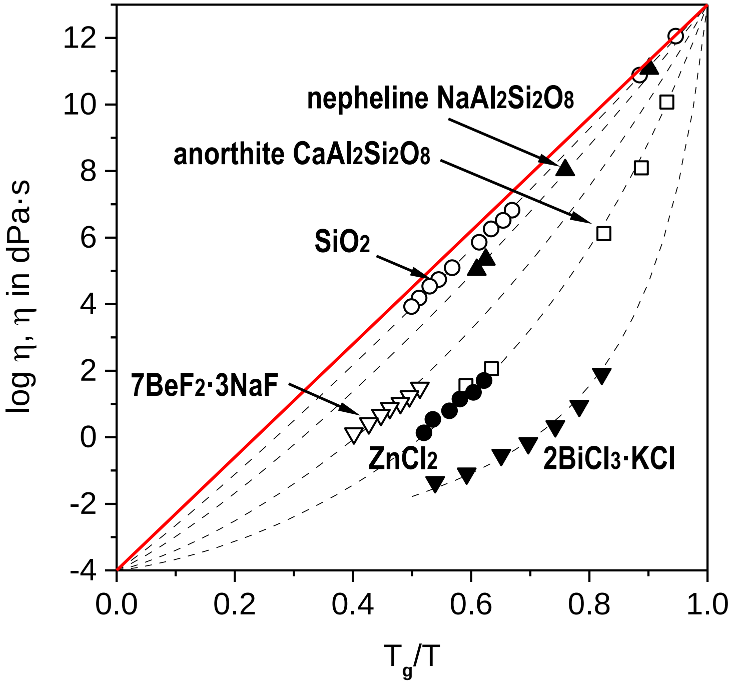
What is „fragility"?

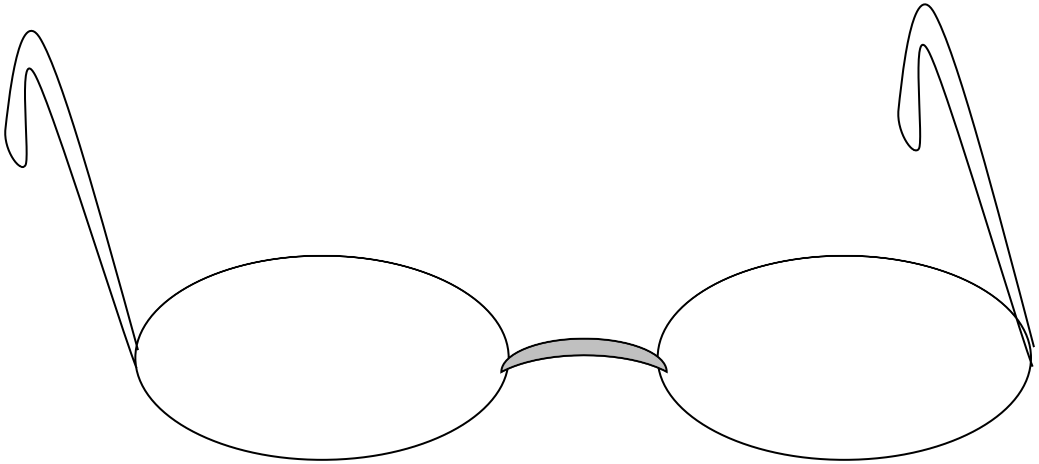
- Technologist call it the „length" of a glass; it determines the working range.
- Fragility is a measure of deviation from an exponential T dependence of relaxation times and transport properties (deviation from Arrhenius behavior).



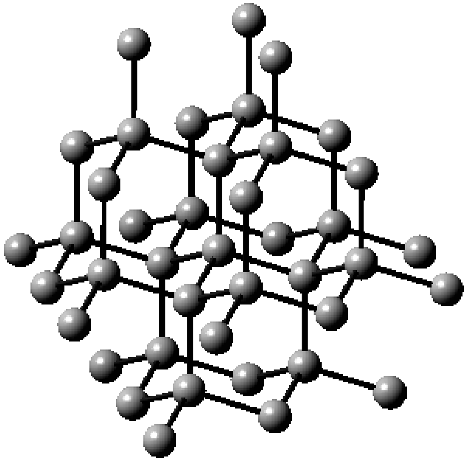
- Fragility may be quantified, e.g., by the slope for $T_g / T \rightarrow 1$ in the so-called Angell plot.
- The non-exponential T dependence is commonly represented by the KWW eq. $\tau \propto \exp B\cdot(T_g/T)^n$, by the VFT eq. $\tau \propto \exp B/(T - T_0)$, etc.
- While the high-T branch reflects a universal feature of liquids, the fragility is likely to reflect the thermodynamics of the liquids.

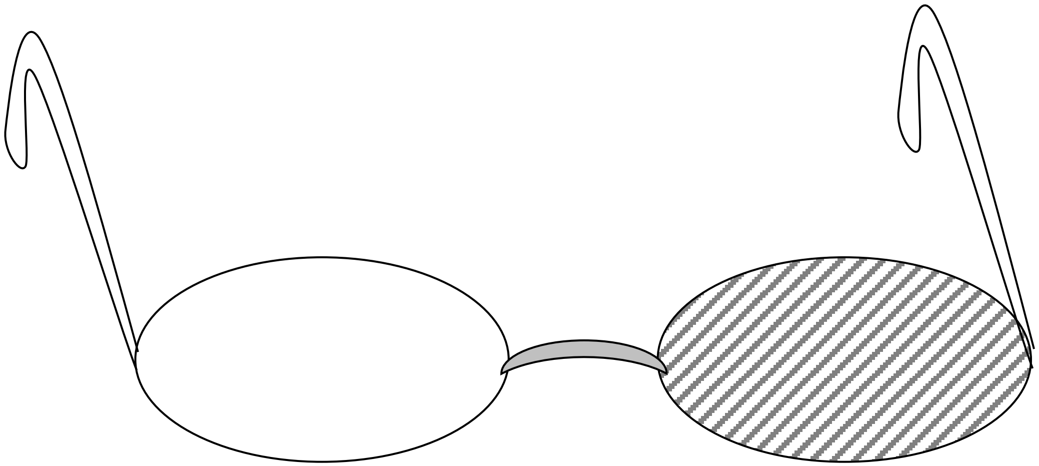


the glassy „state“

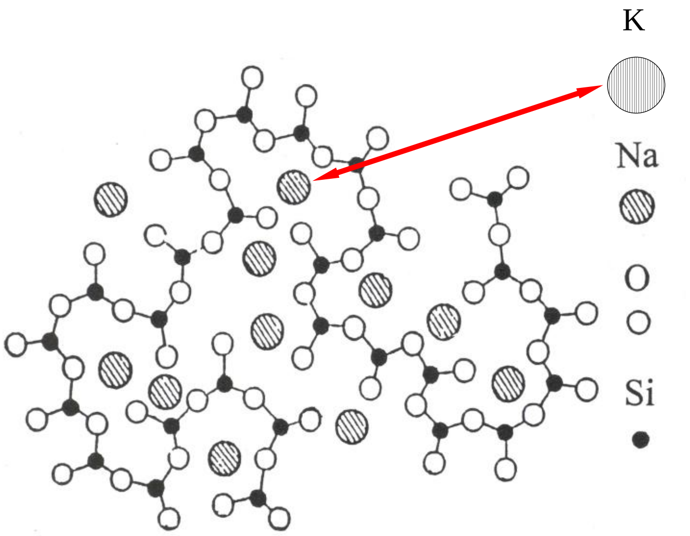


structure	dynamics
topology hkl	energy kT
networks	$c_P(T)$, $\nu(T)$
bonds & coordination	stoichiometry & constitution
field strength	phase diagrams
	ΔH, ΔG, K_P, k^+ , k^-

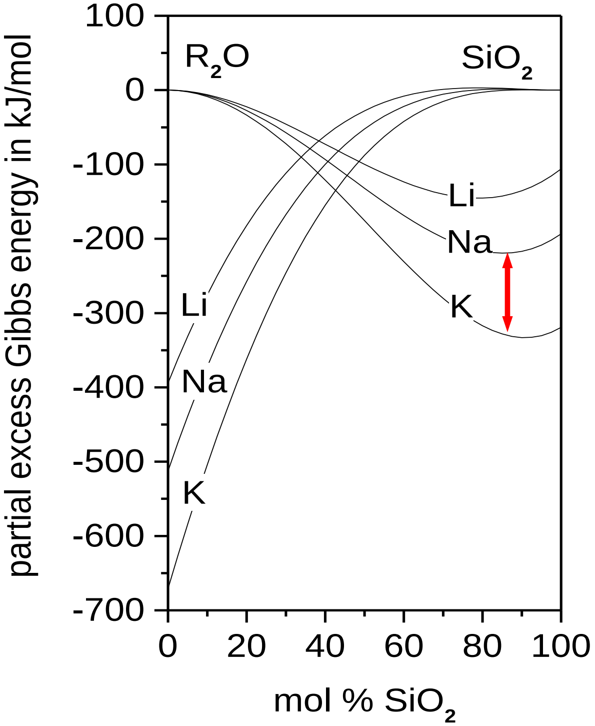




structure



dynamics



matter in internal equilibrium:

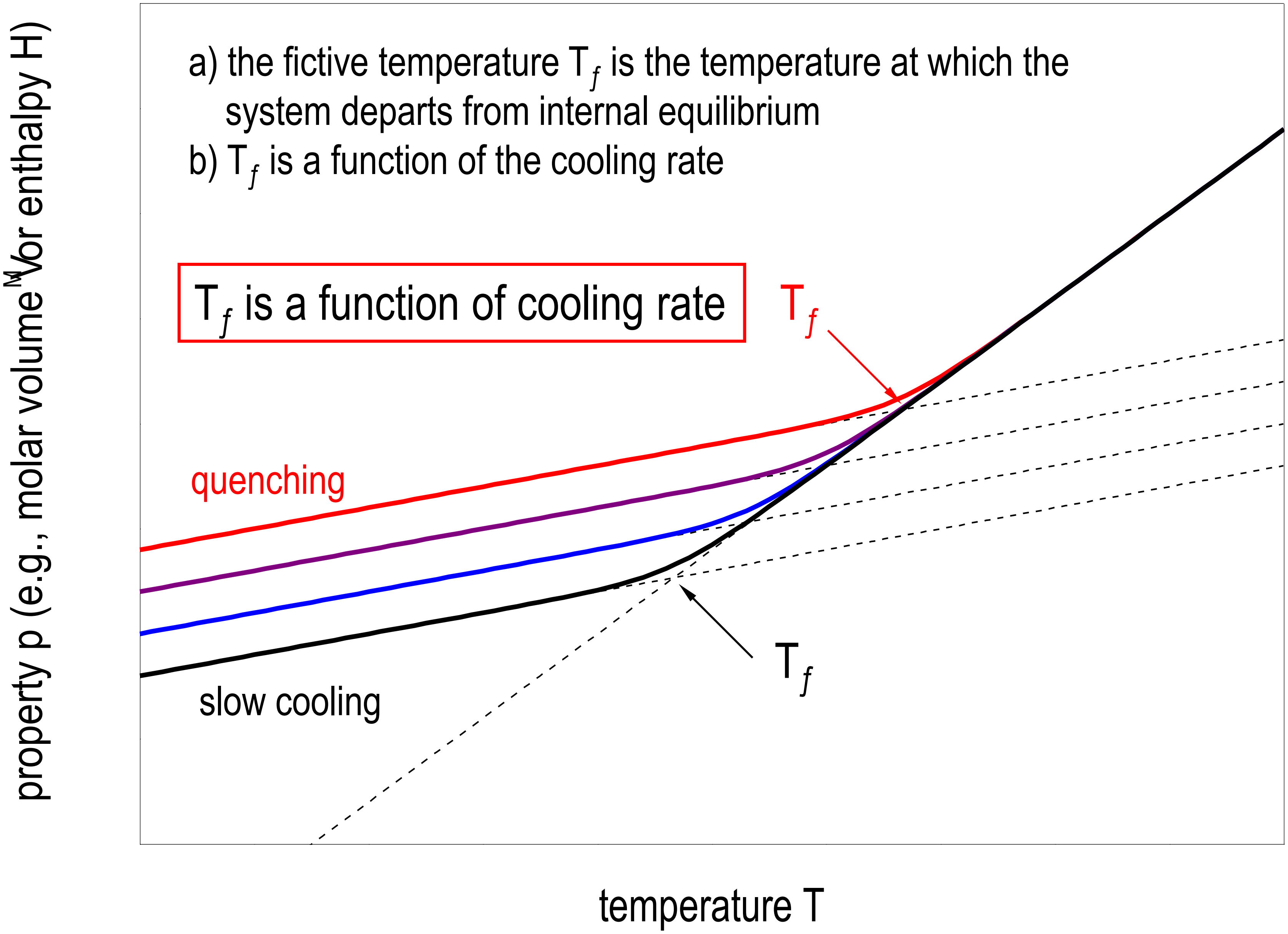
state A: T^A, P^A, n^A_j → state B: T^B, P^B, n^B_j; n_j stands for $\vec{n} = \begin{pmatrix} n_{j=1} \\ : \\ n_{j=N} \end{pmatrix}$ (chemical composition)

- a state depends on variables T, P, n_j only; it is „path independent“; let $Z = Z(T,P,n_j)$ be a property (a „function of state“), then

$$\int_A^B dZ = Z(B) - Z(A); \quad \oint dZ = 0$$

matter at T^B, P^B, n^B_j **not** in internal equilibrium:

- Z is no longer a function of (T^B,P^B,n^B_j) alone; it is path dependent;
- a path may be defined as
  $T^A \rightarrow T^B$, P = const., n_j = const. (e.g., a cooling process)
  $P^A \rightarrow P^B$, T = const., n_j = const. (e.g., an impact process)
  $n^A_j \rightarrow n^B_j$, T = const., P = const. (e.g., a polymerization process)
  or as combinations of T, P, n_j changes;
- the value of T, P, n_j at which the system departs from internal equilibrium is termed fictive temperature T_f, fictive pressure P_f, or fictive composition n_{jf};
- Z is a function of $(T^B, T^B_f; P^B, P^B_f; n^B_j, n^B_{jf})$
- T^B_f, P^B_f, n^B_{jf} depend on the process time



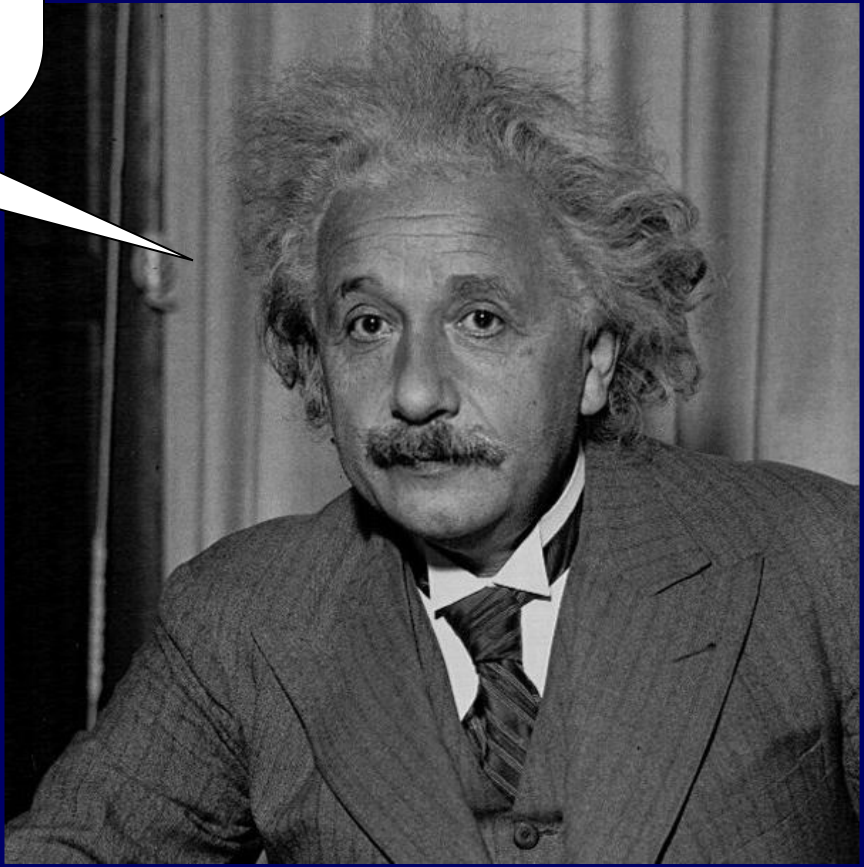
a) the fictive temperature T_f is the temperature at which the system departs from internal equilibrium

b) T_f is a function of the cooling rate

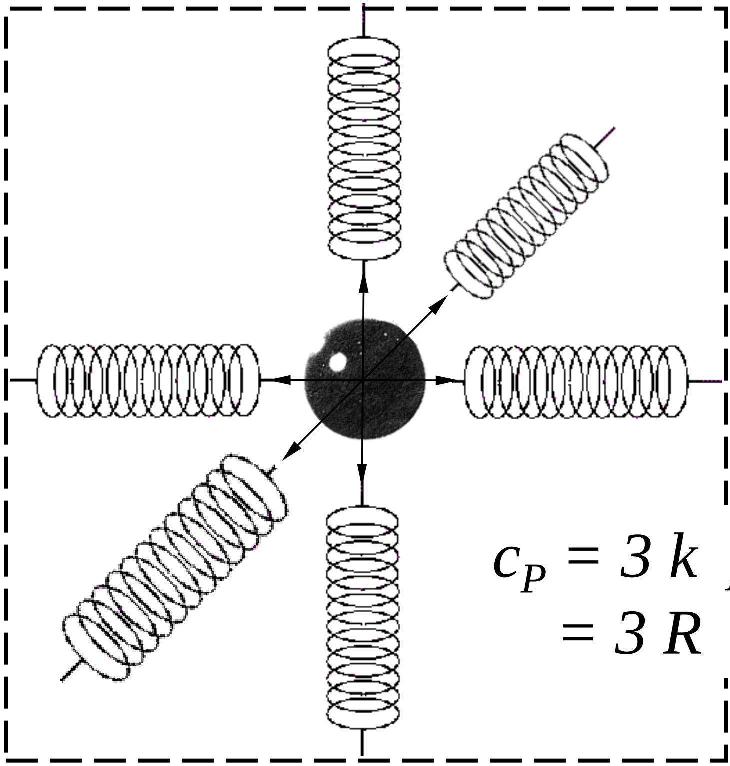
T_f is a function of cooling rate

heat capacities

If you have only one chance to perform a measurement on a material,
then measure c_P!

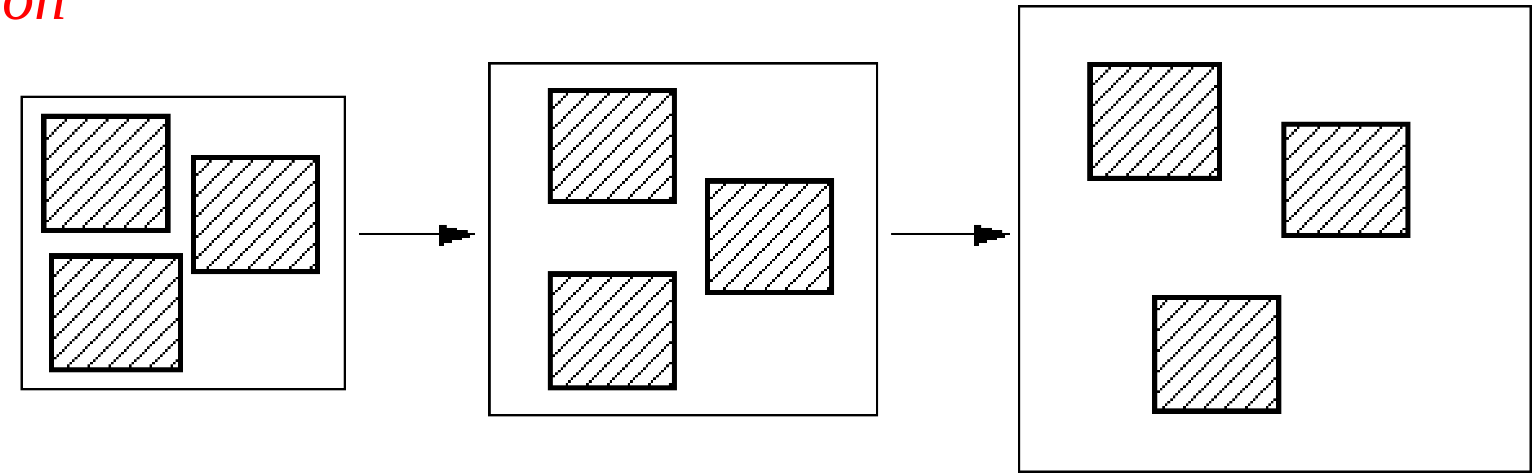


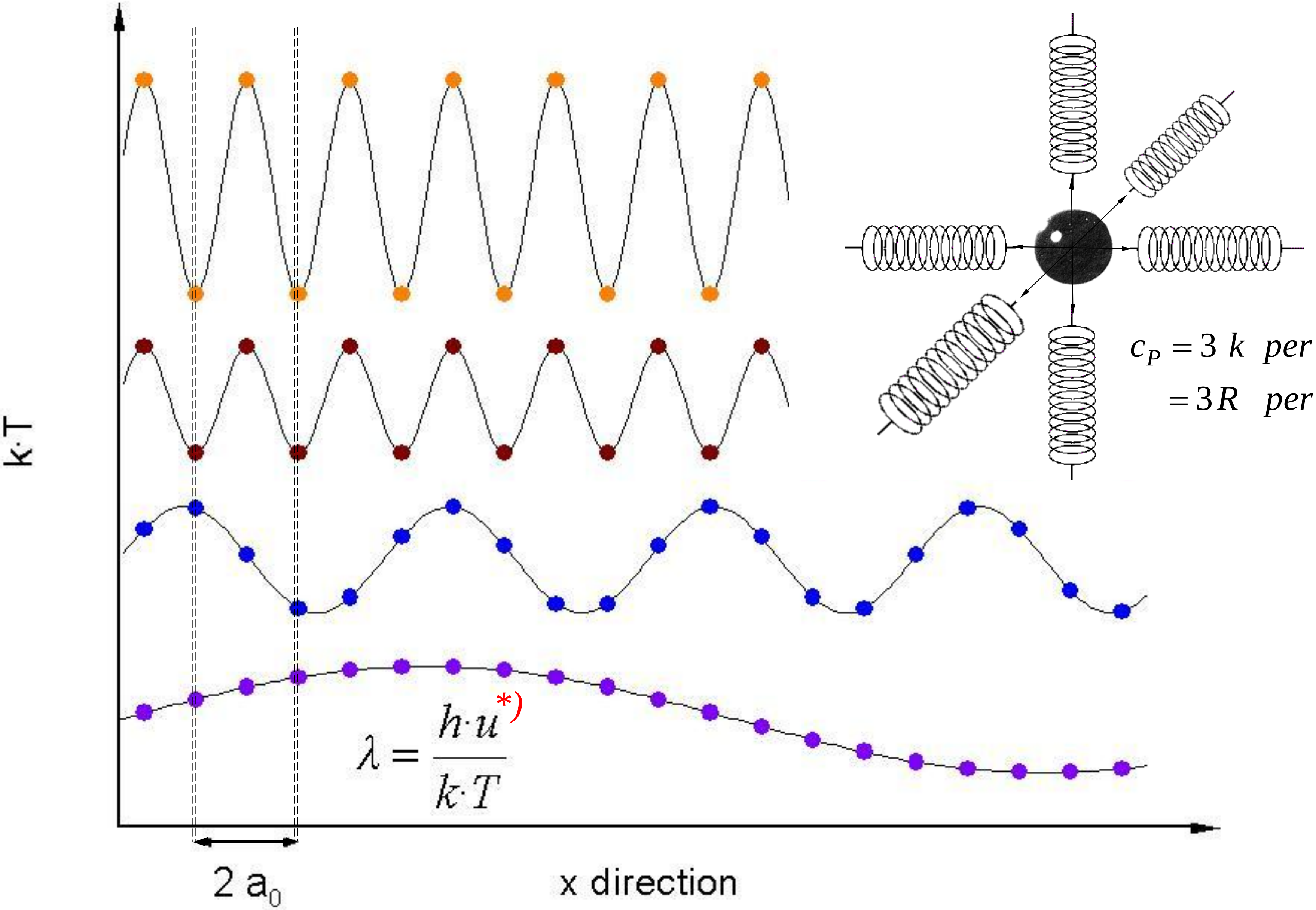
vibration



$$c_P = 3\,k \text{ per atom}$$
$$= 3\,R \text{ per mol}$$

configuration



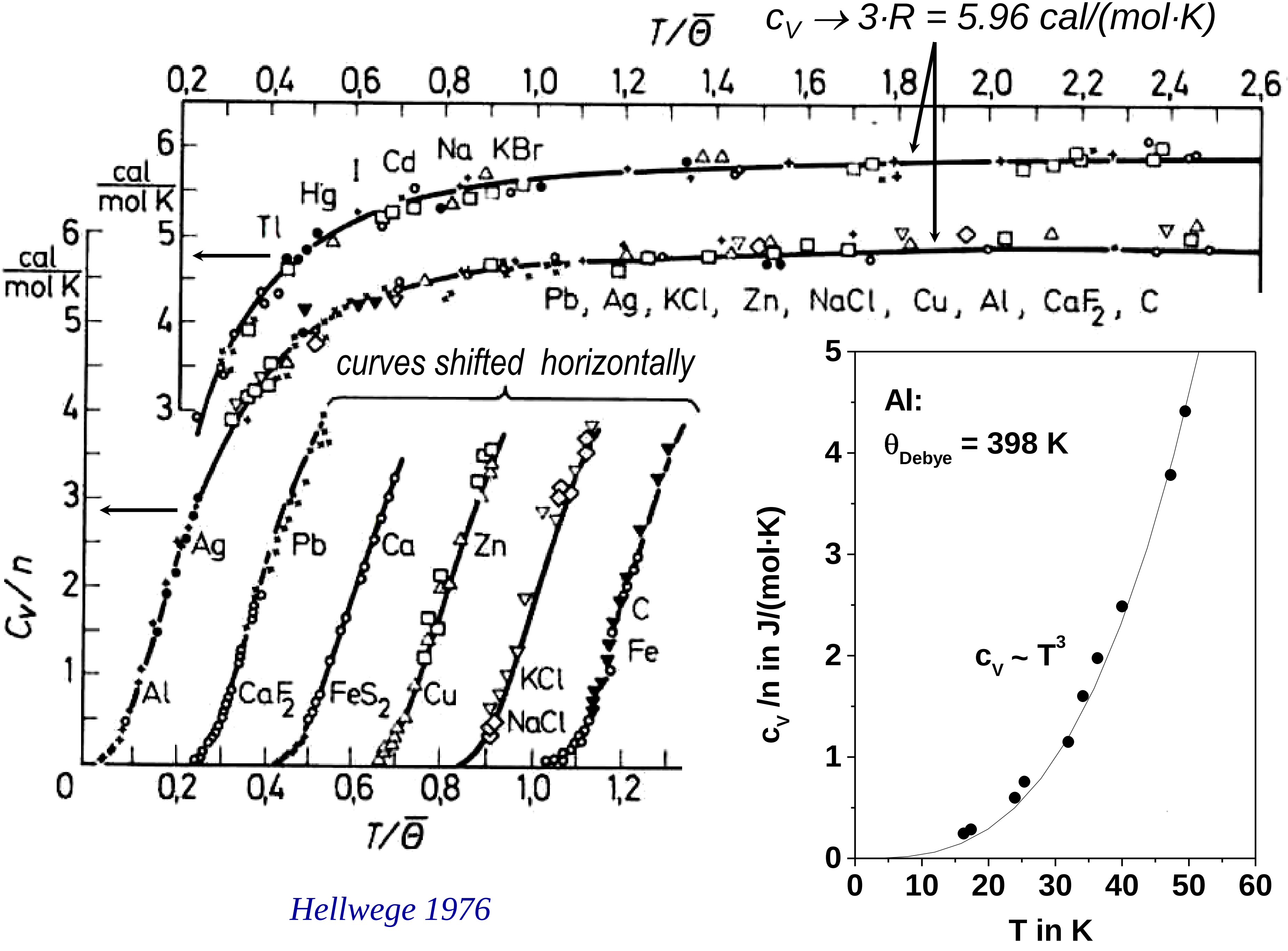


$$\lambda = \frac{h \cdot u}{k \cdot T}\,{}^{*)}$$

$$c_P = 3\,k \quad per\,atom$$
$$= 3R \quad per\,mol$$

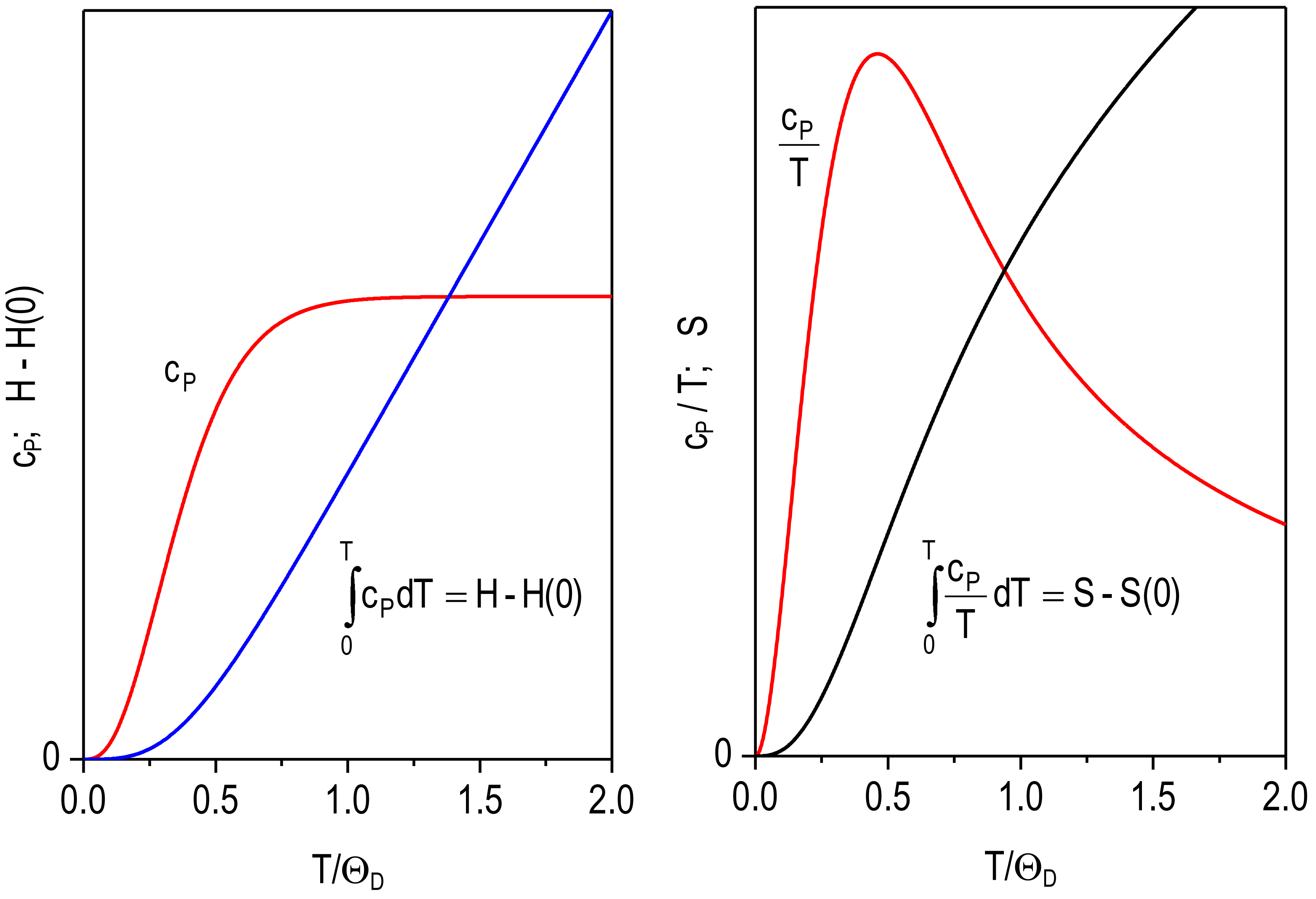
*) u = *sound velocity*

$c_V \rightarrow 3 \cdot R = 5.96$ *cal/(mol·K)*



curves shifted horizontally

Hellwege 1976



c_P; H - H(0)
c_P
∫_0^T c_P dT = H - H(0)
0
0.0
0.5
1.0
1.5
2.0
T/Θ_D
c_P / T; S
c_P / T
∫_0^T (c_P / T) dT = S - S(0)
0
0.0
0.5
1.0
1.5
2.0
T/Θ_D

Example: N_2(g) at boiling point

$$S(T) = \int_0^T \frac{c}{T}\,dT + \sum_i \frac{\Delta H_i}{T_i}, \quad T_i < T$$

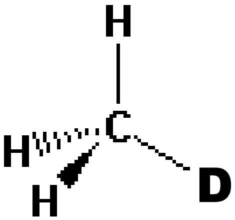
T in K	comment	ΔS in J/(mol·K)
0 – 10	Debye integral	1.916
10 – 35.61	integration of c_P/T	25.246
at 35.61	polym. phase transition	6.427
35.61 – 63.14	integration of c_P/T	23.384
at 63.14	melting point T^m	11.418
63.14 – 77.32	integration of c_P/T	11.414
at 77.32	boiling point T^b	72.120
	sum for N_2(g) at T^b	151.925
	calc. from partition function	152.236

Giauque & Clayton (1933), compiled by Wilks (1963)
other examples: Ar, O_2, Cl_2, HCl, CH_4, C_2H_4, ...

Examples: CO and CH_3D

gas	S(T^b) in J/(mol·K)		
	S_{calc}	S_{exp}	$S_{calc} - S_{exp}$
CO at boiling point T^b	160.33	155.64	4.69
CH_3D at boiling point T^b	165.23	153.64	11.59

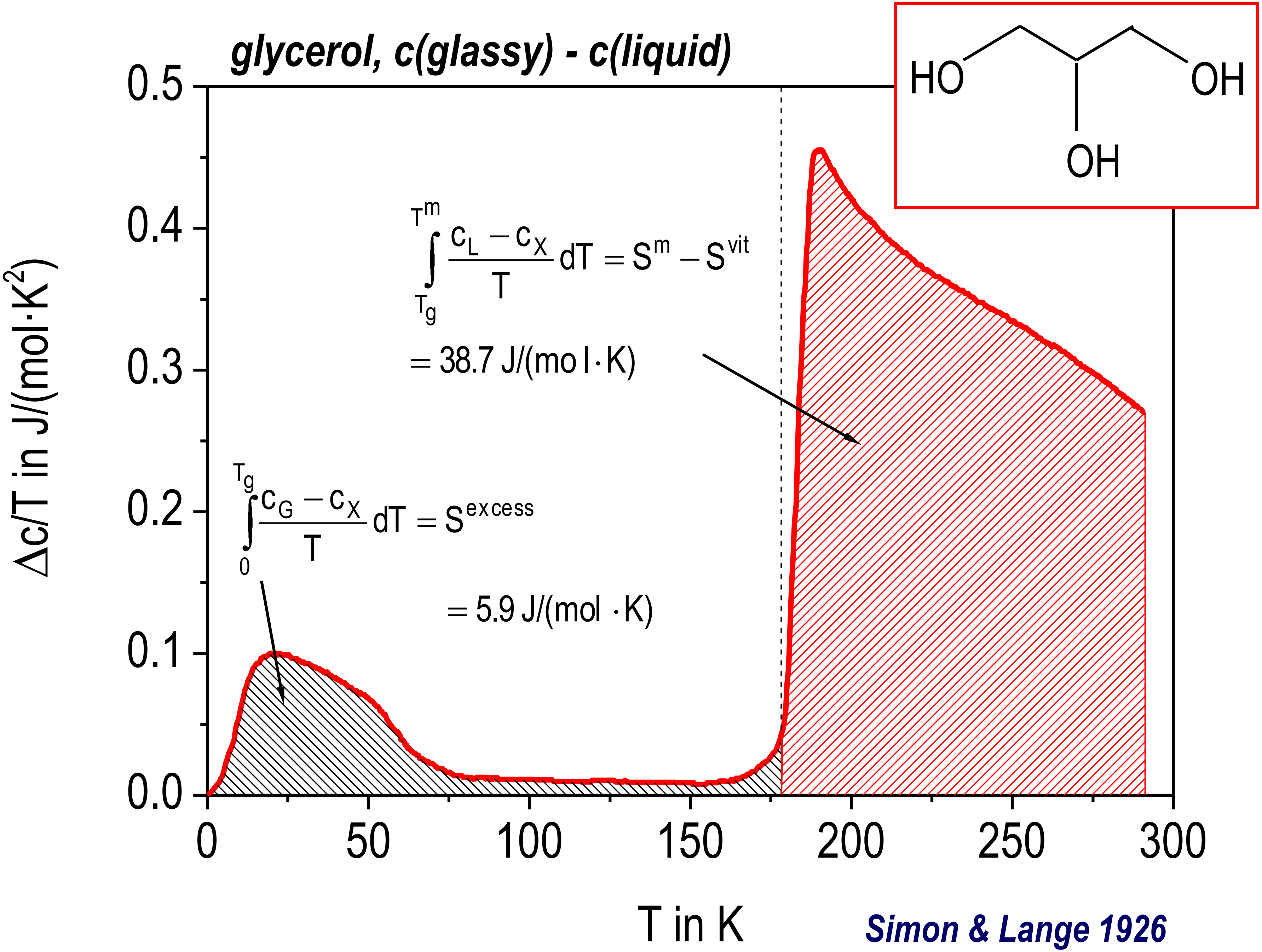
:C≡O: a frozen-in random linear orientation would yield
$\Delta S = -R \ln(½) = 5.76$ J/(mol·K)



a frozen-in random position of D in the molecule would yield
$\Delta S = R \ln(¼) = 11.53$ J/(mol·K)

CO: Clayton & Giauque (1932); CH_3D: Clusius et.al. (1937);
compiled by Wilks (1963); other examples: NO, N_2O, H_2O, D_2O, ...

glycerol, c(glassy) - c(liquid)



$$\int_{T_g}^{T^m} \frac{c_L - c_X}{T} dT = S^m - S^{vit}$$

$$= 38.7 \text{ J/(mol} \cdot \text{K)}$$

$$\int_{0}^{T_g} \frac{c_G - c_X}{T} dT = S^{excess}$$

$$= 5.9 \text{ J/(mol} \cdot \text{K)}$$

Simon & Lange 1926

If c_P data are available for a glass and its isochemical crystal from very low T up to T^m, then the following relations hold:

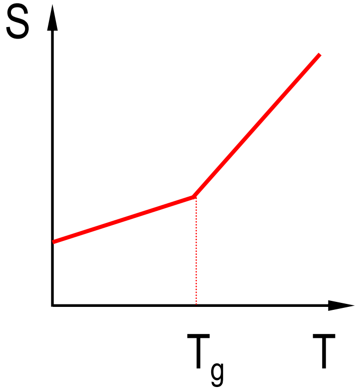
$$\int_0^{T^m+\delta T} \frac{c_{G,L}}{T}\,dT = S_L(T^m) - S_G(0)$$ for the glass,

$$\int_0^{T^m+\delta T} \frac{c_X}{T}\,dT = S^m + S_X(T^m) = S_L(T^m)$$ for the crystal.

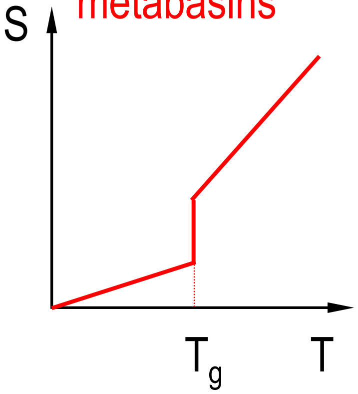
At $T = T^m + \delta T$, both crystal and glass assume the state of eq. liquid. Thus

$$S_G(0) = S_L(T^m) - \int_0^{T^m} \frac{c_{G,L}}{T}\,dT$$

conventional view

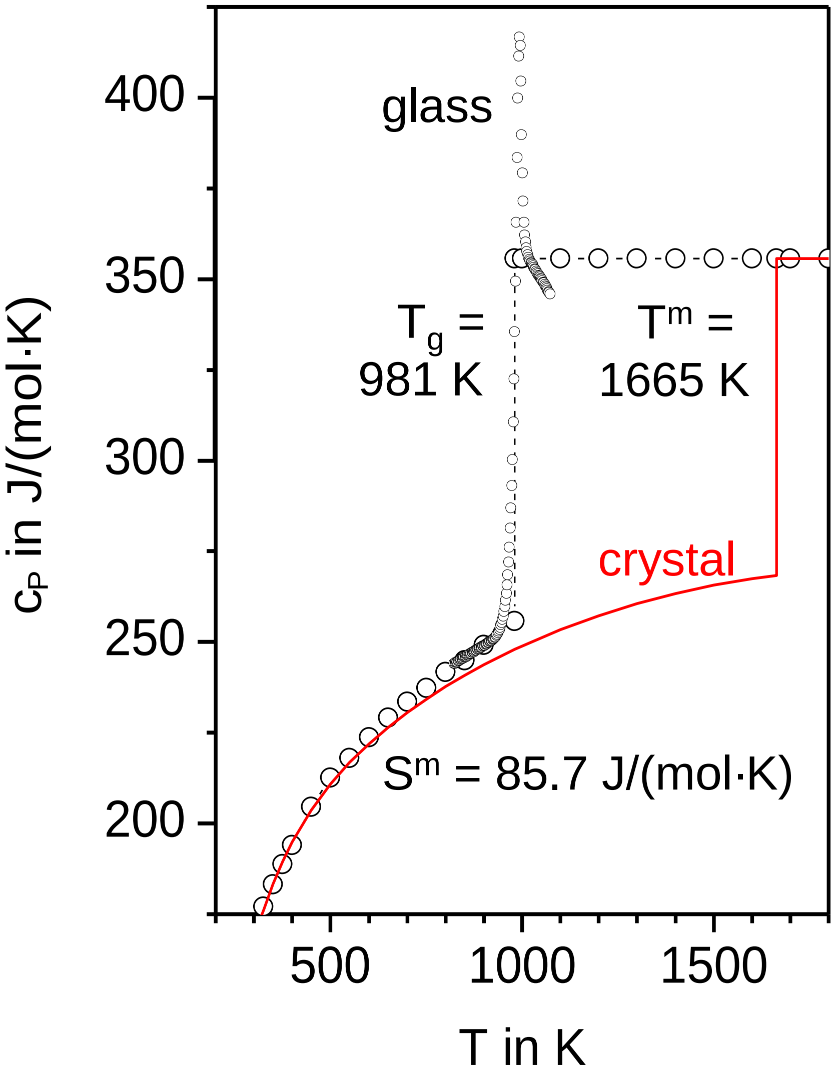


derived via metabasins

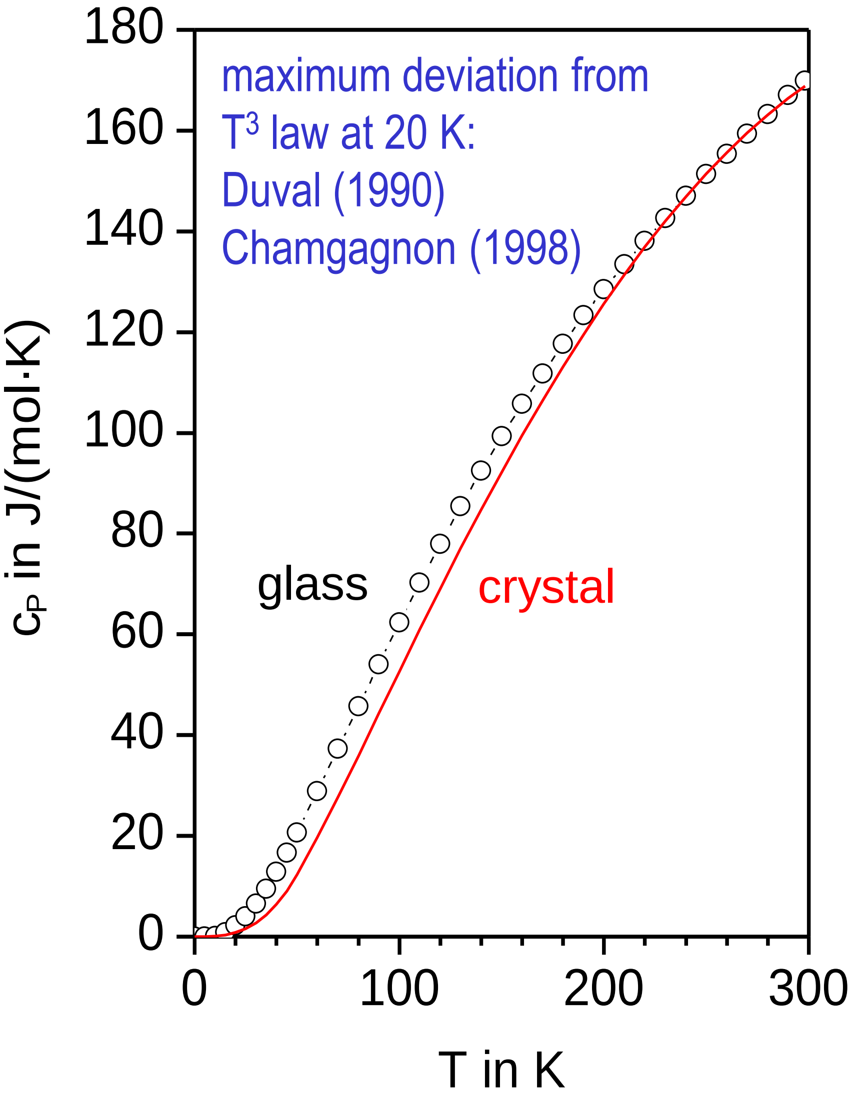


Based on calorimetric data, $S_{glass}(0)$ is found to be > 0. This is the basis of the conventional view of entropy of glasses.

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



Robie et al. (1978); Martens et. al. (1987)
Richet & Bottinga (1995); Courtial et. al. (2000)



maximum deviation from
T^3 law at 20 K:
Duval (1990)
Champagnon (1998)

Krupka, Robie, Hemingway (1985)
Richet, Robie, Heminway (1986)

diopside $CaMg[Si_2O_6]$

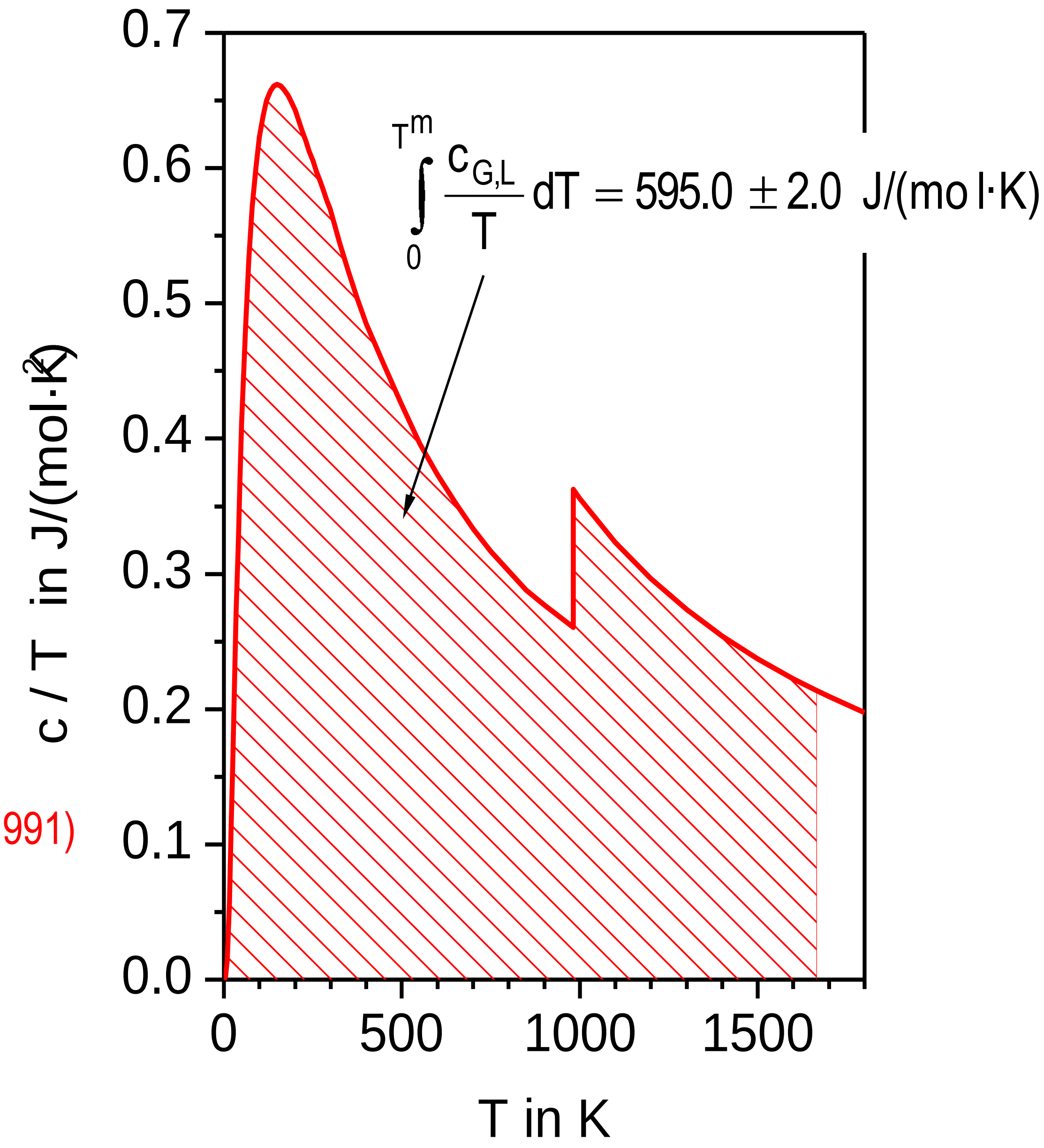
$$S_G(0) = S_L(T^m) - \int_0^{T^m} \frac{c_{G,L}}{T}\,dT$$

$$S_L(T^m) = 619.8 \pm 1.0 \;\; \mathrm{J/(mol\cdot K)}$$ *)

$$\Rightarrow$$

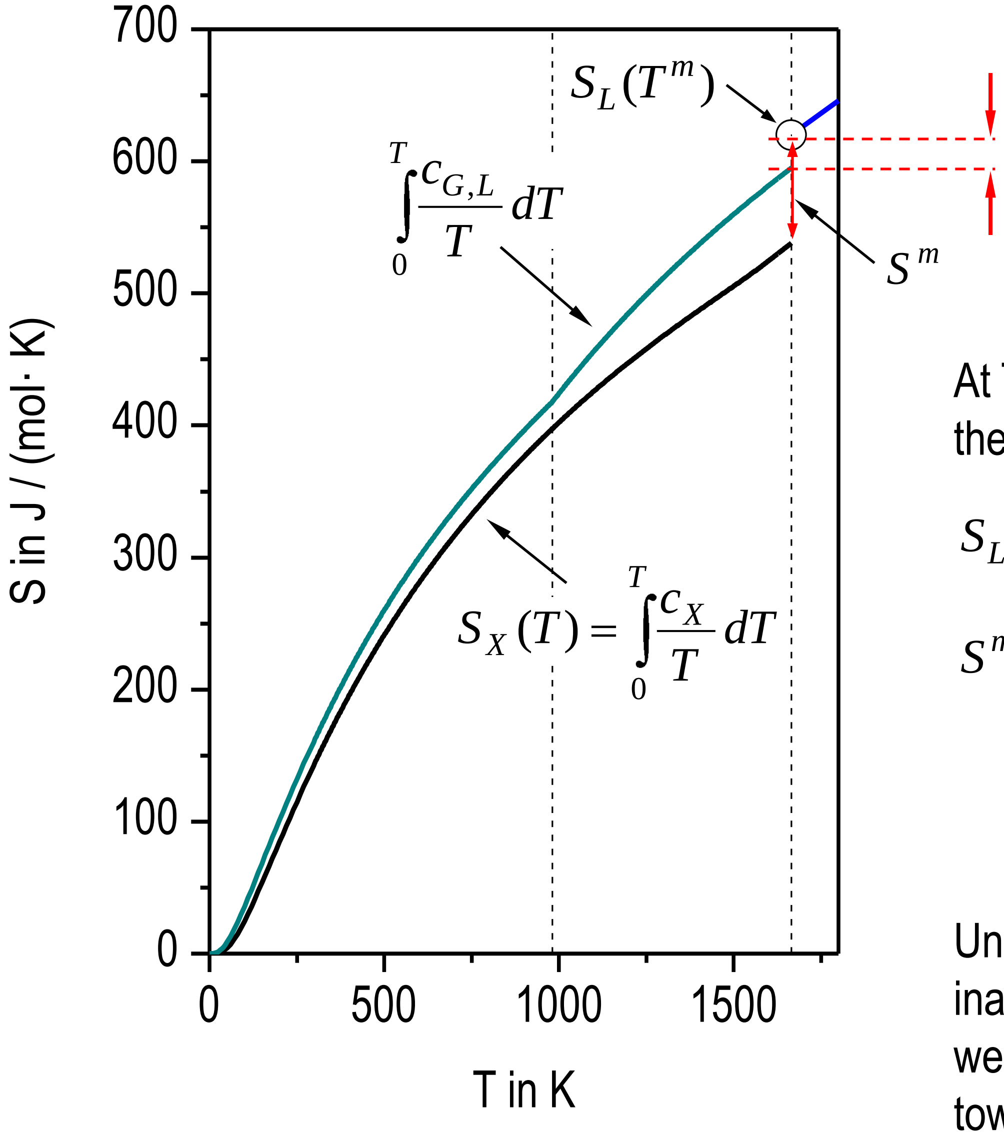
$$S_G(0) = 24.8 \pm 3.0 \;\; \mathrm{J/(mol\cdot K)}$$

*) Knacke, Kubachewski, Hesselmann (1991)



$$\int_0^{T^m} \frac{c_{G,L}}{T}\,dT = 595.0 \pm 2.0 \;\; \mathrm{J/(mol\cdot K)}$$

diopside CaMg[Si$_2$O$_6$]



$$S_L(T^m) - \int_0^{T^m} \frac{c_{G,L}}{T}\,dT = \Delta$$

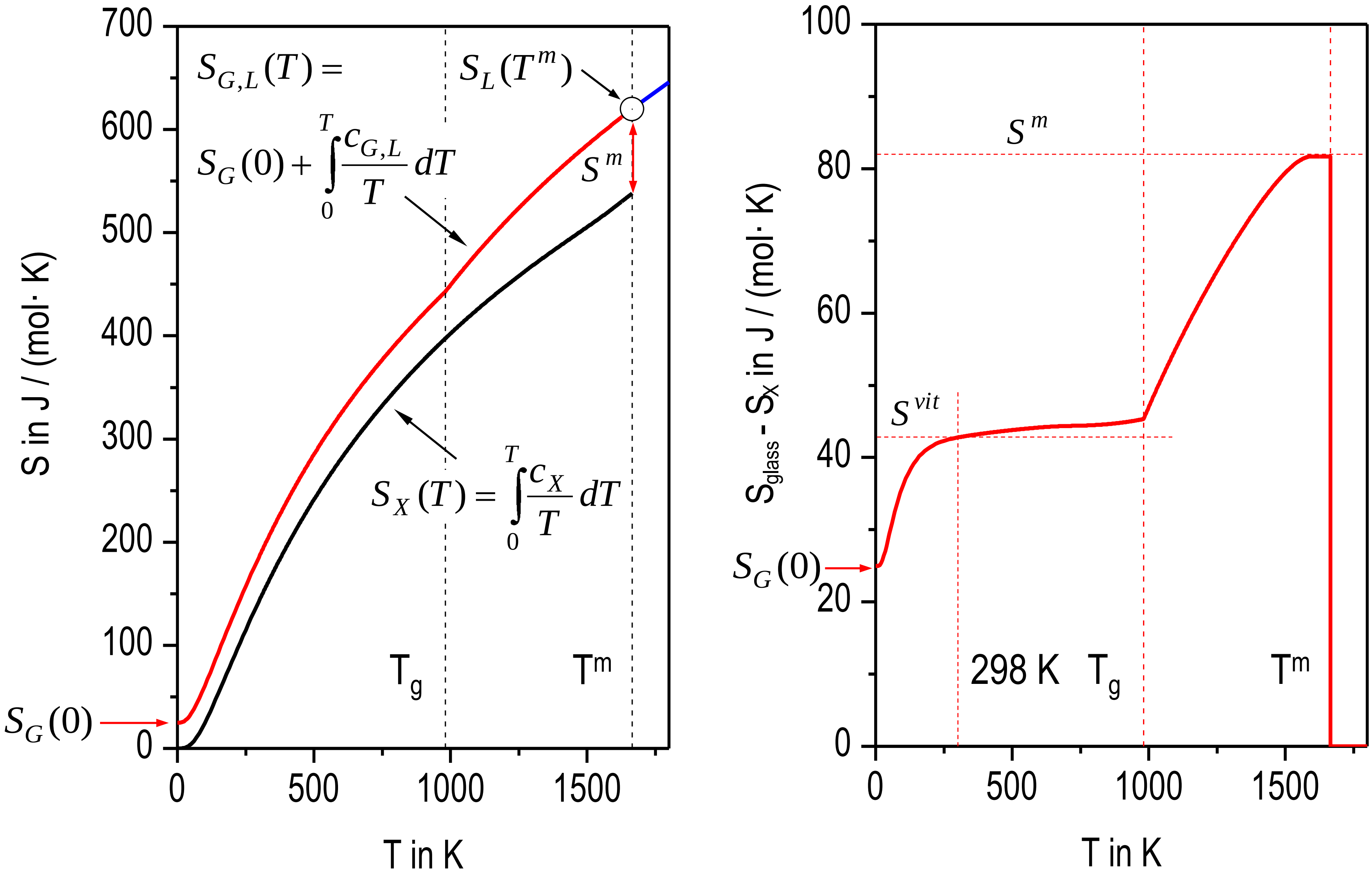
At T^m, both X an G,L must assume the entropy value of the eq. liquid:

$$S_L(T^m) =$$

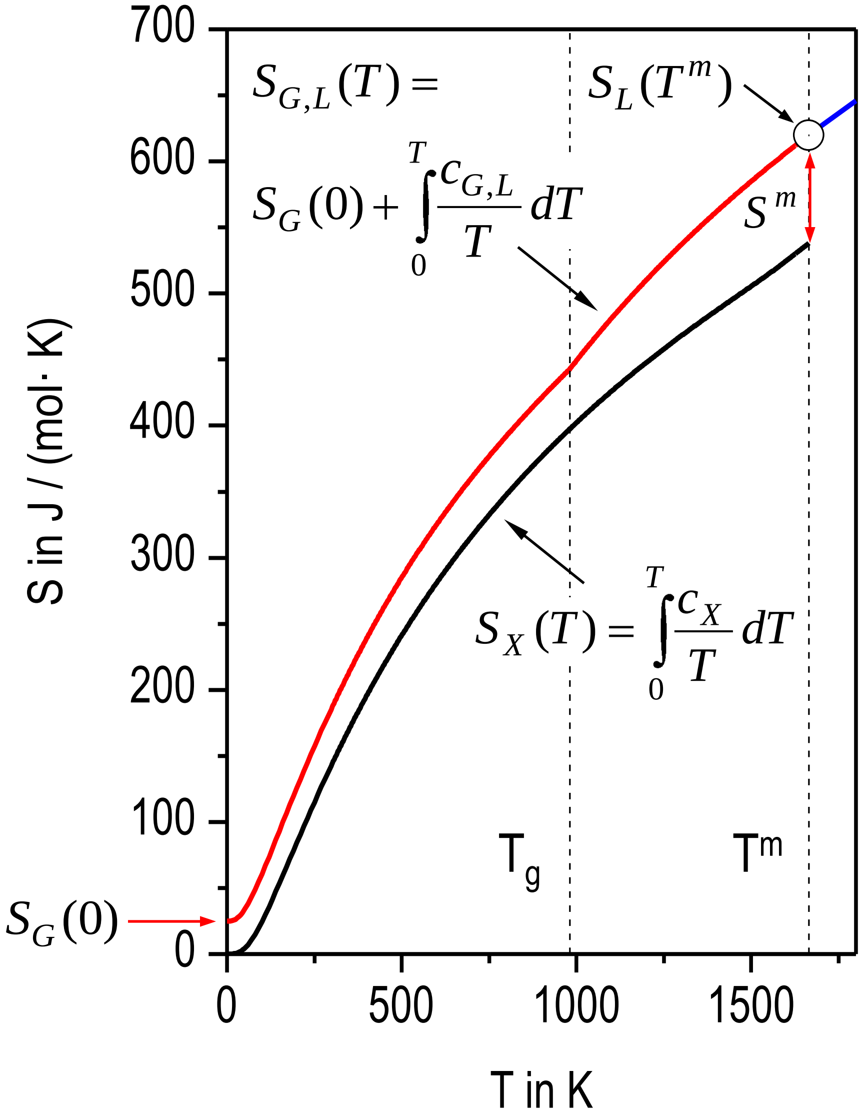
$$S^m + \lim_{T\to T^m}\underbrace{\left(\int_0^T \frac{c_X}{T}\,dT\right)}_{S_X(T)} = \lim_{T\to T^m}\underbrace{\left(\int_0^T \frac{c_{G,L}}{T}\,dT\right)}_{S_{G,L}(T)}$$

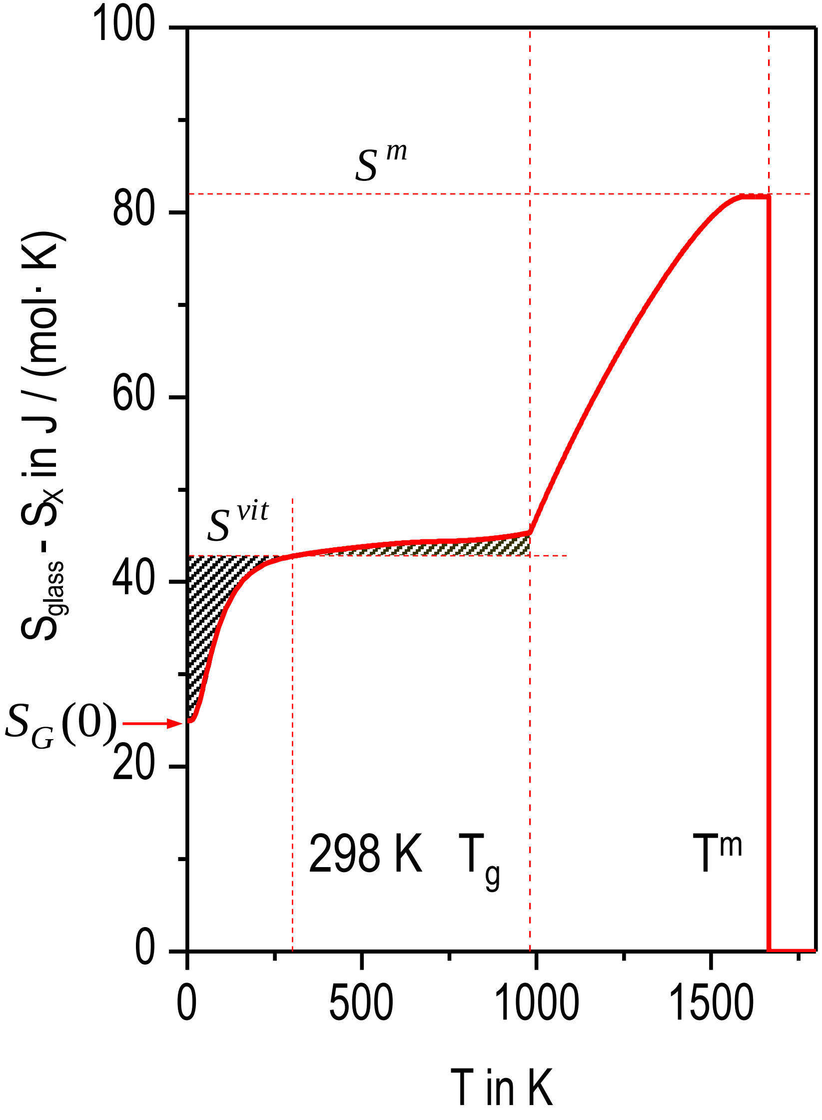
Unless we assume a calorimetrically inaccessible entropy change at T < T^m, we have to shift the green curve by Δ towards the state of the eq. liquid.

diopside $CaMg[Si_2O_6]$

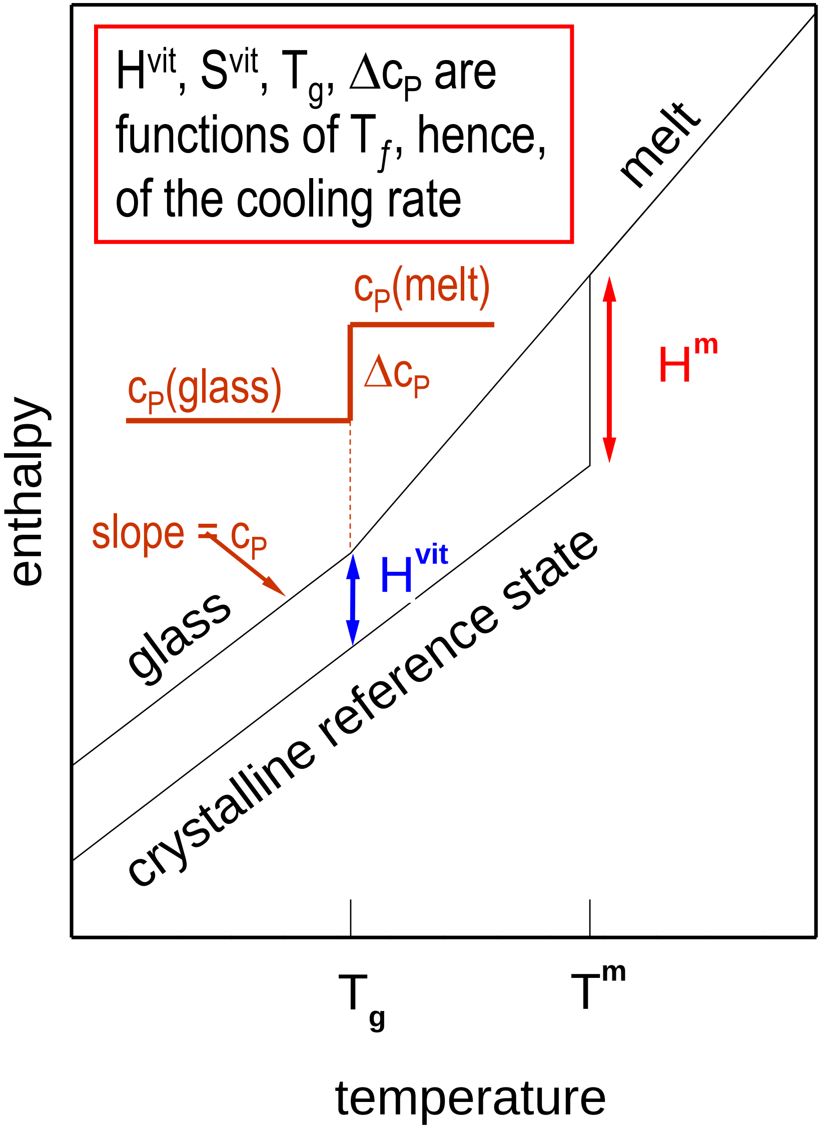


diopside $CaMg[Si_2O_6]$

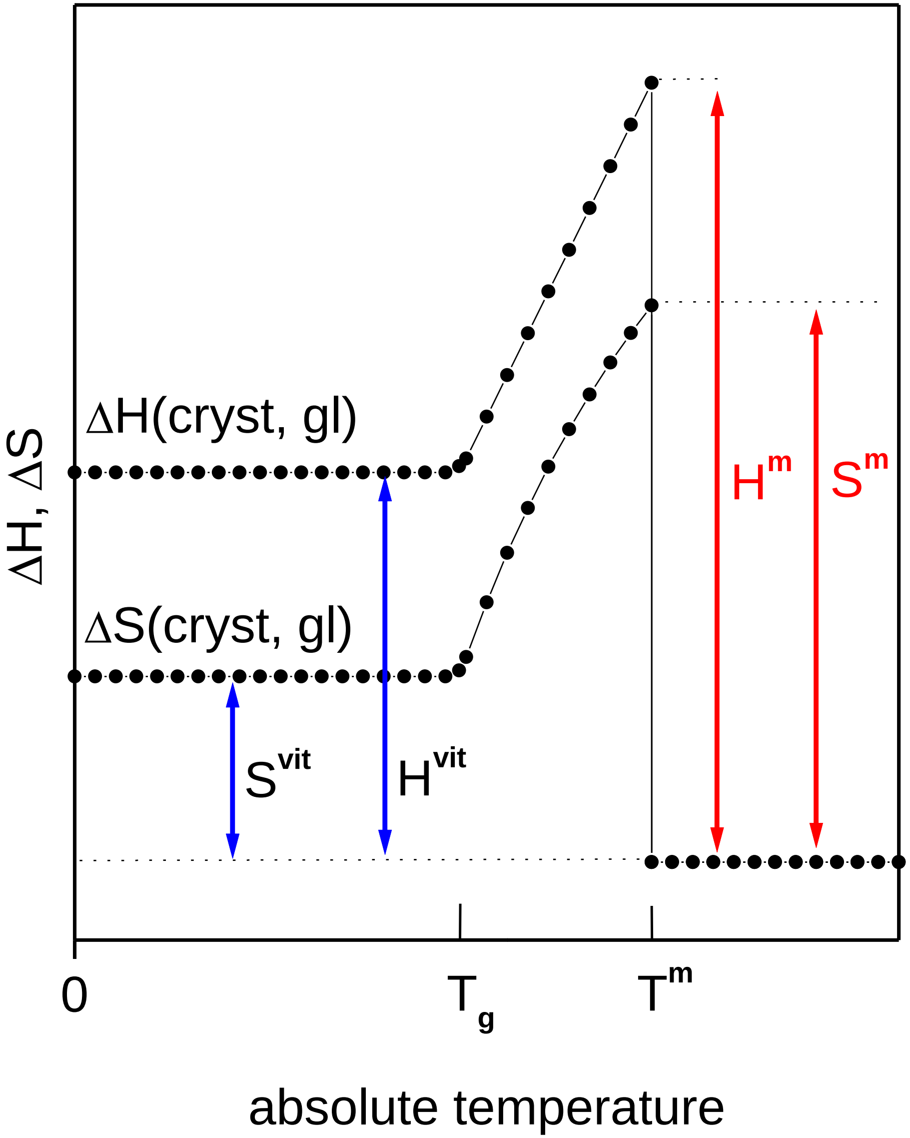


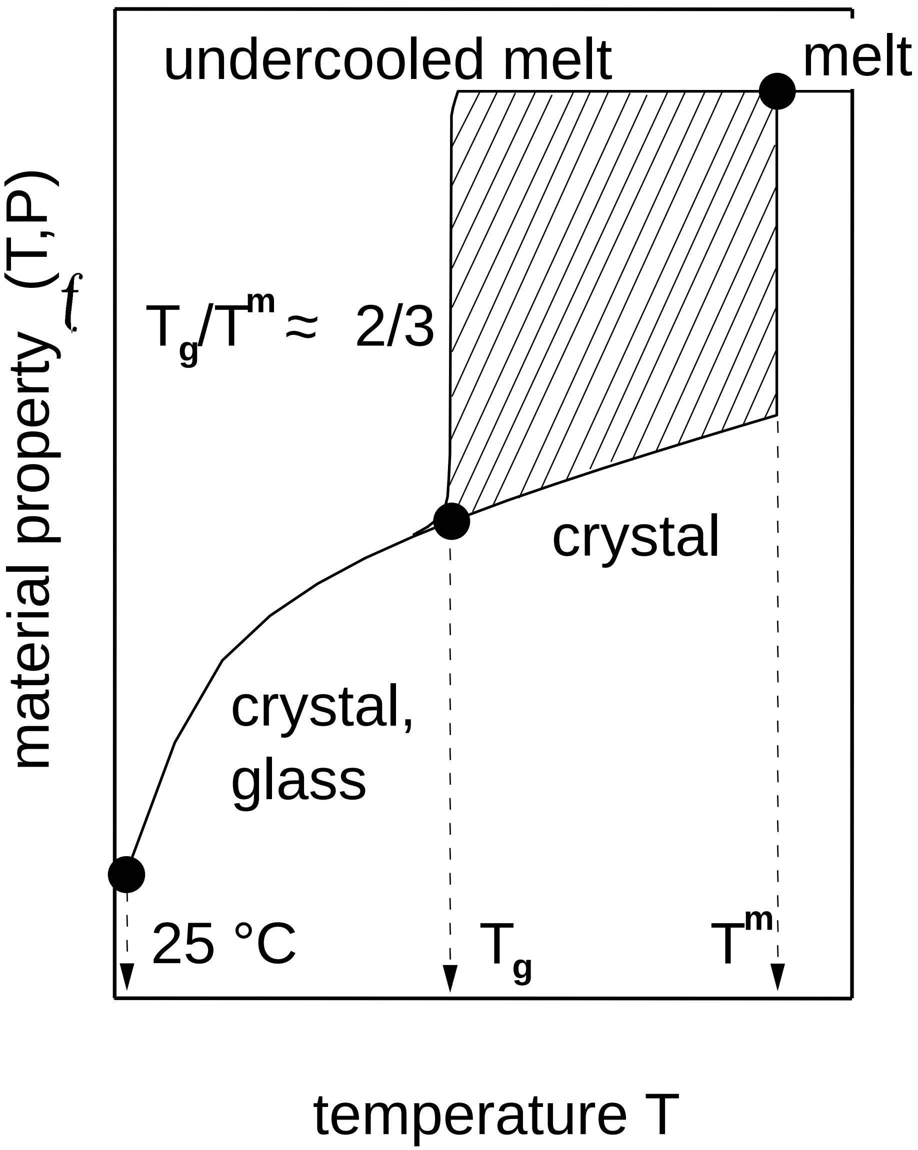


glasses, melts, and the crystalline reference system



H^{vit}, S^{vit}, T_g, Δc_P are functions of T_f, hence, of the cooling rate





$$(G)_{T,P} = \begin{pmatrix} -c_P/T & +V\cdot\alpha_V \\ +V\cdot\alpha_V & -V\cdot\kappa \end{pmatrix}$$

$$c_P = -T\cdot\left(\frac{\partial^2 G}{\partial T^2}\right)_P$$

$$\kappa = -\frac{1}{V}\cdot\left(\frac{\partial^2 G}{\partial P^2}\right)_T$$

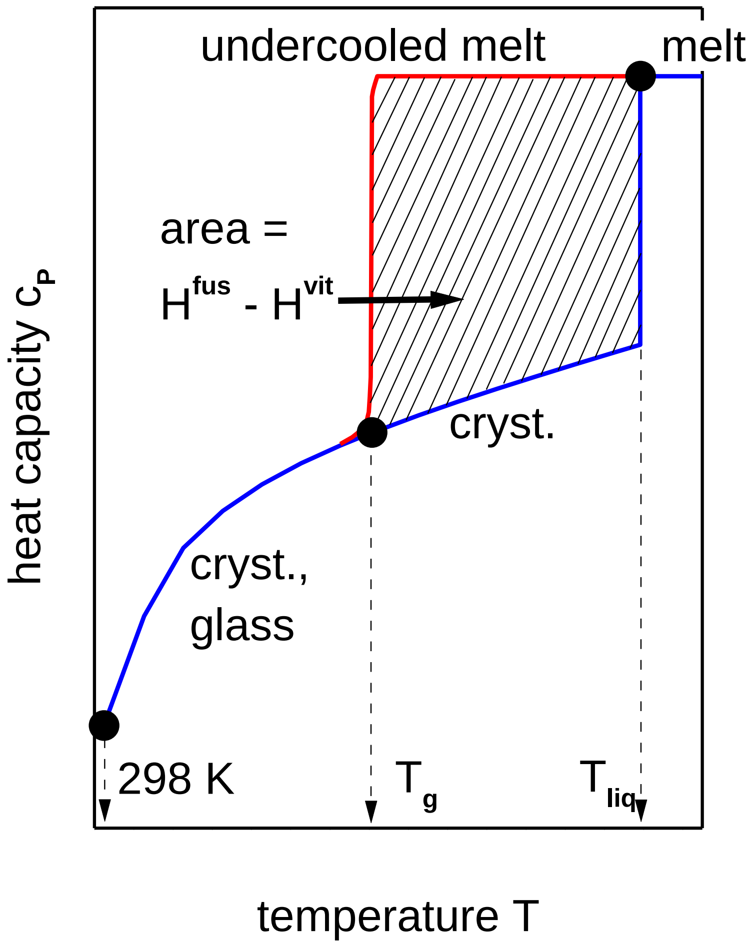
$$\alpha_V = +\frac{1}{V}\cdot\left(\frac{\partial^2 G}{\partial T \partial P}\right)$$

for phases in internal equilibrium:

$$\det(G)_{T,P} = c_P\cdot\kappa\cdot\rho - (\alpha_V)^2\cdot T > 0$$

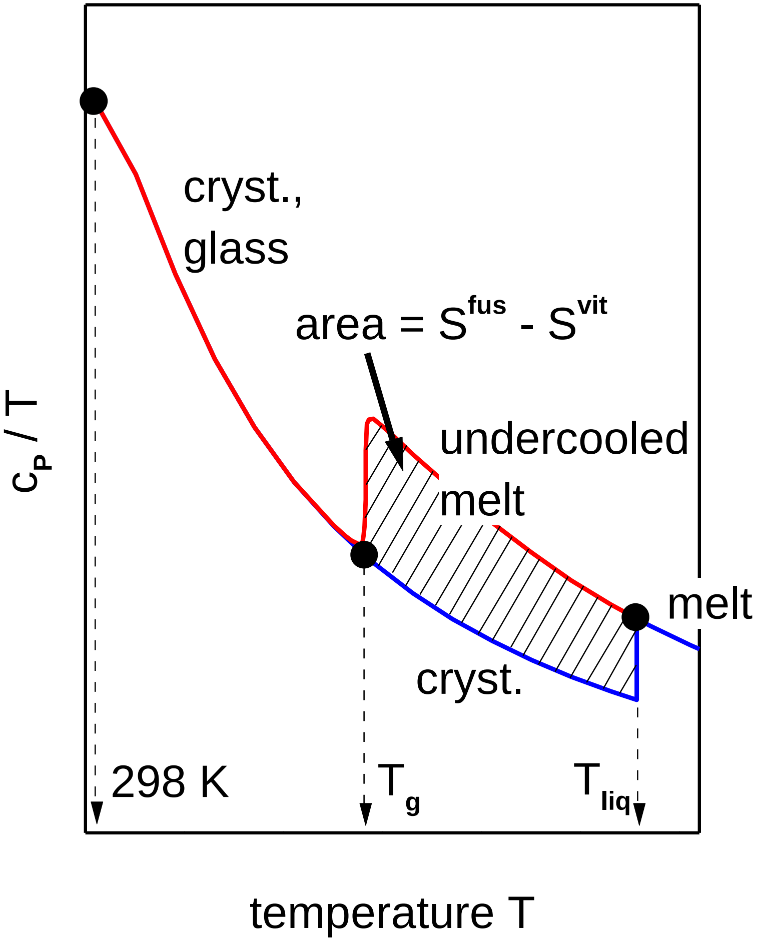
for the glass transition:

$$\Delta c_P\cdot\Delta\kappa\cdot\rho - (\Delta\alpha_V)^2\cdot T > 0$$



$$H_C(T) = \int_{Tg}^{T} \Delta c_P dT$$

$$H^{fus} \approx H^{vit} + \Delta c_P \cdot (T_{liq} - T_g)$$



$$S_C(T) = \int_{Tg}^{T} \frac{\Delta c_P}{T} dT$$

$$S^{fus} \approx S^{vit} + \Delta c_P \cdot \ln \frac{T_{liq}}{T_g}$$

- One-component glasses and glass melts are described in relation to a crystalline reference state by the following data set:
  H^{fus}, S^{fus}, T_{liq}; H^{vit}, S^{vit}, Δc_P, T_g
- The set is redundant: Only 4 out of 7 quantities are independent.
- H^{fus}, S^{fus}, T_{liq} are path-independent equilibrium properties, while H^{vit}, S^{vit}, Δc_P, T_g are path-dependent; they depend on the direction of the path in the (T,P,n_j) space and on the time required to move from state I to state II.

A data set for a one-component glass-forming system thus reads:

H° = standard enthalpy (298 K, 1bar)
for the Xtal stable at T = T_g,
S° = standard entropy (s.a.)
$c_P(T) = A + B \cdot T + C/T^2$

H^{fus} = enthalpy of fusion
S^{fus} = entropy of fusion
T_{liq} = liquidus temperature

$S^{fus} = H^{fus} / T_{liq}$
two independent quantities

H^{vit} = vitrification enthalpy
S^{vit} = vitrification entropy (zero Kelvin entropy)
T_g = glass transition temperature
Δc_P = jump of the heat capacity at T_g

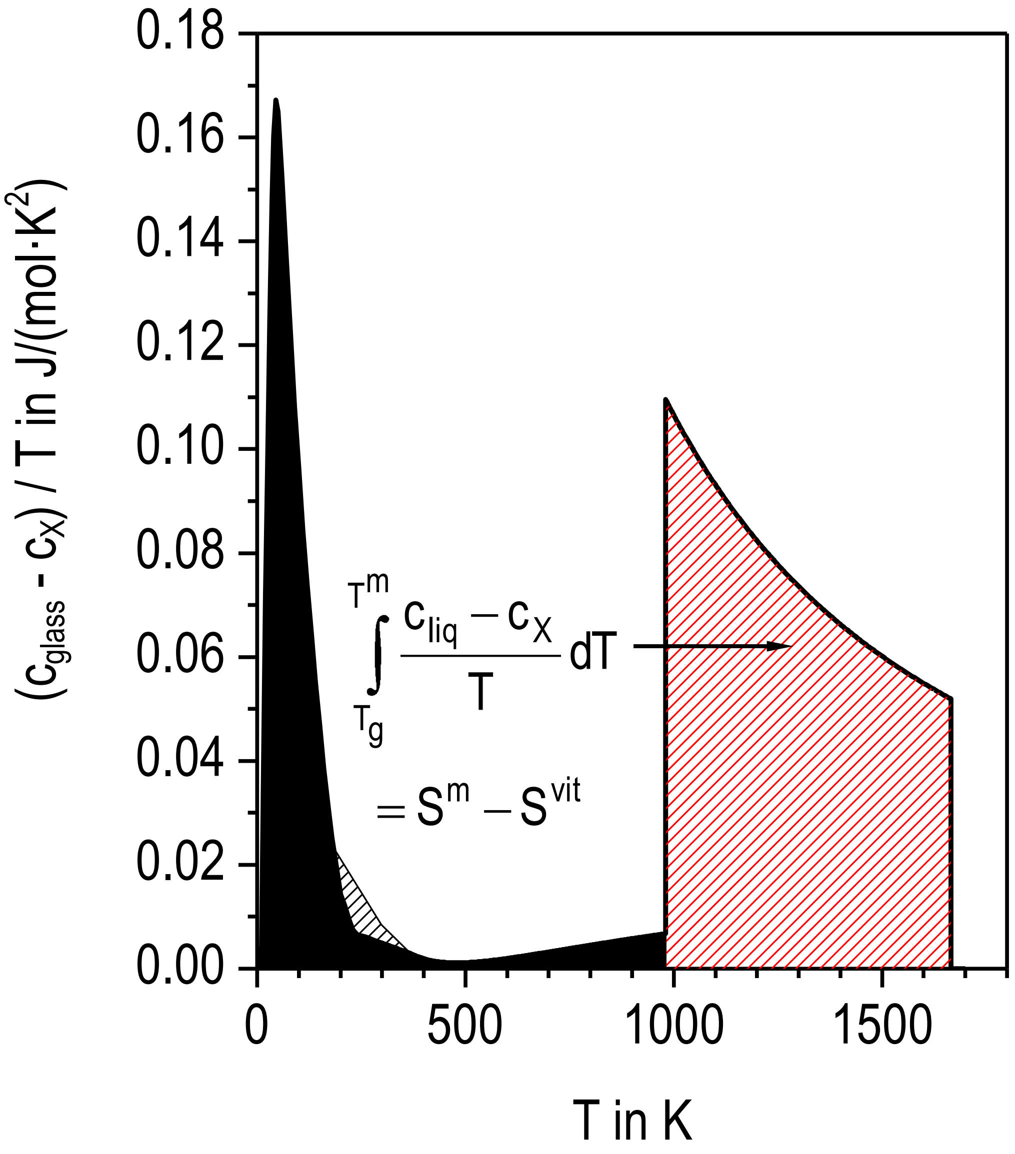
$$H^{vit} \approx H^{fus} - \Delta c_P \cdot (T_{liq} - T_g)$$

$$S^{vit} \approx S^{fus} - \Delta c_P \cdot \ln(T_{liq}/T_g)$$

two independent quantities;
H^{vit}, S^{vit}, T_g, Δc_P are functions of T_f

short excursion: viscosity

diopside $CaMg[Si_2O_6]$



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:

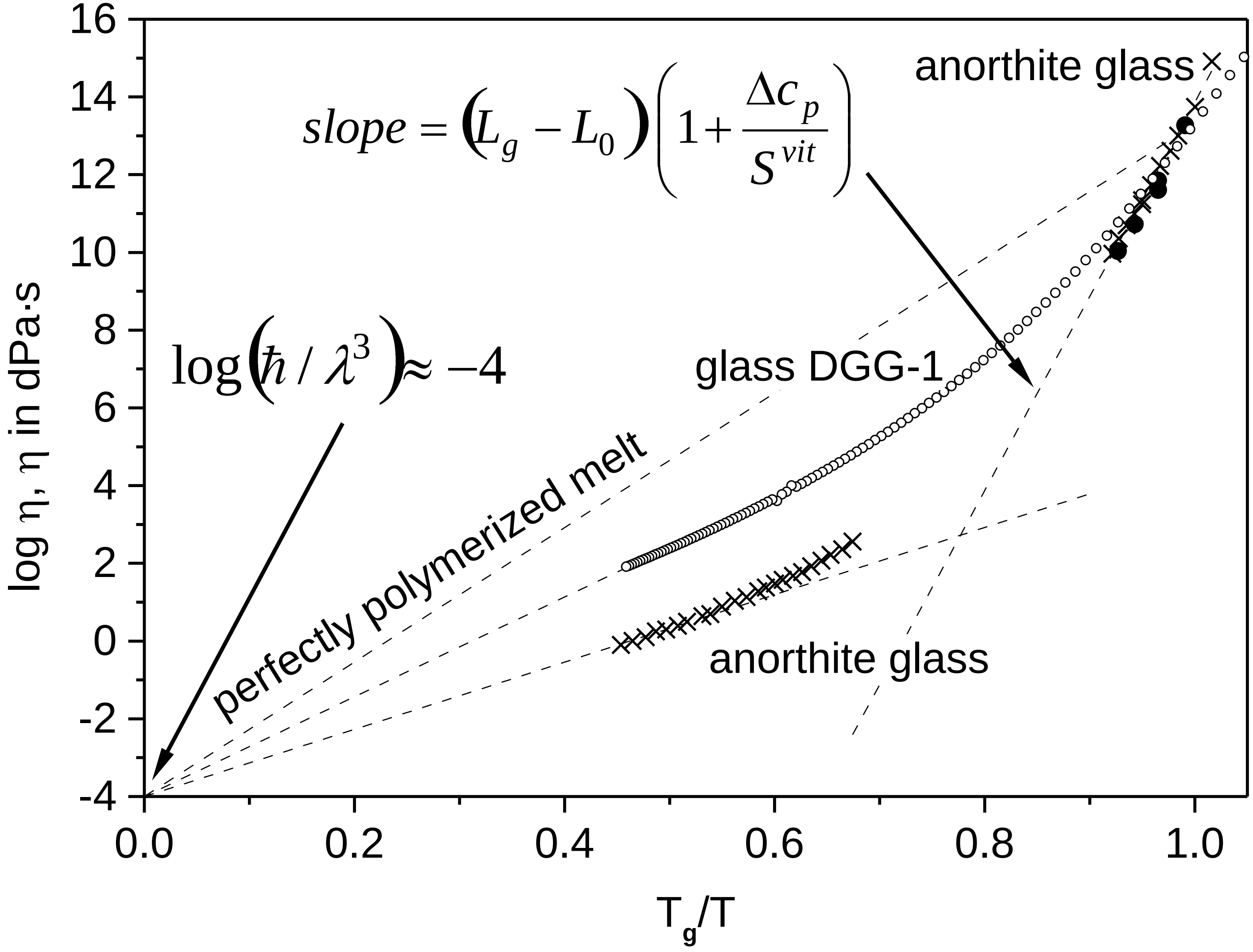
$$L = L_\infty + \frac{C}{T \cdot S_C(T)}; \quad L \equiv \log \eta$$

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

viscosity slope for $T \to T_g$:

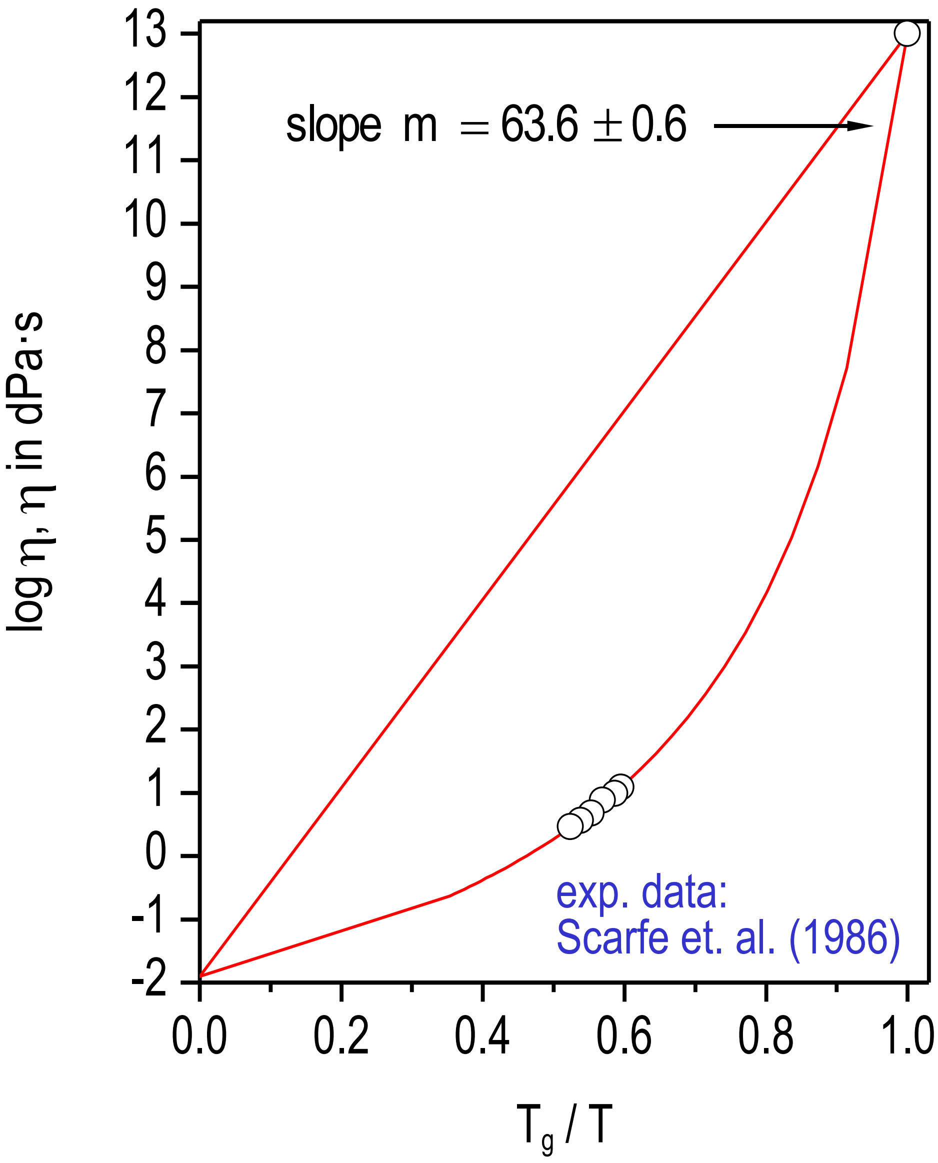
$$\left.\frac{\partial L}{\partial(T_g / T)}\right|_{T=T_g} = \left(L_g - L_\infty\right) \cdot \left(1 + \frac{\Delta c}{S^{vit}}\right)$$

Angell‘s plot of viscosity



high-T limit of diffusion: $D_k^* = \frac{\lambda^2}{3} \cdot \frac{kT}{h}$ Stokes-Einstein: $D_k^* = \frac{kT}{6\pi \cdot \eta \cdot \lambda}$ $\Rightarrow \eta_\infty = \hbar / \lambda^3$

diopside $CaMg[Si_2O_6]$



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

A = -1.899

B = 2493.4

T_0 = 540.6

±δ logη = 0.022

T_g = 708 °C

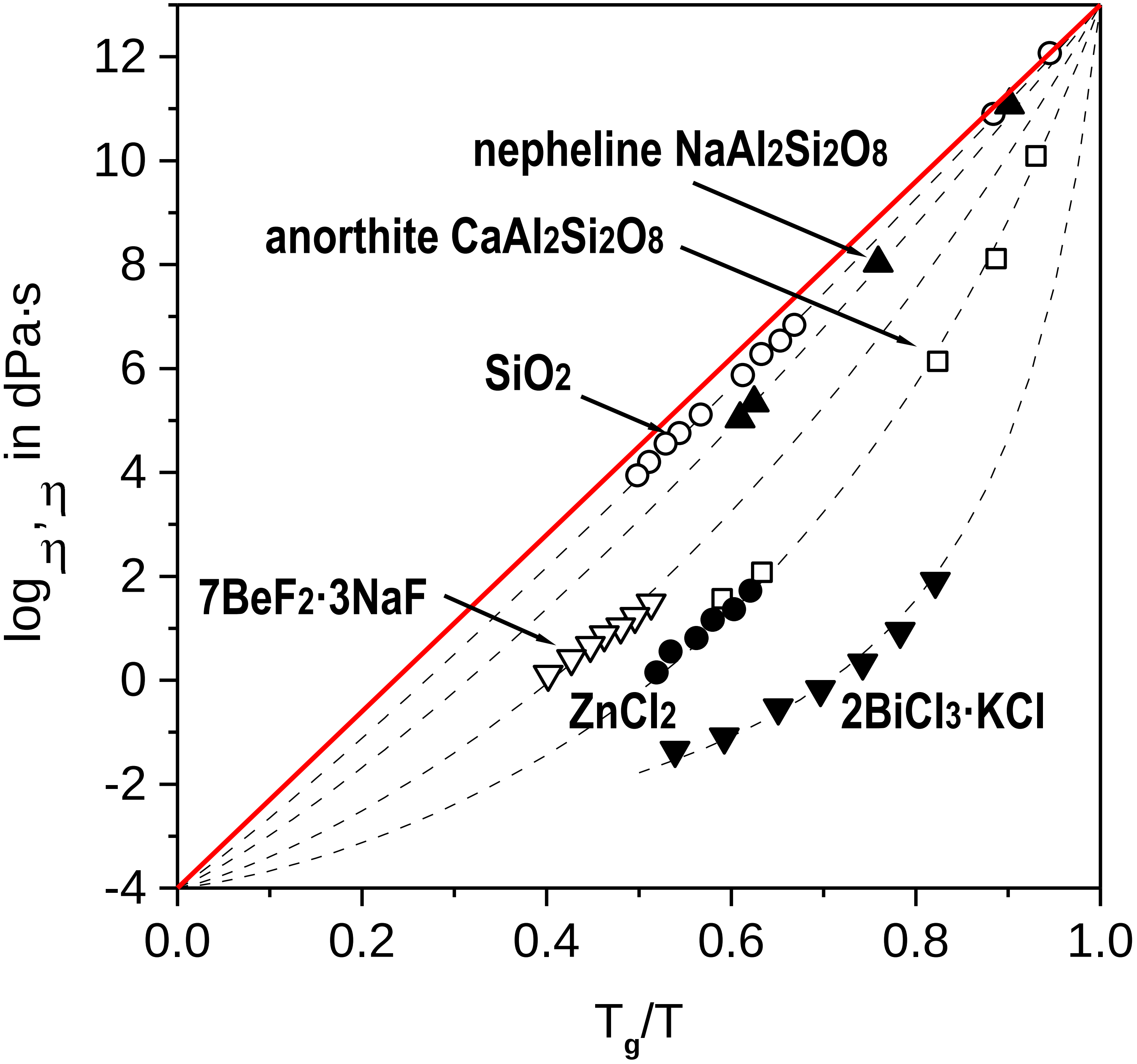
$$\left.\frac{\partial \log\eta}{\partial T_g / T}\right|_{T=T_g} = \frac{T_g \cdot B}{(T - T_0)^2} = m$$

$\Rightarrow$ 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 J/(mol·K)

$\Rightarrow$ m = 63.0

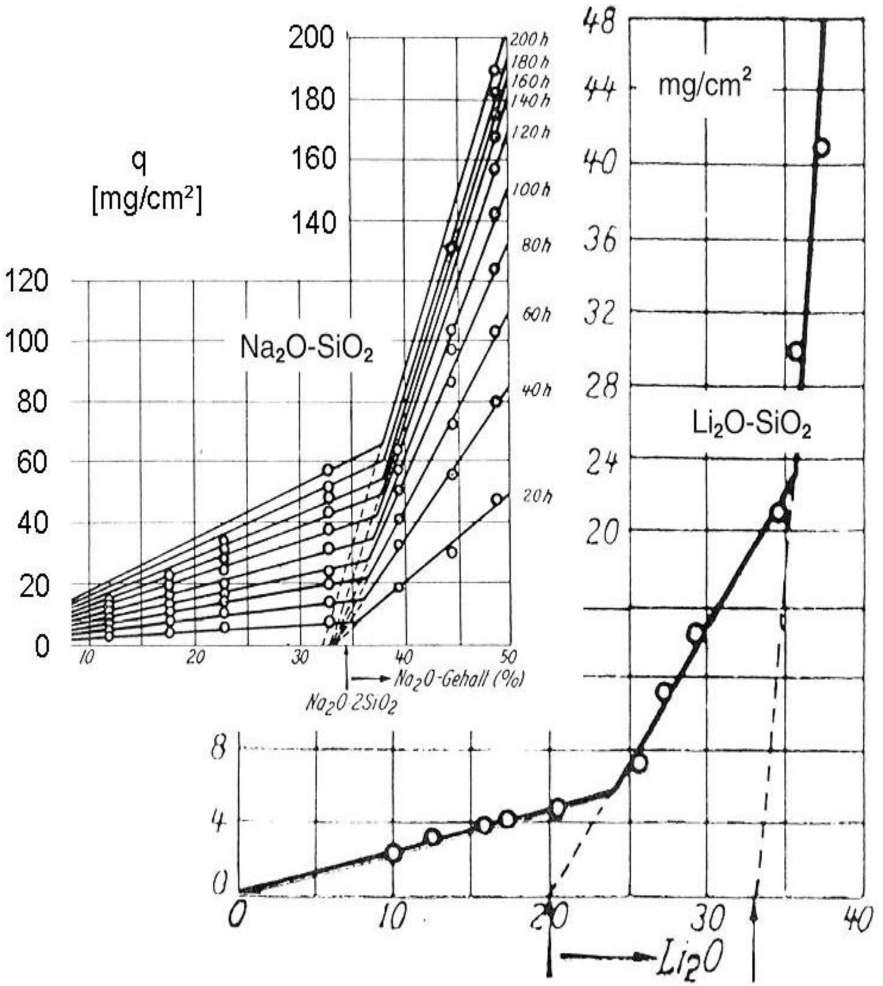


12
10
8
6
4
2
0
-2
-4
0.0
0.2
0.4
0.6
0.8
1.0
log η', η in dPa·s
Tg/T
nepheline NaAl2Si2O8
anorthite CaAl2Si2O8
SiO2
7BeF2·3NaF
ZnCl2
2BiCl3·KCl

the crystalline reference system

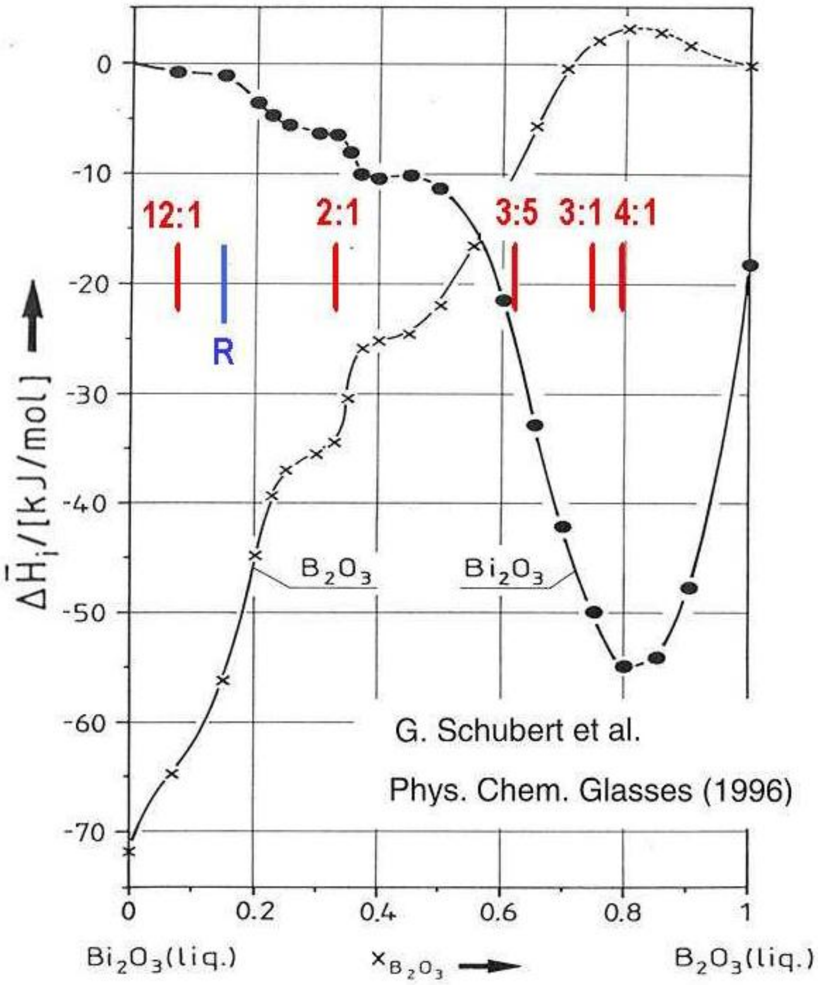
reflections of solid state phase relations clearly seen in the properties of high-T liquids:

evaporation loss by transpiration method



W.E.S. Turner, 1934

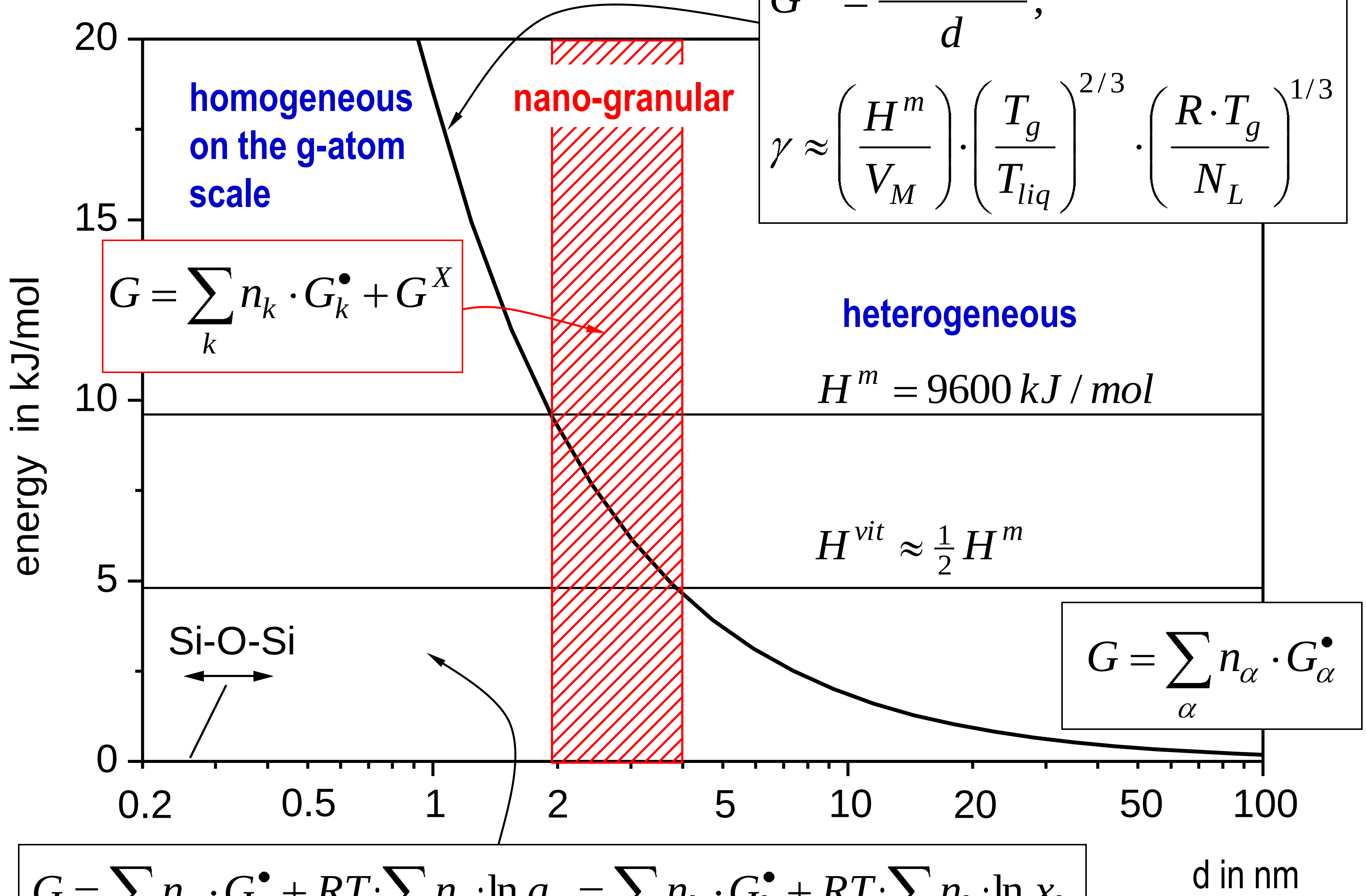
solution calorimetry



G. Schubert et al.
Phys. Chem. Glasses (1996)

see also: Na_2O-MoO_3, -WO_3, -V_2O_3; PbO-B_2O_3
Kaufmann, 2000

glasses, melts, and M.R.O.



$$G^X = \frac{6 \cdot \gamma \cdot V_M}{d};$$

$$\gamma \approx \left(\frac{H^m}{V_M}\right) \cdot \left(\frac{T_g}{T_{liq}}\right)^{2/3} \cdot \left(\frac{R \cdot T_g}{N_L}\right)^{1/3}$$

homogeneous on the g-atom scale

nano-granular

heterogeneous

$$G = \sum_k n_k \cdot G_k^\bullet + G^X$$

$$H^m = 9600\, kJ / mol$$

$$H^{vit} \approx \tfrac{1}{2} H^m$$

Si-O-Si

$$G = \sum_\alpha n_\alpha \cdot G_\alpha^\bullet$$

$$G = \sum_j n_j \cdot G_j^\bullet + RT \cdot \sum_j n_j \cdot \ln a_j = \sum_k n_k \cdot G_k^\bullet + RT \cdot \sum_j n_k \cdot \ln x_k$$

$$H^{\circ}_{glass} = \sum_{k} n_k \cdot (H^{\circ}_k + H^{vit}_k)$$

$$H^{\circ}_{1673,liq} = \sum_{k} n_k \cdot H^{\circ}_{1673,liq,k}$$

$$S^{\circ}_{glass} = \sum_{k} n_k \cdot (S^{\circ}_k + S^{vit}_k)$$

$$S^{\circ}_{1673,liq} = \sum_{k} n_k \cdot S^{\circ}_{1673,liq,k}$$

$$c_{P,liq} = \sum_{k} n_k \cdot c_{P,liq,k}$$

$$H_{T,liq} = H^{\circ}_{1673,liq} + c_{P,liq} \cdot (T - 1673)$$

$$S_{T,liq} = S^{\circ}_{1673,liq} + c_{P,liq} \cdot ln(T / 1673)$$

$$\Delta H_{T,liq} = H_{T,liq} - H^{\circ}_{glass}$$

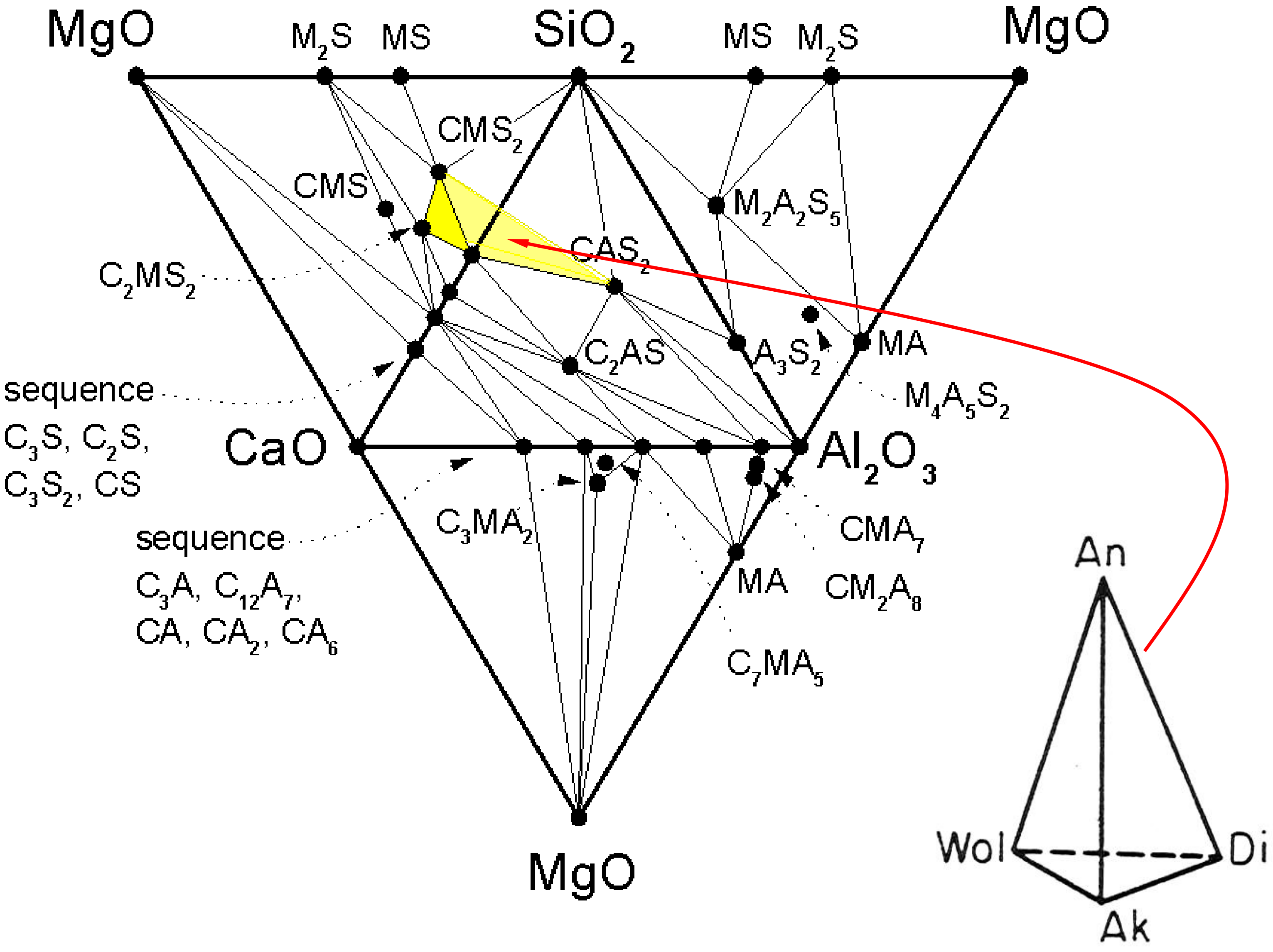
$$ln\ a_j = \sum_{k} \left[A_{jk} \cdot \frac{G^{\circ}_k}{RT} \right] - \frac{G^{\circ}_j}{RT}$$

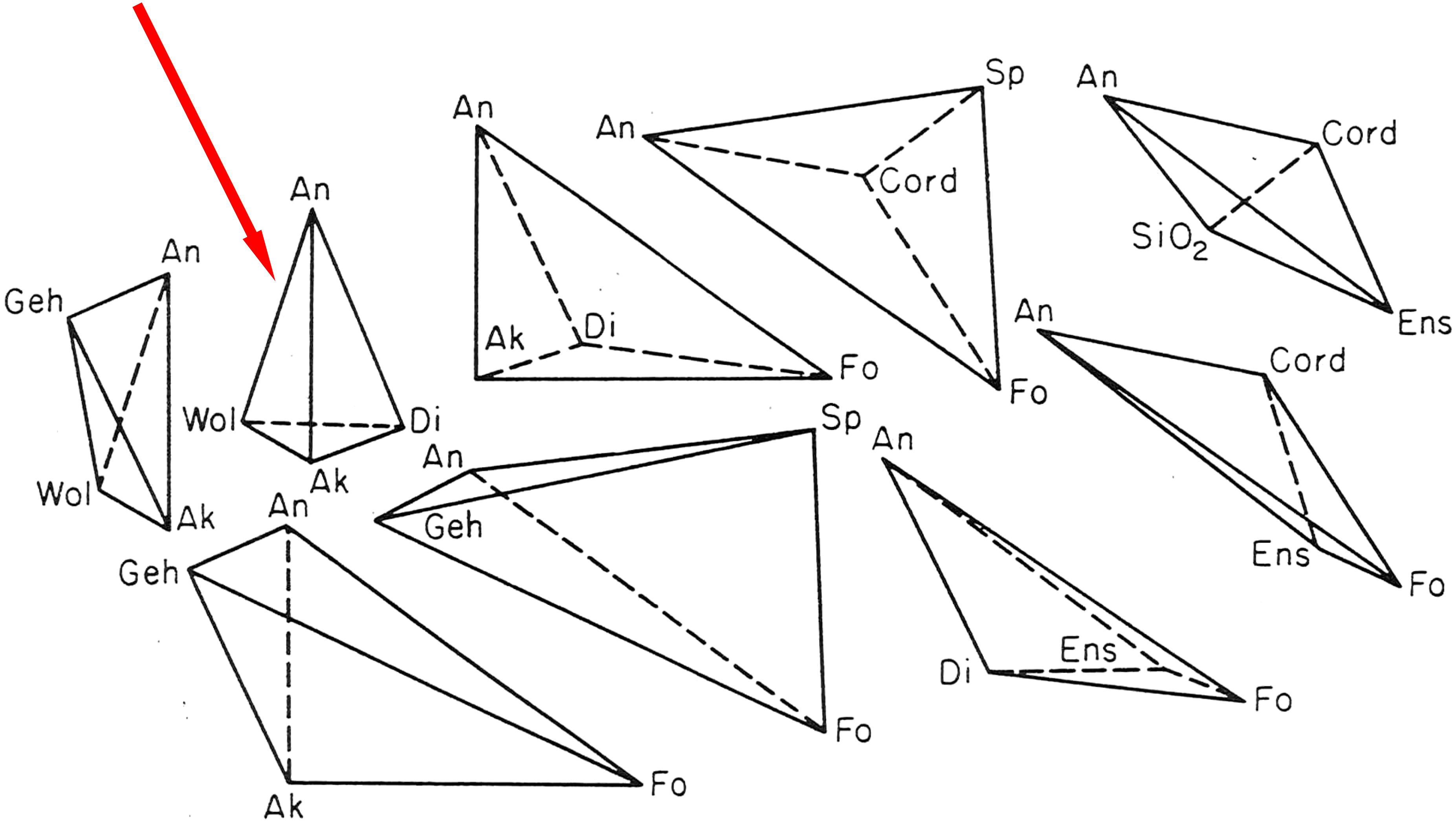
k	-H°	S°	H^{vit}	S^{vit}	$-H_{1673,liq}$	$S_{1673,liq}$	$c_{P,liq}$
$P_2O_5 \cdot 3CaO$	4117.1	236.0	135.1	51.5	3417.1	898.7	324.3
P_2O_5	1492.0	114.4	18.2	9.5	1138.5	586.6	181.6
Fe_2O_3	823.4	87.4	45.2	17.2	550.2	370.3	142.3
$FeO \cdot Fe_2O_3$	1108.8	151.0	82.8	31.4	677.8	579.9	213.4
$FeO \cdot SiO_2$	1196.2	92.8	36.7	13.8	962.3	342.7	139.7
$2FeO \cdot SiO_2$	1471.1	145.2	55.2	20.5	1118.8	512.1	240.6
$MnO \cdot SiO_2$	1320.9	102.5	40.2	15.1	1085.3	345.2	151.5
$2ZnO \cdot SiO_2$	1643.1	131.4	82.4	31.4	1261.1	494.5	174.5
$ZrO_2 \cdot SiO_2$	2034.7	84.5	86.6	32.6	1686.2	381.2	149.4
$CaO \cdot TiO_2$	1660.6	93.7	67.4	25.5	1365.7	360.2	124.7
$BaO \cdot Al_2O_3 \cdot 2SiO_2$	4222.1	236.8	130.5	95.4	3454.3	1198.3	473.2
$BaO \cdot 2SiO_2$	2553.1	154.0	81.6	26.8	2171.1	533.5	241.4
$BaO \cdot SiO_2$	1618.0	104.6	56.5	41.0	1349.8	361.1	146.4
$Li_2O \cdot Al_2O_3 \cdot 4SiO_2$	6036.7	308.8	184.1	12.1	5235.4	1173.2	498.7
$Li_2O \cdot SiO_2$	1648.5	79.9	16.7	6.3	1416.7	339.7	167.4
$K_2O \cdot Al_2O_3 \cdot 6SiO_2$	7914.0	439.3	106.3	29.3	6924.9	1559.4	765.7
$K_2O \cdot Al_2O_3 \cdot 2SiO_2$	4217.1	266.1	80.4	22.1	3903.7	666.5	517.6
$K_2O \cdot 4SiO_2$	4315.8	265.7	26.4	21.3	3697.8	983.7	410.0
$K_2O \cdot 2SiO_2$	2508.7	190.6	12.6	23.9	2153.1	595.4	275.3
$Na_2O \cdot Al_2O_3 \cdot 6SiO_2$	7841.2	420.1	125.0	28.4	6870.1	1512.5	648.1
$Na_2O \cdot Al_2O_3 \cdot 2SiO_2$	4163.5	248.5	92.0	27.9	3614.1	856.9	423.8

kJ/mol;
J/(mol·K)

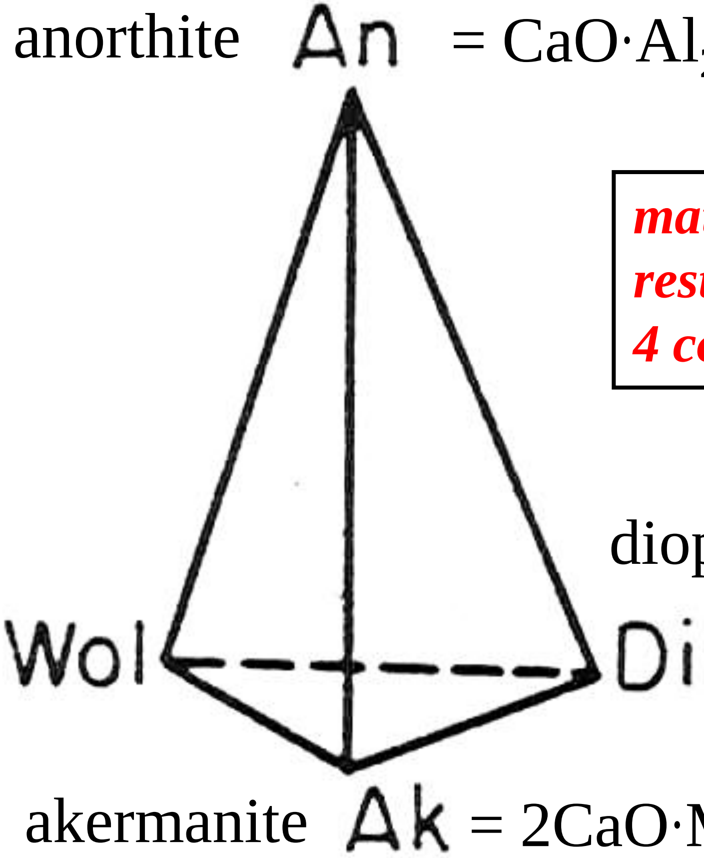
k	-H°	S°	H^{vit}	S^{vit}	$-H_{1673,liq}$	$S_{1673,liq}$	$c_{P,liq}$
B_2O_3	1273.5	54.0	18.2	11.3	1088.7	271.1	129.7
$Na_2O\cdot B_2O_3\cdot 4SiO_2$	5710.9	270.0	42.7	21.1	4988.0	1090.2	637.6
$Na_2O\cdot 4B_2O_3$	5902.8	276.1	58.3	40.1	4986.7	1275.5	704.2
$Na_2O\cdot 2B_2O_3$	3284.9	189.5	48.8	26.6	2735.9	780.3	444.8
$Na_2O\cdot B_2O_3$	1958.1	147.1	43.6	19.5	1585.7	538.7	292.9
$2MgO\cdot 2Al_2O_3\cdot 5SiO_2$	9113.2	407.1	135.8	41.4	7994.8	1606.2	1031.8
$MgO\cdot SiO_2$	1548.5	67.8	46.6	13.6	1318.0	296.2	146.4
$2MgO\cdot SiO_2$	2176.9	95.4	61.4	11.0	1876.1	402.9	205.0
$CaO\cdot MgO\cdot 2SiO_2$	3202.4	143.1	92.3	25.7	2733.4	621.7	355.6
$2CaO\cdot MgO\cdot 2SiO_2$	3876.9	209.2	106.7	32.0	3319.2	775.3	426.8
$CaO\cdot Al_2O_3\cdot 2SiO_2$	4223.7	202.5	103.0	37.7	3628.8	791.2	380.7
$2CaO\cdot Al_2O_3\cdot SiO_2$	3989.4	198.3	129.9	49.4	3374.0	787.8	299.2
$3Al_2O_3\cdot 2SiO_2$	6820.8	274.9	188.3	71.5	5816.2	1231.8	523.4
$CaO\cdot SiO_2$	1635.1	83.1	49.8	18.8	1382.0	329.7	146.4
$2CaO\cdot SiO_2$	2328.4	120.5	101.3	38.5	1868.2	509.2	174.5
$Na_2O\cdot 2SiO_2$	2473.6	164.4	29.3	13.2	2102.5	588.7	261.1
$Na_2O\cdot SiO_2$	1563.1	113.8	37.7	9.8	1288.3	415.1	179.1
$Na_2O\cdot 3CaO\cdot 6SiO_2$	8363.8	461.9	77.3	20.5	7372.6	1555.6	786.6
$Na_2O\cdot 2CaO\cdot 3SiO_2$	4883.6	277.8	57.7	13.4	4240.9	990.4	470.3
$2Na_2O\cdot CaO\cdot 3SiO_2$	4763.0	309.6	87.0	22.6	4029.6	1107.9	501.2
SiO_2	908.3	43.5	6.9	4.0	809.6	157.3	86.2

kJ/mol;
J/(mol·K)


MgO
M_2S
MS
SiO_2
MS
M_2S
MgO
CMS_2
CMS
$M_2A_2S_5$
CAS_2
C_2MS_2
C_2AS
A_3S_2
MA
sequence
C_3S, C_2S,
C_3S_2, CS
$M_4A_5S_2$
CaO
Al_2O_3
C_3MA_2
CMA_7
sequence
C_3A, $C_{12}A_7$,
CA, CA_2, CA_6
MA
CM_2A_8
C_7MA_5
MgO
An
Wol
Di
Ak


Geh
An
Wol
Ak
An
Wol
Di
Ak
An
Ak
Di
Fo
An
Sp
Cord
Fo
An
Cord
SiO$_2$
Ens
An
Cord
Ens
Fo
Sp
An
Geh
Fo
An
Geh
Ak
Fo
An
Ens
Di
Fo

anorthite An $= CaO \cdot Al_2O_3 \cdot 2SiO_2$



matrix calculation is not resticted to spaces with 4 components only!

wollastonite

$CaO \cdot SiO_2 =$ Wol

diopside

Di $= CaO \cdot MgO \cdot 2SiO_2$

akermanite Ak $= 2CaO \cdot MgO \cdot 2SiO_2$

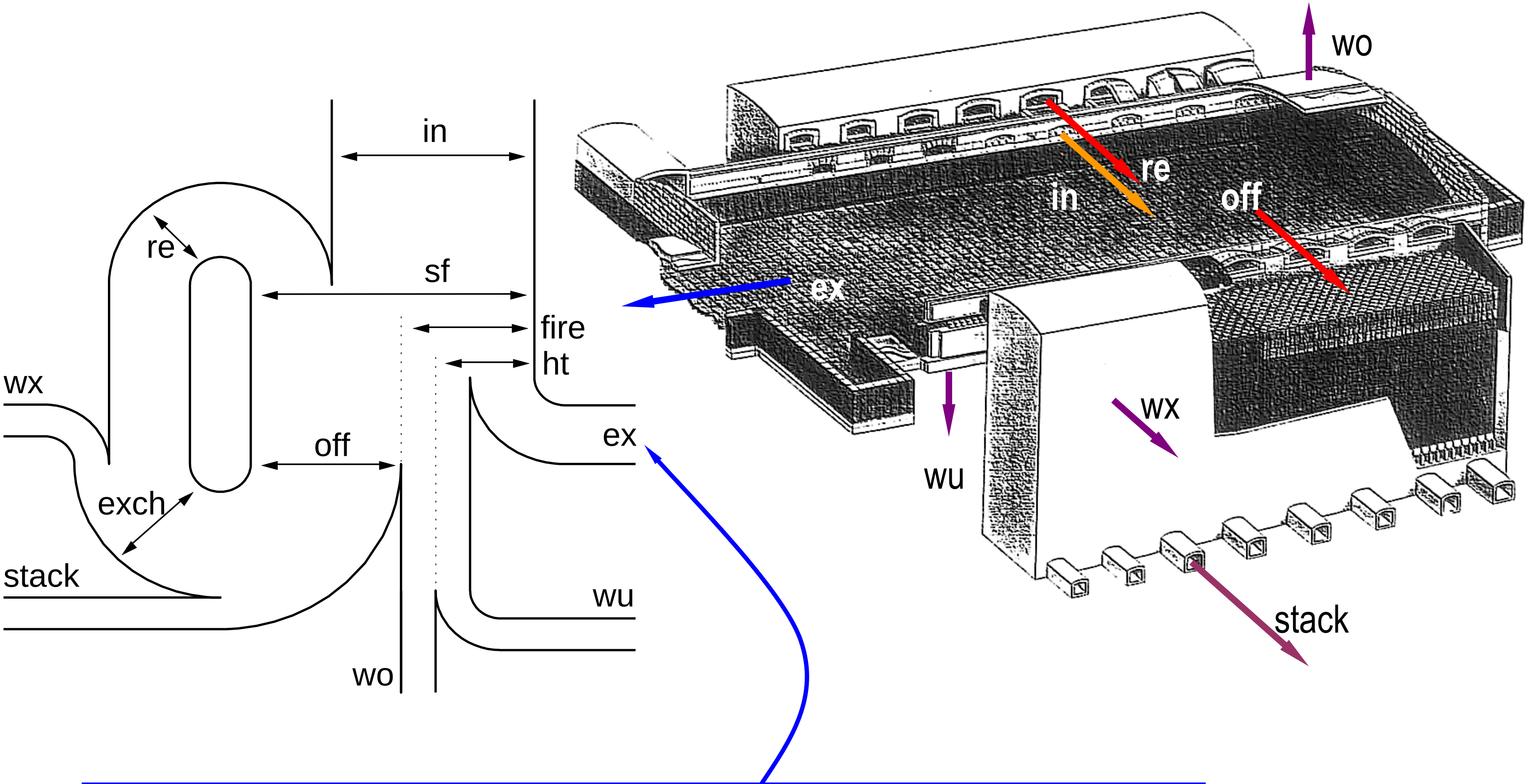
$$\begin{pmatrix} n(an) \\ n(wol) \\ n(ak) \\ n(di) \end{pmatrix} = \begin{pmatrix} 2 & 1 & 2 & 2 \\ 1 & 0 & 0 & 0 \\ 1 & 1 & 2 & 1 \\ 0 & 0 & 1 & 1 \end{pmatrix}^{-1} \cdot \begin{pmatrix} n(SiO_2) \\ n(Al_2O_3) \\ n(CaO) \\ n(MgO) \end{pmatrix}$$

prediction of G^f for 4 mineral fibre compositions

SiO_2-TiO_2-Al_2O_3-Fe_2O_3-FeO-P_2O_5-MgO-CaO-Na_2O-K_2O

	G^f_{el} [kJ/mol]		G^f_{ox} [kJ/mol]	
	exp	calc	exp	calc
glass a	**-852.0**	**-849.6**	**-12.9**	**-10.6**
glass b	**-865.0**	**-867.2**	**-35.4**	**-37.7**
glass c	**-880.8**	**-881.8**	**-34.0**	**-35.0**
glass d	**-885.4**	**-852.7**	**-44.1**	**-41.4**

experiments by Richet et al.



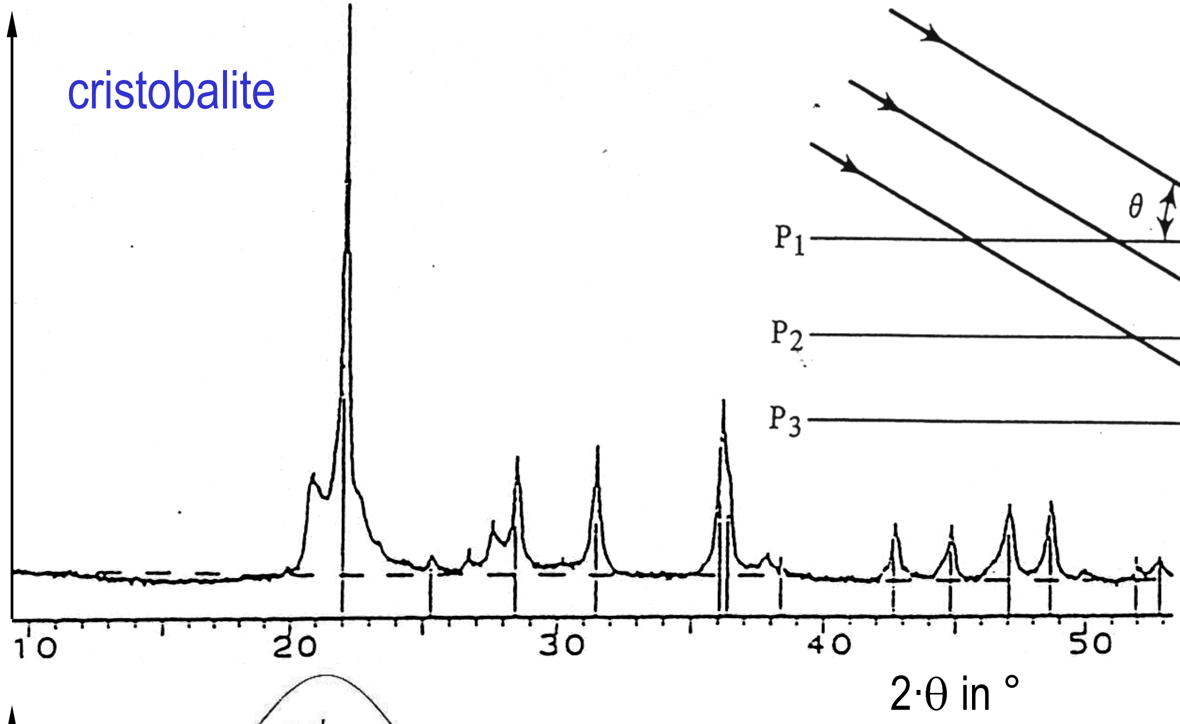
raw materials (25 °C) → glass + batch gases (25 °C) ΔH_{chem}

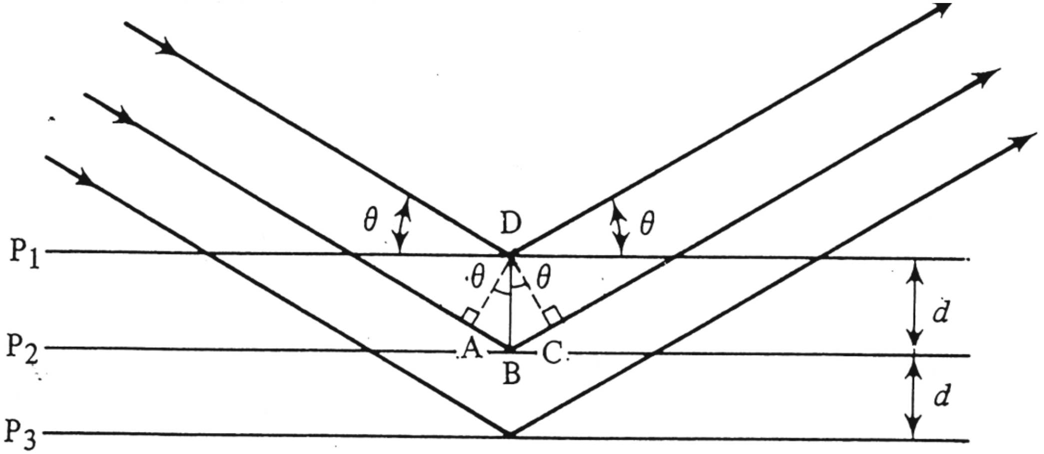
glass (25 °C) → glass melt ($T = T_{ex}$) $\Delta H_{T=Tex}$

$$H_{ex} = (1 - y_C) \cdot \Delta H_{chem} + \Delta H_{T=Tex}$$

structural aspects

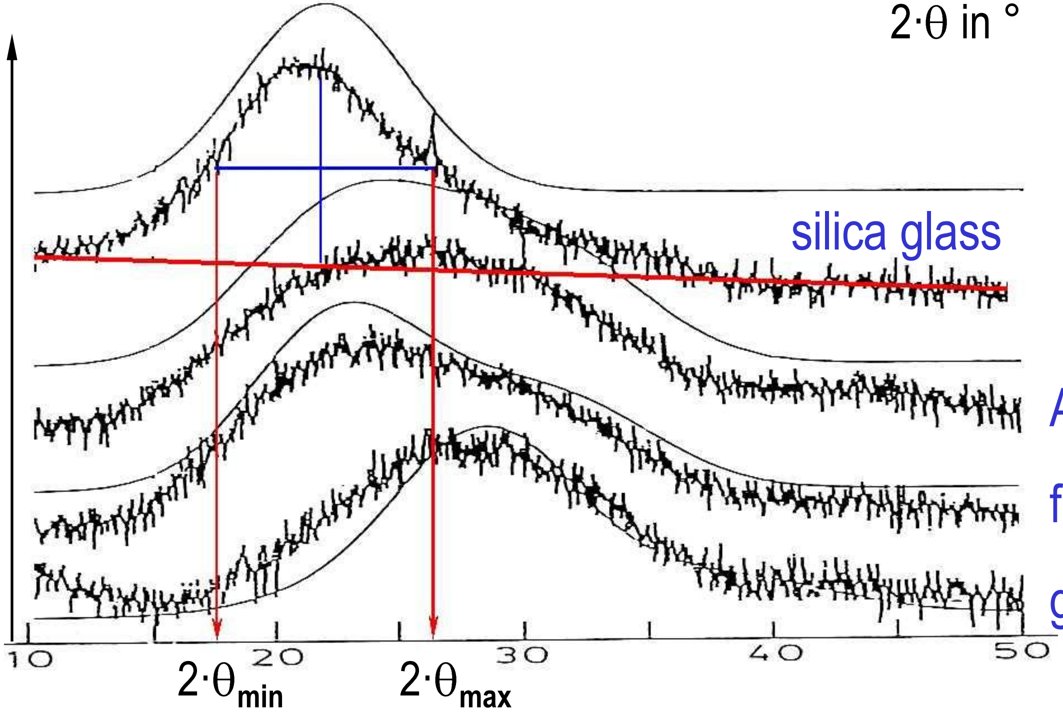
maybe Thursday





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

$$X = 0.154\ldots\ nm\ \ (Cu\ \ K\alpha)$$



peak broadening B

$$B = \frac{1}{2}\cdot(2\cdot\theta_{max} - 2\cdot\theta_{min})\cdot\frac{\pi}{180}$$

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

$$d = \frac{X}{2 \cdot \sin(\frac{1}{2} \cdot 2 \cdot \theta)} \; ; \; X = 0.154\, nm \;\; (Cu \;\; K\alpha)$$

broadening B of diffraction peaks:

$$B = \tfrac{1}{2} \cdot \left(2 \cdot \theta_{\max} - 2 \cdot \theta_{\min}\right) \cdot \frac{\pi}{180} ; \quad (22 \pm 4)^\circ \Rightarrow B = 0.0698$$

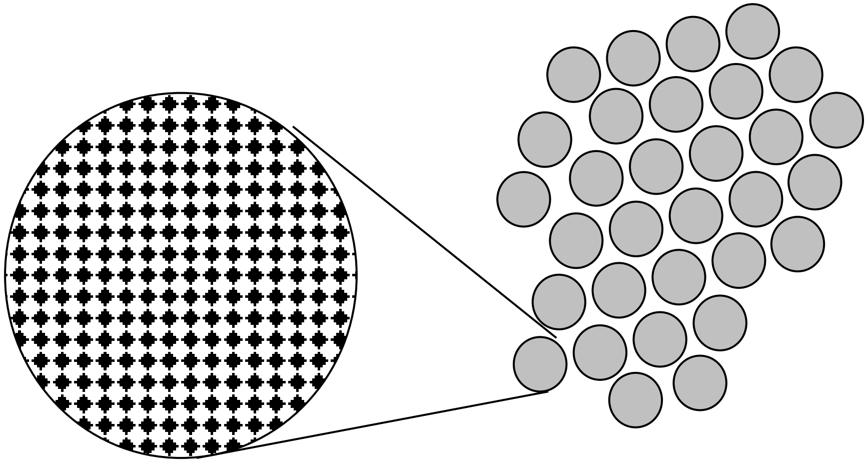
interpretation: peak broadening B ⇔ range b of translational symmetry

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

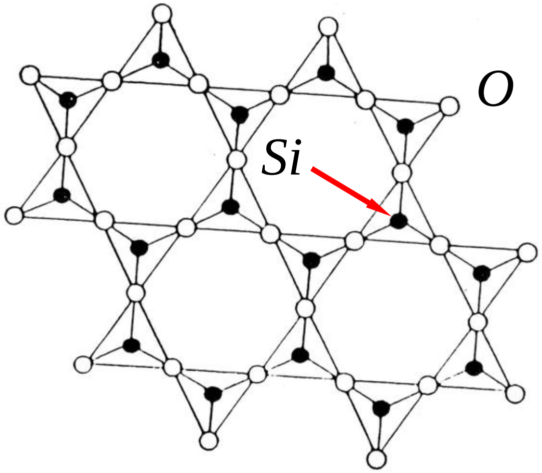
interpretation: peak broadening B ⇔ fluctuation $\varepsilon = \delta d/d$ of lattice spacing

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

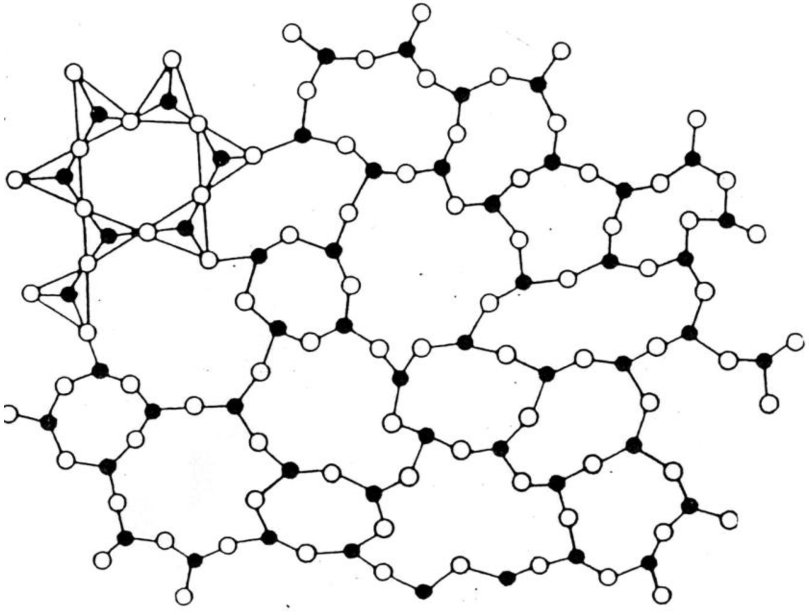
1. *random packing of length-correlated clusters*



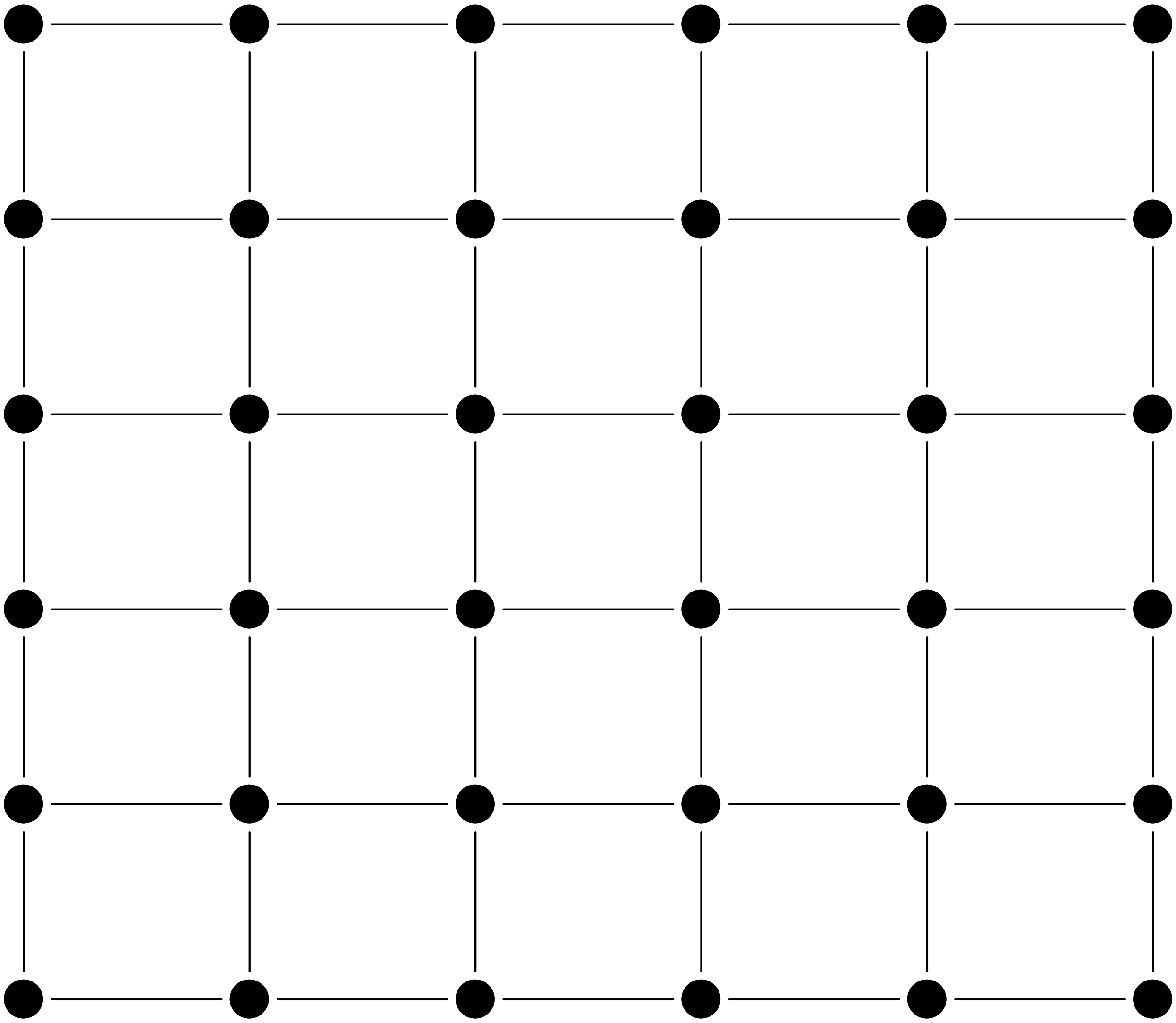
2. *crystalline silica*



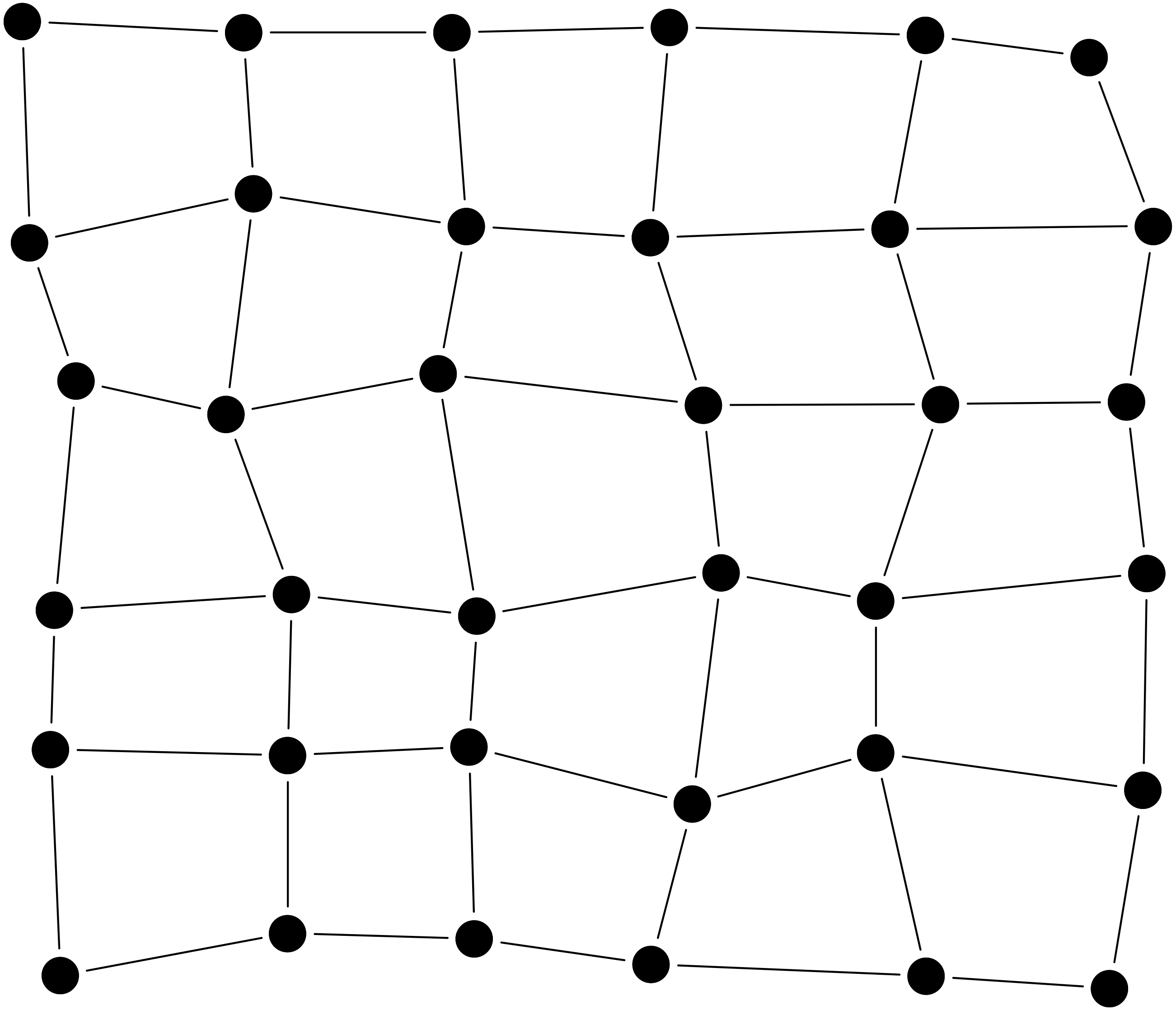
silica glass



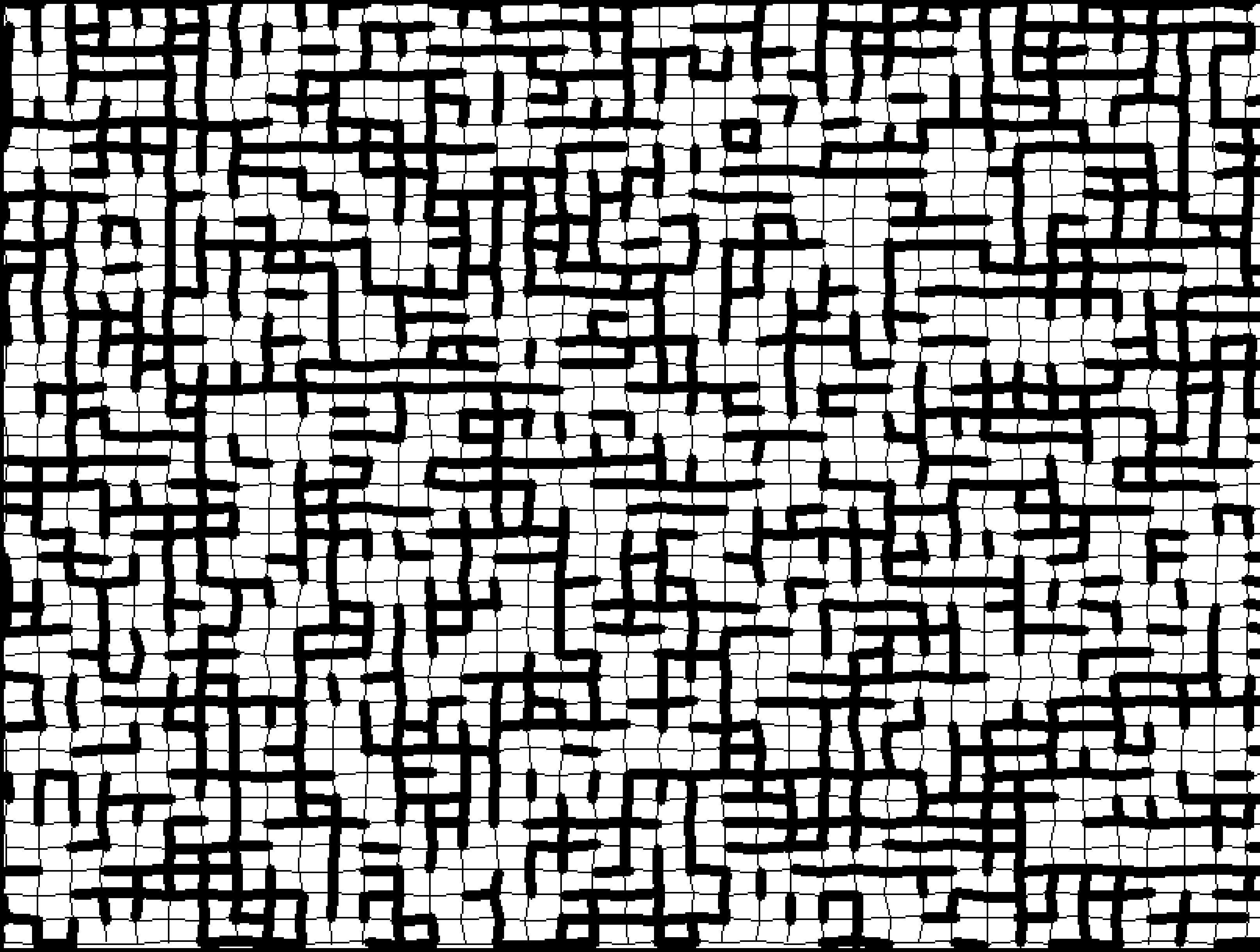
$\varepsilon = \pm 0.00$



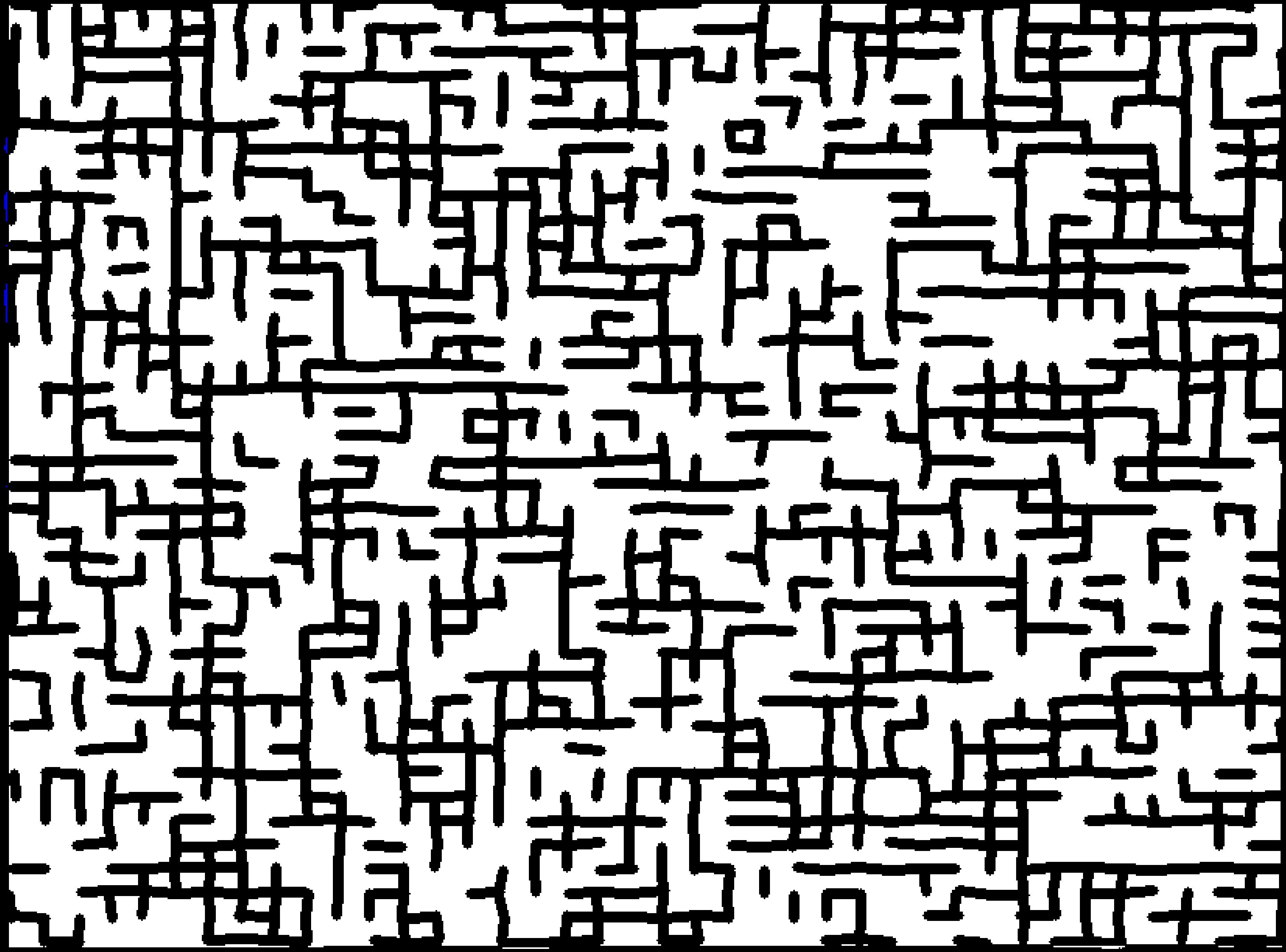
$\varepsilon = \pm 0.09$



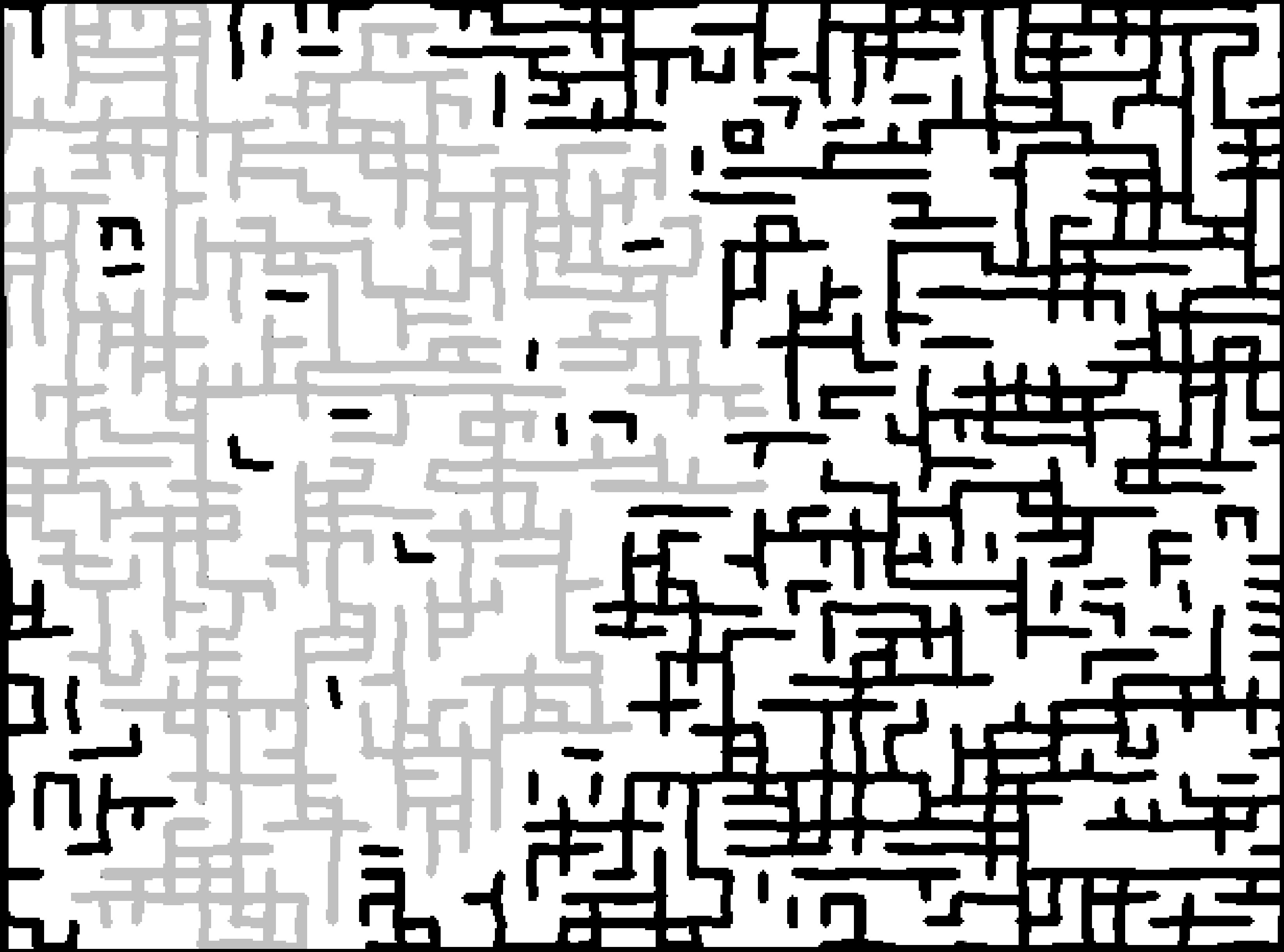
$\varepsilon = 0.09$; $d \leq \varepsilon\cdot\sqrt{2}$ is accepted as bond



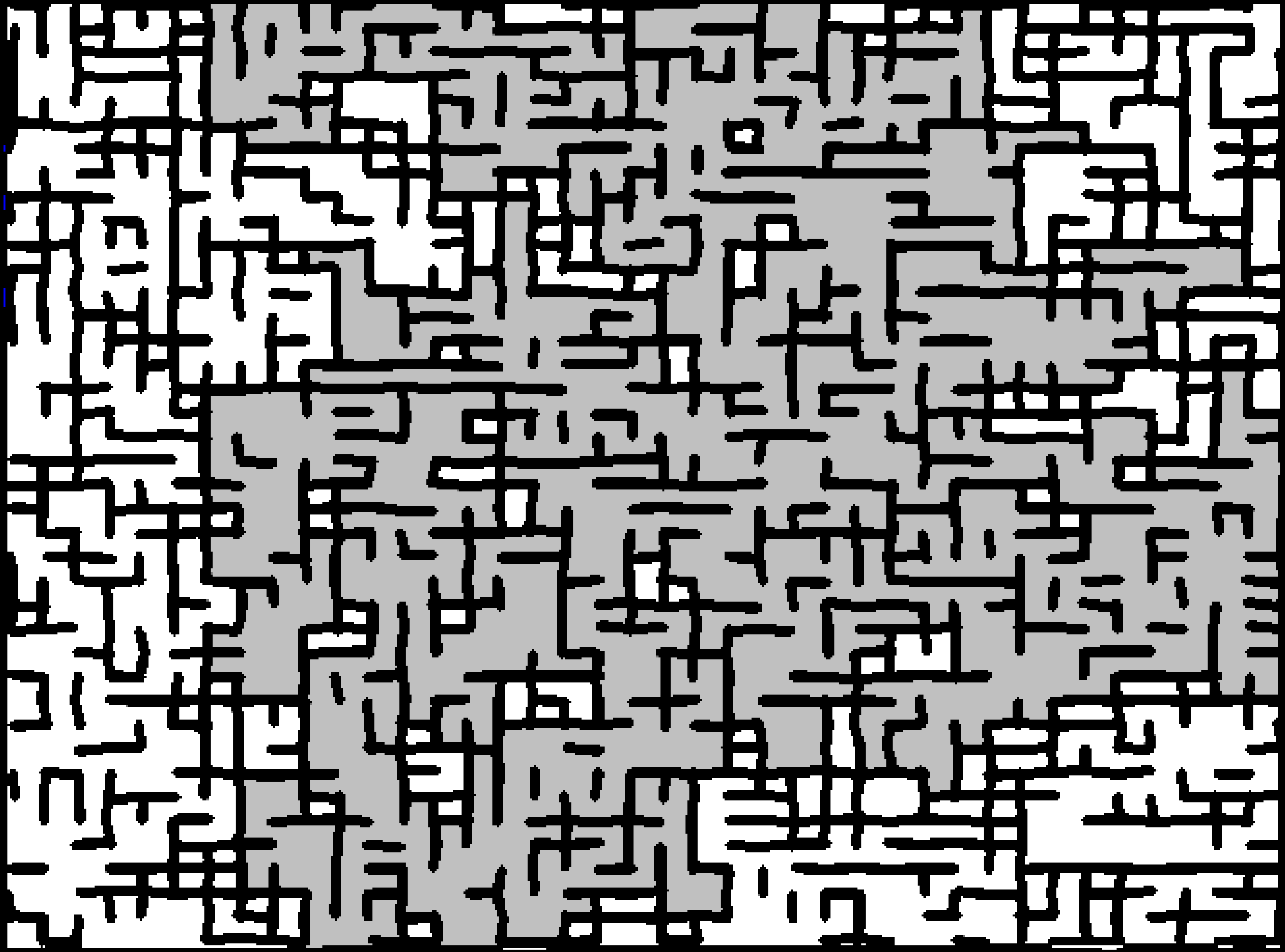
$\varepsilon = 0.09$; $d \le \varepsilon\cdot\sqrt{2}$ is accepted as bond

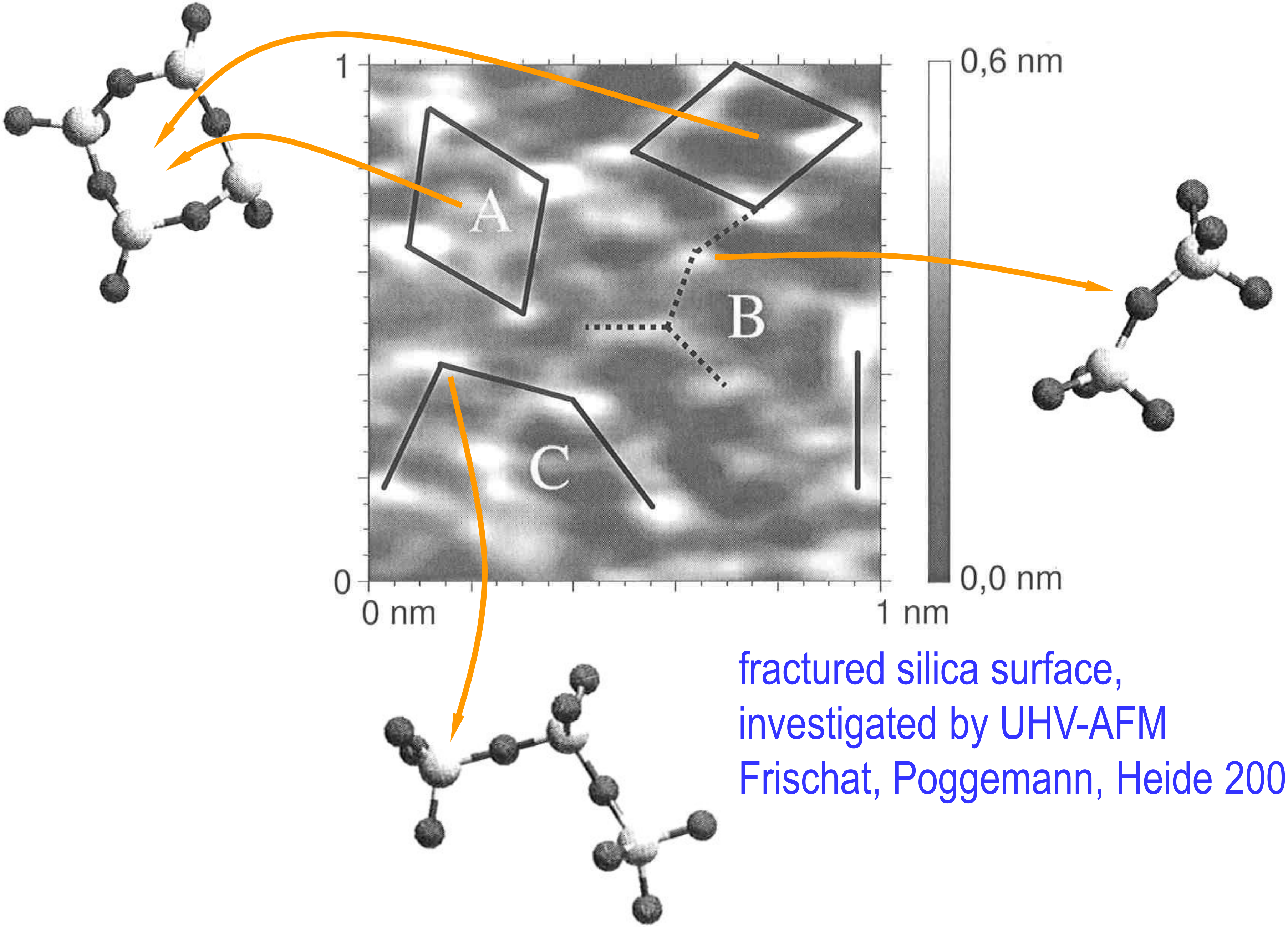


rigidity percolation; see ——

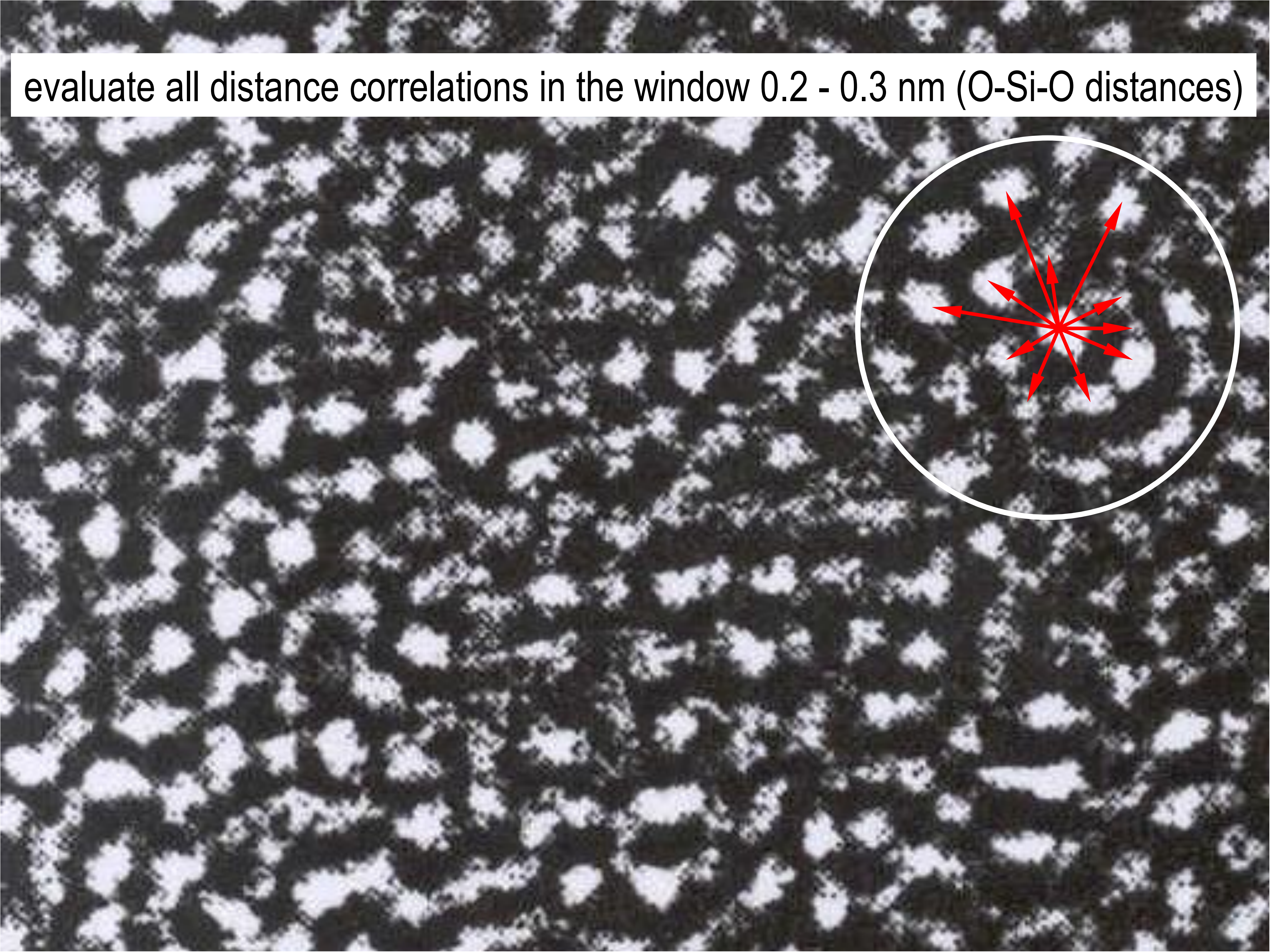


diffusion path percolation; see ▨



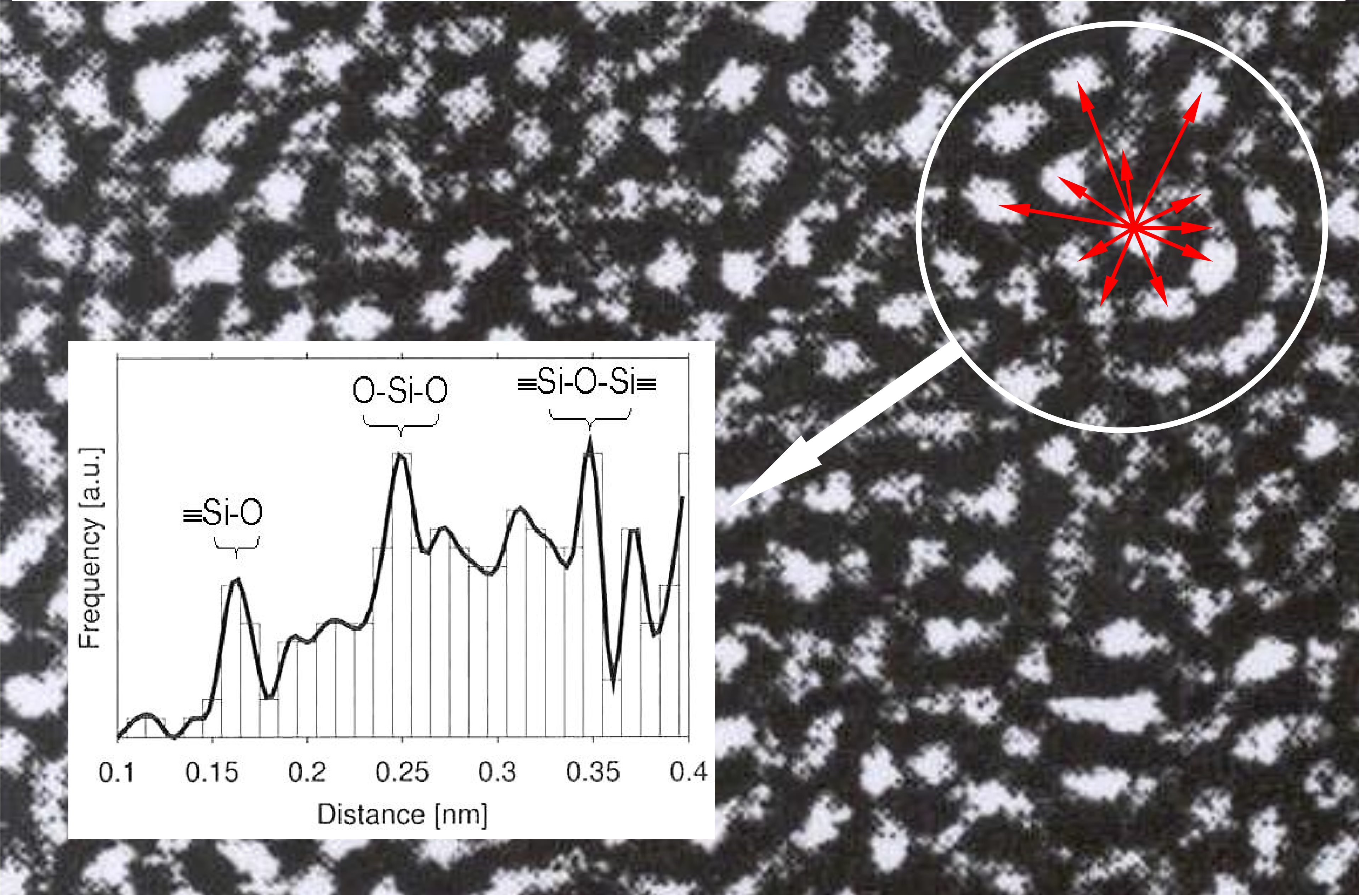


fractured silica surface,
investigated by UHV-AFM
Frischat, Poggemann, Heide 2003

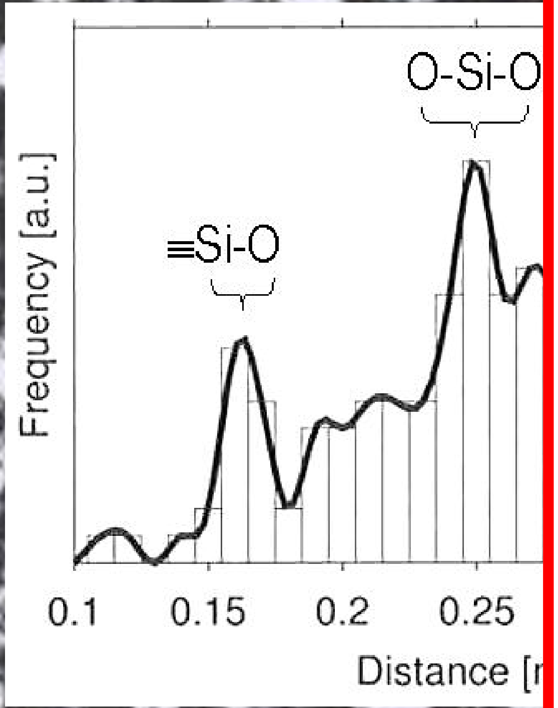


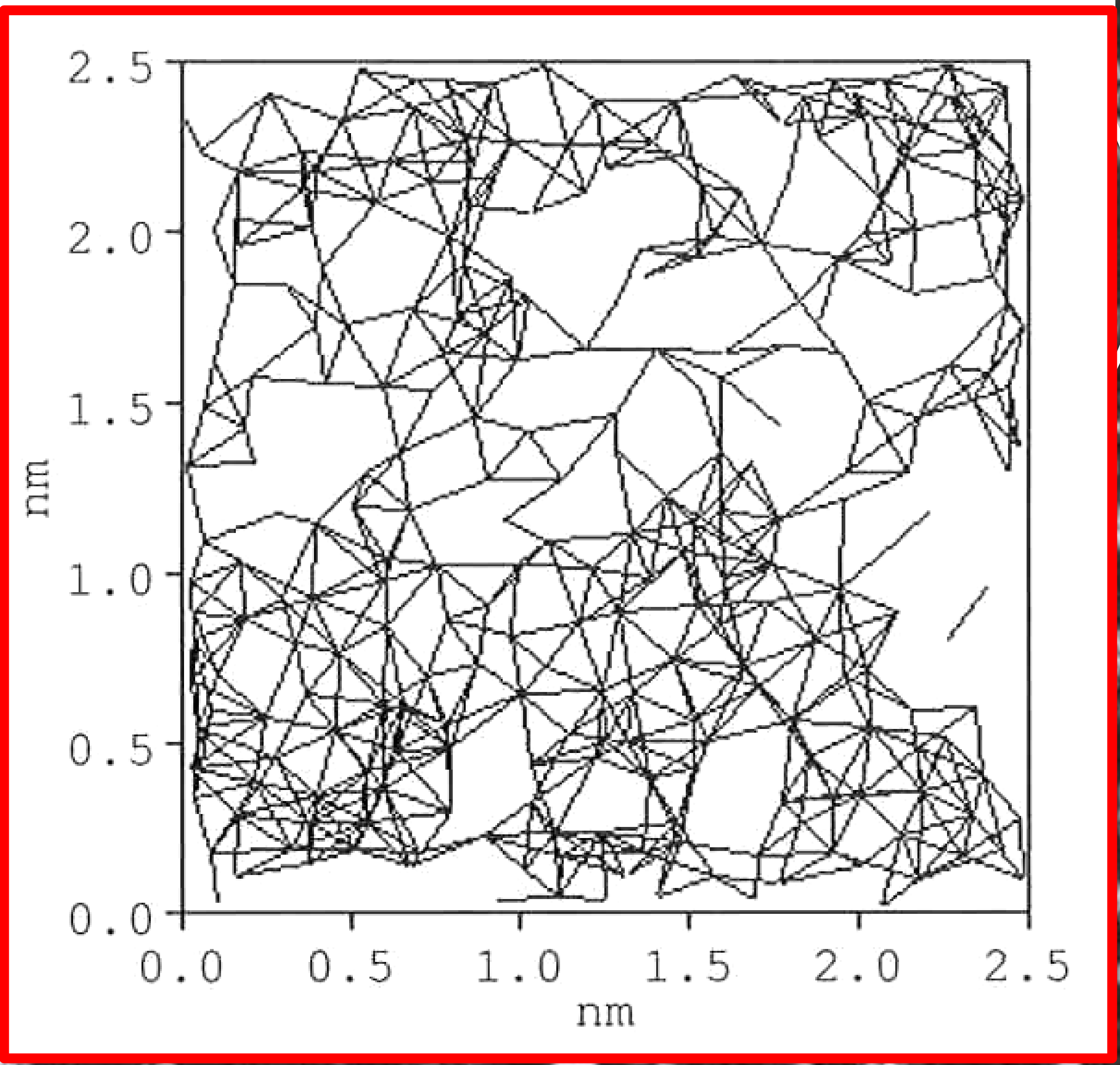
evaluate all distance correlations in the window 0.2 - 0.3 nm (O-Si-O distances)

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)





QUIZ

1.

The c_P of a condensed phase is determined by

- the vibrational and rotational degrees of freedom of its molecular units.
- the vibrational, rotational, andconfigurational degrees of freedom of its molecular units.
- electrons may contribute to c_P.
- More than one answer is correct.

2.

In the glass transition, we observe

- a jump of the heat capacity and the thermal expansion coefficient to higher values.
- a jump of the compression modulus to lower values.
- Both answers are correct.

3.

The c_P of a glass at very low T

- shows an excess over the c_P of the isochemical crystal.
- steadily approaches the value of the isochemical crystal.
- may be larger or smaller than the c_P of the isochemical crystal, depending on the chemical composition.

4.

The properties of frozen-in phases

- are functions of state.
- are unpredictable.
- depend well-defined additional parameters.

QUIZ continued

5.
The c_P jump in the glass transition
- reflects the gain of additional degrees of freedoms.
- influences the fragility of a glass forming system.
- None of thes answers is correct.

6.
Multi-component oxide melts above T^m
- are in perfect disorder.
- still contain quasi-crystalline entities (micro-crystals).
- reflect the constitutional relations found in the crystalline state.

7.
The entropy of condensed phases for $T \rightarrow 0$
- is always zero.
- is zero if the phases are in internal equilibrium.
- can be assessed unequivocally by calorimetry.
- The issue is a yet unresolved controversy of condensed matter physics.

8.
Industrial glasses at 298 K obtained at normalized cooling rates
- cannot be described by thermochemical standard values.
- can be described by the thermochemical standard values of the corresponding crystalline state plus two additional quantities.
- can be described by the thermochemical standard values only if they are one-component systems.

Homework

Derive the enthalpy and entropy (T = 298 K) of a glass of composition (in wt. %)

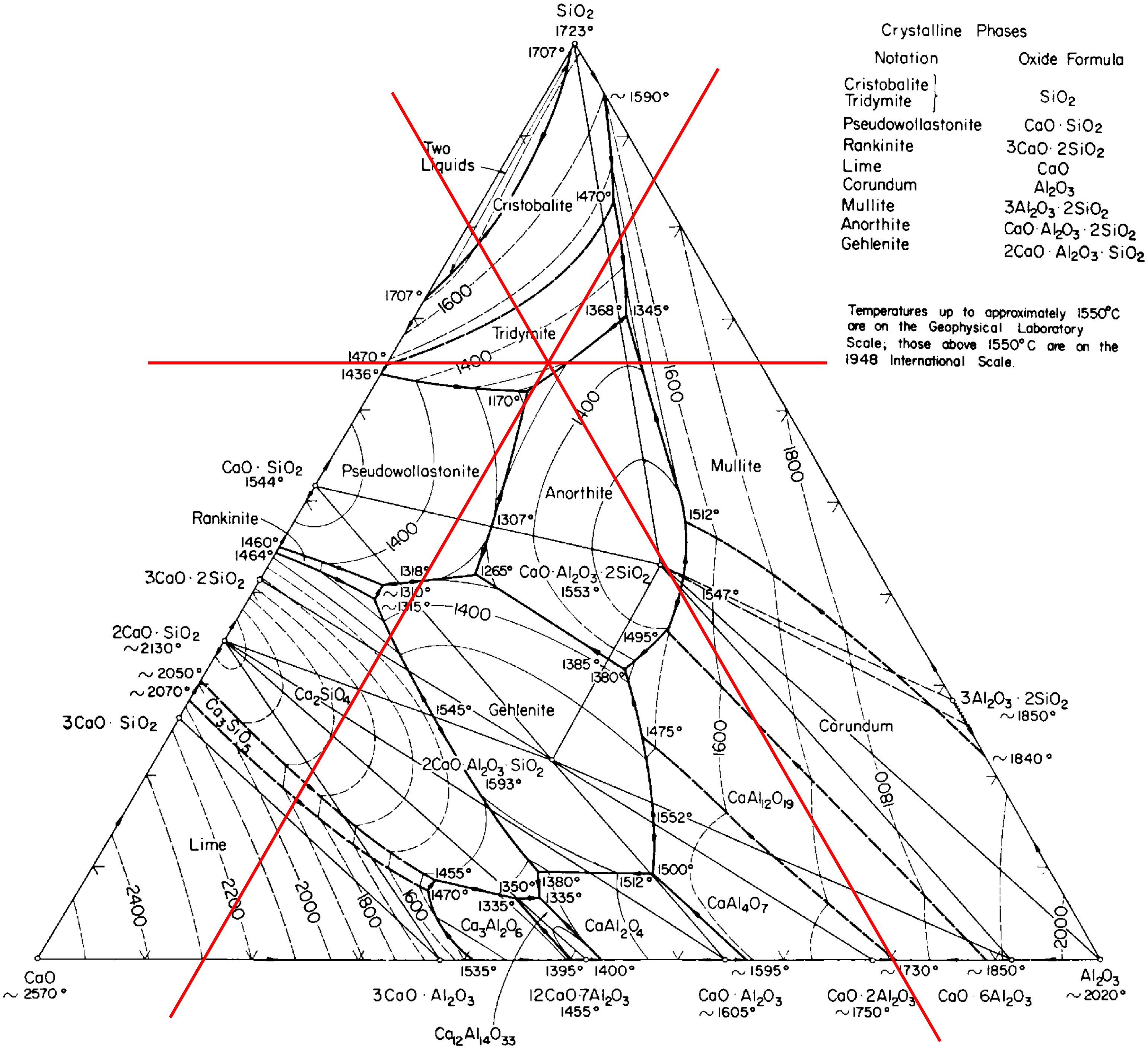
65 SiO_2, 15 Al_2O_3, 20 CaO.

Compare the result to the values of the isochemical (polycrystalline) equilibrium state.

What is the Gibbs energy difference at 298 K?

With a value of T_g = 760 °C and H^{fus} = 475 kJ/kg given, what estimate do you derive for Δc_P?

What is the expected fragility slope?



Crystalline Phases

Notation	Oxide Formula
Cristobalite Tridymite	SiO_2
Pseudowollastonite	$CaO \cdot SiO_2$
Rankinite	$3CaO \cdot 2SiO_2$
Lime	CaO
Corundum	Al_2O_3
Mullite	$3Al_2O_3 \cdot 2SiO_2$
Anorthite	$CaO \cdot Al_2O_3 \cdot 2SiO_2$
Gehlenite	$2CaO \cdot Al_2O_3 \cdot SiO_2$

Temperatures up to approximately 1550°C are on the Geophysical Laboratory Scale; those above 1550°C are on the 1948 International Scale.

Thank you
for your attention