Cauchy Relations in Polymers and Nanocomposites
or
what can the Cauchy Relation tell us about Non-Equilibrium and Nanostructures

School on Polymers and Composites (PCMR), May 2004

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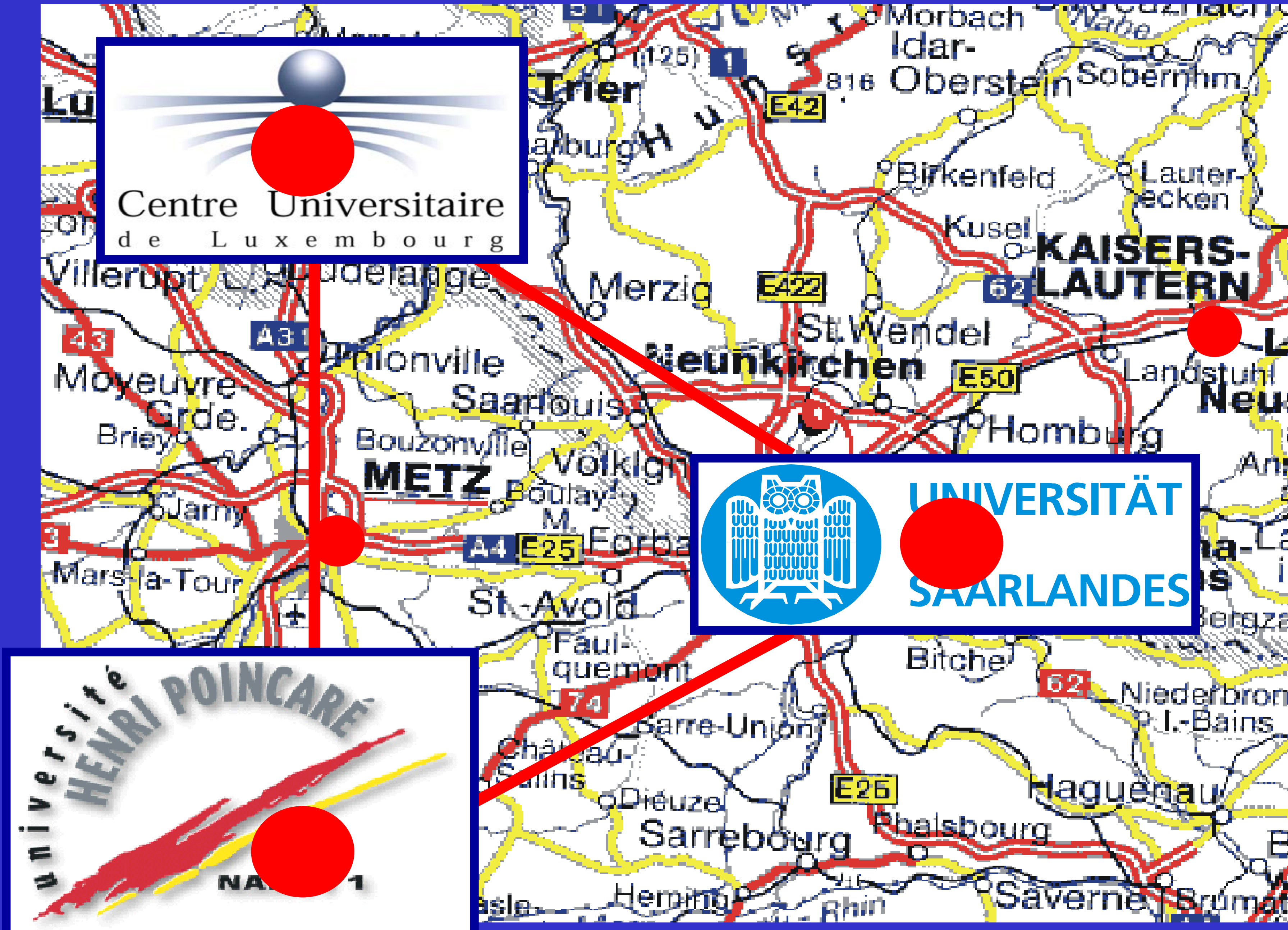
The „Europe of people“ has still to be formed!

Universities, their students and their teachers should be at the front to overcome that challenge!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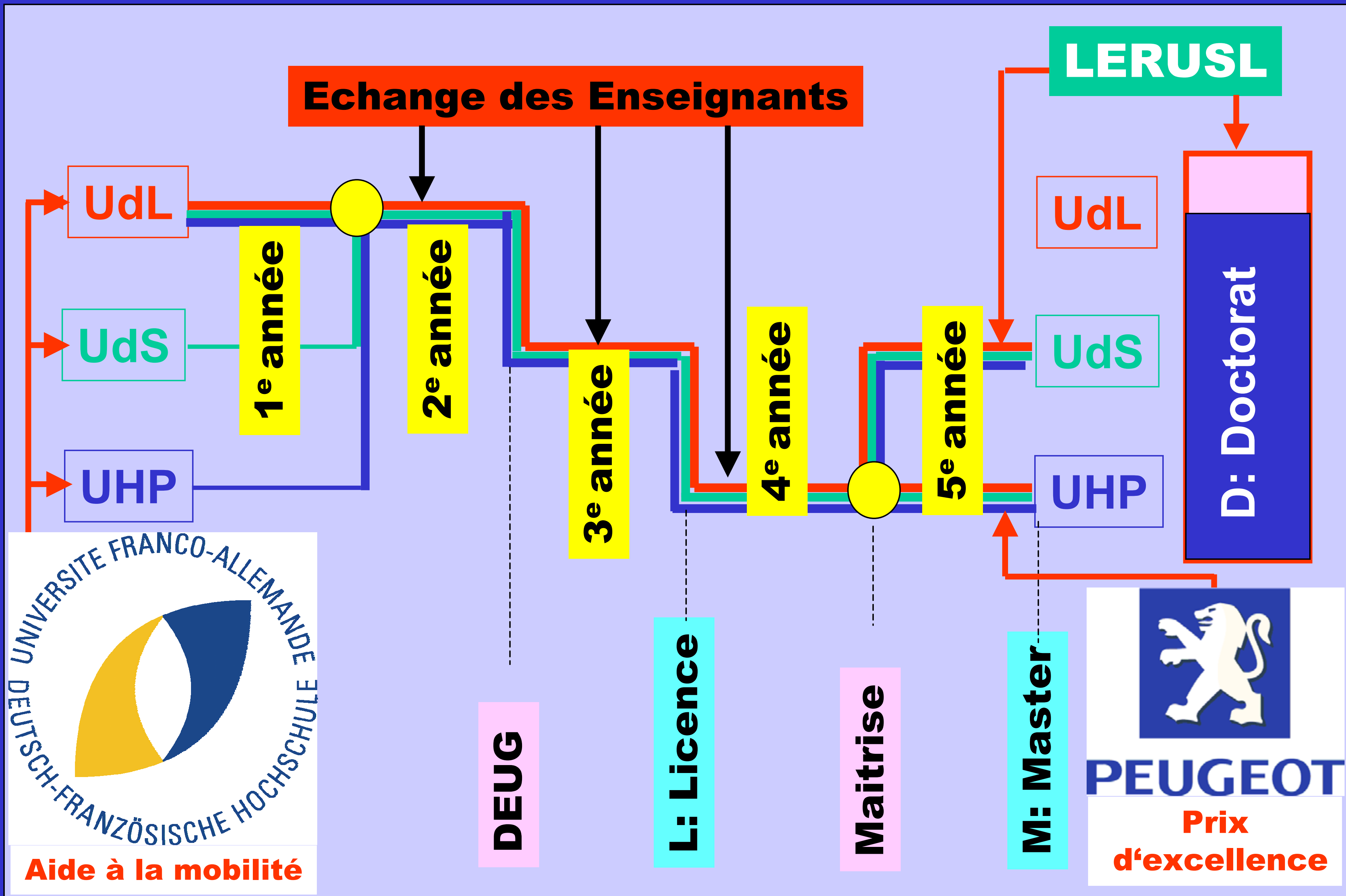
<u>Réponse:</u> Structure du Cursus Intégré „SLLS“ en Physique



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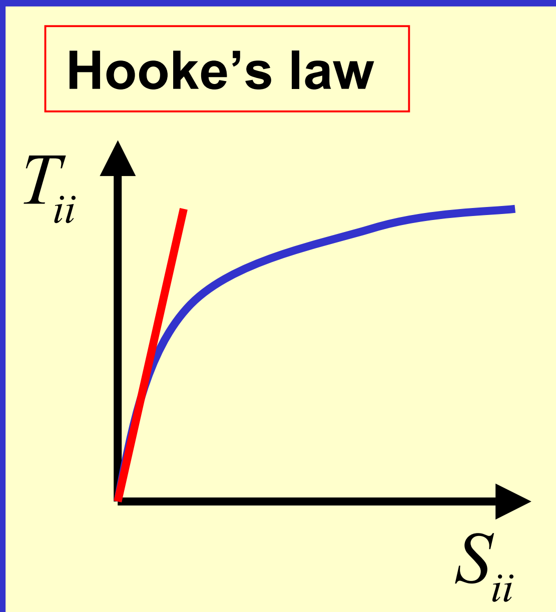
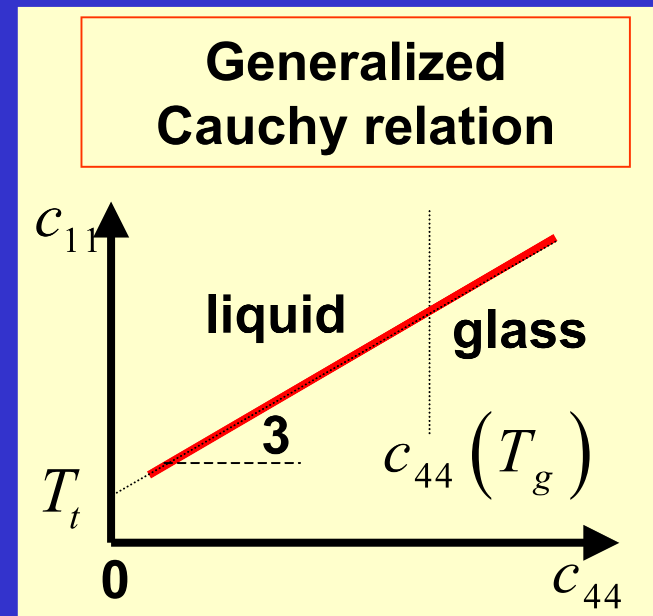
CURSUS INTEGRE SAAR-LOR-LUX EN PHYSIQUE   SAAR-LOR-LUX STUDIENGANG IN PHYSIK

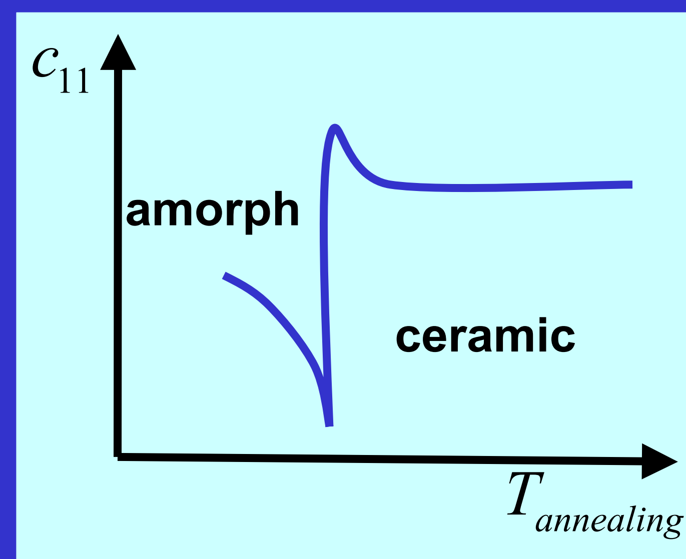
Multinationale Diplom- und Vordiplom Vergabe
Université Henri Poincaré 21. Nov. 2003

What have Hooke's law, the generalized-Cauchy-relations and the nanostructured state in common?





Consolidated nano-CeO2



Hooke's law for a triclinic crystal:

$$\{T_{\alpha\beta}\} = \{c_{\alpha\beta\gamma\delta}\} \cdot \{S_{\gamma\delta}\} \qquad for\ \alpha, \beta = x, y, z$$

$$\begin{bmatrix} T_1 \\ T_2 \\ T_3 \\ T_4 \\ T_5 \\ T_6 \end{bmatrix} = \begin{bmatrix} c_{11} & c_{12} & c_{13} & c_{14} & c_{15} & c_{16} \\ \cdot & c_{22} & c_{23} & c_{24} & c_{25} & c_{26} \\ \cdot & \cdot & c_{33} & c_{34} & c_{35} & c_{36} \\ \cdot & \cdot & \cdot & c_{44} & c_{45} & c_{46} \\ & & & & c_{55} & c_{56} \\ \cdot & \cdot & \cdot & \cdot & \cdot & c_{66} \end{bmatrix} \cdot \begin{bmatrix} S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \\ S_6 \end{bmatrix}$$

Elastic Tensor

Stress Tensor

Strain Tensor

in Voigt notation

21 elastic constants

Hooke's law for a cubic crystal:

$$\begin{bmatrix} T_1 \\ T_2 \\ T_3 \\ T_4 \\ T_5 \\ T_6 \end{bmatrix} = \begin{bmatrix} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ \cdot & c_{11} & c_{12} & 0 & 0 & 0 \\ \cdot & \cdot & c_{11} & 0 & 0 & 0 \\ \cdot & \cdot & \cdot & c_{44} & 0 & 0 \\ & & & \cdot & c_{44} & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & c_{44} \end{bmatrix} \cdot \begin{bmatrix} S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \\ S_6 \end{bmatrix}$$

Elastic Tensor

Voigt notation

Stress Tensor

Strain Tensor

For cubic symmetry there remain only three independent stiffness coefficients:

$$\{c_{11}, c_{12}, c_{44}\}$$

Hooke's law for a isotropic solid (no single crystal any more):

$$\begin{bmatrix} T_1 \\ T_2 \\ T_3 \\ T_4 \\ T_5 \\ T_6 \end{bmatrix} = \begin{bmatrix} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ \cdot & c_{11} & c_{12} & 0 & 0 & 0 \\ \cdot & \cdot & c_{11} & 0 & 0 & 0 \\ \cdot & \cdot & \cdot & c_{44} & 0 & 0 \\ & & & \cdot & c_{44} & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & c_{44} \end{bmatrix} \cdot \begin{bmatrix} S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \\ S_6 \end{bmatrix}$$

Elastic Tensor

Voigt notation

Stress Tensor

Strain Tensor

For isotropic symmetry there remain only two independent stiffness coefficients:

$$\{c_{11}, c_{44}\}$$

But the Isotropy Condition holds: $c_{12} = c_{11} - 2 \cdot c_{44}$

The Prequesites of a Cauchy Relation

Cauchy relations reduces the number of independent elastic constants compared to the number, given by by point symmetry

Additional conditions in order to fulfill a Cauchy relation:

1. **Every lattice particle is a center of inversion.**
2. **There are only central forces between the lattice particles.**
3. **The related equation of motion contains only harmonic terms. Anharmonicity destroys the Cauchy relations Cauchy Relation.**

Cauchy relations: Symmetries beyond crystal symmetries

The symmetry of elastic constants is now higher than the Voigt symmetry and this leads to in general, six additional relations for second order elastic constants, i.e.

$$c_{12} = c_{44}, \quad c_{13} = c_{55} \quad c_{23} = c_{66}$$

$$c_{14} = c_{56} \quad c_{25} = c_{46} \quad c_{36} = c_{45}$$

Crystal with cubic symmetry:

$$c_{12} = c_{13} = c_{23} = c_{66}$$

$$c_{14} = c_{56} = c_{25} = c_{46} = c_{36} = c_{45} = 0$$

Cauchy condition for crystals with cubic symmetry:

$$c_{12} = c_{44}$$

From the cubic to the isotropic elastic state

cubic symmetry →

Three Independent elastic constants

$$c_{11}, c_{12}, c_{44}$$

$$\begin{pmatrix} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{12} & c_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{44} \end{pmatrix}$$

+

isotropy relation

$$c_{12} = c_{11} - 2 \cdot c_{44}$$

→

Isotropic state:

two remaining independent elastic constants

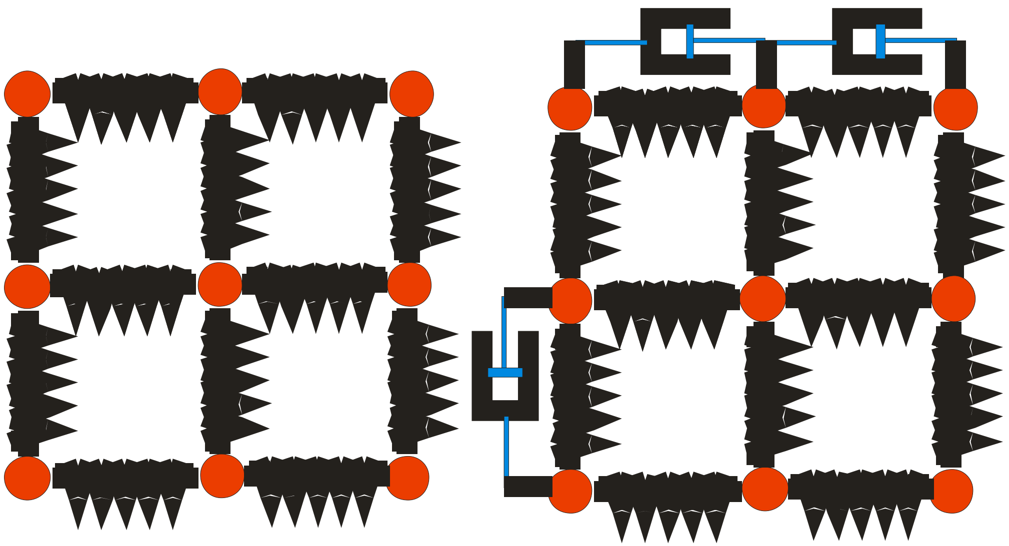
+

Cauchy relation

$$c_{12} = c_{44} \rightarrow c_{11} = 3 \cdot c_{44}$$

one remaining independent elastic constant

Hooke’s elasticity is only part of the truth: ➔ nonlinear elasticity and viscoelasticity of solids



visco-elasic solids ➔ (linear), delayed response

$$c_{ij}^{1} = c_{ij}^{1s} + \frac{\Delta c_{ij}^{1}}{1 + i \cdot \omega \cdot \tau}$$

harmonic solids
➔linear, instanteous
➔ response

anharmonic solids ➔
nonlinear response,
instanteous response

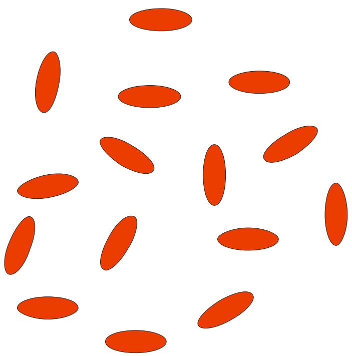
$$\underline{\underline{T}} = \underline{\underline{c}}^{1} \cdot \underline{\underline{S}} + \underline{\underline{S}}^{T} \cdot \underline{\underline{c}}^{2} \cdot \underline{\underline{S}} + \dots.$$

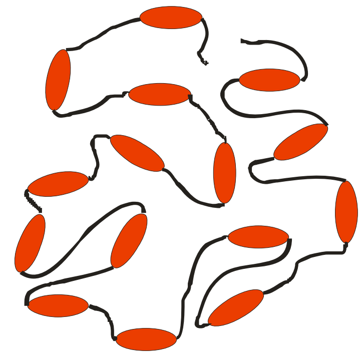
Anharmonicity seen by Grüneisen parameters

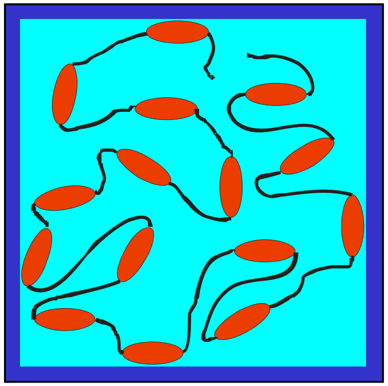
$$\gamma\left(p,\vec{q}\right) = \frac{\partial Ln\left[\omega\left(p,\vec{q}\right)\right]}{\partial Ln\left(\rho\right)}$$

The mechanical properties of amorphous material in the long wavelengt limit

Simple liquid | **Viscous liquid** | **glass**







$$\vec{T} = \underline{\underline{c}}^{1} : \vec{S} + \underline{\underline{\eta}} : \frac{\partial \vec{S}}{\partial t} + \vec{S}^{T} : \underline{\underline{c}}^{2} : \vec{S} + ...$$

but $c_{44} = G \quad ???$

Anharmonicity seen by Grüneisen parameters

$$\gamma(p, \vec{q}) = \frac{\partial Ln\left[\omega(p, \vec{q})\right]}{\partial Ln(\rho)}$$

visco-elastic solids ➔ (linear), delayed response

$$c_{ij}^{1} = c_{ij}^{1s} + \frac{\Delta c_{ij}^{1}}{1 + i \cdot \omega \cdot \tau}$$

$$T_1 = \left(c_{11} + \frac{\partial}{\partial t} \cdot \eta_{11} \right) \cdot S_1$$

$$T_4 = \frac{\partial}{\partial t} \cdot \eta_{44} \cdot S_4$$

$$T_1 = \left(c_{11} + i \cdot \omega \cdot \eta_{11} \right) \cdot S_1$$

$$T_4 = i \cdot \omega \cdot \eta_{44} \cdot S_4$$

What happens, when even the dynamic viscosity relaxes?

$$\eta_{11}^{*} = \eta_{11}^{'} - i \cdot \eta_{11}^{''}$$

$$\eta_{44}^{*} = \eta_{44}^{'} - i \cdot \eta_{44}^{''}$$

Let us use a simple Debye Relaxator:

$$\eta_{11}^{'} = \eta_{11}^{s} + \frac{\Delta \eta_{11}}{1 + \omega^2 \cdot \tau_1^2}$$

$$\eta_{44}^{'} = \eta_{44}^{s} + \frac{\Delta \eta_{44}}{1 + \omega^2 \cdot \tau_4^2}$$

$$\eta_{11}^{''} = \frac{\omega \cdot \Delta \eta_{11}}{1 + \omega^2 \cdot \tau_1^2}$$

$$\eta_{44}^{''} = \frac{\omega \cdot \tau \cdot \Delta \eta_{44}}{1 + \omega^2 \cdot \tau_4^2}$$

The appearance shear stiffness

$$T_4 = i \cdot \omega \cdot \eta^*_{44} \cdot S_4 \longrightarrow T_4 = i \cdot \omega \cdot \left(\eta'_{44} - i \cdot \eta''_{44} \right) \cdot S_4$$

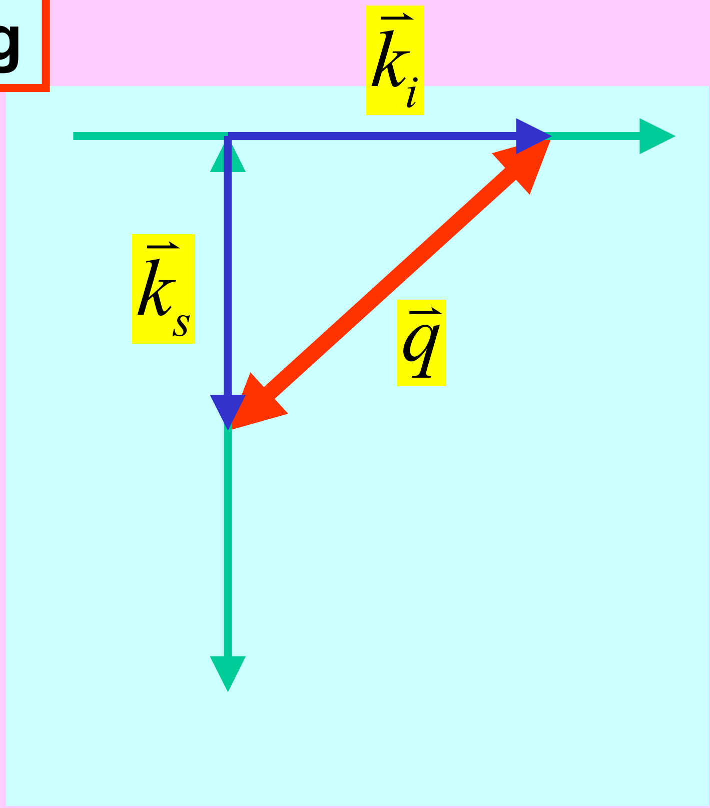
$$T_4 = i \cdot \omega \cdot \left(\eta^s_{44} + \frac{\Delta\eta_{44}}{1+\omega^2 \cdot \tau_4^2} - i \cdot \frac{\omega \cdot \tau_4 \cdot \Delta\eta_{44}}{1+\omega^2 \cdot \tau_4^2} \right) \cdot S_4$$

$$T_4 = \left(\underbrace{\frac{1}{\tau_4} \cdot \frac{\omega^2 \cdot \tau_4^2 \cdot \Delta\eta_{44}}{1+\omega^2 \cdot \tau_4^2}}_{c'_{44}} + i \cdot \omega \cdot \underbrace{\left(\eta^s_{44} + \frac{\Delta\eta_{44}}{1+\omega^2 \cdot \tau_4^2} \right)}_{c''_{44}} \right) \cdot S_4$$

$\omega \cdot \tau_4 << 1$ fast motion → $c'_{44} = 0$

slow motion $\omega \cdot \tau_4 >> 1$ → $c'_{44} = \Delta\eta_{44} / \tau_4$

Kinematic View of Brillouin scattering



momentum conservation

$$\hbar\vec{k}_s = \hbar\vec{k}_i \pm \hbar\vec{q}$$

energy conservation

$$\hbar\omega_s = \hbar\omega \pm \hbar\Omega$$

Sound velocity

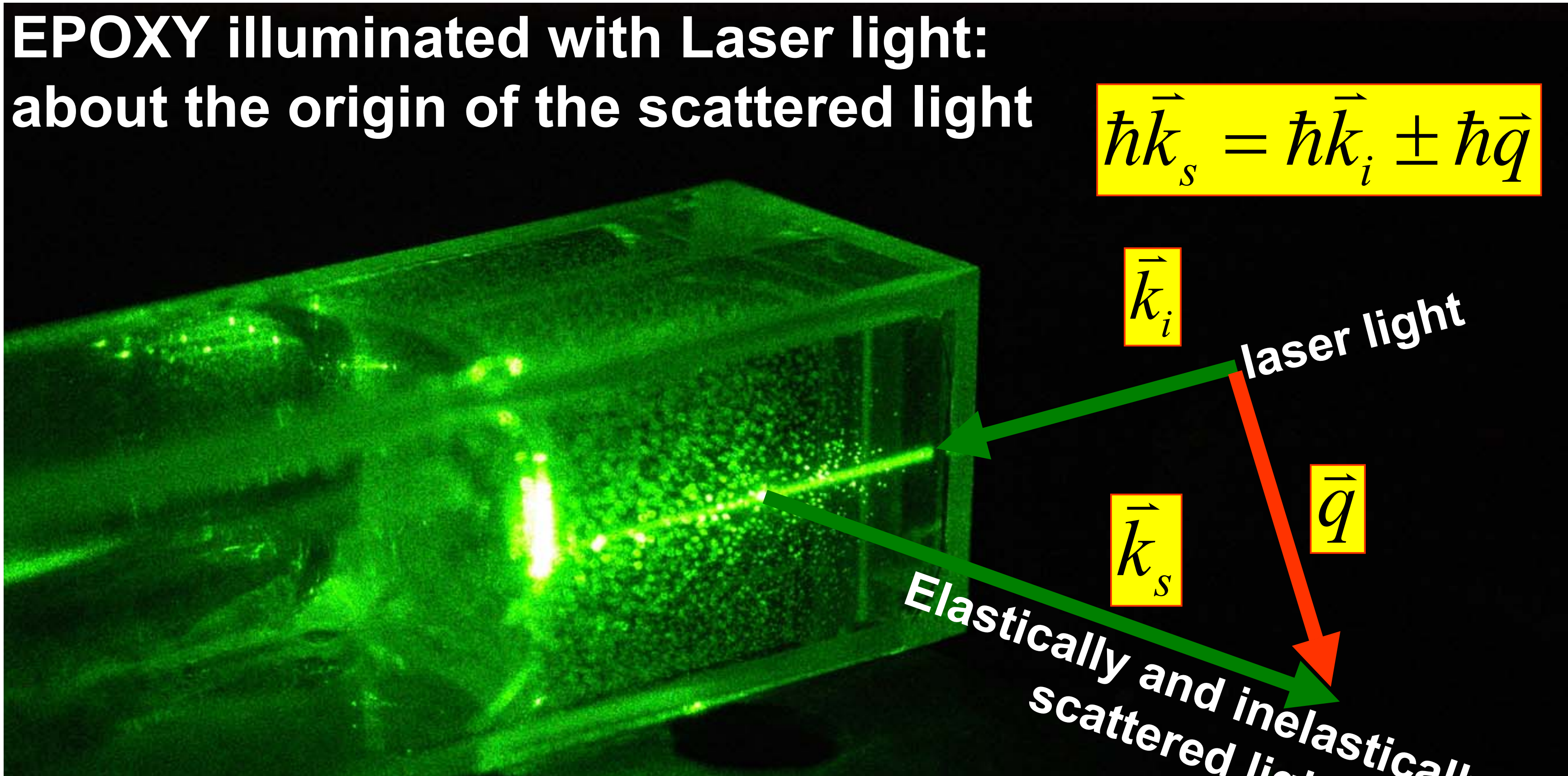
$$V = \frac{\Omega}{q} = f \cdot \left\{ \lambda_\omega \Big/ \left[2 \cdot n \cdot \sin\left[\theta_i / 2 \right] \right] \right\}$$

Elastic constant

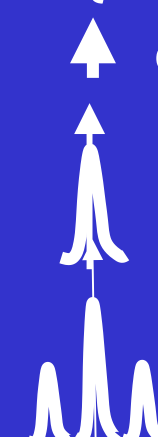
$$c = \rho \cdot V^2$$

EPOXY illuminated with Laser light: about the origin of the scattered light

$$\hbar\vec{k}_s = \hbar\vec{k}_i \pm \hbar\vec{q}$$

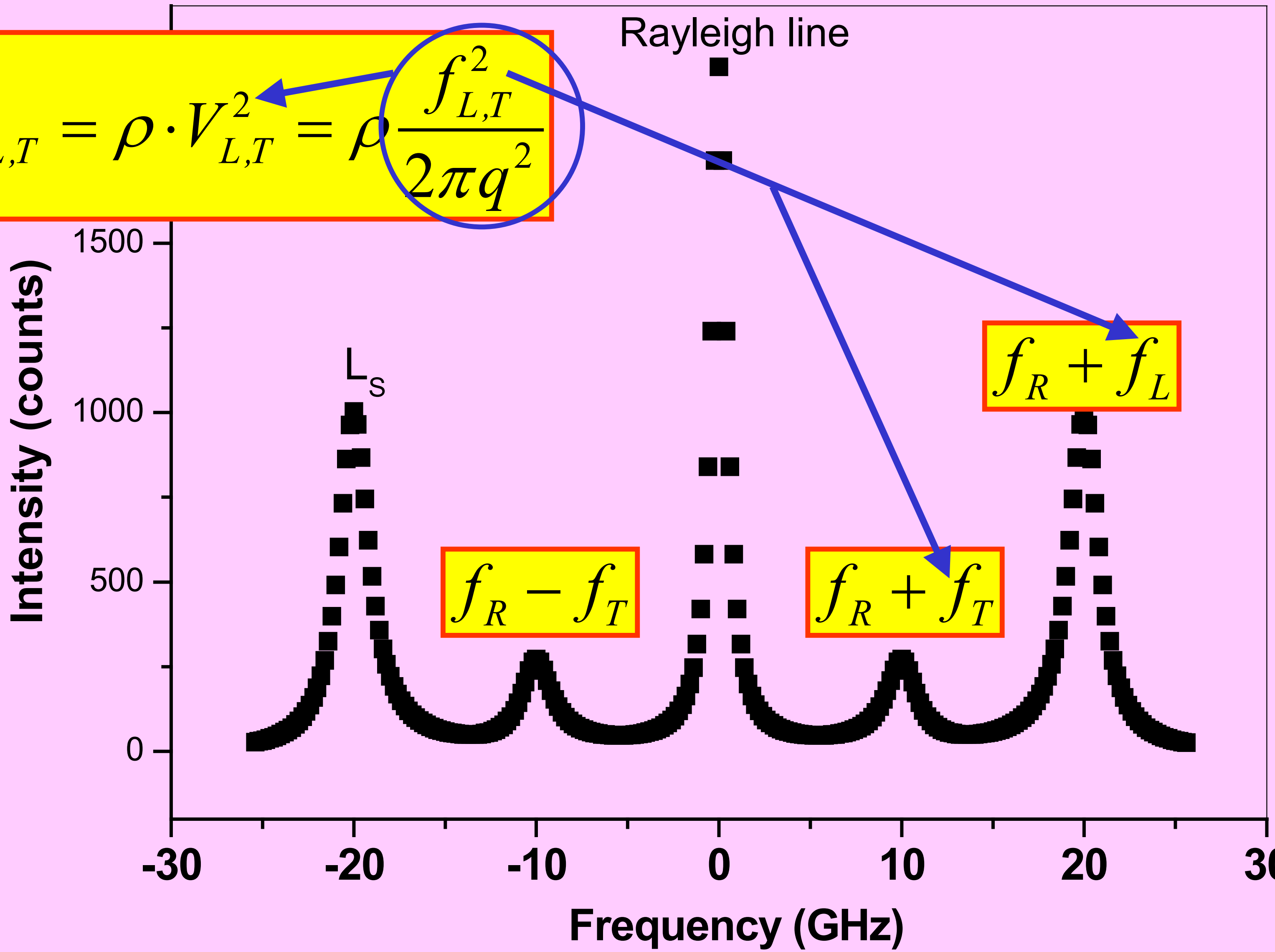


$\left\langle \delta a^*_{kl}(\vec{r}) \cdot \delta a_{mn}(\vec{r}\,') \right\rangle$	static scattering	delta function
$\left\langle \delta a^*_{kl}(t) \cdot \delta a_{mn}(t') \right\rangle$	diffusive scattering	relaxator
$\left\langle \delta a^*_{kl}(\vec{r},t) \cdot \delta a_{mn}(\vec{r}\,',t') \right\rangle$	inelastic scattering	oszillators +relaxator

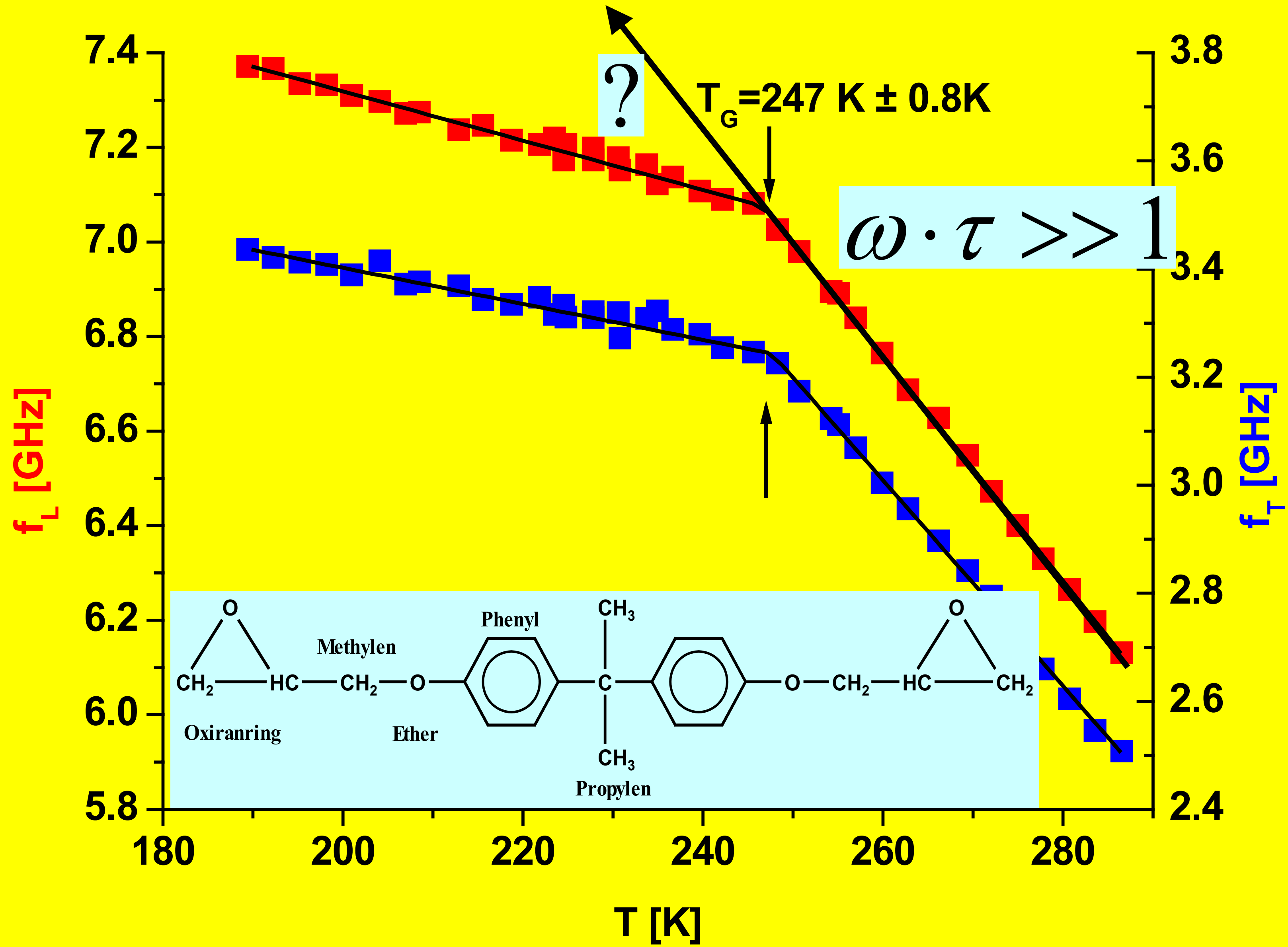


Schematical Brillouin spectrum of an isotropic solid

$$c_{L,T} = \rho \cdot V_{L,T}^2 = \rho \frac{f_{L,T}^2}{2\pi q^2}$$



DGEBA in Langhalsküvette



PRL 2002

Did you ever hear about a Cauchy Relation for Polymers or Liquids at high Frequencies

? $$c_{11} = 3 \cdot c_{44}$$

Cauchy-relation for the high frequency clamped isotropic state of a liquid:

Would reduce the number of elastic constants of isotropic materials from two to one!

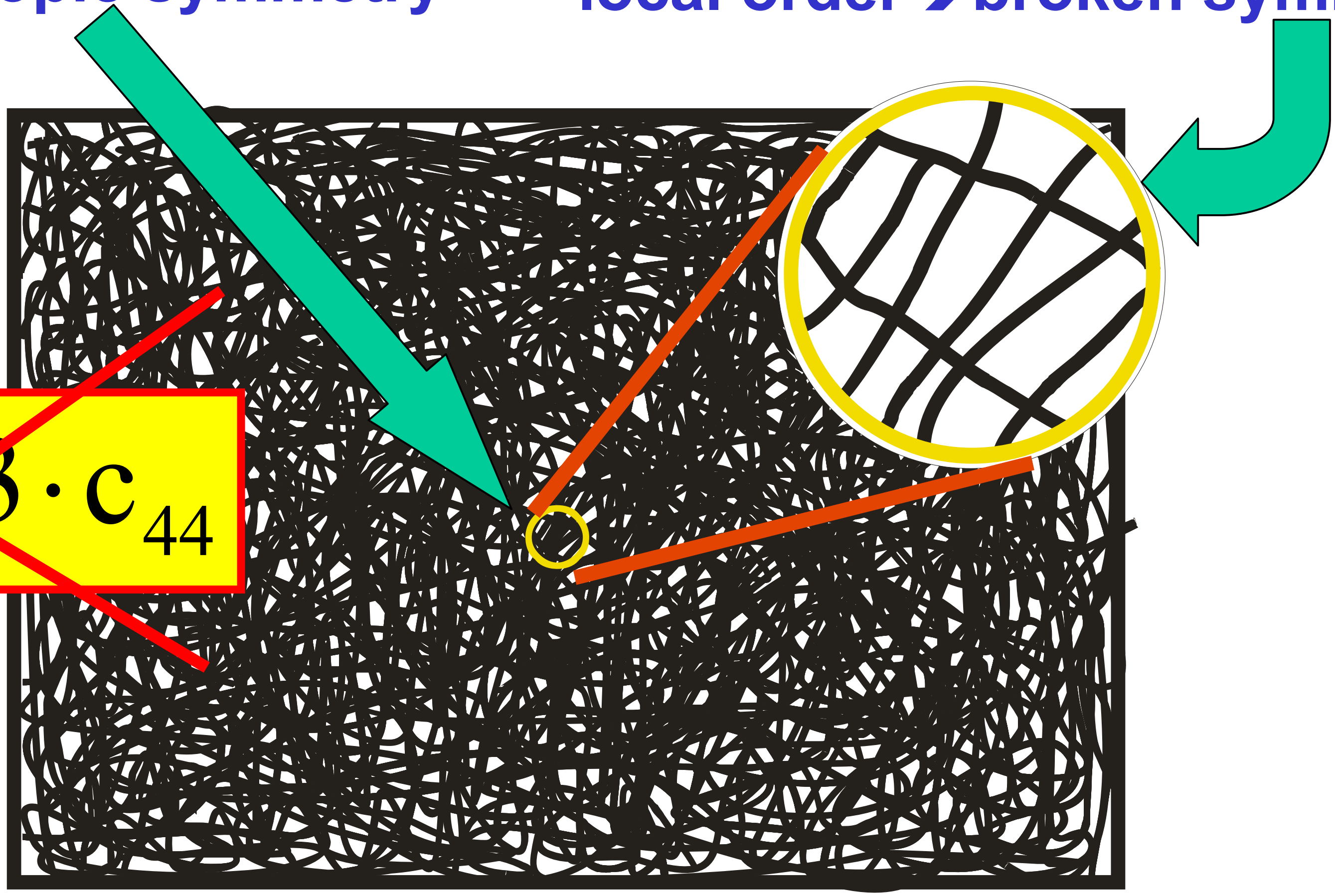
Relations in order to fulfill a Cauchy-relation in the isotropic state:

1. **Every particle is a center of inversion; There are only central forces between the lattice particles.**

2. **The related equation of motion contains only harmonic terms. Anharmonicity destroys the Cauchy relation.**

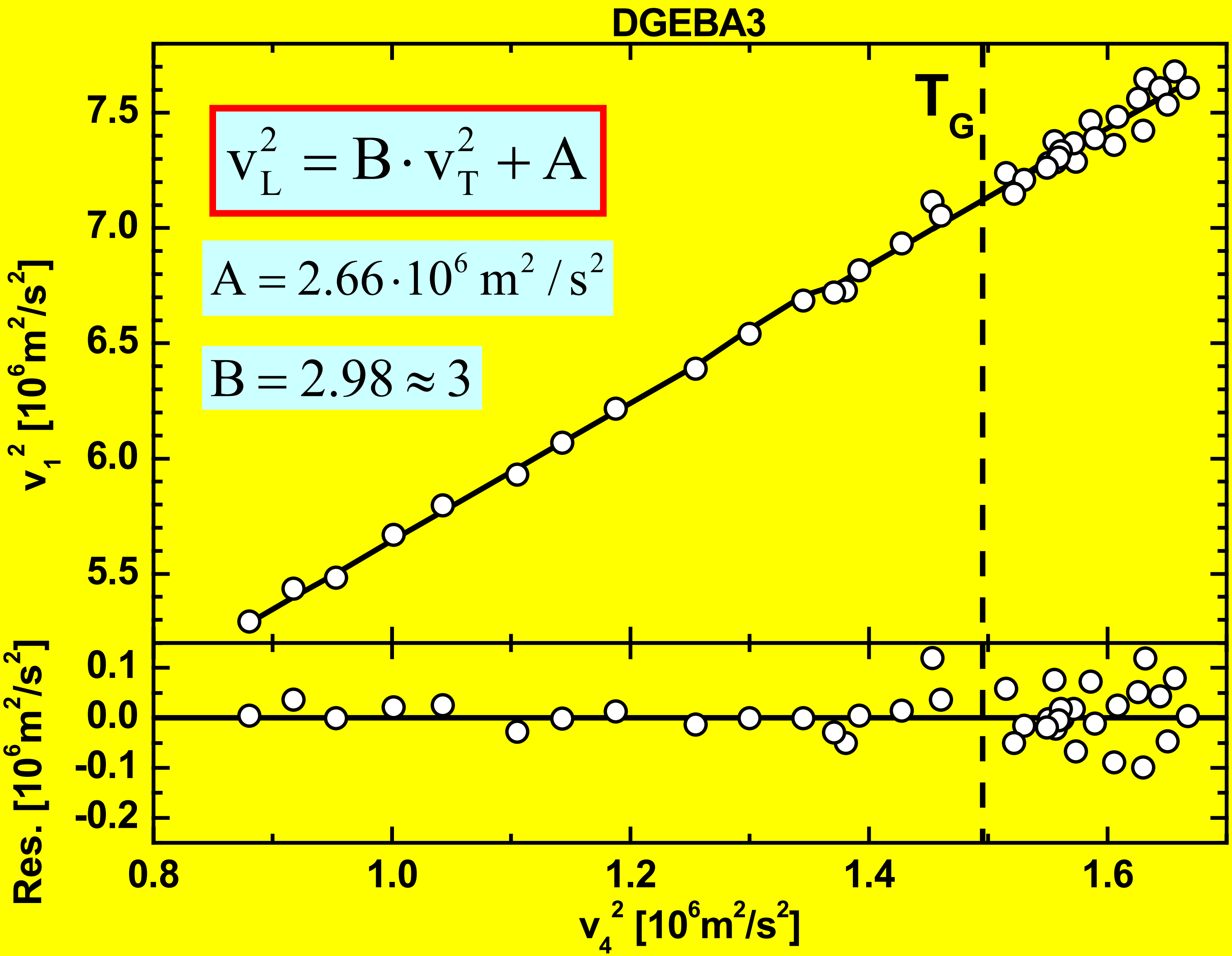
The amorphous state with global isotropic symmetry

The amorphous state with local order→broken symmetry



$$\cancel{c_{11} = 3 \cdot c_{44}}$$

The symmetry changes with the scale ←→
The global symmetry is isotropic, but not the local one!!



Krüger et al.PRB 2002/03

Zwanzig and Mountain (1965) proposed a generalized Cauchy-Relation for the high frequency elastic stiffness coefficients of simple liquids like argon

➔ Generalized Cauchy relation:

Decouples the stiffness constants

$$c_{11} = B \cdot c_{44} + A(P, T, X)$$

B=3

Depending on pressure and Temperature

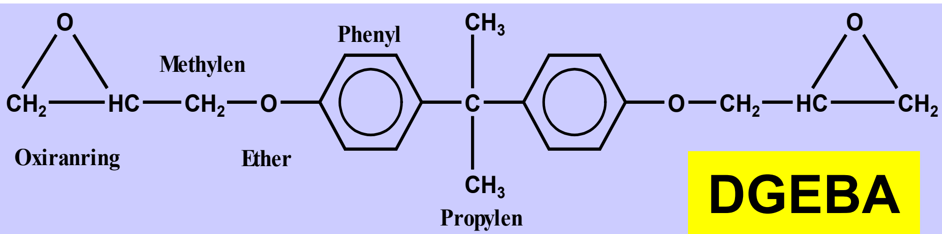
$$c_{11} = c_{11}(c_{44})$$

is not be a linear function

A real experimental and theoretical surprise

A reactive = curing material

Tm=315 K



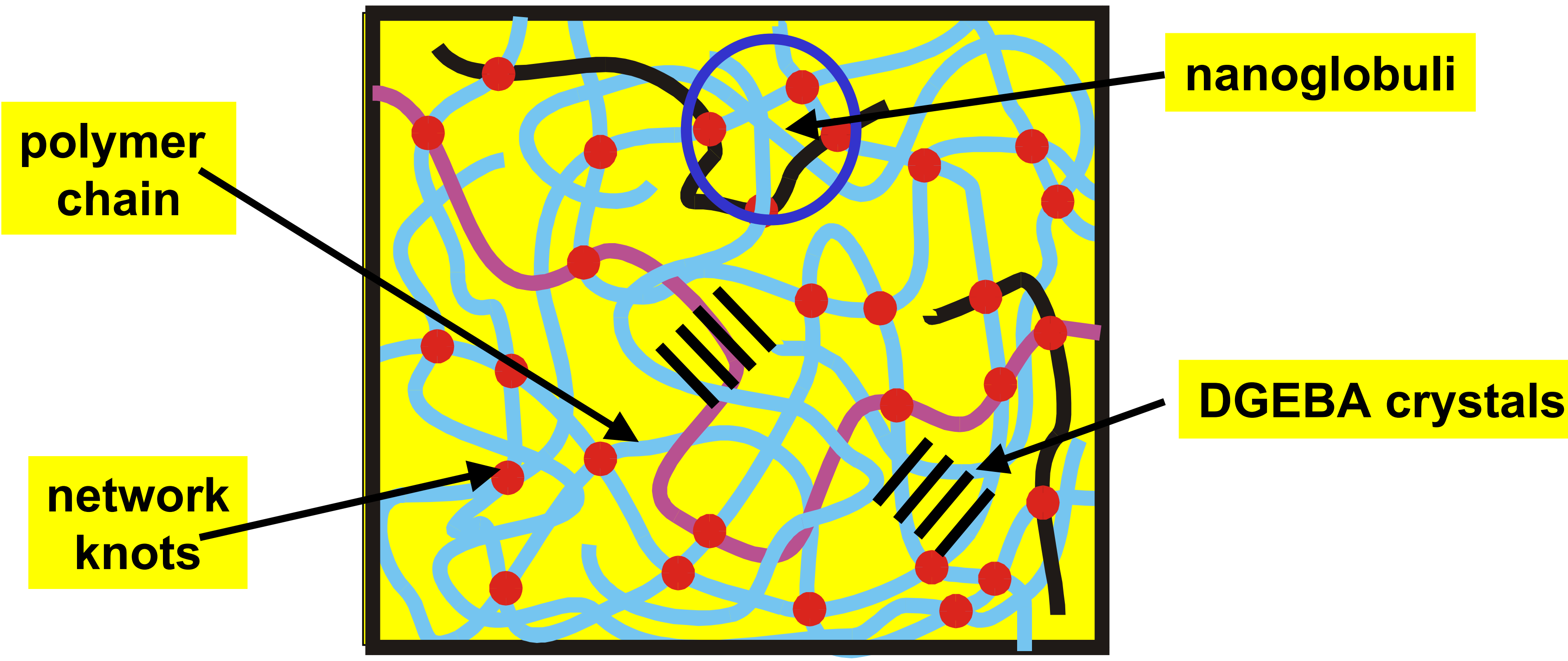
Tm=227 K

H_2N — C_2H_4 — NH — C_2H_4 — NH_2

primäres Amin

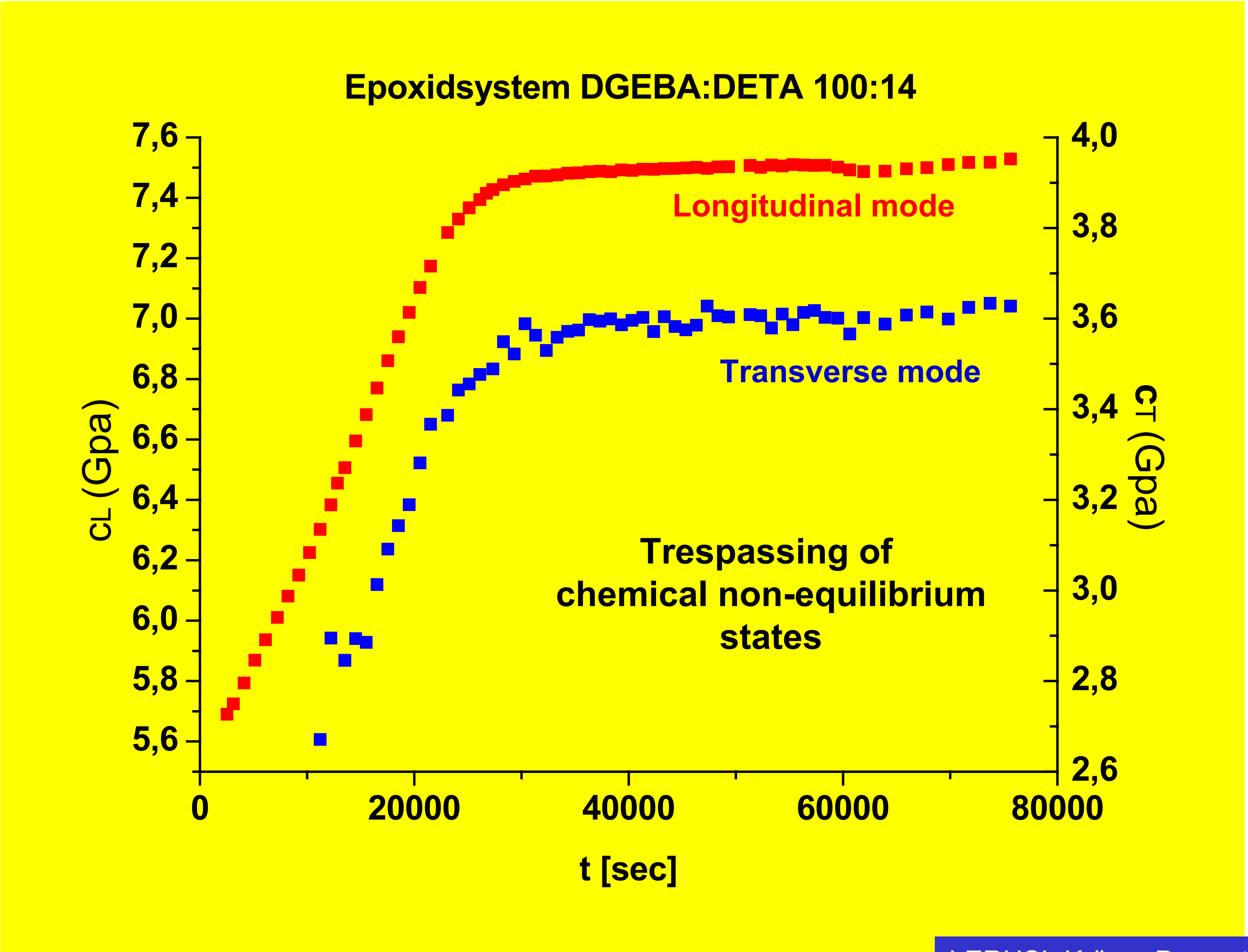
sekundäres Amin

DETA



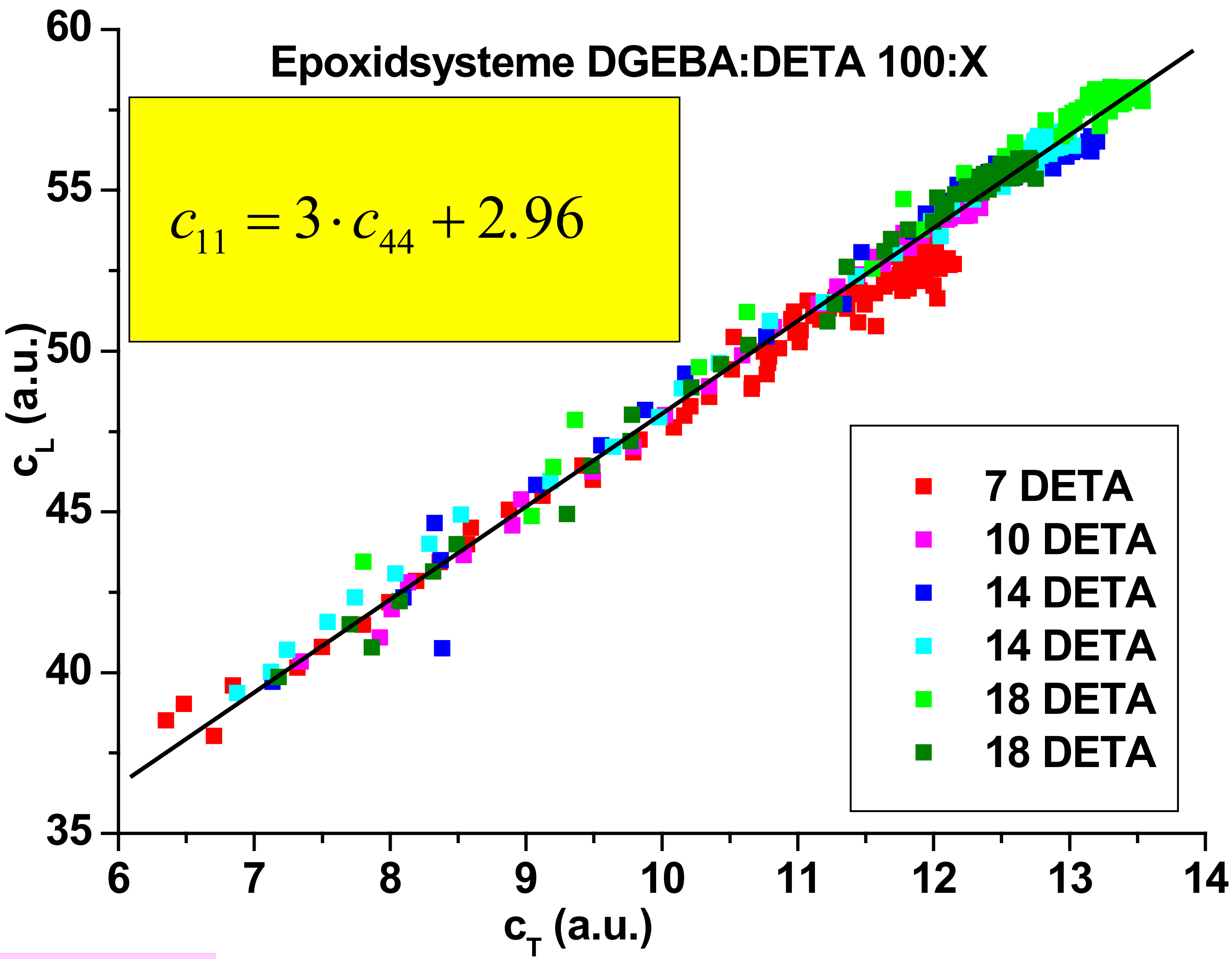
LERUSL Krüger,Possart,Alnot

The curing of an epoxy as seen by the elastic moduli



LERUSL Krüger,Possart,Alnot

Universal Cauchy-Relation in a non equilibrium system



Krüger et al. PRB (2001)

LERUSL Krüger,Possart,Alnot

Generalized Cauchy-Relation

$$\boxed{c_{11}(x) = A + B \times c_{44}(x)}$$

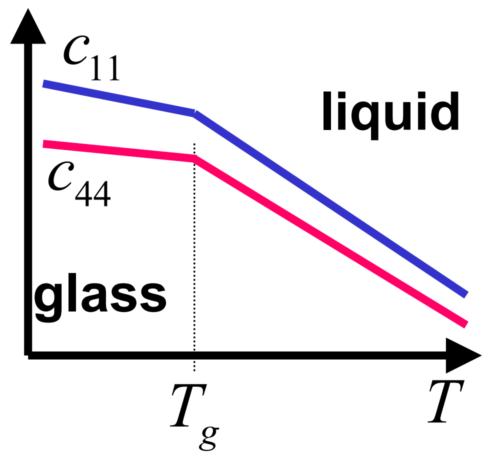
Curing Transition

Substance	A[GPa]	B
epoxy 100:10	3.12	2.96
epoxy 100:14 I	3.77	2.81
epoxy 100:14 II	3.44	2.82
epoxy 100:18 II	3.13	2.96

Glass Transition

	A[GPa]		B
DGEBA		2.92	2.98
PA6-3-T		2.94	2.96
I1	2.41	3.06	
LiCl-solution	4.66	3.15	
CeO_2 /7 at-% Yttrium	51	3.01	

➔ The generalized Cauchy-Relation is not a proportionality but a "linear transformation" with the following implications:



$$c_{11}^{\infty}(x) = A + B \cdot c_{44}^{\infty}(x)$$

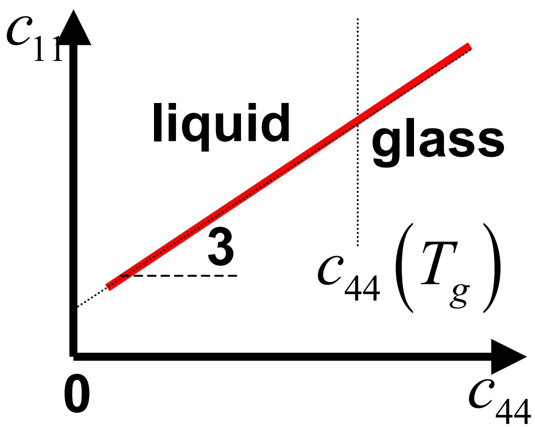
$$B = 3$$

reflects the ideal CR

$$\partial c_{11} / \partial c_{44} = B$$

$$\partial^n c_{11} / \partial x^n = B \cdot \partial^n c_{44} / \partial x^n \qquad n(\geq 1)$$

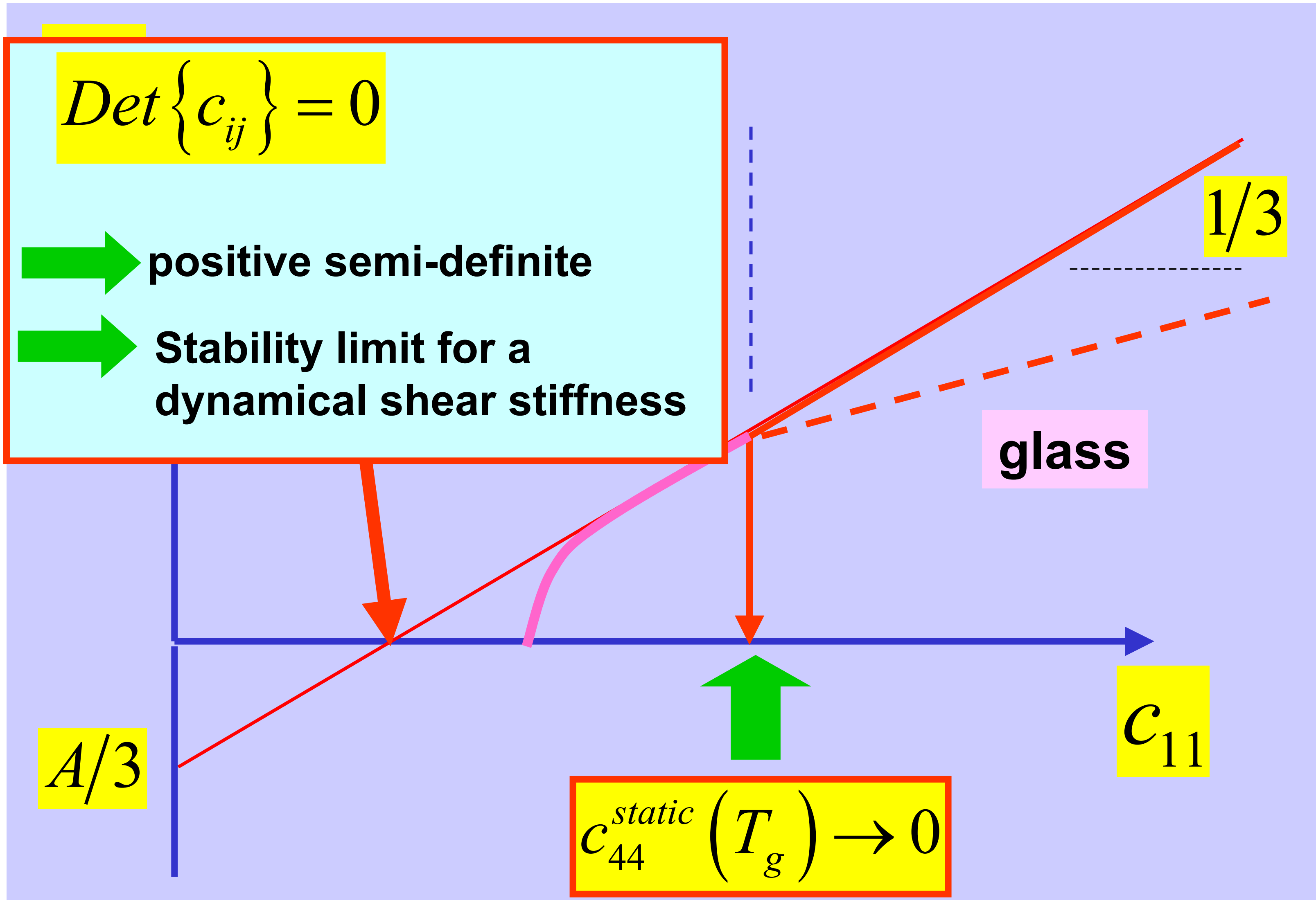
ideal CR



$$\partial c_{11} / \partial x = B \cdot \partial c_{44} / \partial x$$

$$\lim_{c_{44} \to 0} c_{11}^{\infty} = A$$

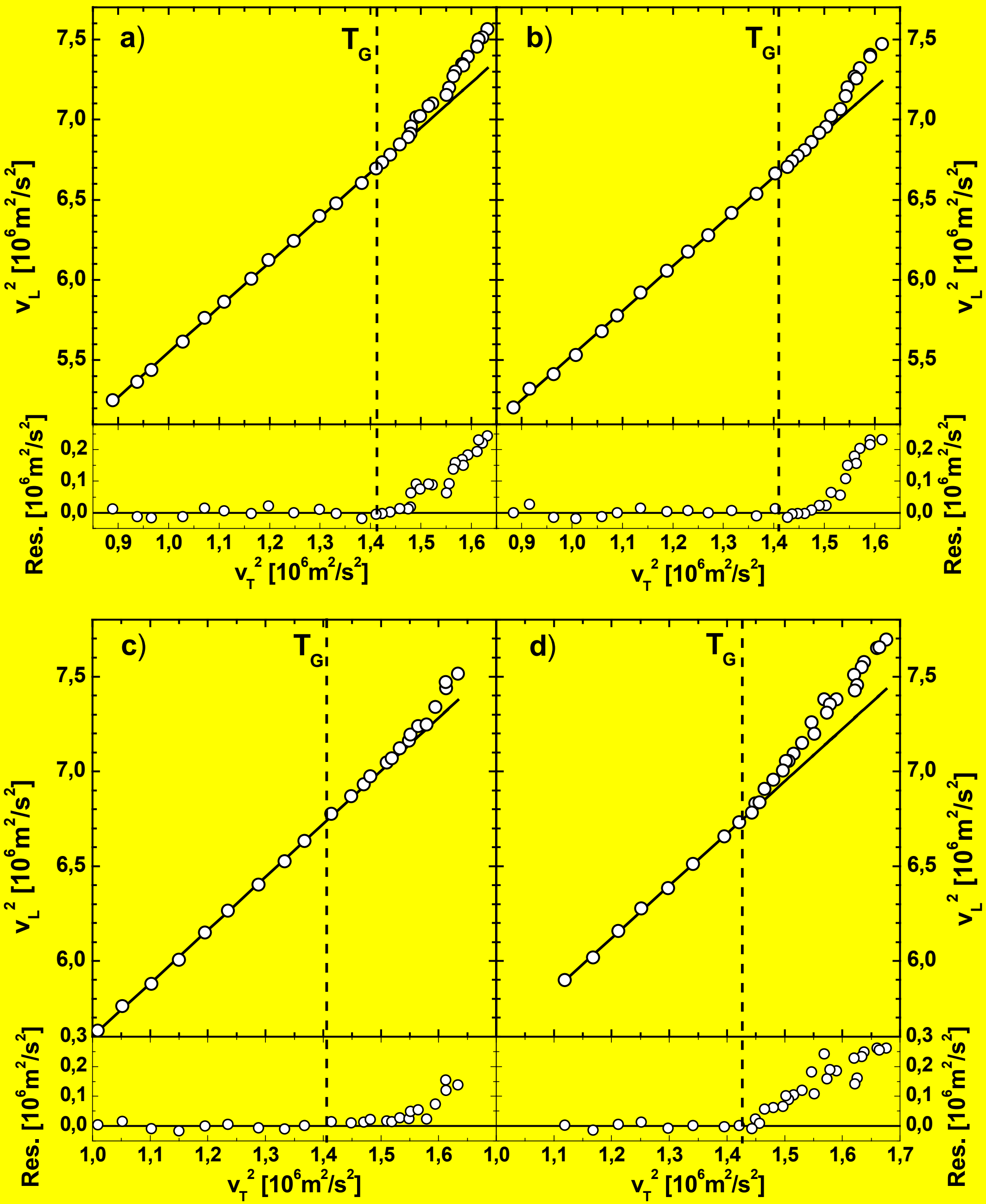
The inverted generalized Cauchy-relation: $c_{44} = B^{-1} \cdot c_{11} - A/B$



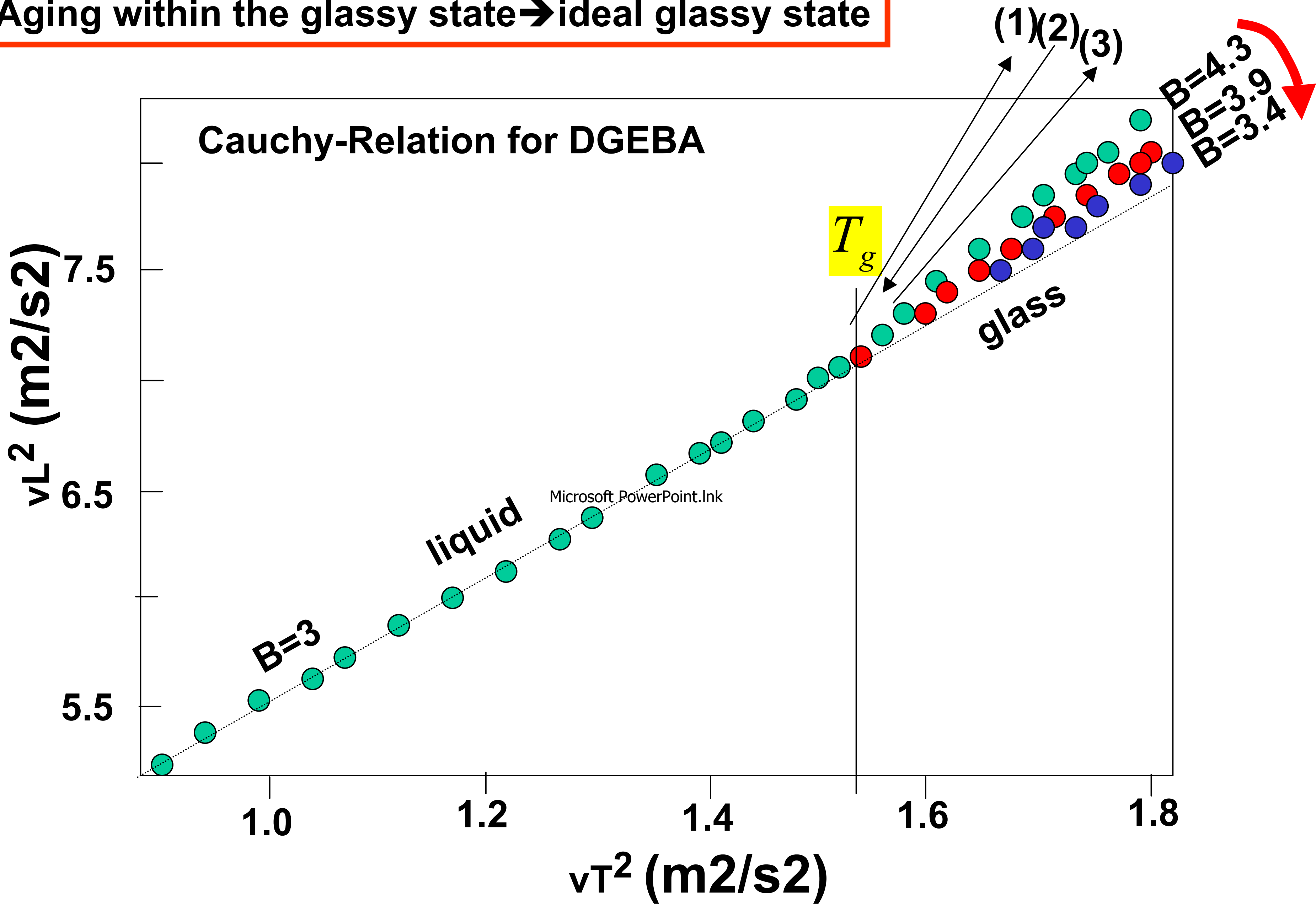
The glassy state is obtained by different quenching ➔

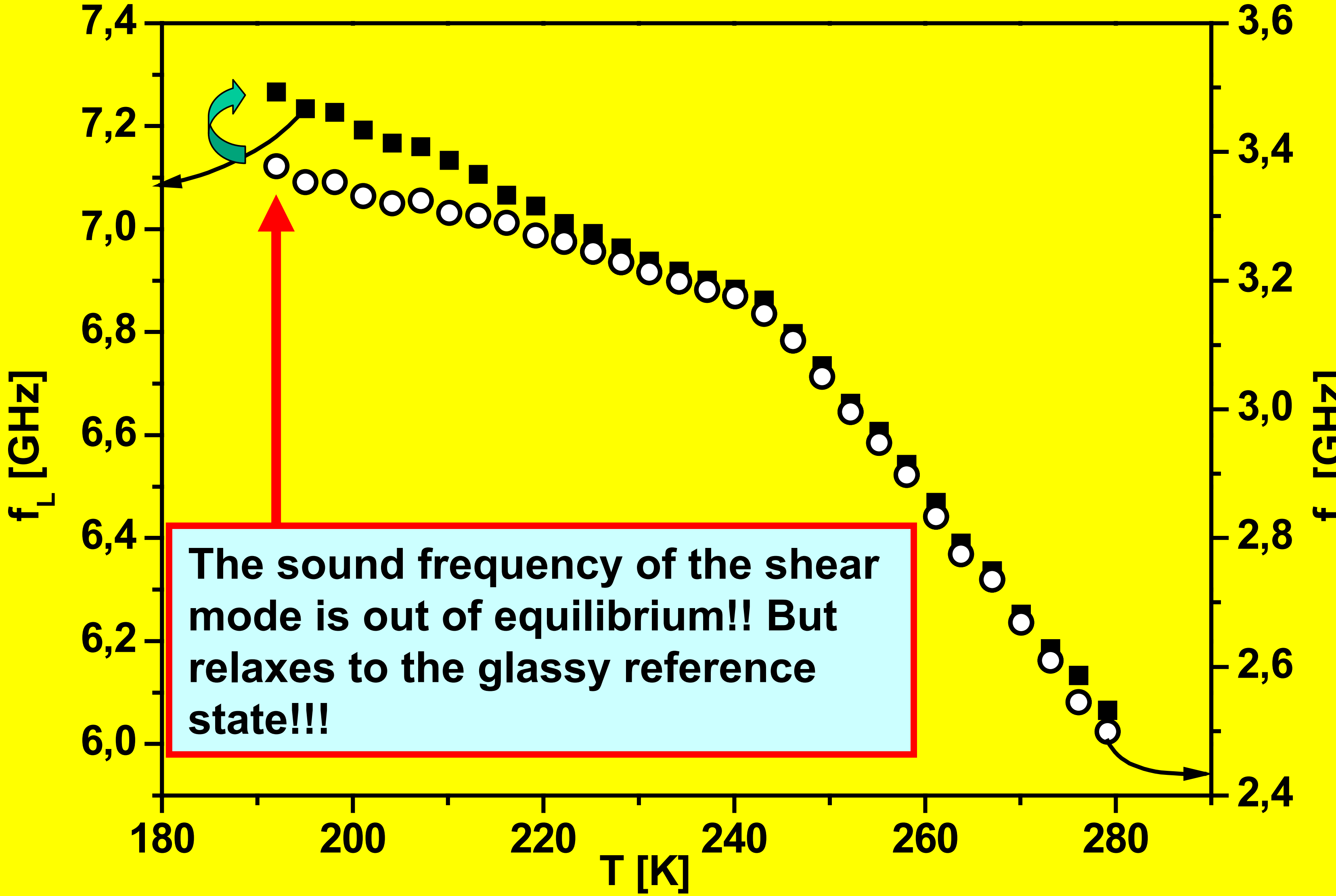
Fast quenching violates the generalized Cauchy-Relation,

Slow cooling yields a glassy reference state!



Aging within the glassy state→ideal glassy state




7,4
7,2
7,0
6,8
6,6
6,4
6,2
6,0
f_L [GHz]
3,6
3,4
3,2
3,0
2,8
2,6
2,4
f_T [GHz]
180
200
220
240
260
280
T [K]
The sound frequency of the shear mode is out of equilibrium!! But relaxes to the glassy reference state!!!

$$c_{11}^{\infty}\left(x\right) = A + B \cdot c_{44}^{\infty}\left(x\right)$$

What is the significance of the parameters A and B?

Do these parameters tell us something about the global and the local symmetry, molecular packing, metastability, etc ?

How do the parameters A and B change, if a material transforms from the amorphous via the nanostructured to the macroscopically ordered state?

Curing of a polymer network with large loops resp. voids which violate the generalized CR

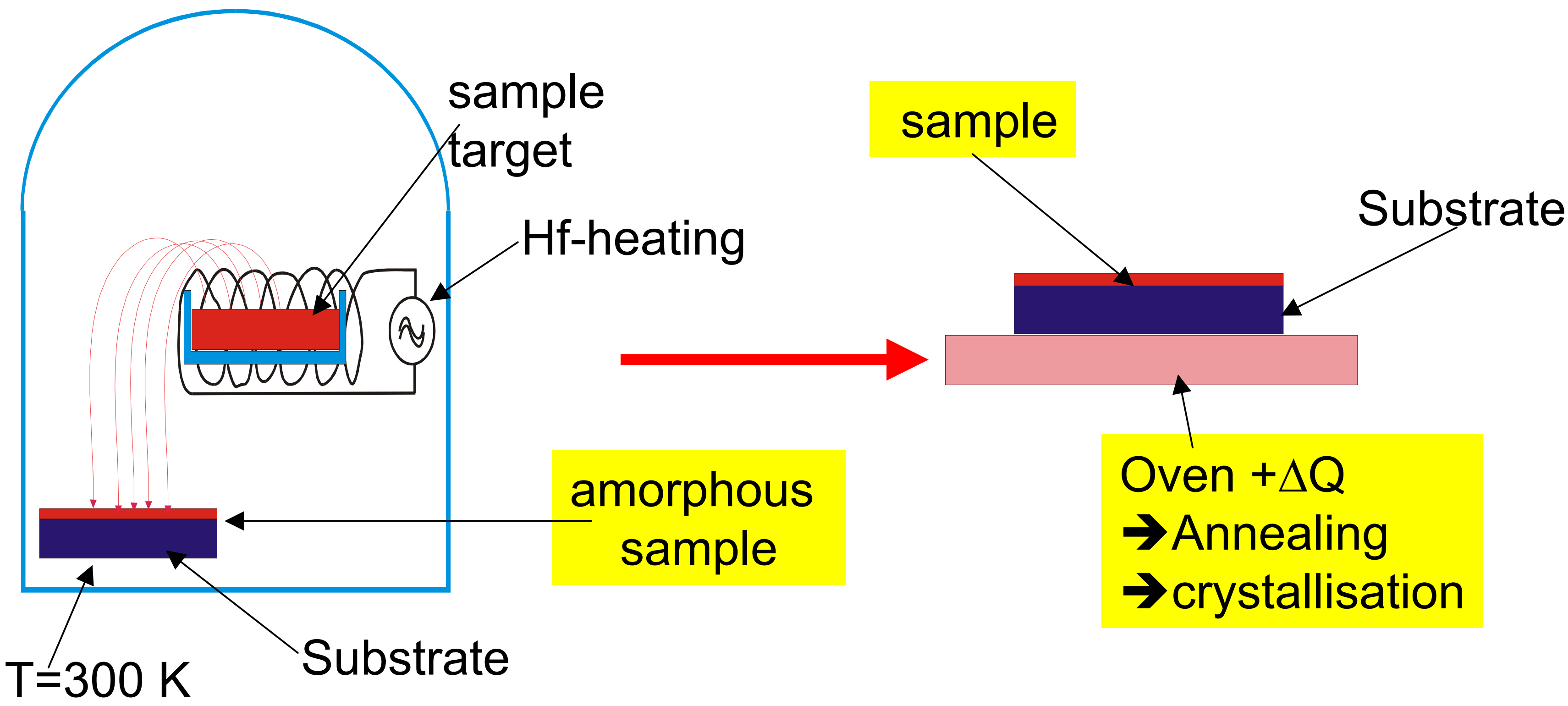
Obviously, the longitudinal stiffness lags behind the shear stiffness during polymerization ➔ B=0.9

This Polyurethane has voids which are ten times as large as found in EPOXies

These voids can be interpreted as „nanoparticles“ within the polymeric matrix.

It should be remembered that to first order shear deformation does not change the volume!
➔ large voids affects rather the longitudinal then the shear stiffness

How to get a **dense** nanocrystalline state: Nanocrystallization by suczessive annealing of the amorphous state

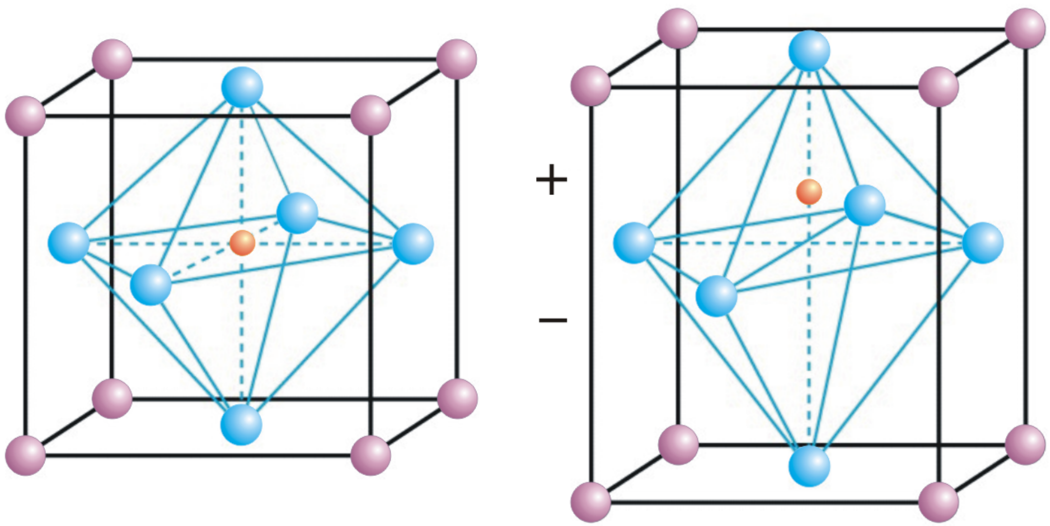


TP B6, Krüger,Schmitt, Rieger

Ca doped Lead Calcium Titanate (PTC) Thin-Film Samples

Perovskite structure

$T > T_C$ $T < T_C$



$T_C = 530$ K

Characteristic of the samples
Thin-films of amorphous PTC were rf-sputtered.
Thickness of the films was 1 μm.

Pb, Ca

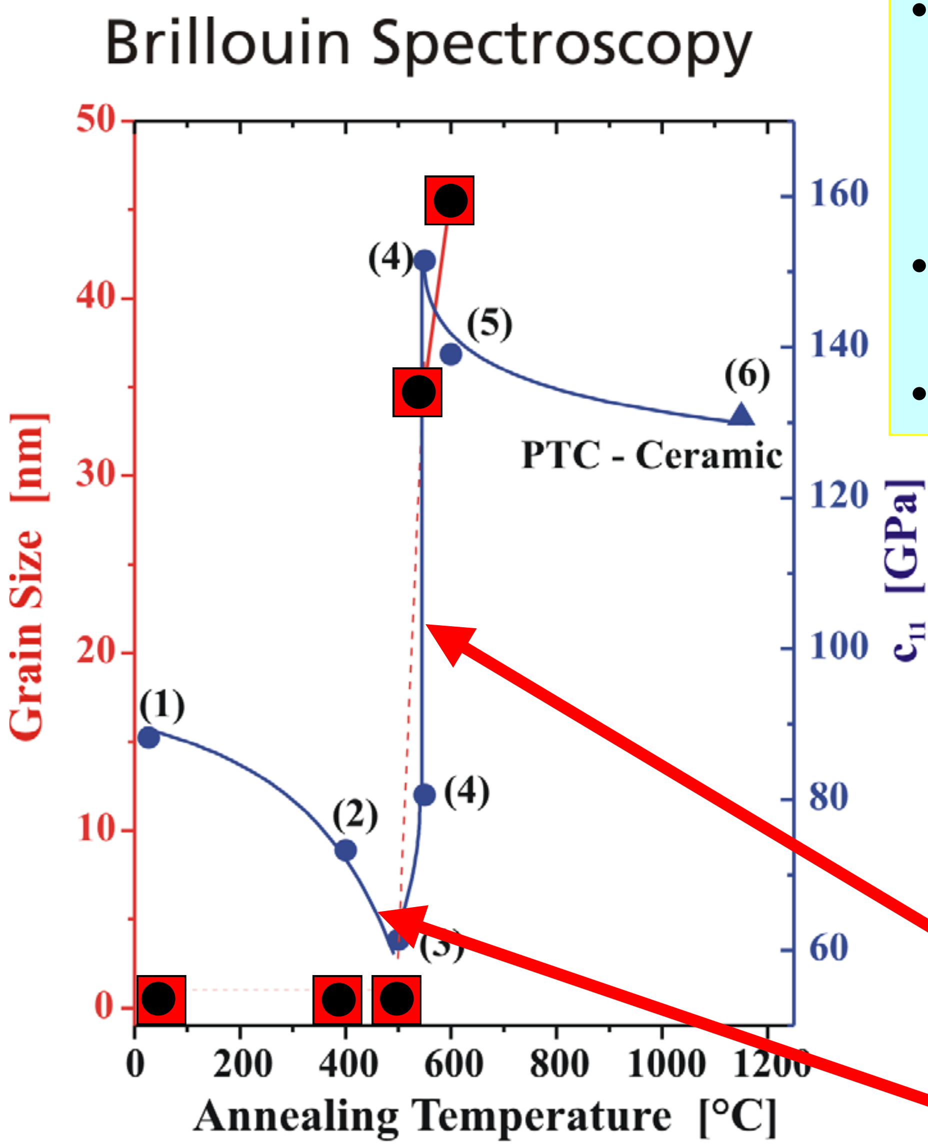
O^{2-}

Ti, Zr

T_C Curie temperature

Sample	Annealing temperature [°C]	Grain size [nm]; (XRD)	State
1	20	-	amorphous
2	400	-	amorphous
3	500	-	amorphous
4	550 (T_{ca})	35	metastable
5	600	46	crystallized
6	650	67	crystallized

TP B6, Krüger,Schmitt, Rieger



- How does the cross-over from the amorphous to the crystalline state takes place?

- An amorphous shows a glass transition!!
- A crystal shows melting!!

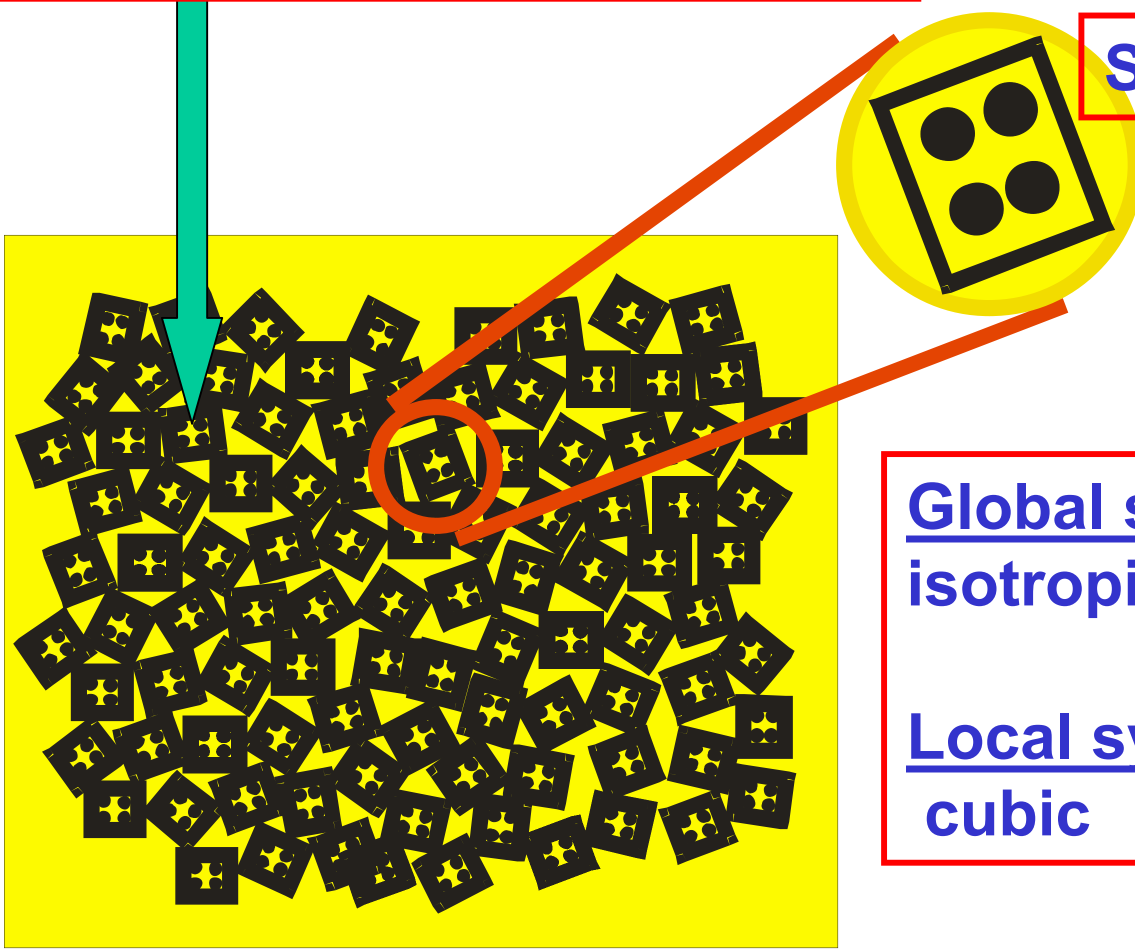
Origin of the discontinuity?

Origin of the softening in the sub-nanometer regime?

Krüger et al. PRL, 78 (1997)

Consolidated nanocrystals with little porosity

The randomly oriented and consolidated single crystals form globally an isotropic state



Single crystal

<u>Global symmetry:</u>
isotropic

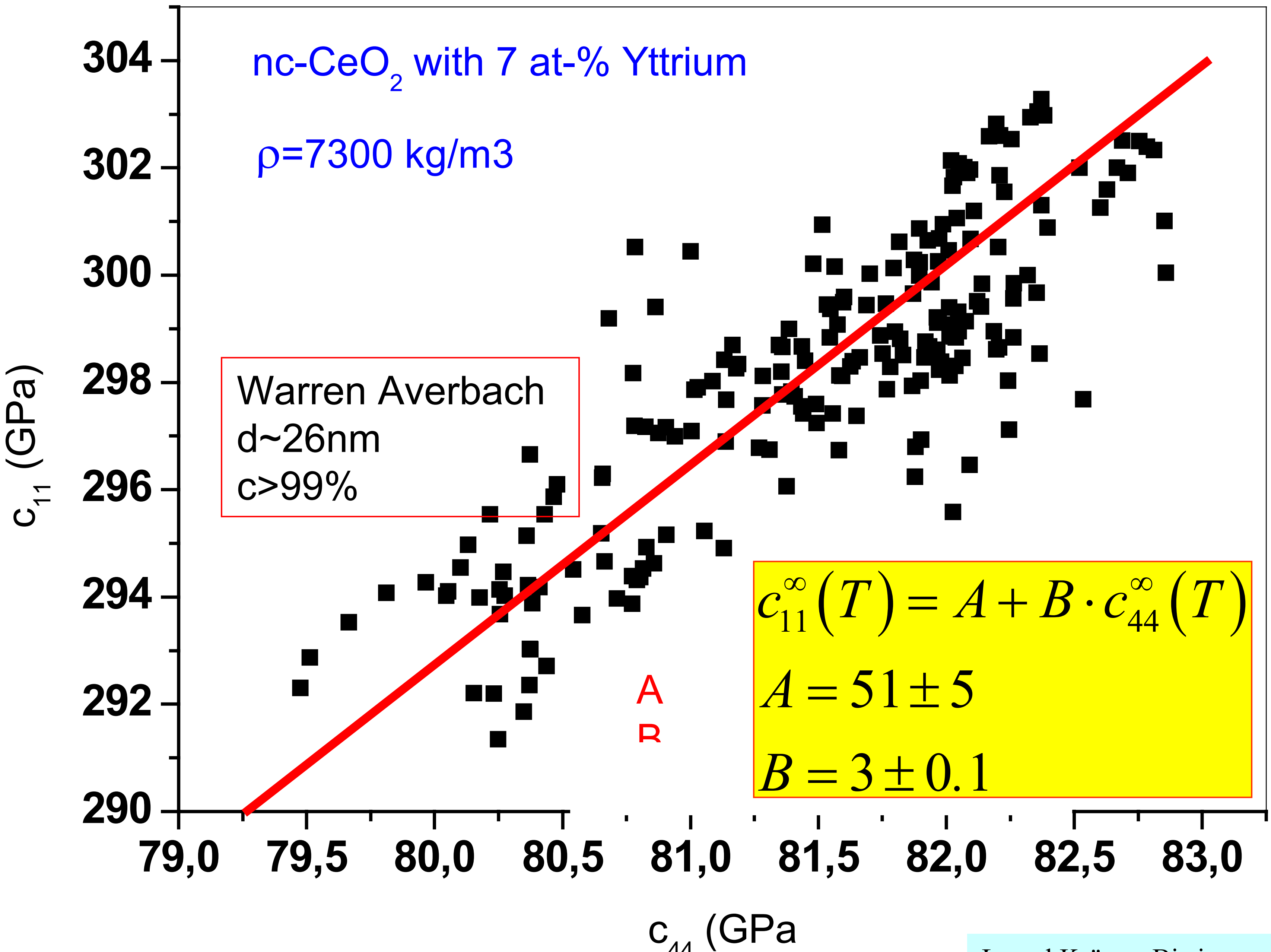
<u>Local symmetry:</u>
cubic

Consolidated CeO_2 with little porosity: One of few samples in the world

we deal with consolidated nanocrystals of cubic structure with macroscopic isotropic symmetry by statistic crystal orientation ⟷ **Does a Cauchy relation hold??**

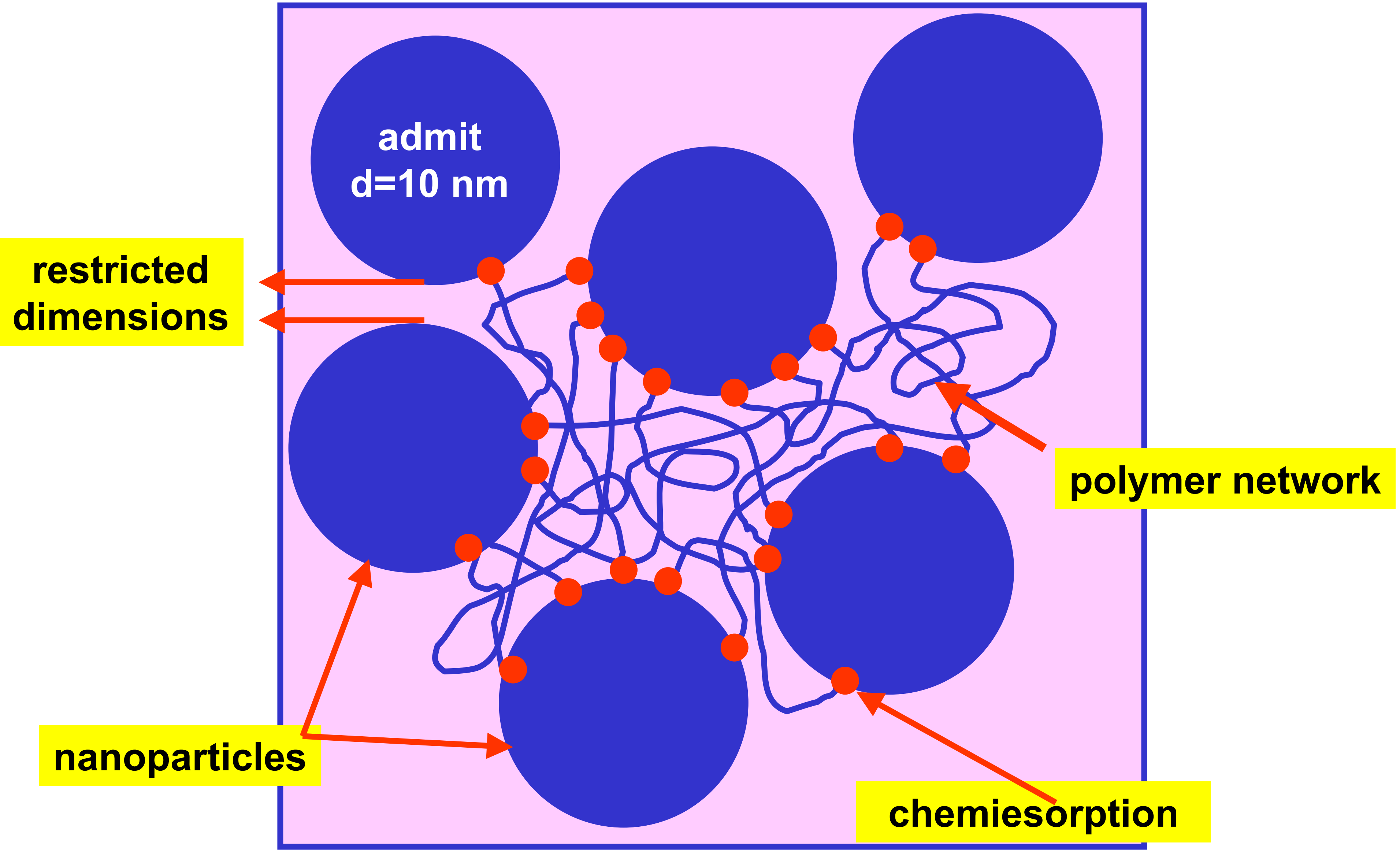
According to Warren Averbach
d=26 nm
c>>99%

Birringer, Tschöpe UdS

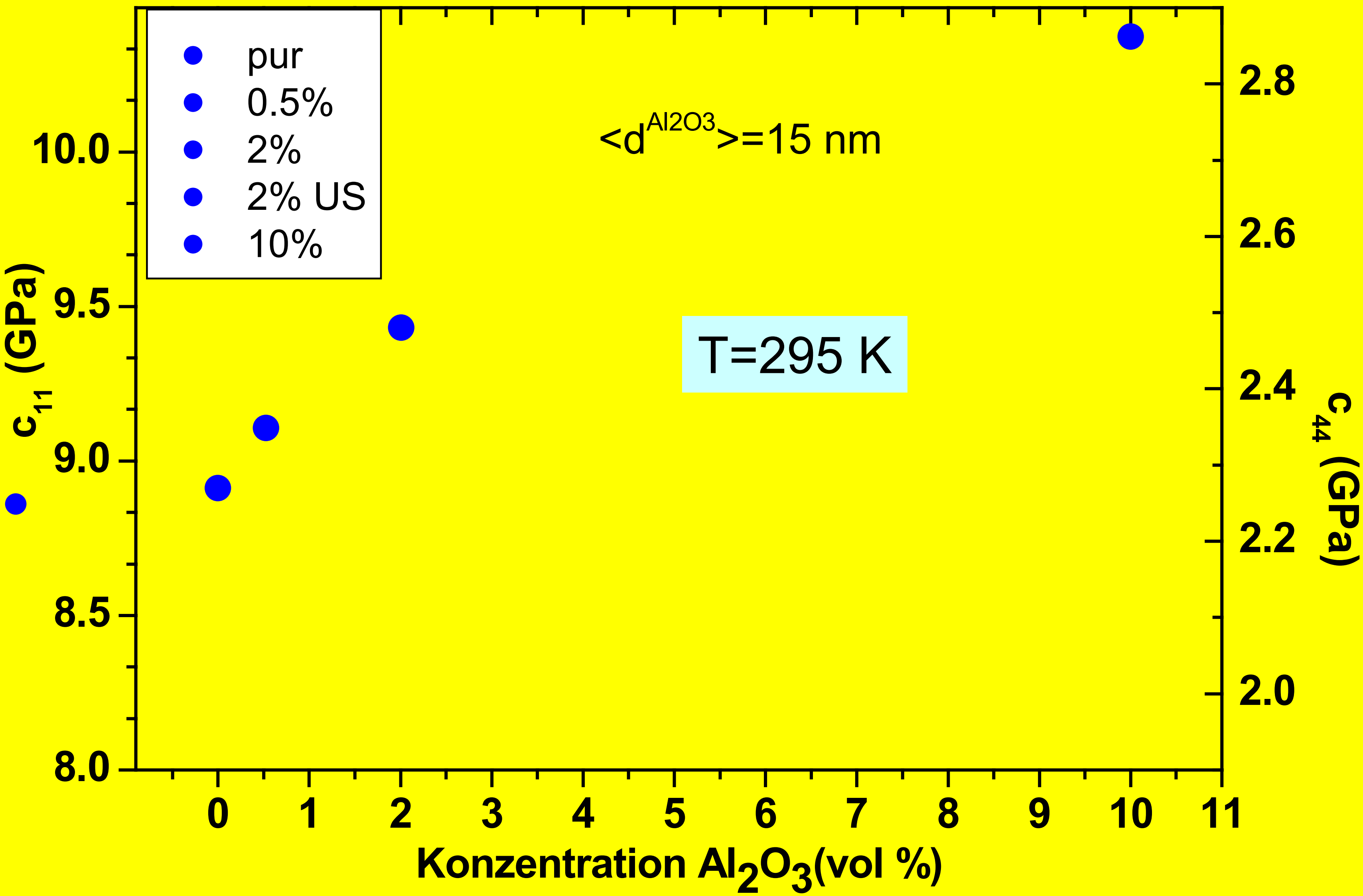


Lerusl Krüger, Birringer, Alnot

Reactive nanocomposite with restricted dimension and selective surface interactions

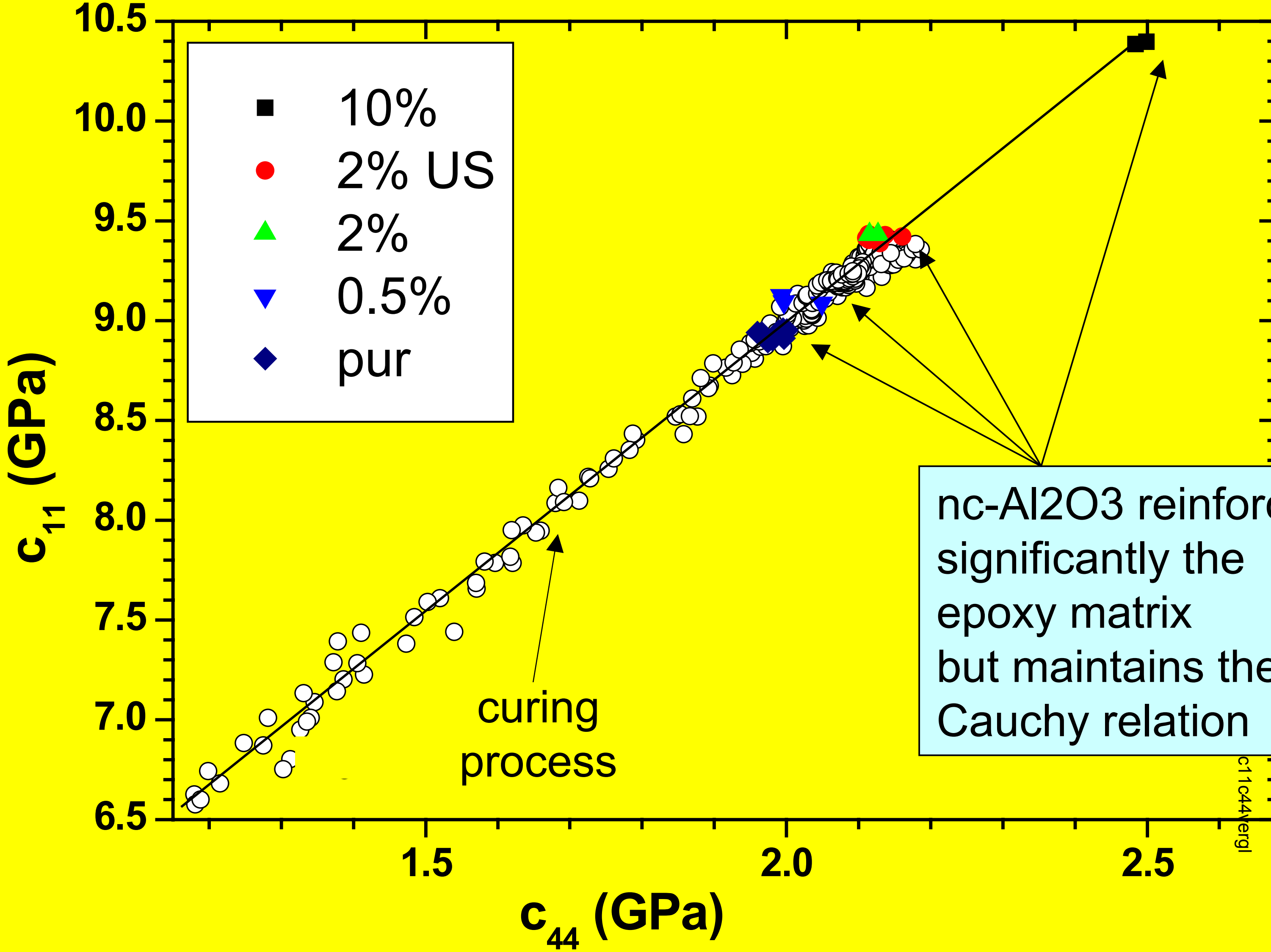


Nano-composite of epoxid & Al2O3 nano-particles



LERUSL Krüger,Wetzel,Possart,Alnot

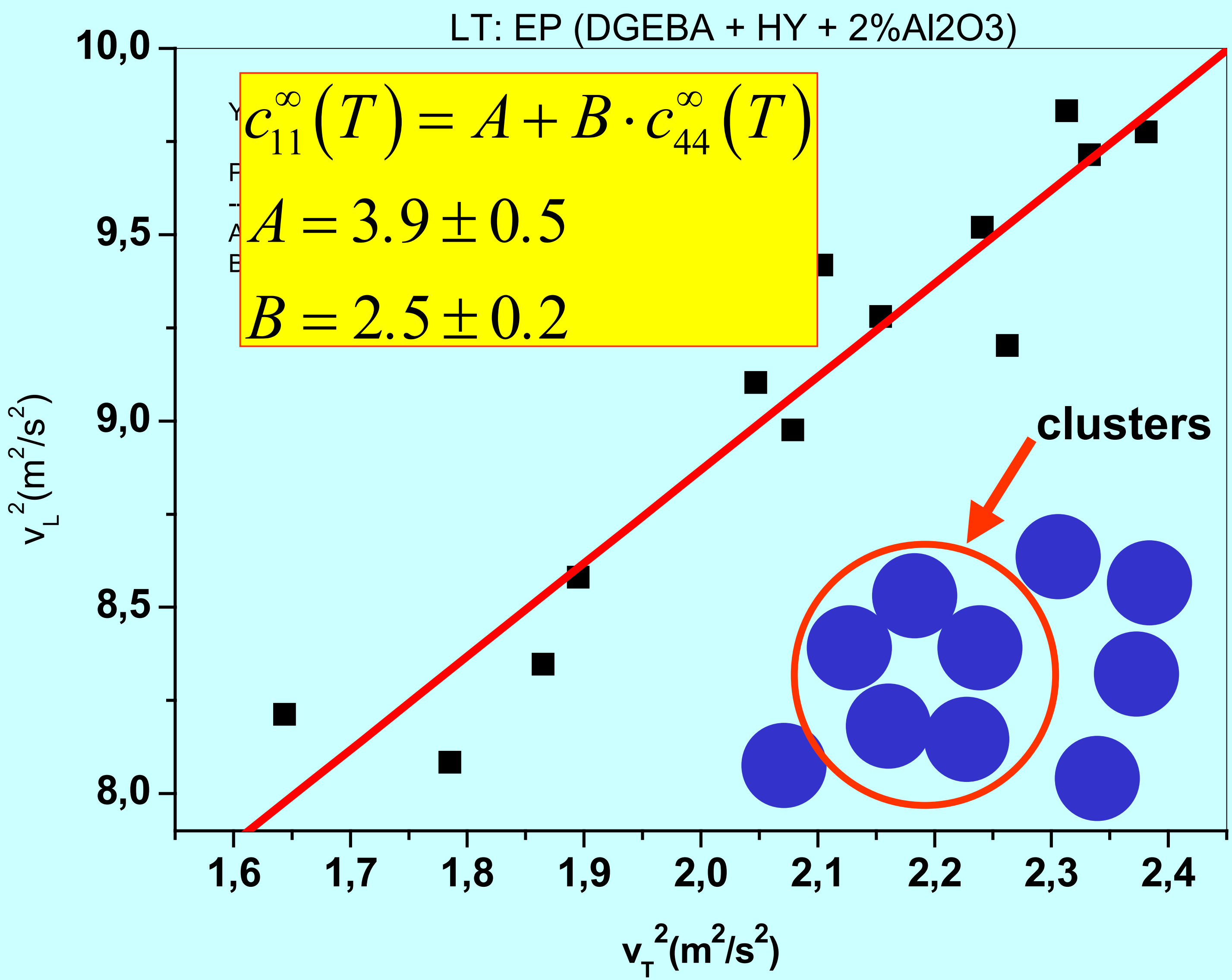
Reinforcement of an epoxy with Al2O3 nanocrystallites
➔ Superelasticity by enhanced network formation

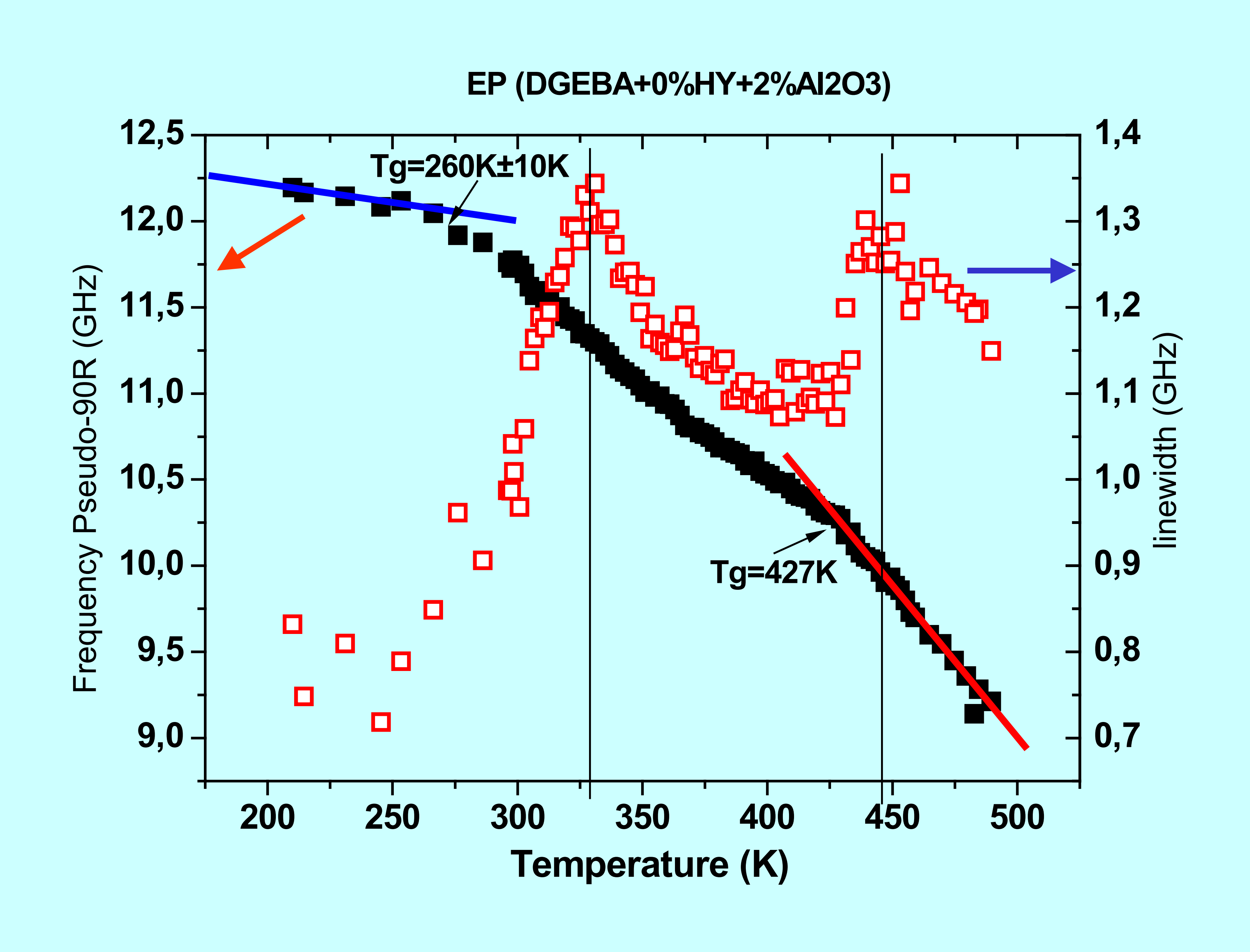


nc-Al2O3 reinforces significantly the epoxy matrix but maintains the Cauchy relation

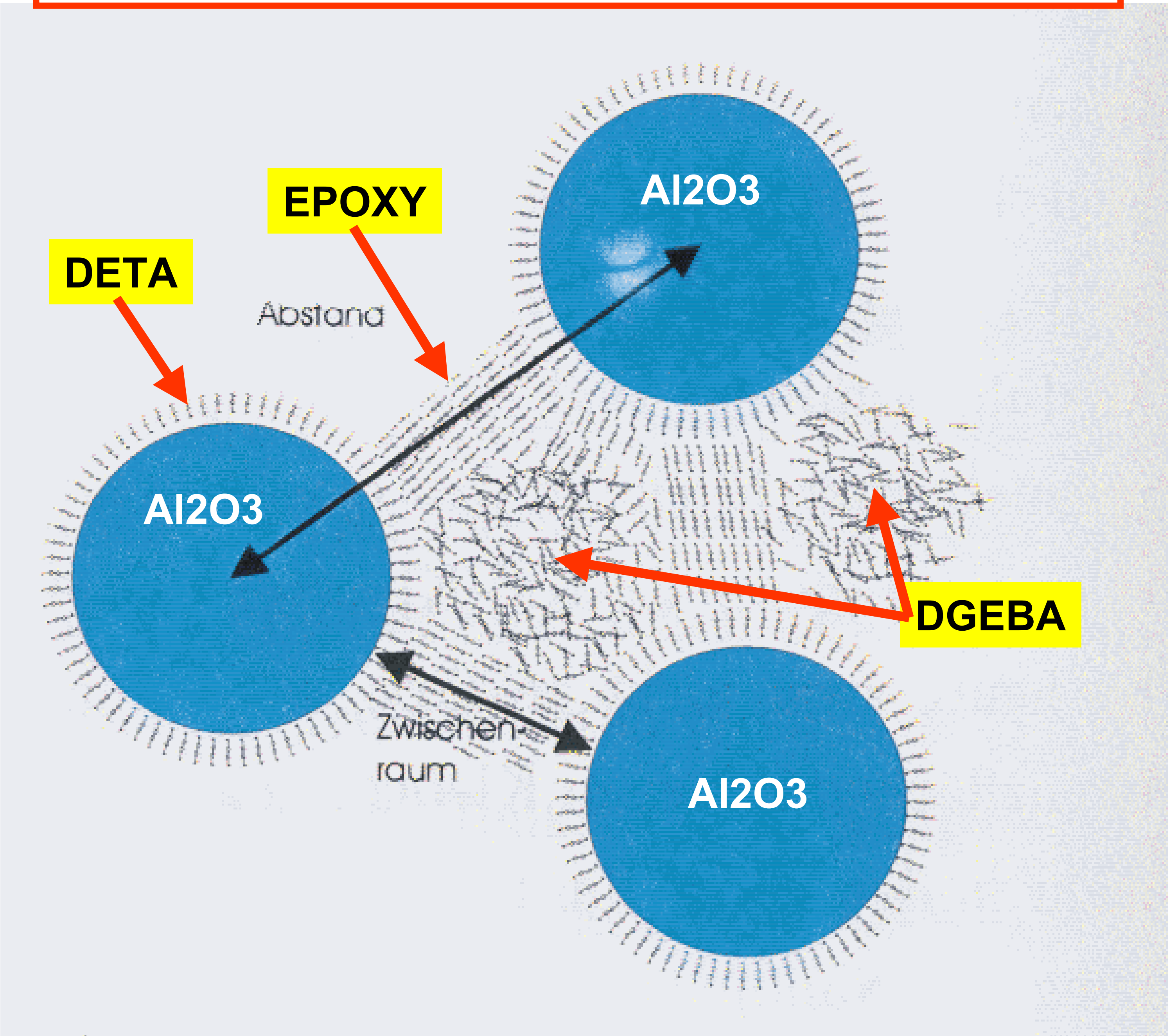
LERUSL Krüger,Wetzel,Possart,Alnot

About the influence selective of selective surface interactions and clusters




EP (DGEBA+0%HY+2%Al2O3)
Tg=260K±10K
Tg=427K
Frequency Pseudo-90R (GHz)
linewidth (GHz)
Temperature (K)
12,5
12,0
11,5
11,0
10,5
10,0
9,5
9,0
1,4
1,3
1,2
1,1
1,0
0,9
0,8
0,7
200
250
300
350
400
450
500

About the morphology of an EPOXY nano-composite



Conclusion

It is interesting to note that in classical physics one can still find quasi universal relations like the generalized CR

It seems that the parameter B is sensitive to the global symmetry but that the parameter A is sensitive to the local symmetry breaking

The generalized CR tells us, that even in nonequilibrium system we can predict the shear properties from the longitudinal one, provided we know one data pair!

Even more, their exist a strict proportionality between the derivatives:

$$\boxed{\partial_x^n c_{11} = B \cdot \partial_x^n c_{44}} \qquad \boxed{n(\geq 1)}$$