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Phase Transitions in Polymers and Their Analysis

Michael Hess

Department of Physical Chemistry

4th UNESCO SCHOOL on MACROMOLECULES AND MATERIALS, UNIVERSITY of STELLENBOSCH 07.04.-08.04.2001

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Talking about Phase Diagrams:

a) p-V-T Diagrams of pure components

b) p(x)-, T(x)-, Bakhuise-Roozeboom-Diagrams of binary (multicomponent) mixtures

- miscible systems
- partially miscible systems
  - systems with an eutecticum
  - systems with UCP and/or LCP

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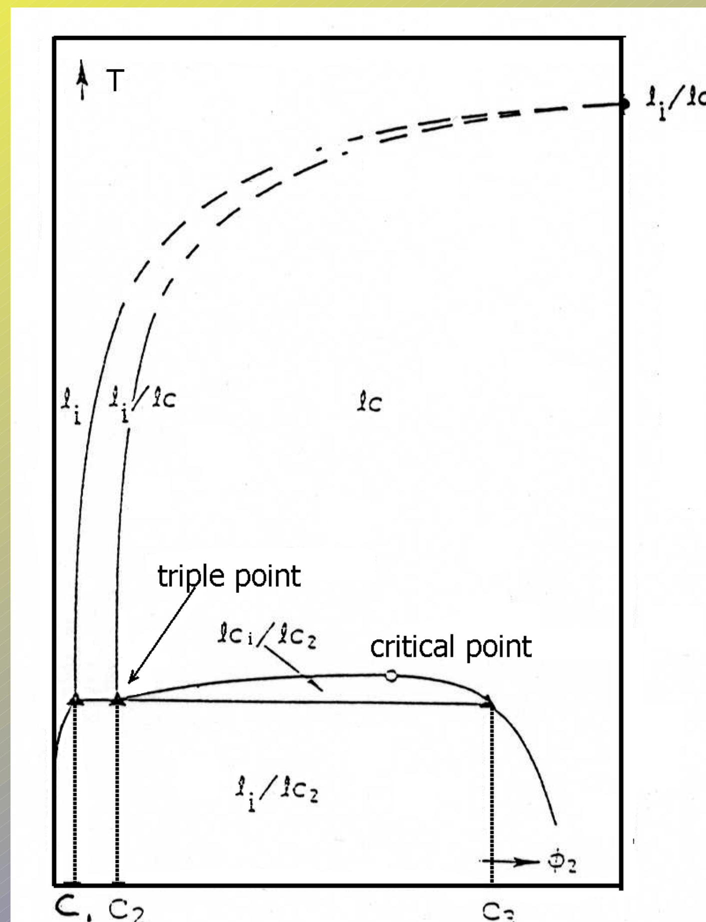
Binary Phase Diagram with a Liquid Crystal



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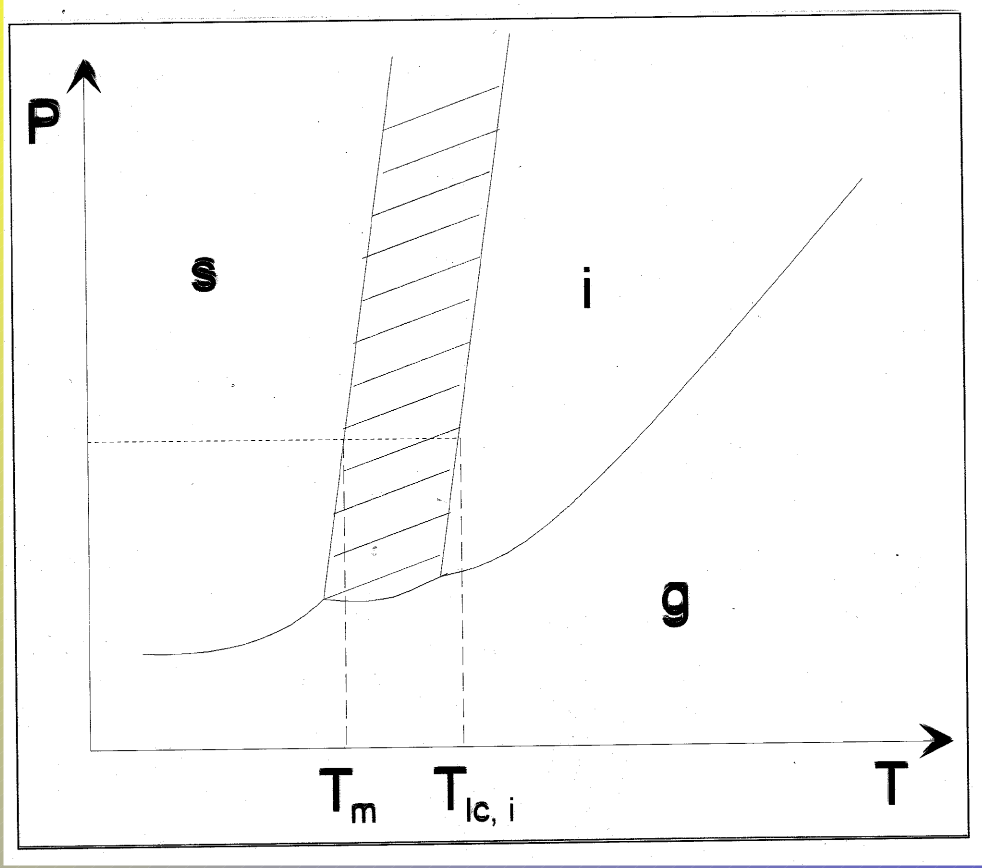

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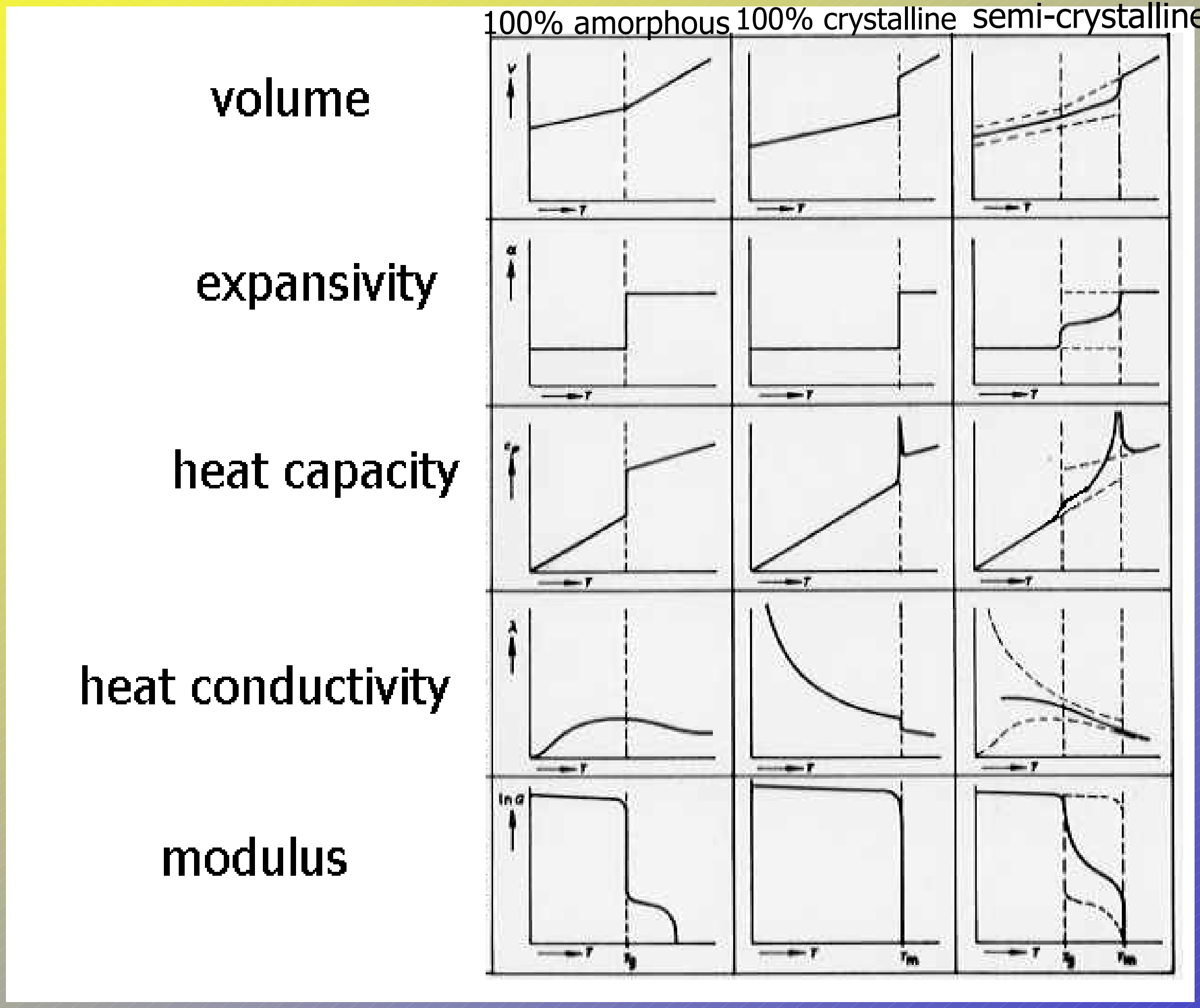

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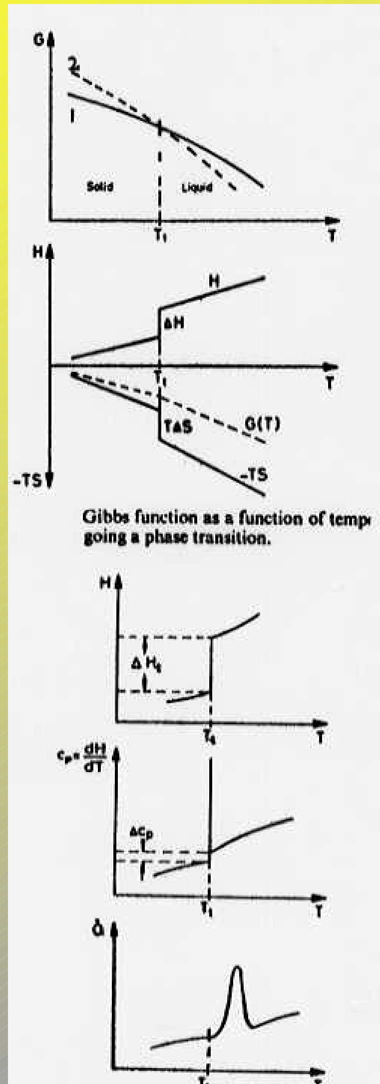
The Gibbs energy energy at a phase transition



What makes things go:

$\Delta_{trans}G < 0$

Calorimeter response

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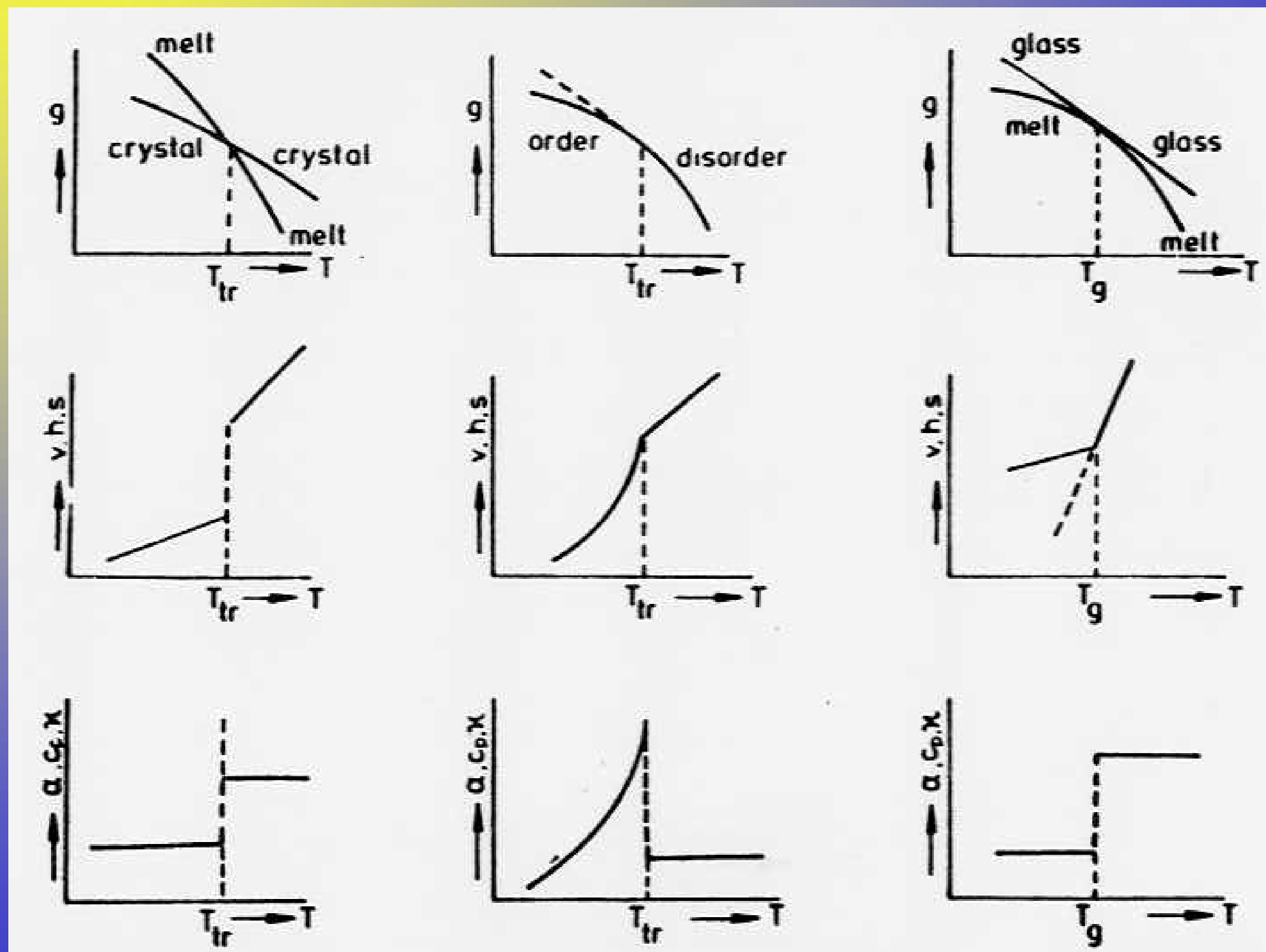

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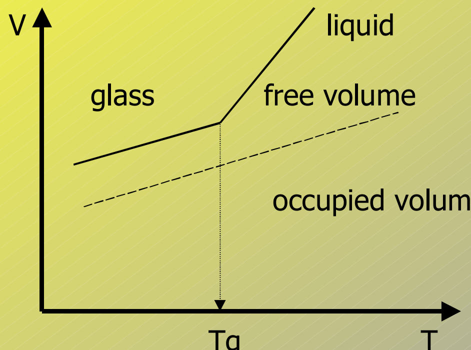
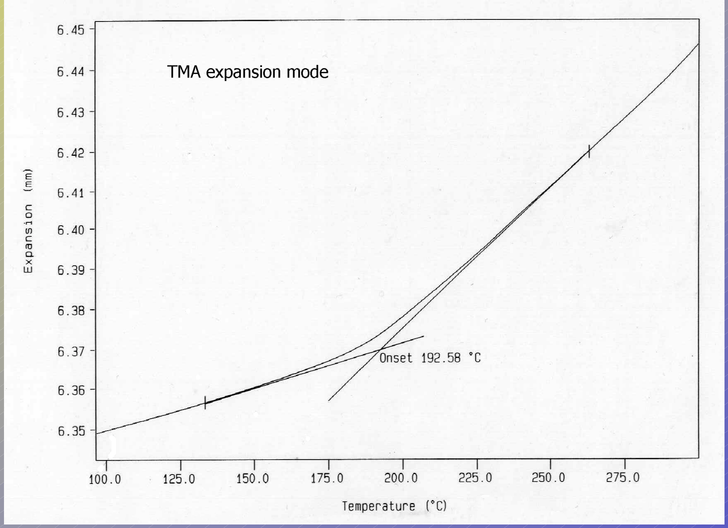
All is free volume and chain mobility



The glassy state can be described as an **iso-free volume state**



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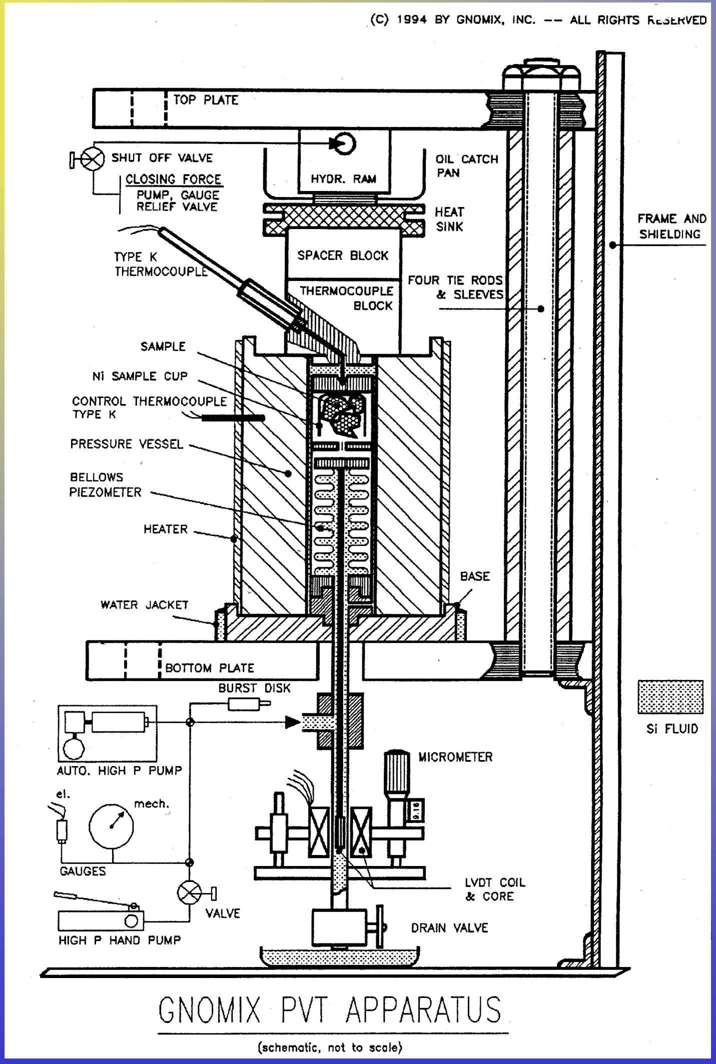
The GNOMIX device for p-v-T experiments



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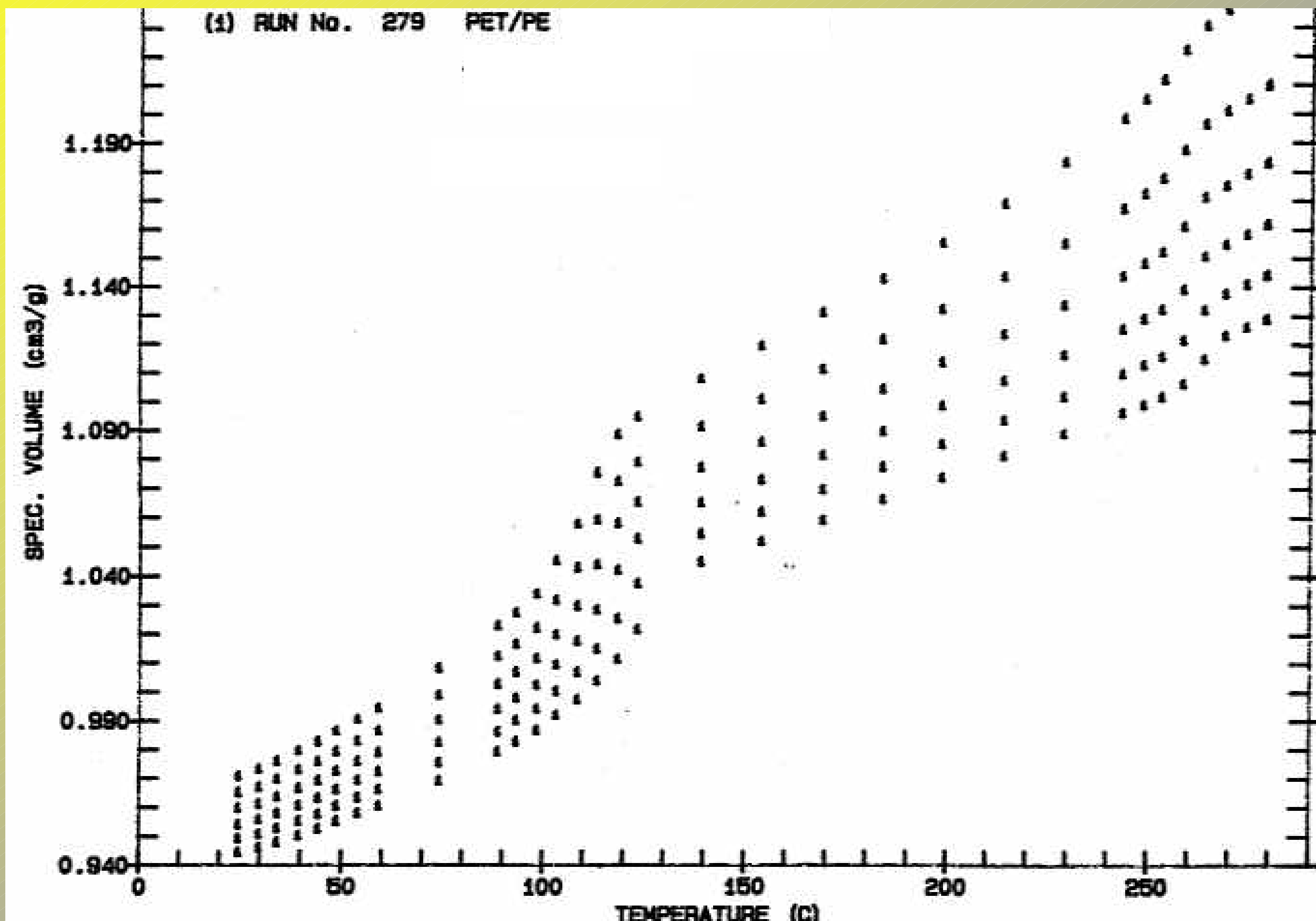

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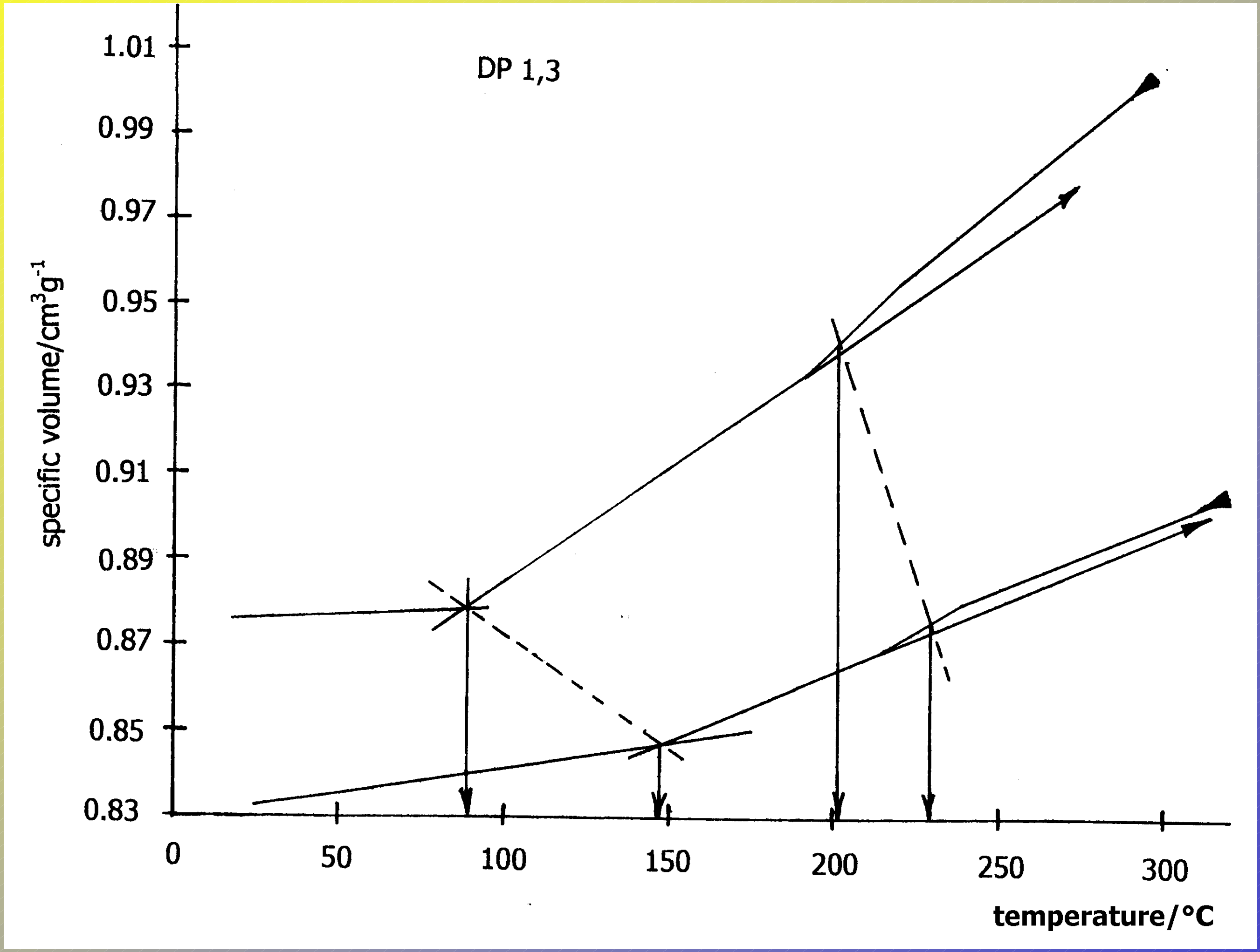

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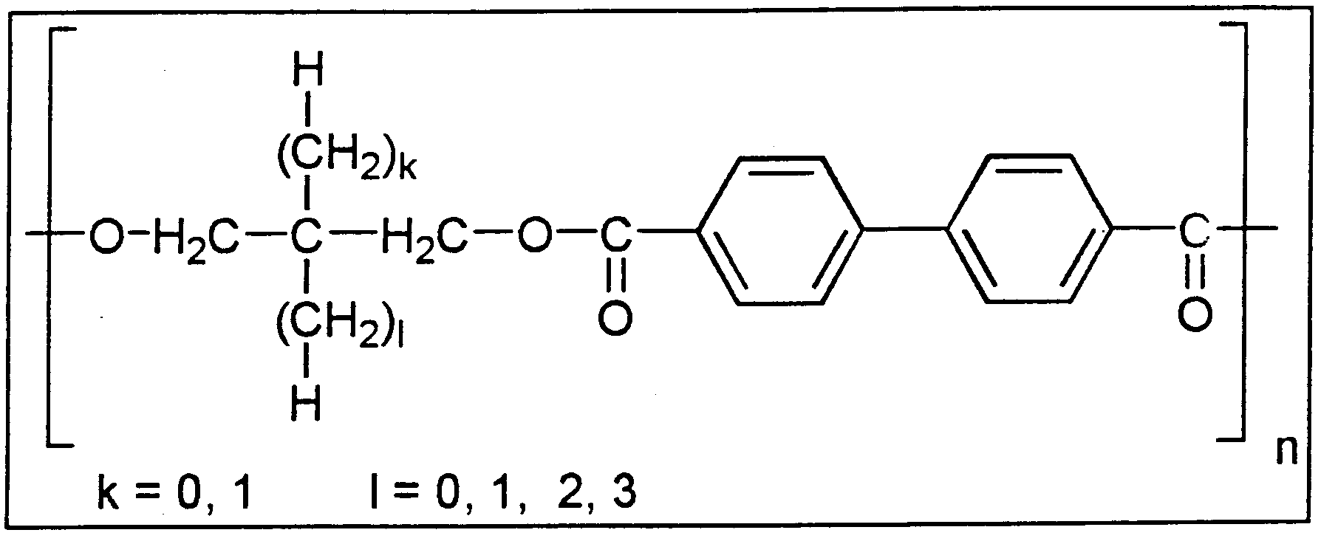

poly[oxy (2, 2' dialkylpropane – 1, 3 – diyl) carboxybisphenyl – 4, 4' – dicarbonyl]

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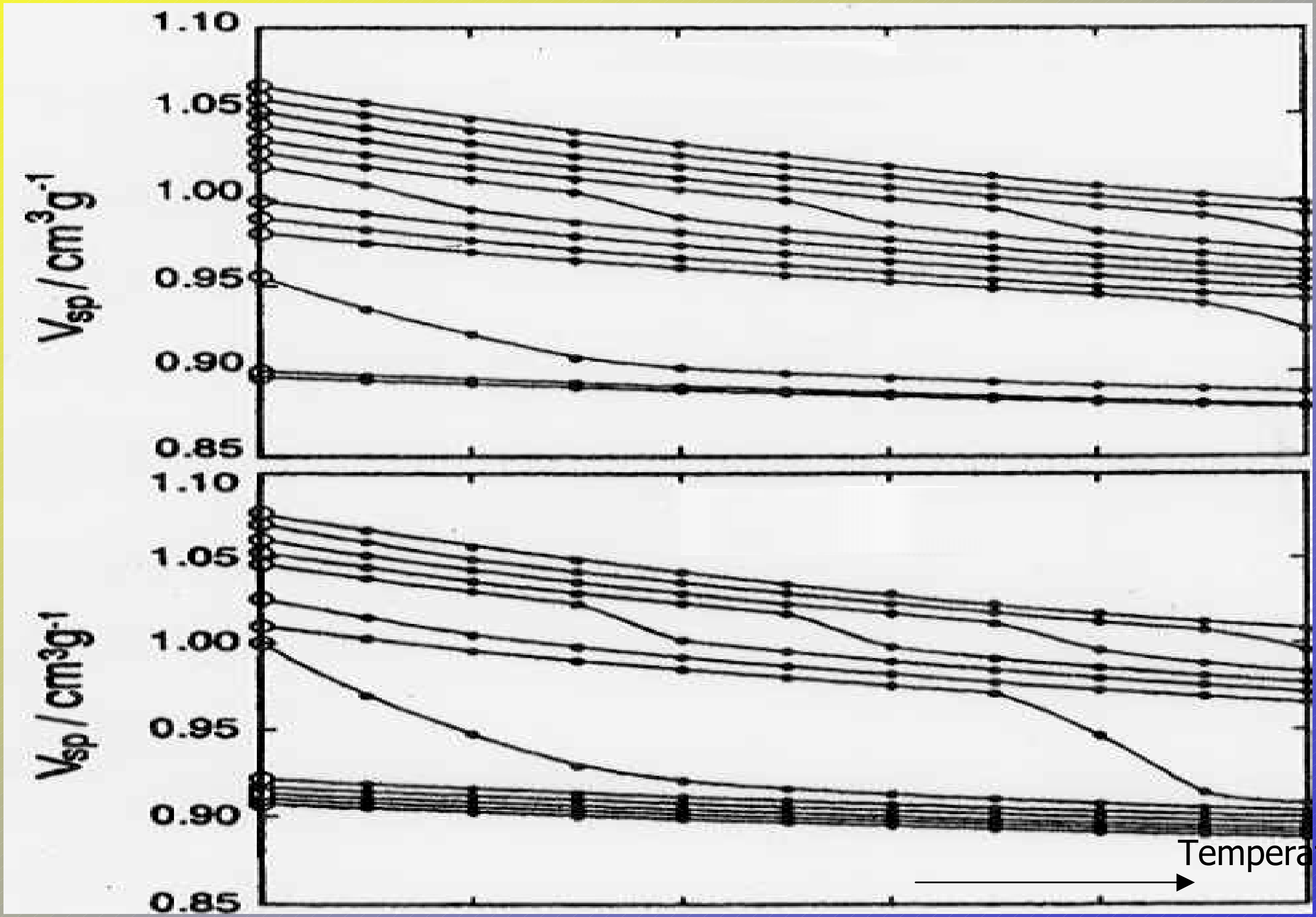
Example for a Strong Pressure/Volume Effect of a LC-Transition



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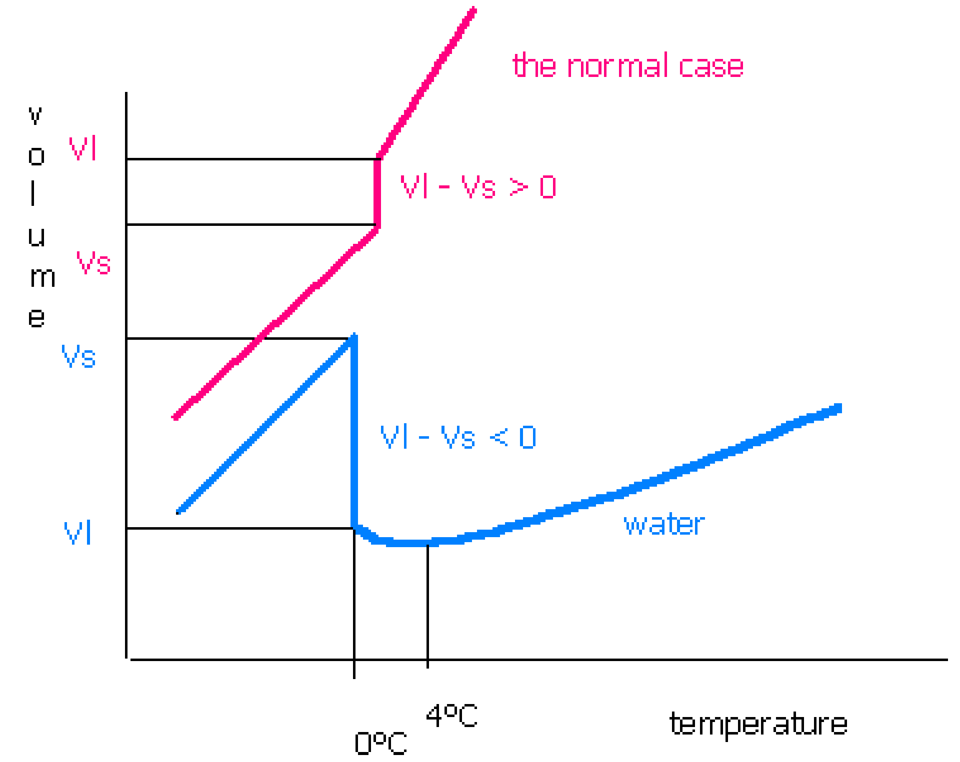

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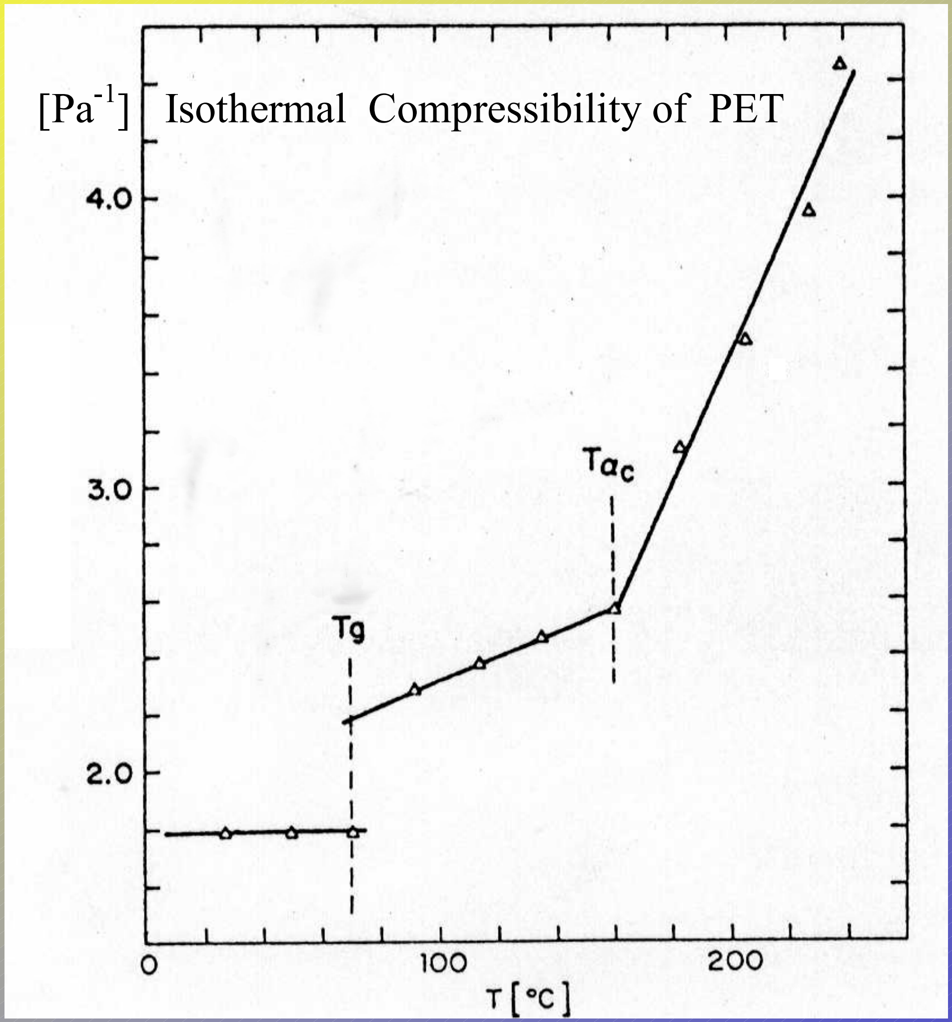

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p-v-T measurements are useful for:

- Basing on the free-volume concepts it is possible to predict service performance and service life of polymeric materials.
- Polymer/polymer miscibility can be predicted.
- Chemical reactions can be followed provided they are accompanied by volume-effects
- Processing parameters can be optimized without a trial and error procedure
- The surface tension of polymer melts can be estimated.

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In all cases one works with two key quantities:

the isobaric expansivity

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

the isothermal compressibility

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

in many cases Ehrenfest's equation holds and the pressure dependence of the glass transition temperature is given by:

$$\frac{dT_g}{dP} = \frac{\Delta\kappa}{\Delta\alpha}$$

although the glass transition is not a second order transition.

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Differential Equations at Phase Transitions

According to Ehrenfest, thermodynamic transitions are classified according to discontinuities in the derivatives of the Gibbs Energy

$$\mathbf{G = H - T \cdot S}; \quad dG = Vdp - SdT = \left(\frac{\partial G}{\partial p}\right)_T dp + \left(\frac{\partial G}{\partial T}\right)_p dT$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -S; \quad \left(\frac{\partial^2 G}{\partial T^2}\right)_p = -\left(\frac{\partial S}{\partial T}\right)_p = -\frac{1}{T}\underbrace{\left(\frac{\partial Q}{\partial T}\right)_p}_{c_p}$$

$c_p \equiv$ heat capacity at constant pressure

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

$$\left(\frac{\partial^2 G}{\partial p \cdot \partial T}\right)_p = \left(\frac{\partial V}{\partial T}\right)_p = \alpha^*$$

$\alpha^* \equiv$ isobaric expansivity, correspondingly $\beta^* \equiv$ isothermal compressibility

1. Order Transition (Discontinuous Thermodynamic Transition)

Bend in G(T) → jump in S(T), V(T) and H(T)

2. Order Transition (Continuous Thermodynamic Transition)

Bend in V(T), H(T) and S(T) → jump in α^*, κ^* and c_p

The Glass Transition (Continuous “Freezing in”, a Kinetic Effect)

Bend in V(T), H(T) and S(T) → jump in α^*, κ^* and c_p
Shape different from a 2^{nd} order transition

First order **thermodynamic** transitions follow the Clausius-Clapeyron Equation:

$$\frac{dp}{dt} = \frac{\Delta H}{\Delta V} \cdot \frac{1}{T}$$

For second order **thermodynamic** transitions Ehrenfest`s Equations are valid

$$\left(\frac{dP}{dT}\right)_{tr} = \frac{\Delta\alpha_{tr}}{\Delta\kappa_{tr}}$$

$$\left(\frac{dP}{dT}\right)_{tr} = \frac{(c_P)_{tr}}{T_{tr} \cdot (V_{spez.})_{tr} \cdot \Delta\alpha_{tr}}$$

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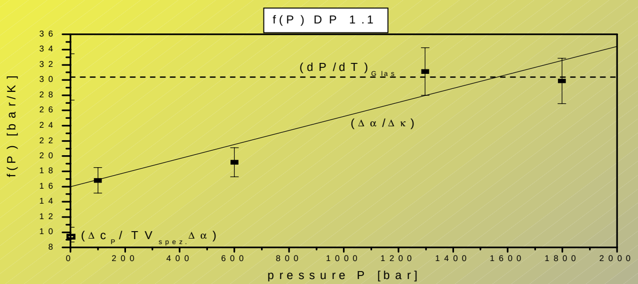
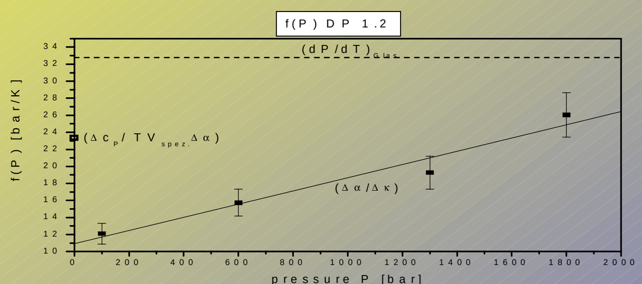
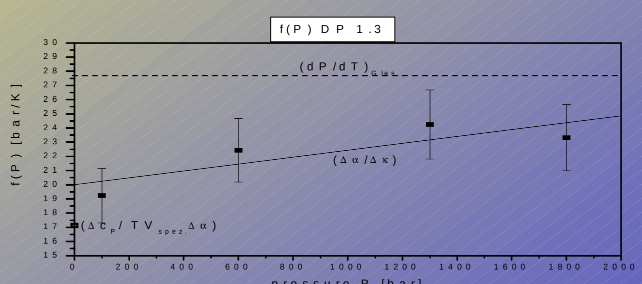
Ehrenfest's Relations of DP 1.1, DP 1.2 and DP 1.3 at T_g







$$\left(\frac{dP}{dT}\right)_{tr} = \frac{\Delta\alpha_{tr}}{\Delta\kappa_{tr}}$$

$$\left(\frac{dP}{dT}\right)_{tr} = \frac{(c_P)_{tr}}{T_{tr}\cdot(V_{spez.})_{tr}\cdot\Delta\alpha_{tr}}$$

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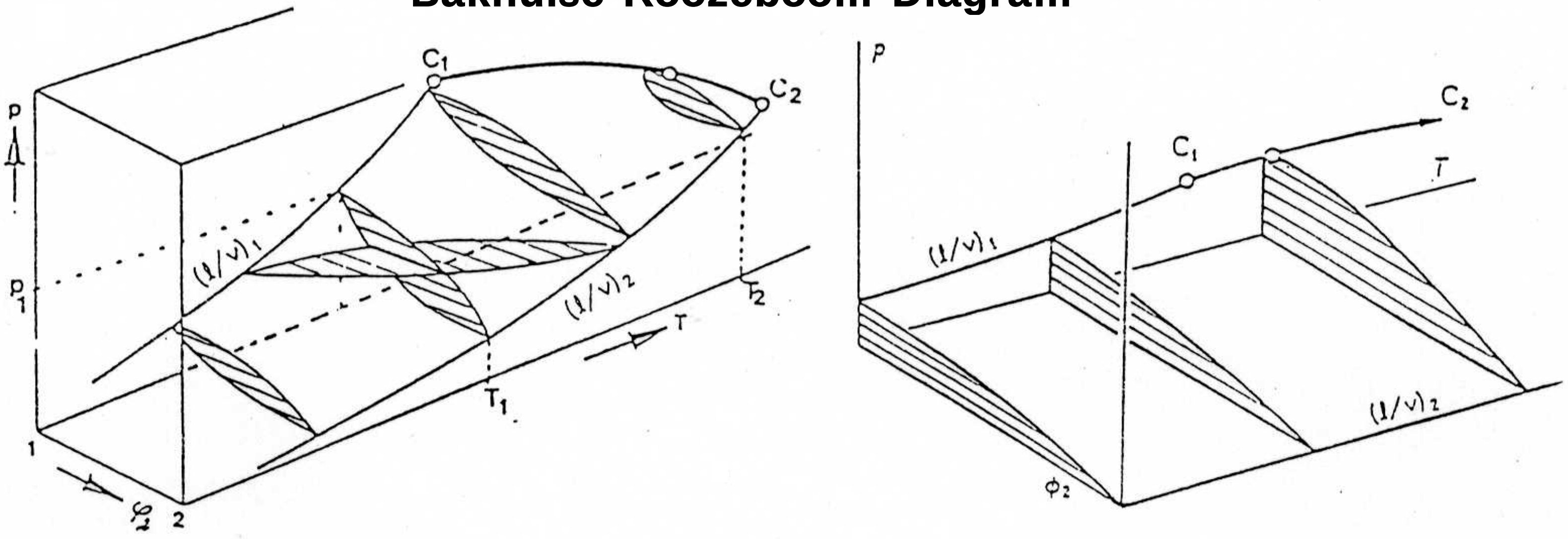
Bakhuise-Roozeboom-Diagram



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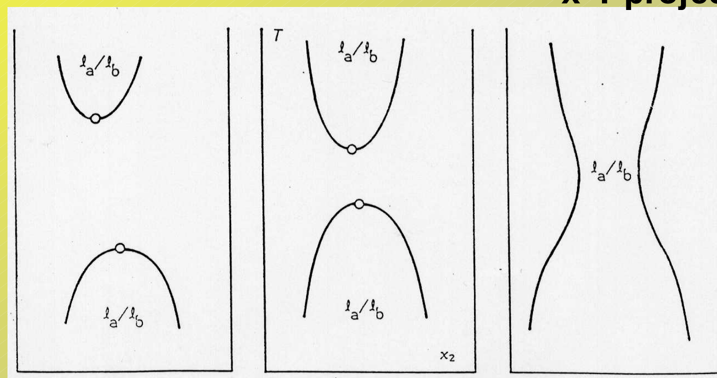
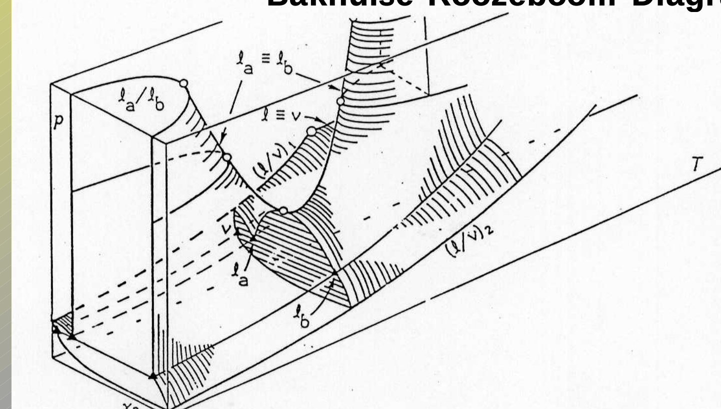
x-T projections



Bakhuise-Roozeboom-Diagram



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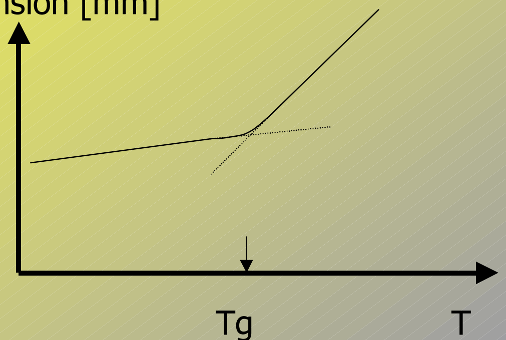
Thermo-Mechanical Analysis

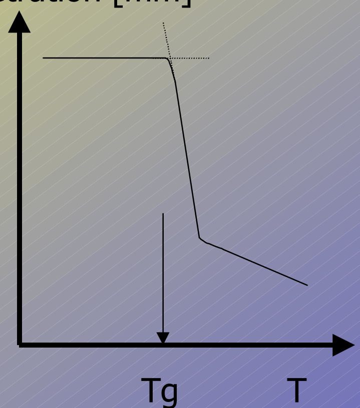
Expansivity: the free volume increases with temperature

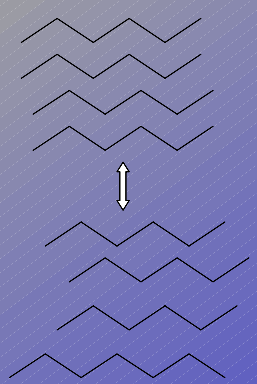
Expansion [mm]



Penetration:

Penetration [mm]





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Dynamic-Mechanical Analysis (Free Oscillating Torsion)

Periodic torsional stress τ ⇒ **periodic deformation γ**

phase shift δ

$$\tau = \tau_0\, e^{i\omega t} \qquad \gamma = \gamma_0\, e^{i(\omega t - \delta)}$$

⇒ **complex torsional modulus**

$$G^* = \frac{\tau}{\gamma} = \frac{\tau_0}{\gamma_0} e^{i\delta} = \underbrace{\frac{\tau_0}{\gamma_0}\cos\delta}_{G'} + i \cdot \underbrace{\frac{\tau_0}{\gamma_0} \cdot \sin\delta}_{G''}$$

Differential equation of the oscillating system:

$$\ddot{\varphi}(t) + a \cdot \dot{\varphi}(t) + b \cdot \varphi(t) = 0; \quad a = \frac{f \cdot G''}{\Theta \cdot \omega_e} \quad b = \frac{f \cdot G' + f_1}{\Theta}$$

$f \equiv$ form factor of the sample; $f_1 \equiv$ form factor of the spring

$\omega_e \equiv$ frequency of the oscillating system

$\Theta \equiv$ momentum of inertia

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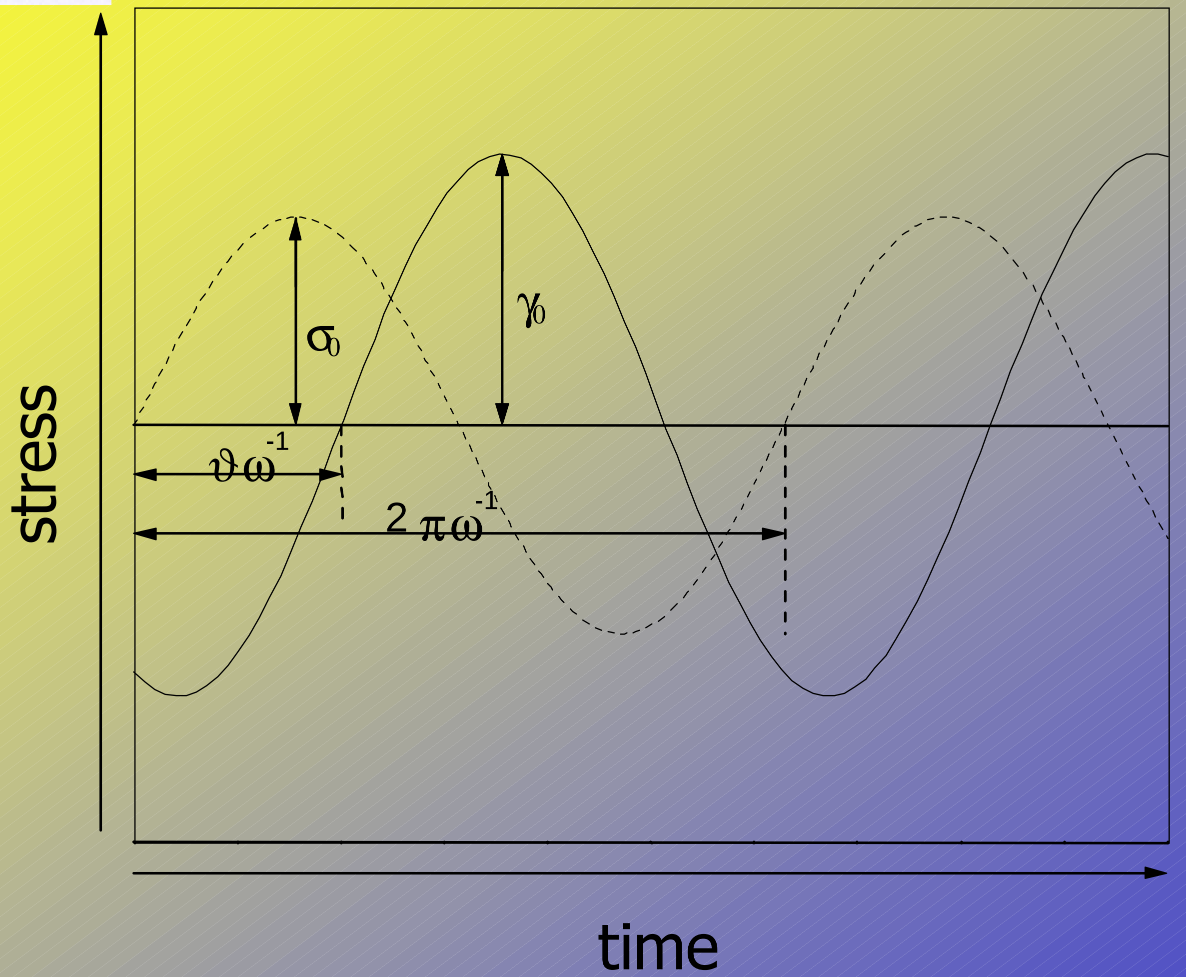

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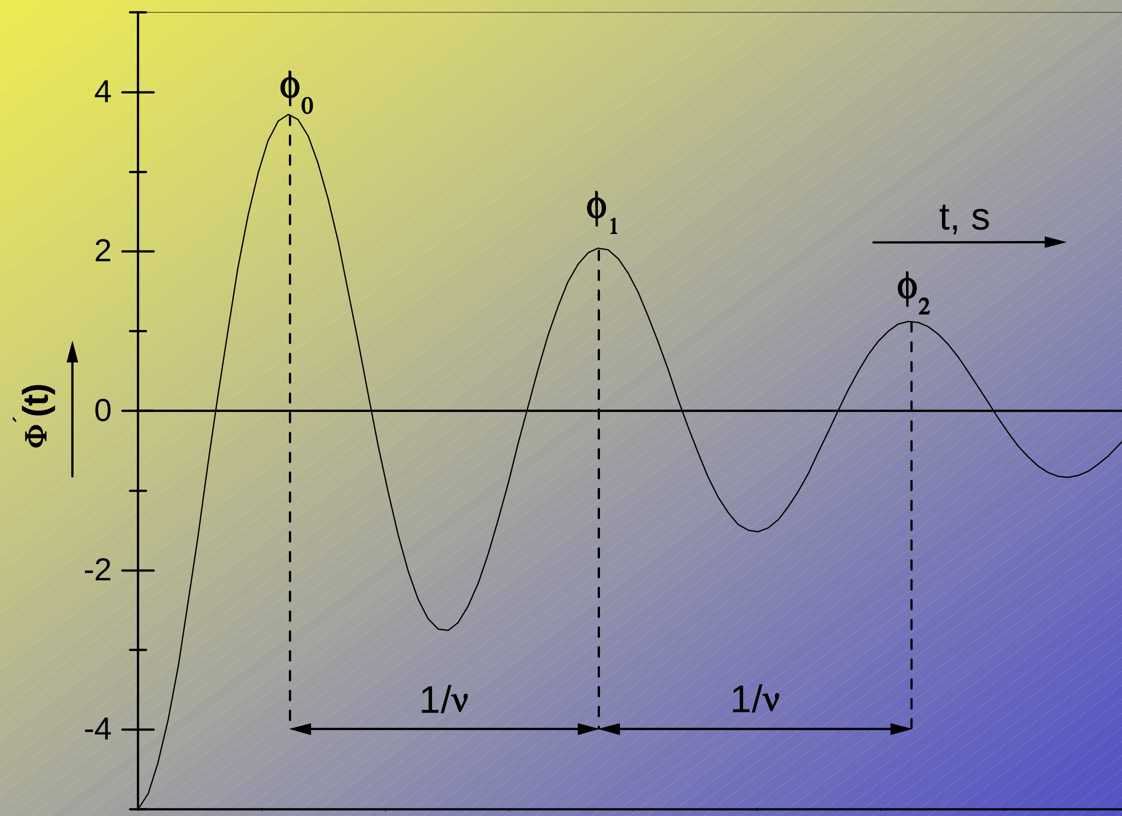
$$\Lambda \equiv \ln\left[\frac{\varphi(t)}{\varphi\left(t+\frac{2\pi}{\omega_e}\right)}\right]$$



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the free damped oscillation is then described by:

$\varphi(t) = \varphi_0 \cdot e^{\frac{-\omega_e \cdot \Lambda}{2\pi} \cdot t}$ **with the logarithmic decrement Λ of the damped oscillation** $\Lambda \equiv \ln\left[\frac{\varphi(t)}{\varphi\left(t + \frac{2\pi}{\omega_e}\right)}\right]$**, so that finally:**

$$G' = \frac{\Theta}{f}\left(\omega_e^2 - \omega_0^2\right) \quad \textbf{and} \quad G'' = \frac{\Theta}{f} \cdot \omega_e^2 \cdot \frac{\Lambda}{\pi}$$

ω_0 is the frequency of the free oscillating system without sample
ω_e is the frequency of the oscillating system with sample

The loss tangent or damping is finally defined by:

$$\tan\delta \equiv \frac{G''}{G'}$$

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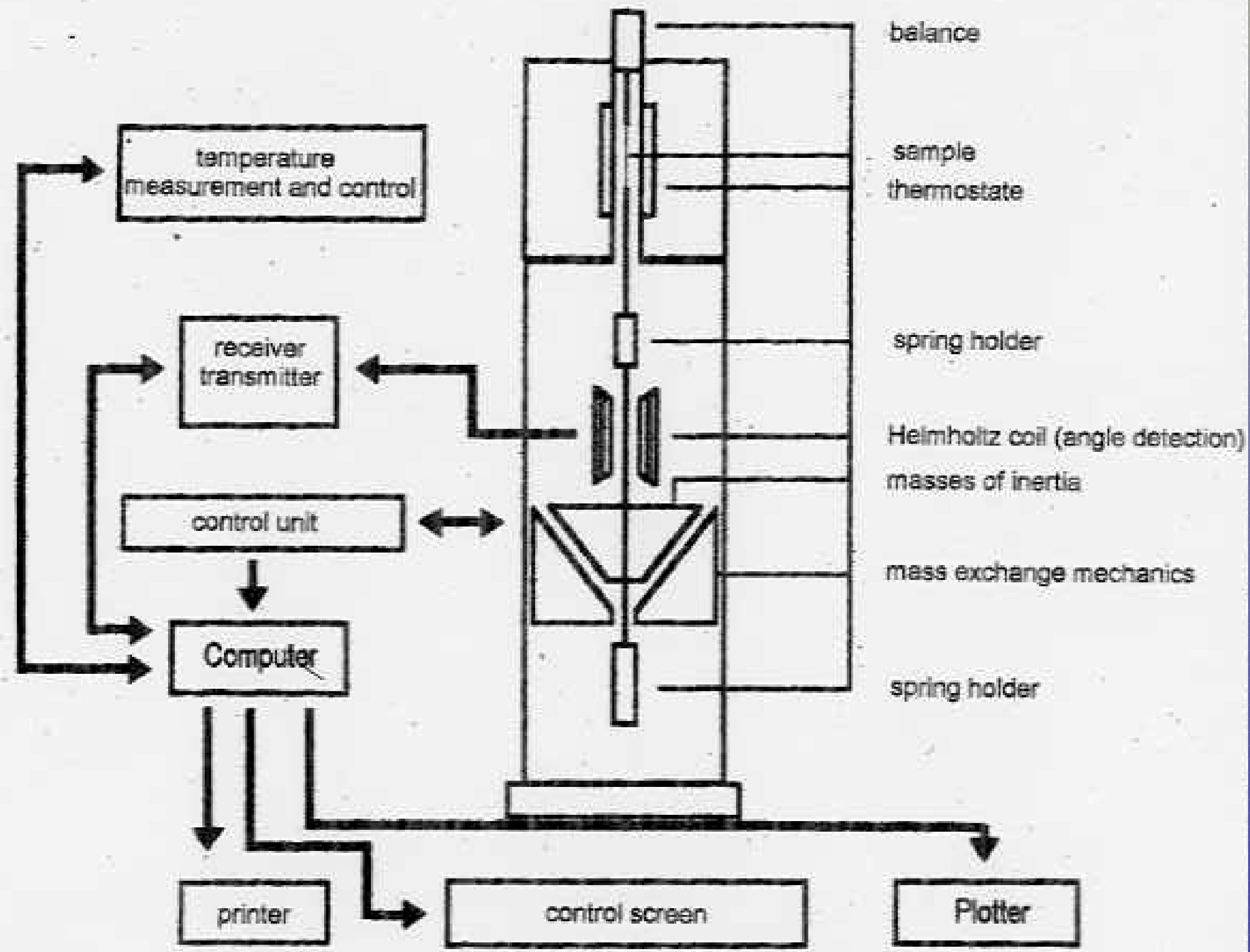

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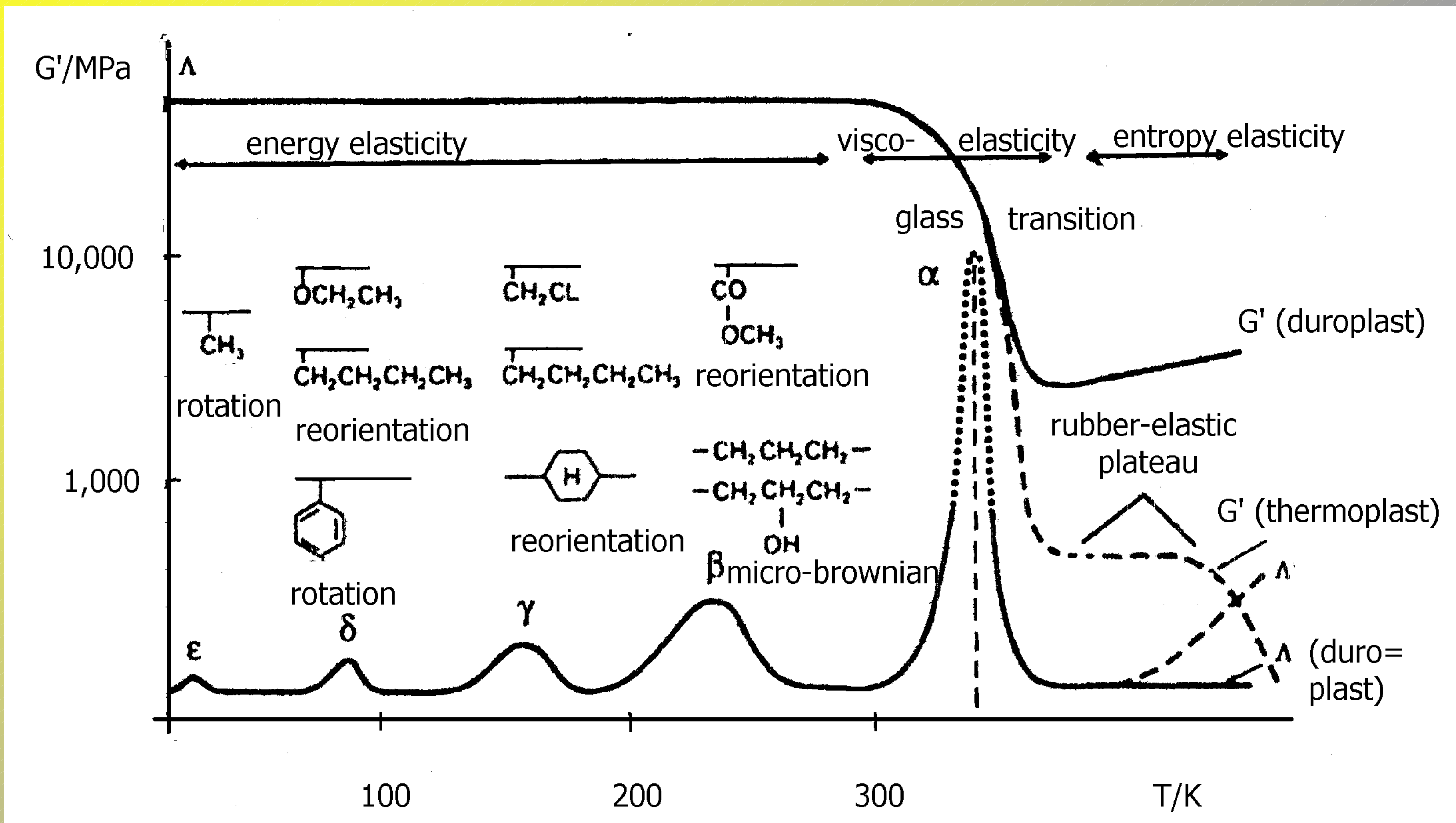

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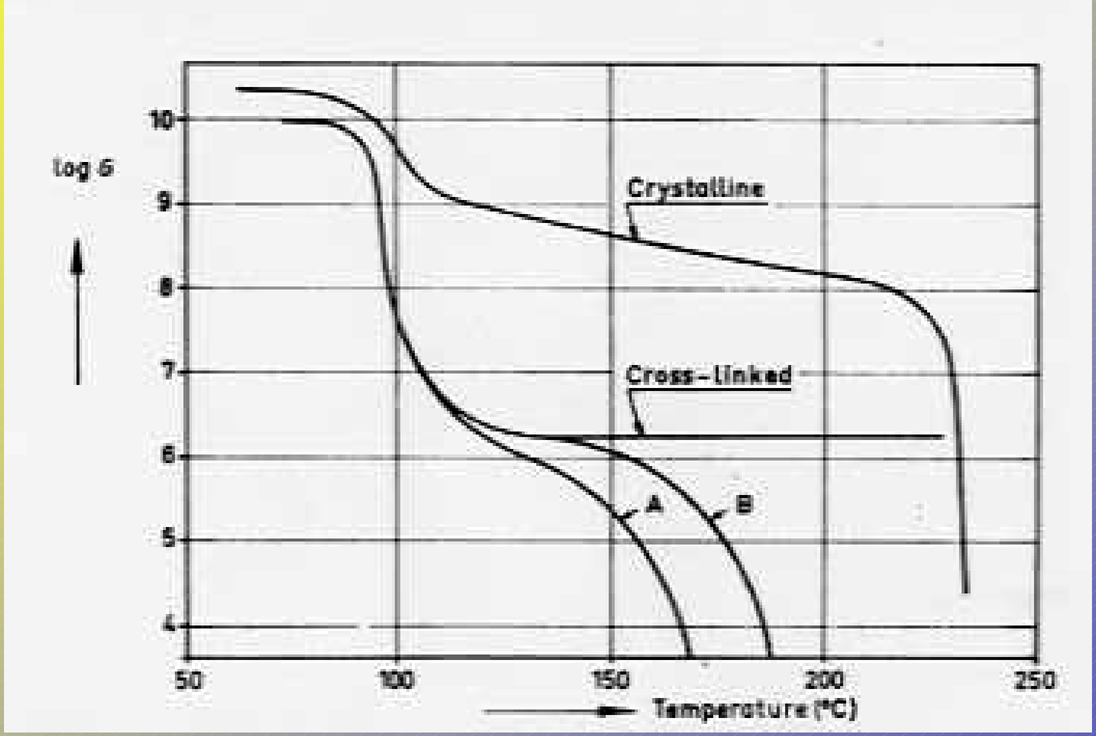
glass-transition, melting and glass-rubber transition



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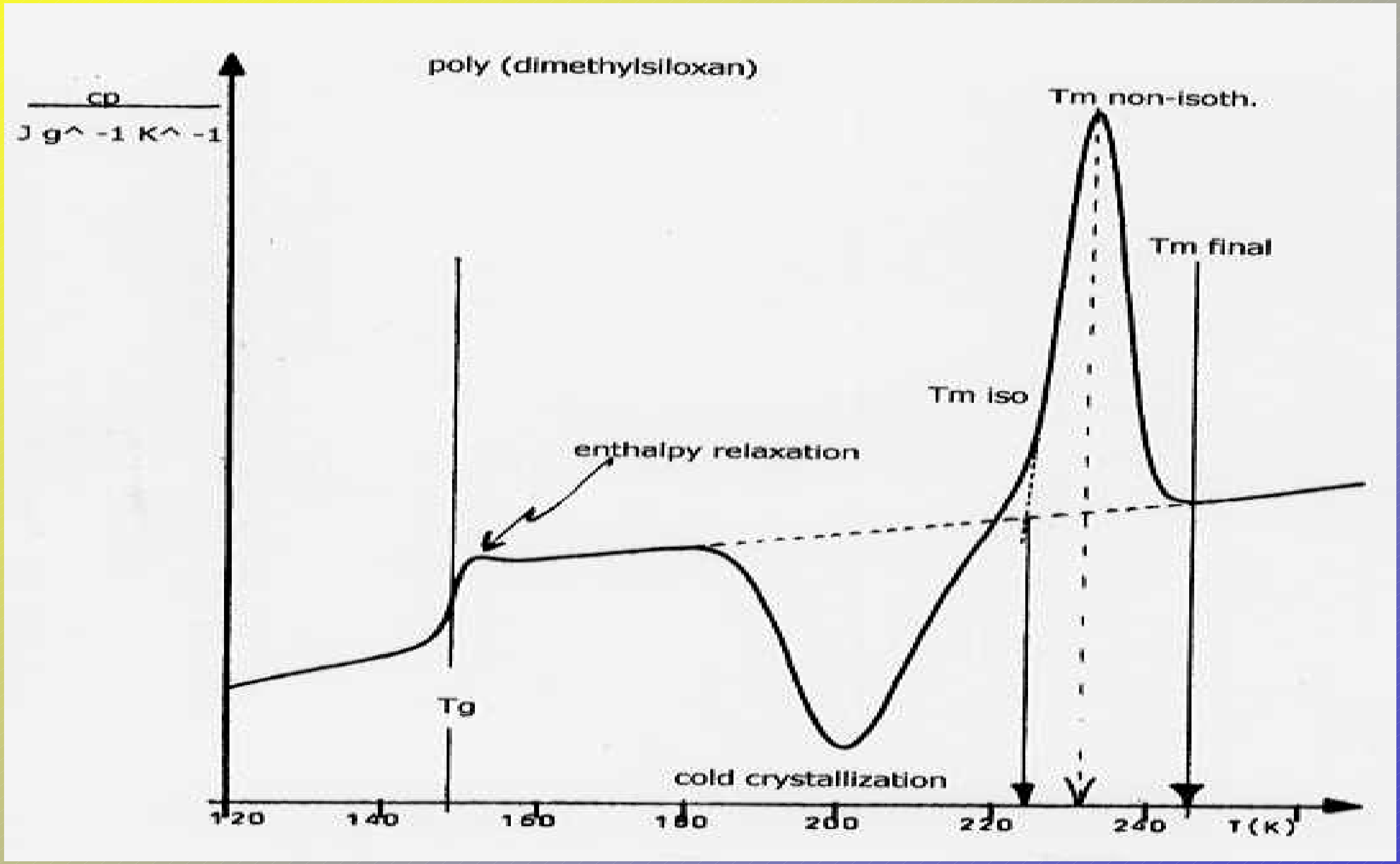

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General Aspects of Binary Phase Diagrams

1. 2 two-phase regions must be separated by either a bivariant one-phase range, or by a part of a non-variant three-phase line.

2. 2 one-phase regions cannot be adjacted, they must be separated by a two-phase region.

3. If there is 2 two-phase region on one side of a three-phase line, there must be 2 two-phase areas on the other side of that line.

4. Metastable extensions beyond the three-phase line must fall within the two-phase ranges in the areas they extend into.

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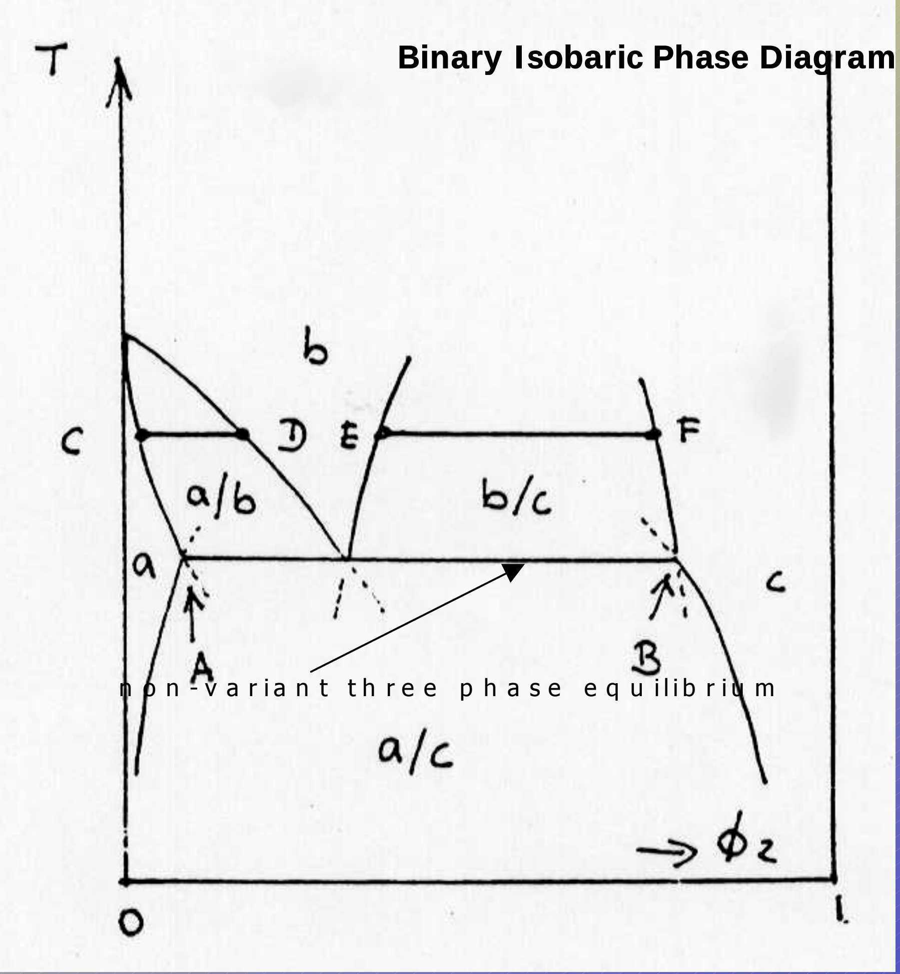

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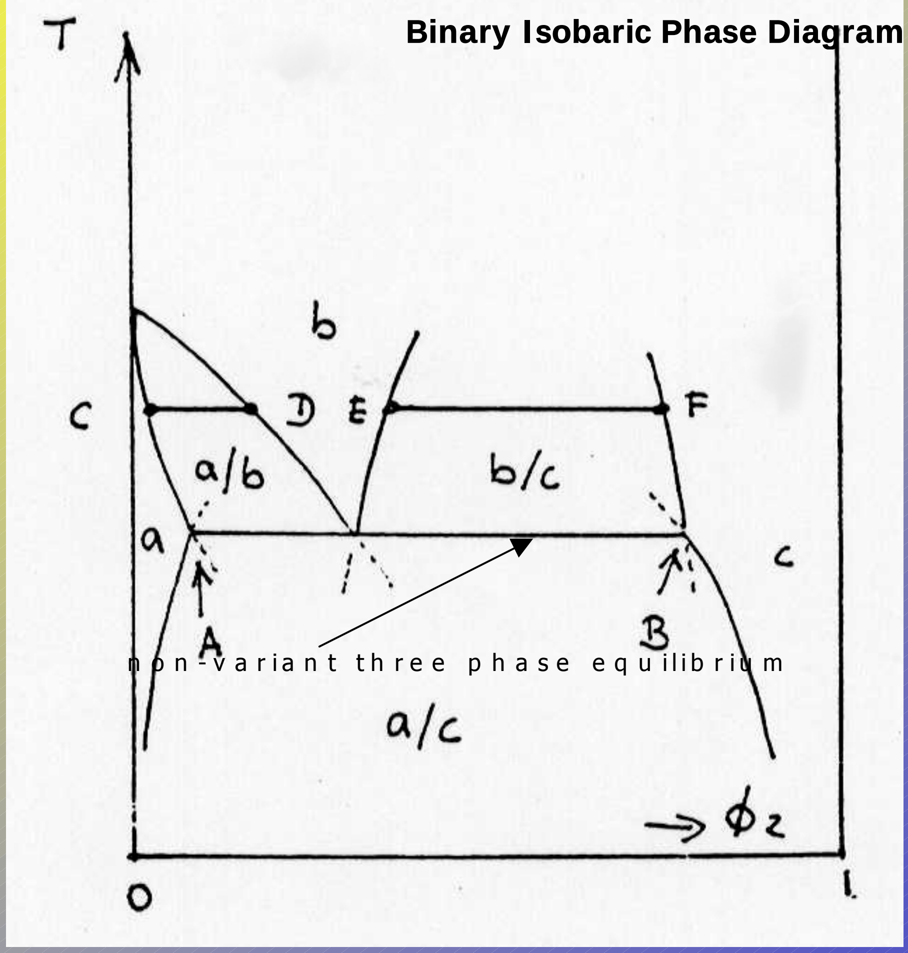
Binary Isobaric Phase Diagram



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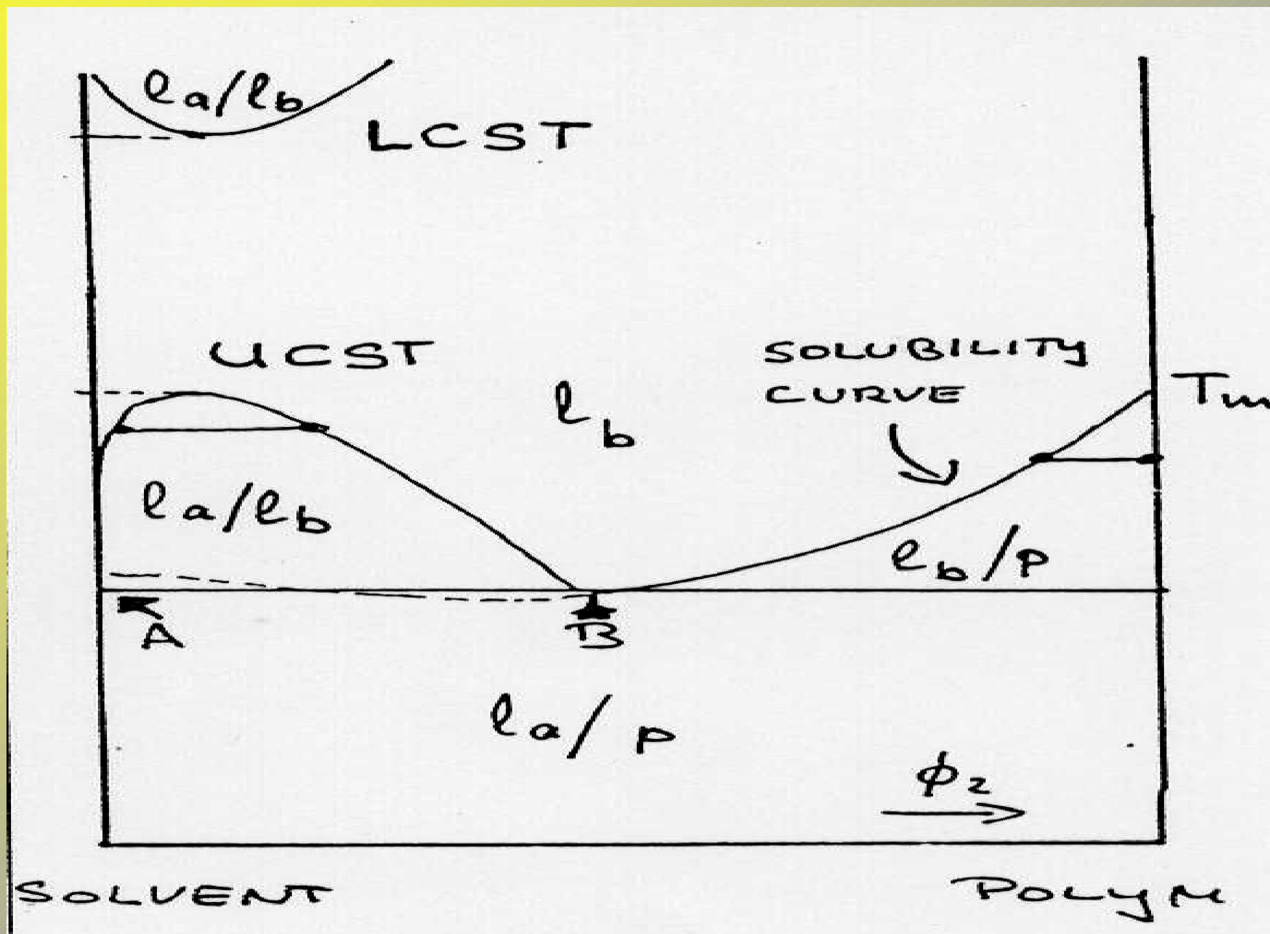
Binary Isobaric Phase Diagram with UCST and LCST



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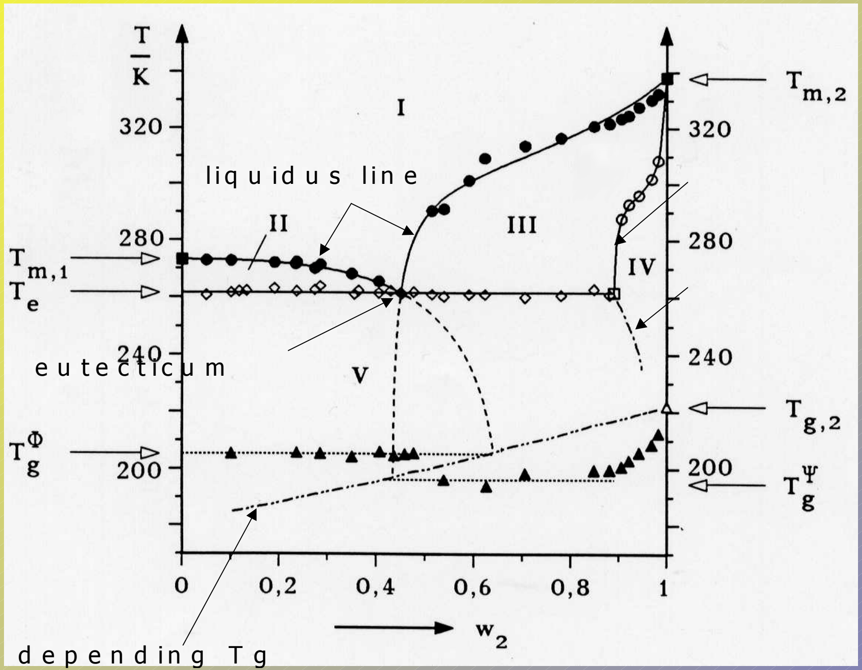

I	liquid phase, homogeneous solution
II	two-phase area, ice/homogeneous solution
III	two-phase area, mixed crystal/homogeneous solution
IV	one-phase area, mixed crystal, PEO-rich
V	two-phase area, ice/mixed crystal

T_g^{Φ} concentration independent glass-transition temperature of the over-saturated solution

T_g^{Ψ} concentration independent glass-transition temperature of eutectic composition

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