High Pressure Dielectric Spectroscopy

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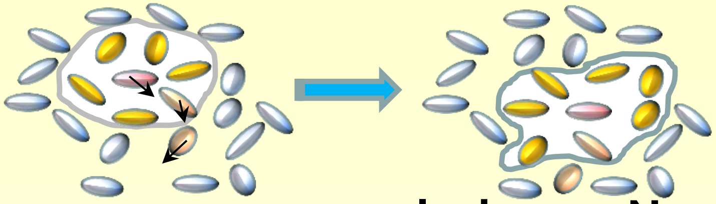
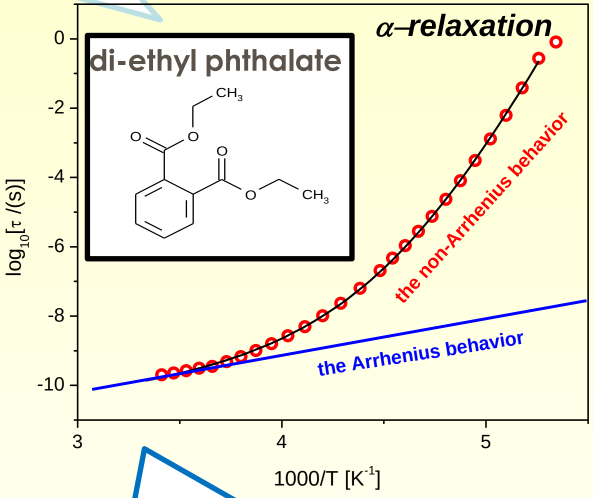
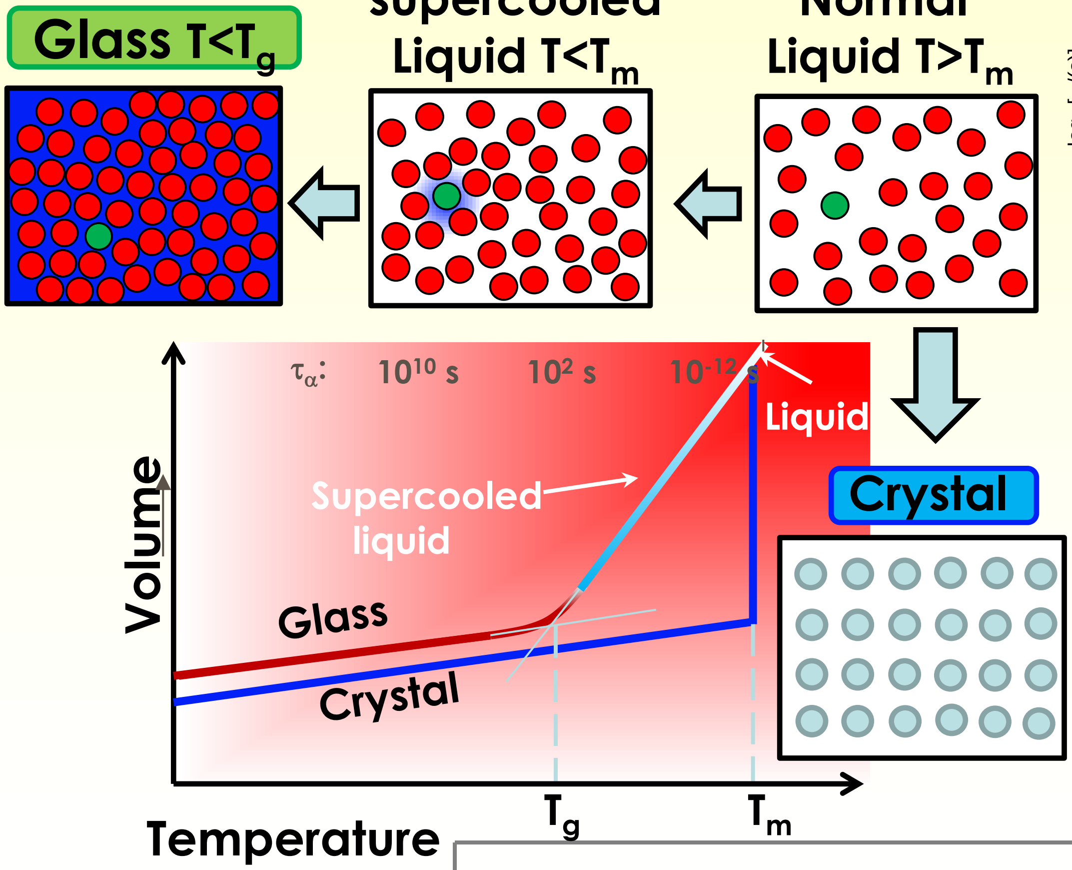
Molecular dynamics of glass-forming liquids

Structural (α-) relaxation



The same pattern of behavior is also observed for viscosity





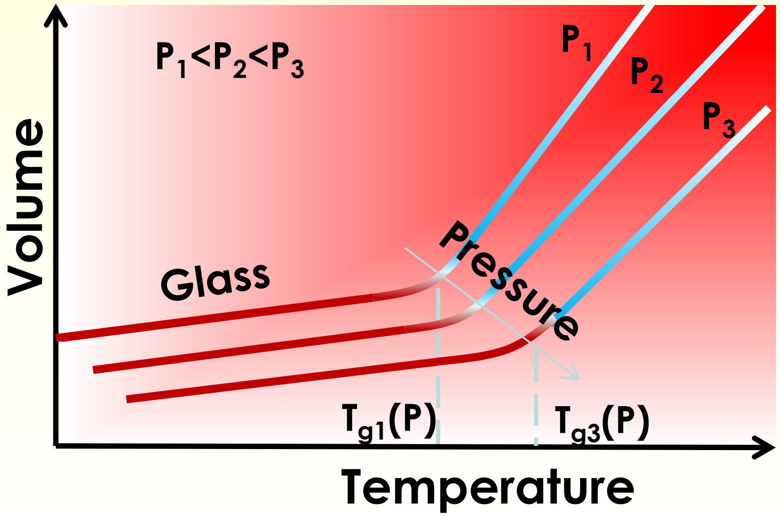
The L-G transition is accompanied by dramatic slowing down of the molecular dynamics as well as viscosity

The Arrhenius law: $\log\tau_\alpha = \log\tau_0 + \frac{E_A}{kT}$

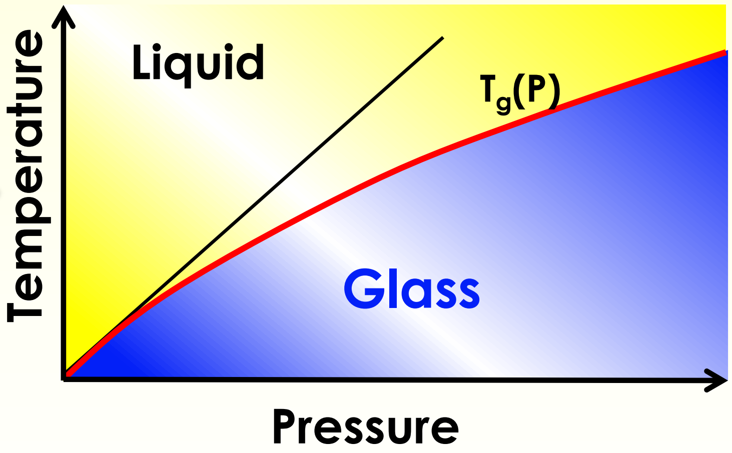
The VFT law: $\log\tau_\alpha = \log\tau_0 + \frac{DT_0}{T - T_0}$

Molecular dynamics studies can be enriched by performing the high pressure experiments.

Pressure brings about an increase of the glass transition temperature.



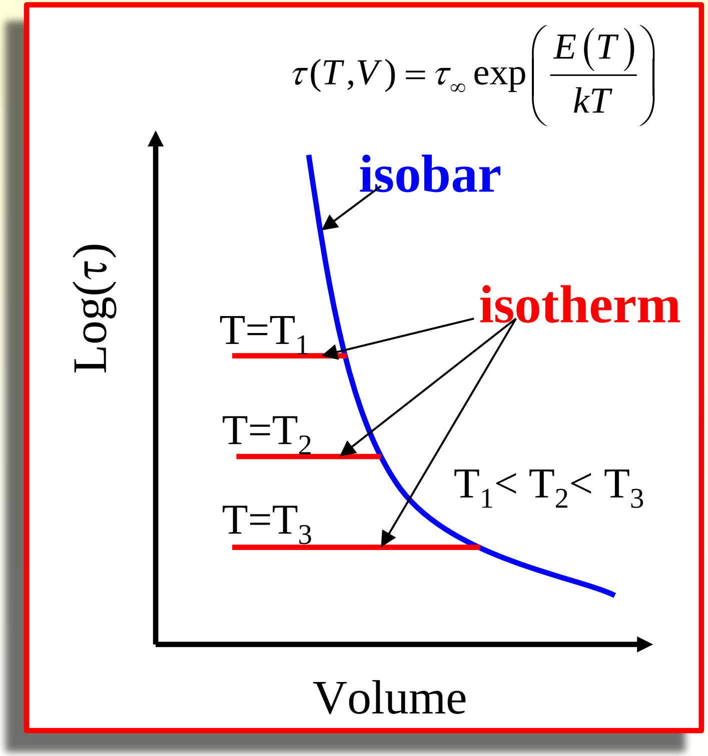
Pressure dependence of T_g exhibits frequently the nonlinear character.



Is the super-Arrhenius behavior near Tg at ambient pressure governed primarily by the decreasing volume, the decreasing temperature, or both ?

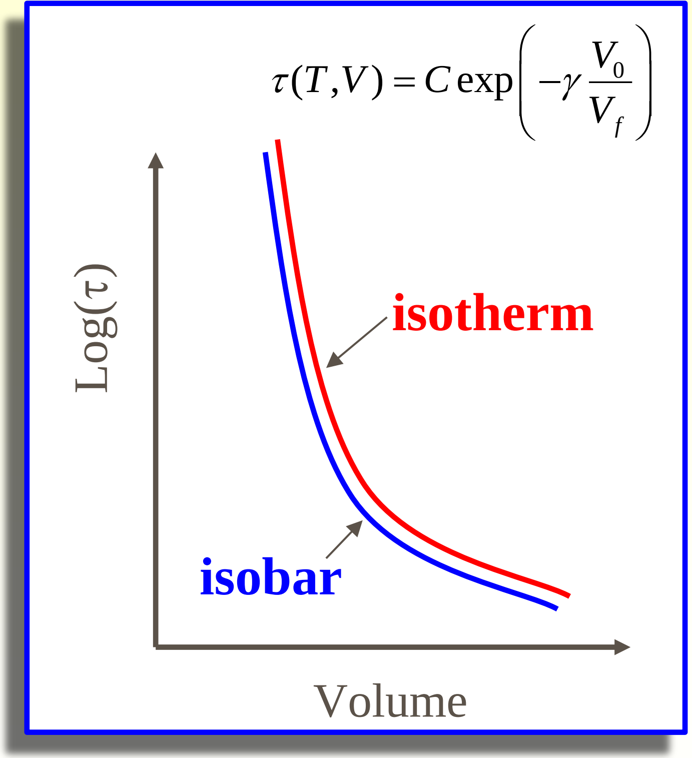
Dominant control variable: Temperature versus Volume

Temperature dominated



$$\tau(T,V)=\tau_\infty \exp\left(\frac{E(T)}{kT}\right)$$

Volume dominated

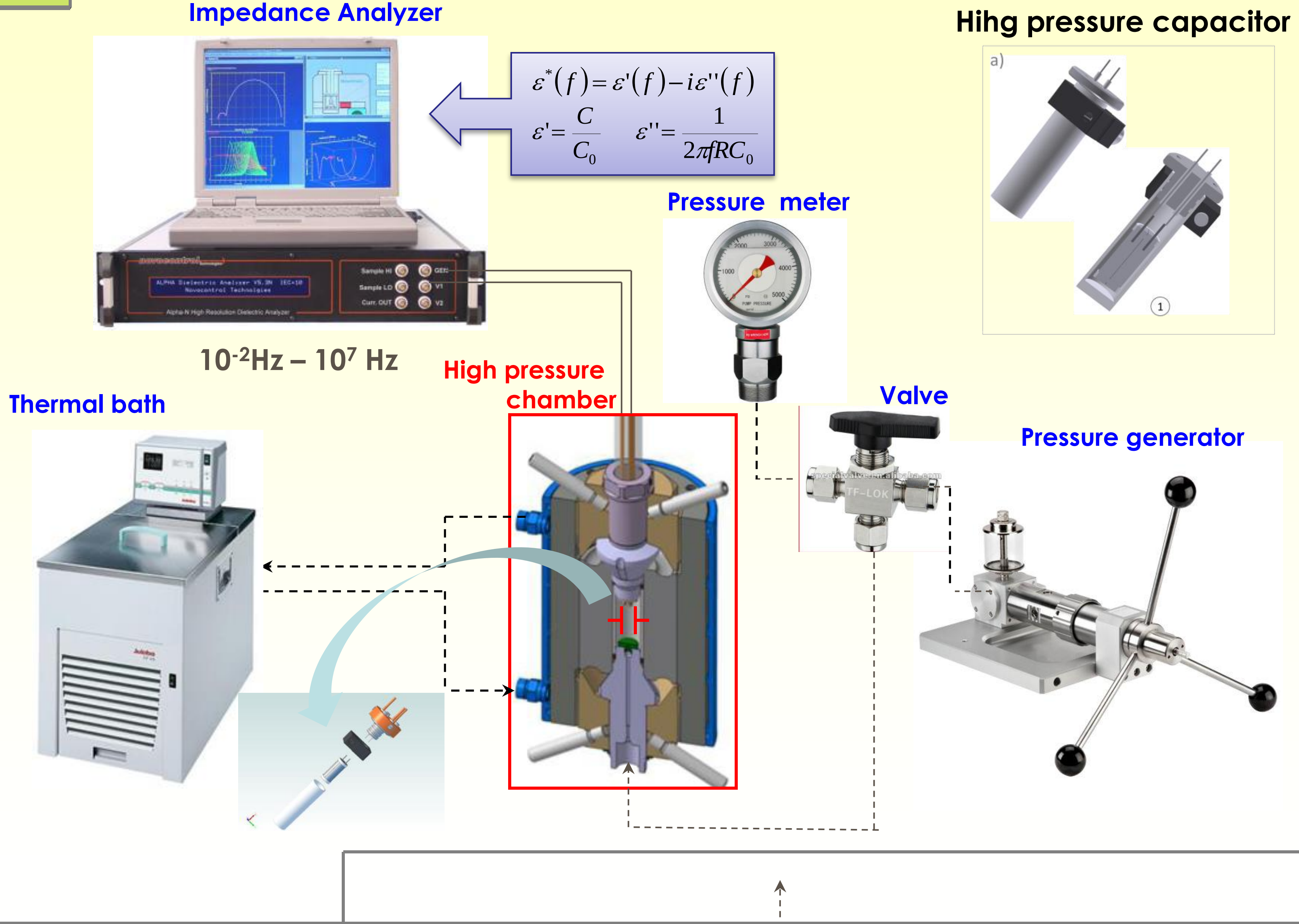


$$\tau(T,V)=C\exp\left(-\gamma\frac{V_0}{V_f}\right)$$

To construct such plot one has to measure pressure dependence of the structural relaxation times and volume as a function of temperature and pressure.

Schematic illustration of the high pressure dielectric set-up

Pressure range: up to 1 GPa



Impedance Analyzer

$$\varepsilon^*(f)=\varepsilon'(f)-i\varepsilon''(f)$$

$$\varepsilon'=\frac{C}{C_0}\qquad \varepsilon''=\frac{1}{2\pi fRC_0}$$

10^{-2}Hz – 10^{7} Hz

Hihg pressure capacitor

Pressure meter

High pressure chamber

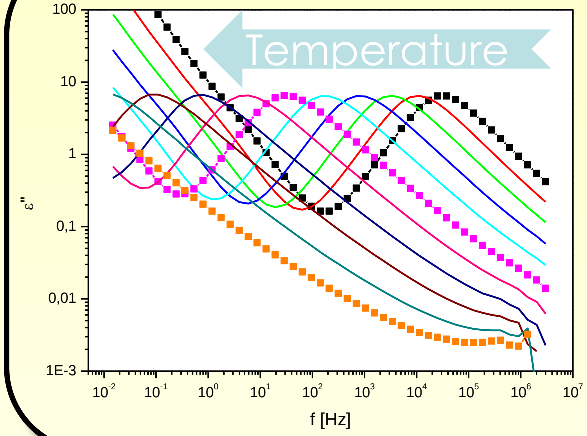
Thermal bath

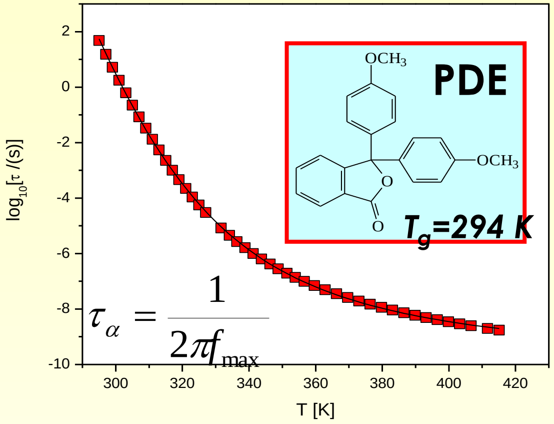
Valve

Pressure generator

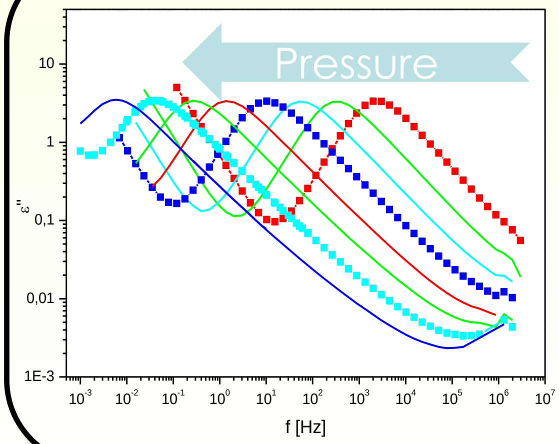
High Pressure Dielectric Measurements of the Structural Relaxation

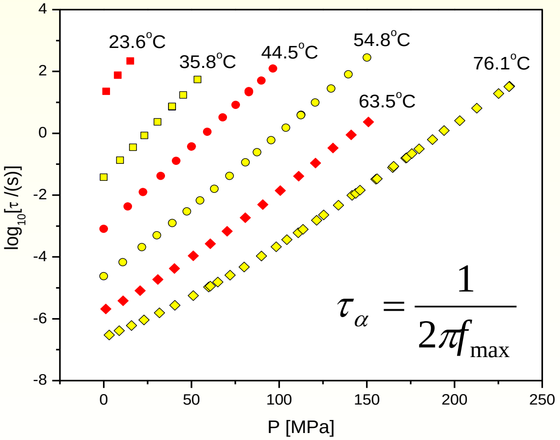
Lowering temprature





Inreasing pressure





PVT measurements:

Tait equation:

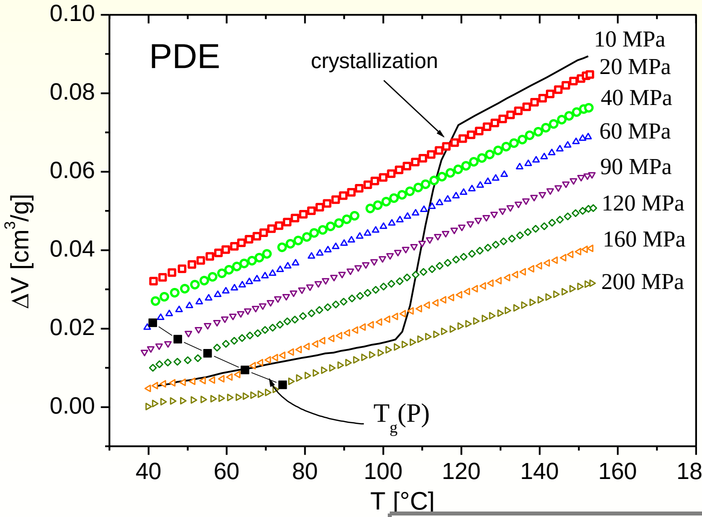
$$V(P,T)=V(0,T)\times[1-0.089]\times\ln\left(1+\frac{P}{C(T)}\right)$$

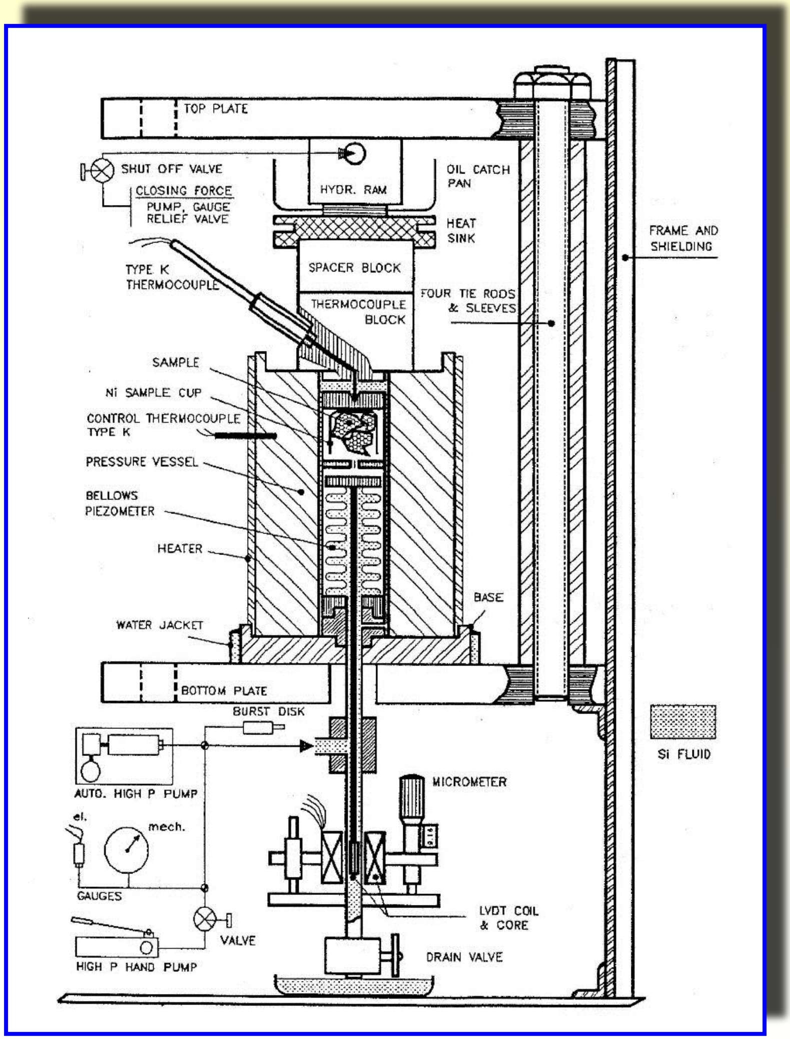
$$V(0,T)=A_0+A_1T+A_2T^2 \quad C(T)=C_0\exp(-C_1T)$$

$$\left(\frac{\upsilon(T,p_0)}{\upsilon(T,p)}\right)^{\gamma_{EOS}}=1+\frac{\gamma_{EOS}}{B_T(p_0)}(p-p_0)$$

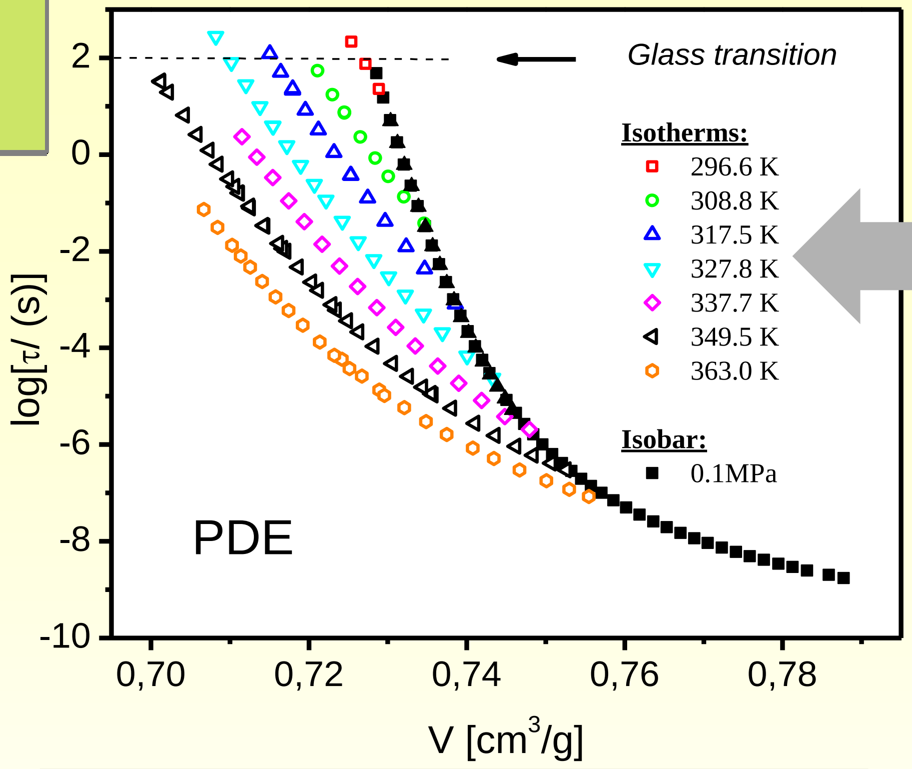
$$\upsilon(T,p_0)=A_0+A_1(T-T_0)$$
$$+A_2(T-T_0)^2$$

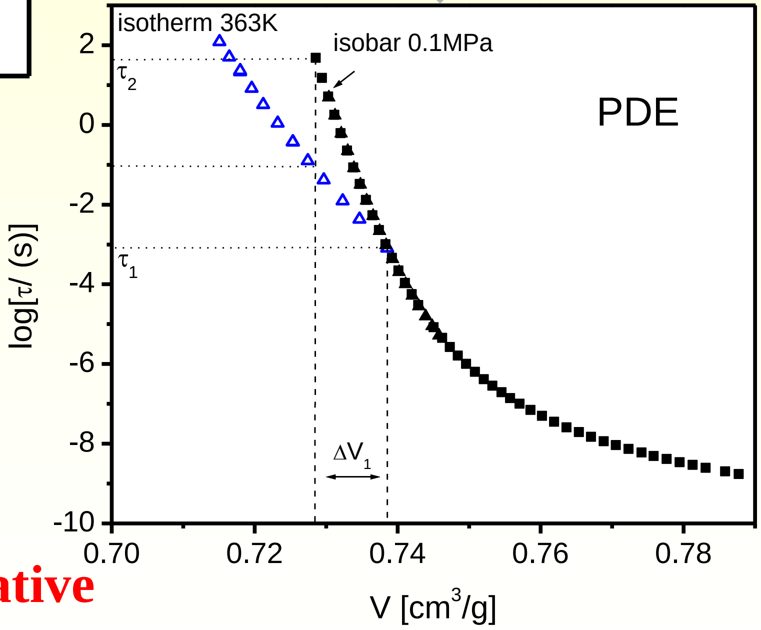
$$B_T(p_0)=B_{T_0}(p_0)\exp(-b_2(T-T_0))$$





Volume dependence of the α-relaxation times





In case of PDE, the super-Arrhenius behavior of the structural relaxation times is governed to the same extent by thermal and volume fluctuations

How to determine quantitatively the relative contribution of both fluctuations?

First approach: Expansion coefficients

$$\left(\frac{\partial \log\tau}{\partial T}\right)_P = \left(\frac{\partial \log\tau}{\partial T}\right)_V + \left(\frac{\partial \log\tau}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

using

$$(\partial \log\tau / \partial T)_V = -(\partial \log\tau / \partial V)_T (\partial V / \partial T)_\tau$$

isochronal expansivity :

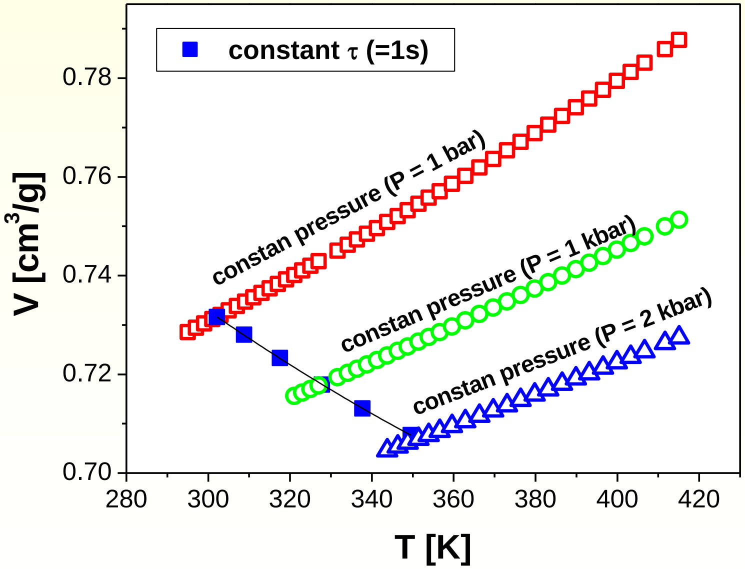
$$\alpha_P = -V^{-1}(\partial V/\partial T)_P$$

isobaric expansivity :

$$\alpha_\tau = -V^{-1}(\partial V/\partial T)_\tau$$

$$\left(\frac{\partial \log\tau}{\partial T}\right)_P = \left(\frac{\partial \log\tau}{\partial V}\right)_T (-\alpha_\tau + \alpha_P)$$

$$\frac{|\alpha_\tau|}{\alpha_P} \begin{cases} >>1 \rightarrow T \text{ dominate} \\ \sim 1 \rightarrow \text{comparable} \\ 0 \rightarrow V \text{ dominate} \end{cases}$$



$$\frac{|\alpha_\tau|}{\alpha_P} \approx 1.25$$

	PDE
1bar	**1.25**
2 kbar	**1.43**

Second approach: Activation energies

Volume ←→ **Temperature**

(steric constraints) ***(thermal fluctuations)***

$$0 \leq E_V/E_P \leq 1$$

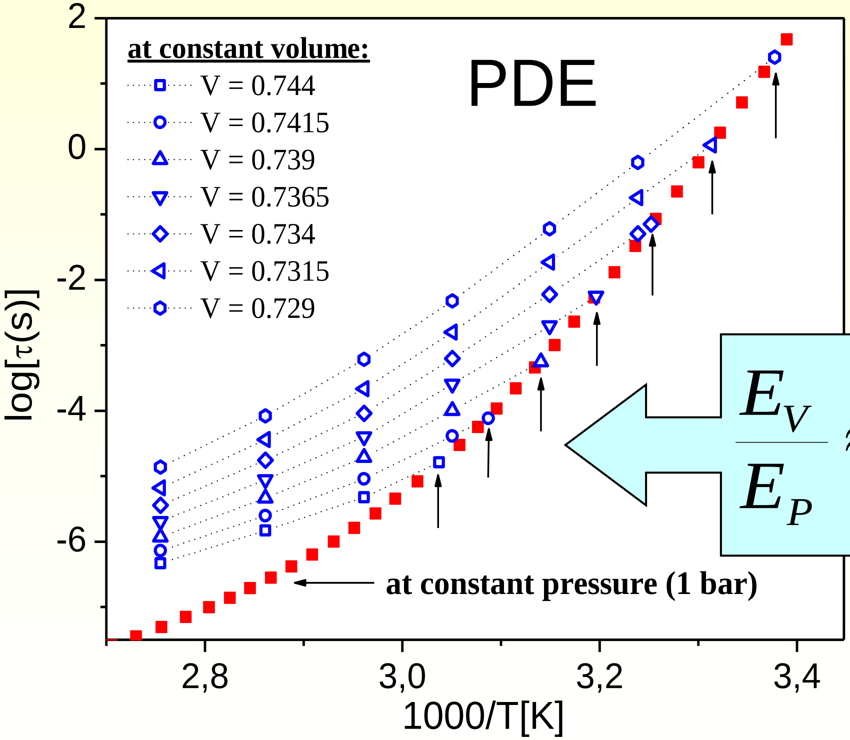
activation energy at constant volume:

$$E_V = \left.\frac{\partial \log \tau}{\partial T^{-1}}\right|_V$$

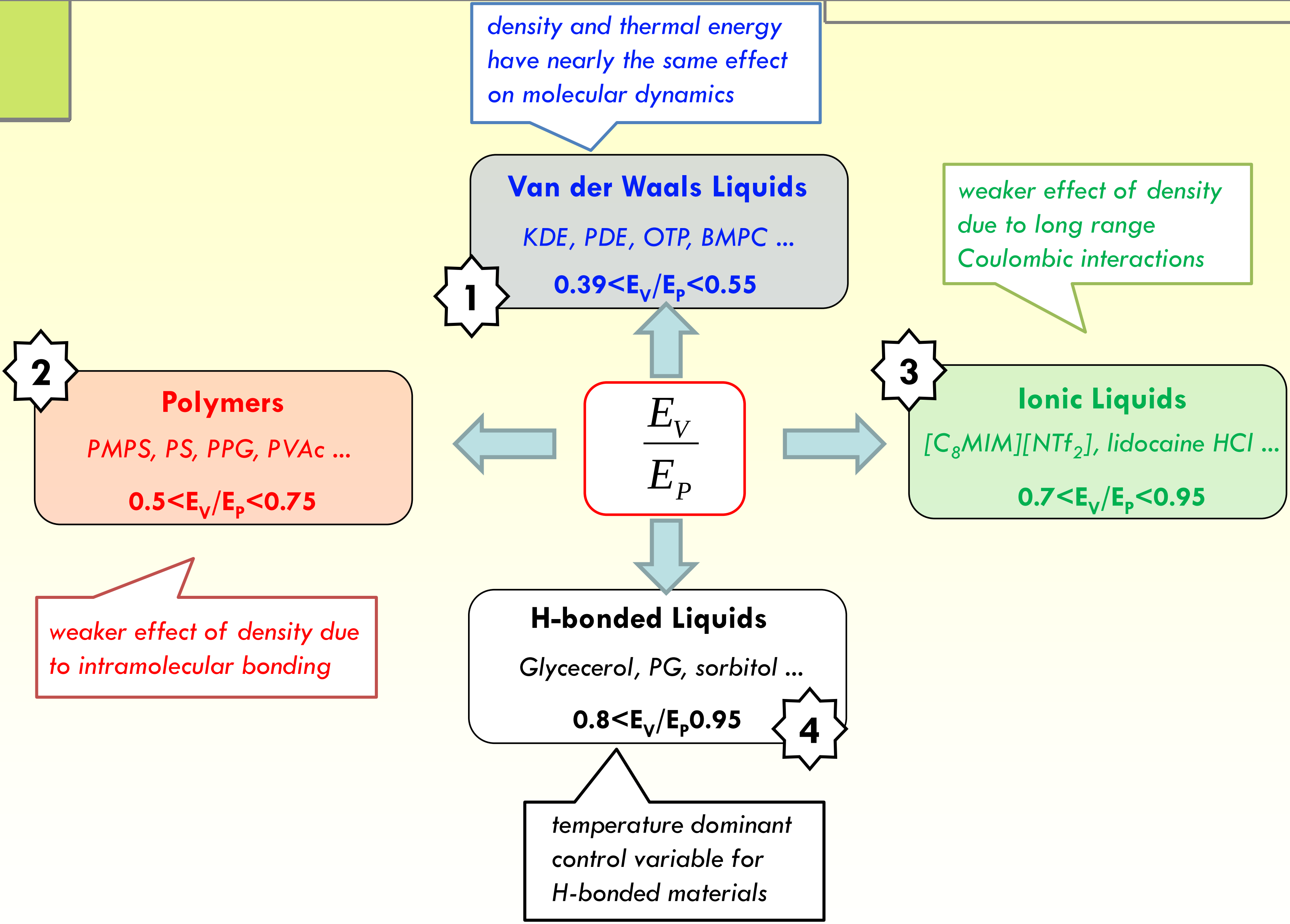
activation energy at constant pressure:

$$E_P = \left.\frac{\partial \log \tau}{\partial T^{-1}}\right|_P$$

$$\boxed{\frac{E_V}{E_P} = \frac{1}{1+\alpha_P/\alpha_\tau}}$$



$$\frac{E_V}{E_P} \approx 0.53$$



density and thermal energy have nearly the same effect on molecular dynamics

1

Van der Waals Liquids

KDE, PDE, OTP, BMPC …

$0.39<E_V/E_P<0.55$

$$\frac{E_V}{E_P}$$

2

Polymers

PMPS, PS, PPG, PVAc …

$0.5<E_V/E_P<0.75$

weaker effect of density due to intramolecular bonding

weaker effect of density due to long range Coulombic interactions

3

Ionic Liquids

$[C_8MIM][NTf_2]$, lidocaine HCl …

$0.7<E_V/E_P<0.95$

H-bonded Liquids

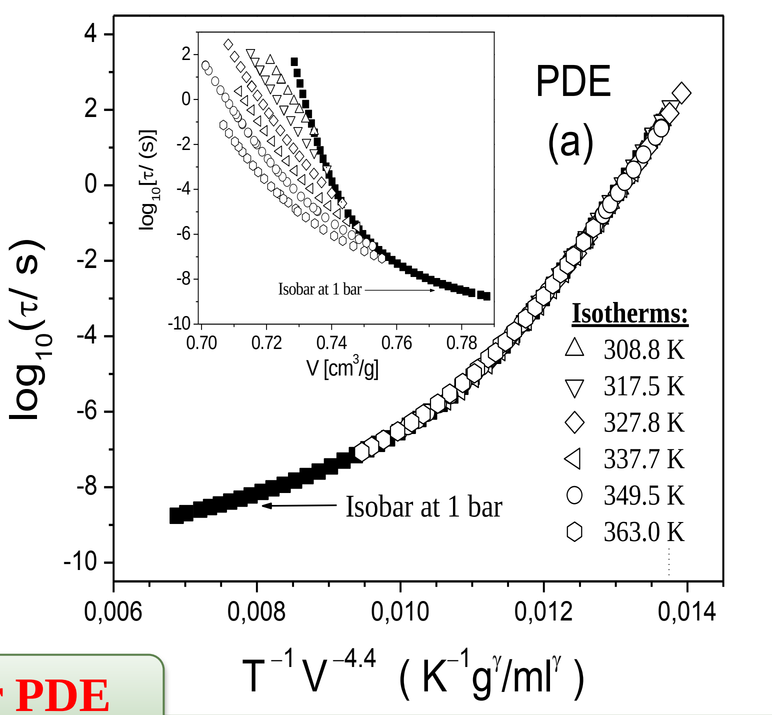
Glycecerol, PG, sorbitol …

$0.8<E_V/E_P0.95$

4

temperature dominant control variable for H-bonded materials

DENSITY SCALING

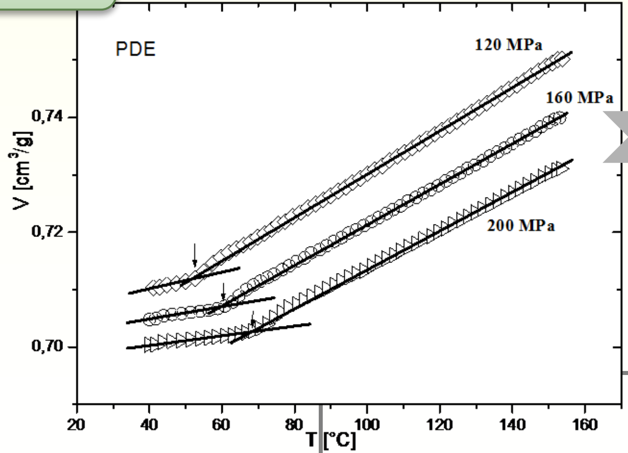


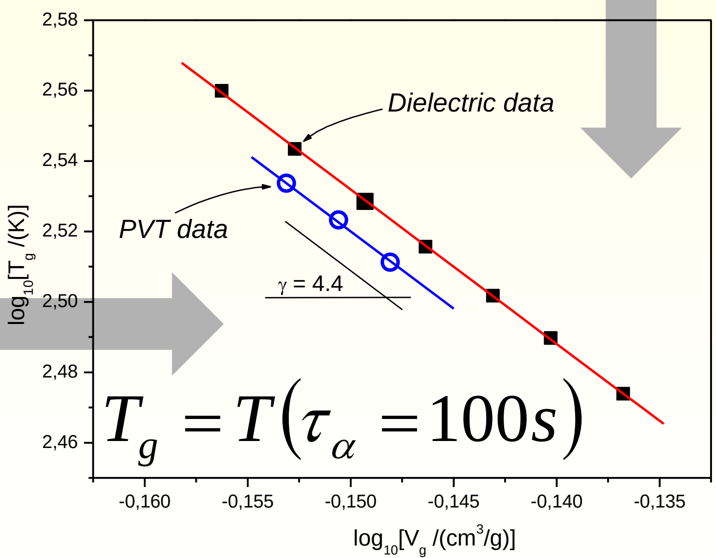
γ=4.4 for PDE

$$\log\tau \text{ vs. } T^{-1}V^{-\gamma}$$

At T=T$_g$ ⇒ $T_g^{-1}V_g^{-\gamma} = const.$

$$\log T_g = A - \gamma \log V_g$$





$$T_g = T(\tau_\alpha = 100s)$$

Relationship between E_V/E_P and γ

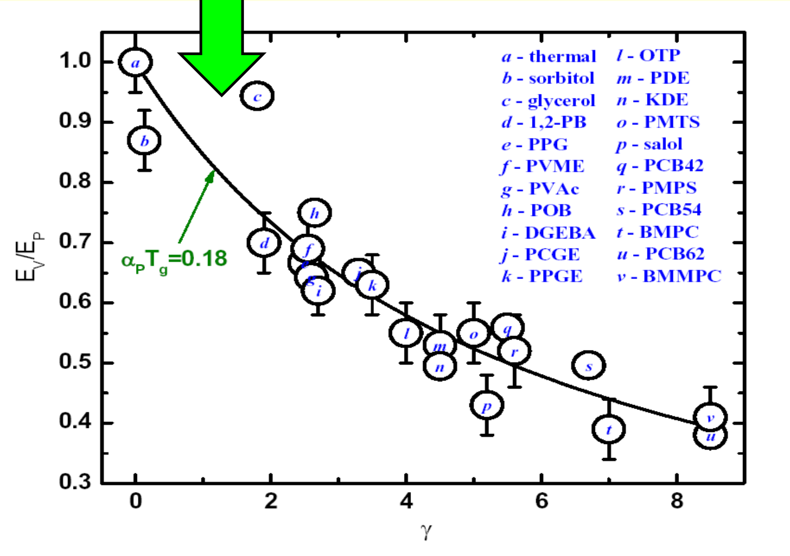
$$\frac{E_V}{E_P} = \frac{1}{1+\alpha_P T_g \gamma}$$

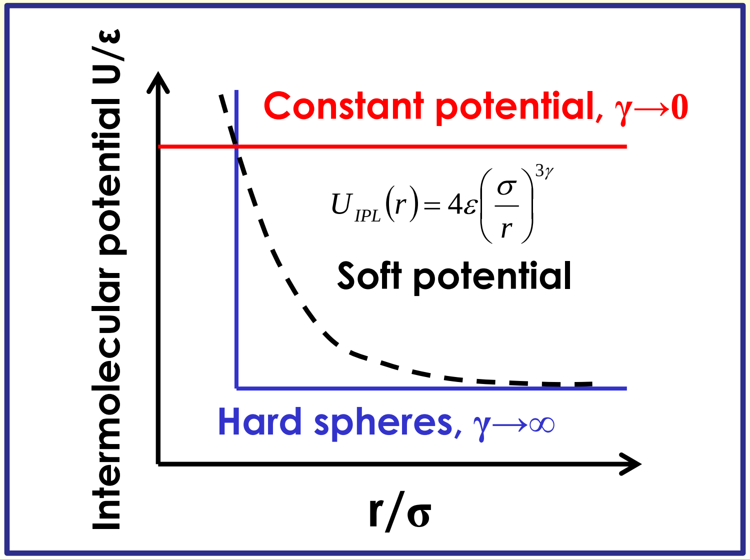
$\alpha_P T_g = 0.18$

Thermaly activated $\gamma \to 0 \Rightarrow \frac{E_V}{E_P} \to 1$

Volume activated $\gamma \to \infty \Rightarrow \frac{E_V}{E_P} \to 0$

Boyer-Spencer rule





$$U_{IPL}(r) = 4\varepsilon\left(\frac{\sigma}{r}\right)^{3\gamma}$$

MD simulations

Intermolecular interactions

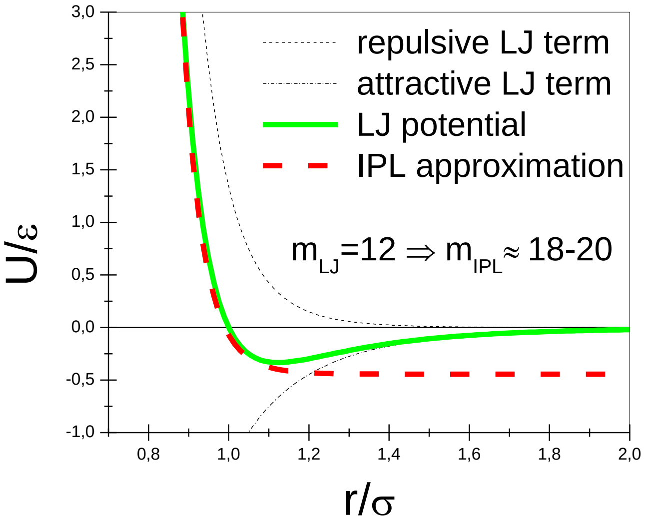
can be described using
Generalized Lennard-Jones potential

$$U_{LJ}(r)=4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{m_{LJ}}-\left(\frac{\sigma}{r}\right)^{n_{LJ}}\right],\quad m_{LJ}=3\gamma\ ,\ n_{LJ}=\frac{3\gamma}{2}$$

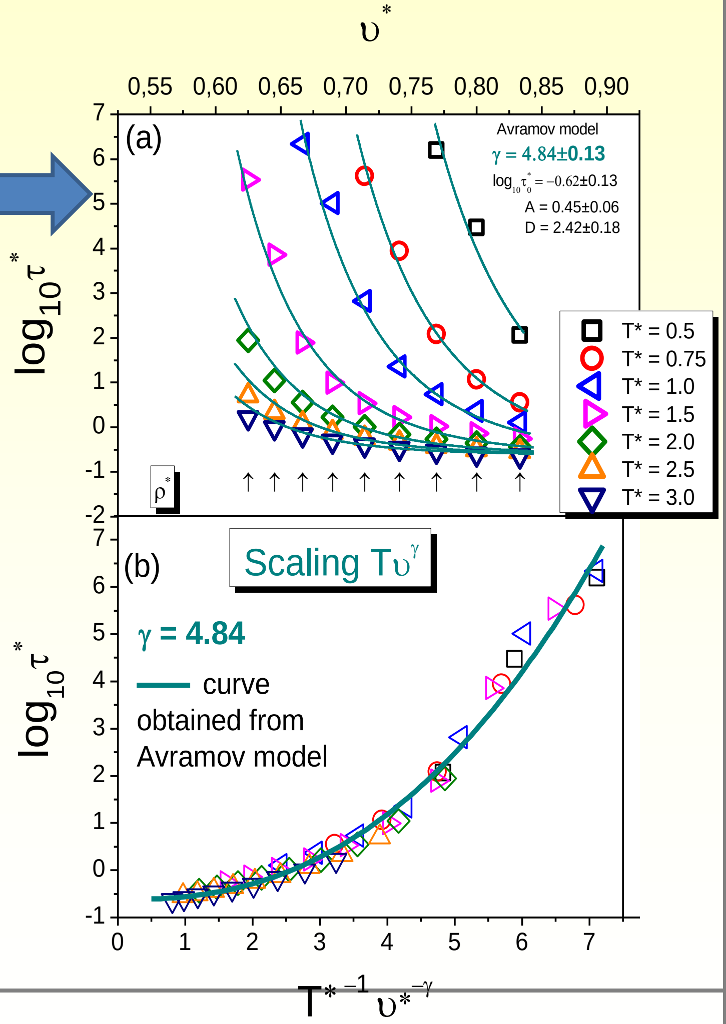
or inverse power law (near T_g)

$$U_{LJ}(r)\approx U_{IPL}(r)=4\varepsilon\left(\frac{\sigma_{IPL}}{r}\right)^{m_{IPL}}-A_t,$$

$$gdzie:\quad m_{IPL}=3\gamma\ ,\ A_t\approx const$$



Simulation of binary system with 1000 particles
A and B in proportion 80:20



Avramov "entropy" model

Assumptions:

1. The motion of the molecules is a thermally activated process with a jump frequency:

$$\nu_i = \nu_0 \exp(-\frac{E_i}{kT})$$

2. There is a distribution of energy barrier

$$W(E) = \left[\sigma - \sigma \exp\left(-\frac{E_m}{\sigma}\right)\right]^{-1} \exp\left[\frac{(E - E_m)}{\sigma}\right]$$

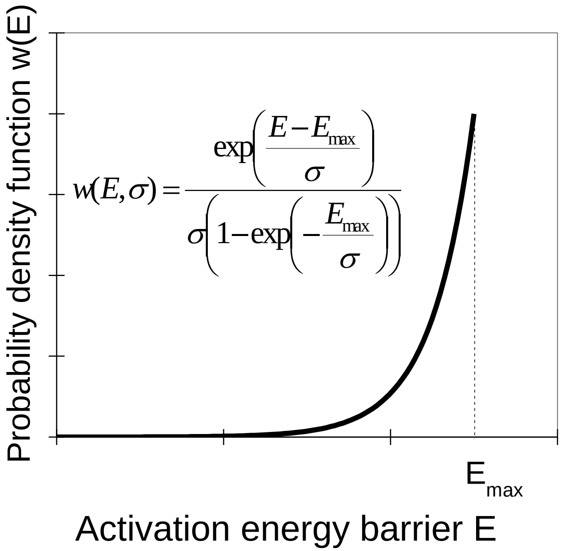
$$\langle \nu \rangle = \int_0^{E_m} \nu(E) W(E) dE$$

$$\langle \nu \rangle = \frac{1}{\tau} = \nu_0 \cdot \exp\left(-\frac{E_m}{\sigma}\right)$$

$E_{\max} = const$ for given material

$$S = -\frac{RZ}{2} \int_0^{E_m} W(E) \ln W(E) dE + const$$

$$S - S_0 \approx -\frac{RZ}{2} \ln \frac{\sigma}{\sigma_0}$$



$$w(E,\sigma) = \frac{\exp\left(\frac{E - E_{\max}}{\sigma}\right)}{\sigma\left(1 - \exp\left(-\frac{E_{\max}}{\sigma}\right)\right)}$$

The original Avramov approach

$$\tau = \tau_0 \exp\left\{30 \exp\left[\frac{2(S-S_0)}{ZR}\right]\right\}$$

$$S = S(T,P)$$

$$\log \tau(T,P) = \log \tau + \left(\frac{T_g}{T}\right)^{\alpha}\left(1+\frac{P}{\Pi}\right)^{\beta}$$

Modified by Avramov, Grzybowski and Paluch

$$\log \tau(T,P) = \log \tau + \left(\frac{T_g}{T}\right)^{\alpha(P)}\left(1+\frac{P}{\Pi}\right)^{\beta}$$

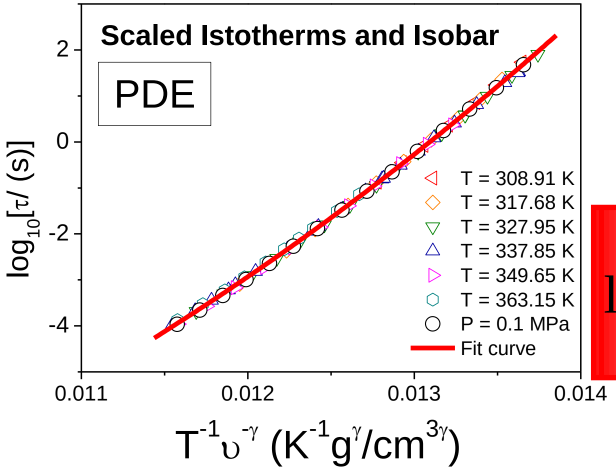
$$\alpha(P) = \left(1 - \frac{c}{c_{p_0}} \ln\left(1+\frac{P}{\Pi}\right)\right)$$

$$S = S(T,V)$$

Derived by Casalini and Roland

$$\log \tau(T,V) = \log \tau_0 + \left(\frac{B}{TV^{\gamma}}\right)^{D}$$

$$\gamma = 4.37 \pm 0.01$$



where: (a) $D = \frac{2c_V}{ZR}$ (b) $\gamma = \frac{c_p/c_v - 1}{\alpha_p T} = \gamma_G$ ✗

What is wrong with the Avramov model ?

For PDE

(calculated using Eq. b)

$$\gamma_G = 0.85$$

???

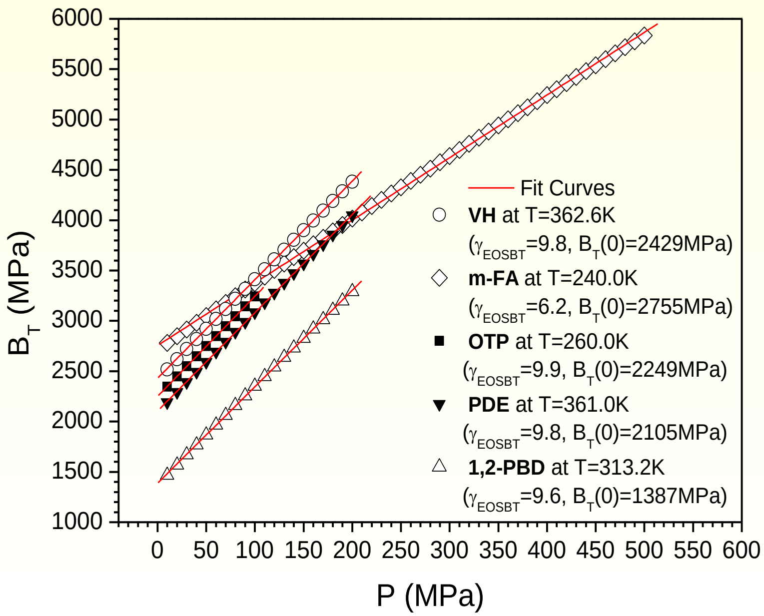
modifications of the Avramov entropic model

$$\rho^{\gamma} \cong 1 + \frac{\gamma}{B} P$$

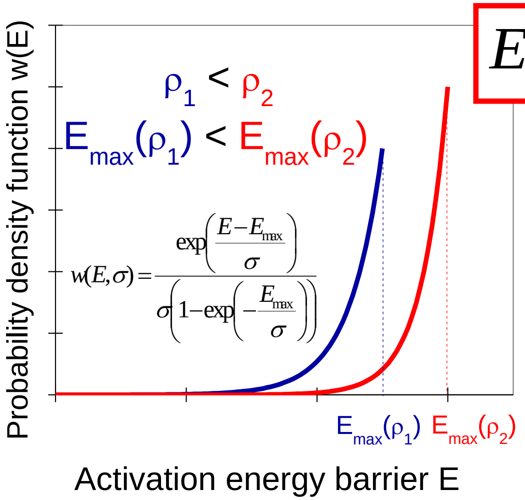
A.N. Papathanassiou, Phys. Rev. E (2009)

Bulk modulus

$$B_T(P) = \gamma P + B$$



$E_{\max} = const$ for a material **in isochoric conditions**



$$w(E,\sigma) = \frac{\exp\left(\frac{E - E_{\max}}{\sigma}\right)}{\sigma\left(1 - \exp\left(-\frac{E_{\max}}{\sigma}\right)\right)}$$

$$E_{\max} = f(\rho)$$

$$\tau = \tau_0 \exp\left[\left(\frac{A}{TV^{\gamma_A}}\right)^{D_A}\right]$$

$$D_A = \frac{2C_V}{ZR}$$

$$E_{\max}(V) = A_E \left(\frac{V_r}{V}\right)^{\gamma_E}$$

$$A = \left(\frac{A_E}{\sigma_r}\right)^{1/D} T_r V_r^{\gamma_A}$$

Our suggested solution

$$\gamma_A = \frac{\gamma_E}{D_A} + \gamma_G$$

The relation $\gamma_A = \frac{\gamma_E}{D_A} + \gamma_G$ where $\gamma_E \approx \gamma_{EOS}$ successfully works for van der Waals liquids at $\tau > \tau_B$

Class of materials	Material	γ_A $\gamma_A (\tau>\tau_B)$	D_A $D (\tau>\tau_B)$	γ_G	γ_E $\gamma_E = D_A(\gamma_A - \gamma_G)$	γ_{EOS}	$\log_{10}\tau_B$
van der Waals liquids	PDE phenylphthalein-dimethylether	4.37 ± 0.01	2.82 ± 0.09	0.85	9.93	9.8 ± 0.2 (low T)	-4.0
	KDE cresolphthalein-dimethylether	4.29 ± 0.03	2.89 ± 0.08	0.85	9.94	9.8 ± 0.1 (low T)	-6.3
	OTP *o*-terphenyl	4.40 ± 0.03	3.1 ± 0.4	1.2	9.92	10.0 ± 0.1	
	PC propylene carbonate	3.91 ± 0.01	3.75 ± 0.25	1.4	9.41	9.4 ± 0.1	-7.3
	BMPC 1,1'-bis(*p*-methoxyphenyl) cyclohexane	7.84	1.74	2.41	9.45	9,9 ± 0.1	-5.0

Pressure dependence of the glass transition temperature

EHRENFEST'S EQUATIOS

$$\frac{dT_g}{dp} = \frac{\Delta\kappa_T}{\Delta\alpha_p} \qquad \text{(1a)}$$

$$\frac{dT_g}{dp} = \frac{T_g \upsilon \Delta\alpha_p}{\Delta C_p} \qquad \text{(1b)}$$

PRIGOGINE-DEFAY RATIO

$$\Pi = \frac{\Delta C_p \Delta\kappa_T}{\upsilon T_g (\Delta\alpha_p)^2} = 1 \qquad \text{(2)}$$

$\frac{dT_g}{dp}$ is the pressure coefficient of the glass transition temperature

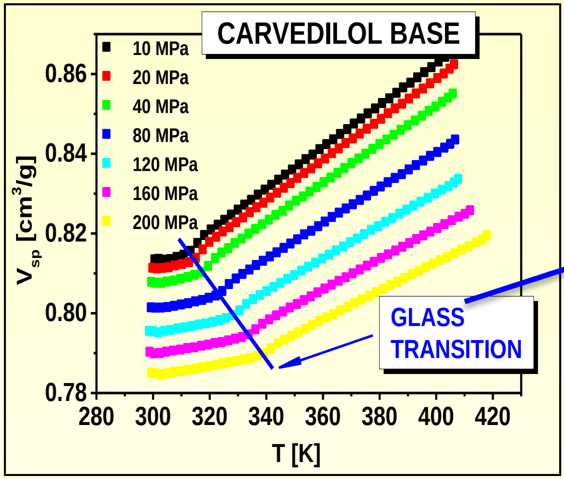
Δ denotes the difference between the properties of the liquid and the glass

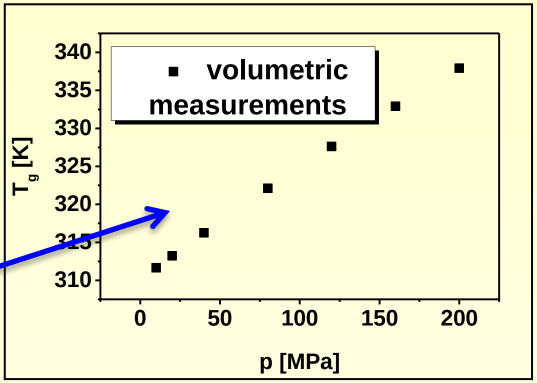
VAST MAJOROTY OF EXPERIMENTAL EXAMINATIONS:

Ehrenfest's equations are **NOT** fulfilled

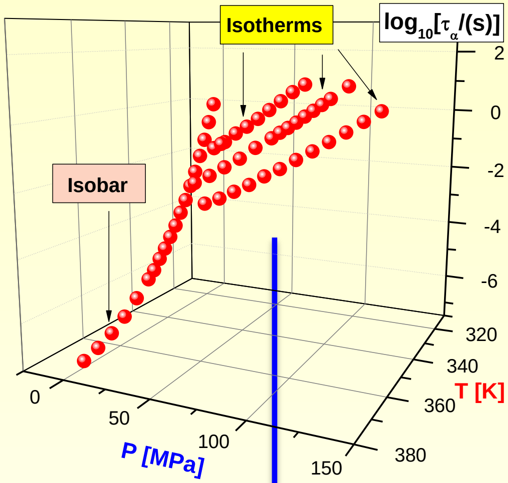
$$\Pi = \frac{\Delta C_p \Delta\kappa_T}{\upsilon T_g (\Delta\alpha_p)^2} > 1$$

More than one order parameter!





$$\log \tau = 1.625$$



$$V(p,T) = \frac{A_0 + A_1(T-T_0) + A_2(T-T_0)^2}{\left[1+(p-p_0)b_1\exp(b_2(T-T_0))\right]^{1/\gamma_{EOS}}}$$

↓ *A. Grzybowski et al., Phys. Rev. E 83, 041505 (2011)*

Phenomenological Andersson-Andersson equation:

$$\frac{dT_g}{dp} = \frac{\Delta\kappa_T}{\Delta\alpha_p} = 0.21[K/MPa]$$

$$\frac{dT_g}{dp} = \frac{T_g \upsilon \Delta\alpha_p}{\Delta C_p} = 0.13[K/MPa]$$

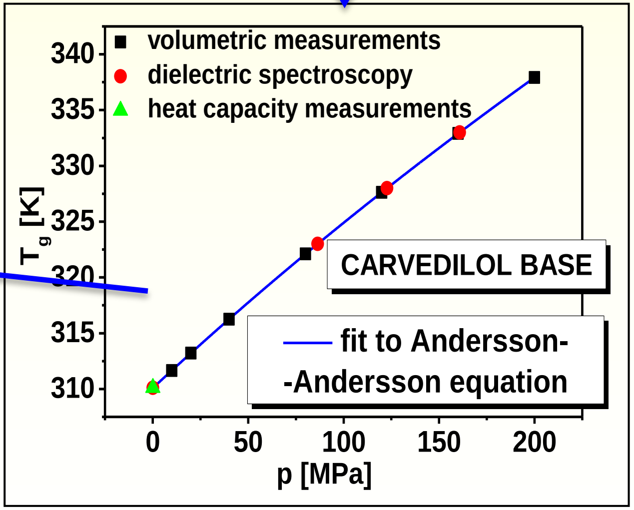
$$\Pi = \frac{\Delta C_p \Delta\kappa_T}{\upsilon T_g (\Delta\alpha_p)^2} = 1.59$$

in the limit of ambient pressure

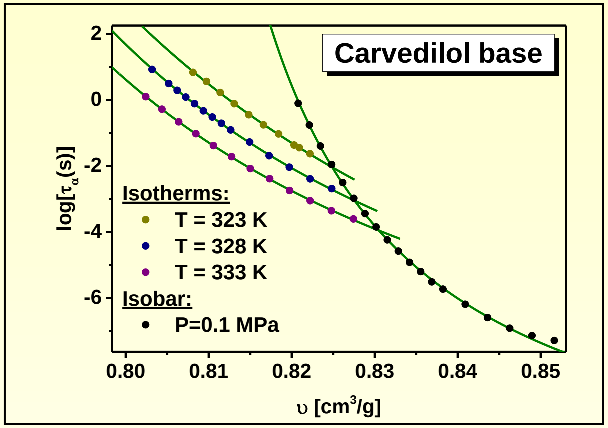
$$T_g(p) = T_g^0\left(1+\frac{p}{k_1}\right)^{k_2}$$

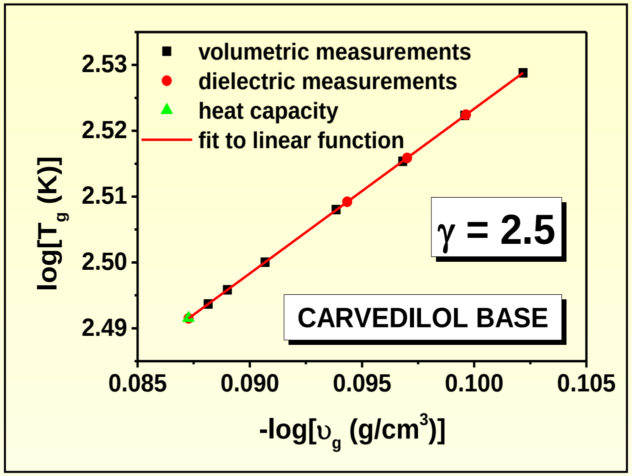
$$\downarrow$$

$$\frac{dT_g}{dp} = 1.6[K/MPa]$$

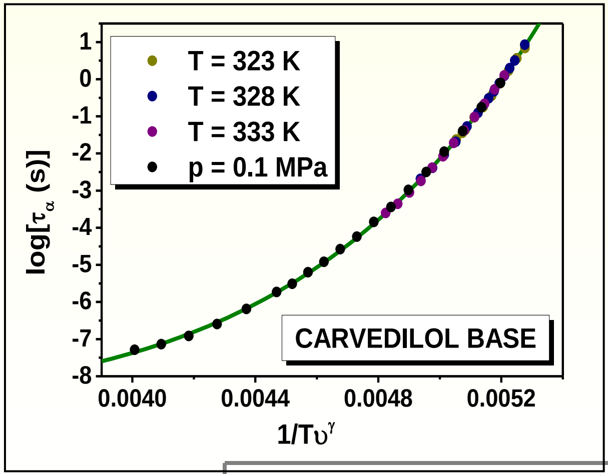


THERMODYNAMIC SCALING





$$\tau = f\left(T\upsilon^{\gamma}\right)$$



$$\tau = const.$$

$$T_\tau \upsilon_\tau^{\gamma} = C$$

$$\log T_\tau = -\gamma \log \upsilon_\tau + C$$

$$\tau_g = const$$

$$C = T_g \upsilon_g^{\gamma}$$

$$\frac{d}{dT} C = \frac{d}{dT}\left(T_g \upsilon_g^{\gamma}\right) = \upsilon_g^{\gamma}\left(1 + T_g \gamma \upsilon_g^{-1}\left(\frac{d\upsilon}{dT}\right)_{\tau}\right) = 0$$

$$d\upsilon = \left(\frac{\partial \upsilon}{\partial T}\right)_p dT + \left(\frac{\partial \upsilon}{\partial p}\right)_T dp$$

$$1 + T_g \gamma \upsilon_g^{-1}\left[\left(\frac{\partial \upsilon}{\partial T}\right)_p + \left(\frac{\partial \upsilon}{\partial p}\right)_T \frac{dp}{dT}\right]_{\tau} = 0$$

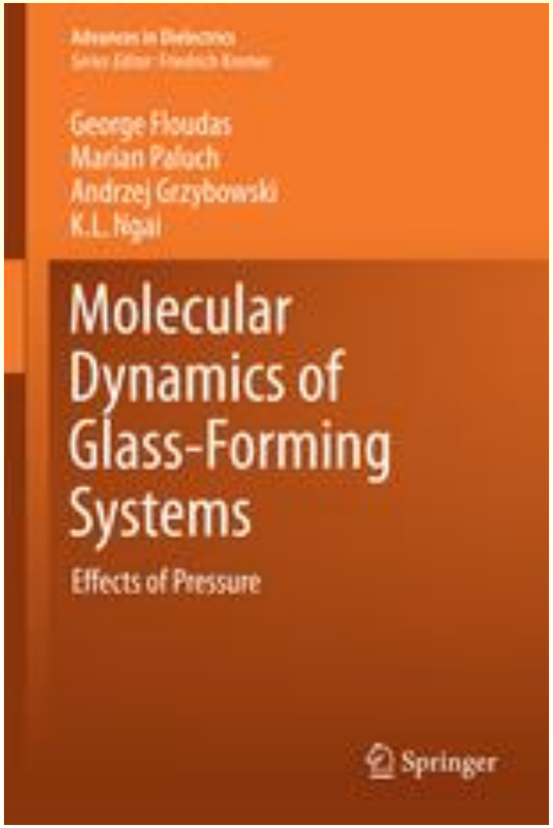
$$\alpha_p = \frac{1}{\upsilon}\left(\frac{\partial \upsilon}{\partial T}\right)_p \qquad \kappa_T = -\frac{1}{\upsilon}\left(\frac{\partial \upsilon}{\partial p}\right)_T$$

$$\boxed{\frac{dT_g}{dp} = \frac{T_g \gamma \kappa_T}{1 + T_g \gamma \alpha_p}} \quad \textbf{(A)}$$

K. Koperwas et al., Phys. Rev. E 86, 041502 (2012)

MATERIAL		ANDERSSON-ANDERSSON	(A)	$\frac{dT_g}{dp} = \frac{\Delta\kappa_T}{\Delta\alpha_p}$	$\frac{dT_g}{dp} = \frac{T_g \upsilon \Delta\alpha_p}{\Delta C_p}$
carvedilol base	CB	0.16	0.16	0.21	0.13
ortho-Terphenyl	OTP	0.26	0.26	0.39	0.17
glibenclamide	GLB	0.21	0.21	0.32	0.14
polystyrene	PS	0.39	0.40	0.50	0.29
telmisartan	TLM	0.28	0.27	0.21	0.30
verapamil hydrochlorine	VH	0.21	0.21	0.21	0.24
glycerol	GLC	0.05	0.06		
1,1’-bis (p-methoxyphenyl) cyclohexane	BMPC	0.24	0.22		
salol	SL	0.20	0.19		
ibuprofen	IBP	0.20	0.20		
indometacin	IND	0.25	0.25		
cresolphthalein-dimethylether	KDE	0.31	0.28		
polyvinylacetate	PVAc	0.25	0.25		
N,N-dimethyl-3-methylbenzamide	DEET		0.15		
mixture of 67% o-terphenyl and 33% o-phenylphenol	OTP-OPP		0.26		

More information about high pressure dielectric spectroscopy and its applications can be found in:



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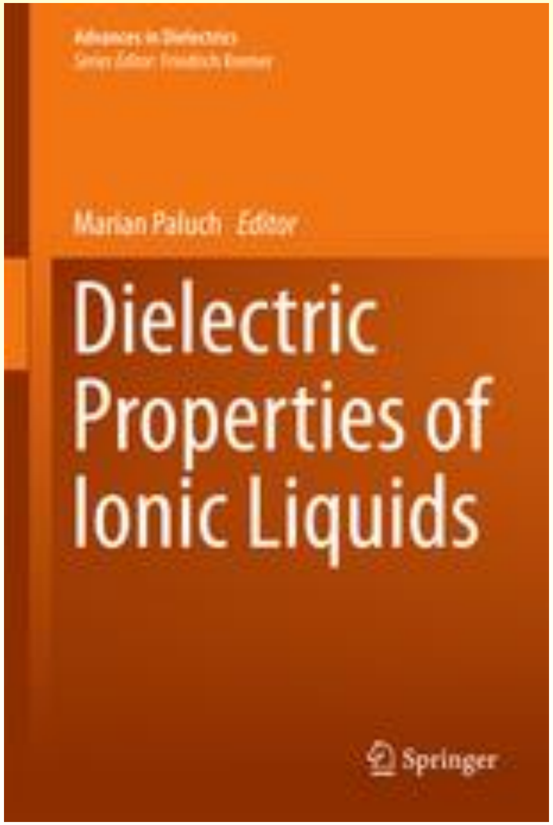

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