Effect of pressure on the fragility parameter: A density scaling point of view and its recent modification.

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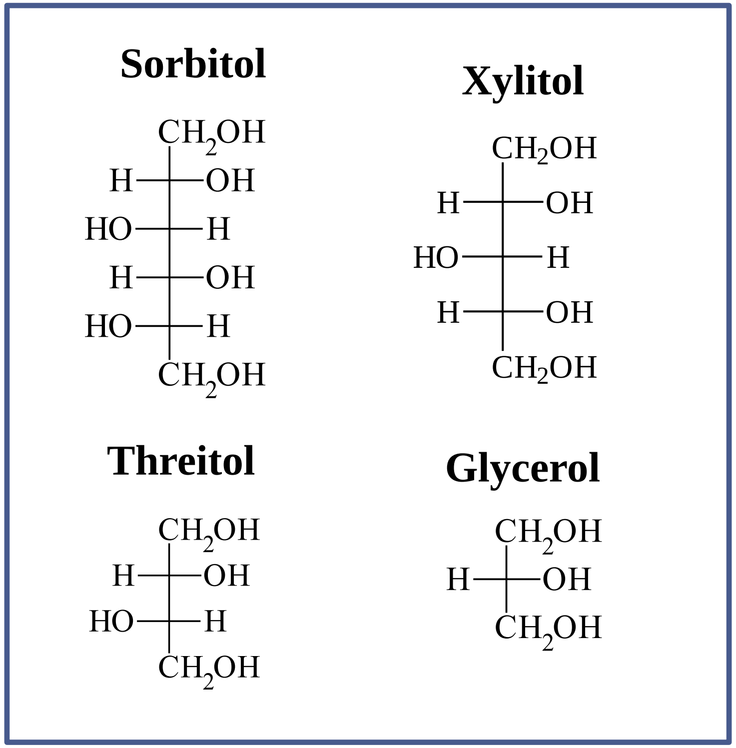
Bengaluru 2014

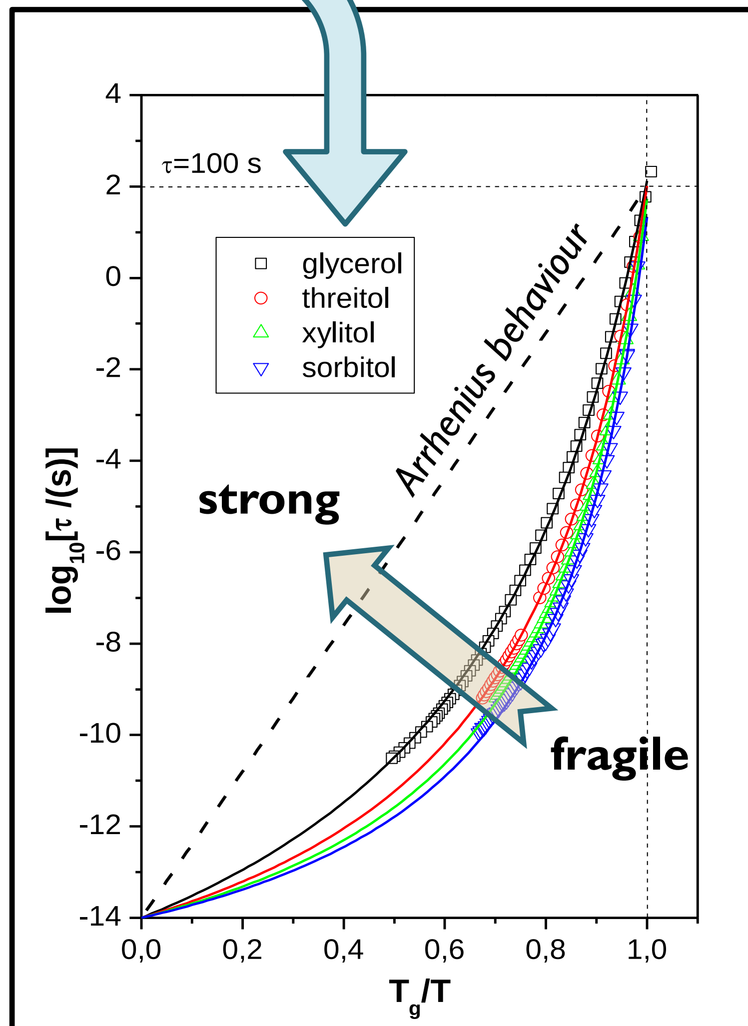
Fragility at ambient pressure

Steepness index

$$m_p = \left.\frac{d\log\tau}{d\left(T_g/T\right)}\right|_{T_g}$$

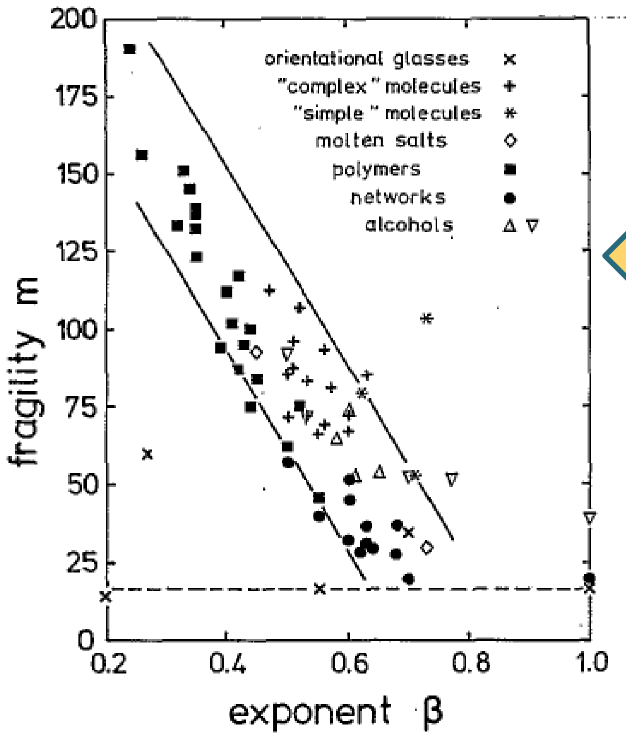


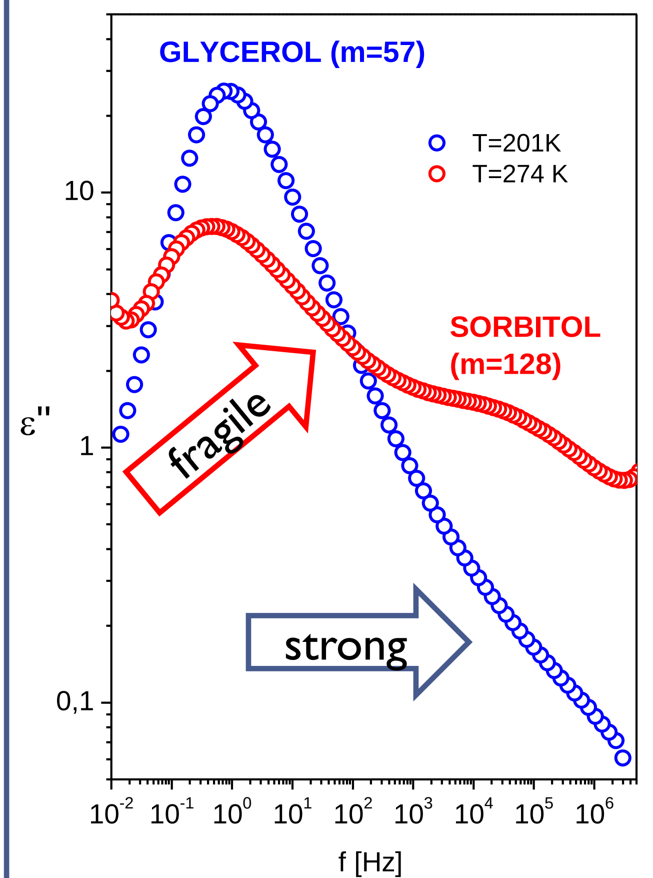
	dT_g/dP	m_p	T_g (at 100s)
glycerol	35±3	57	188.4
threitol	33±5	79	224
xylitol	34±2	94	247
sorbitol	40±5	128	267



Correlation between m and β

R. Bohmer, K. L. Ngai, C. A. Angell, D. J. Plazek, *J. Chem. Phys. 1993*





$$m_p = m_0 + s\beta$$

$$m_0 = 250 \pm 30 \text{ and } s = 320$$

A. Döss, M. Paluch, H. Sillescu, and G. Hinze, *Phys. Rev. Lett.* ***88****, 95701 (2002)*

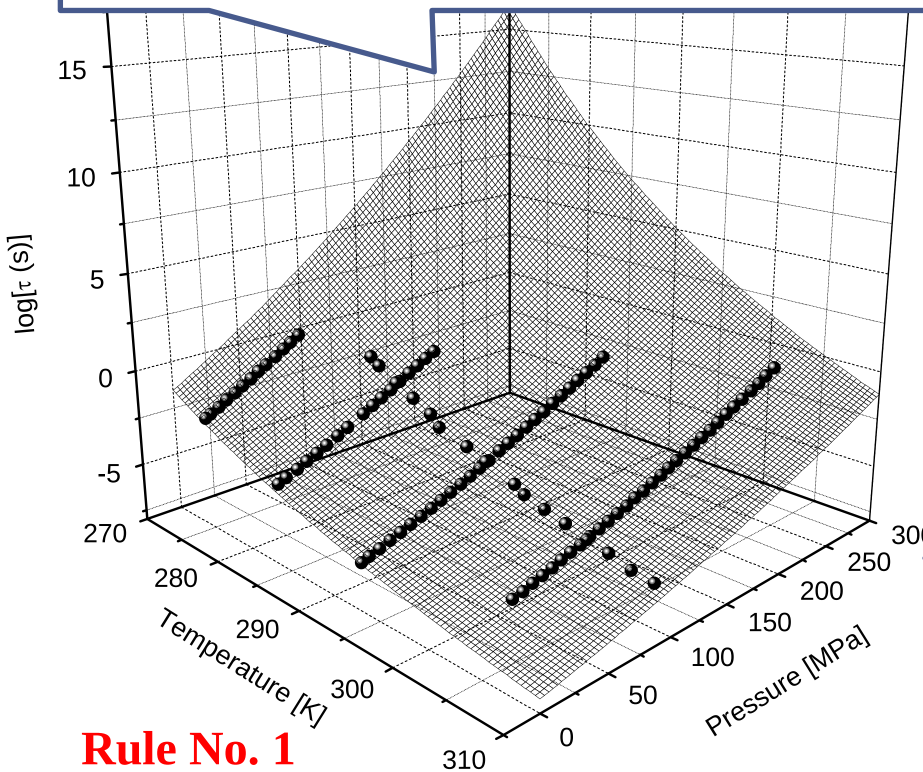
T-P dependence of τ_α

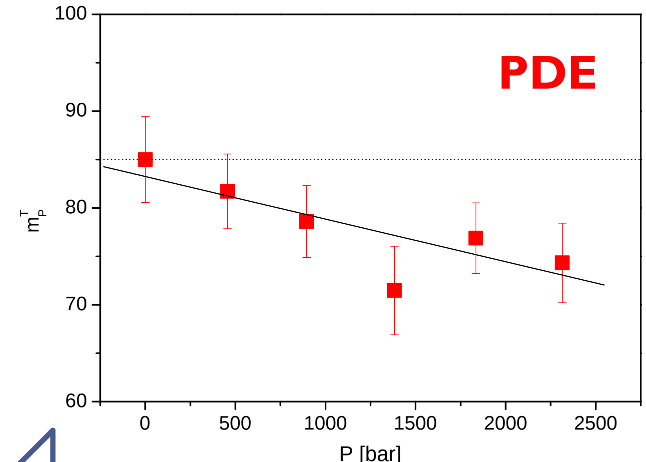
What is the effect of pressure on m_p?

$$m_p^{\,T} = \left.\frac{d\log\tau}{d\left(T_g/T\right)}\right|_{T_g}$$ **at constant P**

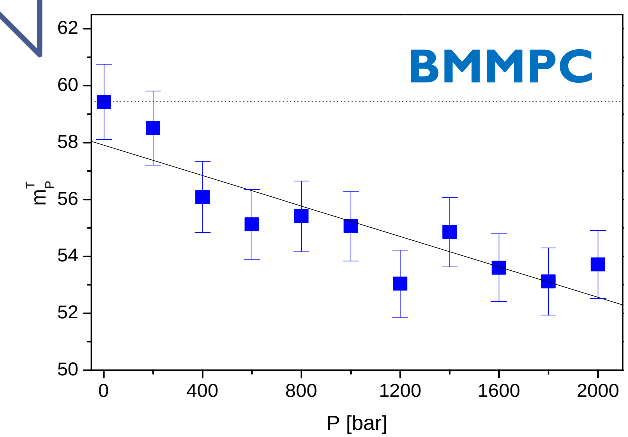
Poly(phenyl glycidyl ether)-co-formaldehyde

M. Paluch, S. Hensel –Bielowka and T. Psurek, J. Chem. Phys. 2000





$$m_p^{\,T} = \frac{\Delta V}{2.303R\,dT_g/dP}$$

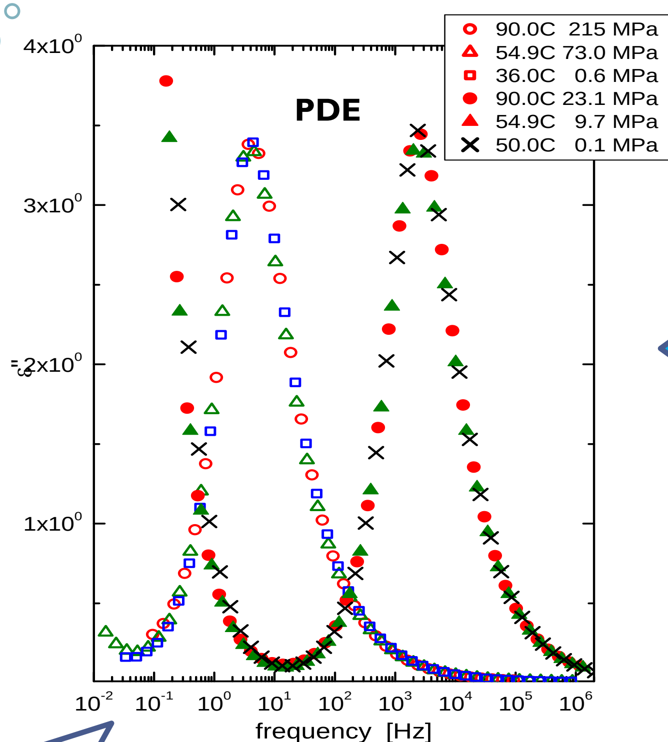


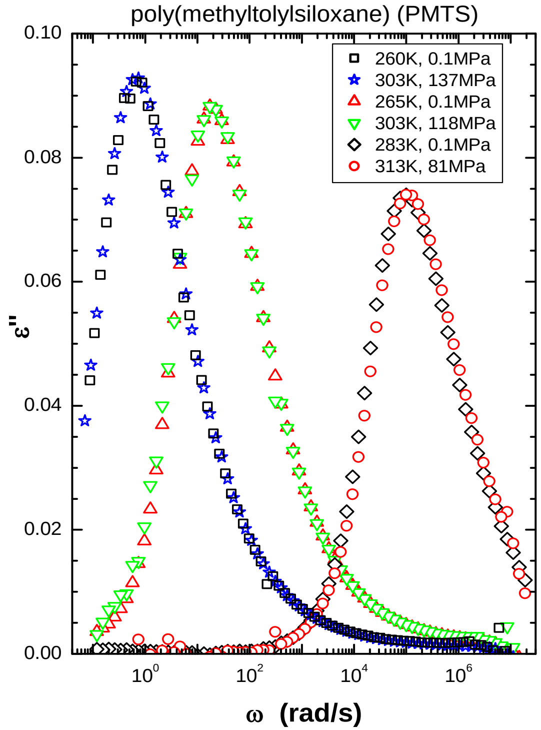
Rule No. 1

Fragility m_p^T of Van der Waals liquids decreases with increasing pressure.

Paluch M, Grzybowska K, Grzybowski A,
J. Phys.-Condens Matter **19** 205117 (2007)

Dielectric spectra of van der Waals liquids at elevated pressure



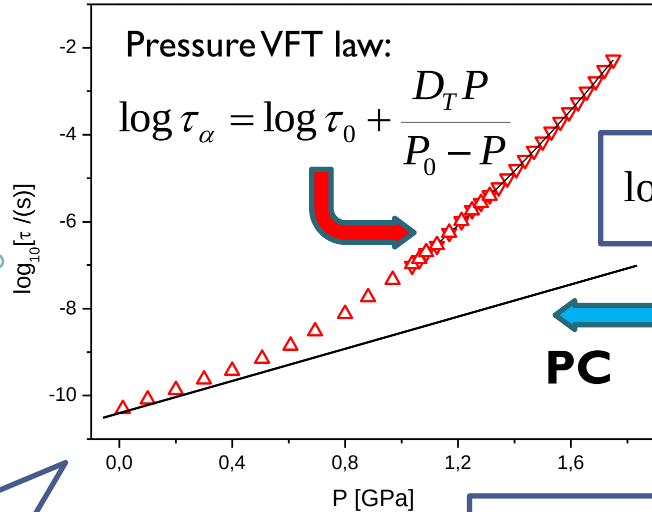


K.L. Ngai, R. Casalini, S. Capaccioli, M. Paluch, C.M. Roland, J. Phys. Chem. B **109** 17356 (2005).

Superposition of dielectric loss spectra at constant τ_α

Breakdown of Correlation between m and β at high pressure

Various fragility indexes



$$\log \tau_\alpha = \log \tau_A + \frac{P\Delta V}{RT}$$

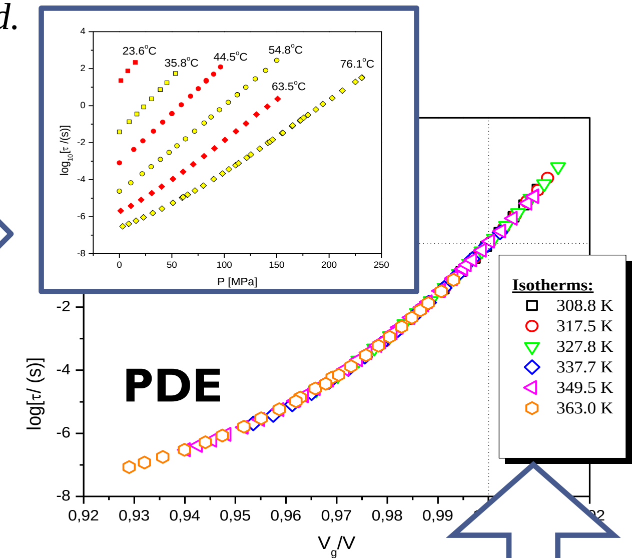
S. Pawlus, R. Casalini, C.M. Roland, M. Paluch, S.J. Rzoska and J. Ziołо, Phys. Rev. E **70**, 061501 (2004)

One can also define **isothermal fragility**:

$$m_T^{\ P} = \left.\frac{d\log\tau}{d\, P/P_g}\right|_{P_g}$$

However it is not a useful parameter because it is not clear at which temperature it should be calculated.

C. M. Roland, S. Hensel-Bielowka, M. Paluch, R. Casalini, Rep. Prog. Phys. 68 1405 (2005).



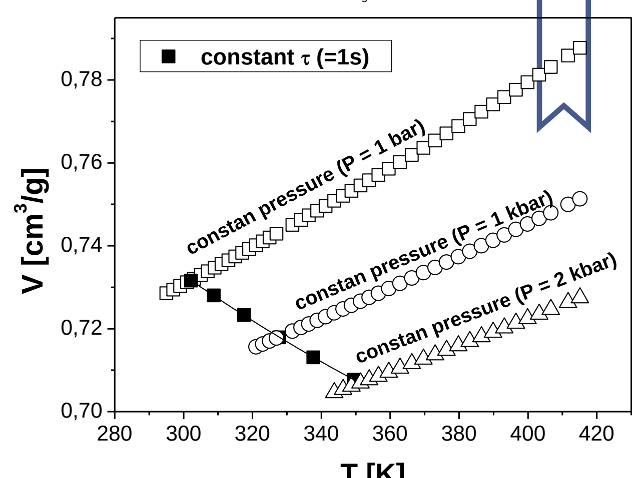
It is better to define **isothermal fragility**:

Rule No. 2

$m_T^{\ V}$ is temperature invariant parameter

$$m_T^{\ V} = \left.\frac{d\log\tau}{d\, V_g/V}\right|_{V_g}$$

T=const



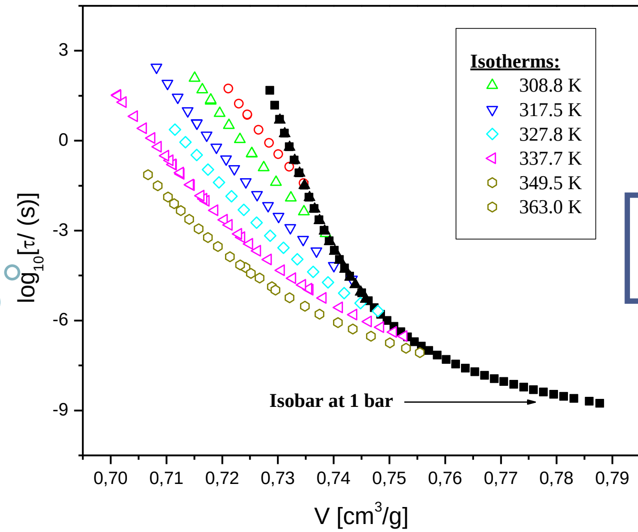
Finally, one can also define **isochoric fragility**:

Rule No. 3

$m_V^{\ T}$ is volume invariant parameter

$$m_V^{\ T} = \left.\frac{d\log\tau}{d\, T_g/T}\right|_{T_g}$$

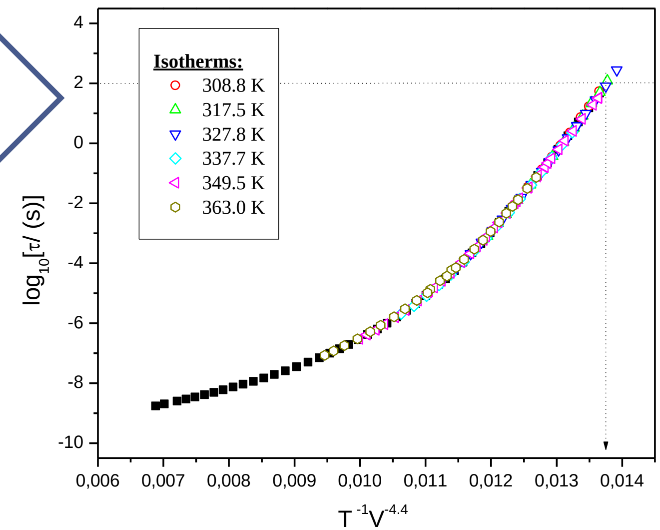
V=const



PDE

$$\log \tau = f\left(TV^{\gamma}\right)$$

Density scaling



and relationship between fragilities

$$m_P^T = m_V^T\left(1 + \gamma T_g \alpha_p\left(T_g\right)\right)$$

$$\frac{E_V}{E_P} = \left[1 + \gamma T_g \alpha_p\left(T_g\right)\right]^{-1}$$

$$\frac{m_V^T}{m_P^T} = \frac{E_V}{E_P}$$

The measure of the relative contribution of theraml and density fluctuations to the super-Arrhenius behaviour

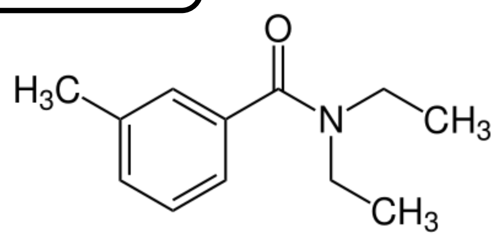
$$\frac{m_P^T}{m_T^V} = \frac{1}{\gamma} + T_g \alpha_p\left(T_g\right)$$

$$\frac{m_T^V}{m_V^T} = \gamma$$

scaling exponent

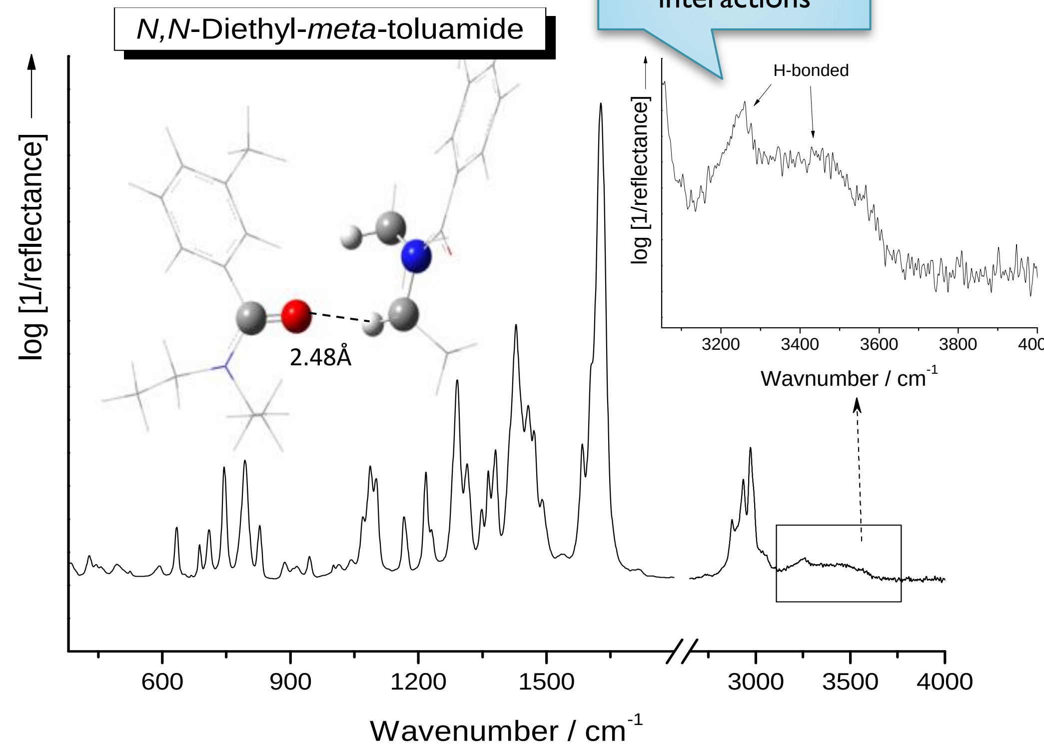
The peculiar behavior of fragility of associated liquids

DEET



***N,N*-Diethyl-*meta*-toluamide**, abbreviated **DEET**, is the most common active ingredient in insect repellents and provides protection against mosquito bites.

Suggest weak H-bonded interactions



Bands related to symetric and asymetric streaching vibrations of OH groups are localized in frequency range:

3400-3600cm^{-1}

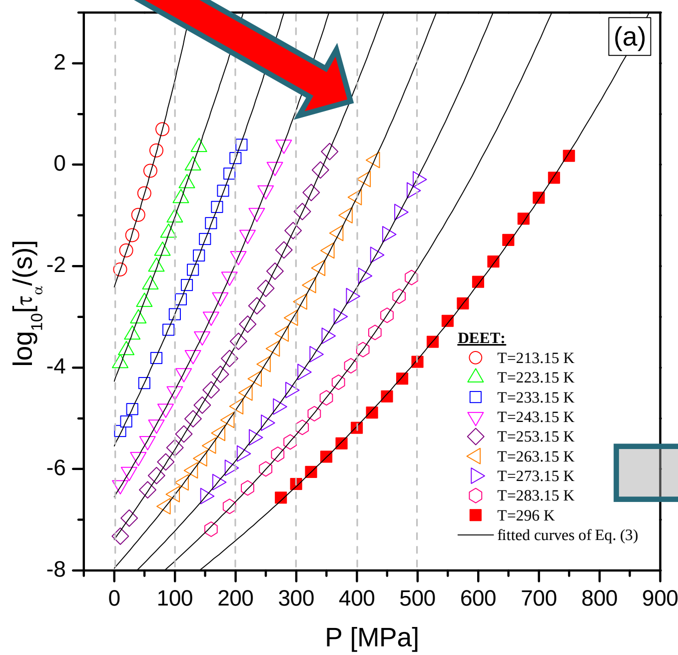
Possible H-bonds:

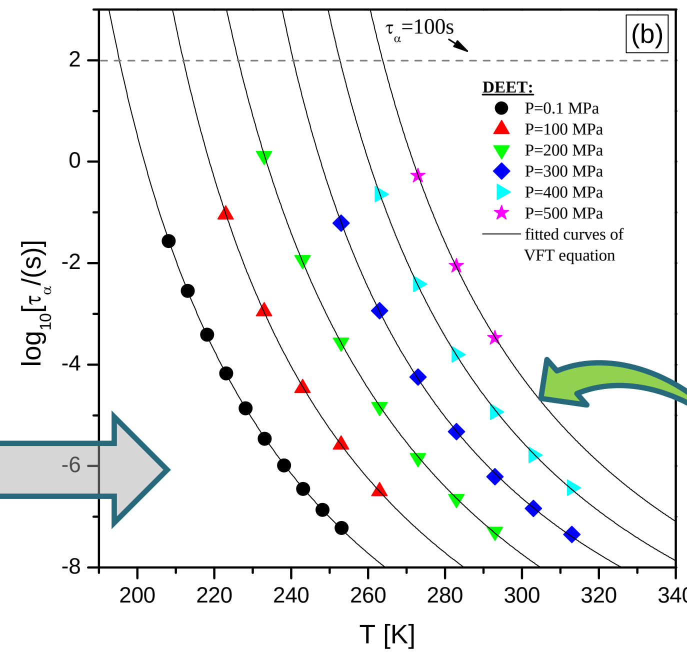
Carbonyl group C=O and group CH2 (near N), groupCH3. hydrogens in benzene ring

The length of H bonds formed: $\mathbf{2.38\dot{A} - 2.48\dot{A}}$

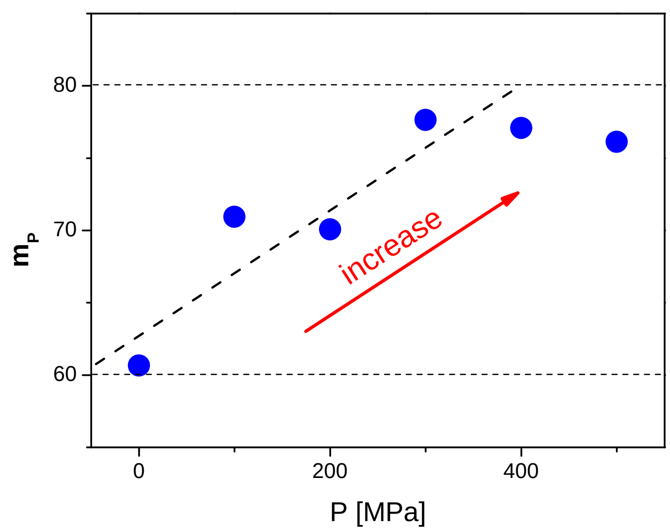
The peculiar behavior of fragility of associated liquids

$$\tau_\alpha = \tau_0 \exp\left(\frac{DP_0}{P_0 - P}\right)$$





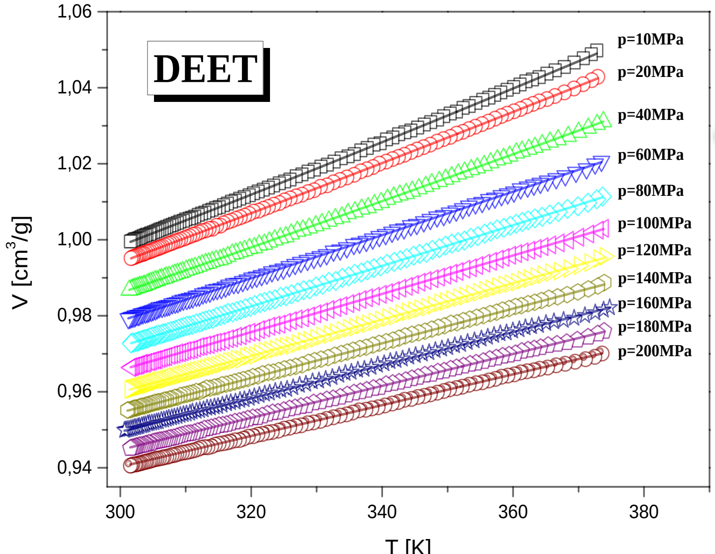
$$\tau_\alpha = \tau_\infty \exp\left(\frac{DT_0}{T - T_0}\right)$$



Fragility increases with compression!

Construction of isochoric curves

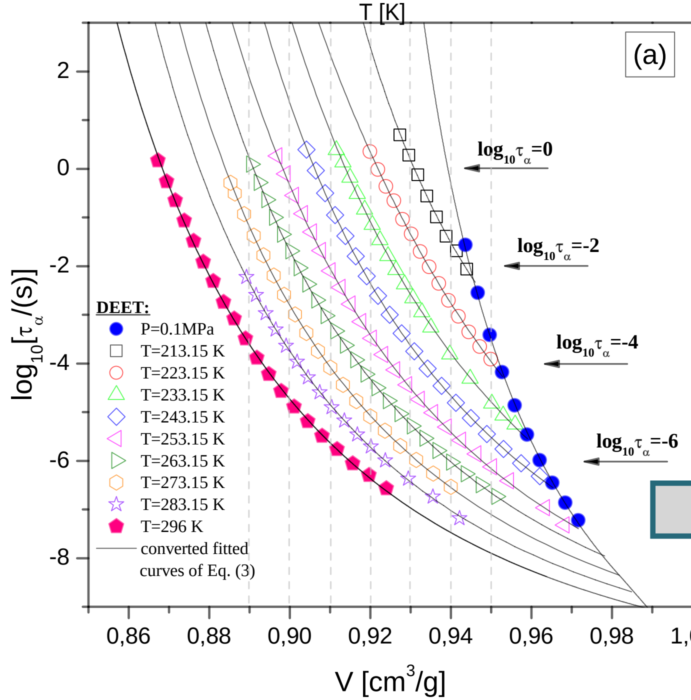
A. Grzybowski, M. Paluch et.al.
J. Phys. Chem. B **113** 7419 (2009)

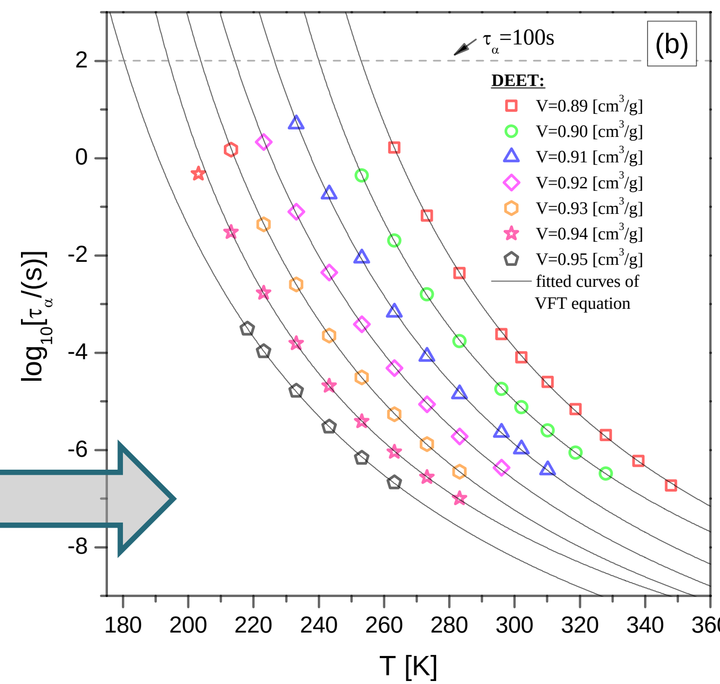


$$\left(\frac{\upsilon(T,p_0)}{\upsilon(T,p)}\right)^{\gamma_{EOS}} = 1 + \frac{\gamma_{EOS}}{B_T(p_0)}(p - p_0)$$

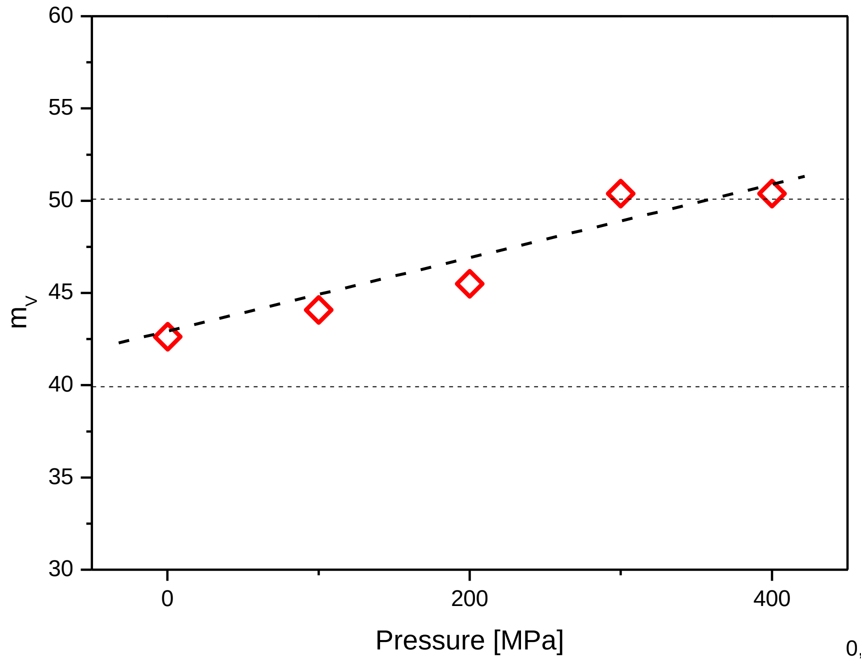
$$\upsilon(T,p_0) = A_0 + A_1(T - T_0) + A_2(T - T_0)^2$$

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





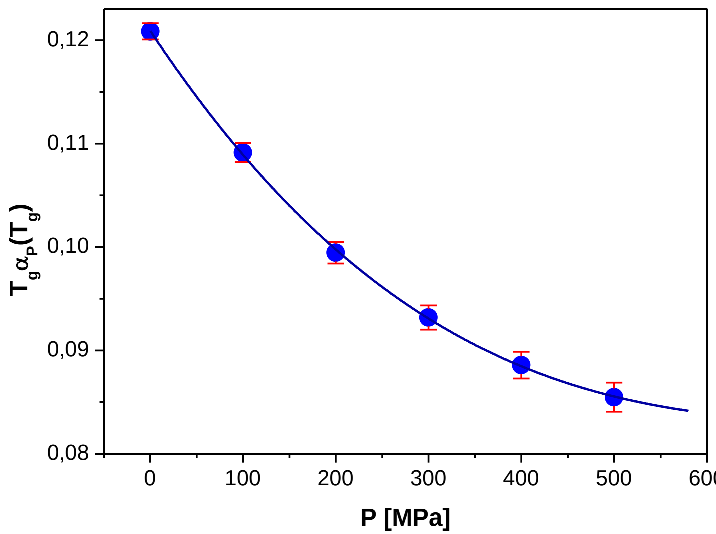
Peculiar behaviour of isochoric fragility



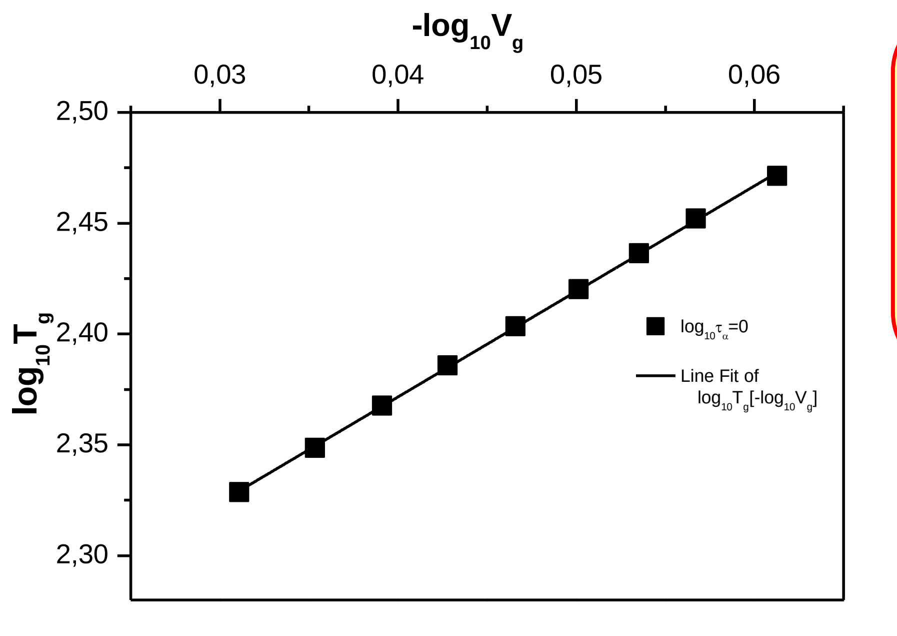
$$m_V^T = \left. \frac{d \log \tau}{d \, {T_g}/{T}} \right|_{T_g}$$

m_V^T increases with pressure

$\alpha_p T_g$ decreases with pressure

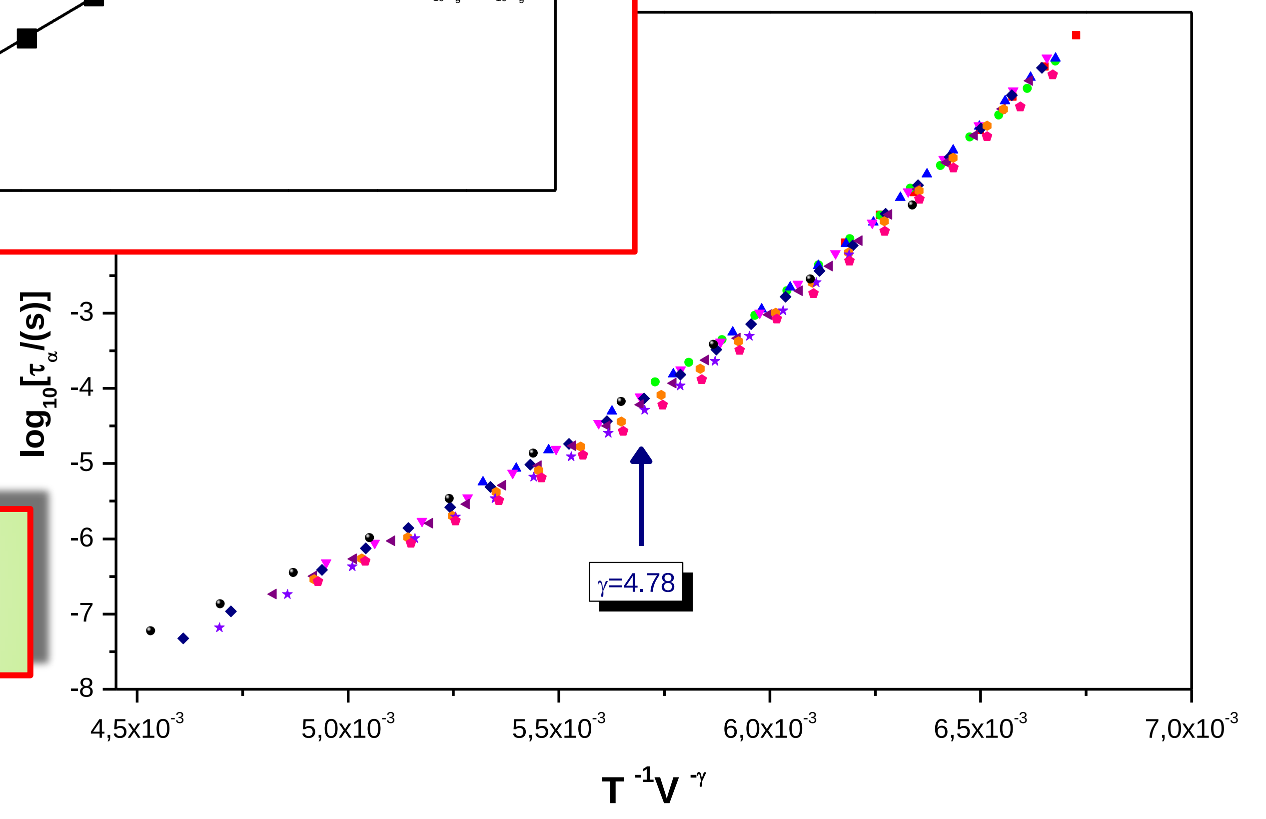


Breakdown of density scaling



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

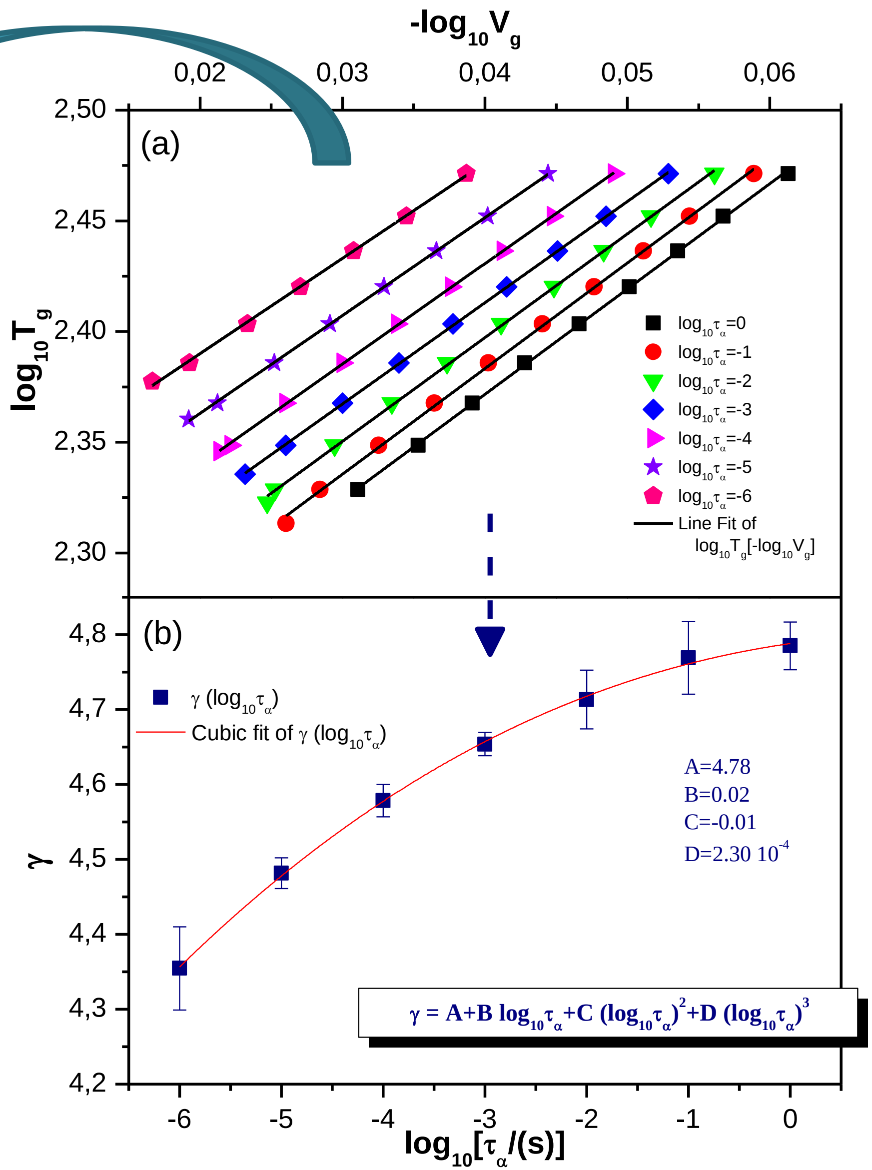
$$\log T_g = A - \gamma \log V_g$$



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

Modified density scaling

The exponent γ depends on the value of the structural relaxation time



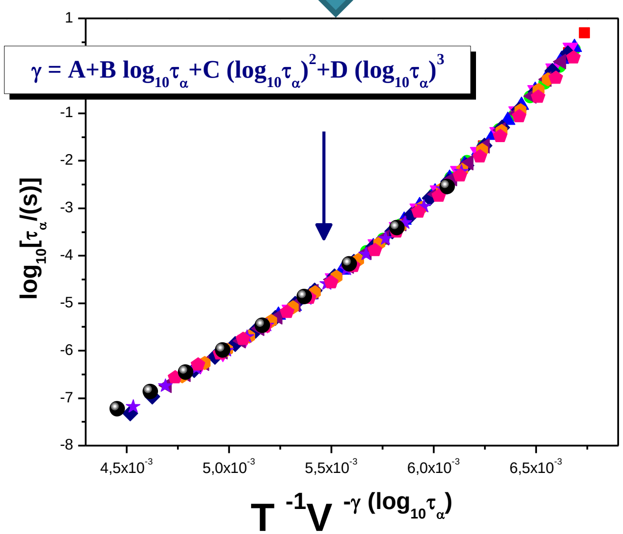
DEET:

Isobar

P=0.1MPa

Isotherms:

T=213.15 K
T=223.15 K
T=233.15 K
T=243.15 K
T=253.15 K
T=263.15 K
T=273.15 K
T=283.15 K
T=296 K



Adam-Gibbs model

$$\tau = \tau_{AG} \exp\left(\frac{A}{TS_c(T)}\right)$$

$$S_c(T,P) = \Delta S_{fus} + \int_{T_K}^{T} \frac{\Delta C_P(T')}{T'} \, dT' - \int_0^P \Delta\left(\frac{\partial V}{\partial T}\right)_{P'} dP'$$

at P =0.1MPa

$$\Delta C_P = K/T$$

$$S_c(T) = \int_{T_K}^{T} \frac{K}{T'^2} dT' = \frac{K}{T_K} - \frac{K}{T} = S_\infty - \frac{K}{T}$$

VFT law:

$$\tau = \tau_{AG} \exp\left(\frac{A}{T - T_0}\right)$$

$$\Delta\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial \Delta V}{\partial T}\right)_P = \left(\frac{\partial\left(V^{melt} - V^{crystal}\right)}{\partial T}\right)_P$$

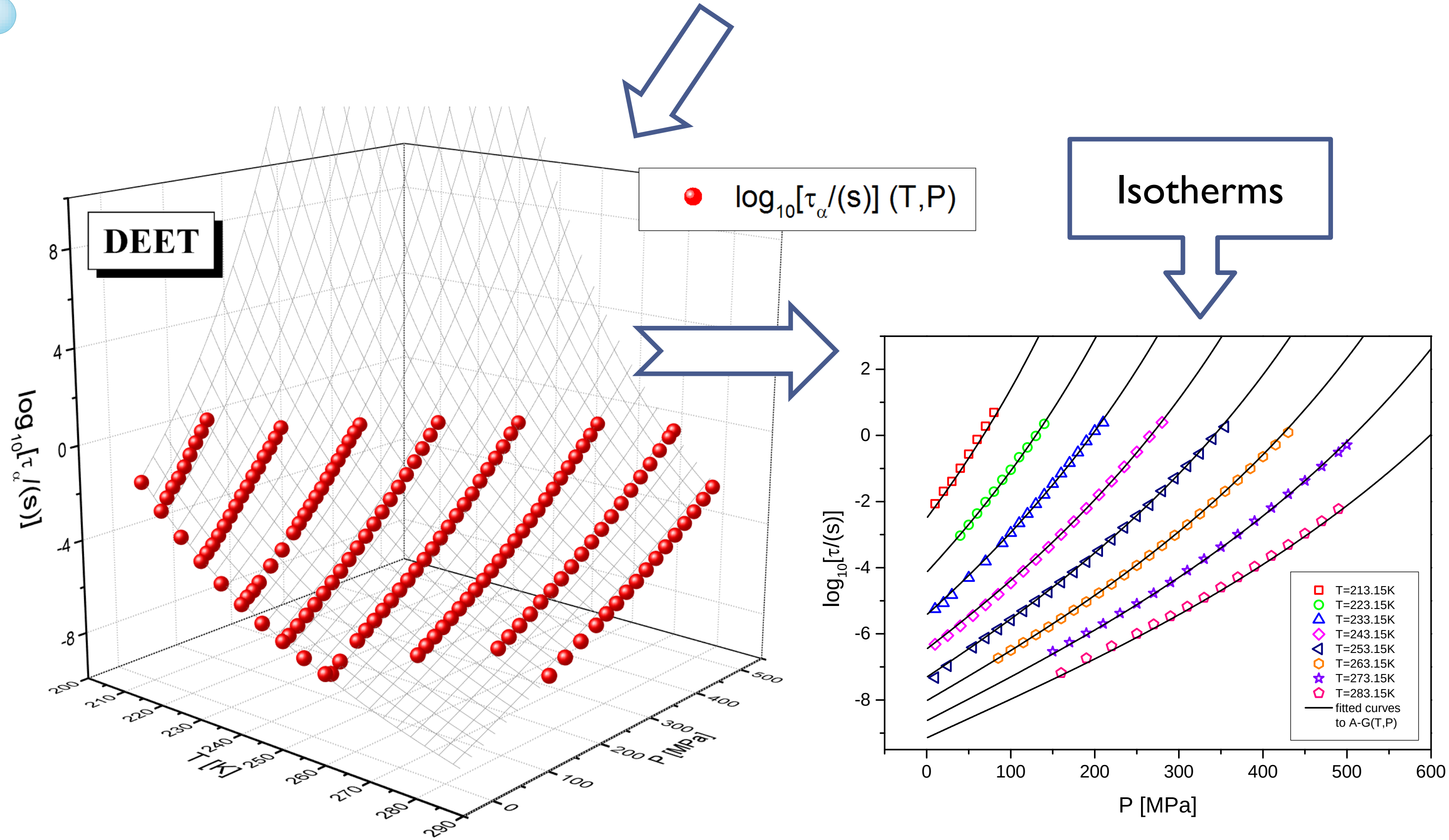
Tait equation:

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

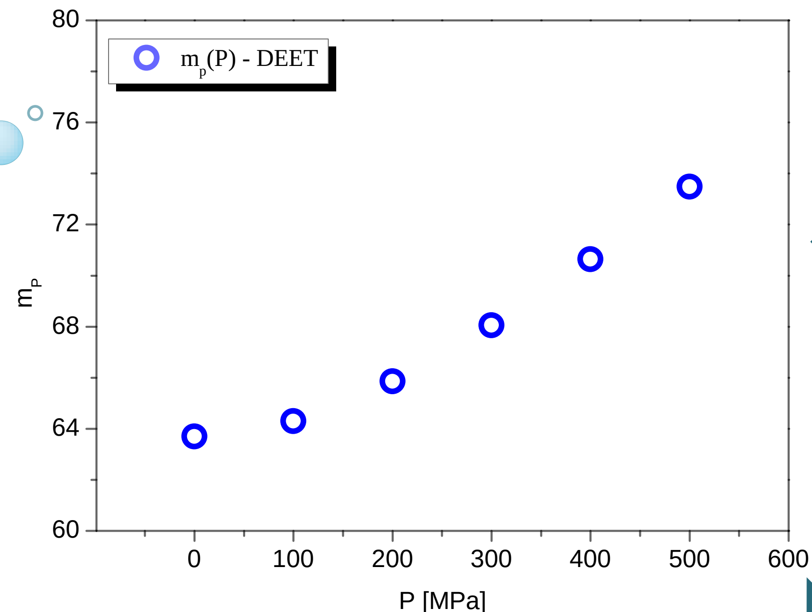
R. Casalini , S. Capaccioli, M. Lucchesi, P. Rolla, M. Paluch, S. Corezzi, D. Fioretto, Phys. Rev. E **64** 1504 (2001).

Generalized AG model

$$\tau(T,P)=\tau_0 \exp\left\{\frac{A}{T-T_0^*+T(\delta/S_\infty)\{-(\beta+\gamma-1)P+(\gamma-1)B(T)\ln(1+[P/B(T)])+\gamma P\ln(1+[P/B(T)])\}}\right\}$$

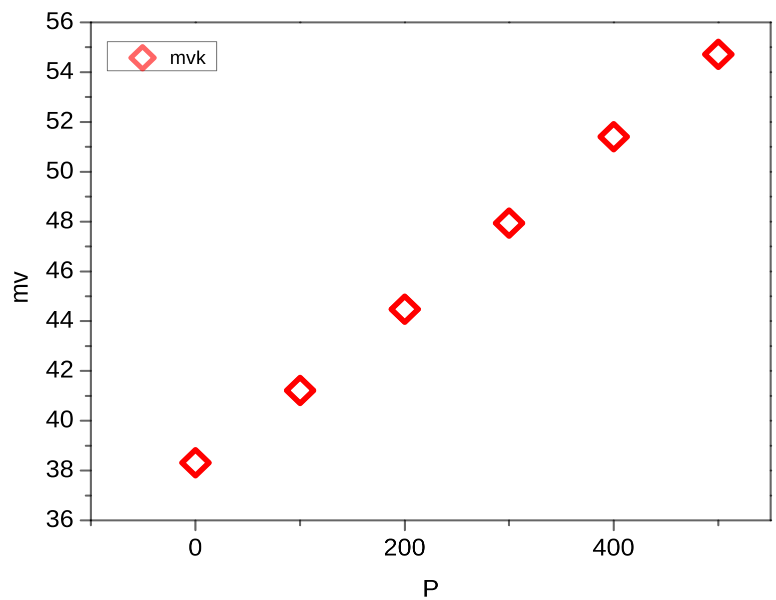


Predictions of AG model



Both isobaric and isochoric frahgilities inceases with compression

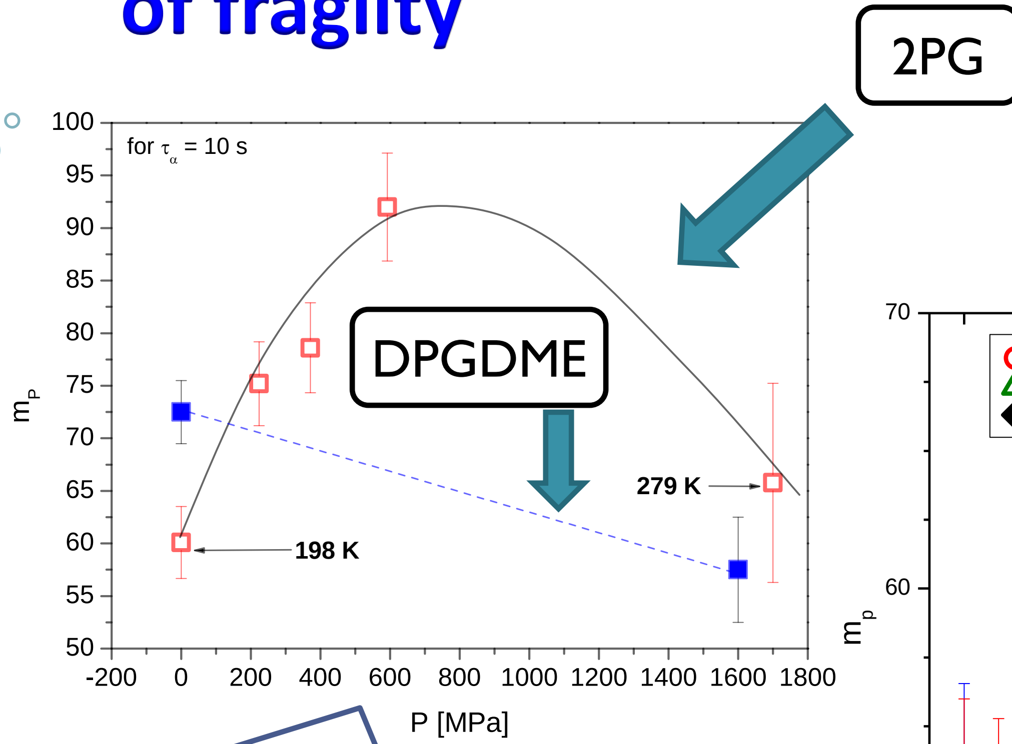
$$\frac{m_V^T}{m_P^T} = \frac{E_V}{E_P}$$

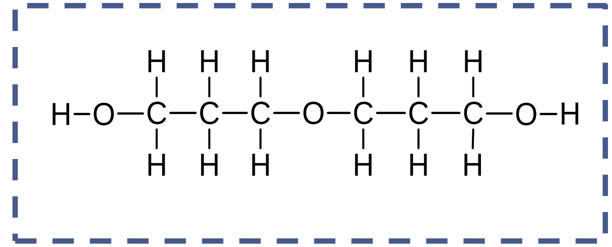


P	mp	mv	mv/mp
0.1	64,41497	38,30952	0,595
100	65,03556	41,21652	0,63
200	66,61965	44,48338	0,67
300	68,83192	47,93754	0.70
400	71,46825	51,40644	0,72
500	74,25285	54,71752	0,74

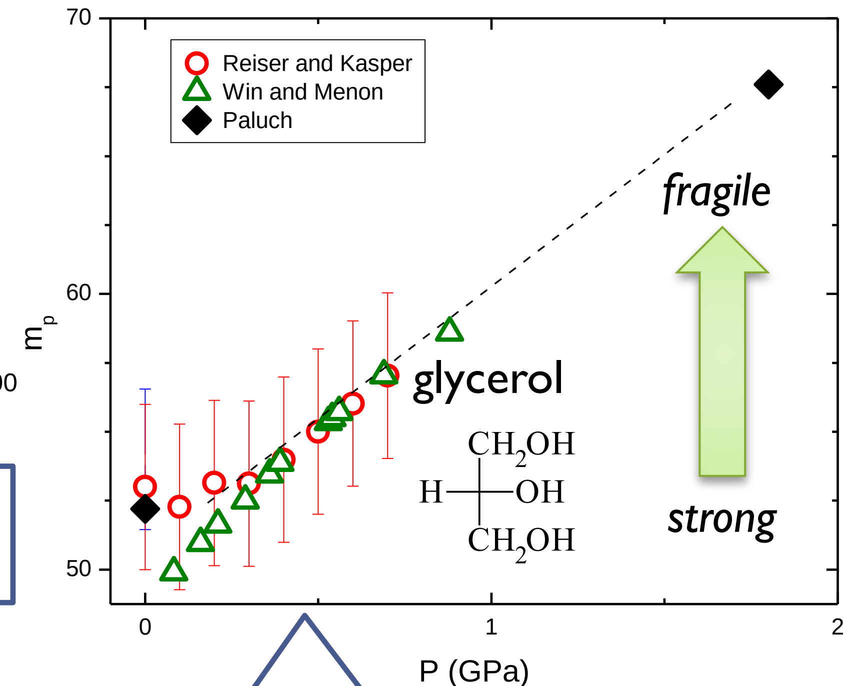
Thermal fluctuations control the molecular dynamics

Further examples of peculiar behavior of fragilty





K. Grzybowska, S. Pawlus, M. Mierzwa, M. Paluch K. L. Ngai, J. Chem. Phys. **125** 144507 (2006)



Effect of pressure on isobaric fragilty is often much more complex for H-bonded than for Van der Waals liquids.

Pawlus S, **M. Paluch**, Ziolo J, Roland CM, J. Phys.: Condensed Matter **21** 332101 (2009)

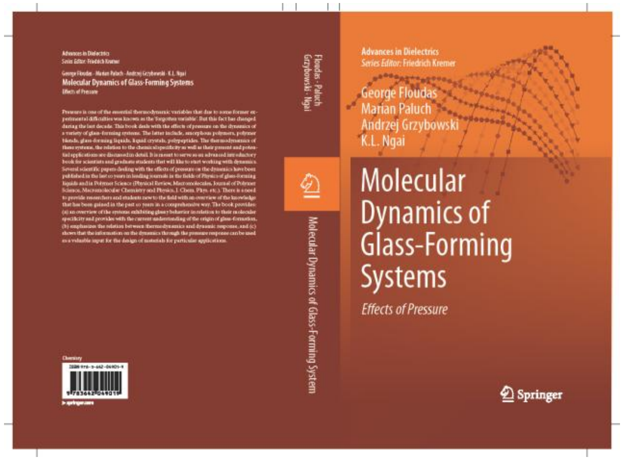
Sumary

Van der Wals Liquids

- Isobaric fragility decreases with pressure whereas isochoric and isothermal fragilities are invariant.
- Structural relaxation times obey density scaling

Asociated liquids

- Isobaric fragility usually increasses with pressure (It is not general rule.)
- Density scaling does not work.



Thank you for your attention