Fragility and Thermodynamics in Complex Glass-Formers

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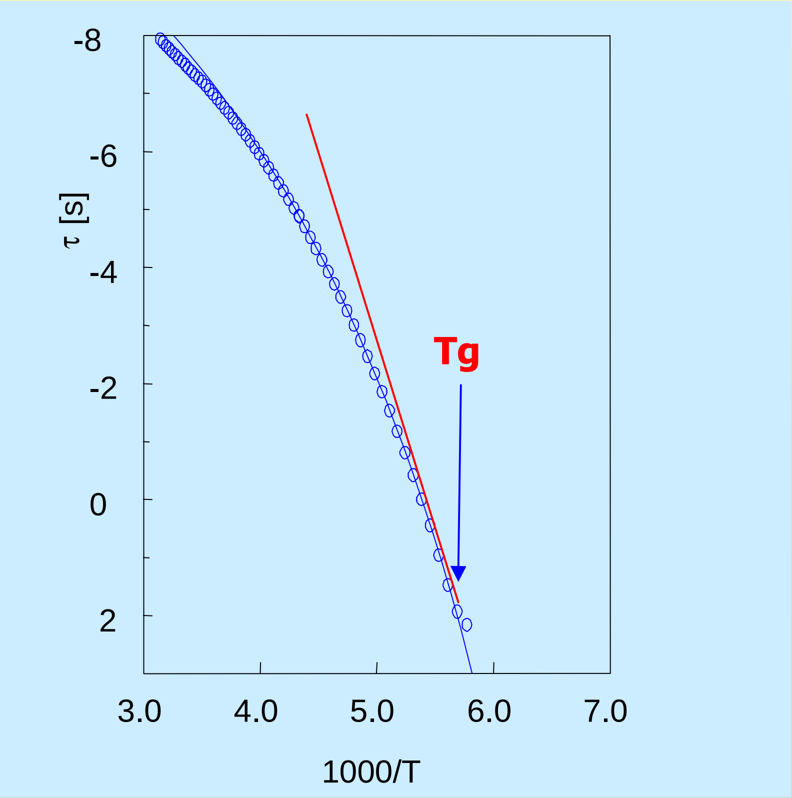
Fragility in glass-forming systems

liquids cooled down below the melting temperature undergoes a rapid increase of the viscosity and the structural relaxation time that eventually leads to structural arrest.



The steepness of the relaxation time variation is normally named "fragility".

Steepness index:

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

"Fragile" liquid → Large *m*

"Strong" liquid → Small *m*

Fragility vs. other properties

- Stretching exponent ;
- Boson peak;
- Non-ergodicity factor;
- Mechanical properties;
- Thermodynamics.

Fragility vs. other properties

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- Non-ergodicity factor;
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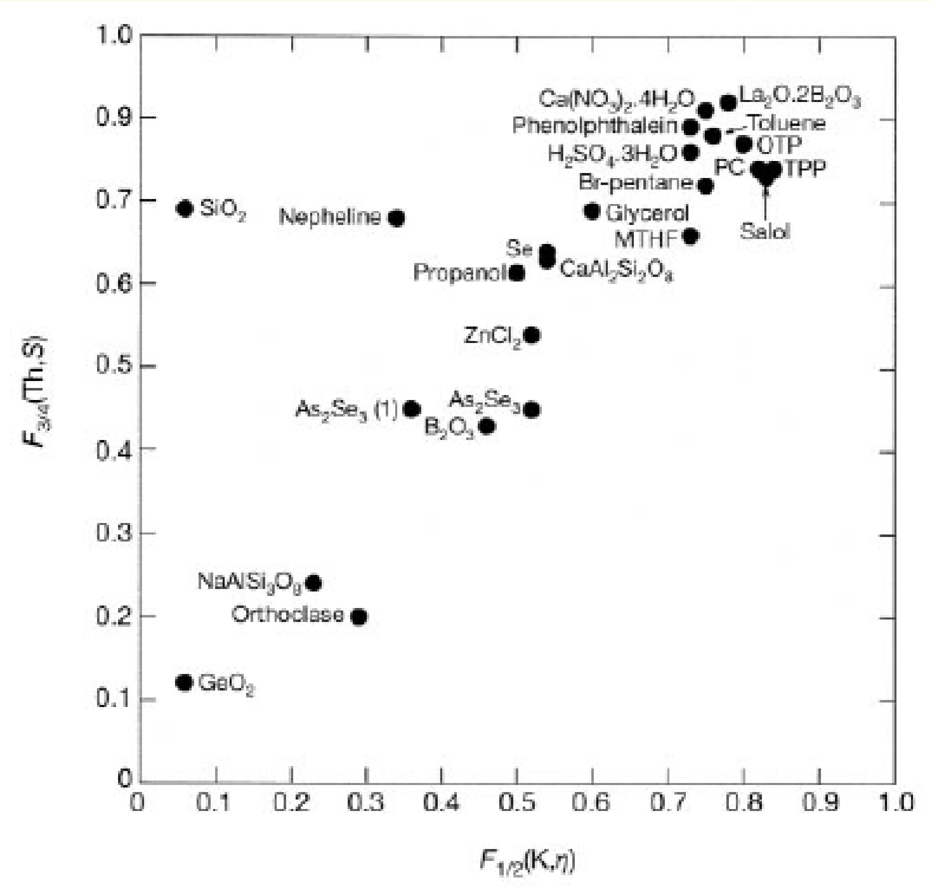
- <u>Thermodynamics.</u>

Connection fragility-thermodynamics: state of the art



AG relation: $$\tau = \tau_0 \exp\left(\frac{C}{TS_c}\right)$$

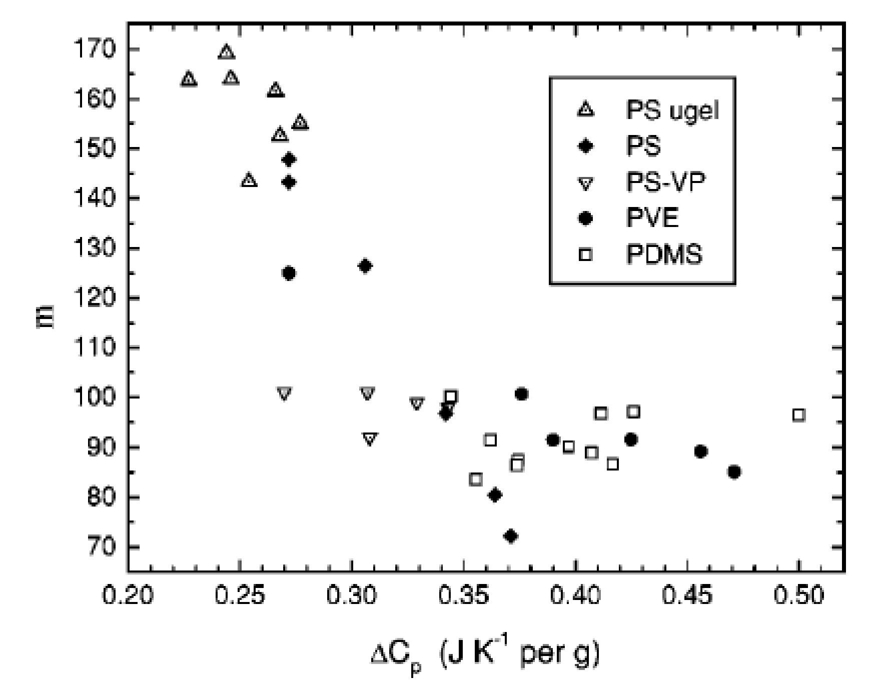
$F_{1/2}$ related to steepness of relaxation time variation

$F_{3/4}$ related to steepness of configurational entropy variation

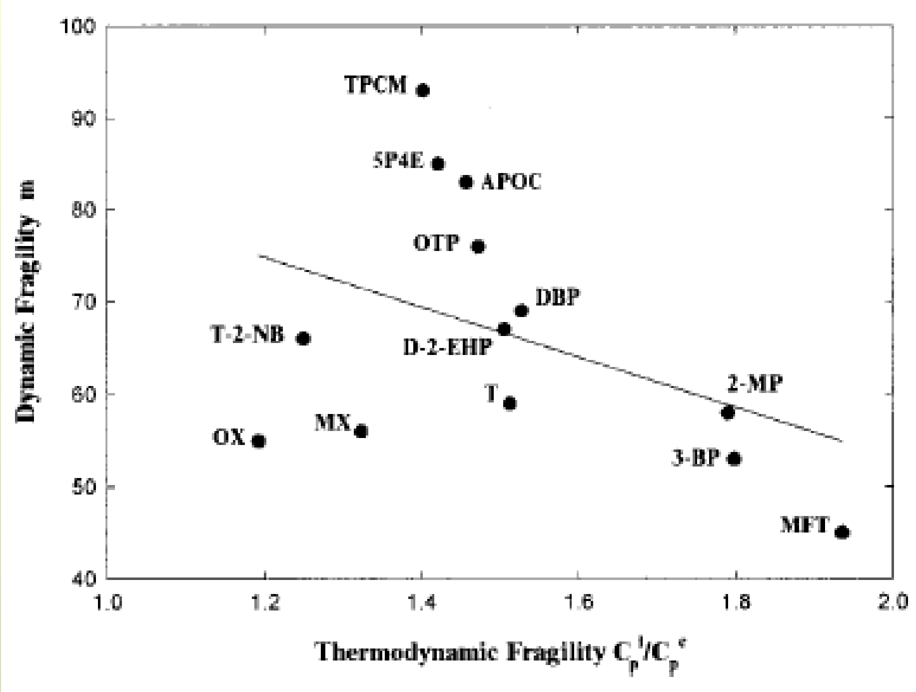
* K. Ito, C. T. Moynihan, and C. A. Angell, Nature **398**, 492 (1999).

Connection fragility-thermodynamics: state of the art

C. M. Roland, P. G. Santangelo, and K. L. Ngai, J. Chem. Phys. **111**, 5593 (1999);



D. Huang and G. B. McKenna, J. Chem. Phys. **114**, 5621 (2001).



fragility vs. the specific heat jump at T_g

NO correlation for polymeric and non-polymeric glass-formers

Connection fragility-thermodynamics from the AG equation

- Connection between fragility and thermodynamics from the AG equation:

AG equation:

$$\tau = \tau_0 \exp\left(\frac{\Delta\mu s_c^*}{k_B T S_c}\right) = \tau_0 \exp\left(\frac{C}{T S_c}\right)$$

Normalized fragility:*

$$m_A = \left.\frac{d\left[\ln\left(\tau(T)/\tau_0\right)/\ln\left(\tau(T_g)/\tau_0\right)\right]}{d\left(T_g/T\right)}\right|_{T=T_g}$$

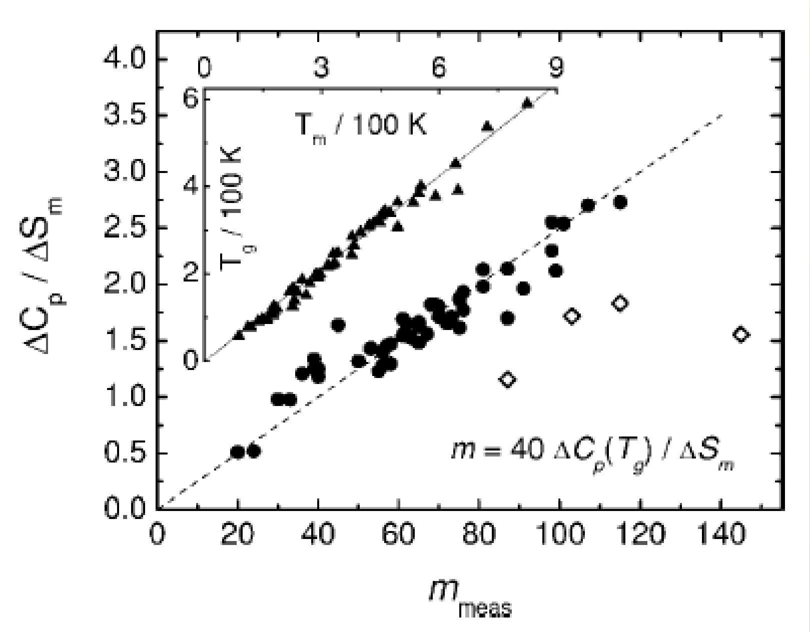
$$m_A = 1 + \frac{\Delta c_p\left(T_g\right)}{S_{ex}\left(T_g\right)}$$

- Configurational properties replaced by excess properties (experimentally accessible);
- Not the same but proportional;
- The specific heat jump at T_g as in previous approaches + $S_{ex}(T_g)$

*R. J. Speedy, J. Phys. Chem. B **103**, 4060 1999.

Connection fragility-thermodynamics from the AG equation

$$m_A = 1 + \frac{\Delta c_p\left(T_g\right)}{S_{ex}\left(T_g\right)} \quad \Longleftrightarrow \quad m_A = 40\frac{\Delta c_p\left(T_g\right)}{S_{ex}\left(T_m\right)}$$



- Analogous to the correlation recently proposed;*
- Verified for a large number of LMWGF

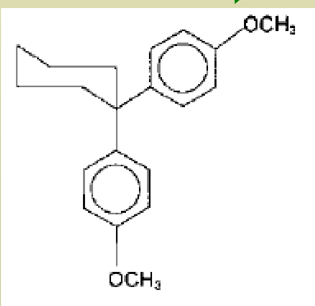
*L.M. Wang, C.A. Angell, and R. Richert, J. Chem. Phys., 125, 074505 (2006).

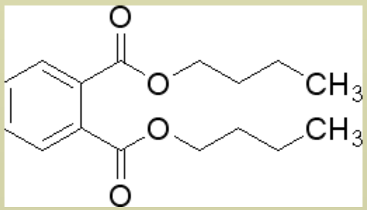
Data for glass-forming polymers

$$m_A = 1 + \frac{\Delta c_p\left(T_g\right)}{S_{ex}\left(T_g\right)}$$

- Structural relaxation times from dielectric spectroscopy;

- Thermodynamics data:
  - for polymers: extensive work of Wünderlich and Pyda;*
  - BCDE and DBP: our data and melting data from NIST database.

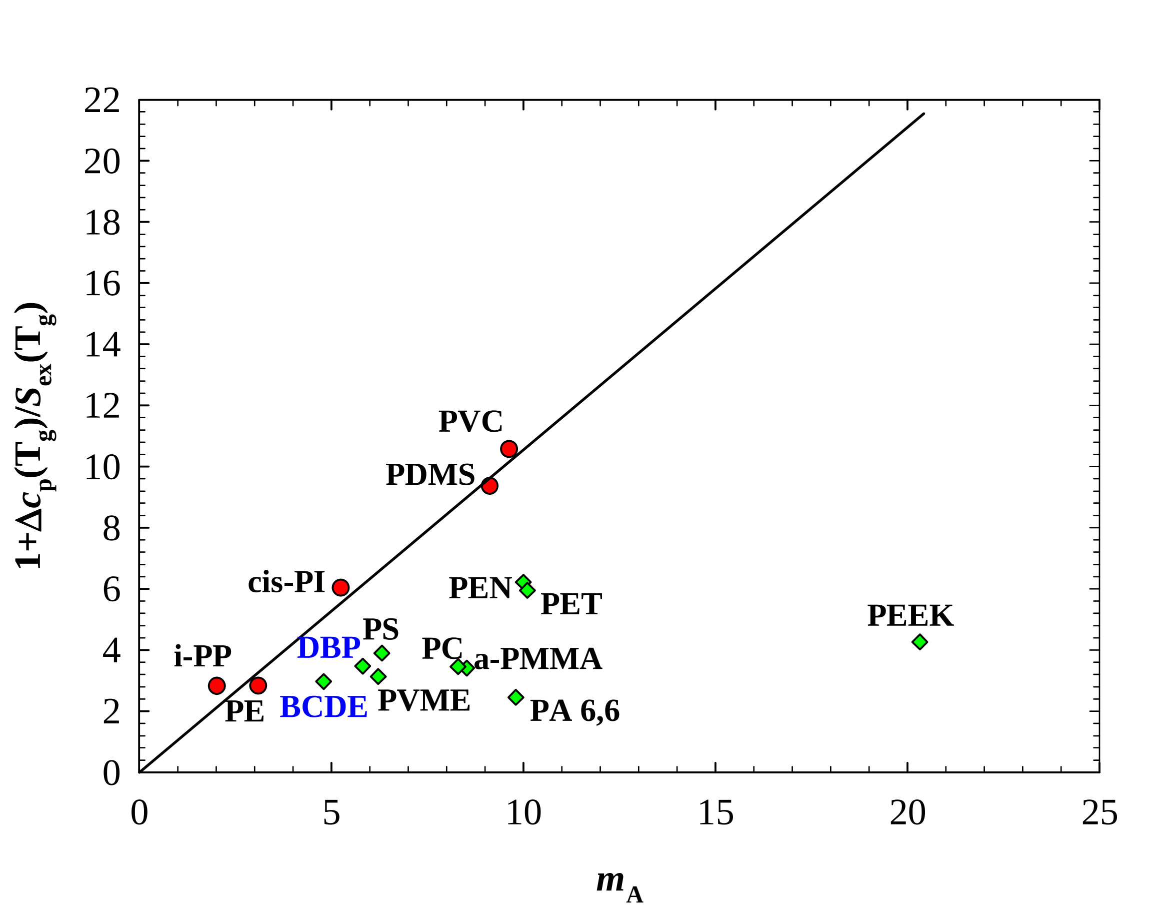




* B. Wünderlich and M. Pyda, ATHAS database, http://web.utk.edu/~athas/ and references therein

B. Wünderlich, Thermal Analysis of Polymeric Materials, Springer-Verlag (Berlin, 2005).

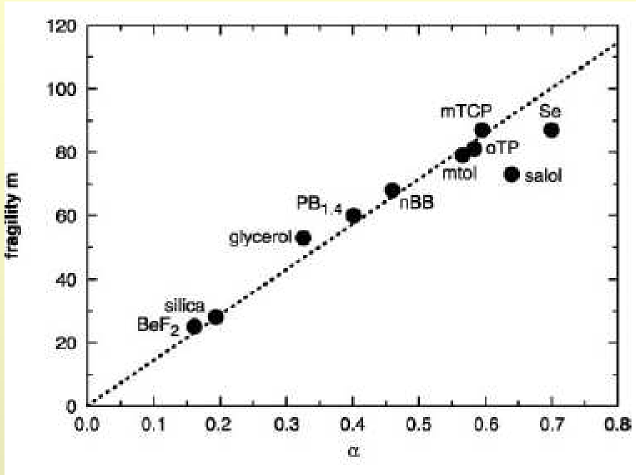
Verification of the fragility relation

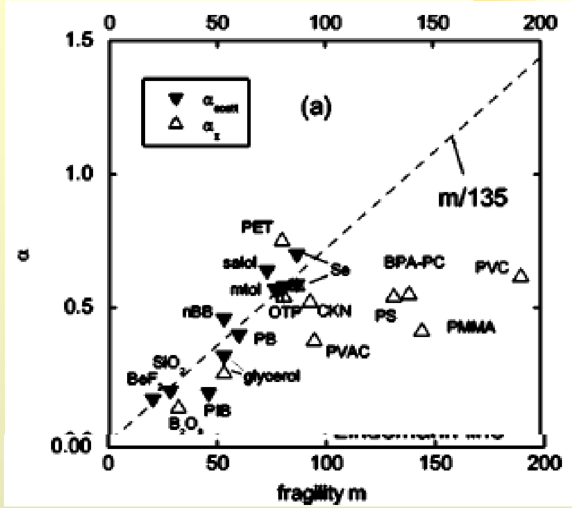


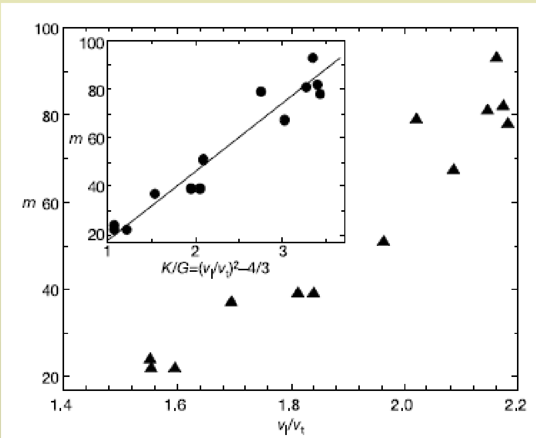
$$m_A = 1 + \frac{\Delta c_p\left(T_g\right)}{S_{ex}\left(T_g\right)}$$

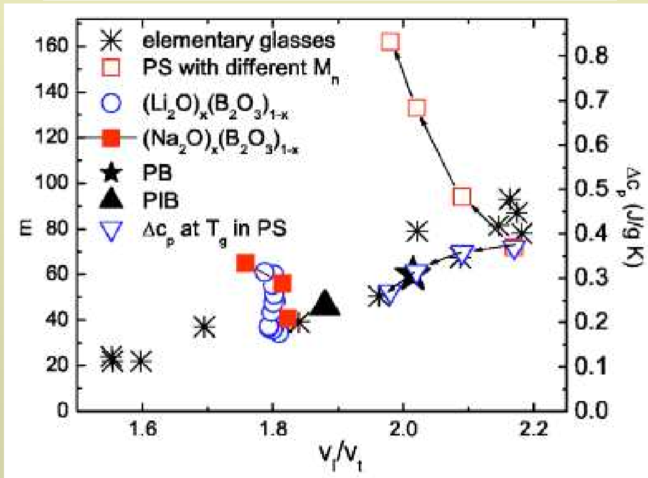
- The fragility relation verified ONLY for some polymers;
- It <u>fails</u> for others and for LMWGF: DBP and BCDE;

Comparison with other approaches







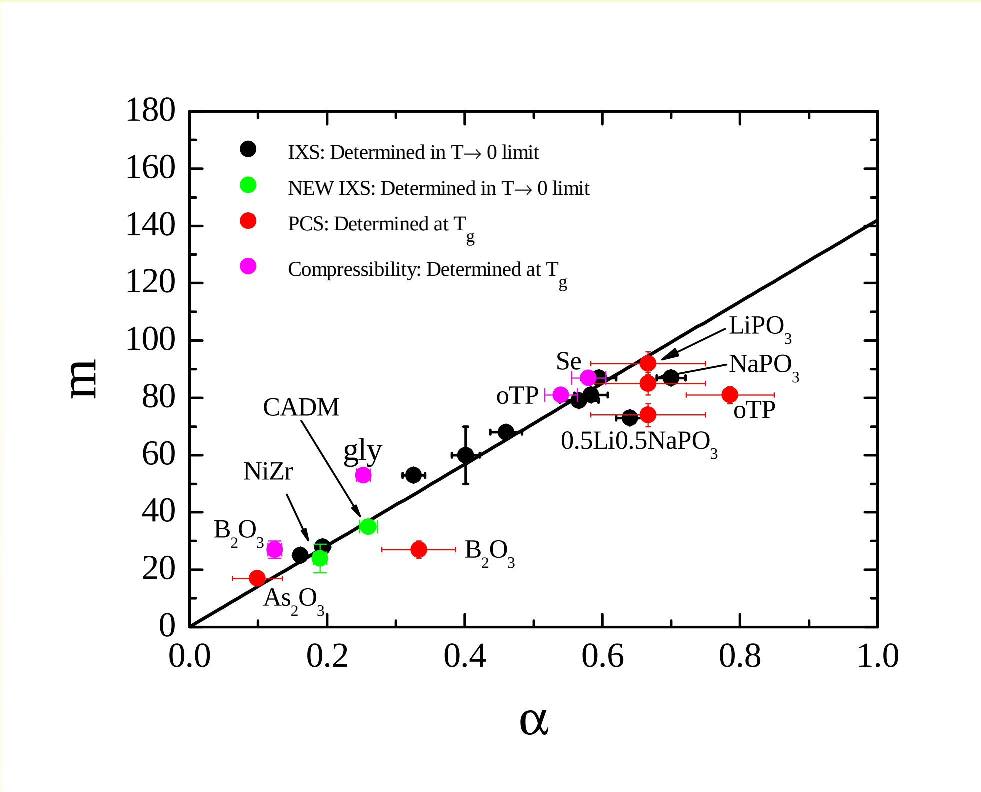


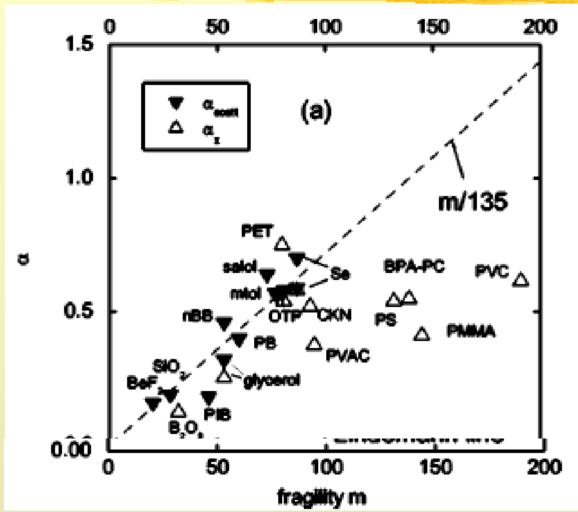
<u>Same deviation of other fragility relations for some glass-forming polymers</u>

* T. Scopigno, G. Rocco, F. Sette, and G. Monaco, Science **302**, 849 (2003); V. N. Novikov and A. V. Sokolov, Nature **431**, 961 (2004)

** U. Buchenau and A. Winschewski, Phys. Rev. B **70**, 092201 (2004); V. N. Novikov, Y. Ding, and A. V. Sokolov, Phys. Rev. E 71, 061501 (2005).

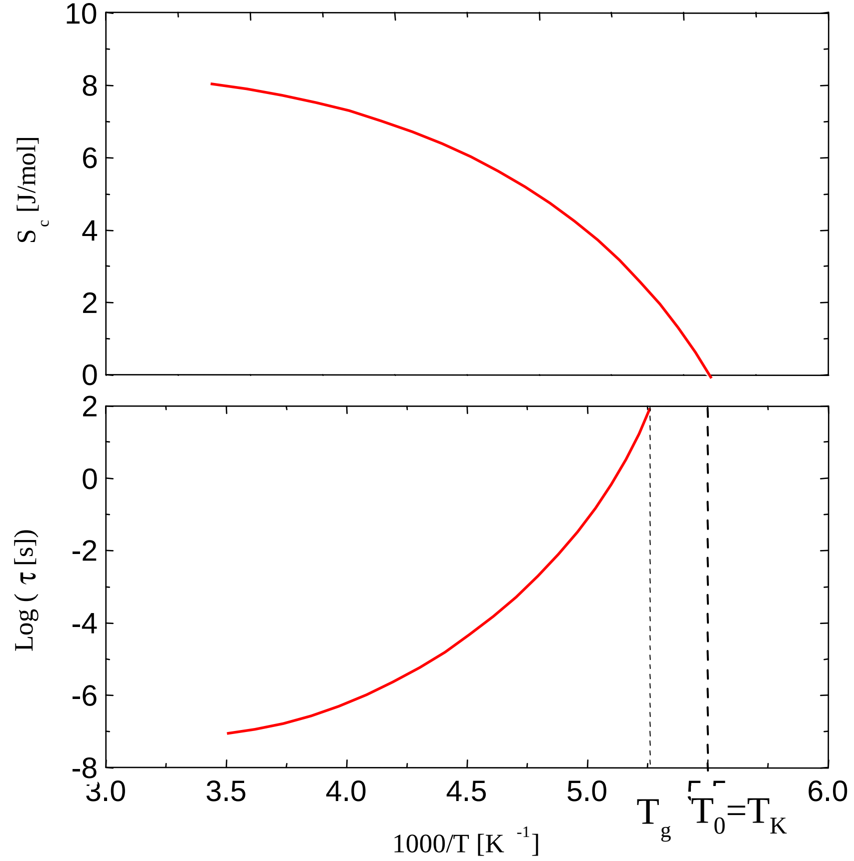
Comparison with other approaches





Deviation only for polymer-like systems

Vogel temperature vs. Kauzmann temperature



$$\tau = \tau_0 \exp\left(\frac{B}{T - T_0}\right)$$

T_0 → $\tau \to \infty$

$$\tau = \tau_0 \exp\left(\frac{C}{TS_{ex}}\right)$$

T_K → $S_{ex} = 0$

$$T_0 = T_K$$

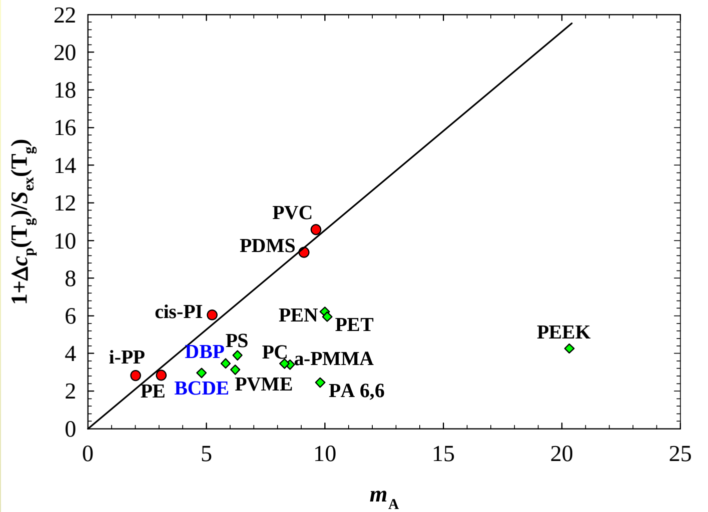
Verified for the vast majority of low-molecular weight glass-formers.*

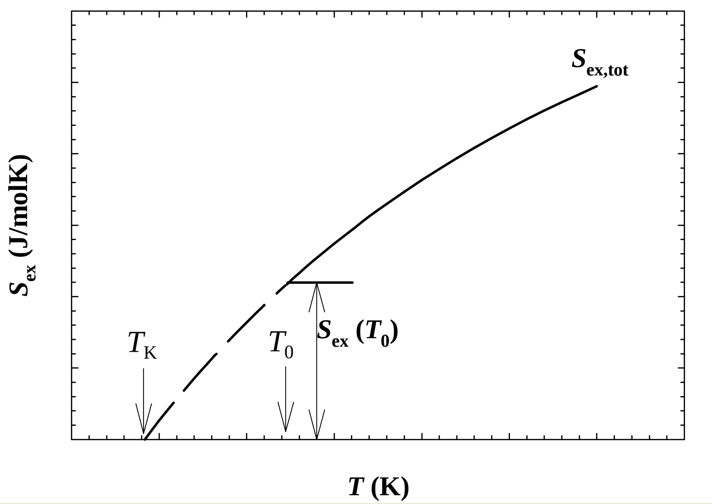
*C.A. Angell, J. Res. Natl. Inst. Stand. Technol. **102**, 171 (1997).

Vogel temperature vs. Kauzmann temperature

Polymer	T_g (K)	T_k (K)	T_0 (K)	S_{ex} (T_0) (J/molK)
i-PP	270	174.5	174	0±1.1
LDPE	237	149	160	1±0.3
cis-PI	200	166.5	162	-0.9±2.6
PVC	354	308	317	0.38±0.2
PDMS	146	130.5	130	0±0.05
PS	373	278	324	6.7±0.3
PEN	390	326	358	9.1±0.4
PET	342	269	308	14.0±0.3
a-PMMA	378	263.5	334	10.7±1.8
PC	420	292	373	21.7±1.4
PEEK	419	324	398.5	22.5±0.7
PA 6,6	323	196	290	64.0±6.8
PVME	244	166.5	205	8±0.5
BCDE	239	146	188.5	26±2
DBP	177.5	126	147	25 ±2

- $T_0 = T_k$ also for those polymer verifying the fragility relation;
- $T_0 > T_k$ for the other polymers and DBP and BCDE;
- Presence of $S_{ex}(T_0)$ unrelated to the α process.





Structure and α relaxation

- Fragility: ONLY related to the <u>α process</u> vs. properties: related to the <u>overall structure</u>;

- <u>ONLY $S_{ex,\alpha}$ related to the α process should be taken into account</u>:

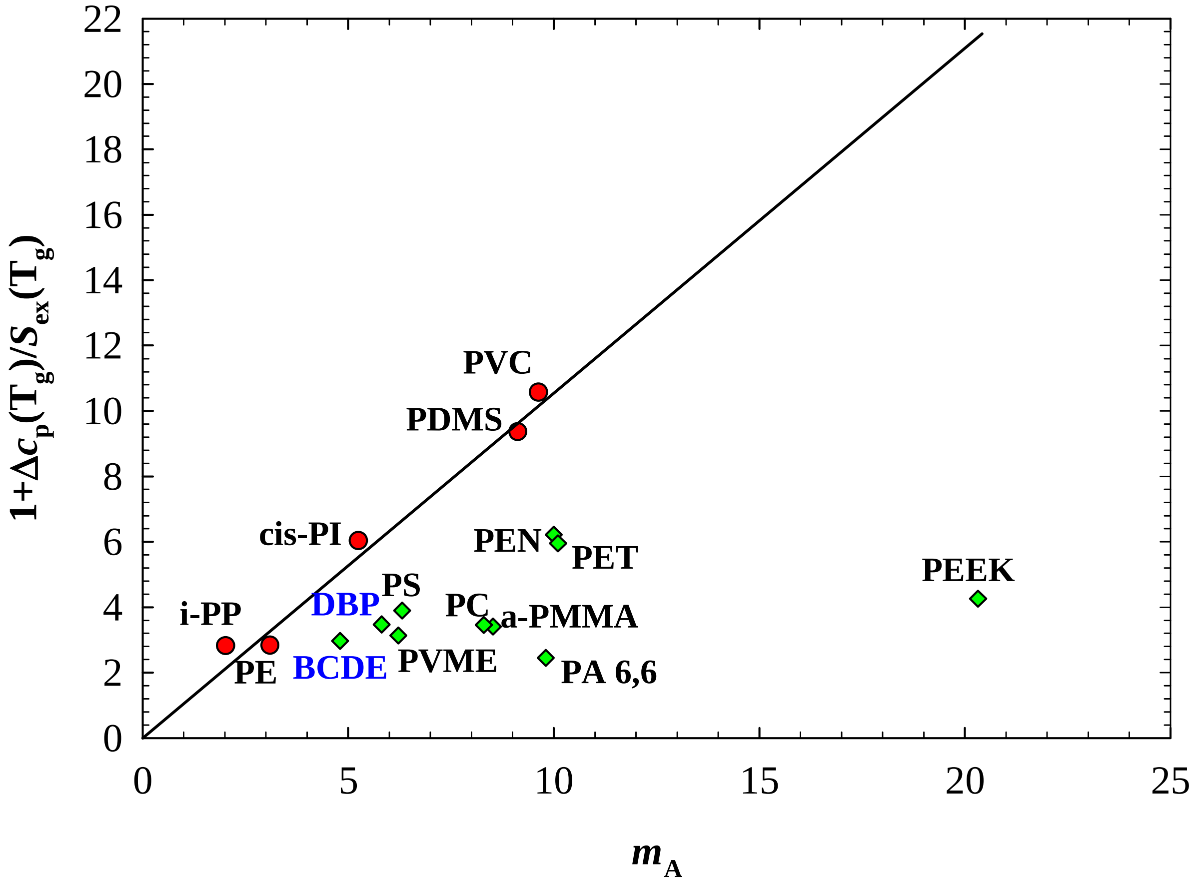
$$m_A = 1 + \frac{\Delta c_p(T_g)}{S_{ex}(T_g)}$$

$$m_A = 1 + \frac{\Delta c_p(T_g)}{S_{ex,\alpha}(T_g)}$$

- $S_{ex,\alpha}$ obtained subtracting the contribution from non-α related processes. At a first approximation equal to $S_{ex}(T_0)$.

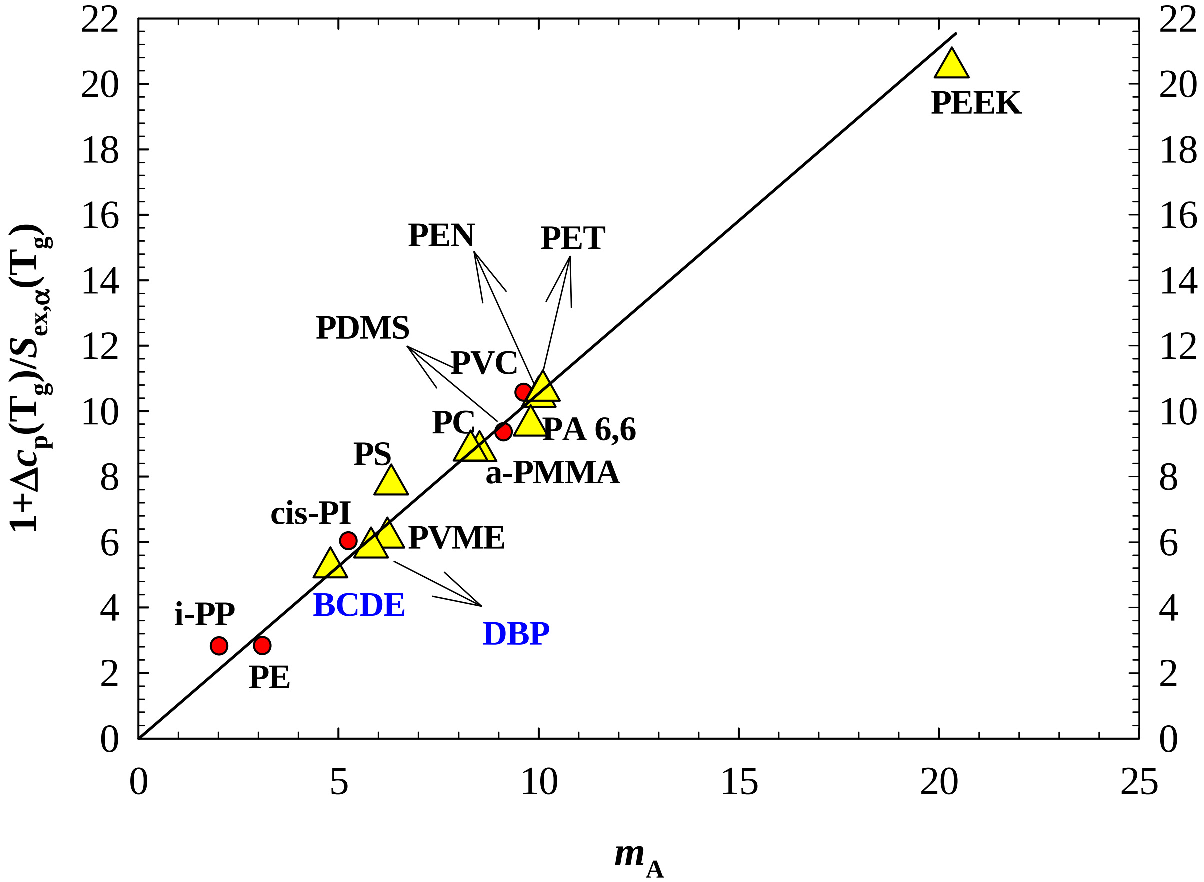
New fragility relation

$$m_A = 1 + \frac{\Delta c_p\left(T_g\right)}{S_{ex,\alpha}\left(T_g\right)} = 1 + \frac{\Delta c_p\left(T_g\right)}{S_{ex,tot}\left(T_g\right) - S_{ex}\left(T_0\right)}$$

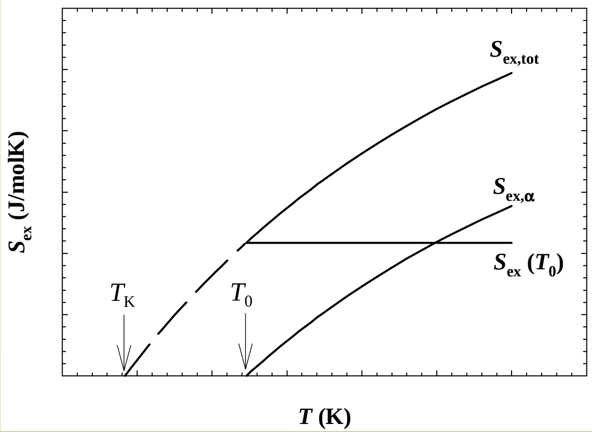


New fragility relation

$$m_A = 1 + \frac{\Delta c_p\left(T_g\right)}{S_{ex,\alpha}\left(T_g\right)} = 1 + \frac{\Delta c_p\left(T_g\right)}{S_{ex,tot}\left(T_g\right) - S_{ex}\left(T_0\right)}$$



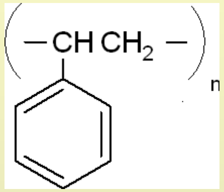
- fragility relation reestablished!;
- Employment of $S_{ex}(T_0)$ for the fragility relation, defined at T_g, not trivial;
- non-α related contribution is temperature independent;



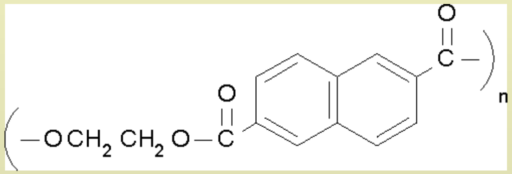
Possible origin of the non-α related contribution to S_{ex}

Glass-formers possessing a non-α related S_{ex} present complicated rather chemical structure:

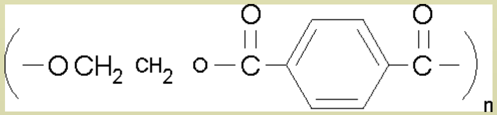
PS



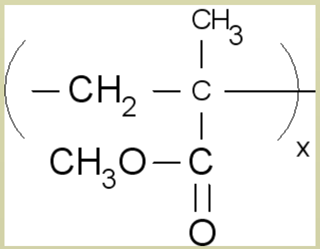
PEN



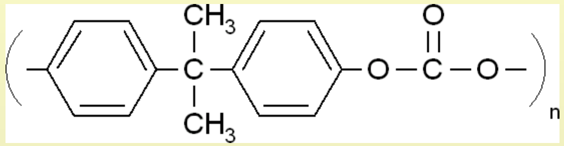
PET



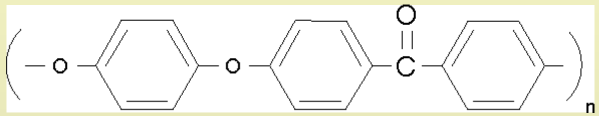
PMMA



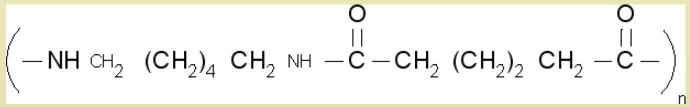
PC



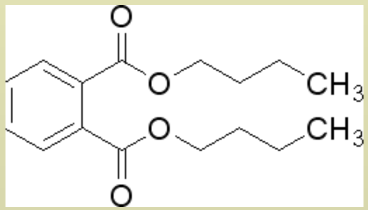
PEEK



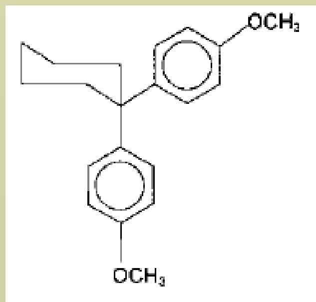
PA 6,6



DBP



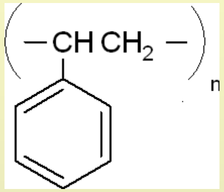
BCDE



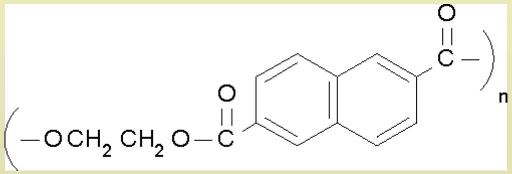
Role of internal degrees of freedom

Motions related to internal degrees of freedom detectable through standard spectroscopic techniques (non-JG secondary relaxations)

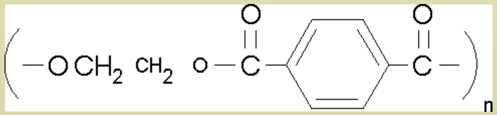
PS



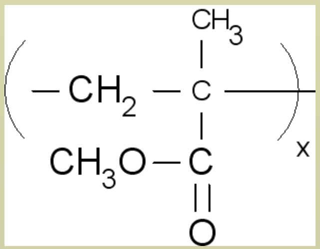
PEN



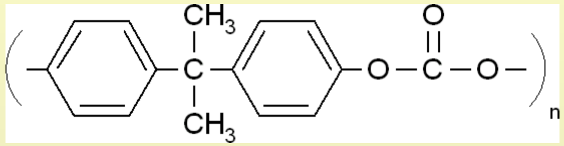
PET



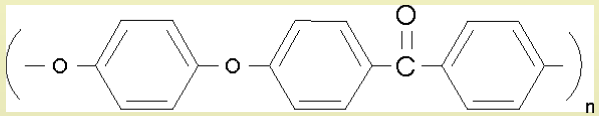
PMMA



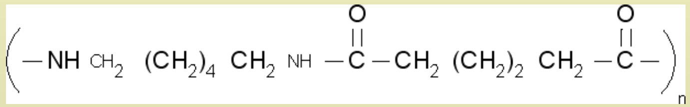
PC



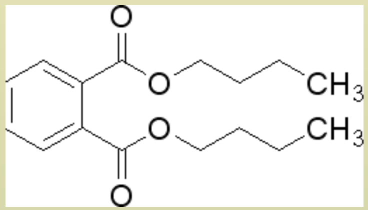
PEEK



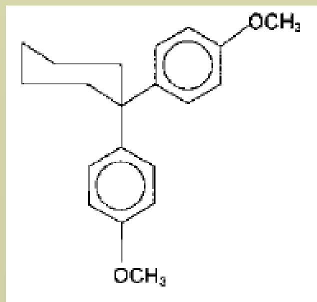
PA 6,6



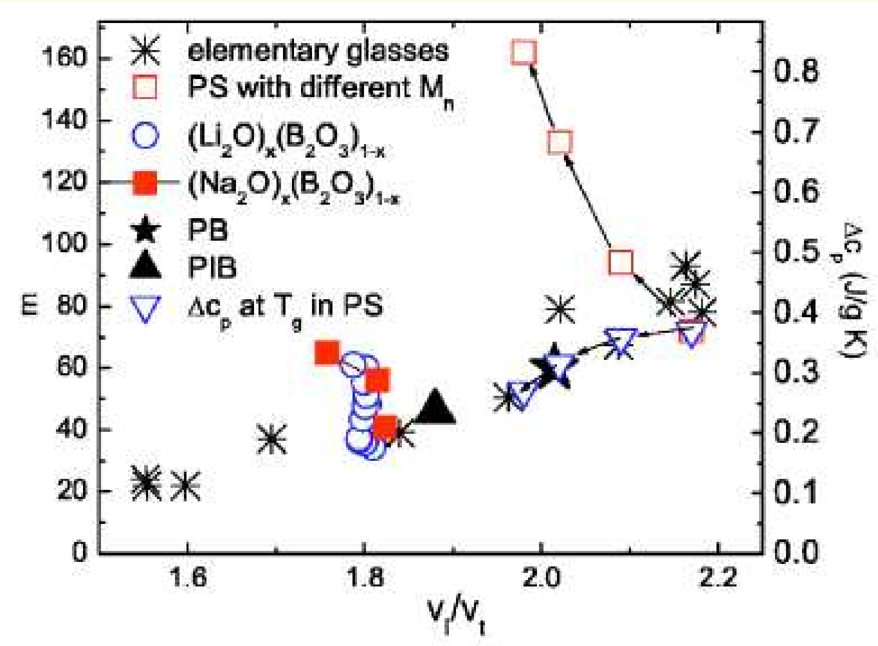
DBP

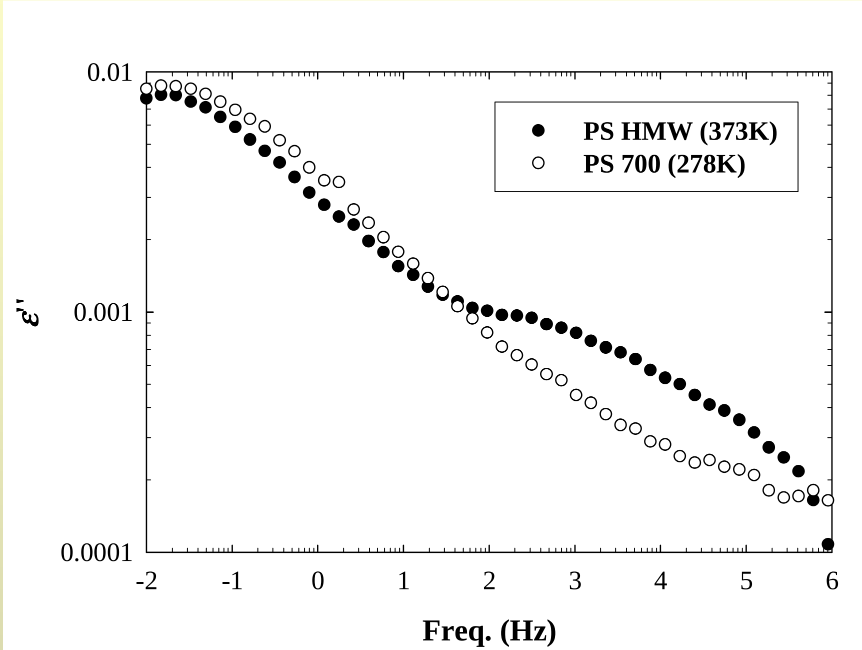


BCDE



Polystyrene secondary relaxation

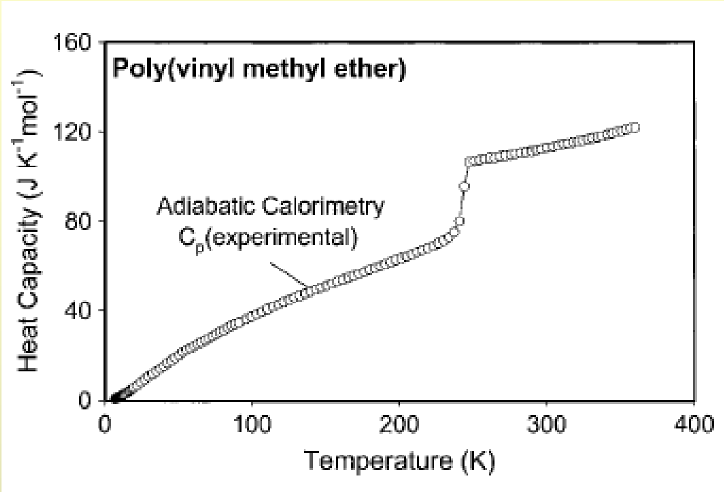




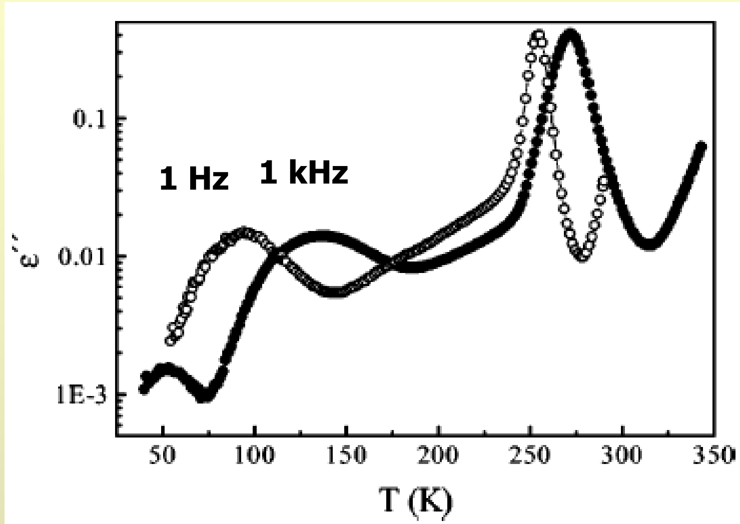
- No detectable secondary relaxation for low molecular weight PS;
- Role of secondary relaxation compatible with the deviation from the correlation between fragility and V_l/V_t;*

* V. N. Novikov, Y. Ding, and A. V. Sokolov, Phys. Rev. E 71, 061501 (2005).

Contribution from calorimetric measurements



PVME*

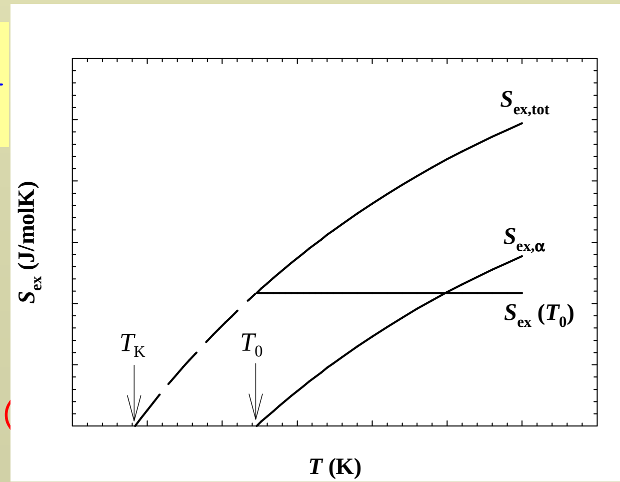


- No specific heat jump at the temperature where secondary relaxation shows up at the same time-scale of the DSC experiment;
- Result compatible with a temperature independent contribution S_{ex} from secondary relaxations.

$$\left.\frac{\partial S}{\partial T}\right|_P = \frac{c_p}{T}$$

- Geometry of motion independent of temperature.
- Entropy of motion between two non equivalent positions:

$$S = k \ln 2 = 5.8 Jmol^{-1}K^{-1}$$



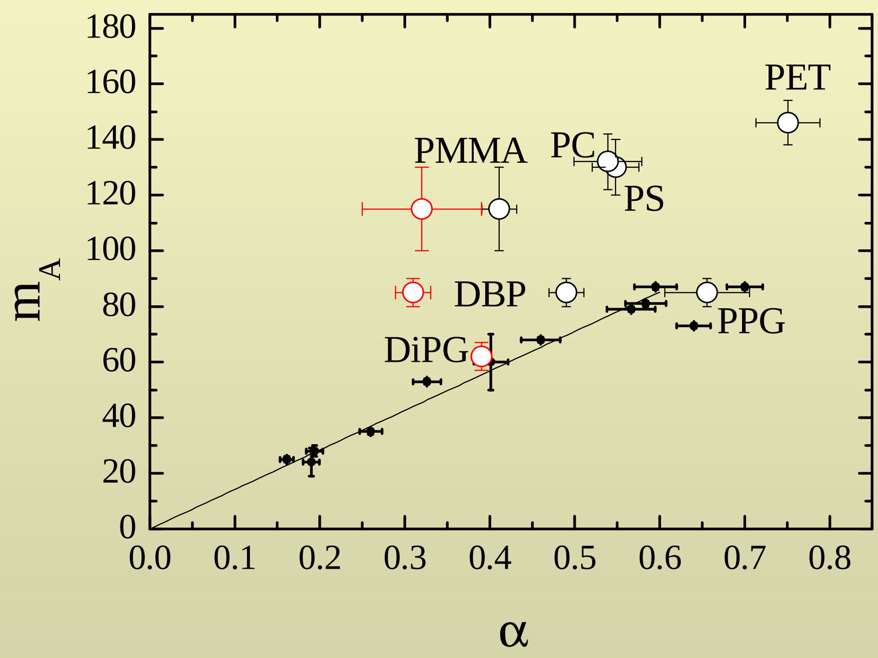
* M. Pyda, K. Van Durme,4 B. Wunderlich, B. Van Mele, J. Pol. Sci. Pol. Phys., 43, 2141 (

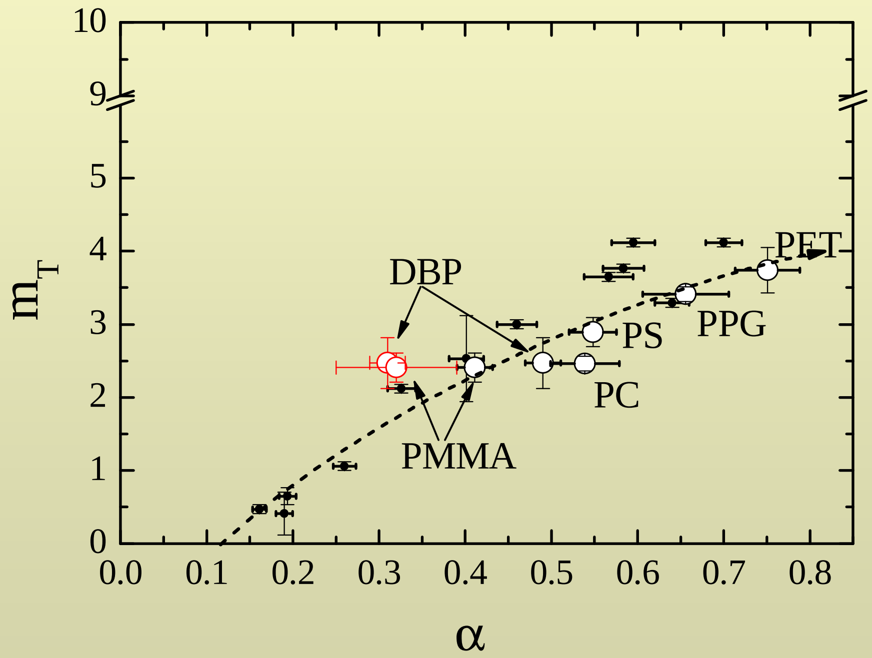
C. Lorthioir, A. Alegria, and J. Colmenero, Phys. Rev. E 68, 031805 (2003).

Uncorrected thermodynamic fragility vs. non-ergodicity factor

$$m_T = 1 + \frac{\Delta c_p(T_g)}{S_{ex\_tot}(T_g)}$$

$$\alpha = \lim_{q\to 0} \frac{d \log f_q(T)}{d(T/T_g)}\Bigg|_{T\to 0}$$





α needs correction too! → $S_{ex}(T_0)$

…collaboration with T. Scopigno, S. Capaccioli and G.C. Ruocco

Summary and Conclusions

- The fragility has been related to thermodynamics starting from the AG relation;
- A positive relation was found only for polymers with simple monomeric structure (also vast majority of LMWGF);
- The relation clearly fails for other polymers, and BCDE and DBP;
- The role of non-α process related relaxations (possibly secondary relaxations) has been highlighted to explain this discrepancy;
- Any correlation between fragility and structure must be taken into account the contribution to the structure on non-α process related relaxations.