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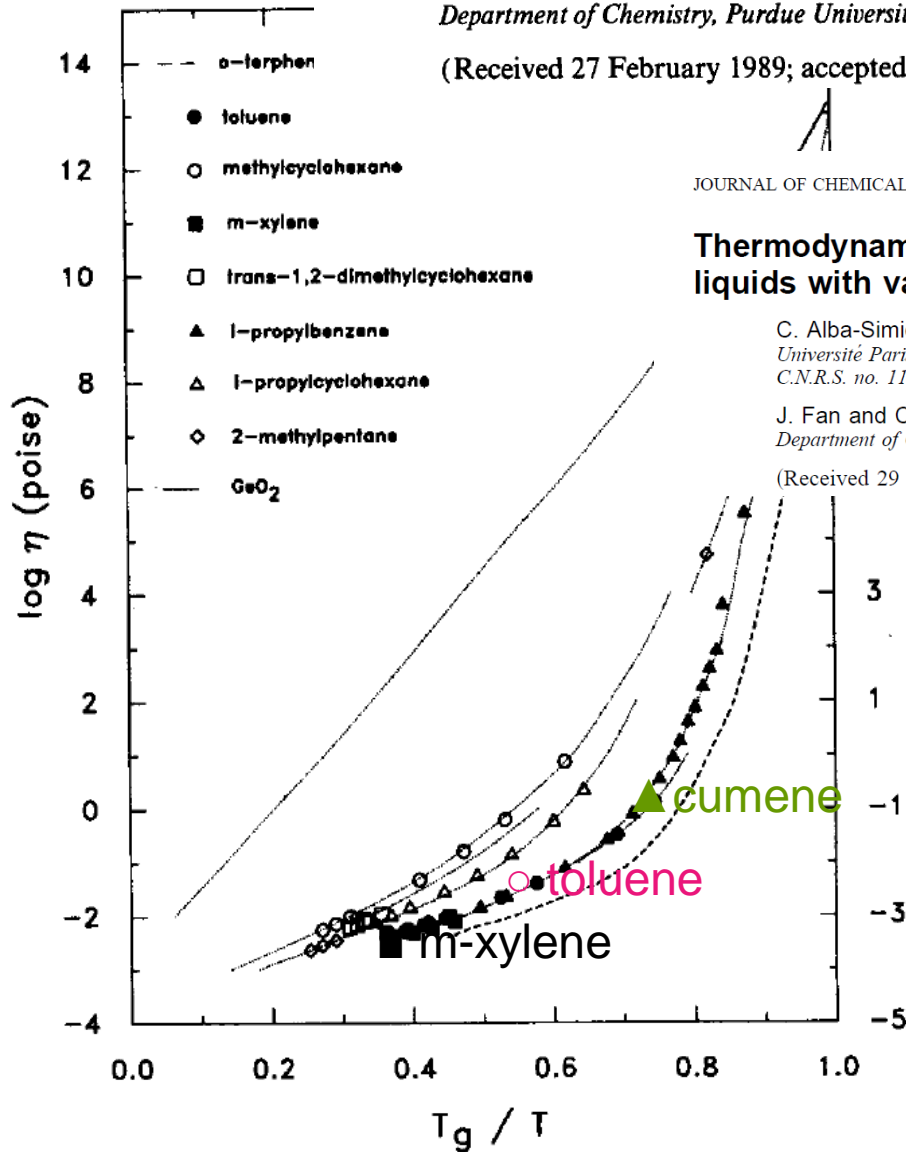
ILL, Grenoble, France.

Thermodynamic aspects of the vitrification of toluene, and xylene isomers, and the fragility of liquid hydrocarbons

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$$m_P = \left. \frac{\partial \log_{10}(\tau)}{\partial T_g/T} \right|_P$$



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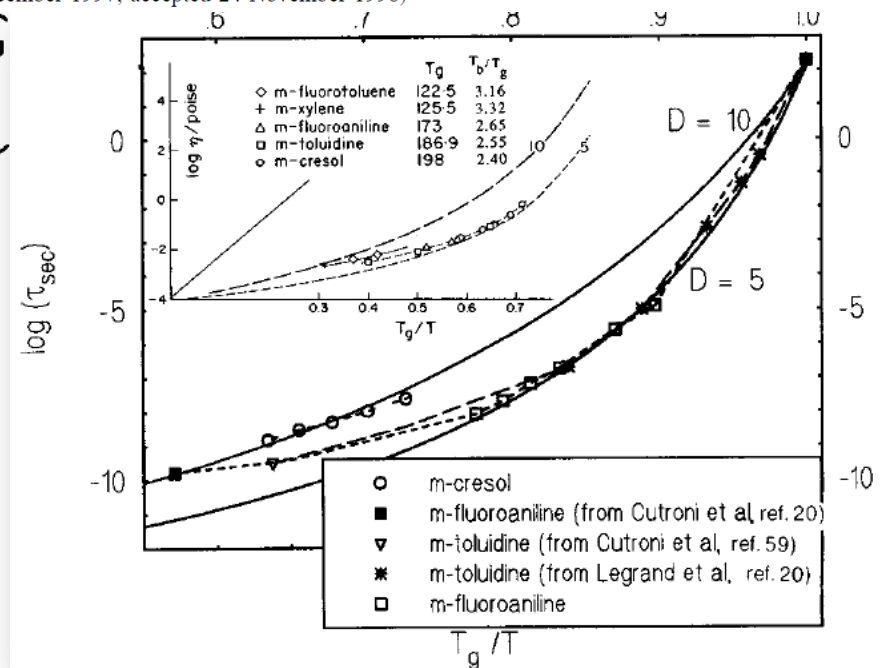
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Thermodynamic aspects of the glass transition phenomenon. II. molecular liquids with variable interactions

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Outline

Goal : Find a molecular liquid with the simplicity close to that of atomic ones yet which is glass-forming

GT is a combination of cooperative effects and local, molecular ones.

Evidence of an Arrhenius behavior with an important effective High Temperature activation energy $E_{\infty} > kT$

Understanding E_{∞} may then help disentangling the two effects and better focus on the purely collective aspect of the slowing down.

Looking for a small value of E_{∞}

High temperature activation energy E_{∞}

At high T (around T_m , T^* , T_c , T_a ...)

⇒ local effect strongly influenced by the molecular details of the system (E_{∞} changes from one molecule to another).

⇒ combined effect of

- the strength of the intermolecular interactions,
- the shape of the molecule,
- the short-range (spatial) correlations associated with the local arrangement of the molecules in the liquid.

Need for more complete information about local structure
Definition of the “simplest” molecular glass-former

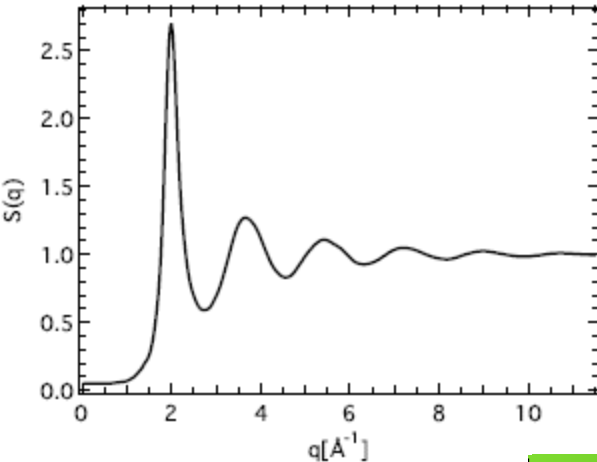
Structure of simple atomic liquids

(here assimilated to a sphere, no additional degrees of freedom)

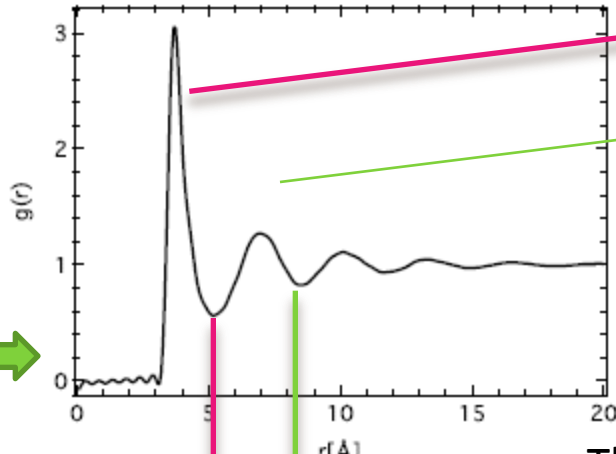
neutron measurement in the Q space (F.T.) \Rightarrow the radial pair correlation function in real space $g(r)$

$$S_M(Q) = f_i(Q) + \frac{4\pi}{Q} \rho_M \int (g_L(r) - 1) r \sin(Qr) dr$$

(a) Structure factor of Argon

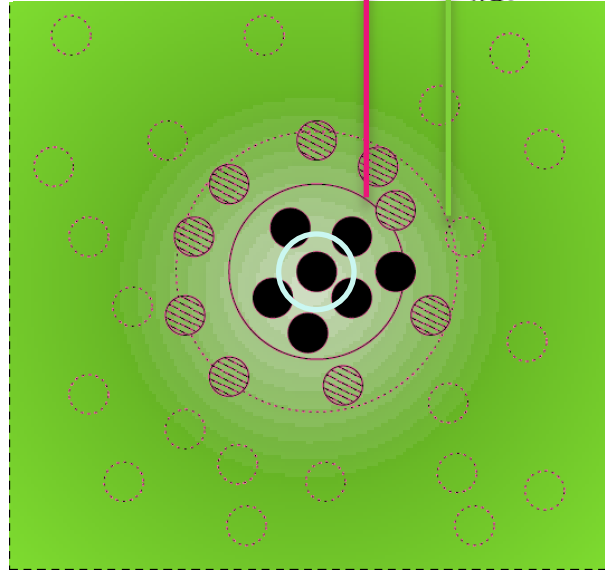


(b) Pair correlation function of Argon



First coordination shell

2nd coordination shell

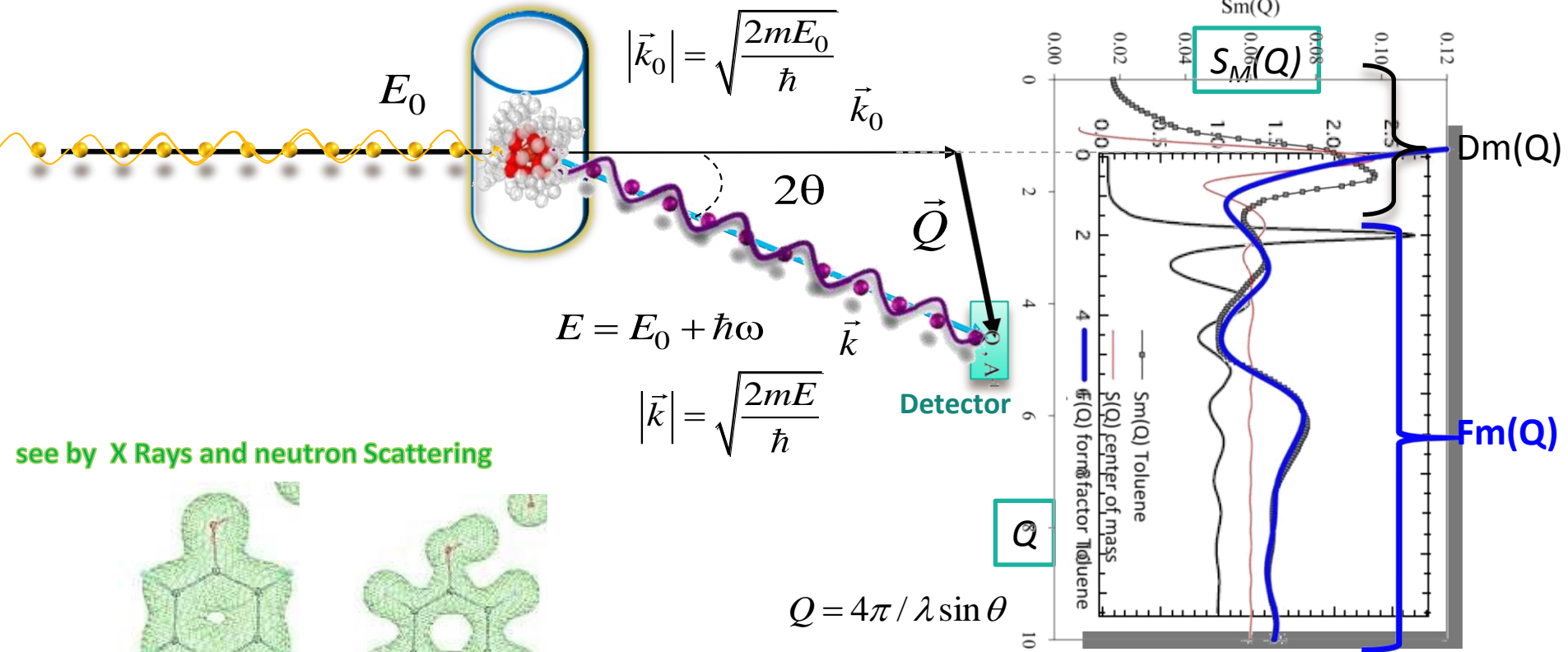


The intermolecular potential governs everything, structure, thermodynamics, dynamics

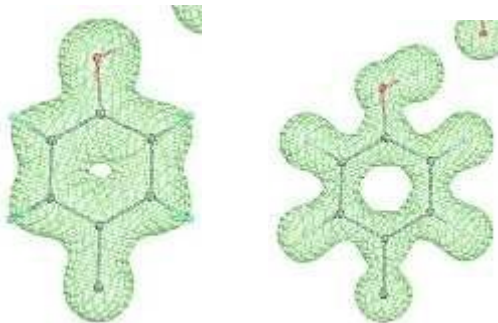
Subtle local arrangement (bond-orientational order, locally preferred structures).

Schematic of a diffraction experiment

$$S_M(Q) = f_i(Q) + \frac{4\pi}{Q} \rho_M \int (g_L(r) - 1) r \sin(Qr) dr$$



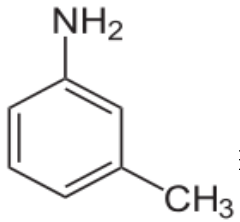
see by X Rays and neutron Scattering



X-ray (H)

Neutron(D)

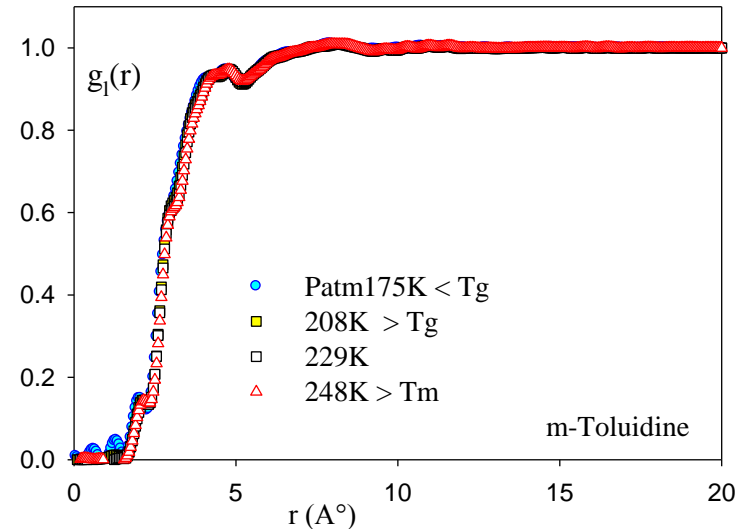
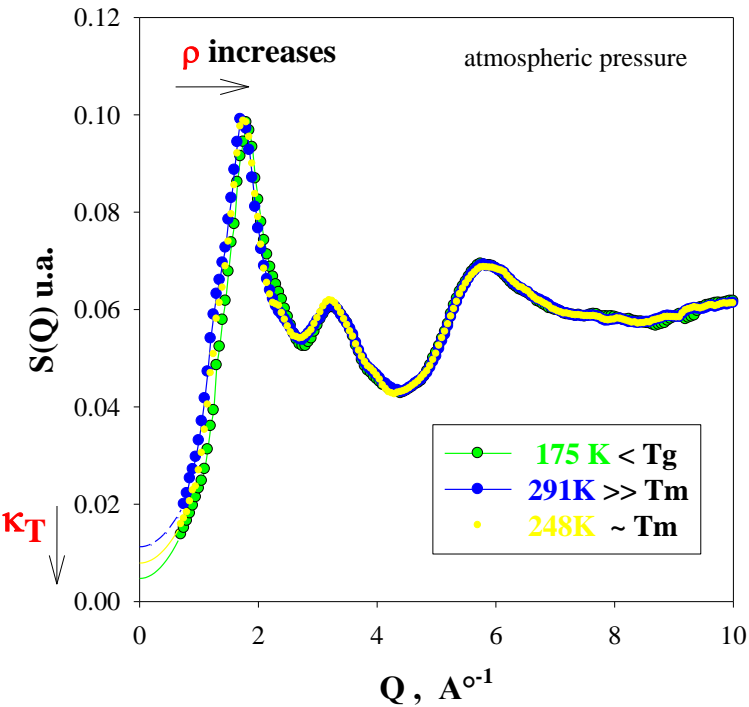
$$S(Q) = D_m(Q) + f_m(Q)$$



Elastic neutron scattering
m-Toluidine

No significant changes in the structure factor around T_g

A shift to higher Q 's (larger density) and a quite featureless pair correlation function



$$S(q) = \frac{1}{\bar{b}^2} \left[\frac{1}{N} \left\langle \left| \sum_i b_i e^{iq \cdot r_i} \right|^2 \right\rangle_t - (\bar{b}^2 - \bar{b}^2) \right]$$

$$\bar{b}^2 = \left| \sum_{\alpha} c_{\alpha} b_{\alpha} \right|^2$$

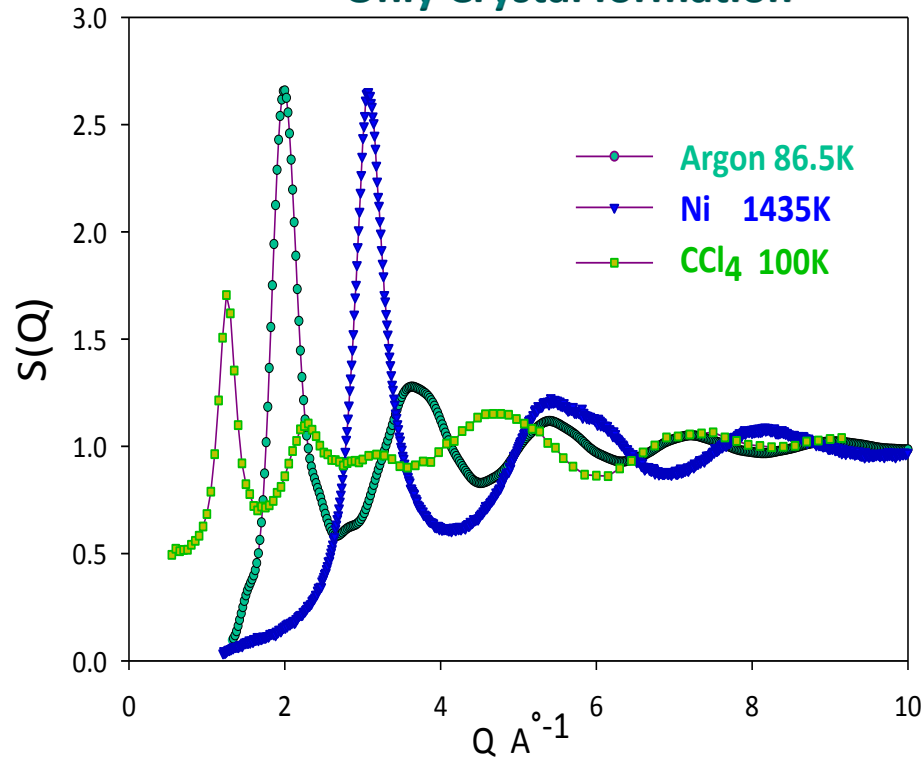
$$\bar{b}^2 = \sum_{\alpha} c_{\alpha} b_{\alpha}^2$$

N = number of atoms in a molecule
 b_i : scattering length of atom i
 r_i position vector
 α, c_{α} atom type and its concentration

$S(Q)$ = a sum of many partial structure factors

Context : two behaviors of the S(Q)

**Very Simple Liquids
(spherical shape)
Only Crystal formation**

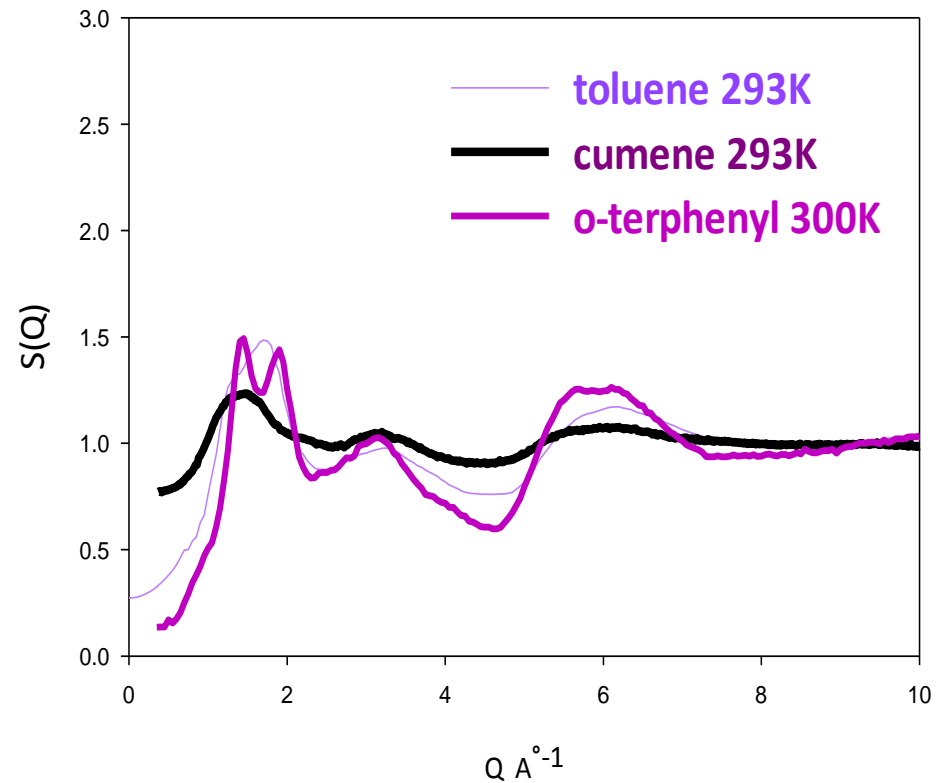


Ar : Yarnell 1973

Ni Holland-Moritz 2008

CCl_4 Pusztai 2009

**Molecular Fragile Glassformers
Liquid, glass, (crystal most of the time)**

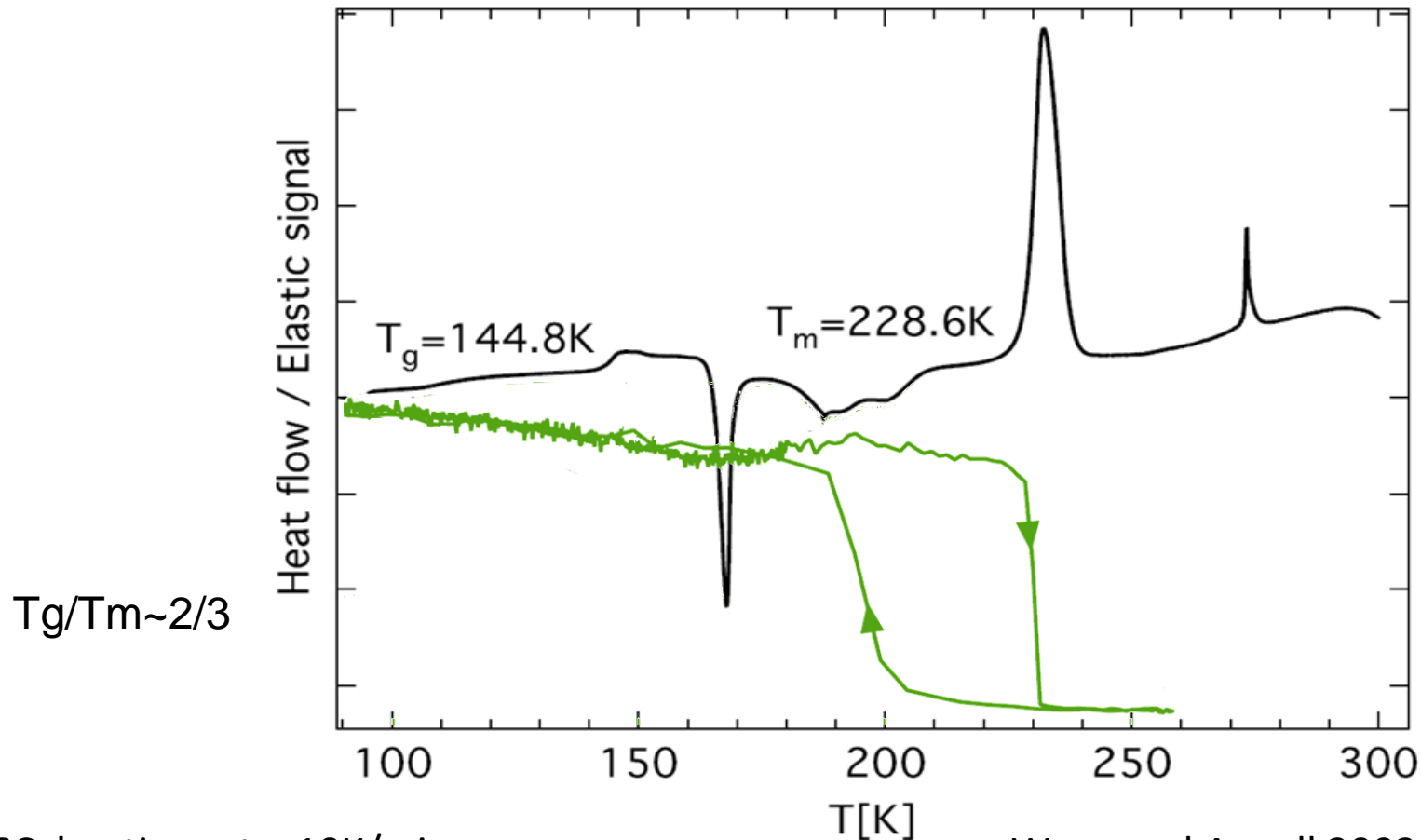


Looking for a simple* molecular system :

- - reducing the number of partial contributions to $S(Q)$ simplifying the shape.
- ➡ - but still able to form a (laboratory) glass and keep some disorder. (resisting to the crystallization).
- ⊙ - low high Temperature activation energy and high fragility?

* Simple = pseudo atomic ?

Glass transition of pure protonated cis-decalin



DSC heating rate 10K/min.

Neutron backscattering heating rate of 1K/min.

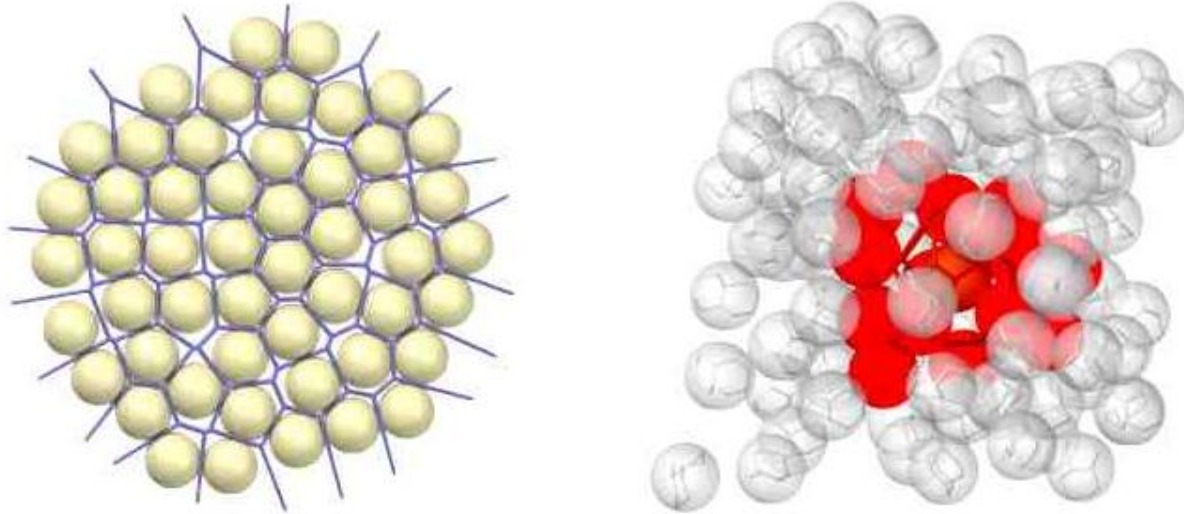
Wang and Angell 2002 :

cis-trans decalin

thermodynamic mp= 145, T_g 137K

Cp crystals see J. P. McCullough, H. L. Finke et al., *J. Phys. Chem.* **61**, 1105-1116 (1957).

Voronoi Tessellation analysis on the MD simulations



Voronoi Tessellation

is a method for allocating space available in a volume to the contained bodies.

This is a geometrically pure way of defining nearest neighbours and allows additional analysis.

Analysis is performed on centre of mass trajectories.

Conclusion

→ **Combining the simplest structure and the glass-forming ability**

→ **A molecule with a Spherical like shape, very high fragility and low E_{∞} at high T**

→ Static structure factor analysis + MD simulations :
Very high compaction of the molecules (not real sphere)
analysis of first neighbors, Voronoi Tessellation.
changes involved at the limit between the 1st and 2nd coordination shells.

→ **Need to be a molecule to define a local orientation order :**
responsible of compaction; very strong correlations between first neighbors
Interpenetrating aggregates in the high viscous regime ($T < T^*$).

→ Having an ingredient against crystallization :
Relation to the crystalline structure (more complex)
where **chirality** does play a role

→ *A model system to link (or not) molecular glassformers and metallic glasses*