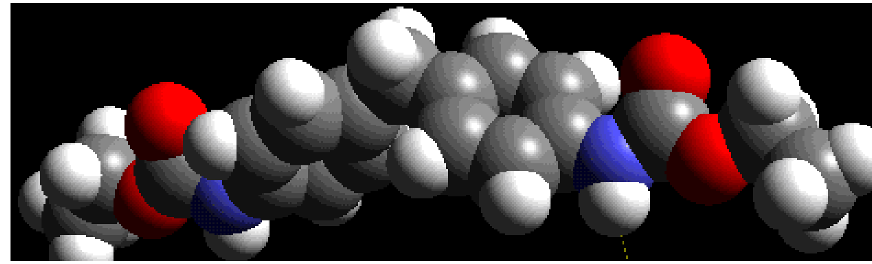
Materials Physics Center
Centro de Física de Materiales
Materialen Fisika Zentroa

Polymer and Soft Matter Group



The glass transition: linear vs non-linear perspective

Daniele Cangialosi

Lisbon
02/09/2024

Outline of the talk

- Linear response in glass forming systems;
- Increasing perturbations: the non-linear regime;
- Relation between linear and non-linear response:
  - Bulk glasses;
  - Confined glasses;
  - Amorphous polymer adsorption

Outline of the talk

- **Linear response in glass forming systems;**
- Increasing perturbations: the non-linear regime;
- Relation between linear and non-linear response:
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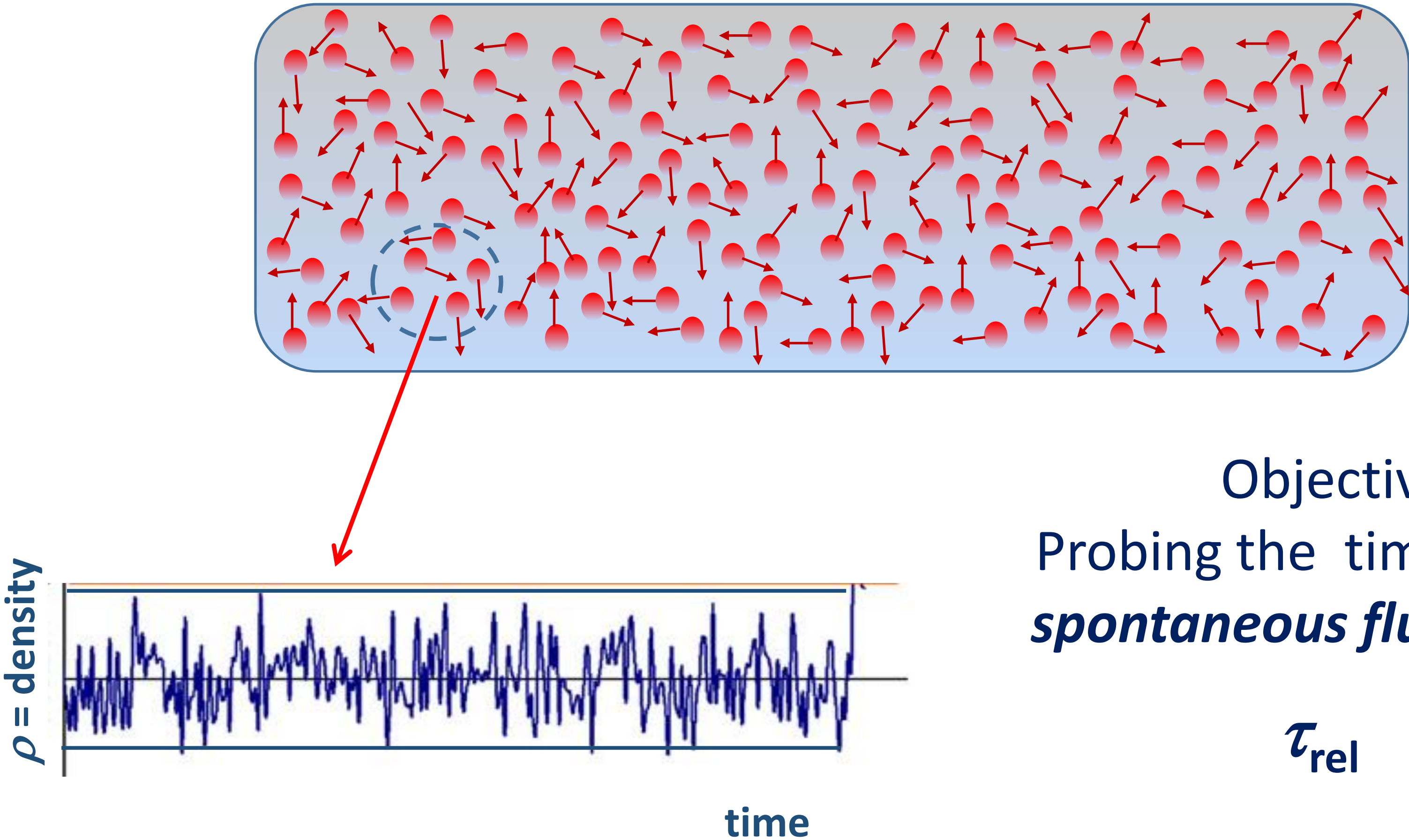
    - Amorphous polymer adsorption

Spontaneous fluctuations in liquids

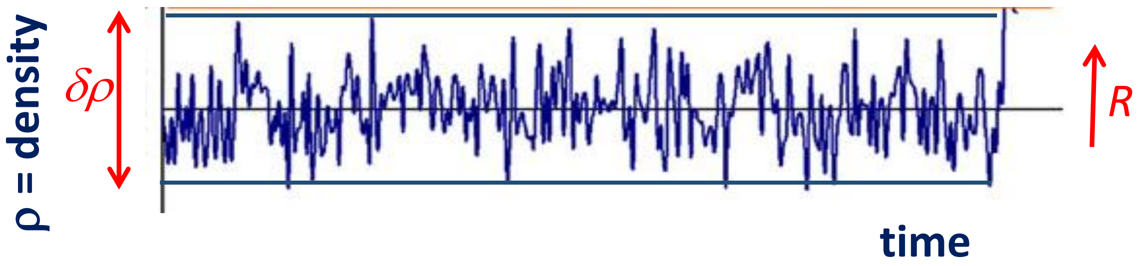


Objective:

Probing the time scale of ***spontaneous fluctuations***

τ_{rel}

Fluctuation Dissipation Theorem (FDT)



$\delta\rho$ = amplitude of (density) fluctuations;
***R* = response to a perturbation**

FDT ⇒ $\delta\rho > R$

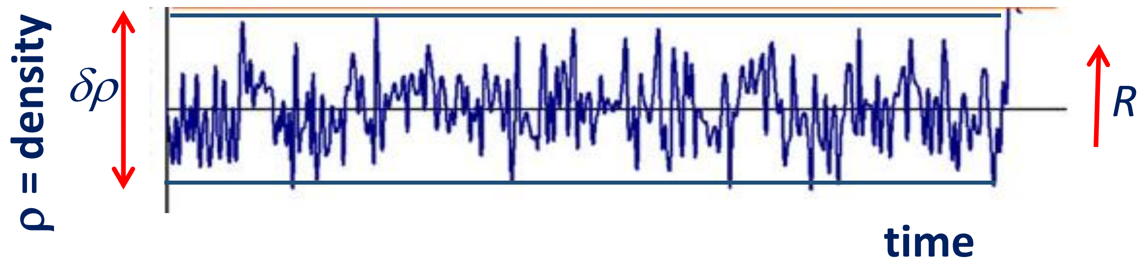
- Application of a ***perturbation***;

- Force field small enough to fulfill the "Fluctuation Dissipation Theorem";

- "Fluctuation Dissipation Theorem": the response of a system in thermodynamic equilibrium to a small applied disturbance (***linear regime***) is the same as its response to a spontaneous fluctuation;

- ***Small*** perturbations adequate to study the fluctuations.

Kinds of perturbation

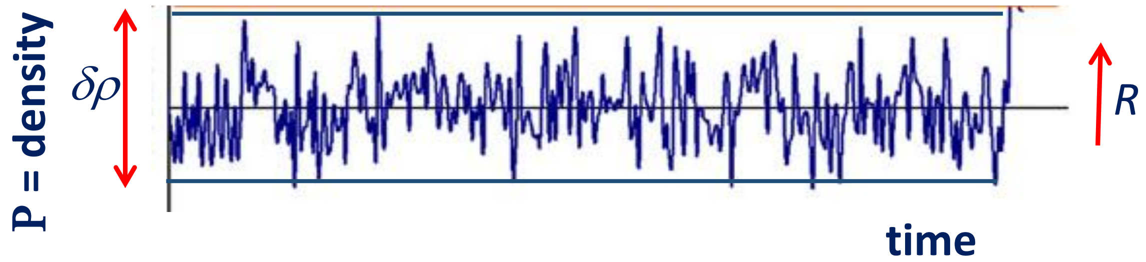


$\delta\rho$ = amplitude of fluctuations;
***R* = response to a perturbation**

FDT ➡ $\delta\rho > R$

- *HYDROSTATIC PRESSURE* ➡ *DENSITY;*
- *Generic MECHANICAL STRESS* ➡ *STRAIN (viscoelasticity);*
- *ELECTRIC FIELD* ➡ *ELECTRIC POLARIZATION;*
- *TEMPERATURE* ➡ *ENTROPY.*

Kinds of perturbation



$\delta\rho$ **= amplitude of fluctuations;**
R **= response to a perturbation**

$$R(t) = \chi(t)\ F(t)$$

Inverse: $F(t) = M(t)\ R(t)$

	Shear mechanical	Dielectric	Calorimetric
Susceptibility	$\gamma = J\ \sigma$	$D = \varepsilon\ \varepsilon_0 E$	$dq = C_p\ dT$
Modulus	$\sigma = G\ \gamma$	$\varepsilon_0 E = M\ D$	$dT = C_p^{-1}\ dq$

SUSCEPTIBILITY: $\chi = J,\ \varepsilon\ \varepsilon_0,\ C_p$

MODULUS: $M = G,\ M,\ C_p^{-1}$

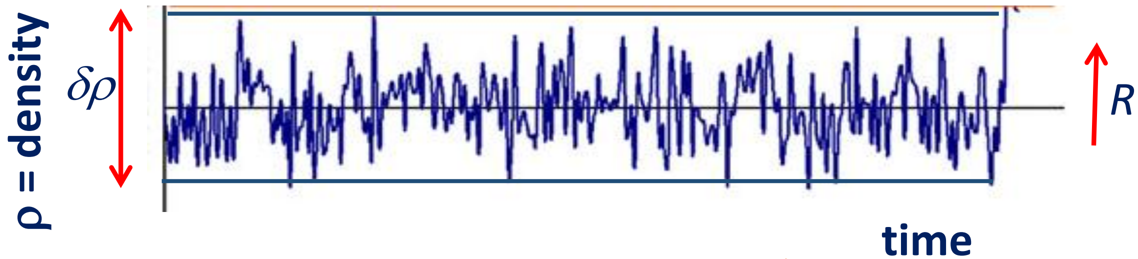
FORCE: $F = \sigma,\ e_0E,\ dT$

RESPONSE: $R = g,\ D,\ dq$

J = COMPLIANCE; G = MECH. MODULUS;
γ = STRAIN; σ = STRESS;
ε = PERMITTIVITY; M = DIEL. MODULUS;
D = DISPLACEMENT; E = ELECTRIC FIELD;
C_p = SPECIFIC HEAT; C_p^{-1} = CAL. MODULUS
dq = HEAT EXCHANGED; dT = T VARIATION;

R. Richert J. Chem. Phys. **149**, 240901 (2018)

Response to simple step perturbation

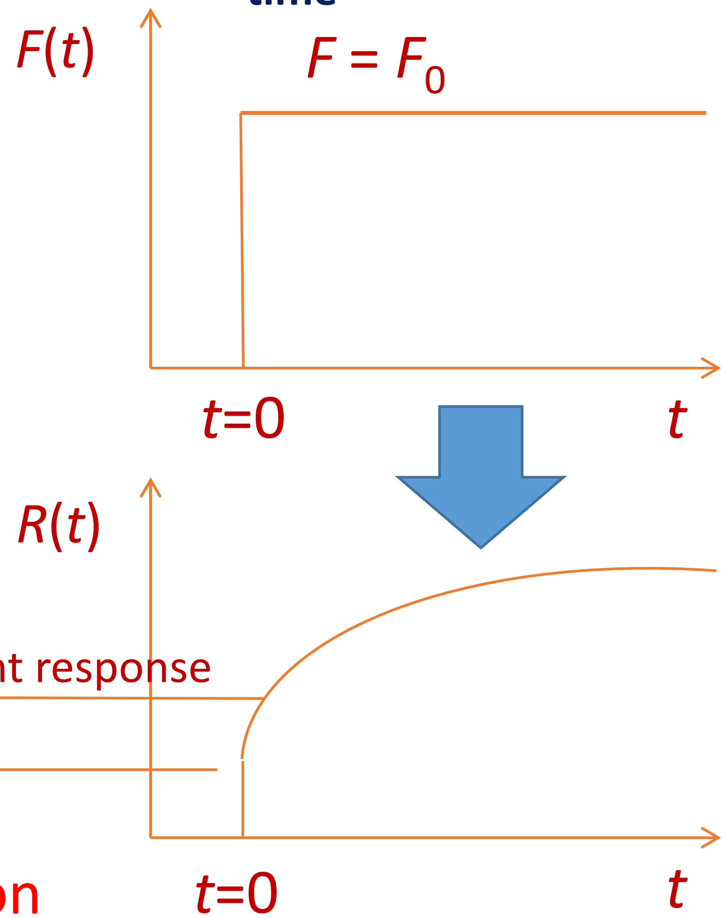


$$R(t) = \chi(t)\,F(t)$$

$$F(t) = 0;\ t < 0$$

$$F(t) = F_0\,;\ t > 0$$

$$R(t) = \chi_\infty\,F_0 + F_0\,(\chi_s - \chi_\infty)\,\phi(t)$$

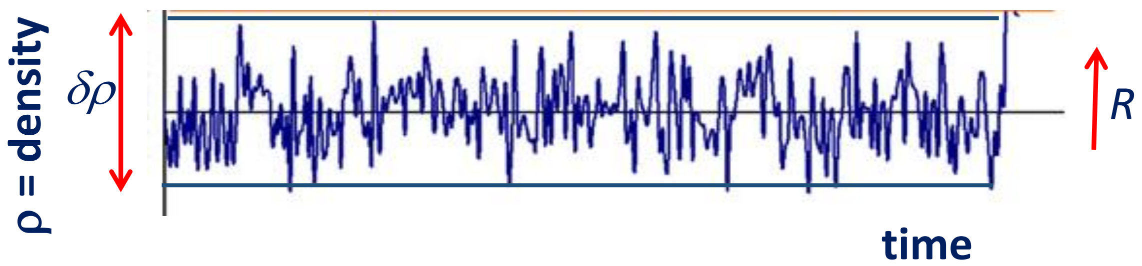


t-dependent response

Instantaneous response

$\phi(t)$ = relaxation (creep) function

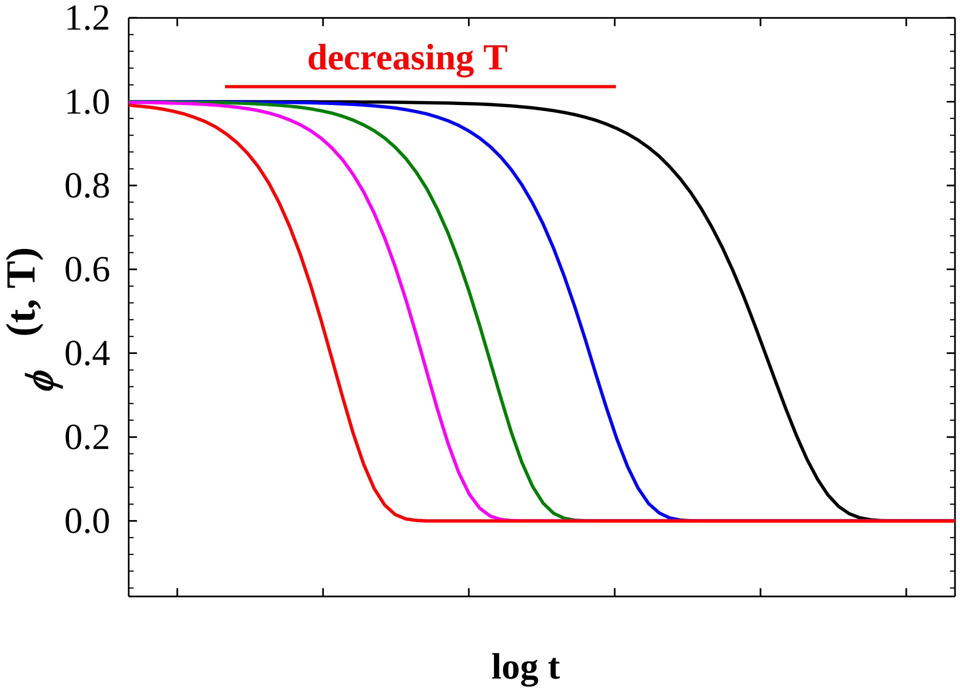
Linear regime: relaxation function

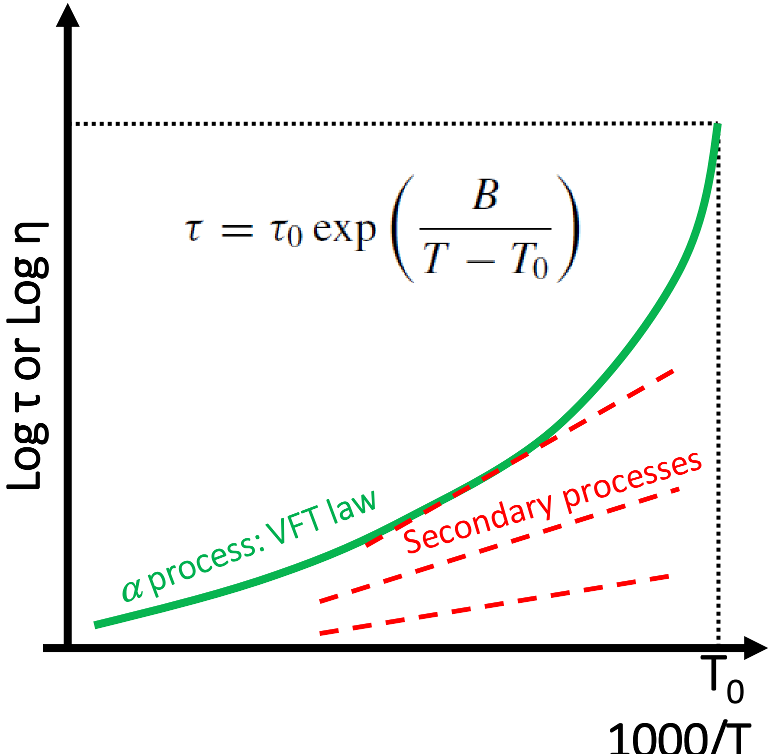


$R(t) = \chi_\infty F_0 + F_0 (\chi_s - \chi_\infty)\, \phi(t)$

$0 < \phi(t) < 1$

Correlation (Relaxation, Retardation) function

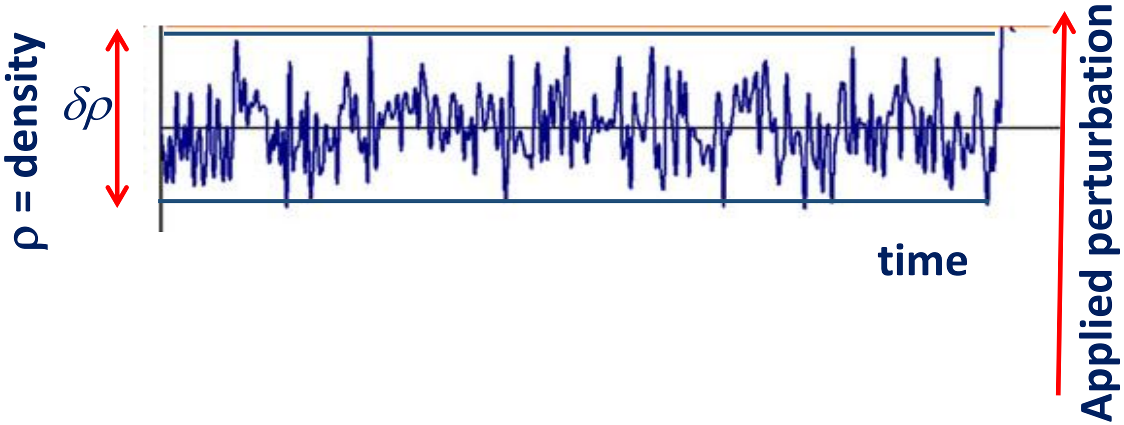




Outline of the talk

- Linear response in glass forming systems;
- **Increasing perturbations: the non-linear regime;**
- Relation between linear and non-linear response:
  - Bulk glasses;
  - Confined glasses;
  - Amorphous polymer adsorption
- Conclusions;

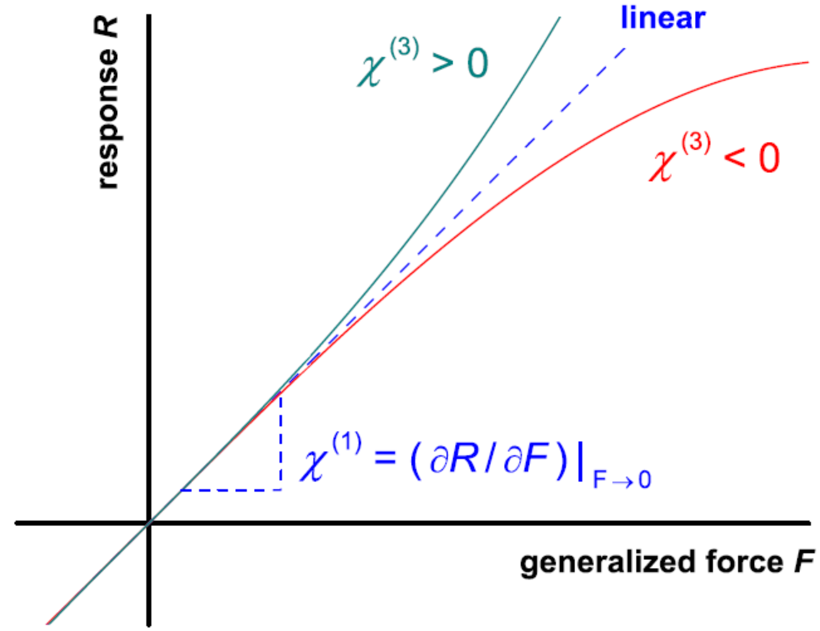
Non-linear regime



Kinetics **of** ***equilibration***
after strong perturbation

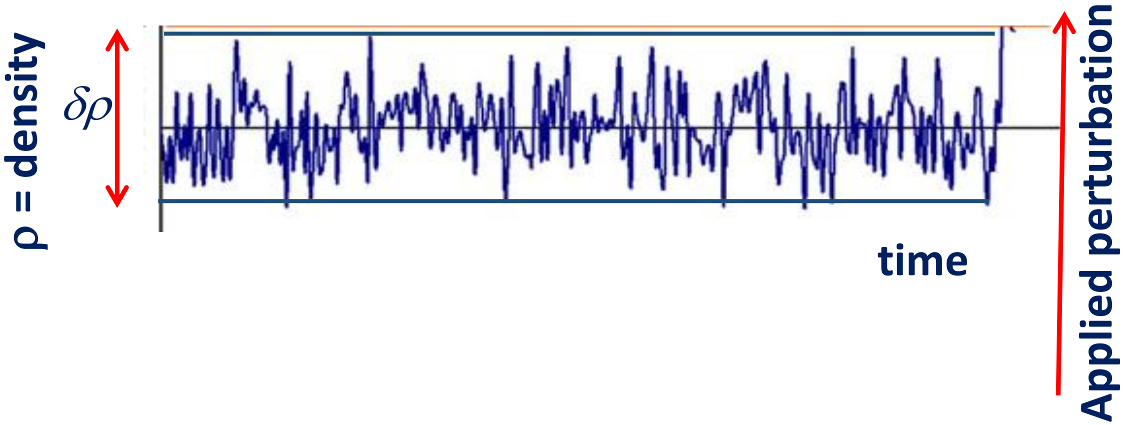
$$R(t) = \chi(t)\,F(t) + \chi(t)^{(2)}\,F(t)^2 + \chi(t)^{(3)}\,F(t)^3\ldots$$

Higher order harmonics
must be included

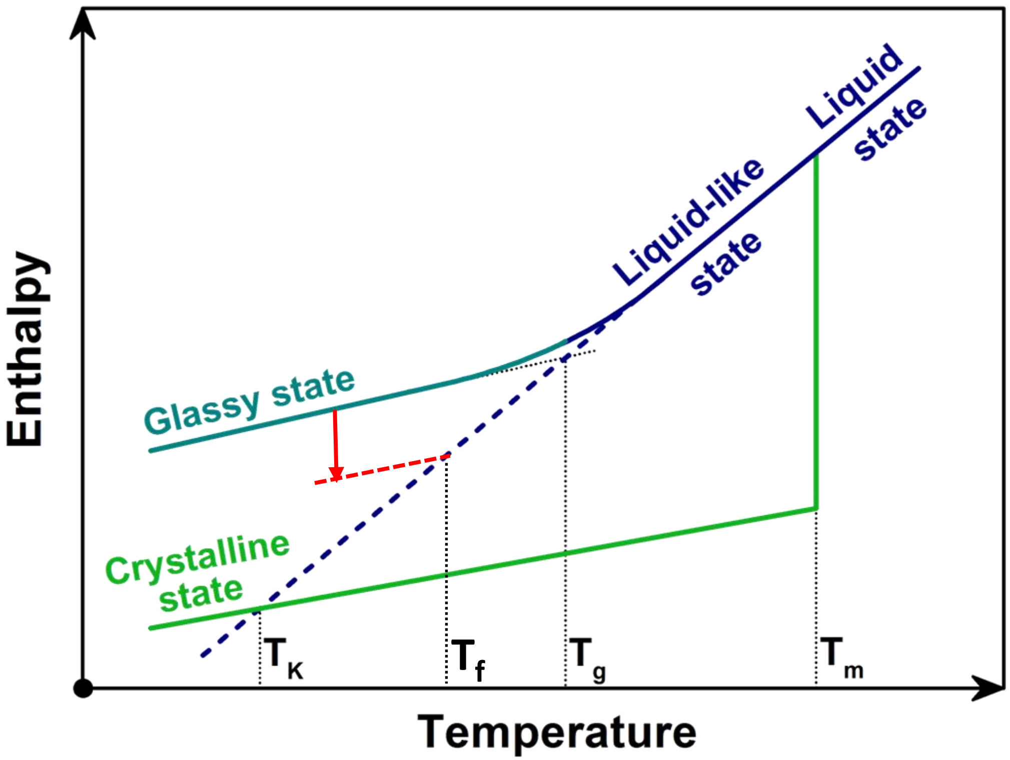


R. Richert J. Chem. Phys. **149**, 240901 (2018)

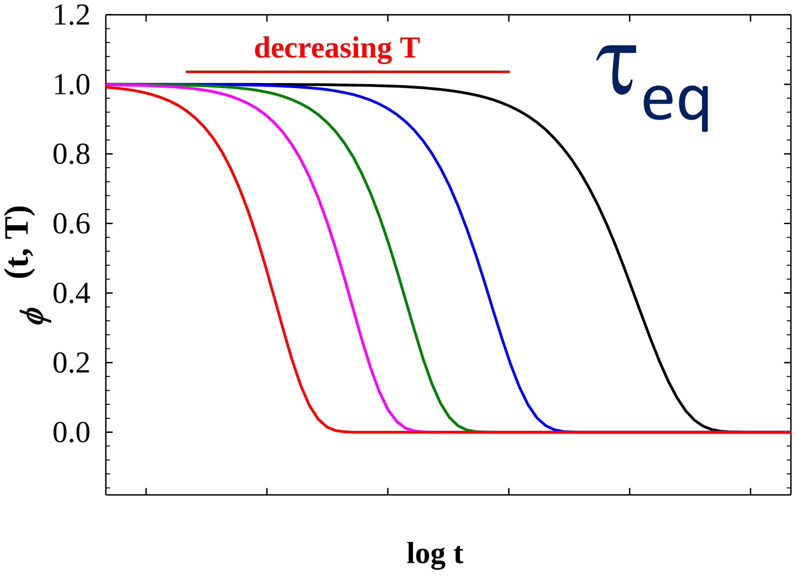
Non-linear regime: physical aging



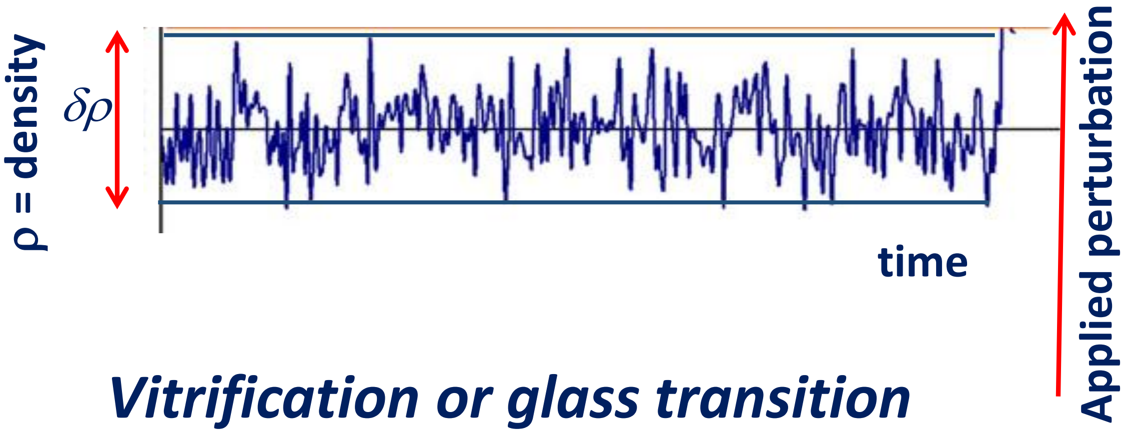
Kinetics of ***equilibration***
after strong perturbation



Recovery (of equilibrium)
function

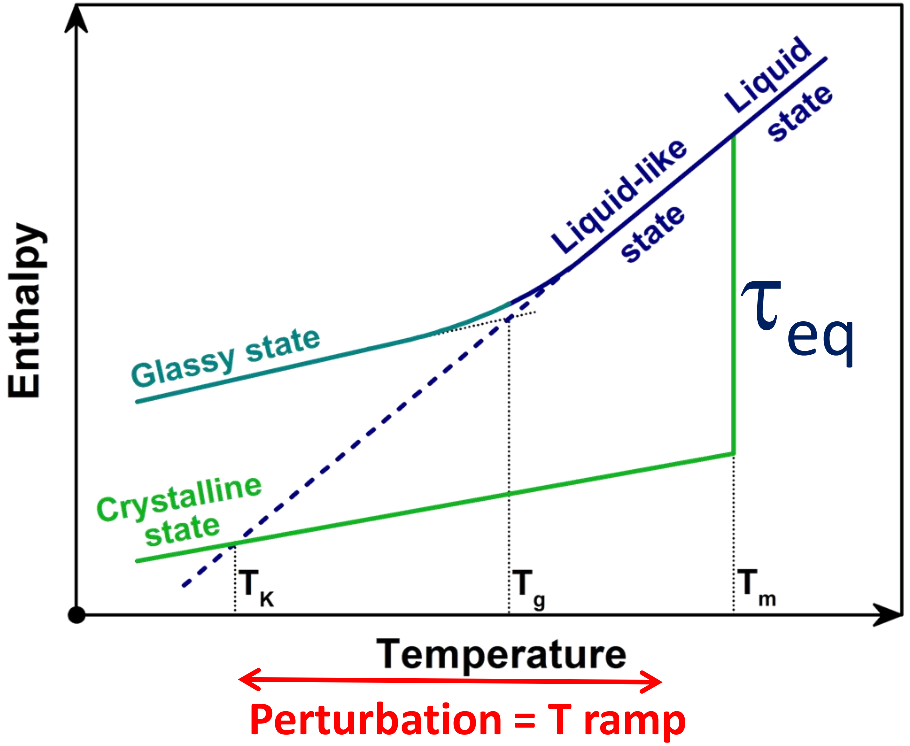


Non-linear regime: vitrification



Equilibrium to ***non-equilibrium kinetic*** transformation

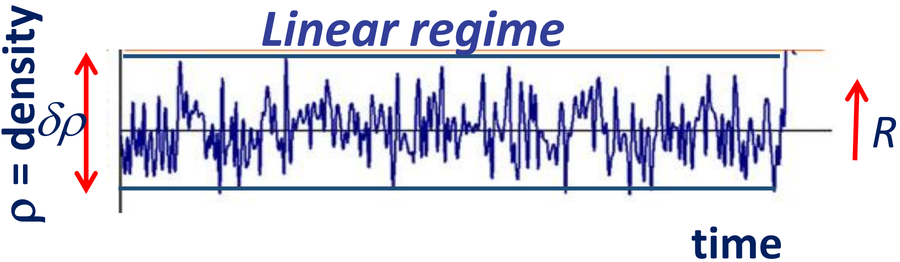
Vitrification or glass transition

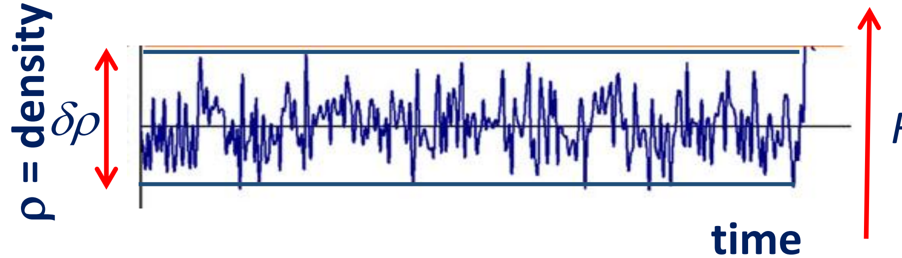


Vitrification induced by the application of a large perturbation

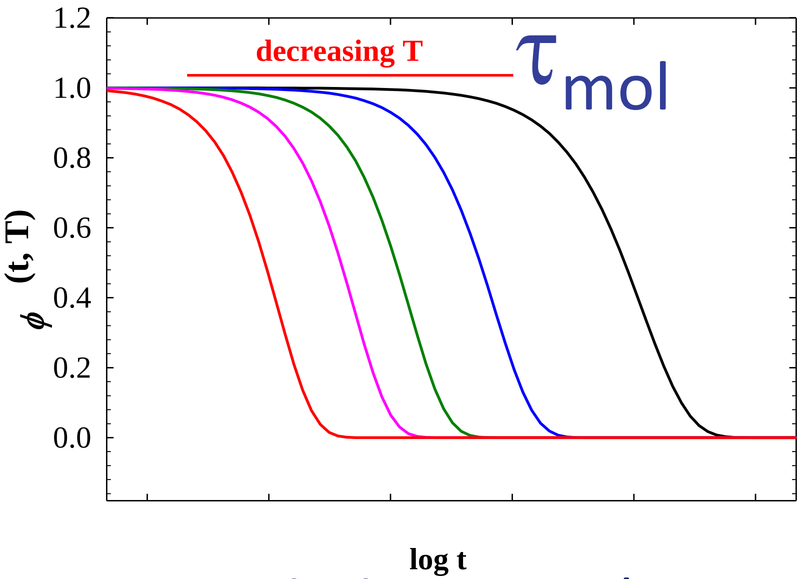
- Thermal
- Mechanical:
  - Pressure;
  - Shear…
- Solvent removal.

Linear and non-linear glass transition



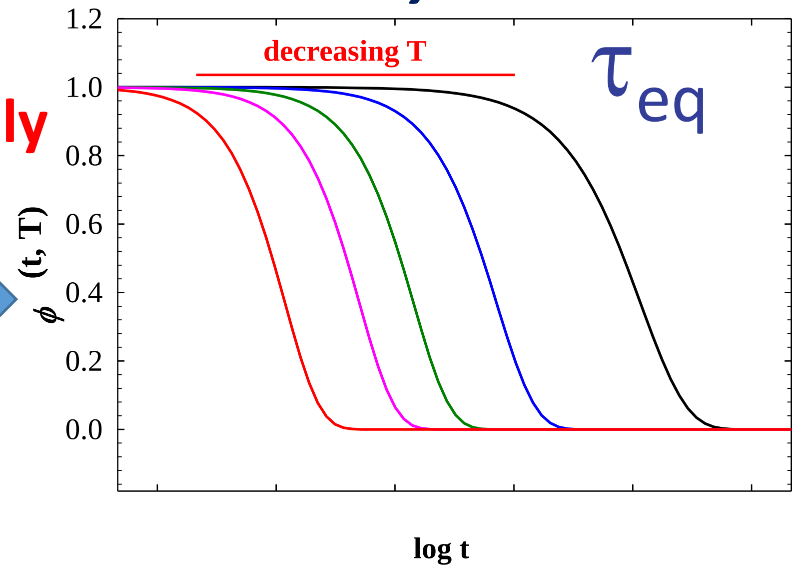


Relaxation function



Conceptually different

Recovery function



- No ***a-priori*** reason why τ_{mol} and τ_{eq} should coincide;
- However, τ_{mol} and τ_{eq} are connected. How?

Outline of the talk

- Linear response in glass forming systems;
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  - Confined glasses;
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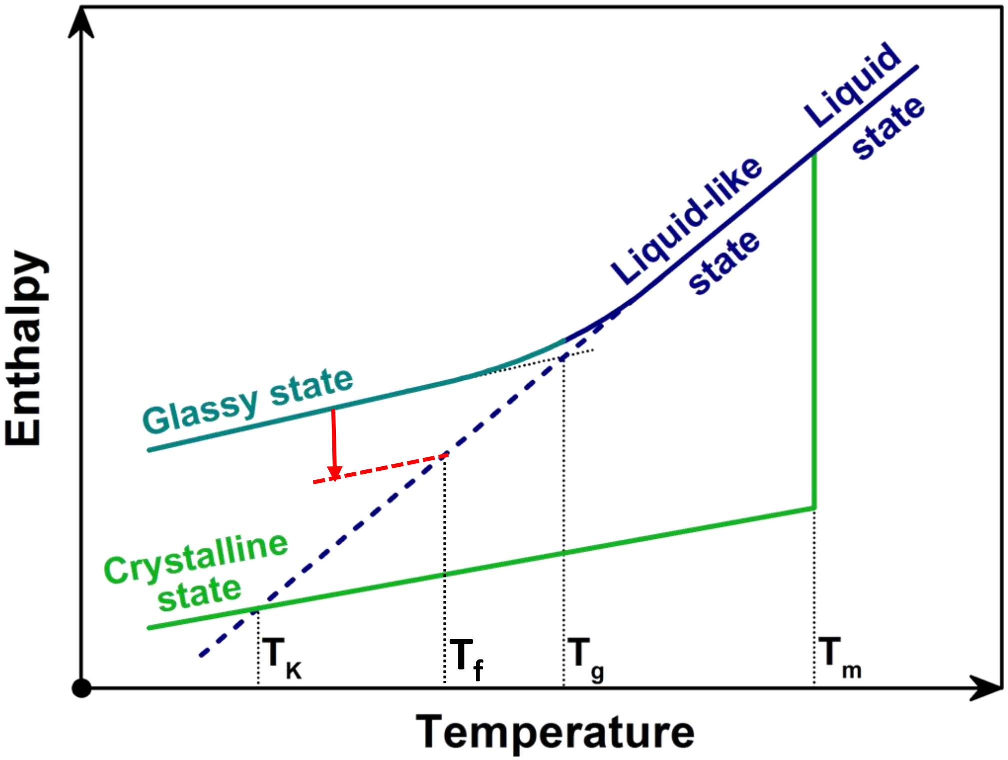
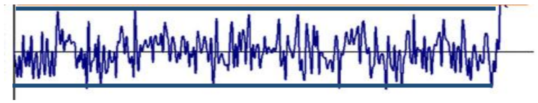
Physical aging *vs* molecular mobility

Non-linear regime

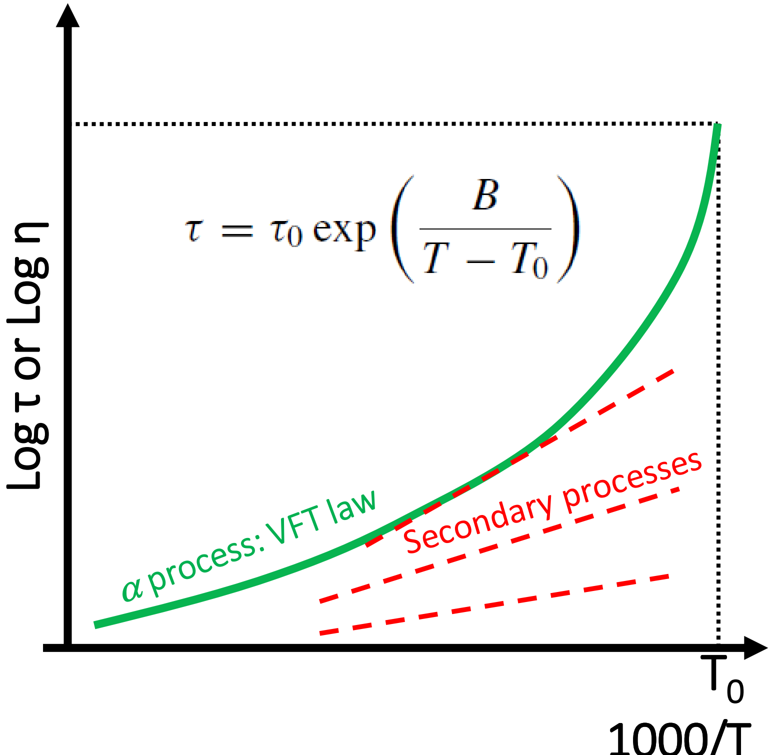


τ_{eq} (time scale of aging) ***depends*** on the time scale of fluctuations τ

Linear regime



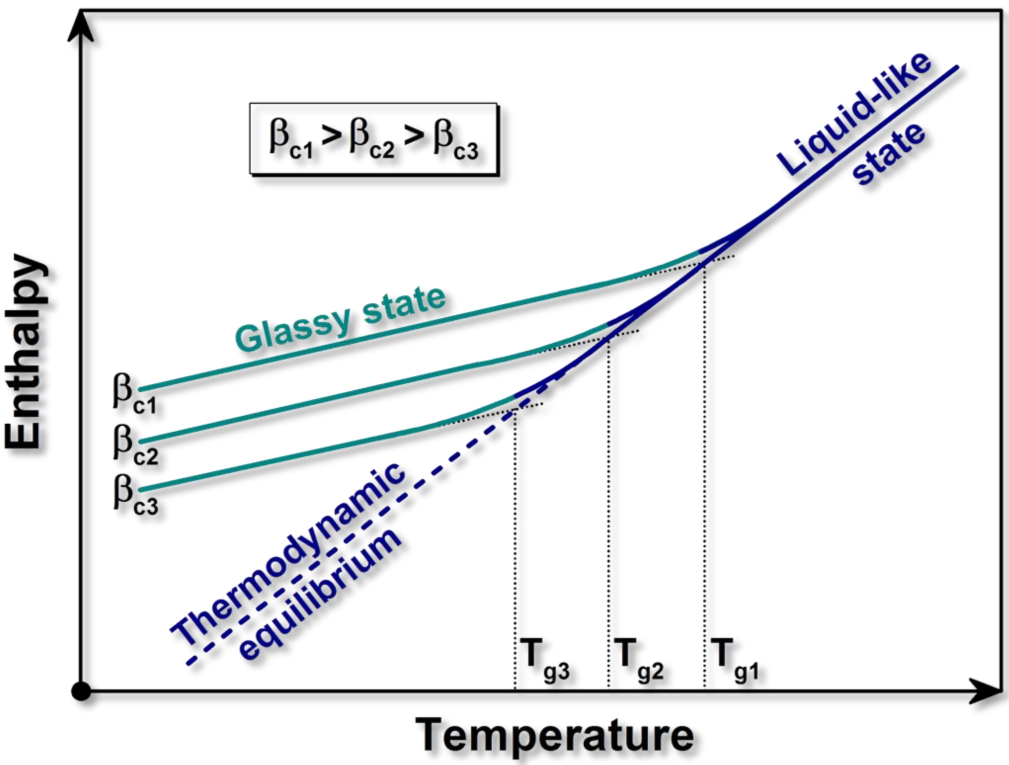
τ = typical time of spontaneous fluctuations



- Conventional wisdom: physical aging ***assisted*** exclusively by τ of the α relaxation
- Role of ***other*** relaxations?
- Connection with physical aging ➡ Talk on Wednesday

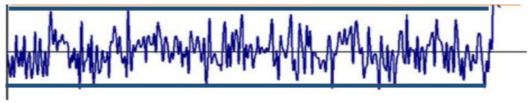
Physical aging *vs* molecular mobility

Non-linear regime

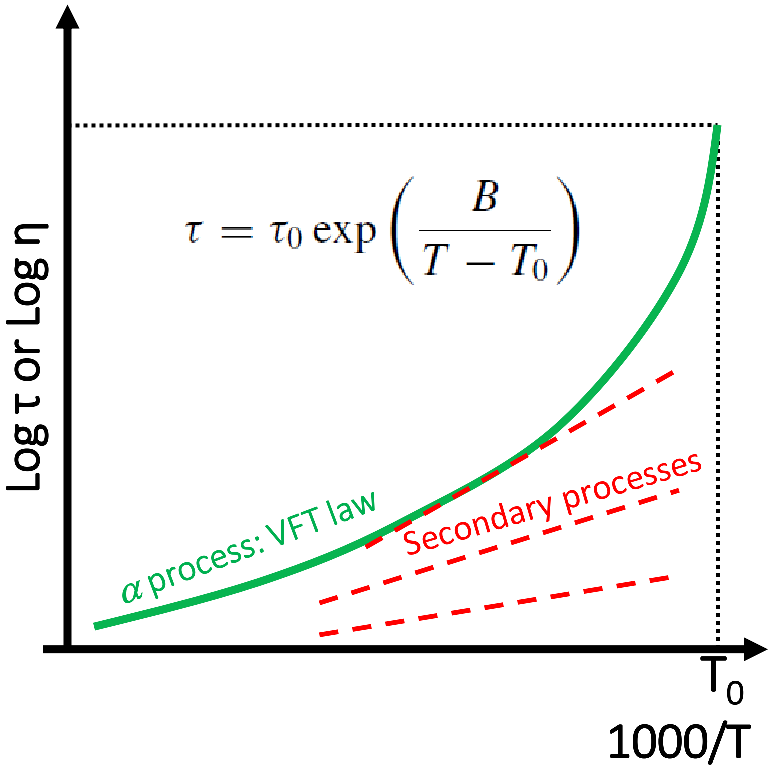


β_c (experimental time scale) ***depends*** on the time scale of fluctuations τ

Linear regime



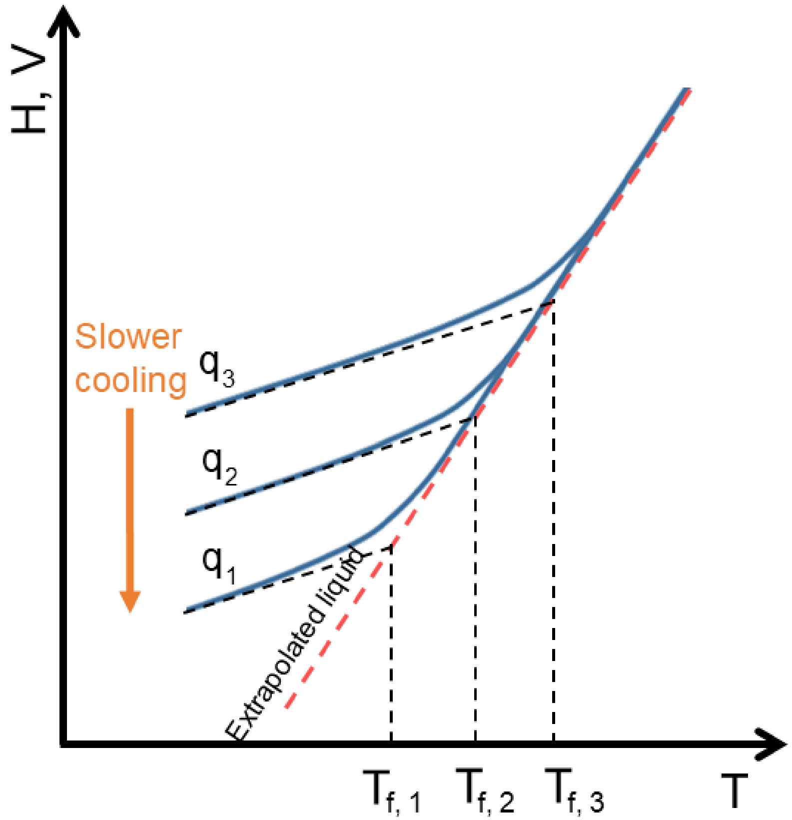
τ = typical time of spontaneous fluctuations



- Conventional wisdom: physical aging ***assisted*** exclusively by τ of the α relaxation
- Role of ***other*** relaxations?

Cooling rate dependent fictive temperature (T_f)

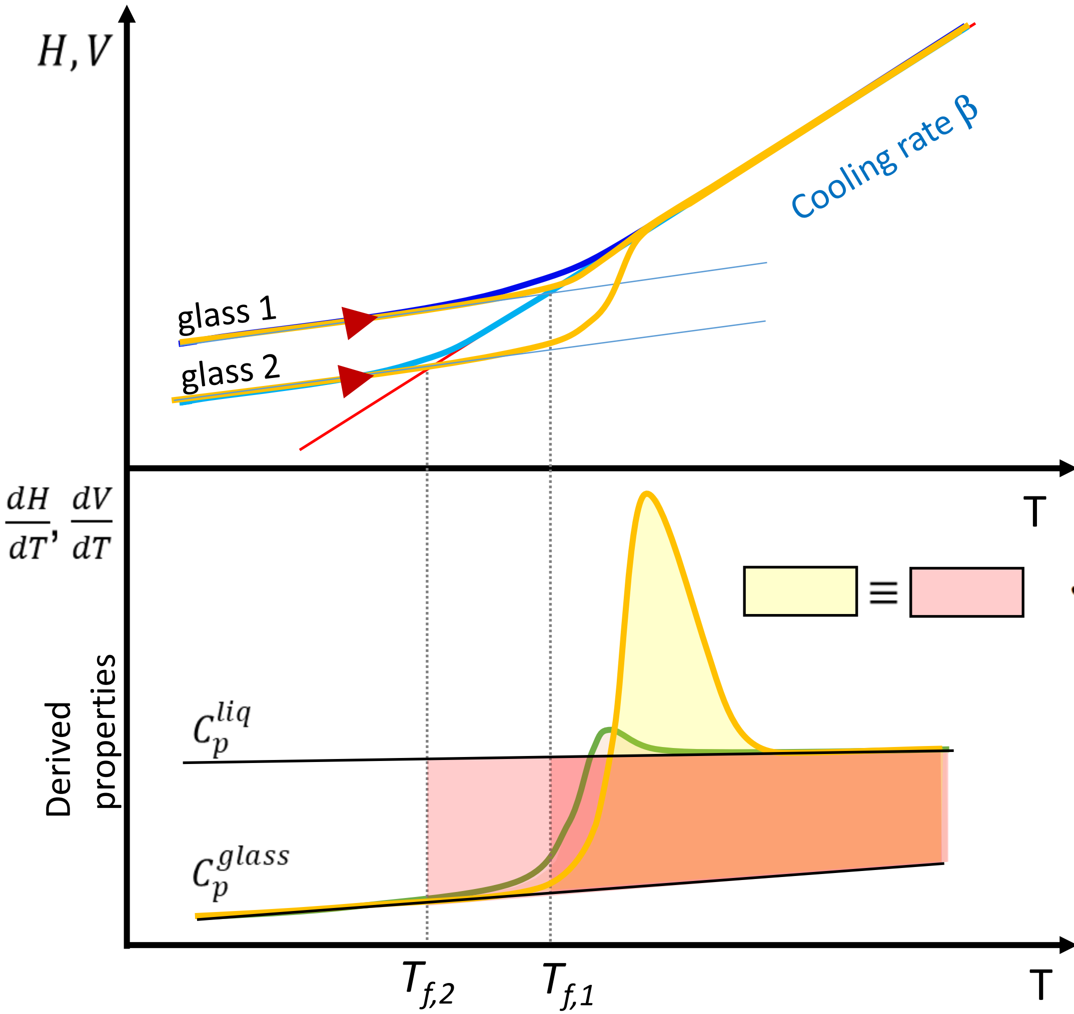
T_f in cooling rate dependent experiments



Cooling Rate Dependent Vitrification

- T_f from ***intersection*** of the glass line to the melt line
- In cooling rate dependent experiments with same rate, $\boldsymbol{T_f \approx T_g}$

T_f Determination: Moynihan method



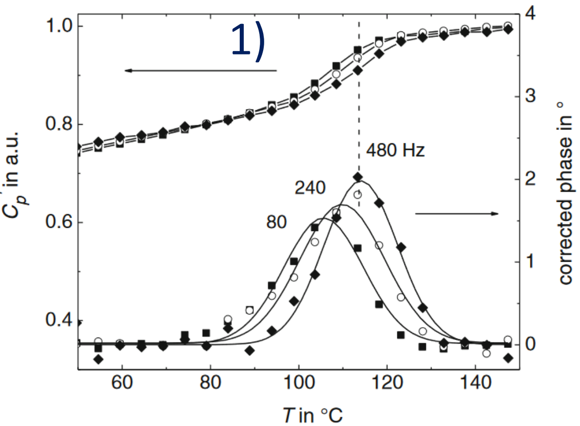
$$\int_{T_f}^{T_1}(c_{p,l}-c_{p,g})dT = \int_{T_2}^{T_1}(c_p-c_{p,g})dT$$

Low T_f correspond to ***large*** endothermic overshoot

C. T. Moynihan et al. Ann. N. Y. Acad. Sci. **279,** 15–35 (1976).

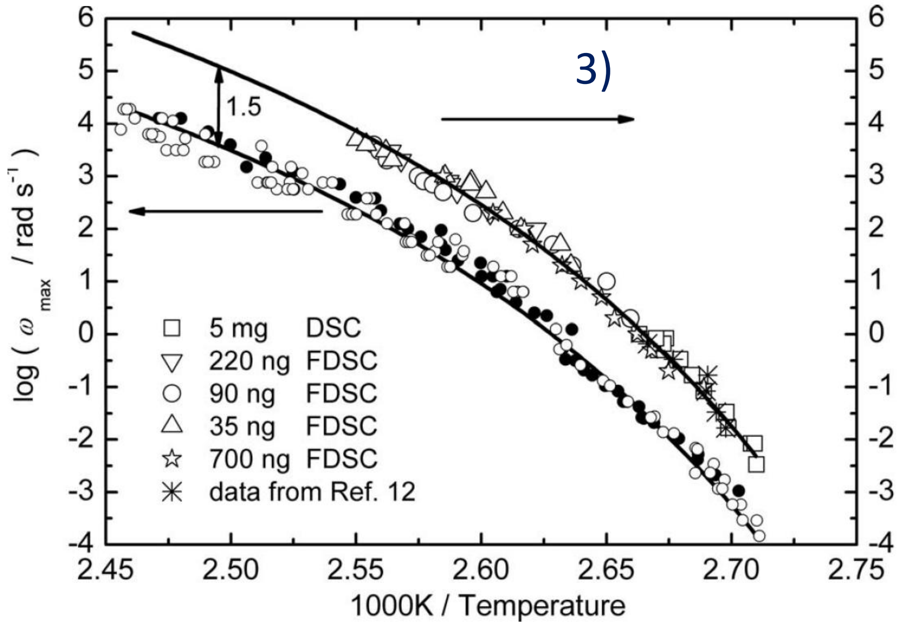
Vitrification (non-linear) vs Molecular mobility (linear)

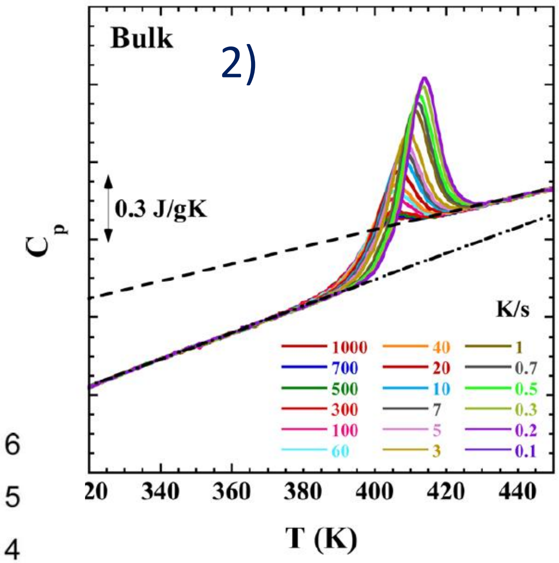
Bulk polystyrene (PS)



Linear regime: ***thermal susceptibility***

$\tau_{mol}=\omega_{max}^{-1}$





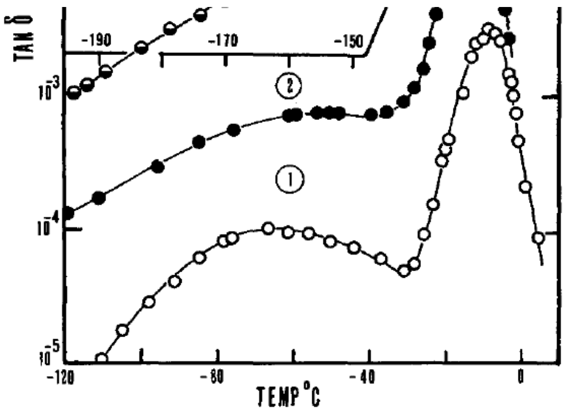
Non-Linear regime: **Cooling rate dependent T_f**

T_f **vs** β

Vitrification ***coupled*** to the α relaxation

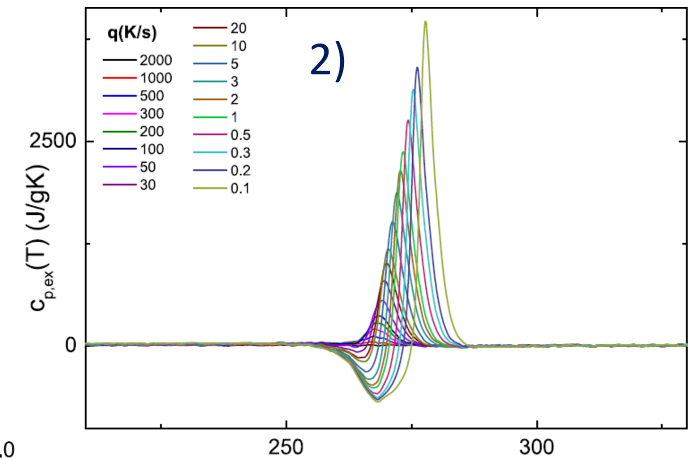
1) Y.Z. Chua, G. Schulz, E. Shoifet, H. Huth, R. Zorn, J.W.P. Schmelzer, C. Schick, Coll. Pol. Sci. 1893, **292**, (2014); 2) N Perez-De Eulate, V. Di Lisio, D. Cangialosi, ACS Macro Lett. 859–863, **6** (2017); 3) J. E. K. Schawe, J. Chem. Phys. 184905, **141** (2014).

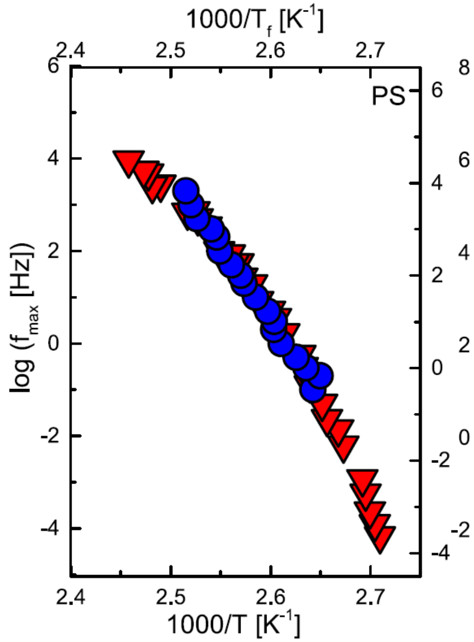
Vitrification (non-linear) vs Molecular mobility (linear)

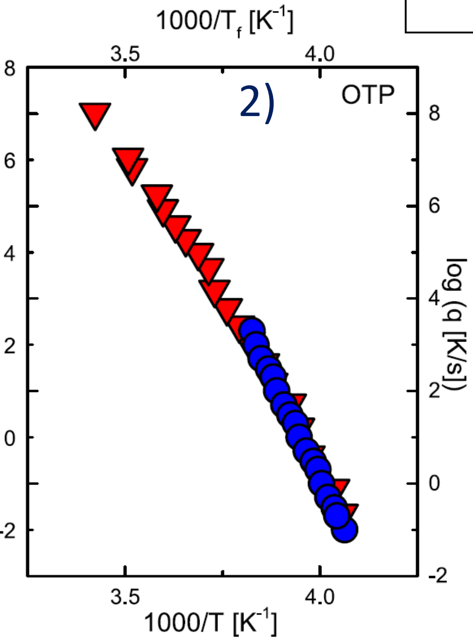


Linear regime: ***dielectric susceptibility***

Bulk polystyrene (PS) and **OTP**







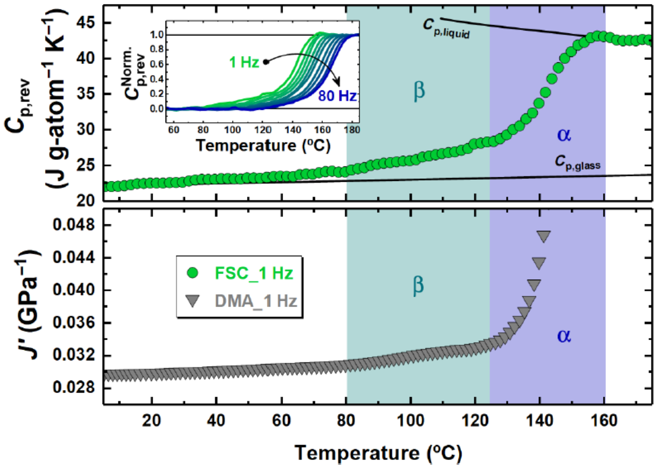
Non-Linear regime: **Cooling rate dependent T_f**

***T_f* vs β**

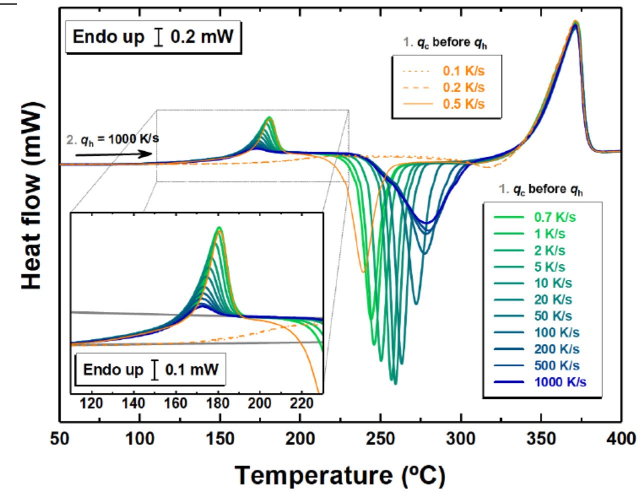
Vitrification ***coupled*** to the α relaxation

1) G.P. Johari, M. Goldstein, J. Chem. Phys. **53**, 2372 (1970); 2) A.A. Abate, S. Napolitano, D. Cangialosi, Thermochim. Acta **707**, 179084, (2022)

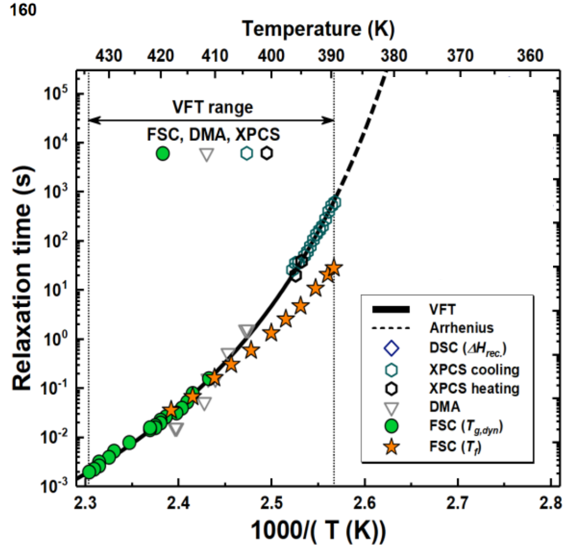
Decoupling between α relaxation and vitrification



Au-based Metallic glass*



Linear regime: ***thermal and mechanical (compliance) susceptibility***

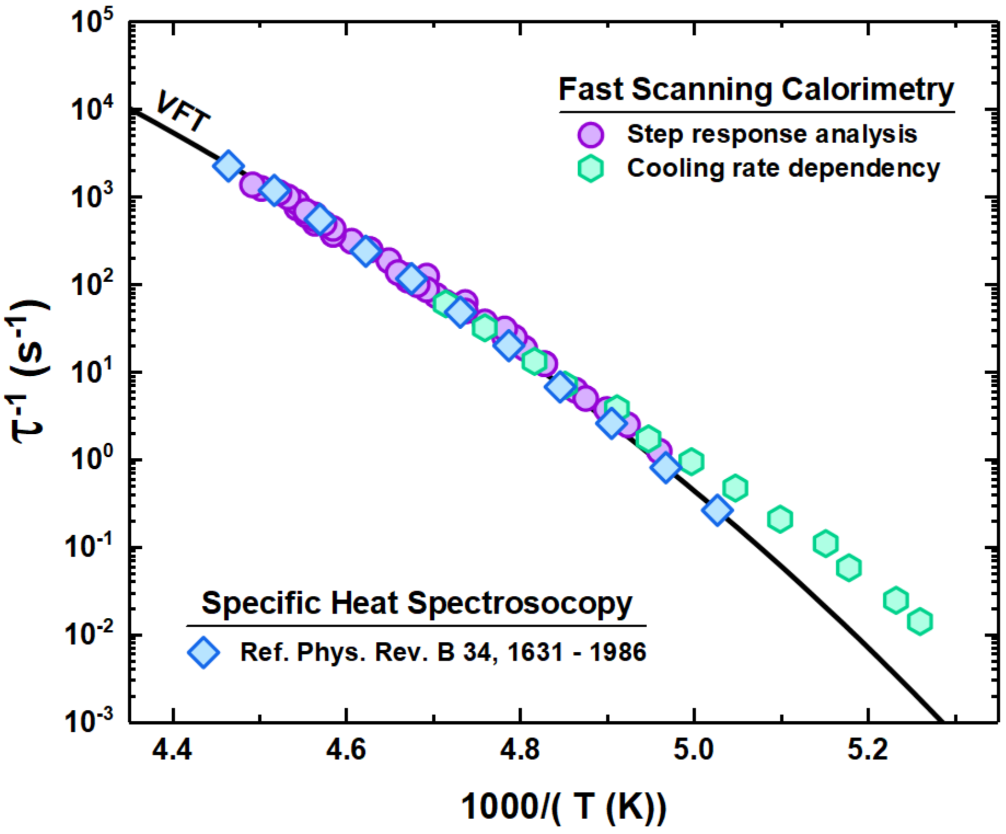


- At low cooling rates T_f lower than expected if ***only*** the α relaxation is accounted for;
- Atomic/molecular mechanisms ***other than*** the α relaxation involved in vitrification.

*X. Monnier, D. Cangialosi, B. Ruta, R. Busch, and I. Gallino, Sci. Adv. 6, eaay1454 (2020)

Decoupling between α relaxation and vitrification

Glycerol



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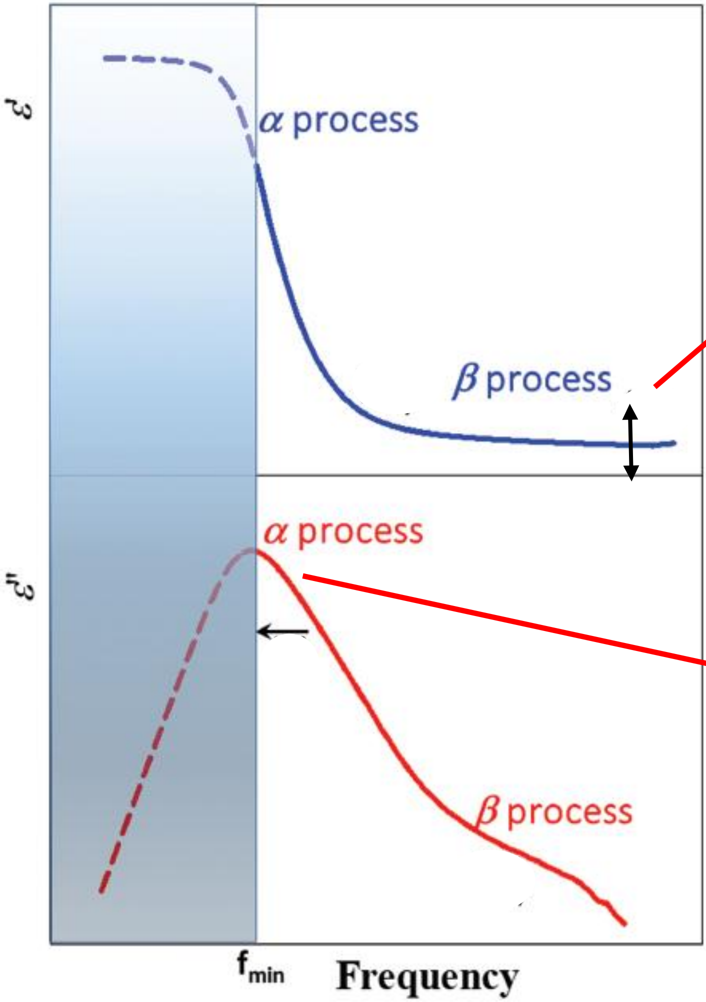
Vitrification vs Molecular mobility in ***thin films***

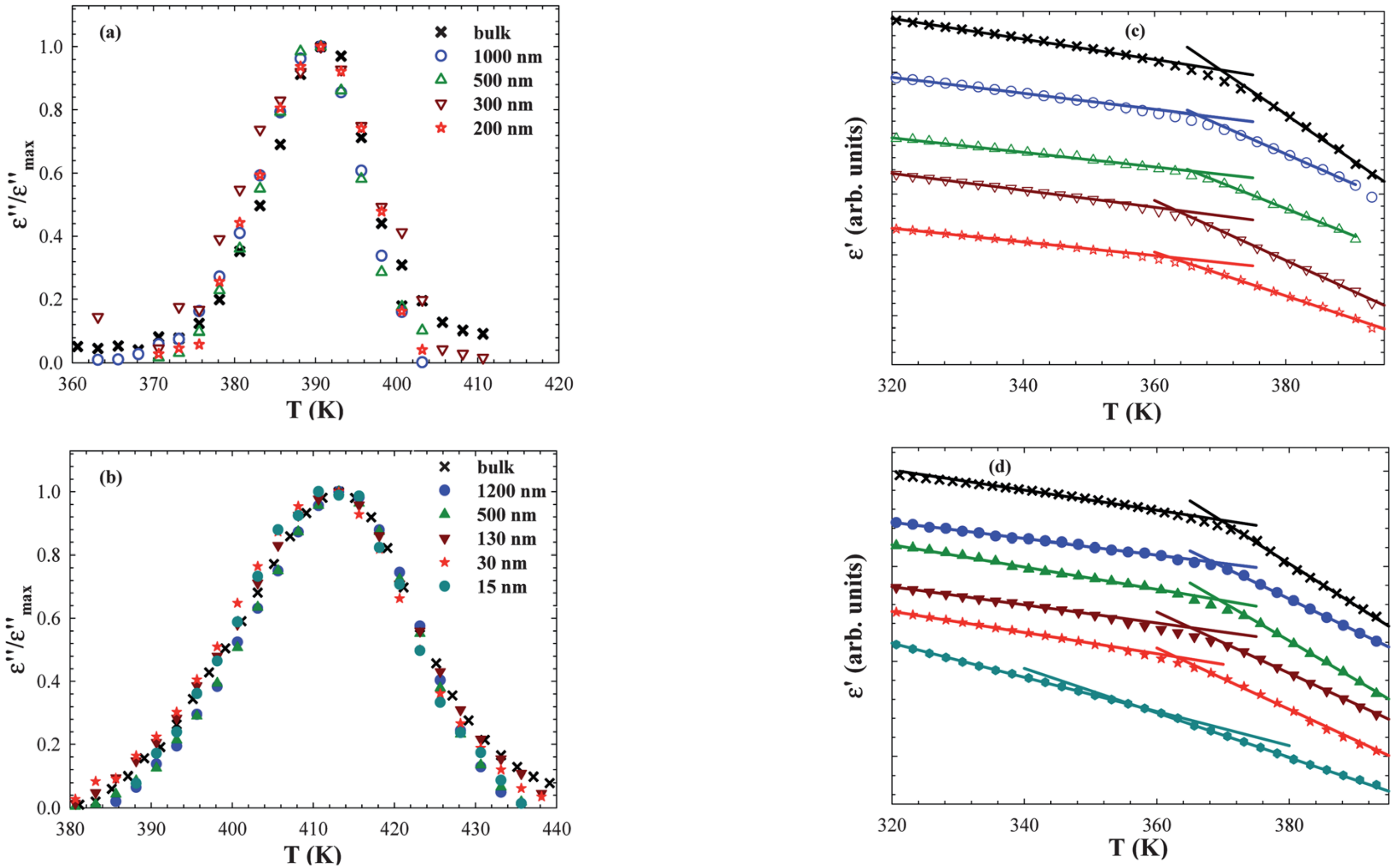


Non-linear response: via Clausius-Mosotti equation density variation as a function of temperature from change in ε'_{∞}

Linear response: α relaxation from frequency shift in dielectric loss with temperature

D. Cangialosi, **ACS Symp. Ser.** 1375, Chapter 6, pp 133-156 (2021)

Vitrification vs Molecular mobility in ***thin films***



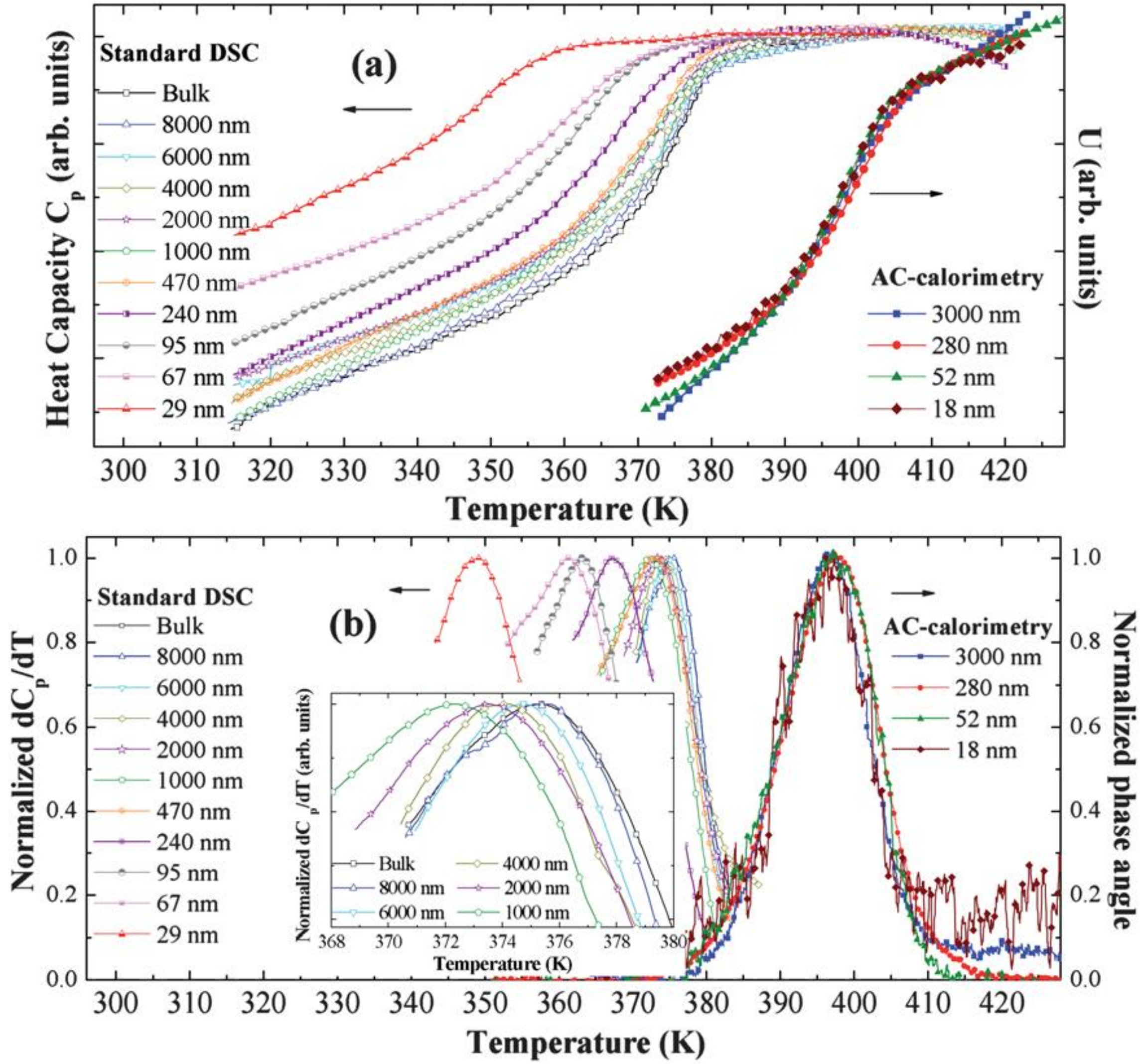
Linear response: thickness ***independent*** α relaxation

Non-linear response: thickness ***dependent*** vitrification

V. M. Boucher D. Cangialosi, H. Yin, A. Schönhals, A. Alegría, J. Colmenero, **Soft Matt.** 8, 5119 (2012)

Vitrification vs Molecular mobility in ***thin films***

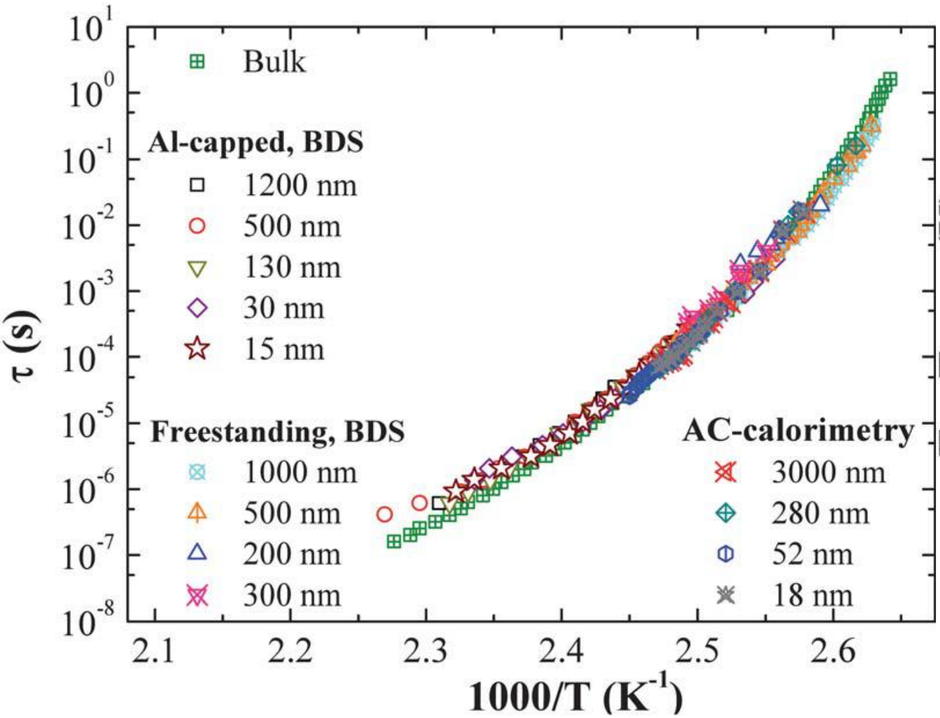
Non-linear response (standard DSC): thickness ***dependent*** vitrification

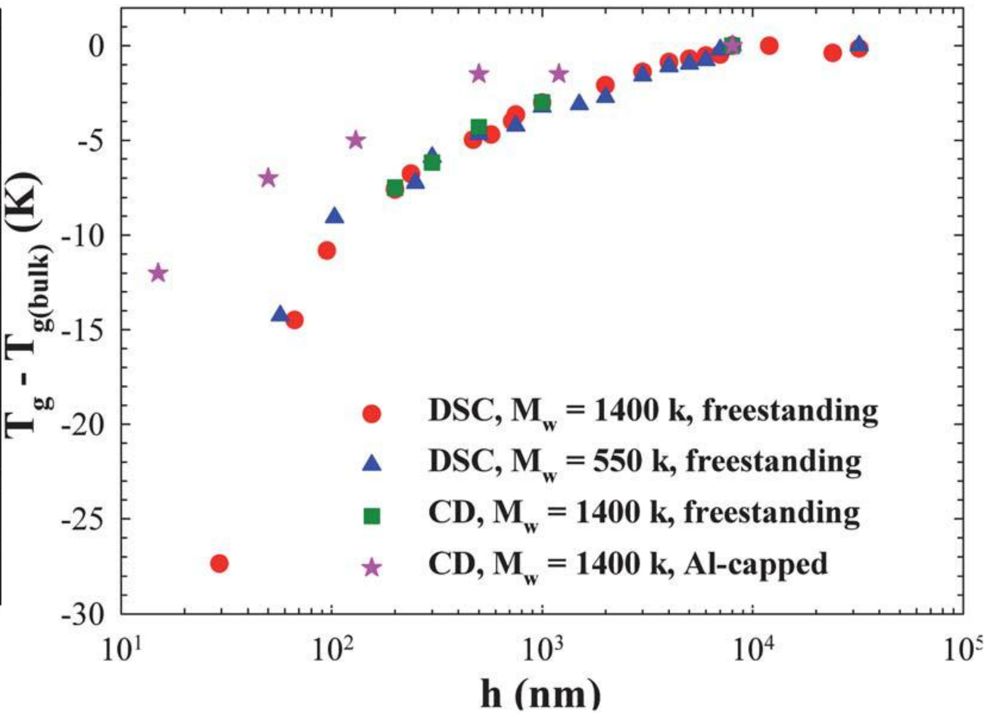


Linear response (AC-calorimetry) thickness ***independent*** α relaxation

V. M. Boucher D. Cangialosi, H. Yin, A. Schönhals, A. Alegría, J. Colmenero, **Soft Matt.** 8, 5119 (2012)

Vitrification vs Molecular mobility in ***thin films***



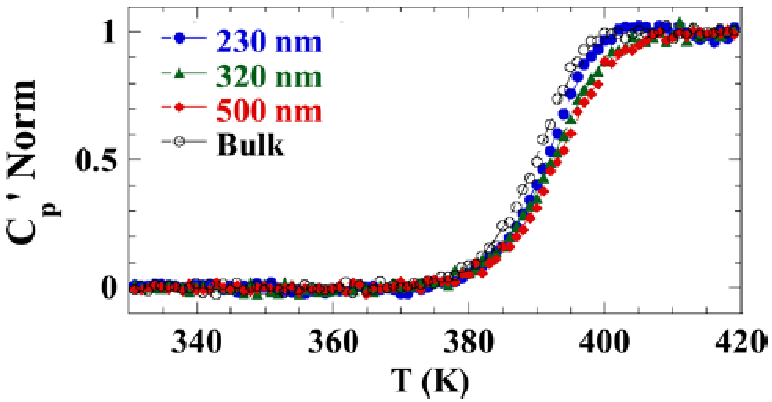


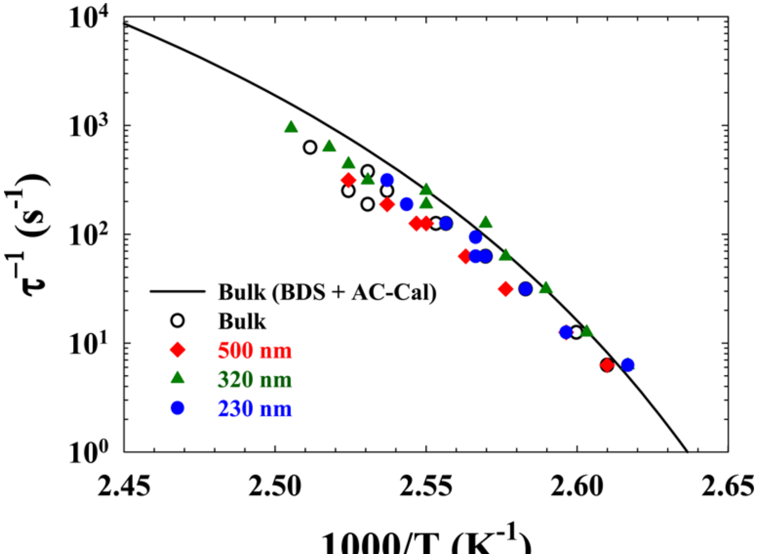
Linear response: thickness ***independent*** α relaxation

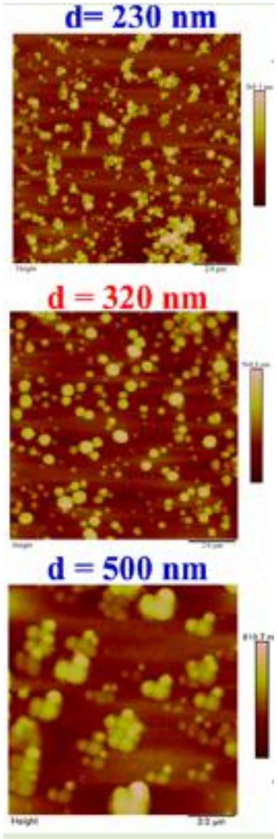
Non-linear response: thickness ***dependent*** vitrification

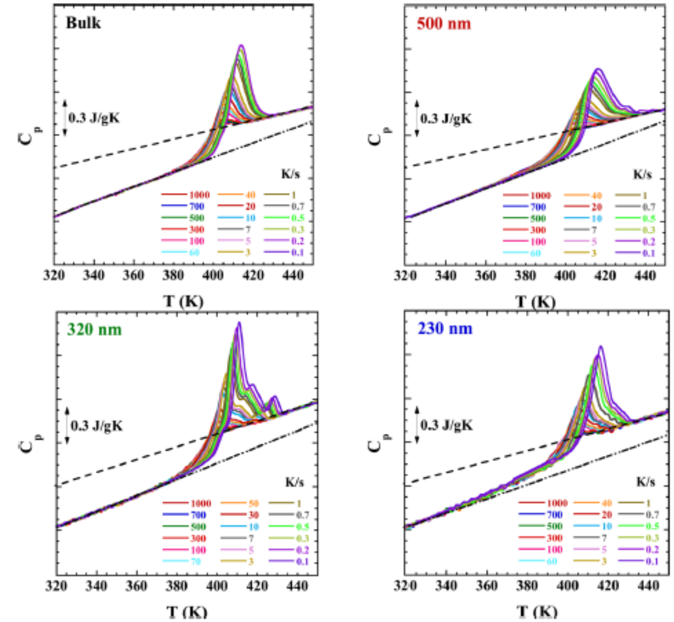
V. M. Boucher D. Cangialosi, H. Yin, A. Schönhals, A. Alegría, J. Colmenero, **Soft Matt.** 8, 5119 (2012)

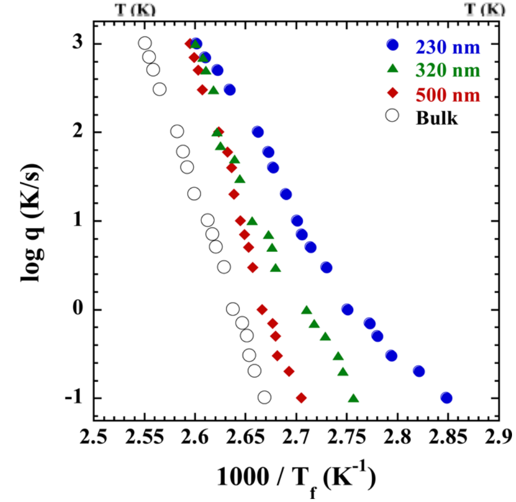
Vitrification vs Molecular mobility in ***PS spheres***











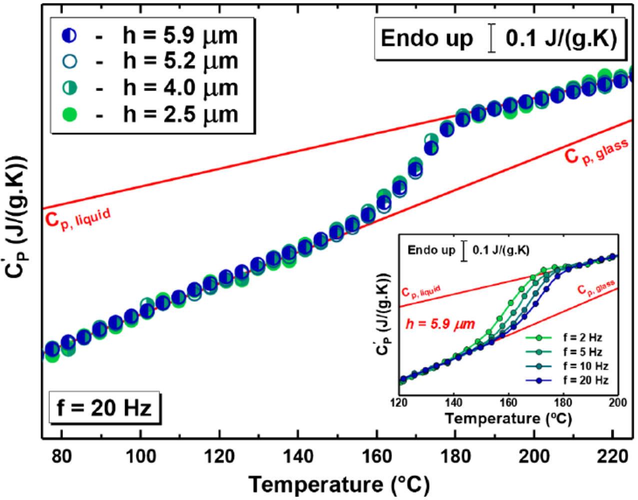
Linear response: size ***independent***

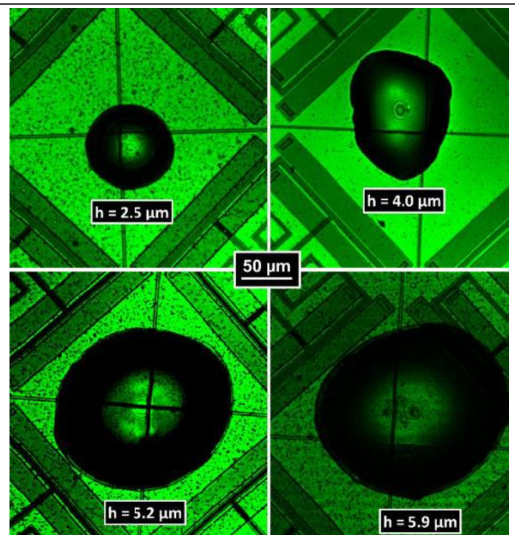
α relaxation

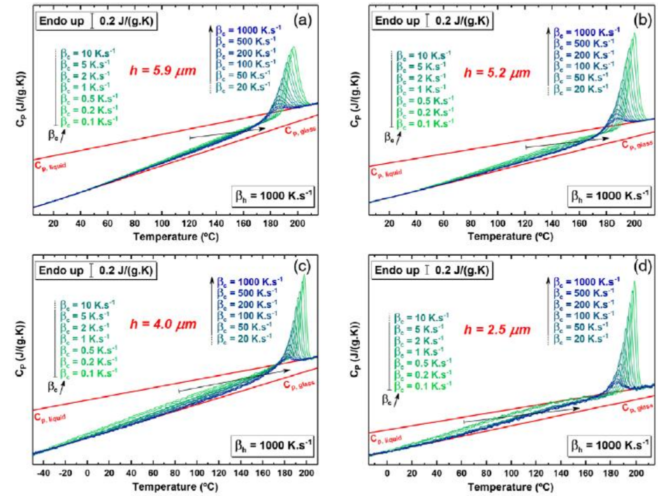
Non-linear response: size ***dependent*** vitrification

D. Cangialosi, V. Di Lisio, N. G. Perez-de-Eulate, **ACS Macro Lett.** 6, 859 (2017)

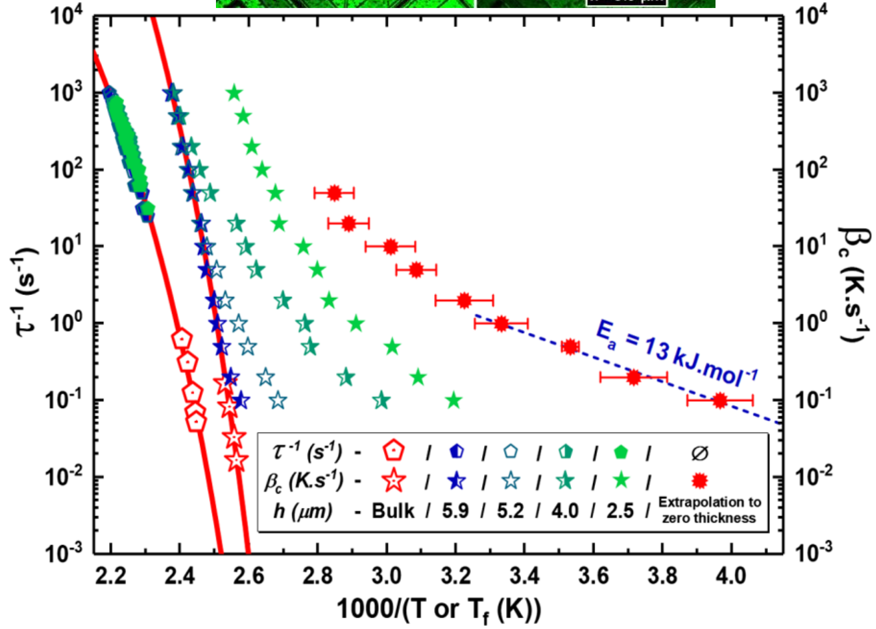
Vitrification vs Molecular mobility in ***micrometric PTBS***







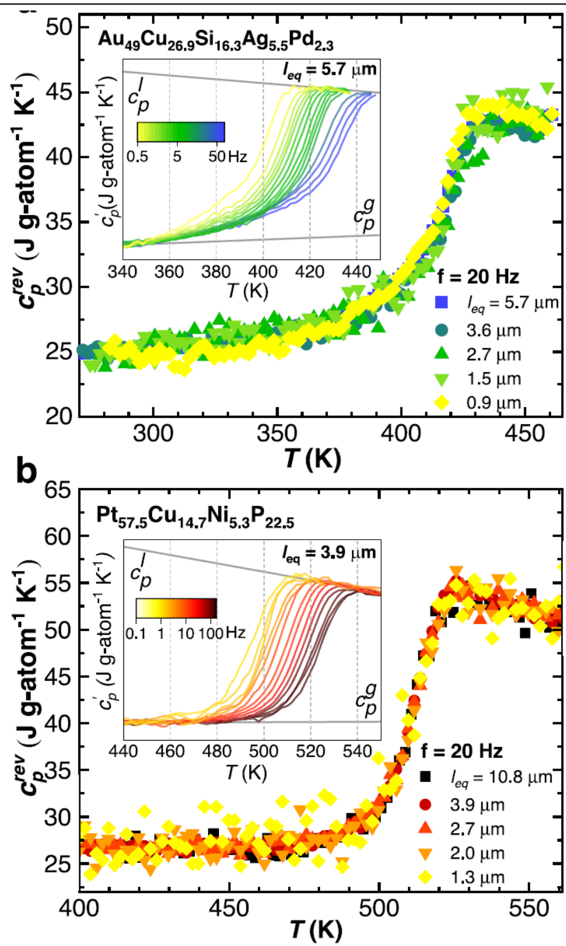
Linear response:
size ***independent*** α
relaxation

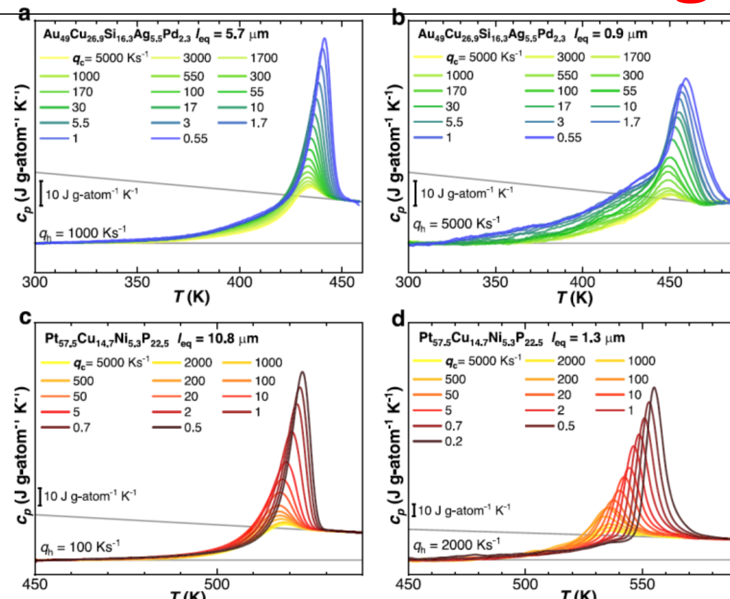


Non-linear response:
size ***dependent***
vitrification

X. Monnier, D. Cangialosi, **Phys. Rev. Lett.** 8, 5119 (2019)

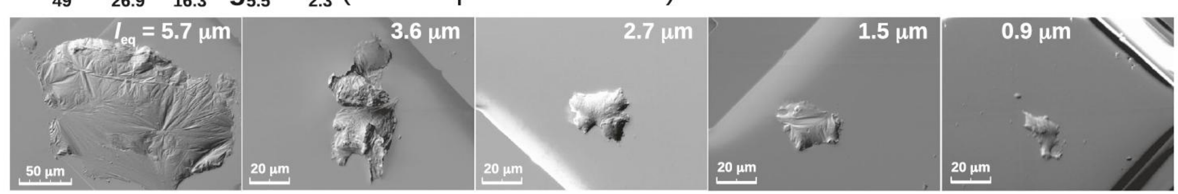
Vitrification vs Molecular mobility in ***micrometric metallic glass***



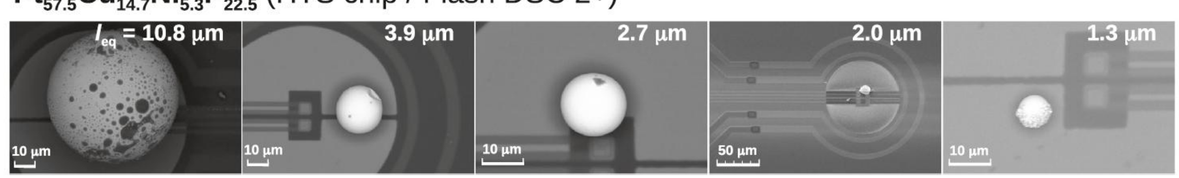


Non-linear response: size ***dependent*** vitrification

Au$_{49}$Cu$_{26.9}$Si$_{16.3}$Ag$_{5.5}$Pd$_{2.3}$ (UFS chip / Flash DSC 1)



Pt$_{57.5}$Cu$_{14.7}$Ni$_{5.3}$P$_{22.5}$ (HTS chip / Flash DSC 2+)

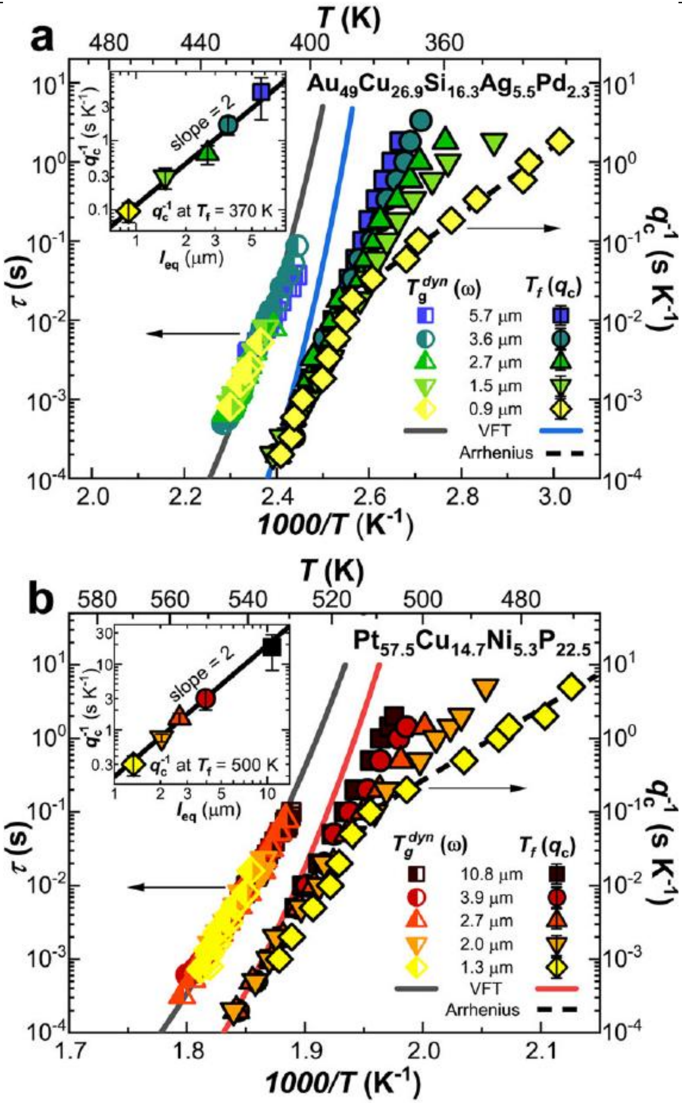


Linear response: size ***independent*** α relaxation

V. Di Lisio, I. Gallino, S.S. Riegler, M. Frey, N. Neuber, G. Kumar, J. Schroers, R. Busch, D. Cangialosi, **Nat. Comm.** 14, 4698 (2023)

Vitrification vs Molecular mobility in ***micrometric metallic glass***

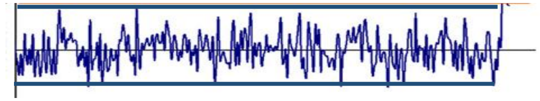
Linear response: size ***independent*** α relaxation



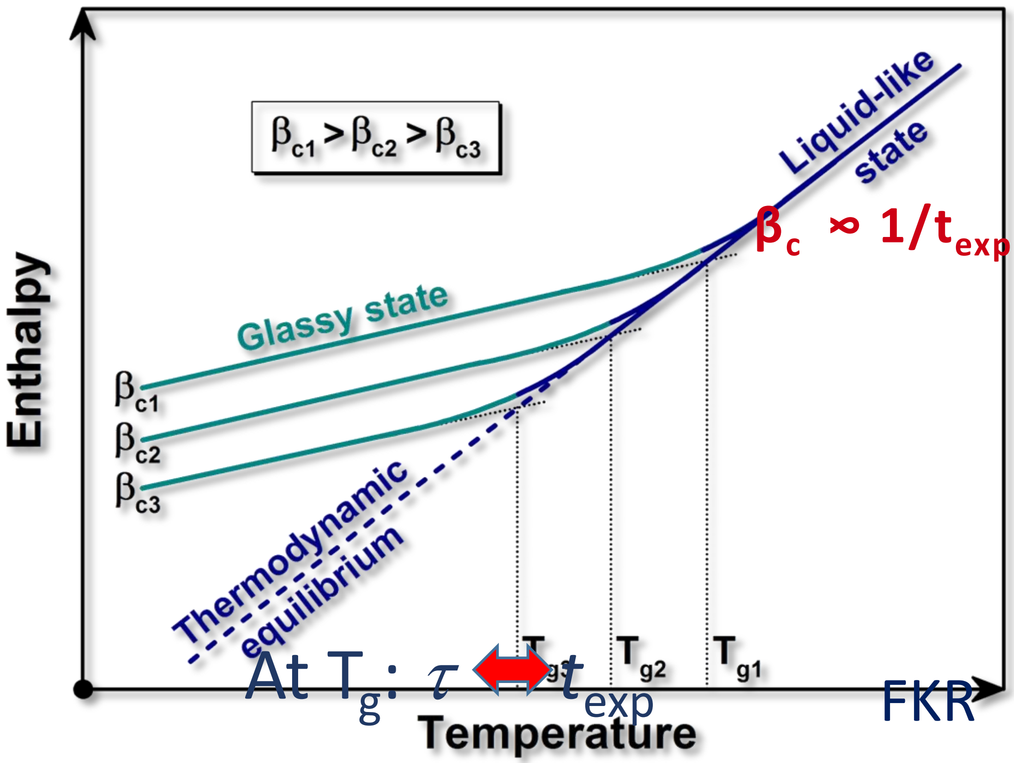
Non-linear response: size ***dependent*** vitrification

V. Di Lisio, I. Gallino, S.S. Riegler, M. Frey, N. Neuber, G. Kumar, J. Schroers, R. Busch, D. Cangialosi, **Nat. Comm.** 14, 4698 (2023)

Vitrification and physical aging *vs* molecular mobility

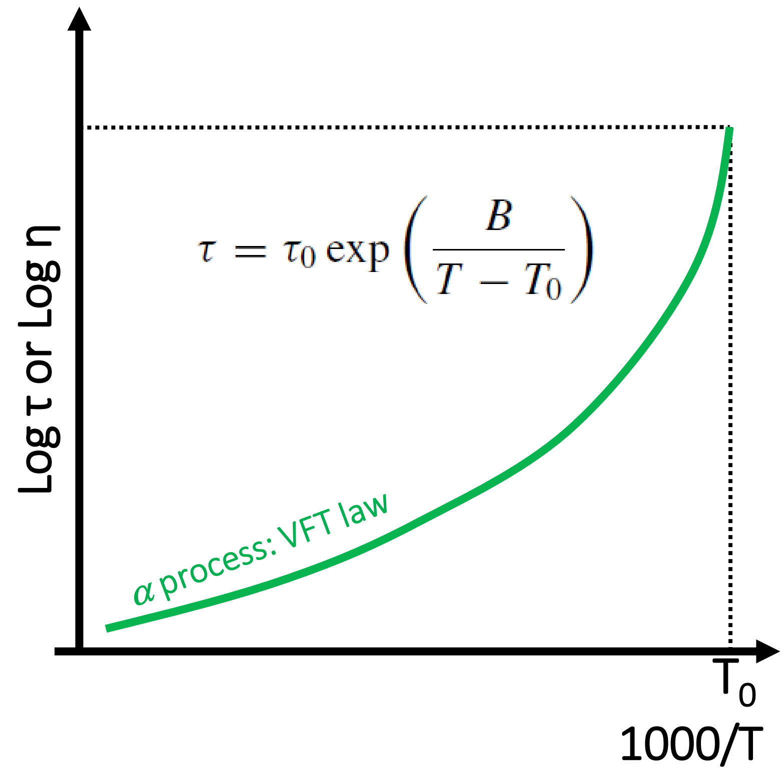


τ = typical time of spontaneous fluctuations



At T_g: $\tau \Leftrightarrow t_{exp}$

FKR



Vitrification, irreversible transformation from the metastable supercooled liquid into the non-equilibrium glass:

Non-linear response

$$\beta^{-1}(T_g) = C(h) * \tau$$

Challenge: underlying physics behind ***C(h)***

Time scale of spontaneous fluctuations:

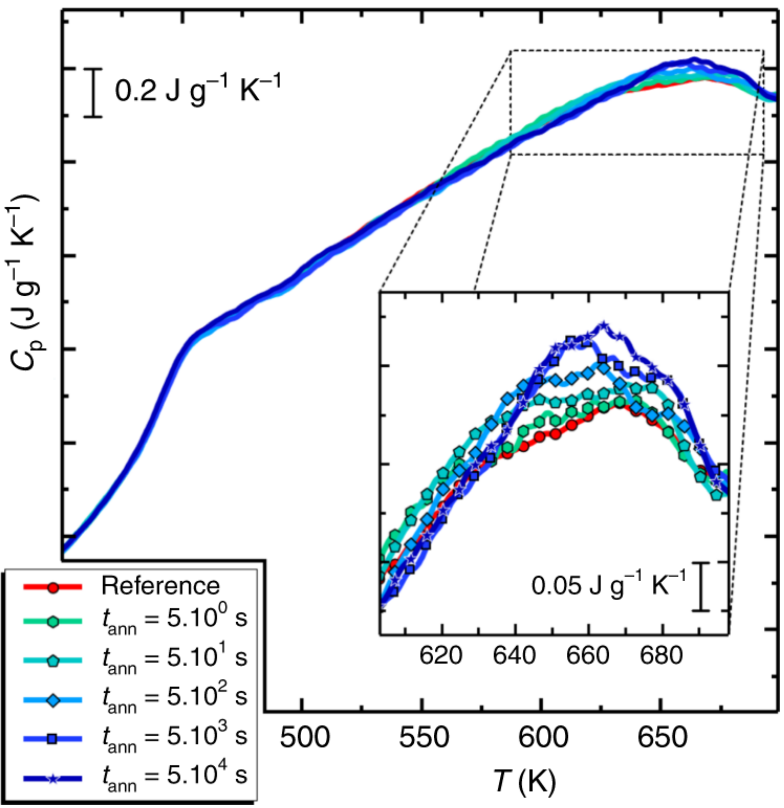
Linear response

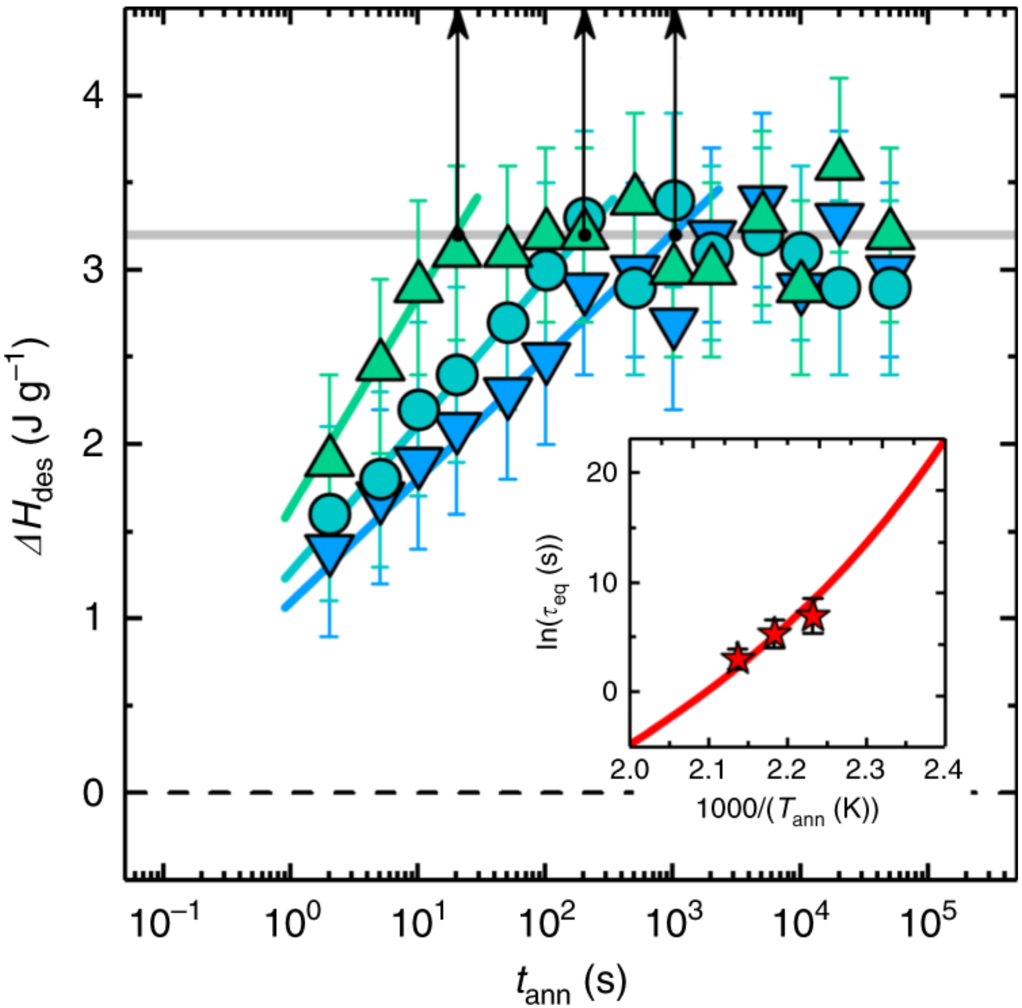
Outline of the talk

- Linear response in glass forming systems;
- Increasing perturbations: the non-linear regime;
- **Relation between linear and non-linear response:**
  - Bulk glasses;
  - Confined glasses;
  - **Amorphous polymer adsorption**

Kinetics of polymer adsoprtion via Fast Scanning Calorimetry

Kinetics of adsorption tracked following ***polymer desorption***





Non-linear kinetics of desorption following temperature dependence of the α relaxation

X. Monnier, S. Napolitano, D. Cangialosi, **Nat. Comm.** 11, 4354 (2020)