The physics of glasses: What have we learnt in the last decade?

J. P. Bouchaud, CFM

with: G. Biroli, L. Berthier & many others!

Preamble

- Sorry for the bombastic title – should be "what have I learnt in the last decade?"

- A partial (=incomplete+biased) view

- Short review on the theory and phenomenology of glasses, with some experimental and simulation results

  + Some open problems, conjectures and interesting experiments to do

- Partly relying on: G. Biroli, J.P. Bouchaud, *The Random First-Order Transition Theory of Glasses: a critical assessment*, arXiv:0912.2542 – 210 refs, among which 140 are $\geq$ 2000 + 5 today...

Outline

- I. Theory: model independent concepts

- II. Theory: first principle approaches

- III. Some phenomenological approaches

  (RFOT, Elastic models, FLD, KCM, etc.)

- IV. Open problems and conjectures

I. Theory – model independent concepts

- Back to basics: glasses (below T_g) are rigid (non zero shear modulus) but amorphous (no apparent long range order)

- The shear modulus can *in principle* be computed as a thermodynamical average

  It is necessarily zero for an ergodic amorphous state (liquid)

- Glasses are thus effectively non-ergodic and stuck around a mechanically stable amorphous configuration

  – as I will argue, some kind of thermodynamic "amorphous order" must propagate at least over medium scales

I. Theory – model independent concepts

- Glasses lose their rigidity as temperature increases not only because the relaxation time scale decreases, but more radically because above some T_c local stability is lost (Goldstein 1969). Below T_c energy barriers grow.

- An explicit scenario for the "cage opening" mechanism: MCT-RFOT (Götze 1985, Kirkpatrick, Thirumalai & Wolynes 1987) – see below

- Local mechanical stability is of paramount importance (but often implied) in all other phenomenological approaches: Elastic (shoving) model (Dyre), Locally Preferred Structures (Frank, Kivelson & Tarjus, Procaccia, etc.), Kinetically Constrained Models (Chandler & Garrahan, ...), etc.

I. Theory – model independent concepts

- Appearance or loss of rigidity is:

  a collective phenomenon (e.g. $z_c = 2d > d + 1$ Maxwell),

  associated to a critical point (MCT, isostatic J-point),

  and diverging susceptibility/correlation length revealing the growth of "amorphous order" (cf. Spin-Glasses)

  where soft-modes are important (Wyart et al.)

I. Theory – model independent concepts

- Rigidity and amorphous order – listen to the Master (P. W. Anderson, 1983)

- *We are so accustomed to this rigidity property that we don't accept its almost miraculous nature, that is an "emergent property" not contained in the simple laws of physics, although it is a consequence of them.*

- *Transitions to rigid, glass-like states, may entail a hidden, microscopic order parameter which is not a microscopic variable in any usual sense, and describes the rigidity of the system. This is the fundamental difficulty of the order-parameter concept: at no point can one be totally certain that one can really exclude a priori the appearance of some new hidden order.*

I. Theory – model independent concepts

- Another crucial ingredient:

- Glasses freeze in a large excess entropy S_{xs} over the crystal ($\sim 1k_B$ per molecule*)

- There is not one but an exponential number of mechanically stable amorphous configurations

- In line with the fact that a minimum amount of complexity/frustration seems to be needed to make a glass

*Note: A fraction of this might be of vibrational origin

I. Theory – correlation lengths and susceptibilities

- A. Dynamical correlations

- Order parameter: $C(t) = \langle \delta\rho(\vec{x},t)\delta\rho(\vec{x},0)\rangle \xrightarrow{1 \ll t \ll \tau} q_{EA} > 0$

- Spatial correlation of temporal correlation:

$$G_4(\vec{x}-\vec{y},t) = \langle \delta\rho(\vec{x},t)\delta\rho(\vec{x},0)\delta\rho(\vec{y},t)\delta\rho(\vec{y},0)\rangle - C(t)^2$$

  Attempts to measure some cooperativity of the dynamics: is the motion at $\vec{x}$ necessary to trigger motion at $\vec{y}$?

- Dynamical susceptibility: fluctuations of correlation:

$$\chi_4(t) = V\langle[\delta C(t)]^2\rangle \equiv \int_{\vec{r}} G_4(\vec{r},t) \propto V_4\, F_4(t/\tau)$$

  defines a dynamic correlation volume $V_4(T)$

I. Theory – correlation lengths and susceptibilities

- B. Dynamical response

- For Newtonian dynamics: measures the correlation between enthalpy fluctuations and dynamics

$$\chi_T(t) = T\frac{\partial C(t)}{\partial T} = \frac{1}{k_B T}\int_{\vec{r}} \left\langle \delta\rho(\vec{r},t)\delta\rho(\vec{r},0)\delta h(\vec{0},0)\right\rangle$$

- A "magic" lower-bound: (Berthier et al.)

$$\chi_4(t) \geq \frac{1}{c_p}\left[\chi_T(t)\right]^2$$

- Allows one to measure V_4 from the temperature dependence of $C(t)$!

I. Theory – correlation lengths and susceptibilities

- Is this too good to be true? – Various remarks

- a) χ_T defines a correlation volume V_T, with $V_4 \propto V_T^2$??

- b) χ_4 in fact depends both on ensemble and dynamics !!

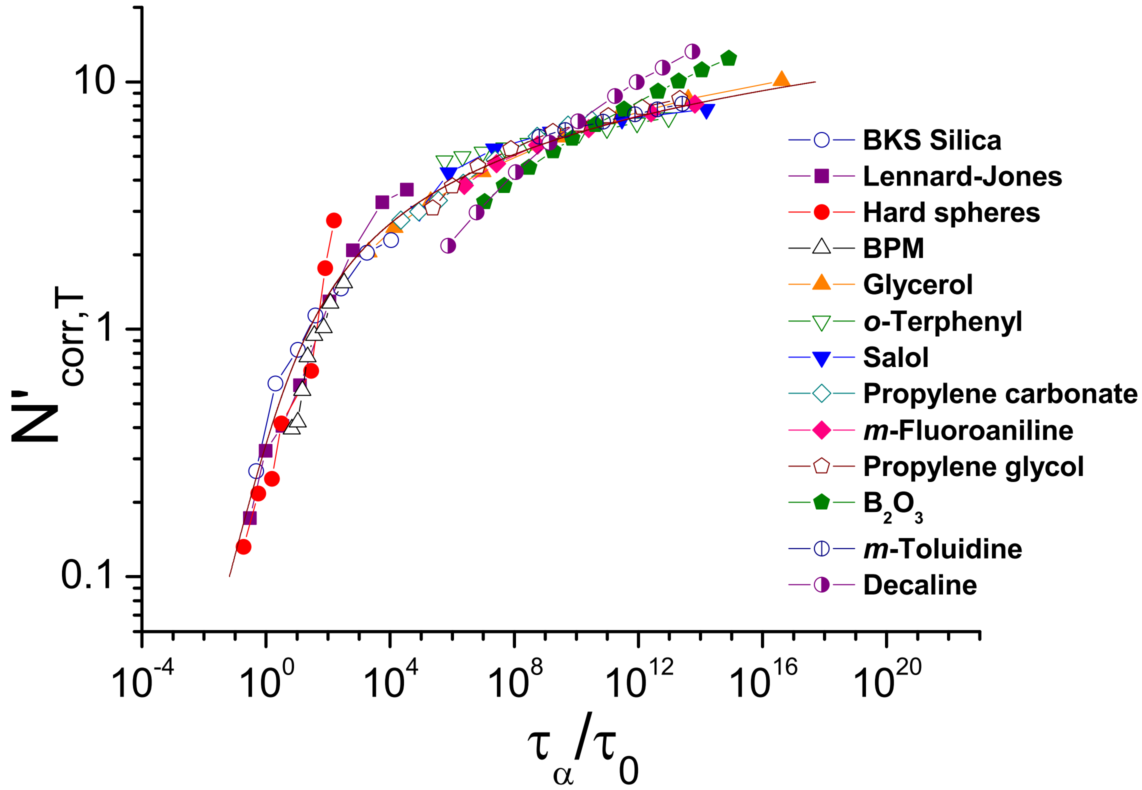
  $$G_4(\vec{q},\tau) \propto \xi_d^{2-\eta} H_1(q\xi_d) + g(q) \left[\xi_d^{2-\eta} H_2(q\xi_d)\right]^2 \qquad V_T = \xi_d^{2-\eta}$$

  $g(q)$ depends on Newtonian/Brownian and Ensemble (NVT/NVE, etc.) For example, $g(q=0)=0$ for NVE...

  $\rightarrow$ the direct interpretation of χ_4 is ambiguous.

- c) χ_T diverges as $1/T$ for a purely Arrhenius system (??)

The dynamical correlation volume



$N_T \propto V_T$; Dalle-Ferrier et al

I. Theory – correlation lengths and susceptibilities

- C. "True" susceptibilities

- $\chi_{\vec{q}}(\vec{k},t)$ measures how the dynamics on scale $1/k$ is affected by a perturbation on scale $1/q$ $(V_T = \xi_d^{2-\eta})$

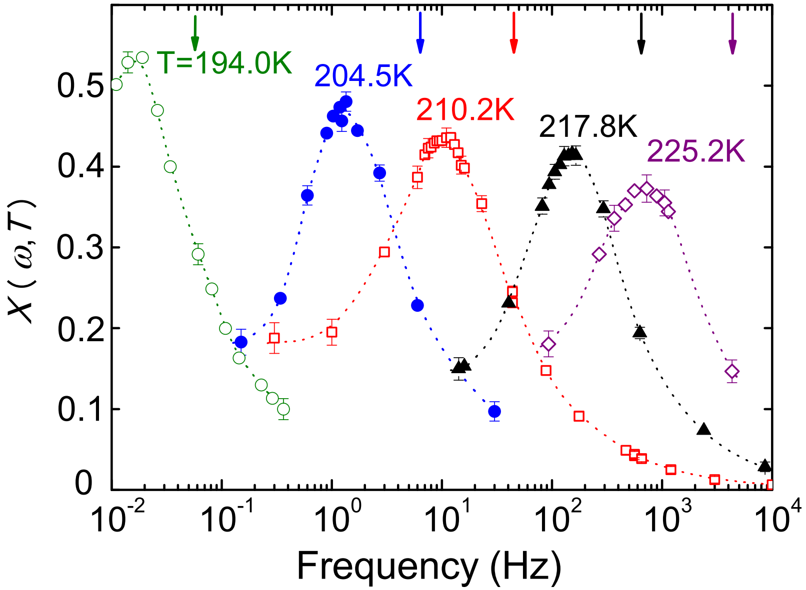
$$\chi_{\vec{q}}(\vec{k},t) = \frac{\partial C(\vec{k},t)}{\partial U(\vec{q})} \propto V_T H(q\xi_d) \qquad \chi_{\vec{q}=0}(\vec{k},t) = \chi_T$$

- Non-linear response χ_3, i.e. non-linear dielectric susceptibility

$$\chi_3(\omega,T) = \frac{\chi_1^2 a^3}{k_B T} V_T \mathcal{H}(\omega\tau),$$

- Much harder to access experimentally

Non-linear dielectric constant



Curves can be rescaled, and variations of height of maximum V_T compatible with the determination from χ_T (Thiberge et al, PRL 2010)

I. Theory – correlation lengths and susceptibilities

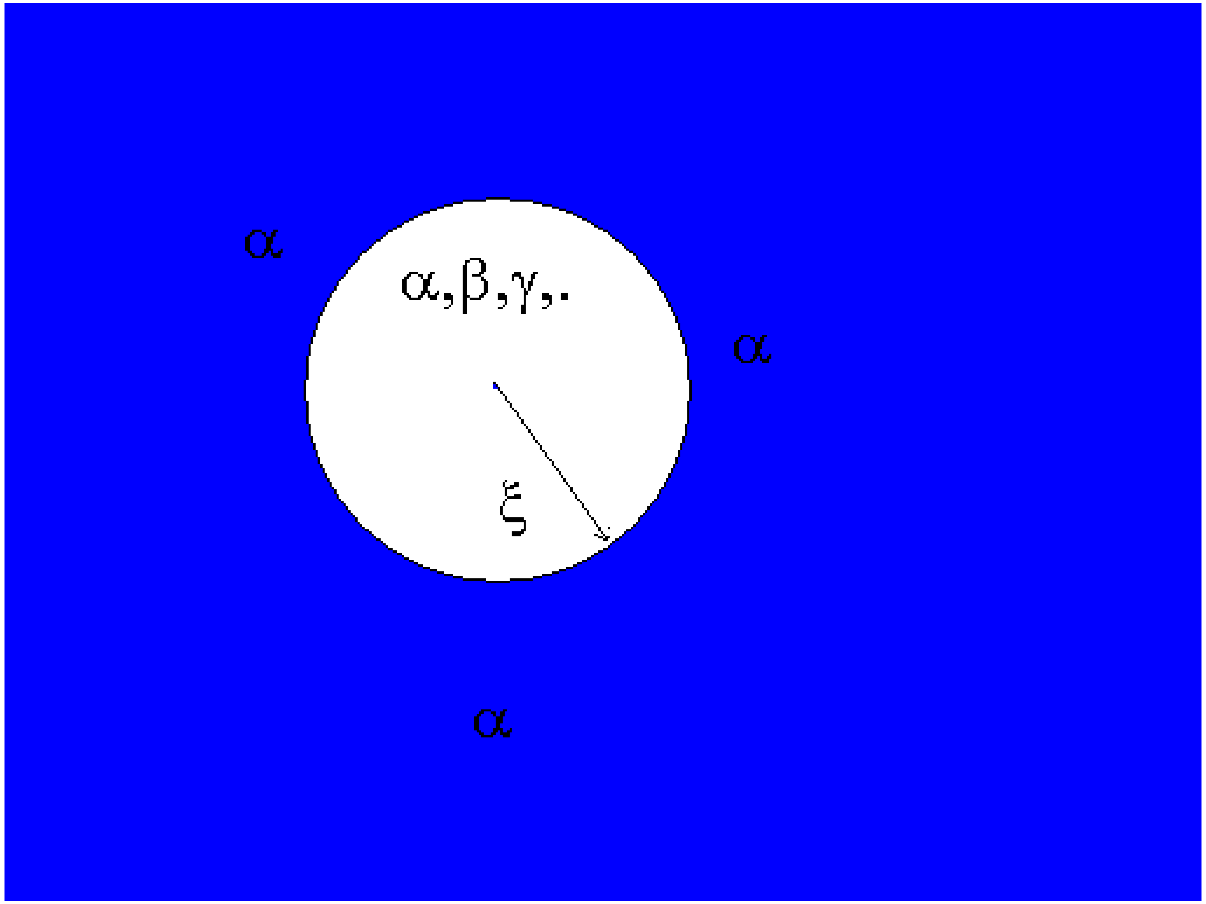
- D. Point-to-set correlation length

- Question: does a free cavity of size ℓ immersed in a frozen state α remain in state α at long times ?

- $\ell < \ell^*$: boundary conditions lock in state α: glass phase – a few configurations dominate: $q(in, \alpha) > 0$

- $\ell > \ell^*$: state α is irremediably lost among the exponential number of other possible states: "entropic melting" towards the liquid: $q(in, \alpha) = 0$

The cavity argument



with G. Biroli – cf also Montanari-Semerjian-Franz

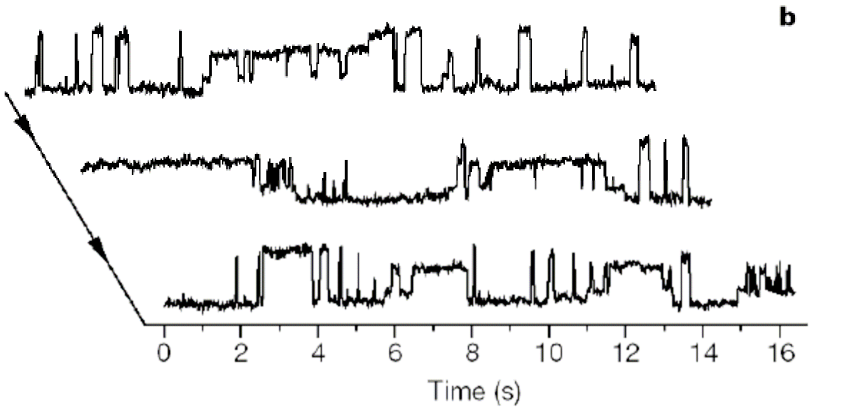
I. Theory – correlation lengths and susceptibilities

- ℓ^*: point-to-set correlation length – a purely static definition

- ℓ^* should also be the dynamical 'cooperative' length since smaller length scales cannot decorrelate without a change of the boundaries (cf. Israeloff experiments)

- This is suggested by a rigorous result by Montanari-Semerjian: τ cannot diverge unless ℓ^* diverges and by a preprint by Cavagna et al. today!!

Observing time dependent ‘states’



A few states dominate, but these states and their relaxation times evolve with time (Vidal-Russel & Israeloff, 2001)

I. Theory – correlation lengths and susceptibilities

- Suggests a "Gedanken experiment" that can be simulated and indeed leads to a growing $\ell^*(T) = 0.85 \to 3.8$ from $1.5T_c$ to $0.9T_c$ (Cavagna et al.)

- Maybe a true experiment someday ?

- What is the relation between ℓ^* and ξ_d? Some facilitation mechanism highly plausible and presumably $\xi_d > \ell^*$

I. Theory – correlation lengths and susceptibilities

- Other length scales ?

  *) FSS length ℓ_G (Karmakar et al.):

  for $\ell < \ell_G$, $P[C(\tau)] \approx \frac{1}{2}\delta(C) + \frac{1}{2}\delta(C - q_E A)$,

  for $\ell \gg \ell_G$, $P[C(\tau)]$ becomes Gaussian

  *) Spatial structure of soft-modes, plastic deformation zones, in particular:

  *) Shear induced reconfiguration of inherent states $\rightarrow \ell_{sh}$ that also seems to grow markedly as T decreases (Mosayebi et al., 2010)

I. Theory – model independent concepts

- More ideas: (but no time!)

- Thermodynamics of space-time trajectories (Ruelle, Garrahan-Chandler-Jack): a probe of the large deviation structure of mobile trajectories and possible phase-transitions

- Isoconfigurational ensemble and dynamic propensity (Harrowell): soft regions (where q_{EA} is anomalously small) appear to be faster

- Etc.

II. Theory – first principle approaches

- A. Mode-Coupling Theory

- MCT – still regarded by many as a first-principle approach that leads to quantitative predictions for the dynamics in terms of the static structure factor $S(\vec{k}) = C(\vec{k}, t = 0)$.

  A transition T_c appears, below which $q_{EA} > 0$ and a non zero shear modulus G_∞

- Well known problem: activated processes kill the MCT transition, replaced by a cross-over (see below)

- Several quantitative successes, in particular for the shape of the plateau $q_{EA}(\vec{k})$ for hard-spheres – although the predicted MCT density 0.52 is quite off the fitted value 0.59

II. Theory – MCT

- Recent results suggest that this quantitative success might be largely coincidental, or needs further justification
  - MCT treatment of hard-spheres in $d > 4$ becomes inconsistent, and catastrophic when $d \to \infty$ (Schmid & Schilling; Ikeda & Miyazaki, 2010)
  - A model where the attraction part of the potential can be turned on and off without changing $S(\vec{k})$ is seen to change dramatically the dynamics (Berthier & Tarjus, 2010)

II. Theory – MCT

- More reasonable to understand MCT as a Landau theory for

$$\delta C(t) = C(t) - q_{EA} \ll 1$$

that in turn describes a generic phase-space transition where local rigidity appears (Andreanov, Biroli, JPB, 2009) –

Mathematical structure of the theory OK, but parameters are ad-hoc!

II. Theory – MCT

- A major progress: the MCT transition is associated with the divergence of a correlation length (expected on physical ground, but strangely denied by the founding-fathers)

- Inhomogenous MCT: $C(\vec{k},t) \to C(\vec{k},\vec{r},t)$ and explicit scaling form for the dynamical response (Biroli, JPB, Miyazaki & Reichman):

$$\chi_{\vec{q}}(\vec{k},t=\tau_\beta) = \xi_d^2 \mathcal{F}_\beta(q\xi_d); \qquad \chi_{\vec{q}}(\vec{k},t=\tau_\alpha) = \xi_d^4 \mathcal{F}_\alpha(q\xi_d)$$

- Single diverging length scale in both regimes: $\xi_d \sim |T - T_c|^{-1/4}$

- The 'cage' β-relaxation is already collective: 'cages' are in fact extended!

II. Theory – MCT

- A necessary consequence: critical fluctuations cannot be neglected close to T_c when $d < 8$ and are expected to change all MCT predictions

- These critical fluctuations interact in an unknown way with:

  – activated events (present even above T_c)

  – 'Harris' fluctuations due to self-induced disorder (also relevant when $d < 8$...)

- Is there *any* regime where MCT makes useful predictions? see below

II. Theory – first principle approaches

- B. Replicas

- Conceptual difficulties at the heart of the glass problem:

  *) no obvious order parameter

  *) exponential number of possible metastable states

- These items are shared by spin-glasses, for which "long range amorphous order" has a precise meaning

II. Theory – first principle approaches

- Replica theory is the natural language to deal with a large number of metastable states

- 1-RSB spin-glass models share an intriguing number of similarities with the phenomenology of glasses (Kirkpatrick, Thirumalai, Wolynes 1980's)

II. Theory: 1-step RSB solution

- Two transition temperatures: $T_c > T_K > 0$

- $T > T_c$: most probable states are unstable saddles that become marginally stable at T_c (cf. the Goldstein phenomenon); the dynamics is exactly described by MCT equations

- $T_K < T < T_c$: system trapped in one of the exponentially numerous state, but thermodynamically $f_{liquid} = f_{state} - TS_c$.

- $T_K < T < T_c$: high frequency shear modulus G_∞ is positive and jumps to zero for $T = T_c^+$

- Below T_K the system is an ideal glass (amorphous ground state), where $S_c = 0$

II. Theory: Replicas

- What can long range interacting spin model with weird interactions ever teach us about molecules that stop jittering around? (Langer)

- Many schematic models of glasses are described by a 1-RSB transition (lattice glass: Biroli-Mézard ; Coniglio et al.)

- Reasonable analytical approximation of model systems ALL lead to a 1-step RSB solution for the thermodynamics and MCT for dynamics [liquids: Stoessel-Wolynes (DFT), Mézard-Parisi-Franz (Replicas); frustrated Coulomb systems: Schmalian et al., Tarjus et al.]

- With some remarkable quantitative predictions, (hard-sphere glass: Parisi-Zamponi ; shear modulus: Yoshino-Mézard)

III. Phenomenology: RFOT

- After a decade of work, 1-RSB seems to be the generic MF theory for systems with a large number of local minima – why not accept it?

- *I do not think these mean-field models can be used to predict the divergence of the viscosity. On the contrary, I think the mechanisms that produce molecular rearrangements in glasses must be localized and that long-range models inevitably fail to describe such mechanisms properly* (Langer)

- Space and locality, absent in mean field, must be restored – this is the whole point of RFOT

III. Phenomenology: RFOT

- Early nucleation arguments by Wolynes et al. can be rephrased in terms of a point-to-set length $\ell^* \propto (\Upsilon/S_c)^{1/d-\theta}$, resulting from a competition between configurational entropy $S_c(T)$ and "surface energy" ΥR^θ

- Mean-field phases can only be given a meaning for small scales $\ell < \ell^*$ but "melt" above ℓ^* – the "mosaic" state

  *) For $d \to \infty$, $\Upsilon \to \infty$ and $\ell^* \to \infty$: mean-field

  *) When $S_c \to 0$ $(T \to T_K)$, $\ell^* \to \infty$: ideal glass

- Picture confirmed by the analysis of Kac models (Franz-Montanari)

III. The mosaic and thermodyn./dyn. connection

- Suppose that energy barriers grow as $\widetilde{\Upsilon}\ell^{\psi}$

- Small scales $\ell < \ell^*$ are fast but cannot decorrelate since only a few states are available

- $\ell \approx \ell^*$ are the fastest droplets that allow the system to explore many zero-overlap states and decorrelate

$$\to \ln \tau(T) = \ln \tau(\ell^*) \sim \frac{\widetilde{\Upsilon}}{T}\left(\frac{\Upsilon}{TS_c}\right)^{\psi/(d-\theta)}$$

- Wolynes: $\psi = \theta = d/2$, $\Upsilon = \widetilde{\Upsilon} = \kappa T$ $\to$ Vogel-Fulcher – super-Arrhenius slowdown comes from the growth of ℓ^*

III. Phenomenology: RFOT

- Is a consistent finite-d interpretation of the natural mean-field (1-RSB) theory of glasses

- Explains naturally the Adam-Gibbs correlations beween thermodynamics and dynamics:

  - Single liquid: $\ln \tau \sim [TS_{xs}(T)]^{-1}$

  - Cross sectional:

$$m = \left.\frac{\partial \log_{10} \tau}{\partial \ln T}\right|_{T_g} \propto \Delta C_p|_{T_g} \propto \beta^{-1}$$

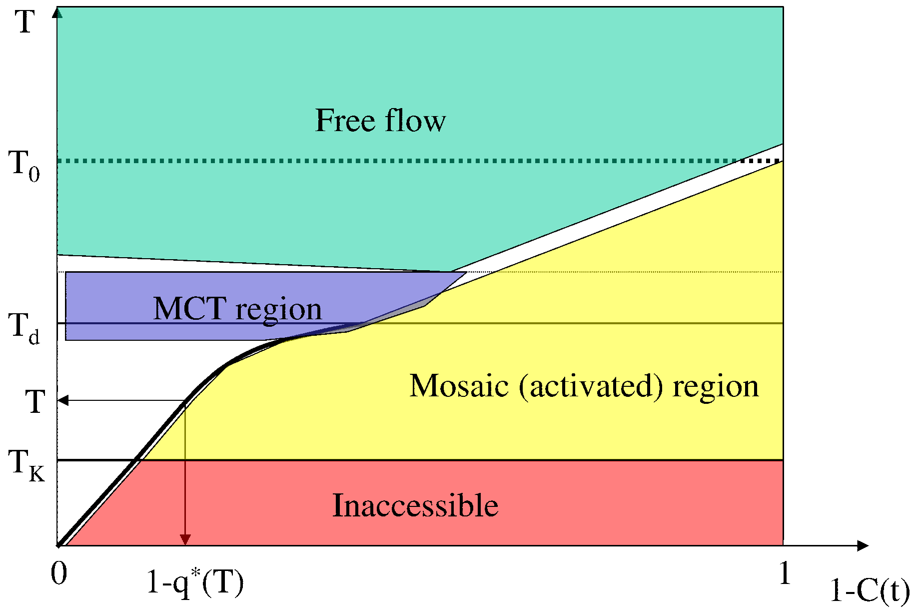
- Accounts for the correlation between fragility m and stretching of the relaxation β

III. Phenomenology: MCT-RFOT

- Deep stable 'glassites' of size ℓ have a finite probability to appear *even above* T_c, and unstable states can be present below T_c

- Activated events are expected above T_c in finite dimensions/size (see e.g. ROM), and on general grounds should dominate the long time dynamics, whereas short times should be governed by MCT

Conjecture – the MCT “sliver”



A quantitative (Ginzburg) calculation?

III. RFOT: a big worry

- Three related comments:
  - a) A very successful formula (Hall & Wolynes, Dyre)

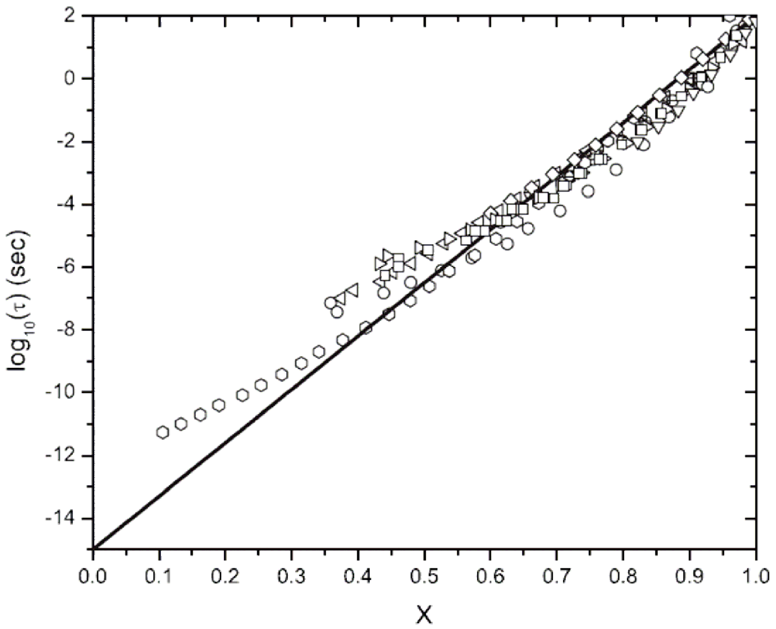
$$\ln \tau(T) = A \frac{a^2}{\langle u^2 \rangle_{pl}(T)} = A' \frac{G_\infty(T) a^3}{k_B T}$$

    Relates short time dynamics to long time dynamics: (see e.g. Niss et al., Torchinsky, ...)

    A large part of the super-Arrhenius slow down is accounted by the (expected) growth of $G_\infty(T)$!!

  - b) Why aren't $\Upsilon, \widetilde{\Upsilon}$ given by $G_\infty(T)$ in RFOT ??
  - c) If $G_\infty(T)$ appreciably changes with temperature, so does the vibrational contribution to S_{xs} and ΔC_p and could mimic Adam-Gibbs correlations (see Wyart, Biroli & JPB)

An Elastic view of glasses



$X = T_g G_\infty(T)/T G_\infty(T_g)$, from Torchinsky et al., 2009

III. Phenomenology: The "shoving" model

- Dyre's model: in order to flow, the system must nucleate a void of volume $\sim a^3$ by "shoving" molecules aside

- Nucleation events are rare but happen fast $\longrightarrow$

$$\Delta E = A' G_\infty(T) a^3$$

- Relies on the proximity of the Goldstein crossover to explain the growth of $G_\infty(T)$

III. Phenomenology: The "shoving" model

- The quantitative Adam-Gibbs relation between $\ln \tau$ and S_c is awkward to explain

- No growth of any cooperative length ℓ^*, not clear why ξ_d should grow or where dynamical heterogeneities come from

- No natural connection between fragility and stretching

- Should revert to Arrhenius at low temperatures: no cooperativity = no singularity!

- Why not mixing RFOT with Dyre's idea, with $\Upsilon \propto G_\infty(T)$ and a mild growth of ℓ^*?

III. Phenomenology: Frustration Limited Domains

- Postulates: Kivelson-Tarjus

  *) A liquid is characterised by a locally preferred structure (LPS) which is different than that of the crystalline phases

  *) Because of geometric frustration, the LPS characteristic of a given liquid cannot tile the whole space

- Common points with RFOT:

  *) Existence of a Goldstein temperature below which the system is locally rigid

  *) The size of the "glassites" ℓ^* grow when T decreases $\rightarrow$ super-Arrhenius behaviour

  *) Microscopic models for FLD lead to a 1-RSB scenario when treated analytically !

III. Phenomenology: Frustration Limited Domains

- Differences:

  *) Finite vs. extensive degeneracy of LPS (metastable states of RFOT are amorphous LPS)

  *) No ideal glass transition or Kauzmann temperature T_K

  *) Difficult to reconcile with the Adam-Gibbs correlations

- Good points:

  *) LPS have been identified in model systems (Coslovich et al.)

  *) Simulations on the hyperbolic plane, where frustration can be tuned, in broad agreement with theory (Sausset et al.)

III. Phenomenology: Kinetically Constrained Models

- Theories start again from the assumption that some local rigidity exists $\rightarrow$ motion is difficult

- Motion is only possible in the presence of a point-like "defect" that itself can only move thanks to the nearby presence of other defects (facilitation)

- The concentration of defects $\propto e^{-J/T}$, *strictly conserved*

- Kinetic constraints can lead to interesting non-Arrhenius behaviour, for example $\tau \propto e^{(J/T)^2}$ and reproduce some of the phenomenology of glasses (Garrahan-Chandler)

III. Issues with Kinetically Constrained Models

- Thermodynamics is forgotten from day one $\longrightarrow$ no Adam-Gibbs correlations –

- What is the physical mechanism underlying local rigidity? (which is after all the main feature of glasses!)

- If KCM represent a coarse-grained description of glasses, what is the coarse-graining scale?

  Shouldn't the size ℓ^* of "glassites" be the elementary scale?

- Why should mobility defects be (nearly) conserved? There are indications that spontaneously generated mobility becomes dominant as the glass is approached

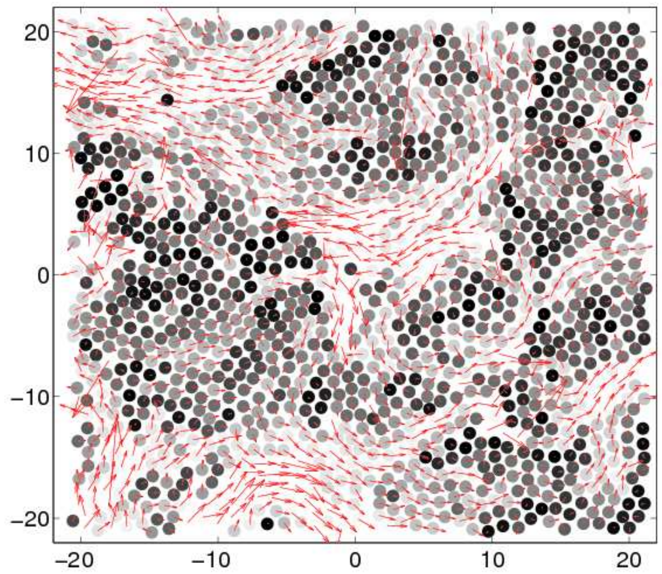
III. Phenomenology: Others

- Chain excitations (Langer et al.)
- Mapping onto a spin-glass in a field (Moore et al.)
- etc.

Summary & partial conclusions

- Some striking experiments
  - Nanoscale experiments revealing the heterogeneous, intermittent nature of the dynamics (Ediger, Israeloff, Kaufmann, Cipelletti)
  - Non-linear susceptibility experiments revealing in a non ambiguous fashion the growth of “amorphous order” as in spin-glasses (Saclay group)
  - Visualization of dynamical heterogeneities (colloids – Weeks, granular – Dauchot)
  - Super-stable glass samples (Ediger) – deep amorphous ground states of RFOT?

Dynamic susceptibility close to Jamming



with F. Lechenault, O. Dauchot, G. Biroli

Summary & partial conclusions

- MCT
  - Should be viewed as a Landau theory of the Goldstein phenomenon: the appearance of stable minima in the free-energy landscape leading to rigidity
  - This is a collective phenomenon, charaterized by a diverging length scale – escape directions of marginally stable saddles involve many particles

Summary & partial conclusions

- RFOT
  - Pros: natural mean-field theory to describe complex systems with many minima, encompassing MCT

    Convincing extension in finite d where configurational entropy limits the size of the 'glassites' and governs the relaxation time

  - Cons: many fuzzy concepts (i.e. "surface tension" Υ) and the related "elastic" problem – the role of $G_\infty(T)$ in the dynamics seems important, is there room left for a growing cooperative scale?

- Conversely, the local elastic picture of Dyre seems to miss the collective effects and point-to-set correlations

Summary & partial conclusions

- Needed

  – Some major analytical progress on a finite d system where RFOT is expected to hold, in particular to understand the MCT-RFOT crossover – a major challenge

  – or at least a finite d system that can be convincingly simulated in both the MCT and activated regime – the finite d candidates unfortunately, can only be simulated above T_c....like all 'hard' models? (ROM Sarlat, Billoire, B&B 2009, lattice glass de Candia, Mauro, Coniglio 2009)

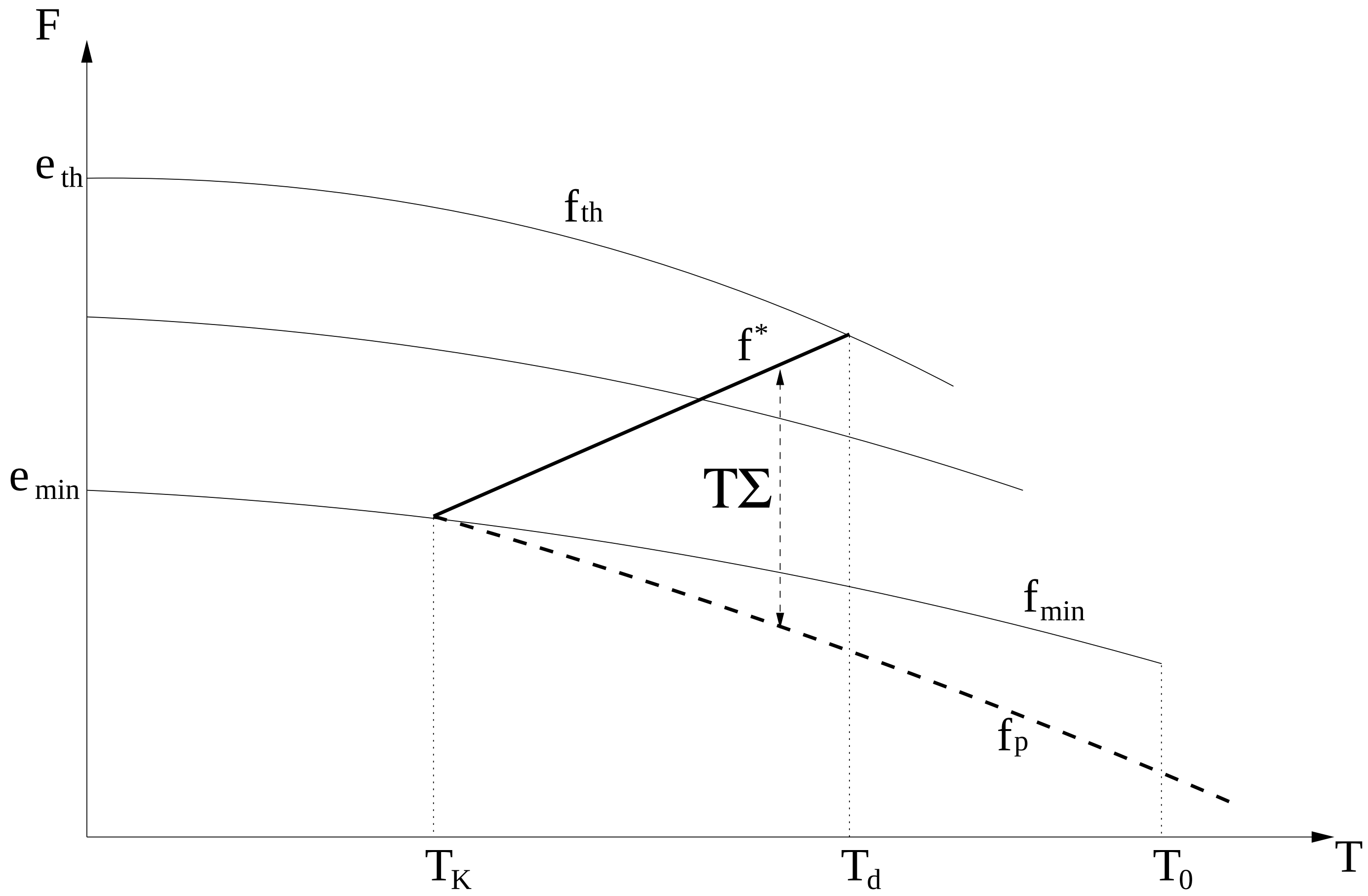
  – A smoking gun experiment? – energy relaxation, role of shear, glass microfluidics, fracture, aging, rejuvenation?

Glasses: too many theories?

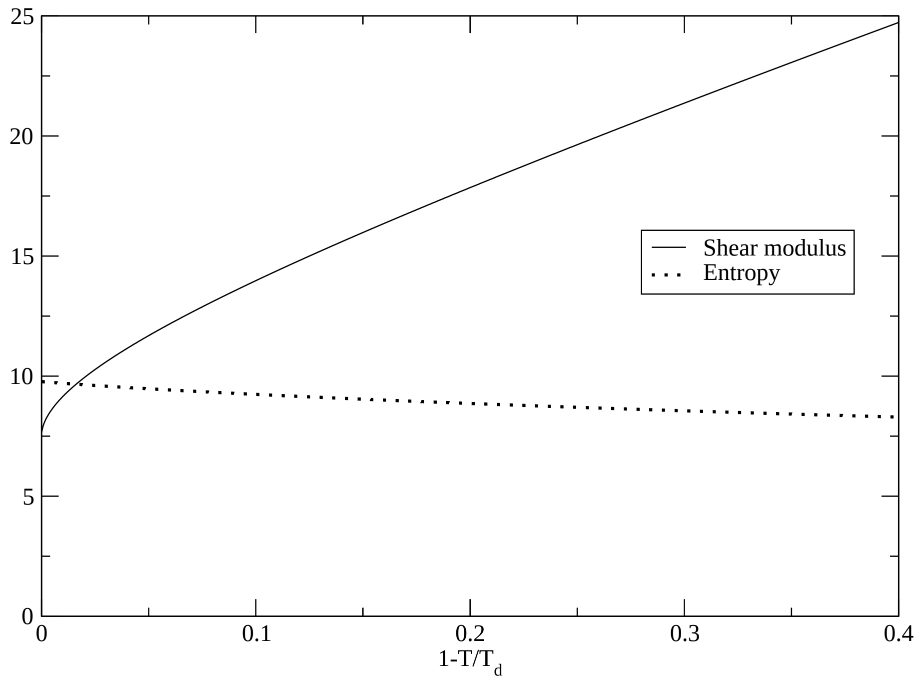
- *Details that could throw doubt on your interpretation must be given, if you know them. You must do the best you can – if you know anything at all wrong, or possibly wrong – to explain it. If you make a theory, for example, and advertise it, or put it out, then you must also put down all the facts that disagree with it, as well as those that agree with it.*

  (R. P. Feynman)

Appendix: The 1-RSB solution



Appendix: Shear modulus



Appendix: measuring surface tension

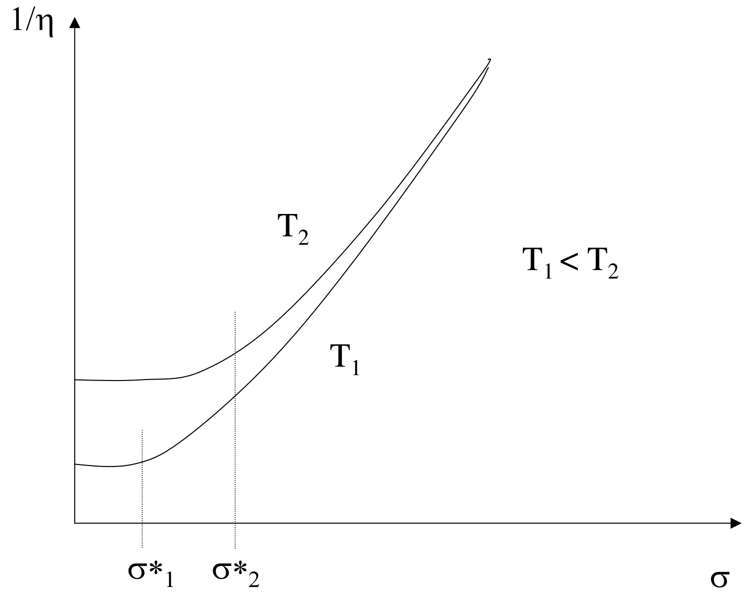
- Within the mosaic scenario, one expects that the excess energy or volume after a quench should be dominated by excess interfaces that disappear and should decay as:

$$e(t) - e_\infty = \frac{\Upsilon \ell^\theta(t)}{\ell^d(t)} F\left[\frac{\ell(t)}{\ell^*(T)}\right] \qquad \ell(t) = \left(\frac{T \ln t}{\widetilde{\Upsilon}}\right)^{1/\psi}$$

- This should give a direct measure of $(d-\theta)/\psi$ and Υ, numerically (Cammarota?) and experimentally (Kovacs?)

- For "point defect" scenarios, the decay should be faster: $t^{-d/z}$ instead of $(\ln t)^{(\theta-d)/\psi}$

Appendix: Flow curves with the RFOT



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with G. Biroli: counter-intuitive evolution of σ_Y $(T_1 < T_2)$, inverse to that of the "shoving" model