Effective theories of the glass transition: thermodynamic versus dynamic approaches

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Warwick 2014

Outline

- In search of an effective theory and an appropriate order parameter for the glass transition: dynamic or thermodynamic?
- Contrasting the dynamical facilitation and the landscape approaches. Enlarging the phase diagram.
- Mean-field dynamical transitions.
- Beyond mean-field: Constraints and pinning fields.

The glass transition: What makes the problem interesting...

There are hints that glass formation involves

- ✳some form of universality
- ✳some form of collective/cooperative behavior

Yet, of an unusual kind...

- ➡Search for **effective theories** of glass-forming liquids
- ➡What is the appropriate **local order parameter**? A **thermodynamic/structural** or a **purely kinetic** approach?

Some theoretical ingredients

- **Frustration**: The energy of a system cannot be minimized by simultaneously minimizing all the local interactions.

  => Multiplicity of low-energy ("metastable") states.

- **Thermal activation in a rugged (free) energy landscape**:

Presence of an exponentially large number of metastable states that may trap the system.

=> Relaxation slowdown is associated with thermally activated escape from metastable states.

- **Dynamical facilitation**: Mobility triggers mobility in nearby regions.

  => Spatial correlations in the dynamics.

Different ways to incorporate the ingredients in a general theory!

Local order parameter(s)

- **Local structural order**: Observables characterizing the locally preferred molecular arrangement in the liquid, if present (e.g., related to bond-orientational order).

  => e.g., poly-tetrahedral/icosahedral in metallic glasses.

- **Similarity or "overlap" between configurations:** Measures of the similarity between two equilibrium configurations of the liquid.

  High overlap => in the same state ("localized")

  Low overlap => in different states ("delocalized")

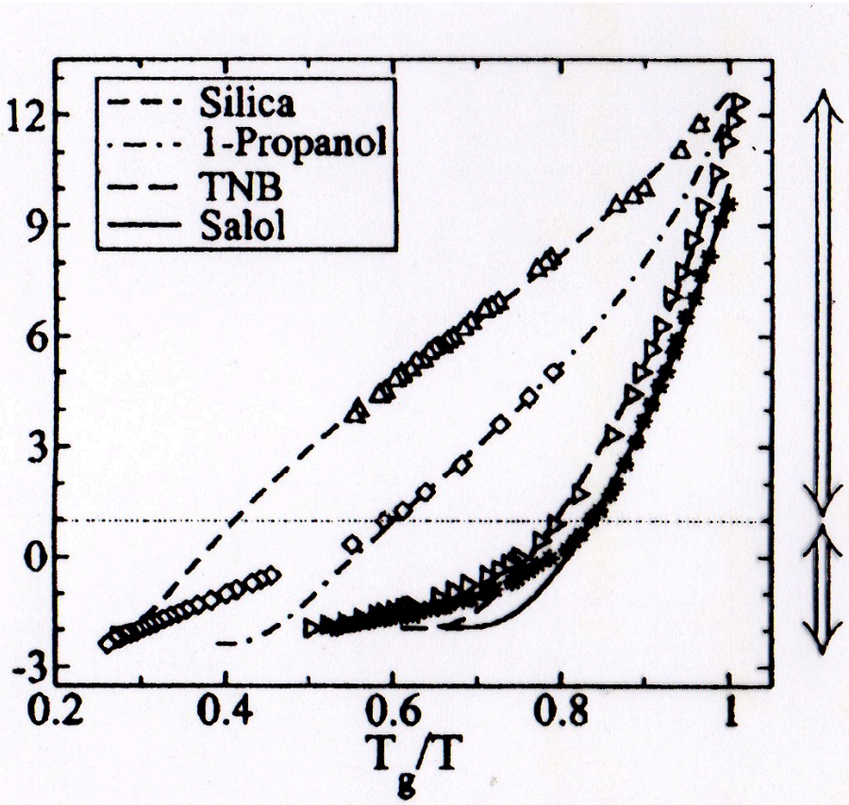
- **Local mobility field**: Mobility or activity defined by following the dynamics in small volumes of space over short periods of time.

  => Easier at low T where mobility is localized and scarce.

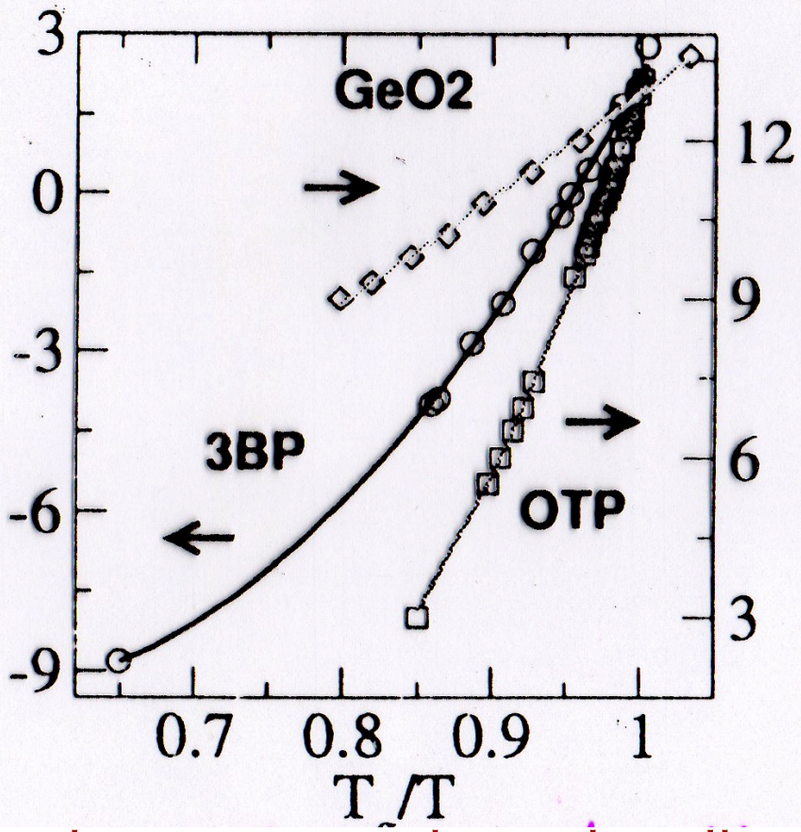
Which is the best starting point to describe glassy liquids?

Weak constraints from comparison to experimental data...

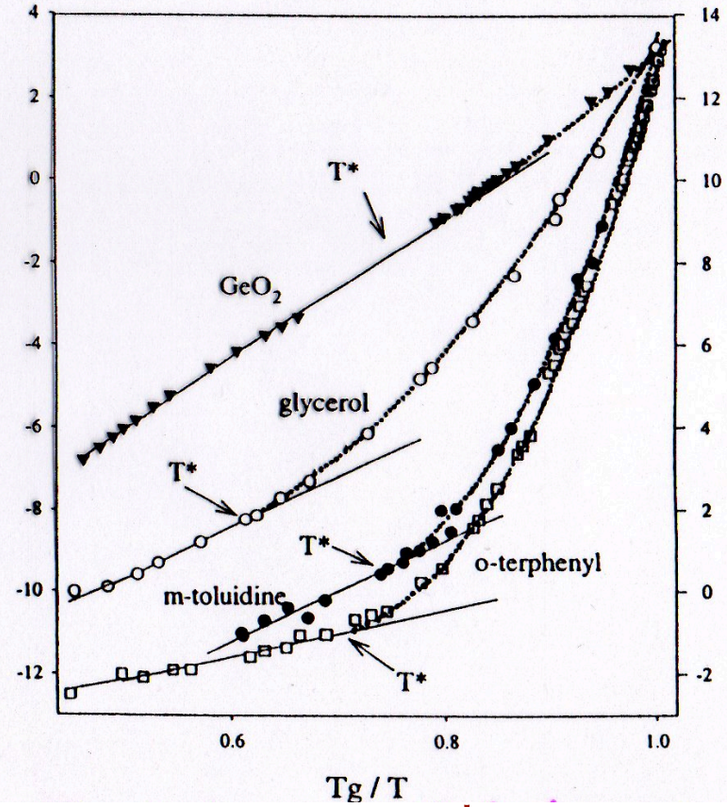
With the help of (unavoidable ?) adjustable parameters, several theories fit the same data equally well



Configurational entropy/RFOT (Wolynes et al.)



Facilitation (Garrahan-Chandler)



Frustration (Kivelson-GT)

log(viscosity or time) vs T_g/T

Focus on:

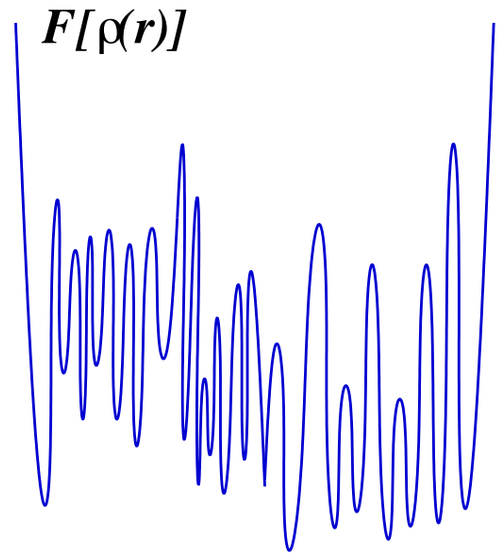
Dynamical facilitation & KCM's
(rarefaction of dynamical paths)
vs
free-energy landscape approach
(rarefaction of metastable states)

Contrasting the predictions by
enlarging the parameter space

The configurational entropy/landscape scenario as the mean-field theory of glass-forming liquids

[Wolynes, Kirkpatrick, Thirumalai, 80's + Parisi-Mezard-Franz +many!!!]

- **Exponentially large number of metastable states** that may trap the liquid (configurational entropy) between two temperatures, a dynamical transition at $\mathbf{T_d}$ and a "random first-order transition" at $\mathbf{T_K}$.
- Order parameter = overlap between equilibrium configurations => build a Landau functional through the replica formalism.



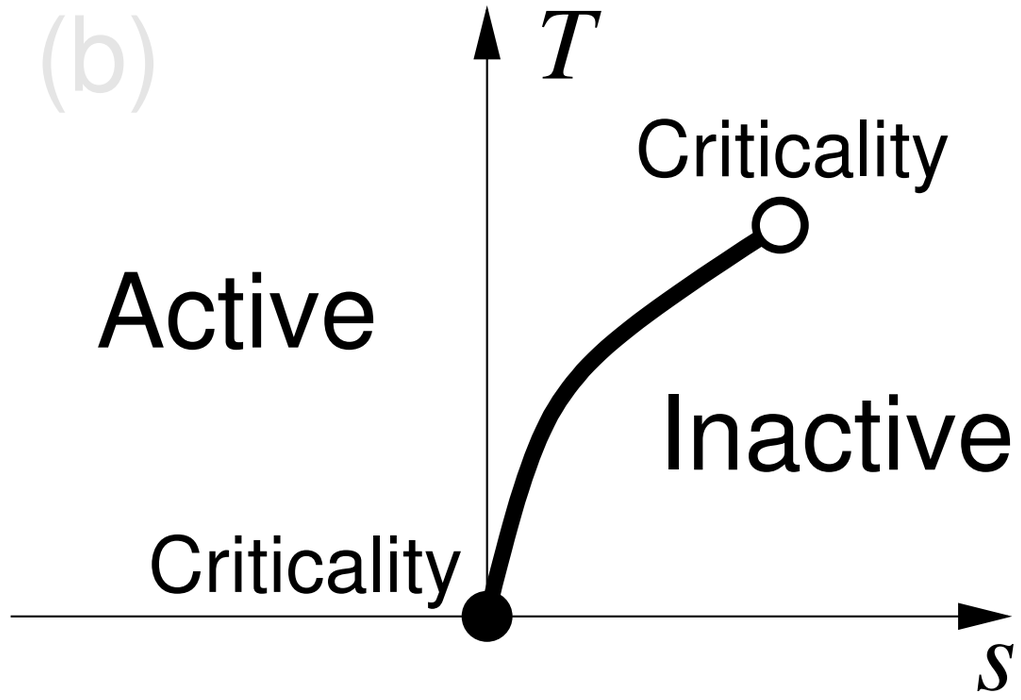
- Found in mean-field spin glasses, in mean-field-like approximations of liquids (HNC, DFT), in **the hard-sphere fluid in the limit of infinite spatial dimension** [Kurchan-Zamponi-Parisi, 2013-14]
- **Role of fluctuations in finite dimensions ???????????**

The importance of adding fields/constraints...

This is a way to enlarge the phase diagram, possibly generating bona fide transitions.

=> One can check qualitative behavior and universality classes without recourse to adjustable parameters.

For instance: In KCM's (dynamical facilitation), add a source ***s*** conjugate to the mobility field



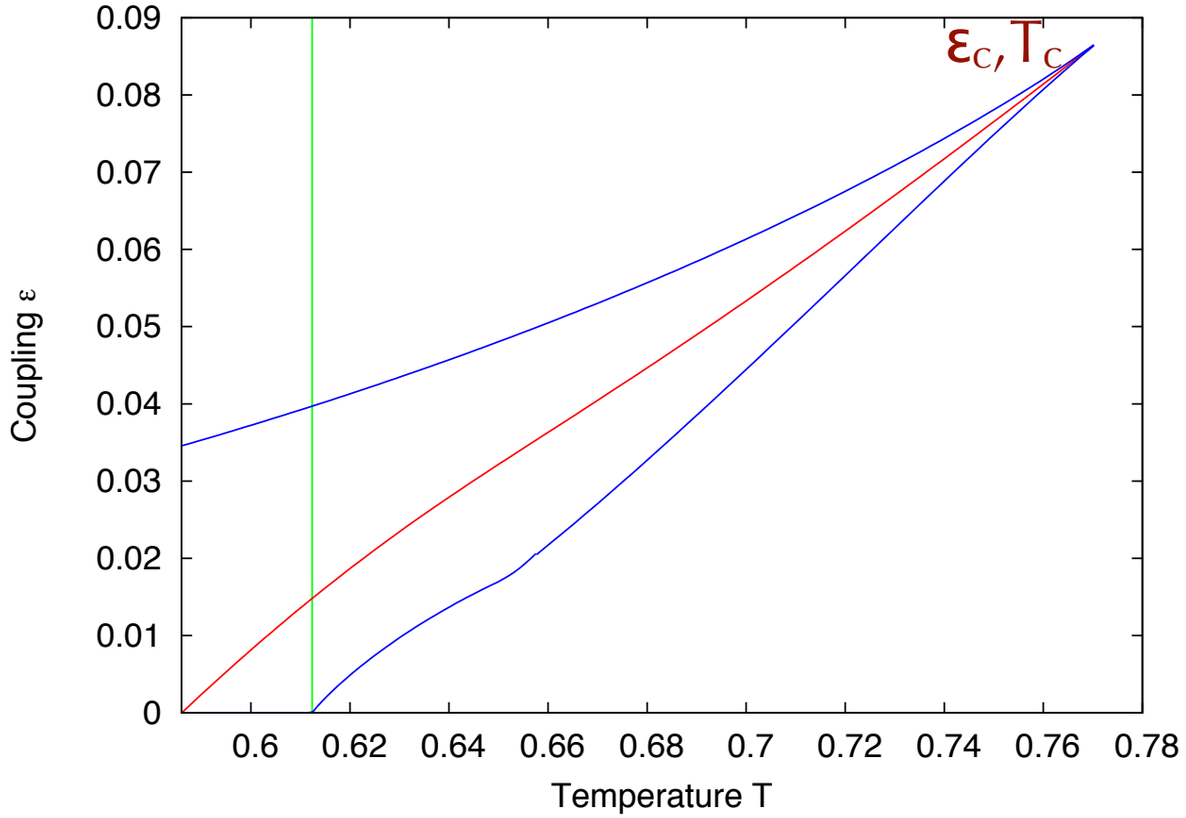
Non-equilibrium phase diagram T versus s [soft constraint, Elmatad et al., PNAS, 2010]

The importance of adding fields/constraints...

Similar spirit yet quite different: Adding equilibrium/ thermodynamic constraints induces new phase transitions and critical points in the **mean-field theory of glass-forming liquids and structural glasses** (random-first order transition scenario)

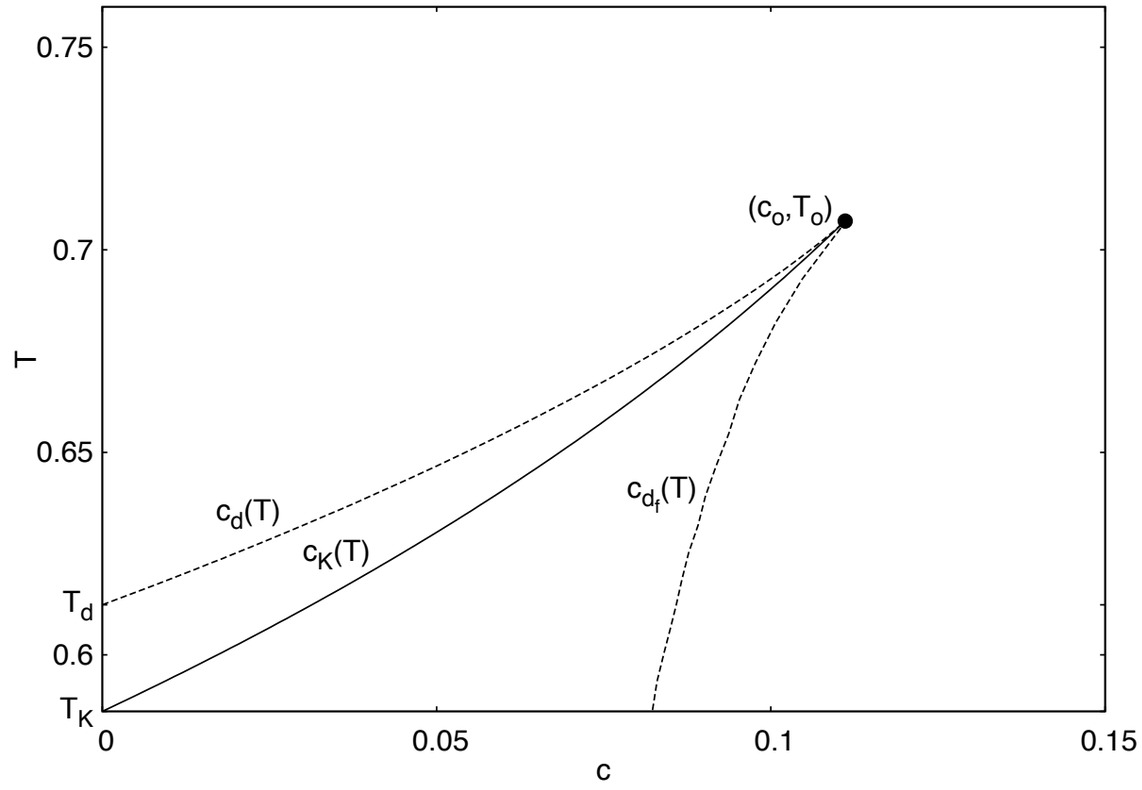
Field ε conjugate to the overlap versus T

[Franz-Parisi, PRL 1997]



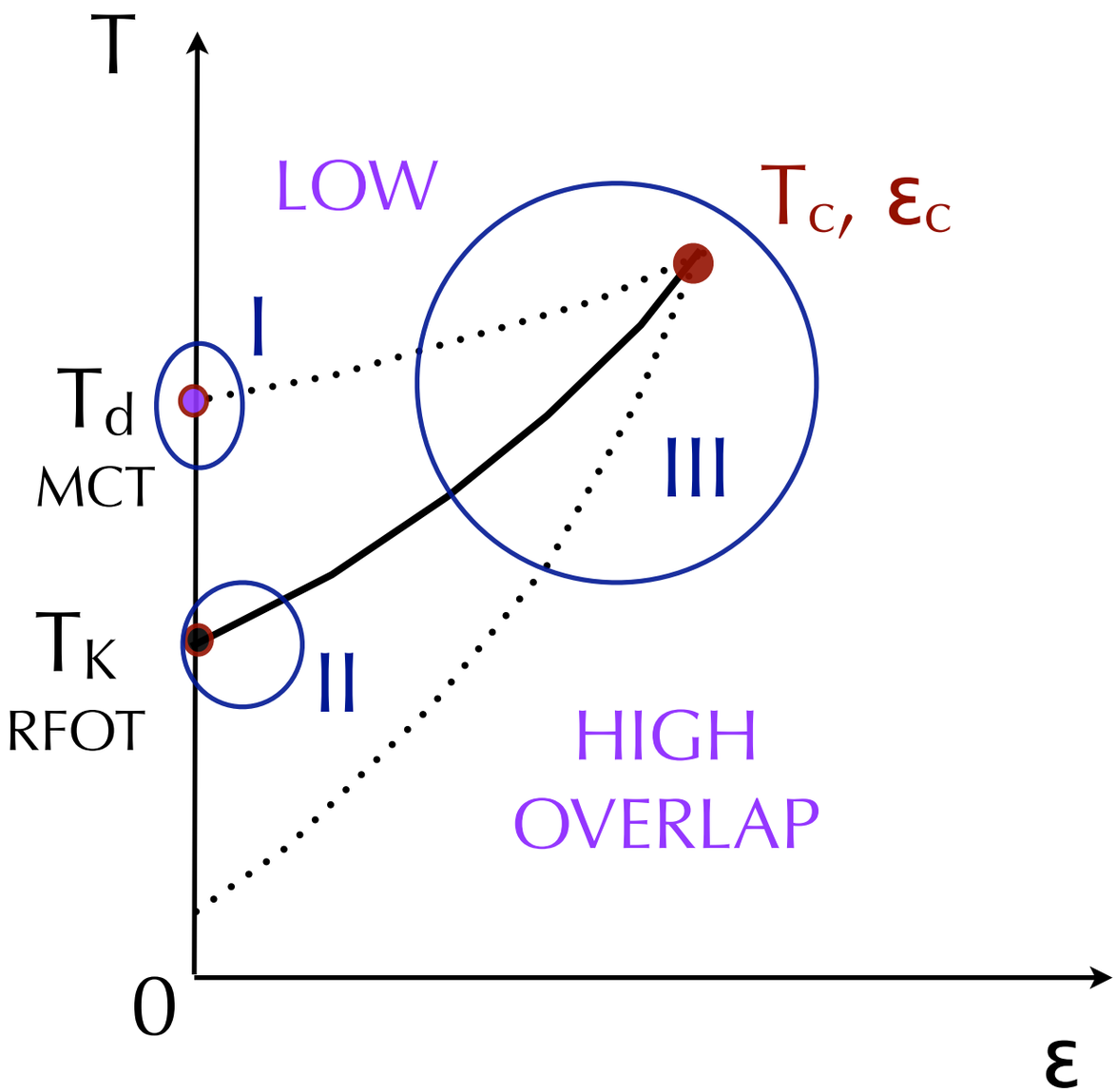
T versus the concentration of randomly pinned particles

[Cammarota-Biroli, PNAS 2012]



Contrasting dynamical-facilitation and configurational-entropy scenarios

Diagram T vs field **ε** conjugate to the overlap (sketch from mean-field theory): **3 regions of interest I, II, III**



—— : First-order transition

• • • • • • : Spinodal(s)

T_c, ε_c : Terminal critical point

T_d : Dynamical (MCT) singularity

T_K : Thermodynamical RFOT

Contrasting dynamical-facilitation and landscape scenarios

Obstacles for a direct comparison:

- Dynamical facilitation and KCM's have trivial thermodynamics.
- The landscape/configurational-entropy approach is essentially formulated at the mean-field level.

=> Introduce a mean-field limit in the dynamical facilitation models.

=> Map back KCM's on models without kinetic constraints and with nontrivial static (multi-spin) interactions.

=> Include fluctuations in the landscape approach.

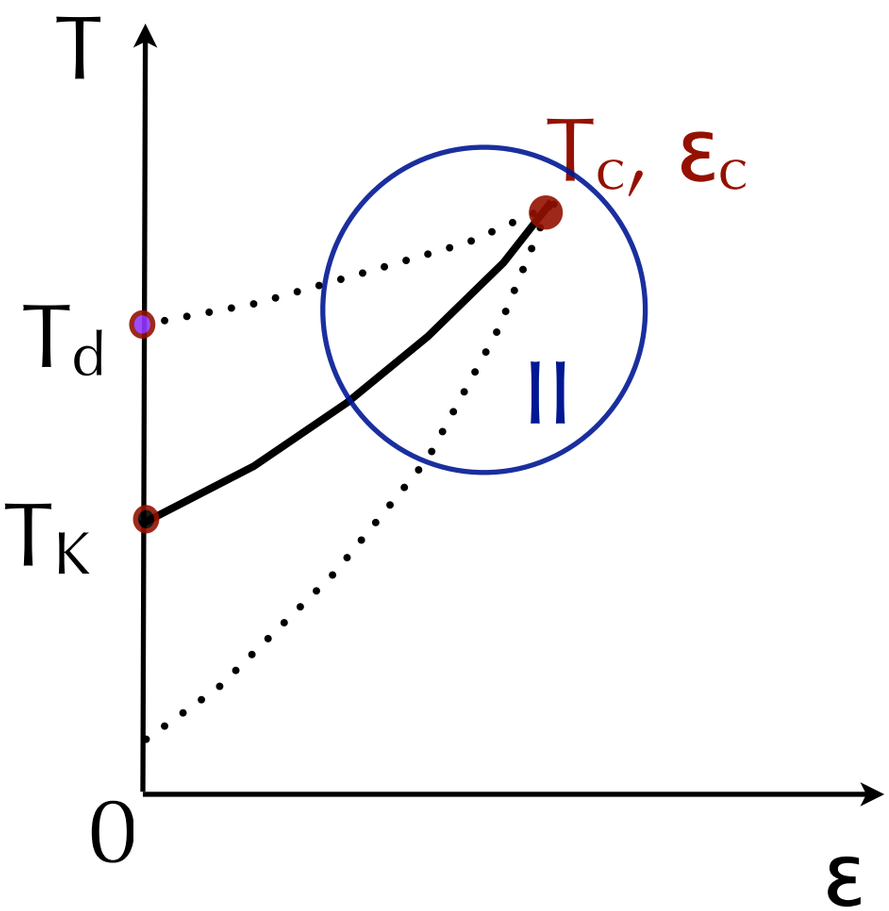
Contrasting ...: Region I near the (mean-field) dynamical glass transition

- **Quasi-equilibrium description of the beta-regime near the MCT transition (T_d):** Critical phenomenon can be described as a cubic field theory in a random source (RFIM spinodal, $d_{sup}=8$) for the **fluctuations of the overlap** between configurations [Franz, Parisi and coll., 2011-2013]
- **KCM's on Bethe lattice and regular random graphs** [a mean-field limit for dynamical facilitation]: The transition has the same character as MCT (discontinuous, relations between exponents, etc).
- **Yet, the order parameters for the quasi-equilibrium description are very different:** "nonlocal mapping" [Foini et al, J. Stat. Mech. 2012, Franz-Sellitto, J. Stat. Mech., 2013]
- Beyond mean-field: seemingly very different behaviors....

+ Digression on KCM's and bootstrap percolation on hyperbolic lattices
[Sausset et al., J. Stat. Phys., 2010]

Contrasting ...: Region II near the terminal critical point in a nonzero applied source coupled to the overlap

Mean-field RFOT-like phase diagram



- **For the landscape/thermodynamic approach:** Add fluctuations to the mean-field description -> Biroli, Cammarota, Tarzia, GT, PRL, 2014

- **For the dynamical-facilitation approach:** Consider spin models with plaquette interactions (duality with KCM's) -> Garrahan, PRE 2014

The overlap between configurations as an order parameter: Sketch of formalism (I)

- **Liquid (N,V,T)**: Hamiltonian $H[\mathbf{r}^N]$, with $\mathbf{r}^N$ = atomic configuration. Pick an equilibrium reference configuration $\mathbf{r_0}^N$ and define the microscopic overlap between $\mathbf{r}^N$ and $\mathbf{r_0}^N$ as

$$\hat{q}_x[\mathbf{r}^N, \mathbf{r_0}^N] = \sum_{i,j=1}^{N} f(|\mathbf{r}^j - \mathbf{r_0}^i|)\delta(\mathbf{x} - \frac{\mathbf{r}^j + \mathbf{r_0}^i}{2})$$

where $f(r) = 0$ for $r > a$ with $a << $ atomic diameter

- Define an overlap field $p(x)$ and its associated effective hamiltonian:

$$S[p; \mathbf{r_0}^N] = -\log \int \frac{d\mathbf{r}^N}{N!}\, \delta[p - \hat{q}[\mathbf{r}^N, \mathbf{r_0}^N]]\, e^{-\beta H[\mathbf{r}^N]}$$

- The correlation functions are generated by the functional $W[\boldsymbol{\varepsilon}; \mathbf{r_0}^N]$:

$$W[\epsilon; \mathbf{r_0}^N] = -\log \int \mathcal{D}p\, e^{-S[p;\mathbf{r_0}^N] + \int_{\mathbf{x}} \epsilon(\mathbf{x})p(x)}$$

Sketch of formalism (II)

- One is interested in the cumulants of $W[\boldsymbol{\varepsilon}; \boldsymbol{r_0}^N]$, $S[p; \boldsymbol{r_0}^N]$, etc, when averaged over $\boldsymbol{r_0}^N$
  => *The reference configuration* $\boldsymbol{r_0}^N$ *plays the role of a* **"quenched disorder"**.

- **Goal:** To derive an effective theory for the overlap field $p(x)$ => approximate form for $S[p; \boldsymbol{r_0}^N]$ or its cumulants by integrating out short-distance fluctuations (through liquid-state theory, general Landau-like arguments, etc).

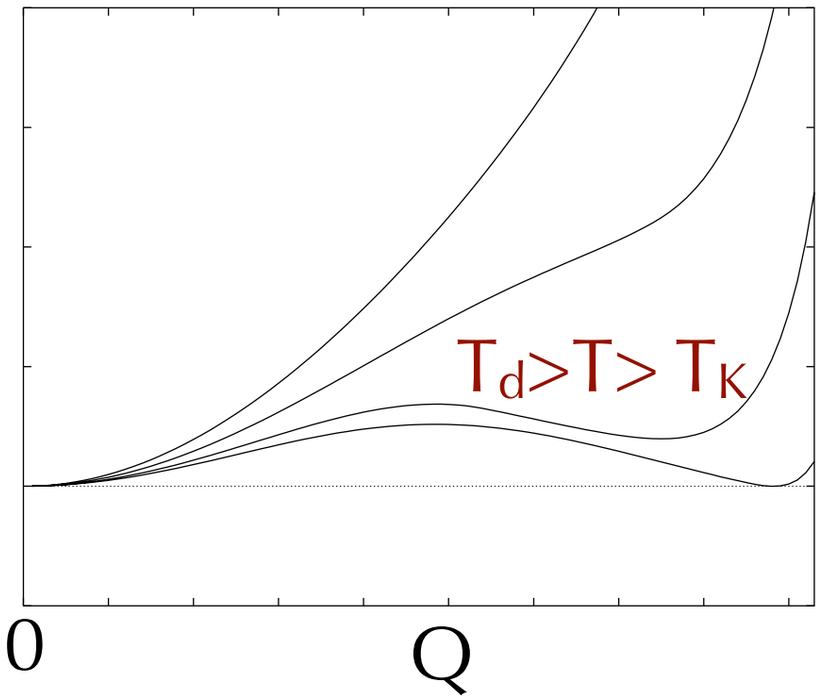
- **To generate the cumulants**: Introduce replicas $\boldsymbol{r_a}^N$, $a=1,\ldots,n$, each coupled to a **distinct** field $\boldsymbol{\varepsilon}_a$
  => Now, one can define replicated overlap fields $\boldsymbol{p_a(x)}$ between $\boldsymbol{r_a}^N$ and $\boldsymbol{r_0}^N$ and overlap fields $\boldsymbol{q_{ab}(x)}$ between $\boldsymbol{r_a}^N$ and $\boldsymbol{r_b}^N$.

Sketch of formalism (III)

- Generically, the effective hamiltonian for the overlap fields $p_a(x)$ is obtained from

$$e^{-S_{rep}[\{p_a\}]} = \overline{\exp(-\sum_{a=1}^{n} S[p_a; \mathbf{r_0}^N])} \propto \int \prod_{ab\neq} \mathcal{D}q_{ab} e^{-\mathcal{S}[\{p_a, q_{ab}\}]}$$

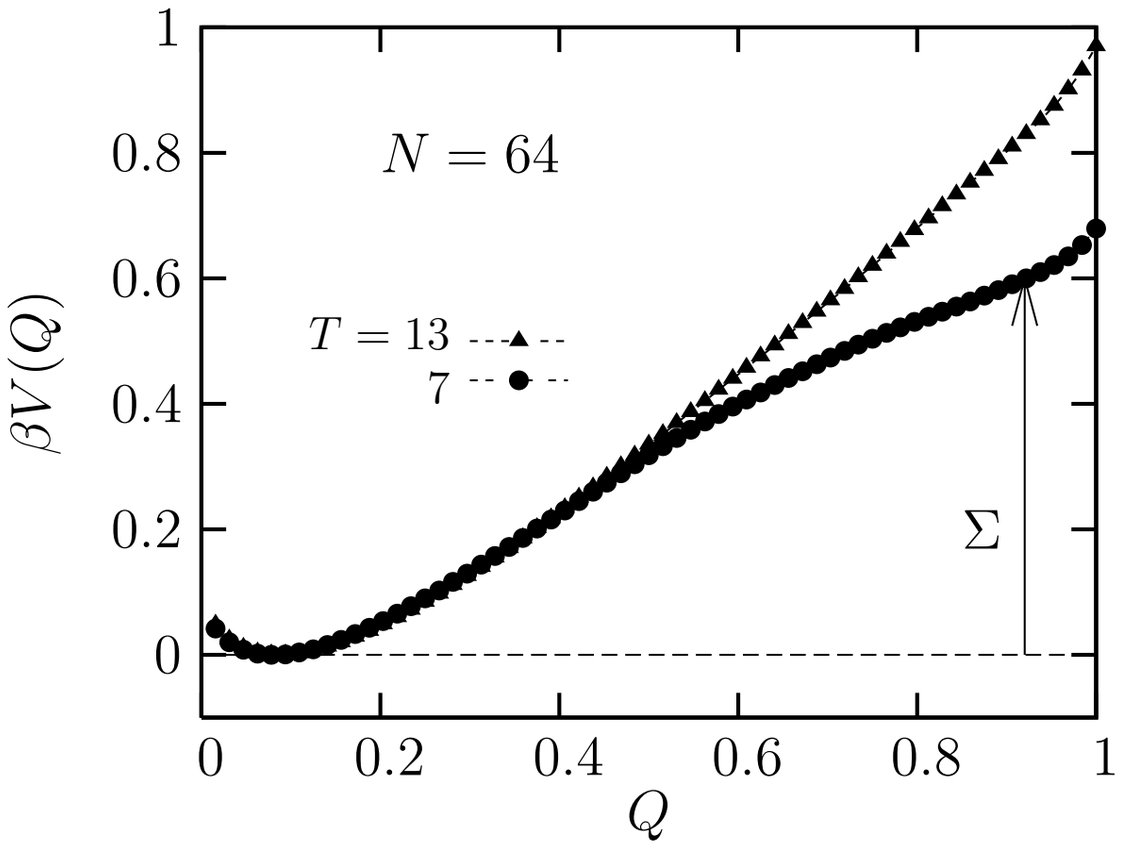
where $S[\{p_a,q_{ab}\}]$ is obtained by integrating out short-distance fluctuations (through liquid-state theory, general Landau-like arguments, etc) and at the Landau level for $p_a=q_{ab}=Q$ has the typical form illustrated here:

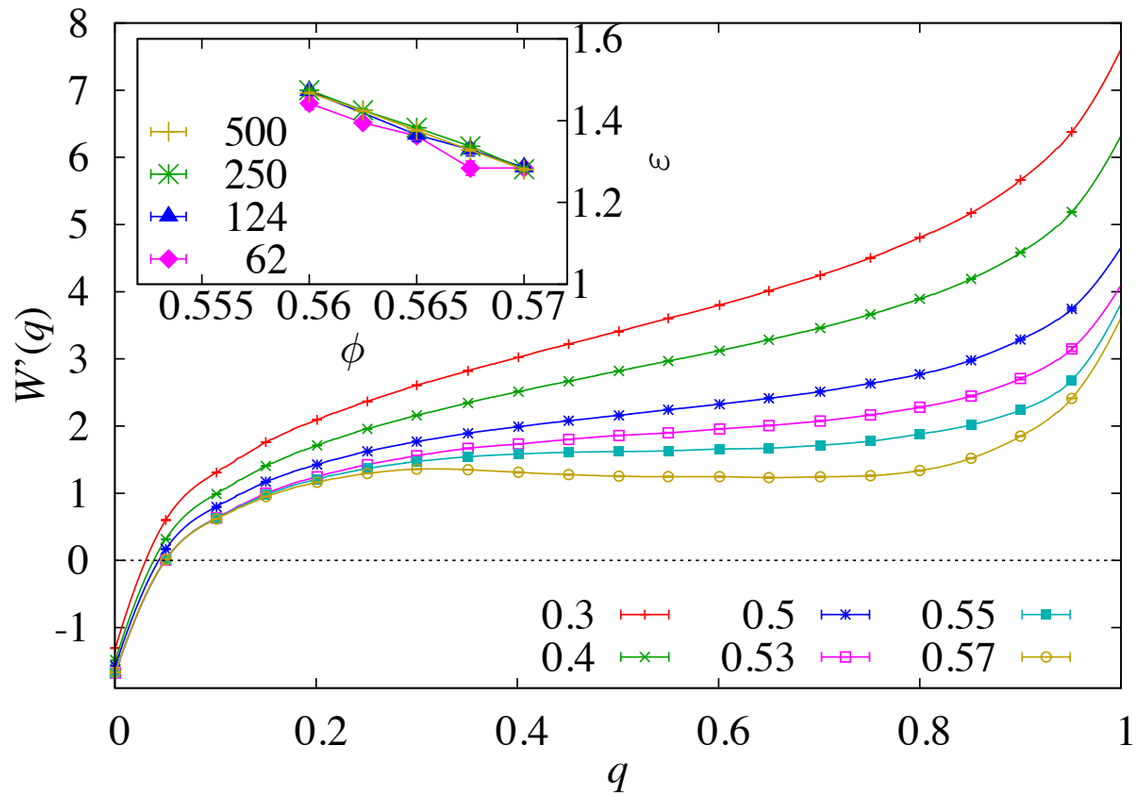


- **Crucial**: The fields p_a can be critical (near the terminal critical point) but never the fields q_{ab} due to the external field provided by the coupling with the p_a's **!!!!!**

Relevance of the 2-state, first-order-like, effective description after integrating out short-distance fluctuations

Evidence from finite-size computer simulations
=> Landau-like potential with cubic term





Effective "annealed" potential (left, Berthier, PRE 2013) and its derivative (right, Parisi-Soane, PRE 2014) for a glass-forming liquid model plotted versus the overlap at different temperatures for a small system size

Results: Universality class

- If present, the terminal critical point is in the **universality class of the RFIM (random field Ising model)**. Effective (disordered) hamiltonian for the overlap fluctuations $\phi(x)=p(x)-p_c$ (up to ϕ^4):

$$S[\phi] = \int_x \left\{ c[\partial\phi(x)]^2 + \frac{r_2}{2}\phi(x)^2 + \frac{r_3}{3!}\phi(x)^3 + \frac{r_4}{4!}\phi(x)^4 \right\}$$

$$+ \int_x \left\{ -h(x)\phi(x) + \frac{\delta r_2(x)}{2}\phi(x)^2 + \frac{\delta r_3(x)}{3!}\phi(x)^3 \right\}$$

h(x) random field (most relevant).Expressions for the parameters

- When one proceeds instead to an "annealed calculation" (just two coupled replicas): universality class of pure Ising model (no quenched disorder)

[Confirmed via a different method by Franz-Parisi: J. Stat. Mech.,2014]

Results: Existence of a critical point in D=3?

One can evaluate the effective parameters of the RFIM description for specific models:

The transition exists if the ratio of the effective disorder strength to the effective interaction (surface tension) is small enough => accounts for long-distance fluctuations.

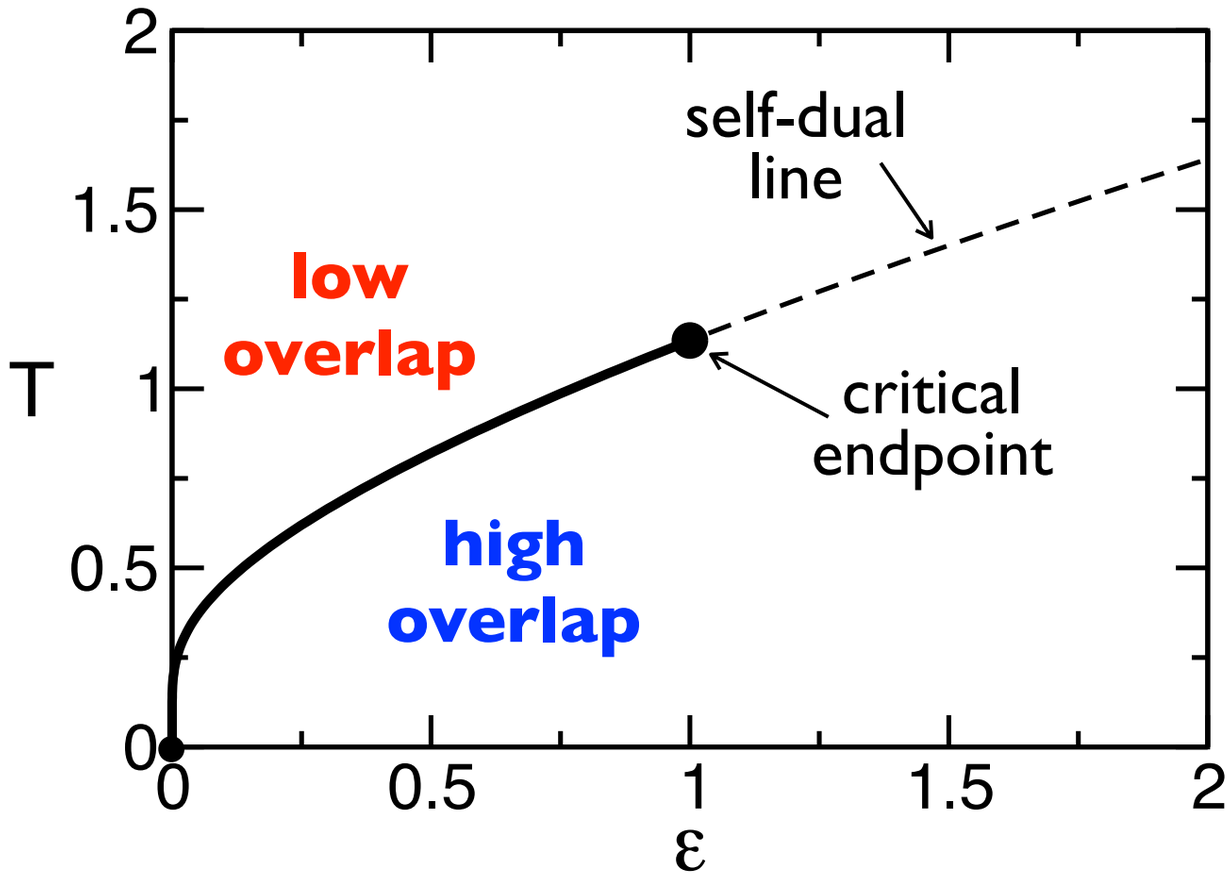
From simulations of the 3D RFIM, the critical ratio ≃ 2.3.

=> The Wolynes et al Landau theory for the fragile glass-forming liquid o-TP: Ratio ≃ 0.94, the transition seems to survive.

=> The disordered p-spin model with p=3, Ratio ≃ 4.48, no transition [cf. also Cammarota et al, PRB 2013]

The terminal critical point in plaquette spin models

Annealed computation (2 coupled replicas) for the 2D triangular plaquette spin model (Garrahan, 2014)



Critical endpoint = **universality class of the 2D 4-state Potts model ≠ 2D Ising model** ($\nu=2/3$, $\alpha=2/3$ *vs* $\nu=1$, $\alpha=0$).

No finite-T transition when $\varepsilon=0$.

Contrasting ...: Region III near the mean-field static transition (RFOT)

- **Interesting per se and to compare with the dynamic facilitation picture:** in the latter, the presence of localized defects destroys any finite-T transition in the absence of constraints.

- Difficulty for deriving an effective theory for the overlap with a reference configuration: **All overlap fields are now affected by the presence of static point-to-set correlations (that precisely diverge in mean-field at the RFOT T_K)** => more tricky to integrate out the q_{ab}'s for fixed p_a's.

- **Work in progress:** indication for a RFIM with a renormalized effective external field (configurational entropy) and antiferromagnetic interactions on top of the ferromagnetic ones.

Conclusion

- Contrasting the dynamical facilitation and the landscape approaches => Enlarging the phase diagram by applying fields/constraints.

- Transitions in the enlarged diagram give info on the structure of the configurations and metastable states. Describable by a 2-state Ising theory or not? Consequences for the nature of the defects?

- Need more systematic investigation in the dynamical-facilitation approach: quenched case, 3D, more models...

- More easily testable in simulations of liquid models.