Theoretical Approaches to the Glass Transition

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SCIENCES ET TECHNIQUES

Encouraging comments of colleagues:

- You will make yourself many enemies
- Bon courage!
- Mission impossible
- ...

Outline of the talk

- Various levels of “theories”
- Examples of *useful* theories/models
- Questions that should be addressed in the future

NB: No glass, no shearing, no shaking, no tapping, no crystallization,...

WELCOME TO THE WORLD OF LIQUIDS!

Various levels of theories

- Fitting functions:
  - Kohlrausch-Williams-Watts function
  - Coupling model (K. Ngai)
  - ...
- Phenomenological models:
  - Adam-Gibbs “theory”
  - Shoving model (J. Dyre)
  - Soft Glassy Material Model (P. Sollich, M.E. Cates, F. Lequeux)
  - trap model (J.-P. Bouchaud)
  - ....
- Theory: Should allow to make a calculation *for a given microscopic Hamiltonian*; calculations might be difficult and approximations might be needed; results might be bad

NB: 1) There are complicated models (e.g. kinetically facilitated Ising models, landscapes,...) that allow to reproduce certain dynamic aspects of real glass-forming liquids; these models are useful to understand certain mechanisms, but they are models and not theories

2) In glass physics the sophistication of approaches/theories spans orders of magnitudes!

Various models/theories for the glass transition

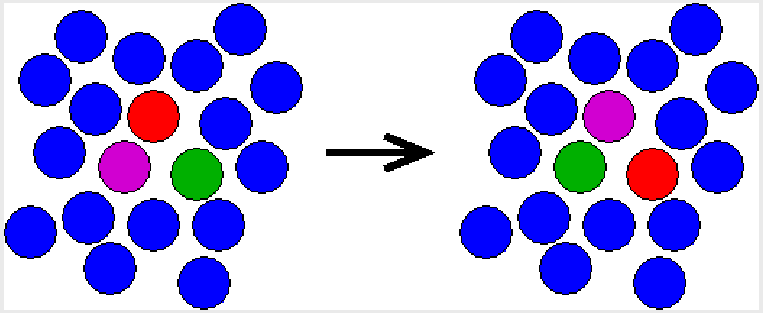
- Adam-Gibbs
- excitation/defect mediated dynamics
- ensembles of histories
- free volume theory
- frustrated domains/avoided criticality
- Gibbs-DiMarzio theory
- mode-coupling theory (comes in various flavors)
- random first order theory
- rigidity percolation
- shoving model
- trap model
- ...

The “theory” of Adam and Gibbs

Basic idea: (Adam and Gibbs 1965)

At low T the relaxation dynamics is a sequence of individual events in which a subregion of the liquid relaxes to a new local configuration. These rearrangements are not single particle jumps (like in a crystal) but cooperative

$\Rightarrow$ Cooperatively rearranging regions (CRR)



Assumptions:

-The CRRs are independent of each other

-The CRRs contain sufficiently many particles to allow to apply the formalism of statistical mechanics

The “theory” of Adam and Gibbs: 2

Consider one CRR that has z particles; one can show that the probability that the CRR rearranges is given by

$$W(z,T) = A \exp(-\beta z \delta\mu)$$

with $\beta = 1/k_b T$ and $\delta\mu$ a constant. Although we have CRR with different sizes (=z), at low T we have $\beta\delta\mu \gg 1$, and thus the relevant CRR will have size z^*

$$W^*(T) = A' \exp(-\beta z^* \delta\mu)$$

where z^* corresponds to the smallest cluster that is able to rearrange.

The “theory” of Adam and Gibbs: 3

What is the value of z^*? At low T we can decompose the dynamics of the particles in vibrations around local minima and transitions between these minima (idea of Goldstein).

$\Rightarrow$The partition function can be factorized into two factors: contribution from vibrations × number of minima with a given energy

$\Rightarrow$The total entropy of the system can be written as a sum of the vibrational entropy, S_{vib}, + configurational entropy S_{conf}

The number of CRRs in a system with N particles is $n(z^*,T) = N/z^*$.
Each CRR has thus a configurational entropy $s_{conf} = S_{conf} / n(z^*,T)$

$$\Rightarrow \quad z^* = N/ n(z^*,T) = N s_{conf}/S_{conf}$$

With $W^*(T)$ = A’ exp(- β z^* δμ) one thus obtains

$$W^*(T) = A' \exp\left[-\frac{\beta N s_{\rm conf}\delta\mu}{S_{\rm conf}}\right] = A' \exp\left[-\frac{C}{TS_{\rm conf}}\right]$$

and assuming that the relaxation time $\tau(T)$ is proportional to $W^*(T)^{-1}$:

$$\tau(T) \propto \eta(T) \propto \exp\left[\frac{C}{TS_{\rm conf}}\right]$$

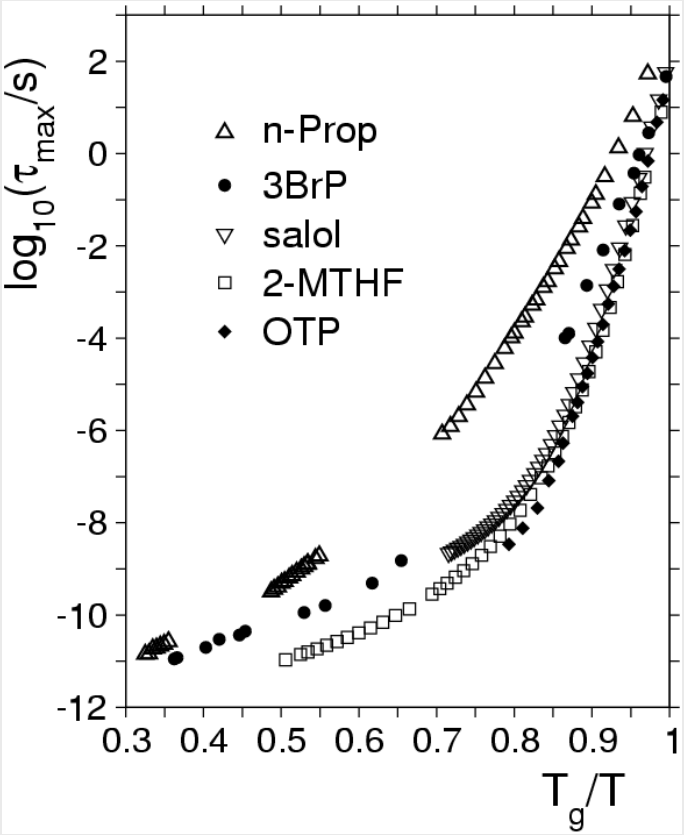
Relation of Adam-Gibbs

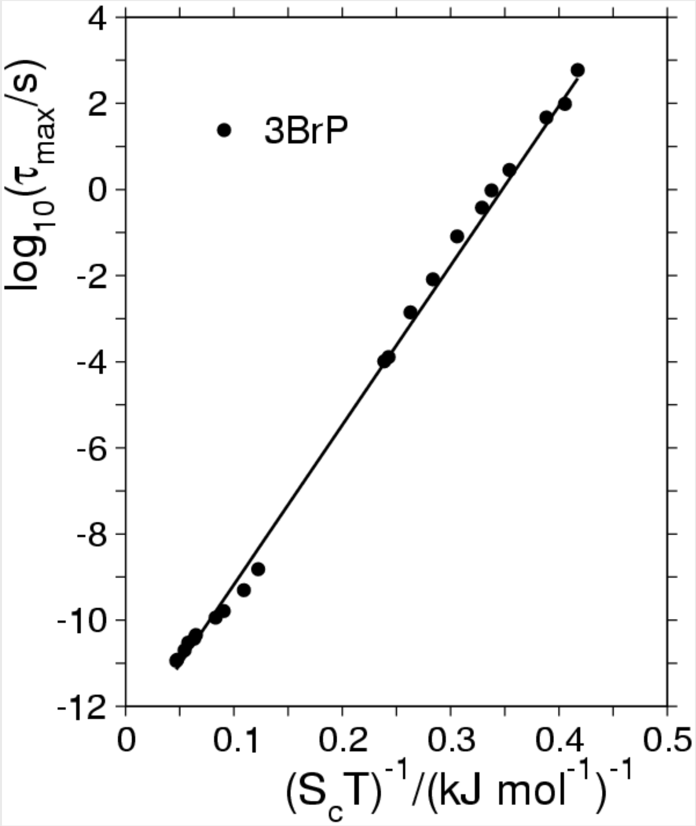
The “theory” of Adam and Gibbs: Validity

One can show that S_{conf} can be determined from the specific heat (Kauzmann)

⇒ The AG-relation can be tested experimentally

$$\tau(T) \propto \eta(T) \propto \exp\left[\frac{C}{T S_{\text{conf}}}\right]$$





Richert and Angell (1998) ⇒ AG works well over a large T-and τ-range (NB: No fit parameter!)

The “theory” of Adam and Gibbs: Consequences

In several glass-forming liquids the excess specific heat $\Delta C_p(T)$ (= spec. heat of liquid – spec. heat of crystal) can be fitted well by

$$\Delta C_p(T) = K/T$$

where K is a constant.

$$\Rightarrow \Delta S(T) = K\,(\,1/T_K - 1/T\,)$$

If we identify $\Delta S(T)$ with $S_{conf}(T)$ we obtain from the AG-relation:

$$\tau(T) \propto \exp\left[\frac{CT_K/K}{T - T_K}\right]$$

$\Rightarrow$ The AG-relation is able to make a connection between dynamics and thermodynamics and to rationalize the Vogel-Fulcher law

Drawbacks of the AG-theory:

- What are the CRRs microscopically???
- Are the CRRs really independent? (NO $\Rightarrow$ RFOT)
- Is it reasonable to assume only one kind of CRRs?
- Almost no predictions for other observables
- ...

Rigidity Percolation

- Phillips, Thorpe, Boolchand (1974--): Idea: A structure of (many) joints and stiff bars becomes rigid if the number of constraints, n_c, equals the number of degrees of freedom, n_d:

$$n_c = n_d$$

Consider a structure of *N* particles with n_r particles having coordination number r (r = 1,...); example $Ge_xS_{1-x-y}I_y$; r = 4, 2, and 1

A counting argument shows that the number of floppy modes (per particle) is

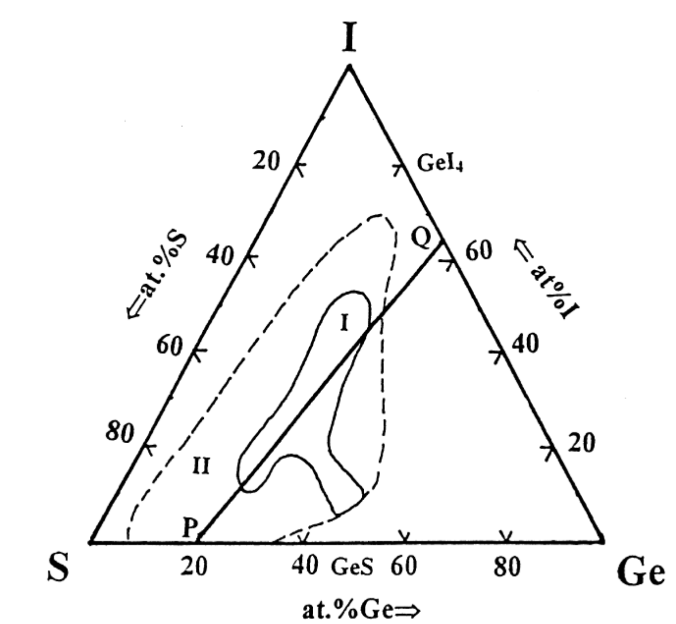
$$F/N = 6 - 5/2 \langle r \rangle - n_1/N$$

with $\langle r \rangle = \sum_{r\geq 1} r\, n_r /N$ (mean coord. number)

$\Rightarrow$ structure is rigid if F=0

$\Rightarrow \langle r \rangle = 2.4 - 0.4\, n_1/N$

$\Rightarrow$ on this composition line glasses form easily



- Glass-formers with HS like structure: Evidence that there are locally favored structures (Egami, Tanaka, Coslovich,..) $\Rightarrow$ Is GT related to rigidity percolation of these structures?

The mode-coupling theory of the glass transition (MCT)

- Consider a system which has degrees of freedom that are fast and slow (good separation of time scales); the Mori-Zwanzig projection operator formalism (1960, 1965) is a method to derive exact equations of motions for the slow dof (by eliminating the fast dof's)

- Glasses: Vibrations (inside the cages) are fast; α-relaxation is slow

$\Rightarrow$ MZ formalism + approximations gives MCT equations

Typical structure of MZ equation: ϕ(q,t) = intermediate scattering function for wave-vector q

$$\ddot{\phi}(q,t)+\Omega^2(q)\phi(q,t)+\Omega^2(q)\int_0^t M(q,t-s)\dot{\phi}(q,s)ds = 0 \quad \text{with} \quad \Omega^2(q) = \frac{q^2 k_B T}{mS(q)}$$

This equation is exact but M(q,t) is horribly complicated $\Rightarrow$ make MCT approximations

$$M^{MCT}(q,t) = \int d^3q' V(q,q')\phi(q',t)\phi(q,t)$$

The mode-coupling theory: 2

$$\ddot{\phi}(q,t) + \Omega^2(q)\phi(q,t) + \Omega^2(q)\int_0^t M^{MCT}(q,t-s)\dot{\phi}(q,s)ds = 0 \quad \text{with} \quad \Omega^2(q) = \frac{q^2 k_B T}{m S(q)}$$

with $$M^{MCT}(q,t) = \int d^3q' V(q,q')\phi(q',t)\phi(q,t)$$

N.B.:

1: By the MZ construction, the vertices V(q,q') depend only on static quantities, such as the density, structure factor, three point correlation functions, …

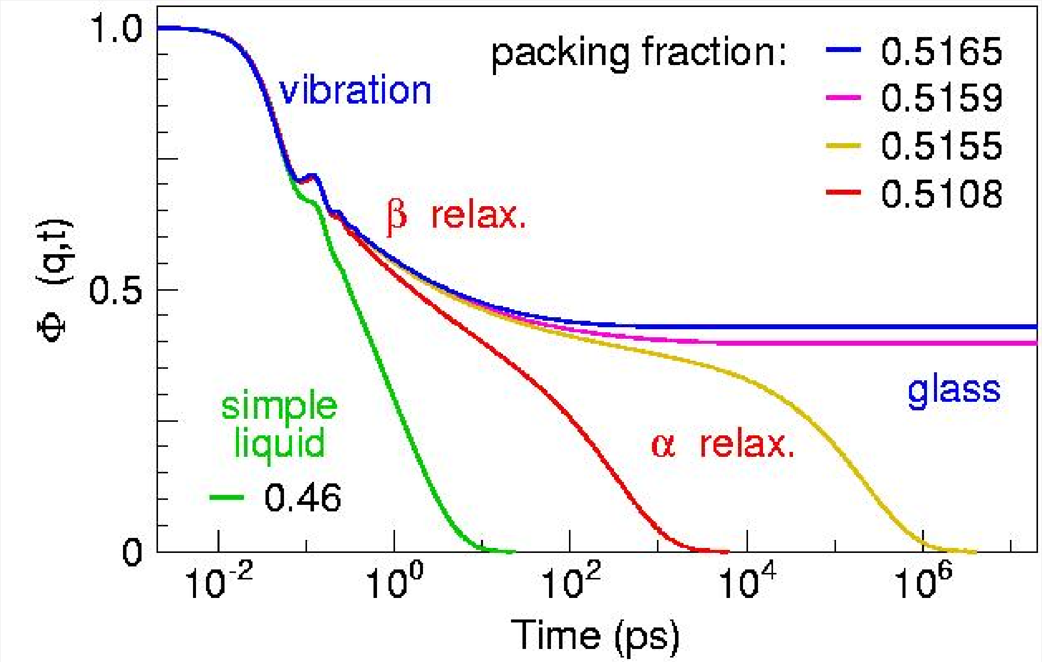
⇒ **THE STATICS GIVES THE DYNAMICS!**

2: If S(q) becomes more peaked, V(q,q') increases, i.e. the memory function increases with increasing density or decreasing temperature.

⇒ With increasing coupling the dynamics is slowed down and ultimately the system can arrest completely ⇒ **ideal glass transition**

Mode-coupling theory: 3

- Consider the MCT solution for a very simple system: hard spheres

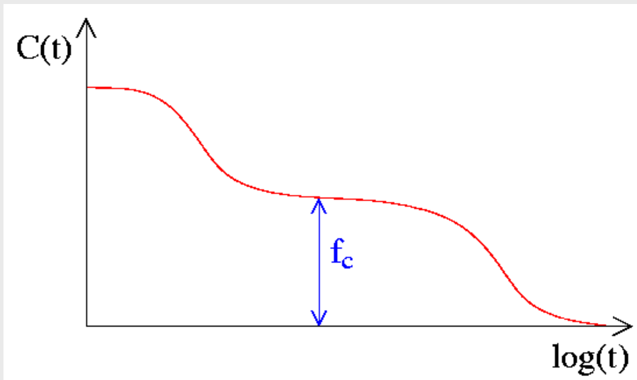


- qualitatively the curves resemble the ones found in experiments

- There exists a critical temperature T_c (or packing fraction) at which the relaxation times increase very quickly
- MCT makes many predictions how the time correlation functions behave close to T_c . These predictions have been tested extensively by means of experiments and computer simulations.

Mode-coupling theory: 4

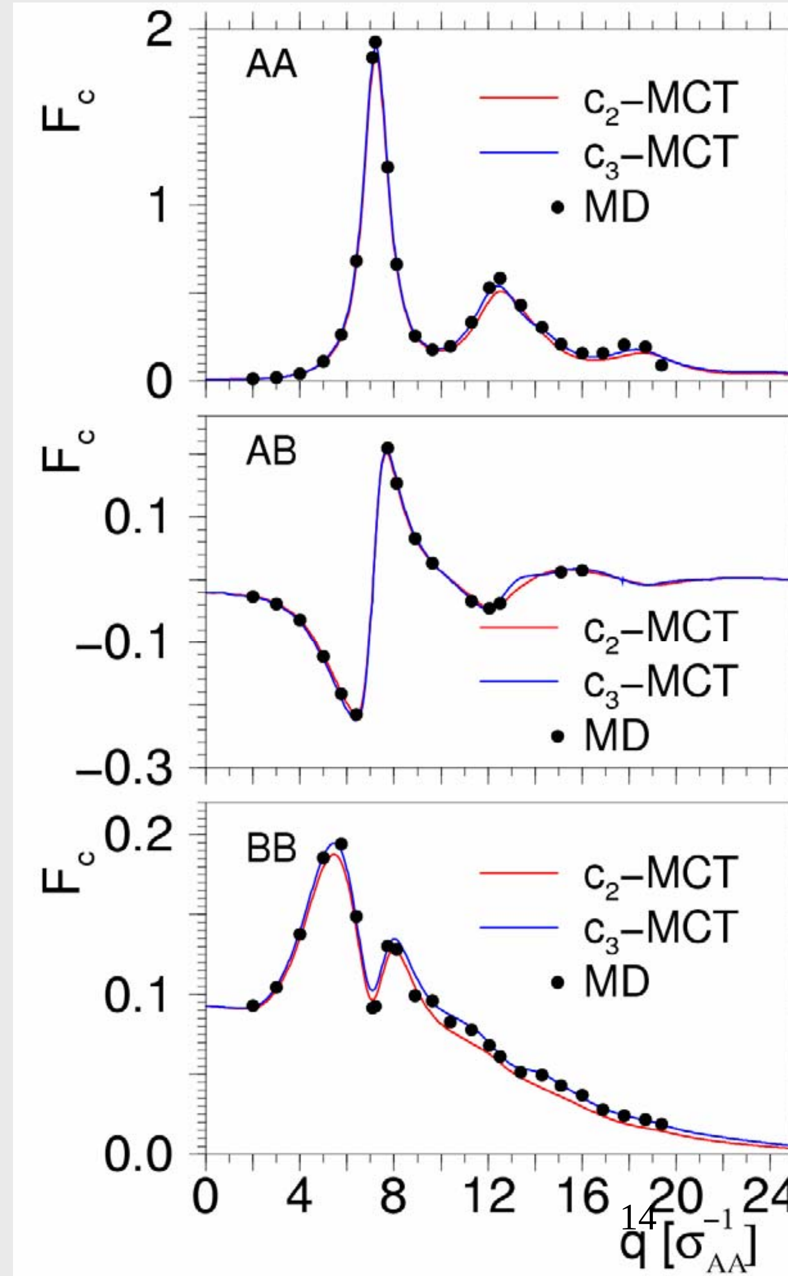
- Nonergodicity parameter (=Debye-Waller factor): height of plateau in time correlation function (also called Edwards-Anderson parameter)



Consider the coherent intermediate scattering function F(q,t):

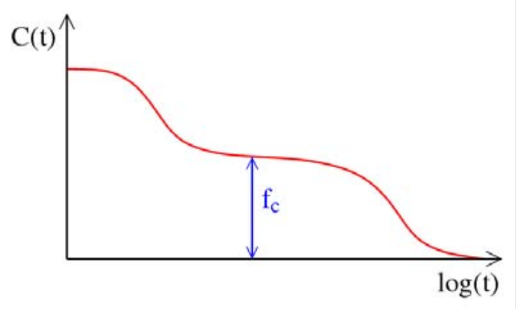
$$F(q,t) = \frac{1}{N} \sum_{k=1}^{N} \sum_{j=1}^{N} \langle \exp\left(i\mathbf{q} \cdot (\mathbf{r}_j(t) - \mathbf{r}_k(0))\right) \rangle$$

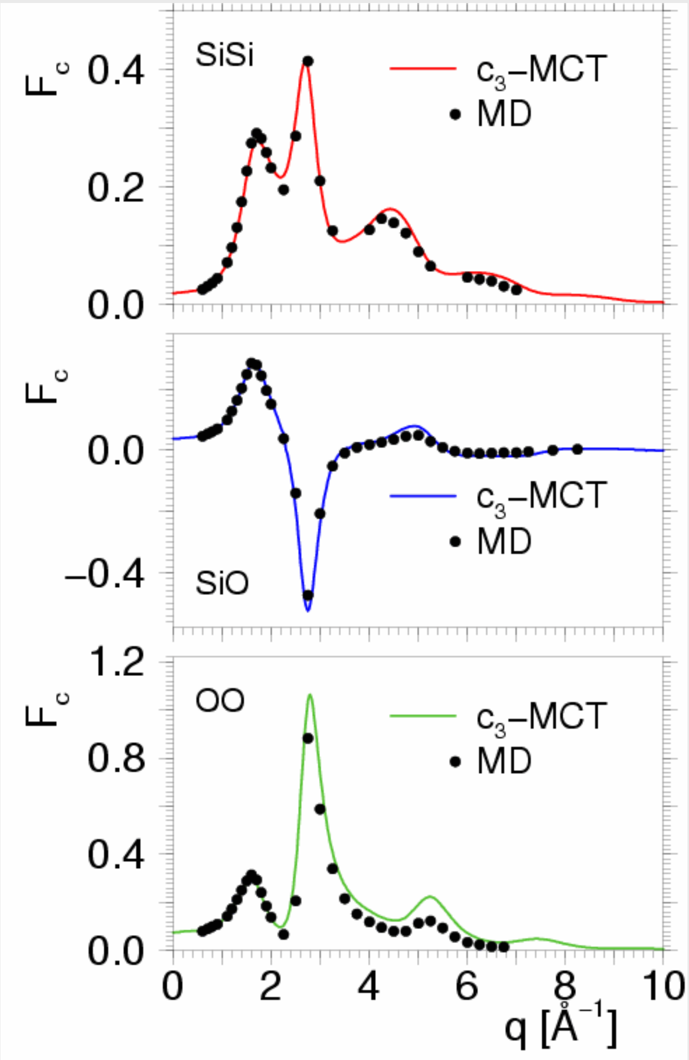
Binary Lennard-Jones system; simulation $\Rightarrow f_c(q)$; Use simulations to obtain the static structure factor $\Rightarrow$ input for MCT



Mode-coupling theory: 5

- Consider silica, SiO_2, a glass-former that has an open network structure





- q-dependence of nonergodicity parameter of the intermediate scattering function
- NO fit parameter!!
- good agreement between MCT and simulation

⇒MCT is also able to make reliable quantitative predictions for “strong” glass-formers

Mode-coupling theory: 6

- The MCT equations are not exact for structural glasses
- In 1986 Kirkpatrick, Thirumalai, and Wolynes studied certain mean-field spin glass models

$$H = -\frac{1}{2}\sum_{i\neq j}^{N} J_{ij}(p\delta_{\sigma_i\sigma_j} - 1) \quad \text{with} \quad \sigma_i \in \{1, \ldots p\}$$

They were able to derive exact equations of motion for C(t), the spin-autocorrelation function: $C(t) = \langle\sigma_i(t)\, \sigma_i(0)\rangle$

These equations have the same mathematical structure as the MCT equations!

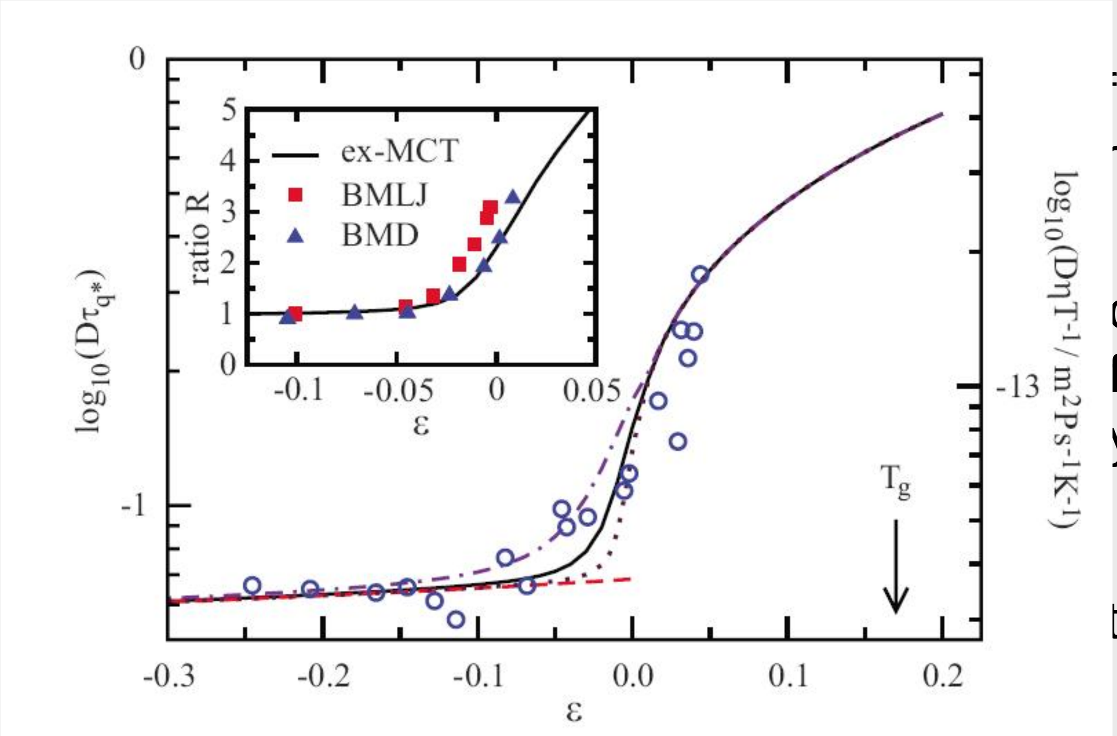
Conclusions:

1. There exist models for which the MCT equations are exact
2. There might be a close connection between spin glasses and structural glasses
3. For the spin glasses models one has a (relatively) good understanding of the (free) energy landscape $\Rightarrow$ dynamic transition at T_c (mode-coupling) and a thermodynamic transition at T_K (= Kauzmann temperature)

Mode-coupling theory: Summary

- MCT is for the moment the only theory that can currently be used to make *quantitative* predictions for a given glass-former

- Failures
  - Gives bad predictions for the value of T_c
  - Often claimed BUT WRONG: MCT predicts a singularity in the dynamics at T_c (which is not seen in real systems) $\Rightarrow$ use extended version of the theory (Götze, Sjögren, Schweizer, Chong)



- Chong 2008 violation of Stokes-Einstein relation

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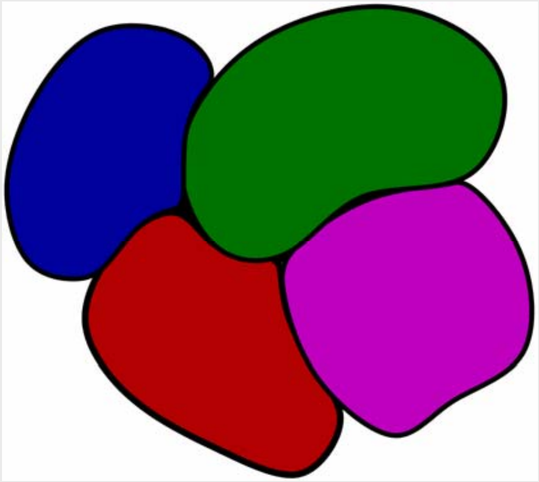
Random First Order Theory

- Decompose the system into the cooperatively rearranging regions of Adam-Gibbs
  $\Rightarrow$ local minima in the free energy
  $\Rightarrow$ "tile" of a mosaic



- Interface tension between neighboring tiles
  $\Rightarrow$ gives size of a tile

- Make assumption on how the interior of a tile relaxes
  $\Rightarrow$ relaxation dynamics of the system

More details: Listen to talk of Jean-Phillipe Bouchaud (15 minutes)

Where are we? Open questions

- There are many approaches that attempt to describe the structure and the glassy dynamics: Some of them are highly sophisticated, some of them are simple minded.

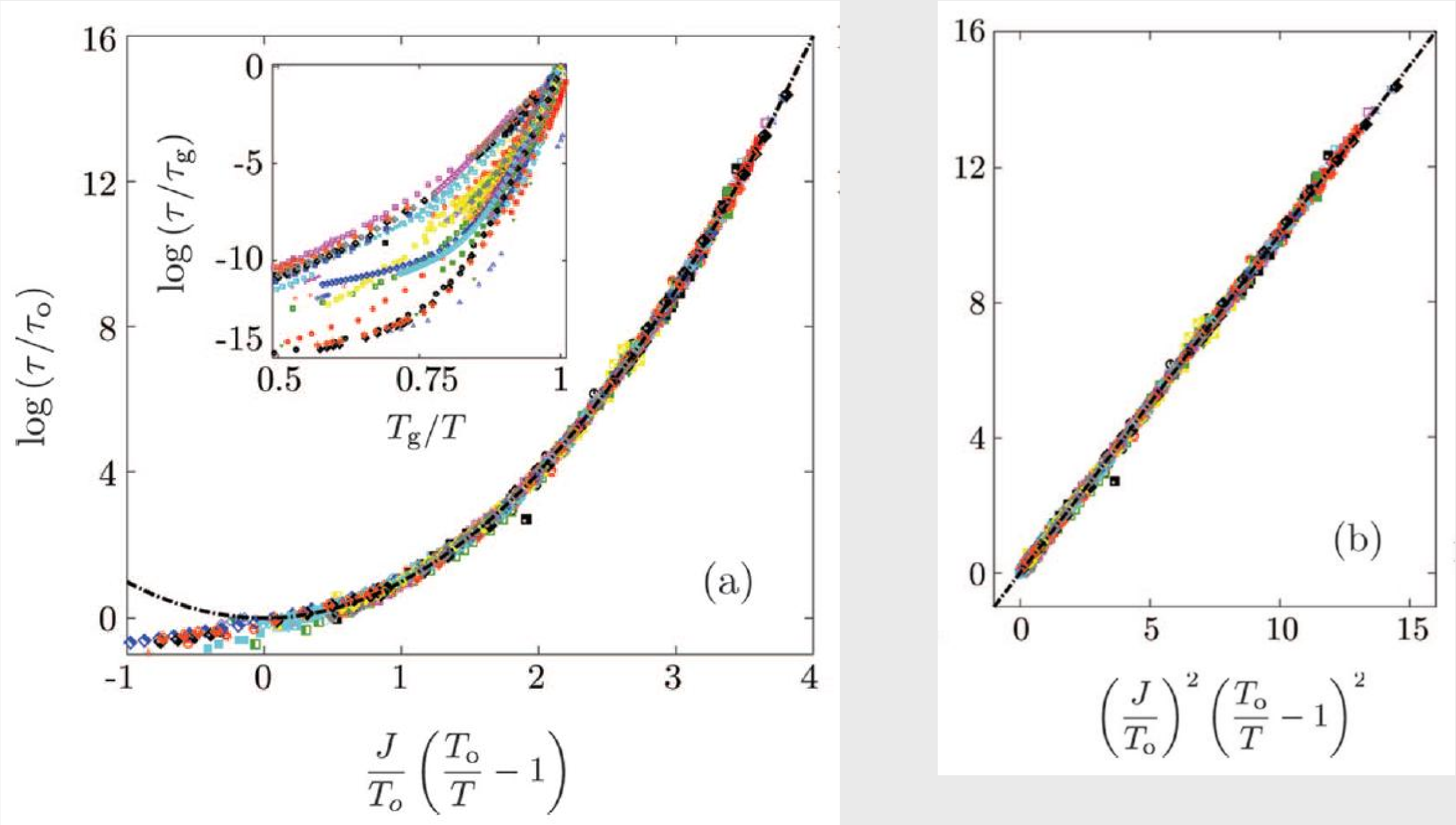
- All of the non-trivial approaches have flaws:
  - Fuzzy concepts: What are the cooperatively rearranging regions of Adam-Gibbs? Does it make sense to talk about an interface tension in the RFOT if the domains are only a few particle diameters?, ...
  - Uncontrolled approximations: MCT takes hopping processes into account in a rudimentary way. What about low T? What is the relevance of mean field results for finite dimensional systems?

- Further questions:
  - Is there a real difference between strong and fragile glass-formers?
  - Do we need to understand dynamical heterogeneities in order to understand the glass-transition? What is the reason for the DH?
  - Are there increasing static length-scales?

- Theories and clever models have helped us to make significant progress in our understanding of glass-forming systems (structure and dynamics).

But there is still a lot to do!

The end of Fragility?



- Elmatad, Garrahan, and Chandler (2009)
- Hess, Rössler and Dingwell (1996)