Survey of Theories of Glassy Behavior

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Outline of the talk

- What is a theory?

- Phenomenological descriptions
    - Structure
        - Continuous Random Network
        - Random close packing
    - Dynamics
        - Adam Gibbs theory
        - Landscapes
        - Free volume theory

- Microscopic descriptions
    - Rigidity percolation
    - Mode Coupling Theory (MCT)
    - Random first order theory (RFOT)

What is a theory?

- Distinguish fitting function and theory!
  - Fitting functions:
    - Kohlrausch-Williams-Watts function
    - Coupling model (K. Ngai)
    - ....
  - Theory: Should allow to make a *microscopic* calculation for a given Hamiltonian; calculations might be difficult and might be approximate; results might be bad

N.B.'s:
1)There are complicated models, e.g. kinetically facilitated Ising models (see talk by Jack), that allow to reproduce a few 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!

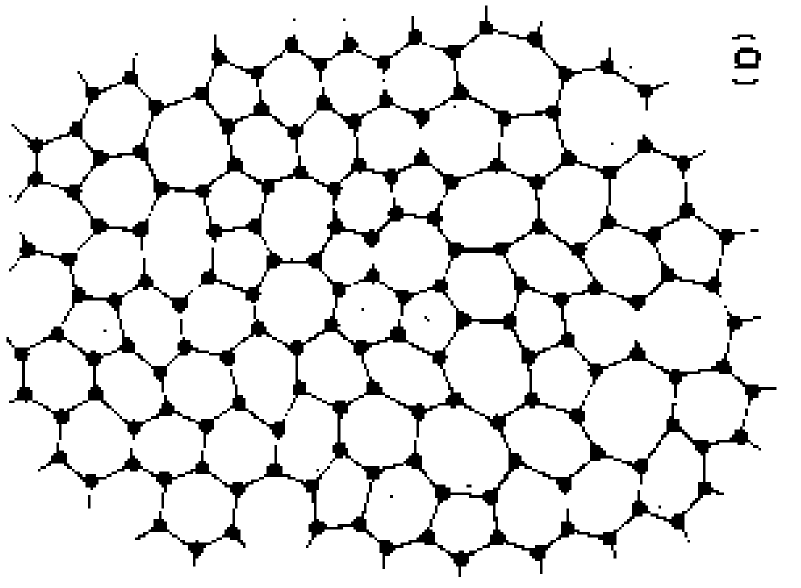
Phenomenological description of the structure: Continuous Random Network

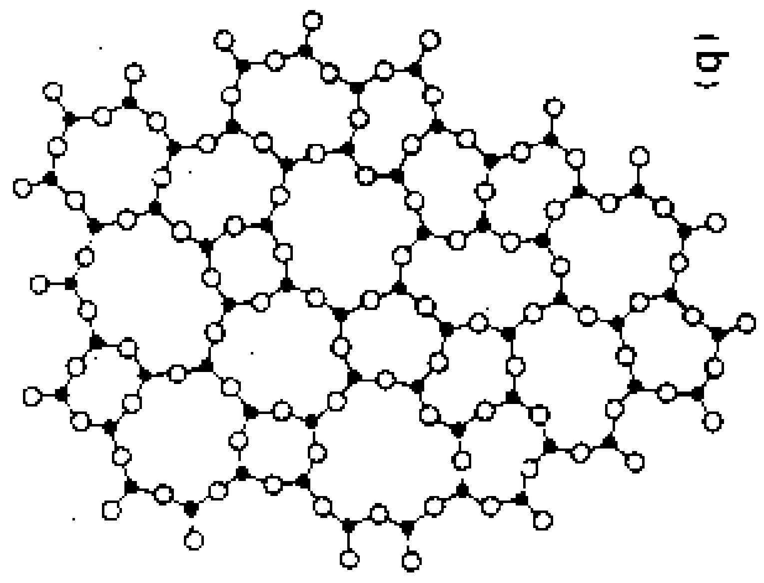
- Covalently bond atoms have a very well defined coordination number
  $\Rightarrow$ well defined local chemical order; Si: z=4, C: z=4; As: z=3,...
- But angles can still vary $\Rightarrow$ local geometrical disorder $\Rightarrow$ random network

- Simple rule to build a random network

For example d=2 random network

- all atoms have z=3
- all nearest neighbor distances are fixed
- no loose ends (=dangling bonds)

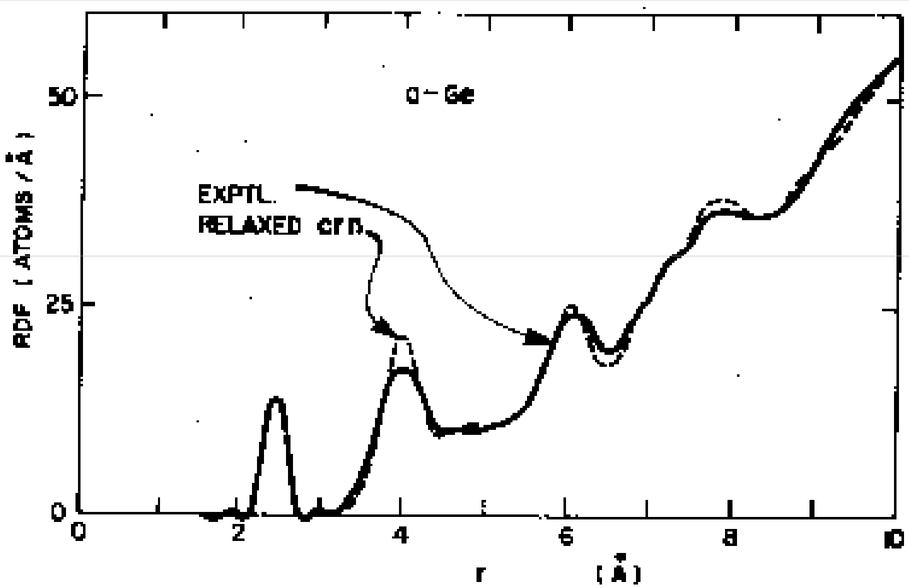




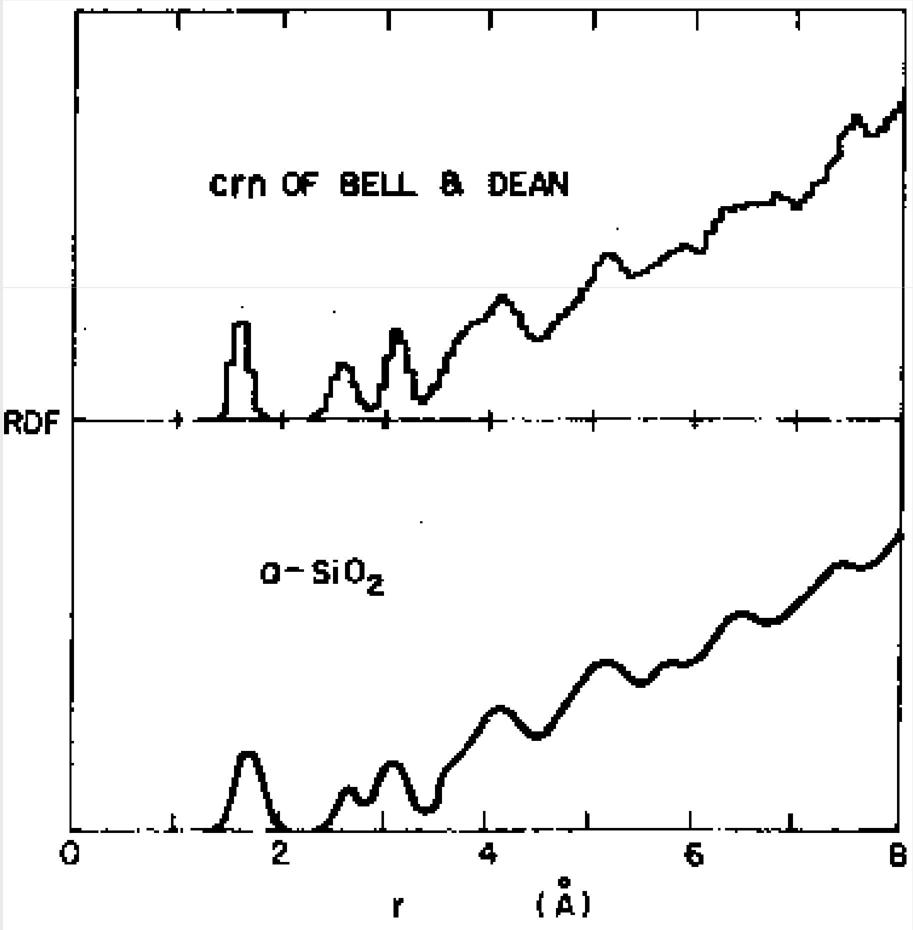
Phenomenological description of the structure: Continuous Random Network: 2

- Comparing structure from CRN with experiments

Amorphous Ge
(Steinhardt et al. 1974)



Amorphous SiO_2
(Bell and Dean 1972)



Phenomenological description of the structure: Random Close Packing

- Approximate atoms as hard spheres; this is ok for many metals (see talks by Kelton and Poole)
- Dimension d=2: Tight packing of hard disks is simple $\Rightarrow$ hexagonal lattice
- Dimension d=3: Local best packing is a tetrahedron; BUT tetrahedra do not allow to fill space uniformly $\Rightarrow$ make local compromise and use icosahedron; BUT icosahedra do not allow to fill space uniformly $\Rightarrow$ random structure (=glass); (see talk by Wales)

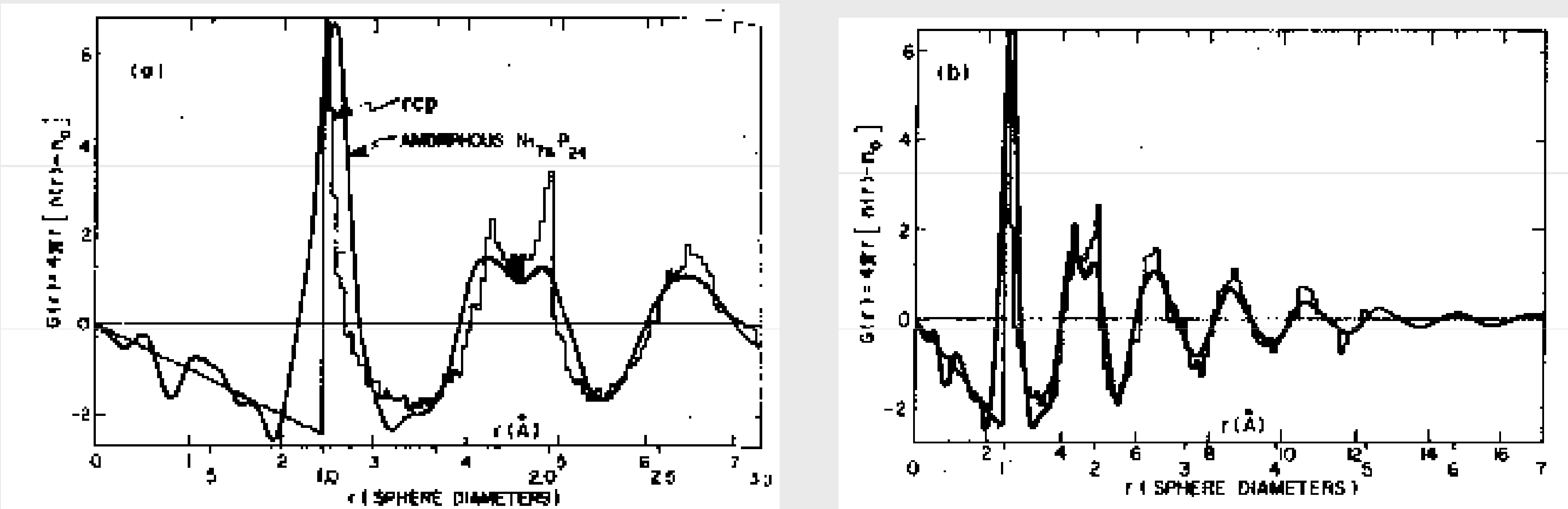
NB: The structure of random close packing is not unique (location of the particles and average density) but depends on the procedure how the structure was created!

- Typical value of the density of RCP: $\rho_{max} \approx 0.64$; compare with tight crystalline packing with : $\rho_{max} \approx 0.74$ (HCP or FCC structure)

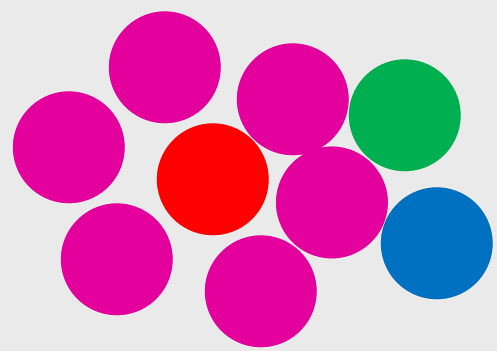
Phenomenological description of the structure: Random Close Packing: 2

- Comparing structure from RCP with experiments:

amorphous $Ni_{76}P_{24}$ (Cargill 1975)



- Reasonably good reproduction of the structure
- Splitting of the second nearest neighbor peak

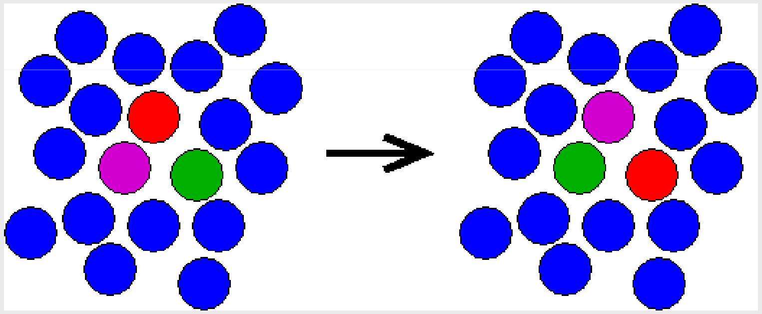


The theory of Adam and Gibbs

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

⇒ 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; the isothermal-isobaric partition function for this subsystem is then

$$\Delta(z,P,T) = \sum_{E,V} w(z,E,V) \exp(-\beta H)$$

where $w(z,E,V)$ is the number of states of the CRR with energy E and volume V, and H is the enthalpy

Not all allowed states can undergo a rearrangement!

$\Rightarrow$ introduce a partition function $\Delta'(z,P,T)$ that considers only the states that can undergo rearrangements

$\Rightarrow$ the fraction of systems that can undergo a relaxation event is

$$f(z,T) = \Delta'/\Delta = \exp(-\beta\,(G-G')) = \exp(-\beta\, z\, \delta\mu)$$

with the Gibbs free energies $G = -k_B T \ln \Delta$ and $G' = -k_B T \ln \Delta'$, and $\delta\mu$ the difference in the chemical potential per particle.

$W(z,T)$, the probability that the system makes a cooperative rearrangement, is proportional to $f(z,T)$ and thus

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

The theory of Adam and Gibbs: 3

Assume that the total system is composed of a collection of $n(k,T)$ CRRs with k particles (k=1,2,...). The average probability that a particle makes a rearrangement is then

$$W^*(T) = N^{-1} \sum_{z=z^*}^{N} z n(z,T) W(z,T)$$

where z^* corresponds to the smallest cluster that is able to rearrange (with $z^*>1$) and N is the number of particles in the system.

$$\Rightarrow \quad W^*(T) = \frac{z^* n(z^*,T) \exp[-\beta z^* \delta\mu]}{N} \sum_{z=z^*}^{N} \frac{z n(z,T)}{z^* n(z^*,T)} A \exp[-\beta(z-z^*)\delta\mu]$$

or, for $\beta\delta\mu >> 1$,

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

$\Rightarrow$ The CRRs relevant for the relaxation dynamics have size z^* since the larger ones are slower by a factor of $O(\exp(-\beta \delta\mu)) << 1$.

The theory of Adam and Gibbs: 4

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^* $\delta\mu$) one thus obtains

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

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

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

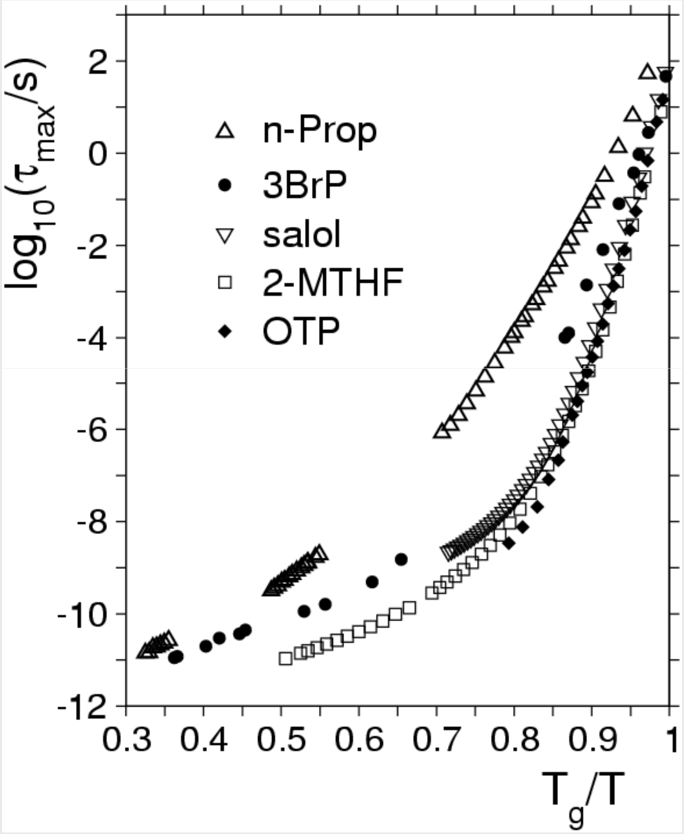
Relation of Adam-Gibbs

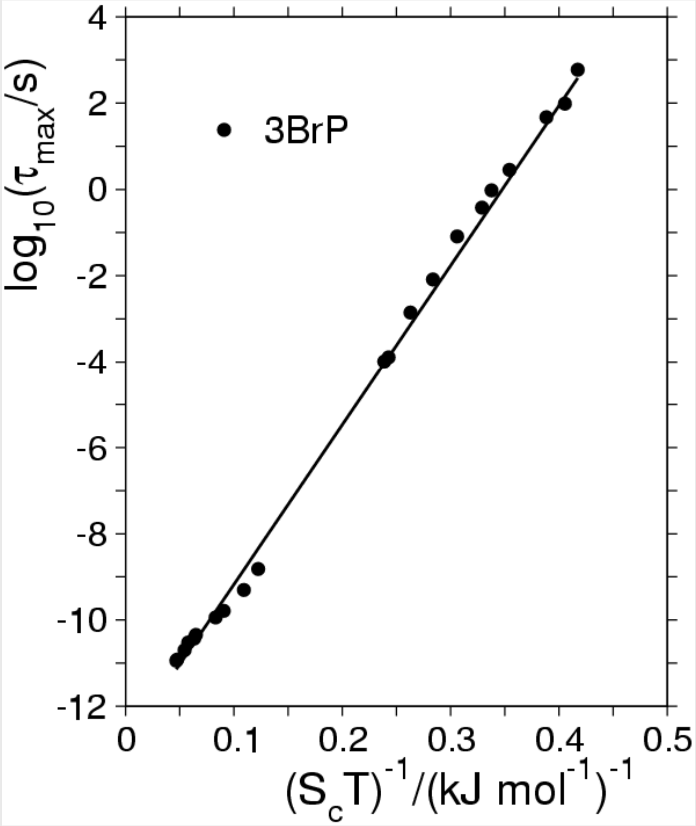
The theory of Adam and Gibbs: Validity

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

⇒ The AG-relation can be tested experimentally

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





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:

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

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

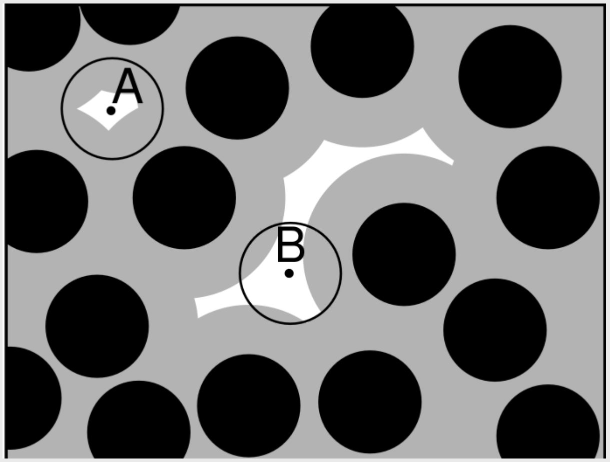
Drawbacks of the AG-theory:

- What are the CRRs microscopically???
- Are the CRRs really independent?
- Is it reasonable to assume only one kind of CRRs?
- No predictions for other observables
- ...

Free Volume Theory

Cohen and Turnbull 1959-1970: Idea: A particle can only change its neighborhood if there is space to do so ⇒ need "free volume"

$$v_f = v - v_0$$



v= volume per particle; v_0 = volume (per particle) accessible only to one particle at a time (= volume of sphere)

Within mean field (= neglect correlations between adjacent free volumes) one can show easily that the probability to find a given free volume v' is given by

$$p(v') = \gamma / v_f \exp(-\gamma v' / v_f) \quad [\gamma = \text{geometric factor}]$$

For a diffusing particle that makes steps of size a with prob. $\Pi(a)$ one can show that the diffusion constant is prop. to $D \propto \int a\, \Pi(a)\, da$

⇒ With $\Pi(a)=p(a)$ one obtains

$$D \propto \exp(-C / v_f)$$

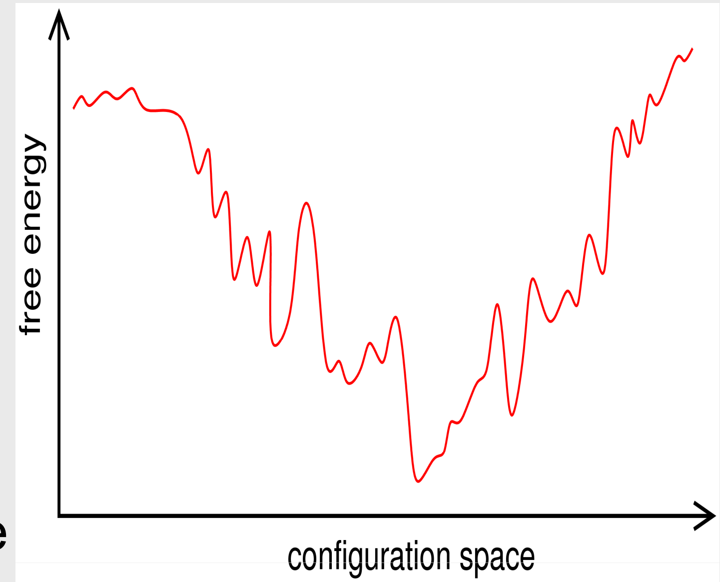
Thus $D \to 0$ if $v_f \to 0$

Thermal systems: $v_f = \alpha(T - T_0)$ ⇒ Vogel-Fulcher law!

Landscapes (see talks Sastry and Wales)

Goldstein 1969: The dynamics of the liquid becomes sluggish because the system has to overcome local barriers in configuration space. With decreasing T these barriers increase ⇒ slowing down is faster than Arrhenius

⇒ At low T the system is moving in a very rough landscape. This can be shown to be exact in mean field spin glasses (see talks by Dasgupta and Mezard). NB: These barriers are in free energy!



What are the properties of this landscape? How many minima at what height? Distribution of barrier height. Is there a hierarchy in the landscape? ....

One can make models of landscapes (e.g. random energy model by Derrida 1980, trap model by Bouchaud et al. 1996) and impose a dynamics ⇒ complex relaxation that shows glassy features

Rigidity Percolation (see talk Elliott)

- 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 glass 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

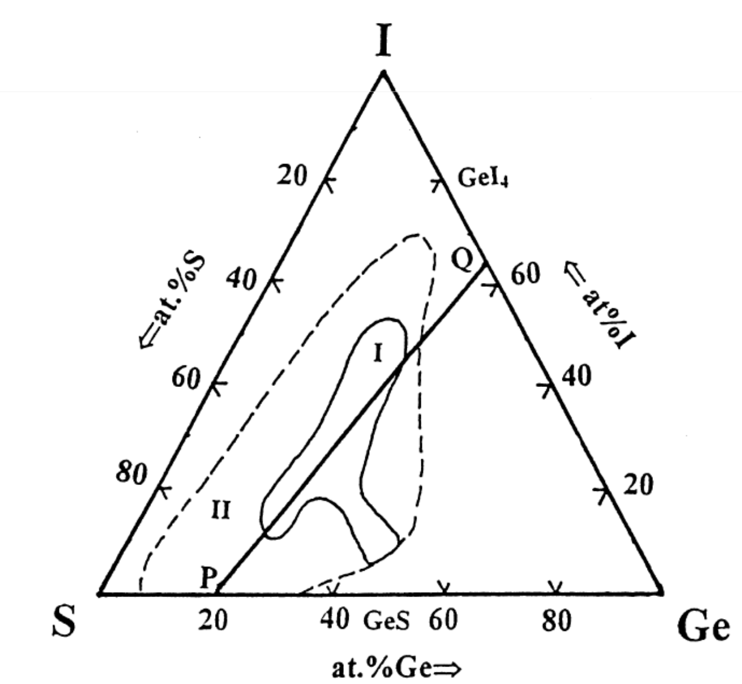
$$F/N = 6 – 5/2 \langle r \rangle - n_1/N$$

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

$\Rightarrow$ structure is rigid if F=0

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

$\Rightarrow$ on this line glasses form easily



The mode-coupling theory of the glass transition (MCT)
see talks of Bagchi, Miyazaki, and Bhattacharyya

- Consider a system which has degrees of freedom that are fast and slow (good separation of time scales); the Zwanzig-Mori 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: $\phi(q,t)$ = intermediate scattering function for wave-vector q

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

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

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

The mode-coupling theory: 2

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

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

N.B.:

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

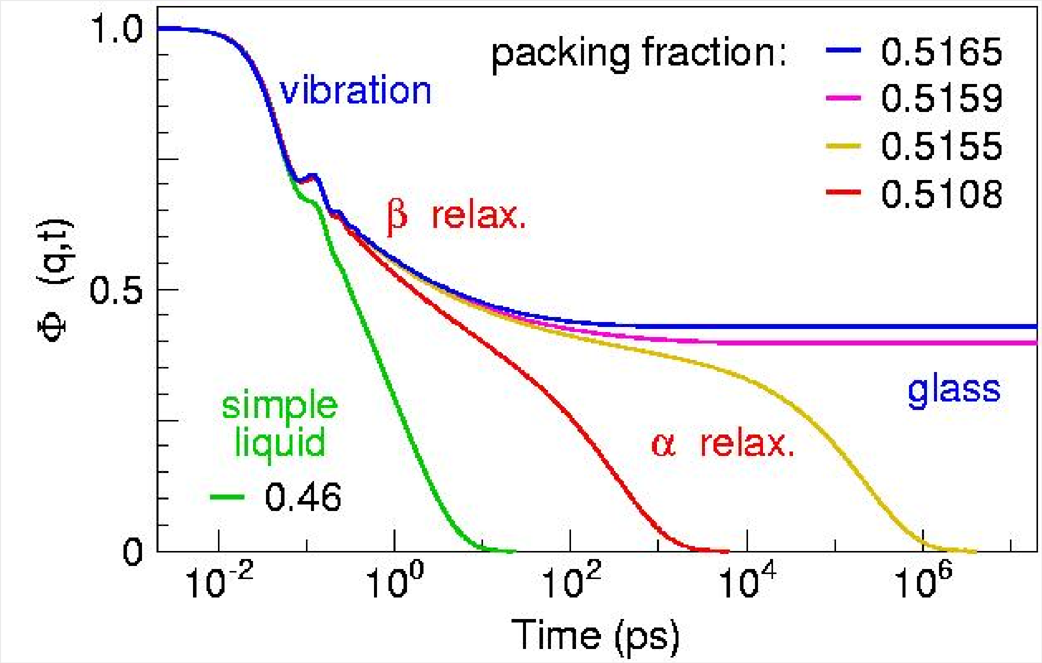
⇒ **THE STATICS GIVES THE DYNAMICS!**

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 ⇒ **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

• Close to T_c the relaxation times show a power-law dependence:

$$\tau \propto (T-T_c)^{-\gamma}$$

Mode-coupling theory: 4

- The MCT equations are not exact for structural glasses
- In 1986 Kirkpatrick, Thirumalai, and Wolynes studied certain mean-field spin glass models (see talks by Dasgupta, Mezard, and Biroli)

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

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

Remark: Cugliandolo and Kurchan generalized 1993 these schematic models to the out-of-equilibrium case (fluct. dissipation theorem is no longer valid!) $\Rightarrow$ Theory for the dynamics of systems in the glass phase (see talks by Kurchan and Franz)

Random First Order Theory

(see talks by Dasgupta, Mezard, Biroli, Bhattacharyya)

Kirkpatrick, Thirumalai, and Wolynes 1980's: Studied the mean field p-spin model:

$$H = -\sum_{i,j,k}^{N} J_{ijk}\sigma_i\sigma_j\sigma_k$$

⇒Landscape has at low T (but above T_K) many different valleys (see also results from replica formalism) ⇒ configuration space can be decomposed into metastable states that have infinite lifetime

⇒partition function can be written as sum over states:

$$Z = \sum_{\sigma} \exp(-\beta H(\sigma)) = \sum_{\alpha=1}^{L}\sum_{\sigma\in\alpha} \exp(-\beta H(\sigma)) = \sum_{\alpha=1}^{L} \exp(-\beta f_\alpha)$$

$$= \int df \exp(-\beta N[f - TS_c(f)]) \quad \text{with} \quad S_c = N^{-1} \log \sum_{\alpha=1}^{L} \delta(f - f_\alpha)$$

⇒ Saddle point approximation ⇒ extremum f* with $S'_c(f^*)=1/T$

Minimum of free energy is $F = f^* - TS_c(f^*)$

Random First Order Theory: 2

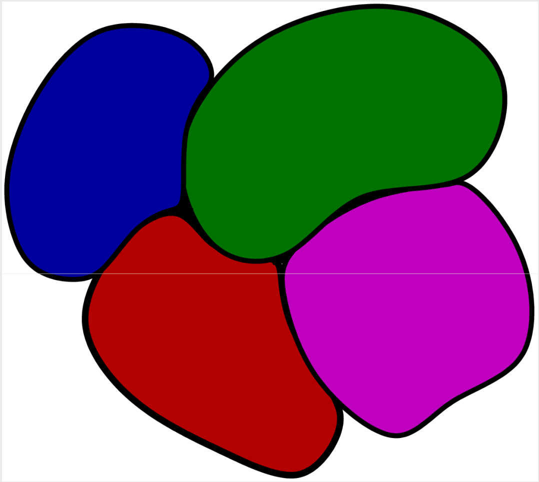
Finite dimensional systems (= finite range of interactions): The metastable states from MF still survive (but have now a finite lifetime)

⇒ different parts of the system will be in different states

⇒ decomposition of the system into patches/tiles that correspond to a local minimum of the free energy

⇒ There is an interface between these patches which costs energy

⇒ surface tension Y(T)



⇒ A patch of size R will have free energy gain ΔF_{gain} and an interface cost ΔF_{cost} with

$$\Delta F_{\text{gain}} = -TS_c(R)R^d \qquad \Delta F_{\text{cost}} = Y(T)R^\theta \quad with \quad \theta \leq d-1$$

Random First Order Theory: 3

The size of the patches ξ will be given by the condition

$$\Delta F_{\text{gain}} = \Delta F_{\text{cost}} \quad \Longrightarrow \xi = \left(\frac{Y(T)}{TS_c(T)}\right)^{\frac{1}{d-\theta}}$$

$\Rightarrow$ length scale that grows with decreasing T!

Connection to dynamics:
Height of free energy barrier Δ to flip a state/patch:

$$\max\,\Delta F = \max\,Y(T)R^{\theta} - TS_cR^{d} \quad \Longrightarrow \Delta = \frac{Y(T)^{\frac{d}{d-\theta}}}{[TS_c(T)]^{\frac{\theta}{d-\theta}}}$$

Assume that process is activated $\Rightarrow$ relaxation time τ is given by

$$\tau = \tau_0 \exp(\Delta/T) = \tau_0 \exp\left(\frac{Y(T)^{\frac{d}{d-\theta}}}{T[TS_c(T)]^{\frac{\theta}{d-\theta}}}\right)$$

If we chose for the exponent θ
we get the expression by Adam and Gibbs

$$\theta = d/2 \quad \Longrightarrow \tau = \tau_0 \exp\left(\frac{C}{TS_c(T)}\right)$$

Summary

!!! CAUTION !!! DON'T GET FOOLED !!!

- 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 small?, ...
  - Uncontrolled approximations: MCT takes hopping processes into account in a rudimentary way. What is the relevance of mean field results for finite dimensional systems

- Theories have helped us to make significant progress in our understanding of glass-forming systems, **but still there is a lot to do**