Energielandschaften, Irrwege und der Glasübergang

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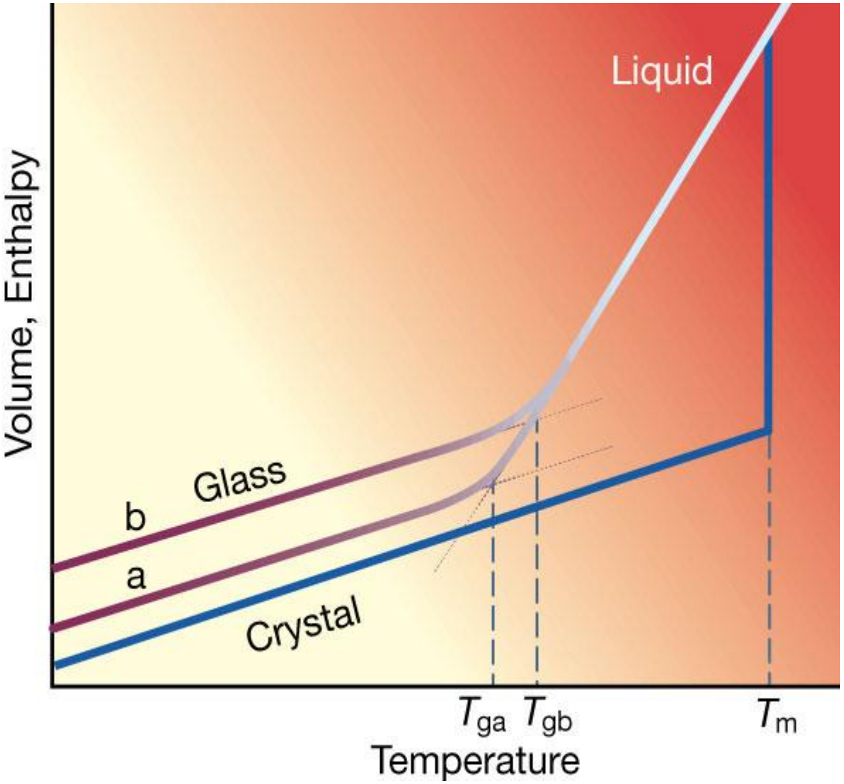
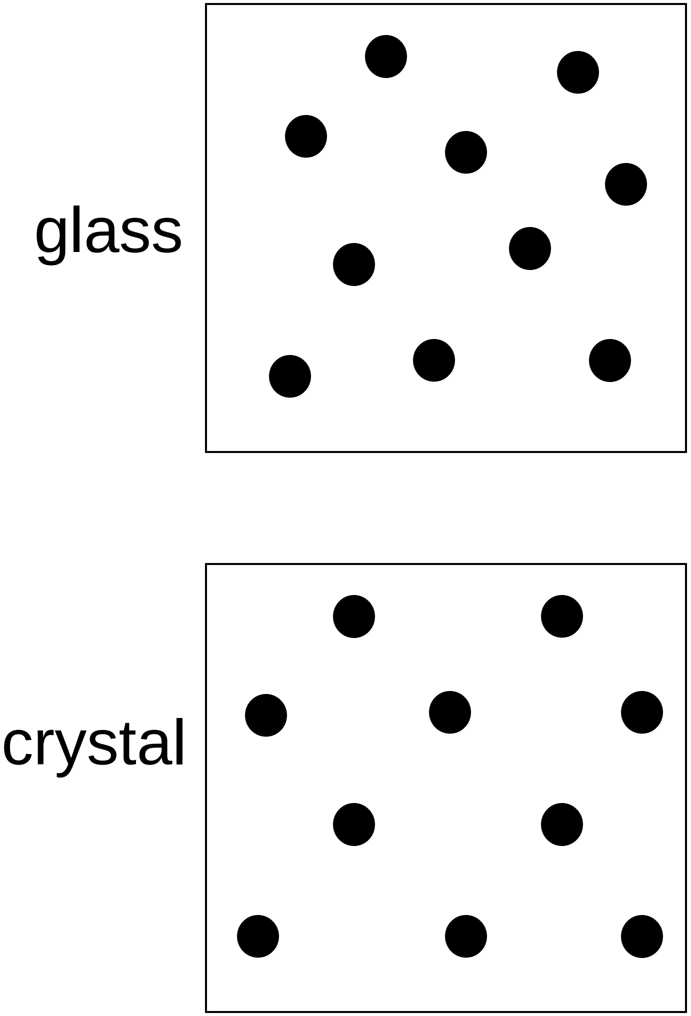
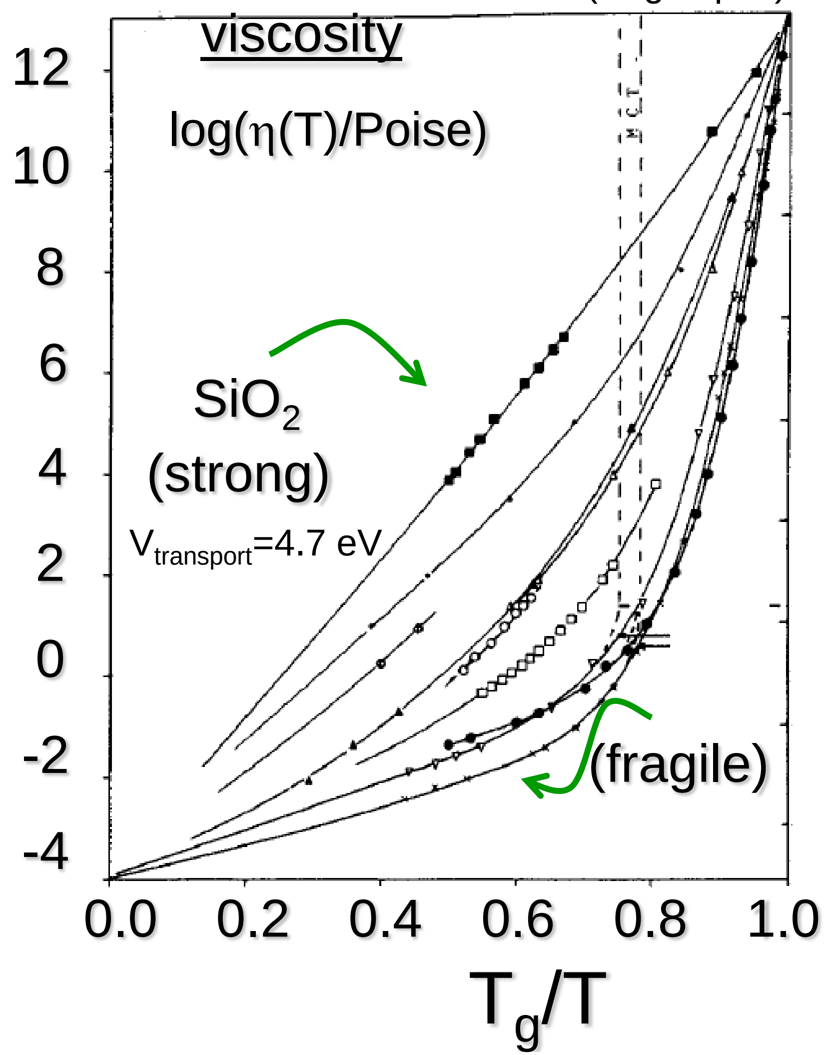
Supercooled liquids and glasses



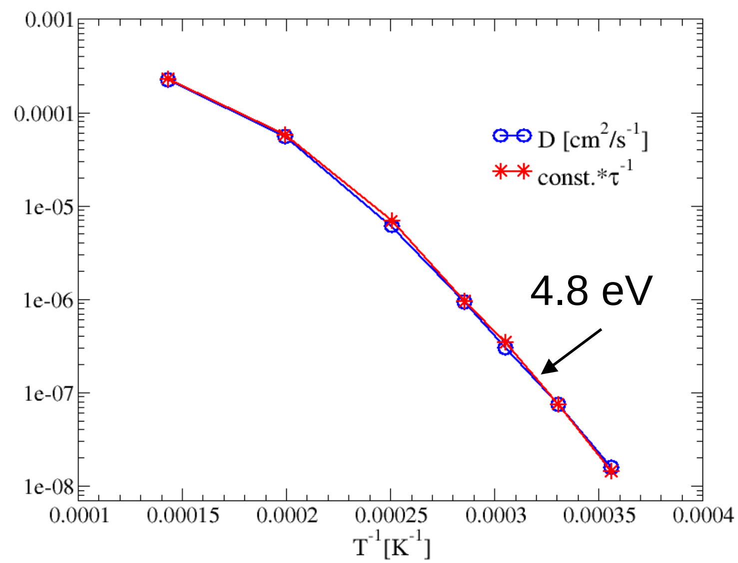


Theoretical understanding of the glass transition

(Angell-plot)



$\eta(T=T_g) = 10^{13}$ Poise



(Horbach, Kob, Binder)

Some model considerations

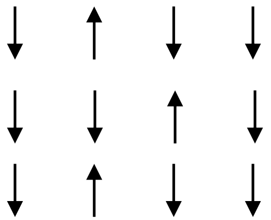
Generally accepted: relaxation processes localized

Dynamics of large system: Relaxation process (CRR) + coupling

Identification of elementary system and coupling?

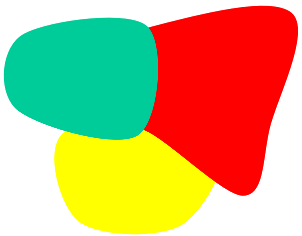
Models:

Faciliated spin models
(Fredrickson, Garrahan, Berthier, Chandler, …)



coupling is everything

Random first order transition theory
(Wolynes, …)



coupling is perturbation

Goal: Simulations => CRR + coupling

Outline

- Discretization of the dynamics

Potential energy landscape

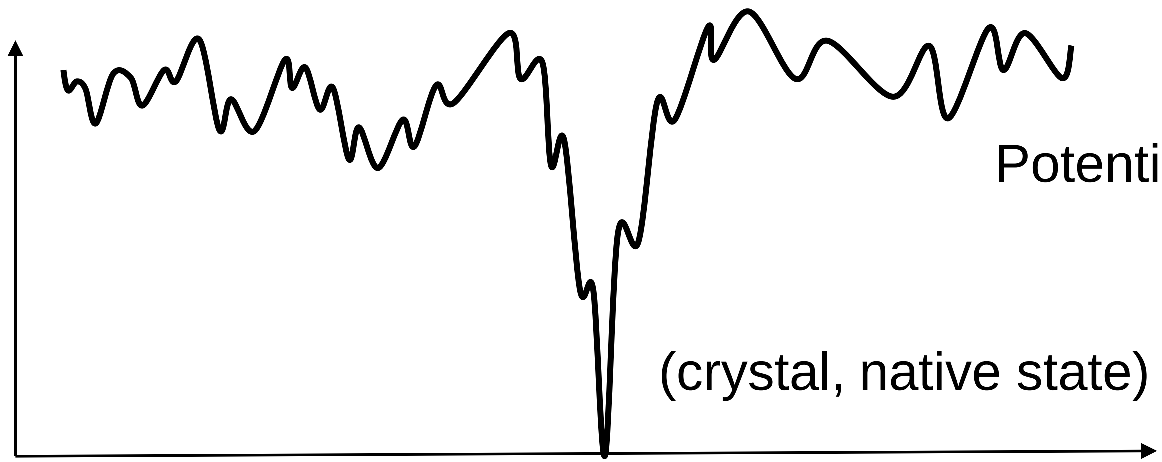
- Dynamics and CTRW

- From the elementary to the macroscopic system

Model systems:

- BKS-silica: pair potential (N=99) (van Beest, Kramer, van Santen)
- Lennard-Jones system (binary) (N=65) (Stillinger and Weber, Kob and Andersen)

Energy landscape



Low temperatures: physical properties governed by minima (statistics, topology)

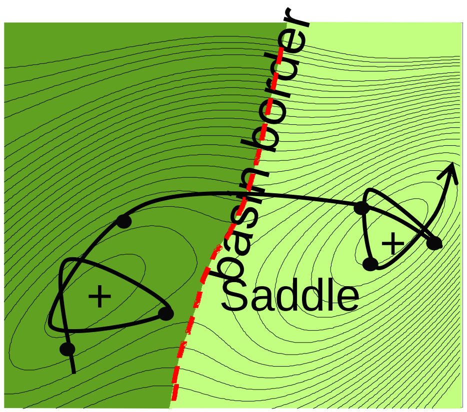
Challenges:

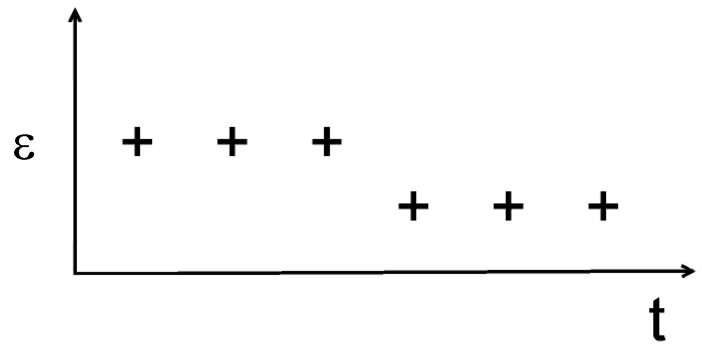
- Exponential number of minima: $\log A = aN + b \log(N) + c + O(\log N/N)$ (analytical exact solution achieved for hard-core model)
- 3N-dimensional configuration space; complex topology

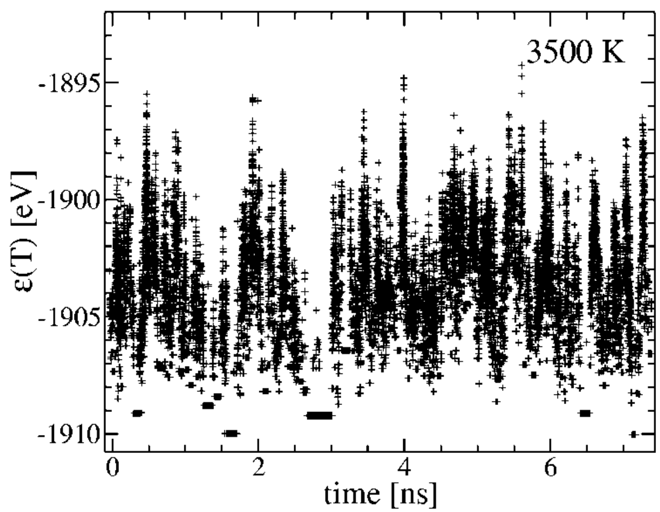
A.H. JPCM(2008)

Exploration of minima for silica

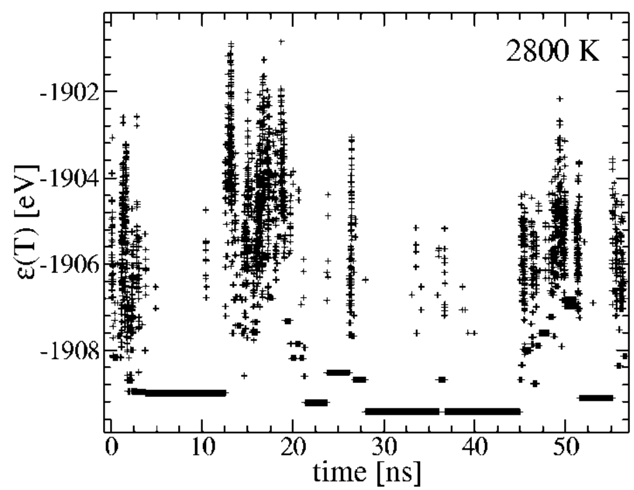
MD simulation + regular quenching







thermodynamics



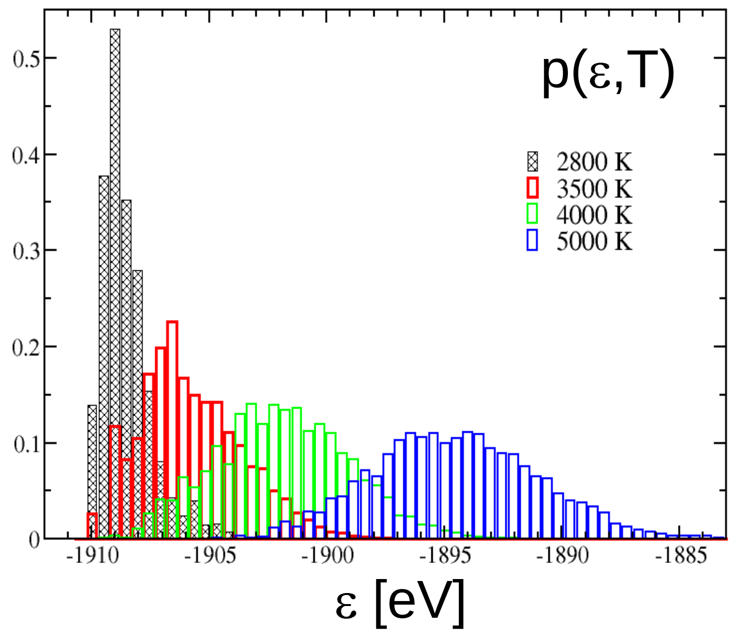
dynamics

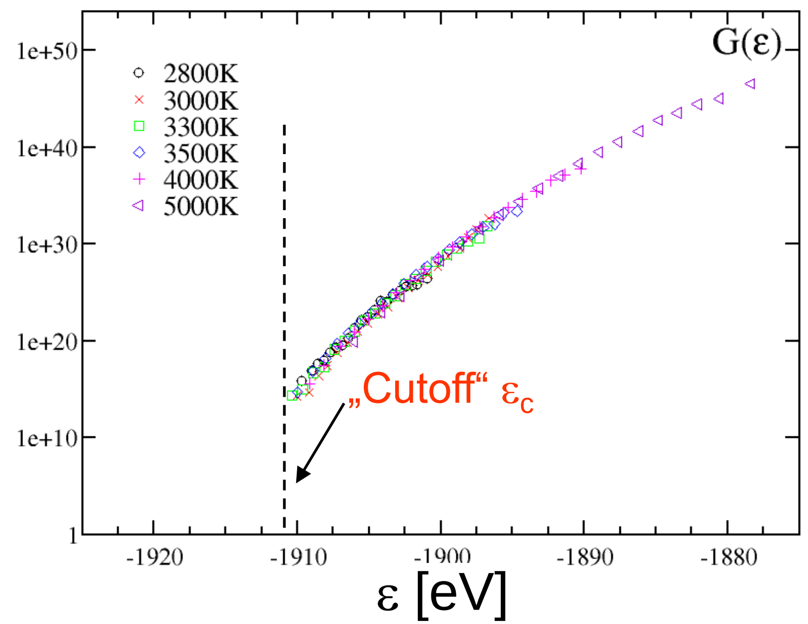
Density of states

$p(\varepsilon,T) \propto G(\varepsilon) \exp(-\beta\varepsilon)$ $\quad$ $G(\varepsilon) \propto p(\varepsilon,T) \exp(\beta\varepsilon)$

SiO_2:

+ thermodynamic integration





For $\varepsilon \approx \varepsilon_c$: defect-free coordination

A. Saksaengwijit, J. Reinisch, A.H., PRL (2004)

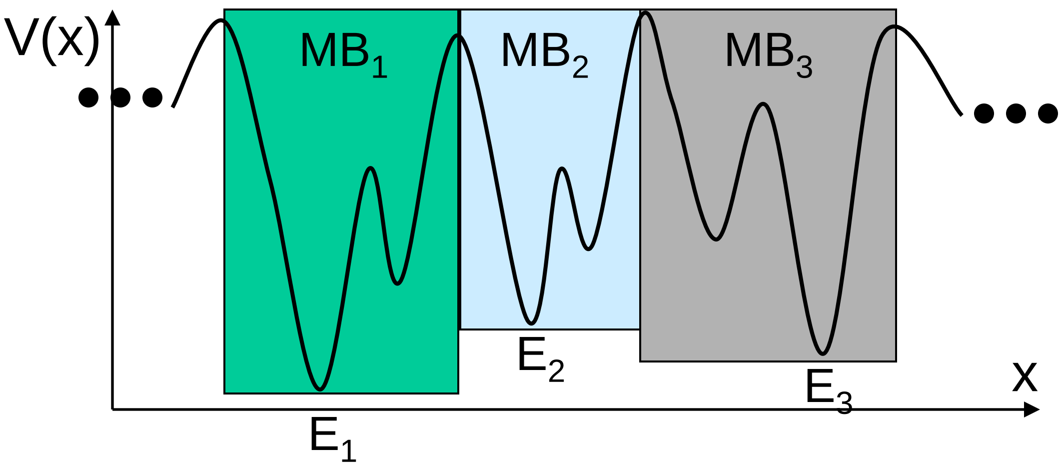
Lennard-Jones:

Gaussian distribution without cutoff (no network constraints)

S. Büchner, A.H., PRL (2000)

Coarse-graining of dynamics

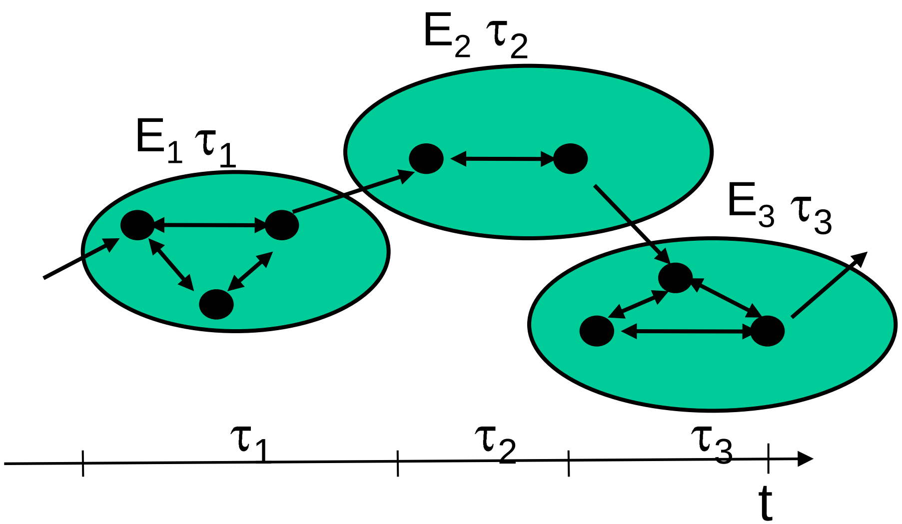
Metabasins



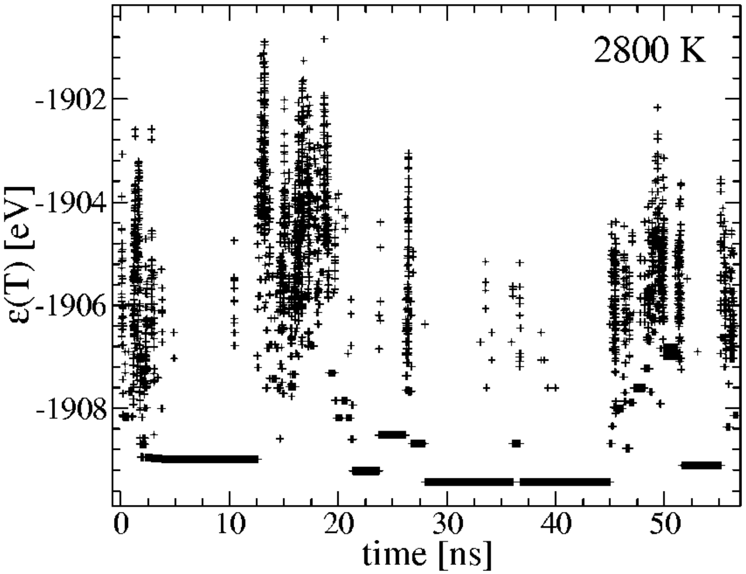
Advantage of metabasins (MBs):

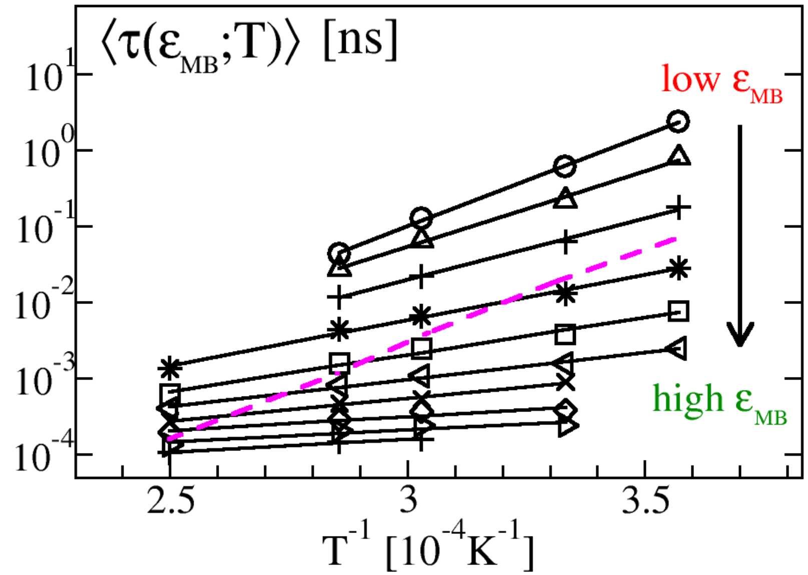
- less forward-backward correlations
- Identification of relevant energies

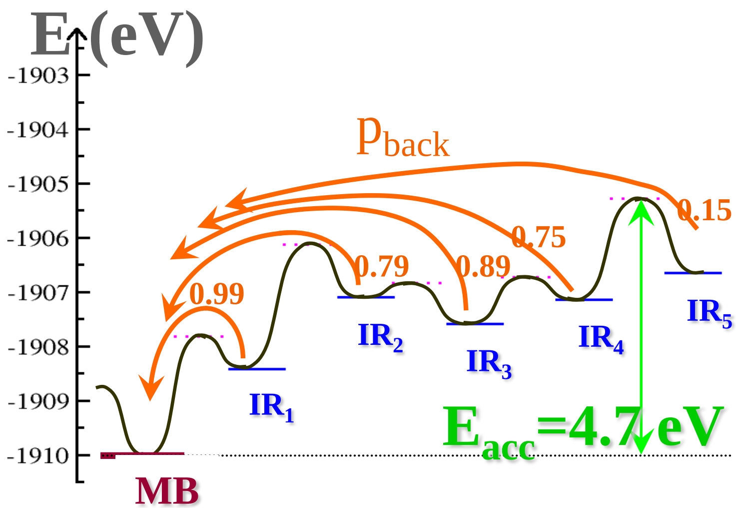
Determination of metabasins for supercooled liquids



Energy-dependent waiting times



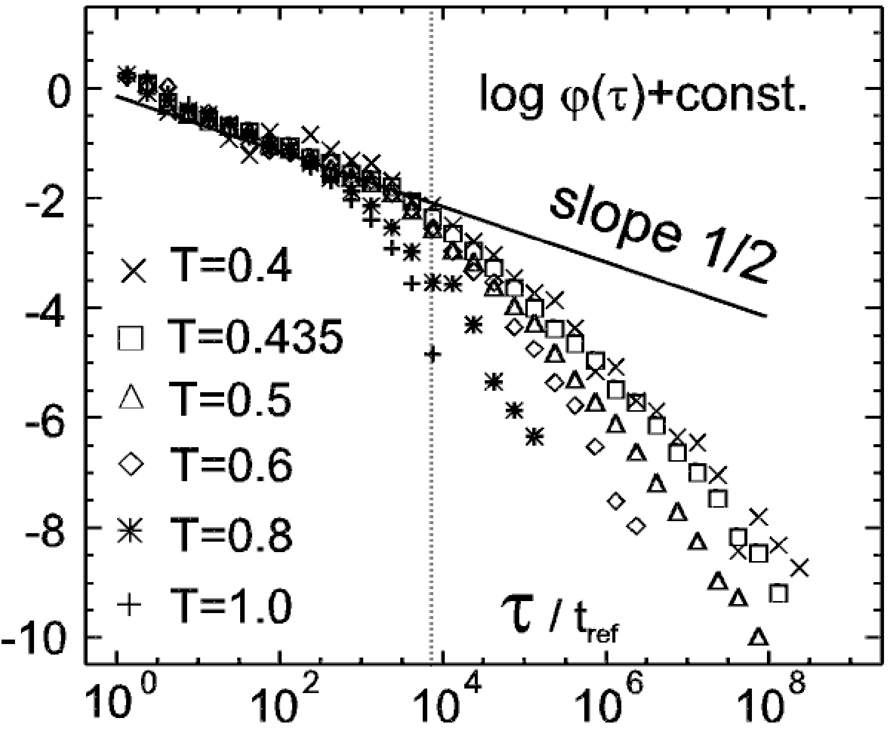


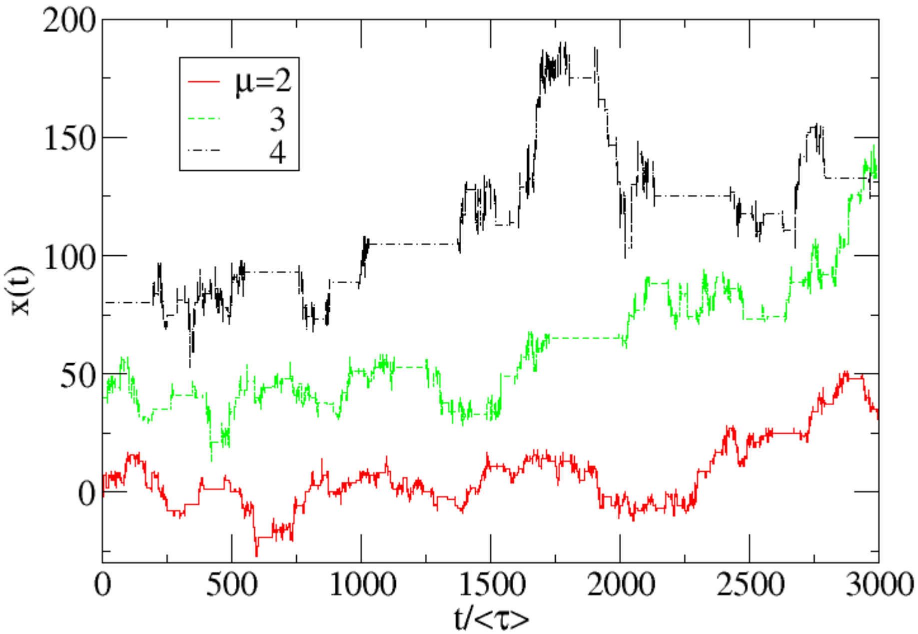


$<\tau(\varepsilon,T)> = \tau_0(\varepsilon) \exp(\beta V(\varepsilon))$

Not a simple bond-breaking mechanism

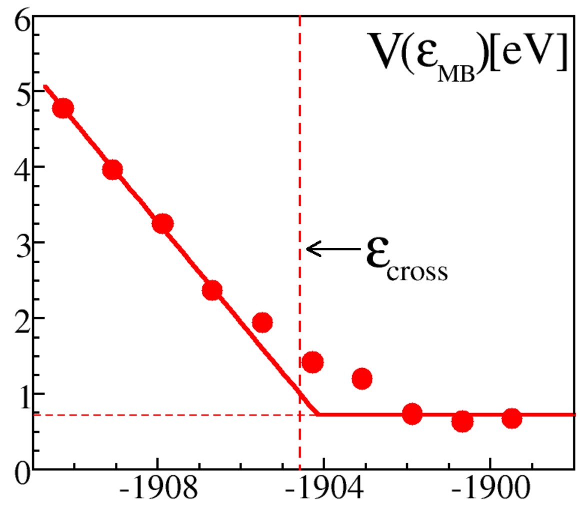
Waiting times from MB



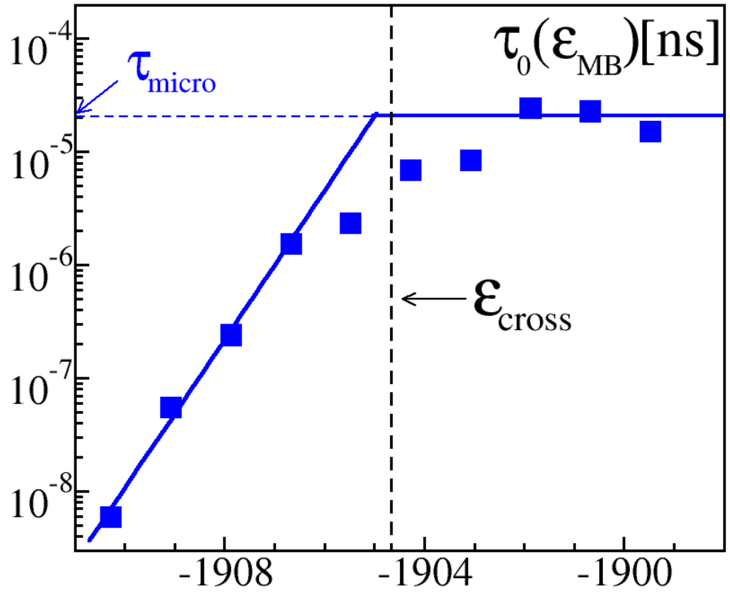


Broad waiting time distribution => Intermittent behavior

Qualitative picture



Entropic contributions



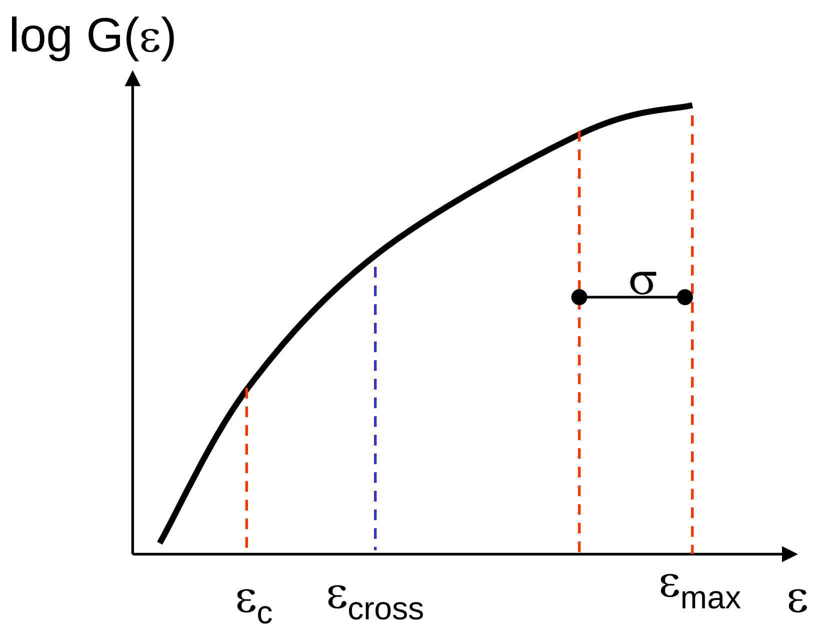
Dramatic increase of attempt frequency $\tau_0(\varepsilon)^{-1}$ (4 orders of magnitude)

Possible explanation: Entropic prefactor $G(\varepsilon_{cross})/G(\varepsilon)$

Quantitative approach

macroscopic dynamics | thermodynamics | microscopic dynamics

$$D(T) = c / \langle \tau(T) \rangle = c \int d\varepsilon \; p(\varepsilon,T) \, / \, \langle \tau(\varepsilon,T) \rangle$$



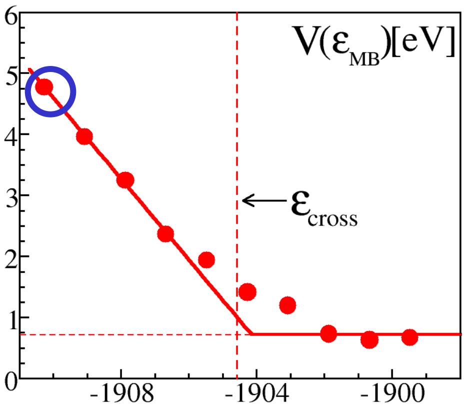
Effect of cutoff

Why does silica display Arrhenius behavior for T < 3000 K?

$$D(T) \propto \int d\varepsilon\, \overset{p(\varepsilon,T)}{\overset{\downarrow}{\delta}}(\varepsilon - \varepsilon_c)\frac{1}{\langle \tau(\varepsilon,T)\rangle} = \frac{1}{\langle \tau(\varepsilon_c,T)\rangle} = \tau_0^{-1}(\varepsilon_c)\exp(-\beta V(\varepsilon_c))$$

Silica is strong because of

- presence of low-energy cutoff of PEL
- Arrhenius behavior of $\langle\tau(\varepsilon_c,T)\rangle$ (Activation energy $V_{diff} \approx V(\varepsilon_c)$)



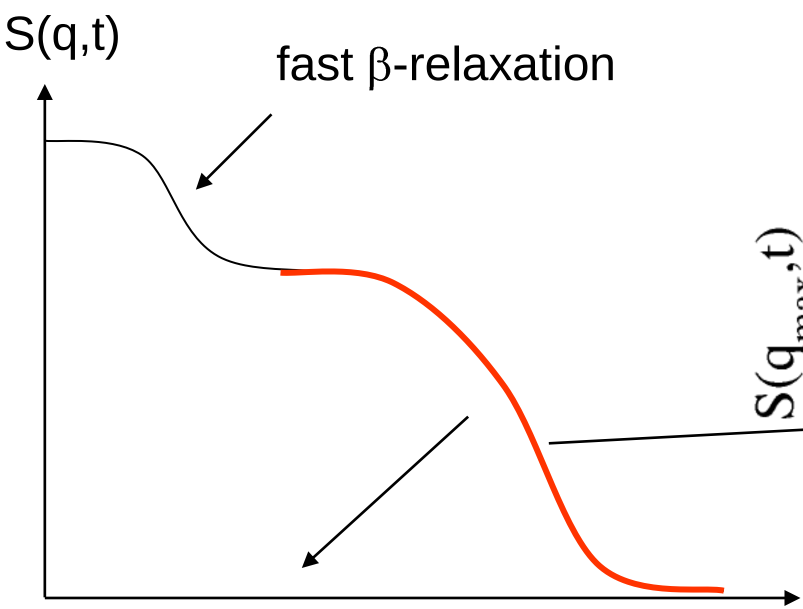
A. Saksaengwijit, J. Reinisch, A.H., PRL (2004); A. Saksaengwijit, A.H., PRE (2006)

Relaxation in supercooled liquids

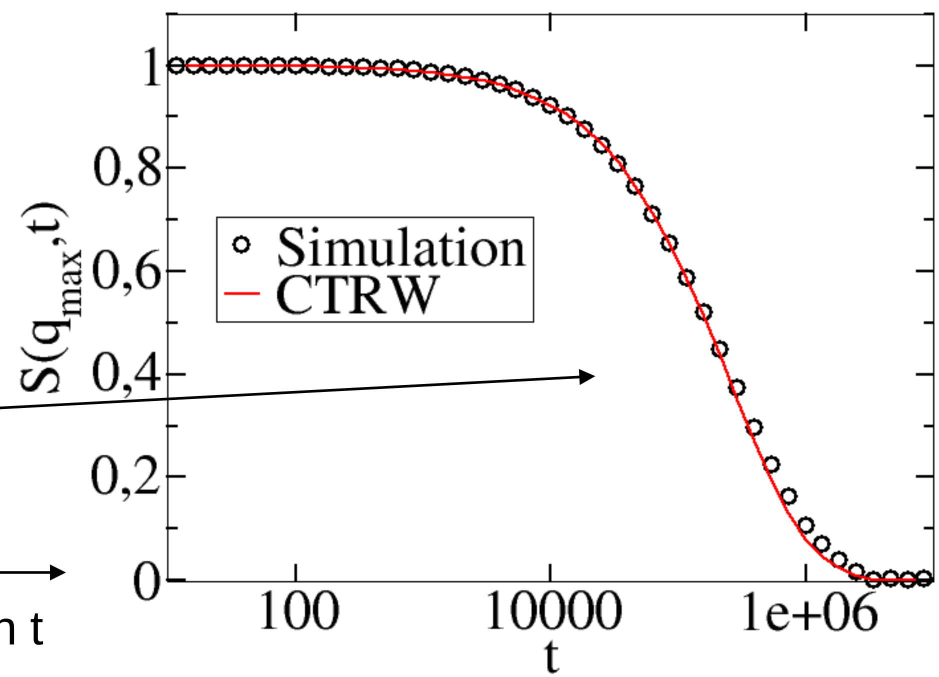
Complex dynamics of supercooled liquids

Observable: $S(q,t) = \langle \cos[q(x(t) - x(0)] \rangle$

(based on inherent structures)



α-relaxation $\propto \exp[-(t/\tau(q))^{\beta(q)}]$ ln t

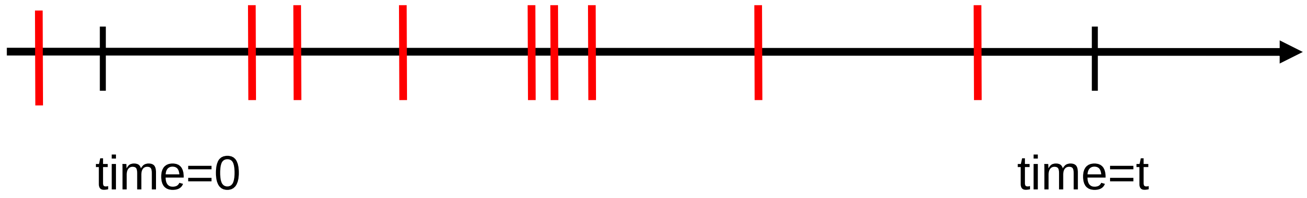


Understanding of $\tau(q),\beta(q)$?

q small: $S(q,t) = \exp(-q^2Dt)$

$D \propto 1/\langle\tau\rangle$

CTRW: General



- (C1) Spatial and temporal properties are independent (☺)
- (C2) Subsequent waiting times are independent (☺)

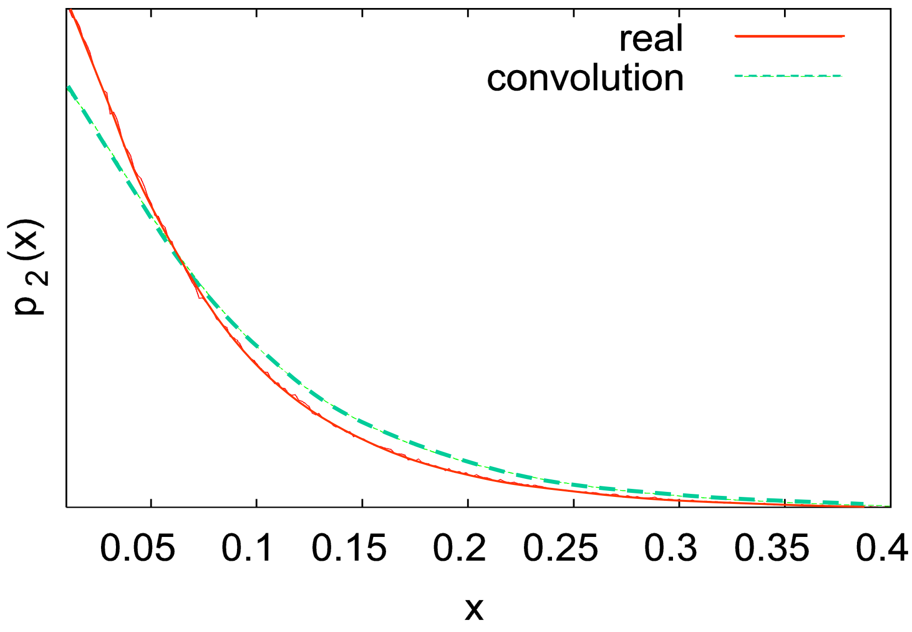
A.H., O. Rubner (PRE, 2008)

- (C3) Subsequent transitions are independent: $p_2(x) = \int dy\, p_1(y)\, p_1(x-y)$

Continuous-time random walk (CTRW): $a^2, \varphi(\lambda) \Rightarrow S(q,\lambda)$ (Montroll, Weiss)

CTRW: condition (C3)

Comparison
$p_2(x)$ vs. $\int dy\, p_1(y)\, p_1(x-y)$



⇒ Minor backward correlations

⇒ Expected deviations at large q

A.H., O. Rubner (PRE, 2008)

Properties of S(q,t)

$S(q,\lambda)$ => $S(q,t)$ in general not possible analytically

Define: $\tau_0 = \int dt\, S(q,t) \cong \tau(q)$

$$\beta_m = \frac{\tau_0^2}{\int dt\, t\, S(q,t)} \cong \beta(q)$$

Introduce:

$$V = \frac{\langle \tau^2 \rangle_\varphi}{2\langle \tau \rangle_\varphi^2} - 1 \qquad T = \frac{\langle \tau^3 \rangle_\varphi}{6\langle \tau \rangle_\varphi} - \frac{\langle \tau^2 \rangle_\varphi^2}{4\langle \tau \rangle_\varphi^2}$$

Result:

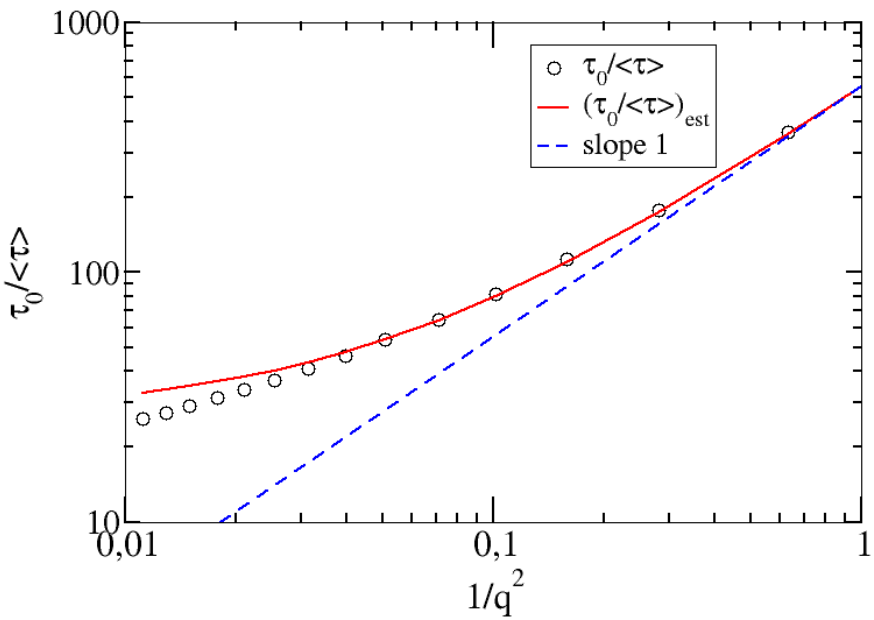
$$\tau_0(q) = \langle \tau \rangle_\varphi \left[V + \frac{2}{q^2 a^2} \right]$$

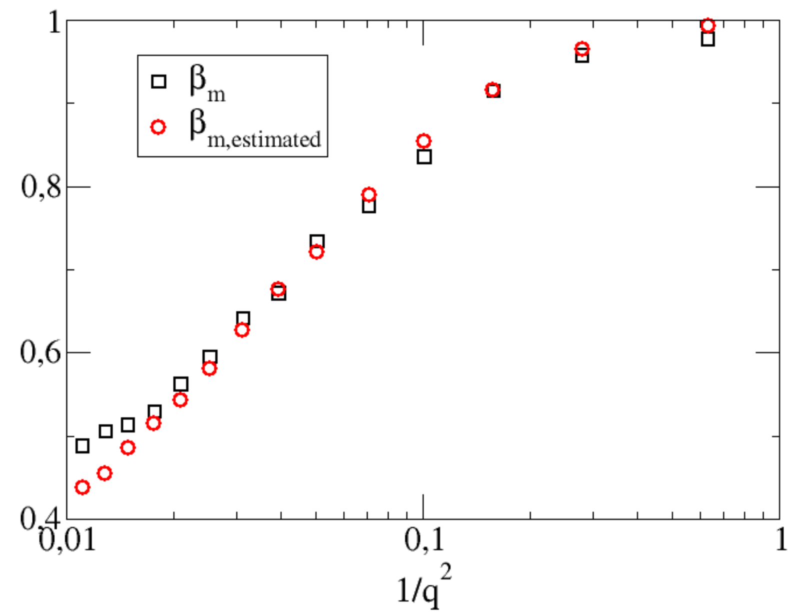
(Berthier, Garrahan et al)

$$\beta_m(q) = \frac{1}{1 + \dfrac{T}{\tau_0(q)^2}}$$

Comparison with numerical data

T=0.5





=> Good agreement

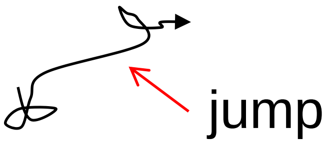
A.H., O. Rubner (PRE, 2008)

Waiting times from real space analysis

Determination of waiting times

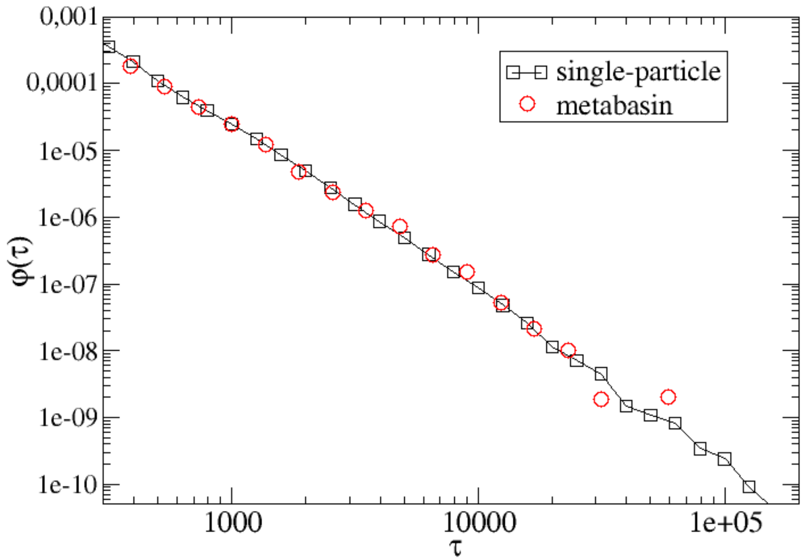
- Configuration space (Metabasins): τ_{MB}

- Real space (Identification of single-particle jumps): τ_{local}



(Vollmayr,Hedges,...)

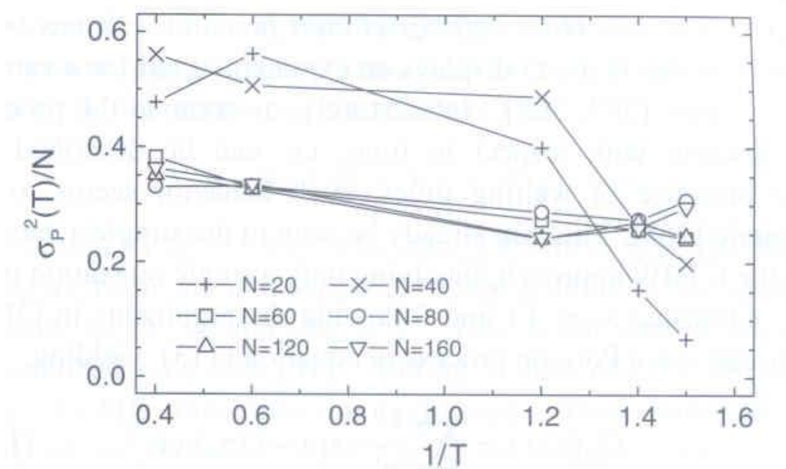
N=65, T=0.5



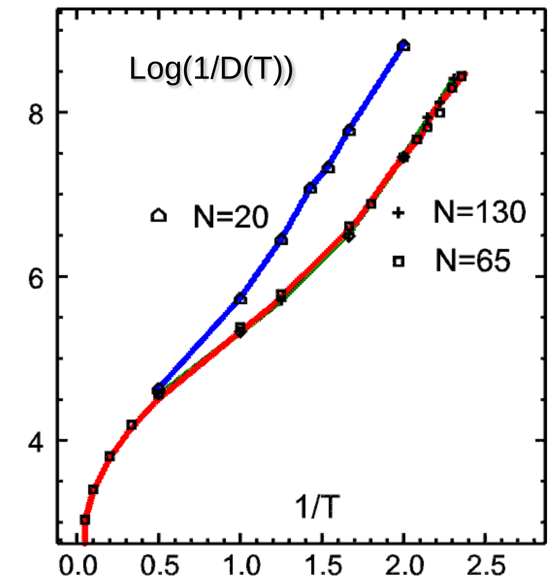
=> Similar properties

Finite-size effects

Thermodynamics



Diffusion

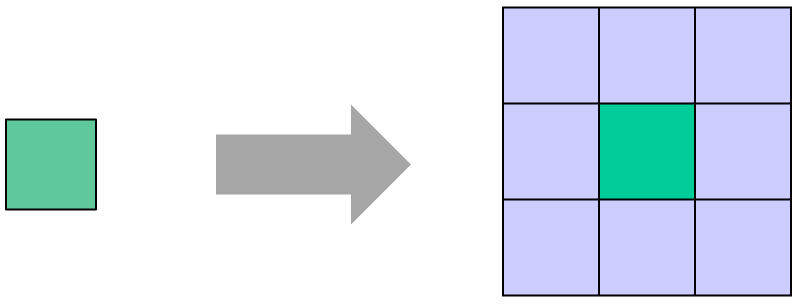


$\Rightarrow$ Minimum system size of approx. 60 particles (roughly 2 CRRs)

But:

- $D\,\tau_\alpha \propto \tau_\alpha^{\ a}$ with a = 2/3 (exp.: a $\approx$ 0.25)
- Significant finite-size effects for τ_α (Fabricius et al, Sastry et al)
- No growing length scales

Size dependence



≙

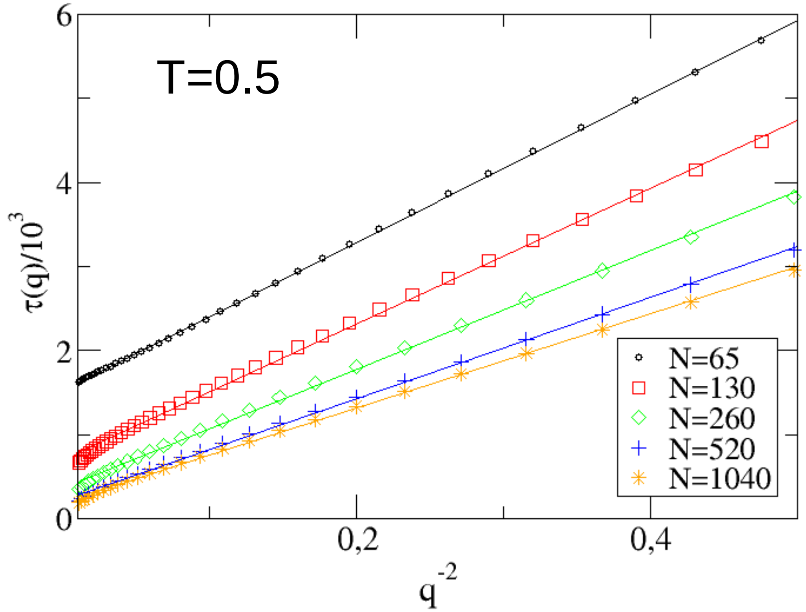
Introduction of coupling

Large N: CTRW description only possible for $\varphi(\tau_{local})$

Underlying reason: S(q,t) is a single-particle observable

Relaxation processes

$\tau(q) = \int dt\, S_{IS}(q,t)$

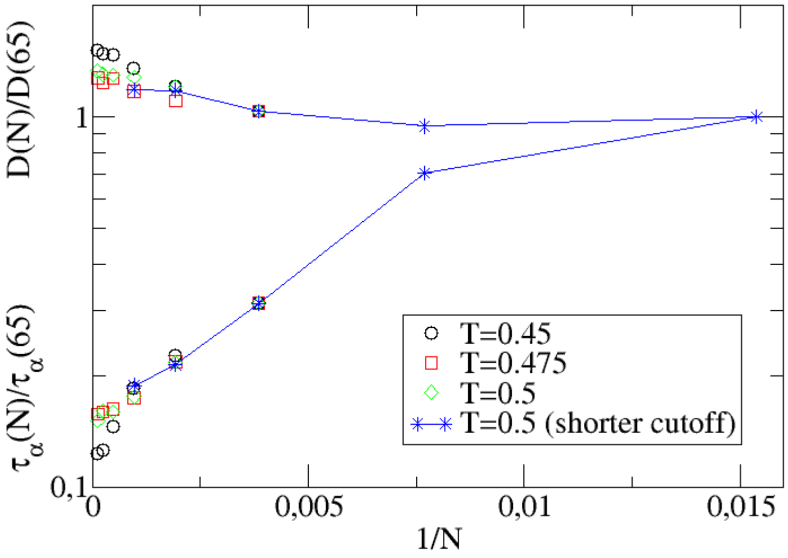


CTRW prediction: $$\tau_0(q) = 3a^2 D \langle \tau^2 \rangle_\varphi + \frac{1}{3Dq^2}$$ (valid for q < 8)

τ_α

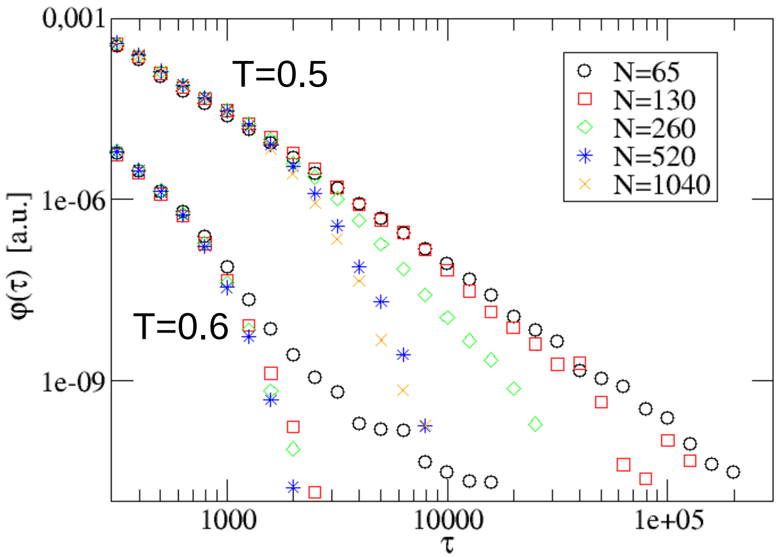
Finite-size effects revisited

65 <= N <= 1040



- Significant finite-size effects for structural relaxation, weak effects for diffusivity
- No general increase of mobility

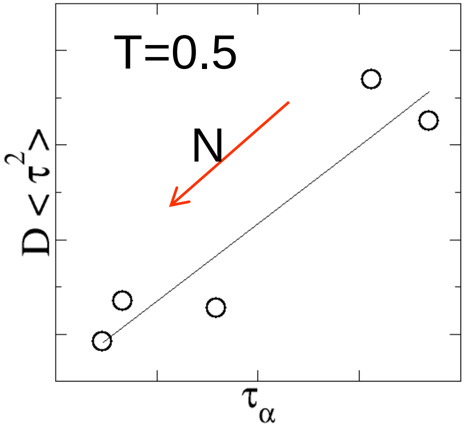
Finite-size effects for w.t.d.



- Major finite-size effects (up to N=520 for T=0.5)

- Second moment strongly N-dependent

- First moment only weakly N-dependent (otherwise D would be strongly N-dependent)



- Theoretical expectation $\tau_\alpha \propto D\langle\tau^2\rangle_\varphi$ fulfilled

From finite-size effects to coupling

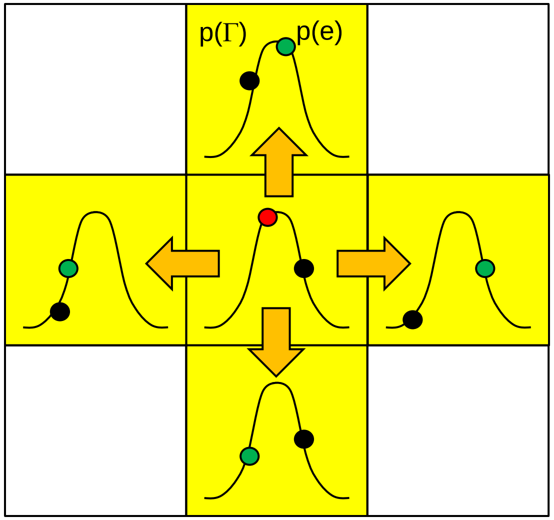
Conditions:

- $<\tau>$ and thermodynamics basically N-independent

- elementary system: approx. 30 particles

- $<\tau^2>$ strongly N-dependent

Idea:



Active & passive processes
=>

- narrowing of waiting time distribution
- identical first moment
- thermodynamics not modified

A.H., J. Phys. Cond. Mat. (2008)

Consequences of coupling

- Finite-size effects

Strong fluctuation limit: $\Gamma \Rightarrow \langle\Gamma\rangle$

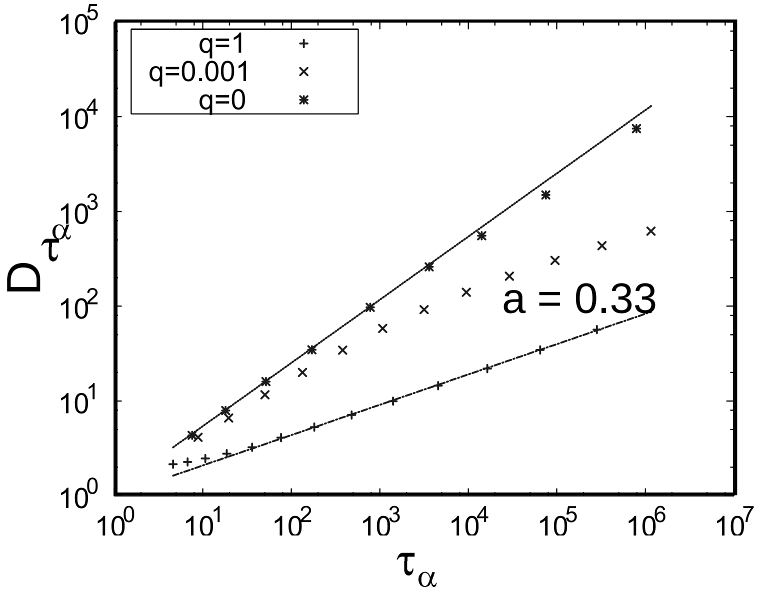
$D_{CRR} \propto 1/\langle\tau\rangle \propto \langle\Gamma\rangle$ => $D \propto \langle \langle\Gamma\rangle \rangle = \langle\Gamma\rangle = D_{CRR}$ => no finite-size effects

$\tau_{\alpha,CRR} \propto D\langle\tau^2\rangle \propto \langle\Gamma^{-1}\rangle$ => $\tau_{\alpha,} \propto \langle \langle\Gamma\rangle^{-1} \rangle = \langle\Gamma\rangle^{-1} \ll \tau_{\alpha,CRR}$

=> finite-size effects

- Violation of Stokes-Einstein relation

$D\,\tau_\alpha \propto \tau_\alpha^{\ a}$ with a=0.33



- Emergence of dynamic length scales

Comparison with facilitation model

Agreement:

- Coupling relevant to explain several key observations (Stokes-Einstein violation; dynamic length scales)
- Clustering of mobile regions
- Diffusion constant not dependent on nature of coupling (FA-model)

Disagreement:

- For BMLJ the minimum system (corresponding to 2-3 spins) already contains important information, e.g., about diffusivity and thermodynamics
- Spontaneous (untriggered) relaxation processes possible

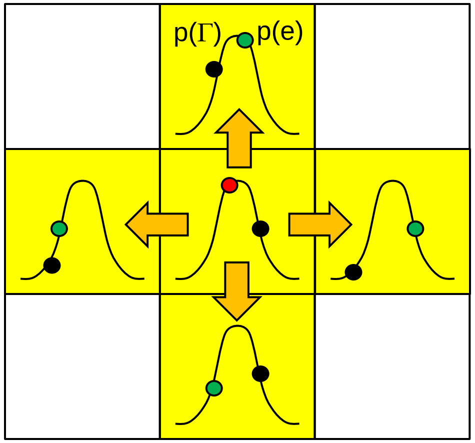
Summary

Energy landscape → Properties of CRR (D,thermodynamics)

CTRW-description → Properties of coupling (τ_α, length scales, Stokes Einstein violation)

Finite-size effects

→ Model of the glass transition



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