Glassy Dynamics in the Potential Energy Landscape

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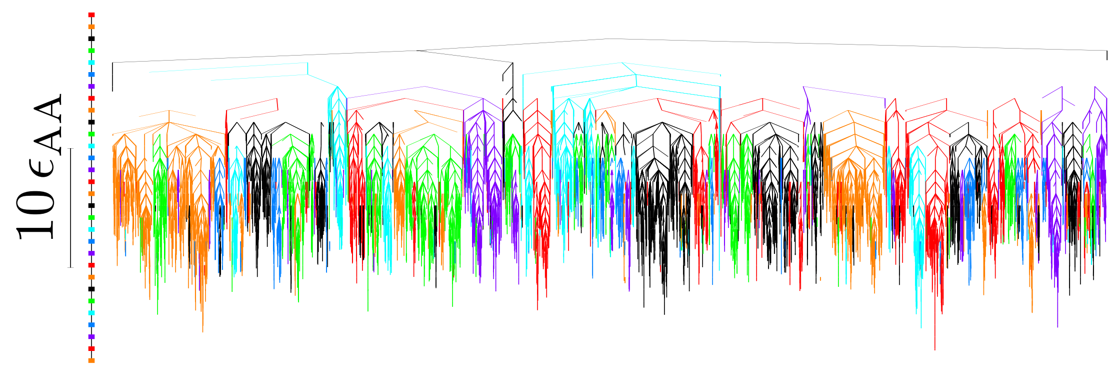


Introduction

- Strong and Fragile Glasses
- Potential Energy Landscape
- Visualising the Potential Energy Landscape

Glassy Dynamics

- Coarse-graining the Landscape - Metabasins
- Cage-breaking
- Reversed and Productive Cagebreaks
- Calculating Diffusion Constants

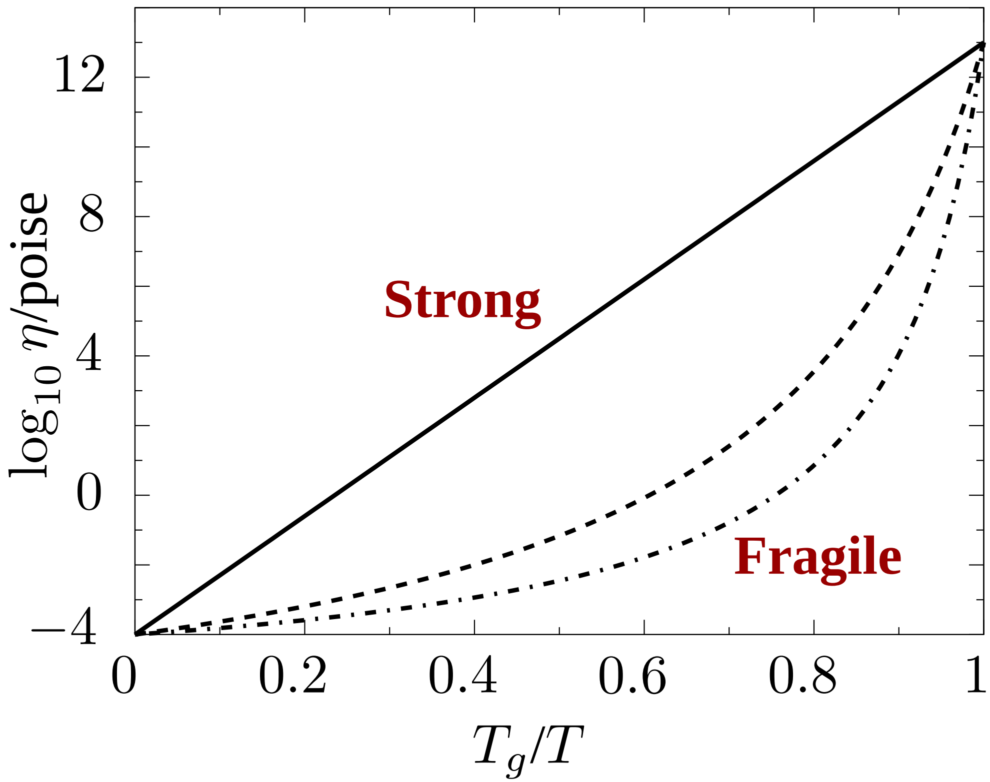
Cage-break Metabasins

- Random Walk
- Metabasins vs. Cagebreaks

'Super-Arrhenius' behaviour

For some supercooled liquids, the temperature dependence of relaxation times or transport properties such as the diffusion constant, D, is stronger than predicted by the Arrhenius law.

	Arrhenius	Super-Arrhenius
Temperature dependence	Arrhenius Law $\eta = \eta_0 \exp[A/T]$	VTF equation $\eta = \eta_0 \exp[A/(T - T_0)]$
Angell's classification	Strong	Fragile



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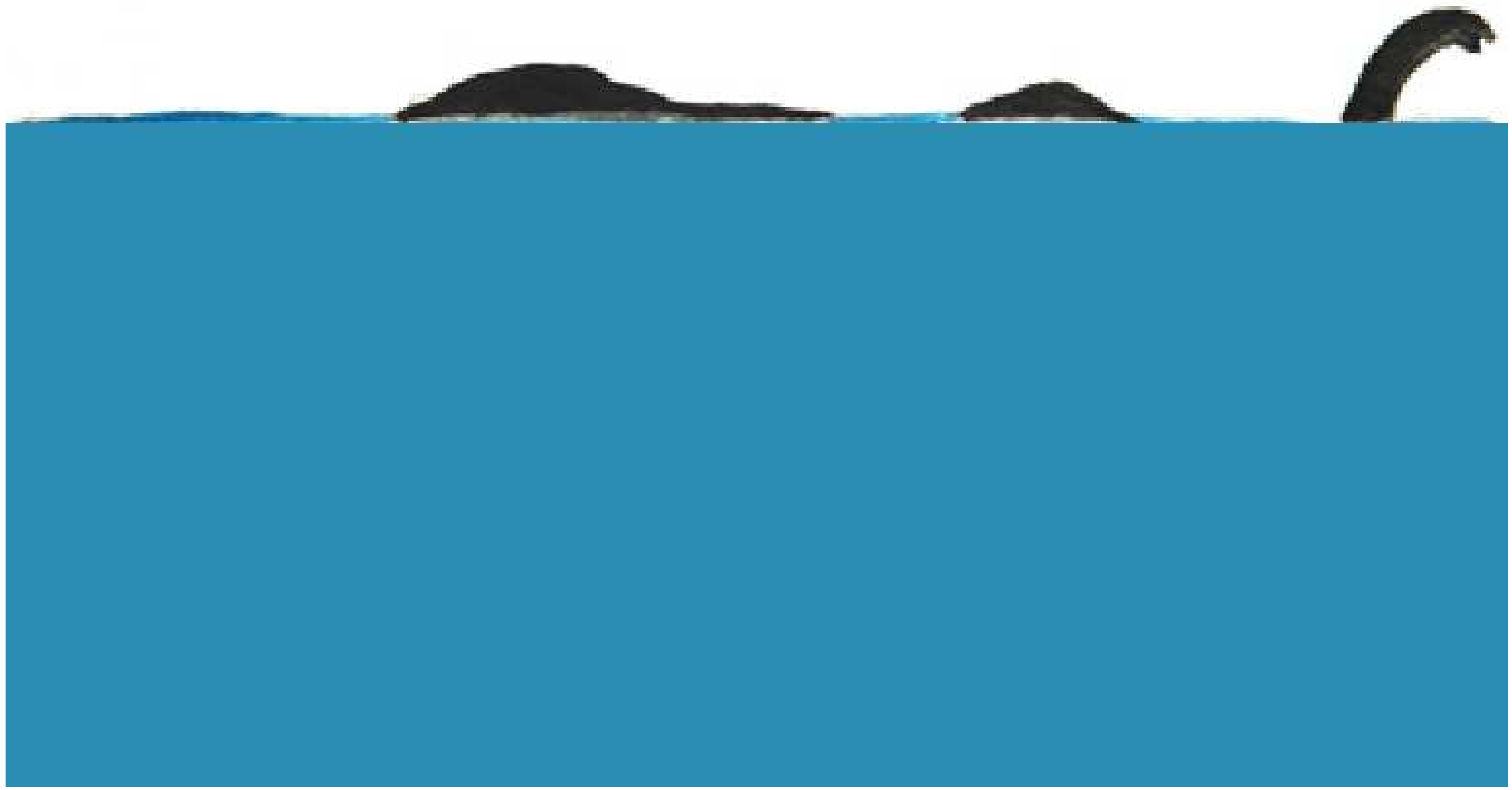
The Loch Ness Monster

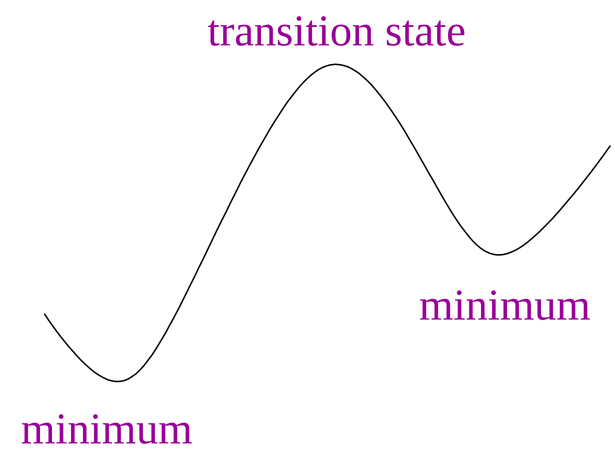



POTENTIAL ENERGY LANDSCAPE

The Loch Ness Monster

Potential Energy Landscapes

Potential Energy Landscape (PEL): the potential energy as a function of all the relevant particle coordinates.

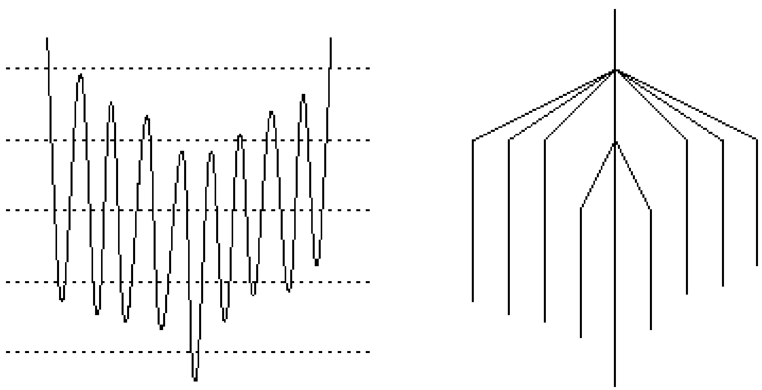


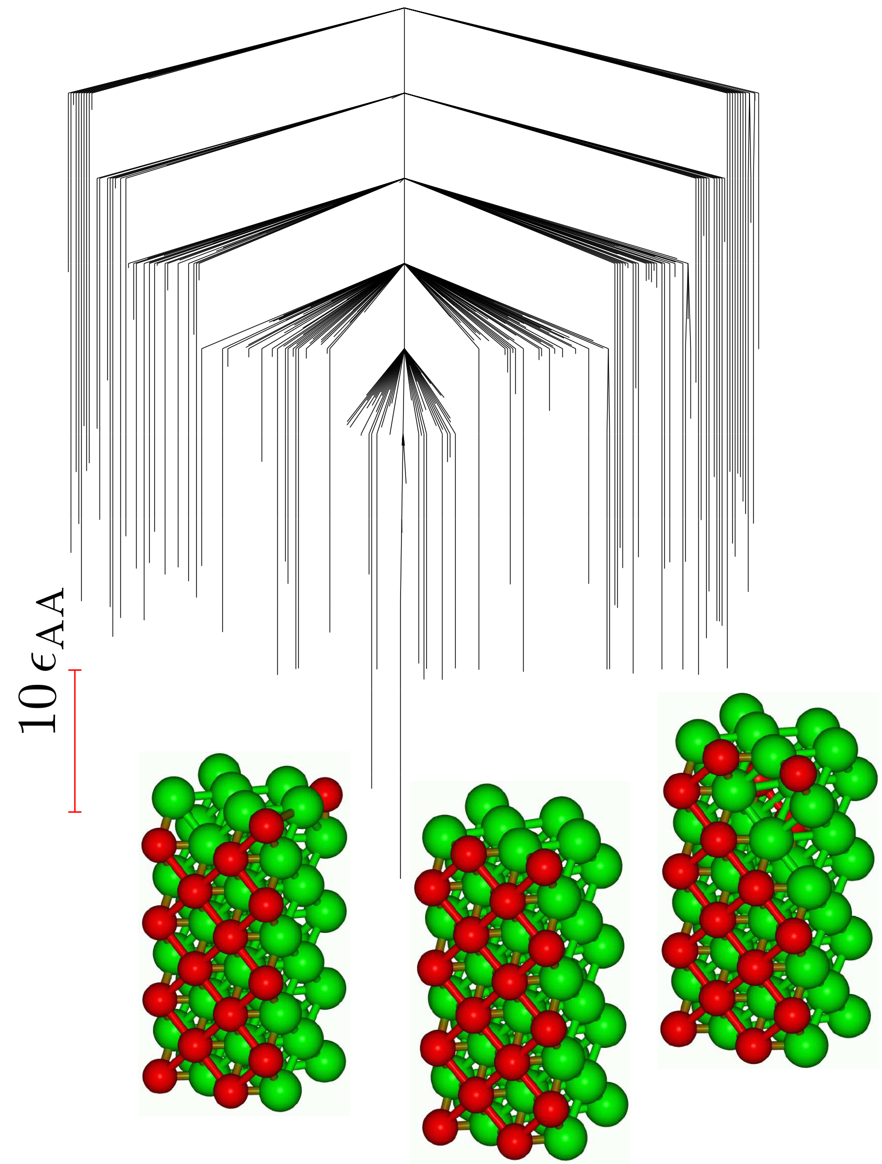
- Any structure can be minimised to find its inherent structure, a minimum on the PEL.
- Discretisation and simplification of configuration space.

Dynamics requires information about transition states, the highest point on the lowest-energy pathway between two minima.

Visualising the Landscape - Crystal Landscapes

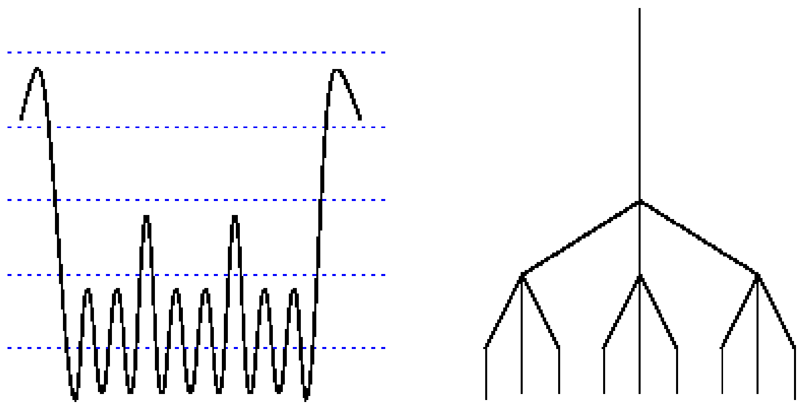
Disconnectivity Graphs



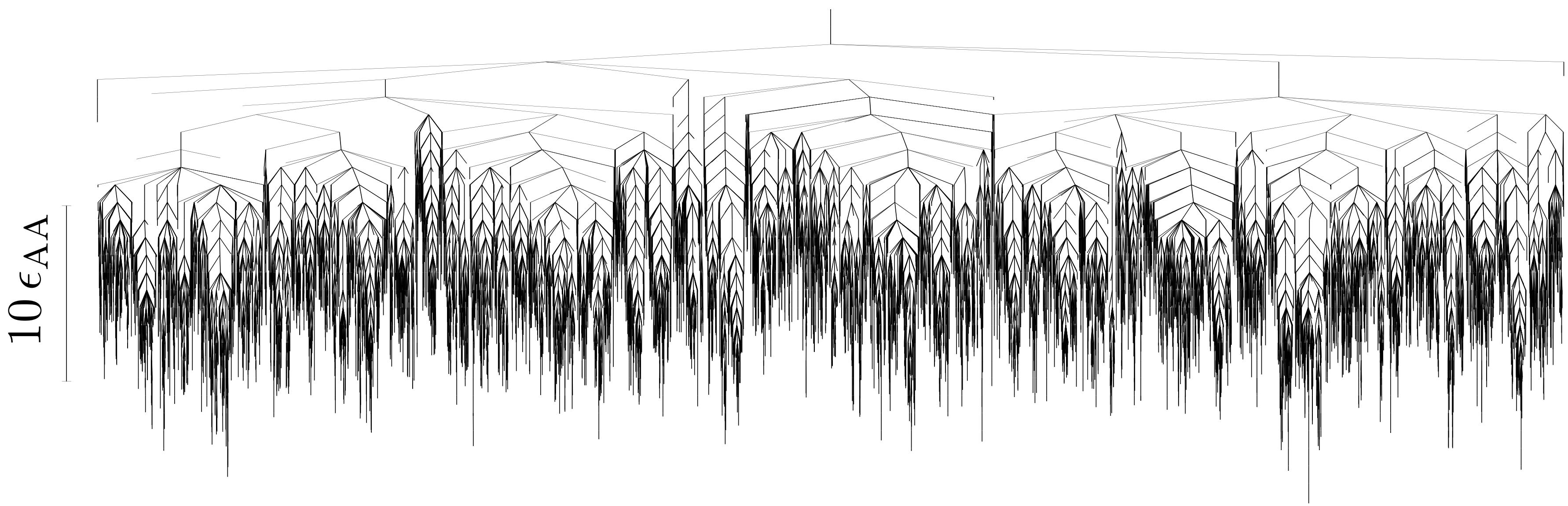


Calvo, Bogdan, de Souza and Wales, JCP 127, 044508 (2007)

Visualising the Landscape - Glassy Landscapes

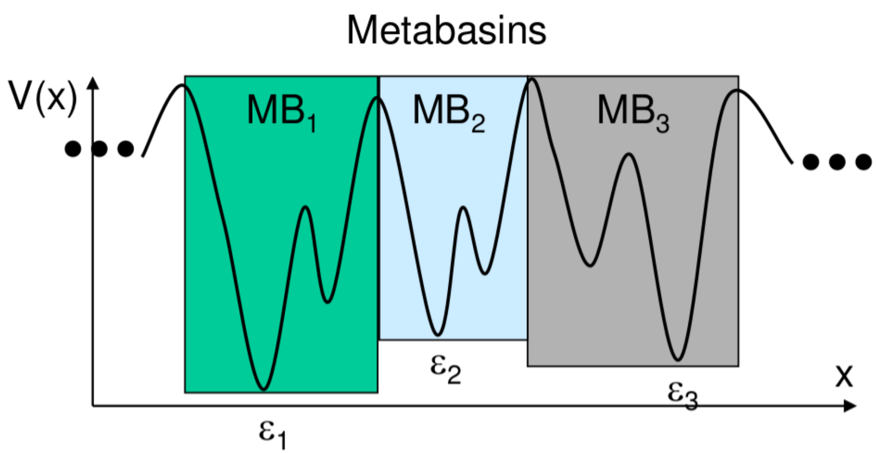


Disconnectivity Graphs



de Souza and Wales, JCP 129, 164507 (2008)

Coarse-graining the landscape



- Transitions between metabasins follow a random walk
- Metabasins are well-characterised by an energy and waiting time
- Diffusion constants can be calculated

Doliwa and Heuer, PRE (2003)

Problems with this approach:

- How but not Why.
- No information about microscopic mechanisms, within metabasins or for transitions between metabasins.
- Identify minima by total system energy, the method cannot be scaled for larger system sizes, restricted to around 65 atoms.

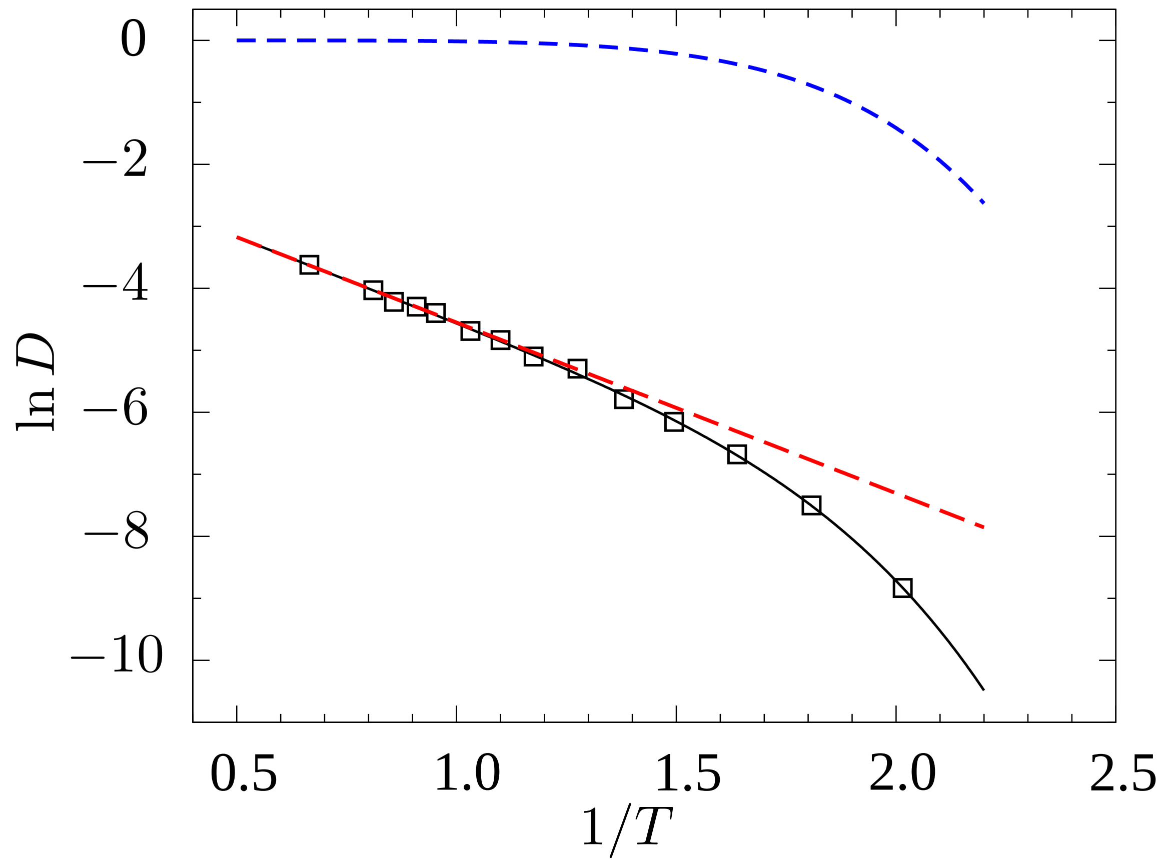
Fitting to Super-Arrhenius Behaviour

- $\ln D_{\text{erg}}(T) = -\left(\frac{m}{T}\right)^n - \frac{c}{T} + \ln D_0$
- Arrhenius component: $-\frac{c}{T} + \ln D_0$
- **Correction:** $-\left(\frac{m}{T}\right)^n$

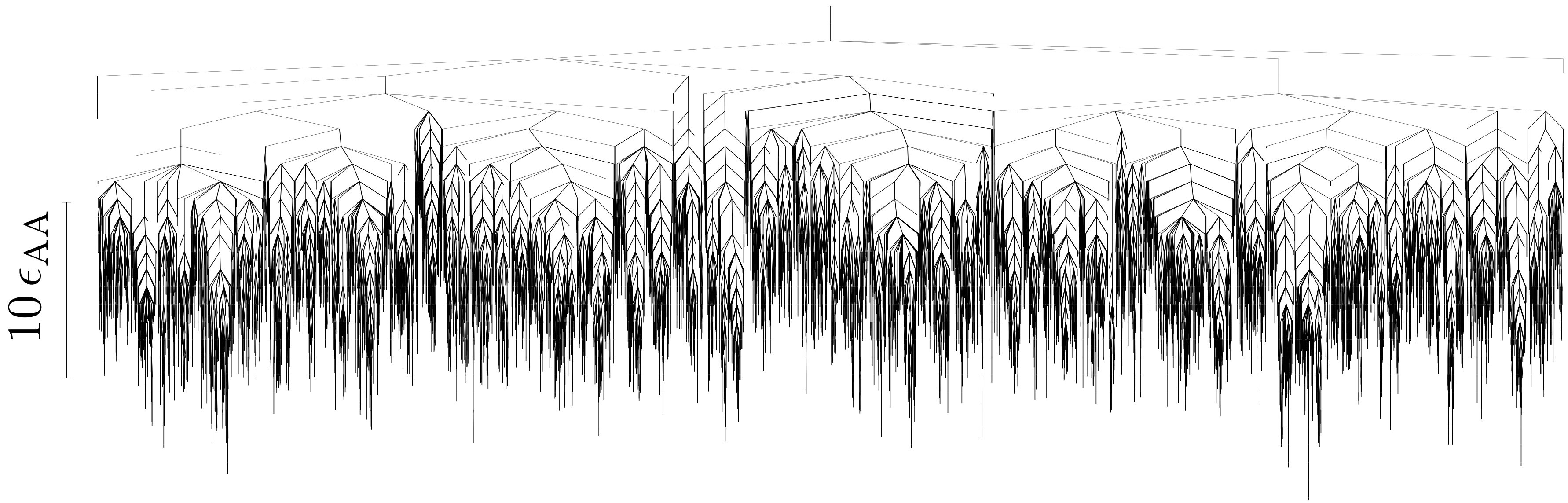
de Souza and Wales

PRB 74, 134202 (2006)

PRL 96, 057802 (2006)



Levels of Coarse-Graining



Negative correlation in Minima-to-Minima Transitions

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Negatively correlated Diffusive Processes

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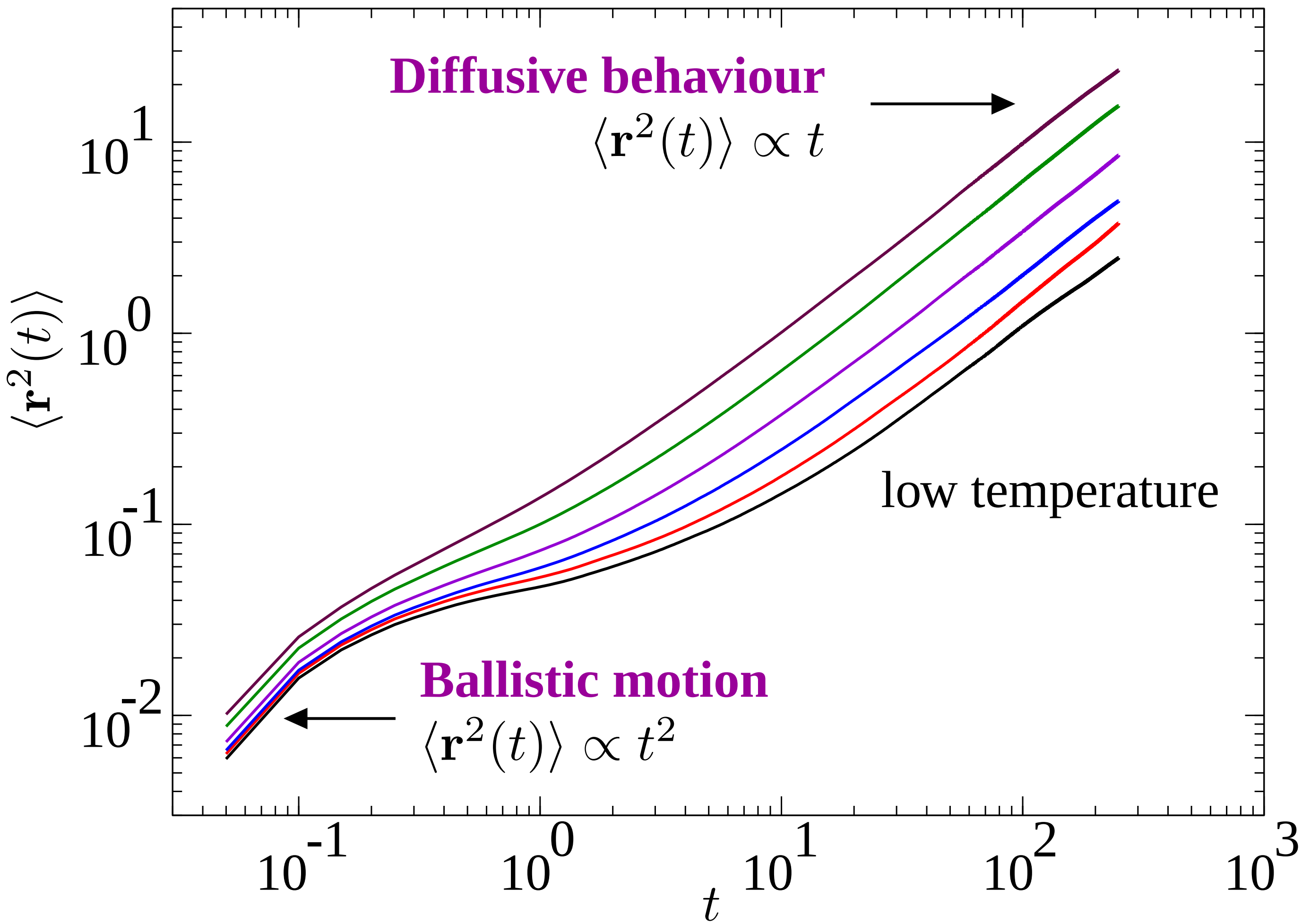
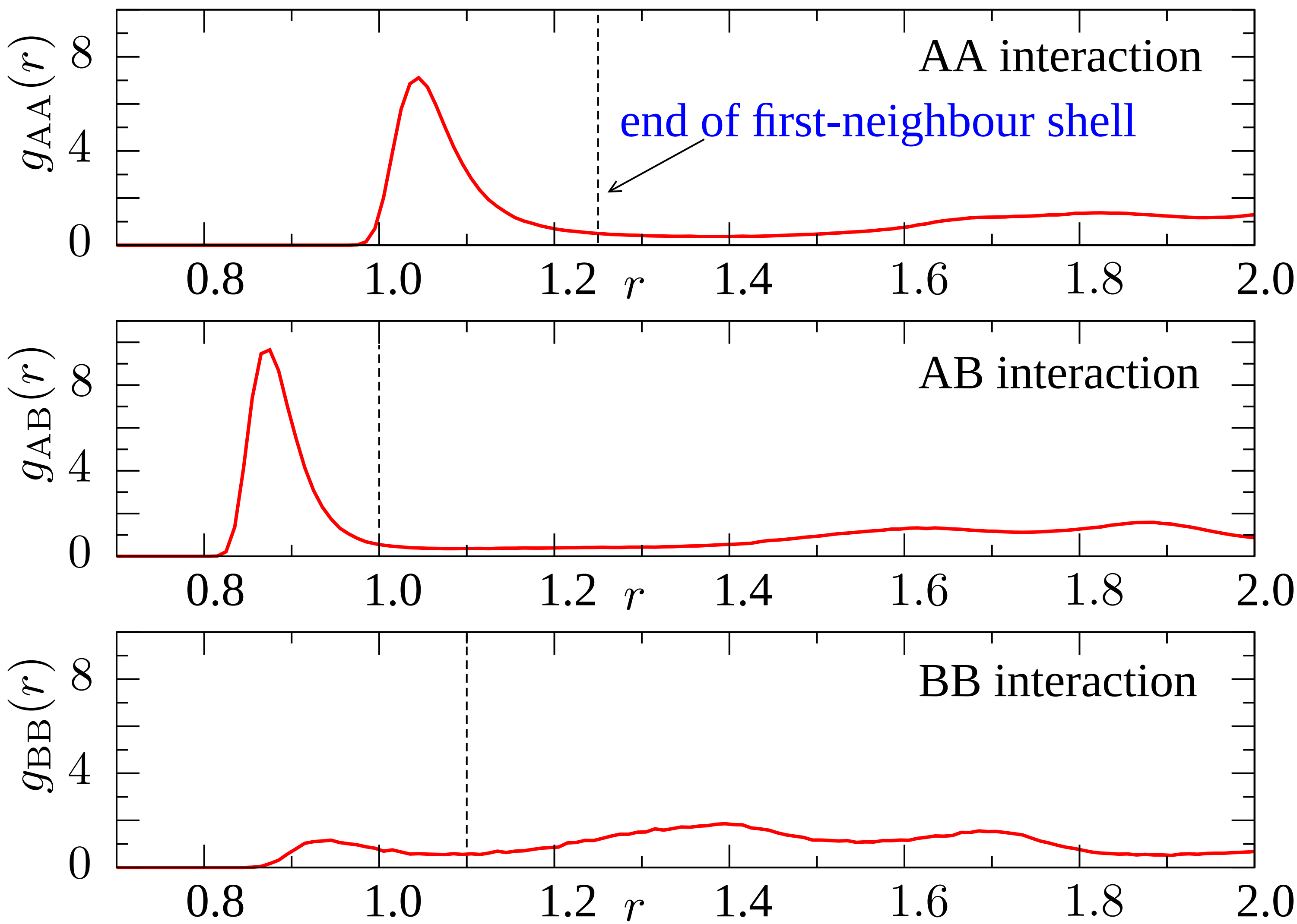
Random Walk between Metabasins

Mean square displacement → Diffusion

Einstein relation: $D = \lim_{t\to\infty} \frac{1}{6t}\langle \Delta \mathbf{r}^2(t)\rangle$



Nearest Neighbours



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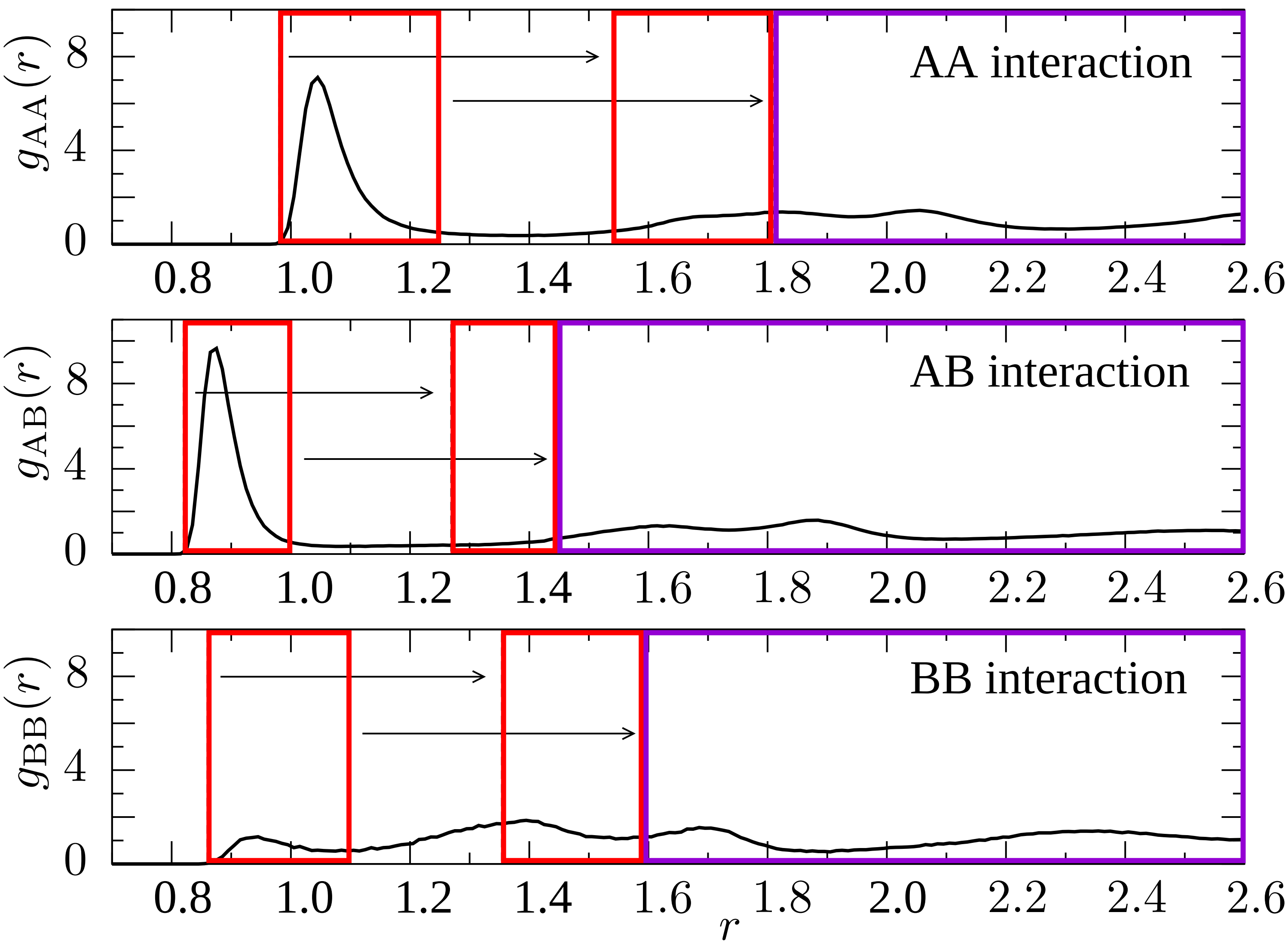
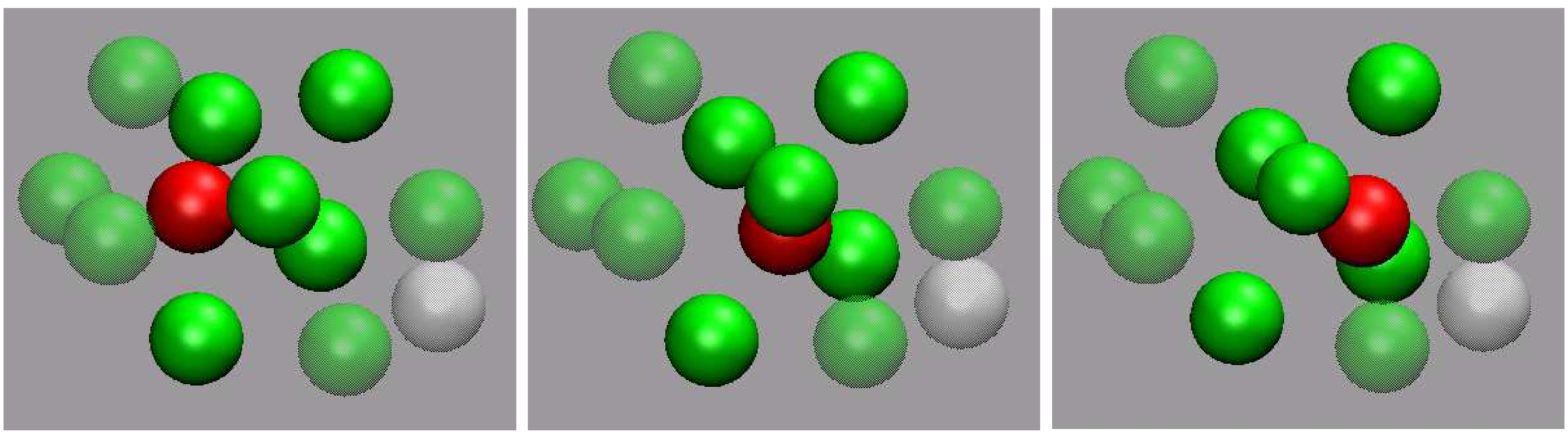


Cage-Breaking Criteria

- Nearest neighbours are within a distance of 1.25 for an AA interaction.
- For the loss of a neighbour, relative distance changes by more than 0.561, which corresponds to half the equilibrium pair separation.
- A cage-break occurs with the loss/gain of at least two neighbours.



- Sequence of minimum – transition state – minimum for a cagebreak.

de Souza and Wales, JCP 129, 164507 (2008)

Reversed Cage-Breaks

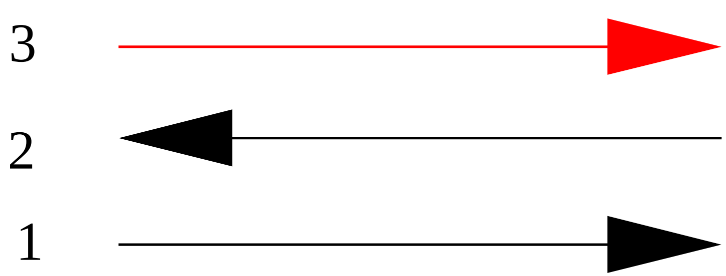
- Identified when the net displacement squared is less than 10^{-5}.
- Chains of repeatedly reversed cage-breaks are found.
- Determine cage-breaks which are Productive towards long-term diffusion:

The cage-break is not followed by the reverse event.

The cage-break is not part of a reversal chain

OR

ends a chain with an even number of reversals.



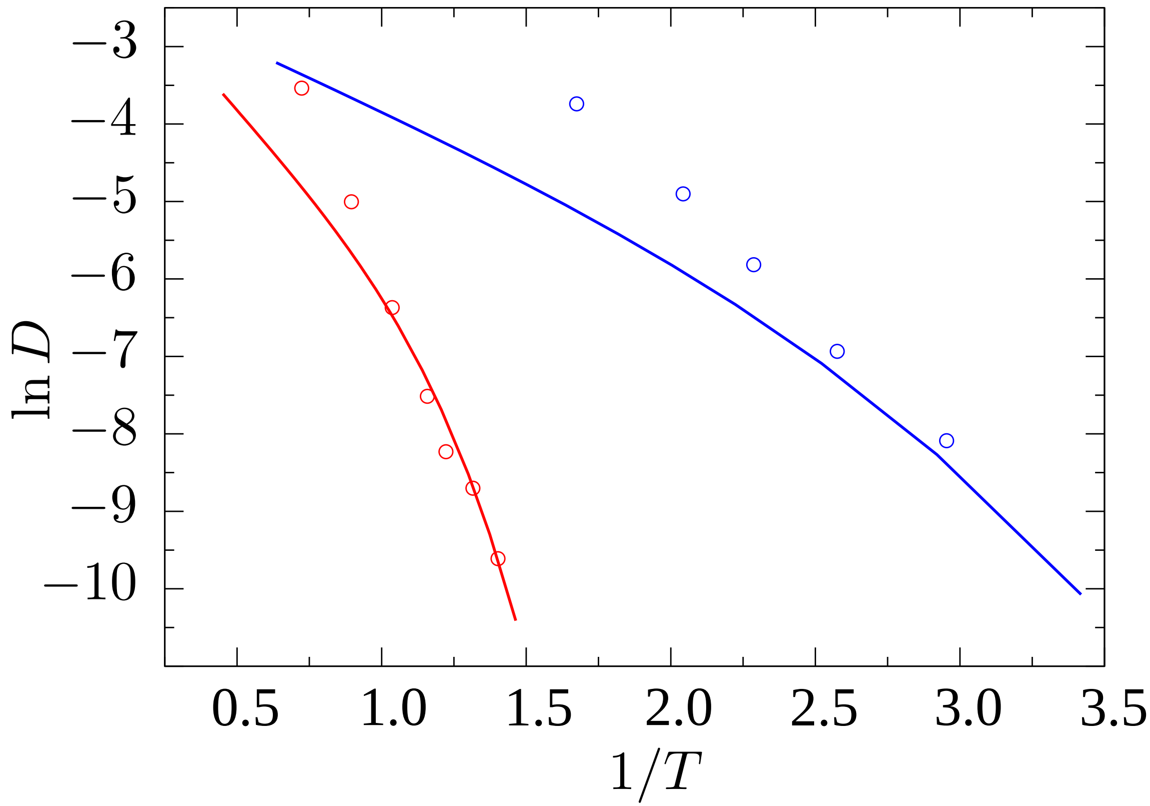
3 cage-breaks

2 reversals

Last cage-break is Productive

Diffusion from Productive Cage-Breaks

Productive Cage-breaks follow a random walk, $\langle \mathbf{r}^2(t) \rangle = \sum_{j=1}^{M} L_j^2$



60-atom binary Lennard-Jones at number densities of 1.3 and 1.1

Landscape-influenced regime $(1/T)$: 0.78 and 1.78

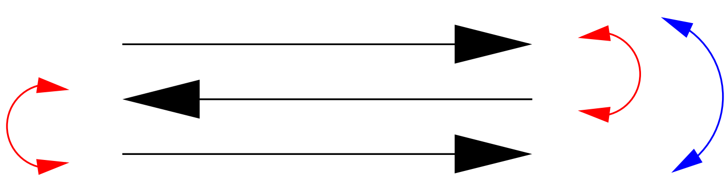
Landscape-dominanced regime $(1/T)$: 1.56 and 3.56

Accounting for correlation

The following simplifications are suggested by our studies of diffusion using Molecular Dynamics trajectories:

- The displacements of cage-breaks are similar and can be represented by a constant, L.
- Correlation arises from direct return events.
- We can account for correlation effects using a count of reversal chains of length z, $n(z)$.

$$\langle \mathbf{r}^2(t) \rangle = ML^2 \left(1 + 2\frac{-n(1) + n(2) - n(3) + \cdots}{M} \right)$$



Reversal chain, z=2.

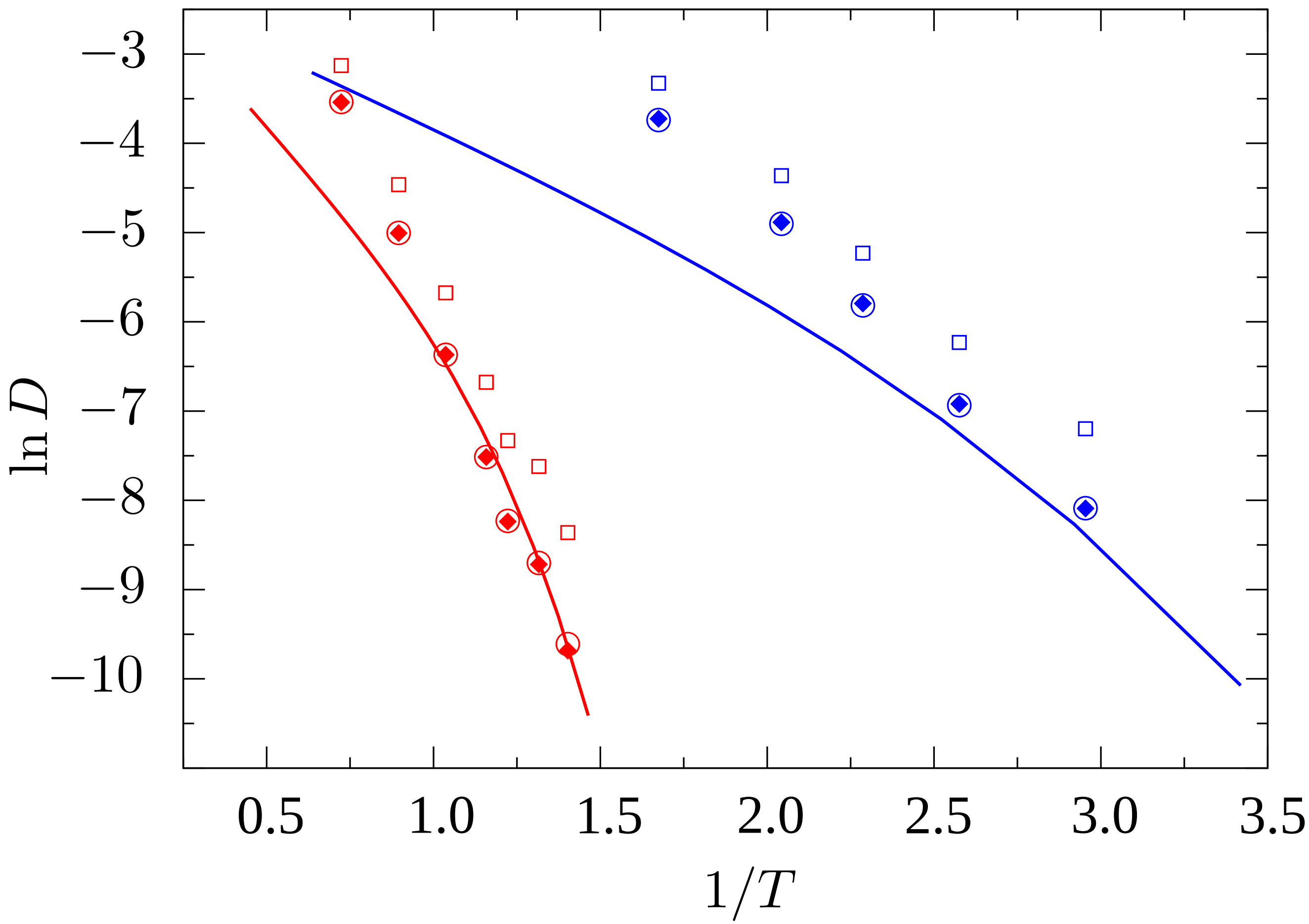
Two reversal chains, z=1.

$n(1) = 2$ and $n(2) = 1$

Diffusion from All Cage-Breaks

$$\langle \mathbf{r}^2(t)\rangle = \sum_{j=1}^{M} L_j^2 \times \left(1 + 2\frac{-n(1)+n(2)-n(3)+\cdots}{M}\right)$$

All Cage-Breaks



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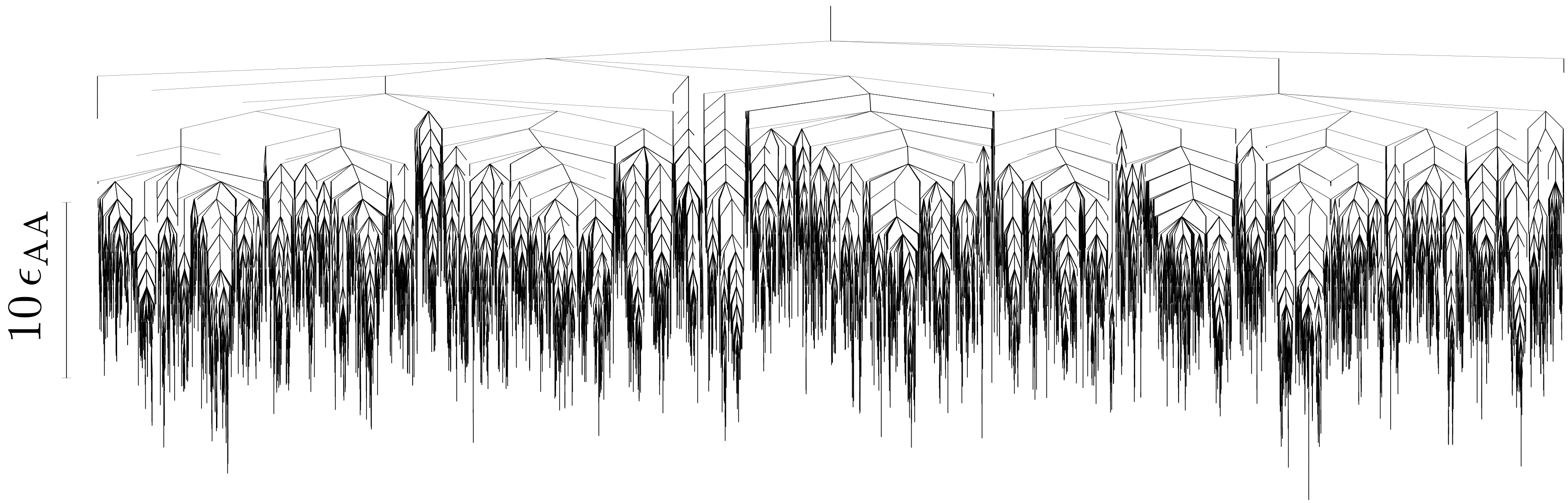

Negative correlation in Minima-to-Minima Transitions

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Negatively correlated Diffusive Processes

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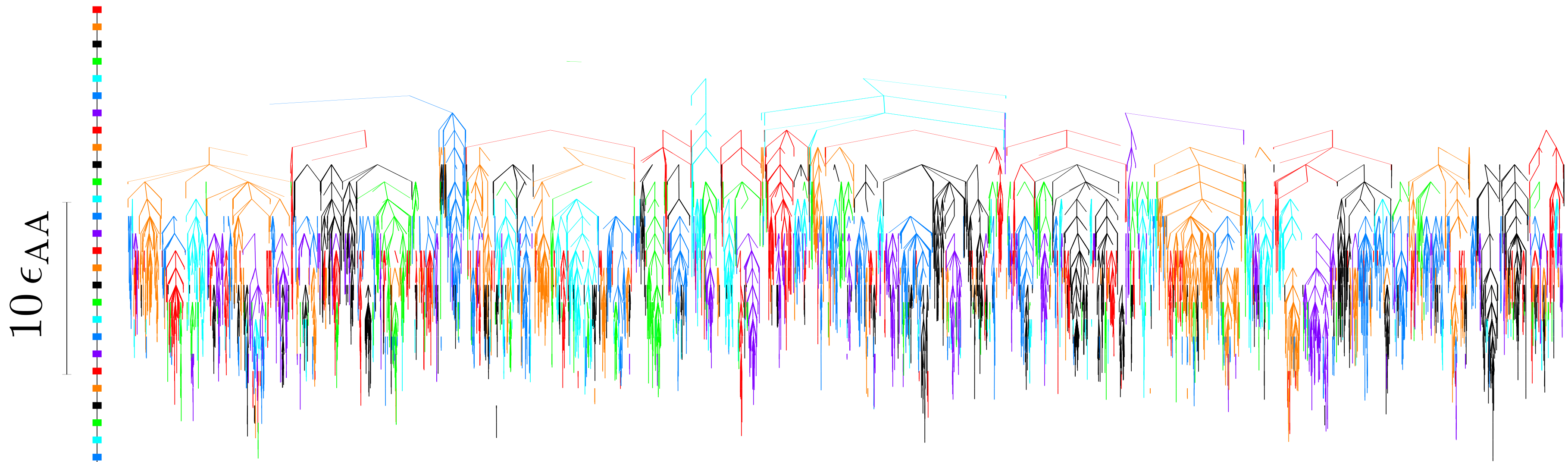
Random Walk between Metabasins

Levels of Coarse-Graining



Negative correlation in Minima-to-Minima Transitions

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Correlated Random Walk of Cage-Breaking events

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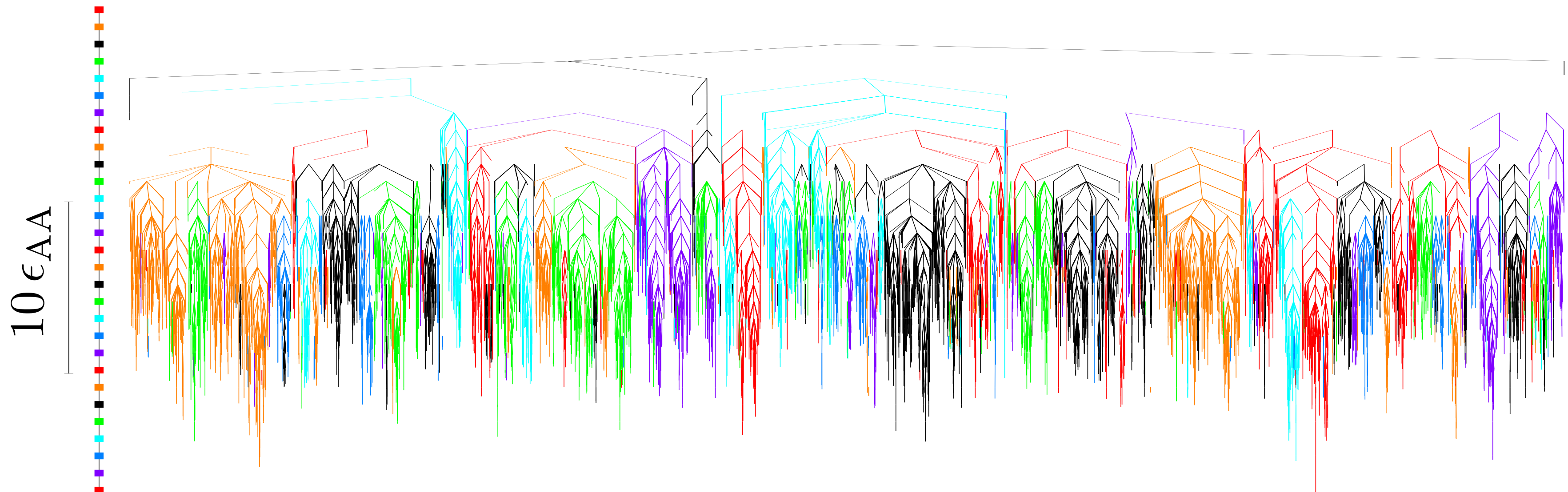
Random Walk between Metabasins

Levels of Coarse-Graining



Negative correlation in Minima-to-Minima Transitions

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Correlated Random Walk of Cage-Breaking events

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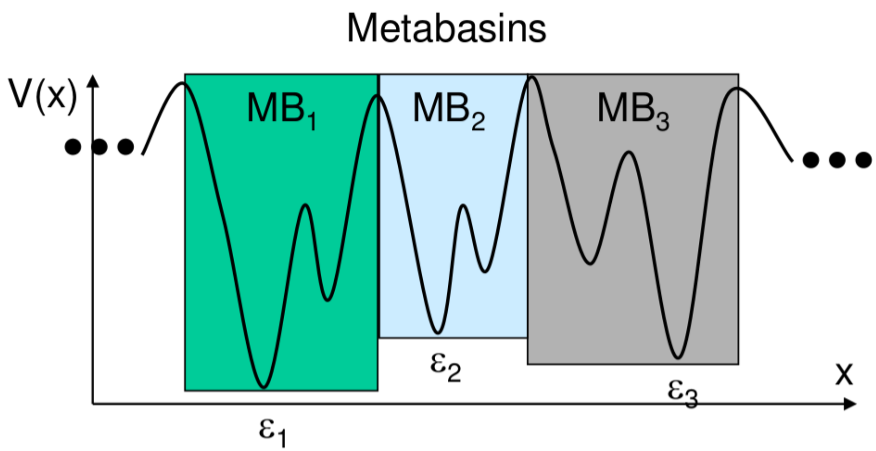
Random Walk of Productive Cage-Breaking events

Metabasins vs. Cagebreaks



- Transitions between metabasins follow a random walk
- Metabasins are well-characterised by an energy and waiting time
- Diffusion constants can be calculated

de Souza, Rehwald and Heuer, in preparation (2013)

Advantages of this method:

- How and Why.
- Information about microscopic mechanisms, within metabasins and for transitions between metabasins.
- Method can be scaled for larger system sizes.

Conclusions

- The Potential Energy Landscape for glass-forming systems is extremely complex.
- The landscape can be coarse-grained into metabasins
- Important transitions such as cagebreaks can be identified
- We have reconciled the two approaches, providing a microscopic description for metabasins within the PEL in the form of productive cagebreaks.
- Microscopic mechanisms <–> Macroscopic properties

The Loch Ness Monster