# ENERGY LANDSCAPE ANALYSIS OF ATOMIC AND POLYMER GLASSES

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GLASSES ARE NON-EQUILIBRIUM MATERIALS

Cooling rate [ºC/min]
- ▽ 1.0
- ◔ 0.5
- ◇ 0.2
- + 0.08
- □ 0.02
- △ 0.0037

LIQUID
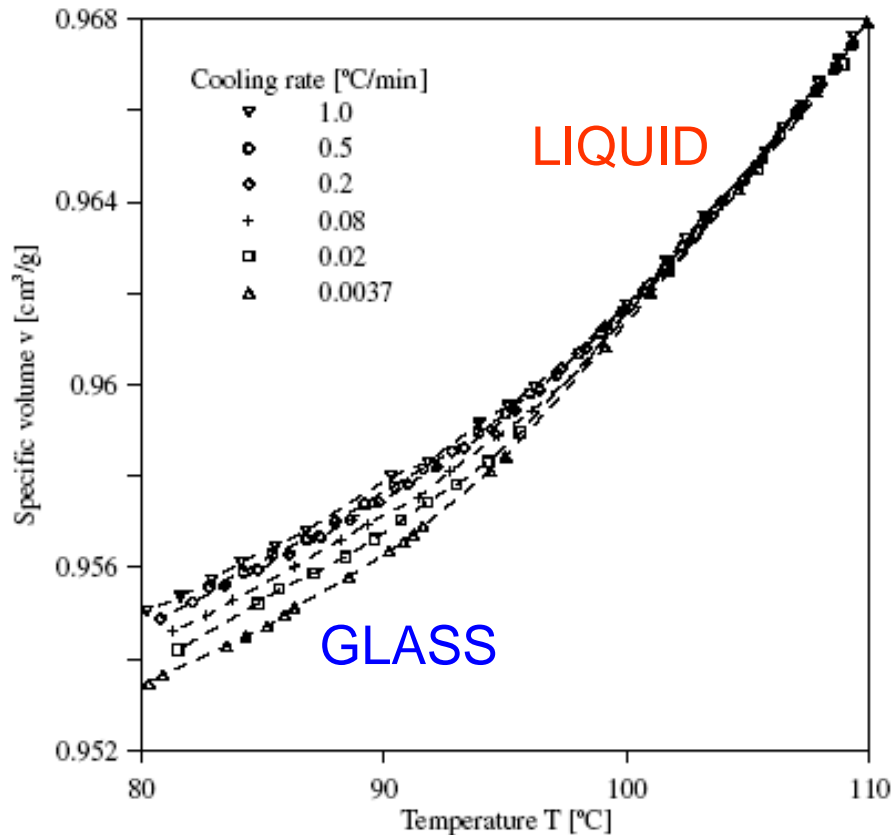
GLASS

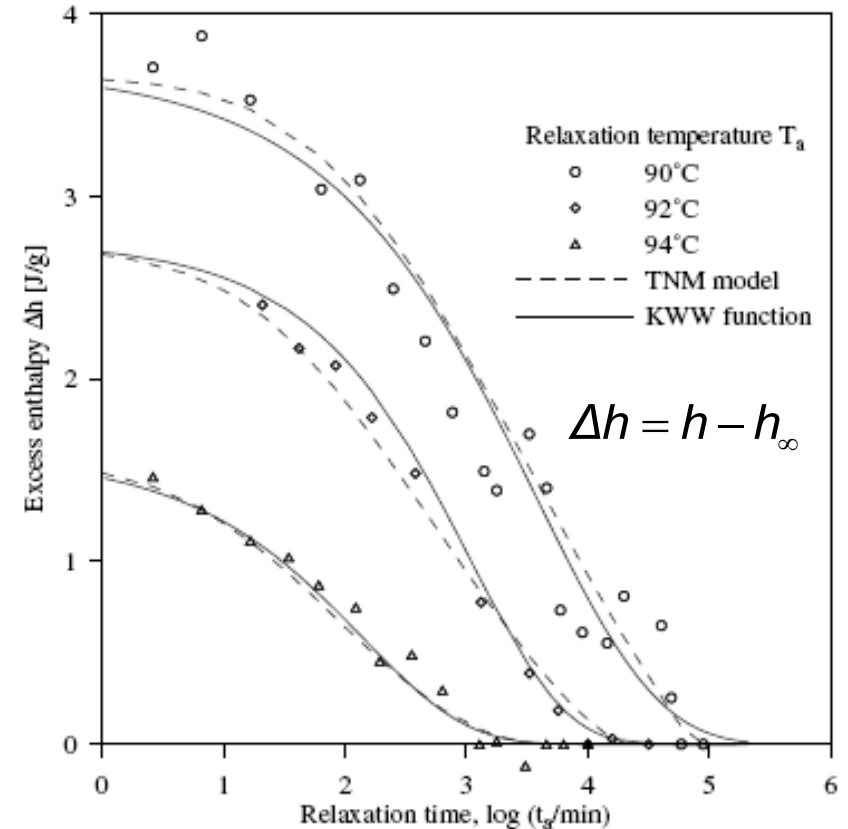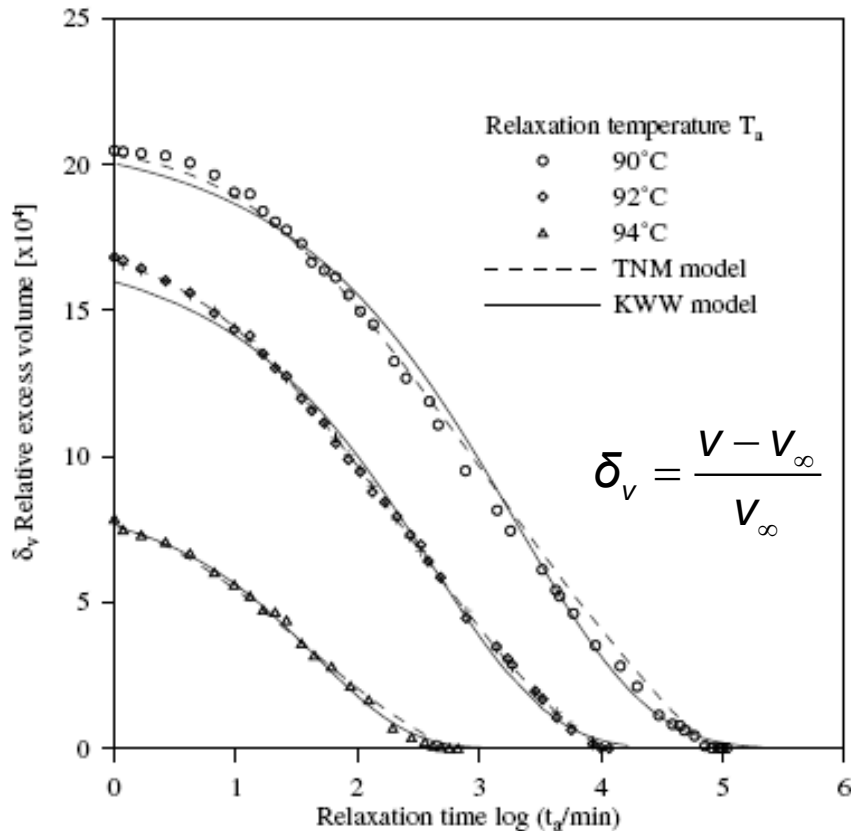atactic Polystyrene (aPS)

M_w=145 kg/mol

M_w/M_w=1.03

Glass structure and properties depend on the rate of cooling from the melt.

J. Hadač, P. Slobodian, P. Říha, P. Sáha, R.W. Rychwalski, I. Emri, J. Kubát, *J. Non-Cryst. Solids*, **353**, 2681-2691 (2007)

GLASSES ARE NON-EQUILIBRIUM MATERIALS

## Glass properties change with time (physical ageing)

aPS, M_w=145 kg/mol, M_w/M_w=1.03, T_g(1°C/min)=97.8±0.2^{o}C

Relaxation temperature T_a
- ○ 90°C
- ◇ 92°C
- △ 94°C
- - - - - TNM model
- —— KWW model

$$\delta_v = \frac{v - v_\infty}{v_\infty}$$

Relaxation temperature T_a
- ○ 90°C
- ◇ 92°C
- △ 94°C
- - - - - TNM model
- —— KWW function

$$\Delta h = h - h_\infty$$

δ$_v$ Relative excess volume [x10^4]

Relaxation time log (t$_a$/min)

Excess enthalpy Δh [J/g]

Relaxation time, log (t$_g$/min)

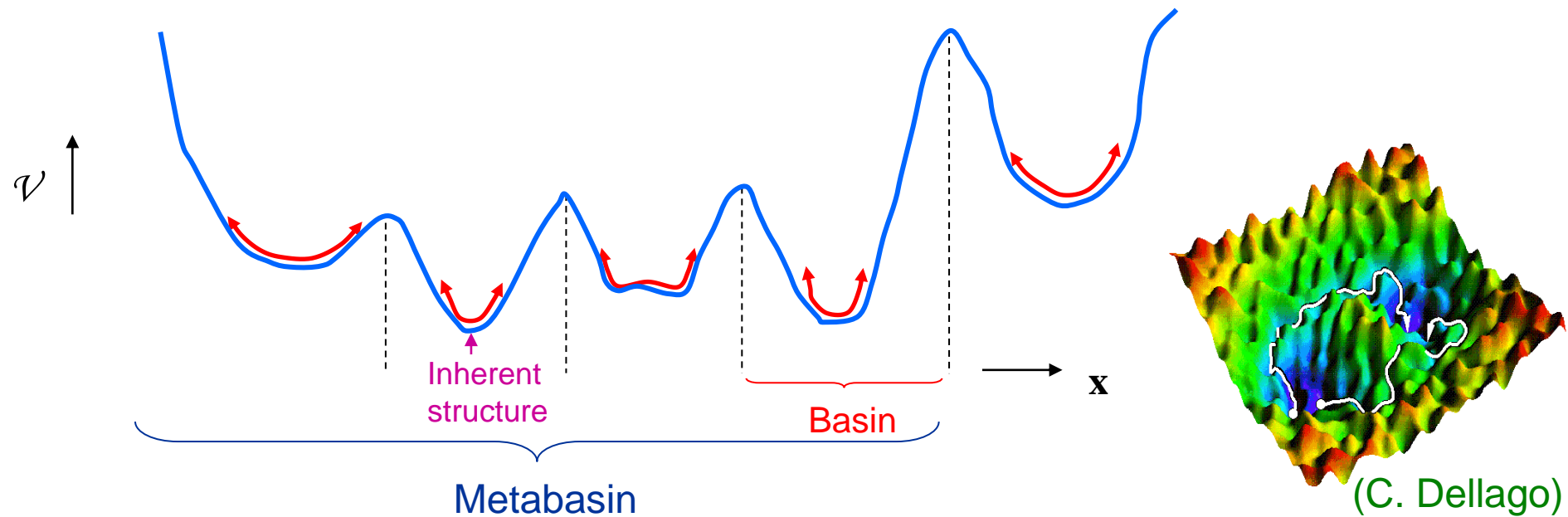# UNITED ATOM MODEL OF GLASSY ATACTIC POLYSTYRENE

A.V. Lyulin, J. DeGroot, M. Michels, *Macromol. Symp*. **191**, 167 (2003).
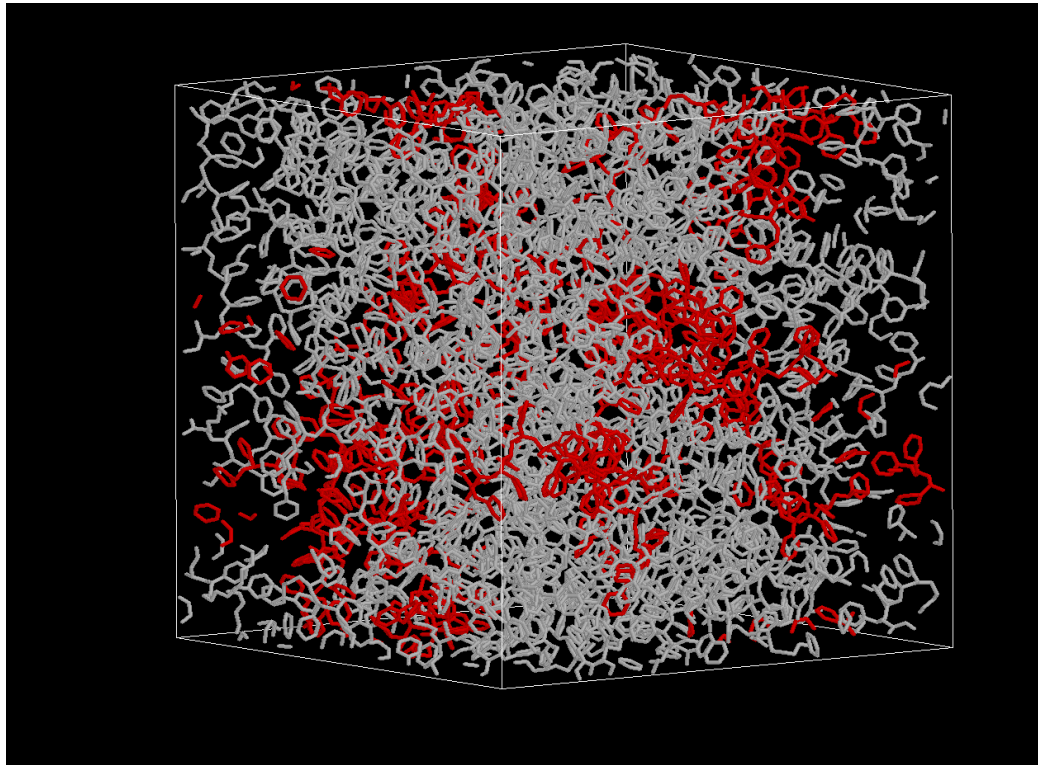
Starting point: Well-equilibrated melt configurations

T. Spyriouni, C. Tzoumanekas, DNT, G. Milano, F. Müller-Plathe, *Macromolecules*, **40**, 3876-3885 (2007).

ENERGY LANDSCAPE PICTURE OF A GLASS

Inherent structure

Basin

Metabasin

(C. Dellago)

Configuration fluctuating in the neighborhood of local energy minima: "Inherent structures" : F. H. Stillinger, *Science* **267**, 1935 (1995).
See also work by P.G. Debenedetti, D.J. Lacks, A. Heuer, G. Parisi, F Sciortino, D. Wales, T. Keyes, T.M. Truskett, DNT and U.W. Suter.

Transitions between minima inhibited by high energy barriers.

Glass properties: arithmetic averages of properties of individual "basins of attraction".   Restricted equilibrium established within each basin.

Ageing: Redistribution in configuration space resulting from infrequent transitions between basins.

IN-BASIN MOTION: QUASI-HARMONIC APPROXIMATION (QHA)

Mass-weighted coordinates

- **Taylor expansion of the energy around the minimum**

$$\mathcal{V}(\mathbf{x}) = \mathcal{V}(\mathbf{x}_o) + \cancel{\nabla_{\mathbf{x}}\mathcal{V}} \cdot (\mathbf{x} - \mathbf{x}_o) + \frac{1}{2}(\mathbf{x} - \mathbf{x}_o)^{\mathrm{T}} \cdot \mathbf{H} \cdot (\mathbf{x} - \mathbf{x}_o)$$

- **Second derivatives of the potential energy**

$$H_{ij} \equiv \partial^2 \mathcal{V} / \partial x_i \partial x_j$$

- **Eigenvalue problem**

$$\mathbf{H} \cdot \mathbf{e} = \lambda \mathbf{e}$$

- **Normal mode frequencies**

$$\omega_i = \sqrt{\lambda_i} \qquad \Rightarrow \qquad q_i^{\mathrm{vib}} = \frac{\exp\left(-\hbar\omega_i / 2k_B T\right)}{1 - \exp\left(-\hbar\omega_i / k_B T\right)}$$

- **Vibrational free energy**

$$A_{\mathrm{vib}} = -k_{\mathrm{B}} T \ln\left(\prod_i q_i^{\mathrm{vib}}\right)$$

$\mathcal{V}(\mathbf{x}_o) = \mathcal{V}_{\mathrm{inh}}$ and ω_i are functions of the spatial extent of the system.

# GIBBS ENERGY MINIMIZATION OF A BASIN UNDER GIVEN STRESS STATE

$$G = \mathcal{V}_{\mathrm{inh}} + A_{\mathrm{vib}} - V_{\mathrm{o}} \sum_{ij} \sigma_{ij}\varepsilon_{ij}$$

Quench from melt by classical MD

$V_k = V_{\mathrm{o}}, \ldots, V_{\mathrm{f}}$

Inherent structure

Vibrational free energy

$\mathbf{G}_k(\boldsymbol{T}, \boldsymbol{P}, \boldsymbol{V}_k)$

Gibbs Free Energy
Classical QHA
T=200 K, P =1 Atm
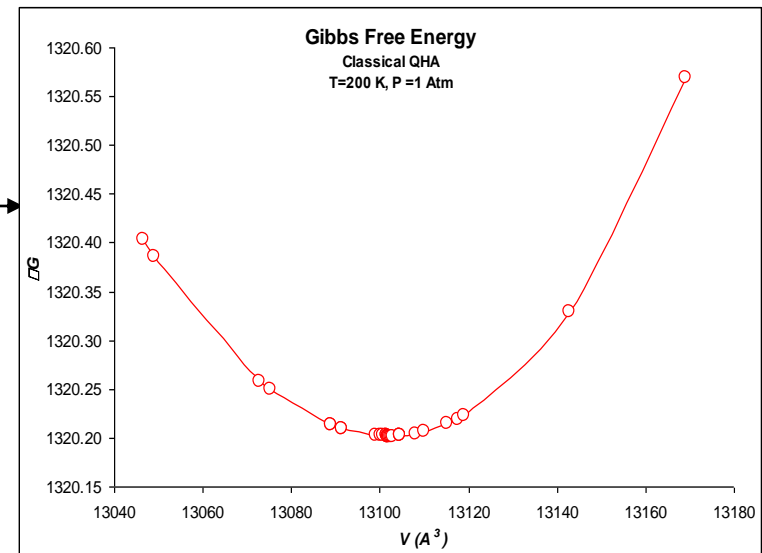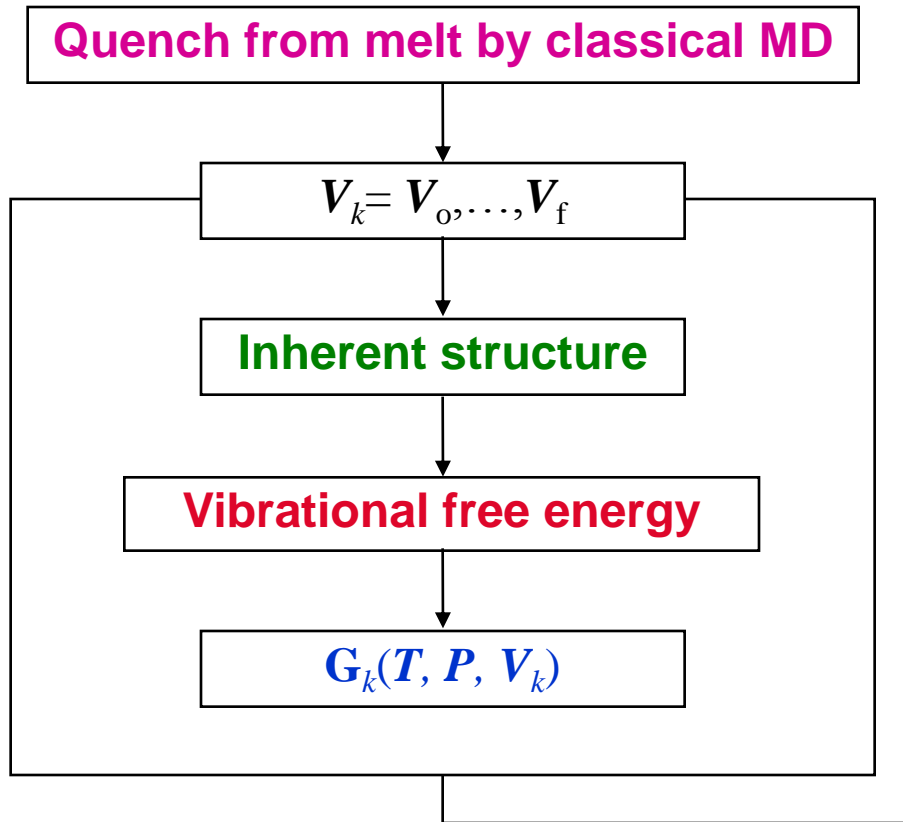
Atatic polystyrene
modified A.Lyulin et al. (2003) model
isotropic dilation/contraction

N.P. Kopsias and DNT, *J. Chem. Phys*. **109**, 8573 (1998).
D. Tsalikis, G.C. Boulougouris, DNT.

VOLUMETRIC BEHAVIOR: QHA vs. MD
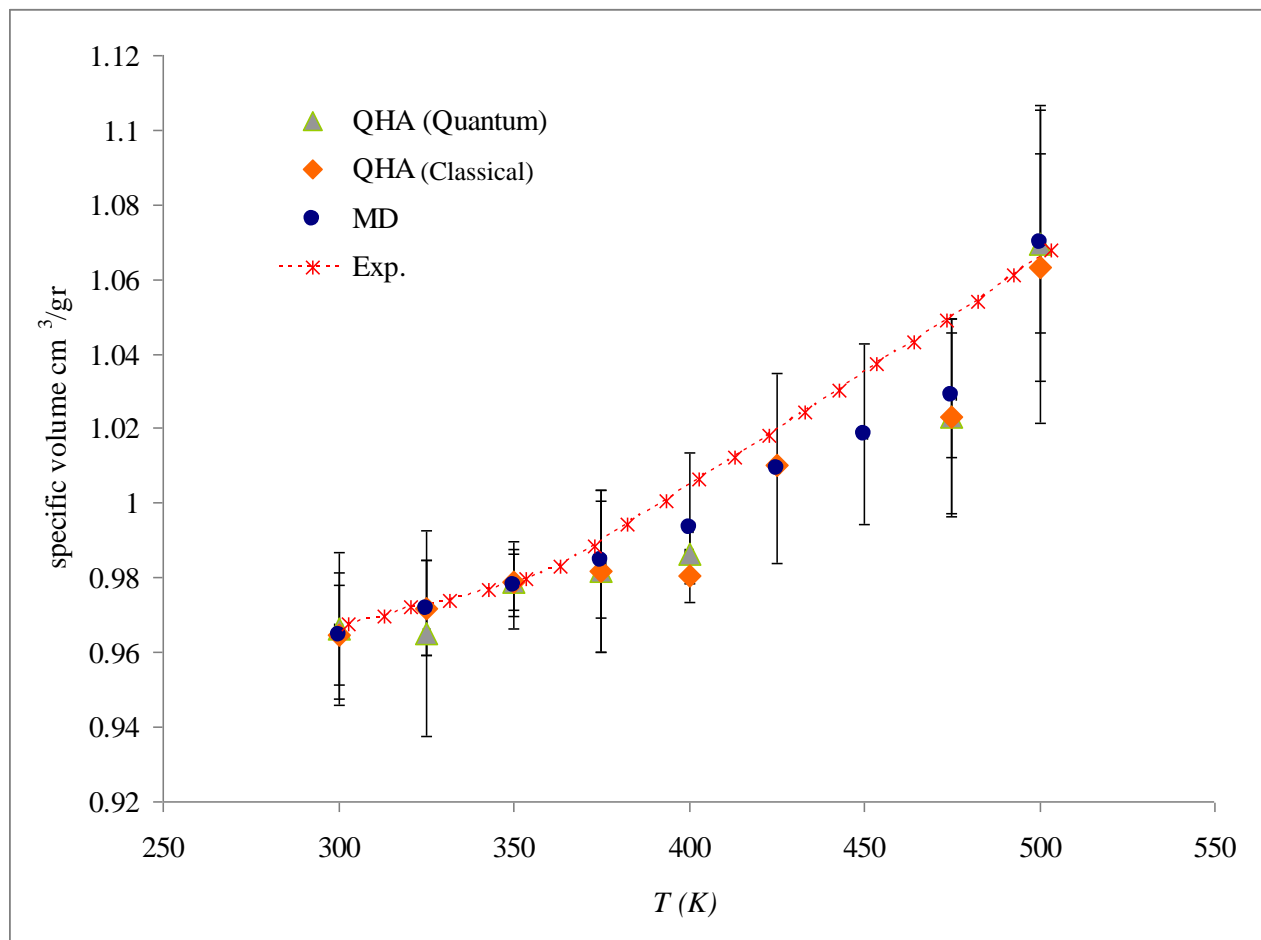
Atactic polystyrene, modified A.Lyulin* model

Pressure 1 bar
MD cooling rate
6.25 K/ns
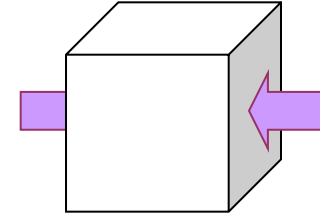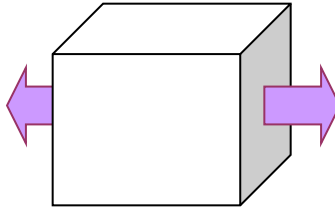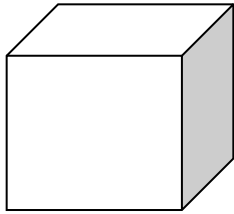
641 united atoms

Averages over 5 inherent structures

D. G. Tsalikis, G.C. Boulougouris, DNT

*A.V. Lyulin, J. DeGroot, M. Michels, *Macromol. Symp*. **191**, 167 (2003).

Exp: P. Zoller, D.J. Walsh (1995). *Standard Pressure-Volume-Temperature Data for Polymers.* Technomic: Lancaster.
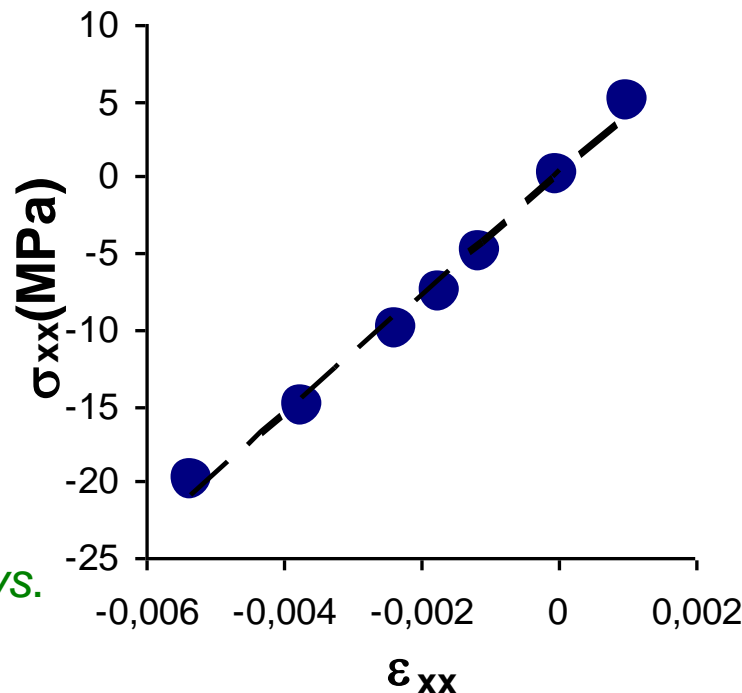
ELASTIC CONSTANTS: QHA

Stress-controlled uniaxial tension-compression experiments: Minimization of in-basin Gibbs energy with respect to spatial dimensions of the model system.

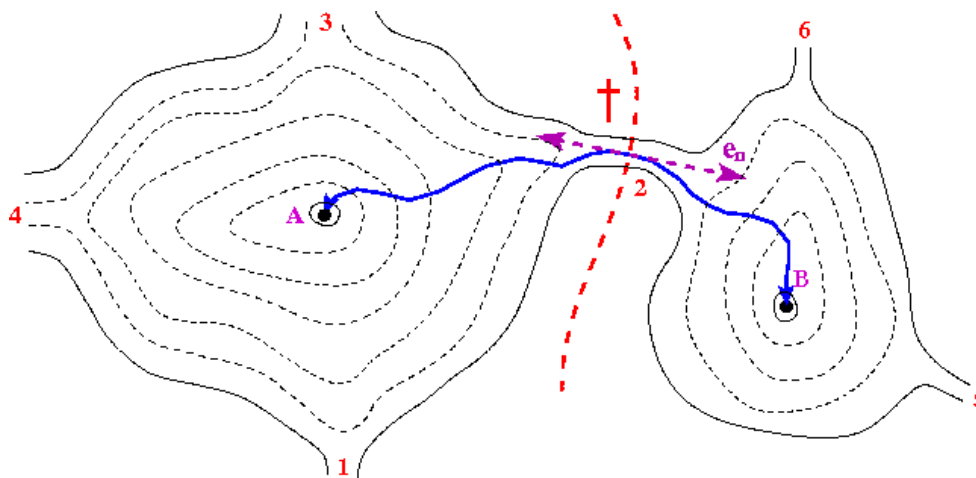Atactic polystyrene, modified A.Lyulin model

641 united atoms

$T = 325$ K

Method: N.P. Kopsias and DNT, *J Chem. Phys.* **109**, 8573 (1998)

Simulation
$E = 3.9$ GPa
$v = 0.35$

Experiment
$E = 3.2\text{-}3.4$ GPa
$v = 0.32$

ELEMENTARY TRANSITIONS BETWEEN BASINS

Determine saddle points (1, 2, 3, 4, …) out of current basin A.

"Dimer method", G. Henkelmann and H. Jónsson, *J. Chem. Phys.* **111**, 7010 (1999).

Through each saddle point, determine reaction path

"Intrinsic Reaction Coordinate", K. Fukui *Acc.Chem.Res.* **14**, 363 (1981).

- First step on either side in the direction of the eigenvector correspon-ding to the negative eigenvalue of the Hessian: $d\mathbf{x} = \pm\, \mathbf{e}_n\; d\tau$

- Subsequent steps in steepest descent direction: $d\mathbf{x} = -\, \nabla_{\mathbf{x}}\mathcal{V}\; d\tau$
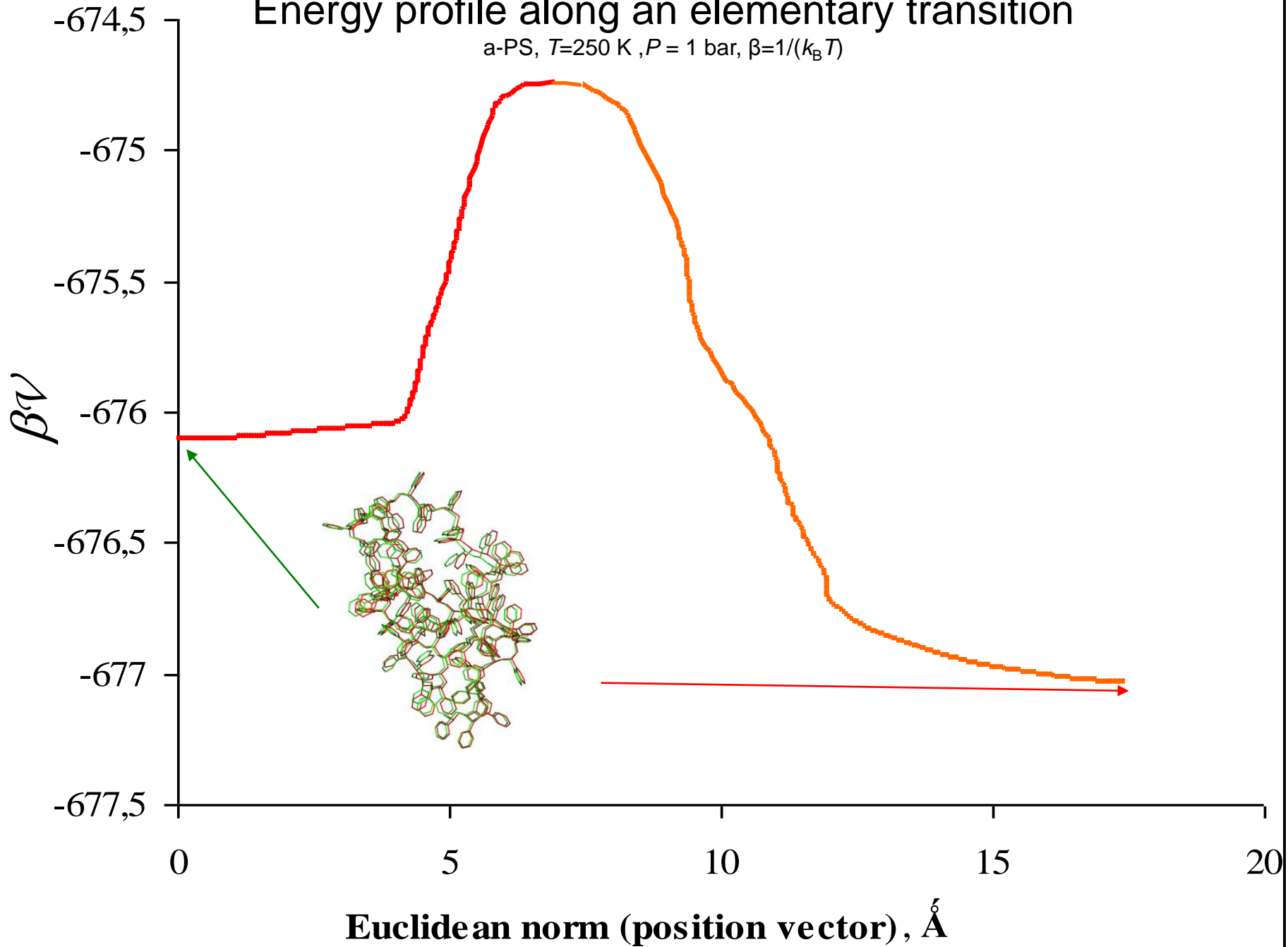
Estimate transition rate constants via Transition State Theory

Quasi-harmonic approximation $\qquad k_{A \to B}^{TST} = \dfrac{k_B T}{h} \exp\left(-\dfrac{G^\dagger - G_A}{k_B T} \right)$
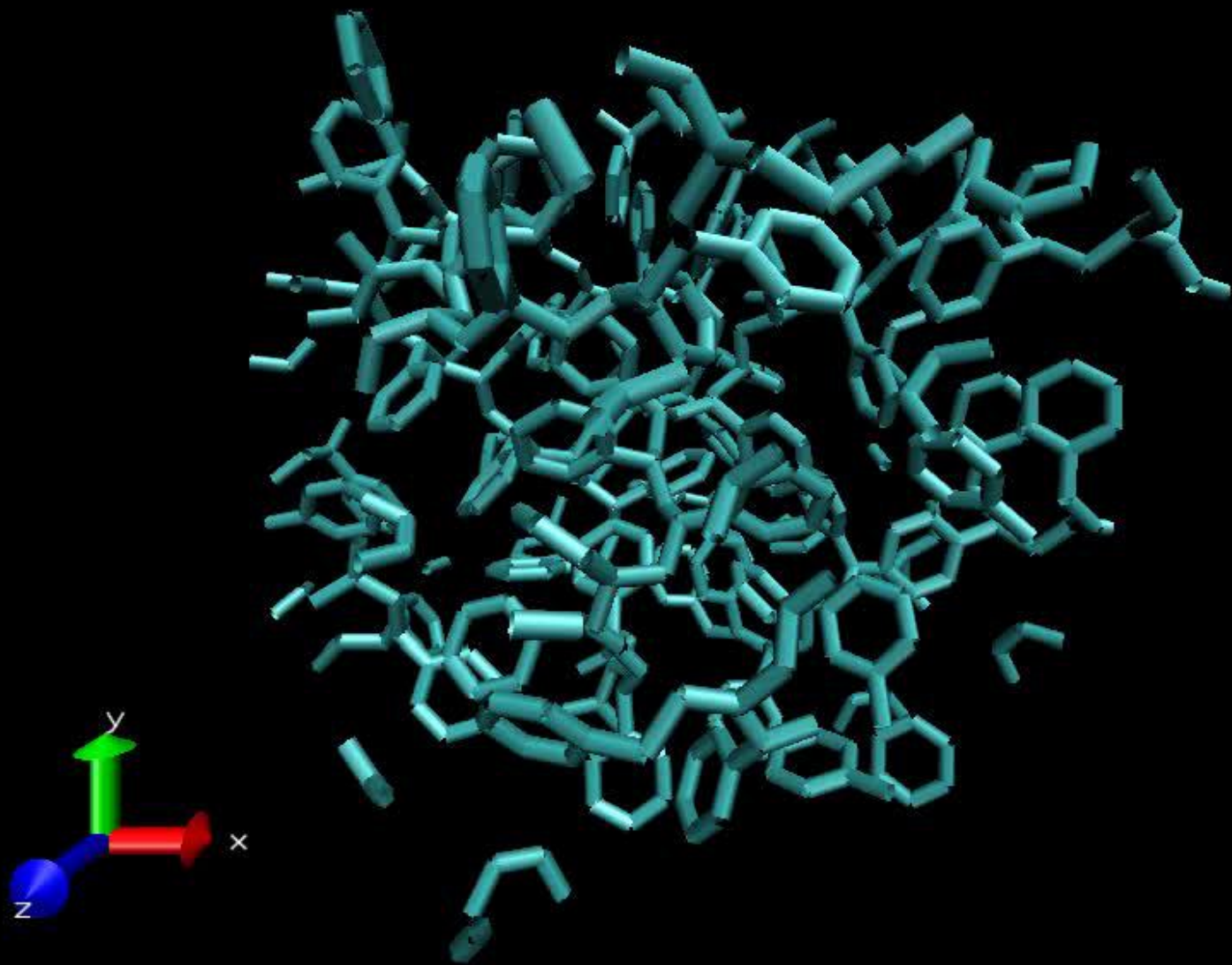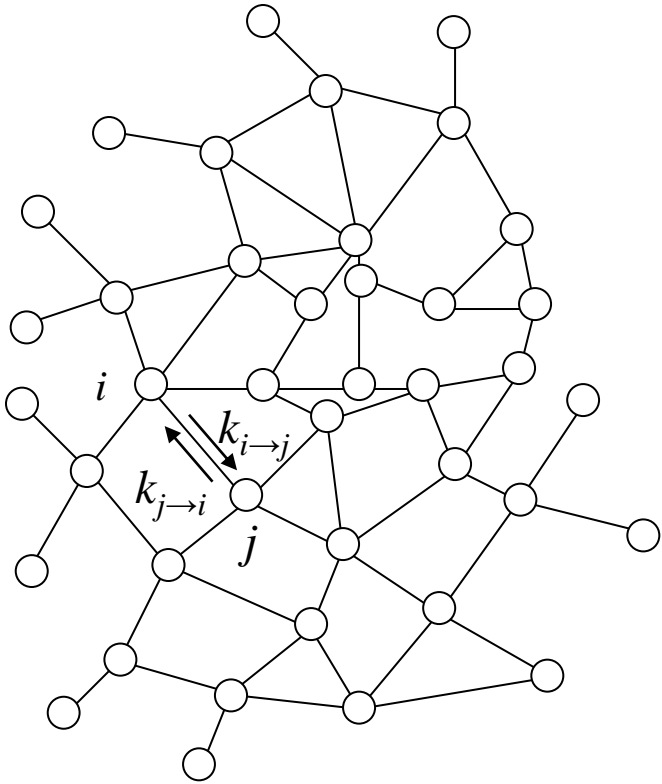
Energy profile along an elementary transition

a-PS, T=250 K, P = 1 bar, β=1/($k_B T$)

$\beta \mathcal{V}$

Euclidean norm (position vector), Å

MASTER EQUATION

n states (basins)

$P_i(t)$:   Probability of being in state i at time t.

$$\frac{dP_i(t)}{dt} = \sum_{j \neq i} P_j(t) k_{j \to i} - P_i(t) \sum_{j \neq i} k_{i \to j}$$

Transition rate constant matrix

or $$\frac{d\mathbf{P}}{dt} = \mathbf{K}\,\mathbf{P}$$ ← vector of state probabilities

$$K_{ij} = k_{j \to i}\ (j \neq i),\ \ K_{ii} = -\sum_{j} k_{i \to j}$$

$t \to \infty : d\mathbf{P}/dt = \mathbf{0},\ \ k_{i \to j}\, P_i(\infty) = k_{j \to i}\, P_j(\infty)$ ← equilibrium state probabilities

(microscopic reversibility)

Need to solve the master equation starting from an initial probability distribution among states $\mathbf{P}(0)$.

MASTER EQUATION: ANALYTICAL SOLUTION

$$\frac{d\mathbf{P}}{dt} = \mathbf{K}\,\mathbf{P}\ , \qquad K_{ij} = k_{j \to i}\ (j \neq i),\ K_{ii} = -\sum_j k_{i \to j}\ , \qquad \mathbf{P}(0)\ \text{given}$$

Define reduced state probabilities: $\tilde{P}_i(t) = P_i(t) / \sqrt{P_i(\infty)}$

$$\frac{d\tilde{\mathbf{P}}}{dt} = \tilde{\mathbf{K}}\,\tilde{\mathbf{P}}\ , \qquad \tilde{K}_{ij} = K_{ij}\ \sqrt{P_j(\infty)} / \sqrt{P_i(\infty)}\ , \qquad \tilde{\mathbf{P}}(0)\ \text{given}$$

Matrix $\tilde{\mathbf{K}}$ is **symmetric** (microscopic reversibility)

Matrix $\tilde{\mathbf{K}}$ is **negative semidefinite**

K.E. Shuler, *Phys. Fluids* **2**, 442 (1959).

J. Wei, C.D. Prater, *Advan. Catal.* **13**, 204 (1962).

N. V. Buchete, G. Hummer, *J. Phys. Chem. B* **112**, 6057 (2008).

G. Boulougouris, DNT, *J. Chem. Phys.* **130**, 044905 (2009).

MASTER EQUATION: ANALYTICAL SOLUTION

Diagonalization of $\tilde{\mathbf{K}}$ permits writing down an analytical solution to the master equation.

Eigenvalues $\lambda_0=0 \geq \lambda_1 \geq \lambda_2 \geq \ldots \geq \lambda_{n-1}$

Eigenvectors $\tilde{\mathbf{u}}_m = \left(\tilde{u}_{1,m}, \tilde{u}_{2,m}, \ldots, \tilde{u}_{i,m}, \ldots \tilde{u}_{n,m}\right)$, $\quad m = 0, 1, 2, \ldots, n-1$

Orthonormality: $\tilde{\mathbf{u}}_m \cdot \tilde{\mathbf{u}}_l = \delta_{ml}$, $0 \leq m, l \leq n-1$, $\sum_{m=0}^{n-1} \tilde{u}_{i,m} \tilde{u}_{j,m} = \delta_{ij}$, $1 \leq i, j \leq n$

Solution of the master equation:

$$\tilde{\mathbf{P}}(t) = \sum_{m=0}^{n-1} \left[\tilde{\mathbf{u}}_m \cdot \tilde{\mathbf{P}}(0)\right] \exp\left(\lambda_m t\right) \tilde{\mathbf{u}}_m \equiv \tilde{\mathbf{P}}(\infty) + \sum_{m=1}^{n-1} \left[\tilde{\mathbf{u}}_m \cdot \tilde{\mathbf{P}}(0)\right] \exp\left(\lambda_m t\right) \tilde{\mathbf{u}}_m$$

$$P_i(t) = \tilde{P}_i(t) \sqrt{P_i(\infty)}$$

K.E. Shuler, *Phys. Fluids* **2**, 442 (1959).

J. Wei, C.D. Prater, *Advan. Catal.* **13**, 204 (1962).

N. V. Buchete, G. Hummer, *J. Phys. Chem. B* **112**, 6057 (2008).

G. Boulougouris, DNT, *J. Chem. Phys.* **130**, 044905 (2009).

EROPHILE: Eigenvalue Representation of Observables and Probabilities in a HIgh-dimensionaL Euclidean space

For any observable $\mathcal{A}$, which has well-defined values $\mathcal{A}_i$ within each state i, nonequilibrium ensemble average value at time t is:

$$\left\langle \mathcal{A}(t) \right\rangle = \sum_{i=1}^{n} P_i(t)\mathcal{A}_i = \left\langle \mathcal{A}(\infty) \right\rangle + \sum_{m=1}^{n-1} a_m\, \beta_m\, \mathrm{e}^{\lambda_m t}$$

Time autocorrelation function is:

$$\left\langle \mathcal{A}(0)\mathcal{A}(t) \right\rangle - \left\langle \mathcal{A}(0) \right\rangle \left\langle \mathcal{A}(\infty) \right\rangle = \sum_{m=1}^{n-1} \beta_m^2 \mathrm{e}^{\lambda_m t} + \left\langle \mathcal{A}(\infty) \right\rangle \sum_{m=1}^{n-1} a_m \beta_m \mathrm{e}^{\lambda_m t} + \sum_{m=1}^{n-1} \beta_m \mathrm{e}^{\lambda_m t} \sum_{l=1}^{n-1} \beta_l \sum_{q=1}^{n-1} \sum_{i=1}^{n} \left[\frac{a_q \tilde{u}_{i,l} \tilde{u}_{i,m} \tilde{u}_{i,q}}{\tilde{P}_i(\infty)} \right]$$

where $a_m = \tilde{\mathbf{u}}_m \cdot \tilde{\mathbf{P}}(0)$, $\beta_m = \tilde{\mathbf{u}}_m \cdot \tilde{\mathcal{A}}$ $(1 \leq m \leq n-1)$

$\lambda_m,\ \tilde{\mathbf{u}}_m$: Eigenvalues and eigenvectors of symmetrized $n \times n$ rate constant matrix $\tilde{\mathbf{K}}$ describing transitions among n explored states (relaxation modes)

$\tilde{P}_i(t) = P_i(t) / \sqrt{P_i(\infty)}$, $\tilde{\mathcal{A}}_i = \mathcal{A}_i \sqrt{P_i(\infty)}$ $(1 \leq i \leq n)$, $\tilde{\mathcal{A}} = \left(\tilde{\mathcal{A}}_1, \tilde{\mathcal{A}}_2, ..., \tilde{\mathcal{A}}_n \right)$

∞: equilibrium among the n explored states.

TRACKING THE EVOLUTION OF THE PROBABILITY DISTRIBUTION AMONG STATES BASED ON A FIRST PASSAGE SAMPLING SCHEME

- Distinguish between "explored" states (paths leading out of them determined), and "boundary" states (connected to explored states but not yet explored themselves).

- Time-dependent probability of occupancy of each explored state determined by analytical solution of master equation:

$$\frac{\partial P_n}{\partial t} = \sum_{m \in E} P_m k_{m \to n} - P_n \sum_{m \in E \cup B} k_{n \to m} , \quad \forall n \in E$$

- Set of explored states augmented by appending a boundary state at an appropriately chosen time based on first passage time analysis.

- Set of boundary states updated by including neighbors of newly added state.

"Dynamical Integration of a Markovian Web" (DIMW): G. Boulougouris and DNT, *J. Chem. Phys.* **127**, 084903 (2007)

○ Explored   ● Boundary
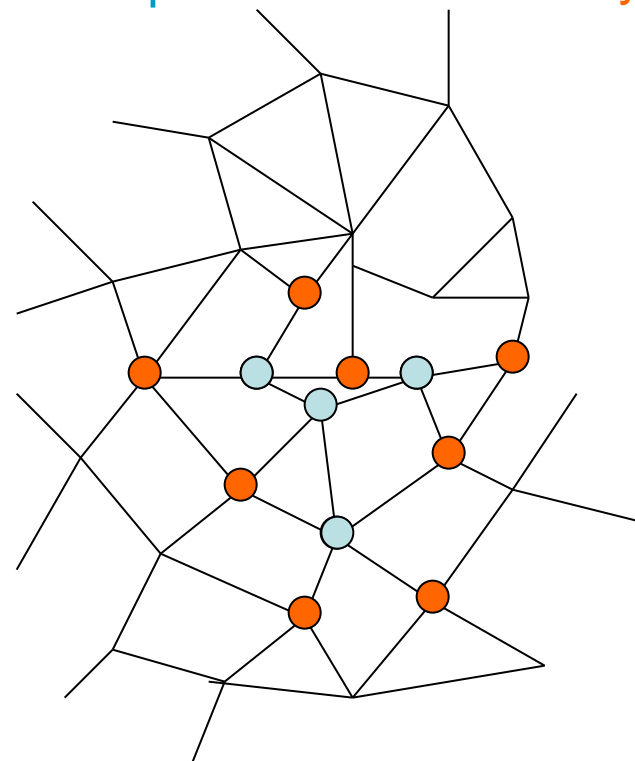
Analytical solution of master equation, with atomistically calculated rate constants, in a network of states that is progressively augmented "on the fly"

a-PS, *T*=250K, *ρ*=0.951g/cm³: EVOLUTION OF THE TIME-DEPENDENT "HELMHOLTZ ENERGY" UNDER CONSTANT VOLUME
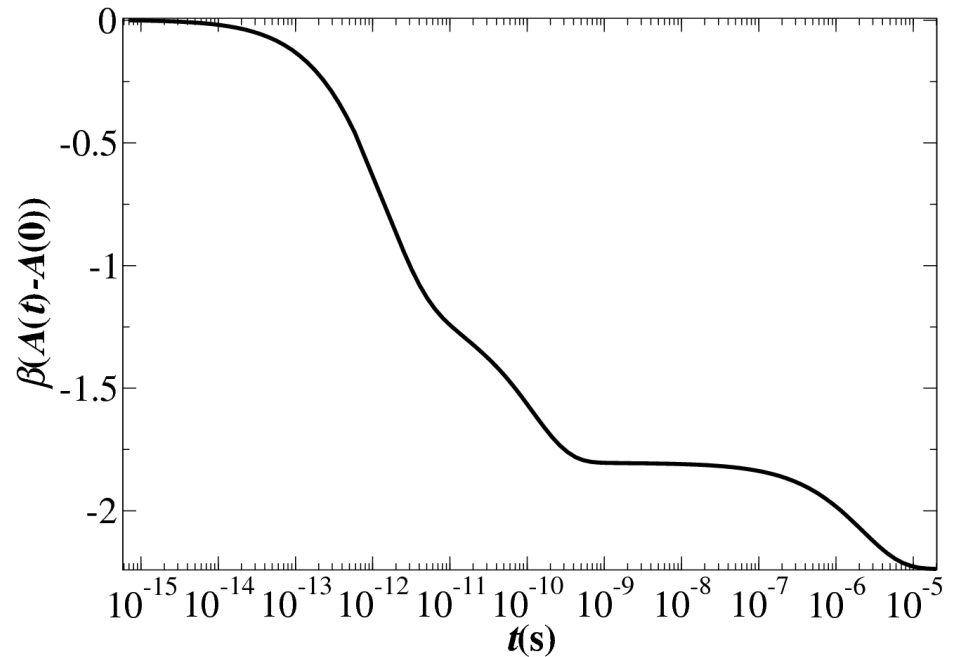
$$A(t) = \sum_i P_i(t) A_i + k_{\mathrm{B}} T \sum_i P_i(t) \ln P_i(t)$$

A_i: Helmholtz energy of basin i (incl. inherent structure energy and vibrational contributions)

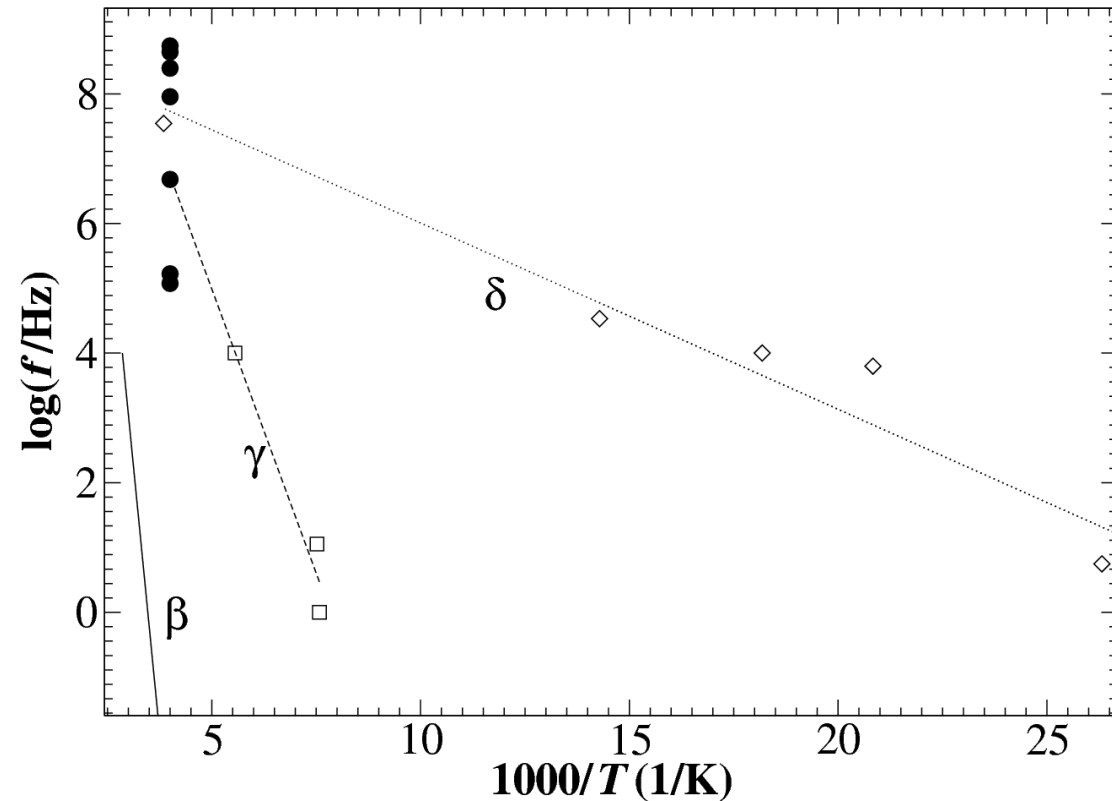$P_i(t)$: fraction of time spent in basin i

240 explored states

2880 saddle point calculations

G. Boulougouris and DNT, *J. Chem. Phys.* **127**, 084903 (2007)
G. Boulougouris and DNT, *J. Chem. Phys.* **130**, 044905 (2009)

CHARACTERISTIC FREQUENCIES FOR SUBGLASS RELAXATIONS

● : Diagonalization of rate constant matrix at 10^{-5}s, landscape, 250 K

□,◇ : Loss modulus measurements (peak frequencies)

ORIENTATIONAL DECORRELATION OF PHENYL STEMS

$$\left\langle \mathbf{v}^x(t) \cdot \mathbf{v}^x(0) \right\rangle$$
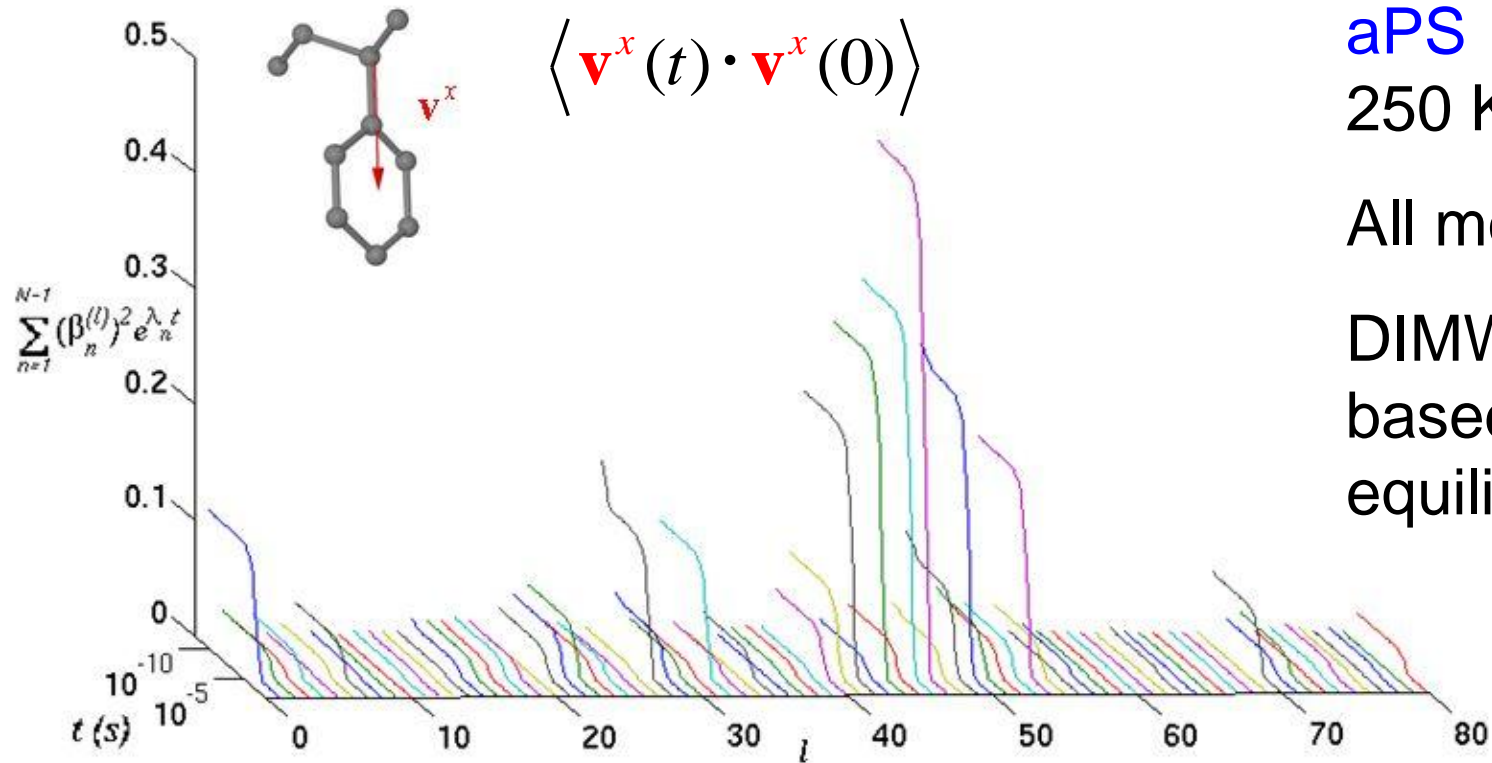
aPS
250 K, 1 bar

All modes

DIMW/EROPHILE based on restricted equilibrium at 10^{-5} s
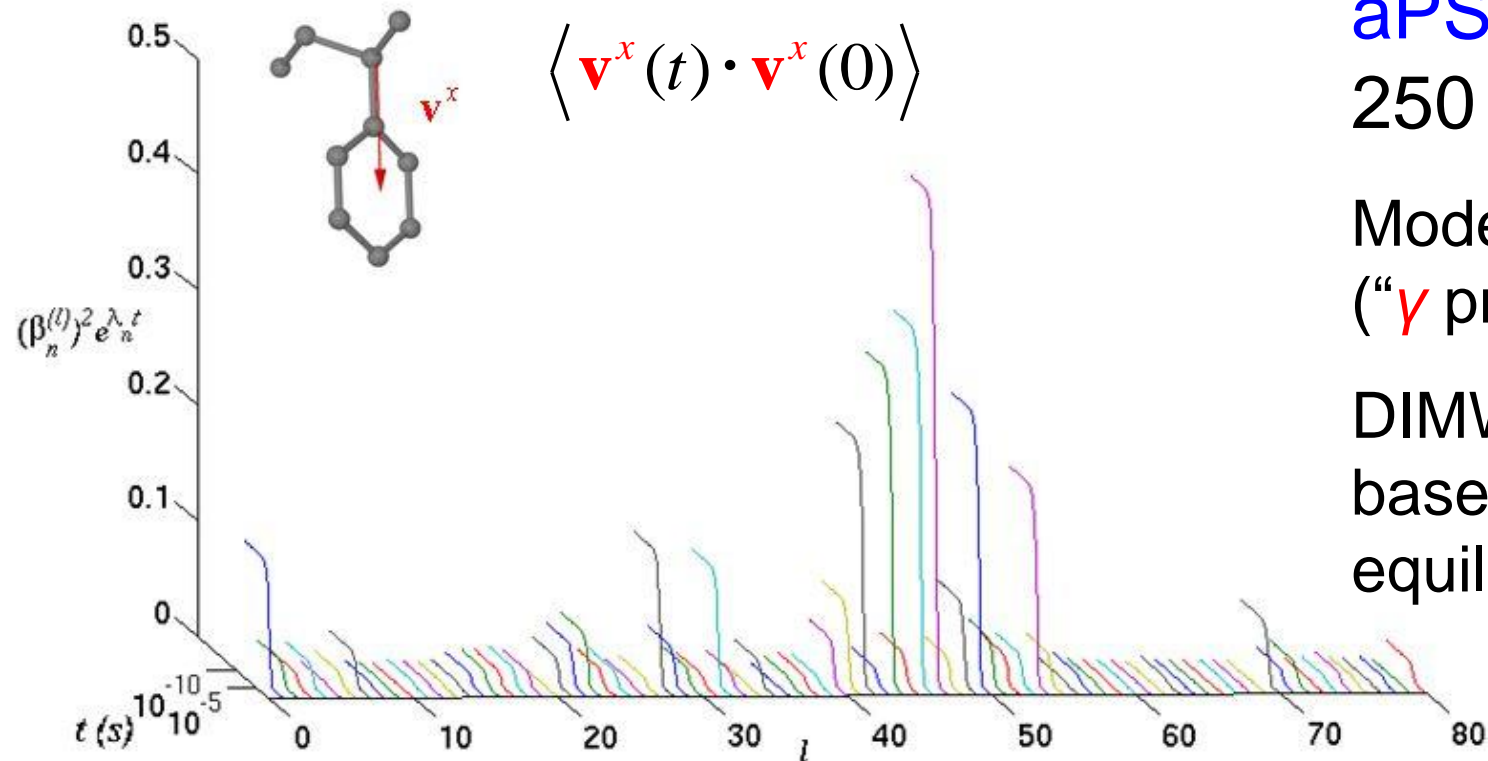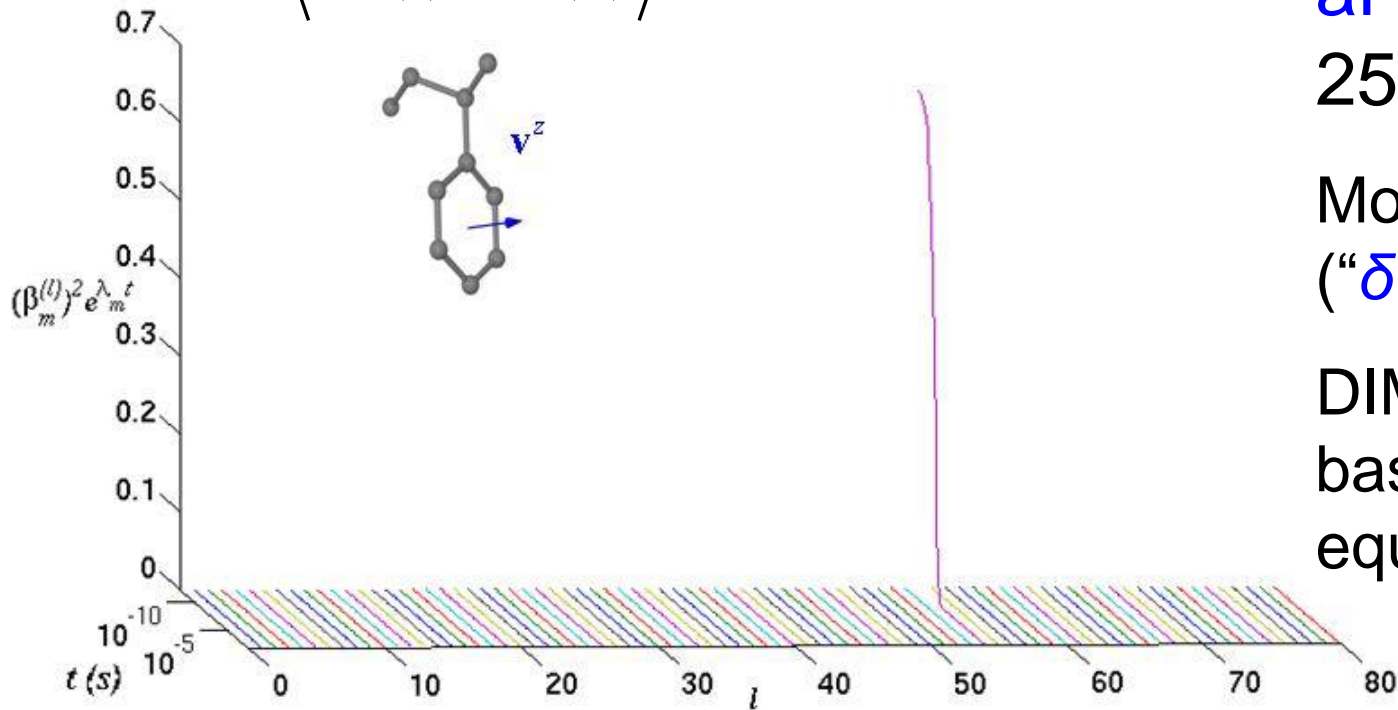
l = index of phenyl along aPS chain

ORIENTATIONAL DECORRELATION OF PHENYL STEMS

$$\left\langle \mathbf{v}^x(t) \cdot \mathbf{v}^x(0) \right\rangle$$

aPS
250 K, 1 bar

Mode $\lambda_n = -10^{5.22}$ s^{-1}
("γ process")

DIMW/EROPHILE based on restricted equilibrium at 10^{-5} s

l = index of phenyl along aPS chain

ORIENTATIONAL DECORRELATION OF VECTORS NORMAL TO PHENYLS

$$\left\langle \mathbf{v}^z(t) \cdot \mathbf{v}^z(0) \right\rangle$$

$(\beta_m^{(l)})^2 e^{\lambda_m t}$

$t \, (s)$

l

aPS
250 K, 1 bar

Mode $\lambda_m = -10^{9.54}$ s^{-1} ("δ process")

DIMW/EROPHILE based on restricted equilibrium at 10^{-5} s

l = index of phenyl along aPS chain

THE LUMPING PROBLEM

- In many systems evolving through infrequent transitions in a network of states (e.g., reacting systems, glasses) the number of states (e.g., molecular species, basins) is enormous

- Because of this large number, one is unable to deal with each state separately

- It is expedient to lump all the states into a few clusters or "equivalence classes" or "lumped classes", and then consider each class as an independent entity

J. Wei, J.C.W. Kuo *I&EC Fundamentals* **8**(1), 114 (1969)

LUMPING ANALYSIS

Lumping = linear transformation of an n-tuple state probability vector, $\mathbf{P}$, into an $\hat{n}$-tuple vector $\hat{\mathbf{P}}$, of smaller dimension with help of a $\hat{n} \times n$ matrix $\mathbf{M}$ of rank $\hat{n}$, where $n > \hat{n}$:

$$\hat{\mathbf{P}} = \mathbf{M} \, \mathbf{P}$$

Properties of lumping matrix **M**:

- Elements are either 0 or 1
- Each column contains exactly one 1

J. Wei, J.C.W. Kuo *I&EC Fundamentals* **8**(1), 114 (1969)

LUMPING ERROR

System whose dynamics follows the master equation

$\dfrac{d\mathbf{P}}{dt} = \mathbf{KP}$ is exactly lumpable by a matrix $\mathbf{M}$ if there

exists a matrix $\hat{\mathbf{K}}$ such that the dynamics of the

lumped system is described by $\dfrac{d\hat{\mathbf{P}}}{dt} = \hat{\mathbf{K}}\hat{\mathbf{P}}$. Then,

$$\boxed{\mathbf{M}}\ \boxed{\mathbf{K}}\ =\ \boxed{\hat{\mathbf{K}}}\ \boxed{\mathbf{M}}$$

Lumping error: $E = \|\mathbf{E}\|_F = \sqrt{\displaystyle\sum_{i=1}^{\hat{n}}\sum_{j=1}^{n}\left|E_{ij}\right|^2},\ \ \mathbf{E} \equiv \mathbf{M}\cdot\mathbf{K} - \hat{\mathbf{K}}\cdot\mathbf{M}$

THE PROBLEM OF OPTIMAL LUMPING

For a system with n states whose dynamics is described by the $n \times n$ matrix $\mathbf{K}$, determine a number of lumped states $\hat{n}$ and a $\hat{n} \times \hat{n}$ lumping matrix $\mathbf{M}$ such that the objective function

$$z(\hat{n}, \mathbf{M}) = z(E, W, \hat{n}) = z_1 W + z_2 E + z_3 \hat{n} \ ,$$

with z_1, z_2, z_3 pre-defined constants, is minimized.

$E =$ lumping error

$W =$ long-time parameter $\quad W = \left\| \hat{\mathbf{K}} \right\|_F = \sqrt{\sum_{i=1}^{\hat{n}} \sum_{j=1}^{\hat{n}} \left| \hat{K}_{ij} \right|^2}$

$$\hat{\mathbf{K}} = \mathbf{M} \cdot \mathbf{K} \cdot \mathbf{A} \cdot \mathbf{M}^{\mathrm{T}} \cdot \hat{\mathbf{A}}^{-1}, \quad \hat{\mathbf{A}} = \mathbf{M} \cdot \mathbf{A} \cdot \mathbf{M}^{\mathrm{T}}$$

$$\mathbf{A} = \mathrm{diag}(P_1(\infty), P_2(\infty), \ldots, P_n(\infty))$$

N. Lempesis, D.G. Tsalikis, G.C. Boulougouris, DNT *J. Chem. Phys.* **135**, 204507 (2011).

THE PROBLEM OF OPTIMAL LUMPING

Problem solved stochastically, using MC moves which change the dimensionality $\hat{n}$ and the form of the lumping matrix $\mathbf{M}$, while respecting the constraints it must satisfy.

Wang-Landau scheme invoked to determine density of matrix $\mathbf{M}$-"states" in the space of variables $(E, W, \hat{n})$. This avoids getting trapped in local minima of the objective function $z(\hat{n}, \mathbf{M})$.
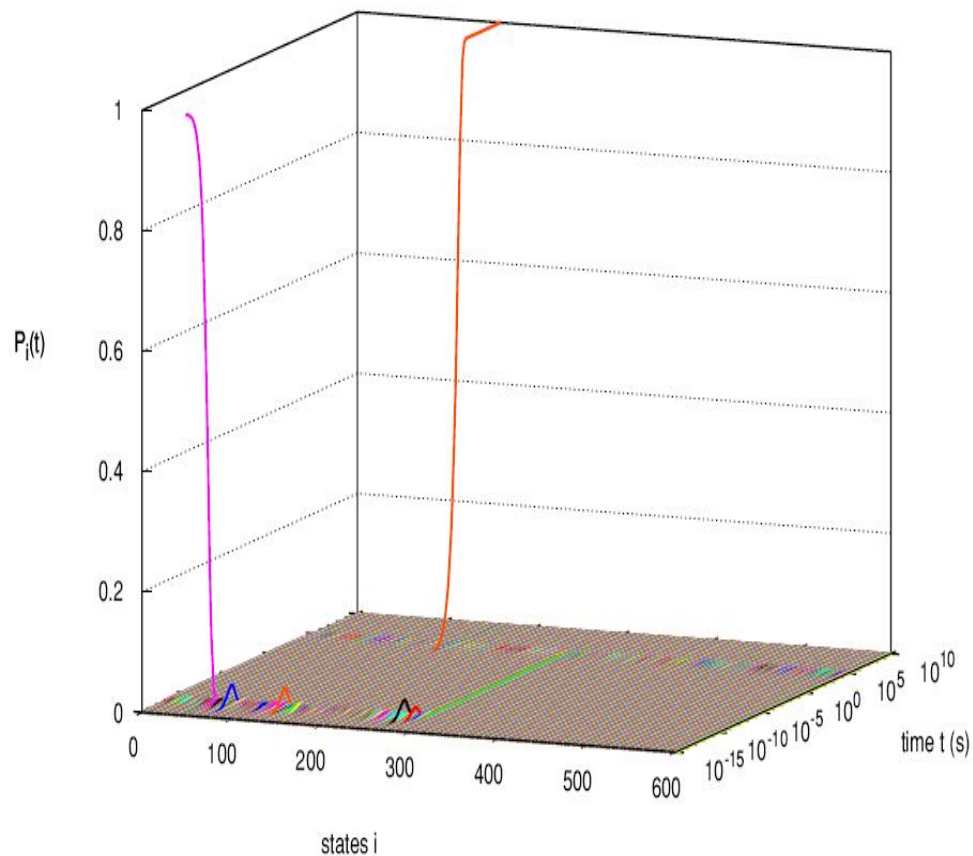
Pick that $\mathbf{M}$ which minimizes the objective function.

N. Lempesis, D.G. Tsalikis, G.C. Boulougouris, DNT *J. Chem. Phys.* **135**, 204507 (2011).

TEST OF LUMPING ALGORITHM
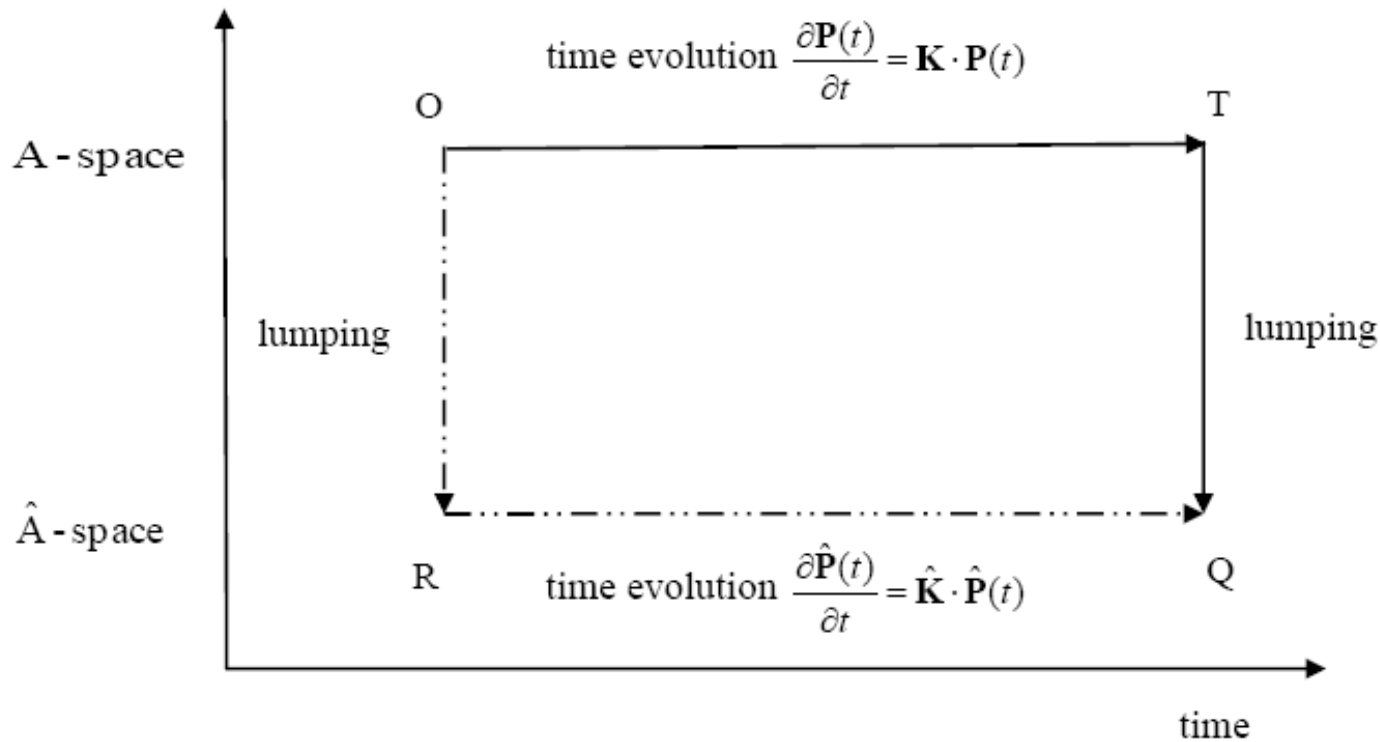
System: 641 particle Lennard-Jones mixture (80%A, 20%B) at 37 K, just below T_g=38.4 K. Original network of n =1503 states (basins) with 51207 transition rate constants between them determined through parallel Temperature Accelerated Dynamics and Histogram reweighting. Final $\hat{n}$ =600.

TEST OF LUMPING ALGORITHM
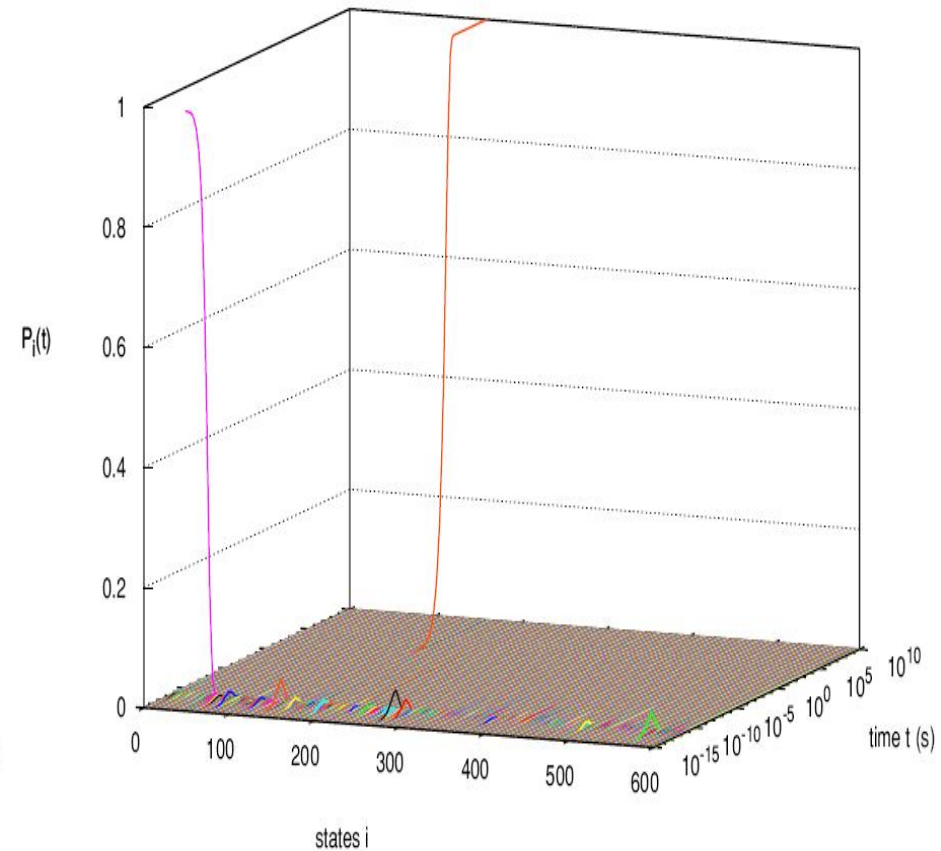
N. Lempesis, D.G. Tsalikis, G.C. Boulougouris, DNT *J. Chem. Phys.* **135**, 204507 (2011).

TEST OF LUMPING ALGORITHM
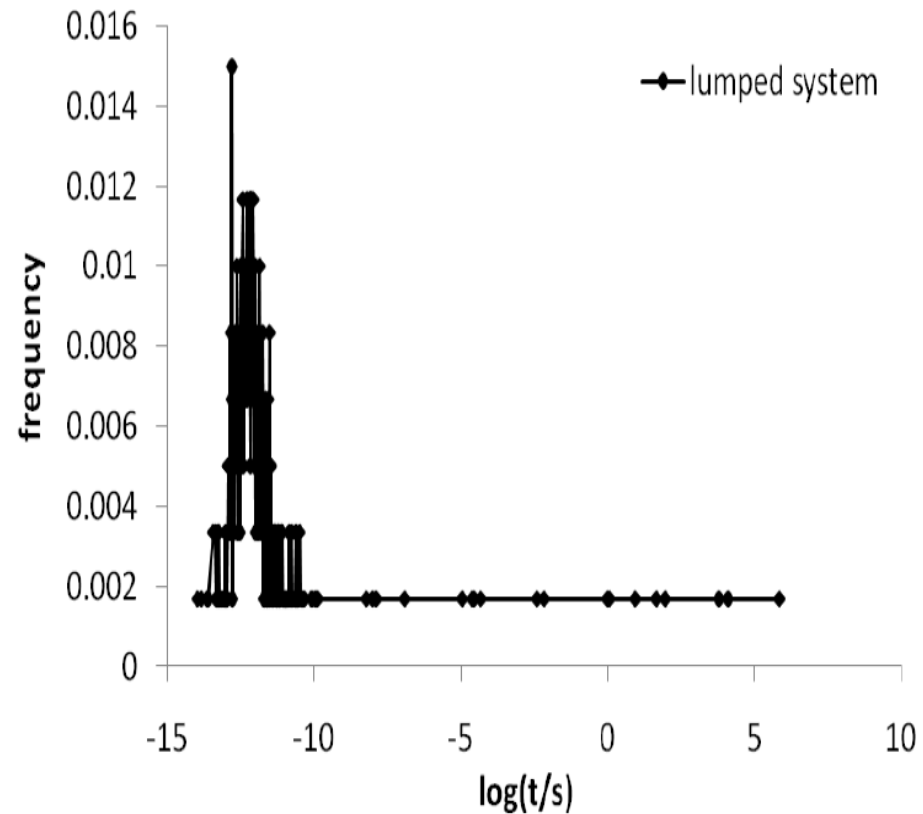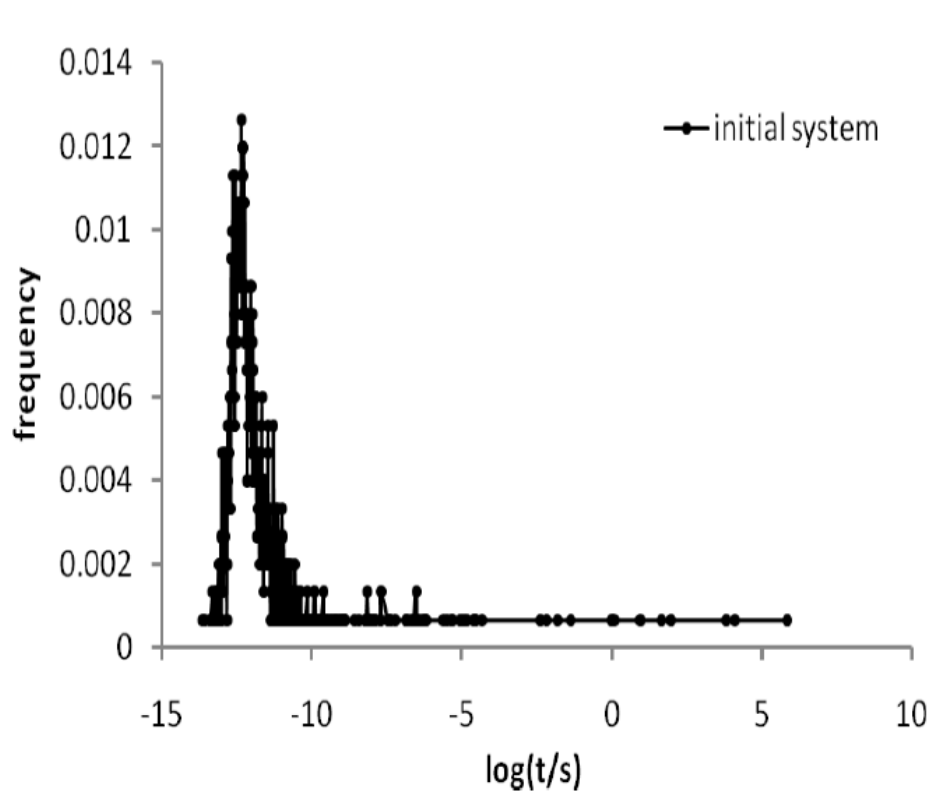
Histograms of inverse opposite eigenvalues of rate constant matrix in original (1503 states) and lumped (600 clusters of states) systems

SUMMARY

- Addressing long-time dynamics is greatly facilitated if system evolution in configuration (or order parameter) space can be reduced to a succession of uncorrelated infrequent events. Rate constants for individual events can be estimated from the (free) energy landscape and the particle masses.

- Analytical solution of the Master Equation starting from a given probability distribution among states can be much more efficient than Kinetic Monte Carlo, when the spectrum of eigenvalues of the rate constant matrix is very broad. Correlation functions for state-dependent observables are readily obtained from the analytical solution (EROPHILE).

- In a glassy system, the Dynamic Integration of a Markovian Web (DIMW) method can track structural relaxation by solving the master equation in a network of explored states which is progressively augmented "on the fly".

- A systematic "lumping" technique has been designed which reduces the number of states that need to be tracked, while preserving the long-time dynamical characteristics of the system.

MOTIVATION

- Atomistic molecular dynamics simulation: µs time scales. [see, however, ms-long simulations of K.Lindorff-Larsen, S. Piana, R.O. Dror, D.E. Shaw, *Science* **334**, 517-520 (2011)].

- Dynamics of most physical, chemical, materials, biological systems: s to years.

- In many cases, dynamics is slow because the system spends most of its time trapped within relatively narrow regions of configuration space and only infrequently jumps from region to region.

RUGGED ENERGY LANDSCAPES

Potential energy $\mathcal{V}(\mathbf{x})$, or

potential of mean force $U(\mathbf{x})$
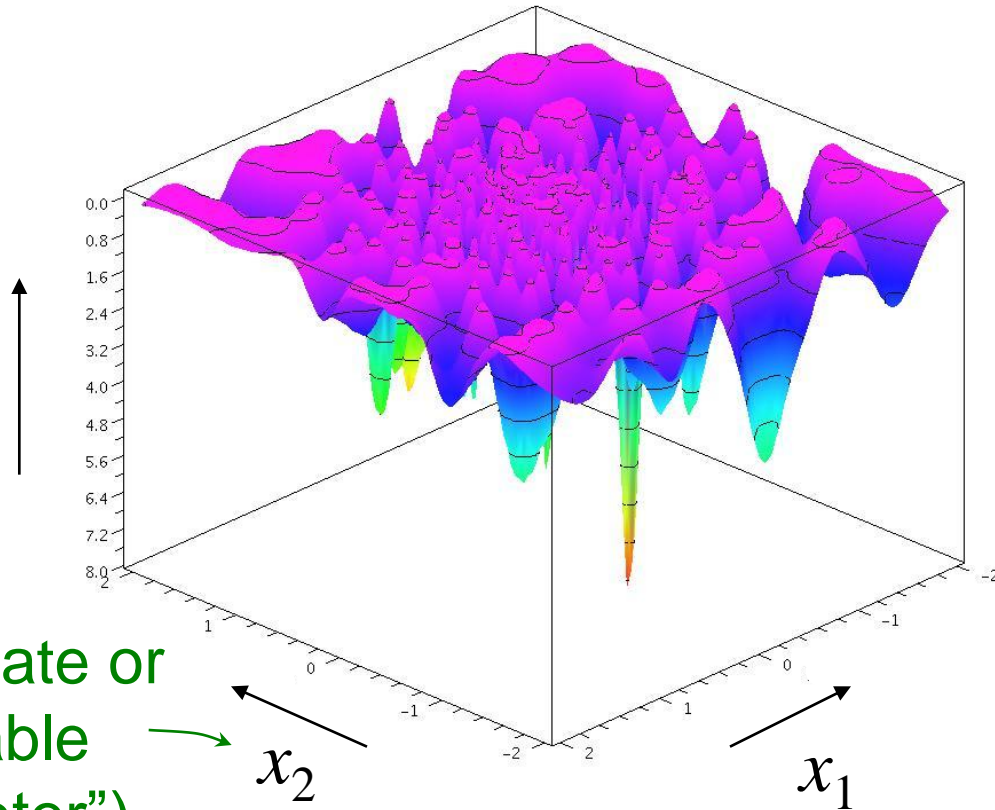
atomic coordinate or collective variable ("order parameter")

x_2

x_1

Minima: "inherent structures" F. H. Stillinger, *Science* **267**, 1935 (1995).

(Collections of) basins of attraction around minima: "states".

The entire $\mathbf{x}$-space can be tessellated into states.

EXAMPLES OF PHENOMENA INVOLVING EVOLUTION ON RUGGED ENERGY LANDSCAPES

- Diffusion of defects and impurities in metals and semiconductors

- Permeation of gas molecules through amorphous polymers

- Diffusion of bulky hydrocarbons in zeolites

- Structural relaxation and plastic deformation of glassy materials

- Protein folding

- Phase transitions in molecular and atomic clusters

- Kinetics of networks of chemical reactions

OUTLINE

- Infrequent events, calculation of transition rate constants

- Kinetic Monte Carlo simulation

- Master Equation: its analytical solution and calculation of time correlation functions

- Low-temperature diffusion of Xe in Silicalite-1: Comparative application of various methods

- The energy landscape picture for glasses

- A method for tracking structural relaxation in glasses: Application to atactic polystyrene

- The lumping problem

TRANSITION RATE CONSTANT
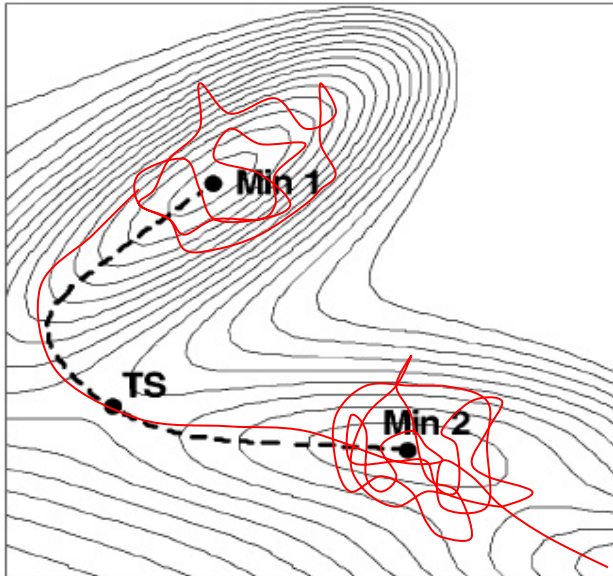
Time scale separation: Mean waiting time for transition out of a state is long in comparison with the time required for system to establish a restricted equilibrium among configurations in the state.

$$t_{cor} << t_{rxn}$$

By the time it exits a state, the system has lost all memory of how it entered there (Markovian character of a sequence of infrequent events).

Rate constant $k_{i \rightarrow j}$: Probability per unit time that a transition to state j will occur, provided the system is in state i.

COMPUTATION OF RATE CONSTANTS

Input: Energy hypersurface and masses associated with degrees of freedom.

- Molecular dynamics (MD), reduction to an inherent structure trajectory and hazard plot analysis [E. Helfand, *J. Chem. Phys*. **69**, 1010 (1978)]

- Temperature-accelerated dynamics [M. R. Sørensen, A.F. Voter, J. Chem. Phys. **112**, 9599 (2000)]

- Transition-State Theory estimate $k_{i\circledR}^{TST}$ from free energy difference between the system confined to the boundary hypersurface of state i and the system allowed to sample the entire state i. Calculation of dynamical correction factor $f_{d,i\circledR j}$ through short MD trajectories initiated on the boundary hypersurface [C.H. Bennett, 1975; D. Chandler, *J. Chem. Phys.* **68**, 2959 (1978), A.F. Voter and J.D. Doll, *J. Chem. Phys*. **82**, 80 (1985)].

COMPUTATION OF RATE CONSTANTS

- Determination of reaction path (e.g., by Fukui's intrinsic reaction coordinate approach) and computation of free energy profile along the path by umbrella sampling or "blue moon ensemble" simulations [T.R. Forester, W. Smith *J. Chem. Soc. Faraday Trans*. **93**, 3249 (1997)]

- Flux-tempered metadynamics [S. Singh, C.C. Chiu, J. de Pablo *J. Stat. Phys*. **144**, 1 (2011); A. Laio, M. Parrinello, *Proc. Natl. Acad. USA* **99**, 12562 (2002)]

- Transition path sampling [P.G. Bolhuis, D. Chandler, C. Dellago, P.L. Geissler *Annu. Rev. Phys. Chem*. **53**, 291 (2002); C. Dellago, P.G. Bolhuis, P. Geissler *Adv. Chem. Phys.* **123**, 1 (2002)]

SEQUENCE OF INFREQUENT EVENTS IS A HOMOGENEOUS POISSON PROCESS

- Numbers of occurrences counted in disjoint time intervals are independent of each other.

- Probability distribution of occurrences counted within any time interval only depends on the length of the interval.

- No counted occurrences are simultaneous.

- Number of observed occurrences within a given time interval follows a Poisson distribution:

$$P[N(t + \tau) - N(t) = n] = \frac{\exp(-k\tau)(k\tau)^n}{n!}$$

- Waiting time until the next occurrence follows an exponential distribution: $\hat{\rho}(\tau) = k \exp(-k\tau)$

- Several Poisson processes i occurring in parallel constitute a Poisson process with rate constant $k = \sum_i k_i$.

KINETIC MONTE CARLO (KMC) SIMULATION

Generation of stochastic trajectories as sequences of transitions between states in a network of n states

Deploy $\mathcal{N} \gg n$ independent walkers among the states according to a prescribed initial probability distribution: $\mathcal{N}_i(t) \approx \mathcal{N} P_i(0)$, $i=1, 2, \ldots, n$

(i)   For each state i that is occupied at time t, calculate expected fluxes $R_{i \to j}(t) = \mathcal{N}_i(t)\, k_{i \to j}$, overall flux $R(t) = \Sigma_i \Sigma_j R_{i \to j}(t)$ and conditional probabilities $q_{i \to j}(t) = R_{i \to j}(t)/ R(t)$.

(ii) Pick time until next transition $\Delta t = -\ln(1-\xi)/R(t)$, where $\xi \in [0,1)$ is a uniformly distributed pseudorandom number. Pick type $i \to j$ of next transition according to $q_{i \to j}(t)$.

(iii) Of the $\mathcal{N}_i(t)$ walkers present in state i pick one with probability $1/ \mathcal{N}_i(t)$ and move it to state j.

(iv) Advance simulation time by Δt. Update array keeping track of current positions of all walkers. Set $\mathcal{N}_i(t+\Delta t) = \mathcal{N}_i(t) - 1$, $\mathcal{N}_j(t+\Delta t) = \mathcal{N}_j(t) + 1$.

(v)   Return to step (i).

EROPHILE: Eigenvalue Representation of Observables and Probabilities in a HIgh-dimensionaL Euclidean space

For any observable $\mathcal{A}$, which has well-defined values $\mathcal{A}_i$ within each state i, nonequilibrium ensemble average value at time t is:

$$\langle \mathcal{A}(t) \rangle = \sum_{i=1}^{n} P_i(t) \mathcal{A}_i = \langle \mathcal{A}(\infty) \rangle + \sum_{m=1}^{n-1} a_m \, \beta_m \, \mathrm{e}^{\lambda_m t}$$

Time autocorrelation function is:

$$\langle \mathcal{A}(0)\mathcal{A}(t) \rangle - \langle \mathcal{A}(0) \rangle \langle \mathcal{A}(\infty) \rangle = \sum_{m=1}^{n-1} \beta_m^2 \mathrm{e}^{\lambda_m t} + \langle \mathcal{A}(\infty) \rangle \sum_{m=1}^{n-1} a_m \beta_m \mathrm{e}^{\lambda_m t} + \sum_{m=1}^{n-1} \beta_m \mathrm{e}^{\lambda_m t} \sum_{l=1}^{n-1} \beta_l \sum_{q=1}^{n-1} \sum_{i=1}^{n} \left[\frac{a_q \tilde{u}_{i,l} \tilde{u}_{i,m} \tilde{u}_{i,q}}{\tilde{P}_i(\infty)} \right]$$

where $a_m = \tilde{\mathbf{u}}_m \cdot \tilde{\mathbf{P}}(0)$, $\beta_m = \tilde{\mathbf{u}}_m \cdot \tilde{\mathcal{A}}$ $(1 \le m \le n-1)$

$\lambda_m, \tilde{\mathbf{u}}_m$: Eigenvalues and eigenvectors of symmetrized $n \times n$ rate constant matrix $\tilde{\mathbf{K}}$ describing transitions among n explored states (relaxation modes)

$$\tilde{P}_i(t) = P_i(t) / \sqrt{P_i(\infty)}, \quad \tilde{\mathcal{A}}_i = \mathcal{A}_i \sqrt{P_i(\infty)} \quad (1 \le i \le n), \quad \tilde{\mathcal{A}} = \left(\tilde{\mathcal{A}}_1, \tilde{\mathcal{A}}_2, ..., \tilde{\mathcal{A}}_n \right)$$

∞: equilibrium among the n explored states.

GLASSES ARE NON-EQUILIBRIUM MATERIALS WITH COMPLEX MECHANICAL BEHAVIOUR
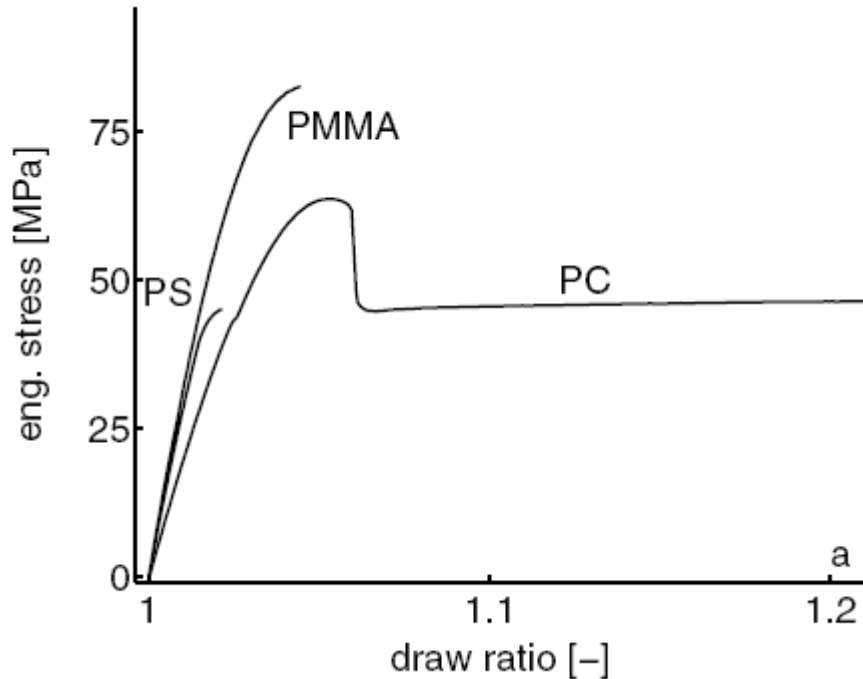
Tension
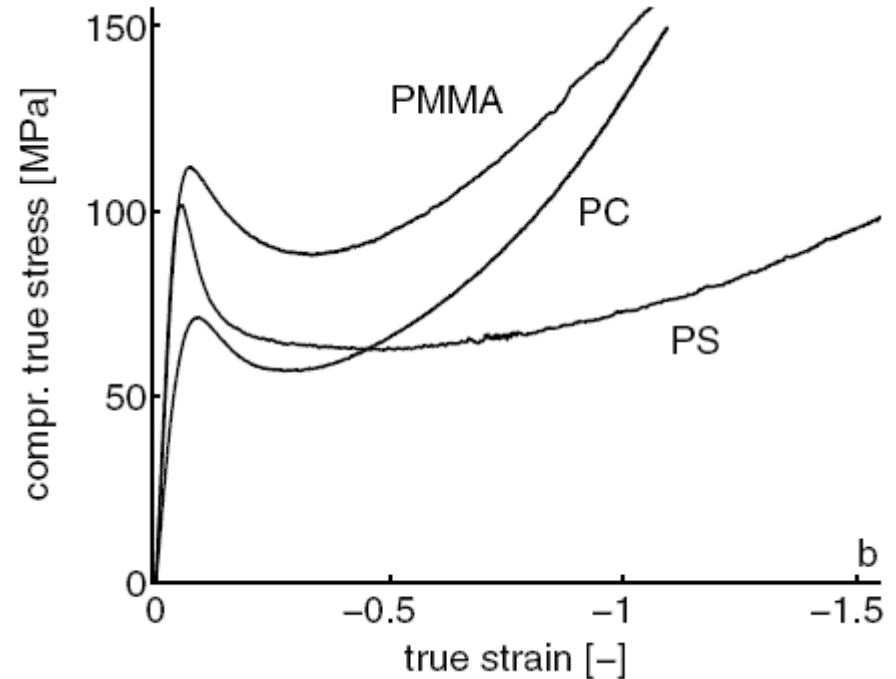
Compression

H. Van Melick, Ph.D. Thesis, Technical University of Eindhoven, 2002

Coarse-grained approaches to the simulation of physical ageing and deformation.

energy landscape important

entanglements important
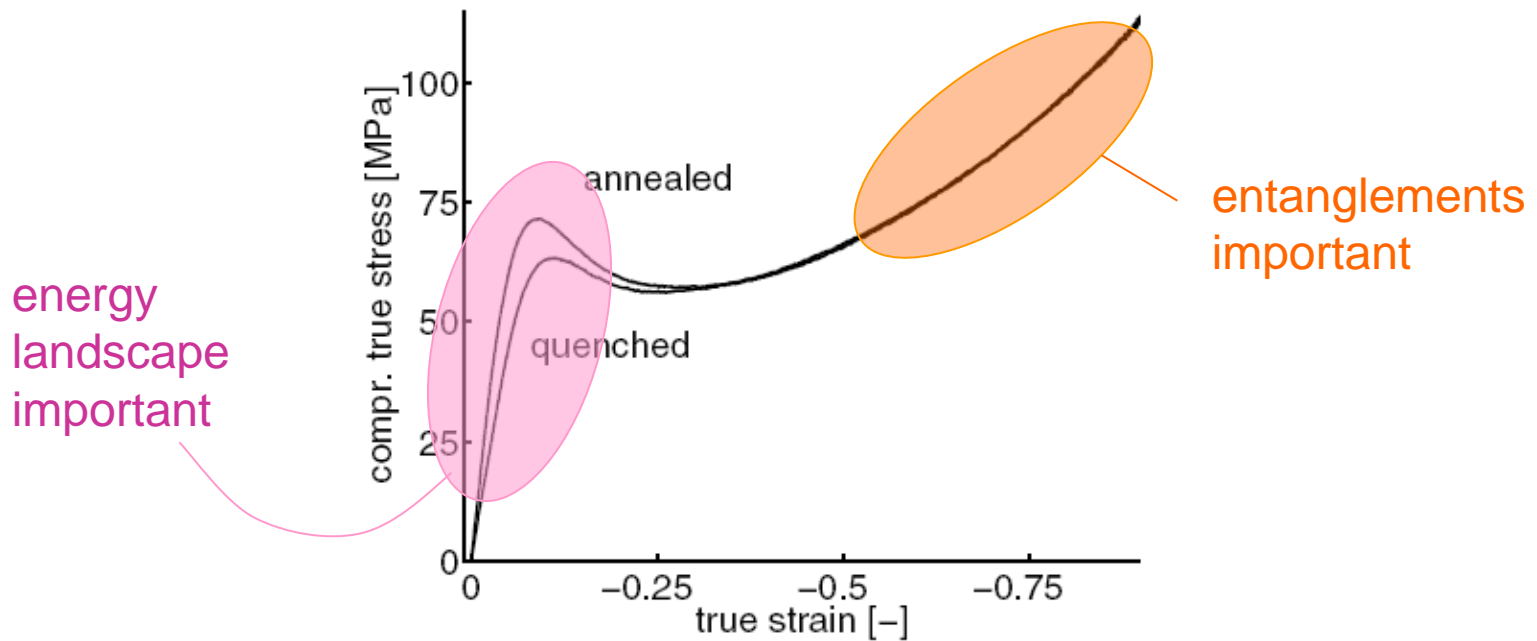
CHALLENGES FOR MOLECULAR MODELLING OF GLASS PROPERTIES

- Atomistic Molecular Dynamics (MD) can address times up to 1 µs and length scales up to 10 nm.

- Impossible to obtain a computer glass with a formation history that is both well-defined and realistic. (Typical MD cooling rates $\geq 10^8$ K/s).

- MD deformation experiments are ultrafast (strain rate $\geq 10^6$ s^{-1}).

OUTLINE

- The energy landscape picture

- Transitions between basins in configuration space: What can be learnt from MD of a Lennard-Jones glass

- From basins to metabasins

- Quasiharmonic approximation: Volumetric properties and elastic constants of glassy aPS

- Estimation of interbasin rate constants by Transition-State Theory

- The DIMW and EROPHILE methods for tracking structural relaxation: Application to glassy aPS

TRANSITIONS BETWEEN BASINS: WHAT CAN BE LEARNT FROM MOLECULAR DYNAMICS

Binary mixture of A (80%) and B(20%) Lennard-Jones spheres. $m_A=m_B$, $\sigma_{BB}=0.88\sigma_{AA}$, $\sigma_{AB}=0.88\sigma_{AA}$, $\varepsilon_{BB}=0.50\varepsilon_{AA}$, $\varepsilon_{AB}=1.50\varepsilon_{AA}$

Kob,W., Andersen, H. C. *Phys. Rev. Lett.* **73**, 1376 (1994).   Shell, S.M., Debenedetti, P.G., Panagiotopoulos, A.Z. *Fluid Phase Equil.* **241**, 147 (2006).

Characteristic temperatures:
Mode coupling $T_c=0.435$ ε_{AA}/k_B = 52.2 K (for A=argon)
Glass temperature $T_g\approx0.32$ ε_{AA}/k_B = 38.4 K

Canonical (*NVT*) and microcanonical (*NVE*) molecular dynamics (MD) simulations at constant density 1.1908 σ_{AA}^{-3}. *N*=641 atoms total. Nosé-Hoover thermostat, Velocity Verlet algorithm. Integration time step 1fs.

Potential energy minimizations with conjugate gradient algorithm used to map MD trajectory onto a corresponding inherent structure trajectory.

STEPWISE COOLING:
INHERENT STRUCTURE ENERGIES
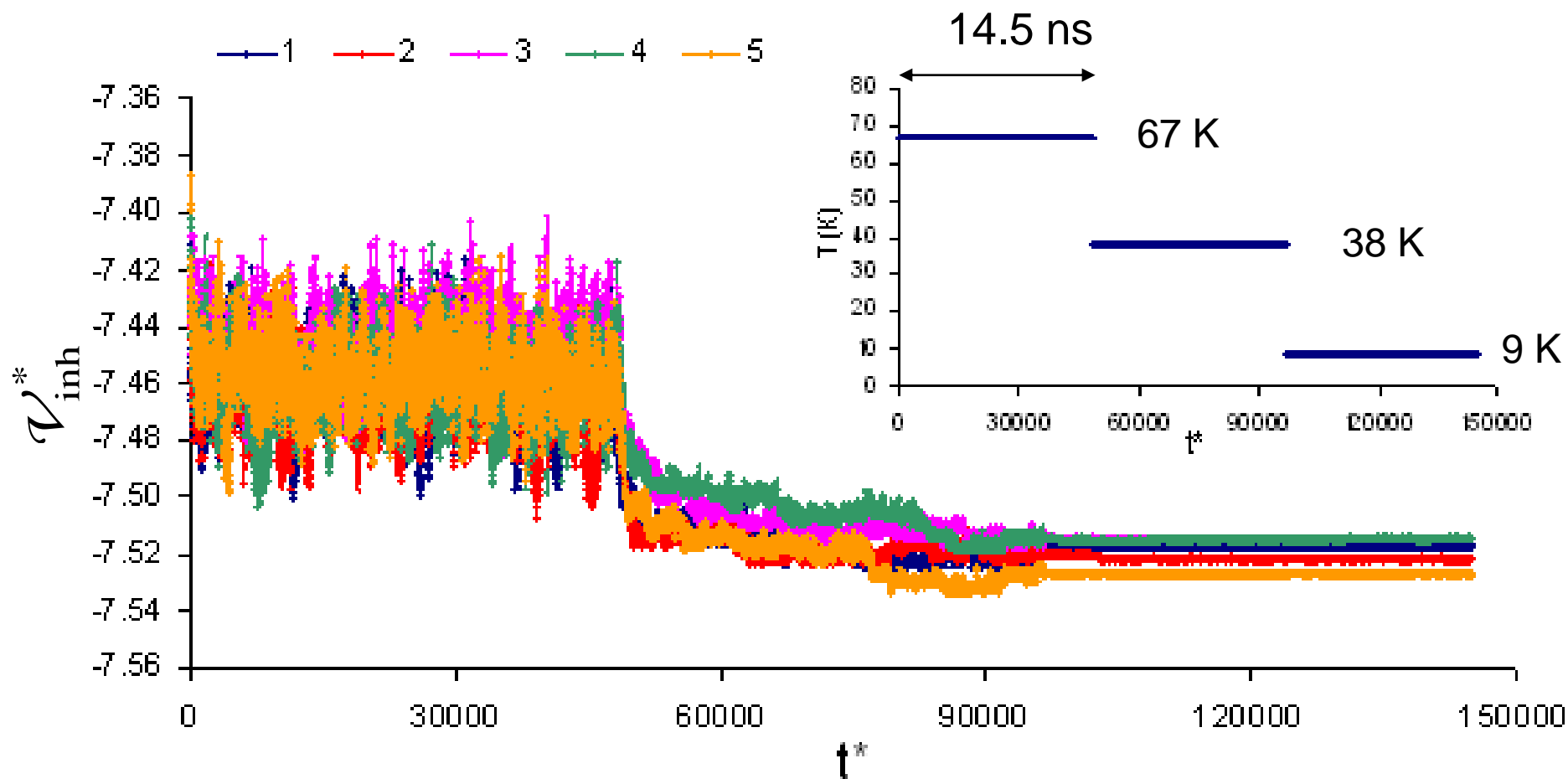
Units: Energy $\varepsilon_{AA} = 0.998$ kJ/mol, time $\left[m_A \sigma_{AA}^2 / (48 \varepsilon_{AA}) \right]^{1/2} = 3.1 \times 10^{-13}$ s

MEAN SQUARE DISPLACEMENT OF A-TYPE ATOMS
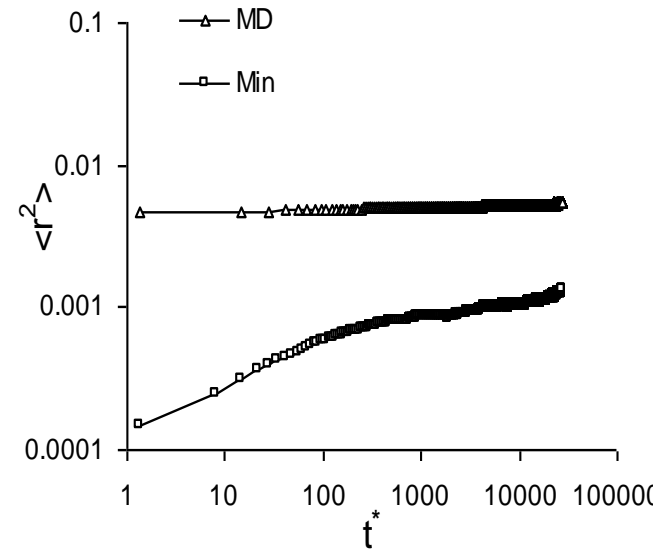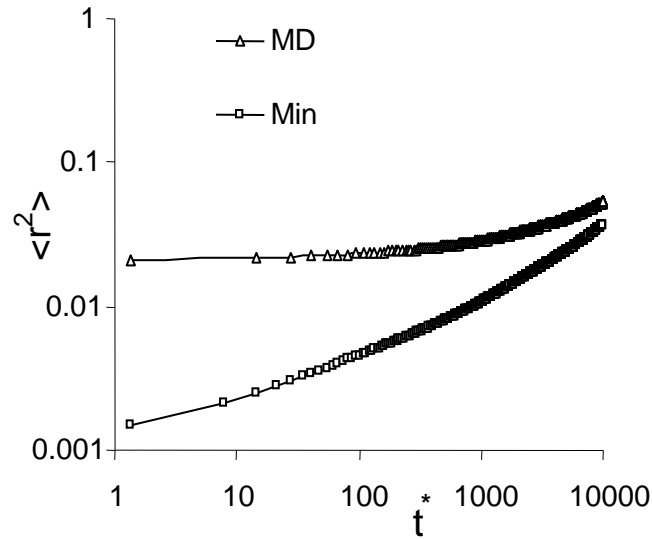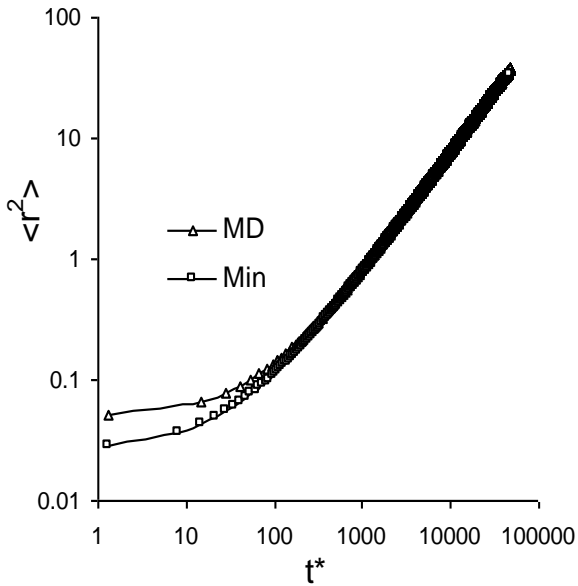
Long-time diffusive motion in the liquid very well captured by inherent structure trajectory.

"Cage effect" at short times, whose duration becomes very long at low T.

Units: Length $\sigma_{AA} = 3.4 \times 10^{-10}$ m,   time $\left[m_A \sigma_{AA}^2 / (48\, \varepsilon_{AA}) \right]^{1/2} = 3.1 \times 10^{-13}$ s

POISSON PROCESS MODEL

- Glassy system starts off with an initial distribution $P_i(0)$ among basins i, which is dictated by its formation history.

- Distribution $P_i(t)$ among basins (states) evolves through successive transitions between basins.

- Transitions are infrequent events: mean waiting time for transition out of a basin is long in comparison to the time required to establish a restricted equilibrium among configurations in the basin.

transition rate constant
from basin i to basin j

Master Equation:

$$\frac{dP_i(t)}{dt} = \sum_{j \neq i} P_j(t)\, k_{j \rightarrow i} - P_i(t) \sum_{j \neq i} k_{i \rightarrow j}$$

vector of basin probabilities

rate constant matrix

$$\frac{d\mathbf{P}}{dt} = \mathbf{K}\mathbf{P}$$

CALCULATING RATE CONSTANTS FOR TRANSITIONS BETWEEN BASINS

Definitions:

Hazard rate $h(t)$: Conditional probability that a system, which has survived a time t since its last transition, will undergo a transition between t and $t+dt$ is $h(t)\,dt$.

Cumulative hazard $H(t)$: $H(t) = \int_0^t h(t')dt'$

Probability that a transition occurs in time less than t since the last transition: $P(t) = 1 - \exp\left[-H(t)\right]$

Poisson process: $h(t) = \lambda$, a constant.
$$H(t) = \lambda t, \quad P(t) = 1 - \exp(-\lambda t)$$

CALCULATING RATE CONSTANTS FOR TRANSITIONS BETWEEN BASINS

Hazard Plot Analysis Helfand, E. *J. Chem. Phys*. **69**, 1010 (1978)

In the course of MD simulation, for any visited basin, β, record residence times between entry to and exit from the basin. Also record the basins γ to which exits from β occur.

Order residence times in β: $\quad t_1 \leq t_2 \leq \ldots \leq t_n$

Estimate cumulative hazard $\hat{H}(t_k)$ corresponding to residence time t_k:

$$\hat{H}(t_k) = \frac{1}{n} + \frac{1}{n-1} + \ldots + \frac{1}{n-k+1}$$

Linear plot $\hat{H}(t_k)$ going through the origin indicates a Poisson process.

Cumulative Hazard vs Residence time t_k (ps)
- □ time interval 0.8ps
- + time interval 2ps

Slope of $\hat{H}(t_k)$ plot, λ_β = total rate constant for exiting basin β.

Rate constant $\quad k_{\beta \to \gamma} = \lambda_\beta \dfrac{\text{Number of times exit from basin } \beta \text{ occurred to basin } \gamma}{n}$

MEAN SQUARE ATOMIC DISPLACEMENT ALONG INHERENT STRUCTURE TRAJECTORY

T=23K
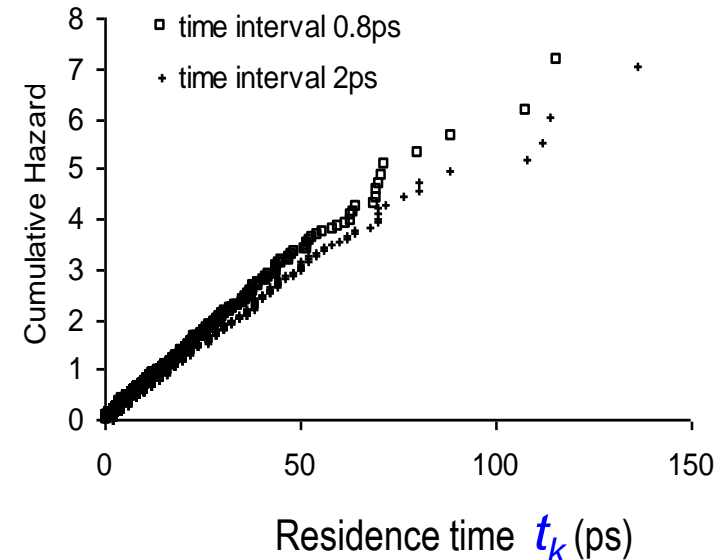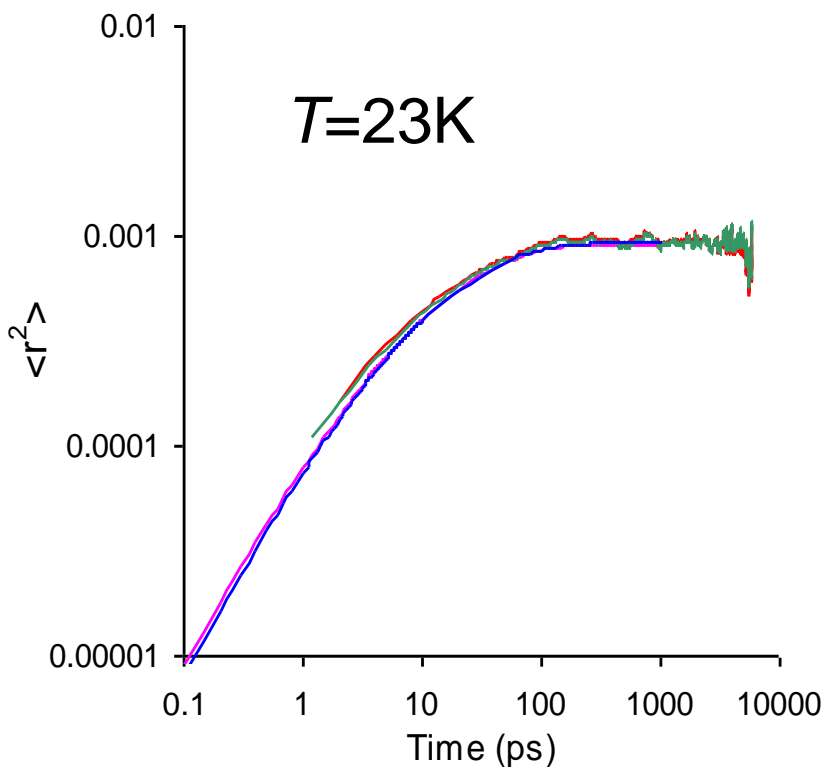
Red line: direct calculation from MD, minimisations every 2ps

Green line: direct calculation from MD, minimisations every 1.2ps

Blue line: Poisson process model, minimisations every 2ps

Purple line: Poisson process model, minimisations every 1.2ps

position of atom i in inherent structure α

Poisson process model:

$$\left\langle r^2\left(\tau\right)\right\rangle = \sum_{\beta}\sum_{\alpha}\left[\frac{\sum_{i}^{N}\left(\mathbf{r}_{i,\beta}^{min}-\mathbf{r}_{i,\alpha}^{min}\right)^2}{N}\right]P_{\alpha\rightarrow\beta}(t)P_{\alpha}(0)$$

$P_{\alpha\rightarrow\beta}(t) = P_{\beta}(t)$ from solution to the Master Equation with initial condition $P_i(0)=\delta_{i\,\alpha}$

OBSERVATION OF METABASINS
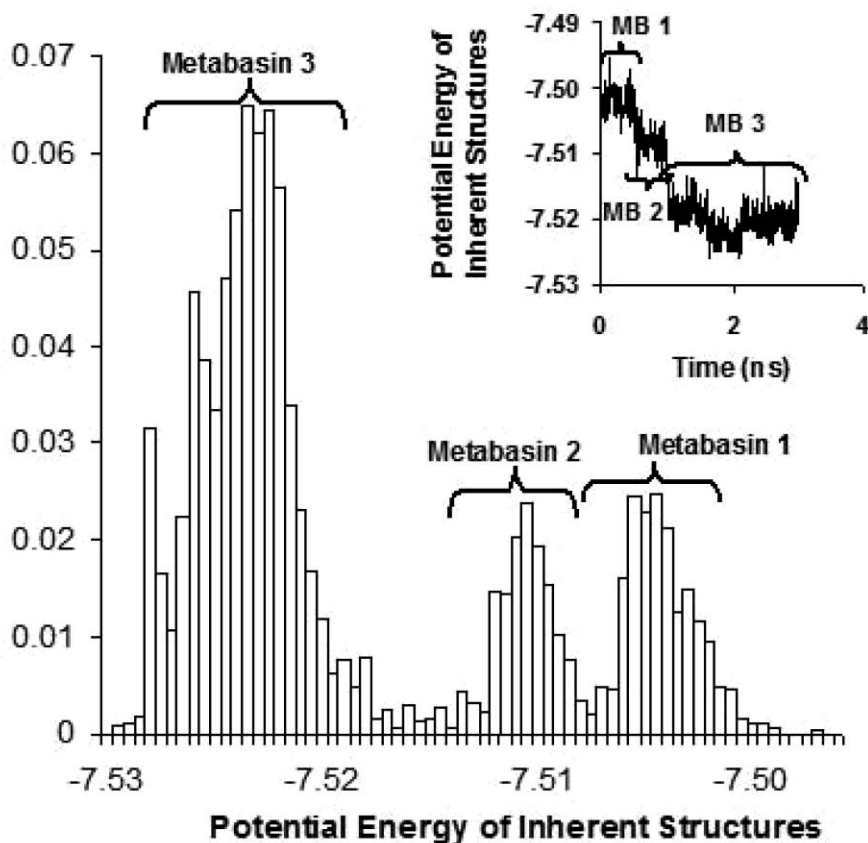
Binary mixture of A (80%) and B(20%) LJ spheres

$m_A = m_B$, $\varepsilon_{BB} = 0.50\varepsilon_{AA}$, $\varepsilon_{AB} = 1.50\varepsilon_{AA}$
$\sigma_{BB} = 0.88\sigma_{AA}$, $\sigma_{AB} = 0.88\sigma_{AA}$.

$\rho = 1.1908\ \sigma_{AA}^{-3}$, $N = 641$ atoms.

Mode coupling $T_c = 0.435\ \varepsilon_{AA}/k_B = 52.2$ K (for A=argon).

Glass temperature $T_g \approx 0.32\ \varepsilon_{AA}/k_B = 38.4$ K

History: Sudden cooling from T=55K to T=37K (3 ns NVT MD trajectory)

Plot: Distribution of potential energies of inherent structures (ISs) visited.

Inset: Time evolution of the IS trajectory.

Three "metabasins" can be identified visually.

Tsalikis, D., Lempesis, N., Boulougouris, G.C., DNT *J. Chem. Theory Comput.* **6**, 1307 (2010)

IDENTIFICATION OF A METABASIN
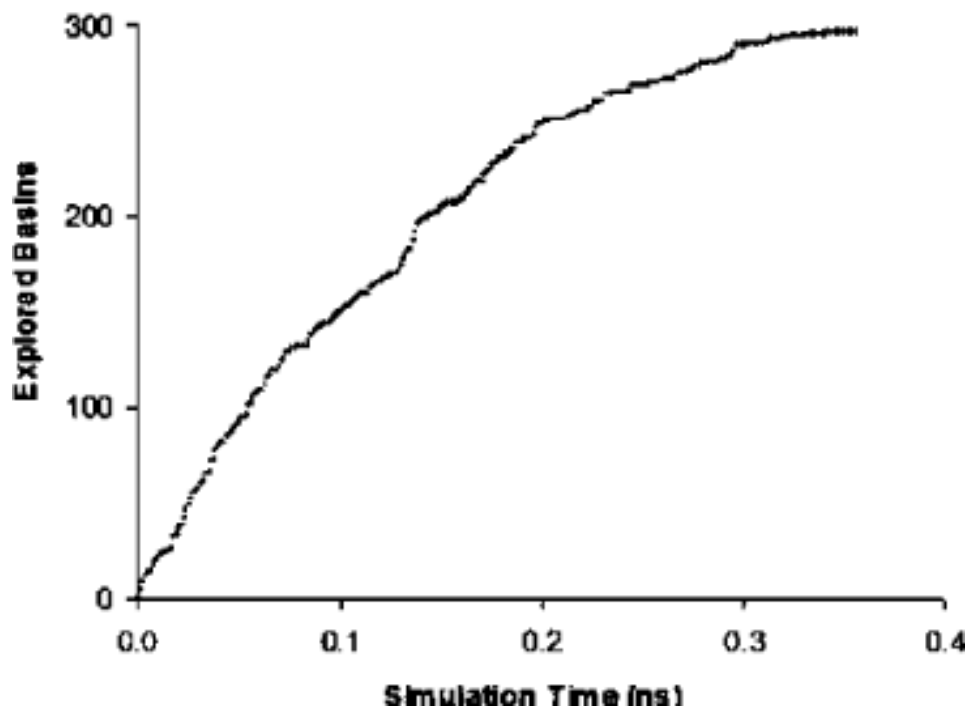
Binary mixture of A (80%) and B(20%) LJ spheres

$m_A=m_B$, $\varepsilon_{BB}=0.50\varepsilon_{AA}$, $\varepsilon_{AB}=1.50\varepsilon_{AA}$ $\sigma_{BB}=0.88\sigma_{AA}$, $\sigma_{AB}=0.88\sigma_{AA.}$

$\rho=1.1908\ \sigma_{AA}^{-3}$, $N=641$ atoms.

Mode coupling $T_c=0.435\ \varepsilon_{AA}/k_B$ = 52.2 K (for A=argon).

Glass temperature $T_g\approx0.32\ \varepsilon_{AA}/k_B$ = 38.4 K

Number of distinct explored minima as a function of time at T=37K. When a plateau is observed for a prefixed time interval (here 0.02 ns), the explored minima are considered to belong to the same metabasin.

Tsalikis, D., Lempesis, N., Boulougouris, G.C., DNT *J. Chem. Theory Comput.* **6**, 1307 (2010)

MD TRAJECTORIES USED FOR THE EXPLORATION OF A METABASIN
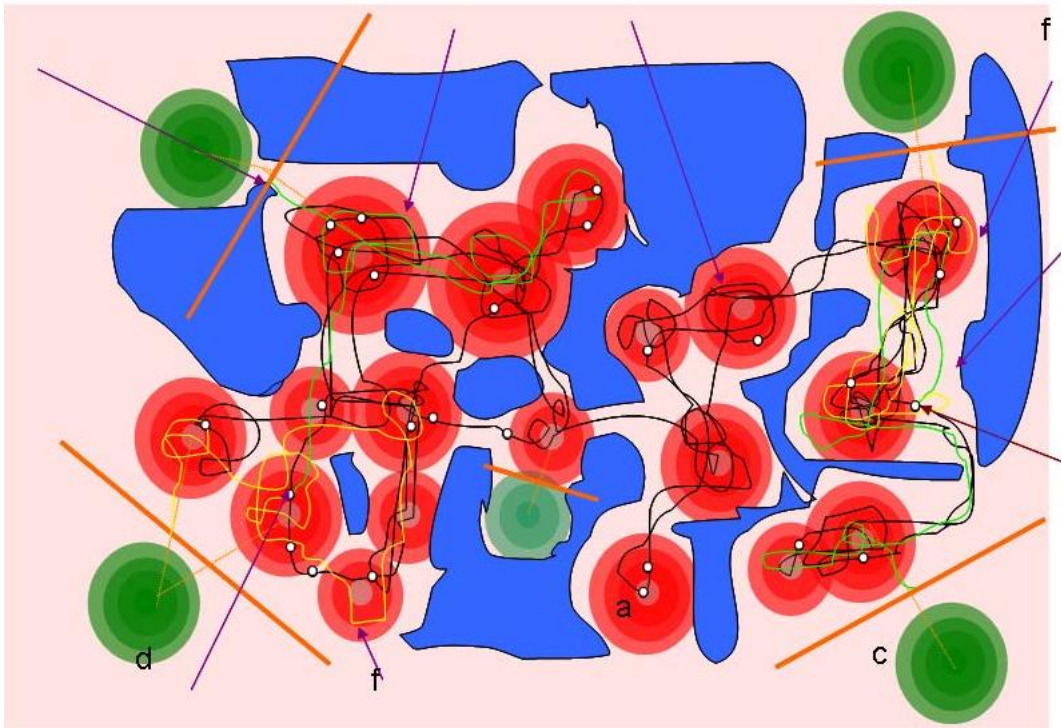
● : basins constituting the metabasin.

● : neighbouring basins, not belonging to the metabasin.

——: configuration-space projection of *NVT* MD trajectory used to define the metabasin.

∘: configuration-space projections of points in phase space sampled during the *NVT* MD trajectory.

Phase-space points ∘ are stored and employed as starting points for generating a swarm of *NVE* MD trajectories trapped in the metabasin.

—— , ——: configuration-space projections of two *NVE* MD trajectories started from two stored phase space points. These may be conducted in parallel.

Tsalikis, D., Lempesis, N., Boulougouris, G.C., DNT *J. Chem. Theory Comput.* **6**, 1307 (2010)

TEMPERATURE-ACCELERATED DYNAMICS[1]

- Define metabasin at $T_0=37$ K

- Conduct long NVT MD simulations trapped within the metabasin at T=37K, 40K, 43K, 46K, 49K, 52K, and 55K.

- Construct swarms of NVE MD trajectories trapped within the metabasin off of each of the NVT MD trajectories. Analyze the NVE trajectories to determine residence time distributions $\hat{P}^\alpha_{NVE}(t)$ within each basin α and conditional probabilities $\Pi^{NVE}_{\alpha\to\beta}$ of transition into other basins β upon exit from α at each energy level E.

- Use histogram reweighting[2] in order to determine energy distribution $p^{est}(E,T_0)$ at the temperature of interest, T_0.

- From $p^{est}(E,T_0)$, $\hat{P}^\alpha_{NVE}(t)$, $\Pi^{NVE}_{\alpha\to\beta}$ determine $\hat{P}^\alpha_{NVT_0}(t)$, $\Pi^{NVT_0}_{\alpha\to\beta}$, hence rate constant $k^{NVT_0}_{\alpha\to\beta}$ for each basin-to-basin transition $\alpha\to\beta$ with α in the considered metabasin, through hazard plot analysis.

[1]F. Montalenti, A.F. Voter, J. Chem. Phys. **116**, 4819 (2002).

[2]A.M. Ferrenberg and R.H. Swendsen, *Phys. Rev. Lett.* **63**, 1195 (1989)

D. Tsalikis, N. Lempesis, G.C. Boulougouris, DNT *J. Phys. Chem. B* **114**, 844 (2010).

DISTRIBUTION OF TRANSITION RATE CONSTANTS BETWEEN BASINS OF A METABASIN (LJ MIXTURE)
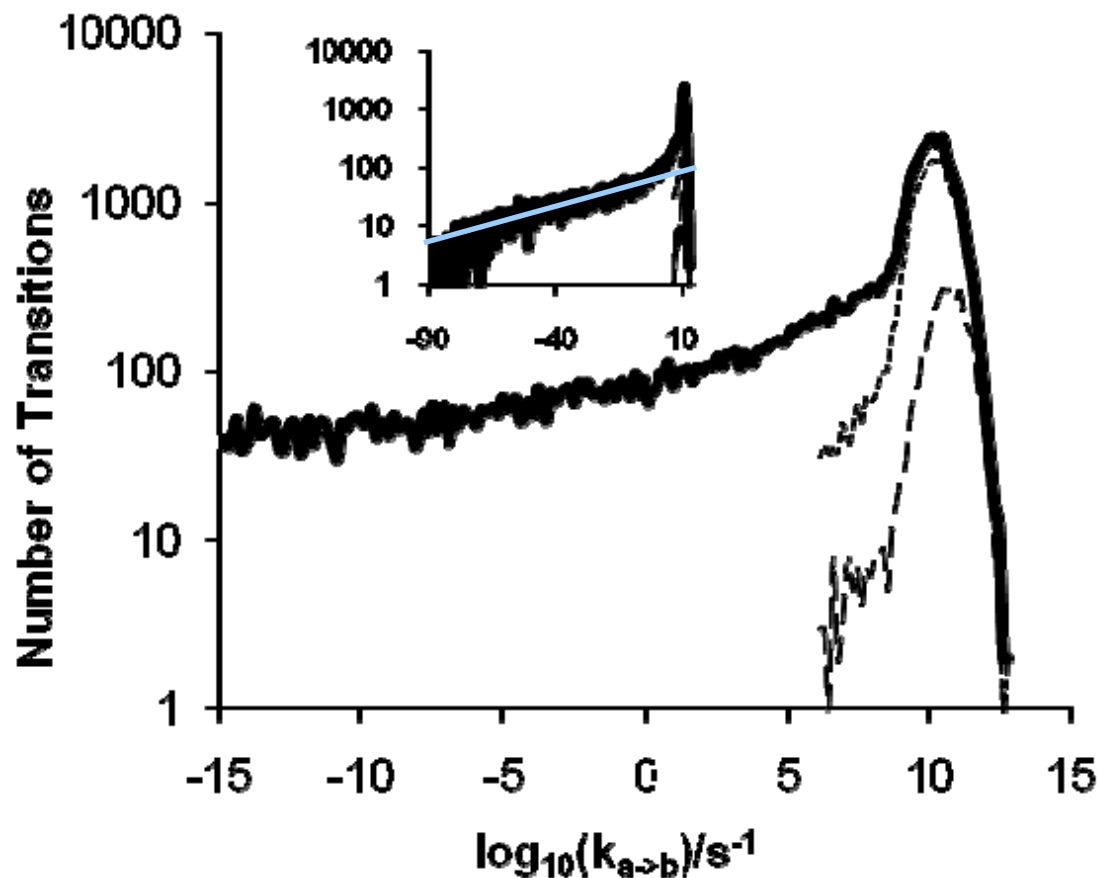
Number of identified distinct transitions between the basins of a specific metabasin at 37K, as a function of their rate constant.

– – – : MD simulation at 37 K, trapped within the metabasin.

-------- : Swarm of NVE trajectories generated in parallel off of an NVT trajectory at 37K.

——— : Temperature-accelerated method, using as input data from swarms of NVE trajectories at temperatures from 37K to 55K.

Inset: same plot for the total range of rate constants sampled by the temperature-accelerated method.

$$\rho(k_{a \to b}/v_0) \approx B\,(k_{a \to b}/v_0)^{\alpha}\,, \quad \alpha \approx 0.01$$

Tsalikis, D., Lempesis, N., Boulougouris, G.C., DNT *J. Phys. Chem. B*, **114**, 7844 (2010).

Distribution similar to that proposed by J. P. Bouchaud, *J. Phys. I France*, **2**, 1705-1713 (1992).

DISTRIBUTION OF TRANSITION RATE CONSTANTS BETWEEN BASINS OF A METABASIN (LJ MIXTURE)

Implication for distribution of barrier heights $E_{a\rightarrow b} = -k_B T \ln(k_{a\rightarrow b}/v_0)$:

$$\rho(E_{a\rightarrow b}) = \frac{B}{k_B T} \exp\left[-(\alpha+1)\frac{E_{a\rightarrow b}}{k_B T}\right]$$

Reminiscent of distribution of trap free energies f in spin glass models, with $E_{a\rightarrow b} = f_0 - f$.
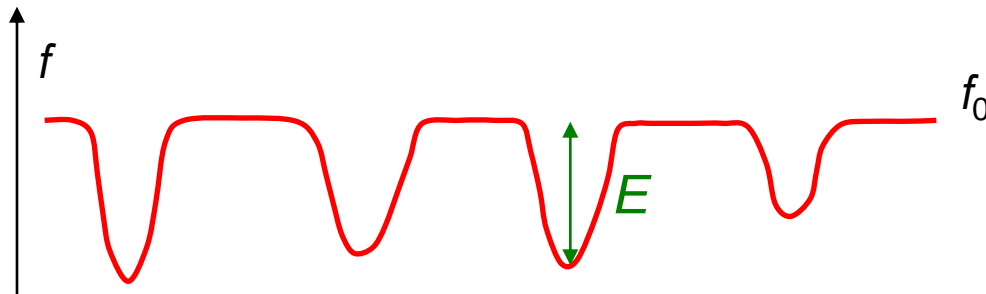
"In the spin glass phase of both the Random Energy Model (REM) and the SK model, the distribution of very low f's is exponential:

$$\rho(f) = \frac{N}{T} \exp\left[x\frac{f-f_0}{T}\right]$$

where x is a temperature-dependent number between 0 and 1, f_0 is the reference level beyond which levels proliferate, and N is a constant. In the REM, $x = T/T_g$, which is connected to the fact that the free energy landscape is temperature independent."

J. P. Bouchaud, *J. Phys. I France*, **2**, 1705-1713 (1992).

BASIN-TO-BASIN TRANSITIONS IN LJ SYSTEM: COOPERATIVITY VS. DISTANCE TRAVERSED
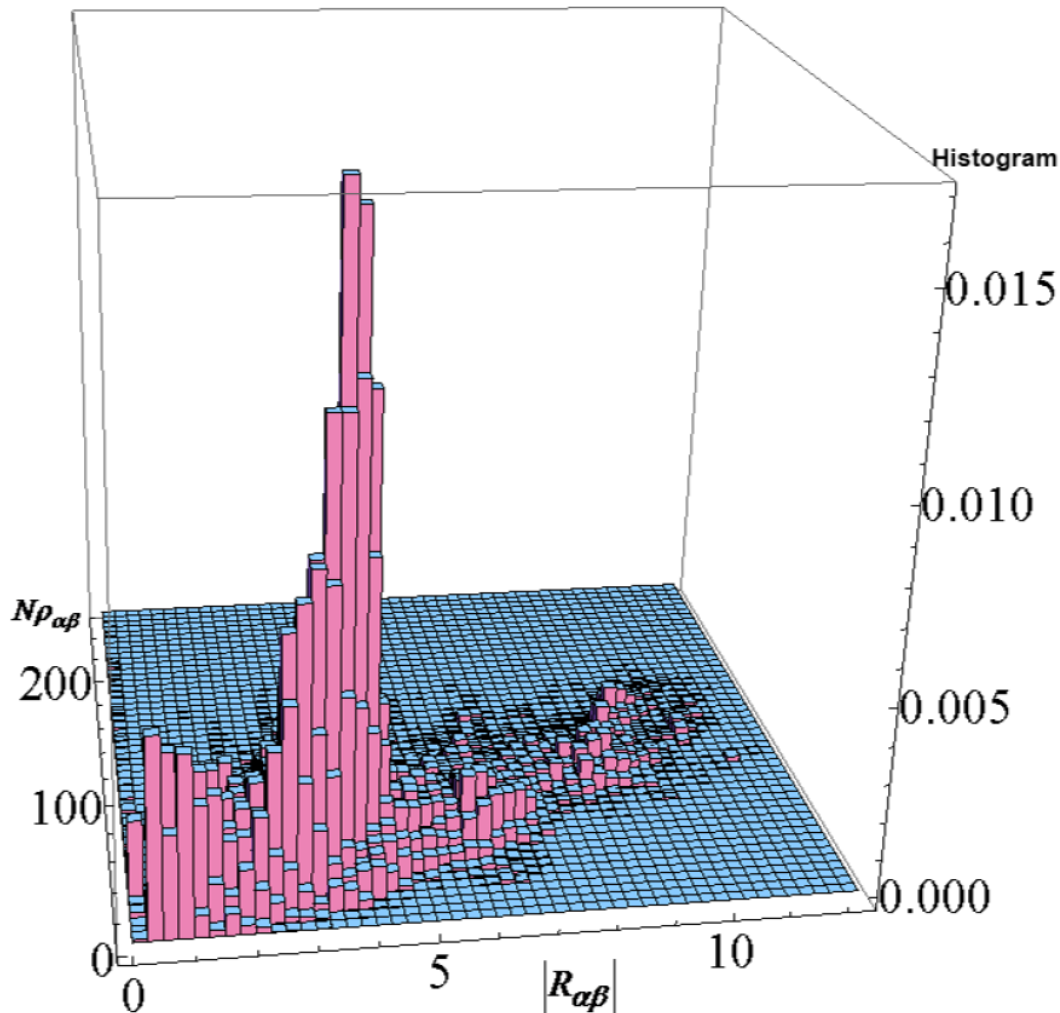
Two-dimensional histogram of 51207 inter- and intra-metabasin transitions explored in the course of sampling 4 metabasins.

$|\mathbf{R}_{\alpha\beta}|$ (r.u.): Euclidean distance traversed between inherent structures in the $3N = 3 \times 641$-dimensional configuration space of the system.

$p_{\alpha\beta}$: Participation ratio

$$p_{\alpha\beta} = \frac{\left[\sum_{i=1}^{N}\left(\mathbf{r}_{\alpha\beta}^{i}\right)^{2}\right]^{2}}{N\sum_{i=1}^{N}\left(\mathbf{r}_{\alpha\beta}^{i}\right)^{4}}$$

displacement vector of atom i between inherent structures α and β

Tsalikis, D., Lempesis, N., Boulougouris, G.C., DNT *J. Phys. Chem. B*, **114**, 7844 (2010).

MECHANISM OF BASIN-TO-BASIN TRANSITIONS (LJ MIXTURE)
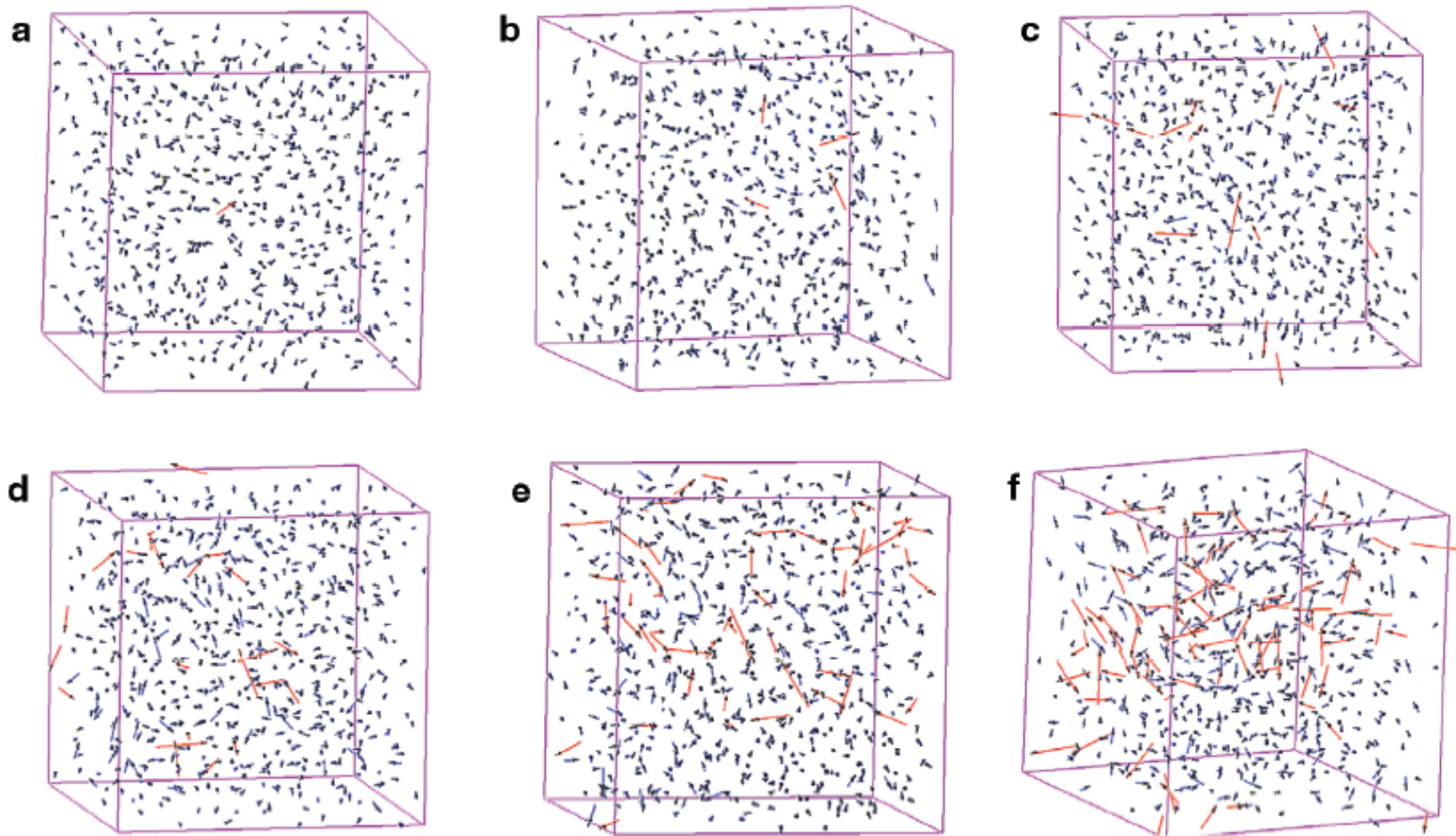
Displacement vectors of all atoms for single transitions with different Euclidean norms |**R**|:
(**a**) 1.7 r.u. (5.8 Å): Isolated cage breaking event.
(**b**) 3.78 r.u.: At this point we start observing more than one cage breaking events within the simulation box.
(**c**) 5.11 r.u.: From this point on, chain formation is evident and transitions are almost entirely inter-metabasin.
(**d**) 7.04 r.u.: From this point on, formation of more than one chains is probable.
(**e**) 7.94 r.u.: At this point there is extended formation of several interlinked chains.
(**f**) 9.50 r.u.: Extensive shear band-like displacement of atoms.
Red colour marks displacements longer than 0.6 r.u. (2 Å).

SOME OBSERVATIONS FROM MD

Structural relaxation below T_g well described as a Poisson process involving successive uncorrelated transitions between basins in configuration space constructed around potential energy minima (inherent structures).

Rate constants describing transitions between any connected basins estimable by hazard plot analysis.

Time-dependent occupancy probabilities for basins and mean square displacement of atoms along inherent structure trajectory captured by Poisson process model in excellent agreement with direct MD.

Mathematical procedure developed for "lifting" the inherent structure trajectory and reproducing the mean squared displacement of atoms as a function of time. Contributions from switches between inherent structures, uncorrelated vibrations in original and destination basins, and in-basin time-dependent motion accounted for.

Results from "lifted" trajectory in excellent agreement with full MD.

T=9K: INHERENT STRUCTURE TRAJECTORY
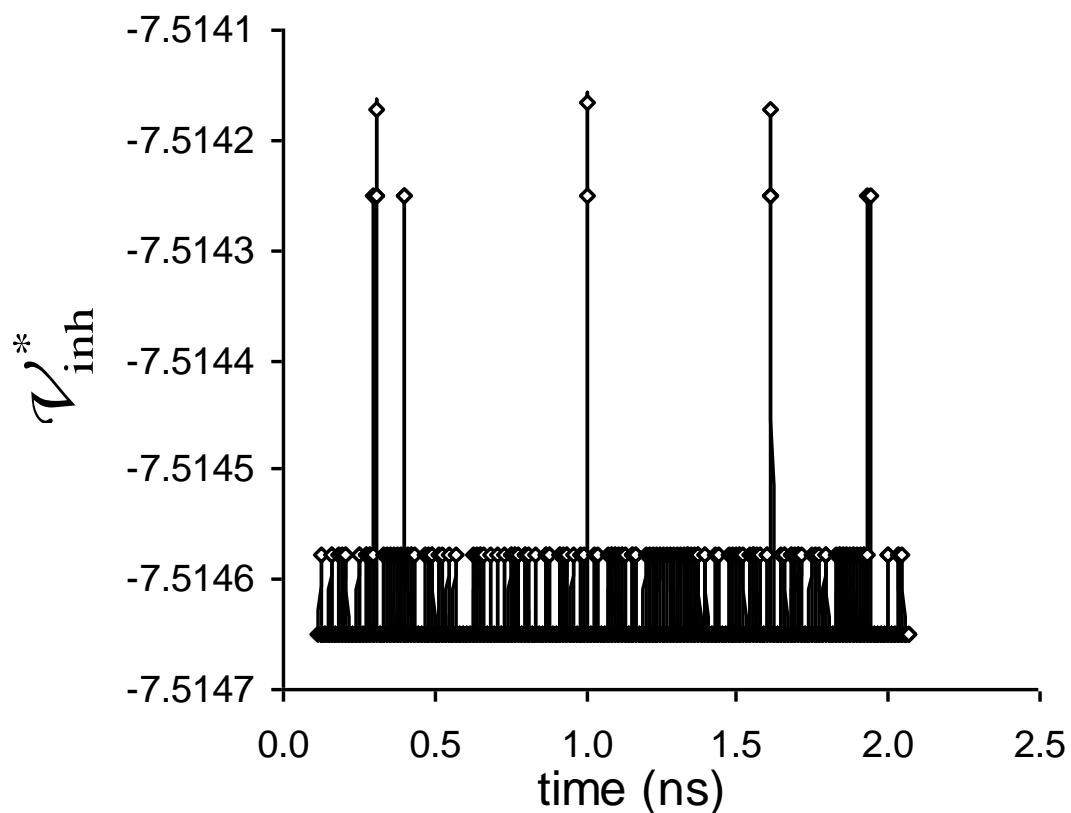
T=9K: BASIN PROBABILITIES
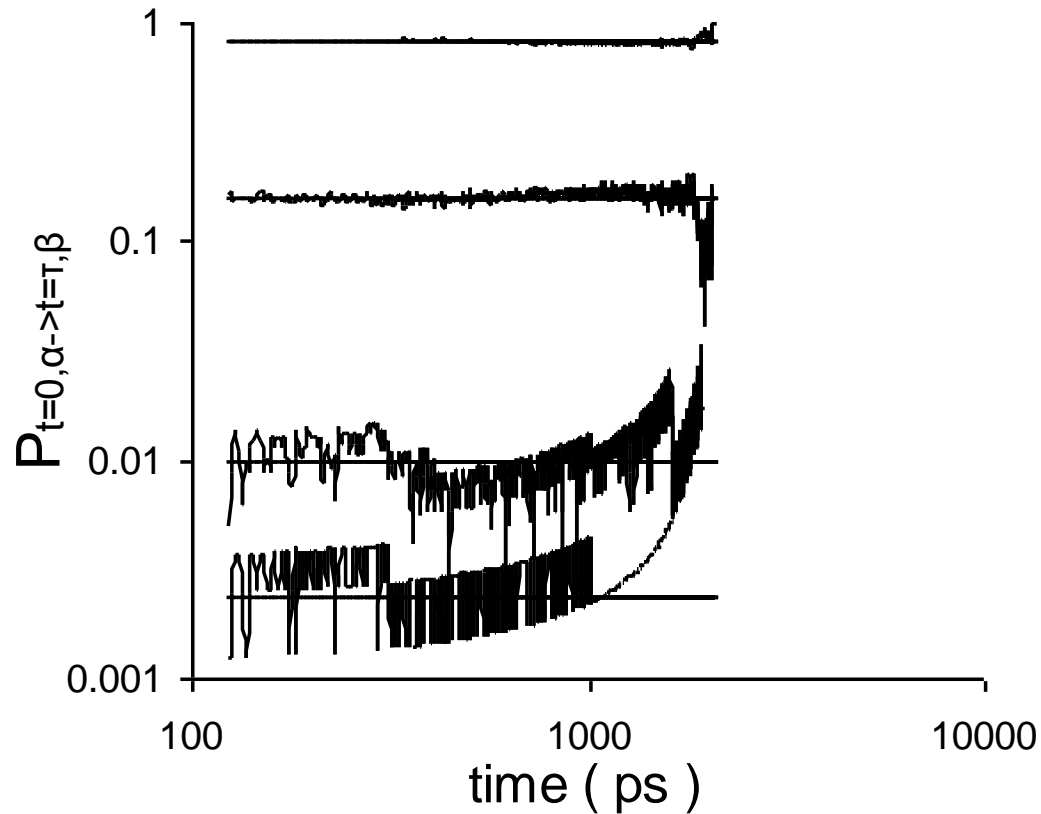
Fluctuating lines: Direct calculation from MD, energy minimization.
Horizontal lines: Based on $k_{\beta \to \gamma}$, solution of the Master Equation.

MEAN SQUARE ATOMIC DISPLACEMENT ALONG INHERENT STRUCTURE TRAJECTORY

T=9K

MD

Poisson process model

T=38K

Energy minimisations every 2 ps
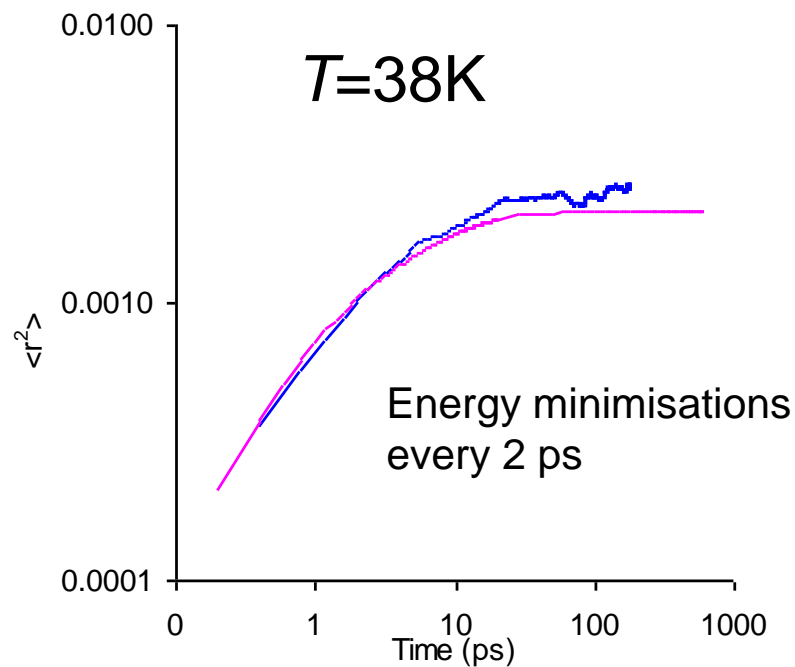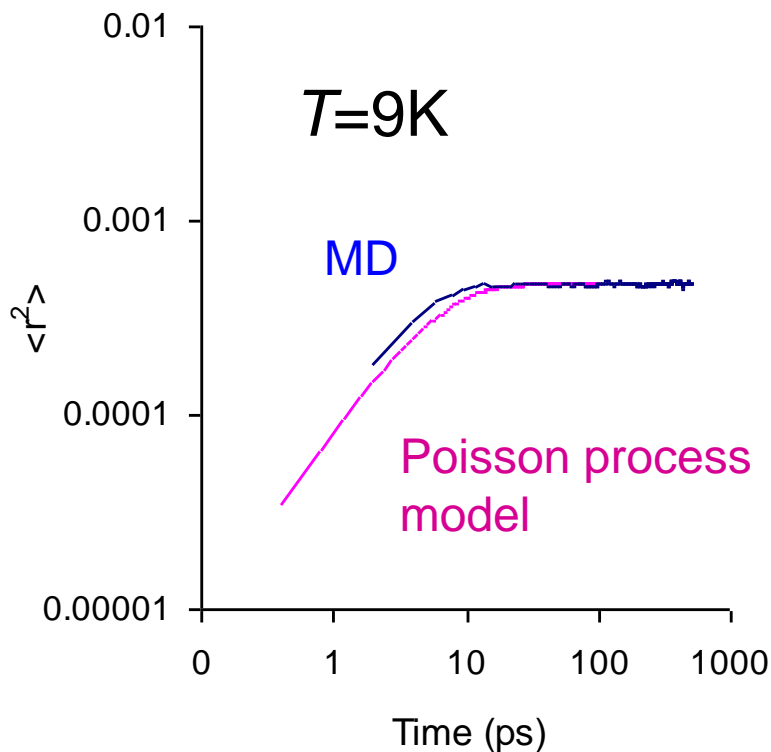
Poisson process model:

$$\left\langle r^2\left(\tau\right)\right\rangle = \sum_{\beta}\sum_{\alpha}\left[\frac{\sum_{i}^{N}\left(\mathbf{r}_{i,\beta}^{\min} - \mathbf{r}_{i,\alpha}^{\min}\right)^2}{N}\right]P_{\alpha\to\beta}(t)P_{\alpha}(0)$$

$P_{\alpha\to\beta}(t) = P_{\beta}(t)$ from solution to the Master Equation with initial condition $P_i(0) = \delta_{i\,\alpha}$

RECONSTRUCTING THE FULL MEAN SQUARE DISPLACEMENT OF ATOMS

Poisson process model:

Term1: MSD Inherent Structures
(inter-basin contribution)

Term 2: Intra-basin Displacement
(final = original minimum)

$$\left\langle \left(\mathbf{r}_i(\tau) - \mathbf{r}_i(0)\right)^2 \right\rangle = \sum_{\alpha=1}^{n} P_\alpha(0) \sum_{\beta=1}^{n} P_{t=0,\alpha \to t=\tau,\beta} \left(\mathbf{r}_{i,\beta}^{\min} - \mathbf{r}_{i,\alpha}^{\min}\right)^2 +$$

$$+ \sum_{\alpha=1}^{n} P_\alpha(0) \sum_{\beta=1}^{n} \left\{ \delta_{\alpha\beta} \int_0^\tau \left[\sum_{\gamma \neq \beta} P_{t=0,\alpha \to t=\tau-\delta\tau,\gamma} k_{\gamma \to \beta} + \delta(\tau - \delta\tau) \right] e^{-\sum_{\gamma \neq \beta} k_{\beta \to \gamma} \delta\tau} \left\langle \left(\mathbf{r}_i^\alpha(\delta\tau) - \mathbf{r}_i^\alpha(0)\right)^2 \right\rangle d\delta\tau \right\} +$$

$$+ \sum_{\alpha=1}^{n} P_\alpha(0) \sum_{\beta=1}^{n} P_{t=0,\alpha \to t=\tau,\beta} \left[\left(1 - \delta_{\alpha\beta}\right) \left(\left\langle \left(\Delta\mathbf{r}_i^\beta\right)^2 \right\rangle + \left\langle \left(\Delta\mathbf{r}_i^\alpha\right)^2 \right\rangle \right) \right]$$

Term 3: Intra-basin Vibrations
around the initial and the final minima
(switch in minimum)

RECONSTRUCTING THE FULL MEAN SQUARE DISPLACEMENT OF ATOMS

Information needed for reconstruction:

Rate constants $k_{\beta \to \gamma}$ describing transitions between any pair of connected basins of the system.

Square of the (continuous) displacement Cartesian distance for all particles between inherent structures, $\left(\mathbf{r}_{i,\beta}^{min} - \mathbf{r}_{i,\alpha}^{min} \right)^2$.

Mean square displacement within each basin as a function of time since entry to the basin, $\left\langle \left(\mathbf{r}_i^{\alpha}(\delta\tau) - \mathbf{r}_i^{\alpha}(0) \right)^2 \right\rangle$.

Equilibrium in-basin variance of atomic positions relative to the energy minimum, $\left\langle \left(\Delta\mathbf{r}_i^{\alpha} \right)^2 \right\rangle$, for each basin.

RECONSTRUCTION OF THE FULL MEAN SQUARE DISPLACEMENT OF ATOMS
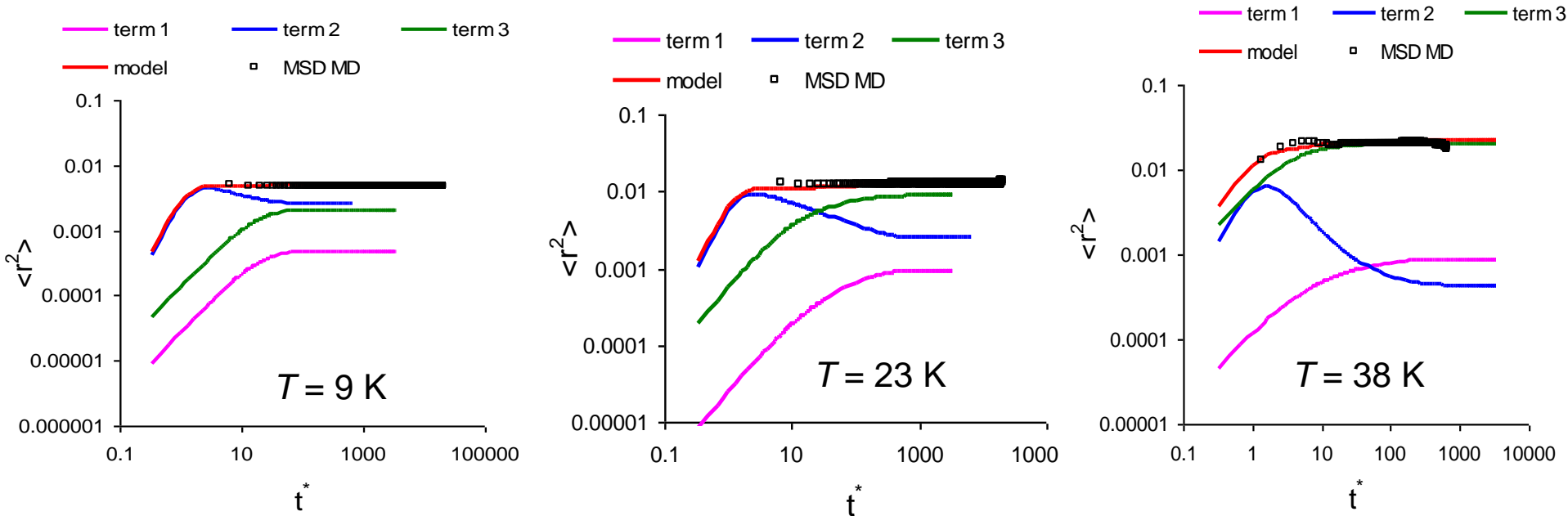
Term 1: Interbasin displacement between inherent structures

Term 2: Intra-basin displacement (final = original minimum)

Term 3: Intra-basin uncorrelated vibrations about original and final minima (switch in minima)

TEMPERATURE-ACCELERATED DYNAMICS IN GLASS-FORMING LJ MIXTURE
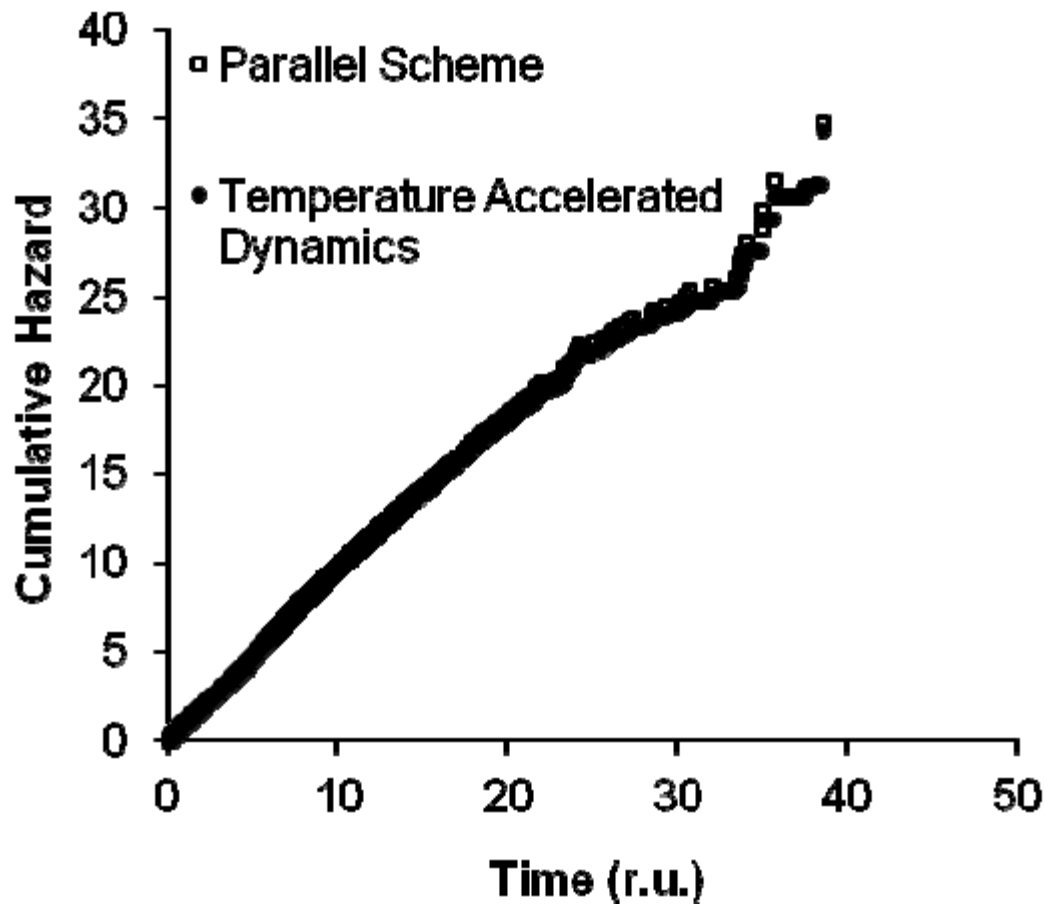
Estimation of transition rate constant $k_{\alpha \to}^{NVT_0} = \sum_\beta k_{\alpha \to \beta}^{NVT_0}$ out of a basin α at T_0=37 K
(a) from a swarm of parallel *NVE* trajectories initiated off of an *NVT* MD run[1] at T_0, and
(b) from a temperature-accelerated dynamics scheme.[2]

[1]Tsalikis, D., Lempesis, N., Boulougouris, G.C., DNT *J. Chem. Theory Comput.* **6**, 1307 (2010)
[2]Tsalikis, D., Lempesis, N., Boulougouris, G.C., DNT *J. Phys. Chem. B* **114**, 7844 (2010).

HAZARD PLOT ANALYSIS: NVT MD vs. SWARM of PARALLEL NVE MD TRAJECTORIES TRAPPED WITHIN A METABASIN
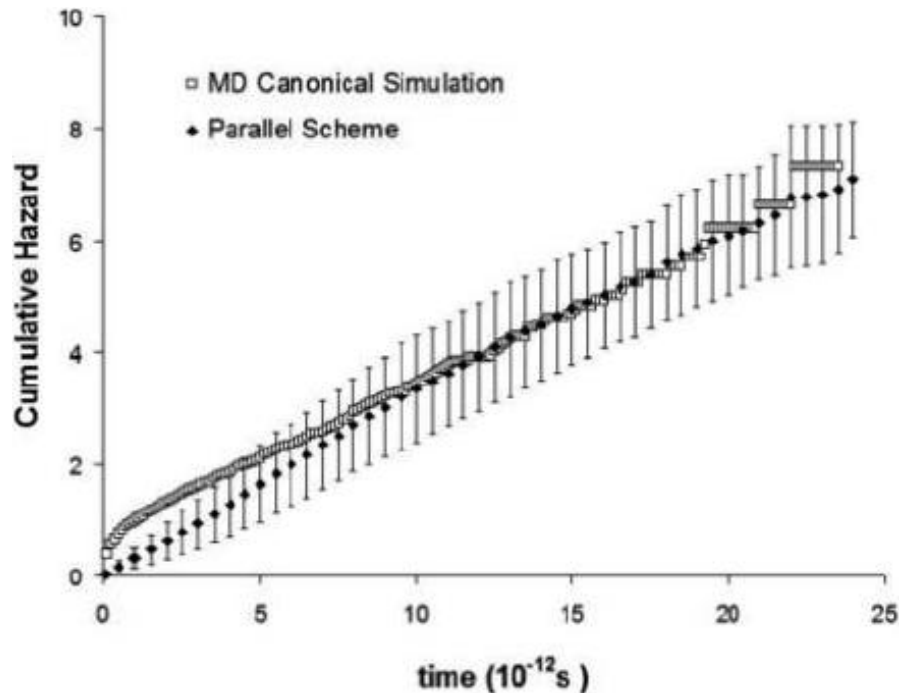
Binary mixture of A (80%) and B(20%) LJ spheres, T=37 K

m_A=m_B, ε_{BB}=0.50ε_{AA}, ε_{AB}=1.50ε_{AA}
σ_{BB}=0.88σ_{AA}, σ_{AB}=0.88σ_{AA}.

ρ =1.1908 σ_{AA}^{-3}, N=641 atoms.

Mode coupling T_c=0.435 ε_{AA}/k_B = 52.2 K (for A=argon).

Glass temperature T_g≈0.32 ε_{AA}/k_B = 38.4 K

Tsalikis, D., Lempesis, N., Boulougouris, G.C., DNT *J. Chem. Theory Comput.* **6**, 1307 (2010)

DISTRIBUTION OF DISTANCES TRAVERSED BY A TRANSITION BETWEEN BASINS (LJ MIXTURE)
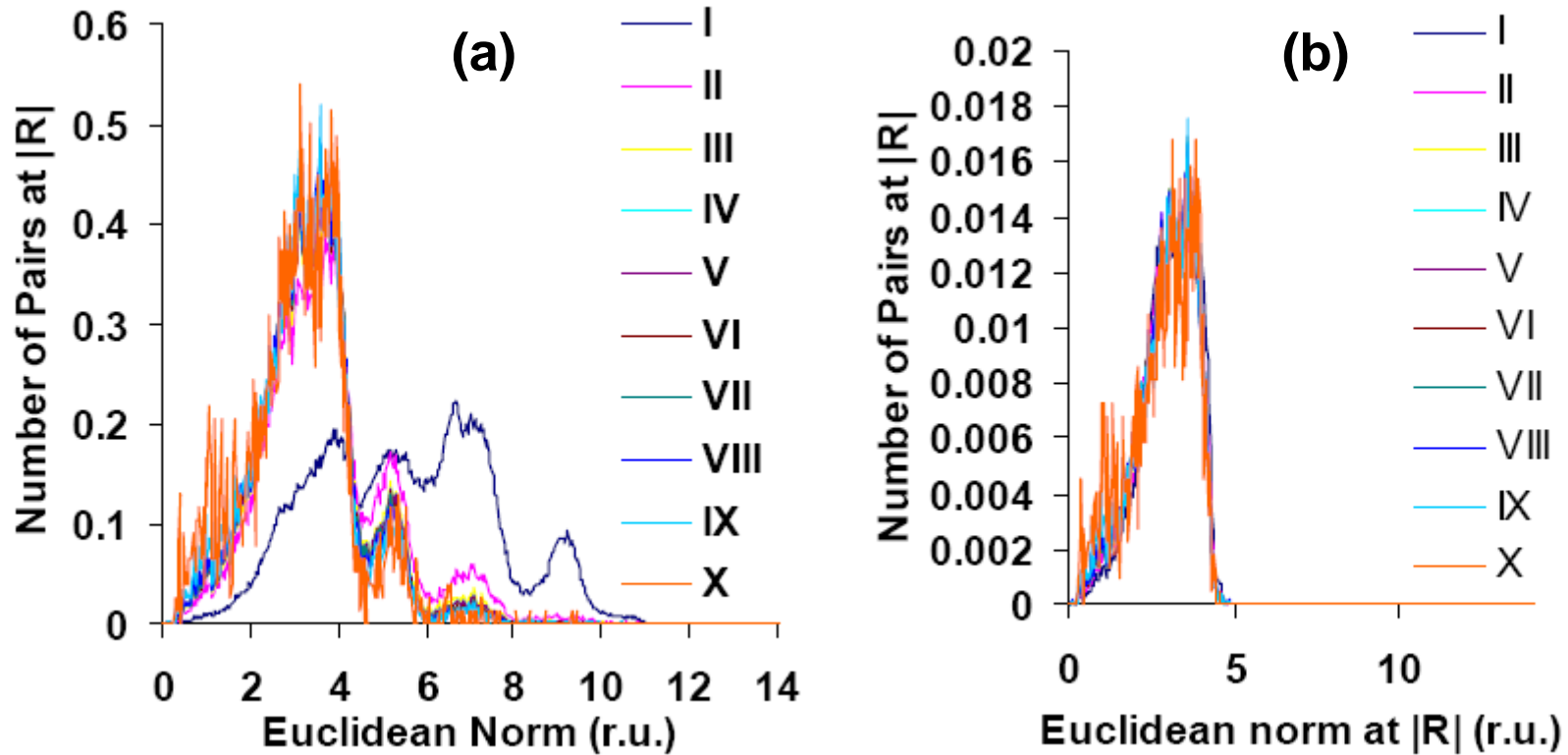
Probability density of Euclidean distances |**R**| between inherent structures (ISs).

(a)   For all ISs, irrespectively of whether they belong to the same metabasin.

(b)   only for ISs belonging to the same metabasin.

   I: with no restriction in respect to direct connectivity (all-to-all).

   II: provided a direct connection was found with the temperature accelerated dynamics.

III-XI: provided a direct connection was found with rate constant $k_{i \rightarrow j}$ at 37 K faster than 10 s^{-1} (III); 10^3 s^{-1} (IV); 10^5 s^{-1} (V); 10^7 s^{-1} (VI); 10^8 s^{-1} (VII); 10^9 s^{-1} (VIII); 10^{10} s^{-1} (IX); 10^{11} s^{-1} (X).

CAGE BREAKING EVENT DURING INTRAMETABASIN TRANSITION

$\rho = 1.1908\ \sigma_{AA}^{-3}$, $T=37$ K

Big spheres: Initial positions
Small spheres: Final positions
Red: first neighbours of central moving atom (also shown in red), both before and after the transition.
Cyan: first neighbours of central moving atom before, but not after the transition.
Blue: atoms which became first neighbours of central moving atom after the transition.
Blue(red) surfaces: Accessible volume to central moving atom before (after) transition.

Tsalikis, D., Lempesis, N., Boulougouris, G.C., DNT *J. Chem. Theory Comput.* **6**, 1307 (2010)
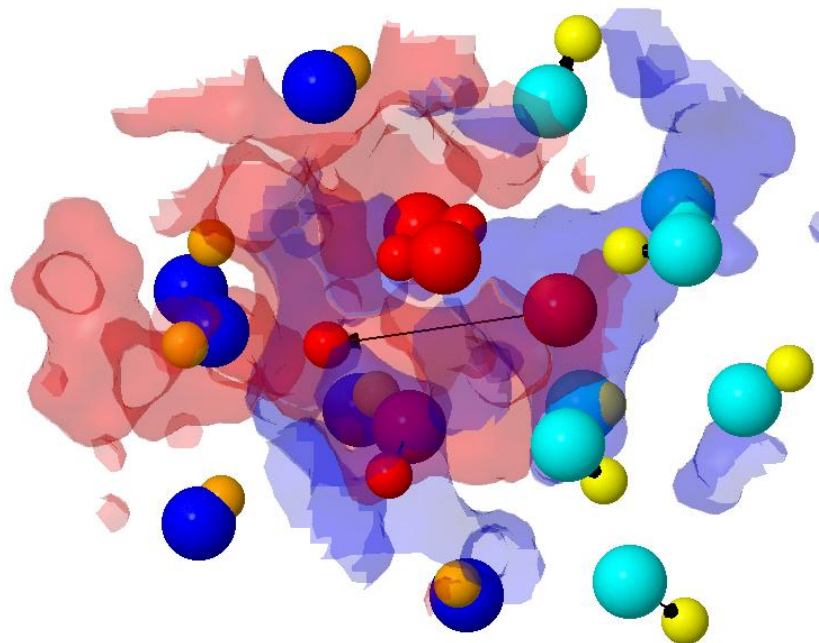
STRINGLIKE MOTION EVENT DURING INTERMETABASIN TRANSITION

Binary LJ mixture
$\rho = 1.1908\ \sigma_{AA}^{-3}$, $T = 37$ K

Initial positions: big spheres
Final positions: small spheres
Red: first neighbours of central moving atom both before and after the transition.
Cyan: first neighbours of central moving atom before, but not after the transition.
Blue: atoms which became first neighbours of central moving atom after the transition.
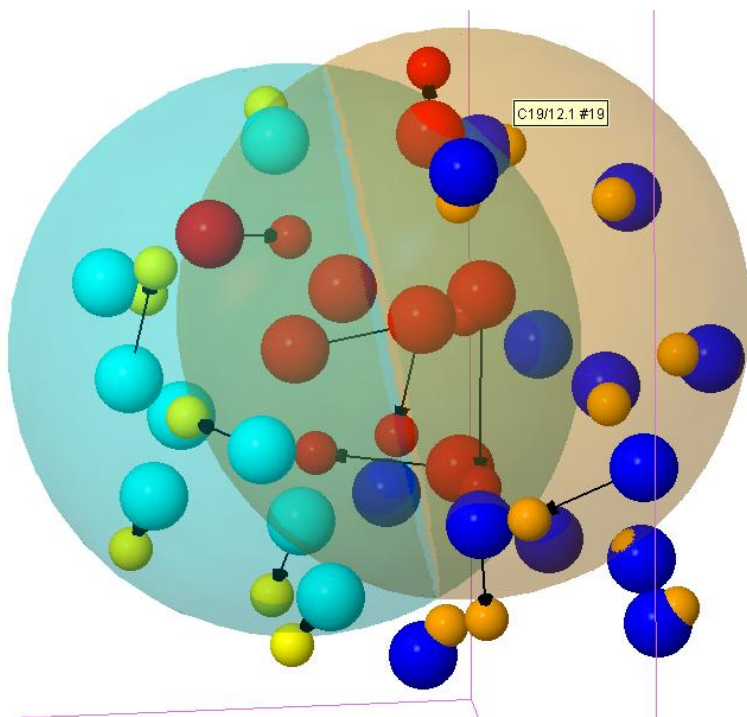
DISTRIBUTION OF RATE CONSTANTS OF TRANSITIONS ENCOUNTERED DURING AGEING SIMULATIONS
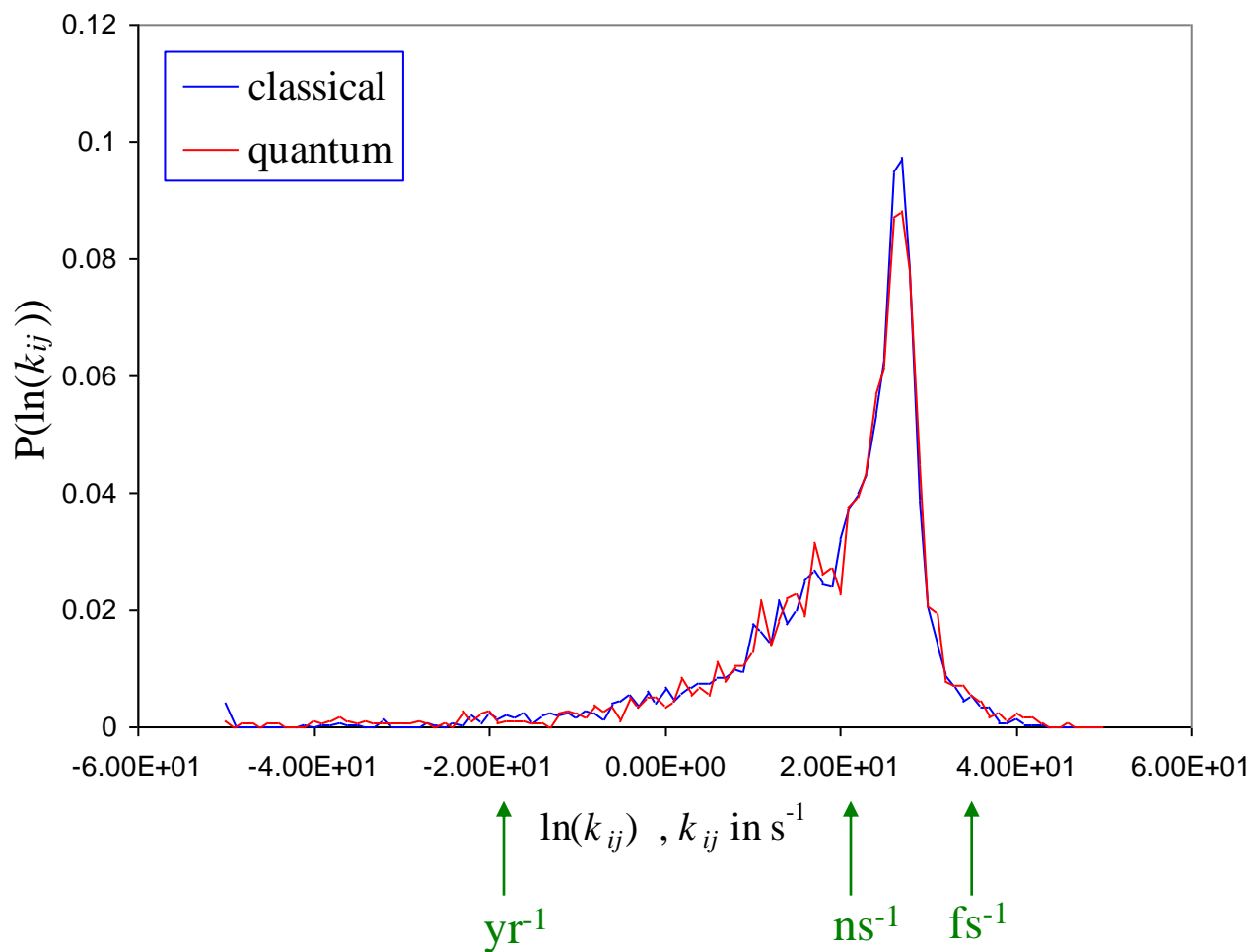
aPS, 250 K, 1 bar

REVERSE MAPPING TO ATOMISTIC LEVEL

Restoration of atomistic detail and relaxation of local packing via a MC procedure employing local moves which preserve chirality and prevent adoption of unrealistic torsional states.

WAXS pattern
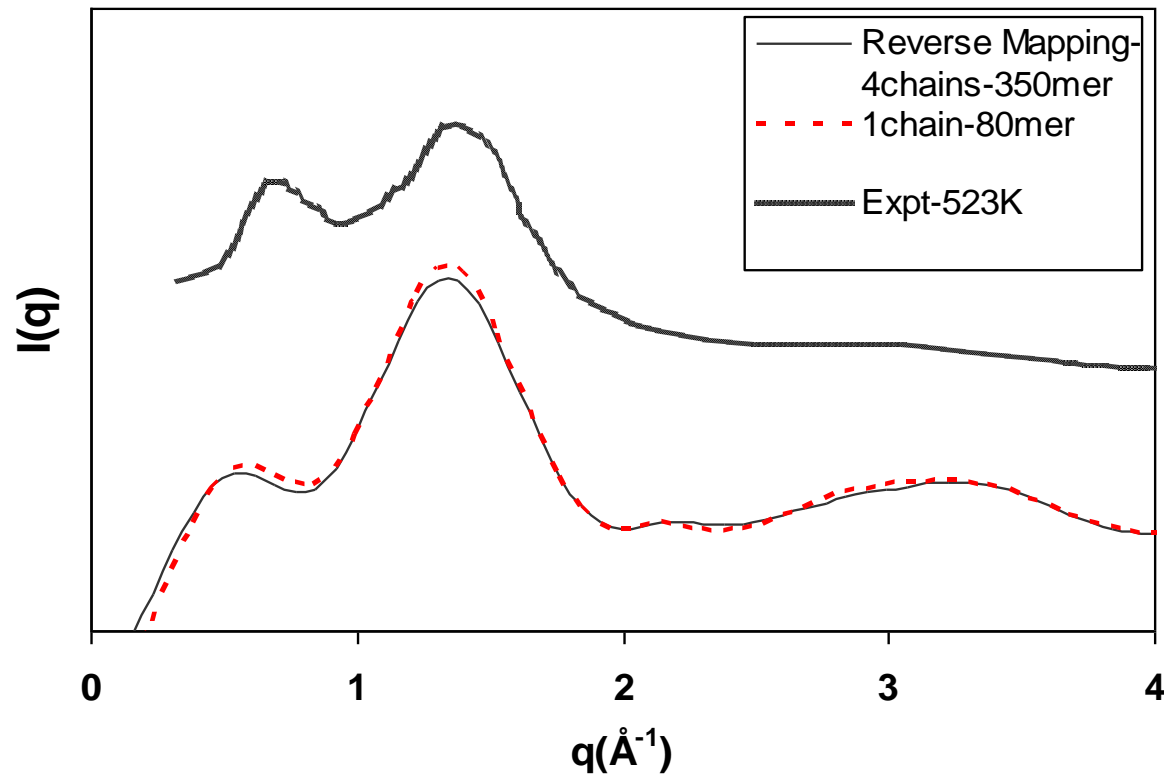
T. Spyriouni, C. Tzoumanekas, DNT, G. Milano, F. Müller-Plathe, *Macromolecules*, **40**, 3876-3885 (2007).

CG PS equilibration

T=500 K, p = 1 bar

$\langle R^2(n_u)\rangle/n_u$ increases monotonically until it reaches a plateau. Excellent agreement with experimental (SANS) and simulation results [1] .

1. Spyriouni, T.; Tzoumanekas, C.; Theodorou, D.N.; Müller-Plathe, F.; G. Milano G. *Macromolecules* **2007**, *40*, 3876.

2. Cotton, J.P.; Decker, D.; Benoit, H.; Farnoux, B.; Higgins, J.; Jannink, G.; Ober, R.; Picot, C.; des Cloizeaux, J. Macromolecules 1974, 7, 863.
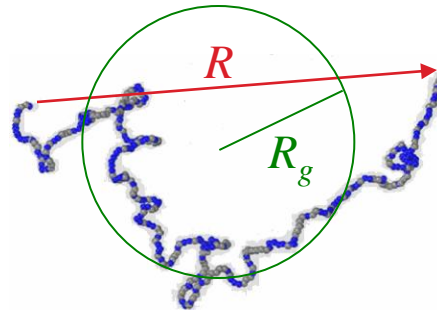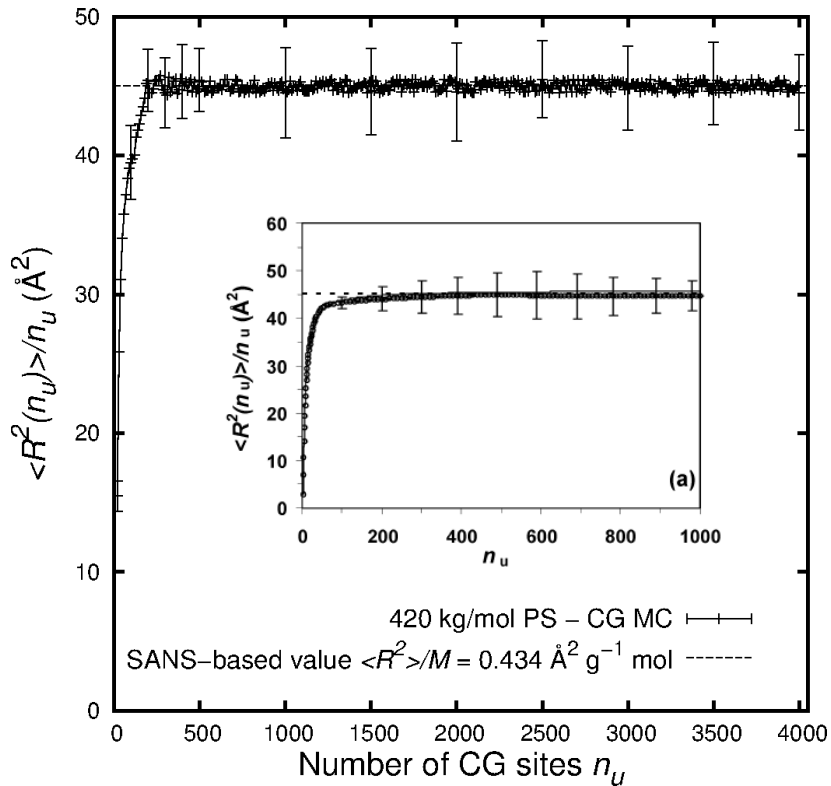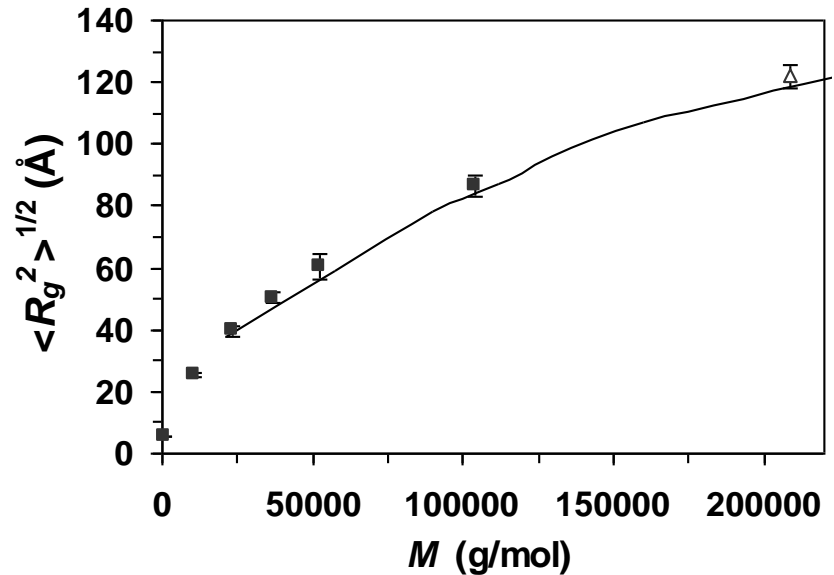
Points: CGMC simulation
line: SANS[2]
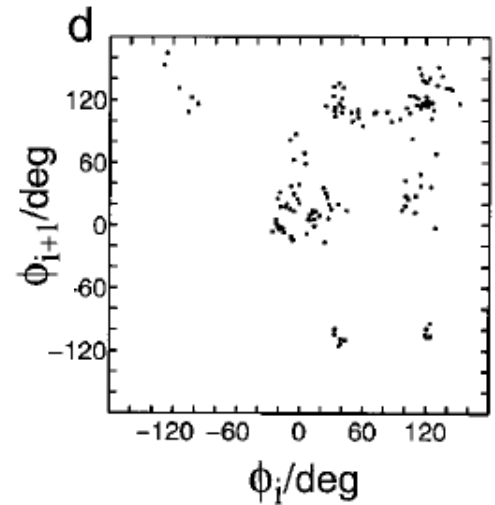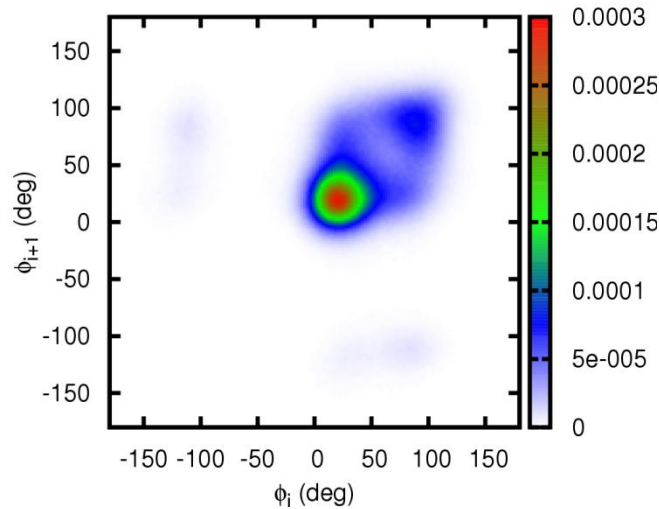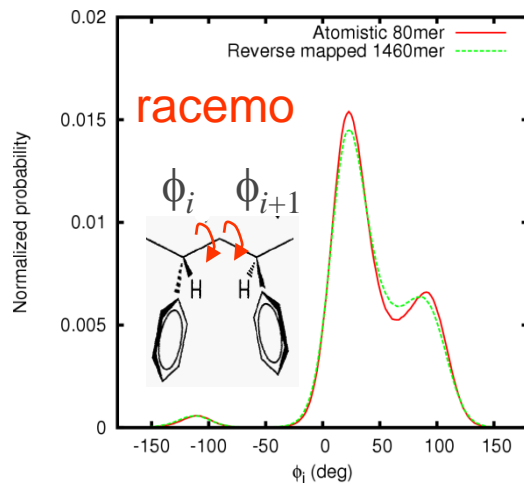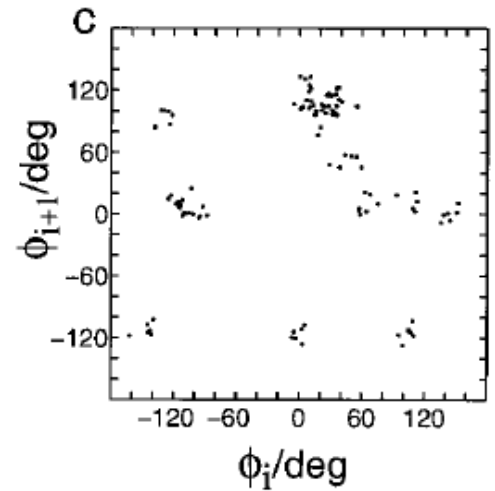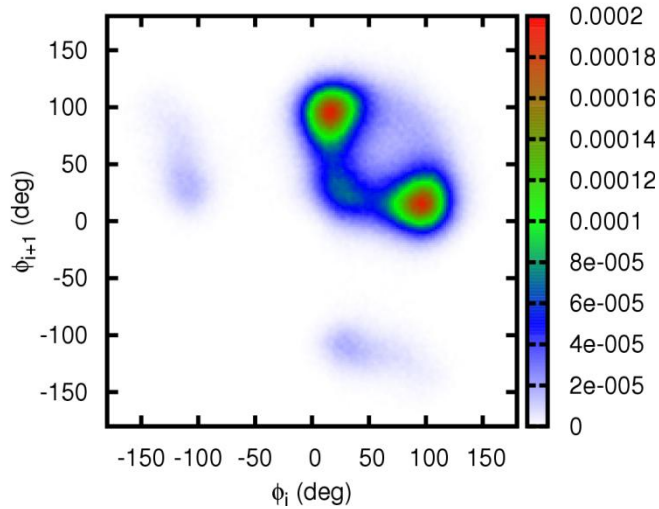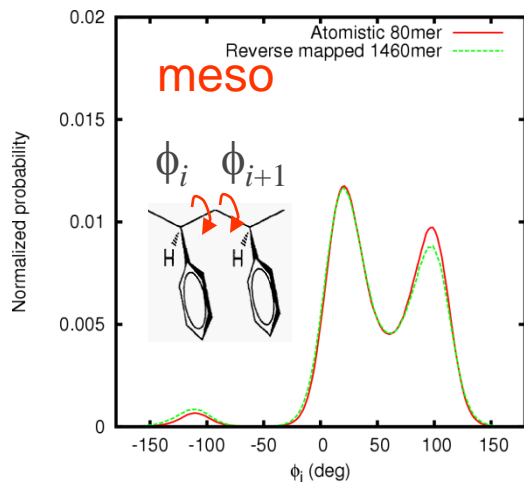
This work, united atom model of
Lyulin, A.V.; Michels, M.A.J.
Macromolecules **2002**, *35*,1463

Robyr, P.; Gan. Z.; Suter, U.W.
Macromolecules **1998**, *31*, 8918.
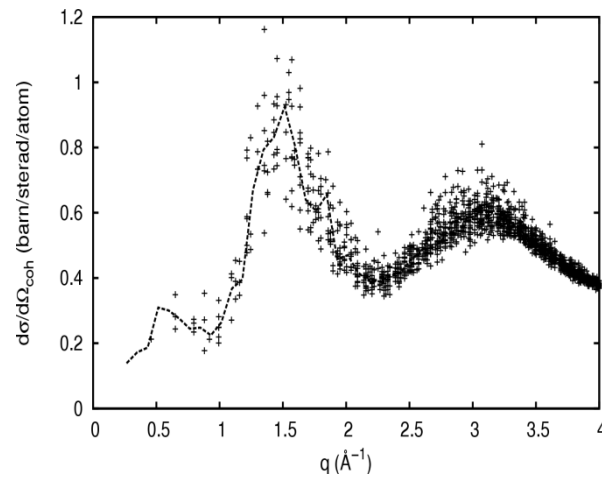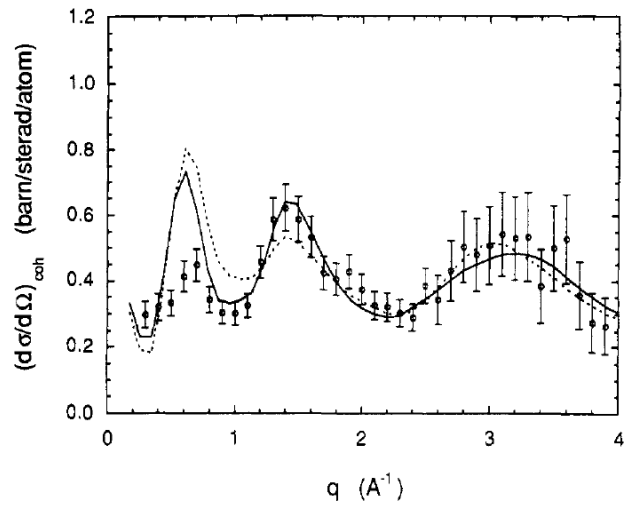
All hydrogens
replaced by
deuteriums
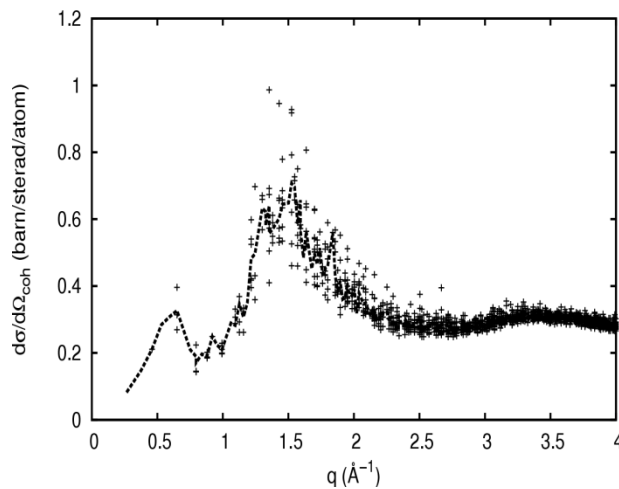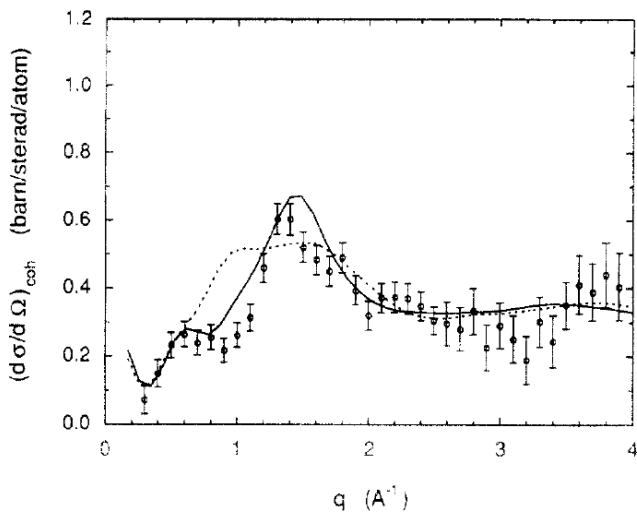
Ring hydrogens
replaced by
deuteriums

Furuya, H.; Mondello, M.; Yang, H-J.; Roe,
R-J.; Erwin, R.W.; Han, C.C.; Smith, S.D.
Macromolecules **1994**, *27*, 5674.

This work

United-atom PS: Segmental Dynamics

This work
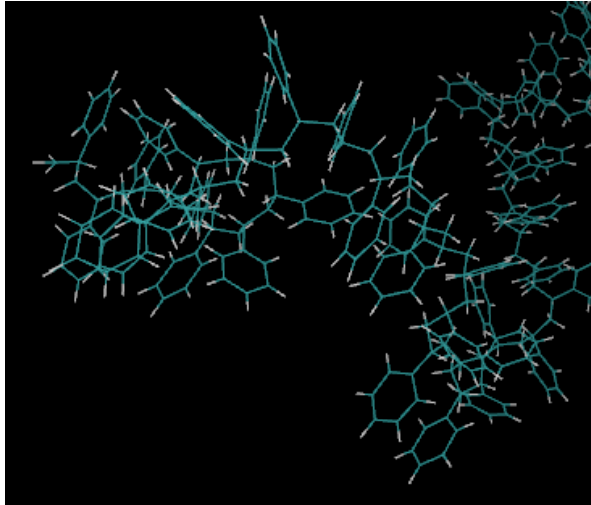
- ▶ Addition of hydrogens during trajectory post-processing [1]

- ▶ Autocorrelation functions for:
  - ◦ C–C bonds along chain backbone
  - ◦ C–CM of the rings
  - ◦ C–H bonds pendant to backbone

- ▶ Good agreement with all atom simulations and experiment at the same temperature (433 K) [2]

1. Ahumada, O.; DNT.; Triolo, A.; Arrighi, V.; Karatasos, C.; Ryckaert, J.-P. *Macromolecules* **2002**, *35*, 7110.
2. Harmandaris, V.A.; Floudas, G.; Kremer, K. *Macromolecules* **2011**, *44*, 393.
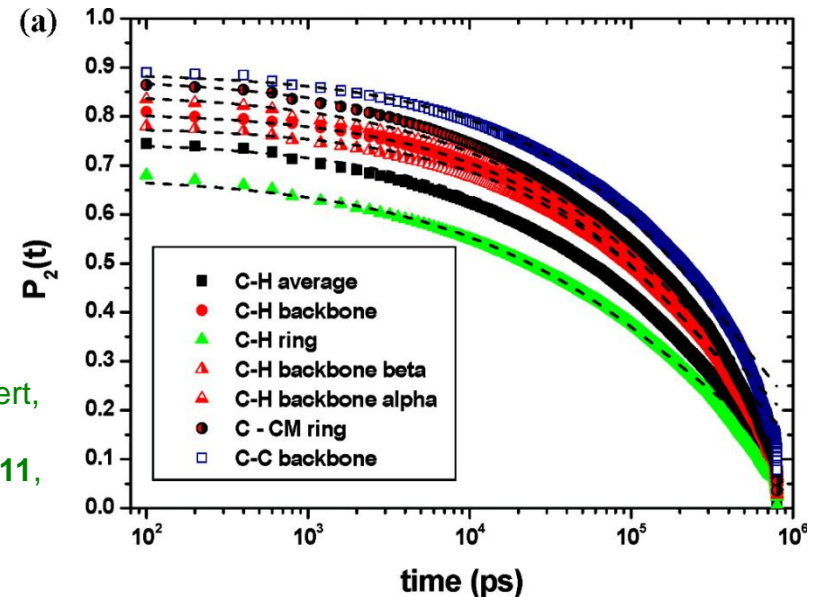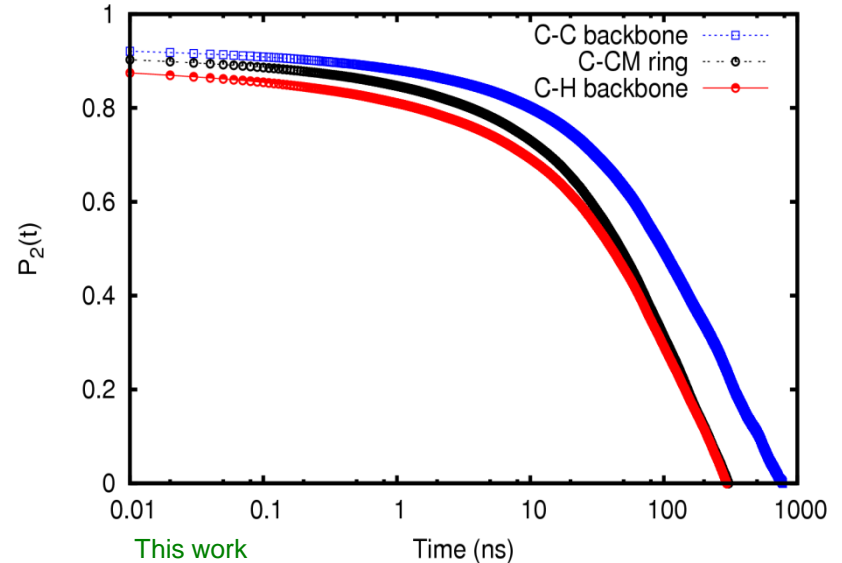
Harmandaris, V.A.; Floudas, G.; Kremer, K. *Macromolecules* **2011**, *44*, 393.

GLASSES ARE NON-EQUILIBRIUM MATERIALS WITH COMPLEX MECHANICAL BEHAVIOUR
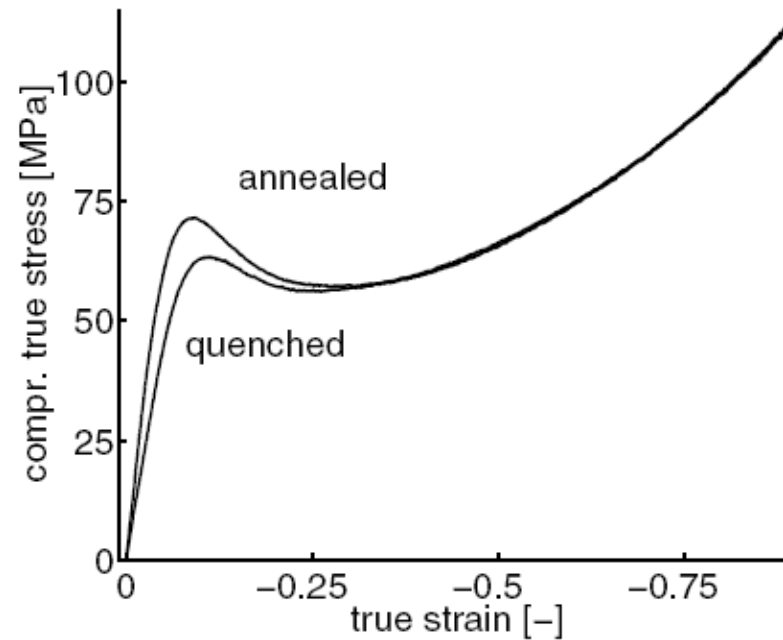
PC in compression: Effect of ageing

H. Van Melick, Ph.D. Thesis, Technical University of Eindhoven, 2002

ELASTIC RESPONSE: QHA

Computational experiment
of Uniaxial Deformation
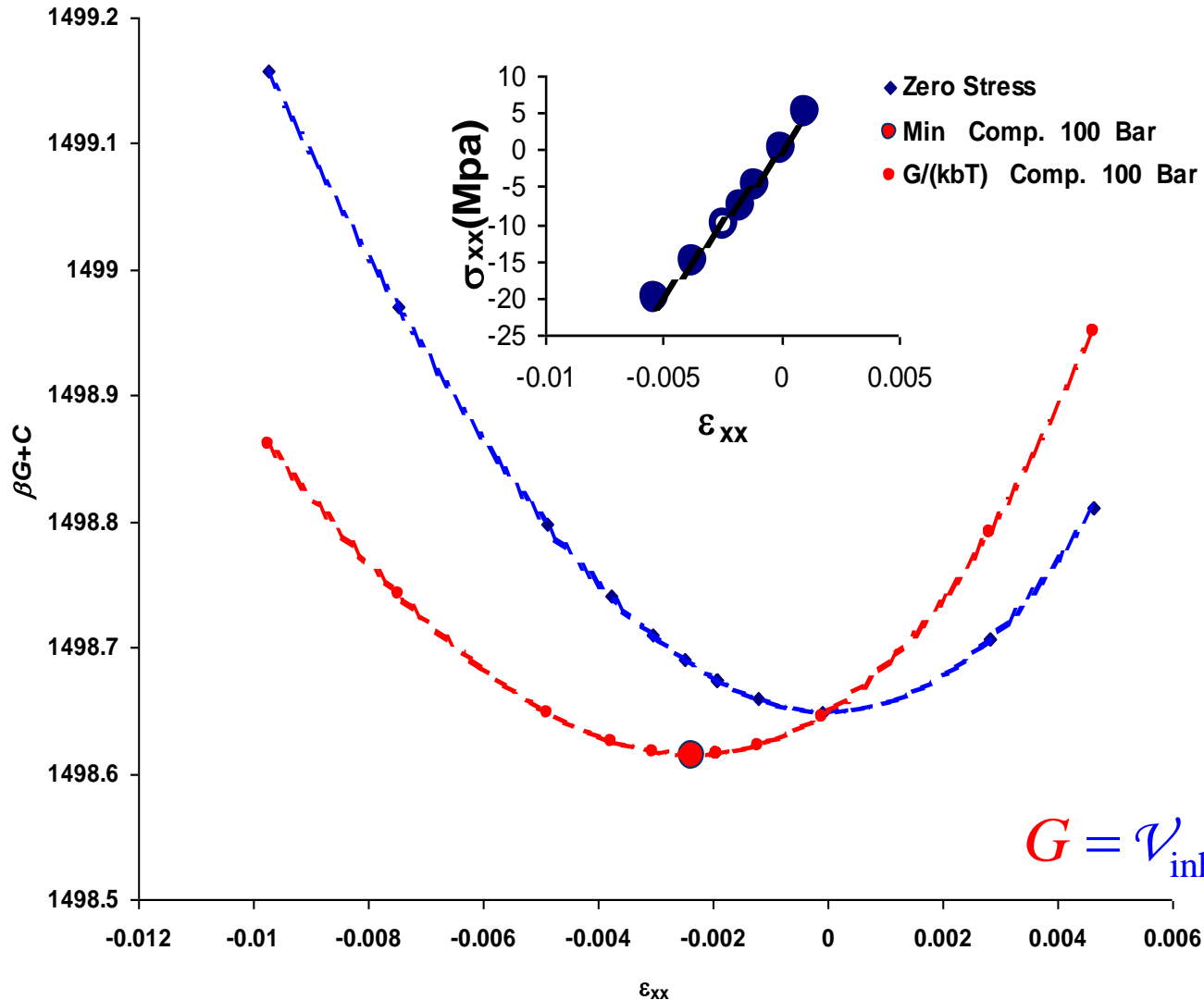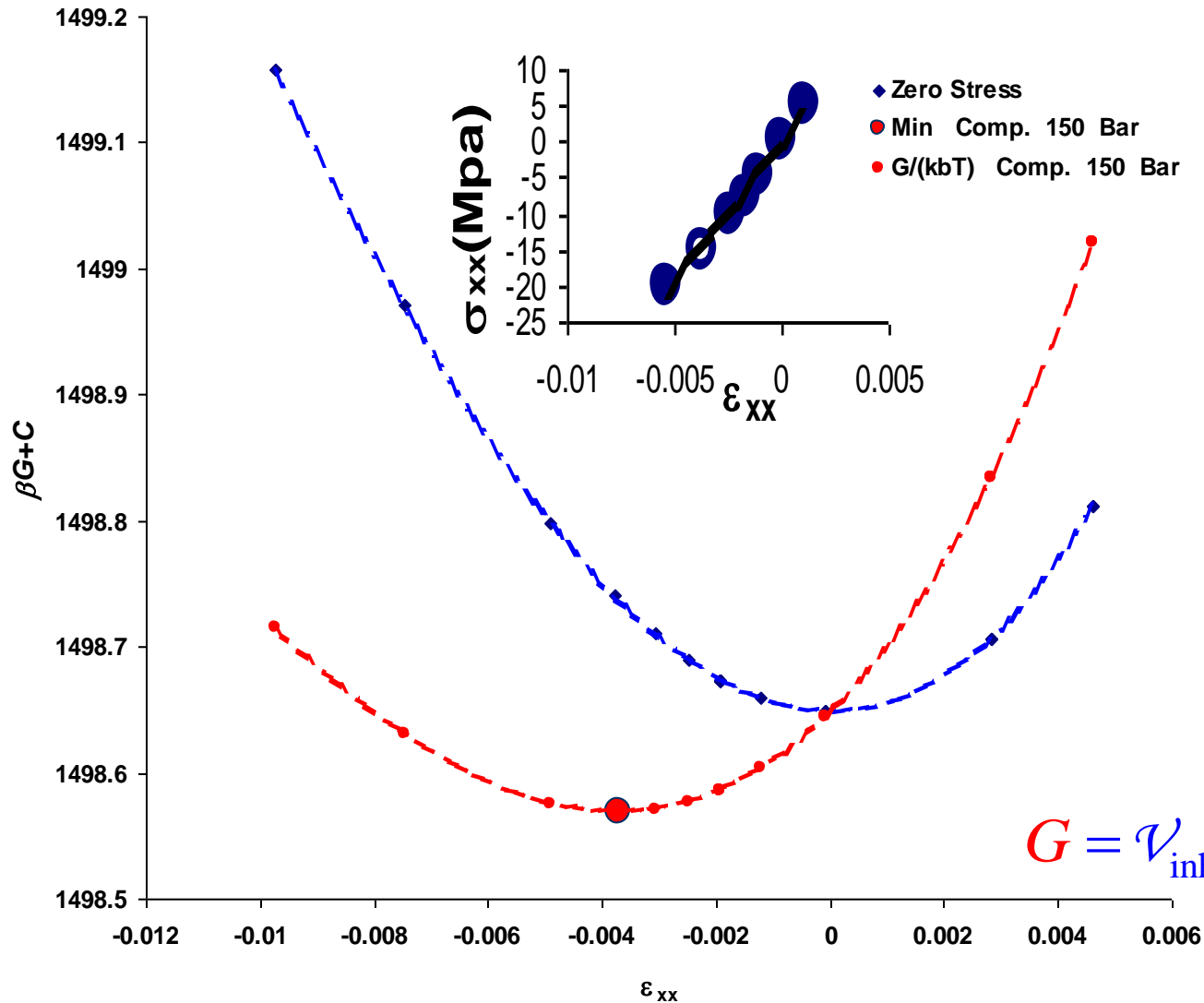(one inherent structure)
Atactic polystyrene
T=325 K, p= 1 bar

$$G = \mathcal{V}_{\text{inh}} + A_{\text{vib}} - V_{\text{o}} \sum_{ij} \sigma_{ij} \varepsilon_{ij}$$

ELASTIC RESPONSE: QHA

Computational experiment
of Uniaxial Deformation
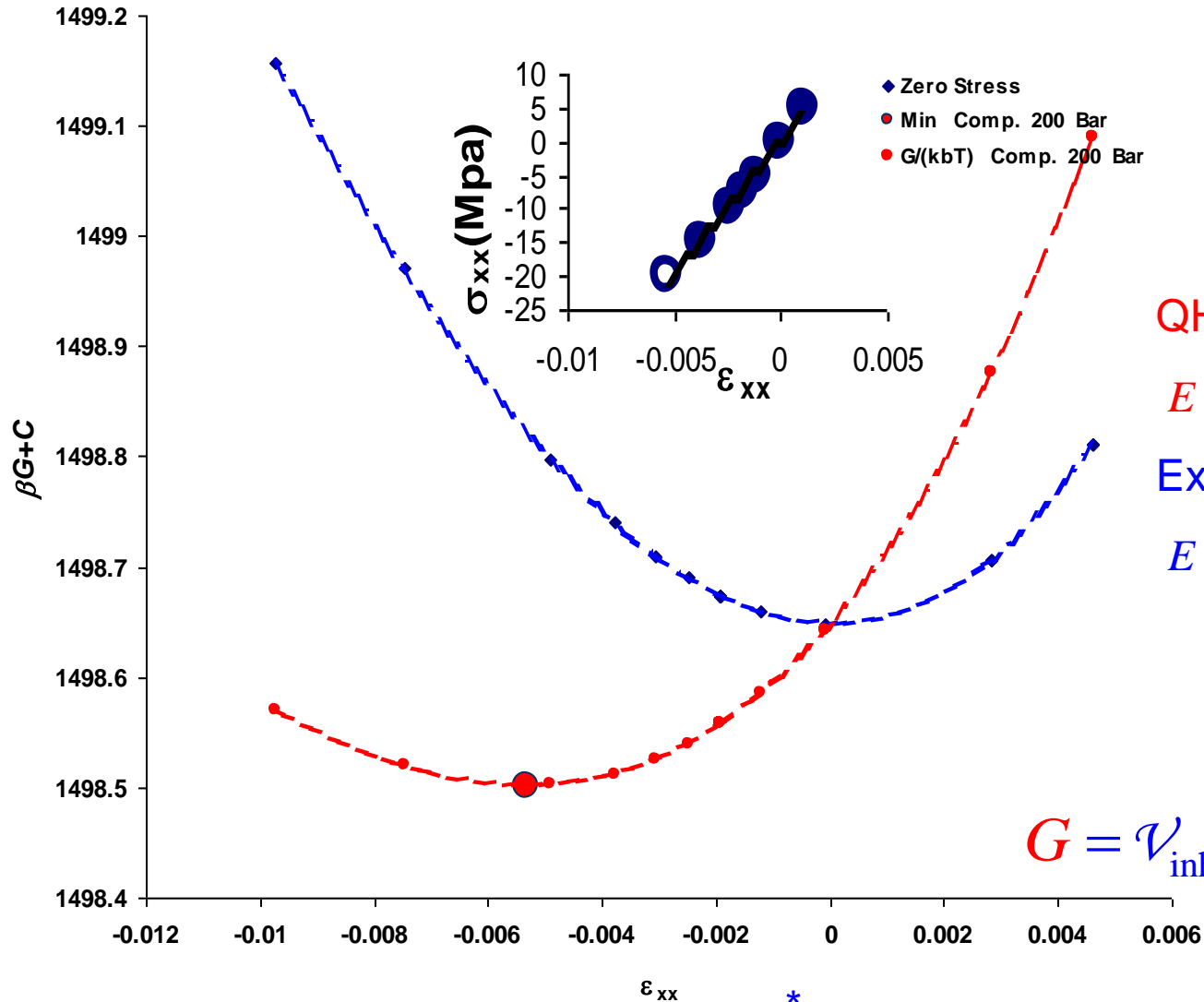(one inherent structure)
Atactic polystyrene
T=325 K, p= 1 bar

$$G = \mathcal{V}_{\text{inh}} + A_{\text{vib}} - V_{\text{o}} \sum_{ij} \sigma_{ij} \varepsilon_{ij}$$

Inset legend:
◆ Zero stress
● Min   Comp. 50 Bar
● G/(kbT)   Comp. 50 Bar

ELASTIC RESPONSE: QHA

Computational experiment
of Uniaxial Deformation
(one inherent structure)
Atactic polystyrene
T=325 K, p= 1 bar

$$G = \mathcal{V}_{\text{inh}} + A_{\text{vib}} - V_{\text{o}} \sum_{ij} \sigma_{ij} \varepsilon_{ij}$$

ELASTIC RESPONSE: QHA

Computational experiment
of Uniaxial Deformation
(one inherent structure)
Atactic polystyrene
T=325 K, p= 1 bar

$$G = \mathcal{V}_{\text{inh}} + A_{\text{vib}} - V_o \sum_{ij} \sigma_{ij} \varepsilon_{ij}$$

ELASTIC RESPONSE: QHA

Computational experiment
of Uniaxial Deformation
(one inherent structure)
Atactic polystyrene
T=325 K, p= 1 bar

$$G = \mathcal{V}_{\text{inh}} + A_{\text{vib}} - V_{\text{o}} \sum_{ij} \sigma_{ij} \varepsilon_{ij}$$

FRACTAL DIMENSION OF THE NETWORK OF INHERENT STRUCTURES (LJ MIXTURE)
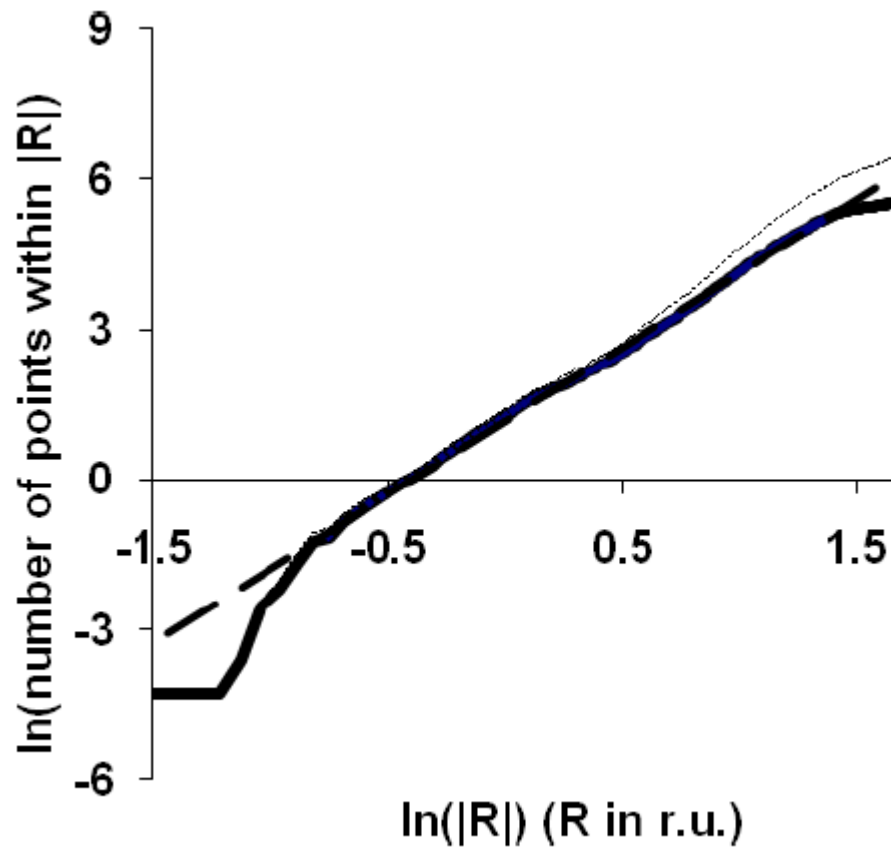
Correlation fractal dimension of the network of potential energy minima of a sampled metabasin and its neighbours.

Config. space is 3×641- dimensional.

Short- dashed line: inclusion of all possible pairs of inherent structures, irrespective of whether they are directly connected or not.

Continuous line: inclusion only of pairs that are directly connected by a transition sampled by our method.

Fractal dimension in both cases is slightly lower than 3 (~2.95).

Tsalikis, D., Lempesis, N., Boulougouris, G.C., DNT *J. Phys. Chem. B*, **114**, 7844 (2010).
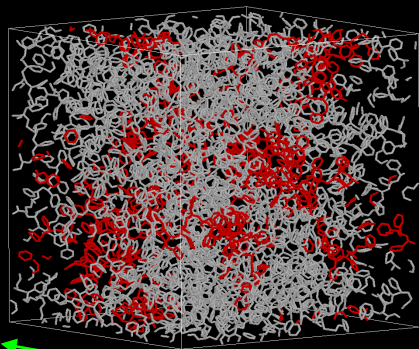
6.3 nm

Atomistic
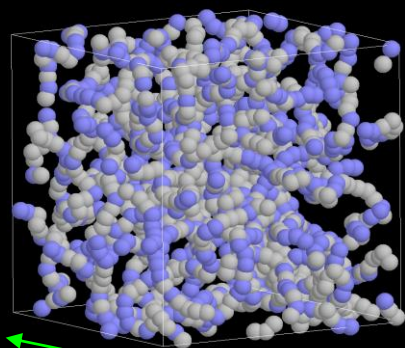
6.3 nm

Coarse-grained
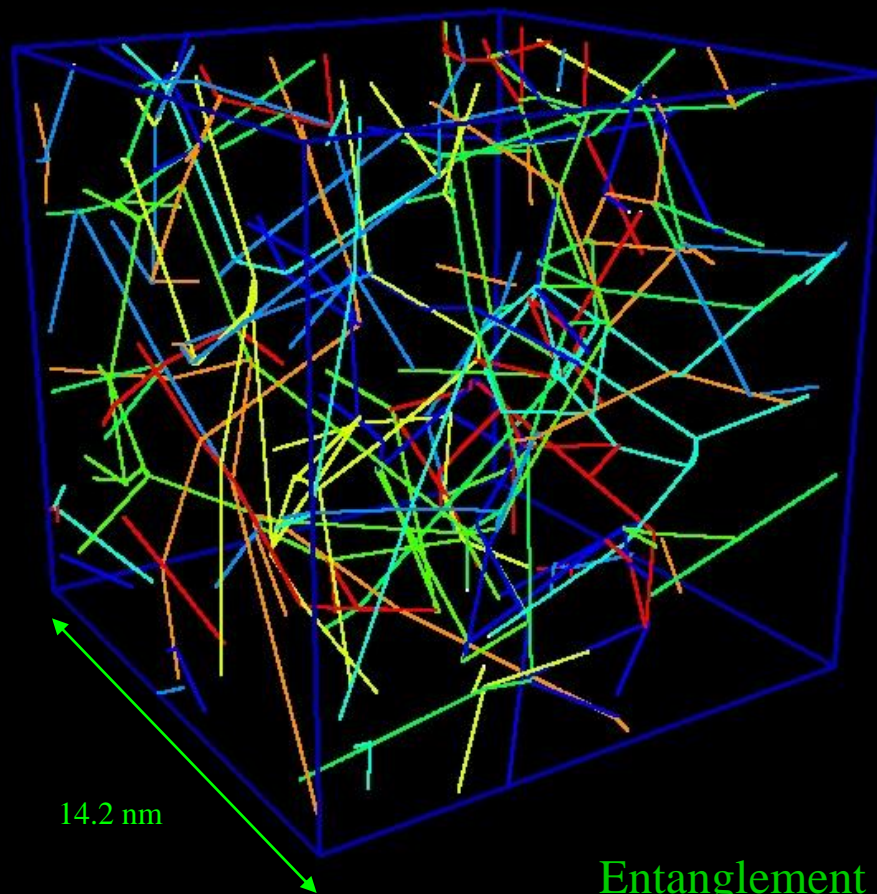
14.2 nm

Entanglement
network

ACKNOWLEDGMENTS

Sponsors