

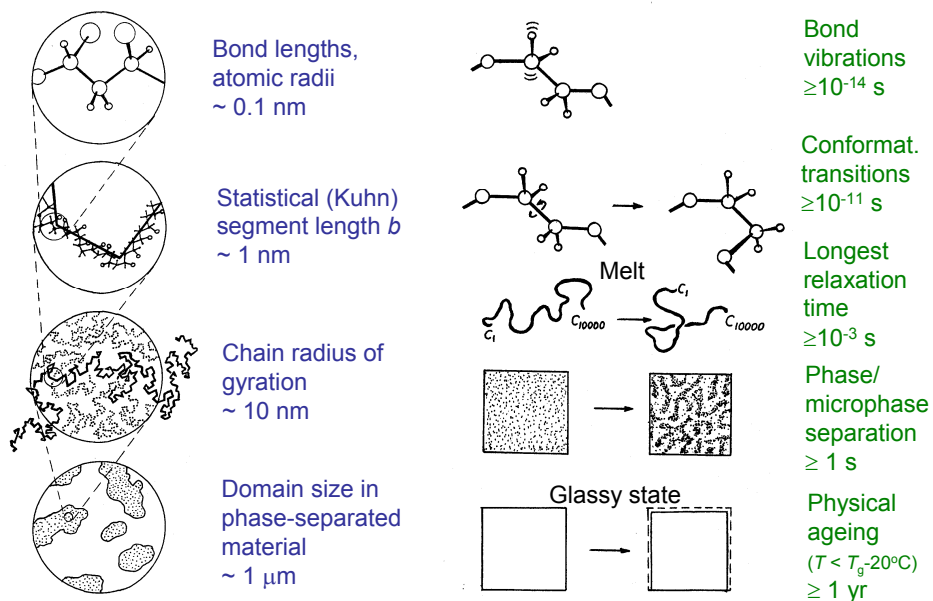
MOLECULAR SIMULATIONS OF SOFT MATTER: MEETING THE CHALLENGE OF LONG TIME SCALES

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Science and Engineering, National Technical University of
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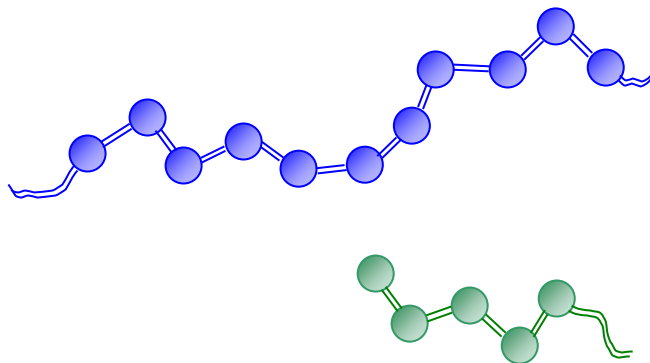
LENGTH AND TIME SCALES IN POLYMERS



OUTLINE

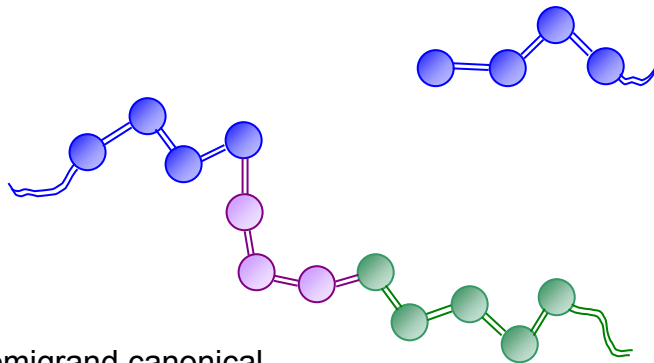
1. Equilibrating long-chain polymer melts with connectivity-altering Monte Carlo: short-chain branched polyethylene.
2. Coarse-graining via Iterative Boltzmann Inversion: atactic polystyrene melts.
3. Topological analysis of entanglements: polyethylene, poly(1,4-butadiene), atactic polystyrene, PET.
4. Invoking the energy landscape picture for glassy polymers: Volumetric properties and elastic constants in atactic polystyrene.
5. Relaxation as a sequence of transitions between basins in configuration space: DIMW and EROPHILE methods.
6. Concluding remarks.

CONNECTIVITY-ALTERING MONTE CARLO: END BRIDGING



P.V.K. Pant & DNT, *Macromolecules* **28**, 7224 (1995)

CONNECTIVITY-ALTERING MONTE CARLO: END BRIDGING



Semigrand canonical
ensemble $[N_{\text{ch}}nPT\mu^*]$

P.V.K. Pant & DNT, *Macromolecules* **28**, 7224 (1995)

COMPUTATIONAL STUDY OF SHORT-CHAIN BRANCHED POLYETHYLENE MELTS

Melts of short-chain branched polyethylene chains

Mean backbone length: 1000 C atoms

Branch length: 4 C atoms

Branches randomly placed along the backbone

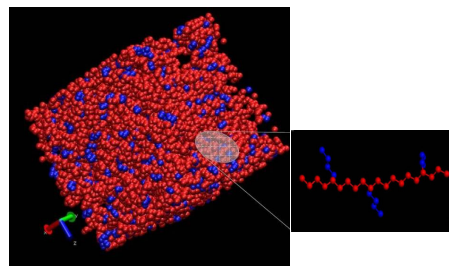
(Random copolymers of ethylene and 1-hexene)

0, 19, 46, 55, 100, 115 branches per 1000 backbone carbons

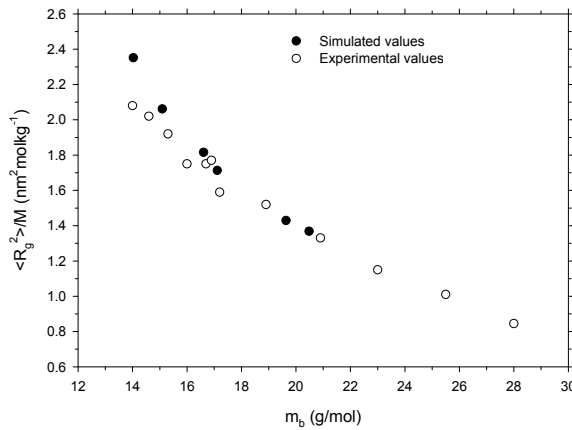
$T=450$ K, $p = 1$ atm

TraPPE force field: M.G. Martin,
J.I. Siepmann, *J. Phys. Chem.*
B. **103**, 4508 (1999)

Javier Ramos, Loukas Peristeras,
DNT, *Macromolecules* **40**, 9640
(2007)



CHAIN STIFFNESS AS A FUNCTION OF THE DEGREE OF BRANCHING



M : number average molar mass

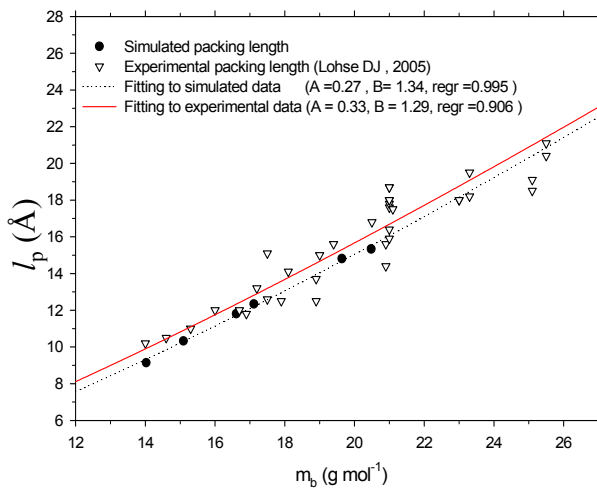
$\langle R_g^2 \rangle$: mean square radius of gyration

m_b : average molar mass per backbone bond

Experimental values: SANS, ethylene–1-butene copolymers
 D.J. Lohse *J. Macromol. Sci. C: Polym. Rev.* **45**, 289 (2005)

PACKING LENGTH AS A FUNCTION OF SCB

$T=450 \text{ K}, p = 1 \text{ atm}, 1000 \text{ backbone C/chain}$



Packing length l_p (\AA)

$$l_p = \frac{V_{\text{occ}}}{\langle R_g^2 \rangle} = \frac{M}{\rho N_A \langle R_g^2 \rangle}$$

Degree of branching

m_b : average molar mass per backbone bond (g/mol)

Empirical correlations

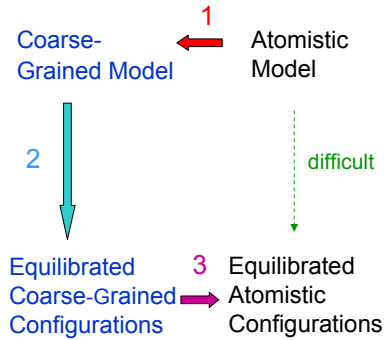
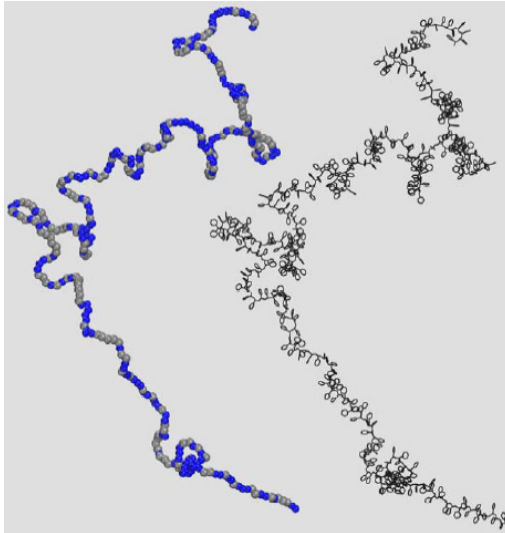
$$l_p = A m_b^B$$

$$M_e = 1.98 N_A \rho l_p^3$$

COARSE-GRAINING MOLECULAR MODELS: ATACTIC POLYSTYRENE

Iterative Boltzmann Inversion (IBI)

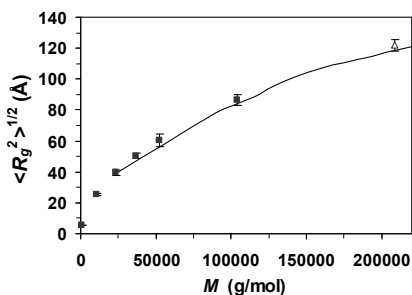
D. Reith, M. Pütz, and F. Müller-Plathe,
J. Comp. Chem. **24**, 1624 (2003).



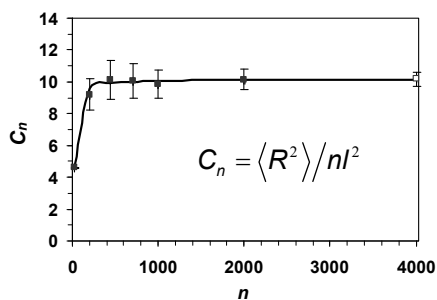
1. Coarse-graining (IBI)
2. Equilibration at coarse-grained level (using connectivity-altering MC)
3. Reverse-Mapping

COARSE-GRAINED SIMULATIONS OF MONODISPERSE aPS MELTS

$T=500$ K and 413 K, $p = 1$ bar
 chain length 9 to 2000 repeat units



Points: simulation
 line: SANS (Cotton et al., 1974)



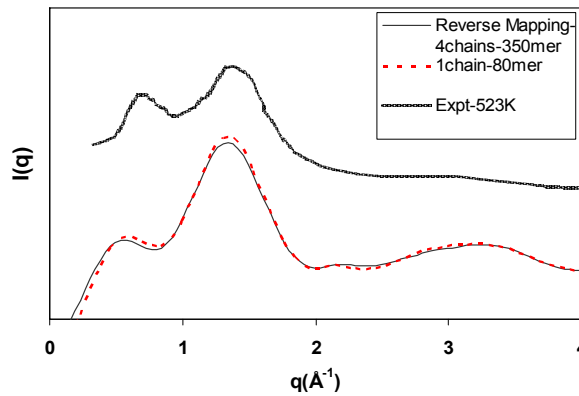
Points: simulation
 line: freely rotating chain model

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

REVERSE MAPPING TO ATOMISTIC LEVEL

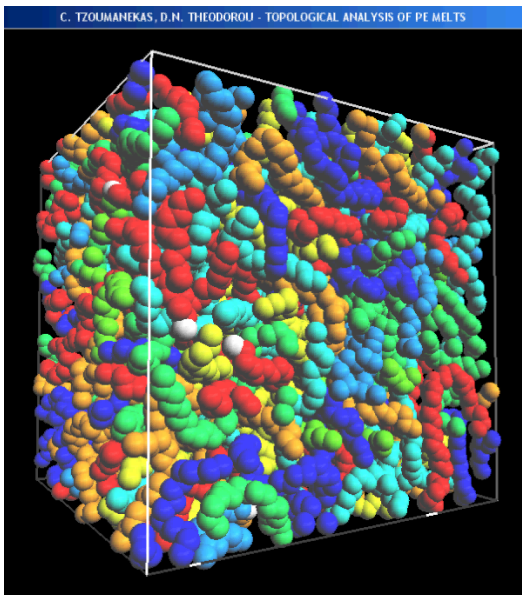
Restoration of atomistic detail and relaxation of local packing via a MC procedure employing local moves which preserve chirality and prevent adoption of unrealistic torsional states.

WAXS
pattern



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

REDUCTION OF MOLECULAR CONFIGURATIONS TO ENTANGLEMENT NETWORKS



CReta Algorithm

C. Tzoumanekas and DNT, *Macromolecules* **39**, 4592 (2006).

Example:

C_{1000} PE, 450 K, 1 atm

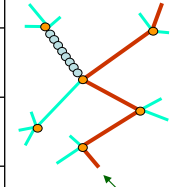
Similar strategies:

R. Everaers, S.K. Sukumaran, G.S. Grest, C. Svaneborg, A. Sivasubramanian, K. Kremer, *Science*, **303**, 823 (2004).

M. Kröger, *Comp. Phys. Comm.*, **168**, 209 (2005).

PRIMITIVE PATH NETWORKS – QUANTITATIVE ESTIMATES

	M (g/mol)	M_e (g/mol)	d (Å)	l_p (Å)
PE (450 K)	7000	1051 (860) ^α	38.4 (36.0) ^α	9.2 (10.1) ^α
PE (450 K)	14000	1037 (860) ^α	36.6 (36.0) ^α	9.9 (10.1) ^α
PB (413 K)	13500	2412 (2346) ^α	42.3 (43.0) ^α	15.5 (14.6) ^α
PET (450 K)	19230	1525 (1171-1450) ^α	33.5 (38.0-35.0) ^α	9.1 (10.6-11.9) ^α
aPS (500 K)	208300	12914 (13310-14780) ^α	75.8 (76.5) ^α	23.6 (23.7) ^α



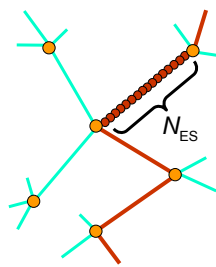
primitive path:
contour length L_{pp}
end-to-end dist. R

$$\text{Kuhn length of primitive path: } d = \frac{\langle R^2 \rangle}{\langle L_{pp} \rangle}, \quad M_e = M \frac{\langle R^2 \rangle}{\langle L_{pp} \rangle^2}$$

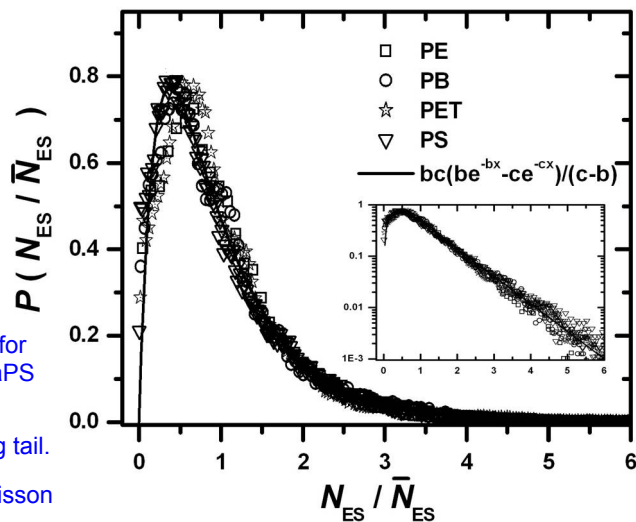
$$\text{Packing length } l_p = \frac{M}{\rho N_A \langle R_g^2 \rangle}, \quad M_e = 1.98 N_A \rho l_p^3$$

^αexp. M_e (from plateau modulus), Fetters et al., *Macromolecules* **24**, 4639 (1994)

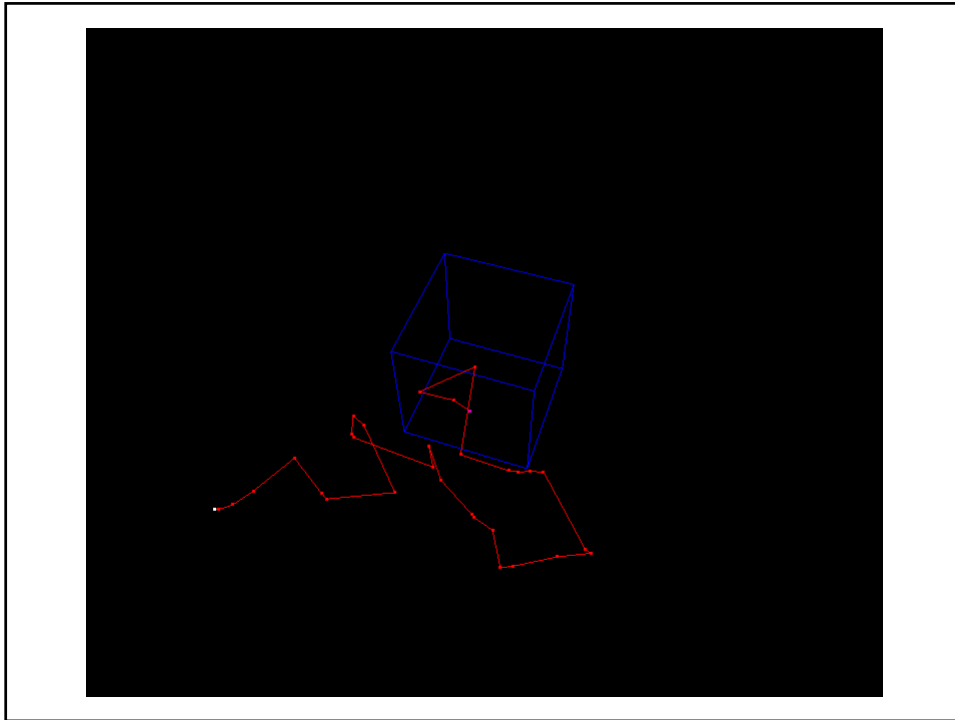
DISTRIBUTION OF STRAND LENGTHS BETWEEN ENTANGLEMENTS



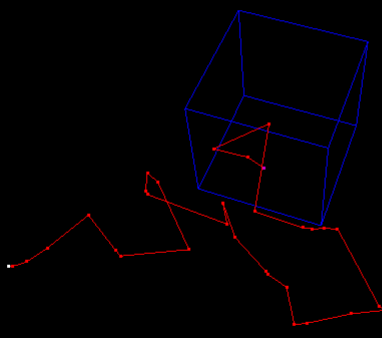
N_{ES} : number of monomers between successive entanglements



- Reduced distributions for PE, cis-1,4 PB, PET, aPS superposable.
- Exponentially decaying tail.
- Convolution of two Poisson processes.

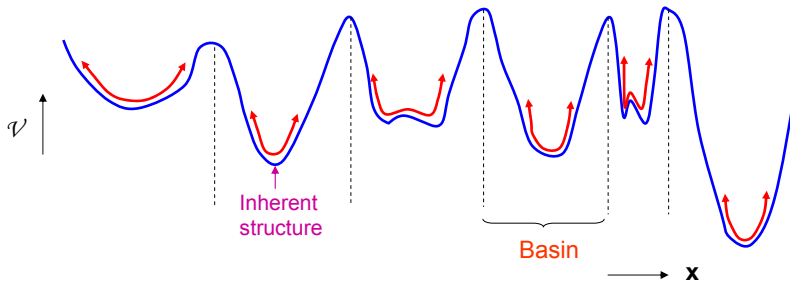


C_{1000} linear PE melt: 150 ns at 450 K, 1 bar



Connection with slip-link simulations of rheological properties, e.g.
Masubuchi, Y.; Takimoto, J.-I.; Koyama, K.; Ianniruberto, G.; Marrucci, G.; Greco, F. *J. Chem. Phys.* **2001**, *115*, 4387-4394.

ENERGY LANDSCAPE PICTURE OF A GLASS



Configuration fluctuating in the neighbourhood of local energy minima:

“Inherent structures” : F. H. Stillinger, *Science* **267**, 1935 (1995).

See also work by D. Wales, A. Heuer, W. Kob, S. Yip, P.G. Debenedetti, D.J. Lacks, T. Keyes, M. Utz, T.M. Truskett, P.Mott, 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.

VOLUMETRIC PROPERTIES AND ELASTIC CONSTANTS OF GLASSY MATERIALS

Configuration trapped in the vicinity of a local minimum of the energy.

Under given stress tensor σ , system will adopt that spatial extent which minimizes

$$G = V'_{inh} + A_{vib} - V_o \sum_{ij} \sigma_{ij} \epsilon_{ij}$$

V'_{inh} : Potential energy at the minimum (inherent structure).

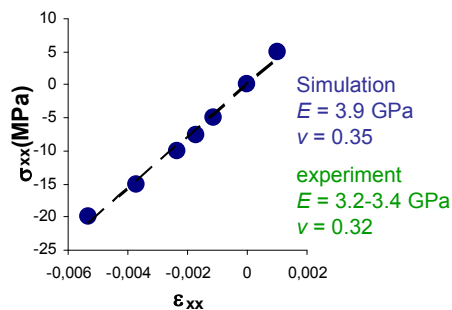
A_{vib} : Vibrational free energy (from normal mode frequencies-quasiharmonic approximation).

ϵ : Strain tensor.

Glassy atactic polystyrene

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

Uniaxial compression-tension



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

D. Tsalikis, G. Boulougouris, DNT

PHYSICAL AGEING: 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 among basins $P_i(t)$ 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.

Master Equation:

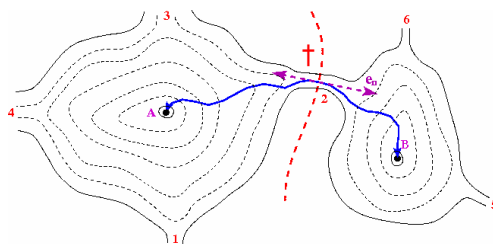
$$\frac{dP_i(t)}{dt} = \sum_{j \neq i} P_j(t) k_{j \rightarrow i} - P_i(t) \sum_{j \neq i} k_{i \rightarrow j}$$

transition rate constant from basin i to basin j
↓

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

vector of basin probabilities
rate constant matrix

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).

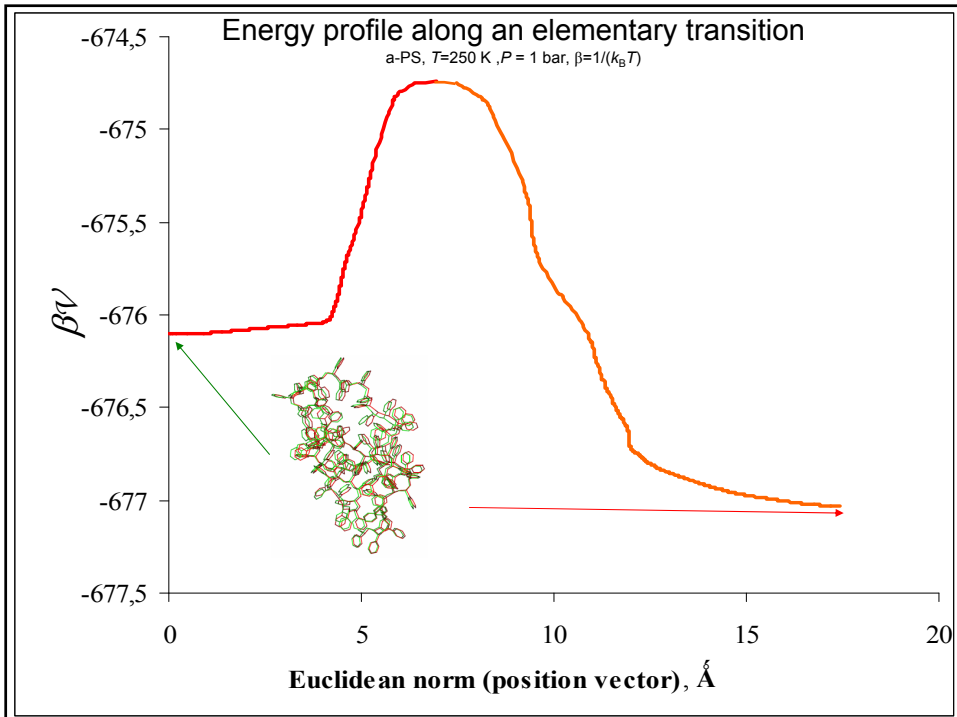
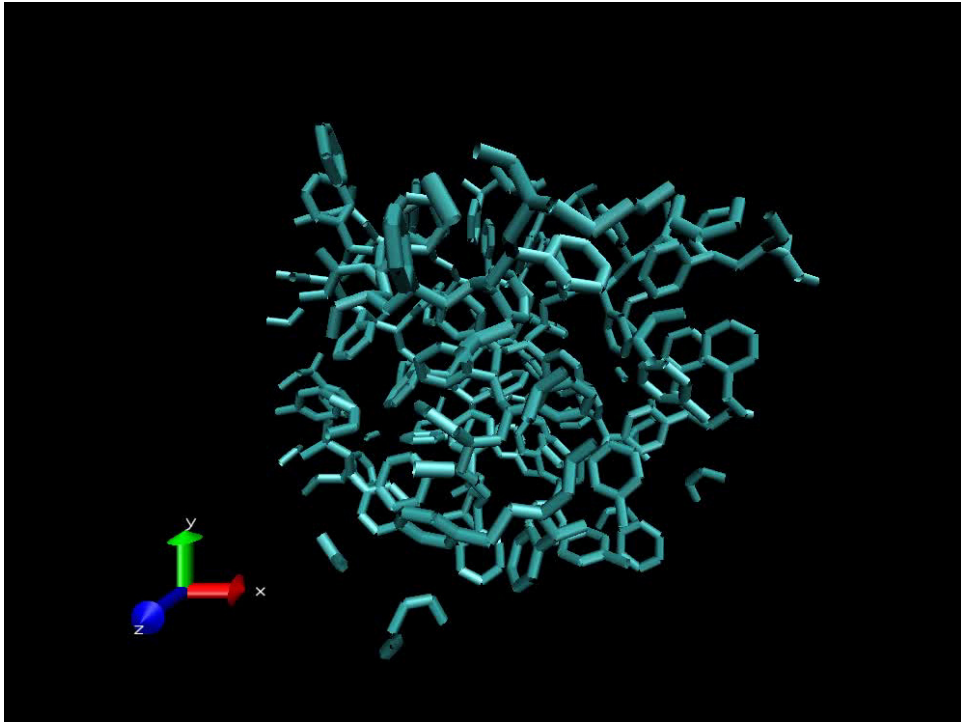
Through each saddle point, determine **reaction path**

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

- First step on either side in the direction of the eigenvector corresponding to the negative eigenvalue of the Hessian: $d\mathbf{x} = \pm \mathbf{e}_n d\tau$
- Subsequent steps in steepest descent direction: $d\mathbf{x} = -\nabla_{\mathbf{x}} \psi d\tau$

Estimate transition rate constants via Transition State Theory

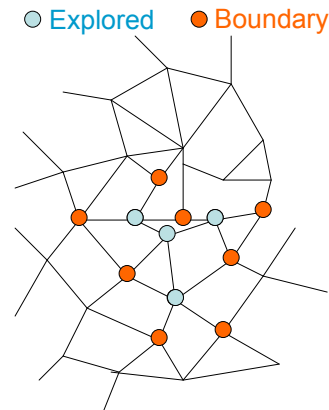
Quasi-harmonic approximation $k_{A \rightarrow B}^{TST} = \frac{k_B T}{h} \exp\left(-\frac{G^\ddagger - G_A}{k_B T}\right)$



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:

$$\frac{\partial P_n}{\partial t} = \sum_{m \in E} P_m k_{m \rightarrow n} - P_n \sum_{m \in E \cup B} k_{n \rightarrow m}, \quad \forall n \in E$$
- 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 neighbours of newly added state.



Analytical solution of master equation, with atomistically calculated rate constants, in a network of states that is progressively augmented “on the fly”

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

a-PS, $T=250\text{K}$, $\rho=0.951\text{g/cm}^3$: EVOLUTION OF THE TIME-DEPENDENT “HELMHOLTZ ENERGY” UNDER CONSTANT VOLUME

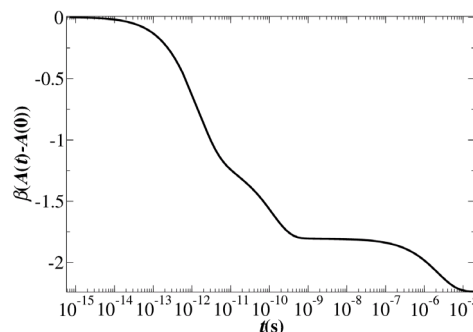
$$A(t) = \sum_i P_i(t) A_i + k_B T \sum_i P_i(t) \ln P_i(t)$$

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

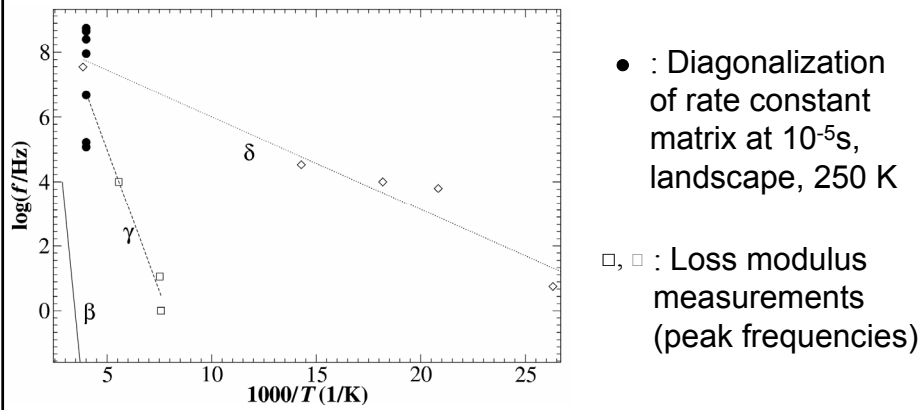
2880 saddle point calculations



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

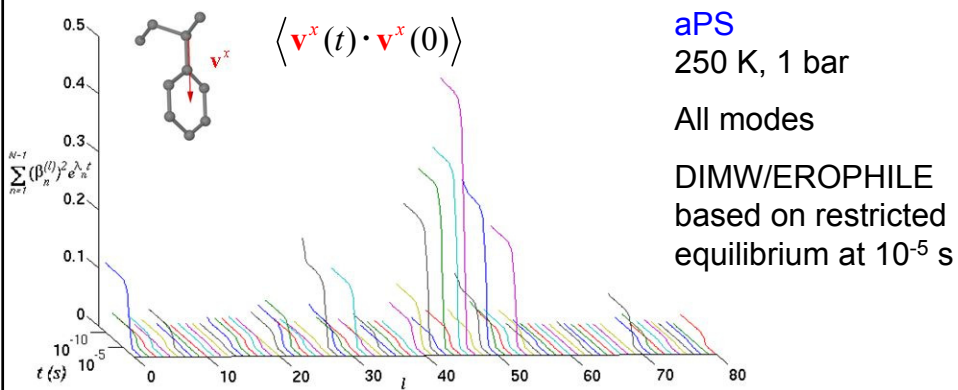
G. Boulougouris and DNT, *J. Chem. Phys.* **130**, 044905 (2009)

CHARACTERISTIC FREQUENCIES FOR PHYSICAL AGEING



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

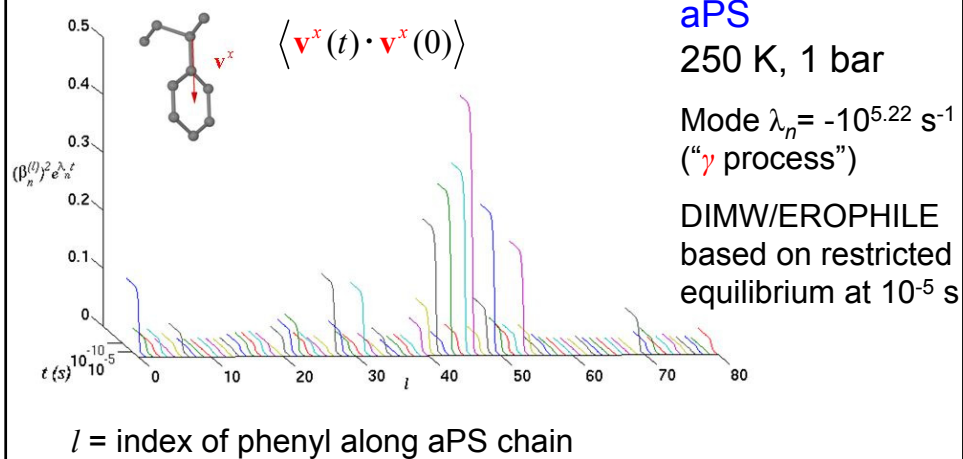
ORIENTATIONAL DECORRELATION OF PHENYL STEMS



l = index of phenyl along aPS chain

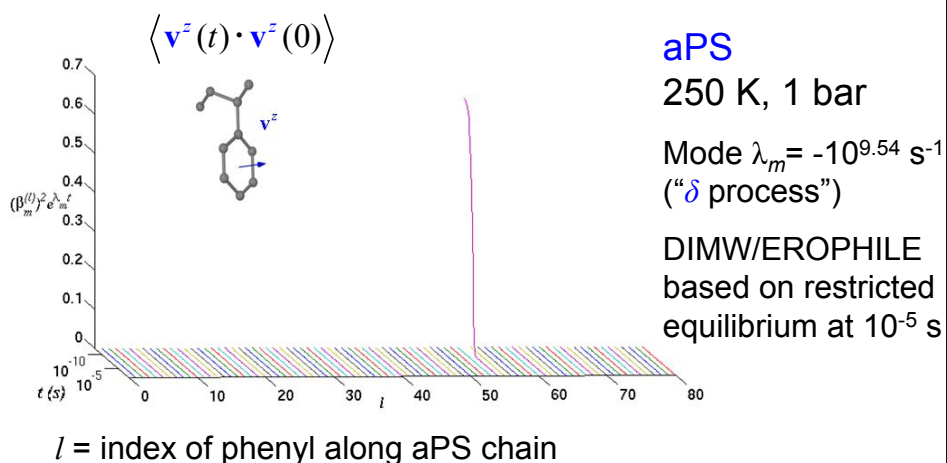
G. Boulougouris and DNT, *J. Chem. Phys.* **130**, 044905 (2009)

ORIENTATIONAL DECORRELATION OF PHENYL STEMS



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

ORIENTATIONAL DECORRELATION OF VECTORS NORMAL TO PHENYLS



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

SUMMARY

- Multiplicity of length and time scales calls for hierarchical approaches in polymer modelling and simulation, based on systematic coarse-graining of the model representation.
- Connectivity-altering Monte Carlo enables the equilibration of long-chain melts at all length scales. For short-chain branched polyethylene, it captures changes in chain dimensions and packing length with branching.
- Combination of connectivity-altering MC with coarse-graining via Iterative Boltzmann Inversion can greatly enhance equilibration efficiency.
- Topological analysis reduces atomistic configurations to entanglement networks, useful in mesoscopic simulations of deformation and flow.
- In a polymer glass (atactic PS), quenched averaging of in-basin properties computed via a quasiharmonic approximation yields reasonable estimates of elastic constants.
- DIMW & EROPHILE methods, which track temporal evolution as a succession of transitions between energy basins in multidimensional configuration space, are promising for predicting and interpreting relaxation in the glassy state.

ACKNOWLEDGEMENTS

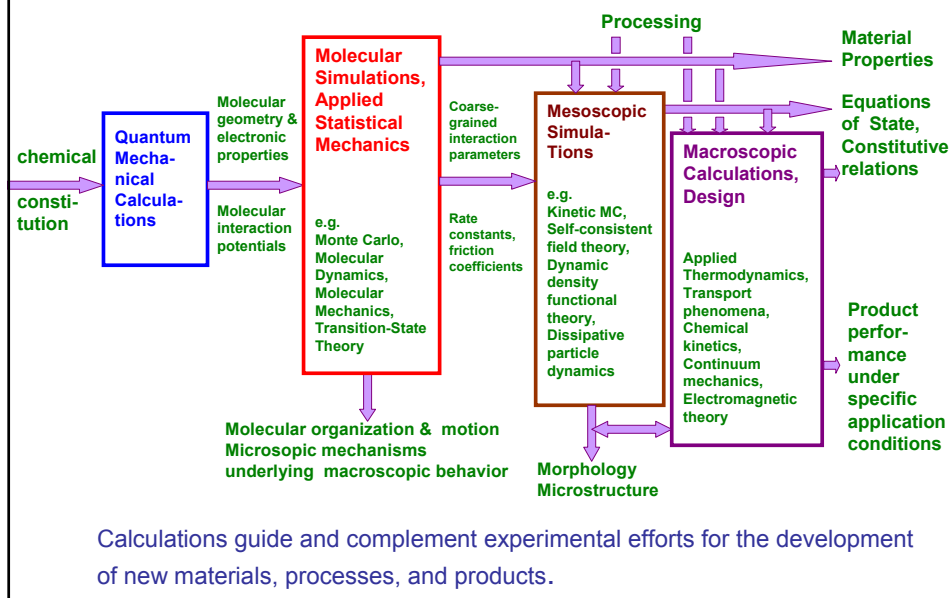
Collaborators

Mr. Stefanos Anogiannakis
Dr. George Boulougouris
Dr. Javier Ramos
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Dr. Dimitris Tsalikis
Dr. Christos Tzoumanekas
Dr. Pino Milano (Salerno)
Prof. Florian Müller-Plathe (Darmstadt)

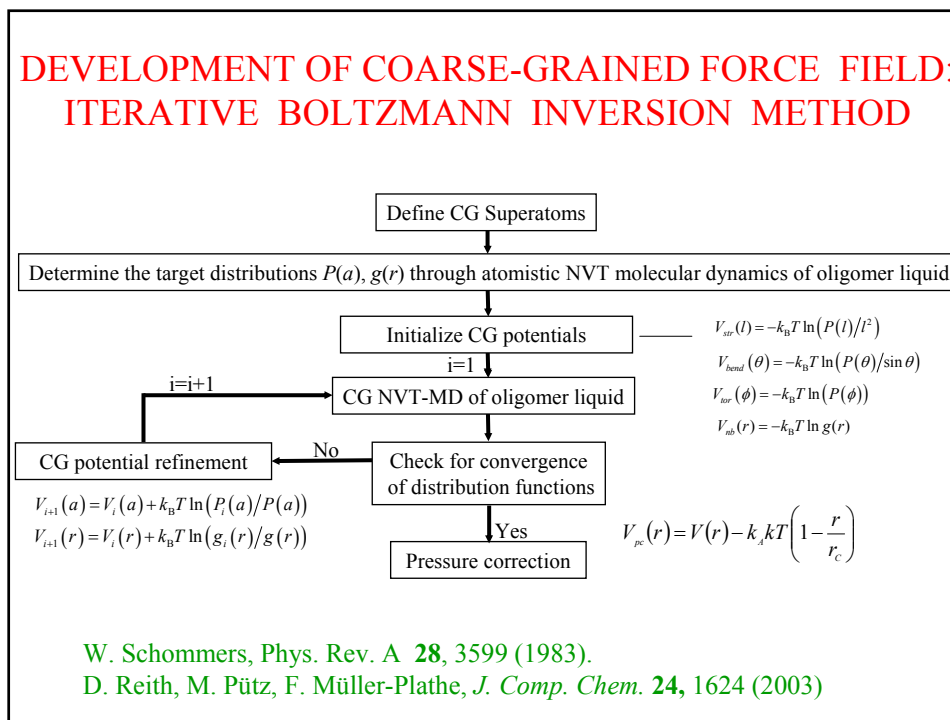
Sponsors

DG12 of the European
Commission, project
SIMGLASS
Dutch Polymer Institute
Mitsui Chemicals
Scienomics SARL
Ministerio de Educacion y
Ciencia, ES
Greek GSRT, PENED and
ENTER programmes

COMPUTATIONAL POLYMER SCIENCE AND ENGINEERING



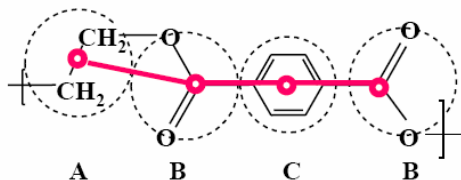
DEVELOPMENT OF COARSE-GRAINED FORCE FIELD: ITERATIVE BOLTZMANN INVERSION METHOD



COARSE-GRAINING: ITERATIVE BOLTZMANN INVERSION OF DISTRIBUTION FUNCTIONS

D. Reith, M. Pütz, and F. Müller-Plathe, *J. Comp. Chem.* **24**, 1624 (2003).

Poly(ethylene terephthalate)



United Atom Model
42 d.o.f./monomer



Coarse-Grained Model
9 d.o.f./monomer

6 bond types
7 angle types
6 torsion types
1 out of plane type
20 unique non-bonded pairs

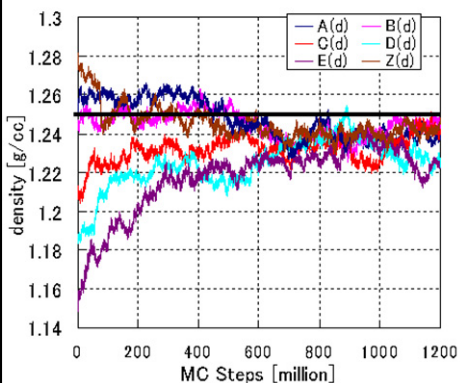
2 bonds A-B, B-B
2 angles A-B-B, B-A-B
2 torsions A-B-B-A, B-A-B-B
6 unique non-bonded pairs

K. Kamio, K. Moorthi, DNT, *Macromolecules* **40**, 710 (2007).

PET PROPERTIES FROM COARSE-GRAINED CONNECTIVITY-ALTERING SIMULATIONS

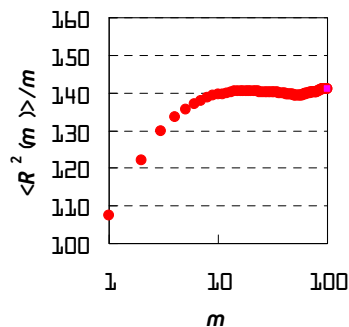
1 atm, 450 K, DP=100

Evolution of density



CG MC: $\rho = 1.24 \pm 0.01 \text{ g/cm}^3$.
Experiment: $\rho = 1.25 \text{ g/cm}^3$

Subchain end-to-end distances



Asymptotic value $\langle R^2(m) \rangle / m = 140 \text{ \AA}^2$, or
 $\langle R^2 \rangle / M = 0.68 \text{ \AA}^2 / (\text{g mol}^{-1})$.
Neutron scattering [Guilmer et al. (1986)]
 $\langle R^2 \rangle / M = 0.61\text{-}0.69 \text{ \AA}^2 / (\text{g mol}^{-1})$.

MODEL AND SIMULATION METHODS

Binary mixture of A (80%) and B(20%) Lennard-Jones spheres.

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

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:

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

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

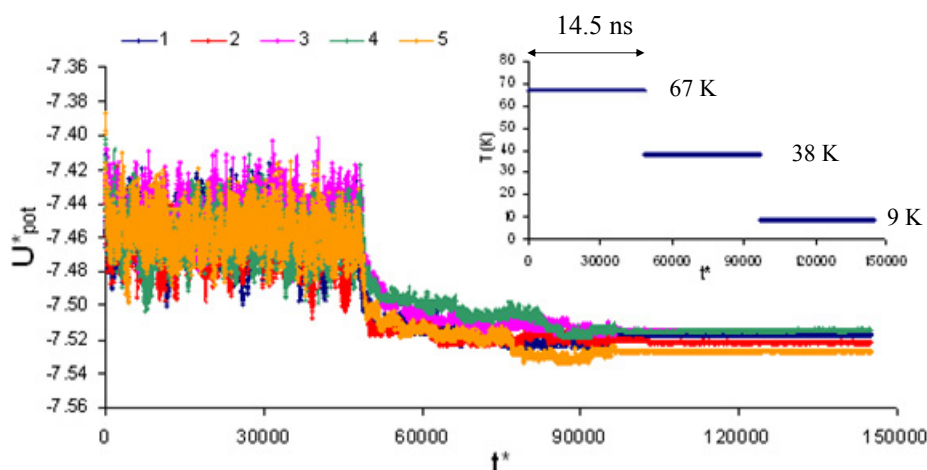
Canonical (NVT) molecular dynamics (MD) simulations at constant density $1.1908 \sigma_{AA}^{-3}$. $N=641$ atoms total.

Nosé-Hoover thermostat, Velocity Verlet algorithm.

Integration time step 1fs.

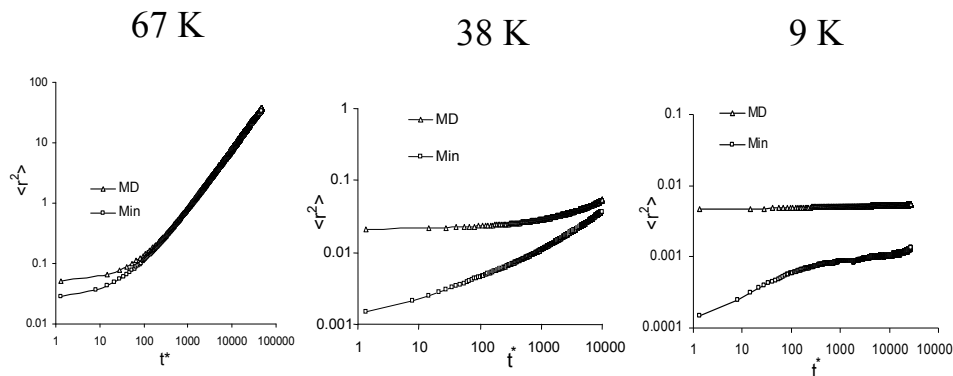
Potential energy minimizations with conjugate gradient algorithm.

STEPWISE COOLING: INHERENT STRUCTURE ENERGIES



Units: Energy $\epsilon_{AA} = 0.998 \text{ kJ/mol}$, time $[m_A \sigma_{AA}^2 / (48 \epsilon_{AA})]^{1/2} = 3.1 \times 10^{-13} \text{ s}$

MEAN SQUARE DISPLACEMENT OF A ATOMS



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

Long-time **diffusive motion** in the liquid very well captured by inherent structure trajectory.

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

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: $P(t) = 1 - \exp[-H(t)]$

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

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 : $t_1 \leq t_2 \leq \dots \leq t_n$

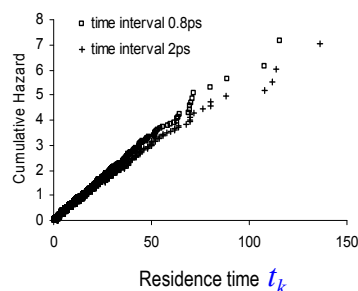
Estimate cumulative hazard $\hat{H}(t_k)$ corresponding to residence time t_k :

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

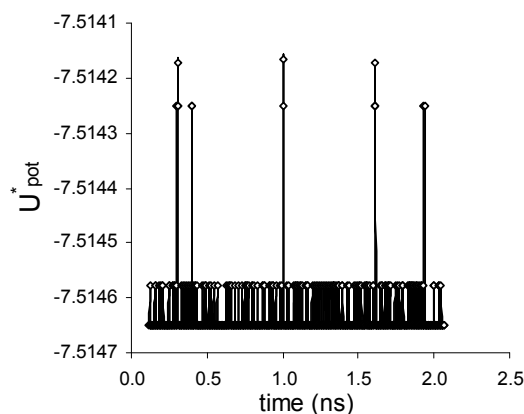
Linear plot $\hat{H}(t_k)$ going through the origin indicates a Poisson process.

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

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

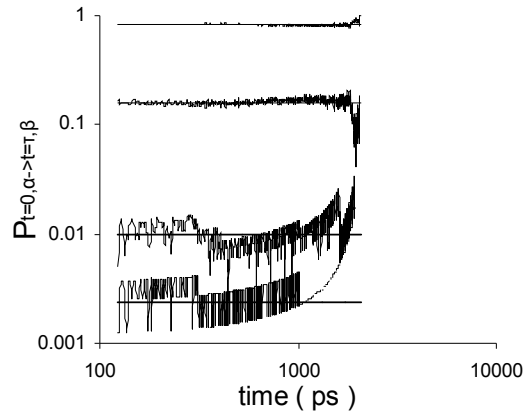


T=9K: INHERENT STRUCTURE TRAJECTORY



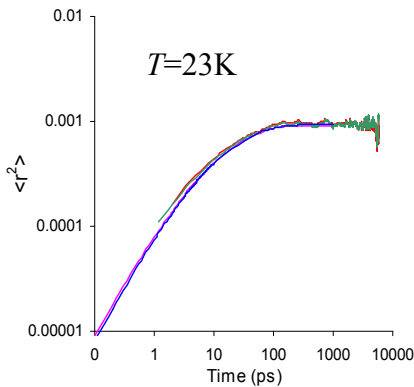
Tsalikis, D., Lempesis, N., Boulougouris, G.C., *DNT J. Phys. Chem. B* **112**, 10619 (2008)

T=9K: BASIN PROBABILITIES



Fluctuating lines: Direct calculation from MD, energy minimization.
 Horizontal lines: Based on $k_{\beta \rightarrow \gamma}$, solution of the Master Equation.

MEAN SQUARE ATOMIC DISPLACEMENT BASED ON INHERENT STRUCTURES



Blue line: Poisson process model, minimizations every 2ps

Purple line: Poisson process model, minimizations every 1.2ps

Red line: direct calculation from MD, minimizations every 2ps

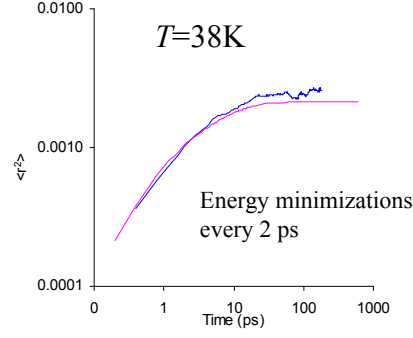
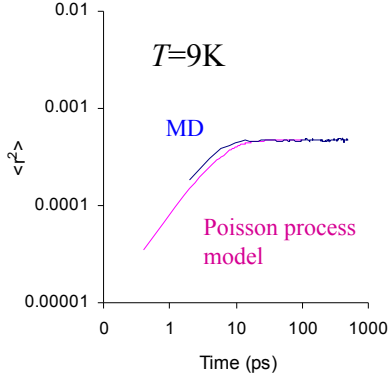
Green line: direct calculation from MD, minimizations every 1.2ps

position of atom i in
inherent structure α

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

$P_{t=0, \alpha \rightarrow t=\tau, \beta}$ from solution to the Master Equation.

MEAN SQUARE ATOMIC DISPLACEMENT BASED ON INHERENT STRUCTURES



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

$P_{t=0, \alpha \rightarrow t=\tau, \beta}$ from solution to the Master Equation.

RECONSTRUCTING THE FULL MEAN SQUARE DISPLACEMENT OF ATOMS

Tsalikis, D., Lempesis, N., Boulougouris, G.C., DNT *J. Phys. Chem. B* **112**, 10628 (2008)

Poisson process model:

Term 1: MSD Inherent Structures
(inter-basin contribution)

$$\langle (\mathbf{r}_i(\tau) - \mathbf{r}_i(0))^2 \rangle = \sum_{\alpha=1}^n P_{\alpha}(0) \sum_{\beta=1}^n P_{t=0, \alpha \rightarrow t=\tau, \beta} (\mathbf{r}_{i,\beta}^{\min} - \mathbf{r}_{i,\alpha}^{\min})^2 + \text{Term 2: Intra-basin Displacement (final = original minimum)}$$

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

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

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

RECONSTRUCTING THE FULL MEAN SQUARE DISPLACEMENT OF ATOMS

Tsalikis, D., Lempesis, N., Boulougouris, G.C., *DNT J. Phys. Chem. B* **112**, 10628 (2008)

Information needed for reconstruction:

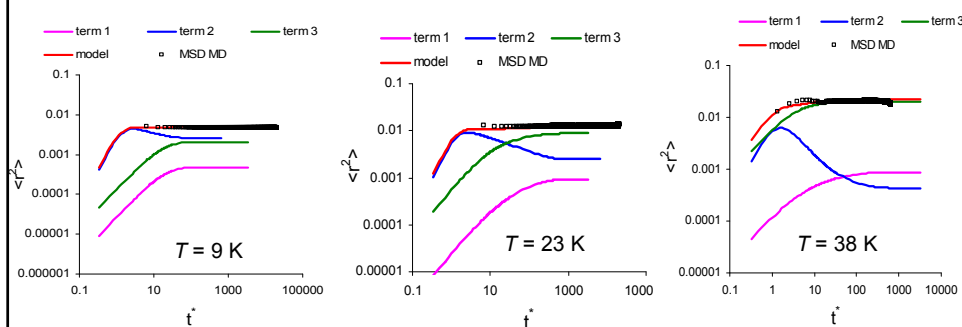
Rate constants $k_{\beta \rightarrow \gamma}$ describing transitions between any pair of connected basins of the system.

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

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

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

RECONSTRUCTION OF THE FULL MEAN SQUARE DISPLACEMENT OF ATOMS



Term 1: Interbasin diffusion 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)

CONCLUSIONS

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). This provides a solid foundation for DIMW.

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.

ACKNOWLEDGMENTS

03EΔ375 research project, implemented within the framework of the Reinforcement Programme Human Research Manpower (PENED) and cofinanced by Greek National and Community Funds (20% from the Greek Ministry of Development – General Secretariat of Research and Technology and 80% from E.U.-European Social Fund.

Senate Committee on Basic Research of the National Technical University of Athens in the form of a PEVE 2006 “Karathéodory” program

Scienomics SARL.

IN-BASIN MOTION: QUASI-HARMONIC APPROXIMATION

- Taylor expansion of the energy around the minimum

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

Mass-weighted coordinates
↓

- 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

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

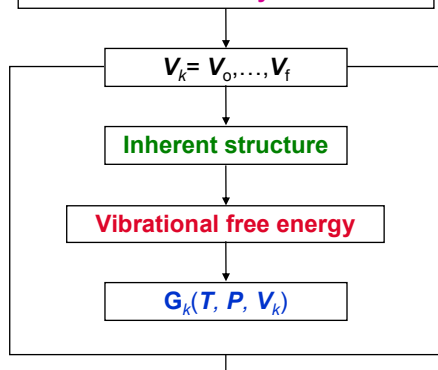
- Vibrational free energy

$$A_{\text{vib}} = -k_B T \ln \left(\prod_i q_i^{\text{vib}} \right)$$

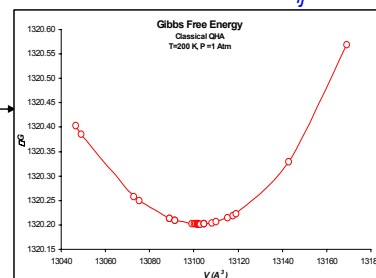
$\mathcal{V}(\mathbf{x}_o) = \mathcal{V}_{\text{inh}}$ and ω_i are functions of the spatial extent of the system.

GIBBS ENERGY MINIMIZATION OF A BASIN UNDER GIVEN STRESS STATE

Quench from melt by classical MD



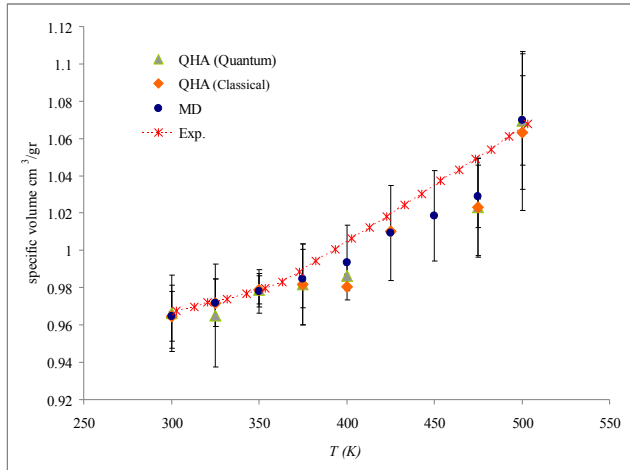
$$G = \mathcal{V}_{\text{inh}} + A_{\text{vib}} - V_o \sum_{ij} \sigma_{ij} \epsilon_{ij}$$



Atactic polystyrene
modified A.Lyulin et al. (2003) model
isotropic dilatation/contraction

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

VOLUMETRIC BEHAVIOUR: QHA vs. MD



Atactic polystyrene,
modified A.Lyulin*
model

Pressure 1 bar
MD cooling rate
6.25 K/ns

641 united atoms

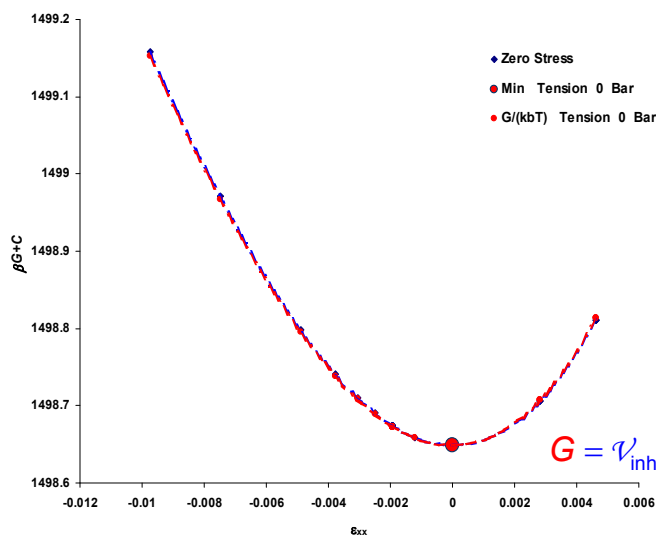
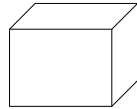
Averages over 5
inherent structures

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

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

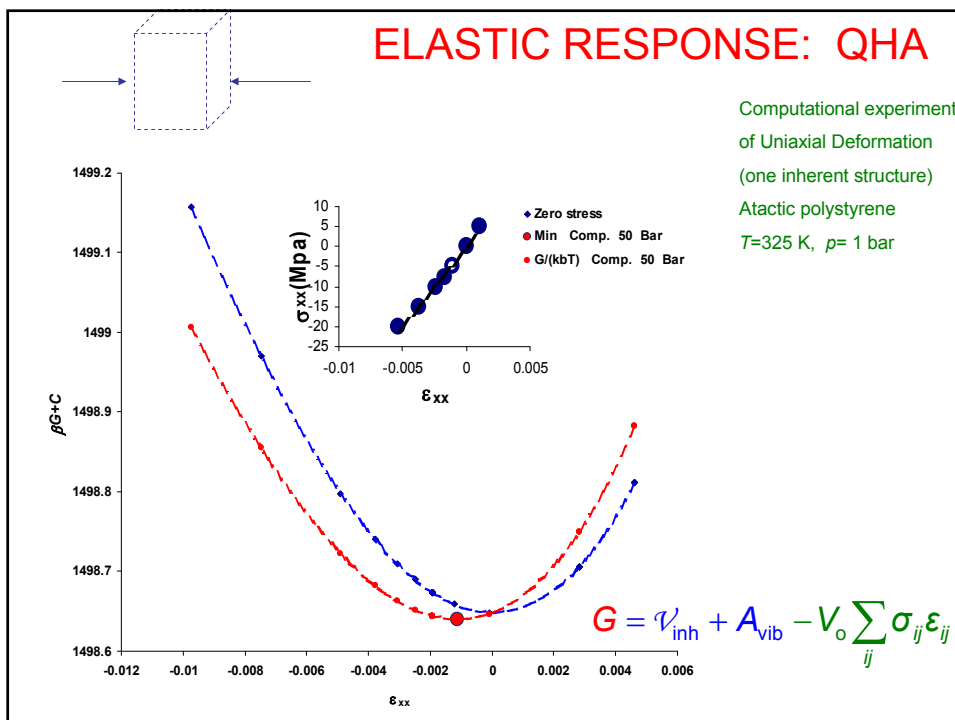
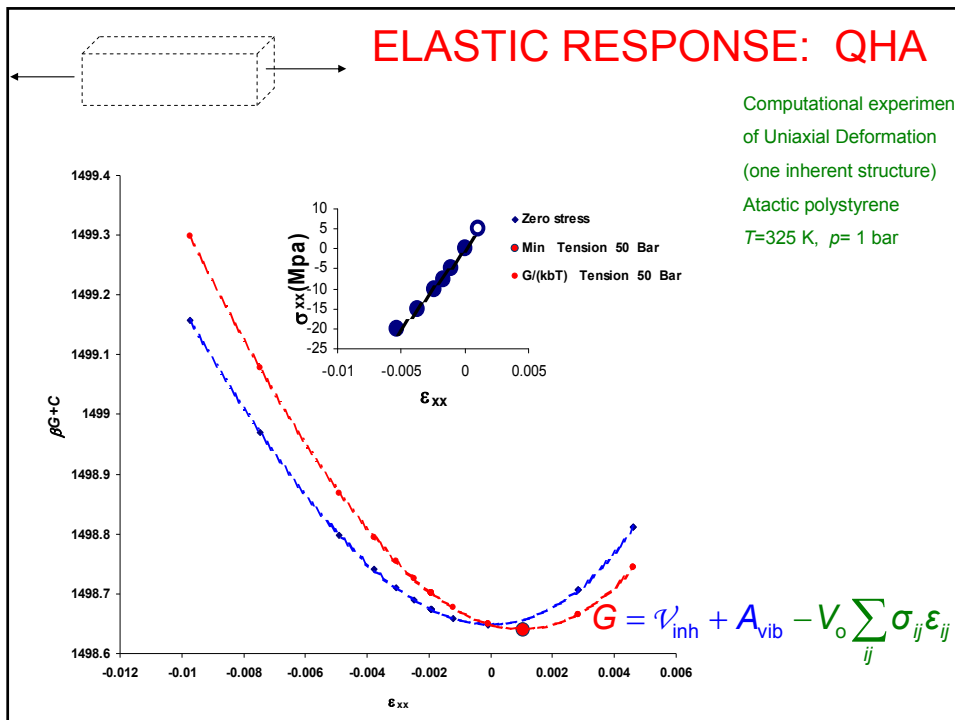
Exp: P. Zoller, D.J. Walsh (1995). *Standard Pressure-Volume-Temperature Data for Polymers*. Technomic: Lancaster.

ELASTIC RESPONSE: QHA



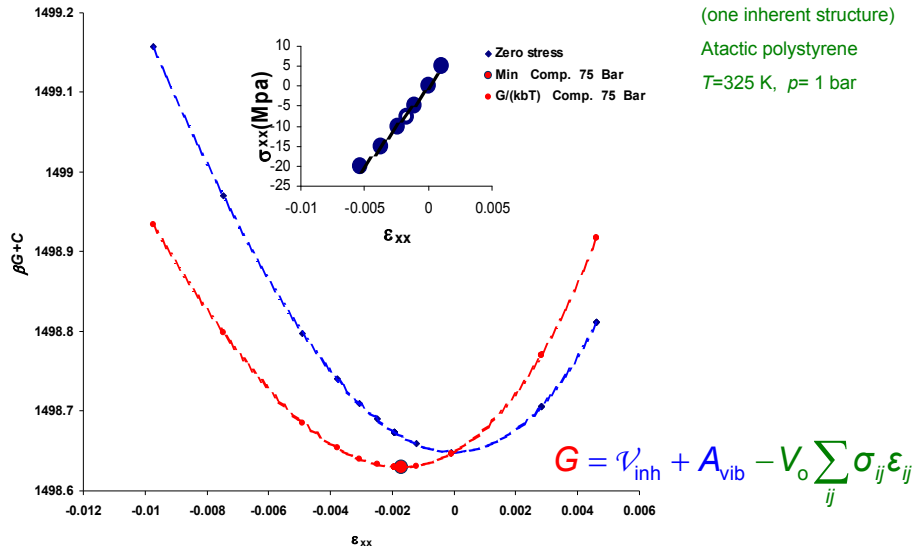
Computational experiment
of Uniaxial Deformation
(one inherent structure)
Atactic polystyrene
 $T=325$ K, $p=1$ bar

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



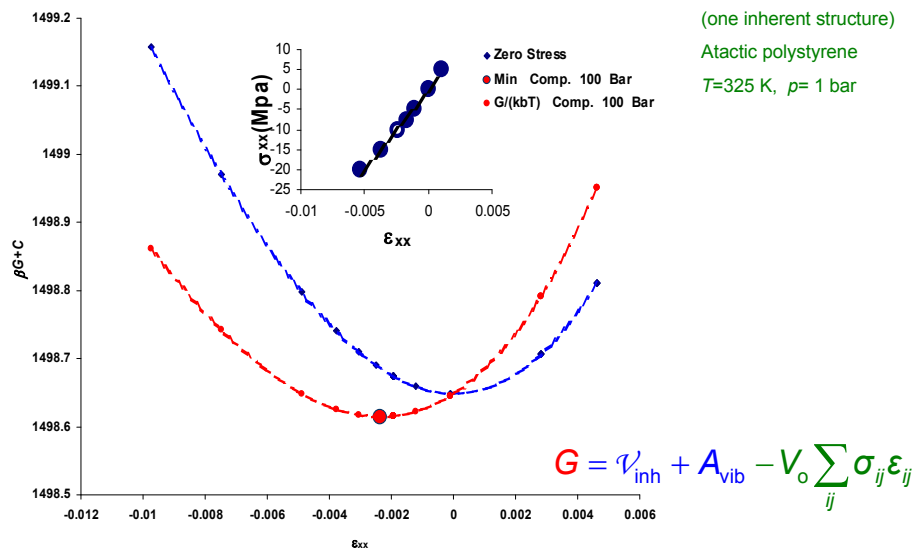
ELASTIC RESPONSE: QHA

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



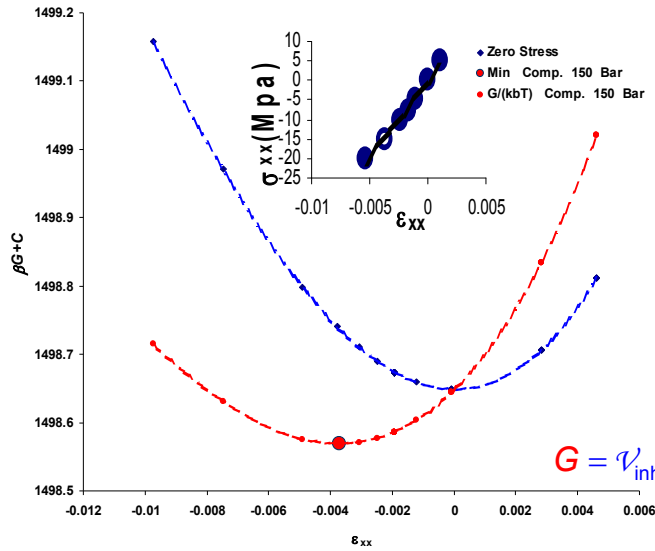
ELASTIC RESPONSE: QHA

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



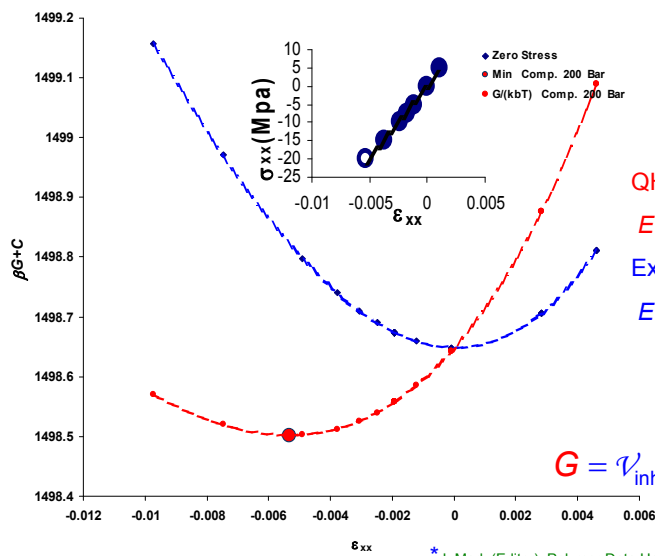
ELASTIC RESPONSE: QHA

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



ELASTIC RESPONSE: QHA

Computational experiment
Of Uniaxial Deformation
(one inherent structure)
Atactic polystyrene
 $T=325\text{ K}$, $p=1\text{ bar}$



QHA predictions:

$E = 3.9\text{ GPa}$, $\nu = 0.35$

Exp. (Room Temp)*:

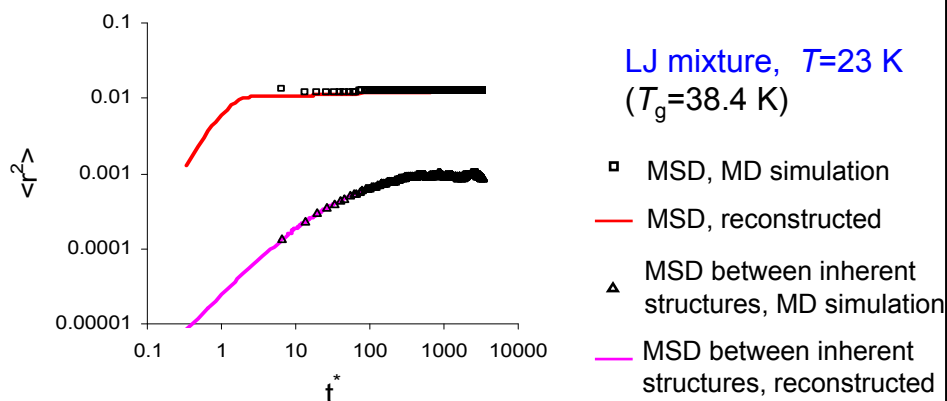
$E = 3.2\text{-}3.4\text{ GPa}$, $\nu = 0.32$

* J. Mark (Editor), Polymer Data Handbook (Oxford University Press, Oxford)

TEST OF POISSON PROCESS MODEL FOR TRANSITIONS BETWEEN BASINS

- Conduct NVT Molecular Dynamics simulation of a simple model glass (Lennard-Jones mixture)
- Generate **Inherent Structure Trajectory** by mapping each visited configuration into the closest local minimum of the potential energy.
- Directly track mean square displacement of atoms along MD trajectory and along Inherent Structure Trajectory.
- Estimate rate constants $k_{i \rightarrow j}$ for transitions between basins (“states”) from the MD via Hazard Plot Analysis.
- Calculate time-dependent basin occupancy probabilities from interbasin transition rate constants by solving **master equation**.
- Reconstruct mean square displacements from Poisson Process model and compare with direct MD estimates.

POISSON PROCESS MODEL: RECONSTRUCTION OF MEAN SQUARE DISPLACEMENT (MSD) OF ATOMS



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

Tsalikis, D., Lempesis, N., Boulougouris, G.C., *DNT J. Phys. Chem. B* **112**, 10628 (2008)

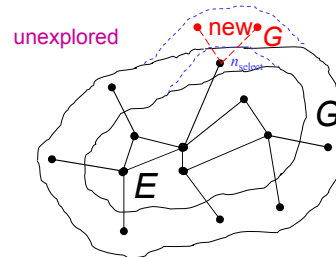
TRACKING THE EVOLUTION OF THE PROBABILITY DISTRIBUTION AMONG STATES BASED ON A FIRST PASSAGE SAMPLING SCHEME.

- Consideration of set of “explored” states E and a set of “boundary” states G . For each explored state n , *all relevant* transitions and the corresponding rate constants k_{nm} out of the state have been evaluated.

- Analytical solution of the master equation with absorbing boundary conditions at all “boundary” states in G .

$$\frac{\partial Q_n(G,t)}{\partial t} = \sum_{m \in E} Q_m(G,t) k_{mn} - Q_n(G,t) \sum_{m \in E \cup G} k_{nm}, \quad \forall n \in E$$

- Evaluation of the time t_{safe} , up to which the presence of “boundary” states does not influence the solution of the master equation, i.e., $P_{\text{alive}}(G,t) = \sum_{n \in E} Q_n(G,t)$ stays practically equal to 1.



- Incremental augmentation of the set of explored states E by including in it a boundary state n_{select} , chosen according to the probability of being reached for the first time from E .

$$f(G,t) = -\frac{\partial P_{\text{alive}}(G,t)}{\partial t} = \sum_{n \in E} \left[Q_n(G,t) \sum_{n_g \in G} k_{nn_g} \right] = \sum_{n_g \in G} f_{n_g}(G,t), \quad \text{where } f_{n_g}(G,t) = \sum_{n \in E} \left[Q_n(G,t) k_{nn_g} \right]$$

EROPHILE: Eigenvalue Representation of Observables and Probabilities in a High-dimensional Euclidean space

For any observable A , which has well-defined values A_i within each state i , nonequilibrium ensemble average value at time t is:

$$\langle A(t) \rangle = \sum_i P_i(t) A_i = \langle A \rangle_{\text{eq}} + \sum_{n=1}^{N-1} a_n \beta_n e^{\lambda_n t}$$

Time autocorrelation function is:

$$\langle A(0)A(t) \rangle - \langle A(0) \rangle \langle A \rangle_{\text{eq}} = \sum_{n=1}^{N-1} e^{\lambda_n t} \beta_n^2 + \langle A \rangle_{\text{eq}} \sum_{n=1}^{N-1} \left[e^{\lambda_n t} a_n \beta_n \right] + \sum_{n=1}^{N-1} e^{\lambda_n t} \beta_n \sum_{m=1}^{N-1} \beta_m \sum_{k=1}^{N-1} \sum_{l=1}^N \left[\frac{a_k \tilde{u}_{l,m} \tilde{u}_{l,n} \tilde{u}_{l,k}}{\tilde{P}_l(\infty)} \right]$$

where $a_n = \tilde{\mathbf{u}}_n \cdot \tilde{\mathbf{P}}(0)$, $\beta_n = \tilde{\mathbf{u}}_n \cdot \tilde{\mathbf{A}}$ ($1 \leq n \leq N-1$)

λ_n , $\tilde{\mathbf{u}}_n$: Eigenvalues and eigenvectors of symmetrized $N \times N$ rate constant matrix describing transitions among N explored states (**relaxation modes**)

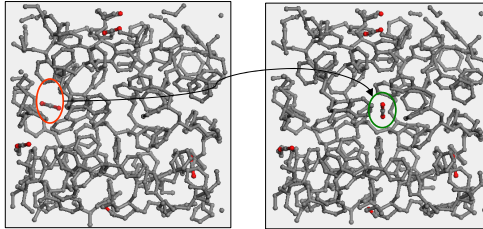
$$\tilde{P}_i(t) = P_i(t) / \sqrt{P_i(\infty)}, \quad \tilde{A}_i = A_i \sqrt{P_i(\infty)} \quad (1 \leq i \leq N)$$

eq, ∞ : restricted equilibrium among the N explored states.

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

SORPTION EQUILIBRIA OF CO₂ IN ATACTIC POLYSTYRENE VIA MOLECULAR SIMULATION

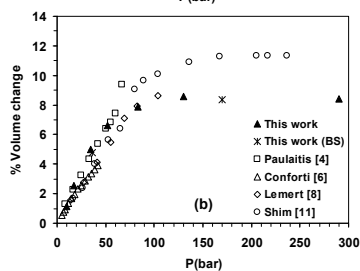
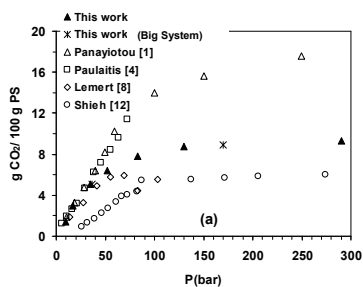
T. Spyriouni, G.C. Boulougouris, DNT, *Macromolecules* **2009**, *42*, 1759-1769.



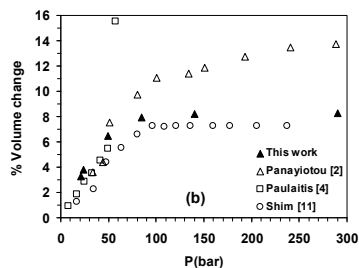
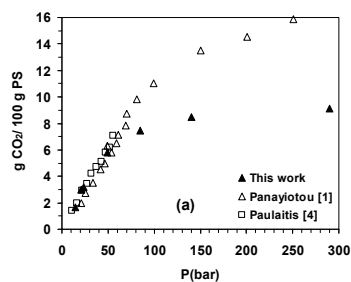
- Molecular Dynamics of PS/CO₂ in the N_1N_2PT ensemble.
- Every 5-6 ns, MC moves that repartition penetrant molecules among accessible volume cavities in the polymer.
- Estimation of CO₂ fugacity via particle deletion (inverse Widom) method Boulougouris, G.C., Economou, I.G., DNT *J. Chem. Phys.* **115**, 8231 (2001).
- Iterative adjustment of P to achieve consistency with CO₂ fugacity in the gas phase

PREDICTED SORPTION AND SWELLING

$T=308\text{ K}$



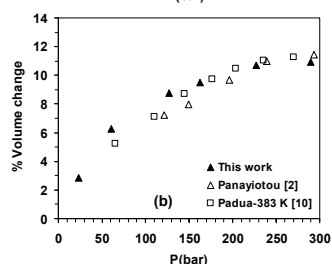
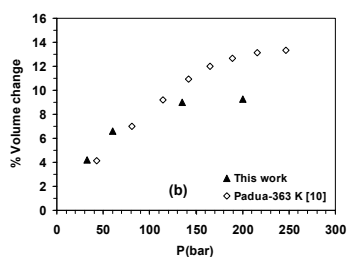
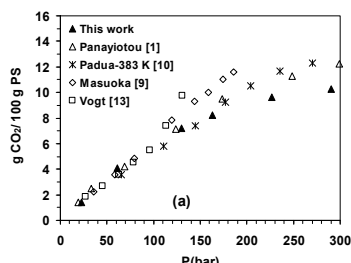
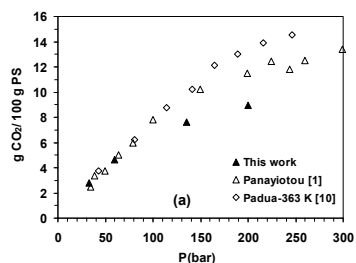
$T=323\text{ K}$



PREDICTED SORPTION AND SWELLING

$T=354\text{ K}$

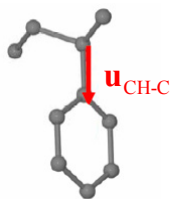
$T=373\text{ K}$



SEGMENTAL DYNAMICS

Orientational Autocorrelation Function of Pendant Bonds

(accumulated during MD as long as no exchange of CO_2 molecules between cavities takes place)



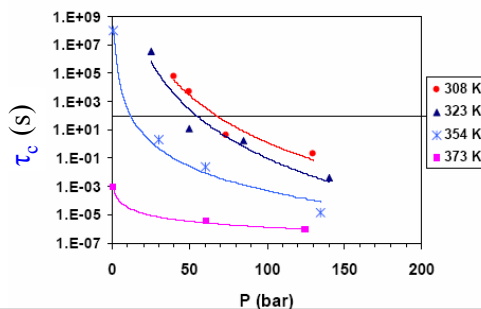
$$P_2(t) = \frac{1}{2} \left\{ 3 \left\langle \left[\mathbf{u}_{\text{CH-C}}(t) \cdot \mathbf{u}_{\text{CH-C}}(0) \right]^2 \right\rangle - 1 \right\}$$

Fit with stretched exponential (KWW) function:

$$P_{\text{KWW}}(t) = \exp \left[- (t / \tau)^\beta \right]$$

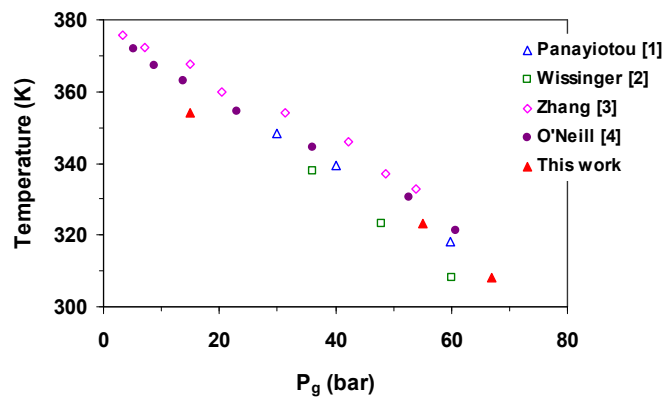
Segmental Correlation Time

$$\tau_c = \int_0^\infty P_2(t) dt = \tau \frac{\Gamma\left(\frac{1}{\beta}\right)}{\beta}$$



SORPTION-INDUCED GLASS TRANSITION

For each temperature, estimate glass transition pressure P_g as the pressure at which segmental correlation time $\tau_c \approx 100$ s



T. Spyriouni, G.C. Boulougouris, DNT, *Macromolecules* **2009**, *42*, 1759-1769.