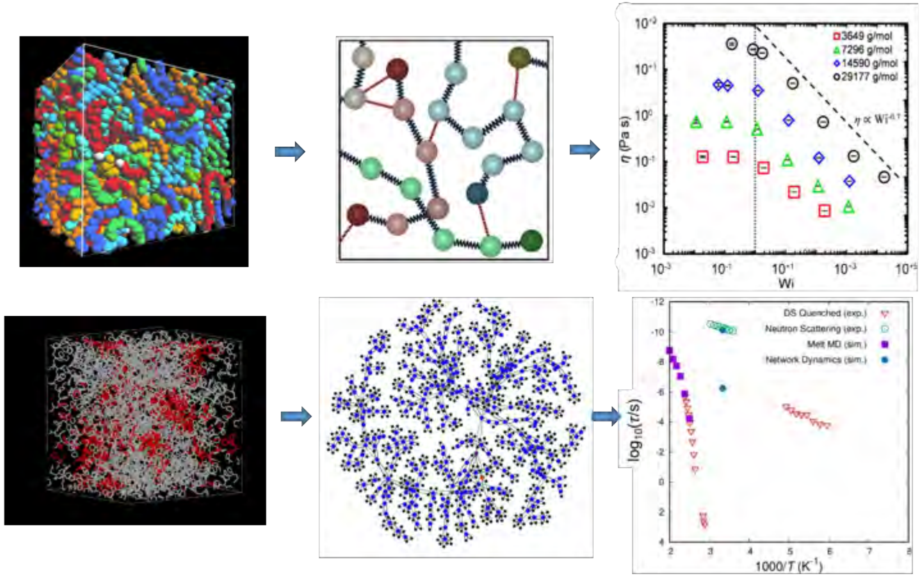
materials design

# Atomistic and Mesoscopic Modeling of Structure-Property Relations in Polymers

## Presented by:
## Doros N. Theodorou

May 24-26, 2022



# Materials Design Webinar Series

- Each session runs several times to accommodate schedules
  - Share the webinar series with your colleagues!
  - Registration details [http://www.materialsdesign.com/webinars](http://www.materialsdesign.com/webinars)
- We will be recording this webinar
  - Watch any of our earlier webinars anytime
  - We will post upcoming webinars on the webinar page
- Vote for the next webinar topic!
  - Take a 2 minutes brief survey at the end of the webinar!
- Audio issues
  - Log out and log back in again
  - Check your audio output
  - Google Chrome (most recent 2 versions) Mozilla Firefox (most recent 2 versions) Apple Safari (most recent 2 versions) Microsoft Edge (most recent 2 versions)

# Please Ask Questions!

full screen

during discussion:
raise hand
to speak

any time during webinar:
type your question here
and then press Send

Q: Can you calculate the gelation point of a polymer?
A: Yes we can! David will address this on an upcoming slide soon.

What forcefields are supported by MedeA?

**Use the raise hand icon to bring attention to your question**

# Webinar Speakers

***Katherine Hollingsworth***

***Dr. Marianna Yiannourakou***

# Professor Doros N. Theodorou

Computational Materials Science and Engineering Group

School of Chemical Engineering

National Technical University of Athens

## Webinar Presenter

# Atomistic and Mesoscopic Modeling of Structure-Property Relations in Polymers

*Doros N. Theodorou*

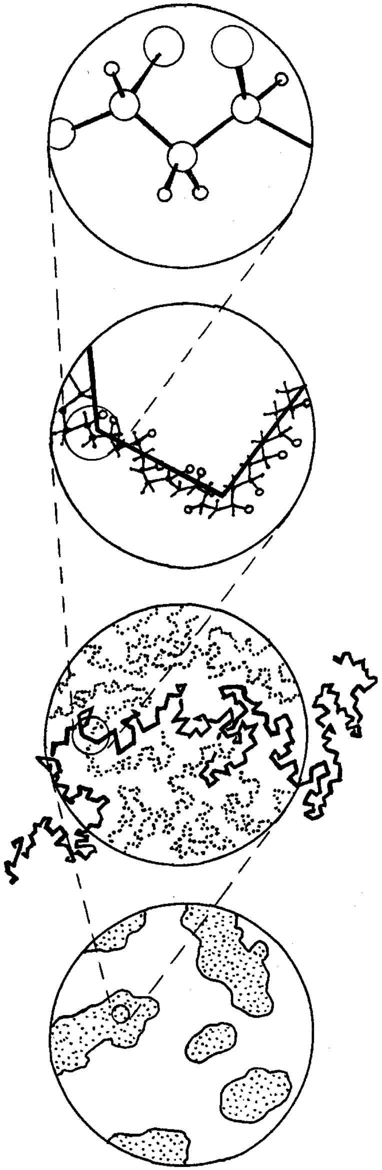
Computational Materials Science and Engineering Group,
School of Chemical Engineering, National Technical University of
Athens, Zografou Campus, 157 80 Athens, GREECE

doros@central.ntua.gr

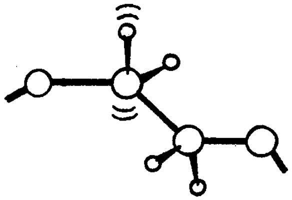
# Outline

- Multiple length and time scales in polymers.
- Polymer melts: packing, entanglements, and rheological properties.
- Polymer glasses: elastic constants, structural relaxation.
- Polymers at Interfaces: surface tension, work of adhesion, interfacial shear strength.
- Summary.

# Length and Time Scales in Polymers

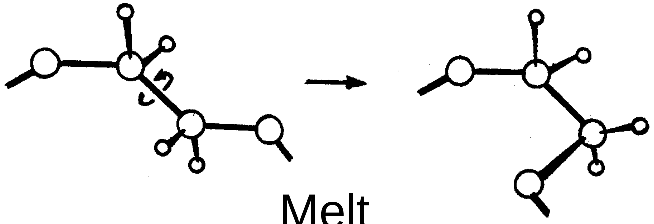


Bond lengths, atomic radii
~ 0.1 nm



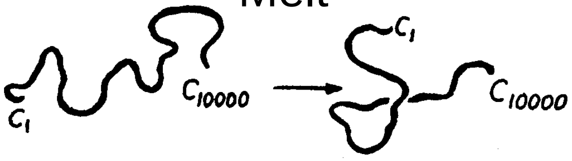
Bond vibrations
≥$10^{-14}$ s

Statistical (Kuhn) segment length *b*
~ 1 nm



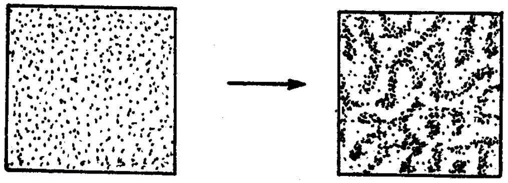
Conformat. transitions
≥$10^{-11}$ s

Melt



Chain radius of gyration
~ 10 nm

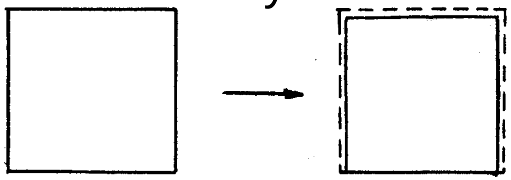
Longest relaxation time
≥$10^{-3}$ s



Phase/ microphase separation
≥ 1 s

Domain size in phase-separated material
~ 1 μm

Glassy state



Physical ageing
($T < T_g$-20°C)
≥ 1 yr

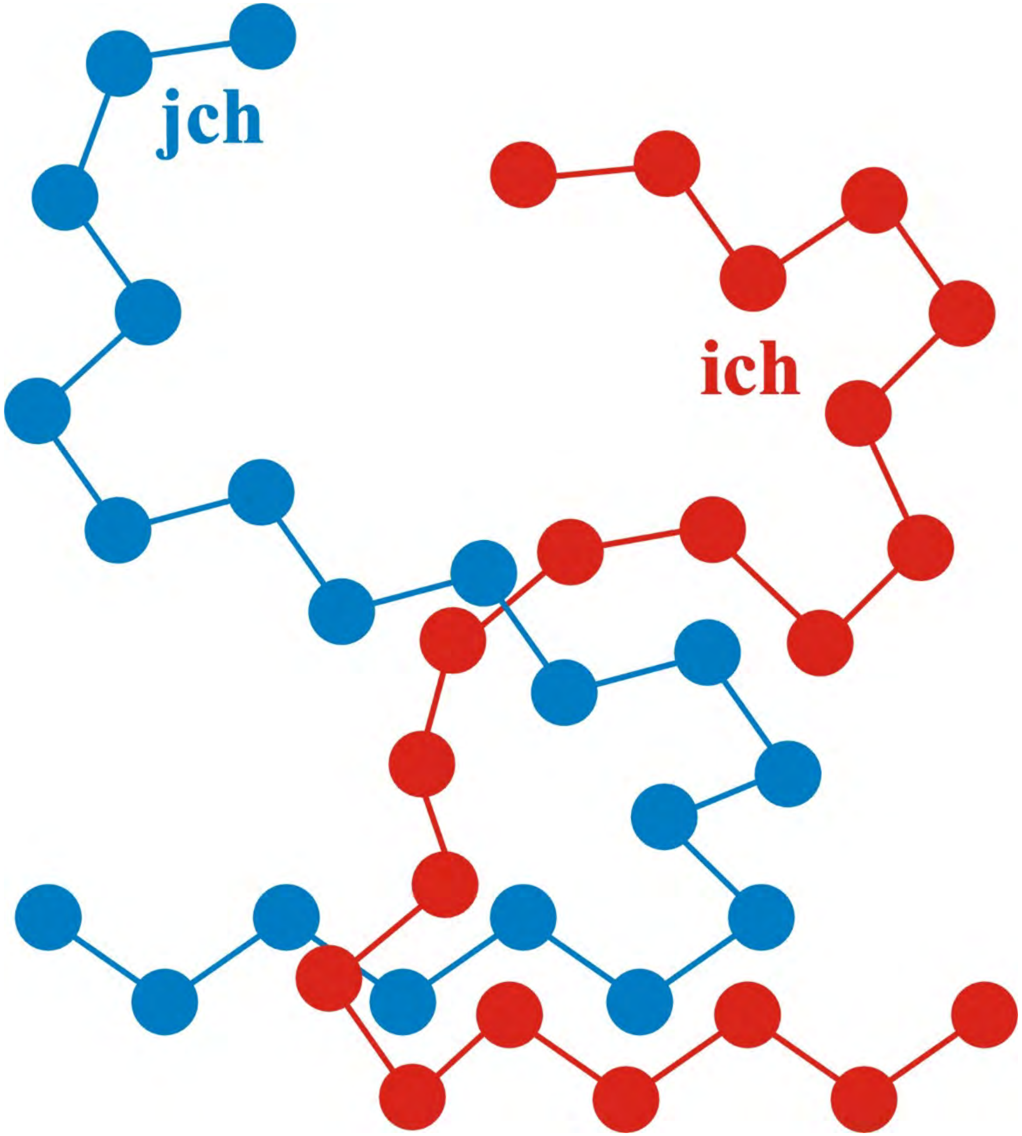
# The Challenge of Long Time Scales

- Atomistic molecular dynamics simulation: μs time scales, ms on special hardware [K.Lindorff-Larsen, S. Piana, R.O. Dror, D.E. Shaw, *Science* **2011**, *334*, 517-520].
- Dynamics of most physical, chemical, materials, biological systems: fs to years.

- Develop hierarchical modeling and simulation methods consisting of many interconnected levels [electronic, atomistic, mesoscopic (>10 nm, > 100 ns), continuum], each level informing the more coarse-grained ones.

# Equilibrating long-chain melts:  connectivity-altering MC

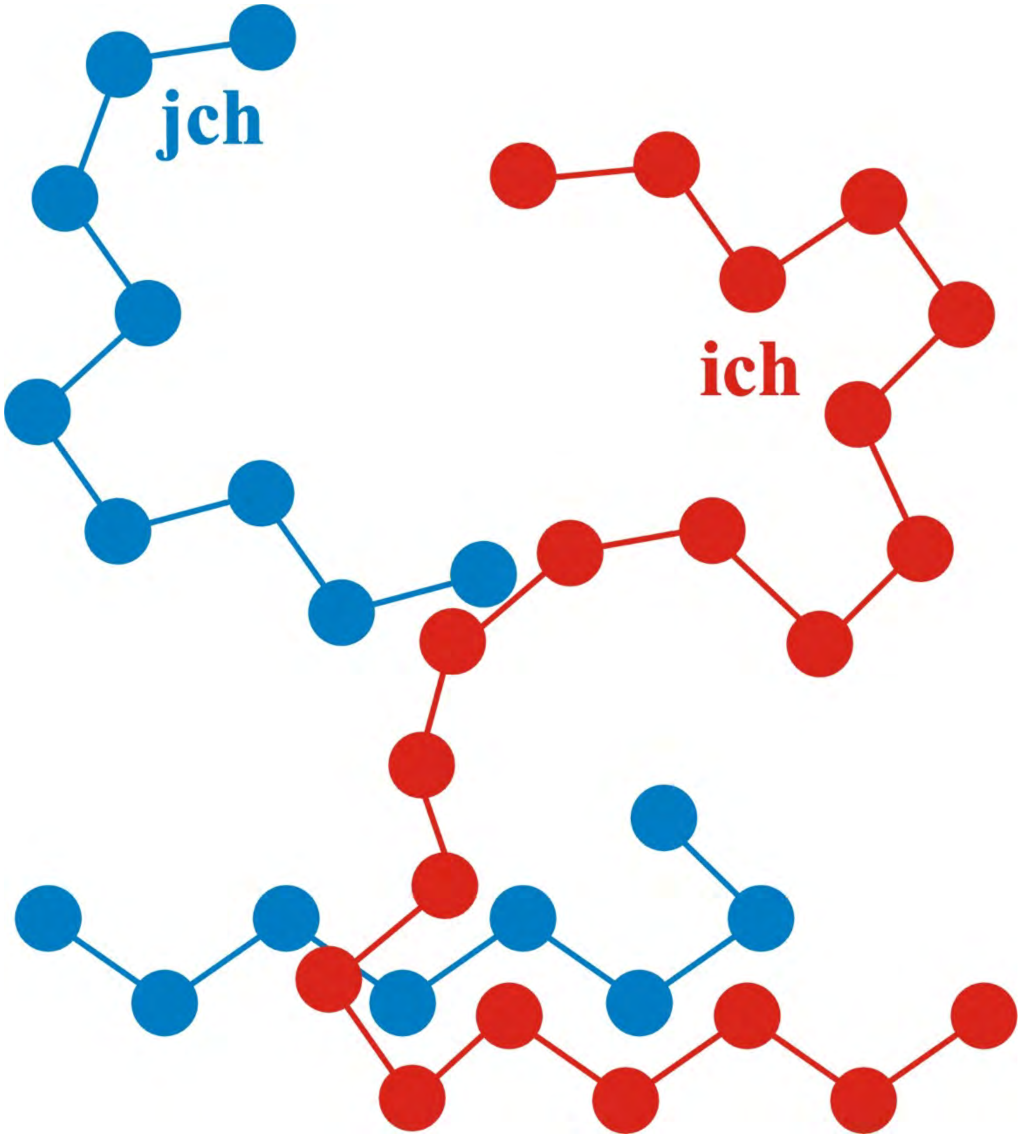
**(DBMC)**



Karayiannis, N., Mavrantzas, V.G., DNT, *Phys. Rev. Lett.* **2002**, *88*, 105503.

# Equilibrating long-chain melts:  connectivity-altering MC

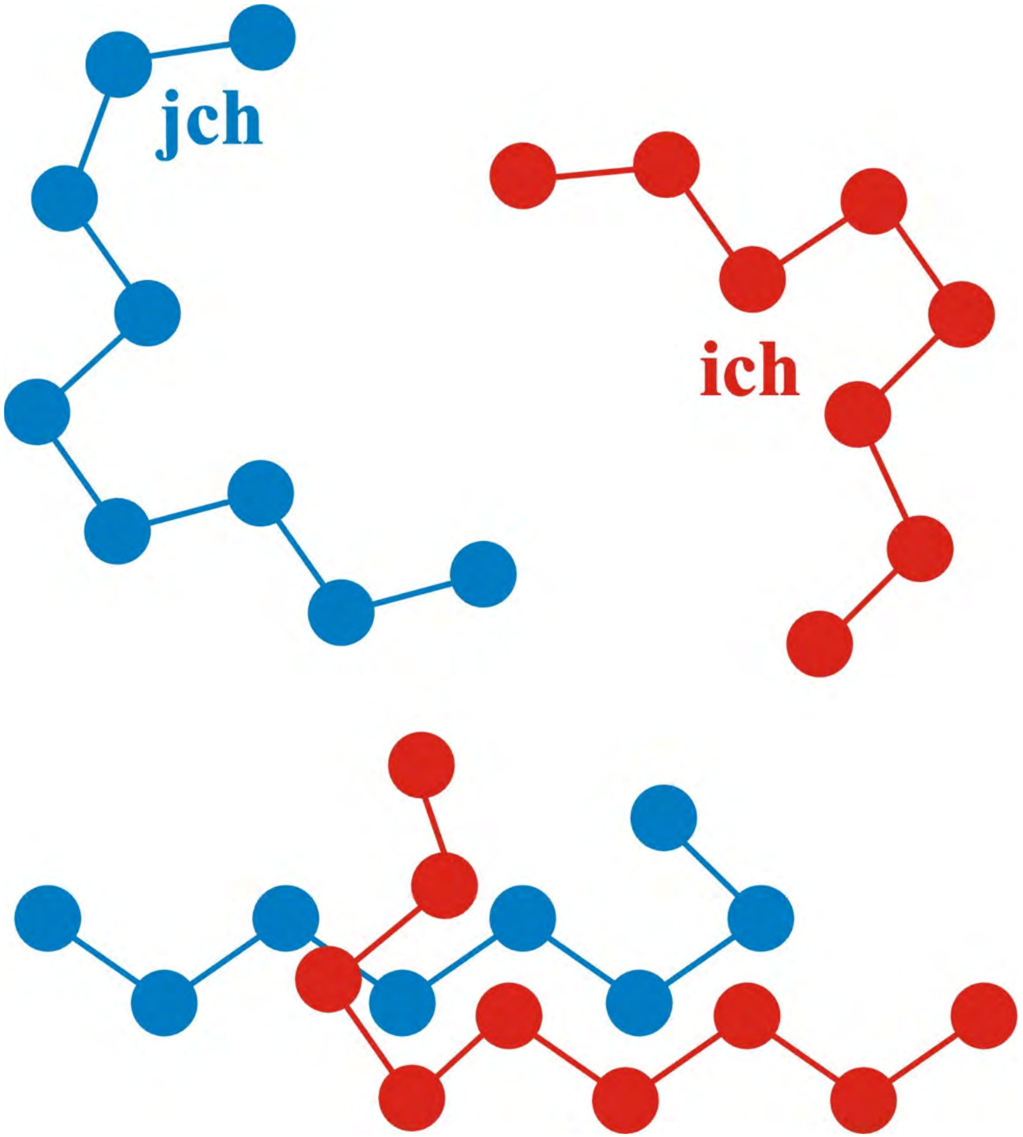
**(DBMC)**



Karayiannis, N., Mavrantzas, V.G., DNT, *Phys. Rev. Lett.* **2002**, *88*, 105503.

# Equilibrating long-chain melts:  connectivity-altering MC

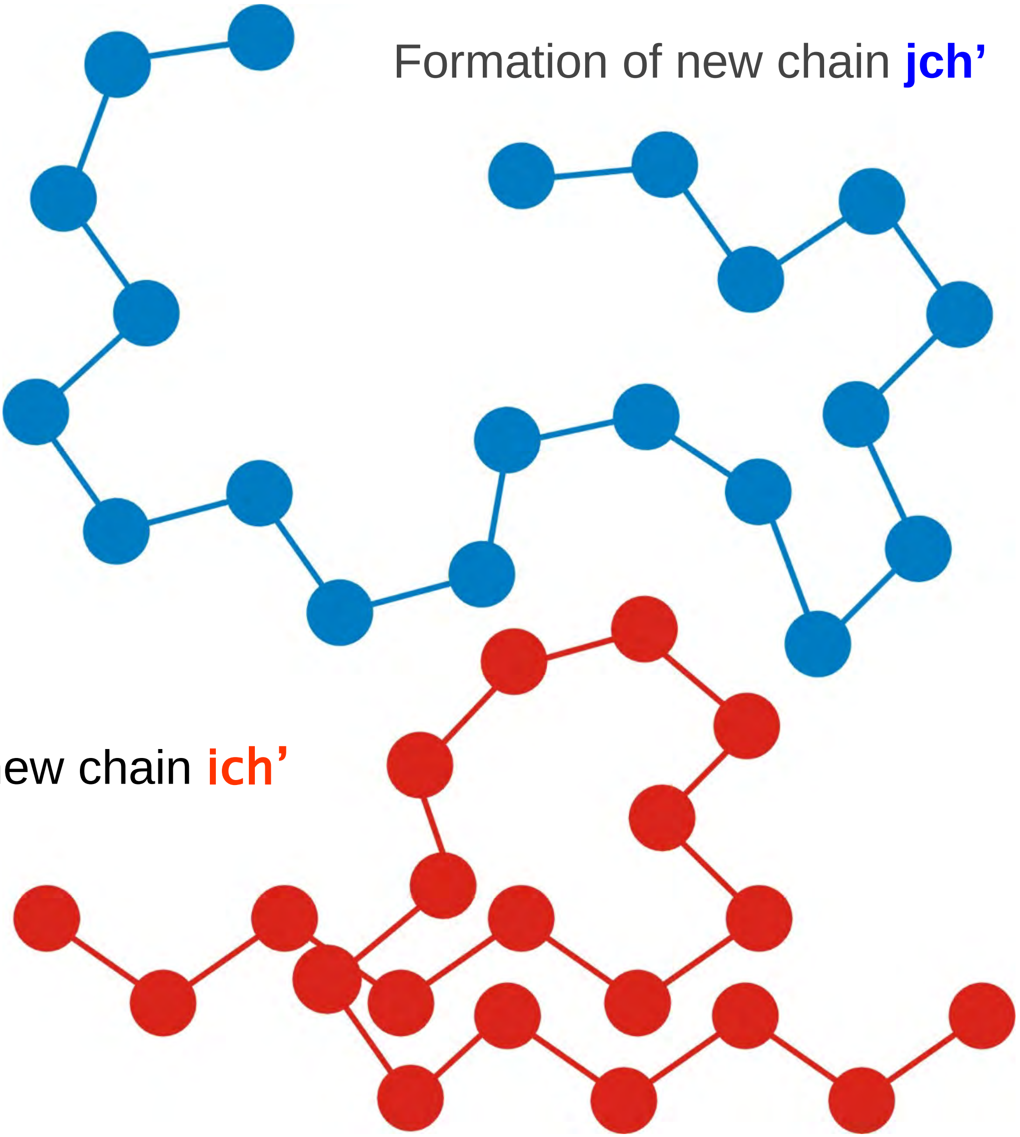
**(DBMC)**



Karayiannis, N., Mavrantzas, V.G., DNT, *Phys. Rev. Lett.* **2002**, *88*, 105503.

# Equilibrating long-chain melts: connectivity-altering MC

**(DBMC)**



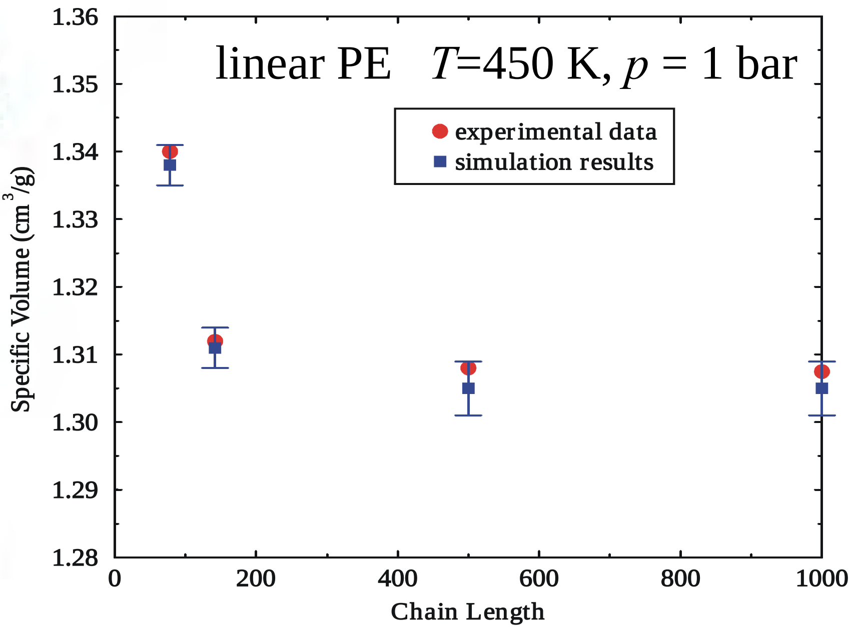
Formation of new chain **jch’**

Formation of new chain **ich’**

Karayiannis, N., Mavrantzas, V.G., DNT, *Phys. Rev. Lett.* **2002**, *88*, 105503.

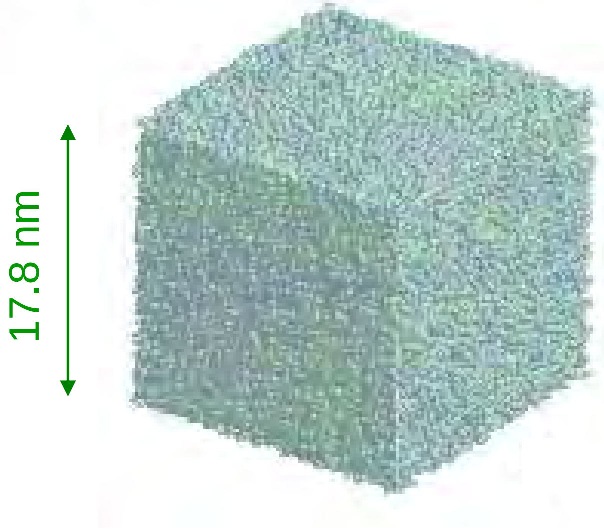
# Structure and $pVT$ properties of polymer melts

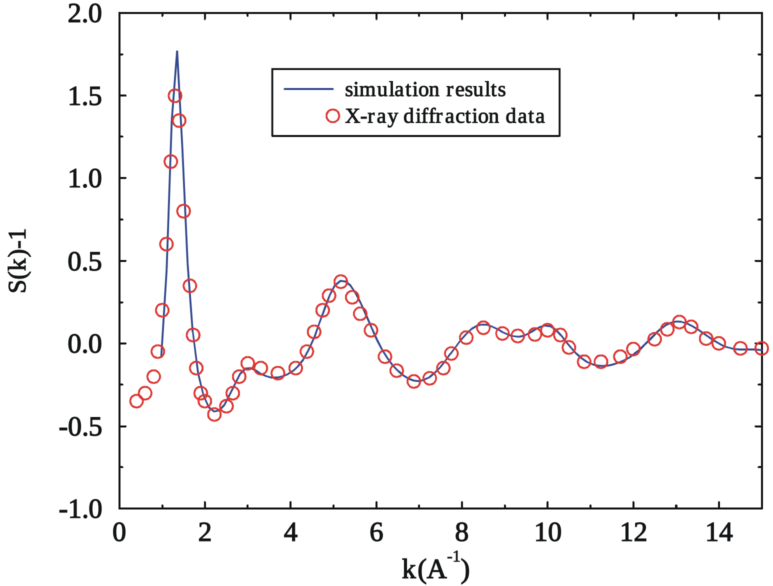
## Connectivity-altering Monte Carlo Simulation



Karayiannis, N.; Mavrantzas, V.G., DNT, *Phys. Rev. Lett.* **2002**, *88*, 105503.

TraPPE force field: Martin, M.G.; Siepmann, J.I. *J. Phys. Chem. B* **1999**, *103*, 4508-4517.





# Entanglement analysis in polymer melts

## CReTA Algorithm

Tzoumanekas, C.; DNT *Macromolecules* **2006,** *39*, 4592.

Example:

$C_{1000}$ PE, 450 K, 1 atm

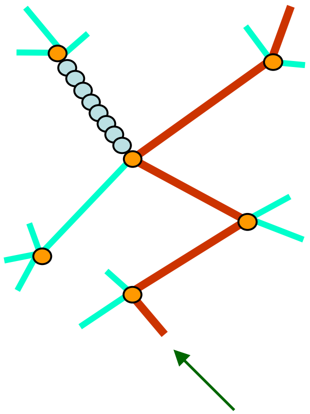
Similar strategies:

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

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

# Primitive path networks: Quantitative estimates

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



primitive path:

contour length $L_{pp}$

end-to-end dist. $R$

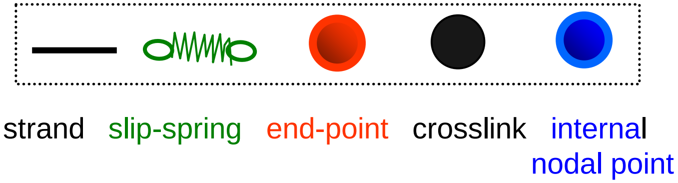
Kuhn length of primitive path: $$d = \frac{\langle R^2 \rangle}{\langle L_{pp} \rangle} \quad , \quad M_e = M \frac{\langle R^2 \rangle}{\langle L_{pp} \rangle^2}$$

Packing length $$l_p = \frac{M}{\rho N_A \langle R_g^2 \rangle}$$

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

[α] exp. $M_e$ (from plateau modulus), Fetters et al., *Macromolecules* **1994**, *24*, 4639

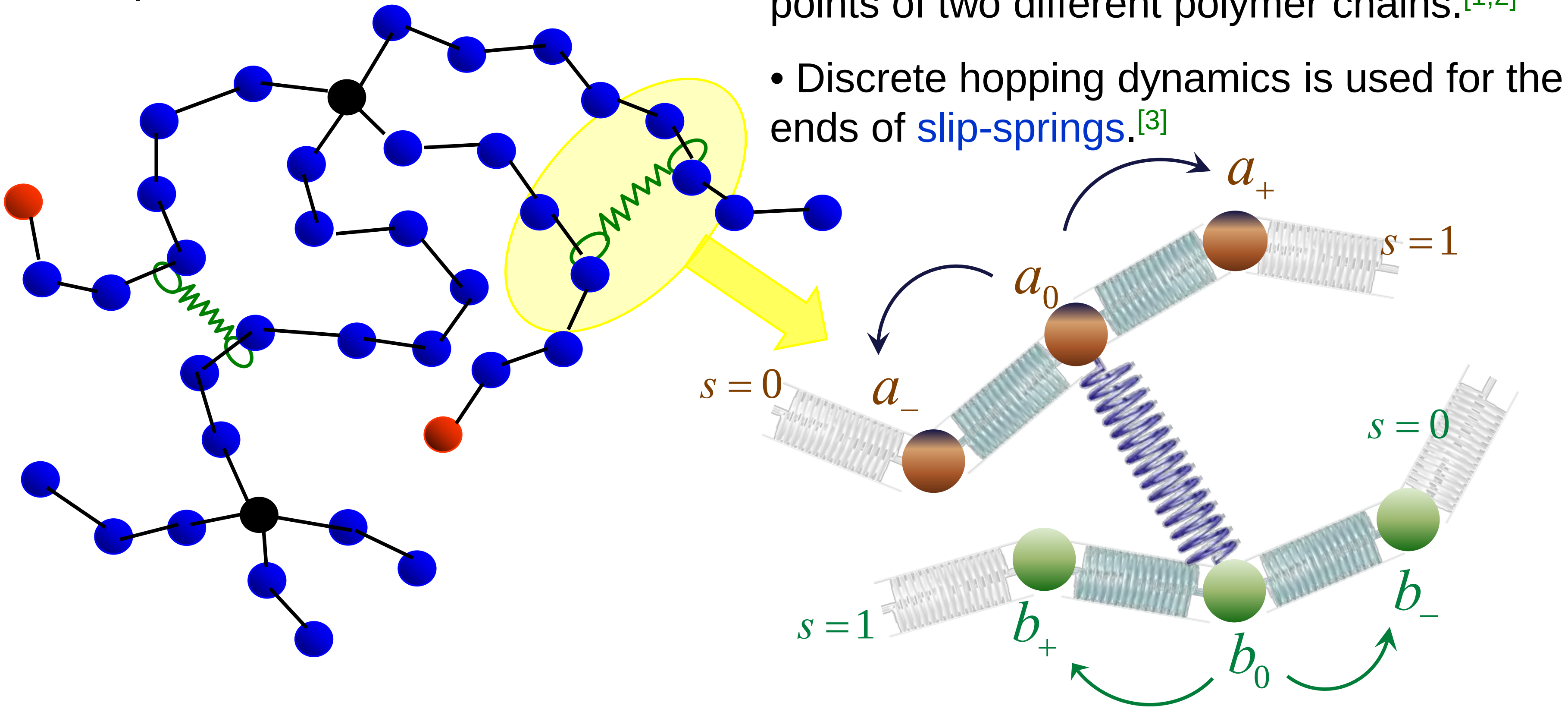
# From entanglement networks to melt rheology



nodal point: ~50 skeletal atoms

**Effect of entanglements introduced by slip-springs.**

- A slip-spring connects two internal nodal points of two different polymer chains.[1,2]
- Discrete hopping dynamics is used for the ends of slip-springs.[3]

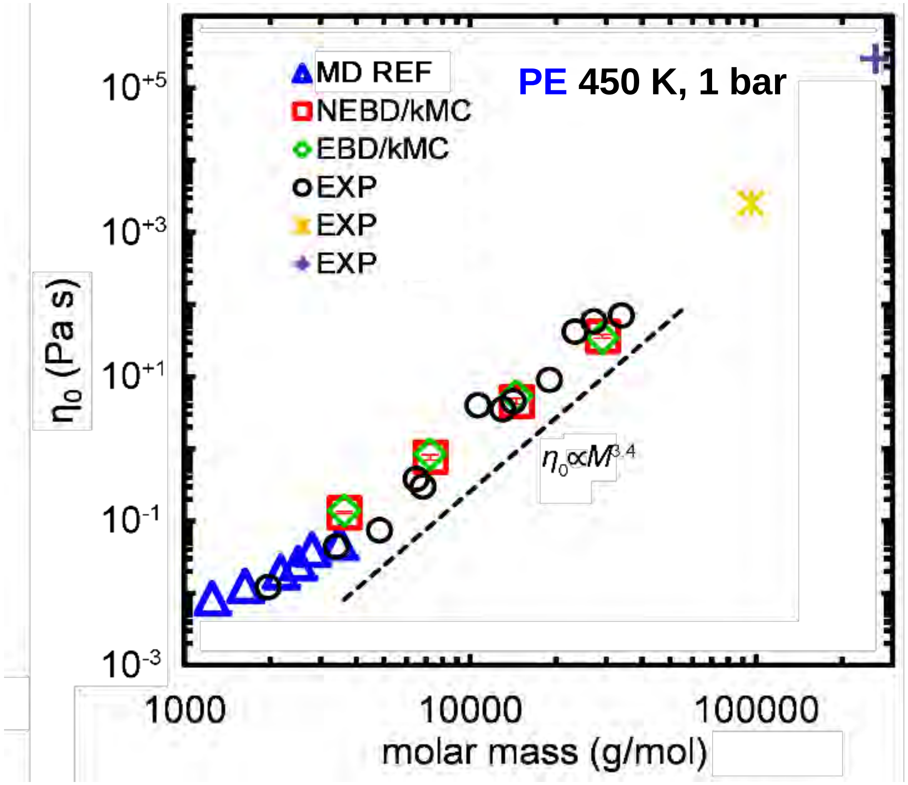


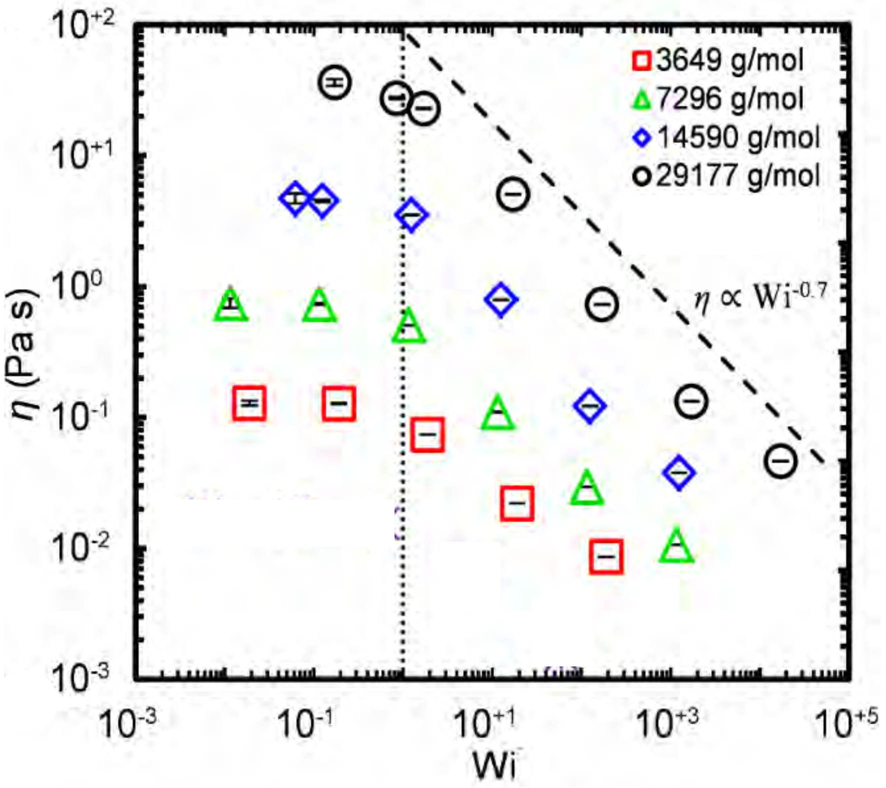
1. Chappa, V.; Morse, D.C.; Zippelius, A. Müller, M. *Phys. Rev. Lett.* **2012**, *109*, 148302.
2. Ramírez-Hernandez, A.; Müller, M; de Pablo, J. J. *Soft Matter* **2013**, *9*, 2030**.**
3. Uneyama, T.; Masubuchi, Y *J. Chem. Phys.* **2012**, *137*, 154902.

# Viscoelastic properties of polymer melts

## Brownian Dynamics/kinetic Monte Carlo simulation

Mesoscopic intrachain effective potentials from atomistic simulations. Local density-dependent nonbonded free energy density from an equation of state (hybrid particle-field approach). Bead friction factors and slip-spring hopping rate constants from atomistic MD.



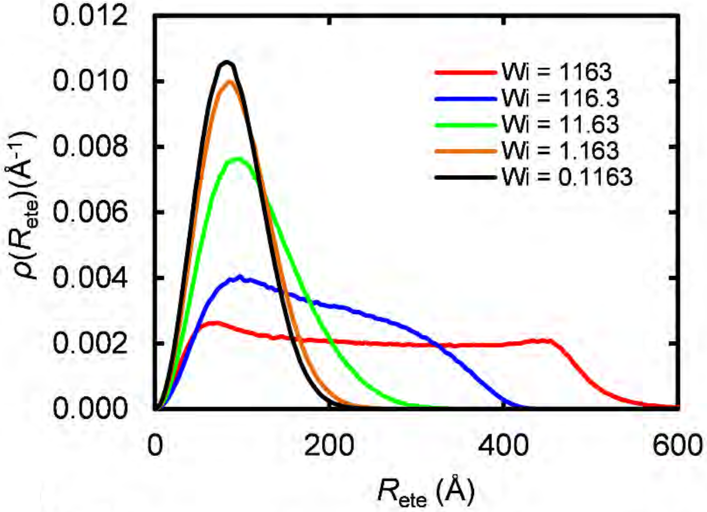


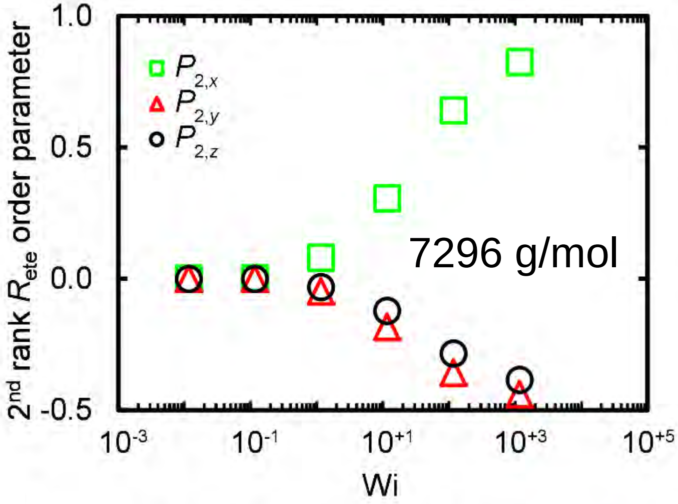
Vogiatzis, G.G.; Megariotis, G.; DNT *Macromolecules* **2017**, *50*, 3004

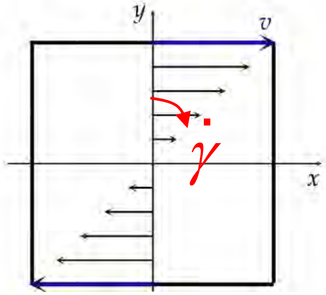
Sgouros, A.P.; Megariotis, G.; DNT *Macromolecules* **2017**, *50*, 4524

# Nonequilibrium BD/kMC: Steady shear flow

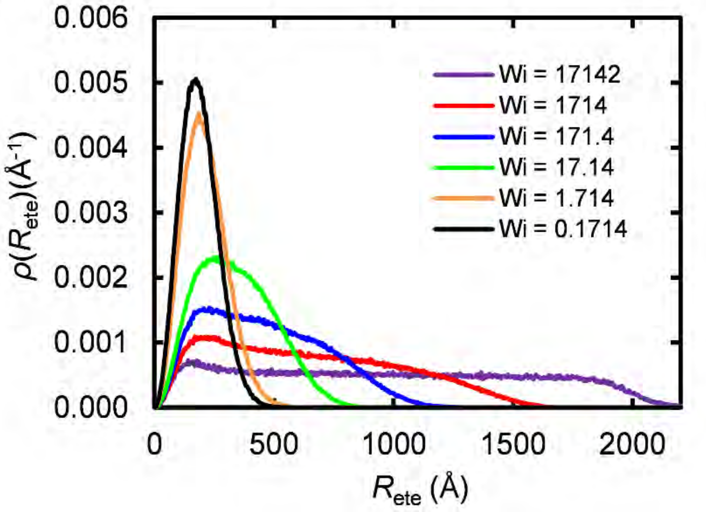
**PE** 450 K, 1 bar

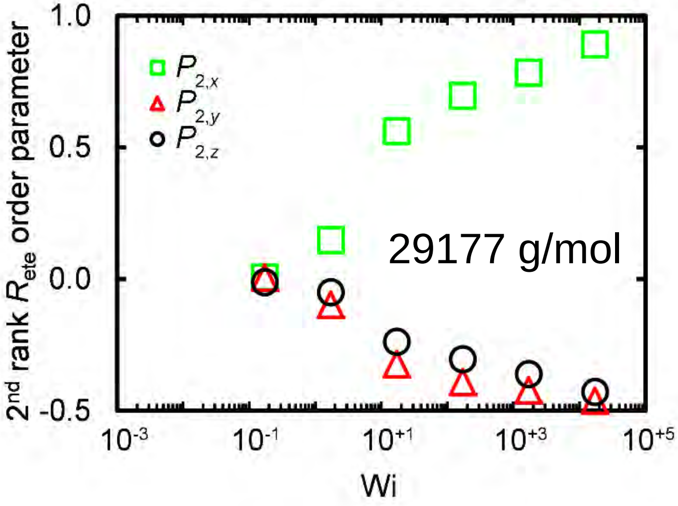


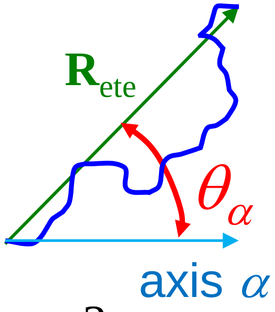




$$\mathrm{Wi} = \dot{\gamma}\tau_1$$







$$P_{2,\alpha} = \frac{3}{2}\left\langle \cos^2\theta_\alpha \right\rangle - \frac{1}{2}$$

Sgouros, A. P.; Megariotis, G.; DNT *Macromolecules* **2017**, *50*, 4524.

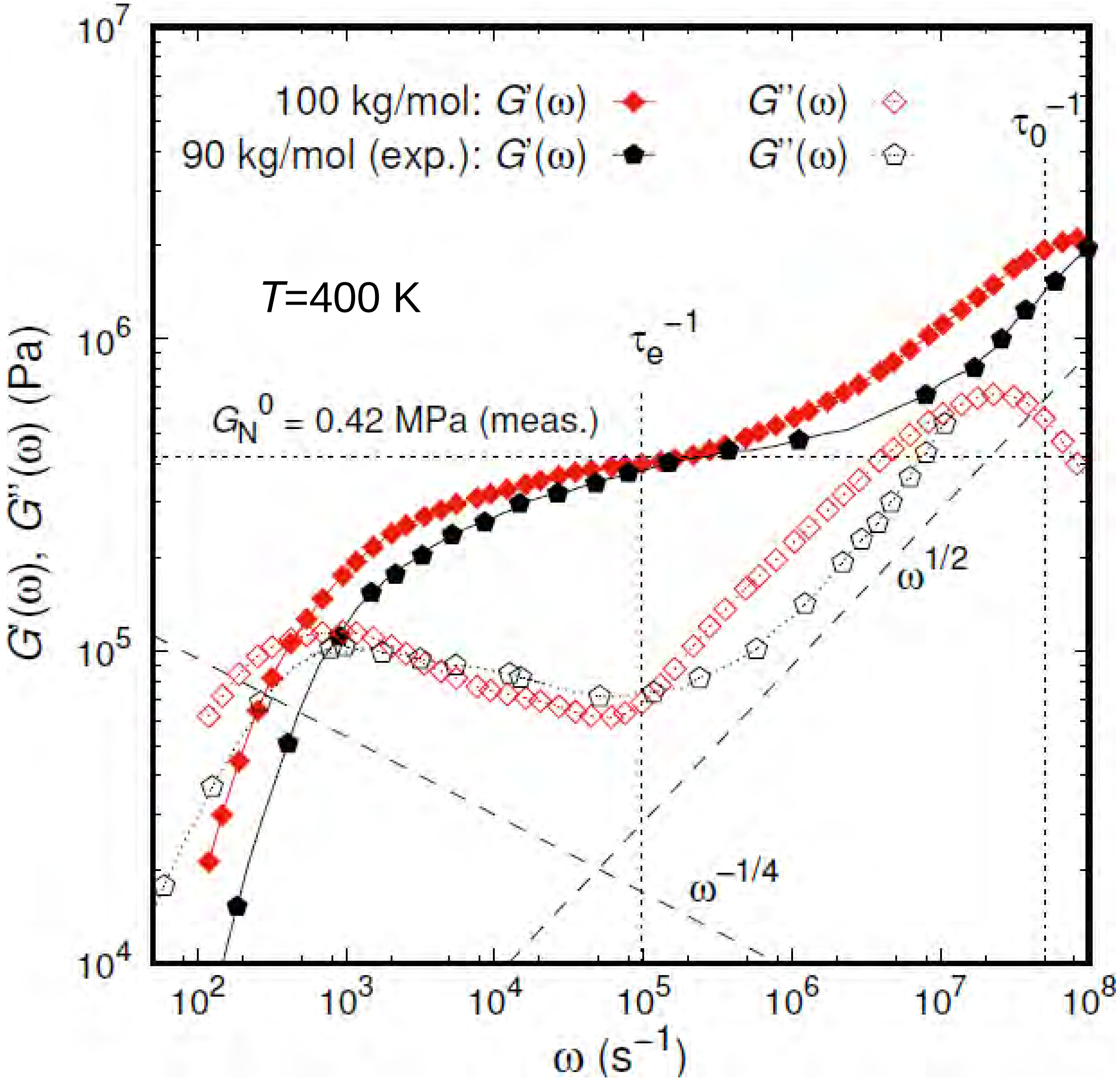
# cis-1,4 polyisoprene melts: dynamic moduli

## Brownian dynamics/kinetic Monte Carlo (BD/kMC)

Stress expression consistent with mesoscopic free energy function.

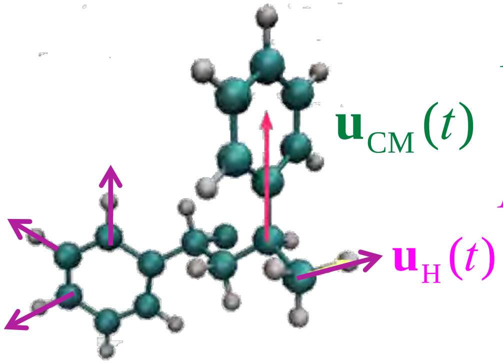
Stress relaxation modulus $G(t)$ from shear stress autocorrelation function at equilibrium.

Vogiatzis, G.G.; Megariotis, G.; DNT *Macromolecules* **2017**, *50*, 3004



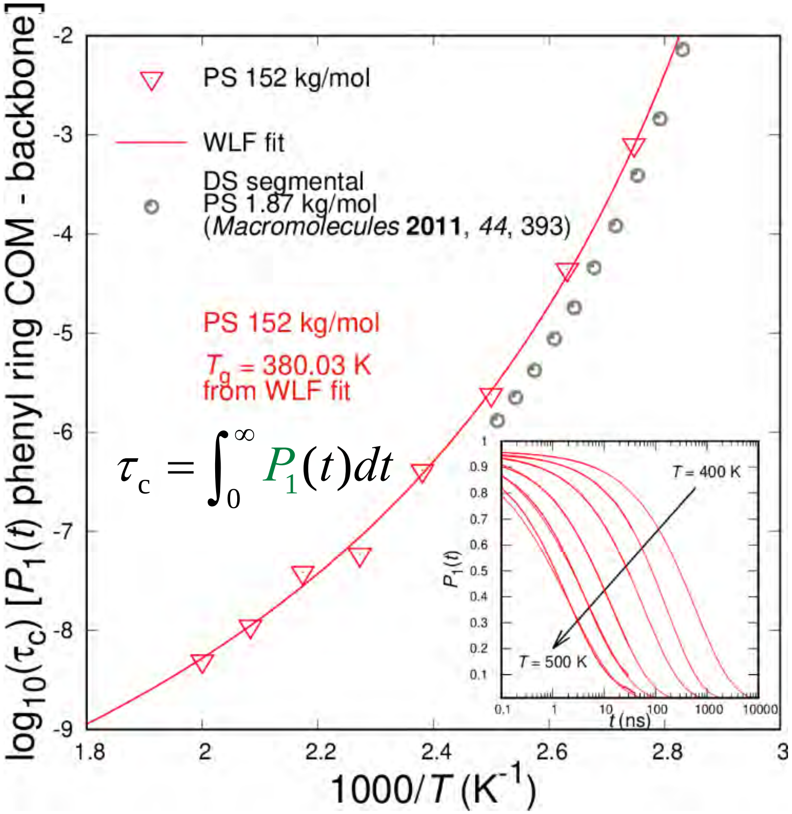
# Segmental Dynamics and Glass Transition: atactic Polystyrene

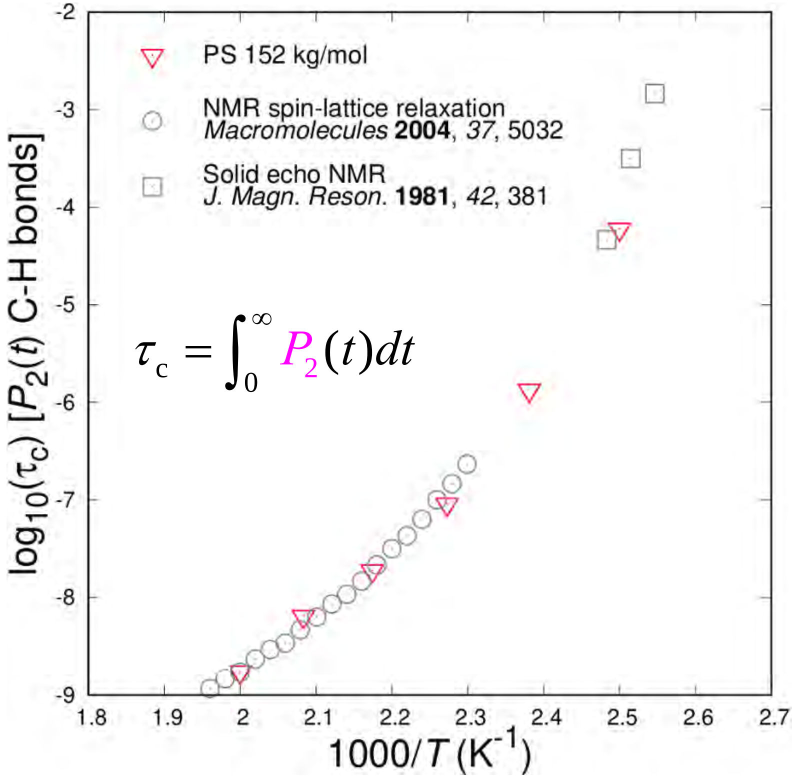
## Atomistic Molecular Dynamics



$$P_1(t) = \left\langle \mathbf{u}_{\mathrm{CM}}(t) \cdot \mathbf{u}_{\mathrm{CM}}(0) \right\rangle$$

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





Fit to empirical Williams–Landel–Ferry relation [1]:

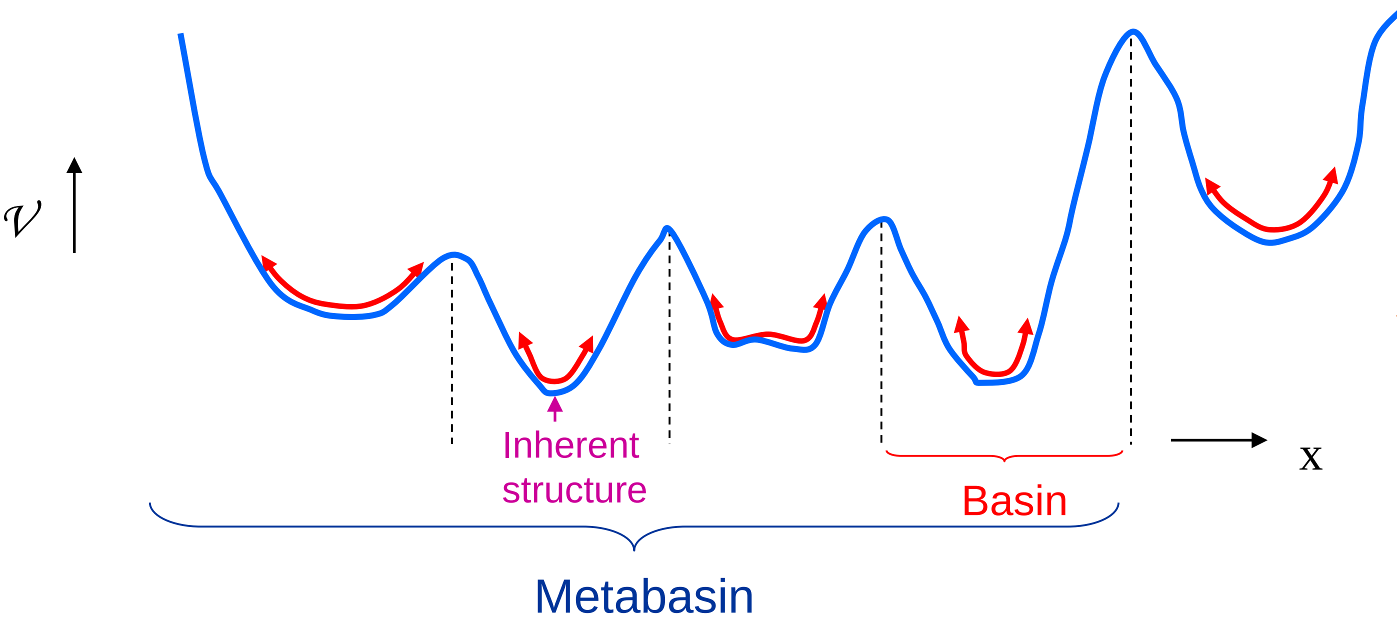
$$\log \tau_c(T) = \log \tau_g - \frac{C_1\left(T - T_g\right)}{C_2 + T - T_g}$$

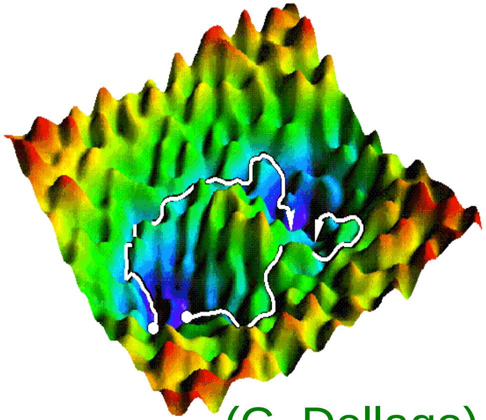
Experimental $T_g$ [2] : 373 K

1. Ferry, J. D. "*Viscoelastic Properties of Polymers", 3rd ed. Wiley, New* York, 1980.
2. Hintermeyer, J. et al. *Macromolecules* **2008**, *41*, 9335.

Vogiatzis G.G.; DNT *Macromolecules* **2014**, *47*, 387.

# Energy Landscape Picture of a Glass





(C. Dellago)

Configuration fluctuating in the neighborhood of local energy minima: "Inherent structures" : Stillinger, F.H. *Science* **1995**, *267*, 1935.
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.

Glassy computer specimens generated by rapid cooling of the melt.

# In-basin motion: Quasi-Harmonic Approximation (QHA)

Mass-weighted coordinates

$$\mathcal{V}(\mathbf{x}) = \mathcal{V}(\mathbf{x}_0) + \cancel{\nabla_{\mathbf{x}}\mathcal{V}} \cdot (\mathbf{x}-\mathbf{x}_0) + \frac{1}{2}(\mathbf{x}-\mathbf{x}_0)^{\mathrm{T}} \cdot \mathbf{H} \cdot (\mathbf{x}-\mathbf{x}_0)$$

- Second derivatives of the potential energy

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

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

- Normal mode angular frequencies

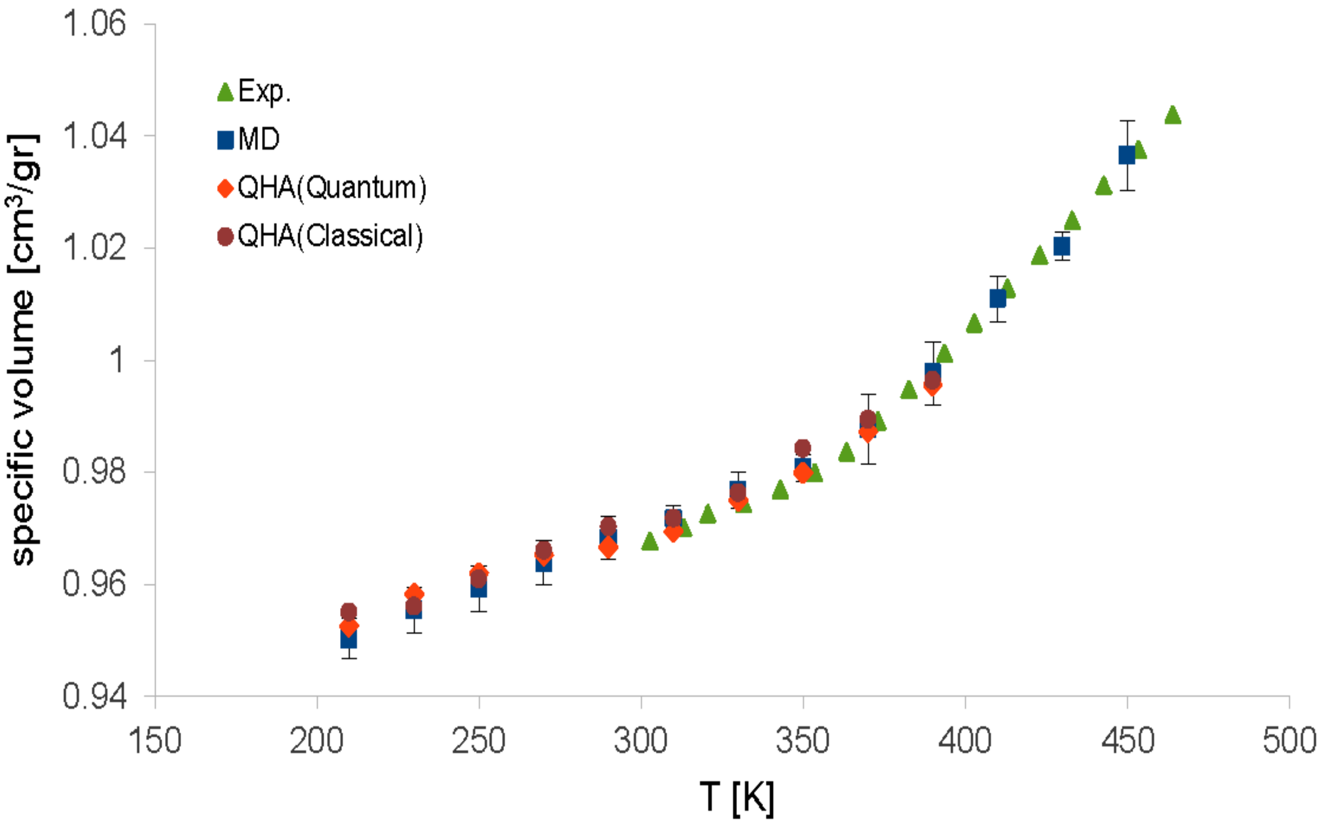
$$\omega_i = \sqrt{\lambda_i} \qquad \Rightarrow \qquad q_i^{\text{vib}} = \frac{\exp\left(-\hbar\omega_i / 2k_B T\right)}{1-\exp\left(-\hbar\omega_i / k_B T\right)}$$

- Helmholtz energy

$$A = \mathcal{V}(\mathbf{x}_0) + A_{\text{vib}} = \mathcal{V}(\mathbf{x}_0) - k_{\mathrm{B}} T \ln\left(\prod_i q_i^{\text{vib}}\right)$$

$\mathcal{V}(\mathbf{x}_0) = \mathcal{V}_{\text{inh}}$ and $\omega_i$ are functions of the spatial extent of the system.

# Volumetric Behavior: QHA vs. MD



Atactic polystyrene, modified A.Lyulin* model

Pressure 1 bar
MD cooling rate
0.5 K/ns

641 united atoms

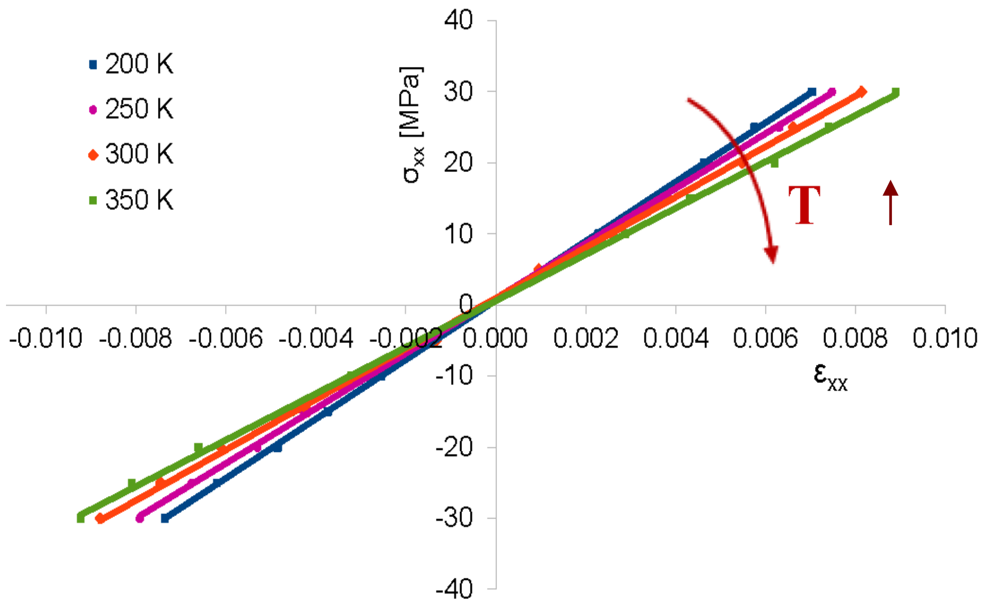
Averages over 5 basins

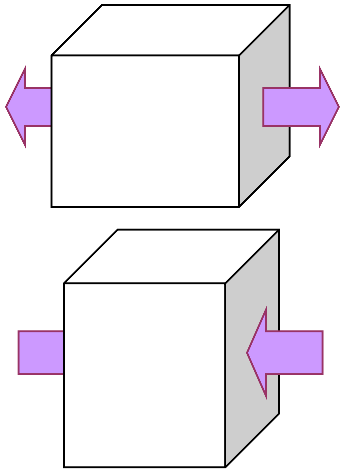
Lempesis, N.; Vogiatzis, G.G.; Boulougouris, G.C.; van Breemen, L.C.A.; Hütter, M.; DNT, *Mol. Phys*. **2013**, *111*, 3430.

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

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

# Elasticity of Polymer Glasses: Quasi-harmonic approximation



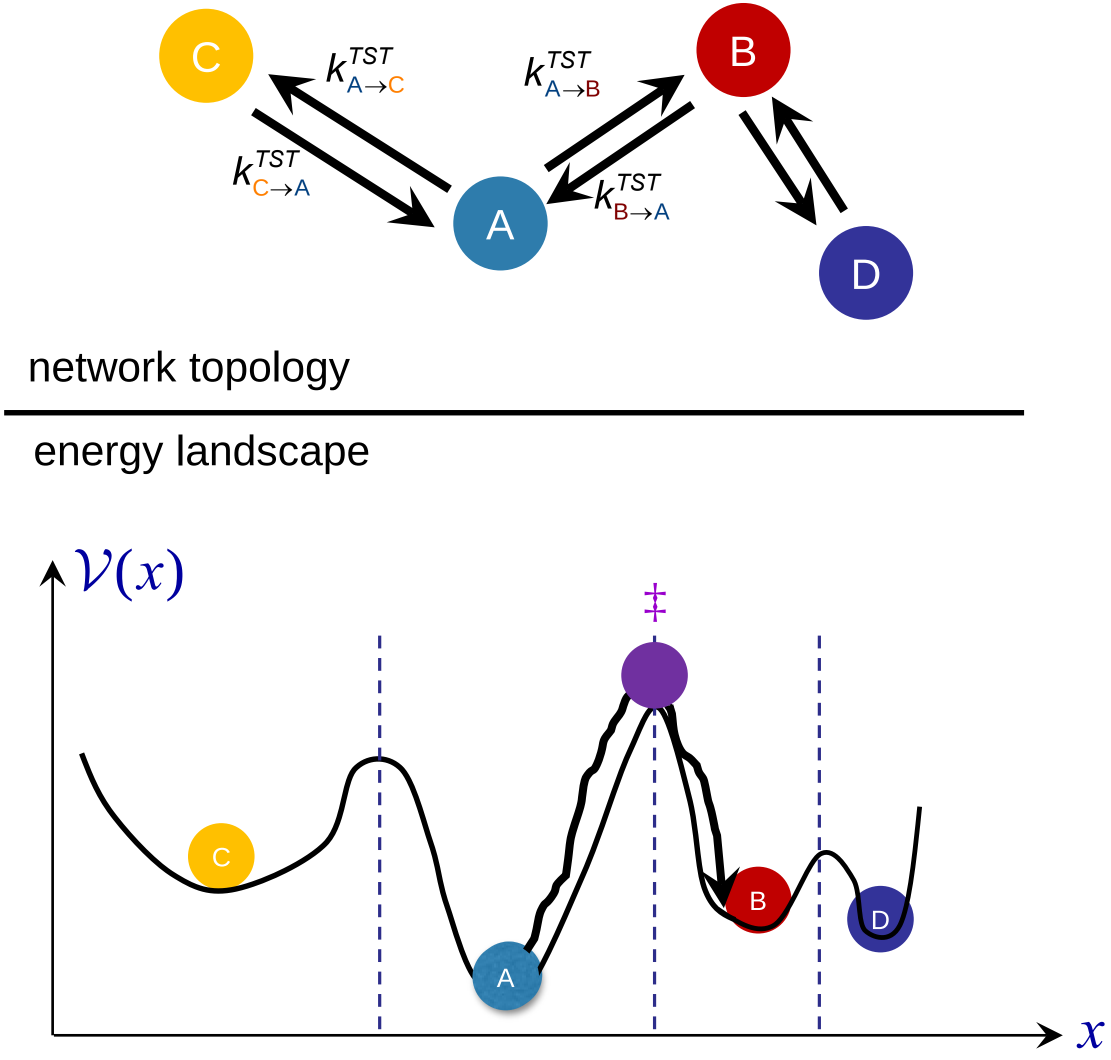


200 computational "specimens", $p$=1 bar

| Glassy atactic polystyrene (PS) | Computation | Experiment |
|---|---|---|
| Young's modulus $E$ (GPa), 300 K | 3.55 | 3.2-3.7 |
| $dE/dT$ (MPa/K) | -6.0 | -4.48 |
| Poisson ratio $\nu$ | 0.35 | 0.33 |
| $d\nu/dT$ ($K^{-1}$) | 0.00022 | 0.00015 |

Lempesis, N; Vogiatzis, G.G.; Boulougouris, G.C.; van Breemen, L.C.A.; Hütter, M.; DNT, *Mol. Phys.* **2013**, *111*, 3430.

# Relaxation in glasses: Energy landscape picture



1.Determine saddle points out of initial basin A.

2. Discover new minima

3.Through each saddle point, determine reaction path

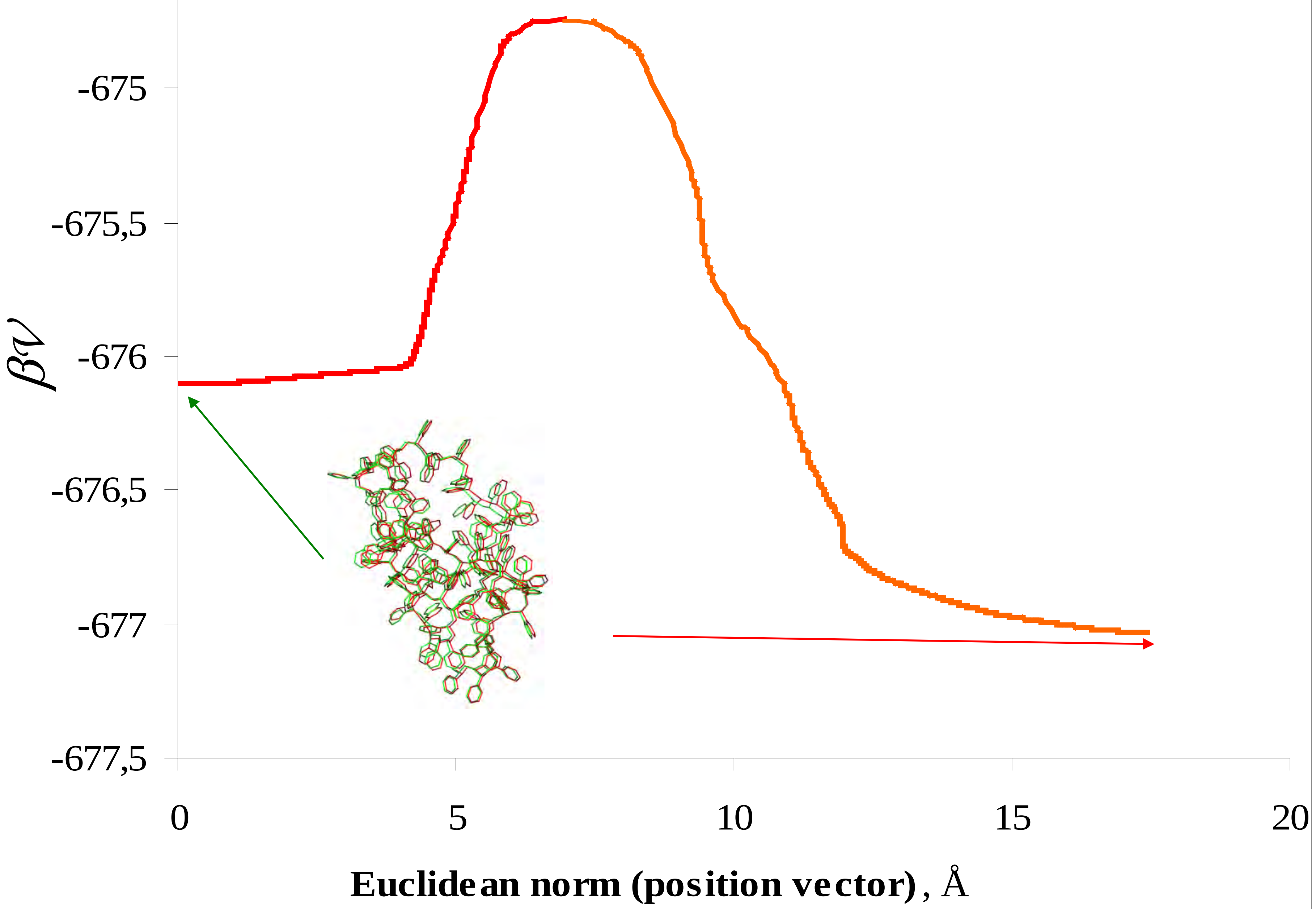
4.Calculate transition rates

$$k^{TST}_{A\to B} \propto \exp\left(-\frac{\mathcal{V}^{\ddagger}-\mathcal{V}_{A}}{k_{B}T}\right)$$

$$k^{TST}_{B\to A} \propto \exp\left(-\frac{\mathcal{V}^{\ddagger}-\mathcal{V}_{B}}{k_{B}T}\right)$$

# Energy profile along an elementary transition

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



# Creating a network of states

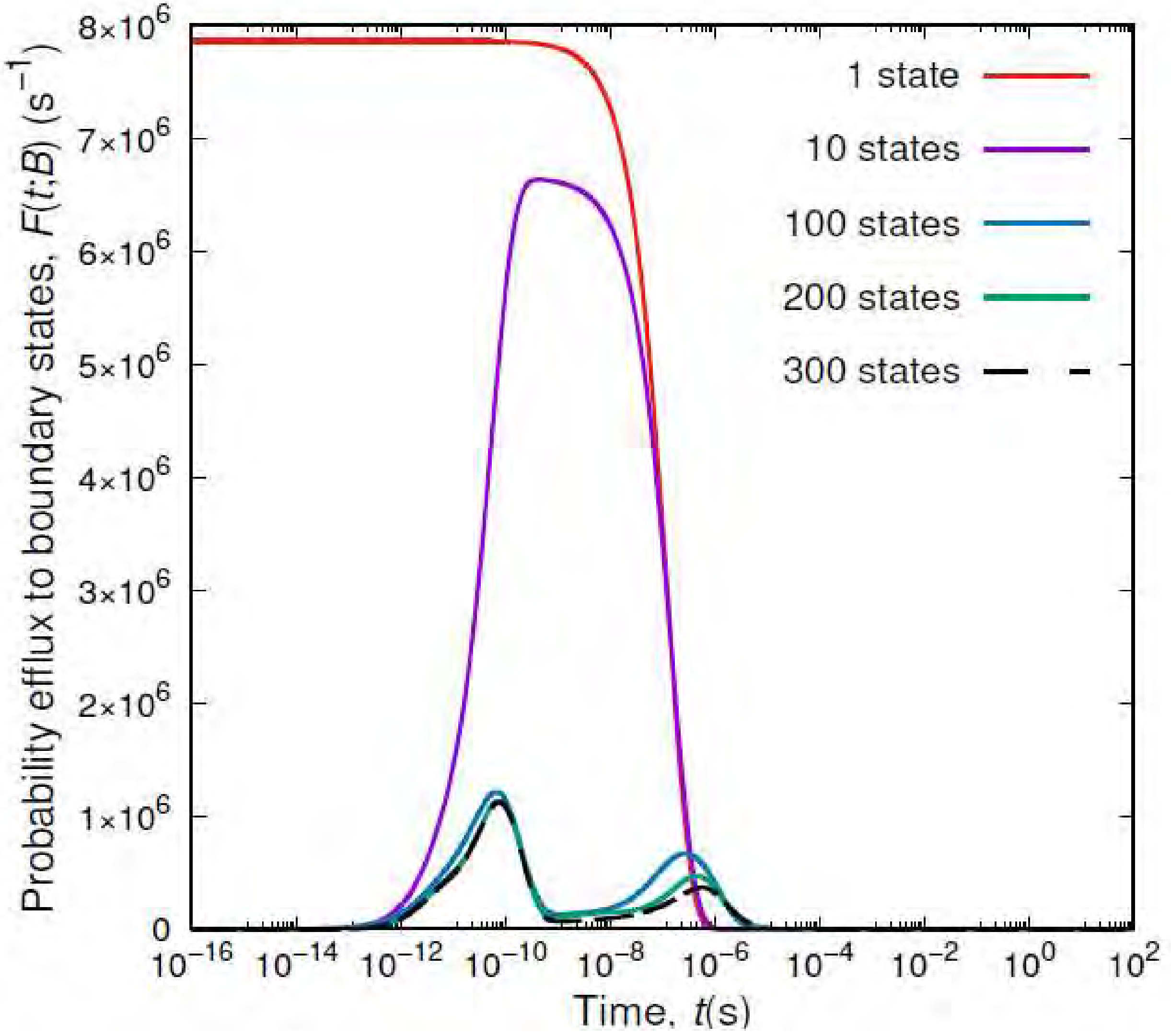
**Graph representation:** Vogiatzis, G.G.; van Breemen L.C.A.; Hütter, M.
*Macromol. Theor. Simul.* **2019**, 190036.

# Evaluating time-dependent probabilities

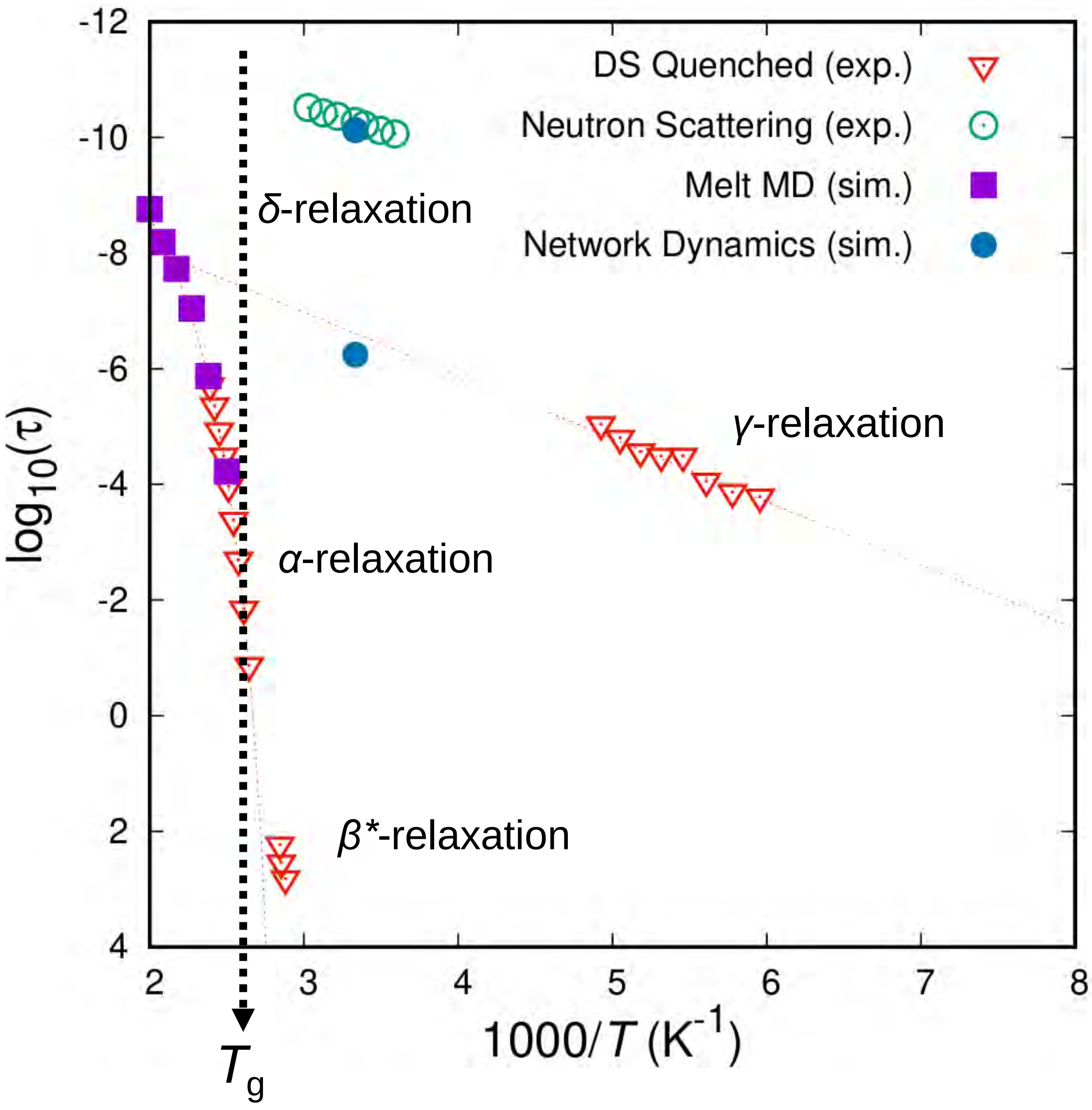
$$\frac{dP_i(t)}{dt} = \sum_{j\neq i} P_j(t)\, k_{j-}$$

Solution of Master Equation for probabilities of occupancy in the network of explored states, which is progressively augmented “on the fly”

# Probability efflux from the current set of explored states



# Revealing the molecular relaxations of atactic PS



Simulations:

**Network Dynamics:** Peaks of the probability efflux from the set of explored states.

**MD:** Characteristic times from orientational autocorrelation function of pendant bonds.

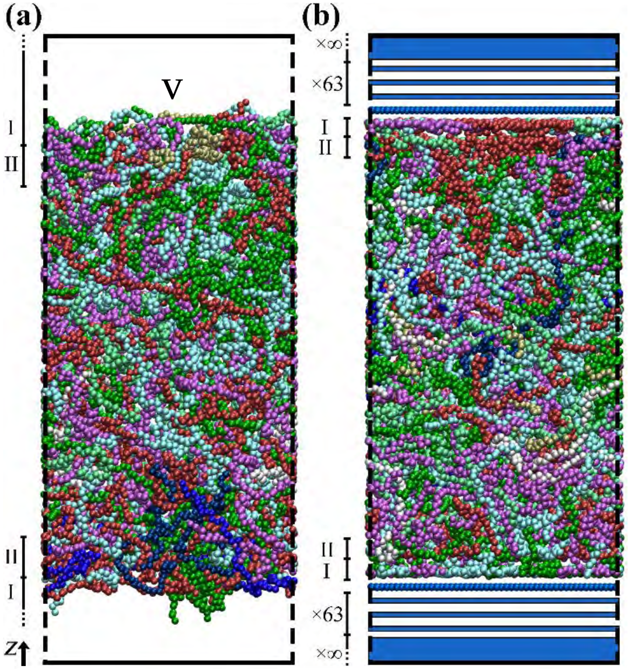
Experimental measurements:

**DS:** Grigoriadi, K.; Putzeys, T.; Wubbenhorst, M.; van Breemen, L.C.A.; Anderson, P.D; Hütter M. *J.Polym.Sci. B Polym. Phys.* **2019**, *57*, 1394.

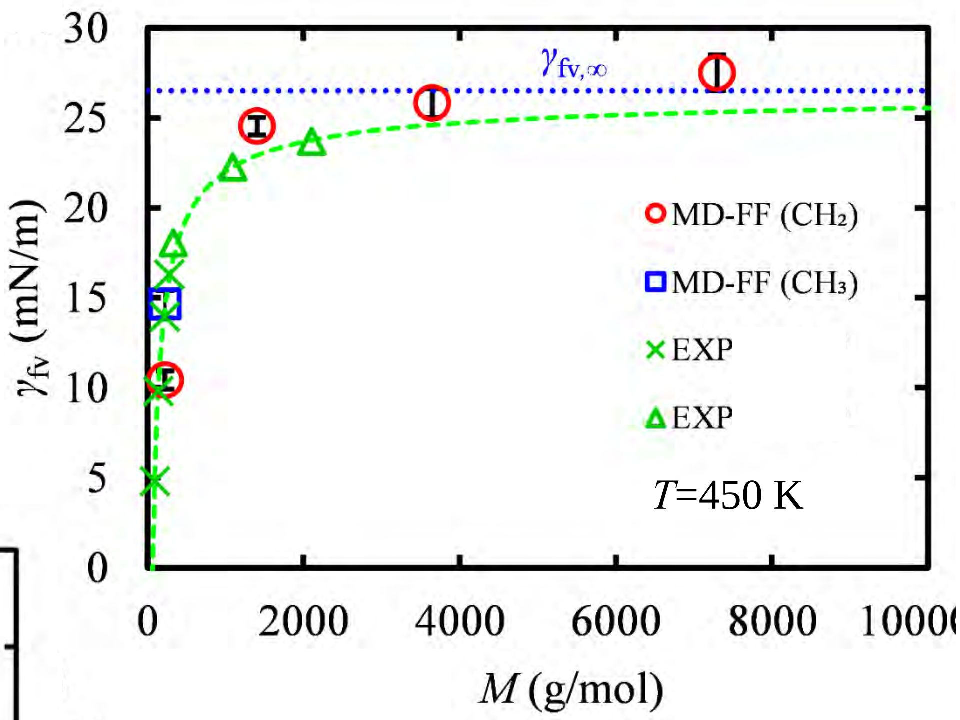
**Neutron Scattering:** Arrese-Igor, S.; Arbe, A.; Frick, B.; Colmenero, J. *Macromolecules* **2011**, *44*, 3161.

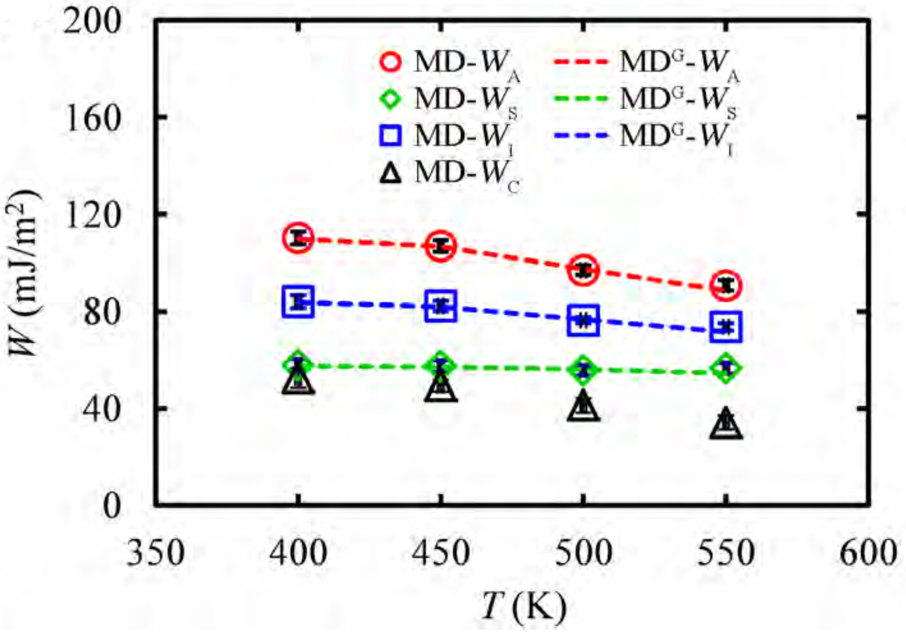
Vogiatzis, G.G.; van Breemen, L.C.A.; DNT; Hütter, M. *Comp. Phys. Comm*. **2020**, 248, 107008.

# Surface and interfacial thermodynamics



## polyethylene (f)/graphite (s)

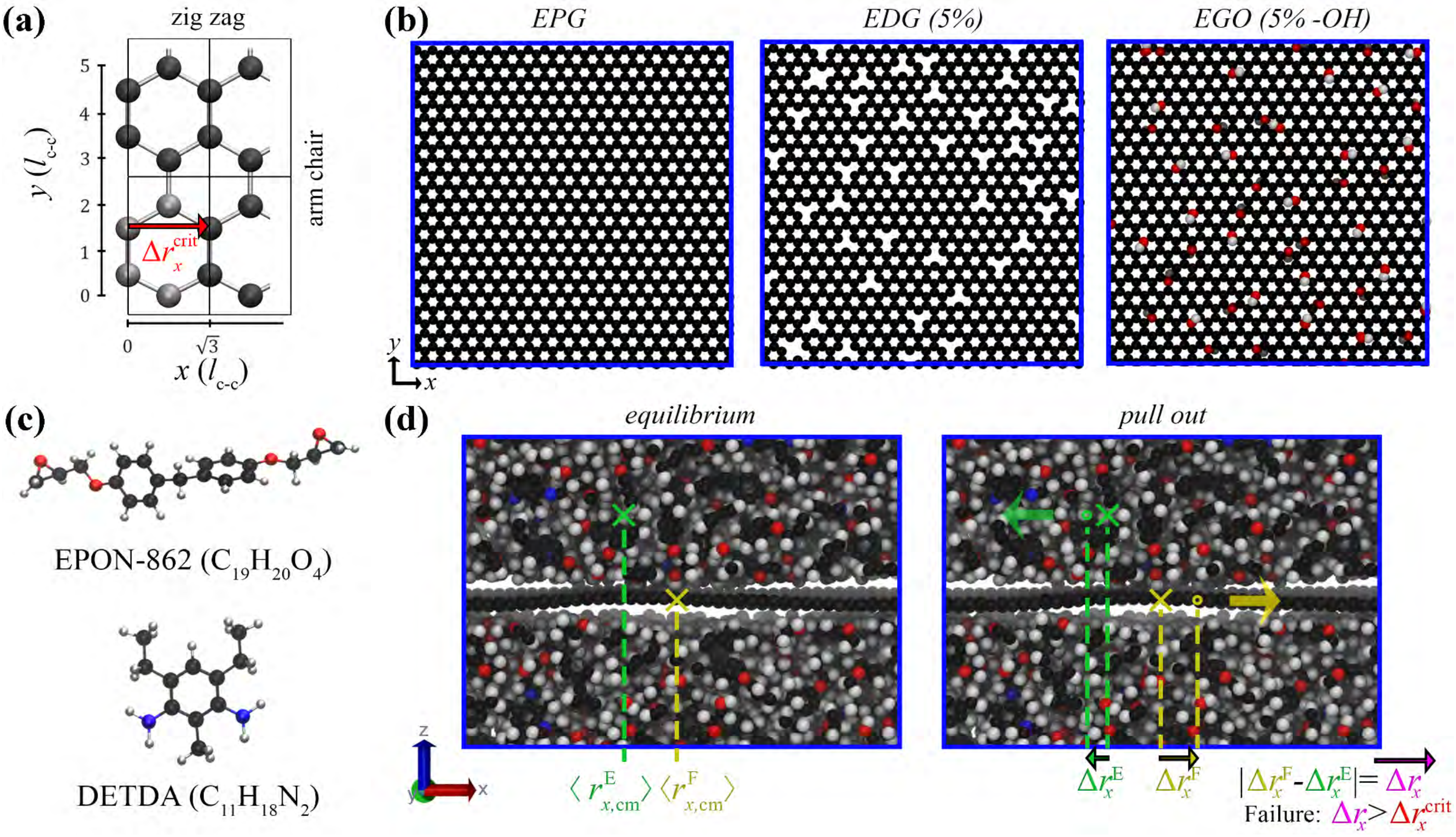




| | |
|---|---|
| $W_A=\gamma_{fv}+\gamma_{sv}-\gamma_{fs}$ | work of adhesion |
| $W_I=\gamma_{sv}-\gamma_{fs}$ | work of immersion |
| $W_S=\gamma_{sv}-\gamma_{fs}-\gamma_{fv}$ | work of spreading |
| $W_C=2\gamma_{fv}$ | work of cohesion |

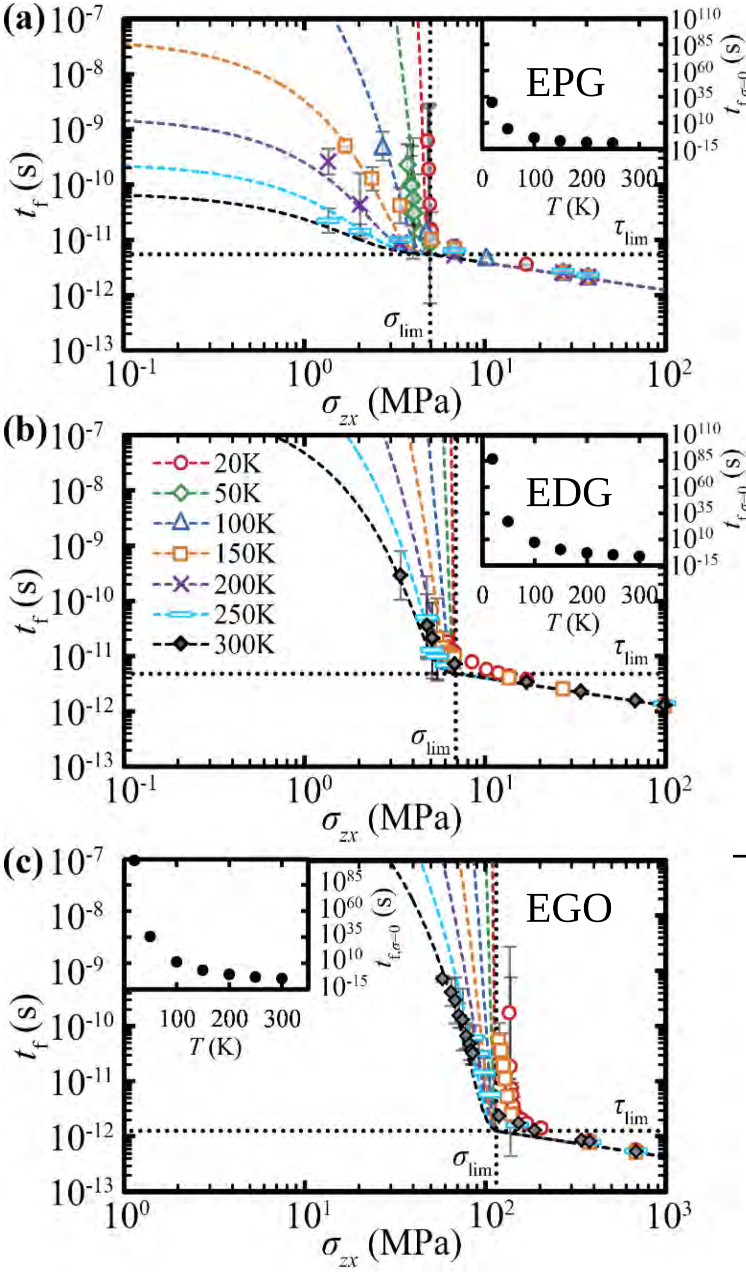
Sgouros, A.P.; Vogiatzis, G.G.;Kritikos, G.; Boziki, A.; Nikolakopoulou, A.; Liveris, D.; DNT *Macromolecules* **2017**, *50*, 8827.

# Epoxy/Graphene Interfacial Shear Strength



Kallivokas, S.V.; Sgouros, A.P. ; DNT *Phys. Rev. E* **2020**, *102*, 030501 (R)

# Epoxy/Graphene Interfacial Shear Strength



MD under shear, hazard analysis of times to failure at various temperatures

## Extended BAZ model (Boltzmann-Arrhenius-Zhurkov)

$$t_\mathrm{f} = \begin{cases} \tau_0 e^{\frac{U_0-\gamma\sigma_{zx}}{k_\mathrm{B}T}} + \tau_{\mathrm{lim}}, & \sigma_{zx} \le \sigma_{\mathrm{lim}} \\ \sqrt{2\rho_A \Delta r_x^{\mathrm{crit}} / \sigma_{zx}}, & \sigma_{zx} \ge \sigma_{\mathrm{lim}} \end{cases}$$

| System | $U_0$ (kcal/mol) | $\gamma$ ($\mathrm{nm}^3$) | $\sigma_{\mathrm{lim}}$ (MPa) | $\tau_{\mathrm{lim}}$ (ps) |
|---|---|---|---|---|
| (a) EPG | 3.9 | 5.4 | 5.0 | 5.5 |
| (b)EDG | 9.1 | 9.2 | 6.9 | 4.8 |
| (c)EGO | 11.1 | 0.7 | 114.9 | 1.2 |

Kallivokas, S.V.; Sgouros, A.P. ; DNT
*Phys. Rev. E*. **2020**, *102*, 030501 (R)

# Epoxy/EGO Interfacial Fracture

# Conclusions

- The challenge of long times and length scales in polymeric materials can be met through careful design of statistical mechanics-based multiscale modeling methods.
- Connectivity-altering Monte Carlo moves equilibrate long-chain melts, allowing topological analysis of entanglements.
- Hybrid particle/field mesoscopic simulations employing slip-springs capture linear and nonlinear viscoelastic properties.
- Structural relaxation in the glassy state can be tracked by solving the master equation for occupancy probabilities in a network of energy basins that is augmented “on the fly” as time elapses.
- Infrequent event analysis quantifies conditions for failure of nanocomposite interfaces under shear.
- Seamless connections between electronic, atomistic, mesoscopic, and continuum approaches, aided by machine learning, are leading to practical computer-aided materials design tools applicable in an industrial setting.

# Acknowledgments

- Dr. Aris Sgouros
- Dr. George Vogiatzis
- Dr. Spyros Kallivokas
- Dr. George Boulougouris
- Dr. Nikos Lempesis
- Dr. Grigorios Megariotis
- Dr. Christos Tzoumanekas
- Dr. Ariadni Boziki
- Ms. Anastasia Nikolakopoulou
- Dr. Stefanos Anogiannakis
- Dr. Krishna Pant
- Dr. Nikos Karayiannis
- Prof. Vangelis Harmandaris, U. Crete & Cyprus Inst.
- Prof. Vlasis Mavrantzas, U. Patras & ETHZ
- Prof. Markus Hütter, T.U. Eindhoven
- Prof. Lambèrt van Breemen, T.U. Eindhoven

LIMMAT STIFTUNG
Bridging Worlds

DPI
The Polymer
Research Platform

SOLVAY
asking more from chemistry®

ΕΛ.Ι.Δ.Ε.Κ.
Ελληνικό Ίδρυμα Έρευνας & Καινοτομίας

ΙΔΡΥΜΑ ΕΥΓΕΝΙΔΟΥ
1954

# Question and Answer Session

***Pr. Doros Theodorou***

National Technical University of Athens

***Dr. Marianna Yiannourakou***

*Materials Design*

# Announcement

## Upcoming

- Next Webinar: **Molecular Modeling of Kerogen Structure, Thermodynamic and Transport Properties**
- Presented by Dr. Marianna Yiannourakou, Materials Design
- June 26-28

# *MedeA* Modules for Polymers

***MedeA* Polymer Builder:** Creates models of isolated polymer chains, providing a foundation for building more complex models

***MedeA GIBBS***: *MedeA GIBBS* focuses on the prediction of fluid properties in various equilibrium conditions such as molecular liquids of complex structure, sorption in natural and industrial adsorbents, solubility of small compounds in polymer materials, and ion exchange.

***MedeA* Thermal Conductivity:** Calculate lattice thermal conductivity with Green-Kubo or non-equilibrium MD Müller-Plathe

***MedeA* Viscosity:** Calculate viscosity with Green-Kubo or non-equilibrium MD Müller-Plathe

***MedeA* Surface Tension:** Calculate surface tension of fluid slabs

***MedeA Amorphous Materials Builder: C***reate condensed phase models based on system chemical composition and target density. It eliminates lengthy mixing and amorphization simulations through realistic sampling of the translational, rotational, and conformational degrees of freedom of component species.

***MedeA* Thermoset Builder:** State-of-the-art methods for creating complex topologies of polymer networks in order to create strain-free molecular models with experimentally observed crosslink densities

***MedeA Mesoscale Builder***: Create models for simulations on the time and length scale of microseconds and tens of nanometers

# *MedeA* Modules for Polymers

***MedeA MT*****:** Elastic, mechanical and thermodynamic properties (also at finite temperature)

***MedeA* Deformation:** Perform deformation beyond the elastic regime

***MedeA* Phonon:** Phonon spectra and thermodynamic functions (vibrational free energy, heat capacities)

***MedeA* Deposition:** Atomistic scale simulation to study deposition, growth, oxidation and etching

***MedeA P3C:*** *C*omputes a wide range of properties using empirical correlations for any desired thermoplastic polymer or copolymer systems using correlative methods

***MedeA* Diffusion:** Automatically calculate diffusivity from mean square displacement

# *MedeA* Past Webinars on Polymer Simulations

**Mesoscale Simulations:** https://www.materialsdesign.com/webinars/recorded/Mesoscale-Simulations

**Use of Polymer Theoretical Concepts in Atomistic Polymer Simulation Software:**
https://www.materialsdesign.com/webinars/recorded/Use-of-Polymer-Theoretical-Concepts-in-Atomistic-Polymer-Simulation-Software

**Computational Polymer Science: Atomistic Modeling Tools and Materials Applications:**
https://www.materialsdesign.com/webinars/recorded/

**Using *MedeA*® to Study Formation and Properties of Polymer Networks:**
https://www.materialsdesign.com/webinars/recorded/Using-MedeA-to-Study-Formation-and-Properties-of-Polymer-Networks

**Use of Polymer Theoretical Concepts in Atomistic Polymer Simulation Software:**
https://www.materialsdesign.com/webinars/recorded/Use-of-Polymer-Theoretical-Concepts-in-Atomistic-Polymer-Simulation-Software

# Question and Answer Session

***Pr. Doros Theodorou***

National Technical University of Athens

***Dr. Marianna Yiannourakou***

*Materials Design*

# Questions about Materials Design Webinars

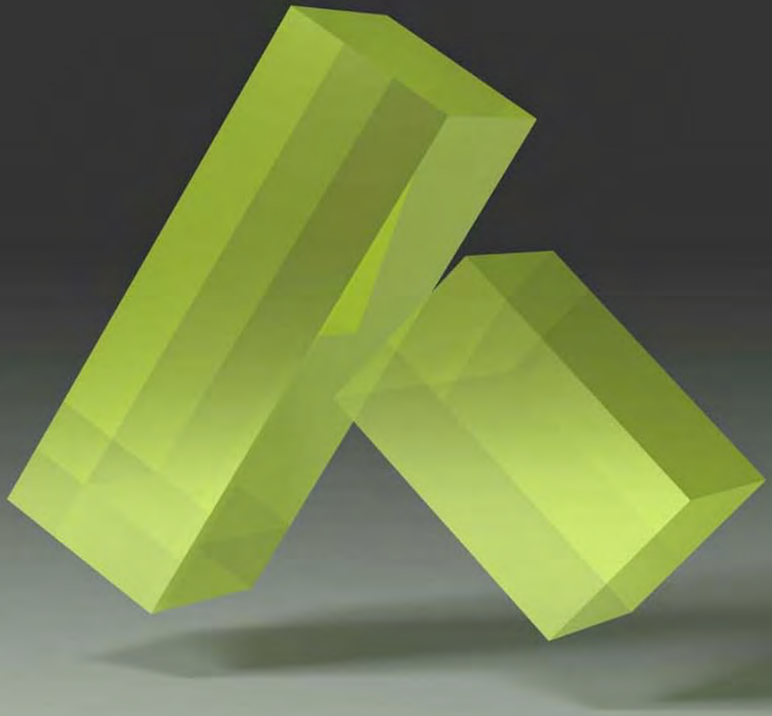
**Katherine Hollingsworth**

*khollingsworth@materialsdesign.com*

materials design

*info@materialsdesign.com*

*www.materialsdesign.com*



# MedeA

Innovation by Simulation