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Methods for Atomistic Simulations of Soft Matter

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Sandia National Laboratories

GSOFT Short Course

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Why do simulations?

Daan Frenkel: ‘In the past, we had to think about the role of simulations because they were expensive, now we have to think because they are (mostly) cheap.’

D. Frenkel, *Simulations: The dark side, Eur. Phys. J. Plus 128, 10 (2013)*

Outline

- why atomistic MD?
- force fields
- practical matters
  - codes
  - building starting states
  - timesteps, thermostats, etc
- properties
- what can we learn? some examples...

Why atomistic MD simulations?

Fundamental insight

- accurate molecular model for a particular material
  - structure-property relationships
  - direct comparisons with experiment
- molecular level information not obtainable from experiment
- new insights into material properties from synergistic work between experimentalists and simulators

Property predictions

- novel materials not yet synthesized
- materials that are difficult to measure
- molecular design

Atomistic MD of soft matter

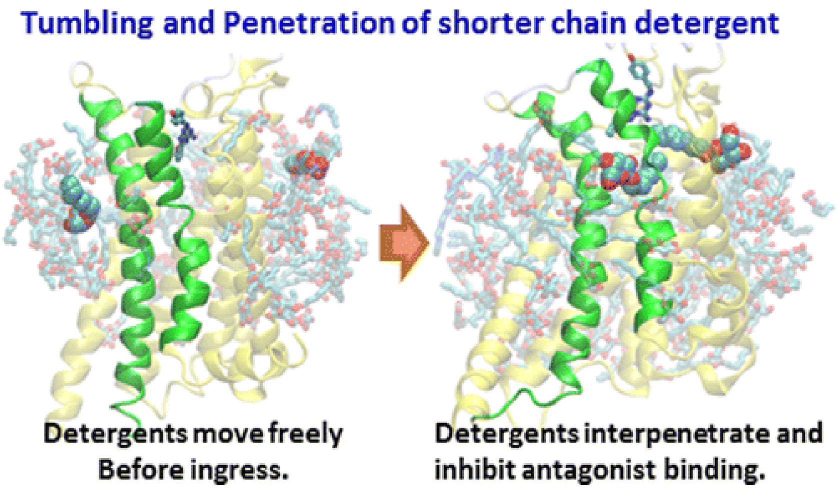
What kinds of systems do people study?

- biomolecules: proteins, peptides, DNA, RNA, lipids, ...
- polymers (often really oligomers)
- surfactants
- liquid crystals
- nanoparticles (often with attached ligands)

Properties/Phenomena

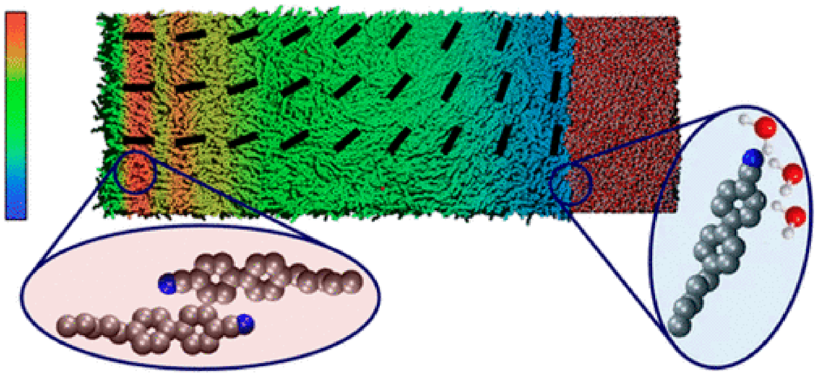
- morphology
- phase behavior
- self-assembly
- dynamics: transport, viscosity, structural transitions, ...

Atomistic MD of soft matter



detergent stabilization of G-protein coupled receptors

Lee, S., Mao, A., Bhattacharya, S., Robertson, N., Grisshammer, R., Tate, C. G., & Vaidehi, N. (2016). *JACS*, *138*, 15425–15433 http://doi.org/10.1021/jacs.6b08742

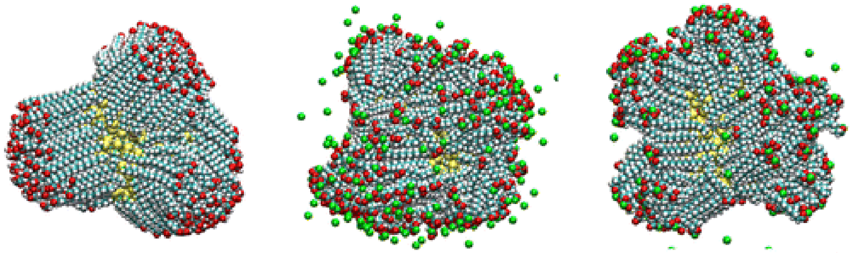


liquid crystals at interfaces

Ramezani-Dakhel, H., Sadati, M., Rahimi, M., Ramírez-Hernández, A., Roux, B., & De Pablo, J. J. (2017). *J Chem Theory Comp*, *13*, 237–244.

Atomistic MD of soft matter

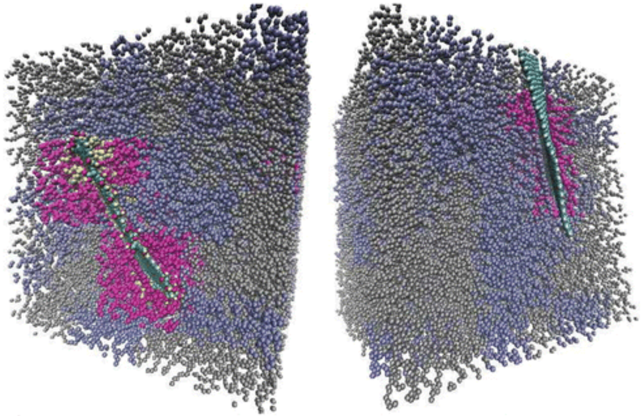
4 nm Gold Nanoparticles in Water



$S(CH_2)_{17}COOH$ $S(CH_2)_{17}COO^-Na^+$ $S(CH_2)_{17}COO^-Ca^{2+}$

gold nanoparticles with different ligands in water

Bolintineanu, D. S., Lane, J. M. D., & Grest, G. S. (2014). *Langmuir*, *30*, 11075–11085.



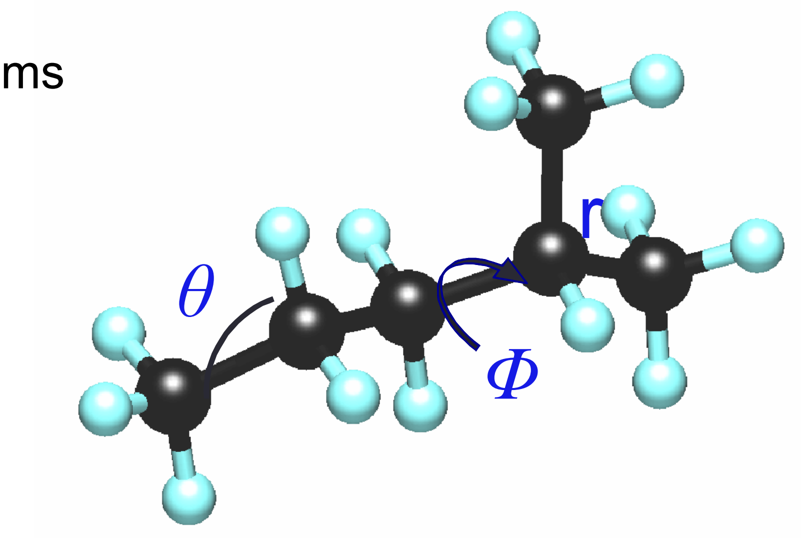
Carboxylated graphene Hydrogenated graphene

graphene sheets in PE or PEO

Bačová, P., Rissanou, A. N., & Harmandaris, V. (2015). *Macromolecules*, *48*(24), 9024–9038.

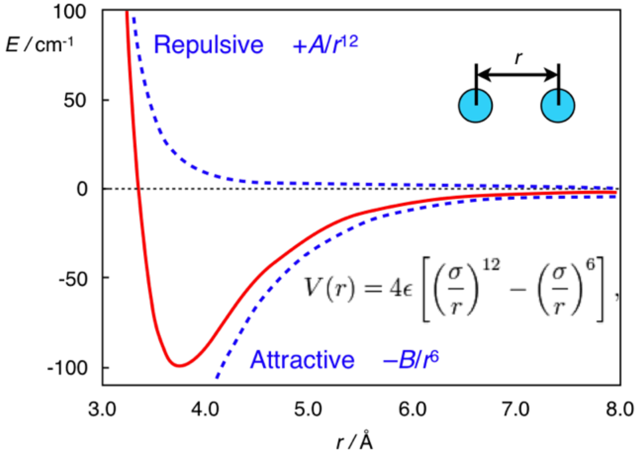
Force fields

interaction potential (energies) between atoms



- intramolecular
  - bonds
  - angles
  - torsions

- intermolecular
  - nonbonded, i.e. van der Waals
  - electrostatics (Coulomb)
  - polarizability



http://chemistry.stackexchange.com/questions/34214/physical-significance-of-double-well-potential-in-quantum-bonding

Typical form of an atomistic ff

example: OPLS-AA (all-atom optimized potentials for liquid simulations)

Jorgensen, W., Maxwell, D., & TiradoRives, J. (1996). *J Amer Chem Soc*, *118*, 11225–11236.

$$E_{bond} = \sum_{bonds} K_b \left(r - r_0\right)^2$$

$$E_{angle} = \sum_{angles} K_\theta \left(\theta - \theta_0\right)^2$$

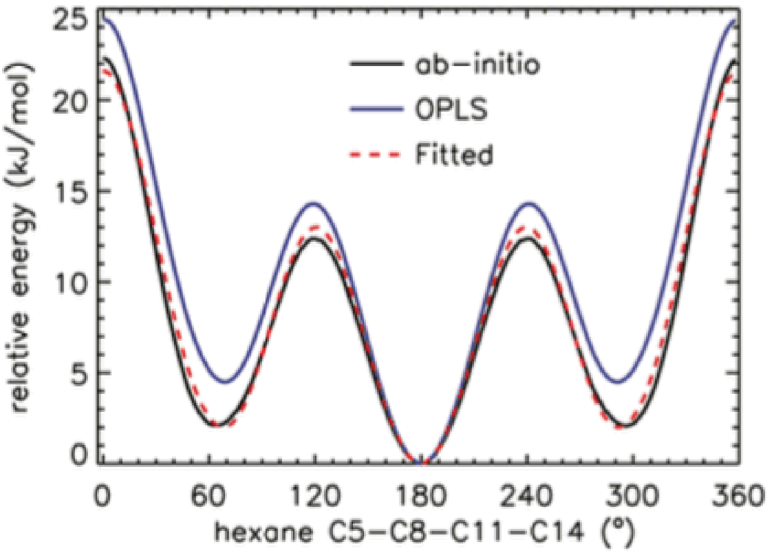
$$E_{torsion} = \sum_i \frac{1}{2} K_1^i \left[1 + \cos(\phi_i)\right] + \frac{1}{2} K_2^i \left[1 - \cos(2\phi_i)\right] + \frac{1}{2} K_3^i \left[1 + \cos(3\phi_i)\right] + \frac{1}{2} K_4^i \left[1 - \cos(4\phi_i)\right]$$

$$E_{ij} = \sum_i \sum_j \left[\frac{q_i q_j e^2}{r_{ij}} + 4\epsilon_{ij} \left(\frac{\sigma_{ij}^{12}}{r_{ij}^{12}} - \frac{\sigma_{ij}^6}{r_{ij}^6} \right) \right]$$

this is a lot of parameters!

Developing force fields

- bonded interactions:
  - bond stretch, angles: from spectroscopy of small molecules or ab initio
- torsions usually fit from *ab initio* (quantum chemistry) calculations
  - calculate energies for a suite of small molecules (gas phase)
  - fit to the functional form of the ff



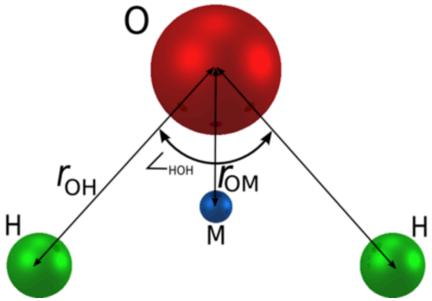
Siu, S. W. I., Pluhackova, K., & Böckmann, R. A. (2012). *J Chem Theory Comput*, *8*, 1459–1470. http://doi.org/10.1021/ct200908r

Developing force fields

- nonbonded interactions
  - often fit to experiment
    - run MD or MC simulation of several (many) molecules
    - compare to: densities, heats of vaporization, hydration energies, ...
    - iterate parameters to get agreement

- partial charges
  - calculate electrostatic potential from quantum chemistry
  - fit partial charges at atom centers

exception: water models often have charge not on an atom, e.g. TIP4P:



$q_M = -2q_H$

http://www.sklogwiki.org/SklogWiki/index.php/TIP4P/2005_model_of_water

More complexity in force fields

class II force fields

anharmonic terms like $H_3(\theta - \theta_0)^3$

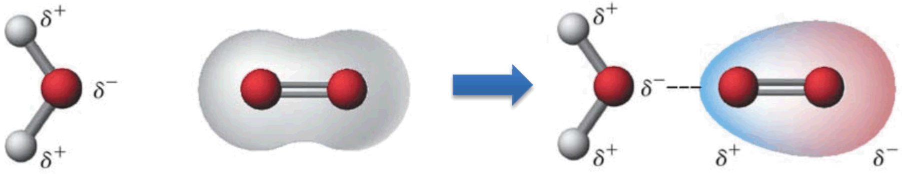
cross-terms like $F_{r\theta}(r - r_0)(\theta - \theta_0)$

polarizability

in reality, charge is not fixed—should respond to environment

include induced dipoles on atoms

$$U_{pol}(\mathbf{r}) = -\frac{1}{2}\sum_i \mu_i \cdot \mathbf{E}_i$$



from Lee-Ping Wang, Stanford

chemical reactions

allow bond formation/breaking

e.g. ReaxFF force field

Common force fields for soft matter

- OPLS-AA (Optimized Potentials for Liquid Simulations-All Atom)
  - Jorgensen group (Yale)
  - transferable; optimized in liquid state
- AMBER (Assisted Model Building with Energy Refinement)
  - originally for biomolecules, Kollman group (UCSF)
  - almost same functional form as OPLS
  - also an MD code
  - http://www.quimica.urv.es/~bo/MOLMOD/General/Forcefields/AMBER.html
- CHARMM (Chemistry at HARvard Macromolecular Mechanics)
  - www.charmm.org; led by Martin Karplus
  - also an MD code; free to academic users
  - for biomolecules

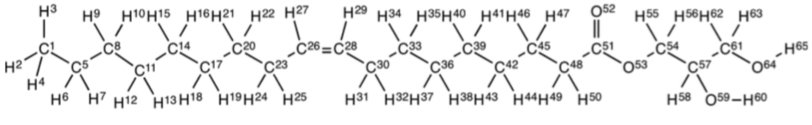
less common:

- COMPASS
  - a class II force field
  - available from Accelrys (not all parameters are published)
- DREIDING
  - Goddard group (CalTech)

Force field strongly affects properties

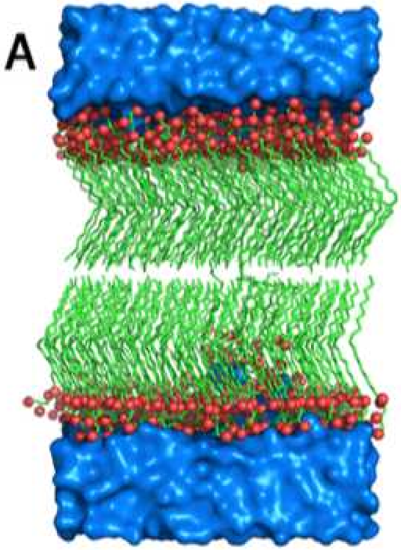
example: LOPLS-AA

refined to better treat long hydrocarbons
corrects phase behavior of surfactants

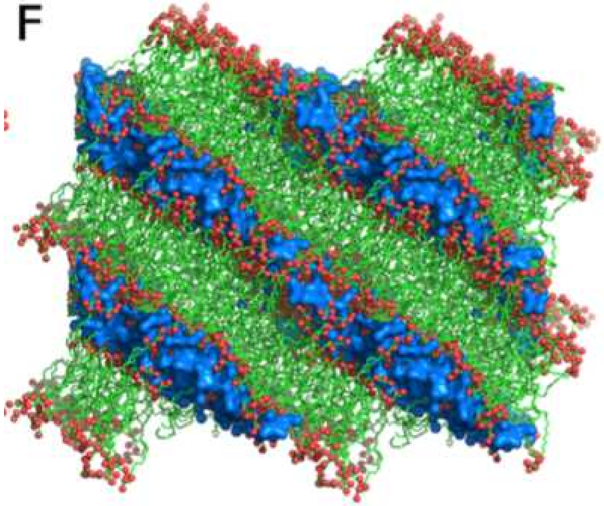


Monoolein (GMO)

incorrect gel phase with OPLS



correct liquid bilayer phase with LOPLS



Pluhackova, K., Morhenn, H., Lautner, L., Lohstroh, W., Nemkovski, K. S., Unruh, T., & Böckmann, R. A. (2015). *J Phys Chem B*, *119*(49), 15287–15299. http://doi.org/10.1021/acs.jpcb.5b08569

Open source MD codes

- LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator)
    - lammps.sandia.gov
    - general code materials science code
    - includes OPLS, CHARMM, Amber ffs
- NAMD (Not Another Molecular Dynamics program)
    - http://www.ks.uiuc.edu/Research/namd/
    - designed for biomolecular systems
    - scales to very large systems
    - integrated with VMD
- GROMACS
    - www.gromacs.org
    - primarily designed for biomolecules
    - faster than LAMMPS for some systems

see also:
https://en.wikipedia.org/wiki/Comparison_of_software_for_molecular_mechanics_modeling

Building starting states

need a good starting configuration for simulations

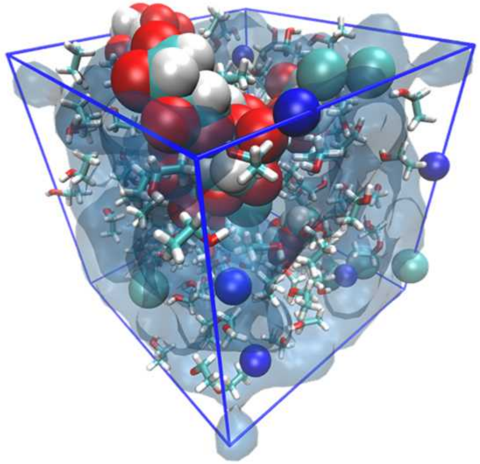
options:

- write your own builder
- use a commercial code like Materials Studio (see: http://accelrys.com/products/collaborative-science/biovia-materials-studio/)
- for biomolecules, download a pdb structure
  - e.g. from the Protein Data Bank, http://www.rcsb.org/pdb/home/home.do
  - can use tools in VMD to fill with water, etc.
- PACKMOL (http://www.ime.unicamp.br/%7Emartinez/packmol/home.shtml)
- build with a Monte Carlo code
  - MCCCS Towhee (http://towhee.sourceforge.net)
  - EMC (http://montecarlo.sourceforge.net)

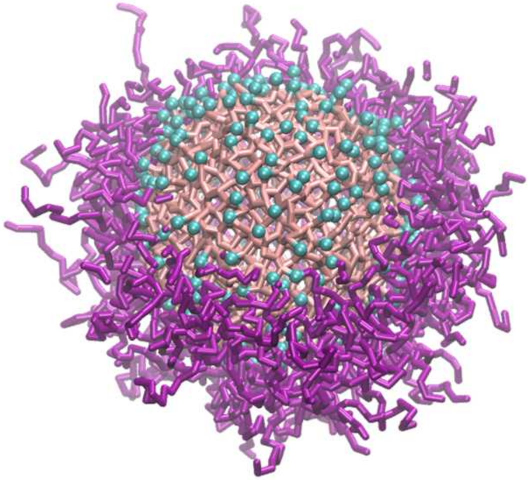
Example: building with EMC

EMC: Found at http://montecarlo.sourceforge.net/

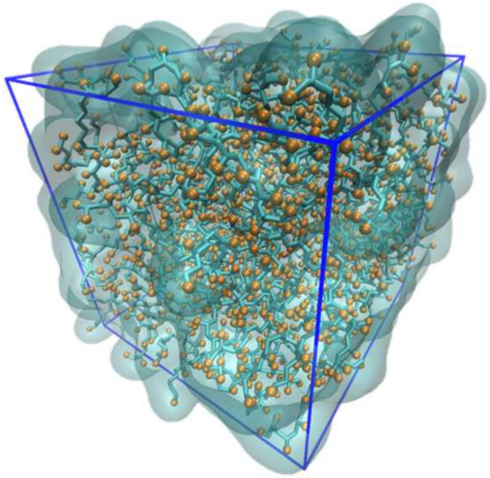
Pieter J. in 't Veld,
ROM/AM, Soft Matter Modeling



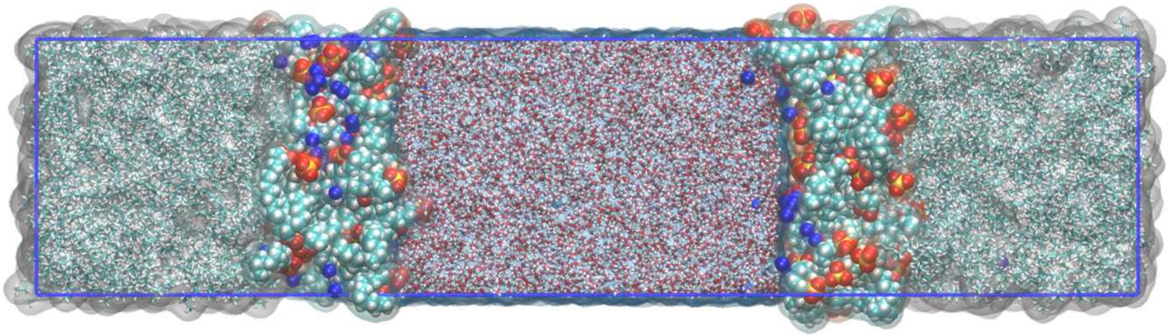
bulk



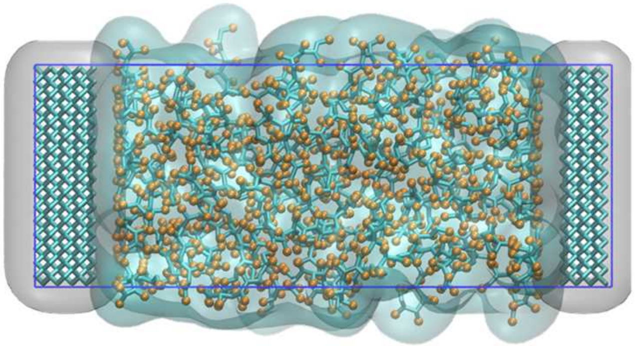
grafting



copolymers



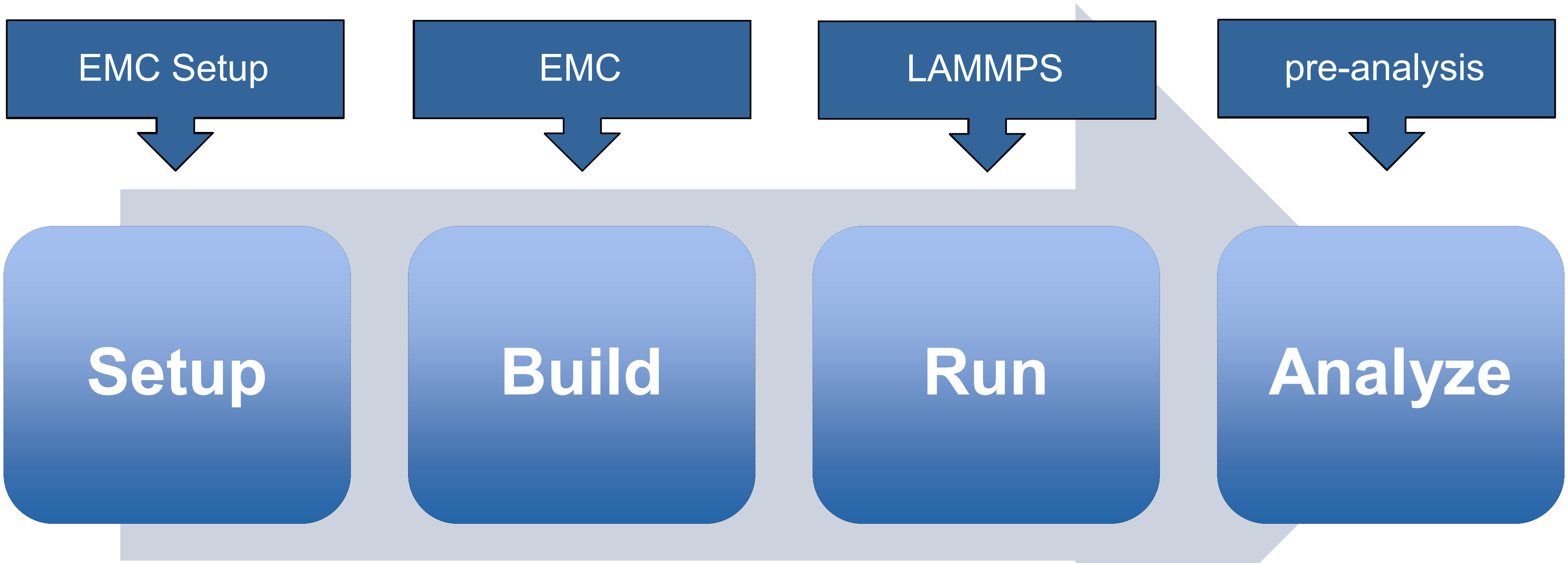
multiphase



surfaces

Workflow for Simulations

Check $EMC_ROOT/examples/setup



- Force field: PCFF, OPLS, CHARMM, TraPPE
- N, P, ρ, T
- Chemical composition
- Selection of phases
- Supports polymers

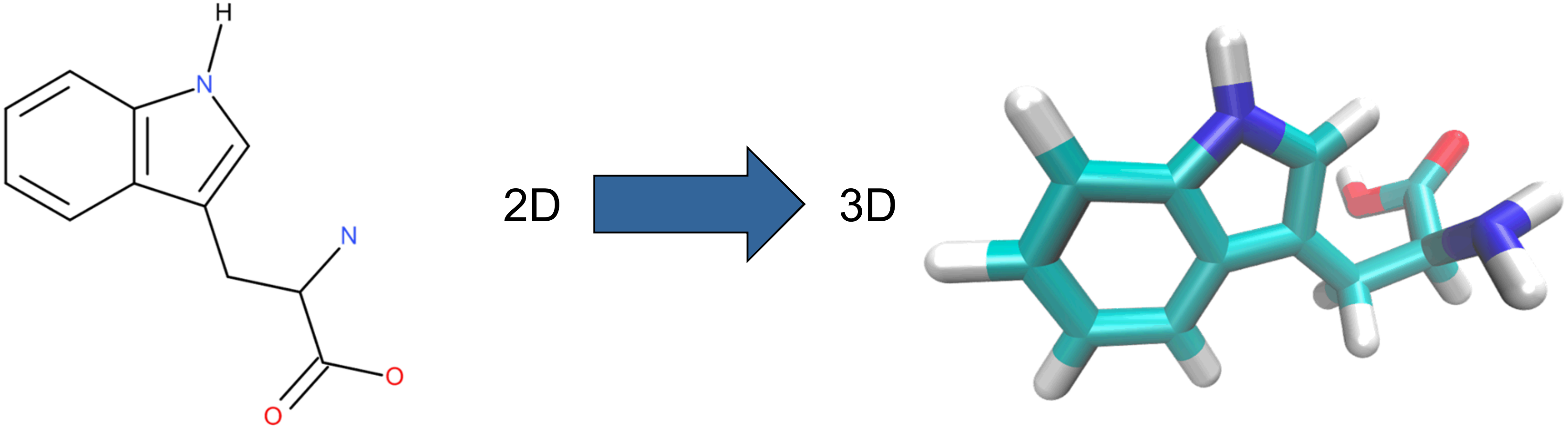
- Input for EMC generated by setup
- Textual format, which can be altered
- Builds condensed phases

- Input for LAMMPS generated by setup
- Holds analysis (e.g. pressure, volume, density profiles etc.)

- Allows for pre-analysis for further data processing

Molecular Structure Investigations

Coupling between 2D and 3D



- Chemical input uses SMILES
- Example: tryptophan (build based on COMPASS force field)
  - Draw structure with Biovia Draw (or JChemPaint (Freeware))
  - Obtain SMILES (both Biovia Draw and JChemPaint convert)
  - Build with EMC (resulting structure dependent on random seed)

Overview

Advantages and Capabilities

- http://montecarlo.sourceforge.net/
- Freeware under GPL v3.1
  - Source code in C
  - Command line with scripting interface
  - Wrap-around setup script
- Advantage over commercial solutions
  - Flexible scripting
  - Can build and graft surfaces in condensed media
  - Can build multiphase systems
- Structure builds in
  - Gas phase
  - Condensed phase (also polymers)
- Algorithms
  - Inverse Monte Carlo (CCB growth)
  - Local spatial incremental relaxation
  - Composite core exclusion
- Applications
  - Atomistic and coarse-grained structures
  - Mechanical, rheological and interfacial properties

Overview

Features

- Documentation
- Setup script (emc_setup.pl) creates
  - EMC build script
  - LAMMPS input script
- Multiple force fields
  - AA (PCFF, OPLS-AA, CHARMM)
  - UA (OPLS-UA, TraPPe)
  - CG (DPD, SDK, MARTINI, Colloidal)

- Algorithms
  - Inverse Monte Carlo (CCB growth)
  - Local spatial incremental relaxation
  - Composite core exclusion
- EMC build script output
  - LAMMPS data files
  - PDB/PSF and VMD script for use with VMD

Thermostats/barostats

- Nosé-Hoover recommended for atomistic simulations
  - add extra variables to equations of motion
    - couple to particle velocities (control T)
    - couple to system dimensions (control P)
  - has a conserved quantity (extended Hamiltonian)
  - generates the NVT/NPT ensemble

    ...in the right conditions (center of mass velocity = 0)

can modify to rigorously generate canonical ensemble with Nosé-Hoover chains
this is the default option in LAMMPS!

damping parameters:
too large: large fluctuations
too small: long time to equilibrate

rules of thumb:
temperature damping ~ 100 timesteps
pressure damping ~1000 timesteps

Berendsen thermostat: does not generate a canonical ensemble
(used to be default in GROMACS)

Time scale issues

in atomistic simulations, need to resolve high frequency oscillations, e.g. C-H bonds

→ time step of 0.1 .... 1 fs

practical time scale of atomistic MD:
ps to 100s of ns (if willing to run a long time...)

heroic MD: μs

can not parallelize time

Time steps

- For polymers, highest frequency modes typically from bond potential:

$$U_b(r) = k_b(r-r_0)^2/2$$

- C-H bond (OPLS)[1]

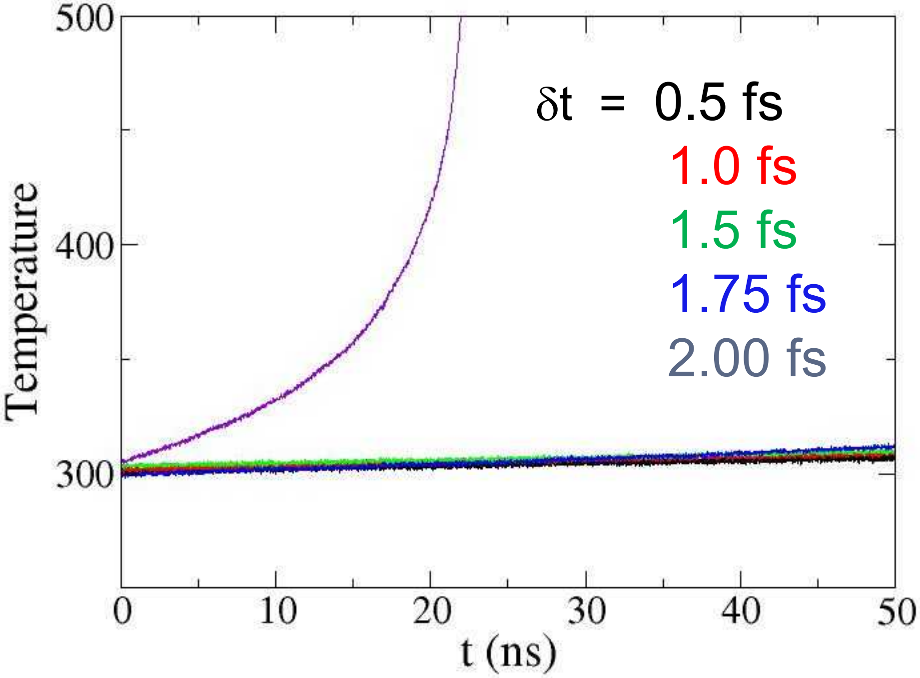
$$k_b = 680 \text{ Kcal mol}^{-1} \text{ Å}^{-2}$$

- $\omega_b \approx 0.5 \text{fs}^{-1}$

  $t_b = 2\pi/\omega_b \approx 12 \text{ fs}$

- High temperature, system becomes anharmonic: $\delta t \downarrow$

Decane T=300K



courtesy of Gary Grest

Ways to accelerate simulations

SHAKE, RATTLE	fix bonds and/or angles allows larger time steps often used on H atoms

rRESPA: Reversible Reference System Propagator Algorithms

Integrate Bond, Angle, Dihedral, van der Waals (LJ), k-space with different time steps
  - LAMMPS – up to 4 time steps

Example: Decane (300K) δt =1.5 fs, 38 ns/day, 64 cores (6400 atoms)
rRESPA – δt =4.5 fs for k-space, 1.5 fs all other interactions, 48 ns/day

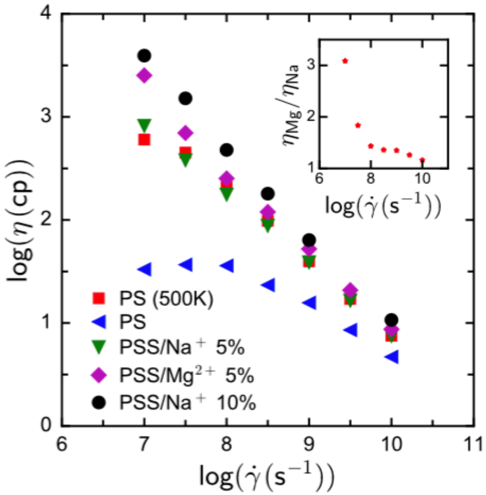
Tuckerman, Berne and Martyna, J. Chem. Phys. 97, 1990 (1992)

Consequences of time scales

- equilibrium: need to run long enough to reach equilibrium
    - not practical for e.g. long polymers (reptation time ~ $N^{3.4}$)
    - biomolecules: may have structural transitions on long time scales

- nonequilibrium:
    - imposed deformations often happen too fast
        - shear or strain rates: often unrealistically fast
        - temperature quenches: orders of magnitude faster than experiment
            - difficult to simulate glassy systems
    - NEMD often in nonlinear regime

viscosity of PSS



Agrawal, A., Perahia, D., & Grest, G. S. (2016). *Phys Rev Lett*, *116*(15), 158001

How do we know if our simulation is accurate?

- compare to experiment
- compare to previous well-established simulation results
- check conservation laws/statistical mechanical relations
  - eg constant energy in NVE ensemble

- calculate the same quantity with two methods
  - example: Green-Kubo expressions vs nonequilibrium simulation

Special techniques

- free energy calculations
  - requires multiple simulations
  - WHAM, thermodynamic integration
- nonequilibrium MD (NEMD)
- parallel tempering
- combined MD-MC
- metadynamics
- ....

Calculating dynamic properties

- from equilibrium fluctuations
  - i.e. time correlation functions with Green-Kubo formalism
  - often best to calculate in NVE ensemble
- from nonequilibrium simulations
  - be careful with thermostatting

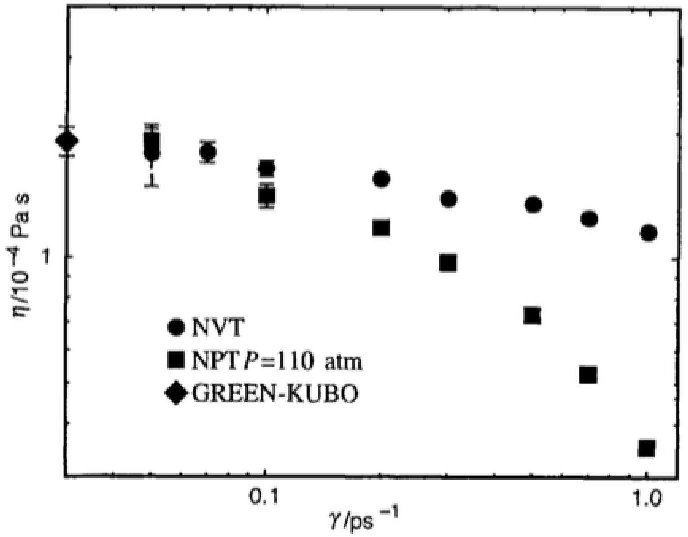
fluctuation-dissipation theorem

example: shear viscosity

Green-Kubo: $\eta = \frac{V}{k_B T} \int_0^\infty \langle P_{xz}(0) P_{xz}(t) \rangle \, dt$

NEMD: $\eta = -\sigma_{xz}/\dot{\gamma}$

shear viscosity of n-decane



Mundy, C. J., Balasubramanian, S., Bagchi, K., Siepmann, J. I., & Klein, M. L. (1996). *Faraday Discussions*, *104*(0), 17–20.

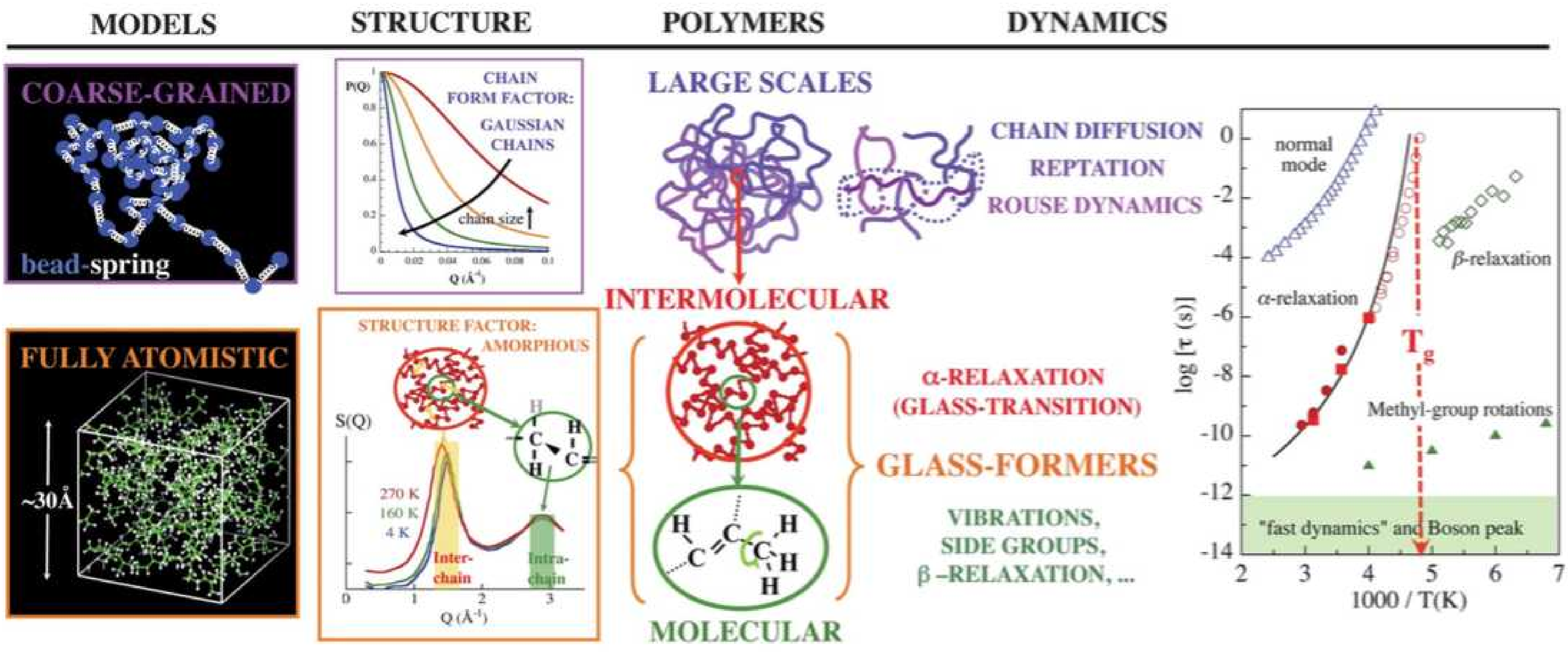
Calculating dynamic properties

- NEMD methods:
  - pro: intuitive to understand, quick to converge
  - con: unphysically large velocity profiles and momentum fluxes

- Green-Kubo method:
  - pro: equilibrium simulation, can use smaller system
  - con: slower to converge
  - con: hard to tell when correlation integral has converged

Atomistic MD and scattering

generally overlap well in length and time scales
many opportunities for collaboration with experimentalists!

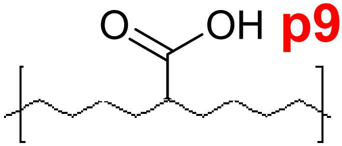


Arbe, A., Alvarez, F., & Colmenero, J. (2012). *Soft Matter*, *8*(32), 8257.

What can we learn?

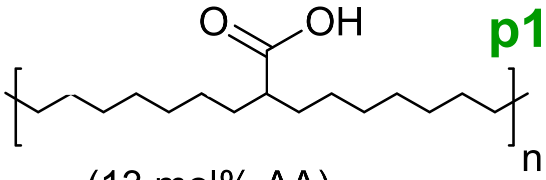
a personal example: atomistic simulations of ionomers

PE backbone with **precisely** spaced carboxylic acid functional groups



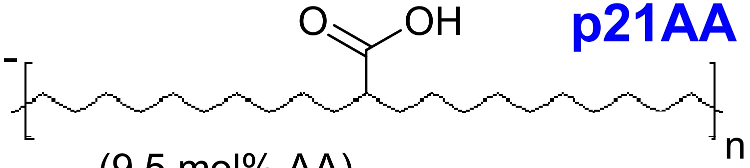
p9AA

(22 mol% AA)



p15AA

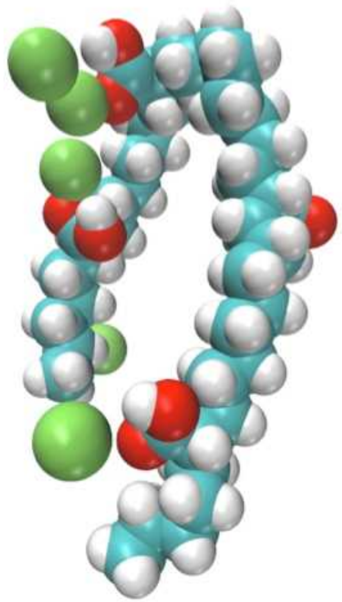
(13 mol% AA)



p21AA

(9.5 mol% AA)

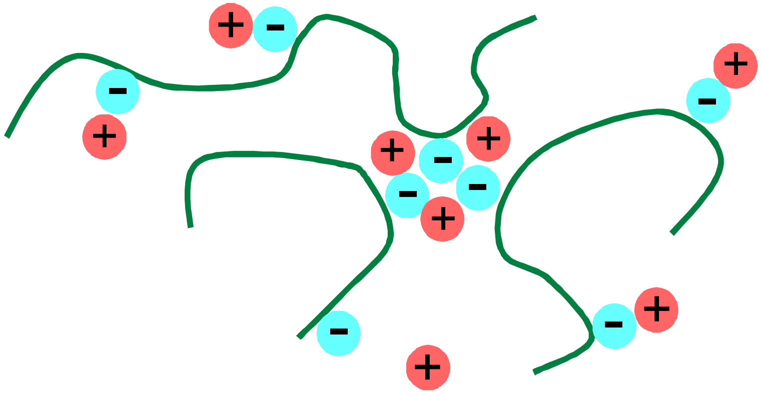
- All atom OPLS-AA force-field
- 80-200 polymers, n = 4 repeat units (4 acid groups)
    - ~ 64 Å box, total of ~25,000 atoms
- NVT ensemble, **150°C → well above T_g**
- 30 ns (400 ns in one case)
- LAMMPS



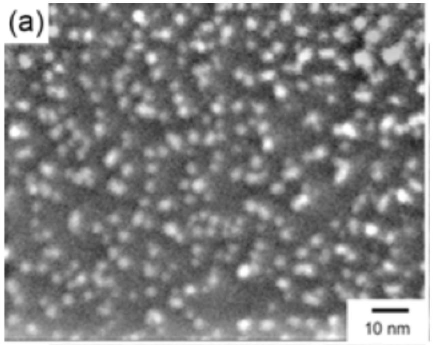
Goals

morphology: understand ion aggregate morphology

Coulombic forces favor aggregates
polymer entropy limits size



nm-scale ionic aggregates



ionic aggregates

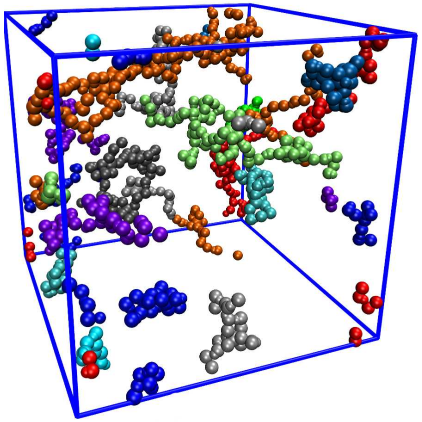
Seitz et al., J Am Chem Soc (2010) 132, 8165

dynamics: understand how morphology impacts polymer, ion dynamics

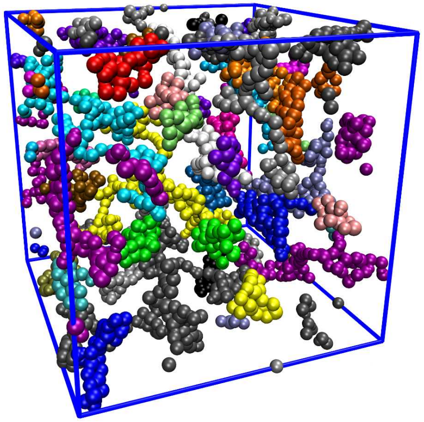
Morphology: Li-neutralized pAA

coloring by cluster

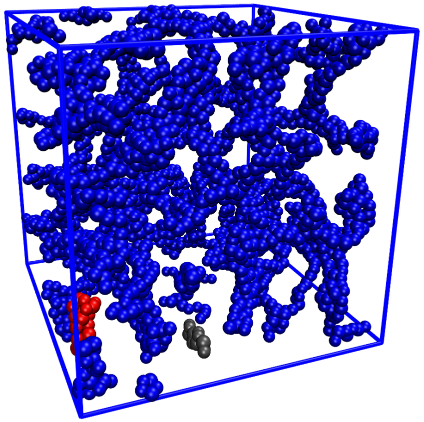
p9AA-10%Li



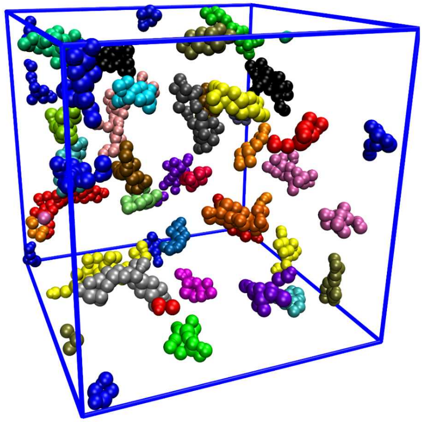
p9AA-43%Li



p9AA-100%Li



p21AA-43%Li



Bolintineanu et al, *ACS Macro Lett*, **2013**

Structure Factors from atomistic MD

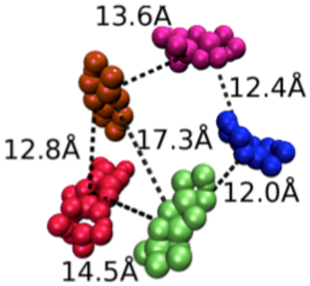
$$S(q) = \sum_i c_i f_i^2 + 4\pi\rho \int_0^\infty \frac{\sin(qr)}{qr} r^2 \sum_{i,j} c_i c_j f_i f_j \left(g_{ij}(r) - 1\right) dr$$

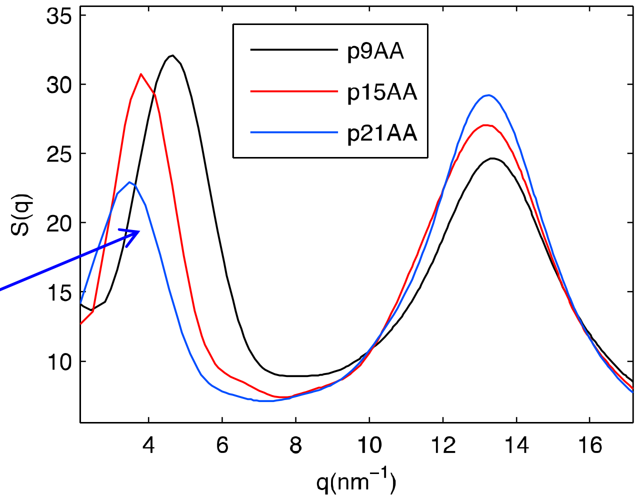
c_i = mole fraction of atom i

f_i = atomic scattering functions for x-rays

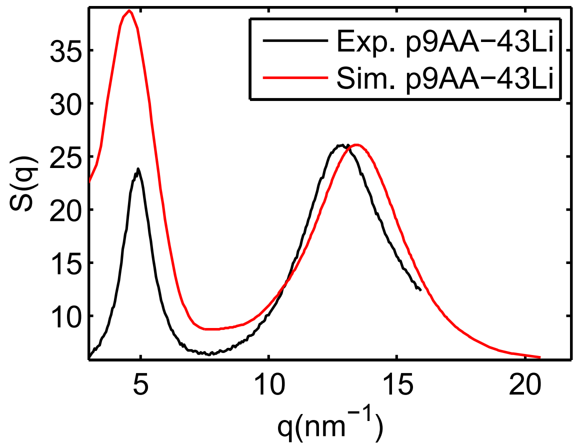
$$f_i = c_i + \sum_{k=1}^{5} a_{ik} \exp(-b_{ik} q_0^2)$$

coefficients are tabulated

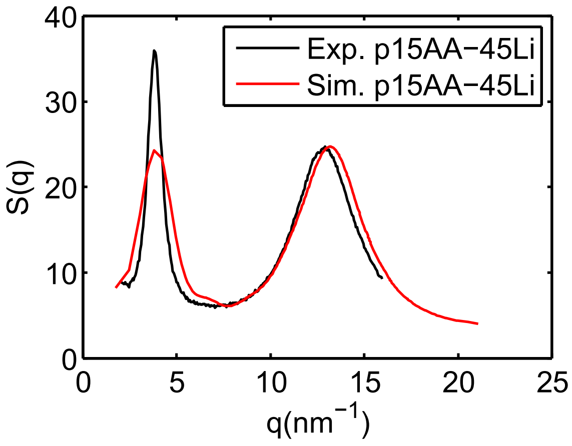




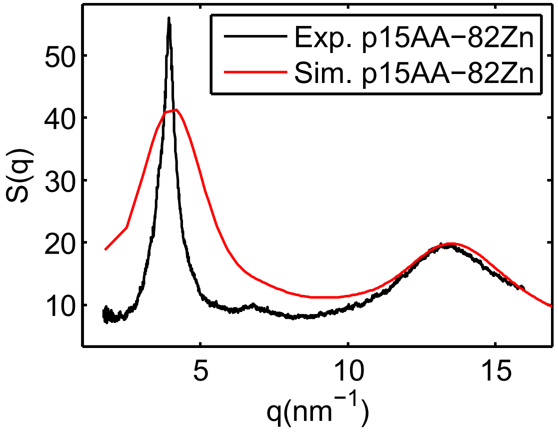
Direct Comparison to X-ray Scattering



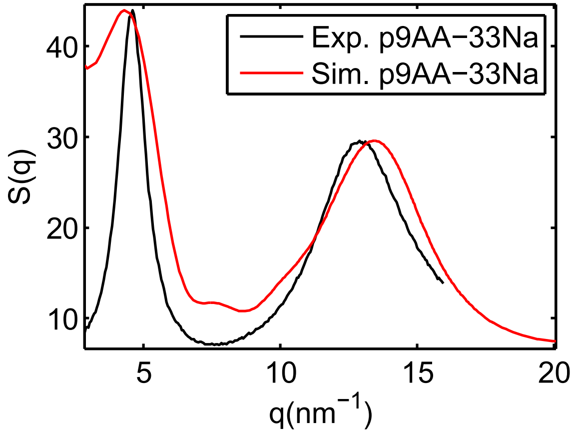
[1]



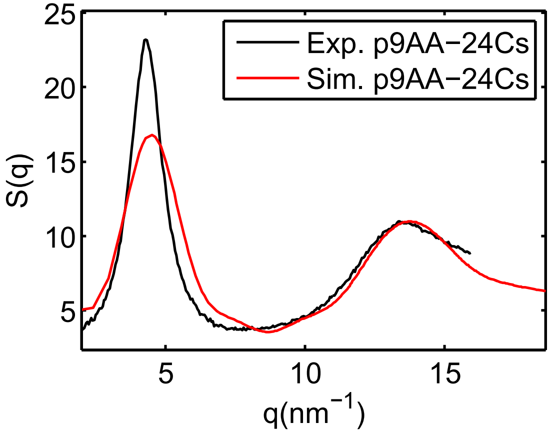
[1]



[2]



[1]



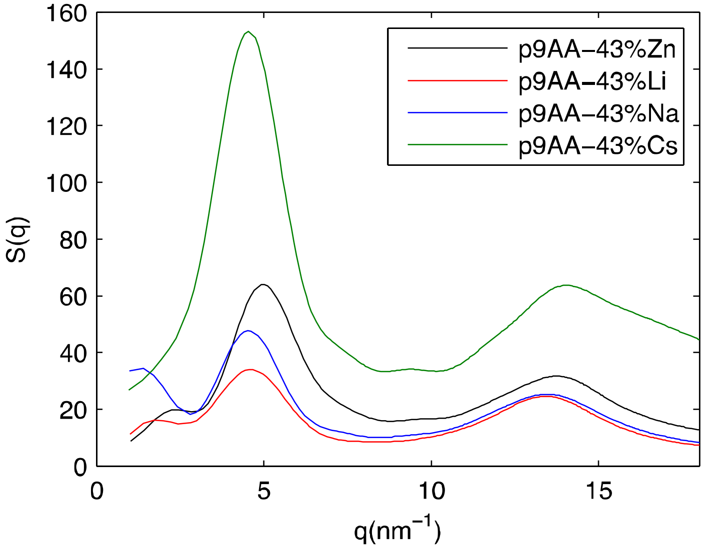
[1]

- 120°C, same neutralization
- S(q) scaled to match amorphous halo height

[1] Buitrago et al, MM 48,1210 (2015)
[2] Seitz et al, JACS 132, 8165 (2010)

- excellent agreement in peak positions
- good agreement in peak shapes

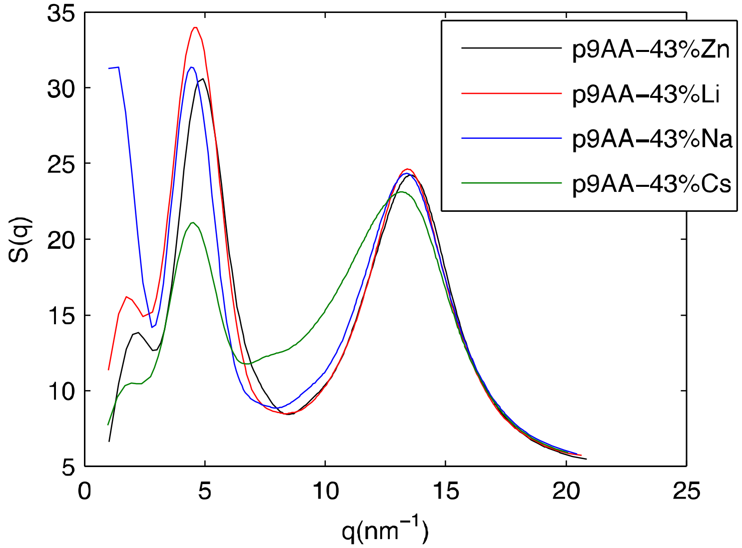
Extra insight from simulation



alchemy

Li$^+$ form factor for all ions

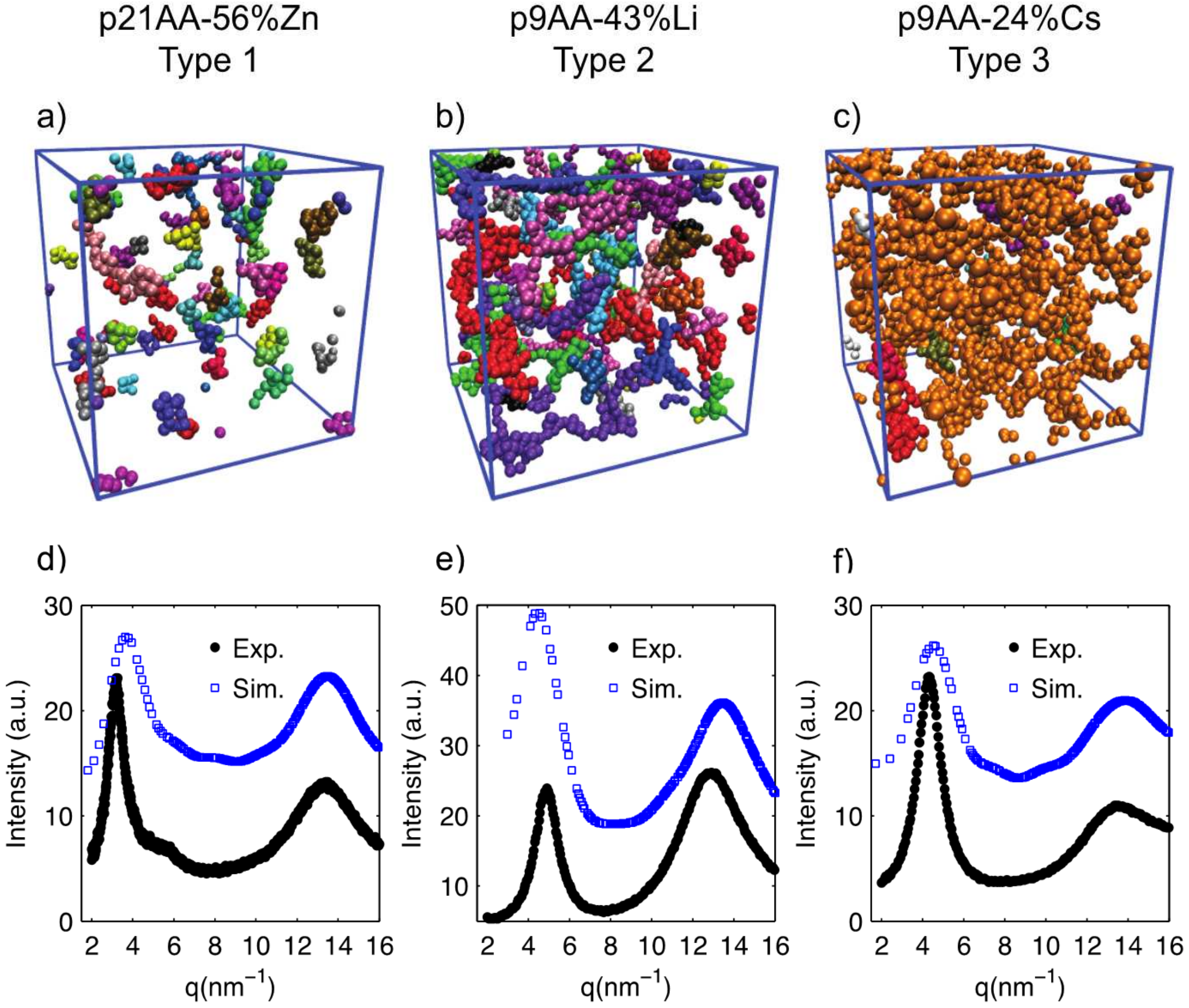
$f_M \rightarrow f_{Li}$



- many differences due to contrast only
- Cs changes short-range structure

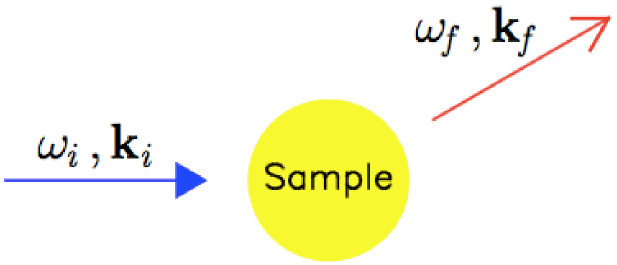
X-ray Scattering Doesn’t Determine Morphology

need simulations or imaging!



Buitrago, C. F. *et al. Macromolecules* **48,** 1210–1220 (2015).

Quasi-Elastic Neutron Scattering



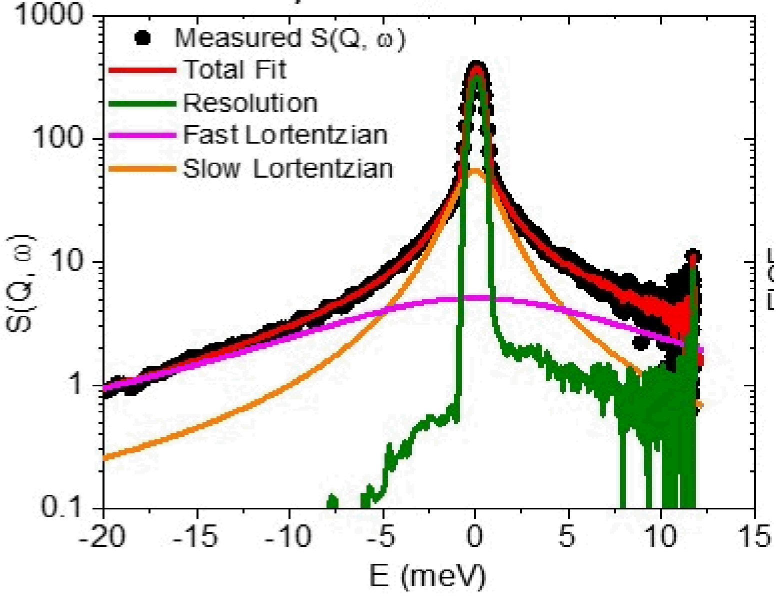
Energy transfer

$$E = \hbar\omega = \hbar(\omega_f - \omega_i)$$

Momentum transfer

$$\mathbf{P} = \hbar\mathbf{Q} = \hbar(\mathbf{k}_f - \mathbf{k}_i)$$

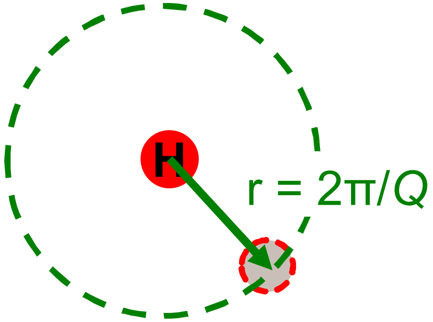
incoherent, inelastic: sensitive to self-motion of hydrogens
scattering intensity proportional to I(Q,ω)


a) DCS QENS

Dynamics: QENS and MD

$$S(Q,t) = \frac{\int S_{exp}(Q,\omega)e^{i\omega t}d\omega}{\int R(Q,\omega)e^{i\omega t}d\omega} \qquad S(Q,t) = \int G_s(r,t)\frac{r\sin(Qr)}{Q}dr$$

$G_s(r,t)$: given an atom was at r=0 at time t=0, the probability that the atom is at r at time t

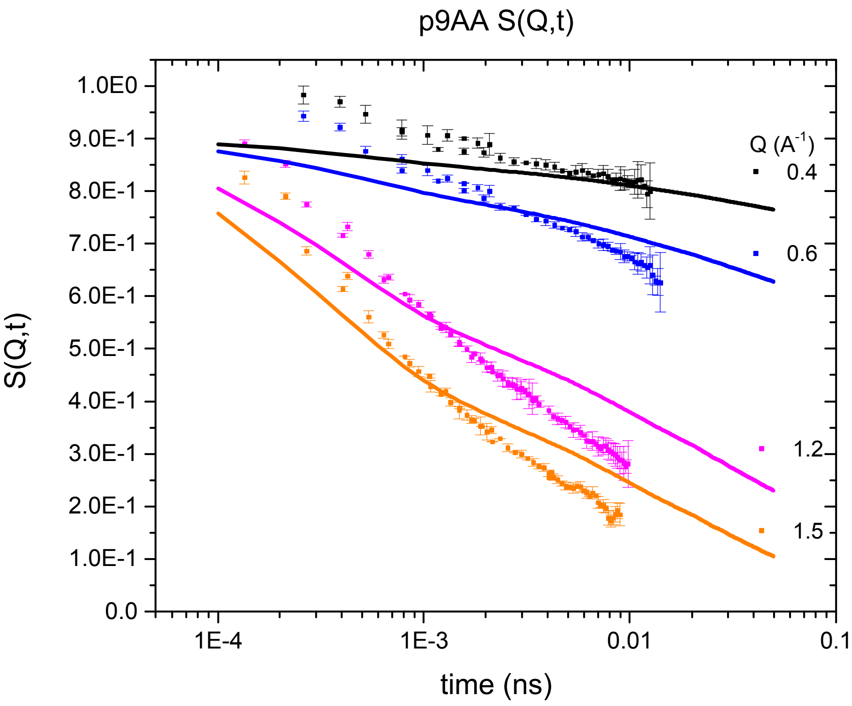


MD simulations

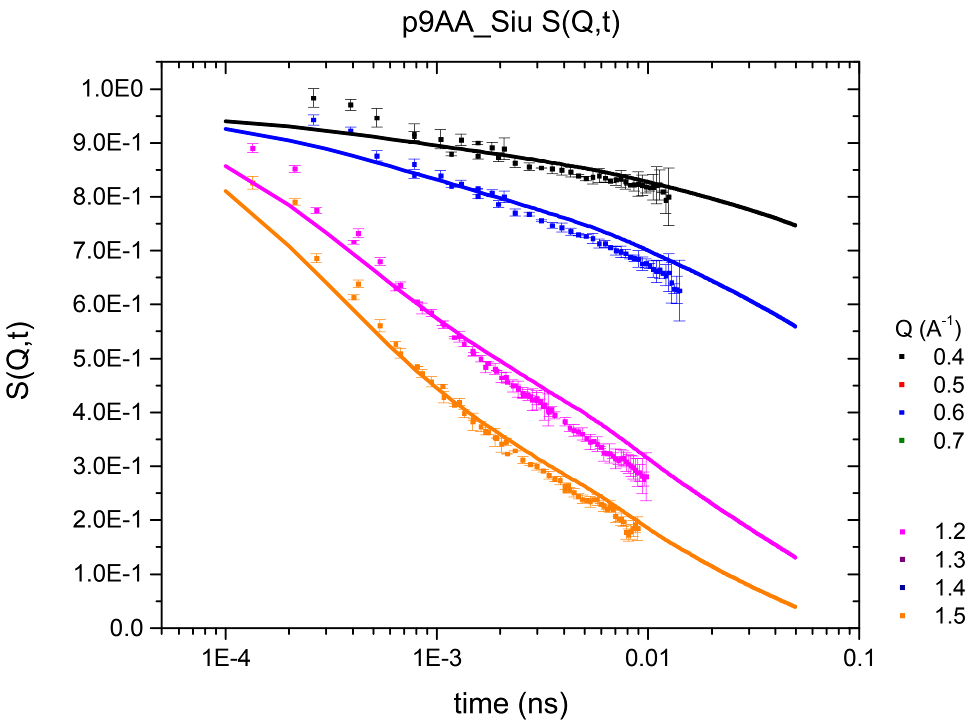
- calculate self-part of van Hove correlation function $G_s(r,t)$ for hydrogens
- exclude chain ends

Comparing to QENS to check force field

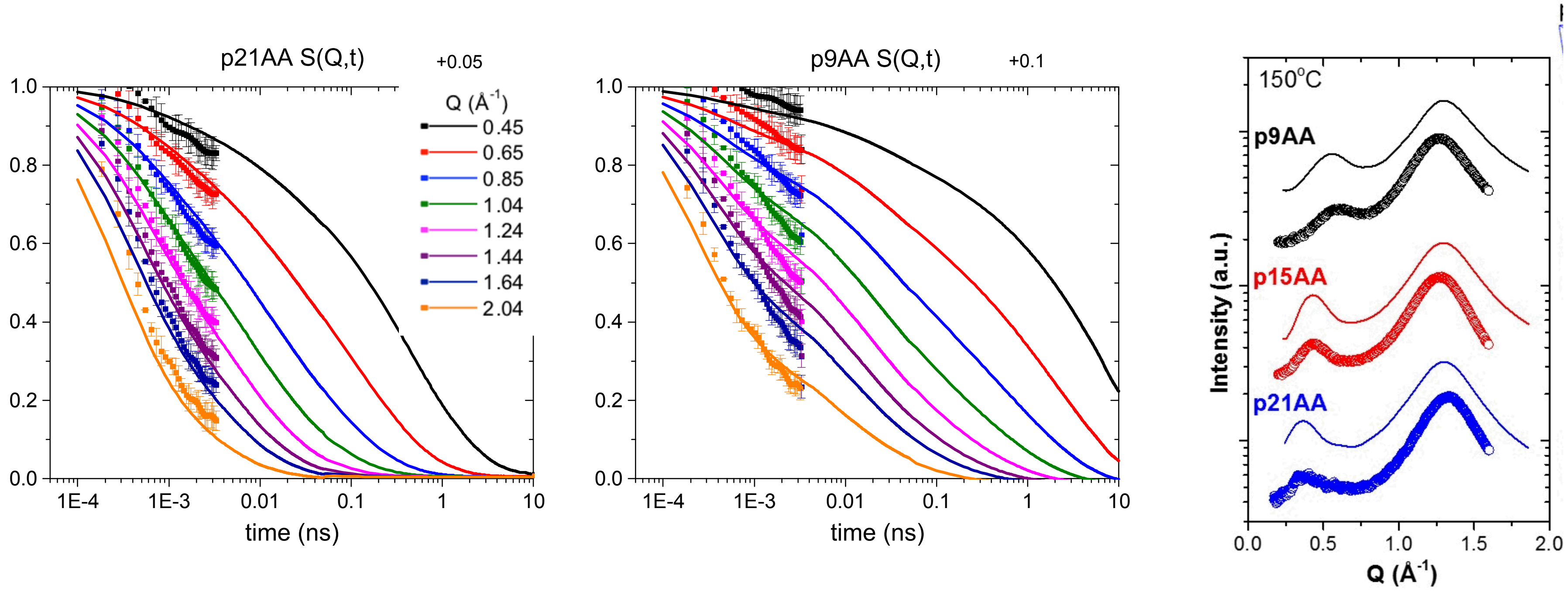
OPLS-AA



LOPLS-AA



Acid Copolymers



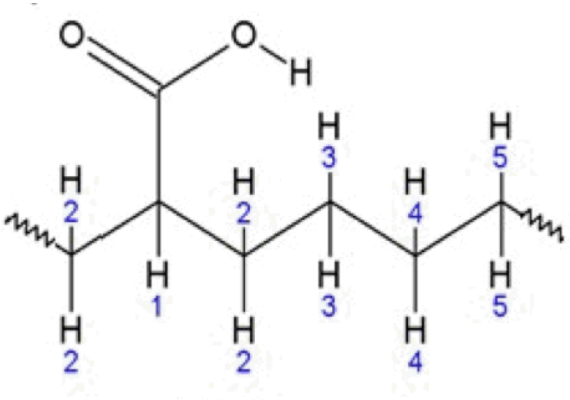
excellent agreement between QENS and MD

relevant length scales:

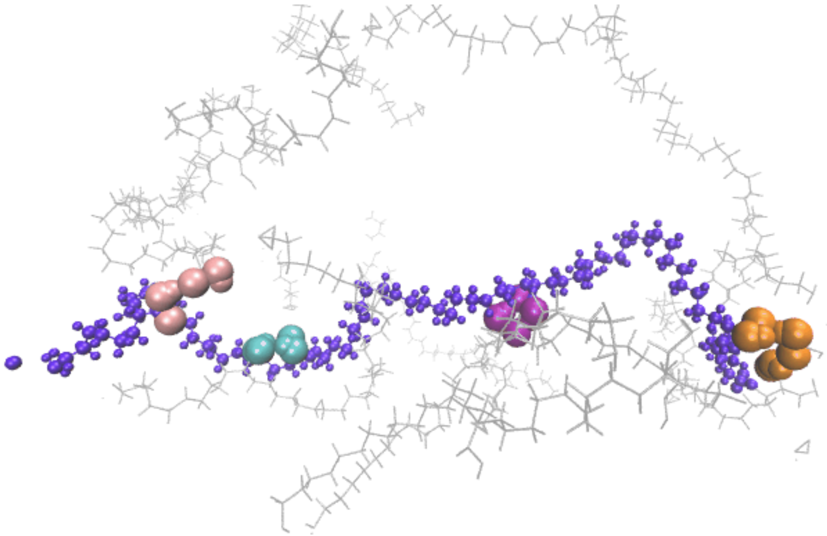
amorphous halo: Q ≈ 1.35 Å^{-1}

ionomer peak: Q ≈ 0.3 – 0.6 Å^{-1}

Local Dynamics

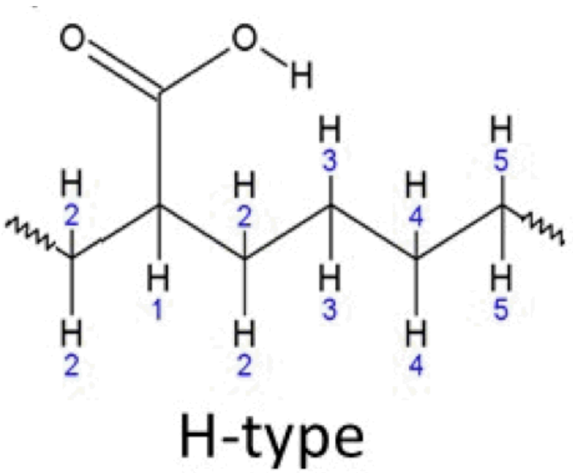


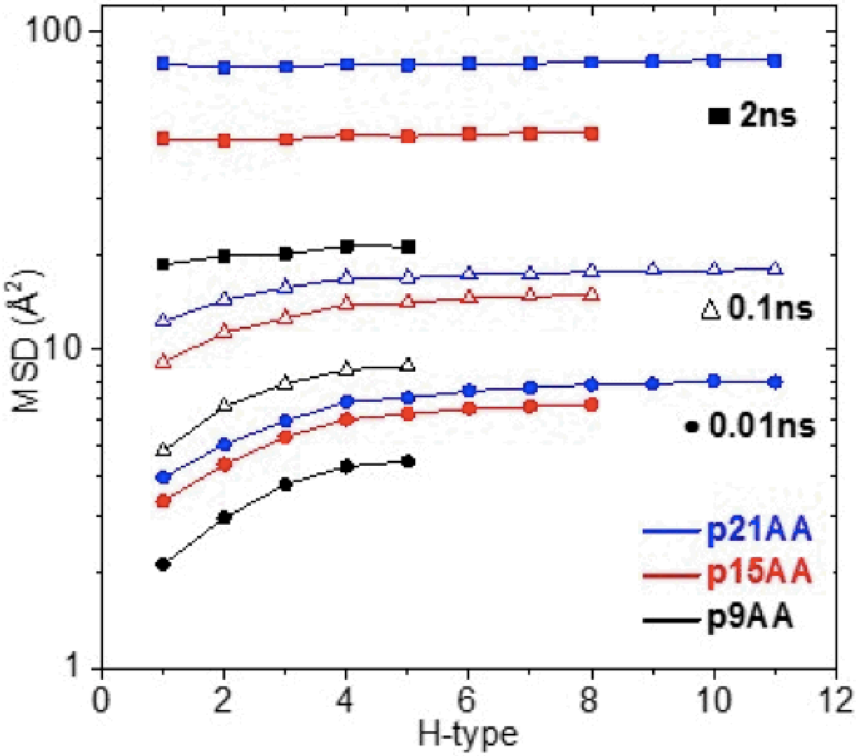
H-type



Middleton, L. R., Tarver, J. D., Cordaro, J., Tyagi, M., Soles, C. L., Frischknecht, A. L., & Winey, K. I. (2016). *Macromolecules*, *49*(23), 9176–9185. http://doi.org/10.1021/acs.macromol.6b01918

Local Dynamics





short times: H1 motion much slower than middle of chain
long times: aggregates rearrange, all H motions similar

Middleton, L. R., Tarver, J. D., Cordaro, J., Tyagi, M., Soles, C. L., Frischknecht, A. L., & Winey, K. I. (2016). *Macromolecules*, *49*(23), 9176–9185. http://doi.org/10.1021/acs.macromol.6b01918

Outlook

Atomistic MD can answer lots of questions in soft matter

Vast field with constantly evolving methods/codes

For related talks this week:

Focus sessions on "Advances in Molecular Dynamics Simulation: From Atomistic to Coarse-Grained Models", sponsored by DCP

- A25: Monday 8 am
- C25: Monday 2:15 pm
- F26: Tuesday 11:15 am
- K25: Wednesday 8 am

References

Books

- M. P. Allen and D. J. Tildesley, *Computer Simulations of Liquids*, Clarendon Press, Oxford, 1987
- Dann Frenkel and Berend Smit, *Understanding Molecular Simulation: From Algorithms to Applications*, Academic Press, 2002
- Tamar Schlick, *Molecular Modeling and Simulation: An Interdisciplinary Guide*, Springer, 2002

Others

- Frenkel, D. (2013). Simulations: The dark side. *The European Physical Journal Plus*, *128*(1), 10
- https://en.wikipedia.org/wiki/Comparison_of_software_for_molecular_mechanics_modeling
- Arbe, A., Alvarez, F., & Colmenero, J. (2012). Neutron scattering and molecular dynamics simulations: synergetic tools to unravel structure and dynamics in polymers. *Soft Matter*, *8*(32), 8257