Engineering Scale Simulation of Non-Equilibrium Network Structures in Copolymer Materials

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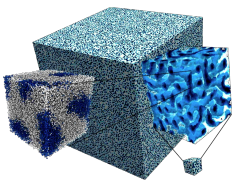
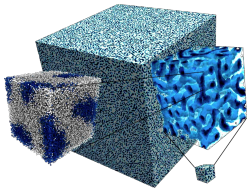
February 27, 2020



Why are complex polymer melts interesting?

Self-assembled nanostructures



Interesting properties for simulations utilizing HPC

SOMA
yes, soft matters

L. Schneider and M. Müller, Comput. Phys. Commun. **235C**, 463–476 (2019)

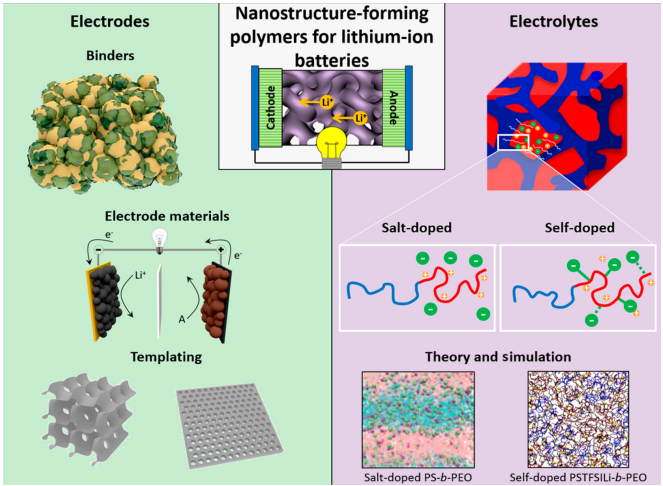
Applications

- battery materials
- molecular sieves
- micro electronics

HPC implementation

- polymers are fractal objects
- straightforward coarse-graining
- short-range vs. long-range phenomena

Next generation of polymeric lithium ion batteries



Goals

- ion conductivity
- mechanical stability

Diblock copolymer materials

- self-assembled nanostructures
- block A: conductivity
- block B: stability

M. A. Morris, H. An, et al., ACS Energy Lett. **2**, 1919–1936 (2017)

Overview

1. How to model and simulate engineering scale polymer melts?
   - Top-down, soft, coarse-grained model
   - SCMF-algorithm and SOMA
2. Large scale metastable networks: battery electrolytes
   - Percolating network structures
   - Diffusive transport properties
3. Future perspective: more atomistic details
   - Mechanical properties

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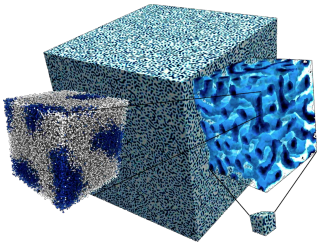

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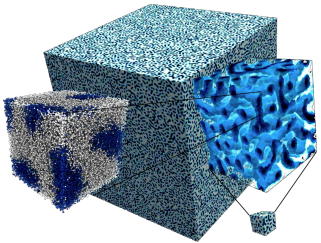
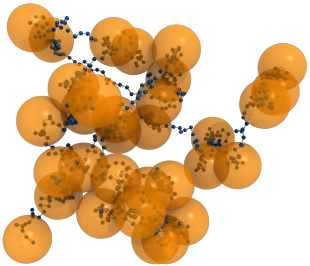
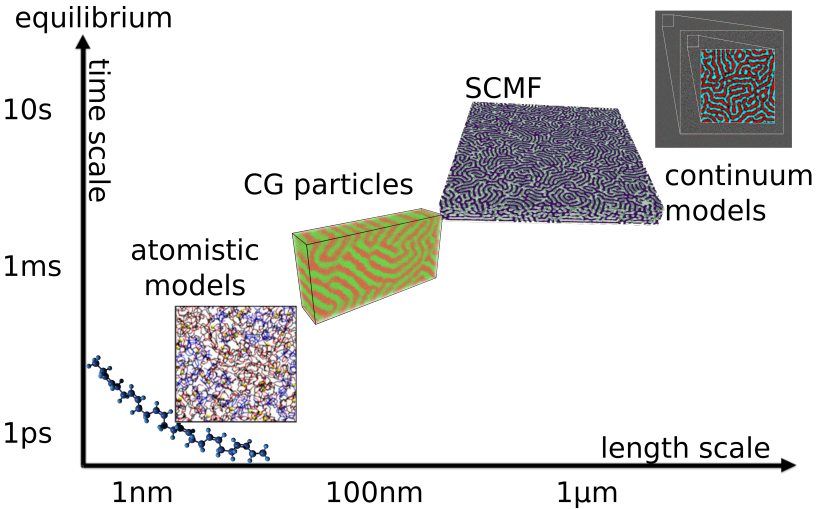




Hierarchy of coarse-grained models

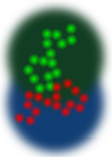


- large scales $\rightarrow$ insertion of atomistic details
- focus on SCMF
- highest length and time scale that includes molecule info
- SCMF unlocks engineering scales
- hard CG models: mechanical properties

Coarse-graining: single bead $\leftrightarrow$ many atoms

Coarse-graining

- Gaussian chain
- fewer degrees of freedom
- universality
- higher parallelism



density $\hat{\phi}_A, \hat{\phi}_B$ based Monte-Carlo

- harmonic bond potential: R_{e0}
  - $V_h(\boldsymbol{r}) = \frac{k_2}{2}\boldsymbol{r}^2$
- restrain density fluctuations: $\kappa_0 N$
  - $\mathscr{H}_{\text{fluc.}}[\hat{\phi}_A, \hat{\phi}_B] \propto \int \mathrm{d}\boldsymbol{r}\ \frac{\kappa_0 N}{2}\left(\hat{\phi}_A(\boldsymbol{r}) + \hat{\phi}_B(\boldsymbol{r}) - 1\right)^2$
- microphase separation: $\chi_0 N$
  - $\mathscr{H}_{\text{sep.}}[\hat{\phi}_A, \hat{\phi}_B] \propto \int \mathrm{d}\boldsymbol{r}\ \chi_0 N\ \hat{\phi}_A(\boldsymbol{r})\hat{\phi}_B(\boldsymbol{r})$

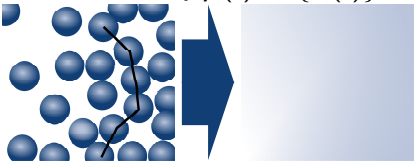
$$N = 2^{14}$$
$$\Downarrow$$
$$N = 2^{7}$$

SOMA
yes, soft matters

https://gitlab.com/InnocentBug/SOMA
L. Schneider and M. Müller, Comput. Phys. Commun. **235C**, 463–476 (2019)

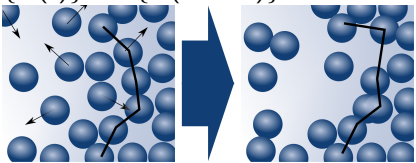
Single-Chain-in-Mean-Field algorithm

1. calculate density $\rho(t) \leftarrow \{\boldsymbol{r}_i(t)\}$



2. bond force-biased Monte-Carlo

$\{\boldsymbol{r}_i(t)\} \overset{\rho(t)}{\rightarrow} \{\boldsymbol{r}_i(t+\Delta t)\}$



3. repeat

K. C. Daoulas and M. Müller, J. Chem. Phys. **125**, 184904 (2006)

Implementation:

Step 1

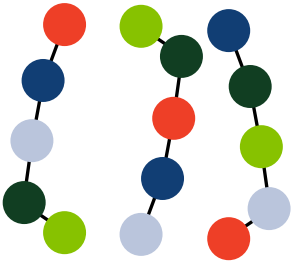
- simple reduction problem
- non-bonded: calculation on a grid

Step 2

- bond force-biased Monte-Carlo
- exact bond energies
- non-bonded particles are independent

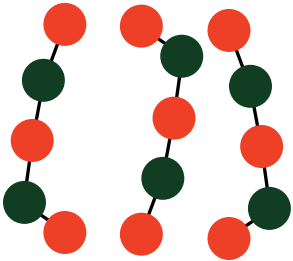
Independent beads: GPU parallel level

Polymer iteration:



- same color: $\Rightarrow$ parallel
- iterate colors
- 3 threads
- 5 iterations

Independent set iteration:



- higher parallelism
- 9 (6) threads
- 2 iterations

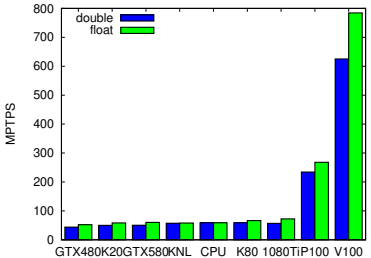
\+ simple independent units
\+ parallelism scales with system
– large polymers (networks)
– no dynamic bonds

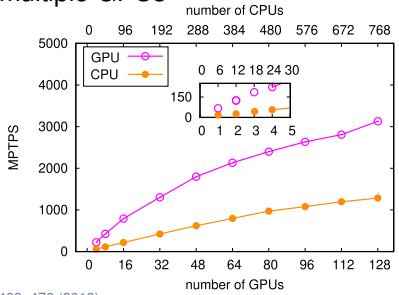
\+ full utilization of parallelism
\+ networks or many nodes
– non-trivial set decomposition
– additional memory and complexity

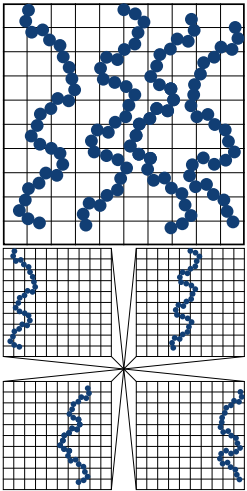
L. Schneider and M. Müller, Comput. Phys. Commun. **235C**, 463–476 (2019)

Multiple GPUs: strong scaling

- good performance on modern GPUs
- next parallel level: multiple GPUs
- distribute molecules across `MPI` ranks
  - `MPI_Allreduce` for density-field
  - automatic load-balance
- straight forward invocation of multiple GPUs







L. Schneider and M. Müller, Comput. Phys. Commun. **235C**, 463–476 (2019)

OpenACC implementation for GPUs

- redesigned for GPU hackathon (2016)
  - 1 team, most without GPU experience
  - mentor support from Nvidia and PGI
  - 1 week $\Rightarrow$ GPU parallel
- growing features over time
- analysis/optimization at more hackathons

OpenACC
More Science, Less Programming

SOMA
yes, soft matters

- C/pragma only implementation
  - accessible to everyone
- CPU/GPU single code base
- open standard
- community support

L. Schneider and M. Müller, Comput. Phys. Commun. **235C**, 463–476 (2019)

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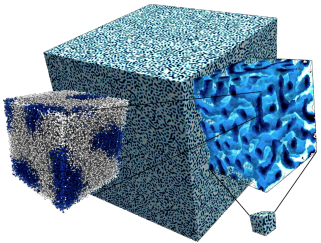
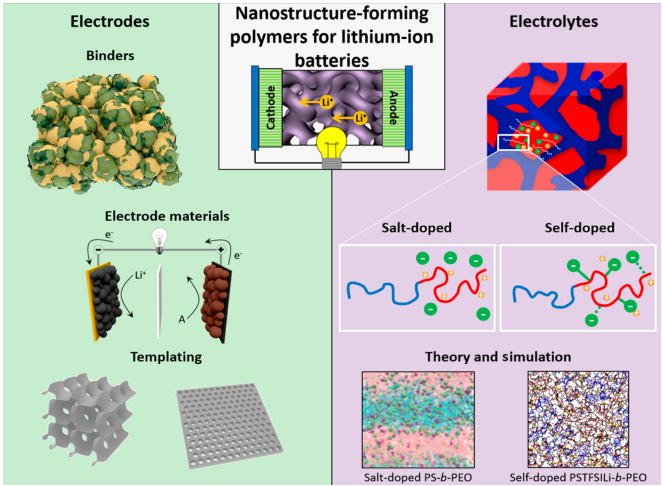


Next generation of polymeric lithium ion batteries



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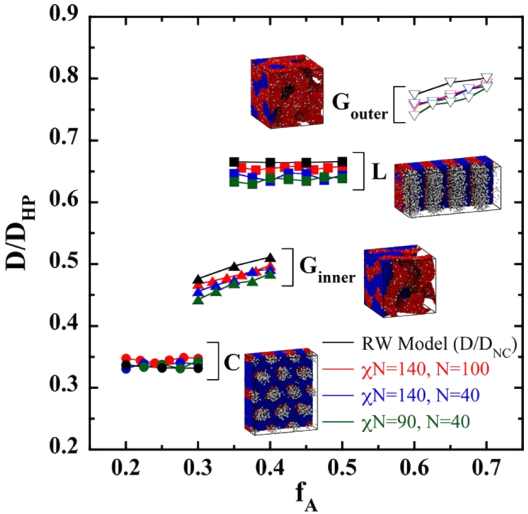
M. A. Morris, H. An, et al., ACS Energy Lett. **2**, 1919–1936 (2017)

Ion transport in polymer electrolytes

- polymer electrolytes: conduction of ions
- recently investigations
  Shen et.al., Alshammasi et.al., and Zhang et.al.
- investigations of molecular details
- interface roughness effects
- equilibrium morphologies

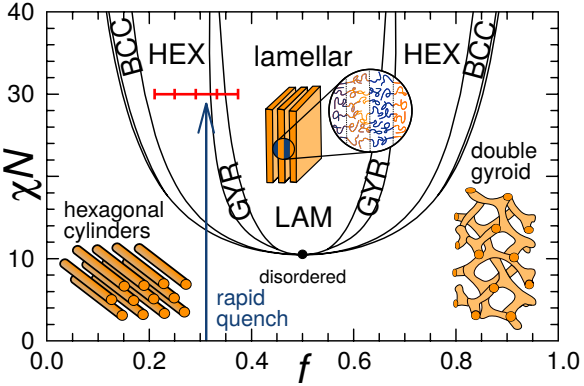
In this talk!

- effect of large-scale morphologies
- non-equilibrium meta-stable states



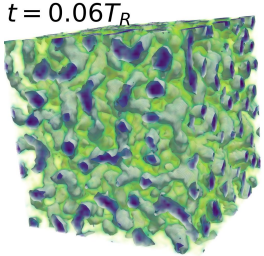
K.-H. Shen, J. R. Brown, et al., ACS Macro Letters **7**, 1092–1098 (2018)
M. S. Alshammasi and F. A. Escobedo, Macromolecules **51**, 9213–9221 (2018)
Z. Zhang, J. Krajniak, et al., ACS Macro Letters **8**, 1096–1101 (2019)

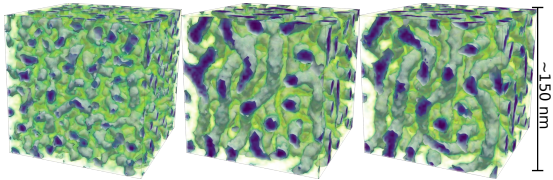
Metastable network phases



- $\chi N = 30$
- $f \in \left[\frac{7}{32}, \frac{12}{32}\right]$

- rapid quench
- metastable
- $t = 6\,T_R$
- 3D diffusion?

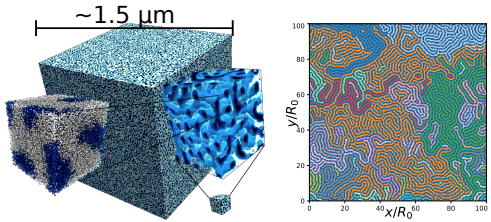




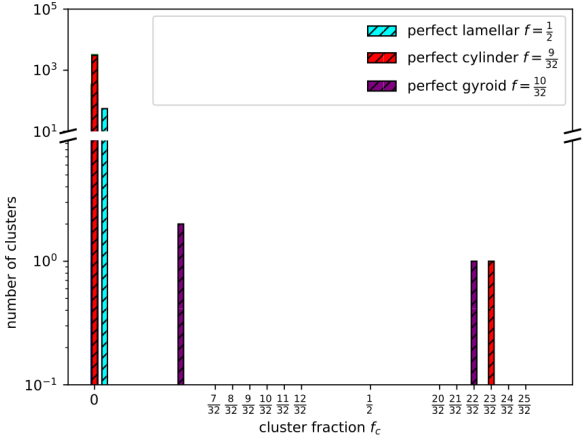
adapted from M. W. Matsen, J. Phys: Condens. Matter **14**, R21 (2001)

L. Schneider and M. Müller, Macromolecules **52**, 2050–2062 (2019)

3D network structures for conductivity and stability



- non-periodic network structures
- $\approx 4.1 \cdot 10^9$ particles
- engineering scale: $L = 0.8\text{-}2.7\mu\text{m}$
- A-phase: omnidirectional diffusion
- B-phase: mechanical stability



- $f > \frac{7}{32}$: 3D percolating cluster for A and B

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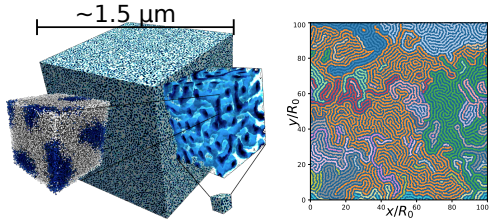

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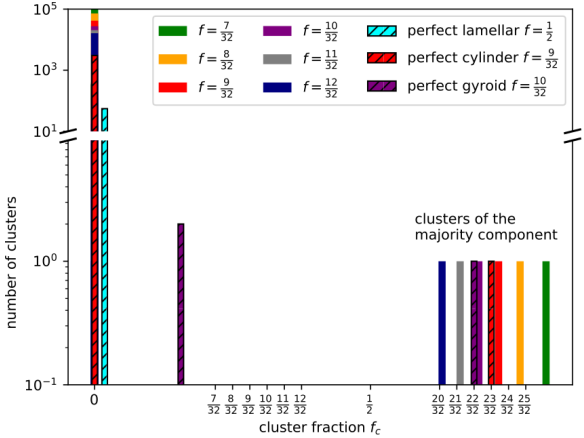

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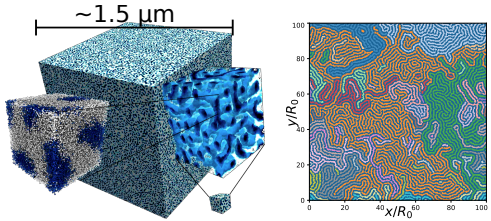

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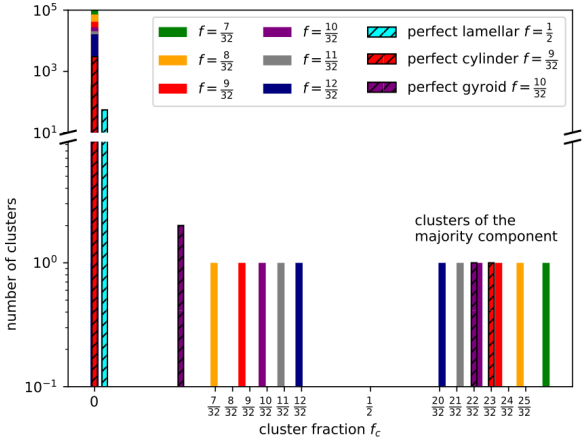

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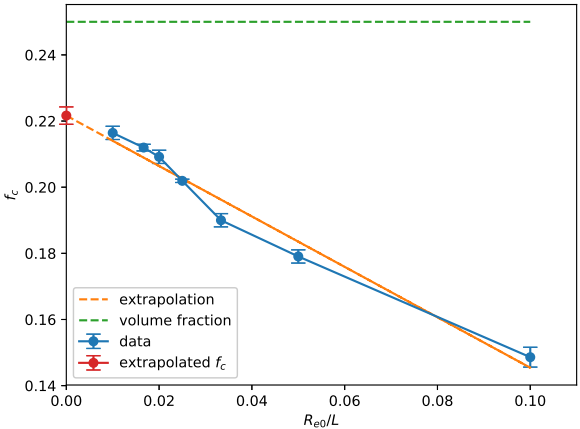
Finite size effect on clusters

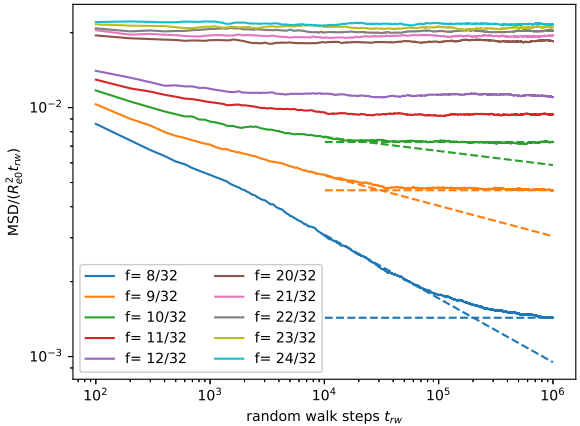


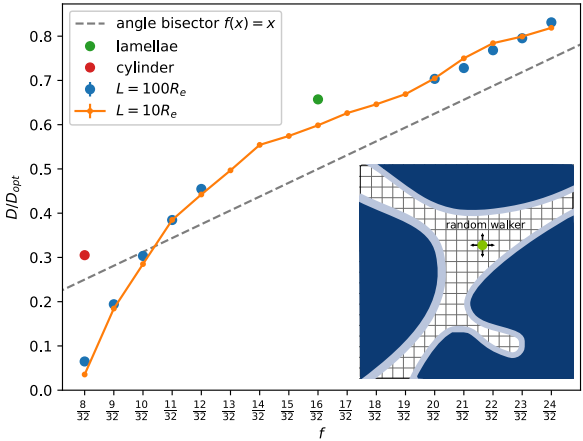
Volume of percolating cluster f_c vs. volume fraction f

- volume cluster $f_c < f$ volume fraction
- small independent cluster

- example: $f = 8/32 = 0.25$
- systematic deviation with system size L
- small simulations underestimate f_c
- extrapolation possible $f_c \propto 1/L$
- extrapolated: $f_c < f$

Diffusive ion transport





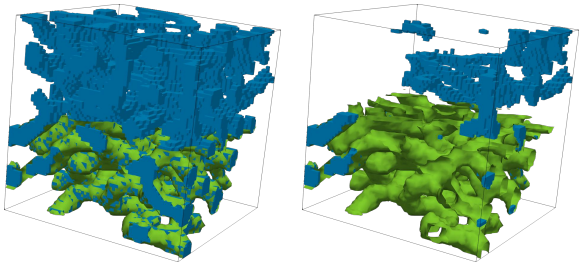
- subdiffusion for $\sqrt{MSD} < (18 \pm 1) R_{e0}$
- linear for $f > 1/2$
- decrease for $f < \frac{13}{32}$

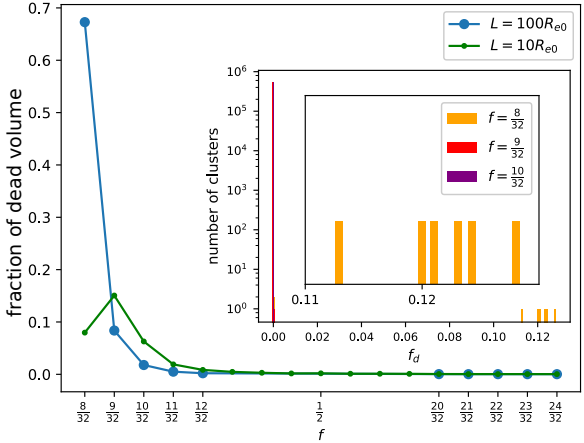
Continuous 3D transport of ions!

L. Schneider and M. Müller, Macromolecules **52**, 2050–2062 (2019)

Dead-end analysis

- diffusion $\neq$ directed transport
- dead-ends in network structures
- impact on small volume fractions f
- underestimated by small simulations





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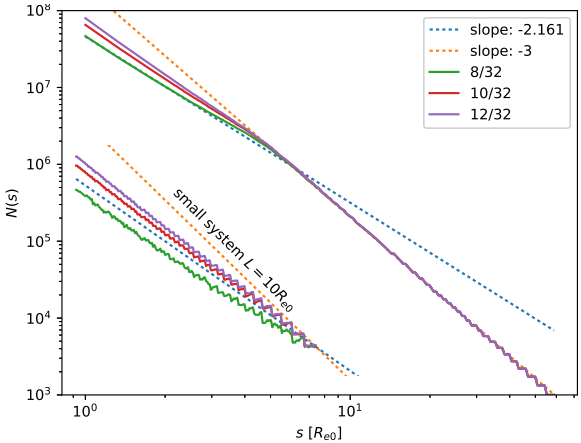
Space-filling characteristics of 3D network structures



- not space-filling $s < s^* \approx (5.4 - 6.4)R_{e0}$
- space-filling on large length scales
- characteristics of an overcritical cluster
- simulations of large sizes required

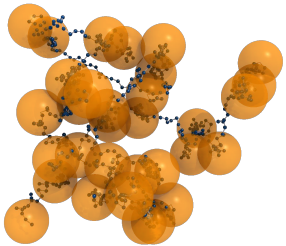
Box counting algorithm

1. divide system if box of length s
2. count boxes that contain structure $N(s)$
   - $N(s) \propto s^{-d_f}$ fractal dimension

D. Ben-Avraham and S. Havlin, Cambridge university press, (2000)

L. Schneider and M. Müller, Macromolecules **52**, 2050–2062 (2019)

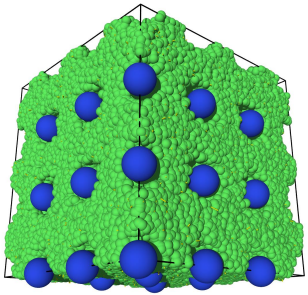
The investigation of some properties require more atomic details



- soft, coarse-grained model: no vitrification
- reinserting degrees of freedom
- finer grained model:
  LJ beads & FENE bonds

G. Zhang, L. A. Moreira, et al., ACS Macro Letters **3**, 198–203 (2014)

- A-block (liquid) and B-block (glass)
- non-equilibrium mechanical tests
- comparison of network phases with equilibrium and “pure” phases
- relevance of the polymer backbone



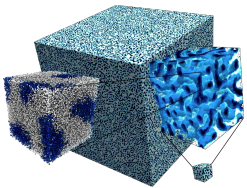
Summary

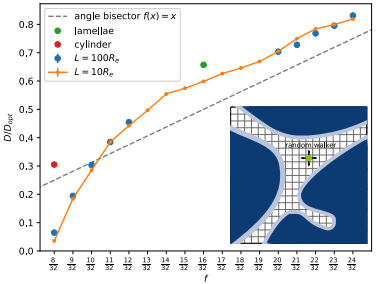
- coarse-grained models
- scaling to many GPUs
- metastable networks
- 3D conductivity

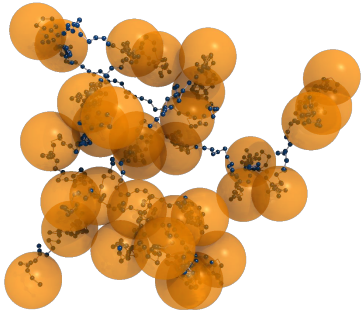
Outlook

- mechanical properties
- remapping to finer grained model

SOMA
yes, soft matters



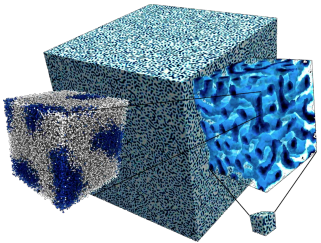


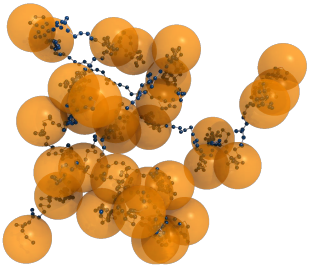


Overview

1. How to model and simulate engineering scale polymer melts?
   - Top-down, soft, coarse-grained model
   - SCMF-algorithm and SOMA
2. Large scale metastable networks: battery electrolytes
   - Percolating network structures
   - Diffusive transport properties
3. Future perspective: more atomistic details
   - Mechanical properties

SOMA
yes, soft matters





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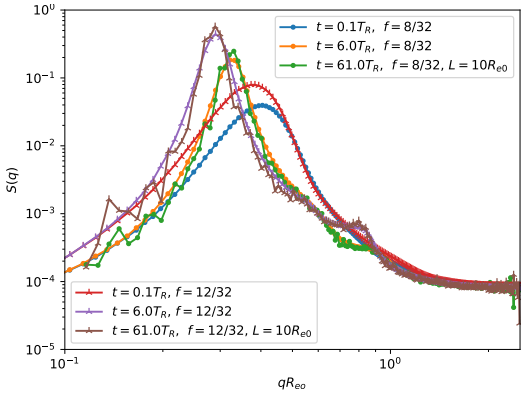
M. Culebras, C. Gómez, et al., Materials **7**, 6701–6732 (2014).

J. Golebiowski, A. Mostofi, et al., in Aps meeting abstracts (2019).

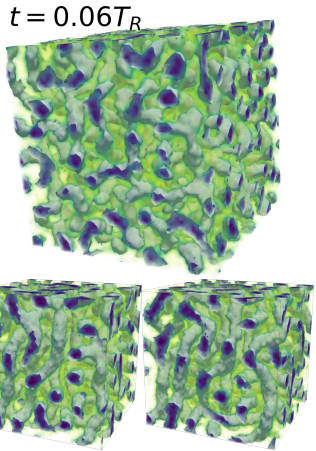
U. Welling and M. Müller, Soft Matter **13**, 486–495 (2017).

Metastable network phases



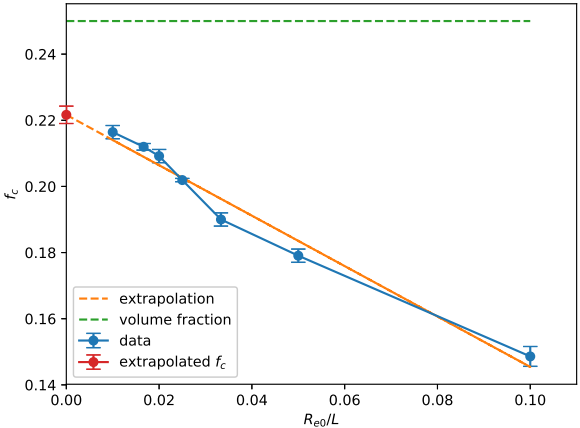
structure factor $S(|\boldsymbol{q}|)$

- rapid quench
- metastable
- $t = 6T_R$
- 3D diffusion?

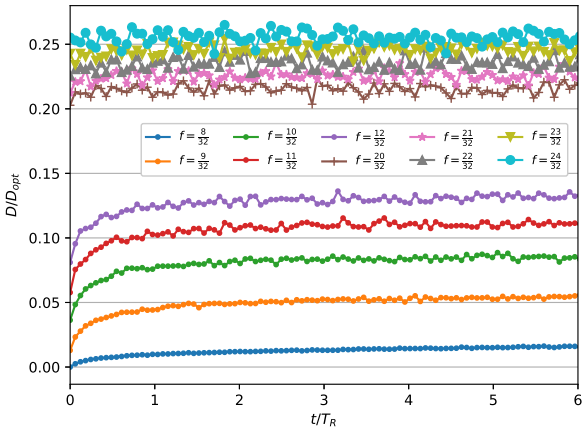


L. Schneider and M. Müller, Macromolecules **52**, 2050–2062 (2019)

Finite-size effect for cluster fraction f_c

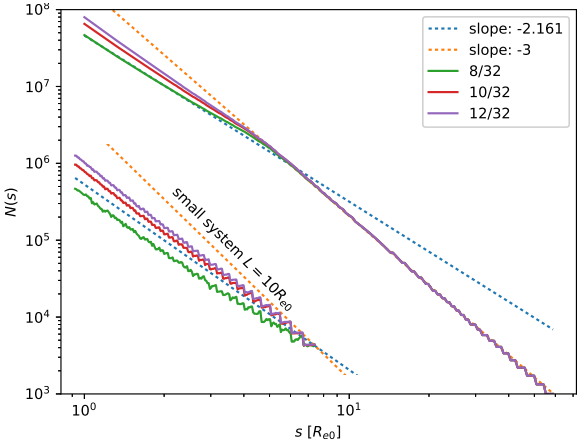


- systematic finite-size effect: $f_c = f_c^* - \alpha/L$



- convergences to plateau after coarsening

Space-filling characteristics of 3D network structures



- not space-filling $s < s^* \approx (5.4 - 6.4)R_{e0}$
- space-filling on large length scales
- characteristics of an overcritical cluster
- simulations of large sizes required

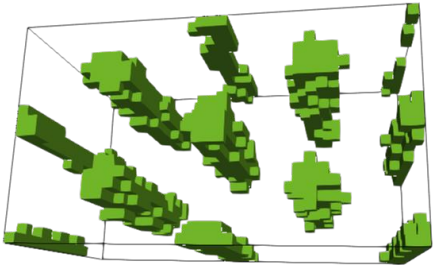
Box counting algorithm

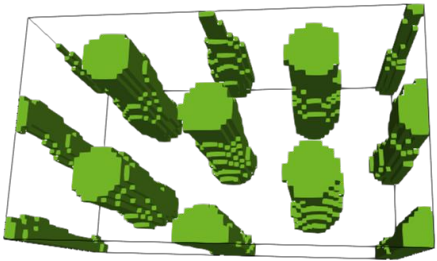
1. divide system if box of length s
2. count boxes that contain structure $N(s)$
- $N(s) \propto s^{-d_f}$ fractal dimension

D. Ben-Avraham and S. Havlin, Cambridge university press, (2000)

L. Schneider and M. Müller, Macromolecules **52**, 2050–2062 (2019)

Grid smoothing for diffusion analysis





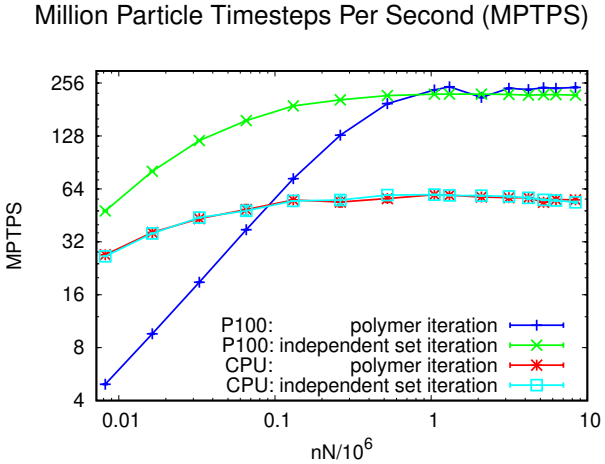
1. time average to reduce fluctuations
2. increase grid resolution
3. apply opening $\bigcirc$ and closing $\bullet$
   - $\rho \bigcirc s = (\rho \ominus s) \oplus s$
   - $\rho \bullet s = (\rho \oplus s) \ominus s$

$$(\rho \ominus s)(\boldsymbol{r}) = \inf_{\boldsymbol{r}' \in s} [\rho(\boldsymbol{r} + \boldsymbol{r}') - s(\boldsymbol{r}')]$$

$$(\rho \oplus s)(\boldsymbol{r}) = \sup_{\boldsymbol{r}' \in s} [\rho(\boldsymbol{r}) - s(\boldsymbol{r} - \boldsymbol{r}')]$$

H. J. Heijmans, SIAM review **37**, 1–36 (1995)

Accelerator saturation

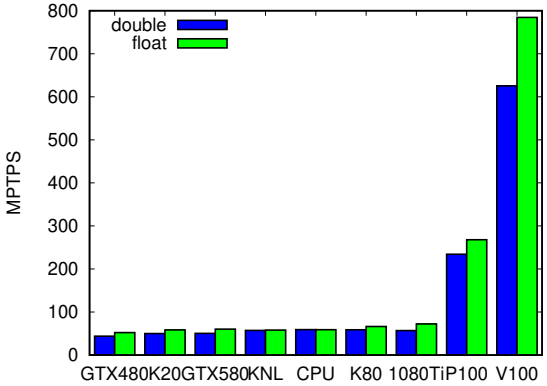


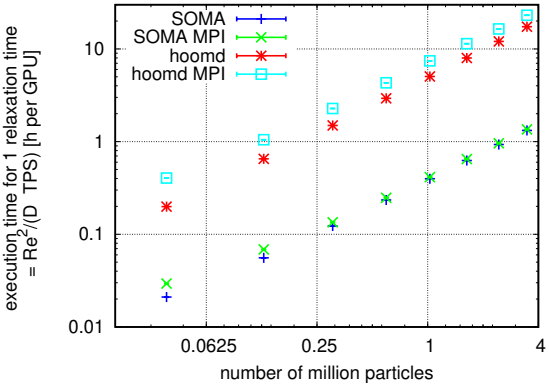
CPU: 2 Intel Xeon E5-2680v3 (24 cores)

P100: Nvidia Pascal P100 GPU

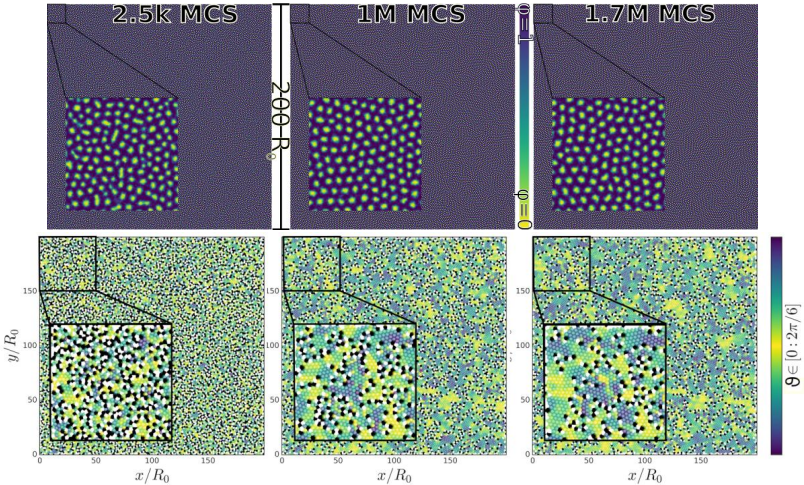
L. Schneider and M. Müller, Comput. Phys. Commun. **235C**, 463–476 (2019)

SOMA performance



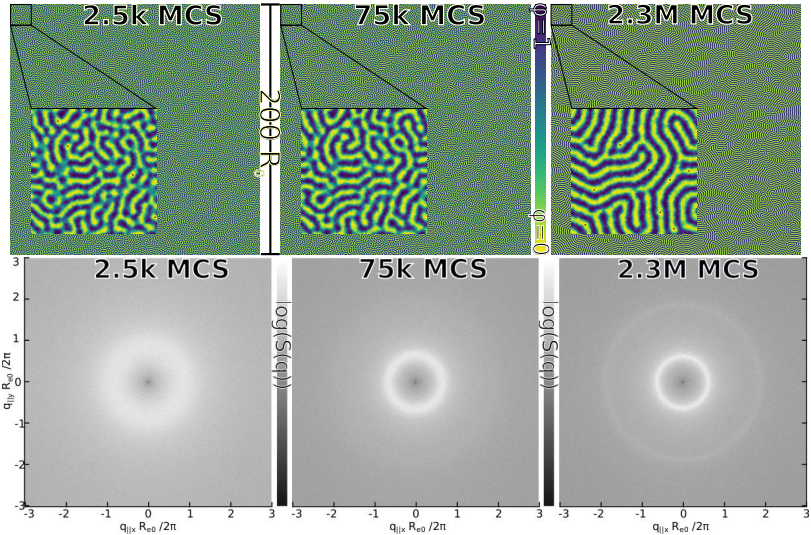


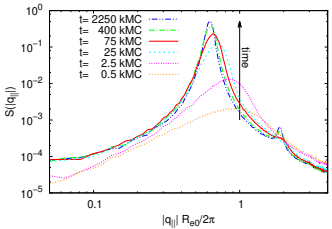
SOMA example: hexagonal cylinders



- $f_A^{\text{hex}} = 0.75$
- $\chi_0 N^{\text{hex}} = 28,$
- $L_x = L_y = 200 R_{e0}$
- $L_z^{\text{lam}} = 0.75 R_{e0}$
- $N = 100$
- $\sqrt{\bar{\mathcal{N}}} \approx 85.7$
- $nN \approx 240 \cdot 10^6$

SOMA example: thin lamellar film

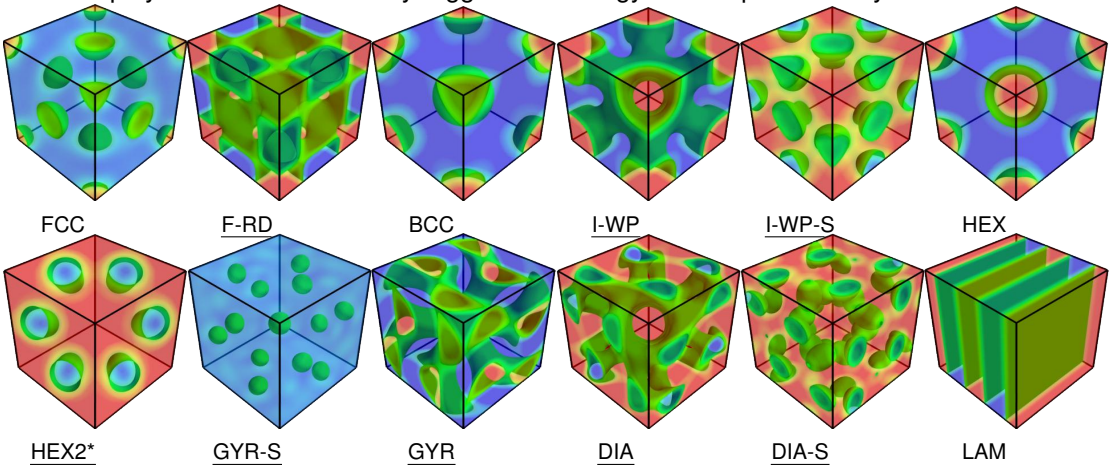




- $f_A^{\text{lam}} = 0.5$
- $\chi_0 N^{\text{lam}} = 17$,
- $L_z^{\text{lam}} = 1.2 R_{e0}$
- $nN \approx 411 \cdot 10^6$

Periodic stable and metastable structures

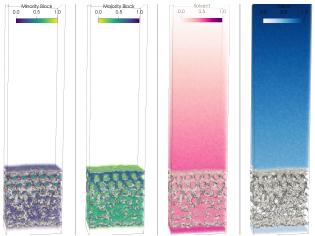
Block copolymer melts have a very rugged free energy landscape. $\Rightarrow$ Many metastable states.



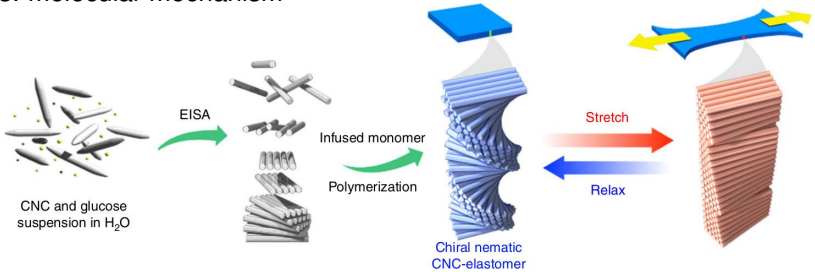
D.-W. Sun and M. Müller, Macromolecules **51**, 275–281 (2017)

Interesting work by Prof. MacLachlan (UBC): CNC in polymer matrix

- cellulose nanocrystals (CNC) in polymer matrix
- EISA: chiral nematic CNC-elastomer
- stretching: change in nematic order
  - optical properties
- simulations: molecular mechanism



evaporation-induced self-assembly (EISA)

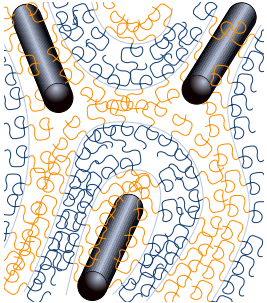


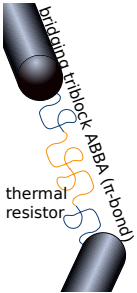
O. Kose, A. Tran, et al., Nature communications **10**, 510 (2019)

Polymer matrix + carbon nano tube: thermoelectric devices?

thermoelectric figure of merit $ZT = \frac{\alpha^2 \sigma}{\kappa} T$

- high electrical conductivity σ
- low thermal conductivity κ





Polymer + CNT nanocomposites

- polymers: low κ
- CNTs: high σ

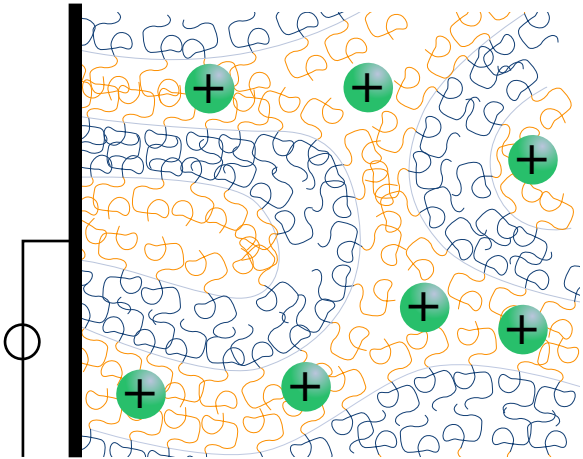
M. Culebras, C. Gómez, et al., Materials **7**, 6701–6732 (2014)

- properties of large scale nanocomposites?
- engineering favorable morphologies?
- mechanical, electrical, and thermal properties?
- model development
  - polymer CNT adsorption
  - thermal transfer @ interface
  - charge transfer @ interface
  - classical and QM contributions

J. Golebiowski, A. Mostofi, et al., in Aps meeting abstracts (2019)

Interface electrode/electrolyte: electronic interactions

- electrode surface may have an ordering effect on morphology
  - length scale and morphology
- directed ion transport in a polymer block
- how does the charge interact with the morphology
- electronic changes in the electrode before/after charge transfer
- repeated charge/discharge cycles
  - long term effects
- SCMF with electrostatics



U. Welling and M. Müller, Soft Matter **13**, 486–495 (2017)