

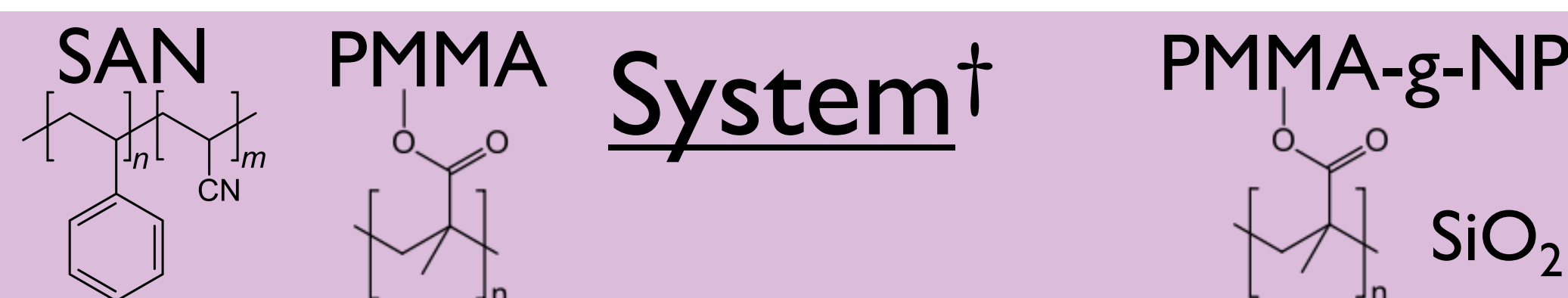


Phase Behavior of Polymer-Grafted Nanoparticles in a Polymer Melt

Motivation

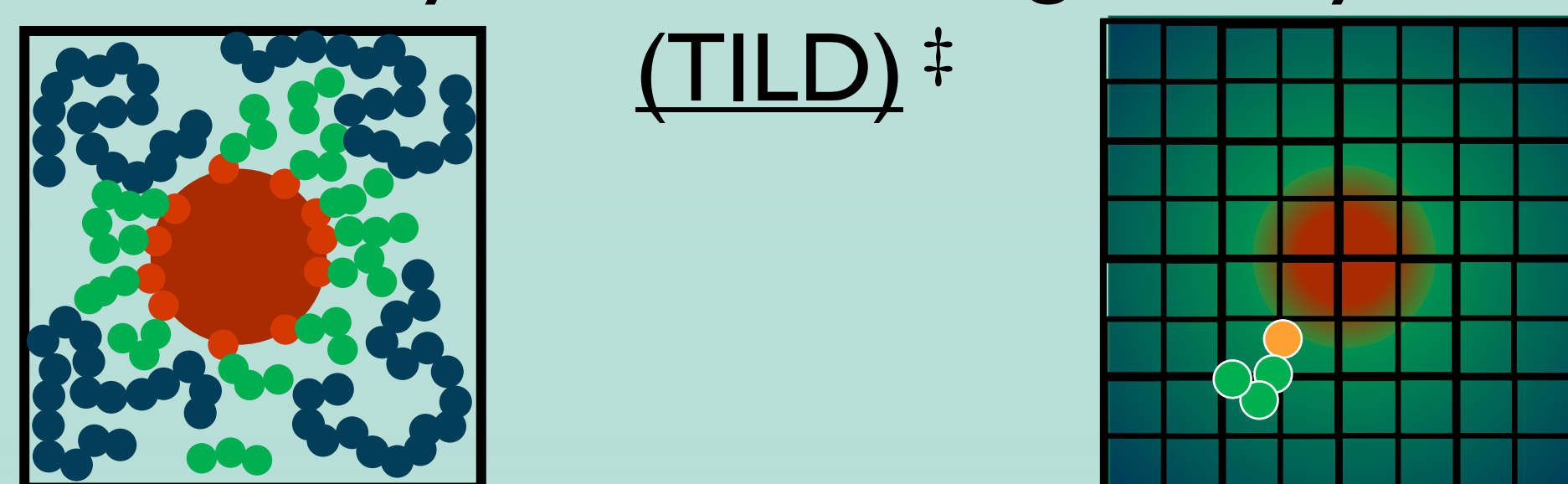
Composites of polymers and nanoparticles aim to form materials that combine the desirable mechanical, electrical, magnetic or other properties from each component.

Successful property combination depends on the overall morphology of the system and the polymer brush grafted to the nanoparticle. The phase behavior, as a function of graft length, nanoparticle size and solvent, is a promising equilibrium control on morphology.



System property	Experimental	TILD sims.
NP radius (SiO ₂)	7.5 nm	3.3 b
Grafting density	0.7 chains/nm ²	3.7 chains/b ²
PMMA mol. weight (graft, matrix)	19 kDa	17 beads
SAN mol. weight (33% AN)	118 kDa	123 beads

Theoretically-Informed Langevin Dynamics



Particle-to-mesh scheme

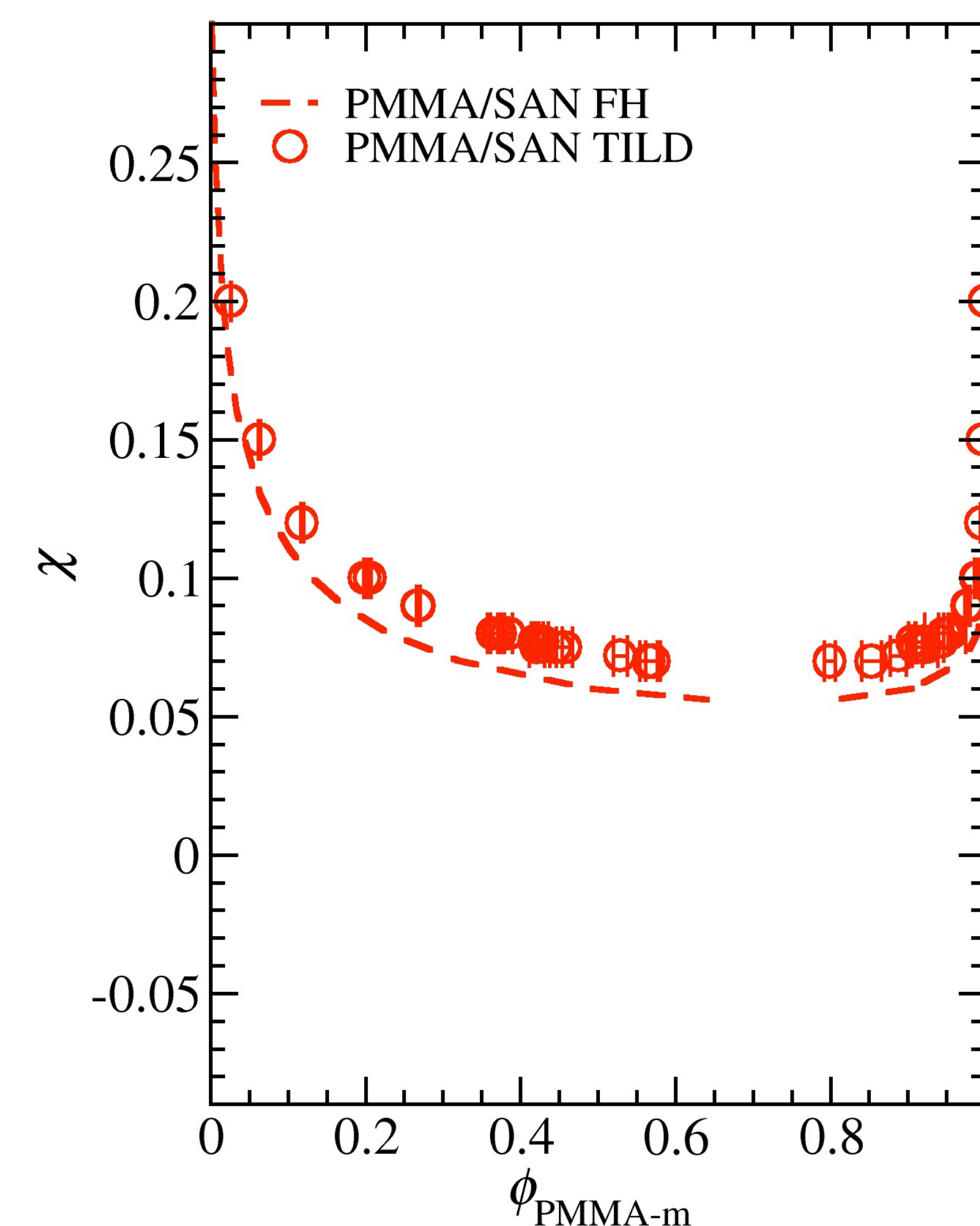
Procedure

- Molecular Dynamics evolves simulation of soft, point-based particles
- T is controlled with Langevin thermostat
- Force on particle is calculated from a field-based interaction

Benefits and losses

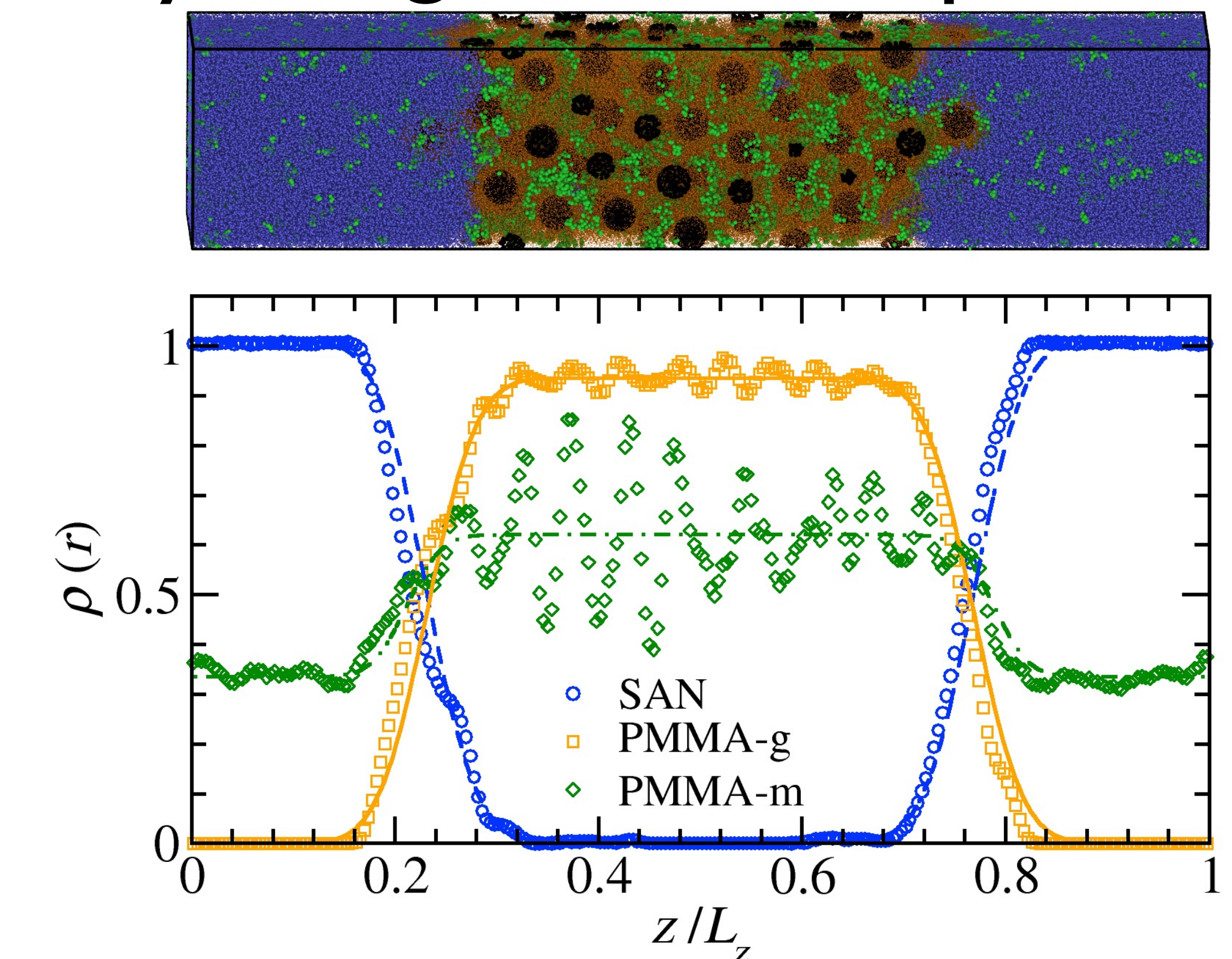
- Fast for particle-based method
- Takes advantage of previous MD developments
- Thermal fluctuations
- No easy accesses to free energy

Homopolymer blend



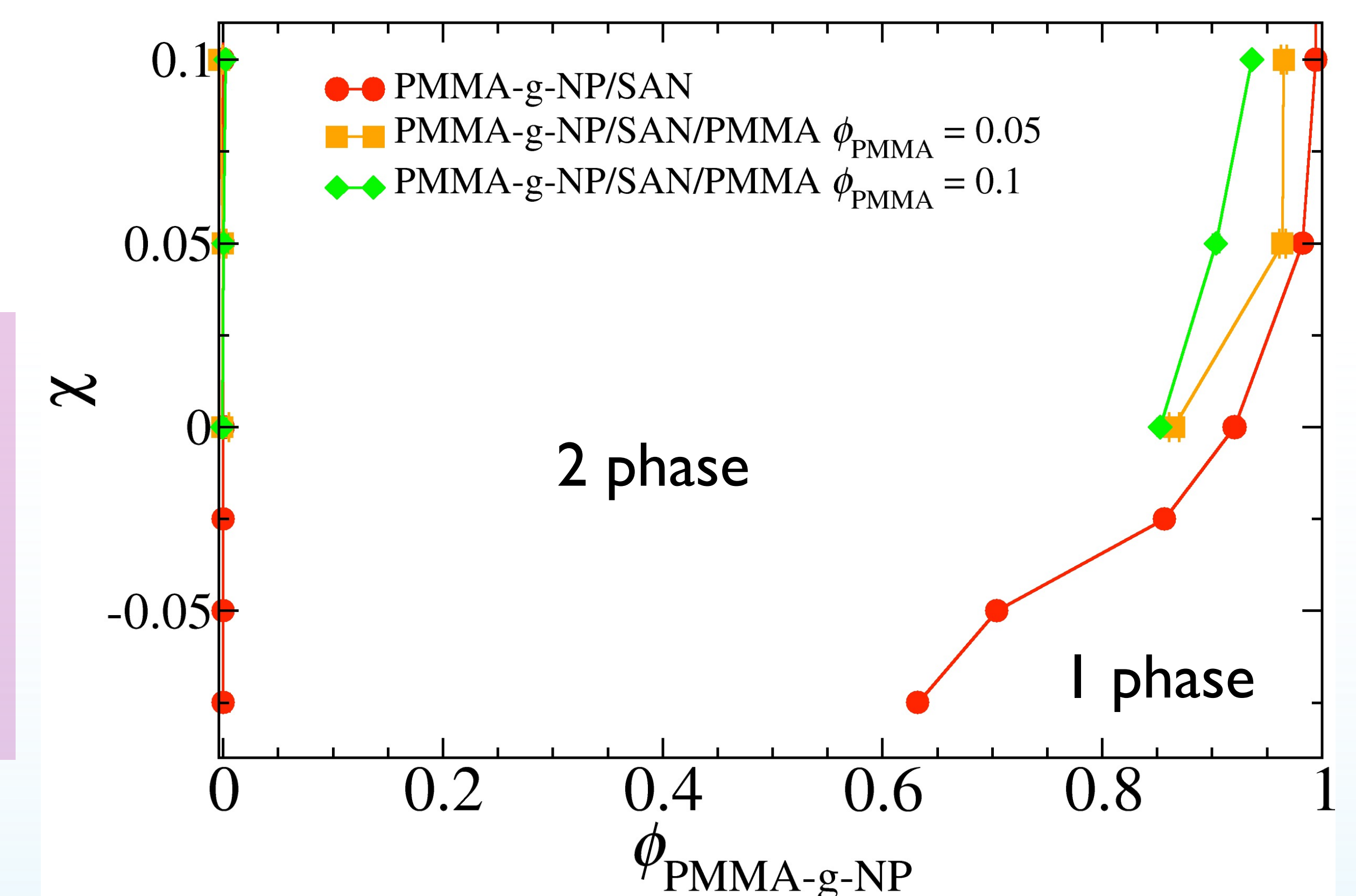
PMMA/SAN phase diagram $\chi(\phi)$

Polymer-grafted nanoparticles



Ex.
config.

Density profile ($\phi_{\text{PMMA-m}}=0.05$, $\chi=0.1$)



Interaction parameter—vol. fraction phase diagram $\chi(\phi)$

Discussion

- Our method equilibrates long polymers in tractable times
- Polymer-grafted NPs drastically change the critical point
- Homopolymer blend behavior controls ternary component
- Adding ternary component increases miscibility

References

- [†]Maguire, S. M., Krook, N. M., Kulshreshtha, A., *et al.* (2021). *Macromolecules*, 54(2), 797–811.
- [‡]Chao, H., Koski, J., & Riggleman, R.A. (2017). *Soft Matter*, 13(1), 239–249.



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- mechanical,
- electrical,
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- plasmonic or
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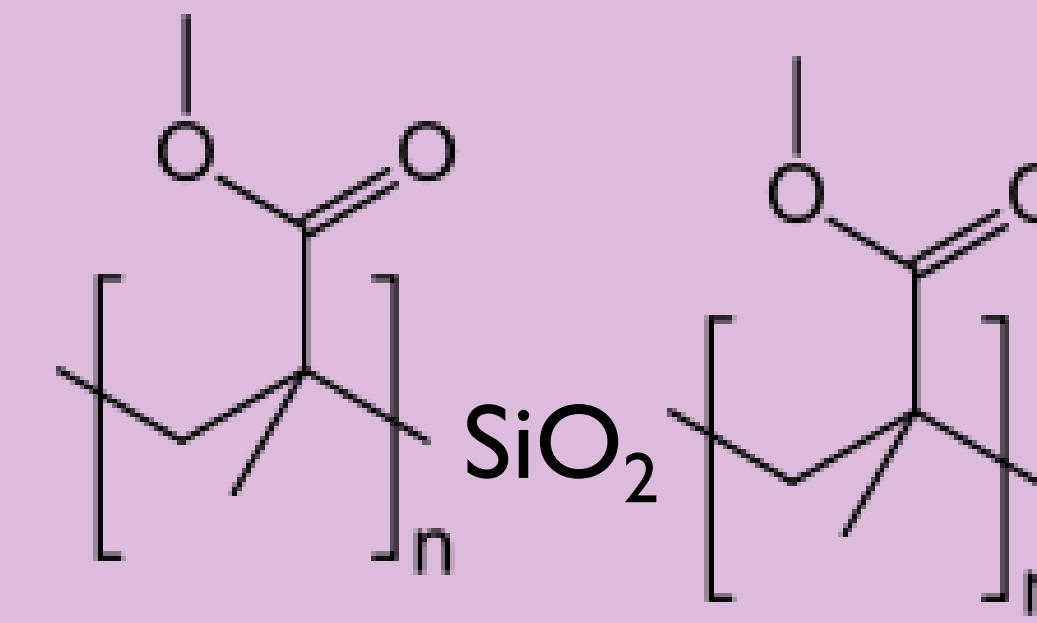
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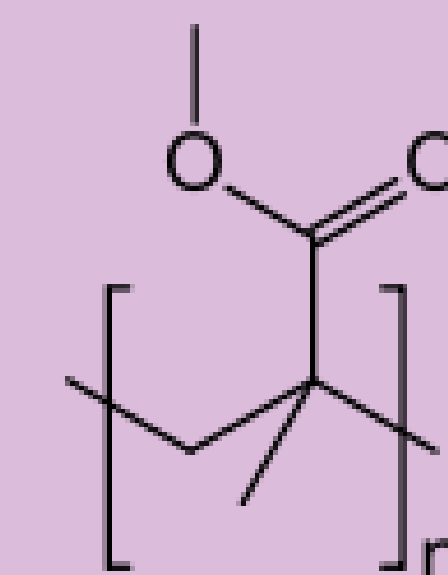
[‡]Chao, H., Koski, J., & Riggleman, R.A. (2017). *Soft Matter*, 13(1), 239–249.

System[†]

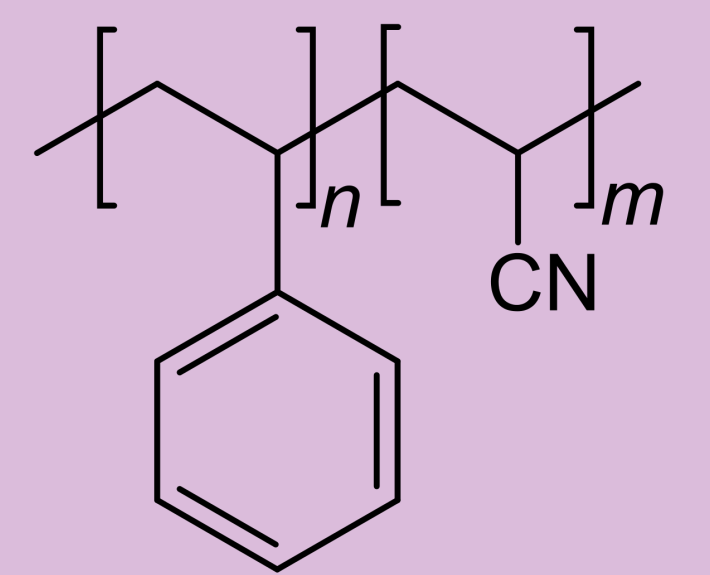
Poly(methy methacrylate)-grafted Silica Nanoparticles in poly(styrene-co-acrylonitrile)



PMMA



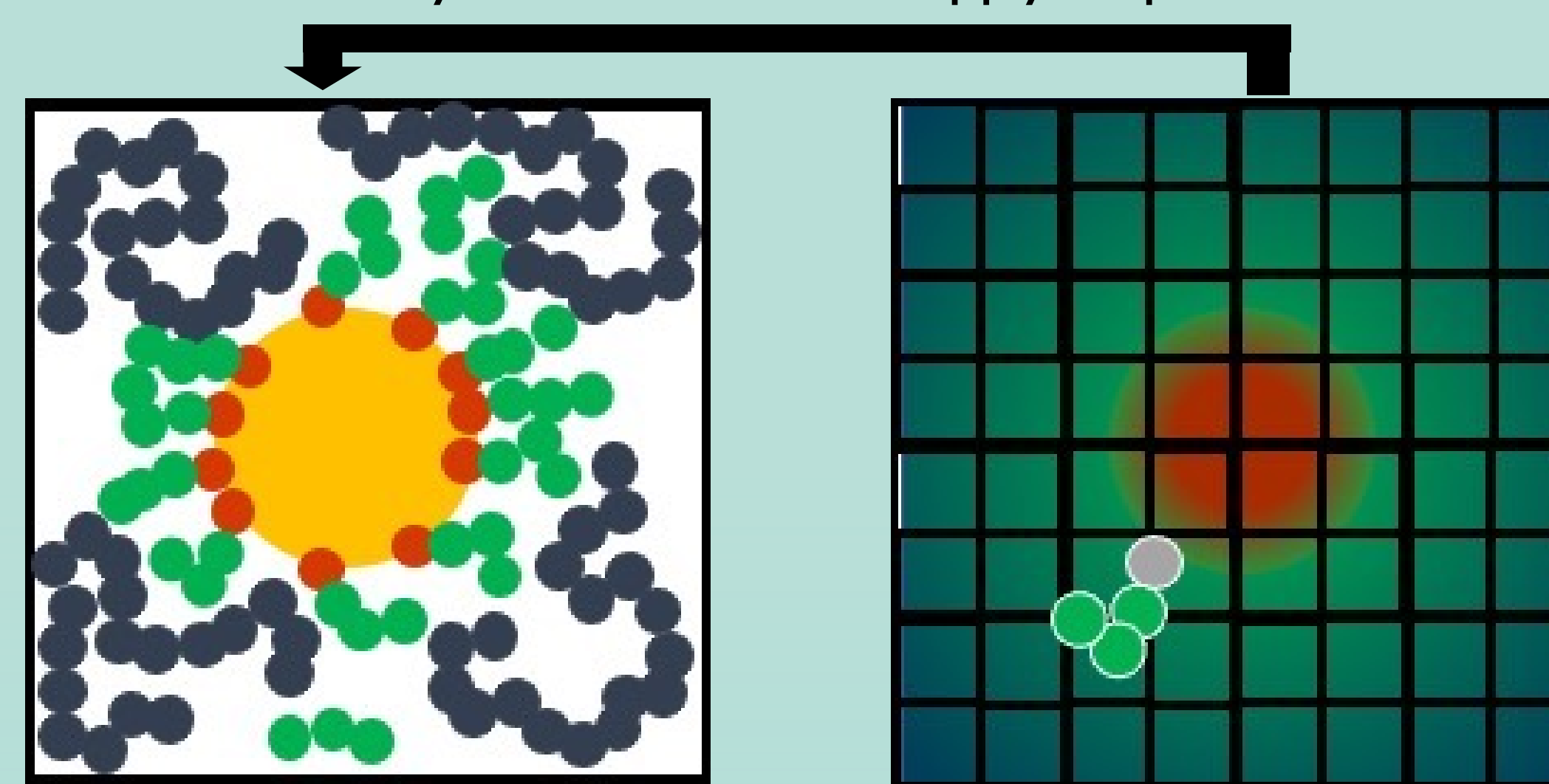
SAN



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Theoretically-Informed Langevin Dynamics (TILD)[‡]

Density-calculated forces apply to particles



Particle-to-mesh

Procedure

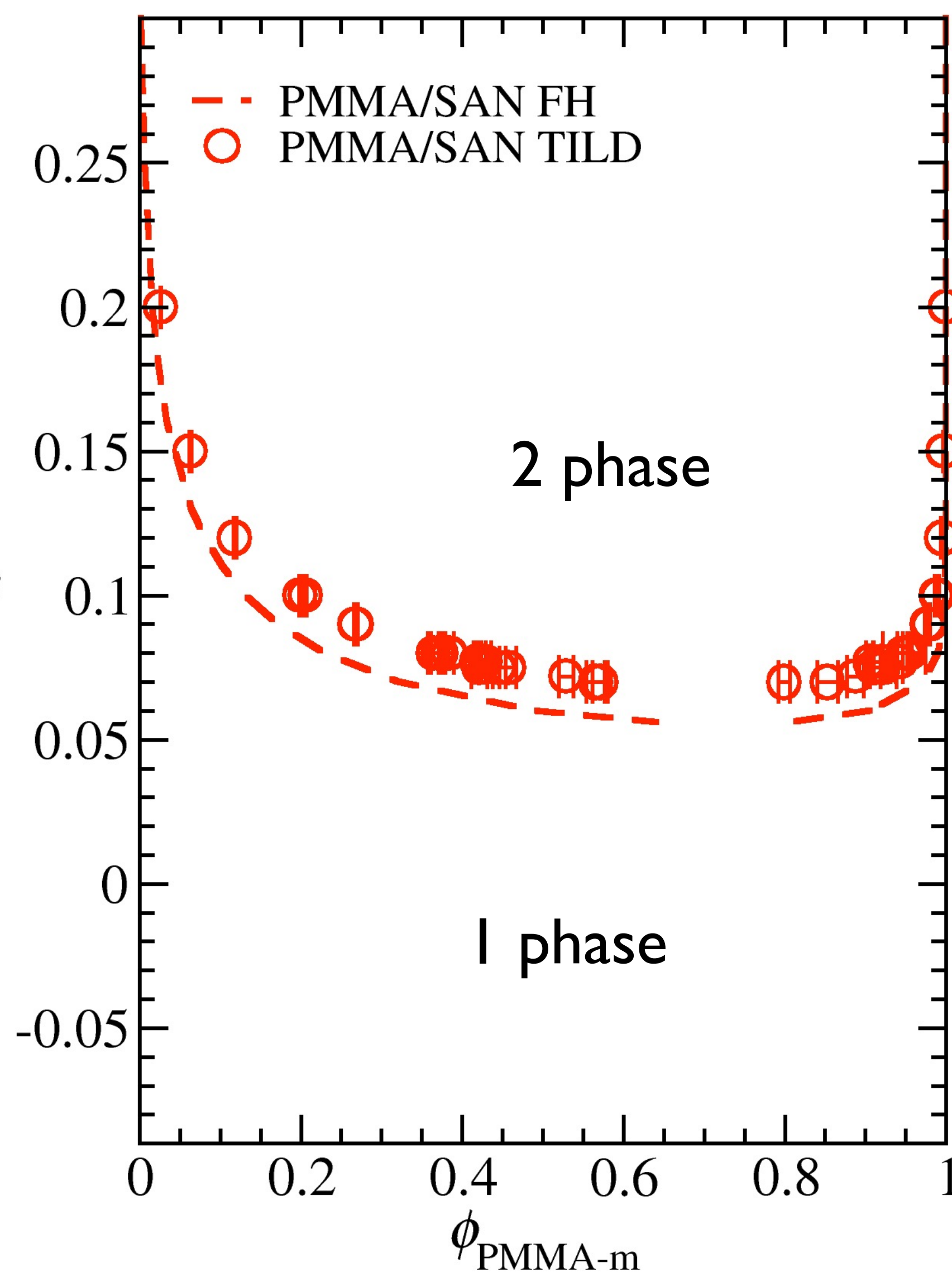
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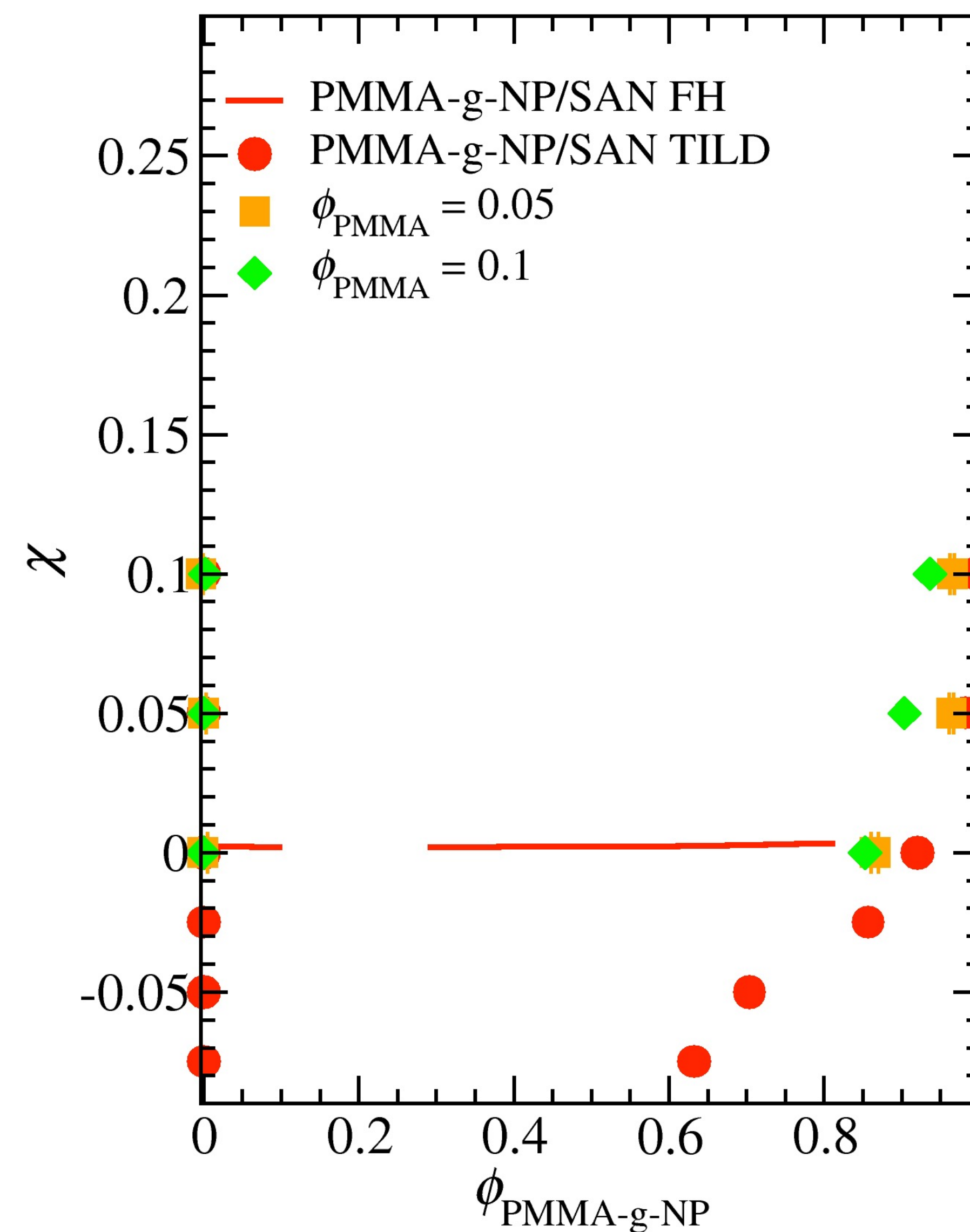


Homopolymer blend



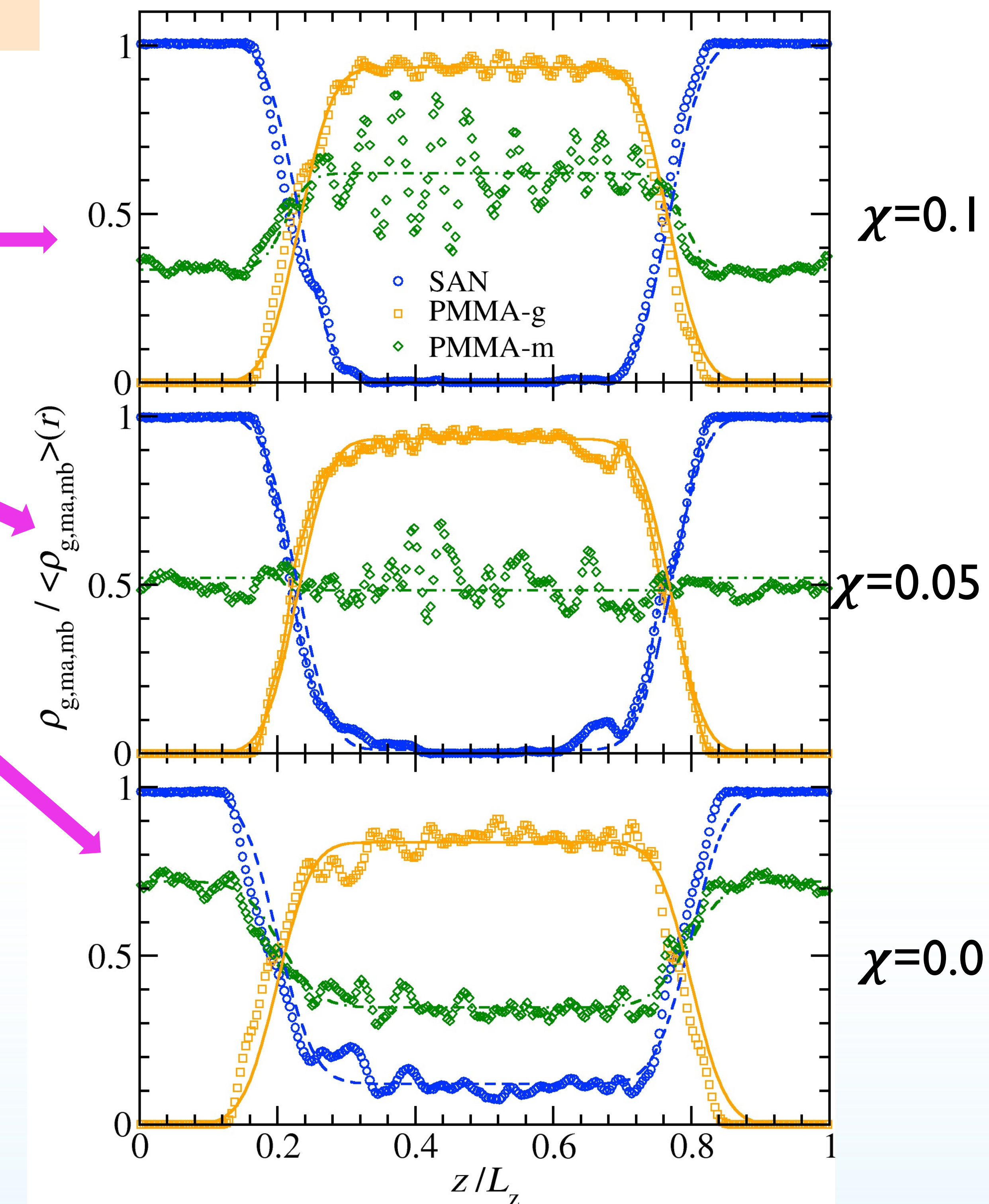
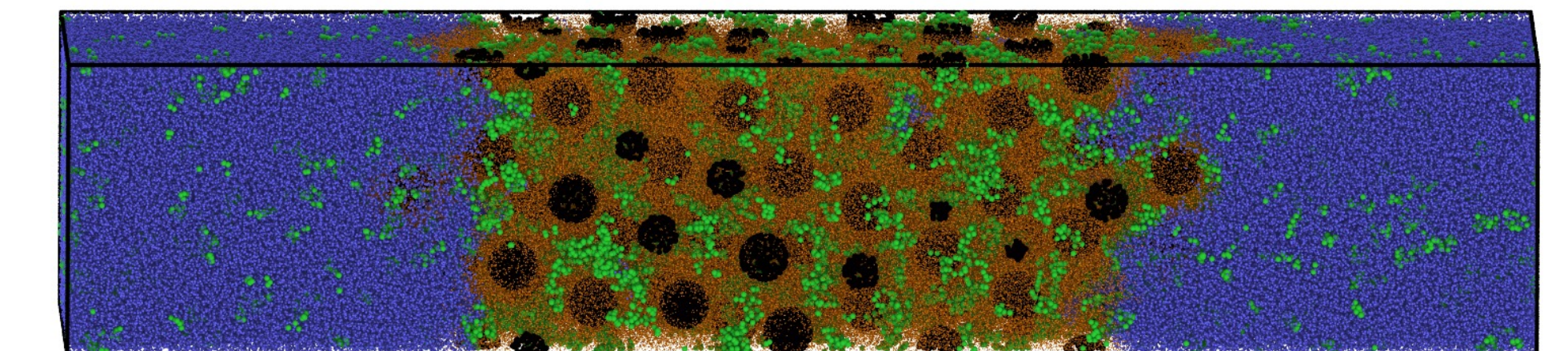
PMMA/SAN phase diagram $\chi(\phi)$

Polymer-grafted nanoparticles



Binary (PMMA-g-NP/SAN) and Ternary (PMMA-g-NP/SAN/PMMA) phase diagram, $\chi(\phi)$, calculated from TILD and Flory-Huggins PGN theory.

Simulation snapshot
($\phi_{\text{PMMA-m}}=0.05$,
 $\chi=0.1$)



Density profiles ($\phi_{\text{PMMA-m}}=0.05$)

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