

Supporting Information for

**Polymeric Solvation Shells around Nanotubes: Mesoscopic
Simulation of Interfaces in Nano-channels**

Ali Gooneie*, and Rudolf Hufenus

Laboratory of Advanced Fibers, Empa, Swiss Federal Laboratories for Materials Science and
Technology, Lerchenfeldstrasse 5, CH-9014 St. Gallen, Switzerland

*Corresponding Authors: ali.gooneie@empa.ch

1. Attractive forces in the biphasic nanofluidic channel

In microscopic approaches, van der Waals forces f_{vdw} between two spheres (or a sphere and a surface) separated by D , are directly proportional to the so-called Hamaker constant A_H as $f_{vdw} \propto \frac{A_H}{D^2}$.¹ This correlation is in fact generally applicable for f_{vdw} between colloids of different shapes.² Consequently, a positive A_H is indicative of an attractive f_{vdw} whereas a negative A_H shows a repulsive f_{vdw} . Despite the significance of the attractive forces in interfacial phenomena, DPD is intrinsically based on soft repulsive interactions and is not equipped with any explicit definitions for the attractive forces.^{3,4} Instead, DPD mimics attraction between two particles as a consequence of the repulsion between them and other surrounding particles. Even though there are some approaches to explicitly incorporate attractive forces into classic DPD (e.g. many-body DPD method), they all depend on additional parameters that can complicate a meaningful design of simulations.^{5,6} Furthermore, we argue that an explicit representation of attractive forces is not needed in the soft polymer models here as the differences in A_H s of several exemplary polymer-nanoparticle combinations are insignificant. In order to calculate A_H values for a number of different material combinations, we used the Lifshitz theory.^{1,2} This theory relates the A_H value of two materials interacting through a medium to their experimental dielectric properties. Based on the published tables of data for different materials,^{1,2} we estimated the A_H s of a number of polymers and muscovite Mica (which is used in most nanofluidic experiments using surface force apparatus devices) interacting through vacuum, see Table S1. As it can be seen, all materials depict attractive f_{vdw} forces of the same order of magnitude. Thus, it is not necessary to distinguish the attractive forces explicitly in soft coarse-grained models of such systems.

Table S1. The Hamaker constants A_H for van der Waals interactions between different polymers and muscovite Mica interacting through vacuum.

System	A_H [10^{-20} J]
Similar polymer-polymer interactions	
PE/PE	6.03
PS/PS	7.17
PMMA/PMMA	6.40
PA6/PA6	7.08
Dissimilar polymer-polymer interactions	
PE/PA6	6.55
PE/PMMA	6.23
PE/PS	6.60
Polymer-Mica interactions	
PE/muscovite Mica	7.58
PS/muscovite Mica	8.33
PMMA/muscovite Mica	7.80
PA6/muscovite Mica	8.21

2. Detachment of nanotube from the interface

For a nanotube with radius R and aspect ratio of AR , the change of free energy of detachment ΔG_d can be expressed by⁷

$$\Delta G_d = \begin{cases} \gamma \pi R^2 (1 - \cos \alpha)^2 \left(1 + \frac{4(AR - 1)(\sin \alpha - \alpha \cos \alpha)}{\pi(1 - \cos \alpha)^2} \right), & \text{for } 0 \leq \alpha \leq 90^\circ \\ \Delta G_d(0 \leq \alpha \leq 90^\circ) + 4\pi \gamma R^2 \cos \alpha \cdot AR, & \text{for } 90^\circ \leq \alpha \leq 180^\circ \end{cases}, \quad (1)$$

with the interfacial tension γ of the two phases, and the contact angle α of one reference phase with the nanotube. The ΔG_d for the detachment of a nanotube with 4 nm radius and AR of 11.25 from a polymer-polymer interface with a typical interfacial tension of 5 mN·m for polymers,⁸ at a reference temperature of 240 °C is plotted in Figure S1. One can see that the energy required to detach the nanotube is 2 orders of magnitude larger than the thermal energy of the system (particularly considering the α values in our simulations that are close to 90°). Thus, the particle

is so-called *surface active* and remains attached at the interface unless an external force is applied.⁹ A more detailed treatment of the free energy changes and partial wetting of the nanotube also suggests that the wetting is marginally close to equal wetting of both phases at equilibrium.¹⁰ Consequently, our simplifying assumption to fix the particle at the interface in our equilibrium simulations is microscopically reasonable. Furthermore, we tested this hypothesis in additional simulations by allowing NT (with parallel orientation to the interface) to freely translate in the z-direction while recording the z-component of its center of mass over time, see Figure S1,b. Considering that NT has a diameter of $4 r_c$, it is clear that it remains at the interface in all systems studied here (note that it was initially fixed at $z = 15 r_c$). One can see that the largest translation of NT occurs in system IV. In this system, the NT partly moves into Poly-L but remains mostly at the interface. This is due to the fact that a full adsorption of NT in Poly-L would result in an increase of less favorable polymer-polymer interactions at their increased interface.

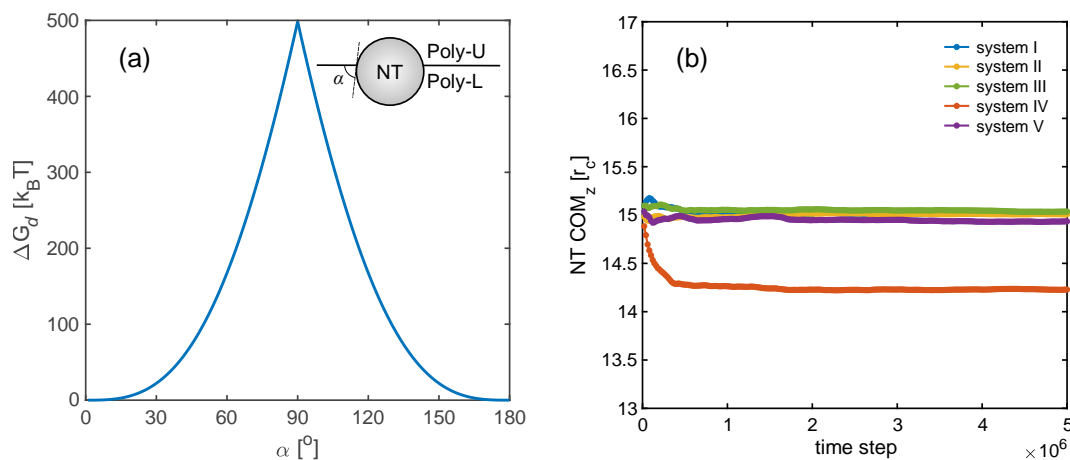


Figure S1. (a) The changes of free energy of detachment of a NT from a typical polymer-polymer interface. (b) The changes in the z-component of center of mass (COM_z) of the NT in different systems as a function of simulation time steps.

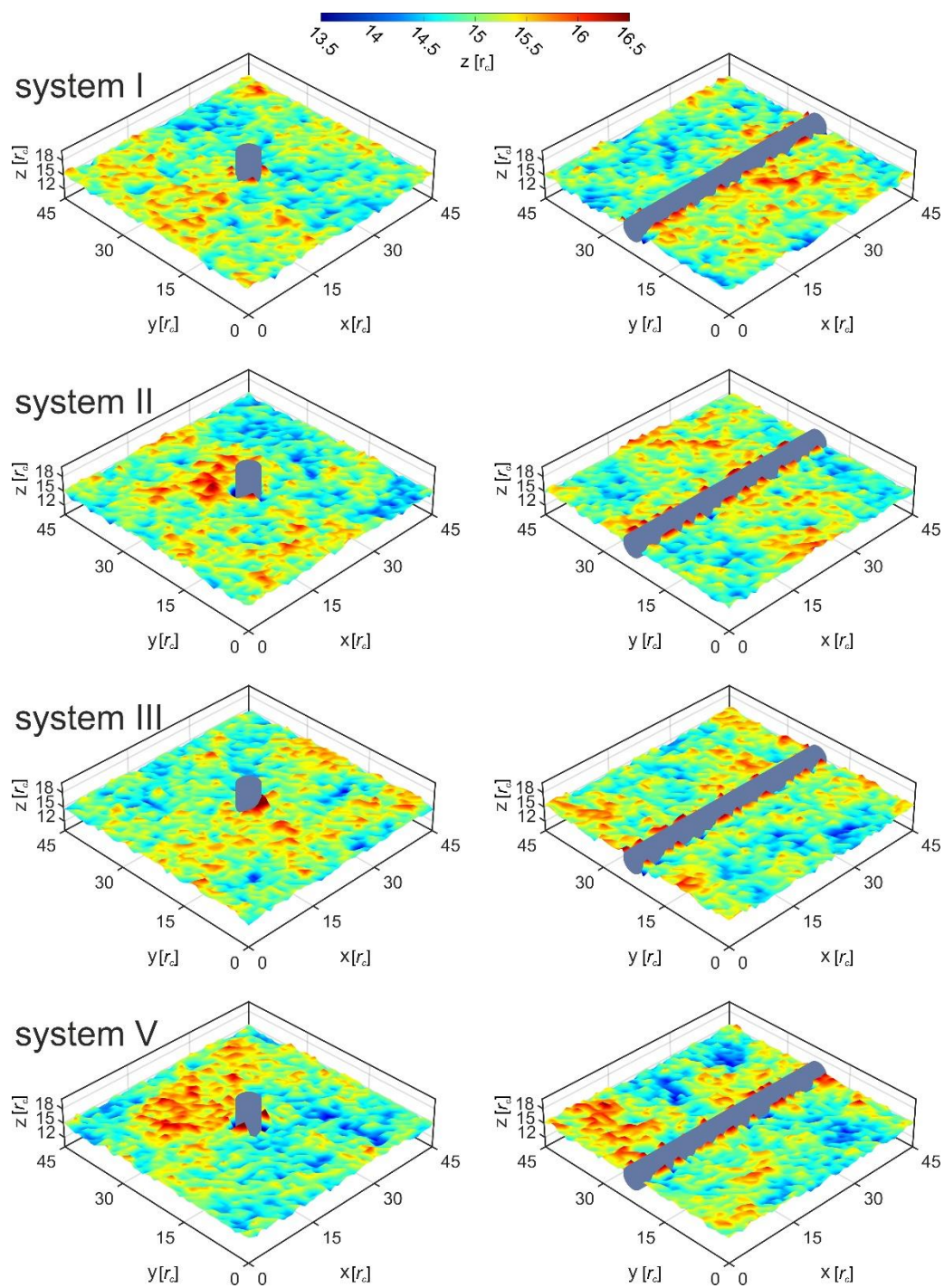


Figure S2. Shape of the interface in different systems.

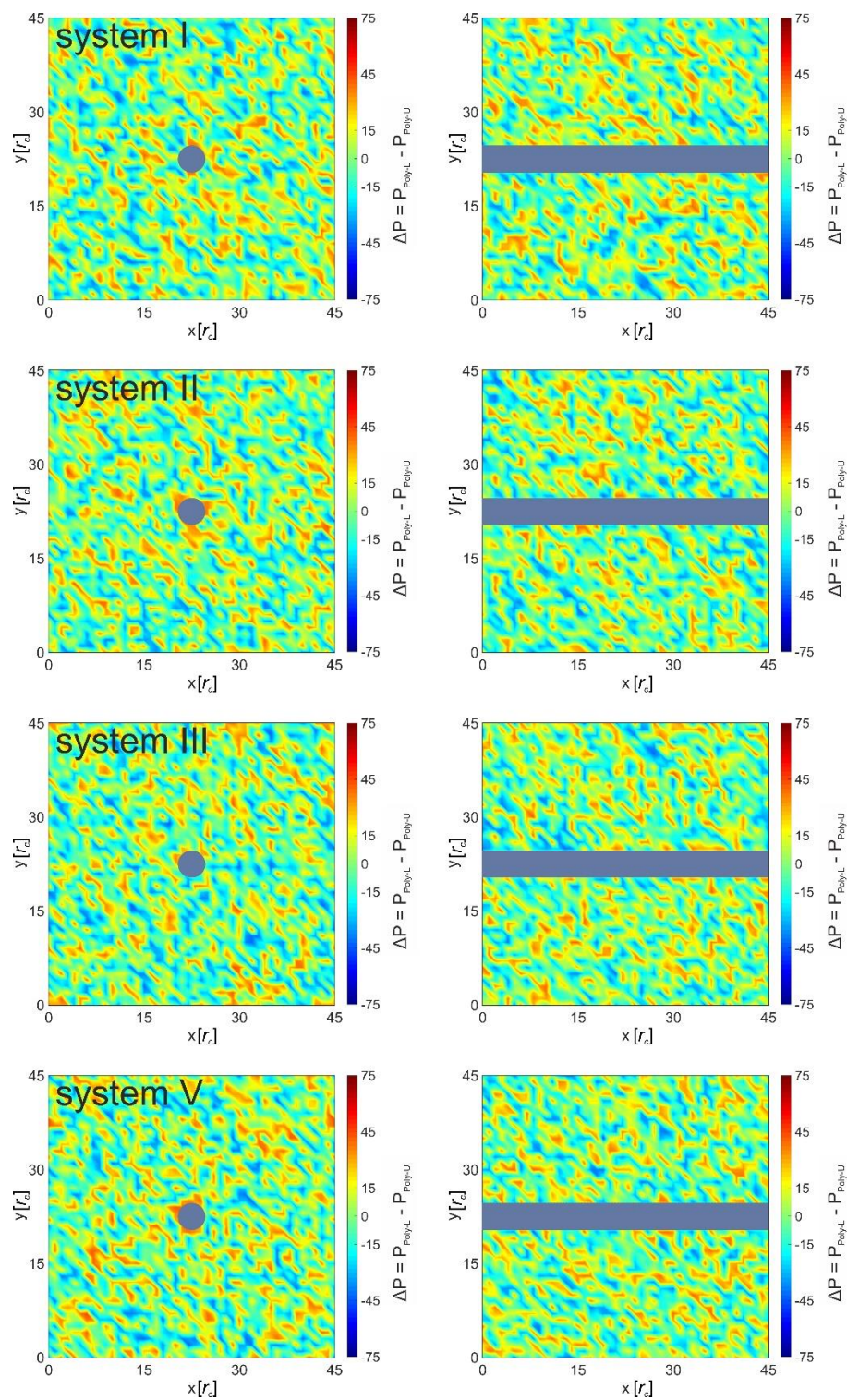


Figure S3. The distribution of pressure differences across the interface ΔP in different systems.

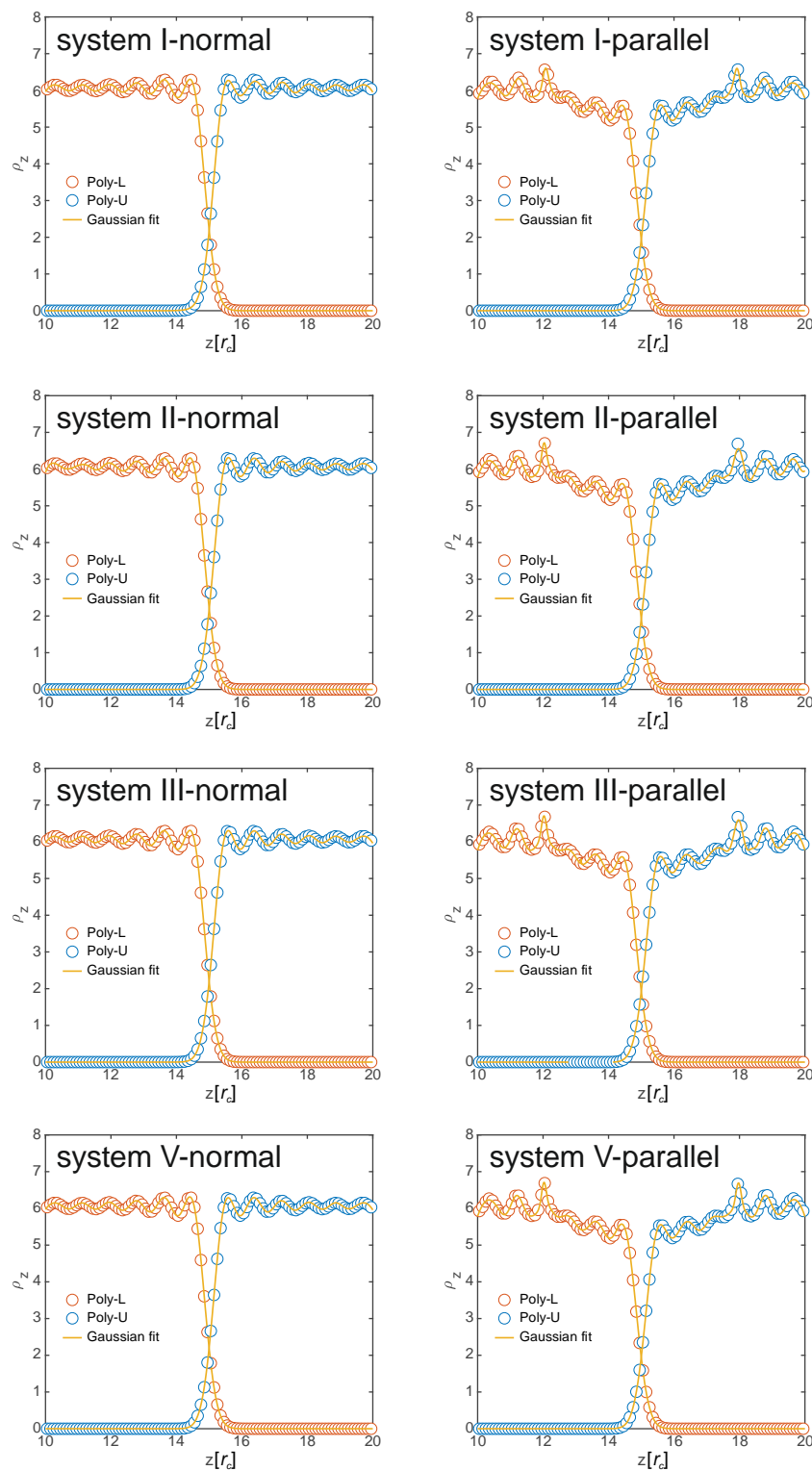


Figure S4. The bead density profiles of the polymers throughout the nanofluidic channel for different systems and nanotube orientations. The profile direction is normal ρ_z to the interface.

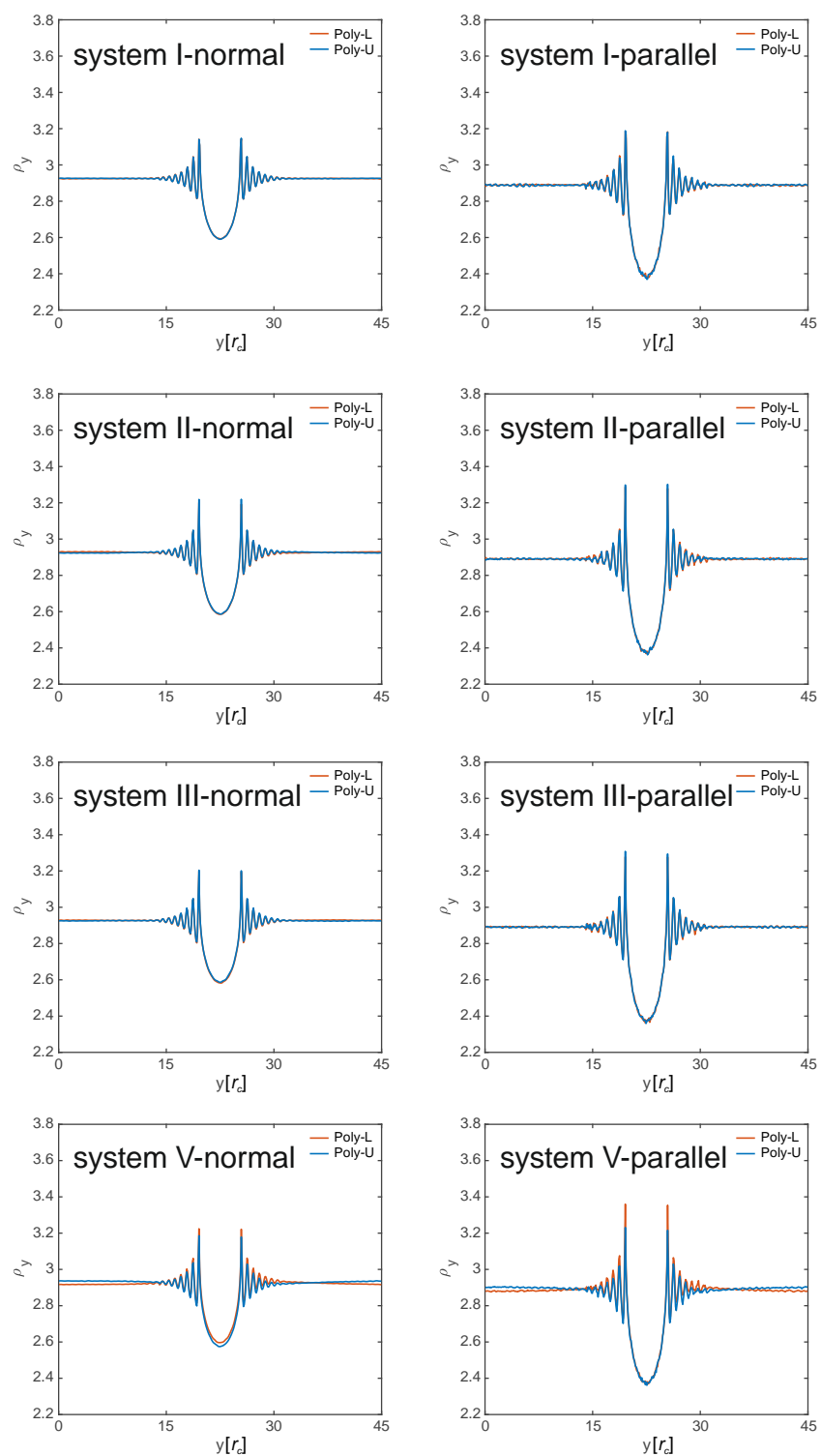


Figure S5. The bead density profiles of the polymers throughout the nanofluidic channel for different systems. The profile direction is parallel ρ_y to the interface.

3. References

- (1) Israelachvili, J. N. *Intermolecular and Surface Forces*; Elsevier, 2011.
- (2) Butt, H.-J.; Graf, K.; Kappl, M. *Physics and Chemistry of Interfaces*, 3rd ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2013.
- (3) Groot, R. D.; Warren, P. B. Dissipative Particle Dynamics: Bridging the Gap between Atomistic and Mesoscopic Simulation. *J. Chem. Phys.* **1997**, *107* (11), 4423–4435.
- (4) Gooneie, A.; Schuschnigg, S.; Holzer, C. A Review of Multiscale Computational Methods in Polymeric Materials. *Polymers (Basel, Switz.)* **2017**, *9* (1), 16.
- (5) Jamali, S.; Boromand, A.; Khani, S.; Wagner, J.; Yamanoi, M.; Maia, J. Generalized Mapping of Multi-Body Dissipative Particle Dynamics onto Fluid Compressibility and the Flory-Huggins Theory. *J. Chem. Phys.* **2015**, *142* (16), 164902.
- (6) Ghoufi, A.; Emile, J.; Malfreyt, P. Recent Advances in Many Body Dissipative Particles Dynamics Simulations of Liquid-Vapor Interfaces. *Eur. Phys. J. E* **2013**, *36* (1), 10.
- (7) Binks, B. P.; Horozov, T. S. Colloidal Particles at Liquid Interfaces: An Introduction. In *Colloidal Particles at Liquid Interfaces*; Binks, B. P., Horozov, T. S., Eds.; Cambridge University Press: Cambridge, 2006; pp 1–74.
- (8) Sperling, L. H. *Introduction to Physical Polymer Science*, 4th ed.; John Wiley & Sons, Inc.: New Jersey, 2006.
- (9) Binks, B. P. Colloidal Particles at a Range of Fluid–Fluid Interfaces. *Langmuir* **2017**, *33* (28), 6947–6963.
- (10) Rapacchietta, A. .; Neumann, A. .; Omenyi, S. . Force and Free-Energy Analyses of Small Particles at Fluid Interfaces I. Cylinders. *J. Colloid Interface Sci.* **1977**, *59* (3), 541–554.