

SUPPORTING INFORMATION

Transferable Coarse-Grained MARTINI Model for Methacrylate-Based Copolymers

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1. Atomistic and Coarse-Grained Force Fields

1.1 Functional Form of the Potentials

The total potential energy of the molecular systems can be described as a sum of intra- (bonded) and intermolecular (nonbonded) interactions:

$$\Phi^{\text{total}}(\mathbf{r}^N) = \Phi^{\text{bon}}(\mathbf{r}^N) + \Phi^{\text{nbon}}(\mathbf{r}^N) \quad (1)$$

For both the GROMOS (atomistic) and MARTINI (CG) force-fields, the nonbonded interactions are modelled as a combination of dispersion (Lennard-Jones, LJ) and electrostatic (Coulomb, C) terms:

$$\Phi^{\text{nbon}}(\mathbf{r}^N) = \Phi^{\text{LJ}}(\mathbf{r}^N) + \Phi^{\text{C}}(\mathbf{r}^N) \quad (2)$$

In the case of GROMOS, bonded or intramolecular interactions are the sum of bond, bond angle, improper and torsional dihedral angle terms:

$$\begin{aligned} \Phi_{\text{GRO}}^{\text{bon}}(\mathbf{r}^N) &= \sum_i \frac{1}{4} K_{b,i} (b_i^2 - b_{0,i}^2)^2 + \sum_i \frac{1}{2} K_{\theta,i} (\cos \theta_i - \cos \theta_{0,i})^2 \\ &+ \sum_i \frac{1}{2} K_{\xi,i} (\xi_i - \xi_{0,i})^2 + \sum_i K_{\phi,i} (1 + \cos(\delta_i) \cos(m_i \phi_i)) \end{aligned} \quad (3)$$

whereas the original MARTINI parameterization only accounts for bond and angle terms (note however that several specific parameterizations usually add torsional potentials to better describe molecular conformations):

$$\Phi_{\text{MAR}}^{\text{bon}}(\mathbf{r}^N) = \sum_i \frac{1}{2} K_{b,i} (b_i - b_{0,i})^2 + \sum_i \frac{1}{2} K_{\theta,i} (\cos \theta_i - \cos \theta_{0,i})^2. \quad (4)$$

1.2 Molecular Parameters

In table 1 we report the energy- and length-scale parameters describing like and unlike LJ interactions between MARTINI water and octanol. The rest of the parameters are provided in the manuscript. Note that the CG particles are treated as electrically neutral LJ sites.

Table 1: LJ potential parameters for interactions of standard MARTINI water and octanol. W denotes the water bead (P_4) whereas OcC and OcA correspond to the octanol building blocks C_1 and P_1 , respectively.

| Pair | ϵ (kJ/mol) | σ (nm) |
|---------|---------------------|---------------|
| W-W | 5.0 | 4.7 |
| OcC-OcC | 3.5 | 4.7 |
| OcA-OcA | 4.5 | 4.7 |
| W-OcC | 2.0 | 4.7 |
| W-OcA | 4.5 | 4.7 |
| OcC-OcA | 2.7 | 4.7 |

In order to represent the copolymer (PEO-*b*-PBMA and PEO-*b*-PMMA) and THF structures at the atomistic level (united-atom approach), eight different GROMOS particles are necessary as illustrated in Figure 1. Parameters for describing nonbonded LJ interactions between like particles are listed in Table 2. The attractive and repulsive terms are given in the standard GROMOS notation ($C^{(6)} = 4\epsilon\sigma^6$ and $C^{(12)} = 4\epsilon\sigma^{12}$). In Tables 3 and 4 the list of parameters for bonds and angles and proper dihedrals are included.

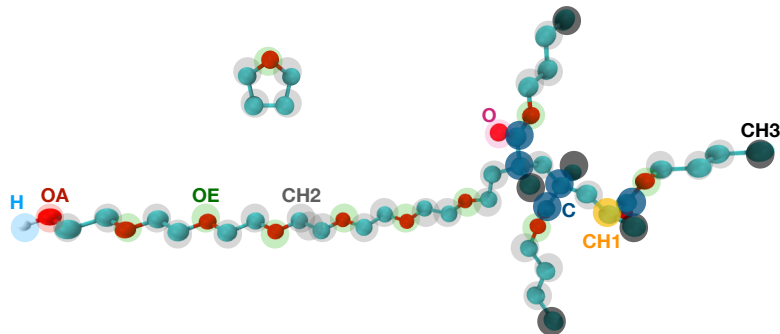


Figure 1: Atomistic representation THF and a PEO-*b*-PBMA chain containing all the different atomic sites described in our work and named according to the GROMOS notation (H, OA, OE, CH2, O, CH1, C and CH3).

Table 2: LJ potential parameters for interactions between all the atomic sites described in our work according to the GROMOS force-field. Unlike interactions are estimated as geometric means: $C_{ij}^{(6)} = \sqrt{C_i^{(6)}C_j^{(6)}}$ and $C_{ij}^{(12)} = \sqrt{C_i^{(12)}C_j^{(12)}}$

| Site | $C^{(6)}$ (kJ nm ⁶ /mol) | $C^{(12)}$ (kJ nm ¹² /mol) |
|------|-------------------------------------|---------------------------------------|
| O | 2.2619536×10^{-3} | 1.0×10^{-6} |
| OA | 2.2619536×10^{-3} | 1.505529×10^{-6} |
| OE | 2.2619536×10^{-3} | 1.21×10^{-6} |
| C | 2.3406244×10^{-3} | 4.937284×10^{-6} |
| CH1 | 6.06841×10^{-3} | 9.70225×10^{-5} |
| CH2 | 7.4684164×10^{-3} | 3.3965584×10^{-5} |
| CH3 | 9.6138025×10^{-3} | 2.6646244×10^{-6} |
| H | 0.0 | 0.0 |

Finally, for creating GROMACS topologies containing optimized parameters we recommend the use of the ATB server. Files for THF can be found at: <https://atb.uq.edu.au/molecule.py?molid=876>.

Table 3: GROMOS bonds and angles parameters

| Interaction | b_0 (nm) / θ_0 (degrees) | K_b (10^6 kJ/(mol nm ⁴)) / K_θ (kJ/mol) |
|---|-----------------------------------|---|
| BONDS | | |
| H-OA | 0.100 | 1.57 |
| CH _n -OE | 0.143 | 8.18 |
| CH _n -OA | 0.143 | 8.18 |
| CH _n -CH _n (including C-C) | 0.152 | 5.43 |
| CH _n -C | 0.153 | 7.15 |
| C-O | 0.123 | 16.6 |
| ANGLES | | |
| CH _n -CH _n -C | 111.0 | 530.0 |
| CH _n -CH _n -Ch _n | 111.0 | 530.0 |
| CH _n -CH _n -OA | 111.0 | 530.0 |
| CH _n -OA-CH _n | 109.5 | 450.0 |
| O-C-CH _n | 121.0 | 685.0 |
| C-CH _n -C | 109.5 | 520.0 |
| H-OA-CH _n | 109.5 | 450.0 |
| C-C-O | 115.0 | 610.0 |
| C-C-OE | 115.0 | 610.0 |
| O-C-OE | 126.0 | 640.0 |

Table 4: GROMOS dihedrals parameters

| Interaction | $\cos(\delta)$ | K_ϕ (kJ/mol) | multiplicity (m) |
|---------------------------------------|----------------|-------------------|----------------------|
| -CH _n -OA- (O, OE) | 1.0 | 1.26 | 3 |
| -CH _n -CH _n - | 1.0 | 5.92 | 3 |
| -CH _n -C- | 1.0 | 5.92 | 6 |
| CH _n -OA-C-CH _n | -1.0 | 24.0 | 2 |

2. PEO₆-*b*-PMMA₇ Bond Length Distributions

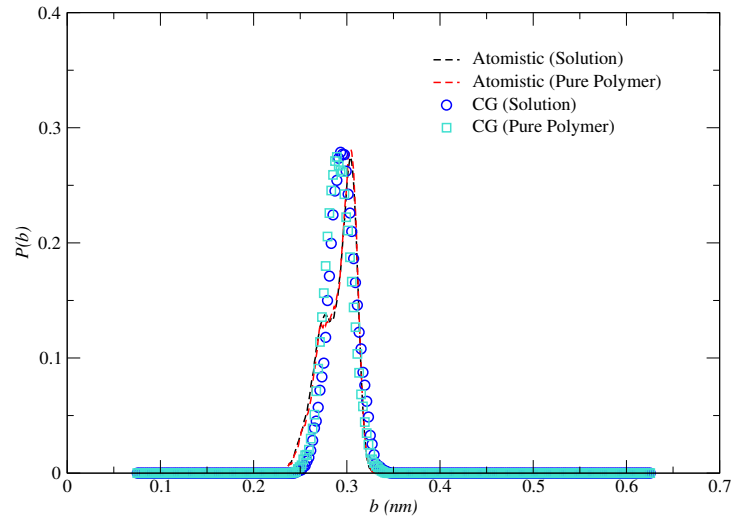


Figure 2: Probability distribution of bond length (b) between EOB and EOT segments sampled by atomistic models representing copolymer chains in THF (black dashed line) and pure polymer systems (red dashed line) along with the CG distributions (empty symbols).

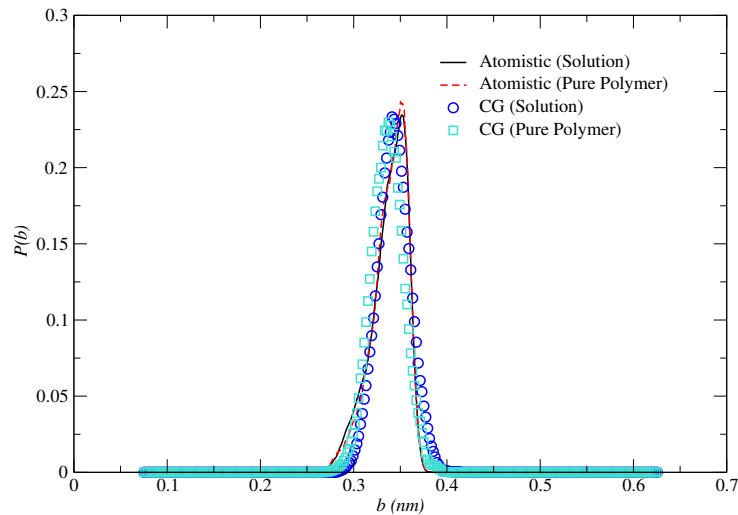


Figure 3: Probability distribution of bond length (b) between EOB and EOB segments sampled by atomistic models representing copolymer chains in THF (black dashed line) and pure polymer systems (red dashed line) along with the CG distributions (empty symbols).

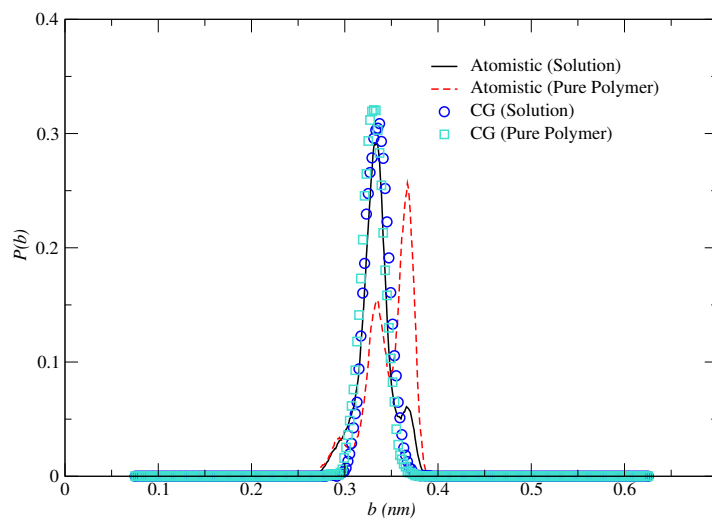


Figure 4: Probability distribution of bond length (b) between EOB and MB segments sampled by atomistic models representing copolymer chains in THF (black dashed line) and pure polymer systems (red dashed line) along with the CG distributions (empty symbols).

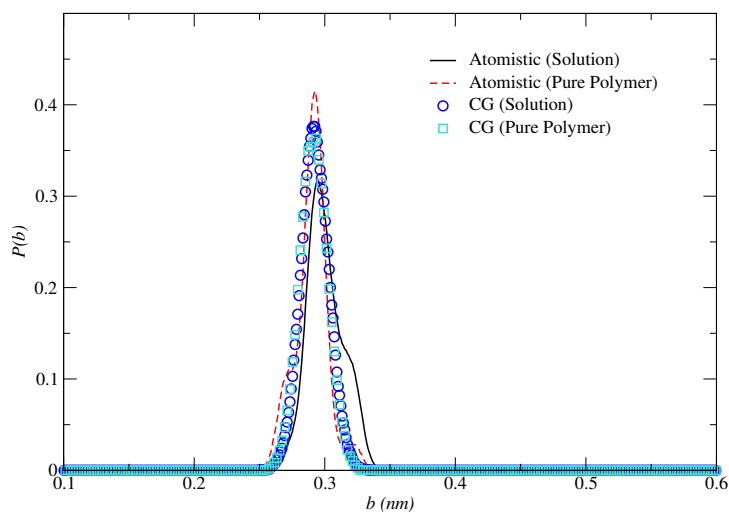


Figure 5: Probability distribution of bond length (b) between MB and MB segments sampled by atomistic models representing copolymer chains in THF (black dashed line) and pure polymer systems (red dashed line) along with the CG distributions (empty symbols).

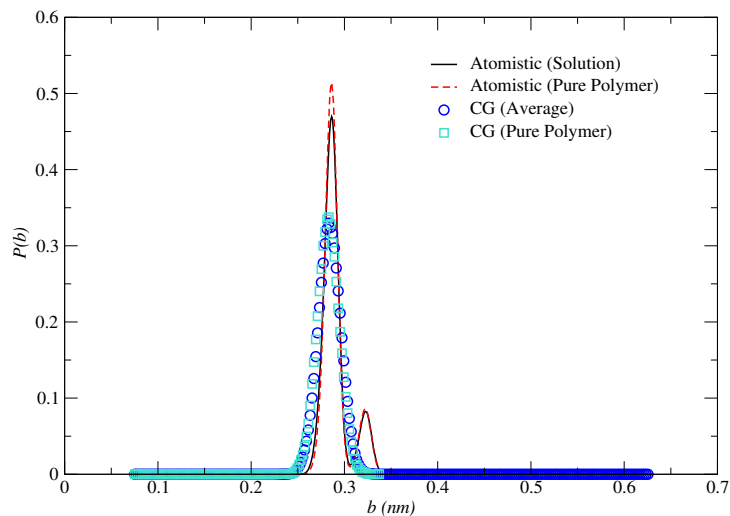


Figure 6: Probability distribution of bond length (b) between MB and ME segments sampled by atomistic models representing copolymer chains in THF (black dashed line) and pure polymer systems (red dashed line) along with the CG distributions (empty symbols).

3. PEO₆- b -PMMA₇ Angle and Dihedral Distributions

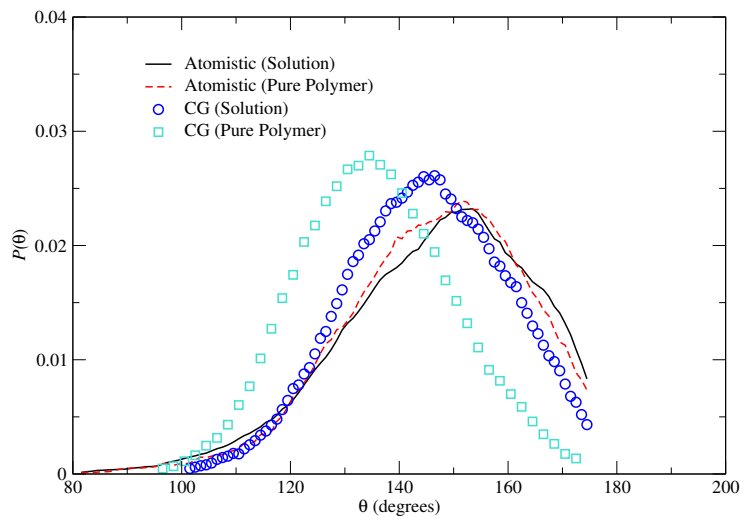


Figure 7: Probability distribution of angle (θ) between EOT-EOB-EOB segments sampled by atomistic models representing copolymer chains in THF (black dashed line) and pure polymer systems (red dashed line) along with the CG distributions (empty symbols).

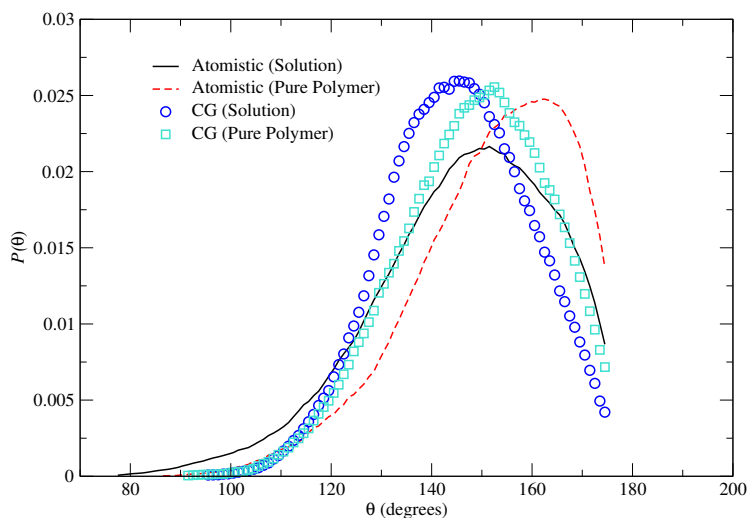


Figure 8: Probability distribution of angle (θ) between EOB-EOB-EOB segments sampled by atomistic models representing copolymer chains in THF (black dashed line) and pure polymer systems (red dashed line) along with the CG distributions (empty symbols).

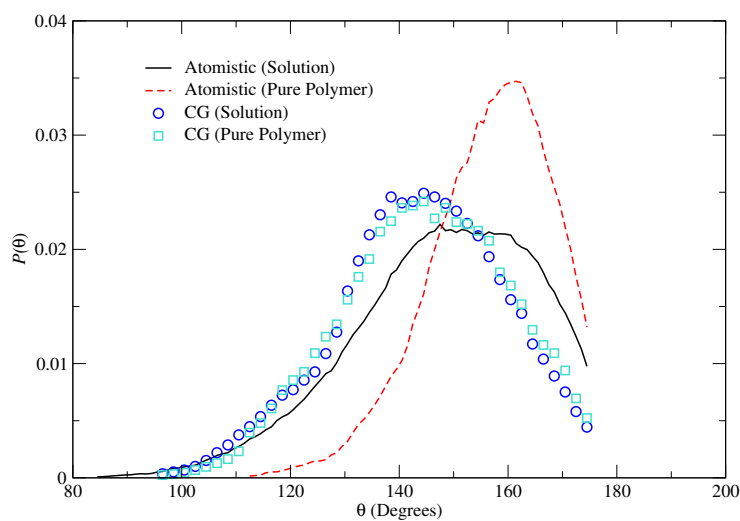


Figure 9: Probability distribution of angle (θ) between EOB-EOB-MB segments sampled by atomistic models representing copolymer chains in THF (black dashed line) and pure polymer systems (red dashed line) along with the CG distributions (empty symbols).

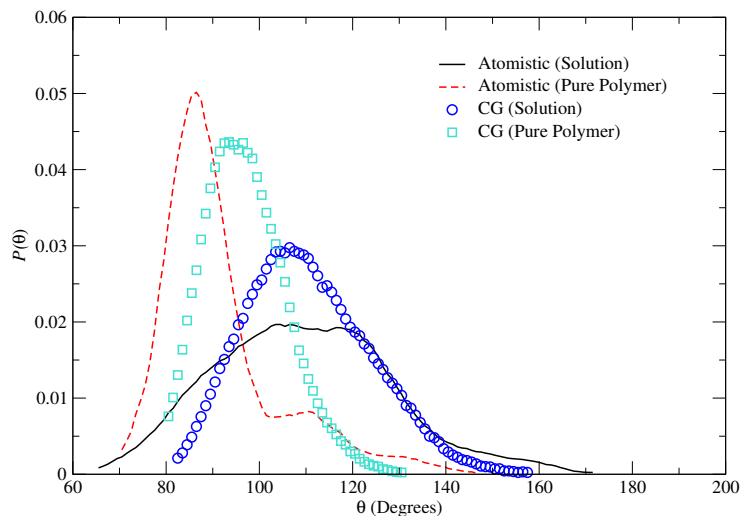


Figure 10: Probability distribution of angle (θ) between EOB-MB-MB segments sampled by atomistic models representing copolymer chains in THF (black dashed line) and pure polymer systems (red dashed line) along with the CG distributions (empty symbols).

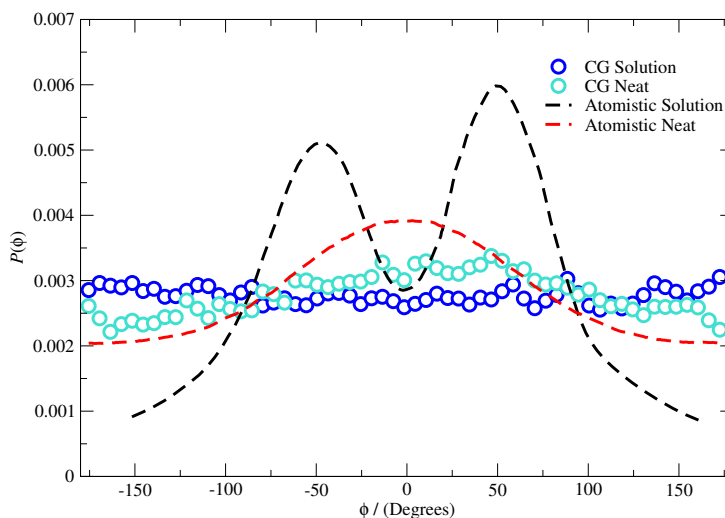


Figure 11: Probability distributions of proper dihedral angles between EOB-EOB-EOB-EOB segments sampled by atomistic models representing copolymer chains in THF (black dashed line) and pure polymer systems (red dashed line) along with the CG distributions (empty symbols).

4. Radius of gyration of PEO_m-*b*-PMMA₆ and PEO_m-*b*-PBMA₆ copolymers.

Table 5: Radius of gyration (R_g) for atomistic and CG PEO_m-*b*-PMMA₆ and PEO_m-*b*-PBMA₆ copolymers in pure polymer and THF solution.

| | Solution | | Pure Polymer | |
|------------------------------|---------------|----------------|---------------|----------------|
| | CG (nm) | Atomistic (nm) | CG (nm) | Atomistic (nm) |
| <i>-b</i> -PMMA ₆ | | | | |
| PEO ₃ | 0.619 ± 0.051 | 0.628 ± 0.053 | 0.608 ± 0.003 | 0.622 ± 0.002 |
| PEO ₇ | 0.894 ± 0.094 | 0.872 ± 0.119 | 0.861 ± 0.002 | 0.852 ± 0.003 |
| PEO ₁₄ | 1.370 ± 0.186 | 1.235 ± 0.213 | 1.295 ± 0.001 | 1.215 ± 0.001 |
| PEO ₁₈ | 1.532 ± 0.276 | 1.376 ± 0.236 | 1.497 ± 0.013 | 1.406 ± 0.005 |
| <i>-b</i> -PBMA ₆ | | | | |
| PEO ₃ | 0.700 ± 0.039 | 0.682 ± 0.042 | 0.698 ± 0.002 | 0.669 ± 0.001 |
| PEO ₇ | 0.933 ± 0.076 | 0.895 ± 0.105 | 0.926 ± 0.003 | 0.882 ± 0.002 |
| PEO ₁₄ | 1.353 ± 0.200 | 1.191 ± 0.235 | 1.377 ± 0.004 | 1.267 ± 0.013 |
| PEO ₁₈ | 1.607 ± 0.237 | 1.370 ± 0.277 | 1.595 ± 0.008 | 1.440 ± 0.007 |

5. Equilibrium Structure of THF

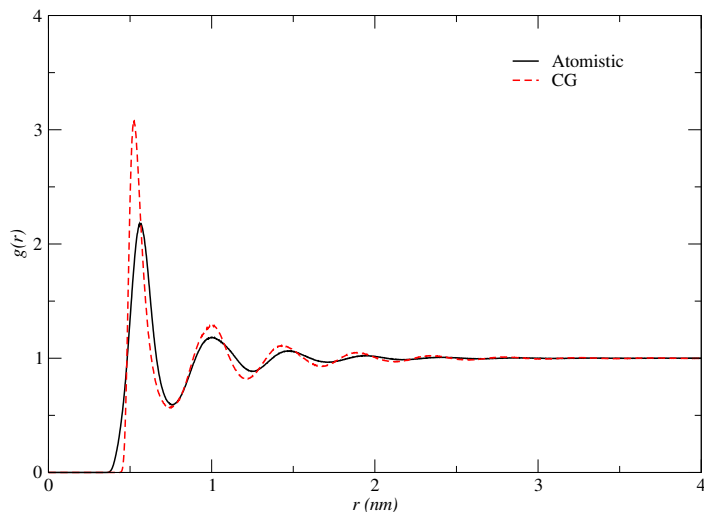


Figure 12: Radial distribution function (RDF) of THF obtained from atomistic (black solid line) and CG (red dashed line) simulations at 300 K and 1 bar. The atomistic RDF has been obtained from the trajectory of the center of mass of THF molecules.

6. Interfacial Properties of THF

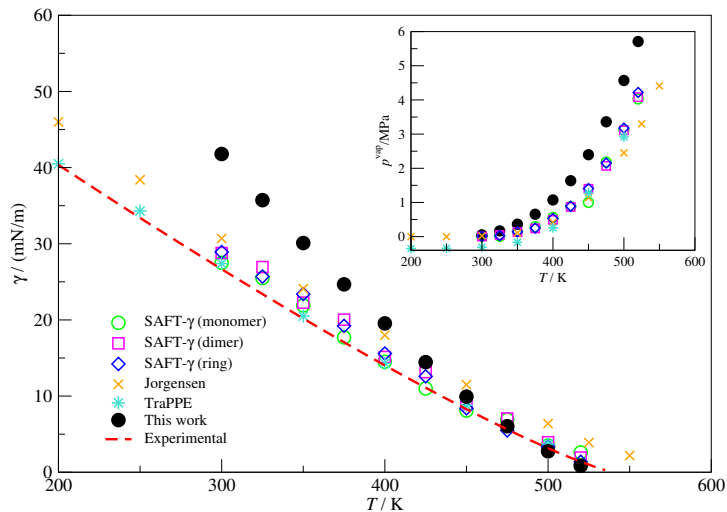


Figure 13: Surface tension and equilibrium vapour pressure (inset plot) as a function of temperature for THF. Experimental values (red dashed lines) and data points indicated for the SAFT- γ (monomer), SAFT- γ (dimer), SAFT- γ (ring), Jorgensen and TraPPE models are compiled from ref [72].