

Multiscale Simulation Scattering Intensity Calculator (MuSSIC)

MuSSIC is a computational tool for calculation of neutron scattering from coarse grain (CG) simulations allowing direct comparison of the simulations to a rigorous benchmark of structural experimental data. It is based on the method introduced by Alan Soper in his paper on coarse-grained Empirical Potential Structure Refinement (Biochimica et Biophysica Acta 1861, 6, 1652-1660, 2017).

The code has been tested for different coarse grain models on simple liquids to complex polymeric systems (examples are given in test_systems). The current version of the code can be used on any CG system like polymer melts or surfactants forming micelles in water (SDS, PEG and CTAB). There is an ongoing usability tests on different systems to test the generality and applicability of the method to other systems. Any development or improvement in the code/method and related examples will be updated on Github page (<https://github.com/disorderedmaterials/MuSSIC>).

Scattering calculation for atomistic simulations

In a neutron scattering experiment, total difference scattering cross section (d.c.s) is measured after suitable correction for beam attenuation, multiple scattering and inelasticity effects. The total structure factor $F(Q)$, which can be related to simple scattering theory to underlying atomistic structure, is obtained from the total differential cross section

$$d.c.s = F(Q) + \sum_{i=1}^N c_i b_i^2 \quad (1)$$

where c_i and b_i are the concentration and scattering length of atom type ' i ' respectively and the sum is over ' N ' number of atom types in the system.

The total structure factor for a system containing M distinct atom types can be written as the weighted sum of all possible partial pair structure factors $S_{ij}(Q)$.

$$F(Q) = \sum_{i=1, j \geq i}^N c_i c_j b_i b_j [S_{ij}(Q) - 1] \quad (2)$$

where c_i and b_i are the concentration and scattering length of atom type ' i ' respectively and $S_{ij}(Q)$ is the partial structure factor related to the correlation between the atom types i and j . Definition of partial structure factor $S_{ij}(Q)$ by Faber and Ziman is given as

$$S_{ij}(Q) - 1 = 4\pi\rho \int_0^\infty r^2 [g_{ij}(r) - 1] \frac{\sin Qr}{Qr} dr \quad (3)$$

where the $g_{ij}(r)$ are the partial radial distribution function of atom types i and j

In atomistic simulations, the partial pair radial distribution functions $g(r)$ are obtained from the atomic positions. A Fourier transform of $g_{ij}(r)$ yields $S_{ij}(Q)$ and $F(Q)$ can be obtained from the sum of neutron weighted $S_{ij}(Q)$. Thus an atomistic structure from the simulation can be validated by comparing the $F^{sim}(Q)$ from simulations with $F^{exp}(Q)$ obtained from experiments. For multicomponent systems, a single diffractogram obtained in experiments contains all the partials that one would like to extract individually. The isotopic substitution technique is used in experiments to obtain partials under the assumption that the structural properties of system are not changed by changing the isotope ratios. It is usually the hydrogen that is replaced by deuterium in neutron scattering experiments. Different ratios of isotope gives different isotopologues.

In simulations, the isotopic substitution can be implemented in simulations simply by changing the neutron scattering length in the coefficient in equation(2) (the product of concentration and scattering length of the atom type and its isotope ratio). The effective scattering length of hydrogen 'H' when substituted by Deuterium 'D' becomes

$$b_H^{eff} = ratio * b_D + (1 - ratio) * b_H$$

where b_H is the scattering length of hydrogen (3.74) is, b_D is the scattering length of deuterium (-6.671) and ' $ratio$ ' is the ratio of hydrogen that is replaced by deuterium in the system.

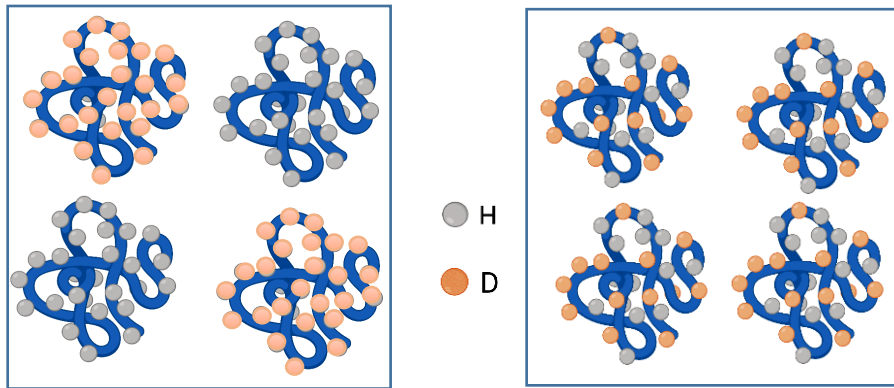


Figure 1 Schematic showing the cases in which hydrogens are not exchangeable (left) and exchangeable (right). H indicates the hydrogen and D indicates the hydrogen which is isotopically substituted.

The scattering weight coefficients change depending on the exchangeability of hydrogens with other hydrogens which are isotope substituted. The scattering weights change for the structure factor arising from intra molecular correlations and intermolecular correlations. To account this correction, the total $F(Q)$ can be separated into two parts. Structure factor computed for bound atoms $F_{intra}(Q)$ i.e., using intra molecular spatial correlation and structure factor computed for unbound atoms $F_{inter}(Q)$ i.e., using inter-molecular spatial correlation.

$$F(Q) = F_{intra}(Q) + F_{inter}(Q)$$

$$F_{inter}(Q) = \sum_{i=1, j \geq i}^N W_{t_{ij}}^{inter} [S_{ij}^{inter}(Q) - 1]$$

$$F_{intra}(Q) = \sum_{i=1, j \geq i}^N W_{t_{ij}}^{intra} [S_{ij}^{intra}(Q) - 1]$$

$S_{ij}^{inter}(Q)$ is the partial structure factor computed by considering only inter molecular spatial correlation between atom types 'i' and 'j' and $S_{ij}^{intra}(Q)$ is computed from intra molecular correlations between atomtypes 'i' and 'j'.

Weighting matrices are calculated for all possible pairs of atom types as below

$$W_{t_{ij}} = (2 - \delta_{ij})c_i c_j b_i b_j$$

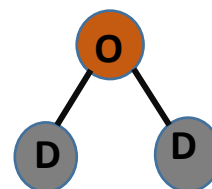
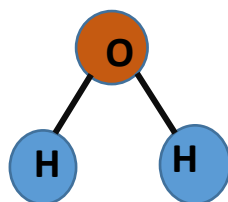
In case of the presence of exchangeable atom types, the scattering lengths are reweighted according to the concentration of total exchangeable atoms

$$b_i = b_i * ex_{conc}$$

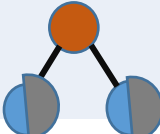
Weighting matrices are same for both 'intra' and 'inter' cases except for those atom types which are not exchangeable and isotopically substituted. Following examples illustrates the difference in the calculation of weighting matrices for partial S(Q)s in the presence of exchangeable hydrogens.

Case1: water molecules

H and D are exchangeable



Scattering lengths and concentration of atom types in different isotopologues

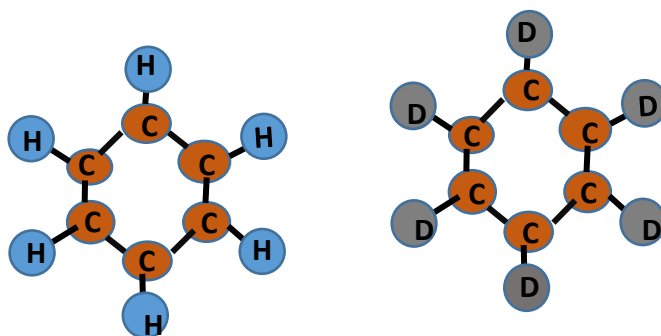
Isotopologue	Atom types	Fraction (c_i)	b_i (inter-molecular)	b_i (intra-molecular)
H ₂ O	O	0.333	0.5803	0.5803
	H	0.666	-0.3739	-0.3739
D ₂ O	O	0.333	0.5803	0.5803
	D	0.666	0.6671	0.6671
HDO (50:50)	O	0.333	0.5803	0.5803
	H and D (exchangeable)	0.666 (0.5H+ 0.5D)	0.1466 (0.5*-0.3739+0.5*0.6671)	0.1466

Weighting matrices

Isotopologue	Atom types	Wt_{ij}^{inter}		Wt_{ij}^{intra}	
H ₂ O	O	0.0374	-0.0964	0.0374	-0.0964
	H		0.0621		0.0621
D ₂ O	O	0.0374	0.172	0.0374	0.172
	D		0.197		0.197
HDO	O	0.0374	0.0378	0.0374	0.0378
	H and D		0.00955		0.00955

Case2: Benzene

H and D are not exchangeable



Scattering lengths and concentration of atom types

Isotopologue	Atom types	Fraction (c_i)	b_i (inter-molecular)	b_i (intra-molecular)
C_6H_6	C	0.5	0.6646	6.646
	H	0.5	-0.3739	-0.3739
C_6D_6	C	0.5	0.6646	0.6646
	D	0.5	0.6671	0.6671
$C_6H_6(50\%)+C_6D_6(50\%)$	C	0.5	0.6646	0.6646
	H	0.5	0.1466	$-0.3739/0.6671$
	D	(0.25H+ 0.25D)	$(0.5*0.3739+0.5*0.6671)$	

Weighting matrices

Isotopologue	Atom types	Wt_{ij}^{inter}		Wt_{ij}^{intra}	
C_6H_6	C	0.110	-0.124	0.110	-0.124
	H		0.0349		0.0349
C_6D_6	C	0.110	0.221	0.110	0.221
	H		0.111		0.111
$C_6H_6(50\%)+C_6D_6(50\%)$	C	0.110	0.0487	0.110	0.0487
	H and D		0.00537		0.0731

Scattering calculation for coarse grained simulations

We define the scattering length density distribution of CG bead type 's' by considering either uniform distribution of atoms or Gaussian distribution of atoms within the bead

$$n_s(r) = \sum_i [N_i^s b_i] \rho(r_s)$$

where N_i^s is the number of atoms of atom type i within bead type 's', b_i is the scattering length density of atom type i and $\rho(r_s)$ is the density distribution of the atoms for bead type 's'

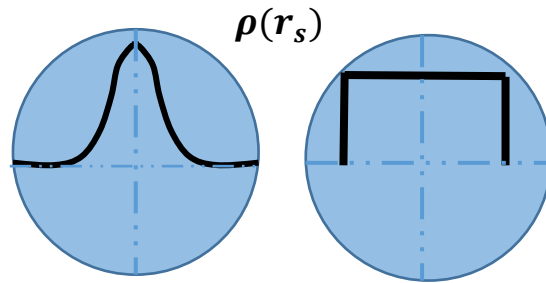


Figure 2 Schematic showing the assumption of Gaussian (left) and uniform distribution (right) of atoms within the bead

The form factor $f_s(Q)$ for bead type 's' is obtained by performing the Fourier transform of the scattering length density distribution

$$f_s(Q) = \sum_i [N_i^s b_i] 4\pi \int [r^2 \rho_s(r_s)] \frac{\sin Qr_s}{Qr_s} dr_s$$

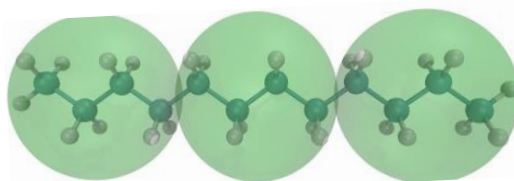


Figure 3 Grouping of certain number of atoms into a bead for CG representation

The total differential scattering cross-section for a CG system containing M distinct CG bead types can be written as

$$d.c.s = \frac{1}{\bar{N}_A} \left[\sum_s^M c_s \sum_i N_i^{(s)} b_i^2 + F_{CG}^{single-bead}(Q) + F_{CG}^{cross-bead}(Q) \right]$$

First term indicates the single atom scattering and the total structure factor for coarse grain systems, $F_{CG}(Q)$, is the sum of single bead scattering $F_{CG}^{single-bead}(Q)$ and cross bead scattering $F_{CG}^{cross-bead}(Q)$. The extra terms in $F_{CG}^{single-bead}(Q)$ takes care of the fact that each bead may contain more than one atom of any given type.

$$F_{CG}(Q) = F_{CG}^{single-bead}(Q) + F_{CG}^{cross-bead}(Q)$$

$F_{CG}^{single-bead}(Q)$ is the scattering from all possible pairs of atom types within the single bead 's', obtained by multiplying effective scattering length with formfactor $f_s(Q)$. Since the atoms in each bead are assumed to be distributed statistically through the particle according to the same $\rho(r_s)$ for all atom types their relative positions within the particle are uncorrelated and the same form factor $f_s(Q)$ applies to all the bead types.

$$F_{CG}^{single-bead}(Q) = \sum_s^M c_s \left[\sum_i N_i^{(s)} (N_i^{(s)} - 1) b_i^2 + 2 \sum_i N_i^{(s)} b_i N_j^{(s)} b_j \right] f_s^2(Q)$$

which can also be written as

$$F_{CG}^{single-bead}(Q) = \sum_s^M c_s \left[\sum_i \sum_{j \geq i} (2 - \delta_{ij}) N_i^{(s)} b_i N_j^{(s)} b_j - \sum_i N_i^{(s)} b_i \right] f_s^2(Q)$$

$F_{CG}^{cross-bead}(Q)$ is the scattering from all possible pairs of bead types, obtained by multiplying effective scattering length of the bead 's' with formfactor $f_s(Q)$

$$F_{CG}^{cross-bead}(Q) = \sum_s^M \sum_{t \geq s}^M (2 - \delta_{st}) c_s c_t \left[\sum_i N_i^{(s)} b_i \right] f_s(Q) \left[\sum_i N_i^{(t)} b_i \right] f_t(Q) (H_{st}(Q) - 1)$$

Similar to the scattering for atomistic models, the total structure factor is divided into $F_{CG}^{intra}(Q)$ and $F_{CG}^{inter}(Q)$

$$F_{CG}^{cross-bead}(Q) = F_{CG}^{intra}(Q) + F_{CG}^{inter}(Q)$$

Intra and Inter molecular scattering are obtained following the same equation as in scattering from atomistic simulations. The only difference is in computation of weights for partial structure factor $S_{CG}(Q)$

$$F_{CG}^{inter}(Q) = \sum_s^M \sum_{t \geq s}^M (2 - \delta_{st}) CGW t_{st}^{inter} f_s(Q) f_t(Q) (H_{st}^{inter}(Q) - 1)$$

$$F_{CG}^{intra}(Q) = \sum_s^M \sum_{t \geq s}^M (2 - \delta_{st}) CGW t_{st}^{intra} f_s(Q) f_t(Q) (H_{st}^{intra}(Q) - 1)$$

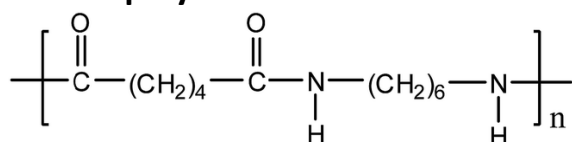
Weighting matrices $CGWt$ are calculated for all possible pairs of bead types as below

$$CGWt_{st} = c_s c_t \left[\sum_i N_i^{(s)} b_i \right] \left[\sum_i N_i^{(t)} b_i \right]$$

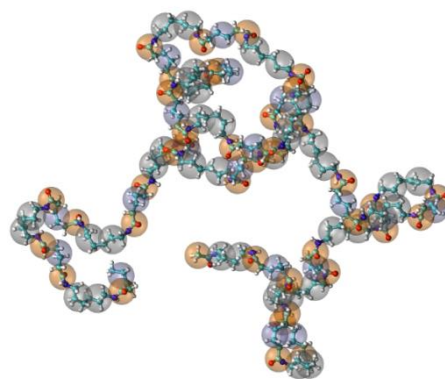
The effective scattering length density of bead type 's' is obtained by summing the scattering length densities of each atom type within the bead multiplied by number of atoms of that atom type. Similar to the scattering from atomistic simulations, scattering length density of hydrogen depends on the isotope ratio 'r' in the isotopologue and exchangeables.

Following examples show scattering lengths and weighting matrices for atomistic representation. Then the scattering lengths of the CG beads are explained using the scattering lengths of the atom types. The differences in weighting matrices $CGWt_{st}$ for inter and intra cases are shown in the presence of exchangeable hydrogens.

Case 3: polyamide66



H and D are not exchangeable when a certain ratio of chains are deuterated



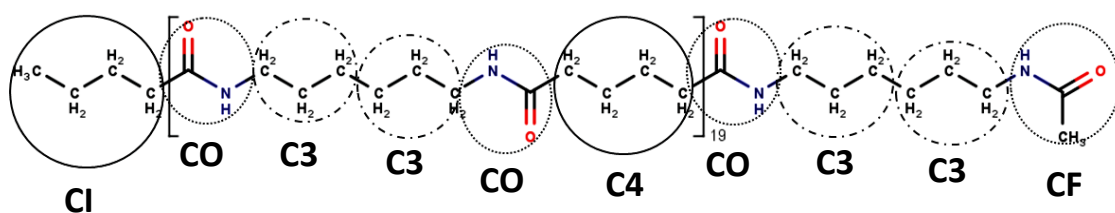
Scattering lengths for atomisitc representation

Isotpologue	Atom types	Fraction (c _i)	b _i (inter-molecular)	b _i (intra-molecular)
natural	C	0.315	0.6646	0.6646
	H	0.5803	-0.3739	-0.3739
	O	0.0522	0.5803	0.5803
	N	0.0522	0.9359	0.9359
Deuterated	C	0.5	0.6646	0.6646
	D	0.5	0.6671	0.6671
	O	0.0522	0.5803	0.5803
	N	0.0522	0.9359	0.9359
50-50 mix	C	0.5	0.6646	0.6646
	H	0.5	0.1466	-0.3739/0.6671
	D	(0.25H+ 0.25D)	(0.5*-0.3739+0.5*0.6671)	
	O	0.0522	0.5803	0.5803
	N	0.0522	0.9359	0.9359

Weighting matrices for atomisitic representation

Isotopologue	Atom types	Wt_{ij}^{inter}				Wt_{ij}^{intra}			
natural	C	0.0438	-0.0908	0.0127	0.0204	0.0438	-0.0908	0.0127	0.0204
	H		0.04709	-0.0131	-0.0212		0.04709	-0.013	-0.0212
	O			0.00092	0.0029			0.00092	0.0029
	N				0.00239				0.00239
Deuterated	C	0.0438	0.1621	0.0127	0.0204	0.0438	0.1621	0.0127	0.0204
	D		0.1499	0.0234	0.03789		0.1499	0.0234	0.03789
	O			0.00092	0.00296			0.00092	0.00296
	N				0.00239				0.00239
50-50 mix	C	0.0438	0.1621	0.0127	0.0204	0.0438	0.1621	0.0127	0.0204
	H and D		0.00724	0.00516	0.00832		0.0985	0.00516	0.00832
	O			0.00092	0.00296			0.00092	0.00296
	N				0.00239				0.00239

CG representation of polyamide66 (~4 carbon per bead case)

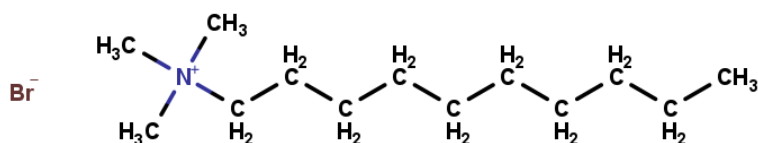


Scattering lengths for CG representation

Isotopologue	bead types	Fraction (c _s)	$\left[\sum N_i^{(s)} b_i\right]$ (inter-molecular)	$\left[\sum N_i^{(s)} b_i\right]$ (intra-molecular)
natural	CI (4b _C +9b _H)	0.01	-0.7067	-0.7067
	C4 (4b _C +8b _H)	0.19	-0.3328	-0.3328
	C3 (3b _C +6b _H)	0.40	-0.2496	-0.2496
	CO (b _C +b _H +b _O +b _N)	0.39	1.8069	1.8069
	CF (2b _C +4b _H b _O +b _N)	0.01	1.3498	1.3498
Deuterated	DI (4b _C +9b _D)	0.01	8.6623	8.6623
	D4 (4b _C +8b _D)	0.19	7.9952	7.9952
	D3 (3b _C +6b _D)	0.40	5.9964	5.9964
	DO (b _C +b _D +b _O +b _N)	0.39	2.8479	2.8479
	DF(2b _C +4b _D +b _O +b _N)	0.01	5.5138	5.5138
50-50 mix (0.5H+ 0.5D)	CI	0.005	3.9778	-0.7067
	DI	0.005	3.9778	8.6623
	C4	0.095	3.8312	-0.3328
	D4	0.095	3.8312	7.9952
	C3	0.20	2.8734	-0.2496
	D3	0.20	2.8734	5.9964
	CO	0.195	2.3274	1.8069
	DO	0.195	2.3274	2.8479
	CF	0.005	3.4318	1.3498
	DF	0.005	3.4318	5.5138

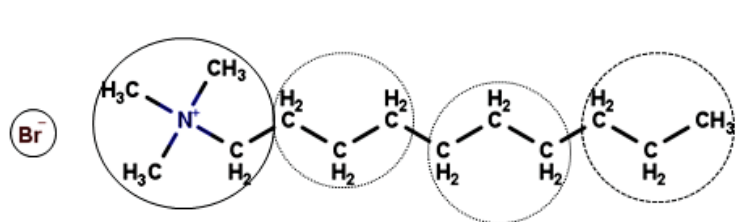
Case4: C₁₀TAB in water

H in C₁₀TAB surfactant is not exchangeable while the hydrogen in water is exchangeable as described in case 1.



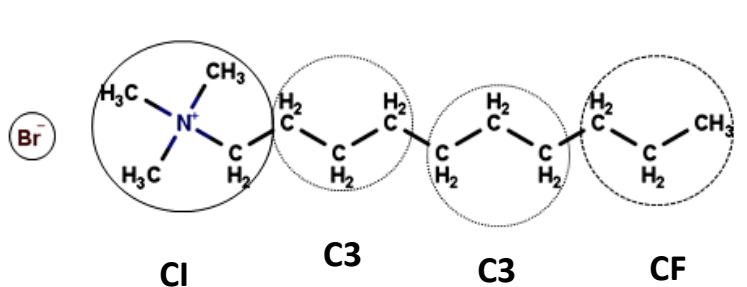
Isotopologue	Atom types	Fraction (c _i)	b _i (inter-molecular)	b _i (intra-molecular)
natural	N	0.00212	0.9359	0.9359
	C	0.02756	0.6646	0.6646
	HC	0.0636	-0.3739	-0.3739
	Br ⁻	0.00212	0.6794	0.6794
	OW	0.3015	0.5803	0.5803
	HW	0.6030	-0.3739	-0.3739
Deuterated	N	0.00212	0.9359	0.9359
	C	0.02756	0.6646	0.6646
	HC	0.0636	0.6671	0.6671
	Br ⁻	0.00212	0.6794	0.6794
	OW	0.3015	0.5803	0.5803
	HW	0.6030	0.6671	0.6671
	Br ⁻	0.0522	0.5803	0.5803

A case is shown where the 50% of the surfactants are deuterated is mixed with 50% of deuterated water.



Isotopologue	Atom types	Fraction (c _i)	b _i (inter-molecular)	b _i (intra-molecular)
50-50 mix of C10TAB in 50-50 mix of water	N	0.00212	0.9359	0.9359
	C	0.02756	0.6646	0.6646
	HC and DC	0.0636	0.1466 (0.5*-0.3739+0.5*0.6671)	-0.3739/0.6671
	Br ⁻	0.00212	0.6794	0.6794
	OW	0.3015	0.5803	0.5803
	HW and DW	0.6030	0.1466	0.1466

CG representation of C₁₀TAB (~3 carbon per bead case)



Isotologue	bead types	Fraction (c _s)	$[\sum N_i^{(s)} b_i]$ (inter-molecular)	$[\sum N_i^{(s)} b_i]$ (intra-molecular)
natural	CI (4b _C +11b _H + b _N)	0.00679	5.2069	-0.5186
	DI (4b _C +11b _D + b _N)		5.206	11.0314
	C3 (3b _C +6b _H)	0.0135	2.8734	-0.2496
	C3 (3b _C +6b _D)		2.8734	5.9964
	CF (3b _C +7b _H)	0.00679	3.02	-0.6235
	DF (3b _C +7b _D)		3.02	6.66350
	Br-	0.00679	0.6794	0.6794
	W	0.966	0.8735	0.8735
	DW		0.8735	0.8735

Verification method

In order to test the accuracy of the method for CG models, the atomistic simulations on selected systems are performed and the scattering data obtained for them is taken as benchmark data. Different CG models/mappings are chosen and trajectories from atomistic simulations are converted to CG trajectories by simply overlaying the beads onto atomic positions. Using MuSSIC code, the scattering data is obtained for the CG trajectories and compared against atomistic benchmark data to test the accuracy.

The comparison is to be done on different CG models (or bead sizes) and form factors. Following figure shows the workflow for the validation tests.

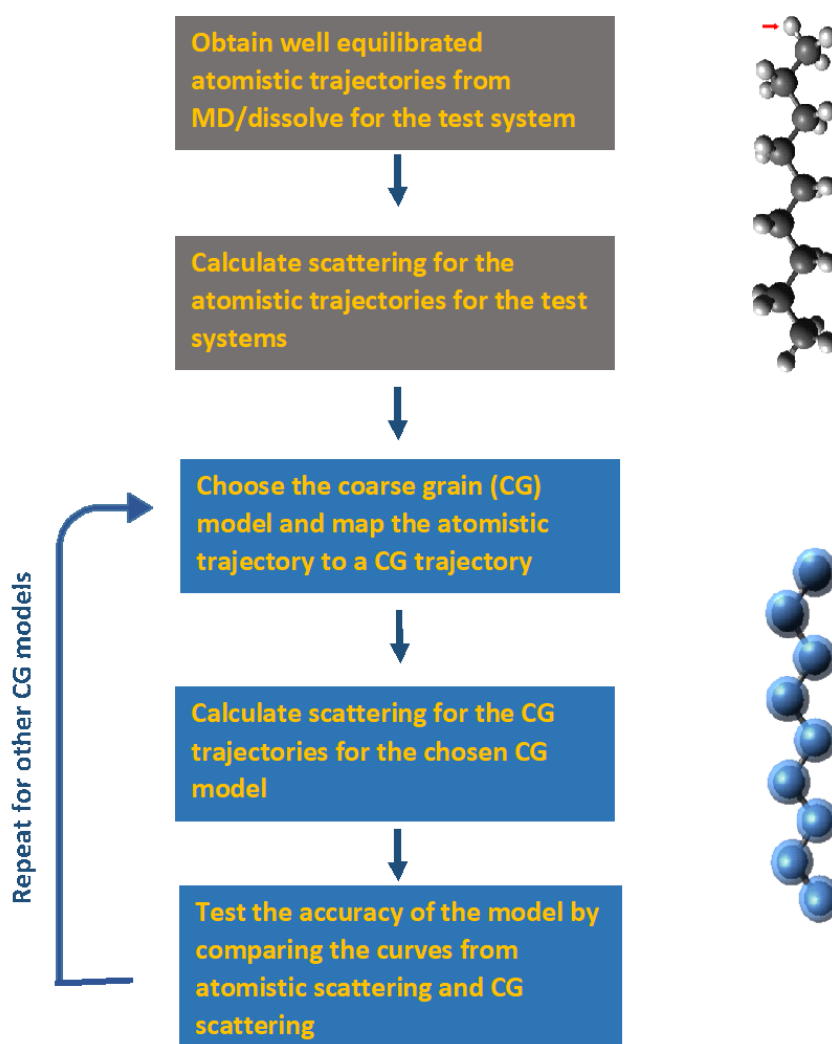
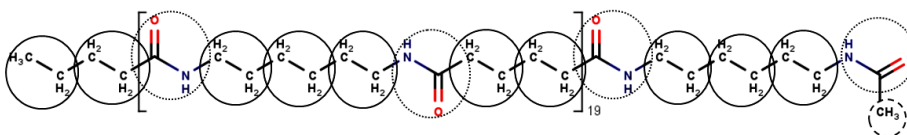


Figure 4 verification method for testing efficacy of MuSSIC

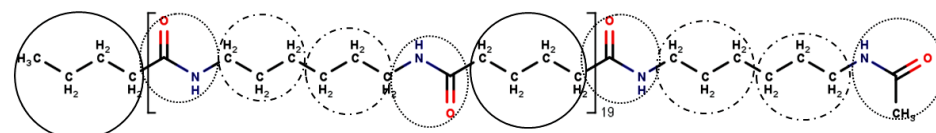
Verification tests

Case 3: polyamide66

~2 carbons per bead



~4 carbons per bead



~6 carbons per bead

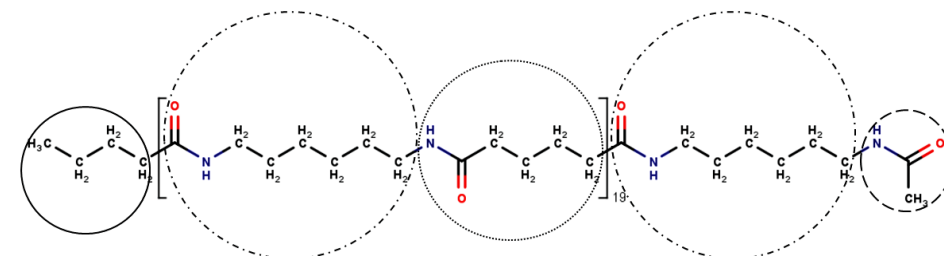


Figure 5 Different mappings between atomistic and CG models of PA-66. The circles denote beads grouping atoms.

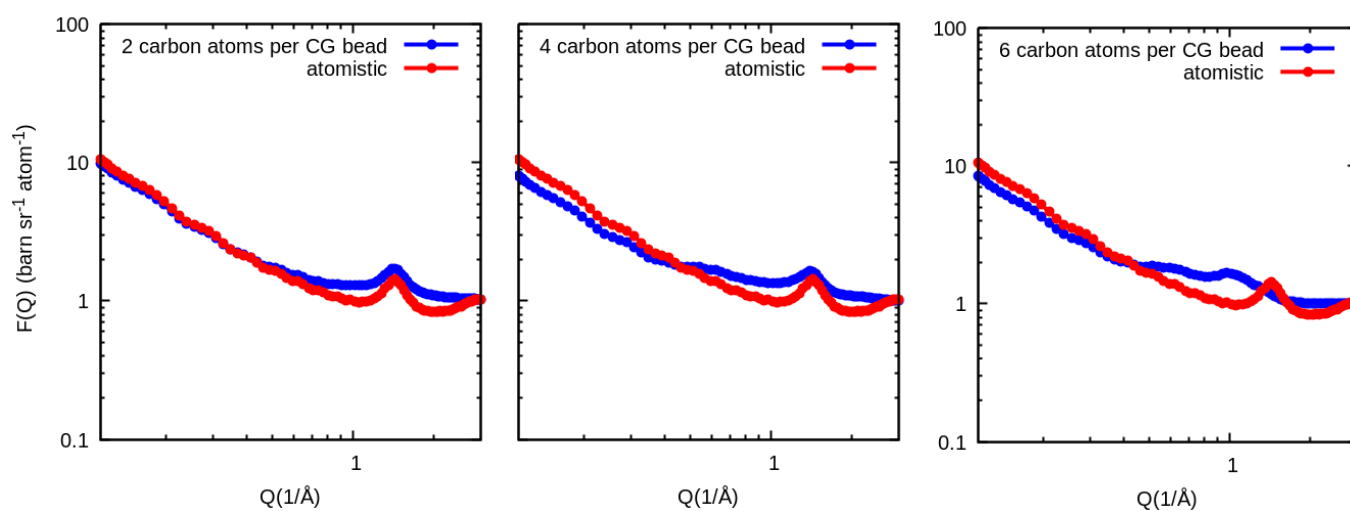


Figure 6: $F_{CG}(Q)$ computed for polyamide-66 and compared with $F(Q)$ for CG mapping shown in the figure 5 ~2 carbon atoms per bead (left) ~4 carbon atoms per bead (middle) and ~6 carbon atoms per bead (right).

Following the verification method shown in the flowchart in figure 4, CG trajectories are generated using different bead sizes shown in figure 5. Figure 6 shows the scattering curves obtained for CG trajectories and compared against atomistic simulations for testing the accuracy. With the increase in the bead size, there is expected divergence at higher Q as we loose the details on spatial resolution with increase in bead size. However the curves are differing slightly at lower Q for CG bead sizes > 3 carbon atoms per bead. Similar results are seen in other dense polymer systems like dodecane. This test shows the limitation on the bead size to ≤ 3 carbon atoms per bead for polymeric systems. The code has been tested for manual deuteration in the CG trajectories for exact proportion of isotope instead of using isotope ratios for $CGWt_{st}$ calculation. This modification in the code in the solved the issue at lower Q . An option is provided in the input file to generate manually deuterated CG trajectories instead of using ratios (details are given in user guide).

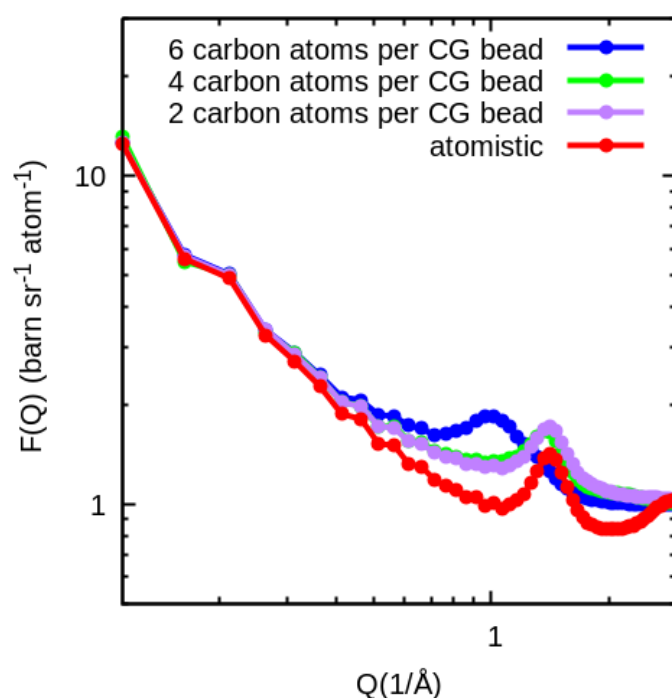


Figure 7 $F_{CG}(Q)$ computed for polyamide-66 and compared with $F(Q)$ for CG mappings 2, 4 and 6 carbons per bead.

Case 4: cetyltrimethylammonium bromide (C₁₀TAB) surfactant in water

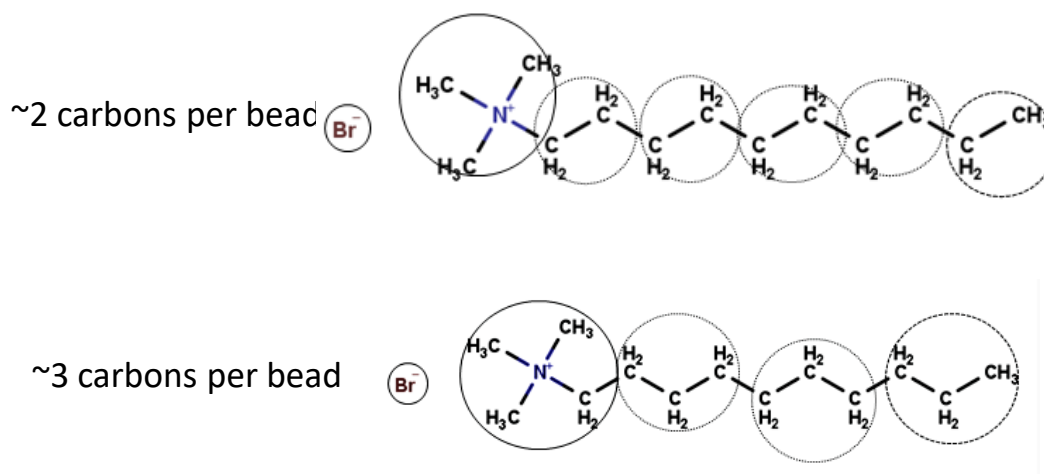


Figure 8 Mapping between atomistic and CG models of C₁₀TAB surfactant. Two different CG mappings showing beads of different sizes

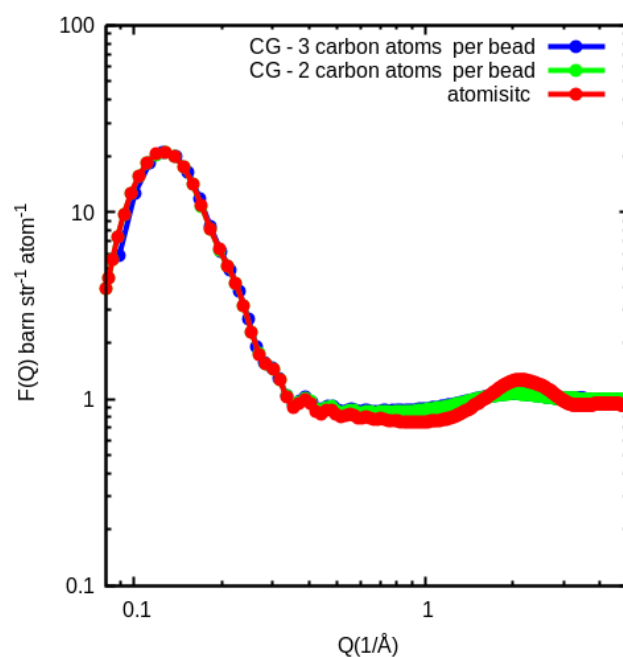


Figure 9 $FCG(Q)$ computed for C₁₀TAB surfactant in water and compared with $F(Q)$ for CG mappings 2 and 3 carbons per bead.

The issue identified with PA66 in lower Q region does not exist for C₁₀TAB micelles in water. In such micellar systems, 90% of the system is filled with water, resulting scattering curves are in perfect agreement with atomistic data in lower Q region.

Usability tests

Case5: cetyltrimethylammonium bromide (C₁₆TAB) in water

Trajectories are obtained after a long DPD simulation of 100mM C16TAB in water (27nm box) performed for $\sim 1.75\mu\text{s}$. The scattering data calculated using MuSSIC is then compared against SANS data. The simulation under estimate the average aggregation number of micelle (~ 40 surfactants) compared to the experiments (~ 70 surfactants). This has been verified by analysing the scattering data on SAS-view application.

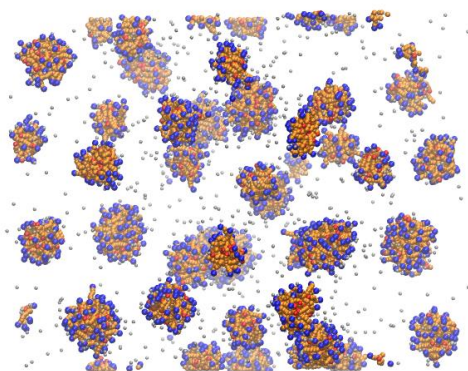


Figure 10 snapshot of C16TAB surfactants in water from DPD simulations

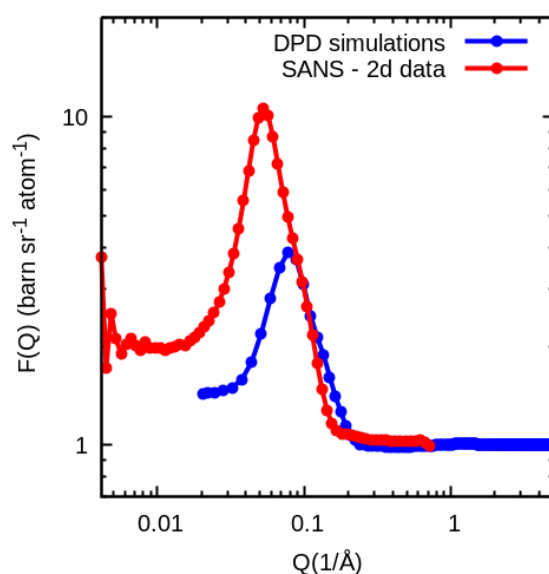


Figure 11 FCG(Q) calculated for C16TAB surfactant in water and compared against small angle neutron scattering data. The trajectories used for the calculation are obtained from $1.75\mu\text{s}$ long DPD simulation

Case6: Sodium dodecyl sulfate (SDS) surfactants in water

Hybrid particle-field simulations are performed on SDS surfactants in water are performed for $1\mu\text{s}$. The scattering curves from MuSSIC are compared with SANS data and found good agreement with the position of peak around $Q = 0.05\text{ (\AA}^{-1}\text{)}$. However the aggregation rate and size appear high in simulations and showing the differences in low Q region.

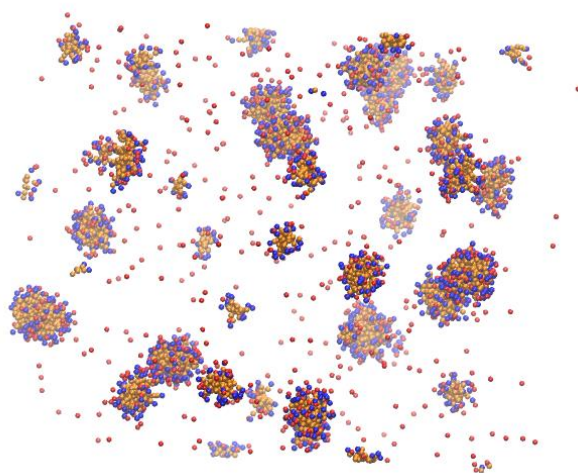


Figure 12 Snapshot of SDS surfactants in water from hybrid particle field simulations

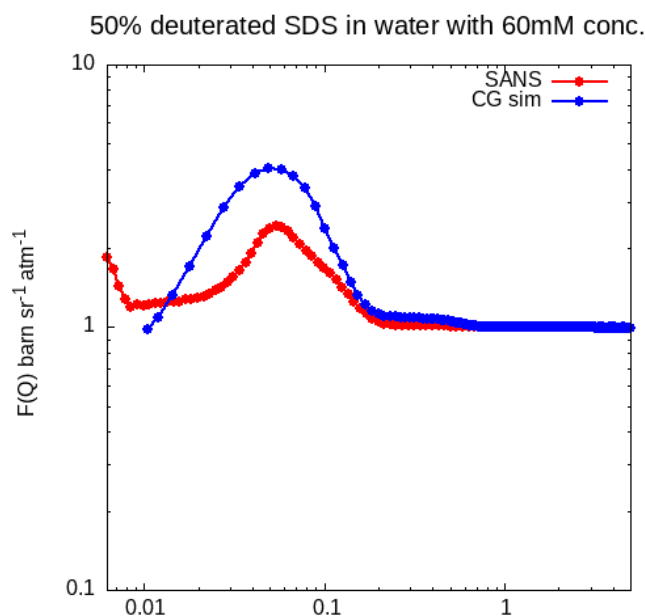


Figure 13 FCG(Q) calculated for the equilibrated structures of 60mM of SDS in water and compared to the data from SANS-2D