Coarse-grained Molecular Dynamics Simulation of Polyethylene Terephthalate (PET)

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Supplementary Information

This supplementary information contains additional derivation and Tables not included in the manuscript file.

The reference numbers in the supplementary information document correspond to the bibliography provided in the published manuscript.

I. Background of the OZPY^{-1} Method

The Ornstein-Zernike Integral Equation with Percus-Yevick approximation (referred to as the OZPY equation[23] here) is

$$\mathrm{y}_{\varphi_1}(r) = 1 + \sum_{\varphi_2}\sum_{\varphi_3} \frac{2\pi\,\mathrm{n}}{r} \int_0^\infty \mathrm{dss}\left[\mathrm{h}_{\phi_2}(s) - \mathrm{y}_{\phi_2}(s) + 1\right] \int_{|r-s|}^{r+s} \mathrm{dtt}\, h_{\varphi_3}(t) \tag{1}$$

With definitions of the cavity functionand total correlation function

$$\mathrm{y}_{\varphi_i}(r,r') = \mathrm{g}_{\varphi_i}(r,r') \exp\left(\frac{\varphi_{\mathrm{i}}(r,r')}{k_B T}\right) \tag{2}$$

$$\mathrm{h}_{\varphi_i}(r,r') = \mathrm{g}_{\varphi_i}(r,r') - 1 \tag{3}$$

In these equations, r, s and t are the displacements of in space; The OZPY equation assumes that there are three interaction sites α, β and γ in the system. The interaction between α and β is represented by φ_1 and φ_1 is always the nonbonded potential, while the summations of φ_2 (represents αγ interaction) and φ_3 (represents γβ interaction) include both nonbonded and bonded potentials (stretching, bending and torsion). Some combinations of φ_2 and φ_3 are not permitted. We will address the allowable combinations shortly. Conceptually, then we measure all pair correlation functions (PCFs), $g_{\varphi_{\mathrm{i}}}(t)$ in the simulation and we solve equation (1) numerically for $\mathrm{y}_{\varphi_1}(r)$ from which the potential can be directly extracted. Previously, we have proved the consistency of the OZPY^{-1} method on monatomic and diatomic fluids. This document shows the procedure to apply this method to chain fluid.

II. Application of OZPY^{-1} Method to Chain Molecules

Similar to the diatomic case,[23] the first thing we need to do is to figure out all allowable combinations for αγβ. As expected, The extension to polyatomic fluid involves more allowable combinations than the diatomic fluid case. A single particle of A in this chain has four types of interactions:

- bond stretching (S) interactions particles separated by one bond
- bond bending (B) interactions with particles separated by two bonds
- bond torsion (T) interactions with particles separated by three bonds
- non-bonded (N) interactions with all other particles, both on the same chain (intramolecular) and on other chains (intermolecular)

Each of these interactions has a distinct interaction potential, $U_S(r)$, $U_B(\theta)$, $U_T(\varphi)$, and $U_N(r)$. On a linear chain, this central particle A interacts with 2 particles of type S, two particles of type B, two particles of type T and all other particles of type N. These include all possible types of interactions. Explicitly, the necessary αγβ combinations (composed of a particle α interacting with particle γ via one type of interaction and particle β interacting with the same particle γ via a second type of interaction) , include SS, SB, ST, SN, BB, BT, BN, TT, TN, and NN.

Some of the combinations are not allowed. Because we use the OZPY^{-1} procedure to generate the nonbonded potential, we always impose that α and β particles are interacting via a nonbonded potential. Under this constraint, both α and β particles cannot be interacting with particle γ via a stretching interaction. Therefore, the αγβ combinations of SS is not allowed. All allowable combinations are listed in Table SI.1 for linear, homonuclear chains. This is provided as a reference and a guide to understanding the more complicated model used for PET. The linear homonuclear chain is not used in this work. All allowable combinations are listed in Table SI.2 for a linear, heteronuclear chain, with structure A(BA)$_n$. This corresponds to our model of PET. There are 34 allowable combinations for this CG PET case.

Second, we need to define an unambiguous pair correlation function for particles interacting via the stretching, bending and torsion potentials. While the bending and torsion potentials are written as functions of the bond angle, if we assume independence between S, B, and T degrees of freedom then we can readily convert the B and T potentials to functions of the separation between the particles. The local density of particles interacting via interaction potential φ_i, $g'_{\alpha\beta,\varphi_i}(r)$, which is directly calculated in an MD simulation,

$$g'_{\alpha\beta,\varphi_i}(r) = n_{\beta,\varphi_i}\, g_{\alpha\beta,\varphi_i}(r) = \frac{N_{\varphi_i,pairs}(r)}{N_\alpha\, V(r)} \qquad (5)$$

where $V(r)$ is the volume of the spherical shell, n_{β,φ_i} is the local density of particles of type β around particles of type α, interacting via φ_i. For the density of atoms interacting via potential φ_i, we used the following function[23],

$$n_{\beta,\varphi_i}(r) = \begin{cases} 0 \; for\, r < r_{\varphi_i,\min} \\ \quad 1/V_{\varphi_i} \qquad for\, r_{\varphi_i,\min} \le r \le r_{\varphi_i,\max} \\ 0 \; for\, r > r_{\varphi_i,\max} \end{cases} \qquad (6)$$

where $r_{\varphi_i,\min}$ is the smallest value for which $g'_{\varphi_i}(r)$ is non-zero, $r_{\varphi_i,\max}$ is the largest value for which $g'_{\varphi_i}(r)$ is non-zero, and the volume accessible to the φ_i atoms is the volume of the spherical shell bound between $r_{\varphi_i,\min}$ and $r_{\varphi_i,\max}$. As mentioned above, φ_i could be S, B, T. In our CG PET case, the corresponding pairs of $r_{\varphi_i,\min}$ and $r_{\varphi_i,\max}$ are (2.8 and 6.5) for stretching, (3.1 and 11.9) for bending ABA, (6.2 and 11.7) for bending BAB and (4.4 and 17.2) for torsion.

After clearing above two uncertainties, we performed the OZPY^{-1} procedure for our CG PET case. The computation process took only a few minutes. The calculated potentials are close to the power law 7-6 type potentials. Using the procedure of reference 23, the calculated potential was fit to 7-6 form to avoid (i) numerical noise and (ii) deficiencies due to the approximate nature of the Percus-Yevick equation. These deficiencies include a softer repulsive potential resulting in greater overlap than observed in the atomistic simulations and an overestimation at in the rate at which the potential rises at separations immediately beyond the first minimum.

This method is ot restricted to the generation of coarse-grained potentials for PET. The following two sections show all of the allowable combinations for a linear homonuclear and linear heteronuclear chain of the form A(BA)$_n$. The procedure is generalizable and can in theory accommodate other structures, including nonlinear chains. All applications of this

$OZPY^{-1}$ procedure as described require unambiguous pair correlation functions of S, B, and T interactions. While not studied here, it is also within the capabilities of the procedure to simultaneously solve for S, B and T, removing the assumptions associated with their independence. We have shown in the PET case that the assumption of independence is reasonable and thus we used the $OZPY^{-1}$ procedure to solve only for the nonbonded interaction.

III. Homonuclear Chain Molecules

The OZPY equation doesn't change from that of the diatomic molecule. The combinations required in the γ summation do change. In Table 1, we list all of the combinations and show that three of them are not allowed. For example, if particles α and γ are interacting via a stretching interaction, and particles β and γ are interacting via a stretching interaction, then particles α and β must be interacting via a bending interaction and not a nonbonded interaction.

Table SI.1. Necessary Combinations for homonuclear chain Case

particle type			**interaction type**			**potentials in summation**	**allowed**
α	β	γ	$\alpha\beta$	$\alpha\gamma$	$\gamma\beta$	$\alpha\gamma\beta$	**allowed**
A	A	A	N	N	N	NN	YES
A	A	A	N	N	S	NS	YES
A	A	A	N	N	B	NB	YES
A	A	A	N	N	T	NT	YES
A	A	A	N	S	N	SN	YES
A	A	A	N	S	S	SS	NO, BEND between α and β
A	A	A	N	S	B	SB	NO, TORSION between α and β
A	A	A	N	S	T	ST	YES
A	A	A	N	B	N	BN	YES
A	A	A	N	B	S	BS	NO, TORSION between α and β
A	A	A	N	B	B	BB	YES
A	A	A	N	B	T	BT	YES
A	A	A	N	T	N	TN	YES
A	A	A	N	T	S	TS	YES
A	A	A	N	T	B	TB	YES

A	A	A	N	T	T	TT	YES

IV. Heteronuclear Chain Molecules of type A-B-A-B-A-

The OZPY equation doesn’t change from that of the heteronuclear chain molecule. There are more combinations required in the γ summation compared to homonuclear chain molecule case. In contrast to the information provided in Table 1 for the homonuclear chain, in which both allowable and disallowed combinations are provided, in Table 2, we provide only the allowable combinations of interaction potentials for the alternating heteronuclear chain.

Table SI.2. Necessary Combinations for heteronuclear chain Case

No.	particle type			potential type			potentials in summation
No.	α	β	γ	$\alpha\beta$	$\alpha\gamma$	$\gamma\beta$	$\alpha\gamma\beta$
1	A	A	A	N_{AA}	N_{AA}	N_{AA}	$N_{AA}N_{AA}$
2	A	A	B	N_{AA}	N_{AB}	N_{AB}	$N_{AB}N_{AB}$
3	A	B	A	N_{AB}	N_{AA}	N_{AB}	$N_{AA}N_{AB}$
4	A	B	B	N_{AB}	N_{AB}	N_{BB}	$N_{AB}N_{BB}$
5	B	B	A	N_{BB}	N_{AB}	N_{AB}	$N_{AB}N_{AB}$
6	B	B	B	N_{BB}	N_{BB}	N_{BB}	$N_{BB}N_{BB}$
7	A	A	B	N_{AA}	S_{AB}	N_{AB}	$S_{AB}N_{AB}$
8	A	B	B	N_{AB}	S_{AB}	N_{BB}	$S_{AB}N_{BB}$
9	B	B	A	N_{BB}	S_{AB}	N_{AB}	$S_{AB}N_{AB}$
10	A	A	B	N_{AA}	N_{AB}	S_{AB}	$N_{AB}S_{AB}$
11	A	B	A	N_{AB}	N_{AA}	S_{AB}	$N_{AA}S_{AB}$
12	B	B	A	N_{BB}	N_{AB}	S_{AB}	$N_{AB}S_{AB}$
13	A	A	A	N_{AA}	B_{AA}	N_{AA}	$B_{AA}N_{AA}$
14	A	B	A	N_{AB}	B_{AA}	N_{AB}	$B_{AA}N_{AB}$
15	B	B	B	N_{BB}	B_{BB}	N_{BB}	$B_{BB}N_{BB}$
16	A	A	A	N_{AA}	N_{AA}	B_{AA}	$N_{AA}B_{AA}$
17	A	B	B	N_{AB}	N_{AB}	B_{BB}	$N_{AB}B_{BB}$
18	B	B	B	N_{BB}	N_{BB}	B_{BB}	$N_{BB}B_{BB}$
19	A	A	B	N_{AA}	S_{AB}	T_{AB}	$S_{AB}T_{AB}$
20	B	B	A	N_{BB}	S_{AB}	T_{AB}	$S_{AB}T_{AB}$
21	A	A	B	N_{AA}	T_{AB}	S_{AB}	$T_{AB}S_{AB}$
22	B	B	A	N_{BB}	T_{AB}	S_{AB}	$T_{AB}S_{AB}$
23	A	A	A	N_{AA}	B_{AA}	B_{AA}	$B_{AA}B_{AA}$
24	B	B	B	N_{BB}	B_{BB}	B_{BB}	$B_{BB}B_{BB}$
25	A	A	B	N_{AA}	T_{AB}	N_{AB}	$T_{AB}N_{AB}$
26	A	B	B	N_{AB}	T_{AB}	N_{BB}	$T_{AB}N_{BB}$
27	B	B	A	N_{BB}	T_{AB}	N_{AB}	$T_{AB}N_{AB}$
28	A	A	B	N_{AA}	N_{AB}	T_{AB}	$N_{AB}T_{AB}$
29	A	B	A	N_{AB}	N_{AA}	T_{AB}	$N_{AA}T_{AB}$
30	B	B	A	N_{BB}	N_{AB}	T_{AB}	$N_{AB}T_{AB}$
31	A	B	A	N_{AB}	B_{AA}	T_{AB}	$B_{AA}T_{AB}$
32	A	B	B	N_{AB}	T_{AB}	B_{BB}	$T_{AB}B_{BB}$
33	A	A	B	N_{AA}	T_{AB}	T_{AB}	$T_{AB}T_{AB}$
34	B	B	A	N_{BB}	T_{AB}	T_{AB}	$T_{AB}T_{AB}$