ma-2010-02084a Coarse-grained Molecular Dynamics Simulation of Polyethylene Terephthalate (PET) by Wang et al.

The authors present a coarse grained model for PET obtained using distribution functions from atomistic simulations together with an integral equation approach to obtain the CG nonbonded interactions. The approach seems interesting and the work leads to new simulation data for dynamics of PET melts.

I cannot assess the quality of the integral equation approach – here the editor will have to rely on an alternative reviewer.

Comments/questions:

1) Line 10: “though” should read “through”
2) Page 2, line 43: “by Hossein and Florian” should be removed (these are the first names of the authors in reference 12)
3) Page 2, line 48: “resources, it beyond” should read “resources, it is beyond”
4) Page 3, line 41: The authors mention two methods to obtain nonbonded CG potentials. Here, the authors should include a recently published single-chain coarse graining method by Fritz *et al.* (Macromolecules (2009) 42, 7579-7588). In this method, the effective pair potential, which describes the interaction between two CG super-atoms, is obtained by calculating the free energy expended to introduce atomistic interactions between all atoms contained by the two CG super-atoms as a function of their center of mass separation distance. This effective pair potential is obtained from atomistic simulations of two oligomers in vacuum which are computationally very cheap. The resulting model provides the melt density and structure (pair correlation functions) as model predictions (unlike iterative Boltzmann inversion and the method reported by the authors of the present work).
5) Page 4, line 23: “On the other hand, it is simple and fast compared to the current methods of comparable accuracy”. The same holds for the single-chain coarse graining method mentioned in my previous point.
6) The time scaling factors are quite small. The authors should point out that this is due to the choice of their “atomistic” model, which, in fact, already is an intermediately coarse grained united atom model. In this context the authors should also discuss how the dynamic properties obtained with the “atomistic” model compare to what is known experimentally. Very often, united atom models explore conformation space faster in comparison to all-atom models, hence the speed up factors would have been significantly larger if the CG model had been parameterized based on an all-atom polymer model (see Ref 18).
7) The authors do not discuss why they have chosen the particular CG mapping scheme shown in figure 1. Although they mention on p.11 that ideally all CG potentials are independent of each other, they do not show that this is indeed the case with their mapping scheme. To better understand the statistical interdependencies, the authors can e.g. plot a 2D-density map of torsion angles sampled by two adjacent torsions along the polymer backbone (see Fig 7 in the reference mentioned under point 4).
8) To validate the CG model in terms of its accuracy in describing the chain structure at local level, the authors should consider presenting the mean square internal distances between CG beads as a function of the number of CG bonds (#bonds) that separate the beads along the chain. For small #bonds this

quantity can be compared with the atomistic model. In their manuscript, the authors compare only the end-to-end distances as a limiting case.

9) The authors systematically use the abbreviation PCF (Pair Correlation Function) for various types of distributions. This is very confusing and needs to be revised ("probability distribution function (PDF)" would be a better choice) because the relevant distribution functions go beyond pair correlations. A "bonded PCF" (p. 11), which involves angles or torsions, is determined by intramolecular correlations that are 3-body or 4-body. Related to this, equation (1) is confusing: it defines a potential $\varphi_{\alpha\beta}\left(r\right)$ based on the PCF $g_{\alpha\beta}\left(r\right)$, which one immediately associates with a radial distribution function. Since the variable *r* is a distance (between sites α and β), the potential must describe a nonbonded interaction or a coarse grained bond. Nonbonded interactions however cannot be obtained by application of eq (1) and are calculated by other means.

10) Equation (2) should contain a logarithm in the second term on the rhs.

11) The discussion on page 6 (in between eqns 1 and 2) is not very clear. The problem the authors try to address plays no role in the iterative Boltzmann inversion method. It also plays no role in the reversible work method of Fritz *et al*. (see point 4). Differences between "fragment molecules and target molecules" play no role in the application of Fritz's method to polystyrene, because the phenyl rings are not isolated, but part of an oligomer. Hence, the mutual ring orientations are consistent with the constraints induced by the backbone. The authors correctly point out that these differences ("fragment molecules and target molecules") may play a role in the work discussed in refs 15 and 20. The discussion at this point should however be revised in order to clarify for what the various methods do account and for what they do not account.

12) page 6, line 18: the term "interaction energy" should not be used when referring to a potential of mean force (which is the case here) or to an effective interaction potential in general. Since degrees of freedom are lost by systematic coarse graining, the final model does not (and should not) reproduce the energy.

13) Page 14. Scaling factors for potential energies are meaningless (see previous point). I disagree with the last sentence of section 3.1.

14) Page 15. Mean square displacement (MSD). To observe diffusion, the quantity MSD/6*t should reach a plateau value (the diffusion constant) in the limit $1/t \rightarrow 0$. A figure with MSD/6*t versus 1/t is more convincing than the double logarithmic plot in Fig 10. Figure 10 shows that the maximum displacement of the longer chains (DP=30-50) is significantly smaller than the average radius of gyration (Table 2). This is a concern, because it indicates that the time scales may not yet be sufficiently large to obtain an accurate diffusion constant.

15) In the figure captions (p.28), the captions of Figures 5 and 6 are reversed.