MECHANICAL BEHAVIOUR OF AMORPHOUS POLYMERS THROUGH SYSTEMATIC COARSE-GRAINED SIMULATIONS

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Summary A general coarse graining (CG) procedure for modelling the uniaxial stress strain behaviour of specific macromolecular archtectures has been proposed. The method has been applied to and verified against polystyrene, an amorphous, glassy polymer. Suggestions to make the procedure better suited for predicting mechanical properties in the glassy regime has been made.

INTRODUCTION

Carefully and appropriately designed Molecular Dynamics (MD) simulations of glassy amorphous polymers not only provide a route to connecting the molecular architecture of these materials to their mechanical properties but open up the possibility of designing architectures for specific property goals. However, most large scale MD simulations reported till date use generic force fields that obfuscate several subtle macromolecular details. Systematic coarse graining (CG) of detailed macromolecular structures is necessary to weed out unnecessary details and retain significant ones in a manner that allows larger timesteps and bigger simulation boxes to be afforded. In this work, we describe our recent attempts at coarse graining several macromolecules using a 'force matching' technique with a view to reproducing their uniaxial stress strain responses. It is pointed out that one of the major bottlenecks in using CG simulations to predict uniaxial behaviour is in the under-estimation of the system's virial—a flaw inherent in all coarse graining schemes. Possible solutions to the above problem of the 'missing virial' is also proposed.

COARSE GRAINING PROCEDURE: THE FORCE MATCHING TECHNIQUE

The structure of a small part of the polystyrene chain is shown in Fig. 1(a) along with the optimized all atom structure of a monomer and its united atom representation. The optimized structure of a PS monomer is well known, an united atom force field is available in Mondello *et al.* [2]. In the coarse graining strategy to be adopted here, we will start by taking one superatom per monomer with a mass of 104 amu. So, a macromolecular PS chain, as shown in Fig. 1(b), in the coarse grained representation is a linear chain of superatoms that are bonded by bond stretching and bending potentials. Moreover, superatoms that do not interact through bonded potentials do so through a non bonded Lenard Jones (LJ) potential. The basic aim of the coarse graining (CG) scheme is to calibrate the bonded and non-bonded potentials with a view to matching some physical property of the system, in this case, the stress strain response in the glassy state.

A superatom I in our case is one whole monomer of PS. The superatom is placed at $\boldsymbol{R}_I$, the mass center of the monomer. We want the force on superatom I to be the vector sum of the forces $\boldsymbol{f}_i$ acting on the p united atoms constituting it, i.e.

$$\boldsymbol{F}_I^{ref} = \sum_{i=1}^{p} \boldsymbol{f}_i. \tag{1}$$

As in Izvekov *et al.* [1], we define an objective function,

$$\Pi = \frac{1}{3LN} \sum_{L=1}^{M} \sum_{I=1}^{N} \left| \boldsymbol{F}_{I,L}^{ref} - \boldsymbol{F}_{I,L} \right|^2, \tag{2}$$

where N is the total number of superatoms in the system and $(\cdot)_{I,L}$ denotes a physical quantity on superatom I in the L-th configuration. The objective then is to find $\boldsymbol{F}_I$ such that Π is a minimum. The force $\mathbf{F}_I$ acting on superatom I is assumed to result from inter and intrachain central pairwise non bonded forces as well as harmonic bond stretching and bending forces with intrachain neighbors.

The non-bonded force on superatom I is of the form

$$\boldsymbol{F}_I^{nb} = \sum_{K=1}^{N_{nb}} F(R_{IK}) \hat{\boldsymbol{R}}_{IK}, \tag{3}$$

where, the summation is taken over the N_{nb}, non-bonded neighbors of atom I. Along with the non-bonded CG force field, we also determine the bonded CG force fields through the force matching technique. Bond stretching force on atom I due to an atom J bonded to it is given by the equation,

$$\boldsymbol{F}_{IJ} = -\frac{1}{R_{IJ}} \left[\frac{\partial}{\partial R_{IJ}} \mathcal{U}_s(R_{IJ}) \right] \boldsymbol{R}_{IJ}, \tag{4}$$

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where the bond stretching potential $\mathcal{U}_s(R_{IJ})$ between two superatoms I and J is taken to be harmonic of the form:

$$\mathcal{U}_s(R_{IJ}) = \frac{1}{2}K_s(R_{IJ} - R_0)^2. \tag{5}$$

The equilibrium bond distance R_0 and the stiffness K_s are yet undetermined.
Finally, the method due to Izvekov *et al.* [1] is closely followed to parametrize the non bonded potential. Several numerical issues are important for the effective coarse graining of a particular molecule. Among them, proper parametrisation of the non bonded force field and sufficient numbers of snapshots over which 2 is taken are the most important.

RESULTS

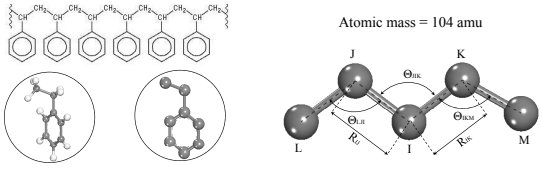
The CG sample at the onset of the equilibration process is constructed on the same detailed PS sample (at 500 K) as described in the last section, with the superatoms being placed at the mass centers of each monomer of the united atom model. Thus the CG system also consists of 14 CG chains with 80 superatoms, each having a mass of 104 amu.
Parameters for the bond stretching and bending potentials are obtained from the minimization procedure. For the specific case of united atom PS, the obtained values are $K_s = 4.5$ kcal/mol$-$ Å^2 and $K_b = 8.827$ kcal/mol while $R_0 = 5$ Å and $\Theta_0 = 122.7°$. These are also obtained by an alternate route following [3] and yield similar values. The non-bonded potential is also calibrated and has a pronounced minima at around 7.5 Å. In our case, even though our method exercises no control on the rdf, the non bonded rdf for the detailed sample is matched remarkably well by the CG sample.
However, the CG sample, at 500 K, does not have the same level of pressure (volume) as the detailed sample when held in a NVT (NPT) ensemble. The atomic virial, that enters the evaluation of the pressure, in the CG sample, is much lower compared to the detailed sample since the intra monomeric contribution to the virial is completely lost during the coarse graining procedure. Obviously, a match in the stresses cannot be expected with such a huge mismatch in the pressure. At this point, we choose to further iteratively refine the non bonded force field at 500 K with a view to equalizing the pressure in the CG and detailed samples. Once the pressures are equalised, the CG sample is quenched at a rate of 1 K$/$ps, undergoes glass transition at $T_g \simeq 268$ K and is deformed in the same manner as the detailed sample at 100 K. The stress strain responses of the detailed and the quenched CG samples are shown in Fig. 2.

OUTLOOK

The handling of the virial in CG procedures is the key to getting a reliable uniaxial response. We have now devised a more robust technique for correcting for the 'missing virial' in our CG scheme. To this end, we modified the objective function as,

$$\Pi = \frac{1}{3NL}\left[\sum_{I=1}^{N}\left|\boldsymbol{F}_{I,L}^{ref} - \boldsymbol{F}_{I,L}\right|^2 + \sum_{I=1}^{N}\left|\boldsymbol{\Sigma}_{I,L}^{ref} - \boldsymbol{\Sigma}_{I,L}\right|^2\right], \tag{6}$$

(where $\boldsymbol{\Sigma}_{I,L}$ is the CG atomic virial and $\boldsymbol{\Sigma}_{I,L}^{ref}$ is the same quantity calculated from the corresponding detailed sample) in order to ensure similar virials between the detailed and the CG systems. The modified procedure is now being tested on various macromolecular systems.



(a) (b)

Figure 1: (a) Chemical structure of the PS molecule, along with the optimum structure of its all atom and united atom monomers; (b) Schematic representation of coarse grained PS.

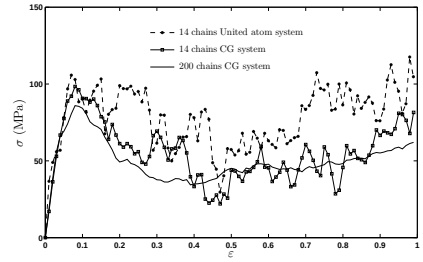


Figure 2: Comparison between the stress strain response of detailed and two CG polystyrene samples deformed at a rate of 0.005ps^{-1} at 100 K.

References

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