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# Reduced Order Molecular Dynamics Model for Polystyrene by Equivalent Structure Coarse Graining

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## Abstract

This paper develops a reduced order equivalent-structure based model for polystyrene (PS) in a rigid body molecular dynamics framework. In general, a coarse grained (CG) model for polymers is obtained by replacing a group of chemically connected atoms by an effective particle and deriving a coarse grained interaction potential that reproduces the structure and dynamics at the desired length and time scale. In the current model, a detailed ( $\sim 16$  atoms) polystyrene monomer referred to as basic structural element (BSE) is replaced by an equivalent model with spherical backbone particles and an ellipsoidal particle that represents the styrene side-group. The governing principals of this homogenization is based on the mass, centroid, angular momentum and energy equivalence between the detailed and the proposed reduced order model. The bonded interactions parameters are readily obtained in the optimization of the equivalent structure from the detailed representation. The non-bonded interactions are treated separately. In order to capture the stereochemistry of the polystyrene molecule, an anisotropic biaxial non-bonded interaction potential function known as RE-squared ( $RE^2$ ) interaction has been used between pairs of ellipsoidal and/or spherical particles in the system. The required calibration of the non-bonded parameters is carried out by matching with the experimental density and the local structure using radial distribution function. This homogenization process scales up the modeling system size significantly as the higher frequency motions like -C-H- vibrations and side-group movements are suppressed. The accuracy of the model is established by comparing with fine-scale simulation with explicit representations

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## I. INTRODUCTION

Molecular simulation methods, e.g. molecular dynamics (MD) have emerged as powerful techniques for studying static and dynamic properties of bulk amorphous polymers such as polystyrene or PS. Short range structure and local heterogeneities at the nanometer scale can be evaluated in great detail using atomic trajectories that are generated from these simulations. The level of sophistication required for modeling polystyrene necessitates more than just linear chain models, because of presence of phenyl groups at alternate backbone carbon atoms. This complex atomic structure poses severe computational challenges, especially when real polymeric systems are concerned. It is prohibitively demanding to solve real polymer physics problems using currently available computational resources. For example, in polymer thin film experiments, the surface layer itself extends to as much as 10 nm [1]. An overall thickness of approximately 40 nm may provide adequate length scale effects in the simulation system to yield an acceptable degree of reliability in the molecular models [2]. In MD simulations, a 40 nm PS thin film system would entail solving a system of equations for around 12,000 monomers. With periodic boundary conditions imposed on the 10nm  $\times$  10nm square region in the lateral plane along the X-Y directions, this is equivalent to solving for  $\sim 200,000$  atoms with explicit representation of hydrogen and carbon atoms or equivalently for  $\sim 100,000$  united atoms [3]. Coarse-grained or reduced order representations of atomic systems are often implemented as a means of reducing computational requirements. In these models, explicit representation of every atom in the atomic system is replaced by "super-atoms" that are units made up of a group of chemically connected atoms. Coarse graining also facilitates MD simulations on longer timescales that are typically necessary for simulating experimentally observed phenomena.

Generally speaking, the objective of coarse graining is to have as many atoms as possible in the reduced-order super-atom unit to achieve maximum advantage in terms of computing at large length and time scales. However, coarse graining too many atoms into a single unit can result in a loss of local information like atomic packing and local arrangement. One of the widely practiced coarse-graining procedures was introduced by Tschope et. al. [4, 5]. The underlying principle in this method is to identify the fast or high frequency internal degrees of freedom from independent simulations of explicit isolated chains, and subsequent averaging. A number of other similar coarse-graining schemes have been proposed for poly-

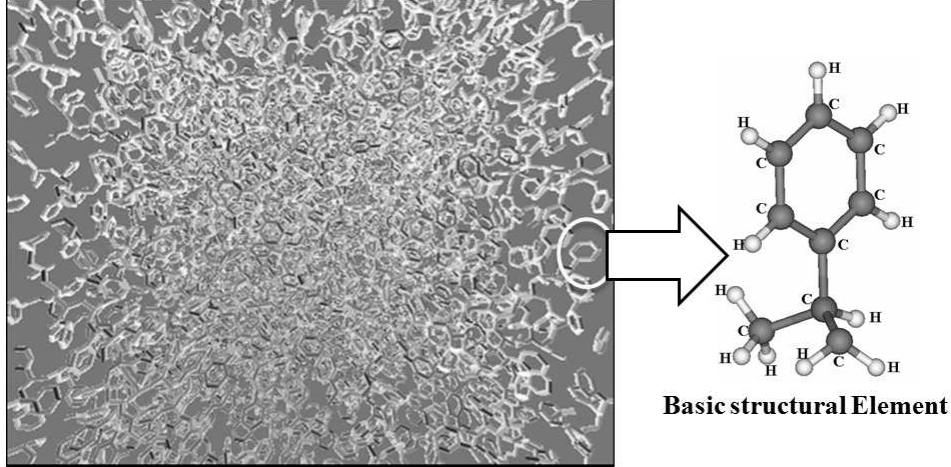


FIG. 1. (a) Representative volume element (RVE) of a polystyrene system, and (b) the basic structural element (BSE) representing the fundamental building block of the molecular chain.

carbonate and polystyrene systems in [6–8]. In particular, a variety of reduced order models have focused on polystyrene [8–12], it being one of the most widely studied polymers with ample opportunity for experimental validation. The models are generally founded upon statistics-based potential of mean force inversion methodology, where interactions are obtained from sampling distributions using explicit atomistic simulation of isolated polymers. Since the sampling distribution functions are temperature dependent, the transferability of these models across a range of temperatures is subject to corrections. Besides temperature dependence, atomistic details like information on stereochemistry and side-group orientation are usually lost with coarse-graining of the polymer structure. For example, such losses are evident in the 2:1 coarse-grained model for PS in [7, 8, 10], where each PS monomer is described by two CG super atoms. The super atoms in this model are spherical in nature with the side-group compressed in the backbone. To improve the stereochemistry representation, some models have made special provisions to account for the different tacticities of adjacent monomers [9]. Different potential functions are defined based on the whether the initial state of monomer pairs was racemic or meso in nature, thus making the method dependent on initial structure. Moreover, since the coarse-grained particle is generally assumed to be spherical, anisotropic phenomena like alignment of polystyrene side-groups in the direction of applied strain [13] cannot be captured using these models.

The proposed coarse-grained model in this study is developed to overcome some of the shortcomings mentioned above. In this model, a monomer is replaced by an equivalent structural element where the side group is configurationally represented as an ellipsoid. The

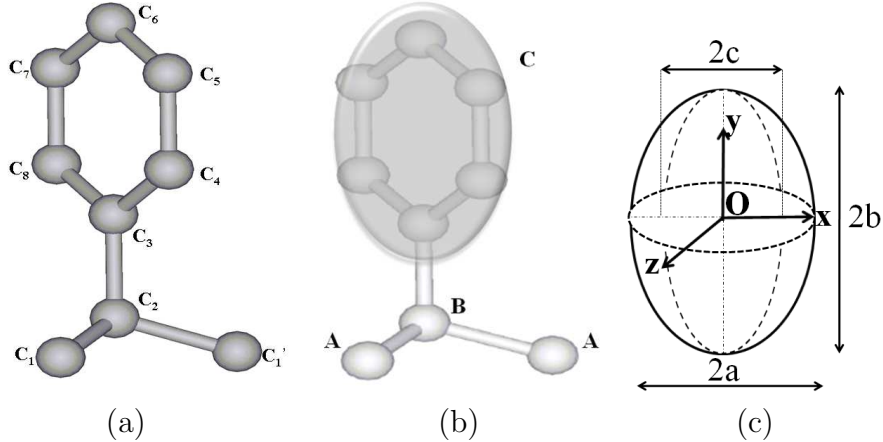


FIG. 2. (a) Stage 1 reduced order: United atom representation, (b) Stage 2 reduced order: Equivalent ellipsoidal representation, and (c) Side group as ellipsoid with axial lengths

three backbone united atoms make up the other units of the basic structural element of the molecular chain structure. To overcome the limitations of orientation dependence associated with conventional coarse-graining methods, a rotational dynamics based MD framework is implemented in the software LAMMPS [14]. The reduced order model is capable of reproducing the basic structural properties like density and pair-correlation function of the explicit MD model. It is expected that it will enable larger polymeric nano-systems ( $\sim 40$ -100 nm) to be studied within the constraints of available computational resources.

## II. REPRESENTATION OF AN EQUIVALENT BASIC STRUCTURAL ELEMENT

Figure 1(a) shows an atomic scale RVE for PS with explicit representation of molecular chains and configurations. The corresponding basic structural element (BSE) delineating the fundamental constitution of the material at this scale is shown in figure 1(b). Coarse graining to generate reduced order MD models of PS is executed in two stages. In the first stage, the BSE which corresponds to an explicit PS monomer consisting of  $\sim 16$  atoms is reduced to a united atom representation as shown in figure 2(a). In this nominally reduced order representation, the chemically connected hydrogen and carbon atoms are consolidated into one united atom that is assumed to be a spherical point with zero volume or no moment of inertia. Subsequently each monomer consists of 9 united atom as shown in 2(a). Detailed studies of PS with this united atom representation has been carried out by the authors in

[3, 15]. In the second stage of coarse graining, the phenyl ring of PS monomer is replaced by an equivalent ellipsoid, and consequently the BSE consists of four structural units as shown in figure 2(b). The three backbone united atoms are represented as spherical particles, whereas the phenyl side group is represented as a single ellipsoidal rigid body. The repeat unit of the BSE are shown in figure 2(b) where backbone atoms are labeled as A and B while the phenyl side group is labeled as C.

The configuration and geometric properties of the ellipsoid are determined from its structural equivalence with the explicit system, i.e. by equating the zero-th, first and second order moments of inertia of the ellipsoid with those of the side-group atoms in the BSE. As shown in figure 2(c), the phenyl side-group in the PS monomer consists of six united atoms in the explicit styrene ring. Equating the zero-th moment of inertia conserves the total mass of the system and determines the volume of the equivalent ellipsoid. Thus,

$$m^{ell} = \sum_{i=1}^6 m_i \quad (1)$$

where  $m^{ell}$  is the total mass of the equivalent ellipsoid and  $m_i$  is the mass of individual particles in the united atom representation. The six atoms are labeled  $C_3$  to  $C_8$  in figure 2(a) with a masses of 12 atomic mass units or *amu* for  $C_3$  and 13 *amu* for the other five resulting in a total ellipsoid mass of 77 *amu*. The bond length between the chemically connected atoms is  $\sim 1.4 \text{ \AA}$ .

Equating the first moment of inertia conserves linear momentum and determines the centroid position of the ellipsoid. The centroidal coordinates  $x_c^{ell}$ ,  $y_c^{ell}$  and  $z_c^{ell}$  of the equivalent ellipsoid are thus expressed as:

$$x_c^{ell} = \frac{\sum_{i=1}^6 m_i x_i}{\sum_{i=1}^6 m_i}, \quad y_c^{ell} = \frac{\sum_{i=1}^6 m_i y_i}{\sum_{i=1}^6 m_i}, \quad z_c^{ell} = \frac{\sum_{i=1}^6 m_i z_i}{\sum_{i=1}^6 m_i} \quad (2)$$

where  $x_i$ ,  $y_i$  and  $z_i$  are the position coordinates of the  $i$ -th united atom in the phenyl side-group.

Finally, equating the second moments conserves angular momentum and determines the principal axes directions. The second moment of inertia for the phenyl group of six atoms

is defined as:

$$\mathbf{I} = \sum_{i=1}^6 m_i (\mathbf{r}_i \otimes \mathbf{r}_i) \quad (3)$$

where  $m_i$  and  $\mathbf{r}_i$  are mass and position vector of the six particles in the united atom representation respectively and  $\otimes$  is the tensor product symbol. While mass and centroid are uniquely determined for the ellipsoid, the nine moments of inertia for the three principal axes and the corresponding three principal directions gives rise to an over-determined system of equations. Consequently, a minimization scheme is employed to obtain the best fitting second moment of  $\mathbf{I}$  for the equivalent ellipsoid from a hexagonal arrangement of atoms. The three eigen-values of the second moment of inertia  $I_1$ ,  $I_2$  and  $I_3$  provide the three principal axis lengths ( $2a$ ,  $2b$  and  $2c$ ) of the equivalent ellipsoid, from the equations:

$$a = \sqrt{\frac{5(-I_1 + I_2 + I_3)}{2m^{ell}}}, \quad b = \sqrt{\frac{5(I_1 - I_2 + I_3)}{2m^{ell}}}, \quad c = \sqrt{\frac{5(I_1 + I_2 - I_3)}{2m^{ell}}} \quad (4)$$

For the polystyrene phenyl ring, the principal axes lengths  $a$ ,  $b$  and  $c$  of the equivalent ellipsoid are found to have values of 3.45 Å, 3.45 Å and 1.0 Å respectively. This corresponds to a spheroid.

The orientations of the three principal axes  $\mathbf{x}'$ ,  $\mathbf{y}'$ ,  $\mathbf{z}'$  can be determined as the eigen-vectors of the second moment of inertia matrix  $\mathbf{I}$ . Various types of orientation representation includes the rotation matrix, axis-angles or Euler angles. Alternatively a singularity free, four parameter quaternion representation, introduced in [16], is implemented for designating orientation. Unlike Euler angles, quaternions do not suffer from the possibility of "gimbal lock" when two planes overlap causing one of the Euler-angles to become ambiguous. Quaternion algebra is numerically more stable and require far less number of parameters to be stored than in the rotation matrix representation. Like real number and complex number systems, quaternions correspond to a number system that can be used to represent a point in space by a single number or quaternions [17].

The quaternion rotation is written as a normalized four-dimensional vector

$$\hat{\mathbf{q}} = [q_0 \ q_1 i \ q_2 j \ q_3 k]^\top. \quad (5)$$



where  $q_1^2 + q_2^2 + q_3^2 + q_4^2 = 1$ . Furthermore, according to the quaternion number system mathematics [16],  $i^2 = j^2 = k^2 = ijk = -1$ . Calculating the quaternion of a given phenyl side group in the reduced order system involves the derivation of a orientation matrix  $\mathbf{Q}$  for the BSE and calculation of its eigen-values and eigen-vectors.

The process is first executed on the starting configuration to generate the initial configuration of the reduced order system. The centroidal position and quaternions of the reduced order system evolves with subsequent increments of the molecular dynamics simulations. The orientation matrix for the ellipsoid is written in terms of three orthogonal basis vectors, derived for the phenyl side group. The  $\mathbf{x}'$  direction is in the plane perpendicular to the phenyl ring, while the line joining atoms C<sub>3</sub> and C<sub>6</sub> in figure 2(a) is assumed to correspond to the  $\mathbf{z}'$  direction. The  $\mathbf{y}'$  direction is constructed from the line joining the bisectors of the lines C<sub>4</sub>-C<sub>5</sub> and C<sub>7</sub>-C<sub>8</sub> respectively.

$$\mathbf{Q} = \begin{bmatrix} x'_1 & y'_1 & z'_1 \\ x'_2 & y'_2 & z'_2 \\ x'_3 & y'_3 & z'_3 \end{bmatrix} \quad (6)$$

The eigenvalues of  $\mathbf{Q}$  are given as:

$$\lambda = \{1, \cos(\theta) + i \sin(\theta), \cos(\theta) - i \sin(\theta)\} \quad (7)$$

where  $\theta$  is the rotation angle. The eigenvector ( $\hat{\mathbf{e}}$ ) corresponding to eigenvalue 1 is an invariant principal axis of rotation. The four components of quaternions are expressed in terms of the principal axis  $\hat{\mathbf{e}} = [e_1 \ e_2 \ e_3]^\top$  and the angle  $\theta$  as:

$$\begin{aligned} q_0 &= \cos(\theta/2) \\ q_1 &= e_1 \sin(\theta/2) \\ q_2 &= e_2 \sin(\theta/2) \\ q_3 &= e_3 \sin(\theta/2) \end{aligned} \quad (8)$$

At any given instance, quaternions can also be used to obtain the rotation matrix as:

$$\mathbf{R} = \begin{bmatrix} -1 + 2q_1^2 + 2q_0^2 & 2(q_1 * q_2 - q_3 * q_0) & 2(q_1 * q_3 + q_2 * q_0) \\ 2(q_1 * q_2 + q_3 * q_0) & -1 + 2q_2^2 + 2q_0^2 & 2(q_2 * q_3 - q_1 * q_0) \\ 2(q_1 * q_3 - q_2 * q_0) & 2(q_1 * q_0 + q_2 * q_3) & -1 + 2q_3^2 + 2q_0^2 \end{bmatrix} \quad (9)$$

The mass, centroidal position, orientation in terms of quaternions, and the principal axes lengths complete the description of the equivalent ellipsoidal rigid body side-group of the PS monomer at any time instance. The other three particles which form the backbone are simply represented by their position vectors with no size (hence zero moment of inertia). Their quaternion parameters  $[q_0 \ q_1 \ q_2 \ q_3]$  stay constant at  $[1 \ 0 \ 0 \ 0]$ . The table I depicts the system size and total degree of freedoms for a system with 8 chains and 320 monomers corresponding to different stages of coarse-graining.

Units/d.o.f.	Explicit Atom System	United Atom System	Equivalent Ellipsoid System
no of units/monomer	16	9	4
d.o.f./monomer	48	24	13
d.o.f.(1x80 monomers)	~ 3840	~ 1920	~ 1040
d.o.f.(8x320 monomers)	~ 122880	~ 61440	~ 33280

TABLE I. Degrees of freedom associated with different stages of reduced order representation of polystyrene in MD simulations

The reduced order system decreases the degrees of freedom by approximately a factor of 3.6 for the 8 chain, 320 monomer model.

### III. POTENTIAL ENERGY FUNCTIONS OF THE REDUCED ORDER SYSTEM

Atoms in the polymeric chains are chemically connected by various springs and joints that provide the bonded interactions and maintain the kinematics and the local morphology of the polymer chain. Besides the bonded interactions, the dynamics of atoms in the polymer chains are also governed by non-bonded interactions. These are non-local in nature and take

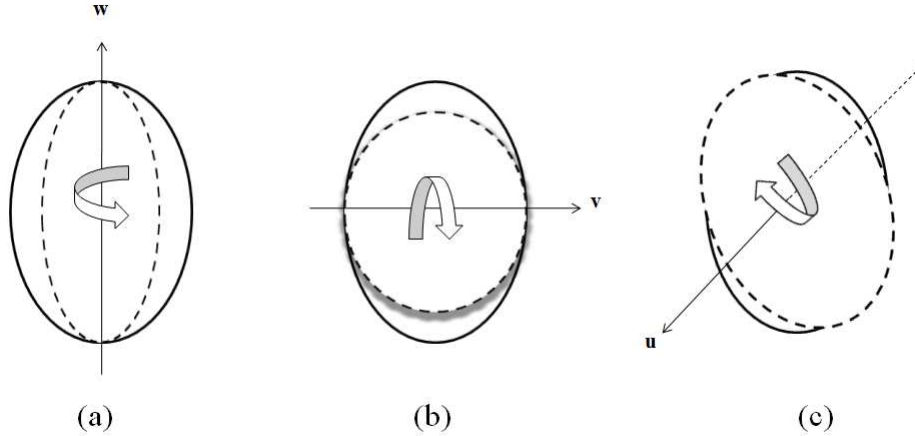


FIG. 3. Modes of deformation: (a) twisting (b) out-of-plane bending (c) in-plane deformation

place between atoms, which are not bonded directly. Thus, the molecular interactions for a polymer system includes bonded energy ( $U_{bd}$ ) and non-bonded energy ( $U_{nb}$ ) terms. The total potential energy ( $U_{total}$ ) of the system is thus written as (see [15]):

$$U_{total} = U_{bd} + U_{nb} \quad (10)$$

The bonded and non-bonded interactions for the reduced order model are discussed next.

### A. Bonded Interactions

The configuration and kinematics in the explicit representation of polymeric chains are effectively modeled by including terms like angular, torsional, improper and out-of-plane interactions along with the spring-like bond interactions as shown in figure 3. The potential function in the explicit model for bonded interaction is given as [3, 15]:

$$U_{bd} = \frac{1}{2}k_b(r - r_0)^2 + \frac{1}{2}k_\theta(\theta - \theta_0)^2 + \frac{1}{2} \sum_{j=1}^3 k_\phi^j [1 + (-1)^{j+1} \cos j(\phi)] + \frac{1}{2}k_\psi(\psi - \psi_0)^2 \quad (11)$$

Here  $r_o$ ,  $\theta_o$  and  $\psi_o$  are the equilibrium bond-length, angle, dihedral angle and improper angle respectively, and  $k_b$ ,  $k_\theta$ ,  $k_\phi$  and  $k_\psi$  are the corresponding stiffness co-efficients.

Development of the functional form for the bonded-potential of the reduced order model is executed in the following steps.

1. MD simulation of the full monomer chain system in its explicit representation is carried out at a given temperature.
2. The centroidal positions of random particle-pairs  $A$  and  $B$  (see figure 2(b)) in the ensemble are determined and their trajectory is sampled for distribution of bond lengths  $AB, BC$ , angles  $ABA$  and  $ABC$  and dihedral angle  $ABA'B'$ . This sampling is done for approximately 1000 temporal instances so that a reliable statistics can be developed for the reduced order model.
3. Distribution functions  $P(r)$ ,  $P(\theta)$  and  $P(\phi)$  for the chains are obtained from the above sampling. Rigorous convergence study is carried out to ensure that these probability distributions are statistically unbiased and independent of the number of sampling points.
4. These probability distributions correspond to the Boltzmann factors of the generalized intra-chain interaction potentials  $U(r)$ . These are written as:

$$P(r) = \exp \left\{ \frac{-U(r)}{k_B T} \right\} \quad (12)$$

$$P(\theta) = \exp \left\{ \frac{-U(\theta)}{k_B T} \right\} \quad (13)$$

$$P(\phi) = \exp \left\{ \frac{-U(\phi)}{k_B T} \right\} \quad (14)$$

where  $k_B$  is the Boltzmanns constant,  $U(r)$  is the bonded length potential of the reduced order chain model, and  $U(\theta)$  and  $U(\phi)$  are the corresponding bond angle and torsion potentials. Thus far there is no fitting procedure needed and it is directly the result of mapping energetic and entropic contributions from the finer scale explicit model.

5. As an example, the coefficient for the assumed bond-stretching potential function of the reduced order model is obtained directly from equation (14) as:

$$U(r) = -k_B T \ln P(r) + C_r \quad (15)$$

The coefficient  $C_r$  is added and evaluated to keep the minimum bond-length potential to zero. Consequently, its value is  $C_r = k_B T \ln P(r_0)$ . The bond-stretching poten-

tial for the reduced order model is assumed to be harmonic. Correspondingly, the coefficient  $K_r$  is obtained from the equation

$$U_r = \frac{K_r}{2}(r - r_0)^2 = -k_B T \ln P(r) + C_r \quad (16)$$

The same procedure is repeated for the other bonded potential functions as well.

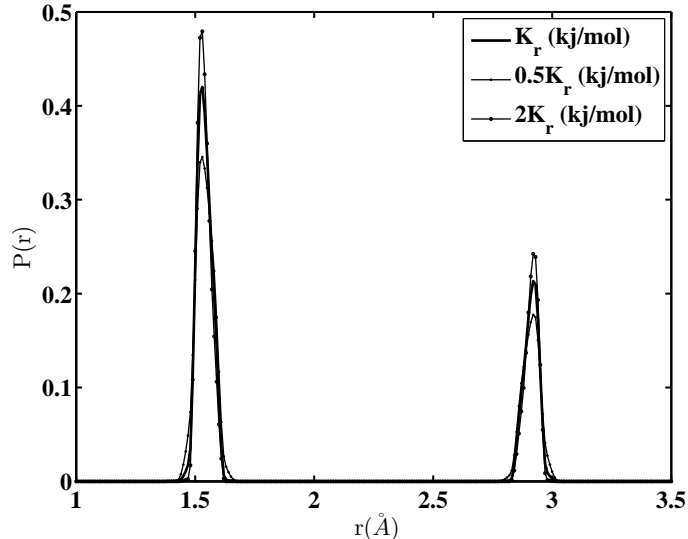


FIG. 4. Probability distribution with respect to bond length. A higher  $K_r$  has sharper and higher peak and narrower spread than a lower  $K_r$ . The figure shows distribution for original stiffness value as well as distribution when the stiffness is halved and doubled.

For bonded interactions, the functional form of bond angle bending modes are described using an harmonic potential, expressed as:

$$U_{angle} = \frac{K_\theta}{2}(\theta_k - \theta_0)^2 \quad (17)$$

Values for the constants  $K_r$ ,  $r_0$ ,  $K_\theta$  and  $\theta_0$  are listed in Table II.

The functional form for the torsional interaction is chosen to describe rotation along the bonds in the backbone carbon atoms in accordance with the Transferable Potentials for Phase Equilibria (TraPPE) potential form [3]:

$$U_{torsion} = \frac{1}{2}\{k_\phi^1(1 + \cos(\phi)) + k_\phi^2(1 - \cos(2\phi)) + k_\phi^3(1 + \cos(3\phi))\} \quad (18)$$

Again the values of the constants are listed in table II. One of the consequences of coarse graining is the possibility of loss of configurational integrity due to removal of hydrogen

<hr/> <i>Chemical Bonds</i> $K_r(\text{kJ/mol}/\text{\AA}^2)$ $r_0(\text{\AA})$ <hr/>			
<i>A - B</i>	666.00	1.54	
<i>B - C</i>	1000.00	2.91	
<hr/> <i>Angular Bonds</i> $k_\theta(\text{kJ/mol}/\text{rad}^2)$ $\theta_0(\text{degree})$ <hr/>			
<i>A-B-A'</i>	520.0	112.0	
<i>A-B-C</i>	1000.0	120.0	
<hr/> <i>Dihedral Bonds</i> $k_\phi^1(\text{kJ/mol})$ $k_\phi^2(\text{kJ/mol})$ $k_\phi^3(\text{kJ/mol})$ <hr/>			
<i>A-B-A'-B'</i>	5.904	-1.124	13.158
<hr/> <i>Improper Bonds</i> $k_\psi(\text{kJ/mol}/\text{rad}^2)$ $\psi_0(\text{degree})$ <hr/>			
<i>B-C-A-A'</i>	167.40	31.00	

TABLE II. Potential function parameters for reduced-order representation of polystyrene system. Different units of angles for equilibrium values (degree) and force constants (radians) is used in the table to maintain consistency with the representation followed in the Molecular Dynamics software package LAMMPS that was used to carry out the simulations.

atoms at the chiral centers. As a result, the four united atoms,  $C_1$ ,  $C_2$ ,  $C_3$  and  $C'_1$  tend to collapse into one plane. In order to prevent this collapse, an improper dihedral-angle interaction potential has been proposed in [8, 18] as,

$$U_{imp} = \frac{K_\psi}{2}(\psi_k - \psi_0)^2 \quad (19)$$

where  $\psi$  is the improper dihedral angle that conserves the structure of chiral center in the molecules modeled as united atoms. The corresponding forces cause the unit normal to the plane ( $C_1, C_2, C_3$ ) to oscillate about its mean position. To coincide with the equilibrium position obtained from MD simulations with explicit structure representation, an equilibrium value  $\psi_0 = 35.04^\circ$  is used with the united atom potential. This is the angle formed with the  $-C_2\text{-H}$ - vector in the equilibrium position. Though  $\psi_0 = 35.04^\circ$  was used for the united atom simulation, the mean value of probability distribution for the equivalent angle in the new representation of C, A, B, A' was found to be  $31^\circ$ . One possible reason for this deviation may be the difference in co-ordinates of site  $C_3$  in united atom representation and site  $C$  in

equivalent coarse-grained representa

## B. Non-bonded Interactions for Rigid Body Systems

Normally, non-bonded interactions between individual atoms are represented in terms of distance-dependent potential functions. An example is the Lennard-Jones potentials, where particles are assumed to be spherical and interactions have radial symmetry. However, approximating a group of atoms as a spherical particle has its shortcomings especially for systems like the phenyl side group, where the six atoms are arranged as part of a co-planar hexagon. If the physical properties are dependent on the stacking direction of the side-group, the spherical assumption may be misleading. In [13], it has been shown that phenyl side groups in polystyrene chains tend to align themselves in the direction of applied tension when a uniaxial load is applied. If the side group is assumed to be spherical, this alignment cannot be captured when the system is subjected to an external load. In order to retain the anisotropy in reduced order model framework, the side groups are assumed to form a rigid body with moments of inertia specified from the explicit atomic structure.

In this work, the styrene side group is represented as a spheroidal rigid body, based on the geometry of phenyl ring as discussed in section II. Gay-Berne [19] have introduced the *ellipsoidal* potential as an extension of L-J potential for anisotropic particles. Parameters of the Gay-Berne potential however lack a well defined physical interpretation and their calibration can be erroneous. A modification to Gay-Berne potential was proposed in [20], where the parameters are related to the equilibrium energy, distance and orientation in a more physical way. This potential is termed as RE<sup>2</sup> potential. The potential energy  $V_{RE^2}$  and is broken down into an attractive  $V_{RE^2}^A$  and a repulsive interaction energy part  $V_{RE^2}^R$  and is expressed as:

$$V_{RE^2}(\mathbf{r}_1, \mathbf{q}_1, \mathbf{r}_2, \mathbf{q}_2) = V_{RE^2}^A(\mathbf{Q}_1, \mathbf{Q}_2, \mathbf{r}_{12}) + V_{RE^2}^R(\mathbf{Q}_1, \mathbf{Q}_2, \mathbf{r}_{12}) \quad (20)$$

where  $\mathbf{Q}_1$  and  $\mathbf{Q}_2$  are the transformation matrices from the global reference frame to the local frame and  $\mathbf{r}_{12}$  is the position vector joining the centroid of the particles. Since the rotational degrees of freedom are also included in this potential function via  $\mathbf{Q}_1$  and  $\mathbf{Q}_2$ , RE<sup>2</sup>

functional form is able to capture and evolve the different modes of deformation for phenyl group as shown in figure 3. As a result, the modes of deformation like twisting, in-plane and out of plane motion of the phenyl group are simulated without explicitly using any bonded potential like torsional spring potentials. Moreover, the selection of parameters with the RE<sup>2</sup> form are very physical in nature. RE<sup>2</sup> form gives the approximate interaction energies between ellipsoids/spheres instead of a modified LJ-based formulation as in the Gay-Berne potential [21]. RE<sup>2</sup> potential is formulated in a way that the orientation dependence decays at large distances and asymptotically reduces to the interaction energy between two spheres. Moreover, it is known to give a more realistic intermediate and close contact interaction [20]. The full details of RE<sup>2</sup> formulation can be obtained from [20, 22].

### C. Numerical values of the Non-bonded parameters

From a purely computational view point, the RE<sup>2</sup> potential interaction between particles in the system can be defined if diagonal shape tensor  $\mathbf{S}_i$  and the relative well-depths values along with the Hamaker constant  $A_{12}$  and the atomic interaction radius  $\sigma$  are known. The shape tensor  $\mathbf{S}_i$  ( $i=1,2$ ) is given in terms of the three principal radii  $a_i$ ,  $b_i$  and  $c_i$  of the ellipsoid as:

$$S_i = \begin{pmatrix} a_i & 0 & 0 \\ 0 & b_i & 0 \\ 0 & 0 & c_i \end{pmatrix} \quad (21)$$

The relative well depth for each site can be expressed as:

$$\epsilon_x = \sigma \cdot \frac{a}{b \cdot c}; \epsilon_y = \sigma \cdot \frac{b}{a \cdot c}; \epsilon_z = \sigma \cdot \frac{c}{a \cdot b} \quad (22)$$

To define non-bonded interactions between ellipsoidal and/or spherical particles using RE<sup>2</sup> anisotropic potential in LAMMPS [14], following parameters must be exactly defined for each pair of atoms:

$A_{12_{ij}}$  = Hamker constant or energy prefactor for the pair (kj/mol)

$\sigma_{ij}$  = radius of the particle that represents excluded volume for the pair (Å)

$\epsilon_{xi}$  = relative well depth of particle i for side-to-side interactions

$\epsilon_{yi}$  = relative well depth of particle i for face-to-face interactions



$\epsilon_{zi}$  = relative well depth of particle i for end-to-end interactions  
 $\epsilon_{xj}$  = relative well depth of particle j for side-to-side interactions  
 $\epsilon_{yj}$  = relative well depth of particle j for face-to-face interactions  
 $\epsilon_{zj}$  = relative well depth of particle j for end-to-end interactions  
 $\sigma_c$  = cutoff distance ( $\text{\AA}$ )

The side and face in the phenyl ring are same and is the plane of the phenyl group. The end-to-end is the normal to the plane of the ring. These are easily obtainable geometric properties of the ellipsoids and spherical sites for the molecule under investigation. The simplification in terms of parameterization is made by using the assumption from Derjaguin expansion [23] where energy well depth parameters are expressed in terms of local curvatures of the ellipsoid.

The three kinds of particles used in the coarse-graining are denoted by A, B and C, where A and B are the spherical backbone atoms and C is the ellipsoidal side group. The calibrated parameters for non-bonded interactions used in this work are presented in table III. A series of calibrations simulations were run with the chosen parameters before arriving the final values. Tests were performed to observe energy conservation and these simulations were validated against radius of gyration, radial distribution function and the density of PS system. The final interaction radius  $\sigma$  for spherical sites is chosen to be 3.95  $\text{\AA}$  and 4.65  $\text{\AA}$  respectively. These values are same as the interaction radius used in united atom representation [3, 8]. A larger value of 5.0  $\text{\AA}$  was chosen for the interaction radius of the ellipsoidal site C. An arithmetic mean is used to obtain interaction values for unlike pairs of particles. The values for relative well depth are obtained using equation 22 for each pair. Geometric mean is used to obtain the relative well depth for unlike sites. The cutoff distance  $\sigma_c$  was chosen to be equal to united atom cut-off distance of 10  $\text{\AA}$  for particles A and B. A value of 12  $\text{\AA}$  was used for ellipsoidal particle C since it has bigger dimension and longer range for non-bonded interactions. The initial values of prefactor A12 of the potential energy term (Hamaker constants) were guessed to be 30 kJ/mol for spherical sites and 80 kJ/mol for the ellipsoidal sites and were optimized by matching the total potential energy of the CG system with the energy from the united atom simulation. The final values are shown in table III

Particle:	<i>A-A</i>	<i>B-B</i>	<i>C-C</i>	<i>A-B</i>	<i>A-C</i>	<i>B-C</i>
$\sigma$	3.95	4.65	5.00	4.30	4.48	4.83
$\epsilon_x$	3.95	4.65	5.00	4.28	4.44	4.82
$\epsilon_y$	3.95	4.65	5.00	4.28	4.44	4.82
$\epsilon_z$	0.3318	0.3906	0.42	0.36	0.3733	0.4050
$A_{12}$	30.24	32.22	86.24	30.22	50.61	50.61
$\sigma_c$	10.00	10.00	12.00	10.00	12.00	12.00

TABLE III. RE<sup>2</sup> parameters for the reduced order model

#### IV. SIMULATION RESULTS AND VALIDATION

Three PS systems containing different number of chains and monomers are studied in this work for coarse graining. They are:

1. system containing one chain of 80 monomers
2. system containing one chain of 320 monomers, and
3. system consisting of eight chains of 320 monomers

The initial configuration of each system is obtained from a fully equilibrated explicit MD system. As discussed in [3, 15], PS molecules in the explicit model are assembled using the augmented Phantom Chain Growth or PCG scheme. In this algorithm, monomers are introduced based on a sampling of a uniform random distribution of the backbone dihedral angle. The total energy change  $\Delta U$  resulting from the introduction of a new site is calculated as the sum of the dihedral and non-bonded interactions. The probability of the acceptance of the new monomer is given by

$$p = \min [1, \exp (-\beta\Delta U)] \quad (23)$$

where  $\beta$  is the product of Boltzmann constant  $k_B$  and the temperature of the system. If a new monomer is not accepted after a certain number of trials, the chain is shortened by removing the previous monomer, and the procedure is repeated.

The initial co-ordinates and the orientation of the ellipsoids are obtained using methods discussed in section II. The initial velocity and angular velocity of the ellipsoids are assigned

randomly such that total momentum is zero and the total kinetic energy is proportional to the desired temperature. The system is validated at 350K. A time-step of 4 fs is chosen for this work and the simulation at each temperature is run for approximately 2 ns. The reduced order model is tested by mapping the coarse-grained trajectory at the end of the simulation to a full scale local structure to confirm if the atomic level topology is retained. Also, the robustness of the potential function developed for the reduced order model is tested through convergence of radial distribution functions and density at a temperature 350K. The simulated densities at different temperature are found to be within a 10% error range.

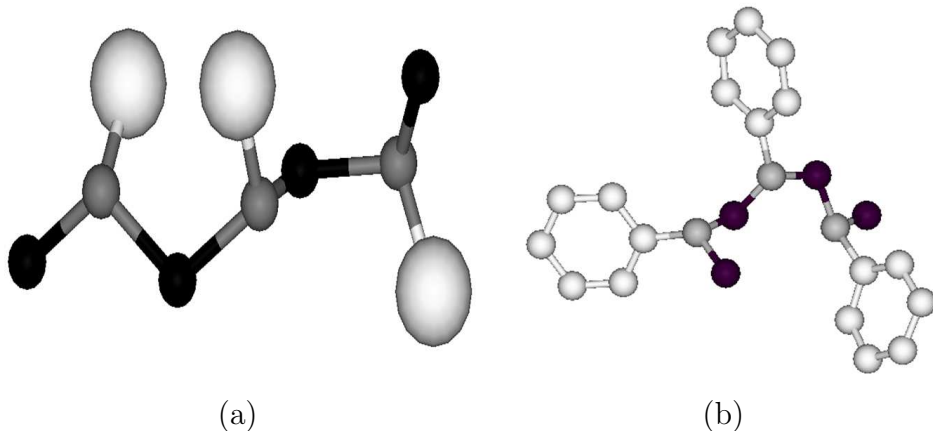


FIG. 5. (a) A 3 monomer sample in the reduced order representation, (b) the reconstructed united atom system at the end of the simulation

Figure 5 exhibits the result of reinsertion of atomic details in the molecular model at the end of the simulation. A 3 monomer strip from the chain of 320 monomers is chosen to highlight the remapping of the reduced order system to the detailed atomic system. Figure 5(a) corresponds to the coarse-grained data obtained from MD simulation at a given time-step. Figure 5(b) shows the 3 monomer system after it has been reconstructed using the information about coordinates and orientation embedded in the reduced order model trajectory. The backbone atoms are trivially mapped as they represent coordinate positions of the same particles in both reduced order and united atom manifestations. The large ellipsoidal particles in the reduced order system contains in itself the evolved centroid and orientation information. Due to this information, the ellipsoid can be mapped back accurately to the corresponding styrene side group as shown in figure. The mathematical details

of this exercise is detailed in section II. The above result shows that, besides retaining the information about the centroid position of the CG site like other sphere based model [7–11], the current model also evolves the orientational degree of freedom because of its anisotropic nature. Consequently, finer all-atom or united atom system can be easily and accurately obtained from the existing coarse-grained system if required.

The radial distribution function for reduced order ellipsoid-ellipsoid system is plotted in figure 6. As demonstrated in the figure, there is a local peak due to near-neighbor correlation, which decays to unity after a length of 10 Å. This behavior is consistent with the theory. It also validates the local structural inhomogeneity and far-field homogenized behavior. Figure 7 shows the density convergence of the reduced order system at 350K. The density converges to experimental values within an error of 10 %. This is acceptable for this significant level of coarse-graining. Furthermore, the rate of convergence of the reduced order model is much faster than what is observed in full scale MD simulation [3], thus establish the advantage of this model.

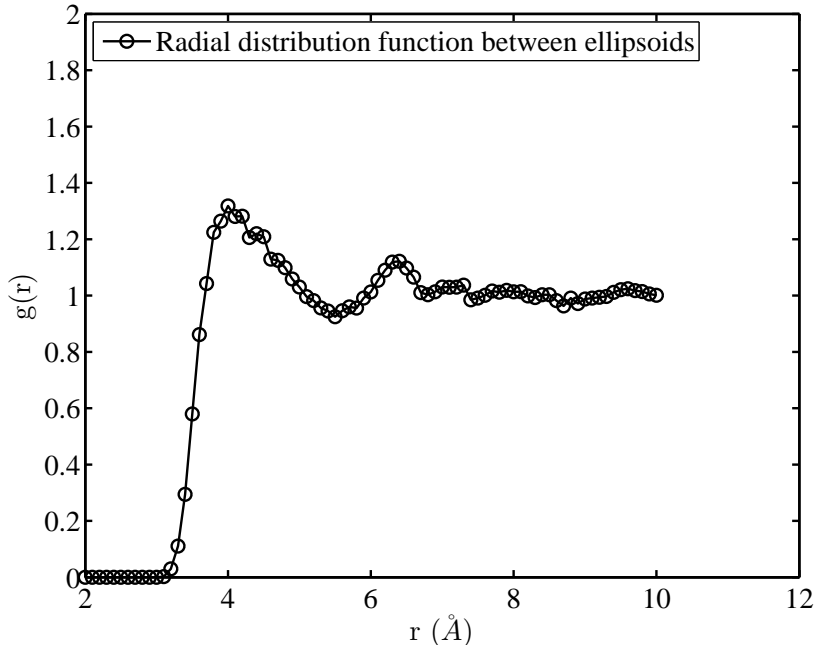


FIG. 6. Radial distribution function of ellipsoidal particle system

One of the primary objectives of this coarse-graining is to facilitate and expedite the process of estimating glass transition temperature  $T_g$  of bulk and thin-film polystyrene systems. For numerical evaluation, the simulation is executed for a temperature range from 300K to 450K in 25K intervals under constant pressure state. Periodic boundary conditions are

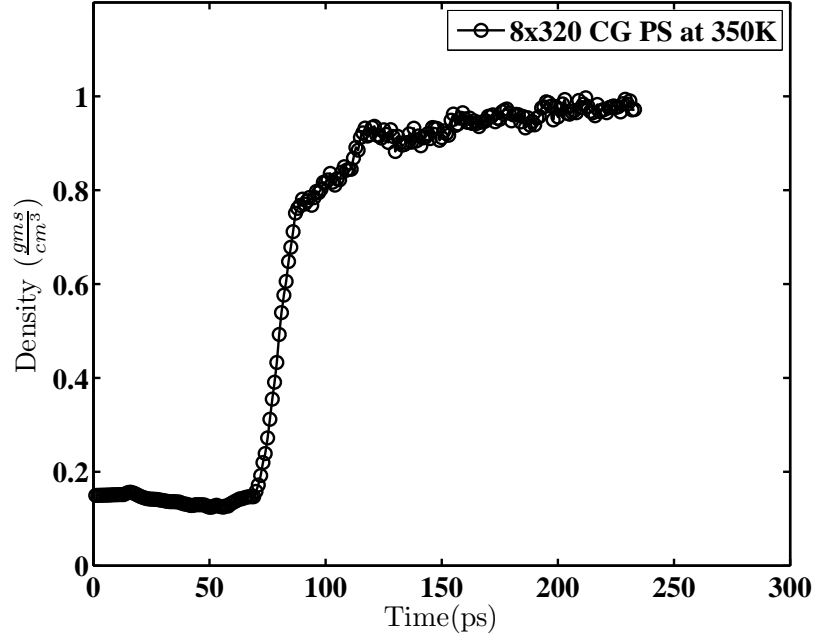


FIG. 7. Convergence in density at 350K with the reduced order model. The initial system has very sparse density(*sim* 0.2 gcc) and the CG model shows a very fast convergence to the the experimental scale density. The experimental density of PS is  $\sim 1.05$  gcc at room temperature.

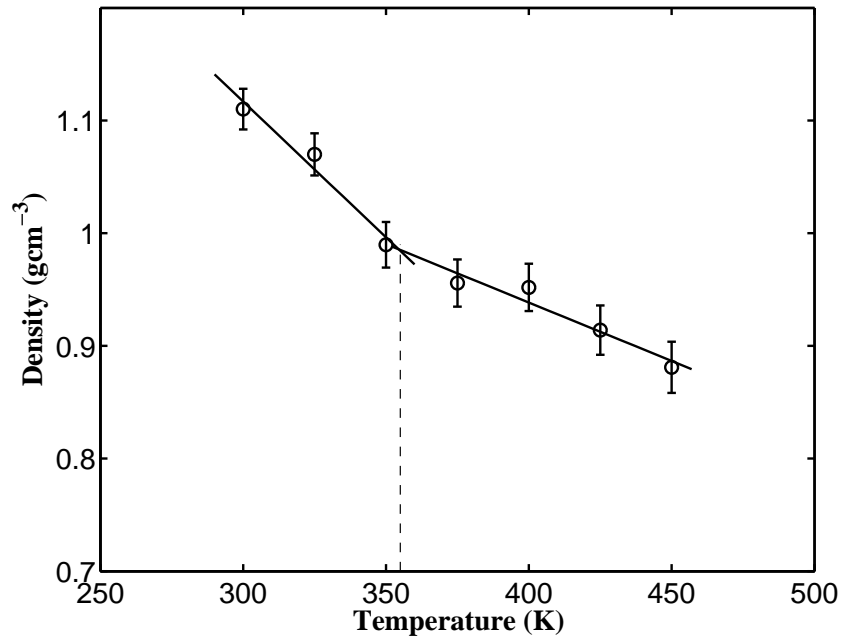


FIG. 8. Density of PS between 300 K and 450 K with the reduced order model. The bold lines are least square fit to the density data. The dashed vertical line is drawn to locate the point of intersection of the two fitted lines, originating from the two ends. Temperature value at the intersection is found to be 355 K. This is taken as the simulation  $T_g$  value, estimated at the temperature where the co-efficient of thermal expansion changes. The experimental value of  $T_g$  is  $\sim 370$  K

applied to the reduced order simulation boxes. The simulation is run for about 2 ns at each temperature until convergence in density is achieved. The densities are plotted as a function temperature in figure 8. The simulation results are within a range of 10 % of the experimental value reported in [24] as 370K. The glass transition is under-predicted by about 15-20K using this method. However, given the scale of coarse-graining involved and the model’s ability to accurately capture the molecular-level anisotropy, the  $T_g$  value is believed to be predicted within an acceptable range. The difference with the experimental value can be attributed to a variety of different factors like cooling rate, sampling limitations of MD along with the parametrization done in this work. However, a reasonable estimate about the glassy phase transition in the polymeric system can be made within a range, based on the density plots, using the current method. Transferability of simulation parameters across temperatures is a known limitation in the coarse-graining literature [12], which makes any prediction pertaining to  $T_g$  debatable. As shown in figure 8, the slope of the curve signifying the coefficient of thermal expansion is observed to change at around  $\sim 350$ K. This temperature can be assumed to signal the onset of the glassy phase and is an estimate of  $T_g$ .

## V. CONCLUSION

A molecular structurally equivalent reduced order model is developed for polymers in this work. The overall intent of this coarse graining is to bridge the gap in length and time-scales between experiments and computational models such that longer time periods may be simulated. A statistically equivalent, reduced order model for polystyrene is arrived at by rigorous sampling of the fine-scale trajectory. The model is shown to reproduce basic structural properties like density and pair-correlation function within acceptable tolerances. While this coarse-graining method has been applied to the polystyrene system only in the current work, the model can be used to study realistic nano-systems ( $\sim 40$ -100 nm) of polymeric materials within the available computational resources.

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