The Caloric Curve of Polymers from the Adaptive Tempering Monte Carlo Method

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1 Introduction

Polypyrrole (PPy) is a prototypical conducting polymer formed by heterocyclic aromatic monomers that are able to change its volume by 30% depending upon its pristine (neutral) or doped (oxidized) chemical phases. Current computational approaches have had difficulty calculating properties that agree well with experimental results. In the past, our group developed a coarse-grained force field for pristine 12 PPy (12 monomers per chain) in which the pyrrole monomers are modeled by a planar 5-member ring with a permanent dipole moment pointing from the monomer center of mass to the nitrogen atom [1]. We have extended that force field for modeling the oxidized phase of PPy, which entails including dopants and taking into account a number of polymer-dopant interactions. The new force field has intra-chain terms similar to the previous model and new interchain interaction components, E_{int}, including the interaction between monomers and dopants, between dopants and dopants, and between monomers in a 12-PPy chain with monomers in a different chain [2]. In total, the full model potential has 15 parameters. Polymer chains with 12 monomers per oligomer (12 PPy) are consistent with the synthetic rendering of this doped polymeric material [3]. Dopants trapped in the polymer matrix result in the oxidized phase of PPy by inducing a charge transfer between the polymer and the dopants. In our case, the dopants acquire negative charge, and the polymer chains lose electrons becoming positively charged. Polymer matrix volume changes are dependent on the size and type of dopants used.

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In this work, we explore with a novel numerical simulation implementation the ability to reproduce the volume expansion of PPy when oxidized. In Sect. 2, we describe the custom parallelization implementation for the calculation of the thermodynamic and mechanical properties of PPy using the newly developed force field. Section 3 provides the calculated PPy properties obtained from the caloric curve for a case system containing chlorine as the atomic dopants. Section 4 concludes this paper.

2 Methods

Although being a molecular component, each 12-PPy monomer will be referred to as a *particle*. Dopants are atoms and will also be referred to as particles. Systems ranging in size from 1024 to 19200 particles were explored for calibrating the size scaling effect on the computational implementation. Simulations were performed with our custom-developed horizontally scalable GPU accelerated Metropolis Monte Carlo (MMC) implementation that utilizes the adaptive tempering Monte Carlo (ATMC) method [4] for the sampling exploration of configuration space as the parallelization strategy for intermolecular energy calculations. The ATMC visits different NPT Gibbs ensembles along with the determination of the caloric curve (enthalpy as a function of temperature). Indeed, the ATMC algorithm drives the evolution of the simulation by selecting which temperature should be explored along the caloric curve. Our numerical implementation supports four simulation modes: NVT-MMC (canonical ensemble), NPT-MMC (isobaric-isothermal ensemble), NVT-ATMC, and NPT-ATMC.

Parallelization of atomistic simulations typically falls into one of the three categories: embarrassingly parallel or replica exchange, domain decomposition, and farm or energy decomposition. The embarrassingly parallel or replica exchange method maintains several independent replicas of the full system configuration, each of them sets at a different temperature. A random walk is achieved by periodic exchanges of configurations at nearby temperatures. The domain decomposition method utilizes a spatial decomposition approach that allows for simultaneous updates of all particles. The latter is accomplished by moving particles that are outside each other's cutoff radius. The farm or energy decomposition approach achieves parallelization by splitting the particles into groupings and then calculating partial energy values for each group. The latter are combined to determine the total system energy. The parallelization approach selected for this research is a variant of the farm or energy decomposition method and contains components of previous MMC parallel implementations [5].

3 Results

3.1 *Parallelization Protocol for the PPy Condensed Phase Analysis*

The parallelization of our new potential model involves three levels of parallelism. The first level of parallelism is provided by the usage of Open MPI, which provides support for distributed memory systems such as computer clusters. The second tier of parallelization is provided by OpenMP, which is designed for shared memory architectures and is effective within one node of a computer cluster. The third tier of parallelization is provided by CUDA. This combination of parallelization technologies allows for an optimal utilization of current and future computational platforms. The combined approach of the three-level parallelization scheme is scalable to any sized system as specific care is taken in selecting the number of nodes and processes so that internodal communication is minimized. The three-level parallelization strategy is accomplished by partitioning the internal summations of the model potential terms into sum segments, with each sum segment assigned to a computational node. Each computational node evaluates partial one-particle energies associated with the sum segment it was assigned. Each node utilizes a combination of OpenMP and CUDA to further speed calculations.

The parallelization performance using the customized energy decomposition approach is schematically shown in Fig. 1, illustrating the processing time of a single MMC passage over all the particles when adopting different loads to the OpenMP (threads), Open MPI (processors), or GPU. As evident from the plot, when the number of particles is below 10000 (Fig. 1 inset), the selection of how to combine processor and thread components is important because the CPU time may be doubled if care is not taken. As the system is scaled up in size to many more particles, the balance processor/thread is still important but not as damaging. Also evident from Fig. 1 is that the processing time performance is the best when using the GPU, if the latter is available. We emphasize that these performance metrics

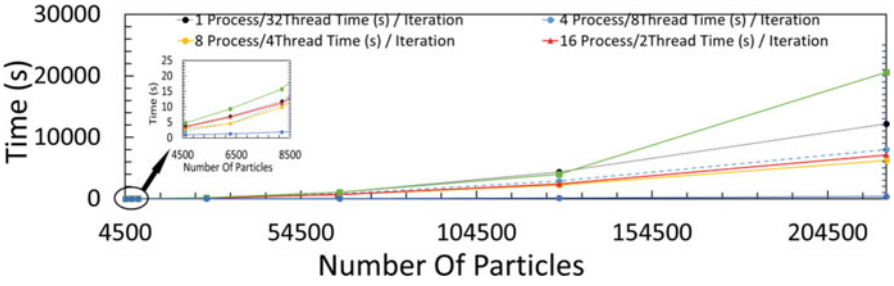

Fig. 1 Performance metrics for the parallelization scheme processing time of one single MMC iteration involving one passage over all the particles in the PPy system. The inset provides a better view of the processing time differences for PPy systems with less than 10000 particles

involve only one MMC step. In a regular simulation for obtaining the physical properties of the PPy system, several millions of these steps are needed.

The overall analysis of the PPy system within a single node with GPU involves a series of steps that we summarize in the flowchart depicted in Fig. 2. The control node initializes the system of particles and then shares the system with worker nodes. If the system is run in one node, the implementation calls one worker (Fig. 2); otherwise, several workers may be called as illustrated in Fig. 3. Once the PPy system is constructed, the spatial coordinates for the monomer and dopants will be distributed to all processing nodes. One node is designated as the control node and will perform all the reduction operations for the partial energies and evaluated the Monte Carlo acceptance step criteria. Initially, the control node is also given a sequence of random numbers and a set of random moves equal to the number of particles in the system. Next, the sum segmentation of model potential terms is determined based on the total number of monomers and dopants in the system and the number of computational nodes available. Next, the random translation/rotation MMC move of each particle is calculated on the control node, and the coordinates of the moved particle are shared with the other computational nodes where the new potential energy is calculated by segments. The computing nodes share their calculated partial energies with the control node where the sum of the partial energies is executed. The workflow enters next into the MMC main loop by accepting or rejecting the monomer or dopant move (translation/rotation). It is the control node that evaluates what action should occur next. If the particle move is accepted, the simulation evolves to the next step of execution. If the particle move is rejected, a reset message is broadcast to all compute nodes to reset values. Although the acceptance/rejection of the particle move is done in the control node, the potential energy associated with the moved particle is distributed between the computing nodes. To accept a move, the control node checks that the new potential energy be lower than the current or if the potential energy is larger, then the decision is done by checking that the change in energy gives a probability $e^{-(E_{new}-E_{old})}/k_BT$ larger or smaller than a random number in the range of 0–1, where k_B is Boltzmann's constant and T is the set system temperature. The particle motion step size is dynamically updated to ensure a 40% to 60% acceptance rate on the particle movement. For efficiency purposes, the control node evaluates the PPy intra-chain terms of the force field. The intra-chain potential energy is parallelized on the control node using OpenMP; this does place more computation on the control node but minimizes internodal communication overhead from Open MPI. The 12-PPy oligomers explored in this research contain 12 monomers only. Thus, the parallelization of the intra-oligomer potential energy represents a minimal gain that, however, could become important if longer polymer chains are considered in the future.

For a multi-compute node configuration, after the initialization step, the work distribution step described previously would occur. Figure 3 illustrates the work distribution for a multi-compute node configuration and a hypothetical number of 60,000 particles. In the multi-compute node configuration, each node is responsible for the evaluation of only part of the E_{int}. In the instance where a GPU is available

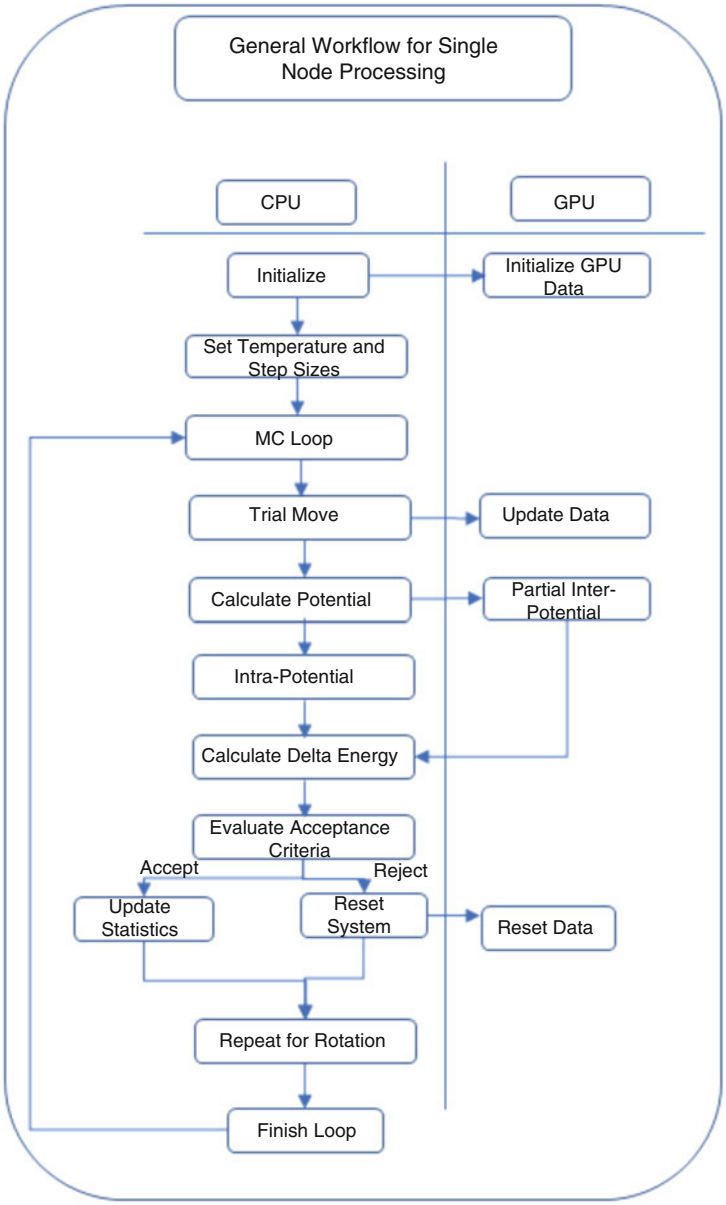

Fig. 2 General process workflow for the simulation utilized in this research

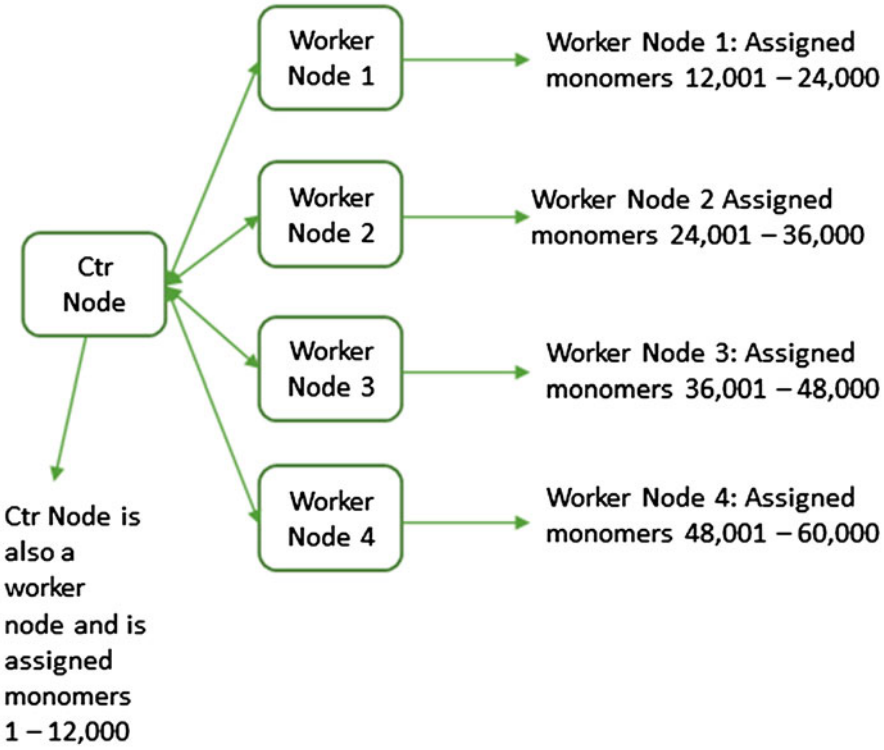

Fig. 3 An example work decomposition using four nodes for a system consisting of 60,000 particles. The control node will be responsible for the delegation and management of all work assignments

on each of the compute nodes, each compute node will off-load the E_{int} evaluation to the GPU.

3.2 PPy Thermodynamic Properties

In this section, we focus primarily on providing the ATMC results for a mid-size oxidized PPy system consisting of 8192 particles. Figure 4 shows the calculated caloric curve for the PPy condensed system. Equilibrium density at ambient temperature is in the range of 1.20 g/cm3 to 1.22 g/cm^3, which is close to the experimentally determined range of 1.30 to 1.46 g/cm^3 [3]; bulk modulus was determined to be in the range of 67–120 MPa, which is within the range of published experimental work of 100–350 MPa [6]; and vector and orientational order parameters indicate that our model reproduces the planar stacking of the polymer chains and specific heat value of 855.93 J kg^{-1}K^{-1} at 300 K that are within the experimental range of values of

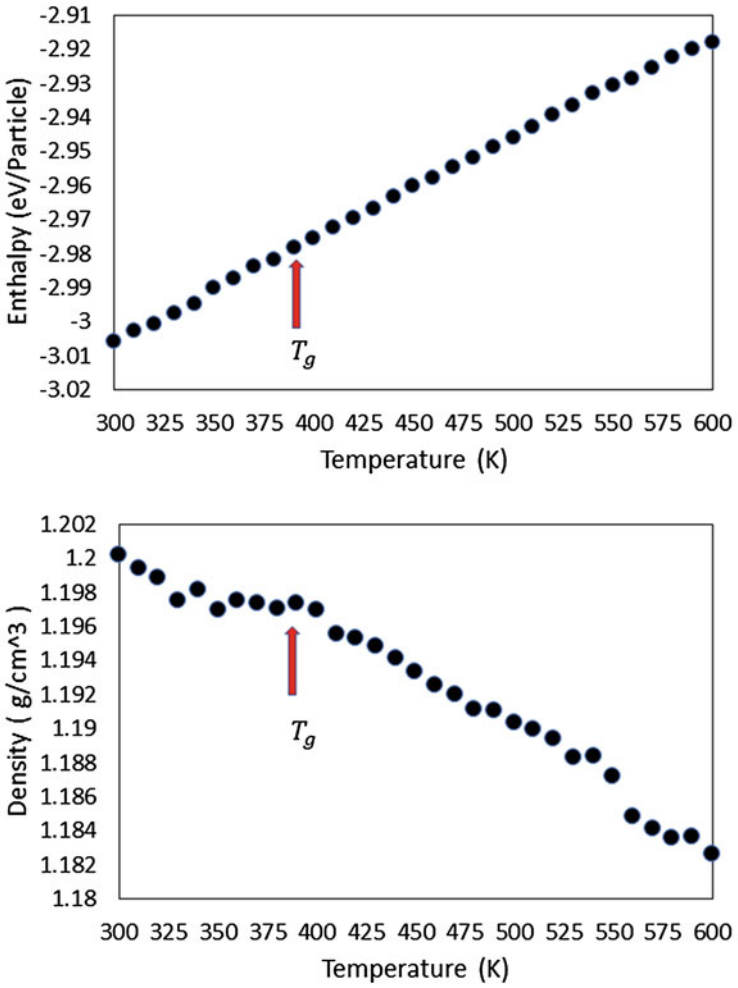

Fig. 4 Caloric curve results from the ATMC simulation beginning at 1000 K and ending at 300 K at 1 atm pressure for a particle system of 6144 pyrrole monomers and 2048 chlorine atom dopants

800–1400 J $kg^{-1}K^{-1}$ [7]. The glass transition temperature was determined to be 400.8 K, which is in very good agreement with the experimentally determined value of 394 K [8].

Concerning the structure of the 12-PPy chains, remarkably, they remain quite stiff along these extensive simulations maintaining a quasi-planar geometry even at high temperatures. The radius of gyration, end-to-end distance, and orientational order parameter change at most by 5% from the initial fully planar conformation.

4 Conclusion

The new force field accurately produces results consistent with values obtained experimentally for oxidized PPy systems. Our model reproduces the stacking of planar PPy chains observed in the experimental microstructure. We predict a glassy structure below the glass transition of 400.8 K. Other calculated properties of this glassy condensed system include the heat capacity, thermal expansion, and structural order parameters, which agree well with experimental and observation data.

The ATMC method provided an efficient and fast method for thoroughly exploring the configuration space of the PPy system. The ATMC provided significant computational time savings even though it visited a larger number of ensembles. The customized energy decomposition approach combined with a hybrid OpenMP-Open MPI multiprocessing strategy allows for the horizontal scalability to accommodate system configurations of a wide range of sizes, accomplished by minimizing data transfers between computational resources. Currently, we are applying this implementation to other complex systems.

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