Short communication

Thermodynamic consistency in the structure-based integral equation coarse-grained method

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M. Dinpajooh, M.G. Guenza[*]

Department of Chemistry and Biochemistry, Institute of Theoretical Science, University of Oregon, Eugene, OR 97403, United States

ABSTRACT

The Integral Equation Coarse-Grained method is an approach that simplifies the representation of a polymer melt into a liquid of coarse-grained chains, considerably speeding up the computation of the melt properties, while reproducing with accuracy structure and thermodynamics of the corresponding atomistic description. In a recent paper [Polymer **111**, 103 (2017)], it was stated that the structure-based Integral Equation Coarse-Grained approach does not give thermodynamic consistency. Here we present new calculations that confirm the validity of this method in predicting consistent pressure and radial distribution functions with atomistic simulations. Other details of the method are also discussed.

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In the recent paper by Wang and Yang, referred hereafter as Paper I [1], the authors state that the thermodynamic consistency of the atomistic and coarse grained (CG) descriptions of homopolymer melts is not possible when our coarse-graining theory, the Integral Equation Coarse-Graining (IECG) theory, is used. In this paper we clarify the issue of thermodynamic consistency and also address other points that are misinterpretations of our work, as they appear in Paper I. Because it would be impossible to address all the details in the incorrect interpretations of our work as they appear in that paper, we refer the interested reader to our original work, about which we will welcome any questions [2–7]. Many of the criticisms in Paper I were already addressed in a previous paper of ours [8], and will not be addressed again here. In a nutshell, when our approach is used incorrectly and/or outside the limits in which it applies, thermodynamic consistency is lost [8]. However, when the approach is used correctly, thermodynamic consistency holds, as we are going to discuss here.

The original IECG formalism is already described extensively in a number of our publications, so it will be summarized only briefly here. The IECG model is a coarse-graining theory based on the solution of the Ornstein-Zernike integral equation [9], extended to macromolecular liquids [11,12]. In the IECG model each polymer in the melt is described as a chain of CG units, positioned at a distance along the chain comparable or larger than the persistence length [13]. Each polymer is partitioned into a number, n_b, of CG units or blobs, with each CG unit representing a number of monomers, N_b, such that the total number of monomers in a chain is $N = n_b N_b$. In the case where $n_b = 1$, the polymer is described as a point particle interacting with a soft potential, i.e. the soft sphere model. The larger the level of coarse-graining, the more significant the speed up in the Molecular Dynamics (MD) simulations that use the IECG representation and potential. Note that Gaussian statistics, which is used in the analytical solution of the IECG theory, is satisfied when N_b is roughly greater than 30 for a melt of polyethylene chains, while different numbers fulfill this condition when polymers of different chemical nature are studied. Also, the direct correlation function, and so the potential, between blobs involves a nonzero tail at relatively large distances, which is more pronounced as the level of coarse-graining increases [3,4]. Structural properties, i.e. the pair distribution function $h(r) = g(r) - 1$, and thermodynamic properties, i.e. compressibility, pressure, internal energy, entropy, Gibbs excess free energy, and Helmholtz excess free energy, were calculated in our previous works for polyethylene melts at different densities and degrees of polymerization [2–7]. Theoretical predictions and results from coarse-grained IECG simulations were compared and tested against united atom (UA) simulations. Structural and thermodynamic properties are consistent, with the exception of the entropy and the internal energy, which depend on the number of blobs in which a chain is partitioned.

We start by addressing with an example the question if it is

* Corresponding author.
E-mail address: mguenza@uoregon.edu (M.G. Guenza).

possible for the CG simulations, which use the structurally-consistent IECG potential, to predict thermodynamic properties consistent with the corresponding atomistic simulations. Reported in Fig. 1 are the results of the pressure calculated in four different MD simulations, performed with different levels of granularity: i) a United Atom simulation (reported in red in the figure), ii) a simulation where each polymer in the melt is represented as a soft sphere ($n_b = 1$, reported in blue), iii) a simulation in which each polymer is represented as a chain of 4 blobs ($n_b = 4$, reported in orange), and iv) one simulation in which each polymer is represented as a chain of 6 blobs ($n_b = 6$, reported in cyan). Each simulation represents a melt of polyethylene chains, with a degree of polymerization $N = 192$, at the temperature of 509 K and at a monomer density of 0.733 gr/cm^3. All the simulations are performed in the canonical ensemble with the Nose'-Hoover thermostat, using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) software program [14].

The UA simulation results are based on the analysis of 8 ns trajectories available from our previous work [3,6]. More details about the UA simulations are reported there. The CG simulations were performed using the IECG potential. The timestep for all was set to 10 fs and the temperature in the Nose'-Hoover thermostat was relaxed in a timespan of 200 fs. The CG particles were allowed to equilibrate for 1 ns before production runs of $6 - 12$ ns were performed to obtain static properties and thermodynamic averages. The IECG potential depends on one non-trivial parameter, the effective monomer-monomer direct correlation function in the limit of zero wavevector k, $C_0 = C^{mm}(k \to 0) = 4\pi \int_0^\infty r^2 C^{mm}(r) dr$, which is directly related to the compressibility of the system. The specific value of C_0 can be determined by different procedures, as described below. In the simulations presented here the value of $C_0 = -10.02$ Å^3. Another important, but trivial, parameter is the polymer squared radius of gyration, which is assumed to be $R_g^2 = 541.0$ Å^2. This value of the radius of gyration was selected from data of Neutron Spin Echo experiments, performed by Richter and coworkers at the given thermodynamic conditions of temperature and density [15]. This value is consistent with a straightforward theoretical estimate given by $R_g^2 = Nl^2/6$, where l is the effective segment length between the center-of-mass of two monomers (4.37 Å for polyethylene). When the theoretical value is used, this results in a R_g^2 value of 611.1 Å^2 for $N = 192$. Simulations performed with this value of R_g^2 and the chains coarse-grained, for example, with six blobs, $n_b = 6$, gives a pressure of 356.15 ± 0.03 atm, which is in excellent agreement with the results obtained using $R_g^2 = 541.0$ Å^2, i.e. a pressure of 356.12 ± 0.03 atm, as reported in Fig. 1.

The cutoff distance for the CG simulations was determined over the range of $r > 0$ from the location of the second extremum of effective intermolecular potential, $V^{bb}(r)$, obtained from the Hypernetted Chain closure (HNC), noting that a small attractive part exists between the first and second extrema [4]. The cutoff values of 269.48 Å, 102.26 Å, and 77.07 Å were used for n_b of one, four, and six, respectively. The simulations with $n_b = 1$ were performed in a box size of 547.8 Å consisting of 27000 blobs, while the simulations with n_b of 4 and 6 were performed in a box size of 273.9 Å, each consisting of 13500 and 20250 blobs, respectively. For n_b of 4 and 6, the effective bond potential between adjacent blobs was taken to be $V_{bond}(r) = 3n_b k_B Tr^2/(8R_g^2) + V^{bb}(r) + k_B T \ln[1 + h^{bb}(r)]$, which enforces the appropriate distributions between adjacent blobs, where k_B is the Boltzmann constant and T is the temperature. The angle potential was calculated using $V_{angle}(\theta) = -k_B T \ln[P(\theta)/\sin(\theta)]$, where Eq. (33) of McCarty et al. [6] was used to obtain $P(\theta)$. All $1 - 2$ and $1 - 3$ pairs of bonded blobs were excluded from the non-bonded interactions.

The top panel of Fig. 1 shows the evolution of the instantaneous pressure, P_i at step i, while the black line represents its instantaneous average: for example at step j, $\langle P_j \rangle = \frac{1}{N_j}\sum_{i=1}^{N_j} P_i$ as N_j is the number of steps up to step j. The bottom panel of Fig. 1 shows in red the probability distribution of the pressure, as obtained from the UA simulation, with the average pressure in black, and the
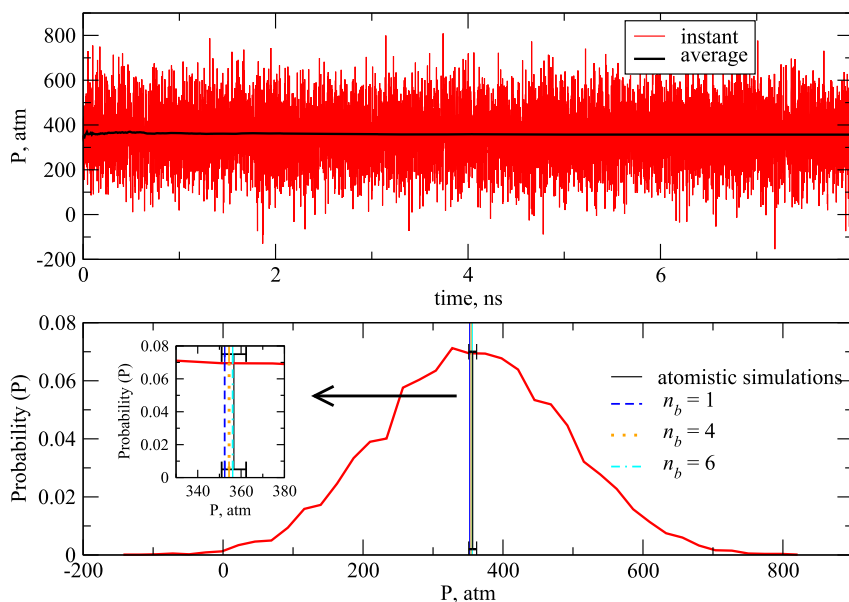

Fig. 1. Top panel: evolution of the instantaneous pressure over the production run of an atomistic simulation of polyethylene with $N = 192$, at 509 K and density 0.733 gr/cm^3 (red curve). Average pressure for the same simulation (black curve). Bottom panel: pressure distribution for the atomistic simulation (red curve). The black line shows the average pressure for atomistic simulations with the simulation error bars (99% confidence interval) obtained from block averages. The dash blue, dot orange, and dash-dot cyan lines show the average pressure for coarse-grained (CG) simulations with one, four, and six CG units per chain, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)