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Comment on "Systematic and simulation-free coarse graining of homopolymer melts: A structure-based study" [J. Chem. Phys. 142, 054905 (2015)]

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In a recent paper by Yang and Wang, referred to hereafter as Paper I,[1] the authors performed a number of calculations using the Integral Equation Coarse-Graining (IECG) theory developed by Guenza, Clark, McCarty, and coworkers.[2–7] While the original IECG formalism is described extensively in the paper, the authors in many instances incorrectly report the assumptions made in the IECG approach. Furthermore they attempt to implement some results from the IECG theory outside of its stated range of validity, which leads to incorrect predictions. In this short communication, we briefly restate the main results of the IECG and bring to the attention of the reader the most relevant misrepresentations of our theory found in Paper I.

The IECG model is a coarse-graining theory based on the integral equation theory of macromolecular liquids.[8] It represents polymer chains in a liquid as chains of coarse-grained units. In the IECG model, each macromolecule is partitioned into an arbitrary number, n_b, of coarse-grained units or blobs. Each CG unit represents a number of monomers, N_b, such that the total number of monomers in a chain is $N = n_b N_b$.[2–4] While there are no limitations to the numerical solution of the IECG potential, Clark *et al.*[3,4] provided also an *analytical solution* of the IECG intermolecular potential. The long-range component of the potential is derived in the limit of $\Gamma = N_b \rho |c_0| \gg 1$, with N_b the number of monomers inside a coarse-grained unit, ρ the monomer density, and c_0 the direct correlation function at $k \to 0$. The latter is directly related to the liquid compressibility.[9] This condition sets limits on the number of monomers included in the coarse-grained unit, N_b, once the thermodynamic parameters of the system are defined. In general, the analytical formalism applies only for CG descriptions where the number of monomer units in the CG unit is much larger than the persistence length of the polymer. Clark *et al.*[3,4] and McCarty *et al.*[5,6] have shown that the IECG approach conserves both structure (see, for example, Figure 8 in Ref. 6 and Figures 1–4 Ref. 7)[7] and thermodynamic properties (see, for example, Figures 9–15 in Ref. 6) as the CG units are represented with variable level of detail. For a full and correct discussion of these results, the reader is advised to refer to Refs. 2, 3, and 5.

Paper I reports in Figures 2–7 calculations for finite size chains, $N = 1000$, and increasing number of CG units in which each chain is partitioned. Care must be taken in comparing the results between our work and Paper I because the variables in Paper I are defined differently than in our papers. The number of CG units in the chain, which is n_b in our notation, is defined in Paper I as N. In a nutshell, Paper I shows that our analytical long-range potential "fails in the limit of large N," which is in the limit of a large number of CG units. Given that the total number of monomers in a chain is fixed, Figures 2–7 in Paper I report values for the limit where the number of CG units is equal or larger than the total number of monomers in the chain. This limit is at odds with the conditions of validity of the analytical solution, just mentioned above. In fact Paper I shows in Figures 2–7 that the analytical solution of the IECG equation is in excellent agreement with the numerical solution *in the limit in which the analytical solution applies*.

It should be stressed that in our work, the analytical potential serves as an approximation, under reasonable assumptions, for the numerical potential that is used in simulations. Having an analytical potential allows one to understand the scaling behavior of the potential with structural parameters, as well as to estimate thermodynamic quantities of interest. Clark *et al.* have shown that the range of parameters for which the analytical representation of the potential agrees quantitatively with the full numerical solution is, as expected, the range of parameters defined by the approximations used in deriving the analytical solutions.[3]

The authors of Paper I also claim that we used the "..the original system of hard-core Gaussian thread model as the input.." to our theory. While the thread model has been extensively investigated in our studies,[7] the three main papers about thermodynamic consistency[3,4,6] are not based on the thread model. The input of our theory is monomer level PRISM theory[8] such that the monomer direct correlation in Fourier space, $\hat{c}^{mm}(k)$ in our notation, varies little over the range of wave vectors that contribute to the effective block-block coarse-grained total and direct correlations. This approximation will be quantitatively accurate so long as the spatial range of the monomer direct correlation is much less than the spatial range of the distribution of monomers about block centers. This is a much less drastic assumption than the monomer thread model, requiring only that the spatial range of the monomer

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interactions be much smaller than the size of the coarse-grained unit, and not infinitesimal. In our main papers about thermodynamic consistency,[3,4,6] the parameter c_0 was taken from either a fit to the pressure from united atom simulations or from numerical PRISM calculation, which have realistic finite-range interactions with hard core repulsive and short range attractive potentials.

In Paper I, the authors state that in their input monomer theory, "both its intrachain non-bonded internal energy per chain and virial pressure diverge." The paper does not provide an explanation for this unphysical result, and intramolecular contributions are subsequently discarded. In our model, the input monomer level system is taken to be a PRISM description[8] of a united atom potential energy model with finite range interactions (with a hard sphere approximation to the repulsive part of the Lennard-Jones potential for computational ease), no unphysical values of the internal energy emerge.[3] Moreover, intramolecular contributions to the internal energy are found to be important in balancing intermolecular components (for a detailed discussion of this point, see Section V D and Figure 11 of Ref. [3]), as they should for a polymer liquid in its equilibrium state.[9]

An analysis demonstrating this effect was performed also for the pressure and reported in the paper by Clark *et al.*[3] Again we found that intra- and intermolecular components tend to balance each other in magnitude and have opposite sign. Thus, they cancel each other leaving the long-range intermolecular contribution as the leading contribution to the pressure (for a detailed discussion of this point, see Section V B and Figure 7 of Ref. [3]). In disagreement with Paper I, we observe that in a molecular liquid, it is essential for the correct evaluation of thermodynamic properties to include both their intramolecular and intermolecular components.

Contrary to the claims in Paper I, our treatment of the pressure and internal energy in Ref. [3] is more rigorous than the treatment presented in Paper I.[3] We are not surprised by the lack of thermodynamic consistency reported by the authors, as they only consider the intermolecular contribution to the pressure. In contrast, our work implicitly includes intramolecular contributions since the pressure is computed directly from molecular dynamics simulations.[10] Likely, in Paper I, the impossibility of observing the correct balancing of intra- and intermolecular terms is a consequence of the unphysical intramolecular chain model used as an input to the theory. When paired with an improper closure, unphysical models lead to well-known "catastrophes" in integral equation theory.[11,12]

In our papers, the analysis of thermodynamic properties is extended to 25 coarse-grained subdivisions on a 1000 monomer system (see, for example, Figures 7 and 11 of Ref. [3] and Figures 11 and 15 of Ref. [6]), contradicting another claim in Paper I that we considered no more than 5 blobs per chain. We also note that the analytical solution of the IECG potential did not require enforcing the Padè approximant, as incorrectly stated in Paper I. As a criticism of our work, Paper I reports

that "the RPA closure fails" in the limit of a highly partitioned CG chain, but this is consistent with our work: for a highly partitioned chain, the total correlation function clearly displays the structure of solvation shells and the RPA mean-field closure should not be used and has not been used in our papers. The RPA/MSA closure was only used to get the approximated form of the potential for $r > R_g$. In that regime the condition $|h^{bb}(r)| \ll 1$ always holds to extremely good approximation in the range of parameters for which our analytical forms are derived.

In our calculations, the numerical evaluation of the potential is input to the molecular dynamics simulations of the CG description. Any comparison of the theory with coarse-grained simulations effectively compares the theory to the implementation of the numerical potential. Often our papers compare four different types of calculations: numerical solutions of the IECG, analytical solutions, united atom simulations, and mesoscale simulations of the coarse-grained description, with the latter using the numerical solution and the HNC closure. Consistency for structural and thermodynamic properties is observed in all comparisons.

Finally, we would like to point out that the IECG method has been tested for realistic polymeric liquids (polyethylene, polyisoprene, and polyisobutadiene) for which united atom simulations are available.[7,13–18] Furthermore we note that the IECG is fully predictive, as CG simulations are performed directly without the need of performing atomistic simulations. The IECG theory has also the advantage of fast performance and accuracy.

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