## Application of PRISM Theory to Determine Thermodynamic Perturbation Terms for Chain Molecules

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Physically based models have their roots in molecular simulation, integral equation theory (IET), density functional theory (DFT), and thermodynamic perturbation theory (TPT). Molecular simulation stands as the ultimate standard by which theories are judged, but it is too slow for common engineering applications and limited to relatively small molecules (~1400 amu) where accurate thermodynamics are concerned. Integral equations have the advantage of providing molecular detail at the level of distribution functions (including "local compositions") while extending to all densities and, in principle, to infinite order in temperature. For the present work, we seek an IET applicable to all orders of molecular weight and temperature while adapting TPT as the basis for expressing the equation of state. This requires the establishment of a rigorous connection between the TPT coefficients and the output of IET. Recently, Ramana et al. have established this connection for spherical molecules. Our goal is to explore the extension to chain molecules. The particular IET of interest applies the polymer adaptation of the "referenced interaction site model" (RISM) theory as the basis for extension to molecular fluids. Polymer RISM theory (PRISM) is applicable in principle to all molecular shapes and sizes. It simply assumes that all pair correlations for a given site type are equivalent, regardless of whether they appear at the end of the chain or in the middle. Our present interest focuses on straight chain models of n-alkanes from ethane to polyethylene, in which case all site types are assumed to be identical in the context of the theory. We find that the first order TPT contribution is fairly accurate regardless of conformational details but the second order TPT contribution is remarkably sensitive to conformation. We can obtain accurate characterization of the second order contribution by varying the persistence length parameter of the semi-flexible chain model. Higher order TPT contributions follow from the second order result and are similarly sensitive to persistence length. The theory would not be "complete," however, without accurate characterization of the TPT reference contribution. We evaluate the compressibility route with various closures to accurately characterize the reference fluid thermodynamics as a function of density, chain length, and bond length. Altogether, the result is an accurate model of all contributions to chain molecular thermodynamics to infinite order in temperature, including the underlying fluid structure.