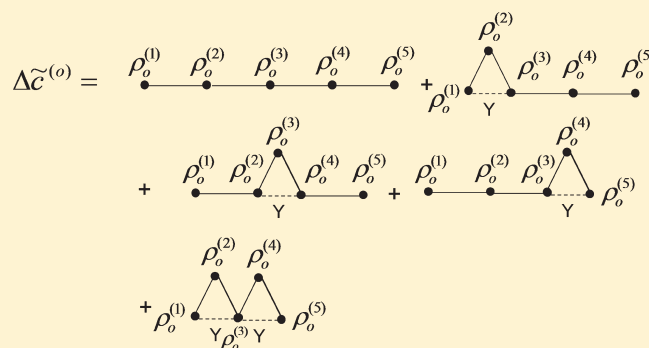


Higher Order Classical Density Functional Theory for Branched Chains and Rings

Bennett D. Marshall and Walter G. Chapman*

Department of Chemical and Biomolecular Engineering, Rice University, 6100 S. Main Houston, Texas 77005, United States

ABSTRACT: We develop a general density functional theory for polyatomic molecules by taking the complete association limit of Wertheim's thermodynamic perturbation theory in a general way. By enforcing the complete association limit at an early point in the derivation and introducing the concept of molecular graphs, a general form for the free energy functional and segment densities are developed for both rigid and semiflexible molecules. The theory is applicable to branched chains, rings, or any other molecular structure. As an example the theory is applied as a second order perturbation theory to the case of molecules with a rigid three segment head and a fully flexible tail in a slit pore where bond angle of the rigid portion is an independent variable.



I. INTRODUCTION

There has been a rapid advance in our theoretical understanding of inhomogeneous polymer systems in the last two decades. Density functional theory has played a pivotal role in this understanding.^{1,2} Perturbation density functional theories add a correction to a reference free energy functional to account for the change in free energy associated with chain formation A^{chain} and then minimize the grand free energy to obtain the density profile. The central task is to determine this correction. Wertheim's thermodynamic perturbation theory (TPT)^{3–7} treated in a complete association limit is an accurate and efficient framework to determine A^{chain} .

Most density functional theories based on TPT calculate A^{chain} in one of three ways;⁸ the first, as suggested by Chapman,⁹ is to treat A^{chain} obtained from TPT in inhomogeneous form as a free energy functional. Kierlik and Rosinberg^{10–12} were the first to develop a perturbation density functional theory using this approach. Their polyatomic density functional theory has been applied to both rigid and flexible linear chains.

A general form for the inhomogeneous free energy functional in TPT1 was first applied for associating fluids by Segura et al.⁸ to a system of associating spheres with four attraction sites. Tripathi and Chapman¹³ and later Jain et al.¹⁴ developed a polyatomic density functional theory based on the inhomogeneous free energy model called modified iSAFT. Modified iSAFT is formulated as a segment density based approach and has been applied to block copolymers,¹⁴ tethered polymers,¹⁵ depletion forces in a polymer/colloid system,¹⁶ and phase transitions in associating polymers.¹⁷

The second approach is to evaluate A^{chain} obtained in the homogeneous version of the theory at some weighted density, such as the weighted densities of fundamental measure theory.¹⁸ This approach was first used by Segura et al.⁸ using the SAFT¹⁹ free energy model in the study of associating fluids near a hard

wall. Later Yu and Wu²⁰ combined this approach in the limit of chain formation with the ideal free energy due to Woodward²¹ to develop a density functional theory for polymers. Their theory has been successfully applied to mixtures of polymeric fluids,²² block copolymers²³ and semiflexible and rigid polymers.²⁴ The third approach is to use density gradient theory or a local density approximation to evaluate A^{chain} obtained in the homogeneous version of the theory. This approach yields accurate results for unconfined systems and has been successfully used to model the liquid vapor interface of associating chain molecules.^{25–27}

These theories have been very successful in modeling fully flexible chain like systems, but little progress has been made in the application of a second order theory or a theory which is capable of describing ring polymers. The theory of Kierlik and Rosinberg¹¹ is written as an Nth order perturbation theory for linear chains, however no attempt was made to approximate the inhomogeneous triplet correlation function and apply it in second order form. Malijevsky et al.²⁸ applied the theory of Yu and Wu to star polymers where a second order homogeneous chain term using weighted densities was added to correct for the second order nature of the central bead treating all other bonds not associated with this bead in first order. An approach similar to this was also adopted by Xu and Cao²⁹ in the study of polydispersity in branched polymers. Adding a second order correction to the homogeneous free energy will result in a more accurate equation of state in the bulk; however the resulting DFT's neglect local three-body correlations since each bond of the branched polymer is still treated independently, as seen by the fact that they use first order recursion relations to evaluate the density profiles.

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Prior to the approach described here, no density functional theory based on Wertheim's theory was capable of describing ring polymers. Ghonasgi and Chapman^{30,31} developed a homogeneous theory which accurately described the behavior of ring molecules. Sear and Jackson³² also developed a homogeneous theory based on TPT for ring molecules by including a ring graph in their graphical expansion. Neither approach has been incorporated into a density functional theory for cyclic molecules or polymers.

In this work we build on the work of Kierlik and Rosinberg^{10–12} and Jain et al.¹⁴ We treat Wertheim's theory in inhomogeneous form to obtain a free energy functional, but we will take a different route to the complete association limit. We enforce the limit of complete association at the starting point of the derivation, and incorporate new molecular graphs that provide insight into the theory. This route allows the density profiles and chain free energy functional to be written in a general form for any molecular structure (chains, branched chains, or rings) at any order of perturbation theory. This general solution of Wertheim's TPT in the complete association limit, which extends previous treatments,^{10–12,14} is the most important contribution of the manuscript. We show that in the complete association limit Wertheim's theory takes a general form irrespective of molecular structure or order of perturbation, and develop a methodology to allow for the simple development of theories for any desired molecular structure.

In section II we review Wertheim's theory and the approach of Kierlik and Rosinberg for linear polymers. In section III we take the limit of complete association of TPT in a general way, and in section IV we develop a general density functional theory for rigid and semiflexible ring and branched molecules. In section V we develop a general homogeneous theory. Lastly, to demonstrate application of the theory, we treat the case of a partially rigid molecule, part rigid and part fully flexible, by treating the rigid portion in second order and the fully flexible portion in first order. We perform calculations for the case of the partially rigid molecule in a slit like pore and show that the results are in excellent agreement with simulation.

II. BACKGROUND

We consider an m component mixture of spherical segments which we bond together to form rings, chains or branched chains of size m . Whichever geometry is formed we will generically call a molecule. Each position on the molecule can only be occupied by a certain species of segment. In this paper the term "segment" represents spherical segments that bond together to form molecules.

The potential model for the spherical segments is composed of a repulsive core and some number of short ranged attraction sites labeled by capital letters. The potential of interaction between segment 1 and 2 of component β and γ is written as³

$$\phi^{(\beta\gamma)}(12) = \varphi_R^{(\beta\gamma)}(12) + \sum_{A \in \Gamma^{(\beta)}} \sum_{B \in \Gamma^{(\gamma)}} \varphi_{AB}^{(\beta\gamma)}(\vec{x}_{AB}) \quad (2.1)$$

Where

$$\vec{x}_{AB} = \vec{r}^{(\gamma)} + \vec{d}_B^{(\gamma)}(\Omega^{(\gamma)}) - \vec{r}^{(\beta)} - \vec{d}_A^{(\beta)}(\Omega^{(\beta)}) \quad (2.2)$$

is the vector connecting site A on segment β to site B on segment γ . $\vec{r}^{(\gamma)}$ is the position vector to the center of segment γ , $\vec{d}_B^{(\gamma)}(\Omega^{(\gamma)})$ is the vector from the center of the segment γ to site B on monomer γ and $\Omega^{(\gamma)}$ defines the orientation of monomer γ . The set of attraction sites on β is represented by $\Gamma^{(\beta)}$ and the notation (12) represents the position and orientation of the segments. If we define $e^{(\beta\gamma)}(12) = \exp(-\beta\varphi^{(\beta\gamma)}(12))$, where $\beta = 1/k_B T$, T is the temperature and k_B is Boltzmann's constant, the Mayer f function is then $f^{(\beta\gamma)}(12) = e^{(\beta\gamma)}(12) - 1$. Following Wertheim the Mayer f function can be decomposed as

$$f^{(\beta\gamma)}(12) = f_R^{(\beta\gamma)}(12) + F^{(\beta\gamma)}(12) \quad (2.3)$$

Where

$$F^{(\beta\gamma)}(12) = e_R^{(\beta\gamma)}(12) \left\{ \prod_{A \in \Gamma^{(\beta)}} \prod_{B \in \Gamma^{(\gamma)}} [1 + f_{AB}^{(\beta\gamma)}(12)] - 1 \right\} \quad (2.4)$$

The subscript R represents the reference system. In Wertheim's theory each bonding state of a segment is treated as a distinct species.⁵ The total number density of component β is given by the sum of the number densities of the bonding states of component β .

$$\rho^{(\beta)}(1) = \sum_{\alpha \subset \Gamma^{(\beta)}} \rho_\alpha^{(\beta)}(1) \quad (2.5)$$

where $\rho_\alpha^{(\beta)}(1)$ is the density of component β bonded at sites α . The improper subset $\alpha = \Gamma^{(\beta)}$ is included in the sum. For simplified notation Wertheim introduced a set of density parameters defined by

$$\sigma_\alpha^{(\beta)}(1) = \sum_{\gamma \subset \alpha} \rho_\gamma^{(\beta)}(1) \quad (2.6)$$

Two important cases of 2.6 are

$$\begin{aligned} \sigma_\circ^{(\beta)}(1) &= \rho^{(\beta)}(1) \\ \sigma_{\Gamma^{(\beta)}}^{(\beta)}(1) &= \rho^{(\beta)}(1) \end{aligned} \quad (2.7)$$

In TPT the change in free energy due to association is

$$\beta(A - A_R) = \sum_{\beta=1}^m \int \left(\rho^{(\beta)}(1) \ln \frac{\rho_\circ^{(\beta)}(1)}{\rho^{(\beta)}(1)} + \rho^{(\beta)}(1) + Q^{(\beta)}(1) \right) d(1) - c^{(\circ)} + c_R^{(\circ)} \quad (2.8)$$

$c^{(\circ)}$ is the sum of all irreducible graphs connected by $F^{(\beta\gamma)}$ and $f_R^{(\beta\gamma)}$ bonds where all points are field points represented by factors of $\sigma_{\Gamma^{(\beta)}-\alpha}^{(\beta)}(j)$ and α is the set of bonded sites of component β at j . The sum of the reference system graphs is given by $c_R^{(\circ)}$. With these definitions the graph sum $\Delta c^{(\circ)} = c^{(\circ)} - c_R^{(\circ)}$ contains only the graphs which contain attraction bonds. Throughout this paper we will adhere to Wertheim's single bonding condition,⁶ where multiple bonding between attraction sites and multiple bonding between segments is forbidden. We will also adhere to a generalization of Wertheim's single chain approximation;⁷ we will only consider graphs with a single path of attraction bonds. The quantity $Q^{(\beta)}(1)$ is defined by

$$\begin{aligned} Q^{(\beta)}(1) &= - \sum_{A \subset \Gamma^{(\beta)}} \sigma_{\Gamma^{(\beta)}-A}^{(\beta)}(1) \\ &+ \sigma_\circ^{(\beta)}(1) \sum_{P(\Gamma^{(\beta)})=\{\gamma, M \geq 2\}} (-1)^M (2-M)! \prod_{\gamma} \frac{\sigma_\gamma^{(\beta)}(1)}{\sigma_\circ^{(\beta)}(1)} \end{aligned} \quad (2.9)$$

Here $P(\Gamma^{(\beta)}) = \{\gamma, M \geq 2\}$ is the proper partition of $\Gamma^{(\beta)}$ into at least 2 subsets. We will also use a series of functions $c_\alpha^{(\beta)}(1)$ defined by

$$c_\alpha^{(\beta)}(1) = \frac{\delta c^{(\alpha)}}{\delta \sigma_{\Gamma^{(\beta)} - \alpha}^{(\beta)}}(1) \quad (2.10)$$

Now the task is to estimate the graph sum $\Delta c^{(\alpha)}$. In first order thermodynamic perturbation theory (TPT1) all graphs are disregarded except those which contain associations between a single pair of segments. Only nearest neighbor interactions along the chain are included yielding results that are independent of bond angle. Kierlik and Rosinberg^{10,11} defined the sum of first order graphs of a mixture of segments with one or two attraction sites to be

$$\Delta c^{(\alpha)} = \sum_{\beta=1}^{m-1} \int \sigma_{-1}^{(\beta)}(1) F^{(\beta, \beta+1)}(12) y_c^{(\beta, \beta+1)}(12) \times (12) \sigma_{+1}^{(\beta+1)}(2) d(1) d(2) \quad (2.11)$$

The graph sum eq 2.11 was defined for the purpose of chain formation. Here $y_c^{(\beta, \beta+1)}(12)$ is the cavity correlation function of the reference system defined by $e_r^{(\beta, \beta+1)}(12) y_c^{(\beta, \beta+1)}(12) = g^{(\beta, \beta+1)}(12)$, where $g^{(\beta, \beta+1)}(12)$ is the two body correlation function of the reference system. Species 1 bonds to species 2, m bonds to $m-1$ and for the other $m-2$ segments internal to the chain segment β bonds to $\beta-1$ and $\beta+1$. The term $\sigma_{-1}^{(\beta)}$ is the density parameter of component β not bonded to component $\beta-1$ and $\sigma_{+1}^{(\beta)}$ is the density parameter not bonded to component $\beta+1$. By definition $\sigma_{+1}^{(m)}(1) = \sigma_o^{(m)}(1)$ and $\sigma_{-1}^{(1)}(1) = \sigma_o^{(1)}(1)$. In this formalism Kierlik and Rosinberg give $Q^{(\beta)}(1)$ as

$$Q^{(\beta)}(1) = -\sigma_{-1}^{(\beta)}(1) - \sigma_{+1}^{(\beta)}(1) + \frac{\sigma_{-1}^{(\beta)}(1) \sigma_{+1}^{(\beta)}(1)}{\rho_o^{(\beta)}(1)} \quad (2.12)$$

Now using the graph sum eq 2.11 and the $Q^{(\beta)}(1)$ defined by eq 2.12 the free energy is minimized with respect to $\sigma_{-1}^{(\beta)}(1)$, $\sigma_{+1}^{(\beta)}(1)$, and $\rho_o^{(\beta)}(1)$ to yield the following mass action equations:

$$\frac{\sigma_{+1}^{(\beta)}(1)}{\rho_o^{(\beta)}(1)} - 1 = \int \sigma_{+1}^{(\beta+1)}(2) F^{(\beta, \beta+1)}(12) y_c^{(\beta, \beta+1)}(12) d(2) \quad (2.13)$$

$$\frac{\rho_o^{(\beta)}(1)}{\rho_o^{(\beta)}(1)} - \frac{\sigma_{-1}^{(\beta)}(1) \sigma_{+1}^{(\beta)}(1)}{(\rho_o^{(\beta)}(1))^2} = 0 \quad (2.14)$$

The mass action equation for $\sigma_{-1}^{(\beta)}(1)$ is obtained by interchanging the label +1 for -1 in 2.13. Defining the “strong association limit” as the limit where the density of segments not bonded at all sites is very small, but nonzero, and association energies are large, but not yet infinite. The limit of complete association corresponds to association energies becoming infinite and the densities of segments not bonded at all sites becoming identically zero. In the limit of strong association the -1 on the left-hand side of eq 2.13 can be neglected and 2.13, 2.14, and 2.11 can be solved recursively to give the following form for $\Delta c^{(\alpha)}$ and segment densities

$$\frac{\Delta c^{(\alpha)}}{(m-1)} = \int \rho_o^{(1)}(1) \dots \rho_o^{(m)}(m) D_1^{(1, 2 \dots m)}(1 \dots m) \times F^{(1, 2 \dots m)}(1 \dots m) d(1) \dots d(m) \quad (2.15)$$

$$\frac{\rho_o^{(j)}(j)}{\rho_o^{(j)}(j)} = \int \rho_o^{(1)}(1) \dots \rho_o^{(j-1)}(j-1) \rho_o^{(j+1)}(j+1) \dots \rho_o^{(m)}(m) \times D_1^{(1, 2 \dots m)}(1 \dots m) F^{(1, 2)}(12) \dots F^{(m-1, m)}(m-1, m) \times d(1) \dots d(j-1) d(j+1) \dots d(m) \quad (2.16)$$

where $D_1^{(1, 2 \dots m)}(1 \dots m)$ is defined by $D_1^{(1, 2 \dots m)}(1 \dots m) \equiv y_c^{(12)}(1, 2) \dots y_c^{(m-1, m)}(m-1, m)$, the subscript 1 denotes first order perturbation theory. Kierlik and Rosinberg¹¹ showed that if the proceeding analysis was repeated for an N 'th order perturbation theory eq 2.16 would remain unchanged except for $D_1^{(1, 2 \dots m)}(1 \dots m) \rightarrow D_N^{(1, 2 \dots m)}(1 \dots m)$. For a detailed description of $D_N^{(1, 2 \dots m)}(1 \dots m)$ the reader is referred to ref 11. The graph sum eq 2.11 can be used to treat linear chains but is fundamentally incapable of describing polymer rings. In order to treat ring polymers Sear and Jackson³² introduced a ring graph to the graph sum. If the possibility of forming chains is neglected the graph sum is composed of a single irreducible ring graph

$$\Delta c^{(\alpha)} = \int \rho_o^{(1)}(1) \dots \rho_o^{(m)}(m) D_1^{(1, 2 \dots m)}(1 \dots m) y_c^{(m, 1)}(m, 1) \times y_c^{(m, 1)}(m, 1) F^{(1, 2)}(12) \dots F^{(m-1, m)}(m-1, m) \times F^{(m, 1)}(m, 1) d(1) \dots d(m) \quad (2.17)$$

In the ring graph all segments have two attraction sites and are fully bonded.

The form of eq 2.17 only allows rings of size m to form. After minimization of the free energy $Q^{(\beta)}(1)$ is found to be $Q^{(\beta)}(1) = -\rho_o^{(\beta)}(1)$ and the segment densities are

$$\frac{\rho_o^{(j)}(j)}{\rho_o^{(j)}(j)} - 1 = \int \rho_o^{(1)}(1) \dots \rho_o^{(j-1)}(j-1) \rho_o^{(j+1)}(j+1) \dots \rho_o^{(m)}(m) \times D_1^{(1, 2 \dots m)}(1 \dots m) y_c^{(m, 1)}(m, 1) F^{(1, 2)}(12) \dots F^{(m-1, m)}(m-1, m) F^{(m, 1)}(m, 1) d(1) \dots d(j-1) d(j+1) \dots d(m) \quad (2.18)$$

In the limit of strong association the monomer density in eq 2.18 will be small and the -1 on the left-hand side can be neglected. It is clear that after the conditions of free energy minimization are enforced and the limit of strong association taken the graph sum used to characterize chain molecules collapses to a form similar to that of the irreducible ring graph with a similar mass action equation. If this similarity can be exploited a general free energy and subsequently general density profile for inhomogeneous systems can be developed.

III. FREE ENERGY FUNCTIONAL FOR LINEAR, BRANCHED, AND RING MOLECULES

To derive a general theory for rings and linear and branched chains, we will take a different route to the limit of strong association; the limit of strong association will be enforced from the outset. There is no restriction on the number of bonding sites on a given segment. We start by defining a graph sum that makes the theory intuitive for nonlinear molecules

$$\Delta \tilde{c}^{(\alpha)} = - \sum_{\beta=1}^m \int Q^{(\beta)}(1) d(1) + \Delta c^{(\alpha)} \quad (3.1)$$

The free energy is now

$$\beta(A - A_R) = \sum_{\beta=1}^m \int \left(\rho^{(\beta)}(1) \ln \frac{\rho_o^{(\beta)}(1)}{\rho^{(\beta)}(1)} + \rho^{(\beta)}(1) \right) d(1) - \Delta\tilde{c}^{(o)} \quad (3.2)$$

Minimizing the free energy with respect to the monomer density produces

$$\frac{\rho^{(\beta)}(1)}{\rho_o^{(\beta)}(1)} = \frac{\delta\Delta\tilde{c}^{(o)}}{\delta\rho_o^{(\beta)}(1)} \quad (3.3)$$

In the limit of strong association the densities of segments not bonded at all sites become small, so their contribution to the total number density of component β becomes negligible and we can write

$$\rho^{(\beta)}(1) = \rho_{\Gamma^{(\beta)}}^{(\beta)}(1) \quad (3.4)$$

Wertheim⁵ gives the relation, which is equivalent to free energy minimization

$$\frac{\rho_{\alpha}^{(\beta)}(1)}{\rho_o^{(\beta)}(1)} = \sum_{P(\alpha)=\{\gamma\}} \prod_{\gamma} c_{\gamma}^{(\beta)}(1) \quad (3.5)$$

where $P(\alpha) = \{\gamma\}$ is the partition of α into nonempty subsets. Using eq 3.4 and 3.5

$$\frac{\rho^{(\beta)}(1)}{\rho_o^{(\beta)}(1)} = \sum_{P(\Gamma^{(\beta)})=\{\gamma\}} \prod_{\gamma} c_{\gamma}^{(\beta)}(1) \quad (3.6)$$

There are also the graphs where $\alpha \neq \Gamma^{(\beta)}$

$$\frac{\rho_{\alpha}^{(\delta)}(1)}{\rho_o^{(\delta)}(1)} = \sum_{P(\alpha)=\{\epsilon\}} \prod_{\epsilon} c_{\epsilon}^{(\delta)}(1) \quad \alpha \neq \Gamma^{(\delta)} \quad (3.7)$$

The statement $\rho^{(\beta)}(1) = \rho_{\Gamma^{(\beta)}}^{(\beta)}(1)$ has allowed us to write down the general density profile at complete association eq 3.6. Now we wish to eliminate the $\sigma_{\Gamma^{(\beta)}-\alpha}^{(\beta)}(1)$'s for $\alpha \neq \Gamma^{(\beta)}$ in eq 3.6 using eq 3.7. In order to do this, we define two types of bonding sets. The first type, type I, is when a set of sites $\{\epsilon\}$ results in an identically zero density $\rho_{\epsilon}^{(\beta)}(1)$ even before the limit of complete association is taken. An example of a type I bonding set can be found in the ring graph eq 2.17; for each specie either both sites are bonded or no sites at all, so the densities $\rho_A^{(\beta)}(1)$ and $\rho_B^{(\beta)}(1)$ are always equal to zero, so $\{A\}$ and $\{B\}$ are bonding sets of type I. Integrated points $\sigma_{\Gamma^{(\beta)}-\epsilon}^{(\beta)}(1)$ where $\{\epsilon\}$ is of type I will never appear in $\Delta c^{(o)}$ and hence do not need to be eliminated. Bonding sets of type II have, in general, nonzero densities when not at complete association. For example any bonding site associated with a segment in a linear or branched chain. At complete association an order of magnitude analysis shows for type II bonding sets that $\sigma_{\alpha}^{(\beta)}(1) = \rho_{\alpha}^{(\beta)}(1)$; with this identification the integrated points in $\Delta c^{(o)}$ are now represented by factors of $\rho_{\Gamma^{(\beta)}-\alpha}^{(\beta)}(1)$ and

$$c_{\alpha}^{(\beta)}(1) = \left(\frac{\delta c^{(o)}}{\delta \rho_{\Gamma^{(\beta)}-\alpha}^{(\beta)}(1)} \right) \quad \alpha \subset \text{type II} \quad (3.8)$$

$$c_{\epsilon}^{(\beta)}(1) = 0 \quad \epsilon \subset \text{type I}$$

Equations 3.6–3.8 can now be used to construct the segmental density profiles for an arbitrarily shaped molecule at any order of

perturbation theory, and this density can then be used to determine $\Delta\tilde{c}^{(o)}$ through eq 3.3. Before proceeding to the general case, to illustrate the method, the simple case of a 5-mer in second order perturbation theory will be considered.

Consider the second order graph sum for a linear chain consisting of $m-2$ segments with two sites A and B, segment 1 has a single site A and segment m has a single site B. Site A on segment β bonds to site B on segment $\beta + 1$, the second order graph sum using Wertheim's chain approximation is then^{7,11}

$$\Delta c^{(o)} = \sum_{\beta=1}^{m-1} \int \sigma_B^{(\beta)}(1) F^{(\beta, \beta+1)}(12) Y^{(\beta, \beta+1)}(12) \sigma_A^{(\beta+1)}(2) d(1) d(2) \\ + \sum_{\beta=1}^{m-2} \int \sigma_B^{(\beta)}(1) \sigma_o^{(\beta+1)}(2) \sigma_A^{(\beta+2)}(3) F^{(\beta, \beta+1)}(12) F^{(\beta+1, \beta+2)}(23) \\ \times Y^{(\beta, \beta+1, \beta+2)}(123) d(1) d(2) d(3) \quad (3.9)$$

where $\sigma_A^{(m)}(1) = \sigma_o^{(m)}(1)$, $\sigma_B^{(1)}(1) = \sigma_o^{(1)}(1)$, $Y^{(\beta, \beta+1)}(12) = y^{(\beta, \beta+1)}(12)$ and

$$Y^{(\beta, \beta+1, \beta+2)}(123) = y^{(\beta, \beta+1, \beta+2)}(123) \\ - y^{(\beta, \beta+1)}(12) y^{(\beta+1, \beta+2)}(23) \quad (3.10)$$

where we have introduced a new s body correlation function $y^{(1...s)}(1...s)$ called the bonding correlation function defined by the reference system correlation function $g^{(1...s)}(1...s)$ as $\prod_{(ij)}^{\text{all bonded pairs}} e_R^{(ij)}(ij) y^{(1...s)}(1...s) = g^{(1...s)}(1...s)$ or alternatively from the cavity correlation function $\prod_{(ij)}^{\text{pairs not bonded}} e_R^{(ij)}(ij) y_c^{(1...s)}(1...s) = y^{(1...s)}(1...s)$ where $y_c^{(1...s)}(1...s)$ is the reference system s body cavity correlation function. For two bonded segments the pair bonding correlation function is $y^{(ij)}(12) = y_c^{(ij)}(12) = g^{(ij)}(12)/e_R^{(ij)}(12)$ and for three segments bonded in a chain where species β bonds to $\beta + 1$ and $\beta + 1$ bonds to $\beta + 2$ the triplet bonding correlation function is given as

$$y^{(\beta, \beta+1, \beta+2)}(123) = \frac{g^{(\beta, \beta+1, \beta+2)}(123)}{e_R^{(\beta, \beta+1)}(12) e_R^{(\beta+1, \beta+2)}(23)} \\ = e_R^{(\beta, \beta+2)}(13) y_c^{(\beta, \beta+1, \beta+2)}(123) \quad (3.11)$$

Now considering the special case of a linear five segment chain in the strong association limit; in this limit the density parameters σ_{α} become densities ρ_{α} and eq 3.9 can be represented graphically as

$$\Delta c^{(o)} = \begin{array}{c} \rho_o^{(1)} \quad \rho_A^{(2)} \quad \rho_B^{(2)} \quad \rho_A^{(3)} \quad \rho_B^{(3)} \quad \rho_A^{(4)} \quad \rho_B^{(4)} \quad \rho_o^{(5)} \\ \bullet \text{---} \bullet + \bullet \text{---} \bullet + \bullet \text{---} \bullet + \bullet \text{---} \bullet \\ \rho_o^{(2)} \quad \rho_A^{(3)} \quad \rho_B^{(3)} \quad \rho_A^{(4)} \quad \rho_B^{(4)} \quad \rho_o^{(5)} \\ \bullet \text{---} \bullet \text{---} \bullet + \bullet \text{---} \bullet \text{---} \bullet + \bullet \text{---} \bullet \text{---} \bullet \\ \rho_o^{(1)} \quad \rho_A^{(2)} \quad \rho_B^{(2)} \quad \rho_A^{(3)} \quad \rho_B^{(3)} \quad \rho_o^{(5)} \\ \bullet \text{---} \bullet \text{---} \bullet \text{---} \bullet \text{---} \bullet \end{array} \quad (3.12)$$

where the first four graphs are the first order graphs and the last three are the second order graphs. The circles represent the appropriate densities and the bonds, lines, represent Mayer functions and correlation functions. The dashed line represents a correlation function bond but no F bond, and the Y means that the correlation function given by eq 3.10 links all three circles. Now evaluating eq 3.6 for segment 1

$$\frac{\rho^{(1)}(1)}{\rho_o^{(1)}(1)} = c_A^{(1)}(1) = \begin{array}{c} \rho_A^{(2)} \\ \bullet \text{---} \bullet \\ (1) \end{array} + \begin{array}{c} \rho_o^{(2)} \\ \bullet \text{---} \bullet \text{---} \bullet \\ (1) \text{ Y } \bullet \end{array} \rho_A^{(3)} \quad (3.13)$$

where the functional derivative is taken by turning all points that the derivative operates on to white, nonintegrated, labeled points (1). Now the density $\rho_A^{(2)}(2)$ is obtained from eq 3.7, we use this equation to eliminate $\rho_A^{(2)}(2)$ from the first order graph in eq 3.13 by superimposing the white circles from the graphs in the sum $\rho_A^{(2)}(2)$ to the point $\rho_o^{(2)}(2)$ in eq 3.13 turning the points black and labeling them with the density $\rho_o^{(2)}(2)$. We repeat this process for $\rho_A^{(3)}(3)$ and $\rho_A^{(4)}(4)$, perform the integration in eq 3.3 and find

$$\Delta c^{(o)} = \rho_o^{(1)} \rho_o^{(2)} \rho_o^{(3)} \rho_o^{(4)} \rho_o^{(5)} + \rho_o^{(1)} \rho_o^{(2)} \rho_o^{(3)} \rho_o^{(4)} \rho_o^{(5)} + \rho_o^{(1)} \rho_o^{(2)} \rho_o^{(3)} \rho_o^{(4)} \rho_o^{(5)} + \rho_o^{(1)} \rho_o^{(2)} \rho_o^{(3)} \rho_o^{(4)} \rho_o^{(5)} + \rho_o^{(1)} \rho_o^{(2)} \rho_o^{(3)} \rho_o^{(4)} \rho_o^{(5)} \quad (3.14)$$

The densities are obtained from eq 3.14 by application of eq 3.3. We see that the graphs $\Delta c^{(o)}$ take on the form of the 5 segment chain, these graphs will be called molecular graphs and the graphs in $\Delta c^{(o)}$ will be called subgraphs. Molecular graphs are reducible graphs which are constructed by “combining” the irreducible subgraphs from $\Delta c^{(o)}$ in such a way to construct a molecular form. For the 5-mer, each molecular graph that could be constructed from the subgraphs in eq 3.12 was constructed and constructed only once. We shall see that this is a general feature of TPT in the strong association limit.

Now the general situation of an arbitrary molecule of m segments will be considered. We will consider s -mer subgraphs in $\Delta c^{(o)}$ which consist of s field points $\rho_{\Gamma(\beta)}^{(\beta)} - \alpha(1)$, where α is the set of bonded sites, a factor $F^{(\alpha, \phi, \dots, \mu, v)}(1 \dots s)$ which is the product of Mayer functions in the subgraph, and a factor $Y^{(\alpha, \phi, \dots, \mu, v)}(1 \dots s)$ which consist of some combination of bonding correlation functions. For instance, in the ring graph $Y^{(\alpha, \phi, \dots, \mu, v)}(1 \dots s)$ is given by the product of m bonding correlation functions $y^{(\alpha, \phi)}(12)$. For branched chains $Y^{(\alpha, \phi, \dots, \mu, v)}(1 \dots s)$ contains the s body bonding correlation function $y^{(\alpha, \phi, \dots, \mu, v)}(1 \dots s)$ combined with lower order bonding correlation functions in such a way to create an irreducible subgraph; specifically for chains of bonds $Y^{(\alpha, \phi, \dots, \mu, v)}(1 \dots s)$ contains the s body bonding correlation function $y^{(\alpha, \phi, \dots, \mu, v)}(1 \dots s)$ and the sum of all products of y 's obtained by partitioning the sequence $1 \dots s$ into subsequences which share the switching point, a factor of -1 is associated with each switching point.^{7,11}

Now, imagine some generic molecule of size m ; assume this molecule has an end segment with one bonding site A, this segment will be labeled (1), and this segment bonds to segment (2) which has four bonding sites, after segment (2) the molecule is arbitrary. Evaluating eq 3.6

$$\frac{\rho^{(1)}(1)}{\rho_o^{(1)}(1)} = \frac{\rho_o^{(2)}(2)}{\rho_o^{(1)}(1)} + \left\{ \begin{array}{l} \text{Sum of higher order subgraphs with a white} \\ \text{circle labelled (1) obtained by functional} \\ \text{differentiation of } \Delta c^{(o)} \text{ w.r.t. } \rho_o^{(1)}(1) \end{array} \right\} \quad (3.15)$$

A bonding path will be defined as a certain way to satisfy the condition that a set of sites are bonded. Depending on the order of perturbation theory a set of sites on a segment can have

multiple bonding paths. This is seen in eq 3.15 where site A in segment (1) is bonded in first order to segment (2) plus bonding with higher order graphs where segment (1) is an end point in the graph. Equation 3.15 then represents all the bonding paths of site A on segment (1). Since each graph in $\Delta c^{(o)}$ is unique, each path taken in eq 3.15 must be unique. Now we wish to eliminate $\rho_{BCD}^{(2)}(2)$ from the first order graph using eq 3.7

$$\frac{\rho_{BCD}^{(2)}(2)}{\rho_o^{(2)}(2)} = c_{BCD}^{(2)}(2) + c_{BC}^{(2)}(2)c_D^{(2)}(2) + c_{CD}^{(2)}(2)c_B^{(2)}(2) + c_{DB}^{(2)}(2)c_C^{(2)}(2) + c_B^{(2)}(2)c_C^{(2)}(2)c_D^{(2)}(2) \quad (3.16)$$

The density $\rho_{BCD}^{(2)}(2)$ is given by the sum of five sets of graphs, a sum of irreducible graphs and four sums of reducible graphs. To eliminate $\rho_{BCD}^{(2)}(2)$ from eq 3.15 the white labeled circle (2) from each of these graphs in eq 3.16 is superimposed onto the black circle of the first order graph in eq 3.15, the circle is turned black and then labeled $\rho_o^{(2)}(2)$, this creates some number of new unique graphs. This sum accounts for all the possible bonding paths allowed by $\Delta c^{(o)}$ to satisfy the condition that the set {BCD} is bonded. The condition that {BCD} is bonded can be satisfied by attaching a triple connection, one of three combinations of a double and single connection or by attaching the combination of three single connections. The partitioning guarantees that each possibility to satisfy this bonding state will be accounted for; every possible path to bond the set {BCD} has been taken, and each path is unique. Now each of these new unique graphs and all of the original higher order graphs have other densities $\rho_{\Gamma(\gamma)-\alpha}^{(\gamma)}$'s that need to be eliminated. Each time one of these densities are eliminated more unique graphs are constructed. Again the partitioning in eq 3.7 assures that each path to satisfy the bonding condition of a set of sites $\Gamma^{(\gamma)} - \alpha$ will be taken. After elimination of all nonmonomer densities, each unique bonding path has been taken each time a density is eliminated which results in the construction of some number of m -mer graphs. These m -mer graphs now consist of a single labeled point (1), monomer density field points for each species 2 through m and Mayer/correlation function bonds. The fact that each bonding path is accounted for, when each density is eliminated, means that each of these m -mer graphs must be unique and that each m -mer graph that could be constructed from a combination of the graphs in $\Delta c^{(o)}$ has been constructed. We perform the integration in eq 3.3 to obtain the molecular graphs in $\Delta \tilde{c}^{(o)}$

$$\Delta \tilde{c}^{(o)} = \{ \text{sum of distinct molecular graphs obtained by combining the subgraphs in } \Delta c^{(o)} \text{ in such a way to construct a distinct } m\text{-mer where all points are integrated points represented by monomer densities} \} \quad (3.17)$$

We can write eq 3.17 in generic form as

$$\Delta \tilde{c}^{(o)} = \int \rho_o^{(1)}(1) \dots \rho_o^{(m)}(m) \tilde{F}(1 \dots m) \tilde{D}(1 \dots m) d(1) \dots d(m) \quad (3.18)$$

where $\tilde{F}(1 \dots m)$ is a product of all bonding Mayer functions and $\tilde{D}(1 \dots m)$ is a sum of product of correlation functions determined by

the specific form of $\Delta c^{(o)}$. The segment densities are obtained from eq 3.3 as

$$\frac{\rho^{(j)}(j)}{\rho_o^{(j)}(j)} = \int \tilde{D}(1\dots m) \tilde{F}(1\dots m) \prod_{\epsilon \neq j} \rho_o^{(\epsilon)}(\epsilon) d(\epsilon) \quad (3.19)$$

Comparing eqs 3.18 and 3.19 we see

$$\Delta \tilde{c}^{(o)} = \int \rho^{(j)}(1) d(1) \quad (3.20)$$

where the species density used in eq 3.20 is arbitrary. The change in free energy is now

$$\beta(A - A_R) = \sum_{\beta=1}^m \int \rho^{(\beta)}(1) \left(\ln \frac{\rho_o^{(\beta)}(1)}{\rho^{(\beta)}(1)} + 1 \right) d(1) - \int \rho^{(j)}(1) d(1) \quad (3.21)$$

Equations 3.19 and 3.21 represent the limit of strong association for Wertheim's TPT applied to mixtures of spherical segments to create a single type of polyatomic molecule. We have shown that Wertheim's theory takes this general form in the strong association limit without defining a specific form of $\Delta c^{(o)}$. Equation 3.21 is written for fixed bond angles, to allow for distributions of bond angles we simply make the substitution⁷

$$\ln \frac{\rho_o^{(\beta)}(1)}{\rho^{(\beta)}(1)} \rightarrow \ln \frac{\rho_o^{(\beta)}(\bar{1})}{\rho^{(\beta)}(\bar{1})} \quad (3.22)$$

When allowing for bond flexibility all bond angles $\{\alpha^{(\beta)}\}$ become internal variables and $\rho^{(\beta)}(\bar{1})$ is the density integrated over all bond angles. The specific details will be considered in section IV C; however, it is important to note that all other results in this section are generally valid for rigid and flexible bonds.

Now we will specifically consider branched chains in TPT2. It is beneficial to think of $\Delta \tilde{c}_{TPT2}^{(o)}$ in the following way. In first order $\Delta \tilde{c}_{TPT1}^{(o)}$ is composed of a single molecular graph consisting of only first order subgraphs, this will be called the spanning tree. In second order, in addition to the spanning tree, there are all the molecular graphs where two adjacent first order subgraphs from the spanning tree have been replaced with a second order graph, then all of the molecular graphs where two pairs of adjacent first order graphs from the spanning tree have been replaced with two second order subgraphs etc.. This process is repeated until the molecular graphs where the maximum number, N_s , of pairs of adjacent first order subgraphs allowed by the form of the spanning tree have been replaced with second order subgraphs. These graphs will be called the filled molecular graphs. Following this method all possible molecular graphs allowed by $\Delta c^{(o)}$ have been constructed. At this point it is clear that $D_2(1\dots m)$ is given by the sum of products of $Y(123)$'s, defined by eq 3.10, and $Y(12)$'s obtained by taking all the ways to partition the molecule into fragments of two and three segments, where fragments share at most one monomer. This was noted by Phan et al.³³ for the case of star molecules in second order perturbation theory. Here it has been shown that this is a general result of TPT2 in the strong association limit.

In this section we have taken the limit of strong association of TPT in a general way. The densities given by eq 3.19 and free energy functional eq 3.21 are valid for any molecular structure at any order of perturbation theory. In the following section density

functional theory will be employed to determine the monomer densities in eq 3.19.

IV. DENSITY FUNCTIONAL THEORY

In this section the density profile for an inhomogeneous system will be developed using the free energy developed in III. Initially the case of fixed bond angle will be considered; extension to flexible systems is straightforward and is considered in IV C. The analysis begins with the definition of the grand free energy at fixed μ , T and V subject to an external field $V_{\text{ext}}(1_r)$

$$\Omega[\{\rho^{(\beta)}(1_r)\}] = A[\{\rho^{(\beta)}(1_r)\}] - \sum_{\beta=1}^m \int d(1_r) \rho^{(\beta)}(1_r) (\mu^{(\beta)} - V_{\text{ext}}^{(\beta)}(1_r)) \quad (4.1)$$

where inhomogeneities in position and orientation are allowed, and $1_r = \{\vec{r}, \Omega_r\}$. Minimization of the grand potential with respect to the segment densities yields the set of Euler–Lagrange equations.

$$\frac{\delta A[\{\rho^{(\beta)}(1_r)\}]}{\delta \rho^{(\gamma)}(1_r)} = \mu^{(\gamma)} - V_{\text{ext}}^{(\gamma)} \quad \forall \gamma = 1, m \quad (4.2)$$

The solution of this set of equations results in the equilibrium density profile of all segments, from which all thermodynamic functions follow. The Helmholtz free energy is given as

$$A[\{\rho^{(\beta)}\}] = A^{\text{id}}[\{\rho^{(\beta)}\}] + A^{\text{molec}}[\{\rho^{(\beta)}\}] + A^{\text{LR,HS,ion}}[\{\rho^{(\beta)}\}] \quad (4.3)$$

where $A^{\text{id}}[\{\rho^{(\beta)}\}]$, $A^{\text{molec}}[\{\rho^{(\beta)}\}]$ and $A^{\text{LR,HS,ion}}[\{\rho^{(\beta)}\}]$ are the contributions from ideal gas and excess contributions due to molecular formation and excess contributions from long-range attractions, hard sphere repulsions and possibly ionic interactions. The ideal gas contribution for a fluid of independent segments is given by

$$\beta A^{\text{id}}[\{\rho^{(\beta)}\}] = \int d(1_r) \sum_{\beta=1}^m \rho^{(\beta)}(1_r) (\ln \rho^{(\beta)}(1_r) - 1) \quad (4.4)$$

The free energy functional for molecular formation produces the correction of the ideal term for linear branched or ring molecules. In the ideal contribution any temperature dependent terms are ignored, this has no affect on fluid structure. The functional derivative of the free energy is interpreted as the inhomogeneous chemical potential whose contributions from the ideal and molecular free energies are

$$\frac{\delta \beta A^{\text{id}}}{\delta \rho^{(\gamma)}(1_r)} = \ln \rho^{(\gamma)}(1_r) \quad (4.5)$$

$$\begin{aligned} \frac{\delta \beta A^{\text{molec}}}{\delta \rho^{(\gamma)}(1_r)} &= \ln \frac{\rho_o^{(\gamma)}(1_r)}{\rho^{(\gamma)}(1_r)} + 1 \\ &+ \sum_{\beta=1}^m \int \rho^{(\beta)}(1) \frac{\delta \left(\ln \frac{\rho_o^{(\beta)}(1)}{\rho^{(\beta)}(1)} \right)}{\delta \rho^{(\gamma)}(1_r)} d(1) - \frac{\delta \Delta \tilde{c}^{(o)}}{\delta \rho^{(\gamma)}(1_r)} \end{aligned} \quad (4.6)$$

Equation 4.6 can be used in conjunction with 3.20 and 3.21 to rewrite the inhomogeneous chemical potential due to molecular formation as

$$\frac{\delta \beta A^{\text{molec}}}{\delta \rho^{(\gamma)}(1_r)} = \ln \frac{\rho_o^{(\gamma)}(1_r)}{\rho^{(\gamma)}(1_r)} - \int \rho_o^{(1)}(1) \dots \rho_o^{(m)}(m) \tilde{F}(1 \dots m) \frac{\delta \tilde{D}(1 \dots m)}{\delta \rho^{(\gamma)}(\vec{r})} \times d(1) \dots d(m) \quad (4.7)$$

where $\rho^{(\gamma)}(\vec{r})$ is the density averaged over all orientations of the segment

$$\rho^{(\gamma)}(\vec{r}) = \int \rho^{(\gamma)}(1_r) d\Omega_r \quad (4.8)$$

With the calculation of the inhomogeneous chemical potentials we have all the information needed to determine the density profile. Equations 4.2, 4.3, 4.5, and 4.7 can be combined to yield

$$\rho_o^{(\gamma)}(1_r) = \exp[\lambda^{(\gamma)}(1_r) + \beta(\mu^{(\gamma)} - V^{(\gamma)}(1_r))] \quad (4.9)$$

where

$$\lambda^{(\gamma)}(1_r) = -\frac{\delta \beta A^{\text{LR, HS, ion}}}{\delta \rho^{(\gamma)}(1_r)} + \int \rho_o^{(1)}(1) \dots \rho_o^{(m)}(m) \times \tilde{F}(1 \dots m) \frac{\delta \tilde{D}(1 \dots m)}{\delta \rho^{(\gamma)}(\vec{r})} d(1) \dots d(m) \quad (4.10)$$

Eliminating the monomer densities in eq 3.19 with eq 4.9 we obtain the inhomogeneous segmental density profiles

$$\rho^{(\gamma)}(\gamma) = \exp[\lambda^{(\gamma)}(\gamma) + \beta(\mu_M - V_{\text{ext}}^{(\gamma)}(\gamma))] I^{(\gamma)}(\gamma) \quad (4.11)$$

where the molecular integral $I^{(\gamma)}(\gamma)$ is

$$I^{(\gamma)}(\gamma) = \int \tilde{F}(1 \dots m) \tilde{D}(1 \dots m) \prod_{\epsilon \neq \gamma}^m \exp[\lambda^{(\epsilon)}(\epsilon) - \beta V_{\text{ext}}^{(\epsilon)}(\epsilon)] d(\epsilon) \quad (4.12)$$

The molecular chemical potential μ_M is defined as the sum of the component chemical potentials $\mu_M = \sum_{\gamma=1}^m \mu^{(\gamma)}$. From eqs 4.11 and 4.12 it is clear that

$$\int d(\gamma) \rho^{(\gamma)}(\gamma) = \int d(\gamma-1) \rho^{(\gamma-1)}(\gamma-1) \quad (4.13)$$

which means global stoichiometry is enforced in the density functional theory. Equation 4.11 is written in a general form for any molecular structure. The specific structure of the molecule is governed by the molecular integral $I^{(j)}$.

As mentioned in III Wertheim's theory was originally conceived for molecules with a fixed bond angle. For clarity of presentation we have derived the general DFT for molecules with fixed bond angles, however the extension to flexible molecules in TP2T is straightforward. We will draw heavily from Wertheim, ref [7]. Wertheim discussed flexibility in the context of a polymerizing fluid with two attraction sites; we will simply generalize his results. We begin by defining a series of bond angle distribution functions $\xi_{\lambda}^{(\beta)}(\alpha_{\lambda}^{(\beta)})$, where $\alpha_{\lambda}^{(\beta)}$ is the λ th bond angle where component β is at the center of a three segment bond. That is component β is at

the apex of the corresponding second order graph. We have the normalization condition

$$\int_0^{\pi} \xi_{\lambda}^{(\beta)}(\alpha_{\lambda}^{(\beta)}) \sin \alpha_{\lambda}^{(\beta)} d\alpha_{\lambda}^{(\beta)} = 1 \quad (4.14)$$

Now we define the quantity

$$\Psi^{(\beta)}(\alpha_1^{(\beta)} \dots \alpha_{\gamma^{(\beta)}}^{(\beta)}) = \xi_1^{(\beta)}(\alpha_1^{(\beta)}) \dots \xi_{\gamma^{(\beta)}}^{(\beta)}(\alpha_{\gamma^{(\beta)}}^{(\beta)}) \quad (4.15)$$

as the product of all of the distribution functions where β is the apex segment. The quantity $\gamma^{(\beta)}$ is the number of triplet bonds for which species β is the apex segment and is given as $\gamma^{(\beta)} = n(\Gamma^{(\beta)})\{n(\Gamma^{(\beta)}) - 1\}/2$ and $n(\Gamma^{(\beta)})$ is the number of bonding sites on species β .

The segment β has each of these bond angles as an internal degree of freedom. The element $d(\beta)$ is now $d(\beta) = \sin \alpha_1^{(\beta)} \dots \sin \alpha_{\gamma^{(\beta)}}^{(\beta)} d\alpha_1^{(\beta)} \dots d\alpha_{\gamma^{(\beta)}}^{(\beta)} d\vec{r}_{\beta} d\Omega_{\beta}$. Clearly, we have the normalization condition

$$\int_0^{\pi} \dots \int_0^{\pi} \Psi^{(\beta)}(\alpha_1^{(\beta)} \dots \alpha_{\gamma^{(\beta)}}^{(\beta)}) \sin \alpha_1^{(\beta)} \dots \sin \alpha_{\gamma^{(\beta)}}^{(\beta)} d\alpha_1^{(\beta)} \dots d\alpha_{\gamma^{(\beta)}}^{(\beta)} = 1 \quad (4.16)$$

In the limit of complete association only two densities appear in the theory $\rho^{(\beta)}$ and $\rho_o^{(\beta)}$ which results in significant simplification. Defining the density integrated over all bond angles of segment β as

$$\rho^{(\beta)}(\vec{r}) = \int \rho^{(\beta)}(\beta) \sin \alpha_1^{(\beta)} \dots \sin \alpha_{\gamma^{(\beta)}}^{(\beta)} d\alpha_1^{(\beta)} \dots d\alpha_{\gamma^{(\beta)}}^{(\beta)} \quad (4.17)$$

Wertheim shows that the monomer density must show the undistorted distribution of bond angles of an isolated segment. Here we generalize his result to a segment with an arbitrary number of attraction sites as

$$\rho_o^{(\beta)}(\beta) = \rho_o^{(\beta)}(\vec{r}) \Psi^{(\beta)}(\alpha_1^{(\beta)} \dots \alpha_{\gamma^{(\beta)}}^{(\beta)}) \quad (4.18)$$

In the fixed bond angle perturbation theory, the reference system density is taken as $\rho_R^{(\beta)}(1) = \rho^{(\beta)}(1)$; however, in the flexible theory, $\rho_R^{(\beta)}(1)$ will have the bond angle dependence of $\Psi^{(\beta)}(\alpha_1^{(\beta)} \dots \alpha_{\gamma^{(\beta)}}^{(\beta)})$ but the density $\rho^{(\beta)}(1)$ has some other dependence. The reference system density is then chosen as $\rho_R^{(\beta)}(1) = \rho^{(\beta)}(1)$. All results of section I remain unchanged except for the following change in the free energy eq 3.21:

$$\ln \frac{\rho_o^{(\beta)}(1)}{\rho^{(\beta)}(1)} \rightarrow \ln \frac{\rho_o^{(\beta)}(1)}{\rho^{(\beta)}(1)} \quad (4.19)$$

The bond angle distribution functions will enter the density functional theory via the monomer densities. For the flexible case the density in the ideal free energy must be the same as the reference system so

$$\beta A^{\text{id, flex}}[\{\rho^{(\gamma)}\}] = \int d(\gamma) \sum_{\gamma=1}^m \rho^{(\gamma)}(\gamma) (\ln \rho^{(\gamma)}(\vec{r}) - 1) \quad (4.20)$$

Now, with eqs 4.19 and 4.20 the grand potential is minimized with respect to $\rho^{(\beta)}(\vec{r})$ and the monomer density is found to be

$$\rho_o^{(\beta)}(\beta) = \Psi^{(\beta)}(\alpha_1^{(\beta)} \dots \alpha_{\gamma^{(\beta)}}^{(\beta)}) \exp[\lambda^{(\beta)}(\vec{r}_{\beta}, \Omega_{\beta}) + \beta(\mu^{(\beta)} - V_{\text{ext}}^{(\beta)}(\vec{r}_{\beta}, \Omega_{\beta}))] \quad (4.21)$$

Now eliminating the monomer densities in eq 3.19 and realizing from eq 4.20 that the thermodynamics depends on $\rho^{(\beta)}(\bar{1})$, eq 4.17 is applied and we obtain

$$\rho^{(\beta)}(\bar{\beta}) = \exp[\lambda^{(\beta)}(\bar{r}_{\beta}, \Omega_{\beta}) + \beta(\mu_M - V_{\text{ext}}^{(\beta)}(\bar{r}_{\beta}, \Omega_{\beta}))] I^{(\beta)}(\bar{r}_{\beta}, \Omega_{\beta}) \quad (4.22)$$

where the molecular integral is now given as

$$I^{(\beta)}(\bar{r}_{\beta}, \Omega_{\beta}) = \int \tilde{F}(1\dots m) \tilde{D}(1\dots m) \Psi^{\text{total}}(\{\alpha_{\gamma}^{(\delta)}\}) \times \prod_{\epsilon \neq \beta}^m \exp[\lambda^{(\epsilon)}(\bar{r}_{\epsilon}, \Omega_{\epsilon}) - \beta V_{\text{ext}}^{(\epsilon)}(\bar{r}_{\epsilon}, \Omega_{\epsilon})] d(\epsilon) \times \sin \alpha_1^{(\beta)} \dots \sin \alpha_{\gamma^{(\beta)}}^{(\beta)} d\alpha_1^{(\beta)} \dots d\alpha_{\gamma^{(\beta)}}^{(\beta)} \quad (4.23)$$

Here $\Psi^{\text{total}}(\{\alpha_{\gamma}^{(\delta)}\})$ is the product of all bond angle distribution functions and remembering $d(\epsilon) = \sin \alpha_1^{(\epsilon)} \dots \sin \alpha_{\gamma^{(\epsilon)}}^{(\epsilon)} d\alpha_1^{(\epsilon)} \dots d\alpha_{\gamma^{(\epsilon)}}^{(\epsilon)} d\bar{r}_{\epsilon} d\Omega_{\epsilon}$. Equations 4.22 and 4.23 represent a general density functional theory for chain molecules with distributions of bond angles. The first order limit of eq 4.23 is defined as the case of a fully flexible molecule where $\xi_{\lambda}^{(\beta)}(\alpha_{\lambda}^{(\beta)}) = 1/2$ for all λ, β .

V. HOMOGENEOUS LIMIT

In addition to interfacial systems, the current methodology allows for the modeling of a wide range of homogeneous systems. Also, the bulk chemical potential is a required input to the density functional theory. For these reasons we find it appropriate to develop a complete homogeneous theory from the analysis presented in III. Here only a pure fluid of homonuclear molecules will be considered. Starting with a stoichiometric proportion of segments in the bulk so the number density of each segment type is equal to that of each other type of segments and equal to that of the molecule which is designated as ρ . The total segment density is $\rho_m = m\rho$. From 3.21 we have

$$\frac{\beta(A - A_R)}{V} = \sum_{\beta=1}^m \rho^{(\beta)} \left(\ln \frac{\rho_o^{(\beta)}}{\rho^{(\beta)}} + 1 \right) - \rho^{(j)} \quad (5.1)$$

To take the limit of complete association the pressure is calculated with

$$\beta(P - P_R) = \rho_m \frac{\partial}{\partial \rho_m} \left(\frac{\beta(A - A_R)}{V} \right)_T - \frac{\beta(A - A_R)}{V} \quad (5.2)$$

which gives

$$\frac{\beta(P - P_R)}{\rho} = m\rho \frac{\partial}{\partial \rho} \ln \frac{\rho_o}{\rho} \quad (5.3)$$

where all monomer densities are treated the same. Using the mass action eq 3.19

$$\rho = \rho_o^m \tilde{F} \tilde{D}[\eta, \{\alpha\}] \quad (5.4)$$

where $\{\alpha\}$ is the set of all bond angles in the molecule. For flexible molecules the integration over correlation and distribution functions is absorbed in $\tilde{D}[\eta, \{\alpha\}]$. Combining eqs 5.3 and 5.4 the change in pressure due to molecular formation is obtained

$$\frac{\beta(P - P_R)}{\rho} = 1 - m - \rho \frac{\partial}{\partial \rho} \ln \tilde{D}[\eta, \{\alpha\}] \quad (5.5)$$

Going back to free energy we obtain the excess free energy of molecular formation

$$\frac{\beta(A^{\text{ex}} - A_R^{\text{ex}})}{N} = -\ln \tilde{D}[\eta, \{\alpha\}] \quad (5.6)$$

where N is the number of molecules, and we obtain the excess chemical potential of molecular formation

$$\beta(\mu^{\text{ex}} - m\mu_R^{\text{ex}}) = -\ln \tilde{D}[\eta, \{\alpha\}] - \rho \frac{\partial}{\partial \rho} \ln \tilde{D}[\eta, \{\alpha\}] \quad (5.7)$$

The homogeneous theory presented in eqs 5.5–5.7 is a general result valid for any molecular structure. Now we will specifically consider linear and branched chains in TPT2. It was found in III that $D_2(1\dots m)$ is obtained by taking all the ways to factor the molecule into dimer and trimer portions. Using this result we can write, for an arbitrarily complex branched molecule in TPT2

$$D_2[\eta, \{\alpha\}] = y(\eta)^{m-1} \sum_{n=0}^{N_b} C_n \lambda^n \quad (5.8)$$

Here C_n is the number ways that n pairs of adjacent first order subgraphs in the spanning tree can be replaced by n second order subgraphs. Equation 5.8 is the rigorous homogeneous solution of TPT2 for all branched molecules in TPT2. For rigid molecules λ is given by

$$\lambda = \frac{y^{(3)}(\eta, \alpha)}{y(\eta)^2} - 1 \quad (5.9)$$

and for flexible molecules

$$\lambda = \int_0^\pi \xi(\alpha) \left(\frac{y^{(3)}(\eta, \alpha)}{y(\eta)^2} - 1 \right) \sin \alpha \, d\alpha \quad (5.10)$$

where $\eta = (m\pi\sigma^3/6)\rho$, $y(\eta) = g(\eta)$ is the homogeneous pair bonding correlation function at contact and $y^{(3)}(\eta, \alpha) = g^{(3)}(\eta, \alpha)$ is the triplet bonding correlation function at contact. Combining eqs 5.5 and 5.7, we obtain the equation of state for an arbitrary branched molecule in TPT2.

$$\frac{\beta(P - P_R)}{\rho} = -(m-1) \left(1 + \eta \frac{\partial}{\partial \eta} \ln y(\eta) \right) - \eta \frac{\partial}{\partial \eta} \ln \left(\sum_{n=0}^{N_b} C_n \lambda^n \right) \quad (5.11)$$

The first term on the right-hand side of eq 5.11 is the first order contribution to the compressibility factor and the second term is the second order correction.

The evaluation of C_n in a general way will be considered in a future work. However it is instructive to consider molecules in which only specific points of the molecule are treated in second order perturbation theory. For instance, consider a trifunctional dendrimer in which only the branch points are treated in second order and the rest of the molecule is treated in first order. Calling N_b the number of branch points C_n is now the number of ways of picking n unordered outcomes from N_b possibilities

$$C_n = \frac{N_b!}{n!(N_b - n)!} \quad (5.12)$$

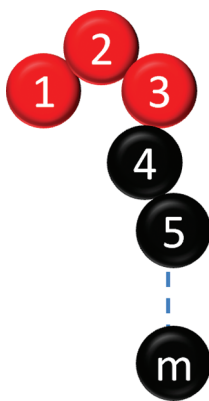


Figure 1. Diagram of partially rigid molecule where segments 1–3 are rigid at a fixed bond angle α and segments 4– m are fully flexible.

With eq 5.12 the sum in eq 5.8 can be easily evaluated yielding the equation of state

$$\frac{\beta(P - P_R)}{\rho} = -(m-1) \left(1 + \eta \frac{\partial}{\partial \eta} \ln y(\eta) \right) - N_b \eta \frac{\partial}{\partial \eta} \ln(1 + \lambda) \quad (5.13)$$

From eq 5.13 it is clear that if molecules with N_b independent branch points are considered, exactly one second order correction per branch point is obtained. This was a simple example, but it illustrates the power of this approach; for an arbitrary branched molecule Wertheim's second order perturbation theory has now been reduced to a counting problem.

VI. PARTIALLY RIGID MOLECULE FROM FRACTIONAL PERTURBATION THEORY

Now as a test of the theory the case of a molecule, see Figure 1, consisting of m spherical segments which has a rigid headgroup consisting of three segments at a fixed bond angle α and a fully flexible tail consisting of $(m-3)$ fully flexible segments will be considered. We begin by considering a linear chain treated in second order perturbation theory. The graph sum $\Delta c^{(o)}$ is given by eq 3.9. The first order limit is defined by taking a linear superposition on the triplet bonding correlation function

$$y^{(\beta, \gamma, \lambda)}(123) \xrightarrow{\text{first order}} y^{(\beta, \gamma)}(12) y^{(\gamma, \lambda)}(23) \quad (6.1)$$

Now the first order limit is taken on all $y^{(\beta, \gamma, \lambda)}(123)$ except for $\{\beta, \gamma, \lambda\} = \{1, 2, 3\}$. So $Y^{(\beta, \gamma, \lambda)}(123) = 0$ for all $\{\beta, \gamma, \lambda\} \neq \{1, 2, 3\}$. We are now left with only one second order graph, a fraction of the original perturbation, and we obtain the graph sum

$$\begin{aligned} \Delta c^{(o)} = & \sum_{\beta=1}^{m-1} \int \sigma_B^{(\beta)}(1) y^{(\beta, \beta+1)}(12) F^{(\beta, \beta+1)}(12) \sigma_A^{(\beta+1)}(2) d(1) d(2) \\ & + \int \rho_0^{(1)}(1) F^{(1,2)}(12) \rho_0^{(2)}(2) F^{(2,3)}(23) \sigma_A^{(3)}(3) Y^{(1,2,3)}(123) d(1) d(2) d(3) \end{aligned} \quad (6.2)$$

Using the method outlined in III we obtain $D(1...m)$ as

$$\tilde{D}(1...m) = y^{(1,2,3)}(123) y^{(3,4)}(34) \dots y^{(m-1,m)}(m-1,m) \quad (6.3)$$

At this point we will assume no orientational inhomogeneities and no orientational dependence in the bonding correlation functions. For the fully flexible bonds the Mayer

functions in the complete association limit are orientationally averaged as

$$\begin{aligned} F^{(\alpha, \gamma)}(\vec{r}_1, \vec{r}_2) &= \lim_{\epsilon_{AB} \rightarrow -\infty} \langle e_R^{(\alpha, \gamma)}(12) f_{AB}^{(\alpha, \gamma)}(12) \rangle \\ &= \lambda \frac{\delta(|\vec{r}_2 - \vec{r}_1| - \sigma^{(\alpha, \gamma)})}{4\pi(\sigma^{(\alpha, \gamma)})^2} \Big|_{\lambda \rightarrow \infty} \end{aligned} \quad (6.4)$$

where λ is the association strength which can be neglected due to cancellation with similar terms in the bulk chemical potential. For the rigid head of the molecule

$$\begin{aligned} F^{(1,2)}(\vec{r}_1, \vec{r}_2) F^{(2,3)}(\vec{r}_1, \vec{r}_2) \\ = \lambda^2 \frac{\delta(|\vec{r}_2 - \vec{r}_1| - \sigma^{(1,2)})}{4\pi(\sigma^{(1,2)})^2} \frac{\delta(|\vec{r}_3 - \vec{r}_2| - \sigma^{(2,3)})}{4\pi(\sigma^{(2,3)})^2} \frac{\delta(\alpha' - \alpha)}{\sin \alpha/2} \end{aligned} \quad (6.5)$$

A delta function in bond angle was added to explicitly show rigidity of the bond. The molecular integral is given by eq 4.12, for segments 3 to m we split the molecular integrals into two parts which can be evaluated with recursion relations

$$I^{(\gamma)}(\vec{r}_\gamma) = I_1^{(\gamma)}(\vec{r}_\gamma) I_2^{(\gamma)}(\vec{r}_\gamma) \quad \gamma \geq 3 \quad (6.6)$$

The $I_1^{(\gamma)}(\vec{r}_\gamma)$'s are evaluated as

$$\begin{aligned} I_1^{(3)}(\vec{r}_3) &= \int \tilde{\rho}_0^{(1)}(\vec{r}_1) \tilde{\rho}_0^{(2)}(\vec{r}_2) F^{(1,2)}(\vec{r}_1, \vec{r}_2) \\ &\times F^{(2,3)}(\vec{r}_2, \vec{r}_3) y^{(1,2,3)}(\vec{r}_1, \vec{r}_2, \vec{r}_3) \\ &\times d\vec{r}_1 d\vec{r}_2 \end{aligned} \quad (6.7)$$

where $\tilde{\rho}_0^{(j)}(\vec{r}_j) = \rho_0^{(j)}(\vec{r}_j) \exp(-\beta\mu^{(j)})$, and for $\gamma > 3$

$$\begin{aligned} I_1^{(\gamma)}(\vec{r}_\gamma) &= \int \tilde{\rho}_0^{(\gamma-1)}(\vec{r}_{\gamma-1}) F^{(\gamma-1, \gamma)}(\vec{r}_{\gamma-1}, \vec{r}_\gamma) \\ &\times y^{(\gamma-1, \gamma)}(\vec{r}_{\gamma-1}, \vec{r}_\gamma) I_1^{(\gamma-1)}(\vec{r}_{\gamma-1}) d\vec{r}_{\gamma-1} \end{aligned} \quad (6.8)$$

The $I_2^{(\gamma)}(\vec{r}_\gamma)$'s are evaluated as

$$I_2^{(m)}(\vec{r}_m) = 1 \quad (6.9)$$

and for $3 \leq \gamma < m$

$$\begin{aligned} I_2^{(\gamma)}(\vec{r}_\gamma) &= \int \tilde{\rho}_0^{(\gamma+1)}(\vec{r}_{\gamma+1}) F^{(\gamma, \gamma+1)}(\vec{r}_\gamma, \vec{r}_{\gamma+1}) \\ &\times y^{(\gamma, \gamma+1)}(\vec{r}_\gamma, \vec{r}_{\gamma+1}) I_2^{(\gamma+1)}(\vec{r}_{\gamma+1}) d\vec{r}_{\gamma+1} \end{aligned} \quad (6.10)$$

For segments 1 and 2

$$I^{(1)}(\vec{r}_1) = \int \tilde{\rho}_0^{(2)}(\vec{r}_2) \tilde{\rho}_0^{(3)}(\vec{r}_3) F^{(1,2)}(\vec{r}_1, \vec{r}_2) \times F^{(2,3)}(\vec{r}_2, \vec{r}_3) y^{(1,2,3)}(\vec{r}_1, \vec{r}_2, \vec{r}_3) \times I_2^{(3)}(\vec{r}_3) d\vec{r}_2 d\vec{r}_3 \quad (6.11)$$

$$I^{(2)}(\vec{r}_2) = \int \tilde{\rho}_0^{(1)}(\vec{r}_1) \tilde{\rho}_0^{(3)}(\vec{r}_3) F^{(1,2)}(\vec{r}_1, \vec{r}_2) \times F^{(2,3)}(\vec{r}_2, \vec{r}_3) y^{(1,2,3)}(\vec{r}_1, \vec{r}_2, \vec{r}_3) \times I_2^{(3)}(\vec{r}_3) d\vec{r}_1 d\vec{r}_3 \quad (6.12)$$

Equations 6.6 through 6.12 give an integration routine to evaluate the molecular integral for the partially rigid molecule.

To obtain numerical results we must approximate the inhomogeneous bonding correlation functions. We begin by approximating the pair bonding correlation function at contact as the average of the potential of mean force^{13,14}

$$y^{(\alpha,\beta)}(\vec{r}_1, \vec{r}_2) = \frac{1}{2} \ln \{ y^{(\alpha,\beta)}(\vec{r}_1) y^{(\alpha,\beta)}(\vec{r}_2) \} \quad (6.13)$$

Evaluating the inhomogeneous cavity correlation functions using weighted densities such as fundamental measure theory has proven to be remarkably successful and has become a standard in the DFT community.^{1,2,8,14,16,20} We will follow the approach used in the iSAFT¹⁴ density functional theory and use the simple weighting

$$\bar{\rho}^{(\gamma)}(\vec{r}_1) = \frac{3}{4\pi\sigma^3} \int_{|\vec{r}_1 - \vec{r}_2| < \sigma} d\vec{r}_2 \rho^{(\gamma)}(\vec{r}_2) \quad (6.14)$$

For homogeneous systems the triplet correlation function for three spheres rigidly bonded at a fixed bond angle Muller and Gubbins³⁴ factored the triplet correlation function as

$$y^{(3)}(\eta, \alpha) = y(\eta) y(\eta) y_o(\eta, \alpha) \quad (6.15)$$

where $y_o(\eta, \alpha)$ was fit to tabular data from Attard's PY3 theory^{35,36} and is given as

$$y_o(\eta, \alpha) = \frac{1 + a\eta + b\eta^2}{(1 - \eta)^3} \quad (6.16)$$

where a and b are constants which depend on bond angle and are presented in tabular form in ref 34. For instance, at a packing fraction of $\eta = 0.3$ $y_o(\eta, \alpha)$ is given as 1.792, 0.995, and 0.977 for $\alpha = 60^\circ$, 120° , and 150° , respectively. The greatest deviation from first order ($y_o = 1$ is the first order result) is seen for a bond angle of 60° . Muller and Gubbins³⁴ compared $y_o(\eta, \alpha)$ from Attard's PY3 theory to simulation results and found that both were in excellent agreement.

In order to estimate the inhomogeneous triplet correlation function Malijevsky et al.²⁸ used eq 6.16 combined with the second order contribution to the homogeneous fluid free energy due to Wertheim⁷ evaluated at a weighted density to obtain a second order correction for a three-arm star polymer. Similarly, Xu and Cao²⁹ used eq 6.16 modified with the weighted densities of fundamental measure theory in the study of polymer polydispersity. Here we will follow the lead of Muller and Gubbins³⁴ and write the inhomogeneous triplet bonding correlation

function as the superposition, assuming a homonuclear rigid three segment head of the molecule

$$y^{(1,2,3)}(\vec{r}_1, \vec{r}_2, \vec{r}_3) = y(\vec{r}_1, \vec{r}_2) y(\vec{r}_2, \vec{r}_3) y_o(\vec{r}_1, \vec{r}_3, \alpha) \quad (6.17)$$

where we approximate $y_o(\vec{r}_1, \vec{r}_3, \alpha)$ using the approximation of eq 6.13 and the weighted densities of eq 6.14. Using eqs 6.13 and 6.17 we can evaluate eq 4.10 as

$$\lambda^{(\gamma)}(\vec{r}_\gamma) = \frac{1}{2} \sum_{\lambda=1}^m \sum_{\lambda'}^{\{\lambda'\}} \int d\vec{r}_1 \rho^{(\lambda)}(\vec{r}_1) \frac{\partial \ln y^{(\lambda,\lambda')}(\vec{r}_1)}{\partial \rho^{(\gamma)}(\vec{r}_\gamma)} - \frac{\delta \beta A^{\text{LR, HS}}}{\delta \rho^{(\gamma)}(\vec{r}_\gamma)} + \frac{1}{2} \int (\rho^{(1)}(\vec{r}_1) + \rho^{(3)}(\vec{r}_1)) \frac{\partial \ln y_o(\vec{r}_1, \alpha)}{\partial \rho^{(\gamma)}(\vec{r}_\gamma)} d\vec{r}_1 \quad (6.18)$$

where $\{\lambda'\}$ is the set of all segments bonded to segment λ .

VII. RESULTS

The DFT derived in VI is now applied to a partially rigid molecule in a slit pore of width $H = 10\sigma$. We use a value for all segments $\sigma = 1$. The external potential is given by

$$V_{\text{ext}}(z) = \begin{cases} \infty & \text{for } z < 0 \text{ or } z > H \\ 0 & \text{otherwise} \end{cases} \quad (7.1)$$

No long-range attractions are included and we use Rosenfeld's fundamental measure theory¹⁸ to model the hard sphere term. We introduce the notation R_3F_n where the subscript 3 refers to there being three rigid head segments and the subscript n represents the number of first order, fully flexible, tail segments. Density profiles were computed for the cases R_3F_0 and R_3F_3 at bond angles of 60° , 120° , and 150° for reduced densities $\eta = 0.1$ and 0.3 .

As a test, density functional theory calculations for the case R_3F_0 are compared to the simulation results from Phan et al.³⁷ Figures 2 and 3 presents profiles for the scaled density $\rho_j^* = \rho_j(z^*)/\rho_{\text{ave}}$ where ρ_{ave} is the average segment density in the pore and $z^* = z/\sigma$. Since the molecule is a rigid trimer the end segments are indistinguishable. We see that for $\eta = 0.1$ there is a depletion effect near wall contact while for $\eta = 0.3$ the trimers accumulate near the wall in an enhancement effect. For angles $\alpha \neq 60^\circ$ the end segments have a higher preference for the wall than the middle segment; this is to be expected due to the fact that there are more molecular orientations where the end segment will be next to the wall than there is for the middle segment.

For a bond angle of 60° , each segment in the trimer should become indistinguishable; however, the density profiles at this bond angle in Figure 2 show very slight differences between the end and middle segment. This can be explained by the definition of the triplet correlation function eq 6.17. Segments 1 and 2 and segments 2 and 3 are bonded by correlation functions $y(\eta)$, whereas segments 1 and 3 are bonded by a correlation function defined by eq 6.16. For each segment to be indistinguishable the correlation between each of the segments must be identical. In order to obtain a completely symmetric trimer ring at 60° we repeated the calculations using the Kirkwood superposition approximation

$$y^{(3)}(\eta, \alpha) = y(\eta) y(\eta) y(\eta) \quad (7.2)$$

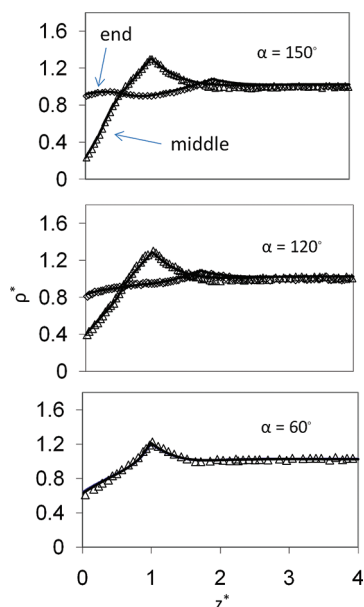


Figure 2. Comparison of density functional theory calculations to simulation results of ref 37 for R_3F_0 molecules at $\eta = 0.1$ in a slit pore of width $H = 10\sigma$. Densities are scaled by the average density in the pore ρ_{ave} .

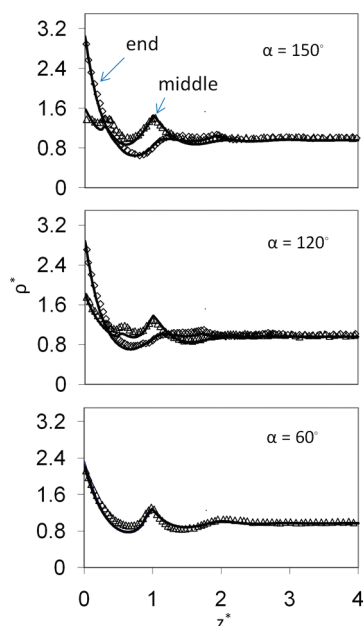


Figure 3. Comparison of density functional theory calculations to simulation results of ref 37 for R_3F_0 molecules at $\eta = 0.3$ in a slit pore of width $H = 10\sigma$.

Figure 4 presents results for a bond angle of 60° using the Kirkwood superposition approximation. As can be seen the end and middle segment density profiles are identical. For the molecule R_3F_3 Kirkwood superposition will be used for $\alpha = 60^\circ$.

As fully flexible segments are added, the symmetry between segment 1 and 3 seen in the rigid trimer is broken. Figures 5 and 6 present density profiles for the molecule R_3F_3 . For segments 1 and 2 the density profiles are only slightly affected by the addition of the extra segments for bond angles of 120° and 150° however

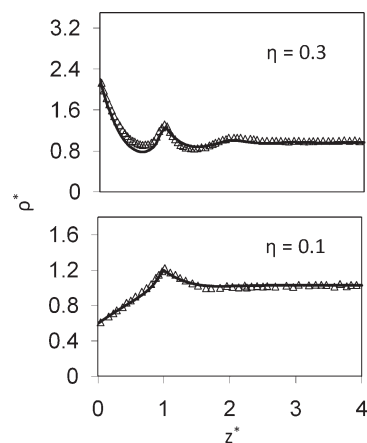


Figure 4. Density profiles for R_3F_0 and $\alpha = 60^\circ$ using Kirkwood superposition approximation.

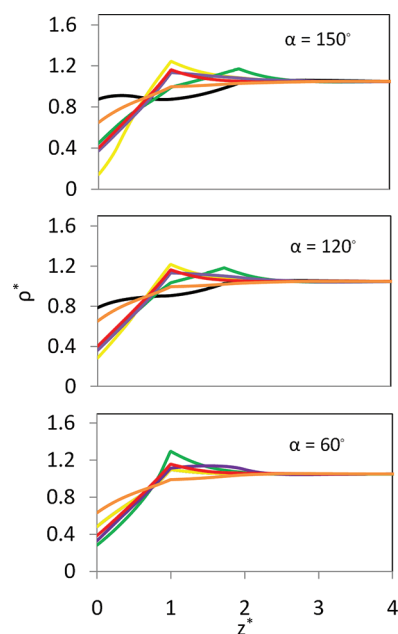


Figure 5. Density profiles for molecule R_3F_3 at a reduced density $\eta = 0.1$. Color code: black = segment 1, yellow = 2, green = 3, purple = 4, red = 5, orange = 6.

there are less orientations where segment 3 can access the wall so we see a decrease in the contact density of this segment. At a bond angle of 60° segments 1 and 2 become indistinguishable and segment 3 shows sharp peaks at $z = \sigma$. For the molecule R_3F_3 at a density $\eta = 0.1$ this sharp peak in the density profile of segment 3 is accompanied by a flat profile for segment 4 for $\sigma < z < 2\sigma$. This effect can be attributed to the fact that segment 3 is somewhat pinned at $z = \sigma$ allowing the fully flexible segment 4 to freely rotate and sweep out a flat profile. This effect is not seen for $\eta = 0.3$ due to packing effects seen at higher density. The enhancement/depletion behavior observed in the case of a rigid trimer is reproduced as additional flexible segments are added, as are the characteristic peaks in the density profiles observed at $z = \sigma$.

In previous TPT1 DFT studies^{24,37} of rigid triatomics against a hard wall inaccurate density wall contact values were obtained at a bond angle of 60° . This inaccuracy is a result of the wall contact

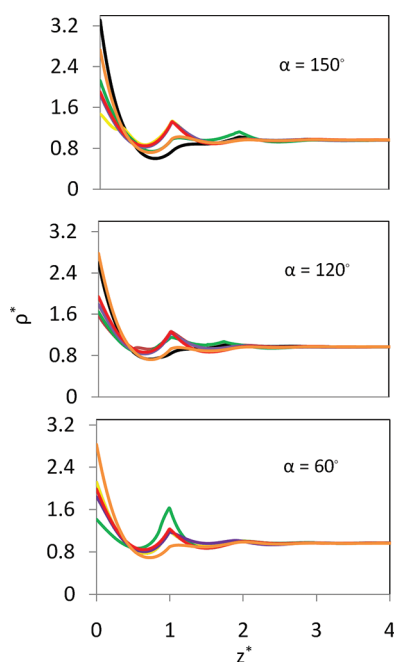


Figure 6. Density profiles for molecule R_3F_3 at a reduced density $\eta = 0.3$. Color code same as Figure 5.

theorem $\beta P = \sum \rho^{(i)}(z=0)$ which states that the total segment density at contact must be equal to the bulk pressure. The previous studies used density functional theories that reduce to a first order equation of state in the bulk, which is least accurate for rigid triatomics at a bond angle of 60° .³⁴ In our approach the second order treatment yields accurate results for density contact values for rigid triatomics even at a bond angle of 60° .

VIII. CONCLUSIONS

We have shown that in the strong association limit Wertheim's theory takes on a general form. Exploiting this generality we have developed a formalism that allows for the derivation of both the bulk and inhomogeneous thermodynamic properties of a polyatomic system in a simple and fast way. The formalism presented in this paper can be easily applied to polyatomic molecules of arbitrary complexity, where the method of Kierlik and Rosinberg^{10–12} would prove prohibitively complex. We also extended Wertheim's theory to allow distributions of bond angles for spheres with an arbitrary number of attraction sites; this extension allows for the development of second order theories for semi-flexible branched polymers. To test the theory we performed calculations for the case of a partially rigid molecule in a slit pore. The results were found to be in excellent agreement with simulation. The applications of this theory are wide ranging; currently, the authors are preparing a manuscript which studies the effect of surfactant bond angle and branching on the oil–water interface using the TPT2 form of the theory. Also, following Segura et al.⁸ and Bymaster and Chapman,¹⁷ association can be included in the theory to study the effect of bond rigidity/flexibility on supramolecular assembly.

AUTHOR INFORMATION

Corresponding Author

*Tel: (1) 713.348.4900. Fax: (1) 713.348.5478. E-mail: wgchap@rice.edu.

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