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Thermodynamic Modeling of Branched Molecular Systems

by

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ABSTRACT

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Presence of branches in the molecular structure results in properties different from that of linear molecules and also leads to special industrial value and diverse novel applications. However, a basic knowledge of thermodynamics of branched molecules is lacking. Experimental data for branched molecules are far less abundant compared with linear molecules and are usually questionable under harsh conditions such as high temperature and high pressure. Therefore, the goal of this thesis is to enhance our understanding of the phase behavior and microstructure of branched molecules using statistical mechanics based theories.

A new equation of state based on statistical associating fluid theory (SAFT) is developed and applied to isomeric alkanes. The branching effect is explicitly accounted and the results are in good agreement with experimental data. The density functional theory (DFT) version of SAFT, modified iSAFT, is applied to study conformations of branched polymers of special architecture, such as dendrimer and bottlebrush polymers. Related parameters such as molecule size, solvent quality and temperature that affect the phase behavior of these polymers have been investigated. The theoretical results are qualitatively consistent with experimental observations and are also validated by molecular simulation. In addition, several functional polymers are studied, where we see potential lower critical solution temperature (LCST) behavior
of an associating dendrimer and partially hidden conformations of an amphiphilic bottlebrush polymer.

The theories and models developed for branched molecules in this thesis are proved to not only be able to explain and support existent experimental results, but also have strong prediction ability where there is no data at all. These models will provide physical insight and helpful guidance for the design and application of branched molecules.
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Chapter 1

Introduction

1.1 Motivation

Molecular architecture affects properties of molecules, and further leads to different applications. A typical example is polyethylene, a popular polymer consisting of ethylene monomers. Commercially, it has three main grades: HDPE, LLDPE and LDPE. HDPE is the high density polyethylene featuring a low degree of short-chain branching. LLDPE is the linear low density polyethylene which has a high degree of short-chain branching. LDPE is the low density polyethylene which has a high degree of both short-chain and long-chain branching. As a result of the different branching structures, they differ in density, permeability, tensile strength and many other properties. Therefore, LDPE is widely used for manufacturing various containers due to its low density. HDPE is used to create sturdy products like PE pipe for its rigidity and impermeability. LLDPE is the best option for plastic bags and sheets based on its high tensile strength and high impact and puncture resistance.

Another example is n-butane and i-butane. Both molecules have four carbon atoms and ten hydrogen atoms, but n-butane is linear and i-butane is branched. As a result, the two molecules have different properties (such as lower melting and boiling points for i-butane). n-butane is typically used as a fuel for cigarette lighters and torches, whereas i-butane is often employed as a refrigerant or as a propellant in spray cans.
The examples above show that difference in molecular architecture, especially in branching pattern, can result in different micro-structures, phase behaviors and thermodynamic properties. Whether it is short chains or long polymers, any property change due to branching matters for industrial processing and practical applications.

1.1.1 Small branched molecules

For small molecules of linear structures, an accurate molecular description of the thermodynamic behavior and phase equilibrium is quite common. However, experimental data and valid models become much fewer for branched structures. Crude oil is composed of literally thousands of compounds of which the paraffin hydrocarbons are the most abundant. The majority of these are isomers, compounds of the same molecular weight but with different molecular structures, such as branching. Energetically, the intermolecular interactions between atoms or groups can be shielded due to the addition of branches. From the entropic respect, different favored conformations might be assumed for different branched structures.[7] All these factors lead to a difference in phase change, fluid structure as well as other thermodynamic properties in a complex way.[4, 3, 5, 8]. Exact knowledge of those property differences, and in addition, knowledge of phase equilibrium is important for the petrochemical industry. Such information is necessary for design of polymerization, supercritical fluid extraction and enhanced oil recovery processes.

The lack of knowledge becomes even more severe for molecules of relatively higher molecular weight. For example, squalane ($C_{30}H_{62}$), a branched isomer of n-triacontane, is widely used in cosmetics. However, experimental measurement of the critical properties of hydrocarbons such as squalane remains an immense challenge[9, 10, 11, 12, 13] since the critical temperatures of hydrocarbons with more than ten carbon atoms are
above 600 K, i.e. in a region where the hydrocarbons become thermally unstable. Even for conditions not that harsh, experiments can be expensive and time consuming. It is impossible to consider the full range of state points and branched structures only from experiments. Practicing engineers many times must estimate fluid properties for components lacking experimental data. This is sometimes done by comparing with reference components that differ in molecular architecture. Therefore, a theoretical model that accurately predicts the effect of branching on thermodynamic properties is needed.

1.1.2 Branched polymers

A polymer is a large molecule composed of many repeated subunits. The repeated subunit is usually named a monomer. The applications of polymers cover almost every area and more novel applications shift towards energy, biotechnology and medical science. The versatility of polymers is largely due to their superior and controllable properties, which depend on both internal and external factors. Internal factors include types of monomers, structure of the polymer, average molecular weight, molecular weight distribution and so on. External factors are mostly environmentally variables, such as temperature, pressure and types of solvents in the case of polymer solutions.

The polymers with branches are called branched polymers. Among all the branched polymers, some have specific branching structures and they are of great industrial value, such as dendrimers and bottlebrush polymers.

Dendrimers are highly uniform, three-dimensional, monodisperse polymers with a tree-like, globular structure. As a result, dendrimers usually have lower viscosity and higher solubility or compatibility than linear polymers. Also, they are amorphous in
the solid state and have no entanglements in their melt form. Bottlebrush polymers contain polymeric side chains attached to a linear polymer backbone, and due to the tunable backbone length, side chain length, side chain composition and grafting density, they have properties like an extended backbone and a very high entanglement molecular weight.

These special structures and unique properties trigger a number of recent studies into the potential applications. Dendrimers are found to be useful in dendritic assemblies, layers, films as well as liquid crystals, in medicine, pharmacy and biology, catalyst, chirality and analytical chemistry.[14] Applications of bottlebrush polymers include drug delivery, photonics, lubricants, rheology modifiers and surface coatings.[15]

Compared with the large body of interdisciplinary research on the applications of dendrimers and bottlebrush polymers, the understanding of the phase behavior of these systems is still in its infancy although the fundamentals are vital for the quality of production and optimization of processing. A thermodynamic model, which is capable of describing both enthalpic and entropic effects, which can explicitly consider the role of molecular structure, solvent, temperature and many other factors, needs to be developed.

1.2 Challenge

It is mentioned in the last section that there are limitations and constraints for the study of branched molecular systems experimentally. Therefore, this section is focused on several simulation and theoretical approaches that people use to study the branched molecules, and their strength and weakness will be discussed.
1.2.1 Molecular simulation

Molecular simulation[16, 17] is a powerful tool to understand experimental results and prove the validity of theory. Depending on which systems are studied, different schemes have been developed for both efficiency and accuracy. As discussed in the review by Juan J. Friere[18], molecular simulations of branched molecules can be roughly divided into three categories: Monte Carlo[19, 20, 21], Molecular Dynamics[22, 23] and Brownian Dynamics[24, 25].

Monte Carlo (MC) methods generate randomly chosen independent configurations and then obtain the required averages of properties by taking into account the equilibrium statistical weights. The advantage of MC is that it can be easily treated in different thermodynamic ensembles. The evolution of the system is based on energy and thus time-independent, which is more computationally friendly. In the molecular dynamics (MD) scheme, the system studied evolves in time based on numerical approximation to classical mechanical equations of motion. To arrive at other ensembles, specific techniques like thermostats need to be used. The principal advantage of MD methods is that both thermodynamic and kinetic properties can be generated. Brownian Dynamics is a useful variety of MD simulations which considers the solvent as a continuous incompressible fluid that exerts stochastic (Brownian) interactions on the frictional units. The technique takes advantage of the fact that there is a large separation in time scales between the rapid motion of solvent molecules and the more sluggish motion of large molecules or polymers. The ability to coarse-grain out these fast modes of the solvent allows one to simulate much larger time scales than in a molecular dynamics simulation.

It should be noted that for a large and complex system, such as a mixture of dendrimers, drug molecules and solvents, molecular simulations are still quite formidable
due to the computational expense. But they can serve as great validation tools for preliminary models.

1.2.2 Theoretical methods

One popular theory to describe, how molecular structure affects fluid properties, is lattice cluster theory (LCT), originally developed by Freed et al.[26, 27] and extended to compressible systems by Dudowicz et al.[28, 29]. LCT uses a double series expansion in the inverse coordination number and the reduced interaction energy to arrive at the free energy of a structured lattice fluid characterized by several combinatorial numbers giving the number of distinct ways to find a given substructure in the molecular architecture of the fluid under consideration. It has been tested against lattice Monte Carlo simulation[30] and extended to include semiflexibility and association interactions in the same lattice formalism[31]. Especially the group of Enders has applied it successfully for polymeric and non-polymeric systems.[32, 33, 34, 35, 36, 37, 38, 39] However, as a lattice theory, LCT sometimes performs weakly for the gas phase. Also the selection of the lattice coordination number can be quite empirical for off-lattice applications.

Another successful category of models is self consistent field theory (SCFT)[40], which is a very powerful theory in polymer field. SCFT models each polymer chain as an ideal chain (or Gaussian chain) in an external field. The mean field is generated by the interactions between the polymer segments. The central approximation in SCFT is that the external field is proportional to the density profile of segments. With an assumed density profile, the external field can be calculated. The density profile can be again updated based on this external field. The iterations continue until the density profile converges to a final stable solution. Different versions of SCFT
have been applied to branched polymers like dendrimers[41, 42, 43] and bottlebrush polymers[44, 45]. SCFT solution provides greater detail (such as the overall monomer and end-monomer density distribution functions) compared with scaling theories. It is computationally efficient and reliable. The drawback of SCFT is that it neglects the compressibility and fluctuation effects. For example, if applied for a mixture of dendrimer and solvents in a confined system, local behavior near surface would be ignored and solvent density distribution would be unavailable.

In sum, despite the extant simulation and theoretical approaches, new thermodynamic models, which combine both computational efficiency and numerical accuracy, which provide both coarse-grained and detailed structure information, which adapt to both normal and extreme conditions, are in great need for branched molecular systems.

1.3 Scope of the Thesis

This thesis is confined to thermodynamic modeling of branched molecular systems. While the discussion and results are mainly for simple chemicals and the molecular model can be somewhat simplified, the thesis contributes to understanding the phase behavior and micro-structure of branched molecules from a molecular viewpoint. The theoretical approaches developed in this thesis can be easily extended to more complex systems and provide insight for molecular design and industrial processing.

Chapter 2 gives an introduction to the statistical association fluid theory (SAFT) equation of state and the interfacial statistical association fluid theory (iSAFT) density functional theory (DFT) approach. Aiming at bulk properties and inhomogeneous properties respectively, these two theories are inherently related.

SAFTD-LJ-Branch, a modified version of SAFT equation of state is developed in
Chapter 3. It is used to study the effect of chain architecture on the thermodynamic properties of isomeric alkanes. It accurately predicts the phase diagram of pure butane, pentane or hexane isomers. Moreover, vapor pressures of n-triacontane and squalane are predicted without further fitting and shown to be in semiquantitative agreement with experimental data. Finally, SAFTD-LJ-Branch is demonstrated to be well applicable to mixtures as we model the vapor-liquid coexistence of binary alkane mixtures containing different hexane isomers and recover the experimental trends.

In Chapter 4, iSAFT is applied to an isolated dendrimer in solvents of varying quality. The detailed structures of isolated dendrimers in implicit solvent are calculated and have a semi-quantitative agreement with simulation results available in the literature. Scaling laws for the radius of gyration is studied. Factors that affect the quality of the solvent are systematically studied in the explicit solvent case. It is found that the solvent size, density, chemical affinity and temperature all play a role in determining a solvent to be good or poor. New molecular dynamics simulations are performed to validate the iSAFT results.

Chapter 5 further discusses the impact of association on the dendrimer system. The existence of association enables uptake of solvent inside the dendrimer even for unfavorable Lennard Jones interaction between solvent and dendrimer. The conformation of the associating dendrimer is greatly affected by temperature. Due to the interplay between association interaction and Lennard Jones attractions, lower critical solution temperature (LCST) behavior of dendrimer is found and it changes as the dendrimer or solvent size changes and the association scheme changes. The results in Chapter 4 and 5 provide insight into the phase behavior of dendrimer solutions as well as guidance in practical applications.

In Chapter 6, iSAFT is extended to bottlebrush polymers in both good and poor
solvent. The detailed structures of side chains in implicit solvent are calculated and have a semi-quantitative agreement with simulation. The average brush heights calculated from the theory agree with well-established scaling theories. An amphiphilic core-shell bottlebrush is also modeled and it turns out the chain length of different blocks has a great impact on the structure and properties of the molecule. These results can aid experimenters in the design and synthesis of functional bottlebrush polymers.

Chapter 7 summarizes the thesis and suggests future research directions.
Chapter 2

Theoretical Background

In the following, details of the statistical associating fluid theory (SAFT) and inhomogeneous statistical associating fluid theory (iSAFT) are described.

2.1 Statistical Associating Fluid Theory (SAFT)

Statistical associating fluid theory (SAFT) is an advanced equation of state (EoS)\cite{46, 47, 48, 49, 50}, which has achieved great success and popularity. SAFT models molecules as chains of spherical segments. It lays its foundation on Wertheim’s first order thermodynamic perturbation theory (TPT1)\cite{51, 52, 53, 54}, which is a rigorous statistical mechanical theory of associating spheres. The excess Helmholtz free energy of a system can be viewed as a sum of the reference fluid contribution plus contributions from chain formation, association, dispersion and other interactions. The perturbation expansion is typically written for a hard sphere reference fluid\cite{46}, Lennard-Jones reference fluid\cite{55} or square well fluid\cite{56}. Depending on the applied interaction potential, different versions of SAFT have been developed, such as PC-SAFT\cite{57, 58}, Soft-SAFT\cite{59} and SAFT-VR\cite{60}.

Different versions of SAFT have been applied for associating or polar molecules such as water\cite{61} and replacement refrigerants\cite{62}, to long-chain alkanes and polyethylene\cite{63}, to more complex substance such as asphaltene\cite{64}. However, in TPT1, only pair correlations are included in the cluster expansion for association or chain formation.
Therefore, interactions between non-nearest neighbors are neglected. As a result, all the major versions of SAFT EoS are implicitly developed for linear chains. There have been several efforts to incorporate branching effect, and they will be discussed in Chapter 3, where a new branched equation of state will be developed as well, with modeling results of isomeric alkanes.

2.2 Inhomogeneous Statistical Associating Fluid Theory (iSAFT)

As a generation of SAFT, iSAFT is a density functional theory (DFT)\cite{65, 66, 67, 68} for inhomogeneous complex polymeric fluids. Based on rigorous statistical mechanics\cite{51, 52, 53, 54}, DFT is proved to provide detailed information for fluid structures at a calculation expense advantageous to simulation methods. Following the work of Segura et al.\cite{69}, polyatomic DFTs were developed based on a bulk free energy\cite{70, 71} for associating molecules or a free energy functional\cite{66}. These DFTs demonstrated that the polyatomic system could be modeled as a mixture of associating atomic fluids in the limit of complete association. A modified DFT is developed to satisfy stoichiometry and got its name as iSAFT by Jain et al.\cite{72} and further extended to study branched molecules\cite{73}, demonstrating the versatility to apply to molecules of different architecture. With appropriate adaptation, iSAFT has been successfully applied to investigate block copolymers in confinement\cite{72}, tethered polymers\cite{74, 75, 76, 77}, polymer-colloid mixtures\cite{78}, and micelle formation\cite{79}. One can also turn to the paper by Emborsky et al.\cite{68} for a good review.

In iSAFT, the polymer is modeled as a flexible chain of tangentially bonded segments. The schematic of a linear polymer consisting of $m$ segments is depicted in Fig. 2.1. Traditional DFTs are formulated for an open system in the grand canonical ensemble. So the system is at fixed volume ($V$), temperature ($T$) and chemical
potential ($\mu$) in the presence of an external field ($V^\text{ext}(r)$). The grand free energy functional $\Omega[\rho]$ for a system of chain fluids can be related to the intrinsic Helmholtz free energy functional $A[\rho]$ as

$$\Omega[\rho_i(r)] = A[\rho_i(r)] - \sum_{i=1}^{m} \int dr' \rho_i(r') (\mu_i - V^\text{ext}_i(r'))$$  \hspace{1cm} (2.1)$$

where $\rho_i$ is the density of segment $i$, $\mu_i$ is its chemical potential, $V^\text{ext}_i$ is the external field acting on segment $i$, and the sum is over all the $m$ segments of the chain. For the system at equilibrium, the grand free energy is minimized. Minimization of the grand free energy with respect to the density of the segments yields a system of variational equations, known as the Euler-Lagrange equations,

$$\frac{\delta A[\rho_i(r)]}{\delta \rho_i(r)} = \mu_i - V^\text{ext}_i(r), \forall i = 1, \ldots, m$$  \hspace{1cm} (2.2)$$

2.2.1 Potential model

In our potential model, segments have a temperature-independent diameter $\sigma$ and they interact through pairwise repulsive, attractive and association contributions,
given by the following pair potential

$$u(r_{12}, \omega_1, \omega_2) = u^{\text{ref}}(r_{12}) + u^{\text{att}}(r_{12}) + \sum_A \sum_B u^{\text{assoc}}_{AB}(r_{12}, \omega_1, \omega_2)$$  \hspace{1cm} (2.3)

where $r_{12}$ is the distance between two segments, $\omega_1$ and $\omega_2$ are the orientations of segment 1 and 2 respectively, and summations are over all association sites in the system.

The reference fluid contribution $u^{\text{ref}}$ is often taken as a hard sphere repulsive interaction

$$u^{\text{ref}}(r_{12}) = u^{\text{hs}}(r_{12}) = \begin{cases} \infty, & r_{12} < \sigma \\ 0, & r_{12} \geq \sigma \end{cases}$$  \hspace{1cm} (2.4)

The intermolecular attractions $u^{\text{att}}$ are described as a cut-shifted Lennard Jones attraction with a Weeks, Chandler, and Andersen (WCA) separation[80, 81],

$$u^{\text{att}}(r_{12}) = \begin{cases} u^{\text{LJ}}(r_{\text{min}}) - u^{\text{LJ}}(r_c) & \text{if } \sigma < r_{12} \leq r_{\text{min}} \\ u^{\text{LJ}}(r_{12}) - u^{\text{LJ}}(r_c) & \text{if } r_{\text{min}} < r_{12} \leq r_c \end{cases}$$  \hspace{1cm} (2.5)

where

$$u^{\text{LJ}}(r_{12}) = 4\epsilon^{\text{LJ}} \left[ \left( \frac{\sigma}{r_{12}} \right)^{12} - \left( \frac{\sigma}{r_{12}} \right)^6 \right]$$  \hspace{1cm} (2.6)

$r_{\text{min}} = 2^{1/6}\sigma$ is the position of the Lennard Jones potential minimum and $r_c = 2.5\sigma$ is the cutoff distance. The sum of $u^{\text{ref}}$ and $u^{\text{att}}$ serves as a good approximation of the cut-shifted Lennard Jones potential.

Finally, Any segment along a chain can have multiple association sites capable of interacting with other sites on other segments. The association contribution is modeled via off centered sites that interact through a square-well potential of short-
range $r_c$. The interactions between site A on one segment and site B on another segment are modeled using the following association potential

$$u_{AB}^{assoc}(r_{12}, \omega_1, \omega_2) = \begin{cases} -\epsilon_{AB}^{assoc}, & r_{12} < r_c; \theta_{A1} < \theta_c; \theta_{B2} < \theta_c \\ 0, & \text{otherwise} \end{cases} \quad (2.7)$$

where $\theta_{A1}$ is the angle between the vector from the center of segment 1 to site A and the vector $r_{12}$ and $\theta_{B2}$ is the angle between the vector from the center of segment 2 to site B and the vector $r_{12}$, as shown in Fig.2.2.

### 2.2.2 Free energies

Following this potential model, the Helmholtz free energy functional can be decomposed into an ideal and excess contribution.

$$A[\rho_i(\mathbf{r})] = A^{id}[\rho_i(\mathbf{r})] + A^{ex,hs}[\rho_i(\mathbf{r})] + A^{ex,chain}[\rho_i(\mathbf{r})] + A^{ex,att}[\rho_i(\mathbf{r})] + A^{ex,assoc}[\rho_i(\mathbf{r})] \quad (2.8)$$
The ideal contribution comes from the ideal gas state of the atomic mixture (id). The excess contribution of the free energy is due to excluded volume effects (hs), chain connectivity (chain), long-range attraction (att), and association (assoc).

The ideal gas functional is known exactly:

$$\beta A^{id}[\rho_i(\mathbf{r})] = \int d\mathbf{r}_1 \sum_{i=1}^{m} \rho_i(\mathbf{r}_1) [\ln \rho_i(\mathbf{r}_1) - 1]$$

(2.9)

The hard sphere contribution $A^{ex,hs}[\rho_i(\mathbf{r})]$ is calculated from Rosenfeld’s fundamental measure theory (FMT)[82] for a mixture of hard spheres:

$$\beta A^{ex,hs}[\rho_i(\mathbf{r})] = \int d\mathbf{r}_1 \Phi[n_\alpha(\mathbf{r}_1)]$$

(2.10)

where $\Phi[n_\alpha(\mathbf{r})]$ is given by

$$\Phi[n_\alpha(\mathbf{r})] = -n_0 \ln(1 - n_3) + \frac{n_1 n_2 - n_{a1} \cdot n_{v2}}{1 - n_3} + \frac{n_3^2 - 3n_2(n_{v2} \cdot n_{v2})}{24\pi(1 - n_3)^2}$$

(2.11)

and $n_\alpha(\alpha = 0, 1, 2, 3, v1, v2)$ are the fundamental measures.

The attraction term $A^{ex,att}[\rho_i(\mathbf{r})]$ is accounted for by the mean field approximation[83]:

$$\beta A^{ex,att}[\rho_i(\mathbf{r})] = \frac{1}{2} \sum_{i=1}^{m} \sum_{j=1}^{m} \int d\mathbf{r}_1 d\mathbf{r}_2 \beta u^{att}_{ij}(|\mathbf{r}_2 - \mathbf{r}_1|) \rho_i(\mathbf{r}_1) \rho_j(\mathbf{r}_2)$$

(2.12)

Wertheim’s TPT1[51, 52, 53, 54], as extended by Chapman[84], is used to calculate $A^{ex,assoc}[\rho_i(\mathbf{r})]$ and $A^{ex,chain}[\rho_i(\mathbf{r})]$. The association free energy functional is

$$\beta A^{ex,assoc}[\rho_i(\mathbf{r})] = \int d\mathbf{r}_1 \sum_{i=1}^{m} \rho_i(\mathbf{r}_1) \times \sum_{\alpha \in \Gamma(i)} \left( \ln \chi^i_\alpha(\mathbf{r}_1) - \frac{\chi^i_\alpha(\mathbf{r}_1)}{2} + \frac{1}{2} \right)$$

(2.13)
The first summation is over all segments \( i \) and the second is over all the association sites on segment \( i \). \( \chi^i_\alpha \) denotes the fraction of segments of type \( i \) that are not bonded at their associating site \( \alpha \), which can be obtained by the law of mass action[84, 69],

\[
\chi^i_\alpha(r_1) = \frac{1}{1 + \int dr_2 \sum_{j=1}^m \rho_j(r_2) \times \sum_{\beta \in \Gamma^{(i)}} \chi^j_\beta(r_2) \Delta^{ij}(r_1, r_2)}
\]  

(2.14)

The association strength \( \Delta^{ij}(r_1, r_2) \) is controlled by

\[
\Delta^{ij}(r_1, r_2) = K F^{ij}(r_1, r_2) y^{ij}(r_1, r_2)
\]  

(2.15)

where \( K \) is a constant geometric factor which accounts for the entropic cost associated with the orientations and bonding volume of two segments. \( F^{ij}(r_1, r_2) \) is the associating Mayer-f function given as[72]

\[
F^{ij}(r_1, r_2) = \exp \left[ \beta \epsilon_0 - \beta v^{ij}_{\text{bond}}(r_1, r_2) \right] - 1
\]  

(2.16)

where \( \epsilon_0 \) is the bond energy and \( v^{ij}_{\text{bond}}(r_1, r_2) \) is the bonding potential. In the complete association limit of \( \epsilon_0 \to \infty \), the chain contribution to the free energy \( A^{\text{ex,chain}}[\rho_i(r)] \) can be obtained. For tangentially bonded segments, the bonding potential is given by

\[
\exp \left[ -\beta v^{ij}_{\text{bond}}(r_1, r_2) \right] = \frac{\delta(|r_1 - r_2| - \sigma^{ij})}{4\pi(\sigma^{ij})^2}
\]  

(2.17)

and \( y^{ij}(r_1, r_2) \) is the cavity correlation function for inhomogeneous hard sphere reference fluid. \( y^{ij}(r_1, r_2) \) is approximated by[72]

\[
\ln y^{ij}(r_1, r_2) = \frac{1}{2} \left\{ \ln y^{ij}[\tilde{\rho}_k(r_1)] + \ln y^{ij}[\tilde{\rho}_k(r_2)] \right\}
\]  

(2.18)
where $\bar{\rho}_k(r_1)$ is the weighted density of segment $k$ at position $r_1$. In the current work a simple weighting is used

$$\bar{\rho}_k(r_1) = \frac{3}{4\pi(\sigma_k)^3} \int_{|r_1-r_2|<\sigma_k} dr_2 \rho_k(r_2)$$

(2.19)

and the expression for $y^{ij}[\bar{\rho}_k(r_1)]$, the cavity correlation function for homogeneous hard sphere fluid, is only needed at contact and can be found in the work of Tripathi and Chapman[66].

2.2.3 Functional derivatives of free energies

The functional derivatives of the free energies are given as

$$\frac{\delta \beta A_{id}[\rho_i(r)]}{\delta \rho_i(r)} = \ln \rho_i(r)$$

(2.20)

$$\frac{\delta \beta A_{ex,hs}^{\text{att}}[\rho_i(r)]}{\delta \rho_i(r)} = \int dr_1 \frac{\delta \Phi[n_\alpha(r_1)]}{\delta \rho_i(r)}$$

(2.21)

$$\frac{\delta \beta A_{ex,att}^{\text{assoc}}[\rho_i(r)]}{\delta \rho_i(r)} = \sum_{j=1}^m \int_{|r-r_1|>\sigma_{ij}} dr_1 \beta u_{ij}^{\text{att}}(|r-r_1|) \rho_j(r_1)$$

(2.22)

$$\frac{\delta \beta A_{ex,assoc}^{\text{assoc}}[\rho_i(r)]}{\delta \rho_i(r)} = \sum_{\alpha \in \Gamma^{(i)}} \ln \chi_\alpha^i(r) - \frac{1}{2} \sum_{j=1}^m \sum_{k=1}^m \int dr_1 dr_2 \rho_j(r_1) \rho_k(r_2)$$

$$\times \sum_{\alpha \in \Gamma^{(j)}} \sum_{\beta \in \Gamma^{(k)}} \chi_\alpha^j(r_1) \chi_\beta^k(r_2) \frac{\delta \Delta^{jk}(r_1, r_2)}{\delta \rho_i(r)}$$

(2.23)

The functional derivative of the association free energy is derived by Bymaster and Chapman[85] and applies to the full range of association. Further applying the
limit of complete association gives

\[
\frac{\delta \beta A^{\text{ex,chain}}[\rho_i(r)]}{\delta \rho_i(r)} = \sum_{\alpha \in \Gamma^{(i)}} \ln \chi^i_\alpha(r) - \frac{1}{2} \sum_{j=1}^{m} \sum_{j'} \int dr_1 \rho_j(r_1) \times \frac{\delta \ln y^{jj'}[\bar{\rho}_k(r_1)]}{\delta \rho_i(r)}
\]  

(2.24)

where \( \{j'\} \) is the set of all segments bonded to segment \( j \). In this equation the first term on the right side enforces stoichiometry. The cavity correlation function is further approximated by its bulk counterpart evaluated at the weighted density as Eq. 2.18.

Substituting the functional derivatives of the free energies in Euler-Lagrange equation Eq. 2.2 gives

\[
\ln \rho_i(r) + \sum_{\alpha \in \Gamma^{(i)}} \ln \chi^i_\alpha(r) = D_i(r) + \beta(\mu_i - V^{\text{ext}}_i(r))
\]  

(2.25)

where \( D_i(r) \) is given by

\[
D_i(r) = -\frac{\delta \beta A^{\text{ex,hs}}[\rho_i(r)]}{\delta \rho_i(r)} - \frac{\delta \beta A^{\text{ex,att}}[\rho_i(r)]}{\delta \rho_i(r)} - \frac{\delta \beta A^{\text{ex,assoc}}[\rho_i(r)]}{\delta \rho_i(r)} + \frac{1}{2} \sum_{j=1}^{m} \sum_{j'} \int dr_1 \rho_j(r_1) \times \frac{\delta \ln y^{jj'}[\bar{\rho}_k(r_1)]}{\delta \rho_i(r)}
\]  

(2.26)

Note that \( \chi^i_\alpha(r) \) in Eq. 2.25 only refer to sites contributing to chain formation, not association. The set of these nonlinear equations can be solved with Eq. 2.14 for the density profile of segments.
The density profile of segment $i$ in a linear chain of $m$ segments is given as

$$\rho_i(r_i) = \exp(\beta \mu_M) \exp[D_i(r_i) - \beta V_i^{\text{ext}}(r_i)] \int \cdots \int dr_1 \cdots dr_{i-1} \exp \left( \sum_{k=1}^{i-1} [D_k(r_k) - \beta V_k^{\text{ext}}(r_k)] \right)$$

$$\times \prod_{k=1}^{k-1} \Delta_{k+1}(r_k, r_{k+1}) \int \cdots \int dr_{i+1} \cdots dr_m \exp \left( \sum_{k=i+1}^{m} [D_k(r_k) - \beta V_k^{\text{ext}}(r_k)] \right) \prod_{k=i}^{m-1} \Delta_{k+1}(r_k, r_{k+1})$$

(2.27)

where $\mu_M = \sum_{i=1}^{m} \mu_i$ is the bulk chemical potential of the chain. The Picard’s iteration method is applied to solve the set of Eq. 2.27 to find the equilibrium density profile and details can be found in the work of Jain et al.[72]

### 2.2.4 Extension to branched molecules

Although iSAFT or DFT has such wide applications, it is somewhat surprising by far there is only limited work devoted to the study of branched molecules[66, 86, 73, 85, 87]. In 2005, Tripathi and Chapman[66] used original iSAFT to model segregation of a blend of linear molecule and branched molecule with the same number of segments. They studied athermal blend and attractive blend respectively and concluded that the different density profiles for two blends are a result of competition between entropy and enthalpy. And the theoretical predictions are in excellent agreement with the simulation results of Yethiraj[88]. Three different DFT formalisms by Malijevsky et al.[86], Jain and Chapman[73], Bymaster and Chapman[85] are developed to study the behavior of star polymers near hard walls. All of them are in good agreement with the simulation results of Yethiraj and Hall[89] and have advantages at different regions. The latter two are both extensions of the modified iSAFT, namely the formalism introduced in this section.
In this thesis, iSAFT will be further extended to study more complex branched polymers such as dendrimers and bottlebrush polymers. Details will be given in corresponding chapters, since the adaptation of theory would depend on or to some extent, take advantage of the structure of the specific molecule.
Chapter 3

Modeling Thermodynamic Properties of Isomeric Alkanes with a New Branched Equation of State

3.1 Introduction

It is mentioned earlier that in general, SAFT is very successful in modeling linear molecules, but not branched molecules. To explicitly include the structural information in the SAFT EoS, a higher level of perturbation theory must be considered, at least a second order perturbation (TPT2)[90]. TPT2 was extended from TPT1 by Wertheim, where all graphs with a single path of two attraction bonds are retained in addition to the graphs retained in TPT1, thus providing information between bonded pairs and next nearest neighbors along the chain. TPT2 differs from TPT1 by a small term and achieves improved agreement with simulation results. Phan et al.[91] firstly derived a TPT2 equation of state for hard sphere chains, including star-like molecules. They were able to predict the pressure of freely rotating chains and that of trimers as a function of the bond angle. Marshall and Chapman[92] extended this approach further to generate a TPT2 correction for any branched molecule. However, it is challenging to evaluate the TPT2 contributions in the above equations of state.

Besides referring to TPT2, another strategy to improve the behavior of the SAFT EoS is using a fluid of dimers as reference fluid. The dimers consist of two spheres bonded at contact and it is assumed that the correlation function for longer chains can be approximated by the dimer correlation function. As a result, in this dimer
scheme, a segment knows the information of nearest neighbor and also the next nearest neighbor. The first SAFT-D was independently developed by Ghonasgi and Chapman[93, 94, 95, 63] and by Chang and Sandler[96] with the reference fluid being hard sphere dimers. With the same strategy, the Lennard Jones (LJ) reference fluid can also be extended to LJ dimer and Johnson[97] used it to predict thermodynamics of pure components. Later, Blas and Vega[98] also demonstrated that Soft-SAFT-D could be applied to mixtures with improvement over Soft-SAFT, which basically uses LJ spheres as the reference fluid. Despite the improvement over the monomer version, no branching effect is taken into consideration for the dimer version.

Recently, Marshall and Chapman[99] proposed a different approach to construct the second order correction to the free energy for branched molecules and showed that a similar form of correction can be applied in a TPT1-D type of equation of state. Specifically, a correction to SAFTD-LJ will yield a new equation of state that not only maintains a simple analytic form but also directly applies to real components. In this work, we follow similar lines and find it possible to further modify the correction to improve predictions for real systems. We name this equation of state as SAFTD-LJ-Branch. We have used SAFTD-LJ-Branch to systematically study the phase behavior of alkane isomers. The phase diagram and vapor pressures of pure isomeric alkanes as well as vapor liquid equilibrium (VLE) of alkane mixtures are modeled. The theoretical predictions agree well with experimental data, validating the new equation of state.

The chapter is organized as follows. In Sec. 3.2, SAFTD-LJ-Branch is developed for branched molecules. In Sec. 3.3, parameters are fitted, correlated and validated. Alkane systems of interest are studied with the application of SAFTD-LJ-Branch. Conclusion is followed in Sec. 3.4.
3.2 Model and Theory

In this section, we introduce SAFTD-LJ[97], and then include the branch correction to obtain SAFTD-LJ-Branch. Finally, the conventional van der Waals one-fluid mixing rules (VdW1)[100] are applied for extension to mixtures.

3.2.1 Formalism of SAFTD-LJ

In the scheme of SAFTD-LJ, if no association exists, the residual Helmholtz free energy of a system can be written as the sum of LJ sphere free energy and chain formation free energy.

\[ A_{res} = A_s + A_{chain} \]  

(3.1)

Three parameters are needed in this model, that is, the number of spherical LJ segments in a molecule \( m \), dispersion energy between LJ segments \( \epsilon \) and segment diameter \( \sigma \). \( \epsilon \) and \( \sigma \) are explicitly included in the LJ potential.

\[ u_{LJ}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \]  

(3.2)

The term \( A_s \) accounts for the contribution from Lennard Jones segments and the term \( A_{chain} \) accounts for the contribution from the effect of segments connected into dimers and then chains of fixed number. We also define \( \rho \) as number density, \( N \) as number of chain molecules or segments, \( V \) as volume, \( T \) as temperature, \( p \) as pressure and \( \mu \) as chemical potential. The subscripts \( s \) and \( c \) refer to segment and chain respectively. In the following formulas, all the quantities will be expressed in reduced forms as below: \( \rho^* = \rho \sigma^3 \), \( T^* = \frac{kT}{\epsilon} \), \( p^* = \frac{p\sigma^3}{\epsilon} \), \( A^* = \frac{A}{NkT} \), \( \mu^* = \frac{\mu}{kT} \).
Now we have the reduced residual Helmholtz free energy.

\[ A_{\text{res}}^* = mA_s^* + A_{\text{chain}}^* \]  

(3.3)

Note that the existence of \( m \) is due to the fact that \( A_s^* \) is reduced with the number of segments while \( A_{\text{res}}^* \) and \( A_{\text{chain}}^* \) are reduced with the number of chains. \( A_s^* \) is proposed by Johnson et al.[101] through correlations of simulation results, and its expression is

\[ A_s^* = \frac{A_s}{N_s kT} = \frac{\sum_{i=1}^{8} a_i \rho_{s_i} \rho_{s_i} + \sum_{i=1}^{6} b_i G_i}{T^*} \]  

(3.4)

where \( a_i, b_i \) are functions of \( T^* \), and \( G_i \) is function of \( \rho_{s_i}^* \).

\( A_{\text{chain}}^* \) is expressed as[97, 98]

\[ A_{\text{chain}}^* = \frac{A_{\text{chain}}}{N_c kT} = -\frac{m}{2} \ln[g_s(\sigma)] + (1 - \frac{m}{2}) \ln[g_d(\sigma)] \]  

(3.5)

Where \( g_s \) and \( g_d \) are the pair radial distribution function of LJ spheres and the site-site distribution function of LJ dimers respectively. Expressions for \( g_s \) and \( g_d \) at contact are also obtained from correlations fit to molecular simulation[102, 97].

\[ g_s(\sigma) = 1 + \sum_{i=1}^{5} \sum_{j=1}^{5} a_{ij} (\rho_{s_i}^*)^i (T^*)^{1-j} \]  

(3.6)

\[ g_d(\sigma) = \sum_{i=1}^{7} \hat{a}_i (T^*)^{1-i} + \sum_{i=1}^{5} \sum_{j=1}^{5} c_{ij} (\rho_{s_i}^*)^i (T^*)^{1-j} \]  

(3.7)

\( a_{ij}, \hat{a}_i \) and \( c_{ij} \) are all sets of constants. Note that in the reference paper[97] \( \hat{a}_i \) is basically \( a_i \). The hat is put here to distinguish from the previous \( a_i \) in Eq. 3.4.
Figure 3.1: Molecules consisting of six segments but with different structures. Molecule (a) has two three-arm articulation segments (gray) and molecule (b) has one four-arm articulation segment (black). Each gray segment receives an NB = 1 and the black segment receives an NB = 3.

3.2.2 Formalism of SAFTD-LJ-Branch

Since the term $A_s$ has no dependence on how the LJ spheres are connected and arranged, to account for branching, we focus on the chain formation term $A_{chain}$.

The reduced chain term in SAFTD-LJ can also be written as

$$A_{chain}^* = \frac{A_{chain}}{N_c kT} = (1 - m) \ln[g_s(\sigma)] - \left(\frac{m - 2}{2}\right) \ln\left[\frac{g_d(\sigma)}{g_s(\sigma)}\right]$$

(3.8)

The first term in the bracket is the chain contribution in SAFT-LJ[102, 55, 103, 104], and the second term is a correction term to incorporate structural information for dimers. If there is no difference between the LJ sphere correlation function and LJ dimer correlation function, then this term vanishes. In SAFTD-LJ, a segment not only knows its nearest neighbor, but also the next nearest neighbor. Thus this term should be proportional to the number of three consecutive segments that can be found in the chain. For a linear chain with $m$ segments, this number is $m - 2$. For branched chains,
we come up with a way to determine this number through observation of articulation segments, that is, the segments with three or more arms. Fig. 3.1 (a) is a branched chain with 6 segments and there are two three-arm articulation segments, colored as gray. The number of three consecutive segments is 6. On the other hand, Fig. 3.1 (b) is also a branched chain with 6 segments and there is one four-arm articulation segment, colored as black. The number of three consecutive segments is 7. Generalizing to a branched chain with \( m \) segments, we introduce a new parameter \( NB \) to reflect the difference in the number of three consecutive segments compared with that of linear isomer (which is \( m - 2 \)). By rule a three-arm articulation segment contributes 1 to \( NB \) and a four-arm articulation segment contributes 3 to \( NB \). For molecules with multiple articulation segments, \( NB \) is additive. Actually, this methodology can also be applied to articulation segments with more arms. However, for the molecules we are most interested in, such as alkanes, the inclusion of three-arm and four-arm articulation segments is enough.

Based on this analysis, we develop a new chain term which takes branched structure into consideration.

\[
A_{\text{chain}}' = \frac{A_{\text{chain}}}{N_c kT} = (1 - m) \ln[g_s(\sigma)] - (\frac{m - 2 + NB}{2}) \ln \left[ \frac{g_d(\sigma)}{g_s(\sigma)} \right]
\]  

(3.9)

When \( NB=0 \), this term is the same as Eq. 3.8, meaning that SAFTD-LJ-Branch simply reduces to SAFTD-LJ for linear chains. This expression is the same as proposed by Marshall and Chapman[99]. They applied the theory to branched alkanes, but not to mixtures.

It is interesting to note that the architecture in LCT is accounted for by a series of combinatorial numbers[31, 37], the number of segments \( m \), the number of bonds...
$m - 1$, the number of two consecutive bonds $N_2$ and the number of three consecutive bonds $N_3$. The impact of architecture on thermodynamics arises starting with the occurrence of $N_2$ in the series expansion of LCT, which is on the same level of approximation as our expression $m - 2 + NB$. This similarity between the two theories is especially striking, because they are derived in a completely different formalism. This strengthens both theoretical results to some extent and it would be interesting to see, if further similarities occur, once trimer and tetramer correlation functions are available.

The resulting SAFTD-LJ-Branch, has four parameters in total, that is $m$, $\sigma$, $\epsilon$ and NB. We assume that to model isomers with different branching structure, $m$, $\sigma$ and $\epsilon$ can be kept the same and the only different parameter is NB. This assumption allows us to predict the phase behavior of numerous chemicals from data for isomers. The approach should be applicable to isomers with similar numbers and types of functional groups, such as alkanes and primary alcohols.

### 3.2.3 VdW1 theory for mixtures

Like other SAFT equations of states, SAFTD-LJ-Branch can be easily extended to mixtures with the approximation of van der Waals One-Fluid Theory[100], which is a well-established conformal solution theory. VdW1 defines parameters of a hypothetical pure fluid $x$ having the same residual properties as the mixture of interest. For $\sigma_x$ and $\epsilon_x$, the mixing rules are:

\[
\sigma_x^3 = \frac{\sum_i \sum_j m_im_jx_ix_j\sigma_{ij}^3}{\sum_i \sum_j m_im_jx_ix_j} \quad (3.10)
\]

\[
\epsilon_x\sigma_x^3 = \frac{\sum_i \sum_j m_im_jx_ix_j\epsilon_{ij}\sigma_{ij}^3}{\sum_i \sum_j m_im_jx_ix_j} \quad (3.11)
\]
Where $x_i$ is the mole fraction of component $i$.

The effective segment number or branching parameter of the conformal fluid are simply the average segment number or branching parameter of the mixture.

$$m_x = \sum_i m_i x_i, \quad NB_x = \sum_i NB_i x_i$$  \hspace{1cm} (3.13)
Table 3.1 : Pure component parameters for normal alkanes from $C_3$ to $C_{10}$

<table>
<thead>
<tr>
<th>carbon number</th>
<th>$m$</th>
<th>$\sigma[A]$</th>
<th>$\epsilon/k[K]$</th>
<th>AAD($p_V$)%</th>
<th>AAD($v_L$)%</th>
<th>$T$ range[K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1.913</td>
<td>3.726</td>
<td>214.3</td>
<td>0.535</td>
<td>0.495</td>
<td>200-350</td>
</tr>
<tr>
<td>4</td>
<td>2.249</td>
<td>3.819</td>
<td>232.1</td>
<td>1.256</td>
<td>2.076</td>
<td>195-420</td>
</tr>
<tr>
<td>5</td>
<td>2.581</td>
<td>3.874</td>
<td>245.3</td>
<td>0.877</td>
<td>1.566</td>
<td>220-460</td>
</tr>
<tr>
<td>6</td>
<td>2.941</td>
<td>3.904</td>
<td>253.9</td>
<td>1.057</td>
<td>1.817</td>
<td>250-500</td>
</tr>
<tr>
<td>7</td>
<td>3.276</td>
<td>3.926</td>
<td>261.8</td>
<td>0.628</td>
<td>0.814</td>
<td>229-501</td>
</tr>
<tr>
<td>8</td>
<td>3.651</td>
<td>3.933</td>
<td>266.7</td>
<td>0.859</td>
<td>0.611</td>
<td>254-526</td>
</tr>
<tr>
<td>9</td>
<td>3.993</td>
<td>3.953</td>
<td>271.5</td>
<td>0.990</td>
<td>0.583</td>
<td>266-554</td>
</tr>
<tr>
<td>10</td>
<td>4.335</td>
<td>3.971</td>
<td>275.3</td>
<td>0.868</td>
<td>0.570</td>
<td>286-574</td>
</tr>
</tbody>
</table>

The equation of state parameters are plotted versus molecular weight (MW) of n-alkanes starting from propane in Fig. 3.2.

We see that the plots of all three parameters show a smooth trend. Inspired by Pedrosa et al.[105], we succeed in correlating the parameters with molecular weight with the following expressions.

\[ m = 0.0248 \text{MW} + 0.8063 \]  \hspace{1cm} (3.14a)

\[ m\sigma^3 = 1.7437 \text{MW} + 23.469 \]  \hspace{1cm} (3.14b)

\[ \frac{\epsilon/k}{MW} = \frac{314.998 \text{MW} - 209.288}{MW + 19.7705} \]  \hspace{1cm} (3.14c)

Figure 3.2 : Parameters of SAFTD-LJ EoS for the series of n-alkanes, correlated from propane to n-decane. Lines are for eye guidance. (a) $m$ as a function of MW. (b) $m\sigma^3$ as a function of MW. (c) $\epsilon/k$ as a function of MW.
### 3.3.2 Phase equilibrium of pure isomeric alkane

**VLE of n-alkanes versus i-alkanes**

In the frame of SAFTD-LJ-Branch, isomeric alkanes share the same parameters except for NB, which is related to the structure of a molecule and determined by the numbers of different types of articulation points.

As a first examination, we model vapor liquid equilibrium for n-alkanes and their corresponding i-alkane isomers. In Fig. 3.3, the predictions for butane, pentane and hexane are compared against NIST values\[1\], which are correlations of experimental data. We observe overall good agreement. The model does extremely well in predicting vapor density and vapor pressure while it underestimates the branching effect on liquid density. Table 3.2 shows the average absolute deviations for predictions of vapor pressure and liquid molar volume in the investigated temperature range. In agreement with experiment, we find that i-alkanes tend to have a higher critical density and a lower critical temperature than its linear isomer. The error in critical temperature can be corrected by including fluctuation\[106\]. Significant deviations are expected if the molecular structure becomes spherical, such as i-butane. This is

<table>
<thead>
<tr>
<th></th>
<th>AAD($p_V$)%</th>
<th>AAD($v_L$)%</th>
<th>$T$ range[K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>i-butane</td>
<td>8.00</td>
<td>3.00</td>
<td>220-387</td>
</tr>
<tr>
<td>i-pentane</td>
<td>3.55</td>
<td>0.52</td>
<td>230-438</td>
</tr>
<tr>
<td>2-methylpentane</td>
<td>3.56</td>
<td>0.45</td>
<td>249-473</td>
</tr>
<tr>
<td>3-methylpentane</td>
<td>5.58</td>
<td>1.09</td>
<td>249-359($p_V$), 343-473($v_L$)</td>
</tr>
<tr>
<td>(2,3)-dimethylbutane</td>
<td>13.20</td>
<td>1.35</td>
<td>244-354($p_V$), 343-473($v_L$)</td>
</tr>
<tr>
<td>(2,2)-dimethylbutane</td>
<td>10.33</td>
<td>1.99</td>
<td>237-346($p_V$), 343-463($v_L$)</td>
</tr>
<tr>
<td>n-triacontane</td>
<td>14.89</td>
<td>2.54</td>
<td>450-780</td>
</tr>
<tr>
<td>squalane</td>
<td>32.51</td>
<td>4.29</td>
<td>450-780</td>
</tr>
</tbody>
</table>
Figure 3.3: Vapor pressures (a, c, e) and temperature/density coexistence curves (b, d, f) for n-butane and i-butane (a, b), n-pentane and i-pentane (c, d), n-hexane and i-hexane (e, f). Squares give NIST values of n-alkanes and triangles give NIST values of i-alkanes[1]. Solid lines give theoretical results of n-alkanes and dashed lines give theoretical results of i-alkanes.
Table 3.3: Parameters of different isomers of hexane

<table>
<thead>
<tr>
<th>Isomer</th>
<th>m</th>
<th>σ[A]</th>
<th>ε/k[K]</th>
<th>NB</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-hexane</td>
<td>2.941</td>
<td>3.904</td>
<td>253.9</td>
<td>0</td>
</tr>
<tr>
<td>2-methylpentane</td>
<td>2.941</td>
<td>3.904</td>
<td>253.9</td>
<td>1</td>
</tr>
<tr>
<td>3-methylpentane</td>
<td>2.941</td>
<td>3.904</td>
<td>253.9</td>
<td>1</td>
</tr>
<tr>
<td>(2,3)-dimethylbutane</td>
<td>2.941</td>
<td>3.904</td>
<td>253.9</td>
<td>2</td>
</tr>
<tr>
<td>(2,2)-dimethylbutane</td>
<td>2.941</td>
<td>3.904</td>
<td>253.9</td>
<td>3</td>
</tr>
</tbody>
</table>

because the branching effect is accounted on the basis of a linear chain model, and increasing sphericity introduces unanticipated symmetry, which affects the thermodynamics of molecules.

**VLE of hexane isomers**

To validate the potential of SAFTD-LJ-Branch being applied to different structures that an alkane isomer may assume, hexane is considered a good choice since it has five isomers. Among the five hexane isomers: n-hexane is linear; 2-methylpentane and 3-methylpentane both have one branch but at different carbon positions; (2,3)-dimethylbutane has two branches located at different positions on the backbone while the two branches of (2,2)-dimethylbutane connect to the same carbon atom. Following the argument in Sec. 3.2.2, it is straightforward to determine the values of NB for each hexane isomer, as is listed in Table. 3.3; the values of parameters m, σ and ε are the same as for n-hexane.

As shown in Fig. 3.4, vapor pressures are modeled for each hexane isomer and plotted as a function of reciprocal temperature. Theoretical results match the NIST values[1] well, especially at low temperatures. Note that using SAFTD-LJ-Branch, 2-methylpentane and 3-methylpentane share the same set of parameters and should yield the same results theoretically. While not identical, the experimental vapor pressures of these two isomers fall very close to each other.
Figure 3.4: Log base 10 vapor pressures for different isomers of hexane versus reciprocal temperature. Symbols give NIST values\cite{1} and lines are theoretical predictions. Upper lines are of higher NB.

Saturated densities at different temperatures for each hexane isomer are plotted in Fig. 3.5 and compared against the values of Kay\cite{2} correlated from experiments. The agreement for densities is not as satisfactory as that for vapor pressures. Overall, the theory overestimates the branching effect on the vapor density while it underestimates that on the liquid density. Moreover, 2-methylpentane and 3-methylpentane show non-negligible differences from the correlations, especially for the liquid density. This indicates that more structural information needs to be included to accurately predict densities of isomers with similar extent of branching. For the prediction of vapor
pressures, the theory seems to be adequate. The tendency of critical properties for different isomers are found to be consistent with experimental data except for the critical temperature of 2-methylpentane, which is exceptionally low experimentally compared with (2,3)-dimethylbutane. The quantitative summary of performance of SAFT-LJ-Branch for different branched hexane isomers is presented in Table. 3.2.

Some may doubt that NB can be determined simply from the structure of hexane since the molecule is modeled as made up of 2.941 effective segments (instead of the carbon number in the backbone) and NB should also be an effective branching
parameter. For the modeling of (2,2)-dimethylbutane, we notice that in Fig. 3.5 the vapor side displays unexpected curvature approaching the critical temperature. We believe that this behavior is a result of the relatively large value of NB (= 3) compared with \( m \). Further, we note that a slightly higher or smaller value of NB can improve the agreement with vapor pressure depending on the component. However, since NB assigned this simple way generates encouraging results, we stick to the parameter values in Table. 3.3 for most of this work. We will discuss the role of NB later where it is not necessarily an integer.

**VLE of n-triacontane versus squalane**

In this section we test our theory for heavier alkanes. One chemical of interest is squalane, an isomer of n-triacontane. It has six methyl branches almost evenly spread over its backbone. To model n-triacontane, we extrapolate the parameters from Eq. 3.14 and we obtain \( m = 11.292, \sigma = 4.069\AA, \epsilon/k = 300.454K \). We use those same numbers for the parameters of squalane with an additional NB = 6. Fig. 3.6 shows the theoretical predictions for vapor pressures of both n-triacontane and squalane, compared against values from NIST[1]. We find the theory does a good job in matching the data at high temperatures, particularly since the parameters are extrapolated. At low temperatures, the predicted vapor pressures of both chemicals begin to deviate from the data points with squalane showing a higher deviation. The average absolute deviations for predicted vapor pressures of n-triacontane and squalane are 14.89% (maximum is 27.67%) and 32.51% (maximum is 61.71%). These numbers are large partly due to the small values of the true vapor pressures when temperature is low. However, the same direction of deviations observed for both chemicals implies a successful capture of the branching effect.
Figure 3.6: Log base 10 vapor pressures of n-triacontane and squalane versus reciprocal temperature. Symbols give NIST values[1]. Solid line gives theoretical results of n-triacontane and dashed line gives theoretical results of squalane.

Due to the unavailability of vapor densities from literature, only the saturated liquid densities of the two isomers are plotted in Fig. 3.7. Contrary to vapor pressures, the theoretical results are more accurate at low temperatures and begin to deviate from NIST values approaching the critical point. There is little difference between the liquid densities of n-triacontane and squalane at low temperatures and as a matter of fact, the theory incorrectly predicts a slightly higher density for squalane until a crossover at high temperature. The inconsistency may be a result of the parameters extrapolated from short chain alkanes or deficiencies of SAFTD-LJ-Branch itself. The
Figure 3.7: Saturated liquid densities of n-triacontane and squalane versus temperature. Symbols give NIST values[1]. Solid line gives theoretical results of n-triacontane and dashed line gives theoretical results of squalane.

Despite defects, the results are still inspiring since the parameters are extrapolated from decane and the only required input is the structure of the chemical. This new equation of state provides semi-quantitatively accurate predictions of the effect of molecular structure for heavier molecules.
3.3.3 Phase equilibrium of alkane mixtures

VLE of isomeric hexane and propane

We further extend the pure component system to mixtures. Vapor liquid equilibrium of isomeric hexane (using parameters in Table. 3.3) and propane are studied at two temperatures (348.15K and 373.15K), as shown in Fig. 3.8. For a better look, the system of n-hexane and propane is compared against the system of (2/3)-methylpentane and propane, system of (2,3)-dimethylbutane and propane, system of (2,2)-dimethylbutane and propane, respectively. In general the model gives a good description of the phase equilibrium compared with experimental data[3] and the branching effect is particularly clear for the dew curve. At 373.15K, the average deviation for the predictions of system of (2,2)-dimethylbutane and propane is 1.90% (maximum is 6.13%) in bubble pressure and 12.06% (maximum is 22.34%) in dew pressure. The systems of propane and other hexane isomers behave similarly or better. At low mole fraction of propane, the theory tends to overestimate pressures while at high mole fraction of propane underestimation occurs. However, the overall tendency is nicely captured. With the same composition, the system with more branching (higher NB) features higher dew pressure and bubble pressure, consistent with the pure component case.

Effect of position where branches grow

In the framework of SAFTD-LJ-Branch, different positions where branches grow are not taken into account as long as the numbers and types of articulation points stay the same. As shown earlier, this was not an issue for mixtures of propane with 2-methylpentane and 3-methylpentane. However, to get some further insight,
Figure 3.8: VLE of the mixture propane + isomeric hexane at 348.15K (lower curves) and 373.15K (upper curves). In each figure, solid lines are theoretical results for mixture propane + n-hexane and dashed lines are theoretical results for mixture propane + branched hexane. Squares give experimental results for mixture propane + n-hexane and triangles give experimental results for mixture propane + branched hexane[3]. (a) Comparison with mixture propane + (2/3)-methylpentane. (b) Comparison with mixture propane + (2,3)-dimethylpentane. (c) Comparison with mixture propane + (2,2)-dimethylpentane.
this section is devoted to understand the nuances between isomers which only differ in the positions where branches grow. We model the mixture of 2-methylpentane and n-octane as well as the mixture of 3-methylpentane and n-octane for vapor liquid equilibrium. The results are shown in Fig. 3.9 and Fig. 3.10. With NB = 1, the theory predicts the phase behavior well and shows some deviations from experiments[4, 5] for both cases. Following the pattern of deviation, we find that a better agreement between prediction and experiments can be obtained when NB is set to around 1.2

Figure 3.9: VLE of the mixture 2-methylpentane + n-octane at various temperatures. Solid lines are theoretical predictions with NB = 1 for 2-methylpentane and dashed lines are theoretical predictions with NB = 1.2 for 2-methylpentane. Symbols are experimental data[4] at 283.15K (squares), 293.15K (triangles), 303.15K (diamonds) and 313.15K (circles).
Figure 3.10: VLE of the mixture 3-methylpentane + n-octane at various temperatures. Solid lines are theoretical predictions with NB = 1 for 3-methylpentane and dashed lines are theoretical predictions with NB = 0.8 for 3-methylpentane. Symbols are experimental data[4, 5] at 283.15K (squares), 293.15K (triangles), 303.15K (diamonds), 313.15K (circles) and 333.15K (crosses).

for 2-methylpentane and 0.8 for 3-methylpentane. This study is interesting as well as intuitive. 2-methylpentane has a ternary carbon atom shielded by two methyl groups while the ternary carbon atom of 3-methylpentane is surrounded by only one methyl group. A stronger shielding effect for 2-methylpentane leads to a stronger branching effect.

Although the most accurate value for NB is dependent on the system studied, we will not try to fit it nor devise a complicated rule of determination for now.
SAFTD-LJ-Branch is developed to provide reasonable solutions to thermodynamics of branched molecules even when no experimental data exists for isomers. We see from the above examples that this model can predict the general trend and provide physically meaningful guidance. In this regard, SAFTD-LJ-Branch is a great tool to study the branched molecules. As we see in the case of 2-methylpentane and 3-methylpentane, NB = 1 tends to be a good average estimate.

In the future, we are interested in a deeper understanding of the relationship between molecular architecture and atoms or groups forming the molecule, potentially leading to better group contribution approaches[107] that explicitly consider molecular architecture.

3.4 Conclusion

This work has a primary focus on thermodynamics of branched molecules. A new equation of state, SAFTD-LJ-Branch is developed through extension of the framework of Marshall and Chapman[99]. The new model is able to predict phase behavior of isomers using a single set of parameters except for the branching parameter, which can be simply obtained from the structure of a molecule. Predictions for pure alkanes and mixtures of alkanes are compared against experimental results with good agreement, especially for the vapor pressures. The accuracy of the predictions is quite surprising considering the simple parameterization scheme and the fact that the branched model adds almost no complexity over the linear model. The theory has strong connections with other popular approaches such as lattice cluster theory and group contribution methods. It also has potential of being applied to associating networks where the effect of branching has been generally neglected.
Chapter 4

Density Functional Study of Dendrimer Molecules in Solvents of Varying Quality

4.1 Introduction

Among all the molecules that feature great potential for applications, dendrimers have received considerable attention[108, 109, 14]. As illustrated in Fig. 4.1, a dendrimer molecule consists of three types of monomer segments: branched (B), linear (L) and terminal (T) segments. The branched segments are bonded more than twice while linear segments are bonded twice and the terminal segments only once. Dendrimers can be characterized by the number of generations $G$, the functionality $b$ of the branched segments and the spacer between the branched segments $n$. To avoid confusion, we use $G$ as the generation of the dendrimer and $g$ as the generation layer a specific segment belongs to. The total number of monomers in a dendrimer (excluding the core monomer) is given by $N = \frac{nb}{G-2}[(b-1)^{G+1} - 1]$.

Because of their well-defined architecture, dendrimers are applied in dendritic assemblies, layers, films as well as liquid crystals[110, 111, 112, 113]. The presence of many terminal groups enables functional modifications to dendrimers, which can be used in medicine, pharmaceuticals[114, 115], catalysts, chirality and analytical chemistry[116, 117]. Among the many properties, the knowledge of the detailed structure of dendrimers is fundamental to synthesis as well as application. Specifically, understanding conformations of dendrimers in solvents of varying quality is of great
Figure 4.1: Schematic of $G_1$ dendrimer with $b = 3$, $n = 3$. The monomers within the concentric shell belong to the same generation $g$. The gray bead represents the core segment and the dark blue group of segments represents one dendron.

importance. Similar to linear polymers, dendrimers tend to swell in good solvents and collapse in poor solvents. However, dendrimers may have quite different solubility for the same solvent compared with linear polymers, even without any modification of terminal groups. Hawker and Fréchet [118] found that dendritic polyesters can exhibit a higher solubility than their linear analogue. For example, in a solubility test with tetrahydrofuran as the solvent, dendritic polyester was found to have a significantly higher solubility than that of analogous linear polyester [119]. On the other hand, unlike linear polymers, dendrimers are considered to be able to encapsulate guest molecules [120, 121] and studying their interaction with solvents might shed some light on drug delivery [115, 122], unimolecular micelles [123, 124], etc.

Triggered by the unique properties and potential applications, researchers have conducted a large body of experimental studies [125, 126, 127, 128] to explore the relationship between dendrimer and solvents. Theory and simulation methods [6, 129,
130, 131, 132, 133, 134] are also applied and a good summary can be found in the review paper by Ballauff and Likos[135]. Using molecular dynamics simulations, Murat and Grest[6] implicitly incorporated the solvent effect and found that the dendrimers would shrink as the solvent became poorer. They also demonstrated that for all solvent conditions considered, dendrimers obey $R_g \sim N^{1/3}$ scaling, where $R_g$ is the radius of gyration. From Flory theory, Sheng et al.[129] conclude that the scaling relation should be $R_g \sim N^{1/5}(G + 1)^{2/5}n^{2/5}$ for good solvent and $R_g \sim N^{1/3}$ for poor solvent, and the latter scaling holds for good solvents only when $n$ is fixed. Based on lattice Monte Carlo and Flory theory, Giupponi and Buzza[130] also claim that a universal form of $R_g \sim N^{1/3}$ is incorrect and they propose a scaling $R_g \sim N^{1/4}(G + 1)^{1/4}n^{1/4}$ for θ solvent in addition to what Sheng et al. [129] obtained. Several other studies were conducted with similar or different conclusions[131, 132, 133, 134]. On the other hand, to what extent the dendrimer is affected by varying quality of solvent remains an active topic for discussion. Several experimental studies[125, 126] found that the solvent effect only plays a role for higher generation dendrimers ($G \geq 4$) and essentially no collapse occurs for lower generation. Topp et al.[127] found that even for $G = 7$, the PAMAM dendrimer showed no apparent sign of collapse from a good solvent (water) to a poor solvent (butanol). On the contrary, using multidimensional NMR techniques, Chai et al.[128] found that even for low generations, DAB dendrimers tend to display extended chain conformations in a good solvent (chloroform) and folded chain conformation in a poor solvent (benzene). Also, a number of theoretical or simulation results[130, 131] lead to the conclusion that a significant collapse of dendrimer takes place for all generations, going from good to poor solvent conditions, although the collapse factor differs case by case. Since there is always ambiguity and controversy over the definition of solvent quality and collapse, plus
the differences in the details of the study methods, no definitive conclusions have been drawn in this regard. Recently, Chen et al.[87] applied classical density functional theory (DFT) to study the conformation of homodendrimers and amphiphilic dendrimers in various solvents and found the existence of dense-core and dense-shell structures under different conditions.

The works mentioned above are more engaged in predicting how dendrimers of different generations or spacer length behave under certain solvent conditions. However, there is also a large parameter space for the solvent, such as the solvent size, density and energetic interactions, which upon change would affect the structure and properties of dendrimers. This facet seems to be overlooked by researchers. Our aim for this work is to perform a systematic analysis on how dendrimers are affected by solvents of varying quality and hopefully, provide some insights on how to construct a good or poor solvent for a specific type of dendrimer.

For this task, we extend inhomogeneous statistical associating fluid theory (iSAFT)[72, 85] to study the structures of dendrimer in both implicit and explicit solvents. For implicit cases, there are no actual solvent molecules around but the effect of solvent is incorporated in the interactions between dendrimer segments. In contrast, in explicit cases, the solvent segments are explicitly modeled. Since simulation results available in literature do not cover the whole range of systems we are interested in, we have also performed molecular dynamics simulations using LAMMPS to justify the iSAFT results, especially for dendrimers in explicit solvents. For clarity, simulation details are included in appendix A.1.

This chapter is organized as follows. In Sec. 4.2, we develop the iSAFT formalism for a dendrimer centered spherically symmetric system. In Sec. 4.3, we firstly model the dendrimers in implicit solvent and compare our results with the simulation re-
results from Murat and Grest[6] and our own. Several scaling analyses have also been carried out. Then we model dendrimer $G5$ in explicit solvent with a discussion of the characteristics of a good or poor solvent, and a comparison of our simulation results. Sec. 4.4 gives our conclusion.

4.2 Model and Theory

The structure of the dendrimer molecule is already introduced and depicted as Fig. 4.1. When explicitly incorporated, solvents are modeled as linear chains which may have favorable or unfavorable interactions with the dendrimer. Solving iSAFT in real space is usually challenging because the density distribution can vary in every dimension. However, in the case of an isolated dendrimer with center core fixed, due to the spherical symmetry of the dendrimer structure, it is possible to simplify a 3D problem to a 1D problem. In such a model, all segment densities are only functions of radial distance from the center core and we are able to focus on a single dendron of the dendrimer, which is the branch formed at the initial branching point (see Fig. 4.1). The interactions between segments follow the same potential model as in Sec. 2.2.1 and association is not considered here. The same equations are used as that in Sec. 2.2.2 and Sec. 2.2.3 except for Eq. 2.27, which is valid only for a linear chain.

To develop the expression of segment density for this dendrimer system, we suppose the center core has a diameter of $\sigma_C$, and all the other monomer or solvent segments have a diameter of $\sigma_D$. We denote the segment that is directly tethered to the center core as segment 1, and the subsequent ones 2,3,\ldots,$m_D$. To be noted is that $m_D$ is not the number of total segments in the dendron but the number of distinguishable segments, which is equal to the path length from segment 1 to a terminal
segment, as illustrated in Fig. 4.2.

Figure 4.2 : Schematic of the way monomer segments are indexed in a dendron of dendrimer. Light gray bead indicates branched segment and the dark gray bead is the core segment. Dashed beads represent segments of other dendrons. \( I_{1,i} \) and \( I_{2,i} \) are pointing outwards and inwards respectively.

It is easy to obtain that \( m_D = (G + 1) \times n \). Segment \( i \) has a total number of \( N_{eq,i} = 2^g \) equivalents in one dendron, for \( gn < i \leq (g + 1)n \). The external field exerted by the center core on the monomer segment 1 is

\[
V_{1}^{\text{ext}}(r) = \begin{cases} 
 u & \text{if } r = \sigma_0 \\
 \infty & \text{otherwise}
\end{cases} \tag{4.1}
\]

Where \( \sigma_0 = \frac{\sigma_C + \sigma_D}{2} \) and \( u \) sets the grafting density or number of arms on the center core segment.
For the other monomer or solvent segments

\[ V_i^{\text{ext}}(r) = \begin{cases} 
\infty & \text{if } r < \sigma_0 \\
0 & \text{otherwise} 
\end{cases} \quad (4.2) \]

The density of dendrimer segments can be expressed as follows. For segment 1,

\[ \rho_1(r_1) = \begin{cases} 
\exp(\beta \mu_D - \beta u) \exp[D_1(\sigma_0)] I_{1,1}(\sigma_0) I_{2,1}(\sigma_0) \delta(r_1 - \sigma_0) & \text{if 1 is a L or T segment} \\
\exp(\beta \mu_D - \beta u) \exp[D_1(\sigma_0)] I_{1,1}(\sigma_0) I_{2,1}^b(\sigma_0) \delta(r_1 - \sigma_0) & \text{if 1 is a B segment} 
\end{cases} \quad (4.3) \]

The delta function \( \delta(r_1 - \sigma_0) \) accounts for the fact that segment 1 is tethered at a fixed distance \( \sigma_0 \) from origin and for the other monomer segments \( i = 2, \ldots, m_D \),

\[ \rho_i(r_i) = \begin{cases} 
\exp(\beta \mu_D - \beta u) \exp[D_i(r_i)] I_{1,i}(r_i) I_{2,i}(r_i) & \text{if i is a L or T segment} \\
\exp(\beta \mu_D - \beta u) \exp[D_i(r_i)] I_{1,i}(r_i) I_{2,i}^b(\sigma_0) & \text{if i is a B segment} 
\end{cases} \quad (4.4) \]

where \( \mu_D \) is “chemical potential” of the dendron imposed by the tether condition. \( I_{1,i} \) and \( I_{2,i} \) are multiple integrals introduced by Jain et al.[72] to facilitate solving the Euler-Lagrange equations for linear chains and further extended to branched chains[73]. The integrals are solved using the following recurrence:

\[ I_{1,1}(\sigma_0) = 1, \quad (4.5) \]

\[ I_{1,2}(r_2) = \begin{cases} 
\exp[D_1(\sigma_0)] \Delta^{(1,2)}(\sigma_0, r_2) & \text{if 1 is a L or T segment} \\
I_{2,1}^b(\sigma_0) \exp[D_1(\sigma_0)] \Delta^{(1,2)}(\sigma_0, r_2) & \text{if 1 is a B segment} 
\end{cases} \quad (4.6) \]
\[ I_{1,i}(r_i) = \begin{cases} \int I_{1,i-1}(r_{i-1}) \exp[D_{i-1}(r_{i-1})] \Delta^{(i-1,i)}(r_{i-1}, r_i) dr_{i-1} & \text{if } i-1 \text{ is a L or T segment} \\
\int I_{1,i-1}(r_{i-1}) I_{2,i-1}^{b-2}(r_{i-1}) \exp[D_{i-1}(r_{i-1})] \Delta^{(i-1,i)}(r_{i-1}, r_i) dr_{i-1} & \text{if } i-1 \text{ is a B segment} \end{cases} \tag{4.7} \]

and

\[ I_{2,m_D}(r_{m_D}) = 1, \tag{4.8} \]

\[ I_{2,i}(r_i) = \begin{cases} \int I_{2,i+1}(r_{i+1}) \exp[D_{i+1}(r_{i+1})] \Delta^{(i+1,i)}(r_i, r_{i+1}) dr_{i+1} & \text{if } i+1 \text{ is a L or T segment} \\
\int I_{2,i+1}^{b-1}(r_{i+1}) \exp[D_{i+1}(r_{i+1})] \Delta^{(i+1,i)}(r_i, r_{i+1}) dr_{i+1} & \text{if } i+1 \text{ is a B segment} \end{cases} \tag{4.9} \]

\[ I_{2,1}(\sigma_0) = \begin{cases} \int I_{2,2}(r_2) \exp[D_2(r_2)] \Delta^{(1,2)}(\sigma_0, r_2) dr_2 & \text{if } 2 \text{ is a L or T segment} \\
\int I_{2,2}^{b-1}(r_2) \exp[D_2(r_2)] \Delta^{(1,2)}(\sigma_0, r_2) dr_2 & \text{if } 2 \text{ is a B segment} \end{cases} \tag{4.10} \]

\( I_{1,i} \) and \( I_{2,i} \) can be considered as integration operators propagating outwards and inwards respectively, as illustrated by Fig. 4.2. In this way, the chemical potential of a segment in a dendron depends on the local chemical potential of all other segments in the dendron. The total density of dendrimer segments is calculated as

\[ \rho_D(r) = \sum_{i=1}^{m_D} N_{eq,i} \rho_i(r) \quad \text{for } r > \sigma_0 \tag{4.11} \]

The value of \( \exp(\beta \mu_D - \beta u) \) can be obtained from the grafting density \( \rho_g \), which is
the number of segments 1 per unit area of the excluding surface.

\[
\int \rho_1(r)dr = \rho_y = \frac{b}{4\pi\sigma_0^2} \tag{4.12}
\]

then we have

\[
\exp(\beta\mu_D - \beta u) = \begin{cases} 
\frac{\rho_y}{\exp[D_1(\sigma_0)I_{1,1}(\sigma_0)I_{2,1}(\sigma_0)]} & \text{if 1 is a L or T segment} \\
\frac{\rho_y}{\exp[D_1(\sigma_0)I_{1,1}(\sigma_0)I_{2,1}^{\sigma_0}]} & \text{if 1 is a B segment}
\end{cases} \tag{4.13}
\]

Substitute the equation into Eq. 4.4 gives the density profile of all the other monomer segments.

The density profile of solvent molecules is more straightforward to obtain since the segments are free to move for \( r > \sigma_0 \). For a solvent consisting of \( m_S \) segments, we have

\[
\rho_j(r_j) = \exp(\beta\mu_S) \exp[D_j(r_j)]I_{1,j}(r_j)I_{2,j}(r_j) \tag{4.14}
\]

Here \( \mu_S \) is the chemical potential of solvent in the bulk and \( I_{1,j}, I_{2,j} \) are following

\[
I_{1,1}(r_1) = 1, \tag{4.15}
\]

\[
I_{1,j}(r_j) = \int I_{1,j-1}(r_{j-1}) \exp[D_{j-1}(r_{j-1})] \Delta^{(j-1,j)}(r_{j-1}, r_j) dr_{j-1} \tag{4.16}
\]

and

\[
I_{2,m_S}(r_{m_S}) = 1, \tag{4.17}
\]

\[
I_{2,j}(r_j) = \int I_{2,j+1}(r_{j+1}) \exp[D_{j+1}(r_{j+1})] \Delta^{(j+1,j)}(r_{j+1}, r_j) dr_{j+1} \tag{4.18}
\]
The total density of solvent segments is calculated as

$$\rho_S(r) = \sum_{j=1}^{m_S} \rho_j(r) \quad \text{for} \; r > \sigma_0$$  \hspace{1cm} (4.19)

For most cases studied we follow the type of dendrimer as constructed in the simulation work of Murat and Grest[6], with $b = 3$ and $n = 7$. The spacer number $n$ is varied for a few cases where we work on scaling. Dendrimers up to $G8$ are modeled using iSAFT. In this work, we consider the sizes of all dendrimer and solvent segments to be the same, such that $\sigma_C = \sigma_D = \sigma_0 = \sigma$. Picard’s iteration method is applied to solve the set of Eq. 4.4 to find the equilibrium density profile.

4.3 Results and Discussion

4.3.1 Dendrimer in implicit solvent

We firstly investigate the case where an isolated dendrimer is immersed in implicit solvent. The simulation results of Murat and Grest[6] show that in the limit of implicit athermal solvent (equivalently, temperature being infinity and non-bonded interaction reducing to pure hard sphere repulsion), dendrimer segments exhibit pure repulsion and the solvent is considered a good solvent since the dendrimer is swollen. As the reduced temperature, $T^* = k_BT/\epsilon_{LJ}$ goes down, the solvent becomes poor and the dendrimer tends to collapse.

With iSAFT we are able to model the structure of dendrimer for the same conditions and make a direct comparison with the simulation. Fig. 4.3 shows radial monomer densities in the implicit athermal solvent from $G5$ to $G8$ with the densities offset by 0.1 for clarity. Overall, the theoretical results are in semi-quantitative agreement with the simulation data. Similar to simulation, the density from iSAFT reaches
Figure 4.3: Radial monomer densities of dendrimers in an implicit athermal solvent. The solid lines represent iSAFT results and the dotted lines are the simulation results of Murat and Grest[6]. Results for G6, G7 and G8 are shifted up by 0.1, 0.2 and 0.3, respectively.

a local minimum before \( r = 5\sigma \) though there is strong oscillation near the origin as a result of packing effect, which is characteristic of DFT methods. The density profile continues to grow and arrives at a region of almost constant density before it drops monotonically and vanishes. Simulation appears to show a slight density maximum where theory shows more even distribution of monomers. While the plateau is more apparent for higher generations from both methods, it is interesting to find that the heights of plateau for all generations are almost the same (\( \rho\sigma^3 \approx 0.1 \) from simulation and \( \rho\sigma^3 \approx 0.08 \) from iSAFT).

Concerning the differences between the theoretical and simulation results, it would
Figure 4.4: Contributions to the overall monomer density profile for G6 dendrimer in an implicit athermal solvent, due to monomers of generation \( g \). Solid lines represent iSAFT results and dotted lines are our MD results.

be instructive to look into the individual density distributions of monomer segments belonging to various generations. To obtain generation by generation density profiles from simulation, we have implemented our LAMMPS code for this system. As we see from Fig. 4.4, for inner generations (small \( g \)), a peak structure is typical, which indicates a relatively localized distribution. However, this kind of localization is not as apparent as that from simulation. From iSAFT, the density profile of every generation rises quickly near the origin and as a result, patterns of plateau structure appear as early as \( g2 \). On the other hand, in simulation, an additional shoulder is formed starting from \( g5 \). This may be accounted by the fact that in iSAFT, although
there is penalty associated with dense packing, there is no constraint on bond angle between segments. This also explains why the overall density profile from iSAFT is slightly flatter than simulation. However, it is clear to see that monomer segments belonging to the outer generations cover the whole range almost uniformly, which is the same case in simulation and confirmed by other works[130, 132, 134]. The folding back of outer generations indicate that although being compact, the dendrimer is quite flexible and open for penetration. We also make a comparison for the radial monomer densities from $G_5$ to $G_8$ at $T^* = 3$. Again, we find semi-quantitative agreement between theory and simulation, as shown in Fig. 4.5. Under this condition, the plateau

![Graph showing radial monomer densities of dendrimers at $T^* = 3$. The solid lines represent iSAFT results and the dotted lines are the simulation results of Murat and Grest[6]. Results for $G_6$, $G_7$ and $G_8$ are shifted up by 0.1, 0.2 and 0.3, respectively.](image)

Figure 4.5: Radial monomer densities of dendrimers at $T^* = 3$. The solid lines represent iSAFT results and the dotted lines are the simulation results of Murat and Grest[6]. Results for $G_6$, $G_7$ and $G_8$ are shifted up by 0.1, 0.2 and 0.3, respectively.
of the density profile from iSAFT is lower than that from simulation \( \rho \sigma^3 \approx 0.3 \) from iSAFT, \( \rho \sigma^3 \approx 0.35 \) from simulation) and wider as well. Individual density distributions of monomer segments belonging to various generations are depicted in Fig. 4.6. The break-down structure is similar to that under athermal conditions except that density profile of each generation is compressed and raised, corresponding to a partially collapsed structure. It should be mentioned that from simulation, \( T^* = 3 \) is identified as the \( \theta \) temperature (at which the dendrimer acts just like an ideal chain and the corresponding solvent is defined as the \( \theta \) solvent) while from iSAFT, it is more like a poor solvent condition. That is, the \( \theta \) temperature from iSAFT tends to be higher. It is also interesting to see how a dendrimer of specific generation behaves

---

**Figure 4.6: Contributions to the overall monomer density profile for G6 dendrimer at \( T^* = 3 \), due to monomers of generation \( g \).** Solid lines represent iSAFT results and dotted lines are our MD results.
differently in solvent of varying quality. In Fig. 4.7, we plot the monomer densities of $G_8$ for athermal condition, $T^* = 4$ and $T^* = 3$ respectively. As the quality of solvent becomes poorer, the dendrimer transitions from a swollen structure to a collapsed one. This is because the monomer segments prefer to aggregate to reduce contact with the solvents when the dendrimer-solvent interaction is unfavorable. With the

Figure 4.7: Radial monomer densities of $G_8$ dendrimers in solvents of varying quality. The solid lines represent iSAFT results and the dotted lines come from the simulation results of Murat and Grest [6].

monomer density profile we are able to calculate the radius of gyration of dendrimer $R_g$ from:

$$R_g^2 = \frac{\int \rho_D(r)r^4dr}{\int \rho_D(r)r^2dr}$$

(4.20)

Results of $R_g$ at different conditions are listed in Table 4.1
To implement some simple scaling analysis, we firstly fix the spacer number $n$ and vary the generation number $G$. As shown in Fig. 4.8, relationships of $R_g$ versus $N$ under different conditions are plotted in a double-logarithmic scale. Dendrimers of $G_5$ through $G_8$ are presented and for the athermal condition, we include $G_1$ to $G_4$ as well. Similar to the results of Murat and Grest[6], for the athermal case, a linear relationship is not formed until some large $G$. Following their way, only points of $G_5$ to $G_8$ are fit to the form $R_g = AN^v$. The value of $v$ is 0.32 for the athermal case and for $T^* = 2$, 0.33 for $T^* = 3$. Inverting the relation, we find $N \sim R_g^3$ for all the cases, which is also consistent with the conclusion of Murat and Grest.

However, as pointed out by several works[129, 130, 131, 132, 133, 134], the scaling law for dendrimers should behave in a more complicated way, and the form of $R_g \sim$
$N^{1/3}$ cannot apply to dendrimers at all conditions. A good way of testing is to repeat the above analysis with fixed generation number $G$ and varied spacer number $n$. $G$ is fixed at 5 in our analysis and the new scaling relation is plotted in Fig. 4.9. As the exact value of $\theta$ temperature is not determined, we only plot the athermal and $T^* = 2$ cases, which should well represent the good and poor solvent cases, respectively. The fitting line shows that $v = 0.61$ for the athermal case and $v = 0.33$ for $T^* = 2$. We also notice that at fixed $G$, the scaling law for good solvent, $R_g \sim N^{1/5}(G + 1)^{2/5}n^{2/5}$ by Sheng et al.[129] reduces to $R_g \sim N^{3/5}$ and the scaling law for poor solvent stays as $R_g \sim N^{1/3}$. The scaling exponents for both cases agree well and we believe the
Figure 4.9: Radius of gyration of the dendrimers as a function of the number of monomers in the dendrimer when generation number $G$ is fixed at 5, on a double-logarithmic scale. The points correspond to the calculated results from iSAFT and the full lines are best fits to the form $R_g = AN^v$.

iSAFT theory to provide meaningful and reasonable scaling of dendrimers. A more complete and systematic study is required to validate any scaling law. For example, dendrimers of a wider range of $G$ should be tested when varying $n$. However, that is not the focus of this work.

4.3.2 Dendrimer in explicit solvent

While the implicit solvent effect is successfully captured and well explained, it is a more realistic model when solvent exists explicitly. In iSAFT, explicit solvent is readily introduced into the system and unlike simulation methods, only little calculation
expense is added to the task. By tuning parameters in the model, we want to understand how both internal (size, density, chemical affinity) and external (temperature) factors have an impact on the solvent quality. Both low and high reduced solvent densities are considered. While the high liquid-like density system is quite common for dendrimer solutions, the low gas-like solvent system can model gas adsorption on dendrimer and provide insights on applications such as chromatography[136], sensor[137] and gas separation[138]. In addition, we learn from the implicit solvent case that dendrimers of different generations behave similarly at a given solvent condition. Therefore, the upcoming results and discussion are based on G5 dendrimers. For some systems, simulation results are provided from our molecular dynamics code.

Figure 4.10 : Density profiles of G5 dendrimer in solvents of different chain length. Solid curves represent dendrimer monomers and dashed curves represent solvent segments. For reference, the dendrimer density profile in implicit athermal solvent is also plotted. (a) $\rho_S \sigma^3 = 0.1$ at bulk. (b) $\rho_S \sigma^3 = 0.6$ at bulk.

We start with a dendrimer made up of hard sphere segments immersed in a hard chain solvent. At this athermal condition, all segments exhibit pure repulsion towards each other. Fig. 4.10a and Fig. 4.10b show the distribution of monomer and solvent
segments at fixed bulk density of solvent segments of 0.1 and 0.6, respectively. The chain length of solvent \( N_S \) ranges from 1 to 100 with bond length equal to \( \sigma \). The density profile of an athermal dendrimer in implicit solvent is plotted as well and it has a more extended structure than any of the explicit cases. The explicit solvent freely penetrates inside the dendrimer. At low solvent density (Fig. 4.10a), we notice that as the solvent chain grows longer, it is more difficult for solvent segments to migrate inside the dendrimer and the dendrimer tends to be more compressed. This is owing to the increased excluded volume of longer chains. A similar trend is observed at high density (Fig. 4.10b) while we see a more facilitated penetration for long chains, which may be accounted by a greater chemical potential exerted by the solvent at a higher bulk density. For both densities, in the case of spherical solvent \( (N_S = 1) \), the solvent density gradually declines from the bulk density when entering the dendrimer, and stays almost constant till near the origin. It is more clearly illustrated by Fig. 4.11a. Here the solvent length is fixed as 1 while bulk density is varied. The solvent density profiles show similar trends and the dendrimer structure is barely affected for any bulk density. On the contrary, in Fig. 4.11b, where the solvent length is 100, the solvent density profile takes a sharp drop and the dendrimer structure is very sensitive to the bulk density of solvent.

Now we introduce the attraction between dendrimer and solvent segments. \( \epsilon_{DD}^{LJ} \), \( \epsilon_{SS}^{LJ} \) and \( \epsilon_{DS}^{LJ} \) are the attraction energy between dendrimer segments, solvent segments, dendrimer and solvent, respectively. We assume \( \epsilon_{DD}^{LJ} = \epsilon_{SS}^{LJ} \) and a spherical solvent for all cases studied. \( \epsilon_{DS}^{LJ} \) is an indicator of the affinity between dendrimer and solvent segments. When \( \epsilon_{DS}^{LJ} = 0 \), there is only pure repulsion between dendrimer and solvent. When \( \epsilon_{DS}^{LJ} = \epsilon_{DD}^{LJ} \), there is no difference between a dendrimer segment and a solvent segment energetically. Fig. 4.12a and Fig. 4.12b show from simulation and theory how
Figure 4.11: Density profiles of G5 dendrimer in solvents at different bulk solvent densities. Solid curves represent dendrimer monomers and dashed curves represent solvent segments. (a) $N_S = 1$. (b) $N_S = 100$.

Figure 4.12: Density profiles of G5 dendrimer in spherical solvents of various affinity with dendrimer. $\beta\epsilon_{DD}^{LJ}$ is fixed as 1. Solid lines represent iSAFT results and dotted lines represent our simulation results. For clarity, density profiles of solvent segments are plotted in the inset with the same coordinates bounds and legends. (a) $\rho_S\sigma^3 = 0.1$ at bulk. (b) $\rho_S\sigma^3 = 0.6$ at bulk.
the structure of dendrimer varies for explicit solvent of different βϵ_{DS} with βϵ_{DD} fixed as 1. As βϵ_{DS} increases, we see a growing influx of solvent into the dendrimer and there is even some enhancement over bulk density at the dendrimer periphery. However, it is a bit surprising that at low density (Fig. 4.12a), the dendrimer still retains a relatively compressed conformation at βϵ_{DS} = 1. On the contrary, at high density (Fig. 4.12b), a well swollen structure is observed at βϵ_{DS} = 1. This finding seems to contradict what we have from Fig. 4.11a and Fig. 4.11b, that the dendrimer tends to be more extended under a lower bulk solvent density when all the other conditions are the same. A proper explanation is that the fluid structure is the result of the interplay between all segments. The attraction between dendrimer segments makes the dendrimer compact at low solvent density and the dendrimer likes to expand to avoid extremely dense packing inside the dendrimer when solvent is abundant. The agreement between iSAFT and simulation results is good except for the case of βϵ_{DD} = 1, βϵ_{DS} = 1 at ρ_σ = 0.1 (blue curve in Fig. 4.12a). The simulation results show a slightly more extended structure of dendrimer and much more enhanced absorption of solvents inside the dendrimer. Again, this is explained by the lack of intramolecular correlation in the iSAFT theory.

The different fluid structures at βϵ_{DD} = βϵ_{DS} = 0 and βϵ_{DD} = βϵ_{DS} = 1 (compare Fig. 4.11a and Fig. 4.12) can also be interpreted as a result of varying temperature for a specific dendrimer and solvent combination. To better understanding the temperature effect, we plot dendrimer-solvent density profiles at various temperatures.

In Fig. 4.13a and Fig. 4.13b, we set ϵ_{DD}/k_b = ϵ_{DS}/k_b = 150K. It shows that the solvent profile does not change much at different temperatures except for T = 150K at ρ_σ = 0.1, where there is apparent enhancement of density inside the dendrimer.
Figure 4.13: Density profiles of $G_5$ dendrimer in spherical solvents at different temperatures. $\epsilon_{DD}/k_b = \epsilon_{DS}/k_b = 150K$. Solid lines represent iSAFT results and dotted lines represent our simulation results. For clarity, density profiles of solvent segments are plotted in the inset with the same coordinates bounds and legends. (a) $\rho_S \sigma^3 = 0.1$ at bulk. (b) $\rho_S \sigma^3 = 0.6$ at bulk.

Figure 4.14: Density profiles of $G_5$ dendrimer in spherical solvents at different temperatures. $\epsilon_{DD}/k_b = 150K$, $\epsilon_{DS}/k_b = 0$. Solid lines represent iSAFT results and dotted lines represent our simulation results. For clarity, density profiles of solvent segments are plotted in the inset with the same coordinates bounds and legends. (a) $\rho_S \sigma^3 = 0.1$ at bulk. (b) $\rho_S \sigma^3 = 0.6$ at bulk.
The dendrimer generally shrinks as temperature decreases while it is not so obvious for the $\rho S \sigma^3 = 0.6$ case, because of the excess solvent inside the dendrimer. In Fig. 4.14a and Fig. 4.14b, we have $\epsilon_{DD}^{ij}/k_b = 150K$, $\epsilon_{DS}^{ij}/k_b = 0$. For all temperatures but the athermal case, where all attractions vanish, the density of solvent inside the dendrimer is reduced greatly due to the unfavored interaction between solvent and dendrimer. As temperature goes down, the separation between dendrimer and solvent becomes more apparent and we see a highly collapsed dendrimer structure. There is semi-quantitative agreement between iSAFT and simulation results except for the case of $\epsilon_{DD}^{ij}/k_b = \epsilon_{DS}^{ij}/k_b = 150K$, $T = 150k$ at $\rho S \sigma^3 = 0.1$ (purple curve in Fig. 4.13a), which is equivalent to the case mentioned before.

It is concluded that for the simple model system considered here, a higher temperature always leads to a higher solubility regardless of the affinity between dendrimer and solvent. However, this is not always the case in reality, since real dendrimers have more interactions (polar, electrostatic, hydrogen bonding, etc.) other than repulsion and dispersion. Incorporating these complex interactions and particularly, understanding the effect of association on dendrimer systems will be the focus of the next chapter.

4.4 Conclusion

We have applied iSAFT to study the conformation of dendrimer molecules in both implicit and explicit solvent. The density distribution of dendrimer in implicit solvent is in semi-quantitative agreement with the simulation data. The generation-by-generation density profile reveals the details of the dendrimer and segments of outer generations are free to fold back to form a dense-core structure. When solvents are explicitly included, we have a large parameter space to explore that can affect
the phase behavior of dendrimer. The solvent quality is affected by the solvent size, density, chemical affinity with dendrimer as well as temperature. Generally, solvents of smaller size and stronger interaction with dendrimer tend to be candidates for good solvents. If only dispersion is considered, a higher temperature always improves the solvent quality. The iSAFT results of dendrimers in explicit solvents are well validated by our simulation results. Compared with molecular simulation, iSAFT has the great advantage of computational efficiency and the future work will look into real applications, such as drug delivery.
Chapter 5

Modeling LCST Behavior of Associating Dendrimers Using Modified iSAFT

5.1 Introduction

Thermoresponsive polymers show sharp and reversible changes in conformations and properties near the lower critical solution temperature (LCST). In aqueous solution, these polymers hydrate and expand below the LCST while they collapse and form aggregates above the LCST. Polyethylene glycol (PEG)[139] and poly(N-isopropylacrylamide) (PNIPAM)[140] are the most often investigated thermoresponsive linear polymers. Nowadays, there is considerable interest in designing thermoresponsive dendritic polymers.[141, 142, 143, 144, 145, 146, 147, 148, 149, 150, 151] Dendritic polymers, unlike linear polymers, are highly branched and therefore, they have a specific spheroid-like shape and multi-functionality. Among all dendritic polymers, dendrimers are perfectly branched and well-defined. With the advantage of structural uniformity, thermoresponsive dendrimers are highly attractive for promising applications, such as drug delivery.[152, 153]

One of the first works for thermoresponsive dendrimers was carried out by Haba et al.[141], where they introduced isobutyramide (IBAM) groups to the chain ends of poly(amidoamine) (PAMAM) or poly(propyleneimine) (PPI) and successfully produced dendrimers with temperature-sensitive water solubility. They further found that LCSTs of IBAM-bearing PAMAM dendrimers varied with different generation
numbers, pH and concentrations. By modifying the terminal segments with functional
groups such as phenylalanine residues[142], Tono et al. successfully synthesized ther-
mosensitive dendrimers that were more suitable for use in biomedical fields. Later
Haba et al.[143] compared the thermosensitive properties of PAMAM dendrimers with
peripheral N-isopropylamide groups and linear polymers with the same functional
groups, and found that although they both featured LCST, there was marked differ-
ence in the transition enthalpy between the linear molecule and dendrimer molecule.
Liu et al.[144] compared the LCST behavior of polyethylenimines (modified with
IBAM) based dendrimers, hyperbranched polymers and linear polymers, and found
that LCSTs of dendrimers were not as sensitive to the molecular weight alteration as
hyperbranched polymer analogues, but more sensitive than linear analogues.

Instead of modifying terminal segments, Parrott et al.[147] encapsulated the hy-
drophobic carborane functionality within the interior of the dendrimer, and also im-
parted LCST behavior to an otherwise fully water-soluble structure. Xu et al.[148]
synthesized H40-poly(N-isopropylacrylamide)-poly(2-(dimethylamino)ethyl methacry-
late) (H40-PNIPAM-PDMA) which exhibited two-stage collapse because PNIPAM
and PDMA have different LCSTs.

These studies in preparing thermoresponsive dendrimers generally fall into two
different strategies. One is the incorporation of temperature responsive groups onto
dendrimers[148, 151] and the other is the grafting of both hydrophobic and hydrophilic
functionalities[141, 142, 143, 144, 147]. The spirits of two strategies are the same in
that the temperature sensitivity is induced as a result of competing interactions.
While the temperature responsive groups have both favorable and unfavorable in-
teractions with the solvent, the second strategy works as well with the appropriate
balance of hydrophilic and hydrophobic moieties.
In terms of applications, Li et al. [152] found that the PAMAM dendrimers modified with alkoxy diethylene glycol not only showed sharply changed surface properties between hydrophilic and hydrophobic at approximate human body temperature, but also had much lower cytotoxicity than that of their parent PAMAM dendrimers, making them a promising material to construct intelligent drug delivery systems. Kimura et al. [150] studied the catalysis activity for a temperature-sensitive dendritic host. The catalysis ability increased above LCST because the incorporated catalyst was accessible to substrates after the dendrimer shrank and in this way, the reaction was controlled by temperature.

Apart from the experimental design and property characterization of thermoresponsive dendrimers, there are also theoretical or simulation works for modeling of dendrimers [6, 130, 135, 87] or thermoresponsive polymers (and polymer brushes) [154, 155, 156, 77]. However, few of them are directly devoted to the study of thermoresponsive dendrimers. This work begins to fill this gap and brings insights to the molecular mechanism of thermoresponsive dendrimers. In last chapter, we have used inhomogeneous statistical associating fluid theory (iSAFT) to study the conformation of an isolated dendrimer in solvents of varying quality and found that the solvent size, density, chemical affinity and temperature all play a role in determining a solvent to be good or poor. [157] Those theoretical results reached semi-quantitative agreement with molecular simulation. An advantage of iSAFT is its ability to describe fluids with association, such as hydrogen bonding, which we believe is of the utmost importance in explaining thermoresponsive behavior of dendrimers. The association sites can be modeled at specific positions of the molecule and explicit bonding are expected within the association range. Therefore, in this work, we use iSAFT to model associating dendrimers and this chapter is organized as follows. In Sec. 5.2, we explain the
Figure 5.1: (a) Schematic of a dendrimer (blue) with a single associating site at each segment. (b) Schematic of a dendrimer (blue) with a single associating site at each inner segment. (c) Schematic of a dendrimer (blue) with a single associating site at each outer segment. For all cases, the solvent (pink) is spherical with a single associating site.

system of interest. In Sec. 5.3, we first explore the hydrogen bond effect on associating dendrimers and then dive into the LCST behavior. Within a vast parameter space, we focus on understanding how dendrimer generation, solvent size and association model would impact the phase behavior. Sec. 5.4 gives our conclusion.

5.2 Model and Theory

The system of interest is depicted as Fig. 5.1a. A single dendrimer is immersed into explicit solvents and the core of the dendrimer is fixed as the origin. The dendrimer molecule takes the same form as that in Chapter 4. So the functionality of branched segments is set as 3 and the spacer between the branched segments is set as 7. While the dendrimer of generation 1 ($G_1$) in Fig. 5.1a is already quite large, its size will increase exponentially as the generation increases. Solvent molecules are explicit and they may have favorable or unfavorable interactions with the dendrimer. The potential model again follows Sec. 2.2.1 and for the association interaction, the radial limits of square-well potential are set to $r_c = 1.05\sigma$ and the angular limit to $\theta_c = 27^\circ$.

With the only difference being the addition of association contribution, the same
formalisms as that in Chapter 4 can be applied. We will not repeat the equations, but present an alternative or probably more rigorous derivation here. It is known that traditional iSAFT DFTs are formulated for an open system in the grand canonical ensemble with fixed volume \((V)\), temperature \((T)\) and chemical potential \((\mu)\). The grand free energy is minimized at equilibrium. However, the system in our study is different from the traditional iSAFT DFT since the number of dendrimer segments is fixed. Therefore, it is more accurate to name such a system as a semi-canonical ensemble where \(V, T, M_D\) (number of dendrimer segments), and \(\mu_S\) (chemical potential of solvent) are fixed. In this semi-canonical ensemble, the equilibrium density profile of polymer and solvent is obtained by minimizing the semi-canonical free energy functional

\[
A' \left[ \rho_i(r) \right] = A \left[ \rho_i(r) \right] + \sum_i \int d\mathbf{r} \rho_i(r) V_{i}^{ext}(\mathbf{r}) - \int d\mathbf{r} \rho_S(\mathbf{r}) \mu_S
\]  

(5.1)

Note that we will use \(D\) and \(S\) as subscripts to represent the properties for dendrimer or solvent. The constraint on the number of dendrimer segments is give by

\[
\int d\mathbf{r} \rho_D(\mathbf{r}) = M_D
\]  

(5.2)

By using the Lagrange multiplier technique, we construct the free energy functional as

\[
A \left[ \rho_i(r) \right] + \sum_i \int d\mathbf{r} \rho_i(r) V_{i}^{ext}(\mathbf{r}) - \int d\mathbf{r} \rho_S(\mathbf{r}) \mu_S - \mu_D \left[ \int d\mathbf{r} \rho_D(\mathbf{r}) - M_D \right]
\]  

(5.3)

where \(\mu_D\) is the “chemical potential” of the dendron (the branch that originates from the central core) imposed by the tether condition that there are three such dendrons.
It is in fact the same $\mu_D$ as that in Eq. 4.3 and Eq. 4.4.

By minimizing the above functional with respect to $\rho_i$, we can obtain

$$\frac{\delta A[\rho_i(r)]}{\delta \rho_D(r)} + V_{\text{ext}}^D(r) - \mu_D = 0 \quad (5.4)$$

$$\frac{\delta A[\rho_i(r)]}{\delta \rho_S(r)} + V_{\text{ext}}^S(r) - \mu_S = 0 \quad (5.5)$$

There are three equations ((5.2),(5.4),(5.5)) with three unknown variables $\rho_D$, $\rho_S$, and $\mu_D$. To obtain the density profiles of each component, we solve these equations simultaneously. The numerical algorithm is the same as in Chapter 4. Note that due to the spherical symmetry of the dendrimer structure, all segment densities are again only functions of radial distance from the center core.

### 5.3 Results and Discussion

#### 5.3.1 Effect of hydrogen bonding on dendrimer structure

To model the effect of hydrogen bonding on dendrimer structure, we firstly adopt the basic association scheme: each dendrimer or solvent segment has one association site and it is limited to bond at most once; association is only possible between a dendrimer segment and solvent segment (see Fig. 5.1a). For simplicity, we set $\epsilon_{DD}/k_b = \epsilon_{SS}/k_b = 150\text{K}$, $\epsilon_{DS}/k_b = 0$ and $\epsilon_{SS}^{assoc}/k_b = 2700\text{K}$. The association energy is similar in magnitude to energies used to model association of alcohols. As shown in Fig. 5.2, at $T = 300\text{K}$, the dendrimer G5 collapses when there is no association and expands with the association on for both low ($\rho_S\sigma^3 = 0.2$, corresponding to a dense gas) and high ($\rho_S\sigma^3 = 0.6$, corresponding to a liquid) solvent densities. This significant change demonstrates that existence of hydrogen bonding is likely to change
the quality of solvent, and in this example, association between dendrimer and solvent results in a good solvent. Similar behaviors are observed from experiments of Chai et al. [128] where they found that DAB (poly-(propylene imine)) would swell in chloroform solutions but collapse in benzene.

Instead of having one association site at each dendrimer segment, it is possible to design a nonuniform distribution of association sites. Particularly, it is of experimenters’ interest to understand how different layouts of functional groups would impact the material properties. Therefore, we also study the case where only the inner segments (excluding the segments of outermost shell) have an associating site per segment (the inner-sites model, see Fig. 5.1b) and the case where only the outer segments (segments of outermost shell) have an associating site per segment (the outer-sites model, see Fig. 5.1c). While the outer-sites model have more associating sites than the inner-sites model, the margin is relatively small compared to the total

Figure 5.2 : Density profiles of G5 dendrimer in spherical solvents at $T = 300K$. $\epsilon_{DD}^{LJ}/k_b = \epsilon_{SS}^{LJ}/k_b = 150K$, $\epsilon_{DS}^{LJ}/k_b = 0$. $\epsilon_{DS}^{assoc}/k_b = 2700K$ when association is on and $\epsilon_{DS}^{assoc}/k_b = 0$ when association is off. Solid curves represent dendrimer monomers and dashed curves represent solvents. (a) $\rho_S \sigma^3 = 0.2$ at bulk. (b) $\rho_S \sigma^3 = 0.6$ at bulk.
numbers of sites when the generation number is high. For reference, we name the dendrimer in Fig. 5.1a as full-sites model. From Fig. 5.3, we see that at 300K, these three different $G_5$ dendrimers (full-sites, inner-sites and outer-sites) show quite different conformations with the same parameters. It is understandable that the full-sites dendrimer would have the most extended conformation because it has nearly twice the number of associating sites compared with the other two dendrimers. What we also find is that the inner-sites dendrimer forms a dense-shell structure and the outer-
sites dendrimer forms a dense-core structure. The controversy of a dendrimer being a dense-shell structure or dense-core structure has been around for decades and it is agreed that the answer varies case by case, depending on the design of dendrimer and also the solvent.[135, 158, 159, 160, 161, 87] While most past studies are focused on amphiphilic dendrimers,[160, 87] this study shows that by imparting hydrogen bonding type interaction at different regions of dendrimer, it is also possible to observe these two different structures.

Figure 5.4: Density profiles of G5 dendrimer in associating spherical solvents at different temperatures. $\epsilon_{DD}^{LJ}/k_b = \epsilon_{SS}^{LJ}/k_b = 150K$, $\epsilon_{DS}^{LJ}/k_b = 0$, $\epsilon_{assoc}^{DS}/k_b = 2700K$, $\rho_S \sigma^3 = 0.2$ at bulk. Solid curves represent dendrimer monomers and dashed curves represent solvents.
In last chapter, we found that if we only consider dispersion, a higher temperature always improves the solvent quality regardless of the affinity between the dendrimer and solvent.[157] Here in Fig. 5.4, we show how temperature affects the system when dispersion and association both exist. We use the full-sites $G_5$ dendrimer and it is found that the dendrimer collapses when temperature is raised from 300K to 450K and becomes less compressed at $T = 600$K. As the temperature goes to infinity, which is the athermal (AS) condition, a fully swollen structure is recovered. This finding is fascinating since it indicates that presence of multiple interactions might cause complex phase behavior.[162, 163, 164] The temperature dependence of this model system can be likened to a dendrimer solution that features both lower critical solution temperature (LCST) and upper critical solution temperature (UCST) with a closed-loop. That is, the solution is miscible for all compositions at low and high temperatures but is prone to phase separation at intermediate temperatures. Unlike LCST behavior, no UCST behavior of dendrimers has been reported yet from literature. It is possible that the dendrimer would decompose before the transition occurs despite that UCST exists theoretically. Therefore, we focus on LCST behavior of dendrimers for the following sections and we stick with the full-sites model for the upcoming results and discussions.

5.3.2 LCST of associating dendrimers

Even the lower critical solution temperature is not that easy to find. LCST is generally believed to be a first order transition and normally a discontinuity or a sharp change in solubility-related properties as the temperature varies would be an indicator of LCST transition, such as the transmittance of solution. We experiment with different combinations of parameters and end up with the following parameter values
Figure 5.5: Results for a full-sites G6 dendrimer in an associating solvent. (a) Density profiles of G6 dendrimer and solvent segments at $T = 282$K. (b) Density profiles of G6 dendrimer and solvent segments at $T = 286$K. (c) Density profiles of bonded dendrimer and solvent segments at $T = 282$K. (d) Density profiles of bonded dendrimer and solvent segments at $T = 286$K. (e) Schematic of swollen dendrimer with solvents. (f) Schematic of collapsed dendrimer with solvents. Other parameters are fixed: $\epsilon_{DD}^{LJ}/k_b = \epsilon_{SS}^{LJ}/k_b = 250$K, $\epsilon_{DS}^{LJ}/k_b = 0$, $\epsilon_{DS}^{assoc}/k_b = 2700$K, $\rho_S\sigma^3 = 0.6$ at bulk.
in search of LCST: $\epsilon_{DD}^{LJ}/k_b = \epsilon_{SS}^{LJ}/k_b = 250K$, $\epsilon_{DS}^{LJ}/k_b = 0$ and $\epsilon_{assoc}^{DS}/k_b = 2700K$. In addition, the bulk solvent density is fixed at 0.6.

For a full-sites $G6$ dendrimer in this type of system, we find that at $T = 282K$, the dendrimer is relatively swollen and there is a substantial amount of solvent inside the interior of dendrimer (Fig. 5.5a). However, as temperature increases to $T = 286K$, we see a dramatic change of the conformation of dendrimer as the dendrimer collapses. Also, the solvent is depleted in the dendrimer (Fig. 5.5b).

The collapse of the dendrimer is due to the LJ attraction between dendrimer segments combined with the unfavorable LJ interaction between dendrimer and solvent segments. When temperature is low, the association between dendrimer and solvent works as a counter force and contributes to the solvation of the dendrimer. As temperature increases, the association between the dendrimer and solvents weakens, and the LJ interaction becomes the dominant factor that makes the dendrimer collapse.

In the interior region of a swollen dendrimer, as we can see from Fig. 5.5c, a substantial amount of dendrimer and solvent segments are bonded. In this case, the association interaction dominates the system and the solvents can easily penetrate inside the dendrimer. By comparison, Fig. 5.5d shows that at $T = 286K$, association only occurs in a very narrow range, at the periphery of the dendrimer. Fig. 5.5e and Fig. 5.5f show the schematics of dendrimer structures at low and high temperatures respectively.

To quantify the structure of dendrimer, we calculate the radius of gyration $R_g$ from Eq. 4.20. For the transition region, we firstly start at a lower temperature with a swollen structure, gradually increasing the temperature and getting a series of swollen structures until the dendrimer collapses. We then start at a higher temperature with a collapsed dendrimer structure, gradually decreasing the temperature
Figure 5.6: $R_g^2$ hysteresis of G6 dendrimer in associating spherical solvents.

and getting a series of collapsed structures until the dendrimer swells. Fig. 5.6 shows the radius of gyration for all these structures. At several temperatures, there are both swollen and collapsed structures so there forms a hysteresis loop. To figure out which structure is actually the stable one at a specific temperature and to pinpoint the exact transition temperature, we calculate the free energy for each state. The semi-canonical free energy difference for two structures versus temperature is plotted in Fig. 5.7. At temperatures lower than 284K, the swollen structure has a lower free energy than the collapsed structure and is the stable one. At temperature higher than 284K, the free energy of collapsed structure is lower, so the dendrimer would collapse. Therefore, for this system, LCST is around 284K. Without using any em-
Figure 5.7: Difference in semi-canonical free energy between the swollen and collapsed structures versus temperatures for $G_6$ associating dendrimer.

empirical temperature dependent parameter, our theory successfully captures the LCST behavior of hydrogen bonding dendrimers. Also note that the formation of hysteresis loop is affected by the step size and error tolerance of the calculation, which may not be found in experiments.

We further study how the generation number of dendrimer would affect the LCST. For dendrimers $G_1$ to $G_3$, there is no apparent LCST transition behavior. This is consistent with the study of Haba et al. [141], where no LCST was observed for lower generations. The LCST of $G_4$ is 306K, and for both $G_5$ and $G_6$, the LCST is 284K. This trend is not quite the same as that of experiments. While Haba et al. [141] found
that LCST decreases as the generation grows, in the study of Parrott et al. [165], LCST of dendrimers showed non-monotonic change with different generations. Considering the different designs for the dendrimers in those experiments and also in our model, we conclude that properties of thermoresponsive dendrimers will be highly dependent on the structures and compositions of the molecules.

Instead of changing the dendrimer size by changing the generation number, we can also model how the LCST varies when the solvent size changes, such as the chain length of a linear solvent. To keep the same amount of bonding sites, each segment of the solvent has a single associating site that can interact with the dendrimer. From Fig. 5.8b we see that when solvent chain length increases, LCST decreases. This trend can be accounted by the entropic effect of the solvents of different sizes. As the solvent molecule gets larger, there must be more favorable energetic gain for the dendrimer to swell, leading to a lower LCST.

Figure 5.8: (a) LCST as a function of dendrimer generation number. Solvent is spherical. (b) LCST as a function of solvent length. Dendrimer is of G5. Other parameters are the same with Fig. 5.7.
5.3.3 Self-association of solvent

In this section, we consider the case that solvent molecules have self-association. This is often the case in real systems. For example, a water molecule is often modeled with either two, three or four association sites with two different types of association sites A and B representing hydrogen or oxygen sites. A site can associate with B site. For our system we consider a two-sites solvent molecule with one A site and one B site. A site can also associate with the C site on the dendrimer. However, no association occurs between B site and C site. While keeping all the other parameters the same as in previous cases, we vary the self-association energy parameter between A site and B site $\epsilon_{AB}^{assoc}$ and see how that affects the phase behavior of the dendrimer at different temperatures.

From Fig. 5.9 we see that for dendrimer of G5, as the self-association strength $\epsilon_{AB}^{assoc}$ increases but still lower than $\epsilon_{AC}^{assoc}$, LCST decreases. This is because of the competition between B site of solvent and C site of dendrimer in associating with the A site of solvent. Fig. 5.10 shows the bonded density profile for those sites at different temperatures. The dendrimer is swollen at 275K and collapsed at 280K. Since $\epsilon_{AB}^{assoc} < \epsilon_{AC}^{assoc}$, site B is less active where dendrimer segments exist, but the introduction of competition tends to drive LCST to the lower temperature. Actually, when we further increase $\epsilon_{AB}^{assoc}$ beyond $\epsilon_{AC}^{assoc}$, the dendrimer would be highly collapsed at all temperatures and the solvents are completely depleted from the dendrimer, and no LCST behavior is observed.
Figure 5.9: LCST of G5 dendrimer for spherical solvents of different self-association energy $\epsilon_{\text{assoc}}^{A_B}$. $\epsilon_{DD}^{LJ}/k_b = \epsilon_{SS}^{LJ}/k_b$ = 250K, $\epsilon_{DS}^{LJ}/k_b = 0$, $\epsilon_{AC}^{\text{assoc}}/k_b$ = 2700K, $\rho_S \sigma^3$ = 0.6 at bulk.

5.4 Conclusion

Understanding the effect of association, such as hydrogen bonding, on the conformation of dendrimers is of great importance for thermoresponsive material design. In this study, we have applied iSAFT to study the structure of a single dendrimer in explicit solvents and found that the inclusion of association will lead to interesting phase behavior that are not observed if only dispersion is considered. The solubility of dendrimer in solvents can be tuned by the association and dispersion strength, and both dense-core and dense-shell conformations of dendrimers can form depending
Figure 5.10: (a) Density profiles of bonded dendrimer and solvent sites at $T = 275K$. (b) Density profiles of bonded dendrimer and solvent sites at $T = 280K$. $\epsilon_{DD}/k_b = \epsilon_{SS}/k_b = 250K, \epsilon_{DS}/k_b = 0, \epsilon_{AC}^{assoc}/k_b = 2700K, \epsilon_{AB}^{assoc}/k_b = 1000K, \rho_S\sigma^3 = 0.6$ at bulk.

on the molecular design. We have also captured the LCST behavior of associating dendrimers at high generations and explored the parameters (i.e., solvent size, self-association of solvent) that can affect the phase behavior. LCST is found to decrease as the solvent size increases or the self-association strength of solvent increases. These results demonstrate iSAFT’s capability to model the hydrogen bonding effect of dendrimer systems and provide guidance in the design and synthesis of real materials.
Chapter 6

Density Functional Study of One- and Two-Component Bottlebrush Molecules in Solvents of Varying Quality

6.1 Introduction

Bottlebrush polymers are another type of branched polymers with increasing research focus. As introduced in Sec.1.1.2, a typical bottlebrush polymer has polymeric side chains attached to a linear polymer backbone. Applications of bottlebrush polymers are wide-ranging; these include photonic materials, lithographic patterning, drug delivery, and tumor detection and imaging.[15]

There have been a few theoretical and simulation studies concerning the conformation of bottlebrush polymers.[166, 167, 168, 169, 170, 171, 172, 173, 174, 175, 176, 177, 178, 179, 180, 45] Emphasis has been laid on both backbone and side chain conformations. Properties concerning backbones include but are not limited to contour length, persistence length and radius of gyration. For the side chain conformations, most interest has been shown in side chain layer thickness and radius of gyration. Backbone and side chains strongly influence each other.[169, 181, 173, 179] For instance, as the grafting density of the side chains increases, the intrinsically flexible backbone is forced into an extended conformation. At the same time, the conformational changes of side chains due to varying solvent quality show different patterns if the backbone itself can extend or contract at various solvent strength. Among all
the models, it is interesting to consider a rigid backbone, which allows a thorough
study of side chain conformations. Although somewhat simplified, the parameter
space remains vast and makes the problem nothing near simple.

One pioneering work under this assumption is the work of Ball et al.[166] in 1991.
They used self-consistent field theory to study the conformations of side chains in melt
conditions and found that the end segments of side chains are excluded from a zone
near the grafting surface. In contrast, Murat and Grest[167], who applied molecular
dynamics simulation for a good solvent case, found no evidence for the existence of
such a “dead zone”. In the following year, Dan and Tirrell[44] utilized self-consistent
field analysis and made an effort to resolve the discrepancies between the two previous
works. They succeeded to some extent but also posted several new results. Later,
Denesyuk[170] used a variational approach with mean-field approximation to calculate
the dominant trajectories of side chains, and found that the segment density in the
center of backbone was only slightly lower than that calculated near the backbone
ends and local properties of bottle-brush polymers were fairly homogeneous. Sheiko
et al.[171] identified different regions of conformations that side chains would fall in.
At low grafting density, the side chains would not overlap with each other. So they
behave like Gaussian coil in good solvent condition and individual globules in poor
solvent condition. At higher grafting density, the side chains would interact with each
other strongly. They become swollen brushes in good solvent and collapsed brush or
pearl-necklace clusters under poor solvent conditions. This classification of different
states has been confirmed by the molecular dynamics simulations of Theodorakis et
al.[176] and they further found that the transition between stretched and collapsed
brushes occurred in a rather gradual manner.

Recently, researchers have paid more attention to the design and synthesis of bot-
tlebrush polymers with side chains consisting of multiple components. As discussed in the review paper of Zhang and Muller[182], popular two-component bottlebrush polymers include block-type, mixed-type and core-shell-type. A block-type bottlebrush polymer has side chains of the same component in a certain range of the backbone while a mixed-type bottlebrush polymer has side chains of both components mixed along the backbone. Depending on the distribution of the two different side chains, their interaction parameters, and the nature of the solvent, side chains of a mixed-type bottlebrush polymer can segregate into two different hemicylinders and these mixed-type bottlebrush polymers are also classified as Janus-type. What these two designs of two-component bottlebrush polymers have in common is that although there are two different components that form the side chains, within a single chain, there is only one component. By contrast, for the core-shell bottlebrush polymer, each side chain is actually the same, but contains blocks of two components.

Due to the distinct properties of components and peculiar structure of the molecule, two-component bottlebrush polymers have diverse applications. In the study of Hong et al.[183], thin films were formed from self-assembly of block-type bottlebrush polymers. Porous templates and scaffolds were further obtained by selective etching of one component. Mixed-type bottlebrush polymers (no Janus structure forming) with hydrophobic polystyrene (PS) and hydrophilic poly(ethylene glycol) (PEG) side chains were synthesized by Li et al.[184] and displayed different surface properties in selective solvents, showing potential as stimuli-responsive coatings. Amphiphilic core-shell bottlebrush polymers may be potentially utilized as unimolecular micelles, have advantages over the conventional micelles from linear amphiphilic diblock copolymers.[185, 186, 187]

Again, with the assumption of a rigid backbone, several theoretical and simulation
studies have been devoted to the study of side chain properties of two-component bottlebrush polymers. Theodorakis et al. [178] used Molecular Dynamics simulation to study the side chain conformations of a Janus-type bottlebrush polymer. They considered a symmetric binary system and found that chains of two different components collapsed independently at low grafting density but formed a Janus dumbbell-type structure at high grafting density. Erukhimovich et al.[180] studied the same type of system and further explored how solvent quality would affect the competition between the tendency of microphase separation to develop periodic order in axial direction and the tendency to form a Janus-type structure. Polotsky et al.[175] used self-consistent field approach to study the structure of core-shell bottlebrush polymer with a solvophobic inner block and a solvophilic outer block. They found that a decrease in the solvent strength for the core block leads to an instability in the cylindrically uniform structure and the appearance of longitudinal undulations in the collapsed core, in agreement with their experimental observations.

To the best of our knowledge, no density functional approaches have been applied to the bottlebrush-type molecules. Therefore, in this work, we extend iSAFT to study the conformations of side chains of a bottlebrush polymer in implicit solvents of various quality. We have also performed molecular dynamics simulations using LAMMPS to justify the iSAFT results. For clarity, simulation details are included in the appendix A.2.

The chapter is organized as follows. In Sec. 6.2, we develop the iSAFT formalism for a cylindrically symmetrical bottlebrush polymer model. In Sec. 6.3, we model the side chains of a bottlebrush polymer in implicit solvent and explore the effect of varying different parameters on chain conformations. Scaling analyses are performed for both good and poor solvent. We also extend the model to a core-shell bottlebrush
polymer and study how varying the chain length of different components would change the molecular structure. Sec. 6.4 gives our conclusion.

6.2 Model and Theory

We assume that the backbone is a rigid hard rod of infinite length. The side chains are uniformly distributed on the surface of backbone and each of them is modeled as a flexible chain of tangentially bonded segments. The density of side chain segments is assumed to vary only along the direction perpendicular to the axis of the backbone, which is set as the origin. As depicted in Fig. 6.1, structural parameters of this model include the grafting density of side chains $\rho_g$, length of side chains (or equivalently, number of side chain segments) $N$, radius of backbone $R_b$ and diameter of segment $\sigma$, which is temperature-independent. The center of tethered segment is right at

Figure 6.1 : Schematic of bottlebrush polymer model.
the backbone surface. The interactions between segments follow the same potential model as in Sec. 2.2.1 except that a different $r_c = 3.5$ is used for the attraction part. Association is not considered here.

To derive the segment density of side chains, we follow Fig. 6.1 to denote segments. Though bottlebrush polymer is highly branched, its side chains are just linear. Therefore, there is no need to treat any branching segment.

The external field exerted by the backbone surface on the tethered segment 1 is

$$V^{\text{ext}}_1(r) = \begin{cases} u & \text{if } r = R_b \\ \infty & \text{otherwise} \end{cases} \quad (6.1)$$

and for other segments

$$V^{\text{ext}}_i(r) = \begin{cases} \infty & \text{if } r < R_b + \sigma/2 \\ 0 & \text{otherwise} \end{cases} \quad (6.2)$$

The density of side chain segments can be expressed as follows. For segment 1,

$$\rho_1(r_1) = \exp(\beta \mu_M - \beta u) \exp[D_1(R_b)] I_{1,1}(R_b) I_{2,1}(R_b) \delta(r_1 - R_b) \quad (6.3)$$

The delta function $\delta(r_1 - R_b)$ accounts for the fact that segment 1 is tethered at the surface and for the other monomer segments $i = 2, \ldots, N$,

$$\rho_i(r_i) = \exp(\beta \mu_M - \beta u) \exp[D_i(r_i)] I_{1,i}(r_i) I_{2,i}(r_i) \quad (6.4)$$

where $\mu_M$ is “chemical potential” of the whole chain imposed by the tether condition.
Similarly, $I_{1,i}$ and $I_{2,i}$ are multiple integrals to facilitate solving the Euler-Lagrange equations for linear chains[72] . The integrals are solved using the following recurrence:

$$I_{1,1}(R_b) = 1,$$  \hspace{1cm} (6.5)

$$I_{1,2}(r_2) = \exp[D_1(R_b)]\Delta^{(1,2)}(R_b, r_2)$$ \hspace{1cm} (6.6)

$$I_{1,i}(r_i) = \int I_{1,i-1}(r_{i-1}) \exp[D_{i-1}(r_{i-1})] \Delta^{(i-1,i)}(r_{i-1}, r_i) dr_{i-1} \hspace{1cm} (6.7)$$

and

$$I_{2,n}(r_n) = 1,$$ \hspace{1cm} (6.8)

$$I_{2,i}(r_i) = \int I_{2,i+1}(r_{i+1}) \exp[D_{i+1}(r_{i+1})] \Delta^{(i,i+1)}(r_i, r_{i+1}) dr_{i+1} \hspace{1cm} (6.9)$$

$$I_{2,1}(R_b) = \int I_{2,2}(r_2) \exp[D_2(r_2)] \Delta^{(1,2)}(R_b, r_2) dr_2 \hspace{1cm} (6.10)$$

The total density of side chain segments is calculated as

$$\rho_M(r) = \sum_{i=1}^{N} \rho_i(r) \hspace{1cm} (6.11)$$

The value of $\exp(\beta \mu - \beta u)$ can be obtained from the grafting density $\rho_g$ as

$$\int \rho_1(r_1) dr_1 = \exp(\beta \mu - \beta u) \exp[D_1(R_b)] I_{1,1}(R_b) I_{2,1}(R_b) = \rho_g \hspace{1cm} (6.12)$$

then we have

$$\exp(\beta \mu - \beta u) = \frac{\rho_g}{\exp[D_1(R_b)] I_{1,1}(R_b) I_{2,1}(R_b)} \hspace{1cm} (6.13)$$

Substituting the equation into Eq. 6.4 gives the density profile of all the other monomer segments. In this work, the radius of backbone $R_b$ is set to be the same as
Figure 6.2: Density profiles of (a) all segments (b) end segment of side chains in solvents of varying quality. $\rho_g = 0.3$, $N = 50$. The solid lines represent iSAFT results and the dotted lines represent simulation results.

We see that the final expressions are very similar and even simpler to that of dendrimer system. However, the cylindrical geometry does post challenges for the solving procedure. The density profile is still solved using Picard’s iteration method while a Fast Hankel Transformation Algorithm is applied to facilitate the iterative evaluation of convolutions, with more details in appendix B.

6.3 Results and Discussion

6.3.1 Bottlebrush polymer in implicit solvent

We start with a grafting density $\rho_g = 0.3$. To find the effect of solvent quality on side chain conformations, we also fix the segment number $N = 50$. As we can see from the Fig. 6.2a, the conformation of side chain transitions from a collapsed structure to a swollen structure as the reduced temperature $T^* = k_b T / \epsilon_{\text{LJ}}$ increases. At athermal
Figure 6.3: Density profiles of all segments for side chains of different length $N$ at (a) athermal condition (b) $T^* = 1$. $\rho_g$ is fixed at 0.3. The solid lines represent iSAFT results and the dotted lines represent simulation results.

condition, which is equivalent to temperature being infinitely high, the side chains are fully swollen, indicating a good solvent. There is good agreement between theoretical and simulation results. We see that iSAFT is also able to predict the oscillation behavior of density profile near the backbone surface, with similar period and number of peaks. Another advantage of iSAFT is that densities of all individual segments are traceable. Fig. 6.2b gives the density profiles of the end segments of side chains at different conditions. Besides the semi-quantitative agreement between theory and simulation, we also see that there are end segments in contact with the backbone and no “dead zone” or “exclusion zone” occurs. This is consistent with the finding of Murat and Grest[167].

Then we would like to see the effect of side chain length $N$ on the conformation of side chains. As shown in Fig. 6.3, whether it is good or poor solvent, an increase in side chain length will mainly result in a horizontal stretch of the density profile and the peak height is almost the same for the same solvent quality. However, we do see a
Figure 6.4: Density profiles of all segments for side chains of different grafting density $\rho_g$ at (a) athermal condition (b) $T^* = 1$. $N$ is fixed at 50. The solid lines represent iSAFT results and the dotted lines represent simulation results.

lower peak height for the density profile of $N = 25$ at $T^* = 1$ compared to the others in Fig. 6.3b, more obviously from the simulation curve. The reason behind may be that the combination of $N = 25, \rho_g = 0.3$ has shifted from a high graft density region to an intermediate density region, and the side chains may assume a different type of conformation.[171, 176]

The effect of grafting density $\rho_g$ on the conformation of side chains can be studied similarly. As shown in Fig. 6.4, with an increase of $\rho_g$, the density profile mainly heightens in athermal case but widens at $T^* = 1$. This is because when the side chains are swollen in a good solvent, they are fully stretched and there is enough space to accommodate more chains. However, in a poor solvent, the sides chains are collapsed and densely packed near the backbone, and addition of new chains have to push segments further away from the surface. Simulation data of $\rho_g = 0.7$ is unavailable because it is rather difficult to graft on such a high density surface. But it is no problem for iSAFT and we see an overall good agreement between theory and
available simulation results.

With the density profile, the average brush height of side chains (or layer thickness) \( \langle h \rangle \) can be calculated from

\[
\langle h \rangle = \frac{\int \rho(r)r^2dr}{\int \rho(r)rdr}
\]  (6.14)

Scaling theory predicts that the scaling variable for \( \langle h \rangle \) changes with solvent quality. For sufficiently large grafting density, the average height \( \langle h \rangle \) is dependent on both grafting density \( \rho_g \) and chain length \( N \). It is predicted that for good solvent, \( \langle h \rangle \sim N^{3/4}\rho_g^{1/4} \) and for poor solvent, \( \langle h \rangle \sim N^{1/2}\rho_g^{1/2} \). Fig. 6.5 shows that iSAFT agrees with these scaling relations.

Figure 6.5: (a) Average Brush height \( \langle h \rangle \) vs \( N^{3/4}\rho_g^{1/4} \) at athermal condition for combinations of \( \rho_g = 0.3, 0.5, 0.7 \) and different side chain length. (b) Average Brush height \( \langle h \rangle \) vs \( N^{1/2}\rho_g^{1/2} \) at \( T^* = 1 \) for combinations of \( \rho_g = 0.3, 0.5, 0.7 \) and different side chain length. Symbols of different shapes are theoretical results at different \( \rho_g \). Dashed curves are linear fits to the data.
Figure 6.6: Density profiles of segments A and B (blue and red lines) when block A is tethered to the backbone. Number of segment A $N_A$ is fixed at 25 and number of segment B $N_B$ is 5 in (a), 15 in (b) and 25 in (c). Other parameters: $\rho_g = 0.3, \epsilon_{AA} = 1, \epsilon_{BB} = 0, \epsilon_{AB} = 0$.

### 6.3.2 Core-shell bottlebrush polymer in implicit solvent

It is easy to extend iSAFT to study the two-component bottlebrush polymer, especially in the case of core-shell bottlebrush polymer since it will usually only have one dimensional density variance. We will study this design in this study and consider the other two for future work.

As for the two types of segments, it is common practice to have one segment as solvent-philic and have the other segment as solvent-phobia. Therefore, for a diblock AB side chain, we set that the interaction energy between segments are $\epsilon_{AA} = 1$, $\epsilon_{BB} = 0$ and $\epsilon_{AB} = 0$. This means that for segment A, the solvent is poor ($T^* = 1$) while for segment B, the solvent is good (athermal). Both diameters of segment A and B are $\sigma$.

We firstly model the case where block A is tethered to the backbone. We fix the number of A segments $N_A = 25$ and vary the number of B segments $N_B$. As we see in Fig. 6.6, the segments of A block are compressed near the surface and we see a extended conformation of block B starting from where A segments vanish. As
we vary $N_B$, there is hardly any change in the conformation of block A but a more stretched structure for block B due to the increase of chain length. It indicates that A segments will simply hide inside the bottlebrush polymer, shielded by the outer layer of B segments.

Then we switch the roles of block A and B, tethering block B to the backbone. Similarly, we fix the number of B segments $N_B = 25$ and vary the number of A segments $N_A$. When $N_A = 5$, we see that A block folds back towards the surface and it is partly shielded by B block. As $N_A$ increases, A block starts to migrate to the exterior of bottlebrush polymer, forming a more and more compressed layer. Although there are still a few B segments around, we see an overwhelming dominance of A segments at the outer layer. These different conformations of side chains are illustrated in Fig. 6.7. In this system, A block is solvent-phobic and would rather stay near the backbone to hide from solvent, while B block likes contact with the solvent. This is the enthalpic effect. On the other hand, folding back of A block creates a region with high density and limits the mobility of B block, resulting in

![Figure 6.7](image)

Figure 6.7: Density profiles of segments A and B (blue and red lines) when block B is tethered to the backbone. Number of segment B $N_B$ is fixed at 25 and number of segment A $N_A$ is 5 in (a), 15 in (b) and 25 in (c). Other parameters: $\rho_g = 0.3, \epsilon_{AA} = 1, \epsilon_{BB} = 0, \epsilon_{AB} = 0$. 
a larger entropic penalty. The different structures presented in Fig. 6.7 are a result of the competition between the enthalpic effect and entropic cost, aiming to reach a minimum free energy.

If we want to study the surface properties of such a core-shell bottlebrush polymer, it is important to know the compositions of the outer layer, and that can be highly dependent on the design of the side chains. In this example, the surface properties of bottlebrush polymers can be B-like for relatively short chains but A-like for longer chains. In the future, we will consider the explicit solvent, which not only makes a more real system, but also introduces other important factors such as solvent size.

6.4 Conclusion

We have applied iSAFT to study the structure of side chains of a bottlebrush polymer in an implicit solvent. Although a rigid backbone is assumed, we have found a variety of conformations for different solvent qualities. In addition, no “dead zone” is discovered for the conditions studied. By changing the grafting density or side chain length, the density profile will shift following a certain pattern. The theoretical results reach a semi-quantitative agreement with our molecular dynamics simulation. The scaling relationship for the brush height at high grafting region is consistent with previous literature. The one-component model is further extended to a two-component model and particularly we explore the surface properties of a core-shell bottlebrush polymer consisting of amphiphilic side chains. The theory predicts that when the inner block is solvent-philic and the outer block is solvent-phobia, the composition of outer layer is dependent on the block length. This type of knowledge is important in the design and application of unimolecular micelles. Compared with molecular simulation, iSAFT has the great advantage of computational efficiency and
the future work will focus on inclusion of explicit solvent and extension of iSAFT to a 2D space, potentially relaxing constraints such as infinite length of backbone, and providing more insights on real applications.
Chapter 7

Concluding Remarks

In this chapter, the thesis work will be summarized and future directions will be proposed.

7.1 Summary

In this thesis, focus has been laid on understanding the branching effect on the thermodynamics of different types of molecules, from simple alkanes to polymers of special architecture.

Firstly, an extension of the statistical associating fluid theory (SAFT) for branched molecules with a Lennard-Jones dimer reference fluid (SAFTD-LJ-Branch) is proposed. The theory successfully predicts how branched architecture affects the attraction and repulsion between molecules. SAFTD-LJ-Branch takes a form similar to SAFTD-LJ with an additional parameter NB introduced to account for the branching effect. We propose an approach relating NB to the number of different types of articulation segments. The theory is used to study the effect of chain architecture on the thermodynamic properties of isomeric alkanes and provides predictions in good agreement with experimental data, for both pure compounds and mixtures. It is also demonstrated to be able to predict the effect of molecular structure for heavier molecules with the only required input being the structure of molecule.

Secondly, modified inhomogeneous statistical associating fluid theory (iSAFT)
density functional theory is extended to dendrimer molecules in solvents of varying quality. The detailed structures of isolated dendrimers in both implicit and explicit solvents are calculated and have a semi-quantitative agreement with simulation results. Radius of gyration is readily obtained and follows the well-established scaling laws. iSAFT predicts that solvents of smaller size and stronger interaction with the dendrimer tend to be candidates for good solvents. By adding association, a hydrogen bonding type interaction, we have discovered more interesting and rich phase behavior. For example, depending on designs of associating sites, the dendrimer can form either a dense-core or dense-shell structure. Also, competition of dispersion and association leads to LCST behavior of dendrimers while the solubility of dendrimer monotonically increases as temperature goes up if there is only dispersion. Those results provide insight into the phase behavior of dendrimer solutions and provide guidance in the design and synthesis of real materials.

In the end, iSAFT is applied to bottlebrush polymers in both good and poor solvents. A vast parameter space is explored to investigate how parameters such as grafting density, chain length will affect the conformation of side chains in implicit solvent. The density profiles and scaling relationship calculated from iSAFT agree well with simulations and other theories. An amphiphilic core-shell bottlebrush polymer is also studied and it is found that when the inner block is solvent-phobia, the periphery of the bottlebrush will always be dominated by the solvent-philic block. However, if the inner block is solvent-philic, the periphery can either be solvent-philic or solvent-phobia, depending on the relative size of each block.
7.2 Future Directions

7.2.1 iSAFT in higher dimensions

The current work has taken advantage of the high symmetry of systems considered (a centered dendrimer or a bottlebrush molecule with an infinitely long rigid backbone). However, if some of these constraints are relaxed, we may get more interesting results as in the experiments or simulations. For example, if we do a 2D iSAFT calculation of side chains of bottlebrush molecules, we may find the pearl-necklace structure along the axial direction besides the radial density profile. And if we further implement the 3D iSAFT calculation, we can even allow the backbone to be fully flexible and study the conformations of backbone and side chains at the same time. The high dimensional iSAFT calculation is obviously more computationally expensive but the computational efforts could be alleviated by utilizing the advanced algorithm, such as the Fast Hankel Transform Algorithm[188, 189, 190].

7.2.2 Higher-order correlation functions and a better functional form

Overall the theories developed in this thesis do a very good job in matching the thermodynamic properties of branched molecular systems with that from experiments and simulations. However, there is still room to improve. SAFTD-LJ-Branch should be easily modified given more structural information, such as trimer and tetramer correlation function. That knowledge might be a remedy to those outliers within the current equation of state. For the inhomogeneous system, the modified iSAFT is based on TPT1 solely. Whether it is dendrimer or bottlebrush polymer, lack of intra-molecular correlation prevents reaching a more accurate result. In addition, those linear or branched chains are modeled as fully flexible chain, not semi-flexible
or stiff chains. To correct this deficiency, one must go to higher order in perturbation theory, which calls for the appropriate triplet correlation functions, or implement a mechanism for adjusting the chain stiffness to fit some known bulk property like the end-to-end distance. Last but not least, from the point of formalism, a better functional form for the long-range attraction contribution $A_{ex,att}[\rho_i(r)]$ can also make a difference since the mean field approximation is widely considered to be not that accurate[191].

7.2.3 More real molecular models

For branched polymers, the molecules constructed throughout the thesis are more of model molecules rather than real molecules. For one thing, model molecules serve the validation purpose very well since simulations of identical or similar conditions are available for comparison. For another, limitation of theory itself prohibits certain complex interactions, such as electrostatic interaction, which is quite common in application of dendrimers[192] and bottlebrush polymers[193]. Still, we are able to consider association to describe the effect of hydrogen bonding. It should not be difficult to extend the current theory to study molecules with segments of different sizes, systems of three or more components (guest macromolecule, solvent, drug molecule). Figuring out a way to incorporate electrostatic and other complex interactions is surely another future direction.

7.2.4 Connections between bulk SAFT and iSAFT

We have demonstrated that SAFT is versatile in that it can be modified and applied in both bulk and inhomogeneous calculations. On one hand, with proper adaptation, the SAFT type equation of state like SAFTD-LJ-Branch is able to solve
VLE or LLE of chemical mixtures. On the other hand, with specific combinations of parameters, we see potential LCST behavior of temperature-sensitive polymers. It would be very interesting to draw connections between the phase behavior obtained from the bulk SAFT EoS and iSAFT density functional theory. To be more specific, does the LCST of associating dendrimer from iSAFT happen to be the temperature where the polymer solution starts phase separation from SAFT? This is very interesting to know.

7.2.5 Kinetic and transport properties

Most versions of density functional theory, including iSAFT, are at the stage of equilibrium calculation. As a result, kinetic and transport properties are usually unavailable. However, sometimes these properties are as important as thermodynamics properties. In terms of the application of dendrimer for drug delivery, not only do people want to know the amounts of drug inside the dendrimer at different conditions, but also they want to know the release rate at different time. The dynamic feature could be added to the current iSAFT by following the spirits of those dynamic density functional theory (DDFT)[194, 195, 196].
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Appendix A

Molecular Dynamic Simulation

In this appendix we outline the details of molecular dynamics simulations for the dendrimer system and bottlebrush polymer system.

A.1 Dendrimer System

Molecular dynamics simulations were used to simulate a single dendrimer in implicit and explicit solvent conditions. The dendrimers were modeled as bead-spring freely jointed united-atom monomers. The solvent molecules were modeled as united atom spheres. The non-bonded interactions are calculated with a truncated and shifted Lennard-Jones potential, which is given as

\[ u_{\text{cs}}^{LJ}(r_{ij}) = u^{LJ}(r_{12}) - u^{LJ}(r_c) \]  \hspace{1cm} (A.1)

\[ u^{LJ}(r_{12}) = 4\epsilon^{LJ} \left[ \left( \frac{\sigma}{r_{12}} \right)^{12} - \left( \frac{\sigma}{r_{12}} \right)^6 \right] \]  \hspace{1cm} (A.2)

where \( \epsilon^{LJ} \) is the well depth, \( \sigma \) is the particle diameter and \( r_c \) is the cutoff radius. The bonded monomer interactions is represented by a harmonic potential

\[ u^{\text{bond}}(r_{12}) = K(r_{12} - r_0)^2 \]  \hspace{1cm} (A.3)

where \( K = 1662\epsilon^{LJ}/\sigma^2 \) is the spring constant\[197\] and \( r_0 = \sigma \) is the equilibrium bond length. For all monomers and solvent particles, mass \( m = 1, \epsilon^{LJ} = 1, \sigma = 1 \) and
\( r_c = 2.5\sigma. \)

We constructed the dendrimers with a series of self-avoiding random walks, using a modified version of the algorithm by Lescanec and Muthukumar [198]. The modification was to ensure that the random walks were outwards from the center of the dendrimer. Hence, the dendrimer created is as open as possible, avoiding any configuration that can lead to monomers being trapped. In this study, we chose the branching factor as \( b = 3 \) and the spacer length as \( n = 7 \).

The simulations were carried using LAMMPS molecular dynamics code[199, 200]. The time step was chosen as \( \Delta t = 0.0006\tau \), where \( \tau = \sigma\sqrt{m/\epsilon_{LJ}} \). The temperature \( T^* = k_B T/\epsilon_{LJ} \) was controlled using Nosé-Hoover thermostat with damping factor of 3\( \tau \). All simulations were minimized using conjugate gradient method and initialized at a temperature of \( T^* = 6.5 \). The system was then cooled to the desired temperature in 3 million time steps. The system was further relaxed for 2 million time steps. A larger time step and/or smaller damping factor can lead to better computational efficiency, which would reduce the equilibration time. The thermostat was then turned off and a production run was carried out for 10 million steps, saving frames every 2000 time steps.

Implicit solvent simulations were carried out with one dendrimer in vacuum. The reduced temperature changes the interactions between the monomers, hence acting like an effective solvent. Explicit solvent simulations were carried out by introducing solvent particles in random to the system. The dendrimer center was fixed at the origin of the cell and periodic boundary conditions were established. The system size was set at \( 70\sigma \), which ensures there is minimum of \( 20\sigma \) space between the dendrimer and its periodic image, avoiding any interactions between them. Solvent particles were inserted into the system in such a way that the total reduced density including
the monomers and the solvents was the desired value.

To model hard sphere interactions, like the case of athermal solvent or no dendrimer-solvent interactions in explicit solvent cases, we changed the cutoff radius to \( r_c = 2^{1/6} \sigma \). It is important to note that those cases correspond to \( \epsilon_{LJ} = 1 \) with \( r_c = 2^{1/6} \sigma \) in simulations, but labeled as \( \epsilon_{LJ} = 0 \) for uniformity. In addition, the temperature for athermal case was fixed\[6] at \( T^* = 1.2 \).

### A.2 Bottlebrush Polymer System

Molecular dynamics simulations were used to simulate a single bottlebrush molecule in implicit solvent. The bottlebrush molecule was modeled as a rod grafted with polymeric side chains at the given density. The side chains are made of bead-spring freely jointed united-atom monomers. The non-bonded interactions and the monomer-rod interactions are calculated with a truncated and shifted Lennard-Jones potential. The 12-6 Lennard-Jones potential form is used.

\[
u_{LJ}(r) = 4\epsilon_{LJ} \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]
\]  

(A.4)

where \( \epsilon_{LJ} \) is the well depth, \( \sigma \) is the particle diameter and \( r \) is the distance. The potential reaches its minimum at \( r_{\text{min}} = 2^{1/6} \sigma \).

The monomer-monomer interactions are given as

\[
u_{ss}(r_{ij}) = u_{LJ}(r_{ij}) - u_{LJ}(r_c)
\]  

(A.5)

where \( r_{ij} \) is the distance between the centers of the two beads. For all monomers, mass \( m = 1 \), \( \epsilon_{LJ} = 1 \), \( \sigma = 1 \), and \( r_c = 3.5\sigma \). For athermal case, we changed the cutoff
radius to \( r_c = r_{\text{min}} \), and the temperature to \( T^* = k_B T/\epsilon_{\text{LJ}} = 1.2 \).

The monomer-rod interactions is given as

\[
 u_{rs}(r_{iz}) = u^{\text{LJ}}(r_{iz} - R_b + 0.5\sigma) - u^{\text{LJ}}(r_{\text{min}}) \tag{A.6}
\]

where \( r_{iz} \) is the distance of the center of the bead from the axis of the rod. \( R_b \) is the radius of the rod or backbone. It should be noted that the grafted bead remains fixed, and do not interact with the rod.

The bonded monomer interactions is represented by a harmonic potential.

\[
 u^{\text{bond}}(r_{ij}) = K(r_{ij} - r_0)^2 \tag{A.7}
\]

where \( K = 1662\epsilon_{\text{LJ}}/\sigma^2 \) is the spring constant and \( r_0 = \sigma \) is the equilibrium bond length.

The initial configuration was constructed as follows. The grafting monomers were randomly placed on the surface of the rod at the given density. The side chains were then grown radially outwards to the given chain length. The simulations were carried using LAMMPS molecular dynamics code\[199\][200]. The rod axis was aligned in the \( z \) direction with the center at the origin of the \( xy \) plane, and periodic boundary conditions were established. The system size in the \( xy \) dimensions were adjusted ensuring there is minimum of \( 20\sigma \) space between the molecule and its periodic image, avoiding any interactions between them. The height of the rod was set at \( 40\sigma \). The time step was chosen as \( \Delta t = 0.0012\tau \), where \( \tau = \sigma\sqrt{m/\epsilon_{\text{LJ}}} \). The temperature \( T^* \) was controlled using Nosé-Hoover thermostat with a damping factor of \( 3\tau \). All simulations were minimized using conjugate gradient method and initialized at a temperature of \( T^* = 6.5 \). The system was then cooled to the desired temperature.
in $5 \times 10^5$ time steps, and further relaxed at the given temperature for $5 \times 10^5$ time steps. The thermostat was then turned off and a production run was carried out for $1 \times 10^6$ steps, saving frames every 1000 time steps.
Appendix B

Fast Hankel Transformation Algorithm

In this appendix we outline the steps to evaluate the weighted densities which are
the convolutions:

\[ n_i^\alpha(\mathbf{r}) = \int \rho_i(\mathbf{r}') \omega^\alpha(R_i - |\mathbf{r} - \mathbf{r}'|) d\mathbf{r}' \]  \hspace{1cm} (B.1)

According to the convolution theorem, the Fourier transformed convolution \( n_i^\alpha(\mathbf{r}) \)
can be expressed as:

\[ \tilde{n}_i^\alpha(\mathbf{k}) = \tilde{\rho}_i(\mathbf{k}) \tilde{\omega}^\alpha(\mathbf{k}) \]  \hspace{1cm} (B.2)

where \( \tilde{\rho}_i(\mathbf{k}) \) and \( \tilde{\omega}^\alpha(\mathbf{k}) \) are the Fourier transformed density distribution and weighting
functions. The basic strategy to evaluate the convolutions in modified iSAFT is to first
evaluate the Fourier transforms of the convolution then perform an inverse transform
to the transformed convolutions.

Following this route, free energy functional derivatives from different contributions
can be numerically evaluated by Fourier transform. The transforms of fundamental
measure theory free energy functional derivatives are given by Sears and Frink[189].
The Fourier transform of mean-field contribution can be expressed as:

\[ \frac{\delta \tilde{A}_{\text{att}}}{\delta \tilde{\rho}_i(\mathbf{k})} = \sum_j \tilde{\rho}_i(\mathbf{k}) \beta \tilde{u}_{ij}(\mathbf{k}) \]  \hspace{1cm} (B.3)

where \( \beta \tilde{u}_{ij}(\mathbf{k}) \) is the Fourier transform of WCA perturbation attractive potential
mentioned before.
There are two contributions to the chain connectivity in modified iSAFT. The first is the direct chain term \( \frac{\delta A_{\text{chain}}}{\delta \rho_i(r)} = -\frac{1}{2} \sum_{m=1}^{m} \sum_{\gamma' \gamma} \int dr' \rho_\gamma(r') \frac{\delta \ln \bar{y}^{\gamma'}}{\delta \rho_i(r)} \). This direction chain term has a Fourier transform:

\[
\frac{\delta \tilde{A}_{\text{chain}}}{\delta \tilde{\rho}_i(k)} = -\frac{1}{2} \sum_{m=1}^{m} \sum_{\gamma' \gamma} \tilde{\rho}_\gamma(k') \frac{\partial \ln \bar{y}^{\gamma'}}{\partial \tilde{\rho}_i(k)} \frac{\delta \tilde{\rho}_i}{\delta \tilde{\rho}_i(k)}
\]

(B.4)

where the Fourier transform of the weighting function for chain term \( \frac{\delta \tilde{\rho}_i}{\delta \tilde{\rho}_i(k)} \) has an analytic form:

\[
\frac{\delta \tilde{\rho}_i}{\delta \tilde{\rho}_i(k)} = \frac{3[\sin(2|k|\sigma_j) - 2|k|\sigma_j \cos(2|k|\sigma_j)]}{(2|k|\sigma_j)^3}
\]

(B.5)

and the Fourier transform of partial derivative of cavity correlation function with respect to weighted density \( \tilde{\rho}_\gamma(k') \frac{\partial \ln \bar{y}^{\gamma'}}{\partial \tilde{\rho}_i(k)} \) has to be numerically evaluated.

The second contribution to chain connectivity in modified iSAFT is the recursive integral \( I_{1,i}(r_i) \) and \( I_{2,i}(r_i) \) as stated previously. The Fourier transforms of those recursive integrals are \( \tilde{I}_{1,i}(k_i) \) and \( \tilde{I}_{2,i}(k_i) \). They are also evaluated in a recursive fashion in Fourier space:

\[
\tilde{I}_{1,i}(k_i) = \mathcal{F}\left\{ \frac{\delta(|r_j - r_{j-1}| - \sigma_{j-1,j})}{4\pi \sigma_{j-1,j}^2} \right\} \mathcal{F}\left\{ I_{1,i}(r_i) \exp[D_{j-1}(r_{j-1})] \right\}
\]

(B.6)

where the first part is body-averaged weighting function and it has an analytic form:

\[
\mathcal{F}\left\{ \frac{\delta(|r_j - r_{j-1}| - \sigma_{j-1,j})}{4\pi \sigma_{j-1,j}^2} \right\} = \frac{\sin(|k|\sigma_{j-1,j})}{|k|\sigma_{j-1,j}}
\]

(B.7)

The Fourier transform of the second part has to be numerically evaluated.