DISSERTATION

NOVEL APPLICATIONS OF ADVANCED INTEGRAL-EQUATION THEORIES TO VARIOUS POLYMERIC SYSTEMS

Submitted by

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In partial fulfillment of the requirements

For the Degree of Doctor of Philosophy

Colorado State University

Fort Collins, Colorado

Fall 2021

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ABSTRACT

NOVEL APPLICATIONS OF ADVANCED INTEGRAL-EQUATION THEORIES TO VARIOUS POLYMERIC SYSTEMS

Since proposed in 1987, the polymer reference interaction site model (PRISM) theory^[1] has been applied to many polymeric systems, including homopolymer melts, solutions, blends, block copolymers, nanocomposites, polyelectrolytes, etc., mainly by the (former) members in the research groups of Schweizer and Curro.^[2-5] It is one of the most successful theories to date for predicting the structure and thermodynamics of homogeneous polymers. Comparing it to the polymer self-consistent field (SCF) theory^[6], which can be considered as the most successful theory for inhomogeneous polymers and has also been applied to a wide variety of systems partly because its numerical calculations have been well developed^[7], we note that few studies on the numerical calculations of the PRISM theory have been reported, which hinders its application by other research groups. As our first step to address this issue, here we focus on the PRISM-PY theory that works well for an important class of coarse-grained models for polymer melts and solutions in an implicit good solvent, where only short-range non-bonded repulsion between polymer segments is employed; all previously reported numerical methods for PRISM calculations are not best suited for this class of models.

Coarse-grained^[8] (CG) models are currently needed to simulate polymeric systems, as full atomistic simulations of many-chain systems used in experiments are in most cases not feasible due to their formidable computational requirements. Polymeric systems are also best suited for coarse graining, as the large number of monomers on each chain allows high levels of coarse graining. Applications of PRISM theory in structure-based coarse graining of multicomponent polymeric systems to diblock copolymer melts have been performed to obtain the structural and thermodynamic properties of both the original and coarse-grained (CG) system, and to quantitatively exam how the effective non-bonded pair potentials between coarse-grained segments and the thermodynamic properties of coarse-grained systems vary with coarse-graining level. The spinodal curve doesn't change, regardless of the original system for symmetric diblock copolymer melts, which was been proved. Using a simple model system for symmetric diblock copolymer melts, we coarse-grained each block as N/2 segments and examined CG systems with N ranging from 2 to 100. Coarse graining increases both the peak value and peak location of the partial structure factor characterizing the composition fluctuations in the CG system. Contrary to the common practice in the literature, CG potentials obtained from short-chain systems can not directly used for long chain systems; this is in fact the transferability problem in coarse graining. The structure-based coarse graining cannot give thermodynamic consistency at any coarse-graining level.

While the polymer self-consistent field theory has gained great success in describing various inhomogeneous polymeric systems, particularly the self-assembled morphologies of block copolymers, for spatially homogeneous systems it reduces to the Flory-Huggins theory and gives the simplest, yet often qualitatively incorrect predictions. Based on the same model system of symmetric DBCs represented as discrete Gaussian chains interacting with soft, finite-range repulsions as commonly used in the dissipative-particle dynamics simulations^[9], we have directly compared, without any parameter-fitting, the thermodynamic and structural properties of the disordered phase obtained from fast off-lattice Monte Carlo (FOMC) simulations^[10], P/RISM theories, and Gaussian-fluctuation theory. The compared quantities include the

internal energy, entropy, Helmholtz free energy, (virial) pressure, constant-volume heat capacity, chain/block dimensions, and various structure factors and correlation functions in the system. Our comparisons unambiguously and quantitatively reveal the consequences of various theoretical approximations and the validity of these theories in describing the fluctuations/correlations in disordered DBCs.

The structure of a polymeric fluid is usually characterized by the intra- and inter-chain pair correlation functions (PCFs), which can be used to determine both the thermodynamic and dynamic properties. Few theories, however, are available to predict such microscopic structures, which require that the segment-segment correlation effects be explicitly considered. In the well-developed self-consistent polymer reference interaction site model (SC-PRISM)^[11], the inter-chain PCFs are approximated by an intra-chain solvation pair potential, thus allowing its prediction of the intra- and inter-chain PCFs. On the other hand, Yu and Wu proposed an extended test-particle method ^[12], enabling prediction of these quantities using polymer density-functional theories (PDFTs). Here we directly compare the intra- and inter-chain PCFs predicted by various versions of PDFTs and SC-PRISM calculations with those obtained from Monte Carlo simulations. A simple model system of tangent hard-sphere chains allows us to unambiguously quantify the accuracy of these predictions as a function of the chain length and hard sphere packing density.

Implicit-solvent (IS) models are widely used in molecular simulations of solutions, with the advantage of dramatically saving the amount of computation and the hope of faithfully reproducing some properties of the corresponding explicit-solvent (ES) model. In practice, however, an IS model often gives qualitatively different results from the corresponding ES model. We take a simple model system of homopolymer solutions as an example to examine the features of the effective coarse-grained^[8] pair potential between polymer segments calculated by Percus-Yevick^[13] and hypernetted-chain (HNC)^[14] closure in the IS model that is designed, using the well-developed polymer reference interaction site model (PRISM)^[15] theory, to reproduce the pair correlation functions between polymer segments in the corresponding ES model. To assess the accuracy of the PRISM theory, we also quantitatively compare its predictions with Monte Carlo (MC) simulation^[16] results, both for the ES model.

ACKNOWLEDGEMENTS

I am eternally grateful to my family, especially my parents Jianzhou Wang and Juxian Hu, for their love and support, my parents never give me any pressure and always encourage me that they are so proud of me. I thank my grandfather and grandmother from the bottom of my heart to give me the power to overcome any difficulties I met. I am greatly thankful to my best partner Ryan Chan for taking care of my daily life during the last two years, I really appreciate that each breakfast, lunch, and dinner you have made for me, therefore I could fully focus on my research and work.

I am deeply indebted to my advisor Professor Qiang Wang. He fully devotes to give guidance and insights on my research, and always provide me the platform to practice and present myself. I got huge growth and found my potential in the past five years. Also, he helped in my life at his best, he already becomes a life friend to me.

I would like to thank all committee members of my Ph.D. defense, Professor Qiang Wang, Professor Christopher Snow, Professor Travis Bailey, and Professor Grzegorz Szamel. Without all of them, I couldn't make my final Ph.D. defense happen. Thanks for spending their precious time in reading and giving suggestions on my research and dissertations.

I owe many thanks to many group members both in Colorado State University and NanKai University. In U.S., especially to Morteza Ziaee, thanks for always coming by to my seat in the office, caring about my life and sharing your research point; to Juntong He, thanks for joining the research team and giving me suggestions on elective courses. In China, to Suyu Wang and Jiawei Zhang, thanks for their kindly help and simulating interactions, they made huge contributions on my dissertation.

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I would like to thank all the faculty and staff of the Department of Chemical and Biology Engineering at the Colorado State University. Especially to Denise Morgan, Claire Lavelle, Tim Gonzales, Tracey Perkins, Ryan Medhurst and Jeff Penn, under your help, I really enjoyed my life, study, and research here.

I also would like to thank my friends in China, especially Yu Gu, Xin Qin, Jundi Wei, Fan Zhang, Chao Zhang and Guoliang Li, I felt a lot of love from you. Thanks for all the calls and chats you made to me to care about my current situations, which means a lot to me. No matter where they are, I wish them all best.

Finally, a huge and special thanks to my best friend Chen Shen and my super lovely dog PALA, thanks for being in my life, keeping me company in every happy and low moments. Without them, I couldn't be so brave to persist until now.

Acknowledgement is made to the donors of The American Chemical Society Petroleum Research Fund for support of this research.

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Chapter 1 Introduction

My PhD research is about applying advanced integral-equation theories to various polymeric systems. In Chap. II, I briefly explain the integral-equation theories, including the reference interaction site model (RISM) theory, polymer reference interaction site model (PRISM) theory, and the self-consistent polymer reference interaction site model (SC-PRISM) theory, used in my research.

In Chap. III, I applied the PRISM theory to the structure-based^[15] coarse graining of diblock copolymer melts. Our group proposed in 2015 the systematic and simulation-free coarse-graining strategy for polymer melts, where we use the well-developed PRISM theory, instead of the commonly used many-chain molecular simulations, for both the original and coarse-grained systems.^[17] This is at least several orders of magnitude faster than those using many-chain simulations, thus effectively solving the transferability problem as coarse graining can now be quickly performed at any conditions needed. Also, since the PRISM theory applies to the thermodynamic limit and can be solved to very high accuracy, our strategy avoids the problems caused by the finite-size effects and statistical uncertainties of many-chain simulations, which are precisely the reasons why we cannot afford such simulations for the original system of long-chain polymer melts. This work is already published.^[18]

In Chap. IV, I built a general polymer reference interaction site model (PRISM) theory algorithm for generic chain models, applying PRISM theory with classic Percus-Yevick^[13] (PY) closure to homopolymer melts of generic models, including Tangent Hard Sphere Chains (THSC), Kremer-Gremer (KG), and Dissipative Particle Dynamic^[9] (DPD) models on different chain length ($N = 1 \sim 120$) and number density ($\rho\sigma^3 = 0.1 \sim 3$) to quantitatively calculate the decay slope of the 3D Fourier Transform of the total correlation function $\hat{h}(q)$ and the direct correlation function $\hat{c}(q)$. Also, we compared our work with a python-based open-source framework for PRISM calculations called "pyPRISM", a faster $\hat{c}(q)$ convergence using our method than python code was proved. We are currently preparing a manuscript on this work for publication.

In Chap. V, we have applied the P/RISM theory to the disordered phase of symmetric diblock copolymers (DBCs). In the dissipative-particle dynamic simulations, model system of symmetric diblock copolymers as discrete Gaussian chains interacting with soft, finite range repulsion is commonly used. The direct comparisons without any parameter-fitting on the thermodynamic and structural properties obtained from fast off-lattice Monte Carlo simulations, reference interaction site model (RISM), polymer reference interaction site model (PRISM) theories, and Gaussian fluctuation theory were made. To reveal the effects of various theoretical assumptions and the validity of these theories in describing the correlations in disordered diblock polymers, internal energy, entropy, Helmholtz free energy, (virial) pressure, constant-volume heat capacity, chain/block dimensions, and various structure factors and correlation functions in the system were calculated and analyzed. The FOMC simulations are performed by a former PhD student in our group, and the theoretical calculations are started by another PhD student in our group; my contribution here is to finish the P/RISM calculations and the manuscript to be submitted for publication.

In Chap. VI, we applied the well-developed self-consistent polymer reference interaction site model (SC-PRISM) theory to a simple model system of Tangent Hard Sphere chains at different chain length $N = 1 \sim 120$ and number density ($\rho\sigma^3 = 0.1 \sim 3$). The interchain pair correlation functions $\hat{h}(q)$ and $\hat{c}(q)$ are approximated by an intra-chain solvation potential, which is then used in single chain simulations. Here directly compared the intra- and inter- chain correlation functions predicted by various versions of PDFTs proposed by Yu and Wu,^[19] and SC-PRISM calculations with those obtained from many- chain Monte Carlo simulations. This model allows us to quantify the accuracy of these predictions as a function of the chain length and hard sphere packing density. The many chains molecular simulations and density-functional theory calculations of the model are being carried out by Suyu Wang and Jiawei Zhang in Nankai University. We are also currently preparing a manuscript on this work for publication.

Finally, in Chap. VII, in this work, we took a simple model system of homopolymer solutions as an example to examine the features of the effective pair potential between polymer segments in the Implicit-Solvent model that is designed, using the well-developed polymer reference interaction site model (PRISM) theory, to reproduce the chain conformations and pair correlation functions between polymer segments in the corresponding Explicit-Solvent model. To assess the accuracy of the PRISM theory, we also quantitatively compare its predictions with Monte Carlo (MC) simulation results, both for the ES model. Note that, we took the Fourier transform of the intra-chain correlation function obtained from MC simulations as input for our method, which can help to focus on the influence generated by theory and closure itself. In our future work, we consider using SC-PRISM algorithm instead of PRISM theory on the IS model to reduce the simulation time to calculate $\hat{\omega}(q)$. The many chains molecular simulations of IS model are being carried out by Suyu Wang in Nankai University.

Chapter 2 Polymer Integral-Equation Theory

For simplicity, here we consider a homogeneous system of *n* homopolymer chains each of *N* interaction sites (either monomers or CG segments) in volume *V*, with the chain number density denoted by $\rho_c \equiv n/V$. Chandler and Andersen proposed the RISM theory in 1972, which generalizes the Ornstein-Zernike (OZ) equation for monatomic systems to molecular systems and is given in the Fourier space as^[20]

$$\hat{\mathbf{h}} = \hat{\boldsymbol{\omega}}\hat{\mathbf{c}}\left(\hat{\boldsymbol{\omega}} + \rho_c\hat{\mathbf{h}}\right)$$
(2.1)

where the symmetric matrices $\hat{\mathbf{h}}$, $\hat{\mathbf{0}}$ and $\hat{\mathbf{C}}$ have $N \times N$ elements of $\hat{h}_{s,s'}$, $\hat{\omega}_{s,s'}$ and $\hat{c}_{s,s'}$, respectively; $c_{s,s'}(r)$ and $h_{s,s'}(r) \equiv g_{s,s'}(r) - 1$ are the interchain direct and total pair correlation functions (PCFs), respectively, between the s^{th} segment on one chain and the s^{th} segment on another, with $g_{s,s'}(r)$ being the interchain radial distribution function; $\omega_{s,s'}(r)$ is the normalized (i.e., $\hat{\omega}_{s,s'}(q=0)=1$) intrachain PCF between the s^{th} and s^{th} segments on the same chain; and we use the short-hand notation $\hat{f} \equiv (4\pi/q) \int_0^{\infty} dr f(r) r \sin(qr)$ to denote the 3D Fourier transform of a radial function f(r) with q being the wavenumber. At given ρ_c and chain conformations $\boldsymbol{\omega}(r)$, Eq.(2.1) must be solved together with a closure relating the interchain direct and total PCFs. The atomic Percus-Yevick (PY) closure^[13] commonly used for systems having short-range, soft, and repulsive non-bonded pair potentials, for example, is given by

$$c_{s,s'}(r) = \left\{1 - \exp\left[\beta u_{s,s'}(r)\right]\right\}g_{s,s'}(r).$$

When N is large (as typical for polymers), it becomes a formidable task to solve $h_{s,s'}(r)$ and

 $c_{s,s'}(r)$ for all (s,s') pairs in the RISM theory. Curro and Schweizer therefore proposed the PRISM theory in 1987, which assumes $h_{s,s'}(r) = h(r)$ and $c_{s,s'}(r) = c(r)$, thus reducing Eq. (2.1) to

$$\hat{h} = \hat{\omega} N^2 \hat{c} \left(\hat{\omega} + \rho_c \hat{h} \right)$$
(2.2)

where $\omega(r) \equiv \frac{1}{N^2} \sum_{s=1}^{N} \sum_{s'=1}^{N} \omega_{s,s'}(r) \omega(r)$. At given ρ_c and $\omega(r)$, Eq.(2.2) again needs to be solved

together with a closure relating h(r) and c(r).

Since the chain conformations (i.e., $\omega(r)$) are not known *a priori*, we use the SC-PRISM theory^[11] to obtain $\omega(r)$. Its basic idea is to replace the intermolecular interactions by an effective intrachain solvation potential w(r), proposed by Chandler and co-workers as^[21, 22]

$$\beta \hat{w} = -\kappa \rho_c N^2 \hat{c}^2 \left(\hat{\omega} + \rho_c \hat{h} \right)$$
(2.3)

where $\kappa \in [0.9, 1.1]$ was introduced by Mendez et al. to obtain the correct behavior of the meansquare chain end-to-end distance^[16]. For an initial guess of $\omega(r)$ (e.g., the ideal-chain conformations), the SC-PRISM calculation proceeds as follows (seen in Fig 2.1):

(a) Solve Eq.(2.2) with a closure, then calculate w(r) from Eq.(2.3).

(b) Perform single-chain Monte Carlo (SCMC) simulation with w(r), the bonded and nonbonded potentials to obtain new $\omega(r)$.

(c) Repeat the above two steps till $\omega(r)$ converges.

We will further use the reweighting scheme^[23, 24] to reuse chain conformations generated in SCMC simulation so that it does not need to be performed at each iteration, thus greatly reducing the SC-PRISM calculation time.



Figure 2.1: The workflow of SC-PRISM Calculations.

Chapter 3 Structure-based Coarse Graining of Diblock Copolymer Melts using PRISM

3.1 Introduction

Recently, our group proposed a systematic and simulation-free strategy for the structure-based coarse graining of multicomponent polymeric systems, where we use the welldeveloped polymer reference interaction site model (PRISM) theory^[11, 15, 25, 26], instead of the commonly used many-chain molecular simulations (MCMS), to obtain the structural and thermodynamic properties of both the original and coarse-grained (CG) systems, and to quantitatively examine how the effective non-bonded pair potentials between CG segments and the thermodynamic properties of CG systems vary with the coarse-graining level^[27]. As examples, our strategy has been applied to both homopolymer melts^[17] and binary polymer blends^[27]; in the latter case, we proved that it does not change the spinodal curve (thus also the critical point) regardless of the original model system, closures, and coarse-graining levels used^[27]. In this work, we apply it to diblock copolymer (DBC) melts. Just like polymer blends, although block copolymer melts have been investigated in many experimental, simulation, and theoretical studies due to their both fundamental and practical importance in polymer science and engineering, their coarse graining has been performed only by a few groups as summarized below.

Ju and co-workers mapped poly(L-lactide) (denoted by A) and polyethylene (PE, denoted by B) blends and DBC melts to the dissipative particle dynamics (DPD) model^[9, 28], where they *set* the volume of each DPD particle (CG segment) V_{seg} =1.15 nm³, which

corresponds to about 6 A monomers ($C_6H_8O_4$) or 24 B monomers (C_2H_4), and the average number of DPD particles per volume of V_{seg} (i.e., the reduced number density of DPD particles) $\rho=3^{[29]}$. To obtain the DPD interaction parameters a_{IJ} ({I,J}^[30]={A,B}), they performed allatom molecular dynamics (MD) simulations of pure A (where each chain consists of 6 monomers) at the thermodynamic temperature T=300 K and various pressures to calculate its dimensionless compressibility κ^{-1} , which then gives ${}^{[31]}a_{AA} = a_{BB} = (\kappa^{-1} - 1)/(2\alpha\rho)$ with $\alpha = 0.1$. They also performed all-atom MD simulations at T=300 K and specified densities of pure A, pure B (where each chain consists of 24 monomers), and their blends (denoted by A/B) at various volume fractions of A (denoted by ϕ_A) to calculate the cohesive energy E_{coh} in volume V, then obtained the solubility parameters for pure systems as $\delta_{\rm I} = \sqrt{(E_{\rm coh}/V)_{\rm I}}$ and $a_{\rm AB}$ from $\chi_{AB} = -0.001 (a_{AB} - a_{AA})^2 + 0.315 (a_{AB} - a_{AA})$,^[32] where they calculated the Flory-Huggins interaction parameter between an and В segment Α а as $\chi_{AB} = \beta V_{seg} \left[\phi_A \delta_A^2 + (1 - \phi_A) \delta_B^2 - (E_{coh} / V)_{A/B} \right] \text{ with } \beta \equiv 1/k_B T \text{ and } k_B \text{ being the Boltzmann}$ constant. With these DPD parameters, they performed DPD simulations of A/B blends and DBCs A-B consisting of A and B chains/blocks of various lengths and at various ϕ_A to study their microphase-separated structure.^[29] In a subsequent paper, Ju and co-workers used this mapping to study the self-assembled structures of linear triblock copolymer (TBC) melts B-A-B at various ϕ_A , where each copolymer chain has N=40 segments. ^[33]

Roy et al. mapped linear TBC melts consisting of two poly((PVBPA) blocks each of 36.5 kg/mol separated by a poly(ether-ether-ketone) (denoted by C) block of 12 kg/mol to the DPD model in three different ways: Model 1 consists of linear TBC A_6 - C_2 - A_6 chains where each A segment represents a portion of the PVBPA block, Model 2 consists of grafted

copolymer (AB)_m-C₂-(AB)_m chains with m=3 or 6 where each A segment on the chain backbone represents the methyl phosphonic acid and each B segment connected as a side group to an A segment represents the styrene, and Model 3 consists of grafted copolymer (AB)_m chains with m=5, 10 or 15 where the middle C₂ block in Model 2 is removed.^[34] They *set* $\rho=3$ and $a_{II}=25$ (I=A,B,C) in all cases, used the same interaction parameter between A and C segments (i.e., A=C) in Model 2, and performed atomistic MD simulations of pure methyl phosphonic acid and ethylbenzene at T=300 K and 1 bar to obtain δ_A and δ_B , respectively, for Models 2 and 3, from which they obtained $\chi_{AB} = \beta V_{seg} (\delta_A - \delta_B)^2$ with V_{seg} being the arithmetic average of the molecular volumes of methyl phosphonic acid and ethylbenzene. While they then calculated $a_{AB}=a_{AA}+3.27\chi_{AB}$,^[31] they also used larger a_{AB} -values in their simulations of Models 2 and 3; similarly, specific a_{AC} -values were used in their simulations of Model 1. With these DPD parameters, they simulated the self-assembled morphology of each model.^[34]

Dieterich and co-workers proposed a Gaussian disphere model for DBC melts, where each block I (=A,B) of $N_{\rm I}$ monomers is coarse-grained as one soft sphere (segment), with parameters $R_{g,\rm I}$ denoting its size and $b = |\mathbf{r}_{\rm A} - \mathbf{r}_{\rm B}|$ the length of the CG bond connecting the two segments located at $\mathbf{r}_{\rm I}$, respectively, on the same chain.^[35] The CG bonded energy of a chain is given by

$$\beta U^{b} = -\ln(P_{A}P_{B}W)$$
, where $P_{I} \equiv p(R_{g,I}/\sqrt{N_{I}-1})/\sqrt{N_{I}-1}$,
 $p(u) \equiv \exp(-u^{2}/a - ad^{2}/u^{2})/uK_{0}(2d)$ with K_{0} denoting the modified Bessel function of order
zero and $a=0.0802$ and $d=1.842$ being the fitted coefficients^[36], and

 $W = \left[\frac{3}{4\pi} \left(R_{g,A}^2 + R_{g,B}^2 \right) \right]^{3/2} \exp\left[-\frac{3b^2}{4} \left(R_{g,A}^2 + R_{g,B}^2 \right) \right]$. The CG non-bonded energy between two segments (including the self-interaction) of type I and J located at \mathbf{r}_{I} and \mathbf{r}_{J} ,

respectively, is given by $\beta U_{u}^{nb} = \varepsilon_{u} \int d\mathbf{r} \rho_{1} (\mathbf{r} - \mathbf{r}_{1}) \rho_{1} (\mathbf{r} - \mathbf{r}_{j})$, where ε_{lJ} is the interaction strength per volume, and $\rho_{1}(\mathbf{r}) = (N_{1}/R_{g,1}^{-3}) f(|\mathbf{r}|/R_{g,1})$ with $f(v) = (3/2\pi)^{3/2} \exp(-3v^{2}/2)$. These CG potentials were obtained based on the ideal conformations of continuous Gaussian chains (CGCs) with additional approximations to yield simple analytical expressions. They then performed canonical-ensemble Monte Carlo (MC) simulations of this model to study the selfassembled morphologies of DBC melts at $\varepsilon_{AA} = \varepsilon_{BB} = 1$ and an average monomer number density $\overline{\rho} = 0.85$ in both bulk and confined films.^[35] This model was later used by Karatchentsev and Sommer to study the stability of the gyroid phase formed by DBC melts at $\varepsilon_{AA} = \varepsilon_{BB} = 1$ and $\overline{\rho} = 0.85$ in bulk.^[37] A similar soft dumbbell model for symmetric DBC melts was proposed by Uneyama based on the ideal conformations of CGCs with additional approximations to yield simple analytical expressions, who then performed Brownian dynamics simulations to study the microphase separation dynamics with and without shear.^[38]

Gross and Paul proposed a soft-quadrumer model for DBC melts, where each block is represented by two CG segments.^[39] Their non-bonded interaction potential between two segments of Ι (=A,B)is type separated at distance r given by $\beta U_{\rm II}^{nb} = 16 \left[1 - 3 \left(r/\sigma_{\rm I} \right)^2 + 2 \left(r/\sigma_{\rm I} \right)^3 \right] / (\chi N + 8) \text{ for } r < \sigma_{\rm I} \text{ and } 0 \text{ otherwise, where } \sigma_{\rm I} = \sqrt{2f_{\rm I}}$ with f_1 being the volume fraction of I-block in DBC melts and $\chi N>0$ is an input parameter characterizing the AB incompatibility, and that between two segments of different types is given by $\beta U_{AB}^{nb} = 2 \left[1 - 3 \left(r / \sigma_{AB} \right)^2 + 2 \left(r / \sigma_{AB} \right)^3 \right]$ for $r < \sigma_{AB} = (\sigma_A + \sigma_B)/2$ and 0 otherwise; they stated that "this form qualitatively reproduces the behavior" of the effective potential between

the centers-of-mass (CoM) of two self- and mutual avoiding (homopolymer) chains found by

Louis et al.^[40, 41], who performed lattice MC simulations of such chains each of 100 and 500 monomers on a simple cubic lattice to obtain the radial distribution function of the chain CoM at several chain number densities up to five times that at the chain overlap (which signals the onset of the semi-dilute regime), then used the Ornstein-Zernike equation with the hyper nettedchain closure to obtain the effective potential. Their bonded potential between two segments of type I is given by $\beta U_{II}^{b} = \beta U_{II}^{nb} + 12.8 (r/\sigma_{I})^{2}/(\chi N + 8)$, and that between two segments of different types is given by $\beta U_{AB}^b = \beta U_{AB}^{nb} + 1.6 (r/\sigma_{AB})^2$; they stated that these bonded potentials reproduce "qualitatively the findings" of Dieterich and co-workers for the distribution of distances between the A and the B block in DBC melts^[35]. They then performed canonical-ensemble MC simulations at the invariant degree of polymerization^[42] $\overline{N} = 216$ and 365, respectively, to construct the phase diagrams of their model in terms of f and χN .^[39] They subsequently extended their work to lamellae of symmetric DBC melts at $\overline{N} = 216$ and $\chi N = 24$ confined between two identical and parallel walls, where they performed MD simulations of an united-atom model of PE chains each of 300 monomers at T=509 K confined between two parallel graphite walls separated at 90 nm, then used the iterative Boltzmann inversion^[43, 44] to obtain the effective potential between the two walls and the CoM of half of a PE chain (corresponding to a polymer segment in their soft-quadrumer model).^[45, 46] This effective potential is repulsive at short distances, has an attractive minimum at a distance about equal to the radius of gyration of half the PE chains, then quickly approaches zero from below; to make the walls selective for A segments, for example, they shifted the potential for A segments so that the minimum value is zero and truncated it at the distance of the minimum. They then performed canonical-ensemble MC simulations at various wall separation and preference to examine the orientation of confined lamellae.^[45, 46]

Finally, Sambriski and Guenza coarse-grained each DBC chain as either one or two connected soft spheres, respectively, representing the CoM of the chain or one of its blocks, using PRISM theory.^[47] While their approach is similar to ours and they also took CGCs as their original model system, they used approximate intrachain pair correlation functions (PCFs) that are both *qualitatively* incorrect and numerically unnecessary, as shown in detail in our Appendix B. Furthermore, for the CG systems, they examined only the interchain total PCFs between the CG segments, not their effective CG potentials nor their thermodynamic properties.^[47]

It is therefore clear that all the previous work on coarse graining of block copolymer melts used only a few (fixed) number of CG segments to represent each copolymer chain and simple analytical expressions for the CG potentials that require additional approximations.^{[29,} ^{34, 35, 38, 39, 47]} In particular, the above mapping^[29, 34] of real block copolymer melts (i.e., with atomistic details) to the DPD model is somewhat *ad hoc* and requires atomistic simulations of the original system, which are computationally very expensive and contradict the purpose of coarse graining^[48]; the much shorter chain length used in the original system than in the CG system further means that they have very different $\overline{\mathcal{N}}$ -values (i.e., chain number densities) controlling the system fluctuations and causes the transferability problem in coarse graining (that is, the CG potentials obtained at one state cannot be directly used at another because they are state functions)^[49]. In contrast, our systematic and simulation-free coarse-graining strategy is quite general and versatile.^[17, 48, 50] It is much faster than those using MCMS, thus effectively solving the transferability problem, and also avoids the problems caused by finite-size effects and statistical uncertainties in MCMS.^[48] Our structure-based coarse graining ensures that the original and CG systems have the same intra- and intermolecular PCFs involving the CG

segments (each representing the CoM of a group of consecutive monomers on the same chain in the original system), *regardless* of the original model system, closures and coarse-graining levels used. Furthermore, our highly accurate numerical CG potentials remove the uncontrolled approximations needed in the previous analytical approaches^[35, 38, 39, 47], and make our strategy equally applicable to more complicated chain models than CGC.^[48] In the following, we present in detail our strategy applied to a simple original model system of DBC melts, and quantitatively examine how the effective non-bonded pair potentials between CG segments and the thermodynamic properties of CG systems vary with the coarse-graining level.

3.2 Model and method

3.2.1 Structure-based coarse graining using PRISM

Here we consider a general original system of *n* diblock copolymer (DBC) A-B chains each of N_m monomers (interaction sites) in volume V at thermodynamic temperature T, where the first $f_A N_m$ monomers on each chain are of species A and the rest $f_B N_m$ monomers are of species B. Let $\rho_I = f_I \rho$ be the number density of monomers of species I (=A, B), where $\rho = nN_m/V$ is the total monomer number density. The PRISM theory^[1] for the original system gives $\hat{\mathbf{H}}^{mm} = \hat{\mathbf{\Omega}}^{mm} \hat{\mathbf{c}}^{mm} \left(\hat{\mathbf{\Omega}}^{mm} + \hat{\mathbf{H}}^{mm} \right), \text{ where } \hat{\mathbf{H}}^{mm} \text{ is a symmetric } 2 \times 2 \text{ matrix with its } \{\mathbf{I}, \mathbf{J}\} \ (= \{\mathbf{A}, \mathbf{B}\})$ element given by $\rho_{\rm I}\rho_{\rm J}\hat{h}_{\rm IJ}^{\rm num}$ and $h_{\rm IJ}^{\rm num}(r)$ being the interchain total pair correlation function (PCF) between two monomers (denoted by the superscript "mm") of species I and J, respectively, $\hat{\mathbf{c}}^{mm}$ is a symmetric 2×2 matrix with its {I,J} element given by \hat{c}_{IJ}^{mm} and $c_{IJ}^{mm}(r)$ being the interchain monomer-monomer direct PCF, $\hat{\Omega}^{mm}$ is a symmetric 2×2 matrix with its {I,J} element given by $\rho N_m \hat{\omega}_{IJ}^{nnm}$ and $\omega_{IJ}^{nnm}(r)$ being the normalized (i.e., $\hat{\omega}_{IJ}^{nnm}(q=0)=1$) intrachain monomer-monomer PCF. and we use the short-hand notation $\hat{f} = (4\pi/q) \int_0^\infty dr f(r) r \sin(qr)$ to denote the 3D Fourier transform of a radial function f(r) with q being the wavenumber.

For given $\hat{\Omega}^{mm}$ and non-bonded pair potentials $\beta u_{IJ}(r)$ between monomers of species I and J, respectively, for all IJ pairs, where $\beta \equiv 1/k_B T$ with k_B being the Boltzmann constant, we solve the above PRISM equation along with a closure for each IJ pair (i.e., an approximate relation among $\beta u_{IJ}(r)$, $c_{IJ}^{mm}(r)$ and $h_{IJ}^{mm}(r)$) to obtain $h_{IJ}^{mm}(r)$, then calculate the structural and thermodynamic properties of the original system. In particular, the partial structure factor characterizing the composition fluctuations in the original system is given by $S_{\psi,m} \equiv S_{AA,m} + S_{BB,m} - 2S_{AB,m}$, where $S_{U,m}$ denotes the {I,J} element of its structure factor matrix $\mathbf{S}_m \equiv (\hat{\mathbf{\Omega}}^{mm} + \hat{\mathbf{H}}^{mm}) / \rho$; after some algebra, we find $S_{\psi,m} / N_m = \delta \omega^{mm} + \sqrt{N} \Gamma_m / \Lambda$, where $\delta \omega^{mm} \equiv \hat{\omega}_{AA}^{mm} + \hat{\omega}_{BB}^{mm} - 2\hat{\omega}_{AB}^{mm}$, the invariant degree of polymerization^[42] $\overline{\mathcal{N}} \equiv (\rho R_{e,0}^{-3} / N_m)^2$ with $R_{e,0}$ denoting the root-mean-square end-to-end distance of an ideal chain in the original system, $\Gamma_m \equiv (\hat{\omega}_{AA}^{mm} - \hat{\omega}_{AB}^{mm})^2 C_{AA} + 2(\hat{\omega}_{AA}^{mm} - \hat{\omega}_{AB}^{mm})(\hat{\omega}_{AB}^{mm} - \hat{\omega}_{BB}^{mm})C_{AB} + (\hat{\omega}_{AB}^{mm} - \hat{\omega}_{BB}^{mm})^2 C_{BB} - \sqrt{\overline{\mathcal{N}}} \delta \omega^{mm} \Delta \omega^{mm} \Delta C$ with $C_{\rm II} \equiv N_m^2 \hat{c}_{\rm II}^{mm} / R_{e,0}^{-3}$ (note that the use of $R_{e,0}$ as the length scale in the above is not essential), $\Delta C \equiv C_{AA} C_{BB} - C_{AB}^{-2}$ and $\Delta \omega^{mm} \Delta C$. The spinodal curve (i.e., the stability limits of the barrier scale sc

stability limit of the homogeneous phase) of the original system is therefore given by

$$\left\{ \frac{\mathrm{d} \left(S_{\psi,m} / N_m \right)}{\mathrm{d} q} \right|_{q^*, \tilde{\chi}^*} = \frac{\mathrm{d} \delta \omega^{mm}}{\mathrm{d} q} \left|_{q^*} + \frac{\sqrt{\mathcal{N}}}{\Lambda} \left(\frac{\mathrm{d} \Gamma_m}{\mathrm{d} q} - \frac{\Gamma_m}{\Lambda} \frac{\mathrm{d} \Lambda}{\mathrm{d} q} \right) \right|_{q^*, \tilde{\chi}^*} = 0 \implies \left. \frac{\mathrm{d} \Lambda}{\mathrm{d} q} \right|_{q^*, \tilde{\chi}^*} = 0 \\ \left. \frac{N_m}{S_{\psi,m}} \right|_{q^*, \tilde{\chi}^*} = \frac{1}{\delta \omega^{mm} (q^*) + \sqrt{\mathcal{N}} \frac{\Gamma_m (q^*, \tilde{\chi}^*)}{\Lambda (q^*, \tilde{\chi}^*)}} = 0 \implies \Lambda (q^*, \tilde{\chi}^*) = 0$$

where the maximum of $S_{\psi,m}$ (occurring at q^*) diverges as the parameter $\tilde{\chi}$ characterizing the repulsion between A and B monomers reaches a certain value (i.e., $\tilde{\chi}^*$); note that, since both $\delta \omega^{nm}$ and Γ_m (and their derivatives with respect to q) are finite, $(d\Lambda/dq)|_{q^*,\tilde{\chi}^*} = 0$ is the only solution to the first equation above (where $\Lambda(q^*, \tilde{\chi}^*) = 0$). This is consistent with Eqs. (8.5~8.7) in Ref. ^[51] obtained by Schweizer.

Coarse-graining each I-block as $N_{\rm I}$ segments, each representing the center-of-mass of $l_{\rm I} = f_{\rm I} N_m / N_{\rm I}$ consecutive I-monomers, and introducing these segments as non-interacting sites into the original system to form the expanded original system, our structure-based coarse graining gives^[50] $\hat{\mathbf{H}}^{ss} \approx \hat{\mathbf{\Omega}}^{sm} (\hat{\mathbf{\Omega}}^{mm})^{-1} \hat{\mathbf{H}}^{mm} (\hat{\mathbf{\Omega}}^{mm})^{-1} \hat{\mathbf{\Omega}}^{ms}$, where $\hat{\mathbf{H}}^{ss}$ is a symmetric 2×2 matrix with its {I,J} element given by $\rho_{\rm I}\rho_{\rm J}\hat{h}_{\rm IJ}^{ss}/l_{\rm I}l_{\rm J}$ and $h_{\rm IJ}^{ss}(r)$ being the interchain total PCF between two segments (denoted by the superscript "ss") of species I and J, respectively, and $\hat{\Omega}^{sm} = (\hat{\Omega}^{ms})^T$ is a 2×2 matrix with its {I,J} element given by $\rho N^2 (f_J / N_J) \hat{\omega}_{IJ}^{sm}$, $N \equiv N_A + N_B$, and $\omega_{IJ}^{sm}(r)$ being the intrachain PCF between a segment of species I and a monomer of species J; note that we have assumed $\hat{\mathbf{c}}^{sm} = \mathbf{0}$, where $\hat{\mathbf{c}}^{sm} = (\hat{\mathbf{c}}^{ms})^T$ is a 2×2 matrix with its {I,J} element given by \hat{c}_{IJ}^{sm} and $c_{IJ}^{sm}(r)$ being the interchain direct PCF between a segment of species I and a monomer of species J in the expanded original system. We also note that a similar result was obtained by Sambriski and Guenza, who considered only the cases of N=1 and 2, with a factor of $4/\omega^2(k)$ ($\omega(k)$ is defined by Eq. (10) in their paper) missing on the right-hand-side of Eq. (11) or (12) in their paper.^[47]

The PRISM theory for the coarse-grained (CG) system gives

 $\hat{\mathbf{c}} = (\hat{\mathbf{\Omega}}^{ss})^{-1} \hat{\mathbf{H}}^{ss} (\hat{\mathbf{\Omega}}^{ss} + \hat{\mathbf{H}}^{ss})^{-1}$, where $\hat{\mathbf{\Omega}}^{ss}$ is a symmetric 2×2 matrix with its {I,J} element given by $\rho N^2 \hat{\omega}_{IJ}^{ss} / N_m$ and $\omega_{IJ}^{ss}(r)$ is the intrachain segment-segment PCF, and $\hat{\mathbf{c}}$ is a symmetric 2×2 matrix with its {I,J} element given by \hat{c}_{IJ} and $c_{IJ}(r)$ being the interchain direct PCF between two segments of species I and J, respectively, in the CG system. Similar to the original system, the partial structure factor characterizing the composition fluctuations in the CG system is given by $S_{\psi} \equiv S_{AA} + S_{BB} - 2S_{AB}$, where S_{IJ} denotes the {I,J} element of its structure factor matrix $\mathbf{S} = (\hat{\mathbf{\Omega}}^{ss} + \hat{\mathbf{H}}^{ss}) N_m / \rho N$; after some algebra, we find

$$S_{\psi}/N = \delta\omega^{ss} + \sqrt{\overline{\mathcal{N}}} \Gamma/\Lambda \text{, where } \delta\omega^{ss} \equiv \hat{\omega}_{AA}^{ss} + \hat{\omega}_{BB}^{ss} - 2\hat{\omega}_{AB}^{ss} \text{ an}$$

$$\Gamma \equiv C_{AA} \left(\hat{\omega}_{AA}^{sm} - \hat{\omega}_{BA}^{sm}\right)^{2} + 2C_{AB} \left(\hat{\omega}_{AA}^{sm} - \hat{\omega}_{BA}^{sm}\right) \left(\hat{\omega}_{AB}^{sm} - \hat{\omega}_{BB}^{sm}\right) + C_{BB} \left(\hat{\omega}_{AB}^{sm} - \hat{\omega}_{BB}^{sm}\right)^{2} - \sqrt{\overline{\mathcal{N}}} \Delta C \left[\hat{\omega}_{BB}^{nm} \left(\hat{\omega}_{AA}^{sm} - \hat{\omega}_{BA}^{sm}\right)^{2} - 2\hat{\omega}_{AB}^{nm} \left(\hat{\omega}_{AA}^{sm} - \hat{\omega}_{BA}^{sm}\right) \left(\hat{\omega}_{AB}^{sm} - \hat{\omega}_{BB}^{sm}\right) + \hat{\omega}_{AA}^{nm} \left(\hat{\omega}_{AB}^{sm} - \hat{\omega}_{BB}^{sm}\right)^{2}\right].$$

$$\Lambda(q^{*}, \tilde{\chi}^{*}) = 0 \text{ and } \left(d\Lambda/dq\right)|_{q^{*}, \tilde{\chi}^{*}} = 0 \text{ therefore give } \left[d\left(S_{\psi}/N\right)/dq\right]|_{q^{*}, \tilde{\chi}^{*}} = 0 \text{ and }$$

 $(N/S_{\psi})\Big|_{q^*,\tilde{\chi}^*} = 0$. In other words, our structure-based coarse graining does not change the spinodal curve of the original system; note that this important conclusion is *independent* of the original model system, the closures for the original and CG systems, and the coarse-graining levels for A and B blocks.

Finally, with closures for the CG system, we obtain the effective non-bonded pair potentials $\beta v_{IJ}(r)$ between segments of species I and J from $c_{IJ}(r)$ and $h_{IJ}^{ss}(r)$ for all IJ pairs, then calculate the structural and thermodynamic properties of the CG system.

3.2.2 A simple model

Due to its simplicity, we choose a specific original model system in this work, which is the DBC counterpart of that for symmetric binary polymer blends used in our previous work^[50]. Here the chain connectivity is described by the continuous Gaussian chain (CGC) model with $N_m \rightarrow \infty$ but finite $R_{e,0}$ and \overline{N} , $\beta u_{AA}(r) = \beta u_{BB}(r) = (\tilde{\kappa}/N_m^2)R_{e,0}^3\delta(r)$ with $\tilde{\kappa} \ge 0$ controlling the system compressibility (we used $\overline{\kappa} = \tilde{\kappa}\sqrt{\overline{N}}$ in our previous work^[48, 50]) and $\delta(r)$ denoting the Dirac δ -function, and $\beta u_{AB}(r) = \left((\tilde{\kappa} + \tilde{\chi})/N_m^2\right) R_{e,0}^{-3} \delta(r)$ with $\tilde{\chi} \ge 0$ controlling the AB incompatibility (we used $\bar{\chi} \equiv \tilde{\chi} \sqrt{N}$ in our previous work^[50]). We refer to this model as the CGC- δ model. It is equivalent to the case of zero interaction range of the model studied by David and Schweizer in Sec. IV of Ref. ^[52] (see our Appendix A for details) and that analyzed with mean-field theories by one of us in Ref. ^[53]. Also, the only difference between this model and the "standard" one^[54, 55] used in polymer field theories for DBC melts is that the latter is incompressible.

Hereafter we consider symmetric (i.e., $f_{\rm I}=1/2$) DBC melts, where the only difference between A and B is their labeling; any quantity with the subscript "AA" is therefore identical to that with the subscript "BB". As in our previous work^[17, 48, 50], we take $R_{e,0}$ as the length scale and define $\tilde{r} \equiv r/R_{e,0}$, assume ideal-chain conformations, and use the (linearized) Percus-Yevick (PY) closure^[56] given by $c_{\rm II}^{nnn}(\tilde{r}) = -(h_{\rm II}^{nnm}(\tilde{r})+1)\beta u_{\rm II}(\tilde{r})$ for all IJ pairs, which leads to constant $C_{\rm IJ}$ solved numerically at given $\bar{\mathcal{N}}$, $\tilde{\kappa}$ and $\tilde{\chi}$ from the following combined PRISM-PY equations:

$$\begin{cases} \frac{2}{\pi^2} \int_0^\infty \mathrm{d}\tilde{q} \,\frac{\tilde{q}^2}{\Lambda} \Big[\Big((\hat{\omega}_{AA}^{nnm})^2 + (\hat{\omega}_{AB}^{mm})^2 \Big) C_{AA} + 2\hat{\omega}_{AA}^{mm} \hat{\omega}_{AB}^{nnm} C_{AB} - \sqrt{\bar{\mathcal{N}}} \,\hat{\omega}_{AA}^{mm} \Delta \omega^{mm} \Delta C \Big] = -\frac{C_{AA}}{\tilde{\kappa}} - 1 \\ \frac{2}{\pi^2} \int_0^\infty \mathrm{d}\tilde{q} \,\frac{\tilde{q}^2}{\Lambda} \Big[\Big((\hat{\omega}_{AA}^{nnm})^2 + (\hat{\omega}_{AB}^{mm})^2 \Big) C_{AB} + 2\hat{\omega}_{AA}^{mm} \hat{\omega}_{AB}^{mm} C_{AA} - \sqrt{\bar{\mathcal{N}}} \,\hat{\omega}_{AB}^{mm} \Delta \omega^{mm} \Delta C \Big] = -\frac{C_{AB}}{\tilde{\kappa} + \tilde{\chi}} - 1 \end{cases}$$

where $\tilde{q} \equiv qR_{e,0}$, and $\hat{\omega}_{AA}^{mm}$ and $\hat{\omega}_{AB}^{mm}$ are given in Appendix B. We can then calculate $S_{\psi,m}/N_m = 2(\hat{\omega}_{AA}^{mm} - \hat{\omega}_{AB}^{mm})/[1 - \sqrt{N}(\hat{\omega}_{AA}^{mm} - \hat{\omega}_{AB}^{mm})(C_{AA} - C_{AB})]$, the interchain internal energy par chain $\beta u^m = -i\sqrt{N}C_{e}/4(1 + \delta_{e})$, where $\delta = 1$ for U = AA and 0 for U = AB, and the

per chain $\beta u_{c,IJ}^m = -\sqrt{N} C_{IJ} / 4(1 + \delta_{IJ})$, where $\delta_{IJ} = 1$ for IJ=AA and 0 for IJ=AB, and the

interchain virial pressure $\beta R_{e,0}^{3} P_{IJ}^{m} = -\bar{N}C_{IJ}/4(1+\delta_{IJ})$ due to the IJ interaction in the original system^[50]. The relation between our solved original system and that by David and Schweizer in Sec. IV of Ref. ^[52] is given in Appendix A.

At given $N_I = N/2$, our structure-based coarse graining gives

$$\left\{ \frac{\hat{h}_{AA}^{ss}}{R_{e,0}^{-3}} = \frac{4}{\Lambda} \left\{ \left((\hat{\omega}_{AA}^{sm})^2 + (\hat{\omega}_{AB}^{sm})^2 \right) C_{AA} + 2\hat{\omega}_{AA}^{sm} \hat{\omega}_{AB}^{sm} C_{AB} - \left[\hat{\omega}_{AA}^{nmm} \left((\hat{\omega}_{AA}^{sm})^2 + (\hat{\omega}_{AB}^{sm})^2 \right) - 2\hat{\omega}_{AB}^{nmm} \hat{\omega}_{AA}^{sm} \hat{\omega}_{AB}^{sm} \right] \sqrt{\mathcal{N}} \Delta C \right\}$$

$$\left\{ \frac{\hat{h}_{AB}^{ss}}{R_{e,0}^{-3}} = \frac{4}{\Lambda} \left\{ 2\hat{\omega}_{AA}^{sm} \hat{\omega}_{AB}^{sm} C_{AA} + \left((\hat{\omega}_{AA}^{sm})^2 + (\hat{\omega}_{AB}^{sm})^2 \right) C_{AB} + \left[\hat{\omega}_{AB}^{nmm} \left((\hat{\omega}_{AA}^{sm})^2 + (\hat{\omega}_{AB}^{sm})^2 \right) - 2\hat{\omega}_{AA}^{nmm} \hat{\omega}_{AA}^{sm} \hat{\omega}_{AB}^{sm} \right] \sqrt{\mathcal{N}} \Delta C \right\}$$

and the PRISM theory for the CG system gives

$$\begin{cases} \frac{\hat{c}_{AA}}{R_{e,0}^{3}} = \frac{\hat{\omega}_{AA}^{ss} \left(\sqrt{N} \Delta h^{ss} - 8 \hat{\omega}_{AB}^{ss} \hat{h}_{AB}^{ss} / R_{e,0}^{3}\right) + 4\left(\left(\hat{\omega}_{AA}^{ss}\right)^{2} + \left(\hat{\omega}_{AB}^{ss}\right)^{2}\right) \hat{h}_{AA}^{ss} / R_{e,0}^{3}}{N^{2} \Delta \omega^{ss} \left[\overline{N} \Delta h^{ss} + 8 \sqrt{N} \left(\hat{\omega}_{AA}^{ss} \hat{h}_{AA}^{ss} / R_{e,0}^{3} - \hat{\omega}_{AB}^{ss} \hat{h}_{AB}^{ss} / R_{e,0}^{3}\right) + 16 \Delta \omega^{ss}}\right]}, \\ \frac{\hat{c}_{AB}}{R_{e,0}^{3}} = \frac{-\hat{\omega}_{AB}^{ss} \left(\sqrt{N} \Delta h^{ss} + 8 \hat{\omega}_{AA}^{ss} \hat{h}_{AA}^{ss} / R_{e,0}^{3}\right) + 4\left(\left(\hat{\omega}_{AA}^{ss}\right)^{2} + \left(\hat{\omega}_{AB}^{ss}\right)^{2}\right) \hat{h}_{AB}^{ss} / R_{e,0}^{3}}{N^{2} \Delta \omega^{ss} \left[\overline{N} \Delta h^{ss} + 8 \sqrt{N} \left(\hat{\omega}_{AA}^{ss} \hat{h}_{AA}^{ss} / R_{e,0}^{3} - \hat{\omega}_{AB}^{ss} \hat{h}_{AB}^{ss} / R_{e,0}^{3}\right) + 16 \Delta \omega^{ss}}\right]}, \end{cases}$$

where $\Delta h^{ss} \equiv (\hat{h}^{ss}_{AA}/R_{e,0}^{3})^2 - (\hat{h}^{ss}_{AB}/R_{e,0}^{3})^2$ and $\Delta \omega^{ss} \equiv (\hat{\omega}^{ss}_{AA})^2 - (\hat{\omega}^{ss}_{AB})^2$, and $\hat{\omega}^{sm}_{AA}$, $\hat{\omega}^{sm}_{AB}$, $\hat{\omega}^{ss}_{AA}$

and $\hat{\omega}_{AB}^{ss}$ are given in Appendix B; we also compare in Appendix B our coarse-graining approach with that used by Sambriski and Guenza^[47]. We then calculate $h_{IJ}^{ss}(\tilde{r})$ and $c_{IJ}(\tilde{r})$ numerically, and obtain $\beta v_{IJ}(\tilde{r})$ with either the PY^[56], hypernetted-chain (HNC)^[14], or randomphase approximation (RPA)^[57, 58] closure for the CG system as

$$\beta v_{IJ}(\tilde{r}) = \begin{cases} \ln \left[1 - c_{IJ}(\tilde{r}) / \left(h_{IJ}^{ss}(\tilde{r}) + 1 \right) \right] & \text{PY} \\ h_{IJ}^{ss}(\tilde{r}) - c_{IJ}(\tilde{r}) - \ln \left(h_{IJ}^{ss}(\tilde{r}) + 1 \right) & \text{HNC} \\ - c_{IJ}(\tilde{r}) & \text{RPA} \end{cases}$$

We further measure the range of CG potentials by their second moment, $\sigma_{IJ} \equiv \sqrt{\int_0^\infty d\tilde{r} \tilde{r}^4 v_{IJ}(\tilde{r}) / \int_0^\infty d\tilde{r} \tilde{r}^2 v_{IJ}(\tilde{r})} \quad \text{. Similar to our previous work}^{[48, 50]}, \text{ we find}$

$$\left(\sigma_{AA}^{RPA}\right)^{2} = \frac{\int d\tilde{\mathbf{r}}\tilde{r}^{2}c_{AA}(\tilde{r})}{\int d\tilde{\mathbf{r}}c_{AA}(\tilde{r})} = \frac{-\nabla_{\tilde{\mathbf{q}}}^{2}\hat{c}_{AA}\Big|_{\tilde{q}=0}}{\hat{c}_{AA}(\tilde{q}=0)} = -\frac{1}{\hat{c}_{AA}(\tilde{q}=0)} \left(\frac{2}{\tilde{q}}\frac{d\hat{c}_{AA}}{d\tilde{q}} + \frac{d^{2}\hat{c}_{AA}}{d\tilde{q}^{2}}\right)\Big|_{\tilde{q}=0} = \frac{1}{3N} + \frac{7\left(1 - C_{AB}/C_{AA}\right)}{30N^{3}}$$

and

$$\left(\sigma_{AB}^{RPA}\right)^{2} = \frac{\int d\tilde{\mathbf{r}}\tilde{r}^{2}c_{AB}(\tilde{r})}{\int d\tilde{\mathbf{r}}c_{AB}(\tilde{r})} = \frac{-\nabla_{\tilde{\mathbf{q}}}^{2}\hat{c}_{AB}\Big|_{\tilde{q}=0}}{\hat{c}_{AB}(\tilde{q}=0)} = -\frac{1}{\hat{c}_{AB}(\tilde{q}=0)}\left(\frac{2}{\tilde{q}}\frac{d\hat{c}_{AB}}{d\tilde{q}} + \frac{d^{2}\hat{c}_{AB}}{d\tilde{q}^{2}}\right)\Big|_{\tilde{q}=0} = \frac{1}{3N} + \frac{7(C_{AA}/C_{AB}-1)}{30N^{3}},$$

where the Taylor expansion of $N^2 \hat{c}_{IJ} / R_{e,0}^{-3}$ given in Sec. 3.2.1 below is our results. We also measure the range of CG potentials by the location of their first root, \tilde{r}_{IJ} , which is the smallest \tilde{r} where $v_{IJ}(\tilde{r}_{IJ}) = 0$; note that $\tilde{r}_{IJ}^{PY} = \tilde{r}_{IJ}^{RPA}$.

Finally, we calculate

$$S_{\psi}/N = 2 \left\{ \hat{\omega}_{AA}^{ss} - \hat{\omega}_{AB}^{ss} + \sqrt{N} \left[\left(\hat{\omega}_{AA}^{sm} - \hat{\omega}_{AB}^{sm} \right)^2 \left(C_{AA} - C_{AB} \right) - \sqrt{N} \left(\hat{\omega}_{AA}^{mm} + \hat{\omega}_{AB}^{mm} \right) \left(\hat{\omega}_{AA}^{sm} - \hat{\omega}_{AB}^{sm} \right)^2 \Delta C \right] / \Lambda \right\},$$

and the interchain internal energy per chain

$$\beta u_{c,\mathrm{IJ}} = \left[\pi \sqrt{N} N^2 / (1 + \delta_{\mathrm{IJ}}) \right] \int_0^\infty \mathrm{d}\tilde{r}\tilde{r}^2 \left(h_{\mathrm{IJ}}^{ss}(\tilde{r}) + 1 \right) \beta v_{\mathrm{IJ}}(\tilde{r}) \quad \text{and} \quad \text{interchain} \quad \text{virial} \quad \text{pressure} \\ \beta R_{e,0}^{-3} P_{\mathrm{IJ}} = \left[\pi \sqrt{N} N^2 / 3 (1 + \delta_{\mathrm{IJ}}) \right] \int_0^\infty \mathrm{d}\tilde{r}\tilde{r}^3 \left(h_{\mathrm{IJ}}^{ss}(\tilde{r}) + 1 \right) \mathrm{d}\beta v_{\mathrm{IJ}}(\tilde{r}) / \mathrm{d}\tilde{r} \quad \text{due to the IJ interaction in the} \\ \text{CG system. We use the same numerical methods as in our previous work}^{[50]}; \text{ note that, due to} \\ \text{a typographical error, } |C_{\mathrm{AA}}| \text{ is missing right after } \sqrt{N} \quad \text{in the twelfth line below Eq. (19) in} \\ \text{Ref.}^{[50]}$$

3.3 Results and Discussion

Here we first present in Secs. 3.1 and 3.2 results of the original and coarse-grained (CG) systems of symmetric diblock copolymer (DBC) melts, respectively, then compare in Sec. 3.3 their thermodynamic properties (i.e., the interchain internal energy per chain and virial pressure). The latter clearly shows that the structure-based coarse graining cannot give thermodynamic consistency at any coarse-graining level, consistent with our previous work on both homopolymer melts^[48, 59] and binary polymer blends^[50].

3.3.1 Original System

Our original system of the CGC- δ model for symmetric DBC melts has three parameters: $\tilde{\kappa}$ controlling the repulsion between all monomers (i.e., the system compressibility), $\tilde{\chi}$ controlling the repulsion between A and B monomers (i.e., the AB incompatibility), and the (finite) invariant degree of polymerization^[42] $\bar{\mathcal{N}}$ controlling the system fluctuations. It reduces to the hard-core CGC- δ model for homopolymer melts^[48, 60] in the limit of $\tilde{\kappa} \to \infty$ and to the soft-core CGC- δ model for homopolymer melts^[48, 50] at $\tilde{\chi} = 0$ and finite $\tilde{\kappa}$, just as the original model system for symmetric binary polymer blends (BPB) used in our previous work^[50]. We therefore consider *finite* $\tilde{\kappa} \ge 0$ and $\tilde{\chi} > 0$, i.e., the soft-core CGC- δ model, which is solved with the ideal-chain conformations and (linearized) Percus-Yevick (PY) closure^[56], in this work.

It is easy to show that the partial structure factor $S_{\psi,m}/N_m$ characterizing the composition fluctuations in our symmetric DBC melts has its maximum at $\tilde{q}^* \approx 4.7656$ (due

to the assumption of ideal-chain conformations), and diverges when $C_{AA} - C_{AB} \approx 10.495 / \sqrt{N}$ (i.e., the spinodal point). In comparison, the mean-field order-disorder transition (ODT) can be obtained with the random-phase approximation (RPA) closure^[57, 58], which gives $\tilde{\chi}_m^* \approx 10.495 / \sqrt{N}$ (i.e., $\bar{\chi}_m^* \approx 10.495$; here the subscript "*m*" denotes the mean-field result), the same as the well-known result of Leibler^[54], who used the "standard" incompressible CGC- δ model; as previously pointed out by one of us, the mean-field ODT does not depend on the system compressibility^[53]. The difference between the spinodal point and the mean-field ODT is therefore due to the PY closure approximately accounting for the fluctuation effects neglected at the mean-field level (i.e., by the RPA closure). Fig. 3.1(a) shows $N_m/S_{\psi,m}(\tilde{q}^*) = \left[1/(\hat{\omega}_{AA}^{mm}(\tilde{q}^*) - \hat{\omega}_{AB}^{mm}(\tilde{q}^*)) - \sqrt{N}(C_{AA} - C_{AB})\right]/2$ vs. $\tilde{\chi}$ at various \tilde{N} (=10³ and 10⁴) and $\tilde{\kappa}$ (=0 and 1); note that $N_m/S_{\psi,m}(\tilde{q}^*) = 1/2(\hat{\omega}_{AA}^{mm}(\tilde{q}^*) - \hat{\omega}_{AB}^{mm}(\tilde{q}^*)) \approx 5.2474$ at $\tilde{\chi} = 0$.

We see that the RPA closure gives straight lines with their slopes depending only on $\overline{\mathcal{N}}$, while the PY closure gives smaller $S_{\psi,m}(\tilde{q}^*)$ than the RPA result (at the same $\tilde{\chi}$ and $\overline{\mathcal{N}}$), indicating that the disordered phase is stabilized by the fluctuations. We also see that the deviation of the PY result from the RPA (mean-field) result increases with increasing $\tilde{\kappa}$ and decreasing $\overline{\mathcal{N}}$. Finally, we note that the PRISM theory used here is applicable only to homogeneous systems and thus cannot give any ODT except the mean-field one. Furthermore, since $\Lambda=0$ at the spinodal point, numerical calculations with the PY closure can only be performed for conditions not too close to it. In the following we consider three cases of symmetric DBC melts at $\tilde{\chi} = 1$ as examples to examine the effects of $\overline{\mathcal{N}}$ and $\tilde{\kappa}$: Case I is at $\tilde{\kappa} = 1$ and $\overline{\mathcal{N}} = 10^4$, Case II is at $\tilde{\kappa} = 1$ and $\overline{\mathcal{N}} = 10^3$, and Case III is at $\tilde{\kappa} = 0$ and $\overline{\mathcal{N}} = 10^4$; note that $C_{AA}=0$ in Case III, which leads to some qualitative differences from Cases I and II as shown in Sec. 3.2.3 below. We also note that $\overline{\mathcal{N}} = 10^3 \sim 2 \times 10^4$ for nearly symmetric DBC melts used in experiments that form lamellae with a bulk period of 20~100 nm.^[61]



Figure 3.1: Inverse of the partial structure factor in the original and coarse-grained system. Inverse of the partial structure factor characterizing the composition fluctuations in (a) the original system of the soft-core CGC- δ model for symmetric DBC melts solved with the idealchain conformations and the PY closure and (b) the corresponding CG system for $\tilde{\kappa} = \tilde{\chi} = 1$ and $\bar{\mathcal{N}} = 10^4$ (i.e., Case I) at its peak position \tilde{q}^* . The straight lines in part (a) are obtained with the RPA closure, and the horizontal lines in part (b) mark the corresponding values for the original system (the solid line is for the left axis and the dashed line for the right axis).

3.3.2 Coarse-grained System

Here we present the interchain total and direct pair correlation functions (PCFs), as well as the partial structure factor characterizing the composition fluctuations, in the CG systems of $2 \le N \le 100$, where each block is coarse-grained as N/2 segments. We also examine the nonbonded CG pair potentials obtained with various closures.
3.3.2.1 Case I: $\tilde{\kappa} = 1$ and $\bar{N} = 10^4$

In this case, we have $C_{AA}\approx -0.90272$, $C_{AB}\approx -1.0046$, and $N_m/S_{\psi,m}(\tilde{q}^*)\approx 0.15439$. The interchain direct PCFs between CG segments $c_{IJ}(\tilde{r})$ (IJ=AA and AB) are qualitatively the same as those for symmetric BPB shown in Fig. 4 of our previous work^[50]; note the Taylor expansion $N^2 \hat{c}_{AA}/R_{e,0}^3 = C_{AA} - [C_{AA}/18 + 7(C_{AA} - C_{AB})/180N^2]q_s^2 + O(q_s^4)$ and $N^2 \hat{c}_{AB}/R_{e,0}^3 = C_{AB} - [C_{AB}/18 - 7(C_{AA} - C_{AB})/180N^2]q_s^2 + O(q_s^4)$ at small $q_s \equiv \tilde{q}/\sqrt{N}$. On

the other hand, Figs. 2(a) and 2(b) show the interchain total PCFs between CG segments $h_{IJ}^{ss}(\tilde{r})$ (IJ=AA and AB) for various *N*, as well as those between monomers $h_{IJ}^{mun}(\tilde{r})$ in the original system.

We see that
$$h_{AA}^{ss}(\tilde{r}) > 0$$
 (except for $N \ge 16$ at $\tilde{r} \approx 0$) and $h_{AB}^{ss}(\tilde{r}) < 0$ for $\tilde{r} \le 0.6$, and that

 $h_{AA}^{ss}(\tilde{r})$ and $h_{AB}^{ss}(\tilde{r})$ collapse, respectively, for $N \gtrsim 10$ and larger \tilde{r} . More importantly, the insets of Figs. 2(a) and 2(b) show that $h_{U}^{ss}(\tilde{r})$ oscillates around 0 (as indicated by the cusps) with a period (measured by $\tilde{r}_{i+2} - \tilde{r}_i$ with \tilde{r}_i denoting the i^{th} root of $h_{U}^{ss}(\tilde{r})$) of about 1.33 (except for the first and last few *i*-values), which is independent of N and slightly larger than $2\pi/\tilde{q}^* \approx 1.318$, and that the extrema of $\tilde{r} |h_{U}^{ss}(\tilde{r})|$ decay exponentially with increasing \tilde{r} . Most of these features clearly originate from $h_{U}^{nnn}(\tilde{r})$, and are qualitatively different from those for symmetric BPB shown in Figs. 3.3(a) and 3.3(b) of our previous work^[50].

Figs. 3.2(a) and 3.2(b) further show that, with increasing N, $h_{IJ}^{ss}(\tilde{r})$ approaches $h_{IJ}^{nun}(\tilde{r})$

in a non-monotonic way; note that $h_{IJ}^{ss}(\tilde{r})$ becomes $h_{IJ}^{mm}(\tilde{r})$ in the limit of $N \rightarrow \infty$ (i.e., without coarse graining). On the other hand, Fig. 1(b) shows that coarse graining (i.e., decreasing N) increases both the peak value of the partial structure factor $S_{\psi}(\tilde{q}^*)/N$ characterizing the composition fluctuations in the CG system and its peak position \tilde{q}^* (or equivalently, decreases the characteristic wavelength $2\pi/\tilde{q}^*$ of the fluctuations); similar results are found for Cases II and III (data not shown).

The effective non-bonded CG pair potentials $\beta v_{IJ}(\tilde{r})$ are calculated from $h_{IJ}^{ss}(\tilde{r})$ and $c_{IJ}(\tilde{r})$ according to the PY^[56], hypernetted-chain (HNC)^[14], or RPA^[57, 58] closure for the CG system. Fig. 3.3(a) shows $\beta v_{IJ}(\tilde{r}=0)$ measuring the strength of the CG potentials; these results are similar to those for symmetric BPB shown in Fig. 3.5 of our previous work^[50], except that $\beta v_{AB}(\tilde{r}=0)$ here monotonically decreases with increasing *N* due to the non-bonded pair potential between monomers $\beta u_{IJ}(\tilde{r}=0) \rightarrow 0$ in the original system of the soft-core CGC- δ model^[48].



Figure 3.2: The interchain total PCFs between CG segments and those between monomers. The interchain total PCFs between CG segments $h_{IJ}^{ss}(\tilde{r})$ and those between monomers $h_{IJ}^{mm}(\tilde{r})$ for symmetric DBC melts at (a,b) $\tilde{\kappa} = 1$ and $\bar{\mathcal{N}} = 10^4$ (i.e., Case I), (c,d) $\tilde{\kappa} = 1$ and $\bar{\mathcal{N}} = 10^3$ (i.e., Case II), and (e,f) $\tilde{\kappa} = 0$ and $\bar{\mathcal{N}} = 10^4$ (i.e., Case III). The (red) dotted curve in each inset show $\tilde{r} \left| h_{IJ}^{mm}(\tilde{r}) \right|$. $\tilde{\chi} = 1$ in all cases.



Figure 3.3: Strength of the non-bonded CG pair potential between AA and AB segments. Logarithmic plot of the strength of the non-bonded CG pair potentials between AA and AB segments obtained with various closures for the CG system, for symmetric DBC melts at (a) $\tilde{\kappa} = 1$ and $\bar{\mathcal{N}} = 10^4$ (i.e., Case I), (b) $\tilde{\kappa} = 1$ and $\bar{\mathcal{N}} = 10^3$ (i.e., Case II), and (c) $\tilde{\kappa} = 0$ and $\bar{\mathcal{N}} = 10^4$ (i.e., Case III); $\tilde{\chi} = 1$ in all cases. In part (c), $v_{AA}^{RPA}(\tilde{r}=0) < 0$, $v_{AA}^{PY}(\tilde{r}=0) < 0$, $v_{AA}^{HNC}(\tilde{r}=0) > 0$, all $v_{AB}(\tilde{r}=0) > 0$, and "LS" denotes "least-squares".

Fig. 3.4 shows the CG potentials $v_{IJ}^{PY}(\tilde{r})$ (IJ \Box AA and AB) obtained with the PY closure for the CG systems, normalized by their strength. We see that $v_{IJ}^{PY}(\tilde{r})$ oscillates around 0 (as indicated by the cusps shown in the inset), and that $v_{IJ}^{PY}(\tilde{r})/v_{IJ}^{PY}(\tilde{r}=0)$ for various *N* approximately collapse when \tilde{r} is normalized by $N^{\Box-k}$ with $\kappa=0.620$; similar results are found for $v_{IJ}^{RPA}(\tilde{r})/v_{IJ}^{RPA}(\tilde{r}=0)$ and $v_{IJ}^{HNC}(\tilde{r})/v_{IJ}^{HNC}(\tilde{r}=0)$ (Data not shown), except that $v_{IJ}^{HNC}(\tilde{r}) > 0$ for *N*≥18.



Figure 3.4: Non-bonded CG pair potentials between AA and AB segments. Non-bonded CG pair potentials between (a) AA and (b) AB segments obtained with the PY closure, for symmetric DBC melts at $\tilde{\kappa} = \tilde{\chi} = 1$ and $\bar{N} = 10^4$ (i.e., Case I).

Finally, Figs. 3.5(a) and 3.5(b) show the range of the CG potentials as a function of *N*; note that our numerical results give $\sigma_{IJ}^{PY} \approx \sigma_{IJ}^{RPA}$ (data not shown), and that \tilde{r}_{IJ}^{HNC} is not calculated for $N \ge 18$. We see that σ_{IJ}^{HNC} exhibits a minimum at N=4, then monotonically increases with increasing *N*, and seems to approach an asymptotic value around 1 for large *N*; the latter clearly contradicts the zero-interaction range of $\beta u_{IJ}(r)$ in the original system, indicating the qualitative failure of the HNC closure for large *N*. On the other hand, we find that $\tilde{r}_{IJ}^{RPA} \propto N^{-0.620\pm0.003}$ using the least-squares fitting of the linearly transformed data; as in our previous work^[48, 50], we normalize \tilde{r} by N^{-k} with k=0.620 for the horizontal axis in Fig. 3.4 above to approximately collapse the CG potentials for various *N*. We also see that \tilde{r}_{IJ}^{HNC} exhibits a minimum at N=12 and that, for $N \le 12$, $\tilde{r}_{IJ}^{HNC} \approx \tilde{r}_{IJ}^{RPA}$ with a maximum deviation of <0.06 (<14%) for IJ=AA and of <0.1 (<23%) for IJ=AB (both occurring at N=12); in all cases, we find $\tilde{r}_{IJ}^{HNC} > \tilde{r}_{IJ}^{RPA}$ as in the case of symmetric BPB^[50].



Figure 3.5: Range of the non-bonded CG pair potentials.

Logarithmic plot of the range of the non-bonded CG pair potentials between (a) AA and (b) AB segments obtained with various closures for the CG system, for symmetric DBC melts at $\tilde{\kappa} = 1$ (i.e., Case I). Part (c) shows the results for symmetric DBC melts at $\tilde{\kappa} = 0$ (i.e., Case III). In all cases, $\tilde{\chi} = 1$ and $\bar{\mathcal{N}} = 10^4$. "LS" denotes "least-squares".

3.3.2.2 Case II: $\tilde{\kappa} = 1$ and $\bar{\mathcal{N}} = 10^4$

In this case, we have $C_{AA} \approx -0.68449$, $C_{AB} \approx -0.86944$, and $N_m / S_{\psi,m}(\tilde{q}^*) \approx 2.3231$. While

the results in this case are qualitatively the same as in Case I, they are *quantitatively different* due to the different \overline{N} -values. Figs. 3.2(c) and 3.2(d), for example, show that $h_{IJ}^{ss}(\tilde{r})$ oscillates

around 0 with a period of about 1.58 and that the extrema of $\tilde{r} |h_{IJ}^{ss}(\tilde{r})|$ decay much faster with increasing \tilde{r} than in Case I, due to the quantitatively different $h_{IJ}^{nm}(\tilde{r})$ in these two cases; note that $N_m/S_{\psi,m}(\tilde{q}^*)$ here is larger than that in Case I. It is therefore clear that, contrary to the common practice in the literature, CG potentials obtained from short-chain (i.e., small- \bar{N}) systems cannot be directly used for long-chain (i.e., large- \bar{N}) systems; this is in fact the transferability problem in coarse graining^[49]. As another example, comparing Figs. 3.3(a) and 3.3(b) shows the quantitative differences in $\beta v_{IJ}(\tilde{r}=0)$ between Cases I and II, and we find that $\tilde{r}_{IJ}^{RPA} \propto N^{-0.564\pm 0.003}$ using the least-squares fitting of the linearly transformed data in Case II.

3.3.2.3 Case III: $\tilde{\kappa} = 0$ and $\bar{\mathcal{N}} = 10^4$

In this case, we have $C_{AA}=0$ and $C_{AB}\approx-0.10481$, and $N_m/S_{\psi,m}(\tilde{q}^*)\approx 6.7456\times 10^{-3}$. Fig. 3.6(a) shows that, at small $q_s \equiv \tilde{q}/\sqrt{N} \lesssim 0.2$, $N^4 \hat{c}_{AA}/R_{e,0}^{-3} < 0$ for various N collapse as

supported by the Taylor expansion

$$N^{4} \frac{\hat{c}_{AA}}{R_{e,0}^{3}} = \frac{7}{180} C_{AB} q_{s}^{2} + \left[\left(\frac{7}{5184} + \frac{C_{AB} \sqrt{N}}{3240} \right) N - \frac{587}{136080} - \frac{7}{2400N^{2}} \right] C_{AB} q_{s}^{4} + O(q_{s}^{6}) \text{ in this}$$

case; with increasing q_s , however, it becomes >0 (after the cusp) and exhibits a maximum around $q_s=5$; and for larger q_s , it quickly approaches 0. This behavior is qualitatively different from Cases I and II above, as well as Case II for symmetric BPB (i.e., $\bar{\kappa} = 0$, $\bar{\chi} = 2$ and $\bar{N} = 10^4$) shown in Fig. 9(a) of our previous work^[50]. Fig. 3.6(b) shows that $c_{AA}(r_s)>0$ at small $r_s \equiv \sqrt{N}\tilde{r} \lesssim 0.5$, again qualitatively different from Cases I and II above. Note, however, that

 $c_{AB}(\tilde{r})$ here is qualitatively the same as in Cases I and II above, as well as Case II for symmetric BPB shown in Fig. 9(d) of our previous work^[50].

On the other hand, Figs. 3.2(e) and 3.2(f) show that $h_{U}^{ss}(\tilde{r})$ oscillates around 0 with a period of about 1.32 (slightly larger than $2\pi/\tilde{q}^*$) and that the extrema of $\tilde{r} |h_{U}^{ss}(\tilde{r})|$ decay much slower with increasing \tilde{r} than in Case I; we therefore increase the number of equally spaced subintervals, denoted by M in our previous work^[50], to 40,000 in order to increase the real-space cut-off in Case III. Note that $N_m/S_{\psi,m}(\tilde{q}^*)$ here is smaller than that in Case I; combining with the corresponding results in Case II, we attribute such changes to how far the system is from its spinodal point (as measured by $N_m/S_{\psi,m}(\tilde{q}^*)$). More importantly, Fig. 3.2(f) shows the unphysical result of $h_{AB}^{ss}(\tilde{r}) < -1$ for $N \leq 10$ at small \tilde{r} ; since $h_{U}^{mm}(\tilde{r}) > -1$ for all \tilde{r} and the PY closure works well for the repulsive potential in the original system, we attribute this unphysical behavior mainly to the use of ideal-chain conformations, which is strictly valid only in the limit of $\bar{N} \to \infty$ or at $\tilde{\chi} = 0$. Similar problem was found in our previous work on homopolymer melts.^[48]

Fig. 3.3(c) shows $\beta v_{IJ}(\tilde{r}=0)$ calculated from $h_{IJ}^{ss}(\tilde{r}=0)$ and $c_{IJ}(\tilde{r}=0)$ according to various closures for the CG system; note that $c_{AA}(r_s=0)>0$ leads to $\beta v_{AA}^{RPA}(\tilde{r}=0)<0$ and $\beta v_{AA}^{PY}(\tilde{r}=0)<0$ (similar results were found for symmetric BPB shown in Fig. 10(a) of our previous work^[50]), while $\beta v_{AA}^{HNC}(\tilde{r}=0)>0$ and all $\beta v_{AB}(\tilde{r}=0)>0$ as in Cases I and II above. We also note that the least-squares fitting of the linearly transformed data gives

 $-\beta v_{AA}^{RPA}(\tilde{r}=0) \propto N^{-1.461\pm0.004}$ and $\beta v_{AB}^{RPA}(\tilde{r}=0) \propto N^{-0.4916\pm0.0008}$; in Fig. 3.6(b), we therefore normalize $c_{AA}(r_s)$ by $N^{-1.461}$ to approximately collapse the results for various N. In addition, for large N, while $\beta v_{IJ}^{PY}(\tilde{r}=0)$ seems to follow the above scaling, $\beta v_{IJ}^{HNC}(\tilde{r}=0)$ levels off and contradicts $\beta u_{IJ}(\tilde{r}=0) \rightarrow 0$ in the original system. We further note that the above unphysical result of $h_{AB}^{ss}(\tilde{r}=0) < -1$ makes $\beta v_{AB}^{PY}(\tilde{r}=0)$ and $\beta v_{AB}^{HNC}(\tilde{r}=0)$ undefined for $N \le 12$.



Figure 3.6: 3D Fourier transform of the interchain direct PCFs between two A-segments in the CG system.

(a) Logarithmic plot of the Fourier transform of the interchain direct PCFs between two A-segments in the CG system \hat{c}_{AA} and (b) linear plot of $c_{AA}(r_s)$ with the inset of $|c_{AA}(r_s)|$ for symmetric DBC melts at $\tilde{\kappa} = 0$, $\tilde{\chi} = 1$ and $\bar{\mathcal{N}} = 10^4$ (i.e., Case III).

Finally, Fig. 3.5(c) shows the range of CG potentials as a function of *N*. Note that our numerical results give $\sigma_{AB}^{PY} \approx \sigma_{AB}^{RPA}$ (data not shown); σ_{AA}^{RPA} , however, cannot be calculated numerically due to $C_{AA}=0$ in this case, and a similar problem is encountered for σ_{AA}^{PY} . Also note that \tilde{r}_{IJ}^{HNC} can be calculated only for *N*=4, 6, and 8 (data not shown). As in Case I above, we see that σ_{IJ}^{HNC} approaches an asymptotic value for large *N*, indicating the *qualitative* failure of the HNC closure for large *N*. On the other hand, we find that $\tilde{r}_{AA}^{RPA} \propto N^{-0.493\pm0.001}$ and

 $\tilde{r}_{AB}^{RPA} \propto N^{-0.513\pm0.001}$ using the least-squares fitting of the linearly transformed data, where the data points at *N*=2 are excluded.

3.3.3 Thermodynamic inconsistency

Here we compare the thermodynamic properties (i.e., the interchain internal energy per chain $u_{c,IJ}$ and the interchain virial pressure P_{IJ} due to the IJ (=AA and AB) interaction) between the original and CG systems. Figs. 3.7(a) and 3.7(b) show their differences for Case I, where we have $\beta u_{c,AA}^m = \beta R_{e,0} P_{AA}^m / 100 \approx 11.284$ and $\beta u_{c,AB}^m = \beta R_{e,0} P_{AB}^m / 100 \approx 25.114$ for the original system, and the RPA and PY closures are used for the CG system. We find that the RPA closure underestimates all these quantities, while the PY closure overestimates $\beta R_{e,0} P_{AA}^m$ (except for $N \ge 82$) and $\beta u_{c,AA}^m$ but underestimates $\beta R_{e,0} P_{AB}^m$ (except for N=4 and $N \ge 34$) and $\beta u_{c,AB}^m$. For large N, the PY closure gives smaller deviations than the RPA closure; as expected, in the limit of $N \rightarrow N_m$, only the PY closure can recover the original system.

Fig. 3.7(c) shows the differences between the thermodynamic properties of the CG system obtained with the HNC closure and those with the RPA closure. Similar to the BPB studied in our previous work^[50], we find that $\beta \left(u_{c,IJ}^{HNC} - u_{c,IJ}^{RPA} \right) \approx \beta R_{e,0}^{-3} \left(P_{IJ}^{HNC} - P_{IJ}^{RPA} \right) / \sqrt{N} > 0$ scales approximately with N^2 for large N, which indicates the *qualitative* failure of the HNC closure in reproducing these thermodynamic properties of the original system for large N; the same reasoning as given in the second paragraph of Sec. 3.3.1 in our previous work^[50] applies here. Similar results are found for Cases II and III (data not shown).



Figure 3.7: Interchain internal energy per chain and virial pressure of the CG system. Logarithmic plot of the interchain internal energy per chain u_c and virial pressure P of the CG system due to (a) the AA and (b) the AB interactions obtained with the RPA and PY closures, for symmetric DBC melts at $\tilde{\kappa} = \tilde{\chi} = 1$ and $\bar{\mathcal{N}} = 10^4$ (i.e., Case I). Part (c) is a logarithmic plot of the difference in these quantities of the CG system obtained between the HNC and RPA closures.

As pointed out in our previous work on homopolymer melts^[48, 59] and BPB^[50], that the structure-based coarse graining cannot give thermodynamic consistency at any coarse-graining level is consistent with the finding by several other groups^[8, 49, 62, 63], and is actually expected due to the fact that the CG pair potentials do not have the many-body nature of the potential of mean force in coarse graining.

3.4 Summary

In this work, we have applied our recently proposed systematic and simulation-free strategy for the structure-based coarse graining of multicomponent polymeric systems^[50] to diblock copolymer (DBC) melts, where we use the well-developed polymer reference interaction site model (PRISM) theory^[1], instead of the commonly used many-chain molecular simulations (MCMS), to obtain the structural and thermodynamic properties of both the original and coarse-grained (CG) systems, and to quantitatively examine how the effective non-bonded pair potentials between CG segments and the thermodynamic properties of CG systems vary with the coarse-graining level. We have proved that our strategy does not change the spinodal curve, regardless of the original model system, closures, and coarse-graining levels for the two blocks.

Due to its simplicity, we have chosen a specific original model system for symmetric DBC A-B melts in this work, which consists of continuous Gaussian chains (CGCs) with the Dirac δ -function interactions and is referred to as the soft-core CGC- δ model. With the root-mean-square end-to-end distance of ideal chains taken as the length scale, this model has only three parameters (which are all finite): $\tilde{\kappa} \ge 0$ controlling the repulsion between all monomers (i.e., the system compressibility), $\tilde{\chi} > 0$ controlling the repulsion between A and B monomers

(i.e., the AB incompatibility), and the invariant degree of polymerization^[42] $\overline{\mathcal{N}}$ controlling the system fluctuations. It is the DBC counterpart of that for symmetric binary polymer blends (BPB) used in our previous work^[50], and its only difference from the "standard" model^[54, 55] used in polymer field theories for DBC melts is that the latter is incompressible (they therefore have the same mean-field ODT, i.e., the well-known Leibler's result^[54]). We have solved this original model system numerically with the assumption of ideal-chain conformations and the (linearized) Percus-Yevick (PY) closure^[56]. The relation between our solved original system and that by David and Schweizer in Sec. IV of Ref. ^[52] is given in Appendix A.

Coarse-graining each block as N/2 segments, We have then examined CG systems with $2 \le N \le 100$ in three cases, all at $\tilde{\chi} = 1$ and in the disordered phase stabilized by the system fluctuations: Case I is at $\tilde{\kappa} = 1$ and $\bar{\mathcal{N}} = 10^4$, Case II is at $\tilde{\kappa} = 1$ and $\bar{\mathcal{N}} = 10^3$, and Case III is at $\tilde{\kappa} = 0$ and $\bar{\mathcal{N}} = 10^4$. In particular, while the interchain direct pair correlation functions (PCFs) between CG segments $c_{IJ}(\tilde{r})$ (IJ=AA and AB) are qualitatively the same as those for symmetric BPB studied in our previous work^[50] in most cases, some qualitative differences in $c_{AA}(\tilde{r})$ are found in Case III. On the other hand, the interchain total PCFs between CG segments $h_{IJ}^{ss}(\tilde{r})$ oscillates around 0 and the extrema of $\tilde{r} \left| h_{IJ}^{ss}(\tilde{r}) \right|$ decay exponentially with increasing \tilde{r} ; we have found that the oscillation period is independent of N and is larger than $2\pi/\tilde{q}^* \approx 1.318$, where \tilde{q}^* denotes the wavenumber at which the partial structure factor characterizing the composition fluctuations in the original system reaches its maximum, and that the period approaches $2\pi/\tilde{q}^*$ and the decay becomes slower as the original system approaches its spinodal point (shown in Fig. 2). Most of these features clearly originate from $h_{IJ}^{nnn}(\tilde{r})$, and are qualitatively different from those for symmetric BPB studied in our previous work^[50]. We have also found that coarse graining (i.e., decreasing N) increases both the peak value and peak location of the partial structure factor characterizing the composition fluctuations in the CG system (see Fig. 3.1(b) for an example).

The effective non-bonded pair potentials $\beta v_{II}(\tilde{r})$ between CG segments of species I and

J are calculated from $h_{IJ}^{ss}(\tilde{r})$ and $c_{IJ}(\tilde{r})$ according to either the PY^[56], hypernetted-chain (HNC)^[14], or random-phase approximation (RPA)^[57, 58] closure for the CG system, and we have analyzed their strength $\beta v_{IJ}(\tilde{r}=0)$ (shown in Fig. 3.3) and range (shown in Fig. 3.5, where the results for Case II are similar to Case I and thus not shown), with the latter quantified by either their second moment σ_{IJ} or their first root \tilde{r}_{IJ} (note that we have obtained σ_{IJ}^{RPA} analytically, and that $\tilde{r}_{IJ}^{PY} = \tilde{r}_{IJ}^{RPA}$). While in most cases $\beta v_{IJ}(\tilde{r}=0)$ approaches 0 with increasing N for large N, consistent with the fact that the strength of the non-bonded pair potential $\beta u_{IJ}(\tilde{r})$ between monomers of species I and J in the original system is 0, $\beta v_{IJ}^{HNC}(\tilde{r}=0)$ in Case III levels off for large N and contradicts this fact. Similarly, while $\sigma_{IJ}^{PY} \approx \sigma_{IJ}^{RPA}$ (data not shown) and $\tilde{r}_{IJ}^{PY} = \tilde{r}_{IJ}^{RPA}$ all approach 0 with increasing N, σ_{IJ}^{HNC} levels off for large N and contradicts the fact that $\beta u_{IJ}(\tilde{r})$ has zero interaction range; note that σ_{AA}^{PY} and σ_{AA}^{RPA} in Case III, as well as $\tilde{r}_{\rm IJ}^{\rm HNC}$ for large N, cannot be calculated. With $\tilde{r}_{\rm IJ}^{\rm RPA} \propto N^{-k}$ obtained from the least-squares fitting of the linearly transformed data, we can approximately collapse $v_{IJ}(\tilde{r})/v_{IJ}(\tilde{r}=0)$ for various N by plotting them vs. $N^k \tilde{r}$ (see Fig. 4 for an example). Quantitative comparisons between Cases I and II, however, show that, contrary to the common practice in the literature, CG potentials obtained from short-chain (i.e., small- $\bar{\mathcal{N}}$) systems cannot be directly used for long-chain (i.e., large- $\bar{\mathcal{N}}$) systems; this is in fact the transferability problem in coarse graining^[49].

Finally, we have compared the thermodynamic properties (i.e., the interchain internal energies per chain and virial pressures) between the original and CG systems and found that

the structure-based coarse graining cannot give thermodynamic consistency at any coarsegraining level. This is consistent with our previous work on homopolymer melts^[48, 59] and BPB^[50], as well as the finding by several other groups^[8, 49, 62, 63], and is actually expected due to the fact that the CG pair potentials do not have the many-body nature of the potential of mean force in coarse graining. Our results clearly indicate the *qualitative* failure of the HNC closure in reproducing these thermodynamic properties of the original system for large *N*.

All the previous work on coarse graining of block copolymer melts used only a few (fixed) number of CG segments to represent each copolymer chain and simple analytical expressions for the CG potentials that require additional approximations.^[29, 34, 35, 38, 39, 47] In particular, the approximate intrachain PCFs for the ideal conformations of CGCs used by Sambriski and Guenza^[47] are both qualitatively incorrect and numerically unnecessary as shown in detail in Appendix B. The mapping^[29, 34] of real block copolymer melts (i.e., with atomistic details) to the dissipative particle dynamics model^[9, 28] is somewhat ad hoc and requires atomistic simulations of the original system, which are computationally very expensive and contradict the purpose of coarse graining^[48]; the much shorter chain length used in the original system than the CG system further causes the transferability problem in coarse graining^[49]. In contrast, our systematic and simulation-free coarse-graining strategy is quite general and versatile.^[17, 48, 50] It is much faster than those using MCMS, thus effectively solving the transferability problem in coarse graining, and also avoids the problems caused by finitesize effects and statistical uncertainties in MCMS.^[48] Furthermore, our highly accurate numerical CG potentials remove the uncontrolled approximations needed in the previous analytical approaches^[35, 38, 39, 47], and make our strategy equally applicable to more complicated chain models than CGC.^[48] Work in this direction will be reported in another publication.

Chapter 4 Numerical Analysis on the PRISM-PY Calculations of Coarse-Grained Polymer Models

4.1 Introduction

As one of the most successful theories, the polymer reference interaction site model (PRISM) theory, developed in 1987, has a wide application for predicting the structural and thermodynamic properties including blends, block copolymers, polyelectrolytes, homopolymer melts, solutions, and nanocomposites. Most of the application were reported by research groups of Schweizer and Curro.^[2-5] However, only a few works have been done on the numerical calculations of the PRISM theory compared with polymer self-consistent field (SCF) theory^[6] as another successful theory. Developing the numerical solution of PRISM model is promising as it is at least several orders of magnitude faster than MCMS, thus solving the transferability problem and those due to the finite-size effects and statistical uncertainties of MCMS. To achieve this, we focused on the PRISM-PY theory which can use used for accurate prediction of polymer melts and solutions in an implicit good solvent, where only short-range non-bonded repulsion between polymer segments is employed. In this work, it has been identified that most of previous works that worked well for PRISM calculations are not ideal for PRISM-PY models.

4.2 Model System and Numerical Methods

Taking the simplest system of *n* homopolymer chains each having *N* segments of diameter (*i.e.*, range of the repulsive part of their non-bonded pair potential $\beta u^{nb}(r)$, where $\beta = 1/k_B T$ with k_B being the Boltzmann constant) σ in volume *V* at thermodynamic temperature *T* as an example, the PRISM equation is given by

$$\hat{h} = N\hat{\omega}\hat{c}\left(N\hat{\omega} + \overline{\rho}\hat{h}\right),\tag{4.1}$$

where $h(\bar{r})$ is the interchain total segment pair correlation function (PCF) with $\bar{r} = r/\sigma$, $\omega(\bar{r})$ is the normalized (i.e., $4\pi \int_0^\infty d\bar{r}\bar{r}^2\omega(\bar{r}) = 1$) intrachain segment PCF, $c(\bar{r})$ is the interchain direct segment PCF, and $\hat{f} = (4\pi/q) \int_0^\infty d\bar{r}\bar{r}f(\bar{r})\sin(q\bar{r})$ denotes the 3D Fourier transform of a radial function $f(\bar{r})$ with q being the wavenumber (in units of $1/\sigma$), and $\bar{\rho} = nN\sigma^3/V$ is the dimensionless segment number density; note that, for monatomic fluids (*i.e.*, N=1), $\hat{\omega} = 1$ and the PRISM equation reduces to the well-known Ornstein-Zernike (OZ) equation^[64]. For given $N, \bar{\rho}$ and ω , to solve for both h and c, a closure is needed; for example, the commonly used atomic Percus-Yevick (PY) closure^[13]

$$c(\overline{r}) = \left[1 - \exp\left(\beta u^{\text{nb}}(\overline{r})\right)\right] \left(1 + h(\overline{r})\right) \tag{4.2}$$

works well for systems where $\beta u^{\rm nb}(\bar{r})$ is purely repulsive.

Analytical solution to the above PRISM-PY theory can be obtained only for the idealized model system of continuous Gaussian chains (where $N \rightarrow \infty$ and the effective bond length between two adjacent segments on a chain $l \rightarrow 0$ at finite ideal-chain root-mean-square end-to-end distance $R_{e,0} = \sqrt{Nl}$) with the Dirac δ -function non-bonded potential (*i.e.*,

 $\beta u^{nb}(r) \propto \delta(r)$ under the Padé approximation for the chain conformations (*i.e.*, $\hat{\omega} = 1/(1+q^2/12)$ with q here in units of $1/R_{e,0}$;^[60, 65] numerical calculations are needed for more complicated cases. In particular, in this work we consider three commonly used $\beta u^{nb}(r)$: The hard-sphere (HS) potential is given by $\beta u^{\text{HS}}(\overline{r}) \rightarrow \infty$ for $\overline{r} < 1$ and 0 otherwise; the Weeks-Chandler-Andersen (WCA) potential is given by $\beta u^{\text{WCA}}(\overline{r}) = \varepsilon (\overline{r}^{-6} - 1)^2$ for $\overline{r} < 1$ and 0 otherwise, which in the limit of the parameter $\varepsilon \to \infty$ becomes $\beta u^{\text{HS}}(\overline{r})$; and the dissipative particle dynamics (DPD) ^[9]potential is given by $\beta u^{\text{DPD}}(\overline{r}) = \varepsilon (1 - \overline{r})^2$ for $\overline{r} < 1$ and 0 otherwise, which in the limit of $\varepsilon \to \infty$ also becomes $\beta u^{\text{HS}}(\overline{r})$. In addition to $\beta u^{\text{nb}}(r)$, two adjacent segments on the same chain also interact with a bonded potential $\beta u^{b}(r)$. The tangent hard-sphere chain (THSC) model uses $\exp(-\beta u^{\rm b}(\bar{r})) = \delta(\bar{r}-1)/4\pi$ and $\beta u^{\rm HS}(\bar{r})$; the Kremer-Grest (KG) model uses $\beta u^{b}(\overline{r}) = -33.75 \varepsilon \ln \left[1 - (\overline{r}/1.5)^{2} \right]$ for $\overline{r} < 1.5$ and ∞ otherwise, and $\beta u^{\text{WCA}}(\bar{r})$ with $\varepsilon=1$ to prevent bond-crossing^[66]; and the DPD model uses $\beta u^{b}(\bar{r}) = 2\bar{r}^{2}$ [67] and $\beta u^{DPD}(\bar{r})$ with $\varepsilon = 37.5/\bar{\rho}$ to mimic the compressibility of water [31]. In the thermodynamic limit, the structural and thermodynamic properties of these three commonly used polymer models are therefore controlled only by N and $\overline{\rho}$; typically, the KG model uses $\overline{\rho} = 0.85$ for polymer melts, and the DPD model uses $\overline{\rho} = 3$ or 5.

In the early PRSM-PY calculations (where the repulsive part of $\beta u^{nb}(\overline{r})$ is $\beta u^{HS}(\overline{r})$), a variational method^[68] was used, where $c(0 \le \overline{r} \le 1^{-})$ is taken as a cubic polynomial with its four coefficients solved numerically. While for HSs (*i.e.*, N=1) this approach gives the exact solution to the OZ-PY theory^[64], for $N \ge 2$ the use of a cubic polynomial leads to systematic error (as shown by our results below). On the other hand, to avoid the expensive calculation of convolutions, the PY closure and the PRISM equation should be computed in the real and the reciprocal space, respectively. One therefore needs to introduce cut-offs and discretize these domains, use the fast Fourier transform (FFT) and the inverse Fourier transform (iFT), which for radial functions are equivalent to the Type-I fast sine transform (FST), to switch between these domains, and solve the PRISM-PY theory using an iterative method.

In 1992, Yethiraj and Schweizer^[69] proposed to use the Picard iteration (also known as the simple mixing, SM), where the interchain indirect PCF $\gamma(\overline{r}) \equiv h(\overline{r}) - c(\overline{r})$ is taken as the independent variables to be solved; with an initial guess $\gamma^{(0)}(\overline{r})$, they (I) calculated $c(\overline{r})$ from the closure and then \hat{c} via the FFT, (II) calculated $\hat{\gamma} = \left[N^2 \hat{\omega}^2 / (1 - N\overline{\rho}\hat{\omega}\hat{c}) - 1\right]\hat{c}$ (obtained from Eq.(4.1)) and then $\gamma(\overline{r})$ via the iFT, and (III) calculate $\gamma^{(1)}(\overline{r}) = \lambda\gamma(\overline{r}) + (1 - \lambda)\gamma^{(0)}(\overline{r})$ for the next iteration, where λ is a constant parameter for the SM. A similar method was implemented in the recently developed pyPRISM^[5], a Python-based open-source framework for PRISM calculations, with the following differences: In Step (II) $\hat{h} = N^2 \hat{\omega}^2 \hat{c} / (1 - N\overline{\rho}\hat{\omega}\hat{c})$ (instead of $\hat{\gamma}$) and $h(\overline{r})$ are calculated, then $\gamma(\overline{r}) = h(\overline{r}) - c(\overline{r})$ is obtained; and in Step (III) a Newton-Krylov based iteration (instead of the SM) is used by default.

For short-range and purely repulsive $\beta u^{nb}(\bar{r})$, the PY closure gives

$$c(\overline{r} \ge 1) = 0; \tag{4.3}$$

solving $c(0 \le \overline{r} < 1)$ therefore gives the least number of independent variables. Furthermore, for the THSC model, both $h(\overline{r})$ and $c(\overline{r})$ are discontinous, in both their value and their 1st-

order derivative, at $\overline{r} = 1$; taking their FFT without accounting for their discontinuities therefor leads to very slow convergence (thus much finer spatial discretization). In contrast, $\gamma(\overline{r})$ is continuous, and $\hat{\gamma}$ decays to 0 much faster than both \hat{h} and \hat{c} (as shown by our results below); it is therefore preferred to take the iFT of $\hat{\gamma}$, which reduces the cut-off in the reciprocal space. Finally, it is well-known that the SM has only linear convergence, thus not suitable for high-accuracy calculations.

The key to numerically solving the PRISM-PY theory is to accurately evaluate the improper integrals in the 3D Fourier transform and its inverse transform. Here we use large enough cut-offs $\overline{r_c}$ (which takes an integer value) and q_c , respectively, for the real and the reciprocal space, such that $\int_0^{\infty} d\overline{rf}(\overline{r}) \approx \int_0^{\overline{r_c}} d\overline{rf}(\overline{r})$ and $\int_0^{\infty} dqf(\overline{q}) \approx \int_0^{\overline{q_c}} dqf(\overline{q})$; the accuracy of these approximations essentially determines that of the numerical solution to the PRISM-PY theory. As aforementioned, it is also important to choose the integrand of these integrals, because its decay rate towards 0 with $\overline{r}(q)$ determines the value of $\overline{r_c}(q_c)$. We therefore use the following approach: We uniformly discretize the real-space interval [0,1] into m subintervals each of length $\Delta \overline{r} \equiv 1/m$; for the KG and DPD models, we take $c(\overline{r_i} \equiv i\Delta \overline{r})$ (i=0,...,m-1) as the independent variables to be solved and our approach has three steps:

I. Given the initial guess of the independent variables, with Eq.(4.3)we calculate $\hat{c}(q_j \equiv j\Delta q) = (4\pi/q_j) \int_0^{\overline{r_c}} d\overline{rrc}(\overline{r}) \sin(q_j\overline{r})$ for j=1,...,M-1 with $M \equiv m\overline{r_c}$ via the FST, which has a computing time of $O(M\ln M)$, and gives $\Delta q = m\pi/M$, $q_M=q_c=m\pi$ and $\hat{c}(q_c)=0$. We also calculate $\hat{c}_0 \equiv \hat{c}(q_0) = 4\pi \int_0^1 d\overline{rr}^2 c(\overline{r})$ via the Romberg integration. Note that the numerical accuracy of $\hat{c}(q_j)$ (*j*=0,...,*M*-1) is determined **only** by *m* (i.e., $\Delta \overline{r}$).

II. We calculate $\hat{\gamma}(q_j) = \left[N^2 \hat{\omega}^2(q_j) / (1 - N \overline{\rho} \hat{\omega}(q_j) \hat{c}(q_j)) - 1 \right] \hat{c}(q_j)$ for j=0,...,M-1 (note that $\hat{\gamma}(q_c) = 0$), then $\gamma(\overline{r_j}) = (1/2\pi^2 \overline{r_j}) \int_0^{q_c} dq q \hat{\gamma}(q) \sin(q \overline{r_j})$ for j=1,...,M-1 via the FST (which gives $\gamma(\overline{r_c}) = 0$) and $\gamma_0 \equiv \gamma(\overline{r_0}) = (1/2\pi^2) \int_0^{q_c} dq q^2 \hat{\gamma}(q)$ via the Romberg integration. Note that the numerical accuracy of $\gamma(\overline{r_j})$ for j=0,...,M-1 is determined by both m (i.e., q_c) and M (i.e., Δq).

III. We calculate $h(\overline{r_i}) = \gamma(\overline{r_i}) + c(\overline{r_i})$ for i=0,...,m-1, then use the residual errors of the PY closure to converge the *m* independent variables via the Anderson mixing (AM), the computing time of which is O(m). Note that, for the KG model, the PY closure gives $h(\overline{r_0}) = -1$.

 $h(\overline{r} \le 1^{-}) = -1$ for $\beta u^{\text{HS}}(\overline{r})$, and. Also note that, at $\overline{r} = 1$, both $h(\overline{r})$ and $c(\overline{r})$ are discontinous for the THSC model. These led to the differences below in our numerical solutions of the three models.

For the THSC model, due to its discontinuity at $\overline{r} = 1$, we take $c(\overline{r_i} = i\Delta \overline{r})$ (*i*=0,...,*m* with $\overline{r_m} = 1^-$) as the independent variables and make the following changes to the above steps: I. Here we use a continuous auxiliary function $c_0(\overline{r}) = \begin{cases} c(\overline{r}) - c_1\overline{r} & \text{if } \overline{r} \leq 1^-\\ c(\overline{r}) & \text{otherwise} \end{cases}$ with $c_1 \equiv c(\overline{r} = 1^-)$ to calculate

$$\hat{c}(q_j) = \left(\frac{4\pi}{q_j}\right) \left[\int_0^{\overline{r_c}} d\overline{rr} c_0(\overline{r}) \sin\left(q_j \overline{r}\right) + c_1 \int_0^1 d\overline{rr}^2 \sin\left(q_j \overline{r}\right) \right]$$
$$= \left(\frac{4\pi}{q_j}\right) \left\{ \int_0^{\overline{r_c}} d\overline{rr} c_0(\overline{r}) \sin\left(q_j \overline{r}\right) + c_1 \left[\left(2 - q_j^2\right) \cos q_j + 2q_j \sin q_j - 2 \right] / q_j^3 \right\}$$

via the FST; note that $\hat{c}(q_c) = (4c_1/m) [(-1)^m (2-m^2\pi^2) - 2]/(m\pi)^3$. We also calculate

 $\hat{c}_0 = 4\pi \int_0^{1^-} d\overline{r} r^2 c(\overline{r})$ via the Romberg integration.

II. Here we use another auxiliary function $\hat{\gamma}_0(q) \equiv \hat{\gamma}(q) - \hat{\gamma}_c$ with $\hat{\gamma}_c \equiv \hat{\gamma}(q_c)$ to calculate

$$\gamma(\overline{r}_{j}) = \left(\frac{1}{2\pi^{2}\overline{r}_{j}}\right) \left[\int_{0}^{q_{c}} \mathrm{d}q q \hat{\gamma}_{0}(q) \sin\left(q\overline{r}_{j}\right) - (-1)^{j} m^{2} \pi \hat{\gamma}_{c}/j\right] \text{ via the FST, which gives}$$
$$\gamma(\overline{r}_{c}) = -(-1)^{j} m^{3} \hat{\gamma}_{c}/2\pi M^{2}.$$

III. Here we take i=0,...,m. Note that the PY closure gives $h(\overline{r_i}) = -1$.

4.3 **Results and Discussion**

In all cases, we take the AM convergence criterion $\varepsilon_c=10^{-10}$ (*i.e.*, the maximum absolute value of the residual errors of the PY closure ovall all $\overline{r_i}$). We use the numerical error of \hat{c}_0 to choose the *m*-value; in particular, for the PRISM-PY theory of the THSC model at N=1 (i.e., the HS model), we have the exact result of $\hat{c}_0^* \equiv \hat{c}_0 (m \to \infty) = \pi (\eta^3 - 4\eta^2 + 2\eta - 8)/6(\eta - 1)^4$ with the HS packing fraction $\eta \equiv \pi \overline{\rho}/6$. Fig. 4.1(a) shows that the numerical error $\Delta \hat{c}_0(m) \equiv |\hat{c}_0^* - \hat{c}_0(m)|$ increases with increasing $\overline{\rho}$ and decays with m^{-2} for HS. We attribute this fast decay to our accounting for the discontinuities of $c(\overline{r})$ in its FFT; as shown in Fig. 4.4 (plotting $\Delta \hat{c}_0(m)$ vs. *m* for HS, KG and DPD model at *N*=1 and $\overline{\rho} = 0.6$) in the Appendix, the decay of $\Delta \hat{c}_0(m)$ with m^{-1} is obtained using pyPRISM^[70].

For the THSC model with $N \ge 2$, since the exact result of $\hat{c}_0(m \to \infty)$ is not known, we take $\hat{c}_0^* = \hat{c}_0(m)$ and found the same behavior of $\Delta \hat{c}_0(m)$; Fig. 4.1(a) further shows the cases for the THSC model with N=24 and 120 at $\bar{\rho} = 0.6$, where we see that $\Delta \hat{c}_0(m)$ increases with increasing *N*. Fig. 4.1(b) shows similar behavior for the KG and DPD models, where $\Delta \hat{c}_0(m)$ decays with m^{-4} at large *m*; numerical calculations of these models are therefore easier (*i.e.*, requires smaller m^*) than the THSC model. According to Figs. 4.1(a) and 4.1(b), we choose the *m*-value (denoted by m^*) in each case to ensure an accuracy of $\Delta \hat{c}_0(m^*) < 10^{-7}$ in our subsequent calculations.



Figure 4.1: Numerical error $\Delta \hat{c}_0(m)$ as a function of the spatial discretization parameter m and Numerical error $\Delta \hat{\gamma}_0(M)$ as a function of M/m.

Parts (a) and (b) show the numerical error $\Delta \hat{c}_0(m)$ as a function of the spatial discretization parameter *m* for (a) the THSC and (b) the KG and DPD models at various dimensionless segment number densities $\overline{\rho}$ and chain length *N*, based on which we choose m^* to ensure $\Delta \hat{c}_0(m^*) < 10^{-7}$ in our subsequent calculations. Similarly, parts (c) and (d) show the numerical error $\Delta \gamma_0(M;m^*)$ as a function of the spatial cut-off $\overline{r}_c = M/m^*$ for (c) the THSC and (d) the KG and DPD models at various $\overline{\rho}$ and *N*, based on which we choose $\overline{r}_c^* \equiv M^*/m^*$ to ensure $\Delta \gamma_0(M^*;m^*) < 10^{-8}$ in our subsequent calculations.

With the above chosen m^* , we similarly use the numerical error $\Delta \gamma_0(M; m^*) \equiv \left| \gamma_0(M; m^*) - \gamma_0(M; m^*) \right|$ to choose the *M*-value (equivalently $\overline{r_c}$); our results are shown in Figs. 4.1(c) and 4.1(d), based on which we choose the *M*-value (denoted by M^*) in each case to ensure that $\Delta \gamma_0(M^*; m^*) < 10^{-8}$ in our subsequent calculations.

Fig. 4.2(a) shows our numerical results of $|\hat{c}(q)|$, $|\hat{h}(q)|$ and $|\hat{\gamma}(q)|$ obtained for the THSC model at N=1 (i.e., the HS model) and $\bar{\rho} = 0.6$, which coincide with the analytical results within our numerical accuracy. Note that (1) the cusps in these logarithmic plots indicates the roots (where $\hat{c}(q)$, $\hat{h}(q)$ or $\hat{\gamma}(q)$ crosses 0), and (2) at large q the local maxima of $|\hat{\gamma}(q)|$ decay towards 0 with q^{-4} , much faster than those of $|\hat{c}(q)|$ and $|\hat{h}(q)|$ decaying with q^{-2} , thus justifying our Step II above; the same are found at other $\overline{\rho}$ -values (data not shown). Fig. 4.2(b) shows N=120, the corresponding results for where $\hat{\omega}(q) = \left\lceil N - B(q) \left(2 + NB(q) - 2B^{N}(q) \right) \right\rceil / N^{2} \left(1 - B(q) \right)^{2}$ with $B(q) = \exp\left(-\beta u^{\rm b}(\bar{r}) - \beta u^{\rm nb}(\bar{r})\right) / \exp\left(-\beta u^{\rm b}(\bar{r}) - \beta u^{\rm nb}(\bar{r})\right) (q=0) = \sin q/q \text{ are used; note}$ that this $\hat{\omega}(q)$ is exact for N=2, and we do not expect any qualitative changes in the decay of $\hat{c}(q)$, $\hat{h}(q)$ and $\hat{\gamma}(q)$ towards 0 at large q for more accurate $\hat{\omega}(q)$. One difference from the N=1 case, however, is that at large q the local maxima of $|\hat{\gamma}(q)|$ now decay towards 0 with q^{-3} ; the same are found at other N ≥ 2 and $\overline{\rho}$ -values (data not shown). Fig. 4.5 in the Summary shows the root-mean-square deviation of $c(0 \le \overline{r} \le 1^{-})$ from its least-square-fitted cubic polynomial $c_3(\overline{r})$, defined as $\Delta c \equiv \sqrt{\int_0^{1^-} d\overline{r} (c(\overline{r}) - c_3(\overline{r}))^2}$ and numerically calculated via the Romberg

integration, vs. $\overline{\rho}$ at various N; we see that the systematic error Δc introduced by variational method^[68] is on the order of 10⁻⁴ and increases with increasing $\overline{\rho}$.



Figure 4.2: 3D Fourier transform of the direct PCF, and that of the total PCF, and that of the indirect PCF for THSC model.

Logarithmic plot of our numerical results of the Fourier transform of the direct PCF $\hat{c}(q)$, that of the total PCF $\hat{h}(q)$, and that of the indirect PCF $\hat{\gamma}(q)$ obtained for the THSC model at (a) N=1 (i.e., the HS model) and (b) N=120; the dimensionless segment number density $\bar{\rho} = 0.6$. Note that *k* denotes the slope of the straight line.

Fig.4.3(a) shows our numerical results of $|\hat{h}(q)|$ and $|\hat{\gamma}(q)|$ obtained for the KG model

at N=1 and 120, where $\overline{\rho} = 0.85$ and

$$B(q) = \frac{\int_{0}^{2^{1/6}} d\overline{r}\overline{r} \sin(q\overline{r}) \Big[1 - (\overline{r}/1.5)^2 \Big]^{33.75} \exp\left[- (2\overline{r}^{-6} - 1)^2 \Big] + \int_{2^{1/6}}^{1.5} d\overline{r}\overline{r} \sin(q\overline{r}) \Big[1 - (\overline{r}/1.5)^2 \Big]^{33.75} - 1.2749384056052096 \times 10^{-10} q \Big]^{33.75} \exp\left[- (2\overline{r}^{-6} - 1)^2 \Big] + \int_{2^{1/6}}^{1.5} d\overline{r}\overline{r} \sin(q\overline{r}) \Big[1 - (\overline{r}/1.5)^2 \Big]^{33.75} - 1.2749384056052096 \times 10^{-10} q \Big]^{33.75} \exp\left[- (2\overline{r}^{-6} - 1)^2 \Big] + \int_{2^{1/6}}^{1.5} d\overline{r}\overline{r} \sin(q\overline{r}) \Big[1 - (\overline{r}/1.5)^2 \Big]^{33.75} \exp\left[- (2\overline{r}^{-6} - 1)^2 \Big] + \int_{2^{1/6}}^{1.5} d\overline{r}\overline{r} \sin(q\overline{r}) \Big[1 - (\overline{r}/1.5)^2 \Big]^{33.75} \exp\left[- (2\overline{r}^{-6} - 1)^2 \Big] + \int_{2^{1/6}}^{1.5} d\overline{r}\overline{r} \sin(q\overline{r}) \Big[1 - (\overline{r}/1.5)^2 \Big]^{33.75} \exp\left[- (2\overline{r}^{-6} - 1)^2 \Big] + \int_{2^{1/6}}^{1.5} d\overline{r}\overline{r} \sin(q\overline{r}) \Big[1 - (\overline{r}/1.5)^2 \Big]^{33.75} \exp\left[- (2\overline{r}^{-6} - 1)^2 \Big] + \int_{2^{1/6}}^{1.5} d\overline{r}\overline{r} \sin(q\overline{r}) \Big[1 - (\overline{r}/1.5)^2 \Big]^{33.75} \exp\left[- (2\overline{r}^{-6} - 1)^2 \Big] + \int_{2^{1/6}}^{1.5} d\overline{r}\overline{r} \sin(q\overline{r}) \Big[1 - (\overline{r}/1.5)^2 \Big]^{33.75} \exp\left[- (2\overline{r}^{-6} - 1)^2 \Big] + \int_{2^{1/6}}^{1.5} d\overline{r}\overline{r} \sin(q\overline{r}) \Big[1 - (\overline{r}/1.5)^2 \Big]^{33.75} \exp\left[- (2\overline{r}^{-6} - 1)^2 \Big] + \int_{2^{1/6}}^{1.5} d\overline{r}\overline{r} \sin(q\overline{r}) \Big[1 - (\overline{r}/1.5)^2 \Big]^{33.75} \exp\left[- (2\overline{r}^{-6} - 1)^2 \Big] + \int_{2^{1/6}}^{1.5} d\overline{r}\overline{r} \sin\left(q\overline{r}\right) \Big] + \int_{2^{1/6}}^{1.5} d\overline{r} \sin\left(q\overline{r}\right) \Big] \exp\left[- (2\overline{r}^{-6} - 1)^2 \Big] + \int_{2^{1/6}}^{1.5} d\overline{r} \sin\left(q\overline{r}\right) \Big] \exp\left[- (2\overline{r}^{-6} - 1)^2 \Big] + \int_{2^{1/6}}^{1.5} d\overline{r} \sin\left(q\overline{r}\right) \Big] \exp\left[- (2\overline{r}^{-6} - 1)^2 \Big] + \int_{2^{1/6}}^{1.5} d\overline{r} \sin\left(q\overline{r}\right) \Big] \exp\left[- (2\overline{r}^{-6} - 1)^2 \Big] + \int_{2^{1/6}}^{1.5} d\overline{r} \sin\left(q\overline{r}\right) \Big] \exp\left[- (2\overline{r}^{-6} - 1)^2 \Big] + \int_{2^{1/6}}^{1.5} d\overline{r} \sin\left(q\overline{r}\right) \Big] \exp\left[- (2\overline{r}^{-6} - 1)^2 \Big] + \int_{2^{1/6}}^{1.5} d\overline{r} \sin\left(q\overline{r}\right) \Big] \exp\left[- (2\overline{r}^{-6} - 1)^2 \Big] + \int_{2^{1/6}}^{1.5} d\overline{r} \sin\left(q\overline{r}\right) \Big] \exp\left[- (2\overline{r} - 1)^2 \Big] + \int_{2^{1/6}}^{1.5} d\overline{r} \cos\left(q\overline{r}\right) \Big] \exp\left[- (2\overline{r} - 1)^2 \Big] + \int_{2^{1/6}}^{1.5} d\overline{r} \cos\left(q\overline{r}\right) \Big] \exp\left[- (2\overline{r} - 1)^2 \Big] + \int_{2^{1/6}}^{1.5} d\overline{r} \cos\left(q\overline{r}\right) \Big] \exp\left[- (2\overline{r} - 1)^2 \Big] + \int_{2^{1/6}}^{1.5} d\overline{r} \cos\left(q\overline{r}\right) \Big] \exp\left[- (2\overline{r} - 1)^2 \Big] + \int_{2^{1/6}}^{1.5} d\overline{r} \cos\left(q\overline{r}\right)$$

are used, and Fig.4.3(b) shows those for the DPD model at N=1 and 10, where $\bar{\rho} = 3$ and

$$B(q) = \frac{\int_0^1 d\overline{rr} \sin(q\overline{r}) \exp\left[-\pi k^{-2/3}\overline{r}^2 - (a/2)(1-\overline{r})^2\right] + \int_1^\infty d\overline{rr} \sin(q\overline{r}) \exp\left(-\pi k^{-2/3}\overline{r}^2\right)}{q\left\{\int_0^1 d\overline{rr}^2 \exp\left[-\pi k^{-2/3}\overline{r}^2 - (a/2)(1-\overline{r})^2\right] + \int_1^\infty d\overline{rr}^2 \exp\left(-\pi k^{-2/3}\overline{r}^2\right)\right\}}$$
are

used. Comparing with Fig. 4.2 for the THSC model, we see that at large q the local maxima of $|\hat{h}(q)|$ (and $|\hat{c}(q)|$, data not shown) now decay with q^{-4} and those of $|\hat{\gamma}(q)|$ decay with q^{-9} (for N=1) or q^{-5} (for $N\geq 2$); the same are found at other $N\geq 2$ (data not shown). Numerical calcuations of the KG and DPD models are therefore easier than those of the THSC model.



Figure 4.3: 3D Fourier transform of the direct PCF, that of the total PCF, and that of the indirect PCF for THSC and DPD model. Logarithmic plot of our numerical results of the Fourier transform of the direct PCF $\hat{c}(q)$, that

of the total PCF $\hat{h}(q)$, and that of the indirect PCF $\hat{\gamma}(q)$ obtained for (a) THSC model at *N*=1, 120 and the dimensionless segment number density $\bar{\rho} = 0.6$. and (b) DPD model at *N*=1,10, and the dimensionless segment number density $\bar{\rho} = 3$; Note that *k* denotes the slope of the straight line.

4.4 Summary



Figure 4.4: The numerical error $\Delta \hat{c}_0(m)$ given by pyPRISM.

The numerical error $\Delta \hat{c}_0(m)$ as a function of the spatial discretization parameter *m* at chain length *N*=1 (*i.e.*, monomers), where the dimensionless monomer number density $\bar{\rho} = 0.6$, 0.85 and 3 for HS, KG and DPD models given by pyPRISM. See the main text for more details.



Figure 4.5: The root-mean-square deviation of $c(0 \le \overline{r} \le 1^{-})$ from its least-square-fitted cubic polynomial.

The root-mean-square deviation of $c(0 \le \overline{r} \le 1^{-})$ from its least-square-fitted cubic polynomial $c_3(\overline{r})$, $\Delta c \equiv \sqrt{\int_0^{1^{-}} d\overline{r} (c(\overline{r}) - c_3(\overline{r}))^2}$, vs. $\overline{\rho}$ at various N for the THSC model. See the main text for more details.



Figure 4.6: PCFs and 3D Fourier transform of PCFS for KG model at $\overline{\rho} = 0.85$. See the main text for more details.



Figure 4.7: PCFs and 3D Fourier transform of PCFS for DPD model at $\overline{\rho} = 3$. See the main text for more details.

Chapter 5 Fluctuation/Correlation Effects in Symmetric Diblock Copolymers: On the Disordered Phase

5.1 Introduction

Block copolymers have attracted great interest not only due to their technical applications (e.g., in nanotechnology) but also the underlying physics especially for their orderdisorder transition (ODT).^[71] While the polymer self-consistent field (SCF) theory has been widely applied to block copolymer systems with great success, it is a mean-field theory that neglects the system fluctuation/correlation (F/C) effects. Such effects are known to play important roles in both the ordered and disordered phases of block copolymers. In particular, SCF theory reduces to the well-known Flory-Huggins theory for the disordered phase, thus giving qualitatively incorrect predictions for the ODT.^[72, 73] On the other hand, the F/C effects studied in conventional molecular simulations of many-chain systems with hard-core repulsions (e.g., the Lennard-Jones repulsion in off-lattice and the self- and mutual-avoiding walk in lattice simulations), where the invariant degree of polymerization^[74] $\overline{N} \equiv (nR_{e_0}^3/V)^2$ controlling the system fluctuations for n monodisperse copolymer chains in volume V with $R_{e,0}$ denoting the root-mean-square end-to-end distance of an ideal chain is at most 100 or so, are not in the experimentally accessible range in most cases (where $\overline{N} > 10^3$).^[72] Using soft potentials that allow particle overlapping, such as done in our previous work^[73] (referred to as Paper I hereafter), is therefore the only way at present to simulate systems of much larger $\bar{\mathcal{N}}$

-values, and is the essence of our fast Monte Carlo simulations proposed several years ago.^[10, 75] This further allows us to directly compare the simulation results and theoretical predictions, based on the same model system without any parameter-fitting, to unambiguously quantify the F/C effects either neglected or treated approximately in the theories.^[75-78]

In Paper I, we reported the first systematic study unambiguously quantifying the ODT shift of a model system of symmetric diblock copolymers (DBC) from the mean-field prediction using fast off-lattice Monte Carlo (FOMC) simulations^[10] with experimentally accessible fluctuations. Here we focus on the disordered phase of the same DBC model system studied in Paper I and quantify the F/C effects on its structural and thermodynamic properties by directly comparing our FOMC results with predictions of both the polymer field theories and integral-equation theories. Systematic loop-expansions can be used to incorporate F/C effects into the field theories.^[79] As the zeroth-order expansion, SCF theory provides a well understood mean-field reference. Since it gives rather trivial predictions for the disordered (homogeneous) phase, however, here we mainly consider the second-order expansion (also known as the one-loop approximation^[80]), i.e., the Gaussian-fluctuation (GF) theory. As shown below, the GF theory predicts the mean-field ODT for symmetric DBC and various diverging behaviors at the ODT.

On the other hand, the integral-equation theories we consider here include both the reference interaction site model (RISM) theory proposed by Chandler and Anderson^[18, 20, 81, 82] and the polymer reference interaction site model (PRISM) theory proposed by Curro and Schweizer.^[25, 83, 84] The former extends the well-known Ornstein-Zernike (OZ) equation^[64] for spherical monatomic fluids to molecular fluids and accounts for both intra- and interchain correlations, and the latter further extends to long-chain systems by assuming that the interchain

total and direct pair correlation functions (PCFs) are independent of the interacting site (segment) positions along the chain, which greatly reduces the computation cost. Given the short chain lengths (*N*=10) used in our FOMC simulations, we explicitly check this approximation by comparing RISM and PRISM results. We also note that both theories require the intrachain PCF as an input, which are taken either as ideal-chain conformations or from our FOMC simulations, and a closure (i.e., an approximation relating the interchain direct PCF and the non-bonded pair potentials between polymer segments), for which we use the atomic random-phase approximation (RPA), Percus-Yevick (PY),^[13] and Zhou closures here; in particular, PRISM theory with the ideal-chain conformations and RPA closure is equivalent to the GF theory as shown below.

PRISM theory has also been widely applied to various polymeric systems. In particular, for conformationally symmetric DBC (A-B) modelled as the continuous Gaussian chains with the Dirac δ -function repulsion between all monomers (i.e., the reference system, denoted by CGC- δ) and an additional Yukawa potential for the AB repulsion, David and Schweizer solved PRISM theory analytically with the reference molecular mean spherical approximation (R-MMSA) and PY (R-MPY) closures, where their reference system was solved with the atomic PY closure^[13] and the Pade approximation for the ideal-chain conformations; in order to compare with the fluctuation theory of Fredrickson and Helfand,^[72] most of their results were obtained under the approximation of either the "literal" or the "effective" incompressibility and other approximations.^[51, 52] In the case where the reference system is the hard-core CGC- δ model, Guenza and Schweizer further simplified these analytical results under the approximations of small range of the Yukuwa potential and large \overline{N} .^[85] The CGC- δ model, however, cannot be directly used in molecular simulations; neither can the "literal"

incompressibility be enforced in off-lattice molecular simulations.

In a subsequent paper, David and Schweizer presented numerical results of the PRISM theory solved with the R-MMSA and R-MPY closures for conformationally symmetric DBC modelled as chains of tangential hard spheres with a modified Lennard-Jones tail potential (see Eq(2.4) there) for the AB repulsion, where they used the ideal-chain conformations.^[86] Later, Donley derived a new closure that is similar to the atomic (linearized) PY closure but incorporates three-body correlations beyond those included in the hypernetted-chain closure, and applied it to study the same model system of symmetric DBC as in Ref.^[86] (again with the ideal-chain conformations).^[87] These theoretical predictions, however, have not been directly compared with molecular simulations.

Our work therefore represents the first direct comparison between PRISM theory and molecular simulations for the disordered phase of block copolymers, where the same model system is used in both the theory and simulations; such comparisons unambiguously reveal the consequences of theoretical approximations and stimulate the development of advanced theories that can quantitatively describe the fluctuation/correlation effects in block copolymers and predict their ODT.

As mentioned early, the F/C effects plays very important role in both ordered and disordered phases for DBC systems. On the other hand, in the comparison among simulations and theories, the SCF theory neglects all the interchain fluctuations and correlations, the GF theory only considers the fluctuations in the Gaussian level, RISM theory with PY closure considers the correlations in the "PY level", and in the FOMC simulations all kinds of fluctuations and correlations are included.

This work is structured as follows. In the second section, we firstly introduce our model system with soft DPD potential and define some notations, where the discrete Gaussian chain (DGC) model is used, following some simple description about FOMC; then the derivation of GF theory and P/RISM theories are simply presented, where the equations of how to calculate the interested structural and thermodynamic properties are also presented. In the third section, these properties are compared among FOMC simulations and theories, including the block/chain mean-square end-to-end distances, the bonded and non-bonded internal energy per chain and (virial) pressure, the Helmholtz free energy per chain, the non-bonded constant-volume heat capacity, and the structure factors. We then make some conclusions and remarks in the fourth section. Some structural and thermodynamic quantities calculated from GF theory is presented in the Appendix. The chain-end effects neglected in the PRISM theory are also discussed in the Appendix.

5.2 Model and Methods

5.2.1 Model Systems

Our model system is the same as in Paper I^[73], where we consider compressible DBC systems of *n* chains in continuum, each consisting of *N* segments at a chain number density $\rho_c \equiv n/V$ with *V* being the system volume. Each chain has N_A A-type segments followed by N_B B-type segments, and $N = N_A + N_B$; for symmetric DBC $N_A = N_B$. The canonical partition function of the system is

$$\mathcal{Z} = \frac{1}{n!} \prod_{k=1}^{n} \prod_{s=1}^{N} \int d\mathbf{R}_{k,s} \cdot \exp\{-\beta \mathcal{H}^{C} - \beta \mathcal{H}^{E}\},$$
(5.1)

where $\mathcal{H}^{C} = \sum_{k=1}^{n} h_{k}^{C}$ is Hamiltonian due to the chain connectivity, with μ_{k}^{C} denoting the contribution of the k^{th} chain, described by the discrete Gaussian chain (DGC) model in 3D, i.e.,

$$\beta h_k^C = \frac{3}{2a^2} \sum_{s=1}^{N-1} \left(\mathbf{R}_{k,s+1} - \mathbf{R}_{k,s} \right)^2,$$
(5.2)

where $\beta \equiv 1/k_B T$ with k_B being the Boltzmann constant and T the thermodynamic temperature, a denotes the effective bond length (assumed to be same for both A and B blocks), and $\mathbf{R}_{k,s}$ denotes the spatial position of the s^{th} segment on the k^{th} chain. The non-bonded Hamiltonian $\mathcal{H}^E = \mathcal{H}^E_{\kappa} + \mathcal{H}^E_{\chi}$, with \mathcal{H}^E_{κ} and \mathcal{H}^E_{χ} given by

$$\mathcal{H}_{\kappa}^{E} = \frac{1}{2\kappa\rho_{0}} \int d\mathbf{r} d\mathbf{r}' \Big[\hat{\rho}_{A}(\mathbf{r}) + \hat{\rho}_{B}(\mathbf{r}) \Big] u_{0} \Big(|\mathbf{r} - \mathbf{r}'| \Big) \Big[\hat{\rho}_{A}(\mathbf{r}') + \hat{\rho}_{B}(\mathbf{r}') \Big] - \frac{nN}{2\kappa\rho_{0}} u_{0}(0), \tag{5.3}$$

$$\mathcal{H}_{\chi}^{E} = \frac{\chi}{\rho_{0}} \int d\mathbf{r} d\mathbf{r}' \hat{\rho}_{A}(\mathbf{r}) u_{0} \left(\left| \mathbf{r} - \mathbf{r}' \right| \right) \hat{\rho}_{B}(\mathbf{r}'), \qquad (5.4)$$
With Eq.(5.3) is due to the system compressibility characterized by the generalized Helfand compressibility \mathcal{K} ,^[88] with the last term used to deduct the self-interaction, and Eq.(5.4) models the repulsion between A and B segments with the generalized Flory-Huggins interaction parameter χ . The average number density of polymer segments is $\rho_0 \equiv nN/V$ and the microscopic densities of A and B segments are defined as $\hat{\rho}_A(\mathbf{r}) \equiv \sum_{k=1}^n \sum_{s=1}^{N_A} \delta(\mathbf{r} - \mathbf{R}_{k,s})$

and
$$\hat{\rho}_{\rm B}(\mathbf{r}) \equiv \sum_{k=1}^{n} \sum_{s=N_{\rm A}+1}^{N_{\rm B}} \delta(\mathbf{r} - \mathbf{R}_{k,s})$$
, respectively.

 $u_0(r) = (15k_BT/2\pi\sigma^3)(1-r/\sigma)^2 \theta(\sigma-r)$ is the dissipative particle dynamic simulations,^[31] with $r \equiv |\mathbf{r}|$ being the separation distance between two segments, the finite interaction range is σ and the Heaviside step-function is $\theta(r)$. The soft, repulsive non-bonded pair potential between two segments *s* and *s'* is therefore given by

$$\beta u_{s,s'} = \begin{cases} (N/\kappa) \beta u_0(r)/\rho_0 N & \text{if } s \text{ and } s' \text{ are of the same type} \\ (N/\kappa + \chi N) \beta u_0(r)/\rho_0 N & \text{otherwise} \end{cases}$$
(5.5)

Which recovers the hard-sphere potential as $N/\kappa \to \infty$.

Alternatively, \mathcal{H}^{E} can be re-written as

$$\beta \mathcal{H}^{E} = \frac{nN}{2\kappa} \left[1 - \frac{\beta u_{0}(0)}{\rho_{0}} \right] + n\chi N f_{A} f_{B} + \frac{N}{\kappa} E_{\kappa} + \chi N E_{\chi}$$
(5.6)

Where

$$E_{\kappa} \equiv (1/2\rho_0) \int d\mathbf{r} d\mathbf{r}' \delta \hat{\boldsymbol{\rho}}(\mathbf{r}) \cdot \mathbf{U}_{\kappa} (|\mathbf{r} - \mathbf{r}'|) \delta \hat{\boldsymbol{\rho}}(\mathbf{r}') \qquad \text{and}$$

 $E_{\chi} \equiv (1/2\rho_0) \int d\mathbf{r} d\mathbf{r}' \delta \hat{\boldsymbol{\rho}}(\mathbf{r}) \cdot \mathbf{U}_{\chi} (|\mathbf{r} - \mathbf{r}'|) \delta \hat{\boldsymbol{\rho}}(\mathbf{r}') \text{ measure the "contact" of all segments and that between A and B segments, respectively, beyond mean field values. Here the vector <math>\hat{\boldsymbol{\rho}}(\mathbf{r}) = [\hat{\rho}_A(\mathbf{r}), \hat{\rho}_B(\mathbf{r})]^T$, $\hat{\boldsymbol{\rho}}(\mathbf{r}) = [\hat{\rho}_A(\mathbf{r}), \hat{\rho}_B(\mathbf{r})]^T$ and $\boldsymbol{\rho}_0 = \rho_0 [f_A, f_B]^T$ with $f_A \equiv N_A/N$ and $f_B = 1 - f_A$ being the average volume fraction of A and B blocks in the copolymer,

respectively, and 2×2 interaction matrices
$$\mathbf{U}_{\kappa}(r) \equiv \left[\beta u_0(r)/N\right] \begin{bmatrix} 1 & 1 \\ 1 & 1 \end{bmatrix}$$
 and

$$\mathbf{U}_{\chi}(r) \equiv \begin{bmatrix} \beta u_0(r)/N \end{bmatrix} \begin{bmatrix} 0 & 1\\ 1 & 0 \end{bmatrix}.$$
 The non-bonded internal energy per chain is then given by
$$\beta u_{c,\text{nb}} \equiv \frac{\langle \beta \mathcal{H}^E \rangle}{n} = \frac{N}{2\kappa} \begin{bmatrix} 1 - \frac{\beta u_0(0)}{\rho_0} \end{bmatrix} + \chi N f_A f_B + \frac{N}{\kappa} \frac{\langle E_{\kappa} \rangle}{n} + \chi N \frac{\langle E_{\chi} \rangle}{n}, \qquad (5.7)$$

The difference in the Helmholtz free energy per chain from the reference state at $\frac{N}{\kappa} = \chi N = 0$

can be calculated via the thermodynamic integration as

$$\beta\Delta f_{c} = \frac{N}{2\kappa} \left[1 - \frac{\beta u_{0}(0)}{\rho_{0}} \right] + \chi N f_{A} f_{B} + \frac{1}{n} \left[\int_{0}^{N/\kappa} dt_{1} \left\langle E_{\kappa} \right\rangle_{N/\kappa=t_{1},\chi N=0} + \int_{0}^{\chi N} dt_{2} \left\langle E_{\chi} \right\rangle_{N/\kappa,\chi N=t_{2}} \right], \quad (5.8)$$

Finally, the fluctuation of E_{κ} and E_{χ} are given by

$$\sigma_{\kappa}^{2} = \left\langle E_{\kappa}^{2} \right\rangle - \left\langle E_{\kappa} \right\rangle^{2} = -\left[\frac{\partial \left\langle E_{\kappa} \right\rangle}{\partial (N/\kappa)} \right]_{\chi N}$$
(5.9)
$$\sigma_{\chi}^{2} = \left\langle E_{\chi}^{2} \right\rangle - \left\langle E_{\chi} \right\rangle^{2} = -\left[\frac{\partial \left\langle E_{\chi} \right\rangle}{\partial (\chi N)} \right]_{N/\kappa}$$
(5.10)

$$\sigma_{\kappa,\chi}^{2} = \left\langle E_{\chi}^{2} \right\rangle - \left\langle E_{\chi} \right\rangle^{2} = -\left[\frac{\partial \left\langle E_{\kappa} \right\rangle}{\partial (\chi N)}\right]_{N/\kappa} = -\left[\frac{\partial \left\langle E_{\chi} \right\rangle}{\partial (N/\kappa)}\right]_{\chi N}, \tag{5.11}$$

from which the constant-volume heat capacity due to the non-bonded interactions is calculated as

$$\frac{C_{V,\text{nb}}}{k_B} = \frac{1}{n} \left[\left(N/\kappa \right)^2 \sigma_{\kappa}^2 + \left(\chi N \right)^2 \sigma_{\chi}^2 + 2 \left(N/\kappa \right) \left(\chi N \right) \sigma_{\kappa,\chi}^2 \right].$$
(5.12)

5.2.2 Fast off-lattice Monte Carlo (FOMC) Simulations

We perform FOMC simulations of the above model system in a canonical ensemble with trial moves of hopping^[75], reptation^[75], pivot^[73], and box-length change^[73], where replica exchange of configurations at different χN is used near ODT to further improve the sampling efficiency; more details are given in Paper I^[73]. Note that our simulations are performed in a variable-length, rectangular parallelepipedal box with the periodic boundary conditions applied in all directions. For the disordered phase close to ODT, the box-length change trial moves are needed to eliminate the effects of the periodic boundary conditions on the system fluctuations.

In our simulations, we calculate

$$E_{\kappa} = (1/2\rho_0 N) \sum_{k=1}^{n} \sum_{k'=1}^{n} \sum_{s=1}^{N} \sum_{s'=1}^{N} \beta u_0 (|\mathbf{R}_{k,s} - \mathbf{R}_{k',s'}|) - n/2 \qquad \text{and}$$

$$E_{\chi} = (1/\rho_0 N) \sum_{k=1}^{n} \sum_{k'=1}^{n} \sum_{s=1}^{N_A} \sum_{s'=N_A+1}^{N} \beta u_0 (|\mathbf{R}_{k,s} - \mathbf{R}_{k',s'}|) - n/4 \text{ ,and their fluctuations}$$

according to Eqs. (5.9)~(5.11) using the second order centered finite difference after their ensemble averages are obtained.

5.2.3 Polymer field theories

Here we start from the same model system as in Sec.5.2.1 and insert the identity $1 = \prod_{P=A,B} \int \mathcal{D}\rho_P \mathcal{D}(\omega_P/2\pi) \exp\left\{\int d\mathbf{r} i \omega_P(\mathbf{r}) [\rho_P(\mathbf{r}) - \hat{\rho}_P(\mathbf{r})]\right\}$ into Eq.(5.1), where $\rho_P(\mathbf{r})$ is the density field constrained to $\hat{\rho}_P(\mathbf{r})$ and $\omega_P(\mathbf{r})$ is the conjugate field imposing this constraint. The partition function can finally be re-written as

$$\mathcal{Z} = \prod_{P} \int \mathcal{D}\rho_{P} \mathcal{D}(\omega_{P}/2\pi) \cdot \exp\left\{-\beta \mathcal{F}\left[\rho_{P}, \omega_{P}\right]\right\}$$

= $\exp\left\{-\beta \mathcal{F}^{id}\right\} \prod_{P} \int \mathcal{D}\rho_{P} \cdot \exp\left\{-\beta \mathcal{H}^{E}\left[\rho_{A}, \rho_{B}\right]\right\}$
 $\times \prod_{P} \int \mathcal{D}(\omega_{P}/2\pi) \cdot \exp\left\{-\beta \mathcal{F}^{en}\left[\rho_{A}, \rho_{B}, \omega_{A}, \omega_{B}\right]\right\},$ (5.13)

where $\beta \mathcal{F}^{id} \equiv -\ln(G^n/n!)$ is the Helmholtz free energy of ideal chains with $G \equiv \prod_{s=1}^{N} \int d\mathbf{R}_s \cdot \exp\{-\beta h^C\}$, and $\beta \mathcal{F}^{en} \equiv -\sum_{p} \int d\mathbf{r} i \omega_p(\mathbf{r}) \rho_p(\mathbf{r}) - n \ln Q[i\omega_A, i\omega_B]$ is the entropic contribution from chain configurations with the single-chain partition function $Q \equiv \prod_{s=1}^{N} \int d\mathbf{R}_s \cdot \exp\{-\beta h^C - i \sum_{s=1}^{N_A} \omega_A(\mathbf{R}_s) - i \sum_{s=N_A+1}^{N} \omega_B(\mathbf{R}_s)\} / G$.

5.2.3.1 Self-consistent field (SCF) theory

The SCF solution, $\mathbf{\omega}^* = \left[\omega_A^*(\mathbf{r}), \omega_B^*(\mathbf{r})\right]^T$ and $\rho^* = \left[\rho_A^*(\mathbf{r}), \rho_B^*(\mathbf{r})\right]^T$, is obtained under the mean-field approximation $\left[\delta \mathcal{F}^{en}/\delta i\omega_P(\mathbf{r})\right]_{\mathbf{\omega}^*, \mathbf{\rho}^*}^T = \left[\delta\left(\mathcal{H}^E + \mathcal{F}^{en}\right)/\delta\rho_P(\mathbf{r})\right]_{\mathbf{\omega}^*, \mathbf{\rho}^*}^T = 0$. In this study we only consider the homogeneous phase, i.e., $\mathbf{\rho}^* = \rho_0$ and $\mathbf{\omega}^* = 0$. SCF theory then gives $\langle E_\kappa \rangle^{\text{SCF}} = \langle E_\chi \rangle^{\text{SCF}} = 0$, $\beta \Delta f_c^{\text{SCF}} = \beta \Delta u_{c,\text{nb}}^{\text{SCF}} = (N/2\kappa) \left[1 - \beta u_0(0)/\rho_0\right] + \chi N f_A f_B$ with $u_{c,\text{nb}}$ being the non-bonded internal energy per chain, the difference in the entropy per chain from the ideal-chain reference state $\Delta s_c^{\text{SCF}}/k_B = \Delta u_{c,\text{b}}^{\text{SCF}} = 1.5(N-1)$ with $u_{c,\text{b}}$ being the bonded energy per chain, the (virial) pressure due to the bonded interaction $\beta P_{c,b}^{\text{SCF}} = \rho_c \left(N/2\kappa + \chi N f_A f_B\right)$, and constant-volume heat capacity $C_V^{\text{SCF}}/k_B = C_{V,b}^{\text{SCF}}/k_B = 1.5(N-1)$ with $C_{V,b}$ being the contribution due to the bonded interaction and that due to the non-bonded interaction $C_{V,\text{ab}}^{\text{SCF}} = 0$. As for the chain dimensions, SCF theory gives random walk for a homogeneous system, e.g.,

$$R_{e,\text{SCF}}^2 = R_{e,0}^2 = (N-1)a^2.$$

5.2.3.2 Random-phase approximation (RPA) and Gaussian-fluctuation

In RPA analysis,^[75, 89, 90] the fields are re-written as $\omega(\mathbf{r}) = \omega^* + \delta \omega(\mathbf{r})$ and $\rho(\mathbf{r}) = \rho^* + \delta \rho(\mathbf{r})$, where $\omega(\mathbf{r})$ and $\rho(\mathbf{r})$ are defined similarly to $\hat{\rho}(\mathbf{r})$. The single-chain partition function can then be expanded to the second order in $\delta \omega(\mathbf{r})$ as

$$\ln Q[i\omega] \approx \ln Q[i\omega^*] - \frac{N}{2V} \int \frac{\mathrm{d}\mathbf{q}}{(2\pi)^3} \delta\hat{\omega}(\mathbf{q}) \cdot \mathbf{S}_1(\mathbf{q}) \delta\hat{\omega}(-\mathbf{q}).$$
(5.14)

where $\delta \hat{\omega}(\mathbf{q})$ denotes the 3D Fourier transform of $\delta \omega(\mathbf{r})$ with \mathbf{q} being wavevector, $\mathbf{S}_{1}(q)$ is the single-chain structure factor matrix with its element $S_{1,\text{PP}'}(q)$ being the average intrachain PCF between two segments on P and P' blocks, respectively, $q = |\mathbf{q}|$. For an ideal DGC, $S_{1,\text{AA}}(q) = NP(f_{\text{A}},q), S_{1,\text{BB}}(q) = NP(f_{\text{B}},q), S_{1,\text{AB}}(q) = S_{1,\text{BA}}(q) = [NP(1,q) - S_{1,\text{AA}}(q) - S_{1,\text{BB}}(q)]/2$

,where

$$P(f,q) = \left[fN - B(q) \left(2 + fNB(q) - 2B(q)^{fN} \right) \right] / N^2 \left(1 - B(q) \right)^2$$
 with

 $B(q) \equiv \exp(-a^2 q^2/6)$.^[75] We then write the second-order term of the statistical weight \mathcal{F} as

$$\beta \mathcal{F}_{\text{RPA}}^{(2)} = \frac{1}{2\rho_0} \int \frac{d\mathbf{q}}{(2\pi)^3} \delta \hat{\boldsymbol{\rho}}(\mathbf{q}) \cdot \left[\mathbf{S}_{\rho}^{\text{RPA}}(q) \right]^{-1} \delta \hat{\boldsymbol{\rho}}(-\mathbf{q}), \qquad (5.15)$$

where $\delta\beta \mathcal{F}_{\text{RPA}}^{(2)} / \delta\delta\hat{\omega}(\mathbf{q}) = 0$ is used, and

$$\mathbf{S}_{\rho}^{\text{RPA}} \equiv \begin{bmatrix} (N/\kappa) \beta \hat{u}_0 / N + S_{1,\text{AA}}^{-1} & (N/\kappa + \chi N) \beta \hat{u}_0 / N + S_{1,\text{AB}}^{-1} \\ (N/\kappa + \chi N) \beta \hat{u}_0 / N + S_{1,\text{AB}}^{-1} & (N/\kappa) \beta \hat{u}_0 / N + S_{1,\text{BB}}^{-1} \end{bmatrix}^{-1} = \left(\mathbf{S}_0 + \mathbf{S}_1^{-1} \right)^{-1}, \quad (5.16) \text{ with } \mathbf{S}_{\rho}^{-1} = \left(\mathbf{S}_0 + \mathbf{S}_1^{-1} \right)^{-1}, \quad (5.16) \text{ with } \mathbf{S}_{\rho}^{-1} = \left(\mathbf{S}_0 + \mathbf{S}_1^{-1} \right)^{-1}, \quad (5.16) \text{ with } \mathbf{S}_{\rho}^{-1} = \left(\mathbf{S}_0 + \mathbf{S}_1^{-1} \right)^{-1}, \quad (5.16) \text{ with } \mathbf{S}_{\rho}^{-1} = \left(\mathbf{S}_0 + \mathbf{S}_1^{-1} \right)^{-1}, \quad (5.16) \text{ with } \mathbf{S}_{\rho}^{-1} = \left(\mathbf{S}_0 + \mathbf{S}_1^{-1} \right)^{-1}, \quad (5.16) \text{ with } \mathbf{S}_{\rho}^{-1} = \left(\mathbf{S}_0 + \mathbf{S}_1^{-1} \right)^{-1}, \quad (5.16) \text{ with } \mathbf{S}_{\rho}^{-1} = \left(\mathbf{S}_0 + \mathbf{S}_1^{-1} \right)^{-1}, \quad (5.16) \text{ with } \mathbf{S}_{\rho}^{-1} = \left(\mathbf{S}_0 + \mathbf{S}_1^{-1} \right)^{-1}, \quad (5.16) \text{ with } \mathbf{S}_{\rho}^{-1} = \left(\mathbf{S}_0 + \mathbf{S}_1^{-1} \right)^{-1}, \quad (5.16) \text{ with } \mathbf{S}_{\rho}^{-1} = \left(\mathbf{S}_0 + \mathbf{S}_1^{-1} \right)^{-1}, \quad (5.16) \text{ with } \mathbf{S}_{\rho}^{-1} = \left(\mathbf{S}_0 + \mathbf{S}_1^{-1} \right)^{-1}, \quad (5.16) \text{ with } \mathbf{S}_{\rho}^{-1} = \left(\mathbf{S}_0 + \mathbf{S}_1^{-1} \right)^{-1}, \quad (5.16) \text{ with } \mathbf{S}_{\rho}^{-1} = \left(\mathbf{S}_0 + \mathbf{S}_1^{-1} \right)^{-1}, \quad (5.16) \text{ with } \mathbf{S}_{\rho}^{-1} = \left(\mathbf{S}_0 + \mathbf{S}_1^{-1} \right)^{-1}$$

the matrix $\mathbf{S}_0 \equiv (N/\kappa) \hat{\mathbf{U}}_{\kappa} + \chi N \hat{\mathbf{U}}_{\chi}$ due to the non-bonded interactions. For symmetric DBC,

 $S_{1,AA} = S_{1,BB}$ and we can diagonalize the matrix $(\mathbf{S}_{\rho}^{RPA})^{-1}$ to obtain Eqs. (A6) and (A7) in Ref. ^[75]. At the mean-field ODT $\chi_{MF}^* N$, $(\mathbf{S}_{\rho}^{RPA})^{-1}$ is singular at the most unstable mode q^* , which gives the corresponding lamellar period $L_{0,MF}^* = 2\pi/q^*$.^[75, 90] Alternatively, we can write

$$\beta \mathcal{F}_{\text{RPA}}^{(2)} = \frac{1}{2\rho_0} \int \frac{d\mathbf{q}}{(2\pi)^3} \delta \hat{\boldsymbol{\omega}}(\mathbf{q}) \cdot \left[\mathbf{S}_{\omega}^{\text{RPA}}(\mathbf{q}) \right]^{-1} \delta \hat{\boldsymbol{\omega}}(-\mathbf{q}), \qquad (5.17)$$

where $\beta \mathcal{F}_{\text{RPA}}^{(2)} / \delta \delta \hat{\mathbf{p}}(\mathbf{q}) = 0$ and $\mathbf{S}_{\omega}^{\text{RPA}} = (\mathbf{S}_{0}^{-1} + \mathbf{S}_{1})^{-1}$; $\chi_{\text{MF}}^{*} N$ and q^{*} can also be obtained from the singularity of q^{*} .

Substituting Eq. (5.14) into Eq.(5.13) and evaluating the Gaussian integrals over $\delta \hat{\omega}(\mathbf{q})$ and $\delta \hat{\mathbf{p}}(\mathbf{q})$, we can approximate the partition function \mathcal{Z} by

$$\mathcal{Z} = \exp\left\{-\beta \mathcal{F}^{id}\right\} \exp\left\{-n\beta \Delta f_c^{\text{SCF}}\right\} \int \mathcal{D}\boldsymbol{\rho} \exp\left\{-\frac{1}{2\rho_0} \int \frac{d\mathbf{q}}{(2\pi)^3} \delta \hat{\boldsymbol{\rho}}(\mathbf{q}) \cdot \mathbf{S}_0(q) \delta \hat{\boldsymbol{\rho}}(-\mathbf{q})\right\}$$
$$\cdot \int \mathcal{D}\left(\frac{\delta \boldsymbol{\omega}}{2\pi}\right) \exp\left\{\int \frac{d\mathbf{q}}{(2\pi)^3} \left[i\delta \hat{\boldsymbol{\omega}}(\mathbf{q}) \cdot \delta \hat{\boldsymbol{\rho}}(-\mathbf{q}) - \frac{\rho_0}{2} \delta \hat{\boldsymbol{\omega}}(\mathbf{q}) \cdot \mathbf{S}_1(q) \delta \hat{\boldsymbol{\omega}}(-\mathbf{q})\right]\right\}$$
$$= \exp\left\{-\beta \mathcal{F}^{id}\right\} \exp\left\{-n\beta \Delta f_c^{\text{SCF}}\right\} \prod_{\mathbf{q}} \left[\det\left[\mathbf{S}_1(q)\mathbf{S}_0(q) + \mathbf{I}\right]\right]^{-1/2},$$
(5.18)

which gives

$$\beta \Delta f_c^{\text{GF}} = \beta \Delta f_c^{\text{SCF}} + \frac{1}{2\rho_c} \int \frac{d\mathbf{q}}{\left(2\pi\right)^3} \ln \det \left[\mathbf{S}_1(q)\mathbf{S}_0(q) + \mathbf{I}\right]$$
(5.19)

with I being the 2×2 identity matrix.

5.2.4 Integral-equation (IE) theories

5.2.4.1 Reference interaction site model (RISM) theory

Due to the small N -values (10 and 20) and thus the large chain-end effects in our study, we employ RISM theory in most cases to study the structural and thermodynamic properties of symmetric DBC in the disordered phase. RISM theory describes the interchain pair correlation functions (PCFs) via the generalized Ornstein-Zernike (OZ) equation given in the Fourier space as^[20]

$$\hat{\mathbf{h}} = \hat{\boldsymbol{\omega}}\hat{\mathbf{c}}\left(\hat{\boldsymbol{\omega}} + \rho_c\hat{\mathbf{h}}\right),\tag{5.20}$$

where the symmetric matrices $\hat{\mathbf{h}}$, $\hat{\mathbf{o}}$ and $\hat{\mathbf{c}}$ have $N \times N$ elements of $\hat{h}_{s,s'}$, $\hat{\omega}_{s,s'}$ and $\hat{c}_{s,s'}$, respectively; $c_{s,s'}(r)$ and $h_{s,s'}(r) \equiv g_{s,s'}(r) - 1$ are the interchain direct and total PCFs, respectively, between the s^{th} segment on one chain and the s^{th} segment on another, with $g_{s,s'}(r)$ being the interchain radial distribution function; $\omega_{s,s'}(r)$ is the normalized (i.e., $\hat{\omega}_{s,s'}(q=0)=1$) intrachain PCF between the s^{th} and s^{th} segments on the same chain; and we use the short-hand notation $\hat{f} \equiv (4\pi/q) \int_0^\infty dr f(r) r \sin(qr)$. to denote the 3D Fourier transform of a radial function f(r).

In this study, we take $\hat{\omega}_{s,s'}$ as an input obtained in two ways: one is calculated directly in FOMC simulations and denoted by $\hat{\omega}_{s,s'}^{\text{FOMC}}$, and the other is given by the ideal DGC model as $\hat{\omega}_{s,s'}^{\text{DGC}} = B(q)^{|s-s'|}$. To assess the theoretical predictions of quantities directly related to the chain conformations (i.e., the chain/block end-to-end distance, internal energy and pressure due to the bonded interaction), however, we use only $\hat{\omega}_{s,s'}^{\text{DGC}}$; while the self-consistent integralequation theories can predict $\hat{\omega}_{s,s'}$, we expect that their results are in-between those obtained using $\hat{\omega}_{s,s'}^{\text{DGC}}$ and $\hat{\omega}_{s,s'}^{\text{FOMC}}$ leave such studies to the future.

Eq. (5.20) must be solved together with a closure relating the interchain direct and total PCFs. Here we use the atomic Percus-Yevick (PY) closure^[13] in most cases, commonly employed for short-range, repulsive non-bonded pair potentials, which for our soft potential [Eq. (5.5)] is given by

$$c_{s,s'}(r) = \left\{ 1 - \exp\left[\beta u_{s,s'}(r)\right] \right\} g_{s,s'}(r).$$
(5.21)

We solve the generalized OZ equation and closure iteratively. For \mathbf{c}^{old} , from Eq. (5.20) we obtain

$$\hat{\boldsymbol{\gamma}} \equiv \hat{\boldsymbol{h}} - \hat{\boldsymbol{c}} = \left(\boldsymbol{I} - \rho_c \hat{\boldsymbol{\omega}} \hat{\boldsymbol{c}}^{\text{old}}\right)^{-1} \left[\hat{\boldsymbol{\omega}} \hat{\boldsymbol{c}}^{\text{old}} \left(\hat{\boldsymbol{\omega}} + \rho_c \hat{\boldsymbol{c}}^{\text{old}} \right) - \hat{\boldsymbol{c}}^{\text{old}} \right],$$
(5.22)

where the symmetric matrix $\hat{\gamma}$ has $N \times N$ elements of interchain indirect PCFs $\hat{\gamma}_{s,s'}$ and **I** identity matrix. We then obtain the new is the $N \times N$ direct PCFs as $c_{s,s'}^{\text{new}}(r) = \left[\gamma_{s,s'}(r) + 1\right] \exp[-\beta u_{s,s'}(r)] - 1 - \gamma_{s,s'}(r)$ from the PY closure; the Anderson mixing method is used with а convergence criterion $\max_{\{s \ge s',r\}} \left\| \left[\gamma_{s,s'}(r) + 1 \right] \exp \left[-\beta u_{s,s'}(r) \right] - g_{s,s'}(r) \right\| \le 10^{-10} \text{ , where } \gamma_{s,s'}(r) \text{ and } g_{s,s'}(r) \text{ are } \beta = 0$ functions of $c_{s,s'}(r)$ from Eq. (22) and we use a cut-off $r_c = 10R_{e,0}$ for $\gamma_{s,s'}(r)$ [i.e., $h_{s,s'}(r)$ and $g_{s,s'}(r)$] and uniformly discretize $[0, r_c]$ into 3200 subintervals.

5.2.4.2 Polymer reference interaction site model (PRISM) theory

To highlight the chain-end effects, we compare the RISM predictions with those from PRISM theory in some cases. Following Schweizer^[52] and replacing the subscript "s, s'" by "sP, s'P'", where $\hat{h}_{sP,s'P'}$, for example, denotes the interchain PCF between the s^{th} segment on P (=A,B) block and the s'^{th} segment on P' block, we can rewrite Eq. (5.20) as

$$\hat{h}_{sP,s'P'} = \sum_{Q=A,B} \sum_{Q'=A,B} \sum_{t=1}^{N_Q} \sum_{t'=1}^{N_Q'} \hat{\omega}_{sP,tQ} \hat{c}_{tQ,t'Q'} \Big(\hat{\omega}_{t'Q',s'P'} + \rho_c \hat{h}_{t'Q',s'P'} \Big).$$
(5.23)

In PRISM theory one assumes $\hat{h}_{sP,s'P'} = \hat{H}_{P,P'} / f_P f_{P'}$ and $\hat{c}_{sP,s'P'} = \hat{C}_{P,P'}$, where $\hat{H}_{P,P'}$ and

 $\hat{C}_{P,P'}$ are the interchain total and direct PCFs between two segments on P and P' blocks, respectively. After some algebra, we finally obtain the PRISM equation from the above as

$$\hat{\mathbf{H}} = \mathbf{S}_{1} \hat{\mathbf{C}} \Big(\mathbf{S}_{1} + \rho_{0} \hat{\mathbf{H}} \Big), \tag{5.24}$$

where the symmetric 2×2 matrices $\hat{\mathbf{H}}$ and $\hat{\mathbf{C}}$ have elements of $\hat{H}_{\mathbf{P},\mathbf{P}'}$ and $\hat{C}_{\mathbf{P},\mathbf{P}'}$, respectively, and we have used $S_{1,\mathbf{PP}'} \equiv \sum_{s=1}^{N_{\mathbf{P}}} \sum_{s'=1}^{N_{\mathbf{P}'}} \hat{\omega}_{s\mathbf{P},s'\mathbf{P}'} / N$.

5.2.4.3 Quantities calculated from IE theories

A. Non-bonded internal energy, (virial) pressure, and free energy

The non-bonded internal energy per chain from IE theories is given by

$$\beta u_{c,\mathrm{nb}}^{\mathrm{IE}} = \beta u_{c,\mathrm{nb}}^{\mathrm{SCF}} + \frac{N}{\kappa} \frac{\langle E_{\kappa} \rangle^{\mathrm{IE}}}{n} + \chi N \frac{\langle E_{\chi} \rangle^{\mathrm{IE}}}{n}, \qquad (5.25)$$

with

$$\frac{\langle E_{\kappa} \rangle^{\text{IE}}}{n} = \frac{2\pi}{\rho_0 N} \sum_{s,s'=1}^{N} \int_0^\sigma dr \Big[\omega_{s,s'}(r) + \rho_c h_{s,s'}(r) \Big] r^2 \beta u_0(r)$$
(5.26)

and

$$\frac{\left\langle E_{\chi}\right\rangle^{\text{IE}}}{n} = \frac{4\pi}{\rho_0 N} \sum_{s=1}^{N_A} \sum_{s'=N_A+1}^{N} \int_0^\sigma dr \Big[\omega_{s,s'}(r) + \rho_c h_{s,s'}(r)\Big] r^2 \beta u_0(r)$$
(5.27)

have both intra- and interchain contributions. Similarly, the non-bonded (virial) pressure from IE theories is given by

$$\beta P_{\rm nb}^{\rm IE} = -\frac{2\pi\rho_c}{3} \sum_{s,s'=1}^N \int_0^\sigma dr \Big[\omega_{s,s'\neq s}(r) + \rho_c g_{s,s'}(r)\Big] r^2 \frac{d\beta u_{s,s'}(r)}{d\ln r}.$$
(5.28)

We then calculate Δf_c^{IE} from Eqs. (5.8), (5.26) and (5.27), and $\Delta s_c^{\text{IE}}/k_B = \beta u_{c,b}^{\text{IE}} - \beta u_{c,b}^{\text{SCF}} + \beta u_{c,nb}^{\text{IE}} - \beta f_c^{\text{IE}}$; the calculation of $\beta u_{c,b}^{\text{IE}}$ is given below. Finally, the

fluctuations of E_{κ} and E_{χ} and the non-bonded constant-volume heat capacity are calculated numerically by the second order centered finite difference according to Eqs. (5.9) ~ (5.12), (5.26) and (5.27).

B. Chain dimensions, internal energy, and pressure due to the bonded interaction, and structure factors

Adopting the method of Wang, ^[91] for two segments e_1 and e_2 on the same chain we introduce an auxiliary parameter η and define $\beta \mathcal{H}^C(\eta) \equiv \beta \mathcal{H}^C + (3\eta/2a^2) \sum_{k=1}^n (\mathbf{R}_{k,e_2} - \mathbf{R}_{k,e_1})^2$. We then have the partition function at given η as

$$\mathcal{Z}(\eta) = \frac{1}{n!} \prod_{k=1}^{n} \prod_{s=1}^{N} \int d\mathbf{R}_{k,s} \cdot \exp\left\{-\beta \mathcal{H}^{C} - \left(3\eta/2a^{2}\right) \sum_{k=1}^{n} \left(\mathbf{R}_{k,e_{2}} - \mathbf{R}_{k,e_{1}}\right)^{2} - \beta \mathcal{H}^{E}\right\}.$$
 (5.29)

The mean-square distance between e_1 and e_2 , $R^2(e_1, e_2)$, is then given by

$$R^{2}(e_{1},e_{2}) = -\frac{2a^{2}}{3n} \frac{\partial \ln \mathcal{Z}(\eta)}{\partial \eta} \bigg|_{\eta=0} = R^{2}_{e,\text{SCF}}(e_{1},e_{2}) + \frac{2a^{2}}{3} \frac{\partial \beta \Delta f_{c}(\eta)}{\partial \eta} \bigg|_{\eta=0},$$
(5.30)

where we numerically evaluate the partial derivative by the second-order centered finite difference after obtaining $\beta \Delta f_c(\eta)$ via Eq. (5.8),; the intrachain PCFs at given η , $\hat{\omega}_{s,s'}(q;\eta,e_1,e_2)$, needed for solving the P/RISM equations are derived in the Appendix A.4. We then have the chain and block mean-square end-to-end distances as $R_{e,\text{IE}}^2 = R_{\text{IE}}^2(1,N)$ and $R_{eb,\text{IE}}^2 = R_{\text{IE}}^2(1,N_A)$,respectively, as well as the mean-square bond length $b_{s,\text{IE}}^2 = R_{\text{IE}}^2(s,s+1)$ for the *s*th bond. The internal energy per chain due to the bonded interaction is then given by $\beta u_{c,b}^{\text{IE}} = (3/2a^2) \sum_{s=1}^{N-1} b_{s,\text{IE}}^2$, from which we calculate the pressure due to the bonded interaction as $\beta P_b = -(2\rho_c/3)\beta u_{c,b}$.

We also calculate the total structure factor $S_t(q) \equiv \sum_{P,P'} S_{PP'}(q)$, where $S_{PP'}(q) \equiv \sum_{s \in P, s' \in P'} \hat{S}_{s,s'} / N$ with $\hat{S}_{s,s'}$ being the (s,s') element of the $N \times N$ matrix $\hat{\mathbf{S}} \equiv \hat{\mathbf{\omega}} + \rho_C \hat{\mathbf{h}} = (\mathbf{I} - \rho_c \hat{\mathbf{\omega}} \hat{\mathbf{c}})^{-1} \hat{\mathbf{\omega}}$. We further calculate the structure factor $S_{\psi}(q) \equiv S_{AA}(q) + S_{BB}(q) - 2S_{AB}(q)$ characterizing the composition fluctuations of $\psi(r) \equiv \left[\rho_A(r) - \rho_B(r)\right] / \rho_0$.

5.2.4.4 Relation among IE, GF, and SCF theories

If we assume $1 - \exp[\beta u_{s,s'}(r)] \approx -\beta u_{s,s'}(r)$ for small $\beta u_{s,s'}(r)$ and set $g_{s,s'}(r) = 1$ in the PY closure [Eq.(5.21)], it is then reduced to $c_{s,s'}(r) = -\beta u_{s,s'}(r)$, the meanspherical approximation (MSA) closure used for penetrable spheres. Since $u_{s,s'}(r)$ satisfies $u_{\rm PP'}(r) = u_{sP,s'P'}(r)$, the RISM equations are then equivalent to the PRISM equations and we have $C_{\rm PP'}^{\rm RPA}(r) = -\beta u_{\rm PP'}(r)$.Eq. (5.24) thus gives the total structure factor matrix $\mathbf{S} \equiv \mathbf{S}_1 + \rho_0 \hat{\mathbf{H}} = (\mathbf{S}_0 + \mathbf{S}_1^{-1})^{-1}$, which is the same as $\mathbf{S}_{\rho}^{\text{RPA}}$. We therefore refer $C_{\rm PP'}^{\rm RPA}(r) = -\beta u_{\rm PP'}(r)$ as the RPA closure. ⁶¹It is clear that, for all calculated structural and thermodynamic quantities, P/RISM theories with the RPA closure (denoted as P/RISM-RPA) and $\omega_{s,s'}^{DGC}(r)$ are the same as GF theory (see Appendix A), which contains only the Gaussianlevel fluctuations. One thing to note is that the above assumption of $g_{s,s'}(r) = 1$ is used only to reduce the PY to the RPA closure; P/RISM-RPA or GF theory does not necessarily give $g_{s,s'}(r) = 1$. On the other hand, in the limit of $\rho_c \to \infty$, Eq. ((5.5)5) gives $\beta u_{s,s'}(r) \to 0$ at finite N/κ and χN , leading to $c_{s,s'}(r) \to 0$ and $h_{s,s'}(r) \to 0$ (or $g_{s,s'}(r) \to 1$) for both and P/RISM-RPA (or GF) theories. In this limit, the interchain P/RISM-PY fluctuation/correlation (F/C) effects can thus be neglected, and both IE and GF theories reduce to SCF theory. From another point of view, all the F/C effects on both structural and thermodynamic properties (beyond the mean-field predictions) for both IE and GF theories are

proportional to ρ_0^{-1} (at large ρ_0 for IE results); this also indicates that both IE and GF theories reduce to SCF theory as $\rho_0 \rightarrow \infty$.

5.3 **Results and Discussion**

Setting the root-mean-square end-to-end distance of an ideal (discrete Gaussian) chain having N segments and an effective bond length a, $R_{e,0} = \sqrt{N-1}a$, as the length scale, we have a total of five parameters in our model system: the invariant degree of polymerization $\overline{N} = (nR_{e,0}^3/V)^2$ for *n* chains in volume *V*, the AB incompatibility χN , the system compressibility N/κ , N, and the range of the (dissipative particle dynamics) interaction potential σ/a (or $\sigma/R_{e,0}$); the first three are physical parameters that can be mapped to an experimental system, and the last two are model parameters characterizing the chain discretization and finite interaction range, respectively. In the following, we fix $\overline{N}=10^4$, N = 10 and $\sigma / a = 0.3$ unless specified otherwise, and examine the effects of N / κ and χN on various structural and thermodynamic properties by comparing the results obtained from different methods in three systems: System I is homopolymers at $\chi N = 0$, and Systems II and III are DBC at $N/\kappa = 0$ and 50, respectively. We use ideal chains at $N/\kappa = \chi N = 0$ as the reference state in all cases. The error bar of each ensemble-averaged quantity from FOMC simulation is estimated as three times its standard deviation with the statistical correlation among samples collected after equilibration considered by the correlation-function method. ⁶²Note that, since the Zhou closure cannot be used for cases of small pair interaction strength, it is only applied for homopolymers at $N/\kappa \gtrsim 12$ and DBC at $N/\kappa = 50$ in this study.

5.3.1 System I: Homopolymer

5.3.1.1 Chain end-to-end distance and bonded internal energy

Fig. 5.1 shows the difference in the mean-square chain end-to-end distances from the ideal-chain reference state, ΔR_e^2 , obtained from various theories and FOMC simulations. We see that ΔR_e^2 obtained from all the methods monotonically increases with increasing N/κ due to the excluded-volume interaction. For small $N/\kappa \lesssim 1$, ΔR_e^2 is proportional to N/κ , which can be found from the Taylor expansion of Eq.(5.36).



Figure 5.1: Difference in the mean-square chain end-to-end distance from the ideal-chain reference state for homopolymers. Logarithmic plot of the difference in the mean-square chain end-to-end distance from the ideal-chain reference state ΔR_e^2 for homopolymers, where "k=1"denotes a straight line of slope 1. N=10, $\overline{N}=10^4$ and $\sigma/a=0.3$.

While our simulation data here are for $N/\kappa \le 50$, as N/κ further increases they are expected to converge to a constant similar to Fig. 5.5(a) in Ref. ^[78] (which is for compressible homopolymers on a 1D lattice). GF (or equivalently P/RISM-RPA with the intrachain PCF for ideal DGC, $\hat{\omega}_{s,s'}^{DGC}$) theory gives surprisingly good results within the entire range of our simulation data, which are also similar to Fig. 5.5(a) in Ref. ^[78]; in contrast, RISM-PY theory with $\hat{\omega}_{s,s'}^{\text{DGC}}$ overestimates ΔR_e^2 for $N/\kappa \gtrsim 2$, and the deviation increases with increasing N/κ and diverges in the limit of $N/\kappa \rightarrow \infty$. With $e_1 = 1$ and $e_2 = N$, Eqs. (5.8), (5.26) and (5.30) give

$$\Delta R_{e,\text{IE}}^{2} = \frac{4\pi a^{2}}{3\rho_{0}N} \sum_{s=1}^{N} \sum_{s'=1}^{N'} \int_{0}^{N/\kappa} d\left(\frac{N}{\kappa}\right) \int_{0}^{\sigma} dr \left[\frac{\partial \hat{\omega}_{s,s'}^{\text{DGC}}(r,\eta)}{\partial \eta} + \rho_{c} \frac{\partial h_{s,s'}(r,\eta,N/\kappa)}{\partial \eta}\right]_{\eta=0} r^{2} \beta u_{0}(r), \quad (5.31)$$

where $\left[\partial \hat{\omega}_{s,s'}^{\text{DGC}}(r,\eta)/\partial \eta\right]_{\eta=0} \ge 0$ is given in Appendix A.4. In the limit of $N/\kappa \to \infty$, PY closure gives $h_{s,s'}(r,\eta,N/\kappa) = -1$ for $0 \le r \le \sigma$ regardless of η , leading to $\left[\partial h_{s,s'}(r,\eta,N/\kappa)/\partial \eta\right]_{\eta=0} = 0$ thus diverging $\Delta R_{e,\text{IE}}^2$ in the limit of $N/\kappa \to \infty$. This divergence is clearly due to the use of ideal-chain conformations. On the other hand, RPA closure $\hat{c}(q) = -(N/\kappa)(\beta \hat{u}_0(q)/\rho_0 N)$ gives $\hat{h}_{s,s'}(q,\eta,N/\kappa)S_1^2(q,\eta)\hat{c}(q)/[1-\rho_0S_1(q,\eta)\hat{c}(q)]$

with
$$S_1(q,\eta) = (1/N) \sum_{s,s'=1}^N \hat{\omega}_{s,s'}(q,\eta)$$
. Eq. (31) then becomes

$$\Delta R_{e,GF}^{2} = \frac{a^{2}}{3\rho_{0}} \int_{0}^{N/\kappa} d\left(\frac{N}{\kappa}\right) \int \frac{d\mathbf{q}}{\left(2\pi\right)^{3}} \left[\frac{\partial S_{1}(q,\eta)}{\partial\eta} + \rho_{0} \frac{\partial \hat{h}(q,\eta,N/\kappa)}{\partial\eta}\right]_{\eta=0} \beta \hat{u}_{0}(q).$$
(5.32)

Since
$$\rho_0 \partial \hat{h}(q,\eta,N/\kappa) / \partial \eta = [1 - \rho_0 S_1(q,\eta) \hat{c}(q)]^{-2} [\partial S_1(q,\eta) / \partial \eta] - [\partial S_1(q,\eta) / \partial \eta]$$
, its

second term then cancels with the first term in the integrand of Eq.(5.32), thus eliminating the divergence of $\Delta R_{e,\text{IE}}^2$ in the limit of $N/\kappa \rightarrow \infty$. With RPA closure,

we finally have

$$\Delta R_{e,GF}^2 = \frac{a^2}{3\rho_0} \int \frac{\mathrm{d}\mathbf{q}}{\left(2\pi\right)^3} \frac{\beta \hat{u}_0(q)}{P(1,q)\beta \hat{u}_0(q) + \kappa/N} \frac{\partial S_1(q,\eta)}{\partial \eta} \bigg|_{\eta=0},\tag{5.33}$$

leading to $\Delta R_{e,GF}^2 / R_{e,0}^2 \approx 0.0141$ in the limit of $N / \kappa \rightarrow \infty$. That $\Delta R_{e,GF}^2$ does not diverge in

the limit of $N/\kappa \rightarrow \infty$ is therefore due to the error cancelation between the use of ideal-chain conformations and RPA closure, which may also be the reason for the surprisingly good prediction of GF theory shown in Fig. 5.1.

The difference in the bonded energy per chain from the reference state (given by $\beta u_{c,b}^{SCF}$), $\beta \Delta u_{c,b}$, exhibits similar behavior to ΔR_e^2 as expected and is therefore not shown.

5.3.1.2 $\langle E_{\kappa} \rangle$, non-bonded internal energy, pressure, and free energy

Fig. 5.2 (a) shows that E_{κ}/n obtained from all the methods monotonically decrease

from
$$(2\pi / \rho_c) \int_0^\sigma dr r^2 \beta u_0(r) \sum_{s,s'=1}^N \omega_{s,s'}^{\text{DGC}}(r) / N^2 \approx 1.2066$$
 at $N / \kappa = 0$ with increasing N / κ ;

this is because polymer segments reduce their contact (overlap) as their repulsion increases. Since $\overline{N}=10^4$ here is below the FCC close packing of these segments (which corresponds to $\overline{N}=2\times10^4$), in the limit of $N/\kappa \to \infty$ we have the ground state of hard-sphere chains with zero non-bonded internal energy, which has no fluctuations (i.e., the presence of multiple energy levels) and gives $E_{\kappa}/n = [\beta u_0(0)/\rho_0 - 1]/2 \approx 0.6937$. There are, however, correlations in the ground state; that is, the segments cannot overlap. We see from Fig. 5.2(a) that RISM-PY theory with $\hat{\omega}_{s,s'}^{\text{DGC}}$ gives very good prediction; even in the limit of $N/\kappa \to \infty$, it gives $E_{\kappa}^{\text{IE}}/n \approx 0.7066$, slightly higher (by <2%) than the above exact value. The deviation is due to the use of ideal chain conformations. In fact, in this limit we have $h_{s,s'}(r < \sigma) = -1$;

Eq. (5.26) then leads to
$$E_{\kappa}^{\text{IE}} / n = (2\pi / \rho_0 N) \sum_{s,s'=1}^{N} \int_{0}^{\sigma} dr \omega_{s,s'}^{\text{DGC}}(r) \beta u_0(r) r^2 - 1/2 \approx 0.7066$$
. We

also note that using $\hat{\omega}_{s,s'}^{\text{FOMC}}$ in RISM-PY theory gives slightly worse (smaller) prediction than using $\hat{\omega}_{s,s'}^{\text{DGC}}$ for N/κ up to 50 (more clearly seen in Fig. 5.2(b)); this unexpected result is actually due to the error cancelation between the use of ideal-chain conformations and PY closure at finite N/κ .



Figure 5.2: The ensemble average of E_{χ} per chain, the non-bonded internal energy per chain, the difference in pressure and the Helmholtz free energy per chain from the reference state. (a) The ensemble average of per chain, (b) the non-bonded internal energy per chain $u_{c,nb}$, (c) the difference in pressure from the reference state due to the non-bonded interactions ΔP_{nb} , and (d) the difference in the Helmholtz free energy per chain from the reference state Δf_c for homopolymers. Note that the horizontal axis in Part (a) is on the logarithmic scale. N = 10, $\overline{N} = 10^4$ and $\sigma/a = 0.3$.

On the other hand, GF theory only works for $N/\kappa \leq 1$ and underestimates E_{κ} at larger N/κ . For large N/κ (up to 10¹⁰) our numerical calculations give $E_{\kappa}^{\text{GF}}/n \propto (N/\kappa)^{-0.25}$. (Data not shown), which is different from the lattice case where $E_{\kappa}^{\text{GF}} / n \propto (N / \kappa)^{-1}$ was found. For $\gamma N = 0$), Eq. (5.39) homopolymers (i.e., can be rewritten as $E_{\kappa}^{\text{GF}} / n = \left(1/4\pi^2 \rho_c\right) \int_0^\infty dq q^2 \beta \hat{u}_0(q) P(1,q) / \left[\left(N/\kappa\right) \beta \hat{u}_0(q) P(1,q) + 1 \right], \text{ which corresponds to}$ Eq. (19) in Ref. ^[78]. With $\beta \hat{u}_0(q) = 1$ on a lattice, we then obtain the "-1" scaling in the limit of $N/\kappa \to \infty$ after the Taylor expansion in terms of κ/N . But for the soft potential used here, $\beta \hat{u}_0(q)$ is not constant and approaches 0 in the limit of $q \rightarrow \infty$, which changes the scaling of E_{κ}^{GF}/n with N/κ . Clearly, $E_{\kappa}^{\text{GF}} = 0$ in the limit of $N/\kappa \to \infty$ indicates that GF theory does not capture the segment correlations in the ground state.

The non-bonded internal energy per chain $\beta u_{c,nb}$ is directly calculated from E_{κ} according to Eq. (5.7) and is shown in Fig. 5.2(b). We see that $\beta u_{c,nb}$ from all the methods is proportional to N/κ at small $N/\kappa \lesssim 1$, and that RISM-PY theory with $\hat{\omega}_{s,s'}^{\text{DGC}}$ can quantitatively predict $\beta u_{c,nb}$ within the range of our simulation data. Its predictions with $\hat{\omega}_{s,s'}^{\text{FOMC}}$, however, are less accurate (smaller) for N/κ up to 50, due to the aforementioned error cancelation between the use of ideal-chain conformations and PY closure at finite N/κ . On the other hand, RISM-PY prediction with $\hat{\omega}_{s,s'}^{\text{DGC}}$ is proportional to N/κ at large N/κ (data not shown), due to the slight deviation of its predicted E_{κ}^{IE}/n from the exact value in the limit of $N/\kappa \to \infty$; in other words, $\beta u_{c,nb}^{\text{IE}}$ diverges instead of approaching 0 in this limit, which is

unphysical and due to the use of ideal-chain conformations. $\hat{\omega}_{s,s'}^{\text{FOMC}}$ is therefore needed at large N/κ to obtain the correct behavior of $\beta u_{c,nb}$. Fig. 5.2(b) also shows that GF theory largely underestimates $\beta u_{c,nb}$ and even gives the wrong trend for $N/\kappa \gtrsim 15$, because it fails to capture the segment correlations. Eq. (5.41) indicates that $\beta u_{c,nb}^{\text{GF}}$ has two parts: the SCF prediction $\beta u_{c,nb}^{\text{SCF}} = (N/2\kappa) [1 - \beta u_0(0)/\rho_0] \approx -0.6937 N/\kappa$ and the GF contribution $(N/\kappa) E_{\kappa}^{\text{GF}}/n \propto (N/\kappa)^{0.75}$ at large N/κ ; the former leads to $\beta u_{c,nb} < 0$ at large N/κ .

Fig. 5.2(c) shows the difference in (virial) pressure from the reference state due to the non-bonded interactions, $\beta \Delta P_{nb} R_{e,0}^3$. We see that $\beta \Delta P_{nb} R_{e,0}^3 \propto N/\kappa$ at small $N/\kappa \lesssim 1$ for all methods, and that RISM-PY theory with $\hat{\omega}_{s,s'}^{\text{DGC}}$ can quantitatively predict $\beta \Delta P_{nb} R_{e,0}^3$ within the range of our simulation data. RISM-PY theory with $\hat{\omega}_{s,s'}^{\text{FOMC}}$, however, gives less accurate (smaller) prediction for N/κ up to 50, due to the same reason for E_{κ}/n or $\beta u_{c,nb}$ discussed above. We also see that GF theory overestimates $\beta \Delta P_{nb} R_{e,0}^3$ at large $N/\kappa \gtrsim 25$, which is different from that for E_{κ}/n or $\beta u_{c,nb}$, due to its failure to capture the segment correlations. On the other hand, while $\beta \Delta P_{nb}^{\text{FOMC}} R_{e,0}^3$ is expected to approach 0 in the limit of N/κ at large N/κ (data not shown), because the SCF contribution, which is proportional to N/κ , dominates at large N/κ ; in other words, they diverge instead of approaching O in the limit of N/κ due to the use of ideal-chain conformations.

Fig. 5.2(d) shows the difference in the Helmholtz free energy per chain from the

reference state, $\beta \Delta f_c$, which is directly calculated from E_{κ} according to Eq.(5.8). We see similar results to those of $\beta u_{c,nb}$ shown in Fig. 5.2(b), but the valid N/κ -range for RISM-PY theory in Fig. 5.2(d) is larger than that in Fig. 5.2(b). On the other hand, the RISM-PY prediction with $\hat{\omega}_{s,s'}^{DGC}$ is proportional to N/κ at large N/κ (data not shown); in other words, βf_c^{IE} diverges in the limit of $N/\kappa \rightarrow \infty$ due to the use of ideal-chain conformations. We also see that $\beta \Delta f_c^{GF}$ exhibits a maximum, which can be found from Eq.(5.8). and the behavior of E_{κ}^{GF} shown in Fig. 5.2(a). In addition, $\beta \Delta f_c^{GF}$ becomes negative at large N/κ (data not shown), where the SCF contribution ($\approx -0.6937N/\kappa$) dominates in Eq.(5.8).

5.3.1.3 σ_{κ}^2 and heat capacity



Figure 5.3: The fluctuation of E_{κ} and σ_{κ}^2 per chain, and the constant-volume heat capacity. Logarithmic plot of (a) the fluctuations of E_{κ} , σ_{κ}^2 , per chain and (b) the constant-volume heat capacity due to the non-bonded interactions $C_{V,nb}$ for homopolymers. In Part (b), "k = 2" denotes a straight line of slope 2. N = 10, $\overline{N} = 10^4$ and $\sigma/a = 0.3$.

Fig. 5.3(a) shows the fluctuations of E_{κ} , σ_{κ}^2 , We see that all the results monotonically decrease from 3.77×10^{-2} at $N/\kappa = 0$ with increasing N/κ . GF theory again only works for $N/\kappa \lesssim 1$, and overestimates σ_{κ}^2 at larger N/κ . For large N/κ , our numerical calculations give $\sigma_{\kappa,GF}^2 \propto (N/\kappa)^{-1.25}$, consistent with the above behavior of E_{κ}^{GF} [see Eq.(5.9)]. In contrast, RISM-PY predictions with both $\hat{\omega}_{s,s'}^{DGC}$ and $\hat{\omega}_{s,s'}^{FOMC}$ are in good agreement with our simulation results, and the former decreases more rapidly with increasing N/κ than GF prediction at large N/κ . While our simulation data are only for $N/\kappa \leq 50$, at larger N/κ they are expected to decrease also more rapidly than GF prediction, as found in the 1D lattice case shown in Fig. 5.3(a) of Ref. ^[78].



Figure 5. 4: The total structure factor and the normalized isothermal compressibility of homopolymers.

(a) The total structure factor $S_t(q)$ and (b) the normalized isothermal compressibility κ_T of homopolymers. N = 10, $\overline{N} = 10^4$ and $\sigma/a = 0.3$.

Analogous to $\beta u_{c,nb}$, the constant-volume heat capacity due to the non-bonded interactions $C_{V,nb}$ is directly calculated from σ_{κ}^2 according to Eq. (5.12) and shown in Fig. 5.3(b). We find that $C_{V,nb}$ from all the methods is proportional to $(N/\kappa)^2$ at small

 $N/\kappa \leq 1$ and monotonically increases with increasing $N/\kappa \leq 50$. At large N/κ , however, $C_{V,nb}^{\text{FOMC}}$. is expected to exhibit a maximum and then decrease to zero in the limit of $N/\kappa \rightarrow \infty$, where the system is in the ground state; while the same is expected for the RISM-PY prediction with $\omega_{s,s'}^{\text{DGC}}$, $C_{V,nb}^{\text{GF}} \propto (N/\kappa)^{0.75}$ and diverges in this limit.

5.3.1.3 Total structure factor and isothermal compressibility

Fig. 5.4(a) shows the total structure factor $S_t(q)$ characterizing the density fluctuations. We see that, for $N/\kappa > 0$, GF theory underestimates On the other hand, $S_t(q)$ predicted by RISM-PY theory with either $\varpi_{s,s'}^{\text{DGC}}$ or $\varpi_{s,s'}^{\text{FOMC}}$ are indistinguishable, and in very good agreement with FOMC results. Note that, with the normalized isothermal compressibility $\kappa_T \equiv -\rho_c k_B T (\partial V/\partial P)_T / V$ and P denoting the total pressure, we have $S_t(q=0)/N = \kappa_T$ which is shown in Fig. 5.4(b). While κ_T cannot be obtained from our canonical-ensemble FOMC simulations performed in a fixed-length box at $\chi N = 0$, we see that κ_T obtained from both GF and RISM-PY theories decrease from 1 for ideal chains (i.e., at $N/\kappa = 0$) with increasing N/κ as expected. Consistent with Fig. 5.4(a), for $N/\kappa > 0$, while GF theory underestimates k_T , RISM-PY theory with $\varpi_{s,s'}^{\text{DGC}}$ gives slightly larger κ_T than that with $\varpi_{s,s'}^{\text{FOMC}}$.

5.3.2 System II: DBC at $N/\kappa = 0$ Chain/block end-to-end distance and bonded internal energy

Fig. 5.5(a) shows that ΔR_e^2 obtained from all the methods monotonically increase with increasing χN (that is, the repulsion between A and B segments causes chain-stretching), and that both GF and RISM-PY theories (with $\hat{\omega}_{s,s'}^{DGC}$) give good predictions for small $\chi N \lesssim 1$, where Taylor expansion of Eq.(5.36) gives $\Delta R_{e,GF}^2 \propto \chi N$ (at $N/\kappa=0$). For $3 \lesssim \chi N \lesssim 8$ GF theory gives better prediction than RISM-PY theory, while for larger χN the opposite occurs. The latter is due to the divergence of $\Delta R_{e,GF}^2$ at the mean-field ODT $\chi_{MF}^* N \approx 10.047$, where the matrix $(\mathbf{S}_{\omega}^{RPA})^{-1}$ becomes singular at the most unstable mode $q_{MF}^* R_{e,0} \approx 4.634$. In contrast, we see that both $\Delta R_{e,FOMC}^2$ and $\Delta R_{e,RISM-PY}^2$ remains finite even at the ODT $\chi^* N \approx 25.67$ determined from FOMC simulations.

Fig. 5.5(b) shows the mean-square block end-to-end distance ΔR_{eb}^2 , with the ideal-chain result given by $R_{eb,0}^2 = (N/2-1)a^2$. We see that ΔR_{eb}^2 obtained from all the methods exhibit a small positive maximum around $\chi N = 2$, and that both theories give good predictions up to $\chi N \lesssim 4$. For larger χN , ΔR_{eb}^2 becomes negative, and GF theory underestimates ΔR_{eb}^2 . mainly due to its divergence to $-\infty$ at $\chi^*_{MF}N$ (again caused by the singularity of $(\mathbf{S}_{\omega}^{RPA})^{-1}$); in contrast, RISM-PY theory $\hat{\omega}_{s,s'}^{DGC}$ overestimates ΔR_{eb}^2 , and both $\Delta R_{eb,FOMC}^2$ and $\Delta R_{eb,RISM-PY}^2$ remains finite at χ^*N . We also note that, for small $\chi N \lesssim 1$, the Taylor expansion of Eq.(5.36) gives $\Delta R_{eb,GF}^2 \propto \chi N$ at $N/\kappa = 0$. Fig. 5.5(c) shows $\beta \Delta u_{c,b}$ obtained from various methods, which is like Fig. 5.5(b) except that $\beta \Delta u_{c,b}^{\text{FOMC}}$ exhibits a minimum before $\chi^* N$. This minimum, absent in R_{eb}^2 , is clearly due to the contribution of A-B bonds: $\Delta R^2 (e_1 = 5, e_2 = 6)$ (data not shown) exhibits similar behavior to ΔR_e^2 shown in Fig. 5.5(a). GF theory, however, cannot capture the minimum in $\beta \Delta u_{c,b}$ due to the divergence to $-\infty$ of other bonds. In contrast, while RISM-PY theory with $\hat{\omega}_{s,s'}^{\text{DGC}}$ overestimates $\beta \Delta u_{c,b}$ for $\chi N \gtrsim 4$, it can capture this minimum. Note, however, that the relative difference $\Delta u_{c,b} / u_{c,b}^{\text{SCF}}$ is very small, meaning that the effect of χN on the bonded energy is negligible compared to the SCF (ideal-chain) contribution although the chain conformations ($\hat{\omega}_{s,s'}^{\text{DGC}}$ and $\hat{\omega}_{s,s'}^{\text{FOMC}}$) are different.





Logarithmic plot of the difference in the mean-square chain end-to-end distance from the idealchain reference state ΔR_e^2 , (b) semilogarithmic plot of the difference in the mean-square block end-to-end distance from the ideal-chain reference state ΔR_{eb}^2 , and (c) semilogarithmic plot of the difference in the bonded energy per chain from the ideal-chain reference state $\beta \Delta u_{c,b}$ for DBC. The vertical lines mark $\chi_{MF}^* N$ (dash-dot-dot) and $\chi_{FOMC}^* N$ (dotted for $N/\kappa = 0$ and solid for $N/\kappa = 50$). In Part (a), "k = 1" denotes a straight line of slope 1. N = 10, $\bar{N} = 10^4$ and $\sigma/a = 0.3$.

5.3.2.2 $\langle E_{\chi} \rangle$, non-bonded internal energy, pressure, and free energy

Fig. 5.6 (a) shows that $\langle E_{\chi} \rangle / n$ obtained from all the methods monotonically decrease

from
$$(4\pi / \rho_c) \int_0^{\sigma} dr r^2 \beta u_0(r) \sum_{s=1}^{N_A} \sum_{s'=N_A+1}^{N} \omega_{s,s'}^{\text{DGC}}(r) / N^2 \approx 3.939 \times 10^{-2}$$
 at $\chi N = 0$ with increasing

 χN ; this is because A and B segments reduce their contact as their repulsion increases. GF theory only works for $\chi N \lesssim 1$, and underestimates E_{χ} at larger χN ; $\langle E_{\chi} \rangle^{\text{GF}}$ diverges to $-\infty$ at $\chi^*_{\text{MF}}N$ due to the singularity of the matrix $(\mathbf{S}^{\text{RPA}}_{\rho})^{-1}$ at the most unstable mode q^* . In contrast, both RISM-PY and FOMC results remain finite even at χ^*N . While RISM-PY theory with both $\hat{\omega}^{\text{FOMC}}_{s,s'}$ and $\hat{\omega}^{\text{DGC}}_{s,s'}$ overestimates $\langle E_{\chi} \rangle$ for $\chi N \gtrsim 15$, using $\hat{\omega}^{\text{FOMC}}_{s,s'}$ gives better prediction than using $\hat{\omega}^{\text{DGC}}_{s,s'}$ as expected.

 $\beta u_{c,nb}$ is directly calculated from $\langle E_{\chi} \rangle$ according to Eq.(5.7) and is shown in Fig. 5.6(b). We see that $\beta u_{c,nb}$ from all the methods is proportional to χN at small $\chi N \lesssim 0.1$ (i.e., where E_{χ} is nearly constant), and exhibits a maximum due to the competing SCF contribution of random mixing (i.e., $\chi N/4$) and the F/C contribution of AB segregation (i.e., the monotonic decrease of $\langle E_{\chi} \rangle$ with increasing χN as shown in Fig. 5.6(a)). These results of $\beta u_{c,nb}$ can be well understood based on those of $\langle E_{\chi} \rangle$ discussed above. The χN -range over which RISM-PY theory gives good predictions for $\beta u_{c,nb}$, however, is smaller than that for $\langle E_{\chi} \rangle$.

Fig. 5.6(c) shows the behavior of $\beta \Delta P_{nb} R_{e,0}^3$, which is $\hat{\omega}_{s,s'}^{DGC}$ like that of $\beta u_{c,nb}$ discussed above. The χN -range over which the theories give good predictions for $\beta \Delta P_{nb} R_{e,0}^3$, however, is larger than that for $\beta u_{c,nb}$. We also note that RISM-PY theory with $\hat{\omega}_{s,s'}^{DGC}$ does not capture the maximum of $\beta \Delta P_{nb} R_{e,0}^3$.



Figure 5.6: The ensemble average of E_{χ} per chain, the non-bonded internal energy per chain, the difference in pressure and Helmholtz free energy per chain from the reference state at $N/\kappa = 0$.

The ensemble average of E_{χ} per chain, (b) the non-bonded internal energy per chain $u_{c,nb}$, (c) the difference in pressure from the reference state due to the non-bonded interactions ΔP_{nb} , and (d) the difference in the Helmholtz free energy per chain from the reference state Δf_c for DBC at $N/\kappa = 0$. The vertical lines mark $\chi^*_{MF}N$ (dash-dot-dot) and $\chi^*_{FOMC}N$ (dotted). Note that the horizontal axis in Part (a) is on the logarithmic scale. N = 10, $\overline{N} = 10^4$ and $\sigma/a = 0.3$.

Fig. 5.6(d) shows that, while $\beta \Delta f_c$ from all the methods are proportional to χN at small $\chi N \lesssim 1$ similar to the behavior of $\beta u_{c,nb}$, they monotonically increase with χN up to $\chi^* N$ ($\chi^*_{MF}N$ for GF theory); this is because the SCF contribution ($\chi N/4$) is always larger than the absolute value of the F/C corrections in Eq.(5.8). We also note that $\beta \Delta f_c^{GF}$ does not

diverge [as evident from Eq.(5.19) or the behavior of E_{χ}^{GF}/n] at χ_{MF}^*N , which means that the entropy per chain $\Delta s_c^{GF}/k_B = \beta u_c^{GF} - \beta \Delta f_c^{GF}$ must diverge just like the non-bonded internal energy, consistent with the divergence of $R_{e,GF}^2$.

5.3.2.3 σ_{χ}^2 and heat capacity

Fig. 5.7(a) shows the fluctuations of E_{χ} , σ_{χ}^2 . We see that GF prediction increases from 1.8756×10^{-2} at $\chi N = 0$ with increasing χN . and diverges to ∞ at $\chi_{MF}^* N$, consistent with the behavior of E_{χ}^{GF} [see Eq.(5.10)]. But even this trend is incorrect, as E_{χ}^{FOMC} decreases with increasing χN . In contrast, RISM-PY theory gives much better predictions, although it underestimates σ_{χ}^2 for $\chi N \gtrsim 10$. RISM-PY theory with $\hat{\omega}_{s,s'}^{FOMC}$ gives the closest prediction to our simulation results as expected, and even captures the small shoulder found in our simulations around $\chi N = 18 < \chi^* N$, which is not captured when ideal-chain conformations are used.

Fig. 5.7(b) shows $C_{V,nb}$ calculated directly from σ_{χ}^2 shown in Fig. 5.7(a) due to the poor performance of GF theory in predicting σ_{χ}^2 , we do not consider it here. We see that $C_{V,nb} \propto (\chi N)^2$ for $\chi N \lesssim 1$, where σ_{χ}^2 is nearly a constant, and that $C_{V,nb}^{\text{FOMC}}$ exhibits a maximum before $\chi^* N$, which is captured by RISM-PY theory with $\omega_{s,s'}^{\text{FOMC}}$ but not with $\omega_{s,s'}^{\text{DGC}}$; the latter behavior can be deduced from that of σ_{χ}^2 .



Figure 5.7: The fluctuations of E_{χ} , σ_{χ}^2 per chain and the constant-volume heat capacity at $N/\kappa = 0$.

(a) Logarithmic plot of the heat capacity due to the non-bonded interaction $C_{V,nb}$ for DBC at $N/\kappa = 0$. The vertical lines mark $\chi^*_{MF}N$ (dash-dot-dot) and $\chi^*_{FOMC}N$ (dotted). N = 10, $\overline{N} = 10^4$ and $\sigma/a = 0.3$.

5.3.2.4 Structure Factor

Fig. 5.8(a) shows the total structure factor $S_t(q)$. As in the case of homopolymers, GF predictions largely underestimate $S_t(q)$ except for the ideal-chain case (data not shown). $S_t(q)$ predicted by RISM-PY theory with either $\omega_{s,s'}^{DGC}$ or $\omega_{s,s'}^{FOMC}$ are indistinguishable; they are in good agreement with the FOMC results for $\chi N \leq 8$ and underestimate the latter for larger χN . Fig. 5.8(b) further shows that, while κ_T given by GF and RISM-PY theories with $\omega_{s,s'}^{DGC}$ monotonically decreases with increasing χN , that given by RISM-PY theories with $\omega_{s,s'}^{FOMC}$ exhibits a minimum around $\chi N = 18.6$.



Figure 5.8: The structure factor and the normalized isothermal compressibility at $N/\kappa = 0$. (a) The structure factor (a) $S_r(q)$ characterizing the density fluctuations, (b) the normalized isothermal compressibility κ_T of diblock copolymers and (c) $S_{\nu}(q)$ characterizing the composition fluctuations in DBC at $N/\kappa = 0$. Part (d) shows the wave-number q^* , where $S_{\nu}(q)$ predicted by RISM-PY theory with the ideal-chain conformations $\omega_{s,s'}^{DGC}$ reaches its maximum, as a function of χ normalized by its ODT-value χ^* determined in FOMC simulations, where the symbol on each curve marks its minimum. N = 10, $\overline{N} = 10^4$ and $\sigma/a = 0.3$.

Fig. 5.8(c) shows the partial structure factor $S_{\psi}(q)$ characterizing the composition

fluctuations. We see a growing peak at the most unstable mode q^* as χN increases, and that the simulation results lie in-between the RISM and RPA predictions. RISM-PY prediction with $\omega_{s,s'}^{\text{FOMC}}$ is hardly better than with $\omega_{s,s'}^{\text{DGC}}$; both underestimates $S_{w}(q)$ (except for ideal chains) and exhibits larger deviation from the FOMC results with increasing χN . This underestimation is consistent with the fact that RISM-PY theory cannot give an ODT (see Sec. 5.3.4 below). On the other hand, RPA prediction largely overestimates $S_{\psi}(q)$, thus giving $\chi^*_{MF}N < \chi^*N$.

Finally, Fig. 5.8(d) shows how the RISM-PY prediction of the peak position q^* of $S_{\psi}(q)$ varies with χ normalized by the ODT determined from simulations, and we see a unexpected minimum (marked by the symbol); the unexpected increase of q^* at large χ signifies the breakdown of RISM-PY theory using $\omega_{s,s'}^{\text{DGC}}$. In contrast, such a minimum is not predicted by RISM-PY theory using $\omega_{s,s'}^{\text{FOMC}}$ (data not shown).

5.3.3 System II: DBC at $N/\kappa = 50$ Chain/block end-to-end distance and bonded internal energy

Fig. 5.5(a) shows that, while $\Delta R_{e,GF}^2$ monotonically increases with increasing χN for small $N/\kappa \lesssim 10$, for larger N/κ it slightly decreases with increasing χN and exhibits a minimum before diverging at $\chi_{MF}^* N$ (which is independent of N/κ). This is consistent with our simulation results at $N/\kappa = 50$, where the GF theory still gives good prediction up to $\chi N \lesssim 6$.

On the other hand, Fig. 5.5(b) shows that, for $N / \kappa \gtrsim 10$, $\Delta R_{eb,GF}^2$ monotonically decreases with increasing χN , which is consistent with our simulation results at $N / \kappa = 50$. Compared to System II, however, GF theory gives good prediction only for $\chi N \lesssim 2$ here. The behavior of $\beta \Delta u_{c,b}$, shown in Fig. 5.5(c), is like System II, except its monotonic decrease with increasing χN for $N/\kappa \gtrsim 10$. Due to the poor performance of RISM-PY theory with $\hat{\omega}_{s,s'}^{\text{DGC}}$ in predicting the chain conformations for System I, we do not consider its predictions here.

We know that larger N/κ makes R_e^2 larger and increasing χN before ODT has two effects: chain stretching leading to larger R_e^2 and formation of clusters leading to smaller R_e^2 that screens the N/κ effect. Therefore, at small N/κ the former effect plays important role, while at large N/κ the latter becomes more significant. The maximum in ΔR_{eb}^2 at $N/\kappa = 0$ results from two competing effects with increasing χN : increased stretching of each block leading to increasing R_{eb}^2 and clusters formed in each block leading to decreasing ΔR_{eb}^2 ; apparently the latter becomes more significant at large χN especially near χ_{MF}^*N . the stretching effect is screened by the larger repulsion because of larger N/κ .

In following, we are currently working on several thermodynamic properties of diblock copolymers at $N/\kappa = 50$, including $\langle E_{\chi} \rangle$, non-bonded internal energy, pressure, free energy, σ_{κ}^2 , heat capacity and structure factor.

5.4 Trends of ODT predicted by RISM-PY method

The mean-field ODT χ_{MF}^* of symmetric DBC is given by RPA, which only accounts for the Gaussian-level fluctuations; $S_{\psi}^{-1}(q^*)$ from RPA is a linear function of χ , and $S_{\psi}^{-1}(q^*)=0$ at χ_{MF}^* . We therefore have $r_{\psi} \equiv S_{\psi}^{-1}(q^*)/S_{\psi}^{-1}(q^*,\chi N=0)=1-\chi/\chi_{MF}^*$ for $\chi \leq \chi_{MF}^*$ from RPA, which does not depend on σ/a and N/κ . On the other hand, this independence is not true for RISM-PY theory, which approximately accounts for the non-Gaussian fluctuations. At finite $\chi > 0$, while r_{ψ}^{PY} predicted by RISM theory with $\omega_{s,s}^{DGC}$ and PY closure is always larger than r_{ψ}^{RPA} and never vanishes (RISM-PY therefore cannot give an ODT) as shown in Fig. 5.9, the qualitative trends of ODT can be inferred from the closeness of r_{ψ}^{PY} to r_{ψ}^{RPA} . In this section we therefore analyze the trends of ODT by comparing the rates at which r_{ψ}^{PY} approaches 0, which captures some of the qualitative behavior of the ODT determined from FOMC simulations in Paper I.^[73]

Fig. 5.9(a) shows the N/κ - and σ/a -dependence of r_{ψ}^{PY} . $\overline{N}=10^4$, where the symbols denote the χN value larger than which RISM-PY theory using $\omega_{s,s'}^{DGC}$ breaks down .We see that, at given σ/a , r_{ψ}^{PY} increases with increasing N/κ and approaches 0 at slower rate. This is because, as N/κ increases, the A-B repulsion characterized by χN becomes relatively weaker, thus requiring larger χN to form lamellae. This behavior is also found for the softcore CGC- δ model of DBC melts used in our recent work, and is consistent with most cases of the FOMC results; note, however, that, at $\sigma/a = 1.15$, χ^*/χ_{MF}^* decreases with increasing

$$N/\kappa$$
 for $\overline{\mathcal{N}} \lesssim 1300$ at $N = 10$ and for $\overline{\mathcal{N}} \lesssim 2500$ at $N = 20$ in FOMC simulations, which

cannot be explained by IE theories. On the other hand, as σ/a increases, the RISM-PY results approach the RPA prediction (i.e., r_{ψ}^{PY} approaches 0 at faster rate), which is consistent with our FOMC results. This is because, as σ/a increases, the AB repulsion becomes effectively larger, thus requiring lower χN to form lamellae.

As $\overline{\mathcal{N}}$ increases, Fig. 5.9(b) shows that, at $N/\kappa = 0$ and $\sigma/a = 0.3$, r_{ψ}^{PY} approaches 0 faster; in other words, as $\overline{\mathcal{N}}$ increases, the system fluctuations approaches Gaussian-level, which is consistent with FOMC results.³



Figure 5.9: Ratio between the inverse of the maximum of structure factor $S_{\psi}(q^*)$ and that $\chi N = 0$ for three different cases.

Ratio between the inverse of the maximum of the structure factor $S_{\psi}(q^*)$ characterizing the

composition fluctuations and that at $\chi N = 0$, predicted by RISM-PY theory with $\omega_{s,s'}^{DGC}$, as a function of χ normalized by its value χ_{MF}^* at the mean-field ODT, for DBC at (a) $\overline{\mathcal{N}} = 10^4$ and N = 10, (b) $N/\kappa = 0$, N = 10, and $\sigma/a = 0.3$, and (c) $\overline{\mathcal{N}} = 10^4$ and $N/\kappa = 0$. In each part, the straight line is the RPA result, and the symbol on each curve marks the χ -value at which q^* reaches the minimum (see Fig. 5.8(d)).

Finally, we also investigate the effects of the chain length N, as shown in Fig.5.9(c). At given $\sigma/a = 0.3$ and $N/\kappa = 0$, r_{ψ}^{PY} decreases with increasing N and approaches 0 at faster rate. But we note that varying N at constant σ/a exhibits both the short-range correlation and chain discretization effects, because changing N also changes $R_{e,0}$. To investigate the latter alone, we compare the case of N = 10 and $\sigma/a = 0.3$ (i.e. $\sigma/R_{e,0} = 0.1$) with that of N = 20 and $\sigma/R_{e,0} = 0.1$. We see that r_{ψ}^{PY} approaches 0 also at faster rate with only increasing the chain discretization, which is consistent with our FOMC results. One may expect that the chain discretization effects diminish quickly and the RISM-PY results approach RPA with increasing chain discretization.

From another point of view, the RPA closure can be obtained from Taylor expansion of PY closure at small $\beta u_{s,s'}(r)$. Since the maximum value of $\beta u_{s,s'}(r)$, achieved at r = 0, is proportional to $(N/\kappa) \overline{\mathcal{N}}^{-1/2} (\sigma/R_{e,0})^3$ (or equivalently $(N/\kappa) \overline{\mathcal{N}}^{-1/2} (\sigma/a)^{-3}$), smaller N/κ or larger $\overline{\mathcal{N}}$ makes $\beta u_{s,s'}(0)$ smaller; Figs. 5.9(a) and 5.9(b) therefore show that, as N/κ decreases $\overline{\mathcal{N}}$ increases, RISM-PY theory approaches RPA results. Similarly, as σ/a
increases at the same N, while the interaction range increases, $\beta u_{s,s'}(0)$ overall decreases; Fig. 5.9(a) therefore shows that RISM-PY theory approaches RPA results with increasing σ/a . Finally, keeping $\sigma/R_{e,0}$ as constant, $\beta u_{s,s'}(0)$ decreases with increasing chain discretization, which is consistent with the middle two curves in Fig. 5.9(c); on the other hand, since increasing N and decreasing $\sigma/R_{e,0}$ have competing effects on $\beta u_{s,s'}(0)$, comparison of the upper two curves in Fig. 5.9(c) shows that the former outweighs the latter in this case.

5.5 Summary

A Calculated quantity from GF theory

A.1 Mean-square end-to-end distances, energy, and pressure due to the bonded interaction

Adopting the method of Wang, for two segments e_1 and e_2 on the same chain we

introduce an auxiliary parameter $\boldsymbol{\eta}$ and define $\beta \mathcal{H}^{C}(\boldsymbol{\eta}) \equiv \beta \mathcal{H}^{C} + (3\boldsymbol{\eta}/2a^{2}) \sum_{k=1}^{n} (\mathbf{R}_{k,e_{2}} - \mathbf{R}_{k,e_{1}})^{2}$

. We then have the partition function at given $\,\eta\,$ as

$$\mathcal{Z}(\eta) = \frac{G(\eta)^n}{n!} \int \mathcal{D}\rho \exp\left\{-\beta \mathcal{H}^E\right\} \int \mathcal{D}\left(\frac{\omega}{2\pi}\right) \exp\left\{\int d\mathbf{r}[i\omega(\mathbf{r}) \cdot \rho(\mathbf{r}) + n \ln Q(\eta)\right\},$$
(5.34)

where

$$Q(\eta) \equiv \prod_{s=1}^{N} \int d\mathbf{R}_{s} \cdot \exp\{-\beta h^{C} - i \sum_{s=1}^{N_{A}} \omega_{A}(\mathbf{R}_{s}) - i \sum_{s=N_{A}+1}^{N} \omega_{B}(\mathbf{R}_{s}) - (3\eta/2a^{2})(\mathbf{R}_{e_{2}} - \mathbf{R}_{e_{1}})^{2}\}/G(\eta)$$

and $G(\eta) \equiv \prod_{s=1}^{n} \int d\mathbf{R}_s \cdot \exp\left\{-\beta h^C - \left(3\eta / 2a^2\right) (\mathbf{R}_{e_2} - \mathbf{R}_{e_1})^2\right\}$. The mean-square distance

between e_1 and e_2 , $R^2(e_1,e_2)$, is then given by

$$R^{2}(e_{1},e_{2}) = -(2a^{2}/3n)\left[\partial \ln \mathcal{Z}(\eta)/\partial \eta\right]_{\eta=0} = \sum_{k=1}^{n} (\mathbf{R}_{k,e_{2}} - \mathbf{R}_{k,e_{1}})^{2}/n.$$

Next, we expand $\ln Q(\eta)$ to the second order in $\delta \omega({f r})$ as

$$\ln Q(\eta) \approx \ln Q^{*}(\eta) - \frac{N}{2V} \int \frac{\mathrm{d}\mathbf{q}}{(2\pi)^{3}} \delta\hat{\omega}(\mathbf{q}) \cdot \mathbf{S}_{1}(q,\eta,e_{1},e_{2}) \delta\hat{\omega}(-\mathbf{q}), \qquad (5.35)$$

where $\mathbf{S}_{1}(q,\eta,e_{1},e_{2})$ is a 2×2 matrix with its (P,P') element being the Fourier transform of $(V/N) \left[\delta^{2} \ln Q(\eta) / \delta i \omega_{P}(\mathbf{r}) \delta i \omega_{P'}(\mathbf{r}') \right]_{\omega^{*}}$. Substituting it into Eq.(5.34) and performing the

Gaussian integrals, we obtain

$$R_{\rm GF}^{2}(e_{1},e_{2}) = R_{\rm SCF}^{2}(e_{1},e_{2}) + \frac{a^{2}}{3\rho_{c}} \int \frac{\mathrm{d}\mathbf{q}}{(2\pi)^{3}} tr \Big[\mathbf{S}_{\omega}^{\rm RPA}(q) \mathbf{S}'_{1,\eta=0}(q,e_{1},e_{2}) \Big],$$
(5.36)

where $R_{SCF}^{2}(e_{1},e_{2}) = (e_{2}-e_{1})a^{2}$ is the SCF prediction, and, at given η , the single-chain structure factor $\mathbf{S}_{1}(q,\eta,e_{1},e_{2})$ and $\mathbf{S}'_{1,\eta=0}(q,e_{1},e_{2}) = \left[\partial \mathbf{S}_{1}(q,\eta,e_{1},e_{2})/\partial \eta\right]_{\eta=0}$ are derived in Sec. A.4. Note that, $\mathbf{S}'_{1,\eta=0}(q,1,N)$ is equivalent to $-\sum_{\mathbf{r},\mathbf{r}'} H(\mathbf{q},-\mathbf{q},\mathbf{r}-\mathbf{r}')/N$ defined in Ref. ^[78];

since RPA [Eq.(5.35)] is the only approximation used here and we obtain the same results as in Ref. ^[78], the additional approximation used in the Appendix of Ref. ^[78] turns out to be exact at the RPA level.

The mean-square chain end-to-end distance can be obtained as $R_{e,GF}^2 = R_{GF}^2(1,N)$, and the mean-square block end-to-end distance $R_{eb,GF}^2 = R_{GF}^2(1,N_A)$ [or $R_{GF}^2(N_A + 1,N)$ for symmetric DBC]. Finally, the bonded energy can be evaluated as

$$\beta u_{c,b}^{\rm GF} = \beta u_{c,b}^{\rm SCF} + \frac{1}{2\rho_c} \int \frac{d\mathbf{q}}{(2\pi)^3} tr \Big[\mathbf{S}_{\omega}^{\rm RPA}(q) \mathbf{S}_{1b^2}(q) \Big],$$
(5.37)

where $\mathbf{S}_{1b^2}(q) \equiv \sum_{s=1}^{N-1} \mathbf{S}'_{1,\eta=0}(q,s,s+1)$, and the pressure due to the bonded interaction is given

by

$$\beta P_{\rm b}^{\rm GF} = \beta P_{\rm b}^{\rm SCF} - \frac{1}{3} \int \frac{\mathrm{d}\mathbf{q}}{(2\pi)^3} \operatorname{tr} \Big[\mathbf{S}_{\omega}^{\rm RPA}(q) \mathbf{S}_{1b^2}(q) \Big].$$
(5.38)

A.2 non-bonded internal energy and non-bonded pressure

Using Eq.(5.18) and the second order cumulant moment of the Gaussian distribution, we obtain the ensemble average of E_{κ} and E_{χ} in GF theory as

$$E_{\kappa}^{\rm GF} = \frac{V}{2} \int \frac{\mathrm{d}\mathbf{q}}{(2\pi)^3} \operatorname{tr} \Big[\mathbf{S}_{\rho}^{\rm RPA}(q) \hat{\mathbf{u}}_{\kappa}(q) \Big], \tag{5.39}$$

$$E_{\kappa}^{\rm GF} = \frac{V}{2} \int \frac{\mathrm{d}\mathbf{q}}{(2\pi)^3} \operatorname{tr} \Big[\mathbf{S}_{\rho}^{\rm RPA}(q) \hat{\mathbf{u}}_{\kappa}(q) \Big],$$
(5.40)

the non-bonded internal energy is then given by

$$\beta u_{c,nb}^{\text{GF}} = \beta u_{c,nb}^{\text{SCF}} + \frac{1}{2\rho_c} \int \frac{d\mathbf{q}}{(2\pi)^3} \operatorname{tr} \left[\mathbf{S}_{\rho}^{\text{RPA}}(q) \mathbf{S}_0(q) \right].$$
(5.41) Alternatively, one can use

$$\beta u_{c,nb}^{\text{GF}} = (N / \kappa) \Big[\partial \beta \Delta f_c^{\text{GF}} / \partial (N / \kappa) \Big] + \chi N \Big[\partial \beta \Delta f_c^{\text{GF}} / \partial (\chi N) \Big] \text{ to obtain the same results.}$$

Similarly, the non-bonded pressure is given by

$$\beta P_{\mathrm{n}b}^{\mathrm{GF}} = \beta P_{\mathrm{n}b}^{\mathrm{SCF}} - \frac{1}{6} \int \frac{\mathrm{d}\mathbf{q}}{(2\pi)^3} \mathrm{tr} \Big[\mathbf{S}_{\rho}^{\mathrm{RPA}}(q) \mathbf{S'}_{0}(q) \Big], (5.42)$$

where
$$\mathbf{S}'_{0} \equiv \left(\beta \hat{u}'_{0}/N\right) \begin{bmatrix} N/\kappa & N/\kappa + \chi N \\ N/\kappa + \chi N & N/\kappa \end{bmatrix}$$
 with $\beta u'_{0}(r) \equiv r d\beta u_{0}(r)/dr$

A.3 non-bonded constant-volume heat capacity

The fluctuations of $\,E_{\kappa}\,$ and $\,E_{\chi}\,$ in GF theory are given by

$$\left(\sigma_{\kappa}^{2}\right)^{\text{GF}} = \frac{V}{2} \int \frac{\mathrm{d}\mathbf{q}}{\left(2\pi\right)^{3}} \mathrm{tr}\left[\left[\mathbf{S}_{\rho}^{\text{RPA}}(q)\hat{\mathbf{u}}_{\kappa}(q)\right]^{2}\right],\tag{5.43}$$

$$\left(\sigma_{\chi}^{2}\right)^{\text{GF}} = \frac{V}{2} \int \frac{\mathrm{d}\mathbf{q}}{\left(2\pi\right)^{3}} \mathrm{tr}\left[\left[\mathbf{S}_{\rho}^{\text{RPA}}(q)\hat{\mathbf{u}}_{\chi}(q)\right]^{2}\right],\tag{5.44}$$

$$\left(\sigma_{\kappa,\chi}^{2}\right)^{\mathrm{GF}} = \frac{V}{2} \int \frac{\mathrm{d}\mathbf{q}}{\left(2\pi\right)^{3}} \mathrm{tr} \left[\mathbf{S}_{\rho}^{\mathrm{RPA}}(q) \hat{\mathbf{u}}_{\kappa}(q) \mathbf{S}_{\rho}^{\mathrm{RPA}}(q) \hat{\mathbf{u}}_{\chi}(q)\right],\tag{5.45}$$

where we have used Eq. (5.18) and the fourth-order cumulant moment of the Gaussian distribution^[80] to calculate the ensemble average; these results can also be obtained from Eqs.(5.9) \sim (5.11). The GF prediction of $C_{V,nb}$ is then given by

$$\frac{C_{V,\text{nb}}^{\text{GF}}}{k_{B}} = \frac{1}{2\rho_{c}} \int \frac{d\mathbf{q}}{(2\pi)^{3}} \text{tr}\left[\left[\mathbf{S}_{\rho}^{\text{RPA}}(q) \mathbf{S}_{0}(q) \right]^{2} \right].$$
(5.46)

Note that at given N/κ and χN , the GF predictions of ΔR_e^2 , ΔR_{eb}^2 , $\beta \Delta u_{c,b}$, $\beta \Delta u_{c,nb}$, $C_{V,nb}$, $\beta \Delta f_c$, and $\Delta s_c / k_B$ are all proportional to ρ_c^{-1} , which is independent of the system dimensionality, and in the limit of $\rho_c \rightarrow \infty$ the SCF prediction is exact.

A.4 Single chain structure factors at given η for R_e^2 calculation

Here we derive $\mathbf{S}'_{1,\eta=0}(q,e_1,e_2) = \frac{\partial \mathbf{S}_1(q,e_1,e_2)}{\partial \eta} \Big|_{\eta=0}$ used for the calculation of $\langle R^2(e_1,e_2) \rangle$ in GF

theory for $e_2 > e_1$. Firstly, for the (A, A) elements, we have

$$\frac{\partial \mathbf{S}_{1,AA}(q,e_{1},e_{2})}{\partial \eta}\Big|_{\eta=0} = \int \mathbf{d}(\mathbf{r}-\mathbf{r}')\frac{\partial}{\partial \eta} \left[\frac{V}{N} \frac{1}{Q^{*}(\eta)} \frac{\delta^{2}Q(\eta)}{\delta i \omega_{A}(\mathbf{r}) \delta i \omega_{A}(\mathbf{r}')} \Big|_{\mathbf{\omega}^{*}} \right]_{\eta=0} \exp\left[-i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')\right] \\
= \frac{3}{2a^{2}N} \sum_{t,t'=1}^{N_{A}} \left[\left\langle \exp\left[-i\mathbf{q}\cdot\left(\mathbf{R}_{t}-\mathbf{R}_{t'}\right)\right] \right\rangle_{0} \left\langle \left(\mathbf{R}_{e2}-\mathbf{R}_{e1}\right)^{2} \right\rangle_{0} - \right] \left\langle \exp\left[-i\mathbf{q}\cdot\left(\mathbf{R}_{t}-\mathbf{R}_{t'}\right)\right] \left(\mathbf{R}_{e2}-\mathbf{R}_{e1}\right)^{2} \right\rangle_{0} \right] \\
= \frac{3}{N} \sum_{t'=1}^{N_{A}-1} \sum_{t=t'+1}^{N_{A}} \left[\left(e_{2}-e_{1}\right) B(q)^{|s'-s|} - \left\langle \exp\left[-i\mathbf{q}\cdot\left(\mathbf{R}_{t}-\mathbf{R}_{t'}\right)\right] \left(\mathbf{R}_{e2}-\mathbf{R}_{e1}\right)^{2} \right\rangle_{0} \right] \\$$
(5.47)

which corresponds to the correlation between $\exp\left[-i\mathbf{q}\cdot(\mathbf{R}_{t}-\mathbf{R}_{t'})\right]$ and $(\mathbf{R}_{e2}-\mathbf{R}_{e1})^{2}$ in the ideal-chain ensemble of ideal-chain system, depending on the positions of relevant segments along a chain. If $e_{2} > e_{1} \ge N_{A}$, apparently, between $\exp\left[-i\mathbf{q}\cdot(\mathbf{R}_{t}-\mathbf{R}_{t'})\right]$ and $(\mathbf{R}_{e2}-\mathbf{R}_{e1})^{2}$ are

uncorrelated, and thus the above equation goes to 0; otherwise, for $e_1 < e_2 \le N_A$, we have

$$\frac{\partial \mathbf{S}_{1,AA}(q,e_{1},e_{2})}{\partial \eta}\bigg|_{\eta=0} = \frac{a^{2}q^{2}}{3N} \begin{cases} \sum_{t'=1}^{e_{1}-1} \sum_{t=e_{1}+1}^{e_{2}} \left(t-e_{1}\right)^{2} B(q)^{t-t'} + \sum_{t'=1}^{e_{1}-1} \sum_{t=e_{2}+1}^{N_{A}} \left(e_{2}-e_{1}\right)^{2} B(q)^{t-t'} \\ + \sum_{t'=e_{1}}^{e_{2}-1} \sum_{t=t'+1}^{e_{2}} \left(t-t'\right)^{2} B(q)^{t-t'} + \sum_{t'=e_{1}}^{e_{2}-1} \sum_{t=e_{2}+1}^{N_{A}} \left(e_{2}-t'\right)^{2} B(q)^{t-t'} \end{cases} \right\},$$
(5.48)

and for $e_1 \le N_A - 1$ and $e_2 \ge N_A + 1$, we have

$$\frac{\partial S_{1,AA}(q,\eta,e_1,e_2)}{\partial \eta}\bigg|_{\eta=0} = \frac{a^2 q^2}{3N} \Biggl\{ \sum_{t'=1}^{e_1-1} \sum_{t=e_1+1}^{N_A} (t-e_1)^2 B(q)^{t-t'} + \sum_{t'=e_1}^{N_A-1} \sum_{t=t'+1}^{N_A} (t-t')^2 B(q)^{t-t'} \Biggr\}.$$
 (5.49)

Similarly, for $e_1 < e_2 \le N_A + 1$, the (B, B) element $\left[\partial S_{1,BB} (q, \eta, e_1, e_2) / \partial \eta \right]_{\eta=0} = 0$; otherwise,

for $e_2 > e_1 \ge N_A + 1$, we have

$$\frac{\partial \mathbf{S}_{1,BB}(q,e_{1},e_{2})}{\partial \eta}\bigg|_{\eta=0} = \frac{a^{2}q^{2}}{3N} \left\{ \sum_{t'=N_{A}+1}^{e_{1}-1} \sum_{t=e_{1}+1}^{e_{2}} \left(t-e_{1}\right)^{2} B(q)^{t-t'} + \sum_{t'=N_{A}+1}^{e_{1}-1} \sum_{t=e_{2}+1}^{N} \left(e_{2}-e_{1}\right)^{2} B(q)^{t-t'} + \sum_{t'=e_{1}}^{e_{2}-1} \sum_{t=e_{2}+1}^{N} \left(e_{2}-t'\right)^{2} B(q)^{t-t'} + \sum_{t'=e_{1}+1}^{e_{2}-1} \sum_{t'=e_{2}+1}^{N} \left(e_{2}-t'\right)^{2} B(q)^{t-t'} + \sum_{t'=e_{1}+1}^{e_{2}-1} \sum_{t'=e_{1}+1}^{N} \left(e_{2}-t'\right)^{2} B(q)^{t-t'} + \sum_{t'=e_{1}+1}^{N} \left(e_{2}-t'\right)^{2$$

and for $e_2 \ge N_A + 2$ and $e_1 \le N_A$, we have

$$\frac{\partial S_{1,BB}(q,\eta,e_1,e_2)}{\partial \eta}\bigg|_{\eta=0} = \frac{a^2 q^2}{3N} \left\{ \sum_{t'=N_A+1t=t'+1}^{e_2-1} \sum_{t'=N_A+1t=e_2+1}^{e_2} (t-t')^2 B(q)^{t-t'} + \sum_{t'=N_A+1t=e_2+1}^{e_2-1} \sum_{t'=N_A+1t=e_2+1}^{N} (e_2-t')^2 B(q)^{t-t'} \right\}.$$
(5.51)

Note that $\left[\partial S_{1,BB}(q,\eta,e_1,e_2)/\partial\eta\right]_{\eta=0}$ is the same as $\left[\partial S_{1,AA}(q,\eta,e_1,e_2)/\partial\eta\right]_{\eta=0}$ for DBC.

symmetric

for $e_1 < e_2 \le N_A$, we have the Finally, crossing terms $\left[\partial S_{1,AB}(q,\eta,e_1,e_2)/\partial\eta\right]_{\eta=0} = \left[\partial S_{1,BA}(q,\eta,e_1,e_2)/\partial\eta\right]_{\eta=0} \text{ as}$ $\frac{\partial S_{1,AB}(q,\eta,e_1,e_2)}{\partial \eta}\bigg|_{n=0} = \frac{q^2 a^2}{6N} \left\{ \sum_{t'=1}^{e_1-1} \sum_{t=N_A+1}^{N} (e_2 - e_1)^2 B(q)^{t-t'} + \sum_{t'=e_1}^{e_2-1} \sum_{t=N_A+1}^{N} (e_2 - t')^2 B(q)^{t-t'} \right\},$ (5.52)

for $N_{\rm A} + 1 \le e_1 < e_2$ we have

$$\frac{\partial S_{1,AB}(q,\eta,e_1,e_2)}{\partial \eta}\bigg|_{\eta=0} = \frac{q^2 a^2}{6N} \left\{ \sum_{t'=1}^{N_A} \sum_{t=e_1}^{e_2-1} (t-e_1)^2 B(q)^{t-t'} + \sum_{t'=1}^{N_A} \sum_{t=e_2}^{N} (e_2-e_1)^2 B(q)^{t-t'} \right\},$$
(5.53)

and for $e_1 \le N_A$ and $e_2 \ge N_A + 1$ we have

$$\frac{\partial \mathbf{S}_{1,AB}(q,e_{1},e_{2})}{\partial \eta}\bigg|_{\eta=0} = \frac{q^{2}a^{2}}{6N} \begin{cases} \sum_{t'=1}^{e_{1}-1} \sum_{t=N_{A}+1}^{e_{2}-1} \left(t-e_{1}\right)^{2} B(q)^{t-t'} + \sum_{t'=1}^{e_{1}-1} \sum_{t=e_{2}}^{N} \left(e_{2}-e_{1}\right)^{2} B(q)^{t-t'} \\ + \sum_{t'=e_{1}}^{N} \sum_{t=N_{A}+1+1}^{e_{2}-1} \left(t-t'\right)^{2} B(q)^{t-t'} + \sum_{t'=e_{1}}^{N} \sum_{t=e_{2}}^{N} \left(e_{2}-t'\right)^{2} B(q)^{t-t'} \\ \end{cases},$$
(5.54)

From the above equations $\mathbf{S}_{1b^2}(q) \equiv \sum_{s=1}^{N-1} \mathbf{S}'_{1,\eta}(q, s, s+1)$ is given by

$$S_{1b^{2},AA} = \frac{a^{2}q^{2}}{3N} \sum_{s=1}^{N_{A}-1} \sum_{t'=1}^{s} \sum_{t=s+1}^{N_{A}} B(q)^{t-t'} = \frac{a^{2}q^{2}}{3} \sum_{s=1}^{N_{A}-1} \frac{\left[B(q)^{s}-1\right]\left[B(q)^{N_{A}}-B(q)^{s}\right]}{NB(q)^{s-1}[1-B(q)]^{2}},$$

$$S_{1b^{2},BB} \frac{a^{2}q^{2}}{3N} \sum_{s=N_{A}+1t'=N_{A}+1t=s+1}^{s} \sum_{k=1}^{N} B(q)^{t-t'} = \frac{a^{2}q^{2}}{3} \sum_{s=1}^{N_{B}-1} \frac{\left[B(q)^{s}-1\right]\left[B(q)^{N_{B}}-B(q)^{s}\right]}{NB(q)^{s-1}[1-B(q)]^{2}},$$

$$S_{1b^{2},AB} = \frac{a^{2}q^{2}}{6N} \left[\sum_{s=1}^{N_{A}} \sum_{t'=1}^{s} \sum_{t=N_{A}+1}^{N} B(q)^{t-t'} + \sum_{s=N_{A}}^{N-1} \sum_{t'=1}^{N_{A}} \sum_{t=s+1}^{N} B(q)^{t-t'}\right]$$

$$= \frac{a^{2}q^{2}}{6N} \left[\sum_{s=1}^{N_{A}} \frac{\left[B(q)^{s}-1\right]\left[B(q)^{N}-B(q)^{N_{A}}\right]}{B(q)^{s-1}[1-B(q)]^{2}} + \sum_{s=1}^{N_{B}-1} \frac{\left[B(q)^{s}-1\right]\left[B(q)^{N}-B(q)^{N_{B}}\right]}{B(q)^{s-1}[1-B(q)]^{2}}\right].$$
(5.55)

Note that, for symmetric DBC, $S_{1b^2,AA}$ is the same as $S_{1b^2,BB}$. In the IE theories, we need the intrachain correlation functions $\hat{\omega}_{t,t'}(q,\eta,e_1,e_2)$ at given η acting on $(\mathbf{R}_{e_2} - \mathbf{R}_{e_1})^2$ on one chain to solve the OZ equation with a closure to obtain $R^2(e_1,e_2)$. Considering one ideal-chain (i.e., without non-bonded interactions), $\hat{\omega}_{t,t'}(q,\eta,e_1,e_2)$, with $t' \ge t$ for example, can be evaluated by Gaussian integral as

Taking the derivative of $\hat{\omega}_{t,t'}(q,\eta,e_1,e_2)$ with respect of η and set $\eta = 0$, we have

$$\frac{\partial \hat{\omega}_{t,t'}(q,\eta,e_{1},e_{2})}{\partial \eta}\Big|_{\eta=0} = \begin{cases} 0, & \text{if } 1 \le t \le t' \le e_{1} \text{ or } e_{2} \le t \le t' \le N; \\ \frac{a^{2}q^{2}}{6} (t'-e_{1})^{2} B(q)^{t'-t}, & \text{if } 1 \le t \le t' \le e_{1} \text{ and } e_{1}+1 \le t' \le e_{2}; \\ \frac{a^{2}q^{2}}{6} (e_{2}-e_{1})^{2} B(q)^{t'-t}, & \text{if } 1 \le t \le t' \le e_{1} \text{ and } e_{2}+1 \le t' \le N; \end{cases} (5.57)$$

$$\frac{a^{2}q^{2}}{6} (t'-t)^{2} B(q)^{t'-t}, & \text{if } e_{1}+1 \le t \le t' \le e_{2}-1; \\ \frac{a^{2}q^{2}}{6} (e_{2}-t)^{2} B(q)^{t'-t}, & \text{if } e_{1}+1 \le t \le e_{2}-1 \text{ and } e_{2} \le t' \le N; \end{cases}$$

which also leads to $\mathbf{S}'_{1,\eta=0}(q,e_1,e_2)$, for example, the (P,P') element is given by $(1/N) \sum_{t\in \mathbf{P},t'\in\mathbf{P}'} [\partial \hat{\omega}_{t,t'}(q,\eta,e_1,e_2)/\partial \eta]|_{\eta=0}.$

B Chain-end effects

The comparison of $\beta u_{c,nb}$ and βP_{nb} between RISM and PRISM theories provides us with the chain-end effects neglected in the PRISM theory, shown as in Fig. [5.10] at $N/\kappa=0$ for instance. We find, with $\omega_{s,s'}^{DGC}$, both $\beta u_{c,nb}$ and βP_{nb} from PRISM-PY method are lower than that from RISM-PY at high χN values, meaning that PRISM-PY gives solutions closer to FOMC simulation than RISM-PY, which is conflict with our expectation and it is probably caused by error cancelation between the chain-end effects and the PY closure.

Chapter 6 PCFs of Polymeric Fluids: A Comparison of Self-Consistent Polymer Reference Interaction Site Model and Polymer Density-Functional Theories

6.1 Introduction

Chain conformations and structures of polymer melts determine their thermodynamic properties. For homopolymer melts of tangent hard-sphere chains, we have compared the intrachain normalized pair correlation function (PCF) $\omega(r)$ (*i.e.*, $\int_{d\mathbf{r}\omega(r)=1}$) and the interchain total PCF h(r) between monomers predicted by the SC-PRISM theory that adjusts its solvation potential strength to reproduce the mean-square chain end-to-end distance R_e^2 given by the corresponding MC simulations^[16] with the SC-PRISM theory that does not adjust its solvation potential strength (denoted by " κ =1"), a polymer density-functional theory based on the modified fundamental measure theory and the second-order thermodynamic perturbation theory^[19, 92] (denoted by "TPT2"), and the corresponding MC simulations for various chain lengths (N_m =3~120) and monomer number densities ($\rho\sigma^3$ =0.1~0.6 with σ being the hard-sphere diameter), establishing it as the most accurate theory for $\omega(r)$ and g(r) to date. The figure below gives an example for N_m =24 and $\rho\sigma^3$ =0.6, where $\omega(r) = \omega(r) - \delta(r)/N_m - 2(N_m - 1)\delta(r-1)/N_m^2$ with $\delta(r)$ denoting the Dirac δ -function.

For homogeneous monatomic fluids, the pair correlation function h(r) is just the familiar radial distribution function g(r)-1. It can be used to determine the structural,

thermodynamic, and dynamic properties of the fluid, and can be measured experimentally. For polymers, there are intra- and inter-chain PCFs, which depend on the segment positions along the chain contour due to the finite chain length. Few theories can predict intra- and inter-chain PCFs; these include polymer integral-equation theories such as the SC-PRISMs and DFTs.

On the other hand, for spatially homogeneous monatomic fluids the Percus' trick is the basis for defining g(r); that is, the radial distribution of other particles around a particle fixed at the origin is inhomogeneous. For polymers Yu and Wu ^[12] proposed the extended Percus' trick, which treats a homogeneous homopolymer system as an inhomogeneous mixture of free chains A and grafted chains C and D. With segment *s*' on a chain fixed at the origin, any polymer DFT can then be used to calculate the number density of segment *s* on type-I chain $\rho_{I,ss'}(r)$ under the spherical symmetry, from which h(r) and $\omega(r)$ are obtained.

Here we use the polymer DFT of Yu and Wu, which combines the modified fundamental measure theory^[93] for hard-sphere correlations and the first-order thermodynamic perturbation theory^[94] for chain correlations; hereafter, we referred to this theory as TPT1. To improve its accuracy, we also replace the first-order thermodynamic perturbation theory by the second order as done in this paper, referred to as TPT2^[92].

6.2 Model and Method

6.2.1 PRISM Calculations

Here we use a simple model system of tangent hard-sphere chains to quantitatively compare the SC-PRISM and DFT predictions of intra- and inter-chain PCFs against manychain Monte Carlo simulation results. In our model system, which consists of *n* homopolymer chains each of N segments in volume V at thermodynamic temperature T. We take the hardsphere diameter σ and $1/\beta \equiv k_B T$ as the units of length and energy, respectively. we have $\beta u^{nb}(\overline{r}) = \begin{cases} \infty & \text{if } \overline{r} < 1\\ 0 & \text{otherwise} \end{cases}$, the bonding potential u^{b} between two adjacent segments on a chain is given by $\exp(-\beta u^b(\overline{r})) = \sigma \delta(\overline{r}-1)/4\pi \implies \int d\overline{r} \exp(-\beta u^b(\overline{r})) = 1$, which fix the bond length to be σ where $\overline{r} \equiv r/\sigma$ and $\overline{\rho} \equiv \rho \sigma^3$. The bonded potential of a chain $V^{b}(\mathbf{R}) = \sum_{s=1}^{N-1} u^{b}(|\mathbf{R}_{s+1} - \mathbf{R}_{s}|)$ sums over all its bonds, where \mathbf{R}_{s} is the spatial position of the sth segment on the chain, and **R** denotes the spatial positions of all segments on the chain, thus its configuration. Note that, $\rho(\mathbf{R})$ is the number density of chains having the configuration **R**, $\rho(\mathbf{r}) \equiv \sum_{s=1}^{N} \rho_s(\mathbf{r})$ is the total segment number density at spatial position \mathbf{r} with

 $\rho(\mathbf{r}) \equiv \sum_{s=1}^{N} \rho_s(\mathbf{r}) \text{ is the total segment number density at spatial position } \mathbf{r} \text{ with}$ $\rho_s(\mathbf{r}) = \prod_{t=1}^{N} \int d\mathbf{R}_t \cdot \delta(\mathbf{r} - \mathbf{R}_s) \rho(\mathbf{R}).$

The PRISM equation gives $\hat{h}/\sigma^3 = N^2 \hat{\omega}(\hat{c}/\sigma^3) \hat{\omega}/[1 - N\bar{\rho}\hat{\omega}(\hat{c}/\sigma^3)]$. The PY closure^[13] gives $c(\bar{r}) = [1 - \exp(\beta u^{nb}(\bar{r}))](1 + h(\bar{r}))$, which leads to $c(\bar{r} \ge \bar{r}_{cut}) = 0$ with $\bar{r}_{cut} = 1$ for the THSC model; it further gives $h(0 \le \bar{r} < \bar{r}_{cut}) = -1$. We therefore only need to

solve for $c(0 \le \overline{r} < \overline{r_{\text{cut}}})$. For an initial guess $c^{\text{old}}(0 \le \overline{r} < \overline{r_{\text{cut}}})$, with σ being the unit of length

and $\frac{\hat{C}^{\text{old}}}{\sigma^3} = N^2 \frac{\hat{c}^{\text{old}}}{\sigma^3}$, we can therefore calculate the 3D Fourier transform of the indirect PCF,

$$\frac{\hat{\gamma}}{\sigma^3} = \frac{\hat{h}}{\sigma^3} - \frac{\hat{c}}{\sigma^3} = \frac{\hat{C}^{\text{old}}}{\sigma^3} \left[\frac{\hat{\omega}^2}{1 - (\bar{\rho}/N)\hat{\omega}(\hat{C}^{\text{old}}/\sigma^3)} - \frac{1}{N^2} \right] \text{ from the PRISM equation, then obtain}$$

 $C^{\text{new}}(r) = N^2 \Big[\exp(-\beta u^{nb}(r)) - 1 \Big] (1 + \gamma(r)), \text{ which reduces to } C^{\text{new}}(\overline{r}) = N^2 (-1 - \gamma(\overline{r})) \text{ for the}$

THSC model. The Anderson mixing is finally used to converge $C(\overline{r})$ with a convergence criterion of $\max_{\{0 \le \overline{r} < \overline{r_{ext}}\}} \left| C^{\text{new}}(\overline{r}) - C^{\text{old}}(\overline{r}) \right| \le 10^{-10}$.

Note that, for hard spheres (i.e., $N_m=1$), the analytical solution is given by

$$c(0 \le \overline{r} < 1) = -\frac{(1+2\eta)^2}{(1-\eta)^4} + \frac{3\eta}{2} \frac{(2+\eta)^2}{(1-\eta)^4} \overline{r} - \frac{\eta}{2} \frac{(1+2\eta)^2}{(1-\eta)^4} \overline{r}^3$$
(6.1)

For a system of *n* hard spheres each of diameter σ in volume *V*, i.e., at the packing (volume) fraction $\eta \equiv \pi \rho \sigma^3/6$ with $\rho \equiv n/V$, the analytical solution to the Ornstein-Zernike equation

$$\hat{h} = \hat{c} \left(1 + \rho \hat{h} \right) \implies \frac{\hat{h}}{\sigma^3} = \frac{\hat{c}/\sigma^3}{1 - (6\eta/\pi)\hat{c}/\sigma^3} \text{ with the Percus-Yevick closure } \begin{cases} h(r < \sigma) = -1\\ c(r \ge \sigma) = 0 \end{cases} \text{ is }$$

given by Eq (6.1), where $\overline{r} \equiv r/\sigma$. We therefore ha

$$\begin{split} \frac{\hat{c}}{\sigma^{3}}(q=0) &= \lim_{q\to 0} \frac{\hat{c}}{\sigma^{3}}(q>0) = \frac{\left(-8+2\eta-4\eta^{2}+\eta^{3}\right)\pi}{6\left(-1+\eta\right)^{4}} \\ \frac{\hat{c}}{\sigma^{3}}(q>0) &= \frac{4\pi}{q\sigma^{3}}\int_{0}^{\infty} drr\sin(qr)c(r) = \frac{4\pi}{\overline{q}}\int_{0}^{1} d\overline{r}\overline{r}\sin(\overline{q}\overline{r})c(\overline{r}) \\ &= \frac{4\pi}{\overline{q}}\int_{0}^{1} d\overline{r}\overline{r}\sin(\overline{q}\overline{r}) \left(-\frac{(1+2\eta)^{2}}{(1-\eta)^{4}} + \frac{3\eta}{2}\frac{(2+\eta)^{2}}{(1-\eta)^{4}}\overline{r} - \frac{\eta}{2}\frac{(1+2\eta)^{2}}{(1-\eta)^{4}}\overline{r}^{3}\right) \\ &= \frac{2\pi}{(1-\eta)^{4}\overline{q}^{6}} \begin{cases} -6\eta(2+\eta)^{2}\overline{q}^{2} + 2\overline{q}\left[12\eta(1+2\eta)^{2}-\left(1-6\eta+5\eta^{3}\right)\overline{q}^{2}\right]\sin\overline{q}} \\ +\left\{24\eta(1+2\eta)^{2}+\left[6\eta\left(2-\eta(4+7\eta)\right)+(1-\eta)^{2}(2+\eta)\overline{q}^{2}\right]\overline{q}^{2}\right\}\cos\overline{q}} \\ -24\eta(1+2\eta)^{2} \end{cases} \\ &= \frac{2\pi}{(1-\eta)^{4}\overline{q}^{6}} \begin{cases} \left[\left(1-\eta\right)^{2}(2+\eta)\overline{q}\cos\overline{q}-2\left(1-6\eta+5\eta^{3}\right)\sin\overline{q}\right]\overline{q}^{2} \\ +6\eta\left\{\left[\left(2-\eta(4+7\eta)\right)\cos\overline{q}-(2+\eta)^{2}\right]\overline{q}+4(1+2\eta)^{2}\sin\overline{q}\right\}\right)\overline{q}} \\ +24\eta(1+2\eta)^{2}(\cos\overline{q}-1) \end{cases} \end{split}$$

(6.2)

$$\begin{aligned} \frac{\hat{h}}{\sigma^{3}}(q=0) &= \lim_{q \to 0} \frac{\hat{h}}{\sigma^{3}}(q>0) = \frac{\left(-8+2\eta-4\eta^{2}+\eta^{3}\right)\pi}{6\left(1+2\eta\right)^{2}} \\ \frac{\hat{h}}{\sigma^{3}}(q>0) &= \frac{2\pi}{-12\eta + \frac{(1-\eta)^{4}\bar{q}^{6}}{\left[\left(1-\eta\right)^{2}(2+\eta)\bar{q}\cos\bar{q}-2\left(1-6\eta+5\eta^{3}\right)\sin\bar{q}\right]\bar{q}^{2}}} \\ &= \frac{\left(1-\eta\right)^{4}\bar{q}^{6}}{\left[\left(1-\eta\right)^{2}(2+\eta)\bar{q}\cos\bar{q}-2\left(1-6\eta+5\eta^{3}\right)\sin\bar{q}\right]\bar{q}^{2}} \\ &= \frac{12\eta}{\left(1-\eta\right)^{2}(2+\eta)\bar{q}\cos\bar{q}-2\left(1-6\eta+5\eta^{3}\right)\sin\bar{q}\right]\bar{q}^{2}} \\ &= \frac{12\eta}{\left(1-\eta\right)^{2}(2+\eta)\bar{q}\cos\bar{q}-2\left(1-6\eta+5\eta^{3}\right)\sin\bar{q}} \\ &= \frac{12\eta}{\left(1-\eta\right)^{2}(2+\eta)\bar{q}\cos\bar{q}-2\left(1-6\eta+5\eta^{3}\right)} \\ &= \frac{12\eta}{\left(1-\eta\right)^{2}(2+\eta)\bar{q}\cos\bar{q}-2\left(1-6\eta+5\eta^{3}\right)} \\ &= \frac{12\eta}{\left(1-\eta\right)^{2}} \\ &= \frac{12\eta}{\left(1-\eta\right)^{2}(2+\eta)\bar{q}\cos\bar{q}-2\left(1-6\eta+5\eta^{3}\right)} \\ &= \frac{12\eta}{\left(1-\eta\right)^{2}} \\ &= \frac{12\eta}{\left(1-\eta\right)^{$$

(6.3)

$$\frac{\hat{\gamma}}{\sigma^{3}}(q=0) = \lim_{q\to 0} \frac{\hat{\gamma}}{\sigma^{3}}(q>0) = \frac{(-4+\eta)^{2} \eta (2+\eta^{2})^{2} \pi}{6(-1+\eta)^{4} (1+2\eta)^{2}}$$

$$\frac{\hat{\gamma}}{\sigma^{3}}(q>0) = \frac{\hat{h}}{\sigma^{3}} - \frac{\hat{c}}{\sigma^{3}} = \frac{6\eta}{\pi} \frac{\hat{c}}{\sigma^{3}} \frac{\hat{h}}{\sigma^{3}}$$

$$= \frac{\frac{24\pi\eta}{(1-\eta)^{4} \bar{q}^{6}} \left\{ \begin{bmatrix} (1-\eta)^{2}(2+\eta)\bar{q}\cos\bar{q}-2(1-6\eta+5\eta^{3})\sin\bar{q} \]\bar{q}^{2} \\ +6\eta \left\{ \begin{bmatrix} (2-\eta(4+7\eta))\cos\bar{q}-(2+\eta)^{2} \]\bar{q}+4(1+2\eta)^{2}\sin\bar{q} \right\} \right\}^{\bar{q}} \right\}^{2} \\ +24\eta(1+2\eta)^{2}(\cos\bar{q}-1)$$

$$= \frac{(1-\eta)^{4} \bar{q}^{6} - 12\eta \left\{ \begin{bmatrix} (1-\eta)^{2}(2+\eta)\bar{q}\cos\bar{q}-2(1-6\eta+5\eta^{3})\sin\bar{q} \]\bar{q}^{2} \\ +6\eta \left\{ \begin{bmatrix} (2-\eta(4+7\eta))\cos\bar{q}-(2+\eta)^{2} \]\bar{q}+4(1+2\eta)^{2}\sin\bar{q} \right\} \right\}^{\bar{q}} \right\}$$

$$(6.4)$$

$$+24\eta(1+2\eta)^{2}(\cos\bar{q}-1)$$

In PRISM calculations, we uniformly discretize $[0, \overline{r}_{cut}]$ into *m* subintervals of width $\Delta \overline{r} = \overline{r}_{cut}/m$. We also use a cut-off $\overline{r}_c = \overline{r}_{cut} M/m$ for $\gamma(\overline{r})$ (i.e., $h(\overline{r})$) and uniformly discretize $[0, \overline{r}_c]$ into *M* subintervals of width $\Delta \overline{r}$. We calculate the 3D Fourier transform $(\hat{c}/\sigma^3)(\overline{q} > 0) = (4\pi/\overline{q}) \int_0^{\overline{r}_c} d\overline{r}c(\overline{r})\overline{r} \sin(\overline{q}\overline{r}) = (4\pi/\overline{q}) \int_0^{\overline{r}_{cut}} d\overline{r}c(\overline{r})\overline{r} \sin(\overline{q}\overline{r})$ using DST (\overline{r}_c instead of \overline{r}_{cut} is used as the upper limit of the first integral to decrease $\Delta \overline{q}$; see below) and using the Romberg integration (i.e., the second integral due to the discontinuity of $c(\overline{r}_{cut})$); $(\hat{c}/\sigma^3)(\overline{q} = 0) = 4\pi \int_0^{\overline{r}_{cut}} d\overline{r}c(\overline{r})\overline{r}^2$ is calculated using the Romberg integration. We also

calculate the 3D inverse Fourier transform $\gamma^{mm}(\overline{r} > 0) = \frac{1}{2\pi^2 \overline{r}} \int_0^{\overline{q}_c} d\overline{q} \, \frac{\hat{\gamma}^{mm}}{\sigma^3} \, \overline{q} \sin(\overline{qr})$ using iDST

(see below) and $\gamma^{mm}(\overline{r}=0) = \frac{1}{2\pi^2} \int_0^{\overline{q}_c} d\overline{q} \, \frac{\hat{\gamma}^{mm}}{\sigma^3} \overline{q}^2$ using the Romberg integration; this introduces $\Delta \overline{q} = \pi/\overline{r_c} = \pi/M\Delta \overline{r}$ and $\overline{q}_c = M\Delta \overline{q} = \pi/\Delta \overline{r}$. We therefore choose *m* to be large enough such

that $\max_{\{0 \le \overline{r} < \overline{r_{cut}}\}} |h(\overline{r}) + 1| \le 10^{-10}$. We also choose M to be large enough such that $\left| h^{mm}(\overline{r_c}) = \frac{1}{2\pi^2 \overline{r_c}} \int_0^{\overline{q_c}} d\overline{q} \, \frac{\hat{\gamma}^{mm}}{\sigma^3} \, \overline{q} \sin(\overline{qr_c}) \right|$ calculated using the Romberg integration is less than 10^{-10} .

To calculate $\frac{\hat{f}}{\sigma^3}(\bar{q}>0) = \frac{4\pi}{\bar{q}} \int_0^{\bar{r}_c} d\bar{r} f(\bar{r}) \bar{r} \sin(\bar{q}\bar{r})$, we use the discrete sine transform

(DST)
$$\hat{F}^{s}(\bar{q}_{k}) \equiv \frac{1}{M} \sum_{j=1}^{M-1} F(\bar{r}_{j}) \sin\left(\frac{\pi jk}{M}\right) = \frac{1}{\bar{r}_{c}} \int_{0}^{\bar{r}_{c}} d\bar{r} F(\bar{r}) \sin(-\bar{q}\bar{r})$$
, where $M+1$ is the number of

equally spaced points at $\overline{r_j} = j\overline{r_c}/M$, for j=0,1,...,M; that is,

$$F(\overline{r}_{j}) = -f(\overline{r}_{j})\overline{r}_{j} \implies \frac{\hat{f}(\overline{q}_{k})}{\sigma^{3}} = \frac{4\pi\overline{r}_{c}}{\overline{q}_{k}}\hat{F}^{s}(\overline{q}_{k}) = \frac{4M(\Delta\overline{r})^{3}}{k}\sum_{j=1}^{M-1}\overline{F}(\overline{r}_{j})\sin\left(\frac{\pi jk}{M}\right)$$
with

 $\overline{F}(\overline{r}_j) = -f(\overline{r}_j)\overline{r}_j / \Delta \overline{r}$ and $\overline{q}_k = \pi k / \overline{r}_c$, for $k=0,1,\ldots,M$. Similarly, to calculate

 $f(\overline{r} > 0) = \frac{1}{2\pi^2 \overline{r}} \int_0^{\overline{q}_c} d\overline{q} \, \frac{\hat{f}}{\sigma^3} \overline{q} \sin(\overline{qr}) , \text{ we use the inverse discrete sine transform (iDST)}$

$$F(\overline{r}_j) \equiv 2\sum_{k=1}^{M-1} \hat{F}^s(\overline{q}_k) \sin\left(\frac{\pi jk}{M}\right) = \frac{2\overline{r}_c}{\pi} \int_0^{\pi M/\overline{r}_c} d\overline{q} \hat{F}^s(\overline{q}) \sin(-\overline{qr}), \text{ which is the same as DST except}$$

that the factor 1/M there is replaced by 2; that is,

$$\hat{F}^{s}(\overline{q}_{k}) = \frac{-\hat{f}(\overline{q}_{k})}{\sigma^{3}}\overline{q}_{k} \implies f(\overline{r}_{j}) = \frac{\tilde{q}_{c}}{4\pi^{2}M\overline{r}_{j}}F(\overline{r}_{j}) = \frac{2}{4M(\Delta\overline{r})^{3}Mj}\sum_{k=1}^{M-1}\overline{F}^{s}(\overline{q}_{k})\sin\left(\frac{\pi jk}{M}\right) \quad \text{with}$$

$$\overline{\hat{F}}^{s}(\overline{q}_{k}) = \frac{-\widehat{f}(\overline{q}_{k})}{\sigma^{3}} \frac{\overline{q}_{k}}{\Delta \overline{q}} \quad . \quad \text{Note that} \quad \overline{q}_{c} = \frac{\pi M}{\overline{r}_{c}} \implies \overline{r}_{c} = \frac{\pi M}{\overline{q}_{c}} \quad , \quad \overline{q}_{k} = \pi k/\overline{r}_{c} = k\overline{q}_{c}/M \quad ,$$

$$\overline{r}_j = j\overline{r}_c/M = \pi j/\overline{q}_c$$
, and that $F(\overline{r}_c = \overline{r}_M) = 2\sum_{k=1}^{M-1} \hat{F}^s(\overline{q}_k)\sin(\pi k) = 0$.

6.2.2 SC-PRISM Calculations

Using only $\beta u^b(\bar{r})$ gives $\tilde{B}_{id}(\bar{q}) = \sin \bar{q}/\bar{q}$ for the THSC model, where $\bar{q} = q\sigma$ with qbeing the wavenumber. Note that, at small \bar{q} , $\tilde{B}_{id}(\bar{q}) \approx 1 - b\bar{q}^2$ with b = 1/6 for the THSC model, leading to $\hat{\omega}_{id}(\bar{q}) = \frac{N_m - \tilde{B}_{id}(\bar{q})(2 + N_m \tilde{B}_{id}(\bar{q}) - 2\tilde{B}_{id}(\bar{q})^{N_m})}{N_m^2(1 - \tilde{B}_{id}(\bar{q}))^2} \approx 1 - \frac{b}{3}\frac{N_m^2 - 1}{N_m}\bar{q}^2$. To avoid division by 0 in the calculation of $\hat{\omega}_{id}(\bar{q})$, we therefore need to set $\hat{\omega}_{id}(\bar{q}) = 1$ for $b\bar{q}^2 \leq \varepsilon \implies \bar{q} \leq \sqrt{\varepsilon/b}$, where $\varepsilon \approx 2.2 \times 10^{-16}$ is the machine ensilon. For the THSC model

 $b\bar{q}^2 < \varepsilon \implies \bar{q} < \sqrt{\varepsilon/b}$, where $\varepsilon \approx 2.2 \times 10^{-16}$ is the machine epsilon. For the THSC model, $\tilde{B}_{\rm NBI}(\tilde{q}) = \tilde{B}_{\rm id}(\tilde{q})$.

Note that we take σ as unit in PRISM and R_e as unit in single chain simulations, we need to make a unit change when we connect these two parts together. Once the PRISM equations are solved for an initial guess of $\hat{\omega}_{old}^{nnn}(\tilde{q})$ (e.g., $\hat{\omega}_{NB1}^{nnn}$), we calculate

$$\beta \frac{\hat{w}}{\sigma^3} = -\kappa \left(\frac{(\rho \sigma^3 / N) (\hat{C} / \sigma^3)^2 \hat{\omega}}{N^2 \left[1 - (\rho \sigma^3 / N) (\hat{C} / \sigma^3) \hat{\omega} \right]} \right) \text{ and then its 3D inverse Fourier transform as in}$$

Sec. 6.2.1 above; we define $d \equiv \sigma_{IJ}/R_e \approx 0.770 N_m^{-1/2}$ (for $N_m < 10$, we use $d = 1/R_e$ with R_e obtained from MD simulations). We transfer \overline{r} to \tilde{r} and $w_0(\overline{r}) = w_0(\tilde{r})$, $\tilde{r} = d\overline{r} = r/R_e$; the solvation potential is then given by $w^{nmn}(\tilde{r}) = \kappa w_0^{nmn}(\tilde{r})$ with κ can be either set to 1, or adjusted (using using the Ridder method) such that the root-mean-square chain end-to-end distance $R_{e,SC}$ obtained from the subsequent single-chain Monte Carlo (SCMC) simulations (or histogram-reweighting, HR) with $w^{nmn}(\tilde{r})$ is equal to R_e , i.e., $|R_{e,SC} - R_e| < \sigma_{R_{e,SC}}$ with σ_A

denoting three times the standard deviation of quantity A given by the SCMC simulations or HR (with the sample correlations accounted for via the correlation-length method). With $\hat{\omega}_{new}^{nmn}(\tilde{q})$ given by the SCMC simulations or HR, transfer \tilde{q} to \bar{q} and $\hat{\omega}_{new}^{nmn}(\bar{q}) \Box \hat{\omega}_{new}^{nmn}(\tilde{q})$, $\bar{q} = d\tilde{q} = q\sigma_{LJ}$ with $\tilde{q} = qR_e$; we finally use the Anderson mixing to converge $\hat{\omega}^{nmn}$, i.e., with $\left|\hat{\omega}_{new}^{nmn}(\tilde{q}) - \hat{\omega}_{old}^{nmn}(\tilde{q})\right| \le \min\left(\sigma_{\hat{\omega}_{new}^{nmn}(\bar{q})}, \sigma_{\hat{\omega}_{old}^{nmn}(\bar{q})}\right)$ satisfied for all \bar{q} .

6.2.3 Monte Carlo Simulations

We also performed many-chain Monte Carlo simulations (MCMS) of tangent hardsphere chains in a canonical ensemble using segment rotation and chain reptation, with configurational bias to increase the acceptance rates of these trial moves. Note that, in MCMS using a cubic simulation box of length *L*, we have $\Delta \bar{q}_{MS} = 2\pi/\bar{L}$ for \hat{h}_{MS} with $\bar{L} \equiv L/\sigma$ due to the PBCs used. We also choose the bin size $\Delta \bar{r}_{MS} = 16p\Delta \bar{r}$ with *p* being an integer in the calculation of $\bar{h}_{MS}(\bar{r})$, so that the Romberg integration can be used with $h(\bar{r})$ obtained from PRISM calculations to calculate the corresponding $h(\bar{r})$ and compare it with $\bar{h}_{MS}(\bar{r})$.

6.2.4 DFT Calculations

Yu and Wu expressed the ideal part of the system Helmholtz free energy due to the combination of chain connectivity, the excess part F^{ex} and the external potential $V(\mathbf{r})$,

$$\Omega = \int d\mathbf{R}\rho(\mathbf{R}) \left(\ln \rho(\mathbf{R}) - 1 + V^{\mathrm{b}}(\mathbf{R}) \right) + F^{\mathrm{ex}}[\rho(\mathbf{r})] + \int d\mathbf{R} \left(\sum_{s=1}^{N} V(\mathbf{R}_{s}) - \mu \right) \rho(\mathbf{R}).$$
(6.5)

with $V(\mathbf{r})$ is external field and μ is chain chemical potential.

 $F^{\rm ex}$ is given by

$$F^{\text{ex}} = \frac{1}{\pi} \int d\mathbf{r} \begin{cases} -\tilde{n}_{2}(\mathbf{r}) \ln(1 - n_{3}(\mathbf{r})) + \frac{\tilde{n}_{2}^{2}(\mathbf{r})\zeta(\mathbf{r})}{2(1 - n_{3}(\mathbf{r}))} + \frac{\nu(\mathbf{r})(3\zeta(\mathbf{r}) - 2)}{36} \\ + \left(\frac{1}{N} - 1\right) \tilde{n}_{2}(\mathbf{r})\zeta(\mathbf{r}) \ln\left[\frac{1}{1 - n_{3}(\mathbf{r})} + \frac{\tilde{n}_{2}(\mathbf{r})\zeta(\mathbf{r})}{4(1 - n_{3}(\mathbf{r}))^{2}} + \frac{\tilde{n}_{2}^{2}(\mathbf{r})\zeta(\mathbf{r})}{72(1 - n_{3}(\mathbf{r}))^{3}}\right] \\ - \frac{1}{N} \tilde{n}_{2}(\mathbf{r})\zeta(\mathbf{r}) \ln\frac{\left[(1 + \Lambda(\mathbf{r}))/2\right]^{N} - \left[(1 - \Lambda(\mathbf{r}))/2\right]^{N}}{\Lambda(\mathbf{r})} \end{cases}$$
(6.6)

$$\zeta(\mathbf{r}) \equiv 1 - \frac{\tilde{\mathbf{n}}_{V2}(\mathbf{r}) \cdot \tilde{\mathbf{n}}_{V2}(\mathbf{r})}{\tilde{n}_{2}^{2}(\mathbf{r})}, \qquad \tilde{n}_{2}(\mathbf{r}) = \int d\mathbf{r}' \delta(1/2 - |\mathbf{r} - \mathbf{r}'|) \rho(\mathbf{r}'),$$

with $v(\mathbf{r}) = \frac{\tilde{n}_{2}^{3}(\mathbf{r})}{n_{3}(\mathbf{r})} \left[\frac{1}{(1 - n_{3}(\mathbf{r}))^{2}} + \frac{\ln(1 - n_{3}(\mathbf{r}))}{n_{3}(\mathbf{r})} \right], \qquad n_{3}(\mathbf{r}) = \int d\mathbf{r}' \Theta(1/2 - |\mathbf{r} - \mathbf{r}'|) \rho(\mathbf{r}'),$
$$\Lambda(\mathbf{r}) \equiv \sqrt{1 + 4 \begin{pmatrix} 0.23363n_{3}(\mathbf{r}) \\ +0.110275n_{3}^{2}(\mathbf{r}) \end{pmatrix}}, \qquad \tilde{\mathbf{n}}_{V2}(\mathbf{r}) = \int d\mathbf{r}' \delta(1/2 - |\mathbf{r} - \mathbf{r}'|) \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \rho(\mathbf{r}'),$$

and $\delta(r)$ is the Dirac δ -function, and $\Theta(r)$ is the Heaviside function.

Minimizing Ω Euler-Lagrange equation, from which we then obtain $\rho(\mathbf{R})$,

$$\frac{\partial\Omega}{\partial\rho(\mathbf{R})} = 0 \implies \rho(\mathbf{R}) = \exp\left(\mu - V^{\mathrm{b}}(\mathbf{R}) - \sum_{i=1}^{N} V(\mathbf{R}_{i}) - \frac{\delta F^{\mathrm{ex}}}{\delta\rho(\mathbf{R})}\right).$$
(6.7)

with $\frac{\delta F^{\text{ex}}}{\delta \rho(\mathbf{R})} = \sum_{t=1}^{N} \frac{\delta F^{\text{ex}}}{\delta \rho(\mathbf{R}_{t})}$ and $\lambda(\mathbf{r}) \equiv \frac{\delta F^{\text{ex}}}{\delta \rho(\mathbf{r})} + V(\mathbf{r})$, we obtain

$$\begin{split} \rho_{s}(\mathbf{r}) &= \prod_{t=1}^{N} \int d\mathbf{R}_{t} \cdot \delta(\mathbf{r} - \mathbf{R}_{s}) \rho(\mathbf{R}) \\ &= \exp(\mu) \prod_{t=1}^{N} \int d\mathbf{R}_{t} \cdot \delta(\mathbf{r} - \mathbf{R}_{s}) \exp\left(-\sum_{t=1}^{N-1} u^{b}(|\mathbf{R}_{t+1} - \mathbf{R}_{t}|) - \sum_{t=1}^{N} \lambda(\mathbf{R}_{t})\right) \\ &= \exp(\mu) \prod_{t=1}^{s-1} \int d\mathbf{R}_{t} \cdot \exp\left(-\sum_{t=1}^{s-2} u^{b}(|\mathbf{R}_{t+1} - \mathbf{R}_{t}|) - \sum_{t=1}^{s-1} \lambda(\mathbf{R}_{t})\right) \\ &\quad \frac{\int d\mathbf{R}_{s} \delta(\mathbf{r} - \mathbf{R}_{s}) \exp\left(-u^{b}(|\mathbf{R}_{s} - \mathbf{R}_{s-1}|) - \lambda(\mathbf{R}_{s})\right)}{\sum_{t=s+1}^{N} \int d\mathbf{R}_{t} \cdot \exp\left(-u^{b}(|\mathbf{R}_{s+1} - \mathbf{R}_{s}|) - \sum_{t=s+1}^{s-1} u^{b}(|\mathbf{R}_{t+1} - \mathbf{R}_{t}|) - \sum_{t=s+1}^{N} \lambda(\mathbf{R}_{t})\right) \\ &= \exp(\mu) \exp\left(-\lambda(\mathbf{r})\right) \prod_{t=1}^{s-1} \int d\mathbf{R}_{t} \cdot \exp\left(-u^{b}(|\mathbf{r} - \mathbf{R}_{s-1}|) - \sum_{t=1}^{s-2} u^{b}(|\mathbf{R}_{t+1} - \mathbf{R}_{t}|) - \sum_{t=1}^{s-1} \lambda(\mathbf{R}_{t})\right) \\ &\cdot \exp\left(\lambda(\mathbf{r})\right) \exp\left(-\lambda(\mathbf{r})\right) \prod_{t=s+1}^{N} \int d\mathbf{R}_{t} \cdot \exp\left(-u^{b}(|\mathbf{R}_{s+1} - \mathbf{r}|) - \sum_{t=s+1}^{s-2} u^{b}(|\mathbf{R}_{t+1} - \mathbf{R}_{t}|) - \sum_{t=s+1}^{s-1} \lambda(\mathbf{R}_{t})\right) \end{split}$$

We can rewrite $\rho_s(\mathbf{r})$ in terms of the propagator $q_s(\mathbf{r})$

$$\rho_{s}(\mathbf{r}) = \exp(\mu + \lambda(\mathbf{r})) \underline{q_{s}(\mathbf{r};[\lambda])} \underline{q_{N-s+1}(\mathbf{r};[\lambda])},$$
(6.9)

where $q_s(\mathbf{r})$ (s = 2,...,N) satisifies

$$q_{s}(\mathbf{r}) = \exp(-\lambda(\mathbf{r})) \int d\mathbf{r}' \exp(-u^{b}(|\mathbf{r}-\mathbf{r}'|)) q_{s-1}(\mathbf{r}') \text{ with } q_{1}(\mathbf{r}) = \exp(-\lambda(\mathbf{r})).$$

6.3 **Results and Discussion**

In the self-consistent PRISM calculations, one converts the interchain PCFs h(r) and c(r) into an intrachain solvation potential w(r) in an approximate way, which is then used in single-chain simulations to iterate $\omega(r)$ till it converges. Note that this parameter κ so that the mean-square chain end-to-end distance here matches that from the many-chain simulations. In Fig 6.1(a), we can see that the SC-PRISM with $\kappa = 1$ overestimates R_e^2 ; as I mentioned before, we can adjust κ to match R_e^2 to the Monte Carlo results. On the other hand, TPT2 underestimates R_e^2 , and TPT1 is even slightly worse than TPT2; these are due to the approximations of the thermodynamic perturbation theories. As the density increases in Fig 6.1 (b) and (c), we see the same qualitative results with smaller R_e^2 in all cases.



Figure 6.1: The mean-square chain end-to-end distance as a function of the number of bonds in a chain at different number density. Parts (a), (b) and (c) show the mean-square chain end-to-end distance Re^2 as a function of the number of bonds in a chain N-1 at different $\rho\sigma^3 = 0.1, 0.4$ and 0.6 on logarithmic plot; the Monte Carlo simulations are shown in black, the self-consistent PRISM results with fixed $\kappa = 1$ are in blue, and the TPT2 results are in red.

Based on Fig 6.1, we may expect that SC-PRISM with κ adjusted gives the smallest, while TPT1 gives the largest, deviation in the intrachain PCF from the Monte Carlo results. This is generally the case, as shown by these two tables here summarizing the results for various *N* and ρ , where the four theories are represented by different colors. SC-PRISM with κ adjusted results are in blue, SC-PRIMS with $\kappa = 1$ results are in green, TPT1 results are in pink and TPT2 results are in red. But there are exceptions. For example, Fig 6.2(a) shows $\omega(r)$ at *N*=24 and a segment number density representing melts. At large enough *r*, the deviations of all theoretical predictions from the Monte Carlo result are smaller than the simulation error, which leads to these empty cells. More importantly, in the first interval of r/σ (ranging from 1 to 2), SC-PRISM gives the largest, while TPT2 gives the smallest, deviation from the Monte Carlo results. This is because in Fig 6.2(c), at small *r*, the bare solvation potential $\beta w_0(r)$ in SC-PRISM calculations is strongly attractive, leading to overestimation of w(r).

Table 6.1: Summary of best theory for $\omega(r)$ in each interval based on the root mean square error between four different theories and MC simulation results.

| Best theory for $\omega(r)$ | | | | |
|-----------------------------|---------------|---------------|-----|-----|
| Ν | Intervals | $ ho\sigma^3$ | | |
| | of r/σ | 0.1 | 0.4 | 0.6 |
| 3 | | | | |
| 4 | | | | |
| 0 | 1~2 | | | |
| | 3 | | | |
| 0 | 4 | | | |
| | 5 | | | |
| 12 | 1 | | | |
| | 2~7 | | | |
| | 8 | | | |
| 24 | 1 | | | |
| | 2~3 | | | |
| | 4 | | | |
| | 5~13 | | | |
| | 14 | | | |
| | 15 | | | |

Table 6.2: Summary of worst theory for $\omega(r)$ in each interval based on the root mean square error between four different theories and MC simulation results.

| The Opposite for $\omega(r)$ | | | | |
|------------------------------|---------------|---------------|-----|-----|
| Ν | Intervals | $ ho\sigma^3$ | | |
| | of r/σ | 0.1 | 0.4 | 0.6 |
| 3 | | | | |
| 4 | 1 | | | |
| | 2 | | | |
| 8 | 1~4 | | | |
| | 5 | | | |
| 12 | 1 | | | |
| | 2~7 | | | |
| | 8 | | | |
| 24 | 1 | | | |
| | 2~13 | | | |
| | 14 | | | |
| | 15 | | | |

Similarly, Table 6.3 and 6.4 summarize the theoretical predictions of the interchain PCF h(r). We observe that TPT2 produces the smallest deviation in h(r) from Monte Carlo results for small segment number densities and r, whereas SC-PRISM with adjusted κ produces the smallest deviation for big ρ or r. On the other hand, SC-PRISM with $\kappa = 1$ produces the biggest deviation for small ρ and r, while TPT1 produces the largest deviation for large ρ or r. As an example, in Fig 6.3 (a) shows h(r) at N=24 and $\rho\sigma^3 = 0.6$ in the semi-logarithmic plot. We see that SC-PRISM with $\kappa = 1$ overestimates h(r), while TPT1 and TPT2 underestimate h(r) for r between 1.2σ and 3σ ; by adjusting κ , SC-PRISM gives overall the best agreement

with the Monte Carlo results.



Figure 6.2: The intra-chain pair correlation function, the deviation of that in each interval between four different methods at N=24 and $\rho\sigma^3 = 0.6$, and the bare solvation potential obtained from SC-PRISM calculations.

Part (a) shows the intra-chain pair correlation function $\omega(r)$ at N=24 and $\rho\sigma^3 = 0.6$ obtained from four different methods in the semi-logarithmic plots; the Monte Carlo simulations are shown in black, the self-consistent PRISM results with fixed κ adjusted are in blue, the selfconsistent PRISM results with fixed $\kappa = 1$ are in green, the TPT1 results are in pink and the TPT2 results are in red. Part (b) shows the deviation of $\omega(r)$ in each interval between four different methods and MC simulation results in the bar plot; the Monte Carlo simulations are shown in black, the self-consistent PRISM results with fixed κ adjusted are in blue, the selfconsistent PRISM results with fixed $\kappa = 1$ are in green, the TPT1 results are in pink and the TPT2 results are in red. Part (c) shows the bare solvation $\beta w_0(r)$ obtained from self-consistent PRISM calculations at different chain length and $\rho\sigma^3 = 0.6$ in the semi-logarithmic plots.

Table 6.3: Summary of best theory for h(r) in each interval based on the root mean square error between four different theories and MC simulation results.

| | | - | | |
|----|---------------|---------------|-----|-----|
| N | Intervals | $ ho\sigma^3$ | | |
| 14 | of r/σ | 0.1 | 0.4 | 0.6 |
| 3 | 1~2 | | | |
| | 3 | | | |
| 4 | 1 | | | |
| | 2 | | | |
| | 3 | | | |
| | 4~5 | | | |
| | 1 | | | |
| 8 | 2 | | | |
| | 3 | | | |
| | 4 | | | |
| | 5~7 | | | |
| | 1 | | | |
| 12 | 2~3 | | | |
| | 4 | | | |
| | 5 | | | |
| | 6~8 | | | |
| | 1 | | | |
| 24 | 2 | | | |
| | 3 | | | |
| | 4 | | | |
| | 5~8 | | | |
| | 9~10 | | | |
| | 11 | | | |

Best theory for h(r)

Table 6.4: Summary of worst theory for h(r) in each interval based on the root mean square error between four different theories and MC simulation results.

| The Opposite for $n(r)$ | | | | |
|-------------------------|---------------|---------------|-----|-----|
| Ν | Intervals | $ ho\sigma^3$ | | |
| | of r/σ | 0.1 | 0.4 | 0.6 |
| 3 | 1~2 | | | |
| | 3 | | | |
| 4 | 1 | | | |
| | 2 | | | |
| 4 | 3 | | | |
| | 4~5 | | | |
| | 1 | | | |
| | 2 | | | |
| 8 | 3 | | | |
| | 4 | | | |
| | 5~7 | | | |
| | 1 | | | |
| | 2 | | | |
| 12 | 3 | | | |
| 12 | 4 | | | |
| | 5 | | | |
| | 6~8 | | | |
| | 1 | | | |
| | 2 | | | |
| | 3 | | | |
| 24 | 4 | | | |
| | 5 | | | |
| | 6~8 | | | |
| | 9~10 | | | |
| | 11 | | | |

The Opposite for h(r)



Figure 6.3: The inter-chain pair correlation function, the deviation of that in each interval between four different methods at N=24 and $\rho\sigma^3 = 0.6$.

Part (a) shows the inter-chain pair correlation function h(r) at N=24 and $\rho\sigma^3 = 0.6$ obtained from several different methods in the semi-logarithmic plots; the Monte Carlo simulations are shown in black, the self-consistent PRISM results with fixed κ adjusted are in blue, the selfconsistent PRISM results with fixed $\kappa = 1$ are in green, the TPT1 results are in pink and the TPT2 results are in red. Part (b) shows the deviation of h(r) in each interval between four different methods and MC simulation results in the bar plot; the Monte Carlo simulations are shown in black, the self-consistent PRISM results with fixed κ adjusted are in blue, the selfconsistent PRISM results with fixed $\kappa = 1$ are in green, the TPT1 results are in pink and the TPT2 results are in red.

6.4 Summary

We performed SC-PRISM with $\kappa = 1$, SC-PRISM with κ adjusted, TPT1, TPT2 and Monte Carlo simulations for various chain lengths ($N_m=3\sim120$) and monomer number densities at $\rho\sigma^3$ (=0.1, 0.4 and 0.6), σ being the hard-sphere diameter, in order to find the best and worst theory for intra-chain pair correlation function $\omega(r)$ and inter-chain pair correlation h(r) based on the deviation between four different theories and MC results. The following figures are used to summary the information for Table 6.1, 6.2, 6.3 and 6.4.



Figure 6.4: The intra- and inter- chain pair correlation function, the deviation of those in each interval between four different methods, and the bare solvation potential obtained from SC-PRISM calculations at N=3 and $\rho\sigma^3 = 0.1$.

Parts (a) and (c) show the intra-chain and inter-chain pair correlation function $\omega(r)$ and h(r) at N=3 and $\rho\sigma^3 = 0.1$ obtained from several different methods; the Monte Carlo simulations are shown in black, the self-consistent PRISM results with κ adjusted are in blue, the self-consistent PRISM results with fixed $\kappa = 1$ are in green, the TPT1 results are in pink and the TPT2 results are in red. Parts (b) and (d) shows the deviation of $\omega(r)$ and h(r) in each interval between four different methods and MC simulation results in the bar plot; the Monte Carlo simulations are shown in black, the self-consistent PRISM results with fixed κ adjusted are in the bar plot interval between four different methods and MC simulation results in the bar plot; the Monte Carlo simulations are shown in black, the self-consistent PRISM results with fixed κ adjusted are in

blue, the self-consistent PRISM results with fixed $\kappa = 1$ are in green, the TPT1 results are in pink and the TPT2 results are in red. Part (c) shows the solvation potential represented by SC-PRISM with $\kappa = 1$, SC-PRISM with κ adjusted and SC-PRISM with κ normalized by κ adjusted.



Figure 6.5: Same with Fig 6.4, but at N=3 and $\rho\sigma^3 = 0.4$.



Figure 6.6: Same with Fig 6.5, but at *N*=3 and $\rho\sigma^3 = 0.6$.



Figure 6.7: Same with Fig 6.5, but at *N*=4 and $\rho\sigma^3 = 0.1$.



Figure 6.8 Same with Fig 6.7, but *N*=4 and $\rho\sigma^3 = 0.4$.



Figure 6.9: Same with Fig 6.8, but at N=4 and $\rho\sigma^3 = 0.6$.



Figure 6.10: Same with Fig 6.9, but at N=8 and $\rho\sigma^3 = 0.1$.



Figure 6.11: Same with Fig 6.10, but at N=8 and $\rho\sigma^3 = 0.4$.


Figure 6.12: Same with Fig 6.11, but at N=8 and $\rho\sigma^3 = 0.6$.



Figure 6.13: Same with Fig 6.12, but at N=12 and $\rho\sigma^3 = 0.1$.



Figure 6.14: Same with Fig 6.13, but at N=12 and $\rho\sigma^3 = 0.4$.



Figure 6.15: Same with Fig 6.14, but at N=12 and $\rho\sigma^3 = 0.6$.



Figure 6.16: Same with Fig 6.15, but at N=24 and $\rho\sigma^3 = 0.1$.



Figure 6.17: Same with Fig 6.16, but at N=24 and $\rho\sigma^3 = 0.4$.

Chapter 7 Structure-based Coarse Graining of Homopolymer Solutions using PRISM Theory: Designing the Implicit-Solvent Model from an Explicit-Solvent Model

7.1 Introduction

Implicit-solvent (IS) models are widely used in molecular simulations of solutions, with the advantage of dramatically saving the amount of computation and the hope of faithfully reproducing some properties of the corresponding explicit-solvent (ES) model. Strictly speaking, the latter can only be achieved when the effective interaction potentials in the IS model are derived from the ES model following some coarse-graining procedure to integrate out the degrees of freedom of the solvent molecules. In practice, however, such a procedure is rarely followed because (1) it makes the effective interaction potentials not pairwise additive and not transferable, and (2) it often requires molecular simulations^[16] of the ES model, which contradicts the purpose of coarse graining. It is therefore not surprising that in practice an IS model often gives qualitatively different results from its "corresponding" ES model.

In this work, we take a simple model system of homopolymer solutions as an example to examine the features of the effective pair potential between polymer segments in the IS model that is designed, using the well-developed polymer reference interaction site model (PRISM)^[15] theory, to reproduce the total pair correlation function (PCF) between polymer segments in the corresponding ES model. To assess the accuracy of the PRISM theory, we also quantitatively compare its predictions with Monte Carlo (MC) simulation^[16] results, both for the ES model. While performing MC simulations of the ES model contradicts the purpose of our structure-based coarse graining, it provides the needed input to the PRISM theory, thus allowing the most stringent test of the theory. This problem can further be avoided by using the self-consistent (SC) PRISM theory^[95] for the ES model, as proposed at the end of this work.

7.2 Models and Methods

7.2.1 PRISM Calculations

As our ES model, let us consider a solution of homopolymer P in an explicit solvent S. Each P chain has N segments (interaction sites), the number density of which is denoted by $\rho \equiv nN/V$ with n being the number of chains and V the system volume. Each S molecule has only one interaction site, the number density of which is denoted by $\rho_{\rm S} \equiv n_{\rm S}/V$ with $n_{\rm S}$ being the number of S molecules. The PRISM equations^[15] for this ES model are given by

$$\begin{cases} \hat{h} = \hat{h}_{\rm PP} = \frac{N^2 \hat{\omega}^2 \left[\hat{c}_{\rm PP} - \left(\hat{c}_{\rm PP} \hat{c}_{\rm SS} - \hat{c}_{\rm PS}^2 \right) \rho_{\rm S} \right]}{1 - N \hat{\omega} \hat{c}_{\rm PP} \rho - \hat{c}_{\rm SS} \rho_{\rm S} + N \hat{\omega} \left(\hat{c}_{\rm PP} \hat{c}_{\rm SS} - \hat{c}_{\rm PS}^2 \right) \rho \rho_{\rm S}} \\ \hat{h}_{\rm PS} = \frac{N \hat{\omega} \hat{c}_{\rm PS}}{1 - N \hat{\omega} \hat{c}_{\rm PP} \rho - \hat{c}_{\rm SS} \rho_{\rm S} + N \hat{\omega} \left(\hat{c}_{\rm PP} \hat{c}_{\rm SS} - \hat{c}_{\rm PS}^2 \right) \rho \rho_{\rm S}} \\ \hat{h}_{\rm SS} = \frac{\hat{c}_{\rm SS} - N \hat{\omega} \left(\hat{c}_{\rm PP} \hat{c}_{\rm SS} - \hat{c}_{\rm PS}^2 \right) \rho}{1 - N \hat{\omega} \hat{c}_{\rm PP} \rho - \hat{c}_{\rm SS} \rho_{\rm S} + N \hat{\omega} \left(\hat{c}_{\rm PP} \hat{c}_{\rm SS} - \hat{c}_{\rm PS}^2 \right) \rho \rho_{\rm S}} \end{cases},$$
(7.1)

where $h(r) \equiv h_{PP}(r)$, $h_{PS}(r)$, and $h_{SS}(r)$ are the intermolecular total PCF between P segments, between P segments and S molecules, and between S molecules, respectively; $c_{PP}(r)$, $c_{PS}(r)$, and $c_{SS}(r)$ are the intermolecular direct PCF between P segments, between P segments and S molecules, and between S molecules, respectively; and $\omega(r)$ is the normalized average intrachain PCF between P segments satisfying $4\pi \int_0^\infty dr r^2 \omega(r) = \sigma^3$ with σ denoting the length unit. For given ρ , ρ_S and $\omega(r)$, to solve the above intermolecular PCFs, we use the atomic Percus-Yevick (PY) ^[13]closure for the ES system given by

$$c_{\rm IJ}(r) = \left\{1 - \exp\left[\beta u_{\rm IJ}(r)\right]\right\} \left[h_{\rm IJ}(r) + 1\right] \text{ with IJ=PP, PS and SS,}$$
(7.2)

where $u_{PP}(r)$, $u_{PS}(r)$ and $u_{SS}(r)$ are the non-bonded pair potentials between P segments, between

P segments and S molecules, and between S molecules, respectively, specified below.

Eliminating all the S molecules in the above ES model, we obtain our IS model, for which the PRISM equation can be written as

$$\hat{c} = \frac{\hat{h}}{N\hat{\omega}\left(N\hat{\omega} + \rho\hat{h}\right)},\tag{7.3}$$

where c(r) is the interchain direct PCF between P segments in the IS model. Note that using the same $\hat{\omega}$ and \hat{h} in Eqs.(7.1) and (7.3) ensures that our IS model exactly reproduces (within our PRISM theory for coarse graining) both the chain conformations and interchain total PCF between polymer segments in the ES model; this is the key to our structure-based coarse graining using the PRISM theory. Finally, to obtain the coarse-grained (CG) or effective nonbonded pair potential v(r) between P segments in the IS model, we use either the PY closure written as

$$\beta v_{\rm PY}(r) = \ln(\gamma(r) + 1) - \ln(h(r) + 1), \qquad (7.4)$$

where $\gamma(r) \equiv h(r) - c(r)$ is the interchain indirect PCF between P segments in the IS model, or the hypernetted-chain (HNC)^[87] closure written as

$$\beta v_{\text{HNC}}(r) = \gamma(r) - \ln(h(r) + 1); \qquad (7.5)$$

since these two closures correspond to different approximations, they give different $\beta v(r)$.

For simplicity, in this work we take P polymers as tangent hard-sphere chains^[96] (THSCs) and S molecules as hard spheres (HSs)^[26] having the same diameter σ ; that is, $\beta u_{IJ}(\bar{r}) \rightarrow \infty$ for $\bar{r} \equiv r/\sigma < 1$ and 0 otherwise with IJ=PP, PS and SS. This also gives $\beta v_{PY}(\bar{r} < 1) \rightarrow \infty$ and $\beta v_{HNC}(\bar{r} < 1) \rightarrow \infty$, and makes Eqs. (7.4) and (7.5) applicable only to $r \ge \sigma$. To obtain the $\hat{\omega}$ needed as the input to Eqs. (7.1) and (7.3), we perform many-chain MC simulations of the ES model. The simulations also give \hat{h}_{IJ}^{MC} at discrete wavenumbers q_{MC} (due to the periodic boundary conditions applied to the simulation box), which are compared with \hat{h}_{IJ} obtained from our PRISM-PY calculations of the ES model to quantitatively assess the accuracy of the theory.

We take σ as the unit of length and uniformly discretize the real-space interval [0,1] into *m* subintervals each of length $\Delta \overline{r} \equiv 1/m$, and take $c_{IJ}(\overline{r_i} = i\Delta \overline{r})$ (*i*=0,...,*m* with $\overline{r_m} = 1^-$) as the independent variables to be solved. Our approach has three steps:

I. Given the initial guess of the independent variables and $c_{IJ}(\overline{r} \ge 1) = 0$ (given by Eq. (7.2),

we use continuous auxiliary functions $c_{IJ,0}(\overline{r}) \equiv \begin{cases} c_{IJ}(\overline{r}) - c_{IJ,1}\overline{r} & \text{if } \overline{r} \leq 1^- \\ c_{IJ}(\overline{r}) & \text{otherwise} \end{cases}$ with

$$c_{IJ,I} \equiv c_{IJ}(\overline{r} = 1^{-}) \qquad \text{to} \qquad \text{calculate}$$

 $\hat{c}_{\mathrm{II}}(q_j) = \left(4\pi/q_j\right) \left\{ \int_0^{r_c} \mathrm{d}\overline{r}\overline{r}c_{\mathrm{II},0}(\overline{r})\sin\left(q_j\overline{r}\right) + c_{\mathrm{II},1}\left[\left(2-q_j^2\right)\cos q_j + 2q_j\sin q_j - 2\right]/q_j^3 \right\} \qquad \text{for}$

j=1,...,M-1 with $M \equiv m\bar{r_c}$ via the fast sine transform (FST), the computing time of which is

 $O(M\ln M)$, use the Romberg integration to calculate $\hat{c}_{IJ}(q_0) = 4\pi \int_0^{1^-} d\overline{rr}^2 c_{IJ}(\overline{r})$, and also calculate $\hat{c}_{IJ}(q_c) = (4c_{IJ,1}/m) [(-1)^m (2-m^2\pi^2) - 2]/(m\pi)^3$; note that the numerical accuracy of $\hat{c}_{IJ}(q_j)$ (j=0,...,M) is determined only by m (i.e., $\Delta \overline{r}$), and that the FST gives $q_j = j\Delta q$ with $\Delta q = m\pi/M$ and $q_M = q_c = m\pi$.

II. We calculate the 3D Fourier transform of the interchain indirect PCFs $\hat{\gamma}_{IJ}(q_j) \equiv \hat{h}_{IJ}(q_j) - \hat{c}_{IJ}(q_j)$ with IJ=PP, PS and SS for *j*=0,...,*M*, where Eq. (7.1) is used to obtain

 $\hat{h}_{\text{U}}. \text{ We then use auxiliary functions } \hat{\gamma}_{\text{U},0}(q) = \hat{\gamma}_{\text{U}}(q) - \hat{\gamma}_{\text{U},c} \text{ with } \hat{\gamma}_{\text{U},c} = \hat{\gamma}_{\text{U}}(q_c) \text{ to calculate } \\ \gamma_{\text{U}}(\bar{r}_j) = \left(\frac{1}{2\pi^2 \bar{r}_j}\right) \left[\int_0^{q_c} \mathrm{d}q q \hat{\gamma}_{\text{U},0}(q) \sin\left(q\bar{r}_j\right) - (-1)^j m^2 \pi \hat{\gamma}_{\text{U},c}/j\right] \text{ for } j=1,...,M-1 \text{ via the FST } \\ \text{(note that } \gamma_{\text{U}}(\bar{r}_c) = -(-1)^j m^3 \hat{\gamma}_{\text{U},c}/2\pi M^2 \text{), calculate } \gamma_{\text{U}}(\bar{r}_0) = \left(\frac{1}{2\pi^2}\right) \int_0^{q_c} \mathrm{d}q q^2 \hat{\gamma}_{\text{U}}(q) \text{ via the } \\ \text{Romberg integration, and also calculate } \gamma_{\text{U}}(\bar{r}_c) = -(-1)^j m^3 \hat{\gamma}_{\text{U},c}/2\pi M^2 \text{ ; note that the numerical } \\ \text{accuracy of } \gamma_{\text{U}}(\bar{r}_j) (j=0,...,M) \text{ is determined by } both m (i.e., q_c) \text{ and } M (i.e., \Delta q). \text{ As shown in } \\ \text{our results below, } |\hat{\gamma}_{\text{U}}(q)| \text{ decays towards 0 much faster than } |\hat{h}_{\text{U}}(q)| \text{ and } |\hat{c}_{\text{U}}(q)| \text{ , thus } \\ \text{requiring a much smaller } q_c. \end{cases}$

III. We calculate $h_{IJ}(\overline{r_i}) = \gamma_{IJ}(\overline{r_i}) + c_{IJ}(\overline{r_i})$ with IJ=PP, PS and SS for *i*=0,...,*m*, then use the residual errors of the PY closures (*i.e.*, $h_{IJ}(\overline{r_i}) + 1$) to converge the 3(*m*+1) independent variables via the Anderson mixing.

Our approach of calculating $\beta v(r)$ for the IS model is as follows:

I. With the above converged $\hat{h}(q_j)$ for j=0,...,M, we calculate $\hat{\gamma}(q_j) \equiv \hat{h}(q_j) - \hat{c}(q_j)$, where Eq. (7.3) is used to obtain \hat{c} .

II. We use an auxiliary function $\hat{\gamma}_0(q) \equiv \hat{\gamma}(q) - \hat{\gamma}_c$ with $\hat{\gamma}_c \equiv \hat{\gamma}(q_c)$ to calculate $\gamma(\overline{r}_j) = (1/2\pi^2 \overline{r}_j) \Big[\int_0^{q_c} dq q \hat{\gamma}_0(q) \sin(q \overline{r}_j) - (-1)^j m^2 \pi \hat{\gamma}_c / j \Big]$ for j=1,...,M-1 via the FST, and also calculate $\gamma(\overline{r}_c) = -(-1)^j m^3 \hat{\gamma}_c / 2\pi M^2$.

III. With the above converged $\gamma_{PP}(\overline{r_j}) = h(\overline{r_j})$ for j=m,...,M, we calculate $\beta_{V_{PY}}(\overline{r_j})$ and $\beta_{V_{HNC}}(\overline{r_j})$ according to Eqs.(7.4) and (7.5), respectively.

7.2.2 MC Simulations

Our many-chain MC simulations^[16] of the ES model are performed in a canonical ensemble using a cubic simulation box with the periodic boundary conditions applied in all directions. Our trial moves include the random displacement of a randomly chosen S molecule (with the maximum displacement adjusted such that the average acceptance rate is about 50%), the random rotation of a randomly chosen P segment under the constraint of fixed bond length, and the reptation of a randomly chosen P chain under the constraint of fixed bond length. For trial moves of an S average acceptance rate is about 50%; for those of an end P segment for $N \ge 3$, when generating its trial position, we avoid its overlap with the third segment on the chain.

Finally, we estimate the error bars of our calculated quantities as three times their standard deviation, with the sample correlations accounted for using the correlation-function method.

7.3 Results and Discussion

For the ES model of THSCs in HSs, we fix the total site number density $\rho_t \equiv \rho + \rho_{\rm S} = 0.6/\sigma^3$, which is representative for liquid solutions. We vary the chain length *N* and the polymer volume fraction $\phi \equiv nN/(nN + n_{\rm S})$ in the solution, and in MC simulations choose the length of the simulation box *L* to be larger than $2R_e$ with R_e denoting the root-mean-square chain end-to-end distance obtained in the simulation.

7.3.1 Chain conformations obtained from MC Simulations

Figs. 7.1(a) and 7.1(b) show

$$\omega^*(\overline{r}) = (2/N^2) \sum_{i=2}^{N-1} (N-i)\omega_i(\overline{r}) = \omega(\overline{r}) - \delta(\overline{r})/N - 2(N-1)\delta(\overline{r}-1)/N^2$$
 (collected using a bin
size of $\delta \overline{r} = 1/32$), where $\omega_i(\overline{r})$ denotes the normalized PCF between segments separated by
i bonds along the same chain satisfying $4\pi \int_0^{\infty} d\overline{r}\overline{r}^2 \omega_i(\overline{r}) = 1$, and $\hat{\omega}(q)$ obtained in many-chain
MC simulations of the ES model for various N and ϕ ; note that for N=2, $\omega^*(\overline{r}) = 0$ and
 $\hat{\omega}(q) = (1 + \sin q/q)/2$ regardless of ϕ . $\omega^*(\overline{r} < 1) = 0$ and $\omega^*(\overline{r} > N - 1) = 0$ are due to the
THSC model, and the discontinuities of $\omega^*(\overline{r})$ at integer values of $\overline{r} = 2,...,N-2$ are due to its
summation of $\omega_i(\overline{r})$, each of which is continuous and takes positive values only for $1 \le \overline{r} \le i$
(and 0 otherwise). We see that $\omega^*(\overline{r})$ at small $\overline{r} \lesssim 3$ decreases with decreasing ϕ , indicating
chain expansion in the athermal HS solvent. This effect becomes more pronounced with

increasing *N*, as can also be seen in Fig. 1(c) showing $R_e^2 = 4\pi \int_0^\infty d\overline{rr}^4 \omega_{N-1}(\overline{r})$ for various *N* and ϕ . On the other hand, $\hat{\omega}(q)$ approaches 1/*N* at large *q* as expected, and the results for various ϕ nearly collapse. As aforementioned, $\hat{\omega}(q)$ is used as the input to our PRISM calculations.



Figure 7.1: The intrachain PCF between P segments at N=8 and N=24 with various ϕ and the corresponding mean-square chain end-to-end distance.

Semi-logarithmic plots of the intrachain PCF between P segments $\hat{\omega}^*(\bar{r})$ (collected using a bin size of $\delta \bar{r} = 1/32$) for the chain length (a) *N*=8 and (b) *N*=24 obtained in many-chain MC simulations of the ES model at various polymer volume fractions ϕ , where the inset shows a semi-logarithmic plot of the corresponding 3D Fourier transform $\hat{\omega}(q)$. Part (c) shows the semi-logarithmic plot of the corresponding mean-square chain end-to-end distance R_e^2 . See main text for details.

7.3.2 Intermolecular PCFs of the ES model

Figs. 7.2~7.4 compare $h_{IJ}(\bar{r})$ for IJ=PP, PS and SS, respectively, obtained from our PRISM-PY calculations and many-chain MC simulations of the ES model at various *N* and ϕ , note that we use the same bin size of $\delta \bar{r} = 1/32$ in PRISM-PY calculations (that is, after obtaining $h_{IJ}(\bar{r})$, we numerically calculate $h_{IJ}((j-1/2)\delta\bar{r}) = \int_{(j-1)\delta\bar{r}}^{j\delta\bar{r}} d\bar{r}\bar{r}^2 h_{IJ}(\bar{r}) / (j(j-1)+1/3)(\delta\bar{r})^3$ and plot it in the figures) as used in the MC simulations. We see that $h(\bar{r}) = h_{PP}(\bar{r})$ exhibits similar oscillations to those for HSs due to the segment packing, and decreases with decreasing ϕ in MC results (for *N*=2, this occurs for $\bar{r} \leq 2$); the latter is the well-known "correlation hole" effect caused by the chain connectivity, and becomes more pronounced at smaller \bar{r} with increasing *N*. In comparison, the PRISM-PY theory overestimates $h(\bar{r})$ at small \bar{r} and even gives its opposite trend with varying ϕ , which is a well-known problem of the PY closure^[13]; this problem becomes more

severe with decreasing ϕ and increasing N.



Figure 7.2: The intermolecular total PCF between P segments $h_{PP}(\overline{r})$ at different chain length and various ϕ .

The intermolecular total PCF between P segments $h(\overline{r}) = h_{PP}(\overline{r})$ obtained (using a bin size of $\delta \overline{r} = 1/32$) from our PRISM-PY calculations and many-chain MC simulations of the ES model at (a) N=2, (b) N=8 and (c) N=24 and various ϕ .

On the other hand, $h_{\rm PS}(\overline{r})$ and $h_{\rm SS}(\overline{r})$ also decrease with decreasing ϕ for $\overline{r} \lesssim 2$ in

MC results, and the PRISM-PY theory gives much better prediction for $h_{PS}(\overline{r})$ and $h_{SS}(\overline{r})$ than for $h(\overline{r})$, although it underestimates $h_{PS}(\overline{r})$ and overestimates $h_{SS}(\overline{r})$ for most $\overline{r} < 2$. We also note that the local maximum of $h_{SS}(\overline{r})$ around $\overline{r} = 2$ shifts to smaller \overline{r} and becomes larger with decreasing ϕ .



Figure 7.3: The intermolecular total PCF between a P segment and an S molecule $h_{PS}(\bar{r})$ segments at different chain length and various ϕ .

The intermolecular total PCF between a P segment and an S molecule $h_{PS}(\bar{r})$ obtained (using a bin size of $\delta \bar{r} = 1/32$) from our PRISM-PY calculations and many-chain MC simulations of the ES model at (a) N=2, (b) N=8 and (c) N=24 and various ϕ .

Figs. 7.9~7.11 in the Summary show the PRISM-PY predictions of $|h_{IJ}(\bar{r})|$ for IJ=PP,

PS and SS, respectively, for the ES model at various N and ϕ , where a bin is not used. Note that (1) the cusps in these semi-logarithmic plots indicates the roots (where $h_{IJ}(\bar{r})$ crosses 0), and (2) at large \bar{r} the local maxima of $|h_{IJ}(\bar{r})|$ exponentially decay towards 0. We see that the local extrema of $|h_{IJ}(\bar{r})|$, particularly those at large \bar{r} , decrease with increasing ϕ . In addition, while at small N and ϕ the roots of $h_{IJ}(\bar{r})$ are nearly evenly spaced, their spacing dramatically increases with increasing N and ϕ . These results are consistent with those shown in Figs. 7.2~7.4.



Figure 7.4: The intermolecular total PCF between S molecules $h_{SS}(\overline{r})$ at different chain length and various ϕ .

The intermolecular total PCF between S molecules $h_{SS}(\overline{r})$ obtained (using a bin size of $\delta \overline{r} = 1/32$) from our PRISM-PY calculations and many-chain MC simulations of the ES model at (a) N=2, (b) N=8 and (c) N=24 and various ϕ .

Fig. 7.5 shows the 3D Fourier transforms of all the intermolecular PCFs, $|\hat{h}_{IJ}(q)|$,

 $|\hat{c}_{IJ}(q)|$ and $|\hat{\gamma}_{IJ}(q)|$ with IJ=PP, PS and SS, for N=2 and ϕ =1/2. Note that (1) the cusps in these logarithmic plots indicates the roots (where $\hat{h}_{IJ}(q)$, $\hat{c}_{IJ}(q)$ or $\hat{\gamma}_{IJ}(q)$ crosses 0), and (2) at large q the local maxima of $|\hat{\gamma}_{PP}(q)|$ and $|\hat{\gamma}_{PS}(q)|$ decay towards 0 with q^{-3} and those of $|\hat{\gamma}_{SS}(q)|$ decay

towards 0 with q^{-4} , much faster than those of $|\hat{h}_{IJ}(q)|$ and $|\hat{c}_{IJ}(q)|$ decaying with q^{-2} , thus justifying the Step II of our numerical approach; these scalings are also consistent with our recent PRISM-PY results for the THSC model. The same scalings are found for other N>1 and ϕ (data not shown).



Figure 7.5: The 3D Fourier transforms of the intermolecular PCFs in the ES model. Logarithmic plots of the 3D Fourier transforms of the intermolecular PCFs in the ES model: (a) $|\hat{h}_{IJ}(q)|$, (b) $|\hat{c}_{IJ}(q)|$ and (c) $|\hat{\gamma}_{IJ}(q)|$ with IJ=PP, PS and SS, for N=2 and ϕ =1/2. The *k*-value gives the slope of the corresponding straight line.

7.3.3 Interchain PCFs and effective pair potential of the IS model

Fig. 7.6 shows $|\hat{c}|$ and $|\hat{\gamma}|$ for N=2 and $\phi=1/2$. We see that, consistent with Fig. 5 and

our recent PRISM-PY results for the THSC model^[26], at large q the local maxima of $\left|\hat{\gamma}(q)\right|$

decay towards 0 with q^{-3} , much faster than those of $|\hat{h}_{pp}(q)|$ and $|\hat{c}(q)|$ decaying with q^{-2} . The same scalings are found for other N>1 and ϕ (data not shown).



Figure 7.6: The 3D Fourier transforms of the intermolecular PCFs in the IS model for N=2 and $\phi = 1/2$.

Logarithmic plot of the 3D Fourier transforms of the intermolecular PCFs in the IS model for N=2 and $\phi=1/2$. The *k*-value gives the slope of the corresponding straight line.

Fig. 7.7(a) shows the effective non-bonded pair potentials between P segments $\beta_{V}(\bar{r})$ calculated from Eqs. (7.4) and (7.5) for N=2 and f=1/2. We see that both $\beta_{V_{\text{PY}}}(\bar{r})$ and $\beta_{V_{\text{HNC}}}(\bar{r})$ are attractive at small $\bar{r} \leq 1.5$ and decay towards 0 with increasing \bar{r} in an

exponentially damped oscillatory manner; compared to $\beta v_{PY}(\overline{r})$, $\beta v_{HNC}(\overline{r})$ is more negative at small \overline{r} and "shifts" to larger \overline{r} . We also see that $\beta v_{HNC}(\overline{r})$ exhibits a discontinuity in its first-order derivative at $\overline{r} = 2$, which is due to the same behavior of $h(\overline{r}) = h_{PP}(\overline{r})$ shown in Fig. 7.2(a). In fact, since $c'(\overline{r})$ is continuous at $\overline{r} = 2$, we find that both $\beta v'_{PY}(\overline{r}) = \left[c(\overline{r}) / (h(\overline{r}) - c(\overline{r}) + 1) (h(\overline{r}) + 1) \right] h'(\overline{r}) - c'(\overline{r}) / [h(\overline{r}) - c(\overline{r}) + 1]$ and

 $\beta v'_{\text{HNC}}(\overline{r}) = \left[h(\overline{r})/(h(\overline{r})+1)\right]h'(\overline{r}) - c'(\overline{r})$ are discontinuous at $\overline{r} = 2$; these are shown in Fig. 7.7(b), where we use a 6th-order accurate finite-difference formula^[50] to calculate the first-order

derivatives.



Figure 7.7: Effective non-bonded pair potential between P segments obtained from PY and HNC Closure and its first derivative.

(a) Effective non-bonded pair potential between P segments $\beta_{V}(\overline{r})$ obtained with the PY and HNC closures in the IS model for N=2 and $\phi=1/2$. (b) The first derivative of $\beta_{V}(\overline{r})$ obtained from PY and HNC closure. (c) $\beta_{V}(\overline{r})$ obtained from HNC closure at different chain length and various ϕ .

The inset of Fig. 7.7(a) shows $|\beta v(\bar{r})|$ on a semi-logarithmic plot; in addition to the exponential decay towards 0 of the extrema of $|\beta v(\bar{r})|$ with increasing \bar{r} , we also see that the location of these extrema and the roots of $\beta v(\bar{r})$ are nearly equally spaced. Fig. 7.8(a) shows that the first (*i.e.*, smallest) two roots of $\beta v_{PY}(\bar{r})$, denoted by $\bar{r}_{1,PY}$ and $\bar{r}_{2,PY}$, respectively, are nearly independent of *N* but increase with increasing ϕ ; similar results are found for other roots, as well as the location of the extrema (except the first extremum at $\bar{r} = 1$), of $\beta v_{PY}(\bar{r})$ (data

not shown).

From Eq. (7.4), it is evident that $\overline{r}_{i,PY}$ are also the roots of $c(\overline{r})$. Fig. 7.8(b) shows that the absolute value of the first three extrema of $\beta v_{PY}(\overline{r})$, denoted by $|\beta v_{i,PY}^*|$, increases with increasing *N* and decreasing ϕ ; similar results are found for other extrema of $\beta v_{PY}(\overline{r})$ (data not shown).While $\beta v_{PY}(\overline{r})$ shown in Fig. 7.7(a) is representative for other *N* and *f*, Fig. 7.7(c) shows that $\beta v_{HNC}(\overline{r})$ becomes more negative for $\overline{r} \lesssim 5$ with increasing *N* and for $2 \lesssim \overline{r} \lesssim 5$ with





Figure 7.8: The first and second roots and the absolute value of the first three extrema $|\beta v_{i,PY}^*|$ of $\beta v_{PY}(\bar{r})$ at different chain length and various ϕ .

(a) Semi-logarithmic plot of the first (*i.e.*, smallest) two roots $\overline{r}_{i,PY}$ (*i*=1,2) and (b) logarithmic plot of the absolute value of the first three extrema $|\beta v_{i,PY}^*|$ (*i*=1,2,3) of $\beta v_{PY}(\overline{r})$ vs. N at various ϕ .

7.4 Summary



Figure 7.9: Semi-logarithmic plots of the intermolecular total PCF between P segments $|h_{PP}(\bar{r})|$ obtained from our PRISM-PY calculations of the ES model. At (a) N=2, (b) N=8 and (c) N=24 and various ϕ .

In this work, we take a simple system of homopolymers in an explicit solvent (ES), modelled as *n* tangent hard-sphere chains (THSCs) each of *N* segments in n_S hard-sphere solvent molecules where all the polymer (P) segments and solvent (S) molecules have the same diameter *s*, as an example to examine the features of the effective pair potential between P segments in the implicit-solvent (IS) model obtained from the structure-based coarse graining using the well-developed polymer reference interaction site model (PRISM) theory^[15]. Our coarse-graining approach, given by Eqs. (7.1)~(7.5), ensures that the IS model exactly reproduces (within the accuracy of the PRISM theory) both the chain conformations and the interchain total pair correlation function (PCF) between P segments in the ES model. We fix the total number density of P segments and S molecules to $0.6/s^3$, which is representative for liquid solutions, and vary *N* and the polymer volume fraction $\phi \equiv nN/(nN + n_s)$ in the solution.



Figure 7.10: Semi-logarithmic plots of the intermolecular total PCF between a P segment and an S molecule $|h_{PS}(\bar{r})|$ obtained from our PRISM-PY calculations of the ES model.

We solve the ES model using the PRISM theory^[15] and the atomic Percus-Yevick (PY) closure^[13], with the intrachain PCF between P segments taken directly from our many-chain Monte Carlo (MC) simulations of the ES model. As expected, chains expand with decreasing f and this effect becomes more pronounced with increasing N. Due to the approximation of the PY closure, the PRISM-PY theory overestimates the interchain total PCF between P segments $h(\bar{r}) = h_{\rm PP}(\bar{r})$ at small $\bar{r} \equiv r/\sigma$ and even gives its opposite trend with varying f (which should decrease with decreasing f) compared to our MC results; this problem becomes more severe

with decreasing f and increasing N. The interchain total PCF between a P segment and an S molecule $h_{PS}(\bar{r})$ and that between S molecules $h_{SS}(\bar{r})$ also decrease with decreasing f for $\bar{r} \leq 2$; the PRISM-PY theory gives much better predictions for $h_{PS}(\bar{r})$ and $h_{SS}(\bar{r})$ than for $h(\bar{r})$,



Figure 7.11: Semi-logarithmic plots of the intermolecular total PCF between S molecules $|h_{SS}(\bar{r})|$ obtained from our PRISM-PY calculations of the ES model.

although it underestimates $h_{PS}(\bar{r})$ and overestimates $h_{SS}(\bar{r})$ for most \bar{r} . At large \bar{r} the local maxima of $|h_{IJ}(\bar{r})|$ (IJ=PP, PS and SS) exponentially decay towards 0. On the other hand, consistent with our recent PRISM-PY results for the THSC model[?], at large wavenumber q the local maxima of the 3D Fourier transforms of the intermolecular indirect PCFs $|\hat{\gamma}_{PP}(q)|$ and

 $|\hat{\gamma}_{PS}(q)|$ decay towards 0 with q^{-3} and those of $|\hat{\gamma}_{SS}(q)|$ decay with q^{-4} , much faster than those of $|\hat{h}_{IJ}(q)|$ and the 3D Fourier transforms of the intermolecular direct PCFs $|\hat{c}_{IJ}(q)|$ (with $\hat{c}_{IJ}(q) = \hat{h}_{IJ}(q) - \hat{\gamma}_{IJ}(q)$) decaying with q^{-2} .

For the IS model, at large q the local maxima of the 3D Fourier transform of the interchain indirect PCF between P segments $|\hat{\gamma}(q)|$ decay towards 0 with q^{-3} , much faster than those of the corresponding $|\hat{h}(q)|$ and $|\hat{c}(q)|$ decaying with q^{-2} . The effective non-bonded pair potentials between P segments $\beta v_{PY}(\bar{r})$ and $\beta v_{HNC}(\bar{r})$ are then obtained from the PY^[13] and the hypernetted-chain (HNC)^[87] closures, respectively, for the IS model. Both $\beta v_{PY}(\bar{r})$ and $\beta v_{HNC}(\bar{r})$ are attractive at small $\bar{r} \leq 1.5$, decay towards 0 with increasing \bar{r} in an

exponentially damped oscillatory manner, and exhibit a discontinuity in their first-order derivative at $\overline{r} = 2$ due to the same behavior of $h(\overline{r}) = h_{\rm PP}(\overline{r})$. Compared to $\beta v_{\rm PY}(\overline{r})$, $\beta v_{\rm HNC}(\overline{r})$ is more negative at small \overline{r} and "shifts" to larger \overline{r} . Both the local extrema of $|\beta v_{\rm PY}(\overline{r})|$ and its roots are nearly equally spaced; their locations are nearly independent of Nbut increase with increasing f (except the first extremum at $\overline{r} = 1$). On the other hand, $\beta v_{\rm HNC}(\overline{r})$ becomes more negative for $\overline{r} \leq 5$ with increasing N and for $2 \leq \overline{r} \leq 5$ with

decreasing f.

Finally, we note that, while performing MC simulations of the ES model contradicts the purpose of our structure-based coarse graining, it provides the needed input (i.e., the chain conformations in the ES model) to the PRISM theory, thus allowing the most stringent test of the theory. On the other hand, this problem can be avoided by using the self-consistent PRISM theory for the ES model; this will be explored in our further work.

Chapter 8 Concluding Remarks and Future Work

In this chapter, I briefly summarize what has been learned from this work and give some suggestions for future work on theoretical studies of polymers.

8.1. We have applied our recently proposed systematic and simulation-free strategy for the structure-based coarse graining of multicomponent polymeric systems to diblock copolymer (DBC) melts, where we use the well-developed polymer reference interaction site model (PRISM) theory, instead of the commonly used many-chain molecular simulations (MCMS), to obtain the structural and thermodynamic properties of both the original and coarsegrained (CG) systems, and to quantitatively examine how the effective non-bonded pair potentials between CG segments and the thermodynamic properties of CG systems vary with the coarse-graining level. We have proved that our strategy does not change the spinodal curve, regardless of the original model system, closures, and coarse-graining levels for the two blocks.

8.2. We have successfully developed a general algorithm to solve a class of coarsegrained models for polymer melts, including THSC, KG and DPD models, using well-known PRISM-PY theory, performed it to different chain length ($N = 2 \sim 120$) and various number density ($\rho\sigma^3 = 0.1 \sim 0.6$), to obtain PCFs and 3D Fourier Transform of those PCFs. Our method has faster decay in the direct correlation function $\hat{c}(q)$ than a recently developed 'pyPRISM', a Python-based open-source framework for PRISM calculations, we attribute this fast decay to our accounting discontinuities of $c(\bar{r})$ and its FFT. What's more, we also found that N = 1 case is a special case for THSC, KG and DPD models, since the indirect correlation function $\hat{\gamma}(q)$ for N = 1 decays fasters than $N \ge 2$ for all methods.

8.3. We have unambiguously quantified the fluctuation/correlation effects on the

the results from MC simulations, PRISM-PY theory, and GF theory. In general, GF theory works only at small N/κ and χN , and RISM-PY theory can give semi-quantitative predictions at larger N/κ and χN . At even larger χN (close to ODT), however, the ideal-chain conformations cannot be used in the RISM-PY theory, which does not give a spinodal point at finite chain number density. At larger N/κ (i.e., $N/\kappa = 50$), we need more future work to support our conclusions.

8.4. We have quantitatively compared the intra- and inter- chain correlation function of tangent hard-sphere chains at various chain length ($N = 2 \sim 120$) and number density $(\rho\sigma^3 = 0.1 \sim 0.6)$, obtained from many-chain Monte Carlo simulations, two SC-PRISM theories with κ either set to 1 or adjusted to match R_e^2 and two polymer DFTs, TPT1 and TPT2. We found that SC-PRISM overestimates R_e^2 , while TPT2 underestimates R_e^2 and slightly improves over TPT1. In general, SC with κ adjusted gives the smallest deviation in intra-chain correlation function from the Monte Carlo results, and TPT1 gives the largest deviation in intrachain correlation function from the Monte Carlo results. There are, however, exceptions caused by the strongly attractively bare solvation potential in SC-PRISM calculations, thus overestimation of intra-chain correlation function at small r. TPT2 gives the smallest deviation in inter-chain correlation function from the Monte Carlo results for small number density and r, and SC-PRISM with κ adjusted gives the smallest deviation at large number density or r. On the other hand, SC-PRISM with $\kappa = 1$ gives the largest deviation in inter-chain correlation function from the Monte Carlo results for small number density and r, and TPT1 gives the largest deviation in inter-chain correlation function from the Monte Carlo result at large number

density or *r*. We will continue working on the long chain length (i.e., N=60 and 120) to summary the relative best method for PCFs.

8.5. We have applied our systematic and simulation-free strategy to the structure-based coarse graining of the well-known Kremer-Grest model for homopolymer melts, where the well-developed Polymer Reference Interaction Site Model theory, instead of the commonly used many-chain molecular simulations, is used for both original and coarse-grained systems. Our self-consistent PRISM calculations well produce the chain conformations in the original system. With increasing chain length, the Percus-Yevick closure used for the original system causes small discrepancies in the interchain total pair correlation functions between monomers. We are currently working to improve the approximate relation employed in the previous structure-based coarse graining using the PRISM theory.

8.6. We have performed our PRISM-PY theory on a simple model system of homopolymer solution at different chain length N = 2, 8, 24, 60 and various $\phi = 0.1, 0.5, 0.9$. We directly compared the total pair correlation functions obtained from our method and manychain Monte Carlo simulations of the corresponding ES model. We found that the intra-chain correlation function $\omega(\bar{r})$ obtained from MC results at small $\bar{r} \leq 3$ decreases with decreasing

 ϕ , indicating chain expansion in the athermal HS solvent. $h_{PP}(\overline{r})$ decreases with decreasing ϕ in MC results (for N=2, this occurs for $\overline{r} \leq 2$) and becomes more pronounced at smaller \overline{r} with increasing N. In comparison, the PRISM-PY theory overestimates $h(\overline{r})$ at small \overline{r} and even gives its opposite trend with varying ϕ , which is a well-known problem of the PY closure; this problem becomes more severe with decreasing ϕ and increasing N. On the other hand, $h_{\rm PS}(\overline{r})$ and $h_{\rm SS}(\overline{r})$ also decrease with decreasing ϕ for $\overline{r} \leq 2$ in MC results, and the PRISM-

PY theory gives much better prediction for $h_{PS}(\overline{r})$ and $h_{SS}(\overline{r})$ than for $h(\overline{r})$, although it underestimates $h_{PS}(\overline{r})$ and overestimates $h_{SS}(\overline{r})$ for most $\overline{r} < 2$. We also note that the local maximum of $h_{SS}(\overline{r})$ around $\overline{r} = 2$ shifts to smaller \overline{r} and becomes larger. What's more, we examined the features of the effective pair potential between polymer segments in the IS model. We found that both $\beta v_{PY}(\overline{r})$ and $\beta v_{HNC}(\overline{r})$ are attractive at small $\overline{r} \leq 1.5$ and decay towards

0 with increasing \overline{r} in an oscillatory manner; also $\beta v_{\text{HNC}}(\overline{r})$ exhibits a discontinuity in its first-order derivative around $\overline{r} = 2$, which is due to the same behavior of $h(\overline{r}) = h_{\text{PP}}(\overline{r})$. In the future work, we consider to use SC-PRISM algorithm we have already developed in the Chapter 6 to reduce the simulation time of obtainnig $\hat{\omega}(q)$, since $\hat{\omega}(q)$ is input for PRISM-PY theory.

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