

Numerical Analysis of PRISM-PY Calculations for Hard- and Soft-Core Generic Polymer Models

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Abstract Generic polymer models capturing the chain connectivity and excluded-volume interactions between polymer segments can be classified, according to whether or not the 3D integral of the latter diverges, into hard- and soft-core models. Taking homogeneous systems of compressible homopolymer melts (or equivalently homopolymer solutions in an implicit, good solvent) in the continuum as an example, we recently compared the correlation effects on the structural and thermodynamic properties of the hard- and soft-core models given by the polymer reference interaction site model (PRISM) theory with the Percus-Yevick (PY) closure (*Polymers* **2023**, 15, 1180). Here we analyzed in detail the numerical errors and behavior of the interchain pair correlation functions (PCFs) given by the PRISM-PY calculations of these models using an efficient numerical approach that we proposed. Our numerical approach has the least number of independent variables to be iteratively solved, analytically treats the discontinuities caused by the non-bonded pair potential (such as that of the hard spheres) and takes only the inverse Fourier transform of the interchain indirect PCF between polymer segments (which is continuous and decays towards 0 with increasing wavenumber much faster than both the interchain direct and total PCFs), and is essential for us to accurately solve the PRISM-PY theory for chain length N as large as 10^6 . To capture the correlation-hole effect, the real-space cut-off in the PRISM calculations should be proportional to the square root of N .

Keywords Generic polymer models; Soft potentials; Polymer reference interaction site model theory

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INTRODUCTION

Generic polymer models are widely used in theoretical and simulation studies in the field of polymer physics as they capture two essential features of all polymers: chain connectivity and excluded-volume interactions. Unlike atomistic models that can represent specific polymers used in experiments, molecular simulations of generic models can reach much larger length and time scales, and theoretical studies of generic models can also be performed. The well-known Edwards model,^[1] for example, is a generic model commonly used in field-theoretic studies (including the widely applied polymer self-consistent field (SCF) theory) of compressible homopolymer melts (or equivalently homopolymer solutions in an implicit, good solvent), where the chain connectivity and excluded-volume interaction between polymer segments are described by the continuous Gaussian chain (CGC) model (here the number of segments on each chain $N \rightarrow \infty$ instead of any finite value such as 1000^[2]) and the Dirac δ -function repulsion with its strength controlled by a *finite* excluded-volume parameter (or the second virial coefficient) v . Depending on whether or not the complete overlapping of polymer segments is allowed, generic polymer models can be classified into soft- and hard-core models.^[3] The Edwards model is a

soft-core model (referred to as the SC CGC- δ model^[4] hereafter), and the corresponding hard-core model is the hard-core Gaussian thread model (referred to as the HC CGC- δ model^[4] hereafter) first studied by Schweizer and Curro,^[5] where $v \rightarrow \infty$ and thus the contact value of the (interchain) radial distribution function between polymer segments $g(r=0)=0$ (note that the ideal chain conformations were assumed in their study).

While these CGC- δ models cannot be used in molecular (*i.e.*, molecular dynamics and Monte Carlo) simulations^[6] and cause the ultraviolet divergence in field-theoretic simulation (FTS),^[7] other generic polymer models designed for such simulations have been used in the literature, including those based on the hard-sphere chain model in the continuum and the self- and mutual-avoiding walk models on a lattice, the Kremer-Grest model,^[8] as well as those used in the dissipative particle dynamics (DPD) simulation,^[9] fast Monte Carlo simulations,^[10–14] FTS,^[15] variants of FTS (under the partial saddle-point approximation),^[16] single-chain-in-mean-field simulation^[17] and hybrid particle field molecular dynamics simulation^[18] (both under the quasi-instantaneous field approximation^[17]). As shown in our recent study,^[3] for compressible homopolymer melts in the continuum with the excluded-volume interaction between polymer segments described by a dimensionless short-range and isotropic pair potential $\beta u^{nb}(r)$, where $\beta \equiv 1/k_B T$ with k_B being the Boltzmann constant and T the thermodynamic temperature of the system, the hard- and soft-core models can be classified according to whether or

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not $\int d\mathbf{r} \beta u^{\text{nb}}(|\mathbf{r}|)$ diverges; the SCF theory can only be applied to soft-core models, where one can define the dimensionless excluded-volume parameter $\varepsilon > 0$ via $u^{\text{nb}}(r) = \varepsilon u_0(r)$ with the normalized pair potential $u_0(r)$ satisfying $\int d\mathbf{r} \beta u_0(|\mathbf{r}|) = \sigma^3$ and σ denoting the unit of length (e.g., the range of $u^{\text{nb}}(r)$). In the limit of the number of chains $n \rightarrow \infty$, in order for the SCF theory to give finite dimensionless non-bonded interaction energy per chain $\beta U^{\text{nb}}/n$, $\varepsilon \propto \rho^{-1}$ is also needed with $\rho \equiv nN/V$ being the average segment number density and V the system volume; this is seen by writing for a **homogeneous** system under the commonly used pairwise additivity $\beta U^{\text{nb}} = \sum_{i < j} \beta u^{\text{nb}}(|\mathbf{r}_i - \mathbf{r}_j|) = (\rho^2/2) \int d\mathbf{r} d\mathbf{r}' \phi(\mathbf{r}) \beta u^{\text{nb}}(|\mathbf{r} - \mathbf{r}'|) \phi(\mathbf{r}') - (nN/2) \beta u^{\text{nb}}(0) = (nN\rho/2) \int d\mathbf{r} \beta u^{\text{nb}}(|\mathbf{r}|) - (nN/2) \beta u^{\text{nb}}(0) = nN\varepsilon \rho \sigma^3/2 - (nN/2) \beta u^{\text{nb}}(0)$, where $\mathbf{r}_i$ denotes the spatial position of the i th segment in the system, $\phi(\mathbf{r}) \equiv \sum_{i=1}^{nN} \delta(\mathbf{r} - \mathbf{r}_i)/\rho = 1$ is the segment volume fraction at $\mathbf{r}$, and the last term deducting the self-interaction of segments gives an unimportant constant. With $\varepsilon \propto \rho^{-1}$, the mean-field approximation inherent in the SCF theory^[19] becomes exact in the above limit, where there are neither fluctuations (which are due to the presence of different energy levels) nor correlations (which are due to the non-zero excluded-volume interaction) in the system; this point was not made as clear as we would like in our recent study.^[3]

Given the wide use of hard- and soft-core generic polymer models, the purpose of our study has two folds: On the one hand, we compare the correlation effects on the structural and thermodynamic properties of hard- and soft-core generic models; except our previous work on the CGC- δ models,^[4] this has not been reported in the literature. For this we choose the polymer reference interaction site model (PRISM) theory proposed by Schweizer and Curro,^[20] which can be considered as the most successful molecular-level theory to date for studying correlations in homogeneous polymeric systems. On the other hand, we examine the numerical calculations of the PRISM theory. Comparing the PRISM theory with the SCF theory, which can be considered as the most successful molecular-level theory for inhomogeneous polymeric systems (e.g., the self-assembled block copolymers) and has been applied to a wide variety of systems partly due to its well-developed numerical calculations,^[21–29] we note that few studies on the numerical calculations of the PRISM theory have been reported,^[30–33] which significantly hinders its application.

As our first step to address the above issues, we limit our study to the PRISM theory with the commonly used Percus-Yevick (PY) closure,^[34] which works well for a simple but important class of generic models for the aforementioned homopolymer melts. With the correlation effects on the structural and thermodynamic properties of two commonly used (one hard- and one soft-core) generic models in this class reported in our recent study,^[3] here we focus on the numerical analysis of the PRISM-PY calculations of these models. We first introduce the PRISM-PY theory and the two generic polymer models in Section **PRISM-PY Theory and Two Generic Polymer Models** below, then show that all previously reported numerical procedures for the PRISM-PY calculations are not

optimal and propose an efficient numerical approach for this class of generic models in Section **Numerical calculations of PRISM-PY theory**. Our numerical results are presented in Section **RESULTS AND DISCUSSION**, and our findings are summarized in Section **CONCLUSIONS**.

MODELS AND METHODS

PRISM-PY Theory and Two Generic Polymer Models

For a model system of n homopolymer chains each having N segments (i.e., interaction sites) in volume V , the PRISM equation is given by

$$\hat{h} = N\hat{\omega}c(N\hat{\omega} + \bar{\rho}\hat{h}) \quad (1)$$

where $h(\bar{r})$ is the interchain total pair correlation function (PCF) between polymer segments with $\bar{r} \equiv r/\sigma$ and σ the segment diameter (i.e., range of the purely repulsive non-bonded pair potential $\beta u^{\text{nb}}(r)$ between polymer segments), $\omega(\bar{r})$ is the normalized (i.e., $4\pi \int_0^\infty d\bar{r} \bar{r}^2 \omega(\bar{r}) = 1$) intrachain PCF, $c(\bar{r})$ is the interchain direct PCF, $\hat{f} \equiv (4\pi/q) \int_0^\infty d\bar{r} \bar{r} f(\bar{r}) \sin(q\bar{r})$ denotes the 3D Fourier transform of a radial function $f(\bar{r})$ with q being the wavenumber (in units of $1/\sigma$), and $\bar{\rho} \equiv nN\sigma^3/V$ is the dimensionless average 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.^[35] For given N , $\bar{\rho}$ and ω , to solve for both h and c , a closure providing an approximate relation between them is needed; here we take the commonly used atomic Percus-Yevick (PY) closure:^[34]

$$c(\bar{r}) = [1 - \exp(\beta u^{\text{nb}}(\bar{r}))](1 + h(\bar{r})) \quad (2)$$

which works well for our class of generic models where $\beta u^{\text{nb}}(\bar{r})$ is short-range and purely repulsive.

Analytical solution to the above PRISM-PY theory for polymers can be obtained only for the idealized Gaussian thread (CGC- δ) model, i.e., a (compressible) system of continuous Gaussian chains (CGCs, 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 $R_{e,0} = \sqrt{N-1}l$) interacting with the Dirac δ -function non-bonded pair potential (i.e., $\beta u^{\text{nb}}(r) \propto \delta(r)$), under the Padé approximation for the chain conformations (i.e., $\hat{\omega} = 1/(1+q^2/12)$ with q here in units of $1/R_{e,0}$).^[4,5] For example, such analytical solutions for both the hard- and soft-core CGC- δ models (the latter is equivalent to the Edwards model^[11]) are given in Appendix B of our previous work,^[4] although the main purpose of that work was to propose a systematic and simulation-free strategy for coarse graining of homopolymer melts.

In this work, we consider two other commonly used generic polymer models, for which the PRISM-PY theory must be solved numerically: the tangent hard-sphere chain (THSC) and the dissipative particle dynamics chain (DPDC) models; the former is a hard-core model that uses $\exp(-\beta u^{\text{b}}(\bar{r})) = \delta(\bar{r}-1)/4\pi$ with $\beta u^{\text{b}}(\bar{r})$ specifying the dimensionless bonded potential between two adjacent segments on the same chain and the hard-sphere (HS) potential $\beta u^{\text{HS}}(\bar{r}) \rightarrow \infty$ for $\bar{r} < 1$ and 0 otherwise as $\beta u^{\text{nb}}(\bar{r})$, and the latter is a soft-core model that uses $\beta u^{\text{b}}(\bar{r}) = 2\bar{r}^2$ and the DPD potential $\beta u^{\text{DPD}}(\bar{r}) = (a/2)$

$(1 - \bar{r})^2$ for $\bar{r} < 1$ and 0 otherwise as $\beta u^{\text{nb}}(\bar{r})$ with the dimensionless interaction parameters $a = A/\bar{\rho}$ and $A=75$ (used hereafter unless specified otherwise) to mimic the compressibility of water;^[9] note that $a=15\epsilon/\pi$ with ϵ defined in **INTRODUCTION**. In the thermodynamic limit, the structural and thermodynamic properties of these two models are therefore controlled only by N and $\bar{\rho}$; molecular simulations of the DPDC model typically use $\bar{\rho} = 3$ or 5. In our recent study,^[3] the DPDC model was simply referred to as the DPD model.

Finally, we note that $\hat{\omega}$ is needed as an input for the PRISM calculations. While in general the chain conformations characterized by $\hat{\omega}$ depend on $\bar{\rho}$, for simplicity here we use the ideal-chain conformations by setting $\hat{\omega}$ to $\hat{\omega}_{\text{id}} = [N - \tilde{B}(q)](2 + N\tilde{B}(q) - 2\tilde{B}(q)^N)/N^2(1 - \tilde{B}(q))^2$ with $\tilde{B}(q) \equiv \int d\bar{r} \exp(i\mathbf{q} \cdot \bar{\mathbf{r}}) \exp(-\beta u^{\text{b}}(|\bar{\mathbf{r}}|)) / \int d\bar{r} \exp(-\beta u^{\text{b}}(|\bar{\mathbf{r}}|)) = \text{sinc } q/q$ for the THSC model and $\exp(-q^2/8)$ for the DPDC model, where $\mathbf{q}$ is the wavevector for the 3D Fourier transform in the numerator with $q=|\mathbf{q}|$; note that $\hat{\omega}_{\text{id}}$ is exact for the THSC model at $N=2$.

Numerical Calculations of PRISM-PY Theory

In the early PRISM-PY calculations (where the repulsive part of $\beta u^{\text{nb}}(\bar{r})$ was $\beta u^{\text{HS}}(\bar{r})$), a variational method^[30] was used, where $c(0 \leq \bar{r} \leq 1^-)$ is taken as a cubic polynomial of $\bar{r}$ with its four coefficients solved numerically. While for HSs (*i.e.*, $N=1$) this approach gives the exact solution to the OZ-PY theory,^[36] for $N \geq 2$ it is difficult to justify the ansatz of $c(0 \leq \bar{r} \leq 1^-)$ being a cubic polynomial. 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 (1) introduce cut-offs and uniformly discretize these domains, (2) use the fast Fourier transform (FFT) and the inverse Fourier transform (iFT), which for radial functions are equivalent to the discrete sine transform of type I (DST),^[37] to switch between these domains, and (3) solve the PRISM-PY theory using an iterative method.

In 1992, Yethiraj and Schweizer proposed to use the Picard iteration (also known as the simple mixing, SM) in the PRISM calculations, where values of the interchain indirect PCF between polymer segments $\gamma(\bar{r}) \equiv h(\bar{r}) - c(\bar{r})$ at discretized positions in the real space are taken as the independent variables to be solved; with an initial guess $\gamma^{(0)}(\bar{r})$, they (I) calculated $c(\bar{r})$ from the closure and then $\hat{c}$ via the FFT, (II) calculated $\hat{\gamma} = [N^2 \hat{\omega}^2 / (1 - N\bar{\rho} \hat{\omega} \hat{c}) - 1] \hat{c}$ (obtained from Eq. 1) and then $\gamma(\bar{r})$ via the iFT, and (III) calculated $\gamma^{(1)}(\bar{r}) = \lambda \gamma(\bar{r}) + (1 - \lambda) \gamma^{(0)}(\bar{r})$ for the next iteration, where λ is a fixed parameter used in the SM to control its convergence.^[31] A similar method was proposed by Talitskikh and Khalatur (albeit for the RISM calculations), who used $Y(\bar{r}) \equiv \bar{r} \gamma(\bar{r})$ and $C(\bar{r}) \equiv \bar{r} c(\bar{r})$ instead of $\gamma(\bar{r})$ and $c(\bar{r})$ (thus $\hat{Y}$ and $\hat{C}$ instead of $\hat{\gamma}$ and $\hat{c}$), in Step (II) calculated $\hat{\gamma}^{(0)}$ via the FFT and $\hat{h}$ via Eq. (1), and in Step (III) calculated $\hat{\gamma}^{(1)} = \lambda \hat{\gamma} + (1 - \lambda) \hat{\gamma}^{(0)}$ and then $\gamma^{(1)}(\bar{r})$ via the iFT for the next iteration (note that when the root-mean-square difference between $\gamma^{(0)}(\bar{r})$ and $\gamma^{(1)}(\bar{r})$ increases during the iteration, they varied $\lambda \in [0, 1]$ to minimize this difference; their iteration method is therefore not the SM).^[32] Another similar method was used by Heine *et al.*, who in Step (II) calculated

$\hat{h} = N^2 \hat{\omega}^2 \hat{c} / (1 - N\bar{\rho} \hat{\omega} \hat{c})$ (instead of $\hat{\gamma}$) from Eq. (1), then $h(\bar{r})$ via the iFT, and $\gamma(\bar{r}) = h(\bar{r}) - c(\bar{r})$.^[33] Their method is implemented in the recently developed pyPRISM,^[38] a Python-based open-source framework for the PRISM calculations, with a Newton-Krylov based iteration (instead of the SM) used by default in Step (III).

For the THSC and DPDC models considered here, the PY closure gives

$$c(\bar{r} \geq 1) = 0 \quad (3)$$

with uniform discretization of the real space, solving $c(0 \leq \bar{r} < 1)$ therefore gives the least number of independent variables (*i.e.*, $\bar{r}_c$ times less than solving $\gamma(0 \leq \bar{r} \leq \bar{r}_c)$, where $\bar{r}_c \gg 1$ denotes the real-space cut-off). Furthermore, when $\beta u^{\text{HS}}(\bar{r})$ is used, both $h(\bar{r})$ and $c(\bar{r})$ are discontinuous, in both their value and their 1st-order derivative, at $\bar{r} = 1$; taking their FFT or iFT without accounting for these discontinuities therefore leads to very slow convergence (thus much finer spatial discretization) as shown in Fig. 1(b) below. In contrast, $\gamma(\bar{r})$ is continuous, and $\hat{\gamma}$ decays to 0 much faster than both $\hat{h}$ and $\hat{c}$ (as shown by our numerical results below); it is therefore preferred to take the iFT of $\hat{\gamma}$, which reduces the cut-off q_c 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 $\bar{r}_c$ (which takes an integer value) and q_c such that $\int_0^\infty d\bar{r} f(\bar{r}) \approx \int_0^{\bar{r}_c} d\bar{r} f(\bar{r})$ and $\int_0^\infty dq f(q) \approx \int_0^{q_c} dq f(q)$; 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 $\bar{r}$ (q) determines the value of $\bar{r}_c$ (q_c). We therefore propose an efficient numerical approach^[3] for the PRISM-PY calculations as described in detail below.

We uniformly discretize the real-space interval $[0, 1]$ into m (thus $[0, \bar{r}_c]$ into $M \equiv m\bar{r}_c$) subintervals each of length $\Delta\bar{r} \equiv 1/m$. For the DPDC model we take $c(\bar{r}_i \equiv i\Delta\bar{r})$ ($i=0, \dots, m-1$) as the independent variables to be solved, and our approach has three steps:

I. Given the initial guess of the independent variables, with Eq. (3) we calculate $\hat{c}(q_j \equiv j\Delta q) = (4\pi/q_j) \int_0^{\bar{r}_c} d\bar{r} c(\bar{r}) \sin(q_j \bar{r})$ ($j=1, \dots, M-1$) via the DST, which has the computational complexity of $O(M \ln M)$ and gives $\Delta q = m\pi/M$, $q_c = q_M = m\pi$ and $\hat{c}(q_c) = 0$. We also calculate $\hat{c}_0 \equiv \hat{c}(q_0) = 4\pi \int_0^1 d\bar{r} \bar{r}^2 c(\bar{r})$ via the Romberg integration (RI).^[39]

II. We calculate $\hat{\gamma}(q_j) = [N^2 \hat{\omega}^2(q_j) / (1 - N\bar{\rho} \hat{\omega}(q_j) \hat{c}(q_j)) - 1] \hat{c}(q_j)$ ($j=0, \dots, M$; note that $\hat{\gamma}(q_c) = 0$), then $\gamma(\bar{r}_j) = (1/2\pi^2 \bar{r}_j) \int_0^{q_c} dq q \hat{\gamma}(q) \sin(q \bar{r}_j)$ ($j=1, \dots, M-1$) via the DST (which gives $\gamma(\bar{r}_c) = 0$) and $\gamma_0 \equiv \gamma(\bar{r}_0) = (1/2\pi^2) \int_0^{q_c} dq q^2 \hat{\gamma}(q)$ via the RI.

III. We calculate $h(\bar{r}_i) = \gamma(\bar{r}_i) + c(\bar{r}_i)$ ($i=0, \dots, m-1$), then use the residual errors of Eq. (2) to converge the m independent variables via the Anderson mixing (AM),^[27] which has the computational complexity of $O(m)$ and can quickly converge

a set of nonlinear equations to a high accuracy even when m is on the order of 10^6 .

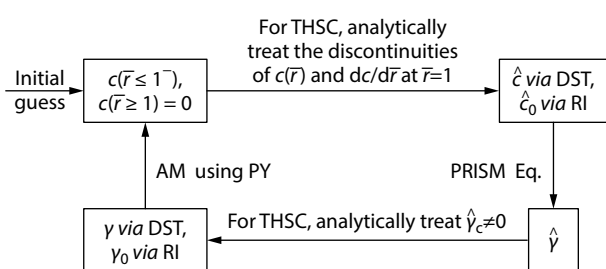
For the THSC model, due to the discontinuities in both $c(\bar{r})$ and its 1st-order derivative at $\bar{r} = 1$, we take $c(\bar{r}_i)$ ($i=0, \dots, m$ with $\bar{r}_m = 1^-$) as the independent variables and make the following changes to the above steps:

I. Here we use an auxiliary function $\tilde{c}(\bar{r}) \equiv c(\bar{r}) - c_1 - c'_1(\bar{r} - 1)$ for $\bar{r} \leq 1^-$ and $c(\bar{r})$ otherwise with $c_1 \equiv c(\bar{r} = 1^-)$ and $c'_1 \equiv (dc/d\bar{r})(\bar{r} = 1^-)$, which is continuous in both its value and 1st-order derivative, to calculate $\hat{c}(q_j) = (4\pi/q_j) \left(\int_0^{\bar{r}_c} d\bar{r} \tilde{c}(\bar{r}) \sin(q_j \bar{r}) + \{c_1 (\sin q_j - q_j \cos q_j) + c'_1 [2(\cos q_j - 1)/q_j + \sin q_j]\}/q_j^2 \right)$ ($j=1, \dots, M$) via the DST; note that we calculate c'_1 via the fourth-order backward finite-difference formula^[40] (which gives the exact c'_1 , apart from the round-off error, when $c(0 \leq \bar{r} < 1)$ is a polynomial of up to the fourth order in $\bar{r}$) unless specified otherwise, and that $\hat{c}(q_c) = [8((-1)^m - 1)c'_1 - 4(-1)^m \pi^2 m^2 c_1]/\pi^3 m^4$ (which gives $\hat{\gamma}_c \equiv \hat{\gamma}(q_c) \neq 0$, thus our change to Step II below). We also calculate $\hat{c}_0 = 4\pi \int_0^1 d\bar{r} \tilde{c}(\bar{r})$ via the RI.

II. Here, we use another auxiliary function $\tilde{\gamma}(q) \equiv \hat{\gamma}(q) - \hat{\gamma}_c$ to calculate $\gamma(\bar{r}_j) = (1/2\pi^2 \bar{r}_j) \left[\int_0^{q_c} dq q \tilde{\gamma}(q) \sin(q \bar{r}_j) - (-1)^j \pi m^2 \hat{\gamma}_c / j \right]$ ($j=1, \dots, M$) via the DST, which gives $\gamma(\bar{r}_c) = -(-1)^j m^3 \hat{\gamma}_c / 2\pi m^2$.

III. Here we take $i=0, \dots, m$, and note that Eq. (2) gives $h(\bar{r}_i) = -1$.

As summarized in Flowchart 1, our proposed numerical approach has the least number of independent variables to be iteratively solved, greatly reduces m (thus M) both by analytically treating the discontinuities in the THSC model and by taking only the iFT of $\tilde{\gamma}$ (which decays towards 0 with increasing q much faster than both $\hat{c}$ and $\hat{h}$), and is essential for us to accurately solve the PRISM-PY theory for N as large as 10^6 (where for the THSC model M is about 8.2×10^6). To the best of our knowledge, analytically treating the discontinuities caused by the HS potential has not even been reported in numerical calculations of the widely studied OZ equation.^[35]



Flowchart 1 Summary of our proposed approach for solving the PRISM-PY theory.

RESULTS AND DISCUSSION

The Hard-sphere (HS) Model

For the HS model (*i.e.*, the THSC model with $N=1$), the PRISM theory reduces to the OZ theory.^[35] with the PY closure, it has the analytical result^[36] of $c^*(\bar{r}) \equiv c(\bar{r}; m \rightarrow \infty, \bar{r}_c \rightarrow \infty) = -(2(1+2\eta)^2 - 3\eta(2+\eta)^2 \bar{r} + \eta(1+2\eta)^2 \bar{r}^3)/2(1-\eta)^4$ for $0 \leq \bar{r} < 1$ with the HS packing fraction $\eta \equiv \pi \bar{\rho}/6$, from which its 3D

Fourier transform $\hat{c}^*$ can be obtained analytically (for example, $\hat{c}_0^* \equiv \hat{c}_0(m \rightarrow \infty, \bar{r}_c \rightarrow \infty) = -\pi(4-\eta)(2+\eta^2)/6(1-\eta)^4$). Due to both the real- and reciprocal-space discretization used in numerical calculations, however, iteration is still needed to solve the OZ-PY theory even when $c^*(\bar{r})$ is used as the initial guess. In

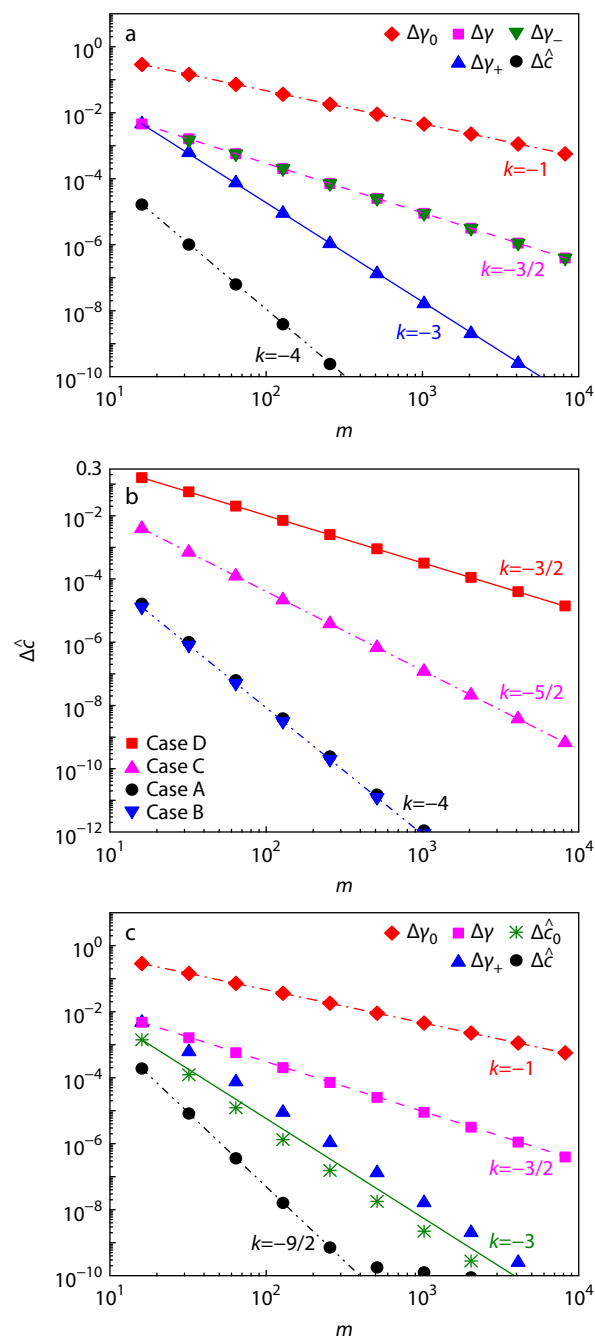


Fig. 1 Logarithmic plots of (a) various numerical errors in Case A and (b) $\Delta\hat{c}$ in various Cases due to the FFT of the analytical result of the direct PCF $c^*(\bar{r})$ and the iFT of that of the indirect PCF $\tilde{\gamma}^*$, as well as (c) various numerical errors in Case A after the AM iteration converges, versus the real-space discretization parameter m for the HS model at the dimensionless average segment (particle) number density $\bar{\rho} = 0.6$. The real-space cut-off $\bar{r}_c = 25$, and the k -value gives the slope of the corresponding straight line.

particular, Fig. 1(a) shows that the numerical error $\Delta\hat{c} \equiv \sqrt{\sum_{j=1}^M (\hat{c}(q_j; m) - \hat{c}^*(q_j))^2} / M$ with $\hat{c}(q_j; m)$ being the FFT of $c^*(\bar{r})$ decays towards 0 at a rate of m^{-4} , where we set c'_1 to the analytical value of $(dc^*/d\bar{r})(\bar{r} = 1^-)$. We attribute this fast decay to the use of $\tilde{c}(\bar{r})$, which is continuous in both its value and the 1st-order derivative at $\bar{r} = 1$, in our calculation of the FFT of $c^*(\bar{r})$ (referred to as Case A). Fig. 1(b) shows that $\Delta\hat{c}$ decays at a rate of $m^{-3/2}$ and $m^{-5/2}$, respectively, when both c_1 and c'_1 are set to 0 (that is, the FFT of $c^*(\bar{r})$ is directly calculated despite the discontinuities of $c^*(\bar{r})$ at $\bar{r} = 1$, referred to as Case D) and when c'_1 is set to 0 (that is, $\tilde{c}(\bar{r})$ is continuous only in its value at $\bar{r} = 1$, referred to as Case C). One could also use $\tilde{c}(\bar{r}) \equiv c(\bar{r}) - c_1 - c'_1(\bar{r} - 1) - c''_1(\bar{r} - 1)^2/2$ for $\bar{r} \leq 1^-$ and $c(\bar{r})$ otherwise with $c'_1 \equiv (d^2c/d\bar{r}^2)(\bar{r} = 1^-)$ set to its analytical value, which is continuous up to the 2nd-order derivative, when calculating the FFT of $c^*(\bar{r})$ (referred to as Case B). Fig. 1(b) further shows that, while $\Delta\hat{c}$ in this case is slightly smaller than in Case A, it decays at the same rate of m^{-4} , thus justifying the Step I of our proposed numerical approach. Table 1 summarizes these four cases. We also note that $\hat{c}_0(m)$ calculated via the RI, which requires m being an integer multiple of 16, is exact; that is, $\Delta\hat{c}_0 \equiv |\hat{c}_0(m) - \hat{c}_0^*|$ is on the order of the double-precision (relative) accuracy of 10^{-15} because $c^*(\bar{r})$ is a cubic polynomial of $\bar{r}$.

On the other hand, convergence of the iFT of $\hat{y}^* = \bar{\rho}\hat{c}^2/(1 - \bar{\rho}\hat{c}^*)$ to its analytical result of $y^*(\bar{r}) = -1 - c^*(\bar{r})$ for $0 \leq \bar{r} < 1$ is more complicated. Fig. 1(a) shows that $\Delta y_0 \equiv |\gamma_0(m) - \gamma_0^*|$, $\Delta y \equiv \sqrt{\sum_{i=1}^m (\gamma(\bar{r}_i; m) - \gamma^*(\bar{r}_i))^2} / m$, $\Delta y_- \equiv \sqrt{\sum_{i=1}^{\bar{r}_+ m-1} (\gamma(\bar{r}_i; m) - \gamma^*(\bar{r}_i))^2} / m$ and $\Delta y_+ \equiv \sqrt{\sum_{i=\bar{r}_+ m}^m (\gamma(\bar{r}_i; m) - \gamma^*(\bar{r}_i))^2} / m = \sqrt{(\Delta y)^2 - (\Delta y_-)^2}$ with $\bar{r}_+ \equiv i_+/m = 1/16$ decay at a rate of m^{-1} , $m^{-3/2}$, $m^{-3/2}$ and m^{-3} , respectively; we also find that both Δy_+ and $\Delta y_1(\bar{r}_+) \equiv |\gamma(\bar{r}_+; m) - \gamma^*(\bar{r}_+)|$ with fixed $\bar{r}_+$ (i.e., independent of m) for any integer $i_+ \in [1, m]$ decay at a rate of m^{-3} (data not shown).

We attribute the slow convergence of $\gamma_0(m)$ calculated via the RI to the highly oscillatory behavior of $\hat{c}^*$ (thus $\hat{y}^*$) as shown in Fig. 2(a), and Fig. 2(b) further shows that the spacing between adjacent roots (where $\hat{c}^* = 0$) and that between adjacent local extrema of $\hat{c}^*$ approach π with increasing q . We also note that $\hat{y}^*$ has the same roots as $\hat{c}^*$ but slightly different locations of local maxima due to its denominator (i.e., $1 - \bar{\rho}\hat{c}^*$), which is always > 0 . DST, on the other hand, is able to converge $\gamma(\bar{r}_+; m)$ for any fixed $\bar{r}_+ > 0$ much faster, which also explains the fast convergence of Δy_+ . The intermediate convergence of Δy_- , which dominates Δy , is finally understood by the fact that, as $\bar{r}_+$ approaches 0, the DST result approaches that of RI. We therefore have the intriguing result that Δy_-

and $\gamma(\bar{r}_+; m)$ converge quite differently for any $\bar{r}_+ > 0$.

Fig. 2(a) further shows that, at large q , the local maxima of $\hat{y}^*$ decay towards 0 with q^{-4} , much faster than the local extrema of $\hat{c}^*$ (and those of $\hat{h}^* = \hat{c}^* + \hat{y}^*$; data not shown) decaying with q^{-2} , thus justifying the Step II of our proposed numerical approach; these can be understood according to $\hat{y}^* = \bar{\rho}\hat{c}^2/(1 - \bar{\rho}\hat{c}^*)$, which is ≥ 0 .

All the above findings also apply to the numerical solution $c(\bar{r}_i; m)$ (and the corresponding $\hat{c}(q_i; m)$ and $\gamma(\bar{r}_i; m)$) converged via the AM iteration, where we use the convergence criterion of $\varepsilon_c < 10^{-10}$ with ε_c denoting the maximum absolute value of the residual errors of the PY closure over all $\bar{r}_i$ ($i=0, \dots, m$), as shown in Fig. 1(c) (where we also use $\bar{r}_+ \equiv i_+/m = 1/16$) with the following exceptions: (1) $\Delta\hat{c}$ decays towards 0 at a slightly faster rate of $m^{-9/2}$ for $m \leq 256$ (the leveling off for larger m is due to our convergence criterion), and (2) $\Delta\hat{c}_0$ decays approximately at a rate of m^{-3} , indicating that the $c(\bar{r}_i; m)$ solved numerically is not exactly a cubic polynomial due to the errors introduced via the real- and reciprocal-space discretization.

For comparison, we note that our numerical approach gives several orders of magnitude more accurate results than the recently developed pyPRISM,^[38] where $c_0 \equiv c(\bar{r}_0)$ and $\hat{c}_0$ are not given and $\Delta\hat{c}$ slowly decays with $m^{-3/2}$.^[3] Our Python script for calculating $\Delta\hat{c}$ using pyPRISM was given in the electronic supplementary information of our recent study;^[3] it gives $\Delta\hat{c}(m = 4096) \approx 1.5 \times 10^{-4}$ at $\bar{\rho} = 0.6$, even higher than $\Delta\hat{c}(m = 4096) \approx 4 \times 10^{-5}$ found in our Case D shown in Fig. 1(b).

The Tangent Hard-sphere Chain (THSC) Model

Based on the above HS results, we use $\Delta\hat{c}_0$ to choose the appropriate real-space discretization and cut-off (i.e., the values of m and $\bar{r}_c$, respectively). Fig. 3(a) shows that $\Delta\hat{c}_0$ decays approximately at a rate of m^{-3} for the THSC model, where we take $\hat{c}_0(m = 4096)$ as $\hat{c}_0^*$ for $N > 1$ at given $\bar{\rho}$. We also see that $\Delta\hat{c}_0$ decreases with increasing N and decreasing $\bar{\rho}$. We therefore take $m = 4096$ in our subsequent calculations for the THSC model, which makes the discretization error comparable to that due to the AM iteration given by the aforementioned convergence criterion. On the other hand, to capture the correlation-hole effect^[41] for polymers, we take $\bar{r}_c$ to be proportional to $\sqrt{N}$; due to our use of ideal-chain conformations, this is the correct scaling for the root-mean-square end-to-end distance of chains (i.e., $N > 1$) regardless of $\bar{\rho}$ and further allows us to include the results for $N = 1$. Fig. 3(b) shows how $\Delta\hat{c}_0$ decays with $\bar{r}_c$ for the THSC model, where for $N = 1$ we take $\hat{c}_0(\bar{r}_c = 11)$ as $\hat{c}_0^*$ at $\bar{\rho} = 0.6$ and $\hat{c}_0(\bar{r}_c = 5)$ as $\hat{c}_0^*$ at $\bar{\rho} = 0.1$, and for $N \geq 100$ we take $\hat{c}_0(\bar{r}_c = 3\sqrt{N})$ as $\hat{c}_0^*$ at given $\bar{\rho}$. We again see that $\Delta\hat{c}_0$ decreases with increasing N (at given $\bar{r}_c/\sqrt{N}$) and decreasing $\bar{\rho}$, and note that $\hat{c}_0$ does not always approach $\hat{c}_0^*$ monotonically with increasing $\bar{r}_c$ (thus

Table 1 Summary of the four cases shown in Fig. 1(b). Note that $\tilde{c}(\bar{r} \geq 1) = c(\bar{r})$.

Case	$\tilde{c}(\bar{r} \leq 1^-) =$	Discontinuity at $\bar{r} = 1$ in	At large m , $\Delta\hat{c} \propto$
A	$c(\bar{r}) - c_1 - c'_1(\bar{r} - 1)$	$d^2\tilde{c}/d\bar{r}^2$	m^{-4}
B	$c(\bar{r}) - c_1 - c'_1(\bar{r} - 1) - c''_1(\bar{r} - 1)^2/2$	$d^3\tilde{c}/d\bar{r}^3$	m^{-4}
C	$c(\bar{r}) - c_1$	$d\tilde{c}/d\bar{r}$	$m^{-5/2}$
D	$c(\bar{r})$	$\tilde{c}(\bar{r})$	$m^{-3/2}$

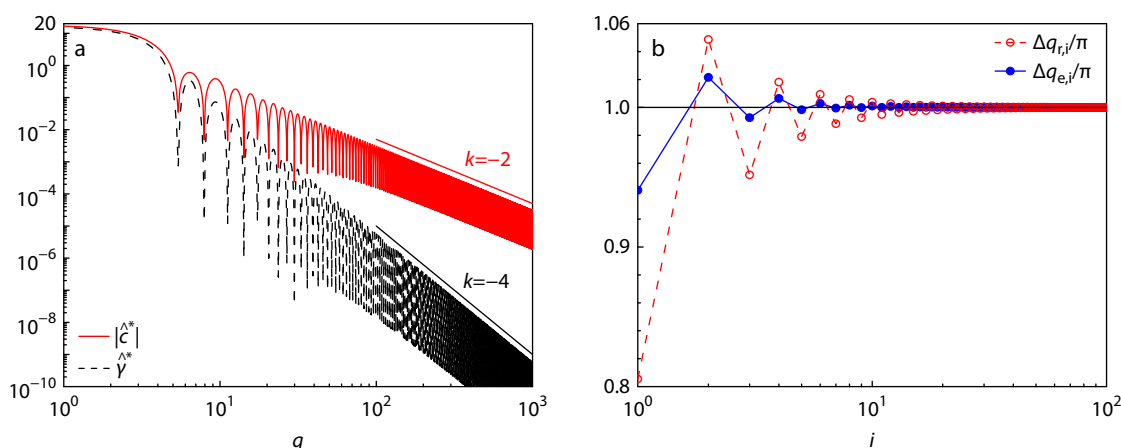


Fig. 2 (a) Logarithmic plot of the 3D Fourier transform of the analytical result of the direct PCF $\hat{c}^*$ and that of the indirect PCF $\hat{y}^*$ versus the wavenumber q , and (b) semi-logarithmic plot of the spacing $\Delta q_{r,i} \equiv q_{r,i+1} - q_{r,i}$ between adjacent roots $q_{r,i}$ and $q_{r,i+1}$, as well as $\Delta q_{e,i} \equiv q_{e,i+1} - q_{e,i}$ between adjacent local extrema located at $q_{e,i}$ and $q_{e,i+1}$, respectively, of $\hat{c}^*$ versus the ordered number i (with $q_{r,1}$ and $q_{e,1}$ being the smallest), for the HS model at the dimensionless average segment (particle) number density $\bar{\rho} = 0.6$. The k -value gives the slope of the corresponding straight line.

the little offset of the point at $\bar{r}_c = 8$ for the case of $N=1$ and $\bar{\rho} = 0.6$). Based on Fig. 3(b), we take $\bar{r}_c \approx 10\sqrt{N}$ (which is rounded to the nearest integer) for $N < 100$ and $2\sqrt{N}$ otherwise in our subsequent calculations for the THSC model, again to be comparable to our aforementioned AM convergence criterion.

With the above chosen discretization parameters and convergence criterion, we then perform PRISM-PY calculations of the THSC model for $N=1 \sim 10^6$ at $\bar{\rho}=0.1$ and 0.6 . Fig. 4(a) shows that, while $c_1 < 0$ and $\hat{c}_0 < 0$ approach their asymptotic value monotonically with increasing N , c_0 exhibits a maximum. We also note that $c_0 < 0$ for too small N (thus not shown in the figure). It seems from our numerical results for $N > 1$ that $c(\bar{r})$ is a monotonic function of $\bar{r} \in [0, 1^-]$ (thus bracketed by c_0 and c_1), same as the case of $N=1$.

In the limit of $N \rightarrow \infty$ and $\sigma \rightarrow 0$ at finite root-mean-square end-to-end distance of the ideal chain $R_{e,0} \equiv \sqrt{N-1}\sigma$, the THSC model becomes the hard-core Gaussian thread model^[5] (HC CGC- δ , where $R_{e,0}$ is taken as the unit of length), which corresponds to its limit of $\bar{\rho} \rightarrow 0$; Fig. 1 of our recent study^[3]

showed how $C_0 \equiv N^2 \hat{c}_0 \sigma^3 / R_{e,0}^3$ (thus the normalized isothermal compressibility $\bar{\kappa}_T = 1 / (1 - \sqrt{N} C_0)$ given by the compressibility equation) and the dimensionless excess (virial) pressure due to the interchain repulsion $\beta R_{e,0}^3 P_{ex} = (2\pi/3) [\bar{N} N^2 / (R_{e,0}/\sigma)^3] (h(\bar{r} = 1) + 1)$ vary with the invariant degree of polymerization^[42] $\bar{N} \equiv (n R_{e,0}^3 / V)^2$ for these two models.

Finally, Fig. 5(a) shows the absolute value of the local extrema of $\hat{c}$ and $\hat{y}$, $\hat{c}_e \equiv \hat{c}(q_e)$ and $\hat{y}_e \equiv \hat{y}(q_e)$, respectively, determined from the cubic polynomial interpolation as explained in **Appendix**, for the THSC model. We see that, for $N \geq 2$, $\hat{y}_e$ decays towards 0 with q^{-3} at large q (which can be compared with Fig. 2(a) for the HS model); this is due to the fact that, at large q , the 3D Fourier transform of the normalized intrachain PCF for the ideal THSC conformations $\hat{\omega} = \hat{\omega}_{id}^{THSC}$ approaches $1/N$ at a rate of q^{-1} (thus $N^2 \hat{\omega}^2$ or equivalently $N^2 \hat{\omega}^2 / (1 - N \bar{\rho} \hat{\omega} \hat{c})$ approaches 1 at the same rate). This decay of $\hat{y}_e$ is still faster than $\hat{c}_e$ (and the local extrema of $\hat{h} = \hat{c} + \hat{y}$;

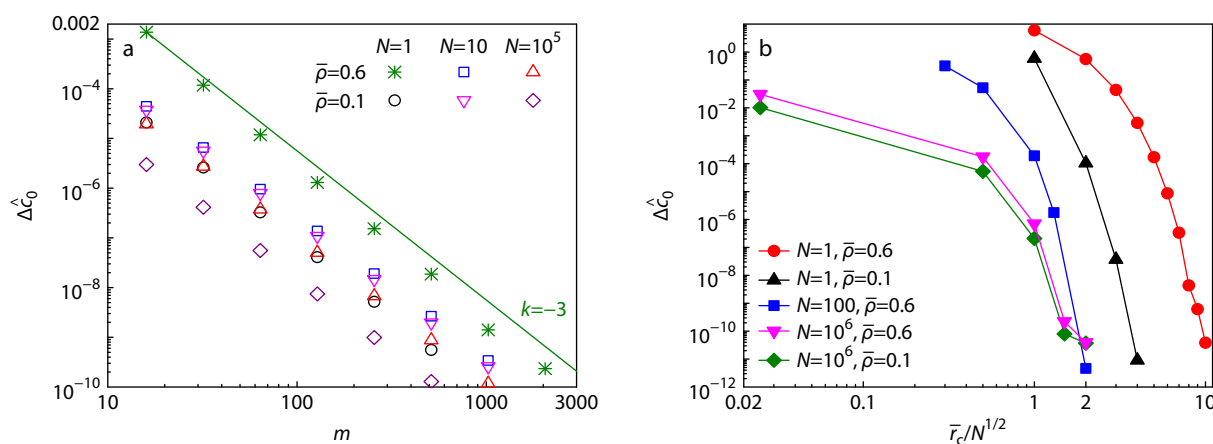


Fig. 3 Logarithmic plot of the numerical error $\Delta \hat{c}_0$ as a function of (a) the real-space discretization parameter m and (b) the real-space cut-off $\bar{r}_c$ for the THSC model at various chain lengths N and dimensionless average segment number densities $\bar{\rho}$. $\bar{r}_c \approx 10\sqrt{N}$ for $N < 100$ and $2\sqrt{N}$ otherwise is used in part (a), and $m=4096$ in (b). The k -value gives the slope of the corresponding straight line.

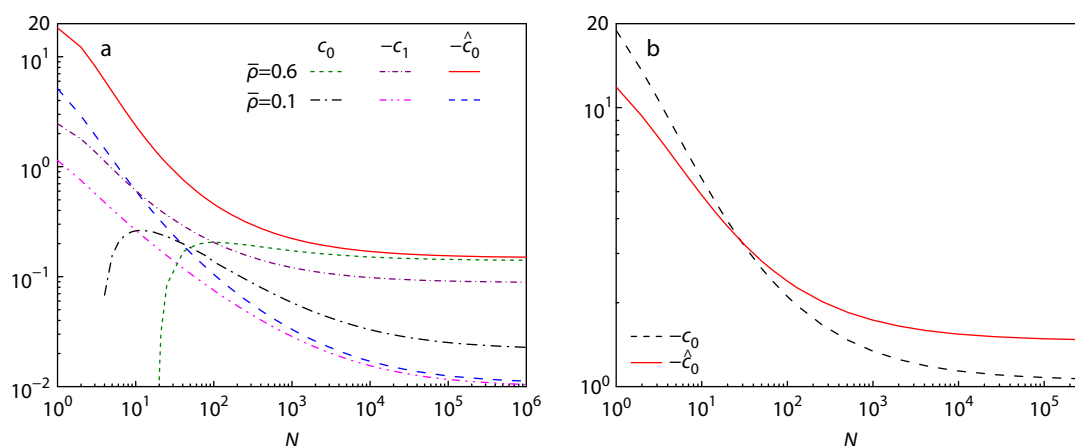


Fig. 4 Logarithmic plots of values of the interchain direct PCF c_0 and $\hat{c}_0$ versus the chain length N for (a) the THSC model at various dimensionless average segment number densities $\bar{\rho}$ and (b) the DPDC model at $\bar{\rho} = 3$. In (a), c_1 is also shown.

data not shown) decaying with q^{-2} . We also note that $\hat{Y}$ is no longer always ≥ 0 ; for small q_e , the local maxima and minima of $\hat{Y}$ scale with q_e differently, leading to the zig-zag behavior shown in the figure. Fig. 5(b) further shows that, while the spacing between adjacent roots (determined from the quadratic polynomial interpolation as explained in **Appendix**) and that between adjacent local extrema of $\hat{c}$ for the THSC model at $N=2$ and $\bar{\rho} = 0.6$ approach π with increasing q as in Fig. 2(b) for the HS model, those of $\hat{y}$ approach $\pi/2$; the same results are found for $N>2$ and other $\bar{\rho}$ (data not shown). We also note that $\hat{y} = [N^2 \hat{\omega}^2 / (1 - N\bar{\rho}\hat{\omega}\hat{c}) - 1] \hat{c}$ has extra roots in addition to those of $\hat{c}$, due to the term in the square brackets.

The Dissipative Particle Dynamics Chain (DPDC) Model

Following the above HS results in Section **The Hard-sphere (HS) Model**, we use $\Delta\hat{c}_0$ to choose the appropriate values of m and $\bar{r}_c$. Fig. 6(a) shows that both $\Delta c_0 \equiv |c_0(m) - c_0^*|$ and $\Delta\hat{c}_0$ de-

cay approximately at a rate of m^{-4} , particularly over the intermediate m -values, for the DPDC model at various N , where we take $c_0(m = 1024)$ and $\hat{c}_0(m = 1024)$ as c_0^* and $\hat{c}_0^*$, respectively. Note that, while Δc_0 here is equivalent to $\Delta\gamma_0$ for the HS model (where $h(\bar{r}_0) = -1$) shown in Fig. 1(c), it decays much faster; $\Delta\hat{c}_0$ also decays faster than shown in Fig. 3(a) for the THSC model. These indicate that the numerical calculations of PRISM-PY theory for the DPDC model are much easier (*i.e.*, need much smaller m) than those for the THSC model; based on Fig. 6(a), we choose $m=512$ in our subsequent calculations for the DPDC model, which makes the discretization error comparable to the convergence criterion of $\varepsilon_c < 10^{-10}$ used for the AM iteration. On the other hand, Fig. 6(b) is similar to Fig. 3(b) and shows that our choice of $\bar{r}_c$ for the THSC model (*i.e.*, $\bar{r}_c \approx 10\sqrt{N}$ for $N < 100$ and $2\sqrt{N}$ otherwise) also works for the DPDC model, where we take $\hat{c}_0(\bar{r}_c)$ as $\hat{c}_0^*$ in our calculation of $\Delta\hat{c}_0$. Finally, we note that our choice of m and $\bar{r}_c$ based on Fig. 6, which is at $\bar{\rho} = 3$, works better for larger $\bar{\rho}$ (data not shown), where the correlations due to

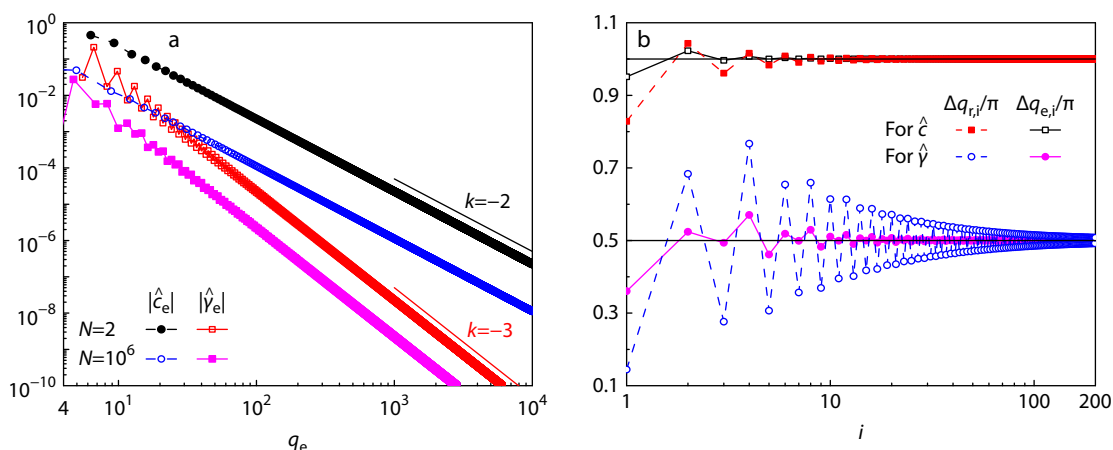


Fig. 5 (a) Logarithmic plot of the absolute value of the local extrema of the interchain direct PCF $\hat{c}$ and indirect PCF $\hat{y}$, $\hat{c}_e \equiv \hat{c}(q_e)$ and $\hat{y}_e \equiv \hat{y}(q_e)$, for the THSC model at various chain lengths N . (b) Semi-logarithmic plot of the spacing $\Delta q_{r,i} \equiv q_{r,i+1} - q_{r,i}$ between adjacent roots $q_{r,i}$ and $q_{r,i+1}$, as well as $\Delta q_{e,i} \equiv q_{e,i+1} - q_{e,i}$ between adjacent local extrema located at $q_{e,i}$ and $q_{e,i+1}$, respectively, of $\hat{c}$ and $\hat{y}$ versus the ordered number i (with $q_{r,1}$ and $q_{e,1}$ being the smallest) for the THSC model at $N=2$. The dimensionless average segment number density $\bar{\rho} = 0.6$ is used, and the k -value gives the slope of the corresponding straight line.

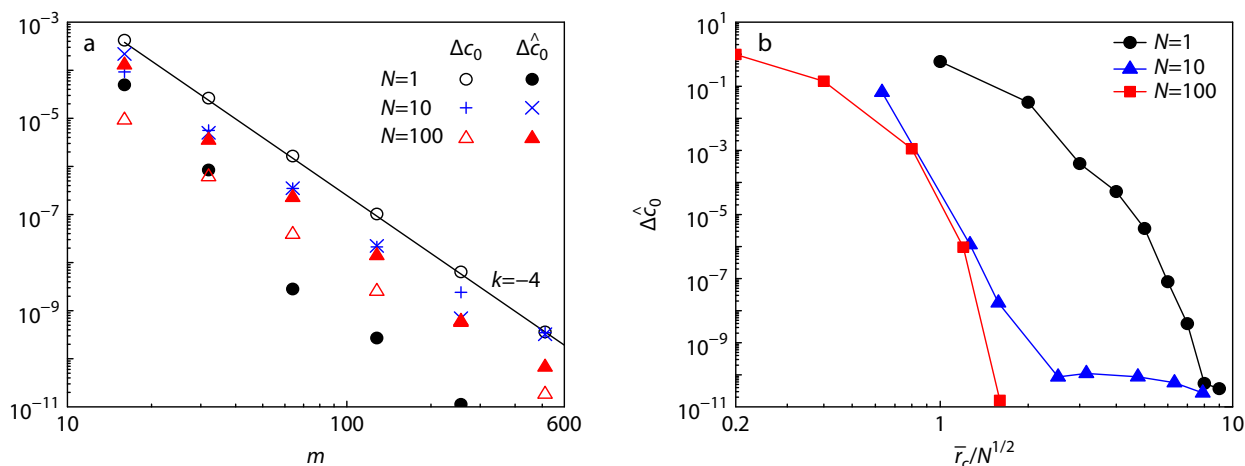


Fig. 6 Logarithmic plot of (a) the numerical error Δc_0 versus (a) the real-space discretization parameter m and (b) the real-space cut-off $\bar{r}_c$ for the DPDC model at various chain lengths N and the dimensionless average segment number density $\bar{\rho} = 3$. In part (a), Δc_0 is also shown and the k -value gives the slope of the corresponding straight line. $\bar{r}_c \approx 10\sqrt{N}$ for $N < 100$ and $2\sqrt{N}$ otherwise is used in part (a), and $m = 512$ in (b).

$\beta u^{\text{DPD}}(\bar{r})$ become weaker.

Results at $N=1$

With the above chosen discretization parameters and convergence criterion, we first note that the PRISM-PY calculations of the DPDC model of $N=1$ (i.e., DPD particles) at $\bar{\rho} = 3$ give the normalized isothermal compressibility via the compressibility equation $\bar{\kappa}_T \equiv \rho_c \kappa_T / \beta = 1 / (1 - \bar{\rho} \hat{c}_0) \approx 0.0273$, where $\rho_c \equiv n/V$ is the chain (particle) number density and $\kappa_T \equiv -(\partial V / \partial P)_{n,\beta} / V$ is the isothermal compressibility with P denoting the system pressure; this is less than half of the $\bar{\kappa}_T = 1/16$ for water at 300 K used by Groot and Warren^[9] to obtain $A=75$. While it is well-known that the PY closure is thermodynamically inconsistent (that is, the above value of $\bar{\kappa}_T$ obtained via the compressibility route is different from $\bar{\kappa}_T = 1 / \left\{ 1 + \left[\partial (\beta \sigma^3 P_{\text{ex}}) / \partial \bar{\rho} \right]_{n,\beta} \right\}$ obtained via the virial route in the PRISM-PY calculations), the approximate equation of state $\beta \sigma^3 P_{\text{ex}} / a \bar{\rho}^2 = 0.101 \pm 0.001$ (i.e., Eq. 16 of Ref. [9]) used by Groot and Warren, which is obtained from their DPD simulations at various values of a and $\bar{\rho}$, also contributes to this discrepancy as it assumes that $\beta \sigma^3 P_{\text{ex}} / a \bar{\rho}^2$ is independent of a (or A) and $\bar{\rho}$. Fig. 7(a) clearly shows that $\beta \sigma^3 P_{\text{ex}} / a \bar{\rho}^2 = (2\pi/3) \int_0^1 d\bar{r}^3 (h(\bar{r}) + 1)(1 - \bar{r})$ obtained from the PRISM-PY calculations varies with both a (or A) and $\bar{\rho}$; while it monotonically increases with increasing $\bar{\rho}$ at fixed A , it exhibits some oscillations at fixed a . Note that the PRISM-PY calculations at fixed a become difficult to converge for large $\bar{\rho}$. We also note that as shown in Fig. 4 of Ref. [9], $\beta \sigma^3 P_{\text{ex}} / a \bar{\rho}^2$ obtained from the DPD simulations at fixed a by Groot and Warren appears to monotonically increase with increasing $\bar{\rho} \in [2, 8]$. Due to the different correlations at different values of a (or A), one cannot justify that $\beta \sigma^3 P_{\text{ex}} / a \bar{\rho}^2$ obtained from the DPD simulations is independent of a (or A) and $\bar{\rho}$.

With increasing $\bar{\rho}$ at fixed A , $\beta u^{\text{DPD}}(\bar{r})$ becomes weaker and the PY closure approaches the random-phase approximation (RPA) closure $c^{\text{RPA}}(\bar{r}) = -\beta u^{\text{DPD}}(\bar{r})$, which gives $c^{\text{RPA}} = -(\pi a/15) \beta \hat{u}_0$ thus $\hat{h}^{\text{RPA}} = -\pi a \beta \hat{u}_0 / (15 + \pi a \bar{\rho} \beta \hat{u}_0)$ according to Eq. (1). In the limit of $\bar{\rho} \rightarrow \infty$, while $\hat{h}^{\text{RPA}}(\bar{r}) = 0$ regardless of whether A or a is fixed, $c^{\text{RPA}}(\bar{r}) = 0$ only when A is fixed

(i.e., $a \rightarrow 0$); the SCF result of $\beta \sigma^3 P_{\text{ex}}^{\text{SCF}} / \bar{\rho} = -(2\pi/3) \bar{\rho} \int_0^1 d\bar{r}^3 (d\beta u^{\text{DPD}}(\bar{r}) / d\bar{r}) = \pi a \bar{\rho} / 30$ is therefore finite in this limit only when A is fixed. Fig. 7(b) shows that when A is fixed, $\beta \sigma^3 (P_{\text{ex}}^{\text{SCF}} - P_{\text{ex}}^{\text{RPA}}) / a \bar{\rho} = -(2\pi/3) \bar{\rho} \int_0^1 d\bar{r}^3 h^{\text{RPA}}(\bar{r})(1 - \bar{r})$ is independent of $\bar{\rho}$ but dependent of A as expected; when a is fixed, however, it is dependent of both $\bar{\rho}$ and a . Similar results are found for the dimensionless excess internal energy per chain (particle), $\beta u_{\text{c,ex}} = \pi a \bar{\rho} \int_0^1 d\bar{r}^2 (h(\bar{r}) + 1)(1 - \bar{r})^2$, as shown in Figs. 7(c) and 7(d); note that $\beta u_{\text{c,ex}}^{\text{SCF}} = \pi a \bar{\rho} / 30$ and $\beta (u_{\text{c,ex}}^{\text{SCF}} - u_{\text{c,ex}}^{\text{RPA}}) / a = -\pi \bar{\rho} \int_0^1 d\bar{r}^2 h^{\text{RPA}}(\bar{r})(1 - \bar{r})^2$. Because correlations exist for $a > 0$ even in the limit of $\bar{\rho} \rightarrow \infty$, hereafter we consider only the DPDC model at fixed A ($=75$), where the SCF theory becomes exact in the limit of $\bar{\rho} \rightarrow \infty$ (where neither fluctuations nor correlations exist).

Results for various N

Next, we perform PRISM-PY calculations of the DPDC model for $N=1-2.6 \times 10^5$ at $\bar{\rho} = 3$. In the case of $N=1$, we see from Fig. 8(a) that, at large q , the local maxima of $\hat{\gamma}$ (i.e., $\hat{\gamma}_e$ determined from the cubic polynomial interpolation as explained in **Appendix**) decay towards 0 with q^{-8} , much faster than the local extrema of $\hat{c}$ (i.e., $\hat{c}_e$ also determined from the cubic polynomial interpolation) and those of $\hat{h} = \hat{c} + \hat{\gamma}$ (data not shown) decaying with q^{-4} ; these can be understood according to $\hat{\gamma} = \bar{\rho} \hat{c}^2 / (1 - \bar{\rho} \hat{c})$ and compared with the HS model. Same as the HS model, we find $\hat{\gamma} \geq 0$ here. Interestingly, the same qualitative behavior is found for $N > 1$, such as the case of $N=10^5$ also shown in Fig. 8(a); this is due to the fact that, at large q , $\hat{\omega} = \hat{\omega}_{\text{id}}^{\text{DPD}}$ approaches $1/N$ exponentially (i.e., $\hat{\omega}(q) - 1/N \propto \exp(-q^2/8)$), thus $N^2 \hat{\omega}^2 / (1 - N \bar{\rho} \hat{\omega} \hat{c})$ approaches $1 / (1 - \bar{\rho} \hat{c})$ (or equivalently $\hat{\gamma} = [N^2 \hat{\omega}^2 / (1 - N \bar{\rho} \hat{\omega} \hat{c}) - 1] \hat{c}$ approaches $\bar{\rho} \hat{c}^2 / (1 - \bar{\rho} \hat{c})$) at the same rate. This explains the much smaller m (thus q_c) needed for the DPDC model than for the THSC model. For small q , however, $\hat{\gamma}$ becomes < 0 for $N \geq 14$ (at $\bar{\rho} = 3$) and monotonically increases with increasing q towards its first local maximum (which is > 0).

Similar to Fig. 2(b) for the HS model, Fig. 8(b) shows that the spacing between adjacent roots (determined from the

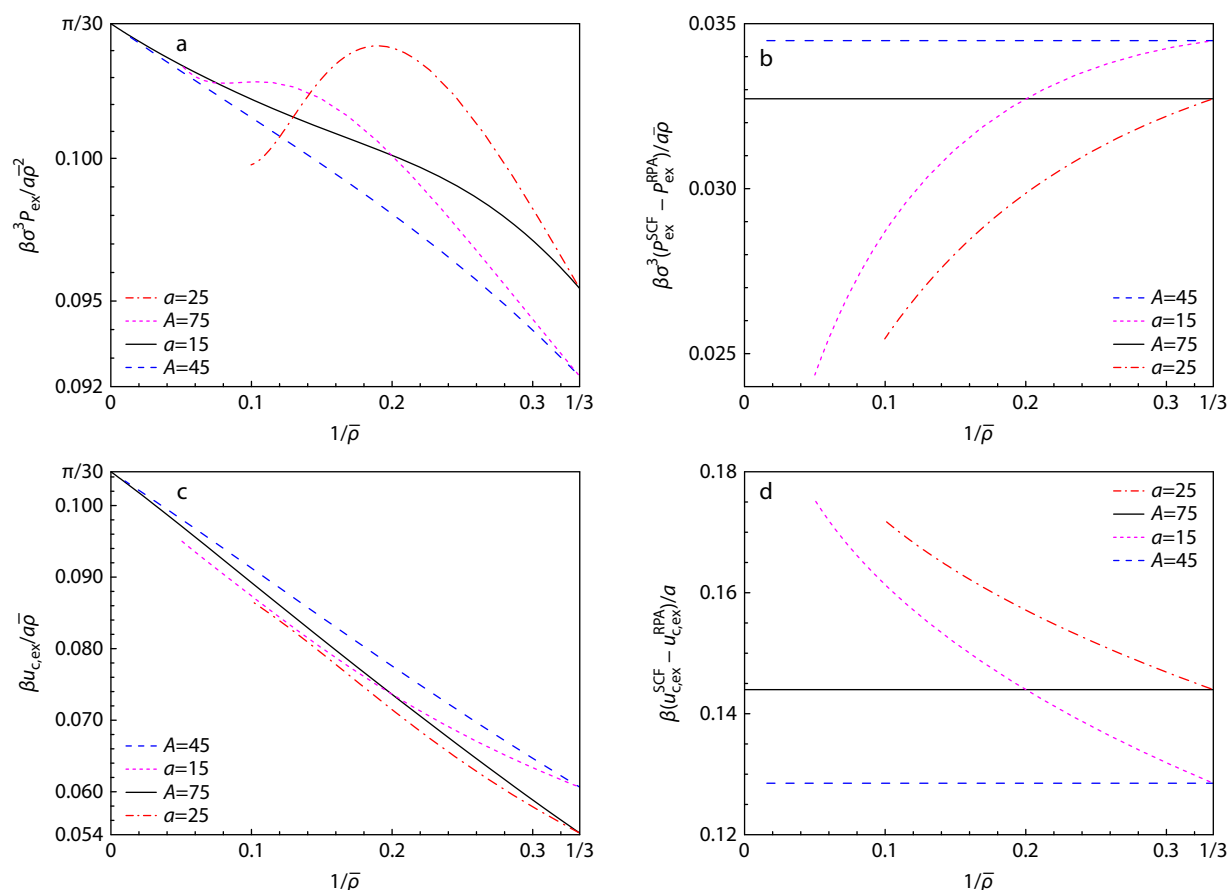


Fig. 7 (a, b) The excess (virial) pressure P_{ex} and (c, d) the excess internal energy per chain (particle) $u_{\text{c,ex}}$ of the DPDC model at $N=1$ versus the dimensionless average segment (particle) number density $\bar{\rho}$ obtained for various a and $A = a\bar{\rho}$ from (a, c) the PRISM-PY calculations and (b, d) the PRISM-RPA calculations, where the SCF results are given by $\beta\sigma^3 P_{\text{ex}}^{\text{SCF}}/a\bar{\rho} = \beta u_{\text{c,ex}}^{\text{SCF}}/a = \pi\bar{\rho}/30$.

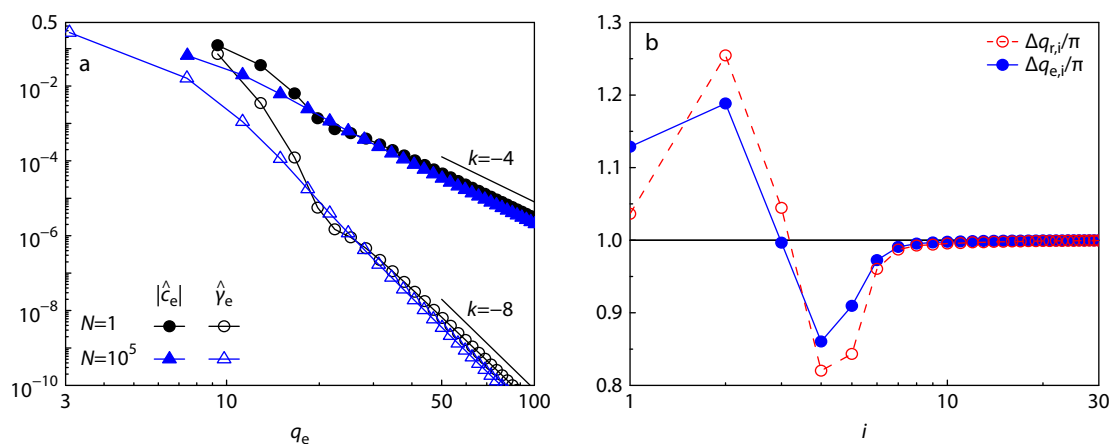


Fig. 8 (a) Logarithmic plot of the absolute value of the local extrema of the interchain direct PCF $\hat{c}_e \equiv \hat{c}(q_e)$ and the local maxima of the interchain indirect PCF $\hat{y}_e \equiv \hat{y}(q_e)$, for the DPDC model at various chain lengths N . (b) Semi-logarithmic plot of the spacing $\Delta q_{r,i} \equiv q_{r,i+1} - q_{r,i}$ between adjacent roots $q_{r,i}$ and $q_{r,i+1}$, as well as $\Delta q_{e,i} \equiv q_{e,i+1} - q_{e,i}$ between adjacent local extrema located at $q_{e,i}$ and $q_{e,i+1}$, respectively, of $\hat{c}$ versus the ordered number i (with $q_{r,1}$ and $q_{e,1}$ being the smallest) for the DPDC model at $N=1$. The dimensionless average segment number density $\bar{\rho} = 3$ is used, and the k -value gives the slope of the corresponding straight line.

quadratic polynomial interpolation as explained in **Appendix**) and that between adjacent local extrema of $\hat{c}$ for the DPDC model of $N=1$ at $\bar{\rho} = 3$ approach π with increasing q ; the same results are found for other N and $\bar{\rho}$ (data not shown). Same as the HS model, $\hat{y}$ for the DPDC model has the

same roots as $\hat{c}$ but slightly different locations of local maxima due to its denominator.

Fig. 4(b) shows that $c_0 < 0$ and $\hat{c}_0 < 0$ approach their asymptotic value monotonically with increasing N for the DPDC model; this can be compared with Fig. 4(a) for the THSC mod-

el. It seems from our numerical results that $c(\bar{r})$ is a monotonic function of $\bar{r} \in [0, 1]$ (thus bracketed by c_0 and $c_1=0$) for the DPDC model. Fig. 1 of our recent study^[3] further showed that the DPDC model at $\bar{\rho} = 3$ gives qualitatively the same behavior of $C_0 \equiv N^2 \hat{c}_0 \sigma^3 / R_{e,0}^3$ (thus $\bar{\kappa}_T = 1 / (1 - \sqrt{N} C_0)$) and $\beta R_{e,0}^3 P_{ex} = -(2\pi/3) [\bar{N} N^2 / (R_{e,0} \sigma)^3] \int_0^1 d\bar{r} \bar{r}^3 (h(\bar{r}) + 1) (d\beta u^{DPD}(\bar{r}) / d\bar{r})$ versus $\bar{N}$ as that for the THSC model.

Finally, Fig. 9 shows that for the DPDC model at large $\bar{\rho}$, c_0 and $\hat{c}_0$ for various N collapse, respectively, and both decay towards 0 at a rate of $\bar{\rho}^{-1}$; in such cases, $\beta u^{DPD}(\bar{r}) = (37.5/\bar{\rho}) (1 - \bar{r})^2 \approx 0$ and the PY closure approaches the RPA closure giving $c_0^{RPA} = -37.5/\bar{\rho}$ and $\hat{c}_0^{RPA} = -5\pi/\bar{\rho}$, independent of N . We then obtain $\bar{\kappa}_T^{RPA} = 1 / (1 - N\bar{\rho}c_0^{RPA}) = 1 / (1 + 5\pi N)$. Fig. 2 of our recent study^[3] showed how $\bar{\kappa}_T = 1 / (1 - \sqrt{N} C_0)$, $\beta \sigma^3 (P_{ex} - P_{ex}^{RPA}) / a\bar{\rho}$ and $\beta (u_{c,ex} - u_{c,ex}^{RPA}) / aN$ obtained from our numerical PRISM-PY calculations for various N vary with $\bar{\rho}$. The central result presented in our recent study^[3] was that the behavior of soft-core models at large $\bar{N}$ depends on how $\bar{N}$ is varied, i.e., whether by changing N at fixed $\bar{\rho}$ (thus the excluded-volume interaction strength ε is fixed) or by changing $\bar{\rho}$ at fixed N (thus ε is also varied as being $\propto \bar{\rho}^{-1}$); in the former case correlations exist even in the limit of $N \rightarrow \infty$, while in the latter case the SCF theory becomes exact in the limit of $\bar{\rho} \rightarrow \infty$ (at finite N). This is analogous to changing $\bar{\rho}$ for the DPDC model of $N=1$ at either fixed a or A discussed in Section Results at $N=1$.

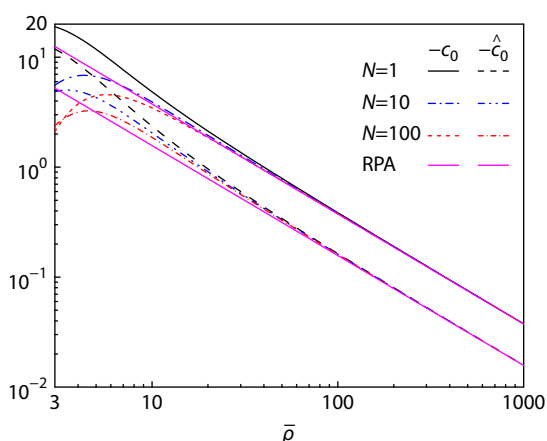


Fig. 9 Logarithmic plot of values of the interchain direct PCF c_0 and $\hat{c}_0$ versus the dimensionless average segment number density $\bar{\rho}$ of the DPDC model at various chain lengths N . The RPA results are given by $c_0^{RPA} = -37.5/\bar{\rho}$ and $\hat{c}_0^{RPA} = -5\pi/\bar{\rho}$.

CONCLUSIONS

In this work, taking homogeneous systems of compressible homopolymer melts (or equivalently homopolymer solutions in an implicit, good solvent) in the continuum as an example, where the excluded-volume interaction between polymer segments is described by a dimensionless short-range, isotropic and purely repulsive pair potential $\beta u^{nb}(r)$, we have examined in detail the numerical calculations of the polymer reference interaction site model (PRISM) theory with the Percus-Yevick (PY) closure for

two commonly used generic polymer models: the tangent hard-sphere chain (THSC) and the dissipative particle dynamics chain (DPDC) models. These two models are classified, according to whether or not $\int d\mathbf{r} \beta u^{nb}(|\mathbf{r}|)$ diverges, as the hard- and soft-core models, respectively.^[3] The correlation effects on the structural and thermodynamic properties of these two models were compared in our recent study.^[3]

Since all previously reported numerical methods for the PRISM calculations^[30–33] are not optimal for our models, we have proposed an efficient numerical approach described in detail in Section Numerical Calculations of PRISM-PY Theory, which enables us to solve the PRISM-PY theory for chain length N as large as 10^6 to an accuracy (i.e., the maximum absolute value of the residual errors of the PY closure) of $\varepsilon_c < 10^{-10}$. In particular, since the PY closure Eq. (2) leads to Eq. (3) for this class of models, with uniform discretization of the real space, the interchain direct pair correlation function (PCF) between polymer segments $c(0 \leq \bar{r} < 1)$, where $\bar{r} \equiv r/\sigma$ with σ being the range of $\beta u^{nb}(r)$, gives the least number of independent variables to be solved via an iteration method, which we choose to be the Anderson mixing^[27] that can quickly converge a large set of nonlinear equations to a high accuracy. For discontinuous $\beta u^{nb}(r)$ such as in the THSC model, analytically treating the corresponding discontinuity in both $c(\bar{r})$ and its 1st-order derivative at $\bar{r} = 1$ gives much more accurate numerical results of its 3D Fourier transform $\hat{c}$, thus greatly reducing the real-space discretization parameter m (i.e., the number of subintervals into which $[0, 1]$ is discretized). Also, since the 3D Fourier transform of the interchain indirect PCF $\hat{\gamma}$ decays towards 0 with increasing wavenumber q much faster than $\hat{c}$ and that of the interchain total PCF $\hat{h} = \hat{c} + \hat{\gamma}$ (as shown below), it is important that the inverse Fourier transform is performed only for $\hat{\gamma}$, which greatly reduces the cut-off of the reciprocal space $q_c = m\pi$. Finally, to capture the correlation-hole effect,^[41] the real-space cut-off $\bar{r}_c$ should be $\propto \sqrt{N}$; we choose the values of m and $\bar{r}_c$ such that the discretization errors are comparable to ε_c . For simplicity, we also use the ideal-chain conformations represented by $\hat{\omega}_{id}$ for the 3D Fourier transform of the intrachain PCF $\hat{\omega}$ needed as the input for the PRISM calculations.

For the THSC model of $N=1$ (i.e., hard spheres), its analytical solution^[36] (denoted by the superscript “*” to the PRISM-PY theory shows that $\hat{c}^*$ is highly oscillatory with the spacing between its adjacent roots and that between its adjacent local extrema approach π with increasing q . $\hat{\gamma}^* = \bar{\rho} \hat{c}^{*2} / (1 - \bar{\rho} \hat{c}^*)$ with $\bar{\rho}$ being the dimensionless average segment (particle) number density has the same roots as $\hat{c}^*$ but slightly different locations of local maxima due to its denominator (which is always > 0). At large q , the local maxima of $\hat{\gamma}^*$ decay towards 0 with q^{-4} , much faster than the local extrema of $\hat{c}^*$ and $\hat{h}^*$ decaying with q^{-2} .

For the THSC model of $N \geq 2$, the local extrema of $\hat{\gamma}$ decay towards 0 with q^{-3} at large q (due to the fact that, at large q , $\hat{\omega}_{id}^{THSC}$ approaches $1/N$ at a rate of q^{-1}), still faster than those of $\hat{c}$ and $\hat{h}$ decaying with q^{-2} . $\hat{\gamma} = [N^2 \hat{\omega}^2 / (1 - N\bar{\rho} \hat{\omega} \hat{c}) - 1] \hat{c}$, however, is no longer always ≥ 0 and has extra roots in addition to those of $\hat{c}$ due to the term in the square brackets. While the spacing between adjacent roots and that between adjacent local extrema of $\hat{c}$ still approach π with increasing q ,

those of $\hat{\gamma}$ approach $\pi/2$. With increasing N , while $c_1 \equiv c(\bar{r} = 1^-) < 0$ and $\hat{c}_0 \equiv \hat{c}(q = 0) < 0$ approach their asymptotic value monotonically, $c_0 \equiv c(\bar{r} = 0)$ exhibits a maximum. It seems from our numerical results that $c(\bar{r})$ is a monotonic function of $\bar{r} \in [0, 1^-]$.

For the DPDC model of $N=1$ (i.e., DPD particles) at $\bar{\rho} = 3$, the PRISM-PY theory gives the normalized isothermal compressibility via the compressibility equation $\bar{\kappa}_T = 1/(1 - \bar{\rho}\hat{c}_0) \approx 0.0273$, less than half of the $\bar{\kappa}_T = 1/16$ for water at 300 K used by Groot and Warren^[9] to obtain $A \equiv a\bar{\rho} = 75$ commonly used in DPD simulations, where a is the dimensionless interaction parameter in the DPD potential $\beta u^{\text{DPD}}(\bar{r}) = (a/2)(1 - \bar{r})^2$ for $\bar{r} < 1$ and 0 otherwise; while the PY closure is thermodynamically inconsistent, the approximate equation of state $\beta\sigma^3 P_{\text{ex}}/a\bar{\rho}^2 = 0.101 \pm 0.001$ (i.e., Eq. 16 of Ref. [9], with P_{ex} denoting the excess virial pressure) used by Groot and Warren also contributes to this discrepancy as it assumes that $\beta\sigma^3 P_{\text{ex}}/a\bar{\rho}^2$ is independent of a (or A) and $\bar{\rho}$. With increasing $\bar{\rho}$ at fixed A , the PY closure approaches the random-phase approximation (RPA) closure. In the limit of $\bar{\rho} \rightarrow \infty$, while $h^{\text{RPA}}(\bar{r}) = 0$ regardless of whether A or a is fixed, $c^{\text{RPA}}(\bar{r}) = 0$ and the SCF results of $\beta\sigma^3 P_{\text{ex}}^{\text{SCF}}/\bar{\rho} = \pi a\bar{\rho}/30$ and the dimensionless excess internal energy per chain (particle) $\beta u_{\text{c,ex}}^{\text{SCF}} = \pi a\bar{\rho}/30$ are finite only when A is fixed. Also when A is fixed, $\beta\sigma^3 (P_{\text{ex}}^{\text{SCF}} - P_{\text{ex}}^{\text{RPA}})/a\bar{\rho}$ and $\beta(u_{\text{c,ex}}^{\text{SCF}} - u_{\text{c,ex}}^{\text{RPA}})/a$ are independent of $\bar{\rho}$. Because correlations exist for $a > 0$ even in the limit of $\bar{\rho} \rightarrow \infty$, we have further considered only the DPDC model at fixed A ($=75$), where the SCF theory can be applied and becomes exact in the limit of $\bar{\rho} \rightarrow \infty$ (where neither fluctuations nor correlations exist).

For the DPDC model at large q , the local maxima of $\hat{\gamma}$ decay towards 0 with q^{-8} regardless of N (due to the fact that, at large q , $\hat{\omega}_{\text{id}}^{\text{DPD}}$ approaches $1/N$ exponentially), much faster than the local extrema of $\hat{c}$ and $\hat{h}$ decaying with q^{-4} . This leads to much smaller m (thus q_c) needed in our PRISM-PY calculations of the DPDC model than those of the THSC model. The spacing between adjacent roots and that between adjacent local extrema of $\hat{c}$ approach π with increasing q . $\hat{\gamma}$ has the same roots as $\hat{c}$ but slightly different locations of local maxima. With increasing N , $c_0 < 0$ and $\hat{c}_0 < 0$ approach their asymptotic value monotonically. It seems from our numerical results that $c(\bar{r})$ is a monotonic function of $\bar{r} \in [0, 1]$. For the DPDC model at large $\bar{\rho}$, c_0 and $\hat{c}_0$ for various N collapse, respectively, and both decay towards 0 at a rate of $\bar{\rho}^{-1}$; in such cases, the PY closure approaches the RPA closure giving $c_0^{\text{RPA}} = -37.5/\bar{\rho}$ and $\hat{c}_0^{\text{RPA}} = -5\pi/\bar{\rho}$, independent of N .

Finally, we note that our numerical approach proposed here can be readily extended to PRISM calculations with other closures and for more complicated systems (e.g., with attractions between polymer segments). Also, an important difference between numerically solving the Ornstein-Zernike equation^[35] for small molecules (i.e., $N=1$, where $\hat{\omega} = 1$) and the PRISM equation for polymers (i.e., $N > 1$) is the behavior of $\hat{\omega}$. These will be the topics of future publications.

Appendix: Finding the Roots and Extrema of Equally Spaced Data using Polynomial Interpolation

We use cubic polynomial interpolation to find all roots of

equally spaced data with spacing h . In particular, for $v_i = v(x_i)$ at $x_i = ih$ ($i=0, 1, 2, 3$), the cubic interpolating polynomial $\tilde{v}(x) = ax^3 + bx^2 + cx + d$ is given by

$$\begin{cases} a = (v_3 - 3v_2 + 3v_1 - v_0)/6h^3 \\ b = -(v_3 - 4v_2 + 5v_1 - 2v_0)/2h^2 \\ c = (2v_3 - 9v_2 + 18v_1 - 11v_0)/6h \\ d = v_0 \end{cases}$$

find all roots of a given series of data points $p_j = p(q_j)$ at $q_j = jh$ ($j=0, \dots, M$) one by one by looping over j : If $p_j=0$ for any j , then q_j is a root. Otherwise, we generally set $v_1=p_j$ such that $v_1 v_2 < 0$ and find the root between q_j and q_{j+1} ; in the case of $p_0 p_1 < 0$ or $p_{M-1} p_M < 0$, we set $v_0=p_0$ or $v_2=p_{M-1}$, respectively.

Similarly, we use quadratic polynomial interpolation to find all extrema of equally spaced data. For $v_i = v(x_i)$ at $x_i = ih$ ($i=0, 1, 2$), the quadratic interpolating polynomial $\tilde{v}(x) = ax^2 +$

$bx + c$ is given by $\begin{cases} a = (v_0 - 2v_1 + v_2)/2h^2 \\ b = -(3v_0 - 4v_1 + v_2)/2h \\ c = v_0 \end{cases}$, the extremum

of which is located at $x_m = -\frac{b}{2a}$ (when $a \neq 0$) with its value being $v_m = c - \frac{b^2}{4a}$. This can then be used to find all extrema of a given series of data points $p_j=p(q_j)$ at $q_j=jh$ ($j=0, \dots, M$) one by one by looping over j : We set $v_1=p_j$ such that $v_1 > v_0$ and $v_1 > v_2$ (that is, (q_{j-1}, q_{j+1}) contains a local maximum) or $v_1 < v_0$ and $v_1 < v_2$ (that is, (q_{j-1}, q_{j+1}) contains a local minimum); note that p_0 and p_M are not considered as local extrema.

Conflict of Interests

The author declares no interest conflict.

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