Coarse-grained Description of Polymer Blends as Interacting Soft-Colloidal Particles

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We present a theoretical approach which maps polymer blends onto mixtures of soft-colloidal particles. The analytical mesoscale pair distribution functions reproduce well data from united atom molecular dynamics simulations of polyolefin mixtures without fitting parameters. The theory exactly recovers the analytical expressions for density and concentration fluctuation structure factors of soft colloidal mixtures (liquid alloys).

I. INTRODUCTION

Polymer blends are systems of fundamental scientific interest. Their structural and dynamical properties change as a function of the proximity to thermodynamic conditions of phase separation (i.e., their spinodal curve). Blends have many practical applications since new materials can be produced with specific physical and chemical properties by simply mixing polymer melt components that have the desired characteristics. Finally, polymeric materials used in daily life are usually mixtures of polymers with different chain length and/or different local structure. Understanding how the mixing of polymer melts modifies their properties has been a relevant and longstanding scientific and technological goal in polymer physics and engineering.\[1,2,3\] From a theoretical perspective, relevant work in this direction has been developed by several groups in recent years.\[4,5,6,7,8,9\]

A great deal of information on the correlation between local (intra- and intermolecular) structure and global fluid properties has been obtained by computer simulations of polymer mixtures.\[10,11,12,13,14\] One of the challenges in simulating polymer blends is the large range of length- and timescales that need to be investigated. Blend properties strongly depend on the local bond lengthscale (short timescale), since mixtures of polymers with different local chemical structure can lead to dramatically different physical properties, including, for example, an opposite trend in demixing with temperature. On the other end, properties need to be investigated on the large lengthscale (long timescale) of concentration fluctuations, which diverges approaching the spinodal decomposition. In this regime, the box size of the system simulated becomes the upper limit in resolution.

To expedite computer simulations, it is useful to renormalize the system by adopting a coarse-grained description of the liquid. The goal is to have a formalism that allows us to simulate macroscopic behavior while retaining information about the detailed atomic chemical structure of polymer chains. The overall behavior of blend materials has to be related, through a well-defined and reversible procedure, to the local chemical structure of the system. As a first step, a convenient approach is to introduce a united atom (UA) description of the polymer chain: a commonly adopted method in simulations of polymer melts and blends.\[12,13,14\] A more drastic renormalization at the lengthscale of the polymer size was proposed by Dautenhahn and Hall\[16\] and later on by Murat and Kremer\[17\], who mapped a blend of polymer chains onto a liquid of colloidal particles interacting through phenomenological soft-core potentials. Recently, Hansen and coworkers have developed a rigorous numerical methodology to derive an effective potential for polymers in solution using liquid state theory.\[18,19\]

An analytical solution of the c.o.m. mean-force potential for a melt was derived by one of the authors.\[20,21\] The potential is qualitatively in agreement with the physical behavior observed in simulation data. For example, when compared with the classical solution by Flory and Krigbaum,\[22\] it has the advantage of correctly predicting greater interpenetration between two chains with increasing degree of polymerization, chain stiffness, and/or liquid density. However, since the derivation does not include explicitly chain connectivity, the analytical solution reproduces the short-scale simulation behavior after fitting the value of the intermolecular potential at complete interpolymer overlap.\[21\] More recently we derived an analytical expression for the potential of mean-force in polymer melts, which reproduces well, and with no adjustable parameters, data from UA Molecular Dynamics (MD) simulations of chains with different degree of polymerization and local chemical structure.\[23\] This coarse-grained potential is an explicit function of atomistic chain parameters, such as degree of polymerization and local semiflexibility, thereby correctly bridging different lengthscales of interest.

It is clearly advantageous to have an analytical form of the potential versus a numerical one, obtained from the inversion of computer simulation data. Since the mean-force potential is a free energy, it depends on the thermodynamic state of the system considered. A numerical calculation of the potential would require us to perform numerical simulations for each thermodynamic state of our system, defeating the purpose of adopting a coarse-grained model to reduce computational time. In this spirit, Krakoviack et al. recently derived an analytical potential for polymers in solution.\[24\]

In this paper we extend the melt theory to derive an analytical expression for the effective interaction potential acting between the centers of mass (c.o.m.) of two polymer chains in a blend. We start from a first-principles liquid
state description, thus limiting our theory to the miscible region of the phase diagram. However, it includes the buildup of concentration fluctuations as the system approaches its spinodal decomposition. It is known that the detailed nature of single-phase blend correlations (pair distribution functions) is sensitive to system-specific factors such as liquid density, temperature, blend composition, and differences in effective unit size and local architectural details of the components. Moreover, many blends of practical relevance are characterized by strong asymmetries in local chemical semiflexibility and architecture. These effects influence local entropic packing of molecules and lead to phase separation upon heating in a blend characterized by a lower critical solution temperature. Our analytical expression describes the interaction between c.o.m. of a pair of polymers in a blend as a function of all the characteristic parameters that govern blend structure and dynamics.

The derived mesoscale pair distribution functions effectively map the polymeric liquid onto a fluid of interacting soft-colloidal particles, thereby correctly reproducing fluctuations in number density and concentration, i.e. structure factors, and recovering the well-known equations for the compressibility and the dilation factor of colloidal mixtures. Moreover, the theory agrees well, without fitting parameters, with data from UA-MD computer simulations for polyolefin blends with different local stiffness, architecture, and blend composition.

Good agreement between the theory of mesoscopic colloidal particle mixtures and microscopic UA computer simulations of polymer blends supports the validity of our analytical renormalization procedure for polymer mixtures. The theory makes predictions on the evolution of the effective interpolymer potentials and chain packing as a function of temperature and blend composition, as well as polymer local structure, semiflexibility, and degree of polymerization.

This paper is divided in the following way: in Sec. II, we derive monomer pair distribution functions for a binary asymmetric polymer blend where differences in bond length, degree of polymerization, and composition are explicitly taken into account. This is followed by a comparison with computer simulation data. In Sec. III, we present a renormalized description of the polymer fluid by deriving c.o.m. pair distribution functions. A brief discussion of the associated mean-force potential at chain-overlap is given in Sec. IV. We then show how our formalism can readily be cast into the language of soft-colloidal systems in Sec. V. In Sec. VI we summarize model calculations for our renormalized description of a binary blend and make comparisons with simulation data. A brief discussion concludes the paper.

II. MONOMER PAIR DISTRIBUTION FUNCTIONS FOR ASYMMETRIC POLYMER BLENDS

In this section we develop the theory for monomer pair distribution functions in an asymmetric polymer blend, which will be inputs to our renormalization approach. The theory is then tested against data from UA-MD simulations. We include the effect of microscopic and macroscopic parameters through a generalized form of the monomer-monomer pair distribution function, as derived from the thread limit in the Polymer Reference Interaction Site Model (PRISM) liquid-state theory by Curro, Schweizer, and coworkers. The choice of the theory representing the monomer pair distribution function is arbitrary, and other analytical approaches could have been chosen as well. The original thread model is implemented here to include the dependence on asymmetries in semiflexibility following a somewhat different procedure than in the original work. No closure approximations are adopted in this derivation, and the miscibility parameter $\chi$ enters as an input to the theory, defining the proximity of the system to its demixing transition (the spinodal temperature). In principle, this approach can describe systems with either Lower (LCST) or Upper (UCST) Critical Solution Temperature.

In the thread model, a single chain is represented as an infinite thread of vanishing thickness with hard core monomer diameter $d \to 0$ and segment number density $\rho \to \infty$, while $\rho d^3$ is finite and of order unity. Although the number of segments is infinite and their size approaches zero, the overall polymer dimension, given by its radius-of-gyration $R_g$ is finite, and enables a direct comparison with data from computer simulations of finite-size polymer chains. This simple chain model gives a very rough description of the liquid on the local segment scale, since it completely averages out solvation shells in the pair distribution function. However, this approximated description of the local structure becomes correct in the limit of long polymer chains, where the fine structure of the distribution function does not appear.

The thread model is the analog of the model investigated in field theory approaches. Although analytically tractable, it has proven to be quite successful in describing properties of polymer melts, block copolymers, and blends. The main reason for its success is that it correctly captures the onset of “correlation hole” effects in the monomer pair distribution functions at the lengthscale of the overall polymer size $R_g$. The presence of the “correlation hole” is a trademark of polymer fluid structure and governs the physics of the system at the chain lengthscale. Since our mesoscopic description of polymer liquids $R_g$ is the lengthscale of interest, the thread model appears to be adequate for the purpose of the theory developed here.

We start from a binary blend of $A$ and $B$ homopolymers, having degrees of polymerization $N_A$ and $N_B$, and unit lengths $\sigma_A$ and $\sigma_B$, respectively. The polymer volume fraction is $\phi = n_A N_A / (n_A N_A + n_B N_B)$, where $n_A$ is the...
number of molecules of type \( A \) in the mixture. Non-bonded interactions are quantified by the single \( \chi \) parameter which describes the “monomer” interchange energy for the blend. The generalized Ornstein-Zernike (OZ) matrix relation for total site-site correlation functions of a binary fluid mixture in Fourier space is

\[
\mathbf{H}(k) = \Omega(k)\mathbf{C}(k)\left[\Omega(k) + \mathbf{H}(k)\right],
\]

where the matrices in Eq. (11) are block matrices of rank 2. Here, \( H_{\alpha\beta}(k) \), \( C_{\alpha\beta}(k) \), and \( \Omega_{\alpha\beta}(k) \) are Fourier transforms of the corresponding correlation functions; for example,

\[
H_{\alpha\beta}(k) = \frac{4\pi}{k} \int_0^\infty r H_{\alpha\beta}(r) \sin(kr) dr.
\]

In real space, \( H_{\alpha\beta}(r) = \rho_\alpha \rho_\beta h_{\alpha\beta}(r) \) is the (chain-averaged) site-site total distribution function matrix; \( C_{\alpha\beta}(r) \) is the intermolecular direct correlation function matrix; and \( \Omega_{\alpha\beta}(r) = \rho_\alpha \omega_\alpha(r) \delta_{\alpha\beta} \) is the intrachain structure factor matrix, with \( \alpha, \beta \in \{A, B\} \) and \( \rho_\alpha = n_\alpha N_\alpha / V \) the number density of monomers \( \alpha \) inside volume \( V \). The site averaged intrachain correlations are described by the Padé approximant to the Debye function (which introduces only a 15% maximum error to the exact expression [31])

\[
\omega_\alpha(k) \approx \frac{N_\alpha}{1 + k^2 R_{\alpha\alpha}^2 / 2}.
\]

Although approximated, Eq. (3) enables an analytically tractable solution to the intermolecular c.o.m.c.o.m. potential, which is the ultimate goal of the theory developed. Moreover, the use of the Padé approximant gives good agreement with simulations for the total pair distribution function in both real and reciprocal spaces [23]. Agreement between the Debye and the Padé forms improves as \( N \) increases.

Partial structure factors are derived from Eq. (11) and \( S(k) = \Omega(k) + \mathbf{H}(k) \) as

\[
S_{AA}(k) = \rho \omega_A(k)(1 - \rho (1 - \phi) \omega_B(k))/\Lambda(k)
\]

\[
S_{BB}(k) = \rho (1 - \phi) \omega_B(k)(1 - \rho \phi \omega_A(k))/\Lambda(k)
\]

\[
S_{AB}(k) = \rho^2 \phi (1 - \rho) \omega_A(k) \omega_B(k) C_{AB}(k)/\Lambda(k)
\]

with \( \rho \) the total segment number density of the blend and

\[
\Lambda(k) = 1 - \rho \phi \omega_A(k) C_{AA}(k) - \rho (1 - \phi) \omega_B(k) C_{BB}(k) + \rho^2 \phi (1 - \rho) \omega_A(k) \omega_B(k) [C_{AA}(k) C_{BB}(k) - C_{AB}^2(k)].
\]

The direct correlation function \( C_{\alpha\beta}(k) \) represents the fluid-averaged intermolecular pair potential, which is short-ranged or independent of \( k \) for \( k \sigma \ll 1 \). Since the lengthscale of interest for a mesoscopic description (\( R_g \)) is larger than \( \sigma \), the direct correlation function can be assumed to be independent of \( k \),

\[
C_{\alpha\beta}(k) \approx C_{\alpha\beta}(k = 0) = C_0^{\alpha\beta} - \epsilon_{\alpha\beta} / \rho.
\]

The first term in Eq. (6), \( C_0^{\alpha\beta} < 0 \), is the hard core repulsion of particles at direct contact (the potential \( (k_B T)^{-1} v(r) \approx -C(r) \)), while the second term, \( \epsilon_{\alpha\beta} / \rho < 0 \), defines the “tail” interaction potential between species \( \alpha \) and \( \beta \). \( C_0^{\alpha\beta} \) governs the pure athermal packing of monomers in the blend, so it contains the entropic contribution that can lead to demixing in the high-temperature region. Consistently with the thread model we assume that the hard core components of the direct correlation function become \( C_0^{\alpha\beta} \approx C_0 \) for any combination of \( A \) and \( B \). Introducing Eq. (6) and Eq. (7) in Eqs. (11) enables the factorization of partial structure factors into two separate contributions related to density and concentration fluctuations

\[
S_{AA}(k) \approx \frac{12 \rho \phi^2}{\sigma_{AB}^2} \left( \frac{1 - \phi}{\phi} \frac{1}{k^2 + \xi_\phi^2} + \frac{\gamma^2}{k^2 + \xi_\rho^2} \right)
\]

\[
S_{BB}(k) \approx \frac{12 \rho (1 - \phi)^2}{\sigma_{AB}^2} \left( \frac{\phi}{1 - \phi} \frac{1}{k^2 + \xi_\phi^2} + \frac{\gamma^{-2}}{k^2 + \xi_\rho^2} \right)
\]

\[
S_{AB}(k) \approx \frac{12 \rho \phi (1 - \phi)}{\sigma_{AB}^2} \left( -\frac{1}{k^2 + \xi_\phi^2} + \frac{1}{k^2 + \xi_\rho^2} \right),
\]
where $\sigma_{AB}^2 = \phi \sigma_B^2 + (1 - \phi) \sigma_A^2$. Density fluctuations are characterized by the correlation length

$$\xi_\rho^2 = -12 \rho C_0 \left[ \frac{\phi}{\sigma_A^2} + \frac{1 - \phi}{\sigma_B^2} \right].$$

(8)

Concentration fluctuations follow an incompressible-like relation $S_{AA} = S_{BB} = -S_{AB}$, and are characterized by the correlation length

$$\xi_\phi = \frac{\sigma_{AB}}{\sqrt{24} \phi (1 - \phi)(\chi_s - \chi)} = \frac{\xi_{cA}}{\sqrt{1 - \chi/\chi_s}} \frac{\sqrt{1 - \phi + \phi \gamma^2}}{\sqrt{1 - \phi + \phi \mu}},$$

(9)

which diverges at the spinodal temperature. Here, $\chi/\rho$ is the analog of the Flory-Huggins interaction parameter given by $\chi = \epsilon_{AB} - (\epsilon_{AA} + \epsilon_{BB})/2$. At the spinodal temperature $\chi \rightarrow \chi_s$, where $\chi_s = \{2N_A \phi\}^{-1} + \{2N_B (1 - \phi)\}^{-1}$. The ratio between $A$ and $B$ chain lengths is given by $\mu = N_A/N_B$, while $\gamma = \sigma_B/\sigma_A$ defines the ratio of local stiffness between species $A$ and $B$. Since the definition of $\gamma$ is arbitrary, for convenience we assume that the stiffest component in the mixture is $B$. Also,

$$\xi_{ca} = R_{go}/\sqrt{2},$$

(10)

is the correlation hole lengthscale for polymer $\alpha$. Eq. (9) implies that asymmetry in the segment length between two components ($\gamma \neq 1$) increases the range of concentration fluctuations.

The total site-site correlation function is derived from the partial structure factors as

$$\rho^2 \phi^2 h_{AA}^{mm}(k) = S_{AA}(k) - \rho \phi \omega_A(k)$$

$$\rho^2 (1 - \phi)^2 h_{BB}^{mm}(k) = S_{BB}(k) - \rho (1 - \phi) \omega_B(k)$$

$$\rho^2 \phi (1 - \phi) h_{AB}^{mm}(k) = S_{AB}(k),$$

(11)

where we introduced the label $mm$ to distinguish monomer correlation functions from those of the c.o.m., which are derived in Section III. Eqs. (11) reduce in real space to the generalized thread expressions for the monomer pair distribution functions of asymmetric polymer blends

$$h_{AA}^{mm}(r) = \frac{3}{\pi \rho r \sigma_{AB}^2} \left[ \frac{1 - \phi}{\phi} e^{-r/\xi_\rho} + \gamma^2 e^{-r/\xi_\phi} - \frac{1}{\phi} \frac{\sigma_{AB}^2}{\sigma_A^2} e^{-r/\xi_{cA}} \right],$$

$$h_{BB}^{mm}(r) = \frac{3}{\pi \rho r \sigma_{AB}^2} \left[ \frac{\phi}{1 - \phi} e^{-r/\xi_\rho} + \gamma^2 e^{-r/\xi_\phi} - \frac{1}{\phi} \frac{\sigma_{AB}^2}{\sigma_B^2} e^{-r/\xi_{cB}} \right],$$

$$h_{AB}^{mm}(r) = \frac{3}{\pi \rho r \sigma_{AB}^2} \left[ -e^{-r/\xi_\rho} + e^{-r/\xi_\phi} \right].$$

(12)

Eqs. (12) describe the distribution of elementary units in a binary blend as a function of the intramolecular structure and thermodynamical parameters. In these expressions, the three lengthscales of interest $\xi_\rho$, $\xi_\phi$, and $\xi_{cA}$ appear uncoupled. Even in the athermal regime where $\chi \ll \chi_s$, the mismatch in size ($\mu \neq 1$) and/or in local semiflexibility ($\gamma \neq 1$) between the two components can lead to non-uniform mixing, corresponding to $h_{AA}(r) \neq h_{BB}(r) \neq h_{AB}(r)$. However, if the system is totally symmetric ($N_A = N_B$ and $\sigma_A = \sigma_B$), Eqs. (12) recover the PRISM equations for a totally symmetric blend, which for athermal conditions recover the melt thread-model equation.

The equations just derived cannot be compared directly with simulation data of monomer pair distribution functions since the thread model does not describe the presence of solvation shells in $g(r) = h(r) + 1$ as observed in simulations. However, a good estimate for the accuracy of the derived expressions can be achieved by comparing with simulations the number of particles included within a sphere of radius $r$, as

$$n_\beta(r) - \delta_{\alpha \beta} = 4\pi \rho_\beta \int_0^r r'^2 g_{\alpha \beta}(r) dr$$

(13)

with $\rho_\beta \in \{\phi \beta, (1 - \phi) \rho \}$ for $\beta \in \{A, B\}$, respectively. Tests of our monomer pair distribution functions are data from UA-MD computer simulations. The simulation procedure has been described in detail in recent papers and will not be discussed here. Systems investigated are blends of isotactic polypropylene (iPP), head-to-head polypropylene (hhPP), polyisobutylene (PIB), syndiotactic polypropylene (sPP), and polyethylene (PE). Simulations and blend parameters are described in the Table.

In the simplified theoretical framework of the previous section, we enforced the limit of large polymer chains, which leads to a single value for the density fluctuation lengthscales, independent of the blend component. Here we
re-introduce finite-size effects, local semiflexibility, and branching, which are specific to each component, through a melt-like description of the local density fluctuation lengthscale as \( \xi_{\rho\alpha}^{-1} = \pi \rho \sigma_{\alpha}^2 / 3 + \xi_{\rho\alpha}^{-1} \) and \( \alpha \in \{A, B\} \). For the cross pair distribution, we have \( \xi_{\rho\alpha\beta}^{-1} = \pi \rho \sigma_{\alpha\beta}^2 / 3 + \xi_{\rho\alpha\beta}^{-1} \). The statistical segment length is calculated from the polymer radius of gyration as \( \sigma_A = R_A \sqrt{6/N_A} \) and \( \sigma_B = R_B \sqrt{6/N_B} \). These formulas hold in the limit of long flexible chains obeying Gaussian statistics. Systems investigated here include linear and branched polyelectrolytes with small, densely-packed pendant groups. It is known that, in general, highly branched polyelectrolytes are more flexible than their linear counterparts having the same degree of polymerization. Moreover, blends of polymers with closely-spaced and/or small-sized pendant groups are characterized by less efficient local packing of units. These effects produce a locally-disordered liquid, consistent with the “random packing” of a Gaussian chain and with the smooth shape of the thread monomer distribution function adopted here.

Most blends considered in the simulations are far from their critical temperature. For some samples, an equation for the \( \chi \) parameter is reported in the literature, as summarized in the Table, and has been used here for the calculation of the concentration fluctuation correlation length. However, the size of effective sites considered in the analysis of the experimental data is in general different for the two components, \( \sigma_A \neq \sigma_B \). In these cases we normalize the value of \( \chi \) by the average number of sites per monomer so as to be consistent with the Flory-Huggins spinodal equation adopted here.

To describe samples for which an equation of \( \chi \) is unknown, we perform calculations in the athermal limit \( (\chi \ll \chi_s) \) where concentration fluctuations are minimized. Most of the blends considered here have cross contributions \( AB \) which could be approximated fairly well by an arithmetic or a geometric average of the self terms, \( AA \) and \( BB \). This is a characteristic of homogeneous liquids, and for blends it occurs in the athermal regime where the components are randomly mixed (if entropic packing effects are not dominant).

Using the procedure just described, we calculated the number of units included in a sphere of radius \( r \) around a tagged polymer \( \alpha \). The theory shows good agreement with simulation data already at an intermolecular distance of a few site lengths (Fig.1). While the thread model cannot reproduce simulation data for \( r \to 0 \), it correctly describes the average liquid structure at intermediate and large \( (R_g) \) lengthscales, which are the lengthscales of interest in our mesoscopic description. We observe that the specific PRISM thread model adopted here tends to overestimate the number of self and cross contacts. For a UCST blend, the self-correlation functions \( AA \) and \( BB \) are best described by the equations in athermal conditions \( (\chi_i << \chi_{is}) \), while the cross-correlation contribution \( AB \) is best represented by the equation in thermal conditions. These trends are visible also in c.o.m. total pair distribution functions presented in Section VI, a feature that appears to depend on the choice of monomer pair distribution functions.

### III. CENTER-OF-MASS SOFT-CORE POTENTIAL IN POLYMER BLENDS

To derive an analytical expression for the c.o.m. intermolecular distribution functions in a polymeric mixture, we extend to polymer blends a procedure outlined by Krakoviack, Hansen, and Louis for homopolymer solutions. While the contribution due to real sites (monomers or effective units) is averaged in the usual PRISM-like fashion, the c.o.m. is included in the OZ relation given by Eq. (11) as an effective “auxiliary” site. For a binary fluid mixture, the matrices in Eq. (11) become block matrices of rank 4. We define the site-site total distribution function matrix as

\[
H(k) = \begin{bmatrix}
H_{mm}(k) & H_{mC}(k) \\
H_{Cm}(k) & H_{CC}(k)
\end{bmatrix},
\]

(14)

In real space \( H_{\alpha\beta}(r) = \rho_\alpha \rho_\beta h_{\alpha\beta}^{cm}(r) \) is the (chain-averaged) site-site total distribution function matrix; \( H_{mC}(r) = \rho_\alpha \rho_{ch,\beta} h_{mC}^{ch}(r) \) and \( H_{Cm}(r) = \rho_{ch,\alpha} \rho_\beta h_{Cm}^{ch}(r) \) are the site-c.o.m. total distribution functions where \( \rho_{ch,\alpha} \) is the number density of chains of species \( \alpha \); finally, \( H_{CC}(r) = \rho_{ch,\alpha} \rho_{ch,\beta} h_{C\beta}(r) \) is the c.o.m.-c.o.m. total distribution function matrix. The direct correlation function matrix,

\[
C(k) = \begin{bmatrix}
C_{mm}(k) & 0 \\
0 & 0
\end{bmatrix},
\]

(15)

includes the condition that direct correlation functions between auxiliary and real sites as well as between two auxiliary sites are negligible, while the “monomer” direct correlation functions are defined in Eq. (10). The intramolecular distribution function matrix is given by

\[
\Omega(k) = \begin{bmatrix}
\Omega_{mm}(k) & \Omega_{mC}(k) \\
\Omega_{Cm}(k) & \rho_{ch}
\end{bmatrix},
\]

(16)
functions between the c.o.m. of two chains in the mixture.

Here a compact notation with the function \( I \) various structure factor \( \alpha \) with \( I \) another structure factor \( \omega \). Eq. (17) formally connects c.o.m. distribution functions to the “monomer” intra- and intermolecular distribution functions, so that it is possible to calculate mesoscale properties from monomeric-scale information. For the intramolecular structure factor \( \omega_{\alpha}^{mm}(k) \), we adopt the Gaussian intrachain distribution of Eq. (3). The “monomer”-c.o.m. intramolecular structure factor \( \omega_{\alpha}^{mC}(k) \), can be approximated well in \( k \)-space by a Gaussian distribution as

\[
\omega_{\alpha}^{mC}(k) = N_{\alpha}e^{-k^2R^{2}/6},
\]

with \( \alpha \in \{A,B\} \). Including Eqs. (13,18) into Eqs. (17) yields the following expressions for the total correlation functions between the c.o.m. of two chains in the mixture.

\[
h_{\alpha\alpha}(r) = \frac{1 - \phi}{\phi} I_{\alpha\alpha}^0(r) + \gamma I_{\alpha\alpha}^0(r),
\]

\[
h_{BB}(r) = \frac{\phi}{1 - \phi} I_{BB}^0(r) + \gamma^{-2} I_{BB}^0(r),
\]

\[
h_{AB}(r) = -I_{AB}^0(r) + I_{AB}^0(r),
\]

where \( I_{\alpha\beta}^0(r) \) and \( I_{\alpha\beta}^0(r) \) identify the concentration and density fluctuation contributions, respectively. We introduce here a compact notation with the function \( I_{\alpha\beta}^0(r) \) defined as

\[
I_{\alpha\beta}^0(r) = \frac{3}{4} \sqrt{\frac{3}{\pi}} \frac{\xi^\prime}{R_{\alpha\beta}} \varphi_{\alpha\beta} \left( \frac{R_{\alpha\beta}}{\xi^\prime \sqrt{3}} + \frac{r \sqrt{3}}{2R_{\alpha\beta}} \right) e^{-r/\xi^\prime} \text{erfc} \left( \frac{R_{\alpha\beta}}{\xi^\prime \sqrt{3}} - \frac{r \sqrt{3}}{2R_{\alpha\beta}} \right)
\]

(23)

and

\[
\varphi_{\alpha\beta} = \frac{1 - \xi^2_{\alpha\beta} / \xi^2}{1 - \xi^2 / \xi^2},
\]

(24)

where \( \xi \in \{\xi, \xi^\prime\} \) and \( \xi^\prime = 3/(\pi \rho \sigma^2_{AB}) \). Radii of gyration in the blend are defined as \( R_{\alpha\beta} = \sqrt{(R_{\alpha}^2 + R_{\beta}^2)/2} = \xi_{\alpha\beta} \sqrt{2} \) so that, for example, if \( \alpha = \beta = A \) then \( R_{AA} = R_{gA} = \xi_{A} \sqrt{2} \) as in Eq. (16).

Eqs. (19) can be further simplified in particular cases. For example, the density fluctuation contribution in both self terms is formally identical to the total distribution function between the c.o.m. of two interacting polymers in a melt

\[
I_{\alpha\beta}^0(r) = h(r) = \frac{3}{4} \sqrt{\frac{3}{\pi}} \frac{\xi^\prime}{R_{\alpha\beta}} \left( 1 - \xi^2 / \xi^2 \right) e^{-3r^2/(4R_{\alpha\beta}^2)} - \frac{1}{2} \frac{\xi^\prime}{R_{\alpha\beta}} \left( 1 - \xi^2 / \xi^2 \right)^2 \text{erfc} \left( \frac{R_{\alpha\beta}}{\xi^\prime \sqrt{3}} - \frac{r \sqrt{3}}{2R_{\alpha\beta}} \right)
\]

(23)

\[
\times \left[ e^{r/\xi^\prime} \text{erfc} \left( \frac{R_{\alpha\beta}}{\xi^\prime \sqrt{3}} + \frac{r \sqrt{3}}{2R_{\alpha\beta}} \right) - e^{-r/\xi^\prime} \text{erfc} \left( \frac{R_{\alpha\beta}}{\xi^\prime \sqrt{3}} - \frac{r \sqrt{3}}{2R_{\alpha\beta}} \right) \right].
\]
This expression can be reduced to a more compact form in the limit of large molecules \((N \rightarrow \infty)\) by expanding the total correlation function as a function of the vanishing parameter \(\xi_\rho/R_g \rightarrow 0\)

\[
h(r) \approx -\frac{39\sqrt{3} \xi_\rho}{16 \sqrt{\pi} R_g} \left(1 + \frac{\xi_\rho}{\xi_c} \right) \left[1 - \frac{9r^2}{26R_g^2} \right] e^{-3r^2/(4R_g^2)} = I^p(r, \xi_\rho/R_g \rightarrow 0). \tag{24}
\]

Since our initial equations of intra- and intermolecular structure factors rely on the assumption of Gaussian-chain statistics, a condition which formally holds only for polymer chains of infinite length, Eq.(24) is entirely consistent with the general description of our system and can be adopted in general for \(N \geq 30\).

The density fluctuation contribution due to cross interactions \(AB\) cannot be simplified to the melt expression, unless the blend is totally symmetric (\(\sigma_A = \sigma_B\) and \(N_A = N_B\)) or only slightly asymmetric. In the totally symmetric case, \(I^p_{AA} = I^p_{BB} = I^p_{AB} = h(r)\). If the system is only slightly asymmetric, the condition \(\vartheta_{AB1} \approx \vartheta_{AB2}\) is still fulfilled, but only for large chains \((N \geq 30)\) and \(\mu = 0.1 - 2\) while \(1 \leq \gamma \leq 2\). For this case, Eqs.(19) simplify to

\[
I^p_{\alpha\beta}(r) \approx \vartheta_{\alpha\beta1} I^p(r, \xi_\rho/R_{g\alpha\beta} \rightarrow 0), \tag{25}
\]

with \(I^p(r, \xi_\rho/R_{g\alpha\beta} \rightarrow 0)\) defined by Eq.(24).

For the concentration fluctuation term, the problem is further complicated by the fact that the functions in Eqs.(19) depend not only on the parameter \(\xi_\rho/R_g \rightarrow 0\), but also on the additional parameter \(\xi_\phi/R_g\) which does not approach zero either in the athermal \((\xi_\phi \rightarrow \xi_c \approx R_g)\) or in the spinodal \((\xi_\phi \rightarrow \infty)\) regions. However, at the spinodal, where the concentration fluctuation lengthscale diverges, the expansion of \(I^\phi_{\alpha\beta}(r)\) in the limit of \(R_{g\alpha\beta}/\xi_\phi \rightarrow 0\) yields:

\[
I^\phi_{\alpha\beta}(r) \approx \frac{\xi_\rho'}{R_{g\alpha\beta}} \left[3 \sqrt{3} \frac{\sqrt{3} e^{-3r^2/(4R_{g\alpha\beta}^2)}}{\pi} + \frac{R_{g\alpha\beta}}{r} \operatorname{erf}\left(\frac{\sqrt{3}}{2} \frac{r}{R_{g\alpha\beta}}\right) - \frac{R_{g\alpha\beta}}{\xi_\phi} + O\left(\frac{R_{g\alpha\beta}^2}{\xi_\phi^2}\right)\right], \tag{26}
\]

where we used the fact that \(\lim_{\xi_\phi \rightarrow \infty} \vartheta_{\alpha\beta i} = 1\) with \(i \in \{1, 2\}\). The first two terms on the r.h.s. of Eq.(26) describe the spinodal decomposition and correspond to the maximum possible contribution to the pair distribution functions due to concentration fluctuations. When the system approaches its spinodal decomposition, contributions in \(R_{g\alpha\beta}/\xi_\phi\) become increasingly small in magnitude, to the point of no longer compensating the first two contributions on the r.h.s. of the equation. In the self terms of the total correlation function, this phenomenon manifests itself as an overshoot in the function, which corresponds to clustering of like species, or attractive interactions between molecules of the same type. Meanwhile, the cross correlation decreases, showing the beginning of phase separation (refer to model calculations in Sec. VI).

In the athermal limit where \(\chi/\chi_s \rightarrow 0\), if the blend is asymmetric, entropic contributions can induce demixing for the mesoscale liquid structure both through density and concentration fluctuation contributions. However, if the blend is symmetric (\(\sigma_A = \sigma_B\) and \(N_A = N_B\)), only density fluctuation contributions \((I^p)\) govern the properties of the mixture, and \(I^\phi_{AA} = I^\phi_{BB} = I^\phi_{AB} = 0\). For symmetric blends, the total correlation functions recover the expression for the melt correlation function.

\section{IV. CHAIN-OVERLAP AND INTERMOLECULAR MEAN-FORCE POTENTIAL}

The overlap value of intermolecular total pair distribution functions provides information on the degree of interpenetration between two chains as a function of monomer density, temperature, blend composition, chain degree of polymerization, and asymmetry ratios (\(\gamma\) and \(\mu\)). In general, the intermolecular potential of mean force for two particles in a liquid is given by \(W_{\alpha\beta}(r) = -k_B T \ln g_{\alpha\beta}(r) \approx -k_B T h_{\alpha\beta}(r)\). For polymer melts, the (repulsive) potential at contact \(W(0)\) is known to decrease with increasing degree of polymerization, increasing density, or increasing polymer stiffness.\cite{13,20} For polymer blends, the situation is more complex since the mismatch in local structure and chain length between the two components can give relevant concentration fluctuation contributions even in the athermal regime.

At contact, the blend density fluctuation term is similar to the melt case. In the limit \(r \rightarrow 0\) and \(N \rightarrow \infty\), Eq.(23) reduces to

\[
\lim_{r \rightarrow 0} I^\rho_{\alpha\beta}(r) \approx -\frac{39}{16} \sqrt{\frac{3}{\pi}} \frac{3}{\rho_\alpha\beta R_{g\alpha\beta}} = I^\rho(0, \xi_\rho/R_{g\alpha\beta} \rightarrow 0) \tag{27}
\]

with \(\vartheta_{\alpha\beta i} = 1\) and \(i \in \{1, 2\}\). Eq.(27) is valid for self correlation functions, and for the cross correlation functions if the system is symmetric or slightly asymmetric. The concentration fluctuation term in the limit \(r \rightarrow 0\) also simplifies.
to
\[
\lim_{r \to 0} I_{\alpha,\beta}^\phi(r) = \frac{3}{4} \sqrt{\frac{3}{\pi}} \frac{3}{\pi \rho \sigma_{AB}^2 R_{\alpha,\beta}} \left( 1 - \frac{\xi_{\alpha,\beta}^2}{\xi_\phi^2} \right) + \\
+ \frac{3}{\pi \rho \sigma_{AB}^2 R_{\alpha,\beta}} \left( 1 - \frac{\xi_{\alpha,\beta}^2}{\xi_\phi^2} \right)^2 \left[ \sqrt{\frac{3}{\pi}} R_{\alpha,\beta}^2 e^{\frac{R_{\alpha,\beta}^2}{3 \xi_\phi^2}} \text{erfc} \left( \frac{1}{\sqrt{3}} R_{\alpha,\beta} / \xi_\phi \right) \right].
\]

(28)

Summarizing, the total correlation functions at contact for structurally symmetric \((\vartheta_{AB1} = 1)\) and slightly asymmetric \((\vartheta_{AB1} \approx 1)\) polymer blends are written in short-hand notation as
\[
\begin{align*}
\lim_{r \to 0} h_{AA}(r) &\approx \frac{1}{\varphi} I_{AA}^\phi(0) + \gamma^2 I^\rho(0, \xi_\rho / R_{gAA} \to 0), \\
\lim_{r \to 0} h_{BB}(r) &\approx \frac{1}{\varphi} I_{BB}^\phi(0) + \gamma^{-2} I^\rho(0, \xi_\rho / R_{gBB} \to 0), \\
\lim_{r \to 0} h_{AB}(r) &\approx -I_{AB}^\phi(0) + \vartheta_{AB1} I^\rho(0, \xi_\rho / R_{gAB} \to 0).
\end{align*}
\]

(29)

For both density and concentration fluctuation contributions, each total distribution function at contact depends on density, stiffness, and degree of polymerization \((I^\rho, I^\sigma, I^\lambda)\). Essentially recovering the melt behavior: an increase in polymer-polymer contact is observed with increasing degree of polymerization \((R_g)\), stiffness \((\sigma\) and \(R_g)\), and liquid density \((\rho)\).

V. MAPPING BLEND CORRELATION FUNCTIONS ONTO A MESOSCOPIC SOFT-COLLOIDAL DESCRIPTION

Our analytical c.o.m. correlation functions effectively map a polymer blend onto a fluid of interacting soft-colloidal particles. To test the quality of our renormalized description we compare its predictions with known properties of colloidal mixtures.

At the mesoscale, a polymer blend is a two-component mixture of colloidal particles of type \(A\) and \(B\) with volume fraction \(\phi = n_A/(n_A + n_B)\), total density \(\rho_{ch} = \rho / N\), and particle size \(R_{gA}\) and \(R_{gB}\). When species \(A\) is chosen to be our reference system, the size mismatch parameter is \(\gamma = R_{gB}/R_{gA}\), and the reduced chain density is \(\rho_{ch} = \rho_{ch} R_{gA}^3\). This renormalized description can be formally obtained from Eqs. (17) by setting the effective number of statistical segments in the two components to be equal, \(N_A = N_B = N\), while the chain asymmetry is completely accounted for by the different statistical segment lengths \(\sigma_A' = R_{gA} \sqrt{6 / N}\) and \(\sigma_B' = R_{gB} \sqrt{6 / N}\). Each effective segment includes the effect of branching and chain semiflexibility, and must be equal or larger than its polymer persistence length, a condition fulfilled by long semiflexible chains.

It is convenient to define universal renormalized quantities which simplify the final equations. The normalized density fluctuation correlation length is \(\hat{\xi}_\rho = \xi_\rho / R_{gA}\), the normalized concentration fluctuation correlation length is \(\hat{\xi}_\phi = \xi_\phi / R_{gA}\), and the normalized concentration fluctuation correlation length is \(\hat{\xi}_\phi = \xi_\phi / R_{gA} = \{[1 - \phi(1 - \gamma^2)]/[2(1 - \chi / \lambda_A)]\}^{1/2}\), and \(\hat{\xi}_\rho = \xi_\rho / R_{gA} = \{2\pi \rho_{ch}[\phi + (1 - \phi) \gamma^2]\}^{-1}\). The total pair distribution functions Eqs. (20) now depend only on mesoscopic reduced variables, including the space coordinate \(\tilde{r} = r / R_{gA}\) as
\[
I_{\alpha,\beta}^\phi(\tilde{r}) = \frac{3}{4} \sqrt{\frac{3}{\pi}} \frac{3}{\pi \rho_a^2} \left( 1 - \frac{a^2}{2 \xi_{\lambda,\beta}^2} \right) b_1 e^{-3 \tilde{r}^2/(4a^2)} - \frac{1}{2} \tilde{\xi}_\rho b_2 e^{a^2/(3 \xi_{\lambda,\beta}^2)}
\times \left[ e^{\tilde{r} / \xi_\lambda \text{erfc} \left( a / \xi_\lambda \sqrt{3} \right)} + e^{-\tilde{r} / \xi_\lambda \text{erfc} \left( a / \xi_\lambda \sqrt{3} \right)} \right],
\]

(30)

where \(\tilde{\xi}_\lambda \in \{\tilde{\xi}_\rho, \tilde{\xi}_\phi\}\). Here \(a = 1\) if \(\alpha = \beta = A\), \(a = \gamma\) if \(\alpha = \beta = B\), and \(a = \sqrt{(1 + \gamma^2)/2}\) for the cross terms. Also \(b_1 = b_2 = 1\) for the self terms, while for the cross terms
\[
b_1 = \frac{\xi_{\lambda,\beta}^2 - \gamma^2/(1 + \gamma^2)}{\xi_{\lambda,\beta}^2 - (1 + \gamma^2)/4},
\]

(31)

and
\[
b_2 = \frac{(2 \xi_{\lambda,\beta}^2 - 1)(2 \xi_{\lambda,\beta}^2 - \gamma^2)}{[2 \xi_{\lambda,\beta}^2 - (1 + \gamma^2)/2]^2}.
\]

(32)
To make contact with the theory of colloidal particle mixtures (e.g., liquid alloys) it is convenient to analyze the properties of the renormalized polymer blend in reciprocal space. The static structure factors for the mixture are defined as

\[ S_{AA}(k) = \phi + \phi^2 \rho_{ch} h_{AA}(k), \]
\[ S_{BB}(k) = 1 - \phi + (1 - \phi)^2 \rho_{ch} h_{BB}(k), \]
\[ S_{AB}(k) = \phi(1 - \phi) \rho_{ch} h_{AB}(k). \]  
(33)

Linear combinations of these functions describe fluctuations in number density and concentration, following Bhatia and Thornton’s formalism. The density fluctuation contribution (\(S^{NN}\) in the conventional notation for “metal alloys”) is given by

\[ S^{\rho\rho}(k) = S_{AA}(k) + S_{BB}(k) + 2S_{AB}(k), \]  
(34)

while the concentration fluctuation contribution (\(S^{CC}\)) is

\[ S^{\phi\phi}(k) = (1 - \phi)^2 S_{AA}(k) + \phi^2 S_{BB}(k) - 2\phi(1 - \phi) S_{AB}(k), \]  
(35)

and their coupling (\(S^{CN}\)) is

\[ S^{\rho\phi}(k) = (1 - \phi) S_{AA}(k) - \phi S_{BB}(k) + (1 - 2\phi) S_{AB}(k). \]  
(36)

Analytical formulas for Eqs. (34-36) follow closely the behavior in reciprocal space observed for colloidal mixtures. For example, \(S^{\rho\rho}(k)\) has a \(k\)-dependence similar to the static structure factor for a single-component liquid. However, since our colloids are soft and can interpenetrate, there is no formation of solvation shells in the mixture and \(S^{\rho\rho}(k)\) becomes a monotonically-increasing function of \(k\). \(S^{\phi\phi}(k)\) and \(S^{\rho\phi}(k)\) oscillate about the values \((1 - \phi)\) and zero, respectively, as observed in colloidal mixtures with oscillations becoming less pronounced in \(S^{\phi\phi}(k)\). A more intuitive picture of the density-concentration fluctuation coupling term can be established by rewriting it as

\[ S^{\phi\rho}(k) = \phi(1 - \phi) \rho_{ch} \int [P_A(r) - P_B(r)] \frac{\sin(kr)}{kr} 4\pi r^2 dr \]  
(37)

where \(P_\alpha(r) = (1 - \phi) g_{BA}(r) + \phi g_{AA}(r)\) is the probability of encountering particle clustering of species \(A\) or \(B\) around the colloid \(\alpha \in \{A,B\}\). In this way, the function \(S^{\phi\rho}(k)\) represents a measure of the difference in local clustering between species \(A\) and \(B\). Maxima and minima in the function point at lengthscales characterized by large asymmetry in the liquid structure due to the mismatch in particle size. If the two species are identical, the mixture is uniform and \(S^{\rho\phi}(k) = 0\) for any \(k\).

In the \(k \to 0\) limit, the density fluctuation contribution and its coupling with concentration fluctuations reduce to the simplified forms

\[ S^{\rho\rho}(0) = \frac{\xi_\rho^2}{\xi_{\rho A}^2} \phi \gamma^2 + 1 - \phi \phi^2, \]  
(38)

\[ S^{\rho\phi}(0) = \phi(1 - \phi) \frac{\gamma^2 - 1}{\gamma^2} \frac{\xi_\rho^2}{\xi_{\rho A}^2}, \]  
(39)

while the concentration fluctuation contribution is

\[ S^{\phi\phi}(0) = \frac{\phi(1 - \phi)}{1 - \chi_s/\chi} + \frac{\phi^2(1 - \phi)^2 (\gamma^2 - 1)^2}{\phi \gamma^2 + 1 - \phi \gamma^2} \frac{\xi_\rho^2}{\xi_{\rho A}^2}. \]  
(40)

For a blend of symmetric polymers, where \(R_{BA} = R_{AB}\) and \(\gamma = 1\), our equations become completely consistent with the theory for a mixture of symmetric colloidal particles; Eq. (39) simplifies to \(S^{\rho\phi}(0) = (\xi_\rho/\xi_{\rho A})^2\) the melt compressibility, \(S^{\rho\phi}(0) = 0\), and the concentration fluctuation contribution becomes

\[ S^{\phi\rho}(0) = \frac{\phi(1 - \phi)}{1 - 2\phi(1 - \phi) \Delta E}. \]  
(41)

Here we introduced Flory’s definition of the spinodal \(\chi_s\), and the renormalized \(\chi\) parameter for the coarse-grained polymer mixture \(\Delta E = N \chi = N \epsilon_{AB} - (N \epsilon_{AA} + N \epsilon_{BB})/2\). For long polymer chains or high density, Eqs. (38-39) vanish since \(\xi_\rho/\xi_{\rho A} \to 0\), while the concentration fluctuation contribution yields \(S^{\rho\phi}(0) = \phi(1 - \phi)/(1 - \chi_s/\chi).\)
In general, asymmetry between the two colloidal species is quantified by the dilution factor [26]

\[ \delta = \frac{v_A - v_B}{\phi v_A + (1 - \phi) v_B} = \frac{S^{\rho\phi}(0)}{S^{\phi\phi}(0)} = \frac{(\phi \gamma^2 + 1 - \phi)(\gamma^2 - 1)}{\phi(1 - \phi)(\gamma^2 - 1)^2 + \gamma^2 \xi_{\rho\rho}^2/\xi_{\rho}^2}. \]  

If the partial molar volumes per particle \( v_\alpha = (\partial V/\partial n_\alpha)_{n_\beta=n_\alpha, \rho, T} \) of the two species are identical (\( \delta = 0 \) and \( \gamma = 1 \)) there is no correlation between the fluctuations in particle number and concentration and \( S^{\rho\phi}(k) = 0 \). At the spinodal, \( S^{\phi\phi}(k) \) diverges and \( \delta \to 0 \).

The isothermal compressibility for a colloidal mixture is defined [26] as

\[ \rho_ch k_B T \kappa_T = S^{\rho\rho}(0) - \frac{S^{\rho\phi}(0)^2}{S^{\phi\phi}(0)} = S^{\rho\rho}(0) - \delta^2 S^{\phi\phi}(0). \]  

Here,

\[ \rho_ch k_B T \kappa_T = \frac{\xi_\rho^2}{\xi_{\rho\rho}^2} \frac{\phi \gamma^2 + 1 - \phi}{\gamma^2} \left[ 1 - \frac{(\gamma^2 - 1)^2 \phi(1 - \phi)}{\phi(1 - \phi)(\gamma^2 - 1)^2 + \gamma^2 \xi_{\rho\rho}^2/\xi_{\rho}^2} \right], \]  

recovers the melt compressibility when the system is composed of colloidal particles of identical size, \( \gamma = 1 \). The compressibility is slightly temperature-dependent through the correction contribution due to \( S^{\rho\phi}(0)/S^{\phi\phi}(0) \). The latter, however, is small for large polymer chains since it scales with degree of polymerization as \( N^{-1} \) in the athermal regime, and vanishes approaching the spinodal curve where the concentration correlation length diverges. This is true at any lengthscale and the \( k \)-dependent blend compressibility can be approximated by its first contribution \( S^{\rho\rho}(k) \) for the entire range of \( k \) and for blends of polymer chains with symmetric or asymmetric size, in agreement with colloidal particle mixtures (Fig.2).

### VI. CENTER-OF-MASS DISTRIBUTION FUNCTIONS: MODEL CALCULATIONS AND COMPARISON WITH UA-MD COMPUTER SIMULATIONS

In this section we present some predictions of our theoretical approach for the clustering and interpenetration of polymer chains in a blend as a function of chain length, semiflexibility, polymer volume fraction, and \( \chi \) dependence by model calculations. In our model calculations, unless otherwise specified, \( N_A = 500, \rho_m = 0.03 \text{ Å}^{-3} \), and \( \sigma_A = 3.0 \text{ Å} \). These parameters have been chosen to be consistent with the UA-MD simulations of polyolefin blends presented below. The chain length, however, has been chosen to be quite large to avoid finite-size effects which could veil the general trend of blend properties. Calculations performed “close to the spinodal condition” are for a \( \chi \) parameter which deviates 0.01% from \( \chi_s \).

As a first study, we look at a structurally symmetric blend for which \( \gamma = 1 \) and \( N_A = N_B \), while varying the blend composition \( \phi \in \{0.25, 0.50, 0.75\} \). In the athermal limit \( \chi \ll \chi_s \), all distribution functions become identical for any blend composition \( \phi \). However, when concentration fluctuations develop (Fig.3), we observe an enhanced clustering and increased number of self contacts in the minority (low \( \phi \)) species, which corresponds to a strong attractive interaction in the mean-force potential. The majority (high \( \phi \)) species increases the number of self-contacts, but still resembles in shape its athermal limit. This effect corresponds to the initial stage of droplet formation in the demixing of compositionally asymmetric mixtures. In general, the extent of demixing increases with increasing asymmetry in blend composition.

To investigate the effect of mismatch in chain flexibility, we analyze blends of polymers with identical degree of polymerization (\( N_A = N_B \)) where component \( A \) is flexible while the stiffness of component \( B \) is increasing (increasing \( R_{gB} \) and \( \gamma \in \{1.0, 1.2, 1.5\} \)). The data from UA-MD simulations analyzed subsequently in this paper (see Table) belong to this group. In general, we observe that an increase in \( \gamma \) enhances the number of \( BB \) and \( AB \) contacts and reduces the number of \( AA \) contacts (Fig.4). This effect is observed in both athermal and thermal mixtures. A stiff chain has a larger \( R_g \) than a flexible molecule with the same degree of polymerization. In this case, the number of chains that can occupy the volume spanned by the stiff component increases with increasing \( R_g \). Furthermore, stiff chains pack better at short distances due to geometric effects (stretched configurations enhance \( BB \) contacts), while flexible chains, which have a coiled configuration, tend to pack more efficiently at distances of order \( R_gA \). Overall, these two effects lead to an enhanced miscibility in mixtures of polymers with different flexibility and same degree of polymerization.
The potential of mean-force for chains of equal length is found to decrease with increasing degree of polymerization in agreement with computer simulations.\cite{16, 18} The effect of mismatch in chain length for polymer species having the same semiflexibility is studied using a blend of polymers with $N_A = 500$ fixed and $N_B \in \{250, 500, 1000\}$, corresponding to $\mu \in \{0.5, 1.0, 2.0\}$ (Fig.5). Analogous effects are observed in both the athermal and the thermal limits. In the athermal limit, the mismatch in chain size prevents the random mixing of the two components and “entropic” effects appear. Trivially, as the $R_g$ of the $B$ component increases the number of chains that can interpenetrate in the volume spanned by $B$ increases. This leads to a larger number of intermolecular contacts for all pair distribution functions $AA$, $BB$, and $AB$. This simple trend is combined with a more subtle behavior: a mismatch in chain length favors interpenetration between different species, so that the number of $AB$ contacts is always higher than the number of $AA$ and $BB$ contacts except for chains of the same length. This property becomes more pronounced when the difference in chain length increases. Also, short flexible chains tend to pack efficiently on the scale of their $R_g$, while these effects are averaged out in large flexible chains, where “solvation shells” do not appear (a behavior analogous to the monomer distribution functions). Our theoretical predictions are in qualitative agreement with off-lattice Monte Carlo simulations of polymer solutions.\cite{16}

To investigate in more detail these effects, we analyze polymer blends which have constant $R_{gA}$ and $R_{gB}$. The change in chain length in the $B$ component is correlated with a change in semiflexibility. For example, the $A$ component is mixed with the component $B$, which is both shorter and stiffer than $A$ ($\mu = 2.00$ and $\gamma = 1.88$), or with a chain $B$ larger than $A$ but with comparable flexibility ($\mu = 0.66$ and $\gamma = 1.09$). In analogy with our previous observation, we see (Fig.6) that stiff chains tend to pack more efficiently than flexible ones at short distances, increasing in this way the number of $BB$ and $AB$ contacts. As a consequence, the number of $AA$ contacts in a mixture of stiff $B$ chains is decreased with respect to the mixture of flexible polymers. Close to the spinodal, flexible chains ($A$ and $B$) are in coiled configurations which tend to pack more efficiently at the distance of their $R_g$. Stiff chains, instead, tend to interpenetrate more efficiently and the number of $BB$ contacts strongly increases in the mixture containing short and stiff $B$ chains.

Next, we compare our analytical expressions against data from UA-MD simulations of polymer blends described in the Table.\cite{13, 14} For each blend considered, the theory agrees with simulation data fairly well. However, we present here only few systems which are representative of our calculations. Input parameters to the theory and the procedure used in the calculations were discussed in Section II.

The c.o.m. total correlation function provides an estimate of the number of molecules interpenetrating at some relative distance $r$. In all the plots (Fig.7) we observe that chains of the stiffest component ($B$), which have extended configurations, tend to pack at short distances $r < R_{gB}$ more efficiently than flexible ones. Flexible molecules, which have coiled configurations, show a high (low) number of “intramolecular” (intermolecular) contacts and pack most efficiently at distances on the order of the overall polymer size, $r \approx 1.5R_{gA}$. The extent of intermolecular chain packing upon blending also depends on polymer flexibility. The theory predicts that the stiff (flexible) component packs better (worse), and the number of self contacts increases (decreases) when mixed with a more flexible (stiffer) polymer, in agreement with simulations.\cite{12}

In general, the agreement between theory and simulations is good with the exception of the PIB/hhPP and PIB/iPP blends for which agreement is only qualitative. For these systems the theory overestimates the number of intermolecular contacts. However, it is well known that PIB blends are usually immiscible blends at these temperatures and for these chain lengths.\cite{14, 15} PIB exhibits very efficient intra- and intermolecular packing which leads to a thermal expansion coefficient and an isothermal compressibility smaller than in other polyolefin blends.\cite{13} This behavior is due to strong attractive interactions between the methyl (–CH$_3$) groups, which in PIB molecules are in very large number (about 50% of the total number of united atoms).\cite{8} However, even for PIB blends, the theory shows very good agreement with simulation data for $r \approx R_g$.

Finally, in Fig.8 we show how the theory can predict the correct qualitative behavior for blends following a LCST phase diagram. At high temperature the blend demixes and shows a distribution function for the $AB$ component that is consistently lower than the $AA$ and the $BB$ contributions. At low temperature, instead, the mixing of the $A$ and $B$ species is enhanced with the $AB$ function being always higher than its $AA$ and $BB$ counterparts.

### VII. CONCLUSIONS

In this paper we present the first analytical solution for the center-of-mass total distribution functions for polymer mixtures. We start from first-principles liquid state theory and derive a set of equations which describe c.o.m. distribution functions between pairs of interacting molecules in the mixture. The mesoscale description of the liquid so obtained depends on local chemical parameters, such as the radius of gyration and bond length. Moreover, mesoscale distribution functions depend on thermodynamic parameters such as density, blend composition, and proximity of the system to its spinodal decomposition.
The analytical c.o.m. total distribution functions quantitatively reproduce data from microscopic united-atom molecular dynamics simulations without the need of fitting parameters. In this comparison, input to the theory are data from the UA-MD simulations. The excellent agreement between analytical theory and simulations in both real and reciprocal space is an indication that our approach provides a reliable mesoscale description of polymer mixtures.

Moreover, our formalism recovers the known analytical functions for the fluctuations in number density and concentration (structure factors) for interacting soft-colloidal mixtures. The one-to-one agreement between the two formalisms supports the validity of our approach as a procedure to map polymer blends onto systems of interacting soft-colloidal particles.

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Table: Polyolefin blends ($T = 453$ K, $N_A = N_B = 96$).

| Blend | $\phi$ | $\rho$ |sites/Å$^3$ | $R_{gA}$ [Å] | $\gamma$ | $\chi$ |
|-------|-------|-------|-------------|--------------|--------|-------|
| iPP/ hhPP | 0.50 | 0.0332 | 11.28 | 1.09 | $-0.00364 + 1.84/T[1]$ |
| hhPP/ sPP | 0.50 | 0.0332 | 12.18 | 1.14 | – |
| PIB/ iPP | 0.50 | 0.0343 | 9.68 | 1.16 | $0.017 + 5.6/T[14]$ |
| sPP/ PE | 0.50 | 0.0328 | 13.89 | 1.19 | – |
| iPP/ sPP | 0.50 | 0.0328 | 11.37 | 1.22 | – |
| PIB/ hhPP | 0.50 | 0.0343 | 9.69 | 1.28 | $0.027 - 11.4/T[14]$, see also[1, 43, 44] |
| hhPP/ PE | 0.50 | 0.0332 | 12.32 | 1.34 | $-0.0294 + 17.58/T[45]$, see also[44] |
| PIB/ sPP | 0.50 | 0.0343 | 9.76 | 1.41 | – |
| PIB/ PE | 0.50 | 0.0343 | 9.76 | 1.68 | $0.00257 + 4.99/T[44]$ |
| iPP/ PE | 0.25 | 0.0328 | 11.35 | 1.47 | $0.005[13]$ |
| iPP/ PE | 0.75 | 0.0328 | 11.33 | 1.48 | $0.01[13]$ |
FIG. 1: Plot of $n_{\alpha\beta}(r)$ against $r$ for the hhPP/PE blend. Theoretical curves for athermal (full lines) and thermal (dashed lines) conditions are compared with simulation data (symbols): $AA$− (circles), $AB$− (diamonds, inset), and $BB$− terms (squares). Arrow indicates the lengthscale $R_gA$.

FIG. 2: Plot of colloid partial structure factors against $kR_gA$ for $\gamma \in \{1.0 \text{ (dashed lines), 1.5} \text{ (full lines)}\}$ with $\mu = 1.0$ and $\phi = 0.5$. Left panel: $S^{\phi\phi}(k)$ with $\chi/\chi_s \in \{0.0, 0.2, 0.4, 0.6, 0.8\}$ from bottom to top. Lower portion: $S^{\rho\phi}(k)$ for $\chi/\chi_s \in \{0.0, 0.2, 0.4, 0.6, 0.8\}$ (curves are indistinguishable in the plot). Right panel also shows $S^{\rho\rho}(k) - \delta^2 S^{\phi\phi}(k)$ (dot-dashed lines) for $\gamma = 1.5$.

FIG. 3: Plots of $h_{\alpha\beta}(r)$ against $r/R_gA$ for a structurally symmetric blend ($\mu = 1.0$ and $\gamma = 1.0$) close to (0.01% from) its spinodal decomposition. Left panel: effect of blend composition for $AA$− term at $\phi \in \{0.25 \text{ (long-dashed line), 0.50} \text{ (dot-dashed line), 0.75} \text{ (full line)}\}$. The behavior for $BB$− term is complementary to the $AA$− term at $1 - \phi$. Right panel: $AB$− term for which curves superimpose onto the full line. Also shown for comparison is the athermal case at $\phi = 0.5$ (dashed lines).

FIG. 4: Plots of $h_{\alpha\beta}(r)$ against $r/R_gA$ for $\gamma \in \{1.0 \text{ (dashed lines), 1.2} \text{ (full lines), 1.5} \text{ (dot-dashed lines)}\}$ with $\mu = 1.0$ and $\phi = 0.5$ for athermal conditions. Left panel: $AA$− (thin lines) and $BB$− terms (thick lines). Right panel: $AB$− terms. Note that $AA = BB$ for the $\gamma = 1$ case.

FIG. 5: Plots of $h_{\alpha\beta}(r)$ against $r/R_gA$ for $\mu \in \{0.5 \text{ (dot-dashed lines), 1.0} \text{ (dashed lines), 2.0} \text{ (full lines)}\}$ with $\gamma = 1.0$ and $\phi = 0.5$ under athermal conditions. Left panel: $AA$− terms; middle panel: $AB$− terms; right panel: $BB$− terms.

FIG. 6: Plots of $h_{\alpha\beta}(r)$ against $r/R_gA$ for systems with different $\mu$ and $\gamma$, but constant radii of gyration $R_gA$ and $R_gB$ at $\phi = 0.5$ for athermal conditions: full lines for $\mu = 2.00$ and $\gamma = 1.88$; dashed lines for $\mu = 1.00$ and $\gamma = 1.33$; dot-dashed lines for $\mu = 0.66$ and $\gamma = 1.09$. Left panel: $AA$− terms; middle panel: $AB$− terms; right panel: $BB$− terms.

FIG. 7: Plots of $h_{\alpha\beta}(r)$ against $r/R_gA$ for blends. Theoretical predictions in athermal (full lines) and thermal (dashed lines) conditions are compared with UA-MD simulations of blends (symbols): $AA$− (circles), $AB$− (diamonds), and $BB$− terms (squares). Blend parameters are given in the Table.

FIG. 8: Plots of $h_{\alpha\beta}(r)$ against $r/R_gA$ for a LCST blend described by $\chi = 0.01125 - 4.75/T$ ($N_A = 96$, $\rho_m = 0.034 \text{ Å}^{-3}$, $\sigma_A = 2.44 \text{ Å}$, $\phi = 0.50$, and $\chi_s = 0.21$). Shown are $AA$− (dot-dashed lines), $AB$− (full lines), and $BB$− terms (dashed lines) at two temperatures: $T = 150 \text{ K} \text{ (thin lines)}$ and $T = 10,000 \text{ K} \text{ (thick lines)}$. 