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# Self-Consistent Integral Equation Theory for the Equilibrium Properties of Polymer Solutions

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ABSTRACT: Self-consistent RISM integral equation theory of polymeric liquids is used to investigate the equilibrium properties of polymer solutions and melts. Density functional formalism is employed to derive the effective medium-induced potential between two sites on a polymer chain. The resulting expression leads to a coupling between the interchain and intrachain pair correlation functions. An approximate method for the calculation of the effective intrachain pair correlations is examined. The method employs Monte Carlo computer simulations of a single polymer chain interacting via local chemical interactions, long-range excluded volume, and the self-consistently determined medium-induced potential in the condensed phase to compute the intrachain pair correlations which are consistent with the interchain packing. Results for solutions of tangent hard-sphere chains are compared to recent off-lattice Monte Carlo simulations for various chain lengths and densities. In particular, it was found that the theory slightly overestimates the average size of the polymers in solution, while the density dependence of the average size of the chains is in good agreement with the Monte Carlo simulations. The inclusion of the self-consistent determination of the intrachain correlations is found to significantly alter the interchain pair correlation function at low and intermediate densities.

## I. Introduction

Recently a numerically tractable, off-lattice, statistical mechanical theory for the equilibrium properties of polymer melts, dense solutions, and alloys was constructed.[1-12] The theory is based on the reference interaction site model (RISM) originally proposed by Chandler and Anderson[13,14] to investigate the structure of fluids composed of small rigid polyatomic molecules. In polymer RISM (PRISM) theory, a polymer chain is viewed as consisting of a collection of spherically symmetric interaction sites or monomeric units covalently bonded together. The calculation of the interchain site–site correlation function, $g(r)$, is rendered tractable in PRISM by explicitly ignoring chain-end effects and invoking the Flory ideality hypothesis, which contends that excluded-volume interactions in dense homopolymer melts are completely screened down to monomeric length scales.[15] The accuracy of the theory, employing the ideality assumption, has been verified through $x$-ray scattering experiments of polyethylene melts[16] as well as molecular dynamics simulations.[17] However, nonideal effects will be important in polymer solutions removed from $\Theta$ conditions. In addition, recent experimental,[18] computer simulation,[19,20] and theoretical[21] studies have identified nonideal behavior in polymer alloys. To address problems where nonideal effects are conceivable, PRISM theory has recently[22] been extended to allow for the self-consistent calculation of the single-chain structure in condensed systems. In the present investigation, self-consistent PRISM integral equation theory will be applied to polymer solutions ranging in concentration from semidilute to concentrated conditions.

In the past, considerable progress has been made in the theory of polymer solutions using the Edwards pseudopotential model[23-26] or, equivalently, the $n$-component Landau–Ginzburg–Wilson field theory, coupled to a constant external field, in the limit $n \rightarrow 0$.[27] The Edwards model suitably describes the properties of long polymer chains on large length scales through a short-range integrable $\delta$ function for the interaction potential between polymer segments. Predictions for the equilibrium properties of dilute and semidilute solutions, based on the Edwards model, have been verified experimentally.[23,28] In addition, the screening of the excluded volume with increasing polymer concentration has also been established.[23] For dense solutions of polymers near the $\Theta$ state, however, one expects the short-range structure of the chains to play an important role in determining the equilibrium properties. Self-consistent PRISM theory offers the potential of treating polymer solutions with any desired level of local chemical detail included. Here we utilize this self-consistent theory to investigate the properties of polymer solutions composed of tangent hard-sphere chains. We will establish that self-consistent PRISM provides an accurate description of the properties of polymer solutions and also correctly accounts for the screening of the excluded volume with increasing concentration.

Previously, it was established that the RISM integral equation could be applied to polymeric systems.[1-5] By explicitly ignoring chain-end effects,[3] the site-averaged intermolecular pair correlation function, $g(r)$, was demonstrated to be specified by a single integral equation, the PRISM equation,

$$h(r) = \int \mathrm{d}\vec{r}'' \int \mathrm{d}\vec{r}'\, \omega(|\vec{r}-\vec{r}'|)\, C(|\vec{r}'-\vec{r}''|)\, [\omega(r'') + \rho_{\mathrm{m}} h(r'')] \tag{1.1}$$

with corrections for chain-end effects being $0\,(1/N^2)$, where $N$ is the number of sites or monomers comprising each polymer. Here $h(r) = g(r) - 1$, $\rho_{\mathrm{m}}$ is the monomer density, and $C(r)$ is the direct correlation function which may be considered as defined through the PRISM equation. $\omega(r)$

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is the intrachain structure factor[1-5] defined by

$$\omega(r) = \frac{1}{N}\sum_{\alpha,\gamma}^{N} \omega_{\alpha\gamma}(r) \tag{1.2}$$

where $\omega_{\alpha\gamma}(r)$ is the normalized probability density for finding sites $\alpha$ and $\gamma$ on the same chain separated by a distance $r$. Typically in the past[1-12,16,17] the solution of eq 1.1 has involved the use of the ideality assumption to specify $\omega(r)$ in eq 1.2 along with an appropriate closure relation. For hard-core interactions of interest in the present work, the Percus–Yevick approximation[14,19] is utilized

$$\begin{aligned} h(r) &= -1 \qquad r < \sigma \\ C(r) &= 0 \qquad r > \sigma \end{aligned} \tag{1.3}$$

where $\sigma$ is the hard-core diameter. At melt densities, where the ideality assumption for $\omega(r)$ is satisfactory, the accuracy of PRISM theory with the Percus–Yevick closure has been established.[6,17] Although PRISM theory provides a powerful tool for elucidating the structure, and hence thermodynamic properties, of polymer fluids in which the single-chain structure is adequately described by an "ideal" model, the theory will find more extensive applications if nonideal behavior is explicitly treated.

Consider a single chain in a homopolymer polymer solution or melt. The interaction potential between sites along the chain consists of the bare hard-core repulsions, interactions due to local chemical details, and a medium-induced potential, $\Delta\mu$, responsible for the influence of the surrounding condensed phase on chain conformations. Rigorously, the medium-induced potential is the excess, with respect to an isolated chain, free energy associated with changing polymer conformations in the condensed phase. Therefore, the single-chain structure factor, $\omega(r)$, will depend on $\Delta\mu$, which in turn depends on the structure of the fluid. The fluid structure is a functional of $\omega(r)$ through the PRISM equation, thus providing the self-consistent link between the intrachain and interchain structure. The explicit calculation of the medium-induced potential was first considered by Chandler and coworkers[30] in the context of a quantum electron solvated by a simple liquid. Recently,[22] the approach has been extended to polymer systems and employed to address local corrections to the ideality approximation for the intrachain structure in dense solutions of semiflexible polymers. In general, the medium-induced potential is a complicated non-pair-decomposable form, making self-consistent calculations of polymer chain structure in condensed phases virtually intractable. However, the determination of $\Delta\mu$ has been rendered tractable through the mean-pair approximation,[30-32] which approximates the medium-induced potential by a pair-decomposable form,

$$\beta\Delta\mu[\{\vec{\mathbf{r}}_i^{(\mathrm{p})}\}] = \sum_{\alpha<\gamma} W_{\alpha\gamma}(|\vec{\mathbf{r}}_\alpha^{(\mathrm{p})} - \vec{\mathbf{r}}_\gamma^{(\mathrm{p})}|) \tag{1.4}$$

where $W_{\alpha\gamma}$ is the medium-induced potential between sites $\alpha$ and $\gamma$ on a given chain and $\vec{\mathbf{r}}_i^{(\mathrm{p})}$ is the position vector of the $i$th site on the polymer. The functional form of $W_{\alpha\gamma}(r)$ was first specified by Chandler et al [30-32] using renormalized perturbation theory truncated at second order. In addition, an expression for $W_{\alpha\gamma}(r)$ identical to Chandler's has been derived from a density functional expansion approach.[33] The medium-induced potential was determined by expanding the free energy of a polymer constrained to a particular conformation in a solvent, in powers of the solvent density. The desired result is obtained by truncating the free energy expansion at second order. In this paper, we provide a different derivation for the medium-induced potential based on the density functional approach. The principal differences between the previous density functional derivation of the medium-induced potential and the one presented in this paper are conveyed in section II. It will become evident that our methodology may easily be extended to multicomponent systems and to higher orders in the functional expansion (i.e., beyond the mean-pair approximation). The resulting nonlinear form of the medium-induced potential in the mean-pair approximation requires the use of approximate methods or computer simulations to determine the chain structure consistent with interchain packing. Here, Monte Carlo simulations of the single chain interacting via bare excluded volume and the medium-induced potential will be used to determine $\omega(r)$ self-consistently.

The rest of the paper is organized as follows. In section II a new derivation of the medium-induced potential using density functional theory is presented. We obtain an expression identical to that that by Chandler using renormalized perturbation theory. Section III describes the methods utilized to calculate the intrachain structure consistent with interchain packing. Monte Carlo simulations of a single chaining interacting via hard-core repulsions and the medium-induced potential are employed to determine the intrachain correlation function self-consistently. Results for solutions of tangent hard-sphere polymer chains are presented in section IV. A comparison is made with recent computer simulations of polymer solutions. We find good agreement between the computer simulations and the self-consistent integral equation theory for the density dependence of the average end-to-end distance of a single chain in solution. With respect to the simulations, the theory slightly overestimates the average size of a chain in solution. Lastly, the main conclusions are summarized in section V.

## II. Derivation of Medium-Induced Potential

The self-consistent calculation of the site–site interchain pair-correlation function, $g(r)$, from eqs 1.1–1.3 requires an expression for the intrachain pair-correlation functions, $\omega_{\alpha\gamma}(r)$, in terms of the bare interactions and the medium-induced potential, $\Delta\mu$. Within the mean-pair approximation,

$$\omega_{\alpha\gamma}(r) = \frac{\int \mathrm{d}\{\vec{\mathbf{r}}_i^{(\mathrm{p})}\}\, \delta(\vec{\mathbf{r}}-\vec{\mathbf{r}}_\alpha^{(\mathrm{p})}+\vec{\mathbf{r}}_\gamma^{(\mathrm{p})}) \mathrm{e}^{-\beta\mathcal{H}_0(\{\vec{\mathbf{r}}_i^{(\mathrm{p})}\})-\sum_{\alpha\le\gamma}\beta W_{\alpha\gamma}(|\vec{\mathbf{r}}_\alpha^{(\mathrm{p})}-\vec{\mathbf{r}}_\gamma^{(\mathrm{p})}|)}}{\int \mathrm{d}\{\vec{\mathbf{r}}_i^{(\mathrm{p})}\}\, \mathrm{e}^{-\beta\mathcal{H}_0(\{\vec{\mathbf{r}}_i^{(\mathrm{p})}\})-\sum_{\alpha<\gamma}\beta W_{\alpha\gamma}(|\vec{\mathbf{r}}_\alpha^{(\mathrm{p})}-\vec{\mathbf{r}}_\gamma^{(\mathrm{p})}|)}} \tag{2.1}$$

where $\mathcal{H}_0(\{\vec{\mathbf{r}}_i^{(\mathrm{p})}\})$ is the configurational Hamiltonian of an isolated polymer chain, $W_{\alpha\gamma}(r)$ is the medium-induced potential between sites $\alpha$ and $\gamma$, and $\int \mathrm{d}\{\vec{\mathbf{r}}_i^{(\mathrm{p})}\}$ represents the sum over all polymer conformations. $\{\vec{\mathbf{r}}_i^{(\mathrm{p})}\}$ denotes a particular conformation of the polymer, and $\beta^{-1}$ is Boltzmann's constant, $k_\mathrm{B}$, times the temperature $T$. We now proceed to derive an expression for $\Delta\mu$ using a density functional expansion approach. In order to simplify the development, the derivation will be formulated for a single polymer in a monatomic solvent. Generalization to a polymeric "solvent" is straightforward and will be presented later.

A definition of the medium-induced potential for a polymer–solvent system is the change in free energy, $\Delta A_{\mathrm{sp}}$, of the solvent, with respect to an isolated polymer having a conformation $\{\vec{\mathbf{r}}_{i,0}^{(\mathrm{p})}\}$ and pure solvent, associated with accommodating the constrained polymer. It has been suggested[30] that an expression for the medium-induced potential, $\Delta\mu$, consistent with the result from second-order renormalized perturbation theory may be attained by constructing a functional expansion of $\Delta A_{sp}$ in powers of the change in the average solvent density, $\rho_s(\vec{r})$, due to the presence of the polymer with constrained conformation, $\{\vec{r}_{i,0}^{(p)}\}$. If the functional expansion is truncated at the quadratic order, an expression for $\Delta\mu$ in agreement with renormalized perturbation theory is obtained. Singh[33] took this approach, specifying $\rho_s(\vec{r})$ using linear response theory.

A different approach may be taken to derive an expression for the medium-induced potential which is in complete agreement with second-order renormalized perturbation theory and does not require recourse to linear response theory. Consider a single polymer chain composed of $N$ interaction sites or monomers immersed in a monatomic solvent. The medium-induced potential, $\Delta\mu$, is given by

$$\Delta\mu[\{\vec{r}_{i,0}^{(p)}\}] = A[\{\vec{r}_{i,0}^{(p)}\},\rho_s(\vec{r})] - A_s^\circ[\rho_s^\circ] - A_p^\circ[\{\vec{r}_{i,0}^{(p)}\}] \tag{2.2}$$

where $A[\{\vec{r}_{i,0}^{(p)}\},\rho_s(\vec{r})]$ is the free energy of the solvent–polymer system with the polymer conformation constrained to $\{\mathbf{r}_{i,0}^{(p)}\}$. $A_s^\circ[\rho_s^\circ]$ and $A_p^\circ[\{\vec{r}_{i,0}^{(p)}\}]$ are respectively the free energies of pure solvent and isolated polymer with conformation $\{\vec{r}_{i,0}^{(p)}\}$. A polymer chain with conformtion $\{\vec{r}_{i,0}^{(p)}\}$ has a segment density profile

$$\rho_p(\vec{r}) = \sum_{i=1}^{N} \delta(\vec{r}-\vec{r}_{i,0}^{(p)}) \tag{2.3}$$

so that eq 2.2 may be written as

$$\Delta\mu[\{\vec{r}_{i,0}^{(p)}\}] = A[\rho_p(\vec{r}),\rho_s(\vec{r})] - A_s[\rho_s^\circ] - A_p[\rho_p(\vec{r})] \tag{2.4}$$

with $\rho_p(\vec{r})$ given by eq 2.3. The objective here is to obtain an expression for $\Delta\mu$ by first considering $A[\rho_p(\vec{r}),\rho_s(\vec{r})]$ for some arbitrary polymer segment density profile, $\rho_{p,a}(\vec{r})$. Next, a functional expansion of $A[\rho_{p,a}(\vec{r}),\rho_s(\vec{r})]$ in powers of both the solvent density, $\rho_s(\vec{r})$, and the polymer segment density, $\rho_{p,a}(\vec{r})$, is performed, truncating the series at second order. The equilibrium or observable solvent density profile, $\rho_{s,\min}(\vec{r})$, is then determined by minimizing $A[\rho_{p,a}(\vec{r}),\rho_s(\vec{r})]$ with respect to variations in $\rho_s(\vec{r})$ at constant $\rho_{p,a}(\vec{r})$. The expression for the medium-induced potential is obtained by substituting $\rho_{s,\min}(\vec{r})$, into $A[\rho_{p,a}(\vec{r}),\rho_s(\vec{r})]$ and, subsequently, specifying the polymer density $\rho_{p,a}(\vec{r})$ to be $\rho_p(\vec{r})$ in eq 2.3. The final expression for $A[\rho_p(\vec{r}),\rho_s(\vec{r})]$ is substituted into eq 2.4 to furnish $\Delta\mu$.

For an arbitrary polymer segment density profile, $\rho_{p,a}(\vec{r})$, the functional Taylor series expansion[14,29] of $A[\rho_{p,a}(\vec{r}),\rho_s(\vec{r})]$ about a uniform density state, $\{\rho_{p,a}^\circ,\rho_s^\circ\}$, yields

$$\begin{aligned} A[\rho_{p,a}(\vec{r}),\rho_s(\vec{r})] = {} & \\ & A[\rho_{p,a}^\circ,\rho_s^\circ] + \int \left.\frac{\delta A}{\delta\rho_{p,a}(\vec{r})}\right|_{\rho_s^\circ,\rho_{p,a}^\circ} \Delta\rho_{p,a}(\vec{r})\, d\vec{r} + \\ & \int \left.\frac{\delta A}{\delta\rho_s(\vec{r})}\right|_{\rho_{p,a}^\circ,\rho_s^\circ} \Delta\rho_s(\vec{r})\, \Delta\rho_s(\vec{r})\, d\vec{r} + \\ & \frac{1}{2}\int\int \left.\frac{\delta^2 A}{\delta\rho_{p,a}(\vec{r})\,\delta\rho_{p,a}(\vec{r}')}\right|_{\rho_s^\circ,\rho_{p,a}^\circ} \Delta\rho_{p,a}(\vec{r})\,\Delta\rho_{p,a}(\vec{r}')\, d\vec{r}\, d\vec{r}' + \\ & \int\int \left.\frac{\delta^2 A}{\delta\rho_{p,a}(\vec{r})\,\delta\rho_s(\vec{r}')}\right|_{\rho_s^\circ,\rho_{p,a}^\circ} \Delta\rho_{p,a}(\vec{r})\,\Delta\rho_s(\vec{r}')\, d\vec{r}\, d\vec{r}' + \\ & \frac{1}{2}\int\int \left.\frac{\delta^2 A}{\delta\rho_s(\vec{r})\,\delta\rho_s(\vec{r}')}\right|_{\rho_s^\circ,\rho_{p,a}^\circ} \Delta\rho_s(\vec{r})\,\Delta\rho_s(\vec{r}')\, d\vec{r}\, d\vec{r}' + \ldots \end{aligned} \tag{2.5}$$

where $A[\rho_{p,a}^\circ,\rho_s^\circ]$ is the free energy of a uniform polymer–solvent system and

$$\Delta\rho_{p,a}(\vec{r}) = \rho_{p,a}(\vec{r}) - \rho_{p,a}^\circ$$

$$\Delta\rho_s(\vec{r}) = \rho_s(\vec{r}) - \rho_s^\circ \tag{2.6}$$

The functional derivatives

$$\left.\frac{\delta A}{\delta\rho_p(\vec{r})}\right|_{\rho_p^\circ,\rho_s^\circ} = \mu_p \quad \text{and} \quad \left.\frac{\delta A}{\delta\rho_s(\vec{r})}\right|_{\rho_p^\circ,\rho_s^\circ} = \mu_s \tag{2.7}$$

are the chemical potentials[34] of the polymer and solvent in the uniform density state, $\{\rho_{p,a}^\circ, \rho_s^\circ\}$. The second-order functional derivatives are identified with

$$\left.\frac{\delta^2 A}{\delta\rho_{p,a}(\vec{r})\,\delta\rho_{p,a}(\vec{r}')}\right|_{\rho_s^\circ,\rho_{p,a}^\circ} = \beta^{-1}\chi_{p,a}^{-1}(|\vec{r}-\vec{r}'|)$$

$$\left.\frac{\delta^2 A}{\delta\rho_s(\vec{r})\,\delta\rho_s(\vec{r}')}\right|_{\rho_s^\circ,\rho_{p,a}^\circ} = \beta^{-1}\chi_s^{-1}(|\vec{r}-\vec{r}'|)$$

$$\left.\frac{\delta^2 A}{\delta\rho_{p,a}(\vec{r})\,\delta\rho_s(\vec{r}')}\right|_{\rho_s^\circ,\rho_{p,a}^\circ} = -\beta^{-1}C_{ps}(|\vec{r}-\vec{r}'|) \tag{2.8}$$

where $\chi_{p,a}^{-1}(r)$ and $\chi_s^{-1}(r)$ are the inverse total density–density correlation functions[8,14,34] for the polymer and solvent, respectively, and $C_{ps}(r)$ is the direct correlation function between sites on the polymer and the solvent,[9] ignoring chain-end effects. To determine the equilibrium density profile of the solvent, $\rho_{s,\min}(\vec{r})$, at fixed polymer segment density profile, $A[\rho_{p,a}(\vec{r}),\rho_s(\vec{r})]$ is minimized with respect to $\rho_s(\vec{r})$:

$$\delta A/\delta\rho_s(\vec{r}) = 0 \tag{2.9}$$

If the functional expansion for $A[\rho_{p,a}(\vec{r}),\rho_s(\vec{r})]$ in eq 2.5 is truncated at quadratic order, $\rho_{s,\min}(\vec{r})$ is given by

$$\rho_{s,\min}(\vec{r}) - \rho_s^\circ = \int d\vec{r}'' \int d\vec{r}'\, \chi_s(|\vec{r}-\vec{r}'|)\, C_{ps}(|\vec{r}'-\vec{r}''|)\, \Delta\rho_{p,a}(\vec{r}'') \tag{2.10}$$

where $\chi_s(|\vec{r}-\vec{r}'|) = \langle\delta\rho_s(\vec{r})\,\delta\rho_s(\vec{r}')\rangle_0$ is the total density–density correlation function of pure solvent.[8,14,34] Combining eqs 2.5, 2.8, and 2.10 and truncating the series at second-order yields

$$\begin{aligned} A[\rho_{p,a}(\vec{r}),\rho_{s,\min}(\vec{r})] = {} & A[\rho_{p,a'}{}^\circ,\rho_{s,\min}{}^\circ] + \\ & \frac{\beta^{-1}}{2}\int d\vec{r}\int d\vec{r}'\, \chi_{p,a}^{-1}(|\vec{r}-\vec{r}'|)\Delta\rho_{p,a}(\vec{r})\,\Delta\rho_{p,a}(\vec{r}') - \\ & \frac{\beta^{-1}}{2}\int d\vec{r}\int d\vec{r}_2\int d\vec{r}_4\int d\vec{r}'\, \{C_{ps}(|\vec{r}-\vec{r}_2|)\,\Delta\rho_{p,a}(\vec{r}_2)\,\times \\ & \chi_s(|\vec{r}-\vec{r}'|)\,\Delta\rho_{p,a}(\vec{r}_4)\,C_{ps}(|\vec{r}'-\vec{r}_4|)\} \end{aligned} \tag{2.11}$$

To determine the medium-induced potential from eq 2.4, $A[\rho_p(\vec{r}),\rho_s(\vec{r})|$ is provided by replacing $\Delta\rho_{p,a}(\vec{r})$ in eq 2.11 with the constrained polymer density profile

$$\Delta\rho_p(\vec{r}) = \sum_{i=1}^{N} \delta(\vec{r}-\vec{r}_{i,0}^{(p)}) - \rho_p^\circ \tag{2.12}$$

and taking the infinite dilution limit, $\rho_p^\circ \to 0$. The resulting expression is then substituted into eq 2.4. Lastly, to remain consistent with the level of the expansion employed for $A[\rho_p(\vec{r}),\rho_s(\vec{r})]$ in eq 2.4, the isolated polymer chain free energy, $A_p[\rho_p(\vec{r})]$, is expanded to quadratic order in $\rho_p(\vec{r})$ and substituted into eq 2.4. The final result for the total medium-induced potential, ignoring chain-end effects for the polymer, becomes

$$\begin{aligned} \beta\Delta\mu[\{\vec{r}_{i,0}^{(p)}\}] = {} & \text{constant} - \\ & \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1 \\ i\neq j}}^{N} \int d\vec{r}\int d\vec{r}'\, C_{ps}(|\vec{r}-\vec{r}_{i,0}^{(p)}|)\,\chi_s(|\vec{r}-\vec{r}'|)\,C_{ps}(|\vec{r}'-\vec{r}_{j,0}^{(p)}|) \end{aligned} \tag{2.13}$$

where $C_{ps}(r)$ is the polymer site–solvent direct correlation function. $\chi_s(|\vec{\mathbf{r}}-\vec{\mathbf{r}}'|) = \rho S(|\vec{\mathbf{r}}-\vec{\mathbf{r}}'|)$ is the total density–density correlation function of pure solvent where $\rho$ is the number density of the solvent and $S(r)$ is the structure factor of pure solvent.[8,14,34] The constant term contains self-interactions of the polymer (i.e., the medium-induced interactions of each site on the polymer with itself) along with other terms that are independent of polymer conformation. It should be stressed that within the present density functional formalism, if the functional expansion for $A[\rho_p(\vec{\mathbf{r}}),\rho_s(\vec{\mathbf{r}})]$ is performed with respect to $\rho_s(\vec{\mathbf{r}})$ only, as was employed previously,[33] the expression obtained for $\Delta\mu$ agrees with the results of Gaussian density field theory. The "Gaussian bath" result arises by assuming the density distribution function for the solvent molecules obeys Gaussian statistics.[31] The expression for $\Delta\mu$ from Gaussian density field theory has the same form as eq 2.13, with $C_{ps}(r)$ replaced by the polymer segment–solvent interaction potential.

Now consider a homopolymer solution or melt. Interactions between sites along a given chain consist of the bare hard-core repulsions, interactions describing local chemical details, and the medium-induced potential, $\Delta\mu$, which takes into account the influence the surrounding chains of the condensed phase have on chain conformations. For this situation, the medium-induced potential may be determined from the present density functional approach by replacing the monatomic solvent in the above derivation with homopolymer consisting of $N$ sites, chemically equivalent to the polymer with constrained conformation $\{\vec{\mathbf{r}}_{i,0}{}^{(p)}\}$. The total medium-induced potential for homopolymer solutions or melts is

$$\beta\Delta\mu[\{\vec{\mathbf{r}}_{i,0}{}^{(p)}\}] = -\frac{1}{2}\sum_{\substack{i=1 \\ i\neq j}}^{N}\sum_{j=1}^{N}\sum_{\alpha,\gamma}^{N}\int \mathrm{d}\vec{\mathbf{r}}\int \mathrm{d}\vec{\mathbf{r}}' \times \\ C_{p\alpha}(|\vec{\mathbf{r}}-\vec{\mathbf{r}}_{i,0}{}^{(p)}|)\ \rho S_{\alpha\gamma}(|\vec{\mathbf{r}}-\vec{\mathbf{r}}'|)\ C_{p\gamma}(|\vec{\mathbf{r}}'-\vec{\mathbf{r}}_{j,0}{}^{(p)}|) \quad (2.14)$$

where the additive constant, independent of polymer conformation, has been omitted. $\rho S_{\alpha\gamma}(|\vec{\mathbf{r}}-\vec{\mathbf{r}}'|) = \chi_{\alpha\gamma}(|\vec{\mathbf{r}}-\vec{\mathbf{r}}'|)$ is the total density–density correlation function between sites $\alpha$ and $\gamma$ of the polymer, and $\rho$ is the number density of homopolymers in solution. $C_{p\alpha}(r)$ is the direct correlation function between site $\alpha$ on the homopolymer and a site on the chain with constrained conformation, ignoring chain-end effects for the constrained polymer. Upon neglecting chain-end effects for the homopolymer surrounding the constrained polymer, the medium-induced potential is given by[22]

$$\beta\Delta\mu[\{\vec{\mathbf{r}}_{i,0}{}^{(p)}\}] = -\frac{1}{2}\sum_{\substack{i=1 \\ i\neq j}}^{N}\sum_{j=1}^{N}\int \mathrm{d}\vec{\mathbf{r}}\int \mathrm{d}\vec{\mathbf{r}}' \times \\ C(|\vec{\mathbf{r}}-\vec{\mathbf{r}}'_{i,0}{}^{(p)}|)\ \rho_m S(|\vec{\mathbf{r}}-\vec{\mathbf{r}}'|)\ C(|\vec{\mathbf{r}}'-\vec{\mathbf{r}}_{j,0}{}^{(p)}|) \quad (2.15)$$

with the medium-induced potential between sites $\alpha$ and $\gamma$ on the polymer being

$$\beta W(|\vec{\mathbf{r}}_\alpha-\vec{\mathbf{r}}_\gamma|) = -\rho_m\int \mathrm{d}\vec{\mathbf{r}}\int \mathrm{d}\vec{\mathbf{r}}'\ C(|\vec{\mathbf{r}}-\vec{\mathbf{r}}_\alpha|)\ S(|\vec{\mathbf{r}}-\vec{\mathbf{r}}'|)\ C(|\mathbf{r}'-\vec{\mathbf{r}}_\gamma|) \quad (2.16)$$

where $C(r)$ is the site–site direct correlation function for the homopolymer liquid defined through the PRISM equation and $\rho_m$ is the density of interaction sites. $S(r)$ is the static structure factor of the polymer liquid, whose Fourier transform is defined[4,5] as

$$\hat{S}(k) = \hat{\omega}(k) + \rho_m\hat{h}(k) \quad (2.17)$$

where $\hat{\omega}(k)$ and $\hat{h}(k)$ are the Fourier transforms of $\omega(r)$ and $h(r) = g(r) - 1$. For a homopolymer solution, the determination of the intrachain structure, $\omega(r)$, consistent with interchain packing is accomplished by the following procedure: (1) The calculation of the intrachain structure factor, $\omega(r)$, requires knowledge of the interchain pair-correlation function, $g(r) = h(r) - 1$. Therefore, $h(r)$ is determined from eq 1.1 using the closure condition (eq 1.3 and some initial "guess" for $\omega(r)$. (2) From eqs 2.1, 2.16, and 2.17 the normalized probability densities, $\{\omega_{\alpha\gamma}(r)\}$, are determined. The $\{\omega_{\alpha\gamma}(r)\}$ are then used in eq 1.2 to determine a "new" estimate for $\omega(r)$. (3) The resulting expression for $\omega(r)$ is utilized to calculate a new $h(r)$ from eq 1.1 with closure condition eq 1.3. Steps 2 and 3 are repeated until the pair correlations, $\omega(r)$ and $h(r)$, have converged. The equilibrium properties may then be determined from the final expressions for $\omega(r)$ and $h(r)$.

## III. Self-Consistent Determination of the Intrachain Correlation Function

We now consider the self-consistent calculation of the intrachain structure for solutions of linear tangent hard-sphere chains. Each chain consists of $N$ interaction sites or monomers with hard-core diameter $\sigma$. For this model the segment bond length, $l$, is equivalent to $\sigma$. Potential interactions between sites on different chains consist only of hard-core repulsions. Pairs of sites within a given chain interact through the bare hard-core repulsions, as well as the medium-induced potential which takes into account the influence of the other chains in solution, and this prevents a closed-form solution of eq 2.1 for $\{\omega_{\alpha\gamma}(r)\}$. To determine $\{\omega_{\alpha\gamma}(r)\}$, we employ Monte Carlo simulations of a *single* chain interacting via long-range excluded volume and the medium-induced potential. Since the self-consistent calculation of the intrachain structure using single-chain simulations coupled to the solutions of the PRISM equation is computationally intensive, one simplification will be adopted. Previously,[6] the pair correlations in dense polymer solutions, calculated from PRISM theory, were demonstrated to be accurately described using a semiflexible chain model for $\omega(r)$, provided the persistence length in the model was adjusted to obtain agreement between the mean-square end-to-end distance, $\langle R^2\rangle$ obtained from computer simulations of dense polymer solutions. The procedure has been extended to polymer solutions[35] and found to accurately described the pair correlations in the system. Here we employ a similar approach; the intrachain structure factor, $\omega(r)$, is determined by performing Monte Carlo simulations of an effective single chain in solution. The $\langle R^2\rangle$ obtained from the simulations is then matched with the $\langle R^2\rangle$ obtained from the semiflexible chain model by adjusting the persistence length, $\xi_p$.

**A. Monte Carlo Simulations.** The effective single chain in solution is modeled as a "pearl-necklace"[36] chain of $N$ sites or beads with diameter $\sigma$, separated by a distance $l = \sigma$. The potential interactions between sites $\alpha$ and $\gamma$ on the chain are described by

$$\phi(|\vec{\mathbf{r}}_\alpha{}^{(p)}-\vec{\mathbf{r}}_\gamma{}^{(p)}|) = \infty, \qquad |\vec{\mathbf{r}}_\alpha{}^{(p)}-\vec{\mathbf{r}}_\gamma{}^{(p)}| < \sigma$$

$$\phi(|\vec{\mathbf{r}}_\alpha{}^{(p)}-\vec{\mathbf{r}}_\gamma{}^{(p)}|) = W(|\vec{\mathbf{r}}_\alpha{}^{(p)}-\vec{\mathbf{r}}_\gamma{}^{(p)}|), \qquad |\vec{\mathbf{r}}_\alpha{}^{(p)}-\vec{\mathbf{r}}_\gamma{}^{(p)}| \geq \sigma \quad (3.1)$$

where $W(r)$ is provided in eq 2.16. The kink-jump method[36] was used to generate chain configurations. A bead is chosen at random, and the chain configuration is changed locally by attempting a rotation of two successive segments around the axis joining their end beads by a random angle, $\phi$, chosen in the interval $(0, 2\pi)$. If an end bead is selected, the terminal segment is rotated to a new position by specifying the angle $\phi$ as before and an angle $\theta$, chosen such that $\cos\theta$ is equally distributed in the interval $(-1, 1)$. Subsequent to a bead move, a test is made for violation of the excluded-volume constraint. Moves that violate the excluded-volume constraint are returned to their initial position, and this is counted as the new configuration. For moves which do not violate the excluded-volume constraint, the Metropolis test[36] is employed to accept configurations. For the purpose of determining the mean-square end-to-end distance, $\langle R^2 \rangle$, samples were taken in intervals $100N$ bead moves and the first $N^2$ moves were discarded. For each run 5000 samples were taken to determine $\langle R^2 \rangle$. At least eight separate simulations were employed to determine the overall $\langle R^2 \rangle$. The resulting $\langle R^2 \rangle$ was then used to determine $\omega(r)$ by equating $\langle R^2 \rangle$ from the simulations to the $\langle R^2 \rangle$ obtained from a semiflexible chain model $\omega(r)$.

**B. Semiflexible Chain Model.** We adopted the semiflexible chain model for the intrachain distribution functions, $\{\omega_{\alpha\gamma}(r)\}$, employed in previous work.[6,22] The intrachain distribution function for sites separated by two segments, referred to as $\omega_{13}(r)$, is treated "exactly" in the sense that the hard-core repulsions between sites $\alpha$ and $\alpha + 2$ are included[22]

$$\omega_{13}(r) = \frac{\epsilon}{4\pi l^2 r} \frac{\exp\left(-2\epsilon\left[1 - \left(\frac{r}{2l}\right)^2\right]\right)}{1 - \exp\left(-2\epsilon\left[1 - \left(\frac{\sigma}{2l}\right)^2\right]\right)} H(r-\sigma)\, H(2l-r) \tag{3.2}$$

where $H(x)$ is the unit step function. $\epsilon$ characterizes the local flexibility of the chain and is related to the persistence length, $\xi_p$, by

$$\xi_p = \frac{l}{1 + \langle \cos\theta \rangle} \tag{3.3}$$

$$\langle \cos\theta \rangle = \frac{1}{\epsilon} - \frac{\exp(\epsilon) + \left(1 - \frac{\sigma^2}{2l^2}\right)\exp\left[-\epsilon\left(1 - \frac{\sigma^2}{2l^2}\right)\right]}{\exp(\epsilon) - \exp\left[-\epsilon\left(1 - \frac{\sigma^2}{2l^2}\right)\right]} \tag{3.4}$$

For $\{\omega_{\alpha\gamma}(r)\}$ with $|\alpha - \gamma| \geq 3$, the Koyama distribution[6,37,38] is employed:

$$\hat{\omega}_{\alpha\gamma}(k) = \frac{\sin(B_{\alpha\gamma}k)}{B_{\alpha\gamma}k} e^{-A_{\alpha\gamma}{}^2k^2} \qquad \text{for } |\alpha - \gamma| \geq 3 \tag{3.5}$$

where $\hat{\omega}_{\alpha\gamma}(k)$ is the Fourier transform of the intrachain distribution function between sites $\alpha$ and $\gamma$. The constants $A_{\alpha\gamma}$ and $B_{\alpha\gamma}$ are given by

$$B_{\alpha\gamma}{}^2 = c_{\alpha\gamma}\langle r_{\alpha\gamma}{}^2 \rangle \qquad A_{\alpha\gamma}{}^2 = \langle r_{\alpha\gamma}{}^2 \rangle \frac{(1 - c_{\alpha\gamma})}{6} \tag{3.6}$$

with

$$c_{\alpha\gamma}{}^2 = \frac{1}{2}\left(5 - 3\frac{\langle r_{\alpha\gamma}{}^4 \rangle}{\langle r_{\alpha\gamma}{}^2 \rangle^2}\right)$$

Here $\langle r_{\alpha\gamma}{}^2 \rangle$ and $\langle r_{\alpha\gamma}{}^4 \rangle$ are the second and fourth moments, respectively, of the Koyama distribution for the distance between sites $\alpha$ and $\gamma$, $\vec{\mathbf{r}}_{\alpha\gamma}$, and are functions of the persistence length $\xi_p$. The expressions for $\langle r_{\alpha\gamma}{}^2 \rangle$ and $\langle r_{\alpha\gamma}{}^4 \rangle$ were provided previously.[6] The Koyama distribution is valid if $\langle r_{\alpha\gamma}{}^4 \rangle / \langle r_{\alpha\gamma}{}^2 \rangle^2 \leq 5/3$. The persistence length $\xi_p$ is determined by matching the mean-square end-to-end distance, $\langle R^2 \rangle$, obtained from Monte Carlo simulations with $\langle R^2 \rangle$ from the Koyama model. It should be mentioned that the semiflexible chain model is globally ideal in the sense that the Koyama model neglects long-range excluded volume. Therefore, there will be discrepancies between the single-chain structure factor of the model, $\hat{\omega}(k)$, and the exact $\hat{\omega}(k)$ in the intermediate scaling regime defined by[28] $R_g{}^{-1} < k < l^{-1}$ where $R_g$ is the average radius of gyration. In the intermediate regime[23,39]

$$\hat{\omega}(k) \propto k^{-1/\nu} \tag{3.7}$$

where $2\nu$ is the scaling exponent for the mean-square end-to-end distance, $\langle R^2 \rangle \propto N^{2\nu}$. For an ideal chain $\nu = {}^1/_2$, while $\nu = {}^3/_5$ for a self-avoiding walk. At high densities where the chain is expected to be ideal, the Koyama model should accurately described the $k$-dependence of the single-chain structure factor, $\hat{\omega}(k)$. However, at low densities some error is introduced in the intermediate scaling regime. Given the previous success of the Koyama model in describing the intrachain correlation in melts and solutions,[6,35] we expect errors incurred by employing the Koyama model for $\omega(r)$ to be small. In addition, the model used here for $\omega(r)$ is expected to accurately describe polymer solutions, since it is in the same spirit as the effective Gaussian model which has been successfully exploited in the past to study polymer solutions.[23,25,40,41]

**C. Solution of PRISM Equation.** The interchain structure needed for the calculation of the medium-induced potential was solved by using the variational scheme of Lowden and Chandler.[42] The PRISM equation and the closure condition (eq 1.3) are equivalent to a variational approach involving the functional

$$I_{\text{RISM}} = \rho_m{}^2 \int C(r)\, d^3r - \frac{1}{8\pi^3}\int d^3k\, \{\rho_m\hat{\omega}(k)\, \hat{C}(k) + \ln[1 - \rho_m\hat{\omega}(k)\, \hat{C}(k)]\} \tag{3.8}$$

and the condition

$$\delta I_{\text{RISM}}/\delta C(r) = 0 \qquad r < \sigma \tag{3.9}$$

As employed previously,[3,6,17] the direct correlation function is assumed to be a cubic polynomial

$$C(r) = \theta(\sigma - r)\sum_{i=1}^{4} a_i\left(\frac{r - \sigma}{\sigma}\right)^{i-1} \tag{3.10}$$

where $\theta(x)$ is the unit step function. $I_{\text{RISM}}$ is minimized with respect to the parameters $\{a_i\}$ in eq 3.10 to obtain the structure of the liquid. The method has been demonstrated[3,6,17] to be very accurate for determining the pair-correlation function, $g(r)$.

The procedure described at the end of section II for the self-consistent calculation of the intrachain structure now becomes the following: (1) Guess an initial value for the persistance length, $\xi_p$, in the semiflexible chain model (SFC). (2) The value of $\xi_p$ is used to determine $\hat{\omega}(k)$ from the (SFC) model described in section IV.B. (3) $\hat{h}(k)$ is determined from the PRISM equation with the Percus–Yevick closure using eqs 3.8, 3.9, and 3.10. (4) Calculate the pairwise medium-induced potential, $W(r)$, from eq 2.16. (5) Perform Monte Carlo simulations of a single chain interacting through excluded volume and the medium-induced potential. Determine $\langle R^2 \rangle$ from the simulations. (6) Match $\langle R^2 \rangle$ determined from the computer simulations with $\langle R^2 \rangle$ obtained from the SFC model by varying $\xi_p$ in the model. Repeat steps 2–6 until $\langle R^2 \rangle$, $\omega(r)$, and $h(r)$ have converged. The mean-square end-to-end distance of a chain in solution is $\langle R^2 \rangle$, and the thermodynamics of the solution are determined from $h(r)$.

## IV. Results for Tangent Hard-Sphere Chains

Recently, Monte Carlo simulations have been performed by Yethiraj and Hall[36] for solutions of tangent hard-sphere chains. Table I provides a comparison between the results of these simulations and the predictions of the present self-consistent PRISM calculations for the mean-square end-to-end distance of a chain in solution, $\langle R^2 \rangle$. The

**Table I. Mean-Square End-to-End Distance, $\langle R^2 \rangle$, as a Function of Packing Density, $\eta = \rho_m(\pi\sigma^3/6)$, and the Number of Sites, *N*, Comprising the Polymers**

| $N$ | $\eta$ | $\langle R^2 \rangle_{\text{PRISM-MC}}$[a] | $\langle R^2 \rangle_{35}$[b] | $\langle R^2 \rangle_{\text{SAW}}$[c] | $\langle R^2 \rangle_{\text{Ideal}}$[c] |
|---|---|---|---|---|---|
| 20 | 0 | | | 50.78 | 30.79 |
| 20 | 0.10 | 45.32 ± 0.61 | 43.01 ± 1.79 | | |
| 20 | 0.20 | 41.92 ± 0.62 | 37.37 ± 1.32 | | |
| 20 | 0.30 | 38.78 ± 0.64 | 34.95 ± 2.81 | | |
| 20 | 0.35 | 35.80 ± 0.66 | 32.23 ± 4.30 | | |
| 50 | 0 | | | 152.03 | 80.80 |
| 50 | 0.20 | 132.10 ± 3.0 | 118.70 ± 4.83 | | |
| 50 | 0.30 | 115.0 ± 5.0 | 106.84 ± 6.05 | | |
| 100 | 0 | | | 348.51 | 164.12 |
| 100 | 0.20 | 285.0 ± 6.0[d] | 242.51 ± 6.53 | | |
| 100 | 0.30 | 247.0 ± 8.0[d] | 220.09 ± 5.08 | | |

[a] $\langle R^2 \rangle_{\text{PRISM-MC}}$ refers to the predictions of self-consistent PRISM integral equation theory where the intrachain structure factor, $\omega(r)$, was determined from Monte Carlo simulations of a single tangent hard-sphere chain interacting via the medium-induced potential, $\beta W(r)$. [b] $\langle R^2 \rangle_{35}$ are the results of many chain Monte Carlo simulations of polymer solutions from ref 35. [c] $\langle R^2 \rangle_{\text{SAW}}$ and $\langle R^2 \rangle_{\text{Ideal}}$ are the corresponding self-avoiding walk and ideal values of the mean-square end-to-end distance, respectively. [d] Recently, more extensive calculations of Yethiraj[43] using a more efficient algorithm suggest that our values of $\langle R^2 \rangle$ for the $N = 100$ case are approximately 5–10% low.

predictions of the theory are in good agreement with the simulations (within 10%) at all densities and chain lengths investigated. Notice the theory properly accounts for the reduction in the average size of the chains with respect to the self-avoiding limit as the density is increased, although, there is still considerable expansion of the polymer coils with respect to $\langle R^2 \rangle$ of ideal chains at the moderate densities investigated.

To quantify the density dependence of $\langle R^2 \rangle$, we fit the data in Table I to the semidilute scaling form

$$\langle R^2 \rangle \propto \eta^{-\alpha} \tag{4.1}$$

where $\eta = \rho_m(\pi\sigma^3/6)$ is the packing density and $\rho_m$ is the density of sites or monomers in solution. For the short chain lengths investigated, the concept of a semidilute regime is somewhat ill defined; however, our main objective is to compare the predictions of self-consistent PRISM with the Monte Carlo simulations of polymer solutions. For $N = 20$ the lowest packing density of 0.10 is in the crossover between the dilute and semidilute regimes, as estimated from the onset of polymer coil overlap,[28] and will not be employed in the analysis. A value of $\alpha = 0.26 \pm 0.04$ was obtained for $\eta > 0.10$ and $N = 20$, while $\alpha = 0.24 \pm 0.08$ was extracted from the simulations.[35] At $N = 50$ and 100, $\alpha$ was determined for the two packing densities studied in the simulations. We obtained $\alpha = 0.34 \pm 0.09$ for $N = 50$ and $\alpha = 0.35 \pm 0.06$ for $N = 100$ both in agreement within statistical error with the simulation results $\alpha = 0.26 \pm 0.10$ ($N = 50$) and $\alpha = 0.24 \pm 0.07$ ($N = 100$). The values of $\alpha$ determined are in fairly good agreement with the scaling predictions, $\alpha = 0.25$, for long chains, although we do not expect a well-defined scaling regime to exist for the short chains studied here. To properly address the semidilute regime, long chains should be considered over a wide range in density. Such calculations are difficult due to the large amount of computing time required for the self-consistent calculation of the intrachain structure factor, $\omega(r)$, from Monte Carlo simulations of a single chain interacting via the medium-induced potential. The interest in the properties of long chains necessitates the use of approximate methods for the self-consistent calculation of $\omega(r)$ which will be the subject of future work.

In Figures 1–4 we compare the site-averaged pair-correlation function, $g(r) = h(r) = 1$, determined from

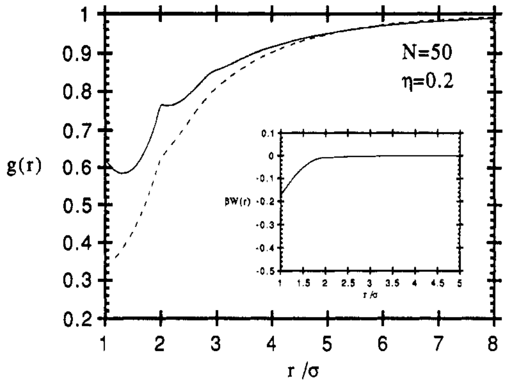

**Figure 1.** Site–site intermolecular correlation function, $g(r)$, for a solution with $N = 50$ and a packing density, $\eta = \rho_m(\pi\sigma^3/6)$, of 0.20. The solid line (—) indicates the prediction of self-consistent PRISM theory, and the inset shows the corresponding medium-induced potential, $W(r)$, for the stated conditions. The dashed line (- - -) is the prediction of PRISM theory assuming the intrachain correlation function, $\omega(r)$, is "ideal".

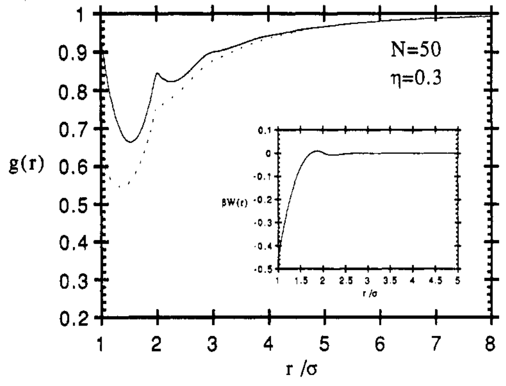

**Figure 2.** Same as Figure 1 but for $\eta = 0.3$.

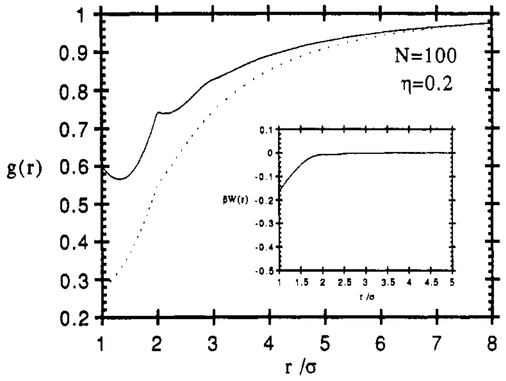

**Figure 3.** Same as Figure 1 but for $N = 100$.

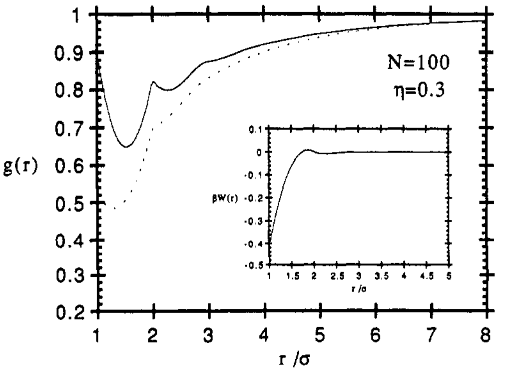

**Figure 4.** Same as Figure 1 but for $N = 100$ and $\eta = 0.3$.

self-consistent PRISM with the predictions of PRISM assuming $\omega(r)$ satisfies the ideality hypothesis. The insets in these figures show the calculated medium-induced potential between two sites within a given chain determined for the conditions where the self-consistent calculations converged. As expected, at the low densities studied here we observe that the self-consistent correction to the ideal structure is quite large for values of $r$ near contact. Since, the thermodynamic properties of systems are directly determined from the pair-correlation function,[3,5,14] the ideality assumption will not accurately describe polymeric systems at low to intermediate densities and including intra/intermolecular self-consistency is necessary. For long chains at meltlike densities, however, we anticipate that the self-consistent correction to PRISM theory using the ideal $\omega(r)$ will be small. This was indeed found to be the case previously[22] based on an approximate treatment using the medium-induced potential in eq 2.15.

It can also be observed from Figures 1–4 that the medium-induced potential $\beta W(r)$ becomes progresively more attractive as the density increases at fixed chain length. This leads to the expected contraction of the chains as the density is increased. As part of this investigation we attempted to perform PRISM/Monte Carlo computations on longer chain systems ($N$ = 150 and 300) at meltlike densities ($\eta = 0.45$ and 0.52). At meltlike packing fractions we observed that $\beta W(r)$ exhibits a deep well at contact ($\beta W(r{=}\sigma) \sim -1$ for $\eta = 0.45$) with subsequent oscillations for larger $r$. Unfortunately, we found that the kink-jump method[36] employed in our simulations was very inefficient in these high-density, large $N$ cases, and, as a result, inordinately large amounts of computer time were required for equilibration with this algorithm. Nevertheless, it should be pointed out that there was a pronounced tendency for the chains to undergo a collapse relative to the ideal state at high densities as the medium-induced potential becomes more attractive. A similar trend has also been observed recently in more extensive calculations of Yethiraj.[44] Such a collapse at meltlike densities is clearly unphysical and may reflect subtle inaccuracies in the medium-induced potential, the PRISM theory, or the simulations at high density. Further investigations are necessary in order to fully understand this effect, although approximate methods,[45] based on a variational procedure at the level of the effective free energy of a single polymer chain in solution, have demonstrated that Gaussian statistics (i.e., $\langle R^2\rangle \propto N$) are recovered at melt densities. Additional research is necessary to ascertain the influence of higher order terms in the free energy expansion (eq 2.5), which lead to the expression for the medium-induced potential (eq 2.13). Recent work by Grayce et al. suggests that the medium-induced potential (eq 2.16) becomes inaccurate at meltlike densities and a new approach has been formulated.[46]

## V. Conclusions

Self-consistent PRISM calculations were performed for polymer solutions composed of tangent hard-sphere chains at various chain lengths and densities. The functional form of the medium-induced potential between pairs of sites was derived using a density functional expansion approach. The nonlinear nature of the medium-induced potential, coupled with the complexity of the excluded-volume interactions, required the use of computer simulations of an effective single chain in solution to determine the intrachain structure factor self-consistently. Good agreement was found between the present calculations and Monte Carlo simulations of polymer solutions for the average size of a polymer chain in solution, $\langle R^2\rangle$, and the density dependence of $\langle R^2\rangle$. However, more research is required to construct a reliable self-consistent theory of very concentrated solutions and melts.

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