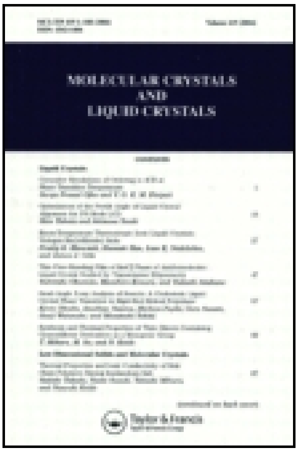

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K. S. Schweizer [a] & J. G. Curro [a]

[a] Sandia National Laboratories, Albuquerque, New Mexico, 87185

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Integral Equation Theory of Polymer Blends†

K. S. SCHWEIZER and J. G. CURRO
Sandia National Laboratories, Albuquerque, New Mexico 87185

An off-lattice microscopic statistical mechanical theory of the equilibrium properties of polymer mixtures is developed based on RISM integral equation methods. A derivation of the RPA scattering function is presented along with a fully microscopic, exact formula for the effective chi-parameter measured in SANS experiments. Numerical results for a hard core Gaussian polymer binary blend are presented. Chi is found to be a sensitive function of concentration, packing fraction, molecular weight, and structural asymmetry.

Experimental study of the intermolecular structure and thermodynamics of polymer liquid mixtures, or blends, has increased dramatically in recent years due primarily to the widespread availability of small angle neutron scattering (SANS) facilities.[1,2] By fitting SANS curves to de Gennes' random phase approximation (RPA) expression for the static structure factor,[3] accurate measurements of the empirically-defined "apparent" Flory chi-parameter, χ, have been made for a wide range of chemical systems, thermodynamic states, and degrees of polymerization. The standard and widely-employed theoretical approach for interpreting the thermodynamic properties of polymer mixtures is the Flory-Huggins (FH) *mean field, lattice* model.[4] The FH theory for the free energy of mixing is characterized by several drastic approximations the most severe of which are:[5] (1) most of the intermolecular and intramolecular correlations are ignored in calculating both the configurational entropy and enthalpy; (2) the lattice is assumed to be incompressible. By employing a novel Monte Carlo scheme Sariban and Binder[5] have recently demonstrated the importance of statistical fluctuations within a *lattice* model of binary blends. The errors incurred by FH theory were found to *increase* with degree of polymerization, and have been attributed primarily to the inadequacies of the random mixing treatment of the entropy. A separate issue is that a simple *lattice* model description of *continuum* blends composed of monomer species of different size, shape, and/or chain flexibility is physically unrealistic. The deficiencies of lattice models in

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describing the equation-of-state of continuum homopolymer melts has been recently documented.[6,7]

In a literal interpretation of the mean field FH model χ is a purely energetic or enthalpic quantity, which is simply proportional to an arithmetic difference in attractive interaction energies (relative to temperature) between the various species. In practice, χ is treated as a phenomenological parameter that reflects all the energetic and entropic contributions to the mixing free energy not accounted for by the ideal, combinatorial entropy of mixing. Recent SANS experiments[1,2,8,9] have now unambiguously documented the fact that the effective χ is in general a complicated function of temperature, density, concentration, intramolecular structure and flexibility, and in some cases degree of polymerization. There are even reports[10] that the SANS-determined χ is not a number but rather a wave vector dependent function. These observations are in fundamental conflict with the mean field FH lattice model. The dual questions of the true microscopic meaning of the apparent χ-parameter being measured in SANS experiments, and the physical factors that determine it, remain largely a mystery due to the lack of a unified, off-lattice statistical mechanical theory of structure and thermodynamics. In the present paper we describe the first tractable microscopic theory[11] of the equilibrium properties of continuum polymer blends.[12]

Our approach is based on a generalization of our reference interaction site model (RISM) integral equation theory of homopolymer melts.[13–15] The polymer molecules are represented as linearly connected sequences of chemical subunits or interaction sites. For simplicity, we consider polymer chains (or rings) composed of identical sites. The intermolecular interaction potential between a site of polymer species M on one chain and a site on another chain of type M' is taken to be a spherically symmetric function composed of a repulsive hard core of diameter $d_{MM'}$ and an attractive tail $v_{MM'}(r)$. As in the homopolymer melt case, the blend structural information is contained in the generalized Ornstein-Zernike nonlinear matrix integral equations proposed by Chandler and Andersen which in Fourier transform space are given by,[16]

$$\underline{\hat{H}}(k) = \underline{\hat{\Omega}}(k)\underline{\hat{C}}(k)\{\underline{\hat{\Omega}}(k) + \underline{\hat{H}}(k)\} \tag{1}$$

where $\underline{H}(r)$, $\underline{C}(r)$, and $\underline{\Omega}(r)$ are square matrices of rank $\sum_{\nu=1}^{p} N_\nu$ (where p = number of distinct species in the multicomponent mixture and N_ν is the number of interaction sites composing a polymer molecule of type ν) with elements $\rho_M\rho_{M'}h_{\alpha M\gamma M'}(r)$, $C_{\alpha M\gamma M'}(r)$, and $\rho_M\omega_{\alpha\gamma M}(r)\,\delta_{M,M'}$, respectively. Here ρ_M is the molecular number density of species M and the multiple subscript notation identifies the two interacting sites and associated polymer species. More specifically, $h_{\alpha M\gamma M'}(r) \equiv g_{\alpha M\gamma M'}(r) - 1$, where $g_{\alpha M\gamma M'}(r)$ is the *inter*molecular site-site radial distribution function between site α on a polymer of species M and site γ of species M', $C_{\alpha M\gamma M'}(r)$ is the corresponding direct correlation function, and $\omega_{\alpha\gamma M}(r)$ is the *intra*molecular probability distribution function for sites α and γ on the same polymer molecule of species M. To uniquely determine $\underset{\sim}{H}(r)$ and $\underset{\sim}{C}(r)$ closure relations for the above integral equations are required. We adopt the simplest scheme that has been successfully employed for atomic and small molecule fluids: the mean spherical approximation (MSA) closure[17]

$$h_{\alpha M \gamma M'}(r) = -1, \qquad r < d_{MM'}, \tag{2a}$$

$$C_{\alpha M \gamma M'}(r) = -\beta v_{MM'}(r), \qquad r > d_{MM'}, \tag{2b}$$

where $\beta = (k_B T)^{-1}$ is the inverse temperature. Equation (2a) is an exact relation for a hard core repulsion and Equation (2b) is the fundamental approximation. In the athermal limit, $v_{MM'}(r) \to 0$, Equations (1) and (2) reduce to the RISM (reference interaction site model) theory of Chandler and Andersen[16] which serves as the basis of our theory for homopolymer melts.[13-15] We refer to Equations (1) and (2) in the presence of attractive forces as the RISM-MSA theory.

As for the homopolymer melt case, there are two fundamental difficulties in applying the RISM-MSA theory to high polymer systems: (1) the need, in principle, to determine the intramolecular ($\Omega(r)$) and intermolecular pair correlations of *flexible* molecules in a self-consistent manner,[15,16] and (2) Equations (1) and (2) are numerically intractable since they correspond to a set of nonlinear, coupled integral equations of order $\left(\sum_\nu N_\nu\right)^2$. A variety of tractable approaches to both these problems have been discussed elsewhere.[13-16] For present purposes, we adopt our optimized perturbation scheme[14] to circumvent the second difficulty which corresponds to ignoring the *explicit* chain end effects. Mathematically this implies $h_{\alpha M \gamma M'}(r) = h_{MM'}(r)$ and $C_{\alpha M \gamma M'} = C_{MM'}(r)$ for all α, γ. This results in an enormous technical simplification of Equation (1) which now reduces to a set of p^2 matrix equations of the *same form* as Equation (1), *but* where the elements of $\underset{\sim}{H}(r)$, $\underset{\sim}{C}(r)$, and $\underset{\sim}{\Omega}(r)$ are now $\bar{\rho}_M \bar{\rho}_{M'} h_{MM'}(r)$, $C_{MM'}(r)$, and $\bar{\rho}_M \omega_M(r) \delta_{MM'}$, respectively. Here, $\bar{\rho}_M = N_M \rho_M$ is the site, or monomer, density of species M and $\omega_M(r)$ is the *intra*molecular structure factor.[14] The corresponding closure relations are the site-index independent versions of Equation (2). Numerical solution of the resulting integral equations is accomplished via the same published procedures employed for the homopolymer melt.[13,14] Relevant details for the blend are given elsewhere.[18]

Before presenting numerical solutions to the RISM-MSA equations for specific models, we first consider the general problem of the static structure factor measured in SANS and other scattering experiments. The general expression for the Fourier-transform of the species-dependent density-density fluctuation correlation functions are

$$\begin{aligned} \hat{\underset{\sim}{S}}(k) &= \hat{\underset{\sim}{\Omega}}(k) + \hat{\underset{\sim}{H}}(k) \\ &= [\underset{\sim}{1} - \hat{\underset{\sim}{\Omega}}(k)\hat{\underset{\sim}{C}}(k)]^{-1}\hat{\underset{\sim}{\Omega}}(k). \end{aligned} \tag{3}$$

The explicit result for the A-species partial structure factor of a binary blend is

$$\begin{aligned}\hat{S}_{AA}(k) &= \bar{\rho}_A\hat{\omega}_A\,(1 - \bar{\rho}_B\hat{\omega}_B\hat{C}_{BB})/\hat{\Lambda} \\ \hat{\Lambda}(k) &\equiv 1 - \bar{\rho}_A\hat{\omega}_A\hat{C}_{AA} - \bar{\rho}_B\hat{\omega}_B\hat{C}_{BB} + \bar{\rho}_A\bar{\rho}_B\hat{\omega}_A\hat{\omega}_B(\hat{C}_{AA}\hat{C}_{BB} - \hat{C}^2_{AB}).\end{aligned} \tag{4}$$

Analogous formulas can be written for the total and other partial structure factors.[18] The above expression is considerably different than the RPA structure factor[3] widely employed to fit SANS data

$$\hat{S}^{-1}(k) = (\phi_A\hat{\omega}_A)^{-1} + (\phi_B\hat{\omega}_B)^{-1} - 2\chi, \tag{5}$$

where $\bar{\rho} = \bar{\rho}_A + \bar{\rho}_B$, $\bar{\rho}_M = \phi_M\,\bar{\rho}$, and χ is the empirical, SANS-determined chi-parameter which is the sole embodiment of *inter*molecular effects. On the other hand, in our microscopic theory intermolecular information enters via the wave vector dependent direct correlation functions which appear in Equation (4) in a variety of combinations. The key to reconciling the differences between the RPA and integral equation expressions for the structure factor lies in the fact that our microscopic theory contains both total density and concentration fluctuations, while the RPA expression has been derived under the assumption of incompressibility. This suggests one should investigate how the integral equation expression is modified by enforcing incompressibility *post facto*. Such a program can be achieved by employing standard functional Taylor series expansion and Legendre transformation techniques. Omitting the details,[18] the following expression for the excess free energy of an *inhomogeneous* binary blend through second order can be derived

$$\beta\delta F = \frac{1}{2}\sum_{M,M'=A,B}\int\frac{d\vec{k}}{(2\pi)^3}\,\hat{S}^{-1}_{MM'}(k)\;\hat{\Psi}_M(k)\hat{\Psi}^*_{M'}(k) \tag{6}$$

where $\hat{S}^{-1}_{MM'}(k)$ is the MM' matrix element of the *inverse* structure factor matrix of Equation (3), and $\hat{\Psi}_M(k)$ is the Fourier-transform of the M-monomer density *fluctuation* field (relative to the homogeneous liquid). Incompressibility can now be enforced *post facto* by requiring $\hat{\Psi}_A + \hat{\Psi}_B = 0$ for all wave vectors. In this limit there is only one independent density fluctuation field in Equation (6), and the quantity multiplying it in the integrand can be identified as the *scalar* $\hat{S}^{-1}(k)$ that describes concentration fluctuations in the blend. Employing Equations (3) and (6), and nondimensionalizing by dividing by the total monomer number density $\bar{\rho}$, one obtains a result for $\hat{S}^{-1}(k)$ *identical in form* to Equation (5), *but* with 2χ replaced by $2\;\hat{\chi}_{\text{eff}}(k)$ defined as[19]

$$2\bar{\rho}^{-1}\,\hat{\chi}_{\text{eff}}(k) \equiv \hat{C}_{AA}(k) + \hat{C}_{BB}(k) - 2\hat{C}_{AB}(k) \tag{7}$$

$$\begin{aligned} &= -\beta[\hat{v}_{AA}(k) + \hat{v}_{BB}(k) - 2\hat{v}_{AB}(k)] \\ &\quad + \hat{C}^{(0)}_{AA}(k) + \hat{C}^{(0)}_{BB}(k) - 2\hat{C}^{(0)}_{AB}(k).\end{aligned} \tag{8}$$

This is an *exact* result within the context of the generalized Ornstein-Zernike formalism and the incompressibility assumption. Our recovery of the RPA *form* provides a more rigorous theoretical justification of its validity. More importantly, the empirical χ-parameter is now a wave vector dependent function in general, and has been given a precise microscopic meaning in terms of a simple combination of the species direct correlation functions. The *form* of Equation (7) is identical to the simple incompressible, mean field lattice expression, *but* the bare attractive interactions relative to the temperature have been replaced by the direct *correlation* functions. Such a result is in accord with the intuitive idea[16] that the direct correlation function (in units of the thermal energy) plays the role of an effective, or renormalized, pair potential in the dense fluid which incorporates many-body structural effects in a nonperturbative manner. In Equation (8) we have employed the specific MSA closure relation thereby explicitly displaying, in accord with phenomenological descriptions,[5] the two fundamentally different contributions to $\hat{\chi}_{\mathrm{eff}}(k)$. The first contribution is inversely proportional to temperature and is the continuous space analog of the Flory-Huggins mean field, purely energetic χ. The second contribution is determined by the direct correlation functions *inside* the hard core (hence the superscript zero). It is primarily an entropic quantity describing the local packing effects in the dense liquid, and in general, is a complex object depending on the specific thermodynamic state and polymer structural details.

To make explicit contact with experimental SANS measurements we note that at relatively small wave vectors, corresponding to the Guinier and intermediate regimes generally probed by SANS, the k-dependence of $\hat{\chi}_{\mathrm{eff}}(k)$ is relatively weak,[14,15] and to a first approximation can be ignored. In this limit we recover precisely the standard RPA form and the apparent chi-parameter extracted from the experimental scattering curves can be identified as the $k \to 0$ limit of $\hat{\chi}_{\mathrm{eff}}(k)$. However, the wave vector dependence of $\hat{\chi}_{\mathrm{eff}}(k)$ may not be negligible for certain polymer systems (as found for a blend containing a very stiff component[10]) and/or larger angle scattering, and can be rigorously included in the context of our theory. A final important general comment is that the post-facto incompressibility approximation still *implicitly* contains density fluctuations via the direct correlation functions, and the *explicit* effects of nonzero compressibility on the thermodynamics and structure can also be included.[18]

A general expression for the free energy of mixing appropriate to our RISM-MSA theory in the *post-facto* incompressible limit can be derived from Equations (5) and (8) by simply integrating $\hat{S}^{-1}(0)$ twice with respect to the A-monomer concentration variable ϕ. The result is[18]

$$
\begin{aligned}
\beta\Delta F_m = {} & \{N_A^{-1}\,\phi\ln(\phi) + N_B^{-1}(1-\theta)\ln(1-\phi)\} \\
& + \chi_a\phi(1-\phi) \qquad (9) \\
& + \{\phi\Delta(1) - \Delta(\phi)\}
\end{aligned}
$$

where

$$\begin{aligned}\Delta(x) &= 2\int_o^x d\phi' \int_o^{\phi'} d\phi''\, \chi_c(\phi)'' \\ 2\chi_a &= \beta^{\bar{\rho}}\, [2\hat{v}_{AB}(o) - \hat{v}_{AA}(o) - \hat{v}_{BB}(o)]\end{aligned} \tag{10}$$

and $2\chi_c$ is the second contribution in Equation (8). The first two contributions in Equation (9) are the standard (ideal) combinatorial entropy of mixing and the (mean field) enthalpy of mixing associated with the bare attractive interactions. The last term contains all the noncombinatorial and correlational contributions to the entropy and internal energy and cannot generally be decomposed any further. An important general point is that the structure of Equation (9) demonstrates that the SANS-determined χ and the empirical χ defined via the standard mean field enthalpy term are *not* equivalent.

As a numerical application of our theory we consider purely athermal binary blends composed of Gaussian chains of different statistical segment lengths $\sigma_A \neq \sigma_B$. Representative results[20] for χ at *fixed* total[15] monomer packing fractions, η_m, are shown in Figure 1 for the simple case of equality of segmental hard core diameter and statistical segment lengths: $d_{AA} = \sigma_A$, $d_{BB} = \sigma_B$, $d_{AB} = (d_{AA} + d_{BB})/2$, and identical degrees of polymerization: $N_A = N_B \equiv N$. In the athermal limit, χ is determined solely by the relative strengths of the species-dependent intermolecular direct correlations induced by the repulsive segmental interactions. There are a number of noteworthy features displayed in Figure 1: (1) χ is negative implying miscibility; (2) χ becomes more negative with increasing total packing fraction and/or structural disimilarity (larger $\gamma \equiv \sigma_B/\sigma_A$); (3) χ is a sensitive function of both concentration (approximately linear) and γ. In particular, χ is significantly more negative for the pure component composed of the smaller statistical segment length. Such a trend has been experimentally observed recently in several blends[8]; (4) the absolute magnitude of χ decreases monotonically with degree of polymerization, but remains nonzero in the asymptotic $N \rightarrow \infty$ limit thereby implying the physical effects involved are primarily *local* in nature. The former trend is a consequence of the suppression of short range *inter*molecular order with increasing N due to the enhancement of self-screening, or "correlation hole," effects as the polymer coils become larger.[13,15] We emphasize that the physical effects calculated here have nothing to do with the standard "equation-of-state" effects[5] associated with a composition-dependent packing fraction and specific attractive interactions in the blend.

A physical interpretation of the general finding of a negative χ, and hence a favorable excess or interaction entropy of mixing, is that the athermal mixture is "more random" than the separate pure components due to a larger variety of possible packing arrangements in a blend composed of polymer chains of different statistical segment lengths. A final comment is that despite the apparent simplicity of the Gaussian model, we have found[18,21] there is a remarkable similarity between our theoretical predictions for χ and SANS measurements[8,9] on a number of polymer mixtures which appear to be dominated by excess entropic effects.

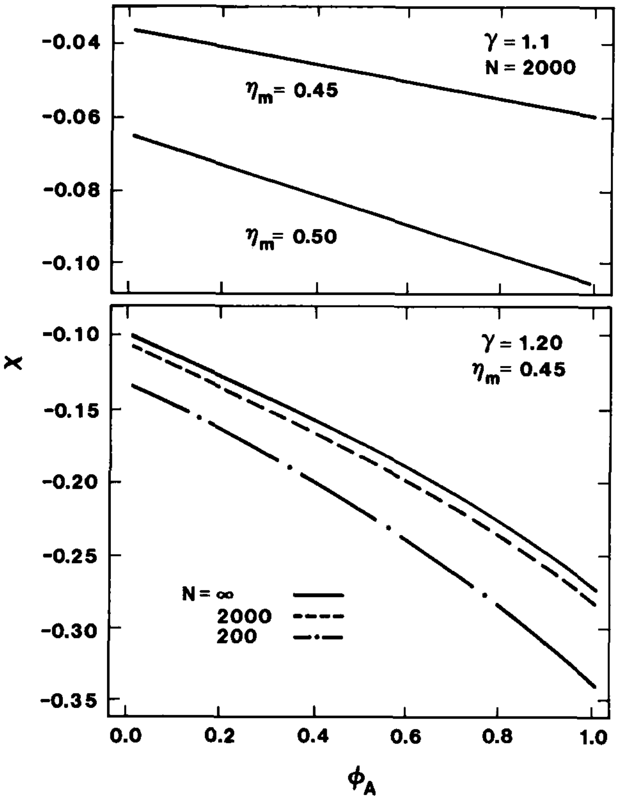

FIGURE 1 Effective chi-parameter as a function of volume fraction of A-monomer species for several values of $\gamma = \sigma_B/\sigma_A$, packing fraction, and degree of polymerization. (See footnote 20).

Other quantities of interest such as the static structure factor, intermolecular radial distribution functions, and free energy of mixing can be straightforwardly computed.[18,21] In addition, a coarse-grained Edwards-like "continuum limit" model[15,22] can be constructed for which the athermal blend integral equations can be solved analytically. Excellent qualitative agreement between the analytical model predictions for χ and the full numerical results are found.[21,22]

In conclusion, we have formulated and implemented the first tractable, microscopic, continuous space statistical mechanical theory of the structure and thermodynamics of polymer blends. Both density and concentration fluctuations, along with intramolecular structural details, are included in general thereby allowing a unified treatment of small and large wavelength phenomena. We believe the theory provides a computationally convenient molecular basis for understanding a wide range of phenomena of experimental interest such as neutron and x-ray scattering, phase separation, and equations of state. Future work will systematically consider isotopic,[18,21] athermal, topological (e.g. ring and chain mixtures),[21] and real chemical blend systems, along with the generalization of the theory to include chain stiffness,[23] self-consistency corrections, and copolymer liquids.

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