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Random phase approximation for compressible polymer blends

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Abstract

The random phase approximation is summarized for compressible polymer blend mixtures in the homogeneous phase region. Similarities with the polymer reference site interaction model are described. The effect of compressibility is also discussed in terms of 'free volume' by introducing an extra component to represent 'small voids'. Variation of the effective Flory–Huggins interaction parameter with composition is found to agree with results obtained using the lattice cluster theory.

1. Introduction

The random phase approximation (RPA) has proven to be very useful in the modeling of small angle neutron scattering (SANS) from polymer blends in the single phase region. Despite its mean field nature, the RPA has been instrumental in obtaining Flory–Huggins 'chi' parameters and mapping out spinodal lines. The RPA formalism has been developed for binary blends [1], and then extended to multicomponent mixtures [2–4]; it can be applied to either compressible or incompressible systems. Extensive details can be found in a recent review article [5]. The 'compressible' RPA equations are reviewed here and applied to a binary blend mixture. The incompressibility constraint will be taken as the very last step after working out the various partial structure factors [4]. Similarities

between the compressible RPA formalism and an Ornstein–Zernike (OZ) approach referred to as the polymer reference site interaction model (PRISM) are discussed. The RPA equations are also used to investigate the effect of compressibility on the composition dependence of the Flory–Huggins interaction parameter.

2. RPA for compressible polymer mixtures

There are two main approaches to derive RPA equations for polymer blend mixtures: the de Gennes [1]–Leibler [6] approach based on linear response theory and the Ohta–Kawasaki approach [7] based on density functional theory. In this paper, the de Gennes–Leibler method is followed. Consider a binary polymer blend (A and B components) of Gaussian chains with degrees of polymerization N_A, N_B , volume fractions ϕ_A, ϕ_B , and monomeric volumes v_A, v_B , respectively. When the blend consists of a homogeneous phase mixture,

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linear response theory yields an expression for the structure factors of the fully interacting system, $S_{AA}(Q)$, $S_{BB}(Q)$, $S_{AB}(Q)$, in terms of those of the 'ideal' (non-interacting) system $S_{AA}^0(Q)$, $S_{BB}^0(Q)$. $S_{AA}^0(Q)$ and $S_{BB}^0(Q)$ are the single chain structure factors (note that $S_{AB}^0(Q) = 0$ because A/B copolymers are not considered here). Assuming effective interaction potentials W_{AA} , W_{BB} and W_{AB} between A and B monomers, the linear responses of the fluctuating densities $\langle \rho_A(Q) \rangle$ and $\langle \rho_B(Q) \rangle$ to externally applied (weakly perturbing) potentials U_A and U_B are given, in reciprocal space, by

$$\langle \rho_A(Q) \rangle = -S_{AA}^0(Q)[U_A + W_{AA}\langle \rho_A(Q) \rangle + W_{AB}\langle \rho_B(Q) \rangle], \tag{1a}$$

$$\langle \rho_B(Q) \rangle = -S_{BB}^0(Q)[U_B + W_{BA}\langle \rho_A(Q) \rangle + W_{BB}\langle \rho_B(Q) \rangle], \tag{1b}$$

where $k_B T$ has been omitted for notation convenience and the fluctuation-dissipation theorem has been used to relate the response functions to the structure factors. Moreover interacting response functions (related to the corresponding structure factors) obey the following relationships:

$$\langle \rho_A(Q) \rangle = -S_{AA}(Q)(U_A - U_B), \tag{2a}$$

$$\langle \rho_B(Q) \rangle = -S_{BB}(Q)(U_B - U_A), \tag{2b}$$

so that the externally applied potentials can be eliminated from these coupled equations. Note that the intermonomer interaction potentials could depend on the scattering wavenumber, Q . The RPA results (for compressible blend mixtures) are, therefore,

$$S_{AA}(Q) = S_{AA}^0(1 + W_{BB}S_{BB}^0)/[(1 + W_{AA}S_{AA}^0) \times (1 + W_{BB}S_{BB}^0) - W_{AB}^2 S_{AA}^0 S_{BB}^0], \tag{3a}$$

$$S_{BB}(Q) = S_{BB}^0(1 + W_{AA}S_{AA}^0)/[(1 + W_{AA}S_{AA}^0) \times (1 + W_{BB}S_{BB}^0) - W_{AB}^2 S_{AA}^0 S_{BB}^0], \tag{3b}$$

$$S_{AB}(Q) = -S_{AA}^0 W_{AB} S_{BB}^0 / [(1 + W_{AA}S_{AA}^0) \times (1 + W_{BB}S_{BB}^0) - W_{AB}^2 S_{AA}^0 S_{BB}^0]. \tag{3c}$$

Here also, $k_B T$ and Q have been omitted. The ideal structure factors are related to the familiar Debye

functions $P_A(Q)$ and $P_B(Q)$ as $S_{AA}^0(Q) = N_A \phi_A v_A P_A(Q)$ and $S_{BB}^0(Q) = N_B \phi_B v_B P_B(Q)$. Fig. 1 shows the variation of the interacting system structure factors for a specific blend mixture. Note that the cross-correlations structure factor, $S_{AB}(Q)$, is negative.

The isothermal incompressibility condition ($\langle \rho_A(Q) \rangle + \langle \rho_B(Q) \rangle = 0$) implies $S_{AA}(Q) = S_{BB}(Q) = -S_{AB}(Q)$ which gives the de Gennes formula

$$1/S_{AA}(Q) = 1/S_{AA}^0(Q) + 1/S_{BB}^0(Q) - 2\chi_{AB}/v_0, \tag{4}$$

where $v_0 = (v_A v_B)^{1/2}$ is a 'reference' volume and the Flory-Huggins interaction 'chi' parameter, χ_{AB} , has been defined as

$$\chi_{AB} = W_{AB} - (W_{AA} + W_{BB})/2. \tag{5}$$

Fig. 2 shows the variation of the sole structure factor, $S_{AA}(Q)$, for an incompressible blend mixture.

This approach has been extended to multicomponent polymer mixtures using an elegant matrix

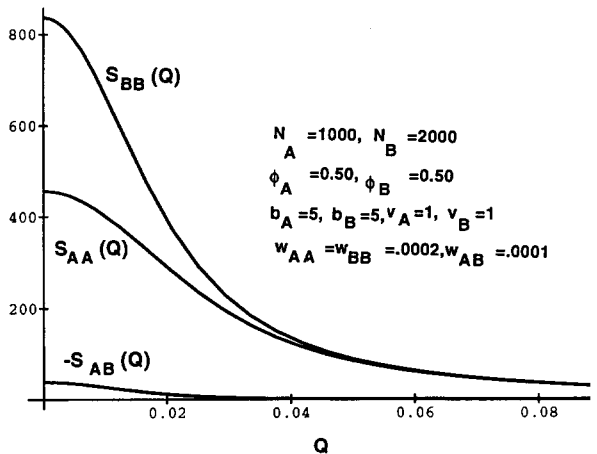


Fig. 1. Partial structure factors for a compressible blend mixture with: degrees of polymerization $N_A = 1000$, $N_B = 2000$; volume fractions $\phi_A = 0.5$, $\phi_B = 0.5$; segment lengths $b_A = b_B = 5 \text{ \AA}$; interaction potentials $W_{AA} = W_{BB} = 0.0002$, $W_{AB} = 0.0001$ ($k_B T = 1$ assumed). Note that monomer volumes have been set to unity ($v_A = v_B = 1$).

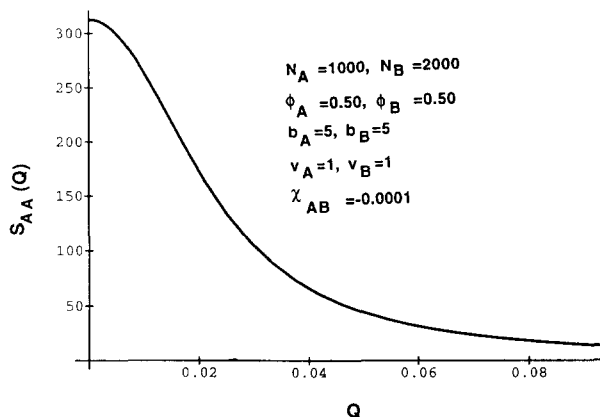


Fig. 2. Partial structure factor for an incompressible blend mixture with the same parameters as in Fig. 1. Here $\chi_{AB} = -0.0001$ has been used and the reference volume has been set to unity ($v_0 = 1$).

notation [3,4]. The main result for compressible mixtures is

$$\mathbf{S}^{-1}(Q) = \mathbf{S}_0^{-1}(Q) + \mathbf{W}(Q) \text{ or}$$

$$\mathbf{S}(Q) = \{1 + \mathbf{S}_0(Q) \cdot \mathbf{W}(Q)\}^{-1} \cdot \mathbf{S}_0(Q) \quad (6)$$

where, for our two-component blend, \mathbf{S} , \mathbf{S}_0 and \mathbf{W} are 2×2 matrices. The incompressibility constraint is imposed by 'sandwiching' \mathbf{S}^{-1} between a 'projector', \mathbf{P}^T , ($= [1, -1]$ for two-component case) and its transpose \mathbf{P} :

$$S_{AA}^{-1}(Q) = \mathbf{P}^T \cdot \{\mathbf{S}_0^{-1}(Q) + \mathbf{W}(Q)\} \cdot \mathbf{P}. \quad (7)$$

This has the effect of adding the diagonal elements and subtracting the off-diagonal elements [4]. In this procedure, the incompressibility constraint is taken as the very last step.

3. The Ornstein-Zernike approach

Defining an interchain structure factor as: $\mathbf{H}(Q) = \mathbf{S}(Q) - \mathbf{S}_0(Q)$, and using the 'compressible' RPA equation, the following relationship is obtained:

$$\mathbf{H}(Q) = -\mathbf{S}_0(Q) \cdot \mathbf{W}(Q) \cdot \mathbf{S}_0(Q) - \mathbf{S}_0(Q) \cdot \mathbf{W}(Q) \cdot \mathbf{H}(Q). \quad (8)$$

This equation is identical to the Fourier transform of the OZ equation used in PRISM calculations [8] except for the fact that, in the OZ equation, the direct correlation functions, $\mathbf{C}(Q)$, replace the potentials $-\mathbf{W}(Q)$ (recall that $k_B T$ has been omitted). This relationship $\mathbf{C}(Q) = -\mathbf{W}(Q)$ is reminiscent of the mean spherical approximation (MSA) closure relation used to solve the OZ equation. A comparable argument showing the similarity of the RPA and OZ approaches was pointed out before [9]. However, incompressible RPA equations were used in that argument.

The RPA and OZ approaches use similar starting equations in direct space. PRISM calculations use the OZ equation along with a closure relation that splits the interaction range into two regions $r < b$ and $r > b$ (b is the segment length) in order to calculate the direct correlation functions (and the intermonomer potentials) 'self-consistently'. The RPA uses the intermonomer interaction potentials as input 'parameters'. The main difference between the two methods is in the modeling of the direct correlation function for low r (local packing). The RPA uses $\mathbf{C}(Q) = -\mathbf{W}(Q)$ even for high Q (low r) while the PRISM with MSA closure assumes that the pair correlation function $g(r) = 0$ for low r . This is tantamount to including multiple contact interactions which are neglected in the RPA. For this reason, PRISM calculations, for example, can predict peaked behaviors for the pair correlation function while the RPA cannot.

4. Compressibility effects on the 'chi' parameter

The issue of compressibility of polymer mixtures has been the focus of much attention. A recent article [10] summarizes the various theoretical approaches used to explain experimentally observed composition dependencies of 'effective' Flory-Huggins chi parameters as measured by SANS [11,12]. It [10] also uses Monte Carlo simulations to investigate such composition dependencies of the effective 'chi' parameter coming from equation of state effects. Among these approaches, the lattice cluster theory [13] predicts mostly peaked behaviors (with a maximum for the variation of chi with composition). A simple incompressible three-component

RPA approach (where the third component is assumed to consist of small 'voids' also referred to as 'free volume') is used here to reproduce similar trends. The reduction of the 'voids' fraction is equivalent to an increase in pressure as considered by Freed and Dudowicz [13]. The incompressible three-component RPA equations are similar to Eqs. (3) except for the fact that intermonomer interaction potentials, W_{AB} s, are replaced by the excluded volumes, V_{AB} s, defined as

$$V_{AA} = 1/S_{CC}^0 - 2\chi_{AC}/v_0$$

$$V_{BB} = 1/S_{CC}^0 - 2\chi_{BC}/v_0$$

$$V_{AB} = 1/S_{CC}^0 + \chi_{AB}/v_0 - \chi_{AC}/v_0 - \chi_{BC}/v_0. \quad (9)$$

Here $S_{CC}^0 = \phi_C v_C$ represents the 'ideal' contribution of the 'voids' and the various chi parameters have the usual definition; $\chi_{IJ} = W_{IJ} - (W_{II} + W_{JJ})/2$ with (I, J) = (A, B). In our application, the voids are assumed not to interact at all ($W_{AC} = W_{BC} = W_{CC} = 0$) and to have sizes equal to the monomer ones (v_C and v_A, v_B are comparable). Following others [10,13], we define an 'effective' chi parameter as

$$\chi_{\text{eff}} = (1/S_{AA}^0 + 1/S_{BB}^0 - 1/S_{AA})/2 \quad (10)$$

at the thermodynamic limit ($Q = 0$). S_{AA} is taken from Eq. (3a). In this approach, 'real' volume fractions are defined ($\phi_A + \phi_B + \phi_C = 1$) as well as 'observed' volume fractions ($\phi_A^0 + \phi_B^0 = 1$) which correspond to the mixing conditions. In order to relate these two sets, the void fraction is assumed to be shared equally between the two components ($\phi_A/\phi_A^0 = \phi_B/\phi_B^0 = 1 - \phi_C$). The variation of χ_{eff} with the 'observed' volume fraction of component A is shown in Fig. 3(a) where the void volume fraction is varied from 0% (horizontal line) to 5% (bottom curve). These curves are similar to those plotted in Ref. [13]. When the void volume fraction is taken to vary linearly with the volume fraction of component A ($\phi_C = 0.08\phi_A^0 + 0.01$), the composition dependence of χ_{eff} is seen to follow a linear behavior at intermediate compositions as shown in Fig. 3(b). This last case is reminiscent of the linear composition dependence of χ_{eff} observed for deuterated polystyrene/polyvinyl methylether [14].

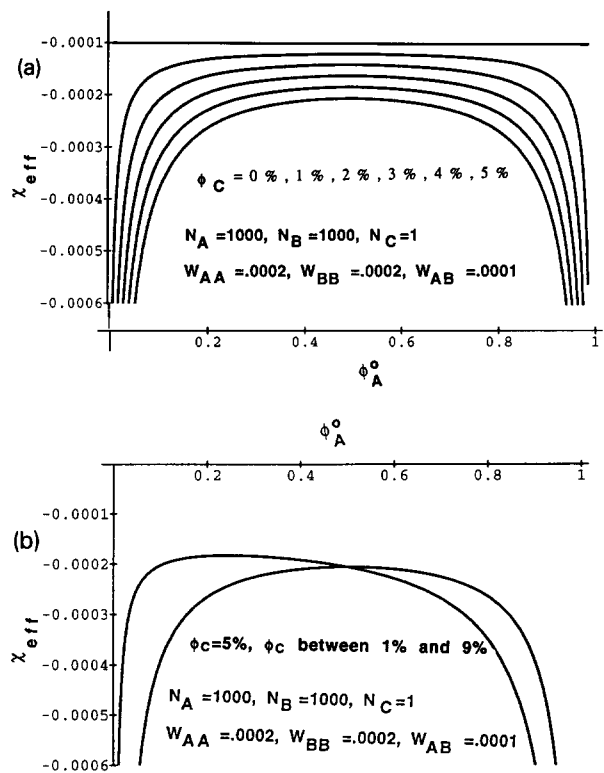


Fig. 3. Composition dependence of the effective chi parameter obtained from the three-component RPA approach where the third component corresponds to small 'voids'. (a) From top to bottom, the curves show the variation of the void fraction, ϕ_C , from 1 to 5%, respectively. The constant line corresponds to a 0% void fraction (i.e., to an incompressible mixture). The monomer volumes have been set to unity ($v_A = v_B = 1$). (b) The two curves correspond to a constant void fraction (symmetric around 50%) and to a void fraction that varies linearly between 1% (pure B) and 9% (pure A) respectively.

Using the simple RPA approach described here, we have not been able to reproduce variations of χ_{eff} that show a minimum with composition as observed in polyolefin blends [11,12].

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