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Reliably estimating bare chi from compressible blends in the grand canonical ensemble

Sagar S. Rane [a,1], P.D. Gujrati [a,b,*]

[a] Department of Polymer Science, The University of Akron, Akron, OH 44325, United States
[b] Department of Physics, The University of Akron, Akron, OH 44325, United States

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Abstract

The bare chi characterizing polymer blends plays a significant role in their macroscopic description. Therefore, its experimental determination, especially from small-angle-neutron-scattering experiments on isotopic blends, is of prime importance in thermodynamic investigations. Experimentally extracted quantity, commonly known as the effective chi is affected by thermodynamics, in particular by polymer connectivity, and composition and density fluctuations. The present work is primarily concerned with studying four possible effective chis, one of which is closely related to the conventionally defined effective chi, to see which one plays the role of a reliable estimator of the bare chi. We show that the conventionally extracted effective chi is not a good measure of the bare chi in *most* blends. A related quantity that does not contain any density fluctuations, and one which can be easily extracted, is a good estimator of the bare chi in all blends except weakly interacting asymmetric blends (see text for definition). The density fluctuation contribution is given by $(\Delta\bar{v})^2/2TK_T$, where $\Delta\bar{v}$ is the difference of the partial monomer volumes and K_T is the compressibility. Our effective chis are theory-independent. From our calculations and by explicitly treating experimental data, we show that the effective chis, as defined here, have weak composition dependence and do not diverge in the composition wings. We elucidate the impact of compressibility and interactions on the behavior of the effective chis and their relationship with the bare chi.

Keywords: Small angle neutron scattering; Thermodynamic interactions; Chi parameter; Bare chi; Polyolefin blends; Ensemble; Equation of state; Light scattering; Lattice theories; Isotopic polymer mixtures; Polymer thermodynamics

1. Introduction

A lattice model of an incompressible polymer mixture of species 1 and 2 is characterized by a dimensionless bare exchange energy parameter $\chi_{12} = q\beta\varepsilon_{12}$. Here q is the coordination number of the lattice, β is the inverse temperature in the units of the Boltzmann constant, $\varepsilon_{ij} = e_{ij} - 1/2(e_{ii} + e_{jj})$ is the microscopic exchange interaction energy, and e_{ij} the bare or van der Waals interaction energy between species i and j. The bare

* Corresponding author. Tel.: +1 330 972 7136; fax: +1 330 972 6918.
E-mail address: pdg@arjun.physics.uakron.edu (P.D. Gujrati).
[1] Present address: Department of Pharmaceutical Sciences, A317 ASTECC Building, University of Kentucky, Lexington, KY 40506-0286, United States.

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exchange energy appears as a parameter in the partition function of the model, where it determines the energy of various configurations in the system. As such, ε_{ij} must be independent of the thermodynamic state, i.e. of composition, molecular weight, free volume, etc. [1,2]. Being a fundamental microscopic parameter, χ_{12} must remain the same in a homopolymer blend, a block copolymer, etc. at the same temperature. Its value, therefore, is of utmost importance in polymer thermodynamics and a great deal of effort has been made to measure it [3–11]. However, what one measures from experiments is not the bare chi, but an effective chi that has been *modified* by thermodynamics. Because of this, it depends on the thermodynamic state of the system. In particular, it develops a composition-dependence, which can be extremely strong in the composition wings if not carefully defined [1].

In the simplest theory, known as the Flory–Huggins (F–H) theory, [12–14] of an incompressible lattice model of polymers, we find that the effective chi is equal to χ_{12} due to the random-mixing approximation (RMA) [15]. (Here, F–H theory will always refer to the above theory of the incompressible model, and not to any of its possible extensions to the compressible model.) The equality is not true in general. Going beyond the RMA [16–20], we find that the effective chi has a weak composition-dependence even in the absence of free volume, with its magnitude close to

$$\chi_{NR} \equiv (q-2)\chi_{12}/q \tag{1}$$

for polymeric fluids with weak interactions, and small amount of free volume. The prefactor $(q-2)/q$ in the definition of χ_{NR} has its origin in the non-randomness (NR) caused by polymer *connectivity* (we ignore end-group effects) and is important for finite q ($\lesssim 12$) expected for real systems. Only when $q \to \infty$, the limit in which the RMA becomes valid, [15] do we expect the connectivity to play no significant role and we expect the effective chi in the incompressible model to be identical to χ_{12}. We, thus, conclude that the composition fluctuations and the polymer connectivity have no effect on the effective chi in the incompressible RMA limit (the F–H theory). To see their effects, one must either consider non-random (NR) theories, or real systems that will always exhibit non-randomness. In an incompressible system, the effective chi is conventionally defined by the following quantity Γ related to the second derivative of the Helmholtz free energy F per site: $\Gamma \equiv (1/2)(\partial^2 \beta F/\partial \phi_{m1}^2)$, where ϕ_{m1}, ϕ_{m2} denote the densities of the two species 1 and 2, with $\phi_{m2} = 1 - \phi_{m1}$. One then subtracts Γ from a reference value

$$\Gamma_{FH,ath} \equiv (1/2)[1/M_1\phi_{m1} + 1/M_2\phi_{m2}] \tag{2}$$

to define the effective chi, known as the F–H chi

$$\chi_{FH} = \Gamma_{FH,ath} - \Gamma. \tag{3}$$

Using this *subtraction scheme* [1,4–11,21–28] we easily find that $\chi_{FH} = \chi_{12}$ in the F–H theory. However, as shown previously (see Eq. 32 and discussion following it in Ref. [1]), this is not true when the compressibility is nonzero, i.e. when the free volume (represented by voids [29]) is *not* zero. In particular, there emerges a divergence in the composition wings. Similarly, if the experimental data is analyzed using Eq. (3), then χ_{FH} invariably exhibits a similar divergence. Such a divergence implies that the effective chi has lost its significance as a measure of χ_{12}. In order to avoid this divergence, it was suggested in Ref. [1] that we use in the subtraction scheme an appropriate reference Γ_{ref} so as to cancel this divergence. It was shown that using the athermal value Γ_{ath} of Γ for Γ_{ref} ensures the *absence of a divergence* in the wings, regardless of whether Γ is calculated in some specific theory or extracted by experiments. Thus, the proposal of Ref. [1] for an effective chi is a *general proposal* applicable to any theory or to any experimental extraction procedure as far as the absence of the divergence is concerned.

The bare chi is required for any first principle calculation or simulation [30]. Only the bare chi can truly characterize the strength and nature of interaction between monomers of two species, regardless of whether we consider a blend or a block copolymer. An effective chi, being dependent on the thermodynamic state, need not be the same in the two systems. Therefore, obtaining a reliable estimator of the bare chi is of utmost importance, and is the central goal of our work. We recall that the aim in Ref. [1] was to demonstrate how to obtain the effective chi without any spurious divergence.

The fluctuations that occur in the system control the quantity Γ. There are composition fluctuations, but no density fluctuations in an incompressible system. In contrast, a compressible system possesses both kinds of fluctuations. The deviation of χ_{FH} from χ_{12} for a compressible system is caused not only by the presence of both fluctuations, but also due to non-randomness [see Eq. (1)]. Since we have no control over the corrections due to non-randomness, we will only investigate the relative contributions due to the two fluctuations in this paper. Thus, our attempt would be to extract a reliable estimator of χ_{NR} in this work.

There exists an unrealistic ensemble, [1] called the A-ensemble (see the Section 2 for relevant details), in which the free volume and the total volume are kept fixed. Thus, there are only composition fluctuations, but no density fluctuations even though the free volume is not zero. This makes the A-ensemble somewhat similar to the incompressible system as far as the fluctuations are concerned. In contrast, the experiments are done in the grand canonical ensemble, called the C-ensemble, [1] which allows for both fluctuations. Compressibility effects in the A-ensemble are due to composition fluctuations alone and are *minimal*, but by no means absent.