A LETTERS JOURNAL EXPLORING
THE FRONTIERS OF PHYSICS

OFFPRINT

Characterization of the Flory-Huggins interaction parameter of polymer thermodynamics

Travis H. Russell, Brian J. Edwards and Bamin Khomami

EPL, **108** (2014) 66003

epl

A Letters Journal Exploring
the Frontiers of Physics

AN INVITATION TO SUBMIT YOUR WORK

www.epljournal.org

The Editorial Board invites you to submit your letters to EPL

EPL is a leading international journal publishing original, innovative Letters in all areas of physics, ranging from condensed matter topics and interdisciplinary research to astrophysics, geophysics, plasma and fusion sciences, including those with application potential.

The high profile of the journal combined with the excellent scientific quality of the articles ensures that EPL is an essential resource for its worldwide audience. EPL offers authors global visibility and a great opportunity to share their work with others across the whole of the physics community.

Run by active scientists, for scientists

EPL is reviewed by scientists for scientists, to serve and support the international scientific community. The Editorial Board is a team of active research scientists with an expert understanding of the needs of both authors and researchers.

www.epljournal.org

epl

ISSN 0295-5075

A Letters Journal Exploring
the Frontiers of Physics

Volume 105 Number 1
January 2014

www.epljournal.org

epl

ISSN 0295-5075

A Letters Journal Exploring
the Frontiers of Physics

Volume 104 Number 1
October 2013

www.epljournal.org

epl

ISSN 0295-5075

A Letters Journal Exploring
the Frontiers of Physics

Volume 103 Number 1
July 2013

www.epljournal.org

epl A LETTERS JOURNAL EXPLORING
THE FRONTIERS OF PHYSICS

www.epljournal.org

OVER
560,000
full text downloads in 2013

24 DAYS
average accept to online publication in 2013

10,755
citations in 2013

"We greatly appreciate the efficient, professional and rapid processing of our paper by your team."

Cong Lin
Shanghai University

Six good reasons to publish with EPL

We want to work with you to gain recognition for your research through worldwide visibility and high citations. As an EPL author, you will benefit from:

1. **Quality** – The 50+ Co-editors, who are experts in their field, oversee the entire peer-review process, from selection of the referees to making all final acceptance decisions.
2. **Convenience** – Easy to access compilations of recent articles in specific narrow fields available on the website.
3. **Speed of processing** – We aim to provide you with a quick and efficient service; the median time from submission to online publication is under 100 days.
4. **High visibility** – Strong promotion and visibility through material available at over 300 events annually, distributed via e-mail, and targeted mailshot newsletters.
5. **International reach** – Over 2600 institutions have access to EPL, enabling your work to be read by your peers in 90 countries.
6. **Open access** – Articles are offered open access for a one-off author payment; green open access on all others with a 12-month embargo.

Details on preparing, submitting and tracking the progress of your manuscript from submission to acceptance are available on the EPL submission website **www.epletters.net**.

If you would like further information about our author service or EPL in general, please visit **www.epljournal.org** or e-mail us at **info@epljournal.org**.

EPL is published in partnership with:

European Physical Society
Società Italiana di Fisica
EDP Sciences
IOP Publishing

www.epljournal.org

A Letters Journal Exploring the Frontiers of Physics

December 2014

EPL, **108** (2014) 66003
doi: `10.1209/0295-5075/108/66003`

`www.epljournal.org`

Characterization of the Flory-Huggins interaction parameter of polymer thermodynamics

Travis H. Russell, Brian J. Edwards[(a)] and Bamin Khomami

Materials Research and Innovation Laboratory, Department of Chemical and Biomolecular Engineering, University of Tennessee - Knoxville, TN 37996, USA

received 8 September 2014; accepted in final form 8 December 2014

PACS `65.20.De` – General theory of thermodynamic properties of liquids, including computer simulation
PACS `64.10.+h` – General theory of equations of state and phase equilibria
PACS `82.35.Lr` – Physical properties of polymers

Abstract – Flory-Huggins theory is the main basis of polymer solution and blend thermodynamics. A key piece of this theory is a parameter quantifying the enthalpic interactions between the components; however, experiments have revealed that this parameter is not composition independent, as originally assumed. This composition dependence has been attributed by some theorists to experimental error; others have tried to explain it based on several competing hypotheses. Here, we use atomistic simulations of isotopic blends based on realistic potentials to study this parameter without making any prior hypotheses. Simulations reveal a composition dependence of this parameter that compares well with experimental data, and serve to verify theoretical relationships between the various forms of this parameter.

In 1942, Paul Flory and Maurice Huggins each independently published seminal articles developing the thermodynamic underpinnings of polymer solution theory [1–3]; *i.e.*, high-molecular-weight macromolecules dissolved in low-molecular-weight solvents. More than seventy years later, this theory has become the foundation of most theoretical understanding of not only polymer-solvent thermodynamics, but also of polymer blend and block copolymer thermodynamics as well. Including Flory, no fewer than five Nobel laureates have contributed to the further development of this theory, and the original papers have been cited well in excess of 10000 times. Its use is ubiquitous in polymer theories and simulations aimed at the description of the phase behavior of polymeric materials, especially for di-block and tri-block copolymer systems where the morphological features of thin films and membranes can be finely tuned to tailor specific nanoscale material properties such as conductance, mechanical and thermal integrity, porosity, absorbance, etc. The universal foundation of Flory-Huggins (FH) theory thus facilitates the development and understanding of many diverse technological applications such as fuel cells, nanofiltration membranes, drug and drug delivery systems, batteries, biochemical sensors, semiconductor microcircuits, etc.

The basic hypothesis of Flory-Huggins theory is that the free energy of mixing of a polymer and solvent can be quantified using a simple lattice model of n unit cells [1–3] according to

$$\frac{\Delta G}{nk_BT} = \frac{\phi_A \ln \phi_A}{N_A} + \frac{\phi_B \ln \phi_B}{N_B} + \chi_T \phi_A \phi_B. \tag{1}$$

In this expression, ΔG is the change in Gibbs free energy of mixing, k_B is the Boltzmann constant, and T is the absolute temperature. ϕ_A and N_A denote the volume fraction and number of monomeric units of the polymer on the lattice, respectively, whereas ϕ_B and N_B denote the volume fraction and number of solvent molecules. Note that $n = N_A + N_B$. In the final term, χ_T is the thermodynamic interaction parameter, which has ultimately become the centerpiece of most theory and simulation of complex polymer phase behavior.

The first two terms on the right side of eq. (1) are the standard (ideal mixture) entropic terms arising solely from the statistical mixing of dissimilar components, assuming all intermolecular interactions are equivalent regardless of the size and energetic nature of the A and B units. This is, of course, an idealization that must be augmented with a suitable expression for the non-ideality of the mixing process that results from the dissimilarity in molecular sizes

---

[(a)] E-mail: `bje@utk.edu` (corresponding author) and the energetic differences between the monomeric units and solvent molecules. Therefore, the final term including the interaction parameter (also known as the Γ-function) was introduced into eq. (1) to account for the enthalpic deviations from ideal mixing. A key point of the Flory-Huggins expression is that χ_T was assumed to be independent of the relative concentrations of polymer and solvent.

Since its origination over seventy years ago, Flory-Huggins theory has been extended to polymer blend and block copolymer systems by assuming that an expression similar to eq. (1) holds once the solvent molecules are replaced by the monomeric units of the juxtaposed polymer. In this case, N_A and N_B are the number of monomeric units of each type of polymer per chain multiplied by the number of chains of each type. These extensions thus define an energetic interaction parameter (χ) to quantify the enthalpic energy of dispersion between distinct components; however, although it is clear in principle that this χ parameter should correspond to the χ_T of eq. (1), this subtle point has often led to confusion as χ_T is not directly amenable to experimental determination. What can be measured directly is a structural version of this parameter, χ_S, which is often used in eq. (1) as if it were the proper thermodynamic interaction parameter.

Thermodynamic and morphological properties of polymer blends, block copolymers, and polymer solutions depend critically on this χ parameter, and, since its introduction, theoretical calculations and molecular simulations have almost exclusively considered it to be independent of the concentrations of the chemical components of the system. However, small-angle neutron scattering experiments on a wide range of isotopic polymer blends (*e.g.*, polyethylene (PE)/deuterated polyethylene (PED)) have shown that the data do not support this assumption [4–6]. In the overwhelming majority of experiments, as the volume fraction of deuterated chains (ϕ_D) in the system entered the ranges of approximately $0.25 > \phi_D > 0.75$, χ dramatically increased displaying a roughly parabolic composition dependence centered around $\phi_D = 0.5$; this dependence appeared to become less pronounced as N was increased toward the mean-field condition of infinite chain length [4–6]. Extensive analyses of excess free energy in isotopic polymer solutions also revealed similar anomalies in FH theory [7–9].

Several possible explanations for the existence of the observed composition dependence of χ have been suggested [4–12], although some theorists have gone so far as to suggest that the observed concentration dependence of this parameter is entirely attributable to experimental error [13]. Alternative explanations for the observed dependence include compressibility effects, concentration fluctuations, non-specifically defined parameters, and minority component structural changes [4–12]. The majority of research has been aimed at the consideration of the effect of concentration fluctuations on χ [4,14–17] using field theoretic techniques of coarse-grained systems of Gaussian or bead-spring chains that represent statistical segments of the polymer chains as opposed to detailed atomistic models of the interactions between the basic elements of the macromolecules. These coarse-grained models of concentration fluctuation effects have helped to understand the basic physics underlying the χ parameter; however, their reliance on coarse-grained approximations of the real polymer chains requires theorists to make assumptions and approximations to derive appropriate relationships between χ and the physical variables of the system. Indeed, the hypothesis that the concentration dependence of χ is due to long- and short-range concentration fluctuations is one such hypothesis. Consequently, while proper calculation of χ_T is vitally important to describing accurately the free energy, only general estimates can be made of this quantity due to the coarse-grained nature of the polymer model employed [18,19]. Additionally, attempting to compute χ_T experimentally requires accurate determination of ΔG, which is generally not possible for complex polymeric systems. Therefore, experimental calculations of the interaction parameter have been restricted to using the structural definition of χ (*i.e.*, χ_S) provided through the Random Phase Approximation (RPA) of de Gennes [20].

RPA is a mean-field theory designed to link light scattering data of intensity, I, *vs.* wave number, q, to structural information provided through the structure factor, $S(q)$ [20]. The structural interaction parameter, χ_S, can be calculated from $S(q)$ through use of the single-chain Debye function, g_D, via the relationships

$$\begin{aligned} I(q) &= \frac{S(q)}{v}(b_B - b_A)^2, && (2)\\ S^{-1}(q) &= [N_A\phi_A g_D(Rg_A, q)]^{-1} \\ &\quad + [N_B\phi_B g_D(Rg_B, q)]^{-1} - 2\chi_S, && (3)\\ g_D(Rg_i, q) &= 2\frac{Rg_i^2 q^2 + \exp(-Rg_i^2 q^2) - 1}{Rg_i^4 q^4}. && (4) \end{aligned}$$

In these expressions, v is a reference volume, b_i is the coherent light scattering length of monomeric unit i, and Rg_i is the radius of gyration of polymer molecule i. Once the structure factor is known, eq. (3) allows calculation of the structural aspect of the interaction parameter, χ_S. $I(q)$ data are measured at $q \approx 0$ to eliminate any wave number dependence [21]. Additionally, the RPA relates $S(0)$ to ΔG as

$$S^{-1}(0) = \frac{\partial^2 \Delta G}{\partial \phi_B^2}. \qquad (5)$$

Equation (5) can then be combined with eqs. (3) and (4) at $q = 0$ to define χ_S as a function of χ_T through the Γ-function of eq. (1) [4,20,22]:

$$\chi_S(\chi_T) = -\frac{1}{2}\frac{\partial^2 \chi_T \phi_A \phi_B}{\partial \phi_A^2}. \qquad (6)$$

For a binary system, $\phi_B = 1 - \phi_A$, which implies that $\chi_S = \chi_T$ when the latter quantity is independent of composition; however, this is not something that should be taken for granted *a priori*.

A number of the previous theoretical efforts cited above have applied the RPA to coarse-grained models of the polymer chains to examine and understand the concentration dependence of χ_S and its relationship to χ_T, *e.g.*, refs. [4,14–17]. However, in each case, approximations and assumptions are made with respect to the coarse graining of the polymer chains, as well as the physical causes and mechanisms responsible for producing the resulting composition dependence of χ_S. In this letter, we describe research that avoids these approximations and assumptions by working in terms of detailed atomistic models of the polymer chains. Once one accepts the plausibility of the atomistic potentials to describe the dynamical properties of the polymer systems, all deductions made from simulations of these potentials are consequences of the underlying system physics, not artifacts of any coarse-graining procedure or assumed physical mechanisms.

Our initial calculations were performed to investigate the composition dependence of χ_S, χ_T, and the functional relationship between the two in a weakly interacting polymer blend modeled on the isotopic mixture of $C_{16}H_{34}$ and $C_{16}D_{34}$. Structural data were produced using Configurational Bias Monte Carlo (CBMC) simulations originally developed by Rosenbluth and Rosenbluth [23] and refined for off-lattice systems by Frenkel and Smit [24]. Calculations of $S(q)$ were performed using the definition provided by Aichele *et al.* [25]. ΔG data for the calculation of χ_T were obtained using Molecular-Dynamics–based Thermodynamic Integration (MDTI) simulations within the open-source Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) platform [26]. Thermodynamic integration was performed in the standard manner [24] by varying an arbitrary parameter, λ, incrementally from the homogeneous PE system to the PE/PED system at the appropriate composition. Ten equal increments of λ were used for all simulations; the suitability of this number was testing by doubling the number of increments for several trial systems, but no noticeable differences were detected —see the dissertation of Russell for further details [27]. Once the C_{16} data were analyzed, N was increased sequentially to 200 ($C_{200}H_{402}$) to investigate the role of chain length on $\chi(\phi_D)$. All simulations were performed using 162 chains in the canonical ensemble using either CBMC or MDTI as the situation warranted. Additional simulations were run in the isobaric-isothermal ensemble to test the accuracy of the Legendre transformation relating the Helmholtz and Gibbs energies, $\Delta G = \Delta A + \Delta(PV)$; both data sets provided statistically equivalent values for ΔG. The simulation density was set at the experimental value of $0.75\,\mathrm{g/cm^3}$, and the temperature was maintained at 323 K for the C_{16} runs and at 450 K for the subsequent chain length analysis.

Accurate united-atom potentials for liquid $C_{16}H_{34}$ are well defined in the literature and have been extensively used for simulations of PE chains [28,29]; these include energetic expressions for the bond-bending, bond-stretching, bond-torsion, and non-bonded intra/intermolecular atomic interactions. Unfortunately, a similar statement cannot be made for deuterated PE liquids. After reviewing scant information on deuterated systems [30,31], we decided to limit variations between the PE and PED potentials to the non-bonded Lennard-Jones (LJ) potentials, under the assumption that intrachain energetics were associated with very stiff elastic constants and not likely to influence phase behavior. This assumption appeared to be supported by several trial runs in which the atomic unit bond length of PE was reduced by 3% relative to the bond length of PED [30,31] with no appreciable change observed in the results. With no explicit knowledge of the exact parameter set for the PED non-bonded potentials, we chose to follow the limited evidence [30,31] available and allow the LJ potential parameters for the $C_{16}D_{34}$ chains (σ_D and ε_D) to vary ±2.5% from their PE values (σ_H and ε_H) [13,28,29]; however, the literature contains contradictions with regard to the relative magnitudes of the Lennard-Jones parameters of hydrogen and deuterium atoms. As such, we examined three specific cases of C_{16} isotopically blended systems:

$$\begin{aligned}&\text{A) } \sigma_D = +2.5\%\,\sigma_H, \quad \varepsilon_D = -2.5\%\,\varepsilon_H,\\ &\text{B) } \sigma_D = +2.5\%\,\sigma_H, \quad \varepsilon_D = +2.5\%\,\varepsilon_H,\\ &\text{C) } \sigma_D = -2.5\%\,\sigma_H, \quad \varepsilon_D = +2.5\%\,\varepsilon_H.\end{aligned}$$

Values of Rg_i^2 of the simulated chains were approximately $22\,\text{Å}^2$ and varied only slightly with parameter set or the composition state point of the system.

As displayed in fig. 1(a), MDTI simulations revealed distinct composition dependences for ΔG across the range of parameter sets. The Gibbs energy has been defined relative to the reference state of pure PE, implying that $\Delta G = 0$ when $\phi_D = 0$; however, in general $\Delta G \neq 0$ at $\phi_D = 1$ since the Gibbs energy of pure PE is not equal to that of pure PED. Whereas eq. (1) can be rewritten to define the thermodynamic interaction parameter in terms of ΔG, fig. 1(b) shows that there are also unique composition dependences of χ_T for each of the simulated parameter sets. Furthermore, the functional forms of $\Delta G(\phi_D)$ and $\chi_T(\phi_D)$ are quite different for each of the three cases. The slope of $\Delta G(\phi_D)$ only varies slowly across the composition range whereas $\chi_T(\phi_D)$ initially displays a modest composition dependence in the low-ϕ_D region which becomes much more prominent as ϕ_D approaches unity. In addition, the functional form of $\chi_T(\phi_D)$ is considerably different from the roughly parabolic form observed in the previous experimental determinations of $\chi_S(\phi_D)$ [4–6]. Furthermore, most theoretical studies aimed at elucidating the concentration dependence of χ_S have nevertheless started by assuming that χ_T was independent of concentration, which is not the case for the present simulations.

Unlike the data for χ_T, the structural interaction parameter calculated according to eq. (3) using the structure factor determined with the CBMC simulations agrees qualitatively with the vast majority of the available experimental data [4–6]. As evident in fig. 2, the values of

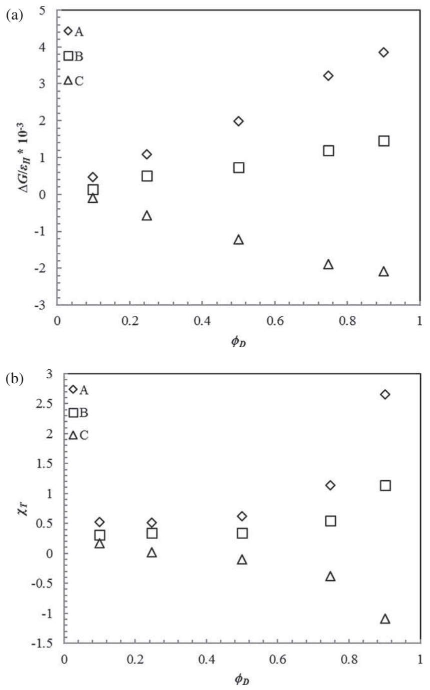

Fig. 1: Composition dependence as a function of ϕ_D of isotopic C_{16} blends with each of the parameter sets, A, B, and C, of (a) ΔG and (b) χ_T. Error bars on the data are believed to be approximately the size of the symbols.

$\chi_S(\phi_D)$ display the established roughly parabolic form. It is worth noting the lack of influence of parameter selection on $\chi_S(\phi_D)$; the data for each parameter set lie on top of each other. As the wave number is inversely proportional to distance, at the relatively long distances associated with $q \approx 0$, the effect of parameter selection along the compositions investigated was negligible. If one views the three parameter sets as corresponding to different isotopic blends, the lack of a parameter-set dependence displayed by the data serves to validate the experimental evidence from 8 of 9 isotopic polymer blends where the data displayed a minimum at $\phi_D = 0.5$ and comparable magnitudes of χ_S over the entire range of ϕ_D [4–6,13].

Having calculated both $\chi_T(\phi_D)$ and $\chi_S(\phi_D)$ for the C_{16} system, eq. (6) was employed to compare the composition dependences of χ_S and $\chi_S(\chi_T)$. The data displayed in fig. 3 show remarkable agreement between these two quantities, and serves to validate the utility of the RPA. In addition to capturing the parabolic form previously reported for $\chi_S, \chi_S(\chi_T)$ also displays the slight influence of parameter selection displayed in fig. 2, thereby leading to the conclusion that eq. (6) remains valid even in the presence of a distinct composition dependence for χ_T. As evident from eqs. (1)–(6), the transition from χ_T to $\chi_S(\chi_T)$ requires calculation of the first and second derivatives of ΔG with respect to ϕ_D. To do this, we regressed the data shown in fig. 1(a) and used a quadratic function to fit $\Delta G(\phi_D)$ for each of the parameter sets, which was the lowest-order polynomial to fit the data within an error tolerance of 0.5%; *i.e.*, $R^2 > 0.995$.

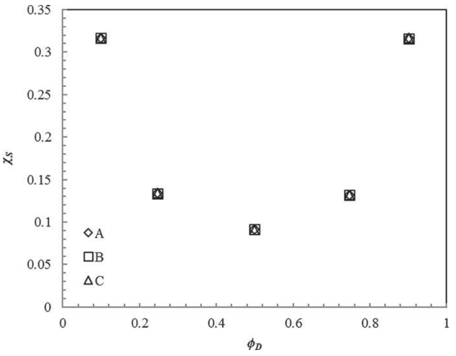

Fig. 2: $\chi_S(\phi_D)$ of C_{16} blends with each of the parameter sets, A, B, and C.

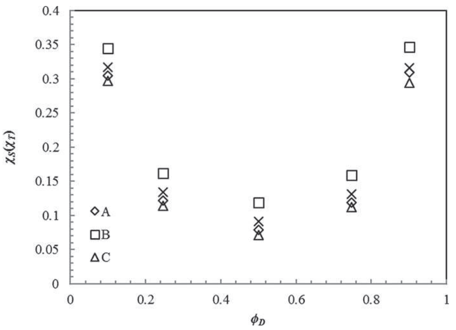

Fig. 3: Composition dependence of $\chi_S(\chi_T)$ as a function of ϕ_D for isotopic C_{16} blends with each of the parameter sets, A, B, and C, and comparison to the common data (χ_S) of fig. 2 (denoted by the symbol ×).

Computational size constraints on the CBMC simulations restricted the smallest measureable wave number in the CBMC simulations to $0.1\,\text{Å}^{-1}$, at the upper limit of the accessible experimental values ($q \in [0.01, 0.1]$) [4–6]. Previous research has shown q to have a minimal impact on the calculation of the interaction parameter within the neighborhood of $q \approx 0$ [21,32], but the exact extent of this region is difficult to determine *a priori*. Data of $\chi_S(\phi_D)$ displayed in fig. 2 were calculated based on the assumption that $q = 0.1\,\text{Å}^{-1} \approx 0$; therefore, to ensure the accuracy of the calculation of $\chi_S(\phi_D)$, the wave number dependence of χ_S was examined down to $q = 0.01\,\text{Å}^{-1}$. $S(q)$ from the CBMC simulations was extrapolated backward to $q = 0.01\,\text{Å}^{-1}$ (using a scaled power-law fit to data in the neighborhood of $q = 0.1\,\text{Å}^{-1}$) and the Debye function was calculated according to eq. (4); these two quantities were then substituted into eq. (3) to obtain $\chi_S(q)$. A comparison between results at $q = 0.1\,\text{Å}^{-1}$ and $0.01\,\text{Å}^{-1}$ revealed that $\chi_S(0.1)$ and $\chi_S(0.01)$ were within an absolute error of ± 0.02, which is believed to be approximately the error of the calculations.

The extrapolation mentioned above allows for an estimation of the q-dependence of the interaction parameter within the range $q \in [0.01, 0.1]$. Figure 4 displays $\chi_S(q)$ for parameter set A at $\phi_D = 0.5$, broken up into separate low-q and high-q plots; the results were once again

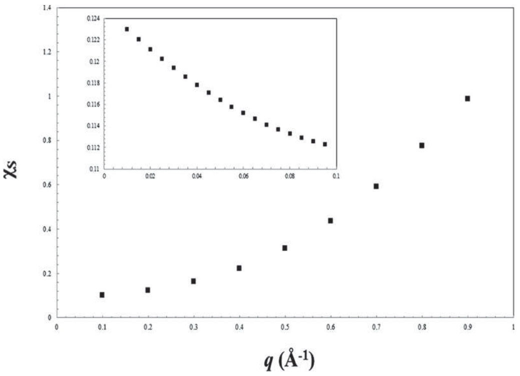

Fig. 4: Wave number dependence of χ_S in an isotopic C_{16} blend with parameter set A at $\phi_D = 0.5$: $q < 0.1\,\text{Å}^{-1}$ (inset) and $q \geq 0.1\,\text{Å}^{-1}$ (main graph).

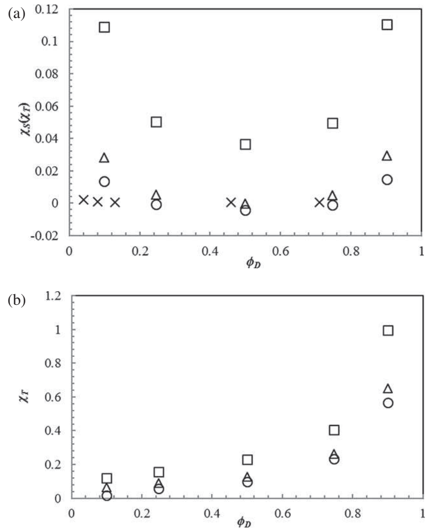

Fig. 5: Composition dependence of C_{50}(□), C_{128}(Δ), and C_{200}(○) blends with parameter set A: (a) $\chi_S(\chi_T)$ and (b) χ_T. Also displayed are experimental data (×) of Londono *et al.* [6] for the PE/PED ($N = 4400$) system for χ_S.

independent of the parameter set used in the simulations. Comparing the main graph and inset of fig. 4, there is an apparent minimum in the curve of $\chi_S(q)$ located at approximately $0.1\,\text{Å}^{-1}$. At low values of q, the response of $\chi_S(q)$ according to eq. (3) is dominated by the approximately quadratic decrease in the structure factor, whereas for larger q, the structure factor decays towards unity while the reciprocal of Debye function increases roughly quadratically, thus producing a rising value of $\chi_S(q)$. Although the location of the minimum in our system is located at $q = 0.1\,\text{Å}^{-1}$, its location is a function of system parameters, such as Rg_i, and as such will vary from case to case. Therefore, the existence and location of this system-specific minimum could explain the differences in $\chi_S(q)$ data observed by Zirkel *et al.* [21] and Balsara *et al.* [32], who observed contradictory results: the former set of authors found χ_S to be a decreasing function of q, whereas the latter authors found it to be an increasing function. Nevertheless, in the very low-q regime, g_D should remain roughly constant regardless of the system studied and any wave number dependence for χ_S in this regime should be slight [21,32].

Having investigated the composition dependence of both χ_S and χ_T in the isotopic C_{16} system, our attention turned to exploring the effect of increased chain length on both $\chi_S(\phi_D)$ and $\chi_T(\phi_D)$. To do this, we chose to use parameter set A, since it produced the largest composition dependence in the C_{16} system displayed in fig. 1(b) and since the parameter-set dependence of χ_S was negligible (see fig. 2). We simulated chain lengths of $C_{50}H_{102}$, $C_{128}H_{258}$, and $C_{200}H_{402}$; because of the excellent agreement shown between the data for these two quantities, as evident from fig. 3, $\chi_S(\phi_D)$ was calculated according to eq. (6) as $\chi_S(\chi_T)$.

As apparent from fig. 5, both the structural and thermodynamic composition dependences weaken as chain length is increased; a result in agreement with experimental findings [4–6]. However, our data seem to indicate that simply increasing chain length will neither produce a composition-independent interaction parameter nor bring χ_S and χ_S into agreement with each other; the effect of increasing chain length wanes as N increases, yet χ_S and χ_T still maintain their unique composition dependences. Because χ_S is defined through the second derivative of the Γ function, in the presence of a composition dependent χ_T there is no combination of parameters that will create agreement between the structural and thermodynamic aspects of χ, and as increasing N does not remove the composition dependence of χ_T, the two aspects of the interaction parameter will not be equivalent. As the value of N is increased in the simulations, χ_S appears to asymptote toward the experimental data of Londono *et al.* at $N = 4400$ [6]. For C_{200}, the characteristic ratio (which describes how the local structure and short-range intramolecular interactions affect the mean-square dimensions of the chains) is within 5% of its infinite chain length value [27], indicating that any further significant decrease of χ_S with increasing chain length is unlikely.

We can examine the behavior of χ_S, and the relationship between this quantity and χ_T, by rewriting eq. (1) with the help of eq. (6):

$$\chi_S(\phi_D) = -\frac{1}{2}\left[\frac{1}{nk_BT}\frac{\partial^2\Delta G}{\partial\phi_D^2} - \frac{1}{\phi_D N_D} - \frac{1}{(1-\phi_D)\,N_H}\right]. \tag{7}$$

As evident from eq. (7), if $\Delta G(\phi_D)$ is described by a weakly nonlinear functional form, as it is here (see fig. 1(a)), $\chi_S(\phi_D)$ will possess a composition dependence that increases dramatically as either composition extreme is approached due to the fact that the last two terms of eq. (7) will dominate the calculation of $\chi_S(\phi_D)$ in those regions [4–6]; this will hold for chains of any length where $\Delta G(\phi_D)$ meets the above criteria, which is expected for isotopic systems in which the Gibbs energy of pure PE should not differ greatly from that of PED. This offers an explanation for the quantitative similarity in the common χ_S values shared by all three parameter sets in fig. 2: although ΔG varies appreciably between the parameter sets (see fig. 1(a)), its composition dependence is only weakly nonlinear in each case, implying that χ_S should be very similar for each parameter set since $\partial^2\Delta G/\partial\phi_D^2$ is approximately constant. However, if $\Delta G(\phi_D)$ is described by a strongly nonlinear function, as would be expected for non-isotopic polymer blends where the difference in the Gibbs energies of the pure states is much larger, $\partial^2\Delta G/\partial\phi_D^2$ may dominate eq. (7) even in the regions of extreme composition. This could account for the experimentally reported linear composition dependence of χ_S in structurally dissimilar polymer blends [33,34]; this possibility was explored by Russell [27], and found to be a valid interpretation of the simulation results for dissimilar (*i.e.*, non-isotopic) polymer blends. Additionally, because $\chi_S(\chi_T)$ relies on the second derivative of $\Delta G(\phi_D)$ while χ_T is defined in terms of ΔG, there is a loss of characteristic information during the transition from χ_T to χ_S. As is the case here, that loss of information can radically change the functional form of the composition-dependent interaction parameter between its thermodynamic and structural definitions.

In conclusion, the simulations described herein have demonstrated that the Flory-Huggins parameter of polymer solution and blend thermodynamics is indeed composition dependent and follows experimental trends established in the literature, without the necessity of approximations arising from coarse graining of the polymeric system nor any *a priori* assumptions of underlying physical mechanisms (such as concentration fluctuations). Indeed, the methodology introduced in this letter provides an avenue by which these approximations and assumptions could be examined critically in comparison to atomistic simulations. Furthermore, the structural and thermodynamic aspects of χ can be very different: the behavior of χ_T varies dramatically between blended systems, whereas the exact form of χ_S is relatively insensitive to the isotopic system under investigation, a feature which is shared by the majority of available experimental data. Also, χ_S and χ_T were found to possess distinct composition dependences at all chain lengths tested, which approached experimental data in the long-chain limit. Although it is possible to transition between χ_S and χ_T, this requires knowledge of the free energy of the system, which can be difficult to calculate experimentally for complex systems. Therefore, purely experimental measurements are generally restricted to determination of the structural interaction parameter and are insufficient for a direct determination of the thermodynamic parameter. This situation is unfortunate, as it is clearly the thermodynamic parameter which should be used in theoretical and simulation studies of polymer blend phase behavior. Therefore, experimentation should be accompanied by some form of realistic simulation of the free energy to ensure that χ is accurately described in terms of both its structural and thermodynamic aspects.

* * *

This research was supported by the National Science Foundation (NSF) under Grant No. DGE-0801470. Computational resources were provided by the NSF to the PolyHub Virtual Engineering Organization and the National Institute for Computational Science.

REFERENCES

[1] Flory P. J., *J. Chem. Phys.*, **109** (1942) 2536.
[2] Huggins M. L., *J. Phys. Chem.*, **46** (1942) 151.
[3] Huggins M. L., *J. Am. Chem. Soc.*, **64** (1942) 1712.
[4] Bates F. S. *et al.*, *J. Chem. Phys.*, **89** (1988) 535.
[5] Krishnamoorti R. *et al.*, *J. Chem. Phys.*, **100** (1994) 3894.
[6] Londono J. D. *et al.*, *Macromolecules*, **27** (1994) 2864.
[7] Jancsó G. *et al.*, *Chem. Soc. Rev.*, **23** (1994) 257.
[8] Luszczyk M. *et al.*, *Macromolecules*, **28** (1995) 745.
[9] Luszczyk M. and Van Hook W. A., *Macromolecules*, **29** (1996) 6612.
[10] Kumar S. *et al.*, *Phys. Rev. Lett.*, **79** (1997) 2265.
[11] Berg L. P. and Painter P. C., *J. Polym. Sci. B: Polym. Phys.*, **41** (2003) 2923.
[12] Sariban A. and Binder K., *J. Chem. Phys.*, **86** (1987) 5859.
[13] Melenkevitz J. *et al.*, *Macromolecules*, **33** (2000) 6869.
[14] Wang Z.-G., *J. Chem. Phys.*, **117** (2002) 481.
[15] Grzywacz P. *et al.*, *Phys. Rev. E*, **76** (2007) 061802.
[16] Qin J. and Morse D. C., *J. Chem. Phys.*, **130** (2009) 224902.
[17] Morse D. C. and Qin J., *J. Chem. Phys.*, **134** (2011) 084902.
[18] Fan C. F. *et al.*, *Macromolecules*, **25** (1992) 3667.
[19] Hildebrand J. H., *The Solubility of Non-Electrolytes* (Reinhold, New York) 1936.
[20] de Gennes P. G., *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca) 1979.
[21] Zirkel A. *et al.*, *Macromolecules*, **35** (2002) 7375.
[22] Sanchez I. C., *Polymer*, **30** (1989) 471.
[23] Rosenbluth M. N. and Rosenbluth A. W., *J. Chem. Phys.*, **23** (1955) 356.
[24] Frenkel D. and Smit B., *Understanding Molecular Simulation: From Algorithms to Applications* (Academic Press, San Diego) 2002.
[25] Aichele M. *et al.*, *Phys. Rev. E*, **69** (2004) 061801.
[26] Plimpton S. J., *J. Comput. Phys.*, **117** (1995) 1.
[27] Russell T. H., *Composition Dependency of the Flory-Huggins Interaction Parameter in Polymer Blends: structural and thermodynamic calculations*, PhD dissertation, The University of Tennessee (2014).
[28] Siepmann J. I. *et al.*, *Nature*, **365** (1993) 330.
[29] Baig C. *et al.*, *J. Chem. Phys.*, **122** (2005) 184906.
[30] Knaap H. and Beenakker J., *Physica*, **27** (1961) 523.
[31] Calado J. C. G. *et al.*, *J. Chem. Phys.*, **100** (1994) 4582.
[32] Balsara N. P. *et al.*, *Macromolecules*, **25** (1992) 6137.
[33] Han C. C. *et al.*, *Polymer*, **29** (1988) 2002.
[34] Nedoma A. J. *et al.*, *Macromolecules*, **41** (2008) 5773.