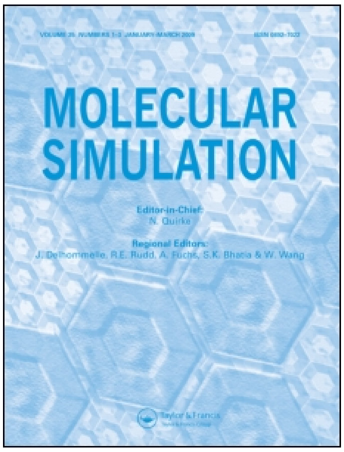

**Molecular Simulation**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

# Molecular dynamics simulation study of compatibility for the polyvinylmethylether/polystyrene mixture

Amirhossein Ahmadi[a]; Juan J. Freire[a]
[a] Departamento de Ciencias y Técnicas Fisicoquímicas, Facultad de Ciencias, Universidad Nacional de Educación a Distancia, Madrid, Spain

**To cite this Article** Ahmadi, Amirhossein and Freire, Juan J.(2008) 'Molecular dynamics simulation study of compatibility for the polyvinylmethylether/polystyrene mixture', Molecular Simulation, 34: 10, 1253 — 1258

**To link to this Article: DOI:** 10.1080/08927020802175233

**URL:** http://dx.doi.org/10.1080/08927020802175233

*Molecular Simulation*
Vol. 34, Nos. 10–15, September–December 2008, 1253–1258

# Molecular dynamics simulation study of compatibility for the polyvinylmethylether/polystyrene mixture

Amirhossein Ahmadi and Juan J. Freire*

*Departamento de Ciencias y Técnicas Fisicoquímicas, Facultad de Ciencias, Universidad Nacional de Educación a Distancia, Madrid, Spain*

(*Received 31 January 2008; final version received 1 May 2008*)

We have performed molecular dynamics simulations for atomistic representations of polyvinylmethylether/polystyrene blends using the 'discover' module of the Materials Studio® software platform with the COMPASS forcefield. The simulation boxes are constructed with the Amorphous Cell module, introducing polymer chains designed with the Visualiser building tools. The simulations yield trajectories files, whose coordinates have been employed to calculate the collective scattering structure factor. Comparison of the numerical data obtained for this property with the predictions of random phase approximation theory, depending on the Flory–Huggins parameter, has allowed us to obtain numerical results for this parameter, commonly accepted as a good indicator of compatibility. The results depend on the method used to assign partial charges though they are always reasonably close to existing data obtained through neutron scattering experiments. The charge equilibration method gives a correct prediction of compatibility in the studied temperature range. Moreover, it shows a positive variation of the Flory–Huggins parameter with temperature, in agreement with the phase behaviour of these blends that show a lower critical temperature. However, the parameter absolute values are too high. When forcefield assigned charges are introduced, the Flory–Huggins parameter are slightly positive and a non-monotonous variation with temperature is found. However, the values for the highest temperatures are remarkably close to the experimental data.

**Keywords:** molecular dynamics; blends; compatibility; scattering

## 1. Introduction

The study of compatibility in polymer mixtures is of great scientific and technological interest, since an accurate prediction of this property can help to the design of new materials with better practical characteristics than the single components [1]. From the experimental point of view, compatibility of blends is explored through the determination of the Flory–Huggins parameter, $\chi$ [2]. This parameter can be extracted from data of the structure scattering factor, obtained in neutron scattering experiments. The random phase approximation (RPA; [3]) provides expressions for the structure factor in terms of $\chi$ and, consequently, numerical values of $\chi$ can be calculated through fits of the experimental data to the RPA prediction [4]. Although the experimental values of $\chi$ evaluated according to this procedure may not be in general agreement with the values obtained from the study of phase separation diagrams, they provide a valuable indication of the mixture compatibility.

A similar approach can be used to obtain theoretical predictions of $\chi$ with numerical data obtained from numerical simulations. Atomistic models of the mixtures can be built in a simulation box, including periodic boundary conditions. Numerical simulations can be performed with these boxes. This way, it is possible to work with realistic representations of the systems, from which different experimental properties are simulated. Molecular dynamics (MD) constitutes the simplest type of simulation for the most detailed systems that require many different interactions between different bonded or non-bonded atoms. These interactions are summarised in the 'forcefield' files.

The MD simulations yield numerical trajectories of polymer blends that constitute statistical samples from which different properties can be calculated. Compatibility clues can be obtained through the study of different structural properties (as the pair distribution functions; [5]). Moreover, the collective 'scattering' structure factors can also be evaluated. Following a procedure similar to that employed in the analysis of the scattering experiments, a subsequent fit of the structure factors to the RPA can provide numerical estimations of $\chi$. This approach has been followed in some recent investigations for polymers with relatively simple molecular structures (composed of alkyl groups) as polypropylene/polyethylene [6] and polyisobutylene/polypropylene [7].

In the present work, we report MD simulation results obtained with module Discover of the Materials Studio® (MS) software platform (Accelrys Software Inc., San Diego, CA, USA) for the structurally more complex polyvinylmethylether/polystyrene (PVME/PS) blends,

---

*Corresponding author. Email: jfreire@invi.uned.es

ISSN 0892-7022 print/ISSN 1029-0435 online

DOI: 10.1080/08927020802175233
http://www.informaworld.com

which have been broadly studied from the experimental point of view. Initial configurations of the blends are prepared with module Amorphous Cell. These systems are especially interesting since they form compatible mixtures at room temperatures, exhibiting a low critical temperature. Moreover, the experimental values of $\chi$ exhibit a significant composition variation [8]. From the molecular point of view, the presence of phenyl groups requires a precise description of interactions and, consequently, the systems may be very sensitive to some model details, in particular the choice of forcefield and the partial charge assignment method. Furthermore, the intermolecular or intramolecular interactions between phenyl groups drastically reduce the mobility of chains [9] requiring larger trajectories to obtain similar statistics. We describe the choice of different simulation and macroscopic variables that allow us to perform efficient simulations for these particular mixtures and compare the final results with existing experimental data. The great advantage of obtaining $\chi$ from the structure factors is that they are calculated from the atom coordinates, having a weak dependence on the energy. Therefore, they are less affected by the choice of potential parameters. We have verified that alternative estimations of $\chi$ based in the direct evaluation of the intermolecular energy between a pair of units averaged over a statistical sample generated through Monte Carlo simulations ([10]; as incorporated in the MS module 'blends') seem to be considerably less precise in the present mixture, depending largely on small details in the forcefield definitions. A similar large dependence on the potential details is found when $\chi$ is obtained from estimations of the cohesive energy density, or the solubility parameter [11], which can be directly evaluated form the MD simulations using the 'analysis' tool incorporated in the Amorphous Cell module.

## 2. Numerical methods

We easily construct the different short PVME and PS chains with the MS Visualiser building tools. We choose atactic configurations for the PS chains. MS module Amorphous Cell allows us to construct relaxed simulation boxes with periodic boundary conditions of size $L$ and a given mean density, $\rho$. We include five chains of each type in the box, which seems to be enough to reproduce the realistic interactions between chains in the small region of the space needed to explore interactions represented by the mean-field parameter $\chi$. The value of $L$ is conveniently chosen to avoid most interactions between replicas of the same chain along the simulation. Another important choice is the number of repeat units of the chains ($N_i$ for chains of type $i$). Using values of $N_i$ corresponding to moderately high molecular weight polymers requires the use of high values of $L$, which considerably increases the computation time required to obtain an adequate statistics. Moreover, longer chains imply a more restricted mobility of the systems. This effect is in addition to the significant reduction of mobility caused by the phenyl group interactions.

Experimental data for the tracer diffusion coefficient of PS [12,13] show values smaller than $10^{-11}\,\mathrm{cm^2\,s^{-1}}$, or $10^{-4}\,\mathrm{Å^2\,ns^{-1}}$, even for PS samples of low molecular weight, $M_w = 4500$ g/mol, at 150°C. The trajectories of these less mobile systems should be long in order to contain an adequate number of significantly different configurations in the resulting statistical sample for the calculation of static properties. Consequently, we have restricted our study to short chains.

We have built PVME chains containing five repeat units and PS chains containing three repeat units. We have verified that both types of chains have a similar root mean square radius of gyration of about 4 Å. Even with this restriction, we expect that, for the interesting range of temperatures covered by the experimental data [4,8,14], the mobility of the systems is very small when, we consider realistic melt densities close to $\rho = 10^3\,\mathrm{kg/m^3}$. Thus, assuming that the reptation model is valid, the diffusion coefficient would be proportional to $M_w^{-2}$, but the diffusion coefficients for our chains would not be higher than $2 \times 10^{-2}\,\mathrm{Å^2\,ns^{-1}}$. (Although the PS mobility may increase in blends, the variation with molecular weight is surely smaller than the reptation prediction for these short chains). Therefore, the chains cannot significantly move along the simulation box and, consequently, the resulting statistical samples are not adequate for the calculation of static properties, unless we employ an extravagant amount of CPU time. We show in Figure 1 some results obtained with our MD simulations for the quadratic displacement of the centre of masses of PS chains in systems of different densities. In accordance with these results, we have decided

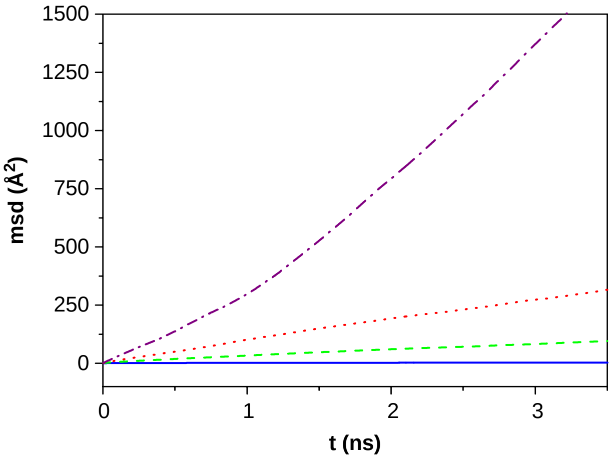

Figure 1. Mean squared displacement, msd, of the centre of masses of PS chains in a PVME/PS mixture at 350 K. Blue solid line, $\rho \cong 1 \times 10^3\,\mathrm{kg/m^3}$; green dash line, $\rho \cong 0.9 \times 10^3\,\mathrm{kg/m^3}$; red dot line, $\rho \cong 0.8 \times 10^3\,\mathrm{kg/m^3}$ and purple dash and dot line, $\rho \cong 0.7 \times 10^3\,\mathrm{kg/m^3}$.

to decrease density to the smaller value of $\rho \cong 0.7 \times 10^3\,\mathrm{kg/m^3}$, which is enough to give a good mobility to the systems.

MD simulations are carried out with the MS module Discover with the COMPASS forcefield [15]. This forcefield is based in *ab initio* quantum mechanical calculations, parameterised to be consistent with condensed phase properties. Partial charges are set according to the 'forcefield assigned' default method that simply considers fixed bond increments provided by the forcefield files and also with the 'charge equilibration' method [16], procedure based in equilibration of atomic electrostatic potentials with respect to a local charge distribution. Differences between the charges obtained with these two methods are important in some cases. It can be observed in Table 1 that the charge equilibration method yields considerable higher absolute charges for all the H atoms, the O atom in PVME, the C atoms in all the methyl and methylene groups and also in the —CH groups of PS. The simulations are performed for constant temperatures $T = 350$, 400 and 450 K using the simple Andersen thermostat [17], valid for static properties. We have verified that both total energy and temperature oscillate around stabilised mean values in the final trajectories used for the calculation of properties. Equilibration times of 4–8 ns are typically required for most systems.

In our study of the atomistic representations of the PVME/PS mixture, we perform several (2 and 3) MD runs from different equilibrated samples, employing a time step of 1.5 fs. This time step is larger than those usually employed to study dynamical properties, 0.5 or 1 fs. But, we have verified that it gives stable trajectories providing similar final results for $\chi$. In each run, the system coordinates are saved and included in the statistical samples every 2000 steps, or 3 ps. Our final statistics combine the results of the different runs, and typically have to cover a total of 60–84 ns in order to obtain a sufficient accuracy in the final results.

Table 1. Forcefield assigned and (averaged for the group) charge equilibration values of partial charges (COMPASS forcefield).

| Type of atom | Forcefield assigned | Charge equilibration |
|---|---|---|
| *PS* | | |
| Carbon 1 in ring | 0 | 0.046 |
| Carbons (2–6) in ring | −0.127 | −0.107 ± 0.013 |
| C in $-\mathrm{CH_3}$ | −0.159 | −0.314 |
| C in $-\mathrm{CH_2}-$ | −0.106 | −0.314 ± 0.001 |
| C in $-\mathrm{CH}-$ | −0.053 | −0.136 |
| H in ring | 0.053 | 0.098 ± 0.010 |
| H in $-\mathrm{CH_3}$ | 0.053 | 0.138 ± 0.010 |
| H in $-\mathrm{CH_2}-$ | 0.053 | 0.13 ± 0.02 |
| H in $-\mathrm{CH}-$ | 0.053 | 0.142 |
| *PVME* | | |
| C in $-\mathrm{O}-\mathrm{CH_3}$ | −0.026 | −0.122 |
| C in final $-\mathrm{CH_3}$ | −0.159 | −0.366 |
| C in final $-\mathrm{O}-\mathrm{CH_2}$ | 0.027 | 0.039 |
| C in $-\mathrm{CH_2}-$ | −0.106 | −0.191 |
| C in $-\mathrm{CH}-$ | 0.080 | 0.116 |
| *O* | −0.266 | −0.549 |
| H in $-\mathrm{O}-\mathrm{CH_3}$ | 0.053 | 0.128 ± 0.021 |
| H in final $-\mathrm{CH_3}$ | 0.053 | 0.134 ± 0.035 |
| H in final $-\mathrm{O}-\mathrm{CH_2}$ | 0.053 | 0.11 ± 0.04 |
| H in $-\mathrm{CH_2}-$ | 0.053 | 0.12 ± 0.04 |
| H in $-\mathrm{CH}-$ | 0.053 | 0.142 |

The collective scattering structure factor is computed as a configurational average, extended over the statistical sample:

$$S(q) = n_\mathrm{s}^{-1}\left\langle \sum_i^{n_\mathrm{s}} \sum_j^{n_\mathrm{s}} f_i f_j \exp\left(i\mathbf{q}\cdot\mathbf{R}_{ij}\right)\right\rangle, \tag{1}$$

where $n_\mathrm{s}$ is the number of scattering units while the terms $f_k$ is the scattering factors, describing the scattering contrast between different types of atoms. In order to give the simplest description of the RPA, we set as scattering units all the non-hydrogen atoms contained in the box and assume that they have opposite signs when the atoms belong to the PVME (A) than when they belong to the PS (B) chains, giving $S(q) = 0$ for $q = 0$ (no scattering with a macroscopic wavelength). Therefore, we set [18]:

$$f_i = n_\mathrm{B}/n_\mathrm{s}, \tag{2a}$$

if atom $i$ belongs to an A chain, or

$$f_i = -n_\mathrm{A}/n_\mathrm{s}, \tag{2b}$$

if atom $i$ belongs to a B chain. $\boldsymbol{R}_{ij}$ is the vector joining centres $i$ and $j$ in a given configuration. Finally, $\mathbf{q}$ is the scattering vector, whose components are conditioned by the box size,

$$q_k = (2\pi/L)n_k, \quad k \equiv x, y, z, \quad n_k = 1, 2, \ldots, \tag{3}$$

## 3. Results and discussion

Figures 2 and 3 contain our $S(q)^{-1}$ versus $q^2$ results for three different temperature calculated from the MD runs with $T = 350\,\mathrm{K}$ with the charge equilibration method and the forcefield assigned partial charges. Similar graphs are obtained for $T = 400$ and 450 K. We compare these data with the theoretical results obtained from the RPA predictions for different values of $\chi$. For our simple choice of scattering factors, the RPA curves are obtained as:

$$V_0 S^{-1}(q) = \frac{1}{N_\mathrm{A}\Phi_\mathrm{A}P_\mathrm{A}(q)} + \frac{1}{N_\mathrm{B}\Phi_\mathrm{B}P_\mathrm{B}(q)} - 2\chi, \tag{4}$$

where $V_0$ is the reference microscopic volume, $V_\mathrm{R}$, normalised with respect to the volume of a scattering unit. Therefore, $V_0 = V_\mathrm{R}/(L^3/n_\mathrm{s})$. The value of $\Phi_i$ is the volume

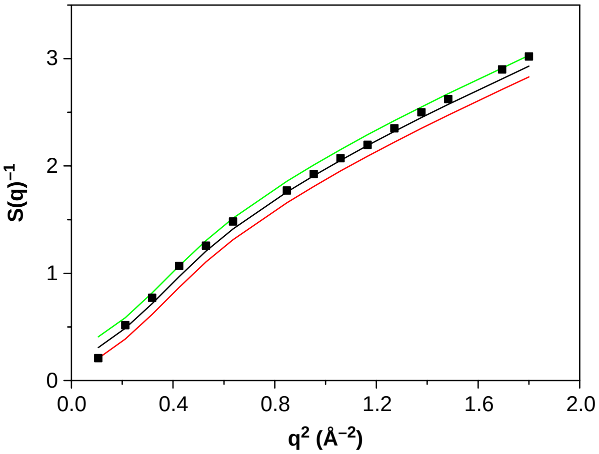

Figure 2. $1/S(q)$ versus $q^2$ from the MD simulation of a PVME/PS mixture at 350 K. The charge equilibration method has been used. Symbols, simulation data; curves correspond to the RPA results from Equation (4), from bottom to top: red line, $\chi/V_0 = 0.05$; black line, $\chi/V_0 = 0$ and green line, $\chi/V_0 = -0.05$.

fraction occupied by $i$ chains, $\Phi_i = (n_s)_i/n_s$, where $(n_s)_i$ is the total number of scattering units belonging to the $i$-type chains and $P_i(q)$ is the form factor corresponding to the $i$ chains, calculated as:

$$P_i(q) = (N_i)^{-2}\left\langle \sum_{i}^{N_i}\sum_{j}^{N_i} \exp\left(i\mathbf{q}\cdot\mathbf{R}_{ij}\right)\right\rangle, \qquad (5)$$

where the average extends now to the different $i$ chains in all the different configurations. In Figures 2 and 3, we compare the simulation results with the RPA curves corresponding to the choices $\chi/V_0 = -0.05$, $\chi/V_0 = 0$ and $\chi/V_0 = 0.05$. It can be observed that the simulation data are generally closer to the $\chi/V_0 = 0$ curve, except in the case of some high-$q$ points. Although, the data show a qualitative variation with $q$ similar to the RPA curves, a slight systematic deviation upwards is observed as $q$ increases. A similar deviation has been found in other systems (see Figure 9 of [6]). In Figure 4, we represent the $S(q)^{-1}$ versus $q^2$ results obtained from the RPA for $\chi = 0$, i.e. only taking into account the form factor contributions, considering the two alternative methods of assigning charges. It can be observed that both sets of results are very close, except for the highest values of $q^2$, corresponding to shorter distances. Therefore, the main influence of the charge assignment method is exerted on the interaction between the two types of chains, directly affecting the determination of mean-field parameter $\chi$.

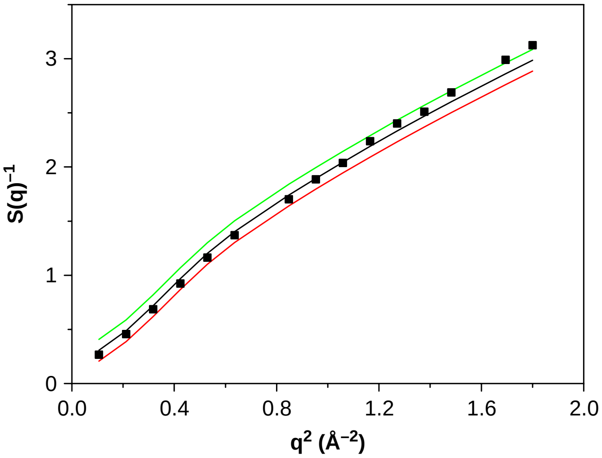

Figure 3. $1/S(q)$ versus $q^2$ from the MD simulation of a PVME/PS mixture at 350 K. Forcefield assigned partial charges have been used. Symbols, simulation data; curves correspond to the RPA results from Equation (4), from bottom to top: red line, $\chi/V_0 = 0.05$; black line, $\chi/V_0 = 0$ and green line, $\chi/V_0 = -0.05$.

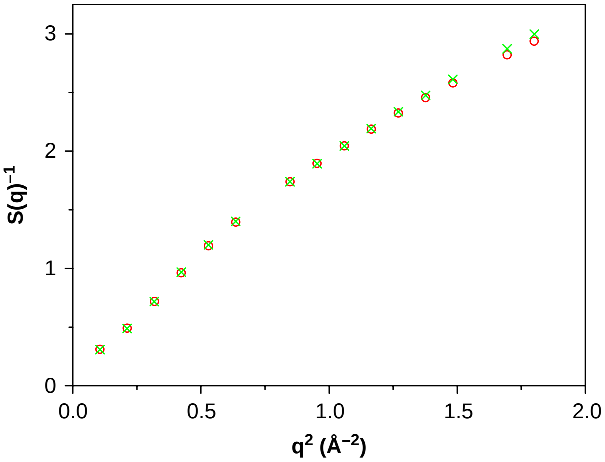

Figure 4. $1/S(q)$ versus $q^2$ determined from Equation (4) with $\chi = 0$. The form factors have been obtained from MD simulations of a PVME/PS mixture at 350 K. Charge equilibration (red circles) and forcefield assigned (green crosses) partial charges have been used.

According to Equation (4), $\chi$ can be calculated from the simulation result, $S_{\mathrm{sim}}(q)$, obtained for any given $q$ value as:

$$(2\chi/V_0) = S_{\mathrm{RPA}}^{-1}(q, \chi = 0) - S_{\mathrm{sim}}^{-1}(q), \qquad (6)$$

where $S_{\mathrm{RPA}}$ $(q,\ \chi = 0)$ is the prediction of the RPA for $\chi = 0$ considering the choice $V_0 = 1$, also implicit in our calculation of the simulation data from Equation (1). This prediction is described by the first two terms on the right hand of Equation (4). Therefore, we can estimate $\chi/V_0$ by evaluating the mean deviation of $S^{-1}(q)$ simulation data corresponding to different $q$ values with respect to the RPA predictions for $\chi = 0$.

In Figure 5, we present the final results obtained for $\chi$ with different temperature values and the two different methods to assign charges, obtained as arithmetic means over all the computed values of $q^2$. In these means, we always exclude two points in the $S(q)$ versus $q^2$

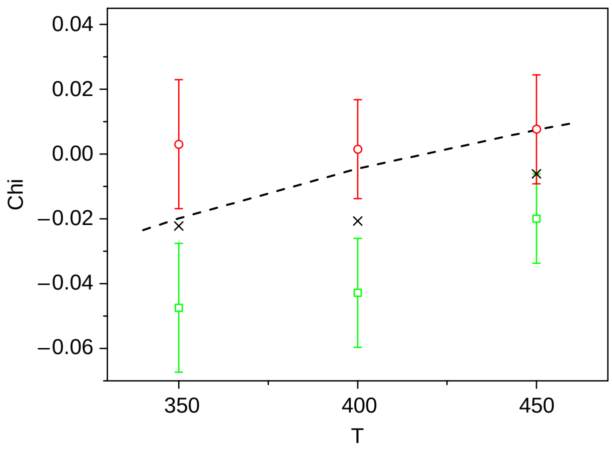

Figure 5. $\chi$ versus $T$ obtained from Equation (6). Green squares, results obtained with the charge equilibration method; red circles, results obtained with forcefield assigned partial charges; black crosses, means from the two methods; line, $-43 + 0.103/T$, fitted equation describing the experimental variation of $\chi$ with $T$ [4,14]. $\chi$ is expressed relative to a reference volume of $100\,\text{Å}^3$. Last two points with $q^2$ higher than 1.5 are excluded in the determination of $\chi$, see text.

representations that correspond to the highest $q^2$, since they systematically show higher deviations; these points correspond to interatomic distances smaller than 5 Å. Our estimations for $\chi$ are compared with a curve describing the experimental values obtained from neutron scattering in the temperature range 60–150°C [4,14]. The results are presented considering a standard reference site volume of $V_R = 100\,\text{Å}^3$. This value, together with $L = 19.3\,\text{Å}$ and $n_s = 220$ yield $V_0 \cong 3.1$.

It can be observed that the simulation results obtained with the forcefield assigned partial charges are always positive but they are in fair quantitative agreement with the experimental curve (taking into account the relatively large error bars). This agreement is particularly good in the high temperature region. The results obtained with the charge equilibration method are systematically smaller, but they are always negative, indicating compatibility. Moreover, they show a positive, variation with temperature, consistent with the trend of the experimental data and also with the experimental detection of a lower critical temperature. In spite of the quantitative discrepancies found between the values obtained with the two methods of assigning charges, it should be observed they bracket the experimental data. In the same plot, we also include means of the values obtained with the two methods. These means are in closer general agreement with the experimental data (though they exhibit a weaker temperature variation). Consequently, the present calculations show that MD simulations can give a reasonable estimation of the $\chi$ parameter, employing an acceptable amount of CPU time, for mixtures of polymer chains with complex chemical structures.

We have verified that other forcefields give worse estimations. In particular, only the COMPASS forcefield is able to provide an adequately small dispersion of the structure factor data with our statistical samples. Thus, the older polymer consistent forcefield (PCFF; [19]), also based in *ab initio* calculations, yields more negative results (with higher error bars) when the charge equilibration method is used. On the other hand, this forcefield together with forcefield assigned partial charges gives higher positive values of $\chi$ (with higher error bars), clearly in disagreement with the compatibility shown by experimental data. In spite of the remarkable increase (about a 100%) of the absolute values of $\chi$ and their error bars with respect to the results obtained with the *Compass* forcefield, the estimations provided by the PCFF also suggest a slight positive variation of $\chi$ with temperature.

The choice of small chain lengths and reduced densities may constitute an important simplification of the real samples. However, we should consider that, at least from the theoretical point of view, parameter $\chi$ is independent of the chain length and density, though variations with both magnitudes have been experimentally observed for real systems. We have investigated this point performing some simulations with blends of simplified models of generic polymer chains, represented by the widely used coarse-grained lattice bond fluctuation model [20]. We have considered blends of chains composed of A units and chains composed of B units. We use the single occupancy condition for the lattice sites, equivalent to a hard core repulsive interaction and three different attractive values of a parameter describing attractive interactions of the types A–A, B–B and A–B between units located in neighbouring sites [21,22]. These parameters have been set to provide results for $\chi$ (referred to the volume of a unit) similar to those expected for our realistic samples. The simplified model allows us to employ the very efficient slithering snake Monte Carlo simulation method and easily explore a variety of densities (some of them reproducing the melt conditions) and chain lengths (up to 100 units). With these specifications, we have calculated parameter $\chi$ from the Monte Carlo simulation statistical samples, following the same procedures used for the MD simulation samples with realistic chains. We have verified that the variation of $\chi$ with chain length and density for the simplified model is small and comparable with the statistical uncertainties.

Table 2 shows the results obtained with the MS module 'blends' based on the method for the direct evaluation of the intermolecular energy between pairs of units described in [10]. It can be observed that the results for parameter $\chi$ are extremely sensitive to the details of the non-bonded potential (as the cut-off value and the method used for assigning charges). Although, one of the choices qualitatively predicts the system compatibility, yielding negative values of $\chi$ and an increase of this parameter with

Table 2. The value of $\chi$ (for a volume of $100\,\text{Å}^3$) obtained from module 'blends' with different cut-off values for the *Compass* forcefield potential, $d_c$ and different charge assignment choices (ffa, forcefield assigned and qeq, charge equilibration).

| $T$ (K) | $d_c = 10\,\text{Å}$ (ffa) | $d_c = 10\,\text{Å}$ (qeq) | No cut-off (ffa) | No cut-off (qeq) |
|---|---|---|---|---|
| 350 | 1.60 | $-1.32$ | 0.49 | 1.04 |
| 400 | 1.17 | $-1.28$ | 0.32 | 0.84 |
| 450 | 0.85 | $-0.72$ | 0.23 | 0.72 |

Table 3. The value of $\chi$ (for a volume of $100\,\text{Å}^3$) obtained from the cohesive energy densities of pure components and mixture with different forcefields and different charge assignment choices (ffa, forcefield assigned and qeq, charge equilibration).

| $T$ (K) | PCFF (ffa) | *Compass* (qeq) |
|---|---|---|
| 350 | $-0.184$ | $-0.112$ |
| 450 | $-0.108$ | $-0.175$ |

temperature, the quantitative results greatly differ from the experimental data. Table 3 shows our estimations for $\chi$ obtained from the cohesive energies of the mixture and the pure components. This method involves performing three different MD simulations for a given system. The method predicts compatible mixtures at the different temperatures, with $\chi$ values dependent on the potential choice and clearly different from the neutron scattering experimental data from the quantitative point of view.

## Acknowledgements

This work has been partially supported by Grant CTQ2006-06446 from DGI-MEC, Spain. A.A. also thanks Fellowships for Graduate Studies from the MAE, Spain, and the Universidad Nacional de Educación a Distancia.

## References

[1] D.R. Paul and C.B. Bucknall (ed.), *Polymer Blends*, Wiley, New York, 1999.

[2] P.-G. de Gennes, *Scaling Concepts in Polymer Physics*, Cornell University, Ithaca, NY, 1979.

[3] D. Schwahn, *Critical to mean field crossover in polymer blends*, Adv. Polym. Sci. 183 (2005), pp. 1–61.

[4] J.E. Mark (ed.), *Physical Properties of Polymers Handbook*, AIP, New York, 1996, pp. 257–268.

[5] D.R. Heine, G.S. Grest, and J.G. Curro, *Structure of polymer melts and blends: comparison of integral equation theory and computer simulations*, Adv. Polym. Sci. 173 (2005), pp. 209–249.

[6] D. Heine, D.T. Wu, J.G. Curro, and G.S. Grest, *Role of intramolecular energy on polyolefin miscibility: isotactic polypropylene/polyethylene blends*, J. Chem. Phys. 118 (2003), pp. 914–924.

[7] E. Jaramillo, D.T. Wu, G.S. Grest, and J.G. Curro, *Anomalous mixing behavior of polyisobutylene/polypropylene blends: Molecular dynamics simulation study*, J. Chem. Phys. 120 (2004), pp. 8883–8886.

[8] C.C. Han, B.J. Bauer, J.C. Clark, Y. Muroga, Y. Matsushita, M. Okada, T.C. Qui, T.H. Chang, and I.C. Sanchez, *Temperature, composition and molecular-weight dependence of the binary interaction parameter of polystyrene polyvinyl methyl-ether blends*, Polymer 29 (1998), pp. 2002–2014.

[9] A. Horta and J.J. Freire, *Block and alternating copolymer chains of styrene-vinylmethylether and styrene-methylmethacrylate by molecular dynamics simulation*, Polymer 45 (2004), pp. 1275–1286.

[10] C.F. Fang, B.D. Olafson, M. Blanco, and S.L. Hsu, *Application of molecular simulation to derive phase-diagrams of binary-mixtures*, Macromolecules 25 (1992), pp. 3667–3676.

[11] T. Spyriouni and C. Vergelati, *A molecular modeling study of binary blend compatibility of polyamide 6 and poly(vinyl acetate) with different degrees of hydrolysis: An atomistic and mesoscopic approach*, Macromolecules 34 (2001), pp. 5303–5316.

[12] T.E. Shearmur, A.S. Clough, D.W. Drew, and M.G.D. van der Grinten, and R.A.L. Jones, *Temperature dependence of the mutual diffusion coefficient of deuterated polystyrene and poly(methyl methacrylate)*, Phys. Rev. E 55 (1997), pp. R3840–R3843.

[13] M.G.D. van der Grinten, A.S. Clough, T.E. Shearmur, M. Geoghedan, and R.A.L. Jones, *Tracer diffusion of deuterated polystyrene into polystyrene-poly(alpha-methyl styrene) studied by nuclear reaction analysis*, Polymer 39 (1998), pp. 3623–3629.

[14] B. Hammouda, R.M. Briber, and B.J. Bauer, *Small-angle neutron-scattering from deuterated polystyrene poly(vinylmethyl ether) protonated polystyrene ternary polymer blends*, Polym. Commun. 33 (1992), pp. 1785–1787.

[15] H. Sun, *COMPASS: An* ab initio *force-field optimized for condensed-phase applications – Overview with details on alkane and benzene compounds*, J. Phys. Chem. B 102 (1998), pp. 7338–7364.

[16] A.K. Rappe and W.A. Goddard, *Charge equilibration for molecular-dynamics simulations*, J. Phys. Chem. 95 (1991), pp. 3358–3363.

[17] D. Frenkel and B. Smith, *Understanding Molecular Simulations*, Academic Press, San Diego, CA, 1996.

[18] A.M. Rubio, J.F.M. Lodge, and J.J. Freire, *Simulation of dynamic scattering from homopolymer and symmetric diblock copolymer solutions with the bond fluctuation model*, Macromolecules 35 (2002), pp. 5295–5303.

[19] H. Sun, S.J. Mumby, J.R. Maple, and A.T. Hagler, *An* ab-initio *cff93 all-atom force-field for polycarbonates*, J. Amer. Chem. Soc. 116 (1994), pp. 2978–2987.

[20] K. Binder (ed.), *Monte Carlo and Molecular Dynamics Simulations in Polymer Science*, Oxford University, New York, 1995.

[21] M. Wittkop, S. Kreitmeier, and D. Göritz, *The collapse transition of a single polymer chain in two and three dimensions: a Monte Carlo study*, J. Chem. Phys. 104 (1996), pp. 3373–3385.

[22] A.M. Rubio, M. Storey, J.F.M. Lodge, and J.J. Freire, *Dynamics of bond-fluctuation model chains in good and theta solvents*, Macromol. Theory Simul. 11 (2002), pp. 171–183.