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On the $N$-scaling of the Ginzburg number and the critical amplitudes in various compatible polymer blends

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Abstract. — The susceptibility related to composition fluctuations in polymer blends can be described by a crossover function derived by Belyakov et al. [2, 3] near and far from the critical temperature $T_c$. This has quite recently been demonstrated by us using neutron and light scattering data [1]. In this paper we discuss consequences of this analysis with respect to the accomplishment of the mean-field approximation far from $T_c$ and the $N$ scaling ($N$ is the degree of polymerization) of the critical amplitudes of the bare correlation length and susceptibility respectively and the Ginzburg number, $G_i$. A quite unexpected $N$ dependence of $G_i$ was found: polymer blends with $N < 30$ give the same $G_i$ as low molecular liquids and at about $N = 30$ an increase of $G_i$ of more than one order of magnitude which is synonymous to an increase of the 3d-Ising regime is observed. For $N \geq 30$ a $G_i \propto 1/N^2$ scaling is found in a range up to $N \approx 400$. The observed $N$ scaling of $G_i$ can be explained by the large entropic contribution of the Flory-Huggins parameter $\Gamma_\alpha$ related to the compressibility or free volume of the system in comparison with the combinatorial entropic term, which was obtained from the analysis of the scattering results with the crossover function.

1. Introduction.

In a recent publication [1] we have used a crossover function which is appropriate to describe the static structure factor $S(Q \rightarrow 0)$, with $Q$ being the scattering vector, for various binary polymer blends at critical composition $\phi_c$ over the whole measured temperature range far from and near to the critical point of phase separation. The crossover function used [2, 3] is an explicit solution to first order in the perturbation parameter $\varepsilon = 4 - d$, with $d$ being the dimensionality of the system, based on a renormalization group analysis. This function links the two limiting cases, namely the mean-field regime valid at temperatures far from the critical $T_c$ and the Ising regime, which is found close to $T_c$ when fluctuations of the composition
become dominant. The crossover function reads

$$\hat{\tau} = (1 + 2.333 \tilde{S}(0)^{3\gamma})^{\gamma - 1} \tilde{S}(0)^{3\gamma - 1} + (1 + 2.333 \tilde{S}(0)^{3\gamma})^{\gamma - 1}$$  \hspace{1cm} (1)$$

with $\hat{\tau} = \tau/G_i$ where $\tau$ is the reduced temperature $\tau = \left| 1/T_c - 1/T \right|/(1/T_c)$, $G_i$ the Ginzburg number and $\tilde{S}(0) = a_0 G_i S(0)$. The critical exponents are those for the 3d-Ising case $\gamma = 1.24$ and $\Delta = 0.51$. The constant $a_0$ is given by the coefficient of the squared term of the order parameter $\psi (x) = \Phi (x) - \phi_c$ in the Landau-Ginzburg-Wilson form of the Gibbs free energy of mixing for second order phase transitions and normalised with $RT$ ($R$ gas constant), hence

$$\frac{\Delta G}{RT} = \int d^3r \left[ \frac{1}{2} a_0 \tau' \psi^2(r) + \frac{1}{4!} u_0 \psi^4(r) + \frac{1}{2} c_0 (\nabla \psi (r))^2 \right]$$  \hspace{1cm} (2)$$

with $\tau' = 1 - T_c(MF)$/$T$ being the reduced mean-field temperature. It can be shown that the Ginzburg number $G_i$ controls the crossover such that for $\tau \ll G_i$ the susceptibility obeys Ising and for $\tau \gg G_i$ mean-field behaviour is observed. $G_i$ is given in terms of the constants $a_0$, $u_0$, and $c_0 = a_0 \xi_0^2$, with $\xi_0$ being the bare correlation length, appearing in equation (2) as [3]

$$G_i = \frac{u_0^2}{32 \pi^4 a_0^4 \xi_0^3 N^2_A}.$$  \hspace{1cm} (3)$$

Using the results from the Flory-Huggins theory [4] for $a_0$ one gets $a_0 = 2 (\Gamma_c + \Gamma_\sigma) = 2 \Gamma_h/\Gamma_c$ with $\Gamma$ the Flory-Huggins interaction parameter $\Gamma = \Gamma_h/\Gamma_\sigma$ ($\Gamma_h$, $\Gamma_\sigma$ being the enthalpic and entropic part, respectively). $\Gamma_c$ indicates the value for $\Gamma$ at the critical point with

$$\Gamma_c = \frac{1}{2} \left[ \frac{1}{V_1 \phi_c} + \frac{1}{V_2(1 - \phi_c)} \right] \text{ and } u_0 = \frac{1}{3} \left[ \frac{1}{V_1 \phi_c^3} + \frac{1}{V_2(1 - \phi_c)^3} \right]$$

with $V_i$ being the molecular volumes of the constituents. Then we can derive from equation (3) [5, 16]

$$\Gamma_c = 1.79 \times 10^{-5} \left[ \frac{1}{V_1 \phi_c^3} + \frac{1}{V_2(1 - \phi_c)^3} \right]^2 / [(1 + \Gamma_\sigma/\Gamma_c) \Gamma_c A^2 N^2_A].$$  \hspace{1cm} (4)$$

$A$ is the flexibility of the chain experimentally obtained by the slope of the Zimm plots e.g. $S^{-1}(Q) = S^{-1}(0) + A \cdot Q^2$. $A$ is identical to $c_0$ in equation (2). With respect to the $N$-dependence of $G_i$, with $N$ the number of monomers per chain, it follows from equation (4) that

$$G_i \propto N^{-1}$$  \hspace{1cm} (5)$$

if $\Gamma_\sigma \ll \Gamma_c$, which is identical to the results from Joanny [6] and de Gennes [7]. In case of $\Gamma_\sigma \gg \Gamma_c$ $G_i \propto N^{-2}$. The $N$ scaling of $G_i$ is determined by the chain length via $\Gamma_c$, $u_0$ and the entropic term $\Gamma_\sigma$ of the Flory-Huggins parameter. This shows that the mean-field like behaviour of polymer mixtures originates in the entropy of the Gaussian chain [8] and the entropy related to the compressibility of the system [19]. However, close to $T_c$ where $\tau \equiv G_i$ the mean-field theory is no longer valid [1-3] and the crossover to the 3-d Ising regime occurs. In this regime we use the expansion of equation (1) for $\tilde{S}(0) \gg 1$, which is essentially the pure Ising case to find [3]

$$S^{-1}(0) = \tau^\gamma / C^+$$  \hspace{1cm} (6)$$
N° 5

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with the critical amplitude

\[ C^+ = \text{Gi}(\gamma^{-1})(1 + 2.333^\gamma d)^{\gamma / (a_0 \cdot 2.333^\gamma d)}. \]  

(7)

This equation can be rearranged to solve for Gi thereby using the fact that \( a_0 \) is given by the inverse of the mean-field critical amplitude \( C_{MF}^+ \) in analogy with equation (6) of the susceptibility to give

\[ \text{Gi} = 0.069\left( \frac{C^+/C_{MF}^+}{1} \right)^{\nu/(\gamma - 1)} \]  

(8)

Hence the Ginzburg number can be expressed by the ratio of the Ising to the mean-field critical amplitudes of the susceptibility. The \( N \) dependence of Gi in this form is given as follows: the \( N \) dependence of \( C^+ \) has been derived by Sariban and Binder [9] to be

\[ C^+ \propto N^{(2 - \gamma)} \]  

(9)

whereas \( C_{MF}^+ \propto N \), if \( \Gamma_\sigma \ll \Gamma_\gamma \) is valid. Then we also obtain \( \text{Gi} \propto N^{-1} \) as already given by equation (5). If, however, \( \Gamma_\sigma \gg \Gamma_\gamma \) the situation becomes more complicated and \( \text{Gi} \) in equation (4) and equation (8) seems to be contradictory in the sense that \( \text{Gi} \propto 1/\Gamma_\sigma \) and \( \text{Gi} \propto \Gamma_\sigma^{(1/\gamma - 1)} \) for \( \text{Gi} \) in equation (4) and equation (8), respectively. In our data analysis we will use equation (8) rather than equation (4) because we have shown [1] that the mean-field description for our polymer blends under study is rather inadequate and the relation for \( \omega_0 \) is only correct in terms of the Flory-Huggins theory. Since the use of the crossover function has shown to model accurately the observed scattering data we will use them to determine the \( N \) scaling of the Gi number (Eq. (8)) and of the critical amplitudes of the bare correlation length and the susceptibility. The paper is organized in the way that first the main properties of the crossover function used are presented and its implications with respect to the traditional mean-field picture are discussed, and second, the \( N \) dependence of the Gi number is presented and discussed on the basis of equation (8).

2. Results.

2.1 THE CROSSOVER FUNCTION. — In order to demonstrate the validity of the crossover function used [2, 3], we have chosen three representative data sets from the studied systems whose characteristic parameters are collected in table I. These data are very different in their behaviour. The system d-PB/PS with \( \langle N \rangle = 23 \) (the mean \( N \) is defined to be \( \langle N \rangle = (\phi_B/N_A + \phi_A/N_B)^{-1} \) according to \( \Gamma_\gamma \)), PPMS/d-PS with \( \langle N \rangle = 50 \), and PVME/d-PS with \( \langle N \rangle = 4200 \). All data sets are plotted in figure 1 in terms of the inverse reduced susceptibility \( \tilde{S}^{-1}(0) \) and the reduced temperature \( \tilde{T} \) as defined in the course of equation (1). The solid line represents the crossover function equation (1). The figure is divided into three parts by three vertical lines. One is the line corresponding to \( \tilde{T} = 1 (\tau = \text{Gi}) \) which marks the crossover from 3d-Ising regime \( (\tilde{T} \ll 1) \) to the crossover range in the middle of the figure. The other line marks the crossover from the crossover range to the mean-field regime and is given by \( \tilde{T} = 300 (\tau = 300 \text{Gi}) \), which arises from the comparison of our prefactor in equation (4) with the prefactor in the corresponding equation originally given by Bates et al. [10] including their constant \( c = 0.3 \). As a further consequence it appears to be difficult even experimentally to reach the true mean-field regime! Most of the data are in the crossover range or even below where \( \tau < \text{Gi} \). This finding is in quantitative agreement with the computer simulations by Deutsch and Binder [11], where it was found that even for \( N > 512 \) no true mean-field behaviour was found. In figure 1 various other relevant limiting lines are plotted. Especially,
Table I.

<table>
<thead>
<tr>
<th>No.</th>
<th>System</th>
<th>$V_A$ (cm$^3$/mol)</th>
<th>$N_A$</th>
<th>$V_B$ (cm$^3$/mol)</th>
<th>$N_B$</th>
<th>$\phi_{C.A}$</th>
<th>$\langle N \rangle$</th>
<th>$G_i$</th>
<th>$C_{MF}^+$ (cm$^3$/mol)</th>
<th>$C^+$ (cm$^3$/mol)</th>
<th>$\xi_0$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>d-PB/PS</td>
<td>1 731</td>
<td>29</td>
<td>1 912</td>
<td>19</td>
<td>0.47</td>
<td>23</td>
<td>1.12 \times 10^{-2}</td>
<td>184</td>
<td>120</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>PPMS/d-PS</td>
<td>2 214</td>
<td>19</td>
<td>8 761</td>
<td>88</td>
<td>0.69</td>
<td>41</td>
<td>3.5 \times 10^{-2}</td>
<td>346</td>
<td>512</td>
<td>8.6</td>
</tr>
<tr>
<td>3</td>
<td>PPMS/d-PS</td>
<td>2 214</td>
<td>19</td>
<td>17 500</td>
<td>176</td>
<td>0.69</td>
<td>50</td>
<td>3.6 \times 10^{-1}</td>
<td>357</td>
<td>530</td>
<td>10.5</td>
</tr>
<tr>
<td>4</td>
<td>PPMS/d-PS</td>
<td>2 214</td>
<td>19</td>
<td>32 743</td>
<td>328</td>
<td>0.84</td>
<td>91</td>
<td>8.8 \times 10^{-2}</td>
<td>465</td>
<td>483</td>
<td>10.2</td>
</tr>
<tr>
<td>5</td>
<td>PDMS/PEMS</td>
<td>19 856</td>
<td>260</td>
<td>30 624</td>
<td>340</td>
<td>0.47</td>
<td>297</td>
<td>1.17 \times 10^{-2}</td>
<td>3333</td>
<td>2 180</td>
<td>16.7</td>
</tr>
<tr>
<td>6</td>
<td>PVME/d-PS</td>
<td>62 800</td>
<td>1 108</td>
<td>693 000</td>
<td>7 219</td>
<td>0.87</td>
<td>4 200</td>
<td>8.75 \times 10^{-5}</td>
<td>472</td>
<td>95.3</td>
<td>10</td>
</tr>
</tbody>
</table>

PB : poly(butadiene) ; PS : poly(styrene) ; PVME : poly(vinylmethylether) ;
PDMS : poly(dimethylsiloxane) ; PEMS : poly(ethylmethylsiloxane) ;
PPMS : poly(phenylmethylsiloxane).

All mixtures are made from components which were anionically polymerized, hence the polydispersity is typically $u = 1.05$ except the PVME which has $u = 2.2$.

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![Graph](image-url)

**Fig. 1.** — Double logarithmic plot $\tilde{S}^{-1}(0)$ versus $\tilde{r}$ for three polymer blends with varying molecular weight (Tab. I). System N° 1 d-PB/PS (O), System N° 6 PVME/d-PS (+), System N° 3 PPMS/d-PS (*). The full line is the crossover function equation (1). Dashed line is the pure 3-d Ising behaviour, dotted line is the pure mean-field behaviour and dash-dotted line is the mean-field expansion (Eq. (8)) of the crossover function. The vertical lines are explained in the text.
as already mentioned before, the dotted line indicates the true mean-field limit. Even the system with \( \langle N \rangle = 4 \, 200 \) does reach the mean-field case only for \( \tau \approx 300 \, \text{Gi} \). Thus, in figures 2a, b we extracted two typical data sets, namely N° 1 and 6 from table I differing in

![Graph showing S\(^{-1}\)(0) versus \( \tau \) for system N° 1 d-PB/PS. Full line is the crossover function (Eq. (1)). The dashed line is the pure Ising case and the dash-dotted line is the mean-field expansion (Eq. (8)) of the crossover function. b) Like 2a) but System N° 6 : PVME/d-PS instead.](image)

Fig. 2. — Plot of \( S^{-1}(0) \) versus \( \tau \) for system N° 1 d-PB/PS. Full line is the crossover function (Eq. (1)). The dashed line is the pure Ising case and the dash-dotted line is the mean-field expansion (Eq. (8)) of the crossover function. b) Like 2a) but System N° 6 : PVME/d-PS instead.
\(\langle N \rangle\) by two orders of magnitude. The data are plotted in terms of \(S^{-1}(0)\) versus \(\tau\). For the d-PB/PS system (Fig. 2a) one recognizes that over the whole temperature range measured the data are almost perfectly matched by the strict Ising case (dashed line). The crossover function (Eq. (1)), however, gives a much better fit for the higher temperatures. The situation is completely different for the PVME/d-PS system (Fig. 2b) where the Ising law fails (dashed line) almost completely. The Ising law has been evaluated from the crossover fit via equation (7). The crossover function fits the data over the whole temperature range studied. With respect to the true mean field behaviour (c.f. Fig. 1) it is interesting to expand equation (1) for \(\tau \gg \Gi\) to get [2, 3]

\[
\hat{S}^{-1}(0) = (\hat{\tau} - 1)(1 - 1.098(\hat{\tau} - 1)^{-0.411}).
\]

Thus the \(\epsilon\)-expansion does not recover the proper square-root of the temperature correction to the classical limit implied by the Ornstein-Zernike theory [3] and given by [12] \(\hat{S}^{-1}(0) = (\hat{\tau} - 1)(1 - (\hat{\tau} - 1)^{-0.5})\). However, this becomes unimportant in practice as one can see in figure 2b, where equation (10) is plotted as a dotted line. Obviously, the expansion is equivalent to the crossover function within the experimental error already for \(\tau\) values smaller than those beyond \(\tau \approx 300\Gi\) in figure 1 where the deviation from mean-field, namely \(\hat{S}(0) = \hat{\tau}\), is smaller than 10% with respect to the crossover function [1].

2.2 The \(\langle N \rangle\) scaling of \(\Gi\). — After having established the crossover function we first focus our attention on the problem whether the \(\langle N \rangle\) calculated and listed in table I is a properly and well defined quantity. One might argue that all systems under study are naturally not completely symmetric with respect to \(N\), \(\phi\), and the segment length of the components. In principle, one could speculate that tedious corrections with respect to the ideal symmetric case are necessary, especially if one wants to compare our results with those obtained by simulations [11]. To test that we have used the predictions of the \(\langle N \rangle\) scaling of \(\xi_0\) given in reference [11]

\[
\xi_0 \propto N^{(1 - \nu)}
\]

with \(\nu = 0.63\). The results are plotted in figure 3. From the obtained agreement between experiment and theory we conclude that our \(\langle N \rangle\) is well defined and no further corrections are necessary. However, the data point for system \(N^*\;6\) (PVME/d-PS) has been dropped because it is completely off. The very asymmetric character of this mixture and the very polydisperse PVME component seems to disturb the mean-field type of equation for determining

![Graph](image-url)

Fig. 3. — Double logarithmic plot of the critical amplitude \(\xi_0\) of the correlation length \(\xi = \xi_0\;\tau^{-\nu}\) as a function of the mean degree of polymerization. For the theoretical prediction see equation (11).
\( \langle N \rangle \) which otherwise worked well. All data points of PVME/d-PS will therefore be dropped from the following considerations.

From the fit of equation (1) to the scattering data (Fig. 1) two parameters are obtained, namely, the mean-field critical amplitude \( C_{MF}^+ = 1/a_0 \) and the Ginzburg number \( Gi \). Both parameters are listed in table I. After having established the mean degree of polymerization (Fig. 3) \( \langle N \rangle \) we will now concentrate on the plot of \( Gi \) versus \( \langle N \rangle \) in a double logarithmic scale as shown in figure 4. First we will discuss the data for \( \langle N \rangle \cong 30 \). Here, the data follow a straight line which scales as \( Gi \propto N^{-\frac{9}{4}} \) This is not predicted by theory (Eq. (5) and (8)) for \( \Gamma_{\sigma} \ll \Gamma_{e} \). In order to add further experimental findings to our data listed in table I we have incorporated a data point by Theobald [13] obtained by light scattering on a similar system to our N° 5 in terms of the crossover function equation (1). The data point for \( \langle N \rangle \cong 30 \) from our system N° 1 has a much smaller \( Gi \) value than the systems 2-3 beyond \( \langle N \rangle \cong 30 \) by about a factor of 30. In order to understand that we first calculate the value for \( Gi \) in the Ornstein-Zernike definition [3]. It is estimated to be \( Gi = 0.01 \) using values for \( a_0 \) and \( u_0 \) appearing in equation (2) and in the definition for \( Gi \) (cf. Eq. (3)) from the van der Waals gas model to be \( a_0 = 9/4 \) and \( u_0 = 27/8 \). Anisimov et al. [3] have furthermore listed values for \( Gi \) for small molecules like \( H_2O \), \( CO_2 \) etc. They range between \( 0.009 < Gi < 0.04 \).

The other besides \( Gi \)-experimentally accessible quantity is (as already mentioned) the amplitude \( C_{MF}^+ = 1/a_0 \) as listed in table I and plotted (and further discussed) in figure 7. Both values, namely \( Gi \) and \( C_{MF}^+ \) immediatly give the Ising critical amplitude according to equation (7). Its \( N \)-dependence is predicted by equation (9) to be \( C^+ \propto N^{0.76} \) as plotted in figure 5. Within a factor of two the data show the predicted \( N \) scaling of the critical amplitude \( C^+ \). From that we furthermore conclude that the determination of \( a_0 \) and \( Gi \) is not ambiguous, although the product \( a_0 \). \( Gi \) enters in fitting equation (1) to the data.
3. Discussion.

One fundamental question which arises while interpreting figure 5 lies in the physical nature of the shaded area at \( \langle N \rangle \approx 30 \). This line obviously separates two completely different regions with respect to the widths of the Ising regime. In order to subsequently discuss all relevant points of the quite complex figure 4 we start with what is relatively settled, that is the behaviour at low \( \langle N \rangle \leq 30 \). There, all available data behave according to the theoretical prediction [12] which further means that a polymer mixture with \( \langle N \rangle = 23 \) (our system 1) is in this sense not a polymer mixture. According to Deutsch and Binder [11] scaling predictions for \( N < 32 \) polymer mixtures are in better agreement with those for semidilute binary blends in a common solvent. Therefore the shaded area separates the region where for \( N < 32 \) excluded volume and end group effects may play an important role. This behaviour might be similar to the case of the determination of the glass transition \( T_g \) of polymers as a function of the degree of polymerization. Since the number of molecular ends is proportional to \( 1/N \), their influence diminishes with increasing \( N \) and accordingly one finds \( T_g = T_g(N \to \infty) + \text{Const.}/N \) [14]. For \( N \approx 30 \) we can reach the \( T_g(N \to \infty) \) within 10% [15] which means that already for such relatively low molecular weights end effects are getting less important. There are furthermore data by Hobbie et al. [17] on a system with \( \langle N \rangle = 20 \) similar to our system 1 which also has been analyzed with equation (1) yielding a value for \( \Gamma = 0.003 \) being even smaller than the theoretical value. This too low value seems not to be reasonable, however, the given trend is confirmed.

![Double logarithmic plot of the critical amplitude C⁺ (Eq. (7)) of the susceptibility as a function of the mean degree of polymerization. The theoretical slope according to equation (9) is shown.](image)

A relevant question remains: is the «step» in \( \Gamma \) at about \( \langle N \rangle = 30 \) already mirrored by the temperature dependence of \( S^{-1}(0) \) or to say do we find in our data this substantial difference in the Ising widths between \( \langle N \rangle < 30 \) and \( \langle N \rangle > 30 \)? This is as more as an important question because from computer simulations [11] such a behaviour is not found. According to these we would have expected a smooth crossover between the \( \langle N \rangle \) smaller and \( \langle N \rangle \) larger than 30 regions. In order to show that this step is indeed our experimental result we have chosen the data sets of our systems \( N^* \) 1 and \( N^* \) 3 which are according to figure 1 almost in the same \( \hat{t} \) range of our crossover plot and have plotted \( S^{-1}(0) \) versus \( 1/T \) in figure 6. The fitted (linear) lines according to the mean-field prediction, although not correct, is sufficient to show the differences of the Ising widths. As one can see from the figure, the width of the Ising regime indicated by \( \Delta T^* \) of the \( \langle N \rangle = 50 \) system is higher by at least a factor of five in comparison to the \( \langle N \rangle = 23 \) system in qualitative agreement with the observed step in \( \Gamma \). Data by Bates et al. [10] with a \( \langle N \rangle = 57 \) and a chemically different system than our systems
2-4 show a crossover width of about $\Delta T^* = 30\, \text{K}$ which is similar to our result of the $N = (50)$ systems. From all these findings we have to conclude that the quantitatively different behaviour of $G_i$ above and below $\langle N \rangle = 30$ is experimentally well settled. This finding also explains why our system 1 with $\langle N \rangle = 23$ had a constant $c$ [16], being proportional to the prefactor in equation (4), which is at least one order of magnitude smaller than the universal value of this prefactor as predicted by Bates et al. [10] for polymer mixtures.

In order to explain the nature of the behaviour of the $\langle N \rangle$ dependence $G_i$ above $\langle N \rangle = 30$ as depicted in figure 4 we will analyze the $\langle N \rangle$ dependence of the respective critical amplitudes appearing in equation (8). In figure 5 the $N$ dependence of $C^+$ has been shown to follow the prediction of equation (9). Then accordingly the $\langle N \rangle$ scaling of $C^+_{\text{MF}}$ which is derived from the $a_0$ values as listed in table I is of immediate interest. The results are shown in figure 7. The data follow within a factor of two the expected $N$ powerlaw. This is about the same accuracy found for the $N$ scaling of the critical amplitude $C^+$ in figure 5. The $N$ dependence of $G_i$ therefore comes from the deviations of both amplitudes within the shaded areas in figures 5 and 7 and the high exponent of $1/(\gamma - 1) = 4.17$ in equation (8). To understand the $N^{-2}$ scaling of $G_i$ above $\langle N \rangle = 30$ we have to analyze further the values of $a_0 = 2(I \sigma_1 + \sigma_2)$. Because the purely combinatorial entropy part $I \sigma_1$ is determined by the molecular volumes and the composition of the components $I \sigma_2$ can be evaluated from $a_0$. In figure 8 both $I \sigma_1$ and $I \sigma_2$ of our systems 1-5 are plotted versus $\langle N \rangle$. The $\langle N \rangle$ dependence of $I \sigma_1$ is $I \sigma_1 \propto N^{-1}$ as expected. The point at $\langle N \rangle = 91$ is a little off which is correlated with its relatively high asymmetric components (Tab. I). The really remarkable effects are the absolute values and the $\langle N \rangle$ dependence of $I \sigma_2$. First of all the absolute values of $I \sigma_1$ and $I \sigma_2$ are comparable over the whole $\langle N \rangle$ range studied and for systems 2-4 $I \sigma_2$ is larger than $I \sigma_1$ by about a factor of three. Hence the inequality $I \sigma_2 \leq I \sigma_1$ which leads to a $G_i \propto N^{-1}$ is never fulfilled. The straightforward calculation of $I \sigma_2$ in the mean field picture leads to values roughly one order of magnitude lower than those shown in figure 8. However,
Fig. 7. — Double logarithmic plot of the critical amplitude $C_{MF}^*$ of the susceptibility as a function of the mean degree of polymerization. The theoretical slope according to equation (9) is shown.

Fig. 8. — Double logarithmic plot of the combinatoric part $\Gamma_c (-\circ -)$ and the entropic part $\Gamma_\alpha (-\times -)$ of the Flory-Huggins parameter as a function of $\langle N \rangle$. $\Gamma_\alpha$ seems to be responsible for the observed $N$ dependence of $\Gamma_c$ because it is of the same size or even larger than $\Gamma_c$.

this discrepancy vanishes within 20 % for our system 6, when $\langle N \rangle$ is so high that we really can measure near the mean-field regime as indicated in figure 1 for $\tau \approx 300 \, \text{Gi}$. We speculate when $\langle N \rangle$ is getting much larger than of the order of the order of 100 that then $\Gamma_\alpha$ is getting more and more unimportant with respect to $\Gamma_c$ and $\Gamma_c \propto N^{-1}$ scaling will then probably hold. This can be seen from figure 8. Secondly, we notice that there is an intermediate $\langle N \rangle$ range (between $30 \leq \langle N \rangle \leq 200$) where $\Gamma_\alpha$ e.g. the free volume
requirements of the quite short chains are dominant. We are not aware of any theoretical description for the \(N\) dependence of \(\Gamma_\sigma\) but could claim that this effect studied here is considered to be of general nature because it is related to the expense to which a given volume is occupied by chain segments and by that characteristic for polymers. These findings get support from quite recent lattice cluster theory computations by Dudowicz et al. \[18\]. They find a two to three orders of magnitude higher \(\Gamma_i\) for compressible polymer mixtures in comparison to results from equation (4) for incompressible systems. These calculations have been performed for PVME/d-PS in the same \(\langle N \rangle\) range of our system. Even though their calculated \(\Gamma_i\) values seems somewhat too high in comparison to our \(\Gamma_i\) in table I for PVME/d-PS these results confirm the influence of \(\Gamma_\sigma\) onto \(\Gamma_i\) and the width of the Ising regime \[20\]. In future work it seems to be interesting to influence the \(\Gamma_\sigma\) term by applying pressure and furthermore, to use systems to span the \(\langle N \rangle\) range studied here \[19\].


In this publication we have discussed the consequences of the analysis of the structure factor at \(Q = 0\) obtained from scattering experiments with neutrons and light for polymer blends in terms of the crossover function derived by Belyakov et al. \[2, 3\]. This analysis has been demonstrated in publication \[1\] and has been performed for various polymer blends with an average degree of polymerization between \(\langle N \rangle = 23\) and \(\langle N \rangle = 4200\) (Tab. I). Our first main result is, as demonstrated in figure 1 and figure 2, that the mean-field regime even for our system 6 with \(\langle N \rangle = 4200\) is never reached! Therefore, this work helps to clarify the meaning of the Flory-Huggins parameter \(\Gamma\) under the influence of fluctuations. Usually, this quantity has been determined by an extrapolation procedure \((\Gamma^{\text{extr}})\) as described in reference \[5\]. This procedure implies a linear behaviour of \(S(0)^{-1} \) vs. \(\tau\) which usually has been identified with the validity of the mean-field theory in the region of the extrapolation. The observed consistency of this description was supported experimentally by the reliable reproduction of the phase diagrams \[21\]. However, it has been demonstrated in our work (Fig. 1) that the mean-field theory holds only at temperatures rather far from \(T_c\), in a region normally inaccessible by the experiment. Instead, the Flory-Huggins parameter was evaluated by a fit of \(S(0)^{-1}\) vs. \(\tau\) by the crossover function derived by Belyakov et al. \[2\] which yields the Ginsburg parameter \(\Gamma_i\) and the critical amplitude \(C_{\text{MF}}\) in equation (1). This leads to the «true meanfield value» \(\Gamma^{\text{MF}}\). Its value may differ considerably from the extrapolated apparent meanfield value \(\Gamma^{\text{extr}}\) described before (see Tab. I in Ref. \[1\]) and demonstrated in figure 8 for \(\Gamma_\sigma\) and \(\Gamma_\nu\), respectively. Only the value of \(\Gamma^{\text{MF}}\) could be identified with a calculation which, e.g., use the mutual interaction between the monomers as in \[18\].

Furthermore, we have discussed the \(\langle N \rangle\) scaling of the Ginsburg number \(\Gamma_i\) and of the critical amplitudes of the bare correlation length and susceptibility. While the critical amplitudes lead to the expected scaling as seen in figures 3, 5, 7 (for the susceptibility within a factor of two) the \(\langle N \rangle\) dependence of \(\Gamma_i\) is quite unexpected. For \(\langle N \rangle < 30\) we find for our system 1 the \(\Gamma_i\) for low molecular liquids and in agreement with the calculated value from the van der Waals model \[3\]. At \(\langle N \rangle \approx 30\) we find a sudden increase of \(\Gamma_i\) by more than one order of magnitude and then for larger \(\langle N \rangle\) a \(\Gamma_i \propto N^{-2}\) scaling law. The increase of \(\Gamma_i\) near \(N = 30\) is clearly observed from the scattering data by the larger width of the Ising regime in figure 6 also in agreement with results from other groups \[10, 17\]. Also the too small \(c\) parameter in the Ginsburg criterion of equation (4) of our system 1 as discussed in reference \[16\] in comparison with those of other \(\langle N \rangle > 30\) polymer mixtures is indicated by the increase of \(\Gamma_i\) at \(\langle N \rangle \approx 30\). A \(\Gamma_i \propto N^{-1}\) scaling is only expected if \(\Gamma_\sigma \ll \Gamma_\nu\), a relation which is usually believed to be fulfilled from conventional analysis in terms of the mean-field approximation. However, according to our analysis of \(S(0)\) with the crossover function of
equation (1) $\Gamma_\sigma$ is found to be of the same order of magnitude as, or even larger than $\Gamma_c$ for $N$ up to 300. There is an indication that $\Gamma_\sigma \ll \Gamma_c$ is fulfilled for $N$ considerably larger than 300. Because $\Gamma_i$ is proportional to the ratio of the critical amplitudes of the susceptibility in Ising and mean-field asymptotic regimes to the power $1/(\gamma - 1) = 4.17$ Gi very sensitively depends on the detailed $N$ dependences of $C^+$ and $C^+_{MF}$ and therefore on $\Gamma_\sigma$ which is the entropic term of the Flory-Huggins parameter and related to the compressibility or the free volume of the system [18]. Because the large value of $\Gamma_\sigma$ in comparison to $\Gamma_c$ seems to be responsible for the increase of $\Gamma_i$ or of the width of the Ising regime at about $\langle N \rangle = 30$, Gi must depend strongly on pressure in this $N$ range. Monte Carlo simulations [11] seem to support our results, because the scaling behaviour similar to good solvent systems is found below $N = 30$.

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References

[20] The Gi number in reference [18] is defined with five times higher prefactor than our Gi. Furthermore their equation (4.2) has to be divided by 9 because of $u_0 = \frac{1}{3} \left[ (V_1 \phi_e^2) + 1/(V_2 (1 - \phi_e)^3) \right]$. 