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# Correlation length and amplitude scaling in critical polymer solutions

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We present a light scattering measurement of the correlation length for a series of critical solutions of polystyrene in methylcyclohexane with different molecular weights. Our results show that the correlation length  $\xi \sim N^{\zeta_\nu} \epsilon^{-0.63}$ , where  $N$  is the polymerization index and  $\epsilon = (T - T_c)/T_c$  is the reduced temperature. The  $N$  exponent  $\zeta_\nu$  is found to be  $0.18 \pm 0.02$ , which is contrary to most earlier direct experimental results but in excellent agreement with theoretical predictions by de Gennes and Stepanow. © 1999 American Institute of Physics. [S0021-9606(99)51142-2]

Polymer solutions near their critical points are well known to exhibit Ising like behavior, i.e., various thermodynamic properties have power-law dependence on the reduced temperature  $\epsilon = (T - T_c)/T_c$  with exponents having the same values as those for simple liquids and ferromagnets. In addition, the amplitudes in front of the temperature factors have power-law dependence on the molecular weight, or the polymerization index  $N$ , of the polymer chains. Thus, apart from a system-dependent constant, a pair of scaling exponents fully characterizes any thermodynamic property of a polymer solution near its critical point. It is also believed that analogous to those between the temperature exponents, similar scaling laws exist for the  $N$  exponents as well and that only two of these exponents are independent, with the one for the correlation length being the most fundamental.<sup>1,2</sup> The correlation length can be expressed as

$$\xi = \xi_0 \epsilon^{-\nu} \propto N^{\zeta_\nu} \epsilon^{-\nu}, \quad (1)$$

where the temperature exponent  $\nu = 0.63$  is well known. The exact non-mean-field value of the  $N$ -exponent  $\zeta_\nu$ , however, remains a long unsettled problem.<sup>2</sup>

Early light scattering measurements from solutions of polystyrene (PS) in cyclohexane (CH) by Debye *et al.*<sup>3</sup> and in methylcyclohexane (MCH) by Shinozaki *et al.*<sup>4</sup> reported the value of  $\zeta_\nu$  to be around 0.28–0.29. Theoretically, de Gennes' scaling argument<sup>5</sup> has led to  $\zeta_\nu \approx 0.185$ , and Stepanow has obtained  $\zeta_\nu \approx 0.17$  using a Landau–Ginsberg–Wilson model.<sup>6</sup> Thus the earlier experimental results do not support the nonclassical theoretical predictions. Interestingly, the above experimental results for  $\zeta_\nu$  seem to be closer to the value of  $\frac{1}{4}$ , which is also put forward by de Gennes based on a modified version of the Flory–Huggins mean-field theory.<sup>7</sup>

Debye, on the other hand, using a ‘‘traditional’’ mean-field theory of the Flory–Huggins type has shown that  $\xi_0^2 \sim R^2$ , where  $R$  is the end-to-end distance of the polymer chain,<sup>8</sup> which implies  $\zeta_\nu = \frac{1}{2}$  for a Gaussian coil ( $R \sim N^{1/2}$ ).

Despite all these complications, the nonclassical values of de Gennes<sup>5</sup> and Stepanow<sup>6</sup> are seen to be more consistent with scaling law estimates based on reliable experimental values for the coexistence curve exponent ( $\zeta_\beta$ ) and interfacial tension exponent ( $\zeta_\mu$ ) which give  $\zeta_\nu = 0.195$ .<sup>2</sup> Widom has also remarked<sup>9</sup> that de Gennes' approximation<sup>5</sup> for  $\zeta_\nu$  (and for  $\zeta_\mu$  for the interfacial tension between the coexisting phases, which has been verified by experiment<sup>2,10</sup>) may be highly accurate. Using the coexistence curve data<sup>11</sup> for PS–MCH, Sanchez deduced  $\zeta_\nu = 0.197$ .<sup>2</sup> However, his result depends on the adoption of a new scaling variable  $\epsilon N^{\zeta_\nu/\nu}$  for polymer solutions. One possible reason for the large values of  $\zeta_\nu$  obtained from the two early light scattering experiments may be that the samples used there were not critical, since both have reported<sup>3,4</sup> using values of  $\phi_c$  that were consistent with  $N^{-1/2}$  rather than the now-generally-accepted  $N^{-(0.37-0.38)}$ .

Attempts have been made in recent years to resolve the above discrepancy. Caylor and Law in a critical adsorption measurement<sup>12</sup> in PS–CH has indirectly determined  $\zeta_\nu$  to be around 0.26, which is again significantly higher than nonclassical theoretical values.<sup>13</sup> In a recent turbidity measurement of polymethyl-methacrylate in 3-octanone (PMMA/3-OCT), however, we found that  $\zeta_\nu$  to be 0.15–0.17 which is in line with the nonclassical theoretical predictions.<sup>14</sup> To fully resolve this issue and also to test the universality assumption about the critical exponent, we have made a direct light scattering determination of  $\zeta_\nu$  in the system PS–MCH, which is reported in this paper.

Narrowly distributed polystyrene standards were purchased from Polymer Laboratories Ltd. Their weight-average

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TABLE I. The weight-averaged molecular weights  $M_w$  and polydispersities  $M_w/M_n$  and critical polymer volume fractions  $\phi_c$  for ten molecular weights of PS in MCH, together with the temperature exponent  $\nu$  and the critical amplitude  $\xi_0$  of the correlation length for seven molecular weights of PS in MCH.  $\xi_0$  in column six are obtained by fixing  $\nu$  to the theoretical value of 0.63.

$M_w$ (g/mol)	$M_w/M_n$	$\phi_c$	$\nu$	$\xi_0$ (nm)	$\xi_0$ (nm) ( $\nu=0.63$ )
10 700	1.02	0.204			
20 500	1.03	0.164			
30 400	1.02	0.143	$0.61 \pm 0.01$	$0.86 \pm 0.02$	$0.74 \pm 0.01$
48 800	1.03	0.118	$0.64 \pm 0.03$	$0.65 \pm 0.05$	$0.78 \pm 0.02$
68 600	1.02	0.104	$0.65 \pm 0.01$	$0.70 \pm 0.01$	$0.83 \pm 0.05$
97 600	1.03	0.092	$0.63 \pm 0.01$	$0.90 \pm 0.02$	$0.91 \pm 0.01$
204 010	1.02	0.070	$0.63 \pm 0.01$	$1.05 \pm 0.01$	$1.02 \pm 0.01$
311 000	1.04	0.059	$0.60 \pm 0.03$	$1.49 \pm 0.07$	$1.13 \pm 0.02$
630 000	1.03	0.046	$0.65 \pm 0.02$	$1.12 \pm 0.04$	$1.25 \pm 0.02$
758 500	1.05	0.043			

molecular weight  $M_w$  and polydispersity  $M_w/M_n$  are provided by the manufacturer, and are listed in Table I. The solvent methylcyclohexane (99.9%+) was purchased from Aldrich Chemical Co. To reduce the shift of critical point due to moisture, the polymer was dried with  $P_2O_5$  and the solvent was distilled with metallic sodium. We made the critical samples by mixing PS and MCH in dry nitrogen atmosphere and then flame sealing them in cylindrical shaped light scattering cells. Afterwards, the cells were mounted on a rotary mixer inside a hot air bath for a few days so that the polymers become fully dissolved in the solvent. At the early stage of the experiment, we made the samples with their critical polymer volume fraction  $\phi_c$  calculated according to<sup>15</sup>  $\phi_c = 6.68 M_w^{-0.38}$ . But when checked with the equal-phase-volume criterion, we found that the concentrations given by this formula are obviously not critical for our samples, despite our observing very stringent procedures in every step of the sample preparation. We therefore redetermined  $\phi_c$  by the above-mentioned criterion for ten molecular weights, which are listed in column three of Table I. The uncertainty in the determination of  $\phi_c$  is about 0.001.<sup>16,17</sup> Figure 1 is a log-log plot of the measured  $\phi_c$  vs  $M_w$  where the solid line represents a least-squares fit of  $\phi_c = (6.42 \pm 0.15) M_w^{-0.37 \pm 0.01}$ . It is seen here that the

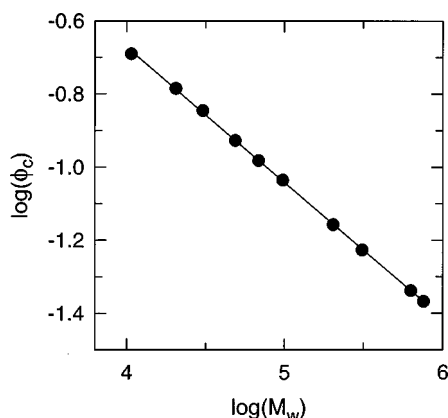


FIG. 1. Log-log plot of the critical volume fraction  $\phi_c$  vs molecular weight  $M_w$  for ten samples of PS-MCH, the solid line is a least-squares fit of  $\phi_c = (6.42 \pm 0.15) M_w^{-0.37 \pm 0.01}$ .

$N$ -exponent  $r(=0.37)$  for  $\phi_c$  is in excellent agreement with its well established experimental and theoretical value,<sup>11,17-19</sup> but the amplitude differs somewhat from that given in Ref. 15. The critical temperature  $T_c$  was taken as the highest phase separation temperature determined in an iterative process as follows. First, the temperature was lowered in steps  $\delta T$  of a few degrees until phase separation occurred. The temperature was then raised back to that of one phase region and the sample thoroughly remixed. This process was repeated with decreasing temperature steps until  $\delta T = 10$  mK. The critical temperature was then taken as the middle value of the range in which phase separation occurred, the uncertainty of  $T_c$  is thus  $\pm 5$  mK. As will be seen below, this precision in  $T_c$  is adequate for our light scattering measurements.

The correlation length  $\xi$  was determined by static light scattering measurement. According to the Ornstein-Zernike theory,<sup>20</sup> the angular distribution of the scattered light intensity  $I(q)$  is given as

$$I(q) \propto (\pi^2/\lambda^4) \phi^2 (\partial n^2/\partial \phi) \frac{\chi}{(1 + \xi^2 q^2)}, \quad (2)$$

where  $\chi$  is the osmotic compressibility,  $\phi$  polymer volume fraction,  $\lambda$  wavelength of the light in vacuum, and  $n$  the refractive index of the solution; and  $q = (4\pi n/\lambda) \sin(\theta/2)$  is the magnitude of the scattering vector with  $\theta$  being the scattering angle. As our scattering intensity was not normalized uniformly for the whole experiment (see below), we can not deduce the value of  $\chi$  from our data. Equation (2) can thus be written as  $I^{-1}(q) = B + Aq^2$  with  $\xi^2 = A/B$ . A series of measurements of  $I(q)$  at different angles and temperatures will, therefore, yield the values of the amplitude  $\xi_0$  and the temperature exponent  $\nu$  in Eq. (1) for a given polymer solution.

Correlation length was measured for seven samples with molecular weights ranging from 30 000 to 630 000, these were shown in Table I along with their  $M_w/M_n$  ratios. Due to the well-known slow drift of critical temperatures,<sup>17</sup> the  $T_c$  for each sample was carefully remeasured before the start of light scattering measurement for that sample. Our angular distribution measurements were done using a high precision goniometer incorporating a thermostated water bath with a

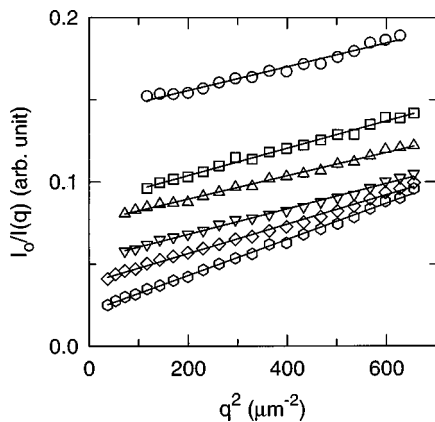


FIG. 2. The inverse of the normalized angular intensity distribution  $I_o/I(q)$  vs  $q^2$  measured at six temperatures for the sample with  $M_w=48\,800$ .  $T-T_c$  for the various data are, from top to bottom, 1.241, 0.891, 0.751, 0.597, 0.404, and 0.178 ( $^{\circ}\text{C}$ ).

temperature stability of  $\pm 2$  mK. The light source was a 10 mW He–Ne laser whose output was attenuated with neutral density filters to a few mW. The scattered light was recorded by a photomultiplier operated in the photon counting mode. Measurements were made in the angular range of  $25^{\circ} < \theta < 130^{\circ}$ , and in the temperature range of  $0.1 < T - T_c < 1.3 (^{\circ}\text{C})$  within which the system is close to the critical point while the multiple scattering effect is still not significant. For each sample, a “background” was first measured in the same angular range at a temperature of about 20–30  $^{\circ}\text{C}$  above the critical temperature (where scattering due to critical fluctuations can be treated as negligible), this was then subtracted from data measured at lower temperatures. If the background is not properly subtracted, its effect will show up more prominently at larger  $\Delta T$  than it is at small  $\Delta T$ . Let us take, as an example, the sample with  $M_w=97\,600$  to estimate this effect. If we used data with  $\Delta T=0.5$ –1.3 only, then  $\nu=0.635$ , whereas  $\nu=0.631$  if all data were used. This shows that any error introduced by using the measured background data as the “true background” is likely to be small for the present purpose.

Figure 2 plots the inverse of the intensity angular distribution  $I_o/I(q)$  versus the squared wave vector  $q^2$  for the sample with  $M_w=48\,800$  at several temperatures above the critical point. The data are seen to be well-fitted by straight lines and the square of the correlation length is given by the ratio of the slope to the intercept ( $\xi^2=A/B$ ). The uncertainties in the determination of  $A$  and  $B$  were estimated to be around 2% and 10%, respectively. These uncertainties yield an uncertainty of 10% in  $\xi^2$  and of 5% in  $\xi$ . The values of  $\xi$  were then fitted to Eq. (1) to obtain the exponent  $\nu$  and the amplitude  $\xi_0$ .

For several samples, two runs of intensity measurement (at different temperatures) were made with slightly different optical setups, one used a power meter for the normalization of the incident light, the other did not. Obviously, the slopes of  $1/I(q)$  vs  $q^2$  for data with different normalization would not be the same, because both the slope  $A$  and the intercept  $B$  contain the overall proportionality constant. But the ratio  $A/B=\xi^2$  should be independent of how the intensity is nor-

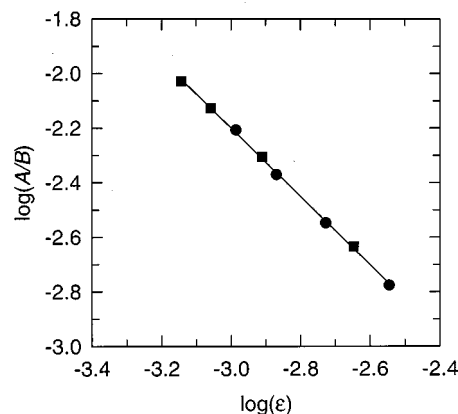


FIG. 3.  $\log(A/B)$  vs  $\log(\epsilon)$  for the sample with  $M_w=204\,010$ . Two sets of data with different normalization of the incident laser intensity are represented with different symbols. The solid line is a least-squares fit to the whole data set, which yields a slope of 1.254 ( $\nu=0.63$ ).

malized, and this is shown in Fig. 3 where  $\log(A/B)$  is plotted against  $\log(\epsilon)$  for the sample of  $M_w=204\,010$ . In the figure, data from the two runs are represented by two types of symbols respectively. A least-squares fit to all data points, shown as the straight line, gives  $2\nu=1.254$  and  $\xi_0=1.05$  nm. The results for all the seven samples are listed in columns four and five of Table I. It is seen that the values of  $\nu$  ranged from 0.60 to 0.65 which are in good agreement with the theoretical prediction of 0.63.

Having verified that the temperature exponent is indeed close to the 3D (three-dimensional) Ising value, we repeated above fitting procedure with a fixed  $\nu=0.63$  for the seven samples to deduce the molecular-weight-dependent amplitude  $\xi_0$ . As the values of amplitudes are known to be sensitively dependent upon the values of exponents in power law fits, using a single value for the temperature exponent allows one to make a meaningful comparison among the amplitudes for different molecular weights.<sup>4</sup>  $\xi_0$  obtained from this fit are listed in column six of Table I. The uncertainties for  $\xi_0$  as listed in the Table are the standard deviations from the fittings, which are smaller than the estimated 5% value. Figure 4 is a plot of  $\log(\xi_0)$  vs  $\log(M_w)$  with the solid line represent-

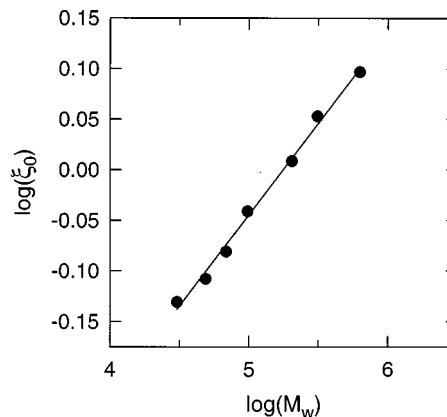


FIG. 4. Log–log plot of  $\xi_0$  vs  $M_w$  for seven molecular weights of PS in MCH. The solid line, representing a least-squares fit, has a slope of  $\zeta_\nu=0.18\pm 0.02$ .



ing a least-squares fit, from which we obtain  $\zeta_\nu = 0.18 \pm 0.02$ . This value is significantly smaller than all previously reported experimental values from light scattering and critical absorption measurements for the same system, but is in excellent agreement with the theoretical predictions of de Gennes<sup>5</sup> and Stepanow,<sup>6</sup> and also agrees well with the one deduced by Sanchez using coexistence curve data.<sup>2</sup> Since Sanchez obtained  $\zeta_\nu$  by adopting  $\epsilon N^{\zeta_\nu/\nu}$  as the fundamental scaling variable for polymer solutions and now that  $\zeta_\nu$  has been directly determined from experiment, one can test whether the proposed scaling variable will yield the correct  $N$  exponent for the order parameter  $\Delta\phi$ , which is the difference in polymer volume fractions between the polymer-rich and the solvent-rich phases. Substituting the theoretical values of  $\nu=0.63$  and  $\beta=0.327$ , as well as  $\zeta_\nu=0.18$  and  $r=0.37$  obtained from the present study, into  $\Delta\phi/\phi_c \sim (\epsilon N^{\zeta_\nu/\nu})^\beta$  (as proposed in Ref. 2), and then comparing it with the definitions  $\Delta\phi \sim N^{-\zeta_\beta\epsilon^\beta}$  and  $\phi_c \sim N^{-r}$ , we obtain  $\zeta_\beta = 0.277 \approx 0.28$ . This is in excellent agreement with the value of  $\zeta_\beta = 0.28$  determined from coexistence curve measurement.<sup>11,21</sup> As the present work determines  $\zeta_\nu$  and  $r$  independently, our results also verifies the relation  $2\zeta_\nu \approx r$  as it should be since this is equivalent to taking  $\epsilon N^{\zeta_\nu/\nu}$  as a scaling variable.<sup>2</sup> Note that, with the interfacial tension exponent  $\zeta_\mu$  taken to be  $0.37-0.39$ ,<sup>2,10</sup> our result is also consistent with the relation  $\zeta_\mu = 2\zeta_\nu$ , as required by the well-known relation  $\sigma \sim \xi^{-2}$  between the interfacial tension and the correlation length.<sup>22</sup> Finally, we note that in a recent theoretical work,<sup>23</sup> Povodyrev *et al.* have shown that the experimentally determined exponents may be effective ones that approach the asymptotic exponents only in the limit of infinite  $N$ . This adds an interesting scenario in the interpretation of experimental results. But because the model is a modified mean field theory, its results could not be readily compared with our current measurement.

Together with the value of  $\zeta_\nu = 0.15-0.17$  obtained from the previous turbidity measurements for the system of PMMA/3-OCT, we conclude that the nonclassical value of

$\zeta_\nu$  should be around  $0.17-0.19$ , which is in a very good agreement with the nonclassical theoretical predictions by de Gennes<sup>5</sup> and Stepanow.<sup>6</sup>

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