

Coexistence curve and diameter of polystyrene in cyclohexane

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We have measured the coexistence curve of a high-molecular-weight ($M_w = 1.56 \times 10^6$) polystyrene in cyclohexane over a temperature range of $4 \times 10^{-5} < (T_c - T)/T_c < 4 \times 10^{-2}$. The concentration difference $X^+ - X^-$, in volume fraction of polystyrene, was well represented by the expression $X^+ - X^- = B\epsilon^\beta + B_1\epsilon^{\beta+\Delta} + B_2\epsilon^{\beta+2\Delta}$ based on the Wegner expansion, where $\beta = 0.327 \pm 0.004$ and Δ is fixed at 0.50. The concentration difference could also be well represented by the expression $X^+ - X^- = B\epsilon^\beta + B'\epsilon^\beta$, where a somewhat higher value of β was required. The diameter in the temperature range $4 \times 10^{-5} < (T_c - T)/T_c < 10^{-2}$ was represented by $(X^+ + X^-)/2 - X_c = A\epsilon^\mu$, where $\mu = 0.860 \pm 0.006$. We have established, for the first time, the value of the asymptotic critical exponent β of even a polymer system to be like that presently calculated for the Ising model. The observed exponent $\mu(= 1 - \alpha)$ is consistent with results of specific-heat measurements.

I. INTRODUCTION

The shape of the coexistence curve for pure liquids and binary-fluid mixtures shows interesting behavior both in diameter and density or concentration difference. It has been found in model calculations¹⁻³ as well as on the basis of thermodynamic arguments^{4,5} that the slope of the diameter of a coexistence curve diverges as the critical temperature is approached. Recent analysis indicates that, in order to explain the coexistence curve data,^{7,8} corrections to simple scaling as proposed by Wegner⁶ are necessary. A deviation from the rectilinear diameter has been observed for binary-fluid systems, carbon disulfide-nitromethane⁹ and polystyrene-cyclohexane.¹⁰ The data of the concentration difference for the system carbon disulfide-nitromethane were well explained by an extended scaling expression due to the Wegner expansion.⁶ In addition, measurements on binary-fluid mixtures^{7,9,11,12} yielded a critical exponent β consistent with renormalization-group calculations.¹³⁻¹⁶ For pure fluids, an anomaly in the diameter near the critical point has been observed in an experiment by Weiner, Langley, and Ford on SF₆.¹⁷ Ley-Koo and Green⁸ analyzed their data on SF₆ in terms of the density difference and the diameter and found that the data could be well represented by the renormalization-group expressions with reasonable values of the exponents. Estler *et al.*¹⁸ analyzed the data on xenon by a simple scaling form with a correction term and obtained the critical exponent β close to the theoretical value. Hocken and Moldover¹⁹ showed that the exponent β obtained for fluids Xe, SF₆, and CO₂ very near their critical points agrees

with theoretical values for the Ising model. A comparison of experimental results between pure fluids and binary-fluid mixtures shows that, by means of simple scaling, larger values of β are observed for pure fluids.²⁰⁻²³ Thus the asymptotic range of simple scaling for binary-fluid mixtures appears to be larger than that for pure liquids.

For polymer solutions it has been known theoretically and experimentally that the shape of the coexistence curve becomes more asymmetric with increasing molecular weight of polymer.²⁴ A highly asymmetric shape of the coexistence curve results in a clear deviation from the law of the rectilinear diameter¹⁰ and suggests a deviation from the simple scaling form for high-molecular-weight polymers. A relationship between a molecular structure and a temperature range of the simple scaling form can be studied with polymer solutions. It would be very interesting to learn whether or not polymer solutions belong to the same universality class as the Ising model. For these reasons we have made coexistence curve measurements on the system polystyrene-cyclohexane using a high-molecular-weight polystyrene sample.

II. EXPERIMENTAL

Polystyrene was prepared by bulk polymerization at 60°C in the presence of α, α -azobisisobutyronitrile for 120 h. The polystyrene was fractionated into 21 fractions in cyclohexane by the fractional solution technique.²⁵ In this investigation, we used a middle-fraction polystyrene with $M_w = 1.56 \times 10^6$. The molecular weight distribution of the sample was inferred as narrow as

$M_w/M_n < 1.03$ from the theory of molecular weight fractionation,^{26,27} where M_w and M_n are the weight- and number-average molecular weight, respectively. The unperturbed mean-square radius of gyration of the polymer obtained by light-scattering measurements also indicated a very narrow molecular weight distribution. Reagent grade cyclohexane was dried over neutral alumina, followed by passing it through a column of silica gel and then fractionally distilled twice under dry nitrogen. Preparation of solutions was performed in a glove box under dry nitrogen. We paid particular attention to avoid moisture in the air.

A detailed description of the apparatus and experimental procedures has been reported elsewhere.¹⁰ The concentration of each of the two coexisting phases was determined by measuring the refractive index difference between the solution and pure cyclohexane. The difference $X^+ - X^-$ and the diameter $\frac{1}{2}(X^+ + X^-)$ were determined with a precision of $\pm 0.02\%$ and 0.01% in the volume fraction, respectively. Our differential cell was set in a thermostated water bath whose temperature could be controlled to within ± 1 mK over a 24-h period. The instrument could also measure concentration as a function of height. Thus, we could ascertain the attainment of an equilibrium state by observing a constant concentration independent of height in each phase. For $T_c - T < 0.01^\circ\text{C}$, we could not measure the coexistence curve because equilibrium could not be achieved within 24 h. In the temperature range of $T_c - T > 0.01^\circ\text{C}$ no concentration gradient caused by gravity could be observed. In the course of the coexistence curve measurements, a slight decrease of the critical temperature was observed. By measuring the molecular weight after the coexistence curve measurements, this decrease was found to be caused by polymer degradation. However, the degradation could be suppressed by adding a small amount (about 0.02% in weight of the solution) of *N*-phenyl-2-naphthylamine to the solution. Such a small amount of impurity did not change the critical temperature and would not affect the shape of the coexistence curve.^{20,21,28,29}

III. RESULTS AND DISCUSSION

The coexistence curves were determined for two experimental runs A and B with overall concentrations of 0.0321 and 0.0324 in the volume fraction of polystyrene, respectively. In each experimental run, the concentrations of the two coexisting phases were measured at 20 temperatures over a temperature range of $0.01 < T_c - T < 11^\circ\text{C}$. The critical temperature was determined to be $30.50 \pm 0.01^\circ\text{C}$. The coexistence curve data

TABLE I. Coexistence curve data for polystyrene-cyclohexane system for overall concentrations X_0 . Concentrations X^+ , X^- , and X_0 are expressed in the volume fraction of polystyrene.

$X_0 = 0.0321$			$X_0 = 0.0324$		
$T_c - T$	X^+	X^-	$T_c - T$	X^+	X^-
0.015	0.0412	0.0229	0.014	0.0413	0.0234
0.022	0.0426	0.0218	0.023	0.0432	0.0217
0.029	0.0439	0.0210	0.032	0.0443	0.0209
0.038	0.0452	0.0203	0.042	0.0454	0.0199
0.048	0.0460	0.0195	0.065	0.0481	0.0181
0.060	0.0475	0.0184	0.082	0.0498	0.0172
0.088	0.0499	0.0167	0.100	0.0513	0.0164
0.142	0.0539	0.0146	0.125	0.0532	0.0155
0.209	0.0581	0.0127	0.182	0.0566	0.0134
0.280	0.0616	0.0114	0.256	0.0609	0.0121
0.402	0.0673	0.0092	0.390	0.0670	0.0094
0.550	0.0733	0.0078	0.530	0.0730	0.0074
0.750	0.0796	0.0065	0.724	0.0794	0.0062
0.995	0.0881	0.0052	0.990	0.0874	0.0047
1.382	0.0986	0.0041	1.350	0.0972	0.0032
1.976	0.1131	0.0022	1.883	0.1103	0.0019
2.983	0.1360	0.0018	3.010	0.1366	0.0015
4.476	0.1650	0.0012	4.493	0.1652	0.0011
7.00	0.2096	0.0009	6.76	0.2083	0.0009
11.04	0.2721	0.0009	10.78	0.2690	0.0009

are given in Table I. Figure 1 shows the coexistence curve and the diameter for run A using a plot of $T_c - T$ versus the volume fraction X of polystyrene. The behavior of X^+ and X^- is quite different and the diameter has a prominent curvature.

A. Difference of coexisting concentration

In Fig. 2 curve (a) represents the coexistence curve for run A given by a log-log plot of $X^+ - X^-$ versus $\epsilon (= (T_c - T)/T_c)$. This plot appears to exhibit a straight-line behavior at asymptotically small values of ϵ and shows a strong curvature at

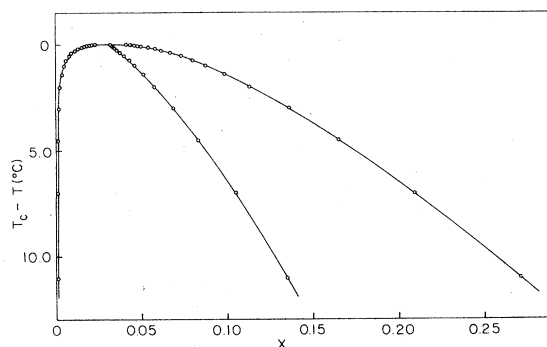


FIG. 1. Coexistence curve and diameter of polystyrene-cyclohexane with an overall concentration of 0.0321 (run A). X is the volume fraction of polystyrene.

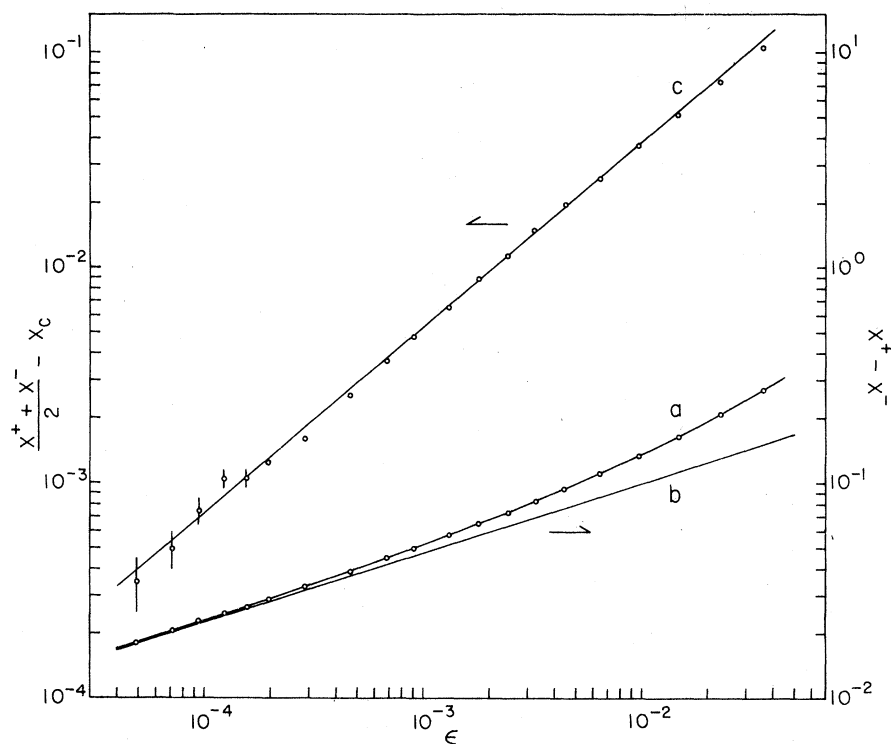


FIG. 2. Log-log plots of concentration difference $X^+ - X^-$ and diameter $\frac{1}{2}(X^+ + X^-) - X_c$ vs reduced temperature $\epsilon = (T_c - T)/T_c$ for run A. The curve (a) and the straight line (c) represent a least-squares fit to the data. The straight line (b) represents the simple scaling form $X^+ - X^- = 0.436\epsilon^{0.322}$.

larger values of ϵ . We have analyzed the difference $X^+ - X^-$ by simple scaling with correction terms according to the Wegner expansion.⁶ Then the difference is fitted to the form

$$X^+ - X^- = B\epsilon^\beta + B_1\epsilon^{\beta+\Delta} + B_2\epsilon^{\beta+2\Delta} \dots, \quad (1)$$

where Δ is fixed at 0.50.^{14,16} In the data analysis for run B we have omitted one of the outermost points and 19 points were used. Analysis by simple scaling with one correction term exhibited

large systematic deviation, but the results are shown in Table II(a). The value of β for this analysis is very small compared with recent measurements on binary-fluid mixtures^{7,9,11,12} and pure fluids.^{8,19} Then we tested simple scaling with two correction terms using a four-parameter least-squares fit. The results are given in Table II(b). The residuals from the fit are shown in Fig. 3(a). Systematic deviation is not observed over the entire range. Since the present study is

TABLE II. Results of an analysis of concentration difference.

(a) $X^+ - X^- = B\epsilon^\beta + B_1\epsilon^{\beta+0.50}$				
	β	B	B_1	
Run A	0.281 ± 0.010	0.293 ± 0.025	2.06 ± 0.023	
Run B	0.281 ± 0.013	0.293 ± 0.031	2.06 ± 0.029	
(b) $X^+ - X^- = B\epsilon^\beta + B_1\epsilon^{\beta+0.50} + B_2\epsilon^{\beta+1.00}$				
	β	B	B_1	B_2
Run A	0.322 ± 0.004	0.436 ± 0.016	1.35 ± 0.08	2.64 ± 0.27
Run B	0.334 ± 0.005	0.491 ± 0.022	1.02 ± 0.12	3.81 ± 0.42
(c) $X^+ - X^- = B\epsilon^\beta + B'\epsilon^{\beta'}$				
	β	B	β'	B'
Run A	0.333 ± 0.004	0.490 ± 0.016	1.01 ± 0.02	3.06 ± 0.14
Run B	0.343 ± 0.005	0.541 ± 0.021	1.09 ± 0.04	3.70 ± 0.30

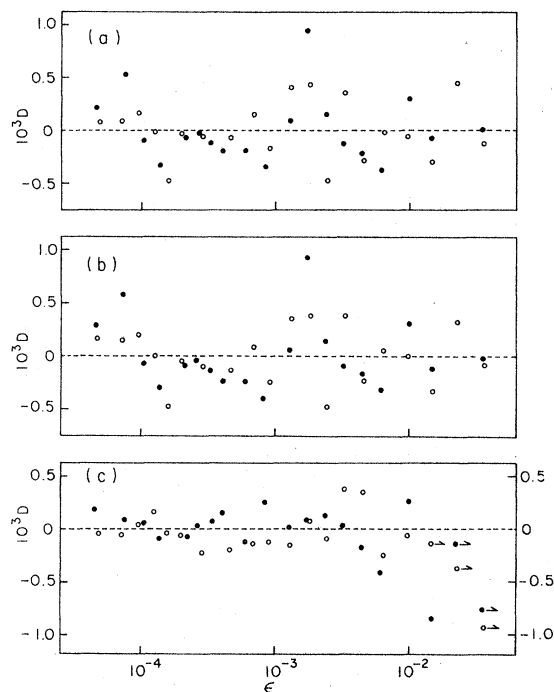


FIG. 3. Residuals of the measurements for polystyrene-cyclohexane with overall concentrations of 0.0321 (run A) \circ , and 0.0324 (run B) \bullet . (a) $D = (X^+ - X^-) - B\epsilon^\beta - B_1\epsilon^{\beta+0.50} - B_2\epsilon^{\beta+1.00}$. (b) $D = (X^+ - X^-) - B\epsilon^\beta - B'\epsilon^{\beta'}$. (c) $D = \frac{1}{2}(X^+ + X^-) - X_c - A\epsilon^\mu$.

not relevant to an accurate estimation of β for lack of data points near T_c , a small disagreement in β for runs A and B is not significant. Therefore, we recommend the average value of $\beta = 0.327 \pm 0.004$ for runs A and B. This value of β is in good agreement with recent experimental values for binary-liquid mixtures and pure fluids and recent renormalization-group calculations for the Ising model.¹³⁻¹⁶ The straight line (b) in Fig. 2, which is described by $X^+ - X^- = B\epsilon^\beta$ with the values of β and B listed in Table II(b), shows that the simple scaling form is valid only in the vicinity of the critical temperature. From the data points in the range of $5 \times 10^{-5} < \epsilon < 5 \times 10^{-4}$ in Fig. 2, we could not observe the effect of the correction terms on account of the scattering of data points. However, an apparent $\beta = d \ln(X^+ - X^-) / d \ln \epsilon$ is calculated as 0.338 and 0.357 at $\epsilon = 5 \times 10^{-5}$ and 5×10^{-4} , respectively. In a previous study,¹⁰ we measured the coexistence curve for the system polystyrene-cyclohexane with molecular weight $M_w = 20 \times 10^4$ over a temperature range of $10^{-5} < \epsilon < 6.7 \times 10^{-3}$. For this system we obtained $\beta = 0.348 \pm 0.003$ and $B = 0.97 \pm 0.01$ by assuming the simple scaling form, because, by visual inspection, a straight line in a plot of $\log_{10}(X^+ - X^-)$ versus $\log_{10}\epsilon$ adequately represented all experi-

mental data over the temperature range ($10^{-5} < \epsilon < 6.7 \times 10^{-3}$). We tried to reanalyze the data for a sample from our previous study with an overall concentration of polystyrene of 0.0688 by simple scaling with one correction term and obtained $\beta = 0.340 \pm 0.005$, $B = 0.896 \pm 0.037$ and $B_1 = 0.39 \pm 0.21$. The value of β by this analysis is close to the present one for $M_w = 1.56 \times 10^6$ and the exponent β for the system polystyrene-cyclohexane appears to be independent of molecular weight. The comparison of the present and the previous study indicates that the ratio of B_1/B becomes large with increasing molecular weight. For high-molecular-weight polystyrene samples the contribution from correction terms will become very large. This means that the temperature range of the simple scaling form depends on molecular weight.

For an analysis of the coexistence curve data, the Wegner expansion⁶ has been applied to a few systems. Greer used the Wegner expansion to the data on the system isobutyric acid-water,⁷ but she obtained no improvement in the fit when the concentration is expressed in volume fraction. It should be mentioned, however, that this data is restricted to be rather near the critical temperature. Greer⁷ also applied the Wegner expansion to the data in volume fraction for the system carbon disulfide-nitromethane⁹ over a wide range of temperatures and showed that simple scaling with two correction terms provides a good fit to the data with a β value in agreement with the Ising model. Ley-Koo and Green⁸ analyzed the data on pure fluid SF_6 (Ref. 17) by Eq. (1) with two correction terms and Δ as an unknown parameter and obtained $\beta = 0.327 \pm 0.001$ and $\Delta = 0.49 \pm 0.04$. The analysis was restricted to the temperature range of $0 < \epsilon < 0.019$ and the deviation was systematic when this analysis was extended to the temperature range of $0 < \epsilon < 0.055$. They showed that the data in the range of $0.019 < \epsilon < 0.055$ obeys an equation of the Van der Waals form. The above data analyses suggest that the Wegner expansion is valid over a larger temperature range for binary-liquid mixtures than for pure fluids. The application of the Wegner expansion to the present system appears to be legitimate because of the reasonable value of β and the small residuals of fit. When we observe the largely curved line (a) in Fig. 2, it seems rather surprising that the data for the present system can be fitted by simple scaling with only two correction terms. It should be noted that for the present system of high-molecular-weight polystyrene the ratio B_1/B is about six times those for the systems carbon disulfide-nitromethane and SF_6 , and B_2 is positive in contrast to those systems.

We also tried to fit the difference $X^+ - X^-$ to the form

$$X^+ - X^- = B\epsilon^\beta + B'\epsilon^{\beta'} \quad (2)$$

The coefficients and exponents in Eq. (2) were determined by a four-parameter least-squares fit and are given in Table II(c). The value of β for this analysis is a little larger than that for simple scaling with two correction terms in Eq. (1). The residuals from this fit given in Fig. 3(b) have the similar behavior as that of Fig. 3(a) and do not show a systematic deviation. The value of β' in Table II(c) may be compared with the theoretical prediction given by Swift and Grover³⁰ but is about twice as large as the current estimates.^{14,16} Different results are reported on the use of Eq. (2) for an analysis of data on xenon. Estler *et al.*¹⁸ fitted their data for $10^{-5} < \epsilon < 5 \times 10^{-2}$ to Eq. (2) with $\beta = 0.332 \pm 0.001$ and $\beta' = 0.61 \pm 0.02$, while in the data analysis by Garland and Thoen²³ the inclusion of this correction term did not change the high value of β . A large deviation from the simple scaling form has been observed for the sodium-ammonia system,³¹ for which the apparent β undergoes a rather abrupt change from 0.50 to 0.34 near $T_c - T = 1.8^\circ\text{C}$. This behavior of the coexistence curve seems to be incompatible with the functional form of Eqs. (1) and (2).

B. Diameter

Recent theories¹⁻⁵ have predicted a deviation from the law of the rectilinear diameter and a leading behavior of the diameter is given by

$$(X^+ - X^-)/2 - X_c = A\epsilon^\mu, \quad (3)$$

where $\mu = 1 - \alpha$. The value of μ could not be determined from the data near the critical temperature, because the diameter $\frac{1}{2}(X^+ - X^-) - X_c$ is very small and affected by a choice of the critical concentration X_c . Therefore, we determined the value of X_c in such a way that the exponent μ has a minimum dependence on the range of ϵ . This was done by repeating the analysis for small

changes in X_c and by varying the range of ϵ . In this analysis the value of X_c , which gives a minimum dependence of μ on the range of ϵ , was found to correspond to the value of X_c , which gives a minimum in the standard deviation. Thus, we obtained $X_c = 0.0317$ for run A, $X_c = 0.0318$ for run B and the results are listed in Table III. The resultant deviation plot is shown in Fig. 3(c) for $\epsilon < 10^{-2}$. No systematic deviation is observed except for six points at $\epsilon > 10^{-2}$. However, these six points which show relatively large deviation in the diameter behave normally in the difference $X^+ - X^-$ as shown in Fig. 3(a). We attribute the deviation of those six points at $\epsilon > 10^{-2}$ in Fig. 3(c) as due partially to the effect of correction terms for simple scaling. For $\epsilon < 10^{-2}$ the diameter can be fitted to a simple scaling form. The weighted average for the three ranges of $\epsilon < 10^{-3}$, 3×10^{-3} , and 10^{-2} give $\mu = 0.860 \pm 0.006$, $A = 1.98 \pm 0.06$ for run A and $\mu = 0.859 \pm 0.006$ and $A = 1.95 \pm 0.06$ for run B. The critical exponent $\alpha = 0.140 \pm 0.006$ deduced from the observed value of μ is compatible with the result of specific-heat measurements on xenon³² and CO_2 .³³ In Fig. 2, $\log_{10}[\frac{1}{2}(X^+ + X^-) - X_c]$ is plotted against $\log_{10}\epsilon$ for data of run A. The straight line c is described with the values of $\mu = 0.860$ and $A = 1.98$.

In our previous study we obtained $\mu = 0.90 \pm 0.03$ and $A = 2.40 \pm 0.34$. The agreement confirms the validity of Eq. (3) even for high-molecular-weight polystyrene ($M_w = 1.56 \times 10^6$) in cyclohexane provided that $\epsilon < 10^{-2}$. The dependence of A on molecular weight should be seen through the ratio A/B , values of which are 2.5 for $M_w = 20 \times 10^4$ and 4.0 for $M_w = 156 \times 10^4$. The large ratio of A/B denotes a very asymmetric coexistence curve as shown in Fig. 1. For ordinary binary-liquid mixtures this A/B ratio is relatively small and precise measurements of the diameter are very difficult.³⁴ The law of rectilinear diameter is not satisfied in the present system over the entire temperature range of our measurements. Deviation from the law of rectilinear diameter has been observed in two systems, a fluid (SF_6) (Ref. 17) and a

TABLE III. Range variation analysis of diameter by $\frac{1}{2}(X^+ + X^-) - X_c = A\epsilon^\mu$.

Range		$\epsilon < 10^{-3}$	$\epsilon < 3 \times 10^{-3}$	$\epsilon < 10^{-2}$	$\epsilon < 4 \times 10^{-2}$
No. points		10	13	17	20
Run A	μ	0.866 ± 0.026	0.879 ± 0.012	0.855 ± 0.006	0.812 ± 0.005
	A	2.02 ± 0.39	2.23 ± 0.16	1.94 ± 0.06	1.56 ± 0.03
Run B	μ	0.870 ± 0.034	0.854 ± 0.012	0.860 ± 0.006	0.822 ± 0.007
	A	2.17 ± 0.56	1.90 ± 0.15	1.95 ± 0.06	1.62 ± 0.05

binary-liquid mixture (carbon disulfide-nitromethane).⁹ However, in both of those systems the anomaly occurs near T_c and the law of rectilinear diameter is obeyed far away from T_c . Ley-Koo and Green⁸ analyzed the data on SF_6 based on the Wegner expansion. They found that the simple scaling with $\mu = 0.850 \pm 0.056$ fits the data only near the critical temperature of $\epsilon < 8.0 \times 10^{-4}$ and the data in the range of $2 \times 10^{-2} < \epsilon < 5.5 \times 10^{-2}$ yields a rectilinear diameter. By comparing their analysis with the present study, we have shown that the range of simple scaling for the diameter is larger for binary-liquid mixtures than that for pure fluids.

In summary, the critical exponent β , when properly evaluated using extended scaling, has a universal value for pure fluids and binary-fluid mixtures including polymer solutions. Furthermore, the value is in excellent agreement with that presently calculated using the Ising model. For the polystyrene-cyclohexane system, the

temperature range over which the simple scaling form remains valid depends upon the polymer molecular weight. If the two components differ more in molecular size, the coexistence curve tends to become more asymmetric. Thus the range of simple scaling for the diameter tends to be larger for binary-fluid mixtures than that for pure fluids. However, in the case of polymer systems, we can vary the polymer molecular size sufficiently to produce a very asymmetric coexistence curve where extended scaling becomes essential even when ϵ is small.

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¹B. Widom and J. S. Rowlinson, *J. Chem. Phys.* **52**, 1670 (1970).

²N. D. Mermin, *Phys. Rev. Lett.* **26**, 169 (1971); **26**, 957 (1971).

³P. C. Hemmer and G. Stell, *Phys. Rev. Lett.* **24**, 1284 (1970); *J. Chem. Phys.* **56**, 4274 (1972).

⁴M. S. Green, M. J. Cooper, and J. M. H. Levelt Sengers, *Phys. Rev. Lett.* **26**, 492 (1971).

⁵N. D. Mermin and J. J. Rehr, *Phys. Rev. Lett.* **26**, 1155 (1971).

⁶F. J. Wegner, *Phys. Rev. B* **5**, 4529 (1972).

⁷S. C. Greer, *Phys. Rev. A* **14**, 1770 (1976).

⁸M. Ley-Koo and M. S. Green, *Phys. Rev. A* **16**, 2483 (1977).

⁹E. S. R. Gopal, R. Ramachandra, P. Chandra Sekhar, K. Govindarajan, and S. V. Subramanyam, *Phys. Rev. Lett.* **32**, 284 (1974).

¹⁰M. Nakata, N. Kuwahara, and M. Kaneko, *J. Chem. Phys.* **62**, 4278 (1975).

¹¹D. T. Jacobs, D. J. Anthony, R. C. Mockler, and W. J. O'Sullivan, *Chem. Phys.* **20**, 218 (1977).

¹²D. A. Balzarini, *Can. J. Phys.* **52**, 499 (1974).

¹³L. P. Kadanoff, A. Houghton, and M. C. Yalabik, *J. Stat. Phys.* **14**, 171 (1976).

¹⁴G. A. Baker, Jr., B. N. Nickel, M. S. Green, and D. I. Meiron, *Phys. Rev. Lett.* **36**, 1351 (1976).

¹⁵G. R. Golner and E. R. Riedel, *Phys. Lett. A* **58**, 11 (1976).

¹⁶J. C. Le Guillou and J. Zimm-Justin, *Phys. Rev. Lett.* **39**, 95 (1977).

¹⁷J. Weiner, K. H. Langley, and N. C. Ford, Jr., *Phys. Rev. Lett.* **32**, 879 (1974).

¹⁸W. T. Estler, R. Hocken, T. Charlton, and L. R. Wilcox, *Phys. Rev. A* **12**, 2118 (1975).

¹⁹R. Hocken and M. R. Moldover, *Phys. Rev. Lett.* **37**, 29 (1976).

²⁰J. M. H. Levelt Sengers, J. Straub, and M. Vincentini-Missoni, *J. Chem. Phys.* **54**, 5034 (1971).

²¹J. M. H. Levelt Senger, *Experimental Thermodynamics of Non-reacting Fluids* (Butterworths, London, 1975), Vol. II, p. 657.

²²J. M. H. Levelt Sengers, W. L. Greer, and J. V. Sengers, *J. Phys. Chem. Ref. Data* **5**, 1 (1976).

²³C. W. Garland and J. Thoen, *Phys. Rev. A* **13**, 1601 (1976).

²⁴H. Tompa, *Polymer Solutions* (Butterworths, London, 1956).

²⁵N. Kuwahara, M. Nakata, and M. Kaneko, *Polymer* **14**, 415 (1973).

²⁶K. Kamide, Y. Miyazaki, and T. Abe, *Makromol. Chem.* **177**, 485 (1976).

²⁷K. Kamide and Y. Miyazaki, *Makromol. Chem.* **176**, 1029 (1975).

²⁸C. S. Bak and W. I. Goldburg, *Phys. Rev. Lett.* **23**, 1218 (1969).

²⁹M. E. Fisher and P. E. Scesney, *Phys. Rev. A* **2**, 825 (1970).

³⁰J. Swift and M. K. Grover, *Phys. Rev. A* **9**, 2579 (1974).

³¹P. Chieux and M. J. Sienko, *J. Chem. Phys.* **53**, 566 (1970).

³²C. Edwards, J. A. Lipa, and M. J. Buckingham, *Phys. Rev. Lett.* **20**, 496 (1968).

³³J. A. Lipa, C. Edwards, and M. J. Buckingham, *Phys. Rev. Lett.* **25**, 1086 (1970).

³⁴A. Stein and G. F. Allen, *J. Phys. Chem. Ref. Data* **2**, 443 (1973).