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Critical behavior of polystyrene-cyclohexane: Heat capacity and mass density

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At temperatures between 7.5 °C and 20 °C as well as 26 °C and 40 °C we have recorded the densities and specific heat at constant pressure for critical mixtures of polystyrene in cyclohexane. The degrees of polymerization were $N=288$ (critical temperature $T_c=9.77$ °C) and $N=6242$ ($T_c=27.56$ °C), respectively. In the two-phase regime a series of reproducible events exists in the specific-heat traces, indicating the existence of nonequilibrium intermediate states as likely resulting from an oscillatory instability of droplet formation. In the one-phase region the critical contribution to the heat capacity follows power law with critical exponent $\alpha=0.11$ compatible with Ising-like criticality. At larger N, however, the critical amplitude of the heat capacity is noticeably smaller than at lower degree of polymerization. This finding may be taken as an indication of different effects from competing mesoscale lengths: the radius of gyration of the polymer and the fluctuation correlation length of the mixture. The density traces reveal marginal deviations from simple linear temperature dependencies. If these deviations are analyzed in terms of critical contributions, different signs in the amplitude result, in conformity with the signs in the pressure dependence of the critical temperature. The absolute values of the amplitudes, however, are substantially larger than predicted from the critical amplitudes of the heat capacities.

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I. INTRODUCTION

Asymptotically close to the critical demixing point polymer solutions, like "simple" low-molecular-weight fluids, belong to the three-dimensional Ising class: the spatial correlation length ξ of order parameter fluctuations has grown so large that it exceeds even the mesoscopic structures of the polymer molecules [1–3]. In correspondence with simple fluids the individual characteristics of polymer solutions, therefore, are largely masked by the fluctuations, so that universal near-critical behavior results. Unfortunately, the range of true asymptotic critical behavior is very small and often hardly accessible to measurements. For most binary fluids, already marginally away from the critical temperature, a trend from Ising-class critical behavior toward mean-field critical behavior becomes obvious. This crossover is especially important in polymer systems [4]. Upon departure from the critical temperature T_c, the fluctuation correlation length of the Ising model decreases according to a power law,

$$\xi = \xi_0 \varepsilon^{-\tilde{\nu}}. \qquad (1)$$

Here,

$$\varepsilon = |T - T_c|/T_c \qquad (2)$$

denotes the reduced temperature and $\tilde{\nu}$ (=0.63) is a critical exponent. Hence, at a temperature T the fluctuation correlation length becomes comparable to the length scale of the mesoscopic structure of the polymer system: ξ competes with the size of the polymer molecules. Normally the radius of gyration R_g of the coiled polymer molecules is considered as a natural size parameter. Competition between ξ and R_g changes the phase separation behavior dramatically. In the crossover region, therefore, significant differences between critical phenomena in high-molecular-weight polymer systems and low-weight fluids emerge.

The radius of gyration is a function of the degree of polymerization N of the molecules. N is thus a parameter that controls the phase behavior of polymer solutions. With increasing N the critical concentration c_c decreases to approach zero, the critical temperature T_c approaches the theta temperature for polymer solutions with large N, and the range of universal Ising-class critical behavior shrinks. Polymer solutions thus allow investigations into the competition of two characteristic mesoscale lengths by tuning the radius of gyration via N and by varying the fluctuation correlation length via T [2,3]. Divergence of ξ and R_g at the theta point and the coupling of both order parameters lead to mean-field-like tricriticality [5].

The possibility to investigate the crossover from asymptotic Ising-class criticality to mean-field tricriticality has inspired considerable interest, both in theory [6–10] and experiment, in the properties of polymer solutions near their consolute points. However, since the pioneering work by Debye and his colleagues [11–14], most experimental studies were by static and dynamic light scattering [15–25]. Small-angle neutron scattering [26] as well as shear viscosity [27] measurements have been performed and heat capacities have been recorded to obtain phase diagrams [28,29]. Surprisingly, however, no determinations of the exponent α in the weak specific-heat divergence near the critical point of polymer solutions have been reported so far. This deficiency has initiated heat-capacity measurements on polystyrene (PS)-cyclohexane (CH) mixtures near their consolute point, using two significantly different molecular weights M_w of the polymer, in order to look for an influence of the degree of polymerization. A careful analysis of the specific heat C_p is ad-

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ditionally stimulated by the relation of its critical amplitude A^+ to the amplitude ξ_0 of the fluctuation correlation length. Using ξ_0 values from the literature A^+ data permits us to inspect the two-scale-factor universality relation [30–32],

$$\xi_0^3 A^+ = k_B X, \tag{3}$$

for any dependence on N. In Eq. (3) k_B is the Boltzmann constant and $X=0.0197$ for low-molecular-weight fluids [30,33]. Furthermore, the temperature dependence of the heat capacity plays a significant role in the description of ultrasonic attenuation spectra of critically demixing liquids [34].

Asymptotically close to the critical demixing point of binary fluids the singular part in the thermal expansion coefficient at constant pressure and constant composition is predicted as weak divergence with critical exponent α of the specific-heat anomaly [1,35,36]. The density thus is expected to have a critical anomaly proportional to $\varepsilon^{(1-\alpha)}$. Since previous measurements did not reveal a critical anomaly in the density of polystyrene-cyclohexane mixtures with number average molar weight $M_w = 35\,800$ [37], we found it interesting to retry density measurements at elevated precision, including a sample of distinctly larger degree of polymerization N. We attempt to relate the amplitudes C^+ and A^+ of the critical terms in the density and specific heat, respectively, to the common relation [1,35,36]

$$C^+ = \frac{-\rho_c A^+}{\alpha(1-\alpha)} \frac{dT_c}{dp}, \tag{4}$$

which is an approximation [38,39]. In Eq. (4) $\rho_c = \rho(c_c, T_c)$ is the density of the mixture at the critical point and dT_c/dp is the slope in the pressure dependence of the critical temperature along the critical line.

II. EXPERIMENT

Samples of polystyrene ($[\text{-CH-C}_6\text{H}_5\text{-CH}_2\text{-}]_N$; ratio of weight-to-number-average molecular weights $\text{MW}/\text{MN} = 1.06$) with molar weights $M_w = 30\,000$ g/mol ($\hat{=} N = 288$) and $650\,000$ g/mol ($\hat{=} N = 6242$) have been purchased from Pressure Chemical Co. (Pittsburgh, PA, USA). The polymers will be named PS_{288} and PS_{6242} in the following. Cyclohexane ($\text{CH}, \text{C}_6\text{H}_{12}, \geq 99.9\%$) was obtained from Sigma-Aldrich (Taufkirchen, Germany). In order to avoid uptake of water from the air the chemicals and samples were always kept under dry nitrogen. Polymer solutions were prepared by weighing appropriate amounts of the constituents into suitable flasks. The critical mass fractions Y_c of the solutions were determined according to the equal-volume criterion ($Y_c = 0.186 \pm 0.001$, PS_{288}; $Y_c = 0.061 \pm 0.001$, PS_{6242}; Y is the mass fraction of polymer). The visually determined lower critical temperatures were $T_c = (282.92 \pm 0.02)$ K (PS_{288}) and $T_c = (300.70 \pm 0.02)$ K (PS_{6242}). These values fit well to data from our density measurements and also to such data from the literature (Fig. 1).

The specific heat at constant pressure, C_p, of the samples has been measured on a differential scanning calorimeter (MicroCal Inc., Northampton, MA). Measurements (sample volume of ≈ 0.5 cm^3) were run in a downscan mode without stirring and with the minimum available scan rate $dT/dt = 0.25$ K/h. In the PS-CH measurements the reference cell was filled with pure cyclohexane. To enable the calculation of absolute specific-heat values we also recorded C_p traces of CH against CH. The specific heat of cyclohexane was taken from the literature data which, for interpolation, may be represented by the following analytical forms:

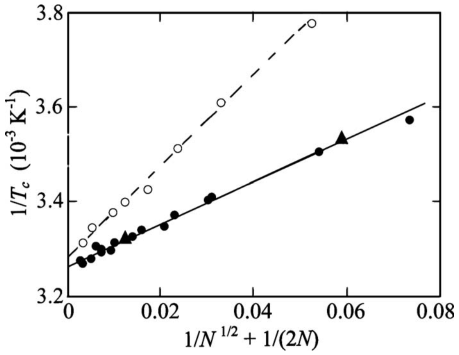

FIG. 1. Flory plot [40]: the reciprocal T_c^{-1} of critical temperature versus $N^{-1/2} + 1/(2N)$ for solutions of polystyrenes in cyclohexane (full symbols: ▲, this paper; ●, [3,13,14,17–19,24,27,37]) and in diethyl malonate (open symbols, Ref. [23]). Full and dashed lines are graphs of Eq. (7) with parameters given in the text.

$$C_p = 36.60 \ \text{J K}^{-1}\,\text{mol}^{-1} + 0.4006T \ \text{J K}^{-2}\,\text{mol}^{-1}, \tag{5}$$

at $278.15 \leq T \leq 298.15$ K [41], and

$$C_p = R\{9.368 + 1.526 \times 10^{-2} T \ \text{K}^{-1} - 3.635 \times 10^{-6} T^2 \ \text{K}^{-2} - 5.621 \times 10^7 T^{-3} \ \text{K}^3 + 23.77 \vartheta^2 e^{\vartheta}(e^{\vartheta} - 1)^{-2}\}, \tag{6}$$

at $T > 298.25$ K [42]. Here, $R = 8.3143$ J K^{-1} mol^{-1} is the universal gas constant and $\vartheta = 2000$ K/T.

Within a range of 10 K above T_c the densities ρ of the mixtures of critical composition have been measured using a high-precision vibrating tube densitometer with built-in reference oscillator and Peltier temperature control (Physica DMA 5000, Anton Paar, Graz, Austria). The temperature of the instrument (sample volume of ≈ 1 cm^3) has been controlled to within 0.001 K. The repeatability in the density measurements was 10^{-6}. Due to imperfect wetting of the vibrating tube the error in absolute density measurements may be larger ($\Delta\rho/\rho \leq 3 \times 10^{-6}$). The densitometer was calibrated against doubly distilled, ultrafiltered, and degassed water.

III. RESULTS AND DISCUSSION

A. Theta temperature

For the critical temperature of a binary solution containing a single polymer species Shultz and Flory derived the relation [40]

$$\frac{1}{T_c} = \frac{1}{T_\theta}\left[1 + \frac{1}{\psi}\left(\frac{1}{N^{1/2}} + \frac{1}{2N}\right)\right], \tag{7}$$

with theta temperature T_θ and with entropy contribution ψ to the thermodynamic interaction parameter. In Fig. 1 for solu-

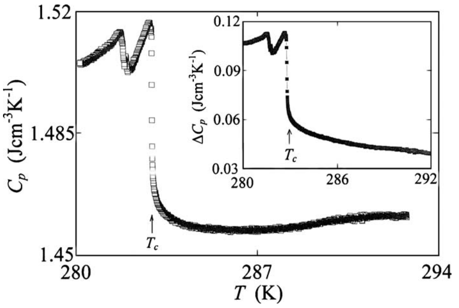

FIG. 2. Heat-capacity profiles for the PS_{288}-CH solution of critical composition. The inset shows the heat-capacity difference $\Delta C_p = C_p - C_{p,ref}$ between the sample and the reference cyclohexane as recorded by the differential scanning calorimeter. In the main part of the diagram the heat capacity $C_p = \Delta C_p + C_{p,ref}$ of the sample with $C_{p,ref}$ according to Eq. (5) is given.

tions of various polystyrenes in cyclohexane and also in diethyl malonate (DEM) inverse critical temperatures are displayed as a function of $N^{-1/2} + (2N)^{-1}$, which—for the large polymers under consideration—is very close to $N^{-1/2}$. For polystyrenes with molar weights between 25 000 and 13 200 000 the data follow the predictions of the Shultz-Flory relation. Extrapolated to infinite molar weight, the critical temperature data yield $T_\theta = 306.56$ K for PS in CH and $T_\theta = 304.69$ K for PS in DEM. The entropy part in the interaction parameter is about twice as large with the former ($\psi = 7.3 \times 10^{-4}$) as with the latter ($\psi = 3.4 \times 10^{-4}$) system.

B. Specific-heat anomaly

In the inset of Fig. 2 an original $\Delta C_p = C_p - C_{p,ref}$ scan of the PS_{288}-CH mixture is presented. The main part of the figure shows the total specific heat, with the heat capacity of the reference liquid according to Eq. (5) added to the experimental difference ΔC_p. Both traces display an increase when approaching the critical temperature from the one-phase region, thus indicating the weak heat-capacity anomaly. A series of events exists in the ΔC_p (and C_p) data at temperatures below T_c. This feature of the specific heat, which had already emerged in two-phase region of the ionic critical system ethylammonium nitrate–*n*-octanol [43] and likewise of the binary critical systems 2-butoxy ethanol–water [44] as well as 2,6-dimethylpyridine–water [45], is reproducible in repeated experiments. It exists also in the heat-capacity profiles of the PS_{6242}-CH mixture of critical composition. This interesting phenomenon of oscillatory phase separation has been modeled by an oscillatory instability of droplet formation driven by supersaturation [46,47]. The focus of this paper, however, is the one-phase region, where the heat capacity of binary critical systems is normally represented by a relation [48–50] that includes a correction-to-scaling term with Wegner exponent [51]. Since only insignificant corrections to scaling were found, the simpler relation

$$C_p = \frac{A^+}{\alpha} \varepsilon^{-\alpha} + E\varepsilon + B \tag{8}$$

has been used in the evaluation of data. The critical exponent of the heat capacity has been either treated as an adjustable parameter, with the critical temperature fixed at the visually determined T_c, or α has been fixed at its theoretical value of 0.11 [48–50] and T_c has been allowed to vary. As we do not fully understand the origin of the small hump in the C_p data of PS_{288} above 288 K (Fig. 2), we evaluated the data at $T < 288$ K only (Fig. 3). For both polystyrenes the results are compiled in Table I and the residuals $C_{p,exp} - C_{p,theor}$ are shown in Fig. 4. With both polystyrenes the residuals are small, and they do not reveal any systematic variations with reduced temperature, thus indicating that the specific heat is well represented by the simplified model.

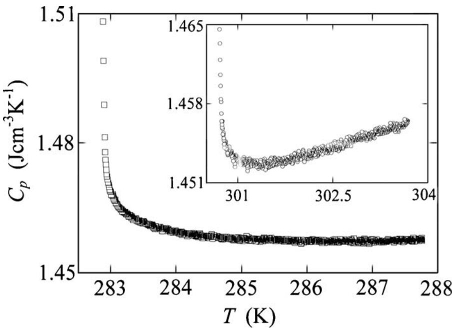

FIG. 3. Heat-capacity data in the one-phase region as used in the regression analysis. Main part: PS_{288}, $1.37 \times 10^{-5} \leq \varepsilon \leq 1.7 \times 10^{-2}$; inset: PS_{6242}, $2 \times 10^{-5} \leq \varepsilon \leq 9.8 \times 10^{-3}$.

The alternative treatment of the critical exponent and the critical temperature as adjustable quantities leads to only marginal variations in α and T_c and also in the other parameters. Quite remarkably, $\alpha = 0.11$ has been obtained with extremely small error from the runs in which the critical expo-

TABLE I. Parameters of the specific-heat relation [Eq. (8)] for critical mixtures of PS_{288} and PS_{6242} with CH. Errors are one standard deviation estimates as provided by the fitting procedure. The fits in which alternatively α or T_c has been fixed have equivalent chi squares.

N	T_c (K)	α	A^+/α (10^{-2} J cm^{-3} K^{-1})	E (J cm^{-3} K^{-1})	B (J cm^{-3} K^{-1})
288	282.916 ± 0.001	$\equiv 0.11$	1.91 ± 0.02	0.30 ± 0.01	1.42 ± 0.01
288	$\equiv 282.915$	0.1100 ± 0.0001	1.91 ± 0.02	0.30 ± 0.01	1.42 ± 0.01
6242	300.709 ± 0.001	$\equiv 0.11$	0.74 ± 0.01	0.77 ± 0.01	1.44 ± 0.01
6242	$\equiv 300.709$	0.1100 ± 0.0001	0.75 ± 0.01	0.77 ± 0.01	1.44 ± 0.01

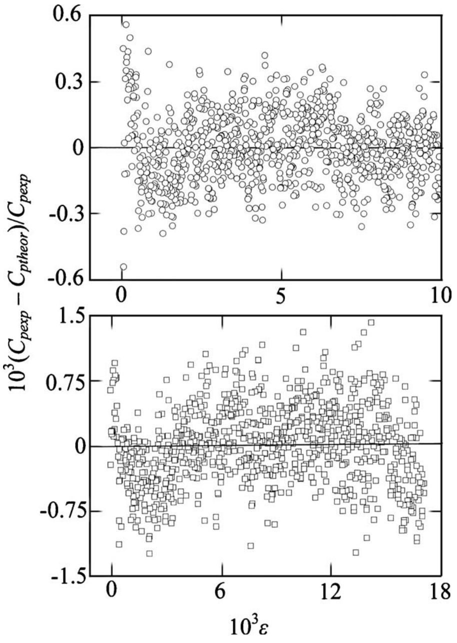

FIG. 4. Residuals $(C_{p,exp}-C_{p,theor})/C_{p,exp}$ for the PS_{6242} (top) and the PS_{288} (bottom) solutions of critical composition. Here, $C_{p,theor}$ denotes the heat capacity according to Eq. (8) with $\alpha \equiv 0.11$ and with the values of the other parameters as listed in Table I.

nent was an adjustable parameter. Hence, we conclude that the specific-heat critical exponent is independent of the polymer molecular weight.

As obvious from the data in Fig. 3, the temperature-dependent part in the background contribution of the specific heat is considerably larger with the PS_{6242}-CH mixture ($E=0.77\ \mathrm{J\ cm^{-3}\ K^{-1}}$) than with the PS_{288}-CH mixture ($E=0.3\ \mathrm{J\ cm^{-3}\ K^{-1}}$) of critical composition. We suppose the stronger temperature dependence in the background contribution to be due to the proximity to the theta temperature: $T_\theta - T_c = 5.85$ K with the PS_{6242} system and $=23.64$ K with the PS_{288} system. Close to the theta point, essentially a symmetrical tricritical point [5], the specific heat obviously increases. Both polymer solutions display also a significant difference in their amplitudes of the critical term. In the most favored sets of data ($\alpha \equiv 0.11$) the amplitude ratio $A^+(PS_{6242})/A^+(PS_{288})$ is as small as 0.39. In contrast to the smaller polymer for which $\xi > R_g$ in the complete range of measurements, ξ exceeds R_g of the larger polymer only close to T_c. Interpolation and extrapolation of radius-of-gyration data by Kostko *et al.* [25] yield $R_g(PS_{288})=4.7$ nm and $R_g(PS_{6242})=21$ nm from which $\xi > R_g(PS_{288})$ at $T-T_c < 12.6$ K and $\xi > R_g(PS_{6242})$ at $T-T_c < 1.5$ K follows. Hence, the small $A^+(PS_{6242})$ value might reflect a competition between both mesoscale lengths: the fluctuation correlation length ξ and the radius of gyration R_g of the polymer. However, no clear-cut conclusions on structural effects can be drawn presently from the amplitude ratio.

C. Two-scale-factor universality relation

It is interesting to compare the difference in the critical amplitude of the specific heat to the literature data for the amplitude ξ_0 [Eq. (1)] of the fluctuation correlation length, using the two-scale-factor universality relation [Eq. (3)]. In a range of different degrees of polymerization, Fig. 5 shows ξ_0 data from recent dynamic light-scattering experiments [3]. The experimental amplitudes nicely agree with the prediction of de Gennes to vary as [5,52]

$$\xi_0 \propto N^{(1-\tilde{\nu})/2}, \tag{9}$$

and are thus preferred to previous data (e.g., [11,13]). As also revealed in Fig. 5, the agreement of the ξ_0 values derived with the aid of Eq. (3) from the heat-capacity critical amplitudes is reasonable but not perfect. Since relation (9) holds for large degrees of polymerization, the deviation at $N=288$ is not surprising. With the PS_{6242}-CH solution of critical composition, however, compatibility with the two-scale-factor universality relation calls for even smaller critical amplitude A^+/α in C_p than derived from the experimental heat-capacity traces.

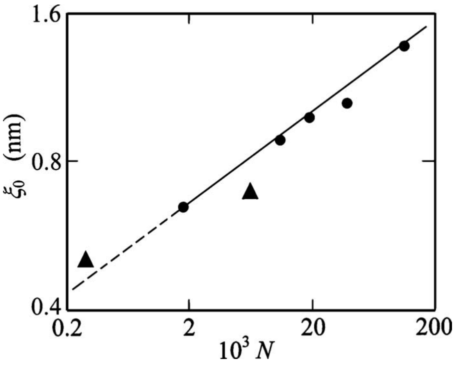

FIG. 5. Amplitude ξ_0 of the fluctuation correlation length versus degree of polymerization for solutions of polystyrene in cyclohexane: ●, data from dynamic light-scattering experiments [3]; ▲, data from application of the two-scale-factor universality relation to the critical amplitude in the specific heat of the PS_{288} and PS_{6242} samples. Due to the small uncertainty of the A^+ values (Table I) the uncertainty in the latter data is smaller than the symbols. The full line represents Eq. (9).

D. Density singularity

In the one-phase region the density of critically demixing binary liquids can be expressed in the same functional form [36,53] as the heat capacity. If again the insignificant correction-to-scaling term is neglected,

$$\rho = C^+\varepsilon^{1-\alpha} + G\varepsilon + \rho_c \tag{10}$$

follows with critical exponent $1-\alpha$ and with $\rho_c=\rho(T_c)$. As the critical term in the density of the PS-CH is very small, we have analyzed the experimental data using the theoretical value $\alpha=0.11$ for the specific-heat critical exponent and fixing the critical temperatures at the visually determined data ($T_c=282.915$ K, PS_{288}; $T_c=300.709$ K, PS_{6242}). The values of the other parameters of Eq. (10) are given in Table II. Without a doubt the absolute values $|C^+|$ of the critical amplitudes are small. However, systematic variations of the residuals $\rho_{exp}-\rho_{theor}$ on the omission of the critical term (Fig.

TABLE II. Parameters of the density relation [Eq. (10)] for critical mixtures of PS_{288} and PS_{6242} with CH. The critical exponent has been fixed at $\alpha=0.11$ and the critical temperatures have been fixed at their visually determined values. Errors are one standard deviation estimates as provided by the fitting procedure.

N	C^{+} (10^{-3} g cm^{-3})	G (10^{-3} g cm^{-3})	ρ_c (10^{-3} g cm^{-3})
288	$-(6.51\pm0.03)$	$-(245.2\pm0.4)$	830.139 ± 0.001
6242	1.37 ± 0.3	$-(284.1\pm0.1)$	785.084 ± 0.001

6) indicate a marginal critical anomaly in the density data.

A noticeable result of the evaluation of density data is the change of sign of the critical term when going from PS_{288} to PS_{6242} (Table II). This finding corresponds to the variation of the pressure dependence of the critical temperature with degree of polymerization. Experimental dT_c/dp data [54] can be represented by the simple relation

$$dT_c/dp = 1.64 \times 10^{-7}\ \text{K/Pa} - 5.38 \times 10^{-8}\ \text{K/Pa} \log N, \tag{11}$$

which yields $dT_c/dp=0.32\times10^{-7}$ K/Pa at $N=288$ and $dT_c/dp=-0.40\times10^{-7}$ K/Pa at $N=6242$. The latter value is in nice agreement with $dT_c/dp=-0.39\times10^{-7}$ K/Pa as measured at $N=5761$ ([55], $M_w=600\,000$). Using these dT_c/dp values and the A^{+}/α data from the evaluation of the heat-capacity profiles (Table I) $C^{+}=-5.5\times10^{-4}$ g/cm^3 ($N=288$) and $C^{+}=2.9\times10^{-4}$ g/cm^3 ($N=6242$) follow from Eq. (4). These values are about ten times smaller than the amplitudes obtained from the temperature-dependent densities (Table II). The reason for the discrepancy may be the fact that the heat capacity at constant volume, C_v, has been neglected relative to C_p when deriving Eq. (4). However, as pointed out by Anisimov *et al.* [56], C_v may also display a critical point anomaly proportional to $\varepsilon^{-\alpha}$. Another reason is the small critical contribution to the density of the polymer solutions which is hardly accessible even to modern high-resolution densitometers.

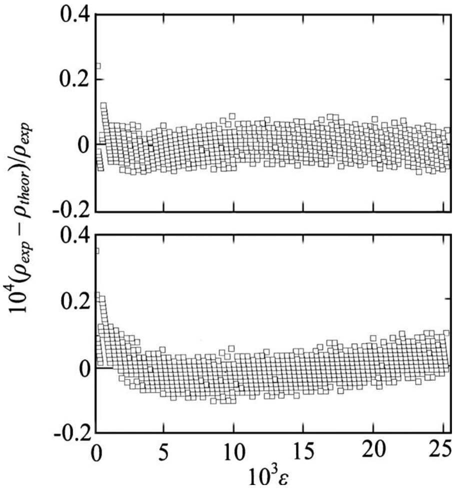

FIG. 6. Residuals $(\rho_{exp}-\rho_{theor})/\rho_{theor}$ for the representation of the PS_{288} data by Eq. (10) with critical term (top) and without critical term ($C^{+}=0$, bottom).

IV. CONCLUSIONS

In the one-phase region polystyrene-cyclohexane mixtures of critical composition show a weak critical anomaly in the specific heat at constant pressure. Whereas the critical exponent α is independent of the degree of polymerization N, small amplitude A^{+}/α of the critical term is significantly smaller at $N=6242$ than at $N=288$. We suggest the reduction in the critical amplitude, a reflection of interferences of two intrinsic length scales, the correlation length of concentration fluctuations, and the radius of gyration of the polymer molecules. Taking the two-scale-factor universality relation for granted, however, an even smaller A^{+}/α value follows for the $N=6242$ sample from the amplitude ξ_0 of the fluctuation correlation lengths, as determined in dynamic light-scattering experiments. At both degrees of polymerization the densities of the mixtures reveal marginal deviations from linear temperature dependences. The signs in the amplitude of the critical term correspond to the signs in the pressure dependence of the critical temperature, as predicted by theory. The absolute values of the critical amplitudes in the densities, however, are noticeably larger than those following from the critical amplitudes in the specific heat at constant pressure. The reason for this discrepancy is not clear presently. Likely the neglect of critical effects in the heat capacity at constant volume may have entailed an incomplete theoretical relation between the density and the specific heat at constant pressure.

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