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Scaled functions of osmotic compressibility and correlation length of polystyrene in diethyl malonate

K. Hamano, N. Kuwahara,* and M. Kaneko
Department of Polymer Science, Hokkaido University, Sapporo, Japan
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The angular distribution of scattered light intensity for polystyrene in diethyl malonate was measured along the isochores near the critical concentration. The zero-angle scattered intensity $I_{c,o}/T$ [i.e., $\lim_{k\to 0}(I_c/T)$ and is directly proportional to the isothermal osmotic compressibility χ_T] and the correlation length ξ were obtained as a function of temperature and composition. The scaled functions of the $I_{c,o}/T$ and ξ were examined as a function of the scaling parameter. The pseudospinodal generalization was found to be valid for even a macromolecular solution. In addition, some considerations concerning the reduced quantities of $I_{c,o}/T$ and ξ in terms of the scaling laws are reported.

I. INTRODUCTION

During the past years, measurements of the equilibrium properties in the critical region have been reported as functions of temperature and composition in both pure fluids and binary-fluid mixtures. More recently the anomalous shear viscosity near the critical point has been analyzed in terms of the scaling-law relation by Izumi and Miyake[1] and D'Arvigo *et al.*[2] The experimental situation has been extensively reviewed by Sengers and co-workers.[3] The phenomenological theory put forward by Widom[17] proved to be quite successful. Because of its simplicity and its successful predictions, it triggered further research and was applied to fluid systems by Green and co-workers.[4] The universality hypothesis exploited by Kadanoff[5] was reformulated by renormalization-group calculations by Wilson.[6]

The relative scattered intensity I_c due to concentration fluctuations within a critical binary mixture is approximated by the relation

$$I_c = A_0 T\chi_T D(k^2\xi^2)\,, \tag{1}$$

where χ_T is the isothermal osmotic compressibility, ξ the long-range correlation length, and $k = (4\pi n/\lambda_0)\sin\frac{1}{2}\theta$ with n, λ_0, and θ being the refractive index of the medium, the wavelength of light in vacuum, and the scattering angle, respectively. A_0 includes $(\partial n/\partial C)^2_{P,T}$ and λ_0^{-4} in which C denotes the concentration expressed in g/cm^3, and $D(k^2\xi^2)$ is the correlation scaling function given by[7]

$$1/D(k^2\xi^2) = 1 + \Sigma_2 k^2\xi^2 - \Sigma_4 k^4\xi^4\,. \tag{2}$$

Values of Σ_2 and Σ_4 are set to unity and zero in the Ornstein-Zernicke (OZ) theory.[7,8] χ_T and ξ along the critical isochore above the critical mixing temperature T_c can be written in terms of the critical-exponent concept:

$$\chi_T = \Gamma\epsilon^{-\gamma}\,, \tag{3}$$

$$\xi = \xi_0\epsilon^{-\nu}\,, \tag{4}$$

in which γ and ν are the critical exponents and ϵ is the reduced temperature $\epsilon = (T - T_c)/T_c$. The zero-angle scattered intensity $I_{c,0}/T$ [i.e., $\lim_{k\to 0}(I_c/T)$ and is directly proportional to χ_T] and the correlation length ξ along the noncritical isochore would diverge on the spinodal curve[9] and hence the extensions of Eqs. (3) and (4) for the noncritical isochore are simply written

$$(I_{c,0}/T) \propto \epsilon_{\mathrm{sp}}^{-\gamma}\,, \tag{3$'$}$$

$$\xi \propto \epsilon_{\mathrm{sp}}^{-\nu}\,, \tag{4$'$}$$

where ϵ_{sp} is the reduced temperature $\epsilon_{\mathrm{sp}} = (T - T_{\mathrm{sp}})/T_c$, with T_{sp} being the pseudospinodal temperature.

The purpose of this work is to attempt a general test of the homogeneity and scaling laws with χ_T and ξ for a macromolecular solution by light scattering experiments over a wide range of the temperature-composition diagram in the critical region. By recent experiments on the angular distribution of scattered light intensity, departure from the OZ theory has been observed in the critical region (i.e., $k\xi \gg 1$).[10,11] Oxtoby and Gelbart[12] have shown that an apparent deviation of the scaling correlation function from the OZ theory can be induced by double scattering. The deviation from the OZ theory may be explained by three different causes[13]: the concentration gradient,[14] double scattering, and genuine deviation from the OZ theory. The gravitational effect should be negligibly small for the system polystyrene-diethyl malonate with a small $1-\bar{v}\rho$ in which $\bar{v}$ denotes the partial specific volume of polystyrene and ρ the density of the mixture. Multiple-scattering effects could be well deduced by use of a capillary cell of 0.5-mm i.d.[15] We have measured the angular distribution of scattered light intensity by use of a 0.5-mm capillary cell in strongly opalescent regions and a 6-mm cell in weakly opalescent regions and thus covered over the range of $0.05_0 \leqslant \phi \leqslant 0.113_5$ and of $0.05 \lesssim k\xi \lesssim 10$, where ϕ is the volume fraction of polymer.

II. EXPERIMENTAL

Polystyrene ($M_w = 2.0\times 10^5$, $M_w/M_n < 1.02$ with M_w and M_n being the weight- and number-average molecular weight, respectively) in diethyl malonate was used. Sample preparation has been described in detail elsewhere.[15] The critical mixing point ($T_c = 10.67$ °C, $\phi_c = 0.083_7$) was established by phase-equilibrium measurements.[15] Capillary cells of 0.5-mm i.d. and cylindrical cells of 6-mm i.d. flame sealed under vacuum immediately after sample preparation were used for light scattering studies. The temperature of a silicone-oil thermostat for the sample cell was controlled to within 1 mK. The angular dependence of scattered intensity was measured by using a specially designed light scattering photometer with a He-Ne laser as a light source.[10] Apertures of 0.6 and 0.2 mm were placed close to the 6-mm cell and the 0.5-mm cell, respectively. The alignment of the photometer has been described in detail elsewhere.[10] Intensity measurements were carried out over the angular range of 25°–135° (21 different angles) along the isochore for eight samples of the 6-mm cell with different concentrations: 0.050_0, 0.064_7, 0.074_6, 0.083_7, 0.087_6, 0.092_4, 0.107_9, 0.113_5, and 25°–115° (15 different angles) along the isochore for six samples of the 0.5-mm cell with 0.073_2 ($\simeq 0.074_6$), 0.081_9, 0.083_0, 0.083_3 ($\simeq 0.083_7$), 0.086_7 ($\simeq 0.087_6$), 0.090_7 ($\simeq 0.092_4$). Intensity readings were corrected for scattering volume, attenuation, and background except for dust, reflection, multiple scattering, etc. The attenuation corrections for the 0.5-mm cell were done within the limit of 17% by means of turbidity measurements by a flat cell of 0.5-mm in optical path length.

III. RESULTS AND DISCUSSION

In order to obtain $(I_{c,0}/T)^{-1}$ and ξ we have analyzed our data by a two-parameter least-squares fit according to the expression Eq. (2).[7] The pseudospinodal temperature T_{sp} for the noncritical isochore was obtained by extrapolating $(I_{c,0}/T)^{-1}$ to (unrealized) states below the phase-separation temperature T_p. The pseudospinodal curve in the temperature-composition diagram is given in Fig. 1 with the coexistence curve. We find a value of 0.35 for the critical exponent β^{+}, which characterizes the shape of the pseudospinodal curve in the neighborhood of the critical mixing point, by a log-log plot of $|\phi-\phi_c|$ vs $(T_c - T_{sp})/T_c$ as shown in Fig. 2. Slopes in a log-log plot of $(I_{c,0}/T)^{-1}$ vs ϵ_{sp} and ξ vs ϵ_{sp} for each the noncritical isochore were found to be independent of concentration over the concentration range of 0.050_0–0.113_5. The results could be well represented by the expressions

$$I_{c,0}/T = B\epsilon_{sp}^{-1.22\pm0.02}, \tag{5}$$

$$\xi = \xi_0\epsilon_{sp}^{-0.64\pm0.02}. \tag{6}$$

The present values of γ and ν are in good agreement with the recent ones for one- and two-component systems[11,13] and for a macromolecular solution.[10] The scaling relation $(2-\eta)\nu = \gamma$, with the critical exponent[16] η, is almost satisfied taking account of $\eta \approx 0.08$ for polystyrene in diethyl malonate.[15]

It is of particular interest to attempt a more general test of the homogeneity and scaling laws with our data in the critical region. Following Sengers and co-workers,[3] the thermodynamic anomalies described by means of the power laws of Eqs. (3) and (4) may be written in terms of scaling laws in the forms

$$A_{\chi}^{*}\chi_T/\Gamma\,|\Delta\phi^{*}|^{-\gamma/\beta} = G_{\chi}(X), \tag{7}$$

$$A_{\xi}^{*}\,\xi/\xi_0\,|\Delta\phi^{*}|^{-\nu/\beta} = G_{\xi}(X), \tag{8}$$

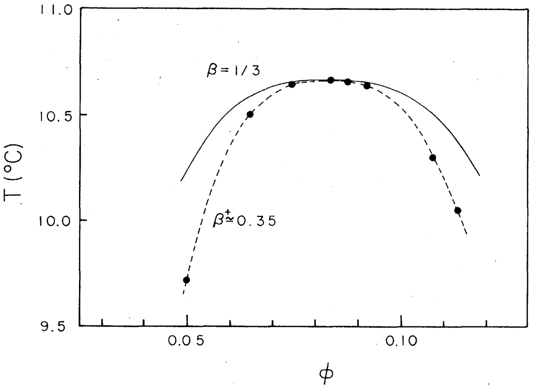

FIG. 1. Coexistence curve with the theoretical value of $\beta = \frac{1}{3}$ (solid line) and the pseudospinodal curve for the system of polystyrene in diethyl malonate (dashed line).

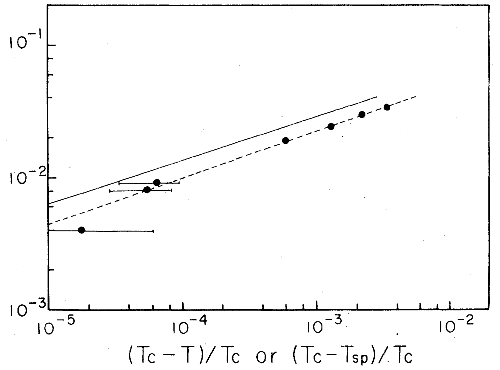

FIG. 2. Logarithmic plots of $|\phi-\phi_c|$ vs $(T_c-T)/T_c$ with $\beta=\frac{1}{3}$ (solid line) and $|\phi-\phi_c|$ vs $(T_c-T_{sp})/T_c$ with $\beta^+=0.35$ (dashed line).

where $G_\chi(X)$ and $G_\xi(X)$ are a function of the scaling parameter $X=\epsilon/|\Delta\phi^*|^{1/\beta}$ with $|\Delta\phi^*|=|\phi/\phi_c-1|$. The scaling parameter X assumes $-Y^{-1/\beta}$ on the coexistence curve because of its asymptotic form $|\Delta\phi^*|=Y(-\epsilon)^\beta$, 0 on the critical isotherm, and ∞ on the critical isochore. A_χ^* and A_ξ^* have been introduced for the assymmetry of χ_T and ξ with the critical mixing concentration ϕ_c. The reduced osmotic compressibility $(I_{c,0}/T)/B$ (i.e., χ_T/Γ) and the reduced correlation length ξ/ξ_0 are given in Fig. 3. In the data analysis, A_χ^* and A_ξ^* were taken to be constant because of the little asymmetry of χ_T and ξ with ϕ_c for each isotherm as shown in Fig. 3. The factors A_χ^* and A_ξ^* should be in principle a function of not only ϕ but also of T. However, the temperature dependence of the factors were also neglected because of the limited ϵ, less than 2% in our work.

A log-log plot of the scaled osmotic compressibility $(I_{c,0}/T)/B|\Delta\phi^*|^{-\gamma/\beta}$ vs X is given by the solid line in Fig. 4 and the scaled correlation length $\xi/\xi_0|\Delta\phi^*|^{-\nu/\beta}$ vs X by the solid line in Fig. 5. In the limit $X\rightarrow 0$ (i.e., critical isotherm), the dimensionless quantity $G(X)$ exhibits an asymptotic behavior for the critical isotherm [i.e., $\partial\log_{10}G(X)/\partial\log_{10}X=0$]. For $X\rightarrow\infty$ (i.e., critical isochore), $G(X)$ exhibits a straight-line behavior with the critical exponent $\gamma\simeq 1.22$ or $\nu\simeq 0.64$. The values of $G(X)$ in the temperature region of $T_p<T<T_c$ along the noncritical isochore are plotted as a function of $X=|-X|$ and are given in closed symbols in Figs. 4 and 5. In the spinodal generalization concept, χ_T and ξ along the noncritical isochore would diverge on the spinodal curve, which is supposed to present the limits of stability of the metastable state. Hence the simple scaling replacing $X=\epsilon/|\Delta\phi^*|^{1/\beta}$ by $X_{sp}=\epsilon_{sp}/|\Delta\phi_{sp}^*|^{1/\beta+}$ with $\Delta\phi^*$ for the pseudospinodal curve, should

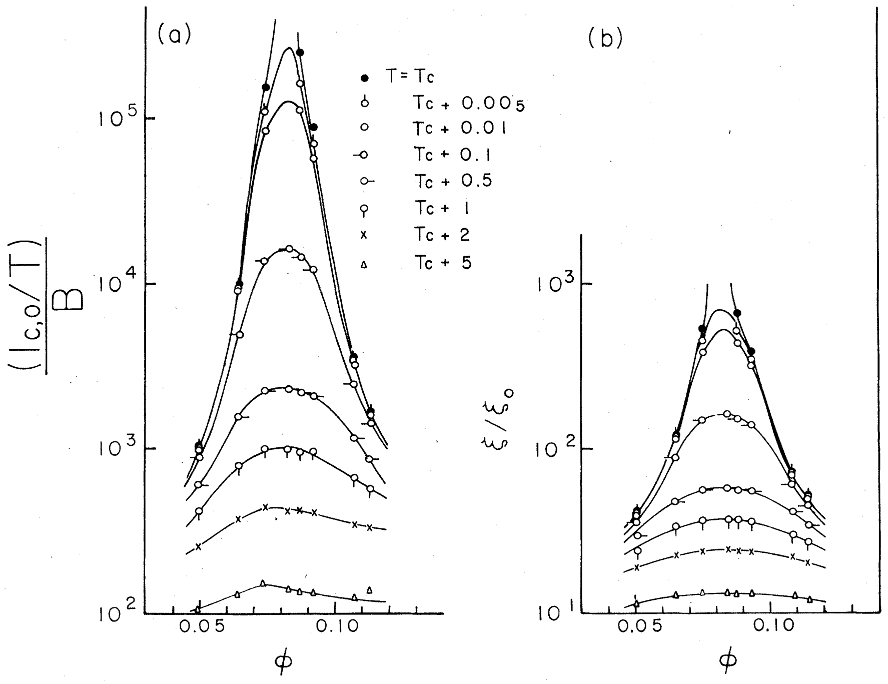

FIG. 3. (a) Plots of $\log_{10}(I_{c,o}/T)/B$ vs ϕ at the isotherms above T_c. (b) Plots of $\log_{10}\xi/\xi_o$ vs ϕ at the isotherms above T_c. The closed circles denote values on the critical isothems.

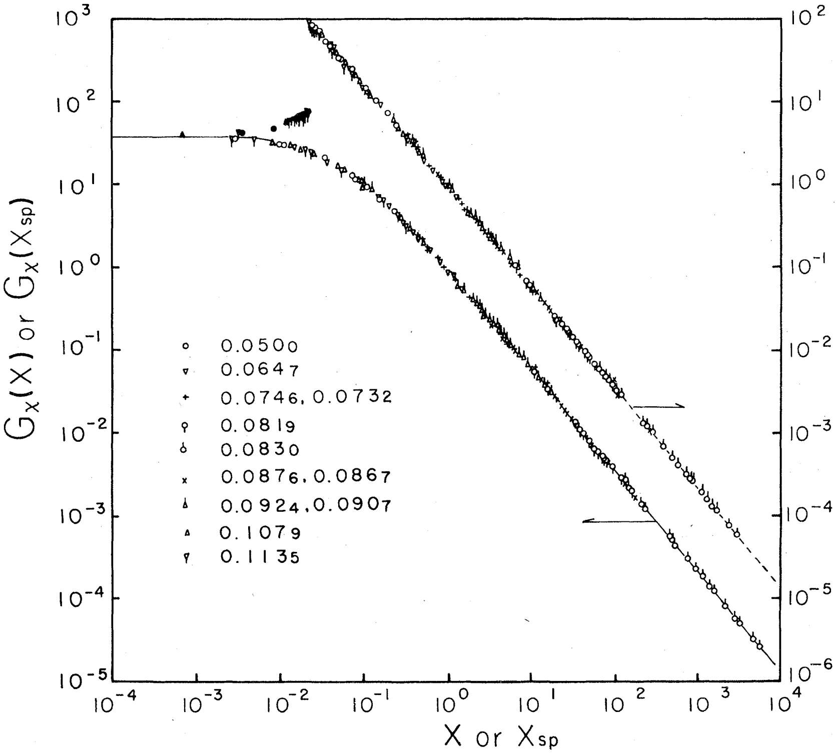

FIG. 4. Logarithmic plots of the scaled osmotic compressibility vs X and X_{sp}. The solid line corresponds to $X=\epsilon/|\Delta\phi^*|^{1/\beta}$, the dashed line to $X_{sp}=\epsilon_{sp}/|\Delta\phi^*_{sp}|^{1/\beta^+}$, and the closed symbols to $X=|-X|$.

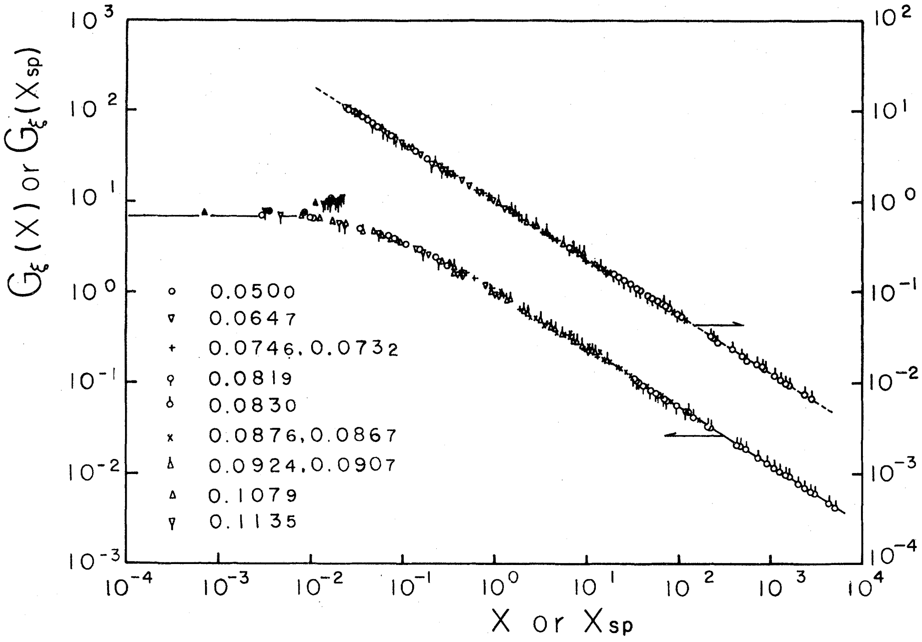

FIG. 5. Logarithmic plots of the scaled correlation length vs X and X_{sp}. The solid line corresponds to $X=\epsilon/|\Delta\phi^*|^{1/\beta}$, the dashed line to $X_{sp}=\epsilon_{sp}/|\Delta\phi^*_{sp}|^{1/\beta^+}$, and the closed symbols to $X=|-X|$.

provide reasonable representations of the experimental results. A log-log plot of $(I_{c,0}/T)/B|\Delta\phi^*_{sp}|^{-\gamma/\beta+}$ vs X_{sp} is given by the dashed line with the slope of 1.22 in Fig. 4 and $\xi/\xi_0|\Delta\phi^*_{sp}|^{-\nu/\beta+}$ vs X_{sp} by the dashed line with 0.64 in Fig. 5. It should be noted that the extension by the spinodal generalization is valid over the entire critical region.

The concentration dependence of the chemical potential μ at the critical isotherm can be expressed as follows:

$$(\partial \mu/\partial \phi)_{T_c} \propto B|\phi - \phi_c|^{\delta-1},$$

where δ is the critical exponent. The value of $\delta - 1 \simeq 3.5$ obtained by a log-log plot of $(I_{c,0}/T)/B$ vs $|\phi - \phi_c|$ for the critical isotherm is in good agreement with the value of $\gamma/\beta^+ = 3.5$ calculated with $\gamma = 1.22$ and $\beta^+ = 0.35$. The concentration dependence of the reduced correlation length ξ/ξ_0 at the critical isotherm could be represented by the expression

$$\xi/\xi_0 \propto |\phi - \phi_c|^{-1.84 \pm 0.10}.$$

On the other hand, ξ/ξ_0 at the critical isotherm obeys the following relation using the critical exponent β^+:

$$\xi/\xi_0 = \epsilon_{sp}^{-\nu} \propto |\phi_{sp} - \phi_c|^{-\nu/\beta^+}.$$

The value of 1.84 obtained by a log-log plot of ξ/ξ_0 vs $|\phi - \phi_c|$ at $T = T_c$ agrees well with the value of $\nu/\beta^+ = 1.83$ calculated with $\nu = 0.64$ and $\beta^+ = 0.35$.

The present values of $\gamma \simeq 1.22$, $\nu \simeq 0.64$, $\beta^+ \simeq 0.35$, and $\delta = 4.5$ are in excellent agreement with the corresponding values for pure fluids and binary-fluid mixtures. We have attempted, for the first time, a test of the universality of the scaled function for a macromolecular solution and established the pseudospinodal generalization to be applicable to even a macromolecular solution in which the two components differ greatly in molecular size. The scaled function $G(X)$ or $G(X_{sp})$ for binary-fluid mixtures should be the same as ours except for only the shift factors on the vertical or the horizontal axis.

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*Present address: Dept. of Polymer Science, Gunma Univ., Kiryu, Japan.

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