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Dynamics of concentration fluctuations along the coexistence curve of a binary mixture

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This work investigates the dynamics of concentration fluctuations in a binary mixture, isobutyric acid in water, when the critical mixing point is approached from within the two-phase region. The scaled diffusion coefficient D^* for both sides of the coexistence curve is in good agreement with the recently proposed dynamic scaling function in the scheme of mode-coupling theory. We find that the dynamic amplitude ratio has the same value $R=1.06\pm0.04$ both above and below T_c, which is in good agreement with a universal value predicted from recent theories and experiments. It is also found that the coefficient ratios $\Gamma/\Gamma^-=4.9\pm2.0$ for the isothermal osmotic compressibility and $\xi_0/\xi_0^-=2.0\pm0.4$ for the correlation length are in good agreement with those suggested by the universality of Γ/Γ^- and of ξ_0/ξ_0^- from scaling theories.

I. INTRODUCTION

Dynamics of the order-parameter fluctuations in pure fluids and binary fluid mixtures has long been a topic of interest. The prediction of critical dynamics has been developed by two theoretical treatments of mode-coupling theory and of renormalization-group theory.[1] These two approaches provide a similar profile for many different systems within the same universality class in terms of having an identical critical exponent and an identical dynamic scaling function.[2] The decay rate Γ associated with the diffusive decay of the order-parameter fluctuations can be determined by measuring the time-dependent correlation function of scattered light. The asymptotic behavior of the diffusion coefficient $D=\lim_{k\to 0}\Gamma/k^2$ can be represented by[3]

$$D=Rk_BT/[6\pi\eta(T)\xi] \quad , \tag{1}$$

where $\xi=\xi_0\epsilon^{-\nu}$ is the correlation length, $\eta(T)$ the shear viscosity, and R a universal amplitude ratio associated with the dynamic scaling relation. Recently most experimental values for R appear to indicate a mode-coupling value with a few percent larger than unity, e.g., $R\simeq1.01$ by Chang and Doiron for ethane[4] and by Burstyn and Sengers for 3-methylpentane + nitroethane,[3] and $R\simeq1.03$ by the authors for polydimenthylsiloxane + diethyl carbonate[5] and for butylcellosolve + water.[6]

The shear viscosity can be represented by

$$\eta(T)=\eta^B(Q_0\xi)^{x_\eta}=\eta^B(Q_0\xi_0)^{x_\eta}\epsilon^{-\phi} \quad , \tag{2}$$

where η^B is the background viscosity, Q_0 the system-dependent wave number, and $\phi=x_\eta\nu$ the critical viscosity exponent. The exponent x_η is related to the dynamic scaling exponent z by the relation $z=3+x_\eta$. The value $x_\eta\simeq0.065$ has been predicted by the renormalization-group theory,[7] which is slightly larger than the value $x_\eta\simeq0.054$ predicted by the mode-coupling theory.[8] The values for x_η in binary fluid mixtures near their critical mixing points have been reported by a number of investigators. The recent experimental values for x_η cover a range from 0.05 to 0.065, in reasonable agreement with the theoretical estimations.[2]

On the other hand, the dynamic light-scattering experiments for the liquid and vapor phases on the coexistence curve have been reported for both CO_2 and xenon.[9] These results have suggested that the decay rate Γ is nearly equal for both branches of the liquid and vapor phases on the coexistence curve and is approximately twice as large as that measured on the critical isochore. In view of recent arguments for dynamic critical phenomena, it is of interest to examine the validity of the dynamic scaling for a binary fluid mixture when the critical mixing point is approached from within the two-phase region. To compare the results in the two-phase region ($T<T_c$) with those in the one-phase region ($T>T_c$), we also report the results obtained for the one-phase region along the critical isochore.

EXPERIMENTAL

Fractionally distilled isobutyric acid and water were used in this work. The coexistence curve for isobutyric acid in water was determined to be the weight-fraction difference $w^+-w^-=Y\epsilon^\beta$ with $Y=1.48_3\pm0.025$ and $\beta=0.317\pm0.003$ using a differential refractometer in the range of $1.67\times10^{-5}\le\epsilon\le9.92\times10^{-3}$, where $\epsilon=|T-T_c|/T_c$. The quoted error represents the standard deviation. The critical weight fraction of the acid was $w_c=0.394_6\pm0.0050$, close to the value 0.3885.[10] The critical temperature was determined to be 299.27 K, consistent with that by Chu.[11] Recent accurate work for the coexistence curve has suggested that the critical exponent β can depend rather sensitively not only on the choice of the composition variable as the order parameter but also on the range of ϵ.[10,12] The difference in the concentration of coexisting phases of isobutyric acid + water was fitted using the other possible composition variables, i.e., volume fraction and mole fraction. The results for these fits to the simple power law yielded the same value of β within experimental errors. The residuals from the fits to the simple power law did not show a noticeable systematic deviation over the entire experimental range of ϵ. Our value for the critical exponent β is in good agreement with that by Greer[10] and also with those found for the fluid systems within the universality class of fluid.[10,12,13]

The light-scattering measurements were performed for a critical mixture of isobutyric acid + water by use of a 6-mm-diam cylindrical cell both along the critical isochore ($T > T_c$) and along the coexistence curve ($T < T_c$). For the one-phase region on the critical isochore the angular distribution of the scattered light was measured over the angular range of $25° \leq \theta \leq 120°$ in the range of $1.27\times10^{-4} \leq \epsilon \leq 3.69\times10^{-3}$ and the autocorrelation functions at $\theta = 60°$, $90°$, and $120°$ were measured in the range of $1.34\times10^{-5} \leq \epsilon \leq 1.33\times10^{-3}$. For the dilute and the concentrated phases on the coexistence curve the angular distribution over the angular range of $25° \leq \theta \leq 135°$ and the autocorrelation functions at $\theta = 45°$, $60°$, $90°$, and $120°$ were measured in the range of $2.67\times10^{-5} \leq \epsilon \leq 8.89\times10^{-4}$. For the system isobutyric acid + water the scattered light due to concentration fluctuations becomes so intense very close to the critical mixing point that the light-scattering data are eventually affected by multiple-scattering contributions. The turbidity measurement, which is scarcely affected by multiple scattering,[14] was also carried out by use of a 5-mm rectangular quartz cell both for the one-phase region in the range of $1.34\times10^{-6} \leq \epsilon \leq 1.73\times10^{-3}$ and for the dilute and the concentrated phases in the range of $3.34\times10^{-6} \leq \epsilon \leq 9.26\times10^{-4}$. The turbidity measurement will be advantageous in obtaining the critical parameters very close to the critical mixing point and also in evaluating approximately multiple scattering contributions to the measured decay rate. The differential refractometer, the light-scattering photometer, sample preparations, and experimental details have been fully described elsewhere.[5,6]

The measurement of the shear viscosity was carried out by use of a modified Ubbelohde-type viscometer along the critical isochore in the range of $1.34\times10^{-5} \leq \epsilon \leq 5.31\times10^{-2}$ and along the off-critical isochores at three different concentrations, i.e., in the range of $3.34\times10^{-5} \leq \epsilon_p \leq 3.41\times10^{-2}$ for $w = 0.263_7$, $1.00\times10^{-5} \leq \epsilon_p \leq 4.48\times10^{-2}$ for $w = 0.358_0$, and $1.67\times10^{-5} \leq \epsilon_p \leq 4.95\times10^{-2}$ for $w = 0.420_4$, where $\epsilon_p = |T - T_p| / T_c$ with the phase separation temperature T_p. The viscosity data have been measured by Woermann and Sarholz for the system isobutyric acid + water at various concentrations near T_p.[15] The shear viscosity data by Woermann and Sarholz, in which T_p has been determined in the concentration range of $0.259 \leq w \leq 0.497$, and the data by us were available to estimate the viscosities associated with the coexistence curve.

RESULTS AND DISCUSSION

In order to obtain the isothermal osmotic compressibility χ_T and the correlation length ξ we have analyzed the angular distribution of the scattered light intensity and the turbidity both along the critical isochore and along the coexistence curve.[14] In a small region of $k\xi$ the Ornstein-Zernike (OZ) correlation function by $1/g(k\xi) = 1 + k^2\xi^2$ gives an excellent representation of the scattered intensity.[16] From the analysis for the angular distribution of the scattered intensity with the OZ function, we have estimated $\xi_0 = (3.5_2 \pm 0.40)\times10^{-8}$ cm and $\nu = 0.62_5 \pm 0.015$ with $\xi = \xi_0\epsilon^{-\nu}$ along the critical isochore in the range of $2.54\times10^{-4} \leq \epsilon \leq 1.46\times10^{-3}$, corresponding to the range of $0.12 \lesssim k\xi \lesssim 1.45$. The intensity data of light scattering very close to T_c were neglected since multiple-scattering effects should be significantly larger. By integration of the scattered light intensity per unit length over all solid angles, the turbidity τ can be written as[17]

$$\tau = \tfrac{1}{2}\pi B\{(1+\beta)\ln[(\sqrt{\beta}+1)/(\sqrt{\beta}-1)] - 2\sqrt{\beta}\} \ , \tag{3}$$

where $\beta = (1 + \frac{1}{2}\alpha^2)^2$ with $\alpha = (k_0\xi)^{-1}$. $B = A\chi_T\alpha^2$ has a weak temperature dependence of $B \propto \epsilon^{\nu\eta}$, where A is nearly independent of temperature in the experimental range of ϵ. The exponent η has a small positive value of the order of a few percent.[18] The $A\chi_T$ for the one-phase region has been calculated from the turbidity τ with the critical parameters ξ_0 and ν obtained by the analysis for the angular distribution of the scattered light intensity. The residuals from the fit to $A\chi_T = \Gamma\epsilon^{-\gamma}$ with $\Gamma = (1.95 \pm 0.03)\times10^{-6}\ \text{cm}^{-1}$ and $\gamma = 1.217 \pm 0.002$ were quite random. The quantity B yields $B = (8.7_0 \pm 0.13)\times10^{-2}\epsilon^{0.033\pm0.002}\ \text{cm}^{-1}$, so that $\eta = 0.053 \pm 0.003$. The multiple-scattering contribution to the measured intensity at $\theta = 90°$ for $\epsilon = 2.54\times10^{-4}$ has been roughly evaluated to be 1.6% for our light-scattering geometry with an average value $\bar{B} = (6.2_0 \pm 0.30)\times10^{-2}\ \text{cm}^{-1}$ and a parameter $\gamma_0 = 2r_0/h \simeq 40$, where r_0 is the radius of the scattering cell and h the height of the observed scattering volume.[19] In the present analysis we have regarded the effect of multiple scattering as an error for determination of the correlation length since a precise calculation is not easy for our experimental arrangement. By considering an almost maximum effect of a 1.6% error we are able to estimate $\xi_0 = (3.5_2 \pm 0.46)\times10^{-8}$ cm and $\nu = 0.62_5 \pm 0.025$ for the correlation length ξ, $\Gamma = (1.95 \pm 0.09)\times10^{-6}\ \text{cm}^{-1}$ and $\gamma = 1.22 \pm 0.04$ for $A\chi_T$, and $\eta = 0.053 \pm 0.005$.

By the same procedure we have analyzed the light-scattering data along both sides of the coexistence curve. The residuals from the fits to $A\chi_T = \Gamma'\epsilon^{-\gamma'}$ for the dilute phase and to $A\chi_T'' = \Gamma''\epsilon^{-\gamma''}$ for the concentrated phase were almost random. We were unable to evaluate the critical exponent η for the two-phase region, because of limited accuracy in the experiment. Our experimental results suggest the symmetric relations for the isothermal osmotic compressibility, the correlation length, and also the turbidity between the two sides of the coexistence curve, i.e., $\Gamma' \simeq \Gamma''$ and $\gamma' \simeq \gamma''$, $\xi_0' \simeq \xi_0''$ and $\nu' \simeq \nu''$, and $\bar{B}' \simeq \bar{B}''$. The averages of the corresponding values between the dilute and the concentrated phases are $\Gamma^- = (4.0 \pm 1.6)\times10^{-7}\ \text{cm}^{-1}$ and $\gamma^- = 1.24 \pm 0.08$ for $A\chi_T$, $\xi_0^- = (1.7_3 \pm 0.22)\times10^{-8}$ cm and $\nu^- = 0.63_4 \pm 0.033$ for ξ, and $\bar{B} = (5.6 \pm 1.0)\times10^{-1}\ \text{cm}^{-1}$ for τ. The exponent values for γ^- and ν^- are in good agreement with the corresponding ones above T_c. We obtain the coefficient ratios $\Gamma/\Gamma^- = 4.9 \pm 2.0$ and $\xi_0/\xi_0^- = 2.0 \pm 0.4$, which are in good agreement with those suggested by recent experiments[20] and by universality of Γ/Γ^- and of ξ_0/ξ_0^- from the scaling theories.[21]

For viscosity measurements in a binary fluid mixture very close to the critical mixing point a lowering of the critical temperature $T_c(S)$ has been observed in the presence of a shear flow with velocity gradient S.[22] The value $T_c(S_{\text{eff}})-T_c(0)$ has been estimated to be approximately -9 mK in terms of an effective velocity gradient for our viscosity measurement very close to the critical mixing point.[5,6] The temperature dependence of the background viscosity η^B has been evaluated with an Arrhenius equation, e.g., for the critical isochore $\eta^B=U\exp(V/T)$ with $U=(3.1_9\pm0.31)\times10^{-7}$ Pa s and $V=(2.67\pm0.03)\times10^3$ in the range of $2.30\times10^{-2}\leq\epsilon\leq5.31\times10^{-2}$. The viscosity data on the critical isochore were well consistent with those obtained by Woermann and Sarholz. The viscosity data along the critical isochore corrected for nonlinear effects[23] were fitted to the power law of Eq. (2). The parameters in Eq. (2) are evaluated to be $Q_0=(2.5_6\pm0.32)\times10^6\ \text{cm}^{-1}$, $\phi=0.040\pm0.002$, and $x_\eta=0.063\pm0.004$. The values for ϕ and x_η are in good agreement with current experimental and theoretical estimations.[2,5–8]

With the aid of the pseudospinodal concept,[24] we have tried to evaluate the viscosities along the coexistence curve for the present system. Recently, Sorensen and Semon have proposed a scaled equation of state on the basis of the pseudospinodal concept, which is valid in the metastable region within the coexistence curve.[25] This equation leads to the universal amplitude ratio, consistent with that deduced from the hypothesis of two-scale-factor universality. In previous work we have confirmed the pseudospinodal concept to be quite useful for the analysis of the diffusion coefficient and the shear viscosity for the off-critical isochore.[6] Though there is no proof whether the concept of the pseudospinodal is acceptable for the dynamical properties in fluid mixtures or not, it should be at least available for the present analysis. Izumi and Miyake have analysed the viscosity data by Woermann and Sarholz in terms of a scaling relation with the assumption of the pseudospinodal.[26] Our procedure to analyze the viscosity data for the off-critical isochores is similar to that applied by them, except for their background estimation. The pseudospinodal curve was determined to be $w^+-w^-=Y^*\epsilon_{\text{sp}}^{\beta^*}$ with $Y^*=1.4_3\pm0.15$ and $\beta^*=0.34_5\pm0.020$ in the range of $2.92\times10^{-5}\leq\epsilon_{\text{sp}}\leq1.60\times10^{-2}$. By extrapolating the viscosity at any isochore to T_p as a smooth function of temperature, i.e., $\eta(T)/\eta^B\propto\epsilon_{\text{sp}}^{-\phi}$, we obtain the viscosities on the coexistence curve in the concentration range of $0.259\leq w\leq0.497$, where $\epsilon_{\text{sp}}=|T-T_{\text{sp}}|/T_c$ with the pseudospinodal temperature T_{sp}. The extrapolation of the background viscosity at any isochore to T_p has been performed in conformity with the Arrhenius equation. The value for the critical temperature by Woermann and Sarholz is 299.45 K, which is 0.06% higher than that by us. It follows a 0.5% larger value in the estimation of the background viscosity as $T\rightarrow T_c$, which is negligibly small in the present analysis. In Fig. 1 we show the viscosity $\eta(T_p)$ and the background viscosity $\eta^B(T_p)$ on the coexistence curve as a function of temperature, where open symbols represent the $\eta(T_p)$ and closed ones the $\eta^B(T_p)$. The symbols of circles and triangles are used to stand for the dilute and the concentrated phases, respectively. Our results are denoted by squares.

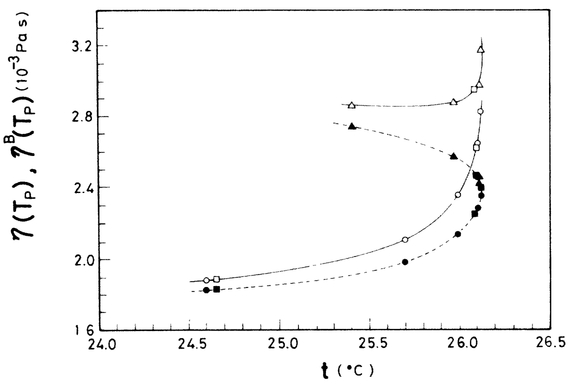

FIG. 1. Extrapolated values deduced from the viscosity data by Woermann and Sarholz and by us for the shear viscosity $\eta(T_p)$ and the background viscosity $\eta^B(T_p)$ on the coexistence curve of isobutyric acid in water as a function of temperature, where open symbols represent the $\eta(T_p)$ and closed ones the $\eta^B(T_p)$. Circles and triangles are used to stand for the dilute and the concentrated phases, respectively. Our values for the $\eta(T_p)$ and the $\eta^B(T_p)$ are denoted by squares.

Log-log plots of $\eta(T_p)/\eta^B(T_p)$ for ϵ collapsed approximately onto a single straight line in the range of $1.00\times10^{-5}\leq\epsilon\leq2.37\times10^{-3}$. In terms of the notation adopted to the viscosity data on the critical isochore we have fitted the data on the coexistence curve to the power law of Eq. (2). The values estimated for the critical parameters are $Q_0^-=(2.9_5\pm0.38)\times10^6\ \text{cm}^{-1}$, $\phi^-=0.036\pm0.003$, and $x_\eta=0.057\pm0.006$, which are in agreement with those obtained for the critical isochore within experimental errors.

In the dynamic light-scattering measurement very close to the critical mixing point, the deviation from the exponential decay law in the time-dependent correlation function of the light undergoing double and higher-order multiple scattering is likely to happen.[27] We have evaluated the contribution of double scattering to the decay rate at $\theta=90°$ as a function of α from the prediction of double-scattering theory.[28] The correction factor $\bar{\epsilon}(C_1-\delta_1C_2)$ with $\bar{\epsilon}=4\pi r_0\bar{B}$ to the decay rate over the entire experimental range of ϵ varies approximately from 0.3% to 2.9% for the one-phase region and from 0.2% to 1.8% for the two-phase region, where $C_1=-0.17\gamma_0^{-1}(\ln\gamma_0-2.2)$ and $C_2=1.12\gamma_0^{-1}(\ln\gamma_0+0.13)/(1+\alpha+\frac{9}{8}\alpha^2)$. The contribution to the decay rate from the higher-order multiple scattering should be negligibly small. The parameter δ_1 has been calculated to be $\frac{4}{3}$ for the slope of the best-fit line to the exponential decay law, in which the time-dependent correlation function includes double-scattering effects. The double-scattering correction to the decay rate at a scattering angle θ has been evaluated from the prediction for the relative contribution of double-scattering decay rate to the single-scattering decay rate.[28]

In terms of the dynamic scaling relation the scaled diffusion coefficient D^* is given by

$$D^*=[6\pi\eta(T)\xi/k_BT](D-D^B)\ .$$

The background diffusion coefficient D^B has been evaluated with the expression $D^B=(k_BT/16\eta^B\xi)[(1+k^2\xi^2)/q_c\xi]$ as a function of temperature and scattering angle.[3,6] The parameter q_c is the system-dependent wave number, which is related to Q_0 in Eq. (2). We have treated q_c as an adjustable parameter with $q_c=2.5\times10^7\ \mathrm{cm}^{-1}$ for the critical isochore, $q_c=6.7\times10^6\ \mathrm{cm}^{-1}$ for the dilute phase, and $q_c=1.6\times10^8\ \mathrm{cm}^{-1}$ for the concentrated phase. At the same $\epsilon=3.34\times10^{-5}$ for $\theta=90°$, for example, these values of q_c yield the relative background contribution D^B/D with the values of 1.8% for the critical isochore, 3.3% for the dilute phase, and 0.2% for the concentrated phase. The experimental scaled diffusion coefficient D^* has been compared with the prediction of the recently proposed dynamic scaling function by[3]

$$\Omega(k\xi)=\Omega_K(k\xi)S(k\xi)^{x_\eta}$$

with the correction $S(y)=a_0(1+b^2y^2)^{1/2}$, where $\Omega_K(y)$ is the original Kawasaki function defined by[29]

$$\Omega_K(y)=(3/4y^2)[1+y^2+(y^3-y^{-1})\tan^{-1}y] \ .$$

The coefficient a_0 is related to the universal amplitude ratio R by $R=a_0^{x_\eta}$. In order to estimate the parameters a_0 and b we have fitted our experimental data to the equation

$$(1/y^2)[D^*/\Omega_K(y)]^{2/x_\eta}=a_0^2(y^{-2}+b^2) \ . \qquad (4)$$

We obtain the values of $a_0=2.5_5\pm0.40$, i.e. $R\simeq1.06$, and of $b=1.0\pm0.4$ for $S(y)$ for the critical isochore. Along both sides of the coexistence curve we obtain the parameter values $a_0=0.9_2\pm0.80$ ($R\simeq1.06$) and $b=1.0\pm0.5$ for the dilute phase, and the values $a_0=2.2_4\pm0.86$ ($R\simeq1.05$) and $b=1.0\pm0.8$ for the concentrated phase. In Figs. 2 and 3 we show the difference between the experimental scaled diffusion coefficient D^* and the dynamic scaling function $\Omega(k\xi)$ with the values estimated for the parameters x_η, a_0, and b. Figure 2 shows the result for the one-phase region and Fig. 3 the result for the two-phase region. In Fig. 3, the values for the dilute and the concentrated phases are denoted by open and solid symbols, respectively. Thus, we find the value of $R=1.06\pm0.02$ for the one-phase region. Along both sides of the coexistence curve we find that $R=1.06\pm0.03$ for the dilute phase and $R=1.05\pm0.05$ for the concentrated phase. It is noted that the values obtained for the amplitude R and the parameter b are identical for both sides of the coexistence curve and also for the critical isochore. Our value for R is in good agreement with the value $R\simeq1.06$ by Beysens *et al.* for three mixtures,[30] and approximately consistent with the value $R\simeq1.01$ found by Burstyn *et al.* for 3-methylpentane + nitroethane (Ref. 3) and by us with the value $R\simeq1.03$ for polydimethylsiloxane + diethyl carbonate (Ref. 5) within a 4% error. The theoretical value for R has been predicted to be $R\simeq1.03$ by Kawasaki and Lo[31] and by Burstyn *et al.*[3] from the mode-coupling theory, and $R\simeq1.07$ by Paladin and Peliti[32] and $R\simeq1.2$ by Siggia *et al.*[7] from the renormalization-group theory. Though we are unable to provide a conclusive reason for the difference between the mode-coupling value of $R\simeq1.03$ and the most recent renormalization-group value of $R\simeq1.07$, our value is compatible with the most recent theoretical estimations, but significantly differs from the value $R\simeq1.2$. A few comments are made about the parameter b. The parameter b is rather sensitive to the exponent value of x_η. For example, a 5% error in the value of x_η leads to an approximate 10% difference in the value b by a least-squares fit to Eq. (4), while the value R is scarcely affected. Taking into account a large error included in the present value of b, our result for the parameter b should be regarded as consistent with the value $b\simeq0.5$ found by Burstyn *et al.* in agreement with the theoretical estimation.[3]

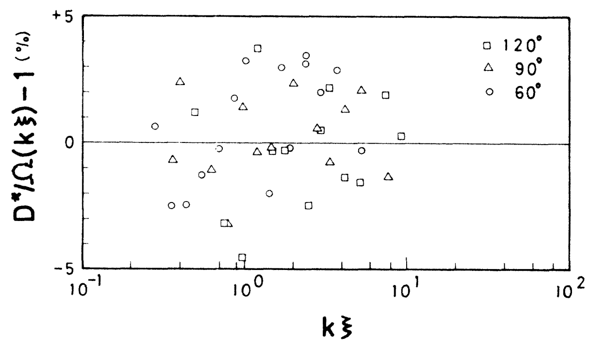

FIG. 2. Comparison between the scaled diffusion coefficient $D^*=[6\pi\eta(T)\xi/k_BT](D-D^B)$ and the dynamic scaling function $\Omega(k\xi)$ with the parameter values $x_\eta=0.063$, $a_0=2.55$, and $b=1.0$ as a function of $k\xi$ above T_c.

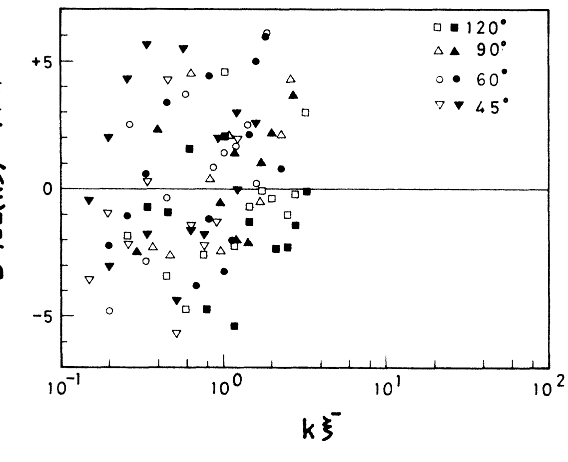

FIG. 3. Comparison of the scaled diffusion coefficient D^* with $\Omega(k\xi^-)$ as a function of $k\xi^-$ below T_c, where the dilute and the concentrated phases are denoted by open and closed symbols, respectively.

In this work we have examined the dynamical behavior in a binary mixture isobutyric acid + water along the coexistence curve below T_c. We find that the asymptotic critical behavior of the diffusion coefficient and of the shear viscosity are quite symmetric between above and below T_c. For an average over the values of the critical parameter determined both above and below T_c we can estimate the values associated with the dynamic scaling function to be $x_\eta = 0.060 \pm 0.005$, $R = 1.06 \pm 0.04$, and $b = 1.0 \pm 0.6$, which are in good agreement with the prediction for the dynamic universality class of a fluid. We also note that $\chi_T / \chi_T^- \simeq 4.9$ for the isothermal osmotic compressibility and $\xi / \xi^- \simeq 2.0$ for the correlation length are verified as functions of temperature when the critical temperature is approached from above and below T_c, in good agreement with the prediction from scaling theories.

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