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Critical exponent for viscosity

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We have measured the critical exponent y characterizing the divergence of the viscosity $\eta \propto |T-T_c|^{-y}$ for carbon dioxide and xenon. The values of y for both fluids fall within the range $y=0.041\pm0.001$ and are consistent with the range $y=0.042\pm0.002$ spanned by our earlier data for four binary liquid mixtures. This agreement is the strongest evidence that pure fluids and binary liquids are in the same dynamic universality class; however, the results for y are inconsistent with the recent theoretical value of 0.032.

The viscosity η is believed to diverge asymptotically near the critical temperature T_c as

$$\eta \propto |T-T_c|^{-y} . \tag{1}$$

The widely accepted hypothesis, that pure fluids near liquid-vapor critical points and binary liquid mixtures near consolute points fall within the same dynamic universality class, leads one to expect the same values of y at both types of critical points.[1] In contrast, previous measurements of y have found smaller values for pure fluids than for binary mixtures.[2] Here, we report measurements near the critical points of both carbon dioxide and xenon, which show that the apparent critical exponent y is in the range of $y=0.041\pm0.001$. This range falls within the larger range $y=0.042\pm0.002$, spanned by our earlier results[3] for four binary liquid mixtures; thus, the present data are consistent with the hypothesis that binary liquid mixtures and pure fluids are in the same dynamic universality class (see Fig. 1).[4]

Theoretical values of y come from several sources. An early calculation using the mode-coupling theory to single-loop order gave the result[5,6] that $y=(8/15\pi^2)\nu \simeq 0.034$, where $\nu \simeq 0.630$ is the exponent for the correlation length ξ. In a more recent two-loop calculation, Bhattacharjee and Ferrell[7] found that $y \simeq 0.032$, and they estimated that the error in this result is "of the order of 1%." Thus this value of y is inconsistent with the present experimental value, within estimates of the combined uncertainties. Bhattacharjee and Ferrell also found that $y \approx 0.34$ from a dynamic renormalization-group calculation to order ϵ^3; however, they argued that the ϵ expansion for the viscosity is less reliable than the mode-coupling theory.

The agreement among the experimental values of y, as displayed in Fig. 1, is remarkable given the varied experimental problems one encounters in determining y for this wide range of fluid systems. One advantage of studying y with pure fluids is that the noncritical background viscosity has a comparatively small temperature dependence, which can be accurately characterized. This is very important, because the small value of y conspires with experimental problems to limit the observable increase in the viscosity near T_c to 20–40 %, as shown in Fig. 2. In pure fluids, the smaller relaxation time τ permits the conditions of low frequency ($\omega\tau \ll 1$) and low shear rate ($\dot{\gamma}\tau \ll 1$), required for measuring the hydrodynamic viscosity, to be more easily met than with binary liquid mixtures. In contrast with binary liquids, the measurement of the critical-point divergence of η in pure fluids is affected by gravity-induced stratification[8] within about $t < 10^{-4}$, where $t \equiv |T-T_c|/T_c$ is the reduced temperature. The stratification is unavoidable on Earth and required us to use a much more elaborate model to analyze the pure fluid data than was needed for the binary liquid data. The model for pure fluids included four additional features: (1) an accepted scaling equation of state to model the stratified density, (2) an established relation be-

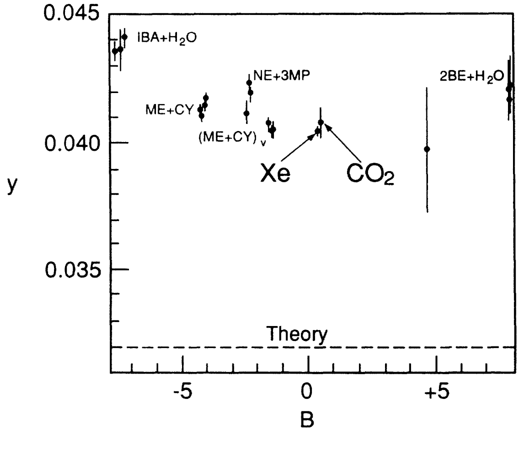

FIG. 1. The viscosity exponent y for four binary mixtures and two pure fluids. The abcissa B, defined by Eq. (7), measures the slope of the noncritical viscosity at T_c. The various fluids, chosen partly for their diverse noncritical viscosities, have exponents that agree with each other better than with the theoretical values of Ref. 7. The label $(\mathrm{ME+CY})_v$ denotes the methanol and cyclohexane data taken at constant volume. The other mixture data are near atmospheric pressure, and the CO_2 and Xe data are taken on their critical isochores. Other nonstandard abbreviations are IBA for isobutyric acid, 2BE for 2-butoxyethanol, NE for nitroethane, and 3MP for 3-methylpentane.

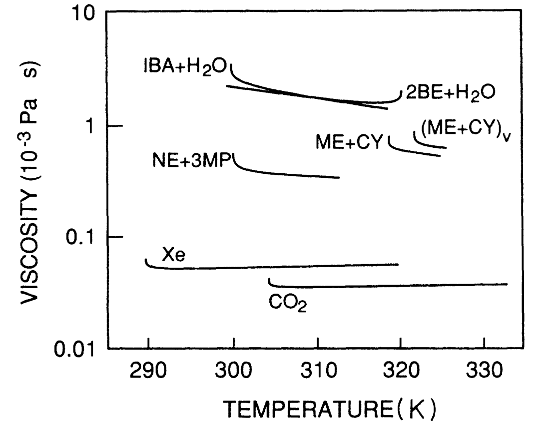

FIG. 2. The viscosities of four binary mixtures and two pure fluids near their critical points. The measured viscosity exponents are shown in Fig. 1.

tween the density, the temperature, and the correlation length, (3) a parametrized function relating the viscosity to the correlation length which incorporates the crossover from critical to noncritical behavior, and (4) a hydrodynamic model to calculate the response of the viscometer to the stratified fluid. Only the last two features are discussed here.

It is now generally accepted[2] that the viscosity very near T_c has the "multiplicative" form of

$$\eta = \eta_0 (Q_0 \xi)^{x_\eta} , \tag{2}$$

where $y \equiv \nu x_\eta$ or, in terms of the reduced temperature t and on the critical isochore,

$$\eta = [\eta_0 (Q_0 \xi_0)^{x_\eta}] t^{-y} . \tag{3}$$

The amplitude of the divergence includes the noncritical background η_0, a characteristic wave vector Q_0, and the correlation length amplitude ξ_0.

To correctly match the purely noncritical viscosity $\eta_0(T)$ far from T_c to the asymptotic form of Eq. (3) requires a "crossover function." For our analysis, we used a crossover function H derived by Bhattacharjee *et al.*,[9] who included the effects of the noncritical contribution to the fluctuation decay rate, as measured by a characteristic wave vector q_C, and cut off the relevant mode-coupling integrals at the finite wave vector q_D. Their expression for the viscosity,

$$\eta = \eta_0 \exp[x_\eta H(q_C \xi_0, q_D \xi_0, \xi)] , \tag{4}$$

has the required asymptotic forms of $\ln(Q_0 \xi)$, close to T_c, and 0, far from T_c. Recently, Olchowy and Sengers[10,11] improved H to allow an accurate and consistent description of thermal diffusivity, as well as viscosity. Because the two crossover functions are equivalent for descriptions of the viscosity,[12] we used the simpler form of Bhattacharjee *et al.*[9]

The present torsion-oscillator viscometer, shown in Fig. 3, is an improved version of the viscometers used for our earlier measurements on binary liquid mixtures.[3,13] All of these viscometers had three important features for nearly critical samples: (1) precise temperature control (<1 mK), which is necessary for acquiring data near T_c, (2) low frequencies (~ 1 Hz), and (3) small oscillation amplitudes to achieve low shear rates (0.1–1 s^{-1}). The low frequency and shear rate also ensured that viscous heating was negligible.

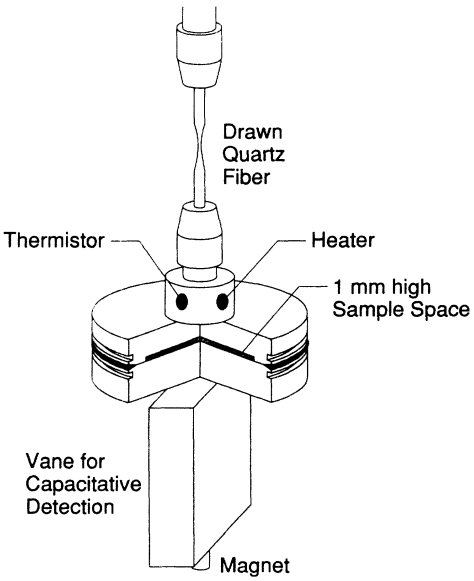

FIG. 3. The CO$_2$ bob, shown sectioned, suspended by a drawn quartz fiber. The xenon bob differed by having a 0.7-mm sample space and a central internal stiffening post.

The sample volumes, contained within the "bobs" of torsion oscillators, were thin and horizontal to reduce the effects of gravitational stratification. Both bobs were filled to a density ρ within $\pm 0.3\%$ of the nominal critical density ρ_c (Refs. 14 and 15), so that, at $t = 10^{-5}$, the maximum error in the critical-point enhancement of the viscosity caused by $\rho \neq \rho_c$ was less than 0.07%.[3]

As with the binary liquid viscometers, the thermostat was comprised of three evacuated, nested, aluminum shells. The heater on the bob was not used during the viscosity measurements. Thus the thermally isolated bob acted as a passive fourth thermostat stage with good temperature stability. During the measurements closest to T_c, the residual temperature gradient across the sample was approximately 200 $\mu\mathrm{K\,m}^{-1}$, three orders of magnitude smaller than the adiabatic gradient that would be present across a convectively stirred sample.

We made decrement measurements by using a capacitance bridge to monitor the freely decaying torsion oscillations. The output of the bridge was assumed to be of the form

$$\theta = \theta_0 \sin(\omega t) e^{-\omega t D/2\pi} . \tag{5}$$

The initial amplitude θ_0 was typically 1 mrad, and the frequency $\omega/2\pi$ was about 1 Hz. The oscillation peaks were measured for 500 periods and then fit by an exponential to obtain the decrement D. The rms scatter in

D was typically $\pm 0.3\%$.

Decrement measurements were made while the bob's temperature slowly relaxed toward the programmed temperature of the inner shell. Near T_c, very slow sweep rates were required to avoid hysteresis attributed to the stratification of the fluid with a time constant of approximately 10^3 s. The results of the slowest negative sweep rates (-0.3 μK/s for xenon and -0.05 μK/s for CO_2, equivalent to -1.6 K/y) were identical to the results of the slowest positive sweeps that started in the two-phase region.

The measured decrements were corrected for the losses D_0 unrelated to the sample's viscosity. For the CO_2 decrements, we either assumed that D_0 was constant and fit only to data within $t < t_{\max} = 0.01$, or we corrected D_0 for temperature-dependent outgassing of the thermostat. (Details of the corrections appear in Ref. 4.) For the xenon measurements, we recorded the residual pressure in the thermostat, and used these data to make corrections to D_0 based on the measured pressure dependence of D_0.

For a homogeneous sample, the relationship between the viscosity and the decrement can be expressed as a function of the viscous penetration depth, $\delta \equiv (2\eta/\rho\omega)^{1/2}$, and the bob's radius R and half-height h. For this function, we used a simple analytic working equation accurate to $O(\delta/R)^2$, which Grouvel and Kestin[16] obtained from an exact solution.[17] Our numerical studies confirmed the accuracy of the analytic approximation; however, the nonlocal nature of the $O(\delta/R)^2$ formula required its careful use when dealing with gravity-induced inhomogeneity near T_c.

We accounted for the effects of stratification by first using the "restricted cubic model"[8,18] equation of state to obtain the vertical profile of the density. From the associated parametric variables, the correlation length as a function of height was also calculated,[8,19] in turn, yielding the vertical profile of the viscosity through Eq. (4). We then used the $O(\delta/R)^2$ working equation to compute the average of the decrements expected if the bob were filled homogeneously with fluid having the viscosity and density found at the bottom and top of the bob. The small contribution to the decrement, resulting from the variation of η and ρ with height along the side wall, was then accounted for by an integral incorporating a simple $O(\delta/R)$ formula.[4]

The noncritical background viscosity η_0 was represented by the *Ansatz*[20]

$$\eta_0(T,\rho) = \eta_{00}(T) + \eta_{01}(\rho) \ . \qquad (6)$$

For $\eta_{00}(T)$, we used the correlations based on kinetic theory developed by Kestin, Ro, and Wakeham.[21,22] For η_{01} of CO_2, we used the description obtained by Iwasaki and Takahashi.[23] For η_{01} of xenon, we combined the correlating function of Jossi, Stiel, and Thodos[24] with the data of Reynes and Thodos.[25]

The total viscosity was represented by the crossover form of Eq. (4). Although the data determining q_C and ξ_0 were available for both CO_2 and xenon, the careful thermal conductivity measurements required to determine q_D were not available for xenon. Thus q_D was treated as an adjustable parameter in fitting the xenon decrement data. For the CO_2 decrement data, one fit was made with q_D fixed, and two fits were made with q_D adjustable.

These considerations were embedded into a fitting program that was used to find the best values of the parameters in Eq. (4) describing the temperature dependence of the viscosity. Figure 4 shows the decrement data and fitted description for xenon.

The four free parameters in our model were T_c, y, q_D, and D_{01}, where D_{01} was the part of D_0 not already accounted for. In practice, we fitted the quantity $\ln(q_D\xi_0)$ to avoid unphysical negative values for q_D. We also tried fixing $\ln(q_D\xi_0)$ at -0.43 ($q_D^{-1} = 0.23$ nm) for CO_2, the value determined by the thermal conductivity data.[10,11] Although the fitted value of q_D was about five times lower than the value determined by thermal conductivity, this had little effect on y. Table I summarizes the results of the various fits, and the insensitivity of y to the fitting procedure is clearly shown. We accounted for correlations between fitting parameters when deriving the error estimates (1σ denotes a 68% confidence level). Also, the assumption of normally distributed errors was verified by calculating the minimum χ^2 for various values of y fixed near the best-fit value.

For both fluids, the absolute viscosity far from T_c was consistent, within the experimental errors, with the noncritical viscosity measured elsewhere.[23,25] (The experimental errors $\Delta\eta/\eta$ were ± 0.015 for CO_2 and ± 0.008 for xenon.)

In Fig. 4, the fitted model for the xenon data is used to illustrate the effects of gravity. The dashed curve is an extrapolation of the xenon fit in the reduced gravity, $10^{-4}g$, where the decrement data at the smallest values of t would fall on a straight line of slope $y/2$. However, in

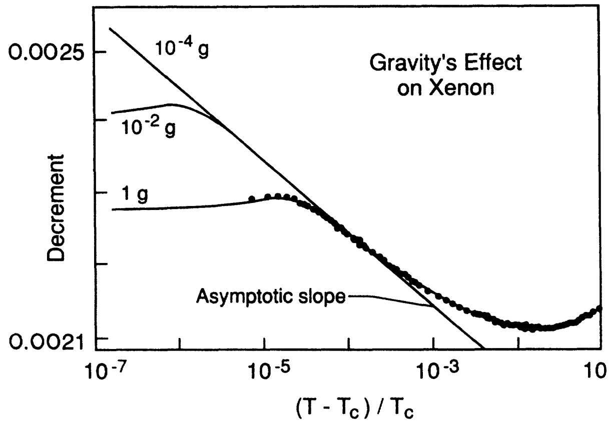

FIG. 4. The decrement of the torsion oscillator filled with xenon as a function of the reduced temperature. The 1g curve is the best fit to the data, and the upper curve shows the decrement expected if the xenon experiment were repeated in low gravity. To first order, the asymptotic slope is $y/2$. Because the asymptotic region is unavailable in 1g, determination of the viscosity exponent y strongly depends on the theory of crossover between the noncritical and critical regions.

TABLE I. Results of four fits to the data, including 1σ error estimates. The upper bound of the fitting range is $t_{\max}$. The fitted viscosity exponent is y, and the fitted cutoff wave vector is q_D.

Fluid	$t_{\max}$	y ($\times 10^3$)	$\ln(q_D \xi_0)$
CO_2	0.01	40.79 ± 0.68	-1.99 ± 2.59
CO_2	0.1	41.66 ± 0.29	-1.65 ± 0.15
CO_2	0.1	40.96 ± 0.21	-0.43 fixed
Xe	0.1	40.50 ± 0.16	-1.75 ± 0.05

$1g$, the decrement data never reach their asymptotic slope! Therefore, a correct model including the effects of both gravity and crossover was necessary for determining the viscosity exponent.

There have been few other pure fluid viscosity measurements made on the critical isochore near T_c. These include measurements on xenon and ethane by Strumpf, Collings, and Pings,[26] on CO_2 by Bruschi and Torzo,[27] and on ^{3}He and ^{4}He by Agosta *et al.*[28]. The results from these groups fell into the range of $0.031 < y < 0.038$.

Previous measurements of y for binary liquids have varied widely. Values from 0.032 to 0.042 were listed in the recent review of Ref. 2, for example. Although much of this variation has been later eliminated by accounting for shear effects, either by limiting the temperature range of the data, as was done by Calmettes,[29] or by applying corrections to the data, as was done by Nieuwoudt and Sengers,[30] our recent low-frequency, low-shear-rate measurements[3] have been the only ones not requiring shear corrections close to T_c. Figure 1 shows the agreement between the binary liquids and pure fluids by plotting y versus the noncritical slope parameter B, defined by

$$B \equiv \left[\left[\frac{T_c}{\eta_0} \right] \left[\frac{d\eta_0}{dT} \right] \right]_{T_c} . \tag{7}$$

We conclude from our study of four binary liquid mixtures and two pure fluids that the viscosity exponent y has a universal value:

$$y = 0.042 \pm 0.002 . \tag{8}$$

This value differs from theory by 30% and has an error of only 5%. We urge that a theoretical effort, commensurate in scale with the present experimental effort, should be made in an attempt to resolve the discrepancy.

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[1] P. C. Hohenberg and B. I. Halperin, Rev. Mod. Phys. **49**, 435 (1977).

[2] J. V. Sengers, Int. J. Thermophys. **6**, 203 (1985).

[3] R. F. Berg and M. R. Moldover, J. Chem. Phys. **89**, 3694 (1988).

[4] R. F. Berg and M. R. Moldover, J. Chem. Phys. **93**, 1926 (1990).

[5] K. Kawasaki, Ann. Phys. (N.Y.) **61**, 1 (1970).

[6] R. Perl and R. A. Ferrell, Phys. Rev. Lett. **29**, 51 (1972); Phys. Rev. A **6**, 358 (1972).

[7] J. K. Bhattacharjee and R. A. Ferrell, Phys. Rev. A **28**, 2363 (1983).

[8] M. R. Moldover, J. V. Sengers, R. W. Gammon, and R. J. Hocken, Rev. Mod. Phys. **51**, 79 (1979).

[9] J. K. Bhattacharjee, R. A. Ferrell, R. S. Basu, and J. V. Sengers, Phys. Rev. A **24**, 1469 (1981).

[10] G. A. Olchowy, Ph.D. thesis, University of Maryland, 1989 (unpublished).

[11] G. A. Olchowy and J. V. Sengers, Phys. Rev. Lett. **61**, 15 (1988).

[12] G. A. Olchowy (private communication).

[13] R. F. Berg and M. R. Moldover, Rev. Sci. Instrum. **57**, 1667 (1986).

[14] M. R. Moldover, J. Chem. Phys. **61**, 1766 (1974).

[15] U. Närger and D. A. Balzarini (private communication).

[16] J. M. Grouvel and J. Kestin, Appl. Sci. Res. **34**, 427 (1978) [note that the second term of Eq. (24) should use $(6+16R/\pi h)$]; see, also, J. C. Nieuwoudt and J. V. Sengers, Physica A **149**, 107 (1988).

[17] J. Kestin and G. F. Newell, Z. Angew. Math. Phys. **8**, 433 (1957); D. A. Beckwith and G. F. Newell, *ibid.* **8**, 450 (1957).

[18] J. T. Ho and J. D. Lister, Phys. Rev. B **2**, 4523 (1970).

[19] J. V. Sengers and J. M. H. Levelt Sengers, in *Progress in Liquid Physics,* edited by C. A. Croxton (Wiley, New York, 1978), Chap. 4.

[20] See review by J. V. Sengers, in *Recent Advances in Engineering Science,* edited by A. C. Eringen (Gordon and Breach, New York, 1968), Vol. III, p. 153.

[21] J. Kestin, S. T. Ro, and W. A. Wakeham, J. Chem. Phys. **56**, 4114 (1972).

[22] J. Kestin, S. T. Ro, and W. A. Wakeham, J. Chem. Phys. **56**, 4119 (1972); J. Kestin, Phys. Chem. Earth (Nobel Symposium) **13-14**, 295 (1982).

[23] H. Iwasaki and M. Takahashi, J. Chem. Phys. **74**, 1930 (1981).

[24] J. A. Jossi, L. I. Stiel, and G. Thodos, AIChE J. **8**, 59 (1962).

[25] E. G. Reynes and G. Thodos, Physica **30**, 1529 (1964).

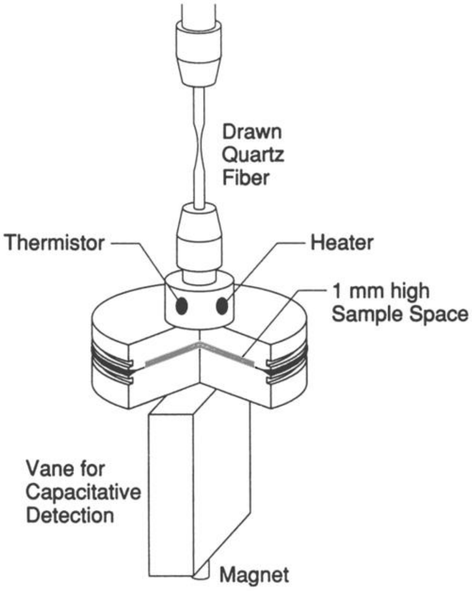
[26] H. J. Strumpf, A. F. Collings, and C. J. Pings, J. Chem. Phys. **60**, 3109 (1974).

[27] L. Bruschi and G. Torzo, Phys. Lett. **98A**, 265 (1983).

[28] C. C. Agosta, S. Wang, L. H. Cohen, and H. Meyer, J. Low Temp. Phys. **67**, 237 (1987).

[29] P. Calmettes, Phys. Rev. Lett. **39**, 1151 (1977).

[30] J. C. Nieuwoudt and J. V. Sengers, J. Chem. Phys. **90**, 457 (1989).



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