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Stokes-Einstein diffusion of critical fluctuations in a fluid

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The diffusion coefficient associated with the order-parameter fluctuations near the critical point of fluids is expected to vanish asymptotically as $D = RkT/6\pi\eta\xi$, where η is the viscosity, ξ the correlation length, and R a universal constant. Our experiments, using 3-methylpentane-nitroethane, yield $R = 1.02 \pm 0.06$, in agreement with the mode-coupling theory of critical fluctuations, but in disagreement with the value $R/6\pi = 1.2/6\pi \simeq 1/5\pi$, recently suggested by several investigators.

I. INTRODUCTION

According to the theory of dynamic critical phenomena, the diffusion coefficient D associated with the order-parameter fluctuations near the critical point of fluids should satisfy a Stokes-Einstein relation of the form[1]

$$D = \frac{RkT}{6\pi\eta\xi}, \tag{1}$$

where k is Boltzmann's constant, T the temperature, η the dynamic viscosity, ξ the correlation length, and R a universal constant independent of the particular fluid under consideration. For fluids near the gas-liquid critical point, D is to be identified with the thermal diffusivity and for liquid mixtures near the consolute point with the binary diffusion coefficient.

In the original derivations of Kawasaki and Ferrell, based on mode-coupling theory, the constant R was found to be unity,[2] while Kawasaki and Lo suggested a value slightly larger than unity.[3] Subsequently, Siggia *et al.* evaluated R to first order in $\epsilon = 4 - d$ (d is the dimensionality) from a renormalization group treatment of critical dynamics; they obtained two estimates, $R = 0.79$ and 1.20, and judged the latter estimate to be more reliable.[4]

An analysis of the thermal conductivity data of carbon dioxide and steam in the critical region[5] seemed to indicate a value of R between 1.15 and 1.20. However, this result was deduced using an empirical modification of (1) to accommodate data in a large range of temperatures and densities around the critical point. An experimental study closer to the critical point was reported by Chen *et al.* for the binary liquid n-hexane-nitrobenzene[6] and by Sorensen *et al.* for the 3-methylpentane-nitroethane system[7]; these authors reported good agreement with the theoretical value $R = 1.20$. This result has been interpreted[6,8] as implying $R/6\pi \simeq 1/5\pi$, which corresponds to Stokes's law for a spherical droplet moving in a medium with the same viscosity as that of the liquid in the droplet.[9]

In order for Eq. (1) to be valid, the critical temperature T_c should be approached closely enough to ensure that the diffusion coefficient D may be identified with its critical part. The presence of an additional background has been well established for fluids near the gas-liquid critical point.[10] A similar background is to be expected in binary liquids near the critical point as argued empirically by Chang *et al.*[11] and demonstrated theoretically by Oxtoby and Gelbart,[12] but it was not considered by Chen *et al.* and Sorensen *et al.* Moreover, the apparent good agreement with the theory, as reported by Sorensen *et al.* was based on viscosity data that differed appreciably from the viscosity data earlier reported by other investigators.[7]

II. LIGHT-SCATTERING MEASUREMENTS

In an attempt to resolve this issue, we have made an analysis of the constant R for the 3-methylpentane-nitroethane system. An accurate determination of the correlation length ξ for this system was reported in a previous publication.[13] Using the same sample and optical cell, we determined the decay rate of the concentration fluctuations by measuring the auto correlation function of the scattered light intensity. Light of a He-Ne laser was focused at the center of the sample cell after passing through an intensity stabilizer, consisting of a variable attenuator with a servo loop. Light scattered at three different scattering angles (29.8°, 89.5°, and 146.8°) was detected by a photomultiplier tube whose signal was analyzed by a clipped correlator with 128 channels connected to a mini computer. From the measured intensity correlation function one can deduce the square of the electric-field correlation function after subtracting the baseline. This baseline was determined from the number of counts in the 128th channel, located at a delay time corresponding to 10 decay times. It was also deduced from the total number of incident counts and clipped counts and the duration of an experimental run. The two determinations agreed within their statistical uncertainty of 0.1%. The variable attenuator enabled us to conduct the measurements as a function of incident intensity and to extrapolate the results to zero intensity, thus eliminating local-heating effects.[7,13] To enhance the accuracy, the signal from the photomultiplier tube was calibrated for any afterpulsing effects by measuring the correlation function of a thermal white light source. In principle, light will be scattered not only from the incident beam, but also from the beam reflected at the cell wall. This effect was negligibly small at the scattering angles of 29.8° and 89.5°, but a correction to the data obtained at 146.8° was required. At most temperatures, the experimental correlation function data could be fit to an exponential decay law yielding a decay rate Γ with a precision of fractions of 1%; however, the accuracy of Γ, as judged from the spread of the data obtained at different scattering angles, is about 2%. Owing to the small scattering cross section of our sample, the effect of multiple scattering on Γ was found to be negligible for the data reported here.

III. VISCOSITY

In Fig. 1 we show the original viscosity data as measured by Stein *et al.*[14] and by Tsai and McIntyre[15] at the critical concentration as a function of temperature. The measurements of Tsai and McIntyre have a high precision, but Stein *et al.* paid more attention to the calibration of the viscosity on an absolute basis. Hence, the most accurate values are obtained by shifting the data of Tsai and McIntyre about 3%, so as to conform to Stein's calibration.[16] Subsequently, Sorensen *et al.* reported viscosity data that were 7% larger[7] and, coincidentally, agreed with preliminary data earlier obtained by Tsai and McIntyre.[17] Hence it became necessary for us to check the viscosity.

The viscosity was measured using the same method earlier used for measuring the viscosity of a mixture near a tricritical point.[18] Mixtures of 3-methylpentane-nitroethane at the critical concentration were prepared and the viscosity was determined from the flow rate of samples of about 1 cm^3 in a syringe with needles of two different gauges (21 and 22) at four different temperatures.

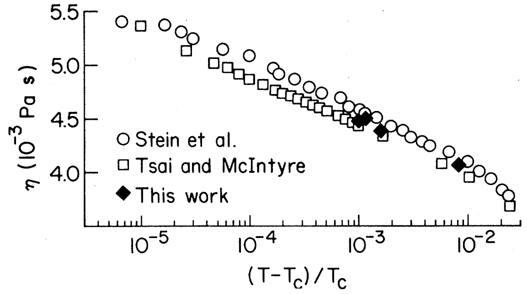

FIG. 1. Viscosity of 3-methylpentane-nitroethane at the critical concentration as a function of temperature.

The method yielded kinematic viscosities which were converted to dynamic viscosities with the densities measured by Greer and Hocken.[19] The results are included in Fig. 1 and they agree within error with the data from the literature as discussed above. Whereas the accuracy of our data is only 2%, they definitely rule out the values suggested by Sorensen *et al.*,[7] so that we can continue to rely on Stein's calibration.[20]

The viscosity η can be represented by an equation of the form[21]

$$\eta = \bar{\eta}(q_D \xi)^{x_\eta} \tag{2}$$

where $\bar{\eta} = A \exp(B/kT)$ is the background viscosity ($A = 2.431 \times 10^{-3}$ Pa s, $B = 1.133$ J), x_η the critical viscosity exponent, and q_D a constant. Representing the correlation length by a power law $\xi = \xi_0 [(T - T_c)/T_c]^{-\nu}$ with $\xi_0 = 0.228$ nm and $\nu = 0.625$ as determined previously,[12] we obtain $x_\eta = 0.0635 \pm 0.0004$ and $q_D = (1.35 \pm 0.18)$ nm^{-1}, where the quoted errors are two standard deviations.

IV. INTERPRETATION OF RESULTS

In order to interpret the data, we separate the decay rate Γ into a critical contribution Γ_c and a background contribution Γ_B as indicated by Oxtoby and Gelbart[12]

$$\Gamma = \Gamma_c + \Gamma_B = \Gamma_c(1 + 3C/4q_D\xi), \tag{3}$$

where, for the range of our data, C may be approximated by the constant value 0.90 to within about 3%. This procedure allows us to estimate Γ_B to within 15%; since at the temperatures of our experiment the contribution of Γ_B to Γ varies from 0.5% to 5%, the resulting errors in Γ_c are within 0.1% to 0.8%.

The decay rate Γ_c is related to the critical part of the diffusion coefficient D, defined in (1), by $D = \lim_{x\to 0}\Gamma_c/q^2$, where q is the wave number and $x = q\xi$. Hence, the coefficient R may be determined from

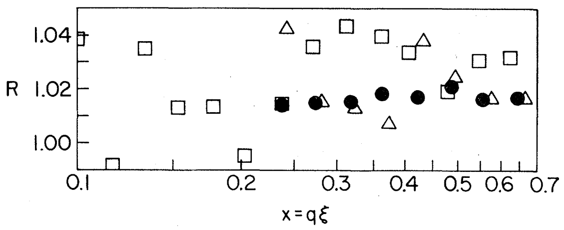

FIG. 2. The coefficient $R(x)$ as a function of x for small values of $x=q\xi$, deduced from the light-scattering measurements at 29.8° (squares), 89.5° (circles), and 146.8° (triangles).

$$R=\lim_{x\to 0} R(x)=\lim_{x\to 0}\left(\frac{\Gamma_c}{q^2 K_0(x)}\right)\frac{6\pi\eta\xi}{kT}, \tag{4}$$

where we have approximated the dependence of Γ_c on x by the Kawasaki function[2]

$$K_0(x)=(3/4x^2)\,[1+x^2+(x^3-x^{-1})\arctan x]\,.$$

Since $\lim_{x\to 0}K_0(x)=1$, this choice does not affect the limiting value of R. In Fig. 2 we show the values of $R(x)$ as deduced from our experimental data as a function of x in the range $0.1\leqslant x\leqslant 0.7$, which corresponds to a temperature range $0.017\leqslant T-T_c\leqslant 0.8$ K. The data in this range are independent of x, within the experimental accuracy, indicating that the Kawasaki function yields a good approximation to the x dependence for small x. Averaging the experimental data, we find $R=1.021\pm 0.026$, where the quoted error represents two standard deviations. Allowing for a 2% error in the correlation length[22] and a 1.5% error in Stein's calibration of the viscosity data, we conclude $R=1.02\pm 0.06$.

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

[2] K. Kawasaki, Ann. Phys. (N.Y.) 61, 1 (1970); R. A. Ferrell, Phys. Rev. Lett. 24, 1169 (1970).

[3] K. Kawasaki and S. M. Lo, Phys. Rev. Lett. 29, 48 (1972).

[4] E. D. Siggia, B. I. Halperin, and P. C. Hohenberg, Phys. Rev. B 13, 2110 (1976).

[5] H. J. M. Hanley, J. V. Sengers, and J. F. Ely, in *Thermal Conductivity 14*, edited by P. G. Klemens and T. K. Chu (Plenum, New York, 1976), p. 383; R. S. Basu and J. V. Sengers in *Proceedings of the 7th Symposium on Thermophysical Properties*, edited by A. Cezairliyan (ASME, New York, 1977), p. 822.

[6] S. H. Chen, C. C. Lai, and J. Rouch, J. Chem. Phys. 68, 1994 (1978).

[7] C. M. Sorensen, R. C. Mockler, and W. J. O'Sullivan, Phys. Rev. Lett. 40, 777 (1978).

[8] D. Beysens, R. Tufeu, and Y. Garrabos, J. Phys. (Paris), Lett. 40, L-623 (1979).

[9] L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Pergamon, New York, 1959), p. 69.

[10] J. V. Sengers and P. H. Keyes, Phys. Rev. Lett. 26, 70 (1971); H. L. Swinney and D. L. Henry, Phys. Rev. A 8, 2586 (1973).

[11] R. F. Chang, P. H. Keyes, J. V. Sengers, and C. O. Alley, Phys. Rev. Lett. 27, 1706 (1971); Ber. Bunsenges. Phys. Chem. 76, 260 (1972).

[12] D. W. Oxtoby and W. M. Gelbart, J. Chem. Phys. 61, 2957 (1974).

[13] R. F. Chang, H. Burstyn, and J. V. Sengers, Phys. Rev. A 19, 866 (1979).

[14] A. Stein, J. C. Allegra, and G. F. Allen, J. Chem. Phys. 55, 4265 (1971).

[15] B. C. Tsai and D. McIntyre, J. Chem. Phys. 60, 937 (1974).

[16] G. F. Allen and D. McIntyre (private communication).

[17] B. C. Tsai, Master's thesis, University of Akron, 1970 (unpublished).

[18] M. W. Kim, W. I. Goldburg, P. Esfandiari, and J. M. H. Levelt Sengers, J. Chem. Phys. 71, 4888 (1979).

[19] S. C. Greer and R. Hocken, J. Chem. Phys. 63, 5067 (1975).

[20] In view of this result Sorensen remeasured the viscosity and also found agreement with Stein *et al.*, (S. C. Sorensen, private communication).

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

[22] This error in ξ is identified with the error in ξ_0 when the light-scattering intensity data in Ref. 13 are fit with fixed exponent values.