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[21] If the Wu and Webb (Ref. 20) viscosity is used, the rms deviation of the data from the theory (with ξ from Ref. 17) is 20%; the deviation is especially large (32%) near T_c.

Spectrum and Intensity of Light Scattered from Sulfur Hexafluoride along the Critical Isochore*

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We have measured the thermal diffusivity (D), the isothermal compressibility (κ_T), and the pressure (P) along the critical isochore of sulfur hexafluoride over the temperature range $0.048°\mathrm{K} < (T - T_c) < 2.4°\mathrm{K}$. We find that $\kappa_T = 1.26 \times 10^{-9}(T/T_c - 1)^{-1.235 \pm 0.015}$ cm^2/dyne and that $(\partial P/\partial T)_V = [7.91 + 0.18(T - T_c) \pm 0.1] \times 10^5$ dyne/cm^2 deg. We discuss our measurements of D in terms of the Kadanoff-Swift-Kawasaki mode-mode coupling theory.

Using the techniques of optical mixing spectroscopy,[1] we have measured the spectrum of light scattered quasielastically from thermal entropy fluctuations in sulfur hexafluoride at critical density over the temperature range $0.048°\mathrm{K} < T - T_c < 2.4°\mathrm{K}$. From these measurements we have deduced the magnitude and temperature dependence of the thermal diffusivity (D) along the critical isochore. From the intensity of the scattered light we have deduced the temperature dependence of the isothermal compressibility (κ_T) along the same path. Finally, we have measured the pressure (P) as a function of temperature and have obtained accurate values for $(\partial P/\partial T)_V$ on the critical isochore.

In our experiment, light from an intensity-stabilized He-Ne laser enters a high pressure optical cell at an incidence angle of 2.42° to the normal of the entrance window. A focusing lens near the exit window of the cell images the scattering region on the entrance aperture of a photomultiplier tube. A second aperture, located in the focal plane of this lens, selects (with angular spread $\Delta\theta/\theta = 0.1$) the scattering angle ($\theta$) and thereby determines the wave vector ($\vec{K}$) of the entropy fluctuation whose scattering is observed. The alignment procedure is such that the scattered rays accepted by the collection optics make the same angle with the window normal as does the transmitted beam. This procedure ensures first that the scattering vector $\vec{K}$ is independent of the index of refraction of the fluid and second that the ratio of the intensity of the scattered light collected to the intensity of the transmitted beam is independent of optical attenuation in the sample. In our experiment, $K = 8380$ cm^{-1}.

The sample cell was filled to within 0.1% of critical density with sulfur hexafluoride of impurity content <20 ppm. Temperatures were measured with a platinum resistance thermometer in accordance with the 1948 International Practical Temperature Scale, and the critical temperature (T_c) was determined to be $318.707 \pm 0.002°\mathrm{K}$ by direct observation of the disappearance of the meniscus.

At constant density, the isothermal compressibility κ_T is proportional to the ratio of the intensity of scattered light to transmitted light.[2] Our data for the temperature dependence of κ_T along the critical isochore are shown in Fig. 1. The compressibility accurately obeys the power law $\kappa_T = C_0(T/T_c - 1)^{-\gamma}$ with $\gamma = 1.235 \pm 0.015$. This value of γ is in good agreement with the results of Puglielli and Ford[3] who obtain $\gamma = 1.225 \pm 0.02$ from turbidity measurements. In plotting Fig. 1, we have chosen a value of $C_0 = 1.26\times10^{-9}$ cm^2/dyne such that our results are in numerical agreement with the PVT data of MacCormack and Schneider[4] at $T - T_c = 1.453$°K.

We have also measured the pressure P at each of our data points using a Baldwin-Lima-Hamilton strain-gauge pressure transducer. Over the temperature range of our measurements $(\partial P/\partial T)_V$ is nearly constant and may be accurately represented by the formula $(\partial P/\partial T)_V = [7.91 + 0.18(T - T_c) \pm 0.1]\times 10^5$ dyne/cm^2 deg along the critical isochore.

The spectrum of the quasielastically scattered light is a Lorentzian of half-width Γ in radians per second. Because our scattering angle θ is small, the Ornstein-Zernike correlation range (ξ) satisfies the inequality $(K\xi)^2 \ll 1$ over the entire temperature range of our measurements. As a result, Γ directly measures the thermal diffusivity $D \equiv \Lambda/\rho c_p$ through the relation $\Gamma = DK^2$.[5] Here Λ is the thermal conductivity, ρ the mass density, and c_p the specific heat per unit mass at constant pressure. The linewidth Γ is determined from the photocurrent spectrum using the technique of self-beating spectroscopy.[1] We are satisfied that the heterodyne contribution to the photocurrent spectrum is negligibly small in our experiment.

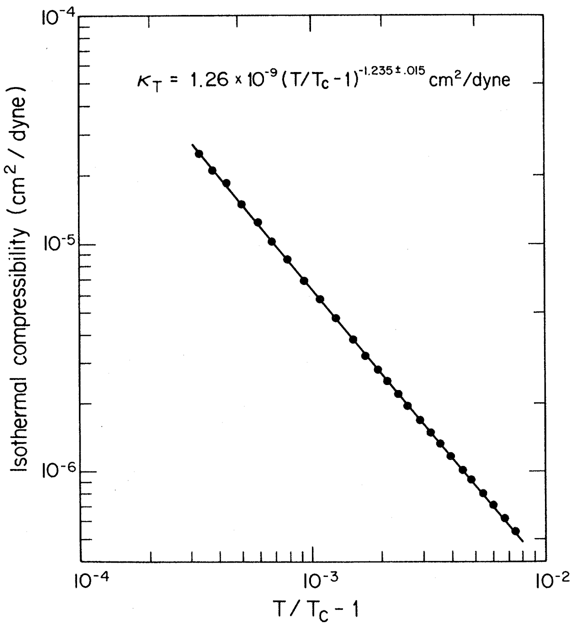

FIG. 1. Isothermal compressibility κ_T along the critical isochore of sulfur hexafluoride as a function of the reduced temperature $(T/T_c - 1)$.

Our measurements of the thermal diffusivity D are shown as a function of $T - T_c$ in the upper portion of Fig. 2. The uncertainty of each value of D is approximately 2%. These results are larger at all temperatures and are different in curvature than results previously reported along the critical isochore by Saxman and Benedek,[1,6] who found $\Lambda/\rho c_p = 1.26\times10^{-2}(T/T_c - 1)^{1.26}$ cm^2/sec for $0.040°\mathrm{K} < T - T_c < 5°\mathrm{K}$. For purposes of comparison, our data can be approximated by the formula $\Lambda/\rho c_p = 1.22\times10^{-3}(T/T_c - 1)^{0.78}$ cm^2/sec in the temperature range $0.048°\mathrm{K} < T - T_c < 0.3°\mathrm{K}$. It should be recognized, however, that a simple power law does not adequately represent our data over the full temperature range, as may be seen from the upper curve in Fig. 3 which is a logarithmic graph of our data for the thermal diffusivity. We have not yet discovered a convincing explanation for the discrepancy between our results and those reported previously. We have observed that large, artificially introduced temperature gradients in the cell can cause the apparent linewidths to approach those of Refs. 1 and 6. However, we feel that the temperature gradients necessary to produce this effect are substantially

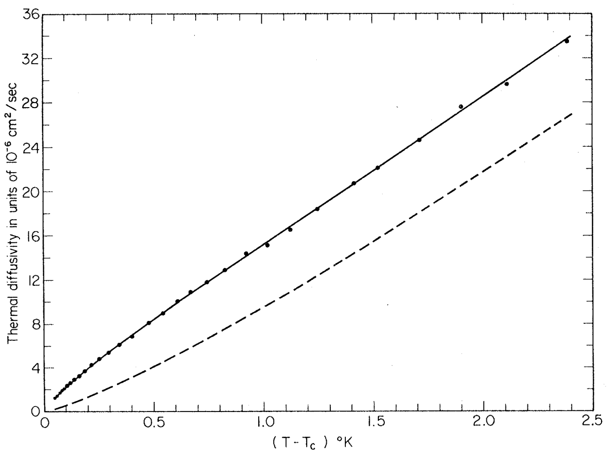

FIG. 2. Upper curve, our data for the thermal diffusivity $D = \Lambda/\rho c_p$ along the critical isochore of SF_6. Lower curve, the background contribution $\Lambda_B/\rho c_p$ to the thermal diffusivity which arises from the nondivergent component of the thermal conductivity.

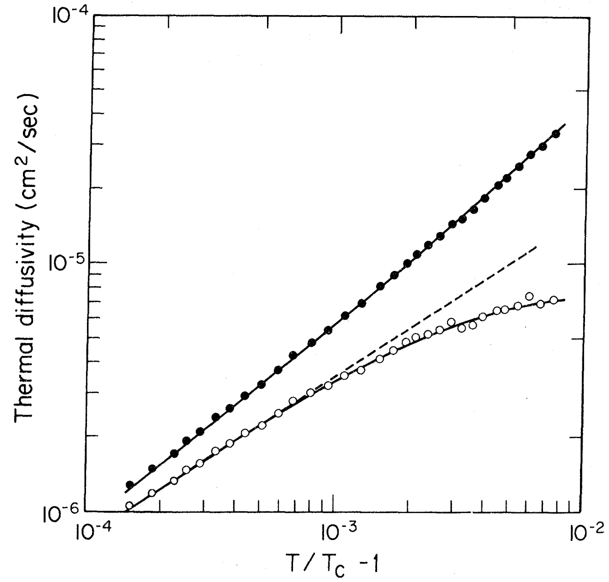

FIG. 3. Upper curve, a logarithmic plot of our data for the total thermal diffusivity D. Lower curve, the critical contribution D_c to the thermal diffusivity obtained from our data by taking account of the background contribution $\Lambda_B/\rho c_p$. The straight (dashed) line represents $k_BT/6\pi\eta^*\xi$ for the values of η^* and ξ discussed in the text.

larger than those encountered by Saxman and Benedek.

We may analyze our data for $D=\Lambda/\rho c_p$ in terms of the Kadanoff-Swift-Kawaskaki mode-mode coupling theory,[7,8] as has already been done for the fluids CO_2[9] and Xe.[10-12] For this purpose, we must take into account the background contribution to the thermal diffusivity which arises from the nondivergent part (Λ_B) of the thermal conductivity.[6,13] This contribution is given by $\Lambda_B/\rho c_p$ and is shown as the lower curve in Fig. 2. The value $\Lambda_B=(3.29\pm0.1)\times10^3$ erg/cm deg sec was obtained from an interpolation[6] of the thermal conductivity data of Tauscher[14] and of Lis and Kellard.[15] The specific heat c_p was determined from the thermodynamic relation $\rho c_p = \rho c_v + T\kappa_T(\partial P/\partial T)_V{}^2$ by using our data for $(\partial P/\partial T)_V$ and κ_T and by estimating c_v from the sound velocity measurements of Fritsch and Carome.[16] The uncertainty in $\Lambda_B/\rho c_p$ is approximately 10%.

The lower curve in Fig. 3 represents our experimental deduction of the critical contribution to the thermal diffusivity $D_c=[(\Lambda/\rho c_p)-(\Lambda_B/\rho c_p)]\times[c_p/(c_p)_s]$. In this formula, $(c_p)_s$ is the divergent or singular component of the specific heat. If, as suggested by Sengers,[13] we identify $(c_p)_s$ with $c_p - c_v$, then the ratio $c_p/(c_p)_s$ is nearly unity over the temperature range of our measurements. According to current interpretations of the mode-mode coupling theory,[9-13] D_c is predicted to be $k_BT/6\pi\eta^*\xi$ in the hydrodynamic regime. Here, k_B is Boltzmann's constant and η^* is a high frequency shear viscosity.

At present it is difficult to determine the validity of the Kawasaki prediction $D_c=k_BT/6\pi\eta^*\xi$ because the value of η^* is not well established and the correlation range ξ has been measured only over a small temperature range.[3] On the other hand, it is interesting to observe that for $0.048°K < T-T_c < 0.5°K$ the exponent describing D_c is 0.64 ± 0.04. This value is consistent with the critical exponent (ν) for the correlation range ξ found by Puglielli and Ford $(\nu=0.67\pm0.07)$ as would be expected for a constant value of η^*. Furthermore, the magnitude of η^* required to fit $k_BT/6\pi\eta^*\xi$ to our data for D_c is approximately 400 ± 50 μP provided we use the values of ξ listed in Ref. 3. On the basis of available low frequency viscosity data,[17] this value of η^* is not unreasonable.[12]

The power law extrapolation of $k_BT/6\pi\eta^*\xi$ is shown as a dashed line in Fig. 3. It is important to observe the marked departure of D_c from a power law behavior for temperatures above $T-T_c=0.5°K$. This rapid departure is not characteristic of the fluids Xe and CO_2 for which a similar analysis is known to apply several degrees above T_c.[9-12]

Preliminary data reported in July 1971 by Mohr and Langley[18] are consistent with the results of this investigation (see also preceding Letter). Braun *et al.* have also reported measurements of the thermal diffusivity along the critical isochore of sulfur hexafluoride.[19]

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Droplet Model Near T_c : Droplet-Droplet Interaction and Correlation Function

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In the equation of state of a real gas near its critical point the "excluded-volume" effect is taken into account for the droplet-droplet interaction in the droplet model. Considering the hard-sphere repulsion between droplets as a small perturbation ("second virial coefficient") we find the scaling laws to be unchanged. No renormalization of the critical exponents occurs. With an additional attraction between the droplets, the corrections to the asymptotic scaling laws are in agreement with those of Green, Cooper, and Levelt Sengers and Mermin and Rehr.

The semiphenomenological mode-mode coupling theory of transport properties near a critical point[1-4] is based on the idea that a transport mode is coupled to two order-parameter fluctuations. The interaction between these order-parameter fluctuations is usually neglected, for example by factorizing a correlation function involving four Fourier components of the fluctuations.[3,4] Nevertheless this simple approximation gives the same critical exponents as the phenomenological theory of dynamical scaling,[5] since the critical behavior is already built into the phenomenological *Ansatz* made for the order-parameter fluctuations. The static analog to the dynamic mode-mode coupling theory seems to us to be the droplet model,[6] where also the interaction between different droplets (which are the analogs of order-parameter fluctuations) is neglected. This model is known to give the static scaling laws[6] and good quantitative agreement[7] with experiment in gases below and at T_c. To support this analogy, we estimate in this Letter the influence of the interaction between the droplets as a small perturbation and show that it does not renormalize the critical exponents. Also the higher-order terms and convergence questions are discussed. From the attractive part of the interaction we find corrections to the asymptotic scaling laws, which are negligible very near T_c; their critical exponents agree with those found by Green, Cooper, and Levelt Sengers[8] and Mermin and Rehr,[9] including the law of the nonanalytic rectilinear diameter. For the density correlation function we also show that one can get the desired scaling behavior (deviations from Ornstein-Zernike theory) if one employs an Ornstein-Zernike-like *Ansatz* for the correlation due to given droplet sizes, the scaling behavior arising because of the summation over all droplet sizes.

The droplet model[6] is based on the idea that a gas near its critical point consists of droplets containing l molecules; the number of droplets per unit volume, n_l, is assumed proportional to $\exp[-(f_l-\mu l)/kT]$. The droplet free energy f_l