SELF-DIFFUSION IN ETHANE NEAR THE CRITICAL POINT[*]

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One of the interesting transport properties of a fluid is its self-diffusion constant D. Yet, insofar as we know, there exist no experimental measurements of D near the critical temperature T_c for any fluid. Furthermore, no theoretical estimates have been published of the anticipated order of magnitude of an anomaly in D near T_c for any fluid. In view of the great interest aroused recently by the success of the lattice gas model in interpreting critical-point phenomena in fluids,[1,2] it seems worthwhile to investigate the behavior near T_c of transport properties such as the diffusion constant.

We present below experimental evidence for the anomalous behavior of D for ethane, C_2H_6, near T_c. It should be said in advance that our samples were not quite pure, approximately 1% of oxygen impurity having been introduced deliberately for experimental reasons to be described below. However, the large effect observed and the specific qualitative nature of the effect may be of assistance in arriving at some understanding at the molecular level of the behavior of fluids near their critical points.

Method of measurement and sample purity.— The well-known spin-echo technique was used for measuring the (spin) self-diffusion constant.[3-5] A factor which limits the accuracy of the measurements in pure ethane is the long proton spin-lattice relaxation time T_1, which is approximately 30 seconds near the critical point. For this reason approximately 1% O_2 was added to the Phillips research-grade (99.99% pure) sample. This reduced T_1 to about 1 second, which made possible an accuracy of better than 5% in the measurement of D. The same procedure has been followed by others[6] in measurements of D in the liquid along the vapor-pressure curve well below T_c. An additional measurement made possible by the nuclear-magnetic-resonance technique, and important in the interpretation of the diffusion data, was the measurement (to within ±2%) of the density ratio ρ_L/ρ_V of the liquid and vapor in equilibrium below T_c from the relative strengths of the nuclear-magnetic-resonance signals. These measurements in pure ethane agreed with density measurements previously reported for pure ethane,[7] which gave $T_c = 32.32°\mathrm{C}$. ρ_L/ρ_V for the pure and impure samples were equal, within experimental error, below 30°C.

Sample geometry and temperature control.— The samples were contained in glass tubing having 1-mm wall thickness, 6-mm outside diameter, and length 8 to 9 cm. The rf measuring coils, each 1 cm long, were wound on the glass tube 3 cm apart. The samples filled to the critical density were mounted vertically in a sample holder whose temperature could be regulated to 0.01°C indefinitely, and in which the maximum temperature gradient across the sample was less than 0.004°C. For most of the measurements near T_c, the sample was first kept at constant temperature for at least 24 hours to establish equilibrium. A second set of measurements was usually made at the same temperature after waiting an additional 24 hours or longer. This precaution was nec-

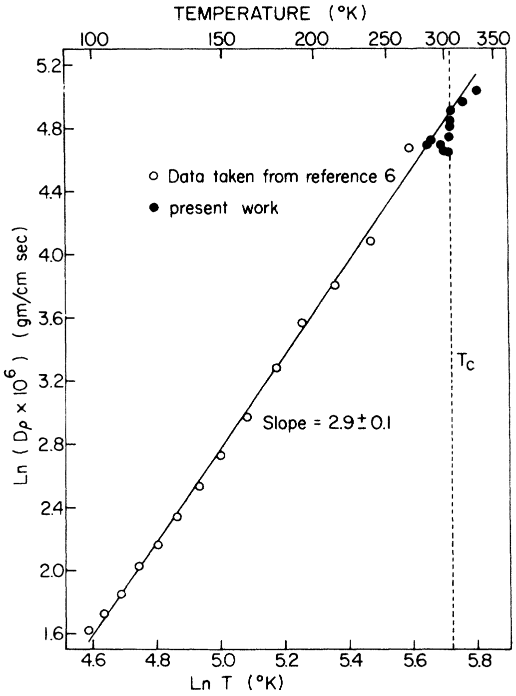

FIG. 1. Plot of $\ln(D\rho)$ versus $\ln T$. The points below 0°C are based on a smooth curve drawn through the diffusion-constant data of reference 6.

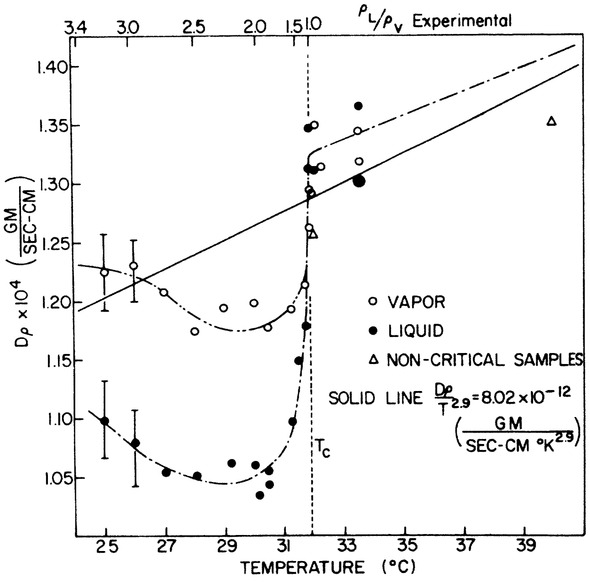

FIG. 2. Temperature dependence of $D\rho$ near T_c. Measured values of ρ_L/ρ_V are also shown. The samples used were loaded to the critical density. Measurements of $D\rho$ based on the slopes of $1/D$-versus-ρ plots at 32 and 40°C using noncritically loaded samples are also shown.

essary. When a sample initially in equilibrium at 23.50°C was quickly warmed to 31.92°C, ρ_L/ρ_V attained a value of 1.6 within less than one hour, and then approached its equilibrium value of unity exponentially with a time constant of eight hours.

Measurements.—Experiments performed at 32 and 40°C in noncritically loaded samples showed that $D \propto \rho^{-1}$ in the range $\frac{1}{2}\rho_c < \rho < 2\rho_c$, where $\rho_c = 0.207$ g/cm³ is the critical density. Thus $D\rho$ is a function of temperature only in this density range. A plot of $\ln(D\rho)$ versus $\ln T$ from just above the melting point at 89.9 to 333°K, approximately 30°K above the critical point, is shown in Fig. 1. The resulting straight line gives $D\rho \propto T^{2.9 \pm 0.1}$. This is an empirical relationship which does not necessarily hold for other substances. Figure 2 gives a plot of $D\rho$ versus T in the temperature region within a few degrees of T_c. A comparison with the results of Fig. 1, as given by the solid line of Fig. 2, shows that $D\rho$ goes through a pronounced minimum for the liquid just below T_c with its minimum value about 20% below the solid line. A similar but smaller effect is observed for the vapor but, unlike the data for the liquid, we cannot say definitely that the vapor minimum is not due to a systematic error, which we estimate to be less than 5%.

It may be seen from the measured values of ρ_L/ρ_V that the anomalous decrease in $D\rho$ as the temperature is increased to 31°C is due primarily to a decrease in ρ_L with very little change in D. Then, the diffusion constant increases by approximately 50% between 31 and 31.9°C. A single measurement of D for a pure sample at 24°C having an error of ±10% agrees with D for the impure sample.

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