SELF-DIFFUSION MEASUREMENTS IN CRITICAL ARGON

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The purpose of this Letter is to present and discuss a set of experimental data on the self-diffusion in critical argon. Such measurements have been performed in order to examine the behavior of a simple fluid in the vicinity of the critical point and decide if any peculiar change of mechanism for self-diffusion is observed.

The method of measurement and the apparatus are described in detail elsewhere.[1,2] The experiments are carried out by means of a tracer technique in argon flowing in a capillary with a mean velocity of about 0.1 mm/sec. An Ar^{36} concentration step is initially produced in the flowing gas at the capillary inlet. The diffusion coefficient D is deduced from the shape of the concentration step at the outlet end of the capillary, as measured by a mass spectrometer. The fluid is maintained at a preset temperature constant within 0.001°C. The absolute temperature is known within 0.05°C. The density ρ is measured with an error of about 1%. The temperature and the density of each run are compared, through a precise pressure measurement, with the available PVT data.[3] The accuracy of the diffusion-coefficient measurements is ±5%. In Fig. 1 the experimental results are reported in a graph of $1/D$ versus ρ; it is seen that within the experimental error no difference exists between the "critical" and "noncritical" data. The data which lie in the temperature range $T=T_C \pm 0.1°\mathrm{C}$ (T_C = critical temperature = 122.29°C) and in the density range $\rho = \rho_C \pm 10\%$ (ρ_C = critical density = 300.4 amagat units) have been considered "critical." A theory of the self-diffusion coefficient of a pure fluid in the neighborhood of the critical point has been developed by Kawasaki,[4] using the Ising lattice model. This calculation shows that a large anomaly in the self-diffusion coefficient is not expected. On the other hand, the author suggests a possible sharp discontinuity in the first derivative of D versus the temperature.

Giterman and Gertsenshtein[5] have studied the effect of the critical fluctuations on the Brownian motion of a particle in a pure substance. From their calculation it can be deduced that the diffusive path is essentially unperturbed as long as diffusion times large in comparison with a characteristic fluctuation time t are considered. This characteristic time is defined as

$$t = (\tfrac{4}{3}\eta + \zeta)\alpha, \tag{1}$$

where η and ζ are the shear and volume viscosities and α is the compressibility of the fluid.

Since α sharply increases to infinity approaching the critical point, from Eq. (1) a sharp change in D as a function of temperature is expected. However, in a typical fluid for $(T-T_C)/T_C = 10^{-5}$, which reasonably is the closest experimental approach to the critical point, t is still about 10^{-4} sec. In an ordinary diffusion measurement the diffusion time ranges from about 1 sec (for nmr techniques) to 10^4 sec (for tracer techniques), so that no appreciable change of D in the neighborhood of the critical point should be observed. A different situation is that of the binary diffusion of impurities in a critical fluid. In this case, consistent with theory,[4] the diffusion coefficient falls to zero[6] approaching the critical point.

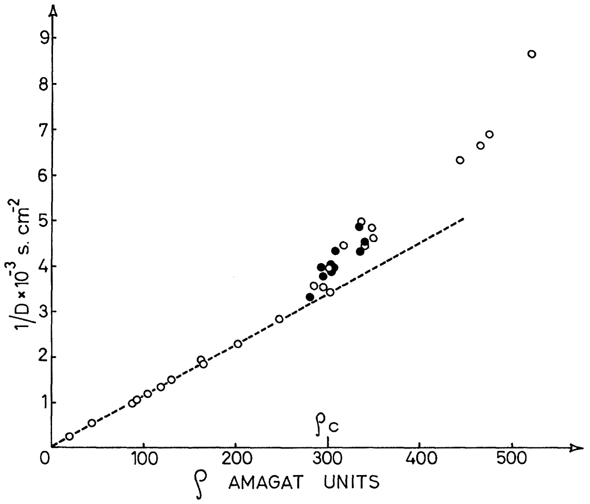

FIG 1. The self-diffusion coefficient of Ar in the critical region. The dotted line represents the behavior of an ideal gas following the Chapman-Enskog theory. Solid circles, critical-region data; open circles, noncritical data.

The critical effects start to be measurable at $(T-T_c)/T_c \sim 10^{-3}$. This behavior is similar to that of the binary diffusion coefficient of two liquids approaching the critical point of separation,[7] which falls to zero as predicted by theory.[8] This similarity is not surprising since there is experimental evidence for a phase separation of impurities in the neighborhood of the critical point of a fluid,[9] arising from the large density fluctuations.

Previous self-diffusion measurements in the critical region have been carried out by a nmr technique on C_2H_6[10] and on CH_4.[11] While in CH_4, as in Ar, no appreciable change in the critical region was observed, in C_2H_6 a decrease of D amounting to about 50% was found. Such a discrepancy could arise from the technique employed for C_2H_6. In fact, to reduce the proton spin-lattice relaxation time, 1% of O_2 was added to the sample. Bearing in mind the above considerations on the behavior of impurities in the critical region, one should regard these data as diffusion of O_2 in C_2H_6.

Finally, Modena and Ricci have recently reported that the mobility of electrons in He^3 shows a smooth decrease of 30% in the critical region.[12] In these measurements the motion of the electronic bubble is due to the driving force of the applied electric field. Unless a frictional mechanism is assumed for the diffusion in the fluid, the resulting viscous motion of the bubble cannot be compared with a diffusive process. The measurements are in good agreement with the observed behavior of viscosity of CO_2, which increases smoothly in the critical region.[13]

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SUPPRESSION OF A TWO-STREAM INTERACTION IN A BEAM-PLASMA SYSTEM BY EXTERNAL ac ELECTRIC FIELDS

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We report an experimental study of the interactions between ion-acoustic waves excited in a beam-plasma system and externally applied ac electric fields. This ac electric field is introduced into the plasma through a beam modulation. The nonlinear interactions described here are the modulation and asynchronous quenching of the ion-acoustic waves and the subharmonic resonance of the applied signals or so-called parametric resonances.[1]

The experimental arrangement is shown in Fig. 1. A cylindrical discharge tube (made of glass) of the hot-cathode type was used with an electron gun. The accelerating electrode E_3 of the gun in Fig. 1 worked as an anode for the main discharge in pair with the hot cathode K. A plasma was produced by means of a hot-cathode mercury discharge at the current I_d from 1 to 100 mA; the plasma density was in the range 10^8-10^9 cm^{-3} at the background pres-