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NEAR-CRITICAL POINT PHENOMENA IN FLUIDS
(19-IML-1)

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Understanding the effects of gravity is essential if we are to predict the behavior of fluids in spacecraft and orbital stations, and, more generally, to give us a better knowledge of the hydrodynamics in these systems. This is the general goal of our study, namely, to understand the behavior of fluids in space. In order to get more general results, we use fluids near their critical point.

What is the critical point?

The simplest way to describe the critical point is to consider the different states of matter: solid, liquid, and gas (Figure 1). These states are delimited by transition lines. It is well known that these lines meet at the 'triple point' where the three phases -- solid, liquid, and gas -- coexist. There is, however, another situation which occurs when liquid and vapor phases coexist. If the temperature and pressure are increased to a high enough level, a point beyond which both liquid and gas phases become indistinguishable is reached. This is the "critical point" where the meniscus between the two phases vanishes. The critical point is located at a particular value of pressure, temperature and density in different substances. The critical point of water, for example, is at a high temperature and pressure (370 °C and 220 bar); it is near room temperature in other substance like carbon dioxide CO_2 (31 °C and 74 bar) or sulphur hexafluoride SF_6 (45 °C and 38 bar).

Universality of critical point behavior

The behavior of all fluids near their critical point becomes the same and is very unusual. The fluid becomes very compressible, fluctuations of density are very large, leading to large fluctuations in the refractive index which means that the system scatters light very much. Fluids look milky, this is the so-called 'critical opalescence' phenomenon.

There is a general reason for these very large fluctuations: the system is so close to the transition point that it "hesitates" between the two equally possible states. The notion of a critical point applies, in fact, to a whole class of systems, where the same kind of behavior can be observed. This applies to all mixtures of partially miscible liquids whose miscibility curve ends in a critical point: mixtures of two simple liquids like water and phenol, or cyclohexane and methanol, micellar solutions (mixtures of water and soap), micro-emulsions (mixtures of water, oil, and soap) and mixtures of molten metals (alloys), as well as to many other fluid systems. In fact all these systems belong to the same 'universal class' whose representative is...a magnet, which undergoes a critical-point transition at the Curie point (the point at which its magnetisation becomes zero). The relevant model is the well known three-dimensional 'Ising model'. All these systems present very close analogies, and the same universal laws apply to their behavior which ultimately depends on the dimensionality of space.

It is important to note that the critical behavior of fluids is not restricted to the immediate vicinity of the critical point. The behavior of fluids can be described in terms of the critical point within a range of more than 100 °C in most of the systems cited above. This is why their study is of interest to many areas, including thermodynamic and transport properties (especially heat and mass transport), and hydrodynamics. The technical implications of these studies are numerous. For example, heat exchangers, oil recovery, the solvent industry, hydrodynamics of two-phase flows, and the processing of polymers, metals and glass, are all dependent on critical point phenomena.

Gravity-sensitive behavior

It is at this point that the experiments in zero-gravity become meaningful. Critical fluids and liquid mixtures are not only critical systems, they are also fluids. And the behavior of fluids on Earth is quite often dictated by gravity. The particularity of critical fluids is that the influence of gravity appears to be very important. This is because some key parameters exhibit extreme values near the critical point:

- compressibility, which makes a pure fluid compressed under its own weight;
- capillary length, where the Earth-bound study of the kinetics of phase separation is governed by gravity flows;
- heat transport, which is slowed down in pure fluids, and mass transport, which also decreases in mixtures of liquids. In pure fluids, the diffusion of heat is so slow that it is the motion of the fluid due to convection that ensures heat transport on Earth.

The liquid mixtures experiment (BEM1) on the IML1 mission

The IML-1 mission offers our team an excellent opportunity to continue our research in this field. We have improved the properties of a naturally near density-matched mixture (cyclohexane and methanol) by partial deuteration of one of the components (cyclohexane) in order to adjust the densities very finely. In this liquid mixture, the critical point is a point of miscibility and the diffusion of the two species is considerably slowed down. Two sounding rocket flights (Texus 11 in 1985 and Texus 13 in 1986) demonstrated that the suppression of gravity effects was effective, at least for the study of the phase separation process by spinodal decomposition (a common process in metallurgy and glass processing). This process occurs in liquid mixtures in the immediate vicinity of the critical point. Thanks to these results, we have been able to carry out a number of ground-based experiments to predict the behavior of phase separating critical mixtures in the absence of gravity. The following areas have in particular been successfully addressed: growth kinetics, the efficiency of partitioning, the effects of capillary and wetting effects by the wall, the influence of a concentration gradient.

For the spinodal decomposition process, the six minutes of microgravity obtained by the use of the Texus rockets were sufficient. However, if the above study is to be extended to the phase separation process in off-critical fluids (nucleation), the kinetics of evolution become much slower and sounding rockets can no longer be used. The aim of the first experiment (BEM1) on IML-1 is, therefore, to check whether the slow growth that is currently observed in the above density-matched system on Earth is due to remaining gravity flows or to a real growth process. For this purpose, a differential experiment will be performed, where the behavior of a slightly off-critical sample of the density-matched mixture of cyclohexane and methanol will be compared with Earth-bound control experiments. For quantitative comparison, the light scattering facility of the CPF will be used in conjunction with the LED illumination (direct observation) and further image analysis. The scenario of the experiment is simple: heat the liquid mixture above its critical temperature (Tc), homogenise it by means of ultrasounds (see Figure 2), lower the temperature to check the value of the critical temperature, and quench the system a few millidegrees below Tc in the unstable region where its phase separates. Then wait to determine the growth kinetics of the two new phases.

The pure fluids experiment (BEM2) on the IML-1 mission

When dealing with pure fluid systems, it is impossible to use the partial deuteration tactic mentioned above since both vapor and liquid are of the same chemical species. Only zero-gravity experiments can remove the effects of gravity. As already noted above, in contrast to liquid mixtures, the liquid-vapor system near its critical point displays a very large anomaly in the heat transport. This anomaly results in very long equilibrium times that are not seen on Earth because heat transport causes very strong convection in the system. The temperature homogenisation of such a system is therefore very important in zero gravity. In order to understand this problem better, we have made a numerical simulation of the hydrodynamic behavior. In this case, our results show that, surprisingly, heat transport is accelerated near the critical point thanks to a phenomenon that we have called the 'Piston Effect'. Our simulation shows that, when heating a fluid to a boundary, only a small layer warms up which expands in the same way as a 'piston'. This 'piston' travels back and forth in the sample cell and converts its energy into heat. Convections accompany this phenomenon and equilibration can be achieved quite rapidly. We have qualitatively demonstrated this effect in an experiment on Texus 25 where thermalisation of a CO_2 sample took less than 10 seconds whereas heat diffusion alone was expected to take 10 days. During the same experiment, we were also able to demonstrate that the kinetics of phase separation of pure fluids, according to the 'spinodal decomposition' process, was the same as that of binary mixtures. No special compressibility effects occurred. It can, therefore, be concluded that all the studies performed with critical density-matched mixtures (see above) can also be applied to pure fluids.

Due to the short duration time of the Texus 25 experiment, valuable information on the long-term homogenization in pure fluids could not be obtained. Moreover, the phase separation of off-critical pure fluids takes too long for investigations to be carried out in sounding rockets. The experiment BEM2 on IML-1 is aimed at investigating these two problems in two samples placed in the same thermostat. The first is filled at a slightly off-critical density with SF_6 for the study of the kinetics of phase separation in off-critical conditions, as in BEM1 but with a pure fluid, and the other is filled with SF_6 at exactly its critical density to study the thermalisation and relaxation of the density inhomogeneities. All samples have a gold thread set inside the cell. This thread is thermally coupled with the thermostat in order to separate the effects in the bulk, around the thread, from the effects of the surface of the window cell. As for the BEM1 experiment, the CPF's light scattering and LED direct observation possibilities will be used with the first cell. Interferometry will be used to measure the density variations in the second cell. In both cases, the scenario will be the same: heating above Tc, waiting until homogenization occurs, stepping down to Tc while studying the relaxation of the density by interferometry, quenching below Tc, and determination, as for the BEM1 experiment, of the kinetics of phase separation.

General results expected from IML-1

What should emerge from the IML-1 mission is a better understanding of the kinetics of growth in off-critical conditions, in both liquid mixtures and pure fluids. This complex phenomenon is the object of intensive investigation in physics and materials sciences area. We also expect that the IML-1 flight will procure key results to provide us with a better understanding of how a pure fluid can be homogenized without gravity-induced convections, and to what extent the 'Piston Effect' is effective in thermalizing the compressible fluids. Ultimately we should be able to decide whether this effect is also responsible for the acceleration of the heat transport on Earth in place of the commonly admitted convection effects.

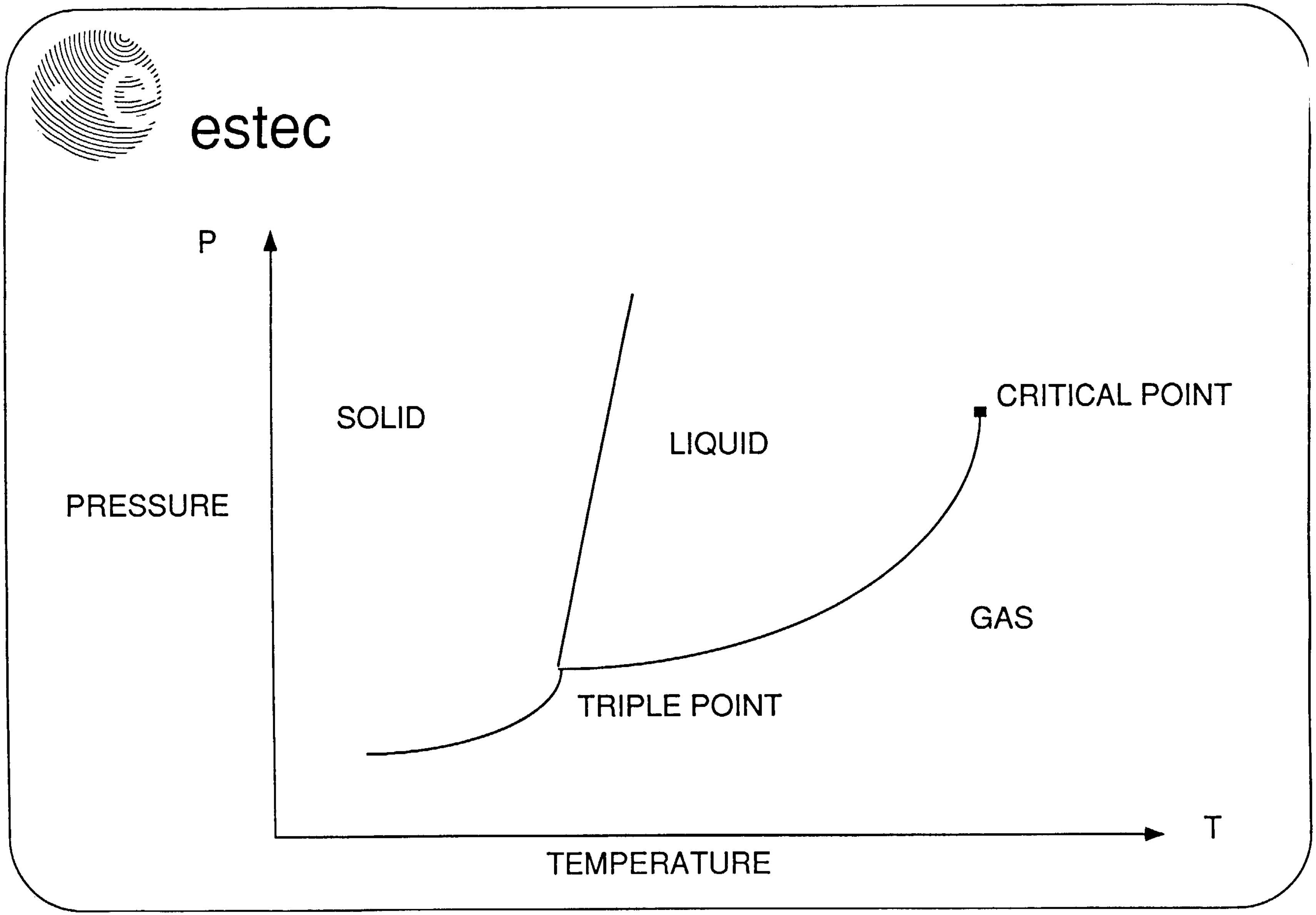

Figure 1. Phase diagram of a pure substance, C.P. = critical point; T.P. = triple point.

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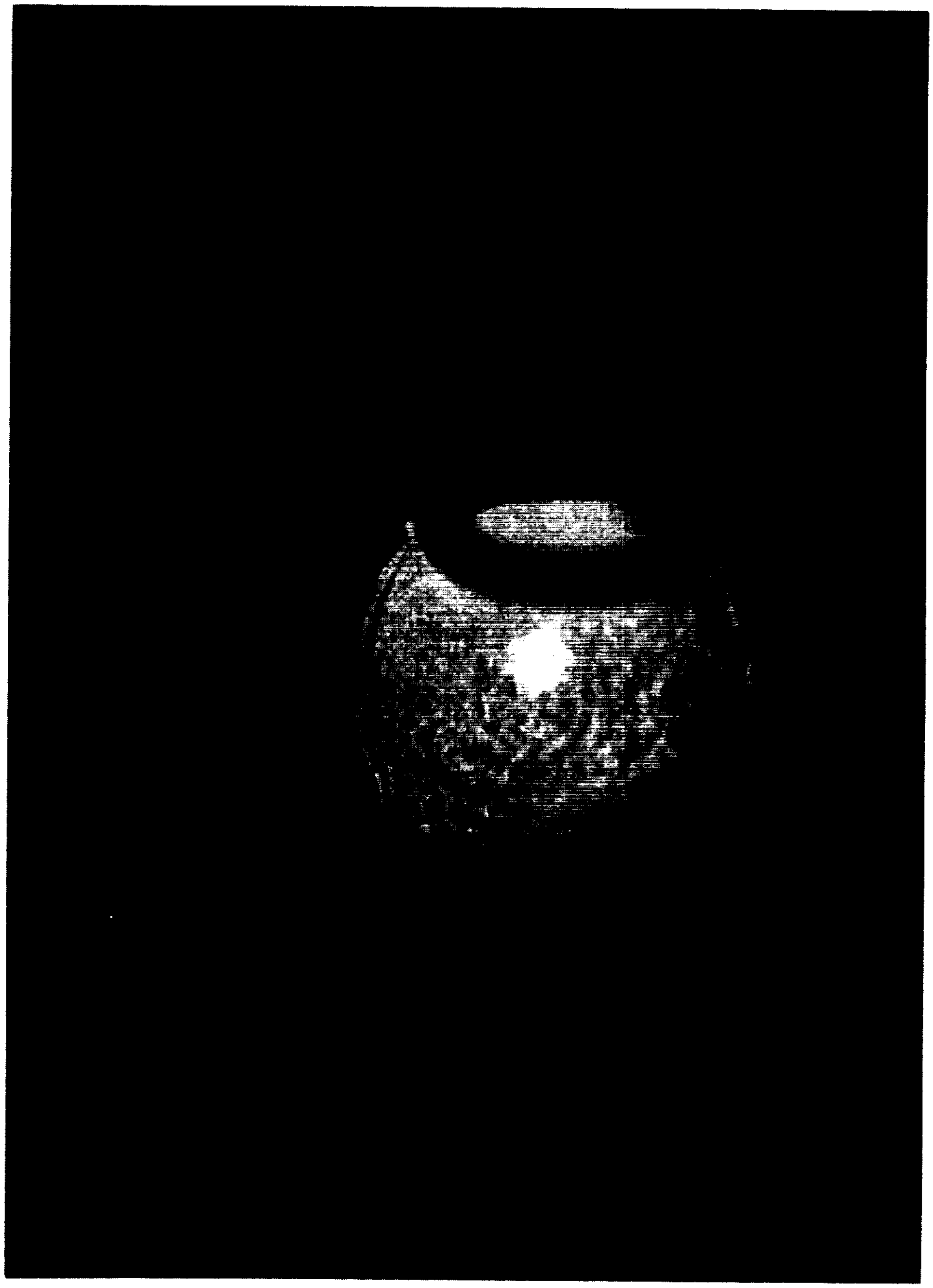

Figure 2. Binary fluid mixture of methanol-deuterated cyclohexane being mixed by ultrasounds with the CPF during ground tests. An air bubble can be seen at the top. The white dot in the middle is the thin laser beam used for scattering diagnostics.

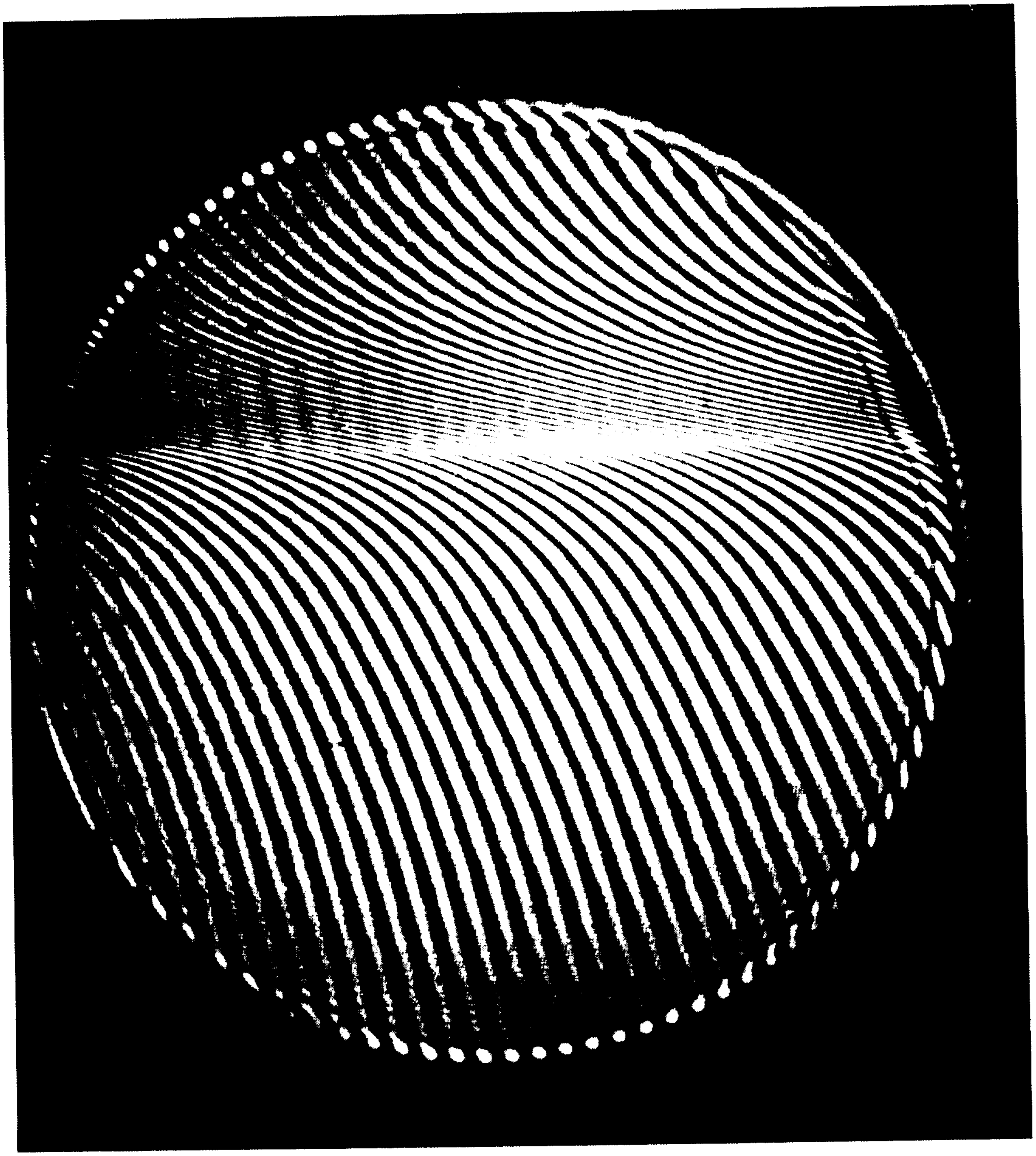

Figure 3. Interferometric pattern of SF_6 just above the critical point showing the fluid compressed by its own weight.