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Temperature propagation in near-critical fluids prior to and during phase separation

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Temperature propagation in a near-critical fluid sample (SF_6) is experimentally studied under reduced gravity in space. Onset of phase separation is indicated by the appearance of a spinodal scattering ring. Critical speeding up of temperature equilibration prior to phase separation and markedly slowed-down temperature equilibration during phase separation are observed.

Thermal relaxation near gas and liquid critical points of single-component fluids was for a long time taken to be governed by thermal diffusivity $D_{\text{th}}=\lambda/c_p$, where λ is the thermal conductivity and c_p is the constant-pressure specific heat per unit volume. D_{th} is proportional to the inverse correlation length, i.e., it goes to zero when the critical point is approached. As a consequence it has been assumed that near the critical-point thermal relaxation is greatly slowed down. Though in the past several experiments were not in agreement with this view, only recent space experiments have led to a revision.[1] Contrary to what was expected, a near-critical fluid sample under reduced gravity in space followed temperature changes of the thermostat nearly instantaneously.[2] Since this phenomenon was observed under reduced gravity, it could not be rationalized by gravity convection. This was usually done in the past when thermal relaxation in earth-bound experiments proceeded faster than estimated by D_{th}.

This main misunderstanding in using D_{th} in relaxation-time estimates was caused by the practice of using D_{th} for samples at constant volume, whereas it should be used only for samples at constant pressure. Onuki, Hao, and Ferrell have pointed out that if the sample volume is fixed and gravity convection is absent, the propagation of temperature changes into the interior region of a fluid near the critical point is mainly proceeding by adiabatic heating. Temperature changes somewhere in the fluid will cause expansion or contraction of the adjacent sample material. This in turn will cause a pressure change throughout the sample volume with the consequence that the sample temperature is changed adiabatically even far from the locus of the initial temperature change.[3] By numerical modeling it has been shown that when cooling a one-dimensional near-critical xenon sample the temperature at the center decreases at the same rate as the temperature at the boundary.[4] Meanwhile, the fast time scale of the adiabatic transient and the phenomenon of critical speeding up of temperature equilibration have been verified experimentally.[5]

Here we report on an experiment in which the spreading of temperature changes through a near-critical fluid sample (SF_6) undergoing a phase transition was studied. The sample was rapidly cooled down from a temperature some millikevins above the critical temperature to a temperature some millikevins below the critical temperature. The experiment was carried out under reduced gravity ($10^{-4}g$) in a sounding rocket of the TEXUS (Technologische Experimente unter Schwerelosigkeit) program. Laser light scattering was used to observe the beginning of the gas-liquid phase separation and to follow its development. In the early stages the transition was of the spinodal-decomposition type.[6] With incipient phase separation a spinodal scattering ring appeared. It was recorded by video. The SF_6 sample of critical overall density ($\rho_c=0.73$ g/cm^3, $T_c=318.5$ K) was housed in a cylindrical copper cell (ø 12×4 mm^2) surrounded by a double thermostat. The sample cell had sapphire windows with a reentrant area (ø 5 mm) in the middle where the laser beam passed the sample. This form of the windows reduced multiple scattering. Fast temperature changes of the sample cell were accomplished by Peltier cooling.

Two thermistors, one in the copper wall of the thermostat and the other immersed in the sample volume, were used to monitor propagation of temperature changes into the interior region of the sample fluid.

The sample cell was equipped with a magnetic stirring bar. It was set into motion from the outside to obtain good homogeneity of the sample.

Three temperature-jump experiments were performed during the reduced gravity period (6 min) of the TEXUS flight. At the starting temperature of 5 mK above T_c of each experiment the sample was homogenized by stirring. The stirring procedure was followed by a quieting period of 30 s. Then the temperature jump was initiated terminating at 5, 2, and 10 mK below T_c, respectively. The temperature versus time curves measured in the copper wall of the thermostat and in the sample fluid, respectively, are given in Fig. 1, jumps 1–3. Time zero in each of the jumps marks the trigger of the quench at the thermostat. Shaded areas indicate appearance of the spinodal ring.

Figure 1 reveals that in the one-phase region above T_c, i.e., prior to the appearance of the spinodal ring, the temperature T_{sa} of the sample fluid follows the thermostat temperature T_{th} with minor delay. When the spindal ring appears, i.e., during the early stages of phase separation, the rate of change of T_{sa} decreases significantly. Prior to the beginning of phase separation the rate of change of

T_{sa} is smaller than that of T_{th} by a factor of 2. During the appearance of the spindal ring the rate of change of T_{sa} is being reduced by a factor of 4–5. Table I gives the three relevant temperature versus time slopes in each of the jumps of Fig. 1: the rate of change of the thermostat temperature during the temperature jump and the rate of change of the sample temperature before and after the spinodal ring period.

At a temperature of some mK around the critical point, as in the present experiments, thermal diffusivity of SF_6 is of the order of some 10^{-7} cm^2/s.[7] This, combined with the thermal length of 2 mm of our sample cell, leads to a thermal relaxation time of the order of about 100 h. In contradiction to this classical estimate, temperature changes in our microgravity-experiment were propagating through the sample within seconds similar to Refs. 2 and 5, though not as fast as predicted for a one-dimensional xenon sample.[4] Our experimental results therefore offer support for the theory of rapid equilibration by adiabatic heating near the critical point, at least in the one-phase region. With incipient phase separation temperature propagation slows down markedly, possibly due to latent heat effects.

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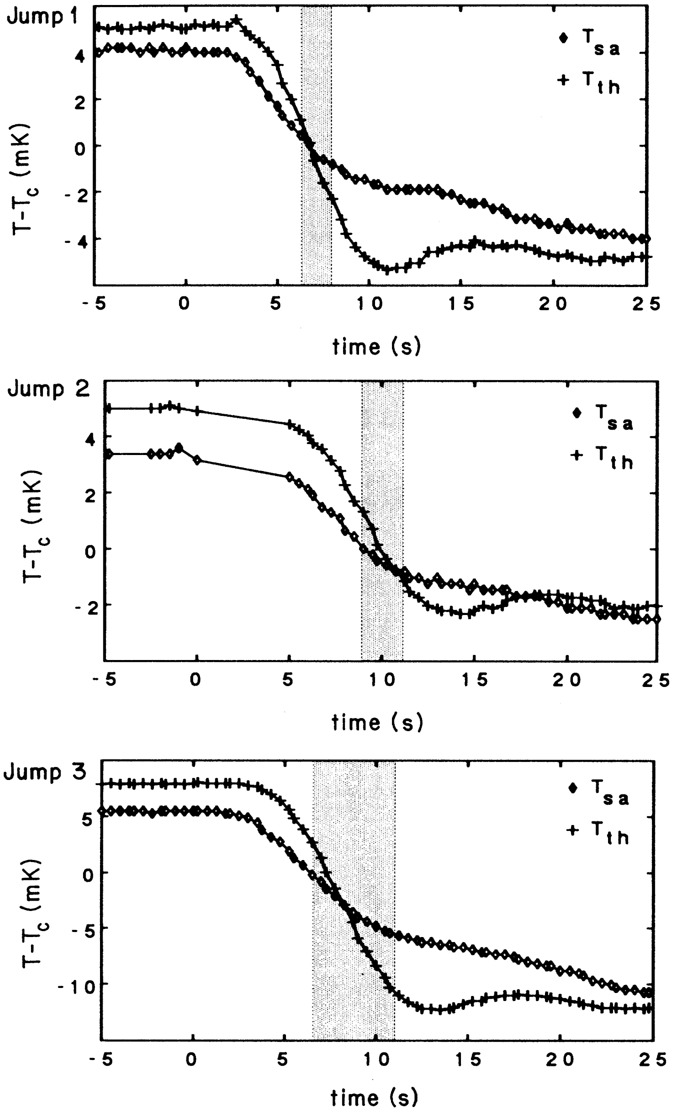

FIG. 1. Temperature vs time curves of three temperature jump experiments in a near critical SF_6 sample. T_c is the critical temperature, T_{sa} the temperature measured in the sample material, and T_{th} the temperature measured in the thermostat. Time zero marks the trigger of the quench, shaded areas indicate the appearance of the spinodal ring.

TABLE I. Three different temperature jumps in near critical SF_6 starting from the thermostat temperature T_{th}^1 and terminating at the thermostat temperature T_{th}^2. $\dot{T}_{\mathrm{th}}$, and $\dot{T}_{\mathrm{sa}}$ are the rates of change of the thermostat and sample temperature, respectively: (a) before, (b) after the appearance of the spinodal ring.

Jump	$T_{\mathrm{th}}^1-T_c$ (mK)	$T_c-T_{\mathrm{th}}^2$ (mK)	$\dot{T}_{\mathrm{th}}$ (mKs^{-1})	$\dot{T}_{\mathrm{sa}}$ (mKs^{-1}) (a)	(b)
1	5	5	1.89	1.03	0.18
2	5	2	1.13	0.67	0.12
3	5	10	3.4	1.65	0.41

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