# Critical Speeding Up Observed

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The extreme compressibility of a fluid near its liquid-vapor critical point significantly alters its dynamic response to temperature changes. Adiabatic processes allow a fluid of constant volume to thermalize in a matter of seconds, compared with the hours or days that thermal diffusion would require. Moreover, the adiabatic transient is faster as the temperature of the fluid approaches the critical temperature. We present experimental measurements of turbidity in critical xenon which show the fast time scale of the adiabatic transient and the phenomenon of critical speeding up.

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The diverging isothermal compressibility of a pure fluid near its critical point profoundly affects the fluid's dynamic response to thermal perturbations. In contrast to the case of the incompressible fluid, where a change in temperature is mediated by thermal diffusion alone, the highly compressible fluid responds in the bulk to a temperature change at the boundary by adiabatic compression. The adiabatic transient, mediated by sound waves, can alter the temperature of the bulk fluid very quickly. The magnitude of the transient and its contribution to thermal equilibration near the critical point have been calculated in several recent papers,[1-4] and some heretofore puzzling experimental observations[5-8] have been elucidated.

In a recent paper[1] we derived equations to describe heat transfer which take into account the high compressibility of the critical fluid. If the total volume $V$ of the sample is fixed and local equilibrium assumed, the following equations express conservation of energy and conservation of mass:

$$\frac{\partial T}{\partial t}-\left(1-\frac{c_V}{c_P}\right)\left(\frac{\partial T}{\partial P}\right)_\rho\frac{\partial P}{\partial t}=\frac{1}{\rho c_P}\nabla\cdot(\lambda\nabla T)\,, \quad (1)$$

$$\int_V \rho\kappa_T\left(\frac{\partial P}{\partial t}\right)dV=\int_V \rho\alpha_P\left(\frac{\partial T}{\partial t}\right)dV\,. \quad (2)$$

$T$, $P$, and $\rho$ are the temperature, pressure, and density fields of the fluid, $\lambda$ is the thermal conductivity, $\alpha_P$ is the isobaric thermal-expansion coefficient, $\kappa_T$ is the isothermal compressibility, and $c_P$ and $c_V$ are the specific heats at constant pressure and volume.

The second term on the left-hand side of Eq. (1) modifies the usual thermal diffusion equation to account for the adiabatic change of temperature and density in the fluid due to variations of pressure with time. As the ratio $\gamma\equiv c_P/c_V$ diverges at the critical point, thermal diffusion is confined to the region very near the fluid boundary and the adiabatic transient dominates the early stage of equilibration. Thermal contraction (or expansion) of the boundary layer causes adiabatic decompression (or compression) throughout the bulk fluid large enough to accomplish most of the temperature change on a time scale of seconds. More remarkably, the transient is faster when the fluid is closer to the critical point.[1,2]

As yet, there has been no experimental study to demonstrate the predictions of Eqs. (1) and (2) for the earliest stage of thermal equilibration. In this paper we present measurements of the turbidity in xenon near its critical point which show that the early stage of thermal response does indeed occur rapidly and uniformly, and which demonstrate the critical speeding up of the adiabatic transient.

We observed the adiabatic transient by measuring the time-dependent transmission of a column of critical xenon following a heat pulse applied at one end. A sample cell made of 6-mm×6-mm square-bore Pyrex tubing[9] contains the 50-mm-long column of xenon. The thickness of the cell wall is approximately 5 mm. Based on the height of the meniscus within the cell, we estimate the density to be approximately 5% above $\rho_c$; the critical density[10] of xenon is $\rho_c=1.11$ g/cm$^3$. One end of the cell is tightly wrapped with a single layer of Manganin wire to form a heater with a total resistance of 93 Ω. Ultraviolet-curing epoxy attaches the heater to the outer cell wall. The heater is insulated on its outer surface by a 2-mm-thick coating of RTV silicone rubber. 2 mm of the xenon column, with a surface area at the wall of 1 cm$^2$, is covered by the heater winding which begins at the extreme end of the Pyrex cell.

We immersed the cell in a well-stirred bath containing 14 l of methanol. To operate near the xenon critical temperature of $-16.6$ °C, the bath was cooled by a chilled mixture of water and ethylene glycol circulating through a Tronac model 101 cooled heater controlled by a Tronac PTC-40 temperature controller. The bath temperature was monitored with a thermistor and was stable to $\pm 0.5$ mK over 2 h.

We measured the transmission $T_x\equiv I/I_0$ of the xenon, the ratio of the intensity $I$ of the beam transmitted through the apparatus as shown in Fig. 1 to the intensity $I_0$ of the beam with the cell removed from the light path. The beam of the 1.8-mW He-Ne laser crossing the 6-mm sample column and the column axis were both per-

 

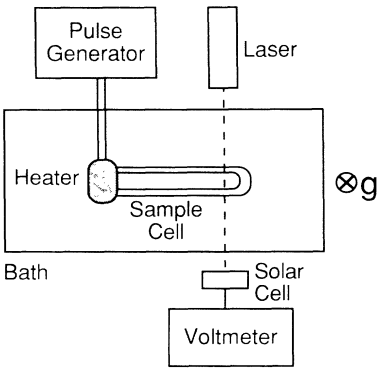


FIG. 1. A schematic top view of the apparatus, showing the laser beam passing through the horizontal column of critical xenon, far from the heater. Gravity is into the page.

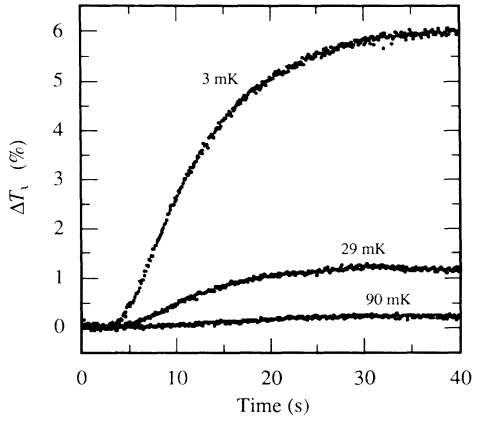


FIG. 2. The change in percent transmission of the xenon as a function of time following a heat pulse applied at time $t=0$ for 1 s. The value of $\Delta T_i$ labels each curve.

pendicular to gravity. A test of the short-term stability of the laser power showed a 0.04% intensity fluctuation over a 5-min period. A 1-in. silicon solar cell detected the transmitted beam. The photocurrent was converted to a voltage and simultaneously recorded on a chart recorder and sampled with a Keithley model 196 digital voltmeter. During measurements of the transient response of the sample, the voltmeter collected intensity readings every 0.1 s into an internal buffer, which were later transferred to a computer for analysis.

We applied the heat pulse to the xenon in a nonequilibrium, but long-lived, state of nearly uniform density[11] which persisted for several hours. By avoiding the equilibrium state with its strong, gravitationally induced density gradient[12,13] we enhanced the amplitude of the dynamic response because more fluid at critical density was in contact with the heated wall. To prepare the initial state, we heated the bath to a temperature 1.4 K above $T_c$ and allowed the xenon time to equilibrate. This far above $T_c$, the compressibility of the xenon is small enough that its vertical density gradient is negligible. We then brought the sample to the desired starting temperature $T_i$ in about 14 min by cooling the bath as quickly as possible. After waiting several minutes with the xenon in this state to be certain that there was no visible flow, we applied the heat pulse which lasted 1 s with a total energy of 0.40 J. This heat pulse was chosen large enough to resolve changes in the transmission of the xenon but small enough so that no convective flows were evident.

Equations (1) and (2) show that the adiabatic response of the fluid at constant volume is independent of the geometry of the cell. Following expansion of the thin boundary layer near the heater, the bulk fluid will show the same compression throughout if the pressure and temperature are uniform. We verified this by measuring the time-dependent transmission at several positions along the cell between 1 mm from the heater and 45 mm from the heater. The measured transient response curves were identical at each position to within the noise.

Figure 2 shows the time dependence of the transmission of the xenon following the heat pulse, measured 45 mm from the heater. Three curves correspond to three initial temperature differences $\Delta T_i \equiv T_i - T_c$: 3, 29, and 90 mK. Following the heat pulse, the transmission varied from 63% to 69%, from 82% to 83.3%, and from 91.5% to 91.8%. The fast adiabatic transient of the xenon is clear in these curves, but the critical speeding up may be obscured by the strong dependence of turbidity on temperature and density.

We have found it possible to analyze the transmission data to obtain the transient temperature response inside the sample. The critical fluctuations, when analyzed, provide a fast temperature probe of the sample interior. We convert the measured intensity values $I$ to turbidity $\tau$ using the relation

$$\tau = -\frac{\ln(I/I_0) - B}{l}, \tag{3}$$

for a path length $l$. The background term $B$, which accounts for reflections from cell surfaces in the beam path, we determined to be $B=0.0251$. The path length of the beam through the xenon was $l=6$ mm.

The relation giving the turbidity as a complicated function of temperature and density has been given by Puglielli and Ford.[14] To evaluate that expression, we used the thermodynamic parameters and the cubic-model equation of state for xenon given in Ref. 10, except for the index of refraction where we used the value $n=1.13665$ reported in Ref. 15.

To establish the density of the xenon in the beam just before the heat pulse, we assume that the xenon is isothermal and that its temperature is the same as the temperature of the bath. Using turbidity values for the initial nonequilibrium state, we fix the temperature and invert the turbidity equation numerically to obtain the corresponding density. Values for the initial density varied between $1.04\rho_c$ and $1.06\rho_c$ depending on the initial tem-

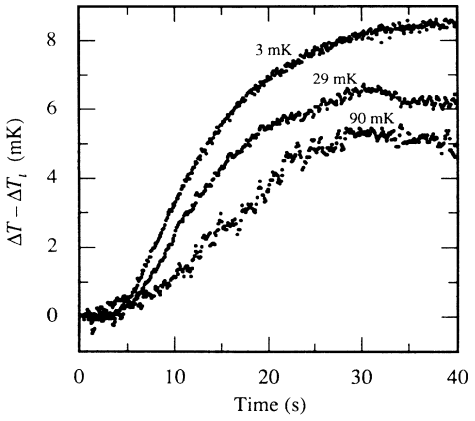


FIG. 3. The temperature change in the xenon as a function of time following a heat pulse applied at time $t=0$ for 1 s. These data were converted from the transmission data shown in Fig. 2 as described in the text. The value of $\Delta T_i$ labels each curve.

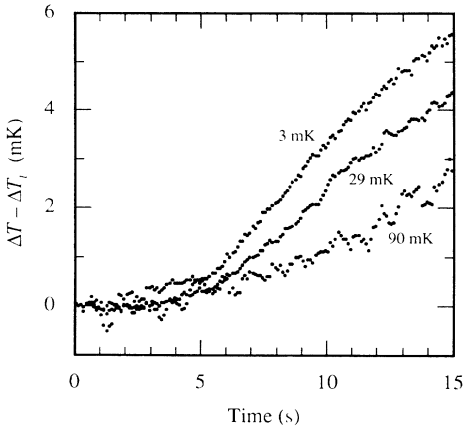


FIG. 4. Detail showing the first 15 s of Fig. 3.

perature. Then, to obtain the temperature curves we fix the density at this initial value and invert the turbidity equation for each turbidity measurement. Although the density change following the heat pulse is large in the boundary layer near the heater, the density change in the remaining fluid is negligible.[1]

Figure 3 is the temperature equivalent of Fig. 2, showing the temperature transient in the xenon following the heat pulse. The three curves correspond to the same three initial temperatures. Each shows an initial delay as the heat pulse diffuses through the 5-mm Pyrex wall with a 5-s diffusive time constant $(L^2/\pi^2 D)$, being shaped into a slower, smooth pulse. Contrast the time scale of the adiabatic transient with the diffusive time constant across the 45 mm between the heater and the observation point which varies between 180 h at $\Delta T_i = 90$ mK and 900 h at $\Delta T_i = 3$ mK.

We show in Fig. 4 the first 15 s of the curves from Fig. 3. Critical speeding up is evident here by the faster temperature response for initial temperatures closer to $T_c$. The predicted form of the adiabatic response is *not* exponential, but algebraic:[2,4] Until the time $t \sim \gamma t_1$, $\Delta T - \Delta T_i \propto (t/t_1)^{-1/2}$, where the time unit $t_1 \propto D^{-1}(\gamma - 1)^{-2} \propto (\Delta T_i)^{1.8}$. We estimate that $\gamma t_1$ is of the order of $10^2$ s in this experiment. Had the cell been insulated from the bath, all three curves would ultimately show the same temperature change, determined by the fixed heat input and the dominant heat capacity of the Pyrex cell. Here, heat loss through the cell walls alters the adiabatic transient well before the time $\gamma t_1$ has been reached. However, the effect of the heat loss is small during the initial response which remains largely adiabatic.

The present results demonstrate three features of the theory relating to the adiabatic response of the fluid: The time scale of the adiabatic transient is seconds, the transient does not depend on position, and the transient speeds up close to $T_c$. Although earlier calculations[1-4] explicitly solved Eqs. (1) and (2) with initial conditions appropriate to the zero-gravity case, it is clear that the presence of gravity does not eliminate the large influence of adiabatic effects. Since it is possible for nearly all of the thermal response to be completed during this early time,[1] there are significant practical implications for the design of terrestrial experiments. Many previous experiments, whose apparent time constants were thought to be limited by fluid diffusivities, may in fact have been limited instead by instrumental thermal time constants. Indeed, the fluid response in the experiment we have described was altered by the thermal diffusivity of the glass sample cell. Recently, Behringer, Onuki, and Meyer[16] reanalyzed earlier measurements of thermal relaxation times in critical $^3$He to show that the measurements had been influenced by adiabatic processes.

Our observations do not contradict other observations of slow relaxation in critical fluids. The adiabatic transient can accomplish most ($\sim$99%) of the temperature change of the fluid, often enough in practice to consider it complete equilibration, but this period is always followed by a diffusive process, albeit at a faster rate than would ordinarily be calculated.[2,4] On Earth the late-stage equilibration is further complicated by the dynamics of establishing the equilibrium density gradient due to gravity. Nevertheless, Eqs. (1) and (2) are entirely adequate for describing the full equilibration process, with gravity or without. The problem remains to apply appropriate boundary conditions with a suitable equation of state to find accurate solutions to the equations for each case of interest.

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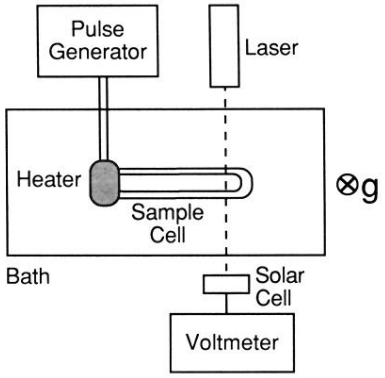


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