High-speed observation of the piston effect near the gas-liquid critical point

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We measured high-speed sound propagation in a near-critical fluid using a ultra-sensitive interferometer to investigate adiabatic changes of fluids on acoustic timescales. A sound emitted by very weak continuous heating caused a stepwise adiabatic change at its front with a density change of order $10^{-7}$ g/cm\textsuperscript{3} and a temperature change of order $10^{-3}$ deg. Very small heat inputs at a heater produced short acoustic pulses with width of order $10\mu$sec, which were broadened as they moved through the cell and encountered with the boundaries. The pulse broadening became enhanced near the critical point. We also examined theoretically how sounds are emitted from a heater and how applied heat is transformed into mechanical work. Our predictions well agree with our data.

Thermal equilibration in one-component fluids takes place increasingly faster near the gas-liquid critical point at fixed volume\textsuperscript{1, 2, 3, 4, 5, 6, 7, 8, 9, 10}, despite the fact that the thermal diffusion constant $D$ tends to zero at the criticality. This is because the thermal diffusion layer at the boundary expands and sounds emitted cause adiabatic compression and heating in the whole cell after many traversals in the container. This heating mechanism is much intensified near the critical point due to the critical enhancement of thermal expansion of the layer. If the boundary temperature $T_w$ is fixed, the interior temperature approaches $T_w$ on the timescale of the piston time\textsuperscript{2}.

$$t_1 = L^2/4(\gamma - 1)^2D,$$

where $L$ is the cell length and $\gamma = C_p/C_V$ is the specific-heat ratio growing near the critical point. This time is much shorter than the isobaric equilibration time $L^2/AD$ by the very small factor $(\gamma - 1)^{-2}$\textsuperscript{11}.

The previous experiments have detected only slow temperature and density changes in the interior region on timescales of order 1 sec. The aim of this letter is to demonstrate that we can detect density changes of order $10^{-8}$ g/cm\textsuperscript{3} taking place on a timescale of $1\mu$sec. In confined fluids, adiabatic changes are usually caused by a mechanical piston, but they can also be achieved by a heat input through a boundary\textsuperscript{1, 2, 3, 4, 5, 6, 7, 8, 9, 10}. The second thermo-acoustic method is particularly efficient near the critical point. These adiabatic processes are very fundamental and ubiquitous, but we are not aware of any experiments detecting the underlying fast acoustic processes.

Our experimental set-up is displayed in Fig.1, where the fluid temperature was controlled with precision of $\pm 1\text{mK}$ using a Pt-thermometer and a four-wire resistance bridge\textsuperscript{12}. The upper and lower plates have area $1\text{ cm}^2$ and are made of Cu with high thermal conductivity $\lambda_{Cu}/k_B = 2.8 \times 10^{23}/\text{cm sec}$. The cell length $L$ was either 10.3mm or 5.5mm. A thin NiCr-foil heater with thickness $3\mu$m was placed $d = 0.5\text{mm}$ below the top plate. The heat capacity of the foil is so small $(C_h/k_B = 8.4 \times 10^{19}/\text{cm}^2\text{ per unit area})$ and the generated heat was almost released to the fluid\textsuperscript{13}. The side walls are made of stainless steel, whose thermal conductivity is 3.9\% of that of Cu. We thus neglect heat flow to the side walls. A laser beam was sent at the cell center and a Twymann-Green interferometer was used to detect small density changes in a slit region of width 0.25mm. Individual signals were very noisy and the data.
points in the following figures are the averages over 418 heat pulses successively generated in 2 seconds. Using sound pulses we first measured the sound speed \( c \). For both \( L = 10.3 \text{mm} \) and \( 5.5 \text{mm} \), our data on \( c \) closely agree with previous ones in the range \( T/T_c - 1 > 10^{-4} \), but become independent of \( T - T_c \) closer to the critical point because of the frequency-effect (inherent to short-time pulses) and/or the gravity effect [13].

In Fig.2 we show acoustic density variations \( \delta \rho(t) \) at the cell center \( x = L/2 \) in a cell of \( L = 1.03 \text{cm} \) at \( T - T_c = 150 \text{mK} \) and 30mK, where \( c \equiv 149 \) and 133m/sec, respectively. Continuous heating was applied in the time region \( 0 < t < 0.2 \text{msec} \) and a sound signal arrived at the cell center for \( t > (L/2 - d)/c \sim 40 \mu \text{sec} \). The total heat supplied was \( Q = 367 \mu \text{erg} \). The inset of Fig.2 displays a rapid relaxation at \( T - T_c = 150 \text{mK} \) after switching-off the heater. Fig.3 illustrates spatial profiles of the pressure deviation \( \delta \rho \), whose inhomogeneity remains small even in the thermal diffusion layers. Notice that \( \delta \rho \) takes large negative values in the layers. The thickness of the layers was only \( 2.6 \times 10^{-5} \text{cm} \) at \( t = 0.2 \text{msec} \) for \( T - T_c = 150 \text{mK} \). Right after switching-off the heater, step-like sounds were emitted on both sides and the one moving upward was reflected at the top at \( t \approx d/c \). The two pulses merged for \( t > 2d/c \sim 10 \mu \text{sec} \).

After sweeping of the sound, we can see a stepwise increase in the density at \( t \approx L/2c, 3L/2c, \) and \( 5L/2c \). After the switching-off at \( t = 0 \mu \text{sec} \), a trapezoidal pulse appeared moving back and forth in the cell. The trapezoidal part should be diminished if the heating time would be a multiple of \( 2L/c \). The interior temperature was slightly increased by \( \delta T = (\partial T/\partial \rho)_s \delta \rho \) and a heat flow was induced through the boundaries. In the present case \( \delta T \sim 0.2T \delta \rho/\rho \sim 10^{-5} \text{deg} \). As can be seen in the inset of Fig.2, the subsequent relaxation in the interior region was very rapid. It is the same as that after cooling of the boundaries on long times scales \( t \gg L/a \), so it is an adiabatic process caused by contraction of the thermal diffusion layers.

In Fig.4 we show \( \delta \rho(t) \) after very short heating in a cell of \( L = 5.5 \text{mm} \) at \( T - T_c = 500 \) and 100mK, where \( c \equiv 149 \) and 133m/sec, respectively. A dc electric current of duration time \( 4.5 \mu \text{sec} \) passed through the heater, where the pulse shape was determined by the relaxation time \( 2 \mu \text{sec} \) of the current amplifier. The total heat supplied was \( Q = 129 \mu \text{erg} \). The pulse directly leaving downward and that reflected at the top can be distinguished since their peaks are separated by \( 2d/c \). The two-peak pulse thus formed moved with speed \( c \) in the cell and was gradually flattened. In Fig.5 we show pulse propagation and its decay at \( T - T_c = 500 \) and 35mK in the cell of 1.03cm on a longer time scale, where the pulses are singly-peak because of the longer pulse-duration time \( 7 \mu \text{sec} \) (\( > 2d/c \)). The pulse broadening and the tendency of homogenization become more enhanced on approaching the critical point. In these experiments, the fluid velocity in the pulse region was of order \( v = c \delta \rho/\rho \sim 10^{-2} \text{cm/sec} \) and the fluid displacement was of order \( \Delta x = v \Delta t \sim 10^{-7} \text{cm} \) with \( \Delta t \sim 10 \mu \text{sec} \) being the pulse-duration time. For such extremely small displacements the film heater did not disturb the sound propagation [14]. We are interested in the adiabatically increased energy \( E_{ad} = p \Delta x \) in the pulse region per unit area. To linear order it is expressed as

\[
E_{ad} = \frac{p}{\rho} \int dx \delta \rho(x, t) = \frac{pc}{\rho} \int dt \delta \rho(x, t). \tag{2}
\]

The ratio of \( E_{ad} \) to the total heat supplied \( Q = \int dt \dot{Q}(t) \) represents the efficiency of transforming applied heat to mechanical work. In our experiments \( E_{ad}/Q \) was about 0.11 – 0.12 at the first arrival of pulses at the cell center over wide ranges of \( T - T_c \) and \( Q \). However, a pulse has a tail persisting in later times and there remains ambiguity of order 10% in the calculation of \( E_{ad} \).

We give theoretical interpretations of the above results neglecting the effect of the bulk viscosity. Let a small amount of heat be supplied to a near-critical fluid at a rate \( \dot{Q}(t) \) per unit area for \( t > 0 \) in a one-dimensional geometry. The volume expansion rate per unit area near
the heater is

\[ \dot{V}_1 = \left( \frac{\partial p^{-1}}{\partial s} \right)_p \frac{\dot{Q}(t)}{T}, \]  

(3)

where \( s \) is the entropy per unit mass. If the heater is attached to the upper plate, this volume change then produces a sound wave propagating downward as \( \delta \rho_{\text{out}}(t - x/c) \), where \( x \) is the distance from the heater and \( \delta \rho_{\text{out}}(t) \) is the density increase in the sound emitted at the heater at time \( t \). Since acoustic disturbances move with the sound speed \( c \), the mass conservation gives the

\[ \delta \rho_{\text{out}}(t) = \frac{\rho}{cT} \frac{\partial T}{\partial p} \dot{Q}(t), \]  

(4)

where the Maxwell relation \( (\partial \rho^{-1}/\partial s)_p = (\partial T/\partial p)_s \) has been used. The adiabatic coefficient \( (\partial T/\partial p)_s \) is nearly equal to the derivative along the coexistence curve \( (\partial T/\partial p)_\text{ex} \) near the critical point \( [\text{II}] \). For CO\(_2\) it is equal to \( T_c/6.98 \mu \text{K} \), and the above relation becomes \( \delta \rho_{\text{out}}/\rho = 1.38 \times 10^{-13} \dot{Q} \) with \( \dot{Q} \) in erg/cm\(^2\) sec. The heating rate used for our data in Fig.2 was \( \dot{Q} = 0.183 \times 10^7 \) and then \( \delta \rho_{\text{out}}/\rho = 2.55 \times 10^{-7} \). This theoretical value fairly agrees with the observed height of the first step \( \sim 2.2 \times 10^{-7} \) in Fig.2. The efficiency of energy transformation discussed below Eq.(2) becomes \( \frac{E_{\text{ad}}}{Q} = \frac{\rho}{T} \left( \frac{\partial T}{\partial p} \right)_s \),

(5)

which is 1/6.98 = 0.14 for near-critical CO\(_2\). On the other hand, the experimental values were in the range 0.11 - 0.12.

As a complicating factor in our experiment, however, the heater is placed \( d = 0.5 \text{mm} \) below the top plate. If \( V_2 \) is the volume expansion rate in the thermal diffusion layer at the top plate, we require \( c \delta \rho_{\text{out}}(t)/\rho = V_1 + V_2 \). In the time region where \( (\partial t)^{1/2} \ll d \ll ct < L \), some calculations yield a modified convolution-type formula,

\[ \dot{\delta \rho}_{\text{out}}(t) = \frac{\rho}{cT} \left( \frac{\partial T}{\partial p} \right)_s \int_0^t dt' \dot{Q}(t - t') \psi(t'/t_2)/t_2, \]  

(6)

where \( t_2 = L^2/4c^2 t_1 \) is a characteristic time of heat exchange between the boundary and sounds in the range \( \lambda/c \ll t_2 \ll t_1 \). The scaling function \( \psi(u) \) is positive and its integral \( \psi(u) = \int_0^u dv \psi(v) \) tends to 1 for large \( u \). The function \( \psi(u) \) itself appeared in the original theory \( [\text{II}] \). Thus Eq.(5) reduces to Eq.(3) when \( \dot{Q}(t) \) changes much slower than \( t_2 \).

We clarify the relationship of the formula (3) and the assumption in the theory of the piston effect \( [\text{II}] \). Let the heat input \( \dot{Q}(t) \) changes slowly compared with the acoustic time \( t_a = L/c \). We suppose a time interval with width \( \delta t \gg t_a \), in which \( \dot{Q}(t) \) is almost unchanged. After many sound traversals, the adiabatic pressure and density increases in the interior region are given by

\[ \delta p = c^2 \delta \rho = c^2 \frac{\delta t}{t_a} \frac{\rho}{cT} \left( \frac{\partial T}{\partial p} \right)_s \dot{Q}, \]  

(7)

as a result of superposition of many steps. In terms of the incremental heat supply \( \delta Q = \dot{Q} \delta t \) we find

\[ \delta p = \frac{\rho}{LT} \left( \frac{\partial T}{\partial p} \right)_s \delta Q = \frac{\delta p}{\rho \beta t a} \frac{\delta Q}{\rho t A}, \]  

(8)

where the Maxwell relation \( (\partial p/\partial s)_p = \rho^2 (\partial T/\partial p)_s \) has been used. If \( \delta p \) is assumed to be homogeneous, Eq.(8)
Temperature deviation is written as \( \delta T = \delta Q/\rho C \) since the space integral of \( \delta s \) is \( \delta T \) and that of \( \delta \rho \) vanishes. In addition, the average temperature deviation is written as \( \langle \delta T \rangle = \delta Q/C_V L \) where \( C_V = \rho T/\delta s/\partial T \rho \) is the isochoric specific heat. From Eq.(3) we may thus reproduce the original theory of the piston effect.

In summary, we have first measured rapid acoustic responses in near-critical \( \text{CO}_2 \) to extremely small heat inputs, which constitute a basis of understanding adiabatic processes in fluids. We demonstrate that adiabatic changes take place on the timescale of \( L/c \). As Fig.2 suggests, it is intriguing that a homogeneous adiabatic change can be achieved almost instantaneously if the heating time is a multiple of \( 2L/c \). The theoretical expressions (3) and (4) are useful to analyze these results and can reproduce the original theory of the piston effect valid on long timescales. The theoretical height of a stepwise sound in Eq.(4) and efficiency \( E_{\text{ad}}/Q \) in Eq.(5) fairly agree with the experimental values. Differences of \( 20 - 30\% \) remain, probably because a fraction of heat escaped to the stainless part and the pulse shape was considerably broadened even at the first arrival at the cell center.

There are a number of unsolved problems. (i) We should understand how a sound pulse is reflected at a boundary wall and how it is damped in the bulk region. In our case, the change of the pulse shape on reflection is apparently more marked than that due to the bulk damping, as can be inferred from comparison of the results for \( L = 5.5\text{mm} \) and those for \( L = 1.03\text{cm} \). This is still the case even very close to the critical point. (ii) The bulk viscosity exhibits strong critical anomaly as \( \zeta \approx 0.03\rho c^2 t_\xi \) \[10\], where \( t_\xi \) is the order parameter relaxation time (18\usec at \( T - T_c = 30\text{mK} \)). It gives a bulk acoustic damping, but it also affects the thickness of the thermal diffusion layer when the typical timescale is longer than \( \gamma \zeta /\rho c^2 \approx 0.03 t_\xi \). The effects of the bulk viscosity on heat transport are not yet well investigated, however. (iii) Upon heat exchange the wall temperature is not fixed when the effusivity ratio \( a_w = (\lambda_w C_w/\lambda p C_p)^{1/2} \) is small \[10\]. Here \( \lambda_w, \lambda, C_w, \) and \( C_p \) are the thermal conductivities and the specific heats (per unit volume) of the solid and fluid, respectively. For finite \( a_w \) the piston time is given by \( t' = [(1 + a_w^{-1})/(\gamma - 1)]^2 L^2/4D \) \[8\], which becomes \( t'_0 \approx C_0^2 L^2/4\lambda c \) if \( a_w \ll 1 \). In our case \( a_w = 3 \times 10^{-3}(T/T_e - 1)^{0.92} \) between Cu and \( \text{CO}_2 \) and \( a_w < 1 \) is reached for \( T - T_e < 50\text{mK} \). This crossover should be studied.

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