RAPID COMMUNICATIONS

PHYSICAL REVIEW A VOLUME 41, NUMBER 4 15 FEBRUARY 1990

Critical speeding up in pure fluids

Hacène Boukari, J. N. Shaumeyer, Matthew E. Briggs, and Robert W. Gammon
Institute for Physical Science and Technology, University of Maryland, College Park, Maryland 20742

(Received 4 August 1989)

We show how the extreme compressibility of a pure fluid near its critical point significantly affects its bulk dynamic response to temperature changes through adiabatic processes. We develop equations that describe the dynamics in the absence of gravity, and illustrate the magnitude of the effect with numerical solutions in one dimension. The results are remarkable: 5 mm of critical xenon, quenched from 20 to 10 mK above its critical temperature, cools by over 99% in less than 5 s. Moreover, adiabatic cooling is *faster* when the fluid is *closer* to the critical point.

A pure fluid near its liquid-vapor critical point exhibits striking anomalies in its thermodynamic response functions. Characterizing these anomalies has been a primary concern of workers in critical phenomena. Until recently, we have little appreciated the implications for the hydrodynamics of critical fluids.[1] In particular, several experiments have measured thermal equilibration times for a fluid near its critical point which appear to be inconsistent with hydrodynamic predictions.[2,3] In this Rapid Communication, we reconcile experiment with hydrodynamics by allowing for the consequences of extreme compressibility in applying the heat transfer equation.

The usual approach to estimating the time to equilibrium has been to apply the thermal diffusion equation[4] to the geometry in question with some appropriate average value of the thermodynamic parameters. The failure of this approach to explain the short times observed is usually ascribed to the influence of convective effects.[2] Given the extreme compressibility of the fluid near its critical point, simply estimating the likely magnitude of the convective effect is difficult.[5] Furthermore, the equilibrium state in gravity has large density gradients whose effect on the dynamics of equilibration is not known, although the equilibrium density profile as a function of temperature is known.[6]

Recent critical-point experiments in low gravity on the U.S. Space Shuttle[7] and Technologische Experimente unter Schwerelosigkeit (TEXUS) sounding rockets,[3] rather than observing unambiguous critical-point behavior with the influence of gravity removed, produced anomalous results. Some of their problems may be traced to not knowing how to predict the time the fluid takes to establish the equilibrium conditions of uniform density and temperature.

In what follows we develop equations appropriate to describe the dynamics of equilibration for a compressible, pure fluid contained in a fixed volume, excluding the effects of gravity and assuming that there is no velocity field. The resulting equation for conservation of energy has a term inducing temperature changes of the fluid through adiabatic changes in the density, in addition to the usual mechanism of thermal diffusion. That compressible fluids are subject to this adiabatic effect is known in other contexts,[8,9] but its vital importance to the equilibration of fluids near the critical point was only recently pointed out by Onuki at a workshop[1] studying this problem. To illustrate the considerable consequence of the adiabatic effect, we present some results from numerical solutions in one dimension for a one-phase critical fluid responding to temperature changes. We find short equilibration times, like those observed experimentally, without the need to introduce convection. Indeed, the adiabatic cooling effect is responsible for accomplishing most of the temperature change in the fluid at a rate remarkably faster than that of thermal diffusion.

Consider a closed cell containing a fluid of constant average density ρ. There is no velocity field, hence no dissipation, and the only source of heat is through the boundary of the fluid. The equation

$$\rho T \frac{\partial s}{\partial t} = \nabla \cdot (\lambda \nabla T) \tag{1}$$

expresses conservation of energy,[10] where s is the entropy per unit mass. The temperature field T is a function of time and the spatial variables; the thermal conductivity λ is allowed to vary with the temperature, hence also with the spatial variables.

Local equilibrium is maintained across a distance L by sound propagation provided that the time scales of interest are larger than $\sim L/v$, where v is the velocity of sound. Although $v \rightarrow 0$ at the critical temperature T_c, v is still larger than 10 m/s for $(T-T_c)/T_c > 10^{-9}$ in a critical fluid.[11] This implies that we can take the pressure P independent of the spatial variables. However, P *is* a function of time, and its value changes during the process of equilibration. We write the change in entropy as

$$\frac{\partial s}{\partial t} = \left(\frac{\partial s}{\partial T}\right)_P \frac{\partial T}{\partial t} + \left(\frac{\partial s}{\partial P}\right)_T \frac{\partial P}{\partial t} . \tag{2}$$

In solving the usual problem of heat conduction in an *incompressible* fluid, changes in the internal energy are due only to temperature variations which result from heat flowing in the fluid. For a *compressible* fluid one must account for the adiabatic change of temperature and density due to the variation of the pressure with time. In the critical fluid the compressibility is so large that the adiabatic effect dominates the process of equilibration.

Combining Eqs. (1) and (2), we apply a Maxwellian relation and thermodynamic transformations to arrive at

$$\frac{\partial T}{\partial t}-\left[1-\frac{c_V}{c_P}\right]\left[\frac{\partial T}{\partial P}\right]_\rho\frac{\partial P}{\partial t}=\frac{1}{\rho c_P}\nabla\cdot(\lambda\nabla T)\,, \qquad (3)$$

where c_P and c_V are the specific heats at constant pressure and volume. Approaching the critical point, the divergence of c_P diminishes the influence of the right-hand side of the equation, confining thermal diffusion to the region very near the fluid boundaries where the temperature gradient is large, while on the left-hand side the ratio $c_V/c_P \rightarrow 0$ and the adiabatic term governs the time dependence of T. Thermal contraction (or expansion) of the fluid at the boundary causes adiabatic decompression (or compression) throughout the rest of the fluid large enough to accomplish most of the temperature change.

The pressure derivative in Eq. (3) can be calculated from the equation of state and conservation of mass. Again assuming local equilibrium, we can write for the change in density

$$\frac{\partial \rho}{\partial t}=\left[\frac{\partial \rho}{\partial T}\right]_P\frac{\partial T}{\partial t}+\left[\frac{\partial \rho}{\partial P}\right]_T\frac{\partial P}{\partial t}\,, \qquad (4)$$

where the first coefficient is proportional to the isobaric thermal expansion, $\alpha_P \equiv -\rho^{-1}(\partial\rho/\partial T)_P$, and the second coefficient to the isothermal compressibility, $\kappa_T \equiv \rho^{-1}\times(\partial\rho/\partial P)_T$. Both of these coefficients diverge at the critical point. In fact, most of the thermodynamic parameters that appear in the equations are strong functions of temperature and density and it is not accurate to treat them as constants in the solution. Instead, they must be allowed to vary as the temperature and density of the sample moves from its initial state, through its intermediate states, to its final state.

Noting that the volume of the sample cell is fixed, we integrate Eq. (4) over the volume of the cell to conserve mass in the system, and the left-hand side of the equation vanishes. Our assumption of mechanical equilibrium means that the pressure and hence $(\partial P/\partial t)$ is spatially constant and so can be moved outside the integral. Rearranging the result gives the pressure derivative,

$$\frac{\partial P}{\partial t}=\frac{\int_V \rho\alpha_P(\partial T/\partial t)dV}{\int_V \rho\kappa_T dV}\,. \qquad (5)$$

This equation shows that the pressure derivative is a weighted average of the temperature derivative over the sample volume. Together with an equation of state, Eqs. (3) and (5) describe the time dependence of the temperature distribution in the enclosed fluid for times longer than the period of the lowest acoustic resonance frequency. These equations are general enough to describe the situation in critical fluids in which the local properties vary greatly through their strong density and temperature dependence. We show below that the pressure term in Eq. (3) determines the transient thermal response of the compressible fluid to temperature changes at its boundary, leading to a response much faster than that from thermal diffusion alone.

We present particular numerical solutions obtained for two cases, a temperature quench and a continuous temperature ramp, which demonstrate the magnitude of the adiabatic effect in the temperature dynamics. In these examples the temperature changes are large enough so that the fluid properties change significantly, and we allow them to vary with temperature and density. Both are modeled using the critical parameters for xenon.

We solve the system of Eqs. (3) and (5) numerically in one spatial dimension. The solution proceeds iteratively. At each time step, the spatial dependence of the temperature field is used in Eq. (5) to obtain the increment in the spatially constant pressure. Then, new values of the thermodynamic response functions are evaluated along the cell by changing the variables T and P to the cubic-model variables r and θ and using relations given in Ref. 12. We calculate background terms of transport coefficients following Swinney and Henry,[13] and the divergent part of λ following Sengers[14] with the shear viscosity taken constant at its background value. With these, the increment in the temperature at each point in the cell is obtained from Eq. (3), the new temperature and density fields are calculated, and the process repeats.

For the temperature quench example we model a xenon sample, 5 mm long and at uniform critical density, whose boundaries are suddenly cooled. Figures 1 and 2 show the temperature and density fields near the fluid boundary at times up to 32 s following a temperature quench from 20 to 10 mK above T_c; the values are calculated at 10-μm intervals. Surprisingly, most of the cooling happens via the adiabatic effect and the center of the fluid accomplishes 99% of its temperature change 4.9 s after the quench. Figure 2 shows how, immediately after the temperature step is applied, the large thermal expansion coefficient causes the density of the fluid near the boundary to increase significantly, resulting in a sudden, adiabatic decompression throughout the fluid, which cools the bulk of the fluid. Although it is not visible at the scale used for Fig. 2, the density is slightly *less* than ρ_c at distances from

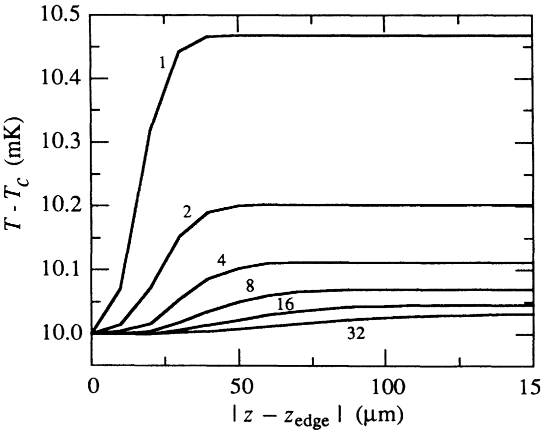

FIG. 1. Temperature profiles are shown near the boundaries, $z_{\rm edge} = \pm 2.5$ mm, of a one-dimensional sample of xenon immediately following a temperature quench from $T - T_c = 20$ mK to $T - T_c = 10$ mK. Throughout the region 0.15 mm $\leq |z - z_{\rm edge}| \leq 2.5$ mm the temperature is spatially constant with the value given at $|z - z_{\rm edge}| = 150$ μm. The time in seconds following the quench labels each profile.

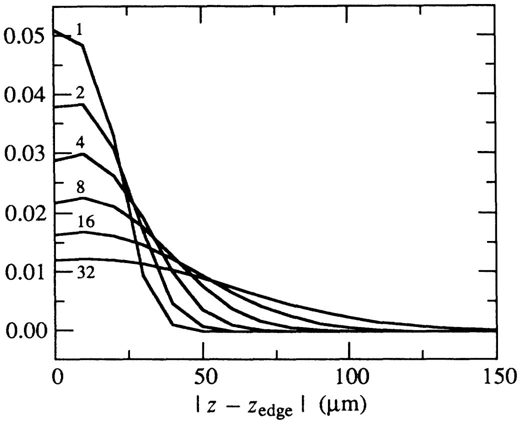

FIG. 2. Density profiles, in reduced units $(\rho/\rho_c)-1$, are shown near the boundaries, $z_{\text{edge}}=\pm 2.5$ mm, of a one-dimensional sample of xenon immediately following a temperature quench from $T-T_c=20$ mK to $T-T_c=10$ mK. The time in seconds following the quench labels each profile.

the wall greater than 150 μm.

Figure 3 shows the pressure as a function of time for three separate quenches; the final temperature of each quench is half the initial temperature, and the sequence approaches T_c logarithmically. The pressure curves, calculated with resolution varying between 2.5 and 10 μm, also reflect the temperature at the center of the fluid. All three quenches show two cooling regimes: a fast one due to the adiabatic process, and a slow one which appears to be due to thermal diffusion.[15] The adiabatic process exhibits two clear trends as the quenches are made closer to T_c. Not only does the fraction of the total pressure (or temperature) change made by the adiabatic process increase in size, but the process also speeds up near the critical point.

This example suggests that the short equilibration times of less than 6 s observed in the one-phase region by Dahl and Moldover[2] in ^{3}He, which differed greatly from relaxation times calculated from thermal diffusion alone, can be accounted for by the adiabatic effect. Although convection may have been present in their sample during temperature changes, it is not needed to explain short equilibration times.

For the temperature-ramp example we model the same xenon sample, 5 mm long, cooled at a constant rate of −1 mK/s at its boundary, starting 100 mK above T_c. Initially, the sample is a uniform critical density. Figure 4 shows the temperature at the boundary and in the center of the fluid during the temperature ramp. At this cooling rate, the temperature at the center of the fluid decreases at the same rate as the temperature at the boundaries. As in the previous example there is no convection in the model; the adiabatic effect is sufficient to cool the fluid rapidly. We can compare this result with the experiment of Nitsche and Straub,[3] performed in a TEXUS sounding rocket, in which a sample of SF_6 was continuously heated from $T_c-0.4$ K to $T_c+0.4$ K at a rate of +2.6 mK/s while the temperature at the center of the fluid was monitored. They found that the temperature at the center of the fluid followed the temperature at the boundary regardless of the presence of gravity. In the earth-bound experiment they observed strong convection which may account for the fast equilibration, but convection could not be the agent in the TEXUS experiment.

A pure fluid in the one-phase state near its critical point is extremely compressible, and this property significantly alters its dynamic response to temperature changes. Changes in temperature at the boundary of the critical fluid are rapidly communicated to the interior of the fluid through adiabatic pressure changes; since the pressure changes are mediated by sound waves, the temperature can change very quickly. In that Eq. (3) still retains a long wavelength, thermal diffusion mode as its long-time solution, the adiabatic response is transient. However, its effect must not be neglected. Depending on the size of the

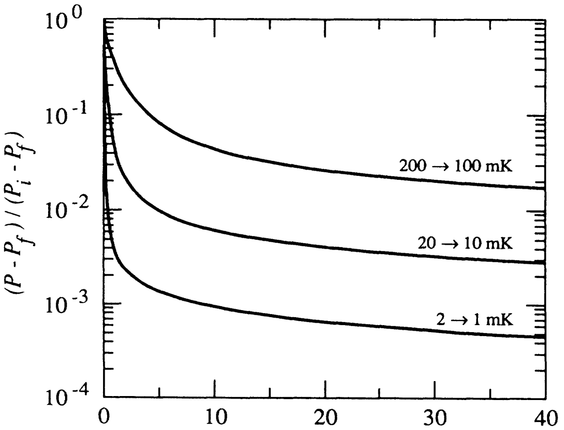

FIG. 3. The pressure, scaled by its initial value P_i and final value P_f, is shown as a function of time after three separate temperature quenches of a one-dimensional sample of xenon, 5 mm long. Each curve is labeled by the initial and final temperature of the corresponding quench, given as differences in mK from T_c.

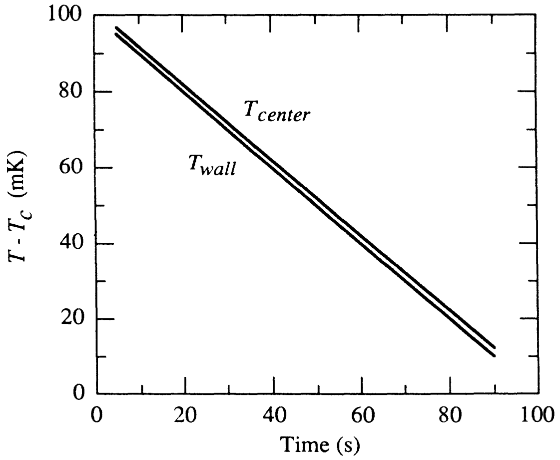

FIG. 4. The temperature, as difference in mK from T_c, at the center of a one-dimensional sample of xenon is shown as a function of time as the boundaries of the sample are cooled continuously at a rate of −1 mK/s. The cooling began with the sample at $T-T_c=100$ mK. The lower curve is the boundary temperature.

temperature change and the resolution of the temperature measurement, the fluid can accurately approach the final temperature and density well before thermal diffusion becomes dominant. In the examples we have presented, equilibrium is effectively reached in a matter of seconds. Perhaps it is most remarkable that, contrary to the precept of critical slowing down, the adiabatic cooling speeds up as the compressibility diverges near the critical point.

The system of Eqs. (3) and (5) is strictly valid only in the absence of gravity; it remains to extend the model to allow for density gradients that are part of the final equilibrium state in a gravitational field. Nevertheless, these equations are immediately applicable to critical-point experiments in low gravity, which are an active part of several space research programs, where the possibility of achieving practical equilibrium in critical fluids in times significantly shorter than through thermal diffusion alone is an important consideration in experiments whose duration is measured in hours.

This research was supported by NASA Contract No. NAS3-25370.

---

[1] *Thermal Equilibration Near the Critical Point,* a NASA sponsored workshop held at the National Institute of Science and Technology, Gaithersburg, Maryland, March, 1989 (unpublished).

[2] D. Dahl and M. R. Moldover, Phys. Rev. A **6**, 1915 (1972).

[3] K. Nitsche and J. Straub, in *Proceedings of the Sixth European Symposium on Material Sciences under Microgravity Conditions, Bordeaux, France, 1986* (European Space Agency, Paris, 1987), Vol. SP-256, p. 109.

[4] M. Sh. Gitterman and V. A. Shteinberg, Teplofiz. Vys. Temp. **10**, 565 (1972) [High Temp. **10**, 501 (1972)].

[5] Moshe Gitterman, Rev. Mod. Phys. **50**, 85 (1978).

[6] J. V. Sengers and J. M. J. van Leeuwen, Physica **116A**, 345 (1982).

[7] H. Klein and B. Feuerbacher, Phys. Lett. A **123**, 183 (1987).

[8] Harold Jeffreys, Proc. Cambridge Philos. Soc. **26**, 170 (1930).

[9] E. A. Spiegel, Annu. Rev. Astron. Astrophys. **10**, 261 (1972).

[10] L. D. Landau and E. M. Lifshitz, *Fluid Mechanics,* 2nd ed. (Pergamon, Oxford, 1987).

[11] C. W. Garland and R. D. Williams, Phys. Rev. A **10**, 1328 (1974).

[12] M. R. Moldover, J. V. Sengers, R. W. Gammon, and R. J. Hocken, Rev. Mod. Phys. **51**, 79 (1979).

[13] Harry L. Swinney and Donald L. Henry, Phys. Rev. A **8**, 2586 (1973).

[14] J. V. Sengers, Int. J. Thermophysics **6**, 203 (1985).

[15] A. Onuki, H. Hao, and R. A. Ferrell, preceding paper, Phys. Rev. A **41**, 2256 (1990).