RAPID COMMUNICATIONS

Fast adiabatic equilibration in a single-component fluid near the liquid-vapor critical point

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Near the liquid-vapor critical point, the diverging thermal-expansion coefficient causes a localized entropy change to produce an immediate temperature change throughout the entire fluid, thereby greatly accelerating the approach to equilibrium.

The experimental study of the critical properties of a single-component fluid near its liquid-vapor critical point is generally hampered by the occurrence of convection. This difficulty can be avoided by carrying out the measurements in a weightless environment, such as is provided by a space vehicle. But then the time required for the fluid sample to come into thermal equilibrium becomes an important consideration. As the diffusion coefficient for the entropy S to be spread through the fluid is $D = \lambda/C_P$, where λ is the thermal conductivity and C_P is the constant pressure specific heat per unit volume, the characteristic relaxation time for the approach to equilibrium is generally taken to be $D^{-1}l^2$, where l is a characteristic length for the sample. As C_P and λ vary nearly as ξ_T^2 and ξ_T, respectively, D^{-1} is proportional to ξ_T, the correlation length, which implies a very long relaxation time when the fluid is brought close to its critical point. It has recently been noted[1] that the above conclusion, appropriate for an unconstrained fluid kept at the critical pressure, is not applicable to a clamped fluid kept at constant volume. In this case, which we examine here in detail, an entropy change anywhere in the fluid leads to a pressure change and, in turn, an adiabatic temperature change throughout the fluid. The resulting long-range correlation in the temperature produces a much more rapid equilibration than would result from diffusion alone. Although implicit in the existing body of knowledge, this effect, which is important for the feasibility of space experiments on the critical properties of fluids in a zero-gravity environment, has until now been overlooked. We therefore begin our exposition of it with a simple heuristic model. (We neglect the effect of gravity and restrict our analysis to small deviations from equilibrium.)

To illustrate the basic physical mechanism, it is convenient to imagine that a quantity of heat ΔQ_1 is introduced into a small subvolume V_1 of the fluid, whose total volume is $V_1 + V_2$. If the fluid is free to expand so as to avoid any change in pressure, the temperature and volume of V_1 will change by

$$\Delta T_1^{(0)} = \frac{\Delta Q_1}{V_1 C_P} \tag{1}$$

and

$$\Delta V_1 = \alpha_P V_1 \Delta T_1^{(0)}, \tag{2}$$

respectively, where α_P is the constant pressure thermal-expansion coefficient. But now, as a second step, we increase the pressure so as to bring the entire volume back to its original value and thereby cancel the expansion represented by Eq. (2). This is accomplished without any entropy exchange, as described by the adiabatic coefficient,

$$V\left(\frac{\partial T}{\partial V}\right)_S = -\frac{\gamma - 1}{\alpha_P}, \tag{3}$$

a familiar thermodynamic relation, where $\gamma = C_P/C_V$ is the specific-heat ratio. Substituting $V = V_1 + V_2$ and $\Delta V = -\Delta V_1$, from Eq. (2) into Eq. (3), yields the temperature rise in V_2,

$$\Delta T_2 = \frac{\Delta V_1}{V_1 + V_2}\frac{\gamma - 1}{\alpha_P} = (\gamma - 1)\frac{V_1}{V_1 + V_2}\Delta T_1^{(0)}. \tag{4}$$

The subvolume V_1 undergoes the same adiabatic temperature increase. The resulting rise in the average temperature $\langle T \rangle$ is the sum of the entropy and adiabatic contributions,

$$\Delta\langle T\rangle = \frac{V_1}{V_1 + V_2}\Delta T_1^{(0)} + (\gamma - 1)\frac{V_1}{V_1 + V_2}\Delta T_1^{(0)}$$

$$= \gamma\frac{\Delta Q_1}{(V_1 + V_2)C_P} = \frac{\Delta Q_1}{(V_1 + V_2)C_V}, \tag{5}$$

and is determined, as to be expected, by C_V, the constant volume specific heat. Dividing up the process envisioned above into two steps is not essential. The pressure and entropy changes can occur simultaneously so as to keep the total volume unchanged at all times. For a fluid close to its liquid-vapor critical point, $\gamma - 1$ is many orders of magnitude greater than 1. The essential point of this paper is that, because of the adiabatic effect, as expressed by the factor of $\gamma - 1$ in Eq. (4), the temperature of V_2, the main bulk of the fluid, which is untouched by any entropy transfer, can share to a considerable degree the temperature change of a small subregion $V_1 \ll V_2$, to which the ac-

tual heat transfer is confined. The approach to equilibrium is thereby considerably facilitated.

The long-range temperature correlation described by Eq. (4) can be analyzed in detail for the one-dimensional case of a sealed fluid kept between two parallel plates at $x = 0$ and $x = 2l$. Let these plates impose a prescribed time dependence for the boundary temperature, $T_B(t)$. The temperature at an arbitrary point in the fluid is $T(x,t)$, with special interest attached to the midplane temperature $T_{mid}(t) \equiv T(l,t)$. Because of the symmetry, we need study only the interval $0 \leq x \leq l$. Our specific goal is to find the relaxing temperature profile $T(x,t)$ for the problem defined by the time-dependent boundary condition $T_B(t) = 1 - \theta(t)$, where $\theta(t)$ is the usual Heaviside step function, zero for $t < 0$ and equal to one for $t > 0$. For convenience, and without loss of generality, we have shifted the zero base line to the final temperature, as well as renormalizing the temperature drop to equal unity, as permitted by linearity. During the initial phase of relaxation, before the adiabatic effect sets in, the temperature profile is represented by the usual error function diffusion formula

$$T^{(0)}(x,t) = \operatorname{erf}\frac{x}{\sqrt{4Dt}} . \tag{6}$$

Integration yields the effective thickness of the relaxed boundary layer as

$$x_{\mathrm{eff}} = \sqrt{(4/\pi)Dt} . \tag{7}$$

Identifying ΔT_2 and $\Delta T_1^{(0)}$ in Eq. (4) with $\Delta T_{mid}(t)$, and -1, respectively, and substituting $V_1/(V_1+V_2) = x_{\mathrm{eff}}/l$ gives

$$\Delta T_{mid}(T) = -(\gamma - 1)\frac{x_{\mathrm{eff}}}{l} = -\frac{2}{\sqrt{\pi}}\sqrt{\tau} , \tag{8}$$

where $\tau = t/t_1$, with the time unit given by

$$t_1 = \frac{D^{-1}l^2}{(\gamma - 1)^2} . \tag{9}$$

The initial drop of T_{mid} plotted versus τ in the upper half of Fig. 1 illustrates Eq. (8). The uppermost curve of the lower half of Fig. 1 shows $T(x,t)$ plotted versus the scaled space coordinate $\xi = (\gamma - 1)x/l$ for $\tau = \frac{1}{16}$. The early temperature profile is accurately represented by Eq. (6) for $\tau \ll 1$.

To carry the problem further we need to generalize Eq. (4) to many subvolumes V_i, and the associated heat transfers, ΔQ_i. These sum to the total volume $V = \sum_i V_i$ and the total heat $\Delta Q = \sum_i \Delta Q_i$, respectively. With all of these contributions pooled, Eq. (4) sums to $(\gamma - 1)\Delta Q/VC_P$, which, added to $\Delta T_i^{(0)}$, the temperature change from heat transfer, gives

$$\Delta T_i = \frac{\Delta Q_i}{V_i C_P} + (\gamma - 1)\frac{\Delta Q}{VC_P} . \tag{10}$$

The change in average temperature, from Eq. (10), is $\Delta\langle T \rangle = \gamma\Delta Q/VC_P = \Delta Q/VC_V$, as required. Using this to eliminate ΔQ from Eq. (10) yields

$$\Delta T_i = \frac{\Delta Q_i}{V_i C_P} + \left(1 - \frac{1}{\gamma}\right)\Delta\langle T \rangle , \tag{11a}$$
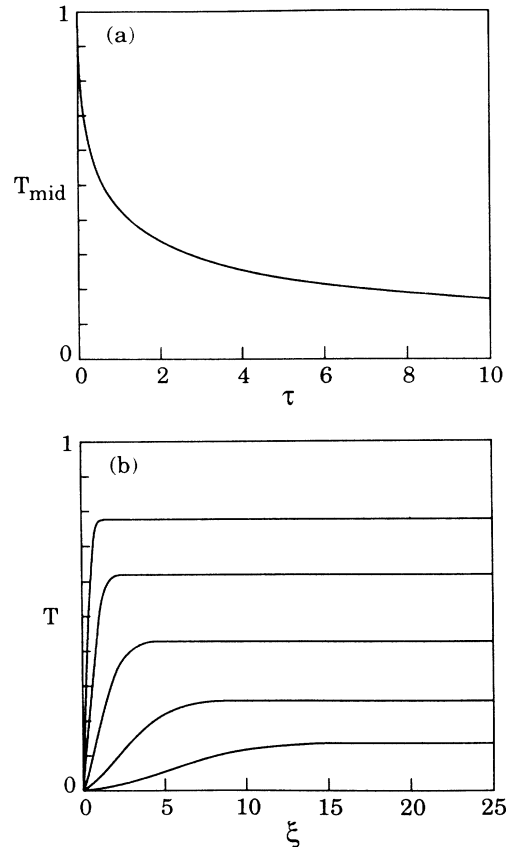

FIG. 1. (a) Midplane temperature T_{mid} vs dimensionless time $\tau = t/t_1$ and (b) temperature vs space variable in units of the fluid thickness $2l$ divided by $2(\gamma - 1)$, where $\gamma = C_P/C_V \gg 1$ is the specific-heat ratio. The profiles are for $\tau = \frac{1}{16}, \frac{1}{4}, 1, 4$, and 16, in descending order from above. The time unit is $t_1 = D^{-1}l^2/(\gamma - 1)^2$, where D is the constant pressure thermal diffusion coefficient.

or, equivalently, the entropy change

$$\Delta S_i = \frac{\Delta Q_i}{T} = \frac{V_i C_P}{T}\left[\Delta T_i - \left(1 - \frac{1}{\gamma}\right)\Delta\langle T \rangle\right] . \tag{11b}$$

For the continuum version of this equation we need to introduce the heat current density $-\lambda\nabla T$. Thus, the heat introduced into V_i in time dt is given by the convergence $\Delta Q_i/V_i = -\nabla\cdot(\lambda\nabla T)dt$, thereby converting Eq. (11a) into the partial integro-differential equation

$$\frac{\partial T}{\partial t} - D\nabla^2 T = \left(1 - \frac{1}{\gamma}\right)\frac{\partial\langle T \rangle}{\partial t} . \tag{12}$$

This equation can also be obtained from Eq. (11b) and the linearized heat conduction equation $\rho\partial\sigma/\partial t = \lambda\nabla^2 T$, where ρ and σ are the mass density and entropy per unit mass, respectively. The application of Eq. (12) to the one-dimensional geometry considered here is facilitated by the identity $\partial\langle T \rangle/\partial t = -(\gamma D/l)\partial T/\partial x|_0$ that follows from integrating over the interval $0 \leq x \leq 2l$ and imposing symmetry about the midplane. This identity expresses the necessary connection, via C_V, of the rise in mean temperature with the influx of heat at the boundary.

With some of the details to be provided elsewhere, we exhibit here the solution of the initial value problem posed by Eq. (12). For $t \geq 0$ the solution can be written as the Fourier integral

$$T(x,t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega f(x,\omega) e^{-i\omega t}, \qquad (13)$$

where the Fourier transform is

$$f(x,\omega) = \frac{1}{Dk^2} \frac{\cos kx - 1 + \tan kl \sin kx}{1 + (\gamma - 1)\tan kl/kl}$$

$$\simeq \frac{1}{Dk^2} \frac{\cos kx - 1 + i \sin kx}{1 + i(\gamma - 1)/kl}$$

$$= \frac{D^{-1}l^2}{(\gamma - 1)^2} \frac{\cos u\xi - 1 + i \sin u\xi}{u(u+i)}. \qquad (14)$$

Here $k^2 = i\omega/D$ and $u = kl/(\gamma - 1)$. As already introduced above, $\xi = (\gamma - 1)x/l$ is the scaled space variable. The approximation in the second line of Eq. (14) is valid for those real values of ω for which $|k| \gg l^{-1}$, so that $\tan kl \simeq i$. This limits the dimensionless time to $\tau \ll (\gamma - 1)^2$. Deforming the contour of integration to pass around the cut along the negative imaginary axis at $\omega = -iDk^2 = -iDl^{-2}(\gamma - 1)^2 u^2$ reduces the integration in Eq. (13) to

$$T(x,t) = \frac{2}{\pi} \int_0^{\infty} \frac{du}{u^2 + 1} e^{-\tau u^2} (1 - \cos u\xi)$$

$$+ \frac{2}{\pi} \int_0^{\infty} \frac{u\, du}{u^2 + 1} e^{-\tau u^2} \sin u\xi. \qquad (15)$$

For $u\xi \gg 1$ the contributions from the oscillating terms in the integrand vanish, leaving

$$T_{\text{mid}}(t) = \frac{2}{\pi} \int_0^{\infty} \frac{du}{u^2 + 1} e^{-\tau u^2} = e^{\tau} \text{erfc} \sqrt{\tau} \simeq \frac{1}{\sqrt{\pi \tau}}, \qquad (16)$$

where $\text{erfc} = 1 - \text{erf}$ is the complementary error function. The final expression in Eq. (16) is an approximation valid for $1 \ll \tau \ll (\gamma - 1)^2$. In this range the denominator of the integrand of Eq. (15) may be approximated by 1, yielding for the profile

$$\frac{T(x,t)}{T_{\text{mid}}(t)} \simeq 1 - \left(1 - \frac{\xi}{2\tau}\right) e^{-\xi^2/4\tau}. \qquad (17)$$

The exact result of the integration is

$$\frac{T(x,t)}{T_{\text{mid}}(t)} = 1 - e^{\xi} \frac{\text{erfc}(\sqrt{\tau} + \xi/2\sqrt{\tau})}{\text{erfc}\sqrt{\tau}}, \qquad (18)$$

which is readily seen to reduce to Eq. (17) for $\sqrt{\tau} \gg 1$ and to Eq. (6) for $\sqrt{\tau} \ll 1$. The function $T(x,t)$ has been computed from Eq. (18) and plotted versus ξ as the five curves in the lower half of Fig. 1, for $\sqrt{\tau} = \frac{1}{4}, \frac{1}{2}, 1, 2$, and 4.

At much longer times, $\tau \gtrsim \gamma^2$, the last stages of equilibrium proceed as a discrete sum of normal modes, having equal strength of $O(\gamma^{-1})$. The relaxation rate of the slowest mode is $D\pi^2 l^{-2}$, four times faster than that of the

fundamental mode in ordinary thermal diffusion. An alternative general treatment of this problem, based on a sum over the discrete modes will appear elsewhere.

Between the long times, $\tau \gtrsim \gamma^2$, and the short times, $\tau = O(1)$, there is a broad intermediate regime which can be characterized by the geometrical mean, $\tau_{\text{int}} \equiv \gamma$, corresponding to a real time of

$$\tau_{\text{int}} = \gamma t_1 = \frac{l^2}{\gamma D} = \frac{C_V}{\lambda} l^2. \qquad (19)$$

It is instructive to rederive Eq. (16) for the intermediate regime by returning to Eq. (4) and the simple picture on which it is based. The subvolume V_1 undergoes the total temperature change

$$\Delta T_1 = \Delta T_1^{(0)} + \Delta T_2 = \left[1 + (\gamma - 1)\frac{V_1}{V_1 + V_2}\right] \Delta T_1^{(0)}. \qquad (20)$$

The fraction by which the temperature in V_2 (inside the fluid) deviates from that in V_1 (the boundary layer) is, therefore,

$$\frac{\Delta T_1 - \Delta T_2}{\Delta T_1} = \frac{\Delta T_1^{(0)}}{\Delta T_1} = \frac{1}{1 + (\gamma - 1)V_1/(V_1 + V_2)}, \qquad (21)$$

which can be identified with $T_{\text{mid}}(t)$. In the intermediate time regime the second term inside the parentheses in Eq. (17) can be neglected, which yields for the effective thickness of the boundary layer

$$x_{\text{eff}}^{\text{int}} \equiv \int_0^{\infty} dx \left[1 - \frac{T(x,t)}{T_{\text{mid}}(t)}\right] \simeq \int_0^{\infty} dx\, e^{-\xi^2/4\tau} = \sqrt{\pi Dt}. \qquad (22)$$

This has the same diffusive time dependence as that of the initial thickness x_{eff} of Eq. (7), and differs from it only by the numerical factor $\pi/2$. Substituting

$$(\gamma - 1)V_1/(V_1 + V_2) = (\gamma - 1)x_{\text{eff}}^{\text{int}}/l = (\pi t/t_1)^{1/2} = \sqrt{\pi \tau}$$

into Eq. (21) gives $T_{\text{mid}} = (\pi \tau)^{-1/2}$ for $\tau \gg 1$ and completes our alternative derivation of Eq. (16) for the intermediate time regime. It is evident that in this regime the approach to equilibrium is dominated by the diffusion, more deeply into the fluid, of the quantity of entropy that has already been received in, or removed from, the boundary region during the earlier stages of the process. Going further, we note that setting $x_{\text{eff}} \simeq \sqrt{Dt}$ gives a good semiquantitative account, within a numerical factor of order unity, for the relaxation process from its very start through the intermediate time regime. The extension of these ideas and methods to the two-phase state and to the nonlinear problem of finite temperature jumps will appear elsewhere. Our results are consistent with some extensive numerical studies[2] as well as some previous observations[3] heretofore not understood.

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

[2]H. Boukari, J. N. Shaumeyer, M. E. Briggs, and R. Gammon, following paper, Phys. Rev. A **41**, 2260 (1990).

[3]D. Dahl and M. R. Moldover, Phys. Rev. A **6**, 1915 (1972); 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, France, 1987), Vol. SP-256, p. 109.