ADIABATIC HEATING EFFECT NEAR THE GAS–LIQUID CRITICAL POINT

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A new feature of macroscopic thermal relaxation processes is investigated in pure fluids near the gas–liquid critical point. If the total volume of the fluid is fixed, an adiabatic heating process can be the dominant temperature equilibration mechanism near criticality. That is, if the boundary temperature is changed, the resultant boundary diffusion layer acts as an efficient piston instantaneously producing an adiabatic volume change in the interior region. As a result, inhomogeneities of the fluid temperature are greatly reduced on a time scale rapidly going to zero at the critical point. On the other hand, when the two phases coexist below $T_c$, the adiabatic process induces a flow of latent heat through the interface. This flow persists for a long time and slows down the equilibration.

1. Introduction

Thermal equilibration processes in fluids near the gas–liquid critical point are known to be complicated and puzzling [1–3], mainly because of the following reasons: (i) Severe density stratification is produced on earth due to the strong divergence of the isothermal compressibility $K_T$ [4]. (ii) In many cases the processes are not described by the linearized hydrodynamic equations due to a number of critical anomalies, such as the divergence of the thermal conductivity $\lambda$ and those of the specific heats, $C_p$ and $C_v$ [3]. (iii) The analysis is very difficult in the presence of the two phases [1, 2]. (iv) Pressure perturbations propagate as sound waves and change rapidly in time, while the entropy (per unit mass) changes diffusively and undergoes critical slowing-down. This leads to an adiabatic heating effect if the total volume of the fluid is fixed [5, 6]. For example, if a sample is warmed from the boundary, a thermal expansion near the boundary instantaneously causes a nearly homogeneous
pressure increase \( \delta p \) throughout the sample. Then the sample is adiabatically warmed by the amount \((\delta T)_a = (\partial T / \partial p)_T \), \( \delta p \) even far from the boundary.

The aim of this paper is to illustrate the essence of this adiabatic effect, which seems to have not been fully discussed in the literature, in the simplest manner. To this end we will mostly neglect the gravity, but we will briefly discuss as to how it blurs the adiabatic effect in subsection 2.6. Our analysis, even in its present form, can explain a seemingly puzzling observation in space by Nitsche and Straub \[7\]. We will also discuss the effect when the two phases coexist. Following a lecture by one of the present authors \[5\], two groups have performed numerical analysis of the effect: Boukari et al \[8\] have presented an illustrative example of the effect near the critical point, and Zappoli et al. \[9\] have examined initial pressure and temperature changes in supercritical fluids. These two papers supplement our previous letter \[6\] and the present paper, because our papers mainly consist of analytic results.

2. Thermal relaxation in the one-phase region at fixed volume

2.1. Linear hydrodynamics

We use the linearized hydrodynamic equations to describe small perturbations in a homogeneous, quiescent, pure fluid. We further neglect the spatial dependence of the pressure deviation \( \delta p \), which is then a function of time \( t \) only. Namely, we are interested in slow processes with time scales much longer than the acoustic time scale \( l/c \), \( I \) being the cell length and \( c \) being the sound velocity. Using the relation

\[
\delta s = \left( \frac{\partial s}{\partial T} \right)_p \delta T + \left( \frac{\partial s}{\partial \rho} \right)_p \delta \rho .
\]

(1)

the thermal diffusion equation can be written as

\[
\frac{\partial}{\partial t} \delta T = \left( \frac{\partial T}{\partial \rho} \right)_p \frac{d}{dt} \delta \rho + D \nabla^2 \delta T .
\]

(2)

Here \( \delta s \) and \( \delta T \) are the deviation of the entropy per unit mass and that of the temperature and \( D = \lambda / \rho C_p \) is the thermal diffusion constant. \( \rho \) being the mass density.

The \( \delta s \) can also be written in terms of the density deviations \( \delta \rho \) and \( \delta p \) as

\[
\delta s = \left( \frac{\partial s}{\partial \rho} \right)_p \delta \rho + \left( \frac{\partial s}{\partial p} \right)_\rho \delta p .
\]

(3)

We consider the case in which the total volume \( V \) of the sample is fixed as in
the case of $C_v$ measurements. Then, we have to first order in the deviation

$$\delta V = \frac{1}{v} \int dr \delta v = -\frac{1}{\rho} \int dr \delta \rho = 0,$$

(4)

where $v = 1/\rho$ is the volume per unit mass and the integral is within the cell. We hereafter denote the spatial average by $\langle \cdots \rangle$,

$$\langle \cdots \rangle = \frac{1}{V} \int dr \langle \cdots \rangle.$$

(5)

Relation (3) yields

$$\delta p = \left( \frac{\partial p}{\partial s} \right)_{\rho} \langle \delta s \rangle = \left( \frac{\partial p}{\partial s} \right)_{\rho} (\rho TV)^{-1} Q(t),$$

(6)

where $Q(t)$ is the total heat supply from the outside to the sample through the boundary. The temperature deviation can then be written in terms of $\delta s$ and $\langle \delta s \rangle$ as

$$\delta T = \left( \frac{\partial T}{\partial s} \right)_{\rho} \delta s + \left( \frac{\partial T}{\partial p} \right)_{s} \delta p = \frac{T}{C_p} \delta s + T \left( \frac{1}{C_v} - \frac{1}{C_p} \right) \langle \delta s \rangle,$$

(7)

where use has been made of the relation

$$\alpha = \left( \frac{\partial T}{\partial p} \right)_{s} = \left( \frac{\partial p}{\partial T} \right)_{s} = 1 - \left( \frac{\partial p}{\partial T} \right)_{s} \left( \frac{\partial \rho}{\partial p} \right)_{s} = 1 - \frac{C_v}{C_p} = 1 - \frac{1}{\gamma}.$$\n
(8)

Hereafter we use the notation

$$\gamma = \frac{C_p}{C_v} > 1.$$

(9)

It follows that $0 < \alpha < 1$. The spatial average of (7) leads to a natural relation for the case of a fixed volume,

$$\langle \delta T \rangle = \left( T/C_v \right) \langle \delta s \rangle = Q(t)/\rho V C_V.$$

(10)

It goes without saying that, if $\rho$ is fixed, $C_p$ appears in (10) instead of $C_v$. Note that the second term of (7) is independent of space and represents the adiabatic temperature change that is present even if $\delta s$ is localized only near the boundary. We also notice that the second term of (7) can be easily much
greater than the first term near the critical point since \( \gamma \rightarrow \infty \) at criticality. Thus the adiabatic heating effect becomes increasingly important on approaching criticality.

If use is made of (6) and (8), the modified heat conduction equation (2) reads

\[
\frac{\partial}{\partial t} \delta T = \alpha \left( \frac{\partial}{\partial t} \delta T \right) + D \nabla^2 \delta T. \tag{11}
\]

The spatial integral of (11) over the cell becomes the equation of the total energy conservation as ought to be the case,

\[
\frac{d}{dt} Q(t) = \rho V C_v \left( \frac{\partial}{\partial t} \delta T \right) = \lambda \int d\sigma \mathbf{n} \cdot \nabla \delta T. \tag{12}
\]

where \( \int d\sigma (\cdots) \) is the surface integral and \( \mathbf{n} \) is the outward normal unit vector at the boundary.

### 2.2. Quick thermal equilibration

The thermal equilibration can be much quickened in the case \( \alpha \equiv 1 \). To show this let us change the boundary temperature by an infinitesimal amount \( T_b = \varepsilon T_c \) at \( t = 0 \). We shall see that the thermal boundary layer has the usual diffusion length \( (Dt)^{1/2} \) in an early stage. Then \( |\nabla \delta T| \sim T_b/(Dt)^{1/2} \) at the boundary and (12) yields

\[
\frac{\partial}{\partial t} \left( \langle \delta T \rangle \right) \sim \frac{\lambda}{L \rho C_v} \frac{T_b}{(Dt)^{1/2}}, \tag{13}
\]

where \( L \) is the characteristic linear size of the cell. This is integrated to give

\[
\frac{1}{T_b} \left( \langle \delta T \rangle \right) \sim \frac{1}{L} \gamma (Dt)^{1/2}. \tag{14}
\]

Owing to the large factor \( \gamma \), the right-hand side of (14) quickly reaches \( \varepsilon (1) \) for \( t \sim t_1 \), where

\[
t_1 = L^2/\gamma^2 D \propto L^2 \xi^{2.7}. \tag{15}
\]

\( \xi \) being the thermal correlation length. Note the relations \( \lambda \propto \xi \), \( C_p \propto \xi^{\gamma \hat{\gamma}} \), and \( C_v \propto \xi^{2\hat{\gamma}} \), and \( t_1 \propto L^2 \varepsilon^{\gamma \gamma} \) with \( \varepsilon = (T - T_c)/T_c \) on the critical isochore. Hereafter \( \hat{\gamma} \), \( \hat{\beta} \), and \( \hat{\alpha} \) are the usual critical exponents. Strikingly the time \( t_1 \) rapidly goes to zero near the critical point, while the usual relaxation time \( L^2/D \) (for
systems at constant pressure) grows as is well known. At $t \sim 1$ the boundary diffusion layer has a thickness of order $(D1)^{1/2} \sim \gamma^{-1}L$ and is still much thinner than the cell length $L$. We may prove that the thickness of the boundary layer remains of order $(D1)^{1/2}$ until the usual entropy diffusion time $t \sim L^2/D = \gamma^21$.

Nitsche and Straub measured the center temperature of a cylinder filled with SF$_6$ as response to the linearly increased wall temperature in space [7]. They found that the difference of the two temperatures stayed unexpectedly small. We believe that our theoretical results provide an explanation for their finding.

To examine the relaxation process more in detail, let us solve (11) in a simple one-dimensional case, $0 < x < L$, under the following boundary conditions:

$$\delta T(x, t) \to 0 \quad \text{as} \quad t \to 0, \quad \delta T(0, t) = \delta T(L, t) = T_1 \quad \text{for} \quad t > 0 .$$

(16)

We assume that $T_1$ is sufficiently small and the linear scheme is applicable. The details of the calculations will be deferred to the appendix and we here summarize the main features. The average temperature deviation behaves as

$$\langle \delta T \rangle / T_1 \equiv 4(t/\pi t_1)^{1/2} \quad \text{for} \quad t \ll t_1 ,$$

(17)

$$1 - \langle \delta T \rangle / T_1 \equiv 2(t_1/\pi t)^{1/2} \quad \text{for} \quad t_1 \ll t \ll \gamma^2 t_1 .$$

(18)

The difference between the average change $\langle \delta T \rangle$ and the change $[\delta T]_{in}$ in the interior region is very small for $t \ll L^2/D = \gamma^2 t_1$. Let us define a normalized temperature deviation,

$$G(x, t) = [T_1 - \delta T(x, t)]/[T_1 - (\delta T)_{in}] ,$$

(19)

which is 0 at $x = 0$ and tends to 1 in the interior region. We may define the effective thickness $x_{eff}(t)$ of the boundary layer by $\langle G \rangle = 1 - 2x_{eff}/L$. Then we shall see in the appendix

$$2x_{eff}/L = [\langle \delta T \rangle - (\delta T)_{in}] /[T_1 - (\delta T)_{in}] \sim (Dt)^{1/2}/L .$$

(20)

In the boundary layer near $x = 0$, the temperature profile is calculated as [6]

$$G(x, t) \equiv \begin{cases} \text{erf}(\hat{x}) & \text{for} \quad t \ll t_1 , \\ 1 - e^{x^2} + \hat{x} e^{-x^2}(t_1/t)^{1/2} & \text{for} \quad t_1 \ll t \ll \gamma^2 t_1 , \end{cases}$$

(21a, 21b)

where

$$\hat{x} = x/(4Dt)^{1/2} .$$

(22)
The third term on the right-hand side of (21b) is dominant near the boundary where \( \dot{x} \ll (t_i/l)^{1/2} \) or \( x \ll L/\gamma \). Therefore, the heat flux \( \lambda \, dT/dx \) at the boundary is equal to \( \frac{1}{2} \lambda (T_1 - [\delta T]_{in}) L/\Delta t \propto t^{3/2} \) in the time region \( t_i \ll t \ll \gamma^2 t_i \), in accord with (12). On the other hand, for \( t \gg \gamma^2 t_i \), we have the following exponential decay:

\[
1 - \delta T(x, t)/T_1 = (2/\gamma)[1 - \cos(2\pi x/L)] \exp(-4\pi^2 \Delta t/L^2).
\]  
(23)

which is the first term, \( n = 1 \), of (A.13) in the limit \( \gamma \to \infty \).

The temperature firstly rises as \( t^{1/2} \) for \( t \ll t_i \), secondly undergoes the polynomial relaxation \( (xt)^{1/2} \) in the wide region, \( t_i \ll t \ll \gamma^2 t_i \), and finally shows the exponential relaxation for \( t \gg \gamma^2 t_i \), with the decay rate \( 4\pi^2 \Delta t/L^2 \), which is four times larger than that of the usual case of fixed pressure. We expect that this is a general aspect in the linear regime, independent of the geometry of the cell, if use is made of a suitably chosen characteristic length \( L \). The temperature profile in the time region \( t \ll \gamma^2 t_i \) is characterized by two distinctly different spatial regions, the boundary layer with thickness \( (\Delta t)^{1/2} \) and the plateau-like interior region. Zappoli et al. [9] aptly described the role of the boundary layer as a piston compressing or expanding the interior region adiabatically.

2.3. Density change

The density change is also of great interest. Using (6) \( \sim (10) \) we obtain the following two expressions:

\[
\delta \rho = \left( \frac{\partial \rho}{\partial T} \right)_p (\delta T - \langle \delta T \rangle)
= \left( \frac{\partial \rho}{\partial s} \right)_p \left( \delta s - \frac{1}{T} C_\gamma \langle \delta T \rangle \right).
\]  
(24)

In the time region \( 0 < t \ll t_i \), \( \langle \delta T \rangle \) is considerably smaller than \( T_1 \) and (24) indicates that the density change at the boundary is of the following order:

\[
(\delta \rho)_b \sim \left( \frac{\partial \rho}{\partial T} \right)_p T_1 \quad \text{for } t \ll t_i.
\]  
(26)

Hereafter \( \cdot \cdot \cdot |_b \) and \( \cdot \cdot \cdot |_n \) denote the value at the boundary and that in the interior region, respectively. In particular, if the fluid was at the critical density \( \rho = \rho_c \) before the temperature change, we have \( \Delta_n = (\delta \rho)_b/\rho_c \sim e^{-\gamma} \epsilon_1 \) (where \( \epsilon_1 = T_1/T_c \)) in the linear regime. As a result the boundary layer can stay within the critical isochore only when \( T_1 \) is very small.

\[
|\epsilon_1| = |T_1/T_c| \ll e^{\beta \gamma^{1/2}}.
\]  
(27)
where $\hat{\beta}$ is also the usual critical exponent nearly equal to $1/3$. In this linear case, (25) shows that the density change in the interior region is much smaller as

$$\langle \delta \rho \rangle_{in} \equiv \left( \frac{\partial \rho}{\partial \rho} \right) \delta s = -\frac{1}{T} \left( \frac{\partial \rho}{\partial s} \right) \rho C_v(\delta T)_{in}.$$  \hspace{1cm} (28)

Since $(\partial \rho/\partial s)_p$ is nearly constant in the critical region, we find the ratio in the form

$$\left| \frac{\langle \delta \rho \rangle_{in}}{\langle \delta \rho \rangle} \right| \sim \gamma^{-1/3} \langle \delta T \rangle / T \ll \gamma^{-1} \text{ for } t \ll t_1.$$  \hspace{1cm} (29)

In terms of $G(x, t)$ defined in (19), the density profile can be written as

$$\delta \rho - \langle \delta \rho \rangle_{in} = \left( \frac{\partial \rho}{\partial T} \right) \rho \left[ T - \langle \delta T \rangle_{in} \right] (1 - G).$$  \hspace{1cm} (30)

In the time region $t_1 \ll t \ll \gamma^2 t_1$, from (18) and (21b) we find

$$\delta \rho - \langle \delta \rho \rangle_{in} = 2 \left( \frac{\partial \rho}{\partial T} \right) \rho T_1 [1 - \hat{x}(t_1/t)]^{1/2} (t_1/\pi t)^{1/2} e^{-\hat{x}^2},$$  \hspace{1cm} (31)

$\hat{x}$ being defined by (22).

2.4. Nonlinear case

If (27) does not hold as in the case of $\epsilon_1 \sim \epsilon$, we should have $(\partial \rho / \partial T)_p \propto \Delta_n^{-\hat{\beta}}$ near the boundary from the scaling consideration, so that

$$\Delta_n = (\delta \rho)_p / \rho_c \sim |\epsilon_1|^{\hat{\beta} / (\hat{\beta} + \hat{\gamma})} \text{ for } |\epsilon_1| \geq \epsilon^{\hat{\beta} + \hat{\gamma}}.$$  \hspace{1cm} (32)

In this nonlinear regime the boundary layer is brought into an off-critical region. There, the linear relations so far cannot be used (at least in their present forms) until $\Delta_n$ decreases down to the order of $\epsilon^{\hat{\beta}}$. However, we may assume that the interior region is still linearly perturbed. This is satisfied for $|\langle \delta \rho \rangle_{in}| \ll \rho_c \epsilon^{\hat{\beta}}$, so that at $[\delta T] \sim T_1$ (28) yields

$$|\epsilon_1| \ll \epsilon^{\hat{\beta} + \hat{\gamma}}.$$  \hspace{1cm} (33)

Then we can make some estimations in the early stage. Note the relation

$$\frac{1}{\rho} \delta \rho = \frac{1}{\rho} \left( \frac{\partial \rho}{\partial s} \right)_p \delta s + \frac{1}{\rho} \left( \frac{\partial \rho}{\partial \rho} \right)_s \delta \rho,$$  \hspace{1cm} (34)
where \((\partial \rho / \partial s)_p = -\rho^2(\partial T / \partial \rho)_s\) is virtually a constant in the critical region, \(|\delta T| \ll T_c\) and \(|\delta \rho| \ll \rho_c\). Integrating (34) over the space we obtain

\[
\delta V = \left(\rho^2 T\right)^{1/2} \left(\frac{\partial \rho}{\partial s}\right)_p Q(t) + \left\langle \frac{1}{\rho} \left(\frac{\partial \rho}{\partial \rho}\right)_s \right\rangle V \delta \rho = 0 .
\]  

(35)

Note that \((\partial \rho / \partial \rho)_s \sim C_v\). In the early stage, in which the boundary layer is much thinner than \(L\), we may replace the average \(\left\langle \rho^{-1}(\partial \rho / \partial \rho)_s \right\rangle\) by the value in the interior region \([\rho^{-1}(\partial \rho / \partial \rho)_s]_m\) to obtain

\[
\delta \rho \equiv \left[\left(\frac{\partial \rho}{\partial s}\right)_p\right]_m (\rho TV)^{-1} Q(t) .
\]  

(36)

The temperature deviation in the interior region is then

\[
(\delta T)_m \equiv \left(\frac{1}{C_v}\right)_m (\rho V)^{-1} Q(t) .
\]  

(37)

Next we calculate the counterpart of the characteristic time \(t_1\), (15), in the nonlinear regime and denote it by \(t_{n1}\). We assume that the heat flux at the boundary is given by \(\lambda T_1/(D t)^{1/2}\) in the early stage \(t \ll t_{n1}\) where \(\lambda\) and \(D\) are the values at the boundary. It decreases as the density deviates from the critical isochore. Then, from (37), the counterpart of (13) becomes

\[
\frac{\partial}{\partial t} (\delta T)_m \sim \frac{1}{\rho L} \left(\frac{\lambda}{D^{1.2}}\right)_b \left(\frac{1}{C_v}\right)_m T_1 t^{1.2} .
\]  

(38)

Integrating (38) and setting \((\delta T)_m \sim T_1\), we find

\[
t_{n1} = \left[L^{2}(D)_b\right] / [(C_v)_m / (C_p)_b]^2
\]  

(39a)

\[
= t_1 (\lambda C_p)_m / (\lambda C_p)_b .
\]  

(39b)

The second line holds when the interior region has only slightly deviated from the initial thermodynamic state. If further use is made of (32), we obtain

\[
t_{n1} \sim t_1 (\epsilon_1 / \epsilon)^{\beta + \gamma} (\nu + \gamma)^{1 + \beta + \gamma} .
\]  

(40)

Hence \(t_{n1} > t_1\) and, if \(\epsilon_1 = \epsilon\), it follows

\[
t_{n1} \sim t_1 \epsilon^{-\beta} \sim L^{2} \epsilon^{1.0} .
\]  

(41)

where \(p = (\beta + \gamma - 1)(\nu + \gamma) / (\beta + \gamma) \equiv 0.71\). At \(t = t_1\), \(\Delta_n(t) / \Delta_n(0)\) decays to
1/2, say. Note that we have not yet examined the subsequent relaxation to the linear regime, in which \( \frac{1}{2} > \frac{\Delta_B(t) / \Delta_B(0)}{\epsilon^2} > \epsilon^2 \).

We notice that the time \( t_{nl} \) generally goes to zero as \( \epsilon \to 0 \) under (33) and is of course much shorter than the entropy diffusion time \( D/L^2 = \gamma^2 t_1 \). Therefore, we may expect that the exponential relaxation still occurs on the time scale of \( \gamma^2 t_1 \) even in the nonlinear case, (32) and (33), despite the initial nonlinear relaxation in the boundary layer.

### 2.5. Adiabatic energy change

It is also of great interest to examine the amount of the internal energy increase in the interior region, which is nothing but the energy transported by acoustic modes from the boundary into the interior region. Far from the boundary the internal energy \( e \) per unit mass changes as

\[
\delta e = -\rho \delta v = \rho^{-2} p \left( \frac{\partial p}{\partial \rho} \right)_s \delta \rho = p \left( \frac{\partial T}{\partial \rho} \right)_s \delta s ,
\]

where \( \delta s = 0 \) and use has been made of (6). The total energy change \( (\delta E)_{in} \) in the interior region is written as

\[
(\delta E)_{in} = V_{in} \rho \delta e = (V_{in} / V) a_s Q ,
\]

where \( V_{in} \) is the volume of the interior region and is nearly equal to the total volume \( V \) in the early stage since \( 1 - V_{in} / V \sim (Di)^{1/2} / L \). Note that (43) holds even in the nonlinear case (32) from (36). The coefficient \( a_s \) is defined by

\[
a_s = \frac{p}{T} \left( \frac{\partial T}{\partial \rho} \right)_s = (1 - \gamma^{-1}) \frac{p}{T} \left( \frac{\partial T}{\partial \rho} \right)_p ,
\]

where use has been made of \( (\partial T/\partial \rho)_s = \alpha (\partial T/\partial \rho)_p \) from (8). As is well known \( (\partial p/\partial T)_\rho \) tends to a constant at the critical point. The value of \( a_s \) at the critical point is 1/6.02 for Xe, 1/6.98 for CO₂, 1/3.92 for \(^4\)He according to ref. [10], and 1/4 from the van der Waals equation of state. We have hence a very simple result,

\[
(\delta E)_{in} \approx a_s Q ,
\]

in the early stage in which \( V - V_{in} \ll V \). From energy conservation the internal energy change in the boundary region is

\[
(\delta E)_b = Q - (\delta E)_{in} \approx (1 - a_s) Q .
\]
The \(a_s\) turns out to be the fraction of energy adiabatically transported into the interior region. Relations (45) and (46) hold even far from the critical point in the early stage, \(V - V_{in} \ll V\), under a fixed total volume.

### 2.6. Gravity effect

We finally consider the adiabatic effect in the presence of gravity. To simplify the problem we neglect both rapid variations occurring on the acoustic time scale \(L/c\) and collective motions triggered by the hydrodynamic instabilities. The geometry is assumed to be one-dimensional in the region, \(0 < x < L\), with the \(x\)-axis in the vertical direction under a fixed total volume \(V\). The velocity field \(v(x, t)\) is supposed to be present only along the \(x\)-axis and is then longitudinal, related to the temporal variation of the density by \(\partial v/\partial x = -\rho^{-1}\partial \rho/\partial t\). In such quasi-stationary situations, the velocity field should be very small and the pressure gradient should be locally balanced with the density variation by

\[
\frac{\partial}{\partial x} p(x, t) = g\rho(x, t).
\]

\(g\) being the gravitational acceleration.

In the case of a fixed volume the pressure is composed of three parts.

\[
p(x, t) = p_{eq}(x) + \delta p_0(t) + \delta p_1(x, t). \tag{48}
\]

The first part \(p_{eq}(x)\) is the equilibrium pressure related to the equilibrium density \(\rho_{eq}(x)\) by \([4, 10]\)

\[
\frac{\partial}{\partial x} p_{eq}(x) = g\rho_{eq}(x) \tag{49a}
\]

or

\[
\frac{\partial}{\partial x} \mu_{eq}(x) = g. \tag{49b}
\]

where \(\mu_{eq}\) is the chemical potential per unit mass in equilibrium. The second part \(\delta p_0(t)\) is the homogeneous pressure change under consideration so far, determined by the fixed volume condition (4). The third part is a new part induced by the density deviation \(\delta \rho(x, t) = \rho(x, t) - \rho_{eq}(x)\) and is determined by (47). Integration of (47) yields

\[
\delta p_1(x, t) = g \int_0^x dx' \delta \rho(x', t). \tag{50}
\]
so that \( \delta p_1(0, t) = \delta p_1(L, t) = 0 \) from (4). This part changes rapidly in the boundary layer and slowly in the interior region.

Since \( C_p \) and \( \lambda \) can strongly depend on the height \( x \) in gravity near the critical point, the heat conduction equation for a small temperature deviation \( \delta T(x, t) \) should be written as

\[
\frac{\partial}{\partial t} \delta T = \left( \frac{\partial T}{\partial p} \right)_s \frac{\partial}{\partial t} \delta p + \frac{1}{\rho C_p} \frac{\partial}{\partial x} \lambda \frac{\partial}{\partial x} \delta T .
\]

(51)

Here \( (\partial T/\partial p)_s \) is nearly a constant, \( \delta p = \delta p_0 + \delta p_1 \) is given by (48), and \( C_p \propto \xi_{/0}^a \) and \( \lambda \propto \xi \) with \( \xi \) being the height-dependent correlation length. We have now a closed set of equations describing the temperature relaxation, although numerical analysis seems to be required in general.

We consider the thermal relaxation after a change of the boundary temperature as in the previous subsections. Notice that, even under gravity, the initial stage of the relaxation should be still characterized by the presence of the boundary layer acting as a piston and the interior region where \( \delta s \approx 0 \). As a simplifying result, furthermore, we can show that the pressure and temperature changes in the interior region are nearly homogeneous in most realistic conditions. To show this we first estimate \( \delta p_1 \). Its maximum in space just after the boundary temperature change is estimated as

\[
|\delta p_1| \leq \left( \frac{\partial T}{\partial p} \right)_s \langle \delta s \rangle L .
\]

(52)

If \(|\delta p_1| \leq |\delta p_0| \) is assumed, (35) still holds and we have

\[
\frac{Q(t)}{\rho TV} = \langle \delta s \rangle \equiv \left( \frac{\partial s}{\partial p} \right)_p \delta p_0 .
\]

(53)

Thus,

\[
|\delta p_1/\delta p_0| \leq gL/\langle c^2 \rangle ,
\]

(54)

where \( \langle c^2 \rangle \) is the spatial average of the square of the sound velocity \( c^2 = (\partial p/\partial \rho)_s \). We assume that the right-hand side of (54) is much smaller than 1. The adiabatic temperature change in the interior region is then given by

\[
(\delta T)_{in} \approx \left( \frac{\partial T}{\partial p} \right)_s \delta p_0 \approx \frac{1}{\langle c_V \rangle} \frac{1}{\rho V} Q(t) ,
\]

(55)

which is a generalization of (10). The flow rate \( \partial Q/\partial t \) is determined by \( \lambda \) and \( D \) at the boundary if the diffusion layer is sufficiently thin (compared to the
inverse of $[\partial \ln \xi/\partial x]$ at the boundary, which characterizes the inhomogeneity due to gravity). Then we have an equation for $\partial(\delta T)_{in}/\partial t$ in the same form as (13) or (38), in which $\langle C_v \rangle$ appears instead of $C_v$ or $(C_v)_{in}$. Similarly to (15) or (39) we find the corresponding relaxation time,

$$t_r \sim \frac{L^2}{(D)_{in}} \frac{\langle C_v \rangle}{(C_p)_{in}}.$$  \hspace{1cm} (56)

The interior region has now been characterized as a medium whose specific heat is effectively given by the average $\langle C_v \rangle$.

3. Thermal relaxation in the two-phase region at fixed volume

So far we have treated a pure fluid in the one-phase region. On the other hand, when two phases coexist, we may expect further interesting effects. Let us suppose a macroscopic interface separating the gas phase and the liquid phase at the center of the cell. The adiabatic process after warming or cooling at the boundary shifts the thermodynamic states of the two phases in the interior region upward for warming (or $\delta p > 0$) and downward for cooling (or $\delta p < 0$) in the $p-T$ phase diagram (or more conveniently in the $s-T$ phase diagram because $s$ is unchanged). The subsequent phenomena are very different depending on the magnitude of $\delta p$. If $\delta p$ is positive and large, the two phases will be shifted into the one-phase region and the interface will vanish eventually. If $\delta p$ is negative and its magnitude is large, we should observe emergence of small domains via nucleation or spinodal decomposition throughout the sample. As the simplest case, if $|\delta p|$ is sufficiently small, the two phases will not exhibit any instability and return to thermodynamic states on the coexistence curve characterized by a new temperature. For simplicity we will focus our attention on the last case assuming that the linear treatments are allowable.

First notice that there should arise a flux of latent heat through the interface. This can be readily understood as follows. The entropy difference between the two phases is given in the initial equilibrium state ($t < 0$) by

$$(\Delta s)_{int} = A_s (T_c - T')^{\hat{\beta}}.$$  \hspace{1cm} (57)

where $A_s$ is a constant. At $t = 0$ the boundary temperature is changed to $T + T_1$ and in the ultimate final state, $t \to \infty$, the entropy difference becomes

$$(\Delta s)_{fin} = A_s (T_c - T - T_1)^{\hat{\beta}}$$

$$\cong (\Delta s)_{int} - \hat{\beta} A_s (T_c - T)^{\hat{\beta} - 1} T_1.$$  \hspace{1cm} (58)
We have assumed \( |T_r| \ll T_c - T \) in the second line. Denoting the volume fraction of the minority phase by \( \phi \), the total amount of latent heat, which flows through the interface, is estimated as

\[
Q_{\text{lat}} \equiv \rho \beta T_c \hat{\beta} A_s (T_c - T)^{\hat{\beta} - 1} T_{\text{f}} \phi V.
\]

This should be compared with the externally given heat (10). The latter will be written as \( Q_{\text{ext}} \). By setting \( \langle \delta T \rangle = T_1 \) (because we are considering the final state), we find

\[
Q_{\text{lat}} / Q_{\text{ext}} \equiv \phi \hat{\beta} T_c A_s (T_c - T)^{\hat{\beta} - 1} / C_v \sim \phi \gamma^{1/2},
\]

where use has been made of \( \hat{\beta} = 1 + \hat{\alpha} = \frac{1}{2}(\hat{\alpha} - \hat{\gamma}) \). The above ratio can well exceed 1 even for small \( \phi \).

We expect that the current through the interface persists for a long time of the order of the diffusion time \( L^2/D \). Then, how is the internal current induced? Recently one of the authors [11] has shown that the gas phase becomes slightly warmer than the liquid phase against a small pressure increase. This is because the thermodynamic derivative \( (\partial T/\partial p) \), takes slightly different values in the two phases,

\[
\left( \frac{\partial T}{\partial p} \right) = \left( \frac{\partial T}{\partial p} \right)_{\text{cri}} \left( 1 \pm \frac{a_c}{\sqrt{\gamma}} + \cdots \right),
\]

where \( (\partial T/\partial p)_{\text{cri}} \) is the critical-point value, the plus sign is for the gas phase, and the minus sign for the liquid phase. The coefficient \( a_c \) is a universal number of order 1 [11]. Therefore, for a pressure change \( \delta p \), the resultant temperature difference between the two phases is

\[
(\Delta T)_{g-\ell} = 2 \left( \frac{\partial T}{\partial p} \right)_{\text{cri}} \frac{a_c}{\sqrt{\gamma}} \delta p
\]

\[
\approx 2 \frac{a_c}{\sqrt{\gamma}} (\delta T)_{\text{in}},
\]

where \( (\delta T)_{\text{in}} = (\partial T/\partial p)_{\text{in}} \), \( \delta T \) is the adiabatic temperature change in the interior region. Recall the relation (18) for \( t_1 \leq t \leq \gamma^2 t_1 \), which indicates that \( T_1 - (\delta T)_{\text{in}} \) decays below \( (\Delta T)_{g-\ell} \) for \( t \leq t_{g-\ell} \). By equating the right-hand sides of (18) and (62), the crossover time \( t_{g-\ell} \) is calculated as

\[
t_{g-\ell} = \gamma t_1 = L^2/\gamma D \propto L^2 \xi^{-0.7}.
\]

For \( t \geq t_{g-\ell} \) the main inhomogeneity in the system turns out to exist near the
interface of the two phases. The diffusion length at \( t \sim t_{g-l} \) is given by \((D_{g-l})^{1/2} \sim L/\gamma^{1/2}\) and is still thinner than the cell size. Notice that \( t_{g-l} \) goes to zero on approaching the critical point.

In the \( C_v \) measurements by Brown and Meyer [1] and by Dahl and Moldover [2], they observed rapid thermal relaxation times in the one-phase case even close to the critical point. We believe that the adiabatic heating effect should have been crucial in their experiments. On the other hand, in two-phase states, they observed markedly different, long relaxation times, which apparently suggested anomalously slow motion of an interface [2, 3]. However, in the light of the adiabatic effect, the slow relaxation can be explained differently: their measured relaxation times are much longer than \( t_{g-l} \), and the two groups should have measured relaxation times of latent heat exchange between gas and liquid regions.

### 4. Concluding remarks

1) The critical speeding up at fixed volume is surprising in view of the well-known critical slowing-down at fixed pressure.

2) The adiabatic effect in the two-phase case is more surprising. The two phases undergo slightly different, adiabatic temperature changes due to relation (61). The resultant slow process of latent heat exchange seems to explain the puzzling findings reported in refs. [1, 2] in the two-phase case. Further experimental investigations on this point should be very informative. It is worth noting that the adiabatic heating process also gives rise to an interesting effect of large enhancement of the sound attenuation when fluids are undergoing phase separation [11]. This is because pressure variations associated with ultrasound induce oscillatory heat flows between the two phases and large dissipation occurs at low frequencies.

3) The space experiment by Nitsche and Straub [7] called for the examination of the adiabatic effect [5]. However, it should be stressed that the effect itself exists even on earth as shown in subsection 2.6. It has not been apparent on earth and has remained unnoticed.

4) In binary mixtures spinodal decomposition experiments have been performed by adiabatically changing the pressure [12, 13]. In pure fluids spinodal decomposition and nucleation can be instantaneously induced almost in the same manner by lowering of the boundary temperature.

5) In this paper we have neglected rapid spatio-temporal variations of the pressure. Such variations have been numerically examined in ref. [9] on the acoustic time scale, which justifies our assumption that the pressure variation is a function of time only.
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Appendix

To solve (11) under (16) we define dimensionless quantities by

\[ X = x/L, \quad \tau = DL^{-2}t, \quad F(X, \tau) = \delta T(x, t)/T_1. \]  (A.1)

The Laplace transformation of \( F(X, \tau) \) will be denoted by

\[ \hat{F}(X, p) = \int_0^\infty d\tau \, F(X, \tau) \exp(-p\tau). \]  (A.2)

Then, (11) becomes

\[ p\hat{F} = \alpha p\langle \hat{F} \rangle + \frac{\partial^2}{\partial X^2} \hat{F}. \]  (A.3)

Using \( \hat{F} = 1/p \) at \( X = 0 \) and 1, we may solve (A.3) in the form

\[ \hat{F} = \alpha \langle \hat{F} \rangle + \left( \frac{1}{p} - \alpha \langle \hat{F} \rangle \right) \frac{\cos[k(2X - 1)]}{\cos k}, \]  (A.4)

where

\[ k = \frac{i}{2} p^{1/2} \quad \text{or} \quad p = -4k^2. \]  (A.5)

The spatial average of (A.4) yields

\[ p \langle \hat{F} \rangle = \gamma \phi(k)/[1 + (\gamma - 1)\phi(k)], \]  (A.6)

where

\[ \phi(k) = \tan(k)/k = \tanh(\sqrt{p}/2)/(\sqrt{p}/2). \]  (A.7)

Substituting (A.6) into (A.4) we find

\[ p \Delta \hat{F} = 1 - p\hat{F} = \left( 1 - \frac{\cos[k(2X - 1)]}{\cos k} \right) / [1 + (\gamma - 1)\phi(k)] \]
\[ = [1 - \cos(2kX) - \tan(k) \sin(2kX)]/[1 + (\gamma - 1)\phi(k)]. \]  (A.8)
Hereafter $\Delta \hat{F}$ is the Laplace transform of $\Delta F = 1 - F$, the amount by which $F(X, \tau)$ has not yet reached its full equilibrium value of 1. Of particular interest is the value of $\Delta F$ in the interior of the fluid, far from the diffusion layers, in the early time region in which the two characteristic spatial regions are well defined. In the interior region the oscillating terms in the numerator of (A.8) disappear leaving the $X$-independent Laplace transform

$$ \Delta \hat{F}_{\text{in}}(p) = \frac{p^{-1}}{1 + (\gamma - 1)\phi(k)} . \quad (A.9) $$

Deforming the contour of integration in the complex-$p$ plane to pass around the poles of $\Delta \hat{F}_{\text{in}}(p)$ that lie along the non-positive real axis of $p$ gives

$$ \Delta F_{\text{in}}(\tau) = \sum_{n=1}^{\infty} e^{-4k_n^2\tau}R_n . \quad (A.10) $$

with

$$ R_n = \frac{2(\gamma - 1)}{\gamma(\gamma - 1) + k_n^2} . \quad (A.11) $$

The contribution from the pole $p = 0$ is given by $\gamma^{-1}$ and has been neglected. The poles in the complex-$p$ plane are located, according to (A.5) and (A.7), at $p_n = -4k_n^2$, where

$$ \tan(k_n) = -\frac{k_n}{\gamma - 1} . \quad (A.12) $$

The values of $k_n$ may be taken to be positive and we find $n - \frac{1}{2} < k_n/\pi < n$. More generally $\Delta F(X, \tau)$ may be expressed as

$$ \Delta F(X, \tau) = \sum_{n=1}^{\infty} R_n [1 - \cos(2k_nX) - \tan(k_n) \sin(2k_nX)] e^{-4k_n^2\tau} . \quad (A.13) $$

For further manipulation of (A.10) and (A.13) we change the summation variable to

$$ u_n = \frac{k_n}{\gamma - 1} \quad (A.14) $$

and the time variable to

$$ \tilde{\tau} = \tau/\tau_1 \quad (A.15) $$
where

\[ \tau_1 \equiv \frac{1}{4(\gamma - 1)^2} . \]  

(A.16)

In the case \( \gamma \gg 1 \), by virtue of (A.12) and (A.14), we have a dense distribution for the summation variable \( u_n \). The spacing of consecutive discrete values is

\[ \Delta u_n \equiv u_{n+1} - u_n = \frac{k_{n+1} - k_n}{\gamma - 1} . \]  

(A.17)

To a first approximation, from (A.13) in the limit \( \gamma \to \infty \), we have \( k_{n+1} - k_n = \pi \), so that

\[ \Delta u_n \approx \frac{\pi}{\gamma - 1} \ll 1 . \]  

(A.18)

The density of terms in the summation is therefore given by

\[ \rho(u) = \frac{1}{\Delta u_n} = \frac{\gamma - 1}{\pi} . \]  

(A.19)

Substitution of this expression into (A.11) gives

\[ \Delta F_{\text{in}} \approx \frac{2}{\pi} \int_0^{\infty} \frac{du}{1 + u^2} e^{-u^2\tau} = e^\tau \text{erfc}(\sqrt{\tau}) , \]  

(A.20)

where \( \text{erfc} = 1 - \text{erf} \) is the complementary error function. For very early times, and for times later than \( \tau_1 \), (A.20) simplifies to

\[ \Delta F_{\text{in}}(\tau) \equiv \begin{cases} 1 - 2(\tau/\pi)^{1/2} & \text{for } 0 \leq \tau \ll 1 , \\ (1/\pi\tau)^{1/2} & \text{for } 1 \ll \tau \ll \gamma^2 . \end{cases} \]  

(A.21a,b)

Similarly, for \( \tau \ll \gamma^2 \), \( \Delta F(X, \tau) \) is approximated by

\[ \Delta F(X, \tau) \approx \frac{2}{\pi} \int_0^{\infty} \frac{du}{1 + u^2} e^{-u^2\tau}[1 - \cos(u\tilde{X}) - u \sin(u\tilde{X})] , \]  

(A.22)

where use has been made of (A.12) and

\[ \tilde{X} = 2(\gamma - 1)X . \]  

(A.23)
The integration with respect to \( u \) in (A.22) is exactly performed to give
\[
\frac{\Delta F(X, \tau)}{\Delta F_{\text{in}}(\tau)} \equiv 1 - \exp(-X^2) \operatorname{erfc}(\sqrt{\tau} + X/2\sqrt{\tau})/\operatorname{erfc}(\sqrt{\tau}) .
\] (A.24)
This yields (21a) and (21b).

The space dependence of the temperature profile near the boundaries will be exhibited explicitly elsewhere [6]. Here we will limit ourselves to those salient features of the profile that can be inferred from the space average of \( \Delta \tilde{F} = 1: \)
\[
p - \tilde{F}.
\]

Thus, the amount by which the average falls below the flat, plateau-like, interior value is
\[
\delta(\Delta \tilde{F}) = \langle \Delta \tilde{F} \rangle - \Delta \tilde{F}_{\text{in}} = \frac{1}{\gamma - 1} \left( \Delta \tilde{F}_{\text{in}} - \frac{1}{p} \right) .
\] (A.26)
so that the inverse Laplace transform yields
\[
\delta(\Delta F) = \langle \Delta F \rangle - \Delta F_{\text{in}} = \frac{1}{\gamma - 1} (\Delta F_{\text{in}} - 1) .
\] (A.27)

We can define an effective thickness of the boundary diffusion layers, \( X_{\text{eff}} \), by
\[
(2X_{\text{eff}})(\Delta F_{\text{in}}) = -\delta(\Delta F) .
\] (A.28)
from \( \langle \Delta F \rangle = (1 - 2X_{\text{eff}}) \Delta F_{\text{in}} \), so
\[
X_{\text{eff}} = \frac{1}{2(\gamma - 1)} \left( \frac{1}{\Delta F_{\text{in}}} - 1 \right) .
\] (A.29)
Substitution of (A.21a, b) gives
\[
X_{\text{eff}} \equiv \begin{cases} 
\frac{1}{\gamma - 1} (\hat{\tau}/\pi)^{1/2} = (4\tau/\pi)^{1/2} , & 0 \leq \tau \leq \tau_1 , \\
\frac{1}{2(\gamma - 1)} (\pi \hat{\tau})^{1/2} = (\pi \tau)^{1/2} , & \tau_1 \leq \tau \leq 1 .
\end{cases}
\] (A.30a)
The early time development expressed by (A.30a) is nothing other than ordinary heat diffusion without any adiabatic effect. The later behavior shown by (A.30b) differs only by a numerical factor indicating that entropy diffusion continues, at these later times, with its penetration depth still of order $\tau^{1/2}$.

For relatively very long times $\tau$ of order 1, (A.30b) indicates that the entropy diffusion penetration depth has grown to be of the same order of magnitude as the total thickness of the fluid sample. For such times the recasting of $\Delta F_{\text{in}}(\tau)$ in the form of an integral becomes inaccurate, and (A.20), (A.21b) and (A.30b) are no longer valid. In fact, as there is no longer any flat, plateau-like interior region, $\Delta F_{\text{in}}$ loses its unique significance and becomes ill-defined. We therefore concentrate our attention on $\langle \Delta F \rangle$ and return to its representation in terms of a sum similar to (A.10),

$$\langle \Delta F \rangle = 2\gamma \sum_{n=1}^{\infty} \frac{1}{\gamma(\gamma-1) + k_n^2} e^{-4\pi k_n^2}. \quad (A.31)$$

For $\tau$ of order 1, only a few terms of the series contribute, and, for these, we have $k_n^2 \ll \gamma(\gamma - 1)$ and can make the additional approximation $k_n = \pi n$. Thus,

$$\langle \Delta F \rangle \approx \frac{2}{\gamma - 1} \sum_{n=1}^{\infty} e^{-4\pi^2\gamma n^2}. \quad (A.32)$$

It is worthwhile to verify that (A.32) joins on smoothly to the results obtained earlier for $\langle \Delta F \rangle$ in the intermediate regime $(\gamma - 1)^{-1} \ll \tau \ll 1$. If $\tau \ll 1$, (A.32) becomes

$$\langle \Delta F \rangle \approx \frac{2}{\gamma - 1} \int_{0}^{\infty} dn \ e^{-4\pi^2\gamma n^2} \approx (1/\pi \tau)^{1/2}, \quad (A.33)$$

which is in complete agreement with (A.21b) for $\gamma \gg 1$.

Note added in proof

Recently Behringer and Meyer [14] have reexamined data of thermal relaxation times in $^3\text{He}$ near the gas–liquid critical point [15, 16] in the light of the adiabatic effect. These experiments were performed at a fixed volume, but the boundary conditions were different from those in this paper. They have found that the adiabatic effect resolves a previously unexplained difference between the data and the calculated relaxation times in the fixed pressure condition.
References