Boiling leading to self-organized convection near the gas–liquid critical point

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Abstract

We present dynamic equations in the Ginzburg–Landau scheme, which govern nonlinear fluid dynamics of pure fluids near the gas–liquid critical point. Above $T_c$ they reduce to those recently proposed to describe supercritical fluid hydrodynamics. Below $T_c$ they can describe phase separation and wetting dynamics in the presence of heat flow and velocity field. This paper predicts some unique effects in boiling near the critical point.

1. Introduction

Static and dynamic critical phenomena in pure fluids are now well understood [1,2]. However, fluid dynamics of near-critical fluids on macroscopic scales is much more complicated and remains mostly unexplored, in which thermal and mechanical disturbances are inseparably coupled [2]. In the simplest case of supercritical fluids ($T > T_c$), thermal equilibration occurs on a rapid time $t_1$ shorter than the macroscopic diffusion time by $\gamma_s^{-2}$ (the piston effect), where $\gamma_s (\gg 1)$ is the specific heat ratio [3]. This is because rapid pressure propagation causes homogeneous adiabatic changes throughout the system at fixed volume. This effect is also crucial in transient behavior in convection of supercritical fluids [4–6].

In this work, we examine a more intriguing situation below $T_c$. Here, we should note that near-critical fluids are very sensitive to the deviation $p - p_c - (\partial p / \partial T)_{cx} (T - T_c)$, when both the pressure and the temperature change in space and time. This quantity represents the distance from the coexistence line with slope $(\partial p / \partial T)_{cx}$. In particular, it changes significantly near a heated or cooled boundary. That is, if the boundary temperature change is larger than $\gamma_s^{-1/2} |T - T_c|$ [7], film boiling can easily be induced
from a liquid near the coexistence line. Also, if the bulk region is in a gas state close to the coexistence line, even slight cooling of the boundary gives rise to condensation of the liquid phase or growth of a wetted liquid layer.

2. Dynamic equations

As in the van der Waals theory, we treat the number density deviation \( \delta n = n - n_c \) as the order parameter. We define the entropy deviation \( \delta s \) by \( n_c T_c \delta s = \delta e - (e_c + p_c) \delta n / n_c \) in terms of the energy density deviation \( \delta e = e - e_c \). Hereafter, the subscript \( c \) denotes taking the critical value and the Boltzmann constant is set equal to 1. Assuming that the critical behavior of fluids is isomorphic to that of Ising systems, we express \( \delta n \) and \( n_c T_c \delta s \) in terms of the spin variable \( \psi \) and the (exchange) energy variable \( T_c m \) in the corresponding Ising system as

\[
\delta n = \psi, \quad n_c \delta s = x_s \psi + m.
\]

The reduced temperature \( \tau = T/T_c - 1 \) is common in the two systems, and then we need to express the pressure deviation \( \delta p = p - p_c \) in terms of \( \tau \) and the (scaled) magnetic field \( h \) in the Ising system. We require the identity \( h \psi + \tau m = (\delta p / n_c T_c) \delta n + \tau n_c \delta s \), which follows from correspondence between the canonical distribution for the Ising system and the grand canonical distribution for the fluid [2]. Then, we find \( x_s = - (\partial p / \partial T)_{ex} / n_c \) and

\[
\delta p = n_c T_c [h - x_s \tau].
\]

The Ginzburg–Landau free energy \( F \) divided by \( T_c \) is the space integral of \( f(\psi, m) = u \psi^4 / 4 + (m + a \psi^2 / 2)^2 / 2C + K |\nabla \psi|^2 / 2 \) for the Ising system, where \( C \) is the specific heat, and \( u, a, \) and \( K \) are positive coefficients. In terms of the density variables \( \psi \) and \( m \), the field variables \( \tau \) and \( h \) are expressed as

\[
\tau = T_c^{-1} \frac{\delta}{\delta m} F = C^{-1} \left[ m + \frac{1}{2} a \psi^2 \right],
\]

\[
h = T_c^{-1} \frac{\delta}{\delta \psi} F = [a \tau - K \nabla^2 + u \psi^2] \psi.
\]

Neglecting inhomogeneity, we calculate the specific heats at constant volume and pressure as \( C_V = C \) and \( C_p = C + (x_s - a \psi)^2 / (a \tau + 3u \psi^2) \). The isothermal compressibility and thermal expansion coefficient become \( K_T = 1 / T_c n_c^2 (a \tau + 3u \psi^2) \) and \( x_p = n_c (x_s - a \psi) K_T \).

In equilibrium \( \tau \) and \( h \) consist of the averages and small thermal fluctuations, so they are usually treated as constants. In nonequilibrium such as in heat-conducting states, they are dynamic variables dependent on space and time. From \( n_c \delta s = C \tau + x_s \psi - a \psi^2 / 2 \), the heat conduction equation is written as

\[
\left( \frac{\partial}{\partial t} + v \cdot \nabla \right) (x_s \psi - \frac{a}{2} \psi^2 + C \tau) = \lambda \nabla^2 \tau,
\]
where $\lambda$ is the thermal conductivity treated as a constant for simplicity. Furthermore, on long time scales of thermal diffusion, sound waves decay to zero and the pressure deviation $p_1(t) \equiv \delta p(r,t) + \rho_c g z$ becomes a function of time only [2]. That is, the pressure gradient is assumed to be equal to the equilibrium gradient $-\rho g \approx -\rho_c g$. The transverse part of the velocity ($\nabla \cdot v = 0$) then obeys

$$\rho_c \left( \frac{\partial}{\partial t} + v \cdot \nabla \right) v = -\nabla p_{\text{inh}} - \left( T_e x_s \psi - \frac{a}{2} \psi^2 \right) \nabla t + \eta \nabla^2 v, \quad (6)$$

where $p_{\text{inh}}$ ensures $\nabla \cdot v = 0$. If low Reynolds number flows are considered, the left-hand side may be set equal to zero (the Stokes approximation). In a steady state under a temperature gradient, Eq. (6) implies that an incompressible velocity is induced by the critical fluctuations [2]. This convective flow gives rise to the well-known critical enhancement of the thermal conductivity.

To check the relative magnitudes of the various terms in these equations, we choose a reference reduced temperature $\tilde{\tau}$ and make the equations dimensionless by scale changes. We introduce scaled reduced temperature $A$, density deviation $\Psi$, and velocity $V$ by

$$A = \tau/\tilde{\tau}, \quad \Psi = \tilde{\psi}/\psi, \quad V = (\xi/D)\nu, \quad (7)$$

where $\tilde{\psi} = (a\tilde{\tau}/u)^{1/2} \sim \tilde{\tau}^\beta$ is the reference density deviation and $D = \lambda a \tilde{\tau}/\chi_0^2 (\cong T_c/6\pi \eta \xi \sim \tilde{\tau}^2)$ is the thermal diffusion constant. Space and time are measured in units of the correlation length $\tilde{\xi} = \xi_{+0} \tilde{\tau}^{-1}$ and the thermal relaxation time $t_{\xi} = \xi^2/D$, where $\xi_{+0}$ is the microscopic length. We rewrite $\tilde{\xi}^{-1} r$ and $t_{\xi}^{-1} t$ as $r$ and $t$ for simplicity. We are interested in the deviations changing slowly compared with $\xi$ in space and $t_{\xi}$ in time, so that the fluctuations with wave numbers greater than $\tilde{\xi}^{-1}$ are assumed to have been coarse grained at the starting point. Then the coefficients in our theory depend on some fractional powers of $\tilde{\tau}$ as $u/K^2 \sim \tilde{\tau}^\gamma, a \sim \tilde{\tau}^{\gamma - 1}, C \sim \tilde{\tau}^{\gamma - 3}$, and $K \sim \tilde{\tau}^{\gamma - 2\gamma}$, and $a_c \equiv (a/C \tilde{\tau})^{1/2} \tilde{\psi}$ is a universal number close to 1 [2]. Using these relations we rewrite (2) and (5) as

$$A + a_c \delta_s [(A - \nabla^2 + \Psi^2)\Psi + Gz] = P_1(t), \quad (8)$$

$$\left( \frac{\partial}{\partial t} + V \cdot \nabla \right) \left( \Psi + \frac{1}{2} a_c \delta_s \Psi^2 - \frac{\delta_s}{a_c} A \right) = \nabla^2 [A - \nabla^2 + \Psi^2] \Psi, \quad (9)$$

where $P_1(t) = p_1(t)/(n_e T_e |x_s|)$ and $\delta_s$ is a small parameter defined by

$$\delta_s = \gamma_s^{-1/2} = (C_V/C_p)^{1/2} \sim \tilde{\tau}^{(\gamma - 2)/2}, \quad (10)$$

with $\gamma_s = \chi_0^2/a\tilde{\tau} C$ being the specific heat ratio at $\tau = \tilde{\tau}$ of the fluid on the critical isochore. The dimensionless gravity $G$ is defined by

$$G = (m_0 \tilde{\tau}/T_e a \tilde{\psi} \tilde{\psi}) g = G_0 \tilde{\tau}^{-(\gamma + \beta + \nu)} g/\text{g}_{\text{earth}}, \quad (11)$$

where $\gamma + \beta + \nu \cong 2.2$ and $g_{\text{earth}}$ is the Earth’s gravity. The coefficient $G_0$ depends on fluids and is $1.3 \times 10^{-14}$ for $^3\text{He}$. Eq. (6) is rewritten as

$$\frac{\tilde{\eta}}{Pr} \left( \frac{\partial}{\partial t} + V \cdot \nabla \right) V = -\nabla P_{\text{inh}} - \left( \frac{1}{a_c \delta_s} \Psi + \frac{1}{2} \Psi^2 \right) \nabla A + \tilde{\eta} \nabla^2 V, \quad (12)$$
where $Pr = \eta/\rho D$ is the Prandtl number, $\tilde{\eta} = \eta Du/T_c(\xi a \tilde{\tau})^2$ is of order $0.1$, and $P_{inh} = [u/T_c(a \tilde{\tau})^2]p_{inh}$. If both $P_1(t)$ in (8) and $P_{inh}$ in (12) are supposed to be of order $1$, the inhomogeneous part $p_{inh}$ is much smaller than the homogeneous part $p_1(t)$ by $a\tilde{\tau}^2/n_c |z_e| \sim \tilde{\tau}^{1-2}$. This justifies the assumption of the homogeneity of $\delta p(r,t)+\rho_c g z \cong p_1(t)$.

The above equations can be simplified in some cases. (i) If the fluid is near equilibrium without heat flux from the boundary, we may take the limit of $\delta_s \to 0$ in (8) and (9) to obtain model $H$ in critical dynamics [1] (without the noise terms here). (ii) We consider small disturbances around an equilibrium state with $A = 1$ on the critical isochore (the average density being at the critical value). In a cell with height $H \equiv L/\xi$ (in units of $\xi$), gravity-induced stratification is weak for $GH \ll 1$ such that the thermodynamic derivatives can be treated to be height independent [5]. Then the deviation $\delta A = A - 1$ obeys

$$\left(\frac{\partial}{\partial t} + V \cdot \nabla - \nabla^2\right) \delta A = (1+\delta_s^2)^{-1}\frac{d}{dt}\delta P - a_c\delta_s G V z. \tag{13}$$

If the cell volume $V$ is fixed, the pressure deviation $\delta P$ here is equal to the space average $\langle \delta A \rangle = \int dr \delta A/V$. Solving the resultant equation for $A$ yields the quick piston time $t_1 = H^2\delta_s^4$. To leading order in $G$, the right-hand side of (12) becomes—$(G/a_c\delta_s)\delta A e_z + \nabla \delta P_{inh}$, where $e_z$ is the unit vector in the $z$ direction. These equations have been used to investigate convection in the supercritical region [5,6]. The Rayleigh number is expressed as $Ra = \rho z_n g L^3/\eta D = [GH^3/\tilde{\tau} a_c \delta_s]A$ with $A \equiv \Delta T/T_c \tilde{\tau} = A_{bot} - A_{top}$. Here $A_{bot}$ and $A_{top}$ are the boundary values of $A$ at $z=0$ and $H$, respectively. In nearly incompressible fluids convection occurs for $Ra > Ra_c = 1708$ (the Rayleigh criterion). In compressible fluids, the above equations yield the Gitterman–Steinberg criterion [5,6,8],

$$A > a_c \delta_s [GH + Ra_c \tilde{\tau}/GH^3]. \tag{14}$$

This was confirmed for $^3$He [4]. When $GH^2 \gg (Ra_c \tilde{\tau})^{1/2} \sim 10$, it follows the Schwarzschild criterion $A/H > a_c \delta_s G$ or $\Delta T/L > a_g \equiv (\partial T/\partial p)_g \rho g$ for convection onset. Here, $a_g$ is called the adiabatic temperature gradient ($=0.034$ mK/cm for $^3$He).

3. Boiling

Heating a liquid at the bottom or cooling a gas at the top triggers boiling or condensation in gravity. Let us prepare a two-phase equilibrium state at $A = -1$ (or $T/T_c - 1 = -\tilde{\tau}$) with a liquid and a gas separated by a horizontal interface. Then we raise the bottom temperature by $\Delta T_b = \tilde{T}_{bot}/(T_c - T)$ at $t = 0$. On long time scale $t \gg 1$, a thermal diffusion layer with thickness $t^{1/2}$ appears at the bottom. If $\delta A_{bot} < \delta_s$, this layer remains in a metastable liquid state with supersaturation of order $\delta A_{bot}/\delta_s$ [7]. If $\delta A_{bot} \gtrsim \delta_s$, the layer becomes a gas and its thickness grows up to the capillary length $(\sigma/\rho \Delta \rho)^{1/2} \sim \tilde{\tau} G^{-1/2}$, where $\sigma$ is the surface tension and $\Delta \rho$ is the density difference between liquid and gas. Then the layer becomes unstable against formation of droplets (the Taylor instability). The droplets are then detached into the bulk, resulting in a two-phase flow. As gas (liquid) droplets move upward (downward) with positive
(negative) excess entropy, heat can be transported very efficiently in the form of latent heat. If $\Delta(=\delta_{\text{bot}}$ here) is larger than the critical value $\Delta_c = a_c \delta_s GL$ (or $\Delta T > a_s L \zeta$) and convection eventually sets in, the average gradient of $A$ in the middle part should be simply given by $-a_c \delta_s$ or

$$ \left( \frac{d}{dz} T \right)_{\text{middle}} \approx -a_g. $$

With increasing $A$, there should appear boundary layers with thickness $\xi_T$ (in units of $\zeta$). The Nusselt number is given by

$$ Nu = 1 + (1 - \Delta_c/A)(H/2\xi_T - 1). $$

For $A \gg \Delta_c$ we have $Nu \approx H/2\xi_T$.

To demonstrate the above effects, we solve (8), (9), and (12) in two dimensions on a $250 \times 250$ cubic lattice by setting $\tau = 1.4 \times 10^{-4}$, $H = 204$, and $a_c = 1$, where $\delta_s = 0.01$, $L = H \zeta = 14 \, \mu m$, and $Pr = 1940$ for $^3$He. The walls at $z = 0$ and $H$ are rigid and the periodic boundary condition is imposed in the $x$ direction. From (11), we obtain $G = 4.1 \times 10^{-4} g/g_{\text{earth}}$. In this work we choose $G = 0.02$ or $g/g_{\text{earth}} = 4.8 \times 10^3$, because the computation time unfortunately becomes very long for very small $G$. Nevertheless, characteristic features disclosed in our simulation should be independent of the size of $G$ and be observable on Earth. As the boundary condition on $\Psi$ we set $\sqrt{2}c\Psi/cz = h_1 + g_1 \Psi$ at $z = 0$ and $\sqrt{2}c\Psi/cz = h_1 - g_1 \Psi$ at $z = H$, where $h_1$ and $g_1$ are parameters characterizing wetting behavior [9]. Here we set $h_1 = 2$ and $g_1 = 1$, for which the boundary is wetted by liquid without heat flow.

In Fig. 1, $A_{\text{bot}}$ is raised from $-1$ to 0 and is held constant thereafter, but $A_{\text{top}}$ is unchanged from $-1$. This means that $T_{\text{bot}} = T_c$ and $T_{\text{top}} = T_c(1 - \tau)$ for $t > 0$. Here convection sets in because $A = 1$ much exceeds $\Delta_c = 0.04$. For $t \lesssim 50$, we can see formation of a gas film at the bottom and a liquid film at the top. For $t \approx 60$, droplets emerge from the films. For $t \gtrsim 70$, the droplets encounter and break up the preexisting interface at the middle, leading to a decrease of the density difference between the upper and lower interior regions. For $t \gtrsim 120$, a dynamical steady state is realized in the whole cell with chaotic density and velocity disturbances, as in the pattern at $t = 200$. In the final state, the middle region is composed of domains with the variance of $\Psi$ about 1, but the density stratification is much reduced than in equilibrium on average. To show this, in Fig. 2, we plot the height-dependent density deviation $\overline{\Psi}(z, t) = \int_0^H dx \Psi(x, z, t)/H$ averaged in the $x$ direction. Here, the Nusselt number $Nu \equiv \lambda_{\text{eff}}/\lambda$ is about 12.5, where $\lambda_{\text{eff}}$ is the effective thermal conductivity in convection and $\lambda$ is that in the reference state ($T/T_c - 1 = \tau$) in the linear regime. The disturbances of $A$ are much smaller than those of $\Psi$ because of large thermal expansion. In Fig. 3, we show the height-dependent reduced temperature $\overline{\Delta}(z, t) \equiv \int_0^H dx A(x, z, t)/H$. In the very initial stage after the piston time $t_1 = H^2 \delta_s^4 = 4 \times 10^{-4}$, $A$ rapidly rises to values about $-0.5$ in the interior and a small temperature difference arises across the interface because of a small difference in $(\partial T/\partial p)$, between the two phases [3]. As expected in (15), the temperature tends to have the adiabatic gradient in the dynamical steady state. Furthermore, even if $A_{\text{bot}}$ and $A_{\text{top}}$ are fixed, the space average $\overline{\langle A \rangle}(t)$ exhibits considerable temporal fluctuations of order 5%, which can be seen by comparison of
Fig. 1. Time-evolution of the density deviation $\Psi(x,z,t)$ for $\langle \Psi \rangle = 0$. The numbers represent the times in units of $t_\xi = \xi^2/D$ after increasing the bottom temperature. We can see a gas film at the bottom and a liquid film at the top, within which the temperature gradient is large.

the two curves at $t=200$ and 300 in Fig. 3. Note that droplets arriving at the boundaries transfer excess heats to the wall and give rise to overall temperature fluctuations in the interior via the piston effect. (In convection above $T_c$, random arrivals of plumes at the boundaries produce a similar noise effect [6].)

The following is suggested. (i) The droplet size is of the order of the boundary layer thickness $\xi/T$. (ii) The Reynolds number defined by $Re \equiv [\langle |V \cdot \nabla V|^2 / |\nabla^2 V|^2 \rangle]^{1/2}/Pr$ remains of order $10^{-2}$ because of the large size of $Pr$. Thus, the viscous force and the buoyancy force are balanced in the interior, so that $\eta(\xi/T)^{-2}v_{\text{drop}} \sim g\Delta\rho$. (iii) In our simulation, the droplet velocity $v_{\text{drop}}$ is of the order of the typical velocity $\sim \sigma/\eta$ in phase separation. Thus, $\xi/T$ is of the order of the capillary length ($\sim \xi G^{-1/2}$). For $T_{\text{bot}} = T_c$ and $T_{\text{top}} = T_c(1 - \tilde{\tau})$ with $\tilde{\tau} \gg \alpha_g L/T_c$ and $G \ll 1$, we find

$$Nu \sim HG^{1/2} \sim L(g\Delta\rho/\sigma)^{1/2} \propto L\tilde{\tau}^{6/2-\nu}.$$  

(17)
Fig. 2. Time evolution of the average density deviation $\bar{\rho}(z,t) = \frac{1}{H} \int_0^H dx \frac{\rho(x,z,t)}{H}$. At $t = 0$ the fluid is in equilibrium in gravity. After increasing the bottom temperature, gas and liquid layers are created at the bottom and the top, respectively. For $t = 80$ and 100 the interior is composed of domains.

Fig. 3. Time evolution of the averaged reduced temperature $\bar{A}(z,t) = \frac{1}{H} \int_0^H dx A(x,z,t)/H$. The temperature gradient is nearly equal to the adiabatic gradient in the interior for the curves at $t = 200$ and 300.
4. Remarks

Competition between gravity and heat flow from below produces intriguing self-organized states below $T_c$. Analogous self-organized heat transport is known in $^4$He near the superfluid transition under gravity and heat flow applied from above [10,11]. In such self-organized superfluid states, high-density vortices can be created such that they produce the temperature gradient $(\partial T/\partial p)_\lambda \rho g \sim 1$ $\mu$K/cm, where $(\partial T/\partial p)_\lambda$ is the slope of the $\lambda$ line.

Our dynamic equations can also be used to investigate wetting dynamics in heat flow. For example, if a gas droplet is put on a solid wall with the bulk region in a liquid state, the contact angle $\theta$ becomes a function of a heat flow $Q$ from the solid wall [12]. With increasing $Q$, the droplet will partially wet the solid ($\theta > 0$) even if the solid was wetted by liquid ($\theta = 0$) for $Q = 0$. For large enough $Q$, we predict a collapse of the droplet changing into a gas film, leading to a transition to film boiling.

References