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Nucleation and Boiling Near the Gas–Liquid Critical Point[1]

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Nucleation near the gas–liquid critical point depends sensitively on whether the pressure or the volume is fixed. We consider near-critical fluids close to the coexistence curve. (i) Upon decompression to a constant pressure with a fixed boundary temperature, bulk nucleation can well be induced from a gas state, whereas from a liquid state boiling is easily triggered in the thermal diffusion layer near the boundary. In this case, bulk nucleation in a metastable gas is described by the classical Lifshitz–Slyozov theory. (ii) Upon cooling of the boundary temperature under the fixed-volume condition, bulk nucleation can be realized in a liquid and a modified Lifshitz–Slyozov theory follows. However, if a gas is cooled from the boundary at a fixed volume, liquid droplets readily appear in the thermal diffusion layer, apparently suggesting no metastability in a gas in agreement with previous experiments. (iii) On the other hand, if a liquid is heated at the boundary wall, boiling readily occurs both at a fixed volume and at a fixed pressure.

KEY WORDS: adiabatic effects; boiling; gas–liquid transition; nucleation.

1. INTRODUCTION

Thermal relaxation in fluids near the gas–liquid critical point is crucially dependent on whether the pressure or the volume of the container is fixed [1, 2]. Under the latter condition, if the boundary temperature is changed, pressure variations propagate as sound waves throughout the container and cause almost instantaneous adiabatic temperature changes (piston effect). The thermal equilibration achieved by this adiabatic mechanism is increasingly important as the critical point is approached. Interestingly,

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thermal relaxation is more complicated in two-phase coexistence, where slow transport of heat and mass takes place through the interface [3]. This indicates that adiabatic effects should also be crucially important in phase separation processes near the gas–liquid critical point, though such effects have not attracted enough attention.

Nucleation near the gas–liquid critical point was first studied by Langer and Turski [4], who assumed a constant pressure (isobaric nucleation) in one-component fluids. Very recently we have examined nucleation near the gas–liquid critical point in more detail both under a constant pressure and in a fixed volume [5]. We assume that the boundary wall of the container is kept isothermal for $t > 0$ after the interior region is brought into a metastable state at $t = 0$. Here there appears a thermal diffusion layer with thickness

$$\ell = (Dt)^{1/2} \tag{1}$$

where D is the thermal diffusion constant. The cell length L is supposed to be sufficiently long that appreciable droplets of the new phase emerge while $L \gg \ell$. We shall see that bulk nucleation in the interior region may be realized when a gas is decompressed at $t = 0$ to a new fixed pressure for $t > 0$ or when a liquid is cooled from the boundary with a fixed volume. In other cases droplets of the new phase appear in the thermal diffusion layer near the boundary wall.

Unfortunately, nucleation experiments on one-componemt fluids near the gas–liquid critical point have not been abundant [6, 7]. Most phase separation experiments have been on fluid binary mixtures near the consolute critical point using a pressure quench method, by which the temperature is changed by $(\partial T/\partial p)_{sx}\,\delta p$ and the critical temperature by $(dT_c/dp)\,\delta p$ adiabatically and hence instantaneously after a pressure change δp [8–10]. As an interesting adiabatic effect, Donley and Langer [11] have recently found a large adiabatic heating in spinodal decomposition of fluid binary mixtures at a constant pressure. It arises from release of the internal energy upon local phase separation and is closely related to the mechanism of the critical acoustic anomaly in binary mixtures [12].

At the present stage of research, we have not yet gained satisfactory understanding of these phase separation phenomena occurring under time-dependent pressure and/or temperature in one- and two-component fluids. Note that most theories so far have assumed isobaric and isothermal conditions in the course of phase separation. This paper treats one-component fluids near the coexistence curve and examines phase separation far from the boundary (bulk nucleation) and within the thermal diffusion layer (boiling or condensation).

2. NUCLEATION FORMULAE

Let a metastable medium of phase 2 be characterized by the temperature deviation $\delta T_{\infty}(t)$ and the pressure deviation $\delta p_{\infty}(t)$. They are measured from a reference state on the coexistence curve and are generally time dependent. Latent heat is absorbed by a growing gas droplet and is released by a growing liquid droplet. The thermal diffusion around the interface gives rise to the evolution equation of the droplet radius $R(t)$ in the standard form [13],

$$\frac{\partial}{\partial t} R = \frac{D}{R}\left[\Delta(t) - \frac{2d}{R} \right] \tag{2}$$

where D is the thermal diffusivity of phase 2 and $\Delta(t)$ is the effective dimensionless supersaturation. Phase 2 is metastable for $0 < \Delta(t) \ll 1$, unstable for $\Delta(t) \gtrsim 1$, and is stable for $\Delta(t) \leqslant 0$. Near the critical point it is expressed as

$$\Delta(t) \cong \tfrac{1}{6} \gamma_s^{1/2} \theta h(t) / (1 - T/T_c) \tag{3}$$

where $\gamma_s = C_p/C_v$ is the specific heat ratio growing as $(1 - T/T_c)^{\alpha - \gamma}$ as $T \rightarrow T_c$, with γ ($\cong 1.25$) and α ($\cong 0.1$) being the usual critical exponents. $h(t)$ represents the distance of medium 2 from the coexistence curve,

$$h(t) = \frac{1}{T}\left[-\delta T_{\infty}(t) + \left(\frac{\partial T}{\partial p} \right)_{\mathrm{cx}} \delta p_{\infty}(t) \right] \tag{4}$$

Hereafter $\theta = 1$ (or -1) if phase 2 is a gas (or liquid) phase. The derivative $(\partial T/\partial p)_{\mathrm{cx}}$ is the slope of the coexistence curve. The length d in Eq. (2) is of order $\xi/6$ in terms of the thermal correlation length ξ on the coexistence curve.

In early-stage nucleation without appreciable droplets, the nucleation rate J is the probability of finding droplets with R larger than the initial critical radius $R_c(0) = 2d/\Delta(0)$ in a unit volume and in a unit time. The classical nucleation theory [4, 14] predicts that J is written in terms of $\Delta(0)$ as

$$J = J_0 \exp\left[-\frac{16\pi}{3} \left(\frac{\sigma d^2}{k_B T} \right) \frac{1}{\Delta(0)^2} \right] \tag{5}$$

where σ is the surface tension.

3. THE ISOBARIC CASE

3.1. Pressure Change

We assume a homogeneous near-critical fluid in a cell with temperature T_0 and a pressure p_0 in the time region $t<0$. If the system is not on the coexistence curve and $\delta T_0 = T_0 - T_{cx}(p_0)$ is nonvanishing, the original supersaturation becomes

$$\Delta(t<0) \cong \tfrac{1}{6}\gamma_s^{1/2}\theta(T_{cx}-T_0)/(T_c-T_{cx}) \tag{6}$$

We assume that $\Delta(t<0)$ is a negative number or a very small positive number to avoid any droplet formation before the experiment. We then change the pressure in a stepwise manner at $t=0$ from p_0 to $p_0+\delta p_\infty$ and keep it constant at later times. The temperature far from the boundary will be adiabatically changed immediately by $\Delta T = (\partial T/\partial p)_s\, \delta p_\infty$. If the boundary temperature is kept at T_0, the temperature profile near the boundary is of the form,

$$T(x, t) = T_0 + (\Delta T)\,\mathrm{erf}(x/2\sqrt{Dt}) \tag{7}$$

where x is the distance from the boundary wall and $\mathrm{erf}(z) = (2/\sqrt{\pi})\int_0^z dp\, \exp(-p^2)$ is the error function tending to 1 for $z \gg 1$. This is the solution of the one-dimensional heat diffusion equation in the semiinfinite case. The interior temperature is higher (or lower) than in the bounder layer for compression $\delta p_\infty > 0$ (or decompression $\delta p_\infty < 0$). The supersaturation given by Eq. (3) is then dependent on x and t as

$$\begin{aligned}\Delta(x, t) &\cong \Delta(t<0) - \frac{1}{6(T_c-T_{cx})}\left(\frac{\partial T}{\partial p}\right)_{cx} \delta p_\infty[1-\theta\gamma_s^{1/2}(1-\mathrm{erf}(x/2\sqrt{Dt}))] \\ &\cong \Delta_\infty + \frac{1}{6}\theta\gamma_s^{1/2}[\Delta T/(T_c-T_{cx})][1-\mathrm{erf}(x/2\sqrt{Dt})]\end{aligned} \tag{8}$$

where $\Delta_\infty = \Delta(t<0) - \Delta T/6(T_c - T_{cx})$ is the supersaturation in the interior region. The interior region can be metastable only for expansion or $\delta p_\infty < 0$. However, $\Delta(x, t)$ can be very large in the thermal diffusion layer. This is discussed for the two cases, $\theta = \pm 1$, separately.

3.1.1. The Gas Case ($\theta = 1$)

For $\delta p_\infty < 0$ the supersaturation is negative in the layer obviously because the boundary temperature is fixed. Therefore, nucleation experiments can well be performed in the bulk region by decompression. Even when a wetting layer of a liquid phase is present at the boundary, it does not grow thicker. Upon compression, $\delta p_\infty > 0$; on the other hand, the boundary becomes cooler than in the interior region and the supersaturation can assume a large positive value within the layer. This indicates liquid condensation near the boundary.

3.1.2. *The Liquid Case* ($\theta = -1$)

For $\delta p_\infty < 0$ the boundary temperature is higher than in the interior region and the supersaturation can be positive and very large in the boundary layer, leading to boiling within the layer. If $\Delta(t<0) \cong 0$, the threshold of boiling is very low and is given by

$$|\Delta T| = (\partial T/\partial p)_\mathrm{s}\, |\delta p_\infty| \gtrsim \gamma_\mathrm{s}^{-1/2}(T_\mathrm{c} - T_\mathrm{cx}) \tag{9}$$

On the contrary, upon compression, $\delta p_\infty > 0$, the entire spatial region remains stable.

3.2. Bulk Nucleation in a Metastable Gas

We discuss bulk nucleation further in the gas case below. Our theory will be valid outside the layer ($x \gtrsim \ell = (Dt)^{1/2}$). Its thickness ℓ is supposed to be much smaller than the cell dimension L and droplet growth occurs before the macroscopic time L^2/D. Namely, the so-called completion time [14] of nucleation is assumed to be shorter than L^2/D. After some calculations the droplet volume fraction $\phi(t)$ satisfies the conservation law [5],

$$\phi(t) + \Delta(t) = \Delta(0) \tag{10}$$

The initial supersaturation $\Delta(0)$ is the bulk value just after the pressure change,

$$\Delta(0) = \Delta(t<0) - \frac{1}{6(T_\mathrm{c} - T_\mathrm{cx})}\left(\frac{\partial T}{\partial p}\right)_\mathrm{cx} \delta p_\infty \tag{11}$$

Now Eqs. (2) and (10) coincide with the original Lifshitz–Slyozov equations [13]. Thus, as the droplets grow, phase 2 slowly approaches the coexistence curve as

$$\Delta(t) \cong (9d^2/Dt)^{1/3} \tag{12}$$

Near the critical point we obtain

$$\delta T_\infty(t) - (\partial T/\partial p)_\mathrm{cx}\, \delta p_\infty \cong -6(T_\mathrm{c} - T_\mathrm{cx})\, \gamma_\mathrm{s}^{-1/2}(9d^2/Dt)^{1/3} \tag{13}$$

The factor $\gamma_\mathrm{s}^{-1/2}$ greatly reduces the above quantity near the critical point.

4. THE CONSTANT-VOLUME CASE

4.1. Change of Boundary Temperature and the Piston Effect

We assume that a fluid near the critical point has a fixed total volume V_0 and is in an equilibrium state on the coexistence curve at a given pressure p_0, whose temperature T_0 is equal to the coexistence temperature $T_{cx}(p_0)$. This state will be chosen as the reference state. The initial deviation $\delta T_0 = T_0 - T_{cx}(p_0)$ can be nonvanishing in experiments, but its effect is only to shift the initial supersaturation by $\Delta(t<0)$. We then slightly change the boundary temperature at $t=0$ and fix it at later times as

$$T_b = T_0 + T_1 \tag{14}$$

In the subsequent relaxation process the thermal diffusion layer plays the role of an efficient piston, giving rise to a nearly homogeneous pressure and temperature on a fast time scale t_1,

$$t_1 = L^2/\gamma_s^2 D \propto (1 - T/T_c)^{1.4} L^2 \tag{15}$$

where L is the system length and γ_s is the specific heat ratio. For $t \gtrsim t_1$ the supersaturation tends to $\frac{1}{6}(-T_1)/(T_c - T_{cx})$ far from the boundary, but it can vary rapidly within the thermal diffusion layer as [5]

$$\Delta(x, t) \cong \frac{1}{6}\left[(-T_1)/(T_c - T_{cx})\right]\left[1 + 2\theta\left(\frac{\gamma_s t_1}{\pi t}\right)^{1/2} \exp(-x^2/4Dt)\right] \tag{16}$$

The inhomogeneity of $\Delta(x, t)$ gives rise to important consequences in experiments.

4.1.1. *The Liquid Case ($\theta = -1$)*

If a liquid phase is cooled from the boundary (namely, $T_1 < 0$), $\Delta(x, t)$ becomes negative within the thermal diffusion layer in the early time region, $t < \gamma_s t_1$. However, for $t \gg \gamma_s t_1$, this inhomogeneity becomes negligible. Fortunately in this case, controlled nucleation experiments may well be performed. That is, for $t \gg t_1$, a nearly homogeneous metastable phase 2 is prepared in the bulk region, where $\delta T_\infty(0) \cong T_1$ and $\delta p_\infty(0) \cong (\partial p/\partial T)_p T_1 \cong (\partial p/\partial T)_s T_1$. On the contrary, if a liquid is slightly heated $(T_1 > 0)$ above the coexistence curve, the thermal diffusion layer can become metastable or even unstable in the time region $t < \gamma_s t_1$, which can lead to boiling. For $t \sim t_1$ and $x \cong 0$, $\Delta(x, t)$ attains a maximum,

$$\Delta_{\max} \sim \gamma_s^{1/2} |T_1|/(T_c - T_{cx}) \tag{17}$$

Therefore, if $\Delta_{\max} \gtrsim 1$ and

$$D\xi^{-2}\gamma_s t_1 \sim (L/\xi)^2/\gamma_s \gg 1 \tag{18}$$

boiling should be induced in the narrow spatial region $x \lesssim (Dt_2)^{1/2} \sim L/\gamma_s^{1/2}$ transiently in the time region $t \lesssim t_2$.

4.1.2. The Gas Case ($\theta = 1$)

Upon cooling $\Delta(x, t)$ attains a large value within the thermal diffusion layer. Its maximum $\Delta_{\max}$ is again given by Eq. (17). This means that phase separation starts to take place within the thermal diffusion layer for $t \gtrsim t_1$ except for very small $|T_1|$ ($\ll (T_c - T_{cx})/\gamma_s^{1/2}$). Under realistic experimental conditions a liquid layer will appear to wet the boundary and no appreciable metastability of a gas phase will be detected. This conclusion is consistent with the experiment at a fixed volume by Dahl and Moldover [6], who observed no metastability in gas states ($\rho < \rho_c$) and expected preferential wetting of a liquid layer at the wall as its physical origin. In addition, upon heating, the gas phase is always stable everywhere in the cell.

4.2. Bulk Nucleation in a Metastable Liquid

Hereafter, we examine the effect of a nonvanishing volume fraction $\phi(t)$ of gas droplets in a metastable liquid in the adiabatic nucleation process. We examine the effects of droplet growth outside the thermal diffusion layer, so we are requiring $\sqrt{Dt} \ll L$. Again, the completion time [14] is assumed to be shorter than L^2/D. With emergence of gas droplets the mass conservation yields the average density deviation $\langle \delta\rho(t) \rangle$ in phase 2 (or outside the droplets) in the form, $\langle \delta\rho(t) \rangle = (\Delta\rho)\, \phi(t)$, where $\Delta\rho = \rho_2 - \rho_1$ and the averaged spatial region includes the thermal diffusion layer. This density change causes adiabatic changes throughout the cell. In other words, the droplets are acting as small pistons. We note that the density change due to the droplet formation is almost homogeneous on spatial scales much longer than the droplet radius and is smaller in the thermal diffusion layer than in the interior region. Therefore, the density change in the interior region in phase 2 is almost given by

$$\overline{\delta\rho}(t) = [\delta\rho]_{\text{in}} + (\Delta\rho)\, \phi(t) \tag{19}$$

where $[\delta\rho]_{\text{in}}$ is the adiabatic interior density change ($\propto T_1$) without droplets. We then note that the average entropy deviation $\overline{\delta s}(t)$ in phase 2 outside the thermal diffusion layer is of the form

$$\overline{\delta s}(t) = (\Delta s)\, \phi(t) \tag{20}$$

We have thus obtained the interior mean deviations, $\overline{\delta\rho}(t)$ and $\overline{\delta s}(t)$, to first order in either T_1 or $\phi(t)$. The average pressure and temperature deviations $\delta p_\infty(t)$ and $\delta T_\infty(t)$ in phase 2 are then related to $\overline{\delta\rho}(t)$ and $\overline{\delta s}(t)$ via the usual thermodynamic relations. The supersaturation $\Delta(t)$ is calculated as

$$\Delta(t) = \Delta(0) - A\phi(t) \tag{21}$$

The coefficient A is expressed in terms of thermodynamic derivatives in phase 2 and is close to 2 near the critical point.

Now Eqs. (2) and (21) constitute a closed set of dynamic equations. We may use the original Lifshitz–Slyozov results simply by rescaling, $\tilde{\Delta}(t) = \Delta(t)/A$, $\tilde{d} = d/A$, and $\tilde{D} = DA$. We can confirm that in later stages, $dDt \gg R_c(0)^3$, $R_c(t)$, and $\Delta(t)$ are independent of A and $\Delta(t)$ behaves as Eq. (12). For the convenience of experimentalists we write $\Delta(0)$ taking account of $\Delta(t < 0)$,

$$\Delta(0) = \tfrac{1}{6}[-T_1 + \gamma_s^{1/2}\theta(T_{cx} - T_0)]/(T_c - T_{cx}) \tag{22}$$

The second term in the brackets arises when the temperature T_0 before cooling deviates from the coexistence temperature $T_{cx} = T_{cx}(P_0)$. The temperature and pressure deviations depend on $\phi(t)$ as

$$\delta T_\infty(t) - (T_1 + \delta T_0) \cong 6(T_c - T_{cx})\,\phi(t) \tag{23}$$

$$\delta p_\infty(t) - \left(\frac{\partial p}{\partial T}\right)_\rho T_1 \cong \left(\frac{\partial p}{\partial T}\right)_\rho [\delta T_\infty(t) - (T_1 + \delta T_0)] \tag{24}$$

where $\delta T_0 = T_0 - T_{cx}$ and $\delta T_\infty(0) = T_1 + \delta T_0$. We should compare Eqs. (4) and (13), which show that the temperature variation in the present adiabatic case is much larger than in the isobaric case by $\gamma_s^{1/2}$. Note that the variations of $\delta T_\infty(t)$ and $\delta p_\infty(t)$ almost cancel in $\Delta(t)$ in the adiabatic case because they move nearly in the parallel direction of the coexistence curve in the p–T phase diagram.

Here we should not forget the condition $\ell < L$ we have assumed. At later times, $t \gtrsim L^2/D$, the fluid tends to an equilibrium state which is equilibrated at the boundary temperature T_b. Thus, the interior mean temperature first approaches to the boundary temperature on the time scale of t_1 due to the piston effect, then increases as Eq. (24) with droplet growth, and finally, returns to the boundary temperature for $t \gtrsim L^2/D$.

5. SUMMARY

We have shown that adiabatic temperature and pressure changes are crucially important in nucleation experiments. Dahl and Moldover's experiment [6] was performed by cooling a liquid from the boundary in a fixed volume. There, the piston effect supercooled the interior region and the adiabatic nucleation discussed in Section 4 proceeded. More systematic experiments are strongly needed under both fixed volume and fixed pressure conditions. Our simple calculation of the supersaturation $\Delta(x, t)$ near the boundary shows that boiling can be triggered easily near the critical point due to large thermal expansion when the boundary temperature is slightly lower than that in the interior liquid region. To describe such boiling phenomena we should also take into account wetting of a liquid on a solid wall [14]. Controlled experiments of boiling near the critical point seem to be promising.

In this paper the dominant heat source far from the boundary is the latent heat produced or absorbed at the interfaces of growing droplets. In adiabatic spinodal decomposition, furthermore, we cannot neglect heat release in its initial stage because the internal energy changes upon local phase separation [11]. Relatively small heat release will also occur in late stages due to the decrease in the interface area with coarsening.

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