PHYSICAL REVIEW E **68**, 026306 (2003)

Supercritical vaporization: Distinguishable fluid regions

Manuel Arias-Zugasti,[1] Jose L. Castillo,[1] and Pedro L. García-Ybarra[2,1]
[1]*Departamento de Física Matemática y Fluidos, UNED, Apartado 60141, 28080 Madrid, Spain*
[2]*Departamento de Combustibles Fósiles, CIEMAT, Avenida Complutense 22, 28040 Madrid, Spain*

(Received 10 December 2002; published 13 August 2003)

The vaporization of a cold fluid pocket suddenly set into a hot, otherwise quiescent, atmosphere at supercritical pressures is analyzed. It is shown that at supercritical but moderate pressures and high ambient temperatures, the position where the thermal expansion coefficient reaches its maximum defines a relatively thin transition region that separates two distinguishable fluid regions: A cold liquidlike region where the heat transport is dominated by conduction, and a hot gaslike region where the heat transport is convective and conductive owed to the thermal expansion induced Stefan flow.

DOI: 10.1103/PhysRevE.68.026306 PACS number(s): 44.25.+f, 44.10.+i, 64.60.Ht

I. INTRODUCTION

Let us consider the vaporization of a cold isolated supercritical fluid package at an initial temperature T_0, instantaneously set into an unconfined, initially quiescent, atmosphere at initial temperature $T_\infty \gg T_0$. In a time scale much larger than the characteristic acoustic time, the vaporization process may be considered as isobaric. Unlike the vaporization process at subcritical pressures, the process at supercritical pressures is a single-phase relaxation event. However, a large number of numerical and experimental experiences on supercritical droplet vaporization (see Refs. [1,2] for a review) show that as the critical pressure is exceeded there are no drastic changes in the vaporization dynamics. Both numerical and experimental evidences suggests that at moderately supercritical pressures there still exist two distinguishable fluid regions (reminiscent of the liquid and gas regions in subcritical vaporization), separated by a relatively thin transition region (reminiscent of the liquid-gas interface but with a nonvanishing thickness), characterized by a relatively large density gradient. On the other hand, at very high supercritical pressures the density variations produced by the temperature changes become smoother, and the two regions can no longer be distinguished. In these latter conditions, the heating of the cold pocket becomes, essentially, a constant density conductive process [3,4], in which the density variations introduce only a small correction [5].

The behavior at supercritical but moderate pressures [6–8] can be explained as a consequence of the *Stefan flow* induced by the thermal expansion in the relatively thin transition region where the thermal expansion coefficient reaches its maximum. The term *Stefan flow* has been chosen for analogy with the subcritical Stefan flow, which is a consequence of the density jump between both phases across the interface. At supercritical but moderate pressures, the Stefan flow induces a convective heat flow of the same order of magnitude (but in the opposite direction) as the conductive heat flow. Hence, the convective thermal flow (produced as a consequence of the thermal expansion by heating) tends to slow down the heating process. The competition between the convective and conductive heat fluxes generates a thin transition layer (where most of the fluid expansion takes place), which recedes through the cold fluid as the vaporization takes place. Consequently, the vaporization process of a cold fluid pocket in a high temperature atmosphere at moderate supercritical pressures differs from a purely conductive heating process (in which the mass flow produced by the heating is absent or negligible), and still keeps some of the features of the subcritical vaporization process. As the pressure at which the vaporization takes place increases, the maximum of the thermal expansion coefficient decreases and broadens. Then, the importance of the thermal expansion induced Stefan flow decreases, and the heating of the cold pocket becomes gradually a purely conductive heating process (equivalent to the heating process of a solid body suddenly immersed in a hot environment).

The main features of the thin transition region (location and thickness) will be analyzed here. Also, the supercritical pressure range in which the transition between slightly supercritical vaporization (characterized by the existence of these two distinguishable fluid regions) and pure conductive heating takes place will be discussed.

II. TRANSITION LAYER TEMPERATURE

When the heating of the cold pocket takes place under supercritical pressures, the intensity of the Stefan flow is determined by the thermal expansion coefficient

$$\beta \equiv -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P, \tag{1}$$

where ρ stands for the fluid density, T the temperature, and P the ambient constant pressure. For illustration purposes, the van der Waals equation of state will be considered. In that case, β is given by

$$\beta T_c = \frac{8}{3}\,\frac{V^2}{\Pi V^3 - 3V + 2}, \tag{2}$$

where Π and V stand for the reduced pressure and reduced specific volume, respectively, and T_c is the critical temperature.

1063-651X/2003/68(2)/026306(5)/$20.00

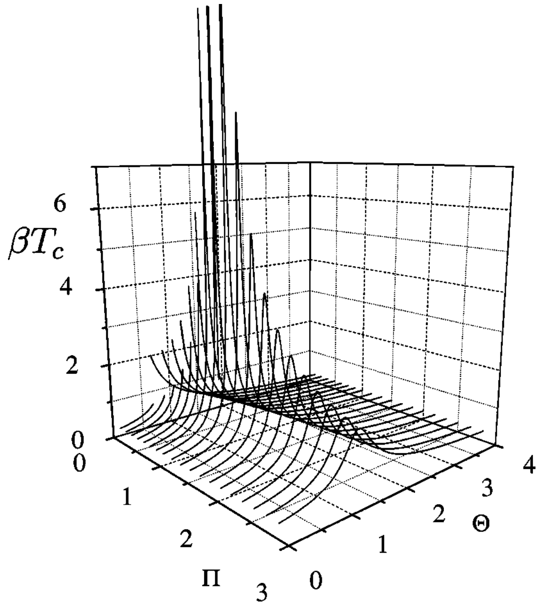

FIG. 1. Thermal expansion coefficient of a van der Waals fluid (times T_c), for reduced temperatures (Θ) between 0 and 4, and reduced pressures between 0 and 3. See Eq. (2).

The product βT_c, given by Eq. (2), is plotted in Fig. 1 as a function of the reduced pressure and temperature. At subcritical pressures, and in the region corresponding to the liquid phase, β is very small and increases as the boiling temperature is approached. On the other hand, in the gas phase β presents much higher values, and decreases with the increasing temperature (indeed $\beta = 1/T$ for an ideal gas). Hence, at subcritical pressures β reaches its maximum at the vapor-liquid interface, where it shows a discontinuity consequence of the density difference between the gas phase and the liquid phase. As the pressure approaches the critical pressure, these maximum values of β at the interface tend to infinity at both sides of the interface (liquid and gas). At pressures above the critical pressure, β is a continuous function of the temperature, which shows a clear maximum. The magnitude of this maximum is quite remarkable at supercritical but moderate pressures, in fact it tends to infinity when the pressure tends to the critical pressure from above. When a fluid particle heated at a constant pressure crosses this maximum of the thermal expansion coefficient, it experiences a relatively large expansion. This volume increase of the heated fluid at slightly supercritical pressures induces an intense Stefan flow.

The position corresponding to this marked thermal expansion coefficient peak at supercritical pressures defines the location of the transition layer. From Eq. (2), the reduced volume (V_E) corresponding to the maximum of β at supercritical pressures is given by

$$V_E = \frac{(2\sqrt{\Pi} + \sqrt{1+4\Pi})^{2/3} - 1}{\sqrt{\Pi}(2\sqrt{\Pi} + \sqrt{1+4\Pi})^{1/3}}. \tag{3}$$

Using the van der Waals equation of state, one finds that the reduced temperature of the transition layer is given by

$$\Theta_E \equiv \frac{T_E}{T_c} = \frac{1}{8}\left(\frac{9}{V_E^2} - \Pi\right). \tag{4}$$

Note that V_E and Θ_E are equal to 1 at the critical pressure $\Pi = 1$.

III. RANGE OF PRESSURES LEADING TO SUPERCRITICAL VAPORIZATION

In the absence of external forces, the isobaric vaporization process of interest here is governed by the continuity equation

$$\frac{\partial \rho}{\partial t} + \vec{\nabla}(\rho \vec{v}) = 0 \tag{5}$$

and the isobaric energy conservation equation

$$\rho c_P\left(\frac{\partial T}{\partial t} + \vec{v}\cdot\vec{\nabla}T\right) = \vec{\nabla}(\kappa \vec{\nabla} T), \tag{6}$$

where $\vec{v}$ stands for the velocity field, t the time, c_P the specific heat at constant pressure, and κ the fluid thermal conductivity.

In the present single-phase thermal relaxation problem, the dependence of the continuity equation on the fluid density may be translated to the dependence on the local temperature. Taking this into account, from Eqs. (5) and (6), by means of Eq. (1) it is easy to derive

$$\vec{\nabla}\cdot\vec{v} = \frac{\beta}{\rho c_P}\vec{\nabla}\cdot(\kappa\vec{\nabla}T). \tag{7}$$

The divergence of the conductive heat flow produced by the temperature gradient acts on Eq. (7) as a volume source term for the (thermal expansion induced) velocity field. From Eq. (7), one can see that $\beta/(\rho c_P)$ is the key coefficient for determining the importance of the thermal expansion induced velocity field.

Taking into account the thermodynamic relation

$$c_P = c_v + \frac{\beta T}{\rho}\left(\frac{\partial P}{\partial T}\right)_\rho, \tag{8}$$

one finds

$$\frac{\beta}{\rho c_P} = \left(1 - \frac{1}{\gamma}\right)\frac{1}{T}\left(\frac{\partial T}{\partial P}\right)_\rho, \tag{9}$$

where $\gamma = c_P/c_v$ is the adiabatic coefficient. For a van der Waals fluid, the ratio is given by

$$\frac{\beta}{\rho c_P} = \frac{1}{P_c}\left(1 - \frac{1}{\gamma}\right)\frac{V^2}{\Pi V^2 + 3}. \tag{10}$$

Recalling that in a supercritical fluid the factor $(1 - 1/\gamma)$ is always of order unity, the order of magnitude of $\beta/(\rho c_P)$ is determined by the factor $V^2/(\Pi V^2 + 3)$. This factor is plotted in Fig. 2 as a function of the reduced temperature for

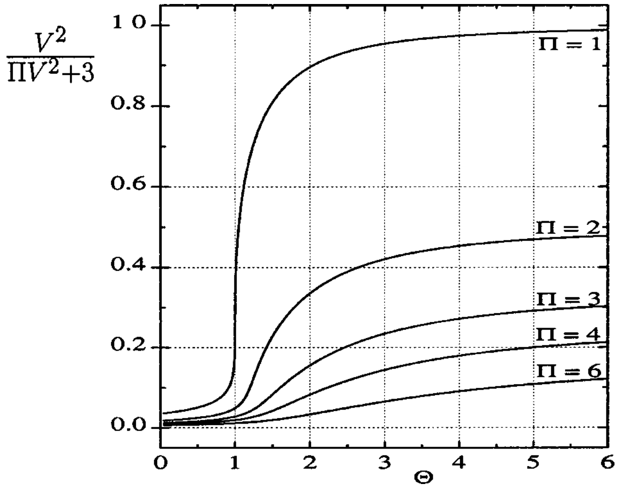

FIG. 2. Factor $V^2/(\Pi V^2+3)$ of a van der Waals fluid as a function of the reduced temperature for several supercritical pressures. See Eq. (10).

several supercritical pressures.

As it may be seen in Fig. 2 that at supercritical but moderate pressures there exist two distinguishable regions separated by a relatively thin transition layer. On one hand, a denser (liquidlike) region can be seen at low temperatures. In this region, which is the supercritical prolongation of the liquid phase, the thermal expansion induced fluid velocity is negligible. There, the thermal expansion induced convective transport is negligible as compared to the conductive heat transport. On the other hand, a lighter (gaslike) region may be recognized at high temperatures. Here, the thermal expansion induced velocity field is much larger than in the liquidlike region, and both the conductive and convective heat transport terms must be retained in the energy conservation equation (6). These two regions are separated by the transition layer, where a strong variation of $\beta/(\rho c_P)$ takes place.

As the pressure increases the transition layer becomes wider, and the relative importance of the convective term linked to the thermal expansion induced Stefan flow decreases, as may be seen in Fig. 2. The ratio between the characteristic values of $\beta/(\rho c_P)$ in the hot ($V \gg 1$) and cold ($V \simeq 1/3$) regions is roughly given by

$$\Delta \equiv \frac{[\beta/(\rho c_P)]_{\Theta \gg 1}}{[\beta/(\rho c_P)]_{\Theta \ll 1}} \simeq 1 + \frac{27}{\Pi}. \tag{11}$$

The liquidlike and gaslike regions remain distinguishable as long as the ratio Δ is large as compared to unity. As a consequence of Eq. (11), the transition between the convective-diffusive vaporization dynamics (characterized by the existence of two distinguishable fluid regions) and the purely conductive dynamics, reached at very high supercritical pressures, occurs gradually. The reduced pressure at which this gradual transition takes place may be roughly estimated by $\Pi_{\max} \simeq 3$, which is the pressure leading to $\Delta \simeq 10$. Moreover, the amplitude of the pressure range where this transition occurs may be roughly estimated by $\delta\Pi_{\max} \simeq 3$. This is the increment of pressure around $\Pi_{\max}$ in which Δ decreases in one order of magnitude. Thus, for pressures below roughly $1.5P_c$, the vaporization dynamics is analogous to that found at subcritical pressures (but without vaporization latent heat) and, for pressures above roughly $4.5P_c$, the Stefan flow is negligible and the heating of the cold supercritical pocket is a purely conductive process.

The temperature that defines the position of the transition layer may also be defined as the temperature corresponding to the inflection point of $\beta/(\rho c_P)$. Taking into account that

$$\frac{\rho c_P}{\beta}\frac{\partial^2}{\partial T^2}\left(\frac{\beta}{\rho c_P}\right) = \frac{\partial}{\partial T}\left(\beta + \frac{\partial \ln \frac{\beta}{c_P}}{\partial T}\right) + \left(\beta + \frac{\partial \ln \frac{\beta}{c_P}}{\partial T}\right)^2 \tag{12}$$

in the supercritical pressure range in which the liquidlike and the gaslike regions may be distinguished, the term $\partial\beta/\partial T$ in Eq. (12) dominates largely over the others. Therefore, in the pressure range in which the transition layer exists, the temperature corresponding to the inflection point of $\beta/(\rho c_P)$ coincides with the temperature at which β reaches its maximum value.

IV. THERMAL THICKNESS OF THE TRANSITION LAYER

The thermal thickness of the transition layer (ΔT_E) is the increment of temperature around T_E needed for the thermal expansion induced convective term in Eq. (6) to become of the same order of magnitude as the conductive term. Thus, at temperatures below roughly $T_E - \Delta T_E/2$, the heat transport is dominated by conduction with a negligible convective heat transport induced by the thermal expansion; whereas for temperatures above roughly $T_E + \Delta T_E/2$, the heat transport is convective and conductive. Inserting Eq. (7) in Eq. (6), the energy conservation equation may be written as

$$\frac{\partial T}{\partial t} + \vec{v} \cdot \vec{\nabla} T = \frac{1}{\beta} \vec{\nabla} \cdot \vec{v}. \tag{13}$$

In the absence of buoyancy for an initially quiescent fluid, and assuming that the thermal expansion induced velocity field is directed along the temperature gradient, the temperature increase across the transition layer needed for the thermal expansion induced convective term in Eq. (13) to become of the same order of magnitude as the conductive term is given by

$$\Delta T_E = 1/\beta_{max}, \tag{14}$$

where β_{max} is the value of β at the transition layer. Therefore, the transition layer thickness vanishes at the critical pressure as a consequence of the critical divergence of the thermal expansion coefficient. Then the transition layer conveys in a continuous way to the physical liquid-gas interphase at the critical point. On the other hand, as the pressure increases the transition layer becomes wider according to the decrease of the maximum of β. From Eqs. (2) and (3), the thermal thickness of the transition layer is given by

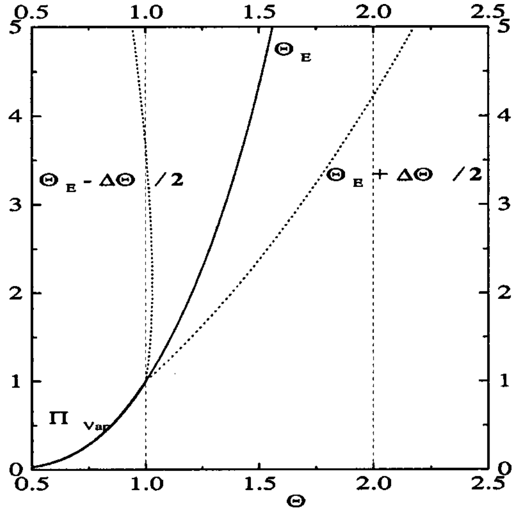

FIG. 3. Transition layer reduced temperature (Θ_E) (solid line) and bounds of the transition layer ($\Theta_E - \Delta\Theta_E/2$, $\Theta_E + \Delta\Theta_E/2$) (dotted line) as a function of the reduced pressure (in ordinates), together with the vaporization pressure (thick line) of a van der Waals fluid.

$$\Delta T_E = T_c \frac{9}{4V_E}\left(\frac{1}{V_E} - 1\right). \tag{15}$$

The ratio between the transition layer thickness

$$\Delta x \equiv \Delta T_E / \left(\frac{\partial T}{\partial r}\right)_{T=T_E} \tag{16}$$

and the characteristic heat conduction length in the hot (gas-like) region,

$$L \equiv (T_\infty - T_E) / \left(\frac{\partial T}{\partial r}\right)_{T=T_E}, \tag{17}$$

is given by

$$\Delta x / L = \Delta T_E / (T_\infty - T_E). \tag{18}$$

As long as this ratio remains a small parameter, the transition layer may be considered as a thin inner transition region, which plays the role of the physical interface in subcritical conditions. Thus, the heating of a supercritical cold pocket set into a much hotter atmosphere at supercritical but moderate pressures is similar to a subcritical vaporization process, but without latent heat nor surface tension. Notwithstanding, in the subcritical vaporization process, the transition region where the Stefan flow is generated belongs to the microscopic scale, while at supercritical pressures this region has a macroscopic thickness which vanishes as the critical pressure is reached from above and which becomes wider as the ambient pressure is increased.

The transition layer reduced temperature (Θ_E) and the transition layer bonds ($\Theta_E - \Delta\Theta_E/2$ and $\Theta_E + \Delta\Theta_E/2$) of a van der Waals fluid are plotted in Fig. 3 as a function of the reduced pressure, together with the subcritical equilibrium vapor pressure. The transition layer may be seen as the natural extension of the vapor-liquid interphase in the supercritical phase. Nevertheless, it is important to remark that the supercritical transition layer separates two regions of the same phase of the fluid.

V. CONCLUSIONS

The heating of a cold fluid pocket suddenly set into a hot, otherwise quiescent, atmosphere at supercritical but moderate pressures is explained here as a consequence of the Stefan flow induced (by thermal expansion) in the relatively thin transition region located where the thermal expansion coefficient reaches its maximum.

At supercritical but moderate pressures, this thermal expansion induced Stefan flow produces a convective heat flow of the same order of magnitude (but in the opposite direction) as the conductive heat flow. Hence, the convective thermal flow tends to slow the heating process.

The competition between the convective and conductive heat fluxes generates the thin transition layer (where most of the fluid expansion takes place), which recedes through the cold fluid as the vaporization takes place. Consequently, the vaporization process of a cold fluid pocket in a high temperature atmosphere at moderate supercritical pressures differs from a purely conductive heating process and resembles the subcritical vaporization process.

As the pressure at which the vaporization takes place increases, the maximum of the thermal expansion coefficient decreases and broadens. Consequently, the importance of the Stefan flow decreases, and the heating of the cold pocket becomes gradually a purely conductive heating process.

Based on the behavior of the thermal expansion coefficient of a van der Waals gas, it is found that the transition between the supercritical vaporization and supercritical conductive heating is a gradual transition that takes place in a pressure band located roughly between $1.5P_c$ and $4.5P_c$.

In order to focus on the main qualitative aspects of the process under study, and to be able to derive some analytical results, the present theoretical analysis has been performed considering the van der Waals equation of state of a pure substance. However, the same analysis may be performed (at least numerically) using any specific equation of state of interest. By means of the corresponding states theory, the qualitative predictions of the present model still hold, during the thermal relaxation period, in the case of vaporization into a multicomponent mixture. However, the dependence of the critical pressure and of the critical temperature with the concentration of dissolved vapors will have a very important effect in that case.

ACKNOWLEDGMENTS

This work has been funded by the Ministerio de Ciencia y Tecnología of Spain, Project Nos. PB98-0142 and DPI2002-04550-C07-01.

[1] S.D. Givler and J. Abraham, Prog. Energy Combust. Sci. **22**, 1 (1996).

[2] J. Bellan, Prog. Energy Combust. Sci. **26**, 329 (2000).

[3] D.B. Spalding, ARS J. **29**, 828 (1959).

[4] D.E. Rosner, AIAA J. **5**, 163 (1967).

[5] A. Chervinsky, AIAA J. **7**, 1815 (1969).

[6] C. Sánchez-Tarifa, A. Crespo, and E. Fraga, Astro. Acta **17**, 685 (1972).

[7] M. Arias-Zugasti, P.L. García-Ybarra, and J.L. Castillo, Phys. Rev. E **60**, 2930 (1999).

[8] M. Arias-Zugasti, P.L. García-Ybarra, and J.L. Castillo, Combust. Sci. Technol. **153**, 179 (2000).