

THERMOPHYSICAL PROPERTIES OF SUPERCRITICAL FLUIDS

Pierre Carlès*

Laboratoire Fluide, Automatique et Systèmes Thermiques
Université Pierre et Marie Curie – Paris 6 / CNRS
Bâtiment 502, Campus Universitaire, 91402 Orsay Cedex, FRANCE
Email : pierre.carles@upmc.fr , Tel : (33)1.69.15.80.48

ABSTRACT

This article presents a general introduction to the physics and dynamics of supercritical fluids and the critical point. It is organized in two parts: In a first section, the nature of the critical point is discussed and its influence on the properties of supercritical fluids is presented; In a second section, we then examine the dynamic processes induced by these peculiar properties, concentrating on heat and mass transfer and more generally on relaxation phenomena.

INTRODUCTION

Although supercritical fluids have been used in various industrial applications for the past 60 years, it is only in the early 70s that their peculiar thermophysical properties have been understood, following the works of Widom, Kadanoff and Wilson. Hence, the understanding of the physics of critical points is a relatively recent result (around 30 years-old). If one now considers the dynamic relaxation phenomena in these fluids (and among them heat transfer and hydrodynamics), then the main discoveries are even younger: a mere 15 years, with lots of open questions remaining. Making a short summary of these recent results seems useful to an application-oriented audience: integrating this recent knowledge may indeed help optimize existing processes, and possibly stimulate the design of new approaches heretofore not considered for lack of a better understanding of what is going on near the critical point.

The aim of this article is to present a brief review of the present knowledge about the thermophysics and dynamics of supercritical fluids, in qualitative terms. For the more technically-oriented reader, a list of key references is provided. In a first part, general considerations about the thermodynamics of supercritical fluids are reminded. In a second part, the most significant mechanisms governing the dynamics of these fluids are introduced.

THE CRITICAL POINT AND SUPERCRITICAL FLUIDS

Phase diagram of a pure component

Following Gibbs phase rule, a pure component in thermodynamic equilibrium can be observed under the form of three different phases (sometimes more), determined by only two independent state variables. The complete set of accessible equilibrium states is thus a surface in the three-dimensions space of state variables. Such a *State Surface* is represented in figure 1 with the particular choice of state variables P (pressure), ρ (mass density) and T (temperature). Most state surfaces of classical components have a similar topology. In figure 1, one can also see the projections of the state surface on the planes (P, T) (Pressure,

Temperature) and $(P, 1/\rho)$ (Pressure, Elementary Volume). The three usual states of matter are represented, separated by *Coexistence Curves*.

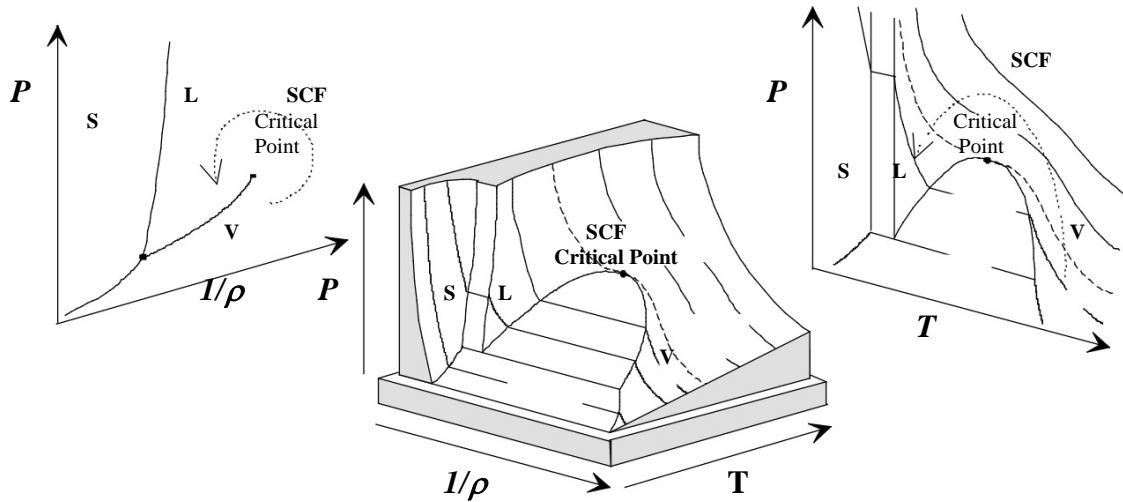


Figure 1 : State Surface of a pure component
 S = Solid, L = Liquid, V = Vapour, SCF = Supercritical Fluid

If the (P, T) set of variables leads to a state located inside a coexistence curve, then the pure component is observed under the form of two coexisting phases. One can observe that the liquid-vapour coexistence curve is not infinite, but presents a maximum. Consequently, the liquid and vapour states cannot be considered as two separated states, but as the extremes of the same continuum (like indicated by the dotted arrow, showing how a continuous transition between vapour and liquid is possible). The first observation of this continuous transition was made in 1822 by Baron Cagniard de la Tour [1]. It stimulated long discussions between Farraday and Herschel in the mid-nineteenth century, but it is only through the works of Andrews [2] and van der Waals in 1873 [3] that a first theoretical model explaining this transition was obtained.

Andrews named the top of the liquid-vapour coexistence curve the *Critical Point*, owing to its singular nature. A fluid whose temperature is higher than the *Critical Temperature* (i.e. the temperature of the critical point) is neither a gas nor a liquid but a *Supercritical Fluid*. Because of their specific position in the phase diagram, fluids in the supercritical domain exhibit peculiar properties, sometimes similar to those of gases and sometimes to those of liquids. Unlike the liquid-vapour coexistence curve, the liquid-solid coexistence curve is considered to be infinite. No maximum has indeed been observed so far on this curve, and many authors consider that the structural symmetries of liquids and solids are too different to allow for a continuous transition [4].

Thermodynamic stability and chemical potentials

A few classical results of thermodynamic stability will now be reminded, which enable a qualitative interpretation of the existence of a critical point and of the peculiar properties observed in its vicinity. Let us consider *Gibbs Potential*, defined as:

$$G = U + P / \rho - T S \quad (1)$$

where U is the *Internal Energy* and S the *Entropy* (per mass unit).

Thermodynamics' second principle implies that G is a thermodynamic potential for systems at constant pressure and temperature [5, 6, 7]. This means that for a given set of

values of variables (P, T) , a system is in a state of equilibrium if G is minimal. Moreover, this equilibrium is stable if G is a convex function of T and P [7]. In other words, the stability of an equilibrium state is governed by the following inequalities:

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_P < 0 \quad \text{and} \quad \left(\frac{\partial^2 G}{\partial P^2}\right)_P < 0 \quad (2)$$

But $dG = -S dT + \frac{1}{\rho} dP$ and $dS = \frac{C_P}{T} dT + \frac{1}{\rho^2} \left(\frac{\partial \rho}{\partial T}\right)_P$, hence:

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_P = -\left(\frac{\partial S}{\partial T}\right)_P = -C_P/T < 0 \quad (3)$$

$$\left(\frac{\partial^2 G}{\partial P^2}\right)_T = -\left(\frac{\partial \rho}{\partial P}\right)_T / \rho^2 = -\kappa_T / \rho < 0 \quad (4)$$

where κ_T is the isothermal compressibility. Consequently, a pure component is in a stable state if, and only if, its isothermal compressibility and heat capacities are positive (conditions (2) and (3)).

Let us now analyse the $(P, 1/\rho)$ projection of the state surface represented in figure 2. Several isotherms have been drawn, below and above the critical temperature. The thin dotted line represents the theoretical extension of the isotherms inside the coexistence curve.

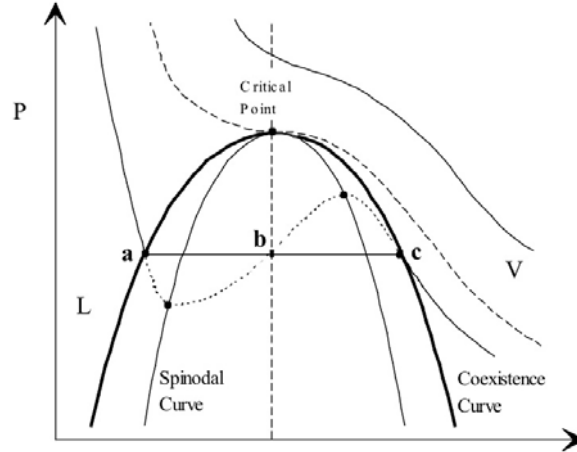


Figure 2 : Coexistence and spinodal curves

Above the critical point, the slope of the isotherms is always negative. In other words, the isothermal compressibility is always positive, and condition (4) is always fulfilled. Let us now consider a fluid container filled with a supercritical fluid at critical density, whose temperature is slowly decreased. In figure 2, one observes that the isotherms tend to become more and more horizontal when the critical point is approached: the compressibility of the fluid is increasing near the critical point. When the critical point itself is reached, the tangent of the isotherm is flat: compressibility is infinite. If the temperature is decreased further, the fluid enters the two-phase zone (for instance reaching point **b**) and a phase separation occurs: the container now contains an equal proportion of liquid (characterised by point **a**) and of gas (characterised by point **c**), both at the same pressure and temperature. At point **b**, the theoretical extension of the isotherm exhibits a positive slope. A one-phase fluid in average conditions **b** would exhibit a negative compressibility, and would thus be mechanically unstable. The process of phase separation along the critical isochore can thus be viewed as a loss of mechanical stability: at the critical point, the single-phase supercritical fluid loses its stability and separates into two stable phases (this happens through what the specialists in non-linear dynamics call a supercritical pitchfork bifurcation [8]).

However, one can observe that part of the isotherms inside the coexistence curve (i.e. the dotted line on figure 2) still maintain a negative slope. The limit of this domain is materialized by a solid line in the figure and called the *Spinodal Curve*. Between the coexistence curve and the spinodal curve, the fluid is locally stable but its Gibbs Potential is not minimal for all possible states at the same pressure and temperature: this is the domain of the *Metastable* state, where a phase can be maintained as long as only very small perturbations take place but which suddenly destabilizes for sufficiently large perturbations. Using the vocabulary of stability, the critical point is defined as the point where mechanical stability becomes neutral, namely:

$$\left(\frac{\partial P}{\partial \rho}\right)_T(T_c, P_c) = 0 \quad (\text{infinite compressibility}) \quad (5)$$

$$\left(\frac{\partial^2 P}{\partial \rho^2}\right)_T(T_c, P_c) = 0 \quad (\text{inflexion point on the critical isotherm}) \quad (6)$$

$$\left(\frac{\partial^3 P}{\partial \rho^3}\right)_T(T_c, P_c) > 0 \quad (\text{stability of the critical isotherm}) \quad (7)$$

Critical phenomena

Heuristic approach

We have just seen that close to the critical point, compressibility goes to infinity. Other physical properties of the fluid also diverge. The divergences of the fluid's thermophysical properties close to the critical point are named *Critical Phenomena*. These phenomena represent the different mechanisms through which the one-phase supercritical fluid « gets prepared » to phase transition.

Let us look back at the behaviour of compressibility, for instance. If one considers a container filled with a fluid in average conditions **b** (figure 2), the fluid inside the container is made of liquid **a** in equilibrium with vapour **c**. If the container is compressed a little (i.e. if its volume is reduced by a small amount), the two-phase equilibrium is displaced towards larger densities, and the amount of liquid is increased while the amount of vapour is decreased. If the change in volume is not too large, this transformation takes place on the **a-c** line, which is both an isotherm and an isobar. Hence, the average density of the fluid inside the cell can be changed without changing its temperature or its pressure : the two-phase system behaves like an infinitely compressible media. The diverging of compressibility close to the critical point can thus be seen as a way for the supercritical fluid to progressively adapts its behaviour to that of a two-phase system. The same analogy could be made with the heat capacity at constant pressure, which also diverges at the critical point. A two-phase system on line **a-c** is such that it can receive energy at constant pressure without any temperature increase: all the energy sent into the system is expended as latent heat in order to change liquid into vapour. Such a system thus behaves like a medium with infinite heat capacity at constant pressure.

Critical divergences

The above description of critical phenomena is only qualitative. However, it illustrates in a clear way how a fluid getting close to the critical point exhibits a singular behaviour. The divergence of the fluid's properties at the critical point, which are universal (in some sense detailed below), can all be written as power laws of a parameter measuring the distance to the critical point. For instance, the divergence of the isothermal compressibility along the critical isochore can be written :

$$\kappa_T = \Gamma / \varepsilon^{-\gamma} \quad \text{with} \quad \varepsilon = (T - T_c) / T_c \quad (8)$$

In this example, the distance to the critical point is expressed by the parameter ε (named the *Reduced Temperature*), and the property diverges with the exponent γ , named *Critical Exponent*. Γ is the *Cofactor* of the power law. In table 1, the critical divergences of the properties of a pure fluid are summarized. As will be seen later, these exponents are the same for all pure fluids, and this universality (*Critical Universality*) is observed even beyond fluid systems.

Property	Thermodynamical Path	Critical Divergence	Critical Exponent
Isothermal compressibility	Critical isochore	$\kappa_T = \Gamma \varepsilon ^{-\gamma}$	$\gamma = 1,239 \pm 0,002$
Heat capacity at constant volume	Critical isochore	$C_v = A^\pm \varepsilon ^{-\alpha}$	$\alpha = 0,110 \pm 0,003$
Density difference between liquid and gas	Coexistence curve	$\rho_l - \rho_g = 2B \varepsilon ^\beta$	$\beta = 0,326 \pm 0,002$
Pressure difference with critical pressure	Critical isotherm	$ \Delta P = D \Delta \rho ^\delta$	$\delta = 4,80 \pm 0,02$
Correlation function ¹	Critical point, large r	$h(r) = r^{2-d-\eta}$	$\eta = 0,031 \pm 0,004$
Correlation length ²	Critical isochore	$\xi = \xi_0 \varepsilon ^{-\nu}$	$\nu = 0,630 \pm 0,001$

Table 1 : Diverging properties close to a critical point and associated critical exponents; given a property X , $\Delta X = (X - X_c) / X_c$ (after [4]) ; d represents the spatial dimension, r the distance away from a given molecule

Several comments can be made about Table 1. First, the critical divergence of a property is defined along a well-defined thermodynamic path. Of course, a diverging quantity will diverge for any thermodynamic path leading to the critical point. It is fairly easy to find the correspondence between the critical exponent along the critical isochore and the critical exponent along the critical isotherm or the coexistence curve for a given property (see [4]). For more complex paths however, this correspondence can be made only through the knowledge of an equation of state. The knowledge of precise equations of states near the critical point is a major difficulty in the study of near-critical fluids (this topic will not be dealt with in this article). The second comment which can be made about Table 1 is that the isothermal compressibility, the heat capacity at constant volume and the correlation length all diverge at the critical point. Several other divergences can be deduced from these three ones. For instance, following generalised Mayer's relation [6]:

$$C_p - C_v = - \frac{T}{\rho^2} \left(\frac{\partial P}{\partial T} \right)_\rho^2 \left(\frac{\partial \rho}{\partial P} \right)_T \quad (9)$$

$(\partial P / \partial T)_\rho$ does not diverge at the critical point and C_v diverges with a small exponent ($\alpha \approx 0,11$). Consequently, C_p diverges like the isothermal compressibility, that is, with an exponent $\gamma \approx 1,24$. Besides, sound velocity c can be expressed as :

¹ Correlation function $h(r)$ measures the statistical correlation between density at a given point and density at a distance r from this point. For large values of r , it goes to zero. Far from the critical point, $h(r)$ can be written as $e^{-(r/\xi)} / r$, where ξ is the correlation length.

² The correlation length, defined in the previous note, measures the spatial extension of density fluctuations.

$$c^2 = \frac{T_c}{\rho_c^2 C_v} \left(\frac{\partial P}{\partial T} \right)_\rho^2 + \left(\frac{\partial P}{\partial \rho} \right)_T \quad (10)$$

Consequently, sound velocity goes to zero at the critical point like $1/\sqrt{C_v}$, that is, with a very weak exponent ($\alpha/2 \approx 0,05$). Finally, the divergence of the correlation length has a strong influence on the critical behaviour of transport properties and of surface tension. Using arguments drawn from statistical physics, it can be shown that shear viscosity η_S and thermal conductivity λ diverge at the critical point, while surface tension between liquid and vapour goes to zero (which can be qualitatively explained by the greater and greater similarity between the two phases close to the critical point). Along the critical isochore, the following relations hold [4] :

$$\lambda \approx \lambda_0 \Delta T^{\nu + \eta - \gamma} \quad (11)$$

$$\eta_S \approx \eta_0 \Delta T^{-\eta} \quad (12)$$

The divergence of thermal conductivity³ should not lead the reader into thinking that a fluid close to the critical point is a better and better heat conductor. Indeed, the diffusive relaxation of temperature is extremely slow, since it depends on the *Thermal Diffusivity* $\lambda / (\rho C_p)$ which goes to zero (the divergence of C_p is indeed stronger than that of λ). This slowing down of the relaxation of entropy at the critical point is classically named the *Critical Slowing Down*. As will be seen later in this chapter, this slowing down contradicts the experimental observation of a *Critical Speeding Up* of temperature relaxation at the critical point. Several authors also predict a critical divergence of the bulk viscosity [9, 10], but it has a practical influence only extremely close to the critical point [11-13]. Hence, this divergence is of little importance in an operational context.

Classical models and their limits

The first model proposed to explain the behaviour of fluids close to their critical point was van der Waals' model, based on a now famous equation [3]. This model was very successful in explaining how microscopic phenomena induced macroscopic divergences at the critical point. It is now seen as a particular case of a broader category, named *Classical* or *Mean Field Models*⁴. These models share the property of having equations of state which are analytical at the critical point (i.e. which can be expanded as Taylor series at the critical point). It can be shown that all equations of state which are analytical at the critical point result in the same (incorrect) critical exponents. Let us consider the equation of state of a fluid, written as $P = f(T, \rho)$ with $f(T, \rho)$ being analytical at the critical point. If the small excursions from the critical co-ordinates are named $\delta T = T - T_c$ and $\delta \rho = \rho - \rho_c$, a third-order Taylor expansion of P at the critical point yields (inserting conditions (4-6)):

$$\begin{aligned} P = & P_c + \left(\frac{\partial P}{\partial T} \right)_\rho^c \delta T + \frac{1}{2} \left(\frac{\partial^2 P}{\partial T^2} \right)_\rho^c \delta T^2 + \left(\frac{\partial^2 P}{\partial T \partial \rho} \right)_\rho^c \delta T \delta \rho + \frac{1}{6} \left(\frac{\partial^3 P}{\partial T^3} \right)_\rho^c \delta T^3 \\ & + \frac{1}{2} \left(\frac{\partial^3 P}{\partial T^2 \partial \rho} \right)_\rho^c \delta T^2 \delta \rho + \frac{1}{2} \left(\frac{\partial^2 P}{\partial T \partial \rho^2} \right)_\rho^c \delta T \delta \rho^2 + \frac{1}{6} \left(\frac{\partial^3 P}{\partial \rho^3} \right)_T^c \delta \rho^3 + \dots \end{aligned} \quad (13)$$

³ $\nu + \eta - \gamma$ is indeed negative.

⁴ Ginzburg-Landau's model also belongs to this category [6]. The name of Mean Field Models comes from the fact that these models are based on the assumption that the molecular interactions globally act as a mean field independent of the molecular distribution.

where the superscript « c » represents the value at the critical point. Looking for exponent δ (which relates ΔP to $\Delta\rho$), one imposes $\delta T = 0$ and obtains :

$$\delta P = \frac{1}{6} \left(\frac{\partial^3 P}{\partial \rho^3} \right)_T^c \delta \rho^3 + \dots \quad , \quad \text{hence} \quad \delta = 3 \quad (14)$$

In the same way, the exponent γ (which measures the divergence of isothermal compressibility along the critical isochore) can be found by deriving eq. (7) with respect to ρ and letting $\delta\rho = 0$:

$$\left(\frac{\partial P}{\partial \rho} \right)_T = \left(\frac{\partial^2 P}{\partial T \partial \rho} \right)_T^c \delta T + \dots \quad , \quad \text{hence} \quad \gamma = 1 \quad (15)$$

The other critical exponents can be calculated in the same way, while the exponents linked with transport properties can be obtained through statistical physics equations. The above results illustrate the failure of classical theories to describe critical phenomena in a proper way, a problem which has been identified as soon as the early 50s [5].

Universality and critical fluctuations

The reason for the failure of mean-field models at the critical point lies in the behaviour of critical fluctuations. Indeed, the thermodynamic formalism is statistical, and all thermodynamic quantities like temperature or internal energy are the result of an averaging process over a large number of molecules. Locally, the properties of the medium can exhibit excursions away from the average values (fluctuations), whose statistics can be predicted using statistical physics [5]. Most macroscopic transport or thermostatic properties are related to the statistical distribution of fluctuations. For instance, the isothermal compressibility is proportional to the root mean square of density fluctuations, while the heat capacity at constant volume is proportional to the root mean square of internal energy fluctuations [5]. Hence, the critical divergence of these two properties (among others) is directly related to the singular behaviour of fluctuations. As the divergence of the correlation length ξ shows, fluctuations become larger and larger near the critical point. Consequently, a critical system is a system where long-range correlations are dominant. This explains why mean-field theories fail (they average these long-range correlations).

The critical divergence of the typical size of fluctuations can be observed experimentally through the phenomenon of *Critical Opalescence* : when a fluid sample is brought close to its critical point, it takes a white and fog-like colour. This phenomenon is observed when the density fluctuations become of the same typical size as the wavelength of visible light : density fluctuations are then large enough to diffuse light. As in the heuristic approach of critical phenomena described above, one can picture the divergence of density fluctuations as a preparation to phase separation : right above the critical point, small domains of high and low density start to form in the fluid; when the coexistence curve is crossed, drops and bubbles nucleate from these domains.

We already said that the critical exponents in Table 1 are the same for all fluid systems. The origin of this *Critical Universality* lies in the divergence of fluctuations. Indeed, macroscopic properties are no longer governed by the local behaviour of molecules but rather by a collective behaviour settling through long-range interactions. Hence, the average properties of the system are no longer functions of the individual nature of its components,

but rather of a given number of global parameters through which *University Classes*⁵ can be defined [7]. Inside a university class, the critical behaviour is identical even if the physical systems are very different.

Scaling laws and renormalisation

The predominance of long-range correlations was the key which allowed the understanding of critical phenomena in the 60s and early 70s. Indeed, if one imagines a system in which long-range correlations dominate, then the exact nature of the local molecular interaction loses relevance and only the collective behaviour at the scale of the correlation length matters. This collective behaviour hides the specificity of systems and leads to a universal behaviour. This observation led several authors into assuming the hypothesis of *Scaling*, which was later formalised through *Renormalisation* techniques. A first illustration of the idea of scaling is Widom's conjecture, proposed in 1963 [14]. Let us write the enthalpy under the following form :

$$G(T, \rho) = G_r(T, \rho) + G_s(\delta T, \delta \rho) \quad (16)$$

where G_r is the *Regular Component* of G and G_s its *Singular Component*. Widom's conjecture was to consider that G_r is analytical while G_s is a generalised homogeneous function, meaning that there exist two real constants p and q such that whatever θ :

$$G_s(\theta^p \delta T, \theta^q \delta \rho) = \theta G_s(\delta T, \delta \rho), \text{ or } G_s(\delta T, \delta \rho) = \delta \rho^{1/q} G_s(\delta T / \delta \rho^{p/q}, 1). \quad (17)$$

In other words, the singular part of the enthalpy is *Self-Similar*, which means that it has the same functional form regardless of the proximity to the critical point, provided the right scaling is made. This assumption leads to several important consequences. Let us for instance calculate the heat capacity at constant volume, by differentiating (17) twice :

$$\left(\frac{\partial^2 G}{\partial T^2} \right)_\rho = \theta^{2p-1} \left(\frac{\partial^2 G_s}{\partial T^2} \right)_\rho (\theta^p \delta T, \theta^q \delta \rho) + \left(\frac{\partial^2 G_r}{\partial T^2} \right)_\rho = - \frac{C_v}{T} \quad (18)$$

By letting $\theta = \delta T^{-1/p}$, one finds on the critical isochore (i.e. for $\delta \rho = 0$) :

$$C_v \approx - T \delta T^{2 - \frac{1}{p}} \left(\frac{\partial^2 G_s}{\partial T^2} \right)_\rho (1, 0) \approx A |\Delta T|^{-\alpha}, \quad \text{hence } \alpha = 2 - \frac{1}{p} \quad (19)$$

As we have just shown, assuming that G_s is homogeneous leads to a relation between a critical exponent and the constants p and q . Through similar calculations, one finds other relations between critical exponents and p and q , which in turn lead to the following equalities once p and q are eliminated [12] :

$$\alpha = 2 - \beta(\delta + 1) \quad \gamma = \beta(\delta - 1) \quad (20)$$

Hence, Widom's conjectures implies that the critical exponents are not independent from one another. Kadanoff in 1966 [15] applied the same self-similarity principle to the study of the Curie point in a discrete model of ferromagnetic solid (the *Ising Model* [16]). This model can easily be transposed to fluid systems, for which it takes the form of a *Lattice-Gas* model (the Curie point is then equivalent to the liquid-vapour critical point). Kadanoff obtained two more relations between the critical exponents, namely:

⁵ A universality class is defined by the spatial dimension d and by the dimension of the *Order Parameter* n . An order parameter is a quantity which is zero above the critical point and finite below. For instance, $\rho - \rho_c$ is chosen as the order parameter for the liquid-vapour critical point (in that case, the order parameter is a scalar).

$$\gamma = \nu(2 - \eta) \qquad d\nu = 2 - \alpha \qquad (21)$$

(with d the dimension of the system). These new relations, added to the ones in (20), leave only two independent critical exponents.

With the works of Kadanoff and Widom, relations between the critical exponents were found, together with a first idea about the origin of the critical universality. But it is only with the work of Wilson in 1971 that a theoretical prediction of the critical exponents was made possible, thanks to the *Renormalisation Group Theory* [17]. The renormalisation group theory enabled Wilson to predict the universal value of the critical exponents. It explained why they are universal, but also predicted that there exists universal relations between the cofactors (or *Critical Amplitudes*) (see Table 1). Critical universality can then be reformulated as:

Inside the universality class of liquid-vapour critical points, consolute critical points and Curie points, the critical behaviour is universally characterized by the definition of two scale factors only. All critical exponents are the same regardless of the system.

This definition means that in order to characterise entirely the critical divergences of a given system, the knowledge of two cofactors is sufficient.

Influence of the critical phenomena far from the critical point

We have just seen that the properties of a fluid become singular close to a critical point. The definitions of critical divergences and of critical universality have been given. These phenomena are described as asymptotic behaviours, but when a supercritical fluid is used in an industrial process, a given finite distance to the critical point is reached. The range of influence of critical phenomena away from the critical point is thus an important practical question. If one examines CO₂ (one of the most used fluid in supercritical processes), several observations can be made (for CO₂, $T_c = 304.13$ K, $\rho_c = 467.8$ kg/m³, $P_c = 7.376$ MPa). First, critical CO₂ is a very dense fluid. In spite of its liquid-like density, critical CO₂ is very compressible: its thermal expansion coefficient is several times that of air at room temperature and pressure in a large vicinity of the critical point (and 41 time larger at $T_c + 1$ K). Hence, even at 100 K above the critical point, CO₂ remains both dense and very compressible. In the same range of temperatures, the vanishing of the thermal diffusivity is clearly visible: even at 100K above the critical point, heat diffusion is 350 slower in CO₂ than in air at ambient conditions (and 11000 time slower at $T_c + 1$ K). These figures show that critical phenomena can generally be felt even far from the critical point itself. Usually, one can consider that the critical divergences affect the fluid significantly in a range of reduced temperatures going from 0 to 0.3 (that is, up to $T/T_c = 1.3$). Even if most industrial processes deliberately avoid the vicinity of the critical point, such figures show that it is always necessary to take into account critical divergences.

Extending these observations to other fluids, the critical density is seen to be typically a few hundreds of kilograms per cubic meters, sometimes more. Such densities are similar to those of usual liquids in ambient conditions. But one should not forget that, unlike liquids, supercritical fluids are extremely compressible media. This observation reminds us that supercritical fluids are media intermediate between gases and liquids, both dense and compressible. One consequence of their large density is to increase their ability to dissolve other components (which is a liquid-like behaviour). But at the same time, the coefficients of mass diffusion are similar to those of gases, so that the transport of dissolved components is very efficient (something normally observed in gases). The association of these two antagonistic characters explains why supercritical fluids have been so widely used in

extraction/separation processes. Finally, due to the critical divergences, the properties of supercritical fluids can be changed with only minute changes of the thermodynamic coordinates. One can thus summarise the typical characters of supercritical fluids by the three points below :

- *Supercritical fluids are dense and compressible at the same time, and heat diffuses slowly while mass diffuses rapidly in them.*
- *The properties of a supercritical fluid can be easily adjusted by small variations of the average temperature and pressure.*
- *Even far from the critical point, the properties divergences at the critical point can be felt and induce unexpected dynamic responses.*

We will now examine the dynamic responses in question (namely, the relaxation processes through which supercritical fluids recover equilibrium after a perturbation).

DYNAMIC RESPONSE OF SUPERCRITICAL FLUIDS

Influence of gravity and anomalous heat transport

The association of a large compressibility and of a large density in the same fluid induces several problems linked with gravity. Indeed, a compressible fluid subjected to a gravity field stratifies in layers of variable densities, just like the atmosphere or the oceans. This stratification is governed by the hydrostatic balance between the pressure gradient and gravity forces, under the well-known form :

$$\partial P / \partial z = - \rho(z) g \quad (22)$$

(where z is the vertical co-ordinate and g the gravitational acceleration). If the fluid is kept at constant temperature and weakly stratified, then this relation can be linearised and solved analytically to yield:

$$\rho(z) = \rho_0 e^{- (\partial \rho / \partial P)_T g z} \quad (23)$$

Let us apply this relation to a one-meter-high container filled with CO₂ at critical density and 1 K above the critical temperature. A relative density difference of 4% between the top and the bottom of the container is observed. It would take 35 meters of ambient air to observe the same amount of stratification. These figures illustrate a fundamental problem of experimental studies in supercritical fluids : the closer one gets to the critical point, the more inhomogeneous the fluid sample becomes. The precise measure of any physical quantity thus gets increasingly difficult as the critical point is approached. In parallel, the strong compressibility of supercritical fluids makes them extremely sensitive to convective instabilities. Even minute temperature differences applied to a fluid close to the critical point lead to strong density inhomogeneities, which in turn give birth to strong convective flows (for instance, strong enough to perturb a precise calorimetric experiment or to destroy delicate products synthesised in supercritical phase). These strong convective flows were for long considered as the reason for the very fast heat transfer observed in supercritical fluid containers despite the vanishing thermal diffusivity. As we will see below, the situation is really more complex.

Due to these problems with gravity, critical fluids very soon appeared as good candidates for microgravity experiments [18]. A particular experiment by Nitsche and Straub in a 1985 flight of the Space Shuttle, though, yielded puzzling results [19]. In a classical thermometry experiment (in which thermal equilibrium should have been reached only

through diffusion owing to the absence of apparent gravity), these authors observed a very fast heat transfer in the fluid, which contradicted the expected critical slowing down of thermal diffusion. This unexpected result demonstrated that the observed anomalous heat transfer in near-critical fluids on the ground was not due to convection as was believed until then.

The Piston Effect and related phenomena

The puzzling observation by Nitsche and Straub was explained only 5 years later, through the work of Onuki [20, 21] and of two other teams working independently [22, 23]. The mechanism leading to the unexpectedly rapid heat transfer was named the *Piston Effect*, and is described qualitatively in figure 4.

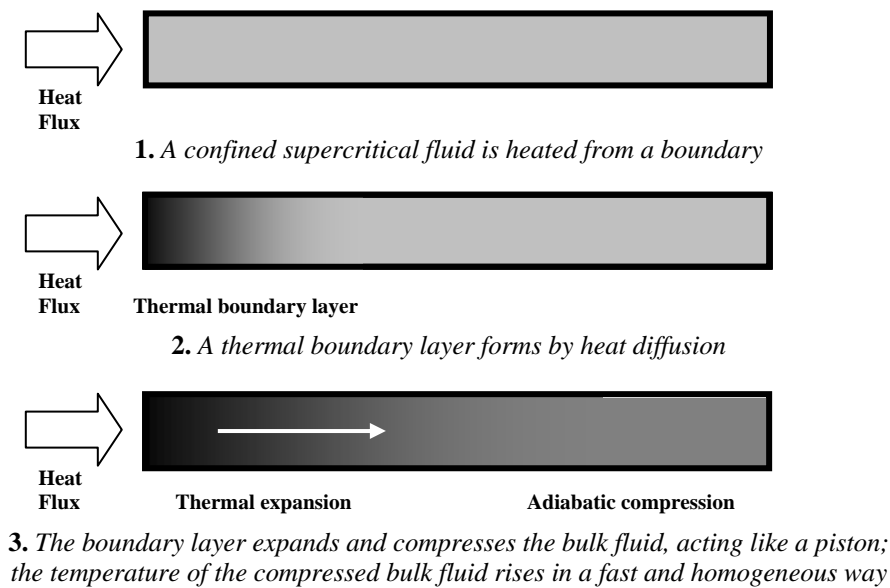


Figure 4 : Qualitative description of the Piston Effect (grey scale represents temperature)

As shown in figure 4, the reason for the rapid heat transfer is the sudden and strong expansion of the thin thermal boundary layer where heat has initially diffused: acting like a piston, it drives an adiabatic compression of the bulk fluid, resulting in a homogeneous temperature increase. Thus, through a purely dynamic phenomena, a fluid with a very small heat diffusivity can nonetheless transfer heat very rapidly. Analyzing the whole process more closely, one concludes that the rapid expansion of the boundary layer drives a field of acoustic waves in the fluid (thermoacoustic convection). The adiabatic compression can be seen as the average effect of these thermoacoustic waves travelling back and forth in the fluid container at a the speed of sound.

Let us briefly summarize Onuki's reasoning [21], which lead to the first quantitative prediction of the typical time of this process. In the absence of convection, the fluid is subjected to pure diffusion, and its temperature evolution should normally be described by a classical heat diffusion equation. However, the effect of the thermal expansion must be added to that picture, under the form of the work of pressure forces. Assuming that the average compression is a slow process compared to the propagation of sound waves, the time-varying pressure in the container can be considered as homogeneous to first order. Then, mass conservation and energetic arguments lead to the formulation of the work of pressure forces

as a term proportional to the average temperature in the cell. The corrected heat transfer equation becomes:

$$\frac{\partial T}{\partial t} = \frac{\gamma - 1}{\gamma} \frac{\partial}{\partial t} \langle T \rangle + D \Delta T \quad (24)$$

where D is the heat diffusivity of the fluid (going to zero at the critical point), $\langle T \rangle$ represents the spatial average of temperature T and γ is the ratio of heat capacities (not to misread as the critical exponent γ , commonly defined with the same notation). The influence of γ on this equation is interesting to observe: if $\gamma = 1$, then the classical equation of heat diffusion is recovered. This corresponds to the particular case of an incompressible fluid, where obviously no piston effect can be observed (indeed, Mayer's generalized relation (9) prescribes that $(\gamma - 1)$ is proportional to the fluid's compressibility). On the other hand, if γ is different from 1 (and it can only be larger), then the middle term of equation (24) represents a new source of temperature variation, associated with the compressive effect of the work of pressure forces. It is interesting to observe that Onuki's reasoning is in no way restricted to supercritical fluids: any fluid with $\gamma > 1$ will be subjected to some degree to the Piston Effect. In other words, when a fluid is confined in a finite-volume cell, then the classical heat equation found in every textbook is only correct for purely incompressible fluids. For compressible fluids, equation (24) is the right equation. The reason why the middle term of equation (24) becomes particularly relevant for supercritical fluids is linked to critical divergences: as shown in the previous section, γ goes to infinity at the critical point, while D goes to zero. As the fluid gets closer and closer to the critical point, the diffusive term becomes smaller and smaller and the work of pressure forces dominates the right-hand side of the equation. This is the reason why the Piston Effect is so dominant in supercritical fluids, although it technically exists in any compressible fluid.

Equation (24) was solved analytically by Onuki [21] in the particular case of a near-critical fluid contained in cell of typical length L , initially at $T = T_0$, and whose boundaries are abruptly heated to $T_0 + \Delta T$. The bulk temperature of the fluid T_{Bulk} then follows the equation:

$$T_{Bulk} = T_0 + \Delta T \left[1 - e^{t/t_{PE}} \operatorname{erfc} \left(\sqrt{t/t_{PE}} \right) \right] \quad (25)$$

$$\text{with } t_{PE} = \frac{t_D}{(\gamma - 1)^2} \quad (26)$$

where t_D is the typical heat diffusion time, here defined as $t_D = L^2/D$. A new typical time appears: t_{PE} , the typical time-scale of the Piston Effect. Interestingly, it goes to zero at the critical point: t_D goes to infinity (critical slowing down), but $(\gamma - 1)^2$ goes to infinity even faster. $t_{PE} \propto \varepsilon^{2\gamma - 2\alpha - \nu - \eta} \approx \varepsilon^{1.6}$ (where γ is now the critical exponent, as defined in table 1). The Piston Effect thus induces a *Critical Speeding Up* of temperature relaxation, contradicting the expected critical slowing down (and explaining Nitsche and Straub's puzzling observation).

The heuristic hypothesis of Onuki and formulas (25-26) have later been confirmed by the asymptotic analysis of Navier-Stokes equations, in the particular case of van der Waals fluids by Zappoli and Carlès [25] and for real fluids by Carlès [12, 26]. It has later been verified experimentally by several teams (see for instance [27]). Note that the definition of t_{PE} is based on a typical length L which should be defined properly. A series of heuristic arguments presented by Carlès [26] lead to a general definition of L yielding good results regardless the geometry of the cell: the appropriate choice for L is the ratio of the total volume of fluid over the area of the heated surface (adiabatic boundaries counting for zero).

In table 2, we compare the values of t_D and t_{PE} for several reduced temperatures, for CO_2 confined at critical density in a 20 cm container. The difference between the two typical times is striking. It is clearly visible on this example that the piston effect (and not diffusion) is responsible for the temperature relaxation in a very large vicinity of the critical point (up to 100 K from T_c here). Hence, heat transfer by the Piston Effect is not restricted to a close vicinity of the critical point, but it affects a large portion of the supercritical domain.

	$T_c + 0,01 \text{ K}$	$T_c + 0,1 \text{ K}$	$T_c + 1 \text{ K}$	$T_c + 10 \text{ K}$	$T_c + 100 \text{ K}$
t_{PE}	3.7 seconds	1 minute 30 seconds	40 minutes	11 hours and 10 minutes	6 days and 5 hours
t_D	19 years and 6 months	3 years and 7 months	246 days	38 days and 16 hours	7 days and 18 hours

Table 2 : Typical heat diffusion time (t_D) and Piston Effect time (t_{PE}) in CO_2 at critical density confined in a 20-cm cell

The figures in Table 2 should not give the impression that a supercritical fluid reaches its complete equilibrium state after a typical time equal to t_{PE} . t_{PE} only measures the typical relaxation time of temperature gradients. As seen above, this fast temperature equilibration is due to the thermal expansion of boundary layers. These boundary layers exhibit strong density gradients which relax only through slow diffusion. In other words, a decoupling appears between the equilibration of temperature and density: temperature gradients relax on the typical time t_{PE} , and density gradients on the typical time t_D .

In figure 5, we have drawn the temperature, pressure, density and velocity profiles obtained by asymptotic analysis of Navier-Stokes equations (from [12]). The fluid is CO_2 , confined in a 1-cm container and subjected to a 1 Wm^{-2} heat flux on its left boundary (its right boundary being insulated). The qualitative evolution described so far is visible in these profiles: temperature exhibits strong gradients close to the heated wall (the thin thermal boundary layer, between $x/L = 0$ and $x/L = 0.05$), and rises in a perfectly homogeneous way everywhere else ; to these strong temperature gradients are associated strong density gradients, which testify of the thermal expansion of the boundary layer ; this thermal expansion gives birth to a velocity field in the cell, which is maximal at the outer edge of the boundary layer (the « piston » velocity) ; finally, one can observe that the pressure in the cell remains homogeneous (but not constant) throughout the whole process. All the above theoretical predictions have been experimentally confirmed in various occasions in the past 10 years: the dynamics of the Piston Effect is now a well-established fact.

It has been mentioned above that the piston-like expansion of the boundary layer drove a series of acoustic waves in the bulk fluid. Although the average effect of these waves is now well-known experimentally, it was only very recently that the underlying thermoacoustic waves were observed and modelled, owing to their extremely small amplitudes (see the 2006 experiments by Miura et al. [28] and model by Carlès [29]).

The peculiar properties of near-critical fluids also give rise to very specific dynamic phenomena which will not be detailed here for lack of space. Among these, one can cite the over-heating phenomenon, by which part of the bulk fluid may reach a higher temperature than that of the “hot” boundaries if the fluid is in a two-phase configuration (see Wunenburger et al., [30]). Other interesting phenomena are the local high-speed jets observed in semi-confined geometries (like small cracks in the container wall), potentially important to explain the fast corrosion observed in supercritical oxidizing media (see Carlès [31] and Frölich et al. [32]). Equally, the response of near-critical fluids to forced oscillation is highly

specific [33], and elements suggest also that particular thermochemical couplings exist [34, 35].

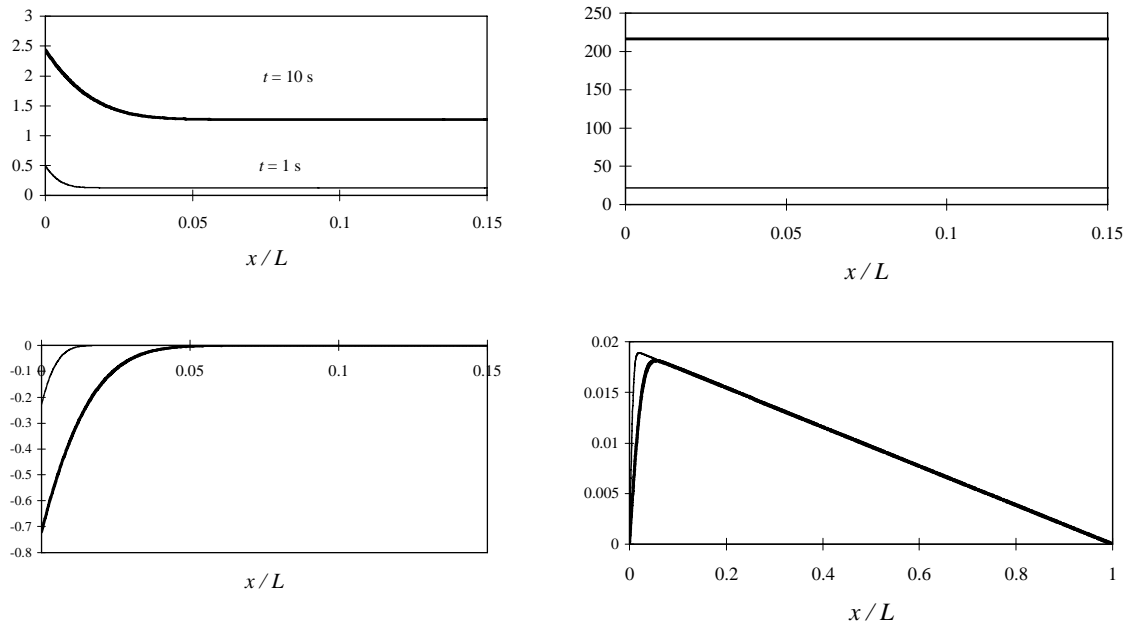


Figure 5 : Temperature, density, pressure and velocity profiles in a cell of 1 cm filled with CO_2 at critical density and at $T_c + 1\text{K}$, subjected on the left boundary to a heat flux of 1 Wm^{-2} while the right boundary is adiabatic

Any “classical” problem of fluid mechanics or thermics gains a new dimension close to the critical point, owing to the specificity of the thermophysical properties. It should thus be expected that many new interesting processes will be discovered in the future.

Supercritical fluids and buoyant convection

The above picture omitted an important element: buoyant convection. In other words, what has been described above is rigorously valid only in the case of a fluid heated from the top, in which no convective current can form. It is therefore legitimate to wonder about whether the above picture remains valid in most practical conditions, namely, when the boundary heating takes place from all boundaries and not just from above. Beyond this initial question, another related issue is the characterization of the conditions under which convection starts in a supercritical fluid.

The question of the coupling between the Piston Effect and natural convection was first studied numerically by Amiroudine [36] and Zappoli et al. [37] in 1995. By conducting two-dimensional direct numerical simulations of a side-heated container filled with a near-critical van der Waals fluid, they showed that convection and the Piston Effect coexist, each retaining more or less its natural time scale. This result was consistent with several ground-based experimental observations of thermal relaxation (see for instance [38]), although no systematic experiment on this problem has been conducted so far (to the best of our knowledge). The same group recently extended these simulations to a full three-dimension geometry [39]. The relative decoupling between convection and the Piston Effect is an important result: it shows that the Piston Effect remains a key mechanism for temperature equilibration near the critical point, regardless of the geometry of the container or of the kind of heating conditions involved. In most cases, the typical time-scale of the Piston Effect is

much faster than that of convection, so that even if convection eventually ensues, most of the thermal equilibration is made by the Piston Effect. Of course, convection drastically speeds up the subsequent density relaxation, which otherwise would take place by slow diffusion.

Let us now examine under which condition buoyant convection starts in a supercritical fluid. As for all Newtonian fluids⁶, any amount of side-heating will trigger convective currents. The real stability issue is thus that of a bottom-heating situation, by which a thin fluid layer at the bottom of the container expands and may (or may not) overcome dissipation and start moving (Rayleigh-Bénard problem). Let us consider the idealized case of a supercritical fluid confined between two infinite horizontal walls, the bottom wall being maintained at a higher temperature than the top one. In a purely conductive configuration, the final steady state presents a constant vertical temperature gradient throughout the fluid (assuming thermal conductivity is roughly constant). Beyond a given gradient threshold though, this steady conductive state becomes unstable and convection ensues. This problem was first studied by Gitterman and Steinberg in 1969 [40], based on heuristic arguments. This last work was recently revisited by Carlès and Ugurtas [41], which gave a rigorous demonstration the following convection criterion :

A supercritical fluid subjected to an adverse temperature gradient $\partial T/\partial z$ in a horizontal container of height L is subjected to buoyant convection if :

$$\frac{\rho g C_v L^4}{\lambda \mu} \left(\frac{\partial \rho}{\partial T} \right)_p \left[\frac{\partial T}{\partial z} + \rho g \left(1 - \frac{C_v}{C_p} \right) \left(\frac{\partial T}{\partial P} \right)_p \right] > Ra_c \quad (27)$$

Ra_c is a critical Rayleigh number, whose value depends on the boundary conditions applied at the top and bottom walls of the container. For fixed-temperature walls, $Ra_c \approx 1708$ (a general list of values of Ra_c can be found in classical stability textbooks _ see for instance Chandrasekhar [36]). Hence, as just presented, the convective stability of a supercritical fluid can be determined by a very simple criterion, consisting in the comparison of the Rayleigh number of the fluid container (the left-hand side of equation (27)) with a critical Rayleigh number determined by the boundary conditions (the right-hand side of equation (27)). Although this criteria is similar to that obtained one century ago for classical incompressible fluids, a significant difference exists : unlike for classical fluids, the correct Rayleigh number here is not simply proportional to the temperature gradient $\partial T/\partial z$ but rather to its difference with $-\rho g (1 - C_v/C_p) (\partial T/\partial P)_p$. This last expression is what meteorologists usually name the *Adiabatic Gradient*. It measures the temperature loss when a fluid particle is forced to climb 1 meter in the hydrostatic pressure gradient without exchanging heat with its environment. As can be seen in equation (27), the temperature gradient $\partial T/\partial z$ is negative in the unstable case (since $(\partial \rho/\partial T)_p < 0$). Subtracting the adiabatic gradient is equivalent to adding a positive term to $\partial T/\partial z$: it thus increase the fluid's stability. This observation is somewhat paradoxical : compressibility is responsible for the convective instability in the first place (the fluid expands when heated), but density stratification (which is also a consequence of compressibility) is a stabilising effect. The validity of criteria (27) has been experimentally confirmed in Helium 3 by Kogan and Meyer in 2001 [43]. In their experimental results, the influence of the adiabatic gradient was dominant, although the horizontal fluid cell was very

⁶ A Newtonian fluid is a fluid in which viscous stresses are proportional to the rate of deformation. Supercritical fluids are generally Newtonian, except very close to the critical point.

thin (1 mm-tall). In classical fluids, the adiabatic gradient correction would only be observed in very large systems such as the atmosphere or the oceans. The surprising thing in the case of supercritical fluids is the fact that the adiabatic gradient is predominant even at the scale of the laboratory or of the industrial plant. This is shown in figure 6, where the critical temperature gradient for convection is drawn for CO₂ as a function of the average temperature and for layers of various heights L . For any container taller than 1 cm, the adiabatic gradient dominates convective stability and criterion (27) simplifies into :

$$-\partial T/\partial z > \rho g (1 - C_v/C_p) (\partial T/\partial P)_\rho \quad (28)$$

The similarity between the effect of gravity on supercritical fluids and on large-scale geophysical systems has driven several authors into proposing the use of supercritical fluids as scaled-down models for geophysical flows. Such an idea was for instance put forward by Berg and co-authors in 1996, who were the first to observe *Internal Gravity Waves*⁷ in small cells filled with supercritical fluids [44], an observation later confirmed and formalised theoretically by Carlès and El Khouri [45]. Although this topic is still very young, a very promising direction of research has been opened.

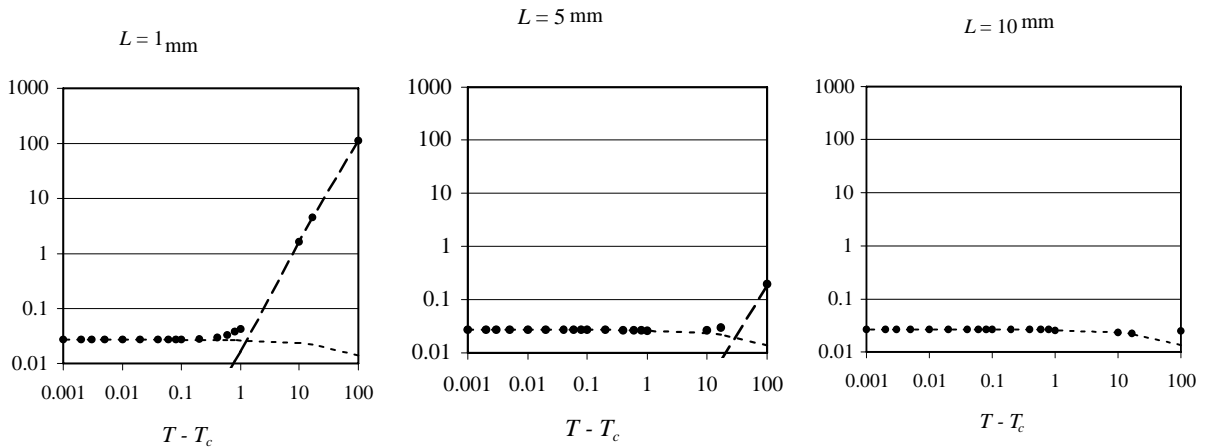


Figure 6 : Critical temperature gradient for convective stability in supercritical CO₂; Black dots represent criterion (27), dotted line criterion (28), and long dotted line the classical Rayleigh criterion ($Ra = Ra_c$).

Summary of relaxation mechanisms in supercritical fluids

As we have just seen, the dynamics of supercritical fluids are governed by a number of mechanisms, some of which are classical while others are the consequence of the peculiar properties of supercritical fluids. Unlike what happens in classical fluids, these different mechanisms are generally decoupled (to a point) and take place on very different time-scales. Hence, as stated above, pressure, temperature or density perturbations in a supercritical fluid usually do not relax following the same laws or on the same time-scales. Table 3 summarises the different relaxation mechanisms : each natural thermodynamic property of the fluid is listed, together with the mechanism governing its relaxation and the typical time-scale on which this relaxation takes place. One can see that pressure perturbations relax on a very short time-scale thanks to acoustic waves, while temperature relaxation is governed by the Piston Effect. Density relaxation finally is governed either by convection or diffusion, depending on the nature of the heating and on geometry. Both these last mechanisms are generally longer

⁷ Internal gravity waves are longitudinal waves propagating in stratified fluid media. They are generally observed in large-scale systems such as the atmosphere or the oceans.

than the Piston Effect, which results in a relative decoupling of temperature and density equilibration processes (something which is never observed in classical fluid systems).


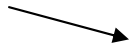
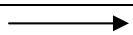

Property	Relaxation mechanism	Typical time	CO ₂ at T _c + 1 K in a 1-cm cell	Asymptotic critical behaviour
Density	Diffusion Convection	$t_D = L^2/D$ $t_C = L^2 \rho/\eta_s$	15 h 20 mn	
Temperature	Piston effect	$t_{EP} = t_D / (C_p/C_v - 1)^2$	6 s	
Pressure	Acoustics	$t_a = L/c$	60 μs	
Fluctuations	Diffusion	$t_\xi = 6 \pi \eta_s \xi^3 / (k_B T)$	30 ns	

Table 3 : Mechanisms governing the relaxation of different properties close to the critical point; in the right-hand-side column, the upward- or downward-facing arrows represent the evolution of the characteristic time as the critical point is approached.

CONCLUSION

In this article, we have presented the thermophysical properties of supercritical fluids and their consequences on supercritical fluids dynamics and thermics. A possible conclusion to this presentation is to look back at the main steps through which the knowledge presented here has been gained. Supercritical fluids were identified as such and first modelled in the late XIXth century. Only 30-35 years ago, the exact origin of their peculiar properties was understood. Dynamic phenomena, in turn, began to be properly understood in the past 15 years (for most of them). It thus clearly appears that most of the existing industrial applications of supercritical fluids were designed (at least in their principle) without the more recent part of the general knowledge reviewed here. It is thus no surprise that these processes tend to avoid as much as possible the vicinity the critical point, still often viewed as « *Terra Incognita* » by most engineers and scientists. But the recent findings made on the critical point should stimulate the search for new applications and processes, which would no longer avoid the critical point but on the contrary try to take benefit of its unmatched characteristics. It can be hoped that with the expanding interest of the scientific community in the study of supercritical fluids, such new « near-critical » applications will soon be proposed.

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