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Supercritical Fluids as Experimental Models for Geophysical Flows[1]

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A pure component is supercritical when its temperature and pressure are above the temperature and pressure of the critical point (CP). In the supercritical domain of the phase diagram, there no longer exists a difference between gaseous and liquid states, and fluids are in an intermediate and somewhat paradoxical state where their thermophysical properties are similar to those of gases for some of them and those of liquids for others. Taking into account the gravity, the diverging compressibility at the CP induces a stable stratification of the fluid density. The stratification is significant, sometimes as much as 10% in a one cm layer. For example, a one cm high cell containing He^3 at 3 mK above its critical temperature is equivalent to a 180 m high column of air or a 7 km high column of water in terms of stratification. Therefore, supercritical fluids (SCFs) at the scale of the laboratory share several features with large geophysical systems. This observation has led several authors into suggesting their use as laboratory models for geophysical flows. However, the peculiarity of near-critical systems could make this analogy fail. In the present work, we have investigated the analogy between both kinds of systems (SCFs at small scale and geophysical flows at large ones) through the study of two examples: the onset of convection in a SCF layer subjected to an adverse temperature gradient, and the generation of internal gravity waves in an isothermal SCF layer. In both cases, the use of asymptotic techniques and of stability analysis has shown that the role of the initial stratification was dominant. At the same time, the fluid flow has been shown to be very similar to that of weakly compressible fluids, the peculiar phenomena specific to SCFs being in this case of second order.

KEY WORDS: adiabatic temperature gradient; critical point; internal gravity waves; linear stability; Rayleigh criterion; supercritical fluids.

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1. INTRODUCTION

A supercritical fluid (SCF) is a fluid in conditions such that the values of the state variables are greater than their critical values. The critical values are those of the coordinates of the top of the liquid-vapor coexistence curve, in a phase diagram. Beyond that curve, the fluid can pass continously from its liquid state to its gaseous state: the fluid is somewhat between a gas and a liquid, which gives it properties that seem paradoxical at first sight. When getting close to the liquid-vapor critical point (CP), the isothermal compressibility diverges (gaseous behavior), the heat capacities at constant pressure or constant volume and the thermal conductivity also diverge, while the density is very large (liquid behavior). A SCF can thus be described as a dense highly compressible fluid in which heat diffuses slower and slower when getting closer to the CP.

By going around the CP, the properties of a SCF can be modified in an easy and continous way by slightly raising or diminishing the temperature or pressure. This property has made SCFs very convenient to a lot of industrial processes such as extraction, food processing, space technology, pharmaceuticals, etc., although their hydrodynamics are still not understood properly. Indeed, it is only in the 1990s that SCF hydrodynamics have known a rebirth of interest with the discovery of a fourth mode of heat transfer, the piston effect (PE) [1–3]. This effect is responsible for the very fast temperature equilibration close to T_c, contradicting the expected critical slowing down of diffusive processes. The unexpectedly rapid heat transfer is due to the high compressibility of a SCF. Indeed, boundary layers form near the heated boundaries which expand or contract depending on whether the wall is hotter or cooler than the fluid. This induces successive adiabatic compressions and expansions of the bulk fluid and, hence, its adiabatic heating or cooling. Moreover, under gravity, a SCF, which is highly compressible and dense, collapses under its own weight to form a large density gradient. For example, density inhomogeneities as large as 10% can easily be observed in centimeter-length cells filled with such a fluid [4, 5]. This stratification gives SCF characteristics that are usually met only in large-scale geophysical flows. For example, it is now well known that convection in an SCF cell subjected to an adverse temperature gradient is dominated by the adiabatic temperature gradient (ATG) [6, 7], a property that is encountered in the atmosphere for air layers of a few tens of meters high or more [8, 9]. In the same way, internal gravity waves (IGW) have been observed in supercritical xenon [5], even in centimeter-length cells.

These observations have suggested that SCFs could be used as experimental models for geophysical flows where stratification effects are dominant [5, 10]. Indeed, in a 1-cm high fluid cell filled with helium 3 mK above its critical point, the relative stratification is equivalent to the one observed in 180 m of air or 7 km of pure water. Meteorologists have shown that the stratification of density within parts of the atmosphere is such that IGW appear, and significally affect certain observed processes, while oceanographers have shown the importance of IGW within regions of the ocean with substantial density stratification [11]. So, experiments conducted in a few cm high cell filled with a stably stratified supercritical fluid (that has the same properties as a large-scale fluid system) could be a better choice than the more common use of stratified salt-water tanks, whose stratification is meant to vanish within a few hours. Up to now, this suggestion has mainly been applied to the study of turbulent convection at large Rayleigh numbers [12, 13]. We wanted to show the relevance of the use of these fluids as experimental models through two examples, the onset of convection and the dynamics of internal gravity waves. To that objective, we used a matched asymptotic analysis to derive linearized perturbation equations from the governing equations of SCF hydrodynamics. A modified Rayleigh criterion was established for the onset of convection [7]. We also checked that the peculiar hydrodynamics of SCFs (PE) did not interefere with the wave generation, and confirmed analytically that a simple system of equations describing incompressible fluids can be used to model the problem [10]. Both these results give credibility to the analogy between SCF hydrodynamics and geophysical fluid flows.

2. ONSET OF CONVECTION IN A RAYLEIGH-BÉNARD CONFIGURATION

2.1. Adiabatic Temperature Gradient

A first condition for convection to be possible is the existence of a negative temperature gradient. A small element of fluid that is displaced upwards will always be at a higher temperature than its neighbors in the upper layers and therefore lighter. Thus, it will tend to move upwards and the motion will be amplified. This simple argument is valid provided two conditions are fulfilled: the dissipative effects must be negligible and the fluid element must remain at a constant density along its movement in the hydrostatic pressure gradient. But in large-scale atmospheres, the latter hypothesis is not true anymore. When a compressible fluid rises, it expands and consequently cools down. So there exists a negative temperature gradient for which an element that rises remains always at the same temperature as the nearby elements. It is called the adiabatic temperature gradient (ATG), or in geophysical usage, the adiabatic lapse rate [9]. Therefore, in order for the instability to take place, the adverse temperature gradient must be greater than the ATG [6].

Consideration of the ATG is usually relevant only in large geophysical flows but not at the laboratory scale. For example, let us consider the adiabatic gradient for air, which at $T \approx 300$ K is approximately 10^{-2} $\mathrm{K \cdot m^{-1}}$. And, in a typical laboratory layer of 3×10^{-2} m, a Rayleigh number of 10^4 (in its classical definition) corresponds to a temperature gradient of around 10^2 $\mathrm{K \cdot m^{-1}}$ which is four orders of magnitude greater than the ATG. Whereas, over a depth of 10 m, (which is the small end of atmospheric scales), such a Rayleigh number is reached for a temperature gradient of about 10^{-8} $\mathrm{K \cdot m^{-1}}$. Hence, the ATG which was completely negligible in air at the centimeter level, becomes overwhelming dominant for layers thicker than 10 m. The classical Rayleigh criterion becomes invalid. Owing to this ATG, it is difficult to model atmospheric flows at laboratory scales.

The more commonly used means to do so is the use of stratified salt-water tanks, enabling large stratifications in reasonnably small containers (a few meters). But, this technique encounters some difficulties, among others, the non-accurate repetitivity of the experiment and the relatively short lapse of time before the salt gets completely mixed. This is the reason why SCFs, which are stably stratified and in which ATG has been observed and measured in small cells [14], are good candidates for laboratory-scaled experiments for geophysical flows. To confirm this suggestion, we had to check that their peculiar hydrodynamics when confined in a cell did not induce notable differences with the usual cases.

2.2. Description of Model

The fluid is confined initially motionless in a thin horizontal cell (see Fig. 1). The density is the critical density ρ_c, and the average temperature T_i is slightly above the critical temperature T_c. An adverse temperature gradient is imposed in the cell by setting the upper thermostated plate at a lower temperature than the lower one. The stratification is assumed to be small enough to insure constant properties of the fluid throughout the cell. The fluid motion is modelled by the Navier–Stokes equations, the fluid is thus treated as a continuous medium. Close to the critical point, the validity of this last assumption is to be verified because of the diverging correlation length. According to Stanley [15], the so-called hydrodynamic limit is located around $(T - T_c)/T_c \approx 10^{-5}$, which means for He^3, $(T - T_c) = 30\ \mu\mathrm{K}$.

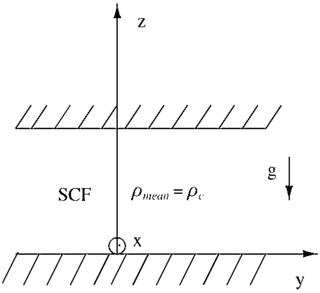

Fig. 1. SCF cell.

The system of equations is formed by the equations of Navier–Stokes, the equation of energy, and an equation of state written in a general form. The system is written in a nondimensional form using the following variables or unknowns (with (x, y, z) the space variables, t, the time variable, and (u, v, w) the components of the velocity) [7]:

$$\begin{gathered} T^* = T/T_c \qquad P^* = P/P_c \qquad \rho^* = \rho/\rho_c \\ (u^*, v^*, w^*) = (u, v, w)/V_{\text{ref}} \qquad t^* = tV_{\text{ref}}/L \\ (x^*, y^*, z^*) = (x, y, z)/L \end{gathered} \tag{1}$$

with the subscript c referring to the critical coordinates of the variable and $V_{\text{ref}} = \eta/(\rho_c L)$, the speed of the viscous diffusion (η is the shear viscousity). The time scale of viscous diffusion was chosen instead of the time scale of temperature diffusion more commonly used. Indeed, at the critical point the heat capacities and the thermal conductivity diverge, making the typical time of heat diffusion longer as the critical point is neared while the shear viscosity is almost constant with respect to the proximity to the critical point. V_{ref} is thus almost independent of T_i, which makes it a good reference velocity.

After having set the system of equations corresponding to the case of a SCF in the initial state described above, a small perturbation is added to the system. Then, an asymptotic expansion is considered where the peculiarities of the SCFs, through the nondimensional coefficients, are taken into account [7].

It is shown that the most general system of perturbation equations compatible with the asymptotic behavior of the fluid properties is (at first order, and where stars have been omitted):

$$\begin{aligned}
\nabla \cdot \mathbf{u}_1 &= 0 \\
\frac{\partial \mathbf{u}_1}{\partial t} &= -\nabla P_1 - \nabla \cdot \tau_1 - \rho_1 \\
\frac{\partial T_1}{\partial t} + \frac{1}{\mathrm{Fr}^2}\left(\frac{\partial T_0}{\partial z} + \mathrm{atg}\right) w_1 &= \frac{1}{\mathrm{Pr}} \triangle T_1 \\
\rho_1 &= -\beta_{\mathrm{p}} \chi_T T_1
\end{aligned} \tag{2}$$

The subscript 0 refers to the base flow, and the subscript 1 is used to label the first order perturbations, τ_1 (nondimensional perturbed fluid stress tensor), $\beta_{\mathrm{p}} = -(T_{\mathrm{c}}/\rho_{\mathrm{c}})\,(\partial \rho/\partial T)_P$ (nondimensional isobaric expansion coefficient), $\chi_T = (P_{\mathrm{c}}/\rho_{\mathrm{c}})\,(\partial \rho/\partial P)_T$ (nondimensional isothermal expansion coefficient), and Pr and Fr are the usual Prandtl and Froude numbers ($\mathrm{Pr} = \eta Cp/\lambda$, $\mathrm{Fr} = V_{\mathrm{ref}}/\sqrt{gL}$), while atg is the nondimensional adiabatic temperature gradient $(L/T_{\mathrm{c}})\,\rho g(\partial T/\partial P)_S$.

2.3. Interpretation

The system in Eq. (2) is equivalent to a linearized Boussinesq system of equations, provided the initial temperature gradient is replaced by $\frac{\partial T_0}{\partial z} + \mathrm{atg}$. Hence, the "corrected" Rayleigh number is written as follows:

$$\frac{\rho g C p L^4}{\lambda \mu}\left(\frac{\partial \rho}{\partial T}\right)_P \left[\frac{\partial T_0}{\partial z} + \rho g\left(\frac{\partial T}{\partial P}\right)_S\right] = \mathrm{Ra}_{\mathrm{corr}}. \tag{3}$$

Thus, convection threshold near the critial point can be approached by the criterion of the "corrected" Rayleigh number: the initial diffusive heat transfer is stable provided that $\mathrm{Ra}_{\mathrm{corr}} < \mathrm{Ra}_{\mathrm{c}}$. Convective instability arises when $\mathrm{Ra}_{\mathrm{corr}} > \mathrm{Ra}_{\mathrm{c}}$. The critical Rayleigh number has the same value as the one obtained with Boussinesq equations. It depends on the boundary conditions which are imposed to the system [16]. The crossover, in the convection onset, from the Rayleigh to the adiabatic temperature gradient regime has been observed by Kogan and Meyer [17], verifying the abovementionned stability criterion.

Because of the corrected Rayleigh number, the criterion for the onset of convection is intermediate between the Rayleigh criterion which is based on the comparison of Ra_{c} to the Rayleigh number and the Schwarzchild criterion which is based on the comparison of the $\frac{\partial T_0}{\partial z}$ with the ATG. Indeed, let us isolate the critical temperature gradient:

$$-\left(\frac{\partial T_0}{\partial z}\right)_c = -\mathrm{Ra}_{\mathrm{c}} \frac{\lambda \mu}{\rho g C p L^4}\left(\frac{\partial T}{\partial \rho}\right)_P + \rho g\left(\frac{\partial T}{\partial P}\right)_S. \tag{4}$$

The second term on the right-hand side of the equation is the ATG, it exhibits little variation with respect to the proximity to the CP. On the other hand, the first term is highly dependent on the proximity to the CP: it is asymptotically small close to T_c and becomes much larger than the ATG far from T_c. Hence, for a SCF confined in a cell, the convective stability will be characterized by the classical Rayleigh criterion far from the CP, and by the Schwarzchild criterion close to the CP. The corrected Rayleigh criterion, as described above, dominates the onset of convection for any initial conditions [7].

3. GENERATION OF INTERNAL GRAVITY WAVES IN AN SCF CELL

As we have already noted, a SCF at rest in a gravity field is a stably stratified fluid, its density decreasing with height. When the fluid is at constant temperature, vertical motions tend to carry a heavier fluid upward and a lighter fluid downward which is a stable situation. A fluid particle which gets displaced vertically is subjected to a buoyancy force tending to pull it back to its initial position. This restoring force is thus responsible for the driving of oscillating motions of the fluid particle. The internal motions are named IGW. An important parameter to take into consideration is the Brunt–Vaïsälä frequency. It can be considered as the superior limitation to the frequency of the IGW. This frequency is obtained as the sum of two terms, one of which is a function of the initial stratification of the fluid and the other a function of its sound velocity. The square of the Brunt–Vaïsälä frequency is classically written as

$$N^2 = -\left(\frac{g}{\rho}\frac{d\rho}{dz} + \frac{g^2}{c^2}\right). \tag{5}$$

3.1. Problem Under Study

We used the same hypothesis and the same nondimensionalised equations as described in Section 2.2 [10]. But this time the fluid is confined at a mean critical density between two thermostated walls separated by a distance L (see Fig. 1). It is subjected to vertical gravity and is initially at thermal and mechanical equilibrium (i.e., motionless and at the same temperature as the walls). The initial configuration is one of hydrostatic density and pressure stratification. Then, small perturbations are added to that fluid configuration and give birth to self-oscillations of the fluid under the form of IGW. The perturbations are functions of the space variables

(x, y, z) and of the typical time scale of IGW, τ, which is still left undetermined but is assumed to be much shorter than the typical time scale of viscous diffusion (for which is defined the variable t).

It is shown that the most general system of equations (where stars have been omitted) compatible with the asymptotic behavior of the fluid properties is then [10]

$$\begin{aligned}\nabla \cdot \mathbf{u}_1 &= 0 + O\left(\frac{1}{\chi_T}\right)\\ \rho_0 \mathbf{u}_{1_\tau} &= -\nabla P_1 - \rho_1 \cdot \mathbf{e}_z + O(\mathrm{Fr})\\ \rho_{1_\tau} + \rho_{0_z} w_1 &= 0 + O\left(\frac{1}{\chi_T}\right)\\ \alpha_\mathrm{p} T_1 + \rho_1 &= \frac{\rho_\mathrm{c}\, \chi_T\, V_\mathrm{ref}^2}{\mathrm{Fr}^2 P_\mathrm{c}} P_1\end{aligned} \tag{6}$$

where the notations used are the same as those in Section 2.2. The typical time scale of the IGW is defined as

$$\tau = \frac{t}{\mathrm{Fr}} \tag{7}$$

$(\rho_\mathrm{c}\, \chi_T V_\mathrm{ref}^2)/(\mathrm{Fr}^2 Pc) = \rho_{0z}/\rho_0$ and can be identified with the square of the Brunt–Väisälä frequency in Eq. (5), in which the acoustic component is negligible (see Ref. 10 for further details).

The system of Eqs. (6) is the classical system governing internal gravity waves in an incompressible, nonviscous, nonconducting fluid. Asymptotic analysis thus shows that SCFs, as far as IGW are concerned, behave at small length scales like weakly compressible fluids (air or water, for example) do at large scales.

3.2. Possible Coupling with the PE

We now must check whether the peculiar hydrodynamics of SCFs interfere with IGW. Indeed, the perturbations inside the SCF cell generate density, pressure, and temperature variations. The difference of temperature induced near the thermostated walls leads to the formation of conductive boundary layers near these walls, in which the fluid temperature adapts to the thermostated walls. Due to the high compressibility of the SCF, these boundary layers expand or contract, which in turn results in a compression or expansion of the bulk fluid (PE mechanism). As a consequence of this dynamic effect, the boundary layers act like a piston moving back and forth from the wall. In other words, the bulk fluid does not bump on a solid boundary but on a moving layer of fluid which oscillates on the time scale of the PE. It must be checked whether this oscillating motion of the boundary layers interferes with the dynamics of the IGW (such a coupling has indeed already been predicted in the case of forced oscillations [18]).

In order to predict whether such a coupling is possible in the case of IGW, it is necessary to calculate the order of magnitude of the velocity in the boundary layers. If it is of the same order as the bulk velocity, then a coupling can appear which will reshape the flow. To check the occurrence of such a coupling, it is necessary to linearize the system describing IGW in a SCF with the time scale of the PE, τ_{PE}, being of the same order of magnitude as the time scale of the IGW. This condition mathematically translates to: $\tau_{\text{PE}} \cong \tau \Leftrightarrow \chi_T \cong 1/\text{Fr}$, with χ_T the timescale of the PE [19]. An order one function, Γ, is thus defined as: $\Gamma = \text{Fr}\,\chi_T = O(1)$. The unknowns $\bar{X}$ are sought as wavelike solutions, periodic in both space and time.

$$\bar{X} = X^{\circ}(z)\, e^{ik_x x}\, e^{ik_y y}\, e^{iw\tau_{PE}}. \tag{8}$$

The following dispersion equation is found:

$$w^{\circ}_{zz} - N^2 w^{\circ}_{z} - k^2\left(1 - \frac{N^2}{\Gamma w^2}\right) w^{\circ} = 0, \tag{9}$$

where $k = \sqrt{k_x^2 + k_y^2}$. When applying a solid-wall condition to the velocity solution, an incompatibility appears: the thermal boundary conditions are not verified anymore. The temperature oscillates close to the walls although the walls should remain at constant temperature. Thermal boundary layers are thus introduced [10], in which heat diffusion is no longer neglected. Different spatial domains are considered: the lower boundary layer (with its own vertical space variable, $\tilde{z} = z/\delta$ with δ the boundary layer thickness), the bulk (where the same space variables (x, y, z) are used), and the upper boundary layer (where a third vertical space variable is defined, $\hat{z} = (z-1)/\delta$). In each domain, the properties of the fluid are decomposed again into the initial hydrostatic profile to which is added a small perturbation. These perturbations vary on the space scale of the corresponding domain. The asymptotic calculations are performed in the lower boundary layer, the bulk, and in the upper boundary layer. The bond between the three regions is ensured by matching conditions:

$$\lim_{\tilde{z}\to\infty} T_{\text{boundary layer}} = \lim_{z\to 0} T_{\text{Bulk}} \qquad \lim_{\hat{z}\to -\infty} T_{\text{boundary layer}} = \lim_{z\to 1} T_{\text{Bulk}}.$$

This leads to the order of magnitude of the velocity in the boundary layers and in the bulk being

$$[u, v, w]_{\text{boundary layer}} = O(\alpha\,\chi_T) \qquad [u, v, w]_{\text{bulk}} = O\left(\frac{\alpha\,\chi_T}{\text{Fr}}\right), \tag{10}$$

where α is the amplitude of the perturbation of the temperature in the bulk and in the boundary layer. With 1/Fr being much larger than one (typically 80 000 for He^3 and 40 000 for CO_2 in centimeter-length cells), the velocity in the boundary layers is always much smaller than the bulk velocity, whatever the proximity to the critical point. Thus, the dynamical response of the boundary layers never interferes with the behavior of the IGW in the bulk fluid. There can never be a coupling between the PE and the IGW, which confirms the analogy between the SCF and geophysical IGW.

4. CONCLUSION

It has been shown in Section 2, that in the case of an initial state of pure conduction the PE plays no role in the onset of convection. The transition between the conductive and convective regimes is simply governed by a corrected Rayleigh criterion, which is equivalent to the classical Rayleigh criterion in which the temperature gradient is corrected by the adiabatic gradient to account for the effect of stratification. It has then been shown in Section 3, that incompressible systems of equations were relevant to describe internal gravity waves in SCF although their compressibility is asymptotically divergent. As in the case of convective stability, PE does not influence the dynamics of the IGW.

SCFs confined in a small cell have hydrodynamical properties which they share with large geophysical flows. It thus seemed very interesting to use them as scaled down experimental models for such flows. But the peculiarity of their properties and hydrodynamics was an issue. In the study presented in this article, we have shown that this peculiar behavior of an SCF does not interfere with IGW or the onset of natural convection. It is perfectly relevant to use SCFs at the laboratory scale to study geophysical IGW and natural convection.

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