A Lagrangian–Eulerian compressible model for the trans-critical path of near-critical fluids

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ABSTRACT

The main objective of the present work is to model the trans-critical path from supercritical to subcritical states near the critical point. The model is based on full compressible sets of equations. The pressure, temperature and density fields are determined in a Lagrangian form through the divergences of velocity and heat flux and advected afterwards in the Eulerian step. Three cases have been considered and are discussed: (i) an isothermal atmosphere in order to validate the model for a perfect gas, (ii) the propagation of sound waves under piston effect timescales for supercritical fluids and the comparison with experimental data from literature and (iii) the third case which constitutes the basis of the present work corresponds to a numerical simulation of the separation of phases from supercritical to subcritical states near the critical point.

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1. Introduction

Near-critical fluids have been extensively used in industrial applications for the past 60 years (Stanley, 1954; Carles, 2010). In recent years, there has been an increased and dedicated research in this area. Near-critical fluids host innumerable possibilities and immense potential for newer and 'cutting-edge' research. The high density of supercritical fluids (SCFs) implies a high dielectric constant which contributes, for example, to a strong dissolution of organic molecules in supercritical CO_2 with high efficiencies. The low viscosity of these fluids allows fast mass transfer and very short analysis times. These singular properties lead to many applications (Williams and Clifford, 2000) such as supercritical chromatography, drying and catalysis, particle formation ranging from nano to macrodimensions, cleaning (purification of water), electronic chip manufacturing or waste and soil decontamination. In space applications, the storage of cryogenic fluids (Oxygen, Hydrogen) is done under supercritical conditions as the management of these fluids is a real problem due to the uncertain localization of gas and liquid phases.

Hydrodynamics of near-critical fluids has gained considerable interest since transport coefficients exhibit singularities which lead to new physical phenomena. Supercritical fluids are as dense as liquids and as compressible and less viscous as gases. The compressibility, heat capacity at constant pressure and thermal expansion coefficient diverge at the critical point as $\sim (\varepsilon)^{-\gamma}$ where $\varepsilon = \frac{T-T_C}{T_C}, T_C$ is the critical temperature and $\gamma \sim 1.24$ is the Ising

critical exponent (Justin, 2002). Some other properties like the thermal conductivity and the heat capacity at constant volume diverge also with lower critical values of the exponents whereas surface tension and thermal diffusivity vanish at the critical point. The vanishing thermal diffusivity slows down the heat transfer processes (termed as "critical slowing down") thus giving a better opportunity to study fluid physics experimentally. The high compressibility implies thermoacoustic or Piston Effect heat transfer (Onuki et al., 1990; Boukari et al., 1990; Zappoli et al., 1990) which is extremely fast near the critical point as opposed to the "critical slowing down".

These singular properties of near-critical fluids have motivated numerous developments on coupled heat and mass transfer like convection in closed cavities (Zappoli et al., 1999), thermal instabilities (Meyer and Kogan, 2002; Chiwata and Onuki, 2001; Amiroudine et al., 2001; Accary et al., 2009) or thermo-vibrational instabilities (Beysens et al., 2005, 2009; Garrabos et al., 2007; Amiroudine and Beysens, 2008).

On the other hand, there has been very little interest on a direct model of the trans-critical path which consists of crossing the critical point from supercritical (subcritical) to subcritical (supercritical) states. The interest of such a modeling is very important in many applications such as the study of the behavior of a CO_2 air-to-water heat pump (Haberschill et al., 2007). In this heat pump system, the evaporation is performed at high temperatures (in the supercritical regime) whereas the condensation is left at the subcritical state. The overall efficiency is increased which is beneficiary in a certain number of applications such as the production of domestic hot water or industrial drying processes. In a more fundamental point of view, some authors (Gopal, 2000; Oaga et al.,

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2004) have also studied the critical opalescence. This phenomenon is a striking light scattering phenomenon, which was elegantly explained by Einstein. In the critical region the light scattering is so large that the substance appears milky white in reflected light and brownish dark in transmitted light. The phenomenon arises from the large fluctuations of the density in the critical region of the substance. On the other hand, there are striking instability phenomena (Wunenburger et al., 1999) which occur when a fluid, below its critical point and under earth's gravity, is heated and subjected to vibrations. This two phase fluid can display stationary or propagating waves on the interface or, in special cases, a stationary relief phenomenon called "frozen waves" for horizontal vibration tangential to the interface (Beysens et al., 2005).

The main objective of the present study is to propose a model that will continuously go from supercritical to subcritical states (and vice versa). The values of thermophysical properties are taken from NIST database (NIST, 2000) and a Lagrange–Euler formulation is used. The major contribution of the present model relies on the fact that it calculates the density from the mass conservation equation itself without having an explicit equation of state whereas in the usual case, the determination of the vapor and liquid densities are deduced from the cubic equation of state (for example van der Waals or Peng-Robinson). It is then numerically impossible to set the right value of the density (vapor or liquid) at each node.

The content of the present paper is organized as follows. Section 2 describes in details the mathematical model of the governing equations together with the initial and boundary conditions. The numerical method is then briefly outlined in Section 3. The results are presented in Section 4 for (i) a first test case of an isothermal atmosphere in order to validate the approach of the mathematical model, (ii) a second test case which compares, with the literature, the piston effect process in supercritical fluids and finally (iii) a third case which constitutes the basis of the present work corresponds to a numerical simulation of the separation of phases from supercritical to subcritical states near the critical point.

2. The mathematical model of the complete set of the compressible governing equations

The following model solves the full set of governing equations in a Lagrangian–Eulerian formulation and is presented hereafter.

Let us consider a Newtonian fluid contained in a domain Ω limited by a surface Γ. This fluid is characterized by its main thermo-physical properties which are the density ρ, the heat capacity at constant volume C_v, the isothermal compressibility $\chi_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T$, the thermal expansion coefficient at constant pressure, $\beta_P = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P$ and the coefficient of the increase of pressure at constant volume, $\alpha_\rho = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_\rho$. The state of a system varies as a function of the velocity (V) and heat flux (ϕ) which can be written in a case of Fourier law assumption, as: $\phi = -k\nabla T$. The thermodynamic state quantities of the system, i.e. the pressure, the temperature and the density will evolve as a function of these two vectors. For example, an applied heat flux to a given system will increase the pressure inside this system or a mechanical compression to the system will lead to an increase of the temperature in it. The infinitesimal variations of the temperature, pressure and the density can be written as follows:

$$\begin{cases} dT = \left(\frac{\partial T}{\partial \rho}\right)_P d\rho + \left(\frac{\partial T}{\partial P}\right)_\rho dP \\ dP = \left(\frac{\partial P}{\partial \rho}\right)_T d\rho + \left(\frac{\partial P}{\partial T}\right)_\rho dT \\ \quad d\rho = -\delta t \rho \nabla \cdot V \end{cases} \quad (1)$$

Here the time constant δt is a characteristic time and corresponds to a very important physical parameter which will be further detailed below. The last equation of the system (1) corresponds to the mass conservation. The state variables (ρ, P and T) are explicitly and respectively calculated from the mass conservation (Eq. (1)), momentum and energy equations (given below). The thermodynamic coefficients (χ_T, β_P, α_ρ) are evaluated from the NIST database (NIST, 2000). There is no need to use an equation of state for the evaluation of these properties as they can simply be obtained by experimental measurements. Thus, the model can be described without any state equation.

2.1. Lagrangian form of the pressure, density and temperature fields

The momentum conservation equation in a non-conservative form and for a Newtonian fluid can be written as follows:

$$\rho \frac{DV}{Dt} = \nabla P + F + \nabla \cdot [\mu(\nabla V + \nabla^t V)] + \nabla(\lambda \nabla \cdot V) \quad (2)$$

where $\frac{D}{Dt}$ is the material derivative, μ and λ correspond to the classical shear viscosity and compression viscosity (or second coefficient of viscosity), F is the volumetric force and P is the equilibrium thermodynamic pressure corresponding to the mechanical equilibrium. The shear viscosity μ is usually and classically given by measurements whereas the second coefficient of viscosity λ verifies the Stoke's law ($\lambda + \frac{2}{3}\mu = 0$).

Considering the stress tensor for a Newtonian fluid, the conservation of the internal energy (e) can be written as:

$$\rho \frac{De}{Dt} = -\nabla \cdot \phi - P\nabla \cdot V + \varphi + q \quad (3)$$

where $\varphi = \lambda(\nabla \cdot V)^2 + 2\mu D_{ij}\frac{\partial V_i}{\partial x_j}$ is the dissipation function with $D_{ij} = \frac{1}{2}\left(\frac{\partial V_i}{\partial x_j} + \frac{\partial V_j}{\partial x_i}\right)$ being the tensor of deformation rate (The Einstein summation convention on repeated indices is applied) and q is the heat source (heat production, radiation...). Considering that $de = C_v dT + [T\left(\frac{\partial P}{\partial T}\right)_v - P]dv$ where v is the specific volume, Eq. (3) can be reformulated as:

$$\rho C_v \frac{DT}{Dt} = -\nabla \cdot \phi - \frac{\beta_P T}{\chi_T}\nabla \cdot V + \varphi + q \quad (4)$$

Eq. (4) can be rewritten as follows, where the temperature is first calculated in a Lagrangian form:

$$T = T^0 - \delta t \left(\frac{\beta_P T}{\rho C_v \chi_T}\right)\nabla \cdot V - \frac{\delta t}{\rho C_v}\nabla \cdot \phi + \frac{\delta t}{\rho C_v}(\varphi + q) \quad (5)$$

where T^0 is the equilibrium temperature at each timestep δt and all the successive terms correspond to the non-equilibrium variations due to the divergence of velocity and heat flux, heat dissipation and any additional heat source.

The momentum Eq. (2) can be re-written as:

$$\rho \frac{DV}{Dt} = -\nabla[P - \left(\lambda + \frac{2}{3}\mu\right)\nabla \cdot V] + F$$
$$+ \nabla \cdot \left[\mu(\nabla V + \nabla^t V - \frac{2}{3}\nabla \cdot V \underline{I})\right] \quad (6)$$

From Eq. (1), the temporal variations of the pressure and density can be derived as:

$$\begin{cases} \frac{DP}{Dt} = -\left(\frac{1}{\chi_T} + \frac{\beta_P^2 T}{\rho C_v \chi_T^2}\right)\nabla \cdot V - \frac{\beta_P}{\rho C_v \chi_T}\nabla \cdot \phi + \frac{\beta_P}{\rho C_v \chi_T}(\varphi + q) \\ \qquad\qquad \frac{D\rho}{Dt} = -\rho\nabla \cdot V \end{cases} \quad (7)$$

The scalar quantities (P and ρ) can be finally written, in a Lagrangian form, as: