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Non-equilibrium phenomena in carbon dioxide expansion

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ABSTRACT

Release of liquid and supercritical carbon dioxide is a fundamental research topic in CCS. Traditional approach is largely based on HEM and, in general, assumes equilibrium from the outlet to the Mach disc. Experimental results have shown that this approach is not always effective in describing the expansion phenomenon; therefore a significant lack of knowledge exists about CO_2 properties at the under-expanded jet zone boundary, which is a main focus in process safety. Here, solid formation, vapour quality, sonic velocity and final temperature are generally calculated according to equilibrium saturation condition, and this is generally incorrect. This article deals with non-equilibrium thermodynamics of liquid and supercritical CO_2 expansion, illustrating relaxation dynamics through the HRM models, and discussing the very specific singularities of CO_2 phase transitions, vapour to liquid and liquid to solid, that result away from the equilibrium condition, due to the rapid phase changes and to the specific properties of CO_2 multi phase thermodynamics, including nucleation and particle growth. Statistical rate theory has been applied with the aim at identifying the phase transition energy barrier, resulting in a significant entropy increase. A case study based on HEM conservation equations integrated with the statistical rate approach has been presented, which covers the gap of the equilibrium hypothesis. The objective of the article is to provide a more accurate method to predict the properties of carbon dioxide following an expansion.

Keywords: CCS; Carbon dioxide; Non-equilibrium thermodynamics; HRM; Metastability; Statistic rate theory; Adiabatic expansion; QRA

1. Introduction

Carbon dioxide uncontrolled depressurisation is the most important incidental scenario potentially resulting in harmful effects. Carbon capture and storage (CCS) has changed traditional carbon dioxide processing and has introduced a significant margin of uncertainty in QRA studies, due to a lack of knowledge concerning both the potential toxicity and the physical chemical behaviour of expanding carbon dioxide from vessels and piping (Parfomak and Folger, 2008; Koornneef et al., 2009, 2010). Thermodynamic trajectories, depressurisation temperatures, dry ice formation, particle nucleation and size, snow-out and sublimation are relatively new aspects related to the CCS process and plant configurations, which significantly affect the operational and emergency scenarios. The relation of the predictable releases from liquid and supercritical states and the very specific physical chemical and thermodynamic properties of carbon dioxide require a complete review of the traditional approach, consisting essentially of the two phase modelling of flashing liquid and dense phase. The present paper analyses the limits of the equilibrium model in describing the multi-phase carbon dioxide expansion from stagnation conditions to atmosphere and proposes a rigorous model to identify carbon dioxide vapour and solid mass fractions, final temperature pressure, enthalpy thermodynamic downstream of the Mach disc, in terms of and entropy, with the aim at carrying out with sufficient accuracy consequence and quantitative risk analysis (QRA) studies. It has to be considered that the approach is based on pure CO_2, whereas impurities such as sulphides, hydrocarbons, hydrogen, hydrates can be contained in carbon dioxide streams. The presence of impurities is known to modify the phase

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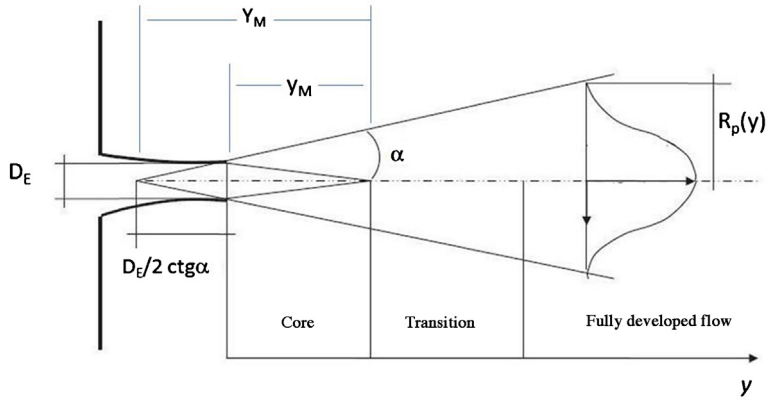

Fig. 1 – Jet flow.

diagram of pure CO_2, as discussed by Seevam et al. (2007) and Demetriades et al. (2012). Methods which are suitable and fast enough for QRA are nevertheless needed and at present software such as DNV PHAST is used for this and is modelled using pure CO_2. Alternative methods which account for impurities are not currently available for such safety studies. Harper et al. (HSE, 2011) consider the use of pure CO_2 a reasonable approximation.

1.1. *Objective and methodology*

The objective of this article is to provide guidance on the prediction of carbon dioxide jet flow characteristics from stagnation conditions to the Mach disc, with specific reference to the effects of non-equilibrium carbon dioxide behaviour around and downstream of the triple point. A general background is presented, dealing with the relaxation properties of the molecular structure and with the inertial behaviour of carbon dioxide. Particular emphasis has been placed to the metastability of the liquid phase and to its effects relative both to the liquid–vapour zone and the solid–vapour zone. The homogeneous relaxation model (HRM) has been illustrated and the statistic rate theory has been applied, justifying and quantifying the energy barriers of the phase transitions. Expansion thermodynamics has been analysed by means of the conservation equations and a triple point non-equilibrium zone has been recognised and described in terms of a structural entropy change along the singularities of multiphase behaviour. Finally, an expansion case study has been presented, with the aim at identifying and applying the findings of this approach.

2. Background of carbon dioxide expansion

2.1. *Equations of conservation*

Carbon dioxide expanding from a liquid or supercritical state is assumed to enter the vapour–liquid zone through the liquid limit or vapour limit curve. After crossing the triple point and the solid–vapour zone, the jet flow will be released to atmosphere. This scenario is not always operationally true, since supercritical carbon dioxide, depending on stagnation pressure and temperature, could depressurise without entering the two phase zone. An under-expanded jet is assumed to flow from a containment outlet through the barrel shaped zone, (Figs. 1 and 2, Benintendi, 2010), which terminates at the Mach disc, at a distance from the outlet generally given by the empirical formula of Ashkenas and Sherman (1966):

$$y_M = 0.67 \times \left(\frac{P_o}{P_a}\right)^{0.67} \quad (1)$$

where P_a is the atmospheric pressure and y is the distance along the jet axis. With reference to the notation included in Fig. 2, the mass, energy and momentum (TNO, 2005) conservation equations are assumed to be valid between the stagnation and the outlet section, and between the stagnation and the Mach disc section:

$$\rho_{l1} \times u_1 \times A_1 = \rho_M \times u_M \times A_M \quad (2)$$

$$\left(H_M + \frac{u_M^2}{2} + z_M \cdot g\right) = \left(H_1 + \frac{u_1^2}{2} + z_1 \cdot g\right) \quad (3)$$

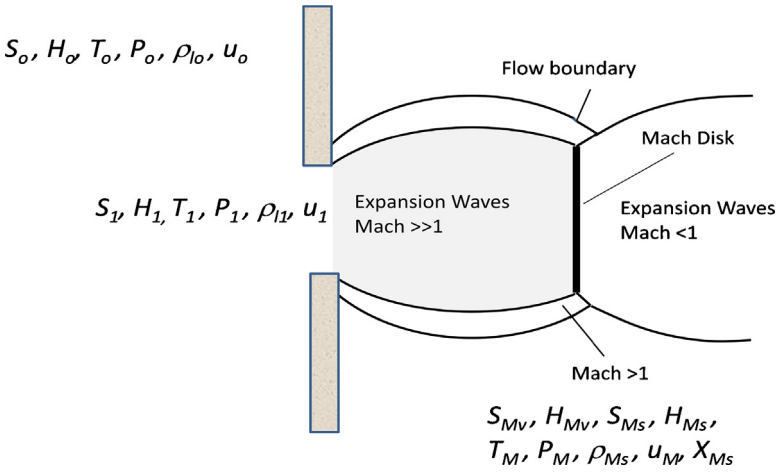

Fig. 2 – Carbon dioxide expansion.