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# Investigating the Validity of the Fundamental Derivative in the Equilibrium and Non-equilibrium Two-Phase Expansion of MM

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**Abstract.** The aim of the work presented in this paper is to explore the validity and possible extent to which non-ideal compressible-fluid dynamic (NICFD) effects may have a role in the expansion of a two-phase mixture of the siloxane MM by expanding the concept of the fundamental derivative to two-phase flows. For the assumption of a homogeneous two-phase mixture under the two limiting cases of thermal equilibrium and frozen thermal states, expressions for the speed of sound are defined. Using these definitions, the fundamental derivative is evaluated within the saturation dome of MM under the assumption of thermal equilibrium. Following this, the variation in the fundamental derivative under thermal equilibrium and frozen thermal states are compared for expansion processes from different reservoir pressures (5, 10 and 15 bar) and vapour qualities (0.1, 0.5 and 0.9). These preliminary results suggest that the fundamental derivative remains below unity throughout the two-phase dome under both limiting cases, with the lowest values obtained in close proximity to the critical point and saturated liquid line. The results also suggest that the deviation between the equilibrium and frozen models increases as the reservoir vapour quality increases. Ultimately, this implies that NICFD effects are likely to be present during the a two-phase expansion of MM within novel turbomachinery. However, further research is necessary to investigate these effects under more realistic assumptions that are relevant to turbomachinery applications (*i.e.*, in-homogeneous and non-equilibrium flow).

**Keywords:** Fundamental derivative · Two-phase flows · Equilibrium flows · Non-equilibrium flows · Organic rankine cycles

## 1 Introduction

The potential benefit of using two-phase expansion within organic Rankine cycles (ORC) has been widely reported within the literature to enhance performance in waste-heat recovery applications [4]. However, the widespread use of two-phase

expansion has not yet been realised due to a lack of two-phase expanders. Existing research has focussed on volumetric expanders, such as twin-screw expanders [8], but these expanders are limited in their built-in volume ratio, which limits them to relatively low temperature applications (typically around 100 °C) that correspond to low expansion volume ratios. Comparatively, turbo-expanders are capable of achieving large expansion ratios over a single stage, but are not designed for two-phase expansion. However, it is postulated here that with the use of molecularly complex working fluids, whose saturated-vapour line has a positive gradient when viewed in the temperature-entropy plane, it could be possible to design a single-stage turbine and confine the two-phase expansion region to the stator vane [3]. Preliminary thermodynamic cycle investigations have identified MM as a suitable working fluid.

However, the use of such fluids introduces the possibility of non-ideal compressible-fluid dynamic (NICFD) effects, particularly around the critical point. The topic of two-phase flows of fluids that may exhibit NICFD effects has been studied previously. For example, the work of Thompson [9,10] has explored shocks in retrograde fluids in which there is a phase transition across the shock. More recently, the work Nannan et al. has evaluated the fundamental derivative  $\Gamma$  of two-phase fluids in the near-critical region [6], and attempted to establish the region in which rarefaction shock waves are admissible [7]. Within these studies the two phases are assumed to be in equilibrium, which can be rationalised in close proximity to the critical point where surface tension, and the difference in density of the phases, are reduced.

Whilst it is unlikely that within an ORC system designed for two-phase expansion the turbine inlet conditions will be sufficiently close to the critical point such that non-classical fluid dynamic behaviour, characterised by  $\Gamma < 0$ , will be present, it is likely that the behaviour of the fluid will be non-ideal, and is likely to be characterised by  $0 < \Gamma < 1$ . However, to the author's knowledge there have not to date been any significant studies that have attempted to investigate the fundamental derivative within two-phase expansion processes relevant to practical two-phase expansion systems. In such systems, the assumption of both thermodynamic and mechanical equilibrium is likely to be an oversimplification owing to the large change in vapour quality across the expansion process, but the inclusion of in-homogeneity and non-equilibrium effects significantly complicates the analysis. Thus, the aim of this paper is initiate investigations into NICFD effects within the two-phase expansion of MM. This is completed by evaluating the fundamental derivative of a homogeneous two-phase mixture of MM under the two limiting cases of thermal equilibrium and frozen thermal states by first defining expressions for the speed of sound for the two-phase mixture. The two cases of thermal equilibrium and frozen thermal states correspond to two extreme cases where heat transfer between the two phases occurs either instantaneously, or is negligible, and in a realistic application it is rationalised that the speed of sound can be approximated as some combination of the two limiting cases [1].

## 2 Modelling

For a single-phase fluid, the possibility of NICFD effects can be investigated by evaluating the fundamental derivative, which can be defined as:

$$\Gamma = 1 + \frac{\rho}{a} \left( \frac{\partial a}{\partial \rho} \right)_s, \quad (1)$$

where  $a$  is the speed of sound,  $\rho$  is the density, and  $s$  refers to an isentropic process. For a single-phase fluid,  $\Gamma$  can be computed from the equation of state. However, for a two-phase expansion, the calculation of  $\Gamma$  requires a suitable definition for the speed of sound, which in turn depends on the extent to which the vapour and liquid phases interact.

Under the assumption of a homogeneous two-phase mixture under thermal equilibrium the flow equations reduce to a single mass, energy and momentum equation for the mixture, and it is possible to derive an expression for the speed of sound and thus compute the fundamental derivative. If the analysis is extended to consider the other extreme case in which the two phases remain homogeneous but expand so rapidly that there is no time to exchange heat, and thus the two-phases can be assumed to remain perfectly insulated such that they both undergo independent isentropic expansions, it is also possible to derive an expression for the speed of sound [1]. Within a more realistic two-phase expansion of a homogeneous fluid it is rationalised that the speed of sound is some combination of the two limiting cases. Unfortunately, for the most realistic case in which the flow is neither homogeneous, or under thermal equilibrium, it becomes necessary to solve separate energy and momentum equations for each phase, and the definition for the speed of sound of the two-phase mixture becomes impossible, and the validity of the fundamental derivative questionable.

Within this work, to enable at least a preliminary quantification of the role of NICFD effects within two-phase expansion it is assumed that the two-phase mixture is in a homogeneous state, which implies that the mixture is well mixed, the size of the disperse particles is sufficiently small such that there is no relative motion between the two phases, and thus the speed of sound is not affected by topological features introduced by an in-homogeneous distribution. Under this assumption, the speed of sound can be defined, and  $\Gamma$  evaluated. Whilst the assumption of homogeneity is likely to be an over simplification for a two-phase expansion within a turbomachine where there is likely to be both a large change in pressure and vapour quality, and hence density of each phase, this assumption does permit a preliminary investigation into NICFD effects within two-phase expansions which can be followed up in later studies.

### 2.1 Homogeneous Equilibrium Modelling

Under the assumption of a homogeneous two-phase mixture, it is assumed that the fluid is well mixed and the size of the disperse particles is sufficiently small such that there is no relative motion between the liquid and vapour phases.

If this is further simplified by neglecting surface tension, then the two-phases can be assumed to be at an equal pressure and travelling at the same velocity (*i.e.*,  $p_L = p_V$ ,  $u_L = u_V$ , where  $p$  is the pressure and  $u$  is the velocity). Similarly, under the assumption of thermal equilibrium the vapour and liquid phases are assumed to transfer heat instantaneously and thus the temperature of both phases is equal to the saturation temperature (*i.e.*,  $T_L = T_V = T_{\text{sat}}$ , where  $T$  is the temperature). Thus, considering the expansion of a homogeneous flow at thermal equilibrium from a defined reservoir condition, defined by the stagnation pressure  $p_0$  and vapour quality  $X_0$ , to a specified discharge pressure  $p$ , the flow conditions can be calculated, assuming an isentropic expansion:

$$u = \sqrt{2(h_0(p_0, X_0) - h(p, s_0))}; \quad (2)$$

$$X = \frac{h(p, s_0) - h_L}{h_V - h_L}, \quad (3)$$

where  $h_0$  and  $s_0$  are the enthalpy and entropy at the reservoir conditions,  $h$  is the static enthalpy of the two-phase mixture,  $u$  is the flow velocity,  $X$  is the vapour mass fraction, and ‘V’ and ‘L’ refer to the vapour and liquid components respectively.

Under the assumption of homogeneous equilibrium flow, the definition of the fundamental derivative used to investigate the presence of non-ideal compressible-fluid dynamic effects within single-phase fluids (Eq. 1), can, in theory, be extended to two-phase fluids. Thus, the variation in  $\Gamma$  along an isentropic expansion can be determined from the variation in the density and speed of sound, which in turn can be computed based on the known pressure  $p$  and mass-fraction  $X$ .

The density of the mixture is given as a volume weighted sum of the vapour and liquid components:

$$\rho = \alpha \rho_V + (1 - \alpha) \rho_L, \quad (4)$$

where  $\alpha$  is the volume fraction of vapour and is related to the mass fraction as follows:

$$\alpha = \frac{1}{1 + \frac{\rho_V}{\rho_L} \left( \frac{1 - X}{X} \right)}. \quad (5)$$

Following the analysis described by Brennen [1], the sound of speed for a homogeneous two-phase flow under thermal equilibrium can be found from:

$$\frac{1}{a^2} = \rho [\alpha g_V + (1 - \alpha) g_L], \quad (6)$$

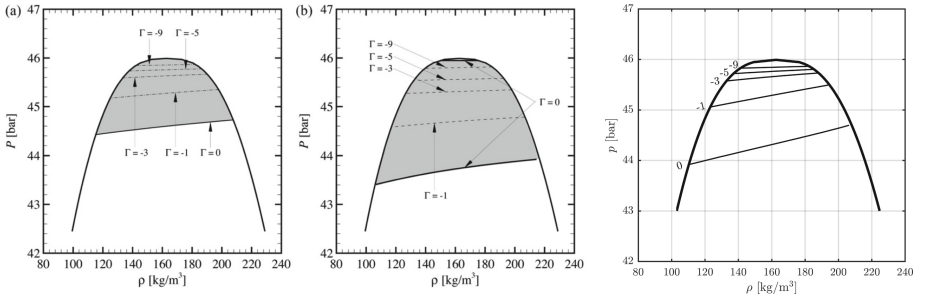
where the parameters  $g_V$  and  $g_L$  are thermodynamic parameters defined by:

$$g_i = \frac{1}{\rho_i} \left( \frac{\partial \rho_i}{\partial p} \right)_e - \frac{1}{h_{LV}} \left( \frac{1}{\rho_V} - \frac{1}{\rho_L} \right) \left( 1 - \rho_i \left( \frac{\partial h_i}{\partial p} \right)_e \right), \quad (7)$$

where the subscript  $i$  refers to the phase of interest,  $h_{LV}$  is the latent heat of vapourisation, and the subscript  $e$  indicates the phase equilibrium derivative.

Together, Eqs. 6 and 7 are equivalent to the expression reported by Nannan et al. [6], albeit expressed in terms of  $\rho$  and  $h$  rather than entropy and specific volume. Throughout this work, the multi-parameter Span-Wagner Helmholtz equation of state [2, 5] is used to determine all fluid properties. This includes the calculation of metastable properties, although the validity of this approach does require further investigation. The partial derivatives in Eq. 7 are computed using the second-order accurate central difference method with a step size of  $\Delta p = 10$  Pa.

Thus, for a given static pressure  $p$  and vapour quality  $X$ , the saturated liquid and vapour enthalpies and densities can be found, which facilitates the calculation of  $\alpha$ ,  $\rho$  and  $a$  through Eqs. 4–7. The derivative  $(\partial a / \partial \rho)_s$  is then computed numerically, again using the central difference method with a step size of  $\Delta p = 10$  Pa, and the fundamental derivative calculated. To validate the method developed here it has been compared to the results previously obtained for the fundamental derivative of methane [6]. The results from the validation are reported in Fig. 1, although it should be noted that the previous results are obtained using analytical expressions, rather than the numerical approach adopted here.



**Fig. 1.** Calculation of  $\Gamma$  in the critical region of methane. The left and centre plots are taken from Nannan et al. [6] and are computed using both the scaled fundamental equation of state (left) and the Wagner-Setzmann Helmholtz-energy-based equation of state (centre). The right plot is generated using the model developed in the present work.

## 2.2 Homogeneous Frozen-State Modelling

Following the same rationale as for the previous section, the assumption of a homogeneous fluid leads to  $p_L = p_V$  and  $u_L = u_V$ . However, rather than assume thermal equilibrium between the phases, the frozen-state model assumes that the two-states do not exchange heat or mass and undergo independent isentropic expansions. Thus, based on the defined reservoir conditions (*i.e.*,  $p_0$ ,  $X_0$ ), the entropy of the liquid and vapour are obtained from the equation of state, namely  $s_L = f(p_0, X = 0)$  and  $s_V = f(p_0, X = 1)$ . Then, following an expansion to a defined pressure,  $p$ , the density of the liquid and vapour follow from  $\rho_L = f(p, s_L)$  and  $\rho_V = f(p, s_V)$ . The speed of sound for each phase follow from the thermodynamic definition:

$$a_i = \sqrt{\left(\frac{\partial p}{\partial \rho_i}\right)_s}, \quad (8)$$

where again  $i$  refers to the phase of interest,  $s$  refers to an isentropic process, and the derivative is computed using the central difference method with a step size of 10 Pa. The speed of sound for the two-phase mixture then follows from [1]:

$$\frac{1}{a^2} = \rho \left[ \frac{\alpha}{\rho_V a_V^2} + \frac{(1 - \alpha)}{\rho_L a_L^2} \right], \quad (9)$$

where  $\rho$  and  $\alpha$  are obtained using Eqs. 4 and 5 respectively, noting that since there is no mass exchange that the vapour quality remains constant (*i.e.*,  $X = X_0$ ). With the speed of sound and density of the two-phase mixture defined along an isentropic expansion, the derivative  $(\partial a / \partial \rho)_s$  is then computed numerically, again using the central difference method with a step size of  $\Delta p = 10$  Pa, and the fundamental derivative calculated.

### 3 Results

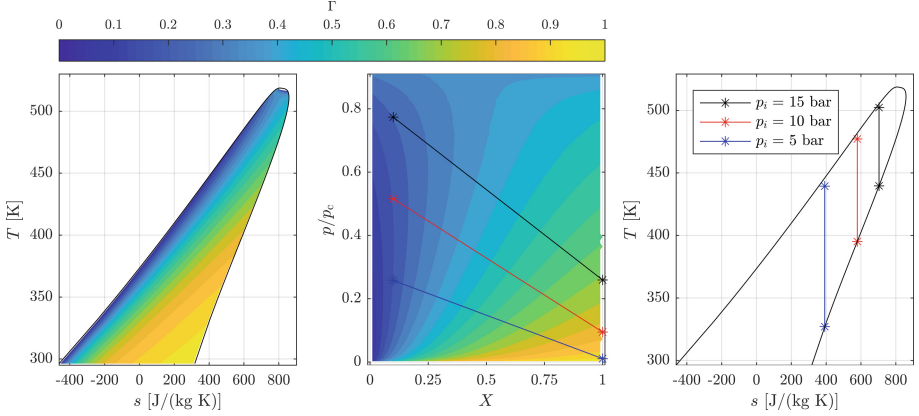
#### 3.1 Fundamental Derivative in Thermal Equilibrium

Under the assumption of thermal equilibrium the fundamental derivative can be determined directly from the equation of state without knowing details of the flow process. Thus, it is possible to directly compute  $\Gamma$  within the two-phase region as a function of pressure  $p$  and vapour quality  $X$ , as reported in Fig. 2. On the left-hand side of this figure, this variation is reported within the  $T$ - $s$  plane, whilst in the centre plot this same variation is reported in the  $p_r$ - $X$  plane, where  $p_r = p/p_c$  with  $p_c$  being the fluid critical pressure.

From Fig. 2, it can be observed that within the two-phase region  $\Gamma$  is always below unity, although the value of  $\Gamma$  does increase as one moves away from the critical point, and further away from the saturated liquid region. In a generalised sense, this implies that under the assumption of homogeneous equilibrium a two-phase flow of MM at any combination of pressure and vapour quality may experience NICFD effects following a sudden small change in pressure.

To aid the discussion relating to turbomachinery applications, and specifically two-phase expansions within a stator vane where the expansion is likely to be relatively rapid, three representative expansions from reservoir pressures of 5, 10 and 15 bar, each with reservoir vapour quality of 0.1, are also reported in the right-hand plot of Fig. 2. For these three expansions the pressure ratios corresponding to an isentropic expansion to a completely vapour state are 24.4, 5.5 and 3.0 for  $p_0 = 5, 10$  and 15 bar respectively, whilst the corresponding volumetric expansion ratios are 155.5, 29.5 and 12.4. Thus, the large expansion ratios, particularly for the lowest reservoir pressure, certainly warrant some caution on whether the assumption of either homogeneity or thermal equilibrium are valid. However, as the reservoir condition moves closer to the critical point, where the densities of the liquid and vapour phases are more similar, the expansion





**Fig. 2.** Variation in  $\Gamma$  within the two-phase region of MM under homogeneous thermal equilibrium reported in the  $T$ - $s$  plane (left) and the  $p$ - $X$  plane (middle). The right plot reports three isentropic expansions from a reservoir vapour quality of 0.1 and reservoir pressures of 5, 10 and 15 bar with corresponding temperatures of 229.2, 204.1 and 166.4 °C.

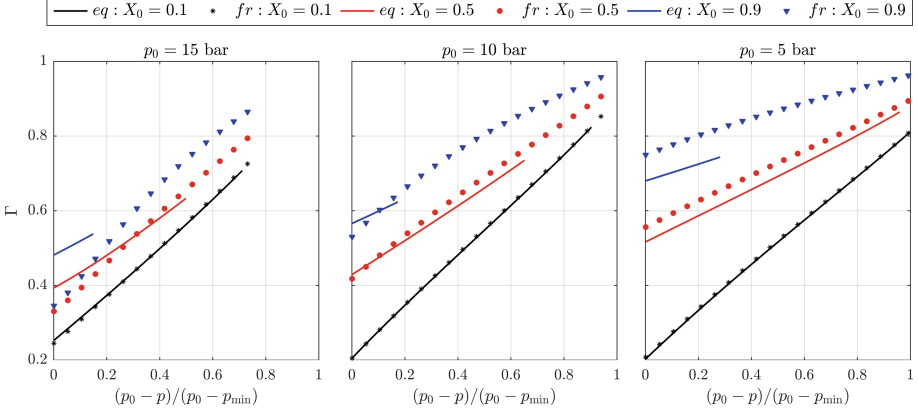
ratios are lower and it is easier to rationalise the assumption of homogeneity and thermal equilibrium. Nonetheless, for the three expansions reported, the results indicate that  $\Gamma$  remains below unity for the whole expansion.

### 3.2 Fundamental Derivative in Frozen and Thermal Equilibrium States

For the three reservoir pressures previously mentioned, a comparison of the variation in  $\Gamma$  during a two-phase expansion of MM from three different reservoir vapour qualities, namely  $X_0 = 0.1, 0.5$  and  $0.9$ , under the assumption of a homogeneous mixture in either a frozen or thermal equilibrium state is reported in Fig. 3. Within this figure, the  $x$ -axis reports the pressure in non-dimensional form where expansion is considered from the reservoir pressure to a minimum pressure  $p_{\min}$  of 1 bar. For the equilibrium cases, the calculation is terminated at the point where the flow becomes saturated vapour.

Considering first the results for the thermal equilibrium cases, it is found that, in line with Fig. 2,  $\Gamma$  increases during the expansion, whilst starting the expansion from a lower reservoir vapour quality leads to lower values for  $\Gamma$  throughout the expansion. The results also reveal that the variation in  $\Gamma$  is more sensitive to the initial reservoir pressure at higher vapour qualities. For example, at  $X_0 = 0.9$  the value of  $\Gamma$  in the initial part of the expansion is around 0.5 and 0.7 for reservoir pressures of 15 and 5 bar respectively, whilst for  $X_0 = 0.1$  the value of  $\Gamma$  is around 0.25 and 0.2 respectively. This behaviour can be rationalised by considering that for a high pressure of 15 bar and  $X_0 = 0.9$ , a significant fraction of the flow is high pressure vapour which is in relatively close proximity to the dense-gas region, whilst at 5 bar and  $X_0 = 0.9$ , the vapour portion of the

flow is much further away from the dense-gas region; for example, for saturated vapour at 15 and 5 bar the corresponding compressibility factors are 0.54 and 0.80 respectively.



**Fig. 3.** Variation in  $\Gamma$  for a two-phase expansion of MM from reservoir pressures of 15, 10 and 5 bar and vapour qualities  $X_0 = 0.1, 0.5$  and  $0.9$  under the assumption of frozen (fr) and thermal equilibrium (eq) states.

Comparing now the equilibrium and frozen cases, a number of observations can be made. Firstly, under both assumptions  $\Gamma$  remains below unity throughout the expansion process, indicating that NICFD effects are likely to be present, irrespective of the thermal interaction between the two phases. It can also be rationalised that in a realistic application, where heat transfer neither occurs instantaneously or is negligible, and the speed of sound can be approximated as some combination of the frozen and equilibrium states [1], that NICFD effects will be present. Secondly, it is observed that at low vapour qualities, the deviation between the two extremes appears negligible, but the deviation increases as the initial vapour quality is increased. For high reservoir pressures, the frozen-state assumptions leads to a lower fundamental derivative than the equilibrium assumption during the initial phase of expansion. In comparison, at lower reservoir pressures the frozen-state assumption leads to higher values of the fundamental derivative. The reason for this behaviour requires further investigation.

In summary, the results reported in Fig. 3 suggest that under the assumptions made within this study, and following the definition of the fundamental derivative for single-phase fluids, NICFD effects are likely within the two-phase expansion of MM from a wide range of reservoir pressures and vapour qualities. This finding holds under both assumptions for the thermal exchange between the two phases. Moreover, the deviation between the frozen-state and thermal equilibrium assumptions increases at higher vapour qualities and appears most significant at high reservoir pressures. In the context of a two-phase ORC turbine, where an optimal expansion would likely begin from a relatively high reservoir pressure and low vapour quality, these preliminary results seem to suggest that

the degree to which NICFD effects are present is not affected by the amount of heat transfer between the two-phases. However, this finding requires further interrogation.

## 4 Conclusions and Future Works

This paper has detailed preliminary investigations into expanding the concept of the fundamental derivative to evaluating NICFD effects within the two-phase expansion of MM under operating conditions relevant to an ORC power system operating with two-phase expansion. For the assumption of a homogeneous two-phase mixture under the two limiting cases of thermal equilibrium and frozen thermal states, expressions for the speed of sound are defined and these are used to evaluate the fundamental derivative. The results have revealed that under both cases the expansion of MM from reservoir pressures of 5, 10 and 15 bar with reservoir vapour qualities of 0.1, 0.5 and 0.9 remains within a region where  $0 < \Gamma < 1$  indicating the presence of NICFD effects. Moreover, it is found that the deviation in the fundamental derivative predicted under the frozen-state and thermal equilibrium assumptions is increased at higher vapour qualities and appears most significant at high reservoir pressures. However, it should be noted that the assumption of a homogeneous two-phase mixture is likely to be an oversimplification, and further investigations are required to fully understand the role of the fundamental derivative within two-phase expansion.

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