



Identification of the phase of a substance from the derivatives of pressure, volume and temperature, without prior knowledge of saturation properties: Extension to solid phase



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ABSTRACT

Venkatarathnam and Oellrich [1] proposed a phase identification parameter (Π) a few years ago to identify the phase of a fluid (vapour or liquid) through the use of the derivatives of pressure, volume and temperature. Currently, this parameter has been found to be the most sensitive parameter for fitting complex equations of state based on the Helmholtz free energy formulation [2,3]. In this paper, it is shown that the phase identification parameter can also be used to identify a solid from a vapour phase, and the mixed (second) derivative of pressure with respect to temperature and volume ($\partial^2 p / \partial v \partial T$), which is already a part of the definition of Π , can be used to distinguish between the solid phase and the liquid/vapour phases. The proposed procedure has applications in fitting equations of state as well as process calculations involving solid phases.

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1. Introduction

Multiphase flows are encountered in a variety of mechanical and chemical engineering applications such as refrigeration, transportation of crude oil and gas over long distances, liquefaction of air, etc. The efficiency of many processes such as the liquefaction of natural gas, separation of air, etc. can be improved by operating closer to the solid-liquid and solid-vapour boundaries; for example, by using larger quantities of higher boiling point components in the refrigerant mixture in the case of natural gas liquefaction processes. There is an increasing interest in the development of equations of state for solid, liquid and vapour phases [4–9] to improve process efficiency and yield.

Many authors have studied methods for the distinction of a liquid phase from a vapour phase without reference to its saturation properties. Poling et al. [10] used the following criteria based on the isothermal compressibility (κ) to identify the phase of a fluid.

$$\text{Liquid phase : } \kappa < 0.005 \text{ atm}^{-1} \quad (1)$$

$$\text{Vapour phase : } \frac{0.9}{p} < \kappa \left(\text{atm}^{-1} \right) < \frac{3.0}{p} \quad (2)$$

The method works only at low pressures, and away from the critical point where the isothermal compressibility of the vapour and liquid phases in equilibrium are very different. Pasad and Venkatarathnam [11] were the first to show that the variation of isothermal compressibility with temperature at constant pressure is different for gases and liquids in the subcritical as well as supercritical region close to the critical point. They proposed the following expression for identifying vapour, liquid and liquid-like vapour phases:

$$\text{Liquid/liquid-like vapour : } \left(\frac{\partial \kappa}{\partial T} \right)_p > 0 \quad (3)$$

$$\text{Vapour phase : } \left(\frac{\partial \kappa}{\partial T} \right)_p \leq 0 \quad (4)$$

More recently, Venkatarathnam and Oellrich [1] simplified the above expression as follows:

$$\text{Liquid/liquid – like vapour : } \Pi > 1 \quad (5)$$

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Vapour : $\Pi \leq 1$ (6)

In the above expression Π refers to the phase identification parameter given by the following expression:

$$\Pi = v \left[\frac{\left(\frac{\partial^2 p}{\partial v \partial T} \right)}{\left(\frac{\partial p}{\partial T} \right)_v} - \frac{\left(\frac{\partial^2 p}{\partial v^2} \right)_T}{\left(\frac{\partial p}{\partial v} \right)_T} \right] \quad (7)$$

The phase identification method described in Eqns. (5) and (6) has been implemented in commercial process simulators such as the Aspen Hysys [12], property programs such as the NIST REFPROP [13], etc. to identify the phase of a fluid at the end of phase equilibrium calculations. The phase identification parameter (Π) has also been found to be extremely useful in the fitting of the multi-parameter Helmholtz energy equations of state [14] that use experimental PVT, speed of sound and calorific measurements. Some of the existing equations of state for different fluids in the NIST REFPROP database have been redone with the phase identification criteria since the publication of Ref. [1], as Eqns. (5) and (6) were not satisfied in some ranges in the older equations. Recent works, based on Helmholtz energy equation of state [2,3,14] and molecular dynamic simulations [15], use the conditions in Eqns. (5) and (6) to fit the equation of state with experimental data. The phase identification parameter Π (also known as PIP in the literature) has currently been established as the most sensitive parameter for fitting high precision equations of state [2,3].

The authors are not aware of a similar method to distinguish solid, liquid and vapour phases, without reference to the properties at phase boundaries. The main aim of this work is to extend the phase identification method of Venkatarathnam and his coworkers [1,11] to cover the solid phase and formulate a procedure to distinguish between solid, liquid and vapour phases without reference to the properties at the phase boundaries.

2. Equations of state for solid phase

There is an increasing interest in the development of equations of state that are valid for liquid and vapour, as well as solid phases. Such equations are expected to improve the efficiency of processes that operate close to phase boundaries [16]. A number of such universal equations of state have been proposed in the past few decades. They can be categorized into three broad groups based on the approach followed:

1. In the most widely used approach, different equations of state are proposed for different phases. Reference [17] is a good example of an equation of state based on the Gibbs energy that works only for the solid phase of carbon dioxide. Refs. [2,3,18] are instances of sophisticated Helmholtz energy formulations valid in the liquid and vapour phases. In such cases, it is necessary to apply equilibrium constraints at phase boundaries while studying phase transitions.
2. The second approach involves modifying the van der Waals form into a higher-order polynomial form [4,6,8,9] to describe the solid, liquid and vapour phases. Multiple volume roots need to be determined at any given pressure and temperature in this approach. These equations also suffer from other deficiencies that have been highlighted by Lee and Yoo [19].
3. In the third approach, proposed by Martynov et al. [7], the traditional Peng-Robinson equation of state is used to describe the PVT relationship of liquid and vapour phases, and a modified Peng-Robinson equation of state is used to describe the PVT

relationship of solid and vapour phases. Both the equations need to be used together to determine the solid-liquid phase boundary.

In this work, all the calculations and analyses have been carried out with the equation of state proposed by Martynov et al. for carbon dioxide. The standard Peng-Robinson equation is used for the liquid and vapour phases:

$$p = \frac{RT}{v-b} - \frac{a}{v(v+b) + b(v-b)} \quad (8)$$

The following standard a and b are used for liquid and vapour phases:

$$a_{LV} = 0.457 \cdot T_c^2 \cdot \alpha(T) / p_c, \quad b_{LV} = 0.0778 \cdot T_c / p_c \quad (9)$$

where $\alpha(T) = (1 + m \cdot (1 - \sqrt{T/T_c}))^2$, $m = 0.37464 + 1.54226\omega - 0.26992\omega^2$, and ω is the acentric factor.

Martynov et al. redefined the two parameters a and b for the solid phase as follows:

$$a_{SV} = a_0(1 - T/T_a), \quad b_{SV} = b_0[1 - c_b \exp(T/T_b)] \quad (10)$$

where $a_0 = 1143 \text{ GPa cm}^6 \text{ mol}^{-2}$, $T_a = 343.55 \text{ K}$, $b_0 = 24.45 \text{ cm}^3 \text{ mol}^{-1}$, $c_b = 0.00035$, and $T_b = 39 \text{ K}$.

The above parameters were fitted with the experimental sublimation and melting line pressure and temperature measurements. The melting and sublimating lines estimated in this work with the above equation matched well with that estimated by the NIST REFPROP [13] for carbon dioxide, with a maximum error of 0.281% along the melting line, and 0.284% along the sublimation line.

3. Variation of isothermal compressibility of solids with temperature at constant pressure

Fig. 1 shows the variation of isothermal compressibility [$\kappa = (-1/v)(\partial v/\partial p)_T$] of solid carbon dioxide with temperature at specified pressures, along with that of the vapour and liquid phases. The calculations with the vapour phase are limited to the sublimation region ($p < 0.517 \text{ MPa}$), and those with the liquid phase to the solid melting region ($p > 0.517 \text{ MPa}$). It can be seen from Fig. 1 that the slopes of the isobars are of the same sign for both the solid and the liquid phases, while those of the vapour are of the opposite sign (relative to the solid and liquid phases). A similar result was also obtained experimentally by Heberlein et al. [20] in the case of solid nitrogen. In the experiment, Heberlein and his coworkers measured changes in length of a solid nitrogen sample with a resolution of 10^{-9} cm by relating a variation of capacitance to dimensional changes. The isothermal compressibility was plotted for a near-zero pressure.

The phase identification criteria developed by Pasad and Venkatarathnam [11] can now be extended to solid phases as follows:

$$\text{Solid/Liquid/Liquid-like vapour : } \left(\frac{\partial \kappa}{\partial T} \right)_p > 0 \quad (11)$$

$$\text{Vapour : } \left(\frac{\partial \kappa}{\partial T} \right)_p < 0 \quad (12)$$

The above criteria are very useful in identifying a vapour phase from liquid and solid phases, but are not useful in identifying a liquid phase from a solid phase.

The phase identification parameter Π is easier to calculate than

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