CALCULATION OF THE THERMODYNAMIC PARAMETERS OF THE SUPERCRITICAL CARBON DIOXIDE BY USING ALTUNIN – GADETSKII EOS

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ABSTRACT

Supercritical fluid technologies are applied on a large industrial scale, e.g. for extractions and reactions. They are used in the food industry, pharmaceuticals and in the cosmetics domain. Carbon dioxide is the most widely used supercritical fluid because of its relatively low critical temperature (31 °C) and pressure (74 bar). In particular, its low critical temperature makes it highly suitable for processing heat-sensitive materials. The control of heat and mass transfer in the supercritical carbon dioxide requires knowledge of these thermodynamic properties. The Altunin and Gadetskii EoS was given to describe the thermodynamic properties of the pure carbon dioxide. The supercritical, the liquid and the gas states of carbon dioxide are represented accurately. The original equation proposed by Altunin and Gadetskii and its tremendous importance in describing the carbon dioxide behavior are analyzed.

INTRODUCTION

A supercritical fluid is any substance at a temperature and pressure above its critical point. It can diffuse through solids like a gas, and dissolve materials like a liquid. In addition, close to the critical point, small changes in pressure or temperature result in large changes in density.Therefore a solute can be extracted at supercritical condition of the solvent, and separated from it by reducing pressure or temperature below the critical parameters of the solvent, yielding a solvent-free extract. By using supercritical solvents having low critical temperatures as carbon dioxide, it is possible to extract thermally labile compounds, specially pharmaceutical and food products. Carbon dioxide is the most widely used supercritical fluid because of its relatively low critical temperature (31 °C) and pressure (74 bar). The control of heat and mass transfer in the supercritical carbon dioxide requires knowledge of these thermodynamic properties.

At present, even in the critical region, thermodynamic behaviour of pure components are most frequently modelled by classical equations of state, including commonly used cubic equations, such as the Redlich–Kwong and Peng–Robinson equations of state. Some non-classical models with theoretical or effective critical exponents are available, such as Bender model and related models that incorporate crossover functions to connect the critical and non-critical regions. Such models are currently used in a correlative rather than a predictive mode, since, in general, they require the critical locus as input as well as a number of adjustable parameters that can be determined only when extensive experimental data are available.

The development of equations of state (EoS) and their application to the correlation and the prediction of phase equilibrium properties is a wide research field. The Altunin and Gadetskii EoS was given to describe the thermodynamic properties of the pure carbon dioxide under its supercritical, liquid and gaseous states.

Whereas, at the vicinity of the critical point, which is characterised principally by the divergence of compressibility, the Altunin and Gadetskii EoS needs other corrective terms to stabilise fitting of the state and calculate accurately thermodynamic functions as the specific heat at constant volume or pressure and the sound celerity.

This work is followed by a numerical estimation of different thermodynamic functions as C_v, at the vicinity of the critical point, using limited development techniques. The domain of validation is showed when comparing results of the calculation and those determined experimentally and given by several authors.

GOVERNING EQUATIONS
Altunin and Gadetskii EoS

To calculate the thermodynamic parameters of the carbon dioxide, we used an equation of state suggested by Altunin and Gadetskii (1971).

This polynomial equation (of degree 6 in 1/T and degree 9 in P was proposed to represent with a good fidelity the experimental results of the IUPAC in particular in the supercritical region.

It is indeed significant to be able to determine with precision, the specific heats, the speed of sound and the derivative of pressure (compared to the thermodynamic quantities) useful for computational fluid dynamics. Traditional equations of state (Van Der Waals, Peng-Robinson, Redlich-Kwong, for example) provide relatively accurate evolutions of the pressure, temperature and density up to the critical point. Nevertheless, in the supercritical field, these evolutions diverge in a significant way of the experimental results (figure II.5). According to Altunin and Gadetskii, the factor of compressibility Z is written:

$$Z = \frac{P}{\rho RT} = 1 + \rho_r \sum_{i=0}^{9} \sum_{j=0}^{6} b_{ij} (\tau - 1)^j (\rho_r - 1)^i$$

Where $\rho_r = \rho/\rho_c$, $\tau = T_c/T$ and b_{ij} are constants related to CO_2 and tabulated by IUPAC.

The Altunin and Gadetski EoS can easily express the thermodynamic quantities as a function of temperature and density necessary for any computer code.

A separate EoS was needed for the critical region within about ± 5 K of the critical temperature. The equation of Schofield et al [3] was chosen for use. This equation is in terms of two variables, r and θ, which may be regarded as polar coordinates centred on the critical point and are related to the density and the temperature by the set of equations:

$$\Delta T = \frac{(T - T_c)}{T_c} = r(1 - b^2\theta^2)$$

$$\Delta \rho = \frac{|\rho - \rho_c|}{\rho_c} = r^\beta g\theta$$

They are related to the pressure by the following parametric equation:

$$\Delta P = \frac{|P_s - P_c|}{P_c} = r^{\beta(\delta+1)}q(\theta) + c\Delta T + ar^{\beta\delta}\theta(1 - \theta^2)$$

Where q is a function of θ, given as follows:

$$q(\theta) = 36.98893 - 82.07960\theta^2 + 56.66053\theta^4 .$$

The complete EoS is formed by combining equations in such a way that one of the other is predominant in its appropriate region using a switching function f(r).

$$P = f(r).P_A + [1 - f(r)]P_S$$

Where f(r) is expressed by:

$$f(r) = 1 - [1 - \exp(-0,01/r)^{n1})][1 - \exp(-0,05/r)^{n2})]$$

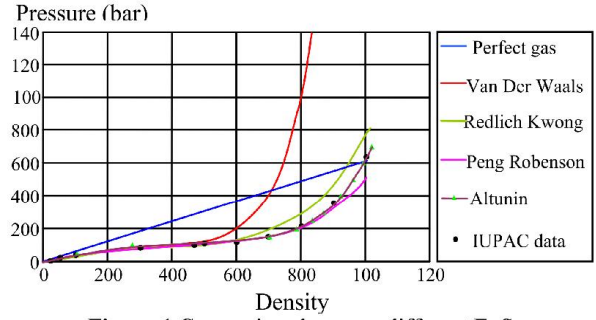A and S indices notice respectively the analytic and the critical expressions of the pressure.

Figure 1 Comparison between different EoS

Heat capacities and sound celerity

Isochoric heat capacity is one of the important thermodynamic characteristics of fluids and fluid mixtures. The EoS does not sufficiently correctly reproduce the values and behaviour of C_v. The role of calorimetric measurements to develop an EoS is very important, especially near the critical and phase transition points. Isochoric heat capacity data contain direct information on second temperature derivatives of pressure $\left(\frac{\partial^2 P}{\partial T^2}\right)_\rho$. For example, heat capacity at constant volume C_v is related to the EoS by:

$$C_v = \left[\frac{\partial U(T,V)}{\partial T}\right]_v$$

U is the internal energy.

That gives: $C_V = C_{V0} - \int_0^\rho \frac{T}{\rho^2}\left(\frac{\partial^2 P}{\partial T^2}\right)_\rho d\rho$.

Where C_{V0} is the ideal gas heat capacity written as: $C_{V0}=C_{P0}-R$

and $C_{P0} = R.\sum_{i=0}^{7} \gamma_i \tau^i$

Where $\tau = T/T_C$ and γ_i are tabulated constants in the IUPAC.

The heat capacity at constant pressure, C_p is related to C_v as follows:

$$C_p = C_v + \frac{T}{\rho^2}\frac{\left(\frac{\partial P}{\partial T}\right)_\rho^2}{\left(\frac{\partial P}{\partial \rho}\right)_T}$$

The sound velocity is a key item in the numerical simulation of any flow of a compressible fluid as we've seen before. This speed is defined as the partial derivative of pressure versus density at constant entropy. The sound velocity C of a pure component can be expressed by the relation:

$$C^2 = \left(\frac{\partial P}{\partial \rho}\right)_S .$$

And as a function of heat capacities we write:

$$C^2 = \frac{C_p}{C_v}\left(\frac{\partial P}{\partial \rho}\right)_T.$$

Taking into account the equation Altunin, we can write:

$$C_v = R\left(-\tau^2 t_3 + t_4 - 1\right)$$

$$C_p = C_v + R\frac{1+\rho_r t_5 - \rho_r t_6}{1+2\rho_r t_5 + \rho_r^2 t_7}:$$

$$C = \left[\frac{C_p}{C_v}RT\left(1+2\rho_r t_5 + \rho_r^2 t_7\right)\right]^{1/2}$$

The coefficients t3, t4, t5, t6 and t7 are given by:

$$t_3 = \left[\sum_{i=0}^{9}\sum_{j=0}^{6} b_{ij}\frac{j(j-1)}{i+1}(\tau-1)^{j-2}(\rho_r-1)^{i+1}\right]_0^\rho$$

$$t_4 = \sum_{i=0}^{7}\gamma_i \tau^i$$

$$t_5 = \sum_{i=0}^{9}\sum_{j=0}^{6} b_{ij}(\tau-1)^j(\rho_r-1)^i$$

$$t_6 = \sum_{i=0}^{9}\sum_{j=0}^{6} b_{ij}\, j(\tau-1)^{j-1}(\rho_r-1)^i$$

$$t_7 = \sum_{i=0}^{9}\sum_{j=0}^{6} b_{ij}\, i(\tau-1)^j(\rho_r-1)^{i-1}$$

β_i and γ_i are constants related to CO_2 and tabulated by IUPAC.

RESULTS AND DISCUSSIONS

The isochoric C_v of pure carbon dioxide is nearly independent of pressure in the high pressure region, indicating that the intermolecular interaction is not sensitive to pressure as the fluid is far from the critical region. In other words, the properties of the fluid far from the critical points do not vary with pressure considerably, which is similar to conventional liquids. The dependence of C_v in the critical region on temperature is more complex. The analytic equation cannot produce the experimental data of Beck et al [12] at this region. Therefore, there exists a maximum in C_v versus temperature curve for CO_2.

As the temperature and the pressure approached the critical point, the compressibility is larger, and the clustering is more pronounced. The heat capacity results from the fact that the fluid absorbs energy as temperature rises. If clusters exist in the fluids, the degree of clustering should be decreased as temperature rises, i.e., some of the members in the clusters enter the bulk, which needs some additional energy. The results near the critical point are not sufficiently close to it using the analytic equation of Altunin. Whereas, the complete formulation of the pressure cannot gives accurate calculation of the second derivatives as mentioned. A longstanding, interesting question is whether the singular behaviour of C_v is related to that of the second derivative of pressure. Future corrections will conserve the good agreement obtained of the pressure estimation in the critical region and will gives an accurate calculation of the second derivative of pressure.

Figure 2 Isochoric heat capacity at different pressure

Figure 3 Isochoric heat capacity at different temperature
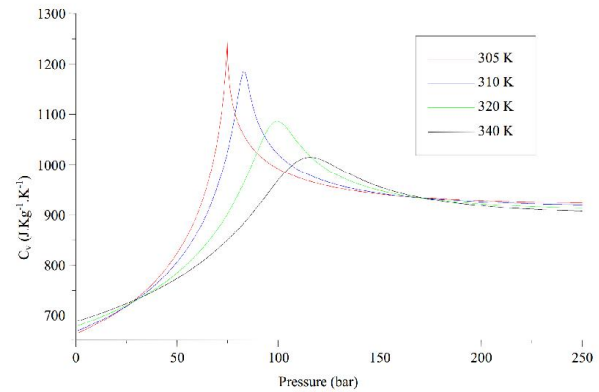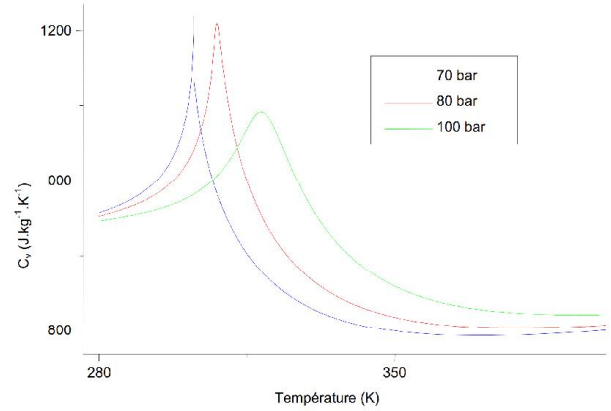
When the isochoric heat capacity is determined, the isobaric capacity can be deduced by calculating first derivatives of pressure. From figure (4), we conclude that C_p is nearly independent of density in both low and high density regions. When the reduced density (ρ/ρ_c) tends to 1, C_p exceeds high values and numerical calculation diverges.

The sound celerity C is an important parameter in fluid dynamics simulation where its accurate estimation is a necessary step in calculation.

Therefore, many researchers have studied fluid dynamics at high density using different expressions of C [13] and [14]. Their results show that shock wave capture in high compressible regions, which is often referred to an important increasing of both Cv and Cp, creates numerical problems and the divergence of calculations. Therefore, figure 6 shows the behaviour of the sound celerity at the critical region and the abrupt discontinuities when the pressure is close to that of the critical point.

Here, the complete equation as presented by Altunin et al. [1] cannot offer accurate value of the parameter C and the variation of derivatives of pressure versus temperature is so perturbed and gives an erroneous function.
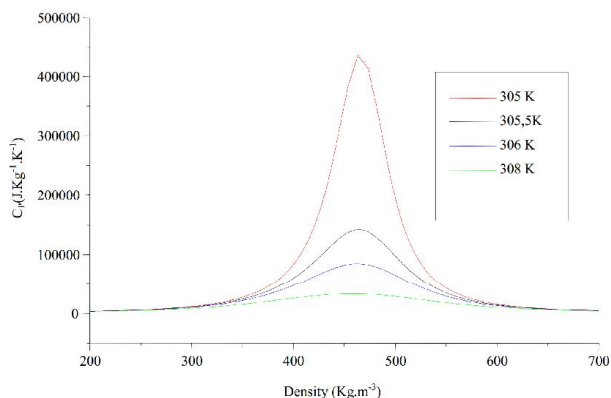
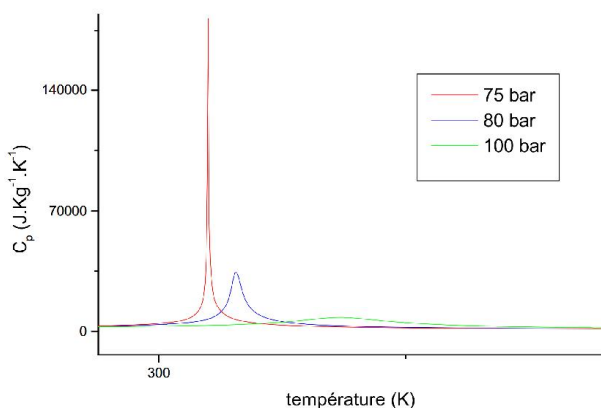**Figure 4** Isobaric heat capacity at different temperature

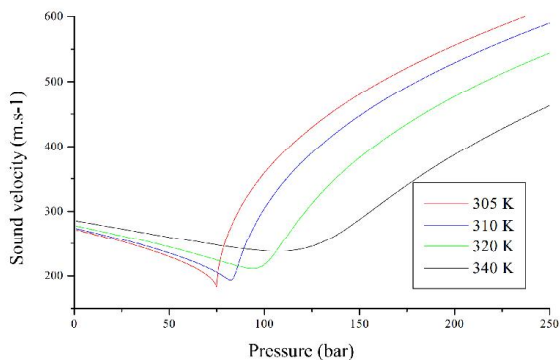**Figure 5** Isobaric heat capacity at different pressure

Figure 6 Sound celerity at different temperature

CONCLUSION

In this contribution, we have considered the integration of heat capacities and sound celerity from the equation of Altunin in the supercritical domain and also at the critical region. The numerical integration evaluates derivatives of the pressure using different high order finite difference techniques. The obtained results showed a good agreement of calculations with the analytic EoS. In contrast, calculation of derivatives of

pressure using the complete equation of state diverges. Therefore, estimation of coefficients of this equation will be undertaken by fitting experimental data of heat capacities at the critical region of carbon dioxide.

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