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Development of a fundamental equation of state for the liquid region of a pure fluid from speed of sound measurements. Application to water

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Abstract

The high level of the experimental precision recently reached in the measurement of speed of sound in the liquid region of fluids, together with the high thermodynamic worth of speed of sound, are the decisive elements increasing the interest in methods which allow to extract complete thermodynamic information from speed of sound data.

This work presents a heuristic approach for the reduction of speed of sound data in the liquid region of a pure fluid into a fundamental dedicated equation of state. Contrarily to the methods reported in the literature for the present purpose, the proposed technique provides an analytical formulation rather than local values of the thermodynamic properties.

A reduction procedure combining linear optimization procedure and non-linear multiproperty fitting was set up. The prediction capability of the method is presented for water as the interest fluid, over an extended pressure and temperature range of the liquid region; the comparisons with the available experimental values of several thermodynamic properties and with the recent IAPWS-95 equation are also given.

The high quality of the obtained results assures that the proposed procedure can be regarded as an effective and robust method to draw a very precise equation of state for the liquid region of a fluid primarily from speed of sound data.

Keywords: Density; Heat capacity; Helmholtz energy equation of state; Liquid measurements; Speed of sound; Water

1. Introduction

The availability of precise thermodynamic models for the accurate calculation of any thermodynamic property in the liquid, vapor and supercritical regions, is a matter of special interest for both scientific and industrial applications. Correspondingly, it is furthermore of fundamental importance to have specific thermodynamic measurements for the enhancement and validation of the models. In fact the development of very precise models following the more effective techniques depends in a large extent on the availability of suitable data in the region of interest.

Among different experimentally accessible data, density and speed of sound stand out in reason of an achievable precision which is at least one order of magnitude higher than the other quantities. However, while density has been commonly used for modeling purposes, the speed of sound has gained an increasing interest for this purpose only recently, particularly as a consequence of the significant improvement of the measuring techniques in a wide range of temperature and pressure in both the vapor and the liquid region. The speed of sound looks then as an attracting quantity because its measurements can now be carried

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Nomenclature

A	Helmholtz energy (kJ kg^{-1})
a	reduced Helmholtz energy (dimensionless)
C_p	isobaric heat capacity (kJ kg^{-1} K^{-1})
C_v	isochoric heat capacity (kJ kg^{-1} K^{-1})
c_i	exponents
d_i	exponents
H	enthalpy (kJ kg^{-1})
ΔH	enthalpy difference (kJ kg^{-1})
I_{Pol}	number of polynomial terms
I_{Exp}	number of exponential terms
M	molecular mass (kg kmol^{-1})
NPT	number of points
n_i	coefficients
P	pressure (MPa)
R	gas constant (kJ kg^{-1} K^{-1})
S	entropy (kJ kg^{-1} K^{-1})
T	temperature (K)
t_i	exponents
U	internal energy (kJ kg^{-1})
w	speed of sound (m s^{-1})
z	generic thermodynamic property

Greek symbols

δ	reduced density (dimensionless)
ρ	density (kg m^{-3})
τ	inverse reduced temperature (dimensionless)
χ^2	objective function

Subscripts

0	reference state
c	critical
calc	calculated
exp	experimental
l	liquid
t	triple point
tot	total

Superscripts

0	ideal gas
R	residual
sat	saturated

out quickly and with high accuracy in a wide range of temperature and pressure, as well in the vapor as in the liquid region.

Several modeling works assuming speed of sound as input data were successfully implemented for the vapor region of pure fluids, taking advantage of the very good accuracies achievable by the recently developed measurement techniques, which allow to get in this region typical uncertainties of less than 0.01%. The thermodynamic properties in vapor can be calculated through numerical integration of the differential equations relating speed of sound to the other quantities [1,2], through virial equations whose coefficients are related to the coefficients of the acoustic virial expansion [3–5], or through regression of a suitable multiparameter equation of state (EoS) directly on speed of sound data [6–9].

When the liquid region is investigated, the attainable experimental uncertainties are usually higher than the former ones for vapor. Typically, an overall uncertainty in the order of few parts per thousand for measurements of speed of sound w in liquid can be obtained by use of a traditional pulse–echo technique for time of flight measurement. A further improvement of this uncertainty has been pursued in the recent development of a microwave resonance technique [10] which allows to determine the internal dimensions of the cylindrical ultrasonic cell at varying temperature and pressure, leading the uncertainty to get a value of 0.05% or lower.

The appearance of these new measurements for the liquid region with accuracy comparable with that of other experimental quantities, typically the density, suggests to study a method to obtain a thermodynamic representation for this phase based on speed of sound data.

In the literature few works about this subject are published [1,11,12] and all of them are based on numerical methods of solution of the differential equations relating the thermodynamic properties. Such procedures have to be locally applied for each condition of interest and consequently a continuous function from which to calculate any thermodynamic function, i.e. an equation of state, cannot be obtained through these methods. Moreover, initial conditions of other properties are required for the numerical integration and, since a second-order partial differential equation is involved, two independent sets of values, usually density and heat capacity, are required along a suitable path.

Therefore, the question here posed is whether a high accuracy dedicated equation of state (DEoS) could be drawn for the liquid region primarily from speed of sound data and what is the more effective procedure to follow for this purpose. In fact the present problem is to verify whether only speed of sound data spread on the range of interest are sufficient to draw a DEoS for the liquid region, similarly to some of the procedures for vapor; alternatively, the goal is to determine which additional experimental quantities have to be included into the regression and with what data distribution.

This approach is different from the current practice for the development of a DEoS for a pure fluid, which considers the whole thermodynamic surface and includes at once