Selected Thermophysical Properties of Dense Fluids Using a General Regularity

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A simple equation of state is used to calculate the bulk modulus, Joule–Thomson inversion temperature, and isobaric expansivity of dense fluids (with density greater than the Boyle density). The EOS predicts the following regularities: (i) the linearity of the bulk modulus versus pressure for each isotherm of a dense fluid for a range of about 100 MPa for subcritical fluids and about 1000 MPa for supercritical fluids, (ii) the linearity of bulk modulus with respect to temperature for each isochore, and (iii) the linearity of inverse isobaric expansivity with pressure for each isochore. The regularities have been found to be consistent with experimental observations. The calculated Joule–Thomson inversion temperature shows good agreement with experimental data in the range of validity of the EOS.

KEY WORDS: dense fluids; bulk modulus; isobaric expansivity; Joule–Thomson inversion temperature.

1. INTRODUCTION

A general regularity has recently been reported for dense subcritical and supercritical fluids [1]. The regularity has been tested with the experimental data for nonpolar, spherical, linear, polar, and quantum fluids, and also fluid mixtures [2], and has been found to be valid for all. In the present work this regularity (EOS) will be used to find analytical expressions for selected thermophysical properties of fluids, and the results will be compared with experiment. A few new regularities will be explored.

The regularity stated is that $(Z-1)v^2$ is linear with ρ^2, where $Z = pv/RT$ is the compression factor, and $\rho = 1/v$ is the molar density. The

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regularity holds for densities greater than the Boyle density and temperatures below about twice the Boyle temperature. The regularity shall be referred to as the "linear isotherm regularity" (LIR).

The LIR is stated as

$$(Z-1)\,v^2 = A + B\rho^2 \tag{1}$$

A simple model was used to obtain the temperature dependence of A and B parameters as [1]

$$A = A_2 - A_1/RT$$

and

$$B = B_1/RT \tag{2}$$

where the constants A_1 and B_1 are related to the intermolecular attraction and repulsion, respectively, and the constant A_2 is related to the nonideal contribution of the thermal pressure.

The LIR, as given by Eq. (1), is shown to be compatible with the van der Waals and the Ihm–Song–Mason [3] equations of state.

2. CALCULATION OF BULK MODULUS

The bulk modulus (reciprocal compressibility) is defined as

$$K = -v(\partial p/\partial v)_T = \rho(\partial p/\partial \rho)_T \tag{3}$$

With Eq. (1) for p as a function of ρ, Eq. (3) reduces to

$$K = RT(\rho + 3A\rho^3 + 5B\rho^5) \tag{4}$$

Empirical observations of Tait in 1888, and their modification by Murnaghan suggested that the bulk modulus for each isotherm of a liquid is linear with respect to pressure [4]. Such a linearity is known as the Tait–Murnaghan equation [5],

$$K = K_0 + K_1\,p \tag{5}$$

where K_0 and K_1 are fluid and temperature dependent. A theoretical basis for this equation is given by Song et al. [6] using an equation of state based on statistical mechanical perturbation theory.

By substituting pv/RT for Z in Eq. (1), and eliminating ρ between Eq. (1) and Eq. (4), the bulk modulus may be obtained in terms of pressure and temperature. It is not obvious that the elimination of ρ will lead to

linear or even nearly linear relation between K and p for each isotherm. However, the elimination will not be performed analytically since it is simple to carry out the elimination of p numerically.

The values of A and B for a fluid can be calculated at any temperature by plotting $(Z-1)\,v^2$ against ρ^2, using experimental p–v–T data for that isotherm. These values along with the density at each T and p can be used to calculate the bulk modulus at that temperature and pressure by Eq. (4). We have used the summary of Stewart and Jacobsen [7] and the experimental data of Robertson et al. [8] to calculate the bulk modulus for Ar. The results for one subcritical and two supercritical isotherms are presented in Fig. 1.

According to the one-fluid approximation [9], it is expected that the LIR can be applied to dense mixtures as well. In this case, the A and B parameters both will depend on the composition of the mixture. Excellent linearity for the $(Z-1)\,v^2$ against ρ^2 plot was obtained from the experimental data of Kubota et al. [10] for the strongly hydrogen-bonded mixture of $H_2O + CH_3OH$. Therefore from knowledge of A and B, the bulk modulus may be calculated for the mixtures for each isotherm and for any particular composition. The results of such a calculation is presented
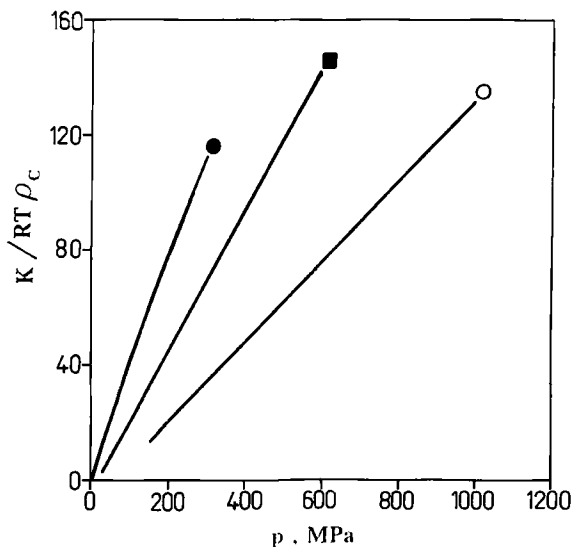

Fig. 1. Reduced bulk modulus versus pressure for isotherms of argon for a subcritical isotherm of 150 K ($\bullet$) and two supercritical isotherms of 200 K ($\blacksquare$) and 308 K ($\bigcirc$).
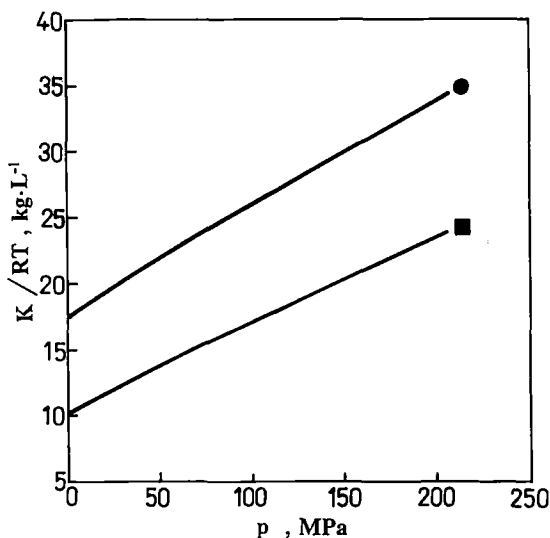
Fig. 2. Bulk modulus (divided by RT) versus pressure isotherms of equimolar mixtures of methanol and water at 283 K (●) and 348 K (■).

for the two isotherms of the $H_2O + CH_3OH$ mixture with equimolar composition in Fig. 2.

The results given in Figs. 1 and 2 suggest that the bulk modulus of dense fluids varies linearly with the pressure for each isotherm at low pressures. However, it is well-known that the linearity deteriorates at high pressures and higher-order terms, i.e., p^2, p^3, etc., must be included in Eq. (5) [5, 6].

It is interesting to note that the Tait–Murnaghan equation [Eq. (5)] is valid in a larger pressure range for supercritical dense fluids (about 1000 MPa) than subcritical dense fluids (about 100 MPa); see Fig. 1. The Tait equation was originally proposed for liquids $(T < T_c)$, and it is interesting to note that it has a greater validity for supercritical dense fluids.

Another important result (regularity) given by the LIR may be seen by expressing the explicit temperature dependence of A and B in Eq. (4):

$$K = p^3(5B_1 p^2 - 3A_1) + pR(1 + 3A_2 p^2) T \qquad (6)$$

This equation shows that the bulk modulus is linear with respect to temperature for each isochore. Values of the bulk modulus reported by Street [11] for argon (interpolated to suitable values) were used to check this
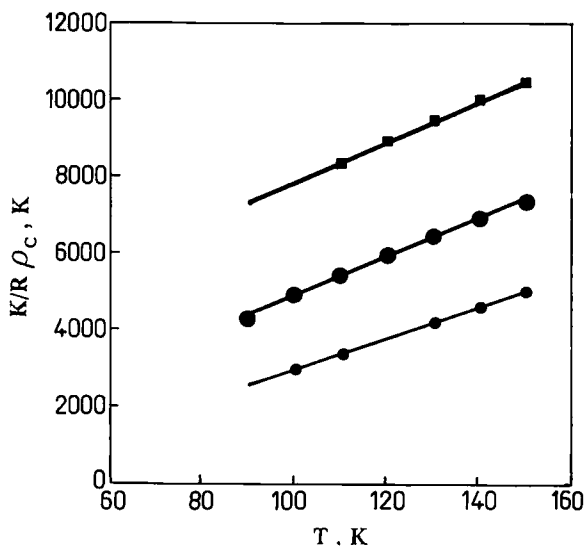
Fig. 3. Bulk modulus (divided by $\rho_c R$) against temperature for argon isochores at $\rho = 33$ (·), $\rho = 35$ (●), and $\rho = 37$ (■) mol·L^{-1}.

prediction. The results are shown in Fig. 3. The prediction seems to hold fairly well in the limited range of data reported.

3. JOULE–THOMSON INVERSION TEMPERATURE

The Joule–Thomson coefficient $\mu_{JT} = (\partial T/\partial P)_H$ is given by

$$\mu_{JT} C_p = T(\partial v/\partial T)_p - v \qquad (7)$$

Using Eq. (1) and substituting pv/RT for Z, one can obtain $(\partial v/\partial T)_p$ and substitute the result in Eq. (7). The final result is

$$\mu_{JT} C_p = \frac{p(3A_1 - 2A_2 RT - 5B_1 \rho^2)}{RT + 3\rho^2(A_2 RT - A_1) + 5B_1 \rho^4} \qquad (8)$$

Therefore, the inversion temperature, T_{inv}, for which $\mu_{JT} = 0$, is given by

$$T_{inv} = (-5B_1 \rho^2 + 3A_1)/2A_2 R \qquad (9)$$

If p is eliminated between Eq. (1) and Eq. (9), the inversion pressure, p_{inv}, may be obtained in terms of T_{inv} as

$$p_{inv} = RT_{inv} \left[\left(\frac{3A_1 - 2A_2 RT_{inv}}{5B_1} \right)^{1/2} + A \left(\frac{3A_1 - 2A_2 RT_{inv}}{5B_1} \right)^{3/2} \right.$$

$$\left. + B \left(\frac{3A_1 - 2A_2 RT_{inv}}{5B_1} \right)^{5/2} \right] \tag{10}$$

The inversion curve for nitrogen is shown along with experimental values [12] in Fig. 4. Equation (10) may be used up to a maximum temperature of $T_{inv} = 3A_1/2A_2R$, above which the expressions in parentheses in Eq. (10) become negative. This temperature corresponds to 392 K for nitrogen. In the range of validity of the LIR (p greater than the Boyle density), the agreement between calculated and experimental curves is satisfactory.
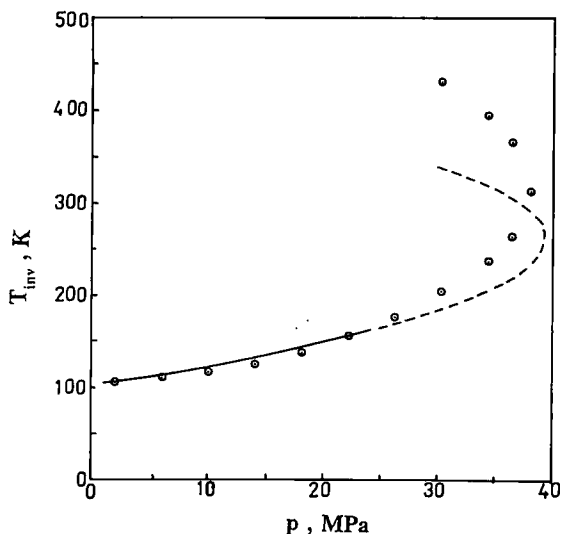

Fig. 4. Experimental and calculated Joule–Thomson inversion temperature versus pressure for nitrogen. The density of points on the solid and dashed portion of the calculated curve are above and below the Boyle density, respectively. The LIR is valid for densities above the Boyle density.

4. ISOBARIC EXPANSIVITY

Equation (1) can be solved to obtain $T(p, \rho)$ as

$$T = \frac{p - (B_1\rho^5 - A_1\rho^3)}{R\rho + A_2\rho^3 R} \qquad (11)$$

This expression may be used to calculate the isobaric expansivity $\alpha = (\partial v/\partial T)_p/v$. A more convenient quantity to calculate would be $1/\alpha$, which can be obtained as

$$\frac{1}{\alpha} = \frac{2\rho^3(B_1 A_2\rho^4 + 2B_1\rho^2 - A_1)}{\rho R(1 + A_2\rho^2)^2} + \frac{1 + 3A_2\rho^2}{\rho R(1 + A_2\rho^2)^2}p \qquad (12)$$

The interesting point about this expression is that it predicts $1/\alpha$ to be linear with pressure for isochores. This prediction (another new regularity) is checked with experimental values of α given by Street [11] (with interpolation to suitable densities). The results are plotted in Fig. 5 and show good linearity in the limited range of data studied.
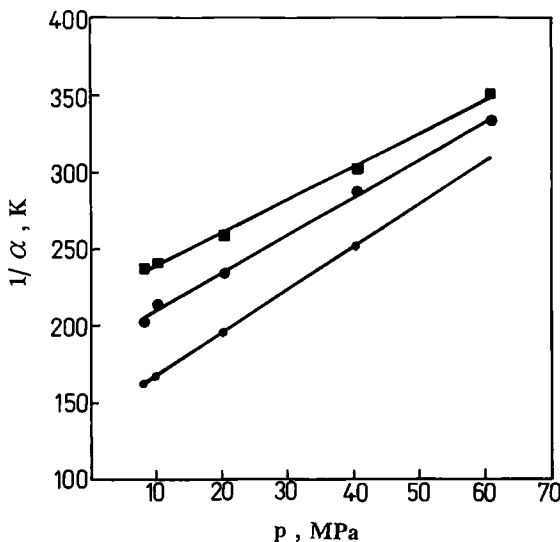

Fig. 5. Inverse isobaric expansivity versus pressure for argon isochores at $\rho = 30$ ($\cdot$), $\rho = 33$ ($\bullet$), and $\rho = 35$ ($\blacksquare$) mol $\cdot$ L^{-1}.

5. DISCUSSION

In spite of the simplicity of the EOS (LIR), it turns out that it is a very powerful equation for dense fluids. Some advantages of LIR over the Tait–Murnaghan EOS have already been examined [2]. In this paper new regularities which are predicted by LIR have been checked with experimental data, and their validity has been verified. Since LIR has no upper density limit, and is valid for the dense supercritical isotherms up to twice the Boyle temperature, it may be expected that the stated regularities will be valid for these fluids as well, even though because of the lack of experimental data they have not explicitly been checked. We may also expect that the regularities will hold for fluid mixtures.

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