

THERMODYNAMIC FLUID EQUATIONS-OF-STATE: NEW SCIENCE-BASED FUNCTIONAL FORMS

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SUMMARY

There is a long history and an extensive literature of cubic equations-of-state, going back 140 years, from van der Waals 2-parameter to current research and compilations with 20+ parameters [1]. As the thermodynamic experimental measurements have improved in accuracy, to 5 or 6 figures, over the decades, these sophisticated cubic equations, that are extensively used for modern thermodynamic property data banks require an ever-increasing complexity and more fitted parameters [1].

The main reason for this progressive inadequacy is that the continuous cubic functional forms are fundamentally inappropriate in the vicinity of T_C and in the supercritical mid-range between gas and liquid phases. A mesophase, confined within percolation loci that bound the existence of gas and liquid phases by higher-order discontinuities, has been identified [2]. A simple numerical differentiation of NIST equations-of-state can demonstrate the the supercritical mesophase and observe the phase bounds, along any isotherm, of any fluid (e.g. CO_2 **Figure 1**) for any of the 200 fluids in the NIST Thermophysical Property data bank [1]. These boundaries have been smoothed over by the equations-of-state used to parameterize the original experimental data. The difference between isothermal rigidity (ω_T) calculated from NIST equation-of-state for CO_2 isotherms by a numerical differentiation, and values of the same property obtained from the velocity of sound (c) tabulation using the thermodynamic identity $\omega_T = Mc^2C_v/C_p$ (M is the molecular weight) can be used to obtain bounds of the mesophase [as defined by equations (1-4) below].

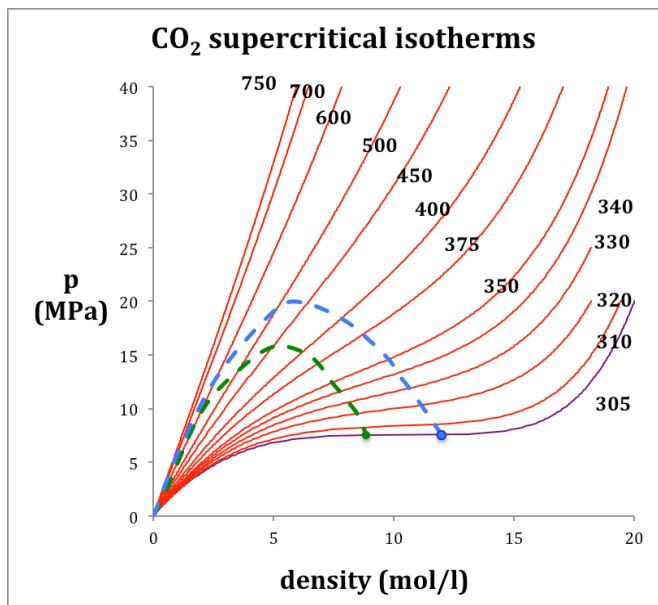


Figure 1: Supercritical isotherms of CO_2 : the temperatures shown are in degrees Kelvin; the green dashed line is the percolation transition locus of bonded clusters (PB) that bounds gas; the blue dashed line is the percolation of available pockets (PA) that bounds the supercritical phase on the liquid side; the green and blue solid circles are the maximum observable gas density, and minimum liquid density along T_c i.e. 305K (purple). The region in between the percolation loci PB and PA is the supercritical mesophase.

Within experimental uncertainties, $p(T)$ is a linear function of ρ in the mesophase region; the origin of the linearity is the colloidal nature of the mesophase [3] with a supercritical linear combination similar to subcritical Lever rule.

When appropriate functional forms are used for each phase separately, we find that the mesophase is linear and the negative and positive deviations for liquid and gas on either side are quadratic, each requiring only known virial coefficients, Boyle temperature (T_B), critical temperature (T_C), coexisting densities along the critical isotherm, and known virial coefficients $b_2(T)$ and $b_3(T)$. A remarkable finding is that for the gas phases below T_B the fourth virial coefficient is everywhere zero within the experimental uncertainty. There is a rigidity symmetry between gas and liquid phases on either side of the mesophase reported previously [4].

Rigidity, $(\omega)_T$, is the work required to isothermally and reversibly increase the density of a fluid; with

dimensions of a molar energy. This simple state function relates directly to the change in Gibbs energy (G) with density at constant T

$$\omega_T = (dp/dr)_T = \rho(dG/d\rho)_T \quad (1)$$

The rigidity isotherms from NIST Thermophysical Properties [1] for CO₂ is shown in **Figure 2**. If equalities (2 to 4) thermodynamically define the percolation loci, it follows that at low density the percolation loci must approach the Boyle temperature (T_B) by its definition. This is the temperature above which the 2nd-virial coefficient is positive and below which it is negative; at T_B, p = ρkT. In the pressure-density plane, the percolation loci exhibit maxima as density decreases and approach zero, i.e. the ideal gas limit at low pressures and densities. The same behavior is seen for other atomic (e.g. argon) and molecular (e.g. water) fluids.

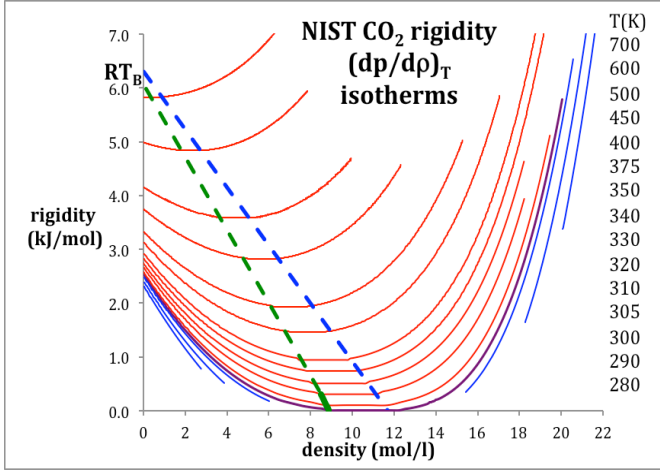


Figure 2: Isotherms for the rigidity of fluid phases of carbon dioxide from NIST thermo-physical tables [4]: the loci of gas and liquid-phase bounds according to the empirical criteria equations (2 to 4) are green (percolation line PB) and blue (percolation line PA) respectively; redlines are supercritical isotherms, blue lines are subcritical isotherms; purple isotherm is T_c (305K): Boyle temperature T_B = 725K corresponding to a rigidity (RT_B) 6.03 kJ/mol where R is the universal gas constant.

are:-

| | | | |
|--------|--------------------------------|-----------------------------------|-----|
| GAS | $\rho < \rho_{PB}$ | $(\delta\omega/\delta\rho)_T < 0$ | (2) |
| MESO | $\rho_{PB} > \rho > \rho_{PA}$ | $(\delta\omega/\delta\rho)_T = 0$ | (3) |
| LIQUID | $\rho > \rho_{PA}$ | $(\delta\omega/\delta\rho)_T > 0$ | (4) |

It is clear from equation (1) that $\omega \geq 0$, i.e. rigidity must always be positive though it can be zero in two phase coexistence regions: Gibbs energy cannot decrease with pressure when T is constant. From these definitions moreover, not only can there be no “continuity” of gas and liquid but the gas and liquid states are fundamentally different in their thermodynamic description. Rigidity is determined by number density fluctuations at the molecular level, which have different but complementary statistical origins in each phase, hence the symmetry [3]. There is a distribution of many small clusters in a gas with one large void; there is a distribution of unoccupied pockets in the liquid with one large cluster.

From **Figure 2** the mesophase rigidity (ω) is obtained in terms of T_B and T_C and then we can represent the density bounds as a function as shown in **Figure 3**.

| | | |
|--------|--|-----|
| GAS | $\rho_{PB}(T) = \rho_G(T_c) [(T_B - T)/(T_B - T_c)]$ | (6) |
| MESO | $\omega_T = T_B [1 - T_B/(T_B - T_c) + T/(T_B - T_c)]$ | (5) |
| LIQUID | $\rho_{PA}(T) = \rho_L(T_c) [(T_B - T)/(T_B - T_c)]$ | (7) |

The observation of linearity is an empirical approximation; a more accurate scrutiny of the original experimental data could result in non-linearity of either or both of these equations for the density bounds. The pressure equations-of-state for any thermodynamic equilibrium state point can be obtained. The gas equation-of-state for an isotherm can be parameterized using the Mayer virial expansion. The mesophase pressure increases linearly with density in the region $0 > T > T_B$ and $\rho_{PB}(T) > \rho < \rho_{PA}(T)$, and for the ‘liquid’ we can use an empirical expansion, for all T and $\rho > \rho_{PA}(T)$. The three equations-of-state are as follows:-

| | | |
|--------|---|------|
| GAS | $p(\rho, T) = kT (1 + b_2(T)\rho + b_3(T)\rho^2 + \dots)$ | (8) |
| MESO | $p(\rho, T) = p_{PB}(\rho, T) + \omega_T(\rho - \rho_{PB})$ | (9) |
| LIQUID | $p(\rho, T) = p_{PA}(\rho, T) + kT[(\rho - \rho_{PA}) + a_2(\rho - \rho_{PA})^2 + a_3(\rho - \rho_{PA})^3 \dots]$ | (10) |

For the temperature-density region $0 > T > T_B$ and $\rho < \rho_{PA}(T)$, equations (5 to 7) are based upon the assumption that there is a phase transition of the third-order at the mesophase bounds with a discontinuity in the density derivative of ω , i.e. the third derivative of Gibbs energy with respect to ρ at constant T along an isotherm. For temperatures above T_B , the equation-of-state “LIQUID”, ρ_{PA} in equation (10) becomes zero and the coefficients a_n are the same as the Mayer virial coefficients $b_n(T)$ in equation (8).

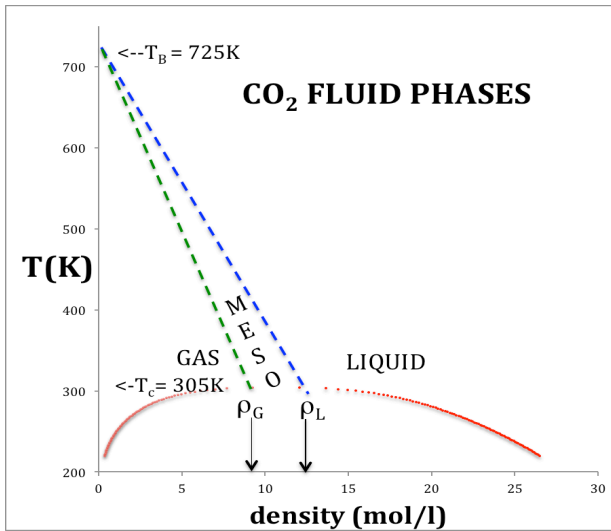


Figure 3: $T(\rho)$ phase diagram for CO_2 using data points obtained from NIST Thermophysical Properties compilation [1] indicating the percolation loci that bound the supercritical liquid and gas states: the green and blue dashed lines are the gas (PB) and liquid (PA) percolation transition loci respectively; coexistence densities are solid red points; the coexisting densities of the gas (ρ_G) and liquid (ρ_L) at the critical temperature (T_c) are indicated by the arrows; T_B is the Boyle temperature.

For the supercritical fluid at temperatures above T_B , equation (8) up to order b_4 is sufficient to reproduce the pressure with 5-figure accuracy, i.e. within the margin of the original experimental uncertainty, with a TRENDLINE regression > 0.999999 , up to temperatures of 1000K and pressures up to 50 Mpa. For the gas phase, at all temperatures below T_B , the 4th virial coefficient is essentially zero, within the uncertainty of the experimental data; all higher terms are negligible. Thus the equation-of-state of the whole ‘gas’ region in **Figure 3** requires just the second and third virial coefficient, in the case of CO_2 .

The above equations-of-state are fundamental to all atomic and molecular fluids and appear to be accurate up to second order, i.e. to quadratic terms for most of the 200 fluids in the NIST data bank for all temperatures below the Boyle temperature. We will report detailed comparisons and virial coefficients for the case CO_2 , and also some preliminary comparisons with experimental data and NIST equations, for the exemplary fluids argon and water.

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