ON WHETHER P,ρ,T SURFACES OF REAL FLUIDS EXHIBIT AN ADDITIONAL CRITICAL POINT IN THE VICINITY OF THE TRIPLE POINT

Marjan Ribarič, J.Stefan Institute, E.Kardelj University, Yu–61000 Ljubljana

Boštjan Žekš, J.Stefan Institute and Institute of Biophysics of Medical Faculty, E.Kardelj University, Yu–61000 Ljubljana

Investigating the global behaviour of P,ρ,T surfaces of real gases, the authors have shown that they exhibit certain analytic properties along the density line $\rho = \rho_{cc} \approx \rho_c$ (critical density) and along the density line $\rho = \rho_{cf} \in [3\rho_c, 5\rho_c]$; in particular, experimental data strongly support the hypothesis that outside the critical region $\rho \approx \rho_c$ and $T \approx T_c$ the isothermal P,ρ dependence of real gases considered should be represented by a rational function, say $P(\rho,T) = A(\rho,T)/B(\rho,T)$, such that

$$\partial^2 A/\partial \rho^2 = \partial^2 B/\partial \rho^2 = \partial^4 A/\partial \rho^4 = \partial^4 B/\partial \rho^4 = 0 \quad \text{for any } T > 0 \qquad (1)$$

at $\rho = \rho_{cc} \approx \rho_c$ and $\rho = \rho_{cf} \in [3\rho, 5\rho_c]$. These relations are new kinds of physical laws, discovered when the authors realized that Thom's theory of catastrophes and van der Waals equation suggest that P,ρ,T surfaces of real gases might indicate the existence of a critical point by displaying some particular analytic properties in the vicinity of the density line $\rho = \rho_{cc} \approx \rho_c$. Accordingly we interpret properties (1) along the density line $\rho = \rho_{cf}$ as an indication that an isothermally compressed real fluid approaching a "discontinuous" liquid–solid phase transition experiences continuous changes such as one would associate with a "continuous" liquid–glas phase transition, cf. Fizika 10, Suppl. 2 (1978) 432–435 and 12 (1980) 41–54; Chem. Phys. 34 (1978) 225–230 and 41 (1979) 221–228.

Continuing investigation of the global behaviour of P,ρ,T surfaces of real gases, we found that their isothermal P,ρ dependences exhibit certain particular analytic properties in the vicinity of the triple point density ρ_{tr}. In particular, for any isotherm $T > T_{tr}$ (triple point temperature) experimental data indicate that

$$\partial^2 \ln(P/\rho)/\partial \rho^2 = 0 \quad \text{and} \quad \partial^4 \ln(P/\rho)/\partial \rho^4 = 0 \qquad (2)$$

at $\rho = \rho_{ac} \approx \rho_{tr} \approx 3\rho_c$, Cryogenics in print. In addition, preliminary results indicate (i) that certain higher order derivatives of pressure P and of the chemical potential μ ρ with respect to density ρ may also have temperature independent zeros at $\rho = \rho_{ac}$, and (ii) that

$$\partial^6 A/\partial \rho^6 = 0 \text{ and } \partial^6 B/\partial \rho^6 = 0 \qquad (3)$$

at $\rho = \rho_{ac}$ for any T.

The triple point ($T = T_{tr}$, $\rho = \rho_{tr}$) is not a critical point itself, though it does have certain attributes associated with a critical point, e.g. the isotherms $T < T_{tr}$ display only a one phase transition (gas – solid), whereas the isotherms $T > T_{tr}$ display two phase transitions (gas – liquid and liquid – solid). Thus the triple point $T = T_{tr}$, $\rho = \rho_{tr}$ is a point where with lowering of temperature the isotherms lose, so to speak, one phase transition. These facts suggest the existence of a particular point, say the anticritical point ($T = T_{ac}$, $\rho = \rho_{ac}$), in the vicinity of which the analytic representations of P,ρ,T surfaces of real fluids exhibit a reverse behaviour to that in the vicinity of the critical point ($T = T_{cc}$, $\rho = \rho_{cc}$), where above–critical isotherms exhibit a monotonous P,ρ dependence, whereas below critical isotherms ($T < T_{cc}$) seem to exhibit wiggles, cf. Fizika 9 (1977) 205–211. In Figs. 1 and 2 isotherms corresponding to two model P,ρ,T surfaces are given schematically such that

$$\partial^i P(\rho,T)/\partial \rho^i = 0 \qquad (4)$$

both at the critical point ($T = T_{cc}$, $\rho = \rho_{cc}$) and at the anticritical point ($T = T_{ac}$, $\rho = \rho_{ac}$) with $i = 1$ and 2 in Fig. 1 and $i = 1,2,3$ and 4 in Fig. 2. In Fig. 1 [2] the behaviour of isotherms along the density lines $\rho = \rho_{cc}$, $\rho = \rho_{ac}$ and $\rho = \rho_{cf}$ is

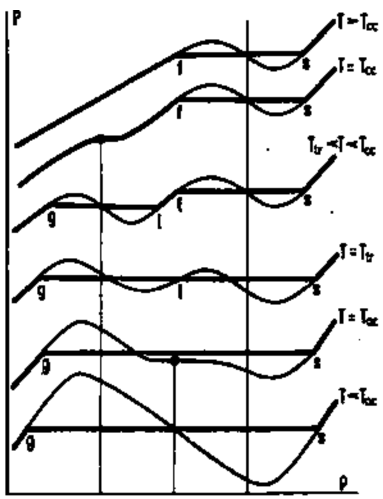

Fig. 1

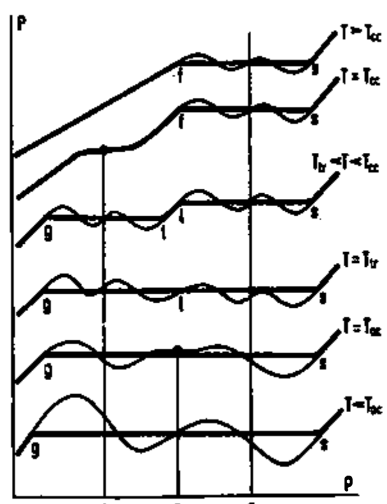

Fig. 2

characteristic of cusp [butterfly] catastrophes. In Figs. 1 and 2 straight lines f – s, g – l, l – s and g – s indicate fluid – solid, gas – liquid, liquid – solid and gas – solid phase transitions, respectively; with lowering of temperature straight lines g – l and l – s approach, coalescing into straight line g – s at the temperature of the triple point. Using full circles we indicated the critical point $T = T_{cc}$, $\rho = \rho_{cc}$ and the anticritical point $T = T_{ac}$, $\rho = \rho_{ac}$. We hope that the available experimental P, ρ, T data of real gases will turn out to be sufficiently abundant and accurate to enable as to verify or disprove the hypothesis proposed, that an analytic representation of the P, ρ, T surface of a real gas exhibits an anticritical point in the vicinity of the triple point.