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PHASE TRANSITIONS OF REAL FLUIDS AND THOM'S THEORY OF CATASTROPHES

Marjan Ribarič, J.Stefan Institute, University of Ljubljana, 61000 Ljubljana, and

Boštjan Žekš, J. Stefan Institute and Institute of Biophysics of the Medical Faculty, University of Ljubljana, 61000 Ljubljana, Yugoslavia

Schulman and Revzen [1] have given reasons why the results of Thom's catastrophe theory could have some bearing on the global behaviour of phase surfaces of real substances outside the critical region, where the effects of fluctuations are negligible and the equations of state are analytic functions. About three years ago we realized [2] that Thom's theory of catastrophes implies a possibility that there are analytic relations between observable physical quantities, say P,ρ,T or μ,ρ,T, such that certain kinds of terms are always missing and not only in the vicinity of the critical point. Absence of certain terms in equations of state of a particular kind would be a kind of physical law if such absence could be experimentally verified for some class of real substances. Unfortunately, Thom's theory of catastrophes itself does not give any indications about the characteristics of those equations of state which would exhibit missing terms.

In particular, if we assume that the liquid-gas transition of real fluids were a kind of Riemann-Hugoniot catastrophe, with $(\rho-\rho_c)$ being an order parameter, provided the effects of fluctuations are negligible, then we know only that P,ρ,T are related by the following analytic relation

$$f_0(T,P) + f_1(T,P)(\rho-\rho_c) + f_3(T,P)(\rho-\rho_c)^3 + \dots = 0, \qquad (1)$$

where the second order term in the order parameter $(\rho-\rho_c)$ is missing, and

$$f_0(T_c,P_c) = 0, \quad f_1(T_c,P_c) = 0 \quad \text{and} \quad f_3(T_c,P_c) \neq 0 . \qquad (2)$$

Now, it is very hard to test assumption (1) against experimental P,ρ,T data of real fluids if we do not know more about the form of functions $f_0(T,P)$, $f_1(T,P)$, $f_3(T,P)$ of control parameters P and T. For suggestions about possible forms of functions $f_i(\rho,T)$ we looked to Van der Waals' equation, since Fowler [3] and Fankhouser [4] have pointed out that it can be written in a particular form of expression (1), having only three terms and with $f_i(T,P)$ depending linearly on P.

Thence we decided to test expression (1) with

$$f_i(T,P) = a_i(T) + P\,b_i(T) \tag{3}$$

against experimental P,ρ,T data of real fluids.

Analysis of the experimental P,ρ,T data of N_2, ethylene, propylene, CO_2 and Xe by a new mathematical technique suggested that outside the critical region (where $|\rho/\rho_c - 1| \ll 1$ and $|T/T_c - 1| \ll 1$) the P,ρ,T surfaces of real gases considered should be represented by the following ansatz

$$P = A(\rho,T)/B(\rho,T)\ , \tag{4}$$

where $A(\rho,T)$ and $B(\rho,T)$ are analytic functions of $\rho > 0$ at any $T > 0$ such that there exists a temperature independent density, say $\rho_{cc} \sim \rho_c$, such that for any $T > 0$ we have

$$\frac{\partial^2 A(\rho,T)}{\partial \rho^2} = 0\ , \quad \frac{\partial^4 A(\rho,T)}{\partial \rho^4} = 0 \tag{5}$$

and

$$\frac{\partial^2 B(\rho,T)}{\partial \rho^2} = 0\ , \quad \frac{\partial^4 B(\rho,T)}{\partial \rho^4} = 0 \quad \text{at} \quad \rho = \rho_{cc}\ ; \tag{6}$$

namely, it turned out that the ansatzes (4) which satisfy conditions (5) and (6) have better fittability than comparative ansatzes not doing so [5,6].
So there are experimental indications that the liquid–gas transitions of real fluids considered are examples of a particular kind of Butterfly catastrophe such that the isothermal P,ρ dependences also exhibit behaviour characteristic of a cusp or Riemann-Hugoniot catastrophe, i.e. such that the corresponding P,ρ,T equations of state are of the form (1) where both second and fourth order terms in order parameter $[\rho - \rho_{cc}]$ are missing.

As real fluids are compressed above a certain, temperature dependent density, say $\rho_f \in [2.5\,\rho_c, 6\rho_c]$, they solidify experiencing a liquid–solid phase transition. Investigating analytic equations of state of N_2, propylene, ethylene, CO_2, Xe — whose parameters have been determined by fitting the experimental P,ρ,T data — in the high density region $\rho \in [2.5\,\rho, 7\,\rho_c]$, we found that the extrapolated P,ρ dependences exhibit behaviour analogous to that found in the vicinity of the critical density ρ_c [7,8]. So we concluded that there are strong indications that isothermally compressed real fluids anticipate their oncoming liquid-solid phase transition as a special kind of Butterfly catastrophe such that their P,ρ,T equations of state are of the form (4), satisfying conditions (5) and (6) at $\rho = \rho_{cc} \sim \rho_c$, and at $\rho = \rho_{cf} \in [2.5\,\rho_c,\ 7\rho_c]$.

Now, it just so happens that Van der Waals' equation has the peculiar property that it can be written in a form (1) also with

$$f_0(T,P) = \mu(T,P) - \mu(T,P_c) = \int_{P_c}^{P} \rho^{-1}\, dP \ , \tag{7}$$

and functions $f_i(T,P)$, $i \geq 1$, being only temperature but not pressure dependent, i.e. the second derivative with respect to density of the chemical potential $\mu(\rho,T)$ associated with the Van der Waals' gas equals zero at $\rho = \rho_c$ for any $T > 0$. We investigated the isothermal dependence of the chemical potential as determined from experimental isothermal P,ρ data of N_2, ethylene, propene, Xe, CO_2, and found strong indications [2,9,10] that, were it not for fluctuations, the chemical potential of real gases considered would be such that

$$\frac{\partial^2 \mu(\rho,T)}{\partial \rho^2} = 0 \quad \text{and} \quad \frac{\partial^4 \mu(\rho,T)}{\partial \rho^4} = 0 \tag{8}$$

for all temperatures $T > 0$ at $\rho = \rho_{cc} \sim \rho_c$. This fact is in accordance with the antisymmetry of the experimentally determined chemical potential of real gases observed by Vicentin–Missoni, Levelt Sengers and Green [11] and Levelt Sengers [12]. Consequently, there are strong indications that also μ,ρ,T surfaces of real gases outside the critical region exhibit behaviour characteristic both of Riemann–Hugoniot and Butterfly catastrophes. We note that relations (8) are equivalent to

$$\frac{\partial}{\partial \rho}\left(\frac{1}{\rho}\frac{\partial P(\rho,T)}{\partial \rho}\right) = 0 \quad \text{and} \quad \frac{\partial^3}{\partial \rho^3}\left(\frac{1}{\rho}\frac{\partial P(\rho,T)}{\partial \rho}\right) = 0 \tag{9}$$

for all temperatures at $\rho = \rho_{cc} \sim \rho_c$.

Following the suggestions of Thom's theory of catastrophes, we have so far discovered altogether ten relations which the isothermal pressure density dependences of real gases seem to satisfy, i.e. relation (5) and (6) at $\rho = \rho_{cc} \sim \rho_c$ and $\rho = \rho_{cf} \in [3\rho_c, 7\rho_c]$ and relations (8) at $\rho = \rho_{cc}$. There are some indications that isothermal P,ρ dependences also satisfy relations (8) at $\rho = \rho_{cf}$, and we are currently investigating this possibility in detail. As a by-product, this investigation should also yield some information as to whether real fluids anticipate their isothermal approach to the liquid–solid phase transition as being above or below critical.

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