

HIGH DENSITY BEHAVIOUR OF EXTRAPOLATED  $P$ ,  $\rho$ ,  $T$  SURFACES  
OF REAL FLUIDS AND BUTTERFLY CATASTROPHE\*

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For  $N_2$ , ethylene, propylene,  $CO_2$  and Xe we found that in the region of high densities,  $\rho \in [3\rho_c, 7\rho_c]$ ,  $\rho_c$  being the critical density, the extrapolated isothermal pressure-density dependences are well described by the following ansatz

$$P(\rho) = [a_0 + a_1(\rho - \rho_0) + a_3(\rho - \rho_0)^3 + a_5(\rho - \rho_0)^5 + a_6(\rho - \rho_0)^6 + \dots] \cdot \\ \cdot [1 + b_1(\rho - \rho_0) + b_3(\rho - \rho_0)^3 + b_5(\rho - \rho_0)^5 + b_6(\rho - \rho_0)^6 + \dots]^{-1}$$

with  $\rho_0 \in [3\rho_c, 7\rho_c]$ .

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## 1. Introduction

Analysing experimental  $P, \rho, T$  data of some real gases we pointed out indications<sup>1,2,3)</sup> that isothermal  $P, \rho$  dependences of real gases should be represented by the following generalisation of a van der Waals equation

$$P(\rho, T, m, n) = A(\rho, T, m) / B(\rho, T, n) \quad (1)$$

where

$$A(\rho, T, m) = \sum_{i=0}^m A_i \rho^i \quad (2)$$

and

$$B(\rho, T, n) = 1 + \sum_{i=1}^n B_i \rho^i \quad (3)$$

are such that

$$\frac{\delta^2 A}{\delta \rho^2} = 0 \quad \text{and} \quad \frac{\delta^2 B}{\delta \rho^2} = 0 \quad (4)$$

at  $\rho = \rho_{cc}$  and  $\rho = \rho_{cf}$ , and such that also

$$\frac{\delta^4 A}{\delta \rho^4} = 0 \quad \text{and} \quad \frac{\delta^4 B}{\delta \rho^4} = 0 \quad (5)$$

at  $\rho = \rho_{cc}$ ; here  $\rho_{cc} \approx$  critical density  $\rho_c$  is a temperature independent constant, whereas  $\rho_{cf} \approx 3\rho_c - 7\rho_c$  is a possibly temperature independent constant. The fact that analytic representations (1) of experimental  $P, \rho, T$  data seem to satisfy conditions (4) and (5) at  $\rho = \rho_{cc} \approx \rho_c$  may be interpreted in terms of Thom's theory of catastrophes as implying that in the absence of fluctuations the liquid-gas transition of real gases could be an example of a special kind of butterfly catastrophe. The indications that condition (4) is satisfied at some possibly temperature independent density  $\rho_{cf}$  can be interpreted as signifying that isothermally compressed real fluids anticipate their liquid-solid phase transition as a kind of Riemann-Hugoniot catastrophe analogous to that displayed by van der Waals' gas at its critical density. In what follows we shall check whether there are experimental indications for representing  $P, \rho, T$  data of real fluids by ansatz (1) satisfying both conditions (4) and (5) at some  $\rho = \rho_{cf} \in [3.5\rho_c, 7\rho_c]$ . So we shall examine whether  $P, \rho, T$  surfaces of real fluids indicate that isothermally compressed real fluids anticipate their oncoming liquid-solid phase transition as a special kind of butterfly catastrophe, analogous to the kind they give indications of exhibiting at their liquid-gas phase transition<sup>1,2)</sup>.

## 2. Analysis of experimental data

To prove the assumption that it makes physical sense to represent the isothermal  $P, \rho$  dependence of real gases by such rational functions (1) as satisfy conditions (4) and (5) at some  $\rho_{cf} \geq 3 \rho_c$ , we have to show the superiority of such ansatzes in fitting experimental data over all (infinitely many) other kinds of ansatzes. This being impossible, we will limit ourself to a check of this assumption by applying the method of osculating functions<sup>1,2,3,4)</sup> to three particular cases. In each case we will consider a polynomial in  $\rho$ , one ansatz (1) satisfying both conditions (4) and (5) at high densities and one ansatz (1) satisfying only condition (4) at high densities. In each case all three ansatzes will have the same number of adjustable parameters (five, four or three) determined in the same way from experimental data. On comparing how the pressure-density dependence of each member of the trio matches the experimentally determined isothermal pressure-density dependence of real gases, we will obtain indications of the physical usefulness of the hypothesis that in the extrapolated high-density region  $\rho > 3\rho_c$ , the analytic representations of experimental isothermal  $P, \rho$  dependences of real gases exhibit behaviour characteristic of a special kind of butterfly catastrophe.

### I. Case

Suppose we have an analytic representation, say  $P_{exp}(\rho, T)$  of experimental isothermal  $P, \rho$  data of the real gas considered. We start the investigation of its qualitative properties using three different ansatzes, each of which will have three parameters adjusted so that it will osculate with  $P_{exp}(\rho, T)$  by having a second order contact. As the first member we take an ansatz such as defined by (1, 2, 3) with  $m = 6$  and  $n = 6$ , denote it as  $P_1(\rho, \rho_0) = A_1(\rho, \rho_0)/B_1(\rho, \rho_0)$ , and determine its 13 parameters so that the following conditions are fulfilled:

- (i)  $P_1$  and  $P_{exp}$  have a second-order contact at  $\rho = \rho_0 \geq 0$ , i. e.,

$$\delta^i P_1(\rho, \rho_0)/\delta \rho^i = \delta^i P_{exp}(\rho)/\delta \rho^i, \text{ for } i = 0, 1, 2 \quad (6)$$

at  $\rho = \rho_0$  for any  $\rho_0 \geq 0$ ;

- (ii) the numerator  $A_1$  and denominator  $B_1$  satisfy relations

$$\delta^2 A_1(\rho = \rho_0, \rho_0)/\delta \rho^2 = 0 \text{ and } \delta^2 B_1(\rho = \rho_0, \rho_0)/\delta \rho^2 = 0, \quad (7)$$

and

$$\delta^4 A_1(\rho = \rho_0, \rho_0)/\delta \rho^4 = 0 \text{ and } \delta^4 B_1(\rho = \rho_0, \rho_0)/\delta \rho^4 = 0 \quad (8)$$

at any point  $\rho_0$  of contact between  $P_1$  and  $P_{exp}$ ;

- (iii) at  $\rho = \rho_c$  we assume in accordance with result of<sup>1,2)</sup> that

$$\delta^2 A_1(\rho = \rho_c, \rho_0)/\delta \rho^2 = 0, \quad \delta^2 B_1(\rho = \rho_c, \rho_0)/\delta \rho^2 = 0, \quad (9)$$

and

$$\delta^4 A_I(\varrho = \varrho_c, \varrho_0)/\delta^4 = 0, \quad \delta^4 B_I(\varrho = \varrho_c, \varrho_0)/\delta^4 = 0 \quad (10)$$

for any  $\varrho_0 \geq 0$ ;

(iv) we assume that

$$P_I(\varrho, \varrho_0, T) = 0 \text{ at } \varrho = 0 \quad (11)$$

and

$$\delta P_I(\varrho, \varrho_0, T)/\delta\varrho = RT \text{ at } \varrho = 0 \quad (12)$$

for any  $\varrho_0 \geq 0$  in agreement with the ideal gas law  $P = \varrho RT$ . These thirteen conditions uniquely determine all 13 constants of ansatz  $P_I(\varrho, \varrho_0)$  as functions of the place  $\varrho_0$  of the second order contact between  $P_I$  and  $P_{exp}$ .

To find out whether the assumption (8) actually makes the functional dependence of  $P_I(\varrho, \varrho_0)$  on  $\varrho$  more close to that of  $P_{exp}(\varrho, T)$  in the vicinity of  $\varrho = \varrho_0$ , we take a completely analogous ansatz, say  $P_{Ic}(\varrho, \varrho_0)$  which differs from  $P_I(\varrho, \varrho_0)$  only in not satisfying condition (8) at  $\varrho = \varrho_0$ . Accordingly we take for  $P_{Ic}$  an ansatz such as defined by (1, 2, 3) with  $m = 5$  and  $n = 5$  whose eleven parameters are determined so that at any  $\varrho_0 \geq 0$  the comparative ansatz  $P_{Ic}$  satisfies conditions (6), (7) and (9) to (12). So both  $P_I$  and  $P_{Ic}$  have a second order contact with  $P_{exp}$  at  $\varrho = \varrho_0$  for any  $\varrho_0 \geq 0$ , and display the same general properties, the only exception being assumption (8) to be investigated in this paper.

To identify those values of  $\varrho_0$  where assumption (8) makes  $P_I(\varrho, \varrho_0)$  more similar to  $P_{exp}(\varrho)$  than  $P_{Ic}(\varrho, \varrho_0)$  is in the vicinity  $[\varrho_0 - h, \varrho_0 + h]$ , we compute the following ratio

$$R(P_I/P_{Ic}, \varrho_0, h, T) \equiv \frac{|P_{exp}(\varrho_0 + h) - P_I(\varrho_0 + h, \varrho_0)| + |P_{exp}(\varrho_0 - h) - P_I(\varrho_0 - h, \varrho_0)|}{|P_{exp}(\varrho_0 + h) - P_{Ic}(\varrho_0 + h, \varrho_0)| + |P_{exp}(\varrho_0 - h) - P_{Ic}(\varrho_0 - h, \varrho_0)|} \quad (13)$$

the reciprocal value of which gives us a measure of how much closer is  $P_I$  to  $P_{exp}$  as compared to  $P_{Ic}$  at the distance  $h$  from the point  $\varrho = \varrho_0$  where both  $P_I$  and  $P_{Ic}$  have a second order contact with  $P_{exp}$ .

In the vicinity  $[\varrho_0 - h, \varrho_0 + h]$  where  $R(P_I/P_{Ic}, \varrho_0, h) \leq 1$ , the experimental data supply indirect evidence in support of hypothesis (8). This evidence, however, would not be physically too credible if the functional dependence of ansatz  $P_I(\varrho, \varrho_0)$  itself were not closer to the functional dependence of  $P_{exp}(\varrho, T)$  on  $\varrho \in [\varrho_0 - h, \varrho_0 + h]$  than that of the most simple polynomial ansatz

$$P_n(\varrho, \varrho_0) = \sum_{i=0}^{n-1} (\varrho - \varrho_0)^i / i! P_n^{(i)} \quad (14)$$

where  $n = 3$  and the parameters

$$P_n^{(b)} = \delta^t P_{exp}(\rho = \rho_0, T) / \delta \rho^t \tag{15}$$

have been determined so that  $P_3(\rho, \rho_0)$  and  $P_{exp}(\rho, T)$  have a second order contact at  $\rho = \rho_0$ . To measure the similarity of  $P_3(\rho, \rho_0)$  and  $P_{exp}(\rho, T)$  we define a ratio, say  $R(P_1/P_3, \rho_0, h)$  in analogy to definition (13). Now, where  $R(P_1/P_3, \rho_0, h) > 1$  there the fact that  $R(P_1/P_{1c}, \rho_0, h) < 1$  does not carry much weight in support of hypothesis (8), since ansatz  $P_I(\rho, \rho_0)$ , being much more complicated than  $P_3(\rho, \rho_0)$  has there no comparative advantages over  $P_3(\rho, \rho_0)$  which does not take any account of hypothesis (8).

### II. Case

We take ansatz (1, 2, 3) with  $m = 6$  and  $n = 6$  and determine the first member, say  $P_{II}(\rho, \rho_0)$  of the second trio of osculating functions in the same way as  $P_I(\rho, \rho_0)$ ; the only difference being that  $P_{II}(\rho, \rho_0)$  is not required to satisfy condition (12) but condition (6) for  $i = 0, 1, 2, 3$ . The comparative ansatz, say  $P_{IIc}(\rho, \rho_0)$  is defined as ansatz (1, 2, 3) with  $m = 5$  and  $n = 5$  which satisfies condition (6) for  $i = 0, 1, 2, 3$  and conditions (7), (9), (10) and (11) but not (8) for all  $\rho_0 \geq 0$ . Both these members of the second trio  $P_{II}$  and  $P_{IIc}$  have a third order contact with  $P_{exp}$  at any  $\rho_0 \geq 0$ . The ratio, say  $R(P_{II}/P_{IIc}, \rho_0, h)$  measuring within the density interval  $[\rho_0 - h, \rho_0 + h]$  the closeness of the functional behaviours of  $P_{II}$  and  $P_{exp}$  as compared to that of  $P_{IIc}$  and  $P_{exp}$  is defined in analogy to definition (13). Further, we also define ratio  $R(P_{II}/P_4, \rho_0, h)$ , measuring the comparative advantage of  $P_{II}(\rho, \rho_0)$  over osculating polynomial  $P_4(\rho, \rho_0)$  of the third order.

### III. Case

We take ansatz (1, 2, 3) with  $m = 6$  and  $n = 6$  and replace its constants by functions of  $\rho_0 \geq 0$  such that now the first member, say  $P_{III}(\rho, \rho_0)$  of the third and the last trio of osculating functions satisfies (6) with  $i = 0, 1, 2, 3, 4$  and con-

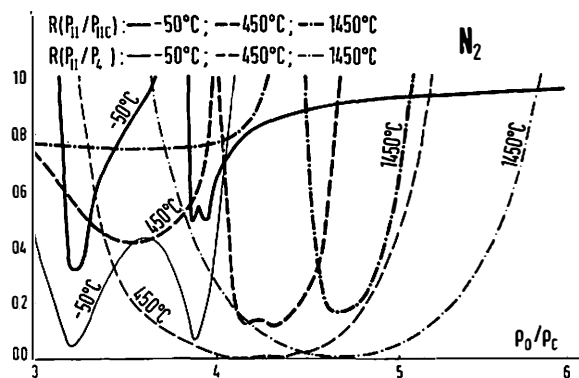


Fig. 1: Ratios  $R(P_{II}/P_{IIc}, \rho_0, h = 0.2 \rho_c, T)$  and  $R(P_{II}/P_4, \rho_0, h = 0.2 \rho_c, T)$  are plotted versus  $\rho_0/\rho_c \in [3, 6]$  for isotherms  $-50^\circ\text{C} = 1.77 T_c$ ,  $450^\circ\text{C} = 5.73 T_c$  and  $1450^\circ\text{C} = 13.65 T_c$  of N<sub>2</sub> fluid.

ditions (7), (8), (9) and (10) at any  $\varrho_0 \geq 0$ . The comparative ansatz, say  $P_{IIIc}(\varrho, \varrho_0)$  is an ansatz (1, 2, 3) with  $m = 5$  and  $n = 5$  which satisfies conditions (6) with  $i = 0, 1, 2, 3, 4$ , (7), (9) and (10) at any  $\varrho_0 \geq 0$ . So both ansatzes  $P_{III}$  and  $P_{IIIc}$  have a fourth order contact with  $P_{exp}$  at any  $\varrho_0 \geq 0$ . We define the associated ratio  $R(P_{III}/P_{IIIc}, \varrho_0, h)$  in analogy to (13). Further, we take osculating polynomial  $P_5(\varrho, \varrho_0)$  defined by (14, 15) and define the associated ratio  $R(P_{III}/P_5, \varrho_0, h)$  in analogy to definition (13).

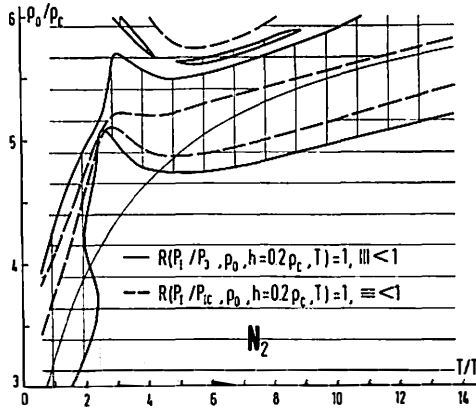


Fig. 2: Regions of the  $\varrho_0/\varrho_c, T/T_c$  plane where ratios  $R(P_1/P_{1c}, \varrho_0, h = 0.2 \varrho_c, T)$  and  $R(P_1/P_3, \varrho_0, h = 0.2 \varrho_c, T)$  of  $N_2$  gas have values smaller than one are shaded horizontally and vertically, respectively. Along the border lines the values of this ratios is equal one.

We took an analytic equation of state for  $N_2$  gas, used by Jacobsen and Stewart<sup>5)</sup> to represent very accurately a wide range of experimental  $P, \varrho, T$  data, and we calculated ratios  $R(P_1/P_{1c}, \varrho_0, h, T)$  and  $R(P_1/P_3, \varrho_0, h, T)$ ,  $R(P_{III}/P_{IIIc}, \varrho_0, h, T)$  and  $R(P_{III}/P_5, \varrho_0, h, T)$ , and  $R(P_{III}/P_{IIIc}, \varrho_0, h, T)$  and  $R(P_{III}/P_5, \varrho_0, h, T)$ , with

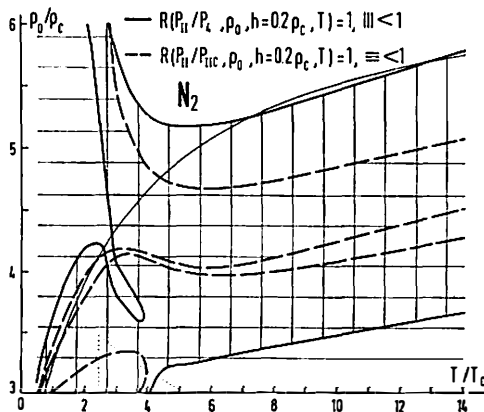


Fig. 3: Regions of the  $\varrho_0/\varrho_c, T/T_c$  plane where ratios  $R(P_{II}/P_{IIc}, \varrho_0, h = 0.2 \varrho_c, T)$  and  $R(P_{II}/P_3, \varrho_0, h = 0.2 \varrho_c, T)$  of  $N_2$  gas have values smaller than one are shaded horizontally and vertically, respectively.

$h/\rho_c = 0.1, 0.2, 0.4, 0.6$  and  $0.8$  as functions of  $\rho_0 \in [3\rho_c, 6\rho_c]$  for 35 isotherms between  $T = -250^\circ\text{C}$  and  $T = 1450^\circ\text{C}$  ( $T_c = -146.89^\circ\text{C}$ ). In all cases we found that these ratios as functions of  $\rho_0$  exhibit minima with values smaller than one, which in general become more pronounced with increasing temperature; for an example see Fig. 1. In Fig. 2 we have indicated in the  $\rho_0/\rho_c, T/T_c$  plane the regions where ratios  $R(P_1/P_{1c}, \rho_0, h = 0.2\rho_c, T)$  and  $R(P_1/P_3, \rho_0, h = 0.2\rho_c, T)$ , by

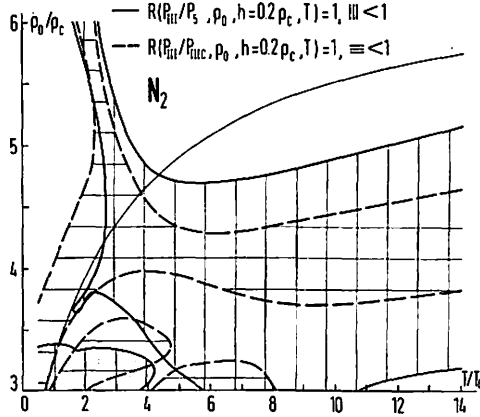


Fig. 4: Regions of the  $\rho_0/\rho_c, T/T_c$  plane where ratios  $R(P_{111}/P_{11c}, \rho_0, h = 0.2\rho_c, T)$  and  $R(P_{111}/P_5, \rho_0, h = 0.2\rho_c, T)$  of  $\text{N}_2$  gas have values smaller than one are shaded horizontally and vertically, respectively.

being smaller than one, support hypothesis (8). Figs. 3 and 4 give analogous results for the second and third case considered. In addition, in Figs. 2, 3 and 4 we have denoted by a thin increasing curve the density of the freezing liquid, say  $\rho_f(T)$  as estimated by equation  $\rho_f(T)/\rho_c = [5.97 + 6.50(T/T_c)]/[2.84 + (T/T_c)]$  ex-

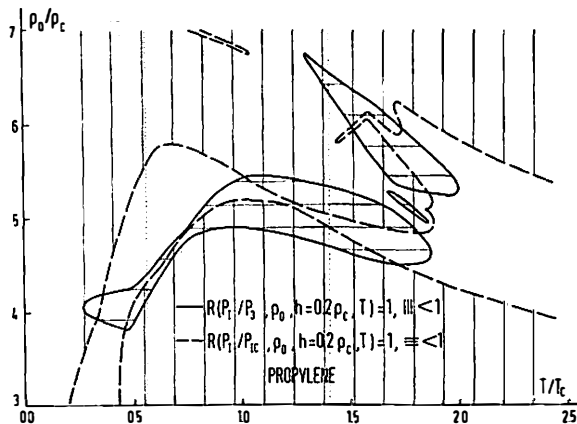


Fig. 5: Regions of the  $\rho_0/\rho_c, T/T_c$  plane where ratios  $R(P_1/P_{1c}, \rho_0, h = 0.2\rho_c, T)$  and  $R(P_1/P_3, \rho_0, h = 0.2\rho_c, T)$  of propylene have values smaller than one are shaded horizontally and vertically, respectively.

trapolating the experimental data collated up to  $T = 1.5 T_c$  by Jacobsen and Stewart<sup>5)</sup>; the thin dotted line indicates the higher-density part of the region of experimental  $P, \rho, T$  data used by Jacobsen and Stewart<sup>5)</sup> in determining the equation of state of  $N_2$  used; rightwards the experimental data used go up to temperature  $T/T_c = 8.7$ , yet with densities less than the critical density. From Figs. 2, 3 and 4 we can obtain an estimate of the value of  $\rho_{cf}$  for  $N_2$  gas. For the high

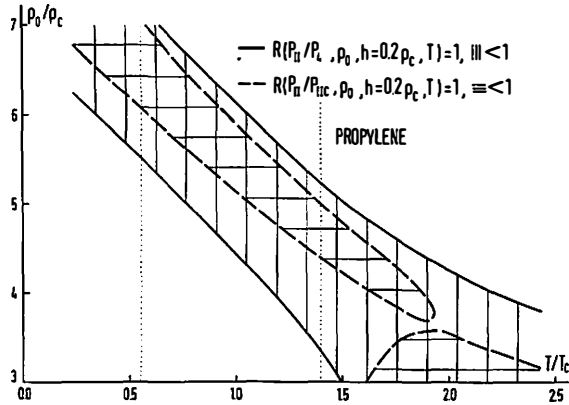


Fig. 6: Regions of the  $\rho_0/\rho_c, T/T_c$  plane where ratios  $R(P_{II}/P_{IIIc}, \rho_0, h = 0.2 \rho_c, T)$  and  $R(P_{II}/P_c, \rho_0, h = 0.2 \rho_c, T)$  of propylene have values smaller than one are shaded horizontally and vertically, respectively.

temperature isotherms  $T \in [3T_c, 14T_c]$  Fig. 1 suggests for  $\rho_{cf}$  values of about  $5\rho_c$  to  $6\rho_c$ , whereas Figs. 2 and 3 suggest somewhat lower values for  $\rho_{cf}(T)$ , say about  $4\rho_c$ . Altogether we could say that for the high temperature isotherms  $T/T_c \in [3, 14]$ , the estimate  $\rho_{cf}(T) \in [3.5\rho_c, 6\rho_c]$  is compatible with Figs. 2, 3 and 4. For

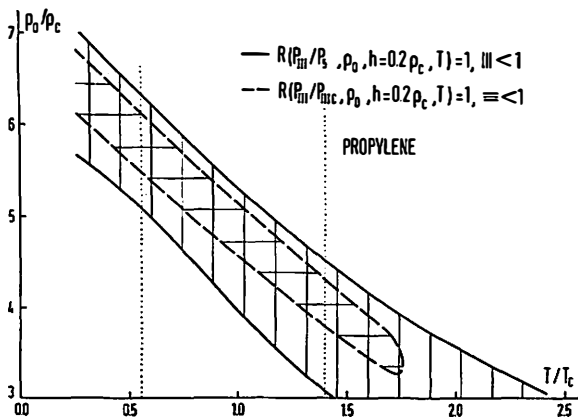


Fig. 7: Regions of the  $\rho_0/\rho_c, T/T_c$  plane where ratios  $R(P_{III}/P_{IIIc}, \rho_0, h = 0.2 \rho_c, T)$  and  $R(P_{III}/P_c, \rho_0, h = 0.2 \rho_c, T)$  of propylene have values smaller than one are shaded horizontally and vertically, respectively.

isotherms  $T < 3T_c$ , Figs. 2,3 and 4 do not give such consistent estimates of the value of  $\rho_{cf}(T)$ . We note, however, that in some numerical experiments where different rational functions, satisfying conditions (4) and (5) at some  $\rho'_0$ , have been analyzed by the oscillating functions defined, the associated ratios sometimes yielded estimates of  $\rho'_0$  which were not mutually compatible and/or were not coinciding with the value of  $\rho'_0$ .

Next we investigated Bender's<sup>6)</sup> analytic equation of state for propylene, and found in all three cases that for  $h/\rho_c = 0.1, 0.2, 0.4, 0.6, 0.8$  the corresponding ratios exhibit well pronounced minima which are smaller than one for the values of  $\rho_0/\rho_c$  indicated in Figs. 5, 6, 7 for  $h = 0.2\rho_c$ . The experimental  $P, \rho, T$  data used by Bender<sup>6)</sup> to determine the considered equation of state for propylene, lie in the temperature interval  $T/T_c \in [0.55, 1.4]$  indicated in Figs. 5, 6, 7 by two thin dotted vertical lines; the density of the data used goes up to  $2.86 \rho_c$ . For isotherms  $T/T_c \in [0.5, 2]$  the results of Fig. 5 suggest for  $\rho_{cf}(T)$  values between  $4 \rho_c$  and  $6\rho_c$ , whereas Figs. 6 and 7 suggest for  $\rho_{cf}(T)$  values from  $7\rho_c$  to  $3\rho_c$ , and even lower; altogether one could make a guess that  $\rho_{cf}(T) \in [3\rho_c, 7\rho_c]$ . We note that Figs. 2, 3 and 4 suggest that  $\rho_{cf}(T)$  of  $N_2$  may be increasing with temperature, whereas Figs. 5, 6 and 7 indicate for  $\rho_{cf}(T)$  of propylene a decreasing tendency. These facts may be due to the empirical equations used and not a physical property of the gases considered.

Both Jacobsen and Stewart's equation of state for  $N_2$  and Bender's, for propylene were fitted to experimental  $P, \rho, T$  data over a region in the  $\rho, T$  plane, and represent the isothermal  $P, \rho$  dependence of  $N_2$  and propylene by the sum of a polynomial in  $\rho$  and of a polynomial in  $\rho$  multiplied by  $\exp \gamma \rho^2$ . To find out whether a different analytic representation of the experimental data would yield a compatible support to the hypothesis (8), we took the isothermal  $P, \rho$  data of a few real gases and fitted them with seven- to ten-degree polynomials in  $\rho$ . Then we analysed these polynomials by computing the corresponding six ratios defined as functions of  $\rho_0 \in [3\rho_c, 6\rho_c]$  for  $h/\rho_c = 0.1, 0.2, 0.3, 0.4, 0.8$ . Proceeding this way we investigated the polynomially extrapolated  $P, \rho$  dependence of:

(i) the isotherms  $T = 150^\circ\text{C}, 125^\circ\text{C}, 100^\circ\text{C}, 75^\circ\text{C}, 50^\circ\text{C}, 25^\circ\text{C}, 0^\circ\text{C}, -25^\circ\text{C}, -50^\circ\text{C}, -75^\circ\text{C}, -100^\circ\text{C}, -125^\circ\text{C}$ , of  $N_2$  gas ( $T_c = -146.89^\circ\text{C}$ ), using  $P, \rho, T$  data collated by Michels, Lunbeck and Wolkers<sup>7)</sup>; here all six ratios computed display minima smaller than one and with a very few exceptions corroborate the estimates of  $\rho_{cf}(T)$  obtained from Jacobsen and Stewart's equation.

(ii) the isotherms  $T = 150^\circ\text{C}, 125^\circ\text{C}, 100^\circ\text{C}$  of propylene ( $T_c = 91.75^\circ\text{C}$ ), using  $P, \rho, T$  data measured by Michels et al.<sup>8)</sup>; here the minima smaller than one of the six ratios computed as functions of  $\rho_0$  suggest an estimate  $\rho_{cf} \in [3.5 \rho_c, 4.7 \rho_c]$ .

(iii) the isotherms  $T = 75^\circ\text{C}, 50^\circ\text{C}, 30^\circ\text{C}, 25^\circ\text{C}, 20^\circ\text{C}, 16^\circ\text{C}, 12.5^\circ\text{C}, 10.5^\circ\text{C}, 6^\circ\text{C}, 0^\circ\text{C}$  of ethylene ( $T_c = 9.3^\circ\text{C}$ ), using  $P, \rho, T$  data obtained by Trappeniers, Wassenaar and Wolkers<sup>9)</sup>; here ratios  $R(P_1/P_{1c})$  and  $R(P_{11}/P_4)$  display minima smaller than one which suggest for  $\rho_{cf}$  of ethylene an estimate  $\rho_c \in [3\rho_c, 6\rho_c]$ , whereas the ratios  $R(P_{11}/P_{11c}), R(P_{111}/P_{111c}), R(P_1/P_3)$  and  $(P_{111}/P_5)$  only seldom display minima smaller than one.

(iv) the isotherms  $T = 150.14^\circ\text{C}, 145.049^\circ\text{C}, 139.830^\circ\text{C}, 125.007^\circ\text{C}, 99.757^\circ\text{C}, 75.260^\circ\text{C}, 49.712^\circ\text{C}, 40.105^\circ\text{C}, 32.075^\circ\text{C}, 29.900^\circ\text{C}, 25.053^\circ\text{C}$  of  $\text{CO}_2$  ( $T_c = 31.04^\circ\text{C}$ ), using  $P, \rho, T$  data obtained by Michels and Michels<sup>10)</sup> and Michels, Michels

and Wouters<sup>11)</sup>; here functional dependences of the six ratios computed suggest for CO<sub>2</sub> gas an estimate  $\rho_{cf} \in [3.5\rho_c, 6\rho_c]$ .

(v) the isotherms  $T = 150^\circ\text{C}$ ,  $125^\circ\text{C}$ ,  $75^\circ\text{C}$ ,  $50^\circ\text{C}$ ,  $25^\circ\text{C}$  of xenon ( $T_c = 16.59^\circ\text{C}$ ) using  $P, \rho, T$  data measured by Michels, Wassenaar and Louwerse<sup>12)</sup>; here an estimate  $\rho_{cf} \in [3.5\rho_c, 5.5\rho_c]$  is indicated by the six ratios computed. In all cases the experimental isothermal  $P, \rho$  data fitted by polynomials in  $\rho$  go up to about three times critical density.

We note that the minima displayed by the six ratios computed from polynomial representation of the isothermal  $P, \rho$  dependence of real gases considered, generally appear less pronounced and distinct than the preceding minima of the ratios computed from analytic equations of state.

In view of the preceding results, it seems that analytic representations of experimental isothermal  $P, \rho$  data of real gases are such that for certain values of the density  $\rho_{cf}(T) \in [3\rho_c, 6\rho_c]$  they can be well approximated within a density interval  $[\rho_{cf}(T) - h, \rho_{cf}(T) + h]$ ,  $h \leq 0.8 \rho_c$ , by rational functions (1) satisfying conditions (4) and (5) at  $\rho = \rho_{cf}(T)$ , i. e. by the following ansatz

$$P(\rho) = [a_0 + a_1(\rho - \rho_{cf}) + a_3(\rho - \rho_{cf})^3 + a_5(\rho - \rho_{cf})^5 + a_6(\rho - \rho_{cf})^6 + \dots] \cdot [1 + b_1(\rho - \rho_{cf}) + b_3(\rho - \rho_{cf})^3 + b_5(\rho - \rho_{cf})^5 + b_6(\rho - \rho_{cf})^6 + \dots]^{-1}. \quad (16)$$

The cases of N<sub>2</sub> gas and propylene considered point out that such values of  $\rho_{cf}(T)$  are not quite independent of the analytic representation; in these two cases they vary up to 25%.

### 3. Discussion

The results of this and the preceding paper<sup>3)</sup> imply that different empirical equations of state of real gases display the same kind of qualitative functional behaviour in the extrapolated, high-density region; we feel this behaviour is due to a physical property of the real gases considered. So we propose the following hypothesis: outside the critical region  $T \approx T_c$  and  $\rho \approx \rho_c$  the isothermal  $P, \rho$  dependence of real gases is a rational function (1) of density  $\rho$  such that its extrapolated behaviour in the high-density region satisfies relations (4) and (5) at some, possibly temperature independent density  $\rho_{cf}(T)$ .

Unfortunately a physical hypothesis can seldom be proved directly by experimental data. What one can do is to check how specific implications of such a hypothesis agree with experimental data, and so obtain circumstantial evidence in support of the hypothesis proposed.

The investigation of this and the preceding paper<sup>3)</sup> can be interpreted as a test against the experimental data of the following implication of the hypothesis proposed: we can interpret any analytic representation of isothermal  $P, \rho$  data of real gases as a result of perturbation of the underlying »true« isothermal equation of state satisfying the hypothesis proposed and so displaying certain analytic properties. Now, these properties should be resistant against small perturbations or else they would not be experimentally observable and so physically insignificant.

Hence we expect these properties or some remnants of them to be present in any accurate mathematical representation of the isothermal  $P, \rho$  data of real gases. In particular, in the extrapolated high density region we expect that such analytic representations will be well approximated by ansatzes taking account of the hypotheses proposed. On considering that the extrapolated behaviour of an analytic representation of the isothermal  $P, \rho$  data depends not only on the experimental data it represents, but also very strongly upon its functional form, we do not expect such an analytic representation necessarily to support the hypothesis considered at densities very close to the presumed density  $\rho_{cf}(T)$  where the »true isothermal equation of state« satisfies the hypothesis considered. In particular, in the case of  $N_2$  we cannot expect the estimates of  $\rho_{cf}(T)$  provided by Figs. 2, 3 and 4 to be very accurate and mutually compatible; and the same goes for the estimates of  $\rho_{cf}(T)$  of propylene provided by Figs. 5, 6, 7. We expect to obtain more accurate estimates of the value of the presumed  $\rho_{cf}(T)$  on fitting experimental isothermal  $P, \rho$  values by a rational function (1) satisfying hypothesis (4) and (5) at some  $\rho_0$  whose optimal value will be determined by optimizing the fit of experimental data. Such an optimal value of  $\rho_0$  will presumably give a better estimate of the true value of  $\rho_{cf}(T)$ , and so supply more information about the temperature dependence of  $\rho_{cf}(T)$ .

In the preceding paper <sup>3)</sup> we have tested only the first part of the hypothesis considered against experimental data, i. e. the assumption that relation (4) is satisfied at some, possibly temperature independent, density  $\rho_{cf}(T)$ . We note that there we obtained estimates for  $\hat{\rho}_{cf}(T)$  which do not contradict the estimates of this paper. If this were not so, all our results obtained in this work would be questionable since they assume and use the results of the preceding paper<sup>3)</sup>.

Investigating the global properties of  $P, \rho, T$  surface of real gases along the critical density line  $\rho = \rho_c$ , we have provided evidence that such  $P, \rho, T$  surfaces are rational functions (1) of density  $\rho$  satisfying conditions (4) and (5) at  $\rho = \rho_{cc} \approx \rho_c$  for any  $T \geq 0$  <sup>1,2)</sup>. In analogy with this result we may supplement the hypothesis proposed by also assuming that  $\rho_{cf}(T)$  is temperature independent. If this were so, then  $P, \rho, T$  surfaces of the real liquids considered would display the structure of a special kind of butterfly catastrophe twice, once around the density  $\rho_{cc} \approx \rho_c$  with  $(\rho - \rho_{cc})$  being an order parameter, and once in the high density region  $\rho > 3\rho_c$  with  $(\rho - \rho_{cf})$  being an order parameter; in both cases  $P$  and  $T$  being the control parameters. According to Thom's theory of catastrophes, such structure of the  $P, \rho, T$  surface along the density line  $\rho = \rho_{cf}$  is associated with some kind of phase transition. The actual occurrence of this phase transition depends on the existence of a critical temperature, say,  $T_{cf}$  analogous to the critical temperature  $T_c$  associated with liquid-gas phase transition. There are three possibilities:

- (i)  $T_{cf}$  is positive and finite, then the  $P, \rho$  isotherm  $T < T_{cf}$  [ $T > T_{cf}$ ] has [no] wiggles around the critical density  $\rho_{cf}$ ,
- (ii)  $T_{cf} = \infty$ , then any  $P, \rho$  isotherm  $T \geq 0$  has wiggles, and
- (iii)  $T_{cf} < 0$ , then no  $P, \rho$  isotherm has any wiggles.

So the question arises whether  $T_{cf} \in (0, \infty)$ , and if so, what kind of phase transition would a real liquid exhibit at some density smaller than  $\rho_{cf}$ , were it compressed along a subcritical isotherm  $T < T_{cf}$ . First we note that for  $N_2$  gas there

are some indications that  $T_{cf} > 0$ , cf. the last paragraph of this section. Then we note that it is quite possible that we might not be able to compress a real liquid sufficiently to observe such a transition, because the compressed liquid could well start crystallizing before that. When  $\rho_{cf}$  is temperature independent and  $T_{cf} > 0$ , we will be sure to observe the corresponding phase transition whenever the density  $\rho_f(T)$  of the freezing liquid becomes larger than the critical value  $\rho_{cf}$ .

In the case of nitrogen, the  $\rho_f(T)$ ,  $T$  data were collated by Jacobsen and Stewart<sup>5)</sup>, pp. 795—922, for the temperature range  $T/T_c \in (0.5, 1.5)$ , the maximal value of  $\rho_f$  being  $3.6 \rho_c$  at  $T = 1.5 T_c$ . For higher temperatures the densities  $\rho_f(T)$  of freezing  $N_2$  are not available, and we can only estimate them by extrapolating the available experimental data, and so see whether they have a tendency to become greater than the value of  $\rho_{cf}$  estimated as  $\rho_{cf} \in (4\rho_c, 7\rho_c)$ . To this end, however an analytic ansatz such as is implied by equations given by Grilly and Mills<sup>13)</sup> and Babb<sup>14)</sup> is of no use, since it automatically assumed that the density  $\rho_f(T)$  of the freezing liquid is an infinitely increasing function of temperature  $T$ . Therefore, we fitted  $\rho_f(T)$ ,  $T$  data collated by Jacobsen and Stewart<sup>5)</sup> with the following ansatz:

$$\rho_f(T)/\rho_c = [a + b(T/T_c)]/[c + (T/T_c)] \quad (17)$$

which assumes the absence of a critical point for the liquid-solid phase transition and a finite maximal density of the freezing liquid. In this way we obtained for the maximal density of the freezing liquid the estimate  $\rho_f(T = \infty) = 6.50 \rho_c$ . This estimate indicates that in the case of  $N_2$  the liquid-solid phase transition and the phase transition associated with the critical density  $\rho_{cf}$  probably occur at about the same density. And so it is quite possible that in the case of  $N_2$  the liquid-solid phase transition always precedes the one associated with  $\rho_{cf}$ , as it actually does in the temperature interval  $T/T_c \in [0.5, 1.5]$  where the experimental  $P$ ,  $\rho$  data have been measured. Now for argon, the experimental  $\rho_f(T)$ ,  $T$  data are available over a wider temperature range  $T/T_c \in [0.56, 2.1]$ , cf. Cheng, Daniels and Crafford<sup>15)</sup>. Proceeding in analogy with  $N_2$ , we obtain  $4.98 \rho_c$  as the estimated value of the maximal density of the freezing argon liquid. If we accept this estimate as valid also for xenon, then the estimate  $P_{cf} \in [4 \rho_c, 6 \rho_c]$  previously obtained for xenon tells us that in the case of xenon it also seems quite possible that the phase transition associated with  $\rho_{cf}$  is always masked by a preceding liquid-solid phase transition. We note that the experimental  $P$ ,  $\rho$ ,  $T$  data leading to the estimate of  $\rho_{cf}$  and the experimental  $\rho_f$ ,  $T$  data leading to the estimate of the maximal possible density of the freezing liquid are not physically directly connected, the first being determined solely by the properties of the liquid and the latter being determined also by the properties of the crystallized solid nitrogen and argon.

The fact that just before freezing, isothermally compressed real fluids have not been observed to experience some other kind of phase transition, and the fact that the estimated values of the presumed critical density  $\rho_{cf}$  and of the estimated maximal values of the freezing liquid are very close, suggest that the liquid-solid phase transition may be always just preceding the presumed phase transition associated with the critical density  $\rho_{cf}$ . These facts suggest that these two phenomena might be physically related, though there seem to be distinct differences. The continuously changing thermodynamic properties of the isothermally compressed li-

quid can hardly indicate directly the oncoming crystallization itself which is accompanied by the abrupt disappearance of the translational symmetry, since this is a discontinuous process. In contrast, the results of this and the preceding paper<sup>3)</sup> can be interpreted as showing that when the real fluids considered are isothermally compressed there occur certain continuous changes which by themselves would lead to a phase transition, possibly from a liquid to an amorphous gel-like (glass-like) state. Ordinarily we do not observe this transition, possibly because physical processes leading to it in an isothermally compressed real fluid are suddenly supplemented by an additional physical process making crystallization thermodynamically more favorable.

From the results of this and the preceding three papers<sup>1,2,3)</sup> we may conclude that there are physical indications that outside the critical region one should approximate isothermal  $P, \rho$  dependence of real gases by an ansatz  $P(\rho, T, m, n)$  defined by (1), (2), (3), which satisfies conditions (4), (5) at  $\rho = \rho_{cc} \approx \rho_c$  and at  $\rho = \rho_{cf} \in [3\rho_c, 6\rho_c]$ , and which in addition also reproduces the ideal gas law (11, 12) in the low density limit. If such a representation  $P(\rho, T, m, n)$  of experimental data, with  $m$  and  $n$  possibly being not finite, is really a kind of physical law, then it should have certain properties which distinguish it from merely empirical equations of state. In a subsequent paper we will investigate the extrapolated high-density behaviour of such equations of state so as to obtain information about the following questions:

(i) Does such an ansatz  $P(\rho, T, m, n)$  display greater fitability than the usual empirical equations of state?

(ii) Is quantity  $\rho_{cf}(T)$  possibly temperature independent. If so, this fact (a physical law) would increase the usefulness of the considered ansatz  $P(\rho, T, m, n)$  in fitting experimental data, because then we would need to determine the value of its parameter  $\rho_{cf}$  only for a few isotherms — possibly only one?

(iii) What is the value of the critical temperature  $T_{cf}$  associated with the critical density  $\rho_{cf}$ ? In particular, is it infinite; in such a case, on being fitted to any isothermal  $P, \rho$  data, the ansatz  $P(\rho, T, m, n)$  would display wiggles in the high-density region around the density  $\rho_{cf}$ , in an analogy to van der Waals' equation displaying wiggles for subcritical isotherms around the critical density. Preliminary investigations indeed show  $P(\rho, T, m, n)$  to have such wiggles. Answers to this and similar questions, by telling how useful is such an ansatz  $P(\rho, T, m, n)$ , will provide a physical test of the underlying hypotheses considered in this and the preceding papers<sup>1,2,3)</sup>, and so show whether these hypotheses physically make sense.

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OBNAŠANJE EKSTRAPOLIRANIH  $P$ ,  $\rho$ ,  $T$  PLOSKEV REALNIH TEKOČIN  
PRI VISOKIH PRITISKIH IN BUTTERFLY KATASTROFA

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Originalno znanstveno delo

Na primerih dušika, etilena, propilena, CO<sub>2</sub> in ksenona smo dognali v področju tri do sedemkratne kritične gostote naslednje obnašanje ekstrapolirane izotermne odvisnosti pritiska od gostote

$$P(\rho) = [a_0 + a_1(\rho - \rho_0) + a_3(\rho - \rho_0)^3 + a_5(\rho - \rho_0)^5 + a_6(\rho - \rho_0)^6 + \dots] \cdot [1 + b_1(\rho - \rho_0) + b_3(\rho - \rho_0)^3 + b_5(\rho - \rho_0)^5 + b_6(\rho - \rho_0)^6 + \dots]^{-1},$$

pri tem je vrednost konstante  $\rho_0$  enaka tri do sedemkratni kritični gostoti.