

GLOBAL BEHAVIOUR OF EXPERIMENTALLY DETERMINED μ , ρ , T
SURFACES OF REAL GASES AND CUSP AND BUTTERFLY
CATASTROPHES^{*)}

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Abstract: Using phenomenological P , ρ , T equations of state of propylene, ethylene, liquid xenon, liquid argon, methane, nitrogen and oxygen, we have analysed the global behaviour of μ , ρ , T surfaces in the noncritical region, looking for experimental evidence in support of catastrophe theory. In addition to the Riemann-Hugoniot (cusp) catastrophe displayed by the Van der Waals equation of state, these experimentally determined surfaces also indicate the possibility of higher order, butterfly catastrophe.

1. Introduction

It has been shown by Fowler¹⁾ and Fankhauser²⁾ that we can rewrite Van der Waals equation as follows

$$\left[\frac{8}{3} \frac{T - T_c}{T_c} - \frac{2}{3} \frac{P - P_c}{P_c} \right] + \left[\frac{8}{3} \frac{T - T_c}{T_c} + \frac{1}{3} \frac{P - P_c}{P_c} \right] \left(\frac{V_c}{V} - 1 \right) + \left(\frac{V_c}{V} - 1 \right)^3 = 0, \quad (1)$$

and so demonstrate that the P , V , T surface of Van der Waals equation exhibits Riemann-Hugoniot catastrophe, which is one of Thom's elementary catastrophes, called cusp catastrophe (Thom³⁾).

^{*)} Preliminary results of this work have been reported at V. Yugoslav Symposium of the Physics of Condensed Matter, Sarajevo, October 1976, *Fizika* 8, Suppl. 1976.

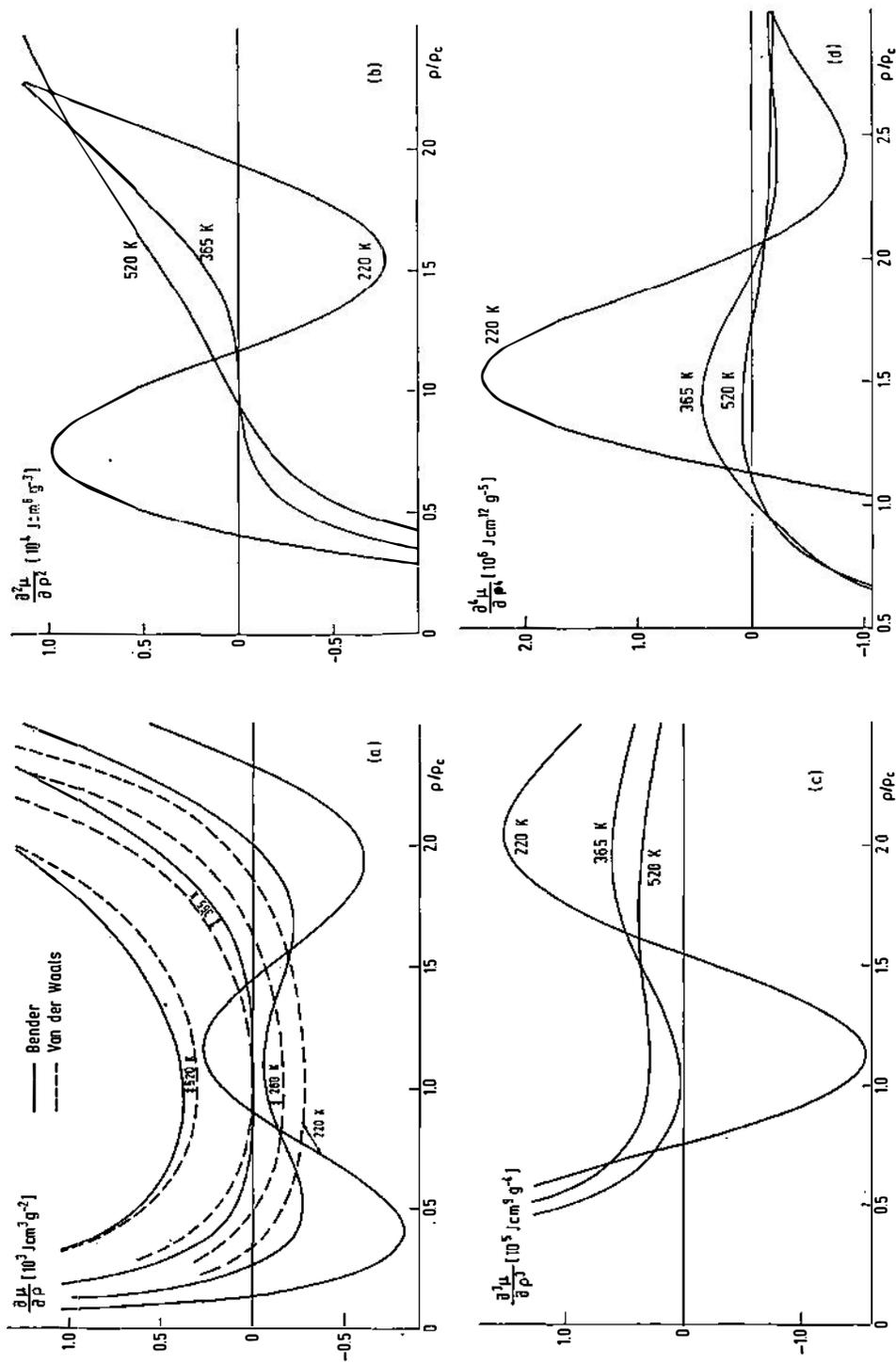


Fig. 1. (a) First derivative of the chemical potential of propylene calculated from Bender's equation ($\partial\mu/\partial\rho$) and from the corresponding Van der Waals equation ($\partial\mu/\partial\rho$) as functions of the reduced density ρ/ρ_c for temperatures above, about and below the critical temperature; (b-d) second, third and fourth derivatives of μ as functions of ρ/ρ_c for three temperatures.

Calculating the first three derivatives of the chemical potential of the Van der Waals gas, say μ_w , with respect to density ρ at $\rho = \rho_c$, we infer from

$$\mu(\rho, T) = \mu(\rho_c, T) + \int_{\rho_c}^{\rho} V dP, \quad (2)$$

($V = 1/\rho$ being the molar volume) and from Van der Waals equation that

$$\begin{aligned} [\mu_w(\rho, T) - \mu_w(\rho_c, T)] - \left[\frac{6P_c V_c^2}{T_c} (T - T_c) \right] (\rho - \rho_c) - \\ - \left[\frac{3}{2} \frac{P_c V_c^4}{T_c} T \right] (\rho - \rho_c)^3 + \text{higher terms in } (\rho - \rho_c) = 0. \end{aligned} \quad (3)$$

Consequently, also the μ_w, ρ, T surface of Van der Waals equation exhibits Riemann-Hugoniot catastrophe.

It has been pointed out by Thom³⁾ and elaborated in more detail by Schulman and Revzen⁴⁾ that the theory of catastrophe would be exactly applicable to the study of thermodynamic surfaces, i. e., to P, P, T or μ, ρ, T surfaces, were it not for the additional, perturbing effect of fluctuations. In particular, in analogy to result (3) we could conclude that the classical behaviour

$$\mu(T_c, \rho) = \mu(T_c, \rho_c) + \frac{1}{n!} (\rho - \rho_c)^n \mu^{(n)}(T_c, \rho_c) + \dots, \quad n = 3, 5, 7, \dots, \quad (4)$$

of the critical isotherm indicates the possibility that real gases exhibit the cusp catastrophe when $n = 3$

$$\mu(T, \rho) = \mu(T, \rho_c) + (\rho - \rho_c) \mu^{(1)}(T, \rho_c) + \frac{1}{6} (\rho - \rho_c)^3 \mu^{(3)}(T, \rho_c) + \dots, \quad (5)$$

for all $T \geq 0$ and $\rho \sim \rho_c$,

where $\mu^{(1)}(T_c, \rho_c) = 0$; or the butterfly catastrophe when $n = 5$

$$\begin{aligned} \mu(T, \rho) = \mu(T, \rho_c) + (\rho - \rho_c) \mu^{(1)}(T, \rho_c) + \frac{1}{2} (\rho - \rho_c)^2 \mu^{(2)}(T, \rho_c) + \\ + \frac{1}{6} (\rho - \rho_c)^3 \mu^{(3)}(T, \rho_c) + \frac{1}{120} (\rho - \rho_c)^5 \mu^{(5)}(T, \rho_c) + \dots, \end{aligned} \quad (6)$$

for all $T \geq 0$ and $\rho \sim \rho_c$,

where $\mu^{(1)}(T_c, \rho_c) = \mu^{(2)}(T_c, \rho_c) = \mu^{(3)}(T_c, \rho_c) = 0$. To wit, there is a possibility that $\partial^2 \mu(\rho_c, T) / \partial \rho^2 = 0$ for $n = 3$ and that for $n = 5$ we have $\partial^4 \mu(\rho_c, T) / \partial \rho^4 = 0$ for all $T \geq 0$.

Since in the case of real gases the fluctuations do influence the shape of the experimentally determined thermodynamic surfaces we cannot expect them to exhibit exactly either the cusp or butterfly catastrophe, especially so in the critical region. We can expect, however, that the topology of μ , ρ , T surfaces of real gases is not distorted beyond recognition by fluctuations and that μ , ρ , T surfaces of real gases would remain sufficiently similar to cusp or butterfly catastrophe (at least outside the critical region) were one of them exhibited in the absence of fluctuations.

2. Analysis of real-gas data

In order to see whether experimentally determined μ , ρ , T surfaces of real gases exhibit cusp-like or butterfly-like behaviour, we took an analytic ansatz (i. e. a classical empirical equation) used by Bender⁵⁾ to reproduce P , ρ , T experimental data of liquid and gaseous propylene, and calculated the first five derivatives of the first five derivatives of the propylene chemical potential $\mu_p(\rho, T)$ with respect to density ρ by Equ. (2) for 30 isotherms over the whole range of experimental data ($220 \text{ K} \leq T \leq 520 \text{ K}$, $0 < \rho/\rho_c \leq 2.71$); first four being plotted in Fig. 1. For comparison we also took the corresponding Van der Waals equation and calculated the first five derivatives of the associated chemical potential μ_w with respect to density and plotted the first one in Fig. 1a. From the behaviour of isothermal derivatives of the chemical potential μ_p as functions of T , we identify four »critical temperatures« as follows (cf. also Fig. 2):

- $T_{c1} = 364.9 \text{ K}$ as the temperature when the graph of $\partial\mu_p(\rho, T)/\partial\rho$ touches the horizontal axis (at $\rho_{c1}/\rho_c = 0.9997$) for the first time with the lowering of temperature, i.e. for $T > T_{c1}$ the equation $\partial\mu_p(\rho, T)/\partial\rho = 0$ does not have a solution for $\rho/\rho_c \in [0, 2.5]$;
- $T_{c2} = 356.7 \text{ K}$ as the temperature at which $\partial^2\mu_p(\rho, T)/\partial\rho^2$ has an inflection point (at $\rho_{c2}/\rho_c = 1.0278$) and below which it displays two local extrema for $\rho/\rho_c \in [0, 2.5]$ at all temperatures $T \in [220 \text{ K}, T_{c2}]$, i. e. at T_{c2} the graph of $\partial^3\mu_p(\rho, T)/\partial\rho^3$ touches the horizontal axis for the first time and thereafter crosses it twice for all temperatures $T \in [220 \text{ K}, T_c]$
- $T_{c3} = 352 \text{ K}$ as the temperature when the graph of $\partial^2\mu_p(\rho, T)/\partial\rho^2$ touches horizontal axis for the first time (at $\rho_{c3}/\rho_c = 1.120$) which it crosses three times for all $T \in [220 \text{ K}, T_{c3}]$, so that for $T \in [220 \text{ K}, T_{c3}]$ the graph of the derivative displays three local extrema: two minima and one maximum; and
- $T_{c4} = 256.6 \text{ K}$ as the temperature at which the local maximum of the first derivative $\partial\mu_p(\rho, T)/\partial\rho$ touches the horizontal axis (at $\rho_{c4}/\rho_c = 1.1285$), so that for all temperatures $T \in [220 \text{ K}, T_{c4}]$ the isotherms of the chemical potential $\mu_p(\rho, T)$ display four local extrema within interval $\rho/\rho_c \in [0, 2.5]$, i.e. two local minima and two maxima.

The zeros of $\partial P/\partial\rho (= \rho\partial\mu/\partial\rho)$ being the same as the zeros of $\partial\mu/\partial\rho$, the corresponding P , ρ isotherms display also two local maxima and two minima for $T < T_{c4}$.

Fig. 1a shows that with lowering of temperature the graph of the first derivative $\partial\mu_p/\partial\rho$ exhibits a general downward movement, getting progressively flatter and flatter and crossing the horizontal axis at $T = T_{c1}$ at the point $\rho = \rho_{c1}$. Within the temperature interval $[T_{c1}, T_{c3}]$ the downward general movement of the graph of $\partial\mu/\partial\rho$ continues. At $T = T_{c3}$ a small part of the graph at $\rho = \rho_{c3}$ starts resting the general downward movements causing a small upwards dent which continues to rise until at $T = T_{c4}$ it reaches the horizontal axis at $\rho = \rho_{c4}$ and keeps rising above it with further lowering of temperature. Fig. 1a clearly brings forth the different behaviour of the first derivative $\partial\mu_w/\partial\rho$ of the chemical potential μ_w associated with the corresponding Van der Waals gas, since for all temperatures $\partial\mu_w/\partial\rho$ as a function of ρ is an upward, parabola-like function moving downwards with the lowering of temperature.

To assist in getting a general view of the way isotherms of $\mu_p(\rho, T)$ change with temperature, we have plotted on Fig. 2 the temperature dependence of the zeros of the fifth, fourth and second isothermal derivatives of the chemical potential $\mu_p(\rho, T)$ with respect to ρ . This picture shows how one zero of $\partial^2\mu_p/\partial\rho^2$ and one zero of $\partial^4\mu_p/\partial\rho^4$ keep more or less together around the critical density for all temperatures $T \in [220 \text{ K}, 520 \text{ K}]$, more so at the critical temperature T_{c1} . Further it is evident that the zero of $\partial\mu_p/\partial\rho$ keeps away from critical density for all temperatures. The way in which two additional zeros of $\partial^2\mu_p/\partial\rho^2$ appear with lowering of temperature at $T = T_{c3}$, in conjunction with the abrupt downward veering of the already existing zero, strongly suggests that this appearance of two additional zeros is actually a masked threeway splitting of the previously simple zero of $\partial^2\mu_p/\partial\rho^2$ above T_{c2} , so that in the undisturbed case we would have $T_{c2} = T_{c3}$. It follows from the definition (6) of butterfly catastrophe that

$$T_{c1} = T_{c2} = T_{c3} = T_{c4} \quad \text{and} \quad \rho_{c1} = \rho_{c2} = \rho_{c3} = \rho_{c4} \quad \text{and} \quad \partial^4\mu(\rho_{c3}, T)/\partial\rho^4 \equiv 0 \quad (7)$$

is the necessary and sufficient condition for the phase transition to be a butterfly catastrophe. Now the temperature dependence of the derivatives of the chemical potential $\mu_p(\rho, T)$ indicates that were $T_{c1} = T_{c2} = T_{c3}$ and $\partial^4\mu(\rho_{c3}, T)/\partial\rho^4 \equiv 0$, relations (7) would hold and there would be a butterfly catastrophe. To sum it up: between T_{c1} and T_{c2} the isotherms of μ_p have one maximum and one minimum as do the isotherms of μ_w ; between T_{c2} and T_{c4} behaviour of isotherm of μ_p gets progressively more and more different from the behaviour of μ_w for $T < T_c$ and below T_{c4} the shape of isotherms of μ_p displays butterfly-like behaviour having two maxima and two minima.

3. Conclusions

As a consequence, if we had to classify the experimentally determined μ_p, ρ, T surface either as a perturbed cusp catastrophe or as a perturbed butterfly catastrophe, we could come to the tentative conclusion that though the behaviour of the μ_p, ρ, T surface is like a perturbed Riemann-Hugeniot catastrophe for temperatures above T_{c2} due to the fact that $\partial^2\mu(\rho_{c3}, T)/\partial\rho^2 \sim 0$ for all T , the overall picture indicates a possibility of a disturbed butterfly catastrophe, disturbance being due either to an inadequate description by Bender's empirical formula, or/and to fluctuations which mask the underlying global behaviour, especially so in the critical region

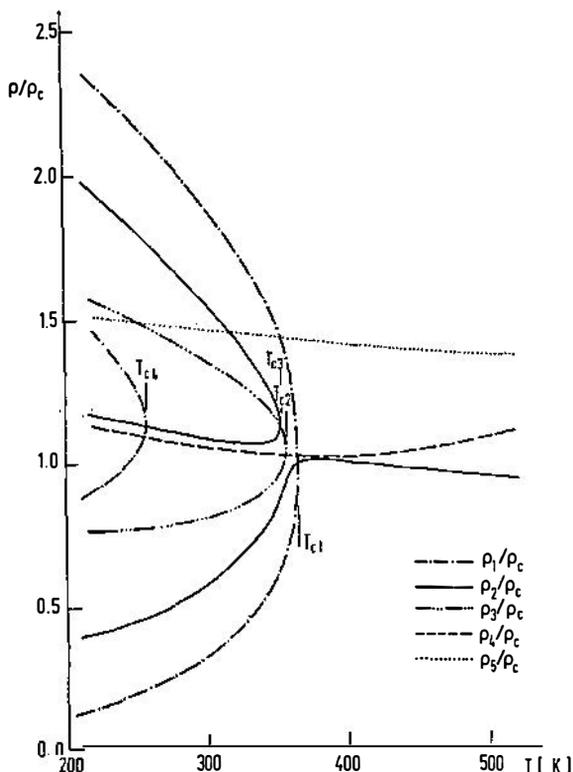


Fig. 2. Zeros of the first, second, third, fourth and fifth derivatives of the chemical potential μ as functions of temperature.

where they render it nonanalytic. Analogous analysis of the empirical formulas of Jacobsen, Stewart and Meyers⁶⁾ for nitrogen and oxygen, Street, Sagan and Staveley⁷⁾ for liquid xenon; Mc Carty⁸⁾ for methane; Street and Staveley⁹⁾ for liquid argon, krypton and xenon; and Bender⁵⁾ for ethylene reveals the same kind of behaviour of associated μ , ρ , T surfaces. Since the analysed empirical formulas do not reproduce experimental data within the measured accuracy, we have analysed directly individual isothermal experimental P , V , T data in order to obtain more precise information and will publish the results separately.

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GLOBALNA OBNAŠANJE EKSPERIMENTALNO DOLOČENIH μ , ρ , T
PLOSKEV REALNIH PLINOV IN »CUSP« IN »BUTTERFLY« KATASTROF

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Vsebina

Da bi dobili eksperimentalno podporo za teorijo katastrof, smo analizirali globalno obnašanje μ , ρ , T ploskev izven kritičnega območja in pri tem uporabili fenomenološke P , ρ , T enačbe stanja za propilen, etilen, tekoči ksenon, tekoči argon, metan, dušik in kisik. Ugotovili smo, da te eksperimentalno določene μ , ρ , T ploskve kažejo poleg značilnosti Riemann-Hugoniot katastrofe še značilnosti »butterfly« katastrofe.