

## CATASTROPHE THEORY AND LIQUID-GAS PHASE TRANSITIONS

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It has been pointed out by Thom 1975 and elaborated in more detail by Schulman and Revzen 1972 that the theory of catastrophes should be applicable to the study of phase transitions in the non-critical region. It is easy to show that the Van der Waals equation of state exhibits the cusp-type of catastrophe in  $\mu$  (chemical potential),  $\rho, T$  representation. We tentatively concluded, therefore, that the classical  $\mu, \rho, T$  equation of state for a gas-liquid phase transition might exhibit the cusp catastrophe:

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

with  $\mu_c^{(1)}(T_c, \rho_c) = 0$  and  $\mu_c^{(3)}(T_c, \rho_c) \neq 0$ ; or the butterfly catastrophe:

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

with  $\mu_B^{(1)}(T_c, \rho_c) = \mu_B^{(2)}(T_c, \rho_c) = \mu_B^{(3)}(T_c, \rho_c) = 0$  and  $\mu_B^{(5)}(T_c, \rho_c) \neq 0$ .

The above expressions imply the following temperature dependence of the first two derivatives of chemical potential: (i)  $\partial \mu_c / \partial \rho$  is a parabola-like function having, in the vicinity of  $\rho = \rho_c$ , only one extremum (minimum) above and below the critical temperature; in contrast  $\partial \mu_B / \partial \rho$  is a parabola-like function having, in the vicinity of  $\rho = \rho_c$ , one extremum (minimum) for  $T \geq T_c$  and three extrema (two minima and one maximum) for  $T < T_c$ . (ii)  $\partial^2 \mu_c / \partial \rho^2$  is an increasing function of  $\rho$ , being zero at  $\rho = \rho_c$ , for all temperatures; whereas  $\partial^2 \mu_B / \partial \rho^2$  is an increasing function for  $T \geq T_c$ , which has two extrema (one minimum and one maximum) for  $T < T_c$ .

In order to see whether  $\mu, \rho, T$  surfaces of real gases show cusp-like or butterfly-like behaviour, we took Bender's (1975) empirical equation reproducing  $\rho, \rho, T$  experimental data of liquid and gaseous propylene and calculated the first five derivatives of the chemical potential  $\mu_{BE}(\rho, T)$  with respect to density for 30 isotherms over the whole range of experimental data ( $220^\circ \text{K} \leq T \leq 520^\circ \text{K}$ ,  $0 < \rho / \rho_c \leq 2.71$ ). Studying the behaviour of the first and second derivative of the chemical potential  $\mu_{BE}(\rho, T)$ , we came to the conclusion that the  $\mu_{BE}, \rho, T$  surface on the whole exhibits more butterfly-like behaviour than cusp-like behaviour.

### References:

Schulman, L.S. and M. Revzen: Phase transitions as catastrophes. *Collective Phenomena* **1**, pp. 43-49 (1972).

Thom, R.: *Structural stability and morphogenesis*, W.A. Benjamin, Inc., Reading, Mass. 1975.