DS 5: The Entropic Fundamental Relation

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1 Deriving the entropic fundamental relation for different systems

(a) We have seen in previous classes that for an ideal gas

$$S = Ns_0 + NR\ln\left[\left(\frac{U}{U_0}\right)^c\left(\frac{V}{V_0}\right)\left(\frac{N}{N_0}\right)^{-(c+1)}\right], \qquad \text{where} \quad s_0 = (c+1)R - \left(\frac{\mu}{T}\right)_0. \tag{1}$$

Does this satisfy the Nernst postulate? What conclusions can you draw from your result?

(b) Now consider an ideal van der Waals fluid, with an equation of state and internal energy given by

$$P = \frac{RT}{v-b} - \frac{a}{v^2}, \qquad \text{and} \qquad u = cRT - \frac{a}{v}, \tag{2}$$

respectively. We will now try to obtain the fundamental relation for such a system.

(i) Prove the *molar relation*

$$\mathrm{d}u = T\mathrm{d}s - P\mathrm{d}v. \tag{3}$$

Hint: "Where is the μ!" you cry? Well, inside the definitions of u, s, and v, of course!

(ii) Write an equation for $\mathrm{d}s$ in terms of v and u. Collect terms *intelligently*, and integrate this equation to get

$$s = Ns_0 + NR\ln\left[(v-b)\left(u+\frac{a}{v}\right)^c\right]. \tag{4}$$

(iii) Does the above answer correspond to the ideal gas entropy when $a \to 0$ and $b \to 0$? Does *this* satisfy the Nernst postulate?

(iv) Using the above relation, find the equation of an van der Waals adiabat (in temperature and volume).

(c) Now, consider a rubber band, which is a bundle of long-chain polymer molecules. The macroscopic quantities we are interested in are the length L, the tension $\mathcal{T}$, the temperature T, and the internal energy U of the rubber band. The length plays a role analogous to volume, and the tension $\mathcal{T}$ is like a negative pressure. The number of moles can represent the number of polymer units, but since that number is fixed in our analysis, we can ignore it.

(i) You are given that for such a system

$$U = cL_0T, \qquad \text{and} \qquad \mathcal{T} = bT\frac{L-L_0}{L_1-L_0}, \quad L_0 < L < L_1, \tag{5}$$

where b and c are constants, L_0 is the un-stretched length of the rubber band, and L_1 represents the elastic limit length.

Find the entropic fundamental relation for such a system.

(ii) For such a rubber band, calculate the fractional change in $(L-L_0)$ that results from an increase of δT in temperature, at constant tension. Express the result in terms of length and temperature.

(iii) If the energy of the unstretched rubber band were to increase *quadratically* with T, find the fundamental equation of the rubber band. Is S extensive in this case?