DS 4:
The Euler and Gibbs-Duhem Relations

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February 15, 2024

1 The Euler relation

(a) Consider the internal energy U in terms of extensive properties $X_1, X_2, \ldots, X_t$. Using the fact that U is an extensive variable, i.e. that

$$U(\lambda S, \lambda X_1, \lambda X_2, \ldots, \lambda X_t) = \lambda U(S, X_1, X_2, \ldots, X_t), \tag{1}$$

show that

$$U(S, X_1, X_2, \ldots, X_t) = \frac{\partial U(\lambda S, \lambda X_1, \ldots)}{\partial(\lambda S)} S + \sum_{j=1}^{t} \frac{\partial U(\lambda S, \lambda X_1, \ldots)}{\partial(\lambda X_j)} X_j. \tag{2}$$

(b) Choosing an intelligent value of λ, show that this just means

$$U = TS + \sum_{j=1}^{t} P_j X_j, \tag{3}$$

where T is the temperature and the P_js are the generalised pressures.

(c) Suppose we have a multicomponent ideal gas with r different types of particles. In this case, show that

$$U = TS - PV + \mu_1 N_1 + \ldots + \mu_r N_r. \tag{4}$$

This is called the *Euler* relation.

(d) Rearrange the above equation to show that in the entropic representation, the Euler relation can be written as

$$S = \sum_{j=0}^{t} F_j X_j. \tag{5}$$

Write out the result for a simple system – say, an r–component ideal gas – in terms of the pressure, temperature, and chemical potentials of the components.

2 The Gibbs-Duhem relation

(i) Show that

$$\mathrm{d}U = T\mathrm{d}S + S\mathrm{d}T + \sum_{j=1}^{t} P_j \mathrm{d}X_j + \sum_{j=1}^{t} X_j \mathrm{d}P_j. \tag{6}$$

(ii) Using the first law of thermodynamics, use your above result to show that

$$S\mathrm{d}T + \sum_{j=1}^{t} X_j \mathrm{d}P_j = 0. \tag{7}$$

(iii) For a single-component system, show that this reduces implies

$$d\mu = -s\,dT + v\,dP. \tag{8}$$

(iv) Let us now see what this implies in the entropy representation. Start by writing the Euler Relation Equation (3) in the entropy representation, and use the differential form of the first law to show that

$$U\,d\left(\frac{1}{T}\right) + V\,d\left(\frac{P}{T}\right) - \sum_{k=1}^{r} N_k\,d\left(\frac{\mu_k}{T}\right) = 0. \tag{9}$$

(v) A particular system obeys two equations of state (A is a constant):

$$\begin{aligned} T &= \frac{3As^2}{v}, \qquad \text{the } \textit{thermal} \text{ equation of state,} \\ P &= \frac{As^3}{v^2}, \qquad \text{the } \textit{mechanical} \text{ equation of state.} \end{aligned} \tag{10}$$

Find μ as a function of s and v, and use it to find U. **Hint:** The Euler relation can be used to find the fundamental relation.

3 An application: electromagnetic radiation

We can apply the Euler relation to the interesting question of electromagnetic radiation. Let us say that you are given the following three facts about electromagnetic radiation:

- $U = bVT^4$, the *Stefan-Boltzmann Law*,
- $P = \dfrac{U}{3V}$,
- $\mu = 0$.

(i) Use the above facts (along with the Euler Relation) to show that

$$S = \frac{4}{3} b^{1/4} U^{3/4} V^{1/4}. \tag{11}$$

(ii) The universe is considered by cosmologists to be an expanding electromagnetic cavity containing radiation that is now at a temperature of $2.7K$. What will be the temperature of the radiation when the volume of the universe is twice its present value? Assume the expansion is isentropic (this being a nonobvious prediction of cosmological model calculations).

(iii) Suppose you could think of radiation as an "ideal gas" of photons (this is highly non-obvious, but imagine that you could). What would be the adiabatic index of such a gas?

(iv) Assuming the electromagnetic radiation filling the universe to be in equilibrium at $T = 2.7K$, what is the pressure associated with this radiation? Express the answer both in pascals and atmospheres. You are given that $b = 7.56 \times 10^{-16} J/m^3K^4$, and 1 Pa = 9.8692×10^{-6} atm.