DS 8:
Engines and Thermodynamic Potentials

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1 The Carnot engine

Consider two identical blocks of metal A and B that are placed inside an insulated container. Suppose that they initially have temperatures are T_{A0} and T_{B0} respectively.

(a) First let us assume that they are simply put into thermal contact with each other, so that heat flows *spontaneously* from one to the other. What is the final temperature? Is any work done? What is the change in the entropy of the system.

(b) Now let us suppose that we try to use this difference in temperature to do useful work. The most efficient way of doing this is by using a Carnot engine. Suppose you naively apply the formula of the Carnot engine: what is the amount of work you would expect to extract from the system? Is this correct? What is wrong in our analysis? (*Answer*: Since the "heat baths" are finite, over one cycle the temperatures of our "reservoirs" has changed.)

(c) To account for this, we need a Carnot cycle that takes and releases *infinitesimal* amounts of heat in each cycle. Let us now suppose that the heat flow between A and B is channelled through a such an engine until they arrive at equilibrium. How does the entropy change? Is any work done? What is the final temperature? *Hint:* For an *infinitesimal* Carnot engine, you have

$$\frac{đQ_H}{đQ_C} = -\frac{T_H}{T_C}, \qquad \text{and} \qquad \mathrm{d}W = đQ_H + đQ_C. \tag{1}$$

2 Free energies

In thermodynamics, a system is defined by the equation of state relating P, V, and T, and one other relation, e.g. the internal energy U as a function of two thermodynamics variables, say T and V. For example, in an ideal gas we have $PV = NT$ and $U = \frac{3}{2}NT$. Both relations can be obtained from the Helmholtz free energy $F = U - TS$.

(a) Show that $\mathrm{d}F = -P\mathrm{d}V - S\mathrm{d}T + \mu\mathrm{d}N$. What are the *natural variables* of F?

(b) Show that

$$P = -\left(\frac{\partial F}{\partial V}\right)_T \qquad \text{and} \qquad U = -T^2\left(\frac{\partial (F/T)}{\partial T}\right)_V, \tag{2}$$

so that both the equation of state and the energy equation can be obtained from F.

(c) What is the physical significance of F, e.g. for a system in a heat bath?