DS 7: Engines and Legendre Transformations

Philip Cherian
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1 A Carnot engine with a van der Waals fluid

(a) Recall that for a van der Waals gas, the entropic fundamental relation is

$$S = Ns_0 + NR\ln\left((v-b)\left(u+\frac{a}{v}\right)^c\right), \qquad \text{and} \qquad u = cRT - \frac{a}{v}. \tag{1}$$

Use the above relations to get the expression for the entropy in terms of T and V.

(b) Compute the work done, the change in internal energy, and the heat exchanged in

(i) The isothermal arms, and

(ii) The adiabatic arms.

(c) Find the net work done in the cycle – and consequently, the efficiency – of this engine.

2 Another engine

(a) Consider an ideal gas that operates in a cycle as follows:

(i) From an initial state (p_1, V_1), it is cooled at constant pressure to (p_1, V_2).

(ii) It is then heated at constant volume to (p_2, V_2).

(iii) The gas then expands adiabatically back to (p_1, V_1).

Sketch the above cycle in PV diagram, and on a TS diagram.

(b) Assuming the heat capacity to be a constant, show that the thermal efficiency of this engine is

$$\eta = 1 - \gamma\left(\frac{(V_1/V_2)-1}{(p_2/p_1)-1}\right). \tag{2}$$

Hint: Remember that along an adiabat pV^γ is a constant, where $\gamma = c_p/c_V$.

3 Thermodynamic potentials

(a) Start with the first law of thermodynamics in its *differential* form:

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N. \tag{3}$$

Convince yourselves that the above equation implies that U is a function of S, V, and N. Now consider the *Helmholtz free energy* F that is a function of T, V, and N. Write down the infinitesimal form of F.

(b) What term would you need to add to $\mathrm{d}U$ so that you get something that looks like $\mathrm{d}F$? Use this to find how one could go from U to F.

(c) Similarly, find an expression for the Gibb's free energy, whose "natural" (or control) variables are T, P, N.

(d) Find an expression for the enthalpy whose natural variables are S, P, N.

(e) Recall that the fundamental equation of an ideal gas in the entropy representation is

$$S = Ns_0 + NR\ln\left[\left(\frac{U}{U_0}\right)^c\left(\frac{V}{V_0}\right)\left(\frac{N}{N_0}\right)^{-(c+1)}\right], \qquad \text{where} \quad s_0 = (c+1)R - \left(\frac{\mu}{T}\right)_0. \tag{4}$$

Use this to find $U(S, V, N)$.

(f) Use your expression for U to get the expression for the Helmholtz free energy $F(T, V, N)$. Find the "equations of state" in this representation.

(g) Repeat the above process in the enthalpy and Gibbs free energy representations.