Sheet 03

Discussion: Thursday 23.05.2024

Exercise 1 Legendre(-Fenchel) transformations (see Chapter 9.2)

Represent the pressure of a simple fluid as a Legendre transform of the energy density E/V.

Exercise 2 Long-range interactions

In Chapters 26 and 27 we have considered internal energies E with short-ranged interactions, which we used to justify the weak-coupling assumption and in consequence the extensivity of E in thermodynamically large systems. Here, we will derive the Gibbs-Duhem relation for long-ranged interactions.

1. For long-ranged interactions, i.e. electromagnetic or gravitational interactions, the interaction energy is
$$E_{\mathrm{lr}} = \frac{\alpha}{2} \int \mathrm{d}^3\mathbf{x} \int \mathrm{d}^3\mathbf{x}' \, \frac{\rho(\mathbf{x})\rho(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|}. \tag{1}$$
What is α, ρ?

2. Express the interaction energy using a potential $\phi(\mathbf{x})$. Split both potentials ϕ and ρ into contributions from the system $\mathcal{S}$ and the environment $\mathcal{E}$.

3. Now terms with different combinations of $\phi_{\mathcal{S}(\mathcal{E})}$, $\rho_{\mathcal{S}(\mathcal{E})}$ occur in E_{lr}. We neglect the energy contribution from interactions within $\mathcal{E}$. We assume that $\mathcal{S}$ is small enough (and sources are distributed in a way) that we can assume constant $\phi_{\mathcal{S}}$, $\rho_{\mathcal{S}}$. Rewrite E_{lr} and $\mathrm{d}E_{\mathrm{lr}}$ in terms of the integrated density $Q_{\mathcal{S}}$. You should arrive at
$$\mathrm{d}E_{\mathrm{lr}} = \phi \mathrm{d}Q_{\mathcal{S}} + Q_{\mathcal{S}} \mathrm{d}\phi_{\mathcal{E}}. \tag{2}$$

4. Consider an electromagnetic potential ϕ^{el}. In the electrostatic case, $Q = zFn$ with z the charge number, F the Faraday constant and $n = N/N_A$ with the number of atoms N.
   - Write down the expression for the total energy E and the respective Gibbs-Duhem relation. The former can be brought into the same form as for short-ranged interactions by renaming $\mu \to \eta$.
   - Furthermore, derive the equilibrium condition by applying a Legendre transformation to a suitable thermodynamic potential.

5. Do the same for the gravitational potential ϕ^{gr}. As we assume small $\mathcal{S}$ we can neglect one of the contributions.