LMU Munich
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Exercises on Mathematical Statistical Physics
Math Sheet 5

Problem 1 (Virial and equipartition theorem). We consider a classical system governed by the Hamilton function $\mathcal{H}(x)$, with $x = (x_1, ..., x_{6N}) = (q, p) = (q_1, ..., q_{3N}, p_1, ..., p_{3N}) \in \mathbb{R}^{6N}$. We denote the time average of a function $f(t)$ by

$$\langle f \rangle := \lim_{T\to\infty} \frac{1}{2T} \int_{-T}^{T} f(t)dt.$$

The classical equipartition theorem states that

$$\left\langle x_i \frac{\partial \mathcal{H}}{\partial x_j} \right\rangle = \delta_{ij} k_B T.$$

a) Prove this statement using the canonical ensemble. Give an argument why this is a sensible way of reasoning. (*You may assume* $\mathcal{H}(x) \to 0$ *for large* $|x|$.)

b) We specialize to a Hamiltonian of the form $\mathcal{H}(q,p) = \sum_{i=1}^{3N} p_i^2 + V(q)$, where V is a *homogeneous function* of degree $n \in \mathbb{Z} \setminus \{0\}$, i.e. satisfies $V(\lambda q) = \lambda^n V(q)\ \forall \lambda > 0$. Prove that the averages of the kinetic and the potential energy are related by the following equation,

$$\langle E_{kin} \rangle = \frac{n}{2} \langle V \rangle,$$

also known as the **virial theorem**.

Problem 2 (H-functional and entropy). We consider a discretized phase space of total volume 1, partitioned into M boxes of volume V. The total number of particles is $N = \sum_{j=1}^{M} n_j$ and we assume that each n_j, the number of particles in box j, is so large that we may apply Stirling's approximation. For this situation, show that the H-functional and the Boltzmann entropy S agree up to a constant shift and a constant prefactor (i.e. $S = C_1 H + C_2$).

Problem 3 (Entropy of an ideal gas). Derive the Sackur-Tetrode equation

$$S = k_B N \ln\left(\frac{V}{N}\left(\frac{4\pi m E}{3h^2 N}\right)^{\frac{3}{2}}\right) + \text{const.} \cdot N$$

for the entropy of an ideal gas with volume V, total energy E and particle number N directly from Boltzmann's formula $S = k_B \ln(W)$. Here, W denotes the phase space volume belonging to the given macro-state. You should assume that the particles are indistinguishable and introduce an auxiliary constant h for dimensional reasons. What if h is chosen differently?

Problem 4 (A different ensemble).

a) Why do we use the word *ensemble*? In the canoncial ensemble, the probability measure is given by

$$\mathbb{P}(A) = \frac{1}{Z}\int_A d^{6N}x e^{-\beta\mathcal{H}(x)}.$$

Z is called canonical partition function. What is Z here, and why is it sufficient for many calculations of average values to know the partition function of an ensemble?

b) An gas of N particles is kept at fixed temperature T and fixed pressure p in a piston with variable volume. We want to calculate average values using the *isothermal-isobaric ensemble*. Understand why the partition function is given by

$$\Delta(p, N, T) = \frac{1}{N! h^{3N} V_0}\int_0^\infty \mathrm{dV} \int \mathrm{d^{6N}x}\; e^{-\beta(\mathcal{H}(x)+pV)}$$

(You need not derive it in any way, but motivate why it has to look like this.)

c) Calculate the average value $\langle V\rangle$ of the volume.

d) Express the volume fluctuations $(\Delta V)^2$ (i.e. the variance of V) by the compressibility (here the thermodynamic quantities, i.e. the average values, are used)

$$c := \frac{1}{V}\frac{\partial V(T, N, p)}{\partial p}.$$

How do they scale with V and what does that have to do with the equivalence of ensembles?

Recommended Reading: There is a link on the website to a short and very interesting review on irreversibility and the Boltzmann equation by Herbert Spohn.

The solutions to these exercises will be discussed on Friday, June 10 and on Monday, June 13.