Mathematical Statistical Physics – LMU München, summer semester 2012

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Homework sheet 5 – due on 25.05.2012 – and exercises for the class on 18.05.2012

5.1 *Grand canonical reference measure and identical particles.* In the grand canonical description of a particle system in the container $\Lambda \subset \mathbb{R}^d$, we "try to" use the phase space

$$\Omega^\Lambda := \dot{\cup}_{n\geq 0}\Omega_n^\Lambda,$$

where Ω_n^Λ is the phase space of an n-particle system, so

$$\Omega_n^\Lambda = (\lambda \times \mathbb{R}^d)^n.$$

We "try to" equip this phase space with the reference measure

$$\lambda^\Lambda = \sum_{n\geq 0} \lambda_{\Omega_n^\Lambda},$$

where $\lambda_{\Omega_n^\Lambda}$ is the Lebesgue measure on Ω_n^Λ, that is $\lambda_{\Omega_n^\Lambda} = (\lambda_\Lambda \otimes \lambda_{\mathbb{R}^d})^{\otimes n}$. Now the Liouville theorem ensures that this measure is invariant under any Hamiltonian dynamics.

(a) Show that the choice of the phase space is consistent in the sense that if $\Lambda = \Lambda_1 \dot{\cup} \Lambda_2$, then $\Omega^\Lambda = \Omega^{\Lambda_1} \times \Omega^{\Lambda_2}$ (with suitable natural identifications).

(b) However, show that the choice of λ^Λ is inconsistent: $\lambda^\Lambda \neq \lambda^{\Lambda_1} \otimes \lambda^{\Lambda_2}$.

(c) Notice that in our choice of the measure we have some "freedom": If we want the Liouville theorem to ensure that the measure is invariant, then any measure of the form

$$\lambda^\Lambda = \sum_{n\geq 0} c_n \lambda_{\Omega_n^\Lambda}$$

will do, with $0 < c_n \in R$. How should we choose the sequence c_n, if we want to ensure also that $\lambda^\Lambda = \lambda^{\Lambda_1} \otimes \lambda^{\Lambda_2}$?

(d) What has this got to do with indistinguishability of the particles?

5.2 *Canonical entropy and patrition function.* The canonical measures $\mu_{\Lambda,\beta,N}$ describing a Hamiltonian particle system (with Hamiltonian $\mathcal{H}$) of N particles in the container $\Lambda \subset \mathbb{R}^d$ are probability measures on the phase space Ω_N^Λ which are absolutely continuous w.r.t. $\lambda_{\Omega_N^\Lambda}$ (see footnote [1]), and have density

$$\rho_{\Lambda,\beta,N}(x) = \frac{1}{Z(\Lambda,\beta,N)} e^{-\beta\mathcal{H}(x)}.$$

See the first exercise for notation. β is a parameter and $Z(\Lambda,\beta,N)$ is the suitable normalizing factor called the "partition function". The canonical entropy S^{can} is defined as the relative entropy

$$S^{can}(\Lambda,\beta,N) = H(\mu_{\Lambda,\beta,N}; \lambda_{\Omega_N^\Lambda}),$$

where H stands for relative entropy (not to be mixed with the Hamiltonian $\mathcal{H}$).

[1] If we want to get "correct dependence on N", we better use $c_N\lambda_{\Omega_N^\Lambda} = \frac{1}{N!}\lambda_{\Omega_N^\Lambda}$ as the reference measure, as we learned from Exercise 5.1 and 4.7

(a) Let E denote the expectation of $\mathcal{H}$ w.r.t. $\mu_{\Lambda,\beta,N}$. Express S^{can} in terms of β, E and Z

i. using the definition of relative entropy,

ii. using the maximum entropy principle.

(b) What is the physical meaning of $\log Z$?

5.3 **(homework)** *Grand canonical entropy and patrition function.* The grand canonical measures $\mu_{\Lambda,\beta,\beta'}$ describing a Hamiltonian particle system (with Hamiltonian $\mathcal{H}$) in the container $\Lambda \subset \mathbb{R}^d$ are probability measures on the phase space Ω^Λ which are absolutely continuous w.r.t. λ^Λ, and have density

$$\rho_{\Lambda,\beta,\beta'}(x) = \frac{1}{Z(\Lambda,\beta,\beta')} e^{-\beta\mathcal{H}(x)-\beta' N(x)}.$$

See the first exercise for notation. Here N denotes the particle counting function $N : \Omega^\Lambda \to \mathbb{N}$, $N(x) = n$ if $x \in \Omega^\Lambda_n$. β and β' are parameters and $Z(\Lambda,\beta,\beta')$ is the suitable normalizing factor called the "partition function". The grand canonical entropy S^{gr} is defined as the relative entropy

$$S^{gr}(\Lambda,\beta,\beta') = H(\mu_{\Lambda,\beta,\beta'}; \lambda^\Lambda),$$

where H again stands for relative entropy (not to be mixed with the Hamiltonian $\mathcal{H}$).

(a) Let E denote the expectation of $\mathcal{H}$ and $\bar{N}$ denote the expectation of N w.r.t. $\mu_{\Lambda,\beta,\beta'}$. Express S^{gr} in terms of β, E, β', $\bar{N}$ and Z

i. using the definition of relative entropy,

ii. using the maximum entropy principle.

(b) What is the physical meaning of $\log Z$?

Solution:

(a) i. For transparency, we omit the non-important arguments of the functions. By definition,

$$S^{gr}(\Lambda,\beta,\beta') = H(\mu_{\Lambda,\beta,\beta'}; \lambda^\Lambda) = -\int_{\Omega^\Lambda} \rho \log \rho \, \mathrm{d}\lambda^\Lambda.$$

Of this, $-\log \rho(x) = \log Z + \beta\mathcal{H}(x) + \beta' N(x)$, so

$$\begin{aligned} S^{gr}(\Lambda,\beta,\beta') &= \log Z \int_{\Omega^\Lambda} \rho \, \mathrm{d}\lambda^\Lambda + \beta \int_{\Omega^\Lambda} \mathcal{H}\rho \, \mathrm{d}\lambda^\Lambda + \beta' \int_{\Omega^\Lambda} N\rho \, \mathrm{d}\lambda^\Lambda = \\ &= \log Z \int_{\Omega^\Lambda} 1 \, \mathrm{d}\mu + \beta \int_{\Omega^\Lambda} \mathcal{H}(x) \, \mathrm{d}\mu(x) + \beta' \int_{\Omega^\Lambda} N(x) \, \mathrm{d}\mu(x) = \\ &= \log Z + \beta E + \beta' \bar{N}. \end{aligned}$$

ii. We use the notation of Exercise 4.6. We apply the maximum entropy principle with $\Omega = \Omega^\Lambda$, $\nu = \lambda^\Lambda$, $n = 2$, $X_1 = \mathcal{H}$, $X_2 = N$, $m_1 = E$, $m_2 = \bar{N}$, $t_1 = \beta$ and $t_2 = \beta'$. With this substitution, the theorem ensures exactly that our grand canonical measure is the measrure on Ω^Λ which has maximum relative entropy w.r.t. λ^Λ, under the constraints $\mathbb{E}_\mu \mathcal{H} = E$ and $\mathbb{E}_\mu N = \bar{N}$. The final statement of the theorem ensures that the relative entropy is

$$S = \beta E + \beta' \bar{N} + \log Z.$$

(b) In thermodynamics, the "grand free energy" or "free entalpy" is defined as

$$G = E - TS - \kappa \bar{N}$$

where T is the temperature and κ is the chemical potential. (The chemical potential is normally denoted by μ, but I would like to avoid confusion.) With our notation, $\beta = \frac{1}{T}$ and $\beta' = -\beta\kappa$, so $G = E - \frac{S}{\beta} + \frac{\beta'}{\beta}\bar{N} = -\frac{1}{\beta}\log Z$, so the physical meaning of $\log Z$ is

$$\log Z = -\beta G = -\frac{G}{T}.$$

5.4 **(homework)** *Canonical description of the free gas.* Consider the free gas with the Hamiltonian given in Exercise 4.7.

(a) Describe the canonical distribution.

(b) Calculate the canonical partition function. Keep the footnote in mind.

(c) Calculate the canonical entropy.

(d) Set $V = Nv$ where V is the volume of Λ, so $S^{can}(\Lambda, \beta, N)$ becomes $S^{can}_{\beta,v}(N)$. How does $S^{can}_{\beta,v}(N)$ scale with N? Compare with the result of Exercise 4.7.

Solution:

(a) According to the canonical distribution, the configurational positions of the n particles are (mutually) independent and identically distributed on Λ (apart from the identification of permutations due to the indistinguishability of the particles). The $d \cdot N = 3N$ moment components are also mutually independent of each other and the configurational positions, and have identical Gaussian distribution with expectation 0 and variance $\frac{m}{\beta}$.

(b) We set $d = dim(\Lambda) = 3$.

$$\begin{aligned} Z(\Lambda, \beta, N) &= \frac{1}{N!} \int\limits_{\Lambda^N \times (\mathbb{R}^3)^N} e^{-\sum_{i=1}^N \frac{\beta}{2m}\vec{p}_i^2} \, \mathrm{d}^{3N}q \, \mathrm{d}^{3N}p = \frac{1}{N!} V^N \left(\int_{-\infty}^{\infty} e^{-\frac{\beta}{2m}p^2} \, \mathrm{d}p \right)^{3N} = \\ &= \frac{V^N}{N!} \left(\frac{2\pi m}{\beta} \right)^{3N/2}. \end{aligned}$$

(c) From Exercise 5.2 we know that $S_{can}(V, \beta, N) = \beta E + \log Z(V, \beta, N)$ where E is the expectation of the energy H with respect to the canonical distribution. E can be calculated in many different ways. Maybe the the easiest is to read it out from the description in point (a):

$$E = \frac{1}{2m} \sum_{i=1}^{N} \sum_{\alpha \in \{x,y,z\}} \mathbb{E}_{can} p_{i\alpha}^2 = \frac{3N}{2m} \mathrm{Var}(p_{1x}) = \frac{3N}{2m}\frac{m}{\beta} = \frac{3N}{2\beta},$$

so

$$S_{can}(V, \beta, N) = \frac{3N}{2} + N \log V - \log N! + \frac{3N}{2} \log \frac{2\pi m}{\beta}.$$

(d) From the Stirling formula $\log N! = N \log N - N + O(\log N)$, so

$$S_{can}(V, \beta, N) = \frac{3N}{2} + N \log V - N \log N + N + \frac{3N}{2} \log \frac{2\pi m}{\beta} + O(\log N),$$

and

$$
\begin{aligned}
S^{can}_{\beta,v}(N) &= N\left(\frac{5}{2}+\log\frac{V}{N}+\frac{3}{2}\log\frac{2\pi m}{\beta}\right)+O(\log N)= \\
&= N\left(\frac{5}{2}+\log v+\frac{3}{2}\log\frac{2\pi m}{\beta}\right)+O(\log N).
\end{aligned}
$$

In particular,

$$
\lim_{N\to\infty}\frac{S^{can}_{\beta,v}(N)}{N}=\frac{5}{2}+\log v+\frac{3}{2}\log\frac{2\pi m}{\beta}.
$$

This is in perfect agreement with the result of Exercise 4.7 if we substitute u – which denotes the (deterministic) energy per particle in that exercise – with $\frac{E}{N}=\frac{3}{2\beta}$, which is the (expectation of the) same quantity here.

5.5 *Grand canonical description of the free gas.* Consider the free gas with the Hamiltonian given in Exercise 4.7.

(a) Describe the grand canonical distribution.

(b) Calculate the grand canonical partition function. Keep the footnote in mind.

(c) Calculate the grand canonical entropy.

(d) Let V be the volume of Λ. How does $S^{gr}(V,\beta,\beta')$ scale with V? Compare with the result of Exercise 4.7. and the previous exercise.

5.6 **(homework)** *Free gas with several types of particles.* Consider a container which is devided into k parts, separated by thin walls. Each part has volume V_k and contains N_k identical particles of a free gas, which, however, differ from the particles in other compartments. The system is in equilibrium as much as it can be: exchange of energy is allowed. Now we remove the walls, and wait for equilibrium to be reached again. How much does the entropy change?

Solution 1: using the strict definition, avoiding unnecessary calculations. Before the solution, one is welcome to choose between the microcanonical and the canonical description of the free gas. Both approaches lead to a correct solution, and the result will be the same. The canonical description may be a little easier from a conceptual point of view.

The question is only about the *change* in the entropy, so an explicit calculation of the entropy is not needed – it is enough to understand the V-dependence. With that in mind, there is no serious difference between the microcanonical and the canonical description:

- In the microcanonical description we are interested in the V_i-dependence of

$$
S(V_1,V_2,\ldots,V_k,N_1,N_2,\ldots,N_k,E)
$$

while E and the N_i are kept fixed.

- In the canonical description we are interested in the V_i-dependence of

$$
S(V_1,V_2,\ldots,V_k,N_1,N_2,\ldots,N_k,\beta)
$$

while β and the N_i are kept fixed.

In both cases, it's enough to consider the change in the value of $\log Z$:

- In the microcanonical description $S = \log Z$,
- In the canonical description $S = \beta E + \log Z = \frac{3}{2}(N_1 + \cdots + N_k) + \log Z$, and the particle numbers don't change.

The partition function Z is an integral, over the phase space, of some "weight function". The domain of that integral (the phase space itself) is different in the microcanonical and the canonical setting, and so is the function to integrate. However, in both settings, they have two crucial properties:

- the phase space is a product of the configuration space and the velocity space,
- the weight function we are integrating *does not depend on the configuration point.* (Here it is important that the particles are noninteracting, so the Hamiltonian doesn't depend on the configuration.)

As a result, in the integral Z, the volume of the configuration space appears as a *factor* multiplying the rest of the integral. But the configuration space is nothing else than the Cartesian product of the domains into which the $N = N_1 + \cdots + N_k$ particles are confined (apart from some identification of the particles), so its volume is just the product of these N volumes (apart from some normalizing factors coming from the idetification, which do not depend on the V_i). Thus

- $Z_{micr}(V_1, V_2, \ldots, V_k, N_1, N_2, \ldots, N_k, E) = V_1^{N_1} V_2^{N_2} \ldots V_k^{N_k} \cdot z_{micr}(N_1, N_2, \ldots, N_k, E)$,
- $Z_{can}(V_1, V_2, \ldots, V_k, N_1, N_2, \ldots, N_k, \beta) = V_1^{N_1} V_2^{N_2} \ldots V_k^{N_k} \cdot z_{can}(N_1, N_2, \ldots, N_k, \beta)$.

In both cases, removing the walls means replacing every V_i with $V := V_1 + \cdots + V_k$, so

$$\begin{aligned} S_{after} - S_{before} &= \log Z_{after} - \log Z_{before} = \log \frac{Z_{after}}{Z_{before}} = \\ &= \log \left(\left(\frac{V}{V_1} \right)^{N_1} \cdots \left(\frac{V}{V_k} \right)^{N_k} \right) = \sum_{i=1}^{k} N_i \log \frac{V}{V_i}. \end{aligned}$$

Solution 2: using the canonical distribution, understanding what it is. If we use the canonical measure to describe the free gas, then all the positions and velocities of all the particles are completely (mutually) independent – see Exercise 5.4. (One only has to be careful about non-distinguishability of the particles.) So, according to the canonical measure, the k subsystems (containig N_k particles each) are mutually independent, i.e. they "don't know about each other", even after the walls are removed. To be precise: the joint distribution is a product measure, Z is just the product of the Z_i-s of the subsystems, and S is exactly the sum of the S_i. So one can rigorously write **in the canonical setting**

$$\Delta S = \sum_{i=1}^{k} \Delta S_i,$$

where

$$\Delta S_i = S_{can}(V, N_i, \beta) - S_{can}(V_i, N_i, \beta) = N_i \log V - N_i \log V_i$$

from Exercise 5.4. This gives

$$S_{after} - S_{before} = \sum_{i=1}^{k} N_i \log \frac{V}{V_i}.$$

(Note that this argument *does not work in the microcanonical setting*: the "entropy of the subsystems" doesn't really make sense, since there is only one total energy E.)

Solution 3: canonical setting, by explicit calculation of the entropy. The calculation of Exercise 5.4 can easily be repeated with k different kinds of particles, with particle numbers N_i, masses m_i and constrained to the domains Λ_i each. A possible overlap of these domains plays no role, and the result is

$$S(V_1, \ldots, V_k, N_1, \ldots, N_k, \beta) = \sum_{i=1}^{k} \left[\frac{3N_i}{2} + N_i \log \left(V_i \left(\frac{2\pi m_i}{\beta} \right)^{d/2} \right) - \log N_i! \right].$$

So

$$S_{after} - S_{before} = S(V, \ldots, V, N_1, \ldots, N_k, \beta) - S(V_1, \ldots, V_k, N_1, \ldots, N_k, \beta) = \sum_{i=1}^{k} N_i \log \frac{V}{V_i}.$$

Solution 4: microcanonical setting, by explicit calculation of the entropy. If all masses are equal, the explicit calculation of the microcanonical entropy as done in the solution of Exercise 4.7, can be repeated in the setting of several kinds of particles. If the masses are *not equal*, the calculation is more difficult, since the constant energy surface is no longer a sphere in the velocity space, and $|\nabla H|$ is not constant. After overcoming that difficulty, we get

$$Z_{micr}(V_1, \ldots, V_k, N_1, \ldots, N_k, E) = \frac{1}{E} \frac{E^{3N/2}}{\Gamma(\frac{3N}{2})} \prod_{i=1}^{k} \frac{V_i^{N_i} m_i^{3N_i/2}}{N_i!}.$$

So

$$S_{after} - S_{before} = \log \frac{Z_{micr}(V, \ldots, V, N_1, \ldots, N_k, E)}{Z_{micr}(V_1, \ldots, V_k, N_1, \ldots, N_k, E)} = \sum_{i=1}^{k} N_i \log \frac{V}{V_i}.$$

5.7 *Grand canonical description of the free gas and the Poisson process.* Consider the grand canonical ensamble of the free gas in a container Λ with parameters β, β'.

(a) Let $\Lambda_1 \subset \Lambda$. What is the distribution of the (random) number N_1 of particles that are in Λ_1?

(b) Let Λ_1 and Λ_2 be two *disjoint* subsets of Λ. (That is, $\Lambda_1, \Lambda_2 \subset \Lambda$, $\Lambda_1 \cap \Lambda_2 = \emptyset$.) Let N_i denote the (random) number of particles in Λ_i ($i = 1, 2$). What is the *joint distribution* of N_1 and N_2?