Tutorial, 15 Nov 2013

This is the second edition of tutorial. It differs by presence of question 4.c and absence of section 8 (which was not compulsory). Other changes are only to give extra hints and to clarify questions.

You are free to ask any questions about this tutorial or about any HomeWork assignments now, or after the classes. You can also contact me with your questions any other time by vel145@gmail.com.

It is possible to schedule meeting during off-lecture hours to discuss any subject that you don't understand (including homework). E-mail me or ask me in person for that. However, I expect that you do basic preparatory work before such meeting.

1. **Method of Lagrange multiplier.**

   Example explained: Find the maximum of the function $F(x, y) = x\,y$ if x and y satisfy constraint $x^2 + y^2 - 1 = 0$ (i.e. they describe a point on a circle of unit radius).

   A possible **straightforward solution** is to explicitly solve the constraint by $y = \pm\sqrt{1 - x^2}$, and make F depending only on the one variable x: $F(x, y(x)) = \pm x\,\sqrt{1 - x^2}$. Then we can find extrema of F by equating its derivative to zero:

   $$
   \begin{aligned}
   0 &= \frac{d}{dx}\left(\pm x\,\sqrt{1 - x^2}\right) = \pm\left(\sqrt{1 - x^2} - \frac{x^2}{\sqrt{1 - x^2}}\right) \\
   &= \pm\left(\frac{1 - 2x^2}{\sqrt{1 - x^2}}\right)
   \end{aligned}
   \tag{1}
   $$

   Hence we get 4 extremal points given by $\{x = \pm 1/\sqrt{2}, y = \pm 1/\sqrt{2}\}$. Then it is obvious to find the maximal value: $F = 1/2$.

   Solution of the same problem **using the Lagrange multiplier** goes as follows. One considers equations[1]

   $$
   \begin{aligned}
   0 &= \frac{\partial}{\partial x}\left(F + \lambda \times \text{constraint}\right) = \frac{\partial}{\partial x}(xy + \lambda(x^2 + y^2 - 1)) = y + 2\,\lambda\,x\,, \\
   0 &= \frac{\partial}{\partial y}\left(F + \lambda \times \text{constraint}\right) = \frac{\partial}{\partial y}(xy + \lambda(x^2 + y^2 - 1)) = x + 2\,\lambda\,y\,.
   \end{aligned}
   \tag{2}
   $$

   The introduced above unknown constant λ is called Lagrange multiplier. It multiplies the constraint we want to satisfy.

   We solve equations (2) together with the constraint $x^2 + y^2 - 1 = 0$, i.e. we solve 3 equations on 3 variables (x, y, λ). For instance, from (2) we see that $\lambda = -\frac{y}{2x} = -\frac{x}{2y}$, therefore $x = \pm y$, and we immediately conclude from the constraint that $x^2 = y^2 = 1/2$, i.e. the same answer as using the straightforward method.

   In many situations the method of Lagrange multiplier is easier to apply than the straightforward method because it does not require explicit solution of imposed constraints.

   Generic situation. The method of Lagrange multiplier allows one to find an extremum of a function $F(x_1, x_2, \ldots, x_n)$ under condition that n variables x_i are not independent, i.e. that they satisfy relations $C_\alpha(x_1, x_2, \ldots, x_n) = 0$ for $\alpha \in \overline{1, k}$; k is the number of constraints imposed. In the above-discussed example $C = x^2 + y^2 - 1$.

   To solve such problem, one introduces k new parameters λ_α (Lagrange multipliers) and solve the following system of equations:

   $$
   \frac{\partial}{\partial x_i}\left(F + \sum_\alpha \lambda_\alpha C_\alpha\right) = 0\,, \quad i \in \overline{1, n}\,,
   \tag{3}
   $$

   $$
   C_\alpha = 0\,.
   \tag{4}
   $$

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[1] partial derivative in x means that y is fixed and vice versa.

These are $n + k$ equations to fix $n + k$ quantities (x's and λ's). In equations (3) constraint $C_\alpha = 0$ is imposed *after* differentiation, therefore, generically, $\frac{\partial C_\alpha}{\partial x_i} \neq 0$.

Exercises[2]:

(a) Find positions on the curve $2x^2 + xy + 2y^2 = 1$ which are the closest and the furthest from the origin (hint: it is easier to work with the square of the distance than with the distance itself).

(b) We discussed on the last lecture that the statistical weight of the configuration in which n_α subsystems are in α-s eigenstate is given by

$$W = \frac{M!}{\prod_\alpha n_\alpha!} \, . \tag{5}$$

Two constraints should be satisfied:

$$\sum_\alpha n_\alpha \;=\; M \quad \text{(number } M \text{ of subsystems is fixed)}, \tag{6a}$$

$$\sum_\alpha n_\alpha E_\alpha \;=\; E \quad \text{(total energy } E \text{ is fixed)}. \tag{6b}$$

E_α above is the energy of the α-s eigenstate.

Using the method of Lagrange multiplier and approximating $\log x! \simeq x \log x - x$, derive the canonical ensemble distribution:

$$n_\alpha = \text{const} \times e^{-\beta\, E_\alpha}, \tag{7}$$

where "const" and β are numbers that are the same for all α's.

You are not required to find "const" and β explicitly.

Hint: it is technically easier to maximize $\log W$ than W.

(c) Repeat the same consideration as above, but for the case when the number of particles in a given subsystem can change. For this consider labeling α that labels both number of particles in the subsystem, N_α, and an eigenstate with energy E_α. Total number of particles should be conserved, this produces you an extra constraint.

Derive the grand canonical ensemble distribution:

$$n_\alpha = \text{const} \times e^{-\beta E_a + \beta\, \mu\, N_\alpha} \tag{8}$$

μ is called chemical potential.

2. When the number of particles is not constant, change of energy can be also due to the change of number of particles:

$$dE = TdS - PdV + \mu\, dN. \tag{9}$$

Consider two systems that are separated by a movable barrier which allows both heat and particle transfer between two systems. Show that if these systems are in equilibrium with each other, they have the same value of P, T, μ.

Use that, because the two systems are fully isolated from outside world, the total entropy $S = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2)$ is maximal and total $E = E_1 + E_2$, $V = V_1 + V_2$, $N = N_1 + N_2$ are constant.

3. **Basics about averages**

Suppose that for quantity X you know all its n-th moments[3]: $\langle X^n \rangle$. Denote by $\bar{X} \equiv \langle X \rangle$.

(a) Compute mean square deviation[4] of X ($\langle (\delta X)^2 \rangle \equiv \langle (X - \bar{X})^2 \rangle$) in terms of moments.

(b) For Y being mean over M measurements of X ($Y = \frac{1}{M}(X_1 + X_2 + \ldots X_M)$), compare $\frac{\langle (\delta X)^2 \rangle}{\langle X \rangle^2}$ and $\frac{\langle (\delta Y)^2 \rangle}{\langle Y \rangle^2}$.

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[2]If you want to practice more, type "Lagrange multiplier" in any research engine and you will immediately get hundreds of exercises.

[3]Here moments are understood in the sense of statistics (type "moment (mathematics)" for definition in wikipedia. Do not confuse with particle momentum.

[4]Also known as variance

4. **Microcanonical ensemble**

   (a) *Skip this question if you did it in the problem set N5.* Find the surface area σ_D of $(D-1)$-dimensional sphere (sphere surrounding D-dimensional ball) of unit radius. Check your result against known low-dimensional answers: $\sigma_1 = 2$, $\sigma_2 = 2\pi$, $\sigma_3 = 4\pi$.

   Hint: compute the product of integrals $\prod_{i=1}^{D} \int_{-\infty}^{+\infty} e^{-x_i^2} dx_i$ directly and by passing to spherical coordinates: $d^D x = r^{D-1} dx\, d\Omega$, where Ω is spherical angle. You do not need to write $d\Omega$ explicitly (like $d\Omega = \sin\theta\, d\theta\, d\phi$ in $D = 3$), it is enough to know that $\int d\Omega = \sigma_D$.

   If in doubt, try explicit cases with $D = 1, 2, 3$ first.

   (b) During lecture we discussed that the entropy is directly computable in the microcanonical ensemble:

   $$e^{S(E)} = \int \delta(E - \mathcal{H}(\Gamma))\, d\Gamma, \tag{10}$$

   where the integral is over whole phase space.

   Consider the classical ideal gas of N particles that occupies volume V in D dimensions (real-world case is $D = 3$). The Hamiltonian of the ideal gas is given by $\mathcal{H} = \sum_{i=1}^{N} \frac{p_i^2}{2m}$ and the measure of integration is given by $d\Gamma = \prod_{i=1}^{N} \frac{d^D p_i\, d^D q_i}{(2\pi\hbar)^D}$. When necessary use that $N \gg 1$, in particular use Stirling formula.

   Task: Compute the entropy of the ideal gas using (10). You should get:

   $$S = N \log\left[V \left(\frac{2mE}{(2\pi\hbar)^2}\right)^{D/2}\right] + \log \sigma_{N\times D} = N \log\left[V \left(\frac{E}{N}\right)^{D/2} \times \left(\frac{m\,e}{\pi\hbar^2 D}\right)^{D/2}\right]. \tag{11}$$

   Hint: it is convenient to consider all momenta as one $N \times D$-dimensional vector and integrate over this $N \times D$-dimensional space by introducing spherical coordinates.

   Hint: if in doubt, first consider some small explicit values of N and D, e.g. $N = 1, D = 1$.

   (c) The answer above is obviously wrong because it is not extensive quantity.
   We therefore should correct (10). Can you guess how? (Hint: particles are indistinguishable).

   (d) On the previous step you should obtain $S(E, V)$ as a function of energy and volume. Compute the temperature of the system using the *definition* of the temperature:

   $$\frac{1}{T} \equiv \frac{\partial S}{\partial E}_{|V} \tag{12}$$

   Use the obtained answer to express energy in terms of temperature.

   (e) From the knowledge of $S(E, V)$, express energy as $E(S, V)$. Compute pressure of the ideal gas using this expression and $P = -\frac{\partial E}{\partial V}_{|S}$. Obtain equation of state for the ideal gas.

   (f) Compute C_P and C_V for the ideal gas.

5. (Problem 5.2 from K. Huang) A room of volume $3 \times 3 \times 3\, m^3$ contains air at $T = 300K$ and $P = 10^5$Pa. Estimate the probability that you will find a $1cm^3$ volume somewhere in the room totally devoid of air, due to statistical fluctuations. Do the same for a $10^{-30} m^3$ volume. Will this probability change if we heat the gas keeping its volume fixed?

6. **Saddle point approximation.** In the integral of type $\int_{-\infty}^{+\infty} f(x)^N dx$, if $N \gg 1$, the value of the integral is approximated by its value at maximum of f. More precisely, consider:

   $$\int dx f(x)^N = \int dx e^{N \log f(x)} \simeq e^{N \log f(x_{max})} \times \int dx\, e^{\frac{(x - x_{max})^2}{2} N \partial_x^2 \log f}, \tag{13}$$

   where $x_{\max}$ is the value of x at which f has its maximum. For this reason second derivative should be negative, and we get the gaussian integral which can be taken. So our approximation is:

   $$\int_{-\infty}^{+\infty} f(x)^N dx \simeq e^{N \log f(x_{\max})} \sqrt{\frac{2\pi}{-N \partial_x^2 \log f}} \left(1 + \mathcal{O}(1/\sqrt{N})\right). \tag{14}$$

Task: Compute, using the saddle point approximation:

$$\mathcal{I}(N) = \int_{-\infty}^{+\infty} \left(\frac{1}{1+x^2} \right)^{\pi N} dx \,. \tag{15}$$

To check your result, compare it with numerical data for various N:

N	1	4	9	16	25	36
$\mathcal{I}$	1.14308	0.515566	0.337837	0.251885	0.200961	0.167222

Note: saddle point approximation is typical for statistical physics. We have the natural large parameter N – the number of particles.

7. **Canonical ensemble** Let $\rho(\Gamma)d\Gamma = e^{-\beta \mathcal{H}(\Gamma)}d\Gamma$ is non-normalized probability density distribution. The normalized version would be then $\chi(\Gamma)d\Gamma = \frac{1}{Z}\rho(\Gamma)d\Gamma$, where

$$Z = \int \rho(\Gamma)\,d\Gamma \,. \tag{16}$$

Z is called partition function. It will be one of the tasks below to show that $\mathcal{F} \equiv -T \log Z$ is nothing but the thermodynamic's Free energy. For the moment consider $\mathcal{F}$ as it is defined above. Clearly, it is a function with natural variables T and V

(a) Express $\bar{E} \equiv \langle E \rangle \equiv \int \mathcal{H}(\Gamma)\chi(\Gamma)\,d\Gamma$ in terms of derivatives of $\mathcal{F}$ or Z with respect to T.
Hint: consider $\partial_\beta Z$ to get an idea.

(b) Express $\langle (\delta E)^2 \rangle$ in terms of derivatives of $\mathcal{F}$ or Z with respect to T. Assuming that $\mathcal{F}$ is extensive quantity discuss how $\sqrt{\langle (\delta E)^2 \rangle}/\langle E \rangle$ depends on the number of particles.

(c) Find $\mathcal{F}$, $\langle E \rangle$, $\langle (\delta E)^2 \rangle$ for the ideal gas. Definitions for $\mathcal{H}$ and $d\Gamma$ are the same as above.

(d) Show that Z can be computed as follows:

$$Z = \int_0^E dE\, e^{-\frac{E}{T}+S(E)} \,, \tag{17}$$

where $S(E)$ is defined by (10). Hence $e^{-E/T+S(E)}$ is the probability distribution for possible values of energies.

(e) Using explicit expressions for the ideal gas, plot $e^{-E/T+S(E)}$ against E. Observe how the structure of the plot changes if we change $N \times D$ from $N \times D = 1$ to $N \times D \gg 1$.

(f) The definition of entropy as $S = \log W$ is valid for the case when all microstates of the system are equally probable. In general, if the probability function P_Γ (or density distribution $\chi(\Gamma)d\Gamma$ in continuous case) is non-constant, one should use more generic definition:

$$\mathbf{S} = -\sum_\Gamma P_\Gamma \log P_\Gamma \quad \text{for discrete case}\,,$$

$$\mathbf{S} = -\int \chi(\Gamma) \log \chi(\Gamma)d\Gamma \quad \text{for continuous case}\,. \tag{18}$$

Show that $\mathbf{S}$ defined in such a way is still an additive quantity (provided that $\chi(\Gamma)$ is normalized: $\int \chi d\Gamma = 1$. Check that for $P_\Gamma = \text{const}$ we recover definition $S = \log W$.

(g) Using $\mathbf{S}$ defined by (18) for canonical ensemble, show that $\mathcal{F} = \langle E \rangle - T\,\mathbf{S}$. Find $\mathbf{S}$ in terms of derivatives of $\mathcal{F}$ with respect to T (make this derivation based on definition (18)).

(h) Verify for ideal gas that $\mathbf{S}$ for canonical ensemble coincides with S defined by (10).

(i) Recall that $e^{-E/T+S(E)}$ is extremely picked around $E = \langle E \rangle$. Use this fact to explain why S and $\mathbf{S}$ are actually the same quantities (recall saddle point approximation).