L3 et Magistère de physique fondamentale — Université Paris-Sud

Partial Exam of Statistical Physics

March 14, 2019

Duration : **2 hours.**

The use of documents, mobile phones, calculators, . . . , is forbidden.

Recommendations :

Read the text carefully and **write** out your answers as *succinctly* and as *clearly* as possible. Check your calculations (dimensional analysis, etc.) ; do not forget to **reread yourself**.

⚠ Check the **informations at the end of the text** ⚠

Question related to the lectures : Entropy (~ 15mn)

1/ We consider an ensemble of occupation probabilities of microstates denoted by $\{P_\ell\}$. Give the Gibbs-Shannon entropy, $S(\{P_\ell\})$, for this probability distribution.

2/ Deduce the expression of the microcanonical entropy S^* by applying the above expression to the microcanonical distribution $P^*_\ell = 1/\Omega$ for $\ell = 1, \cdots, \Omega$ (the total number of available microstates).

3/ We now consider the canonical distribution $P^{\rm c}_\ell = (1/Z)\,\mathrm{e}^{-\beta E_\ell}$ with $\beta \stackrel{\rm def}{=} 1/(k_B T)$. Give the definition of the free energy F and recover the expression of the canonical entropy $S^{\rm c}$ in terms of F and the average energy $\overline{E}^{\rm c}$.

4/ Show that $S^{\rm c} = -\frac{\partial F}{\partial T}$.

1 The virial theorem ($\sim 20 + 40$mn)

We consider a system of N atoms whose $6N$ coordinates are denoted by $\vec{\Gamma} \equiv (q_1, \cdots, q_{3N}, p_1, \cdots, p_{3N})$ and its Hamiltonian reads $H(\vec{\Gamma})$. In this problem, we consider an **isolated** system, at equilibrium, described within the **classical** framework.

⚠ The parts **A** and **B** are independent (however treating part **A** could help for part **B**) ⚠

A. Preliminaries : the classical perfect gas.— In this part, we assume that the N atoms interact weakly enough to justify the perfect gas hypothesis, i.e. $H(\vec{\Gamma}) = H_{\rm kin}(p_1, \cdots, p_{3N}) = \sum_{i=1}^{3N} \frac{1}{2m} p_i^2$. The atoms are confined in a box of volume V.

1/ Express the number $\Phi_N(E)$ of microstates of energy less than E as an integral in phase space. Calculate this integral.

2/ If the energy is fixed within some uncertainty δE, provide the relation between the number of available microstates $\Omega_N(E)$ and $\Phi_N(E)$.

3/ Show that the microcanonical entropy $S^*(E,N,V)$ can be expressed as a function of $\Phi_N(E)$ (when supposing $N \gg 1$). Deduce an expression for $S^*(E,N,V)$ emphasizing the *extensivity* property of the entropy.

4/ Recall the definition of the microcanonical temperature T^*. Calculate T^* for the monoatomic gas.

B. The virial theorem

Introduction.— In the framework of *classical mechanics*, Rudolf Clausius obtained in 1870 a relation (the virial theorem) between the two following time averages :

$$\overline{H_{\mathrm{kin}}}^{(\mathcal{T})} = -\frac{1}{2}\overline{\sum_{k=1}^{N} \vec{r}_k \cdot \vec{F}_k}^{(\mathcal{T})} \,, \tag{1}$$

which is valid for an isolated stable system (in a macroscopic equilibrium) of N particles ; $\vec{r}_k$ and $\vec{F}_k$ are the position of the particle k and the resultant forces exerted on it, respectively. The goal of this part **B** is to obtain a relation analogous to Eq. (1) however in the framework of *statistical physics*.

We consider an Hamiltonian in the form $H(\vec{\Gamma}) = H_{\mathrm{kin}}(p_1, \cdots, p_{3N}) + U(q_1, \cdots, q_{3N})$, where U gathers the effect of an external potential and the interactions, if any. The *only* necessary hypothesis is that the system must be confined in a finite area of space and be at equilibrium. We introduce

$$V_N(E) \stackrel{\mathrm{def}}{=} \int \theta_{\mathrm{H}}(E - H(\vec{\Gamma}))\, \mathrm{d}^{6N}\vec{\Gamma} \quad \text{et} \quad \Sigma_N(E) \stackrel{\mathrm{def}}{=} V_N'(E) = \int \delta(E - H(\vec{\Gamma}))\, \mathrm{d}^{6N}\vec{\Gamma} \tag{2}$$

where $\theta_{\mathrm{H}}(x)$ denotes the Heaviside function ($\theta_{\mathrm{H}}(x) = 1$ for $x > 0$ and $\theta_{\mathrm{H}}(x) = 0$ for $x < 0$).

1/ Recall the expression for the microcanonical distribution $\rho^*(\vec{\Gamma})$.

2/ Justify that the microcanonical average can be written under the following form

$$\left\langle q_i \frac{\partial H}{\partial q_j} \right\rangle = \frac{1}{\Sigma_N(E)} \int q_i \frac{\partial H(\vec{\Gamma})}{\partial q_j}\, \delta(E - H(\vec{\Gamma}))\, \mathrm{d}^{6N}\vec{\Gamma} \tag{3}$$

3/ Justify that $\lim_{q_i \to \pm\infty} \theta_{\mathrm{H}}\left(E - H(\vec{\Gamma})\right) = 0$ (and also $\lim_{q_i \to \pm\infty} q_i\ \theta_{\mathrm{H}}\left(E - H(\vec{\Gamma})\right) = 0$).

4/ Deduce that

$$\left\langle q_i \frac{\partial H}{\partial q_j} \right\rangle = \delta_{i,j} \frac{V_N(E)}{\Sigma_N(E)} \tag{4}$$

5/ Justify that in the limit $N \gg 1$, we can write the microcanonical entropy $S^* \simeq k_B \ln V_N(E) +$ const, up to a constant independent of E. To which thermodynamic quantity is related the ratio $V_N(E)/\Sigma_N(E)$?

6/ Deduce

$$\sum_{i=1}^{3N} \left\langle q_i \frac{\partial H}{\partial q_i} \right\rangle = c\, T^* \,, \tag{5}$$

and provide the expression of the constant c as a function of N and k_B. Discuss the relation with the equation (1) of the virial theorem obtained in the Newtonian framework.

7/ Which other famous theorem of statiscal physics can be eventually seen as a particular case of this relation (for a specific form of the Hamiltonian) ?

2 Fluctuations of energy ($\sim$ 40mn)

We consider a system in contact with a thermostat which fixes its temperature T. A microstate is indexed by one (or several) indices ℓ and its energy is noted E_ℓ.

1/ Recall the definition of the canonical partition function Z where we introduce $\beta \stackrel{\text{def}}{=} 1/(k_B T)$.

2/ Show that the average energy is given by $\overline{E}^{\text{c}} = \big(-\frac{\partial}{\partial\beta}\big)\ln Z$.

3/ We recall that the energy variance is given by $\kappa_2 \stackrel{\text{def}}{=} \overline{(E-\overline{E}^{\text{c}})^2}^{\text{c}} = \big(-\frac{\partial}{\partial\beta}\big)^2 \ln Z$. Show that it is related to the specific heat $C_V \stackrel{\text{def}}{=} \frac{\partial\overline{E}^{\text{c}}}{\partial T}$.

4/ The third cumulant (which corresponds to the centered moment) is defined by $\kappa_3 \stackrel{\text{def}}{=} \overline{(E-\overline{E}^{\text{c}})^3}^{\text{c}} = \big(-\frac{\partial}{\partial\beta}\big)^3 \ln Z$. Show that

$$\kappa_3 = 2k_B^2 T^3\, C_V + k_B^2 T^4 \frac{\partial C_V}{\partial T} \tag{6}$$

5/ Application to the (classical) monoatomic perfect gas : We provide the dependence in temperature of the partition function of the partition monoatomic perfect gas $Z \propto T^{3N/2}$. Deduce $\overline{E}^{\text{c}}$, $\kappa_2/\big(\overline{E}^{\text{c}}\big)^2$ et $\kappa_3/\big(\overline{E}^{\text{c}}\big)^3$.

6/ Justify that this is legitimate to consider that the energy distribution is Gaussian.

Reread yourself ! ($\sim$ 5mn)

Appendice :

- Volume of the hypersphere of unit radius in $\mathbb{R}^D$:

$$\mathscr{V}_D = \frac{\pi^{D/2}}{\Gamma(\frac{D}{2}+1)}$$

- Stirling formula :
  $\ln N! \simeq N\ln N - N + \mathcal{O}(\ln N)$ for $N \gg 1$ where $\ln\Gamma(z+1) \simeq z\ln z - z + \mathcal{O}(\ln z)$ pour $z \to \infty$.
- Fundamental constants : $k_B \simeq 1.38\times 10^{-23}$ J/K ; $\hbar \simeq 10^{-34}$ J.s ;
- Fundamental identity of *thermodynamics* : $\mathrm{d}E = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\,\mathrm{d}N + \cdots$

Solutions on the webpage of the main lecture : see
`http://lptms.u-psud.fr/christophe_texier/`