Homework 3: Phys 7230 (Spring 2022)

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***Problem* 1** (Derivation of ensembles)**:**
(a) Grand canonical ensemble
Start with the expression

$$W\left[\left\{n_q\right\}\right] = \frac{\mathcal{N}!}{\prod_q n_q!} \tag{1.1}$$

for the number of configurations in a grandcanonical ensemble consisting of $\mathcal{N}$ systems with a set $\left\{n_q\right\}$ describing the number of systems with energy E_q and number of particles N_q, discussed in lectures. Utilizing lowest order Stirling approximation, maximize $W\left[\left\{n_q\right\}\right]$ over n_q, subject to three constraints,

$$\sum_q n_q = \mathcal{N}, \qquad \sum_q n_q E_q = E\mathcal{N}, \qquad \sum_q n_q N_q = N\mathcal{N}, \tag{1.2}$$

imposed via Lagrange multiplier γ, β, α, with E and N the average energy and particle number in the ensemble, derive the most likely n_q^* and thereby obtain the grandcanonical probability distribution $P_q = n_q^*/\mathcal{N}$.

Hint: Maximizing $\ln W$ may be more convenient.

Solution.

First, using Stirling approximation, we write

$$\ln W = \mathcal{N}\ln\mathcal{N} - \mathcal{N} - \sum_q \left(n_q \ln n_q - n_q\right) = \mathcal{N}\ln\mathcal{N} - \sum_q n_q \ln n_q. \tag{1.3}$$

Extremizing this function, we calculate

$$\begin{aligned}\boldsymbol{\nabla}(\ln W) - \gamma\boldsymbol{\nabla}\left(\sum_q n_q - \mathcal{N}\right) - \beta\boldsymbol{\nabla}\left(\sum_q n_q E_q - E\mathcal{N}\right) - \alpha\boldsymbol{\nabla}\left(\sum_q n_q N_q - N\mathcal{N}\right)& \\ = \ln\mathcal{N} - 1 - \ln n_q + 1 + \beta(E - E_q) + \alpha(N - N_q) = 0.&\end{aligned} \tag{1.4}$$

Inverting, we get

$$\frac{n_q}{\mathcal{N}} = e^{\beta(E-E_q)+\alpha(N-N_q)}. \tag{1.5}$$

By the normalization condition,

$$1 = \sum_q \frac{n_q}{\mathcal{N}} = e^{\beta E + \alpha N} \sum_q e^{-\beta E_q - \alpha N_q} = e^{\beta E + \alpha N} \mathcal{Z}. \tag{1.6}$$

where $\beta = 1/k_B T$ and $\alpha = -\mu\beta$. Then, letting $n_q = n_q^*$, the most probable state satisfying (1.5), we can write the probability distribution as

$$P_q = \frac{n_q^*}{\mathcal{N}} = \frac{e^{-\beta E_q - \alpha N_q}}{\mathcal{Z}}. \tag{1.7}$$

□

(b) Derivation redux

Let us rederive all three ensembles distributions in a more streamlined way by focusing on P_q and noting that P_q can be determined by maximizing the (Shannon's) entropy $S = -k_B \sum_q P_q \ln P_q$ subject to the appropriate number of constraints for each ensemble. Thus, derive

(i) Microcanonical ensemble subject to its one constraint, showing that it is just given by a normalized *constant* $P_q = 1/\Omega$.

(ii) Canonical ensemble subject to its two constraints, showing that it is given by the Gibbs form.

(iii) Grandcanonical ensemble subject to its three constraints, showing that it is given by the Gibbs form.

Solution.

(i) The constraint for the microcanonical ensemble is the normalization condition

$$\sum_q P_q = 1. \tag{1.8}$$

Then, we differentiate to find P_q that extremizes S

$$\boldsymbol{\nabla}(S) - \lambda \boldsymbol{\nabla}\left(\sum_q P_q - 1\right) = -k_B\big(\ln P_q + 1\big) - \lambda_1 \Rightarrow P_q = e^{-1-\lambda/k_B}. \tag{1.9}$$

Plugging this back into the normalization condition, we get

$$\sum_q P_q = e^{-1-\lambda_1/k_B} \sum_q 1 = e^{-1-\lambda_1/k_B}\Omega, \tag{1.10}$$

where $\Omega = \sum_{\{q_i\}} 1$ is the multiplicity of the system. Then we can rewrite the probability distribution function

$$P_q = \frac{1}{\Omega}, \tag{1.11}$$

which is a constant, indicating a uniform distribution. Also, we can invert to solve for λ_1

$$\lambda_1 = S_t - k_B, \tag{1.12}$$

where $S_t = k_B \ln \Omega$ is the thermodynamic entropy.

(ii) In addition to the normalization condition (1.8), we add a constraint

$$\sum_q E_q P_q = E, \tag{1.13}$$

where E is the average energy of the system. Then, the P_q that extremizes S satisfies

$$-k_B\big(\ln P_q + 1\big) - \lambda_1 - \lambda_2 E_q = 0 \Rightarrow P_q = e^{-1-\lambda_1/k_B - \lambda_2 E_q/k_B}. \tag{1.14}$$

Applying the normalization,

$$1 = \sum_q P_q = e^{-1-\lambda_1/k_B} \sum_q e^{-\lambda_2 E_q/k_B} = e^{-1-\lambda_1/k_B} \sum_q e^{-\beta E_q} \Rightarrow e^{-1-\lambda_1/k_B} = \frac{1}{Z}, \tag{1.15}$$

where we have let the constant $\lambda_2 = 1/T$, with T the equilibrium temperature, and Z is the partition function of the canonical ensemble. It then follows that the distribution function

$$P_q = \frac{e^{-\beta E_q}}{Z} \tag{1.16}$$

has the Gibbs form.

(iii) The third constraint to add is

$$\sum_q N_q P_q = N, \tag{1.17}$$

where N is the average number of particles per partition. Then P_q extremizing S satisfies

$$-k_B\big(\ln P_q + 1\big) - \lambda_1 - \lambda_2 E_q - \lambda_3 N_q = -k_B \ln P_q - S_t - E_q/T - \lambda_3 N_q = 0, \tag{1.18}$$

where we have replaced the first two Lagrange multipliers with physical quantities derived in (i-ii). The probability distribution function is

$$P_q = e^{-S-\beta E_q - \lambda_3 N_q/k_B} = e^{-S-\beta E_q + \beta\mu N_q}, \tag{1.19}$$

where we have let the constant $\lambda_3 = -\mu/T$. Then, with the normalization condition,

$$1 = e^{-S} \sum_q e^{-\beta(E_q + \mu N_q)} = e^{-S} \mathcal{Z}, \tag{1.20}$$

and the probability distribution function can be written as

$$P_q = \frac{e^{-\beta(E_q+\mu N_q)}}{\mathcal{Z}}, \tag{1.21}$$

which has the Gibbs form. $\square$

(c) Recall the expression for $\Omega(E)$ for the microcanonical ensemble of a 3d ideal Boltzmann gas of N particles. Using it, calculate the probability P_ϵ of a *particular* particle to have energy in the neighborhood of $\epsilon \ll E$.

From your answer for P_ϵ and comparing it with the standard Boltzmann-Gibbs weight, read off the corresponding effective temperature of this single particle in terms of E and N.

Hint: (i) From above total $\Omega(E)$ first think about the number of states (sub-multiplicity) $\Omega_\epsilon(E)$ for one of the particle to have energy ϵ and the remaining $N-1$ sharing the remaining energy. (ii) Note that $P_\epsilon = \Omega_\epsilon/\Omega$. (iii) Use Stirling's approximation and $\epsilon \ll E$ to simplify your answer.

Solution.

From Sackur-Tetrode, we can write the multiplicity as $\Omega = e^{S/k_B} = (V^N/N!)f(N,E)$ where

$$f(N,E) = e^{5N/2}\left(\frac{4\pi m E}{3Nh^2}\right)^{3N/2}. \tag{1.22}$$

Then, we note that there is only one way to distribute an energy of ϵ into a particular particle. Thus, the multiplicity for the entire system of one particle of energy ϵ and $N-1$ particles of energy $E-\epsilon$ is

$$\begin{aligned}\Omega_\epsilon &= \frac{V^{N-1}}{(N-1)!}f(N-1,E-\epsilon)\\ &= \frac{V^{N-1}}{(N-1)!}e^{5(N-1)/2}\left(\frac{4\pi m(E-\epsilon)}{3(N-1)h^2}\right)^{3(N-1)/2}\\ &\approx \frac{V^{N-1}}{(N-1)!}e^{5(N-1)/2}\left(\frac{4\pi m(E-\epsilon)}{3Nh^2}\right)^{3(N-1)/2}.\end{aligned} \tag{1.23}$$

The probability is thus

$$\begin{aligned}P_\epsilon &= \frac{\Omega_\epsilon}{\Omega}\\ &\approx \frac{N}{V}e^{-5/2}\left(\frac{4\pi m E}{3Nh^2}\right)^{-3/2}\left(1-\frac{\epsilon}{E}\right)^{3(N-1)/2}\\ &\approx \frac{N}{V}e^{-5/2}\left(\frac{4\pi m E}{3Nh^2}\right)^{-3/2}e^{-3(N-1)\epsilon/2E},\end{aligned} \tag{1.24}$$

which follows the Gibbs form if the effective temperature is defined as

$$k_B T_{\text{eff}} = \frac{2E}{3(N-1)}. \tag{1.25}$$

□

(d) Variance (i.e., mean-squared fluctuations) in the number of particles N in the grand canonical ensemble is given by $\left\langle(\Delta N)^2\right\rangle$. Show that quite generally it is given by

$$N_{\text{rms}}^2 = \left\langle(\Delta N)^2\right\rangle = -\left.\frac{\partial \overline{N}}{\partial \alpha}\right|_{\beta,V} = \left.\frac{\partial^2(\ln \mathcal{Z})}{\partial \alpha^2}\right|_{\beta,V} \tag{1.26}$$

Solution.

First, from $\mathcal{Z}$, we can calculate

$$\frac{\partial \mathcal{Z}}{\partial \alpha} = \frac{\partial}{\partial \alpha} \sum_q e^{-\beta E_q - \alpha N_q} = -\sum_q N_q e^{-\beta E_q - \alpha N_q} = -\langle N \rangle \mathcal{Z}, \tag{1.27}$$

and

$$\frac{\partial^2 \mathcal{Z}}{\partial \alpha^2} = \sum_q N_q^2 e^{-\beta E_q - \alpha N_q} = \left\langle N^2 \right\rangle \mathcal{Z}. \tag{1.28}$$

Differentiating (1.27) again, we get

$$\left\langle N^2 \right\rangle \mathcal{Z} = -\frac{\partial \langle N \rangle}{\partial \alpha} \mathcal{Z} + \langle N \rangle^2 \mathcal{Z} \Rightarrow \left\langle (\Delta N)^2 \right\rangle = \left\langle N^2 \right\rangle - \langle N \rangle^2 = -\frac{\partial \langle N \rangle}{\partial \alpha}. \tag{1.29}$$

Also,

$$\frac{\partial (\ln \mathcal{Z})}{\partial \alpha} = -\langle N \rangle . \tag{1.30}$$

So taking the differentation again leads us to the second equality

$$\frac{\partial^2 (\ln \mathcal{Z})}{\partial \alpha^2} = -\frac{\partial \langle N \rangle}{\partial \alpha}. \tag{1.31}$$

□

***Problem* 2** (Ultra-relativistic gas)**:** Consider a non-interacting 3d gas of identical ultra-relativistic particles (i.e., ignoring their mass), with a dispersion $\epsilon_i = p_i c$, at temperature T and chemical potential μ, where $p_i = |\mathbf{p}_i| = \sqrt{p_{xi}^2 + p_{yi}^2 + p_{zi}^2}$.

Following similar steps that we did in class for nonrelativistic Boltzmann gas, compute:

(a) Grandcanonical partition function, $\mathcal{Z}(\mu, T)$ by first computing the canonical one, $Z(N, T)$, introducing fugacity and then summing over N.

Hint: it is nice to do the integral in the spherical coordinate system.

Solution.

$\square$

(b) Grandcanonical free energy $\mathcal{F}(\mu, T)$.

Solution.

$\square$