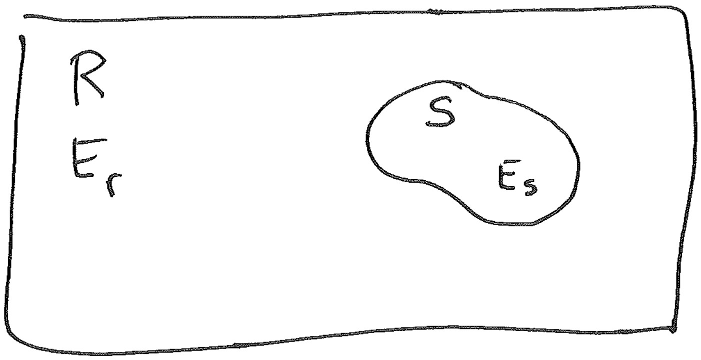
Phys. 528 Lecture 6

Canonical Ensemble



System divided into large reservoir R and subsystem S.

$$E = E_r + E_s = \text{const.}$$

The probability to find the subsystem S in a particular quantum state s whose energy is E_s is

$$P_s \propto \Omega_R(E_r) \times 1 = \Omega_R(E - E_s)$$

$$\ln \Omega_R(E - E_s) \simeq \ln \Omega_R(E) - \frac{\partial \ln \Omega_R}{\partial E} E_s$$

$$= \ln \Omega_R(E) - \beta E_s$$

where

$$\beta \equiv \left.\frac{\partial \ln \Omega}{\partial E}\right|_{N,V}$$

$$P_s \propto e^{-\beta E_s}$$

$$1 = \sum_s P_s = C \sum_s e^{-\beta E_s}$$

Let $Z = \sum_s e^{-\beta E_s}$ be the <u>partition function</u> of subsystem S (from the German Zustandssumme = sum over states).

$$\boxed{P_s = \frac{e^{-\beta E_s}}{Z}}$$

Importantly, the result does not depend on the nature of R, only on β.

2) Thermodynamics in the canonical ensemble

$$E = \sum_s P_s E_s = \text{average energy of (sub)system } S.$$

Since the reservoir has now moved into the background, described only by the single parameter β, I will often ~~refer~~ refer to S as simply the "system."

$$\boxed{E \equiv \langle E_s \rangle = \frac{\sum_s E_s e^{-\beta E_s}}{\sum_s e^{-\beta E_s}} = -\frac{\partial \ln Z}{\partial \beta}.}$$

The thermodynamics may be derived from the Helmholtz free energy

$$\boxed{F = E - TS.}$$

$$dF = dE - TdS - SdT$$

$$= \cancel{TdS} - pdV + \mu dN \cancel{-TdS} - SdT$$

$$dF = -SdT - pdV + \mu dN$$

$$\boxed{\begin{aligned} &F = F(N, V, T) \\ &S = -\frac{\partial F}{\partial T}\Big|_{N,V} \qquad P = -\frac{\partial F}{\partial V}\Big|_{N,T} \\ &\mu = \frac{\partial F}{\partial N}\Big|_{V,T} \end{aligned}}$$

$$E = F + TS = F - T \left.\frac{\partial F}{\partial T}\right|_{V,N}$$

$$E = -T^2 \frac{\partial}{\partial T}\left(\frac{F}{T}\right)\Big|_{N,V}$$

$$\boxed{F = -k_B T \ln Z \quad , \quad \beta = \frac{1}{k_B T}}$$

This constitutes the fundamental result of the canonical ensemble. All of the thermodynamics of the system can be derived from this.

e.g. $$C_V = T \left.\frac{\partial S}{\partial T}\right|_{N,V} = -T \left.\frac{\partial^2 F}{\partial T^2}\right|_{N,V}$$

A useful expression for the entropy of the system may be determined as follows:

$$P_s = \frac{e^{-\beta E_s}}{Z} \quad , \quad \ln P_s = -\ln Z - \beta E_s$$

$$\langle \ln P_s \rangle = -\ln Z - \beta \langle E_s \rangle = -\ln Z - \beta E$$

$$= \beta (F - E) = -\frac{S}{k_B}$$

$$\boxed{S = -k_B \langle \ln P_s \rangle = -k_B \sum_s P_s \ln P_s}$$

<u>Third law of thermodynamics</u> (Nernst theorem)

$$\lim_{T \to 0} P_s = \begin{cases} 1, & E_s = E_0 \text{ (ground state)} \\ 0, & \text{otherwise} \end{cases}$$

Then $\lim_{T \to 0} S(T) = 0$, provided g.s. is nondegenerate. otherwise

$$\lim_{T \to 0} P_s = \begin{cases} 1/g, & E_s = E_0 \text{ (degeneracy } g) \\ 0, & \text{otherwise} \end{cases}$$

$$\lim_{T \to 0} S(T) = -k_B \sum_{i=1}^{g} \frac{1}{g} \ln \frac{1}{g} = k_B \ln g$$

3) Alternative formulation of the canonical ensemble

Rather than a single system exchanging energy with a reservoir, we can study many copies of the system with the average energy per system fixed. Let $\mathcal{N} \gg 1$ be the # of systems in the ensemble sharing a total energy $\mathcal{E}$. Let n_s denote the # of systems in the ensemble in a particular state of energy E_s at a give instant.

For a given set $\{n_s\}$, there are a large # $W\{n_s\}$ of ensembles that realize it:

$$W\{n_s\} = \frac{\mathcal{N}!}{n_0!\, n_1!\, n_2! \cdots}$$

$\{n_s\}$ satisfies the constraints

$$\sum_s n_s = \mathcal{N} \qquad (1)$$

$$\sum_s E_s n_s = \mathcal{E} = \mathcal{N} E \qquad (2)$$

The most probable distribution is that which maximizes W subject to the two constraints.

$$\ln W = \ln N! - \sum_s \ln(n_s!)$$

In the limit $\mathcal{N} \to \infty$, all states for which $P_s = \frac{n_s}{\mathcal{N}} > 0$ also have $n_s \to \infty$, so we can use Stirling's formula:

$$\ln W \simeq \mathcal{N} \ln \mathcal{N} - \sum_s n_s \ln n_s$$

Using the method of Lagrange multipliers, the most probable distribution must satisfy

$$0 = \delta \ln W - \alpha \sum_s \delta n_s - \beta \sum_s E_s \delta n_s$$

$$0 = \sum_s \left[-(\ln n_s^* + 1) - \alpha - \beta E_s \right] \delta n_s$$

$$\ln n_s^* = -(\alpha+1) - \beta E_s$$

$$n_s^* = C e^{-\beta E_s}$$

C and β may be determined from

$$\frac{n_s^*}{N} = \frac{e^{-\beta E_s}}{\sum_s e^{-\beta E_s}}$$

$$\frac{\mathcal{E}}{N} = E = \frac{\sum_s E_s e^{-\beta E_s}}{\sum_s e^{-\beta E_s}} .$$

By comparison with our previous results, we see that $\beta = \frac{1}{k_B T}$.

The most probable distribution thus coincides with the average distribution (found previously) in the limit $N \to \infty$.

4) Ensemble entropy

We can define an entropy for the ensemble via

$$\frac{S}{k_B} = \frac{1}{N} \ln W \simeq \ln N - \sum_s \frac{n_s}{N} \ln n_s$$

$$= - \sum_s \frac{n_s}{N} (\ln n_s - \ln N)$$

$$= - \sum_s \frac{n_s}{N} \ln \frac{n_s}{N}$$

$$\boxed{S = -k_B \sum_s P_s \ln P_s}$$

Notice that this definition does not require equilibrium; it holds for arbitrary ensembles that may be far from equilibrium.

i) This result agrees with the result for the equilibrium entropy of the canonical ensemble.

ii) This result agrees with the definition of entropy in the microcanonical ensemble :

$$S = k_B \ln \Omega$$

$$P_s = \frac{1}{\Omega} \; ; \qquad S = -k_B \sum_s \frac{1}{\Omega} \ln \frac{1}{\Omega}$$

$$= k_B \ln \Omega \quad \checkmark$$

The canonical probability distribution can be found by maximizing S subject to the constraints :

$$\sum_s P_s = 1 ,$$

$$\sum_s P_s E_s = E .$$