CHM 421/621
Statistical Mechanics

Lecture 22 Canonical Ensemble

Formalisms of Statistical Mechanics

Lecture Plan

Ensembles

Canonical Ensemble

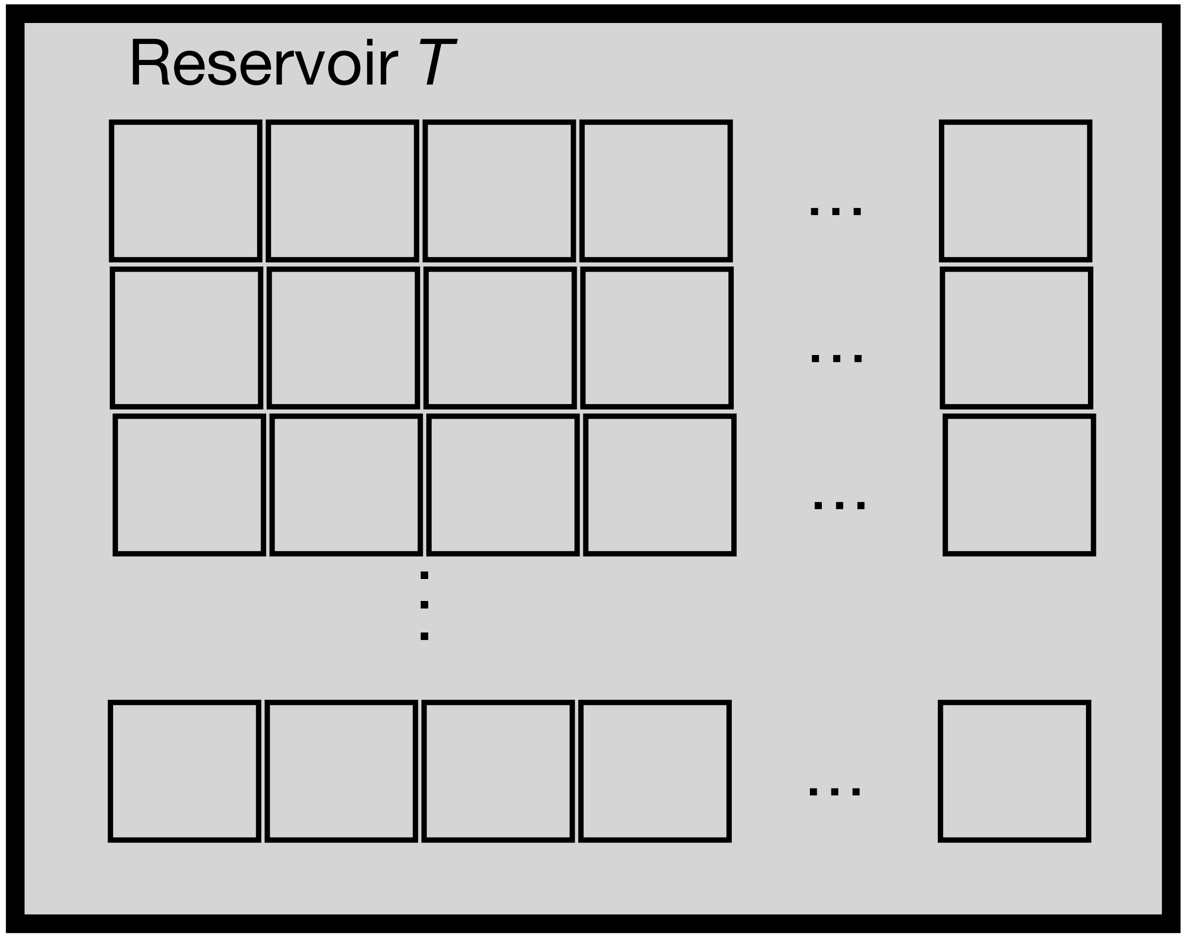
We are generally interested not in isolated systems but those in contact with a thermal (or other) reservoir, capable of exchanging energy with one another.

An ensemble of such (identically prepared) systems at the same temperature (T) is called a **canonical ensemble**.

The total energy of the ensemble with reservoir is fixed: $U_{tot} = \mathcal{E} + U_r$

=> various microstates where $\mathcal{E}$ and U_r are different, keeping U_{tot} constant, are possible.

Even for a given $\mathcal{E}$ there are multiple ways of distributing the energy across the members of the ensemble. We are actually interested in this distribution.



Ensembles

Canonical Ensemble

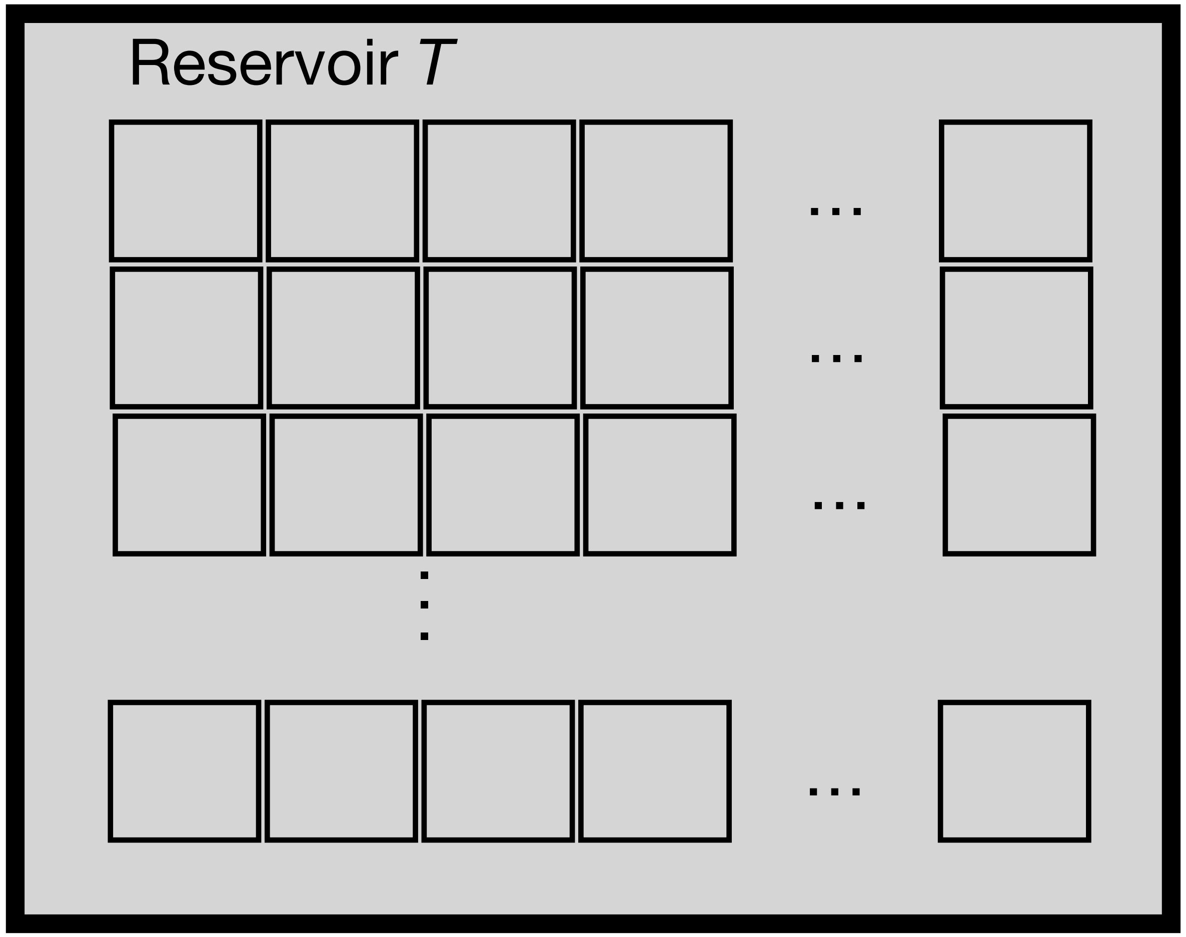
What is the probability that a system in such an ensemble is in a particular microstate *k* with energy E_k?

From the basic postulate we can see that the probability must depend on the energy of the microstate only. i.e.

Discrete $P_k \equiv P(E_k)$

Classical $f(\{\vec{r},\vec{p}\}) \equiv f(E(\{\vec{r},\vec{p}\})$

This can also be understood in terms of grouping the systems into various **micro-canonical ensembles** (hence the name).



Ensembles

Canonical Ensemble

What is the probability that a system in such an ensemble is in a particular microstate *k* with energy E_k?

Joint probability of combined system A+B

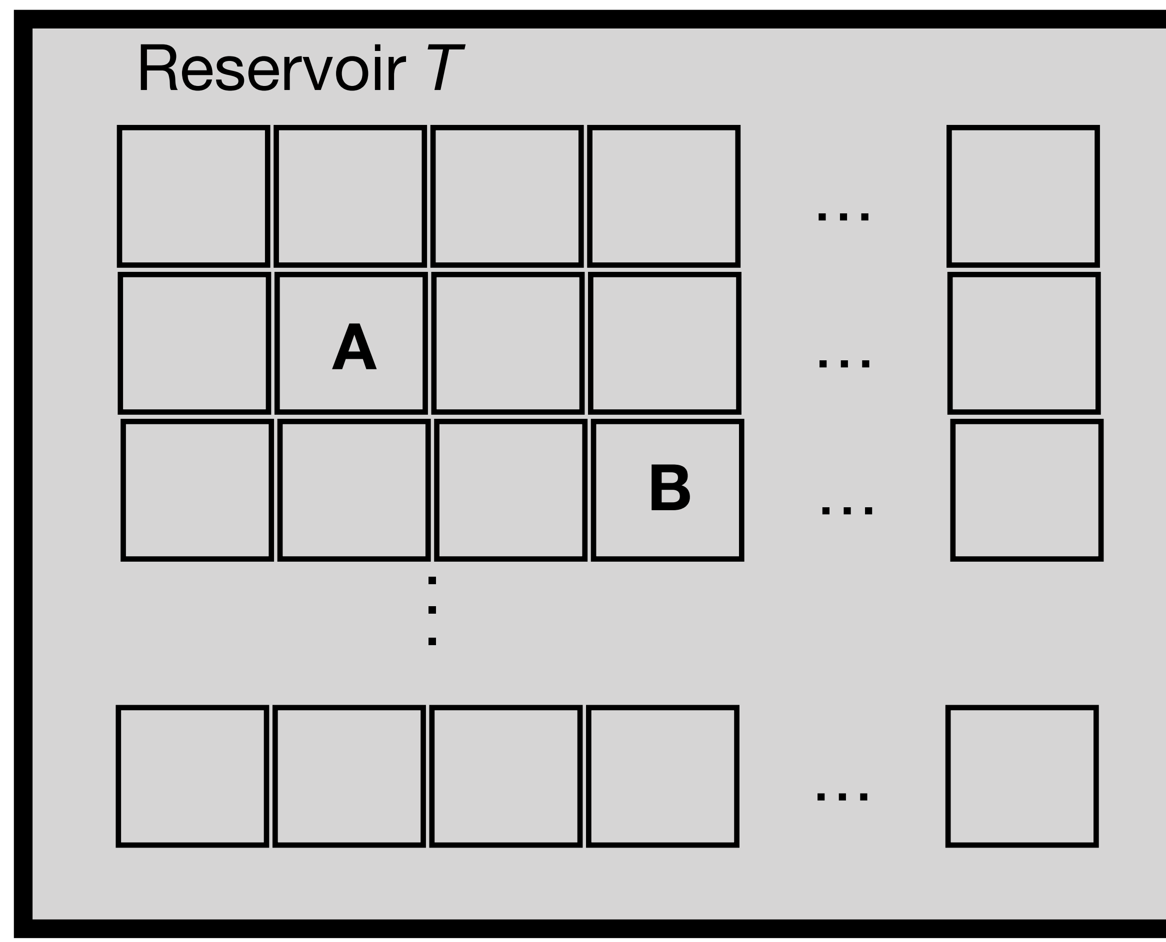
$$P_{A+B}(E_{A+B}) \approx P_{A+B}(E_A + E_B)$$
$$= P_A(E_A) \times P_B(E_B)$$

since E_A and E_B are independent events.

Now,

$$\frac{\partial P_{A+B}(E_{A+B})}{\partial E_A} = \frac{\partial P_{A+B}(E_{A+B})}{\partial E_B}$$
$$\implies P'_A(E_A)P_B(E_B) = P_A(E_A)P'_B(E_B)$$
$$\implies \frac{P'(E)}{P(E)} = \text{constant}$$

Since A and B were arbitrarily chosen.



Ensembles

Canonical Ensemble

What is the probability that a system in such an ensemble is in a particular microstate *k* with energy E_k?

$$\frac{dP(E_k)}{P(E_k)} = C \times dE$$

C is a constant

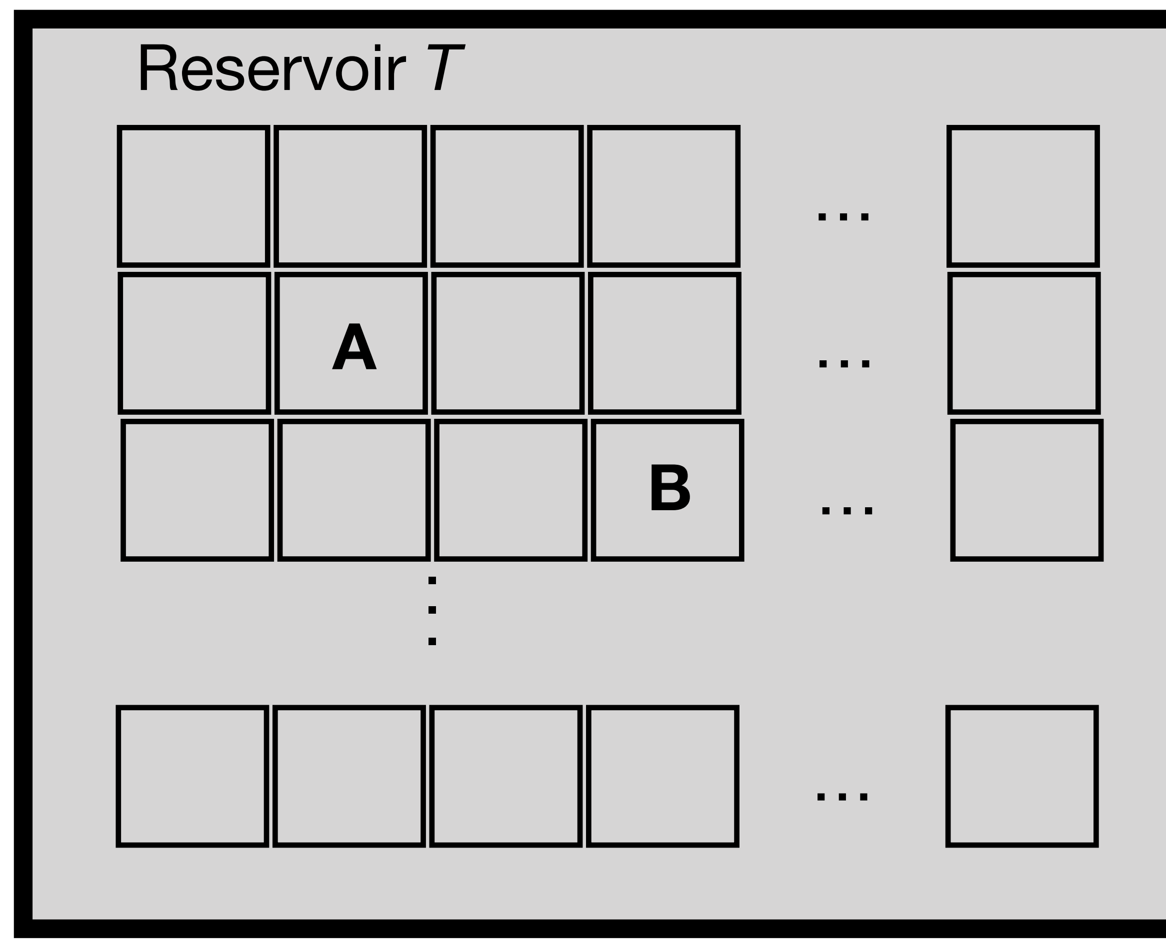
$$\implies \ln P(E_k) = C\ E_k + \ln D$$

D is a constant of integration

$$\implies \boxed{P(E_k) = D\ \exp(C\ E_k)}$$

$$\sum_k P(E_k) = 1$$

$$\implies D = \boxed{Z^{-1} = 1/\sum_k \exp(CE_k)}$$



Z is called the **canonical partition function.**

Ensembles

Canonical Ensemble

What is the probability that a system in such an ensemble is in a particular microstate *k* with energy E_k?

For a discrete (quantum) system

$$P(E_k) = \frac{1}{Z}\exp(-\beta E_k)$$

$$Z = \sum_k \exp(-\beta E_k)$$

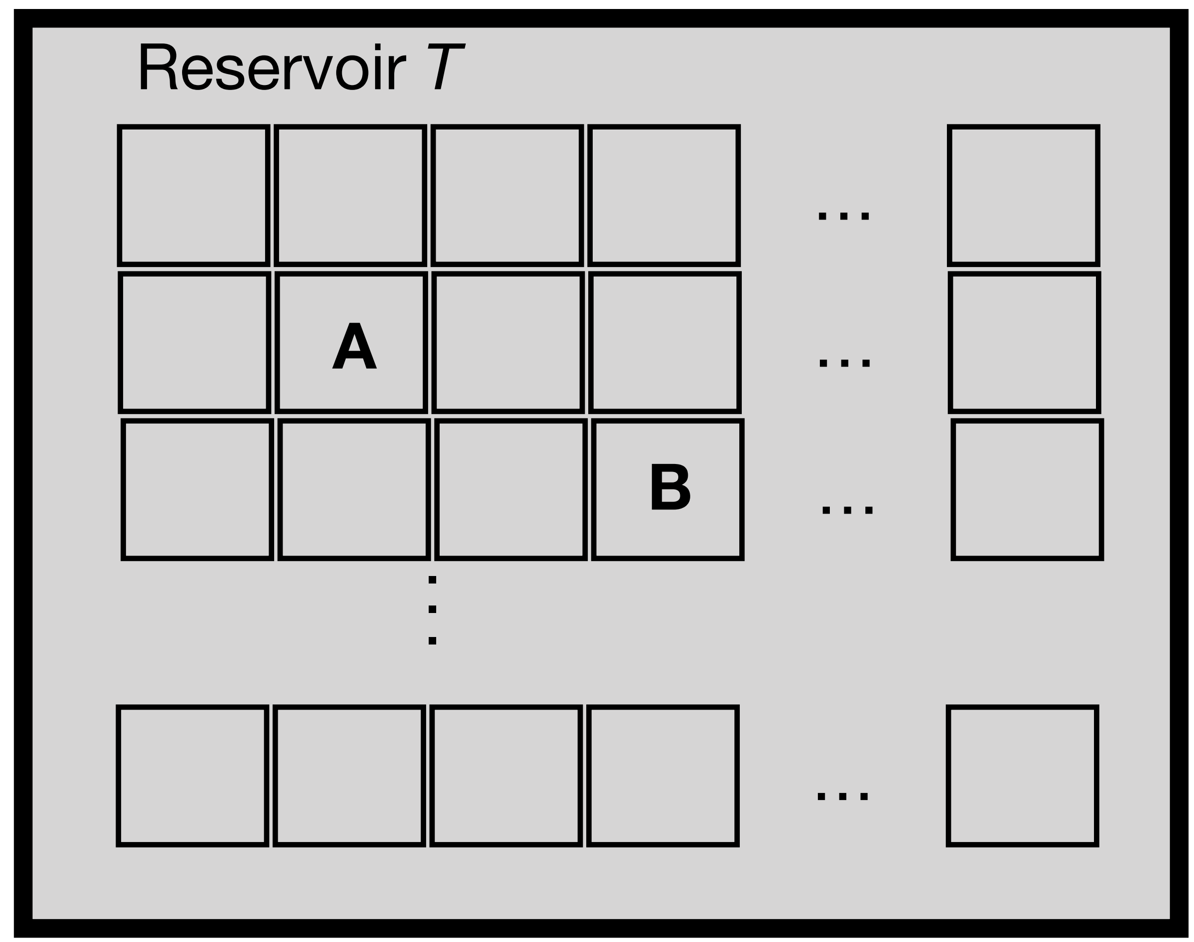
(Setting $C = -\beta$)

For a continuous (classical) system

$$f(E(\{\vec{r},\vec{p}\}) = \frac{1}{Z}\exp(-\beta E(\{\vec{r},\vec{p}\})$$

$$Z = A \int d^{3N}r \int d^{3N}p \, \exp(-\beta E(\{\vec{r},\vec{p}\})$$

$$A = \frac{1}{N!h^{3N}}$$



β must be related to reservoir only!

Ensembles

Canonical Ensemble

Computing averages

$$U \equiv \overline{E} = \frac{1}{Z} \sum_k E_k \exp(-\beta E_k)$$

For classical systems we can write

$$U \equiv \overline{E} = \frac{1}{Z\ h^{3N}} \int d^{3N}x \int d^{3N}p\ E\ \exp(-\beta E)$$

In practice the factor is immaterial as it cancels out (except for the indistinguishability). So we can ignore it by setting it to 1 in the appropriate units.

$$U \equiv \overline{E} = \frac{1}{Z} \int d^{3N}x \int d^{3N}p\ E\ \exp(-\beta E)$$

Ensembles

Canonical Ensemble

Computing averages

In either case a simplification to the energy expression is

$$U = -\frac{\partial \ln Z}{\partial \beta}$$

Ensembles

Canonical Ensemble

Ideal gas at finite temperature *T*

$$E = \sum_{i=1}^{N} p_i^2/2m$$

$$\begin{aligned} Z(\beta, V, N) &= \int d^{3N}x \int d^{3N}p \, \exp(-\beta \sum_{i=1}^{N} p_i^2/2m) \\ &= \left(\int d^3x \int d^3p \, \exp(-\beta \frac{\mathrm{p}^2}{2\mathrm{m}}) \right)^N \\ &\equiv (z)^N \end{aligned}$$

where *z* is called the molecular partition function.

$$z = V \left(\frac{2\pi m}{\beta} \right)^{\frac{3}{2}} \Longrightarrow u = U/N = -\frac{\partial \ln z}{\partial \beta}$$

$$= \frac{3}{2\beta}$$

Comparing with the known result of $u = \frac{3}{2} k_B T$

We have $\boxed{\beta = \frac{1}{k_B T}}$