# CHM 421/621 Statistical Mechanics

## Lecture 26 Grand Canonical Ensemble

# Ensembles

**Lecture Plan**

**Generalisation of the Ensemble Idea** (An alternative derivation)
**Open systems: Grand Canonical Ensemble**

# Ensembles

**Canonical Ensemble**

Distinguishable and indistinguishable particles

Distinguishable

$$Z(N,V,T) = z(V,T)^N$$

Boltzmann statistics

Indistinguishable

$$Z \approx \frac{z^N}{N!}$$

Approximate and valid for
non-degenerate systems

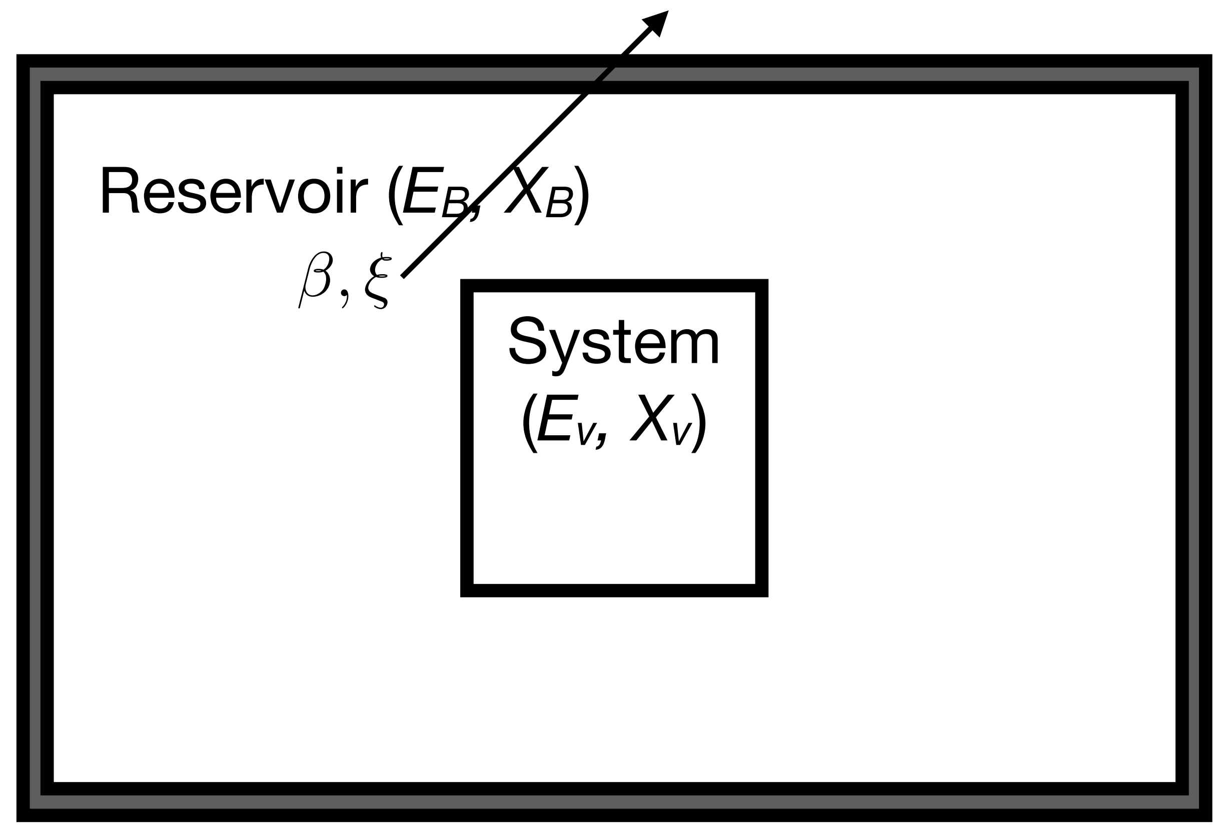
# Ensembles

**A General Ensemble**

Alternative derivation (see D. Chandler or D. Callen)

$$k_B \xi = \frac{\partial S}{\partial X}$$

$$k_B^{-1} dS = \beta dE + \xi dX$$
$$E_{tot} = E_B + E_v$$
$$X_{tot} = X_B + X_v$$




For a fixed system micro state *v*, the number of micro states possible for the system+reservoir is

$$\Omega(E_{tot}, X_{tot}; E_B, X_B) = \Omega(E_{tot} - E_v, X_{tot} - X_v)$$

Given $E_B >> E_v, X_B >> X_v$ we can write

# Ensembles

**A General Ensemble**

Alternative derivation (see D. Chandler or D. Callen)

$$
\begin{aligned}
&\ln\Omega(E_{tot} - E_v, X_{tot} - X_v) \\
&\qquad \approx \ln\Omega(E_{tot}, X_{tot}) - E_v \frac{\partial \ln\Omega}{\partial E} - X_v \frac{\partial \ln\Omega}{\partial X} + \ldots \\
&\qquad = \ln\Omega(E_{tot}, X_{tot}) - \beta E_v - \xi X_v
\end{aligned}
$$

Assuming that all micro states with the same E and X are equally likely, we have

$$
\begin{aligned}
P_v &\propto \exp\left(\Omega(E_{tot} - E_v, X_{tot} - X_v)\right) \\
&= \exp\left(\Omega(E_{tot}, X_{tot})\right) \times \exp\left(-\beta E_v - \mu X_v\right)
\end{aligned}
$$

Normalising the probability we get

$$
P_v = \exp\left(-\beta E_v - \xi X_v\right) / \Xi
$$

where

$$
\Xi(\beta, X) \equiv \sum_v \exp\left(-\beta E_v - \xi X_v\right)
$$

# Ensembles

**Gibbs Entropy Formula**

For the generalised ensemble consider the expression

$$\mathcal{S} \equiv -k_B \sum_v P_v \ln P_v$$

Using the general distribution we derived, we can write this as

$$\begin{aligned}\mathcal{S} &= k_B \sum_v P_v \left(\ln\Xi + \beta E_v + \xi X_v\right) \\ &= k_B \left(\ln\Xi + \beta \langle E\rangle + \xi \langle X\rangle\right)\end{aligned}$$

This is just a Legendre transform of the partition function into function of *U* and *X*.

$$d\mathcal{S} = k_B \beta dU + \xi dX$$ This is just the entropy!!

Therefore,

$$S = -k_B \sum_v P_v \ln P_v$$

# Ensembles

**Open systems**

Grand canonical probability distribution

Consider a system at constant temperature with volume *V* and with particle permeable walls. System is in contact with a thermal (T) and particle (chemical potential) reservoir.

Here, $k_B \xi = -\beta \mu$

Therefore, the distribution we get is

$$P_v = \exp\left(-\beta E_v + \beta \mu N_v\right) / Z_G$$

$$Z_G(\beta, \mu, V) = \sum_{N=0}^{\infty} \sum_{k} \exp\left(-\beta E_v + \beta \mu N_v\right)$$

This is called the Grand Canonical Ensemble (or distribution).

# Ensembles

**Open systems**

Average number of particles in the system

$$\overline{N} = \sum_{N=0}^{\infty} \sum_{k} P(E_k, N)\ N$$
$$= Z_g^{-1} \sum_{N=0}^{\infty} \sum_{k} \exp(-\beta(E_k - \mu N))N$$
$$= \frac{1}{\beta} \left( \frac{\partial \ln Z_g}{\partial \mu} \right)_{\beta, V}$$

Similarly, we can show that

$$-\left( \frac{\partial \ln Z_g}{\partial \beta} \right)_{\mu, V} = \overline{E} - \mu \overline{N}$$

# Ensembles

**Open systems**

$$Z_g \equiv Z_g(\beta, \mu, V)$$

$$d(\ln Z_g) = \left(\frac{\partial \ln Z_g}{\partial \beta}\right)_{\mu,V} d\beta + \left(\frac{\partial \ln Z_g}{\partial \mu}\right)_{\beta,V} d\mu + \left(\frac{\partial \ln Z_g}{\partial V}\right)_{\beta,\mu} dV$$

$$= -(\overline{E} - \mu\overline{N})d\beta + \beta\overline{N}d\mu + \left(\frac{\partial \ln Z_g}{\partial V}\right)_{\beta,\mu} dV$$

$$d(\ln Z_g + \beta\overline{E} - \beta\mu\overline{N}) = \beta d\overline{E} - \beta\mu d\overline{N} + \left(\frac{\partial \ln Z_g}{\partial V}\right)_{\beta,\mu} dV$$

$$k_B T d(\ln Z_g + \beta\overline{E} - \beta\mu\overline{N}) = d\overline{E} - \mu d\overline{N} + k_B T \left(\frac{\partial \ln Z_g}{\partial V}\right)_{\beta,\mu} dV$$

Using
$\beta = 1/k_B T$

Comparing with

$$TdS = dU - (u - Ts + Pv)dN + PdV$$

we get …

# Ensembles

**Open systems**

$$\mu = G/N = u - Ts + Pv$$

Gibbs free energy per particle
or the chemical potential

$$U = \overline{E} = -\frac{\partial \ln Z_g}{\partial \beta} + \mu k_B T \frac{\partial \ln Z_g}{\partial \mu}$$

$$S = k_B(\ln Z_g + \beta\overline{E} - \beta\mu\overline{N})$$

$$P = k_B T \left(\frac{\partial \ln Z_g}{\partial V}\right)_{T,\mu}$$

Using these we can show that

$$PV = k_B T \ln Z_g \implies Z_g = e^{\beta PV}$$

So the grand canonical distribution can also be written as

$$P(E,N) = e^{-\beta(E - \mu N + PV)}$$

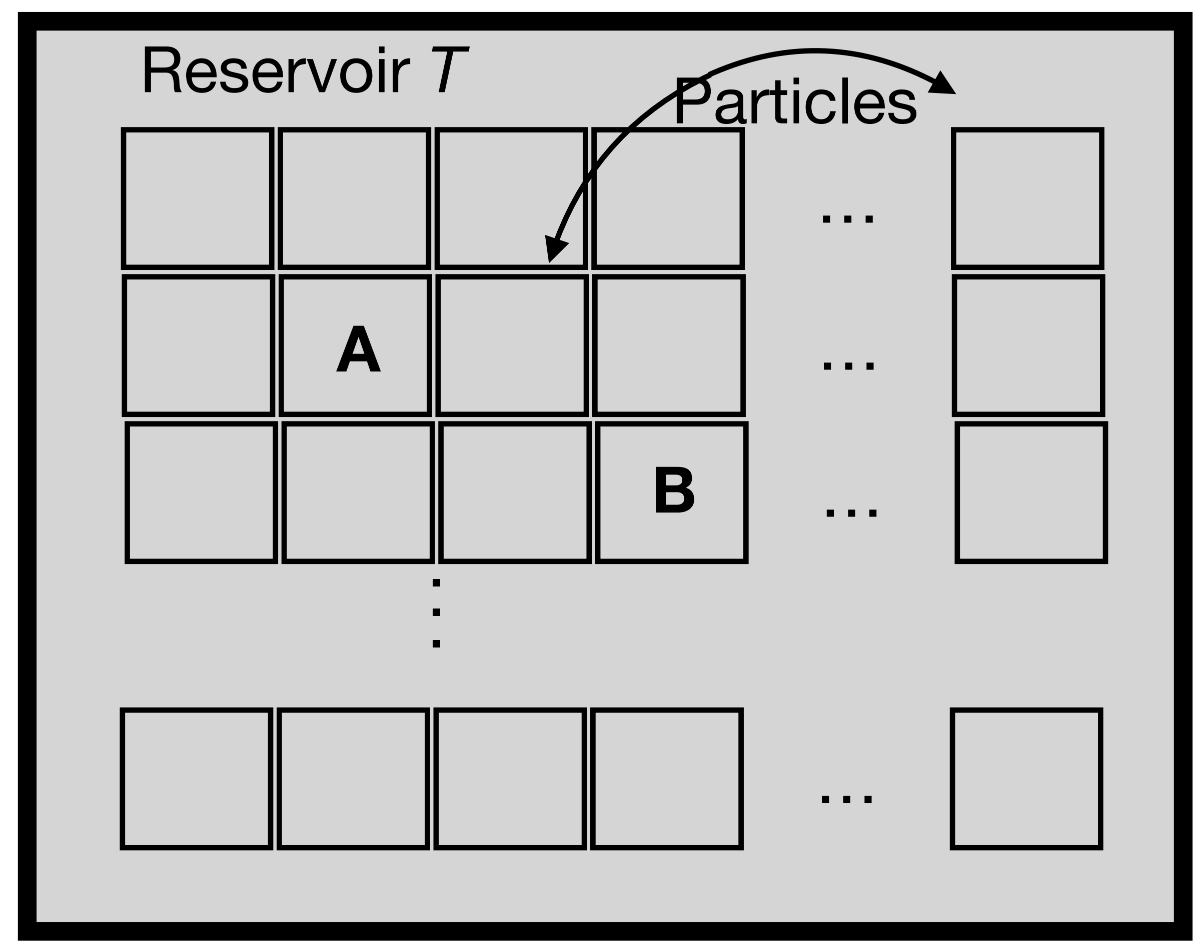
# An Alternative Derivation

**Open systems**

Grand canonical probability distribution

Consider a system at constant temperature with volume *V* and with permeable walls.

All microstates with the same energy *E* and the same number of particles *N* are assumed to be equally probable.




$$P_{A+B}(E_A + E_B, N_A + N_B) = P_A(E_A, N_A) \times P_B(E_B, N_B)$$

$$P_A(E_A, N_A)\frac{\partial P_B(E_B, N_B)}{\partial E_B} = \frac{\partial P_A(E_A, N_A)}{\partial E_A} P_B(E_B, N_B)$$

$$P_A(E_A, N_A)\frac{\partial P_B(E_B, N_B)}{\partial N_B} = \frac{\partial P_A(E_A, N_A)}{\partial N_A} P_B(E_B, N_B)$$

# An Alternative Derivation

**Open systems**

Grand canonical probability distribution

$$\frac{\partial \ln P_A}{\partial E_A} = \frac{\partial \ln P_B}{\partial E_B} \qquad \Longrightarrow \ln P(E_A, N_A) = -\beta E_A + C_A(N_A)$$

$$\frac{\partial \ln P_A}{\partial N_A} = \frac{\partial \ln P_B}{\partial N_B} \qquad \Longrightarrow \ln P(E_A, N_A) = \beta \mu N_A + C_A(N_A)$$

By substituting second eqn. into the first we get

$$C_A(N_A) = \beta \mu N_A + D_A$$

$$P_A(E_A, N_A) = e^{D_A} \; e^{-\beta E_A + \beta \mu N_A}$$
$$\equiv Z_g^{-1} e^{-\beta E_A + \beta \mu N_A}$$

$$Z_g^{-1} = \sum_{N=0}^{\infty} \sum_{k} e^{-\beta E_k + \beta \mu N}$$

Grand canonical partition function