# CHM 421/621
# Statistical Mechanics
## Lecture 23 Canonical Ensemble

# Ensembles

**Lecture Plan**

**Canonical Ensemble**

**Gibbs Ensemble Postulates**

**Entropy and pressure in canonical ensemble**

**Molecular Interpretation of work and heat**

# Ensembles

**Canonical Ensemble**

<u>Gibbs Ensemble Postulates</u>

This refers to the identification of averaged quantities in the ensemble with the corresponding thermodynamic property. In particular,

$$U \equiv \overline{E}$$

$$P \equiv \overline{P}$$

$$\mu \equiv \overline{\mu}$$

Where the averages are over the canonical ensemble at temperature *T*.

# Ensembles

**Canonical Ensemble**

Entropy and pressure in the canonical ensemble

We have that $$Z \equiv Z(\beta, V, N)$$

At constant *N*, we can write

$$d(\ln Z) = \left(\frac{\partial \ln Z}{\partial \beta}\right) d\beta + \left(\frac{\partial \ln Z}{\partial V}\right) dV$$
$$= -U d\beta + \left(\frac{\partial \ln Z}{\partial V}\right) dV$$

Adding $d(\beta U)$ on both sides

$$d(\ln Z + \beta U) = \beta dU + \left(\frac{\partial \ln Z}{\partial V}\right) dV$$

Multiplying both sides by $k_B T$ and rearranging

$$dU = k_B \; d(\ln Z + \beta U) - k_B T \left(\frac{\partial \ln Z}{\partial V}\right) dV$$

Comparing with

$$dU = TdS - PdV$$

We can write

$$P = k_B T \left(\frac{\partial \ln Z}{\partial V}\right)$$

$$dS = k_B \; d(\ln Z + \beta U)$$

# Ensembles

**Canonical Ensemble**

Entropy and pressure in the canonical ensemble

The definition for pressure also makes sense from an averaging perspective

$$
\begin{aligned}
P &= \frac{1}{Z} \sum_k P_k \exp(-\beta E_k) \\
&= \frac{1}{Z} \sum_k - \left( \frac{\partial E_k}{\partial V} \right) \exp(-\beta E_k) \\
&= \frac{1}{Z} \frac{1}{\beta} \frac{\partial}{\partial V} \sum_k \exp(-\beta E_k) \\
&= k_B T \left( \frac{\partial \ln Z}{\partial V} \right)
\end{aligned}
$$

This relation is just the mechanical equation of state for the systems

For an ideal gas this implies

$$P = k_B \, T \, \frac{N}{V}$$

$$P = k_B T \left( \frac{\partial \ln Z}{\partial V} \right)$$

$$dS = k_B \, d(\ln Z + \beta U)$$

# Ensembles

**Canonical Ensemble**

Entropy and pressure in the canonical ensemble

The entropy can obtained by integration

$$S = k_B \ \ln Z + \frac{U}{T} + \ \text{constants}(N, \textit{other extensive parameters})$$

The constant term (in the absence of other extensive parameters) depends only on *N.* Since in practice only differences in *S* and *U* are actually measured, the constant can be set to 0. This is the convention we shall follow.

$$\boxed{S = k_B \ \ln Z + \frac{U}{T}}$$

This convention poses problems when we require extensivity of *S*. But not for d*S.* (See Appendix D in Atlee Jackson and pg. 46 of McQuarrie.)

# Ensembles

**Canonical Ensemble**

<u>Entropy and pressure in the canonical ensemble</u>

Rearranging the equation for entropy we get

$$-k_B\ T\ \ \ln Z = U - T\ S \equiv F$$

Thus, we can now assign a thermodynamic meaning to the canonical partition function

$$\boxed{F = -k_B T\ \ \ln Z}$$

The definitions of entropy and pressure are now consistent with their thermodynamic analogues

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \qquad\qquad P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$$

# Ensembles

**Canonical Ensemble**

Molecular interpretation of work and heat

Consider the function $f = \ln Z \equiv f(\beta, \{E_k\})$

$$
\begin{aligned}
df &= \left(\frac{\partial f}{\partial \beta}\right)_{\{E_k\}} d\beta + \sum_k \left(\frac{\partial f}{\partial E_k}\right)_\beta dE_k \\
&= -\overline{E}\ d\beta + \frac{1}{Z}\sum_k -\beta\ \exp(-\beta E_k)\ dE_k \\
&= -\overline{E} d\beta - \beta \sum_k P(E_k) dE_k
\end{aligned}
$$

This can be written as

$$
d(f + \beta \overline{E}) = \beta \left( d\overline{E} - \sum_k P(E_k) dE_k \right) = \beta \sum_k E_k dP(E_k)
$$

# Ensembles

**Canonical Ensemble**

Molecular interpretation of work and heat

Consider carrying out two processes on the ensemble:

1. Changing volume of all systems equally by *dV*, and in turn changing the $E_k$*'s* for all systems alike.
2. Changing the temperature of the ensemble (by switching to another heat reservoir with temperature $T + dT$)

The work done on any system in changing its energy from $E_j$ to $E_j$+$dE_j$ (through the volume change) is $dE_j$.

Therefore the ensemble averaged reversible work done in the volume change process is

$$\delta W_{rev} = \sum_k P(E_k) dE_k$$

Reversible work is done on a canonical ensemble when the energies of the states of the systems are changed infinitesimally without changing their *populations* (or probabilities).

# Ensembles

## Canonical Ensemble

Molecular interpretation of work and heat

Since $d\overline{E}$ is the average change in total energy we must have that

$$\begin{aligned}\delta Q_{rev} &= d\overline{E} - \delta W_{rev} \\ &= d\overline{E} - \sum_k P(E_k) dE_k \\ &= \frac{1}{\beta} d(f + \beta \overline{E}) \\ &= \sum_k E_k dP(E_k)\end{aligned}$$

Reversible heat supplied to a canonical ensemble alters the *populations* (probabilities) of the states of the systems without changing their energies.

# Ensembles

**Canonical Ensemble**

Summary of thermodynamic relations

$$U = \overline{E} = k_B T^2 \left( \frac{\partial \ln Z}{\partial T} \right)_{V,N}$$

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

$$S = k_B T \left( \frac{\partial \ln Z}{\partial T} \right)_{V,N} + k_B \ln Z$$

$$F = -k_B T \ln Z(N,V,T)$$