PHY 341/641
Thermodynamics and Statistical Physics

Lecture 15

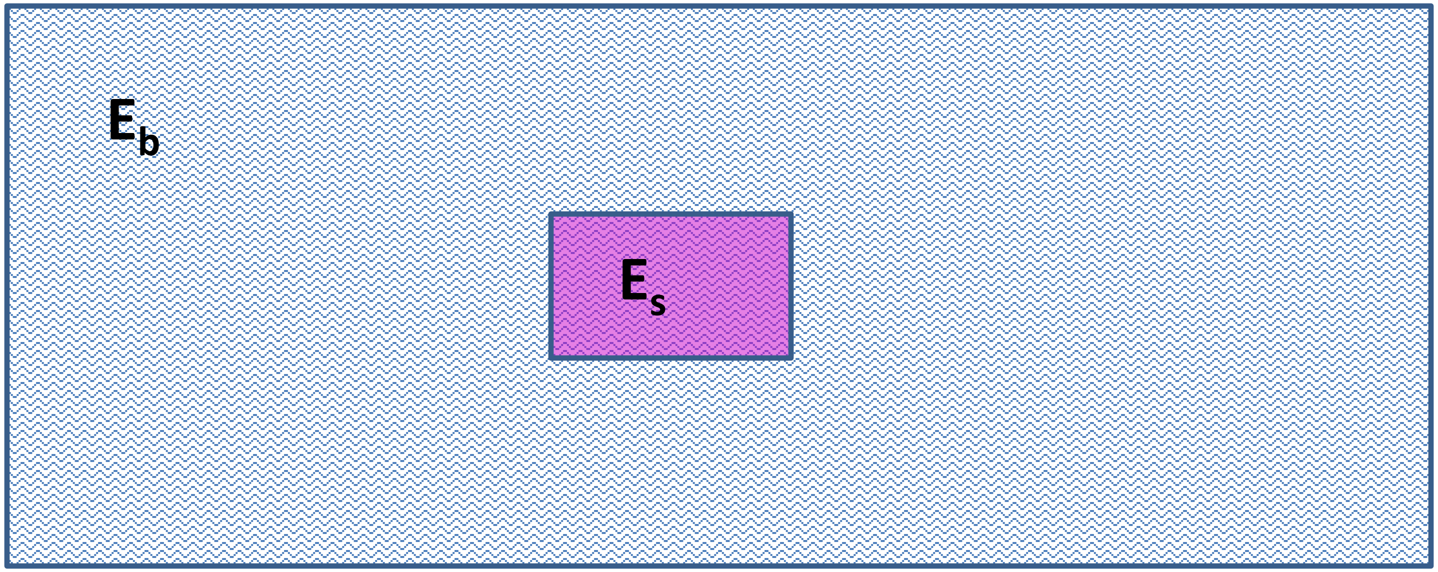
Methodologies of statistical mechanics. (Chapter 4 in STP)

A. Canonical ensemble
B. Grand canonical ensemble

5	1/27/2012	Entropy	2.15-2.19	HW 5	1/30/2012
6	1/30/2012	Thermodynamic Potentials	2.20-2.21	HW 6	2/1/2012
7	2/01/2012	Thermodynamic Potentials	2.22-2.24	HW 7	2/3/2012
8	2/03/2012	Introduction to probability theory	3.1-3.3	HW 8	2/6/2012
9	2/06/2012	Probability distributions	3.4-3.5	HW 9	2/8/2012
10	2/08/2012	Continuous distributions/Central limit theorem	3.6-3.10	HW 10	2/10/2012
11	2/10/2012	Introduction to statistical mechanics	4.1-4.2	HW 11	2/13/2012
12	2/13/2012	Enumeration of microstates	4.3	HW 12	2/15/2012
13	2/15/2012	Many particle systems	4.4-4.5	HW 13	2/17/2012
14	2/17/2012	Microcanonical ensemble	4.6	HW 14	2/20/2012
15	2/20/2012	Canonical ensemble	4.7-4.8	HW 15	2/22/2012
16	2/22/2012	Grand canonical ensemble	4.9-4.12	HW 16	2/24/2012
17	2/24/2012	Review			
	2/27/2012	APS -- no class; take-home exam			
	2/29/2012	APS -- no class; take-home exam			
	3/02/2012	APS -- no class; take-home exam			
	3/05/2012				

Review:

Canonical ensemble:



Canonical ensemble (continued)

$$E_{tot} = E_s + E_b \qquad\qquad E_s << E_b$$

Probability that system is in microstate s:

$$\mathcal{P}_s = \frac{\Omega_b\left(E_{tot} - E_s\right)}{\sum_{s'} \Omega_b\left(E_{tot} - E_{s'}\right)}$$

$$\ln \mathcal{P}_s \approx C + \ln \Omega_b\left(E_{tot}\right) - E_s \left(\frac{\partial \ln \Omega_b\left(E\right)}{\partial E}\right)_{E_{tot}} + \cdots$$

$$\ln \mathcal{P}_s \approx C + \ln \Omega_b\left(E_{tot}\right) - E_s \left(\frac{1}{kT}\right) + \cdots$$

$$\Rightarrow \mathcal{P}_s = C' e^{-E_s/kT} = \frac{1}{Z} e^{-E_s/kT}; \quad Z = \sum_{s'} e^{-E_{s'}/kT}$$

Name	Potential	Differential Form
Internal energy	$E(S,V,N)$	$dE = TdS - PdV + \mu dN$
Entropy	$S(E,V,N)$	$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN$
Enthalpy	$H(S,P,N) = E + PV$	$dH = TdS + VdP + \mu dN$
Helmholtz free energy	$F(T,V,N) = E - TS$	$dF = -SdT - PdV + \mu dN$
Gibbs free energy	$G(T,P,N) = F + PV$	$dG = -SdT + VdP + \mu dN$
Landau potential	$\Omega(T,V,\mu) = F - \mu N$	$d\Omega = -SdT - PdV - Nd\mu$

Canonical ensemble

Partition function (note: $P_s \equiv$ pressure here; keep N constant)

$$Z \equiv \sum_{s'} e^{-E_{s'}/kT} \equiv \sum_{s'} e^{-\beta E_{s'}} = Z(T,V) \equiv Z(\beta,V)$$

$$d\left(\ln Z(\beta,V)\right) = \left(\frac{\partial \ln Z}{\partial \beta}\right)_{V,N} d\beta + \left(\frac{\partial \ln Z}{\partial V}\right)_{T,N} dV$$

$$d\ln Z = \qquad -\left\langle E_s \right\rangle d\beta \qquad + \beta \left\langle P_s \right\rangle dV$$

$$d\left(\ln Z + \left\langle E_s \right\rangle \beta\right) = d(\ln Z) + d\left(\left\langle E_s \right\rangle \beta\right)$$

$$= \beta\left(\left\langle dE_s \right\rangle + \left\langle P_s \right\rangle dV\right)$$

$$= \beta\left(\left(TdS - \left\langle P_s \right\rangle dV\right) + \left\langle P_s \right\rangle dV\right)$$

$$d\left(\ln Z + \left\langle E_s \right\rangle \beta\right) = \beta\left(TdS\right)$$

$$d\left(\ln Z + \langle E_s \rangle \beta\right) = \beta\left(TdS\right)$$

$$\Rightarrow d\left(-k \ln Z\right) = d\left(\frac{\langle E_s \rangle}{T} - S\right)$$

$$\Rightarrow -k \ln Z = \frac{\langle E_s \rangle}{T} - S$$

$$\Rightarrow -kT \ln Z = \langle E_s \rangle - TS = F(T,V) \quad \text{Helmholz Free Energy}$$

$$F(T,V,N) = -kT \ln Z\left(T,V,N\right)$$

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = -S = \left(\frac{-\partial\left(kT \ln Z\right)}{\partial T}\right)_{V,N} = -k \ln Z - kT\left(\frac{\partial\left(\ln Z\right)}{\partial T}\right)_{V,N}$$

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

$$\left(\frac{\partial F}{\partial N}\right)_{T,V} = \mu = -kT\left(\frac{\partial\left(\ln Z\right)}{\partial N}\right)_{T,V}$$

Example: Canonical distribution for free particles

Classical canonical distribution for N free particles of mass m moving in d dimensions in box of length L

$$Z(T,V,N) = \frac{1}{N!h^{dN}} \int_{0\le r_i \le L} d^{dN} r \int d^{dN} p \, e^{-\frac{\beta}{2m}\left(\sum_i p_i^2\right)}$$

$$= \frac{L^{dN}}{N!h^{dN}} \left(2\pi mkT\right)^{dN/2}$$

$$= \frac{1}{N!} (L)^{dN} \left(\frac{2\pi mkT}{h^2}\right)^{dN/2}$$

For $d = 3$, $L^3 \equiv V$

$$Z(T,V,N) = \frac{V^N}{N!} \left(\frac{2\pi mkT}{h^2}\right)^{3N/2}$$

Compare with microcanonical ensemble:

$$\Gamma(E,V,N) = \frac{V^N}{N!\Gamma\left(\frac{3N}{2}+1\right)} \left(\frac{2\pi mE}{h^2}\right)^{3N/2}$$

Example of a canonical ensemble consisting of 2 particles (Example 4.2 of your textbook)

Consider a system consisting of 2 distinguishable particles. Each particle can be in one of two microstates with single-particle energies 0 and Δ. The system is in equilibrium with a heat bath at temperature T.

s	ε_1	ε_2	E_s
1	0	0	0
2	0	Δ	Δ
3	Δ	0	Δ
4	Δ	Δ	2Δ

$$Z = \sum_s e^{-E_s/kT} = 1 + e^{-\Delta/kT} + e^{-\Delta/kT} + e^{-2\Delta/kT} = 1 + 2e^{-\Delta/kT} + e^{-2\Delta/kT}$$

$$Z = \sum_s e^{-E_s/kT} = 1 + e^{-\Delta/kT} + e^{-\Delta/kT} + e^{-2\Delta/kT} = 1 + 2e^{-\Delta/kT} + e^{-2\Delta/kT}$$

$$\langle E_s \rangle = -\frac{\partial \ln Z}{\partial \beta} = \frac{2\Delta e^{-\Delta/kT} + 2\Delta e^{-2\Delta/kT}}{1 + 2e^{-\Delta/kT} + e^{-2\Delta/kT}} = \frac{2\Delta e^{-\Delta/kT}}{1 + e^{-\Delta/kT}}$$

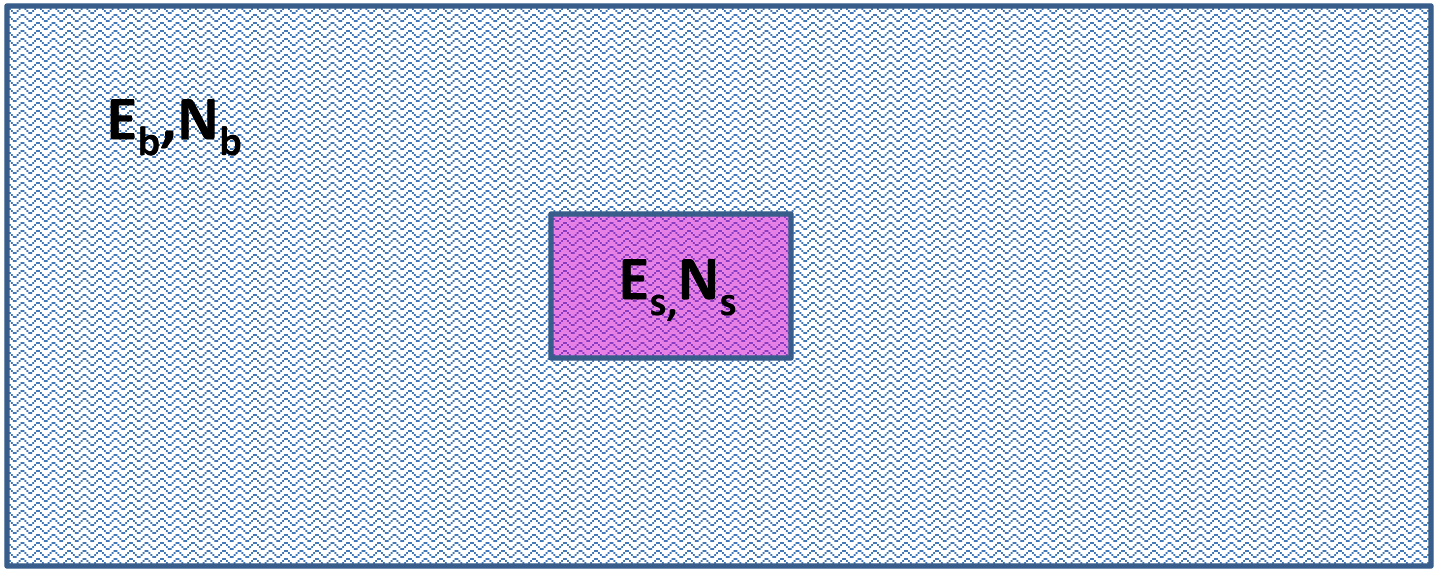
$$F = -kT \ln Z = -2kT \ln\left(1 + e^{-\Delta/kT}\right)$$

Note: This example of 2 independent identical particles has the simplifying property:

$$Z_{tot} = \sum_s e^{-E_s/kT} = 1 + e^{-\Delta/kT} + e^{-\Delta/kT} + e^{-2\Delta/kT} = 1 + 2e^{-\Delta/kT} + e^{-2\Delta/kT}$$

$$= \left(1 + e^{-\Delta/kT}\right)^2 = Z_1^2$$

Grand canonical ensemble



Assume $E_s << E_b$, $N_s << N_b$

$$E_{tot} = E_s + E_b \qquad E_s << E_b$$

$$N_{tot} = N_s + N_b \qquad N_s << N_b$$

Probability that system is in microstate s:

$$\mathcal{P}_s = \frac{\Omega_b\left(E_{tot} - E_s, N_{tot} - N_s\right)}{\sum_{s'} \Omega_b\left(E_{tot} - E_{s'}, N_{tot} - N_{s'}\right)}$$

$$\ln \mathcal{P}_s = C + \ln \Omega_b\left(E_{tot} - E_s, N_{tot} - N_s\right)$$

$$\approx C + \ln \Omega_b\left(E_{tot}, N_{tot}\right) - E_s \left(\frac{\partial \ln \Omega_b}{\partial E}\right)_{E_{tot}, N_{tot}} - N_s \left(\frac{\partial \ln \Omega_b}{\partial N}\right)_{E_{tot}, N_{tot}} \cdots$$

Grand canonical ensemble (continued):

Again recall :

$$S(E,V,N) = k \ln \Omega(E,V,N)$$

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T} = k\left(\frac{\partial \ln \Omega}{\partial E}\right)_{V,N}$$

$$\left(\frac{\partial S}{\partial N}\right)_{E,V} = -\frac{\mu}{T} = k\left(\frac{\partial \ln \Omega}{\partial N}\right)_{E,V}$$

$$\Rightarrow \ln \mathscr{P}_s = C + \ln \Omega_b\left(E_{tot} - E_s, N_{tot} - N_s\right)$$

$$\approx C + \ln \Omega_b\left(E_{tot}, N_{tot}\right) - E_s\left(\frac{\partial \ln \Omega_b}{\partial E}\right)_{E_{tot},N_{tot}} - N_s\left(\frac{\partial \ln \Omega_b}{\partial N}\right)_{E_{tot},N_{tot}} \cdots$$

$$\approx C + \ln \Omega_b\left(E_{tot}, N_{tot}\right) - E_s \frac{1}{kT} + N_s \frac{\mu}{kT}$$

$$\Rightarrow \mathscr{P}_s = C' e^{-\left(E_s - \mu N_s\right)/kT} \equiv C' e^{-\beta\left(E_s - \mu N_s\right)} \equiv \frac{1}{Z_G} e^{-\beta\left(E_s - \mu N_s\right)}$$

where : $\quad Z_G \equiv \sum_{s'} e^{-\beta\left(E_{s'} - \mu N_{s'}\right)}$

Grand canonical ensemble (continued):

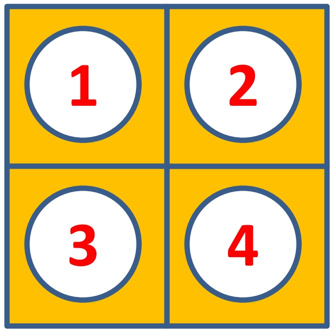
$$\Rightarrow \mathscr{P}_s = \frac{1}{Z_G} e^{-\beta(E_s - \mu N_s)}$$

$$\text{where:} \qquad Z_G \equiv \sum_{s'} e^{-\beta(E_{s'} - \mu N_{s'})}$$

$$\text{Note that } \Omega_{Landau}(T,V,\mu) = F - \mu N = -kT \ln Z_G$$

	Partition function	Thermodynamic potential
Microcanonical	$\Omega(E,V,N)$	$S(E,V,N)=k\ln(\Omega)$
Canonical	$Z(T,V,N)$	$F(T,V,N)=-kT\ln(Z)$ $F=E-TS$
Grand canonical	$Z_G(T,V,\mu)$	$\Omega_{Landau}(T,V,\mu)=-kT\ln(Z_G)$ $\Omega_{landau}=F-\mu N$

Example of a grand canonical ensemble:



Consider a system with 4 sites, each of which can be unoccupied or occupied (n_i=0 or 1) with corresponding site energies ε_i=0 or Δ.

s	Config.	#	E_s	N_s
1	0 0 0 0	1	0	0
2	1 0 0 0	4	Δ	1
3	1 1 0 0	6	2Δ	2
4	1 1 1 0	4	3Δ	3
5	1 1 1 1	1	4Δ	4

$$Z_G = 1 + 4e^{-\beta(\Delta-\mu)} + 6e^{-2\beta(\Delta-\mu)} + 4e^{-3\beta(\Delta-\mu)} + e^{-4\beta(\Delta-\mu)}$$

$$Z_G = 1 + 4e^{-\beta(\Delta-\mu)} + 6e^{-2\beta(\Delta-\mu)} + 4e^{-3\beta(\Delta-\mu)} + e^{-4\beta(\Delta-\mu)}$$

$$= \left(1 + e^{-\beta(\Delta-\mu)}\right)^4$$

$$\langle N_s \rangle = \sum_{s'} N_{s'} \mathcal{P}_{s'}$$

$$= \frac{1\cdot 4e^{-\beta(\Delta-\mu)} + 2\cdot 6e^{-2\beta(\Delta-\mu)} + 3\cdot 4e^{-3\beta(\Delta-\mu)} + 4\cdot e^{-4\beta(\Delta-\mu)}}{Z_G}$$

$$= \frac{4e^{-\beta(\Delta-\mu)}\left(1 + 3e^{-\beta(\Delta-\mu)} + 3e^{-2\beta(\Delta-\mu)} + e^{-3\beta(\Delta-\mu)}\right)}{\left(1 + e^{-\beta(\Delta-\mu)}\right)^4}$$

$$= \frac{4e^{-\beta(\Delta-\mu)}}{\left(1 + e^{-\beta(\Delta-\mu)}\right)}$$

Solving for μ:

$$\mu = \Delta - kT \ln\left(\frac{4}{\langle N_s \rangle} - 1\right)$$