

PHY 341/641 Thermodynamics and Statistical Physics

Lecture 15

Methodologies of statistical mechanics. (Chapter 4 in STP)

- A. Canonical ensemble
- B. Grand canonical ensemble

2/20/2012

PHY 341/641 Spring 2012 -- Lecture 15

1

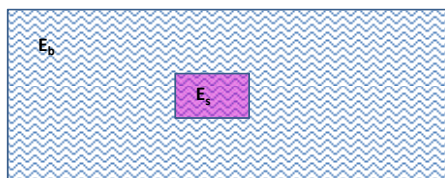
5	1/27/2012	Entropy	2.15-2.19	HW 5	1/30/2012
6	1/30/2012	Thermodynamic Potentials	2.20-2.21	HW 6	2/1/2012
7	2/6/2012	Thermodynamic Potentials	2.22-2.24	HW 7	2/3/2012
8	2/6/2012	Introduction to probability theory	3.1-3.3	HW 8	2/6/2012
9	2/6/2012	Probability distributions	3.4-3.5	HW 9	2/8/2012
10	2/6/2012	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			
	3/2/2012	APS -- no class, take-home exam			
	3/5/2012				

2/20/2012

PHY 341/641 Spring 2012 -- Lecture 15

2

Review:
Canonical ensemble:



2/20/2012

PHY 341/641 Spring 2012 -- Lecture 15

3

Canonical ensemble (continued)

$$E_{tot} = E_s + E_b \quad E_s \ll E_b$$

Probability that system is in microstate s :

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

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

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

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

2/20/2012

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4

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	$\Omega(T, V, \mu) = F - \mu N$	$d\Omega = -SdT - PdV - N d\mu$

2/20/2012

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5

Canonical ensemble

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

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

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

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

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

$$= \beta \langle dE_s \rangle + \langle P_s \rangle dV$$

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

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

2/20/2012

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6

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

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

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

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

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

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

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

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

2/20/2012

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7

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

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

$$= \frac{L^{dN}}{N! h^{dN}} (2\pi m k T)^{dN/2}$$

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

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

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

Compare with microcanonical ensemble:

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

2/20/2012

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8

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

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

2/20/2012

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9

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

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

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

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

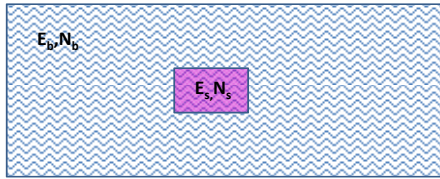
$$Z_{tot} = \sum_s e^{-E_s/kT} = 1 + e^{-\Delta/kT} + e^{-\Delta/kT} + e^{-2\Delta/kT} = 1 + 2e^{-\Delta/kT} + e^{-2\Delta/kT} = (1 + e^{-\Delta/kT})^2 = Z_1^2$$

2/20/2012

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10

Grand canonical ensemble



Assume $E_s \ll E_b$, $N_s \ll N_b$

2/20/2012

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11

$$E_{tot} = E_s + E_b \quad E_s \ll E_b$$

$$N_{tot} = N_s + N_b \quad N_s \ll N_b$$

Probability that system is in microstate s :

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

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

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

2/20/2012

PHY 341/641 Spring 2012 -- Lecture 15

12

Grand canonical ensemble (continued):

Again recall:

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

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

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

$$\Rightarrow \ln \mathcal{P}_s = C + \ln \Omega_b(E_{tot} - E_s, N_{tot} - N_s) \\ \approx C + \ln \Omega_b(E_{tot}, N_{tot}) - E_s \left(\frac{\partial \ln \Omega_b}{\partial E} \right)_{E_{tot}, N_{tot}} - N_s \left(\frac{\partial \ln \Omega_b}{\partial N} \right)_{E_{tot}, N_{tot}} \dots$$

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

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

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

2/20/2012

PHY 341/641 Spring 2012 -- Lecture 15

13

Grand canonical ensemble (continued):

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

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

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

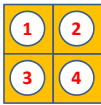
	Partition function	Thermodynamic potential
Microcanonical	$\Omega(E, V, N)$	$S(E, V, N) = k \ln \Omega$
Canonical	$Z(T, V, N)$	$F(T, V, N) = -kT \ln Z$ $F = E - TS$
Grand canonical	$Z_G(T, V, \mu)$	$\Omega_{\text{Landau}}(T, V, \mu) = -kT \ln Z_G$ $\Omega_{\text{Landau}} = F - \mu N$

2/20/2012

PHY 341/641 Spring 2012 -- Lecture 15

14

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 $\epsilon_i=0$ 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

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

2/20/2012

PHY 341/641 Spring 2012 -- Lecture 15

15

$$\begin{aligned}
 Z_G &= 1 + 4e^{-\beta(\Lambda-\mu)} + 6e^{-2\beta(\Lambda-\mu)} + 4e^{-3\beta(\Lambda-\mu)} + e^{-4\beta(\Lambda-\mu)} \\
 &= (1 + e^{-\beta(\Lambda-\mu)})^4 \\
 \langle N_s \rangle &= \sum_{s'} N_{s'} \mathcal{P}_{s'} \\
 &= \frac{1 \cdot 4e^{-\beta(\Lambda-\mu)} + 2 \cdot 6e^{-2\beta(\Lambda-\mu)} + 3 \cdot 4e^{-3\beta(\Lambda-\mu)} + 4 \cdot e^{-4\beta(\Lambda-\mu)}}{Z_G} \\
 &= \frac{4e^{-\beta(\Lambda-\mu)}(1 + 3e^{-\beta(\Lambda-\mu)} + 3e^{-2\beta(\Lambda-\mu)} + e^{-3\beta(\Lambda-\mu)})}{(1 + e^{-\beta(\Lambda-\mu)})^4} \\
 &= \frac{4e^{-\beta(\Lambda-\mu)}}{(1 + e^{-\beta(\Lambda-\mu)})}
 \end{aligned}$$

Solving for μ :

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