PHY 341/641
Thermodynamics and Statistical Physics

Lecture 12

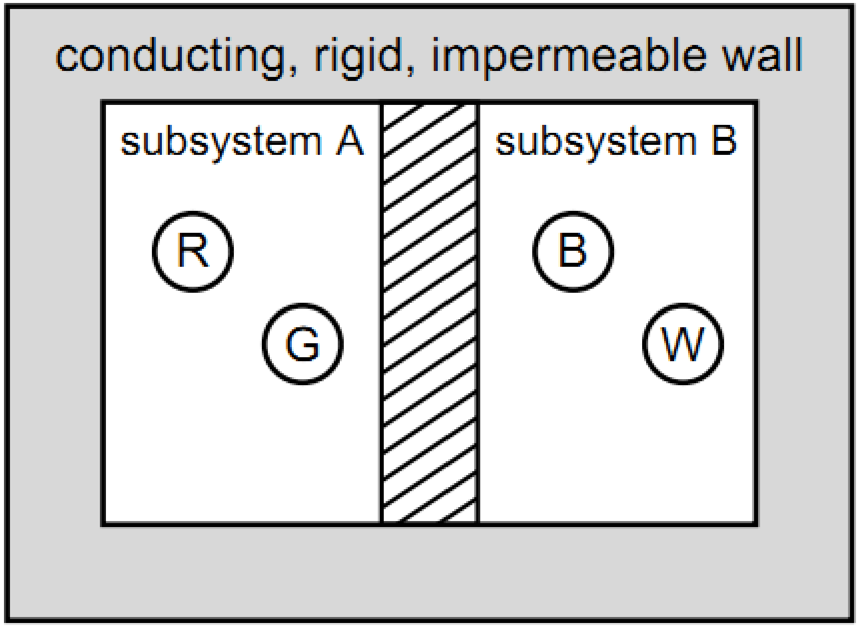
Methodologies of statistical mechanics. (Chapter 4 in STP)

A. Examples of macrostates and microstates
B. $S=k \ln(\Omega)$
C. Counting microstates

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
	2/17/2012				
	2/20/2012				
	2/22/2012				
	2/24/2012				
	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 from Lecture 11 – 2 subsystems sharing total energy

N_A=2, N_B=2



$$E_{tot} = E_A + E_B = 6$$

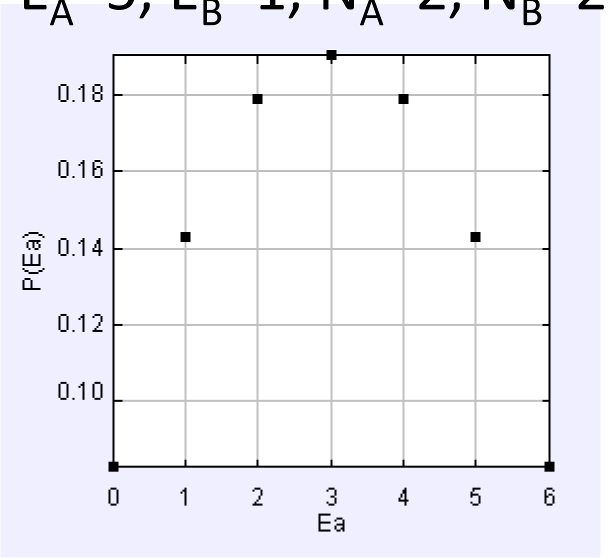
$$\Omega_{tot} = \sum_{E_{tot}=6} \Omega_A(E_A)\Omega_B(E_B) = 84$$

E_A	microstates	$\Omega_A(E_A)$	E_B	microstates	$\Omega_B(E_B)$	$\Omega_A \Omega_B$	$P_A(E_A)$
6	6,0 0,6 5,1 1,5 4,2 2,4 3,3	7	0	0,0	1	7	7/84
5	5,0 0,5 4,1 1,4 3,2 2,3	6	1	1,0 0,1	2	12	12/84
4	4,0 0,4 3,1 1,3 2,2	5	2	2,0 0,2 1,1	3	15	15/84
3	3,0 0,3 2,1 1,2	4	3	3,0 0,3 2,1 1,2	4	16	16/84
2	2,0 0,2 1,1	3	4	4,0 0,4 3,1 1,3 2,2	5	15	15/84
1	1,0 0,1	2	5	5,0 0,5 4,1 1,4 3,2 2,3	6	12	12/84
0	0,0	1	6	6,0 0,6 5,1 1,5 4,2 2,4 3,3	7	7	7/84

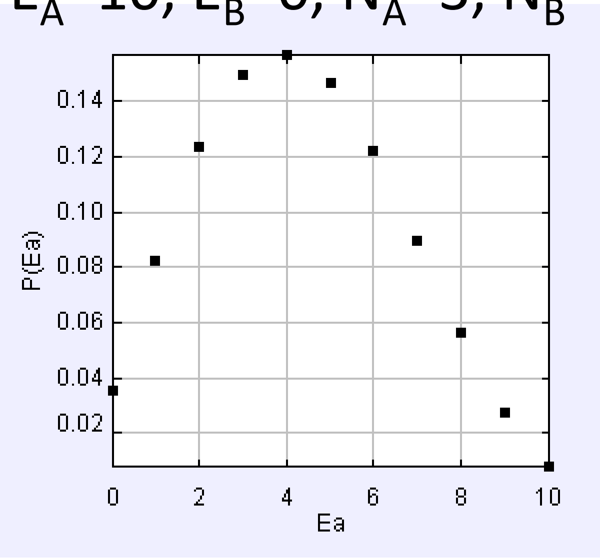
Table 4.3: The 84 equally probable microstates accessible to the isolated composite system composed of subsystems A and B after the removal of the internal constraint. The total energy is $E_{\text{tot}} = E_A + E_B = 6$ with $N_A = 2$ and $N_B = 2$. Also shown are the number of accessible microstates in each subsystem and the probability $P_A(E_A)$ that subsystem A has energy E_A.

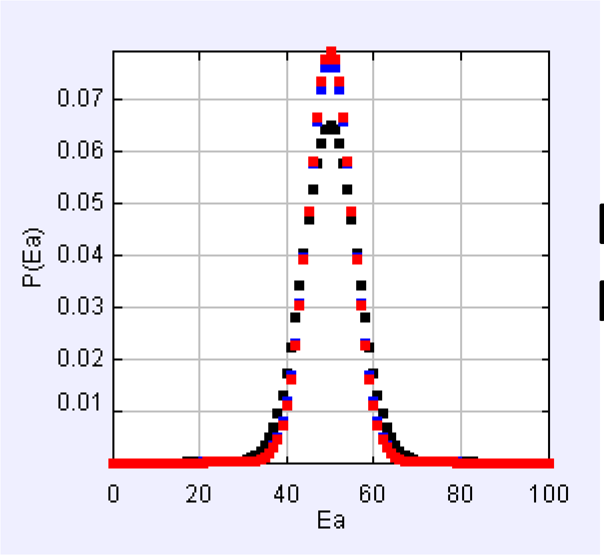
Simulation program [stp_EinsteinSolids.jar]

E_A=5, E_B=1, N_A=2, N_B=2



E_A=10, E_B=0, N_A=3, N_B=4





E_A=100, E_B=0,
N_A=N_B=100,1000,10000

Properties of microstate number function:

$$\Omega_{\text{tot}}(E_{tot}) = \sum_{E_A} \Omega_A(E_A)\Omega_B(E_{tot} - E_A)$$

For large N_A, N_B :

$$\Omega_{\text{tot}}(E_{tot}) \approx \Omega_A(\tilde{E}_A)\Omega_B(E_{tot} - \tilde{E}_A)$$

where $\tilde{E}_A \equiv$ most probable E_A

$$\Rightarrow \ln\Omega_{\text{tot}}(E_{tot}) \approx \ln\Omega_A(\tilde{E}_A) + \ln\Omega_B(E_{tot} - \tilde{E}_A)$$

Properties of Boltzmann entropy function

$$S_{tot} = k\ln\Omega_{\text{tot}} \approx k\ln\Omega_A(\tilde{E}_A) + k\ln\Omega_B(E_{tot} - \tilde{E}_A)$$

$$S_{tot} \approx S_A + S_B$$

Other examples of microstate analysis for both classical and quantum systems.

For N particles moving according to the classical mechanical (Newton's) laws of physics in d-dimensional space (d=1,2,3), Liouville's theorem shows that phase space $d^{dN}r\ d^{dN}p$ spans all possibilites. In order to count the number of microstates, it is useful to define:

The number of microstates with energy less than or equal to E:

$$\Gamma(E) \propto \int_{Energy \leq E} d^{dN}r\ d^{dN}p$$

The number of microstates with energy between E and $E + dE$:

$$g(E) = \frac{d\Gamma}{dE}$$

Relationship between classical and quantum microstate analyses:

Classical $\qquad\qquad\qquad\qquad$ Quantum

$$\frac{1}{N!h^{dN}}\int d^{dN}r \; d^{dN}p \;\Rightarrow\; \sum_n$$

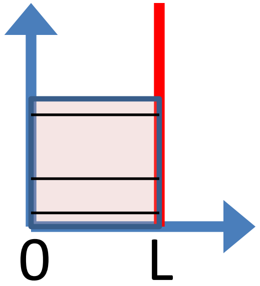
Example for quantum particle in 1-dimensional box:

Classical

$$\frac{p_x^2}{2m} \le E$$

Quantum

$$\varepsilon_{\mathrm{n}} = \frac{h^2 n^2}{8mL^2} \le E$$



Example: single particle of mass m confined within a 1 dimensional box of length L; d=1, N=1:

Classical treatment :

$$0 \le x \le L :$$

$$-\sqrt{2mE} \le p_x \le \sqrt{2mE}$$

$$\Gamma_{Cl}(E) = \int_0^L dx \int_{-\sqrt{2mE}}^{\sqrt{2mE}} dp_x = 2L\sqrt{2mE}$$

Quantum treatment :

Discrete energies : $\varepsilon_n = \dfrac{h^2 n^2}{8mL^2} \quad n = 1,2,3\cdots$

$$\Gamma_Q(E) = \sum_{n=1}^{\varepsilon_n \le E} = \frac{2L}{h}\sqrt{2mE}$$

Example: single particle of mass m confined within a 2-dimensional square box of length L; d=2, N=1:

Classical treatment:

$$\Gamma_{Cl}(E) = \iint_{Energy \le E} d^2r\, d^2p = L^2 \int_0^{2\pi} dp_\varphi \int_0^{\sqrt{2mE}} p_r dp_r = \pi L^2 (2mE)$$

Quantum treatment:

Discrete energies: $\varepsilon_{n_x,n_y} = \dfrac{h^2\left(n_x^2 + n_y^2\right)}{8mL^2} \quad n_x, n_y = 1,2,3\cdots$

$$\Gamma_Q(E) = \sum_{n_x,n_y=1}^{\varepsilon_{n_x,n_y} \le E} = \frac{\pi L^2}{h^2}(2mE)$$

Discretization effects in quantum case:

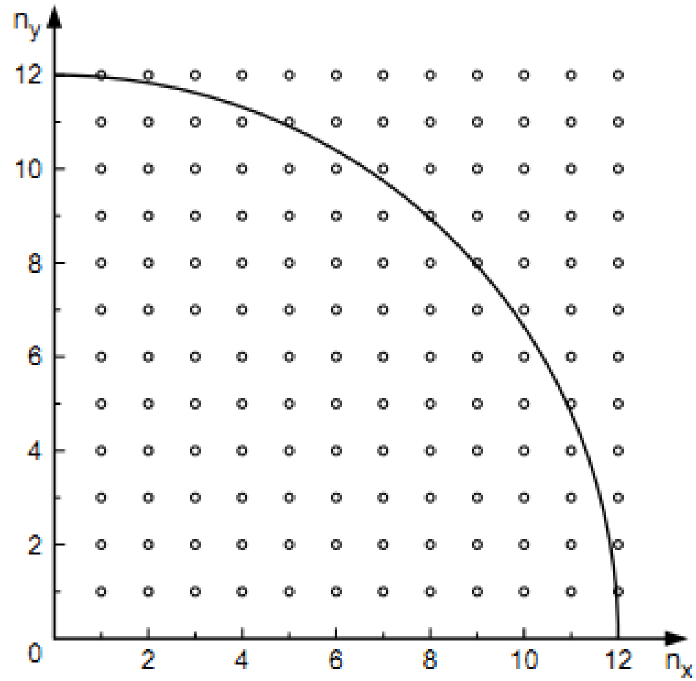


Figure 4.6: The points represent possible values of n_x and n_y. Note that n_x and n_y are integers with $n_x, n_y \geq 1$. Each point represents a single-particle microstate. What is the total number of states for $R \leq 12$? The corresponding number from the asymptotic relation is $\Gamma(E) = \pi\, 12^2/4 \approx 113$.

$$\text{For} \quad E = \frac{h^2 12^2}{8mL^2} \quad \frac{1}{h}\Gamma_{Cl} = 36\pi^2 = 113.097$$

$$\Gamma_Q = 98$$

Example: single particle of mass m confined within a 3-dimensional square box of length L; d=3, N=1:

Classical treatment:

$$\Gamma_{Cl}(E) \iiint_{Energy\leq E} d^3r\, d^3p = \frac{4\pi L^3}{3}\left(2mE\right)^{3/2}$$

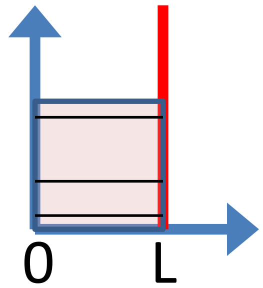
Quantum treatment:

Discrete energies: $\varepsilon_{n_x,n_y,n_z} = \dfrac{h^2\left(n_x^2+n_y^2+n_z^2\right)}{8mL^2} \quad n_x, n_y, n_z = 1,2,3\cdots$

$$\Gamma_Q(E) = \sum_{n_x,n_y,n_z=1}^{\varepsilon_{n_x,n_y,n_z}\leq E} = \frac{4\pi L^3}{3h^3}\left(2mE\right)^{3/2}$$

Many particles; N>1

Consider N=2, d=1



Quantum

$$\varepsilon_{n_i} = \frac{h^2 n_i^{\,2}}{8mL^2}$$

$$\Gamma_Q(E) = \sum_{\varepsilon_{n_1}+\varepsilon_{n_2}\le E}$$

distinguishable particles		Bose statistics		Fermi statistics	
n_1	n_2	n_1	n_2	n_1	n_2
1	1	1	1		
2	1	2	1	2	1
1	2				
2	2	2	2		
3	1	3	1	3	1
1	3				
3	2	3	2	3	2
2	3				
3	3	3	3		
4	1	4	1	4	1
1	4				
4	2	4	2	4	2
2	4				
4	3	4	3	4	3
3	4				
4	4	4	4		

Table 4.8: The microstates of two identical noninteracting particles of mass m in a one-dimensional box such that each particle can be in one of the four lowest energy states. The rows are ordered by their total energy. If the particles obey Fermi statistics, they cannot be in the same microstate, so $n_1 = 1$, $n_2 = 1$ is not allowed. There is no such restriction for Bose statistics. Because the particles are identical and hence indistinguishable, $n_1 = 1$, $n_2 = 2$ and $n_1 = 2$, $n_2 = 1$ are the same microstate.

distinguishable particles		Bose statistics		Fermi statistics		
n_1	n_2	n_1	n_2	n_1	n_2	
1	1	1	1			$n_1^2+n_2^2=2$
2	1	2	1	2	1	$n_1^2+n_2^2=3$
1	2					
2	2	2	2			$n_1^2+n_2^2=4$
3	1	3	1	3	1	$n_1^2+n_2^2=10$
1	3					
3	2	3	2	3	2	$n_1^2+n_2^2=13$
2	3					
3	3	3	3			$n_1^2+n_2^2=18$
4	1	4	1	4	1	$n_1^2+n_2^2=17$
1	4					
4	2	4	2	4	2	$n_1^2+n_2^2=20$
2	4					
4	3	4	3	4	3	$n_1^2+n_2^2=25$
3	4					
4	4	4	4			$n_1^2+n_2^2=32$

Table 4.8: The microstates of two identical noninteracting particles of mass m in a one-dimensional box such that each particle can be in one of the four lowest energy states. The rows are ordered by their total energy. If the particles obey Fermi statistics, they cannot be in the same microstate, so $n_1 = 1$, $n_2 = 1$ is not allowed. There is no such restriction for Bose statistics. Because the particles are identical and hence indistinguishable, $n_1 = 1$, $n_2 = 2$ and $n_1 = 2$, $n_2 = 1$ are the same microstate.