PHY 341/641
Thermodynamics and Statistical Physics

Lecture 13

Methodologies of statistical mechanics. (Chapter 4 in STP)

A. Evaluation of Γ(E) for N>1
B. Microcanonical ensemble
C. Evaluation of temperature

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				

Relationship between classical and quantum microstate analyses:

Classical — Quantum

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

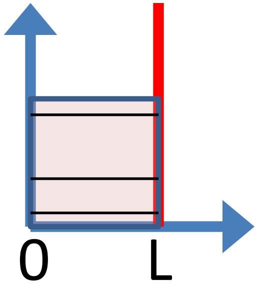
Example for quantum particle in 1-dimensional box:

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:

$$0 \leq x \leq L:$$

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

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

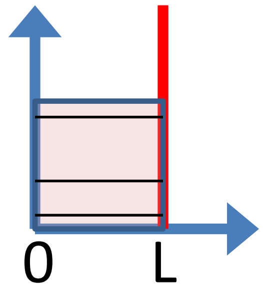
Quantum treatment:

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

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

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			$n_1^2+n_2^2=32$

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Classical analysis for Γ(E) for d=1, N=2

Classical treatment :

$$0 \le x_1 \le L \qquad 0 \le x_2 \le L$$

$$0 \le p_{x,1}^2 + p_{x,2}^2 \le 2mE$$

$$\Gamma_{Cl}(E) = \int_0^L dx_1 \int_0^L dx_2 \iint_{0 \le p_{x,1}^2 + p_{x,2}^2 \le 2mE} dp_{x,1} dp_{x,2}$$

Trick: Map problem into general problem of finding volume of ν dimensional hypersphere of radius R (see Section 4.14.1 of STP)

$$V_\nu(R) \equiv \iiint\limits_{x_1^2+x_2^2+\cdots x_\nu^2 \le R^2} dx_1 dx_2 dx_3 dx_4 \cdots dx_\nu = C_\nu R^\nu$$

Note that: $V_1(R) = 2R$

$$V_2(R) = \pi R^2$$

$$V_3(R) = \frac{4\pi}{3} R^3$$

In terms of constant C_ν:

$$V_\nu(R) = \nu C_\nu \int_0^R r^{\nu-1} dr$$

Clever trick to find C_ν:

Note that: $I_\nu \equiv \left(\int_{-\infty}^{\infty} dx\, e^{-x^2} \right)^\nu = \pi^{\frac{\nu}{2}}$

This can be written in the form:

$$I_\nu = \int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dx_2 \cdots \int_{-\infty}^{\infty} dx_\nu\, e^{-x_1^2 - x_2^2 \cdots - x_\nu^2} = \nu C_\nu \int_0^\infty r^{\nu-1} e^{-r^2} dr$$

$$I_\nu = \pi^{\frac{\nu}{2}} = \nu C_\nu \int_0^\infty r^{\nu-1} e^{-r^2} dr$$

Gamma function: $\Gamma(\alpha) \equiv \int_0^\infty dt\, t^{\alpha-1} e^{-t}$

$$\Rightarrow \int_0^\infty r^{\nu-1} e^{-r^2} dr = \frac{1}{2}\Gamma\left(\tfrac{\nu}{2}\right)$$

$$\nu C_\nu \frac{1}{2}\Gamma\left(\tfrac{\nu}{2}\right) = \pi^{\frac{\nu}{2}}$$

$$\Rightarrow C_\nu = \frac{2\pi^{\frac{\nu}{2}}}{\nu\Gamma\left(\frac{\nu}{2}\right)} = \frac{\pi^{\frac{\nu}{2}}}{\Gamma\left(\frac{\nu}{2}+1\right)}$$

Note: $\alpha\Gamma(\alpha) = \Gamma(\alpha+1)$

ν	$\Gamma(\nu/2)$	C_ν
1	$\sqrt{\pi}$	2
2	1	π
3	$\frac{1}{2}\sqrt{\pi}$	$\frac{4\pi}{3}$

Result for Γ(E) for d=1, N=2

$$\Gamma_{Cl}(E) = \int_0^L dx_1 \int_0^L dx_2 \iint_{0\leq p_{x,1}^2+p_{x,2}^2\leq 2mE} dp_{x,1}dp_{x,2}$$

$$= L^2\pi\left(2mE\right)$$ (same as result for d=2, N=1)

Check:

$$\text{Let } E \equiv \frac{h^2\kappa^2}{8mL^2} \quad \text{so that} \quad \frac{1}{h^2}\Gamma_{Cl}(\kappa^2) = \frac{\pi}{4}\kappa^2$$

$$\frac{1}{h^2}\Gamma_{Cl}(\kappa^2) = \frac{\pi}{4}\kappa^2 \qquad \Gamma_Q(\kappa^2) = \sum_{n_1^2+n_2^2\leq\kappa^2}$$

κ^2	Γ_{Cl}	Γ_Q
2	1.571	1.000
5	3.927	3.000
8	6.283	4.000
10	7.854	6.000
13	10.210	8.000
17	13.352	10.000
18	14.137	11.000
20	15.708	13.000
25	19.635	16.000

Microstate count for N particles in d-dimensions

Classical microstate distribution

$$\Gamma(E) = \frac{1}{N!h^{dN}} \int_{\sum_i \frac{p_i^2}{2m} \leq E} d^{dN}r \; d^{dN}p$$

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

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

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

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

Boltzmann entropy function

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

For 3-dimension system of N indepent particles

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

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

Stirling approximation for $x \to \infty$:

$$x! \equiv \Gamma(x+1) \approx x \ln x - x + \tfrac{1}{2}\ln(2\pi x)$$

To leading order in N:

$$S(E,V,N) = Nk\left(\ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln\left(\frac{4\pi mE}{3Nh^2}\right) + \frac{5}{2}\right)$$

$$\text{Note:} \quad \text{more correct analysis would use:}$$

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

$$\text{where } \Omega(E,V,N) = \frac{d\Gamma(E,V,N)}{dE}$$

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

$$\frac{d\Gamma(E,V,N)}{dE} = \Gamma(E,V,N)\frac{3N}{2E}$$

$$\ln\frac{d\Gamma(E,V,N)}{dE} = \ln\Gamma(E,V,N) - \ln\frac{2E}{3N}$$

$$\underset{N\to\infty}{\approx} \ln\Gamma(E,V,N)$$

$$S(E,V,N) = Nk\left(\ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln\left(\frac{4\pi mE}{3Nh^2}\right) + \frac{5}{2}\right)$$

Relation to temperature and other thermodynamic variables

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{3}{2} Nk \frac{1}{E}$$

$$\Rightarrow E = \frac{3}{2} NkT \qquad \text{Recall}: U = \frac{NkT}{\gamma - 1}$$

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N} = Nk \frac{1}{V}$$

$$\Rightarrow PV = NkT$$