PHY 341/641
Thermodynamics and Statistical Physics

Lecture 14

Methodologies of statistical mechanics. (Chapter 4 in STP)

A. Microcanonical ensemble
B. Canonical ensemble

Schedule and assignments

Note: This schedule may need to be modified -- please check for changes and additions frequently.

No.	Lecture Date	Topic	Text Sections	Problem Assignments	Assignment Due Date
1	1/18/2012	Introductory concepts	1.1-1.5	HW 1	1/23/2012
2	1/20/2012	Introductory concepts	1.6-1.12	HW 2	1/23/2012
3	1/23/2012	First Law of Thermodynamics	2.1-2.11	HW 3	1/25/2012
4	1/25/2012	Second Law of Thermodynamics	2.12-2.14	HW 4	1/27/2012
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
	2/20/2012				
	2/22/2012				
	2/24/2012				

Microstate count for N particles in d-dimensions – microcanonical distribution

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

$$\Gamma(E,V,N)=\frac{1}{N!h^{dN}}\int_{0\le r_i\le L} d^{dN}r \int_{\sum_i \frac{p_i^2}{2m}\le E} d^{dN}p$$

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

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

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

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

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

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

$$\Rightarrow PV = NkT$$

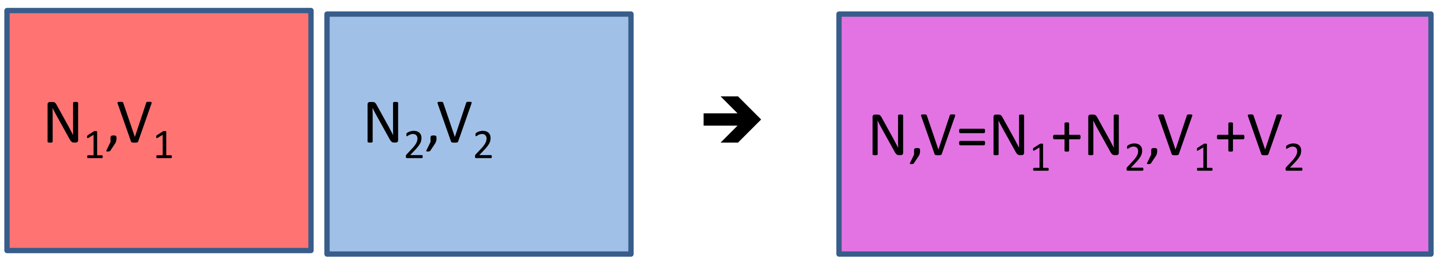
Also note:

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

For ideal gas of N particles in 3-dimensional box of volume V :

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

Gibb's paradox :



$N_1/V_1=N_2/V_2=N/V$

$$\Delta S \equiv S(E,V,N) - \left(S(E_1,V_1,N_1) + S(E_2,V_2,N_2)\right)$$

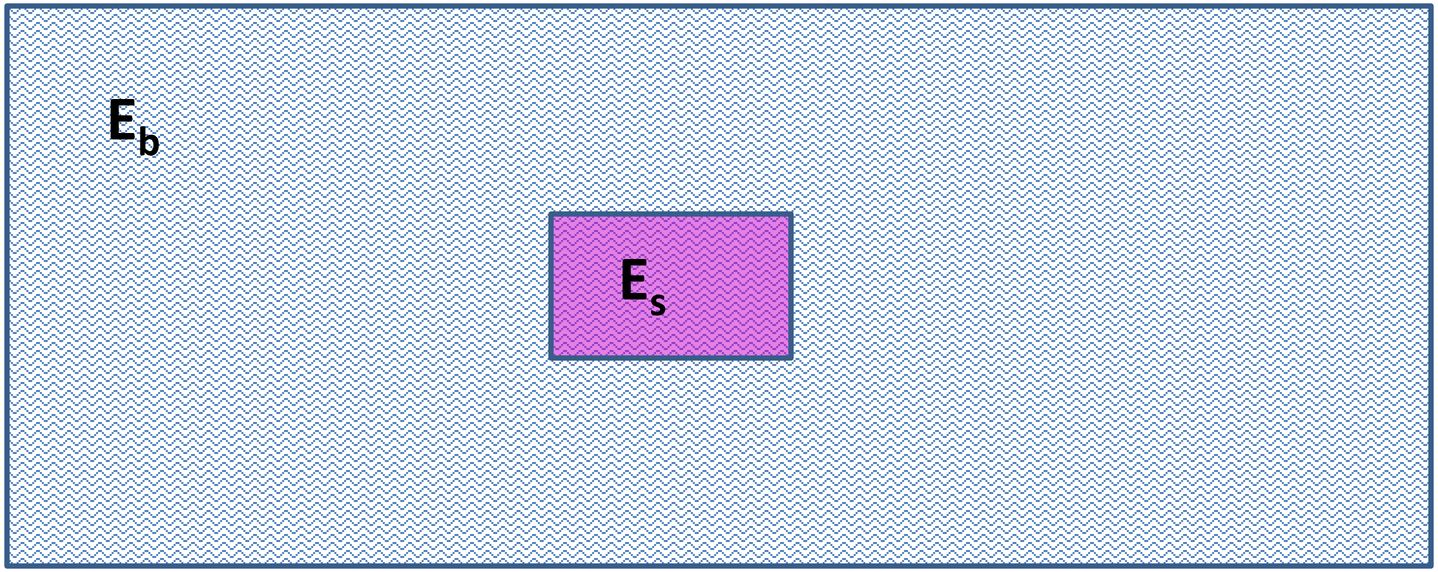
$$\text{If} \quad m_1 = m_2 \quad \text{and} \quad \frac{E_1}{N_1} = \frac{E_2}{N_2} = \frac{E}{N} \quad \Rightarrow \Delta S = 0$$

Microcanonical ensemble:

For ideal gas of N particles in 3-dimensional box of volume V:

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

Canonical ensemble:



Canonical ensemble (continued)

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

Probability that system is in microstate s:

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

$$\ln P_s = C + \ln \Omega_b\left(E_{tot} - E_s\right)$$

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

Canonical ensemble (continued)

$$\ln P_s = C + \ln \Omega_b\left(E_{tot} - E_s\right)$$

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

$$\left(\frac{\partial k \ln \Omega_b\left(E\right)}{\partial E}\right)_{E_{tot}} \approx \left(\frac{\partial S_b(E)}{\partial E}\right)_{V,N} = \frac{1}{T_b}$$

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

$$\Rightarrow \boxed{P_s = C' e^{-E_s/kT}}$$

Canonical ensemble:

$$P_s = C' e^{-E_s/kT}$$

$$= \frac{1}{Z} e^{-E_s/kT}$$

$$\text{where:} \quad Z \equiv \sum_{s'} e^{-E_{s'}/kT} \quad \text{"partition function"}$$

Calculations using the partition function :

$$Z \equiv \sum_{s'} e^{-E_{s'}/kT} = \sum_{s'} e^{-\beta E_{s'}} \quad \text{where } \beta = \tfrac{1}{kT}$$

Canonical ensemble continued – average energy of system:

$$\langle E_s \rangle = \frac{1}{Z}\sum_{s'} E_{s'} e^{-E_{s'}/kT} = \frac{1}{Z}\sum_{s'} E_{s'} e^{-\beta E_{s'}}$$

$$= -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta}$$

Heat capacity for canonical ensemble:

$$C_V = \frac{\partial \langle E_s \rangle}{\partial T} = \frac{1}{kT^2}\frac{\partial \langle E_s \rangle}{\partial \beta}$$

$$= -\frac{1}{kT^2}\frac{\partial^2 \ln Z}{\partial \beta^2} = -\frac{1}{kT^2}\left(\frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} - \left(\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right)^2\right)$$

$$= \frac{1}{kT^2}\left(\langle E_s{}^2 \rangle - \langle E_s \rangle^2\right)$$

First Law of Thermodynamics for canonical ensemble

$$\langle E_s \rangle = \frac{1}{Z}\sum_{s'} E_{s'} e^{-\beta E_{s'}} = \sum_{s'} E_{s'} P_{s'}$$

$$d\langle E_s \rangle = \sum_{s'} E_{s'} dP_{s'} + \sum_{s'} P_{s'} dE_{s'}$$

$$= \sum_{s'} E_{s'} dP_{s'} + \sum_{s'} P_{s'} \frac{dE_{s'}}{dV} dV$$

- Pressure associated with state s

$$d\langle E_s \rangle = \sum_{s'} E_{s'} dP_{s'} - \langle P \rangle dV$$

$$d\langle E_s\rangle = \sum_{s'} E_{s'} dP_{s'} - \langle P\rangle dV$$

First law:

$$dE = TdS - PdV \qquad \Rightarrow TdS = \sum_{s'} E_{s'} dP_{s'}$$

where $P_{s'} = \frac{1}{Z} e^{-\beta E_{s'}}$

note that: $E_{s'} = -\frac{1}{\beta} \ln ZP_{s'} = -\frac{1}{\beta}\left(\ln Z + \ln P_{s'}\right)$

$$\Rightarrow \sum_{s'} E_{s'} dP_{s'} = -kT\left(\sum_{s'} (\ln Z) dP_{s'} + \sum_{s'} \ln P_{s'} dP_{s'}\right)$$

=0

$$TdS = \sum_{s'} E_{s'} dP_{s'} = -kT\left(\sum_{s'} \ln P_{s'} dP_{s'} \right)$$

$$dS = -k\left(\sum_{s'} \ln P_{s'} dP_{s'} \right) = -d\left(k \sum_{s'} P_{s'} \ln P_{s'} \right)$$

$$\Rightarrow S = S_0 - k \sum_{s'} P_{s'} \ln P_{s'}$$

We also note that :

$$TdS = C_V dT$$

Recap:

$$\text{Microcanonical ensemble: Internal energy } U \Leftrightarrow E$$

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

$$E(S,V,N) \quad \Rightarrow dE = TdS - PdV + \mu dN$$

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

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

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

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)

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

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

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

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

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

Note: Using first law: $\left\langle dE_s \right\rangle = TdS - \left\langle P_s \right\rangle dV$

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

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

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

$$\Rightarrow -kT\ln Z = \langle E_s\rangle - TS = F(T,V)$$ 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

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

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

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

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:

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