

PHY 341/641
Thermodynamics and Statistical Physics

Lecture 14

Methodologies of statistical mechanics. (Chapter 4 in STP)

- A. Microcanonical ensemble
- B. Canonical ensemble

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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	1/29/2012	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				

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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

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

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

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

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

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

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Boltzmann entropy function

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

For 3-dimension system of N independent particles

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

Stirling approximation for $x \rightarrow \infty$:

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

To leading order in N :

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

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Note: more correct analysis would use:

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

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

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

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

$$\begin{aligned} \ln \frac{d\Gamma(E, V, N)}{dE} &= \ln \Gamma(E, V, N) - \ln \frac{2E}{3N} \\ &\approx \ln \Gamma(E, V, N) \end{aligned}$$

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

Relation to temperature and other thermodynamic variables

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

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

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

$$\Rightarrow PV = NkT$$

Also note:

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

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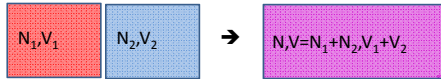
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For ideal gas of N particles in 3-dimensional box of volume V :

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

Gibb's paradox :



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

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

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

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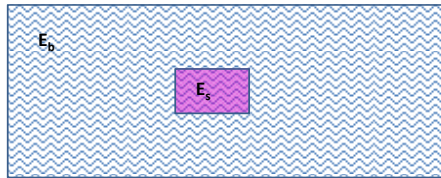
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Microcanonical ensemble :

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

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

Canonical ensemble:



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Canonical ensemble (continued)

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

Probability that system is in microstate s :

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

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

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

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Canonical ensemble (continued)

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

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

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

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

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Canonical ensemble:

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

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

Calculations using the partition function:

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

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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:

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

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

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

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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

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

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

First law:

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

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

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

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

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

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

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

We also note that:

$$TdS = C_V dT$$

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Recap:

Microcanonical ensemble : Internal energy $U \Leftrightarrow E$

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

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

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

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

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

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

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Canonical ensemble

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

$$Z \equiv \sum_s e^{-E_s/kT} \equiv \sum_s e^{-\beta E_s} = Z(T, V) \equiv Z(\beta, V)$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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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

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

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

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

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:

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

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