PHY 770 -- Statistical Mechanics
11 AM – 12:15 & 12:30-1:45 PM TR Olin 107

Instructor: Natalie Holzwarth (Olin 300)
Course Webpage: http://www.wfu.edu/~natalie/s14phy770

Lecture 10-11 -- Chapter 5
Equilibrium Statistical Mechanics
Canonical ensemble

- **Probability density matrix**
- **Canonical ensembles; comparison with microcanonical ensembles**
- **Ideal gas**
- **Lattice vibrations**

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	Lecture date	Text Reading	Topic	Assign.	Due date
1	Tue: 01/14/2014	Chap. 3	Review of macroscopic thermodynamics	#1	02/04/2014
2	Thu: 01/16/2014	Chap. 3	Review of macroscopic thermodynamics	#2	02/04/2014
3	Tue: 01/21/2014	Chap. 3	Thermodynamic potentials	#3	02/04/2014
4	Tue: 01/21/2014	Chap. 3	Thermodynamic stability	#4	02/04/2014
5	Thu: 01/23/2014	Chap. 3	Thermodynamic stability	#5	02/04/2014
	Tue: 01/28/2014		NAWH out of town - no class		
	Thu: 01/30/2014		NAWH out of town - no class		
6	Tue: 02/04/2014	Chap. 4	Phase transitions	#6	02/11/2014
7	Thur: 02/06/2014	Chap. 2	Microscopic analysis of entropy	#7	02/11/2014
8	Thur: 02/06/2014	Chap. 2	Microscopic analysis of entropy	#8	02/11/2014
9	Tue: 02/11/2014	Chap. 2	Microscopic analysis of entropy	#9	02/18/2014
	Thur: 02/13/2014		Class cancelled due to weather		
10	Tue: 02/18/2014	Chap. 5	Equilibrium Statistical Mechanics	#10	02/27/2014
11	Tue: 02/18/2014	Chap. 5	Equilibrium Statistical Mechanics	#11	02/27/2014
12	Thur: 02/20/2014	Chap. 5	Equilibrium Statistical Mechanics	#12	02/27/2014
13	Thur: 02/20/2014	Chap. 5	Equilibrium Statistical Mechanics	#13	02/27/2014
	Tue: 02/25/2014		NAWH out of town -- no class		
14	Thur: 02/27/2014	Chap. 5	Equilibrium Statistical Mechanics		
15	Thur: 02/27/2014	Chap. 5	Equilibrium Statistical Mechanics		
	Tue: 03/04/2014	*APS Meeting*	Take-home exam (no class meeting)		
	Thur: 03/06/2014	*APS Meeting*	Take-home exam (no class meeting)		
	Tue: 03/11/2014		Spring break (no class meeting)		
	Thur: 03/13/2014		Spring break (no class meeting)		
16	Tue: 03/18/2014	Chap. 6	(Exam due)		

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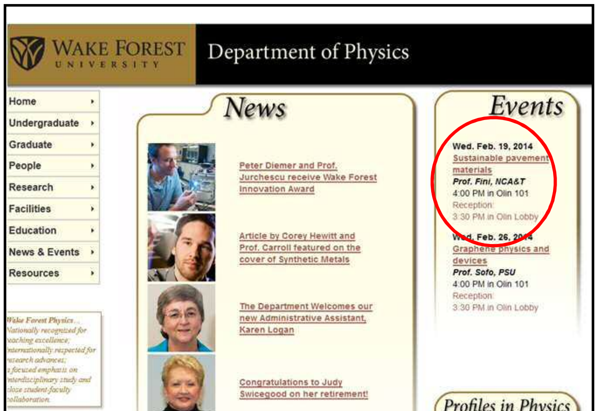

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WFU Physics Colloquium

TITLE: Production and Characterization of Bio-based Adhesives for Construction Applications

SPEAKER: Professor Elham (Ellie) H. Fini,

Department of Civil Engineering,
North Carolina A&T University

TIME: Wednesday February 19, 2014 at 4:00 PM

PLACE: Room 101 Olin Physical Laboratory

Refreshments will be served at 3:30 PM in the Olin Lounge. All interested persons are cordially invited to attend.

ABSTRACT

To enhance economic, environmental and social well-being both private and public agencies are emphasizing the need for adopting more "sustainable" practices and products in design, construction, and maintenance of infrastructure, including pavements. The trend toward sustainable pavements has led the pavement industry to place more emphasis on application of new materials such as warm mix asphalt (WMA), half-warm mix asphalt (HWMA) and cold mix asphalt (CMA) in order to reduce carbon footprints of pavement and to reduce fuel consumption and CO2 emission. Depleting aggregate resources and a stricter regulatory environment also led exploitation schemes to evolve towards greater recycling emphasizing on increasing percentages of reclaimed asphalt pavements (RAP),

Microscopic definition of entropy – due to Boltzmann

Consider a system with *N* particles having a total energy *E* and a macroscopic parameter *n*.

$\mathcal{N}_N(E,n)$ denotes the multiplicity of microscopic states having the same parameters. Each of these states are assumed to equally likely to occur.

$$\Rightarrow S(N,E,n) = k_B \ln\left(\mathcal{N}_N(E,n)\right)$$

Alternative description of entropy in terms of probability density (attributed to Gibbs)

$$\Rightarrow S = -k_B \,\mathrm{Tr}\left[\hat{\rho}\ln(\hat{\rho})\right]$$

Probability density -- continued

Normalization: $\mathrm{Tr}\left[\hat{\rho}\right] = 1$

Average value of X: $\langle X \rangle = \mathrm{Tr}\left[\hat{\rho} X\right]$

Classical treatment (in 3 dimensions):

$$\hat{\rho} \Rightarrow \rho(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N, \mathbf{p}_1, \mathbf{p}_2, \ldots \mathbf{p}_N, t)$$

$$\mathrm{Tr} \Rightarrow \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \ldots d^3\mathbf{r}_N d^3\mathbf{p}_1 d^3\mathbf{p}_2 \ldots d^3\mathbf{p}_N$$

Example of classical treatment of microstate analysis of *N* three dimensional particles in volume *V* with energy *E*

Classical microstate distribution:

$$\mathcal{N}(E,V,N)=\frac{1}{N!h^{3N}}\int d^{3N}r\;\; d^{3N}p\;\;\delta\left(\sum_i \frac{p_i^2}{2m}-E\right)$$

$$\approx\frac{1}{N!h^{3N}}\int d^{3N}r\;\; d^{3N}p\;\;\Theta\left(\sum_i \frac{p_i^2}{2m}-E\right)$$

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

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

Example of classical treatment of microstate analysis of *N* three dimensional particles in volume *V* with energy *E* -- continued

Rough statement of equivalence of Boltzmann's and Gibbs' entropy analysis for this and similar cases:

Boltzmann: $S(E,V,N)=k_B\ln\left(\mathcal{N}(E,V,N)\right)$

Gibbs: $\hat{\rho}\approx\frac{1}{\mathcal{N}(E,V,N)}$

$$S(E,V,N)=-k_B\mathrm{Tr}\left[\hat{\rho}\ln\hat{\rho}\right]=-k_B\left(\sum_i^{\mathcal{N}}\right)\left(\frac{1}{\mathcal{N}(E,V,N)}\right)\ln\left(\frac{1}{\mathcal{N}(E,V,N)}\right)$$

$$=k_B\ln\left(\mathcal{N}(E,V,N)\right)$$

Quantum representation of density matrix

Hamiltonian operator: $\hat{H}$

Probability amplitude: $|\psi_i(t)\rangle$

Schroedinger equation: $i\hbar\frac{\partial|\psi_i(t)\rangle}{\partial t}=\hat{H}|\psi_i(t)\rangle$

Density operator: $\hat{\rho}(t)=\sum_i\rho_i|\psi_i(t)\rangle\langle\psi_i(t)|$

Evaluation of average value of operator $\hat{O}$ in terms of eigenstates $|a_i\rangle$:

$$\left\langle\hat{O}\right\rangle=\mathrm{Tr}\left[\hat{\rho}(t)\hat{O}\right]=\sum_{i,j}\langle a_i|\hat{\rho}(t)|a_j\rangle\langle a_j|\hat{O}|a_i\rangle$$

Microcanonical ensemble:

Consider a closed, isolated system in equilibrium characterized by a time-independent Hamiltonian $\hat{H}$ with energy eigenstates $|E_n\rangle$. This implies that the density matrix is constant in time and is diagonal in the energy eigenstates:

$$\langle E_n|\hat{\rho}(t)\hat{O}|E_n\rangle = \langle E_n|\hat{\rho}|E_n\rangle\langle E_n|\hat{O}|E_n\rangle \equiv \hat{\rho}_{nn}\hat{O}_{nn}$$

Note that, in this case: $\langle E_n|\ln(\hat{\rho})|E_n\rangle = \ln(\hat{\rho}_{nn})$

Hint for $|x-1|\leq 1$: $\ln(x) = (x-1) + \frac{1}{2}(x-1)^2 + \frac{1}{3}(x-1)^3 + ...$

$$\Rightarrow S = -k_B Tr\left[\hat{\rho}\ln(\hat{\rho})\right]$$
$$= -k_B \sum_{n=1}^{N_{max}}\left(\hat{\rho}_{nn}\ln(\hat{\rho}_{nn})\right)$$

Microcanonical ensemble -- continued

$$\Rightarrow S = -k_B \sum_{n=1}^{N_{max}}\left(\hat{\rho}_{nn}\ln(\hat{\rho}_{nn})\right)$$

General analysis of probability density matrix elements $\hat{\rho}_{nn}$:

Find $\hat{\rho}_{nn}$ which maximizes S and satisfies $\sum_{n=1}^{N_{max}}\hat{\rho}_{nn} = 1$

$$\delta\left(\sum_{n=1}^{N_{max}}\left(-k_B\hat{\rho}_{nn}\ln(\hat{\rho}_{nn}) + \alpha\hat{\rho}_{nn}\right)\right) = 0$$

$$\sum_{n=1}^{N_{max}}\delta\hat{\rho}_{nn}\left(-k_B + \alpha - k_B\ln(\hat{\rho}_{nn})\right) = 0$$

$$\Rightarrow \hat{\rho}_{nn} = \exp\left(\frac{\alpha}{k_B} - 1\right) = \text{(constant)} = \frac{1}{N_{max}}$$

$$S = -k_B \sum_{n=1}^{N_{max}}\left(\hat{\rho}_{nn}\ln(\hat{\rho}_{nn})\right) = k_B\ln(N_{max})$$

Summary of results for microcanonical ensemble –
Isolated and closed system in equilibrium with fixed energy *E*:

Equilibrium implies that $S = -k_B \sum_{n=1}^{N_{max}}\left(\hat{\rho}_{nn}\ln(\hat{\rho}_{nn})\right)$ is maximum

Analysis finds $\hat{\rho}_{nn} = \frac{1}{N_{max}}$ where $E = \sum_{n=1}^{N_{max}} E_n$

$$\Rightarrow S = k_B\ln(N_{max})$$

Now consider a closed system which can exchange energy with surroundings – canonical ensemble

Two viewpoints
- Optimization with additional constraints
- Explicit treatment of effects of surroundings

Canonical ensemble – derivation from optimization

Find form of probability density which optimizes S with constraints

Maximize: $S = -k_B \,\mathrm{Tr}\left[\hat{\rho}\ln(\hat{\rho})\right]$

Constrain: $\mathrm{Tr}(\hat{\rho}) = 1$ and $\mathrm{Tr}(\hat{\rho}\hat{H}) = \langle E \rangle$

$$\delta\left(\mathrm{Tr}\left[-k_B\hat{\rho}\ln(\hat{\rho}) + \alpha\hat{\rho} + \gamma\hat{\rho}\hat{H}\right]\right) = 0$$

$$\delta\hat{\rho}\left(-k_B + \alpha + \gamma\hat{H} - k_B\ln(\hat{\rho})\right) = 0$$

$$\Rightarrow \hat{\rho} = \exp\left(\frac{\alpha}{k_B} - 1\right)\exp\left(\frac{\gamma}{k_B}\hat{H}\right) \equiv \frac{1}{Z}\exp\left(\frac{\gamma}{k_B}\hat{H}\right)$$

$$\mathrm{Tr}[\hat{\rho}] = 1 \quad \Rightarrow Z = \mathrm{Tr}\left[\exp\left(\frac{\gamma}{k_B}\hat{H}\right)\right] \equiv Z(\gamma)$$

Canonical ensemble from optimization – continued

$$\hat{\rho} = \frac{\exp\left(\frac{\gamma}{k_B}\hat{H}\right)}{Z(\gamma)}$$

$$S = -k_B\,\mathrm{Tr}\left[\hat{\rho}\ln(\hat{\rho})\right] = -k_B\,\mathrm{Tr}\left[\hat{\rho}\left(\frac{\gamma}{k_B}\hat{H} - \ln(Z(\gamma))\right)\right]$$

$$= -k_B\left(\frac{\gamma}{k_B}\langle E\rangle - \ln(Z(\gamma))\right)$$

$$\Rightarrow k_B\ln(Z(\gamma)) = S + \gamma\langle E\rangle$$

Recall that for a closed system (fixed number of particles), the Helmholz free energy is given by: $A = U - TS$

$$\Rightarrow \langle E\rangle + \frac{1}{\gamma}S = U - TS = -k_B\,\mathrm{T}\ln(Z(\gamma)) \quad \text{for } \frac{1}{\gamma} = -T \text{ and } \langle E\rangle = U$$

Canonical ensemble from optimization – summary of results

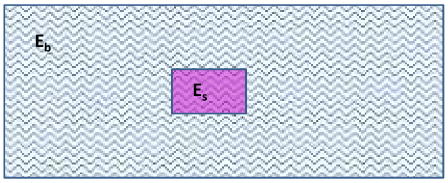
$$\hat{\rho} = \frac{\exp\left(-\frac{\hat{H}}{k_BT}\right)}{Z(T)} \quad \text{where } Z(T) = \mathrm{Tr}\left[\exp\left(-\frac{\hat{H}}{k_BT}\right)\right]$$

$$A = -k_BT\ln(Z(T))$$

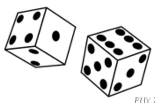
$$S = -k_B\,\mathrm{Tr}\left[\hat{\rho}\ln(\hat{\rho})\right]$$

$$U = \mathrm{Tr}\left[\hat{\rho}\hat{H}\right]$$

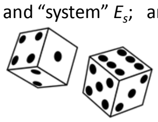
Canonical ensemble -- explicit consideration of effects of "bath" E_b and "system" E_s:



Analogy (thanks to H. Callen, *Thermodyanmics and introduction to thermostatistics*)

bath:  system: 

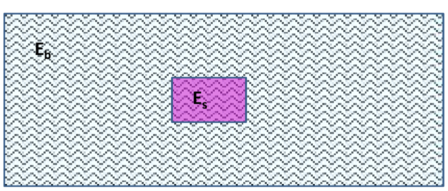
Canonical ensemble -- explicit consideration of effects of "bath" E_b and "system" E_s; analogy with 3 dice

bath: E_b  system: E_s 

For every toss of the 3 dice, record all outcomes with a sum of 12→E_{tot} as a function of the red dice representing E_s.

E_s	E_b	$\mathcal{P}_s$
1	5+6,6+5	2/25
2	4+6,6+4,5+5	3/25
3	3+6,6+3,4+5,5+4	4/25
4	2+6,6+2,3+5,5+3,4+4	5/25
5	1+6,6+1,2+5,5+2,3+4,4+3	6/25
6	1+5,5+1,2+4,4+2,3+3	5/25

Canonical ensemble -- explicit consideration of effects of "bath" E_b and "system" E_s:



Estimation of probabilty function:

$$\mathcal{P}_s = \frac{\mathcal{N}_b\left(E_{tot} - E_s\right)}{\sum_{s'} \mathcal{N}_b\left(E_{tot} - E_{s'}\right)}$$

Canonical ensemble (continued)

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

Probability that system is in microstate s:

$$\mathcal{P}_s = \frac{\mathcal{N}_b\left(E_{tot} - E_s\right)}{\sum_{s'} \mathcal{N}_b\left(E_{tot} - E_{s'}\right)}$$

$$\ln \mathcal{P}_s = C + \ln \mathcal{N}_b\left(E_{tot} - E_s\right)$$

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

Canonical ensemble (continued)

$$\ln \mathcal{P}_s = C + \ln \mathcal{N}_b\left(E_{tot} - E_s\right)$$

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

Recall that: $\left(\frac{\partial\left(k_B \ln \mathcal{N}_b\left(E\right)\right)}{\partial E}\right)_{E_{tot}} \approx \left(\frac{\partial S_b(E)}{\partial E}\right)_{V,N} = \frac{1}{T_b}$

$$\ln \mathcal{P}_s \approx C + \ln \mathcal{N}_b\left(E_{tot}\right) - E_s\left(\frac{1}{k_B T}\right) + \cdots$$

$$\Rightarrow \boxed{\mathcal{P}_s = C' e^{-E_s/k_B T}}$$

Canonical ensemble (continued):

$$\mathcal{P}_s = C' e^{-E_s/k_B T}$$

$$\equiv \frac{1}{Z} e^{-E_s/k_B T}$$

where: $Z \equiv \sum_{s'} e^{-E_{s'}/k_B T}$ "partition function"

Calculations using the partition function:

$$Z \equiv \sum_{s'} e^{-E_{s'}/k_B T} = \sum_{s'} e^{-\beta E_{s'}} \quad \text{where } \beta = \tfrac{1}{k_B T}$$

Canonical ensemble continued – average energy of system:

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

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

Heat capacity for canonical ensemble:

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

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

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

First Law of Thermodynamics for canonical ensemble (*T* fixed)

$$\langle E_s\rangle = \sum_{s'} E_{s'}\mathcal{P}_{s'} = U \quad \text{(internal energy)}$$

$$d\langle E_s\rangle = \sum_{s'} E_{s'} d\mathcal{P}_{s'} + \sum_{s'} \mathcal{P}_{s'} dE_{s'}$$

$$= \sum_{s'} E_{s'} d\mathcal{P}_{s'} + \sum_{s'} \mathcal{P}_{s'} \frac{dE_{s'}}{dV} dV$$

- Pressure associated with state s

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

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

First law of thermodynamics:

$$dU = TdS - PdV \quad \Rightarrow TdS = \sum_{s'} E_{s'} d\mathcal{P}_{s'}$$

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

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

$$\Rightarrow \sum_{s'} E_{s'} d\mathcal{P}_{s'} = -k_BT\left(\left(\ln Z\right)\sum_{s'} d\mathcal{P}_{s'} + \sum_{s'} \ln \mathcal{P}_{s'} d\mathcal{P}_{s'}\right)$$

=0

$$TdS = \sum_{s'} E_{s'} d\mathcal{P}_{s'} = -k_B T \left(\sum_{s'} \ln \mathcal{P}_{s'} d\mathcal{P}_{s'} \right)$$

$$dS = -k_B \left(\sum_{s'} \ln \mathcal{P}_{s'} d\mathcal{P}_{s'} \right) = -d\left(k_B \sum_{s'} \mathcal{P}_{s'} \ln \mathcal{P}_{s'} \right)$$

$$\Rightarrow S = S_0 - k_B \sum_{s'} \mathcal{P}_{s'} \ln \mathcal{P}_{s'}$$

$$\text{where} \quad \mathcal{P}_{s'} = \frac{1}{Z} e^{-\beta E_{s'}} \equiv \frac{1}{Z} e^{-E_{s'}/k_B T}$$

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Canonical ensemble – summary and further results

Partition function:

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

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

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

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

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

Note: Using first law: $d\langle E_s \rangle = dU = TdS - PdV$

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

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

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

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

$$A(T,V,\{N_i\}) = -k_B T \ln Z\left(T,V,\{N_i\}\right)$$

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Summary of relationship between canonical ensemble and its partition function and the Helmholz Free Energy:

$$A(T,V,\{N_i\}) = -k_B T \ln Z\left(T,V,\{N_i\}\right)$$

$$\left(\frac{\partial A}{\partial T}\right)_{V,\{N_i\}} = -S = \left(\frac{-\partial\left(k_B T \ln Z\right)}{\partial T}\right)_{V,\{N_i\}} = -k_B \ln Z - k_B T\left(\frac{\partial\left(\ln Z\right)}{\partial T}\right)_{V,\{N_i\}}$$

$$\left(\frac{\partial A}{\partial V}\right)_{T,\{N_i\}} = -P = -k_B T\left(\frac{\partial\left(\ln Z\right)}{\partial V}\right)_{T,\{N_i\}}$$

$$\left(\frac{\partial A}{\partial N_i}\right)_{T,V,\{N_j\}} = \mu_i = -k_B T\left(\frac{\partial\left(\ln Z\right)}{\partial N_i}\right)_{T,V,\{N_j\}}$$

Canonical ensemble in terms of probability density operator

$$\hat{\rho} = \frac{\exp\left(-\frac{\hat{H}}{k_B T}\right)}{Z(T)} \qquad \text{where } Z(T) = \mathrm{Tr}\left[\exp\left(-\frac{\hat{H}}{k_B T}\right)\right]$$

$$A = -k_B T \ln\left(Z(T)\right) \Rightarrow \hat{\rho} = \exp\left(-\frac{\hat{H}-A}{k_B T}\right) \equiv \exp\left(-\beta(\hat{H}-A)\right)$$

$$S = -k_B \,\mathrm{Tr}\left[\hat{\rho}\ln\left(\hat{\rho}\right)\right]$$

$$U = \mathrm{Tr}\left[\hat{\rho}\hat{H}\right]$$

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

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

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

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

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

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

Compare with microcanonical ensemble:

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

Example: Canonical distribution for free particles -- continued

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

$$A(T,V,N)=-k_BT\ln\left(Z(T,V,N)\right)\approx -k_BTN\left(1+\ln\left(\frac{V}{N}\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}\right)\right)$$

$$S(T,V,N)=-\left(\frac{\partial A}{\partial T}\right)_{V,N}=\frac{5}{2}Nk_B+Nk_B\ln\left(\frac{V}{N}\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}\right)$$

Canonical ensemble of indistinguishable quantum particles

Indistinguishable quantum particles generally must obey specific symmetrization rules under the exchange of two particle labels (see Appendix D of your textbook)

$$P_{i,j}\,|k_1,k_2.....k_i...k_j...k_N\rangle=\pm|k_1,k_2.....k_j...k_i...k_N\rangle$$

$+$ ➔ Bose-Einstein particles

$-$ ➔ Fermi-Dirac particles

General notation:

P denotes permutation operator

p denotes 0 or 1 for even or odd permutations

$|k_1,k_2...k_N\rangle^{\pm}$ denotes symmetrized (anti symmetrized wavefunction)

$$\Rightarrow|k_1,k_2...k_N\rangle^{\pm}=\frac{1}{\sqrt{N!}}\sum_P(\pm)^p\,P\,|k_1,k_2...k_N\rangle$$

Canonical ensemble of indistinguishable quantum particles

Example: 3-body ideal gas confined in large volume *V* with momenta ***k*₁**, ***k*₂** and ***k*₃**,

$$|k_1,k_2,k_3\rangle^{\pm}=\frac{1}{\sqrt{3!}}\big(|k_1,k_2,k_3\rangle+|k_3,k_1,k_2\rangle+|k_2,k_3,k_1\rangle$$
$$\pm\left(|k_2,k_1,k_3\rangle+|k_1,k_3,k_2\rangle+|k_3,k_2,k_1\rangle\right)\big)$$

Partition function for single particle:

$$Z_1(T)=\mathrm{Tr}[\exp(-\hat{H}/k_BT)]=\frac{V}{h^3}\int d^3p\ e^{-\mathbf{p}^2/(2mk_BT)}$$
$$=V\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}\equiv\frac{V}{\lambda_T^3}\quad\text{where }\lambda_T\text{ is the "thermal wavelength"}$$

Partition function for three particles:

$$Z_3(T)=\mathrm{Tr}[\,^{\pm}\langle\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3|\exp(-\hat{H}/k_BT)|\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3\rangle^{\pm}]$$

Canonical ensemble of indistinguishable quantum particles

Example: 3-body ideal gas confined in large volume *V* with momenta $\mathbf{k_1}$, $\mathbf{k_2}$, and $\mathbf{k_3}$,

Note that $\langle \mathbf{k_1} | \mathbf{k_2} \rangle = (2\pi)^3 \delta^3(\mathbf{k_1} - \mathbf{k_2})$

$$\Rightarrow Z_3(T) = \frac{1}{3!}\left(\left(Z_1(T) \right)^3 \pm 3 Z_1(T) Z_1\left(\frac{T}{2}\right) + 2 Z_1\left(\frac{T}{3}\right) \right)$$

$$= \frac{1}{3!}\left(\frac{V}{\lambda_T^3}\right)^3 \left(1 \pm \frac{3}{2^{3/2}}\left(\frac{\lambda_T^3}{V}\right) + \frac{2}{3^{3/2}}\left(\frac{\lambda_T^3}{V}\right)^2 \right)$$

$$\underset{\rightarrow \text{semiclassical}}{=} \frac{1}{3!}\left(\frac{V}{\lambda_T^3}\right)^3$$

Reduced single particle density matrix and the Maxwell-Boltzmann distribution

Reduced single particle density matrix:

$$n_R(\mathbf{k_1}) \equiv \langle \mathbf{k_1} | \hat{\rho}_{\mathbf{R}} | \mathbf{k_1} \rangle = \frac{1}{(N-1)!} \sum_{\mathbf{k}_2 \ldots \mathbf{k}_N} {}^{\pm}\langle \mathbf{k}_1, \mathbf{k}_2 \ldots \mathbf{k}_N | \hat{\rho} | \mathbf{k}_1, \mathbf{k}_2 \ldots \mathbf{k}_N \rangle^{\pm}$$

$$\hat{\rho} = \frac{\exp\left(-\frac{\hat{H}}{k_B T}\right)}{Z(T)} \quad \text{where } Z(T) = \mathrm{Tr}\left[\exp\left(-\frac{\hat{H}}{k_B T}\right)\right], \quad \hat{H} = \sum_i \frac{\hat{\mathbf{p}}_i^2}{2m}$$

We have previously shown in the semi-classical limit:

$$Z(T, N) = \frac{1}{N!}\left(\frac{V}{\lambda_T^3}\right)^N$$

$$\Rightarrow n_R(\mathbf{k_1}) = N\left(\frac{\lambda_T^3}{V}\right)\exp\left(-\frac{\hbar^2 \mathbf{k}_1^2}{2 m k_B T}\right)$$

Reduced single particle density matrix and the Maxwell-Boltzmann distribution -- continued

$$n_R(\mathbf{k_1}) = N\left(\frac{\lambda_T^3}{V}\right)\exp\left(-\frac{\hbar^2 \mathbf{k}_1^2}{2 m k_B T}\right) \quad \text{where } \lambda_T \equiv \sqrt{\frac{h^2}{2\pi m k_B T}}$$

Note that $\sum_{\mathbf{k_1}} n_R(\mathbf{k_1}) = \frac{V}{(2\pi)^3}\int d^3k \; n_R(\mathbf{k}) = N$

$$= N\int d^3v \, F(\mathbf{v})$$

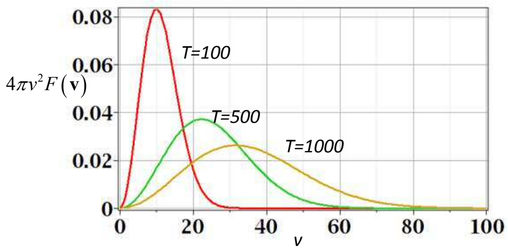
$\Rightarrow$ Maxwell-Boltzmann velocity distribution:

$$F(\mathbf{v}) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{m\mathbf{v}^2}{2 k_B T}\right)$$

Reduced single particle density matrix and the Maxwell-Boltzmann distribution -- continued

Maxwell-Boltzmann velocity distribution:

$$F(\mathbf{v}) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{m\mathbf{v}^2}{2k_B T}\right)$$



Canonical ensemble example: Einstein solid revisited

Consider *N* independent harmonic oscillators (in general *N=3 x number of lattice sites*) with frequency ω

Hamiltonian: $\hat{H} = \hbar\omega \sum_{i=1}^{N} \left(\hat{n}_i + \frac{1}{2}\right)$

$$Z(T,N) = \sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\cdots\sum_{n_N=0}^{\infty} \langle n_1 n_2 ... n_N | \exp\left(-\beta\hbar\omega \sum_{i=1}^{N}\left(\hat{n}_i + \frac{1}{2}\right)\right) | n_1 n_2 ... n_N \rangle$$

$$= \left(\sum_{n_1=0}^{\infty} \langle n_1 | \exp\left(-\beta\hbar\omega\left(\hat{n}_1 + \frac{1}{2}\right)\right) | n_1 \rangle\right)^N = \left(\frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}}\right)^N$$

$$A(T,N) = -k_B T \ln(Z(T,N)) = N\left(\frac{\hbar\omega}{2} + k_B T \ln\left(1-e^{-\beta\hbar\omega}\right)\right)$$

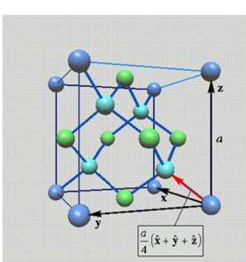
$$U = A + TS = A - T\left(\frac{\partial A}{\partial T}\right)_N = N\hbar\omega\left(\frac{1}{2} + \frac{e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}\right)$$

Consistent with result from microcanonial ensemble

More realistic model of lattice vibrations

Lattice vibrations for 3-dimensional lattice

Example: diamond lattice



Ref: http://phycomp.technion.ac.il/~nika/diamond_structure.html

Atoms located at the positions:

$$\mathbf{R}^a = \mathbf{R}_0{}^a + \mathbf{u}^a$$

Potential energy function near equilibrium:

$$\Phi\left(\left\{\mathbf{R}^a\right\}\right) \approx \Phi\left(\left\{\mathbf{R}_0{}^a\right\}\right) + \frac{1}{2}\sum_{a,b}\left(\mathbf{R}^a - \mathbf{R}_0{}^a\right)\cdot\left.\frac{\partial^2\Phi}{\partial\mathbf{R}^a\partial\mathbf{R}^b}\right|_{\left\{\mathbf{R}_0{}^a\right\}}\cdot\left(\mathbf{R}^b - \mathbf{R}_0{}^b\right)$$

Define:

$$D_{jk}^{ab} \equiv \left.\frac{\partial^2\Phi}{\partial\mathbf{R}_j{}^a\partial\mathbf{R}_k{}^b}\right|_{\left\{\mathbf{R}_0{}^a\right\}}$$

so that

$$\Phi\left(\left\{\mathbf{R}^a\right\}\right) \approx \Phi_0 + \frac{1}{2}\sum_{a,b,j,k} u_j^a D_{jk}^{ab} u_k^b$$

Lagrangian: $L\left(\left\{u_j^a, \dot{u}_j^a\right\}\right) = \frac{1}{2}\sum_{a,j} m_a\left(\dot{u}_j^a\right)^2 - \Phi_0 - \frac{1}{2}\sum_{a,b,j,k} u_j^a D_{jk}^{ab} u_k^b$

$$L\left(\left\{u_j^a, \dot{u}_j^a\right\}\right) = \frac{1}{2}\sum_{a,j} m_a\left(\dot{u}_j^a\right)^2 - \Phi_0 - \frac{1}{2}\sum_{a,b,j,k} u_j^a D_{jk}^{ab} u_k^b$$

Equations of motion:

$$m_a \ddot{u}_j^a = -\sum_{b,k} D_{jk}^{ab} u_k^b$$

Solution form:

$$u_j^a(t) = \frac{1}{\sqrt{m_a}} A_j^a e^{-i\omega t + i\mathbf{q}\cdot\mathbf{R}_0^a}$$

Details: $\mathbf{R}_0^a = \boldsymbol{\tau}^a + \mathbf{T}$ where $\boldsymbol{\tau}^a$ denotes unique sites and $\mathbf{T}$ denotes replicas

Define:

$$W_{jk}^{ab}(\mathbf{q}) = \sum_{\mathbf{T}} \frac{D_{jk}^{ab} e^{i\mathbf{q}\cdot\left(\boldsymbol{\tau}^a - \boldsymbol{\tau}^b\right)}}{\sqrt{m_a m_b}} e^{i\mathbf{q}\cdot\mathbf{T}}$$

Eigenvalue equations:

$$\omega^2 A_j^a = \sum_{b,k} W(\mathbf{q})_{jk}^{ab} A_k^b$$

In this equation the summation is only over unique atomic sites.

$\Rightarrow$ Find "dispersion curves" $\omega(\mathbf{q})$

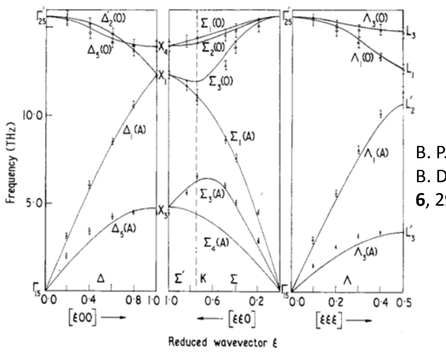


Figure 1. Dispersion curves for silicon. Experimental points are due to Doll: △ and ○ show the longitudinal and transverse modes, respectively.

B. P. Pandey and B. Dayal, *J. Phys. C* **6**, 2943 (1973)

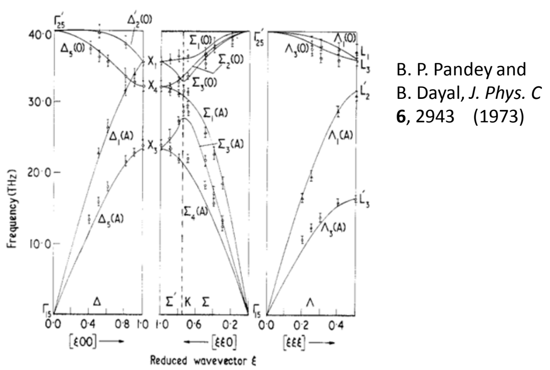


Figure 2. Phonon dispersion curves of diamond. Experimental points are due to Warren *et al* (1965, 1967). △ and ○ represent the longitudinal and transverse modes, respectively.

B. P. Pandey and B. Dayal, *J. Phys. C* **6**, 2943 (1973)

Lattice vibrations – continued

Classical analysis determines the normal mode frequencies $\omega_{\nu\mathbf{q}}$ and their corresponding modes

In general, for a lattice with M atoms in a unit cell, there will be 3M normal modes for each **q** . While the normal mode analysis for $\omega_{\nu\mathbf{q}}$ and the normal mode geometries are well approximated by the classical treatment, the quantum effects of the vibrations are important. The corresponding quantum Hamiltonian is given by:

$$\hat{H} = \sum_{\nu\mathbf{q}} \hbar\omega_{\nu\mathbf{q}} \left(\hat{n}_{\nu\mathbf{q}} + \frac{1}{2} \right) \qquad \text{where } \hat{n}_{\nu\mathbf{q}} \text{ denotes number operator}$$

Eigenvalues of $\hat{n}_{\nu\mathbf{q}}$ are 0, 1, 2, ...∞

Lattice vibrations continued

$$\hat{H} = \sum_{\nu\mathbf{q}} \hbar\omega_{\nu\mathbf{q}} \left(\hat{n}_{\nu\mathbf{q}} + \frac{1}{2} \right) \quad \text{where } \hat{n}_{\nu\mathbf{q}} \text{ denotes number operator}$$

Eigenvalues of $\hat{n}_{\nu\mathbf{q}}$ are 0, 1, 2, ...∞

Partition function:

$$Z(T) = \mathrm{Tr}\left[e^{-\beta\hat{H}} \right] = \prod_{\nu\mathbf{q}} \left(\sum_{n_{\nu\mathbf{q}}=0}^{\infty} \exp\left(-\beta\hbar\omega_{\nu\mathbf{q}} \left(n_{\nu\mathbf{q}} + \frac{1}{2} \right) \right) \right)$$

$$= \prod_{\nu\mathbf{q}} \left(\frac{e^{-\beta\hbar\omega_{\nu\mathbf{q}}/2}}{1 - e^{-\beta\hbar\omega_{\nu\mathbf{q}}}} \right)$$

Average energy associated with lattice vibrations

$$\langle E \rangle = -\left(\frac{\partial \ln(Z)}{\partial\beta} \right) = \sum_{\nu\mathbf{q}} \hbar\omega_{\nu\mathbf{q}} \left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega_{\nu\mathbf{q}}} - 1} \right) \equiv \sum_{\nu\mathbf{q}} \hbar\omega_{\nu\mathbf{q}} \left(\frac{1}{2} + \langle n_{\nu\mathbf{q}} \rangle \right)$$

Lattice vibrations continued

Average energy associated with lattice vibrations

$$\langle E \rangle = \sum_{\nu\mathbf{q}} \hbar\omega_{\nu\mathbf{q}} \left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega_{\nu\mathbf{q}}} - 1} \right)$$

$$= \sum_{\nu} \left(\frac{V}{(2\pi)^3} \int d^3q \; \hbar\omega_{\nu\mathbf{q}} \left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega_{\nu\mathbf{q}}} - 1} \right) \right)$$

$$= \int d\omega \; g(\omega) \; \hbar\omega \left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1} \right)$$

Phonon density of states

$$g(\omega) = \sum_{\nu} \left(\frac{V}{(2\pi)^3} \int d^3q \;\; \delta(\omega - \omega_{\nu\mathbf{q}}) \right)$$

Note that: $\int d\omega \, g(\omega) = 3M$

Lattice vibrations continued

Debye model for $g(\omega)$

$$g_D(\omega) = \begin{cases} \dfrac{V\omega^2}{2\pi^2} \left(\dfrac{2}{c_t^3} + \dfrac{1}{c_l^3} \right) \equiv \dfrac{9M\omega^2}{\omega_D^3} & \text{for } \omega \le \omega_D \\ 0 & \text{otherwise} \end{cases}$$

$$\langle E \rangle_D = \int_0^{\omega_D} d\omega \; g_D(\omega) \; \hbar\omega \left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1} \right)$$

$$= 9\mathrm{M} \left(\frac{\hbar\omega_D}{8} + \frac{1}{\omega_D^3} \int_0^{\omega_D} d\omega \;\; \frac{\hbar\omega^3}{e^{\beta\hbar\omega} - 1} \right)$$

Heat capacity

$$C_D = \frac{9Mk_B}{(\hbar\beta\omega_D)^3} \int_0^{T_D/T} dx \frac{x^4 e^x}{(e^x - 1)^2} \quad \text{where } T_D = \hbar\omega_D / k_B$$