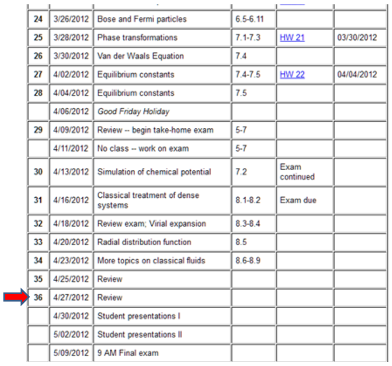
PHY 341/641
Thermodynamics and Statistical Physics

Lecture 36

Review and examples

- Review of general principles
- Review of specific examples



24	3/26/2012	Bose and Fermi particles	6.5-6.11		
25	3/28/2012	Phase transformations	7.1-7.3	HW 21	03/30/2012
26	3/30/2012	Van der Waals Equation	7.4		
27	4/02/2012	Equilibrium constants	7.4-7.5	HW 22	04/04/2012
28	4/04/2012	Equilibrium constants	7.5		
	4/06/2012	*Good Friday Holiday*			
29	4/09/2012	Review -- begin take-home exam	5-7		
	4/11/2012	No class -- work on exam	5-7		
30	4/13/2012	Simulation of chemical potential	7.2	Exam continued	
31	4/16/2012	Classical treatment of dense systems	8.1-8.2	Exam due	
32	4/18/2012	Review exam; Virial expansion	8.3-8.4		
33	4/20/2012	Radial distribution function	8.5		
34	4/23/2012	More topics on classical fluids	8.6-8.9		
35	4/25/2012	Review			
36	4/27/2012	Review			
	4/30/2012	Student presentations I			
	5/02/2012	Student presentations II			
	5/09/2012	9 AM Final exam			

4/30– Laurence, Zac, Eric

5/2 -- Kristen, Audrey, Griffin

Fundamental principles of thermodynamics and statistical mechanics

- This course focused on “thermostatics” and statistical mechanics of systems in equilibrium
- Thermal equilibrium ←→fixed temperature
- First law of thermodynamics

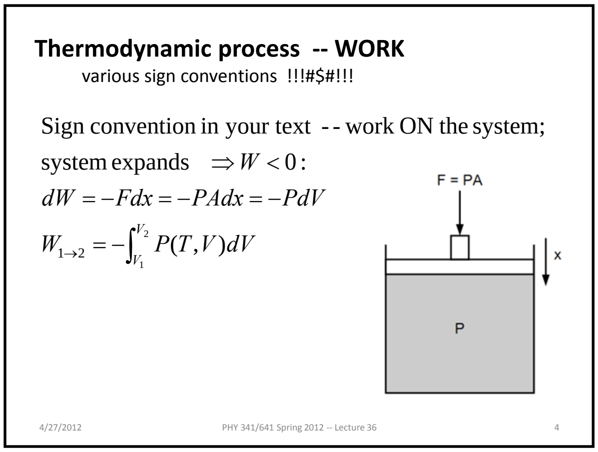
$$E_2 - E_1 \equiv \Delta E = Q + W$$

For heat added TO the system: $Q > 0$

For heat withdrawn FROM the system: $Q < 0$

For work done TO the system (contraction): $W > 0$

For work done BY the system (expansion): $W < 0$



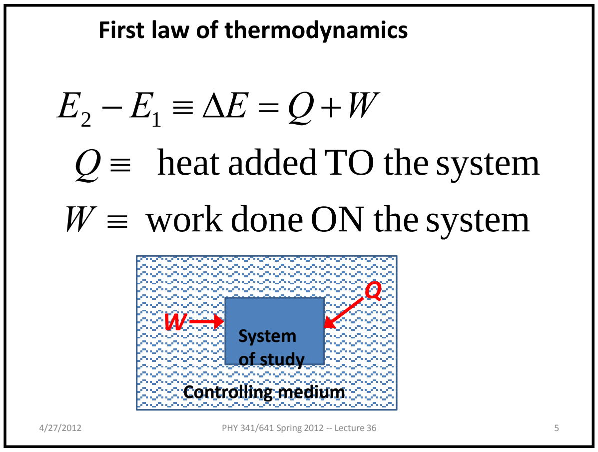
Thermodynamic process -- WORK

various sign conventions !!!#$#!!!

Sign convention in your text -- work ON the system; system expands $\Rightarrow W < 0$:

$$dW = -Fdx = -PAdx = -PdV$$

$$W_{1\to 2} = -\int_{V_1}^{V_2} P(T,V)dV$$

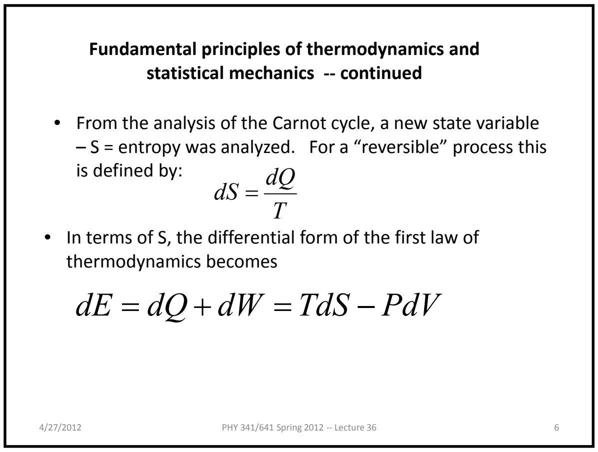


First law of thermodynamics

$$E_2 - E_1 \equiv \Delta E = Q + W$$

$Q \equiv$ heat added TO the system

$W \equiv$ work done ON the system



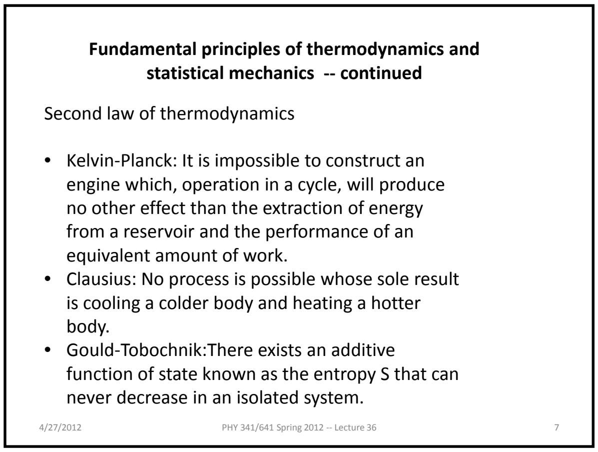
Fundamental principles of thermodynamics and statistical mechanics -- continued

- From the analysis of the Carnot cycle, a new state variable – S = entropy was analyzed. For a “reversible” process this is defined by:

$$dS = \frac{dQ}{T}$$

- In terms of S, the differential form of the first law of thermodynamics becomes

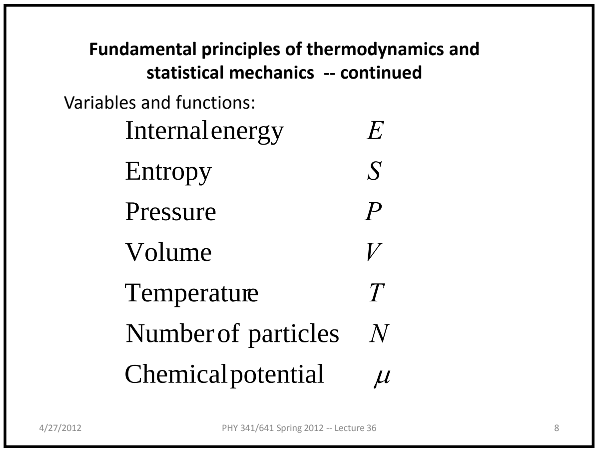
$$dE = dQ + dW = TdS - PdV$$



Fundamental principles of thermodynamics and statistical mechanics -- continued

Second law of thermodynamics

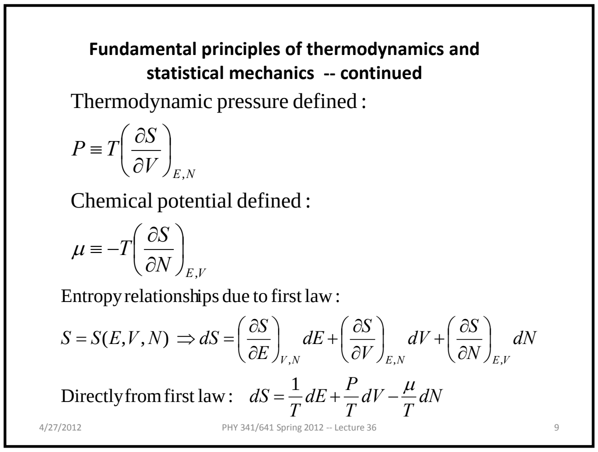
- Kelvin-Planck: It is impossible to construct an engine which, operation in a cycle, will produce no other effect than the extraction of energy from a reservoir and the performance of an equivalent amount of work.
- Clausius: No process is possible whose sole result is cooling a colder body and heating a hotter body.
- Gould-Tobochnik:There exists an additive function of state known as the entropy S that can never decrease in an isolated system.



Fundamental principles of thermodynamics and statistical mechanics -- continued

Variables and functions:

Internal energy	E
Entropy	S
Pressure	P
Volume	V
Temperature	T
Number of particles	N
Chemical potential	μ



Fundamental principles of thermodynamics and statistical mechanics -- continued

Thermodynamic pressure defined :

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

Chemical potential defined :

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

Entropy relationships due to first law :

$$S = S(E,V,N) \Rightarrow dS = \left(\frac{\partial S}{\partial E}\right)_{V,N} dE + \left(\frac{\partial S}{\partial V}\right)_{E,N} dV + \left(\frac{\partial S}{\partial N}\right)_{E,V} dN$$

Directly from first law : $dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN$

Fundamental principles of thermodynamics and statistical mechanics -- continued

Analysis of differential form of First Law of Thermodyamics --

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

$$dE = \left(\frac{\partial E}{\partial S}\right)_{V,N} dS + \left(\frac{\partial E}{\partial V}\right)_{S,N} dV + \left(\frac{\partial E}{\partial N}\right)_{V,S} dN$$

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

Fundamental principles of thermodynamics and statistical mechanics -- continued

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

From the mathematical properties of these functions, we can derive the "Maxwell relations". For example, simplifying to fixed N:

Gibbs free energy : $G = G(T,P) = F + PV$

$$dG = dF + PdV + VdP = -SdT + VdP = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP$$

$$\Rightarrow S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad V = \left(\frac{\partial G}{\partial P}\right)_T$$

$$\left(\frac{\partial}{\partial P}\right)_T \left(\frac{\partial G}{\partial T}\right)_P = \left(\frac{\partial}{\partial T}\right)_P \left(\frac{\partial G}{\partial P}\right)_T$$

$$\Rightarrow \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

Maxwell relation

Summary of Maxwell's relations for a fixed number of particles

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

Properties of extended Maxwell's relations

Check consistency:

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

From internal energy: $\mu = \left(\frac{\partial E}{\partial N}\right)_{V,S}$

Is this consistent???

$$dE = TdS - PdV + \mu dN = \left(\frac{\partial E}{\partial S}\right)_{V,N} dS + \left(\frac{\partial E}{\partial V}\right)_{S,N} dV + \left(\frac{\partial E}{\partial N}\right)_{S,V} dN$$

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

Categories of functions and variables
Extensive ➔ depends on system size
Intensive ➔ independent of system size

Extensive		Intensive	
Number of particles	N	Temperature	T
Volume	V	Pressure	P
Entropy	S(E,V,N)	Density	ρ
Internal energy	E(S,V,N)	Chemical potential	μ
Enthalpy	H(S,P,N)		
Helmholz Free energy	F(T,V,N)		
Gibbs Free energy	G(T,P,N)		

Special relationship of μ to $G(T,P,N)$:

Argue that: $G(T,P,N) = Ng(T,P)$

$$\left(\frac{\partial G}{\partial N}\right)_{T,P} = \mu = g(T,P) \qquad \Rightarrow \mu = \frac{G(T,P,N)}{N}$$

In terms of Gibbs free energy density $g(T,P)$ (intensive function) --

Gibbs-Duhem equation:

$$dg = d\mu = \left(\frac{\partial g}{\partial T}\right)_P dT + \left(\frac{\partial g}{\partial P}\right)_T dP$$

$$dg = d\mu = -\frac{S}{N}dT + \frac{V}{N}dP \equiv -sdT + vdP$$

Some materials parameters based on thermodynamic variables and functions

Heat capacity at constant V:

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

In fact, this should be easy, but as we have seen the "natural" variables of E are *E=E(S,V,N)* and *S=S(E,V,N)*.

$$T = \left(\frac{\partial E}{\partial S}\right)_V \qquad \left(\frac{\partial T}{\partial S}\right)_V = \left(\frac{\partial^2 E}{\partial S^2}\right)_V$$

$$\Rightarrow C_V = \frac{T}{\left(\partial^2 E/\partial S^2\right)_V} = \frac{\left(\partial E/\partial S\right)_V}{\left(\partial^2 E/\partial S^2\right)_V}$$

Other useful thermodynamic derivatives

Isothermal compressibility:

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N}$$

Isobaric expansion:

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

Fundamental principles of thermodynamics and statistical mechanics -- continued

The connection between the macroscopic viewpoint of thermodynamics and the microscopic viewpoint of statistical mechanics was made by Boltzmann using the statistical properties of large systems.

In analyzing a system, Boltzmann introduced the notion of the number of microstates Ω_{tot} and postulated its relationship to entropy:

$$S_{tot} = k \ln \Omega_{\text{tot}}$$

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 $E + dE$:

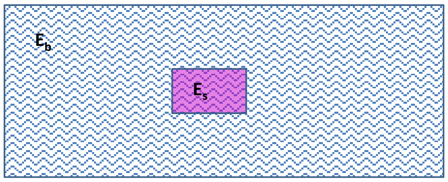
$$g(E) = \frac{d\Gamma}{dE} \rightarrow \Omega(E)$$

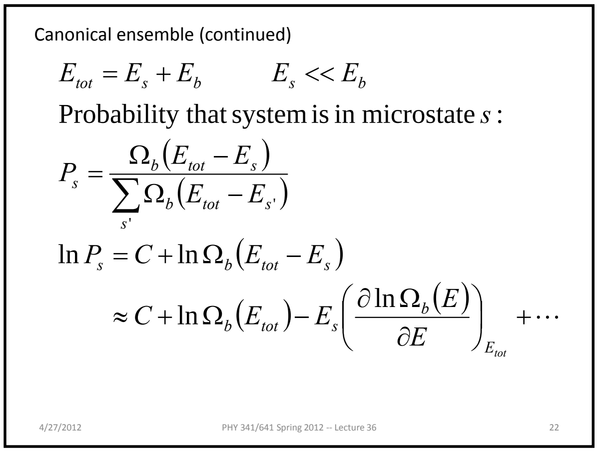
Note that for large N, $k \ln \Gamma \approx k \ln \Omega = S$

Fundamental principles of thermodynamics and statistical mechanics -- continued

Extending Boltzmann's analysis of "microcanonical" ensemble where E is controlled to "canonical" ensemble where T is controlled

Canonical ensemble:





Canonical ensemble (continued)

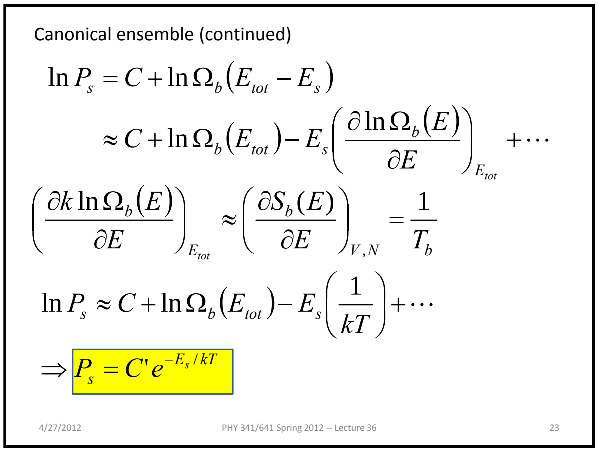
$$E_{tot} = E_s + E_b \qquad E_s << E_b$$

Probability that system is in microstate s :

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

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

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



Canonical ensemble (continued)

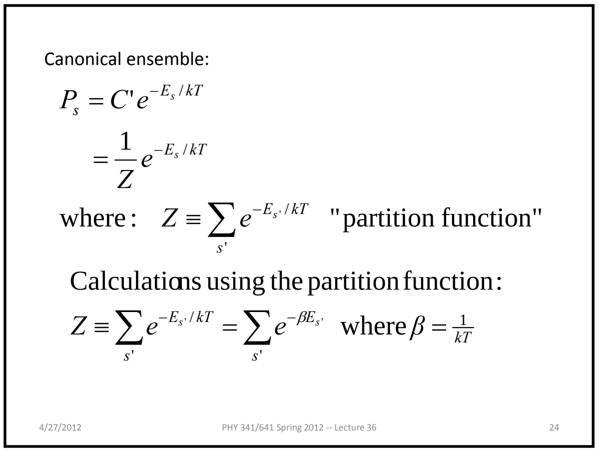
$$\ln P_s = C + \ln \Omega_b(E_{tot} - E_s)$$

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

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

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

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



Canonical ensemble:

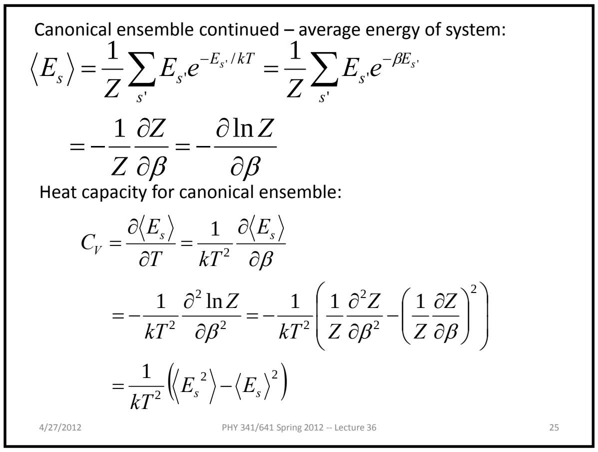
$$P_s = C' e^{-E_s/kT}$$

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

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

Calculations using the partition function:

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



Canonical ensemble continued – average energy of system:

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

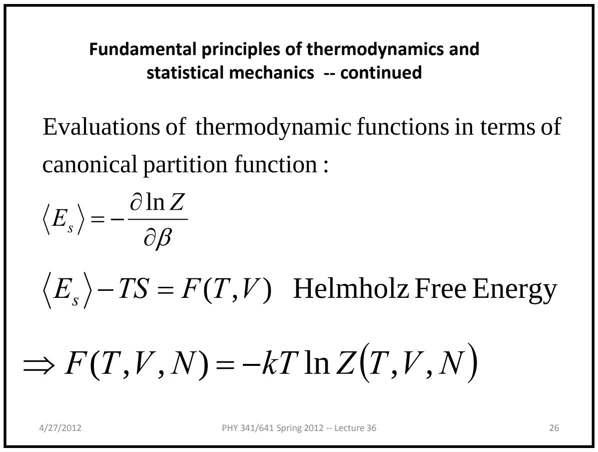
$$= -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta}$$

Heat capacity for canonical ensemble:

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

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

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



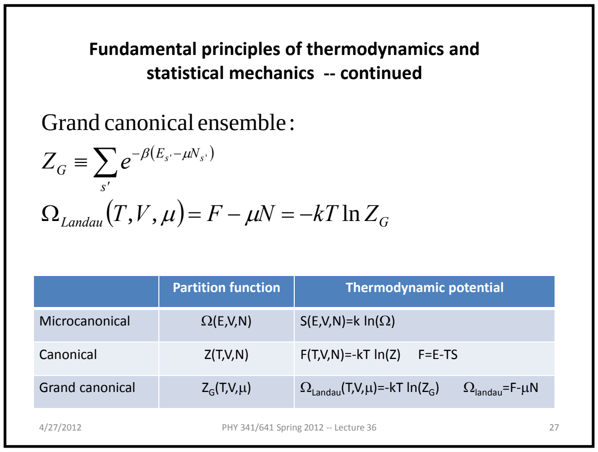
Fundamental principles of thermodynamics and statistical mechanics -- continued

Evaluations of thermodynamic functions in terms of canonical partition function :

$$\langle E_s \rangle = -\frac{\partial \ln Z}{\partial \beta}$$

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

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



Fundamental principles of thermodynamics and statistical mechanics -- continued

Grand canonical ensemble :

$$Z_G \equiv \sum_{s'} e^{-\beta(E_{s'} - \mu N_{s'})}$$

$$\Omega_{Landau}(T,V,\mu) = F - \mu N = -kT \ln Z_G$$

	Partition function	Thermodynamic potential
Microcanonical	$\Omega(E,V,N)$	$S(E,V,N)=k \ln(\Omega)$
Canonical	$Z(T,V,N)$	$F(T,V,N)=-kT \ln(Z)$ $F=E-TS$
Grand canonical	$Z_G(T,V,\mu)$	$\Omega_{Landau}(T,V,\mu)=-kT \ln(Z_G)$ $\Omega_{landau}=F-\mu N$

Fundamental principles of thermodynamics and statistical mechanics -- continued

Statistics of non-interacting quantum particles

Single particle states : ε_k

Single particle occupation numbers : n_k

Bose particles (integer spin) : $n_k = 0,1,2,3,\cdots$

Fermi particles ($\frac{1}{2}$ integer spin) : $n_k = 0,1$

Grand partition function for these systems:

$$Z_G(T,\mu) = \sum_s e^{-\beta(E_s - \mu N_s)} \text{ summing over all microstates } s$$

Grand partition function for these systems:

$$Z_G(T,\mu) = \sum_s e^{-\beta(E_s - \mu N_s)} \text{ summing over all microstates } s$$

$$E_s = \sum_k n_k^s \varepsilon_k \qquad N_s = \sum_k n_k^s$$

$$Z_G(T,\mu) = \prod_k \left(\sum_s e^{-\beta\left(n_k^s \varepsilon_k - \mu n_k^s\right)} \right)$$

$$\equiv \prod_k Z_{G,k}(T,\mu)$$

$$\text{where } Z_{G,k}(T,\mu) \equiv \sum_s e^{-\beta\left(n_k^s \varepsilon_k - \mu n_k^s\right)}$$

Fermi particle case : $n_k^s = 0,1$

$$Z_{G,k}(T,\mu) \equiv \sum_s e^{-\beta\left(n_k^s \varepsilon_k - \mu n_k^s\right)}$$

$$= 1 + e^{-\beta(\varepsilon_k - \mu)}$$

Landau potential for this case :

$$\Omega_k = -kT \ln Z_{G,k} = -kT \ln\left(1 + e^{-\beta(\varepsilon_k - \mu)}\right)$$

Mean occupancy numbers :

$$\langle n_k \rangle = -\frac{\partial \Omega_k}{\partial \mu} = \frac{1}{e^{\beta(\varepsilon_k - \mu)} + 1}$$

Self − consistency condition : $N = \sum_k \langle n_k \rangle \Rightarrow$ defines μ

Bose particle case : $n_k^s = 0,1,2,3,4,\cdots$

$$Z_{G,k}(T,\mu) \equiv \sum_s e^{-\beta\left(n_k^s\varepsilon_k - \mu n_k^s\right)}$$

$$= \sum_{n_k^s=0}^{\infty} e^{-\beta(\varepsilon_k-\mu)n_k^s} = \frac{1}{1-e^{-\beta(\varepsilon_k-\mu)}}$$

Landau potential for this case:

$$\Omega_\mathrm{k} = -kT\ln Z_{G,k} = kT\ln\left(1-e^{-\beta(\varepsilon_k-\mu)}\right)$$

Mean occupancy numbers:

$$\langle n_k\rangle = -\frac{\partial\Omega_\mathrm{k}}{\partial\mu} = \frac{1}{e^{\beta(\varepsilon_k-\mu)}-1}$$

In some cases: $N = \sum_k \langle n_k\rangle \Rightarrow$ defines $\mu \le 0$

Fundamental principles of thermodynamics and statistical mechanics -- continued

Thermodynamic description of the equilibrium between two forms "phases" of a material under conditions of constant *T* and *P*

Review of Gibb's Free energy:

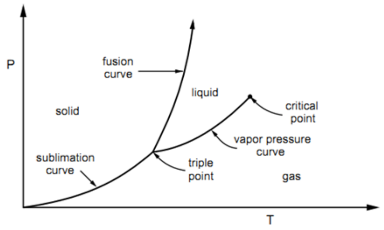
$$G = G(T,P,N) \equiv E - TS + PV = F + PV$$

$$dG = -SdT + VdP + \mu dN$$

$$\mu = \mu(T,P) = \frac{G}{N} \equiv g(T,P)$$

$$\left(\frac{\partial g}{\partial T}\right)_P = -\frac{S}{N} \qquad \left(\frac{\partial g}{\partial P}\right)_T = \frac{V}{N}$$

Example of phase diagram :



Clausius - Clapeyron Equation

$$g_A(T,P) = g_B(T,P)$$

$$dg_A(T,P) = dg_B(T,P)$$

$$\left\{\left(\frac{\partial g_A}{\partial T}\right)_P - \left(\frac{\partial g_B}{\partial T}\right)_P\right\} dT + \left\{\left(\frac{\partial g_A}{\partial P}\right)_T - \left(\frac{\partial g_B}{\partial P}\right)_T\right\} dP = 0$$

$$-\left\{\frac{S_A}{N_A} - \frac{S_B}{N_B}\right\} dT + \left\{\frac{V_A}{N_A} - \frac{V_B}{N_B}\right\} dP = 0$$

$$\Rightarrow \frac{dP}{dT} = \frac{\Delta(S/N)}{\Delta(V/N)}$$

Examples of systems studied using STP principles

The van der Waals equation of state
-- More realistic than the ideal gas law; contains some of the correct attributes for liquid-gas phase transitions.

Ideal gas equation of state : $PV = NkT$

van der Waals equation of state : $\left(P + a\frac{N^2}{V^2}\right)(V - bN) = NkT$

here a, b are material - dependent parameters

Dimensionless variables :

$$\tilde{P} \equiv 27\left(\frac{b^2}{a}\right)P \quad \tilde{T} \equiv \frac{27}{8}\left(\frac{b}{a}\right)kT \quad \tilde{\rho} \equiv 3b\frac{N}{V}$$

van der Waals equation of state : $\tilde{P} = \frac{8\tilde{\rho}\tilde{T}}{3-\tilde{\rho}} - 3\tilde{\rho}^2$

Summary of results for classical fluid with pair potential:

Equation of state in terms of pair correlation function :

$$\frac{PV}{NkT} = 1 - \frac{2\pi N}{3kTV}\int dr\, r^3 \frac{du(r)}{dr} g(r) = 1 - \frac{2\pi\beta\rho}{3}\int dr\, r^3 \frac{du(r)}{dr} g(r)$$

Equation of state in terms of virial expansion at low density :

$$\frac{PV}{NkT} \approx 1 + \rho B_2(T) + \cdots$$

$$B_2(T) = -\frac{2\pi\beta}{3}\int dr\, r^3 \frac{du(r)}{dr} e^{-\beta u(r)}$$

$\Rightarrow$ At this limit : $g(r) \approx e^{-\beta u(r)}$