PHY 341/641 Thermodynamics and Statistical Mechanics

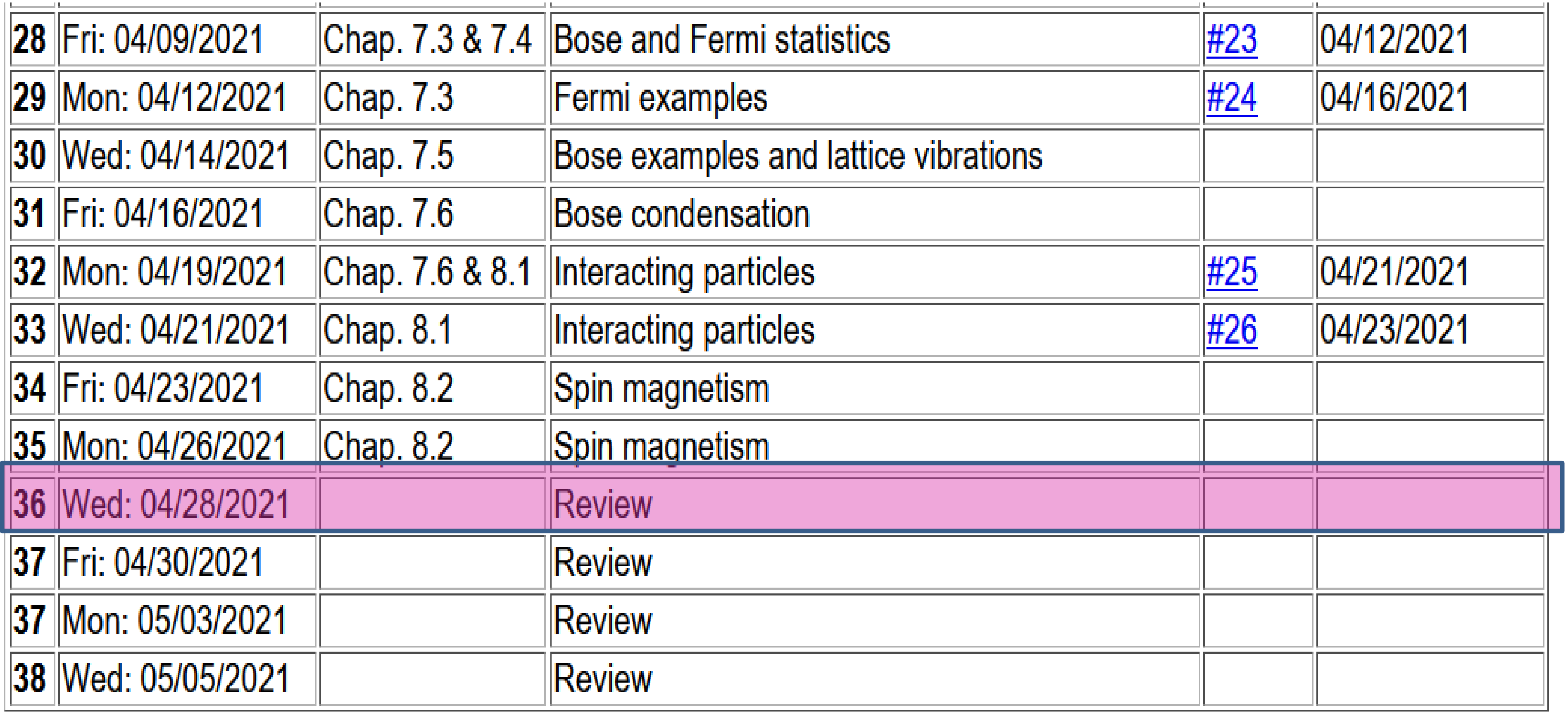
MWF: Online at 12 PM & FTF at 2 PM

Record!!!

Discussion for Lecture 36:

Review Part 1

1. Overview
2. Variables and functions of thermodynamics
3. Various macroscopic and microscopic viewpoints



28	Fri: 04/09/2021	Chap. 7.3 & 7.4	Bose and Fermi statistics	#23	04/12/2021
29	Mon: 04/12/2021	Chap. 7.3	Fermi examples	#24	04/16/2021
30	Wed: 04/14/2021	Chap. 7.5	Bose examples and lattice vibrations		
31	Fri: 04/16/2021	Chap. 7.6	Bose condensation		
32	Mon: 04/19/2021	Chap. 7.6 & 8.1	Interacting particles	#25	04/21/2021
33	Wed: 04/21/2021	Chap. 8.1	Interacting particles	#26	04/23/2021
34	Fri: 04/23/2021	Chap. 8.2	Spin magnetism		
35	Mon: 04/26/2021	Chap. 8.2	Spin magnetism		
36	Wed: 04/28/2021		Review		
37	Fri: 04/30/2021		Review		
37	Mon: 05/03/2021		Review		
38	Wed: 05/05/2021		Review		

Important dates: Final exams available < May 6; due May 14

Outstanding work due May 14

Review 1 & 2 Summary of concepts/equations

Review 3 & 4 Examples

Timelines –

May 5 – Review 4 & take home exam available
May 14 – all course materials due; outstanding homework, and completed exams

Please note that the complete lecture slides are posted on the course webpage and the zoom recordings are available on the shared google drive.

Colloquium this week is joint with Chemistry on Wed. at 4 PM

Chemistry Department Seminar
Joint Seminar with Physics
Wednesday, April 28, 2021 at 4 P.M.

Dr. Miles Silman
Professor of Biology
Andrew Sabin Family Foundation Professor of Conservation Biology
Director, Center for Energy, Environment, and Sustainability
Wake Forest University

The electromagnetic spectrum and carbon nanomaterials in Andean and Amazonian conservation

Dr. Silman received a B.S. in Biology from the University of Missouri and his Ph.D. in Zoology from Duke University.
His primary interests are community composition and dynamics of Andean and Amazonian tree communities in both space and time. The lab's current research focuses on combining modern- and paleoecology to understand tree distributions and plant-climate relationships in the Andes and Amazon.

WAKE FOREST UNIVERSITY
Department of Biology

Variables of thermodynamics

- ☐ Temperature – $T \geq 0$ in Kelvin scale
- ☐ Volume – V in units of m^3
- ☐ Pressure – P in units of Pascals (Newtons/m^2)
- ☐ Entropy – S in units of Joules/K
- ☐ Mass – M in units of kg
- ☐ Number of particles – N
- ☐ Chemical potential – μ in units of Joules

Various thermodynamic functions and their interrelationships

Internal energy $U = U(S,V,N)$ $dU = TdS - PdV + \mu dN$

Entropy $S = S(U,V,N)$ $dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN$

Enthalpy $H = H(S,P,N)$

Helmholtz free energy $F = F(T,V,N)$

Gibbs free energy $G = G(T,P,N)$

Grand potential $\Omega = \Omega(T,V,\mu)$

Using the Legendre transformation method:

$$H(S,P,N) = U + PV \qquad dH = TdS + VdP + \mu dN$$

$$F(T,V,N) = U - ST \qquad dF = -SdT - PdV + \mu dN$$

$$G(T,P,N) = F + PV \qquad dG = -SdT + VdP + \mu dN$$

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

Summary of thermodynamic functions

Internal energy	$U = U(S,V,N)$	$dU = TdS - PdV + \mu dN$
Entropy	$S = S(U,V,N)$	$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN$
Enthalpy	$H = H(S,P,N)$	$dH = TdS + VdP + \mu dN$
Helmholtz free energy	$F = F(T,V,N)$	$dF = -SdT - PdV + \mu dN$
Gibbs free energy	$G = G(T,P,N)$	$dG = -SdT + VdP + \mu dN$
Grand potential	$\Omega(T,V,\mu)$	$\mathrm{d}\Omega = -SdT - PdV + Nd\mu$

Some first derivative relationships --

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} = \left(\frac{\partial H}{\partial S}\right)_{P,N} \qquad P = -\left(\frac{\partial U}{\partial V}\right)_{S,N} = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = -\left(\frac{\partial \Omega}{\partial V}\right)_{T,\mu}$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = -\left(\frac{\partial G}{\partial T}\right)_{P,N} = -\left(\frac{\partial \Omega}{\partial T}\right)_{V,\mu} \qquad V = \left(\frac{\partial H}{\partial P}\right)_{S,N} = \left(\frac{\partial G}{\partial P}\right)_{T,N}$$

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{V,S} = \left(\frac{\partial H}{\partial N}\right)_{P,S} = \left(\frac{\partial F}{\partial N}\right)_{V,T} = \left(\frac{\partial G}{\partial N}\right)_{T,P} \qquad N = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V}$$

Note that these relationships are in principle general; describing both the macroscopic and microscopic aspects of our thermodynamic systems. While all of the thermodynamic potentials are valid in general, there is usually one function that most expedient for a given situation.

The system that we spent a lot of time on is the mono atomic ideal gas.

Microcanonical ensemble for a mono atomic ideal gas. Here we have N particles of mass M in a volume V and internal energy U. Note that in the this and some following slides Ω denotes the microcanonical multiplicity function.

Microstate: the "distribution" of particles in phase space:

$$\Rightarrow D\left(\{q_1 \cdots q_{3N}\},\{p_1 \cdots p_{3N}\},t\right)$$

Macrostate multiplicity based on total ("internal") energy U:

$$\Omega(N,U) = \frac{1}{h^{3N}N!}\int d^{3N}q\,d^{3N}p\,D\left(\{q_i\},\{p_i\}\right)\delta\left(H\left(\{q_i\},\{p_i\}\right)-U\right)$$

Phase space density, taken to be constant

Dirac delta function

Hamiltonian

Since the atoms are in a box of volume *V*:

$$\int d^{3N}q \Rightarrow V^N$$

For an ideal gas with *N* atoms of mass *M*:

$$H\left(\{q_i\},\{p_i\}\right) = \frac{1}{2M}\sum_{i=1}^{3N} p_i^2$$

Impose constraint that the only non-trivial contributions

come from $\frac{1}{2M}\sum_{i=1}^{3N} p_i^2 = U.$ In order simplify the mathematics,

first perform an intermediate calculation for

$$X(N,U) \equiv \int d^{3N}p\ \Theta\Big(U - H\left(\{q_i\},\{p_i\}\right)\Big)$$

$$\delta(x-a) \leftrightarrow \frac{d\Theta(x-a)}{dx}$$

delta
function

step
function

Define a radial variable for the $3N$ momentum space

$$\rho = \sqrt{\sum_{i=1}^{3N} p_i^2}$$

$$X(N,U) = \int d^{3N}p\ \Theta\Big(H\big(\{q_i\},\{p_i\}\big) - U\Big)$$

$$= \int (\text{angular part}) \int_0^{\sqrt{2MU}} d\rho\ \rho^{3N-1}$$

$$= \frac{(2\pi MU)^{3N/2}}{\Gamma\left(\frac{3N}{2}\right)}$$

⇦

Special mathematical function

$\Gamma(n) = (n-1)!$ for integer n

When the dust clears --

$$\Omega(N,V,U)=\frac{V^N 2\pi M}{h^{3N}N!}\frac{\left(2\pi MU\right)^{3N/2-1}}{\Gamma\left(\frac{3N}{2}\right)}$$

$$\approx\frac{V^N}{h^{3N}N!}\frac{\pi^{3N/2}}{\left(3N/2\right)!}\left(\sqrt{2MU}\right)^{3N}$$

Boltzmann's idea was to use the multiplicity function to calculate the entropy --

$$S = k_B \ln(\Omega(N,V,U))$$

$$\Omega(N,V,U) \approx \frac{V^N}{h^{3N} N!} \frac{\pi^{3N/2}}{(3N/2)!} \left(\sqrt{2MU}\right)^{3N}$$

$$\approx \left(\frac{V}{N} \left(\frac{4\pi MU}{3Nh^2} \right)^{3/2} e^{5/2} \right)^N$$

Using Stirling approximation

$$S(N,V,U) \approx Nk_B \left(\ln\left(\frac{V}{N} \left(\frac{4\pi MU}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right)$$

Sachur-Tetrode equation

Helmholtz free energy for monoatomic ideal gas

For monoatomic ideal gas --

Equation of state: $PV = Nk_BT$

Internal energy: $U = \frac{3}{2}Nk_BT$

Entropy: $$S = Nk_B\left(\ln\left(\frac{V}{N}\left(\frac{4\pi MU}{3Nh^2}\right)^{3/2}\right)+\frac{5}{2}\right)$$

Helmholtz: $$F = U - TS = -Nk_BT\left(\ln\left(\frac{V}{N}\left(\frac{2\pi MNk_BT}{Nh^2}\right)^{3/2}\right)+1\right)$$

Helmholtz μ: $$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -k_BT\left(\ln\left(\frac{V}{N}\left(\frac{2\pi Mk_BT}{h^2}\right)^{3/2}\right)\right)$$

Gibbs free energy for monoatomic ideal gas

[We have only worked out the entropy for this case.]

For monoatomic ideal gas --

Equation of state: $PV = Nk_BT$

Internal energy: $U = \frac{3}{2}Nk_BT$

Entropy: $$S = Nk_B\left(\ln\left(\frac{V}{N}\left(\frac{4\pi MU}{3Nh^2}\right)^{3/2}\right)+\frac{5}{2}\right)$$

Gibbs: $$G = U - TS + PV = -Nk_BT\left(\ln\left(\frac{V}{N}\left(\frac{2\pi MNk_BT}{Nh^2}\right)^{3/2}\right)\right)$$

$$= -Nk_BT\left(\ln\left(\frac{k_BT}{P}\left(\frac{2\pi Mk_BT}{h^2}\right)^{3/2}\right)\right)$$

Gibbs μ: $$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P} = -k_BT\left(\ln\left(\frac{k_BT}{P}\left(\frac{2\pi Mk_BT}{h^2}\right)^{3/2}\right)\right)$$

One further comment about chemical potential using ideal gas example

$$\text{Gibbs:} \qquad G = -Nk_BT\left(\ln\left(\frac{k_BT}{P}\left(\frac{2\pi Mk_BT}{h^2}\right)^{3/2}\right)\right) = G(T,P,N)$$

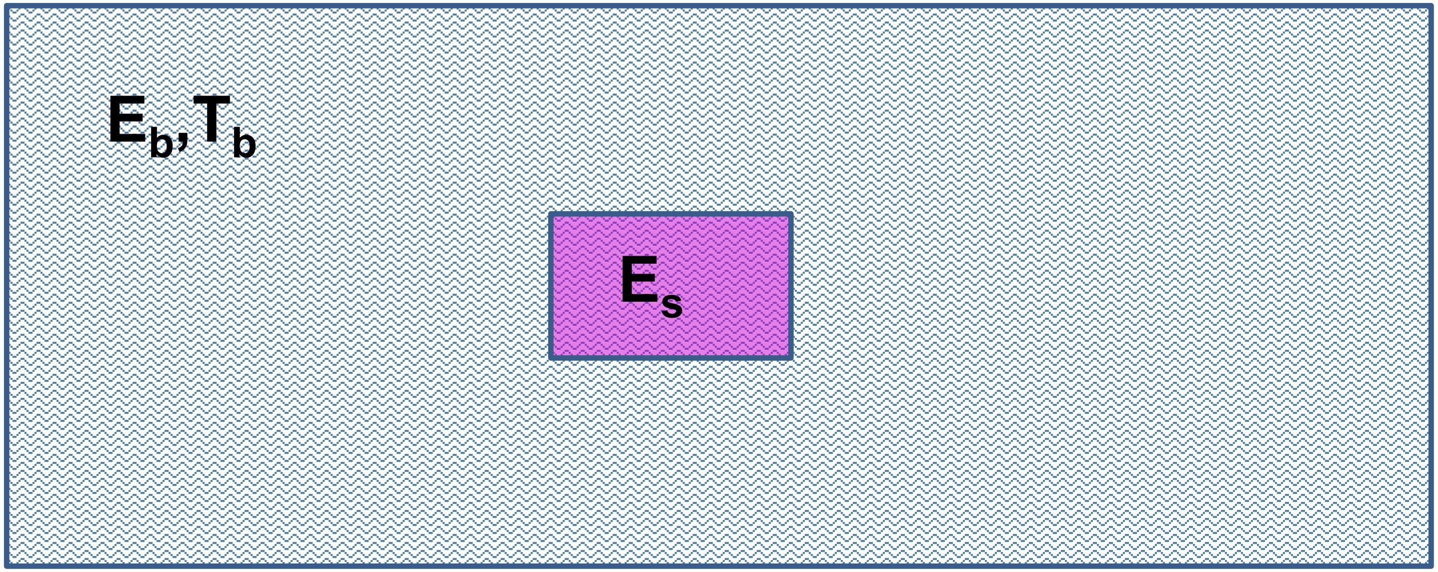
$$\text{Gibbs } \mu\text{:} \qquad \mu = \left(\frac{\partial G}{\partial N}\right)_{T,P} = -k_BT\left(\ln\left(\frac{k_BT}{P}\left(\frac{2\pi Mk_BT}{h^2}\right)^{3/2}\right)\right) = \mu(T,P)$$

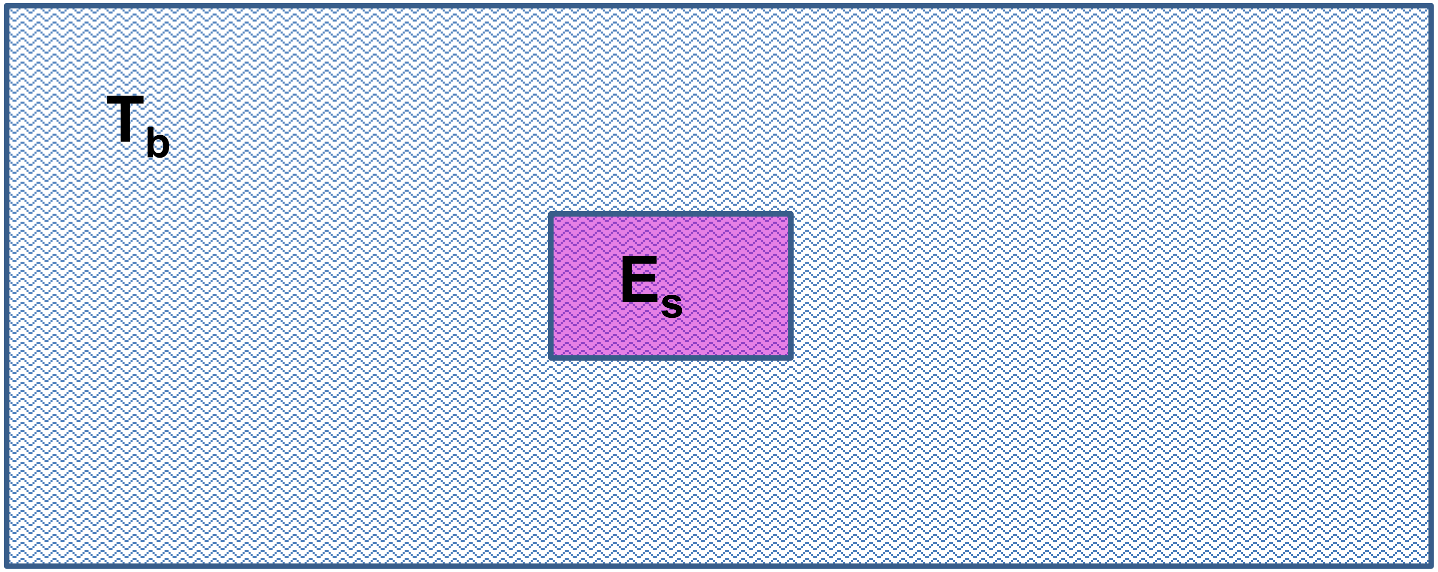
Also note that $G(T,P,N) = N\mu(T,P)$

Note that all of these results were derived from a knowledge of the entropy of our microcanonical mono atomic ideal gas

Now, we would like to extend the analysis of an isolated system to that of a system within a heat bath. The system within the heat bath will be analyzed in terms of a “canonical ensemble” --

Canonical ensemble:





In this case, we argue that the probability $\mathscr{P}_s$ of our system being in state s depends on the internal energy U_s and the bath temperature T_b :

$$\mathscr{P}_s = \frac{1}{Z(T_b)} e^{-U_s/k_B T_b} \qquad \text{where the "partition" function is } Z(T_b) = \sum_s e^{-U_s/k_B T_b}$$

This enables us to determine the "canonical" average of system properties. For example, the average internal energy of our system is given by

$$\langle U \rangle = \sum_s U_s \mathscr{P}_s = \frac{1}{Z(T_b)} \sum_s U_s e^{-U_s/k_B T_b}$$

Interestingly, the average Helmholtz free energy is given by

$$\langle F \rangle = \langle U \rangle - T \langle S \rangle = -k_B T_b \ln\left(Z(T_b)\right)$$

Evaluating the canonical partition function for the N particle mono atomic ideal gas

$$Z(T) = \sum_s e^{-U_s/kT} = \frac{1}{h^{3N} N!} \int d^3 r_1 d^3 r_2 \ldots d^3 r_N \int d^3 p_1 d^3 p_2 \ldots d^3 p_N \; e^{-\sum_i p_i^2/(2mkT)}$$

$$= \frac{V^N}{h^{3N} N!} \left(\int_{-\infty}^{\infty} dp_x e^{-p_x^2/(2mkT)} \right)^{3N} = \frac{V^N}{h^{3N} N!} \left(2\pi mkT\right)^{3N/2}$$

Analysis of a canonical ensemble for a mono atomic ideal gas

$$F(T,V,N) = -kTN\ln\left(\frac{V}{h^3}\left(2\pi mkT\right)^{3/2}\right) + kTN(\ln N - 1)$$

Stirling approx.

$$= -kTN\left(\ln\left(\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right) + 1\right)$$

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

$$U = F + TS = \frac{3}{2}NkT$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} = \frac{3}{2}Nk$$

Analysis of a canonical ensemble for a mono atomic ideal gas -- continued

$$F(T,V,N) = -kTN\left(\ln\left(\frac{V}{N}\left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right) + 1 \right)$$

Chemical potential --

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V} = -kT\ln\left(\frac{V}{N}\left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right)$$

Note that these results are for a classical ideal gas without internal degrees of freedom. Additional considerations are needed when considering internal degrees of freedom and/or quantum particle (Fermi or Bose) effects.

Possible topics for next time –

1. Effects of internal degrees of freedom for classical ideal gas
2. Bose or Fermi ideal gas; grand partition function
3. Ideal gas systems in thermodynamic cycles (heat engines and refrigerators).
4. Magnetic/spin systems
5. Phase transitions and chemical reactions