PHY 341/641
Thermodynamics and Statistical Physics

Lecture 29

Review (Chapters 5-7 in STP)

- Magnetic systems; Ising model
- Fermi statistics
- Bose statistics
- Phase transformations
- Chemical equilibria

20	3/09/2012	Phase transformation	5.8-5.10		
	3/12/2012	*Spring Break*			
	3/14/2012	*Spring Break*			
	3/16/2012	*Spring Break*			
21	3/19/2012	Many particle systems	6.1-6.2	HW 19	03/23/2012
22	3/21/2012	Fermi and Bose particles	6.3-6.4		
23	3/23/2012	Bose and Fermi particles	6.5-6.11	HW 20	03/28/2012
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	1-7		
	4/11/2012	No class -- work on exam	1-7		
30	4/13/2012	Classical gases and liquids	8.1-8.2	Exam due	
	4/16/2012				

Second exam: April 9-13

-- student presentations 4/30, 5/2 (need to pick topics)

Review of statistical mechanics of spin ½ systems -- Chapter 5 in STP

Fist consider system with independent particles in a magnetic field:

Microstates:

$\varepsilon_i = -\mu s_i B$ where $s_i = \pm 1$, $\mu B \equiv$ spin alignment energy

$\mu \equiv \frac{1}{2} g \mu_B = -9.28 \times 10^{-24} J/T$

$$Z_N = \sum_{s_1=\pm1} \sum_{s_2=\pm1} \sum_{s_3=\pm1} \cdots \sum_{s_N=\pm1} e^{\beta\mu B\left(\sum_{i=1}^{N} s_i\right)}$$

$$= \left(\sum_{s_1=\pm1} e^{\beta\mu B s_1} \right)^N = (Z_1)^N$$

Calculation of Z_1

$$Z_1 = \sum_{s_1=\pm1} e^{\beta\mu B s_1} = e^{-\beta\mu B} + e^{\beta\mu B} = 2\cosh(\beta\mu B)$$

Thermodynamic functions:

$$F = -kT\ln(Z_1)^N = -NkT\ln Z_1 = -NkT\ln\big(2\cosh(\beta\mu B)\big)$$

$$\langle E\rangle = -N\frac{\partial \ln Z_1}{\partial\beta} = -N\mu B\tanh(\beta\mu B)$$

$$C = \left(\frac{\partial\langle E\rangle}{\partial T}\right)_B = kN(\beta\mu B)^2\operatorname{sech}^2(\beta\mu B)$$

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Magnetic field dependence of Z:

$$Z_N(T,N,B) = \big(2\cosh(\beta\mu B)\big)^N$$

Magnetization :

$$M = \mu\sum_{i=1}^{N}\langle s_i\rangle$$

$$\langle s_i\rangle = \frac{\sum_{s_1=\pm1} s_1 e^{\beta\mu B s_1}}{\sum_{s_1=\pm1} e^{\beta\mu B s_1}} = \frac{1}{\beta\mu}\frac{\partial\ln Z_1}{\partial B}$$

$$\Rightarrow M = N\mu\tanh(\beta\mu B) = -\frac{\partial F}{\partial B}$$

$$\chi \equiv \left(\frac{\partial M}{\partial B}\right)_T = -\left(\frac{\partial^2 F}{\partial B^2}\right)_T = N\mu^2\beta\operatorname{sech}^2(\beta\mu B)$$

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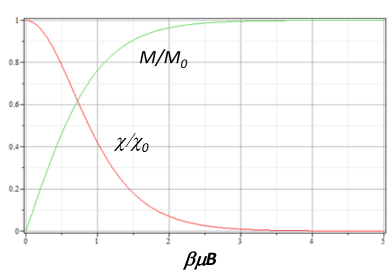
Magnetization and susceptibility of independent spin ½ particles



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Effects of interactions between particles:

Independent particle system

Microstate s :

$$E_s = -\sum_{i=1}^{N} \mu s_i B \equiv -H \sum_{i=1}^{N} s_i$$

Interacting particle system – Ising model

Microstate s :

$$E_s = -J \sum_{i,j(nn)}^{N} s_i s_j - H \sum_{i=1}^{N} s_i$$

For one dimension : $E_s = -\sum_i \left(J s_i s_{i+1} + \frac{1}{2} H \left(s_i + s_{i+1}\right)\right)$

Partition function for 1-dimensional Ising system of N spins with periodic boundary conditions (s_{N+1}=s_1)

$$Z_N = \sum_s \exp\left[\beta J \sum_{i=1}^{N} s_i s_{i+1} + \frac{\beta H}{2} \sum_{i=1}^{N} \left(s_i + s_{i+1}\right)\right]$$

$$\equiv \sum_{s_1, s_2, s_3 \cdots s_N} f(s_1, s_2) f(s_2, s_3) \cdots f(s_{N-1}, s_N) f(s_N, s_{N+1})$$

where :

$$f(s, s') = \begin{pmatrix} f(1,1) & f(1,-1) \\ f(-1,1) & f(-1,-1) \end{pmatrix}$$

$$\equiv \begin{pmatrix} e^{(\beta J + \beta H)} & e^{(-\beta J)} \\ e^{(-\beta J)} & e^{(\beta J - \beta H)} \end{pmatrix} \equiv \mathbf{T}$$

1-dimensional Ising system of N spins with periodic boundary conditions (s_{N+1}=s_1) (continued)

$$Z_N = \sum_{s_1, s_2, s_3 \cdots s_N} f(s_1, s_2) f(s_2, s_3) \cdots f(s_{N-1}, s_N) f(s_N, s_{N+1})$$

$$= \sum_{s_1, s_2, s_3 \cdots s_N} T_{s_1 s_2} T_{s_2 s_3} T_{s_3 s_4} T_{s_4 s_5} \cdots T_{s_N s_{N+1}}$$

where :

$$\mathbf{T} \equiv \begin{pmatrix} e^{(\beta J + \beta H)} & e^{(-\beta J)} \\ e^{(-\beta J)} & e^{(\beta J - \beta H)} \end{pmatrix}$$

$$Z_N = \mathrm{Tr}\left(\mathbf{T}^N\right)$$

1-dimensional Ising system of N spins with periodic boundary conditions (s_{N+1}=s_1) (continued)

Some tricks from linear algebra :

1. Any symmetric matrix $\mathbf{T}$ can be diagonalized by a transformation of the type $\mathbf{U}^{-1}\mathbf{T}\mathbf{U}=\mathbf{\Lambda}\equiv\begin{pmatrix}\lambda_1 & 0 & \cdots & 0\\ 0 & \lambda_2 & \cdots & 0\\ \cdots & \cdots & \cdots & \cdots\\ 0 & 0 & 0 & \lambda_n\end{pmatrix}$.
2. $\mathbf{TTT}\cdots\mathbf{T}=\mathbf{TUU}^{-1}\mathbf{TUU}^{-1}\mathbf{TU}\cdots\mathbf{U}^{-1}\mathbf{T}$
3. $\mathrm{Tr}(\mathbf{TTT}\cdots\mathbf{T})=\mathrm{Tr}(\mathbf{U}^{-1}\mathbf{TTT}\cdots\mathbf{TU})=\mathrm{Tr}(\mathbf{\Lambda\Lambda}\cdots\mathbf{\Lambda})$

$$\Rightarrow \mathrm{Tr}(\mathbf{T}^N)=\lambda_1^N+\lambda_2^N+\lambda_3^N\cdots\lambda_n^N$$

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1-dimensional Ising system of N spins with periodic boundary conditions (s_{N+1}=s_1) (continued)

In this case :

$$\mathbf{T}\equiv\begin{pmatrix}e^{(\beta J+\beta H)} & e^{(-\beta J)}\\ e^{(-\beta J)} & e^{(\beta J-\beta H)}\end{pmatrix}$$

$$\mathbf{\Lambda}=\begin{pmatrix}\lambda_1 & 0\\ 0 & \lambda_2\end{pmatrix}$$

$$\lambda_1=e^{\beta J}\left\{\cosh(\beta H)+\left[\sinh^2(\beta H)+e^{-4\beta J}\right]^{1/2}\right\}$$

$$\lambda_2=e^{\beta J}\left\{\cosh(\beta H)-\left[\sinh^2(\beta H)+e^{-4\beta J}\right]^{1/2}\right\}$$

$$Z_N=\mathrm{Tr}\left(\mathbf{T}^N\right)=\lambda_1^N+\lambda_2^N$$

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1-dimensional Ising system of N spins with periodic boundary conditions (s_{N+1}=s_1) (continued)

$$Z_N=\mathrm{Tr}\left(\mathbf{T}^N\right)=\lambda_1^N+\lambda_2^N=\lambda_1^N\left(1+\left(\frac{\lambda_2}{\lambda_1}\right)^N\right)$$

$$F(T,J,H)=-kT\ln Z_N=-NkT\ln\lambda_1-kT\ln\left[1+\left(\frac{\lambda_2}{\lambda_1}\right)^N\right]$$

$$\approx -NkT\ln\lambda_1$$

$$=-NJ-kT\ln\left[\cosh(\beta H)+\left[\sinh^2(\beta H)+e^{-4\beta J}\right]^{1/2}\right]$$

$$M(T,J,H)=-\frac{\partial F}{\partial H}=\frac{N\sinh(\beta H)}{\left[\sinh^2(\beta H)+e^{-4\beta J}\right]^{1/2}}$$

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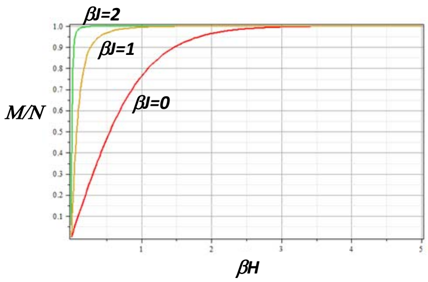
$$M(T,J,H) = \frac{N\sinh(\beta H)}{\left[\sinh^2(\beta H) + e^{-4\beta J}\right]^{1/2}}$$



Mean field approximation for 1-dimensional Ising model

Exact macrostate energy :

$$E_s = -J\sum_{i=1}^{N} s_i s_{i+1} - H\sum_{i=1}^{N} s_i$$

Mean field macrostate energy :

$$E_s^{MF} = -J\sum_{i=1}^{N} s_i\langle s_i\rangle - H\sum_{i=1}^{N} s_i$$

$$= -(J\langle s_i\rangle + H)\sum_{i=1}^{N} s_i$$

$$\equiv -H_{eff}\sum_{i=1}^{N} s_i$$

Mean field partition function and Free energy:

$$F^{MF} = -kT\ln\left(Z_1^{MF}\right)^N = -NkT\ln Z_1^{MF} = -NkT\ln\left(2\cosh(\beta H_{eff})\right)$$

$$H_{eff} = J\langle s_i\rangle + H$$

Consistency condition :

$$\langle s_i\rangle = \frac{1}{Z_1}\sum_{s_i} s_i e^{-\beta H_{eff} s_i} = \tanh\left[\beta\left(J\langle s_i\rangle + H\right)\right]$$

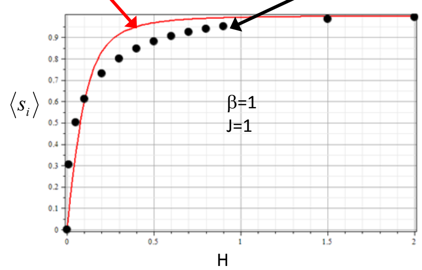
One dimensional Ising model with periodic boundary conditions:

Exact solution :

$$\langle s_i \rangle \equiv \frac{M}{N} = \frac{\sinh(\beta H)}{\left[\sinh^2(\beta H) + e^{-4\beta J}\right]^{1/2}}$$

Mean field solution :

$$\langle s_i \rangle = \tanh\left[\beta\left(J\langle s_i \rangle + H\right)\right]$$



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Summary of qualitative results of Ising model systems :

- Exact solutions of one-dimensional system show no phase transitions
- Exact solution by Onsager for two-dimensions system shows phase transitions as a function of T in zero magnetic field
- Mean field approximation shows phase transitions for all dimensions as a function of T in zero magnetic field
- Mean field approximation for fixed T as a function of magnetic field is qualitatively similar to exact solution for one dimension

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Self-consistency condition for mean field treatment for general system with *q* nearest neighbors

$$H_{eff} \equiv J\sum_{j=1}^{q} s_j + H$$

$$\langle H_{eff} \rangle = Jq\langle s_j \rangle + H \equiv Jqm + H$$

$$Z_1 = \sum_{s_1=\pm 1} e^{\beta \langle H_{eff} \rangle s_1} = 2\cosh\left(\beta\left(Jqm + H\right)\right)$$

$$\frac{F}{N} = -kT \ln Z_1$$

$$m = -\frac{1}{N}\frac{\partial F}{\partial H} = \tanh\left(\beta\left(Jqm + H\right)\right)$$

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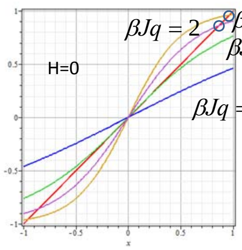
Mean field self-consistency condition:

$$m = \tanh\left(\beta\left(Jqm + H\right)\right)$$



Condition for non-trivial solution for m at $H = 0$:

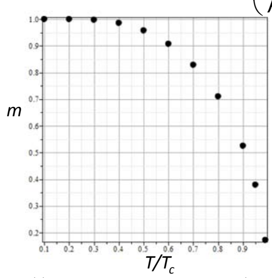
$$\beta Jq \geq 1$$

➔Mean field solutions exhibit "critical behavior" (phase transition) at $\beta_c Jq=1$.

Mean field self-consistency condition for H=0: $m = \tanh\left(\beta\left(Jqm\right)\right)$

Define : $\beta_c Jq = 1$

$$m = \tanh\left(\beta\left(Jqm\right)\right) = \tanh\left(\frac{\beta}{\beta_c} m\right) = \tanh\left(\frac{T_c}{T} m\right)$$



$$m = \begin{cases} \tanh\left(\frac{T_c}{T} m\right) & \text{for } T \leq T_c \\ 0 & \text{for } T > T_c \end{cases}$$

Summary of results for mean field treatment of Ising model

Internal energy for $H = 0$:

$$E = -NJqm^2$$

where $m = \tanh\left(\beta\left(Jqm\right)\right)$

Heat capacity :

$$C = \left(\frac{\partial E}{\partial T}\right)_N = 2Nk\beta^2 Jqm\left(\frac{\partial m}{\partial \beta}\right)_N$$

$$\left(\frac{\partial m}{\partial \beta}\right)_N = \left(Jqm + \beta Jq\left(\frac{\partial m}{\partial \beta}\right)_N\right)\operatorname{sech}^2\left(\beta\left(Jqm\right)\right)$$

$$\left(\frac{\partial m}{\partial \beta}\right)_N = \frac{Jqm}{\cosh^2\left(\beta\left(Jqm\right)\right) - \beta Jq}$$

$$C = \frac{2Nk\beta^2 J^2 q^2 m^2}{\cosh^2\left(\beta\left(Jqm\right)\right) - \beta Jq}$$

Behavior of magnetic susceptibility (in scaled units):

$$m = \tanh\left(\beta(Jqm + H)\right)$$

$$\chi(T,H) = \left(\frac{\partial m}{\partial H}\right)_T$$

$$\left(\frac{\partial m}{\partial H}\right)_T = \left(\beta + \beta Jq\left(\frac{\partial m}{\partial H}\right)_T\right)\text{sech}^2\left(\beta(Jqm + H)\right)$$

$$\chi(T,H) = \left(\frac{\partial m}{\partial H}\right)_T = \frac{\beta}{\cosh^2\left(\beta(Jqm+H)\right) - \beta Jq}$$

For $H = 0$:

$$\chi(T,0) = \frac{1}{Jq}\frac{\frac{T_c}{T}}{\cosh^2\left(\frac{T_c}{T}m\right) - \frac{T_c}{T}}$$

Behavior of magnetic susceptibility (in scaled units) -- continued:

$$\chi(T,0) = \frac{1}{Jq}\frac{\frac{T_c}{T}}{\cosh^2\left(\frac{T_c}{T}m\right) - \frac{T_c}{T}}$$

For $T > T_c$; $m = 0$

$$\chi(T,0) = \frac{1}{Jq}\frac{\frac{T_c}{T}}{1 - \frac{T_c}{T}} = \frac{T_c}{Jq}\frac{1}{T - T_c} \quad \text{Curie - Weiss relation}$$

For $T < T_c$ and $T \approx T_c$; $m \approx \sqrt{3}\left(\frac{T}{T_c}\right)\left(1 - \frac{T}{T_c}\right)^{1/2}$

$$\cosh^2\left(\frac{T_c}{T}m\right) \approx 1 + 3\left(1 - \frac{T}{T_c}\right)$$

$$\chi(T,0) \approx \frac{1}{Jq}\frac{\frac{T_c}{T}}{\left(1 - \frac{T}{T_c}\right)\left(3 - \frac{T_c}{T}\right)} \approx \frac{T_c}{2Jq}\frac{1}{T_c - T}$$

Many particle systems with translational degrees of freedom – Chapter 6 of STP

Interacting systems – N identical particles of mass m:
Classical treatment

$$Z(T,V,N) = \frac{1}{N!h^{3N}}\int d^{3N}r \int d^{3N}p\, e^{-\frac{\beta}{2m}\left(\sum_i \mathbf{p}_i^2\right) - \beta V(\{\mathbf{r}_i\})}$$

$$Z(T,V,N) = \frac{1}{N!h^{3N}}\int d^{3N}r e^{-\beta V(\{\mathbf{r}_i\})} \int d^{3N}p\, e^{-\frac{\beta}{2m}\left(\sum_i \mathbf{p}_i^2\right)}$$

$$\mathbf{p}_i = m\mathbf{v}_i \qquad d^3p = 4\pi m^3 v^2 dv$$

$$\int d^{3N}p\, e^{-\frac{\beta}{2m}\left(\sum_i \mathbf{p}_i^2\right)} = \left(4\pi m^3 \int v^2 dv e^{-\beta m v^2/2}\right)^N$$

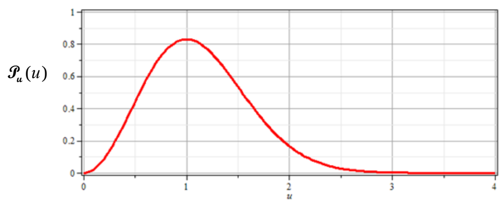
Probability of finding particle of velocity between v and $v + dv$:

$$\mathcal{P}(v) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}$$

Maxwell velocity distribution

$$\mathcal{P}(v) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}$$

$$\mathcal{P}(v)dv = \mathcal{P}_u(u)du = \frac{4}{\sqrt{\pi}}u^2 e^{-u^2}du \quad \text{where } u \equiv \sqrt{\frac{m}{2kT}}v$$



➔ For classical particles the Maxwell velocity distribution is the same for all particle interaction potentials.

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:

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

Grand partition function for these systems:

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

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

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

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

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

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 :

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

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 :

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

Mean occupancy numbers :

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

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

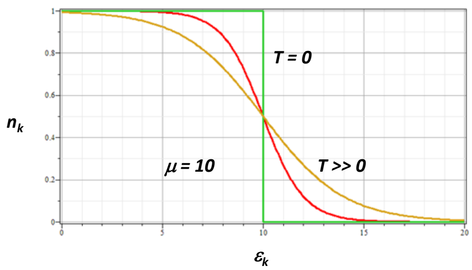
Note a detail:

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

Note that the summation of the geometric series implies that $e^{-\beta(\varepsilon_k - \mu)} < 1$

$\Rightarrow e^{\beta\mu} < 1$ or $\mu < 0$

Case of Fermi particles



Case of Fermi particles

Non-interacting spin ½ particles of mass *m* at *T=0* moving in 3-dimensions in large box of volume $V=L^3$:
Assume that each state e_k is doubly occupied (due to spin)

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

Example : particles in 3-dimensional box of length L

$$\varepsilon_{n_x,n_y,n_z} = \frac{h^2\left(n_x^2+n_y^2+n_z^2\right)}{8mL^2} \quad n_x, n_y, n_z = 1,2,3\cdots$$

In the limit $L \to \infty$, $\varepsilon_k \to \frac{\hbar^2 k^2}{2m}$

$$\sum_k \to 2\left(\frac{L}{2\pi}\right)^3 \int d^3k$$

spin degeneracy

Case of Fermi spin ½ particles for *T →0* in 3-dimensional box.

$$\langle n_k \rangle = \frac{1}{e^{\beta(\varepsilon_k-\mu)}+1} \approx \begin{cases} 1 & \text{for } \varepsilon_k < \mu \\ 0 & \text{for } \varepsilon_k > \mu \end{cases}$$

$$N = \sum_k \langle n_k \rangle \to 2\left(\frac{L}{2\pi}\right)^3 \int_{\varepsilon_k<\mu} d^3k = 2\left(\frac{L}{2\pi}\right)^3 \frac{4\pi}{3} k_F^3$$

$$\mu = \frac{\hbar^2 k_F^2}{2m} \equiv \varepsilon_F$$

$$N = \frac{V}{3\pi^2}\left(\frac{2m\varepsilon_F}{\hbar^2}\right)^{3/2}$$

$$\Rightarrow \varepsilon_F = \frac{\hbar^2}{2m}\left(3\pi^2 \frac{N}{V}\right)^{2/3}$$

Case of Bose particles

Non-interacting spin 0 particles of mass *m* at low *T* moving in 3-dimensions in large box of volume $V=L^3$:

Assume that each state e_k is singly occupied.

$$N=\sum_k \langle n_k\rangle = \sum_k \frac{1}{e^{\beta(\varepsilon_k-\mu)}-1}$$

$$\varepsilon_{n_x,n_y,n_z}=\frac{h^2\left(n_x^2+n_y^2+n_z^2\right)}{8mL^2} \quad n_x,n_y,n_z=1,2,3\cdots$$

$$\text{In the limit } L\to\infty,\ \varepsilon_k \to \frac{\hbar^2k^2}{2m}$$

$$\sum_k \to \left(\frac{L}{2\pi}\right)^3\int d^3k=\int d\varepsilon\, g_B(\varepsilon)$$

$$g_B(\varepsilon)=\frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{\varepsilon}$$

Critical temperature for Bose condensation:

$$N=\langle n_0\rangle+\int_0^\infty d\varepsilon\, g_B(\varepsilon)\frac{1}{e^{\beta(\varepsilon-\mu)}-1}$$

condensate "normal" state

$$\text{If } N=\int_0^\infty d\varepsilon\, g_B(\varepsilon)\frac{1}{e^{\beta(\varepsilon-\mu)}-1}, \text{ there is no "condensate"}$$

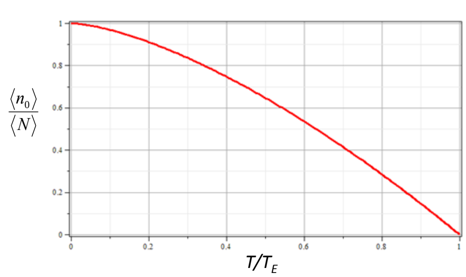
The temperature at which the above equality is satisfied is called the Einstein condensation temperature T_E.

Approximate value:

$$N\approx\frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty d\varepsilon\sqrt{\varepsilon}\frac{1}{e^{\beta_E\varepsilon}-1}=\frac{V}{4\pi^2}\left(\frac{2mkT_E}{\hbar^2}\right)^{3/2}\int_0^\infty dx\sqrt{x}\frac{1}{e^x-1}$$

$$N\approx\frac{V}{4\pi^2}\left(\frac{2mkT_E}{\hbar^2}\right)^{3/2}2.612\frac{\sqrt{\pi}}{2} \quad \Rightarrow kT_E=\left(\frac{N/V}{2.612}\right)^{2/3}\frac{2\pi\hbar^2}{m}$$

$$\text{For } T\le T_E \quad \frac{\langle n_0\rangle}{\langle N\rangle}=1-\left(\frac{T}{T_E}\right)^{3/2}$$



Other systems with Bose statistics

Thermal distribution of photons -- blackbody radiation:

In this case, the number of particles (photons) is not conserved so that μ=0.

$$\langle n_k \rangle = \frac{1}{e^{\beta\varepsilon_k} - 1}$$

$$\varepsilon_k = \hbar\omega = \hbar c k = h\nu$$

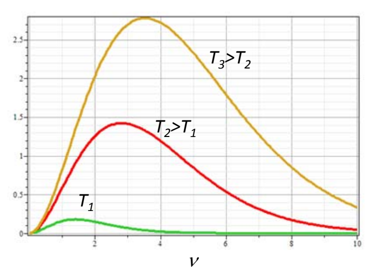
$$\sum_k \rightarrow \left(\frac{L}{2\pi}\right)^3 \int d\varepsilon \int d^3k\, \delta(\varepsilon - \hbar c k) = \frac{V}{\pi^2 \hbar^3 c^3} \int d\varepsilon\, \varepsilon^2$$

Distribution of radiated energy:

$$\langle E \rangle = \sum_k \langle n_k \rangle \varepsilon_k = \frac{V}{\pi^2 \hbar^3 c^3} \int d\varepsilon \frac{\varepsilon^3}{e^{\beta\varepsilon} - 1} = \frac{8\pi h V}{c^3} \int d\nu \frac{\nu^3}{e^{\beta h \nu} - 1}$$

$$\langle E \rangle = \frac{8\pi^5 V (kT)^4}{15 (hc)^3}$$

Blackbody radiation distribution:



Other systems with Bose statistics

Thermal distribution of vibrations -- phonons:

In this case, the number of particles (phonons) is not conserved so that μ=0.

$$\langle n_k \rangle = \frac{1}{e^{\beta\varepsilon_k} - 1}$$

$$\varepsilon_k = \hbar\omega$$

For Einstein solid, the fundamental frequency ω vibrates in 3 directions for all N particles.

$$\langle E \rangle = 3N\hbar\omega \left(\frac{1}{e^{\beta\hbar\omega} - 1} + \frac{1}{2} \right)$$

$$C = \left(\frac{\partial \langle E \rangle}{\partial T} \right) = 3Nk \left(\frac{\hbar\omega}{kT} \right)^2 \frac{e^{\beta\hbar\omega}}{\left(e^{\beta\hbar\omega} - 1\right)^2}$$

Other systems with Bose statistics -- continued
Thermal distribution of vibrations -- phonons:

$$\langle n_k \rangle = \frac{1}{e^{\beta\varepsilon_k}-1}$$

$$\varepsilon_k = \hbar\omega$$

For Debye solid, the fundamental frequency $\omega = \bar{c}k$, where $\bar{c}$ denotes the speed of sound (assumed here to be the same in 3 directions).

$$\langle E \rangle = \frac{3V\hbar}{2\pi^2\bar{c}^3}\int_0^{\omega_D}\frac{\omega^3 d\omega}{e^{\beta\hbar\omega}-1} = 9NkT\left(\frac{T}{T_D}\right)^3\int_0^{T_D/T}\frac{x^3 dx}{e^x-1}$$

Thermodynamic description of the equilibrium between two forms "phases" of a material under conditions of constant *T* and *P* -- Chapter 7 in STP

Review of Gibb's Free energy:

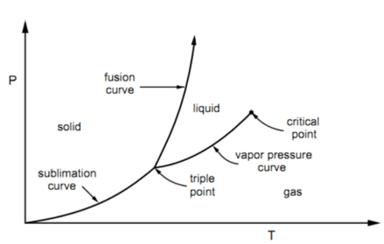
$$G = G(T,P,N) \equiv E - TS + PV = F + PV$$

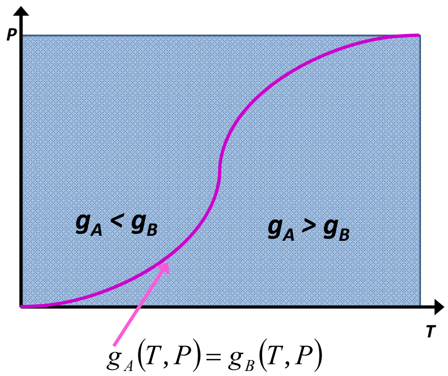
$$dG = -SdT + VdP + \mu dN$$

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

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

Example of phase diagram :





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Clausius - Clapeyron Equation

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

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

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

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

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

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Clausius - Clapeyron Equation

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

For a phase change involving the "Latent Heat":

$$\Delta S = \frac{L_{AB}}{T}$$

$$\frac{dP}{dT} = \frac{L_{AB}}{T(V_A - V_B)}$$

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Clausius - Clapeyron Equation - - approximate *P(T)* for liquid - gas coexistence

$$\frac{dP}{dT} = \frac{L_{AB}}{T\left(V_A - V_B\right)}$$

Example: A ≡ vapor B ≡⟹ water

$$L_{AB} = 2.257\times10^{6}\ J/kg = 40.7\times10^{3}\ J/mole \qquad T \geq 373.15K$$

$$V_A \approx \frac{R_M T}{P} \text{ (per mole)} \qquad R_M = kN_{Avo}$$

$$V_B \approx 0$$

$$\frac{dP}{dT} = \frac{L_{AB}}{R_M}\frac{P}{T^2} \quad \Rightarrow \quad \frac{dP}{P} = \frac{L_{AB}}{R_M}\frac{dT}{T^2}$$

$$\ln(P) = \text{constant } -\frac{L_{AB}}{R_M T} \quad \Rightarrow \quad P(T) = P_0 e^{-L_{AB}/R_M T}$$

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Other topics

- Van der Waals equation of state
- Chemical equilibria

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