PHY 770 -- Statistical Mechanics
12:00* -1:45 PM TR Olin 107

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Course Webpage: http://www.wfu.edu/~natalie/s14phy770

Lecture 13
Chap. 5 – Canonical esemble

- ❑ **Partition function**
- ❑ **Ising model in 1d and mean field approximation**

Chap. 6 – Grand canonical ensemble

- ❑ **Grand partition function**
- ❑ **Classical and quantum ideal gases**

***Partial make-up lecture -- early start time**

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	The Ising model (class 12-1:45 PM)	#12	02/27/2014
	Tue: 02/25/2014		NAWH out of town -- no class		
13	Thur: 02/27/2014	Chap. 5	(class 12-1:45 PM)		
	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)		
14	Tue: 03/18/2014	Chap. 6	(Exam due)		

Summary of results for the canonical ensemble

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

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

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

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

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

$$\mathcal{H}_{\text{Ising}} = -\varepsilon \sum_{i=1}^{N} s_i s_{i+1} - \frac{\mu B}{2} \sum_{i=1}^{N} (s_i + s_{i+1})$$

$$Z_N = \text{Tr}\left[\exp\left(\beta\varepsilon \sum_{i=1}^{N} s_i s_{i+1} + \frac{\beta\mu B}{2} \sum_{i=1}^{N} (s_i + s_{i+1})\right)\right]$$

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

where:

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

$$\equiv \begin{pmatrix} e^{(\beta\varepsilon + \beta\mu B)} & e^{(-\beta\varepsilon)} \\ e^{(-\beta\varepsilon)} & e^{(\beta\varepsilon - \beta\mu B)} \end{pmatrix} \equiv \overline{\mathbf{P}}$$

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

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

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

where:

$$\overline{\mathbf{P}} \equiv \begin{pmatrix} e^{(\beta\varepsilon + \beta\mu B)} & e^{(-\beta\varepsilon)} \\ e^{(-\beta\varepsilon)} & e^{(\beta\varepsilon - \beta\mu B)} \end{pmatrix}$$

$$Z_N = \text{Tr}\left[\overline{\mathbf{P}}^N\right]$$

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. $\text{Tr}(\mathbf{TTT}\cdots\mathbf{T}) = \text{Tr}(\mathbf{U}^{-1}\mathbf{TTT}\cdots\mathbf{TU}) = \text{Tr}(\mathbf{\Lambda\Lambda}\cdots\mathbf{\Lambda})$

$$\Rightarrow \text{Tr}\left[\overline{\mathbf{P}}^N\right] = \lambda_1^N + \lambda_2^N$$

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

In this case:

$$\overline{\mathbf{P}} \equiv \begin{pmatrix} e^{(\beta\varepsilon+\beta\mu B)} & e^{(-\beta\varepsilon)} \\ e^{(-\beta\varepsilon)} & e^{(\beta\varepsilon-\beta\mu B)} \end{pmatrix}$$

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

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

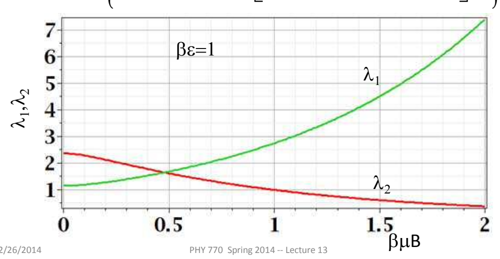
$$\lambda_2 = e^{\beta\varepsilon}\left\{\cosh\left(\beta\mu B\right) - \left[\sinh^2\left(\beta\mu B\right) + e^{-4\beta\varepsilon}\right]^{1/2}\right\}$$

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

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

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

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



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

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

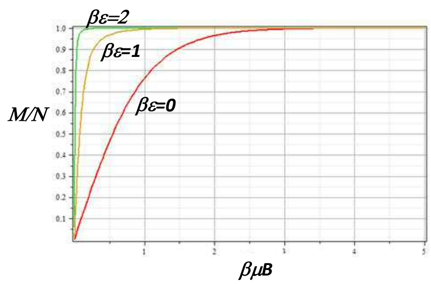
$$A(T,\varepsilon,B) = -kT\ln Z_N = -NkT\ln\lambda_1 - kT\ln\left[1 + \left(\frac{\lambda_2}{\lambda_1}\right)^N\right]$$

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

$$= -N\varepsilon - kT\ln\left[\cosh\left(\beta\mu B\right) + \left[\sinh^2\left(\beta\mu B\right) + e^{-4\beta\varepsilon}\right]^{1/2}\right]$$

$$M(T,\varepsilon,B) = -\frac{\partial A}{\partial B} = \frac{N\mu\sinh\left(\beta\mu B\right)}{\left[\sinh^2\left(\beta\mu B\right) + e^{-4\beta\varepsilon}\right]^{1/2}}$$

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



Mean field approximation for 1-dimensional Ising model

Exact Hamiltonian:

$$\hat{H}_{Ising} = -\varepsilon \sum_{i=1}^{N} s_i s_{i+1} - \mu B \sum_{i=1}^{N} s_i$$

Mean field approximation:

$$\hat{H}^{MF}_{\text{Ising}} = -\varepsilon \sum_{i=1}^{N} s_i \langle s_i \rangle - \mu B \sum_{i=1}^{N} s_i$$

$$= -\left(\varepsilon \langle s_i \rangle + \mu B\right) \sum_{i=1}^{N} s_i$$

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

Mean field partition function and Free energy:

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

$$H_{eff} = \varepsilon \langle s_i \rangle + \mu B$$

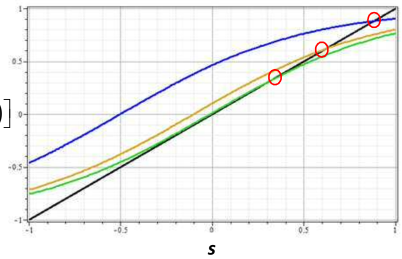
Consistency condition:

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

Consistency condition:

$$\langle s_i \rangle = \tanh\left[\beta\left(\varepsilon\langle s_i\rangle + \mu B\right)\right]$$

$\tanh\left[\beta\left(\varepsilon\langle s_i\rangle + \mu B\right)\right]$



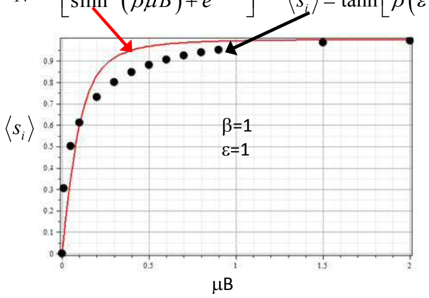
One dimensional Ising model with periodic boundary conditions:

Exact solution:

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

Mean field solution:

$$\langle s_i \rangle = \tanh\left[\beta\left(\varepsilon\langle s_i\rangle + \mu B\right)\right]$$



Extension of mean field analysis to more complicated geometries

Ising model:

$$\hat{H}_{Ising} = \sum_{i,j(nn)}^{N} \epsilon_{ij} s_i s_j - \mu B \sum_{i=1}^{N} s_i \Rightarrow -\epsilon \sum_{i,j(nn)}^{N} s_i s_j - \mu B \sum_{i=1}^{N} s_i$$

Ising model in mean field approximation:

$$\hat{H}_{Ising}^{MF} = -\epsilon \frac{\nu}{2} \sum_{i}^{N} s_i \langle s_j \rangle - \mu B \sum_{i=1}^{N} s_i$$

$\nu \equiv$ number of nearest neighbors

$$\hat{H}_{Ising}^{MF} = -\left(\epsilon \frac{\nu}{2}\langle s_j\rangle + \mu B\right)\sum_{i=1}^{N} s_i \equiv -H_{eff}\sum_{i=1}^{N} s_i$$

Extension of mean field analysis to more complicated geometries -- continued

Mean field partition function and Free energy:

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

$$H_{eff} = \varepsilon\frac{\nu}{2}\langle s_i\rangle + \mu B$$

Consistency condition:

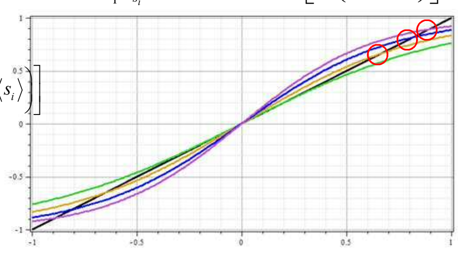
$$\langle s_i\rangle = \frac{1}{Z_1}\sum_{s_i} s_i e^{-\beta H_{eff} s_i} = \tanh\left[\beta\left(\varepsilon\frac{\nu}{2}\langle s_i\rangle + \mu B\right)\right]$$

Extension of mean field analysis to more complicated geometries -- continued

Consistency condition for B=0:

$$\langle s_i\rangle = \frac{1}{Z_1}\sum_{s_i} s_i e^{-\beta H_{eff} s_i} = \tanh\left[\beta\left(\varepsilon\frac{\nu}{2}\langle s_i\rangle\right)\right]$$

$$\tanh\left[\beta\left(\varepsilon\frac{\nu}{2}\langle s_i\rangle\right)\right]$$



Extension of mean field analysis to more complicated geometries -- continued

Consistency condition for B=0:

Define: $s_0 = \tanh\left[\beta\left(\varepsilon\frac{\nu}{2}s_0\right)\right]$

$$Z_N = \begin{cases} (2)^N & \text{for } \langle s\rangle = 0 \\ \left(2\cosh(\beta\varepsilon\nu/2)\right)^N & \text{for } \langle s\rangle = \pm s_0 \end{cases}$$

$$U = -\left(\frac{\partial\ln(Z_N)}{\partial\beta}\right) = -\frac{1}{2}N\nu\varepsilon s_0^2$$

Extension of mean field analysis to more complicated geometries -- continued

Consistency condition for B=0:

Define: $s_0 = \tanh\left[\beta\left(\varepsilon\frac{\nu}{2}s_0\right)\right]$

Heat capacity:

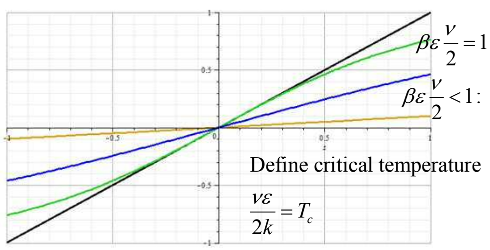
$$C_N = \left(\frac{\partial U}{\partial T}\right)_N = -\left(\frac{\partial \ln(Z_N)}{\partial \beta}\right) = N\nu\varepsilon\beta^2 s_0\left(\frac{\partial s_0}{\partial \beta}\right)_N$$

$$C_N = \frac{Nk\nu^2\varepsilon^2\beta^2 s_0^2}{2\cosh^2(\beta\nu\varepsilon s_0/2) - \beta\nu\varepsilon}$$

Extension of mean field analysis to more complicated geometries -- continued

For: $s_0 = \tanh\left[\beta\left(\varepsilon\frac{\nu}{2}s_0\right)\right]$

Note that there is no solution for $\beta\varepsilon\frac{\nu}{2} < 1$:



Define critical temperature

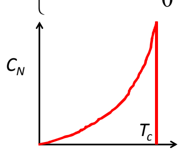
$$\frac{\nu\varepsilon}{2k} = T_c$$

Extension of mean field analysis to more complicated geometries -- continued

$$T_c \equiv \frac{\nu\varepsilon}{2k}$$

Heat capacity in terms of critical temperature:

$$C_N = \begin{cases} \dfrac{2Nks_0^2\left(T_c/T\right)^2}{\cosh^2\left(s_0\left(T_c/T\right)\right) - T_c/T} & \text{for } T < T_c \\ 0 & \text{for } T > T_c \end{cases}$$



Comment on mean field heat capacity

Heat capacity in terms of critical temperature:

$$C_N = \begin{cases} \dfrac{2Nks_0^2\left(T_c/T\right)^2}{\cosh^2\left(s_0\left(T_c/T\right)\right) - T_c/T} & \text{for } T < T_c \\ 0 & \text{for } T > T_c \end{cases}$$

Note that: $s_0 = \tanh\left[\beta\left(\varepsilon\frac{\nu}{2}s_0\right)\right] = \tanh\left(s_0\frac{T_c}{T}\right)$

Your text claims that: $C_N(T = T_c^-) = 3Nk_B$

Hint: $s_0(T = T_c^-) \approx \sqrt{3}\,\frac{T}{T_c}\sqrt{\frac{T_c - T}{T_c}}$

Comment about 1-dimensional case

One can show (rigorously) that for one dimensional systems, there can be no phase transitions! (Mean field results are qualitative correct for 2 and 3 dimensions.)

Canonical ensemble – derivation from optimization

Find form of probability density which optimizes *S* with constraints

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

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

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

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

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

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

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

Generalization: Grand canonical ensemble – derivation from optimization

Find form of probability density which optimizes S with constraints

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

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

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

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

$$\Rightarrow \hat{\rho}=\exp\left(\frac{\alpha}{k_B}-1\right)\exp\left(\frac{\gamma}{k_B}\hat{H}+\frac{\lambda}{k_B}\hat{N}\right)\equiv\frac{1}{Z_\mu}\exp\left(\frac{\gamma}{k_B}\hat{H}+\frac{\lambda}{k_B}\hat{N}\right)$$

$$\mathrm{Tr}\left[\hat{\rho}\left(-k_B+\alpha+\gamma\hat{H}+\lambda\hat{N}-k_B\ln\left(\hat{\rho}\right)\right)\right]=\left(-k_B+\alpha\right)+\gamma\langle E\rangle+\lambda\langle N\rangle+S$$

Grand partition function -- continued

$$\mathrm{Tr}\left[\hat{\rho}\left(-k_B+\alpha+\gamma\hat{H}+\lambda\hat{N}-k_B\ln\left(\hat{\rho}\right)\right)\right]=\left(-k_B+\alpha\right)+\gamma\langle E\rangle+\lambda\langle N\rangle+S$$

Recall the grand potential:

$$\Omega\left(T,V,\mu\right)=U-TS-\mu N$$

$$\Rightarrow \gamma=-\frac{1}{T} \qquad \lambda=\frac{\mu}{T}$$

$$\Rightarrow \Omega\left(T,V,\mu\right)=-k_BT\ln\left(Z_\mu\left(T,V,\mu\right)\right)$$

where $Z_\mu\left(T,V,\mu\right)=\mathrm{Tr}\left[e^{-\beta(\hat{H}-\mu\hat{N})}\right]$

$$\hat{\rho}=e^{-\beta(\hat{H}-\mu\hat{N}-\Omega)}=\frac{e^{-\beta(\hat{H}-\mu\hat{N})}}{\mathrm{Tr}\left[e^{-\beta(\hat{H}-\mu\hat{N})}\right]}$$

Examples of grand canonical ensembles – ideal (non-interacting) quantum particles in a cube of length L with periodic boundary conditions

Single particle Hamiltonian:

$$\hat{H}_1\,|\,\varepsilon_{\mathbf{p}}\rangle=\frac{\mathbf{p}^2}{2m}\,|\,\varepsilon_{\mathbf{p}}\rangle; \qquad \mathbf{p}=\frac{2\pi\hbar}{L}\left(l_x\hat{\mathbf{x}}+l_y\hat{\mathbf{y}}+l_z\hat{\mathbf{z}}\right) \quad \text{where } -\infty\le l_i\le\infty$$

$$\sum_{\mathbf{p}} \Rightarrow \left(\frac{L}{2\pi\hbar}\right)^3\int d^3p=\frac{V}{\left(2\pi\right)^3}\int d^3k$$

Extension to multiparticle case:

For particles which obey Fermi-Dirac statistics:

1. Each single particle momentum eigenstate $|\,\varepsilon_{\mathbf{p}_\alpha}\rangle$ has an occupancy $n_\alpha=0$ or 1
2. Each momentum eigenstate $|\,\varepsilon_{\mathbf{p}_\alpha}\rangle$ has a spin degeneracy $g=2s+1$, where $s=\text{(integer)}+\frac{1}{2}$

Examples of grand canonical ensembles – ideal (non-interacting) quantum particles in a cube of length *L* with periodic boundary conditions -- Fermi-Dirac case

In the absence of a magnetic field, the particle spin does not effect the energy spectrum, and only effects the enumeration of possible states

$$Z_\mu^{FD}(T,V,\mu) = \mathrm{Tr}\left[e^{-\beta(\hat{H}-\mu\hat{N})}\right] = \prod_{\mathbf{p}_i}\left(\sum_{n_{\mathbf{p}_i}=0}^{1} e^{-\beta n_{\mathbf{p}_i}(\varepsilon_{\mathbf{p}_i}-\mu)}\right)^g$$

$$= \prod_{\mathbf{p}_i}\left(1+e^{-\beta(\varepsilon_{\mathbf{p}_i}-\mu)}\right)^g$$

$$\Omega_{FD}(T,V,\mu) = -k_BT\ln\left[\prod_{\mathbf{p}_i}\left(1+e^{-\beta(\varepsilon_{\mathbf{p}_i}-\mu)}\right)^g\right]$$

$$= -k_BTg\sum_{\mathbf{p}_i}\ln\left(1+e^{-\beta(\varepsilon_{\mathbf{p}_i}-\mu)}\right)$$

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Examples of grand canonical ensembles – ideal (non-interacting) quantum particles in a cube of length *L* with periodic boundary conditions -- Fermi-Dirac case -- continued

$$\Omega_{FD}(T,V,\mu) = -k_BTg\sum_{\mathbf{p}_i}\ln\left(1+e^{-\beta(\varepsilon_{\mathbf{p}_i}-\mu)}\right)$$

Self-consistent determination of μ:

$$\langle N\rangle = -\left(\frac{\partial\Omega_{FD}}{\partial\mu}\right)_{T,V} = \sum_{\mathbf{p}_i}\frac{g}{e^{\beta(\varepsilon_{\mathbf{p}_i}-\mu)}+1}$$

Recall:

$$\sum_{\mathbf{p}} \Rightarrow \left(\frac{L}{2\pi\hbar}\right)^3\int d^3p = \frac{V}{(2\pi\hbar)^3}4\pi\int_0^\infty p^2dp \quad \text{since } \varepsilon_{\mathbf{p}} \text{ is isotropic in } \mathbf{p}$$

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Examples of grand canonical ensembles – ideal (non-interacting) quantum particles in a cube of length *L* with periodic boundary conditions -- Fermi-Dirac case -- continued

$$\langle N\rangle = -\left(\frac{\partial\Omega_{FD}}{\partial\mu}\right)_{T,V} = \sum_{\mathbf{p}_i}\frac{g}{e^{\beta(\varepsilon_{\mathbf{p}_i}-\mu)}+1}$$

Let $z = e^{\beta\mu}$: $\langle N\rangle = \frac{Vg}{(2\pi\hbar)^3}4\pi\int_0^\infty p^2dp\ \frac{z}{e^{\beta p^2/2m}+z}$

Let $x^2 \equiv \beta\frac{p^2}{2m}$ $\quad \lambda_T \equiv \frac{2\pi\hbar}{\sqrt{2\pi mk_BT}}$ $\quad \langle N\rangle = \frac{Vg}{\lambda_T^3}f_{3/2}(z)$

Here: $f_{5/2}(z) \equiv \frac{4}{\sqrt{\pi}}\int_0^\infty dx\ x^2\ln\left[1+ze^{-x^2}\right] = \sum_{\alpha=0}^{\infty}(-1)^{\alpha+1}\frac{z^\alpha}{\alpha^{5/2}}$

$$f_{3/2}(z) \equiv \frac{4}{\sqrt{\pi}}\int_0^\infty dx\ x^2\frac{z}{e^{x^2}+z} = \sum_{\alpha=0}^{\infty}(-1)^{\alpha+1}\frac{z^\alpha}{\alpha^{3/2}} = z\frac{df_{5/2}(z)}{dz}$$

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Examples of grand canonical ensembles – ideal (non-interacting) quantum particles in a cube of length *L* with periodic boundary conditions -- Fermi-Dirac case -- continued

Low temperature behavior: for $\mu > 0 \Rightarrow$ z $\to \infty$ for $T \to 0$

$$\langle N \rangle = \frac{Vg}{(2\pi\hbar)^3} 4\pi \int_0^{\sqrt{2m\mu}} p^2 dp$$

$$\Rightarrow \mu(T=0) = \frac{\hbar^2}{2m}\left(\frac{6\pi^2}{g}\frac{\langle N \rangle}{V}\right)^{3/2} \qquad \equiv \varepsilon_F$$

Examples of grand canonical ensembles – ideal (non-interacting) quantum particles in a cube of length *L* with periodic boundary conditions -- Fermi-Dirac case -- continued

Keeping more terms in low temperature expansion:

$$\Rightarrow \mu(T) \approx \varepsilon_F \left(1 - \frac{\pi^2}{12}\left(\frac{k_B T}{\varepsilon_F}\right)^2 + \ldots\right)$$

$$U = \langle \hat{H} \rangle \approx \frac{3}{5}\langle N \rangle \varepsilon_F \left(1 + \frac{5\pi^2}{12}\left(\frac{k_B T}{\varepsilon_F}\right)^2 + \ldots\right)$$

$$C_V \approx \frac{\langle N \rangle k_B^2 \pi^2}{2\varepsilon_F} T$$

Examples of grand canonical ensembles – ideal (non-interacting) quantum particles in a cube of length *L* with periodic boundary conditions -- Fermi-Dirac case -- continued

Behavior of occupancy parameter:

$$\langle n_{\mathbf{p}} \rangle = \frac{g}{e^{\beta(\varepsilon_{\mathbf{p}} - \mu)} + 1} \equiv \frac{gz}{e^{\beta\varepsilon_{\mathbf{p}}} + z}$$