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

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

Lecture 14

Chap. 6 – Grand canonical ensemble

- ❑ **Fermi-Dirac distribution function**
- ❑ **Bose-Einstein distribution**

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

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	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. 6	Grand partition function (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	Fermi and Bose particles (class 12-1:45 PM; Exam due)	#13	03/25/2014
15	Thur: 03/20/2014	Chap. 6	Fermi and Bose particles (class 12-1:45 PM)	#14	03/25/2014

Reminder:

Please think about the subject of your computational project – due next week.

Suggestions available upon request.

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 spin (*g*)

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

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

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

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

Fermi-Dirac case -- continued

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

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:

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

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

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

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

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

Fermi-Dirac case -- continued

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

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

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

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Fermi-Dirac case -- continued

Keeping more terms in low temperature expansion:

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

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

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

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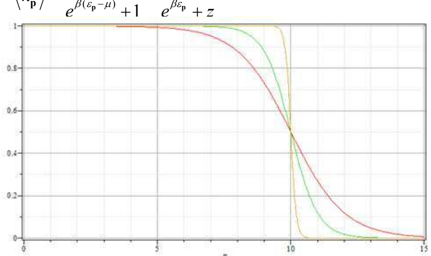
Fermi-Dirac case -- continued

Behavior of occupancy parameter:

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



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Examples of grand canonical ensembles – ideal (non-interacting) quantum particles in a cube of length *L* with periodic boundary conditions -- Bose-Einstein case (assumed to have spin 0)

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

$$\Omega_{BE}(T,V,\mu) = -k_B T \ln\left[\prod_{\mathbf{p}_i}\left(\frac{1}{1-e^{-\beta(\varepsilon_{\mathbf{p}_i}-\mu)}}\right)\right] = k_B T \sum_{\mathbf{p}_i}\ln\left(1-e^{-\beta(\varepsilon_{\mathbf{p}_i}-\mu)}\right)$$

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Bose-Einstein case

$$Z_\mu^{BE}(T,V,\mu) = \prod_{\mathbf{p}_i}\left(\sum_{n_{\mathbf{p}_i}=0}^{\infty} e^{-\beta n_{\mathbf{p}_i}(\varepsilon_{\mathbf{p}_i}-\mu)}\right) = \prod_{\mathbf{p}_i}\left(\frac{1}{1-e^{-\beta(\varepsilon_{\mathbf{p}_i}-\mu)}}\right)$$

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

$$\Omega_{BE}(T,V,\mu) = k_B T \ln(1-z) - \frac{k_B T V}{\lambda_T^3} g_{5/2}(z)$$

$$\text{where } g_{5/2}(z) \equiv -\frac{4}{\sqrt{\pi}}\int_0^\infty x^2 dx \ln(1-ze^{-x^2})$$

$$\lambda_T \equiv \sqrt{\frac{2\pi\hbar^2}{mk_BT}}$$

Fermi-Dirac case

$$Z_\mu^{FD}(T,V,\mu) = \prod_{\mathbf{p}_i}\left(\sum_{n_{\mathbf{p}_i}=0}^{1} e^{-\beta n_{\mathbf{p}_i}(\varepsilon_{\mathbf{p}_i}-\mu)}\right)^g = \prod_{\mathbf{p}_i}\left(1+e^{-\beta(\varepsilon_{\mathbf{p}_i}-\mu)}\right)^g$$

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

$$\Omega_{FD}(T,V,\mu) = -\frac{g k_B T V}{\lambda_T^3} f_{5/2}(z)$$

$$\text{where } f_{5/2}(z) \equiv \frac{4}{\sqrt{\pi}}\int_0^\infty x^2 dx \ln(1+ze^{-x^2})$$

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Bose-Einstein case

$$g_{5/2}(z) \equiv -\frac{4}{\sqrt{\pi}}\int_0^\infty x^2 dx \ln(1-ze^{-x^2})$$

$$g_{3/2}(z) \equiv \frac{4}{\sqrt{\pi}}\int_0^\infty x^2 dx \frac{z}{e^{x^2}-z}$$

$$P = -\frac{\Omega_{BE}}{V} = -\frac{kT}{V}\ln(1-z) + \frac{kT}{\lambda_T^3} g_{5/2}(z)$$

$$\frac{\langle N\rangle}{V} = \frac{1}{V}\frac{z}{1-z} + \frac{kT}{\lambda_T^3} g_{3/2}(z)$$

Fermi-Dirac case

$$f_{5/2}(z) \equiv -\frac{4}{\sqrt{\pi}}\int_0^\infty x^2 dx \ln(1+ze^{-x^2})$$

$$f_{3/2}(z) \equiv \frac{4}{\sqrt{\pi}}\int_0^\infty x^2 dx \frac{z}{e^{x^2}+z}$$

$$P = -\frac{\Omega_{FD}}{V} = \frac{gkT}{\lambda_T^3} f_{5/2}(z)$$

$$\frac{\langle N\rangle}{V} = \frac{gkT}{\lambda_T^3} f_{3/2}(z)$$

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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.

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

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

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

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

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

Case of Bose particles at low *T*

$$N = \sum_k \langle n_k \rangle = \langle n_0 \rangle + \sum_{k>0} \frac{1}{e^{\beta(\varepsilon_k - \mu)} - 1}$$

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

Note that for low T a consistent solutions exists such that $N \approx \langle n_0 \rangle$

$$\langle n_0 \rangle = \frac{1}{e^{\beta(-\mu)} - 1} \approx \frac{1}{1 - \beta\mu - 1} = \frac{1}{-\beta\mu} \text{ assuming } |\mu| \text{ small}$$

In this case, $\mu \approx -\frac{kT}{N}$

Critical temperature for Bose condensation:

$$N = \underbrace{\langle n_0 \rangle}_{\text{condensate}} + \underbrace{\int_0^\infty d\varepsilon \, g_B(\varepsilon) \frac{1}{e^{\beta(\varepsilon - \mu)} - 1}}_{\text{“normal” state}}$$

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

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

Approximate value of T_E:

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

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

Case of Bose particles at low *T*

$$N = \sum_k \langle n_k \rangle = \langle n_0 \rangle + \sum_{k>0} \frac{1}{e^{\beta(\varepsilon_k - \mu)} - 1}$$

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Critical temperature for Bose condensation:

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Approximate value:

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

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Summary:

Define $z \equiv e^{\beta\mu} \leq 1 \qquad \lambda_T \equiv \left(\frac{2\pi\hbar^2}{mkT}\right)^{1/2}$

The Landau potential for the Bose system can be written:

$$\Omega_{BE}(T, V, \mu) = kT \ln(1 - z) + \frac{4kT}{\sqrt{\pi}} \frac{V}{\lambda_T^3} \int_{\lambda_T\sqrt{\pi}/L}^\infty dx \, x^2 \ln\left(1 - ze^{-x^2}\right)$$

$$\langle N \rangle = -\left(\frac{\partial \Omega_B}{\partial \mu}\right) = \underbrace{\frac{z}{1 - z}}_{\langle n_0 \rangle} + \frac{4}{\sqrt{\pi}} \frac{V}{\lambda_T^3} \int_{\lambda_T\sqrt{\pi}/L}^\infty dx \, x^2 \left(\frac{z}{e^{x^2} - z}\right)$$

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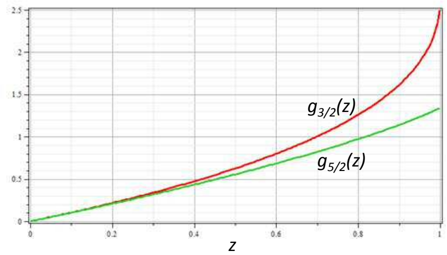
Some convenient integrals

$$g_{5/2}(z) \equiv \frac{4}{\sqrt{\pi}}\int_0^\infty dx\, x^2 \ln\left(1 - z e^{-x^2}\right) = \sum_{n=1}^{\infty} \frac{z^n}{n^{5/2}}$$

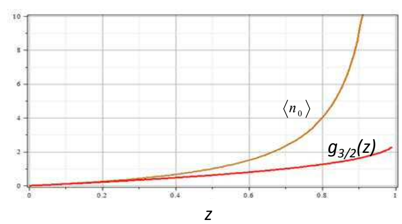
$$g_{3/2}(z) \equiv \frac{4}{\sqrt{\pi}}\int_0^\infty dx\, x^2 \left(\frac{z}{e^{x^2} - z}\right) = z\frac{d}{dz} g_{5/2}(z) = \sum_{n=1}^{\infty} \frac{z^n}{n^{3/2}}$$



$$\langle n_0 \rangle = \frac{z}{1-z} \qquad \text{where } z \equiv e^{\beta\mu} \le 1 \qquad \lambda_T \equiv \left(\frac{2\pi\hbar^2}{mkT}\right)^{1/2}$$

$$\langle N \rangle - \langle n_0 \rangle = \frac{4}{\sqrt{\pi}}\frac{V}{\lambda_T^3}\int_{\lambda_T\sqrt{\pi}/L}^{\infty} dx\, x^2\left(\frac{z}{e^{x^2}-z}\right) = \frac{V}{\lambda_T^3}\left(g_{3/2}(z) - \frac{4}{\sqrt{\pi}}\int_0^{\lambda_T\sqrt{\pi}/L} dx\, x^2\left(\frac{z}{e^{x^2}-z}\right)\right)$$

$$\langle N \rangle - \langle n_0 \rangle \approx \frac{V}{\lambda_T^3} g_{3/2}(z) \qquad \text{note that } \lim_{z\to 1} g_{3/2}(z) = 2.612$$



Equation for z:

$$\langle N \rangle = \langle n_0 \rangle + \frac{V}{\lambda_T^3} g_{3/2}(z)$$

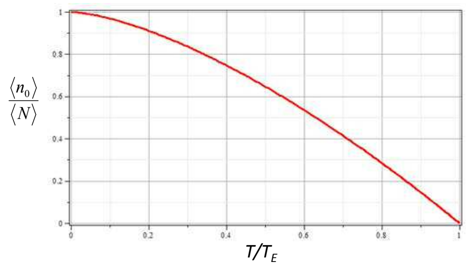
Define Einstein temperature

$$\langle N \rangle = \frac{V}{\lambda_{T_E}^3} g_{3/2}(1) = \frac{V}{\lambda_{T_E}^3} 2.612$$

For $T > T_E$, $\langle n_0 \rangle << \langle N \rangle$ and $\langle N \rangle = \frac{V}{\lambda_T^3} g_{3/2}(z)$ has a solution for $z < 1$

For $T \le T_E$, $z \to 1^-$ and $\langle N \rangle = \langle n_0 \rangle + \frac{V}{\lambda_T^3} g_{3/2}(1)$

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



$$\frac{\langle n_0 \rangle}{\langle N \rangle} = 1 - \frac{\lambda_{T_E}^3}{\lambda_T^3} = 1 - \left(\frac{T}{T_E}\right)^{3/2}$$

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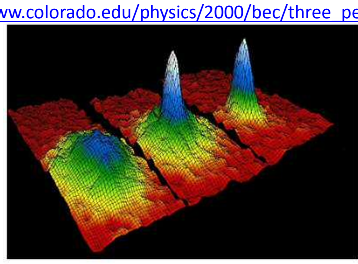
http://www.colorado.edu/physics/2000/bec/three_peaks.html



Bose-Einstein Condensation at 400, 200, and 50 nano-Kelvins

^{87}Rb atoms (~2000 atoms in condensate)

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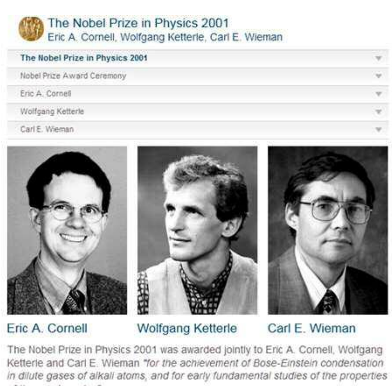

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Other systems with Bose statistics

Thermal distribution of photons -- blackbody radiation:

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

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

$$\varepsilon_k = \hbar\omega = \hbar ck = h\nu$$

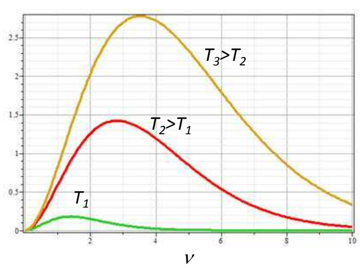
$$\sum_k \rightarrow \left(\frac{L}{2\pi}\right)^3 \int d\varepsilon \int d^3k\,\delta(\varepsilon - \hbar ck) = \frac{V}{\pi^2\hbar^3c^3}\int d\varepsilon\,\varepsilon^2$$

Distribution of radiated energy:

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

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

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).

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

Effects of interactions between particles – classical case

$$\hat{H} = \sum_{i=1}^{N} \frac{\hat{\mathbf{p}}_i}{2m} + \sum_{i,j}^{N(N-1)} V\left(\hat{\mathbf{r}}_{ij}\right) \equiv \hat{T}^N + \hat{V}^N$$

Canonical partition function : $Z_N\left(T\right) = \mathrm{Tr}\left[e^{-\beta\hat{H}}\right] = \frac{1}{N!}\frac{1}{\left(\lambda_T\right)^{3N}} Q_N(T,V)$

where $Q_N(T,V) \equiv \int d\mathbf{r}_1 \int d\mathbf{r}_2 .... \int d\mathbf{r}_N e^{-\beta\hat{V}^N}$

Grand canonical partition function :

$$Z_\mu\left(T\right) = \sum_{N=1}^{\infty} Z_N\left(T\right) e^{\beta N\mu} = \sum_{N=1}^{\infty} \frac{1}{N!}\frac{1}{\left(\lambda_T\right)^{3N}} Q_N(T,V) e^{\beta N\mu}$$

Effects of interactions between particles – classical case -- continued

$$\hat{V}^N = \sum_{i,j}^{N(N-1)} V\left(\hat{\mathbf{r}}_{ij}\right)$$

$$Q_N(T,V) \equiv \int d\mathbf{r}_1 \int d\mathbf{r}_2 .... \int d\mathbf{r}_N e^{-\beta\hat{V}^N}$$

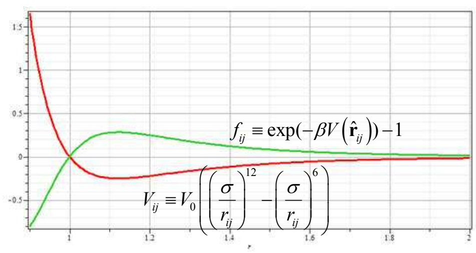
$$= \int d\mathbf{r}_1 \int d\mathbf{r}_2 .... \int d\mathbf{r}_N e^{-\beta \sum_{i,j}^{N(N-1)} V\left(\hat{\mathbf{r}}_{ij}\right)}$$

$$\approx \int d\mathbf{r}_1 \int d\mathbf{r}_2 .... \int d\mathbf{r}_N W_N\left(\mathbf{r}_1, \mathbf{r}_2 ... \mathbf{r}_N\right)$$

$$W_N\left(\mathbf{r}_1, \mathbf{r}_2 ... \mathbf{r}_N\right) \equiv \prod_{i,j}^{N(N-1)} (f_{ij} + 1)$$

$$f_{ij} \equiv \exp(-\beta V\left(\hat{\mathbf{r}}_{ij}\right)) - 1$$

Effects of interactions between particles – classical case -- continued



Effects of interactions between particles – classical case -- continued

$$Z_\mu(T,V) = \sum_{N=0}^{\infty} \frac{1}{N!}\frac{1}{\lambda_T^{3N}} e^{\beta N\mu} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \ldots \int d\mathbf{r}_N W_N(\mathbf{r}_1, \mathbf{r}_2 \ldots \mathbf{r}_N)$$

$$W_N(\mathbf{r}_1, \mathbf{r}_2 \ldots \mathbf{r}_N) \equiv \prod_{i,j}^{N(N-1)} (f_{ij} + 1)$$

$$f_{ij} \equiv \exp(-\beta V(\hat{\mathbf{r}}_{ij})) - 1$$

Note that:

$$W_1 = 1 \qquad W_2(\mathbf{r}_1, \mathbf{r}_2) = 1 + f_{12}$$

$$W_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = (1 + f_{12})(1 + f_{13})(1 + f_{23})$$

Effects of interactions between particles – classical case -- continued

$$Z_\mu(T,V) = \sum_{N=0}^{\infty} \frac{1}{N!}\frac{1}{\lambda_T^{3N}} e^{\beta N\mu} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \ldots \int d\mathbf{r}_N W_N(\mathbf{r}_1, \mathbf{r}_2 \ldots \mathbf{r}_N)$$

In terms of cumulant expansion:

$$Z_\mu(T,V) = \exp\left(\sum_{\nu=0}^{\infty} \frac{1}{\nu!}\frac{1}{\lambda_T^{3\nu}} e^{\beta\nu\mu} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \ldots \int d\mathbf{r}_\nu U_\nu(\mathbf{r}_1, \mathbf{r}_2 \ldots \mathbf{r}_\nu)\right)$$

Typical cluster functions:

$$U_1(\mathbf{r}_1) = W_1(\mathbf{r}_1)$$

$$U_2(\mathbf{r}_1, \mathbf{r}_2) = W_2(\mathbf{r}_1, \mathbf{r}_2) - W_1(\mathbf{r}_1) W_1(\mathbf{r}_2)$$