WMPH029-05 Statistical Mechanics Lecture 11

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Theory of Condensed Matter Group

(Computational Spectroscopy)

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Bosons

- Photons
- Phonons
- Bose-Einstein Condensation and Imperfect Bose gas

Next time Chapter 14 (Ising spin model)

Bose Systems

 As we can fill as many Bosons in the same quantum level as we want they behave very differently from Fermions and in at zero temperature all Bosons well be in the lowest energy state giving rise to phenomena as Bose-Einstein condensation.

We will consider a few Bose systems

- What is the partition function for photons?
- What is the internal energy and equation of state for photons?
- How do we derive the Planck equations for black body radiation?

- Photons are bosons and the first type of particles for which quantum effects were reported
- The Hamiltonian for a free electric field can be modeled as a collection of quantum harmonic oscillators

$$(n+\frac{1}{2})\hbar\omega, \qquad n=0,1,2,\ldots$$

N then enumerates the number of photons with a given frequency

Photons are massless

Energy =
$$\hbar \omega$$

Momentum = $\hbar \mathbf{k}$, $|\mathbf{k}| = \frac{\omega}{c}$
Polarization vector = $\mathbf{\epsilon}$, $|\mathbf{\epsilon}| = 1$, $\mathbf{k} \cdot \mathbf{\epsilon} = 0$

- Associated field $\mathbf{E}(\mathbf{r}, t) = \epsilon e^{i(\mathbf{k} \cdot \mathbf{r} \omega t)}$
- Transverse $\nabla \cdot \mathbf{E} = 0$ $\epsilon \cdot \mathbf{k} = 0$ Two perpendicular polarizations (or left and right polarized)

$$\mathbf{k} = \frac{2\pi\mathbf{n}}{L}$$

 $\mathbf{n} = \mathbf{a}$ vector whose components are $0, \pm 1, \pm 2, \dots$

Density of states

$$\frac{V}{\left(2\pi\right)^3}4\pi k^2\,dk$$

Total energy

$$E\{n_{\mathbf{k},\,\epsilon}\} = \sum_{\mathbf{k},\,\epsilon} \hbar \omega n_{\mathbf{k},\,\epsilon}$$
$$\omega = c|\mathbf{k}|$$
$$n_{\mathbf{k},\,\epsilon} = 0, 1, 2, \dots$$

Partition function

$$Q = \sum_{\{n_{\mathbf{k},\epsilon}\}} e^{-\beta E\{n_{\mathbf{k},\epsilon}\}}$$

No limit on the occupation numbers!

The partition function

$$Q = \sum_{\{n_{\mathbf{k},\epsilon}\}} \exp\left(-\beta \sum_{\mathbf{k},\epsilon} \hbar \omega n_{\mathbf{k},\epsilon}\right) = \prod_{\mathbf{k},\epsilon} \sum_{n=0}^{\infty} e^{-\beta \hbar \omega n} = \prod_{\mathbf{k},\epsilon} \frac{1}{1 - e^{-\beta \hbar \omega}}$$

$$\log Q = -\sum_{\mathbf{k}, \epsilon} \log (1 - e^{-\beta \hbar \omega}) = -2\sum_{\mathbf{k}} \log (1 - e^{-\beta \hbar \omega})$$

The average occupation numbers

$$\langle n_{\mathbf{k}} \rangle = -\frac{1}{\beta} \frac{\partial}{\partial (\hbar \omega)} \log Q = \frac{2}{e^{\beta \hbar \omega} - 1}$$

Internal energy

$$U = -\frac{\partial}{\partial \beta} \log Q = \sum_{\mathbf{k}} \hbar \omega \langle n_{\mathbf{k}} \rangle$$

To find the pressure we rewrite the partition function

$$\log Q = -2\sum_{n} \log (1 - e^{-\beta \hbar c 2\pi |\mathbf{n}|V^{-1/3}})$$

• The pressure is then $P = \frac{1}{\beta} \frac{\partial}{\partial V} \log Q = \frac{1}{3V} \sum_{\mathbf{k}} \hbar \omega \langle n_k \rangle$

• Equation of state $PV = \frac{1}{3}U$

 $\frac{V}{\left(2\pi\right)^3}4\pi k^2\,dk$

• In limit of infinite volume:

$$U = \frac{2V}{(2\pi)^3} \int_0^\infty dk \, 4\pi k^2 \frac{\hbar ck}{e^{\beta \hbar ck} - 1} = \frac{V\hbar}{\pi^2 c^3} \int_0^\infty d\omega \, \frac{\omega^3}{e^{\beta \hbar \omega} - 1}$$

This is infinite so we examine the internal energy density

$$\frac{U}{V} = \int_0^\infty d\omega \, u(\omega, T) \qquad u(\omega, T) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\beta \hbar \omega} - 1}$$

Integrate [x^3/(Exp[a*x]-1), x]
$$\frac{x^3 \log[1-e^{-ax}]}{a} - \frac{3 x^2 \operatorname{PolyLog}[2, e^{-ax}]}{a^2} - \frac{6 x \operatorname{PolyLog}[3, e^{-ax}]}{a^3} - \frac{6 \operatorname{PolyLog}[4, e^{-ax}]}{a^4}$$

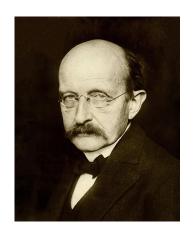
$$\frac{\pi^4}{15 a^4}$$

 This integral can be solved exactly and gives the energy density of photons with frequency
 ω

$$\frac{U}{V} = \frac{\pi^2}{15} \frac{\left(kT\right)^4}{\left(\hbar c\right)^3}$$

This is Planck's radiation law

$$P = \frac{U}{3V} = \frac{\pi^2}{45} \frac{(kT)^4}{(\hbar c)^3}$$



Max Planck (1858-1947) Nobel Prize 1918

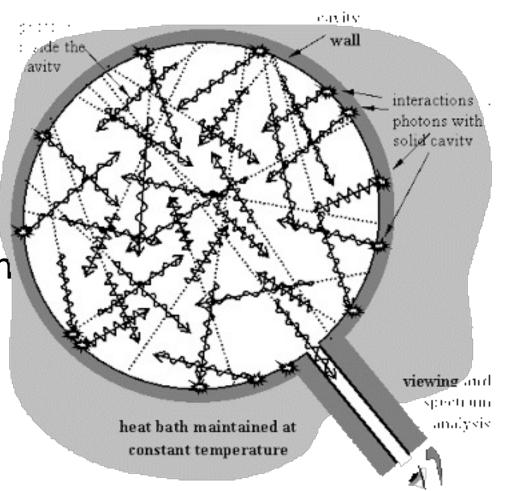
The heat capacity is then

$$c_V = \frac{4\pi^2 k^4 T^3}{15(\hbar c)^3}$$

 As the number of particles is not bounded this goes to infinity with infinite temperature

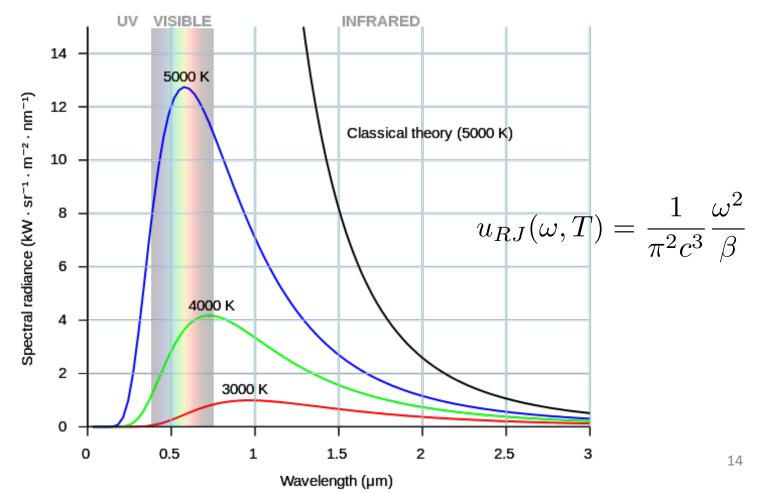
 For black body cavity with a hole

 Intensity of radiation emitted at specific frequency per unit area of hole



$$I(\omega, T) = c \int \frac{d\Omega}{4\pi} u(\omega, T) \cos \theta = \frac{c}{4} u(\omega, T)$$

• The black body spectrum
$$u(\omega, T) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\beta \hbar \omega} - 1}$$



Integrated of over all frequencies

$$I(T) = \int_0^\infty d\omega \, I(\omega, T) = \sigma T^4$$
$$\sigma = \frac{\pi^2 k^4}{60\hbar^3 c^3}$$

Stefan's law and Stefan's constant



Josef Stefan (1835–1893)

- What are phonons?
- How to describe vibrations in solid lattices?
- What is the heat capacity of a solid?

• Extended waves of vibrations $e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}$

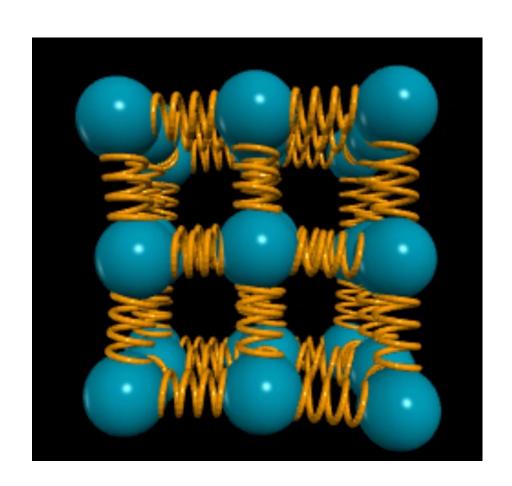
$$\hbar\omega_i$$

$$\omega_1, \omega_2, \ldots, \omega_{3N}$$

$$\mathbf{k} = (2\pi/L)\mathbf{n}$$

$$0, \pm 1, \pm 2, \dots$$

$$|\mathbf{k}| = \frac{\omega}{c}$$



Approximations:

- Well approximated to be harmonic far below the melting temperature
- We will consider an isotropic elastic sample
- Speed of sound considered isotropic and independent of polarization of modes

 Debye considered elastic continuum. The frequency distribution become continuous

$$f(\omega) d\omega = \frac{\text{no. of normal modes with}}{\text{frequency between } \omega \text{ and } \omega + d\omega} = \frac{3V}{(2\pi)^3} 4\pi k^2 dk$$

$$f(\omega) d\omega = V \frac{3\omega^2}{2\pi^2 c^3} d\omega$$



Peter Debye (1884-1966)Nobel Prize 1936

 As the number of modes is 3N the highest frequency is $\int_0^{\omega_m} f(\omega) d\omega = 3N$

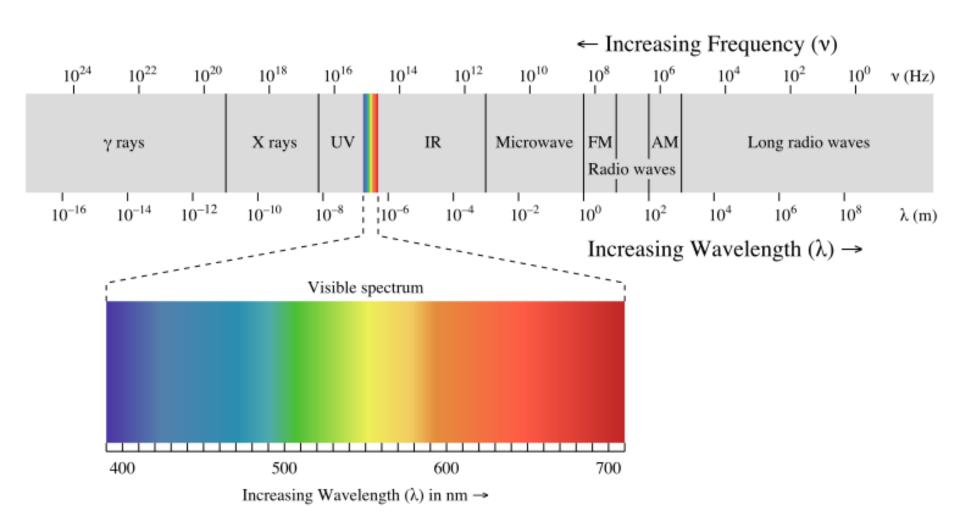
$$\omega_m = c \left(\frac{6\pi^2}{v} \right)^{1/3}$$

The max frequency corresponds to a minimum wavelength

$$\omega_m = c \left(\frac{6\pi^2}{v}\right)^{1/3}$$
 $\lambda_m = \frac{2\pi c}{\omega_m} = \left(\frac{4}{3}\pi v\right)^{1/3} \approx \text{interparticle distance}$

- Wavelengths below the inter atom distance would be meaning less
- Inversely, knowing the typical atomic distances and sound speed we can estimate the max frequency

- Speed of sound in various materials:
 - Gold 3240 m/s
 - Glass 4540 m/s
 - Aluminum 6320 m/s
 - Beryllium 12900 m/s
 - Ice 4000 m/s
- Shortest atomic distance in crystals ~1Å



• The energy is $E\{n_i\} = \sum_{i=1}^{3N} n_i \hbar \omega_i$

The resulting partition function

$$Q = \sum_{\{n_i\}} e^{-\beta E\{n_i\}} = \prod_{i=1}^{3N} \frac{1}{1 - e^{-\beta \hbar \omega_i}}$$

Or the logarithm of the partition function

$$\log Q = -\sum_{i=1}^{3N} \log (1 - e^{-\beta \hbar \omega_i})$$

The average occupation numbers are then

$$\langle n_i \rangle = -\frac{1}{\beta} \frac{\partial}{\partial (\hbar \omega_i)} \log Q = \frac{1}{e^{\beta \hbar \omega_i} - 1}$$

 And the internal energy ("integral energy" typo in book, just above eq. 12.33)

$$U = -\frac{\partial}{\partial \beta} \log Q = \sum_{i=1}^{3N} \hbar \omega_i \langle n_i \rangle = \sum_{i=1}^{3N} \frac{\hbar \omega_i}{e^{\beta \hbar \omega_i} - 1}$$

 $t = \beta \hbar \omega$

In limit of infinite volume

$$U = \frac{3V}{2\pi^{2}c^{3}} \int_{0}^{\omega_{m}} d\omega \, \omega^{2} \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \qquad \frac{U}{N} = \frac{9(kT)^{4}}{(\hbar\omega_{m})^{3}} \int_{0}^{\beta\hbar\omega_{m}} dt \, \frac{t^{3}}{e^{t} - 1}$$

Debye function

$$\frac{U}{N} = \frac{9(kT)^4}{(\hbar\omega_m)^3} \int_0^{\beta\hbar\omega_m} dt \, \frac{t^3}{e^t - 1}$$

$$D(x) = \frac{3}{x^3} \int_0^x dt \, \frac{t^3}{e^t - 1} = \begin{cases} 1 - \frac{3}{8}x + \frac{1}{20}x^2 + \cdots & (x \ll 1) \\ \frac{\pi^4}{5x^3} + O(e^{-x}) & (x \gg 1) \end{cases}$$

$$x = \beta \hbar \omega_m$$

Debye temperature
$$kT_D = \hbar \omega_m = \hbar c \left(\frac{6\pi^2}{v}\right)^{1/3}$$

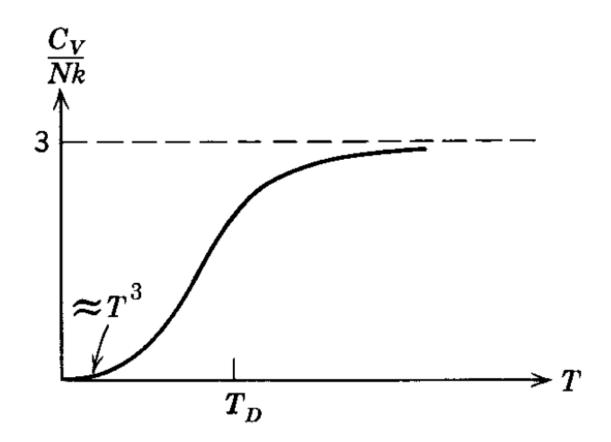
$$\frac{U}{N} = 3kTD(\lambda) = \begin{cases} 3kT\left(1 - \frac{3}{8}\frac{T_D}{T} + \cdots\right) & (T \gg T_D) \\ 3kT\left[\frac{\pi^4}{5}\left(\frac{T}{T_D}\right)^3 + O(e^{-T_D/T})\right] & (T \ll T_D) \end{cases}$$

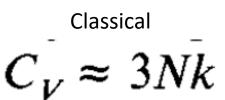
• From this we find the heat capacity $\lambda \equiv T_D/T$

$$\frac{C_V}{Nk} = 3D(\lambda) + 3T \frac{dD(\lambda)}{dT} = 3\left[4D(\lambda) - \frac{3\lambda}{e^{\lambda} - 1}\right]$$

$$\frac{C_{V}}{Nk} = \begin{cases} 3 \left[1 - \frac{1}{20} \left(\frac{T_{D}}{T} \right)^{2} + \cdots \right] & (T \gg T_{D}) \\ \frac{12\pi^{4}}{5} \left(\frac{T}{T_{D}} \right)^{3} + O(e^{-T_{D}/T}) & (T \ll T_{D}) \end{cases}$$

Temperature dependence





 Einstein proposed model with one single frequency

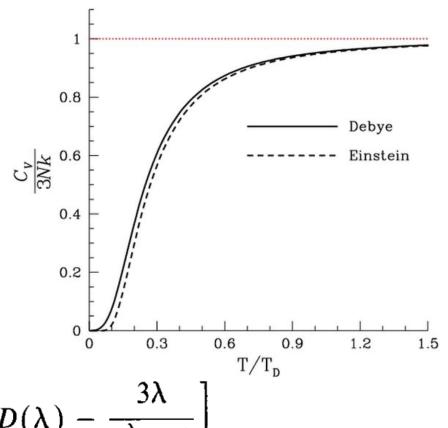
Einstein

$$\frac{C_V}{Nk} = 3\left(\frac{T_E}{T}\right)^2 \frac{e^{T_E/T}}{(e^{T_E/T} - 1)^2}$$

Debye

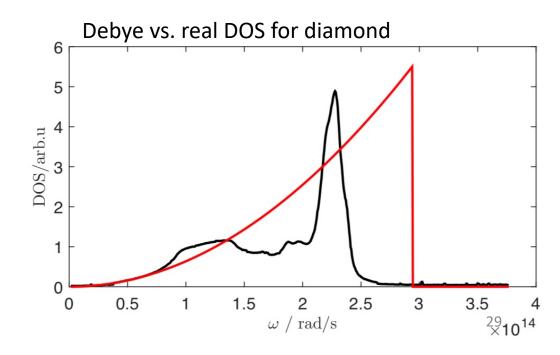
$$\frac{C_V}{Nk} = 3D(\lambda) + 3T \frac{dD(\lambda)}{dT} = 3\left[4D(\lambda) - \frac{3\lambda}{e^{\lambda} - 1}\right]$$

$$T_E = T_D \left(\frac{\pi}{6}\right)^{3/2}$$



- In real solids different types of modes are often present.
- Debye temperatures of simple atomic solids
 - Beryllium 1440 K
 - Iron 470 K
 - Silver 210 K
 - Gold 170 K
 - Cesium 38 K

$$\omega pprox rac{1}{2\pi} \sqrt{rac{k}{m}}$$



- How does the ideal Bose gas behave at very low temperature?
- Can all particles be in the ground state?
- What is the presure of the BEC?
- Real gasses interact, how does that affect BEC?

Equation of state for the ideal Bose gas

$$\begin{cases} \frac{P}{kT} = \frac{1}{\lambda^3} g_{5/2}(z) - \frac{1}{V} \log(1 - z) & \lambda = \sqrt{2\pi\hbar^2/mkT} \\ \frac{1}{v} = \frac{1}{\lambda^3} g_{3/2}(z) + \frac{1}{V} \frac{z}{1 - z} & g_n(z) \equiv \sum_{l=1}^{\infty} \frac{z^l}{l^n} \end{cases}$$

• g is bounded, positive, and monotonically increasing for real z, $0 \le z \le 1$

$$g_n(z) = Li_n(z)$$

For low fugacities

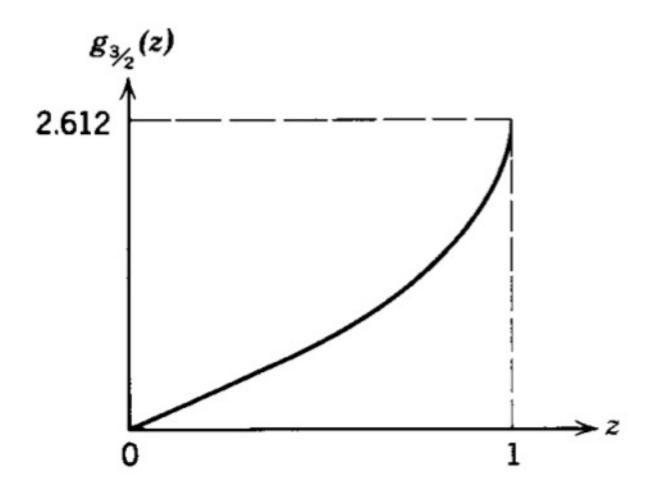
$$g_{3/2}(z) = z + \frac{z^2}{2^{3/2}} + \frac{z^3}{3^{3/2}} + \cdots$$

For z=1 (Riemann zeta function)

$$g_{3/2}(1) = \sum_{l=1}^{\infty} \frac{1}{l^{3/2}} = \zeta(\frac{3}{2}) = 2.612...$$

• For all positive z where the function is not diverging $0 \le z \le 1$

$$g_{3/2}(z) \leq 2.612\dots$$



The equation of state can be rewritten

$$\lambda^3 \frac{\langle n_0 \rangle}{V} = \frac{\lambda^3}{v} - g_{3/2}(z)$$

• When $\frac{\lambda^3}{v} > g_{3/2}(1)$

• The occupation of the state with p=0 is a (large) finite fraction $\langle n_0 \rangle / V > 0$

 This means that the system consist of two parts, one with p=0 and another with |p|>0

The p=0 part is a Bose-Einstein condensate

• The equation $\frac{\lambda^3}{v} = g_{3/2}(1)$ define the boundary

$$\left(\sqrt{2\pi\hbar^2/mkT}\right)^3 > 2.612v$$

Critical Temperature

$$kT_c = \frac{2\pi\hbar^2/m}{\left[vg_{3/2}(1)\right]^{2/3}}$$

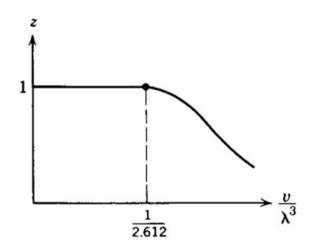
Critical volume

$$v_c = \frac{\lambda^3}{g_{3/2}(1)}$$

Low temperature, low mass favor groundstate

• For infinite volume we have

$$z = \begin{cases} 1 & \left(\frac{\lambda^3}{v} \ge g_{3/2}(1)\right) \\ \text{the root of } g_{3/2}(z) = \lambda^3/v & \left(\frac{\lambda^3}{v} \le g_{3/2}(1)\right) \end{cases}$$

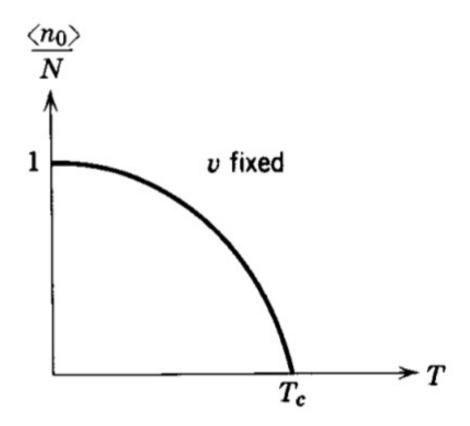


The occupation fraction of the p=0 level

$$\frac{\langle n_0 \rangle}{N} = \begin{cases} 0 & \left(\frac{\lambda^3}{v} \le g_{3/2}(1)\right) \\ 1 - \left(\frac{T}{T_c}\right)^{3/2} = 1 - \frac{v}{v_c} & \left(\frac{\lambda^3}{v} \ge g_{3/2}(1)\right) \end{cases}$$

$$\langle n_0 \rangle = z/(1-z)$$

Occupation of the p=0 level



For the Bose gas the fugacity is

$$g_{3/2}(z) = \frac{\lambda^3}{v}$$

• For the BEC z=1

$$g_{3/2}(z) = \frac{\lambda^3}{v}$$
$$\frac{g_{3/2}(z)}{g_{3/2}(1)} = \frac{v_c}{v}$$

Equations of state

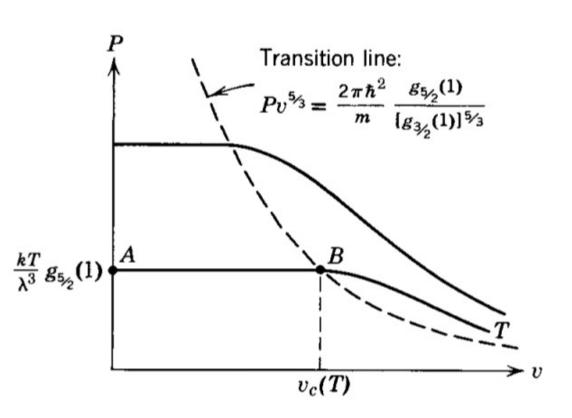
$$\frac{g_{3/2}(z)}{g_{3/2}(1)} = \left(\frac{T_c}{T}\right)^{3/2}$$

$$\frac{P}{kT} = \begin{cases} \frac{1}{\lambda^3} g_{5/2}(z) & (v > v_c) \\ \frac{1}{\lambda^3} g_{5/2}(1) & (v < v_c) \end{cases}$$

$$g_{5/2}(1) = \zeta(\frac{5}{2}) = 1.342...$$

PV diagram

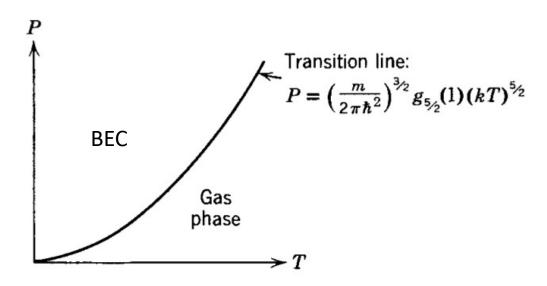
 The points A and B indicate the coexisting BEC and normal Bose gas states



The vapor pressure of the BEC is

$$P_0(T) = \frac{kT}{\lambda^3} g_{5/2}(1)$$

$$\frac{dP_0(T)}{dT} = \frac{5}{2} \frac{kg_{5/2}(1)}{\lambda^3} = \frac{1}{Tv_c} \left[\frac{5}{2} kT \frac{g_{5/2}(1)}{g_{3/2}(1)} \right]$$



- The change in specific volume is $\Delta v = v_c$
- From the Clapeyron equation we get the latent heat per particle
- The BEC transition is a first-order phase transition

$$\frac{dP}{dT} = \frac{L}{T\Delta v}$$

$$L = \frac{g_{5/2}(1)}{g_{3/2}(1)} \frac{5}{2} kT$$

 Other relevant thermodynamic functions for ideal Bose gas/BEC

$$\frac{U}{N} = \frac{3}{2}Pv = \begin{cases}
\frac{3}{2} \frac{kTv}{\lambda^3} g_{5/2}(z) \\
\frac{3}{2} \frac{kTv}{\lambda^3} g_{5/2}(1)
\end{cases}$$

$$-\frac{A}{NkT} = \begin{cases}
\frac{v}{\lambda^3} g_{5/2}(z) - \log z \\
\frac{v}{\lambda^3} g_{5/2}(1)
\end{cases}$$

$$\frac{C_V}{Nk} = \begin{cases}
\frac{15}{4} \frac{v}{\lambda^3} g_{5/2}(z) - \frac{9}{4} \frac{g_{3/2}(z)}{g_{1/2}(z)}
\end{cases}$$

$$\frac{G}{NkT} = \begin{cases} \log z \\ 0
\end{cases}$$

$$\frac{G}{NkT} = \begin{cases} \log z \\ 0
\end{cases}$$

$$\frac{15}{4} \frac{v}{\lambda^3} g_{5/2}(1)$$

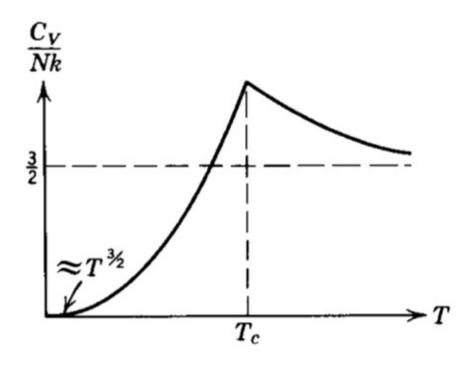
$$\frac{15}{4} \frac{v}{\lambda^3} g_{5/2}(1)$$

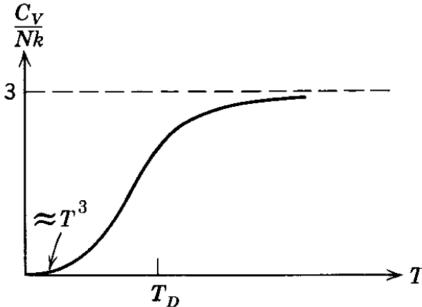
$$\frac{15}{4} \frac{v}{\lambda^3} g_{5/2}(1)$$

$$\frac{15}{4} \frac{v}{\lambda^3} g_{5/2}(1)$$

Heat capacity
 BCE and ideal Bose gas

Phonons





- Requirements
 - Conservation of particle numbers
 - Low temperature
 - Low mass

Imperfect Bose gas

- Zero specific volume seem rather unphysical
- In reality bosons feel each other
- Binary scattering events with scattering length a can be included

$$E_n \equiv \left(\Phi_n, \mathcal{H}'\Phi_n\right) = \sum_{\mathbf{p}} \frac{p^2}{2m} n_{\mathbf{p}} + \frac{4\pi a\hbar^2}{m} \left(\Phi_n, \sum_{i < j} \delta(\mathbf{r}_i - \mathbf{r}_j) \Phi_n\right)$$

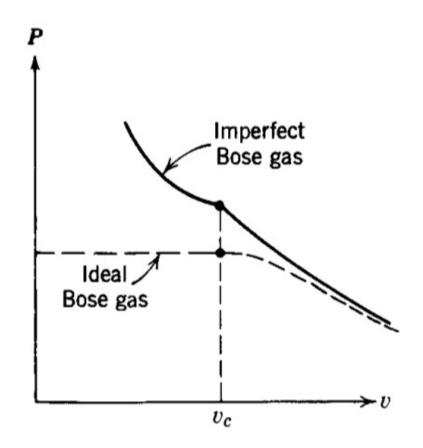
$$E_{n} = \sum_{\mathbf{p}} \frac{p^{2}}{2m} n_{\mathbf{p}} + \frac{4\pi a\hbar^{2}}{mV} \left(N^{2} - \frac{1}{2} \sum_{\mathbf{p}} n_{p}^{2} \right)$$

Imperfect Bose gas

 The PV diagram for the imperfect Bose gas

$$P = P^{(0)} + \frac{4\pi a\hbar^2}{m} \left[\frac{1}{v^2} \left(1 - \frac{1}{2}\bar{\xi}^2 \right) + \frac{1}{v} \bar{\xi} \frac{\partial \bar{\xi}}{\partial v} \right]$$

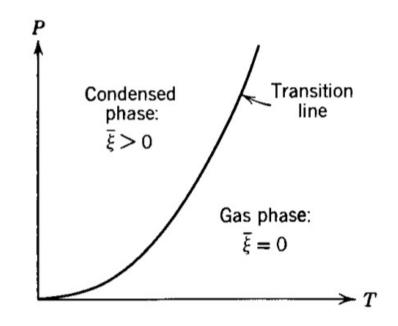
 Second-order phase transition



Imperfect Bose gas

 The PT diagram for the imperfect Bose gas

$$P = \begin{cases} P^{(0)} + \frac{4\pi a\hbar^2}{mv^2} & (v > v_c, T > T_c) \\ P^{(0)} + \frac{2\pi a\hbar^2}{m} \left(\frac{1}{v^2} + \frac{1}{v_c^2}\right) & (v < v_c, T < T_c) \end{cases}$$



 Heat capacity change at transition point

$$\frac{\Delta C_V}{Nk} = \frac{9a}{2\lambda_c} g_{3/2}(1)$$

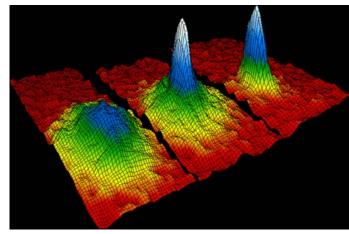
 Using a gas of ~2000 rubidium-87 atoms at 170 nK produced in 1995



Carl Wieman (1951-present) Nobel Prize 2001



Eric Cornell (1961-present) Nobel Prize 2001



Velocity distribution

~200000 sodium-23 atoms also in 1995



Wolfgang Ketterle (1951-present) Nobel Prize 2001

Quiz Leaderboard

Average score: (19702) Standard deviation: (10566)

Midterm Assignment

Statistical Mechanics

Midterm Assignment 2023



Thanks to Carlos Baiz, U. Texas at Austin, for allowing the use of the picture "Boltzmann in front of his laptop".

Midterm Assignment

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For the midterm assignment you can use the book and other course material including your own notes. You are encouraged to solve the exercises using a colab (jupyter) notebook, but this is not a requirement. Mathematica, MATLAB, or another numerical language of choice may also be used. You may use existing libraries as NUMPY and SCIPY. Any code used must be included in the answers and the code handed in should be directly executable (use .ipynb, .m or .n format not .pdf). You are welcome to discuss with other students, but each student must hand in an individually written answer (including individual written code). Answers will be checked for plagiarism and use of ChapGPT. All provided numbers must include the proper units. All plots must include axis-labels including units. The answers must be given in English and typed. Handwritten answers are not accepted. The final report must be uploaded in the teaching environment as a single .ipynb, .m or .n file including both the answers and the used code. The code must run out of the box, and produce the figures shown in the report.

Norm:

The table below shows the number of points to be given for each of the questions. For the midterm score the total score, M, is converted to the mark using the max score (M_{max} =70) according to the formula $\frac{9M}{M_{\text{max}}} + 1$. The midterm counts for 1/3 of the grade for the full course.

Subquestion A B C D E F G H I J Points 5 5 5 10 5 5 10 10 5 10

Two polarizations Two Spin States of Photon (S=1)

A system is only in an eigenstate of spin around an axis if a rotation about the axis doesn't change the system. Take z to be the direction of travel, then for a spin 1 system the S_z = 0 state would be symmetric to a rotation about an axis normal to the direction of travel. But this can only be the case if the momentum is zero i.e. in the rest frame. If the system has a non-zero momentum any rotation will change the direction of the momentum so it won't leave the system unchanged.

For a massive particle we can always find a rest frame, but for a massless particle there is no rest frame and therefore it is impossible to find a spin eigenfunction about any axis other than along the direction of travel. This applies to all massless particles e.g. gravitons also have only two spin states.

Next Time

Note this will be 17-19 not in the morning!

- What is the Ising Model? (And 1D solution)
- The Bragg-Williams Approximation
- The Bethe-Peierls Approximation
- Real materials:
 - The Onsager Solution (from Chapter 15)
 - Monte Carlo