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STATISTICAL PHYSICS LECTURE NOTES

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Lecture Notes 7

1. Overview of the canonical ensemble

The canonical ensemble procedure to determine the thermodynamics of a system is contained in the following two equations. First we calculate the partition function, Eq(1), and then we calculate the Helmholtz free energy, Eq. (2):

$$Z(T,V,N) = \sum_j e^{-\frac{U_j(V,N)}{k_B T}} \tag{1}$$

$$F(T,V,N) = -k_B T \ln(Z) \tag{2}$$

2. Electromagnetic Radiation

Figure 1: Max Karl Ernst Ludwig Planck (1858 – 1947) was a German theoretical physicist who discovered the energy quanta.

Electromagnetic standing waves are contained in a container with metallic walls at a temperature T. According to Planck (1900), this radiation is composed of photons of energy $\varepsilon = h\upsilon = \bar{h}\omega$, where υ is the frequency. The photon momentum is: $|p| = \frac{\varepsilon}{c} = \frac{h}{\lambda} = \frac{\bar{h}\omega}{c}$, where λ is wavelength, and $\frac{c}{\upsilon} = \lambda$.

The energy of a standing wave, labelled m, is $u_m = n_m \bar{h}\omega_m$ where $n_m = 0, 1, 2\ldots$ is the number of photons. The partition function, given in Eq. (1), can be factorized:

$$Z = \sum_{(u_1, u_2 \ldots)} e^{-\frac{(u_1 + u_2 + \cdots)}{k_B T}} = \prod_m (\sum_{n_m=0}^{\infty} e^{-n_m \frac{\bar{h}\omega_m}{k_B T}}) = \prod_m [\frac{1}{1 - e^{-\frac{\bar{h}\omega_m}{k_B T}}}]$$

I used the geometric sum, see Appendix.

The free energy, from Eq. (2), is:

$$F = k_B T \sum_m \ln\left[1 - e^{-\frac{\bar{h}\omega_m}{k_B T}}\right] \tag{3}$$

The entropy is:

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = -k_B \sum_m \ln\left[1 - e^{-\frac{\bar{h}\omega_m}{k_B T}}\right] + k_B \sum_m \frac{e^{-\frac{\bar{h}\omega_m}{k_B T}}}{1 - e^{-\frac{\bar{h}\omega_m}{k_B T}}} \frac{\bar{h}\omega_m}{k_B T} \tag{4}$$

or:

$$S = -k_B \sum_m \ln\left[1 - e^{-\frac{\bar{h}\omega_m}{k_B T}}\right] + k_B \sum_m \frac{1}{e^{\frac{\bar{h}\omega_m}{k_B T}} - 1} \frac{\bar{h}\omega_m}{k_B T} \tag{5}$$

The energy using Eqs. (3), (5) and $U = F + TS$ is:

$$U = \sum_m \frac{\bar{h}\omega_m}{e^{\frac{\bar{h}\omega_m}{k_B T}} - 1} \tag{6}$$

Since the energy of a standing wave (mode) is $n\bar{h}\omega$, the average number of photons of angular frequency ω is:

$$n = \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1} \tag{7}$$

This is the Bose-Einstein distribution.

Figure 2: Satyendra Nath Bose (1894 – 1974) was an Indian theoretical physicist who discovered the statistics governing integer spin particles. They are called bosons in his honor.

The total number of photons from all standing waves is:

$$N = \sum_m \frac{1}{e^{\frac{\bar{h}\omega_m}{k_B T}} - 1} \tag{8}$$

The sums above can be estimated by using the integral approximation. The validity of this approximation will be discussed later in the lecture. We start with a linear container of length L. The standing waves satisfy: $L = m\lambda/2$, $m = 1, 2, 3...$

Then: $\Delta m = 2L\Delta(1/\lambda) = 2(L/h)\Delta|p|$, where $|p| = h/\lambda$ is photon momentum absolute value. When we integrate we will consider the vector momentum (positive and negative values of p). Hence we drop the factor of two: $\Delta m = (L/h)\Delta p$. We next generalize to a container in three dimensions:

$$\Delta m_x \Delta m_y \Delta m_z = g\frac{V}{h^3}d^3p \tag{9}$$

The degeneracy factor is g. The electromagnetic waves are transverse waves. Hence there are g =2 independent directions for the vibrations. Equation (9) is general and it holds for all systems. The integral approximation is:

$$\sum_{m_x,m_y,m_z}(\dots) \approx \frac{gV}{h^3}\iiint d^3p(\dots) \tag{10}$$

Using the dispersion equation: $|p| = \frac{\bar{h}\omega}{c}$ we calculate d^3p:

$$d^3p = 4\pi p^2 dp = \frac{4\pi\bar{h}^3}{c^3}\omega^2 d\omega$$

Then (10) becomes:

$$\sum_{m_x,m_y,m_z}(\dots) \approx \int d\,\omega D(\omega)(\dots) \tag{11}$$

where the density of standing waves per angular frequency is:

$$D(\omega) = \frac{V\omega^2}{\pi^2 c^3} \tag{12}$$

We apply the integral approximation to the free energy Eq. (3):

$$F = \frac{k_B TV}{\pi^2 c^3}\int_0^\infty d\omega\omega^2\ln(1 - e^{-\frac{\bar{h}\omega}{k_B T}}) \tag{13}$$

We change the variable of integration to $x = \frac{\bar{h}\omega}{k_B T}$ and get:

$$F = \frac{k_B TV}{\pi^2 c^3}(\frac{k_B T}{\bar{h}})^3\int_0^\infty dx x^2\ln(1 - e^{-x}) \tag{14}$$

As we see in Computer Lab 4, the integral on the right hand side of Eq. (14) is equal to: $-\frac{\pi^4}{45}$

Then Eq (14) can be written as:

F= - (a/3)VT⁴ (15)

The constant a is called the Stefan constant and it is equal to:

$$a = \frac{\pi^2 k_B{}^4}{15(c\bar{h})^3} = 7.56 * 10^{-16}j/m^3 K^4 \tag{16}$$

Exercise: Check that the numerical value of the Stefan constant is 7.56*10⁻¹⁶j/m³K⁴.

Since: $dF = -SdT - pdV + \mu dN$, we get:

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = \frac{4a}{3}VT^3 \qquad (17)$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{a}{3}T^4 \qquad (18)$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = 0 \qquad (19)$$

The energy is:

$$U = F + TS = -\frac{a}{3}VT^4 + \frac{4a}{3}VT^4 = aVT^4 \qquad (20)$$

The heat capacity is:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = 4aVT^3 \qquad (21)$$

Equations (17) to (21) were derived in the thermal physics course (lecture 10) starting from the assumption that the chemical potential of photons is zero. The Stefan constant value is found here to be determined by the fundamental constants h, c, k_B.

The number of photons, applying the integral approximation to the sum in Eq. (8), is:

$$N = \frac{V}{\pi^2 c^3}\int_0^\infty d\omega\, \omega^2 \frac{1}{e^{\frac{\hbar\omega}{k_B T}}-1} = \frac{VT^3 k_B^3}{\pi^2 c^3 \hbar^3}\int_0^\infty dx\, \frac{x^2}{e^x-1} = 2.404\frac{k_B^3}{\pi^2 c^3 \hbar^3}VT^3 = 2.026*10^7 VT^3 \quad (22)$$

The numerical evaluation of the integral in Eq. (22) is done in Computer Lab 4.

Exercise: Check that the numerical constant on the right hand side of Eq. (22) is $2.026*10^7 (m*K)^{-3}$.

The energy can be written using the integral approximation, Eqs. (6) and (12), as:

$$U = \frac{V\hbar}{\pi^2 c^3}\int_0^\infty d\omega\, \frac{\omega^3}{e^{\frac{\hbar\omega}{k_B T}}-1} \qquad (23)$$

The energy per frequency interval $\frac{dU}{d\omega}$ is called spectral energy density u_ω .

$$u_\omega = \frac{V\hbar}{\pi^2 c^3}\frac{\omega^3}{e^{\frac{\hbar\omega}{k_B T}}-1} \qquad (24)$$

For high temperatures (classical regime): $\frac{\hbar\omega}{k_B T} \ll 1$:

$$u_\omega \approx \frac{V\omega^2}{\pi^2 c^3}k_B T \qquad (25)$$

This formula is obtained in the classical version of statistical mechanics and is called the Rayleigh-Jeans law. Note that integrating this u_ω for all frequency gives an infinite value. This is known as the ultraviolet catastrophe. It is an artifact of the classical approximation.

It shows the need for quantum mechanics to explain electromagnetic radiation.

For low temperatures (quantum regime) $\frac{\bar{h}\omega}{k_BT} \gg 1$, we get the Wien law:

$$u_\omega \approx \frac{V\bar{h}\omega^3}{\pi^2c^3}e^{-\frac{\bar{h}\omega}{k_BT}} \qquad (26)$$

The spectral energy density per wavelength is obtained from: $u_\lambda = u_\omega|d\omega/d\lambda|$:

$$u_\lambda = \frac{8hc\pi V}{\lambda^5(e^{\frac{hc}{\lambda k_BT}}-1)} \qquad (27)$$

u_λ exhibits a maximum at a wavelength given by the Wien displacement law:

$\lambda_{max}T = 2.898*10^{-3}$mK. This is derived in Computer Lab 4. We show u_λ vs λ in Figure 3.

$u_\lambda (\lambda , 1 , 2.7)$

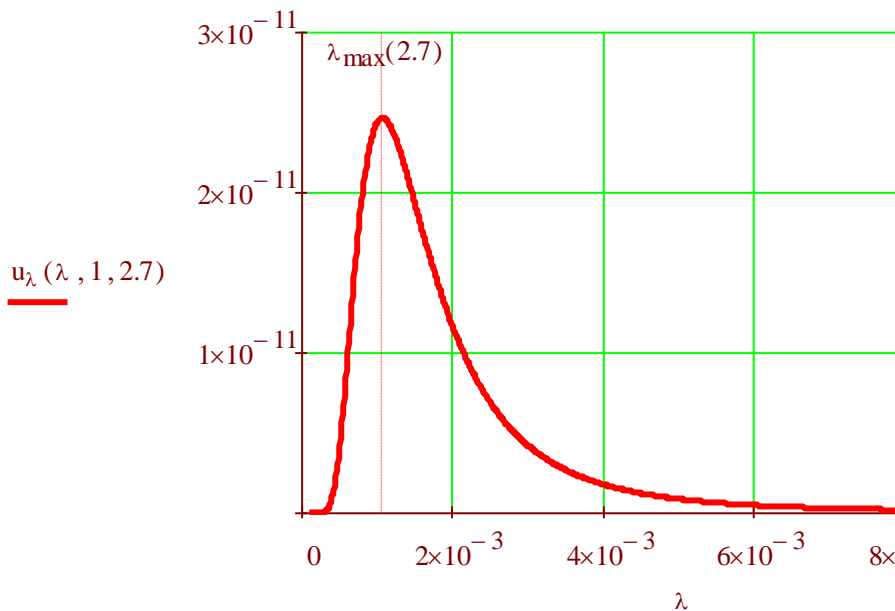*Figure 3: Spectral energy vs wavelength for background radiation*
T = 2.7K. Maximum occurs at wavelength of 1mm, in the microwave
part of the spectrum.

Validity Range for the Integral Approximation

The integral approximation, Eqs. (10), (11), is: $\sum_{modes}(...) \approx \int d\,\omega D(\omega)(...)$

It is valid provided:

$$1 \gg \frac{\bar{h}\Delta\omega_{mode}}{k_BT} \qquad (28)$$

The standing waves in a cube of size L*L*L have angular frequencies:

$\omega_{m_x,m_y,m_z} = \frac{c\pi}{L}\sqrt{m_x{}^2 + m_y{}^2 + m_z{}^2}$ with m_x, m_y, m_z = 1, 2. 3... We estimate the frequency

change to be of the order of the fundamental frequency: $\Delta\omega_{mode} \sim \omega_{1,1,1} = \frac{c\pi}{L}\sqrt{3}$. Then the

inequality becomes: $\frac{c\pi}{L}\sqrt{3} \ll \frac{k_B T}{\hbar}$ or

$$TL \gg \frac{ch}{k_B}\frac{\sqrt{3}}{2} = 1.25 * 10^{-2} K * m \tag{29}$$

Exercise: Check the numerical value on the right hand side of Eq. (29).

For a cube of volume 1liter, L = 0.1m. According to Eq. (29), the integral approximation works

for: T $\gg$ 0.125K. At room temperature T = 300K, the integral approximation works (according

to Eq. (29)) for: L $\gg$ 42microns.

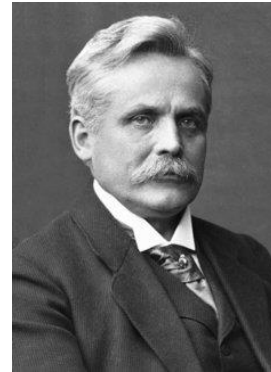Appendix: The geometric sum: $\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$ if $|x| < 1$. Indeed:

$(1-x)\sum_{n=0}^{\infty} x^n = \sum_{n=0}^{\infty} x^n - \sum_{n=1}^{\infty} x^n = 1.$
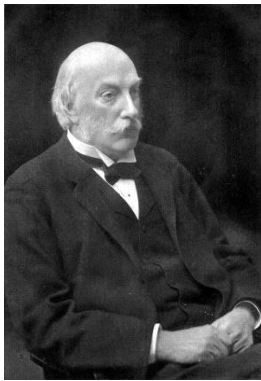
Figure 4:
John William Strutt,
baron Rayleigh
(1842 – 1919),
English physicist.

Figure 5:
James Hopwood Jeans
(1877 – 1946)
English physicist.

Figure 6:
Wilhelm Wien
(1864 – 1928)
German physicist.

<u>Readings</u>
Callen Ch. 16 Sec. 8.
Problem Sets 7.
Computer Lab 4.

Lecture Notes 8

1. Grand canonical ensemble

We study a system in contact with a large reservoir. The system and the reservoir exchange heat and matter. The total system is insulated.
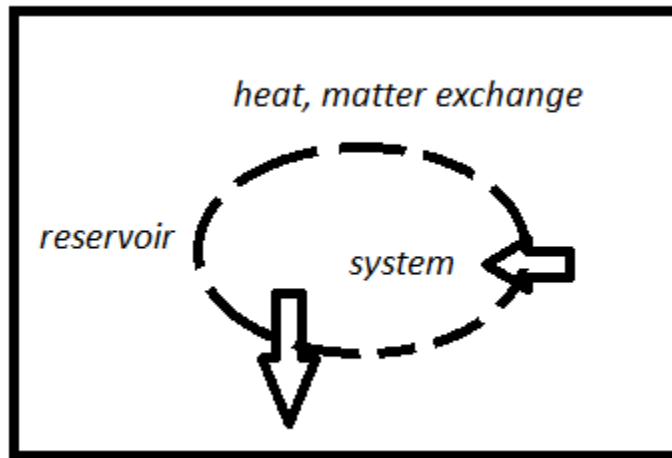

Figure 1: The (large) reservoir exchanges energy and matter with the (small) system under study. The total system (reservoir plus system) is insulated.

The system microstates are labeled by j. The system energy and number of particles in microstate j are respectively U_j and N_j. Since the total system is insulated: $U_{res} = U_{tot} - U_j$, $N_{res} = N_{tot} - N_j$

Corresponding to the microstate j, the reservoir can occupy a large number of microstates $\Omega_{res}(U_{tot}-U_j, N_{tot} - N_j)$. Since according to the first postulate of statistical mechanics the insulated total system microstates are equally probable, the probability for the system under study to be in microstate j, without regard to the state of the reservoir, is:

$$Pj = \Omega_{res}(U_{tot}-U_j, N_{tot} - N_j)/\Omega_{tot}(U_{tot}, N_{tot}) \tag{1}$$

We then use the second postulate (Boltzmann) to express the number of microstates in terms of the entropy:

$$P_j = \exp[(S_{res}(U_{tot}-U_j, N_{tot} - N_j) - S_{tot}(U_{tot}, N_{tot}))/k_B] \tag{2}$$

We use the Taylor expansion for the reservoir entropy. The small parameters are $U - U_j$, and $N - N_j$, where U is the average system energy and N is the average system number of particles:

Sres(U$_{tot}$-U$_j$, N$_{tot}$ − N$_j$) - Stot(U$_{tot}$, N$_{tot}$)≃ Sres(U$_{tot}$-U, N$_{tot}$ − N) + (δSres/δUres)(U - U$_j$) +

$$(δSres/δNres)(N - N_j) - Stot(U_{tot}, N_{tot}) \qquad (3)$$

The higher contributions to the Taylor expansion are small in view if the fact that the reservoir is huge compared to the system. Since the entropy is additive:

Stot(U$_{tot}$, N$_{tot}$) = S(U, N) + Sres(U$_{tot}$-U, N$_{tot}$ − N) $\qquad$ (4)

Furthermore: δSres/ δUres = 1/Tres and δSres/δNres = -µres/Tres , At equilibrium Tres = T and µres = µ. Hence, we can now express the microstate probability of Eq. (2) as:

P$_j$ = exp{[-S + (U − U$_j$)/T - µ(N − N$_j$)/T]/k$_B$}= exp(Ω /k$_B$T)exp[-(U$_j$ - µN$_j$)/k$_B$T] $\qquad$ (5)

The grand-canonical thermodynamic potential is: Ω = U –TS - µN. We denote:

exp(Ω /k$_B$T) = 1/Z. Hence:

Ω = -k$_B$Tln(Z) $\qquad$ (6)

The probabilities add up to unity:

$$1 = \sum_j P_j = \frac{1}{Z}\sum_j e^{-\frac{U_j - µN_j}{k_B T}}$$

Hence the partition function Z is:

$$Z(T,V,µ) = \sum_j e^{-\frac{U_j - µN_j}{k_B T}} \qquad (7)$$

Equations (6) and (7) provide a roadmap for determining the thermodynamics of any system. Given the energy levels U$_j$, that depend on the volume, one first computes from Eq. (7) the partition function Z(T,V,µ). Then by substituting this on the right hand side of Eq. (6) one gets the grand-canonical potential: Ω = Ω(T,V,µ). This is a fundamental equation and all thermodynamic quantities are obtained by using:

dΩ = -SdT – pdV –Ndµ. $\qquad$ (8)

2. Classical version of the grand canonical ensemble

Niels Bohr's correspondence principle states that for large quantum numbers, systems behave according to the laws of classical physics. In the classical physics limit, the sum over microstates is replaced by an integral over the phase space. This is the space spanned by positions and momenta. The Heisenberg uncertainty principle states that the smallest ΔxΔp is of the order of the Planck constant h. Then the partition function is:

$$Z \approx \sum_N \frac{e^{\frac{\mu N}{k_B T}}}{N!} \int \dots \int \frac{d^3 x_1 \dots d^3 x_N d^3 p_1 \dots d^3 p_N}{h^{3N} j} e^{-\frac{H(x_1 \dots x_N, \, p_1 \dots p_N)}{k_B T}} \tag{9}$$

In the case of undistinguishable particles one includes the N! factor in the denominator of Eq. (9). If the particles are distinguishable this factor is not present. The Hamiltonian H is the energy expressed in terms of positions and momenta.

Application: Classical ideal gas

The ideal gas is a low density gas whose energy is approximated by its kinetic energy only. The Hamiltonian is:

$$H = \sum_{j=1}^{N} \frac{\vec{p}_j^{\,2}}{2m} \tag{10}$$

The classical partition function from Eqs. (9) and (4) becomes:

$$Z = \sum_{N=0}^{\infty} \frac{e^{\frac{\mu N}{k_B T}} V^N}{N! h^{3N}} \left[\int_{-\infty}^{\infty} e^{-\frac{p^2}{2m k_B T}} dp \right]^{3N} = \sum_{N=0}^{\infty} \frac{e^{\frac{\mu N}{k_B T}} V^N}{N! \lambda_T^{3N}} \tag{11}$$

where the thermal wavelength is:

$$\lambda_T = \frac{h}{\sqrt{2\pi m k_B T}} \tag{12}$$

The sum on the right hand side of (11) is (see Appendix):

$$Z = \exp\left(\frac{V}{\lambda_T^3} e^{\frac{\mu}{k_B T}}\right) \tag{13}$$

Using Eqs. (6) and (13) we get the fundamental equation:

$$\Omega = -k_B T \frac{V}{\lambda_T^3} e^{\frac{\mu}{k_B T}} \tag{14}$$

According to the Euler equation the grand canonical potential is: $\Omega = U - TS - \mu N = -pV$. Hence equation (14) becomes:

$$p = \frac{k_B T}{\lambda_T^3} e^{\frac{\mu}{k_B T}} \tag{15}$$

or

$$\mu = k_B T \ln\left(\frac{p \lambda_T^3}{k_B T}\right) \tag{16}$$

Application: Determine the equation of state, by using Eq.(16).

Since dμ = -sdT +vdp, $v = \left(\frac{\partial \mu}{\partial p}\right)_T = \frac{k_B T}{p}$ $\tag{17}$

The classical version of statistical physics is applicable provided the quantum (de Broglie) thermal wavelength is short compared to the characteristic distance, i.e. the mean distance

between atoms: $\lambda_T \ll (\frac{V}{N})^{1/3}$. In view of the equation of state $\lambda_T \ll (\frac{k_B T}{p})^{1/3}$, Then by using Eq.(16) we find that in the classical limit the chemical potential is negative: $\mu \ll 0$.

Appendix: The sum: $\sum_{n=0}^{\infty} \frac{x^n}{n!} = e^x$ for any x.

Readings
Callen Ch. 17
Problem Set 8.