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STATISTICAL PHYSICS LECTURE NOTES

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Lecture Notes 4

1. Canonical Ensemble

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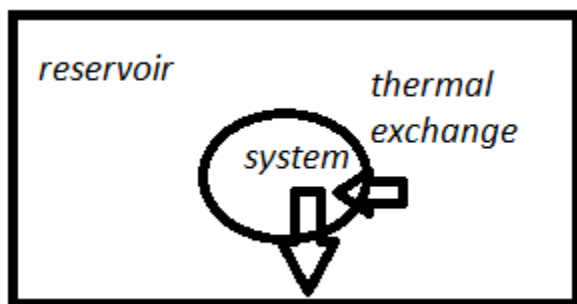

Figure 1: The reservoir (large) exchanges energy with the system (small) under study. The total system (reservoir plus system) is insulated.

The system microstates are labeled by j. The system energy in microstate j is U_j. Since the total system is insulated: $U_{res} = U_{tot} - U_j$. Corresponding to the microstate j, the reservoir can occupy a large number of microstates $\Omega_{res}(U_{tot}-U_j)$. 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 reservoir, is:

$$P_j = \Omega_{res}(U_{tot}-U_j)/\Omega_{tot}(U_{tot}) \tag{1}$$

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

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

We use the Taylor expansion of the reservoir entropy. The small parameter is $U - U_j$, where U is average system energy:

$$S_{res}(U_{tot}-U_j) - S_{tot}(U_{tot}) \simeq S_{res}(U_{tot}-U) + (\delta S_{res}/\delta U_{res})(U - U_j) - S_{tot}(U_{tot}) \tag{3}$$

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:

$$S_{tot}(U_{tot}) = S(U) + S_{res}(U_{tot}-U) \tag{4}$$

Furthermore: $\delta S_{res}/\delta U_{res} = 1/T_{res}$ and at equilibrium $T_{res} = T$. We can now express the microstate probability of Eq. (2) as:

$P_j = \exp\{[-S + (U - U_j)/T]/k_B\} = \exp(F/k_BT)\exp(-U_j/k_BT)$ (5)

The Helmholtz free energy is $F = U - TS$.   We denote: $\exp(F/k_BT) = 1/Z$. Hence:

$F = -k_BT\ln(Z)$ (6)

The probabilities add up to unity:

$$1 = \sum_j P_j = \frac{1}{Z}\sum_j e^{-\frac{U_j}{k_BT}}$$

Hence the partition function Z is:

$$Z = \sum_j e^{-\frac{U_j}{k_BT}}$$ (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 V and number of particles N, one first computes from Eq. (7) the partition function $Z(T,V,N)$. Then by substituting this on the right hand side of Eq. (6) one gets Helmholtz free energy: $F = F(T,V,N)$.

2. Energy fluctuation, Gibbs-Einstein Equation

We start from the average energy formula:

$$U = \sum_j P_j U_j$$ (8)

where:

$$P_j = e^{\frac{F-U_j}{k_BT}}$$ (9)

and $F = F(T,V,N)$ according to Eq.(6) and U_j depends on V and N but not on T.

Differentiate both sides of Eq.(8) with respect to T:

$$\left(\frac{\partial U}{\partial T}\right)_{V,N} = \sum_j P_j \left[-\frac{F-U_j}{k_BT^2} + \frac{1}{k_BT}\left(\frac{\partial F}{\partial T}\right)_{V,N}\right]U_j$$ (10)

Use on the right hand side of Eq.(10): $\left(\frac{\partial F}{\partial T}\right)_{V,N} = -S$ and $F + TS = U$. On the left hand side of

Eq. (10) use: $\left(\frac{\partial U}{\partial T}\right)_{V,N} = C_V$. We find:

$$C_V = \frac{1}{k_BT^2}\sum_j P_j\left[U_j - U\right]U_j = \frac{1}{k_BT^2}\left(\overline{U_j^2} - U^2\right) = \frac{\overline{(U_j-U)^2}}{k_BT^2}$$ (11)

or: $var(U_j) = \overline{(\Delta U)^2} = k_BT^2C_V$.   This equation was discovered independently by Gibbs and Einstein. The variance of energy is a statistical measure of the energy fluctuations. The isochoric heat capacity therefore measures the energy fluctuations. Note that Eq. (11) implies the isochoric heat capacity is positive.
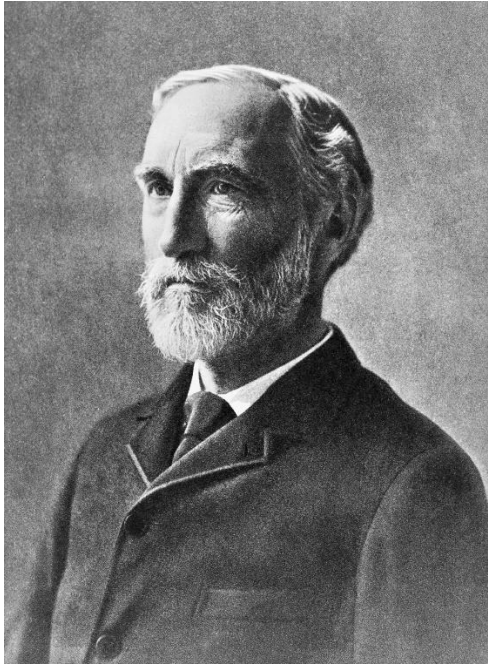
s:

Figure 2: Josiah Willard Gibbs (1839 –1903) created statistical mechanics, proving that the thermodynamics laws follow from the ensemble statistics. He has also discovered the vector calculus.

The fractional energy fluctuation is defined below. Since U and C_V are extensive quantities (i.e. they are proportional to the number of particles N) while T is an intensive quantity, the fractional energy fluctuation scales as $1/N^{1/2}$:

$$\sqrt{\frac{\overline{(\Delta U)^2}}{U^2}} = \sqrt{\frac{k_B T^2 C_V}{U^2}} \sim \frac{1}{\sqrt{N}} \tag{12}$$

This means that the energy fluctuation in the canonical ensemble is small for a large number of particles.

Application: Calculate the fractional energy fluctuation for the classical ideal gas.

Start with: $U = (i/2)N k_B T$; $C_V = (i/2)N k_B$. Substitute in Eq.(12).

$$\sqrt{\frac{\overline{(\Delta U)^2}}{U^2}} = \sqrt{\frac{k_B T^2 C_V}{U^2}} = \sqrt{\frac{2}{iN}}$$

<u>Readings</u>
Callen Ch. 16 Sec. 1. 2; Ch.19 Sec.2
Problem Set 5.

3

Lecture Notes 5

1. Classical version 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):

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

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

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 $\Delta x \Delta p$ is of the order of the Planck constant h. Then the partition function is:

$$Z \approx \int \ldots \int \frac{d^3 x_1 \ldots d^3 x_N d^3 p_1 \ldots d^3 p_N}{h^{3N}} e^{-\frac{H(x_1 \ldots x_N, \, p_1 \ldots p_N)}{k_B T}} \tag{3}$$

The Hamiltonian H is the. energy expressed in terms of positions and momenta.

Figure 1: Niels Bohr (1885 – 1962) and Werner Heisenberg (1901-1975) pioneers of quantum physics.

2. Classical ideal gas

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

$$H = \sum_{j=1}^{N} \frac{\vec{p}_j^{\,2}}{2m} \tag{4}$$

The classical partition function from Eqs. (3) and (4) becomes:

$$Z = \frac{V^N}{h^{3N}} \left[\int_{-\infty}^{\infty} e^{-\frac{p^2}{2mk_BT}} dp \right]^{3N} = \frac{V^N}{\left(\frac{h}{\sqrt{2\pi mk_BT}} \right)^{3N}} \tag{5}$$

We denote:

$$\lambda_T = \frac{h}{\sqrt{2\pi mk_BT}} \tag{6}$$

λ_T is called the thermal wavelength. It estimates the size of de Broglie wavelength:

$\lambda = h/p \sim h/(3mk_BT)^{1/2}$.

Figure 2: Prince Louis-Victor de Broglie (1892-1987), French physicist who predicted the wave character of matter.

Substituting Eqs (5), (6) into (2), one gets $F = -Nk_BT\ln(V/\lambda_T^3)$. This formula violates the expected thermodynamics scaling $F = Nf(T,V/N)$, since F, V, N are extensive variables and T is an intensive quantity. This is a problem known as the Gibbs paradox. The solution of the paradox is provided by the quantum mechanical idea that the N particles are indistinguishable. Hence we over-counted the number of states in Eq (5) by a factor of N!, the number of permutations of the N identical particles. The classical partition function for the ideal gas is then:

$$Z = \frac{V^N}{(\lambda_T)^{3N} N!} \tag{7}$$

The free energy F is obtained from Eqs. (7) and (2):

$$F = -Nk_B T \left[ln\left(\frac{V}{N}\right) + 1 - 3\ln(\lambda_T) \right] = -Nk_B T \left[ln\left(\frac{V}{N}\right) + 1 + \frac{3}{2}\ln\left(\frac{2\pi m k_B T}{h^2}\right) \right] \tag{8}$$

Entropy is:

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = Nk_B \left[ln\left(\frac{V}{N}\right) + 1 + \frac{3}{2}\ln\left(\frac{2\pi m k_B T}{h^2}\right) \right] + \frac{3}{2} Nk_B \quad \text{or}$$

$$S = Nk_B \left[ln\left(\frac{V}{N}\right) + \frac{5}{2} + \frac{3}{2}\ln\left(\frac{2\pi m k_B T}{h^2}\right) \right] \tag{9}$$

Equation (9) was derived independently, in 1912, by the Dutch physicist Hugo Martin Tetrode (1895 - 1931) and by the German physicist Otto Sackur (1880-1914).

The equation of state is obtained by calculating the pressure:

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{Nk_B T}{V} \tag{10}$$

The energy is obtained from Eqs.(8) and (9):

$$U = F + TS = \frac{3}{2} Nk_B T \tag{11}$$

The chemical potential can be obtained by using the Euler equation:

$$\mu = u - Ts + pv = \frac{3}{2} k_B T - k_B T \left[ln\left(\frac{V}{N}\right) + \frac{5}{2} + \frac{3}{2}\ln\left(\frac{2\pi m k_B T}{h^2}\right) \right] + k_B T$$

or:

$$\mu = -k_B T \left[ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln\left(\frac{2\pi m k_B T}{h^2}\right) \right] = -k_B T ln\left(\frac{V}{N\lambda_T^3}\right) \tag{12}$$

Appendix

The Gaussian integral is:

$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}} \quad \text{for a} > 0.$$

We prove this result next. We denote the integral I. Then:

$$I^2 = \iint_{-\infty}^{\infty} e^{-a(x^2+y^2)} dxdy = \frac{1}{a}\int_0^{\infty} e^{-r^2} 2\pi r dr = \frac{\pi}{a} \tag{13}$$

Hence: $I = \sqrt{\frac{\pi}{a}}$

3. Two-state model in the canonical ensemble

We analyze now a system of N distinguishable particles that can occupy two energy states. The system is in equilibrium with a heat reservoir at temperature T. The particles are distinguishable by their location. Each atom that has a spin ½ so in the presence of an external magnetic field H its energy is either $-\varepsilon = -\mu_B H$ or $\varepsilon = +\mu_B H$. The Bohr magneton is $\mu_B = eh/(4\pi m) = 9.27*10^{-24}$ j/T, where e is the electron's charge and m is the electron's mass.

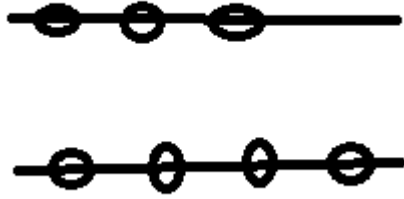*Figure 3:* Example of two-state system: 3 atoms have each an energy ε and 4 atoms have each an energy $-\varepsilon$.

The partition function, given in Eq.(1), can be factorized:

$$Z = \sum_{(u_1,\ldots,u_N)} e^{-\frac{(u_1+u_2+\cdots+u_N)}{k_B T}} = \left(\sum_{u=-\varepsilon}^{\varepsilon} e^{-\frac{u}{k_B T}}\right)^N = \left[2\cosh\left(\frac{\varepsilon}{k_B T}\right)\right]^N \tag{14}$$

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

$$F = -Nk_B T ln\left[2\cosh\left(\frac{\varepsilon}{k_B T}\right)\right] \tag{15}$$

The entropy is:

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = Nk_B ln\left[2\cosh\left(\frac{\varepsilon}{k_B T}\right)\right] - Nk_B \frac{\varepsilon}{k_B T} tanh(\frac{\varepsilon}{k_B T}) \tag{16}$$

The energy is:

$$U = F + TS = -N\varepsilon tanh(\frac{\varepsilon}{k_B T}) \tag{17}$$

The isochoric heat capacity is:

$$C_V = \frac{\partial U}{\partial T} = Nk_B (\frac{\varepsilon}{k_B T})^2 [1 - (tanh(\frac{\varepsilon}{k_B T}))^2] \tag{18}$$

Eqs.(17) and (18) are identical to the microcanonical calculations for energy and heat capacity, see Lecture 2, Eqs.(8) and (9).

Readings
Callen Ch. 16 Sec. 2, 9. 10
Problem Sets 5, 6

Lecture Notes 6

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):

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

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

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. Since $\Delta x \Delta p > h$, the classical partition function includes a factor of h^{-3N} :

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

The Hamiltonian H is the. energy expressed in terms of positions and momenta.

2. Classical solid

The solid includes 3N linear oscillators. The energy of harmonic oscillator includes the kinetic energy and the elastic energy. The Hamiltonian is:

$$H = \sum_{j=1}^{N}\left(\frac{\vec{p_j}^2}{2m} + \frac{k\vec{x_j}^2}{2}\right) \tag{4}$$

The classical partition function from Eqs. (3) and (4) is:

$$Z = \frac{1}{h^{3N}}\left[\int_{-\infty}^{\infty} e^{-\frac{p^2}{2mk_B T}} dp\right]^{3N} \left[\int_{-\infty}^{\infty} e^{-\frac{kx^2}{2k_B T}} dx\right]^{3N} = \left(\frac{\sqrt{2\pi mk_B T}\sqrt{\frac{2\pi k_B T}{k}}}{h}\right)^{3N} = \left(\frac{2\pi k_B T}{h\omega}\right)^{3N}$$

Where $\omega = \sqrt{\frac{k}{m}}$ is the angular velocity. Denoting $\bar{h} = \frac{h}{2\pi}$ we get the following formula for the partition function:

$$Z = \left(\frac{k_B T}{\bar{h}\omega}\right)^{3N} \tag{5}$$

Substituting Eqs (5) into (2), one gets:

$$F = -3Nk_B T\ln\left(\frac{k_B T}{\bar{h}\omega}\right) \tag{6}$$

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Note that since the atoms are distinguishable by location there is no factor of N!, the number of permutations of the N particles. This term was needed for the ideal gas.

The entropy is:

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = 3Nk_B\left[ln\left(\frac{k_BT}{\hbar\omega}\right) + 1\right] \tag{7}$$

The energy is obtained from Eqs.(8) and (9):

$$U = F + TS = 3Nk_BT \tag{8}$$

The heat capacity is:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = 3Nk_B \tag{9}$$

For 1 mole of any solid: $C_V = 3R = 25j/°C*mole = 6cal/°C*mole$. This was discovered experimentally, in 1819, by Dulong and Petit.

Since there is no volume dependence in Eq (6), the pressure is zero: $p = 0$. The chemical potential can be obtained by using the Euler equation:

$$\mu = u - Ts + pv = 3k_BT - 3k_BT\left[ln\left(\frac{k_BT}{\hbar\omega}\right) + 1\right]$$

or:

$$\mu = -3k_BTln(\frac{k_BT}{\hbar\omega}) \tag{10}$$

3. Einstein solid in the canonical ensemble

The Einstein solid consists of N atoms or 3N independent linear harmonic oscillators. All oscillators are assumed to have the same frequency ω. The quantized energy of a linear harmonic oscillator is:

$$u_j = (n_j + \tfrac{1}{2})\hbar\omega \qquad j = 1, 2,..., 3N \tag{11}$$

$\bar{h} = h/2\pi$ where h is the Planck constant.

The quantum numbers $n_j = 0, 1, 2...$. The 3N linear oscillators are labelled: $j = 1, 2,...., 3N$.

The partition function, given in Eq.(1), can be factorized:

$$Z = \sum_{(u_1,...,u_{3N})} e^{-\frac{(u_1+u_2+\cdots+u_{3N})}{k_BT}} = (\sum_{n=0}^{\infty} e^{-(n+\frac{1}{2})\frac{\hbar\omega}{k_BT}})^{3N} = [e^{-\frac{\hbar\omega}{2k_BT}}\frac{1}{1-e^{-\frac{\hbar\omega}{k_BT}}}]^{3N}$$

Or:

$$Z = \left[2\sinh\left(\frac{\hbar\omega}{2k_BT}\right)\right]^{-3N} \tag{12}$$

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

$$F = 3Nk_BT\ln[2\sinh\left(\frac{\hbar\omega}{2k_BT}\right)] \tag{13}$$

The entropy is:

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = -3Nk_B\ln\left[2\sinh\left(\frac{\hbar\omega}{2k_BT}\right)\right] + 3Nk_B\frac{\hbar\omega}{2k_BT}\cotanh(\frac{\hbar\omega}{2k_BT}) \tag{14}$$

The energy is:

$$U = F + TS = 3N\frac{\hbar\omega}{2}\cotanh(\frac{\hbar\omega}{2k_BT}) \tag{15}$$

Check that we can rewrite Eq. (15) as:

$$U = 3N\frac{\hbar\omega}{2} + 3N\frac{\hbar\omega}{e^{\frac{\hbar\omega}{k_BT}}-1} \tag{16}$$

The first term in the right hand side of Eq.(16) is the zero point energy, while the second term corresponds to the thermal average of $n_j\hbar\omega$ for each of the 3N oscillators. Hence the mean quantum number:

$$\bar{n} = \frac{1}{e^{\frac{\hbar\omega}{k_BT}}-1} \tag{17}$$

The isochoric heat capacity is:

$$C_V = \frac{\partial U}{\partial T} = 3Nk_B(\frac{\hbar\omega}{2k_BT})^2\frac{1}{[\sinh\left(\frac{\hbar\omega}{2k_BT}\right)]^2} \tag{18}$$

Eqs.(16), (17) and (18) are identical to the microcanonical calculations for energy and heat capacity, see Lecture 3, Eqs.(12), (13) and (14). This is a general result of statistical mechanics: a large system has the same thermodynamics in the different ensembles. The reason is that the fractional fluctuations are very small, of the order of N$^{-1/2}$, see lecture 4 Eq.(12).

In the classical limit: $T \gg \frac{\hbar\omega}{k_B} = T_E$, the energy from Eq.(16) and the heat capacity from Eq.(18) are approximated as: $U \approx 3Nk_BT$ and $C_V \approx 3Nk_B$. Those are the equations derived in the classical version of the canonical ensemble, Eqs.(8) and (9).

In the quantum regime: $T \ll \frac{\hbar\omega}{k_B} = T_E$, Eq. (14) can be approximated to show that the entropy S $\simeq$ 0, consistent with the third law of thermodynamics.

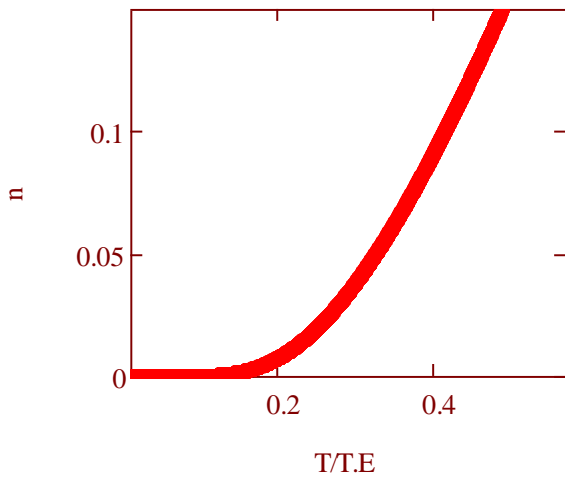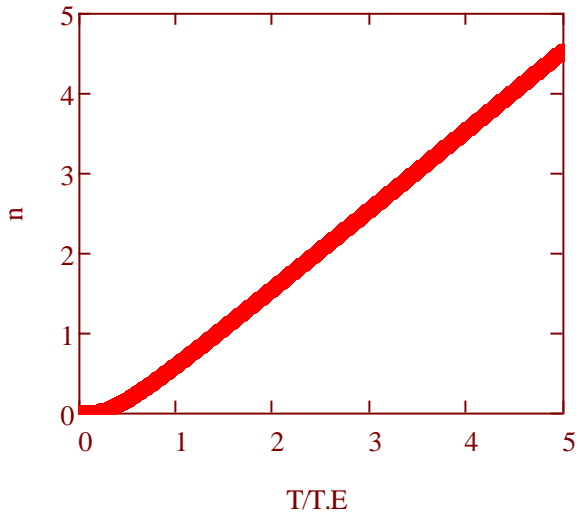We show next the average quantum number dependence on T/T$_E$.

Figure: n vs T/T$_E$. For high temperatures (top graph) n ~ T/T$_E$. For low temperatures (bottom graph) n approaches zero exponentially fast.

Readings
Callen Ch. 16 Sec. 2, 9
Problem Sets 5, 6