

8.08 Statistical Physics II — Spring 2019

Recitation Note 1

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1 Canonical Ensemble

1.1 Derivation from Microcanonical Ensemble

According to the fundamental assumption of statistical mechanics, each quantum state in an isolated system is equally probable in the (microcanonical) ensemble. We would like to know what is the probability of a quantum state in a system that is not isolated, but in thermal equilibrium with a heat bath / reservoir.

Consider a system that is in contact with a heat bath. Energy is free to transfer between the system and the bath. The system has energy E_1 and the bath has energy E_2 . Assume the heat bath is much larger than the system such that $E_2 \gg E_1$ (since energy is an extensive quantity). The system and the bath as a whole is an isolated system with energy $E = E_1 + E_2$. Therefore, we can apply the principles of microcanonical ensemble. The probability that the system is in a state with energy E_1 is

$$P_1(E_1) = \frac{\Gamma_2(E - E_1)}{\Gamma(E)} = \frac{\exp\left(\frac{S_2(E - E_1)}{k_B}\right)}{\Gamma(E)}, \quad (1)$$

where $\Gamma_i(E)$, $i = 1, 2$ is the number of states in the energy range $(E, E + \delta E)$ in the system and in the bath respectively. $S_i(E)$, $i = 1, 2$ is the entropy of the system and the bath respectively. We have used the definition of entropy $S = k_B \ln \Gamma$.

Since $E > E_2 \gg E_1$, we can expand S_2 around E :

$$S_2(E - E_1) \approx S_2(E) - \frac{\partial S_2}{\partial E} E_1. \quad (2)$$

Here we **define** the temperature T to be

$$\frac{1}{T} \equiv \frac{\partial S_2}{\partial E}. \quad (3)$$

It is not yet clear what is the physical significance of this quantity (namely, the first order derivative of entropy with respect to energy). But we will see very soon below.

Insert Eq. (2) and (3) back into (1). we have

$$P_1(E_1) = \frac{\exp\left(\frac{S_2(E)}{k_B}\right) \exp\left(-\frac{E_1}{k_B T}\right)}{\Gamma(E)} = \frac{1}{Z} \exp\left(-\frac{E_1}{k_B T}\right). \quad (4)$$

Note that only E_1 is the variable of interest. The remaining E_1 independent terms can be summarized as $1/Z$, which is the normalization factor of the probability distribution P_1 . It is chosen such that $\sum_n P_1(E_{1,n}) = 1$. Here $E_{1,n}$ is the energy of the n -th state of the system. It is not hard to see

$$Z = \sum_n \exp\left(-\frac{E_{1,n}}{k_B T}\right) = \sum_n \exp(-\beta E_{1,n}). \quad (5)$$

Equation (4) is called the Boltzmann distribution. β is a common notation for the inverse temperature $\beta \equiv 1/k_B T$.

1.2 Partition Function and Helmholtz Free Energy

The quantity Z we defined in Eq. (5) is not only a normalization factor, but also has deep physical meaning. To see this,

$$Z = \sum_n e^{-\beta E_{1,n}} \quad (6)$$

$$= \int_{-\infty}^{+\infty} dE \sum_n \delta(E - E_{1,n}) e^{-\beta E} \quad (7)$$

$$= \int_{-\infty}^{+\infty} dE e^{-\beta(E - T S_1(E))}, \quad (8)$$

where $\delta(x)$ is the Dirac delta function. We have used the fact that

$$\sum_n \delta(E - E_{1,n}) = \Gamma_1(E) = e^{S_1(E)/k_B}. \quad (9)$$

In the following, we drop the subscript 1 in the entropy when S is clearly referred to the entropy of the system.

Both E and S are extensive quantities, i.e. $E, S \propto N$. They are overwhelmingly large in a typical system where $N \sim 10^{23}$. This allows us to use the saddle point approximation to simplify the integral.

The saddle point approximation is a general method to approximate integrals of the following form

$$I = \int_{-\infty}^{+\infty} dx e^{-f(x)} \approx \int_{-\infty}^{+\infty} dx e^{-f(x_0) - \frac{1}{2} f''(x_0)(x-x_0)^2} = e^{-f(x_0)} \sqrt{\frac{2\pi}{f''(x_0)}}, \quad (10)$$

where we have expanded $f(x)$ around the saddle point x_0 , i.e., the point where $f'(x_0) = 0$. The approximation is valid because if the exponential decays so fast around its minimum that only its value around the minimum contributes significantly to the integral.

Insert Eq. (10) into (8), and denote $F(E) = E - TS(E)$, we have

$$Z = e^{-\beta F(E_0)} \sqrt{\frac{2\pi}{-T \frac{\partial^2 S}{\partial E^2}(E_0)}}, \quad (11)$$

where E_0 is the solution to

$$F'(E_0) = 1 - T \frac{\partial S}{\partial E}(E_0) = 0. \quad (12)$$

We make several comments to the above result:

1. Physically, the saddle point approximation means the Boltzmann distribution is extremely sharply peaked. Averaging over states with the most probable energy is as good as averaging over all the states.
2. Combining Eq. (12) with (3), it follows

$$\frac{1}{T} = \frac{\partial S_2}{\partial E} = \frac{\partial S_1}{\partial E}. \quad (13)$$

Therefore T is indeed the usual thermodynamic temperature: Two systems that are in thermal equilibrium share the same temperature.

3. Note that $F(T) = E_0(T) - TS(E_0(T)) = \tilde{F}(T, E_0(T))$ is exactly the Helmholtz free energy. (Here we have slightly abused the notation. When E_0 is fixed by Eq. (12), F is ultimately a function of T . $\tilde{F}(x, y) = y - xS(y)$ is a formal expression of F to emphasize the functional form and the variable dependency of F .) The system minimizes the free energy to reach the thermal equilibrium.
4. Taking the logarithm of both sides of Eq. (11),

$$\ln Z = -\beta F + \frac{1}{2} \ln(2\pi) - \frac{1}{2} \ln \left(-T \frac{\partial^2 S}{\partial E^2} \right). \quad (14)$$

Since F is extensive $F \propto N$ while $\partial^2 S / \partial E^2 \propto 1/N$, we can neglect the last two terms. We end up having

$$F = -\frac{1}{\beta} \ln Z = -k_B T \ln Z. \quad (15)$$

Partition function is directly related to the free energy of the system.

2 Thermodynamic Quantities

2.1 Thermodynamic Approach

We can compute all the thermodynamic quantities from the state function of the system. Below is some standard exercises in the thermodynamics.

In the microcanonical ensemble, the state function is the entropy $S(U, V)$. We already know the temperature is defined as

$$T = \left(\frac{\partial S}{\partial U} \right)_V^{-1}. \quad (16)$$

To compute the pressure of the system, consider an adiabatic expansion process,

$$0 = dS = \left(\frac{\partial S}{\partial U} \right)_V dU + \left(\frac{\partial S}{\partial V} \right)_U dV = \left[-\frac{p}{T} + \left(\frac{\partial S}{\partial V} \right)_U \right] dV, \quad (17)$$

where we have used the fact $dU = -pdV$. Thus

$$p = T \left(\frac{\partial S}{\partial V} \right)_U. \quad (18)$$

In the canonical ensemble, the state function is the free energy $F(T, V)$. Let us first compute the its first order derivatives,

$$\left(\frac{\partial F}{\partial T} \right)_V = \left(\frac{\partial \tilde{F}}{\partial E} \right)_{T,V} \Big|_{E=E_0} \frac{dE}{dT} + \left(\frac{\partial \tilde{F}}{\partial T} \right)_V = -S, \quad (19)$$

$$\left(\frac{\partial F}{\partial V} \right)_T = \left(\frac{\partial \tilde{F}}{\partial E} \right)_{T,V} \Big|_{E=E_0} \frac{dE}{dV} + \left(\frac{\partial \tilde{F}}{\partial V} \right)_T = -T \left(\frac{\partial S}{\partial V} \right)_E = -p. \quad (20)$$

This can be summarized by the familiar differential relation $dF = -SdT - pdV$.

The total energy of the system can be computed by

$$E_0 = F + TS(E_0, V) = F - T \left(\frac{\partial F}{\partial T} \right)_V. \quad (21)$$

Finally, let us compute one of the second order derivatives. The heat capacity of the system is

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = \left(\frac{\partial F}{\partial T} \right)_V + S + T \left(\frac{\partial S}{\partial T} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V. \quad (22)$$

2.2 Statistical Approach

The thermodynamic quantities can also be computed directly from the ensemble. The expectation value of any quantity X , denoted as $\langle X \rangle$ can be computed directly by

$$\langle X \rangle = \sum_n X_n P_n, \quad (23)$$

where $P_n = e^{-\beta E_n} / Z$ is the Boltzmann distribution.

As an example, we compute the expectation of the energy:

$$\langle E \rangle = \sum_n E_n P_n = \sum_n \frac{E_n e^{-\beta E_n}}{Z} = \sum_n \frac{-\frac{\partial}{\partial \beta} e^{-\beta E_n}}{Z} = \frac{-\frac{\partial}{\partial \beta} Z}{Z} = -\frac{\partial}{\partial \beta} \ln Z. \quad (24)$$

To see Eq. (24) is equivalent to (21), insert Eq. (15). It follows

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z = -\frac{\partial}{\partial \beta} \beta F = F + \beta \frac{\partial F}{\partial \beta} = F - T \frac{\partial F}{\partial T} = E_0. \quad (25)$$

This is within our expectation since the Boltzmann distribution is sharply peaked. The most probable energy should be the same as the average energy.

2.3 Example: Quantum Harmonic Oscillator

The energy level of a quantum harmonic oscillator is

$$E_n = \left(n + \frac{1}{2} \right) \hbar \omega, \quad (26)$$

where $n = 0, 1, 2, \dots$. Let us assume the oscillator is in thermal equilibrium with a heat bath of temperature T . The partition function is

$$Z = \sum_{n=0}^{\infty} e^{-\beta E_n} = e^{-\beta \epsilon/2} \sum_{n=0}^{\infty} e^{-n\beta \epsilon} = \frac{e^{-\beta \epsilon/2}}{1 - e^{-\beta \epsilon}} = \frac{1}{2 \sinh(\beta \epsilon/2)}, \quad (27)$$

where we have defined $\epsilon \equiv \hbar \omega$. Straightforward computation gives the energy expectation

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = \frac{\epsilon}{2} \coth \left(\frac{\beta \epsilon}{2} \right), \quad (28)$$

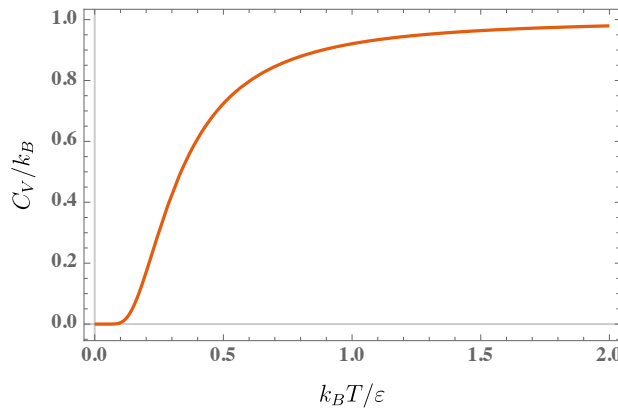
and the heat capacity

$$C_V = \frac{\partial \langle E \rangle}{\partial T} = k_B \left(\frac{\beta \epsilon}{2} \right)^2 \frac{1}{\sinh^2 \left(\frac{\beta \epsilon}{2} \right)} = k_B \left(\frac{\epsilon}{2k_B T} \right)^2 \frac{1}{\sinh^2 \left(\frac{\epsilon}{2k_B T} \right)}. \quad (29)$$

Although the final result looks complicated, it is worthwhile to consider two limits:

- Low temperature $k_B T \ll \epsilon$. When $x \gg 1$, $\sinh x \approx e^x/2$. Therefore $C_V \sim k_B \exp(-\epsilon/k_B T)$ decays exponentially with inverse temperature.
- High temperature $k_B T \gg \epsilon$. When $x \ll 1$, $\sinh x \approx x$. Therefore $C_V \sim k_B$ is a constant.

The plot of C_V as a function of $k_B T/\epsilon$ confirms the above results.



3 Energy Cost of Information

3.1 Flexible Chain

Consider a flexible chain with N links. Each link can independently point right or left. There is no interaction between the links. The length of the chain is $L = N_R - N_L$, where $N_{R/L}$ is the number of links pointing right/left.

Although the chain has zero internal energy, it does have entropy as a function of the chain length L . Let us consider two limits.

- $L = 0$. In this case $N_R = N_L = L/2$. The entropy is

$$S(L = 0) = k_B \ln \frac{N!}{N_R!N_L!} = k_B \left(N \ln N - 2 \frac{N}{2} \ln \frac{N}{2} \right) = k_B N \ln 2, \quad (30)$$

where we have used the Stirling approximation $\ln N! \approx N \ln N$.

- $L = N$. In this case $N_R = N$ and $N_L = 0$. The entropy is $S(L = N) = k_B \ln 1 = 0$.

Now, suppose the chain is in thermal equilibrium with a heat bath of temperature T . What is the energy cost of stretching the chain from $L = 0$ to $L = N$, assuming the stretching is a reversible process such that during the whole process the chain is in thermal equilibrium with the bath? The answer is that

$$\Delta E_{\text{bath}} = T \Delta S_{\text{bath}} = k_B T N \ln 2. \quad (31)$$

It is the same as the free energy change of the system:

$$\Delta F = F(N) - F(0) = T(S(0) - S(N)) = k_B T N \ln 2. \quad (32)$$

We make several comments to the above result:

1. There is an energy cost of information (decreasing the entropy);
2. The system tends to lower the free energy by shrinking;
3. When stretching the chain, there is effectively a restoring force $f \equiv -\partial F/\partial L$. This type of force is called the “entropic force”.

3.2 Hard Disk

Setting a random bit on the hard disk to a particular value decreases the entropy of the hard disk by $k_B \ln 2$, which costs free energy $k_B T \ln 2$ if the hard disk is in thermal equilibrium with temperature T . This sets a theoretical power consumption bound for information writing.

A typical today’s hard disk has power about $P = 1\text{W}$. By the above bound, at room temperature it can write

$$N = \frac{P}{k_B T \ln 2} \sim \frac{1}{1.38 \times 10^{-23} \cdot 300 \cdot 0.7} \sim 10^{22} \text{bit/s} \sim 10^8 \text{TB/s}. \quad (33)$$

While in reality the writing speed is of order 1GB/s. There is huge room for improving the efficiency of our hard disks.

The similar principle is also applicable to irreversible computation.