

# 8.08 Statistical Physics II — Spring 2019

## Recitation Note 3

Huitao Shen  
huitao@mit.edu

Feb 25, 2019

### Contents

<b>1</b>	<b>Equivalence of Ensembles</b>	<b>2</b>
1.1	Case Study: Spin 1/2 in the Magnetic Field . . . . .	2
1.2	Energy Fluctuations in the Canonical Ensemble . . . . .	3
<b>2</b>	<b>Adiabatic Demagnetization Revisited</b>	<b>3</b>
<b>3</b>	<b>Diatomic Ideal Gas</b>	<b>4</b>

# 1 Equivalence of Ensembles

We have already learned the microcanonical ensemble and the canonical ensemble.

The microcanonical ensemble is an ensemble of isolated systems. The entropy as a function of the total energy  $S(E)$  fully determines the thermodynamic property of the system.

The canonical ensemble is an ensemble of systems in contact with a large heat bath. The free energy as a function of the temperature  $F(T)$  fully determines the thermodynamic property of the system.

Although the two ensembles are seemingly very different, the thermodynamic property of a system is independent of which ensemble is used to model it in the thermodynamic limit.

## 1.1 Case Study: Spin 1/2 in the Magnetic Field

We demonstrate the equivalence by considering  $N$  spins with  $S = 1/2$  in the magnetic field. The Hamiltonian is  $H = \sum_{i=1}^N g\mu_B B S_i^z$ .

1. Microcanonical ensemble. Suppose the total energy of the system is  $E$ . It follows

$$E = \frac{\Delta}{2}(n_{\uparrow} - n_{\downarrow}) = \frac{\Delta}{2}(2n_{\uparrow} - N), \quad (1)$$

where  $\Delta \equiv g\mu_B B$  is the energy gap of the system and we have used  $N = n_{\uparrow} + n_{\downarrow}$ . The entropy of the system is

$$S(E) = k_B \ln \binom{N}{n_{\uparrow}} \approx k_B [N \ln N - n_{\uparrow} \ln n_{\uparrow} - (N - n_{\uparrow}) \ln(N - n_{\uparrow})]. \quad (2)$$

The temperature is

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{1}{\Delta} \frac{\partial S}{\partial n_{\uparrow}} = \frac{k_B}{\Delta} \ln \frac{N - n_{\uparrow}}{n_{\uparrow}} = \frac{k_B}{\Delta} \ln \frac{N/2 - E/\Delta}{N/2 + E/\Delta}, \quad (3)$$

which can be simplified as

$$E = -\frac{N\Delta}{2} \tanh\left(\frac{\beta\Delta}{2}\right). \quad (4)$$

After some algebra, one can further combine Eq. (1), (2) and (4) to rewrite entropy as a function of temperature:

$$S = Nk_B \left[ \ln 2 + \ln \cosh\left(\frac{\Delta\beta}{2}\right) - \frac{\Delta\beta}{2} \tanh\left(\frac{\Delta\beta}{2}\right) \right]. \quad (5)$$

2. Canonical ensemble. The partition function is

$$Z = (e^{-\beta\Delta/2} + e^{\beta\Delta/2})^N = 2^N \cosh\left(\frac{\Delta\beta}{2}\right). \quad (6)$$

The average energy is

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = -\frac{N\Delta}{2} \tanh\left(\frac{\Delta\beta}{2}\right), \quad (7)$$

which is consistent with Eq. (3). The average entropy is

$$S = -\frac{\partial F}{\partial T} = Nk_B \left[ \ln 2 + \ln \cosh\left(\frac{\Delta\beta}{2}\right) - \frac{\Delta\beta}{2} \tanh\left(\frac{\Delta\beta}{2}\right) \right], \quad (8)$$

which is consistent with Eq. (5).

Several comments are given in order:

- To compute the thermodynamic property of a system in contact with a heat bath  $T$ , one can use the microcanonical ensemble, as long as the total energy is correctly identified through  $E(T)$ , which in the above example is given by Eq. (4).
- Conversely, to compute the thermodynamic property of an isolated system, one can use the canonical ensemble, as long as the temperature is correctly identified through  $T(E)$ , which in the above example is given by Eq. (3).
- Since the two ensembles are “equivalent” (more about the meaning of “equivalence” in the next section), we are free to choose whichever ensemble that is computationally easier. In the above example, both approaches are easy. In the first problem of pset 1 (defects in a crystal), using a microcanonical ensemble is easier because summing the partition function there is hard. Later in this course we will see some examples when doing the summation is actually easier.

## 1.2 Energy Fluctuations in the Canonical Ensemble

The energy in the microcanonical ensemble is a constant, while the energy in the canonical ensemble is a random variable. We just showed that by choosing the proper temperature, one can make  $\langle E \rangle(T) = E$ , such that the two ensembles gives the same thermodynamic property of the system. It is natural to ask the question: What is the variance/fluctuation of  $E$  in the canonical ensemble?

Note that  $\text{Var}(E) = \langle E^2 \rangle - \langle E \rangle^2$ . To compute  $\langle E^2 \rangle$ , we use the same trick when deriving the expression of  $\langle E \rangle$ :

$$\langle E^2 \rangle = \sum_n E_n^2 P(E_n) = \frac{1}{Z} \sum_n E_n^2 e^{-\beta E_n} = \frac{1}{Z} \frac{\partial^2}{\partial \beta^2} e^{-\beta E_n} = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}. \quad (9)$$

Thus

$$\text{Var}(E) = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \left( -\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right)^2 = \frac{\partial}{\partial \beta} \left( \frac{1}{Z} \frac{\partial Z}{\partial \beta} \right) = -\frac{\partial \langle E \rangle}{\partial \beta} = k_B T^2 C_V. \quad (10)$$

Two comments come in order:

- The above equation is an example of the fluctuation-dissipation theorem, which relates the fluctuation (LHS) and the response of the system (RHS). In this way, we also prove  $C_V > 0$  always holds true.
- The relative energy fluctuation is

$$\frac{\Delta E}{E} = \frac{\sqrt{\text{Var}(E)}}{E} \propto \frac{1}{\sqrt{N}} \rightarrow 0, \text{ as } N \rightarrow \infty. \quad (11)$$

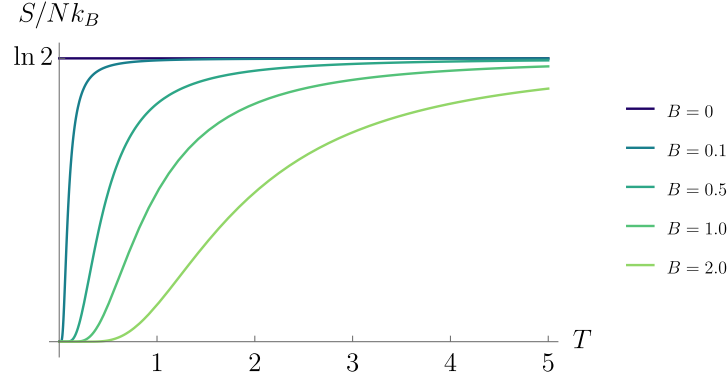
This means in the thermodynamic limit, the microcanonical ensemble and the canonical ensemble are strictly equivalent.

## 2 Adiabatic Demagnetization Revisited

We revisit the last problem in the second pset.

Consider  $N$  spin-1/2 spins in a magnetic field  $B$ . Initially, the system has a temperature  $T$ . If we slowly reduce the magnetic field to  $B/2$ , what becomes the temperature of the system? If we slowly reduce the magnetic field to zero, what becomes the temperature of the system? (Hint: the entropy remains unchanged in the above adiabatic process.)

We have already computed the entropy of this system in Eq. (5) and (8). It is instructive to plot the  $S(T)$  curve, where we have set  $g\mu_B/2k_B = 1$ :



- $B \neq 0$ . At zero temperature, all spins are antiparallel to the magnetic field. There is only one state, thus  $S \rightarrow 0$  as  $T \rightarrow 0$ . At high temperature, the magnetic field is irrelevant and spin directions are completely random, thus  $S \rightarrow Nk_B \ln 2$  as  $T \rightarrow \infty$ .
- $B = 0$ . Since there is no energy difference between spin states, spin directions are always completely random.

Start from any initial state  $(B_i, T_i)$ , when the magnetic field is reduced adiabatically, we are only allowed to move left horizontally on the  $S - T$  plot, so the temperature will decrease. Since entropy is only a function of  $\Delta\beta$ ,  $B/T = \text{const.}$  through out the process. Thus when  $B_f = B_i/2$ ,  $T_f = T_i/2$ . The temperature is lowered by reducing the magnetic field adiabatically.

The situation becomes problematic as  $B \rightarrow 0$ . When  $B = 0$ , the entropy is always  $k_B N \ln 2$  independent of the temperature. However, unless we start from  $T = \infty$ , the initial entropy is always smaller than this value. To resolve this issue, note that an adiabatic process must be a reversible process such that the entropy of the system does not increase due to irreversibility. This requires the system to be at thermal equilibrium all the time. Microscopically, this means the thermalization time  $\tau \rightarrow 0$ . However, the two limits  $B \rightarrow 0$  and  $\tau \rightarrow 0$  do not commute:

- If we take  $B \rightarrow 0$  first then  $\tau \rightarrow 0$ , the system cannot thermalize, which means the even when  $B = 0$  and  $\Delta = 0$ , the spin distribution is not completely random and depends on the previous direction of  $B$  when  $B \neq 0$ . The resulting state-energy distribution does not obey any distribution in the microcanonical/canonical ensemble. Therefore, one can say the system is not in thermal equilibrium and the temperature is not well-defined.
- If we take  $\tau \rightarrow 0$  first then  $B \rightarrow 0$ , the system indeed thermalizes and extracts entropy from the environment. Therefore, the adiabatic condition is violated.

### 3 Diatomic Ideal Gas

Previously, we have studied monoatomic ideal gas. We now consider diatomic ideal gas, which involves internal degrees of freedom. The Hamiltonian of diatomic gas is

$$H_N = \sum_{i=1}^N \left[ \frac{\mathbf{p}_{A,i}^2}{2m_A} + \frac{\mathbf{p}_{B,i}^2}{2m_B} + \frac{k}{2} (\mathbf{x}_{A,i} - \mathbf{x}_{B,i})^2 \right], \quad (12)$$

where the attractive interaction is expanded around the minimum of the interatomic potential. Note that we only consider the interaction within a molecule and neglect the inter-molecule interaction. In this way, the partition function factorizes as  $Z = Z_1^N / N!$ .

To compute the partition function of a single molecule, we rewrite the Hamiltonian in the center-of-mass frame. Define

$$\mathbf{R} \equiv \frac{\mathbf{x}_A m_A + \mathbf{x}_B m_B}{m_A + m_B}, \quad \mathbf{r} \equiv \mathbf{x}_A - \mathbf{x}_B, \quad (13)$$

the Hamiltonian becomes

$$H = \frac{\mathbf{p}_{\mathbf{R}}^2}{2M} + \frac{\mathbf{p}_{\mathbf{r}}^2}{2\mu} + \frac{kr^2}{2}, \quad (14)$$

where total mass  $M \equiv m_A + m_B$  and reduced mass  $1/\mu \equiv 1/m_A + 1/m_B$ . The center of mass motion is represented by  $H_{\text{trans}} = \mathbf{p}_{\mathbf{R}}^2/2M$ . The remaining terms represents the internal degrees of freedom of the molecule. To this end, it is convenient to switch to the spherical coordinate  $\mathbf{r} = (r \sin \theta \cos \varphi, r \sin \theta \sin \varphi, r \cos \theta)$ , such that

$$\frac{\mathbf{p}_{\mathbf{r}}^2}{2\mu} + \frac{kr^2}{2} = \frac{\mu}{2}(\dot{r}^2 + r^2\dot{\theta}^2 + r^2 \sin^2 \theta \dot{\varphi}^2) + \frac{kr^2}{2} = \underbrace{\frac{1}{2I}(p_{\theta}^2 + \frac{p_{\varphi}^2}{\sin^2 \theta})}_{H_{\text{rot}}} + \underbrace{\frac{p_r^2}{2\mu} + \frac{kr^2}{2}}_{H_{\text{vib}}}, \quad (15)$$

where we have decomposed the internal degrees of freedom into a rotation part and a vibration part. Here  $I \equiv \mu \langle r^2 \rangle$  is the moment of inertia of the molecule<sup>1</sup>.

To summarize,  $H = H_{\text{trans}} + H_{\text{rot}} + H_{\text{vib}}$  and the partition function also factorizes out as  $Z_1 = Z_{\text{trans}} Z_{\text{rot}} Z_{\text{vib}}$ . We now consider each term separately.

- Translation.  $H_{\text{trans}}$  is identical to the Hamiltonian of monoatomic ideal gas. Thus

$$Z_{\text{trans}} = \frac{V}{\lambda_T^3}, \quad (16)$$

where  $\lambda_T = \sqrt{2\pi\hbar^2/Mk_B T}$ . The heat capacity is  $C_{V,\text{trans}} = 3k_B/2$ .

- Vibration.  $H_{\text{vib}}$  is the Hamiltonian of a harmonic oscillator. At low temperature, it should be treated quantum mechanically. We have already computed this in the previous recitation, and the partition function is

$$Z_{\text{vib}} = \sum_{n=0}^{\infty} \exp \left[ - \left( n + \frac{1}{2} \right) \beta \hbar \omega \right] = \frac{\exp(-\Theta_v/2T)}{1 - \exp(-\Theta_v/T)}, \quad (17)$$

where  $\omega \equiv \sqrt{k/\mu}$  and we have defined the characteristic temperature of vibration  $\Theta_v \equiv \hbar\omega/k_B$ .

At low temperature, the heat capacity decreases exponentially with temperature. At high temperature,  $C_{V,\text{vib}} = k_B$  because of the existence of both kinetic energy and potential energy.

At high temperature, the system can also be treated semiclassically, giving the partition function:

$$Z_{\text{vib}} = \frac{1}{h} \int_{-\infty}^{+\infty} dp \exp \left( -\frac{\beta p^2}{2\mu} \right) \int_{-\infty}^{+\infty} dx \exp \left( -\frac{\beta k x^2}{2} \right) = \frac{k_B T}{\hbar \omega}. \quad (18)$$

Note the similarity between  $Z_{\text{vib}}$  at high temperature and  $Z_{\text{trans}}$ .

- Rotation.  $H_{\text{rot}}$  is the Hamiltonian of a rigid rotor. At low temperature, it should be treated quantum mechanically. After quantization (See this [wikipedia page]), the rotation energy level is

$$E_l = \frac{\hbar^2}{2I} l(l+1), \quad (19)$$

where the angular momentum  $l = 0, 1, \dots$ . Each level has degeneracy of  $g_l = 2l + 1$ . The partition function is then

$$Z_{\text{rot}} = \sum_{l=0}^{\infty} (2l+1) \exp \left( -l(l+1) \frac{\Theta_r}{T} \right), \quad (20)$$

where we have defined the characteristic temperature of rotation  $\Theta_r \equiv \hbar^2/2Ik_B$ . This summation cannot be performed analytically. At low temperature, one can simply preserve the first two terms in the summation. The

<sup>1</sup>Here we actually used an approximation to treat  $I$  as a constant. Otherwise  $H_{\text{rot}}$  and  $H_{\text{vib}}$  are correlated.

system should behave similarly as a harmonic oscillator at low temperature. The heat capacity should thus decrease exponentially.

At high temperature, the spectrum can be approximated as a continuum:

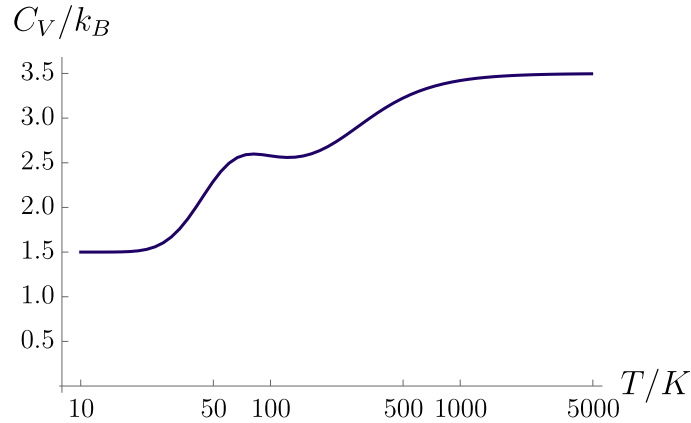
$$Z_{\text{rot}} \approx \int_0^{\infty} dl(2l+1) \exp\left(-l(l+1)\frac{\Theta_r}{T}\right) = \int_0^{\infty} d(l(l+1)) \exp\left(-l(l+1)\frac{\Theta_r}{T}\right) = \frac{T}{\Theta_r}. \quad (21)$$

At high temperature, the system can also be treated semiclassically:

$$Z_{\text{rot}} = \frac{1}{h^2} \int_0^{2\pi} d\varphi \int_{-\infty}^{+\infty} dp_{\theta} \exp\left(-\frac{\beta p_{\theta}^2}{2I}\right) \int_0^{\pi} d\theta \int_{-\infty}^{+\infty} dp_{\varphi} \exp\left(-\frac{\beta p_{\varphi}^2}{2I \sin^2 \theta}\right) = \frac{2I}{\beta h^2} = \frac{T}{\Theta_r}, \quad (22)$$

yielding the same result. Note the similarity between  $Z_{\text{rot}}$  at high temperature and  $Z_{\text{trans}}$ . The heat capacity at high temperature is thus  $C_{V,\text{rot}} = k_B$ .

For a typical diatomic molecule  $\Theta_r \approx 10 - 100\text{K}$  while  $\Theta_v \approx 10^3\text{K}$  (try to estimate these number by yourself!). Therefore the  $C_V - T$  curve for diatomic gas has the following form:



When the temperature becomes even higher, the atomic bonding between the atoms breaks (in other words, the harmonic approximation in the Hamiltonian Eq. (12) fails), and a diatomic molecule becomes two monoatomic molecules, whose heat capacity in total is  $3k_B/2 \cdot 2 = 3k_B$ . The heat capacity decreases compared with the fully excited diatomic gas!