Tutorial 3, Statistical Mechanics: Concepts and applications
2019/20 ICFP Master (first year)

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Tutorial exercises

1. **Two level system.** *[Source: Problem 6.3 from Statistical Mechanics 2nd edition by Kerson Huang, 1987]*

   Consider a system of N free particles in which the energy of each particle can assume two and only two distinct values 0 and ϵ ($\epsilon > 0$). Denote by n_0 and n_1, the occupation numbers of the energy level 0 and ϵ, respectively. The total energy of the system is E.

   HINT # 1: Use ϵ as the unit of energy (i.e., set ϵ to 1) to simplify your expressions.

   HINT # 2: You may find Stirling's approximation useful:

$$\ln x! \approx x \ln x - x$$

   (a) Find the entropy of such a system.

   (b) Find the temperature as a function of E, and show that it can be negative. What happens when a system of negative temperature is allowed to exchange energy with a system of positive temperature?

: *(a)* $n_1 = E$; $n_0 = N - E$

Number of ways to choose n_1 particles out of N is the binomial coefficient

$$\binom{N}{n_1} = \frac{N!}{n_1!(N-n_1)!}$$

Using Stirling's approximation,

$$\frac{S}{k} = N \ln N - E \ln E - (N-E)\ln(N-E)$$

(b)

$$\frac{1}{T} = \ln \frac{N-E}{E}$$

$T < 0$ when $N/E < 2$: temperature is negative when there are more particles in the upper energy level E than in the lower level, 0. When put in thermal contact with a $T > 0$ system, the system with $T < 0$ will increase its temperature by (counterintuitively!) increasing the number of particles in the lower energy level n_0.

2. **Pauling residual entropy.** *[Source: Pauling, J. Am. Chem. Soc.* **12** *(2680-2684), 1935.]*

   Water molecules in ice are arranged in such a way that for every oxygen atom, there are two hydrogen atoms nearby, and two further away from it, as shown in Fig. 1(A). In 1935 Pauling used this to estimate the value of **residual entropy** - a nonzero value of entropy that systems, which can take multiple configurations at or near absolute zero, are said to have.

   (a) Estimate the value of residual entropy for an ice block containing N water molecules.

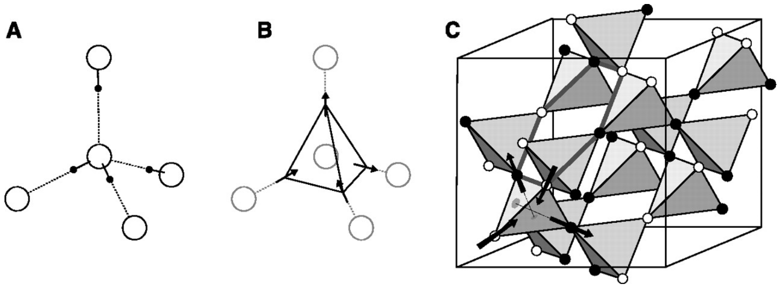

FIG. 1. (A) Local arrangement in water ice, showing oxygen ions (large white circles) and hydrogen ions (small black circles). (B) The corresponding picture for spin ice. (C) Pyrochlore lattice of corner-sharing tetrahedra, as occupied by the magnetic rare-earth ions in the spin ice materials $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$. *Source: Bramwell, Gingras, Science* **294** *(1495-1501), 2001.*

This problem came to a new light in 1999, when Ramirez and collaborators found that a rare-earth magnetic compound, $Dy_2Ti_2O_7$, reached the same value of residual entropy as water ice as the temperature tended towards zero. The source of the ground state degeneracy comes from the similar so-called ice-rule, which states that for every tetrahedron, making up the pyrochlore lattice [Fig. 1(C)] that Dy ions live on, there are two magnetic moments pointing in, and two pointing out [Fig. 1(B)].

: *Each of 4 hydrogens has 2 possible positions with respect to a given oxygen* → *16 ways to arrange all four*
Only 6 out of 16 ways satisfy the 2-near 2-far condition → $\frac{6}{16} = \frac{3}{8}$ *of configurations are permitted*
We can approximate the number of possible configurations for N water molecules ($2N$ hydrogen atoms) as

$$\left(\frac{3}{8}\right)^N \left(2^{2N}\right) = \left(\frac{3}{2}\right)^N .$$

Therefore, $S = Nk \ln \frac{3}{2}$.

3. **Pressure.**

Reminder: There is an important relation between the thermodynamic energy $\bar{E}$ and the system Hamiltonian $E\left(\{q\},\{p\},\lambda\right)$:

$$\overline{\frac{\partial E\left(\{q\},\{p\},\lambda\right)}{\partial \lambda}} = \left.\frac{\partial \bar{E}}{\partial \lambda}\right|_S , \tag{1}$$

where λ is a parameter and the second derivative is performed at fixed entropy S.

Consider a given body and an external force acting on it. Let the external parameter λ in Eq. (1) be $\vec{r}$, the radius of some surface element $d\vec{s}$. The force acting on that surface element is then given by

$$\vec{F} = -\frac{\partial E\left(\{q\},\{p\},\vec{r}\right)}{\partial \vec{r}} . \tag{2}$$

(a) Find the mean force on a surface element. The magnitude of the force per unit area is called the **pressure**.

Hint: Change in volume is given by $d\vec{s} \cdot d\vec{r}$

(b) Consider two parts, in contact with one another, of a closed system in equilibrium. What can you say about the pressures of the two parts, P_1 and P_2?

: *(a)*

$$\bar{F} = -\overline{\frac{\partial E\left(\{q\},\{p\},\vec{r}\right)}{\partial \vec{r}}} = -\left.\frac{\partial \bar{E}}{\partial \vec{r}}\right|_S = \left.\frac{\partial \bar{E}}{\partial V}\right|_S \frac{\partial V}{\partial \vec{r}}$$

$$\bar{F} = \left.\frac{\partial \bar{E}}{\partial V}\right|_S d\vec{s}$$

Pressure is given by

$$P = \left.\frac{\partial \bar{E}}{\partial V}\right|_S$$

(b) $V_1 + V_2 =$ *constant. In equilibrium, entropy is maximized - also with respect to changes in, e.g.,* V_1*:*

$$\frac{\partial S}{\partial V_1} = \frac{\partial S_1}{\partial V_1} + \frac{\partial S_2}{\partial V_2}\frac{\partial V_2}{\partial V_1} = \frac{\partial S_1}{\partial V_1} - \frac{\partial S_2}{\partial V_2} = 0$$

$$dE = TdS - PdV$$

$$dS = \frac{dE}{T} + \frac{P}{T}dV$$

$$\frac{\partial S}{\partial V} = \frac{P}{T}$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

Since $T_1 = T_2$ *in thermal equilibrium, the condition for mechanical equilibrium is* $P_1 = P_2$.

4. **Maxwell distribution.**

(a) Derive the probability distribution for the momentum of a non interacting particle.

(b) What is the mean kinetic energy of the particle?

(c) Find the mean square fluctuation of the velocity.

: *(a) Gibbs distribution (setting $k = 1$):*

$$\rho(\{q\}, \{p\}) = Ae^{-E(\{q\},\{p\})/T} \tag{3}$$

where A is found from the normalization condition $\int \rho \quad dpdq = 1$.
For a non interacting particle, there is only kinetic energy $E = (p_x^2 + p_y^2 + p_z^2)/2m$. Substitute this energy into Eq. (3) and use the Gaussian integral

$$\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}} \tag{4}$$

to find the normalization constant A. This results in the following momentum probability distribution:

$$dw_{\vec{p}} = \frac{1}{(2\pi mT)^{3/2}} e^{-(p_x^2+p_y^2+p_z^2)/2mT} dp_x dp_y dp_z. \tag{5}$$

(b) To find the mean kinetic energy, take a $\partial/\partial\alpha$ of Eq. (4):

$$\int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx = -\frac{\partial}{\partial\alpha} \int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}} \frac{1}{2\alpha}. \tag{6}$$

$$\bar{p}_x^2 = \frac{1}{\sqrt{2\pi mT}} \int_{-\infty}^{\infty} p_x^2 e^{-p_x^2/2mT} dp_x = Tm \tag{7}$$

Therefore, the mean kinetic energy is $3 \times p_x^2/2m = 3T/2$.
(c)

$$\langle(\Delta v)^2\rangle = \overline{v^2} - \bar{v}^2 \tag{8}$$

The first term was calculated in part (b) and is equal to $3T/m$. For the second term, remember that the calculation needs to be carried out for the absolute value *of the velocity - i.e., the limits of integration are from 0 to ∞. One can derive a useful general expression for integrals of the form $\int_0^\infty x^n e^{-\alpha x^2} dx$ using substitution of variables $y = \alpha x^2$:*

$$\int_0^{\infty} x^n e^{-\alpha x^2} dx = \frac{1}{2} \alpha^{-(n+1)/2} \Gamma\left(\frac{1}{2}(n+1)\right). \tag{9}$$

$$\langle(\Delta v)^2\rangle = \frac{T}{m}\left(3 - \frac{8}{\pi}\right)$$