

# PHYS 427 - Thermal and Statistical Physics - Discussion 04

Feb 18, 2025

Last week we introduced thermodynamics in the **canonical ensemble**. In this formalism, the probability that a system is in microstate " $i$ " is given by

$$p_i = \frac{e^{-\beta \varepsilon_i}}{Z} \quad (1)$$

where  $\varepsilon_i$  is the energy of the system in state " $i$ ",  $\beta \equiv 1/k_B T$ , and  $Z$  is the **partition function**:

$$Z \equiv \sum_i e^{-\beta \varepsilon_i} \quad (2)$$

When carrying out calculations in the canonical ensemble, it turns out to be useful to work with a so-called "thermodynamic potential" known as the **Helmholtz free energy**:

$$F \equiv U - TS \quad (3)$$

The Helmholtz free energy takes on a particularly nice form in the canonical ensemble. One can show from the definition of  $U (= \sum_i p_i \varepsilon_i)$  and  $S (= -k_B \sum_i p_i \ln p_i)$  that

$$F = -k_B T \ln Z \quad (4)$$

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1. **Helmholtz free energy**: In our previous studies of closed systems, the entropy was naturally expressed as a function of the energy, volume, particle number, etc.:

$$S = S(U, V, N, \dots). \quad (5)$$

We defined temperature  $T$ , pressure  $p$  and chemical potential  $\mu$  as derivatives of the entropy:

$$\frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_{V,N} \quad p = T \left( \frac{\partial S}{\partial V} \right)_{U,N} \quad \mu = -T \left( \frac{\partial S}{\partial N} \right)_{U,V}. \quad (6)$$

When  $U$ ,  $V$  and  $N$  change by small amounts  $dU$ ,  $dV$  and  $dN$ , the corresponding change in  $S(U, V, N)$  is, by the chain rule,

$$dS = \left( \frac{\partial S}{\partial U} \right)_{V,N} dU + \left( \frac{\partial S}{\partial V} \right)_{U,N} dV + \left( \frac{\partial S}{\partial N} \right)_{U,V} dN \quad (7)$$

$$= \frac{1}{T} dU + \frac{p}{T} dV - \frac{\mu}{T} dN. \quad (8)$$

This is called the **fundamental thermodynamic relation** (FTR) and it's commonly rearranged as

$$\boxed{dU = T dS - p dV + \mu dN.} \quad (9)$$

- (a) Using the FTR, derive an expression for  $dF$ . Conclude that the Helmholtz free energy is naturally expressed as a function of  $T$ ,  $V$  and  $N$
  - (b) Express  $S$ ,  $p$  and  $\mu$  as derivatives of the Helmholtz free energy.
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2. **Two-state systems:** The simplest (non-trivial) quantum systems are two-state systems. Examples of these systems include a particle with a spin-1/2 degree of freedom, a photon with two polarization states, a neutrino oscillating between two of its flavours (e.g. electron and muon), a qubit in quantum computing, and more!

Consider a lattice of  $N$  sites. At each site there is a two-state system with states  $|0\rangle$  and  $|1\rangle$  whose energies are 0 and  $\Delta$  respectively (assume the two-state systems don't interact with one another). The system is in thermal equilibrium with a heat bath at temperature  $T$ .

- (a) Compute the partition function of the system:  $Z(T, N)$ .
- (b) Compute the Helmholtz free energy of the system:  $F(T, N) = -k_B T \ln Z$ .
- (c) From the Helmholtz free energy, compute the entropy:  $S = -(\partial F / \partial T)_N$ .
- (d) From the Helmholtz free energy, compute the chemical potential:  $\mu = (\partial F / \partial N)_T$ .
- (e) Compute the energy of the system using the following two approaches:
  - i. The standard approach in the canonical ensemble:  $U = -\frac{\partial}{\partial \beta} \ln Z$ .
  - ii. The definition of the Helmholtz free energy:  $F = U - TS$ .

Your two answers should agree!

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Unlike quantum mechanics, in classical mechanics one can simultaneously specify the position  $\vec{x}$  and momentum  $\vec{p}$  of a particle. The partition function of a classical particle in  $D$ -dimensions is given by

$$Z = \int \frac{d^D x d^D p}{(2\pi\hbar)^D} e^{-\beta H(\vec{x}, \vec{p})} \quad (10)$$

where  $H(\vec{x}, \vec{p})$  is the particle's Hamiltonian and we denote the manifold with coordinates  $\{x_1, \dots, x_D, p_1, \dots, p_D\}$  as **phase space**. The factor of  $2\pi\hbar$  is necessary in order to keep the partition function dimensionless — one can see this factor arise by starting with the quantum partition function and then treating the position and momentum as commuting operators in the so-called "classical limit":  $\hbar \rightarrow 0$ . Regardless, multiplying the partition function by a constant won't affect our results as we ultimately take derivatives of  $\ln Z$ .

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3. **3D classical harmonic oscillator:** Consider a classical system with a three-dimensional oscillator in thermal equilibrium with a reservoir at temperature  $T$ . The oscillator's Hamiltonian is  $H(\vec{x}, \vec{p}) = \frac{1}{2m} \vec{p}^2 + \frac{1}{2} m \omega^2 \vec{x}^2$ .

- (a) Show the partition function of the oscillator is

$$Z = \left( \frac{k_B T}{\hbar \omega} \right)^3 \quad (11)$$

- (b) Compute the energy of the oscillator and check that your answer agrees with the equipartition theorem.

- (c) The probability that the oscillator will occupy a small region in phase space about the point  $(\vec{x}, \vec{p})$  is

$$P(\vec{x}, \vec{p}) = \frac{e^{-\beta H(\vec{x}, \vec{p})}}{Z} \frac{d^3x d^3p}{(2\pi\hbar)^3} \quad (12)$$

Integrate over the possible position values and momentum orientations of the oscillator. Thus, show that the probability the magnitude of the oscillator's momentum is between  $p$  and  $p + dp$  is given by

$$P(p) = 4\pi \left( \frac{1}{2\pi m k_B T} \right)^{3/2} p^2 \exp\left( -\frac{p^2}{2m k_B T} \right) dp \quad (13)$$


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