

# UWaterloo 2026 Winter PHYS359 - Statistical Mechanics

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# 1 Einstein Solid and Oscillators

Lecture on 5/1/2026 by ()�.

Consider

# 2 Stirling's Approximation

Lecture on 7/1/2026 by ()�.

**Definition 2.1** (Gamma Function). *The Gamma function is defined as*

$$\Gamma(n) = \int_0^\infty dt t^{n-1} e^{-t} \quad (1)$$

for  $n > 0$ .

The gamma function is related to the factorial function via  $\Gamma(n+1) = n!$  for integers  $n \geq 0$ . Consider

$$n! = \Gamma(n+1) = \int_0^\infty dt t^n e^{-t} = \int_0^\infty dt e^{n \ln t - t}. \quad (2)$$

Since the complexity of calculating the factorial function grows rapidly with  $n$ , we look for an approximation for large  $n$ . The integrand is sharply peaked around  $t = n$  for large  $n$  because the exponent  $n \log t - t$  attains its maximum there.

**Proposition 2.1** (Stirling). *For large  $n$ , we have*

$$n! = \sqrt{2\pi n} \left( \frac{n}{e} \right)^n \left( 1 + \frac{1}{12n} + O\left(\frac{1}{n^2}\right) \right). \quad (3)$$

In asymptotic notation, this is written as  $n! \sim \sqrt{2\pi n} e^{-n} n^n$ . The exponent  $n \log t - t$  may be Taylor expanded about  $t = n$  and write the remainder terms as . . . :

$$\begin{aligned} n \log t - t &= n \log \left( n \cdot \frac{t}{n} \right) - t \\ &= n \log n + n \log \left( 1 + \frac{t-n}{n} \right) - t \\ &= n \log n + n \left( \frac{t-n}{n} - \frac{1}{2} \left( \frac{t-n}{n} \right)^2 + \frac{1}{3} \left( \frac{t-n}{n} \right)^3 - \frac{1}{4} \left( \frac{t-n}{n} \right)^4 + \dots \right) - t \\ &= n \log n - n - \frac{1}{2n}(t-n)^2 + \frac{1}{3n^2}(t-n)^3 - \frac{1}{4n^3}(t-n)^4 + \dots . \end{aligned} \quad (4)$$

Then, the integral becomes

$$\begin{aligned} n! &= \int_0^\infty dt e^{n \log n - n} e^{-\frac{1}{2n}(t-n)^2} e^{\frac{1}{3n^2}(t-n)^3} e^{-\frac{1}{4n^3}(t-n)^4} \dots \\ &= n^n e^{-n} \int_0^\infty dt e^{-\frac{1}{2n}(t-n)^2} e^{\frac{1}{3n^2}(t-n)^3} e^{-\frac{1}{4n^3}(t-n)^4} \dots \\ &= n^n e^{-n} \int_0^\infty dt e^{-\frac{1}{2n}(t-n)^2} \left( 1 + \frac{1}{3n^2}(t-n)^3 - \frac{1}{4n^3}(t-n)^4 + \dots \right) \\ &= n^n e^{-n} \left\{ \int_0^\infty dt e^{-\frac{1}{2n}(t-n)^2} + \frac{1}{3n^2} \int_0^\infty dt e^{-\frac{1}{2n}(t-n)^2} (t-n)^3 - \frac{1}{4n^3} \int_0^\infty dt (t-n)^4 e^{-\frac{1}{2n}(t-n)^2} + \dots \right\} \\ &\equiv n^n e^{-n} (I_1 + I_2 + I_3 + \dots) . \end{aligned}$$

Since most of the Gaussian is centered about  $t = n > 0$ , we may extend the lower limits of integration to  $-\infty$ . Then,  $I_1 = \sqrt{2\pi n}$ ,  $I_2 = 0$  since the integrand is odd, and  $I_3$  may be evaluated as follows:

### 3 Entropy

Lecture 3 on 14/1/2026 by ()�.

Entropy is a physical measure of disorder in a system. The Boltzmann entropy formula is given by

$$S = k_B \ln \Omega, \quad (5)$$

where  $\Omega$  is the number of microstates corresponding to a macrostate, and  $k_B \approx 1.38 \times 10^{-23} \text{ J/K}$  is the Boltzmann constant.

**Example 3.1** (Einstein solid). The number of microstates in an Einstein solid consisting of  $N$  oscillators and  $q$  energy quanta is given by

$$\Omega(N, q) = \left( \frac{qe}{N} \right)^N \quad (6)$$

for large  $N$  and  $q$ . The entropy of the Einstein solid is therefore

$$S = k_B \ln \Omega = k_B N (\ln q - \ln N + 1). \quad (7)$$

Since  $q = E/\hbar\omega$  and  $E/N \propto k_B T$ , the term  $qe/N$  in the logarithm is proportional to  $k_B T/\hbar\omega$ .

”There is no dumb questions, but there is a dumb time to ask a question.”

### 4 Canonical Ensemble

Consider a system  $\mathcal{A}$  in thermal equilibrium with a heat reservoir  $\mathcal{R}$  at (constant) temperature  $T$ . If the temperature of  $\mathcal{A}$  is not equal to  $T$ , then energy will flow between  $\mathcal{A}$  and  $\mathcal{R}$  until thermal equilibrium is reached. The combined system  $\mathcal{A} + \mathcal{R}$  is isolated, so its total energy  $E_{\text{tot}} = E_{\mathcal{A}} + E_{\mathcal{R}}$  is constant, and hence the total system  $\mathcal{U}$  satisfies

$$\Omega_{\mathcal{U}} = \Omega_{\mathcal{A}} \Omega_{\mathcal{R}}. \quad (8)$$

For a fixed temperature, or microstate, of  $\mathcal{A}$ , we can count the number of microstates of  $\mathcal{R}$  consistent with that microstate of  $\mathcal{A}$ . That is, for microstate  $\mathcal{A}_1$  of  $\mathcal{A}$ ,  $\Omega(\mathcal{A}_1) = \Omega_{\mathcal{R}}(\mathcal{A}_1)$ ,  $\Omega(\mathcal{A}_2) = \Omega_{\mathcal{R}}(\mathcal{A}_2)$ , and so on.

By the Fundamental Assumption, the probability of finding the system  $\mathcal{A}$  in microstate  $\mathcal{A}_i$  is proportional to the number of microstates of the reservoir consistent with that microstate of  $\mathcal{A}$ :

$$\frac{P(\mathcal{A}_i)}{P(\mathcal{A}_j)} = \frac{\Omega_{\mathcal{R}}(\mathcal{A}_i)}{\Omega_{\mathcal{R}}(\mathcal{A}_j)}. \quad (9)$$

Therefore,

$$\frac{P(\mathcal{A}_i)}{P(\mathcal{A}_j)} = \exp \left[ \frac{1}{k} (S_{\mathcal{R}}(\mathcal{A}_i) - S_{\mathcal{R}}(\mathcal{A}_j)) \right]. \quad (10)$$

Recall that

$$dU = T dS - P dV + \mu dN, \quad (11)$$

so that at constant volume and particle number, we have

$$\Delta S = \int \frac{dU}{T} = \frac{\Delta U}{T}, \quad (12)$$

since temperature is constant for the reservoir. Thus,

$$\frac{P(\mathcal{A}_i)}{P(\mathcal{A}_j)} = e^{\frac{1}{kT} [U_{\mathcal{R}}(\mathcal{A}_i) - U_{\mathcal{R}}(\mathcal{A}_j)]} = e^{-\frac{1}{kT} [U_{\mathcal{A}}(\mathcal{A}_i) - U_{\mathcal{A}}(\mathcal{A}_j)]} = \frac{e^{-\frac{1}{kT} U_{\mathcal{A}}(\mathcal{A}_i)}}{e^{-\frac{1}{kT} U_{\mathcal{A}}(\mathcal{A}_j)}}. \quad (13)$$

The probability of finding the system  $\mathcal{A}$  in microstate  $\mathcal{A}_i$  is therefore proportional to  $e^{-\frac{1}{kT}U_{\mathcal{A}}(\mathcal{A}_i)}$ , which is known as the *Boltzmann factor*.

**Example 4.1** (thermal excitation). The energy of an hydrogen atom in the  $n$ th energy level is given by

$$E_n = -\frac{13.6}{n^2} \text{ eV}. \quad (14)$$

For a hydrogen atom at  $T = 300$  K, we have

$$\frac{P(2s)}{P(1s)} = \frac{e^{-\beta E_{1s}}}{e^{-\beta E_{2s}}} = \frac{e^{-\beta(-3.4 \text{ eV})}}{e^{-\beta(-13.6 \text{ eV})}} = e^{-\beta(10.2 \text{ eV})} \approx 10^{-171}, \quad (15)$$

where we have used the notation  $\beta = (kT)^{-1}$ , known as the *thermodynamic beta* or *coldness*. It is helpful to remember that  $kT \approx \frac{1}{40}$  eV at room temperature. On the surface of the sun,  $T_{\text{sun}} = 6000$  K =  $20T_{\text{RT}}$ , we have

$$\frac{P(2s)}{P(1s)} = e^{-\beta(10.2 \text{ eV})} \approx 2.8 \times 10^{-9}. \quad (16)$$

Now the probability is just one in a billion, and we expect hydrogen  $1s \rightarrow 2s$  transitions to occur often on the surface of the sun due to thermal excitation.

”...and I can’t do this anymore. I don’t mean teaching of course.”

”Thank goodness the number is only e to the power of -395 and not 10 to the power of -408.”

”How many hydrogen atoms are there in the sun? I dunno, a bunch?”

It turns out that the Boltzmann factor is not the actual probability, as it is not normalized. Defining the *partition function*  $Z$  as

$$Z = \sum_i e^{-\frac{1}{kT}E_{\mathcal{A}}(\mathcal{A}_i)}, \quad (17)$$

the probability of finding the system  $\mathcal{A}$  in microstate  $\mathcal{A}_i$  is given by

$$P(\mathcal{A}_i) = \frac{1}{Z} \exp \left[ -\frac{1}{kT} E_{\mathcal{A}}(\mathcal{A}_i) \right]. \quad (18)$$

The partition function  $Z$  is a constant, in that it does not depend on the state. However, it still depends on  $\beta$ , and hence the name *partition function*. Moreover, shifting  $E$  by a constant does not change the probability.

”At some point I tried becoming a zed player. It didn’t work. So will just call it zee, but you will hear zed being thrown around randomly here and there throughout the course.”

*Remark.* When we are thinking microscopically, we tend to use  $E$ , and when we are thinking macroscopically we tend to use  $U$ .

The probability of a microstate of a system in contact with a heat reservoir depends on the energy of the microstate. The equal likelihood assumption only applies to an isolated system.

## 5 Random Walk

TA Class on 12/1/2026 by ()�.

Consider the following problem:

**Example 5.1** (1D random walk). **Question:** A particle is confined to move on a line starting at the origin. The experimenter flips a fair coin  $N$  times and moves the particle one unit to the right for heads and one unit to the left for tails. What is the formula for  $\Omega(x)$  of the number of ways to reach position  $x$  after  $N$  steps?

Let  $N_R$  and  $N_L$  be the number of steps to the right and left, respectively. Then, we have

$$N = N_R + N_L, \quad x = N_R - N_L. \quad (19)$$

We can then solve for  $N_R$ , and

$$\Omega(x) = \binom{N}{N_R} = \frac{N!}{N_R! N_L!}, \quad (20)$$

and in fact

$$\Omega(x) = \binom{N}{\frac{N+x}{2}} = \frac{N!}{\left(\frac{N+x}{2}\right)! \left(\frac{N-x}{2}\right)!}. \quad (21)$$

Let's find the first derivative of  $\Omega(x)$  with respect to  $x$ . Suppose  $N \gg x$ , i.e.  $N, (N+x)/2, (N-x)/2 \gg 1$ , then we can apply Stirling's approximation without the prefactor:  $n! \sim n^n e^{-n}$ . Then,

$$\begin{aligned} \Omega(x) &= \frac{N!}{\left(\frac{N+x}{2}\right)! \left(\frac{N-x}{2}\right)!} \\ &\sim \frac{\left(\frac{N}{e}\right)^N}{\left(\frac{N+x}{2e}\right)^{\frac{N+x}{2}} \left(\frac{N-x}{2e}\right)^{\frac{N-x}{2}}} \\ &= \frac{(2N)^N}{(N+x)^{\frac{N+x}{2}} (N-x)^{\frac{N-x}{2}}} \\ &= \left(\frac{2N}{N+x}\right)^{\frac{N+x}{2}} \left(\frac{2N}{N-x}\right)^{\frac{N-x}{2}}. \end{aligned} \quad (22)$$

Since  $\ln$  is a monotonic function, we can find the extrema of  $\Omega(x)$  by finding the extrema of  $\ln \Omega(x)$ . We have

$$\begin{aligned} \ln \Omega(x) &\sim \left(\frac{N+x}{2}\right) \ln \left(\frac{2N}{N+x}\right) + \left(\frac{N-x}{2}\right) \ln \left(\frac{2N}{N-x}\right) \\ &= \left(\frac{N}{2}\right) \ln (4N^2) - \left(\frac{N}{2}\right) \ln [(N+x)(N-x)] + \left(\frac{x}{2}\right) \ln \left(\frac{N-x}{N+x}\right). \end{aligned} \quad (23)$$

Then,

$$\begin{aligned} \frac{\partial \ln \Omega}{\partial x} &\sim -\frac{Nx}{(N+x)(N-x)} + \frac{1}{2} \ln \left(\frac{N-x}{N+x}\right) - \frac{Nx}{(N+x)(N-x)} \\ &= -\frac{2Nx}{(N+x)(N-x)} + \frac{1}{2} \ln \left(\frac{N-x}{N+x}\right) \\ &= \frac{1}{2} \ln \left(\frac{N-x}{N+x}\right) + O\left(\frac{1}{N}\right). \end{aligned} \quad (24)$$

Setting this to zero, we find that the maximum occurs at  $x = 0$ . Therefore, the most probable position after  $N$  steps ( $N \gg 1$ ) is the origin.

Let's set  $N - x = \delta \ll 1$ . Then, we have