

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 \dots :

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

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 Ω 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

$$dU = TdS - PdV + \mu dN, \quad (11)$$

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 $T = 300 \text{ K}$, 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 $kT \approx \frac{1}{40} \text{ eV}$ at room temperature. On the surface of the sun, $T_{\text{sun}} = 6000 \text{ K} = 20T_{\text{RT}}$, 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 β , 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