# Physics 415 - Lecture 1: Statistical Mechanics (Preview)

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In statistical mechanics, we will be interested in the laws governing the behavior of "macroscopic" systems.

- Macroscopic = composed of many constituent particles (atoms, molecules, etc.)
- Typical # $\sim 10^{23}$ particles.

In principle, if "microscopic" (M-scopic) laws are known, then properties of systems of a large # of particles can be deduced by solving the M-scopic equations.

**Example:** Classical system of N particles:

$$m_i \ddot{\vec{r}}_i = \vec{F}_i(\vec{r}_1, \ldots, \vec{r}_N), \quad i = 1, \ldots, N$$

(where $\dot{} \equiv \frac{d}{dt}$, $\ddot{} \equiv \frac{d^2}{dt^2}$, etc.) Given initial conditions $\vec{r}_i(t=0)$ and $\vec{v}_i(t=0)$ $(\vec{v}_i = \dot{\vec{r}}_i)$, we have complete knowledge of the state of the system at any time $t$.

However, for macroscopic N ($N \sim 10^{23}$), this is not feasible.

- Even if we could solve the equations of motion (EOM), simply recording all initial conditions is not practical.
- Indeed, knowing the state of each particle is not even useful or interesting info.
- When the # of particles is large, we'd rather have info about the "average" properties of the system.

Thus, in statistical mechanics, we will abandon such M-scopic determinism in favor of a statistical (or probabilistic) description.

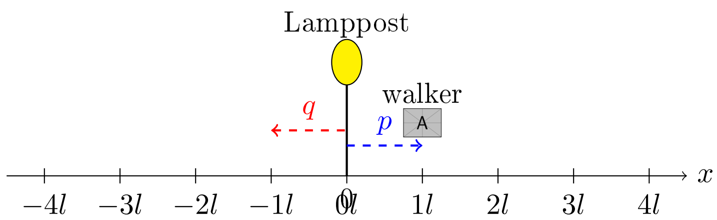
We will find that, precisely because of the large # of particles involved, new laws & types of regularities will appear that govern the macroscopic behavior.

- Notions like "entropy" & "temperature" will emerge, that have no analog in particle mechanics & are purely of statistical nature.

Since statistical notions will be important for understanding macroscopic systems, we'll spend some time reviewing basics of probability. This will be mostly math (not physics). We'll illustrate important ideas through an important example:

## 1D Random Walk

(A good starting point for understanding a variety of phenomena).



- Walker starts from lamppost at $x = 0$.
- Taking random steps of length $l$ at regular intervals.
- Each step is independent of the last.
- Probability $p$ to step to the right & probability $q = 1 - p$ to step to the left.

**Question:** After taking $N$ steps, what is the probability that the walker is at a position $x = ml$ ($m$ = integer)? (For another example of a 1D random walk, see "probability board" demo at Ingersoll museum).

We want to calculate the probability $P_N(m)$ that the walker is at position $x = ml$ after $N$ steps.

- Let $n_1 = \#$ of steps right, $n_2 = \#$ of steps left.
- Total steps: $N = n_1 + n_2$.
- Final position: $ml = n_1 l - n_2 l \implies m = n_1 - n_2$.
- Note: $-N \leq m \leq N$. Also, $N$ and $m$ must have the same parity ($N - m = 2n_2$ is even).
- From the above, we can express $n_1$ and $n_2$ in terms of $N$ and $m$: $n_1 = (N + m)/2$ $n_2 = (N - m)/2$

The probability of taking a specific sequence of $n_1$ steps right and $n_2$ steps left is:

$$(\underbrace{p \times p \times \cdots \times p}_{n_1 \text{ times}}) \times (\underbrace{q \times q \times \cdots \times q}_{n_2 \text{ times}}) = p^{n_1} q^{n_2}$$

Of course, there are many different ways (sequences) in which the walker could take $n_1$ steps right & $n_2$ steps left.

**Example:** $N = 3$, $m = 1$. Then $n_1 = (3+1)/2 = 2$, $n_2 = (3-1)/2 = 1$. Possible sequences: a) $\rightarrow\rightarrow\leftarrow$ b) $\rightarrow\leftarrow\rightarrow$ c) $\leftarrow\rightarrow\rightarrow$ There are 3 ways.

In general, the number of ways is given by the binomial coefficient:

$$\# \text{ of ways} = \binom{N}{n_1} = \frac{N!}{n_1!(N - n_1)!} = \frac{N!}{n_1! n_2!}$$

Check above example: $N = 3, n_1 = 2, n_2 = 1 \implies \binom{3}{2} = \frac{3!}{2!1!} = 3$. ✓

Therefore, the total probability $P_N(m)$ is (number of ways) $\times$ (probability of one way):

$$P_N(m) = \frac{N!}{n_1! n_2!} p^{n_1} q^{n_2}$$

This is the "binomial distribution".

Using $n_1 = (N + m)/2$ and $n_2 = (N - m)/2$:

$$P_N(m) = \frac{N!}{[(N + m)/2]![(N - m)/2]!} p^{(N+m)/2} (1 - p)^{(N-m)/2}$$

Recall the binomial theorem: $(p + q)^N = \sum_{n_1=0}^{N} \frac{N!}{n_1!(N-n_1)!} p^{n_1} q^{N-n_1}$. Comparing with the formula for $P_N(m)$ (summed over $n_1$ or $m$) explains the name.

**Example:** $p = q = 1/2$ (unbiased walk).

$$P_N(n_1) = \frac{N!}{n_1! n_2!} \left(\frac{1}{2}\right)^N$$

Let's consider $N = 10$. The probability $P_{10}(n_1)$ is plotted below. Note: $m = n_1 - n_2 = n_1 - (N - n_1) = 2n_1 - N$.

| $n_1$ | Approx $P_{10}(n_1)$ |
|---|---|
| 0 | $\approx 0.001$ |
| 1 | $\approx 0.01$ |
| 2 | $\approx 0.044$ |
| 3 | $\approx 0.12$ |
| 4 | $\approx 0.21$ |
| 5 | $\approx 0.25$ |

After $N = 10$ steps, probability is largest for the particle to be near the origin ($m = 0$, or $n_1 = 5$). Probability to be far from the origin is small.

## General Notions

Let $X$ be a random variable, taking $K$ possible values $x_1, x_2, \dots, x_K$, with associated probabilities $P(x_1), P(x_2), \dots, P(x_K)$. ($0 \le P(x_i) \le 1$ and $\sum_{i=1}^{K} P(x_i) = 1$).

### Mean

The "mean" (average) of $X$ is: $\overline{X} = \sum_{i=1}^{K} P(x_i)x_i$. For a function $f(X)$: $\overline{f(X)} = \sum_{i=1}^{K} P(x_i)f(x_i)$.

### Variance

Suppose we want to know how much measurements of $X$ "fluctuate" about the mean value. The "variance" (second moment, dispersion) is defined as:

$$\mathrm{Var}(X) = \sigma_X^2 = \overline{(X - \overline{X})^2} = \sum_{i=1}^{K} P(x_i)(x_i - \overline{X})^2$$

We square the deviation $(x_i - \overline{X})$ since fluctuations can have either sign. Note the useful identity:

$$\overline{(X - \overline{X})^2} = \overline{X^2 - 2X\overline{X} + (\overline{X})^2} = \overline{X^2} - 2\overline{X}\,\overline{X} + (\overline{X})^2 = \overline{X^2} - (\overline{X})^2$$

We also define the root-mean-square (RMS) deviation (or standard deviation):

$$\Delta X_{rms} = \sigma_X = \sqrt{\overline{(X - \overline{X})^2}} = \sqrt{\overline{X^2} - (\overline{X})^2}$$

**Example:** Binomial Distribution Properties (results to be shown in discussion section/homework)

- Average # of steps to the right: $\overline{n_1} = N \times p$
  (= (total # of steps) $\times$ (prob. of step right))
- Variance: $\mathrm{Var}(n_1) = \overline{n_1^2} - (\overline{n_1})^2 = N \times pq$
- RMS deviation: $\Delta n_{1,rms} = \sqrt{Npq}$
- The relative width is:
  $$\frac{\Delta n_{1,rms}}{\overline{n_1}} = \frac{\sqrt{Npq}}{Np} = \sqrt{\frac{q}{p}} \times \frac{1}{\sqrt{N}}$$
- This shows the distribution becomes sharply peaked (relative width $\to 0$) when $N \gg 1$.