Lecture 10: The Central limit Theorem and related topics (concluded)+More

Reading Assignment for Lectures 10-12: PKT Chapter 6
I am handing out a partial Problem Set 2, due week Friday, Oct. 8, just so you can get started. Full Problem Set will be posted on the website soon.
I handed this out at the beginning of the period. If you wee not there, you did not get it. Come by my office and pick up a copy. And, ***PLEASE, COME TO CLASS ON TIME!***

Important Comments on the results for the random-walk/coin-toss result (continued):

4. The Random walk in 1D and in 3D:
Note: This is also freely joined polymer chain in 1D/3D.
The relationship between the random walk and the coin toss:
N tosses = N steps
length of each step = a
Total length of walk along contour L=Na
Net end-to-end length X = aM
Substitute (taking care with normalization):

$$\boxed{P_N(X) = \frac{1}{\sqrt{2\pi Na^2}} e^{-\frac{X^2}{2Na^2}}.} \quad \text{(1D)}$$

Note that $\begin{cases} \langle X \rangle = a\langle M \rangle = 0 \\ \langle X^2 \rangle = a^2 \langle M^2 \rangle = Na^2 \end{cases}$

To generalize this to three dimensions, imagine a 3D walk with 1/3 of the steps in each direction, so $N_x = N_y = N_z = N/3$, $X = aM_x, Y = aM_y, Z = aM_z$, etc.

$$P_N(X,Y,Z) = \frac{1}{\sqrt{2\pi N_x a^2}} e^{-\frac{X^2}{2N_x a^2}} \cdot \frac{1}{\sqrt{2\pi N_y a^2}} e^{-\frac{Y^2}{2N_y a^2}} \cdot \frac{1}{\sqrt{2\pi N_z a^2}} e^{-\frac{Z^2}{2N_z a^2}}$$

$$\boxed{= \left(\frac{3}{2\pi Na^2}\right)^{3/2} e^{-\frac{3R^2}{2Na^2}}} \qquad (3D)$$

with $\langle \vec{R}^2 \rangle = a^2 \langle M_x^2 + M_y^2 + M_z^2 \rangle = Na^2$

As for the coin toss, this form is much more general than single steps length a along the axes. All that changes is the step length $a \to a_{eff}$.

5. Random walks in time:
Imagine each step to taking place in a time interval:
Time per step = τ, total elapsed time t = Nτ, so, $N \to \frac{t}{\tau}$ and the probability distribution represents the probably outcome after time t for a single particle which starts at the origin or, equivalently, for a cloud of (non-interacting) particles, each one undergoing a random walk.
In this representation, we find by substitution (1D):

$$P(X,t) = P_{N=t/\tau}(X) = \sqrt{\frac{\tau}{2\pi t a^2}}\, e^{-\frac{X^2\tau}{2ta^2}}. \tag{10.2}$$

So far time and space are discrete. We now imagine going to a continuum limit with $a \to 0, \tau \to 0$ with $\frac{a^2}{\tau} \to 2D$. D is the "diffusion constant" (note units)
The constant 2 is conventional, but see below for reason.

Thus, $$\boxed{P(X,t) = \frac{1}{\sqrt{4\pi D t}}\, e^{-\frac{X^2}{4Dt}}}$$

with $\boxed{\left\langle X^2 \right\rangle = 2Dt.}$ 1D

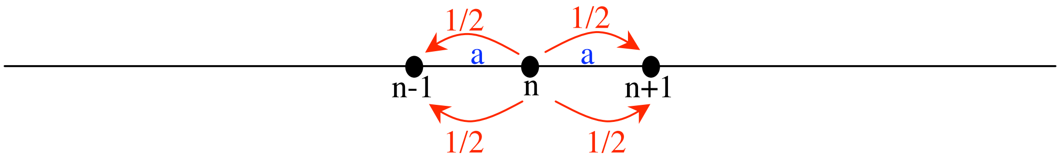
Probability distribution for a particle localized at x=0 at t=0 and subject to continuum random walk.
Or, in 3D:

$$\boxed{P(\vec{R},t) = \left(\frac{1}{4\pi D t}\right)^{3/2} e^{-\frac{1}{4Dt}\left(X^2+Y^2+Z^2\right)} = \left(\frac{1}{4\pi D t}\right)^{3/2} e^{-\frac{R^2}{4Dt}}}$$

with $\boxed{\left\langle R^2 \right\rangle = \left\langle X^2 \right\rangle + \left\langle Y^2 \right\rangle + \left\langle Z^2 \right\rangle = 6Dt}$

c.f., diffusion at Lecture 4.9.

6. Random walks and diffusion:
Consider a set of sites spaced along the x-axis at $x_n = na$ for $n = 0, \pm 1, \pm 2, \ldots$



Imagine a particle executing a random walk among these sites such that, during each time-step τ, the particle moves one step right or left randomly with probability ½ for each direction. Let $\left\{P_n(t)\right\}_{n=-\infty}^{\infty}$ be the discrete probability distribution at time time t. Then, at time t+τ,

$$P_n(t+\tau) = P_n(t) + \frac{1}{2}\left[P_{n+1}(t) + P_{n-1}(t) - 2P_n(t)\right].$$

Now, assume a and τ small and variations smooth $P_n(t) \to P(x = na, t)$ (I'll take a continuum limit in just a minute), so we can Taylor expand:

$$P(na, t+\tau) = P(na,t) + \tau \frac{\partial P(na,t)}{\partial t} + \frac{\tau^2}{2}\frac{\partial^2 P(na,t)}{\partial t^2} + \ldots$$

$$P((n\pm 1)a, t) = P(na,t) \pm a \frac{\partial P(na,t)}{\partial x} + \frac{a^2}{2}\frac{\partial^2 P(na,t)}{\partial x^2} + \ldots$$

Substituting these expressions above gives,

$$\tau \frac{\partial P(na,t)}{\partial t} + \frac{\tau^2}{2}\frac{\partial^2 P(na,t)}{\partial t^2} + .. = \frac{a^2}{2}\frac{\partial^2 P(na,t)}{\partial x^2} + \frac{a^3}{6}\frac{\partial^3 P(na,t)}{\partial x^3} + \ldots$$

Now, divide by τ and take the limit $a,\tau \to 0$ with $\frac{a^2}{2\tau} \to D$ (finite), giving

$$\boxed{\frac{\partial P}{\partial t} = D\frac{\partial^2 P}{\partial x^2},} \quad \text{(the diffusion equation)}$$

i.e., in (this) continuum limit the probability distribution satisfies the diffusion equation.

Notes:

(a) Satisfy yourself that the Gaussian distribution above satisfies this equation.

(b) The corresponding equation in 3D is $\frac{\partial P}{\partial t} = D\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)P \equiv D\nabla^2 P$.

(c) More on this topic in PKT Chapter 13

Thermodynamics and Statistical Mechanics

My objective here is not to duplicate the content of PHYS 344 and 445.
What I will do: Summarize for you some important results and make some important connections.
I want you to understand the meaning of these results and how to use them. I will not derive them for you but I will try to point you in the direction of understanding where they come from.

Systems:
Thermodynamics and statistical mechanics typically treat systems of one of two distinct types:

(A) A large system composed of many identical subsystems or a small number of different kinds of subsystems with many identical copies of each.
Examples:
N monatomic gas molecules in a volume V
N_A molecules of type A, N_B molecules of type B, N_C molecules of type C
Note: if the chemical reaction $A + B \Leftrightarrow C$ is possible, then only two numbers are fixed, say, N_A-N_B and $2N_C$+N_A+N_B.

(B) A small system which is "in contact" with a large system at "equilibrium."
Typically, the large system fixes the value of one or more "intensive" variables (like T, μ, P) by exchanging energy, particles, volume with the small system.
Terminology: In this situation the large system is often called a "bath" or "reservoir," e.g., a "thermal bath."
Examples:
A single small (e.g., protein) molecule with many internal conformations weakly interacting with a larger environment at temperature T.

For both A and B the subsystems may or may not interact with one another. In real life, interactions are typically present. In some situations they play an important role; in others they do not. Of course, theoretical treatment is always simpler when interaction effects ("correlations") are absent. Whether or not the approximation of neglecting interactions is valid depends on the situation.

Microstates:
To describe the system we need some set of coordinates which completely describe its "microstate."

Example: for the classical gas $\{\vec{r}_k, \vec{p}_k\}_{k=1}^{N}$ (with N~10^{23}) plus other internal coordinates for non-monatomic molecules (or for monatomic molecules at higher energies, where other internal degrees of freedom are being probed).

Microstates are described by the laws of mechanics or quantum mechanics, whichever is applicable.
It is a (surprising) fact of quantum mechanics that for particles in a finite volume—however large—the states of the system are always discrete (countable), so they can be labeled by an integer n. Thus, we can assign an energy E_n to each microstate n.
Note: The energy E_n here refers to the total energy of all N subsystems, including interaction energies. It is the sum of the energies of the individual subsystems if and only if there are no interactions between the subsystems.

Measurements:
All measurements are made on microstates.
For small systems (B), measurements are typically not exactly predictable/reproducible; however, we can hope—for sufficiently well-characterized systems—to detect well defined averages and distributions.
For large systems (A) at "equilibrium," single measurements of certain kinds of variables often produce well-defined, reproducible values. These variables are like the averages in the coin-toss experiment.
Example: pressure in a gas at temperature T.
The basic reason for this is statistics (like the Central Limit Thm): The probability that you have happened upon an "unusual" microstate gets very small for large N. It is not that anomalous states don't exist; it is just that the probability that you find one of them is vanishingly small.
Example: pressure in a gas at temperature T.
But, note:
(a) It is easy to prepare anomalous states, if you want to. (Use a fan!)
(b) Some kinds of measurements do not give well-defined reproducible values.
Ex.: What is the position of the particle k=100?