Theo. 4. Statistical Physics
Lecture 8.
Felix Yu
November 13, 2023.

Last time: Kinetic theory of gases
Maxwell-Boltzmann distribution
Equipartition theorem.

Today: More on equipartition theorem.
Virial theorem
Moments & cumulants of probability distrib. fins.

From the end of last time, we saw that the Maxwell-Boltzmann distribution for velocities gave an expectation value of $\langle v^2 \rangle$ of $\frac{3 k_B T}{m}$, and so the corresponding $\langle E_{kin} \rangle = \frac{3}{2} k_B T$ for each particle.

We recognized that this provided a way of counting the 3 spatial degrees of freedom and thus motivated the ansatz that any dof. with a quadratic form for energy, i.e. the internal / potential energy or the kinetic energy depends quadratically on a parameter, would have $\langle E_{dof} \rangle = \frac{1}{2} k_B T$. This is the central principle of the equipartition theorem:

Blundell & Blundell   If the energy of a classical system is the sum of n quadratic modes and that system is in contact with a heat reservoir at temp. T, the mean energy of the system is $\frac{n}{2} k_B T$.

Comments:

This is a remarkably insightful theorem, since it directly connects a macroscopic coordinate (temperature) to the microscopic expression (average squared speed or energy more generally). At its heart, this connection between the intensive nature of temperature to the statistical average of mean kinetic energy is because of the differential nature of the Boltzmann factor in determining the Boltzmann dist.

Thought experiment:

Consider an arbitrary subsystem that locally exhibits an average $\langle E_{kin} \rangle$ that is higher than the $\langle E_{kin}^{sys} \rangle$ of the system. The probabilistic nature of the Boltzmann dist. dictates that on average (in the time domain), this overfluctuation in $\langle E_{kin} \rangle$ is matched by an equivalent (probabilistic weight) underfluctuation of $\langle E_{kin} \rangle$ smaller than $\langle E_{kin}^{sys} \rangle$. Since this is valid for any subsystem size, we can immediately see that thermal equilibrium dictates a macroscopic average that allows / forces local fluctuations according to subsystem size. The smaller the subsystem, the farther from $\langle E_{kin}^{sys} \rangle$ you can deviate.

This logic is at the heart of understanding why the canonical ensemble equilibrates temperature, regardless of the subsystem size.

Wide applicability of the equipartition theorem:

The equipartition theorem presumes that energy (potential or kinetic) has quadratic dependence on a coordinate. This is the essence of <u>harmonic motion</u> (for ~~potential~~ potential energy), since for any <u>stable</u> extremum of a potential, a small enough displacement of the particle in the potential can be approximated by a harmonic oscillator. Recall that the extremum condition requires the first derivative of the Taylor series to vanish, and so the leading dynamic term of $V(x)$ expanded around x_0 gives $\frac{V''(x)}{2}(x-x_0)^2$.

Of course, the global behavior of $V(x)$ could lead to significant corrections to harmonic motion, which would cause an invalidation of the assumption used in the equipartition theorem.

Another assumption in the equipartition theorem is that the energy is effectively continuous for the given T. We know, however, that a small T and a quantized energy spectrum will cause a possibility that the discrete nature of system energies are not all accessible given the temperature, ~~Such~~ or even resulting in such dofs. being forced to their ground state + cannot be excited. This is called "freezing out" and <u>is</u> central to studies of "gapped" systems such as semiconductors, transition edge sensors, etc.

There is a related thm. about the tradeoff of potential + kinetic E.

This is the virial theorem (which is generally derived from considering Hamiltonian evolution), which states that the total kinetic energy of a stable system of particles bound by "conservative force" (work done is path independent") is $\frac{1}{2}$ the total potential energy of the system. Note the virial theorem holds even for systems not in thermal equilibrium, but given that classical kinetic energy is always quadratic with velocity squared, we can use the virial theorem and the equipartition theorem to analyze non-harmonic potentials.

We return to the connection of T and microscopic probabilistic statements such as $\langle v \rangle = \sqrt{\frac{8 k_B T}{\pi m}}$ and $\langle v^2 \rangle = \frac{3 k_B T}{m}$.

These expectation values are emblematic of a <u>moment</u> <u>decomposition</u>, which is a way to analyze the behavior of convolution integrals (generally) as a family of expectation values.

Specifically, for a probability ~~p~~ distribution, the leading moments (also called ~~cu~~ cumulants) are the <u>mean</u>, <u>variance</u>, <u>skewness</u>, <u>kurtosis</u>, etc. Since it will be central to calculate statistical averages of probability distributions via convolutions, we now pivot to a discussion of statistics.

We have seen how the Boltzmann distribution dictated the Maxwell-Boltzmann velocity distribution simply by requiring the density of states for the velocity distribution to obey Boltzmann factor scaling. More generally, we treated $g(v)\,dv$ as the probability and $g(v)$ as the ~~prod~~ probability density function. Generally, $p(x) \equiv dP(x)/dx$ for $P(x)$ as cumulative probability fcn.

We then define moments of the probability density function as

$$m_n \equiv \langle x^n \rangle = \int dx\, p(x)\, x^n.$$

This is related to the characteristic function which generates moments:

$$\tilde{p}(k) = \langle e^{-ikx} \rangle = \int dx\, p(x)\, e^{-ikx}$$

This is related to the PDF via Fourier transform:

$$p(x) = \frac{1}{2\pi} \int dk\, e^{+ikx}\, \tilde{p}(k)$$

The key point is that the Taylor series (being entire) can read off successive moments:

$$\tilde{p}(k) = \left\langle \sum_{n=0}^{\infty} \frac{(-ik)^n}{n!} x^n \right\rangle = \sum_{n=0}^{\infty} \frac{(-ik)^n}{n!} \langle x^n \rangle$$

and also enable shifts to study any expansion pt. x_0:

$$e^{ikx_0}\,\tilde{p}(k) = \langle e^{-ik(x-x_0)} \rangle$$

$$= \sum_{n=0}^{\infty} \frac{(-ik)^n}{n!} \langle (x-x_0)^n \rangle$$

Finally, the cumulants are built from moments:

mean	$\langle x \rangle_c = \langle x \rangle$
variance	$\langle x^2 \rangle_c = \langle x^2 \rangle - \langle x \rangle^2$
skewness	$\langle x^3 \rangle_c = \langle x^3 \rangle - 3\langle x^2 \rangle\langle x \rangle + 2\langle x \rangle^3$
kurtosis	$\langle x^4 \rangle_c = \langle x^4 \rangle - 4\langle x^3 \rangle\langle x \rangle - 3\langle x^2 \rangle^2 + 12\langle x^2 \rangle\langle x \rangle^2 - 6\langle x \rangle^4$

This is built from the cumulant generating fcn. which is the log of the characteristic fcn.

$$\ln \tilde{p}(k) = \sum_{n=1}^{\infty} \frac{(-ik)^n}{n!} \langle x^n \rangle_c$$

$$\left[\text{Recall} \quad \ln(1+\epsilon) = \sum_{n=1}^{\infty} (-1)^{n+1} \frac{\epsilon^n}{n!} \right]$$

Aside: it is helpful to consider an arbitrary convolution integral & consider a Taylor series expansion of one fcn. with the other fcn. as a probability dist.

Regarding discrete + continuous probability distributions, you should already be familiar with Gaussian PDFs, the binomial distr. & related multinomial distrib., and Poisson distrib. We have also introduced the Boltzman distrib. Given so many random distributions, how can we analyze the statistics of individual dofs if they obey different PDFs?

Fortunately, for sums of random variables, we have the central limit theorem that the total PDF of many random variables tends to a normal distribution. This can be seen, for example, by an analysis of the moments or cumulants and how they scale for diff. distribs. (See Kardar, section 2.5). The key is that the Gaussian = normal distrib. only has the ~~...~~ mean + variance as non-zero cumulants. All $\langle x^3 \rangle$ + $\langle x^4 \rangle$ + higher moments are arranged in such a way that $\langle x^3 \rangle_c = \langle x^4 \rangle_c = \ldots = 0$.

Next time: Analyze specific statistical distributions of particles, expand on notion of ensemble, work with partition fcn.