Maxwell-Boltzmann distribution in statistical physics

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This notes is meant to be a supplement and not a substitute for standard text books.

1 Why statistical physics ?

Consider the following problem. A box of volume V has N particles, where $N >> 1$, typically of the order of Avagadro's number. How to determine the position and momenta of all these classical particles as a function of time ? The Newton's equation of motion for all the particles must be solved. To do this, we need to specify the initial conditions, position and momenta, of all the particles. This is not possible in general. Hence we resort to using statistical methods.

The trade-off : In the normal course, when we do calculations with Newton's equations we can get detailed predictions for the future state of the classical system. Now that when $N >> 1$, we are taking recourse to statistical methods, we have to give up asking detailed questions. Instead we ask questions about the average behaviour of the system.

A little bit of thought and you can figure out that statistical questions are relatively easy to handle if the averages are independent of time. In the physics context, this means that while dynamical variables of interest (like pressure, energy etc.) can fluctuate, they should necessarily fluctuate about a well-defined average. Under the conditions of equilibrium, statistical physics gives predictions for average behavior of system's variables.

A canonical example : Weakly interacting gas enclosed in volume V and in thermal equilibrium with reservoir at temperature T. If the ideal gas in a enclosure is our system S of interest, the reservoir R represents, in principle, the rest of the universe. Our system S can exchange thermal energy, but not particles, with the reservoir. Since thermal energy is exchanged all the time, as shown in fig 1, energy at every instant of time fluctuates. However, thanks to thermal equilibrium, it fluctuates about some average value (see the red line in fig 1). The main programme of equilibrium statistical physics is to compute these averages.

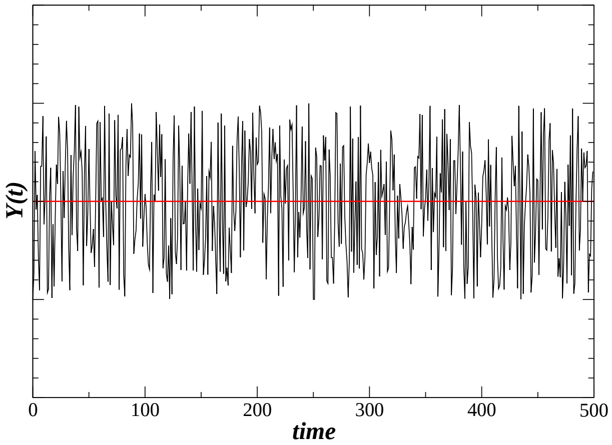

Figure 1: *A caricature of dynamical variable $y(t)$, say, the energy of system S, measured as a function of t. The red line is the average $\langle y \rangle$.*

To make analysis simple, we assume our gas to be dilute and only weakly interacting sufficient enough to continually exchange energy among themselves but not strong enough that inter-molecular interactions begin dominate. Dilute gas also means that every molecule can be assumed to be distinguishable. This distinguishability will break down when the quantum effects begin to dominate. Thus, this is the scenario for classical treatment of the system.

2 Maxwell-Boltzmann distribution

To compute the average energy, we need to know the distribution of energy. In other words, what is the probability that the system S is in state s with energy E_s ?

The fundamental postulate of statistical physics asserts that an isolated system is likely to be found in any of its accessible states with equal probability.

Isolated system : An isolated system does not exchange energy or particles with the environment. In our example, the combined system consisting of S and R constitutes an isolated system.

state of system: A state of a classical particle is specified by its position and momentum. Its quantum mechanical state is specified by its wave function.

accessible states : For a given energy E, only a fraction of the entire phase space is available to the particle. Accessible states are those states that the particle can access consistent with its energy E.

All these can be illustrated with a particle in harmonic oscillator potential with energy E. This is an isolated system whose energy E is a constant. State of the particle is given by its position and momenta. Consistent with constant energy E, the harmonic oscillator can access all the states in the ellipse labelled by E in figure 2. The fundamental postulate asserts that the particle has equal probability of being found anywhere on the ellipse (shown in red colour in figure 2).

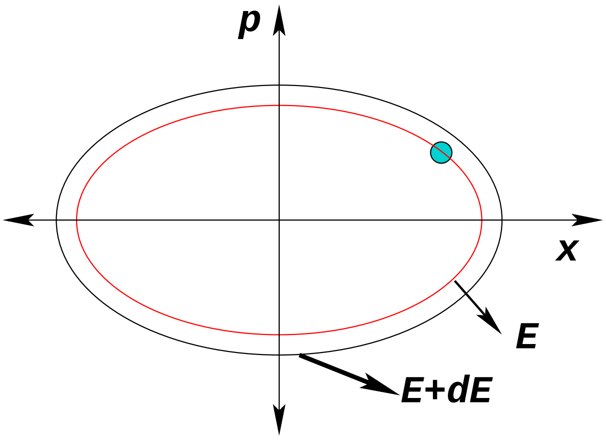

Figure 2: *Phase space of harmonic oscillator. The solid dot is position of the particle with energy E. The particle has equal probability of being found at any point on the red line.*

If the particle has energy lying between E and $E + dE$, then the particle could be found anywhere inside the two ellipses shown in figure 2. In this case, the accessible phase space is the area lying between the two ellipses.

Starting from the fundamental postulate, we can obtain the probability that the system (in equilibrium with reservoir at temperature T) is in a state s with energy E_s.

This is given by,

$$P_s = \frac{e^{-E_s/kT}}{\sum_s e^{-E_s/kT}} \tag{1}$$

where k is the Boltzmann constant and T is the temperature. This distribution, called Maxwell-Boltzmann distribution, is the central result of equilibrium statistical physics.

Example 1: Max Planck assumed that the energy exchange between the oscillators on the walls of the black body cavity and the standing waves takes place in discrete quanta given by, $\epsilon_n = nh\nu$, where h is the Planck's constant. Using this energy expression in the distribution in Eq. 1 he obtained the average energy to be,

$$\bar{\epsilon} = \frac{\sum_{n=0}^{\infty} nh\nu \; e^{-nh\nu/kT}}{\sum_{n=0}^{\infty} e^{-nh\nu/kT}} = \frac{h\nu}{e^{h\nu/kT} - 1} \tag{2}$$

The quantity, $\sum_r e^{-\beta E_r}$, where $\beta = 1/kT$, is called the partition function. From the knowledge of the partition function, all other averages can be calculated.

Example 2: For the ideal gas of N particles in an enclosure in equilibrium at temperature T, calculate the number of particles lying in the range of energy between E and $E + dE$.

Number of particles with energy lying in $[E, E + dE]$ is the product of number of accessible states in energy range $[E, E+dE]$ and the probability that the state (with energy E) is occupied by a particle. It can be written as,

$$n(E)\; dE = C\; [\Omega(E)\; dE]\; P_E.$$

where C is the normalisation constant. Since the system is in thermal equilibrium with a reservoir at temperature T, the gas particles do not occupy all the accessible states but preferentially occupy only a fraction of the accessible states. That is given by P_E (Eq. 1). Finally, we determine C from the requirement that there are N gas particles in the system. Thus, we have

$$\int_0^{\infty} n(E)\; dE = C \int_0^{\infty} e^{-E/kT} \Omega(E)\; dE = N.$$

Example 3: Energy of particle in one-dimensional box of length L is $E = C\; n^2$, where C is a constant. Find $\Omega(E)\; dE$, the number of states in range $[E, E + dE]$.

Number of states that have energy less than or equal to E is $\sqrt{E/C}$.
Hence $\Omega(E)\; dE$ = number of states in the range $[E, E + dE]$ is given by

$$\Omega(E)\; dE = \left(\frac{d}{dE}\sqrt{E/C}\right)\; dE = \frac{E^{-1/2}}{2\sqrt{C}}\; dE$$
