Gibbs Distribution

From Liouville theorem it is just one step to the Gibbs distribution, the cornerstone of the equilibrium Statistical Mechanics. The standard statement of an equilibrium Stat. Mech. problem is as follows. Imagine a large mechanical system with virtually infinite number of microscopic degrees of freedom. This system is supposed to be in equilibrium in the sense that all its macroscopic motions have relaxed, so that the time evolution is nothing but repeating microscopically different, but macroscopically equivalent states. We will refer to such a system as a heat bath. Suppose then that we have a system $A$ weakly coupled to the heat bath. The precise meaning of weak coupling is that the interaction term in the Hamiltonian of the compound system “heat bath + system $A$” is much smaller than the bare Hamiltonian of the system $A$. Under these conditions, the evolution of the system $A$ is almost free at timescales characteristic to its internal dynamics. At larger timescales, the presence of the heat bath becomes relevant, since it leads to the non-conservation of the energy of the system $A$. In the limit of infinitely large time, the system $A$ will try all possible energies with corresponding probabilities. In Statistical Mechanics, we are interested in the distribution of the states of the system $A$ in the phase space. Given this distribution, we can evaluate all the thermodynamic properties of the system.

To derive the distribution of the states of the system $A$ we employ the idea of statistical ensemble. We make snapshots of the state of the system $A$ with equal time intervals, $\Delta t$. For each snapshot we introduce a corresponding point in the phase space, so that after making a very large number of snapshots we have an ensemble of points in the phase space representing the distribution of the states of the system $A$. What are the properties of our ensemble? We can make sure that this is a steady-state ensemble with respect to internal dynamics of the system $A$. To this end we take $\Delta t$ small enough to guarantee that during this period the interaction with the heat bath is negligible (does not significantly affect the form of the trajectory). Then we realize that if we allow our ensemble to evolve during the time $\Delta t$, then the position of the 1-st point will be equal to the original position of the 2-nd point, and so forth: $j$-th point takes the position of the $(j+1)$-th point. Hence, the ensemble reproduces itself and thus its distribution function $W_A$ does not change with time. In accordance with the Liouville theorem, it means that $W_A(p_s, q_s)$ is some constant of motion of
the system \( A \). Moreover, we will find this function!

Along with the system \( A \) we can consider another system, \( B \), also interacting with the same heat bath, as well as with the system \( A \), all the interactions being infinitesimally small. The smallness of the interaction between \( A \) and \( B \) means that there distributions \( W_A \) and \( W_B \) are independent. Hence, if we consider the system \( A + B \), then the distribution function \( W_{AB} \) for this composite system will be simply

\[
W_{AB} = W_A W_B .
\]

(1)

It is this simple relation—if combined with the fact that all the three distributions are the constants of motion for the systems, \( A + B \), \( A \), and \( B \), respectively—allows one to establish the explicit form for the distributions. Let us take logs from both sides of Eq. (1)

\[
\ln W_{AB} = \ln W_A + \ln W_B .
\]

(2)

Any function of a constant of motion is also a constant of motion, we conclude that the log of distribution is an additive constant of motion. But in a general case there is only one (up to a global scaling factor and a trivial constant term) additive constant of motion, the energy. So,

\[
\ln W_A = -\beta H_A + \text{const} ,
\]

(3)

where \( H_A \) is the Hamiltonian of the system \( A \), \( \beta \) is some parameter of the dimensionality of inverse energy, and the constant is fixed by the normalization condition. The parameter \( \beta \) is the only free parameter of the problem, it characterizes the heat bath and, in accordance with (2), is one and the same for all systems that are in thermodynamic equilibrium with the given heat bath. Our final result—Gibbs distribution—reads:

\[
W_A(\{p_s, q_s\}) \propto e^{-\beta H_A(\{p_s, q_s\})} .
\]

(4)

What is the physical meaning of the parameter \( \beta \)? A hint is given by the following definition. The quantity

\[
T = 1/\beta
\]

(5)

is called temperature. The relevance of the quantity \( T \) to, say, kinetic energy of an atom of a gas will become clear later on, as a direct consequence of the distribution (4).

A comment is in order here on the issue of units. From the definition (5) we see that the dimensionality of temperature is the same as that of energy.
If we measure energy in Joules (J), then \( T \) should be also measured in Joules. Nevertheless, there is a practice of measuring temperature in Kelvins (K). There is a historical reason for that (the notion of temperature appeared prior to Gibbs distribution), but there is also a physical reason. The energy scale of 1J is good for typical macroscopic objects, while the scale of 1K is good for a single atom. The relation between the two units is as follows

\[
T(J) = k_B T(K),
\]

where the parameter

\[
k_B = 1.3807 \cdot 10^{-23} \text{J/K}
\]

is called Boltzmann factor. If we measure \( T \) in Kelvins, then we simply need to replace \( T \) with \( k_B T \) in Gibbs distribution. In this course, we measure energy and temperature in the same units. [In the final answers, one can always replace \( T \) with \( k_B T \), if necessary.]

Consider Gibbs distribution for the system of interacting particles described by the Hamiltonian

\[
H = \sum_{j=1}^{N} \frac{p_j^2}{2m} + \sum_{j=1}^{N} V(r_j) + \sum_{i<j} U(r_i - r_j).
\]

We have

\[
W \propto \exp \left( -\sum_{j=1}^{N} \frac{p_j^2}{2mT} \right) \exp \left( -\sum_{j=1}^{N} \frac{V(r_j)}{T} - \sum_{i<j} \frac{U(r_i - r_j)}{T} \right).
\]

We see that the distributions of momenta and coordinates are statistically independent. And this is an amazing counterintuitive fact, since dynamically these variables are strongly coupled! The distribution of momenta is especially simple, since not only the momenta of different particles are statistically independent, but even the components of the momentum of one and the same particle are independent. Hence, without loss of generality we can consider the distribution of momentum (or velocity, since the two are just proportional to each other) of a single one-dimensional particle. This distribution is

\[
W \propto e^{-p^2/2mT} \propto e^{-mv^2/2T}.
\]

This distribution is called Maxwell distribution.

**Problem 14.** Find the expectation value for the kinetic energy of a 1D, 2D, and 3D particle at temperature \( T \).
If particles are non-interacting, then the spatial distribution significantly simplifies:

\[ W \propto \prod_{j=1}^{N} e^{-V(r_j)/T}. \] (11)

All the coordinates—but, generally speaking, not their components—are now statistically independent. This is Boltzmann distribution.

**Problem 15.** Find the expectation value for the potential energy of a 3D harmonic oscillator at temperature \( T \). Reminder: The potential energy of a 3D harmonic oscillator reads: \( U(r) = Ax^2 + By^2 + Cz^2 \), where \( A \), \( B \), and \( C \) are some parameters.