

Where does the Gibbs distribution come from

Haozhe Shan*

December 1, 2020

The Gibbs distribution states that at constant temperature, the probability of a system being in a specific state s is related to the energy of this state $H(s)$ by

$$Prob(s) \propto e^{-\frac{H(s)}{k_B T}}, \quad (1)$$

where T is temperature and k_B is the Boltzmann constant. Why does it have this specific form?

1 A system with fixed energy

Let \mathbf{s} denote state of the system. For example, if the system is composed of N particles in 3D space, \mathbf{s} may be a $6N$ -dimensional vector with the first $3N$ describing momenta and the second $3N$ describing positions.

As the particles move around, \mathbf{s} will change over time. Their dynamics are governed by Newtonian laws, but analyzing their trajectories over time will be difficult. We take advantage of the fact that total energy of all balls is conserved, and think about all the possible \mathbf{s} that give the same energy¹.

Intuitively, the “number” of possible \mathbf{s} depends on E . For example, if the particles only have kinetic energy and $E = 0$, there is only one possible state where all particles have zero momenta. On the other hand, for $E > 0$ we can have all the balls moving slowly, one ball moving quickly, or something in between. We would like to rigorously define this “number” as a state space density.

Think about the space of all \mathbf{s} ². Let $V(E)$ denote the volume in this space corresponding to all \mathbf{s} with energy **less or equal to** E . Then define density as

$$\Omega(E) = \frac{dV(E)}{dE} = \lim_{\delta E \rightarrow 0} \frac{V(E + \delta E) - V(E)}{\delta E}. \quad (2)$$

*Center for Brain Science, Harvard, 2020

¹Physicists call this collection of \mathbf{s} giving rise to the same energy the **microcanonical ensemble**.

²We are assuming that \mathbf{s} takes on continuous values

Given this, the volume of possible \mathbf{s} with energy between $E, E + \delta_E$ is given by $\delta_E \Omega(E)$. For brevity, this will be referred to as the volume at E^3 .

So far, we haven't said anything about probabilities. Here we make a crucial assumption: for a given system E , the probability density function (PDF) of \mathbf{s} is zero outside the $\delta_E \Omega(E)$ volume and uniform inside it. Before seeing how this leads to the Gibbs distribution, we first need to give a careful definition of temperature.

2 A definition of temperature

Intuitively, two objects in contact with each other will stop transferring heat when they have the same temperature. Here we see how we can define temperature in a way that this observation arises from our analysis above.

Arbitrarily divide the system into two parts, described by $\mathbf{s}_1, \mathbf{s}_2$. Energy of each part is given by $H_1(\mathbf{s}_1) = E_1$ and $H_2(\mathbf{s}_2) = E_2$. Since the total energy is fixed, $E_1 + E_2 = E$. Clearly, E_1 can take on different values. What is the probability density function of it? We can derive it by again thinking about volumes in state space.

If the first part is at \mathbf{s}_1 , the second part should have energy $H_2(\mathbf{s}_2) = E - E_1$. We can now just look at the volume in \mathbf{s}_2 space at $E - E_1$. Repeating the calculation in Eq.2, we can express this volume as $\delta_E \Omega_2(E - E_1)$, where Ω_2 is a density function for \mathbf{s}_2 . Analogously, we have a density function for \mathbf{s}_1 , $\Omega_1(E_1)$, such that $\delta_E \Omega_1(E_1)$ is the volume in \mathbf{s}_1 space at E_1 .

To derive the volume associated with $H_1(\mathbf{s}_1) = E_1$, we express $\Omega(E)$ in terms of $\Omega_1(E_1)$ and $\Omega_2(E_2)$. Let $H(\mathbf{s})$ denote energy of the entire system.

$$\Omega(E) = \delta_E^{-1} \int_{E < H(\mathbf{s}) < E + \delta_E} d\mathbf{s} = \delta_E^{-1} \int_{E < H(\mathbf{s}) < E + \delta_E} d\mathbf{s}_1 d\mathbf{s}_2 \quad (3)$$

$$= \int d\mathbf{s}_1 \left(\delta_E^{-1} \int_{E - H_1(\mathbf{s}_1) < H_2(\mathbf{s}_2) < E + \delta_E - H_1(\mathbf{s}_1)} d\mathbf{s}_2 \right) \quad (4)$$

$$= \int d\mathbf{s}_1 \Omega_2(E - H_1(\mathbf{s}_1)) \quad \text{split the space of } \mathbf{s}_1 \text{ into volumes of all possible energy levels} \quad (5)$$

$$= \int dE_1 \left(\delta_E^{-1} \int_{E_1 < H_1(\mathbf{s}_1) < E_1 + \delta_E} d\mathbf{s}_1 \right) \Omega_2(E - H_1(\mathbf{s}_1)) = \int dE_1 \Omega_1(E_1) \Omega_2(E - E_1). \quad (6)$$

Note that the integrand is the volume corresponding to E_1 . Thus

³Strictly speaking, since \mathbf{s} takes on continuous values, the volume of \mathbf{s} related to every energy is 0. By volume at E , I'm referring to energy between E and $E + \delta_E$. This is analogous to how the probability of a continuous random variable taking on any value is 0, but the probability density is non-zero.

$$Prob(E_1) = \frac{\Omega_1(E_1)\Omega_2(E-E_1)}{\Omega(E)}. \quad (7)$$

It turns out that $Prob(E_1)$ is sharply peaked around its maximum⁴. The value of E_1 that maximizes it, E_1^* , should satisfy

$$0 = \frac{d}{dE_1} \Omega_1(E_1)\Omega_2(E-E_1) \Big|_{E_1^*} = \frac{d\Omega_1}{dE_1} \Big|_{E_1^*} \Omega_2(E-E_1^*) + \frac{d\Omega_2}{dE_1} \Big|_{E_1^*} \Omega_1(E_1^*) \quad (8)$$

$$= \frac{d\Omega_1}{dE_1} \Big|_{E_1^*} \Omega_2(E-E_1^*) - \frac{d\Omega_2}{dE_2} \Big|_{E-E_1^*} \Omega_1(E_1^*) \quad (9)$$

$$\Rightarrow \frac{1}{\Omega_1(E_1^*)} \frac{d\Omega_1}{dE_1} \Big|_{E_1^*} = \frac{1}{\Omega_2(E-E_1^*)} \frac{d\Omega_2}{dE_2} \Big|_{E-E_1^*}. \quad (10)$$

Define $S(E) = k_B \log \Omega(E)$ ⁵. The above equation can be rewritten with S

$$\frac{dS_1}{dE_1} \Big|_{E_1^*} = \frac{dS_2}{dE_2} \Big|_{E-E_1^*}. \quad (11)$$

What does E_1^* mean? It means that the first part will very likely have energy level E_1^* and stay there, and the second part will have $E - E_1^*$. In other words, they are not transferring energy to each other. Thus, this equality is something satisfied when both parts have the same T . We thus define the temperature as

$$\frac{1}{T} = \frac{dS}{dE} \Big|_{V,N}, \quad (12)$$

where we specify that this derivative is taken assuming constant volume, V , and number of particles N .

3 Gibbs distribution: system at constant temperature

So far we have focused on systems with a fixed total energy. We now consider systems at a fixed temperature⁶. A more concrete way to think about it is to think about a system in a heat bath. This is now like the pair of systems we considered above, with state vectors $\mathbf{s}_1, \mathbf{s}_2$. However, here we are going to focus on the first system. What is the probability of our system being in state \mathbf{s}_1 ? It

⁴This can be checked by Taylor expansion around E_1

⁵This is the thermodynamic entropy.

⁶Canonical ensembles

should the volume of system 2 having energy $E - E_1$, divided by the volume of the entire system having energy E .

$$Prob(\mathbf{s}_1) \propto \Omega_2(E - E_1) = e^{S_2(E - E_1)/k_B}. \quad (13)$$

Now consider two states, $\mathbf{s}_1 = \mathbf{s}_A$ and $\mathbf{s}_1 = \mathbf{s}_B$. To see which state is more likely, we can take the ratio of their probability density, yielding

$$\frac{Prob(\mathbf{s}_A)}{Prob(\mathbf{s}_B)} = e^{k_B^{-1}[S_2(E - E_A) - S_2(E - E_B)]}. \quad (14)$$

I mentioned previously that fluctuation in E_1 is small. Therefore, $E - E_A$ and $E - E_B$ are close. In addition, we assume the temperature of system 2, i.e. our heat bath, to be constant. In other words,

$$\left. \frac{dS_2}{dE_2} \right|_{E_2 = E - E_A} = \left. \frac{dS_2}{dE_2} \right|_{E_2 = E - E_B} = \frac{1}{T}. \quad (15)$$

We thus write

$$S_2(E - E_A) - S_2(E - E_B) \approx \frac{dS_2}{dE_2}(E_B - E_A) = T^{-1}(E_B - E_A). \quad (16)$$

Plugging this back into Eq.14, we have

$$\frac{Prob(\mathbf{s}_A)}{Prob(\mathbf{s}_B)} = e^{k_B^{-1}T^{-1}(E_B - E_A)}. \quad (17)$$

In other words,

$$Prob(\mathbf{s}_A) \propto e^{-k_B^{-1}T^{-1}E_A}. \quad (18)$$

4 Further reading

Chapter 3, 6 in James Sethna's Statistical Mechanics: Entropy, Order Parameters, and Complexity.