Deriving the Thermal State in Quantum Mechanics

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Abstract

We will derive the canonical thermal state for a quantum system with a given Hamiltonian, using *the principle of maximum entropy inference*, following ideas from by E. T. Jaynes.

1 The thermal state

Here we will follow ideas from E. T. Jaynes [1, 2], and employ *the principle of maximum entropy inference*, to motivate and derive the canonical thermal state of a quantum system, with Hamiltonian $\hat{H}$.

$$\rho = \frac{\mathrm{e}^{-\beta\hat{H}}}{\mathfrak{Tr}\big[\mathrm{e}^{-\beta\hat{H}}\big]} \tag{1}$$

In this derivation we can assume a mix of the "objective" and "subjective" attitude towards probabilities [1] in physical systems—meaning that when we calculate a probability of some state, we deal with it as *our expectation* that this state will be physically realized, and if we wanted to experimentally verify our calculated probabilities we would need an ensemble of identical systems, on which a frequency measurement of the state would approach our calculated probability (in the limit of an infinite ensemble). Put differently, we consider probabilities as calculated from our state of knowledge, but, if we wanted to, we also expect to be able to prepare an ensemble of physical systems that would correlate with our expected probabilities in a frequency measurement.

We then define a "thermal state", for a system with Hamiltonian $\hat{H}$, as one where we only have information about its state in our knowledge about its average energy $\langle E\rangle$.[1] Note that an average energy does not imply some *unique* state ρ, nevertheless, we are looking for exactly such a state.[2] To single out one particular choice of ρ, we follow [1] and include one additional condition. We require is that the state ρ should—not only give the correct average energy $\langle E\rangle$, but also—maximize the von Neumann entropy $S(\rho)$ of the distribution.

$$S(\rho) := -\mathfrak{Tr}\big[\rho \ln \rho\big] \tag{2}$$

From an information theoretic perspective, entropy can be interpreted as the amount of uncertainty in our state, or in other words, the amount of information that has to be supplied in order to reduce the state to a pure state (with no ambiguity, or zero entropy).

To motivate why we wish to *maximize the entropy* (a.k.a. uncertainty), imagine the following scenario, for simplicity only with with *classical* probabilities, and *Shannon* entropy: The only information we have about a physical state is the average energy $\langle E\rangle$, and we have two viable candidate probability distributions $P_1(E_i)$ and $P_2(E_i)$ over a set of energies $\{E_i\}$, such that the (classical) Shannon entropy $H(P)$ is maximized for P_1, and it is strictly smaller for H_2.

$$H(P_1) > H(P_2) \tag{3}$$

Here, the probability distribution P_2 must incorporate some *biased* assumptions (additional information that we do not really have) compared to distribution P_1,

[1] Such an average energy $\langle E\rangle$, is best thought of as an ensemble average.

[2] There are plenty of freedom in our choice of ρ. For instance, we can consider states corresponding to different probability distribution between the eigenvalues of the Hamiltonian $\hat{H}$, $\{P(E_i)\}$, and we can introduce entanglement in our state, without changing the distribution between eigenvalues $\{P(E_i)\}$.

since P_2 is in a sense "closer" to the definite (pure) state than P_1. Therefore P_1 is the only distribution for which we cannot argue that some extraneous information was incorporated. This is *the principle of maximum entropy inference* [1].

Here (in the quantum case), we want to determine the state ρ, that maximizes the von Neumann entropy, but is subject to our constraints $\mathfrak{Tr}[\rho] = 1$, and $\mathfrak{Tr}[\hat{H}\rho] = \langle E \rangle$. To this end, we will use the method of Lagrange multipliers, $\lambda_1 \neq 0$, $\lambda_2 \neq 0$, and we construct the function $f(\rho, \lambda_1, \lambda_2)$.

$$f(\rho, \lambda_1, \lambda_2) = -k\,\mathfrak{Tr}\big[\rho \ln \rho\big] + \lambda_1 \big(1 - \mathfrak{Tr}\big[\rho\big]\big) + \lambda_2 \Big(\langle E \rangle - \mathfrak{Tr}\Big[\rho \hat{H}\Big]\Big) \tag{4}$$

We begin by using the spectral theorem and rewrite our state ρ, and the energy operator $\hat{H}$ on their diagonal form, using some diagonalizing basis $\{|\psi_i\rangle\}$, and $\{|\phi_i\rangle\}$, with their eigenvalues $\{p_i\}$ and $\{E_i\}$, respectively.

$$\rho = \sum_i p_i \, |\phi_i\rangle\langle\phi_i| \tag{5}$$

$$\hat{H} = \sum_i E_i \, |\psi_i\rangle\langle\psi_i| \tag{6}$$

Then $\mathfrak{Tr}[\rho \ln \rho]$ becomes a simple sum over eigenvalues $\sum_i p_i \ln p_i$, the trace over ρ is just the sum of the eigenvalues $\{p_i\}$, and finding the expression for $\mathfrak{Tr}[\rho \hat{H}]$ requires very few steps.

$$f(\rho, \lambda_1, \lambda_2) = -k \sum_i p_i \ln p_i + \lambda_1 \Big(1 - \sum_i p_i\Big) + \lambda_2 \Big(\langle E \rangle - \sum_{i,j} p_i \, E_j \, |\langle \psi_i | \phi_j \rangle|^2\Big) \tag{7}$$

We then want to take the derivatives of this expression with respect every degree of freedom in ρ, and also with respect to $\lambda_1 \neq 0$ and $\lambda_2 \neq 0$, then set all equations equal to 0. Since the term that includes $|\langle \psi_i | \phi_j \rangle|^2$ is the only one affected by an infinitesimal rotation of the state-basis $\{|\psi_i\rangle\}$, if the derivative equals zero, the matrix elements $\langle \psi_i | \phi_j \rangle$ must be indifferent (in the linear, first-order sense) to such a rotation. This is only possible if the bases $\{|\psi_i\rangle\}$, and $\{|\phi_i\rangle\}$ coincide (up to an irrelevant phase for each basis vector). Thus $|\langle \psi_i | \phi_j \rangle|^2 = \delta_{ij}$, and we can conclude that ρ is a diagonal matrix in the eigenbasis of the Hamiltonian, $\{|\phi_i\rangle\}$.

$$\begin{aligned} & f(p_1, \cdots, p_n, \lambda_1, \lambda_2) = \\ & = -k \sum_i p_i \ln p_i + \lambda_1 \Big(1 - \sum_i p_i\Big) + \lambda_2 \Big(\langle E \rangle - \sum_i p_i E_i\Big) \end{aligned} \tag{8}$$

The remaining degrees of freedom of f are the ones with respect to the probability eigenvalues $\{p_i\}$, and of course λ_1 and λ_2. We take the derivative with respect each of them, and set all equations equal to 0.

$$\frac{\partial f}{\partial p_i} = -k\big(\ln p_i + 1\big) - \lambda_1 - \lambda_2 E_i = 0 \qquad \Rightarrow \tag{9}$$

$$\ln p_i = -1 - \frac{\lambda_1}{k} - \frac{\lambda_2 E_i}{k} \qquad \Rightarrow \tag{10}$$

$$p_i = \frac{\mathrm{e}^{-\lambda_2 E_i / k}}{\mathrm{e}^{1 + \lambda_1 / k}} \quad ; \quad \forall\, i \tag{11}$$

Then the derivatives with respect to λ_1 and λ_2, and we gather the results in a system of equations.

$$\begin{cases} p_i = \dfrac{\mathrm{e}^{-\lambda_2 E_i/k}}{\mathrm{e}^{1+\lambda_1/k}} \quad ; \quad \forall\, i & (12) \\ \displaystyle\sum_i p_i = 1 & (13) \\ \displaystyle\sum_i p_i E_i = \langle E \rangle & (14) \end{cases}$$

Since we know that the basis $\{|\phi_i\rangle\}$ diagonalizes both ρ and $\hat{H}$ we can rewrite these equations in terms of ρ and $\hat{H}$.

$$\begin{cases} \rho = \dfrac{\mathrm{e}^{-\lambda_2 \hat{H}/k}}{\mathrm{e}^{1+\lambda_1/k}} & (15) \\ \mathfrak{Tr}\big[\rho\big] = 1 & (16) \\ \mathfrak{Tr}\Big[\rho\hat{H}\Big] = \langle E \rangle & (17) \end{cases}$$

In equation (15) we have two unknowns, λ_1 and λ_2, that are uniquely specified by the two conditions in equation (16) and (17). To find an expression for $\mathrm{e}^{1+\lambda_1/k}$, we take the trace of equation (15) and set it equal to 1.

$$1 = \frac{1}{\mathrm{e}^{1+\lambda_1/k}} \mathfrak{Tr}\Big[\,\mathrm{e}^{-\lambda_2 \hat{H}/k}\Big] \quad \Rightarrow \quad \frac{1}{\mathrm{e}^{1+\lambda_1/k}} = \frac{1}{\mathfrak{Tr}\big[\,\mathrm{e}^{-\lambda_2 \hat{H}/k}\big]} =: \frac{1}{Z} \tag{18}$$

As shown, the denominator in equation (15), $\mathrm{e}^{1+\lambda_1/k} \in (0, \infty)$, can be seen as a normalization of the numerator, we name this normalization *the partition function*, and denote it with $Z := \mathfrak{Tr}\big[\,\mathrm{e}^{-\lambda_2 \hat{H}/k}\big]$.

$$\begin{cases} \rho = \dfrac{\mathrm{e}^{-\lambda_2 \hat{H}/k}}{\mathfrak{Tr}\big[\,\mathrm{e}^{-\lambda_2 \hat{H}/k}\big]} & (19) \\ \mathfrak{Tr}\Big[\rho\hat{H}\Big] = \langle E \rangle & (20) \end{cases}$$

Then λ_2 is a constant that is fixed by $\langle E \rangle$, and a dimensional analysis of λ_2/k gives that it has the physical dimensions of the standard reciprocal temperature $\beta(\langle E \rangle) = 1/kT(\langle E \rangle)$. Thus we can call $\lambda_2/k \equiv \beta$, and we arrive at our thermal state for ρ.

$$\rho = \frac{\mathrm{e}^{-\beta \hat{H}}}{\mathfrak{Tr}\big[\,\mathrm{e}^{-\beta \hat{H}}\big]} \tag{21}$$

We conclude that the thermal state is a diagonal matrix—in the eigenbasis of the Hamiltonian—where the probability eigenvalues correspond to the classical canonical distribution (when treated as a function of their energies, $p_i(E_i)$).

Finally, we should mention one technicality. The method with Lagrangian multipliers can only find *candidate points* for extremum values. In this case, the ρ that we found really is a maximum of the von Neumann entropy, however, a rigorous proof of this will be arduous, so here it is left as an exercise for the restless reader.

2 References

[1] E. T. Jaynes, Information Theory and Statistical Mechanics, Physical Review, Vol. 106, Num. 4, May 15 1957.

[2] E. T. Jaynes, Information Theory and Statistical Mechanics II, Physical Review, Vol. 108, Num. 2, October 15 1957.