

# 10.40 Appendix

## Connection to Thermodynamics and Derivation of Boltzmann Distribution

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### Outline

- Canonical ensemble
- Maximum term method
- Most probable distribution
- Ensembles continued: Canonical, Microcanonical, Grand Canonical, etc.
- Connection to thermodynamics
- Relation of thermodynamic quantities to Q

### 0.1 Canonical ensemble

In the *Canonical ensemble*, each system has constant  $N, \underline{V}$ , and  $T$ .

After equilibration, remove all of the systems from the bath, and put them all together:

Apply postulate 2 to the ensemble of systems, also called a *supersystem*.

Let  $n_j$  = number of systems with energy  $\underline{E}_j$ . Also,  $\mathcal{N} = \sum_j n_j$  and  $\underline{E}_{tot} = \sum_j n_j \underline{E}_j$ .

If we know all  $\underline{E}_j$ 's, then the state of the entire ensemble would be well-defined.

For example, let's analyze an ensemble with 4 systems, labeled A, B, C, and D, where

A	B	C	D
$\underline{E}_2$	$\underline{E}_3$	$\underline{E}_2$	$\underline{E}_1$

Then,  $\underline{E}_{tot} = \underline{E}_1 + 2\underline{E}_2 + \underline{E}_3$

Also, the distribution of the systems,  $\vec{n} = (n_1, n_2, n_3, \dots) = (1, 2, 1)$ .

But there are many different supersystems consistent with this distribution. In fact, the number of supersystems consistent with this distribution is

$$\Omega_{tot}(\vec{n}) = \frac{\mathcal{N}!}{\prod_j n_j!} = \frac{4!}{1!2!1!} = 12$$

What is the probability of observing a given quantum state, e.g.  $\underline{E}_j$ ? In other words, what is the fraction of systems in the ensemble in the state  $\underline{E}_j$ ?

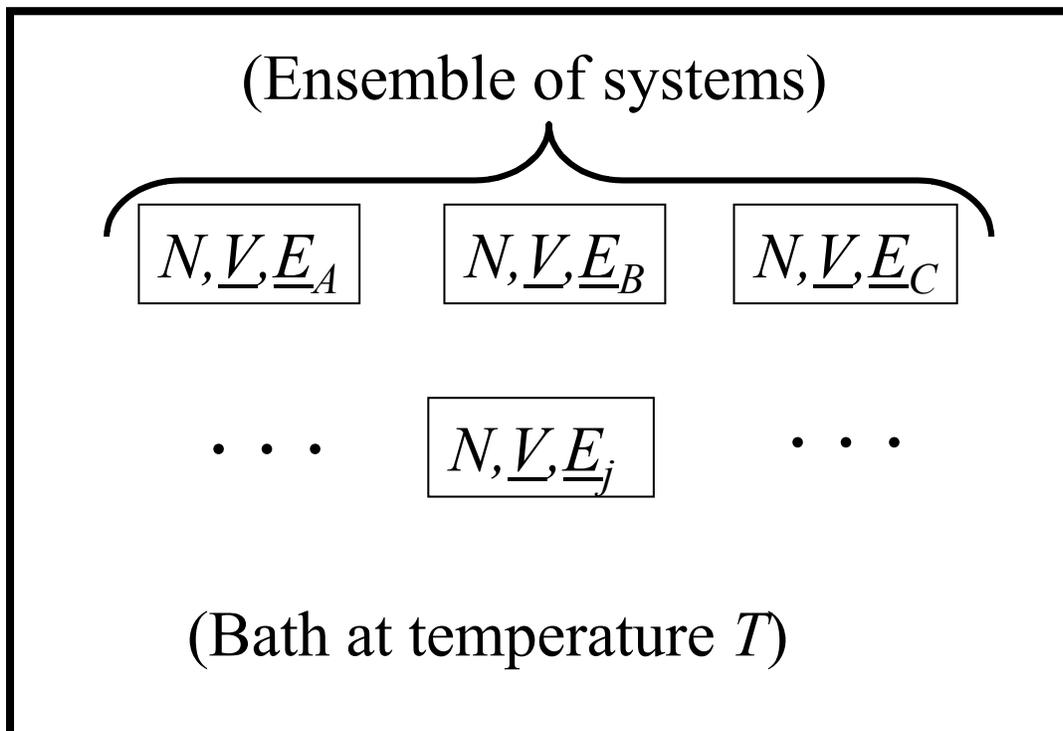


Figure 1: Canonical ensemble

The answer is  $\frac{n_j}{\mathcal{N}}$ .

However, it may be the case that many distributions fulfill the conditions of the ensemble,  $(N, \underline{V}, \underline{E}_{tot})$ .

For example, assume that there are two:

$$n_1 = 1, n_2 = 2, n_3 = 1; \Omega_{tot} = 12$$

and

$$n_1 = 2, n_2 = 0, n_3 = 2; \Omega_{tot} = 6$$

Then the probability of observing, for example,  $\underline{E}_3$  is  $\frac{1}{4}$  in the first distribution and  $\frac{1}{2}$  in the second.

The probability in the case where both distributions make up the ensemble is:

$$p_3 = \left(\frac{1}{4}\right) \frac{1 \times 12 + 2 \times 6}{12 + 6} = \frac{1}{3}$$

In general,

$$p_j = \left(\frac{1}{\mathcal{N}}\right) \frac{\sum_{\vec{n}} \Omega_{tot}(\vec{n}) n_j(\vec{n})}{\sum_{\vec{n}} \Omega_{tot}(\vec{n})}$$

where the sum is over all distributions satisfying the conditions of  $(N, \underline{V}, \underline{E}_{tot})$ .

Then, for example, we could compute ensemble averages of mechanical quantities:

$$\underline{E} = \langle \underline{E} \rangle = \sum_j P_j \underline{E}_j$$

$N, \underline{V}, \underline{E}_A$	$N, \underline{V}, \underline{E}_B$	$N, \underline{V}, \underline{E}_C$
. . .	$N, \underline{V}, \underline{E}_j$	. . .

Figure 2: Canonical ensemble forming its own bath

and

$$P = \langle P \rangle = \sum_j p_j P_j,$$

where  $p$  is the pressure.

## 0.2 Maximum term method

Recall:

$$p_j = \left( \frac{1}{\mathcal{N}} \right) \frac{\sum_{\vec{n}} \Omega_{tot}(\vec{n}) n_j(\vec{n})}{\sum_{\vec{n}} \Omega_{tot}(\vec{n})}$$

where

$$\Omega_{tot}(\vec{n}) = \frac{\mathcal{N}!}{\prod_j n_j!}.$$

As  $\mathcal{N} \rightarrow \infty$ ,  $n_j \rightarrow \infty$ , for each  $j$ .

Thus, the *most probable distribution* becomes dominant. We can call this distribution,  $\vec{n}^*$ .

Let  $n_j^* = n_j$  in the  $\vec{n}^*$  distribution. Then

$$p_j = \frac{1}{\mathcal{N}} \frac{\Omega_{tot}(\vec{n}^*) n_j^*}{\Omega_{tot}(\vec{n}^*)} = \frac{n_j^*}{\mathcal{N}}$$

## 0.3 Most probable distribution

Which distribution gives the largest  $\Omega_{tot}$ ?

Solve via method of undetermined multipliers:

Take natural log of  $\Omega_{tot}$ .

$$\ln(\Omega_{tot}(\vec{n})) = \ln\left(\frac{\mathcal{N}!}{\prod_i n_i!}\right) = \left(\sum_i n_i\right) \ln\left(\sum_i n_i\right) - \sum_i n_i \ln n_i,$$

where we have switched the index from  $j$  to  $i$  and used Stirling's approximation, which becomes exact as  $n_i \rightarrow \infty$ :

$$\ln y! \approx y \ln y - y.$$

We wish to find the set of  $n_j$ 's, which maximize  $\Omega_{tot}(\vec{n})$  and hence  $\ln(\Omega_{tot}(\vec{n}))$ :

$$\frac{\partial}{\partial n_j} \left[ \ln(\Omega_{tot}(\vec{n})) - \alpha \sum_i n_i - \beta \sum_i n_i E_i \right] = 0, j = 1, 2, 3, \dots$$

where  $\alpha$  and  $\beta$  are the undetermined multipliers. Carrying out the differentiation yields

$$\ln \left( \sum_i n_i \right) - \ln n_j^* - \alpha - \beta \underline{E}_j = 0, j = 1, 2, 3, \dots$$

or

$$n_j^* = \mathcal{N} e^{-\alpha} e^{-\beta \underline{E}_j}, j = 1, 2, 3, \dots$$

Recalling that

$$\mathcal{N} = \sum_j n_j^*$$

yields

$$\sum_j e^{-\alpha} e^{-\beta \underline{E}_j} = 1$$

or

$$e^{\alpha} = \sum_j e^{-\beta \underline{E}_j}.$$

Also,

$$\langle \underline{E} \rangle = \frac{\sum_j n_j^* \underline{E}_j}{\mathcal{N}} = \frac{\sum_j \mathcal{N} e^{-\alpha} e^{-\beta \underline{E}_j} \underline{E}_j}{\mathcal{N}} = \frac{\sum_j e^{-\beta \underline{E}_j} \underline{E}_j}{\sum_j e^{-\beta \underline{E}_j}}$$

and

$$p_j = \frac{n_j^*}{\mathcal{N}} = e^{-\alpha} e^{-\beta \underline{E}_j} = \frac{e^{-\beta \underline{E}_j}}{\sum_j e^{-\beta \underline{E}_j}},$$

where

$$Q = \sum_j e^{-\beta \underline{E}_j}$$

and, as we discussed in the last lecture, is the *partition function*, the normalization factor.

#### 0.4 Canonical ensemble continued and connection to thermodynamics

Recall from last time, via the maximum-term method in the canonical ensemble:

$$\langle \underline{E} \rangle = \frac{\sum_j n_j^* \underline{E}_j}{\mathcal{N}} = \frac{\sum_j \mathcal{N} e^{-\alpha} e^{-\beta \underline{E}_j} \underline{E}_j}{\mathcal{N}} = \frac{\sum_j e^{-\beta \underline{E}_j} \underline{E}_j}{\sum_j e^{-\beta \underline{E}_j}}$$

and

$$p_j = \frac{n_j^*}{\mathcal{N}} = e^{-\alpha} e^{-\beta \underline{E}_j} = \frac{e^{-\beta \underline{E}_j}}{\sum_j e^{-\beta \underline{E}_j}},$$

where,

$$Q = \sum_j e^{-\beta \underline{E}_j},$$

as we discussed in the last lecture, is the *partition function*, the normalization factor.

In addition, as we have shown:

$$\underline{E} = \langle \underline{E} \rangle = \sum_j p_j \underline{E}_j$$

and

$$P = \langle P \rangle = \sum_j p_j P_j,$$

where  $P$  is the pressure.

If we differentiate the equation for  $\langle E \rangle$ ,

$$\begin{aligned} d\langle E \rangle &= \sum_j \underline{E}_j dp_j + \sum_j p_j d\underline{E}_j \\ &= -\frac{1}{\beta} \sum_j (\ln p_j + \ln Q) dp_j + \sum_j p_j \left( \frac{\partial \underline{E}_j}{\partial \underline{V}} \right)_N d\underline{V}. \end{aligned} \quad (1)$$

Recall that the pressure,

$$P = \left( \frac{\partial E}{\partial V} \right)_N$$

or

$$P_j = \left( \frac{\partial \underline{E}_j}{\partial \underline{V}} \right)_N.$$

This yields for equation 1

$$d\langle E \rangle = -\frac{1}{\beta} \sum_j \ln p_j dp_j - \frac{1}{\beta} \sum_j \ln Q dp_j + \sum_j p_j P_j d\underline{V}.$$

[Note that

$$\begin{aligned} &d \left( \sum_j p_j \ln p_j \right) \\ &= \sum_j \ln p_j dp_j + \sum_j p_j d(\ln p_j) \\ &= \sum_j \ln p_j dp_j + \sum_j p_j \frac{dp_j}{p_j}. \end{aligned} \quad (2)$$

Since,

$$\begin{aligned} \sum_j p_j &= 1, \\ \sum_j dp_j &= 0. \end{aligned}$$

Thus, the right term in equation 2 is equal to 0. This yields

$$d\langle E \rangle = -\frac{1}{\beta} d \left( \sum_j p_j \ln p_j \right) - \langle P \rangle d\underline{V}.$$

Recalling from the combined first and second laws (in intensive form, noting that since  $N$  is a constant, intensive and extensive forms are equivalent):

$$dU = TdS - PdV$$

Since  $U \leftrightarrow \langle E \rangle$  and  $p \leftrightarrow \langle p \rangle$ ,

$$TdS \leftrightarrow -\frac{1}{\beta} d \left( \sum_j p_j \ln p_j \right).$$

Let

$$X = - \sum_j p_j \ln p_j.$$

Then,

$$dS = \frac{1}{\beta T} dX. \quad (3)$$

We know that the left side of the equation is an exact differential, so the right side must be too, and thus,  $\frac{1}{\beta T}$  must be a function of  $X$ . This means that

$$dS = \phi(X) dX = df(X).$$

Integrating,

$$S = f(X) + \text{const}, \quad (4)$$

where we can set the arbitrary constant, *const*, equal to 0 for convenience.

Now we can make use of the additive property of  $S$ , and we can divide a system into two parts,  $A$  and  $B$ . This yields:

$$S = S^A + S^B = f(X^A) + f(X^B). \quad (5)$$

Note that

$$X^{A+B} = - \sum_{i,j} p_{i,j} \ln p_{i,j},$$

where  $i$  is the index for the possible states of  $A$  and  $j$  is the index for the possible states of  $B$ . Then

$$\begin{aligned} X^{A+B} &= - \sum_{i,j} p_i^A p_j^B (\ln p_i^A + \ln p_j^B) \\ &= - \sum_i p_i^A \ln p_i^A - \sum_j p_j^B \ln p_j^B \\ &= X^A + X^B. \end{aligned}$$

Thus, from equation 5,

$$S = f(X^A) + f(X^B) = f(X^A + X^B).$$

For this to be so,

$$f(X) = kX,$$

where  $k$  is a constant. Thus,

$$S = -k \sum_j p_j \ln p_j. \quad (6)$$

From equations 3 and 4,

$$\frac{1}{\beta T} = k,$$

and thus,

$$\beta = \frac{1}{kT}.$$

We designate  $k$  as Boltzmann's constant, a universal constant.

## 0.5 Microcanonical, Grand Canonical, and other ensembles

Recalling the formulation for  $S$  from equation 6, and noting that in the microcanonical ensemble,

$$p_j = \frac{1}{\Omega},$$

where we recall that  $\Omega$  is the total number of states with the same energy, then

$$\begin{aligned} \underline{S} &= -k \sum_j p_j \ln p_j = -k \sum_j \frac{1}{\Omega} \ln \frac{1}{\Omega} \\ &= k \ln \Omega(N, \underline{V}, \underline{E}). \end{aligned}$$

This is Boltzmann's famous formula for the entropy.

In the Grand Canonical ensemble, the number of particles in each system is allowed to fluctuate, but  $\mu$  is kept constant. This is called the  $(\underline{V}, T, \mu)$  ensemble. Also, there are other ensembles, such as  $(N, P, T)$ , etc. Note that from an analysis of fluctuations (Lecture 27), we shall see that in the macroscopic limit of a large number of systems, all of these ensembles are equivalent.

## 0.6 Relation of thermodynamic quantities to $Q$

Recall that

$$\begin{aligned} \underline{S} &= -k \sum_j p_j \ln p_j \\ p_j &= \frac{e^{-\beta \underline{E}_j}}{Q} \\ Q &= \sum_j e^{-\beta \underline{E}_j} \end{aligned}$$

Plugging in the formula for  $p_j$  into that for  $\underline{S}$  yields

$$\begin{aligned} \underline{S} &= -k \sum_j \frac{e^{-\beta \underline{E}_j}}{Q} \ln \frac{e^{-\beta \underline{E}_j}}{Q} \\ &= -k \sum_j \frac{e^{-\beta \underline{E}_j}}{Q} \left( -\frac{\underline{E}_j}{kT} - \ln Q \right) \\ &= \frac{\langle \underline{E} \rangle}{T} + k \ln Q \end{aligned}$$

Recalling our definitions from macroscopic thermodynamics and the fact that  $U \leftrightarrow \langle E \rangle$  yields

$$\boxed{\underline{A} = -kT \ln Q}$$

Similarly,

$$\begin{aligned} \underline{S} &= - \left( \frac{\partial \underline{A}}{\partial T} \right)_{\underline{V}, N_i} = kT \left( \frac{\partial \ln Q}{\partial T} \right)_{\underline{V}, N_i} + k \ln Q \\ \underline{P} &= - \left( \frac{\partial \underline{A}}{\partial \underline{V}} \right)_{T, N_i} = kT \left( \frac{\partial \ln Q}{\partial \underline{V}} \right)_{T, N_i} \\ \underline{U} &= \underline{A} + T\underline{S} = kT^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{\underline{V}, N_i}. \end{aligned}$$

Thus, all thermodynamic properties can be written in terms of the partition function,  $Q(N, \underline{V}, T)$ !

In order to compute  $Q$ , all we need are the possible energy levels of the system. We can obtain these from solving the equations of quantum mechanics.