10.40 Lecture 30

Postulates of statistical mechanics, Gibbs ensembles, partition function

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Outline

- Ensembles
- Postulates of statistical mechanics
- Microcanonical ensemble
- Canonical ensemble
- Maximum term method
- Most probable distribution

30.1 Ensembles and ensemble averages

An *ensemble* is an assembly of microstates or of systems. Imagine a very large collection of systems evolving in time. A snapshot of the state of each of these systems at some instant in time forms the ensemble. As an example, the one-dimensional random walk could also be viewed as a large collection of random lines, on each of which the particle takes C steps either to the left or to the right. We can then create an ensemble, and thence determine an ensemble average, by measuring the number of steps to the right or to the left on each line, and then averaging all of these results together to obtain a complete average.

30.2 Two postulates of statistical mechanics

Most of statistical mechanics results from two different postulates, both of which state very simple, but very important concepts.

1. Time averaging is equivalent to ensemble averaging.
2. For possible states with the same $N, \underline{V}$,and $\underline{E}$, all states are equally likely. (Atkins calls this the "principle of equal *a priori* probabilities.")

Postulate 1 states that the result of averaging an observable property across many measurements taken across time can be replaced with the related result of averaging a property at a single time across a large number of systems, as defined by an ensemble. Postulate 2 tells us that if we have multiple states with the same energy, they are all equally likely. This applies to only states within a given energy level, but does not generalize across energy levels.

30.3 Microcanonical ensemble

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

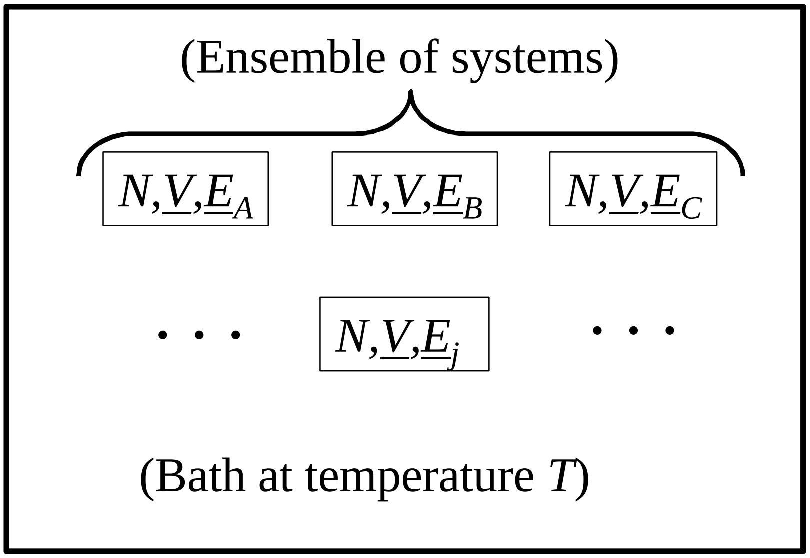

Figure 1: Microcanonical ensemble

By Postulate 2, the probability that any given system is in a particular state, j, is $\frac{1}{\mathcal{N}}$, where $\mathcal{N}$ is the total number of possible states. It is important to note that the microcanonical ensemble consists of all unique states with $N, \underline{V}$,and $\underline{E}$ held constant.

30.4 Canonical ensemble

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

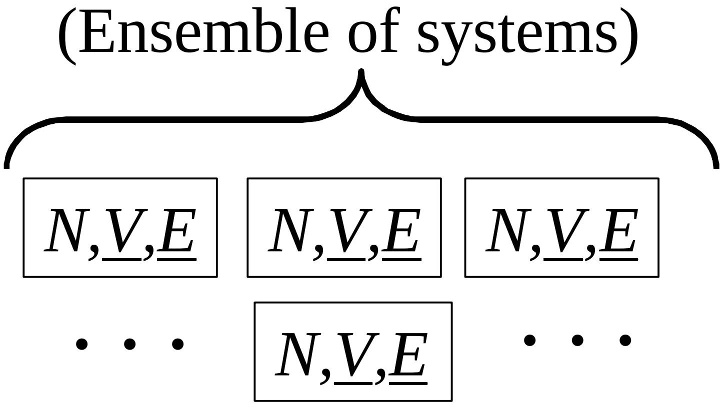

Figure 2: Canonical ensemble

we can remove all of the systems from the bath, and put them all together:

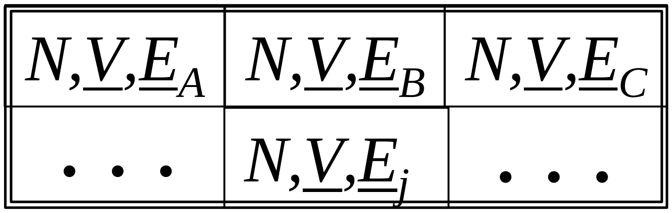

Figure 3: Canonical ensemble acting as its own heat bath

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

Let n_j be the number of systems with energy $\underline{E}_j$. Also, the number of systems is given by

$$\sum_j n_j = \mathcal{N},$$

while the total energy of the ensemble is given by

$$\underline{E}_{tot} = \sum_j n_j \underline{E}_j.$$

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

As an 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 system can be described as a vector $\overrightarrow{n} = (n_1, n_2, n_3, ...) = (1, 2, 1)$.

This particular arrangement is not unique, however: there are many different supersystems consistent with this distribution. In fact, the number of supersystems consistent with this distribution are

$$\text{-}_{tot}(\overrightarrow{n}) = \frac{\mathcal{N}!}{\prod_j n_j!} = \frac{4!}{1!2!1!} = 12.$$

Each of these configurations is equivalent, and have the same total energy, and are indistinguishable in terms of their behavior. If we want to know the probability of observing a given quantum state, such as $\underline{E}_j$, we can determine the fraction of systems in the ensemble in the state $\underline{E}_j$. We can clearly show that this probability is just $n_j/\mathcal{N}$. However, we may still find that many distributions fulfill the conditions of the ensemble, $(N, \underline{V}, \underline{E}_{tot})$.

For example, assume that there are two such distributions

$$n_1 = 1, n_2 = 2, n_3 = 1; \text{-}_{tot} = 12.$$

and

$$n_1 = 2, n_2 = 0, n_3 = 2; \text{-}_{tot} = 6.$$

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.

If these two distributions were the only ones available to us in the ensemble, then the probability of observing $\underline{E}_3$ is given by

$$P\left(\underline{E}_3\right) = \frac{\left(\frac{1}{4}\right) \times 12 + \left(\frac{2}{4}\right) \times 6}{12 + 6} = \frac{1}{3}.$$

More generally, we can express this result as

$$P_j = \left(\frac{1}{\mathcal{N}}\right) \frac{\sum_{\overrightarrow{n}} -_{\ tot}(\overrightarrow{n}) n_j(\overrightarrow{n})}{\sum_{\overrightarrow{n}} -_{\ tot}(\overrightarrow{n})}, \qquad (1)$$

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:

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

and

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

where p is the pressure.

30.5 Maximum term method

In the canonical ensemble, we have lots of different probability distributions, which makes it very difficult to calculate the the complete partition function.

Recall that in (1), $-_{\ tot}\left(\vec{n}\right)$ is given by

$$-_{\ tot}(\overrightarrow{n}) = \frac{\mathcal{N}!}{\prod_j n_j!}.$$

As $\mathcal{N} \to \infty$, $n_j \to \infty$, for each j. Under these conditions, what we find is that a single distribution, the *most probable distribution*, denoted $\vec{n}^*$, becomes dominant over all others. We can call this distribution, $\overrightarrow{n}^*$. For the systems in the j^{th} state, in the most probable distribution $\vec{n}^*$, we obtain

$$P_j = \frac{1}{\mathcal{N}} \frac{-_{\ tot}(\overrightarrow{n}^*) n_j^*}{-_{\ tot}(\overrightarrow{n}^*)} = \frac{n_j^*}{\mathcal{N}}.$$

30.6 Most probable distribution

We can now show how to find the distribution that gives the largest $-_{\ tot}$. The method is known as the method of *Lagrange multipliers*, or *undetermined multipliers*. Before we begin, though, we find it simpler to start with the natural logarithm of $-_{\ tot}$, rather than $-_{\ tot}$ itself:

$$\ln\left(-_{\ tot}(\overrightarrow{n})\right) = \ln\left(\frac{\mathcal{N}!}{\prod_i n_i!}\right) = \left(\sum_i n_i\right) \ln\left(\sum_i n_i\right) - \sum_i n_i \ln n_i, \qquad (2)$$

where in (2) we have switched the index from j to i and used Stirling's approximation, which becomes exact as $n_i \to \infty$:

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

We wish to find the set of n_j's which maximize $-_{\ tot}(\overrightarrow{n})$ and therefore, also maximize $\ln\left(-_{\ tot}\left(\overrightarrow{n}\right)\right)$. To do this, we note that our constraints are:

1. The number of states in our system $\sum_i n_i$ is constant.
2. The total energy of the system $\sum_i n_i E_i$ is constant.

Including these constraints in our system gives us the objective function

$$f(\vec{n}) = \ln\left(-\ _{tot}(\vec{n}) - \alpha \sum_i n_i - \beta \sum_i n_i E_i \right). \tag{3}$$

Taking the derivative of (3) with respect to a given n_j, we have

$$\frac{\partial}{\partial n_j}\left[\ln\left(-\ _{tot}(\overrightarrow{n})\right) - \alpha \sum_i n_i - \beta \sum_i n_i E_i = 0 \right],$$

for each $j = 1, 2, 3, \ldots$, where α and β are the undetermined multipliers. Carrying out the differentiation yields

$$\ln\left(\sum_i n_i\right) - \ln n_j^* - \alpha - \beta E_j = 0,$$

or

$$n_j^* = \mathcal{N} e^{-\alpha} e^{-\beta E_j}. \tag{4}$$

If we recall that

$$\mathcal{N} = \sum_j n_j^*, \tag{5}$$

then we find from (4) and (5) that

$$\sum_j e^{-\alpha} e^{-\beta E_j} = 1,$$

which we can rewrite as

$$e^{\alpha} = \sum_j e^{-\beta E_j}. \tag{6}$$

From (6), we therefore find that e^{α} defines the normalization factor of the system, which we will show can be associated with the canonical partition function Q.

Also, the average energy of a system in the ensemble is given by

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

while the probability of observing a given state in the system is

$$P_j = \frac{n_j^*}{\mathcal{N}} = e^{-\alpha} e^{-\beta E_j} = \frac{e^{-\beta E_j}}{Q},$$

where

$$Q = \sum_j e^{-\beta E_j} \tag{7}$$

is the *partition function*, or normalization factor, as we discussed in the previous lecture. What we have not yet determined, however, is the coefficient β in (7), which serves to "scale" the energy coefficients: we will shortly show, however, that $\beta = 1/k_B T$.