Lecture 2: Canonical Ensemble and the Partition Function

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Probability Distribution:
Probability distribution functions are at the heart of statistical mechanics. All observables (thermodynamic) can be expressed as functions of averages over a distribution.

\[
F(\theta) = F \left( \int \theta(X) P(X) \, dX \right) \equiv F(\langle \theta \rangle)
\]

Single observation
Probability
Average of all

\[
F(\langle \theta \rangle) = E, G, H, \mu, C_p, k, \ldots \text{ for example}
\]

When we determine the \( \theta(X) \) and \( P(X) \), we can calculate the observable \( F(\langle \theta \rangle) \).

Let's derive now the probability distribution corresponding to the chemical ensemble. The physical picture of the chemical ensemble is the following.
Ensemble and Canonical Ensemble:

Ensemble:
An idealization consisting of a large number of similar systems

Canonical Ensemble:
An ensemble with the same Number of molecules, Volume and Temperature, but different Energy per system. \((N, V, T)\)

Step 1: Ensemble placed in heat bath to equilibrate at \(T\).

Step 2: Ensemble surrounded by thermal insulation: Total energy fixed.

In principal, these are energy eigenvalues of quantum states

<table>
<thead>
<tr>
<th>systems</th>
<th>(a_1)</th>
<th>(a_2)</th>
<th>(a_3)</th>
<th>...</th>
<th>(a_n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>energy</td>
<td>(E_1)</td>
<td>(E_2)</td>
<td>(E_3)</td>
<td>...</td>
<td>(E_n)</td>
</tr>
</tbody>
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The set \(\{a_i\}\) is the distribution of the energies \(\{E_i\}\) over the ensemble
**Constraints on the distribution**

- Total number of members of the ensemble fixed: \( \sum_i a_i = A \)
- Total energy of the ensemble fixed: \( \sum_i a_i E_i = E_{TOT} \)

Any distribution which satisfies constraints above is a possible distribution for the ensemble.

**Most probable distribution:**

**Q:** what is the most probable distribution \( \{a_i\} \) for the canonical ensemble? (canonical distribution).

**A:** Count the number of ways of realizing each distribution \( \{a_i\} \) over the ensemble. The canonical distribution (most probable) is that distribution which can be realized in the largest number of ways.

In general, \( W(\{a_i\}) \equiv \) number of ways of realizing the distribution over the ensemble

\[
= \frac{A!}{a_1!a_2!a_3!\cdots}
\]

\( \iff \) If each energy level is distinct

\( \iff \) Eliminating over counting

In order to get the most probable distribution, we seek to maximize \( W(\{a_i\}) \) subject to two constraints above.
Simplification:

(1). \( \{a_i\} \) are integers but may be treated as continuous variables.

(2). Maximizing \( \ln W(\{a_i\}) \) equals maximizing \( W(\{a_i\}) \)

(3). \( \ln a! = a \ln a - a \) (stirling’s approximation when \( a \) is a large number)

\[
(1) \quad \ln W = A \ln A - A - \sum a_i \ln a_i - \left( -\sum a_i \right) \\
(2) \quad \delta \ln W = \sum \frac{\partial \ln W(\{a_i\})}{\partial a_i} \delta a_i \\
= - \sum \frac{\partial}{\partial a_i} (a_i \ln a_i) \delta a_i = - \sum (\delta a_i + \ln a_i \delta a_i)
\]

The two constraints can be expressed:

(3) \( \sum_i \delta a_i = 0 \) \quad (4) \( \sum_i E_i \delta a_i = 0 \)

From (2) and (3)

(5) \( \delta \ln W = - \sum \ln a_i \cdot \delta a_i = 0 \)
From (5), use method of Lagrange undetermined multipliers to introduce constraints (3) and (4) in to the equation

\[
(6) \quad \sum_i \ln a_i \cdot \delta a_i + \alpha \sum_i \delta a_i + \beta \sum_i E_i \delta a_i
\]

\[
= \sum_i (\ln a_i + \alpha + \beta E_i) \delta a_i = 0
\]

\[
\ln a_i^* + \alpha + \beta E_i = 0 \\
a_i^* = e^{-\alpha} e^{-\beta E_i}
\]

Where \(\{a_i^*\}\) distribution that maximizes \(W\)

We need to evaluate \(\alpha\) and \(\beta\) in (7), from the first constraint (3)

\[
\sum_i a_i = A \rightarrow e^{-\alpha} = \frac{A}{\sum_i e^{-\beta E_i}}
\]

Now, the probability of a system in the ensemble having energy \(E_i\) is:

\[
(7) \quad P(E_i) \equiv \frac{\# \text{ systems in ensemble with energy } E_i}{\text{Total } \# \text{ systems in the ensemble}} = \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}
\]

The sum in the denominator \(\sum_i e^{-\beta E_i}\) \textbf{Canonical partition function} \(Q\) is very important in statistical Thermodynamics,

\[
(8) \quad Q(N, V, \beta) = \sum_i e^{-\beta E_i(N, V)} \quad \text{Or } Z(N, V, \beta)
\]
Canonical partition function:
Partition functions are used in statistical mechanics to connect microscopic properties with macroscopic properties

\[ P(E_i) = \frac{e^{-\beta E_i}}{Q} \tag{7} \]

\[ Q(N, V, \beta) = \sum_i e^{-\beta E_{i(N,V)}} \tag{8} \]

If differentiate \( \ln Q_N \) with respect to \( \beta \):

\[ \frac{\partial \ln Q}{\partial \beta} = \frac{\partial Q}{Q \partial \beta} = \frac{\sum_i (-E_i)e^{-\beta E_i}}{Q} = -\sum_i E_i P(E_i) = -\langle E \rangle \tag{9} \]

Define **thermodynamic limit** to be:

\[ N \to \infty \quad \text{# molecules in each system} \]

\[ V \to \infty \quad \text{Volume of each system} \]

\[ N|V = \text{constant} \]

Stat Mech:
Average statistical mechanical energy

\[ \langle E \rangle = E \]

Thermodynamics Internal Energy
What is $\beta$?
(You can check the supplementary materials for the proof.)

$$\beta = \frac{1}{k_B T} \quad k_B = 1.3906 \times 10^{-16} \text{ erg} \cdot \text{deg}^{-1}$$

Also Mc Quarries derives:

(10) \[ S = k_B \ln Q + \frac{E}{T} \]

(11) \[ A(T, V) = E - TS = -k_B T \ln Q \]
We will show that: \[ \beta \propto \frac{1}{T} \]

Consider \( \ln Q \), the natural log of canonical partition function:
\[
f(\beta, E, E_2 \ldots) = \ln Q = \ln \left( \sum_i e^{-\beta E_i} \right)
\]

The total differential of \( f \) is:
\[
df = \left( \frac{\partial f}{\partial \beta} \right)_{\{E_i\}} d\beta + \sum_j \left( \frac{\partial f}{\partial E_j} \right)_{\{\beta, E_{i\neq j}\}} dE_j
\]

Let’s evaluate the partial derivative of \( f \) with respect to \( \beta \) and \( \{E_i\} \)

From (9)
\[
\left( \frac{\partial f}{\partial \beta} \right)_{\{E_i\}} = -\langle E \rangle = -\bar{E}
\]
\[
\left( \frac{\partial f}{\partial E_j} \right)_{\beta, E_{i\neq j}} = \frac{1}{Q} \cdot \frac{\partial}{\partial E_j} \sum_i e^{-\beta E_i} = -\frac{\beta}{Q} e^{-\beta E_j} = -\beta P(E_j)
\]
Supplementary material

So, total differential of f is:

\[ df = -\overline{E} \, d\beta - \beta \sum_j P(E_j) \, dE_j \]

\[ d(\overline{E} \, \beta) = \overline{E} \, d\beta + \beta \, d\overline{E} \]

When we combine the equation above:

\[ d(f + \beta \overline{E}) = \beta \left( (d\overline{E}) - \sum_j P(E_j) \, dE_j \right) \]

From \( Q(N, V, \beta) = \sum_i e^{-\beta E_i(N,V)} \):

\[ dE_i = \frac{\partial E_i}{\partial V} \, dV = -P_j \, dV \]

Put it back to the total differential:

\[ d(f + \beta \overline{E}) = \beta \left( (d\overline{E}) - \sum_j P(E_j) \, dE_j \right) = \beta (dQ_{rev}) \]

Pressure on system

Work done on the system

Change of ensemble internal energy

Work
The left hand side is a state function because the integral of a total differential depends only on the end points. So $\beta(dQ_{rev})$ is a state function.

By 2nd law of thermodynamics, $\frac{dQ_{rev}}{T}$ is a state function: $1/T$ is the integration factor that makes product $\frac{dQ_{rev}}{T}$ a state function, so:

$$\beta \propto \frac{1}{T}$$

Also, since $\frac{dQ_{rev}}{T} = dS$, by second law,

$$d(f + \beta E) = \frac{dS}{k_B}$$

$$\frac{S}{k_B} = f + \beta E + \text{constant} = \ln Q + \beta E + \text{constant}$$

$$S = k_B \ln Q + \frac{E}{T} + \text{constant}$$

Since we cares the change of $S$ not the absolute $S$, we can set the constant 0,

$$S = k_B \ln Q + \frac{E}{T}$$