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A Simple System Analyzed on the
Canonical and Microcanonical
Ensembles

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1. The Problem Statement

Consider a system of \( N \) distinguishable, independent particles, each of which can exist in two states separated by an energy \( \varepsilon \).

We specify the state of the system, \( \psi \) by

\[
\psi = (N_1, N_2, N_3, \ldots, N_N), \quad N_j = 0 \text{ or } 1
\]

where \( N_j \) = state of the particle \( j \). The energy of a given state is given by

\[
E_\psi = \sum_{i=1}^{N} N_i \varepsilon,
\]

where I have chosen the ground state energy as 0.

2. Analysis on the Canonical Ensemble

Starting from

\[
Z = \sum_\psi e^{-\beta E_\psi}
\]
and

$$F = -kT \ln Z$$

we can write

$$-\beta F = \ln \sum_{\psi} e^{-\beta E_{\psi}}.$$ 

Now, the energy of a given state is given by

$$E_{\psi} = \sum_{j=1}^{N} N_j \varepsilon_j,$$

then entering this into the expression for the partition function, we get

$$Z = \sum_{\psi} e^{-\beta E_{\psi}}$$

so

$$Z = \sum_{N_1, N_2, \ldots, N_N = 0 \text{ or } 1} \exp \left( -\beta \sum_{i=1}^{N} N_i \varepsilon_i \right).$$
Section 2: Analysis on the Canonical Ensemble

We can use $e^{a+b} = e^a e^b$ to write the rewrite the partition function as

$$Z = \sum_{N_1, N_2, \ldots, N_N = 0 \text{ or } 1} (e^{-\beta N_1 \varepsilon}) (e^{-\beta N_2 \varepsilon}) \ldots$$

or

$$Z = \left( \sum_{N_1 = 0 \text{ or } 1} e^{-\beta \varepsilon N_1} \right) \left( \sum_{N_2 = 0 \text{ or } 1} e^{-\beta \varepsilon N_2} \right) \ldots \left( \sum_{N_N = 0 \text{ or } 1} e^{-\beta \varepsilon N_N} \right).$$

We can rewrite this as a product

$$Z = \prod_{j=1}^{N} \sum_{N_j = 0, 1} e^{-\beta \varepsilon N_j}.$$ 

The sum contained in this product can be evaluated easily,

$$\sum_{N_j = 0, 1} e^{-\beta \varepsilon N_j} = \frac{1}{N_j = 0} + e^{-\beta \varepsilon} \frac{1}{N_j = 1},$$

which reduces to

$$Z = (1 + e^{-\beta \varepsilon})^N.$$
Section 2: Analysis on the Canonical Ensemble

Now that we have the partition function, we are in a position to calculate the properties of the system. Recall

\[
\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}
\]

and

\[
F = -kT \ln Z(T, V, N)
\]

so

\[
-\beta F = \ln Z.
\]

Thus, in the current example we have

\[
-\beta F = \ln \left(1 + e^{-\beta \varepsilon}\right)^N = N \ln \left(1 + e^{-\beta \varepsilon}\right)
\]

and

\[
\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = -\frac{\partial}{\partial \beta} N \ln \left(1 + e^{-\beta \varepsilon}\right)
\]
\[ \begin{align*}
\frac{N}{(1 + e^{-\beta \varepsilon})} \partial \frac{\partial}{\partial (1 + e^{-\beta \varepsilon})} \\
\varepsilon Ne^{-\beta \varepsilon} \\
\frac{N \varepsilon}{e^{\beta \varepsilon} + 1}.
\end{align*} \]

Thus we have

\[ E = E(T) \]

We can draw some simple conclusions from this expression.

At \( T = 0 \), \( e^{\beta \varepsilon} \to \infty \Rightarrow E \to 0 \).

Thus at \( T = 0 \) all particles are in the ground state.

As \( T \to \infty \), \( e^{\beta \varepsilon} \to 1 \), since \( \beta \varepsilon \to 0 \), and \( E = NE/2 \).

Thus as \( T \to \infty \) all states are equally likely.
3. Analysis on the Microcanonical Ensemble

Consider the state $m$, with $m$ upper levels occupied, its multiplicity is the number of ways of choosing $m$ objects from $N$, the identity is immaterial.

$$C(N,m) = \Omega(E,N) = \frac{N!}{m!(N-m)!}.$$  

For the state $m$, we can write $E = m\varepsilon$, or $m = E/\varepsilon$.

Combining this with $S = k \ln \Omega(E,N)$ and $\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_{V,N}$, we get,

$$\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_{V,N} = \left( \frac{\partial (k \ln \Omega)}{\partial E} \right)_{V,N}$$

or

$$\frac{1}{kT} = \beta = \left( \frac{\partial (\ln \Omega)}{\partial E} \right)_{V,N}.$$
But $E = m\varepsilon$, $\varepsilon = \text{constant}$, so $dE = \varepsilon dm$, and
\[
\beta = \frac{1}{\varepsilon} \left( \frac{\partial (\ln \Omega)}{\partial m} \right)_{V,N},
\]
where $N$ must be large enough for $\Omega$ to be a continuous function of $m$.

We must now relate this to system functions
\[
\left( \frac{\partial (\ln \Omega)}{\partial m} \right)_{V,N} = \frac{\partial}{\partial m} \ln \left( \frac{N!}{m!(N-m)!} \right)_N
\]
but $\ln N! = N \ln N - N$, so
\[
\ln \frac{N!}{m!(N-m)!} = N \ln N - N - [(N-m) \ln(N-m) - (N-m)
+ m \ln m - m]
= N \ln N - (N-m) \ln(N-m) - m \ln m
\]
\[
\left( \frac{\partial \ln \Omega}{\partial m} \right)_N = 0 - \frac{\partial}{\partial m} (N-m) \ln(N-m) - \frac{\partial}{\partial m} \ln m
\]
\[
\begin{align*}
= \ln(N - m) - \frac{(N - m) \partial(N - m)}{\partial m} - \ln m - \frac{m \partial m}{\partial m} \\
= \ln(N - m) + 1 - \ln m - 1 \\
= \ln \left( \frac{N - m}{m} \right) \\
= \ln \left( \frac{N}{m} - 1 \right).
\end{align*}
\]

But,
\[
\beta = \frac{1}{\varepsilon} \left( \frac{\partial \Omega}{\partial m} \right)_{N,V},
\]
so
\[
\varepsilon \beta = \ln \left( \frac{N}{m} - 1 \right)
\]
and
\[
\exp(\varepsilon \beta) = \frac{N}{m} - 1, \\
m = \frac{N}{1 + \exp(\varepsilon \beta)}.
\]
and finally, using $E = m \varepsilon$ we get the same result that we got earlier by performing the analysis on the canonical ensemble:

$$E = \frac{N_\varepsilon}{1 + e^{\varepsilon \beta}}.$$