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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 ε.

We specify the state of the system, ψ by

$$\psi = (N_1, N_2, N_3, \ldots, N_N), \qquad N_j = 0 \text{ or } 1$$

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

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

and

$$F = -kT \ln Z$$

we can write

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

Now, the energy of a given state is given by

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

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

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

so

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

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

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

or

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

We can rewrite this as a product

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

The sum contained in this product can be evaluated easily,

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

which reduces to

$$Z = \left(1 + \mathrm{e}^{-\beta \varepsilon}\right)^N.$$

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

$$<E>= -\frac{\partial \ln Z}{\partial \beta}$$

and

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

so

$$-\beta F = \ln Z.$$

Thus, in the current example we have

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

and

$$\begin{aligned} <E> &= -\frac{\partial \ln Z}{\partial \beta} \\ &= -\frac{\partial}{\partial \beta} N \ln \left(1 + \mathrm{e}^{-\beta\varepsilon}\right) \end{aligned}$$

$$
\begin{aligned}
&= -\frac{N}{(1+\mathrm{e}^{-\beta\varepsilon})}\frac{\partial}{\partial\beta}\left(1+\mathrm{e}^{-\beta\varepsilon}\right) \\
&= \frac{\varepsilon N \mathrm{e}^{-\beta\varepsilon}}{(1+\mathrm{e}^{-\beta\varepsilon})} \\
{<}E{>} &= \frac{N\varepsilon}{\mathrm{e}^{\beta\varepsilon}+1}.
\end{aligned}
$$

Thus we have

$$E = E(T)$$

We can draw some simple conclusions from this expression.

At $T = 0$, $\mathrm{e}^{\beta\varepsilon} \to \infty \Rightarrow E \to 0$.
Thus at $T = 0$ all particles are in the ground state.

As $T \to \infty$, $\mathrm{e}^{\beta\varepsilon} \to 1$, 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 $E = m\varepsilon$, $\varepsilon =$ constant, so $\mathrm{d}E = \varepsilon \mathrm{d}m$, and

$$\beta = \frac{1}{\varepsilon}\left(\frac{\partial\left(\ln\Omega\right)}{\partial m}\right)_{V,N},$$

where N must be large enough for Ω to be a continuous function of m.

We must now relate this to system functions

$$\left(\frac{\partial\left(\ln\Omega\right)}{\partial m}\right)_{V,N} = \frac{\partial}{\partial m}\ln\left(\frac{N!}{m!(N-m)!}\right)_N$$

but $\ln N! = N\ln N - N$, so

$$\begin{aligned}
\ln\frac{N!}{m!(N-m)!} &= N\ln N - N - [(N-m)\ln(N-m) - (N-m) \\
&\quad + m\ln m - m] \\
&= N\ln N - (N-m)\ln(N-m) - m\ln m
\end{aligned}$$

$$\left(\frac{\partial\ln\Omega}{\partial m}\right)_N = 0 - \frac{\partial}{\partial m}(N-m)\ln(N-m) - \frac{\partial}{\partial m}\ln m$$

$$
\begin{aligned}
&= \ln(N-m) - \frac{(N-m)}{(N-m)}\frac{\partial(N-m)}{\partial m} - \ln m - \frac{m}{m}\frac{\partial m}{\partial m} \\
&= \ln(N-m) + 1 - \ln m - 1 \\
&= \ln\left(\frac{N-m}{m}\right) \\
&= \ln\left(\frac{N}{m} - 1\right).
\end{aligned}
$$

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

$$\mathrm{e}^{\varepsilon\beta} = \frac{N}{m} - 1,$$

$$m = \frac{N}{1 + \mathrm{e}^{\varepsilon\beta}},$$

and finally, using $E = m\varepsilon$ we get the same result that we got earlier by performing the analysis on the canonical ensemble:

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