The Grand Canonical Partition Function

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1 Introduction to the Grand Canonical Ensemble

Last week, we introduced systems for which the number of particles is not fixed. Instead, the system can exchange particles with a large reservoir at fixed chemical potential μ and temperature T. The role of the reservoir is to maintain the system at fixed T and fixed μ. We would like to understand the properties of such a system.

Question: What is the probability distribution governing this system?

Answer: The grand canonical ensemble.

The probability of finding the system in a specific microstate $|n\rangle$ depends on both the energy E_n of that state and the number of particles N_n occupying that state:

$$p(n) = \frac{e^{-\beta(E_n - \mu N_n)}}{\mathcal{Z}} \tag{1}$$

where μ is the chemical potential, $\beta = 1/(k_B T)$, and $\mathcal{Z}$ is the normalization factor.

2 The Grand Canonical Partition Function (Gibbs Sum)

Here, $\mathcal{Z}$ is the **grand canonical partition function** (also called the Gibbs sum). It is obtained by summing over *all possible microstates* of the system:

$$\mathcal{Z} = \sum_n e^{-\beta(E_n - \mu N_n)}. \tag{2}$$

Note that this includes summing over all possible occupation N_n of each state $|n\rangle$.

3 Useful Relations

Just as the canonical partition function Z acts as a generating function for the average energy, the grand canonical partition function $\mathcal{Z}$ generates averages for both energy and particle number.

3.1 Energy and Particle Number Relation

Let us take the derivative of the natural logarithm of $\mathcal{Z}$ with respect to β:

$$\begin{aligned}
-\frac{\partial}{\partial\beta}\ln\mathcal{Z} &= -\frac{1}{\mathcal{Z}}\frac{\partial\mathcal{Z}}{\partial\beta} \\
&= -\frac{1}{\mathcal{Z}}\sum_n \frac{\partial}{\partial\beta}\left[e^{-\beta(E_n-\mu N_n)}\right] \\
&= -\frac{1}{\mathcal{Z}}\sum_n -(E_n-\mu N_n)e^{-\beta(E_n-\mu N_n)} \\
&= \sum_n (E_n-\mu N_n)\left[\frac{e^{-\beta(E_n-\mu N_n)}}{\mathcal{Z}}\right]
\end{aligned}$$

Recognizing the term in the brackets as the probability $p(n)$:

$$\begin{aligned}
-\frac{\partial}{\partial\beta}\ln\mathcal{Z} &= \sum_n (E_n-\mu N_n)p(n) \\
&= \sum_n E_n p(n) - \mu\sum_n N_n p(n)
\end{aligned}$$

$$\boxed{-\frac{\partial}{\partial\beta}\ln\mathcal{Z} = \langle E\rangle - \mu\langle N\rangle} \tag{3}$$

Here, $\langle E\rangle$ is the average energy of the system and $\langle N\rangle$ is the average number of particles in the system.

3.2 Average Number of Particles

Now, let us take the derivative of the natural logarithm of $\mathcal{Z}$ with respect to the chemical potential μ:

$$\begin{aligned}
\frac{\partial}{\partial\mu}\ln\mathcal{Z} &= \frac{1}{\mathcal{Z}}\frac{\partial\mathcal{Z}}{\partial\mu} \\
&= \frac{1}{\mathcal{Z}}\sum_n \frac{\partial}{\partial\mu}\left[e^{-\beta(E_n-\mu N_n)}\right] \\
&= \frac{1}{\mathcal{Z}}\sum_n e^{-\beta(E_n-\mu N_n)}(\beta N_n) \\
&= \beta\sum_n N_n\left[\frac{e^{-\beta(E_n-\mu N_n)}}{\mathcal{Z}}\right] \\
&= \beta\sum_n N_n p(n)
\end{aligned}$$

Since $\sum_n N_n p(n)$ is the average number of particles $\langle N\rangle$, we get:

$$\frac{\partial}{\partial\mu}\ln\mathcal{Z} = \beta\langle N\rangle \tag{4}$$

Rearranging to solve for $\langle N\rangle$:

$$\boxed{\langle N\rangle = \frac{1}{\beta}\frac{\partial}{\partial\mu}\ln\mathcal{Z}} \tag{5}$$

or equivalently:

$$\langle N \rangle = k_B T \frac{\partial \ln \mathcal{Z}}{\partial \mu} \tag{6}$$