To consider theories for fluctuations in the number of particles we require an ensemble that keeps $V$, $T$, and the chemical potential, $m$ constant, a grand canonical ensemble. To construct the grand canonical ensemble, the system is enclosed in a container that is permeable both to heat and to the passage of particles. The number of particles in the system can range over all possible values. As in the canonical ensemble we have occupation numbers $a_{nj}$ describing the number of systems that have energy $E_j$ and $N$ particles. There are two indices for summation since neither the energy of the system nor the number of particles is the same in all of the systems. We can specify the state of the ensemble by specifying that $a_{n1}$, $a_{n2}$, $a_{n3}$, of the systems are in states 1, 2, 3, ..., respectively, with energies $E_{n1}$, $E_{n2}$, $E_{n3}$,... depending on $N$, the number of particles in each system. In the grand canonical ensemble the occupation numbers obey three conditions.

Following the principle of a priori probabilities, we assume that every distribution of occupation number is equally probable. As we have seen for the canonical ensemble we can use the method of the most probable distribution to derive the form of the distribution function and the partition function for the grand ensemble.

The number of ways $W(a)$ or $W(a_{n1}, a_{n2}, a_{n3},....)$ that any particular distribution of $a_{nj}$’s can be achieved is given by

As before we assume that the systems are macroscopic and are distinguishable objects that can be distributed among available states. In any particular distribution $a_{nj}/A$ is the fraction of systems of the canonical ensemble in the $j$th energy state containing $N$ particles. The overall probability $P_{nj}$ that a system is in the $j$th quantum state with $N$ particles is obtained by averaging $a_{nj}/A$ over all the allowed distributions.

The notation of summing over $a$ means that the value of $a_j$ depends on the distribution and that the summations are over all distributions that satisfy the constraints. The most probable distribution is the distribution that maximizes $W$. The maximum $W$ will be found by setting the derivative $\frac{\partial \ln W(a_{nj})}{\partial a_{nj}} = 0$ subject to the constraints above that the $a_{nj}$ must sum to $A$, the total energy $E$ is equal to the sum of $a_{nj}E_j$, and the total number of particles $N$ is $a_{nj}N$. This implies that
In other words, there is no change in the total number of systems $A$, total energy $E$, and the total number of particles, $\mathbf{N}$ with respect to changes in the occupation numbers. The procedure followed here is analogous to that used for the canonical ensemble; we maximize $W$ subject to the constraints. The difference is that there is one addition constraint on the number of particles, $\mathbf{N}$ that was not present in the canonical ensemble.

To maximize subject to constraints we use the method of LaGrange undetermined multipliers.

where we have moved the summation symbol in front of the three terms. The constants $a$, $\mathbf{b}$, and $g$ are the undetermined multipliers. We first carry out the derivative and then find the value of the multipliers.

We can evaluate

$$\left(\frac{\partial \ln W}{\partial a_{N_i}}\right) = \left(\frac{\partial \ln A!}{\partial a_{N_i}}\right) - \sum N S_j \left(\frac{\partial \ln a_{N_j}}{\partial a_{N_i}}\right)$$

using Stirling's approximation: $\ln x! \approx x\ln x - x$.

To simplify $\left(\frac{\partial \ln W}{\partial a_{N_i}}\right)$ the first step is to note that

$$\ln W = \ln A! - \sum N S_j \ln a_{N_j} = \ln A - A - \sum N S_j a_{N_j} \ln a_{N_j} - \sum N S_j \ln a_{N_j}$$

Since $A = \sum N S_j a_{N_j}$ the last two terms cancel to give

$$\ln W = \ln A - \sum N S_j a_{N_j} \ln a_{N_j}$$

Note that exactly the same procedure and algebra are used to show that the derivative of $\ln W$ is equal to the most probable distribution in the canonical ensemble, and so we have:
The most probable distribution is:

Now we only need to find the undetermined multipliers $a$, $b$, and $g$.

By summing both sides the indices $N$ and $j$ we can obtain $a$.

The left-hand side is equal to one and $e^{a} = \frac{1}{X}$ where $X$ is the grand canonical partition function or the grand partition function (for short).

The Boltzmann distribution in this ensemble can be written

The star indicates that this is the most probable distribution as shown above by maximizing $W$ with respect to the occupation numbers.

The averages of mechanical properties $E$, $P$, and $N$ are
We have shown that \( b = \frac{1}{k_B T} \) where \( k_B \) is Boltzmann’s constant. This is true for all of the ensembles. A similar approach can be used to show that \( g = \frac{-m}{k_B T} \). The differential of the grand partition function is

Using the definitions of mechanical properties from above we have

The last term is the ensemble-averaged work done by the system.

We add \( d(b \bar{\epsilon} \bar{n}) + d(g N) \) to both sides

The thermodynamic equation

\[ dE = TdS - PdV + m \, dN \]

can be rearranged to
TdS = dE - m dN + PdV

Comparing these two equations by dividing through by $b$ we find that

$$g = -mb = -m/kT$$ from the second term in each equation.

Since we can replace $g/b$ by $-m$ we have

which gives the entropy as

Since

$$G = m N = E + PV - TS$$

We can use the above equation to determine that

There are several ways to express the grand partition function. Starting with the definition,

we can define the canonical partition function for N particles as

and then insert this expression into the grand partition function
We know also that \( e^g = e^{m/kT} \). The quantity \( e^{m/kT} \) is often denoted \( l \).

For indistinguishable particles \( Q = q^N/N! \) where \( q \) is the molecular partition function. Therefore,

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