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The Grand Canonical Ensemble

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1. Systems with Variable Particle Numbers

We have developed an expression for the partition function of an ideal gas.

2. Review of the Ensembles

2.1. Microcanonical Ensemble

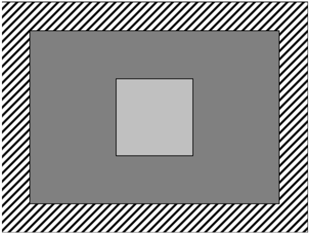
The system is isolated. This is the first bridge or route between mechanics and thermodynamics, it is called the *adiabatic* bridge.

E, V, N are fixed $\quad S = k \ln \Omega(E, V, N)$

2.2. Canonical Ensemble

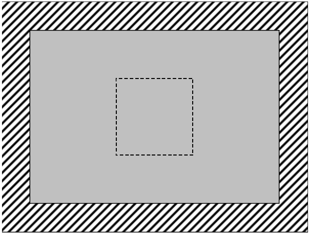
System in contact with a heat bath. This is the second bridge between mechanics and thermodynamics, it is called the *isothermal* bridge. This bridge is more elegant and more easily crossed.

T, V, N fixed, E fluctuates. $F = -kT \ln Z(T, V, N)$



2.3. Grand Canonical Ensemble

System in contact with heat bath/paricle reservoir. This third bridge is called the *open* bridge. T, V, μ fixed, E and N fluctuate. $\Omega = -kT\ln\Xi = -kT\ln\mathcal{Z}$, where Ω is the grand potential and $\Xi(=\mathcal{Z})$, is the grand partition function.



3. Average Values on the Grand Canonical Ensemble

For systems in thermal and diffusive contact with a reservoir, let $x(N,r)$ be the value of x when the system has N particles and is in state Nr. The thermal average is thus

$$\langle x\rangle = \sum_{N,r} x(N,r)p_{Nr} = \frac{\sum\limits_{N,r} x(N,r)\mathrm{e}^{\beta(N\mu - E_{Nr})}}{\mathcal{Z}}$$

3.1. Average Number of Particles in a System

$$\langle N\rangle = \frac{\sum\limits_{N,r} N\mathrm{e}^{\beta(N\mu - E_{Nr})}}{\mathcal{Z}}$$

We can evaluate this by differentiating $\mathcal{Z}$.

$$\frac{\partial \mathcal{Z}}{\partial \mu} = \sum_{N,r} N \beta \mathrm{e}^{\beta(N\mu - E_{Nr})}$$

$$\frac{\partial \mathcal{Z}}{\partial \mu} = \beta \sum_{N,r} N \mathrm{e}^{\beta(N\mu - E_{Nr})}.$$

Now we can rewrite our equation for $\langle N \rangle$ as

$$\mathcal{Z}\langle N \rangle = \sum_{N,r} N \mathrm{e}^{\beta(N\mu - E_{Nr})}$$

and we see that

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

$$\langle N \rangle = \frac{1}{\beta \mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \mu}$$

$$\langle N \rangle = \frac{1}{\beta} \frac{\partial (\ln \mathcal{Z})}{\partial \mu}.$$

Now it is useful to introduce the *absolute activity* λ at this point. We define the absolute activity as

$$\lambda = \mathrm{e}^{\beta\mu}.$$

We use this to rewrite the expressions for $\mathcal{Z}$ and $\langle N \rangle$.

$$\begin{aligned}
\mathcal{Z} &= \sum_N \sum_r \mathrm{e}^{\beta(N\mu - E_{Nr})} \\
&= \sum \sum \mathrm{e}^{\beta N\mu} \mathrm{e}^{-E_{Nr}} \\
&= \sum \sum \lambda^N \mathrm{e}^{-E_{Nr}}.
\end{aligned}$$

So we can rewrite our our expression for $\langle N \rangle$

$$\langle N \rangle = \frac{1}{\beta} \frac{\partial(\ln \mathcal{Z})}{\partial \mu},$$

using $\lambda = \mathrm{e}^{\mu\beta}$. Starting from $\lambda = \mathrm{e}^{\mu\beta}$, we find

$$\frac{\partial \lambda}{\partial \mu} = \beta \mathrm{e}^{\mu\beta} = \lambda\beta.$$

So

$$\frac{1}{\beta}\frac{\partial(\ln\mathcal{Z})}{\partial\mu} = \frac{1}{\beta}\frac{\partial(\ln\mathcal{Z})}{\partial\lambda}\frac{\partial\lambda}{\partial\mu} = \frac{\lambda\beta}{\beta}\frac{\partial(\ln\mathcal{Z})}{\partial\lambda} = \lambda\frac{\partial(\ln\mathcal{Z})}{\partial\lambda}$$

This is a result of practical importance. We can find λ by matching $\langle N\rangle$ to N the actual number of particles in the system.

In chemistry, it is common to introduce the fugacity at this point. The definition is close to the definition of the absolute activity, we define the *fugacity* f as

$$f = \mathrm{e}^{\frac{\mu}{k}}.$$

We will not make further use of the fugacity.

In calculating the thermal properties of systems, the ensemble on which we choose to make the calculations is a matter of convenience. We choose the ensemble independently of the actual environment. This is possible because fluctuations tend to be small. Since $N =$ const is mathematically awkward, the grand ensemble is often the most convenient approach.

4. The Grand Canonical Ensemble and Thermodynamics

Starting from

$$\mathcal{Z} = \sum_{N,r} \mathrm{e}^{\beta(N\mu - E_{Nr})}$$

and

$$p_{Nr} = \frac{\mathrm{e}^{\beta(N\mu - E_{Nr})}}{\mathcal{Z}},$$

we relate the grand canonical ensemble to thermodynamics using the Gibbs entropy formula

$$S = -k \sum_{r} p_r \ln p_r.$$

In this case we write the Gibbs entropy formula as

$$S = -k \sum_{N,r} p_{Nr} \ln p_{Nr}.$$

Inserting the Gibbs distribution, we get

$$\begin{aligned}
S &= -k \sum_{N,r} p_{Nr} \ln \left(\frac{\mathrm{e}^{\beta(N\mu - E_{Nr})}}{\mathcal{Z}} \right) \\
&= -k \sum_{N,r} p_{Nr} \ln \left(\ln \left(\frac{1}{\mathcal{Z}} \right) + \beta N \mu - \beta E_{Nr} \right) \\
&= -k \sum_{N,r} p_{Nr} \ln \frac{1}{\mathcal{Z}} - k \sum_{N,r} p_{Nr} \beta N \mu + k \sum_{N,r} p_{Nr} \beta E_{Nr} \\
&= -k \ln \frac{1}{\mathcal{Z}} \sum_{N,r} p_{Nr} - k\beta\mu \sum_{N,r} p_{Nr} N + k\beta \sum_{N,r} E_{Nr} p_{Nr} \\
S &= k \ln \mathcal{Z} - k\beta\mu \langle N \rangle + k\beta \langle E \rangle.
\end{aligned}$$

And, after rearranging

$$\ln \mathcal{Z} = \frac{S}{k} + \beta\mu\langle N \rangle - \beta\langle E \rangle,$$

which will normally be written as

$$\ln \mathcal{Z} = \frac{S}{k} + \beta\mu N - \beta E,$$

where, as usual, we have written $E = \langle E \rangle$ and $N = \langle N \rangle$.

This expression can be further simplified. To simplify it we will make use of the Legendre transform.

5. Legendre Transforms

Legendre transforms are widely used in mechanics and thermodynamics. Legendre transforms transform are most easily explained in one dimension. For each function $f(x)$ define a new function $\mathcal{L}f(z)$, the Legendre transform, as follows:
Define

$$z = \frac{\mathrm{d}f}{\mathrm{d}x}$$

thus relating the new variable z to the old variable x. We require that

$$\frac{\mathrm{d}^2 f}{\mathrm{d}x^2} \neq 0$$

to guarantee that we can find the inverse function $x(z)$. Hence we have a unique relation between x and z. The Legendre transform can be written as

$$\mathcal{L}f(z) = zx(z) - f\left(x(z)\right)$$

So we simultaneously change our variable to the derivative and modify the function. Note that in physics the transform is often defined as the negative of the function above (e.g. $F = E - TS$) The mathematical definition of the transform is “better” as there is no minus sign in the inverse transformation. But in thermodynamics we want to keep the meaning of the transformed function in terms of energy, and $TS - E$ would be awkward. Thus we have seen Legendre transforms but have not defined them.

That completes the theory as I’ll present it, if you are interested you can easily find the complete theory worked out (usually in terms of mappings) and explicit calculations of the inverse transform. I'm going to show you how to figure it out practically for two variables.

5.1. Legendre Transforms for two variables

Consider a function of two variables $f(x, y)$ so that the differential of f is of the form

$$\mathrm{d}f = \frac{\partial f}{\partial x}\mathrm{d}x + \frac{\partial f}{\partial y}\mathrm{d}y$$

or

$$\mathrm{d}f = u\mathrm{d}x + v\mathrm{d}y$$

where $u = \frac{\partial f}{\partial x}$ and $v = \partial f \partial y$. Our task is change the independent variables x, y to the independent variables u, y. The differential quantities will be expressed in terms of $\mathrm{d}u$ and $\mathrm{d}y$. to effect the change let

$$g = f - ux$$

then

$$\mathrm{d}g = \mathrm{d}f - u\mathrm{d}x - x\mathrm{d}u$$

but

$$\mathrm{d}f = u\mathrm{d}x + v\mathrm{d}y$$

so

$$\mathrm{d}g = v\mathrm{d}y - x\mathrm{d}u.$$

This is the form we desire. The quantities x and v are now functions of u and y and are given by

$$x = -\frac{\partial g}{\partial u} \text{ and } v = \frac{\partial g}{\partial y}.$$

In this case, these are our inverse transforms. The transformation of the Lagrangian of mechanics to the Hamiltonian is an example of such a transformation.[1]

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[1] See for example: Herbert Goldstein, *Classical Mechanics*, Addison-Wesley, 1950, Chapter 7

5.2. Helmholtz Free Energy as a Legendre Transform

We want to transform from $E(S, V, N)$ to $F(T, V, N$ so using

$$\mathcal{L}f(z) = f\left(x(z)\right) - zx(z)$$

we know $T = \left(\frac{\partial E}{\partial S}\right)_{V,N}$ so we write

$$\mathcal{L}E(N, V, T) = E(N, V, S(T))\frac{\partial E}{\partial S}S$$

or

$$F = E - TS.$$

calculating the differential shows that we have changed the independent variable from S to T.

6. Legendre Transforms and the Grand Canonical Ensemble

Recall we have found

$$\ln \mathcal{Z} = \frac{S}{k} + \beta\mu N - \beta E$$

we can rewrite this as

$$-kT \ln \mathcal{Z} = E - TS - \mu N.$$

Rewriting this as

$$-kT \ln \mathcal{Z} = F - \mu N$$

we recognize this as another Legendre transform, as we know that μ is the conjugate variable of N. Thus we are transforming to a quantity that is a function of μ rather than being a function of N. Such potentials are called grand potentials. This one happens to be the most useful. So defining

$$\Omega(T, V, \mu) = F(T, V, N(\mu)) - \frac{\partial F}{\partial N} N$$

we have

$$\mathrm{d}\Omega = \mathrm{d}F - \mu \mathrm{d}N - N\mathrm{d}\mu = S\mathrm{d}T - p\mathrm{d}V - N\mathrm{d}\mu$$

The grand potential is the available energy for a system in contact with a reservoir that provides the energy necessary to keep the system at constant temperature and the particles necessary to keep it at constant chemical potential.

We can now relate Ω and$\mathcal{Z}$ by writing

$$\Omega = -kT \ln \mathcal{Z}.$$

This result is the open bridge between thermodynamics and statistical mechanics. This equation will form the basis of our strategy for deriving thermodynamics from the grand canonical ensemble.

Since we have used the methods before, I am going to summarize the strategy as you will appreciate the terminology. You wouldn't have before we had studied the canonical ensemble.

7. Solving Problems on the Grand Canonical Ensemble

1. Find $\mathcal{Z}$ as a function of T, V, μ. (Other mechanical extensive variables could replace V.

2. Find the grand potential from $\Omega = -kT \ln \mathcal{Z}$.

3. Find the entropy of the system from

   $$S = -\left(\frac{\partial \Omega}{\partial T}\right)_{V,\mu}$$

   and the number of particles from

   $$N = \langle N \rangle = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{V,T}$$

4. Use

   $$p = -\left(\frac{\partial \Omega}{\partial V}\right)_{\mu,T}$$

to find the equation of state.

5. Find any useful thermodynamic potential from

$$F = \Omega + \mu N$$

$$E = F + TS = \Omega + \mu N + TS$$

$$G = E + pV - TS = F + pV$$

$$H = E + pV$$

6. Study the system using thermodynamics.