Apr. 15

Grand Canonical Ensemble

At the end of the previous lecture, I introduced the *grand potential*

$$\Xi = F - \mu N$$

appropriate to situations in which the number of particles is not fixed. This quantity satisfies

$$N = -\left.\frac{\partial \Xi}{\partial \mu}\right|_{T,V}$$

In this lecture, I will derive this quantity as the logarithm of an appropriate partition function, and I will discuss some applications of the corresponding ensemble.

To begin our discussion, go back to the description of a system of many particles by the microcanonical ensemble with fixed E and N. In the previous lecture, we considered a situation in which a large system exchanges energy with a small system under study. We can generalize this discussion to a situation in which the larger system can exchange both *energy* and *particles*. We describe the composite of the large and small system by a microcanonical ensemble with total energy $\mathcal{E}$ and total number of particles $\mathcal{N}$. The phase space volume is

$$\Omega_*(\mathcal{E},\mathcal{N}) = \sum_N \int dE \; \Omega(E,N)\, \Omega_{Bath}(\mathcal{E}-E, \mathcal{N}-N)$$

Following the logic of the previous lecture, represent the phase space volume of the large system as

$$\Omega_B(E,N) = e^{S_B(E,N)}$$

and then expand the entropy of the large system in the relatively small quantities E and N, the energy and particle number in the small system. For the bath,

$$\left.\frac{\partial S_B}{\partial E}\right|_{V,N} = \frac{1}{T} \qquad \left.\frac{\partial S_B}{\partial N}\right| = -\frac{\mu}{T}$$

so that

$$S_B(\mathcal{E}-E, \mathcal{N}-N) = S_B(\mathcal{E}, \mathcal{N}) - \frac{1}{T}E + \frac{\mu}{T}N$$

The quantity

$$e^{S_B(\mathcal{E},\mathcal{N})}$$

factors out as an overall constant, independent of the particular state of the small system. The states of the small system should then appear with the probability

$$P \propto e^{-\frac{E}{T} + \frac{\mu}{T}N}$$

This average over states is called the *grand canonical ensemble.* Averages over observables are given by the formula

$$\langle \mathcal{O}(q,p,N)\rangle = \frac{\sum_N \int \left(\frac{dq\,dp}{2\pi\hbar}\right)_N \mathcal{O}(q\,p\,N)\, e^{-\beta[H(q,p)-\mu N]}}{\sum_N \int \left(\frac{dq\,dp}{2\pi\hbar}\right)_N e^{-\beta[\mathcal{H}(q,p)-\mu N]}}$$

The denominator in this formula is the *grand partition function*

$$\Xi = \sum_N \int \left(\frac{dq\,dp}{2\pi\hbar}\right)_N e^{-\beta[H-\mu N]} \qquad \beta = \frac{1}{T}$$

The *grand potential* is then defined by

$$\log \Xi = -\beta \Phi \qquad \text{or} \qquad \Phi = -T \log \Phi$$

analogously to our definition of F in the previous lecture. If the small system is macroscopic, we can make use of the fact that the fluctuations about the equilibrium state are very small. Then the grand canonical weight factor is strongly peaked about its value for the most probable configurations. This implies that the relationship between Φ and the entropy is

$$-\beta \Phi = S - \beta E + \beta \mu N$$

so this indeed implies the formula

$$\Phi = E - TS - \mu N = F - \mu N$$

presented at the end of the previous lecture.

In thermodynamics, the *chemical potential* μ is the conjugate quantity to particle number N. In statistical mechanics, we see that the factor

$$e^{\beta \mu N}$$

gives the relative weight of states with different values of N. By adjusting μ, we can shift the expectation value $\langle N \rangle$. Typically, our strategy in working with the grand canonical ensemble will be to choose μ so that the expectation value $\langle N \rangle$ gives the desired number of particles in the system.

From the definition of Ξ, this quantity is the generating function of correlations of energy and particle number. Analogously to the result for the partition function of the canonical ensemble,

$$\langle E-\mu N \rangle = -\frac{\partial}{\partial\beta}\log\Xi\Big|_{V,\mu} = \frac{\sum_N \int \frac{dq\,dp}{2\pi\hbar}(H-\mu N)e^{-\beta(H-\mu N)}}{\sum_N \int \frac{dq\,dp}{2\pi\hbar}\; e^{-\beta(H-\mu N)}}$$

Here we have also

$$\langle N \rangle = \frac{1}{\beta}\frac{\partial}{\partial\mu}\log\Xi\Big|_{T,V} = \frac{\sum_N \int \frac{dq\,dp}{2\pi\hbar}\; N\; e^{-\beta(H-\mu N)}}{\sum_N \int \frac{dq\,dp}{2\pi\hbar}\; e^{-\beta(H-\mu N)}}$$

And, just as for the energy, the second derivative of the log of the partition function gives the mean square fluctuation in particle number,

$$\frac{1}{\beta^2}\frac{\partial^2}{\partial\mu^2}\log\Xi = \langle N^2 \rangle - \langle N \rangle^2$$

The quantity $\log\Xi$ is extensive, and μ and β are intensive, so the left-hand side of this equation is proportional to N. On the right-hand side, each term is proportional to N^2, but the difference must be proportional to N. This is consistent with the idea that the mean square deviation in particle number is of the order of $\sqrt{N}$.

As a first application of this formalism, we can evaluate Ξ for an ideal gas.

$$\Xi = \sum_N \int\left(\frac{dq\,dp}{2\pi\hbar}\right)_N e^{-\beta H}\, e^{\beta\mu N}$$

$$= \sum_N \frac{1}{N!} V^N \left[\int\frac{d^3p}{(2\pi\hbar)^3}\, e^{-\beta\frac{p^2}{2m}}\right]^N e^{\beta\mu N}$$

In writing the phase space volume of N particles, I include a factor $1/N!$ to account for the equivalence of configurations obtained by exchanging identical particles.

$$\Xi = \sum_N \frac{1}{N!} V^N \left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2 N} e^{\beta\mu N}$$

Then the expression for the grand partition function can be recognized to sum to an exponential

$$\Xi = \exp\left[V \left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2} e^{\beta\mu} \right]$$

Finally,

$$\Phi = -V T^{5/2} \left(\frac{m}{2\pi\hbar^2}\right)^{3/2} e^{\beta\mu}$$

This formula does not have an obvious interpretation on its own. To form an interpretation, it will be useful to eliminate μ in favor of the expected number of particles N. These are connected by the relation

$$N = \frac{1}{\beta}\frac{\partial}{\partial\mu}\log\Xi\Big|_{T,V} \quad \text{or} \quad N = -\frac{\partial\Phi}{\partial\mu}\Big|_{T,V}$$

Differentiating the expression above, we find

$$N = V T^{3/2} \left(\frac{m}{2\pi\hbar^2}\right)^{3/2} e^{\beta\mu}$$

Then

$$\mu = T \log\left[\frac{N}{V}\left(\frac{2\pi\hbar^2}{mT}\right)^{3/2}\right]$$

and, quite simply,

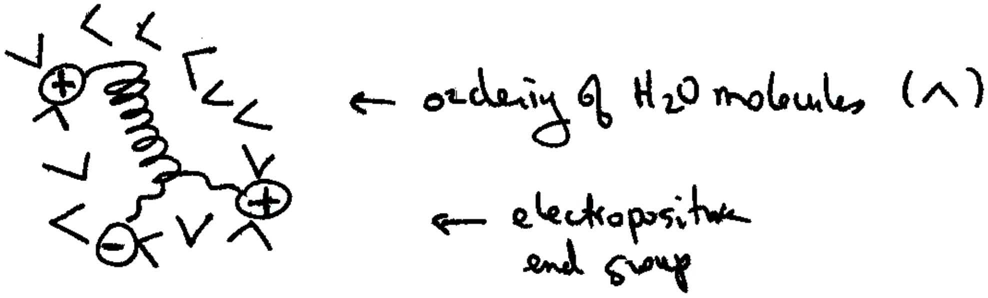
$$\Phi = -NT$$

Since, as we derived in the previous lecture, $\Phi = -pV$, we find

$$pV = NT$$

which is the correct result for an ideal gas.

This example illustrates that the grand canonical ensemble makes calculation for the idea gas much easier than in either of our previous formalisms. It also gives a remarkable bonus: It implies that the ideal gas law actually applies to systems that are far from ideal. Consider, as a target for a statistical mechanics description, a dilute solution, with N_S solute molecules – even a solution of complex molecules such as proteins – interacting with a solvent, for example water. The solute-solvent interaction can be very complicated.



Howver, as long as the solution is sufficiently dilute that we can ignore the interaction of *solute* molecules with one another, we can analyze this system simply in the grand canonical ensemble for N_S. Under this assumption, the statistical weight of configurations in the sum over N_S has the form

$$\Xi = \sum_{N_S} \frac{1}{N_S!} V^{N_S} [\mathcal{Z}]^{N_S} e^{\beta \mu_S N_S}$$

where $\mathcal{Z}$ is a very complicated integral over the relative positions of solvent molecules surrounding one molecule of solvent. This integral is independent of the concentration of solute. It depends on T and other thermodynamic parameters of the solvent. So, give it a name:

$$\mathcal{Z} = e^{-\beta f_S(T)}$$

The function $f_S(T)$ is the *effective free energy* of a solute molecule. The grand partition function is then

$$\Xi = \exp[V e^{-\beta f_S(T)} e^{\beta \mu_S}]$$

Working from this expression following the logic that we used to study the ideal gas,

$$N_S = V e^{-\beta f_S(T)} e^{\beta \mu_S}$$

and

$$\mu_S = T \log \frac{N_S}{V} + f_S(T)$$

so that

$$\Phi = -N_S T$$

and the pressure due to the presence of the solute is

$$P_S = \frac{N_S T}{V}$$

It is difficult to compute $f_S(T)$ from first principles, but we could determine it experimentally under some standard conditions. Often, we will want to work with constant *pressure* instead of fixed volume. In that case, we would convert Φ to the analogue of a Gibbs free energy and quote an effective Gibbs free energy per particle. Also, instead of working with

$$N_S/V = \text{molecules}/\text{cm}^3$$

it is often more convenient to work with the *concentration*

$$c_S = \text{moles}/\text{cm}^3$$

absorbing the conversion factor into $f_S(T)$. For the rest of this lecture, I will write the formula for μ above in the standard form

$$\mu_S = T \log c_S + f_S(T)$$

The result for the pressure due to the solute

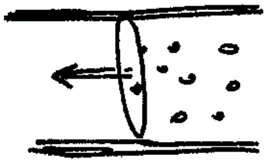
$$P_S = \frac{N_S}{V} T$$

is remarkably simple. This pressure can be measured. Set up a *semipermeable membrane*, that is, a membrane that is freely permeable to solvent molecules but impermeable to molecules of the solute.

The solvent molecules can pass back and forth through the membrane to equalize their pressure, but for the solute molecules, this is not possible. So there is a net force acting on the membrane. This force points to the left in the figure. This force per unit area, called *osmotic pressure* is given by

$$P = \frac{N_s T}{V}$$

This is *van't Hoff's law*. Osmotic pressure can be used to operate an engine and extract work. Indeed, this is the means of turning stored energy into work in many biological systems.

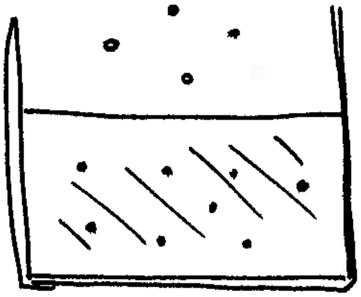


It is interesting that the driving force here comes from *entropy*. Increasing the volume of the right-hand side of the container at the expense of the left-hand side increases the entropy of the solute. This lowers the total free energy, since

$$F = E - TS$$

Most biological membranes are selectively permeable, and most of these contain protein molecules that pump ions up a concentration gradient to maintain a concentration difference across the membrane.

Now consider a solute in equilibrium with a gas outside the solvent, for example, CO_2 dissolved in water in equilibrium with CO_2 gas.



The chemical potential of CO_2 in each phase is

$$\text{gas:} \quad \mu_g = T \log c_g + f_g(T)$$

$$\text{liquid:} \quad \mu_\ell = T \log c_\ell + f_\ell(T)$$

where

$$f_g(T) = \frac{3}{2} \log \frac{2\pi\hbar^2}{mT} + \left(\begin{array}{c}\text{rotational}\\ \text{free energy}\end{array}\right) + \log N_A$$

and $f_\ell(T)$ is much harder to compute. But, still, the general structure of these equations tells us something about the equilibrium. Think of the two systems, CO_2 in gas and CO_2 dissolved in water, as two statistical systems in equilibrium with a large reservoir of particles. Then each system much have the same chemical potential as that of the reservoir. Then, for equilibrium,

$$\mu_g = \mu_\ell$$

This implies

$$\log c_\ell = \log c_g + f(T)$$

this is

$$c_\ell = K(T)\ c_g$$

In other words, the concentration of CO_2 dissolved in the water is proportional to the partial pressure of CO_2 in the gas. This relation is called *Henry's law.* We can measure the coefficient $K(T)$ at some standard conditions and then apply it to *any* situation in which c_ℓ is sufficiently small.

We can use the same method to analyze the distributionof molecules in a gravitational field in a gas at a fixed temperature. I will first give the standard analysis of this problem based on the canonical ensemble. For an ideal gas in a gravitational field, ther eis an energy associated with the gravitational potential. Then molecules at different positions have a different Boltzmann weight

$$\int d^3x \cdot 1 \quad \rightarrow \quad \int d^3x\ e^{-\beta m g z}$$

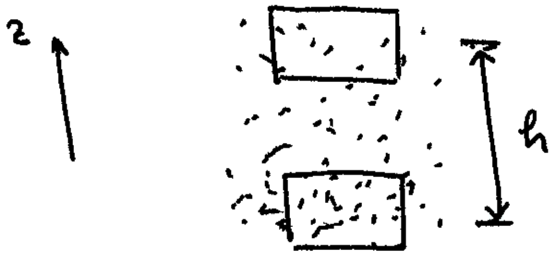
From this, we see that

$$\frac{(\text{Prob of a molecule at } z = z_0 + h)}{\text{Prob of a molecule at } z = z_0} = e^{-\beta m g h}$$

The result still holds for a gas in which the molecules have an intermolecular interaction, as long as the range ℓ of the interactions satisfies

$$\beta m g \ell \ll 1$$

We can look at this problem in another way by considering regions of gas at different heights as independent systems that can exchange particles.



If these systems are at the same temperature, the formulae for μ in the two systems will differ only by the change in density and by the change in gravitational potential energy

$$\mu(z_0) = T \log c(z_0) + f_S(T, z_0)$$

$$\mu(z_0+h) = T \log c(z_0+h) + f_S(T, z_0) + mgh$$

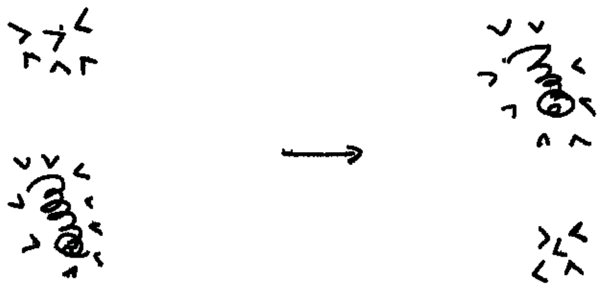
If the two systems are in equilibrium with a common particle bath, or just in equilibrium with one another,

$$\mu(z_0) = \mu(z_0+h)$$

This implies

$$\frac{c(z_0+h)}{c(z_0)} = e^{-mgh/T}$$

In this form, the argument generalizes to molecules in a dilute solution. Here it is not so obvious what the correct value of m should be, since when a solute molecule changes its height, it displaces some solvent.



But it must be that the solute free energy difference at differnt heights will be proportional to g and h, and so

$$f_s(T, z_0+h) = f_s(T, z_0) + Mgh$$

for some value of M, which we might call the *effective gravitational mass* of the solute molecule. Then the argument we gave for an ideal gas applies, and we conclude that

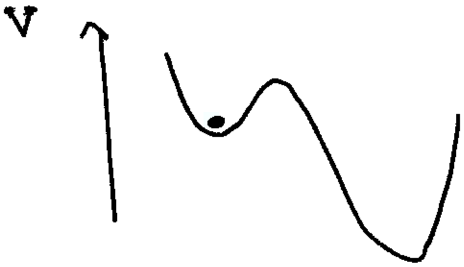
$$\frac{c_s(z_0+h)}{c_s(z_0)} = e^{-Mgh/T}$$

After measurement of M under standard conditions, this equation can be used to analyze the separation of protein molecules in solution in a centrifuge.

These ideas generalize much further. Consider a chemical reactions, for definiteness

$$2H_2 + O_2 \longrightarrow 2H_2O$$

If we start with a chamber that contains H_2 and O_2 in the gas phase at low temperature, nothing happens. There is a potential energy barrier that keeps these molecules from interacting, so the system stays in only a limited volume of its potential phase space.



Now introduce a spark as a catalyst. The reaction runs in the forward direction, seeking a more typical point on the energy surface.

Eventually, we come to a new equilibrium. What are the relative amounts of H_2, O_2, and H_2O in equilibrium?

Here are two arguments for the formulae that determine the answers to this question. First, we start from the canonical ensemble with a fixed number of H and O atoms. The reaction runs to maximize the phase space volume or to minimize the free energy F. Write the chemical potential of the molecular species as

$$\mu_i = \left.\frac{\partial F}{\partial N_i}\right|_{T,V} \qquad i = H_2, O_2, H_2O$$

Let n be the *reaction coordinate*, a value that parametrizes the extent to which the forward reaction has been carried out,

$$dN_{H_2} = -2\,dn \qquad dN_{O_2} = -dn \qquad dN_{H_2O} = +2\,dn$$

We need to minimize F with respect to this variable. That is,

$$\frac{\partial F}{\partial n} = 0$$

This implies

$$\begin{aligned} 0 &= \frac{\partial F}{\partial N_{H_2}} \cdot \frac{dN_{H_2}}{dn} + \frac{\partial F}{\partial N_{O_2}} \cdot \frac{dN_{O_2}}{dn} + \frac{\partial F}{\partial N_{H_2O}} \frac{dN_{H_2O}}{dn} \\ &= \mu_{H_2} \cdot (-2) + \mu_{O_2} \cdot (-1) + \mu_{H_2O} \cdot (+2) \end{aligned}$$

so that, finally,

$$2\mu_{H_2} + \mu_{O_2} = 2\mu_{H_2O}$$

We can derive this equation in another way from the grand canonical ensemble. I will set up the grand canonical ensemble for the three molecular species H_2, O_2, and H_2O,

$$\Xi = \sum_{N_{O_2} N_{H_2} N_{H_2O}} Z(N_{O_2}, N_{H_2}, N_{H_2O}) \cdot e^{\beta\mu_{H_2} N_{H_2}} e^{\beta\mu_{O_2} N_{O_2}} e^{\beta\mu_{H_2O} N_{H_2O}}$$

The factor with μ_i constrains the number of type i molecules. However, this equation has one too many constraints. The reaction coordinate should be unconstrained so that the system can adjust itself to maximize the statistical weight. To arrange this, we must insist that the vector

$$(\mu_{H_2}, \mu_{O_2}, \mu_{H_2O})$$

is *orthogonal* to the reaction coordinate

$$(-2dn, \quad -dn, \quad +2dn)$$

This gives again the equation

$$0 = -2\mu_{H_2} - \mu_{O_2} + 2\mu_{H_2O}$$

These two derivations apply to any chemical reaction

$$a_1X_1 + a_2X_2 + \cdots \longrightarrow b_1Y_1 + b_2Y_2 + \cdots$$

where X_1, X_2, ..., Y_1, Y_2, ... are species and a_1, a_2, ... and b_1, b_2, ... are integers. For any such reaction, the equilibrium condition is

$$\sum_i a_i \mu_{X_i} = \sum_j b_j \mu_{Y_j}$$

This equation applies not only to chemical reactions but to reactions of all sorts. For example, in a *very* hot gas, with $T \gg$ MeV, we have electron-positron pair creation and annihilation by thermal processes

$$\gamma + \gamma \rightleftarrows e^+ + e^-$$

and gamma-ray emission and absorption

$$e^- + e^- \rightleftharpoons e^- + e^- + \gamma$$

If the second reaction is in equilibrium, then

$$\mu(\gamma) = 0$$

This implies that, if the first reaction is in equilibrium

$$\mu(e^+) = -\mu(e^-)$$

Quite generally, in thermal equilibrium a particle that can be freely created and destroyed has

$$\mu = 0$$

Particles and antiparticles f and $\overline{f}$ have

$$\mu(f) + \mu(\bar{f}) = 0$$

These equations apply, for example, to thermal equilibrium in the early universe.

We can make a further analysis of the equilibrium conditions for chemical reactions involving molecules in a gas phase or in dilution solutions. In these cases,

$$\mu_i = T \log c_i + f_i(T)$$

The equilibrium conditions become

$$-\sum_i a_i \log c_i + \sum_j b_j \log c_j = \sum_i \frac{a_i}{T} f_i(T) - \sum_j \frac{b_j}{T} f_j(T)$$

Taking the exponential of this equation

$$\frac{\prod_j (c_j)^{b_j}}{\prod_i (c_i)^{a_i}} = K(T)$$

The parameter $K(T)$ is called the *equilibrium constant.* For example, for the reaction $2\,H_2 + O_2 \to 2\,H_2O$,

$$\frac{c_{H_2O}^2}{c_{H_2}^2\, c_{O_2}} = K(T)$$

This relation—which you probably learned in high-school chemistry—is called the *law of mass action.* The equilibrium constant $K(T)$ can be measured at some standard conditions and then applied more generally. Even better, $K(T)$ factorizes,

$$K(T) = \frac{\prod_j e^{-b_j f_j(T)/T}}{\prod_i e^{-a_i f_i(T)/T}}$$

so we can determine the species free energies $f_i(T)$ individually and assemble them to compute $K(T)$.

For reactions of gases, we have an explicit formula for $f_i(T)$. Taking into account also the contribution from the chemical binding energy,

$$f_i(T) = \frac{3}{2} T \log \frac{2\pi\hbar^2}{m_i T} + \varepsilon_i$$

Then

$$K(T) = (\text{const}) \cdot T^{\frac{3}{2}\left(\sum_j b_j - \sum_i a_i\right)} e^{-\frac{1}{T}\left[\sum_j b_j \varepsilon_j - \sum_i a_i \varepsilon_i\right]}$$

The exponential tells us that the equilibrium favors the side of the reaction with the smaller energy, taking into account the chemical binding energy. The power of T accounts for the influence of *entropy* on $K(T)$. It favors the side of the reaction with more products. These two effects compete with one another to favor the side that corresponds to lower free energy.

If we perturbe the equilibrium by adding some reagent, the reaction will run to a new equilibrium in which the equilibrium ratio of products is restored. This will necessarily decrease the amount of the reagent that was added. If we raise the temperature, the equilibrium will be shifted toward the side this higher total free energy. The entropy term will have a larger effect, and so the relation will shift away from the term with chemical binding energy and heat will be absorbed. Both effects illustrate the general principle of chemical reactions called *Le Chatelier's principle*: When a chemical equilibrium is disturbed, the reaction runs in a direction that opposes the perturbation[1].

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[1] This principle is due to Henry-Louis Le Chatelier, a 19th century French chemist. He is not to be confused with the 18th century French physicist Emilie du Châtelet, the first person to enunciate the principle of conservation of energy.