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Canonical Ensemble

In our discussion of statistical mechanics up to this point, we have been analyzing systems of many particles that are isolated from the rest of the universe. More often, we are interested in systems that can exchange energy with other systems with which they are in contact. A very useful idealization is that the system we wish to study is in contact with a much larger system that has already reached its equilibrium state. I will call such a large system a *heat bath*. If this system is very large, the smaller system that we are studying will lose heat to or gain heat from the heat bath without making any change in its properties. Our small system will then come to a thermal equilibrium at the temperature of the heat bath.

The description of a system in contact with a heat bath in statistical mechanics is simpler than the statistical mechanics of an isolated system. In this lecture, I will work out the statistical desccription of a system in contact with a heat bath and work through some elementary applications of this construction.

We begin by constructing the microcanonical ensemble composed of the small system under study and the heat bath. The small system is modelled by the microcanonical average over the energy surface, with

$$\Omega(E) = \int dq\, dp\; \Theta(q,p,E)/\delta E = e^{S(E)}$$

The heat bath can be modelled in the same way, with

$$\Omega_B(E_B) = \int d\bar{q}\, d\bar{p}\; \Theta(\bar{q},\bar{p},E_B)/\delta E = e^{S_B(E_B)}$$

The heat bath is in thermal equilibrium. Thus it is characterized by a temperature T such that

$$\frac{1}{T} = \left.\frac{\partial S_B}{\partial E_B}\right|_{V,N}$$

Now allow the small system to exchange energy with the heat bath, so that the two systems come to a joint equilibrium. This is described in the microcanonical ensemble by an average over the joint energy surface, whose area is

$$\Omega_+(\mathcal{E}) = \int dE\ \Omega(E)\,\Omega_B(\mathcal{E}-E)$$

$$= \int dE\ e^{S(E)}\ e^{S_B(\mathcal{E}-E)}$$

If the heat bath is large, the amount of energy transfered to it from the small system will be insignificant in comparison to its total energy. Then we can approximate

$$S_B(\mathcal{E}-E) = S_B(\mathcal{E}) - E\left.\frac{\partial S_B}{\partial \mathcal{E}}\right|_{V,N} + \cdots$$

Entropy is extensive, so $S_B \sim N_B$. The second term in this expansion is of the order of the size of the small system $N \ll N_B$. Higher terms in the expansion are suppressed by further powers of N/N_B, so they can be neglected. Then the expression for the area of the joint energy surface becomes

$$\Omega_+(\mathcal{E}) = \int dE \int dq\,dp\ \frac{\Theta(q,p,E)}{\delta E}\ e^{+S_B(\mathcal{E})}\ e^{-E\cdot\frac{1}{T}}$$

or

$$\frac{\Theta(q,p,E)}{\delta E} \approx \delta(H(q,p)-E)$$

$$\Omega_+(\mathcal{E}) = e^{S_B(\mathcal{E})} \int dq\,dp\ e^{-\frac{1}{T}\cdot H(q,p)}$$

The prefactor depends only on the properties of the heat bath and, if the properties of the bath are fixed, this term is a constant. We thus derive that phase space points in the small system are weighted by the factor

$$dq\,dp\;\; e^{-H(q,p)/T}$$

and expectation values of observables in the small system are computed by the prescription

$$\langle O(q,p)\rangle = \frac{\int dq\,dp\;\; O(q,p)\, e^{-H(q,p)/T}}{\int dq\,dp\;\; e^{-H(q,p)/T}}$$

This is the *canonical ensemble.* The factor

$$e^{-H(q,p)/T}$$

is called the *Boltzmann factor.*

It is important that, in this derivation of the canonical ensemble, we never needed to assume that the system under study was large. We only needed to assume that the heat bath was large. The canonical ensemble applies even to *single atoms* exchanging energy with a heat bath in equilibrium.

As a first application of the canonical ensemble, I will compute the properties of an ideal gas in equilibrium with a heat bath at temperature T. For each particle of the gas, the probability distribution of $\vec{q}$ and $\vec{p}$ is proportional to

$$\int d^3q\, d^3p\;\; e^{-|\vec{p}|^2/2mT}$$

The probability is independent of position and is a Gaussian distribution for momentum. The normalized momentum distribution is

$$\int d^3p\, f(\vec{p}) = \int d^3p\; \frac{1}{(2\pi mT)^{3/2}}\; e^{-|\vec{p}|^2/2mT}$$

This derivation reproduces the results that we obtained from our analysis of the ideal gas in the microcanonical ensemble, except that, instead of struggling with factorials, here we could just write down the answer. There are important differences in the two derivations, however. The result for the microcanonical ensemble applied to an isolated system, but was only valid for the limit in which this system contains a large number of particles. In the canonical ensemble, the result applies to a system of any size as long as the heat bath is large. The total energy of the gas is not fixed; rather, it fluctuates as energy passes back and forth between the gas and the heat bath. However, while for one atom

$$\left\langle \frac{|\vec{p}|^2}{2m} \right\rangle = \frac{3}{2}T$$

with fluctuations in energy of order 1, for a system of N atoms the total energy is

$$\left\langle \sum_j \frac{|\vec{p}_j|^2}{2m} \right\rangle = \frac{3}{2}NT$$

with fluctuations of relative size $1/\sqrt{N}$. For $N \sim 10^{20}$ or even 10^{12}, we can ignore the distinction between fixed energy and energy regulated by a heat bath.

We can equally well apply the rules of the canonical ensemble to other simple classical model systems. A standard example is the harmonic oscillator

$$H = \frac{p^2}{2m} + \frac{m}{2}\omega^2 q^2$$

The canonical ensemble gives points in the phase space of a harmonic oscillator the weights

$$\int dq\,dp \; \frac{e^{-\frac{1}{T}\left[\frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2\right]}}{(2\pi m T)^{1/2}\left(2\pi T/m\omega^2\right)^{1/2}}$$

I have supplied a normalization factor so that the total probability is 1. From the properties of Gaussian integrals, we can read off directly

$$\langle p^2 \rangle = mT \qquad \langle q^2 \rangle = \frac{1}{m\omega^2}$$

Then

$$\left\langle \frac{p^2}{2m} \right\rangle = \left\langle \frac{1}{2} m\omega^2 q^2 \right\rangle = \frac{T}{2}$$

The average thermal energy of the oscillator is

$$\langle H(q,p) \rangle = T$$

A very similar result applies to a classical rigid rotator. For definiteness, consider rotations about a fixed axis. For this system,

$$H = \frac{L^2}{2I}$$

in which L is a phase space coordinate

$$dq\,dp = d\phi\, dL$$

Then the canonical ensemble gives a probability distribution for ϕ and L

$$\int d\phi dL \; e^{-\frac{1}{2}\frac{L^2}{IT}}$$

The expectation value $\langle L^2 \rangle = IT$. Then the expectation value of the energy is

$$\left\langle \frac{L^2}{2I} \right\rangle = \frac{T}{2}$$

Very generally, any classical phase space degree of freedom p whose Hamiltonian is a quadratic form has the thermal energy

$$\langle H(p) \rangle = \frac{T}{2}$$

This is called the *equipartition theorem.*

The small amount of theory that we have just derived already has an interesting application. Consider a diatomic molecule like N_2 or O_2, the main constituents of air. Such a molecule has internal degrees of freedom. It can vibrate and rotate.

To work out the statistical mechanics of a gas of such molecules, I will need to invoke two results that I will derive later from our discussion of quantum statistical mechanics. First, although classically the equipartition theorem applies for any relation between the temperature T and the frequency of a harmonic oscillation ω, in quantum mechanics the excited states of an oscillator are not excited if

$$\hbar\omega \gg T$$

We will see that the equipartition theorem applies in the limit

$$T \gg \hbar\omega$$

Second, some motions that exist classically do not change the quantum-mechanical wavefunction of a molecule. These do not contribute to the statistical mechanics.

The vibrational oscillations of a diatomic molecule are typically in the frequency range $\hbar\omega \sim eV$, in the near UV. These oscillations do not contribution to the statistical mechanics of the diatomic gas at room temperature. The rotational motions of a diatomic molecule are typically in the classical limit to which equipartition applies when $T \gg 5°$ K (except for the case of H_2, for which temperatures above about 100° K are required). However, the rotations around the axis of the molecule do not change the Schrödinger wave function of the molecule, so this rotational degree of freedom does not exist in the quantum theory.

The result is that there are precisely 2 internal degrees of freedom with quadratic Hamiltonians that are relevant for diatomic gases at room temperature. Then the energy per molecule at temperature T is

$$\langle E/N \rangle = \left\langle \frac{|\vec{p}|^2}{2m} \right\rangle + \left\langle \frac{L^2}{2I} \right\rangle$$

$$= \frac{3}{2}T + \frac{2}{2}T = \frac{5}{2}T$$

Our argument that $pV = NT$ is still true for this diatomic gas, but the relation for adiabatic expansion discussed in the previous lecture is affected. Under adiabatic compression or expansion, we now find

$$dE = -pdV = \frac{5}{2}NdT$$

so that

$$-\frac{dV}{V} = \frac{5}{2}\frac{dT}{T}$$

or

$$\left(\frac{V_1}{V_2}\right) = \left(\frac{T_1}{T_2}\right)^{-5/2} \qquad \left(\frac{P_1}{P_2}\right) = \left(\frac{V_1}{V_2}\right)^{-7/5}$$

The final result is that adiabatic expansion is governed by the general formula

$$pV^{\gamma} = (\text{const})$$

but now with

$\gamma = \frac{5}{3}$ atoms, $\frac{7}{5}$ diatomic molecules, $\frac{8}{6} = \frac{4}{3}$ complex molecules.

It is amazing that the microscopic properties of gas particles can affect the macroscopic properties of the gas in a way that is observable in the compressible fluid dynamics of the gas, for example, in the speed of sound.

Now I will discuss some more formal aspects of the canonical ensemble. In analogy to what we did for the microcanonical ensemble, I will give a name to the denominator in the canonical expectation value. This is the *canonical partition function*, defined by

$$Z = \int dq\,dp\; e^{-\beta H(q,p)}$$

with

$$\beta = \frac{1}{T} \qquad \text{or} \qquad = \frac{1}{k_B T}$$

The partition function Z is the *generating function* for correlations of the energy,

$$-\frac{\partial}{\partial\beta}\log Z = \frac{\int dq\,dp\; e^{-\beta H}\cdot H(q,p)}{\int dq\,dp\; e^{-\beta H}} = \langle H(q,p)\rangle = E$$

The quantity $(\partial E/\partial T)$ is called the *specific heat.* To be more precise, I define

$$C_V = \left.\frac{\partial E}{\partial T}\right|_{V,N}$$

In terms of the partition function,

$$C_V = \frac{\partial E}{\partial T} = \frac{\partial\beta}{\partial T}\frac{\partial E}{\partial\beta} = \frac{1}{T^2}\frac{\partial^2}{\partial\beta^2}\log Z$$

It is interesting to compute this from the definition of the partition function

$$\frac{\partial^2}{\partial\beta^2}\log Z = -\frac{\partial}{\partial\beta}\left[\frac{\int dq\,dp\; H\, e^{-\beta H}}{\int dq\,dp\; e^{-\beta H}}\right]$$

There are two terms in the derivative here, because β appears in both the numerator and the denominator. Then

$$\frac{\partial^2}{\partial\beta^2}\log Z = \frac{\int dq\,dp\; H^2 e^{-\beta H}}{\int dq\,dp\; e^{-\beta H}} - \frac{\left(\int dq\,dp\; H e^{-\beta H}\right)\left(\int dq\,dp\; H e^{-\beta H}\right)}{\left(\int dq\,dp\; e^{-\beta H}\right)^2}$$

Thus,

$$C_V = \frac{1}{T^2}\left(\langle E^2\rangle - \langle E\rangle^2\right)$$

We see that C_V is proportional to the mean square fluctuation in energy. Notice that $\langle E\rangle \sim N$ so $\langle E\rangle^2 \sim N^2$, but the mean square fluctuation is of the order of N, so C_V is properly extensive, $C_V \sim N$. We will see similar connections between thermodynamic derivatives and mean square fluctuations at several point in this course.

The logarithm of the canonical partition function is called the *Helmholtz free energy*

$$F = -\frac{1}{\beta}\log Z \quad \text{or} \quad Z = e^{-\beta F}$$

The quantity F expresses the phase space volume of the canonical ensemble in the same way that the entropy S expresses the volume of phase space included in the microcanonical average. To understand how F and S differ, go back to the derivation of the canonical ensemble from the formula

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

If *both* systems are very large (with the heat bath, still, much bigger), the integral can be well approximated by keeping only the region near the huge maximum value of the integrand. If E_* is the value of E that maximizes the integrand, then

$$\Omega_*(\mathcal{E}) \approx \left[e^{S(\mathcal{E})} \; e^{S_B(\mathcal{E}) - E \cdot \frac{1}{T}} \right]\Big|_{E_*}$$

In this situation, the expectation value of E in the integral is well approximated by E_*. We had previously set

$$\Omega_*(\mathcal{E}) = e^{S(\mathcal{E})} \cdot \mathcal{Z}$$

Thus

$$\mathcal{Z} = e^{-\beta F} = e^{S} \, e^{-\beta E}$$

or

$$F = E - TS$$

For a small system in contact with a heat bath, I will take this equation to be the *definition* of S.

This definition is consistent with the general expression for entropy that I wrote in the previous lecture. In the canonical ensemble, we integrate not only over a surface of fixed energy but over all of phase space. The probability associated with a given cell in phase space is, for a system with D degrees of freedom,

$$\mathcal{P}(q,p) = \frac{(2\pi\hbar)^D}{\mathcal{Z}} \cdot e^{-\beta H(q,p)}$$

Then we can evaluate

$$S = -\sum_{\text{cells}} p \log p$$

$$= -\int dq\,dp\ \frac{1}{Z} e^{-\beta H} \left[-\beta H(q,p) - \log \frac{Z}{(2\pi\hbar)^D} \right]$$

This gives

$$S = \beta E - \beta F$$

The final result is just the expression for the entropy S given by the equation above.

There is another way to look at the formula

$$F = E - TS \quad \text{or} \quad S = -\frac{F}{T} + \frac{E}{T}$$

that is typically used in discussion of thermodynamics. For this discussion, we consider large systems for which the microcanonical and the canonical ensemble are equivalent. In our discussion of the microcanonical ensemble, we considered

$$S(E, V, N)$$

as a *state function* with a unique value for each (E, V, N), from which the macroscopic properties of the system could be derived. In a similar way, we can consider $F(T, V, N)$ to be a state function with a unique value for each choice of (T, V, N). This would be a more convenient description of the system if we are able to control T, rather than E, externally. In some sense, F should be connected to S by a change of variables. The precise connection is via a *Legendre transformation.* Since

$$\frac{1}{T} = \frac{\partial S}{\partial E}$$

we can construct the function

$$S - \frac{1}{T}E$$

If we differentiate this function with respect to E, there are two sources of E-dependence, first, the explicit dependence on E, second, the implicit dependence on E through the dependence on T.

$$\frac{d}{dE} = \frac{d}{dE}\Big|_{\text{explicit}} + \frac{dT}{dE}\frac{d}{dT}$$

The Legendre transformation is constructed so that the explicit dependence on E cancels,

$$\frac{d}{dE}\Big|_{\text{explicit}}\left(S - \frac{1}{T}E\right) = \frac{dS}{dE} - \frac{1}{T} = 0$$

so that the result can be considered purely as a function of T. If we multiply the above by $(-T)$, this conclusion is not changed, so

$$F = E - TS$$

can be considered as a pure function of T. In particular,

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

For the microcanonical ensemble, we gave a physical interpretation to all three first derivatives of the state function $S(E, V, T)$.

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

It is convenient to express these relations as differentials of S with respect to its three variables.,

$$dS = \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN$$

Then

$$dF = d(E - TS)$$

$$= -SdT - pdV + \mu dN$$

From this expression, we can read off the three first derivatives of F with respect to its arguments,

$$\left.\frac{\partial F}{\partial T}\right|_{V,N} = -S \qquad \left.\frac{\partial F}{\partial V}\right|_{T,N} = -p \qquad \left.\frac{\partial F}{\partial N}\right|_{T,V} = \mu$$

These expressions gives an explicit way to compute S, p, and μ in practice. We obtain a value for F by computing the canonical partition function, and then differentiate F as indicated.

The three first derivative relations also generate nontrivial relations among the derivatives of thermodynamic quantities. These relations, called *Maxwell relations*, are generated by the use of the partial derivative identity

$$\frac{\partial}{\partial x}\frac{\partial f}{\partial y} = \frac{\partial}{\partial y}\frac{\partial f}{\partial x}$$

For example,

$$\left.\frac{\partial S}{\partial V}\right|_{T,N} = \left.\frac{\partial p}{\partial T}\right|_{V,N}$$

The Maxwell relations are nontrivial and sometimes are quite surprising in their form.

To work in terms of other sets of variables, we can take further steps with Legendre transformations. Chemists like to work at fixed pressure rather than at fixed volume. They define the *Gibbs free energy* by

$$G = F + pV$$

From this definition, it follows that

$$dG = -S\,dT + V\,dp + \mu\,dN$$

leading to

$$\left.\frac{\partial G}{\partial T}\right|_{p,N} = -S \qquad \left.\frac{\partial G}{\partial p}\right|_{T,N} = V \qquad \left.\frac{\partial G}{\partial N}\right|_{T,p} = \mu$$

Similarly, the quantity

$$\mathcal{H} = E + pV$$

is called the *enthalpy.*

We can also use the Legendre transformation to discuss a system that is in contact with a large reservoir of particles, in such a way that particles can be exchanged between the system and this large source. The value of the chemical potential μ for the system that we are studying will then come into equilibrium with the value of μ in the reservoir. To describe this situation, we define the *grand potential*

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

which is a function of (T, V, μ). For this state function

$$d\Phi = -SdT - pdV - Nd\mu$$

$$\left.\frac{\partial \Phi}{\partial T}\right|_{V,\mu} = -S \qquad \left.\frac{\partial \Phi}{\partial V}\right|_{T,\mu} = -p \qquad \left.\frac{\partial \Phi}{\partial \mu}\right|_{T,V} = -N$$

Since Φ is extensive and T and μ are intensive, Φ must be of the form

$$\Phi = V \cdot f(T, \mu)$$

Then the derivative of Φ with respect to V given above implies

$$\Phi = -V \cdot p(T, \mu)$$

After we discuss the computation of Φ, we will find this a very convenient way to obtain the pressure for a large system of particles.