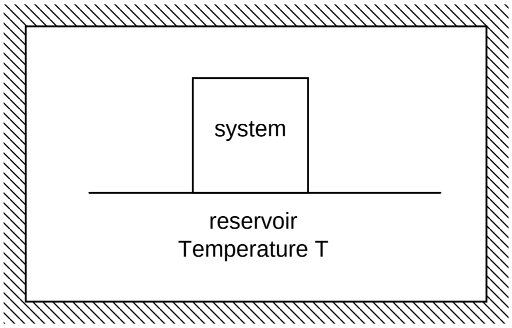
Physics 127a: Class Notes

Lecture 6: Canonical Ensemble

Discussion and Derivation

A system that can exchange energy via very weak contact with a temperature bath eventually comes to equilibrium. The *canonical ensemble* describes the statistical distribution in such a system. Why is very weak contact with the reservoir important? Because now the energy E that is *conserved* by the internal dynamics is no longer rigorously fixed as it is in an isolated system—note that although the coupling with the reservoir is weak, we wait arbitrarily long for the system-reservoir to come to equilibrium. The dynamics of the system remains dominated by the internal interactions, so the derivation of the phase-space distribution in lecture 3 remains correct. Thus we must have $\rho(q, p) = \rho(E)$ but now E may change, and we need to find the energy dependence. Another way of saying this: $\rho(q, p)$ is constant over the constant energy surface as in the microcanonical ensemble, and we need to relate the ρ on different energy surfaces.



To find the probability distribution over the states of the *system* in the *canonical* ensemble we consider the *combined* system+reservoir as isolated, and described by the *microcanonical* ensemble.

We will calculate the probability P_j of finding the system in a particular microstate j with energy E_j. The probability P_j is proportional to the number of microstates of the *reservoir* consistent with this system microstate, since for the combined system+reservoir each microstate is equally likely. The number of microstates available in the reservoir depends on j through the energy: if the reservoir has energy $E^{(r)}$ when the system is in microstate i it will have energy $E^{(r)} - \Delta E$ with $\Delta E = E_j - E_i$ when the system is n microstate E_j.

Consider the ratio of probabilities for microstates j and i

$$\frac{P_j}{P_i} = \frac{1 \times \Omega^{(r)}(E^{(r)} - \Delta E)}{1 \times \Omega^{(r)}(E^{(r)})} = \exp\left\{\left[S^{(r)}(E^{(r)} - \Delta E) - S^{(r)}(E^{(r)})\right]/k\right\} \tag{1}$$

(the number of microstates is one for the system multiplied by Ω for the reservoir), and in the second expression we have introduced the entropy of the reservoir $S^{(r)} = k \ln \Omega^{(r)}$. Since the reservoir is assumed large, ΔE is small compared to $E^{(r)}$ for any system change i to j, and so we can evaluate the quantity inside the exponential as the first term in a Taylor expansion, to find

$$\frac{P_j}{P_i} = \exp\left[-\frac{E_j - E_i}{kT}\right] \tag{2}$$

with T the temperature of the reservoir

$$\frac{1}{T} = \frac{\partial S^{(r)}}{\partial E^{(r)}}. \tag{3}$$

This gives us the result for the probability of system microstate j in the canonical ensemble

$$P_j \propto e^{-\beta E_j} \qquad \text{with} \qquad \beta = \frac{1}{kT}. \tag{4}$$

The proportionality constant is fixed by normalizing the sum of probabilities to unity. It turns out to be useful to focus the calculation on this sum, and we define this as the *canonical partition function* Q_N

$$Q_N(T, V, N) = \sum_j e^{-\beta E_j} \tag{5}$$

and then

$$P_j = Q_N^{-1} e^{-\beta E_j}. \tag{6}$$

Further we define the free energy $A(T, V, N)$

$$A = -kT \ln Q_N. \tag{7}$$

Note that the probability distribution of the system in contact with the reservoir only depends on the properties of the reservoir through the single parameter T. Also, we have not made use of any argument depending on the *system* being macroscopic, just that the reservoir is very large. The system may in fact be microscopic, even a single state. The temperature T in the expression is the temperature of the reservoir—for a microscopic system its temperature is not well defined from internal quantities, and so is often *defined* to be that of the reservoir.

Relationship to Other Quantities and Thermodynamics

An obvious question is what is the ensemble average of the fluctuating energy of the system in the canonical ensemble. We call this the internal energy U.

$$U = \langle E \rangle = \sum_j P_j E_j = \frac{\sum_j E_j e^{-\beta E_j}}{\sum_j e^{-\beta E_j}} = -\frac{1}{Q_N}\frac{\partial Q_N}{\partial \beta}. \tag{8}$$

Thus we have various useful expressions

$$U = -\frac{\partial}{\partial \beta} \ln Q_N = \frac{\partial(A/T)}{\partial(1/T)} = -T^2 \frac{\partial}{\partial T}\left(\frac{A}{T}\right), \tag{9}$$

with all the partials taken at fixed N, V.

For a macroscopic system we expect all quantities to be dominated by the most probable value, and then the mean is given by this value. Let's look at this in more detail.

For a macroscopic system the energy levels become closely spaced, and we can introduce a continuous density $g(E)$ giving the number of microstates per unit energy interval. Then

$$Q_N = \sum_j e^{-\beta E_j} = \int dE\, g(E) e^{-\beta E}. \tag{10}$$

Comparing with the calculation of the entropy in an isolated system

$$g(E) = e^{S(E)/k}/\Delta \tag{11}$$

where Δ is the energy band we defined for counting the number of states "at" energy E. So

$$Q_N = \int \frac{dE}{\Delta} e^{-\beta[E - TS(E)]}. \tag{12}$$

(Similarly, we identify the probability of finding the system in *any* microstate at energy E as $P(E) \propto \exp\{-\beta[E - TS(E)]\}$, where the energy is from the Boltzmann factor and the entropy from counting the states at this energy.) Now for a macroscopic system E and S are extensive quantities of $O(N)$, and so the exponential function is *very* strongly peaked about the energy $\bar{E}$ maximizing the function, determined by minimizing $E - TS(E)$, i.e. the value $\bar{E}$ given by

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_{E=\bar{E}}. \tag{13}$$

The integral may then be evaluated, and will be given by the height times a width W. Taking logs

$$A = -kT \ln Q_N = \bar{E} - TS(\bar{E}) - kT \ln\left(\frac{W}{\Delta}\right). \tag{14}$$

The last term is of order $1/N$ compared to the others, and may be ignored, so that

$$A \simeq \bar{E} - TS(\bar{E}). \tag{15}$$

Furthermore because the width of the distribution over energies is very narrow

$$U \simeq \bar{E}, \tag{16}$$

and so

$$A \simeq U - TS(U). \tag{17}$$

Equation (17) is what leads us to call A the free energy. Note that Eq. (13) gives us the usual equality of the temperature of system and reservoir in equilibrium, with the temperature of the system defined in terms of the energy derivative of the entropy at the most probable value of the energy $\bar{E}$. Equation (16) is an example of the statement that we can replace average quantities by their most probable values. Very strictly, A is defined absolutely for the system in the canonical ensemble, and is not a fluctuating quantity, On the other hand the energy, the entropy defined as $S(E)$, the temperature defined as $(\partial S/\partial E)^{-1}$, are fluctuating quantities, and we would usually characterize them by their mean values. However the range of fluctuations is of relative order $1/\sqrt{N}$, and so the fluctuations are negligible in a macroscopic system.

Thermodynamic Identity

From Eq. (17) we have

$$dA = dU - TdS - SdT. \tag{18}$$

But the thermodynamic identity (strictly at energy $\bar{E}$ and then replacing $\bar{E}$ by U) is

$$dU = TdS - PdV + \mu dN. \tag{19}$$

Together these give

$$dA = -SdT - PdV + \mu dN. \tag{20}$$

Note again the T, V, N appear as the natural variables for the dependence of A.

Equation (20) immediately gives us an alternative root for calculating thermodynamic quantities

$$S = -\left(\frac{\partial A}{\partial T}\right)_{N,V}, \qquad P = -\left(\frac{\partial A}{\partial V}\right)_{T,N}, \qquad \mu = \left(\frac{\partial A}{\partial N}\right)_{T,V}. \tag{21}$$

The free energy tells us the work available at constant temperature (and N)

$$dA = -pdV|_{T,N} \tag{22}$$

the reason for its name.

Return to the ideal, monatomic, classical gas

For the ideal, monatomic, classical gas

$$H = \sum_{i=1}^{3N} \frac{p_i^2}{2m} \qquad \text{and} \qquad \sum_j \rightarrow \frac{1}{N! h^{3N}} \int \dots \int d^{3N}x d^{3N}p \tag{23}$$

where p_i are the $3N$ momentum components of N particles in 3 dimensions. Thus

$$Q_N = \frac{1}{N!}\left[\frac{1}{h^{3N}} \int d^{3N}x \int d^{3N}p \exp\left(-\beta \sum \frac{p_i^2}{2m}\right)\right]. \tag{24}$$

The quantity in the [ ] factorizes, so that

$$Q_N = \frac{1}{N!}\left[\frac{1}{h^3} \int d^3x \int dp_x\, e^{-\beta p_x^2/2m} \int dp_y\, e^{-\beta p_y^2/2m} \int dp_z\, e^{-\beta p_z^2/2m}\right]^N. \tag{25}$$

The d^3x integral gives the volume V, and each momentum integral is easy to do

$$\int_{-\infty}^{\infty} dp_x e^{-\beta p_x^2/2m} = (2mkT)^{1/2} \int_{-\infty}^{\infty} e^{-s^2} ds = (2\pi mkT)^{1/2}. \tag{26}$$

Finally

$$Q_N = \frac{1}{N!}\left[V\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right]^N \tag{27}$$

giving for the free energy, using Stirling's approximation $\ln N! \simeq N \ln N - N$,

$$A = -kT \ln Q_N = NkT\left\{\ln\left[\frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{3/2}\right] - 1\right\}. \tag{28}$$

Note the role of the *thermal length*

$$\lambda = \sqrt{\frac{h^2}{2\pi mkT}} \tag{29}$$

which is the de Broglie wavelength of a particle with kinetic energy about kT. In terms of λ and the density $\rho = N/V$

$$A = NkT\left[\ln\left(\rho\lambda^3\right) - 1\right]. \tag{30}$$

The classical limit, where this is a good description, is precisely $\rho\lambda^3 \ll 1$, i.e. small probability of finding two particles in the *degeneracy volume* λ^3. If this is violated, we have to worry about quantum statistics (Bose v. Fermi) and do a fully quantum calculation.

The thermodynamic properties of the ideal gas are now easily calculated

$$U = -T^2 \frac{\partial}{\partial T}\left(\frac{A}{T}\right)_{N,V} = \frac{3}{2}NkT, \tag{31}$$

$$S = -\left(\frac{\partial A}{\partial T}\right)_{N,V} = Nk\left\{\ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right] + \frac{5}{2}\right\}, \tag{32}$$

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{T,V} = kT \ln\left[\frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{3/2}\right]. \tag{33}$$

These should be compared with the results derived in the microcanonical ensemble, using Eq. (31) to relate $E \simeq U$ to T—they are, of course, identical. The relative ease of the canonical calculation compared with the microcanonical one should be noted.