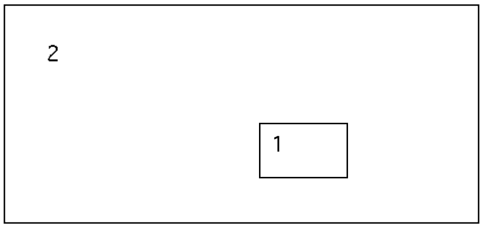
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Physics Department

8.044 Statistical Physics I Spring Term 2013

Notes on the Canonical Ensemble

The fundamental basis of statistical mechanics is the postulate of equal a priori probabilities in the equilibrium state of a completely isolated system. In such a system, referred to as a microcanonical ensemble, the total internal energy E is fixed. We have seen that such an ensemble can, in principle, be used to determine both microscopic probabilities and thermodynamic information such as the energy function and the equations of state. In all but the simplest systems, however, the process is too difficult to carry out.

There is another approach which arrives at the same information in a much simpler manner. It deals with a system which is in thermal equilibrium with a large bath. Since energy can flow to and from the bath, the system is described by the bath temperature T rather than by a fixed internal energy E. Such a system, and the statistical method based on it, are referred to as a canonical ensemble. We demonstrate here how its properties can be derived from the more fundamental assumption associated with the microcanonical ensemble.



Imagine a large closed system represented by a microcanonical ensemble. Within it is a small subsystem, 1, which may be so small that it has only one microscopic degree of freedom or so large that a set of thermodynamic variables can be defined on it. The rest of the large system is referred to as the remainder, 2. The subsystem is not closed (isolated) but can interact with the remainder. A phase space can be made up for 1 and another for 2. They are non-overlapping and the phase space for the whole system is the tensor product of the two. Even though 1 and 2 will not separately be represented by microcanonical ensembles (their energies E_1 and E_2 are not fixed), one can define a phase space volume for each in the same way one would if dealing with a microcanonical ensemble. Thus one can find (or at least imagine) $\Omega_1(E_1$, and other variables) and $\Omega_2(E_2$, and other variables).

The microcanonical ensemble gives the probability density for the microscopic variables of a closed system (E and N fixed). The canonical ensemble gives the probability density for the microscopic variables of a system in thermal equilibrium with a fixed reservoir at temperature T. In the case of the situation we have constructed, the system is 1 with N_1 fixed and E_1 free to vary, and the remainder 2 is the reservoir which is assumed to be so large that its temperature is insensitive to the state of 1. Let $\{p_1, q_1\}$ indicate the set of microscopic variables associated with 1. We wish to find the joint probability density $p(\{p_1, q_1\})$.

For the entire system (microcanonical) one has

$$p(\text{system in state X}) = \frac{\text{volume of accessible phase space consistent with X}}{\Omega(E)}$$

In particular, for our case

$$\begin{aligned} p(\{p_1, q_1\}) &\equiv p(\text{subsystem at } \{p_1, q_1\}; \text{ remainder undetermined}) \\ &= \frac{\Omega_1(\{p_1, q_1\})\Omega_2(E - E_1)}{\Omega(E)} \end{aligned}$$

Note that giving fixed values to all the microscopic variables in 1, $\{p_1, q_1\}$, means that it is constrained to a single state (point) in its phase space. Therefore $\Omega_1(\{p_1, q_1\}) = 1$.

$$k \ln p(\{p_1, q_1\}) = \underbrace{k \ln \Omega_1}_{k \ln 1 = 0} + \underbrace{k \ln \Omega_2(E - E_1)}_{S_2(E - E_1)} - \underbrace{k \ln \Omega(E)}_{S(E)}$$

We rewrite the second term on the right by expanding the function S_2 about the point where the energy of the remainder equals E. [Note: Don't worry, we are not *physically* putting all the energy of the system into the remainder; we are simply imagining evaluating the function S_2 at a point somewhat removed from its most probable value.]

$$S_2(E - E_1) \approx S_2(E) - \underbrace{\frac{\partial S_2(E_2)}{\partial E_2}}_{\text{evaluated at } E_2 = E} E_1$$

The partial derivative $(\partial S_2/\partial E_2)$ is by definition $1/T_2$ when it is evaluated at the equilibrium value of E_2. But 2 is so large that the derivative changes little if evaluated at E instead of at $< E_2 >$. T_2 is now simply referred to as T, the temperature of the "reservoir". The specific details of the microscopic state of the subsystem enter the expression through the energy E_1 which is the Hamiltonian of the subsystem evaluated at $\{p_1, q_1\}$: $E_1 = \mathcal{H}_1(\{p_1, q_1\})$. Using these considerations in the above expression gives

$$k \ln p(\{p_1, q_1\}) = \underbrace{-\frac{\mathcal{H}_1(\{p_1, q_1\})}{T}}_{\text{depends on specific state of the subsystem}} + \underbrace{S_2(E) - S(E)}_{\text{depends on the reservoir and average properties of the subsystem}}$$

It could be that 1 is so small that thermodynamics does not apply to it. That is, the number of particles is too small for macroscopic variables such pressure and temperature to be defined for the subsystem. [Note, however, that the bath has a temperature and it is that temperature that enters into the first term on the right above.] Under these circumstances all that we can do is find the probability density of the microscopic variables of the subsystem 1:

$$\begin{aligned} p(\{p_1, q_1\}) &\propto \exp[-\frac{\mathcal{H}_1(\{p_1, q_1\})}{kT}] \\ &= \exp[-\frac{\mathcal{H}_1(\{p_1, q_1\})}{kT}] \Big/ \int \exp[-\frac{\mathcal{H}_1(\{p_1, q_1\})}{kT}]\{dp_1, dq_1\} \end{aligned}$$

If thermodynamics does apply to 1, one can proceed further and get all of the thermodynamic information about the subsystem from the normalization constant associated with the microscopic probability density. The additive nature of entropy requires

$$S(E) = S_1(< E_1 >) + S_2(< E_2 >).$$

$E_1 + E_2 = E$ due to the way we have divided up the subsystem and the remainder within a microcanonical whole. It follows that $< E_1 > + < E_2 >= E$. We can now simplify the reservoir dependent part of the expression for $\ln p$.

$$S_2(E) - S(E) = \underbrace{S_2(E) - S_2(< E_2 >)}_{\approx (\partial S_2(E_2)/\partial E_2) < E_1 >=< E_1 > /T} - S_1(< E_1 >)$$

$$k \ln p(\{p_1, q_1\}) = -\frac{\mathcal{H}_1(\{p_1, q_1\})}{T} + \frac{< E_1 >}{T} - S_1$$

$$p(\{p_1, q_1\}) = \underbrace{\exp[\frac{(< E_1 > -TS_1)}{kT}]}_{\equiv 1/Z} \exp[-\frac{\mathcal{H}_1(\{p_1, q_1\})}{kT}]$$

Note that $< E_1 >$ is what one means by the thermodynamic internal energy of the system. Also, $T = T_1$ since 1 and 2 are in thermal equilibrium. Thus

$$< E_1 > -TS_1 = U_1 - T_1 S_1 = F_1$$

where F_1 is the Helmholtz free energy. From now on only the subsystem need be considered and the subscripts are dropped.

$$p(\{p, q\}) = Z^{-1} \exp[-\frac{\mathcal{H}(\{p, q\})}{kT}]$$

$$\begin{aligned}
Z_N(T,V) &= \int \exp[-\frac{\mathcal{H}(\{p,q\})}{kT}]\{dp,dq\} \qquad \text{the partition function} \\
&= \exp[-\frac{(E-TS)}{kT}] = \exp[-\frac{F(T,V,N)}{kT}]
\end{aligned}$$

$$\begin{aligned}
F(T,V,N) &= -kT \ln Z_N(T,V) \\
S(T,V,N) &= -\left(\frac{\partial F}{\partial T}\right)_{V,N} \\
P(T,V,N) &= -\left(\frac{\partial F}{\partial V}\right)_{T,N}
\end{aligned}$$

We see that in the case of the canonical ensemble, the connection between statistical mechanics and thermodynamics is made through the partition function.

Note that in the development above, we have assumed that the internal energy of a system, E, is equal to the expected value of the Hamiltonian for that system: $E = < \mathcal{H}(\{p,q\}) >$. Though true for most systems, this is not always true. It is not true, for example, for a simple paramagnet. We will examine paramagnets in detail later in the course. It is fair to say that this fact is not well understood by many students, and can cause confusion and consternation when the application of the above formalism to a magnet gives the wrong answer for the internal energy and the entropy.

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