8.044 Statistical Physics I   Spring Term 2003

Notes on the Microcanonical Ensemble

The object of this endeavor is to impose a simple probability density on the phase space, classical or quantum, of the many particle system and to use it to obtain both microscopic and macroscopic information about the system. The microscopic information includes the probability densities for individual microscopic coordinates or states. The macroscopic information will consist of a statistical mechanical definition of the temperature, the second law of thermodynamics and all the necessary equations of state.

1. The System

The system we will consider consists of N particles in a volume V subject to enough mechanical and electromagnetic constraints to specify the thermodynamic state of the system when combined with the additional constraint that the total energy of the system is restricted to a very narrow range Δ above a reference energy E.

$$E < \text{energy} \le E + \Delta$$

The number of items in the list of fixed quantities, including E, is the number of independent macroscopic variables. For simplicity we will carry along only 3 in most of these notes: E, N and V.

Fixed:
  E
  V
  N
  $\vec{M}$ or $\vec{H}$
  $\vec{\mathcal{P}}$ or $\vec{\mathcal{E}}$
  .
  .
  .

2. The Probability Density

Here we choose the simplest of all possible forms (at least conceptually) for the probability density: a constant for all of the accessible states of the system. The "accessible" states are those microscopic states of the system consistent with the constraints $(E, V, N, \cdots)$. This choice is known as the "postulate of equal a priori probabilities". It is in fact the fundamental basis of all of statistical mechanics.

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Classical version:

$$
\begin{aligned}
p(\{p,q\}) &= 1/\Omega && E < \mathcal{H}(\{p,q\}) \le E + \Delta \\
&= 0 && \text{elsewhere}
\end{aligned}
$$

$$
\Omega \equiv \int_{\text{accessible}} \{dp, dq\} = \Omega(E, V, N)
$$

Quantum version:

$$
\begin{aligned}
p(k) &= 1/\Omega && E < \langle k|\mathcal{H}|k \rangle \le E + \Delta \\
&= 0 && \text{elsewhere}
\end{aligned}
$$

$$
\Omega \equiv \sum_{k,\ \text{accessible}} (1) = \Omega(E, V, N)
$$

In the quantum case Ω is dimensionless. It is the total number of microscopic states accessible to the system. Classically Ω is the accessible volume of phase space. It can be made dimensionless by dividing by $\hbar^m$ where m is the number of canonically conjugate momentum-coordinate pairs (p, q) in the phase space. In most of what follows the classical version will be employed.

Microscopic information is obtained by integrating the unwanted variables out of the joint probability density $p(\{p, q\})$. For example if one wants the probability density for a single coordinate q_i

$$
\begin{aligned}
p(q_i) &= \int_{q \ne q_i} p(\{p, q\}) \, \{dp, dq\} \\
&= \frac{1}{\Omega} \int_{q \ne q_i} \{dp, dq\} \\
&= \frac{\Omega'(\text{all but } q_i \text{ axis})}{\Omega}
\end{aligned}
$$

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For a more complex state of the system, X, involving specification of a subset $\{p'', q''\}$ of the microscopic variables

$$
\begin{aligned}
p(X) &= \int_{\text{except } \{p'', q''\}} p(\{p, q\}) \{dp, dq\} \\
&= \frac{1}{\Omega} \int_{\text{except } \{p'', q''\}} \{dp, dq\} \\
&= \frac{\Omega'(\text{consistent with } X)}{\Omega} \\
&= \frac{\text{volume of accessible phase space consistent with } X}{\text{total volume of accessible phase space}}
\end{aligned}
$$

We will see later that the thermodynamic information about the system is obtained from the dependence of Ω on the constraints, $\Omega(E, V, N)$.

3. Quantities Related to Ω

$$
\begin{aligned}
\Phi(E, V, N) &\equiv \int_{\mathcal{H}\{p, q\} < E} \{dp, dq\} \\
&= \text{cumulative volume in phase space}
\end{aligned}
$$

$$
\begin{aligned}
\omega(E, V, N) &\equiv \frac{\partial \Phi(E, V, N)}{\partial E} \\
&= \text{density of states as a function of energy}
\end{aligned}
$$

$$
\Rightarrow \Omega(E, V, N) = \omega(E, V, N)\Delta
$$

3

4. Entropy

In general Ω increases exponentially with the size of the system. It is convenient to work with an extensive measure of the phase space volume, one which is additive as two systems are brought together in mutual equilibrium. A logarithmic measure of Ω satisfies this criterion.

$$\begin{aligned}
S(E,V,N) &\equiv& k \ln \Omega(E,V,N) \\[2ex]
&\approx& k \ln \Phi(E,V,N) \\[2ex]
&\approx& k \ln \omega(E,V,N)
\end{aligned}$$

The two approximate expressions hold due to the fact that for large N the error can be shown to be of order $\ln N$ while the given term is proportional to N.

$S(E,V,N)$ is called the entropy.

- It is a state function.

- It is extensive.

- It is a logarithmic measure of the microscopic degeneracy associated with a macroscopic (that is, thermodynamic) state of the system.

- k is Boltzmann's constant with units of energy per ^0K.

5. Statistical Mechanical Definition of Temperature

Bring together two arbitrary systems 1 and 2, each represented by its own micro-canonical ensemble and therefore having well defined phase space volumes Ω_1 and Ω_2. While isolated from the rest of the world they are allowed to interact thermally, $dQ_1 = -dQ_2$, but not mechanically, $dW_1 = dW_2 = 0$. The interaction is weak enough that the two systems maintain their identities, thus the individual phase space volumes (and the microscopic variables on which they are defined) still make sense. Since the sum of the two systems is isolated it also can be represented by its own microcanonical ensemble with phase space volume Ω. Since Ω must take into account

all the possible ways the total energy E can be divided between the two subsystems $\Omega(E)$ can be expressed in terms of their individual phase space volumes as follows:

$$\Omega(E) = \int_0^E \Omega_1(E') \, \Omega_2(E - E') \, dE'$$

Consider the following reasonable question. What is the most probable value for E_1 when equilibrium has been reached? We can determine this from $p(E_1)$.

$$p(E_1) = \frac{\Omega_1(E_1) \, \Omega_2(E - E_1)}{\Omega(E)}$$

Note that this expression is consistent with the normalization of $p(E_1)$.

$$\int_0^E p(E_1) \, dE_1 = \frac{\int_0^E \Omega_1(E_1) \, \Omega_2(E - E_1) \, dE_1}{\Omega(E)} = \frac{\Omega(E)}{\Omega(E)} = 1$$

Now find where $p(E_1)$ has its maximum by finding where its derivative vanishes.

$$
\begin{aligned}
0 &= \frac{d}{dE_1} \left(\Omega_1(E_1) \Omega_2(E - E_1) \right) \\[2mm]
&= \frac{d\Omega_1(E_1)}{dE_1} \Omega_2(E - E_1) + \Omega_1(E_1) \frac{d\Omega_2(E - E_1)}{dE_1} \\[2mm]
&= \frac{d\Omega_1(E_1)}{dE_1} \Omega_2(E_2) - \Omega_1(E_1) \frac{d\Omega_2(E_2)}{dE_2} \\[2mm]
&= \frac{1}{\Omega_1(E_1)} \frac{d\Omega_1(E_1)}{dE_1} - \frac{1}{\Omega_2(E_2)} \frac{d\Omega_2(E_2)}{dE_2} \\[2mm]
&= \frac{d}{dE_1} \ln \Omega_1(E_1) - \frac{d}{dE_2} \ln \Omega_2(E_2)
\end{aligned}
$$

Thus the maximum of $p(E_1)$ occurs when

$$\left(\frac{\partial S_1}{\partial E_1} \right)_{\mathchar'26\mkern-10mu dW_1 = 0} = \left(\frac{\partial S_2}{\partial E_2} \right)_{\mathchar'26\mkern-10mu dW_2 = 0}$$

Solving would give the most probable value of E_1. More important is the fact that this expression specifies the equilibrium condition. Therefore

$$\left(\frac{\partial S}{\partial E} \right)_{\mathchar'26\mkern-10mu dW = 0} = f(T) \equiv \frac{1}{T} \qquad \text{(in equilibrium)}$$

The specific choice of $f(T)$

- agrees with the T defined empirically by the ideal gas law,

- agrees with the T defined thermodynamically by the efficiency of Carnot cycles.

6. Two Fundamental Inequalities

Consider the two systems in section 5. when they are not necessarily at the same temperature before contact. Let E_1 be the energy of system 1 before the contact is made and E_1^* be its energy after the combined system has reached mutual equilibrium. When contact is first made the following relationship holds between the probabilities of finding system 1 at those energies; the equality only holds if the two systems were in equilibrium before contact, which would require $E_1 = E_1^*$.

$$p(E_1) \ \leq \ p(E_1^*)$$

$$\Omega_1(E_1)\Omega_2(E - E_1) \ \leq \ \Omega_1(E_1^*)\Omega_2(E - E_1^*)$$

$$1 \ \leq \ \frac{\Omega_1(E_1^*)}{\Omega_1(E_1)} \ \frac{\Omega_2(E - E_1^*)}{\Omega_2(E - E_1)}$$

$$0 \ \leq \ \underbrace{S_1(E_1^*) - S_1(E_1)}_{\Delta S_1} + \underbrace{S_2(E - E_1^*) - S_2(E - E_1)}_{\Delta S_2}$$

But entropy is additive, so the entropy change for the entire system is $\Delta S = \Delta S_1 + \Delta S_2$. Thus we have found the important result

- $\Delta S \geq 0$ for spontaneous changes in an isolated system

Now consider the special case where system 2 is so large compared to system 1 that the heat added to it, $\dbar Q_2$, does not change its temperature. System 2 is then referred to as a temperature bath or thermal reservoir and $T_2 \equiv T_{\text{bath}}$. This assumption allows us to find an explicit relation for small changes in the entropy of system 2:

$$dS_2 \ = \ \frac{dE_2}{T_2} \qquad \text{statistical definition of temperature}$$

$$= \ \frac{\dbar Q_2}{T_2} \qquad \text{since no work is done}$$

$$= \ -\frac{\dbar Q_1}{T_{\text{bath}}}$$

We can now rewrite the inequality derived above as it applies to this special case.

$$
\begin{aligned}
0 &\leq dS_1 + dS_2 \\
0 &\leq dS_1 - \frac{\dbar Q_1}{T_{\text{bath}}}
\end{aligned}
$$

From this we conclude that

- $dS_1 \geq \dfrac{\dbar Q_1}{T_{\text{bath}}}$ \qquad when exchanging heat with a reservoir

The two inequalities indicated by bullets, taken together, form the second law of thermodynamics.

7. <u>Entropy as a Thermodynamic Variable</u>

The work done on a system is given by the expression

$$
\begin{aligned}
\dbar W &= \left\{ \begin{array}{c} -PdV \\ \mathcal{S}dA \\ \mathcal{F}dL \end{array} \right\} + HdM + \mathcal{E}d\mathcal{P} + \cdots \\
&\equiv \sum_i X_i \, dx_i
\end{aligned}
$$

Here for convenience we have introduced the notation of a generalized "force" X_i conjugate to some generalized external parameter x_i.

In the microcanonical ensemble the energy is fixed at E. In general the internal energy of a system is the average of the energy over all the accessible microstates, so in this case U is identical to E and we can write the first law as

$$
dE = \dbar Q + \dbar W
$$

Now we examine the consequences of the statistical mechanical definition of entropy.

$$
S \equiv k \ln \Omega = S(\underbrace{E, V, M, \cdots}_{})
$$

constraints when computing Ω, a
complete set of independent ther-
modynamic variables

$$
= S(E, \{x_i\})
$$

where we have <u>chosen</u> to use the x_i
as the constraints

The statistical mechanical expression for the entropy can be inverted to give E as a function of S.

$$S(E, V, M, \cdots) \quad \leftrightarrow \quad E(S, V, M, \cdots)$$

$$S(E, \{x_i\}) \quad \leftrightarrow \quad E(S, \{x_i\})$$

$$dE|_{dW=0} = \not{d}Q \quad \text{from the first law}$$

$$dE|_{dW=0} \leq T dS \quad \text{utilizing the second law} \qquad \text{[the equality only holds for equilibrium (reversible) changes]}$$

Therefore

$$dE = \not{d}Q + \not{d}W$$

$$\leq T dS + \not{d}W$$

$$\leq T dS + \left\{ \begin{array}{c} -P dV \\ \mathcal{S} dA \\ \mathcal{F} dL \end{array} \right\} + H dM + \mathcal{E} d\mathcal{P} + \cdots$$

The final line above is a fundamental result which expresses the combined first and second laws of thermodynamics. We continue our development by solving this expression for the differential of the entropy.

$$dS \geq \frac{1}{T} dE - \frac{1}{T} \not{d}W = \frac{1}{T} dE - \frac{1}{T} \sum_i X_i \, dx_i$$

$$\geq \frac{1}{T} dE + \frac{P}{T} dV - \frac{H}{T} dM - \frac{\mathcal{E}}{T} d\mathcal{P} + \cdots$$

This expression leads to two fundamental results. The first is a restatement of the second law of thermodynamics.

The only changes which can occur in an isolated system $(dE = dx_i = 0)$ are those which increase the entropy or, at best, leave it unchanged.

The second result is that the connection between statistical mechanics and thermo-dynamics in the microcanonical ensemble is through the entropy. In particular, if one knows the entropy as a function of the constraints $S(E, \{x_i\})$, or what is equivalent the phase space volume $\Omega(E, \{x_i\})$, then one can find expressions for the generalized forces in terms of those same variables by taking the appropriate derivative. The resulting expressions are the equations of state for the system. In particular

$$\left(\frac{\partial S}{\partial x_j}\right)_{E, x_i \neq x_j} = -\frac{X_j}{T}$$

$$\left(\frac{\partial S}{\partial V}\right)_{E, M, \mathcal{P}} = \frac{P}{T}$$

$$\left(\frac{\partial S}{\partial M}\right)_{E, V, \mathcal{P}} = -\frac{H}{T}$$

$$\left(\frac{\partial S}{\partial \mathcal{P}}\right)_{E, V, M} = -\frac{\mathcal{E}}{T}$$