Lecture 7: Fluctuations

1 Introduction

In a canonical or grand canonical equilibrium ensemble the system members of interest exchange conserved quantities with the environment. As a consequence the total of such quantities fluctuates in a random fashion about the ensemble mean. A closed system may be subdivided into equal open subregions. If the whole system is in statistical equilibrium then the subsystem conserved quantities will have equal means. On the other hand, the subsystem totals for the conserved quantities will also fluctuate for the same reason as canonical ensemble member totals vary (they are open systems). In this lecture we examine the nature of such fluctuations. We begin with the grand canonical ensemble.

2 Grand canonical ensemble fluctuations

The standard deviation of total energy E and molecular number N are non-zero for such an ensemble and give a measure of how the such quantities fluctuate among members. From Lecture 5 we can write the probability density of the ensemble as

$$
\begin{aligned}
P_G &= Z_G^{-1} \exp\left(-\beta E - \alpha N\right) \\
\beta &\equiv T^{-1} \\
\alpha &\equiv -\mu T^{-1}
\end{aligned}
$$

Now the mean energy E_0 is

$$
\begin{aligned}
E_0 &= \langle E \rangle_{P_G} = Z_G^{-1} \sum_{N=0}^{\infty} \int_{R^{6N}} E \exp\left(-\beta E - \alpha N\right) dV \\
dV &= \frac{d^N \boldsymbol{p}\, d^N \boldsymbol{q}}{\hbar^{3N} N!}
\end{aligned}
$$

where the angle brackets denote the expectation with respect to the subscripted density. Differentiating E_0 with respect to the inverse temperature β we obtain

$$
\frac{\partial E_0}{\partial \beta} = \frac{\partial Z_G^{-1}}{\partial \beta} \sum_{N=0}^{\infty} \int_{R^{2N}} E \exp\left(-\beta E - \alpha N\right) dV - \left\langle E^2 \right\rangle_{P_G}
$$

but using the definition of the partition function Z_G we easily obtain

$$
\frac{\partial Z_G^{-1}}{\partial \beta} = Z_G^{-1} \langle E \rangle_{P_G}
$$

and so

$$
\frac{\partial E_0}{\partial \beta} = \langle E \rangle_{P_G}^2 - \left\langle E^2 \right\rangle_{P_G} = -variance(E) \tag{1}
$$

in an entirely analogous fashion we can obtain

$$\frac{\partial \overline{N}}{\partial \alpha} = \langle N \rangle_{P_G}^2 - \langle N^2 \rangle_{P_G} = -variance(N)$$

It is of interest to consider what happens to fluctuations as the mean number of molecules increases i.e. as the thermodynamical limit is approached. Similarly to the previous lecture one may introduce an energy density i.e. the mean energy per molecule:

$$\epsilon \equiv \frac{E_0}{\overline{N}} \tag{2}$$

If ϵ is held fixed and the number of molecules increased then we simply obtain a larger version of the original system. Substitution of (2) into (1) leads to

$$\Delta_E \equiv \frac{sd(E)}{E_0} = \frac{1}{\sqrt{\overline{N}}\epsilon} \left(-\frac{\partial \epsilon}{\partial \beta} \right)^{\frac{1}{2}}$$

which shows that as the size of the system increases the ratio of fluctuations of energy to system mean energy drops off as the inverse of the square root of the mean number of molecules. Some simple calculations for an ideal gas using the formulae of the previous lecture reveals that energy fluctuations for "everyday" gas volumes are less than $10^{-10} joules$ which is close to the limit of experimental detectability.

3 Boltzmann entropy

We turn now to the case of a closed system with fixed energy and molecule number. If this system is divided up into a significant number of subsystems then as time progresses fluctuations in the subsystem macroscopic quantities will occur and these will become, by the arguments of the previous section, larger as the subsystem size becomes smaller.

In order to analyze this situation we introduce a new version of entropy appropriate to systems not in equilibrium since such macroscopic fluctuations indicate a system slightly out of equilibrium thermodynamically. The definition of entropy outlined in the first lecture was intended for equilibrium systems and in that context corresponded with the Shannon/Gibbs ensemble entropy. The non-equilibrium version uses a similar approach but relies fundamentally on the concept of coarse grained or observable variables for it's definition. It is commonly called the (non-equilibrium) Boltzmann entropy.

A coarse grained variable may be defined by first identifying some functions $A_j(\boldsymbol{p}_i, \boldsymbol{q}_i)$ of the system configuration (phase space) variables. Secondly the possible values of such functions are assigned to a countable set of intervals on the real line. Denote the set of these interval memberships by the vector $\boldsymbol{a}$. The specific details of such intervals are not important to the entropy definition (but of course must be concretely specified). The basic point here is that there are a multitude of <u>configuration</u> values for each vector coarse grained variable outcome

$\boldsymbol{a}$. This basic fact enables a suitable definition of entropy. A useful example is our closed system with subsystem total energies E_j mapped to intervals of equal length ΔE.

Now, as noted in earlier lectures, the set of possible configuration variables for a closed system is a submanifold of R^{6N} however within this submanifold one can identify a set of values of the configuration variables that are consistent with a particular $\boldsymbol{a}$. This may be the empty set of course if the outcome violates the total energy constraint. Denote the volume (or Lebesgue measure) of the set of consistent variables by $\Omega(\boldsymbol{a})$ then we define the Boltzmann entropy of the coarse grained outcome vector by

$$\begin{aligned} S_B(\boldsymbol{a}) &\equiv& \log \Omega(\boldsymbol{a}) + C \\ C &=& -\log\left[(2\pi\hbar)^N N!\right] \end{aligned} \tag{3}$$

where the additive constant is chosen for dimensional consistency and to subsume the indistinguishability (quantum) issue discussed earlier. A variant of this equation is inscribed on the gravestone of Ludwig Boltzmann in Vienna. For the remainder of the lecture we drop the subscript B.

4   Boltzmann principle

We now invoke the quasi-ergodic hypothesis for the microcanonical ensemble. This states that in an equilibrium situation for a closed system the probability that the configuration is within any particular finite volume subset of the submanifold of possible configuration values is actually proportional to the subset volume. Such a hypothesis enables us to invert Boltzmann's equation (3) and obtain the probability of any particular outcome vector $\boldsymbol{a}$:

$$P(\boldsymbol{a}) = D \exp\left(S(\boldsymbol{a})\right) \tag{4}$$

This relation was due originally to Einstein in 1904 but is commonly called the Boltzmann principle. It has been of fundamental importance in statistical physics. The significance is that once the entropy function is known then the probability of coarse grained outcomes may be computed, a situation first appreciated by Einstein[1].

An immediate consequence of equation (4) is that the most probable macrostate $\boldsymbol{a}_M$ is that of maximum Boltzmann entropy S_{max}. In a loose sense deviations from $\boldsymbol{a}_M$ are only of significant probability when they are small i.e. the probability distribution over macroscopic $\boldsymbol{a}$ is "very sharply peaked". A mathematical peculiarity of our definition above is that S is a function over a countable set

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[1]Computation of the entropy function from first principles from the microcanonical ensemble of a given dynamical system is a non-trivial undertaking as a moments reflection shows however in the thermodynamical limit it is possible to make contact with the Clausius definition of entropy. This is a rather subtle matter which we leave the interested reader to pursue in the literature beginning with the Penrose reference given in Lecture 1.

(the domain of the outcomes $\boldsymbol{a}$) rather than a continuum. In order to regularize the situation we assume there exists a suitable differentiable interpolating function which extends the entropy function to all possible (real) values of the original vector variable $\boldsymbol{A}$ with the property that the (unique) maximum of this interpolation function occurs within the maximal coarse-graining interval.

Consider now the small deviation from the maximum entropy case by expanding the entropy function with a Taylor series about $\boldsymbol{A}_M$ the value of the coarse-grained variable which maximizes entropy. Now the gradient of S with respect to the coarse grained variables vanishes at this point because of the maximality assumption so we can write to second order accuracy:

$$
\begin{aligned}
S &\approx S_{max} + \frac{1}{2} \sum_{ij} s_{ij} \Delta A_i \Delta A_j \\
s_{ij} &\equiv \left. \frac{\partial^2 S}{\partial A_i \partial A_j} \right|_{\boldsymbol{A}_M} \\
\Delta \boldsymbol{A} &\equiv \boldsymbol{A} - \boldsymbol{A}_M
\end{aligned}
\tag{5}
$$

Note that the maximal condition also means that the matrix s_{ij} is negative definite. Substitution of (5) into (4) shows that to the degree that the approximation made is valid, the probability distribution governing fluctuations of the coarse grained variables is Gaussian with mean $\boldsymbol{A}_M$ and covariance matrix s^{-1} i.e. the sharply peaked normal distribution is peaked at the outcomes giving maximum Boltzmann entropy and the covariance of fluctuations is given by the matrix s^{-1}. Notice also that the Boltzmann entropy fluctuates and is not a fixed ensemble value as it was for the microcanonical ensemble with the Gibbs/Shannon equilibrium entropy.

5   Simple application

Consider a closed system divided into two sections which exchange only energy. The coarse-grained variables of interest to us will be the total energies of each section E_1 and E_2. We have then

$$
E_1 + E_2 = E_0
$$

where E_0 is fixed but clearly E_1 and E_2 fluctuate and our interest is in their statistics. Since E_0 is constant there is only one independent random variable describing the system. Further we have

$$
\begin{aligned}
\langle E_1 \rangle + \langle E_2 \rangle &= E_0 \\
\Delta E_1 + \Delta E_2 &= 0
\end{aligned}
$$

from which it follows easily that the covariances satisfy

$$
r \equiv \langle \Delta E_1 \Delta E_1 \rangle = \langle \Delta E_2 \Delta E_2 \rangle = - \langle \Delta E_1 \Delta E_2 \rangle
$$

so the entropy function for the combined system may be written approximately[2] as

$$S(E_1) = S_{max} - \frac{1}{2}r^{-1}(\Delta E_1)^2 \tag{6}$$

Now the Boltzmann entropy like the thermodynamical and equilibrium entropies discussed in earlier lectures may be shown (see Chapter 5 of the book by Penrose) to be additive for compound systems. Thus we have

$$S = S_1 + S_2 \tag{7}$$

where the subscripts refer to the two sections of our closed system. The most probable state for the combined system occurs when S is maximized but this may not correspond with maximal entropies for the interacting two sections seperately because of the thermal interaction. Thus in terms of the independent random variable E_1 a quadratic expansion for both sections of the system must include a linear term in ΔE_1 as well as a quadratic term. We have then

$$
\begin{aligned}
S_1 &= S_{1m} + \eta_1 \Delta E_1 - \frac{1}{2}\gamma_1 (\Delta E_1)^2 \\
S_2 &= S_{2m} + \eta_2 \Delta E_1 - \frac{1}{2}\gamma_2 (\Delta E_1)^2
\end{aligned} \tag{8}
$$

Combining (6), (7) and (8) we obtain for the introduced constant parameters

$$
\begin{aligned}
S_{max} &= S_{1m} + S_{2m} \\
\eta_1 &= -\eta_2 \\
r^{-1} &= \gamma_1 + \gamma_2
\end{aligned} \tag{9}
$$

Now in a similar way as we did in the thermodynamics Lecture 2 we can introduce a temperature function as

$$T_i^{-1} \equiv \frac{dS_i}{dE_i}$$

Comparison of this with (8) and (9) shows that when $\Delta E_1 = 0$ i.e. when $S = S_{max}$ then

$$T_1 = T_2 \equiv T = \eta_1^{-1}$$

but otherwise small fluctuations about this most likely maximum entropy temperature occur. Differentiating (8) twice w.r.t. E_1 and using (9) gives

$$
\begin{aligned}
r^{-1} &= -\frac{d^2 S_1}{dE_1^2} - \frac{d^2 S_2}{dE_1^2} \\
&= -\left[\frac{dT_1^{-1}}{dE_1} + \frac{dT_2^{-1}}{dE_2}\right]
\end{aligned}
$$

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[2]Note that for this system there is only one independent variable so the Taylor expansion in (5) involves only ΔE_1 and not $\Delta E_2 = E_0 - \Delta E_1$.

where we are using the definition of temperature on the second line and the fact that $E_1 + E_2$ is a constant. Now an important thermodynamical quantity (which we have not introduced yet) is the specific heat which is given by

$$C_i = \frac{dE_i}{dT_i}$$

and this is close to independent of temperature for many important fluids. Thus to a good approximation we may write

$$r^{-1} = \left(C_1^{-1} + C_2^{-1}\right) T^{-2}$$

where we are also neglecting the small difference between T_1 and T_2 for normal fluctuations. Thus the variance of E_1 is given by

$$r = T^2 \frac{C_1 C_2}{C_1 + C_2}$$

a result which may be found [3] in many texts on thermodynamics. The above derivation illustrates the power of Boltzmann's entropy in dealing with system fluctuations and there exist many other important examples of it's usage.

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[3] after the addition of Boltzmann's constant to convert temperature to Kelvin