The Gibbs approach
PH431 Lecture 9, Monday 10 March 2014, Adam Caulton (a.caulton@lse.ac.uk)

1 The basics of the Gibbs approach

1.1 The ensemble

The central notion in the Gibbsian approach to statistical mechanics is the ensemble. Instead of considering a single joint system, as in the Boltzmannian approach, and defining e.g. equilibrium and entropy as belonging to a system in a definite state, we consider instead a probability distribution over joint states, a.k.a. an ensemble.

An ensemble is not an assembly! An assembly is a single system, consisting of many parts, e.g. particles, that interact. An ensemble is a fictional construction of many “mental copies” of a system (usually an assembly!), which do not interact.

An ensemble may be represented by a function \( \rho : \Gamma_\gamma \rightarrow \mathbb{R} \) on the joint phase space. Since it is a probability density, the function is normalised; i.e. \( \int_{\Gamma_\gamma} \rho(x) \, d\mu_L(x) = 1 \), where \( \mu_L \) is (as usual) the Lebesgue measure on \( \Gamma_\gamma \).

1.2 Phase averages

We may use the probability density \( \rho \) to calculate expectation values, or phase averages, of physical quantities. Recall that any quantity for the joint system can be represented by a real-valued function \( f : \Gamma_\gamma \rightarrow \mathbb{R} \) on the joint phase space. Then its phase average is given by

\[
\bar{f} := \int_{\Gamma_\gamma} f(x) \rho(x) \, d\mu_L(x) \tag{1}
\]

Think of \( \bar{f} \) as the mean value of \( f \) for the ensemble.

1.3 Equilibrium

The definition of equilibrium is different in the Boltzmannian and Gibbsian approaches. In the Gibbsian approach, equilibrium is a feature of an ensemble.

- Constancy of the macroscopic quantities. This rough idea is common to the definition of equilibrium in thermodynamics, but here takes the exact form that the phase averages of all macroscopic quantities be constant over time.
- Stationarity of \( \rho \); i.e. \( \frac{\partial \rho}{\partial t} = 0 \). This was Gibbs’ original condition. Given (1), this condition entails the one above; but the converse entailment does not hold. This will be important later!

1.4 Entropy and the maximum entropy principle

The Gibbs entropy is also defined for ensembles:

\[
S_G(\rho) := -k_B \int_{\Gamma_\gamma} \rho(x) \log \rho(x) \, d\mu_L(x) \tag{2}
\]
Note the general “$-\sum_i p_i \log p_i$” form of this expression, familiar from the Boltzmann entropy for an assembly of “identical” systems (week 7’s lecture), and similar to many definitions of entropy in other fields. But beware!: in the Boltzmannian expression, the $p_i$ refer to the relative frequencies for “identical” constituent systems in single assembly; here the $\rho(x)$ refers to a probability density over different states for a joint system.

Gibb’s maximum entropy principle states that, if the ensemble is in equilibrium, then $\rho$ has the Gibbs entropy that is maximal amongst all other distributions that satisfy the constraints on the system. So, given the above, Gibbs defined an ensemble to be in equilibrium iff: (i) $\rho$ is stationary; and (ii) $S_G(\rho)$ is maximal, given the constraints.

Different constraints lead to different equilibrium distributions for $\rho$:

- **Microcanonical ensemble.** $E$ and $n$ held constant. The resulting equilibrium distribution is $\rho \propto \delta(H(q_1, \ldots, q_n; p_1, \ldots, p_n) - E)$. This is rather like a “principle of indifference” applied (according to the Lebesgue measure) to the energy hypersurface $\Gamma_E$.

- **Canonical ensemble.** $E$ varied; $n$ held constant.

- **Grand canonical ensemble.** $E$ and $n$ varied.

## 2 Why does the Gibbs approach work?

The above machinery is enormously successful in generating empirically successful predictions for a variety of systems. But its success is *prima facie* something of a mystery…

### 2.1 Ensembles vs. real world systems

What relation do ensembles have to real world systems? How are the probability densities described by $\rho$ to be interpreted, especially given that we know that there is only one system?

### 2.2 Whence the maximum entropy principle?

The maximum entropy principle is set down independently of any details about the dynamics of our system. But what justifies this principle? Is it just the principle of indifference applied to statistical mechanics?

### 2.3 Why does phase averaging work?

The success of the Gibbs approach relies on the assumption that the macroscopic quantities observed in experiments are phase averages. But how can that be?

A traditional answer is that, if the system is ergodic, then its phase average for any quantity equals its time average (remember ergodicity from last week); and time averages are what are observed in real experiments. (It is thought that the time-scale of a macroscopic experiment is enormous compared to the microscopic changes of the system.) But:

- **Ergodicity too strong.** Many systems for which the Gibbs approach works are *not* ergodic!
• **Finite vs. infinite time averages.** If we grant that experiments measure time averages, then they surely measure finite time averages, but phase averages for ergodic systems are equal to infinite time averages!

• **Do measurements really measure time averages?** (Surely we need to know much more about the measurement process until we may justifiably assume that.)

There are three main responses to this problem:

1. **Malament & Zabell (1980).** Phase averaging will work approximately well if: (i) the values $f(x)$ of the quantities we are interested in do not vary much about their phase average $\bar{f}$; and (ii) $\rho(x)$ represents the probability density of finding the system, at any given time, in state $x$. See Frigg (2008, 64-66) for more discussion about this approach.

   A related proposal, due to Vranas (1998) is to weaken the requirement of ergodicity to $\epsilon$-ergodicity (roughly: “ergodic behaviour in most of the phase space”). Vranas’s guiding idea is that $\epsilon$-ergodicity, which is a weaker condition, suffices to account for the empirical success of the Gibbs approach.

2. **Khinchin (1949).** We need not assume ergodicity for our system; we need only assume that ergodic-like behaviour holds: (i) for the macroscopic quantities of interest, which we may assume are all sum functions (i.e. we may ignore interaction terms); (ii) in the limit of very many degrees of freedom (e.g. $n$ large). This behaviour is called $K$-ergodic.

   (i) leads to the “methodological paradox” that equilibrium cannot be reached without particle interactions, despite assuming that interaction terms may be ignored. Attempts to justify the latter fall under the Thermodynamic Limit Programme, and mostly involve the assumption that $n, V \to \infty$, while $\frac{n}{V} \approx \text{const.}$

3. **The Jaynes approach.** More of which next week…

### 2.4 The approach (?) to equilibrium

Gibbs defined equilibrium for ensembles as the probability density that is: (i) stationary and (ii) has maximal entropy, given the constraints. But if the probability density is stationary, then not only does it never change in the future, it can never have changed in the past. Non-equilibrium distributions, on this definition, remain non-equilibrium distributions. So what becomes of the minus-first law?

I will consider two responses to this problem (I ignore the interventionist strategy; for which see Frigg (2008, §3.5.2, pp. 83-86)):

1. **Coarse-graining the phase space.** The proposal is to coarse-grain the joint phase space $\Gamma_\gamma$, and define a Gibbs entropy for the coarse-grained counterpart to the ensemble $\rho$.

   The guiding idea is that the Hamiltonian flow on the joint phase space leads a non-equilibrium ensemble to qualitatively “look more and more like” an equilibrium ensemble over time: e.g. the region of phase space given non-zero probability in a constant energy, non-equilibrium state becomes ever more warped and tentacular within $\Gamma_E$, so that eventually, FAPP it is like a flat distribution over $\Gamma_E$; i.e. the microcanonical ensemble.

   It has been proved that, for mixing systems, the coarse-grained Gibbs entropy never decreases. (But mixing is a stronger condition than ergodicity!)
2. **Redefining equilibrium.** We can retrench from Gibbs’ condition that an equilibrium state be stationary—after all, all we need is that the macroscopic quantities not vary (or not vary too much) over time.

2.5 **Companions in guilt**

Remember that many of the philosophical issues facing the Boltzmann account also face the Gibbs account! In particular, their success in reducing thermodynamics relies on what constitutes the successful reduction of one theory to another.

3 **Reading for discussion**

*Required reading:*


*Further reading:*