10.40 Lecture 22
Postulates of statistical mechanics, Gibbs ensembles

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(In preparation for Lecture 22, also read T&M, 10.1.4).

Outline

- Ensembles
- Postulates of statistical mechanics
- Gibbs Ensembles: Microcanonical ensemble
- Gibbs Ensembles: Canonical ensemble
- Gibbs Ensembles: Grand Canonical and others

  Note that the derivations of the relationships between the thermodynamic quantities and the statistical quantities are presented in the Appendix.

22.1 Ensembles and ensemble averages

An *ensemble* is an assembly of microstates or systems. Imagine a very large collection of systems evolving in time. A snapshot of the state of each of these systems at some instant in time forms the ensemble.

22.2 Two postulates of statistical mechanics:

1. time averaging is equivalent to ensemble averaging
2. for possible states with the same $N, \underline{V}$, and $\underline{E}$, all states are equally likely. Atkins: "principle of equal *a priori* probabilities"

22.3 Gibbs Ensembles: Microcanonical ensemble

In the *microcanonical ensemble*, each system has constant $N, \underline{V}$, and $\underline{E}$.

By Postulate 2, the probability that any give system is in a particular state, j, is $\frac{1}{\Omega(N,\underline{V},\underline{E})}$, where $\Omega(N, \underline{V}, \underline{E})$ is the total number of possible states. It turns out (see the Appendix for derivations) that the connection to macroscopic thermodynamics is through the entropy:

$$\underline{S} = k \ln \Omega(N, \underline{V}, \underline{E}).$$

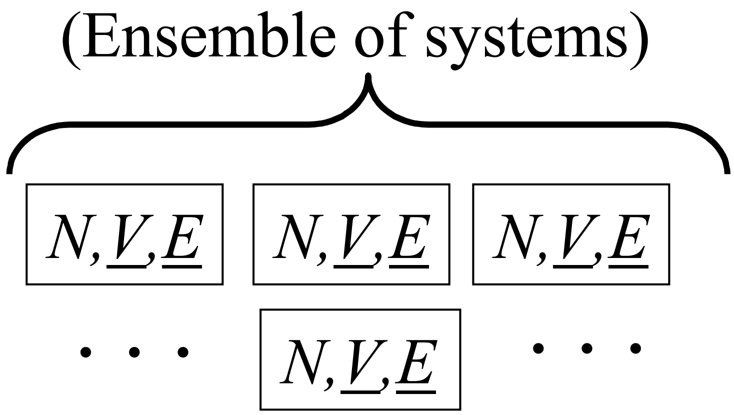

Figure 1: Microcanonical ensemble

22.4 Gibbs ensembles: Canonical ensemble

In the *Canonical ensemble*, each system has constant $N, \underline{V}$,and T.

After equilibration, remove all of the systems from the bath, and put them all together:

Here, the connection is through the Helmholtz Free Energy:

$$\boxed{\underline{A} = -kT \ln Q(N, \underline{V}, T)}$$

Similarly,

$$\begin{aligned} \underline{S} &= -\left(\frac{\partial \underline{A}}{\partial T}\right)_{\underline{V},N} = kT\left(\frac{\partial \ln Q}{\partial T}\right)_{\underline{V},N} + k\ln Q \\ P &= -\left(\frac{\partial \underline{A}}{\partial \underline{V}}\right)_{T,N} = kT\left(\frac{\partial \ln Q}{\partial \underline{V}}\right)_{T,N} \\ \underline{U} &= \underline{A} + T\underline{S} = kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{\underline{V},N}. \end{aligned}$$

Thus, all thermodynamic properties can be written in terms of the partition function, $Q(N, \underline{V}, T)$! In order to compute Q, all we need are the possible energy levels of the system. We can obtain these from solving the equations of quantum mechanics.

22.5 Gibbs Ensembles: Grand Canonical and others

In the Grand Canonical ensemble, the number of particles in each system is allowed to fluctuate, but μ is kept constant. This is called the $(\underline{V}, T, \mu)$ ensemble. Also, there are other ensembles, such as (N, P, T), etc. Note that from an analysis of fluctuations (Lecture 27), we shall see that in the macroscopic limit of a large number of systems, all of these ensembles are equivalent. The choice of which one to use is made for convenience.

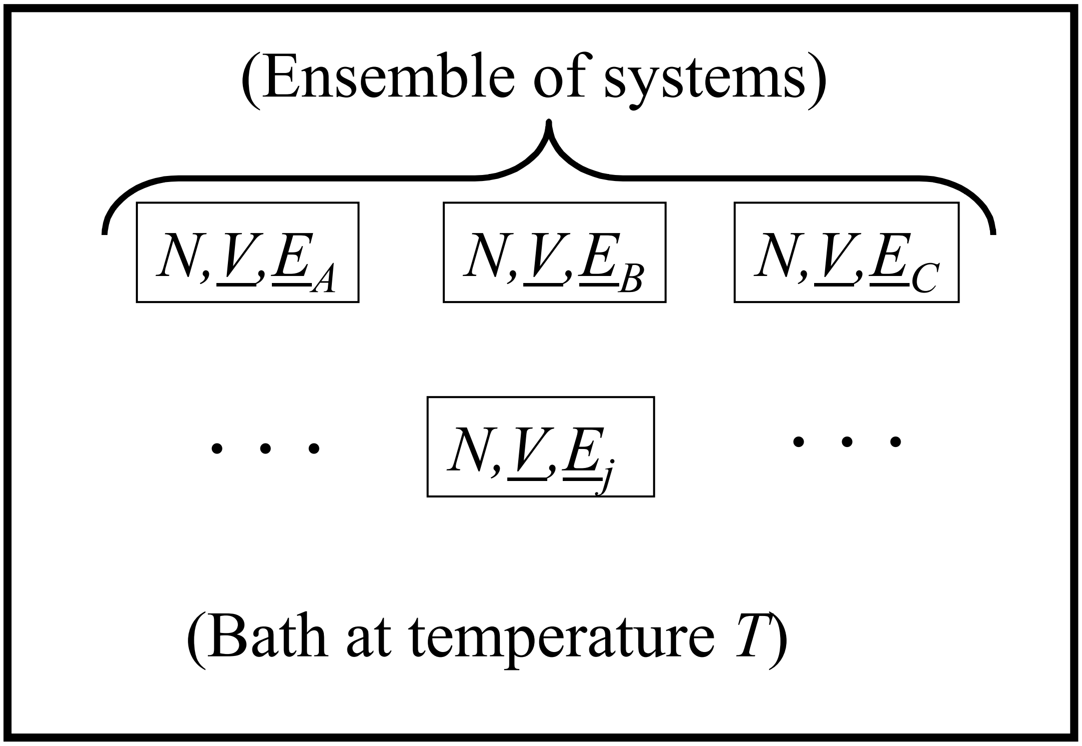

Figure 2: Canonical ensemble

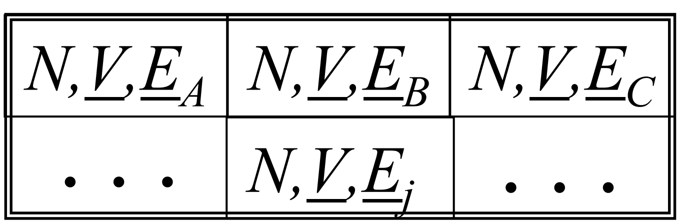

Figure 3: Canonical ensemble forming its own bath