

CHM 421/621

Statistical Mechanics

Lecture 2

Introduction and Review

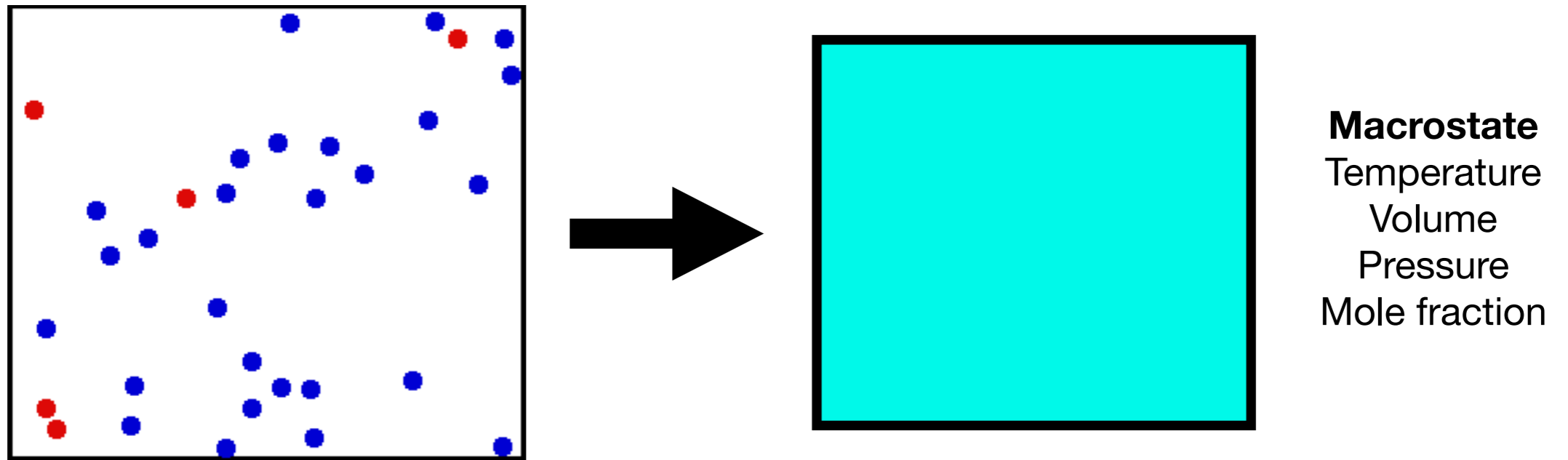
Lecture Plan

- Nature and Scope of thermodynamics
- Need for statistical mechanics
- Basic assumption of statistical mechanics
- A familiar example

Nature of Thermodynamics

Thermodynamics deals with properties of and processes undergone by macroscopic (bulk) systems.

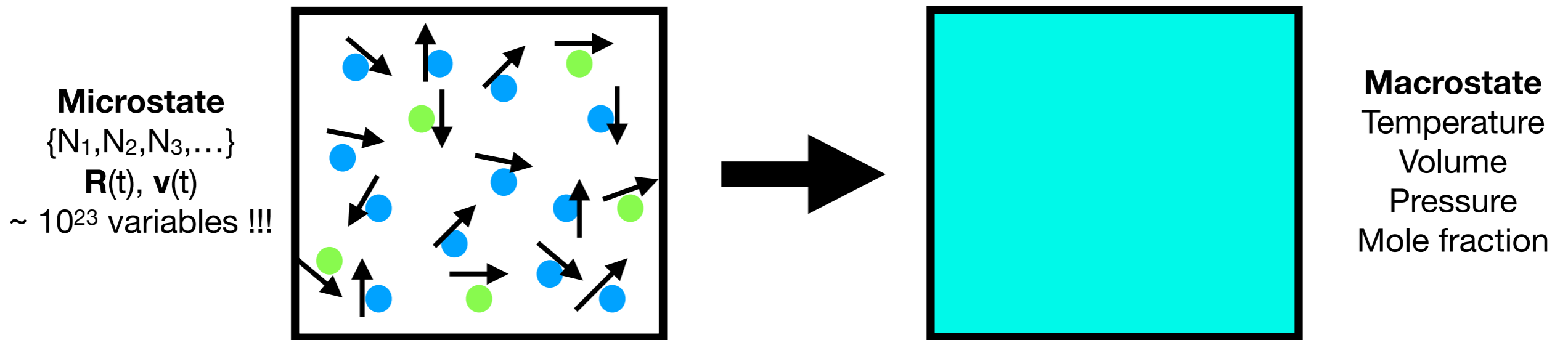
E.g. Volume, temperature, pressure, internal energy, conversion of heat to work, criteria for spontaneity, etc.



Macroscopic variables: Parameters that are deemed sufficient to completely describe the macroscopic state (**macrostate**) of a thermodynamic system.
(T, V, N, P, etc.)

Nature of Thermodynamics

Thermodynamic equilibrium => spatial uniformity, static nature, chemical homogeneity



But real systems are hardly every uniform and certainly not static!

Microstate: A particular microscopic configuration a system may be in at any instant of time. Specified, for example, by positions, velocities, etc. or by a set of quantum numbers.

Nature of Thermodynamics

The macroscopically “relevant” variables are picked out by the resolution limits of typical macroscopic measurements.

For instance, typical macroscopic temporal resolutions maybe in microseconds (10^{-6}), while atomic processes could be in femtoseconds (10^{-15}). Thus, any measurement would essentially be oblivious to such fast processes.

Similarly, the deviations in positions at the level of Angstroms (10^{-10} m) would not be visible to macroscopic measurements with resolutions limits in mm (10^{-3} m).

This enormous simplification is both an advantage and a disadvantage.

Scope of Thermodynamics

Thermodynamics provides mathematical relations between the experimentally measured macroscopic state variables.

E.g.

$$C_p - C_v = \left[p + \left(\frac{\partial E}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_p$$

Note that such relations are quite generally valid, being independent of any microscopic details of the system.

Thus, predictions of thermodynamics have a wide scope spanning Chemistry, Physics, Biology, Astrophysics, Computer Science, Engineering, etc.

However, thermodynamics is in itself incapable of providing physical interpretations or quantitative prediction of macroscopic properties.

For this we need to look beyond the macroscopic description.

Need for Statistical Mechanics

How do we bring in the microscopic details into consideration?

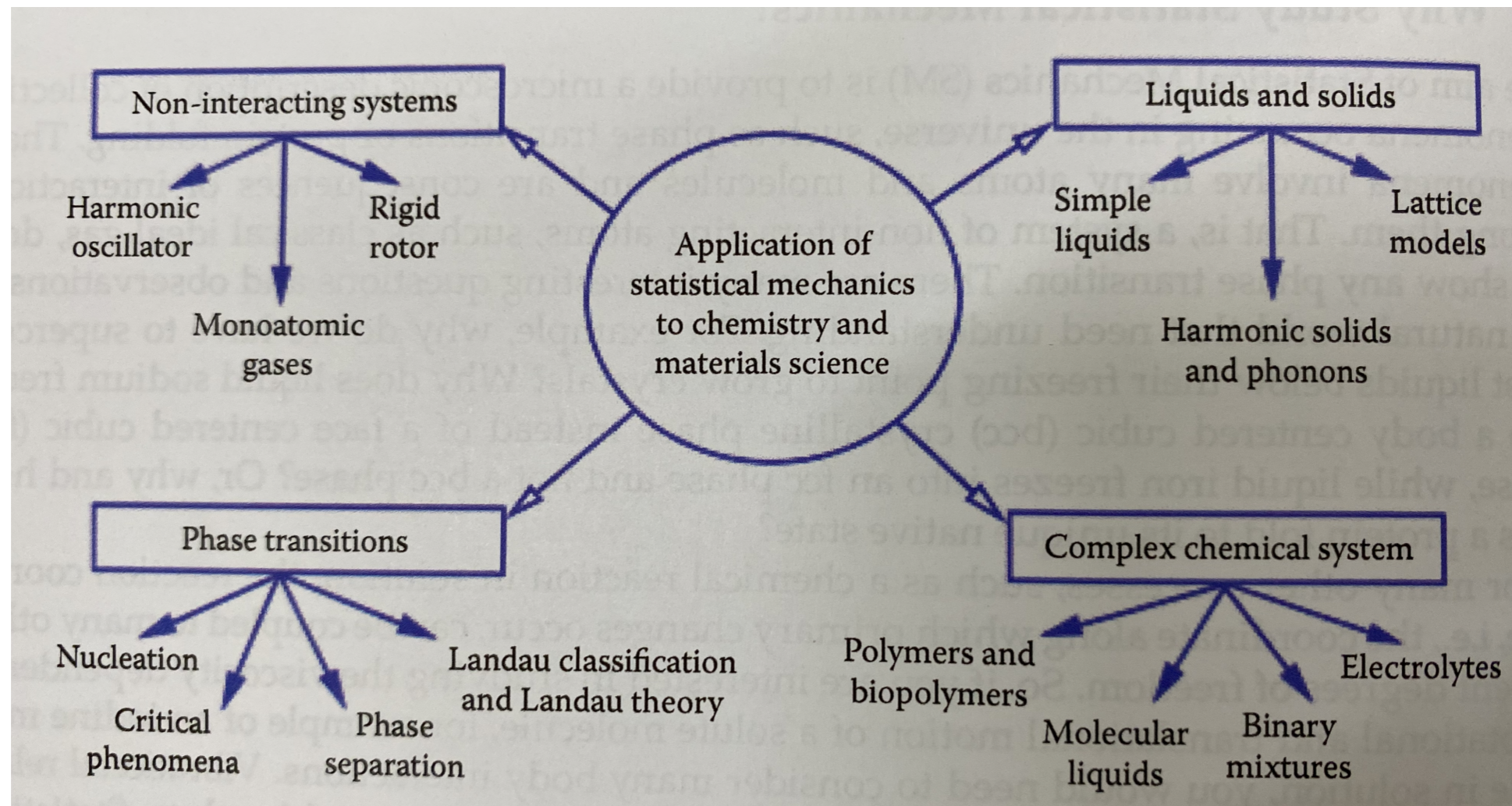
Basic Assumption:

The physical properties of a macroscopic system depend only on the average behaviour of all the atoms in that system.

Program of Statistical Mechanics

- (1)** Assume a microscopic model for the system.
- (2)** Assume/Derive a probability distribution for the various micro states possible under the given external constraints (thus bringing in the macroscopic variables).
- (3)** Compute weighted averages of desired properties.

Scope of Statistical Mechanics



A familiar example

Classical microstates - set of instantaneous coordinates and velocities.

System: Consider a system of N particles moving independently of each other and inside a closed container of volume V . The container (and hence the particles) is assumed to be in thermal contact with a reservoir at temperature T .

Model:

$$H(\{\mathbf{p}_i(t), \mathbf{r}_i(t)\}) = \sum_{i=1}^N \frac{1}{2m} p_i^2$$

Probability distribution:

$$\rho(\{\mathbf{p}_i, \mathbf{r}_i\}) = \frac{1}{Q(N, V, T)} \exp(-\beta H(\{\mathbf{p}_i, \mathbf{r}_i\}))$$

A familiar example

Probability distribution:

$$\rho(\{\mathbf{r}_i, \mathbf{p}_i\}) = \frac{1}{Q(N, V, T)} \exp(-\beta H(\{\mathbf{r}_i, \mathbf{p}_i\}))$$

Meaning:

The probability of finding the system in a microstate with the momenta of the particles between \mathbf{p}_i and $\mathbf{p}_i + d\mathbf{p}_i$ and their positions between \mathbf{r}_i and $\mathbf{r}_i + d\mathbf{r}_i$ is given by

$$\rho(\{\mathbf{r}_i, \mathbf{p}_i\}) d^{3N} r_i d^{3N} p_i$$
$$\Rightarrow \int \rho(\{\mathbf{r}_i, \mathbf{p}_i\}) d^{3N} r_i d^{3N} p_i = 1$$

So what is $Q(N, V, T)$?

A familiar example

$$Q(N, V, T) = AV^N \left(\frac{2\pi m}{\beta} \right)^{\frac{3N}{2}}$$

Here A is a constant to ensure the correct dimensions. We will show later that

$$A = \frac{1}{h^{3N}}$$

$$Q(N, V, T) = \left(\frac{V}{\Lambda^3} \right)^N$$

With $\Lambda = \frac{h}{\sqrt{2\pi m k_B T}}$

In this case, the normalisation equation becomes

$$\frac{1}{h^{3N}} \int \rho(\{\mathbf{r}_i, \mathbf{p}_i\}) d^{3N} r_i d^{3N} p_i = 1$$

Average Energy

Calculate

$$U = \langle H \rangle = \int d\mathbf{r} \int d\mathbf{p} H(\{\mathbf{r}_i, \mathbf{p}_i\}) \rho(\{\mathbf{r}_i, \mathbf{p}_i\})$$

Answer

$$U = \frac{3}{2} N k_B T$$