

Chapter 3: Summary

Chapter 3 introduces basics of statistical approach and then apply to isolated systems. Non-isolated systems are the focus of Chapter 4.

1. **Macrostates** of a thermodynamic system are given by a set of only a few thermodynamic variables. For example, values of three variables (E, V, N) specify the macrostate of an isolated system. The description of a **microstate** of a thermodynamic system however requires a large set of numbers specifying every single constituent particle's motion. For example, the microstates of a classical gas are given by the set of $6N$ components of positions and momenta,

$$(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; \mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N),$$

which is usually referred to as phase space.

Statistical approach is to find a distribution and take averages over the microstates. These averages give the observed values of the corresponding thermodynamic variables.

2. Two basic assumptions in statistical physics: (a) the postulate of equal a priori probabilities and (b) Boltzmann's formula for entropy

$$S = k_B \ln \Omega(E, V, N)$$

where Ω is the statistical weight, or the total number of microstates for a given macrostate (E, V, N) of an isolated system.

Three **ensemble** approaches employed in statistical physics:

- Microcanonical ensemble: isolated systems with fixed (E, V, N) ;
 - Canonical ensemble for systems in heat bath with fixed (T, V, N) ;
 - Grand canonical ensemble for open systems, a topic for a 3rd year course.
3. Statistical mechanics of isolated system (microcanonical ensemble):
 - First, find $\Omega(E, V, N)$;
 - Use Boltzmann formula to find entropy $S = k_B \ln \Omega(E, V, N)$;

- Use thermodynamic relations

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{V,N}$$

to find energy equation and the other relation

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

to find the equation of state.

Take a paramagnetic solid of spin-1/2 system in an applied magnetic field B as example, where macrostate $(E, V, N) \rightarrow (n_{\uparrow}, B, N)$ with n_{\uparrow} the number of spin-up atoms. The statistical weight is given by

$$\Omega(n_{\uparrow}, N) = \frac{N!}{n_{\uparrow}!(N - n_{\uparrow})!}$$

Stirling approximation $\ln M! \approx M \ln M - M$ for large M useful for calculations. Details in example sheet.

4. The **correspondence** between classical and quantum mechanics in statistical weight for a particle of a gas is given by the following formula

$$\int d\Omega_1 = \frac{1}{h^3} \int d^3 r_1 d^3 p_1,$$

where h is the Planck constant. This is useful in Chapter 4.