## Chapter 4: Summary

This chapter covers main part of statistical physics: the canonical ensemble for non-isolated systems - systems at constant temperature $T$. The key quantity is the partition function from which all other thermodynamic quantities can be calculated.

1. **Boltzmann distribution** of a system at $i$-th microstate with energy $E_i$ is given by

$$p_i = \frac{1}{Z_N} e^{-E_i/k_B T},$$

where the normalization factor $Z_N$ is usually referred to as **partition function** of the $N$-body system

$$Z_N = \sum_i e^{-E_i/k_B T}.$$

Thermodynamic quantities are calculated as average values over the Boltzmann distribution. For example, the internal energy $E$ is given by

$$E = \langle E \rangle = \sum_i E_i p_i = \frac{1}{Z_N} \sum_i E_i e^{-E_i/k_B T}.$$

2. In the **independent-particle approximation**, where interactions between particles are ignored (e.g., ideal gases, ideal paramagnet, etc.), the $N$-body partition function can be written in terms of an one-body function $Z_1$ as:

   - For $N$ distinguishable particles (models of solids such as paramagnet)

$$Z_N = (Z_1)^N;$$

   - For $N$ indistinguishable particles (models of classical gases), in a further **classical approximation**

$$Z_N \approx \frac{1}{N!}(Z_1)^N,$$

where the **one-body partition function** is defined as

$$Z_1 = \sum_{k_1} e^{-\epsilon_{k_1}/k_B T}$$

with one particle state $k_1$ and energy $\epsilon_{k_1}$.

3. A typical calculation for a system at temperature $T$ (canonical ensemble):

   - First calculate partition function $Z_N$ (e.g., using the independent-particle approximation).
   - Then Helmholtz free energy by $F = -k_B T \ln Z_N$.
   - Using thermodynamic relations to determine other quantities, such as

     $$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}, \quad P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}.$$

   - The internal energy is obtained by, with definition $\beta = 1/k_B T$,

     $$E = -\left(\frac{\partial \ln Z_N}{\partial \beta}\right)_{V,N}$$

     or simply using $E = F + TS$.

4. Example. The spin-1/2 ideal paramagnet in a field: only two single-particle energy levels. Partition function, internal energy, heat capacity and entropy. The low and high temperature behaviors and their physical meanings.

5. Example. The classical ideal gases: single-particle states are specified by continuous variables $(\mathbf{r}, \mathbf{p})$. Partition function, equation of state, energy and entropy. The unphysical results at the limit $T \to 0$ (e.g., violation of the third law). The vibrational and rotational contributions to the internal energy per diatomic molecule - quantum treatment and classical limits.

6. Revisit: the equipartition theorem and Maxwell velocity distribution.