

Classical and Quantum Statistics

(Lecture 13)

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Advanced Thermodynamics (M2794.007900)
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(* Some materials in this lecture note are borrowed from the textbook of Ashley H. Carter.

Dilute Gases and the Maxwell-Boltzmann Distribution

→ Let's find the **Maxwell-Boltzmann distribution** for **dilute gases**.

(Assumptions for dilute gases)

1. For all energy levels, the occupation numbers are very small compared with the available number of quantum states (or most quantum states are empty).

$$N_j \ll g_j, \text{ for all } j$$

2. It is extremely unlikely that more than one particle will occupy a given state. Thus, it is irrelevant whether or not the particles obey the Pauli exclusion principle, and both Fermi-Dirac and Bose-Einstein statistics are approximately identical.

Then, for Fermi-Dirac statistics, $\frac{g_j!}{(g_j - N_j)!} = g_j(g_j - 1)\dots(g_j - N_j + 1) \approx g_j^{N_j}$

$$w_{FD} = \prod_j \frac{g_j!}{(N_j)!(g_j - N_j)!} \approx \prod_j \frac{g_j^{N_j}}{N_j!} = w_{MB} \quad \text{Maxwell-Boltzmann statistics}$$

Dilute Gases and the Maxwell-Boltzmann Distribution

→ Continue on.

For Bose-Einstein statistics, $\frac{(g_j + N_j - 1)!}{(g_j - 1)!} = g_j(g_j + 1)\dots(g_j + N_j - 1) \approx g_j^{N_j}$

$$w_{BE} = \prod_j \frac{(g_j + N_j - 1)!}{N_j!(g_j - 1)!} \approx \prod_j \frac{g_j^{N_j}}{N_j!} = w_{MB} \quad \text{Maxwell-Boltzmann statistics}$$

Compare with Boltzmann statistics, $w_B = N! \prod_{j=1}^n \frac{g_j^{N_j}}{N_j!}$

$$w_B = N! w_{MB} \quad \leftarrow \text{Additional microstates with distinguishable particles}$$

For Maxwell-Boltzmann distribution, the method of Lagrange multipliers is applied.

$$\frac{\partial S_L}{\partial N_j} = \frac{\partial \ln w}{\partial N_j} + \alpha + \beta \epsilon_j = 0$$

Dilute Gases and the Maxwell-Boltzmann Distribution

→ Continue on.

Boltzmann statistics and Maxwell-Boltzmann statistics result in the same distribution.

$$f_j = \frac{N_j}{g_j} = \frac{N e^{-\frac{\epsilon_j}{kT}}}{Z} \quad \text{where} \quad Z = \sum_{j=1}^n g_j e^{-\frac{\epsilon_j}{kT}} \quad \leftarrow \text{Maxwell-Boltzmann distribution}$$

(cf.) Because the two distributions are identical, Boltzmann statistics and Maxwell-Boltzmann statistics are frequently confused with each other. Boltzmann statistics assumes distinguishable particles (largely applied to solids and some liquids), while for gases Fermi-Dirac or Bose-Einstein statistics applies and Maxwell-Boltzmann statistics is a very useful approximation for a dilute gas.

The Connection between Classical and Statistical Thermodynamics

- Let's relate the properties in statistical thermodynamics to those in classical thermodynamics.

The statistical expression for internal energy is,

$$U = \sum_{j=1}^n N_j \varepsilon_j$$
$$\rightarrow dU = \sum_{j=1}^n \varepsilon_j dN_j + \sum_{j=1}^n N_j d\varepsilon_j$$

From the energy states of translational kinetic energy,

$$\varepsilon_{tr} = \left(\frac{h^2}{8mV^{2/3}} \right) (n_x^2 + n_y^2 + n_z^2) \quad \text{or} \quad \varepsilon_j = \varepsilon_j(V)$$

In general,

$$\varepsilon_j = \varepsilon_j(X) \quad \text{where } X : \text{an extensive property of the system}$$

The Connection between Classical and Statistical Thermodynamics

→ Continue on.

$$dU = \sum_{j=1}^n \varepsilon_j dN_j + \sum_{j=1}^n N_j d\varepsilon_j \quad \text{and} \quad \varepsilon_j = \varepsilon_j(X)$$

Here,

$$d\varepsilon_j = \left(\frac{d\varepsilon_j}{dX} \right) dX \rightarrow \sum_{j=1}^n N_j d\varepsilon_j = \left[\sum_{j=1}^n N_j \left(\frac{d\varepsilon_j}{dX} \right) \right] dX = -YdX$$

$$\text{where } Y \equiv - \sum_{j=1}^n N_j \left(\frac{d\varepsilon_j}{dX} \right)$$

Then,

$$dU = \sum_{j=1}^n \varepsilon_j dN_j - YdX \quad \text{or} \quad (dU)_X = \sum_{j=1}^n \varepsilon_j dN_j$$

To compare with classical counterparts or Gibbs equation,

$$dU = TdS - YdX \quad \text{or} \quad (dU)_X = TdS$$

Finally,

$$\sum_{j=1}^n \varepsilon_j dN_j = TdS \quad \text{and} \quad \sum_{j=1}^n N_j d\varepsilon_j = -YdX$$

The Connection between Classical and Statistical Thermodynamics

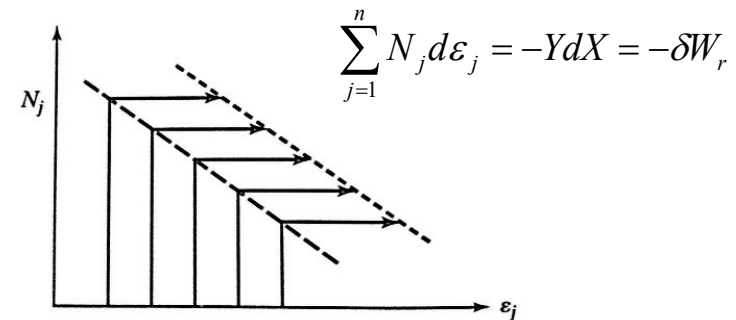
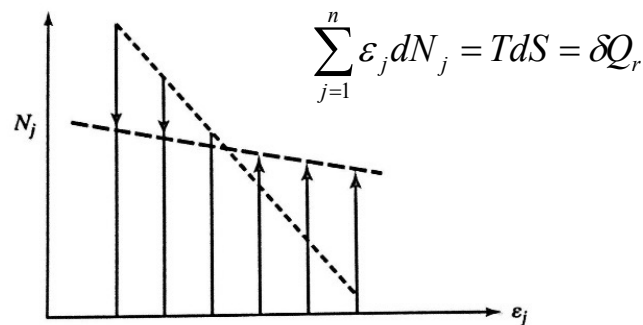
→ Continue on.

$$\sum_{j=1}^n \varepsilon_j dN_j = TdS \quad \text{and} \quad \sum_{j=1}^n N_j d\varepsilon_j = -YdX$$

For a reversible process,

$$\sum_{j=1}^n \varepsilon_j dN_j = TdS = \delta Q_r \quad \text{and} \quad \sum_{j=1}^n N_j d\varepsilon_j = -YdX = -\delta W_r$$

1. The first equation states that heat transfer is energy resulting in a net redistribution of particles among the available energy levels, involving no work.
2. The second equation states that when the reversible work is done on the system, the energy levels are shifted to higher values with no redistribution of the particles among the levels.



The Connection between Classical and Statistical Thermodynamics

→ Let's derive the chemical potential.

The change in internal energy in classical thermodynamic is,

$$dU = TdS - PdV + \tilde{\mu}dN \quad (\tilde{\mu} : \text{chemical potential per particle})$$

Using the Helmholtz function,

$$F = U - TS$$

$$\rightarrow dF = dU - TdS - SdT = TdS - PdV + \tilde{\mu}dN - TdS - SdT$$

$$\rightarrow dF = -SdT - PdV + \tilde{\mu}dN$$

$$\rightarrow \tilde{\mu} = \left(\frac{\partial F}{\partial N} \right)_{T,V}$$

We'll evaluate the entropy, the Helmholtz function, and the chemical potential for Maxwell-Boltzmann statistics.

The Connection between Classical and Statistical Thermodynamics

→ Continue on.

The Maxwell-Boltzmann statistics is given by,

$$w_{MB} = \prod_j \frac{g_j^{N_j}}{N_j!} \quad \text{with} \quad \frac{N_j}{g_j} = \frac{N e^{-\frac{\epsilon_j}{kT}}}{Z}$$

Then,

$$S = k \ln w = k \left[\sum_j N_j \ln g_j - \sum_j N_j! \right] \approx k \left[\sum_j N_j \ln g_j - \sum_j N_j \ln N_j + \sum_j N_j \right] = k \left[N - \sum_j N_j \ln \left(\frac{N_j}{g_j} \right) \right]$$

Combining these expressions,

$$S = k \left[N - \ln N \sum_j N_j + \ln Z \sum_j N_j + \frac{1}{kT} \sum_j N_j \epsilon_j \right]$$

$$\rightarrow S = \frac{U}{T} + Nk(\ln Z - \ln N + 1)$$

$$\rightarrow F = U - TS = -NkT(\ln Z - \ln N + 1)$$

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The Connection between Classical and Statistical Thermodynamics

→ Continue on.

$$F = -NkT(\ln Z - \ln N + 1) \quad \text{and} \quad \tilde{\mu} = \left(\frac{\partial F}{\partial N} \right)_{T,V}$$

Then, the chemical potential is given by,

$$\tilde{\mu} = \frac{\partial}{\partial N} [-NkT(\ln Z - \ln N + 1)]_{T,V} = -kT(\ln Z - \ln N + 1) - NkT \left(-\frac{1}{N} \right) = kT \ln \left(\frac{N}{Z} \right)$$

Thus,

$$\tilde{\mu} \sim T \quad \text{and} \quad \tilde{\mu} \sim \ln \left(\frac{N}{Z} \right) \sim \ln \left(\frac{N}{V} \right) \sim \frac{N}{V}$$

The chemical potential increases with higher temperature and concentration.

Finally,

$$\frac{N}{Z} = e^{\tilde{\mu}/kT} \quad \text{or} \quad \frac{N_j}{g_j} = \frac{N e^{-\frac{\epsilon_j}{kT}}}{Z} = \frac{1}{e^{\frac{\epsilon_j - \tilde{\mu}}{kT}}} \quad \leftarrow \text{Maxwell-Boltzmann distribution}$$