

III Introduction to Statistical Physics

class schedule: March 31, April 1

reading assignments: S15F-H, S18D, R7.6, R7.7

examples marked with * are important and should be studied carefully.

III.2 Equipartition and Specific Heats

III.2.1 Equipartition and specific heats in classical limit

In the classic limit, when the spacing between energy states becomes very small (like in an ideal gas with not too low temperature), we can derive the mean values by integration over the phase space,

$$y_{mean} = \frac{\int y e^{-\beta \epsilon} dq_1 dq_2 dq_3 dp_1 dp_2 dp_3}{\int e^{-\beta \epsilon} dq_1 dq_2 dq_3 dp_1 dp_2 dp_3}$$

Where q_1, q_2, q_3 are space coordinates, and p_1, p_2, p_3 are momentum coordinates.

Example 1: the average kinetic energy ϵ_x in X-dimension for an ideal gas particle is

$$\epsilon_x = \frac{\sum_{n=0}^{\infty} \frac{n^2 h^2}{2mL^2} e^{-\frac{n^2 h^2}{2mL^2 kT}}}{\sum_{n=0}^{\infty} e^{-\frac{n^2 h^2}{2mL^2 kT}}}$$

In classical limit,

$$\epsilon_x = \frac{\int_{-\infty}^{\infty} e^{-\frac{p_x^2}{2mkT}} \frac{p_x^2}{2m} dp_x}{\int_{-\infty}^{\infty} e^{-\frac{p_x^2}{2mkT}} dp_x} = \frac{1}{2} kT$$

In general, if the energy of a system stored in a certain degree of freedom can be written in the form of bq^2 , where q refers to x, y, z or p_x, p_y, p_z , i.e., the position or momentum coordinate, the average energy in each degree of freedom is $\epsilon = \frac{1}{2} kT$, or the **equipartition theorem**. The total mean energy is therefore $E = \nu N \epsilon = \frac{1}{2} \nu N kT$, where ν is the degree of freedom per particle.

The **heat capacity** is calculated by $C_V = \frac{\partial E}{\partial T} = \frac{1}{2} \nu N k$, and the molar specific heat $c_V = \frac{1}{2} \nu N_a k = \frac{1}{2} \nu R$.

Example 2: in the classical limit, the molar specific heat is $\frac{3}{2} R$ for a mon-atomic ideal gas and $\frac{7}{2} R$ for a di-atomic gas.

III.2.2 Specific heats: quantum mechanics effects at low temperatures

The equipartition theorem does not hold any more when quantum effects start to dominate, for example, for di-atomic gas and solids at low temperatures, namely, when $\epsilon \sim kT$.

Example 3: the molar specific heat of a di-atomic ideal gas: the quantum mechanics limit. The specific heat for many di-atomic gases at low temperature is found to be $\frac{5}{2} R$ other than $\frac{7}{2} R$, because

gas particles are at the ground state of the vibrational energy, and the 2 degrees of freedom of vibrational energy vanish.

*Example 4: the mean energy of a 1D harmonic oscillator $\epsilon_n = \hbar\omega(n + \frac{1}{2})$ is calculated to be

$$\epsilon = \frac{\sum_{n=0}^{\infty} \hbar\omega(\frac{1}{2} + n)e^{-\frac{\hbar\omega(\frac{1}{2}+n)}{kT}}}{\sum_{n=0}^{\infty} e^{-\frac{\hbar\omega(\frac{1}{2}+n)}{kT}}}$$

*Example 5 (Reif 7.7): the specific heats of solids: the **Einstein model** and **Einstein temperature**. At low temperatures, namely, temperatures lower than the Einstein temperature, the specific heat of a solid is smaller than $3R$. As T approaches zero, the specific heat is reduced toward zero.