

## Chapter 8

# Canonical Ensemble $(E, V, N)$

### 7. Different physical systems in Canonical Ensemble

#### Ideal gas in a Box

We consider now the ideal gas in the canonical ensemble, for which the Hamilton function,

For single particle in 3D

$$H = \frac{p^2}{2m} + 0, \quad Z_1(T, V) = \int \frac{d^3 q d^3 p}{h^3} e^{-\beta \frac{p^2}{2m}}$$

Where,  $d^3 q = dx dy dz$ ,  $d^3 p = dp_x dp_y dp_z$

$$Z_1(T, V) = \iiint \frac{dx dp_x}{h} e^{-\beta \frac{p_x^2}{2m}} \iiint \frac{dx dp_y}{h} e^{-\beta \frac{p_y^2}{2m}} \iiint \frac{dx dp_z}{h} e^{-\beta \frac{p_z^2}{2m}}$$

$$Z_1(T, V) = \left[ \frac{L}{h} \int_{-\infty}^{\infty} dp_x e^{-\beta \frac{p_x^2}{2m}} \right]^3 \quad -\infty < p_x < \infty; -\infty < p_y < \infty; -\infty < p_z < \infty$$

$$Z_1(T, V) = \left[ \frac{L}{h} \sqrt{\frac{\pi}{\beta/2m}} \right]^3 = \frac{V}{h^3} (2\pi m k_B T)^{3/2}$$

For N indistinguishable Particles,

$$Z_N(T, V) = \frac{1}{N!} \left[ \frac{V}{h^3} \sqrt{2\pi m k_B T} \right]^N$$

Alternate Method, For N particles in 3D

$$H = \sum_{i=1}^N \frac{p_i^2}{2m}, \quad Z_N(T, V) = \int \frac{d^{3N} q d^{3N} p}{h^{3N} N!} e^{-\beta \sum_{i=1}^N \frac{p_i^2}{2m}} \quad (15)$$

contains just the kinetic energy. Since Ideal gas potential P.E. = 0

**(a) Factorization.** The integral leading to  $Z_N$  factorizes in (15):

$$Z_N(T, V) = \frac{V^N}{N!} \left( \int_{-\infty}^{+\infty} \frac{dp}{h} e^{-\beta \frac{p^2}{2m}} \right)^{3N} = \frac{V^N}{N!} \left( \sqrt{\frac{2\pi m k_B T}{h}} \right)^{3N} \quad (16)$$

$$\int_{-\infty}^{+\infty} dx e^{-ax^2} = \sqrt{\frac{\pi}{a}} \quad (17)$$

**(b) Thermal wavelength.** Evaluating (16) explicitly with the help of (17) we get

$$Z_N(T, V) = \frac{V^N}{N!} \left( \frac{\sqrt{2\pi m k_B T}}{h} \right)^{3N} = \frac{1}{N!} \left( \frac{V}{\lambda_T^3} \right)^N \quad (18)$$

where we have defined the thermal wavelength  $\lambda_T$  as

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

For air (actually nitrogen,  $N_2$ , with  $m = 4.65 \times 10^{-26} \text{ kg}$ ) at  $T = 298 \text{ K}$ , the thermal wavelength is  $0.19 \text{ \AA}$ , which is actually smaller than the Bohr radius. Quantum mechanical effects start to play a role only once  $\lambda_T$  becomes larger than the typical interparticle separation.

**(c) Thermal momentum:** Heisenberg's uncertainty principle  $\Delta x \cdot \Delta p \sim h$  allows to define a thermal momentum  $p_T$  as

$$p_T = \frac{h}{\lambda_T} = \sqrt{2\pi m k_B T}, \quad \frac{p_T^2}{2m} = \pi k_B T = \frac{2\pi}{3} E_{kin}, \quad E_{kin} = \frac{3}{2} k_B T$$

The thermal momentum  $p_T$  is hence of the same order of magnitude as the average momentum  $\bar{p}$  of the gas, as defined by  $E_{kin} = p^2 / (2m)$ , but not identical.

**(d) Free energy:** From (18) we obtain (with  $\log N! \approx N \log N - N$ )

$$\begin{aligned} F(T, V, N) &= -k_B T \ln \left( \frac{1}{N!} \left( \frac{V}{\lambda_T^3} \right)^N \right) = -k_B T \left( \ln \frac{1}{N!} + \ln \left( \frac{V}{\lambda_T^3} \right)^N \right) \\ &= -k_B T \left( -N \ln N + N + N \ln \frac{V}{\lambda_T^3} \right) \end{aligned} \quad (19)$$

and hence

$$F(T, V, N) = -N k_B T \left\{ \ln \left( \frac{V}{N \lambda_T^3} \right) + 1 \right\} = -N k_B T \left\{ \ln \left( \frac{V (2\pi m k_B T)^{3/2}}{N h^3} \right) + 1 \right\}$$

for the free energy of the ideal gas

**(e) Entropy:** Using,

$$F(T, V, N) = -N k_B T \left\{ \ln \left( \frac{V (2\pi m k_B T)^{3/2}}{N h^3} \right) + 1 \right\}$$

We then have,

$$S = - \left( \frac{\partial F}{\partial T} \right)_{V, N} = N k_B \left[ \ln \left( \frac{V}{N \lambda_T^3} \right) + 1 \right] + N k_B T \left[ \frac{3}{2T} \right]$$

This results in the Sackur-Tetrode equation

$$\boxed{S = N k_B \left\{ \ln \frac{V}{N \lambda_T^3} + \frac{5}{2} \right\}} \quad (20)$$

Comparing (20) with the microcanonical Sackur-Tetrode equation

$$S = k_B N \left\{ \ln \left[ \left( \frac{4\pi m E}{3h^2 N} \right)^{3/2} \frac{V}{N} \right] + \frac{5}{2} \right\}$$

one finds that they coincide when  $\frac{E}{N} = \frac{3k_B T}{2}$ .

**(f) Chemical potential.** The chemical potential  $\mu$  is

$$\begin{aligned}\mu &= \left( \frac{\partial F}{\partial N} \right)_{T,V} = -k_B T \left[ \ln \frac{V}{N \lambda_T^3} + 1 \right] + N k_B T \left[ \frac{V}{N \lambda_T^3} \cdot \frac{\lambda_T^3}{V} \right] \\ &= -k_B T \ln \left( \frac{V}{N \lambda_T^3} \right) = k_B T \ln \left( \frac{V}{N} \right) \left( \frac{\sqrt{2\pi m k_B T}}{h} \right)^3\end{aligned}$$

The previous expressions were much simpler obtained than when calculated in the microcanonical ensemble.

**Equivalence of ensembles.** In the thermodynamic limit the average value of an observable is in general independent of the ensemble (microcanonical or canonical).

$$N \rightarrow \infty, \quad V \rightarrow \infty, \quad \frac{N}{V} = \text{constant}$$

is taken. One therefore usually chooses the ensemble that is easier to work with.

**Fluctuations of Observables:** Fluctuations of observables,  $\langle A^2 \rangle - \langle A \rangle^2$ , may however be ensemble dependent! An example for an observable for which this is the case is the energy, which is constant, by definition, in the microcanonical ensemble, but distributed according to (9) in the canonical ensemble.

### Energy Fluctuations

We evaluated the representation (12) for the specific heat in a first step:

$$\begin{aligned}\frac{C_V}{T} &= \left( \frac{\partial S}{\partial T} \right)_V = - \frac{\partial^2 F}{\partial T^2} = \frac{\partial^2}{\partial T^2} (k_B T \ln Z_N); \quad \frac{C_V}{T} = \frac{\partial^2}{\partial T^2} [k_B T \ln Z_N] \\ &= \frac{\partial}{\partial T} \left[ k_B \ln Z_N + \frac{k_B T}{Z_N} \frac{\partial Z_N}{\partial \beta} \frac{\partial \beta}{\partial T} \right] \quad \frac{\partial \beta}{\partial T} = \frac{-1}{k_B T^2} \\ &= \frac{\partial}{\partial T} \left[ k_B \ln Z_N - \frac{1}{T Z_N} \frac{\partial Z_N}{\partial \beta} \right].\end{aligned}$$

**Second derivatives.** The remaining derivative with respect to the temperature  $T$  is

$$\begin{aligned}\frac{\partial}{\partial T} k_B \ln Z_N &= \frac{-1}{T^2 Z_N} \frac{\partial Z_N}{\partial \beta} \\ \frac{\partial}{\partial T} \frac{-1}{T Z_N} \frac{\partial Z_N}{\partial \beta} &= \frac{1}{T^2 Z_N} \frac{\partial Z_N}{\partial \beta} + \left[ \frac{1}{T Z_N^2} \left( \frac{\partial Z_N}{\partial \beta} \right)^2 - \frac{1}{T Z_N} \frac{\partial^2 Z_N}{\partial \beta^2} \right] \frac{-1}{k_B T^2}\end{aligned}$$

With the first two terms cancelling each other, we find

$$C_V = \frac{1}{k_B T^2} \left[ \frac{1}{Z_N} \frac{\partial^2 Z_N}{\partial \beta^2} - \left( \frac{1}{Z_N} \frac{\partial Z_N}{\partial \beta} \right)^2 \right] \quad (21)$$

for the specific heat  $C_V$  as a function of derivatives of the partition function  $Z_N$ .

**Derivatives of the partition function.** The definition (10) for the partition function

Corresponds to

$$\frac{1}{Z_N} \frac{\partial Z_N}{\partial \beta} = - \frac{\int d^{3N} q d^{3N} p \frac{H e^{-\beta H(q,p)}}{h^{3N} N!}}{\int d^{3N} q d^{3N} p \frac{e^{-\beta H(q,p)}}{h^{3N} N!}}, \quad Z_N = \int d^{3N} q d^{3N} p \frac{e^{-\beta H(q,p)}}{h^{3N} N!}$$

viz to

$$\frac{1}{Z_N} \frac{\partial Z_N}{\partial \beta} = -\langle E \rangle, \quad \frac{1}{Z_N} \frac{\partial^2 Z_N}{\partial \beta^2} = \langle E^2 \rangle \quad (22)$$

**Specific heat.** Our results (21) and (22) lead to the fundamental relation

$$\boxed{C_V = \frac{1}{k_B T^2} [\langle E^2 \rangle - \langle E \rangle^2]} \quad (23)$$

between the specific heat  $C_V$  and the fluctuations  $\langle E^2 \rangle - \langle E \rangle^2$  of the energy.

– Both the specific heat  $C_V \sim N$  and the right-hand side of (23) are extensive. The later as a result of the central limit theorem discussed, which states that the variance of independent processes are additive.

– The specific heat describes the energy exchange between the system and a heat reservoir. It hence makes that sense that  $C_V$  is proportional to the size of the energy fluctuations.

**Relative energy fluctuations.** The relative energy fluctuations,

$$\frac{\sqrt{\langle E^2 \rangle - \langle E \rangle^2}}{\langle E \rangle} \sim \frac{1}{\sqrt{N}} \quad (24)$$

vanish in the thermodynamic limit  $N \rightarrow \infty$ .

– The scaling relation (24) if a direct consequence of (23) and of the fact that both  $C_V$  and the internal energy  $U = \langle E \rangle$  are extensive.

– Eq. (24) is consistent with the demand that the canonical the microcanonical ensembles are equivalent in the thermodynamic limit  $N \rightarrow \infty$ . Energy fluctuations are absent in the microcanonical ensemble.