Partition Function

• *One-particle partition function:* For a particle of mass m in a box of volume V at temperature T,

$$Z_1 = \zeta = \int_\Gamma \mathrm{d}^3q\, \mathrm{d}^3p\, \mathrm{e}^{-\beta H(q,p)} = \int_V \mathrm{d}^3q \Big(\int_{\mathbb{R}} \mathrm{d}p_x\, \mathrm{e}^{-\beta p_x^2/2m} \Big)^3 = V \left(\frac{2\pi m}{\beta} \right)^{3/2}.$$

• *N-particle partition function:* For N particles of the same type, the natural partition function to write is

$$Z_N = \int_\Gamma \mathrm{d}^3q_1 ... \mathrm{d}^3q_N\, \mathrm{d}^3p_1 ... \mathrm{d}^3p_N\, \mathrm{e}^{-\beta \Sigma_i H_i(q,p)} = V^N \left(\frac{2\pi m}{\beta} \right)^{3N/2} = \zeta^N .$$

Derivation of Thermodynamics

• *Mean energy and temperature:* The mean energy associated with Z_N is

$$\bar E = -\frac{1}{Z_N} \frac{\partial Z_N}{\partial \beta} = -\frac{1}{\zeta^N} V^N \frac{3N}{2} \Big(\frac{2\pi m}{\beta} \Big)^{3N/2-1} \Big(-\frac{2\pi m}{\beta^2} \Big) = \tfrac{3}{2}\, N k_{\rm B} T .$$

• *Equation of state:* The pressure can be found from the Helmholtz free energy F, which gives, as expected,

$$F = -k_{\rm B}T \ln Z_N = -k_{\rm B}T\, N \big[\ln V + \tfrac{3}{2} \ln(2\pi m\, k_{\rm B} T) \big]$$
$$p = -\frac{\partial F}{\partial V}\Big|_{T,N} = -(-k_{\rm B}T\, N)\, \frac{1}{V} , \quad \text{which gives} \quad pV = N k_{\rm B} T .$$

• *Entropy and Gibbs paradox:* As we saw previously, from $S = -\partial F/\partial T|_{V,N}$ we get

$$S = \frac{1}{T} \bar E + k_{\rm B} \ln Z_N = N k_{\rm B} (\ln V + \tfrac{3}{2} \ln V + \sigma) , \qquad \sigma := \tfrac{3}{2} (1 + \ln 2\pi m k_{\rm B}) ,$$

which means that S is not additive. To avoid the Gibbs paradox, from now on we will use a modified partition function.

Final Form of Partition Function

• 1*-particle partition function:* We need to start from the quantum partition function; as we will see, this will motivate us to rescale the one-particle partition function by $\zeta \mapsto (1/h^3)\, \zeta$. So, from now on,

$$\zeta = \frac{V}{h^3} \Big(\frac{2\pi m}{\beta} \Big)^{3/2} = \frac{V}{\lambda^3} ,$$

a dimensionless expression, where $\lambda := h/\sqrt{2\pi m k_{\rm B} T}$ is the thermal wavelength. This rescaling by itself has no effect on any of the above thermodynamical considerations.
• *N-particle partition function:* In terms of the rescaled ζ, the N-particle partition function turns out to be

$$Z_N = \frac{\zeta^N}{N!} = \frac{V^N}{\lambda^{3N} N!} .$$

The mean energy and equation of state are not affected by this redefinition, because of the derivatives with respect to β and V, respectively, of $\ln Z_N$, but the entropy is affected and the Gibbs paradox no longer arises.

Relevant Sections: Phys 731; Chandler; Halley, Ch 4 and beginning of Ch 5; Reif; Schwabl.