Physical applications

one-dimensional box of length L:

$$Z = \frac{1}{h}\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dp\ \exp\left(-\beta\left[\frac{p^2}{2m} + U(x)\right]\right) = \frac{1}{h}\int_0^L dx \int_{-\infty}^{\infty} dp\ \exp\left(-\beta\frac{p^2}{2m}\right)$$
$$= \frac{L}{h}\sqrt{\frac{2\pi m}{\beta}} = \frac{L}{\lambda}$$

Gaussian integral: $1 = \int_{-\infty}^{\infty} \exp(-x^2/2\sigma^2)/\sqrt{2\pi\sigma^2}$
thermal de Broglie wavelength:

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

Ideal gas:

$$Z = \frac{1}{N!}\left(\frac{L}{h}\sqrt{\frac{2\pi m}{\beta}}\right)^{3N} = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N$$
$$\langle E\rangle = -\frac{\partial \ln Z}{\partial \beta} = \frac{3}{2}Nk_BT$$
$$A(T) = -k_BT\ln Z = Nk_BT\left(\ln\frac{\lambda^3}{V} + \ln N - 1\right) = Nk_BT\left(\ln\left(\rho\lambda^3\right) - 1\right)$$
$$S = -\frac{\partial A}{\partial T} = Nk_B\left(\frac{5}{2} - \ln(\rho\lambda^3)\right)$$

Recall MaxEnt results when $f(X;\alpha)$ depended on parameter α:

$$-\frac{\partial \log Z}{\partial \alpha} = \sum_{k=1}^{m}\lambda_k\left\langle\frac{\partial f(X;\alpha)}{\partial\alpha}\right\rangle$$

if we use

$$\alpha = V, \qquad \frac{\partial f(X;\alpha)}{\partial \alpha} = \frac{\partial E_i}{\partial V} = -p$$

we get

$$-\frac{\partial \ln Z}{\partial V} = -\frac{\partial \ln\left(\frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N\right)}{\partial V} = -\frac{N}{V} = -\beta\langle p\rangle$$

or in a better recognised form: (equation of state)

$$Nk_BT = \langle p\rangle V$$

Harmonic oscillator:

$$\ddot{x} + \underbrace{\frac{k}{m}}_{\omega^2} = 0 \qquad \Rightarrow \qquad x = A\sin(\omega t + \phi_0)$$

its energy:

$$E = \frac{1}{2}mv^2 + \frac{1}{2}kx^2 = \frac{p^2}{2m} + \frac{m\omega^2}{2}x^2$$

so:

$$Z = \frac{1}{h}\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dp e^{-\beta\frac{p^2}{2m}} e^{-\beta\frac{m\omega^2}{2}x^2} = \frac{1}{h}\sqrt{\frac{2\pi m}{\beta}}\sqrt{\frac{2\pi}{m\omega^2\beta}} = \frac{1}{\hbar\omega\beta}$$

where we introduced $\hbar = h/(2\pi)$.

$$\langle E\rangle = -\frac{\partial \ln Z}{\partial\beta} = -\frac{\partial}{\partial\beta}\ln\frac{1}{\beta} = k_B T \qquad \text{and} \qquad C_V = \frac{\partial\langle E\rangle}{\partial T} = k_B$$

equipartition: each harmonic half-degree of freedom contributes $k_B T/2$ to the average energy.

Solids: many-body potential is quadratic far from melting; using $\mathbf{x} = (x_1, x_2, \ldots, x_{3N})$:

$$V(\mathbf{x}) = V_0 + \sum_{i=1}^{3N}\frac{\partial V}{\partial x_i}(x_i - x_i^0) + \frac{1}{2}\sum_{i,j=1}^{3N}\frac{\partial^2 V}{\partial x_i \partial x_j}(x_i - x_i^0)(x_j - x_j^0) + \ldots$$

leading to $C = 3Nk_B$ (Dulong-Petit), correct at high T.
Quantum harmonic oscillator: discrete energy levels $E_i = \left(i + \frac{1}{2}\right)\hbar\omega$

$$Z = \sum_{i=0}^{\infty} e^{-\beta\left(i+\frac{1}{2}\right)\hbar\omega} = e^{-\frac{1}{2}\beta\hbar\omega}\frac{1}{1 - e^{-\beta\hbar\omega}} = \frac{1}{2\sinh\left(\frac{\beta\hbar\omega}{2}\right)}$$

$$\langle E\rangle = -\frac{\partial \ln Z}{\partial\beta} = \frac{\hbar\omega}{2}\coth\frac{\hbar\omega}{2k_B T}$$

$$C = \frac{\partial\langle E\rangle}{\partial T} = k_B\left(\frac{\hbar\omega}{2k_B T}\right)^2\frac{1}{\sinh^2\frac{\hbar\omega}{2k_B T}}$$

high T (low β): $\sinh x \sim x, \quad C \to k_B$ (classical)
low T (high β): $\sinh x \sim \frac{1}{2}e^x, \quad C \to k_B\left(\frac{\hbar\omega}{k_B T}\right)^2 e^{-\frac{\hbar\omega}{k_B T}}$ (exponential suppression)
Einstein solid: $C = 3Nk_B\left(\frac{\hbar\omega}{2k_B T}\right)^2\frac{1}{\sinh^2\frac{\hbar\omega}{2k_B T}}$, still incorrect.
Correct: Debye (spectrum of frequencies)

The grand canonical ensemble

The MaxEnt solution for two constraints:

$$\langle f_1(X)\rangle = F_1, \qquad \langle f_2(X)\rangle = F_2$$
$$Z(\lambda_1,\lambda_2) = \sum_{i=1}^{n} e^{-\lambda_1 f_1(x_i)-\lambda_2 f_2(x_i)}$$
$$p_i = \frac{1}{Z} e^{-\lambda_1 f_1(x_i)-\lambda_2 f_2(x_i)}$$
$$S(F_1,F_2) = \log Z(\lambda_1,\lambda_2) + \lambda_1 F_1 + \lambda_2 F_2$$

grand canonical ensemble: $f_1(x_i) = E_i,\ f_2(x_i) = N_i,\ F_1 = \langle E\rangle,\ F_2 = \langle N\rangle,$ $\lambda_1 = \beta = 1/(k_B T),\ \lambda_2 = -\mu\beta = -\mu/(k_B T),\ S = S_{GC}/k_B,\ Z = \Xi$:

$$\Xi(\beta,\mu) = \sum_i e^{-\beta(E_i-\mu N_i)}$$
$$p_i = \frac{1}{\Xi} e^{-\frac{1}{k_B T}(E_i-\mu N_i)}$$
$$S_{GC}(\langle E\rangle,\langle N\rangle) = k_B \ln \Xi + \frac{\langle E\rangle}{T} - \frac{\mu\langle N\rangle}{T}$$

from MaxEnt results:

$$\langle E\rangle = -\left.\frac{\partial \ln \Xi}{\partial \beta}\right|_{\mu\beta} = -\left.\frac{\partial \ln \Xi}{\partial \beta}\right|_{\mu} + \left.\frac{\partial \ln \Xi}{\partial \mu}\right|_{\beta} \mu k_B T$$
$$\langle N\rangle = -\left.\frac{\partial \ln \Xi}{\partial -\mu\beta}\right|_{\beta} = k_B T \left.\frac{\partial \ln \Xi}{\partial \mu}\right|_{\beta}$$
$$\frac{1}{T} = \left.\frac{\partial S_{GC}}{\partial \langle E\rangle}\right|_{\langle N\rangle}$$
$$-\frac{\mu}{T} = \left.\frac{\partial S_{GC}}{\partial \langle N\rangle}\right|_{\langle E\rangle}$$

fluctuations:

$$\sigma_N^2 = \mathrm{Var}(N) = \left.\frac{\partial^2 \ln \Xi}{\partial(-\mu\beta)^2}\right|_{\beta} = k_B T \left.\frac{\partial \langle N\rangle}{\partial \mu}\right|_{\beta}$$

reciprocity relations:

$$\left.\frac{\partial \langle E\rangle}{\partial -\mu\beta}\right|_{\beta} = \left.\frac{\partial \langle N\rangle}{\partial \beta}\right|_{\mu\beta}$$

or

$$-k_B T \left.\frac{\partial \langle E\rangle}{\partial \mu}\right|_{\beta} = \left.\frac{\partial \langle N\rangle}{\partial \beta}\right|_{\mu} - \mu k_B T \left.\frac{\partial \langle N\rangle}{\partial \mu}\right|_{\beta}$$

grand free energy:

$$\Phi(T,\mu) = -k_B T \ln \Xi = \langle E\rangle - \mu\langle N\rangle - T S_{GC}$$

partial trace:

$$e^{-\beta\Phi} = \Xi = \sum_i e^{-\beta E_i} e^{\beta\mu N_i} = \sum_{N=0}^{\infty} e^{\beta\mu N} \sum_j e^{-\beta E_{j,N}} = \sum_N e^{-\beta\left(A(T;N)-\mu N\right)}$$