2.9 The classical ideal gas

Calculation of the micro canonical state sum (phase volume)
For the calculation of the thermodynamic potential of a classical ideal gas we need the partition function, i.e. the phase volume of the "free particles", which are in a box with volume V:

$$\begin{aligned}\Phi(E,V_s,N) &= \frac{1}{N!h^{3N}} \int\limits_{H=\sum_i \frac{p_i^2}{2m}+H_{wall}} d^3p_1...d^3p_N d^3r_1...d^3r_N \\ &= \frac{V^N}{N!h^{3N}} \frac{\pi^{\frac{3N}{2}}}{\left(\frac{3N}{2}\right)!}(2mE)^{\frac{3N}{2}} \approx v^N \left(\frac{4\pi m}{3h^2}\epsilon\right)^{\frac{3N}{2}} e^{\frac{5N}{2}}\end{aligned} \tag{2.58}$$

here we have used the Stirling formula $N! \approx N^N e^{-N} = \left(\frac{N}{e}\right)^N$.
Finally we get with $\epsilon := \frac{E}{N}$

$$\begin{aligned}S(E,N,V) = k\ln(\Phi(E,V_s,N)) &= k\ln\left(v^N \left(\frac{4\pi m}{3h^2}\epsilon\right)^{\frac{3N}{2}} e^{\frac{5N}{2}}\right) \\ &= Nk\ln(v) + \frac{3}{2}Nk\ln(\epsilon) + k\ln\left(\left(\frac{4\pi m}{3h^2}\right)^{\frac{3N}{2}} e^{\frac{5N}{2}}\right)\end{aligned} \tag{2.59}$$

By differentiating we find:

$$\frac{1}{T} = \frac{\partial S(E,N,V)}{\partial E} = \frac{3}{2}\frac{kN}{E} \qquad \text{leading to} \qquad E = \frac{3}{2}NkT \qquad , \tag{2.60}$$

and

$$\frac{p}{T} = \frac{\partial S(E,N,V)}{\partial V} = \frac{kN}{V} \qquad \text{leading to} \qquad pV = kNT \qquad . \tag{2.61}$$

Let

$$\lambda(T) := \frac{h}{\sqrt{2\pi mkT}} \qquad , \tag{2.62}$$

then we get

$$S(T,V,N) = kN\left[\ln\left(\frac{v}{\lambda^3(T)}\right) + \frac{5}{2}\right] \qquad , \tag{2.63}$$

or

$$F(T,V,N) = E - TS = \frac{3}{2}NkT - NkT\left[\frac{5}{2} + \ln\left(\frac{v}{\lambda^3(T)}\right)\right] = -NkT\left[1 + \ln\left(\frac{v}{\lambda^3(T)}\right)\right] \qquad . \tag{2.64}$$

The function $\lambda(T)$ is except for the factor $\sqrt{\frac{2\pi}{3}}$ the de Broglie wavelength (see above) of a particle with the thermal energy $\epsilon = \frac{3}{2}kT$. So our results only hold if $\lambda^3(T) \ll \frac{V}{N}$.

Summing up all approximations:

- Each particle occupies a volume which is much bigger than the uncertainty in space. That the particles are not distinguishable (the symmetry relations) is not important any more.
- Not only the states with the lowest energy levels will be occupied in the phase space, i.e. we must not count the states exactly.
- We need high temperatures and extremely diluted gases.

The grand canonical potential and variations of the number of particles
Starting with

$$\mu = \frac{\partial F}{\partial N} = \frac{F}{N} + kT = -kT\ln\left(\frac{v}{\lambda^3(T)}\right) \text{ , i.e. } \quad N = \frac{V}{\lambda^3(T)}e^{\frac{\mu}{kT}} \qquad , \tag{2.65}$$

we get

$$\Omega(T,V,\mu) = F - \mu N = -NkT = -\frac{kT}{\lambda^3(T)}Ve^{\frac{\mu}{kT}} \qquad . \tag{2.66}$$

Generally holds:

$$\Omega(T,V,\mu) = -kT\sum_i \ln\left(\sum_{n_i}\exp\left(-n_i\frac{\epsilon_i-\mu}{kT}\right)\right) \quad\text{and}\quad \langle N\rangle = -\frac{\partial\Omega}{\partial\mu} = \sum_i \frac{\sum_{n_i} n_i \exp\left(-n_i\frac{\epsilon_i-\mu}{kT}\right)}{\sum_{n_i}\exp\left(-n_i\frac{\epsilon_i-\mu}{kT}\right)} \quad . \tag{2.67}$$

Consequently we find

$$\frac{\partial^2\Omega}{\partial\mu^2} = -\frac{\partial\langle N\rangle}{\partial\mu} = \frac{1}{kT}\left[\left\langle N^2\right\rangle - \langle N\rangle^2\right] \quad . \tag{2.68}$$

Using Eq. (2.66) we get

$$\frac{\partial\Omega}{\partial\mu}(T,V,\mu) = -\frac{1}{\lambda^3(T)}Ve^{\frac{\mu}{kT}} \quad\text{and}\quad \frac{\partial^2\Omega}{\partial\mu^2}(T,V,\mu) = -\frac{1}{kT}\frac{1}{\lambda^3(T)}Ve^{\frac{\mu}{kT}} \tag{2.69}$$

The relative variance of the particle number is therefor

$$\frac{\left\langle N^2\right\rangle - \langle N\rangle^2}{\langle N\rangle^2} = \frac{kT}{\langle N\rangle^2}\frac{\partial^2\Omega}{\partial\mu^2} = \frac{1}{\langle N\rangle} \quad , \tag{2.70}$$

which is the solution for the Poisson distribution. For macroscopic systems with $N \approx 10^{23}$ particles the variance in N is negligible small.

Equivalent results hold for all other "generalizes forces" in thermodynamics. Although we only fix the "generalizes coordinates" of a system the forces are extremely well defined. The Legendre transformation just switches from coordinates to forces, which are in both contacts well defined and contain the same information. A random process leads to an extremely reliable result, if the involved numbers are large enough. Thermodynamic is just mathematics and its results are almost as exact as pure mathematics.