

4.4 The probability of finding a system in the Grand Canonical Ensemble to have Energy E_s and particle number N_r is given by 4.2.9:

$$P(N_r, E_s) = \frac{e^{-\alpha N_r} e^{-\beta E_s}}{\sum_{r,s} e^{-\alpha N_r} e^{-\beta E_s}} \quad \text{with } \alpha = \frac{-\mu}{kT}, \text{ and } \beta = \frac{1}{kT}$$

Thus, the probability of finding a system to have exactly N particles can be found by letting $N_r \rightarrow N$, and summing over E_s :

$$P(N) = \sum_s \frac{e^{-\alpha N} e^{-\beta E_s}}{\sum_{r,s} e^{-\alpha N_r} e^{-\beta E_s}} = \sum_s \frac{z^N e^{-\beta E_s}}{\sum_s (z^N e^{-\beta E_s/kT})} \quad \text{by 4.3.11 } (e^{-\alpha} = z)$$

by 3.3.8, $Q_N(V, T) = \sum_s e^{-E_s/kT}$, so $P(N) = \frac{z^N Q_N(V, T)}{\sum_r z^{N_r} Q_{N_r}(V, T)}$

by 4.3.15, the denominator is simply the grand partition function, so we end up with

$$P(N) = \frac{z^N Q_N(V, T)}{\Omega(z, V, T)}$$

For a classical ideal gas, $Q_N(V, T) = \frac{(Vf(T))^N}{N!}$ using 4.4.1, and 4.4.2.

and by 4.4.3, $\Omega(z, V, T) = e^{zVf(T)}$

$$P(N) = \frac{z^N (Vf(T))^N}{N! e^{zVf(T)}} = \frac{z^N e^{-zVf(T)} (Vf(T))^N}{N!} = \frac{[zVf(T)]^N e^{-[zVf(T)]}}{N!}$$

This is a poisson distribution.

In general, $P(k) = \frac{\lambda^k e^{-\lambda}}{k!}$. Here we let $\lambda \rightarrow zVf(T)$, and $k \rightarrow N$, and we recover the boxed expression.

For an unbiased estimator like ΔN , the root mean square deviation ($\sqrt{(\Delta N)^2}$) is the same as the square root of variance $\sqrt{\text{var}(\Delta N)}$ (also called "Standard Error").

For a poisson distribution, the variance is simply λ .

$$\therefore \sqrt{\text{var}(\Delta N)} = \sqrt{\lambda} = \sqrt{zVf(T)}$$

General formula

Meanwhile, by 4.5.3, $(\Delta N)^2 = kT \left(\frac{\partial \bar{N}}{\partial \mu} \right)_{T, V} \Rightarrow \sqrt{(\Delta N)^2} = \sqrt{kT \left(\frac{\partial \bar{N}}{\partial \mu} \right)_{T, V}}$

We know for a classical ideal gas, $\bar{N} = zVf(T)$ (by 4.4.6)

$$\sqrt{(\Delta N)^2} = \sqrt{kT \left(\frac{\partial}{\partial \mu} zVf(T) \right)} = \sqrt{kT \left(\frac{\partial}{\partial \mu} e^{\mu/kT} \right) Vf(T)} = \sqrt{\frac{kT}{kT} zVf(T)} = \sqrt{zVf(T)}$$

These two methods agree!!!

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Note: if we assume the ideal gas to be monatomic, $f(T) = (2\pi m kT)^{3/2} / h^3$