5.2: Energy and the number of particles

First of all, note that fluctuations of macroscopic variables depend on particular conditions.[2] For example, in a mechanically- and thermally-insulated system with a fixed number of particles, i.e. a member of a *microcanonical* ensemble, the internal energy does not fluctuate: $\delta E = 0$. However, if such a system is in thermal contact with the environment, i.e. is a member of a *canonical* ensemble (Figure $2.4.1$), the situation is different. Indeed, for such a system we may apply the general Equation ($2.1.7$), with W_m given by the Gibbs distribution ($2.4.7$)-($2.4.8$), not only to E but also to E^2. As we already know from Sec. 2.4, the first average,

$$\langle E\rangle = \sum_m W_m E_m, \quad W_m = \frac{1}{Z}\exp\left\{-\frac{E_m}{T}\right\}, \quad Z = \sum_m \exp\left\{-\frac{E_m}{T}\right\}, \tag{5.2.1}$$

yields Equation ($2.4.10$), which may be rewritten in the form

$$\langle E\rangle = \frac{1}{Z}\frac{\partial Z}{\partial(-\beta)}, \quad \text{where } \beta \equiv \frac{1}{T}, \tag{5.2.2}$$

more convenient for our current purposes. Let us carry out a similar calculation for E^2:

$$\langle E^2\rangle = \sum_m W_m E_m^2 = \frac{1}{Z}\sum_m E_m^2 \exp\{-\beta E_m\}. \tag{5.2.3}$$

It is straightforward to verify, by double differentiation, that the last expression may be rewritten in a form similar to Equation ($5.2.2$):

$$\langle E^2\rangle = \frac{1}{Z}\frac{\partial^2}{\partial(-\beta)^2}\sum_m \exp\{-\beta E_m\} \equiv \frac{1}{Z}\frac{\partial^2 Z}{\partial(-\beta)^2}. \tag{5.2.4}$$

Now it is easy to use Eqs. ($5.1.4 - 5.1.5$) to calculate the variance of energy fluctuations:

$$\left\langle \tilde{E}^2\right\rangle = \langle E^2\rangle - \langle E\rangle^2 = \frac{1}{Z}\frac{\partial^2 Z}{\partial(-\beta)^2} - \left(\frac{1}{Z}\frac{\partial Z}{\partial(-\beta)}\right)^2 \equiv \frac{\partial}{\partial(-\beta)}\left(\frac{1}{Z}\frac{\partial Z}{\partial(-\beta)}\right) = \frac{\partial\langle E\rangle}{\partial(-\beta)}. \tag{5.2.5}$$

Since Eqs. ($5.2.1$)-($5.2.5$) are valid only if the system's volume V is fixed (because its change may affect the energy spectrum E_m), it is customary to rewrite this important result as follows:

Fluctuations of E:

$$\boxed{\langle \tilde{E}^2\rangle = \frac{\partial\langle E\rangle}{\partial(-1/T)} = T^2\left(\frac{\partial\langle E\rangle}{\partial T}\right)_V \equiv C_V T^2.} \tag{5.2.6}$$

This is a remarkably simple, fundamental result. As a sanity check, for a system of N similar, independent particles, $\langle E\rangle$ and hence C_V are proportional to N, so that $\delta E \propto N^{1/2}$ and $\delta E/\langle E\rangle \propto N^{-1/2}$, in agreement with Equation ($5.1.13$). Let me emphasize that the classically-looking Equation ($5.2.6$) is based on the general Gibbs distribution, and hence is valid for any system (either classical or quantum) in thermal equilibrium.

Some corollaries of this result will be discussed in the next section, and now let us carry out a very similar calculation for a system whose number N of particles in a system is not fixed, because they may go to, and come from its environment at will. If the chemical potential μ of the environment and its temperature T are fixed, i.e. we are dealing with the *grand canonical ensemble* (Figure $2.7.1$), we may use the grand canonical distribution ($2.7.5$)-($2.7.6$):

$$W_{m,N} = \frac{1}{Z_G}\exp\left\{\frac{\mu N - E_{m,N}}{T}\right\}, \quad Z_G = \sum_{N,m}\exp\left\{\frac{\mu N - E_{m,N}}{T}\right\}. \tag{5.2.7}$$

Acting exactly as we did above for the internal energy, we get

$$\langle N\rangle = \frac{1}{Z_G}\sum_{m,N} N \exp\left\{\frac{\mu N - E_{m,N}}{T}\right\} = \frac{T}{Z_G}\frac{\partial Z_G}{\partial\mu}, \tag{5.2.8}$$

$$\langle N^2\rangle = \frac{1}{Z_G}\sum_{m,N} N^2 \exp\left\{\frac{\mu N - E_{m,N}}{T}\right\} = \frac{T^2}{Z_G}\frac{\partial^2 Z_G}{\partial \mu^2}, \tag{5.2.9}$$

so that the particle number's variance is

Fluctuations of N:

$$\boxed{\left\langle \widetilde{N}^2\right\rangle = \langle N^2\rangle - \langle N\rangle^2 = \frac{T^2}{Z_G}\frac{\partial Z_G}{\partial \mu} - \frac{T^2}{Z_G^2}\left(\frac{\partial Z_G}{\partial \mu}\right)^2 = T\frac{\partial}{\partial \mu}\left(\frac{T}{Z_G}\frac{\partial Z_G}{\partial \mu}\right) = T\frac{\partial\langle N\rangle}{\partial \mu},} \tag{5.2.10}$$

in full analogy with Equation (5.2.5).

In particular, for an ideal classical gas, we may combine the last result with Equation $(3.2.2)$. (As was already emphasized in Sec. 3.2, though that result has been obtained for the canonical ensemble, in which the number of particles N is fixed, at $N>>1$ the fluctuations of N in the grand canonical ensemble should be relatively small, so that the same relation should be valid for the *average* $\langle N\rangle$ in that ensemble.) Easily solving Equation $(3.2.2)$ for $\langle N\rangle$, we get

$$\langle N\rangle = \text{const}\times\exp\left\{\frac{\mu}{T}\right\}, \tag{5.2.11}$$

where "const" means a factor constant at the partial differentiation of $\langle N\rangle$ over μ, required by Equation (5.2.10). Performing the differentiation and then using Equation (5.2.11) again,

$$\frac{\partial\langle N\rangle}{\partial\mu} = \text{const}\times\frac{1}{T}\exp\left\{\frac{\mu}{T}\right\} = \frac{\langle N\rangle}{T}, \tag{5.2.12}$$

we get from Equation (5.2.10) a very simple result:

Fluctuations of N: classical gas

$$\boxed{\langle\widetilde{N}^2\rangle = \langle N\rangle, \qquad \text{i.e. } \delta N = \langle N\rangle^{1/2}.} \tag{5.2.13}$$

This relation is so important that I will also show how it may be derived differently. As a by-product of this new derivation, we will prove that this result is valid for systems with an arbitrary (say, small) N, and also get more detailed information about the statistics of fluctuations of that number. Let us consider an ideal classical gas of N_0 particles in a volume V_0, and calculate the probability W_N to have exactly $N \leq N_0$ of these particles in its part of volume $V \leq V_0$ – see Figure $5.2.1$.

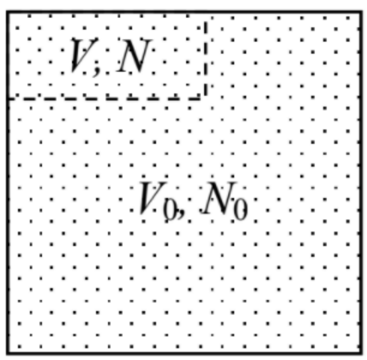

Figure 5.2.1: Deriving the binomial and Poisson distributions.

For one particle such probability is $W = V/V_0 = \langle N\rangle/N_0 \leq 1$, while the probability to have that particle in the remaining part of the volume is $W' = 1 - W = 1 - \langle N\rangle/N_0$. If all particles were distinguishable, the probability of having $N \leq N_0$ *specific* particles in volume V and $(N - N_0)$ *specific* particles in volume $(V - V_0)$, would be $W^N W'^{(N_0-N)}$. However, if we do not want to distinguish the particles, we should multiply this probability by the number of possible particle combinations keeping the numbers N and N_0 constant, i.e. by the binomial coefficient $N_0!/N!(N_0-N)!$.[3] As the result, the required probability is

Binomial distribution:

$$\boxed{W_N = W^N W'^{(N_0-N)}\frac{N_0!}{N!(N_0-N)!} = \left(\frac{\langle N\rangle}{N_0}\right)^N\left(1-\frac{\langle N\rangle}{N_0}\right)^{N_0-N}\frac{N_0!}{N!(N_0-N)!}.} \tag{5.2.14}$$

This is the so-called *binomial probability distribution*, valid for *any* $\langle N\rangle$ and N_0.[4]

Still keeping $\langle N\rangle$ arbitrary, we can simplify the binomial distribution by assuming that the whole volume V_0, and hence N_0, are very large:

$$N_0 >> N, \tag{5.2.15}$$

where N means all values of interest, including $\langle N\rangle$. Indeed, in this limit we can neglect N in comparison with N_0 in the second exponent of Equation (5.2.14), and also approximate the fraction $N_0!/(N_0 - N)!$, i.e. the product of N terms, $(N_0 - N + 1)(N_0 - N + 2)\ldots(N_0 - 1)N_0$, by just N_0^N. As a result, we get

$$W_N \approx \left(\frac{\langle N\rangle}{N_0}\right)^N \left(1-\frac{\langle N\rangle}{N_0}\right)^{N_0} \frac{N_0^N}{N!} \equiv \frac{\langle N\rangle^N}{N!}\left(1-\frac{\langle N\rangle}{N_0}\right)^{N_0} = \frac{\langle N\rangle^N}{N!}\left[(1-W)^{\frac{1}{W}}\right]^{\langle N\rangle}, \tag{5.2.16}$$

where, as before, $W = \langle N\rangle/N_0$. In the limit (5.2.15), $W \to 0$, so that the factor inside the square brackets tends to $1/e$, the reciprocal of the natural logarithm base.[5] Thus, we get an expression independent of N_0:

Poisson distribution:

$$\boxed{W_N = \frac{\langle N\rangle^N}{N!} e^{-\langle N\rangle}.} \tag{5.2.17}$$

This is the much-celebrated *Poisson distribution*[6] which describes a very broad family of random phenomena. Figure $5.2.2$ shows this distribution for several values of $\langle N\rangle$ – which, in contrast to N, are not necessarily integer.

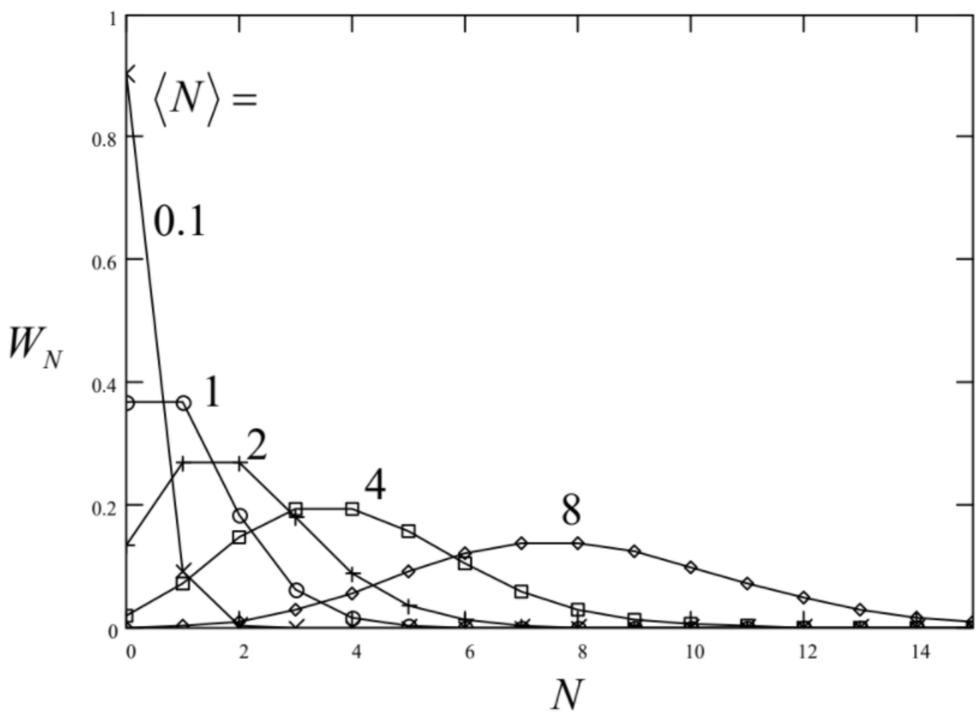

Figure $5.2.2$: The Poisson distribution for several values of $\langle N\rangle$. In contrast to that average, the argument N may take only integer values, so that the lines in these plots are only guides for the cyc.

Gaussian distribution:

$$\boxed{W_N = \frac{1}{(2\pi)^{1/2}\delta N}\exp\left\{-\frac{(N-\langle N\rangle)^2}{2(\delta N)^2}\right\}.} \tag{5.2.18}$$

(Note that the Gaussian distribution is also valid if both N and N_0 are large, regardless of the relation between them – see Figure $5.2.3$.)

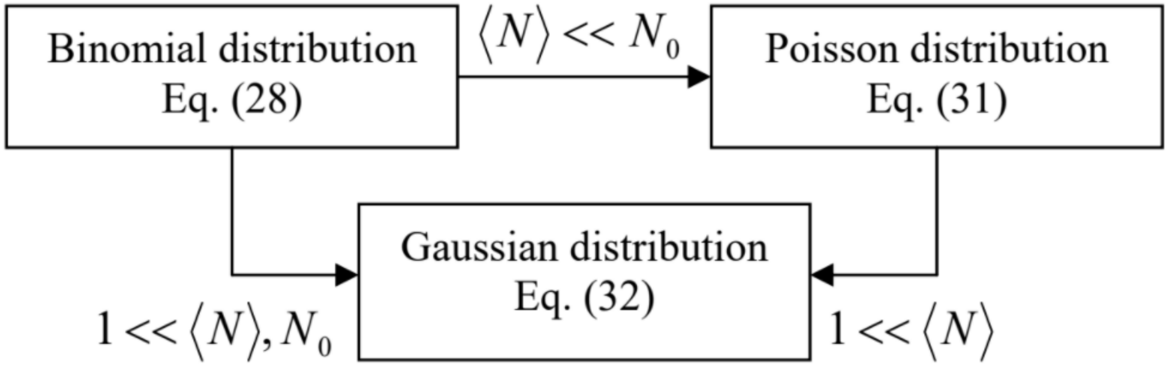

Figure 5.2.3: The hierarchy of three major probability distributions.

A major property of the Poisson (and hence of the Gaussian) distribution is that it has the same variance as given by Equation (5.2.13):

$$\langle \tilde{N}^2 \rangle \equiv \left\langle (N - \langle N \rangle)^2 \right\rangle = \langle N \rangle. \tag{5.2.19}$$

(This is not true for the general binomial distribution.) For our current purposes, this means that for the ideal classical gas, Equation (5.2.13) is valid for *any* number of particles.
