5.1: Characterization of Fluctuations

At the beginning of Chapter 2, we have discussed the notion of averaging, $\langle f\rangle$, of a variable f over a statistical ensemble – see Eqs. $(2.1.7)$ and $(2.1.10)$. Now, the *fluctuation* of the variable is defined simply as its deviation from such average:

Fluctuation:

$$\boxed{\tilde{f} \equiv f-\langle f\rangle;} \tag{5.1.1}$$

this deviation is, generally, also a random variable. The most important property of any fluctuation is that its average (over the same statistical ensemble) equals zero:

$$\langle\tilde{f}\rangle \equiv\langle f-\langle f\rangle\rangle=\langle f\rangle-\langle\langle f\rangle\rangle=\langle f\rangle-\langle f\rangle \equiv 0. \tag{5.1.2}$$

As a result, such an average cannot characterize fluctuations' *intensity*, and the simplest characteristic of the intensity is the *variance* (sometimes called "dispersion"):

Variance: definition

$$\boxed{\langle\tilde{f}^{2}\rangle=\langle(f-\langle f\rangle)^{2}\rangle.} \tag{5.1.3}$$

The following simple property of the variance is frequently convenient for its calculation:

$$\langle\tilde{f}^{2}\rangle=\langle(f-\langle f\rangle)^{2}\rangle=\langle f^{2}-2 f\langle f\rangle+\langle f\rangle^{2}\rangle=\langle f^{2}\rangle-2\langle f\rangle^{2}+\langle f\rangle^{2}, \tag{5.1.4}$$

so that, finally:

Variance via averages:

$$\boxed{\langle\tilde{f}^{2}\rangle=\langle f^{2}\rangle-\langle f\rangle^{2}.} \tag{5.1.5}$$

As the simplest example, consider a variable that takes only two values, ± 1, with equal probabilities $W_{j}=1/2$. For such a variable, the basic Equation $(2.1.7)$ yields

$$\langle f\rangle=\sum_{j} W_{j} f_{j}=\frac{1}{2}(+1)+\frac{1}{2}(-1)=0, \quad \text{but } \langle f^{2}\rangle=\sum_{j} W_{j} f_{j}^{2}=\frac{1}{2}(+1)^{2}+\frac{1}{2}(-1)^{2}=1 \neq 0 \tag{5.1.6}$$
$$\text{so that } \left\langle\tilde{f}^{2}\right\rangle=\langle f^{2}\rangle-\langle f\rangle^{2}=1.$$

The square root of the variance,

r.m.s. fluctuation:

$$\boxed{\delta f \equiv\langle\tilde{f}^{2}\rangle^{1/2},} \tag{5.1.7}$$

is called the *root-mean-square (r.m.s.) fluctuation*. An advantage of this measure is that it has the same dimensionality as the variable itself, so that the ratio $\delta f/\langle f\rangle$ is dimensionless, and may be used to characterize the *relative intensity* of fluctuations.

As has been mentioned in Chapter 1, all results of thermodynamics are valid only if the fluctuations of thermodynamic variables (internal energy E, entropy S, etc.) are relatively small.[1] Let us make a simple estimate of the relative intensity of fluctuations for an example of a system of N independent, similar particles, and an extensive variable

$$\mathscr{F} \equiv \sum_{k=1}^{N} f_{k}. \tag{5.1.8}$$

where all single-particle functions f_{k} are similar, besides that each of them depends on the state of only "its own" (k^{th}) particle. The statistical average of such $\mathscr{F}$ is evidently

$$\langle \mathscr{F} \rangle = \sum_{k=1}^{N} \langle f \rangle = N\langle f \rangle, \tag{5.1.9}$$

while its fluctuation variance is

$$\left\langle \widetilde{\mathscr{F}}^2 \right\rangle \equiv \langle \widetilde{\mathscr{F}}\widetilde{\mathscr{F}} \rangle \equiv \left\langle \sum_{k=1}^{N} \tilde{f}_k \sum_{k'=1}^{N} \tilde{f}_{k'} \right\rangle \equiv \left\langle \sum_{k,k'=1}^{N} \tilde{f}_k \tilde{f}_{k'} \right\rangle \equiv \sum_{k,k'=1}^{N} \left\langle \tilde{f}_k \tilde{f}_{k'} \right\rangle. \tag{5.1.10}$$

Now we may use the fact that for two independent variables

$$\left\langle \tilde{f}_k \tilde{f}_{k'} \right\rangle = 0, \quad \text{for } k' \neq k; \tag{5.1.11}$$

indeed, this relation may be considered as the mathematical definition of their independence. Hence, only the terms with $k' = k$ make substantial contributions to the sum (5.1.10):

$$\left\langle \widetilde{\mathscr{F}}^2 \right\rangle = \sum_{k,k'=1}^{N} \left\langle \tilde{f}_k^2 \right\rangle \delta_{k,k'} = N \left\langle \tilde{f}^2 \right\rangle. \tag{5.1.12}$$

Comparing Eqs. (5.1.9) and (5.1.12), we see that the relative intensity of fluctuations of the variable $\mathscr{F}$,

Relative fluctuation estimate:

$$\boxed{\frac{\delta \mathscr{F}}{\langle \mathscr{F} \rangle} = \frac{1}{N^{1/2}} \frac{\delta f}{\langle f \rangle},} \tag{5.1.13}$$

tends to zero as the system size grows $(N \rightarrow \infty)$. It is this fact that justifies the thermodynamic approach to typical physical systems, with the number N of particles of the order of the Avogadro number $N_A \sim 10^{24}$. Nevertheless, in many situations even small fluctuations of variables are important, and in this chapter we will calculate their basic properties, starting with the variance.

It should be comforting for the reader to notice that for some simple (but very important) cases, such calculation has already been done in our course. In particular, for any generalized coordinate q and generalized momentum p that give quadratic contributions of the type $(2.2.28)$ to the system's Hamiltonian (as in a harmonic oscillator), we have derived the equipartition theorem $(2.2.30)$, valid in the classical limit. Since the average values of these variables, in the thermodynamic equilibrium, equal zero, Equation (5.1.7) immediately yields their r.m.s. fluctuations:

$$\delta p = (mT)^{1/2}, \quad \delta q = \left(\frac{T}{\kappa}\right)^{1/2} \equiv \left(\frac{T}{m\omega^2}\right)^{1/2}, \quad \text{where } \omega \left(\frac{\kappa}{m}\right)^{1/2}. \tag{5.1.14}$$

The generalization of these classical relations to the quantum-mechanical case $(T \sim \hbar\omega_j)$ is provided by Eqs. $(2.5.13)$ and ($2.5.16$):

$$\delta p = \left[\frac{\hbar m\omega}{2} \coth \frac{\hbar\omega}{2T}\right]^{1/2}, \quad \delta q = \left[\frac{\hbar}{\hbar m\omega} \coth \frac{\hbar\omega}{2T}\right]^{1/2,}. \tag{5.1.15}$$

However, the intensity of fluctuations in other systems requires special calculations. Moreover, only a few cases allow for general, model-independent results. Let us review some of them.