

## Solutions Problem Set 0: The Thermodynamic Limit

For a thermodynamic system with  $N$  particles, the thermodynamic limit is the case where one takes  $N \rightarrow \infty$ , so there are an infinite number of degrees of freedom. Most of what we will do in this course involves systems in the thermodynamic limit. The discussion presented here illustrates why the thermodynamic limit is so important, and why it is so fundamental to the subject of thermodynamics.

In our first discussion session we watched simulations of a gas of  $N = 8$  particles and a gas of  $N = 1024$  particles. We observed that as  $N$  increased, the relative fluctuations in the number of particles in any given partition of the system box decreased. Here we want to give a simple argument to show why that might be. First we will consider the total energy of the particles in the gas, and then later we will consider the number of particles in the partition.

Let  $\epsilon_i = \frac{1}{2}mv_i^2$  be the kinetic energy of particle  $i$ . We will assume that the probability for this energy to have the value  $\epsilon$  is given by a probability density  $\mathcal{P}(\epsilon)$ .

The *average* energy  $\langle \epsilon \rangle$  of a single particle is then,

$$\langle \epsilon \rangle = \int_0^\infty d\epsilon \mathcal{P}(\epsilon) \epsilon \quad \text{and similarly} \quad \langle f(\epsilon) \rangle = \int_0^\infty d\epsilon \mathcal{P}(\epsilon) f(\epsilon) \quad (1)$$

If we define  $\delta\epsilon \equiv \epsilon - \langle \epsilon \rangle$ , then  $\langle \delta\epsilon \rangle = 0$ , and the *variance* of the energy of a single particle is defined as,

$$\sigma_\epsilon^2 \equiv \langle \delta\epsilon^2 \rangle = \langle (\epsilon - \langle \epsilon \rangle)^2 \rangle = \langle \epsilon^2 - 2\epsilon\langle \epsilon \rangle + \langle \epsilon \rangle^2 \rangle = \langle \epsilon^2 \rangle - 2\langle \epsilon \rangle\langle \epsilon \rangle + \langle \epsilon \rangle^2 = \langle \epsilon^2 \rangle - \langle \epsilon \rangle^2 \quad (2)$$

The square root of the variance is the *standard deviation*  $\sigma_\epsilon$ . The standard deviation is a measure of the width of the distribution  $\mathcal{P}(\epsilon)$  about its average.

The total energy of the gas of  $N$  particles is then,

$$E = \sum_{i=1}^N \epsilon_i \quad (3)$$

We now assume that the particles are all the same, so that we can view the different  $\epsilon_i$  as each being described by the same probability distribution  $\mathcal{P}(\epsilon)$ ; and we will assume that the interactions between the particles is sufficiently weak that we can regard the energies of the different particles as being uncorrelated. In the language of probability, we say the  $\epsilon_i$  are independent, identically distributed, random variables.

The average total energy is then,

$$\langle E \rangle = \left\langle \sum_{i=1}^N \epsilon_i \right\rangle = \sum_{i=1}^N \langle \epsilon_i \rangle = N \langle \epsilon \rangle \quad (4)$$

and the variance of the total energy is,

$$\sigma_E^2 \equiv \langle (E - \langle E \rangle)^2 \rangle = \left\langle \left[ \sum_{i=1}^N (\epsilon_i - \langle \epsilon_i \rangle) \right]^2 \right\rangle = \left\langle \left[ \sum_{i=1}^N \delta\epsilon_i \right]^2 \right\rangle = \left\langle \sum_{i=1}^N \sum_{j=1}^N \delta\epsilon_i \delta\epsilon_j \right\rangle \quad (5)$$

$$= \sum_{i=1}^N \sum_{j=1}^N \langle \delta\epsilon_i \delta\epsilon_j \rangle = \sum_{i=1}^N \langle \delta\epsilon_i^2 \rangle + \sum_{i \neq j} \langle \delta\epsilon_i \delta\epsilon_j \rangle = \sum_{i=1}^N \langle \delta\epsilon_i^2 \rangle + \sum_{i \neq j} \langle \delta\epsilon_i \rangle \langle \delta\epsilon_j \rangle \quad (6)$$

where, in the last line, we split the double sum over  $i$  and  $j$  into the terms where  $i = j$  and the terms where  $i \neq j$ . We then used the assumption that  $\delta\epsilon_i$  is uncorrelated with  $\delta\epsilon_j$ , and so when  $i \neq j$  we have  $\langle \delta\epsilon_i \delta\epsilon_j \rangle = \langle \delta\epsilon_i \rangle \langle \delta\epsilon_j \rangle$ . This last result can be shown as follows: for two random variables  $x$  and  $y$ , with a joint probability distribution  $\mathcal{P}(x, y)$ , then the variables are statistically independent if the joint probability factors, i.e.  $\mathcal{P}(x, y) = \mathcal{P}_x(x) \mathcal{P}_y(y)$ . Then,

$$\langle xy \rangle = \int dx \int dy \mathcal{P}(x, y) xy = \int dx \int dy \mathcal{P}_x(x) \mathcal{P}_y(y) xy = \left( \int dx \mathcal{P}_x(x) x \right) \left( \int dy \mathcal{P}_y(y) y \right) = \langle x \rangle \langle y \rangle \quad (7)$$

Next we use that  $\langle \delta\epsilon_i \rangle = 0$ , and by definition  $\sigma_\epsilon^2 = \langle \delta\epsilon^2 \rangle$ . We therefore get,

$$\sigma_E^2 = \sum_{i=1}^N \langle \delta\epsilon_i^2 \rangle = \sum_{i=1}^N \sigma_\epsilon^2 = N\sigma_\epsilon^2 \quad \Rightarrow \quad \sigma_E = \sqrt{N}\sigma_\epsilon \quad (8)$$

So finally we have for the relative fluctuation in the total energy of the gas,

$$\frac{\sigma_E}{\langle E \rangle} = \frac{\sqrt{N}\sigma_\epsilon}{N\langle \epsilon \rangle} = \frac{1}{\sqrt{N}} \frac{\sigma_\epsilon}{\langle \epsilon \rangle} \sim \frac{1}{\sqrt{N}} \quad (9)$$

Thus the relative fluctuation in the total energy of the gas vanishes as  $N \rightarrow \infty$ . This is called the *thermodynamic limit*, where the relative fluctuation away from the average becomes negligible. The key point behind this result is the assumption that the particles are weakly interacting, and so their energies are uncorrelated.

## The Random Walk

You may have recognized that the above arguments are the same as one uses in describing the *random walk*.

A walker takes a step every after every  $\Delta t$  time. The distance of the step  $x$  is sampled from a probability distribution  $\mathcal{P}(x)$ . Each step is described by exactly the same  $\mathcal{P}(x)$ , and the distance traveled in any given step is uncorrelated with the distance traveled in any other step. Let  $X$  be the distance traveled after  $N$  steps. If  $x_i$  is the distance traveled in step  $i$ , then

$$X = \sum_{i=1}^N x_i. \quad (10)$$

The average distance traveled in any given step is

$$\langle x \rangle = \int_{-\infty}^{\infty} dx \mathcal{P}(x) x \quad (11)$$

and the standard deviation  $\sigma_x$  of the distance in one step is given by,

$$\sigma_x^2 = \langle (x - \langle x \rangle)^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2 \quad (12)$$

Then the average distance traveled in  $N$  steps is,

$$\langle X \rangle = N\langle x \rangle \quad (13)$$

and the standard deviation  $\sigma_X$  of the distance traveled after  $N$  steps is given by,

$$\sigma_X^2 = N\sigma_x^2 \quad (14)$$

If  $\langle x \rangle \neq 0$  this is called a *biased* random walk. The walker is more likely to travel in one direction than the other. As the number  $N$  of steps increases, the relative fluctuation in the total distance traveled decreases as,

$$\frac{\sigma_X}{\langle X \rangle} = \frac{1}{\sqrt{N}} \frac{\sigma_x}{\langle x \rangle} \sim \frac{1}{\sqrt{N}} \quad (15)$$

But if  $\langle x \rangle = 0$  this is called an *unbiased* random walk. The walker is just as likely to travel in one direction as in the reverse direction. After  $N$  steps the average distance traveled is  $\langle X \rangle = N\langle x \rangle = 0$ . On average, i.e. averaging over many such random walks, the walker goes nowhere! But in any given random walk, the distance the walker is likely to be from the origin after  $N$  steps is given by the *root mean square distance*,

$$\sigma_X = \sqrt{\langle X^2 \rangle} = \sqrt{N}\sigma_x \quad (16)$$

The time after  $N$  steps is  $t = N\Delta t$ , and so for an unbiased random walk one has,

$$\sqrt{\langle X^2 \rangle} \sim \sqrt{t} \quad (17)$$

This is the behavior of a *diffusing* particle.

## Number of Particles in a Partition of the Box

We can now return to the original problem that stimulated this discussion. How many particles of the gas will be found in a given partition of the system box?

Let us define a variable  $s_i$  for particle  $i$ , such that  $s_i = 1$  if particle  $i$  is in the partition, and  $s_i = 0$  if particle  $i$  is not in the partition. Since  $s$  can take only two values, we can write for its probability distribution,

$$\mathcal{P}(s) = \begin{cases} p & \text{for } s = 1 \\ 1 - p & \text{for } s = 0 \end{cases} \quad (18)$$

where  $p$  is the probability that the particle is in the desired partition. The average of  $s$  is then,

$$\langle s \rangle = \sum_{s=0}^1 \mathcal{P}(s)s = (1)P(1) + (0)P(0) = p \quad (19)$$

and the standard deviation  $\sigma_s$  of  $s$  is given by,

$$\sigma_s^2 = \langle s^2 \rangle - \langle s \rangle^2 = \sum_{s=0}^1 \mathcal{P}(s)s^2 - p^2 = p - p^2 = p(1 - p) \quad (20)$$

For a system with  $N$  particles, the total number of particles  $S$  that are in the partition of the system box is then,

$$S = \sum_{i=1}^N s_i \quad (21)$$

We can now write the statistics of  $S$  in terms of the average and standard deviation of the single particle variable  $s$ . If we assume that the particles are only weakly interacting, so that we can take the  $s_i$  as independent random variables, we then have,

$$\langle S \rangle = N \langle s \rangle = Np \quad (22)$$

and

$$\sigma_S^2 = N \sigma_s^2 = Np(1 - p) \quad (23)$$

So the relative fluctuation of the number of particles in the partition is,

$$\frac{\sigma_S}{\langle S \rangle} = \frac{\sqrt{Np(1 - p)}}{Np} = \frac{1}{\sqrt{N}} \sqrt{\frac{1 - p}{p}} \quad (24)$$

For the simulation we saw in the discussion session, the box was divided into three equal partitions, so  $p = 1/3$ , and,

$$\frac{\sigma_S}{\langle S \rangle} = \frac{1}{\sqrt{N}} \sqrt{\frac{2/3}{1/3}} = \sqrt{\frac{2}{N}} \quad (25)$$

In all these examples, the key assumption that leads to the result, that relative fluctuations decay as  $1/\sqrt{N}$ , is that the degrees of freedom are statistically independent of each other. This will be true when the degrees of freedom are only very weakly interacting. Later on, in Unit 4 where we discuss phase transitions, we will see that this assumption is not always true!

The discussions above illustrate several reasons why the thermodynamic limit is important:

1) For a gas of particles we found that  $\sigma_E/\langle E \rangle \sim 1/\sqrt{N}$ . In other words, once  $N$  is large enough, we can ignore fluctuations in the total energy of the gas, since the relative fluctuations about the average total energy become

negligible. Thus, in providing a thermodynamic description of the gas it is sufficient to consider only the average  $\langle E \rangle$  and we don't need to worry about higher moments  $\langle E^n \rangle$ .

2) For describing the gas it does not matter which of two different physical situations corresponds to the actual system: (i) We might have that the gas is in total isolation from the rest of the universe, in which case energy  $E$  is conserved and so fixed to a constant value. There are no fluctuations in  $E$  at all. This is called the *microcanonical ensemble*. In this ensemble the energies  $\epsilon_i$  cannot all truly be independent of one another since their sum  $\sum_i \epsilon_i = E$  is constrained to be a constant. (ii) Or we might have the case that the box containing the system allows heat to be transported across its walls, and the system is then in contact with a thermal reservoir (the world outside the box) that can exchange energy with the system. In this case  $E$  is not fixed but can fluctuate. We will see that in this case the system and reservoir must have the same temperature. This is called the *canonical ensemble*. Since there is no constraint that  $E$  is fixed, we can now regard the  $\epsilon_i$  as independent when interactions are weak. However, because in this case  $\sigma_E/\langle E \rangle \sim 1/\sqrt{N}$ , these fluctuations in  $E$  can be ignored and the system will behave the same as in (i) where  $E$  is fixed. Thus, in the thermodynamic limit, we can do calculations in either the microcanonical or canonical ensemble, whichever is mathematically easiest, regardless of whether the true physical system is in thermal isolation from the rest of the world or whether it is contact with a thermal reservoir.

3) Our result also indicates why it is possible to determine the average value of a random variable by taking a large number of repeated measurements. Suppose we have a random variable  $x$ , and we make  $N$  independent measurements of its value. Call these measurements  $x_i$ . Then the observed average of these  $N$  measurements is,

$$\bar{x} = \frac{1}{N} \sum_i x_i \quad (26)$$

If we write  $X = \sum_i x_i$ , so that  $\bar{x} = X/N$ , then we can write

$$\langle X \rangle = \sum_i \langle x_i \rangle = N \langle x \rangle \quad \Rightarrow \quad \langle x \rangle = \frac{\langle X \rangle}{N} = \left\langle \frac{X}{N} \right\rangle = \langle \bar{x} \rangle \quad (27)$$

and

$$\sigma_X^2 = N \sigma_x^2 \quad \text{and so} \quad \sigma_{\bar{x}}^2 = \langle \bar{x}^2 \rangle - \langle \bar{x} \rangle^2 = \left\langle \left( \frac{X}{N} \right)^2 \right\rangle - \left\langle \frac{X}{N} \right\rangle^2 = \frac{\sigma_X^2}{N^2} = \frac{N \sigma_x^2}{N^2} = \frac{\sigma_x^2}{N} \quad (28)$$

So the relative fluctuation in our measurement  $\bar{x}$  behaves as,

$$\frac{\sigma_{\bar{x}}}{\langle \bar{x} \rangle} = \frac{\sigma_x}{\sqrt{N}} \frac{1}{\langle x \rangle} = \frac{1}{\sqrt{N}} \frac{\sigma_x}{\langle x \rangle} \sim \frac{1}{\sqrt{N}} \quad (29)$$

That is, the more measurements  $N$  we make, the closer a particular measurement of  $\bar{x}$  will be to the true  $\langle x \rangle$ .