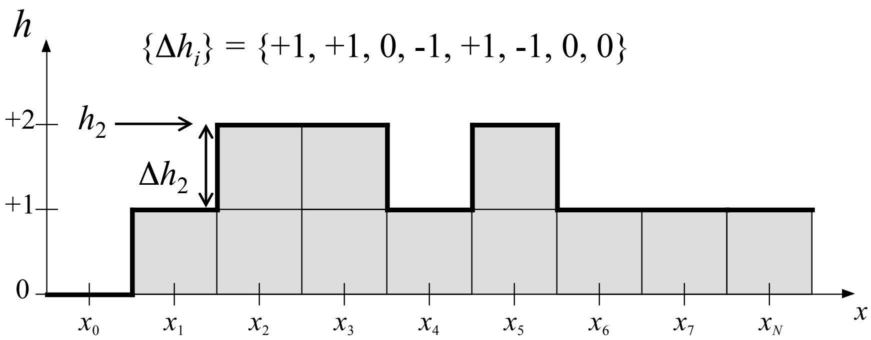
Discussion Session 4

Let us discuss a simple model of a one-dimensional interface between a two dimensional solid and the vacuum. We imagine building the solid by adding square building blocks along a line of equally spaced discrete sites $\{x_i\}$, $i = 0$ to N, as in the sketch below. The blocks have a side length of unity. At each site x_i the height of the interface h_i is just the number of blocks piled up at the site.



We can define $\Delta h_i \equiv h_i - h_{i-1}$ as the step height, i.e. the change in height, as we go from site x_{i-1} to site x_i. The energy of the interface we will take to be a surface tension, proportional to the length of the interface,

$$E = \epsilon \sum_{i=1}^{N} |\Delta h_i| + \epsilon(N+1) = \epsilon \sum_{i=1}^{N} |\Delta h_i| + E_0 \tag{1}$$

The first term gives the lengths of the vertical segments of the interface, while the second term gives the lengths of the horizontal segments. From a knowledge of just the step heights $\{\Delta h_i\}$ and the initial height h_0, we can construct the heights of the interface,

$$h_i = h_0 + \sum_{j=1}^{i} \Delta h_j = h_0 + (h_1 - h_0) + (h_2 - h_1) + \cdots + (h_{i-1} - h_{i-2}) + (h_i - h_{i-1}) = h_i \tag{2}$$

To keep the problem simple, we image that the height at the left most site x_0 is fixed to be $h_0 = 0$, and the steps can be at most one unit of height difference, so they can take only the values $\Delta h_i = 0, \pm 1$. The heights h_i are free to go positive or negative, according to the steps taken.

1) What is the entropy $S(E, N)$ of this interface at fixed E and N?

We treat this problem in the microcanonical ensemble. For fixed N, for each value of E there will be a number of different possible configurations. If we count the total number $\Omega(E, N)$ of all such configurations with energy E, then the entropy will be $S = k_B \ln \Omega$.

If n is the number of sites which have $\Delta h_i \neq 0$, then the energy of the interface will be,

$$E = \epsilon n + E_0 \tag{3}$$

because the energy cost is the same whether we take a step up, $\Delta h_i = +1$, or a step down, $\Delta h_i = -1$. So for a fixed E, the number of such sites is,

$$n = \frac{E - E_0}{\epsilon} \tag{4}$$

The number of possible configurations with total energy E is then just,

$$\Omega(E, N) = \frac{N!}{n!(N-n)!} \, 2^n \qquad \text{where } n = \frac{E - E_0}{\epsilon} \tag{5}$$

The first combinatoric factor is just the number of ways to choose which of the N sites are the n sites which have $\Delta h_i \neq 0$. Then for each of the n sites with $\Delta h_i \neq 0$ we have two possible choices, $\Delta h_i = +1$ or $\Delta h_i = -1$; this gives the second factor of 2^n. The entropy is then,

$$S(E,N) = k_B \ln \Omega(E,N) = k_B \left[n \ln 2 + \ln N! - \ln n! - \ln(N-n)! \right] \tag{6}$$

Using Stirling's approximation, $\ln N! = N \ln N - N$, we then get,

$$S(E,N) = k_B \left[n \ln 2 + N \ln N - N - n \ln n + n - (N-n)\ln(N-n) + N - n \right] \tag{7}$$

$$= k_B \left[n \ln 2 + N \ln N - n \ln n - (N-n)\ln(N-n) \right] \tag{8}$$

$$= k_B \left[n \ln 2 + n \ln N + (N-n)\ln N - n \ln n - (N-n)\ln(N-n) \right] \tag{9}$$

$$= k_B \left[n \ln 2 + n \ln\left(\frac{N}{n}\right) + (N-n)\ln\left(\frac{N}{N-n}\right) \right] \qquad \text{where } n = \frac{E - E_0}{\epsilon} \tag{10}$$

We could then find the temperature of the interface by,

$$\frac{1}{T(E,N)} = \left(\frac{\partial S}{\partial E}\right)_N = \left(\frac{\partial S}{\partial n}\right)_N \left(\frac{\partial n}{\partial E}\right) = \frac{1}{\epsilon}\left(\frac{\partial S}{\partial n}\right)_N \qquad \text{and invert to get} \quad E(T,N) \tag{11}$$

which gives the energy of the interface when the temperature is fixed to temperature T.

Alternatively, we could take the energy of Eq. (1) and compute the canonical partition function,

$$Q_N(E) = \sum_{\{\Delta h_i\}} \mathrm{e}^{-\left(\epsilon \sum_{i=1}^N |\Delta h_i| + E_0\right)/k_B T} = \mathrm{e}^{-E_0/k_B T} \prod_{i=1}^N \left(\sum_{\Delta h_i = 0, \pm 1} \mathrm{e}^{-\epsilon |\Delta h_i|/k_B T} \right) \tag{12}$$

From $Q_N(E)$ we can then get the Helmholtz free energy,

$$A(T,N) = -k_B T \ln Q_N(E) \tag{13}$$

and then from $A(T,N)$ we can get the entropy and energy of the interface,

$$S(T,N) = -\left(\frac{\partial A}{\partial T}\right)_N \qquad \text{and} \qquad E(T,N) = -\left(\frac{\partial(-A/T)}{\partial(1/T)}\right)_N = -\left(\frac{\partial(-\beta A)}{\partial \beta}\right)_N \tag{14}$$

I leave it to you to do this exercise! You should find that you get the same $E(T,N)$ in both canonical and micro-canonical calculations, and that you also get the same entropy $S(E,N)$. To get $S(E,N)$ in the canonical calculation, you have to invert $E(T,N)$ to get $T(E,N)$ and insert that into $S(T,N)$; you should then find just the same result as in Eq. (10).

2) How much does the interface fluctuate?

We will assume that N and E are both fixed, i.e. we will work in the microcanonical ensemble.

The left end of the interface is pinned at $h_0 = 0$, but the right end h_N is free to fluctuate up or down depending on the sequence of steps taken. We have,

$$h_N = \sum_{i=1}^N \Delta h_i \tag{15}$$

The average height of the right end of the interface will then be,

$$\langle h_N \rangle = \left\langle \sum_{i=1}^N \Delta h_i \right\rangle = \sum_{i=1}^N \langle \Delta h_i \rangle = 0 \tag{16}$$

where the last step follows from $\langle \Delta h_i \rangle = 0$ since the energy cost of a step up is exactly the same as the energy cost of a step down, so on average there should be just as many steps up and steps down.

But, as a measure of the fluctuations, we now want to measure the variance of h_N,

$$\sigma_{h_N}^2 = \langle h_N^2 \rangle - \langle h_N \rangle^2 = \langle h_N^2 \rangle \tag{17}$$

We have,

$$\langle h_N^2 \rangle = \left\langle \left(\sum_{i=1}^N \Delta h_i \right)^2 \right\rangle = \sum_{i=1}^N \sum_{j=1}^N \langle \Delta h_i \Delta h_j \rangle \tag{18}$$

When $i \neq j$ we have $\langle \Delta h_i \Delta h_j \rangle = 0$ since Δh_i is independent of Δh_j. So the only terms that contribute to the above double sum are those when $i = j$, and we get,

$$\langle h_N^2 \rangle = \sum_{i=1}^N \langle \Delta h_i^2 \rangle \tag{19}$$

Now since we are at fixed E, only $n = (E - E_0)/\epsilon$ of the N sites have $\Delta h_i \neq 0$, and these are equally likely to have $\Delta h_i = +1$ as $\Delta h_i = -1$. So we have,

$$\langle h_N^2 \rangle = \sum_{i=1}^N \langle \Delta h_i^2 \rangle = n \langle \Delta h_i^2 \rangle = n \left(\frac{1}{2}(+1)^2 + \frac{1}{2}(-1)^2 \right) = n \tag{20}$$

where the term in the parenthesis represents the 1/2 probability that the step goes up and the 1/2 probability that the step goes down. So finally,

$$\sigma_{h_N} = \sqrt{\langle h_N^2 \rangle} = \sqrt{n} = \sqrt{\frac{E - E_0}{\epsilon}} \tag{21}$$

If we insert into the above $E(T, N)$ from Eq. (11), then we will get $\sigma_{h_N}(T, N)$, and see how much the interface fluctuates when it is in equilibrium at temperature T. Because E is an extensive variable, we expect to find $E - E_0 \propto N$, and then we will get the result $\sigma_{h_N} \propto \sqrt{N}$.

You should notice that our calculation of σ_{h_N} is exactly the same calculation we did in discussing an unbiased random walk! The connection comes from viewing the x-axis like a time axis, and the height h_i is then the distance traveled at time i.

3) What is the entropy $S(E, N)$ if we now also pin the right end of the interface to $h_N = 0$?

In this case, we still must have exactly n sites with $\Delta h_i \neq 0$, where $n = (E - E_0)/\epsilon$, but now exactly half of those steps $m = n/2$ must be up, and half must be down, so that the interface comes to $h_N = 0$ after the N steps. How many such configurations are there?

The number of configurations is given by the multinomial coefficient,

$$\Omega(E, N) = \frac{N!}{m!m!(N - 2m)!} \tag{22}$$

This is because there are $\dfrac{N!}{n!(N-n)!}$ ways to chose which $n = 2m$ of the N sites have $\Delta h_i \neq 0$, and then there are $\dfrac{n!}{m!m!}$ ways to choose which of those n sites are the m steps up and which are the m steps down. The product of these two factors gives the multinomial coefficient above.

In general, for N total objects, the number of ways one can choose n_1 objects to put in jar 1, n_2 objects to put in jar 2, n_3 objects to put in jar 3, ..., and n_m objects in jar m, with $n_1 + n_2 + \cdots + n_m = N$, is,

$$\frac{N!}{n_1! n_2! n_3! \cdots n_m!} \tag{23}$$

We can now get the entropy,

$$S(E,N) = k_B \ln \Omega(E,N) = k_B \left[\ln N! - 2\ln m! - \ln(N-2m)!\right] \tag{24}$$

Using Stirling's approximation this becomes,

$$S(E,N) = k_B \left[N\ln N - N - 2m\ln m + 2m - (N-2m)\ln(N-2m) + N - 2m\right] \tag{25}$$

$$= k_B \left[(2m + N - 2m)\ln N - 2m\ln m - (N-2m)\ln(N-2m)\right] \tag{26}$$

$$= k_B \left[2m\ln\left(\frac{N}{m}\right) + (N-2m)\ln\left(\frac{N}{N-2m}\right)\right] \tag{27}$$

Using $m = n/2$ we can write this as,

$$S(E,N) = k_B \left[n\ln\left(\frac{N}{n/2}\right) + (N-n)\ln\left(\frac{N}{N-n}\right)\right] \tag{28}$$

$$= k_B \left[n\ln 2 + n\ln\left(\frac{N}{n}\right) + (N-n)\ln\left(\frac{N}{N-n}\right)\right] \qquad \text{with } n = \frac{E-E_0}{\epsilon} \tag{29}$$

This is exactly the same result we found in Eq. (10) for the case where the right end of the interface was *not* pinned to $h_N = 0$.

Why doesn't the entropy depend on whether or not we pin the right side of the interface? It would seem that if we pin both sides of the interface there should be fewer allowed configurations for a given E than if we pin only one side. Hence we would expect that Ω should be different in the two cases, and hence S should be different in the two cases.

The reason is that the difference between the two cases is a change of the *boundary conditions*. In one case we pin both ends, in the other case we pin only one end. But if the system is sufficiently long, we don't expect that what we do at the ends should effect what happens in the bulk of the system in the middle. Any difference in S should go away as $N \to \infty$.

But our results seemed to be the same for *any* value of N, not just in the $N \to \infty$ limit! The answer to this paradox lies in the fact that, when we used Stirling's approximation to evaluate $\ln N!$, we were in essence taking the large N limit. To see this consider the ratio of the number of states Ω. Let Ω^{I} be the case with only one end pinned, and Ω^{II} be the case with both ends pinned. We then have,

$$\frac{\Omega^{\mathrm{I}}}{\Omega^{\mathrm{II}}} = \frac{N!}{n!(N-n)!}\,2^n\,\frac{(n/2)!(n/2)!(N-n)!}{N!} = \frac{(n/2)!(n/2)!}{n!}\,2^n \tag{30}$$

where $n = (E-E_0)/\epsilon$, and in case II we used $m = n/2$. The above is clearly *not* zero!

We then have for the entropy difference,

$$S^{\mathrm{I}} - S^{\mathrm{II}} = \Delta S = k_B \ln\left(\frac{\Omega^{\mathrm{I}}}{\Omega^{\mathrm{II}}}\right) = k_B \ln\left(\frac{(n/2)!(n/2)!}{n!}\,2^n\right) = k_B\left[n\ln 2 + 2\ln(n/2)! - \ln n!\right] \tag{31}$$

We will now use Stirling's approximation, but keeping the next order term. From Notes 2-10 we have

$$\ln n! = n\ln n - n + \frac{1}{2}\ln n + \cdots \tag{32}$$

We then get

$$\Delta S/k_B = n\ln 2 + 2(n/2)\ln(n/2) - 2(n/2) + 2\frac{1}{2}\ln(n/2) - n\ln n + n - \frac{1}{2}\ln n \tag{33}$$

$$= n\ln 2 + n\ln n - n\ln 2 - n + \ln n - \ln 2 - n\ln n + n - \frac{1}{2}\ln n \tag{34}$$

$$= \frac{1}{2}\ln n - \ln 2 = \frac{1}{2}\ln\left(\frac{n}{4}\right) > 0 \tag{35}$$

So the entropy of the case with only one end pinned is indeed larger than the entropy of the case with both ends pinned. But the finite difference between the two cases comes from the *third* term in Stirling's expansion for $\ln n!$.

Now since E is extensive, we expect $n = (E - E_0)/\epsilon$ is also extensive, so $n \propto N$. Thus $\Delta S/k_B \propto \ln N$. However S is also extensive, so $S \propto N$. Thus the relative difference in entropy between the two cases is,

$$\frac{\Delta S}{S} \propto \frac{\ln N}{N} \to 0 \qquad \text{as} \qquad N \to \infty \tag{36}$$

Thus, in the thermodynamic limit $N \to \infty$, the entropy of the two cases become equal to leading order. The boundary condition that we choose does not effect the thermodynamic behavior in the thermodynamic limit!