

Chapter 1. Model System

1 Introduction

The quantum state of a physical system at any instant of time can be written as a linear combination of the *stationary quantum states*, the states in which all observable quantities are independent of time. We usually drop the term stationary.

Be sure to distinguish between states and energy levels. Degenerate states with the same energy must be counted separately when we enumerate the number of states available to a physical system, *e.g.* H, Li or B atoms, particle in a box. The number of degenerate states is called the *multiplicity*. For particle in a cubic box

$$\epsilon = \frac{1}{2M} \left(\frac{\hbar\pi}{L} \right)^2 (n_x^2 + n_y^2 + n_z^2).$$

2 Binary model system

We will use a simple binary system to illustrate some of the basic principles of statistical mechanics. In order to do this we must start by working out the statistical properties of this system.

System of N particles (sites), each of which can be in state 1 or -1, *i.e.* has 2 possible states. This might be seen as a simple model for a system of spin 1/2 particles, but could also represent any collection of microscopic systems having only 2 possible states. A set of trap sites that can be either occupied or unoccupied; a collection of 2 level “atoms”; *etc.*

We will carry the spin analogy, and say that if the system is in state +1 it has a magnetic moment of m and if it is in state -1 it has a magnetic moment of $-m$.

Each of the particles may independently be in ± 1 states, so that there are 2^N possible states for the system of N particles.

We can denote a single state of the system as, *e.g.* $\uparrow\uparrow$ 00010111 ..., or explicitly labelling the particles $\uparrow_1\uparrow_2\downarrow_3\downarrow_4\downarrow_5\uparrow_6\downarrow_7\uparrow_8\uparrow_9\uparrow_{10}$...

With this notation we can compactly denote all states of the system by

$$(\uparrow + \downarrow)_1(\uparrow + \downarrow)_2(\uparrow + \downarrow)_3 \dots (\uparrow + \downarrow)_N,$$

where each term in the product represents one possible state of the system. For example, for 3 particles $(\uparrow + \downarrow)_1(\uparrow + \downarrow)_2(\uparrow + \downarrow)_3$ gives the 8 terms:

3 spins up — $\uparrow\uparrow$ 1

2 spins up — $\uparrow\uparrow$ 0 $\uparrow\downarrow$ 1 $\downarrow\uparrow$ 1

1 spin up — $\uparrow\downarrow$ 0 $\downarrow\uparrow$ 0 $\downarrow\downarrow$ 1

0 spins up — $\downarrow\downarrow$ 0

The total magnetic moment of the system varies from $-Nm$ to $+Nm$ in steps of $2m$.

While there are 2^N states of this system, there are only $N + 1$ possible values for M , and for large N , $2^N \gg N + 1$ so there must be a lot of degeneracy.

2.1 Multiplicity function

We will assume N is even (for convenience) and write the number of up spins as $N_\uparrow = \frac{1}{2}N + s$ and the number of down spins as $N_\downarrow = \frac{1}{2}N - s$. The range of s is then $-\frac{1}{2}N, -\frac{1}{2}N + 1, \dots, 0, \dots, \frac{1}{2}N - 1, \frac{1}{2}N$. The nett positive spin of the system, the *spin excess*, is $N_\uparrow - N_\downarrow = 2s$.

We can exploit this compact notation to enumerate the number of states of the system having a given spin excess. Ignoring the ordering of the terms, we might write one of the states of the system

as $\uparrow^{N_{\uparrow}}\downarrow^{N_{\downarrow}}$, and we see that, apart from the ordering of factors, we may regard the listing of the states of the system

$$(\uparrow + \downarrow)^N$$

as a binomial expansion in which each term summarizes all of the states with a given spin excess. The number of such states is then

$$g(N, s) = \binom{N}{N_{\uparrow}} = \binom{N}{\frac{1}{2}N + s} = \frac{N!}{(\frac{1}{2}N + s)!(\frac{1}{2}N - s)!},$$

and is known as the *multiplicity function* (or the *density of states*).

(Of course, more directly, we might just note that the number of ways of choosing exactly $N_{\uparrow}$ upward spins from a set of N particles is defined to be $\binom{N}{N_{\uparrow}}$.)

A few sets of binomial coefficients:

n	
1	1 1
2	1 2 1
3	1 3 3 1
4	1 4 6 4 1
5	1 5 10 10 5 1
6	1 6 15 20 15 6 1
7	1 7 21 35 35 21 7 1
8	1 8 28 56 70 56 28 8 1
9	1 9 36 84 126 126 84 26 6 1
10	1 10 45 120 210 252 210 120 45 10 1

2.2 Another system: a binary alloy

A different system with the same statistical properties is a binary alloy where the atoms occupying the sites in a crystal lattice can be either A or B. In this case we may identify the number of A atoms with $N_{\uparrow}$ *etc.*, and then the mathematics is identical.

2.3 Sharpness of the multiplicity function for large N

We approximate $g(N, s)$ for large N , in the case when $|s| \ll N$. We start from the approximation for $n!$ known as *Stirling's formula*,

$$n! \simeq \sqrt{2\pi n} n^n \exp\left(-n + \frac{1}{12n}\right).$$

This is an example of an asymptotic expansion. Its precision is greatest for large n .

(The enumeration of states frequently involves factorials and in the limit of large numbers we will always use Stirling's formula to approximate them. Stirling's formula has very wide use in statistical mechanics.)

We expand $\ln g$, retaining terms to $O(1/N)$, so

$$\ln N! \simeq \frac{1}{2} \ln(2\pi) + (N + \frac{1}{2}) \ln N - N$$

and

$$\ln N_{\uparrow}! \simeq \frac{1}{2} \ln(2\pi) + (N_{\uparrow} + \frac{1}{2}) \ln N_{\uparrow} - N_{\uparrow}.$$

Combining these, remembering that $N = N_{\uparrow} + N_{\downarrow}$, gives

$$\ln g \simeq -\frac{1}{2} \ln(2\pi) + (N_{\uparrow} + \frac{1}{2}) \ln \left(\frac{N}{N_{\uparrow}} \right) + (N_{\downarrow} + \frac{1}{2}) \ln \left(\frac{N}{N_{\downarrow}} \right) - \frac{1}{2} \ln N.$$

Replacing $N_{\uparrow}$ and $N_{\downarrow}$ in terms of s and expanding the log ($\ln \overline{1+x} = x - x^2/2 \dots$)

$$\ln \left(\frac{N_{\uparrow}}{N} \right) \simeq -\ln 2 + \frac{2s}{N} - \frac{2s^2}{N^2}$$

and similarly for $\ln(N_{\downarrow}/N)$ (note that this approximation assumes $|s| \ll N$). We then get

$$\ln g \simeq \frac{1}{2} \ln \left(\frac{1}{2\pi N} \right) + (N_{\uparrow} + \frac{1}{2}) \left(\ln 2 - \frac{2s}{N} + \frac{2s^2}{N^2} \right) + (N_{\downarrow} + \frac{1}{2}) \left(\ln 2 + \frac{2s}{N} + \frac{2s^2}{N^2} \right),$$

which reduces to

$$\ln g \simeq \frac{1}{2} \ln \left(\frac{2}{\pi N} \right) + N \ln 2 - \frac{2s^2}{N}$$

after dropping terms $O(1/N)$. Exponentiating this,

$$g(N, s) \simeq g(N, 0) \exp \left(\frac{-2s^2}{N} \right),$$

where

$$g(N, 0) \simeq \sqrt{\frac{2}{\pi N}} 2^N.$$

In short g is approximately Gaussian when $|s| \ll N$.

We can approximate the sum over s by an integral, and then (after extending the limits to infinity)

$$\int_{-\infty}^{\infty} g(N, s) ds = 2^N,$$

so that the normalization of g is preserved by the approximations. For $N = 50$, $g(50, 0) = 1.264 \times 10^{14}$ while our approximation gives 1.270×10^{14} . The approximation is poor when $|s| \rightarrow \frac{1}{2}N$, *i.e.* when g is small.

A measure of the width of the Gaussian approximation for g is the value of s where g falls to $1/e$ times its peak value, that is where

$$s_e = \sqrt{\frac{N}{2}}.$$

The fractional width of the peak in g is then

$$\frac{s_e}{N} = \sqrt{\frac{1}{2N}},$$

as we have already anticipated. This is very small for large values of N . This very narrow peak in the density of states is a characteristic of the statistical behaviour of systems of large numbers of particles.

3 Mean values

If S is a random variable and the probability that $S = s$ is $P(s)$, then if $f(S)$ is any function of S the mean value of $f(S)$ is

$$\langle f \rangle = \sum_{\text{alls}} f(s) P(s)$$

(provided that P is normalized, *i.e.* $\sum_s P(s) = 1$).

With the basic assumption that all accessible states of the system are equally likely, for the binary model system

$$P(N, s) = \frac{g(N, s)}{2^N}.$$

Using our approximation for g and replacing the sum with an integral again, we can calculate the mean value of s^2 ,

$$\begin{aligned} \langle s^2 \rangle &\simeq \int_{-\infty}^{\infty} s^2 P(N, s) ds \\ &\simeq \sqrt{\frac{2}{\pi N}} \int_{-\infty}^{\infty} s^2 \exp\left(\frac{-2s^2}{N}\right) ds \\ &= \sqrt{\frac{2}{\pi}} \frac{N}{8} \int_{-\infty}^{\infty} x^2 e^{-\frac{1}{2}x^2} dx \\ &= \frac{N}{4}. \end{aligned}$$

The spin excess is $2s$, so that the root-mean-squared spin excess is simply

$$\langle 4s^2 \rangle^{\frac{1}{2}} = \sqrt{N}$$

and the fractional fluctuation in the spin excess is this divided by N , *i.e.* $1/\sqrt{N}$.

The peak in the density of states is both *narrow* (it has a small fractional width) and *sharp* ($g(N, s)$ dies away rapidly from its peak).

3.1 Energy of the binary system

When dealing with the thermal properties of a physical system the energies of the various states of the system are of significance: sometimes fixed; sometimes variable. The potential energy of a magnet of moment $\mathbf{m}$ in a magnetic field of strength $\mathbf{B}$ is

$$U = -\mathbf{m} \cdot \mathbf{B}.$$

Assuming that the 2 “spin” states for each of the elementary magnets are either aligned or antialigned with the field, the total magnetic energy of such a system is

$$U = \sum_{i=1}^N U_i = - \sum_i \mathbf{m}_i \cdot \mathbf{B} = -(N_{\uparrow} - N_{\downarrow})mB = -2smB = -MB,$$

where M is the total magnetic moment of the system. The spacing between adjacent energy levels is constant, $\Delta\epsilon = 2mB$.

(This model ignores possible interaction between the spins.)

3.2 Another example system:

The simple harmonic oscillator of frequency ω has energy eigenvalues

$$\epsilon_n = n\hbar\omega$$

for any integer $n \geq 0$. (We use our freedom to choose the zero point of energy to ignore the ground state — zero point — energy.) The multiplicity of every state is 1. We are interested in the number of ways $g(N, n)$ that a fixed total energy $\epsilon = n\hbar\omega$ can be distributed among N oscillators.

We will use a generating function to get the answer. First, define

$$f(N, t) = \sum_{n=0}^{\infty} g(N, n)t^n.$$

The *generating function* f considered as a function of t contains the same information as g when considered a function of n . By its definition we get

$$g(N, n) = \frac{1}{n!} \left. \frac{d^n f(N, t)}{dt^n} \right|_{t=0}.$$

Now $g(1, n) = 1$, so that

$$f(1, t) = \sum_{n=0}^{\infty} t^n = \frac{1}{1-t},$$

for $|t| < 1$. (Here the derivation deviates from the book.) First note that

$$g(N+1, n) = \sum_{k=0}^n g(N, n-k),$$

where k represents the possible states for the additional oscillator. Using this then

$$\begin{aligned} f(N+1, t) &= \sum_{n=0}^{\infty} g(N+1, n)t^n = \sum_{n=0}^{\infty} t^n \sum_{k=0}^n g(N, n-k) \\ &= \sum_{k=0}^{\infty} \sum_{n=k}^{\infty} g(N, n-k)t^n = \sum_{k=0}^{\infty} \sum_{s=0}^{\infty} g(N, s)t^{s+k} \\ &= \sum_{k=0}^{\infty} t^k \sum_{s=0}^{\infty} g(N, s)t^s = \frac{1}{1-t} f(N, t). \end{aligned}$$

We have the simple result

$$f(N, t) = \left(\frac{1}{1-t} \right)^N,$$

which then gives

$$g(N, n) = \frac{1}{n!} N(N+1) \dots (N+n-1) = \frac{(N+n-1)!}{n!(N-1)!} = \binom{N+n-1}{n}.$$

This result will be used later.