

MICRO- AND MACROSTATES IN THERMAL PHYSICS

FYS2160

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1. INTRODUCTION

This is a brief study of micro- and macrostates in thermal physics and statistical mechanics¹. In statistical mechanics, a microstate is a specific microscopic configuration of a thermodynamic system that the system may occupy with a certain probability in the course of its thermal fluctuations. In contrast, the macrostate of a system refers to its macroscopic properties, such as its temperature, pressure, volume and density. Two models are introduced in this study; *the Einstein crystal*, which could represent a silicone crystal, and the *spin system*, which could represent a system of magnetic dipoles

2. THE EINSTEIN CRYSTAL

2.1. Theoretical background. In a real crystal, individual atoms oscillate around an equilibrium position while interacting mostly with its nearest neighbors. A simplified model for such a system can be represented by a harmonic oscillator potential in three dimensions

$$(1) \quad U_i(\mathbf{r}_i) = \frac{1}{2}k_x(x_i - x_{i,eq})^2 + \frac{1}{2}k_y(y_i - y_{i,eq})^2 + \frac{1}{2}k_z(z_i - z_{i,eq})^2$$

From quantum mechanics, we know that the energy of a harmonic oscillator is

$$(2) \quad \epsilon_i = n_i \Delta \epsilon$$

where n_i is an integer describing the state of oscillator i . The entire system of N such (non-interacting) oscillators will have total energy

$$(3) \quad U = \sum_{i=1}^N \epsilon n_i$$

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¹I have come to realise that these two terms are somewhat interchangeable

For simplicity the energy is measured in units of ϵ .

$$(4) \quad q = \frac{U}{\epsilon} = \sum_{i=1} n_i$$

This is equivalent to equation 3, but implies that a specific system will have constant total energy, yet the energy distribution may change.

A microstate of the Einstein crystal is described by the numbers n_i for each oscillator

$$(5) \quad \{n_1, n_2, \dots, n_N\}$$

For example, for a system with $N = 4$ and $q = 4$, a possible microstate is $\{1, 0, 2, 1\}$.

2.2. Simple microstates. In a system with $N = 3$ and $q = 3$ there are ten possible microstates

$$\{0, 0, 3\}, \{3, 0, 0\}, \{0, 1, 2\}, \{1, 0, 2\}, \\ \{1, 2, 0\}, \{2, 1, 0\}, \{2, 0, 1\}, \{2, 1, 0\}, \{1, 1, 1\}$$

For an easy case like this it is relatively easy to write out all the different microstates. When the system is bigger, with higher N , a human may not be up for the task.

The general formula for computing the number of microstates for N oscillators with q units of energy is

$$(6) \quad \Omega(N, q) = \binom{q + N - 1}{q} = \frac{(q + N - 1)!}{q!(N - 1)!}$$

Plugging in for $N = 3$ and $q = 3$ indeed yields the expected result

$$\Omega(3, 3) = \binom{3 + 3 - 1}{3} = \binom{5}{3} = \frac{5!}{3!2!} = \frac{5 \cdot 4}{2} = 10$$

2.3. Two subsystems in thermal contact. Consider two initially isolated subsystems, system A with $N_A = 2$ oscillators and energy $q_A = 5$; and system B with $N_B = 2$ oscillators and energy $q_B = 1$. Subsystem A has the following six possible microstates

$$(7) \quad \{0, 5\}, \{1, 4\}, \{2, 3\}, \{3, 2\}, \{4, 1\}, \{5, 0\}$$

and subsystem B will have the following two microstates

$$(8) \quad \{0, 1\}, \{1, 0\}$$

All the microstates from one of the subsystems can be combined with any from the other system giving a total number of $6 \cdot 2 = 12$ possible microstates.

Now, let the two subsystems be put in thermal contact. This means that they can exchange energy, but that the number of particles and volume of each subsystem does not change. The total energy ($q = q_A + q_B = 6$) can be distributed between the two subsystems. The possible values of $q_k = q - q_{k^c}$ where $k \in \{A, B\}$. k^c is the complement of k , whatever k is not. It follows that the possible energy values must be $q_k \in [0, q] = [0, 6]$.

We call a state with a given q_A for a *macrostate* of the combined system. This means that there are a total of seven macrostates in the system, listed in table 1

These values have been calculated using the binomial coefficient in equation 6. The full number of microstates for a given macrostate q_A are given in the last column as the total multiplicity $\Omega_{tot} = \Omega_A \Omega_B$.

The following source code listing provides a way to compute the same numbers with a class in Python.

TABLE 1. Macrostates and multiplicities of a system with two Einstein crystals

q_A	Ω_A	q_B	Ω_B	Ω_{tot}
0	1	6	7	7
1	2	5	6	12
2	3	4	5	15
3	4	3	4	16
4	5	2	3	15
5	6	1	2	12
6	7	0	1	7
Sum:				84

```

class EinsteinCrystal:

    def __init__(self, q, N_A, N_B):

        # Arguments
        self.q = q
        self.N_A = N_A
        self.N_B = N_B

        # Initializing data structures
        self.q_A = np.asarray(range(0, q+1))
        self.omega_A = np.zeros(q+1)
        self.q_B = np.zeros(q+1)
        self.omega_B = np.zeros(q+1)
        self.omega_tot = np.zeros(q+1)

        # Computation loop
        for i in range(0, self.q+1):

            self.omega_A[i] = \
                scipy.misc.comb(self.q_A[i] + self.N_A-1, self.q_A[i])
            self.q_B[i] = self.q - self.q_A[i]
            self.omega_B[i] = \
                scipy.misc.comb(self.q_B[i] + self.N_B-1, self.q_B[i])

```

An object of this class defines a system consisting of two subsystems, A and B . To get information about the states and multiplicity of the system I have written the following method². This method displays information about smaller systems quite well.

```

def table(self):
    # Printing header
    print("{:>5} {:>7} {:>5} {:>7} {:>10}"
          .format("q_A", "omega_A", "q_B", "omega_B", "omega_tot"))

```

²I am uncertain what names to use: object or class instance; and method or function. My sincere apologies to the reader if some other words than the ones I have chosen are the norm for Python.

```

# Printing data
for i in range(0, self.q+1):
    print("{:>5.0f} {:>7.0f} {:>5.0f} {:>7.0f} {:>10.0f}" \
          .format(self.q_A[i], self.omega_A[i], \
                  self.q_B[i], self.omega_B[i], self.omega_tot[i]))

# Total multiplicity

```

To compute probability of every state and to plot det probability density function I have writting this next method method which computes the probabilities for the macrostates q_A . The probability are computed by dividing all possible microstates for a given macrostate by every possible micorstate.

$$(9) \quad p(q_A) = \frac{\Omega_{i,tot}}{\sum \Omega_{i,tot}}$$

```

def PDF(self):

    # Array for probabilities
    self.probs = np.zeros(self.q+1)

    # Computing probabilities
    for i in range(self.q+1):
        self.probs[i] \
        = self.omega_tot[i] / np.sum(self.omega_tot)

    # Printing probabilities if the system is not too large
    if self.q <= 20:
        print("{:>5} {:>7}".format('q_A', 'P(q_A)'))
        for i in range(self.q+1):
            print("{:>5.0f} {:>7.4f}" \
                  .format(self.q_A[i], self.probs[i]))

```

The method prints to terminal the probabilities that are given in table 2.

TABLE 2. Probabilities of the macrostates for two Einsten crystals where $q = 6$ and $N_A = N_B = 2$

q_A	$P(q_A)$
0	0.0833
1	0.1429
2	0.1786
3	0.1905
4	0.1786
5	0.1429
6	0.0833
Sum:	1.0

The maximum number of microstates before the two crystals came in thermal contact was only $\sum \Omega_{i,tot} = 12$. For the interconnected system, the number of allows microstates have risen dramatically to $\sum \Omega_{i,tot} = 84$. Another aspect to draw attention to is that the highest number of possible microstates for a givin macrostate is highest when the energy in the crystals, q_A and q_b are similar. This is clear from looking at table 1. It would be intersting to see if the same holds true

for an even larger system. Figure 1 shows the an approximation of a probability density function for the two crystals when the parameters are increased to $q = 100$ and $N_A = N_B = 50$. The tendency is very clear, as we see the graph forms a characteristic bell curve with a peak at $q_A = 50$, where the energy of the two crystals are most similar. The probability for this exact macrostate is $p(q_A = 50) \approx 5.6\%$.

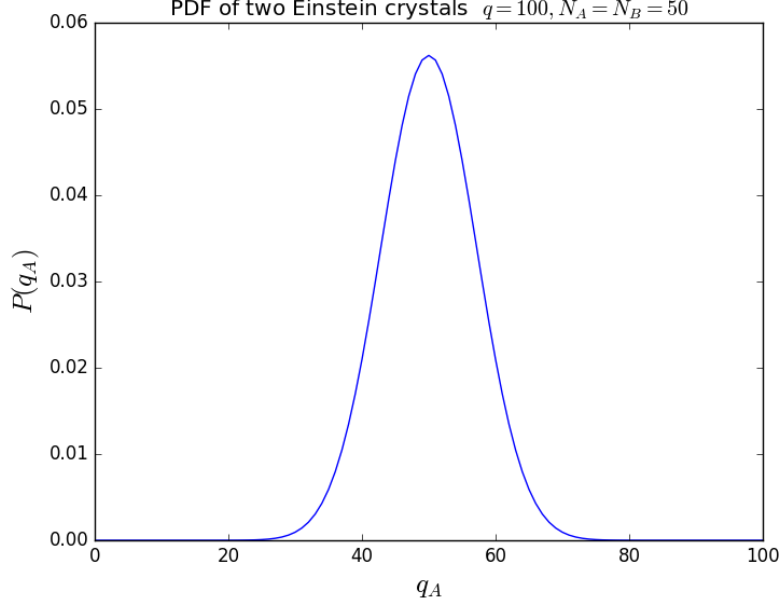


FIGURE 1. Probability density function for two interconnected Einstein crystals with $q = 100$ and $N_A = N_B = 50$

2.4. Thermodynamic properties. Equation 6 gives us the multiplicity of a system as a binomial coefficient

$$\Omega(N, q) = \binom{q + N - 1}{q} = \frac{(q + N - 1)!}{q!(N - 1)!}$$

Using Stirlings's approximation, $\ln x! = x \ln x - x$, this expression can be simplified for large N . First of all the exact formula can be simplified

$$(10) \quad \frac{(q + N - 1)!}{q!(N - 1)!} \approx \frac{(q + N)!}{q!N!}$$

Now we take the natural logarithm and apply Stirling's approximation

$$(11) \quad \ln \Omega \approx \ln \left(\frac{(q + N)!}{q!N!} \right) = \ln(1 + n)! - \ln q! - \ln N!$$

$$(12) \quad \approx (q + N) \ln(q + N) - (q + N) - q \ln q + q - N \ln N + N$$

$$(13) \quad = (q + N) \ln(q + N) - q \ln q - N \ln N$$

$$(14) \quad = (q + N) \ln q \left(1 + \frac{N}{q} \right) - q \ln q - N \ln N$$

$$(15) \quad = (q + N) \left(\ln q + \ln \left(1 + \frac{N}{q} \right) \right) - q \ln q - N \ln N$$

A Taylor expansion will reveal that $\ln(1+x) \approx x$. Then we have

$$\begin{aligned}\ln \Omega &\approx (q+N)\left(\ln q + \frac{N}{q}\right) - q \ln q - N \ln N \\ &= q \ln q + N + N \ln q + \frac{N^2}{q} - q \ln q - N \ln N \\ &= N \ln \left(\frac{q}{N}\right) + N + \frac{N^2}{q}\end{aligned}$$

Assuming $N/q \ll 1$, then N^2/q will quickly approach zeros, and we are left with a very neat expression for the natural logarithm of the multiplicity

$$(16) \quad \ln \Omega(N, q) \approx N(\ln(q/N) + 1)$$

From equation 16 one can see that the multiplicity of a large Einstein solid must be

$$(17) \quad \Omega(N, q) \approx e^{N \ln(q/N)} e^N = \left(\frac{eq}{N}\right)^N$$

For a variety of systems, particles and energy tend to rearrange themselves until the multiplicity is at or very near its maximum value. The fact that the multiplicity tends to increase is a simple way to state the *second law of thermodynamics*.

Since multiplicities are very large numbers, one usually deals with the natural logarithm to the multiplicity instead. This was the reason for the rather large algebraic exercise war performed above. For historical reasons, one also multiply by a factor of Boltzmann's constant. This provides a quantity called the *entropy*.

$$(18) \quad S \equiv k \ln \Omega$$

For a large Einstein crystal the entropy must be

$$(19) \quad S = k \ln(eq/N)^N = Nk[\ln(q/N) + 1]$$

One nice property of entropy is that the total entropy of a system of several subsystems is the sum of the entropy of the subsystems. For a two-part system a quick proof will be something like this

$$(20) \quad S_{tot} = k \ln \Omega_{tot} = k \ln(\Omega_A \Omega_B) = k \ln \Omega_A + k \ln \Omega_B = S_A + S_B$$

Consider a thermal equilibrium of two Einstein crystals in thermal contact. At equilibrium the entropy, as a function of energy, of the two crystals must be at maximum. In other words, algebraically speaking

$$(21) \quad \frac{\partial S_A}{\partial U_A} + \frac{\partial S_B}{\partial U_B} = 0$$

where $U_k = \epsilon q_K$ (the energy of each particle times the unit of energy³).

The definition of *temperature* of a system is the reciprocal of the slope of its entropy vs energy graphs. Again, algebraically speaking

$$(22) \quad T \equiv \left(\frac{\partial S}{\partial U}\right)^{-1}$$

By expanding upon the expression for entropy of an Einstein crystal (equation 19)

$$(23) \quad S = Nk[\ln(q/N) + 1] = Nk \ln U - Nk \ln(\epsilon N) + Nk$$

one will find the temperature of the Einstein crystal to be

$$(24) \quad T = \left(\frac{\partial S}{\partial U}\right)^{-1} = \left(\frac{Nk}{U}\right)^{-1} = \frac{U}{Nk}$$

³This follows from equation 3 and 4

3. THE SPIN SYSTEM

The spin system is different from a system of Einstein crystals, but can be addressed in a somewhat similar approach. For a paramagnetic system with binary spins, each particle can be in two possible states $S = +1$ or $S = -1$. Alternatively, one can call these states "spin up" and "spin down" states, borrowing terminology from quantum mechanics⁴. The energy of such a dipole depends on its orientation relative to an external magnetic field B . The simplest system we can consider consists of N independent dipoles/spins, S_i .

If we define N_{\uparrow} to be the number of dipoles that point up, and N_{\downarrow} to be the number of dipoles that point down, the total number of dipoles is $N = N_{\uparrow} + N_{\downarrow}$. For a system of a given N , there will be one macrostate for each possible value of N_{\uparrow} from 0 to N . It is easy to see that the number of different systems is governed by combinatorial mathematics and the multiplicity of any given macrostate is therefore given by the binomial coefficient

$$(25) \quad \Omega(N_{\uparrow}) = \binom{N}{N_{\uparrow}} = \frac{N!}{N_{\uparrow}!(N - N_{\uparrow})!} = \frac{N!}{N_{\uparrow}!N_{\downarrow}!}$$

which is another way of saying; "how many different systems of a given number of spin up can I have?". I have supplied an attempt at a derivation of the binomial coefficient in appendix A, for the keen reader⁵.

For the sake of symmetry, the energy levels of a single dipole in an ideal two-state paramagnet are $-\mu B$ for spin up and μB for spin down. The total energy of the system is

$$(26) \quad U = \mu B(N_{\downarrow} - N_{\uparrow})$$

denoting the net spin by ν , it is given by the relation $2\nu = N_{\uparrow} - N_{\downarrow}$. It can be beneficial to write the total energy as a function of the net spin:

$$(27) \quad U = -2\mu B\nu$$

By rewriting the number of spin up dipoles

$$(28) \quad N_{\uparrow} = N - N_{\downarrow} = \frac{N}{2} + \frac{N}{2} + N_{\downarrow} = \frac{N}{2} + \frac{N_{\uparrow}}{2} + \frac{N_{\downarrow}}{2} - \frac{2N_{\downarrow}}{2} = \frac{N}{2} + \frac{N_{\uparrow} - N_{\downarrow}}{2} = \frac{N}{2} + \nu$$

and similarly for spin down dipoles

$$(29) \quad N_{\downarrow} = N - N_{\uparrow} = \frac{N}{2} + \frac{N}{2} + N_{\downarrow} = \frac{N}{2} + \frac{N_{\uparrow}}{2} + \frac{N_{\downarrow}}{2} - \frac{2N_{\uparrow}}{2} = \frac{N}{2} - \frac{N_{\uparrow} - N_{\downarrow}}{2} = \frac{N}{2} - \nu$$

This in turn allows one to rewrite the multiplicity as a function of the net spin

$$(30) \quad \Omega(N, \nu) = \frac{N!}{\left(\frac{N}{2} + \nu\right)! \left(\frac{N}{2} - \nu\right)!}$$

Now I wish to approximate this function for $N \gg 1$. I have tried to do this with my pencil on a piece of paper, but I was quickly lost in the algebraic jungle. Instead I turn to Python symbolic computation package:

```
In [1]: from sympy import *
In [2]: nu = symbols('nu')
In [3]: N = symbols('N')
```

⁴This quickly becomes a study of a spin-1/2 particle system

⁵Another way to denote the number of spin up dipoles is by S_{+} . I find this to be easily confused with the entropy S and therefore use the notation N_{\uparrow} used many other places, like Schroeder's Introduction to Thermal Physics

```

In [4]: omega = factorial(N) /
( factorial(N/2+nu)*factorial(N/2-nu))

In [5]: lnOmega = log(omega)

In [6]: TlnOmega = series(lnOmega, nu, n=3)

In [7]: simplify(TlnOmega)
Out [7]: log(factorial(N)/(factorial(N/2))**2)
- nu**2*polygamma(1, N/2 + 1) + O(nu**3)

```

And there we have it, at least most of it. The Polygamma-function is a function which can roughly be approximated by

$$(31) \quad \Psi(x) \approx \ln x - (1/2x) - (1/12x^2) + \dots$$

The first argument in the sumpy Polygamma function is the order of differentiation, while the second is the evaluation point. From the listing above, written in a plainer mathematical typeset, we have

$$(32) \quad \ln \Omega(N, \nu) = \ln \left(\frac{N!}{\frac{N}{2}! \frac{N}{2}!} \right) - \frac{2\nu^2}{N}$$

The first of these terms is $\Omega(N, 0)$, which is easy to see from equation 30. The second term remains as it is, and we can write

$$(33) \quad \Omega(N, \nu) = \Omega(N, 0)e^{-2\nu^2/N}$$

It would be interesting to see how this approximation compares with a numerical approximation of a similar situation. The following class written in Python provides a framework where M microstates are generated randomly for a system of N dipoles.

```

class RandomSpin():
    """Generates M microstates randomly for a system
    of N u/down (+1 or -1) spins"""
    def __init__(self, M, N):

        self.M = M
        self.N = N

        # mu and B are set to 1 as default.
        # In reality for a two-state paramagnet
        # mu is the Bohr magneton
        self.mu = 1.0
        self.B = 1.0

        self.microstates = np.zeros(shape=(M,N))

        for i in range(M):
            for j in range(N):
                # Generates ranom numbers -1 or +1
                self.microstates[i,j] = np.random.randint(2)*2 -1

    def energyHistogram(self, binsNumber=10):
        net_spin = np.zeros(self.M)
        for i in range(self.M):

```



```

net_spin[i] = float(sum(self.microstates[i,:])) / 2

# Energy
U = - 2 * self.mu * self.B * net_spin

# Analytical solution
nu = np.linspace(-self.N, self.N, self.M)
prob = self.M * \
    scipy.misc.comb(self.N, self.N/2) * \
    np.exp(-nu * nu / self.N) / \
    2 ** (self.N)

plt.hist(U, bins=binsNumber, label="Numerical")
plt.plot(nu, prob, label="Analytical", linewidth=2)
plt.title("Histogram of M = " + str(self.M) \
    + " and N = " + str(self.N))
plt.xlabel("Frequency")
plt.ylabel("Energy (U)")
plt.xlim([-self.N/2, self.N/2])
plt.legend()
plt.show()

```

Additionally, the class includes two simple set-methods, in order to change the value for μ and B . An object of this class can be made with for example $M = 10000$ and $N = 50$. Running the `energyHistogram(binsNumber)` method will render a figure that compares the randomly generated spin systems to the analytical version in equation 33, shown in figure 2.

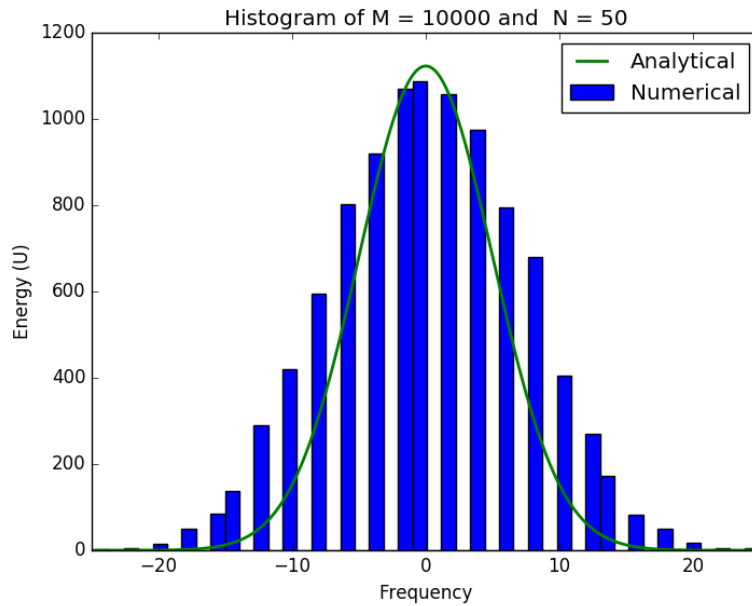


FIGURE 2. Histogram of $M = 10000$ randomly generated microstates in a binary spin system of $N = 50$ dipoles.

Figure 2 shows that the randomly generated microstates are close to the analytical approximation for large N . The randomly generated microstates seems to have a distribution with slightly larger kurtosis.

Now, we will return to describing the system using exact, and not the approximate, multiplicity. The *entropy* S as a function of N and N_\uparrow will, using Stirling's approximation, be

$$(34) \quad \frac{S}{k} = \ln \left(\frac{N!}{N_\uparrow! N - N_\uparrow!} \right) = \ln N! - \ln N_\uparrow! - \ln(N - N_\uparrow)!$$

$$(35) \quad \approx N \ln N - N - N_\uparrow \ln N_\uparrow - N_\uparrow - (N - N_\uparrow) \ln(N - N_\uparrow) - (N - N_\uparrow)$$

$$(36) \quad = N \ln N - N_\uparrow \ln N_\uparrow - (N - N_\uparrow) \ln(N - N_\uparrow)$$

The *temperature* is given by

$$(37) \quad \frac{1}{T} = \frac{\partial S}{\partial U} = \frac{\partial S}{\partial N_\uparrow} \frac{\partial N_\uparrow}{\partial U}$$

To solve this I first need to rearrange the energy in equation 26 a bit

$$(38) \quad U = \mu B(N_\downarrow - N_\uparrow) = \mu B(N - 2N_\uparrow) \rightarrow N_\uparrow = \frac{1}{2} \left(N - \frac{U}{\mu B} \right)$$

Knowing this, the first factor on the right hand side of equation 37 is

$$(39) \quad \frac{\partial S}{\partial N_\uparrow} = k[-\ln N_\uparrow - 1 + \ln(N - N_\uparrow) + 1]$$

$$(40) \quad = k \ln \left(\frac{N - N_\uparrow}{N_\uparrow} \right) = k \ln \left(\frac{N + U/\mu B}{N - U/\mu B} \right)$$

and the second factor is

$$(41) \quad \frac{\partial N_\uparrow}{\partial U} = -\frac{1}{2\mu B}$$

Putting the pieces together, the reciprocal of the temperature must be

$$(42) \quad \frac{1}{T} = -\frac{k}{2\mu B} \ln \left(\frac{N + U/\mu B}{N - U/\mu B} \right)$$

Appendices

A. DERIVING THE BINOMIAL COEFFICIENT

This outline may not be rigorous enough to satisfy a mathematician, but it serves its purpose, in the true spirit of a physicist.

Say we have an n element set and want to make ordered lists of length k from this set. There will be n ways to pick the first element, $n - 1$ ways to pick the second, and $n - k$ ways to pick the k th element. Alternatively, there are

$$(43) \quad n(n - 1) \dots (n - k) = \frac{n!}{(n - k)!}$$

such sequences. This is all nice and dandy, but we are in reality dealing with *unordered* lists. This means that we want to identify the $k!$ permutations of its elements, each of which was counted separately above as the same list. The fix is simple - divide by $k!$

$$(44) \quad \frac{\frac{n!}{(n - k)!}}{k!} = \frac{n!}{k!(n - k)!}$$

This is the binomial coefficient.