Statistical and Low Temperature Physics (PHYS393)

2. Distinguishable particles

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Contents

Aim

To use the Lagrange multiplier method to derive the distribution of microstates for distinguishable particles.

Objectives

1. To explain what distinguishable particles are.

2. To count microstates for particles with more than two energy levels.

3. To describe and use the Lagrange multiplier method.

4. To explain Boltzmann's postulate for entropy.

5. To derive the Boltzmann distribution.

2.1 Microstates and Macrostates

Two particles are distinguishable if you can tell them apart. A 1 p coin and a 2 p coin would be distinguishable particles.

If you have two identical coins, they may be indistinguishable. However, you may stick a label on one, then they become distinguishable particles again.

You cannot stick labels on identical atoms or electrons. So those are indistinguishable particles.

However, there is a special case for atoms. When atoms are fixed in a solid, you can use their difference in location to tell one atom from another.

Just remember the position, and you can always get back to the same atom. So atoms in a solid are distinguishable particles.

We have previously looked at the tossing of coin, and used this as an analogy for a particle with two energy levels.

A real particle could have more than two energy levels. We need to look at the problem of how to specify the macrostates, and how to count them. In order to do so, we need to develop some notations. We shall start with the coin.

A coin has 2 sides: head and tail. Suppose we toss the coin $N = 2$ times. The result is $n_1 = 2$ heads, and $n_2 = 0$ tails. Now lets rephrase that.

Consider a particle with 2 energy levels: ε_1 and ε_2. Suppose we have $N = 2$ particles. And there are $n_1 = 2$ particles at energy level ε_1, and $n_2 = 0$ at ε_2.

So for the particle with energy levels ε_1 and ε_2, we have specified the macrostate using numbers $(n_1, n_2) = (2, 0)$.

So we can specify the macrostate using the number of particles at each energy level.

Lets write down all the macrostates and microstates for the coin:

(n_1, n_2) Microstates

(2, 0) $[H, H]$
(0, 2) $[T, T]$
(1, 1) $[H, T]$, $[T, H]$

and rephrase this for the particle:

(n_1, n_2) Microstates

(2, 0) $[\varepsilon_1, \varepsilon_1]$
(0, 2) $[\varepsilon_2, \varepsilon_2]$
(1, 1) $[\varepsilon_1, \varepsilon_2]$, $[\varepsilon_2, \varepsilon_1]$

Note, for example, $[\varepsilon_1, \varepsilon_2]$ would mean that particle 1 is at level ε_1 and particle 2 is at level ε_2.

We are ready to take the next step.

Consider a particle with 3 energy levels: ε_1, ε_2 and ε_3. Suppose there are $N = 2$ particles. And there are $n_1 = 2$ at energy level ε_1, $n_2 = 0$ at ε_2, and $n_3 = 0$ at ε_3.

We have again specified the macrostate using the number of particles at each energy level $(n_1, n_2, n_3) = (2, 0, 0)$.

Lets write down a useful relation:

$$N = n_1 + n_2 + n_3$$

The total number of particles is equal to the sum of the particles at each level.

These are all possible macrostates and microstates:

(n_1, n_2, n_3) Microstates

(2, 0, 0) $[\varepsilon_1, \varepsilon_1]$
(0, 2, 0) $[\varepsilon_2, \varepsilon_2]$
(0, 0, 2) $[\varepsilon_3, \varepsilon_3]$
(1, 1, 0) $[\varepsilon_1, \varepsilon_2]$, $[\varepsilon_2, \varepsilon_1]$
(0, 1, 1) $[\varepsilon_2, \varepsilon_3]$, $[\varepsilon_3, \varepsilon_2]$
(1, 0, 1) $[\varepsilon_1, \varepsilon_3]$, $[\varepsilon_3, \varepsilon_1]$
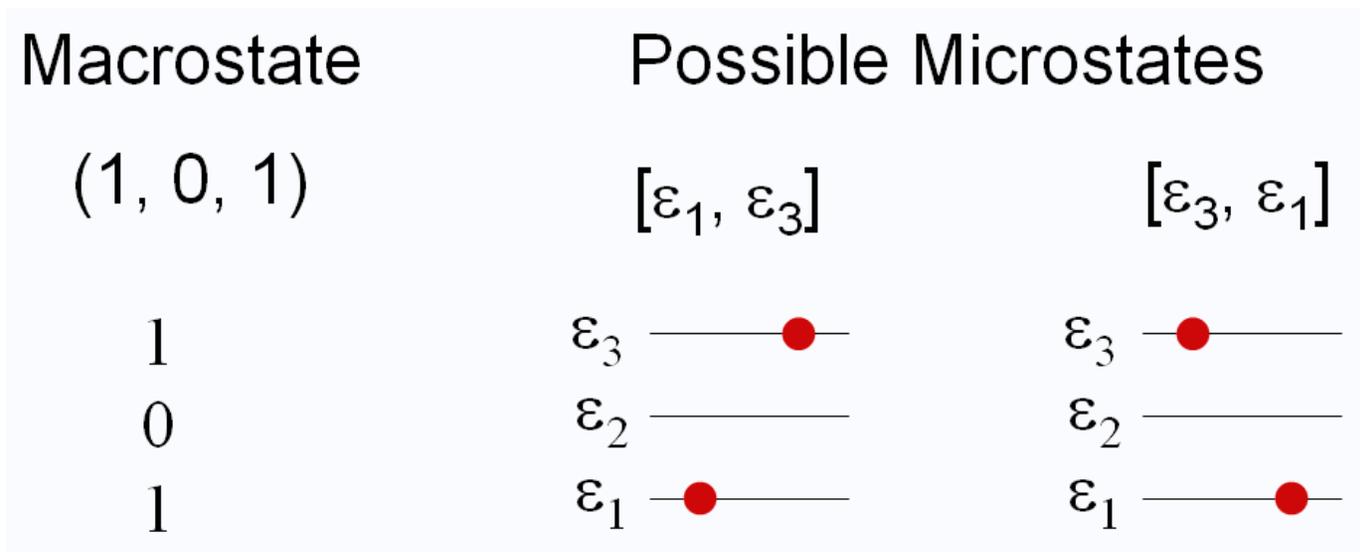
For example, for the macrostate (1, 0, 1), we can have 2 microstates:

$[\varepsilon_1, \varepsilon_3]$ means particle 1 at ε_1 and particle 2 at ε_3.
$[\varepsilon_3, \varepsilon_1]$ means particle 1 at ε_3 and particle 2 at ε_1.

Another way of representing these microstates is to use a picture like this:

Macrostate	Possible Microstates	
(1, 0, 1)	$[\varepsilon_1, \varepsilon_3]$	$[\varepsilon_3, \varepsilon_1]$
1	ε_3 ——●——	ε_3 ●——
0	ε_2 ————	ε_2 ————
1	ε_1 ●——	ε_1 ——●—

Each of the red circles represents a particle.

The full list is shown on the next silde.

Macrostate	Possible Microstates

It quickly gets complicated if we increase the number of levels. Fortunately, we usually need to know the number of microstates, but not the actual arrangements.

There is a formula for this number. We return to the coin tossing example:

"A coin has 2 sides: head and tail. Suppose we toss the coin $N = 2$ times. The result is $n_1 = 2$ heads, and $n_2 = 0$ tails."

We have already seen the formula previously. The number of microstates for the macrostate (n_1, n_2) is

$$\Omega = \frac{N!}{n_1! n_2!}$$

It is simply the number of ways of putting N different objects into 2 boxes.

So we can think of the particles as different objects, and the energy levels as boxes. With this idea, the formula can be easily extended to the particle example:

"Consider a particle with 3 energy levels: ε_1, ε_2 and ε_3. Suppose there are $N = 2$ particles. And there are $n_1 = 2$ at energy level ε_1, $n_2 = 0$ at ε_2, and $n_3 = 0$ at ε_3."

We want to know the number of microstates in the macrostate (n_1, n_2, n_3). This would be the number of ways of putting N different objects into 3 boxes, since there are 3 energy levels. The answer is

$$\Omega = \frac{N!}{n_1! n_2! n_3!}$$

The formula generalises to of energy levels, for any number particles:

$$\Omega = \frac{N!}{n_1! n_2! n_3! ... n_i! ...}$$

or

$$\Omega = \frac{N!}{\prod_i n_i!}$$

We now have to consider how we want to use this formula.

Previously, we have drawn an analogy between coin tossing and atoms in a cup of tea. There is a parallel between the number of heads, and the total energy of the atoms.

We have seen that when there is a very large number of tossing or of atoms, the most probably macrostate becomes almost the only macrostate.

If we can find this macrostate, we would know the number of particles at each energy level. This would allow us to find the total energy, the heat capacity, and other thermodynamic quantities, which is what we set out to do.

So we want to use the formula for the number of microstates,

$$\Omega = \frac{N!}{\prod_i n_i!},$$

to find the most probable macrostate.

In order to do so, there are 2 more equations we need to include.

The total number of particles is N. The macrostate is specified by the number of particles at each energy level: $(n_1, n_2, ..., n_i, ...)$. So the total number must the the sum of the particles at each level:

$$N = \sum_i n_i$$

We consider an isolated system, e.g. a cup of tea that is very well insulated from the surrounding. Then the total energy U of the particles would remain constant.

There are n_1 particles at energy level ε_1, so the total energy of these particles is $n_1 \varepsilon_1$. Adding up the energy of the particles at all energy levels, we have the energy of the whole system:

$$U = \sum_i n_i \epsilon_i$$

Lets write down all the equations we have.

For a macrostate n_i, specified by the number of particles in each energy level: $(n_1, n_2, ...)$:

The number of microstates is given by

$$\Omega = \frac{N!}{\prod_i n_i!}$$

We assume that the total number of particles is fixed:

$$N = \sum_i n_i$$

Assuming that the system is isolated, the total energy is also fixed:

$$U = \sum_i n_i \epsilon_i$$

Ω is a function of the variables $(n_1, n_2, ...)$.

There are 2 conditions, or constraints, on these variables:

(i) the total number of particles is a constant, and
(ii) the total energy is also a constant.

In order to maximise Ω, we can use the method of Lagrange multipliers.

The procedure is as follows:

1. We maximise $\ln \Omega$ instead of Ω. The result would be the same because when $\ln \Omega$ is a maximum, so is Ω.

2. The reason is that $\ln \Omega$ can be simplified for very large N using the Stirling's theorem.

3. Write down the Lagrange function $\ln \Omega + \lambda_1 N + \lambda_2 U$.

4. λ_1 and λ_2 are new parameters called Lagrange multipliers.

5. Differentiate this with respect to every n_i.

6. Set the derivative to zero and solve for n_i, λ_1 and λ_2.

7. This gives the macrostate $(n_1, n_2, ...)$.

2.2 Lagrange Multipliers
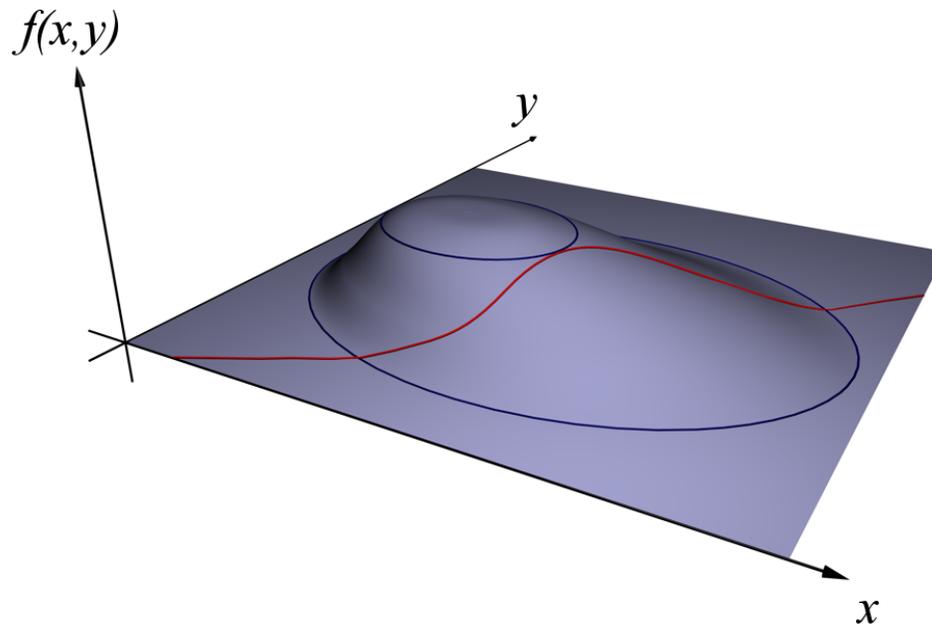
1. Suppose you want to find the highest point along a road that does not quite go over the top of a hill.

2. The highest point on the road must be just touching one of the the contours of the hill.
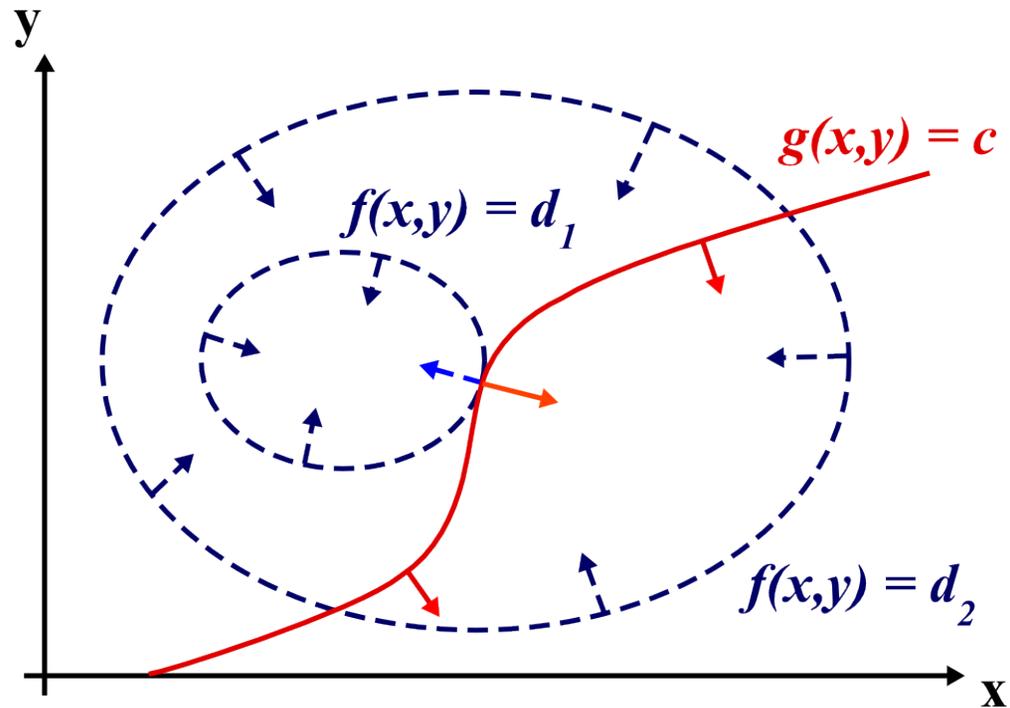
1. Represent the road as a graph $g(x, y) = 0$

2. This turns the road itself into a contour of the function $g(x, y)$. It is the contour when this function is zero.

3. At the highest point the contours touch, the normals to the contours are aligned.

1. Suppose the hill is represented by the function $f(x, y)$.

2. It is possible to find a vector with the following properties:

   - pointing in the direction of greatest slope,

   - with a magnitude equal to the gradient of that slope.
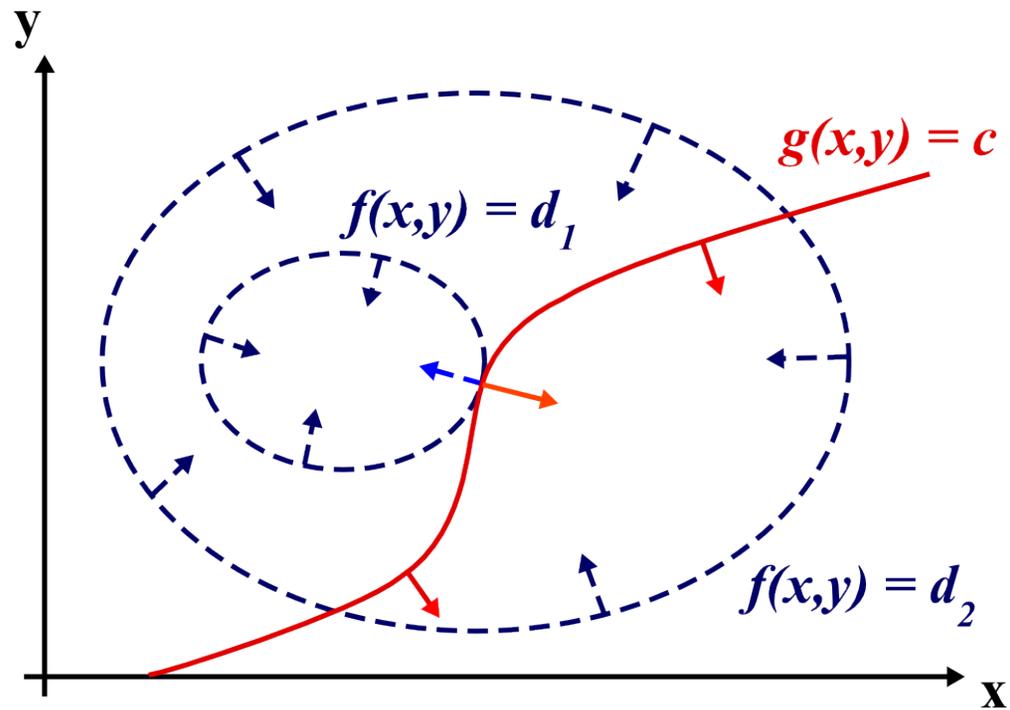
1. This means that the vector must be perpendicular to the contour.

2. This vector, also simply called "gradient", is calculated using $\nabla f(x, y) = (\frac{\partial f}{\partial x}, \frac{\partial f}{\partial y})$
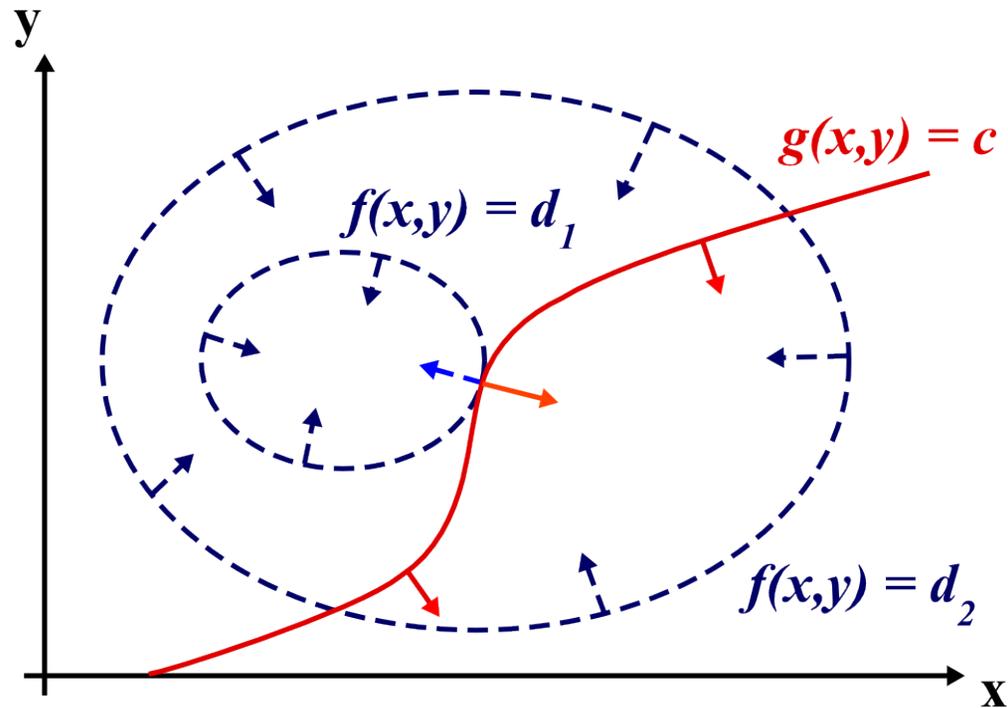
1. At the point where the contours touch, the gradient vectors of both $f(x, y)$ and $g(x, y)$ are aligned.

2. This means that we can find λ such that

$$\nabla f(x, y) + \lambda \nabla g(x, y) = 0 \qquad (1)$$

1. Problem: Maximise $f(x, y)$ subject to the constraint $g(x, y) = 0$.

2. Solution: Write down the Lagrange function $f(x, y) + \lambda g(x, y)$ and find its gradient. The parameter λ is called the Lagrange multiplier.

3. We have 3 equations now. The gradient gives 2 equations:

$$\frac{\partial f(x, y)}{\partial x} + \lambda \frac{\partial g(x, y)}{\partial x} = 0 \tag{2}$$

$$\frac{\partial f(x, y)}{\partial y} + \lambda \frac{\partial g(x, y)}{\partial y} = 0 \tag{3}$$

and the constraint gives one:

$$g(x, y) = 0 \tag{4}$$

4. Solve for x, y and λ.

1. The method can be extended to any number of variables and constraints. Suppose we have a function of n variables, $f(x_1, x_2, ..., x_n)$.

2. Suppose we have two constraints, $g(x_1, x_2, ..., x_n) = 0$ and $h(x_1, x_2, ..., x_n) = 0$.

3. Write down the Lagrange function $f(x_1, x_2, ..., x_n) + \lambda_1 g(x_1, x_2, ..., x_n) + \lambda_2 h(x_1, x_2, ..., x_n)$, and find its gradient. Note that each constraint has one Lagrange multiplier.

4. The gradient gives n equations, and the constraints give 2. We have n unknowns from the variables $x_1, x_2, ..., x_n$ and 2 from the multipliers λ_1 and λ_2.

5. Solve the equations for all the unknowns.

If we need to find the maximum of a function, like Ω, subject to constraints like fixed N and fixed U, we use the Lagrange multipliers.

First, we use $\ln \Omega$ instead of Ω. When one is maximum, so is the other, so it makes no difference for this problem. The Stirling's theorem is used to simplify $\ln \Omega$.

Then we write down the Lagrange function $\ln \Omega + \lambda_1 N + \lambda_2 U$ and maximise with respect to n_i.

The Stirling's Theorem is used for large factorials.

For real objects, N may be the number of atoms. This could be as big as 10^{30}, and it takes a long time to calculate.

Fortunately, there is a simple, approximate formula that is very accurate for large numbers:

$$\ln N! \approx N \ln N - N$$

This formula is the Stirling's Theorem.

We need to maximise

$$\ln \Omega + \lambda_1 N + \lambda_2 U$$

In order to do so, we need to differentiate this. Start with

$$N = n_1 + n_2 + ... + n_i + ...$$

Differentiating with respect to n_i gives

$$\frac{\partial N}{\partial n_i} = 1.$$

Next, we differentiate

$$U = n_1 \epsilon_1 + n_2 \epsilon_2 + ... + n_i \epsilon_i + ...$$

This gives

$$\frac{\partial U}{\partial n_i} = \varepsilon_i.$$

Next we need to differentiate $\ln \Omega$.

Start with the formula

$$\Omega = \frac{N!}{n_1! n_2! ... n_i! ...}$$

Then take the logarithm,

$$\ln \Omega = \ln N! - \ln n_1! - \ln n_2! - ... - \ln n_i! - ...$$

and apply Stirling's theorem:

$$\ln \Omega = N \ln N - N - (n_1 \ln n_1 - n_1) - (n_2 \ln n_2 - n_2) - ... - (n_i \ln n_i - n_i) - ...$$

Differentiating, we get

$$\frac{\partial \ln \Omega}{\partial n_i} = \ln N - \ln n_i$$

Note that in this differentiation, N is to be treated as a function of n_i and not a constant. The condition that N is a constant should be imposed afterwards.

These are what we have obtained:

$$\frac{\partial N}{\partial n_i} = 1$$

$$\frac{\partial U}{\partial n_i} = \varepsilon_i$$

$$\frac{\partial \ln \Omega}{\partial n_i} = \ln N - \ln n_i$$

To maximise the Lagrange function $\ln \Omega + \lambda_1 N + \lambda_2 U$, we need to differentiate this and set the derivative to zero:

$$\frac{\partial \ln \Omega}{\partial n_i} + \lambda_1 \frac{\partial N}{\partial n_i} + \lambda_2 \frac{\partial U}{\partial n_i} = 0$$

Substituting the above results, we get:

$$\ln N - \ln n_i + \lambda_1 + \lambda_2 \varepsilon_i = 0$$

We have obtained

$$\ln N - \ln n_i + \lambda_1 + \lambda_2 \varepsilon_i = 0$$

Soving for n_i gives the solution:

$$n_i = A \exp(\lambda_2 \epsilon_i)$$

where $A = N \exp(\lambda_1)$.

Next, we need to determine λ_1, or A, and λ_2.

A can be obtained using

$$N = \sum n_i,$$

the condition that the total number of particles is N. This is called the normalisation condition. Substituting, we get

$$N = A \sum \exp(\lambda_2 \epsilon_i).$$

Rearranging this gives

$$A = \frac{N}{\sum \exp(\lambda_2 \epsilon_i)}.$$

Next, we need to find λ_2. In principle, we can use the next constraint

$$U = \sum n_i \epsilon_i$$

Substituting the solution

$$n_i = A \exp(\lambda_2 \epsilon_i)$$

we get

$$U = \sum A \epsilon_i \exp(\lambda_2 \epsilon_i)$$

Then solve for λ_2.

Unfortunately, this equation is very difficult to solve. Instead, we need to take another approach. That is to make use of our knowledge of thermodynamics.

2.3 Boltzmann Postulate

The purpose of doing all these calculations is to find a way to calculate thermodynamic quantities like entropy and heat from first principles.

Instead of solving for λ_2 directly, we can try and find it in terms of known quantities in thermodynamics. We shall start by stating the result:

$$\lambda_2 = -\frac{1}{k_B T}.$$

where k_B is the Boltzmann constant and T is the temperature.

There are many ways to determine this. We shall look at the following approach:

1. Use entropy to show that λ_2 is related to T.
2. Use the ideal gas law to obtain the above equation.

To relate λ_2 to the entropy formula

$$dQ = TdS,$$

we look at the Lagrange function $\ln \Omega + \lambda_1 N + \lambda_2 U$ again.

Previously, we have taken the derivative to find the set of numbers $(n_1, n_2, ...)$ that would maximise the function. We have found the solution for n_i, except for the unknown λ_2.

For small variations about this solution $(n_1, n_2, ...)$, the change in the Lagrange function would be zero, since it is at a maximum. So

$$d(\ln \Omega) + \lambda_1 dN + \lambda_2 dU = 0$$

Suppose we impose the condition that the total N is fixed, but we give some heat dQ to the system so that U increases a little.

Since U increases, we are going beyond the original problem statement, in which U is fixed. We are going to modify the constraints on N and U.

Injecting the heat would cause the numbers $(n_1, n_2, ...)$ to change. Particles at the lower energy levels would be excited to higher energies.

However, we are making use of the results from the original problem. We a small change from the point $(n_1, n_2, ...)$ where the Lagrange function is at a maximum.

This means that that any change in the function should remain zero to first order:

$$d(\ln \Omega) + \lambda_1 dN + \lambda_2 dU = 0.$$

By injecting the heat dQ, we have modified the constraint U.

We shall require that the constraint on N remain the same, that is the number of particles remain fixed.

The numbers n_i in the individual levels can change. For example, n_1 may decrease slightly, and n_2 may increase, so that the energy U increases.

Then $dN = 0$ and $dU = dQ$, and we have

$$d(\ln \Omega) + \lambda_1 dN + \lambda_2 dU = d(\ln \Omega) + \lambda_2 dQ = 0$$

Rearrange this to compare with the entropy formula

$$
\begin{aligned}
dQ &= -\frac{1}{\lambda_2} d(\ln \Omega) \\
dQ &= T dS.
\end{aligned}
$$

Comparing the 2 equations:

$$dQ = -\frac{1}{\lambda_2}d(\ln \Omega)$$
$$dQ = TdS.$$

gives

$$TdS = -\frac{1}{\lambda_2}d(\ln \Omega)$$

This implies that

$$T = -\frac{1}{k\lambda_2}$$
$$S = k \ln \Omega,$$

for some constant k. We can verify these by substitution:

$$TdS = -\frac{1}{k\lambda_2}d(k \ln \Omega) = -\frac{1}{\lambda_2}d(\ln \Omega)$$

The constant k simply make the expressions for T and S more general.

Therefore, we have shown that λ_2 is indeed related to T. The value of the constant k would have to wait.

We shall see later, in the lectures on ideal gas, that k is the Boltzmann constant

$$k_B = \frac{R}{N_A} = 1.3807 \times 10^{-23} \text{J K}^{-1},$$

where R is the ideal gas constant and N_A is Avogadro's constant. So

$$\lambda_2 = -\frac{1}{k_B T}$$

We now have the complete solution for the macrostate $(n_1, n_2, ...)$:

$$n_i = A \exp(\lambda_2 \varepsilon_i) = A \exp\left(-\frac{\varepsilon_i}{k_B T}\right)$$

The most probable macrostate is given by

$$n_i = A \exp\left(-\frac{\varepsilon_i}{k_B T}\right)$$

The following symbol is often used in statistical mechanics:

$$\beta = \frac{1}{k_B T}$$

so we would also see the macrostate in this form:

$$n_i = A \exp(-\beta \varepsilon_i)$$

where

$$A = \frac{N}{\sum \exp(-\beta \varepsilon_i)}$$

Note that we have not arrived at this by solving the problem mathematically.

We have assumed that our macrostate idea is an accurate description of a real system, and then we have used our knowledge of thermodynamics to find the unknown Lagrange multiplier λ_2.

As we shall see in these lectures, the predictions of this formula has been verified by many experiments. It is from these empirical results that we can finally accept that the ideas about macrostates and microstates are a good description of how energies and distributed among atoms and electrons.

The solution for the macrostate tells us how the number of particles are distributed in different energy levels:

$$n_i = A \exp\left(-\frac{\varepsilon_i}{k_B T}\right).$$

It is called the Boltzmann distribution.

We have arrived at the expression for the Lagrange multiplier λ_2 by comparing these 2 equations:

Recall that when we compare these 2 equations

$$
\begin{aligned}
dQ &= -\frac{1}{\lambda_2} d(\ln \Omega) \\
dQ &= T dS.
\end{aligned}
$$

we have arrived at 2 results:

$$
\begin{aligned}
T &= -\frac{1}{k\lambda_2} \\
S &= k \ln \Omega,
\end{aligned}
$$

One is an expression for the Lagrange multiplier λ_2. The other is something even more exciting:

$$
S = k_B \ln \Omega.
$$
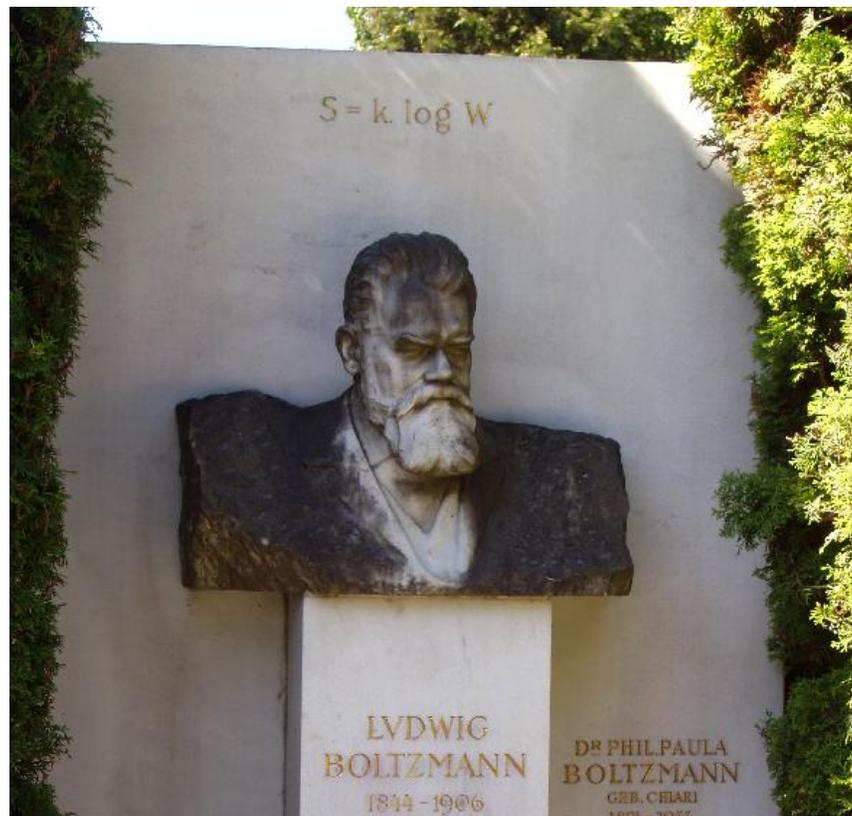
We have found a formula for entropy!

Historically, the formula

$$S = k_B \ln \Omega.$$

was first postulated by Boltzmann. It is so important that it is engraved on his tombstone ...

As with the Boltzmann distribution, we know that the entropy formula

$$S = k_B \ln \Omega$$

is correct because it works. Again, as we shall see in the following lectures, it agrees with many experiments when we use it to predict thermodynamic quantities.

Even so, it helps to see that this formula, based on the number of microstates Ω, agrees with some of the properties that we know about the entropy S:

1. We know that entropy tends to increase. We know that a system tends towards the macrostate with the greatest number of microstates.

2. We get the total entropy of two systems by adding. We get the number of microstates Ω by multiplying, but the logarithm of multiplcation becomes addition.

A note on the recommended text

If you are using the recommended text:

Statistical Mechanics - A Survival Guide,
by A. M. Glazer and J. S. Wark

please note that the Lagrange multiplier method given on pages 15 and 16 is incorrect.

Please use the version given in these lectures.

1. We study an isolated system of N particles. We hope that this can be used to describe a real system of electrons or atoms.

2. We assume that as long as the total energy U is fixed, the system is equally likely to be in any microstate.

3. To find the most probable macrostate, we maximise $\ln \Omega$, where Ω is the number of microstates in a macrostate specified by $(n_1, n_2, ...)$.

4. We formulate this as a problem to find the answer $(n_1, n_2, ...)$ for which the function $\ln \Omega$ is a maximum, subject to the constraints that N and U are constants.

5. With the help of the formula $dQ = TdS$, we find that the most probable macrostate is the Boltzmann distribution,

$$n_i = A \exp(-\varepsilon_i / k_B T).$$

6. This also leads to a formula or postulate for entropy

$$S = k_B T \ln \Omega,$$

which has to be verified by experiments.

7. We assume that because N is very large, the probability of a different macrostate from the Boltzmann distribution is extremely small. It should be possible to demonstrate this in the same way that we have done previously for the tossing of coins.
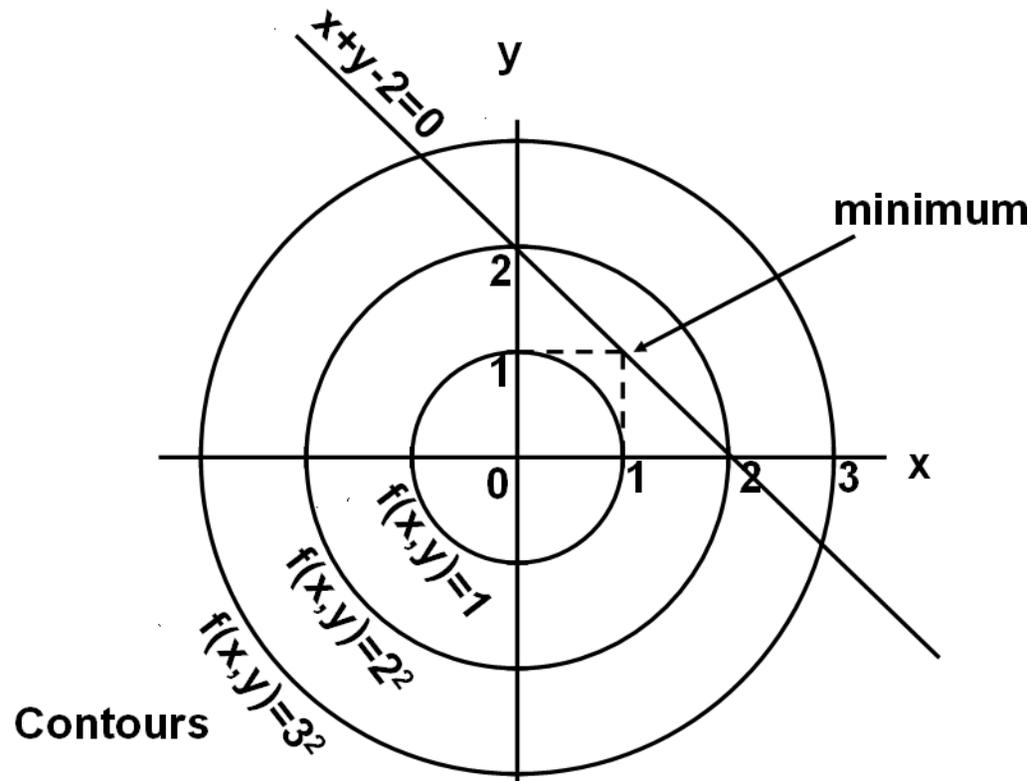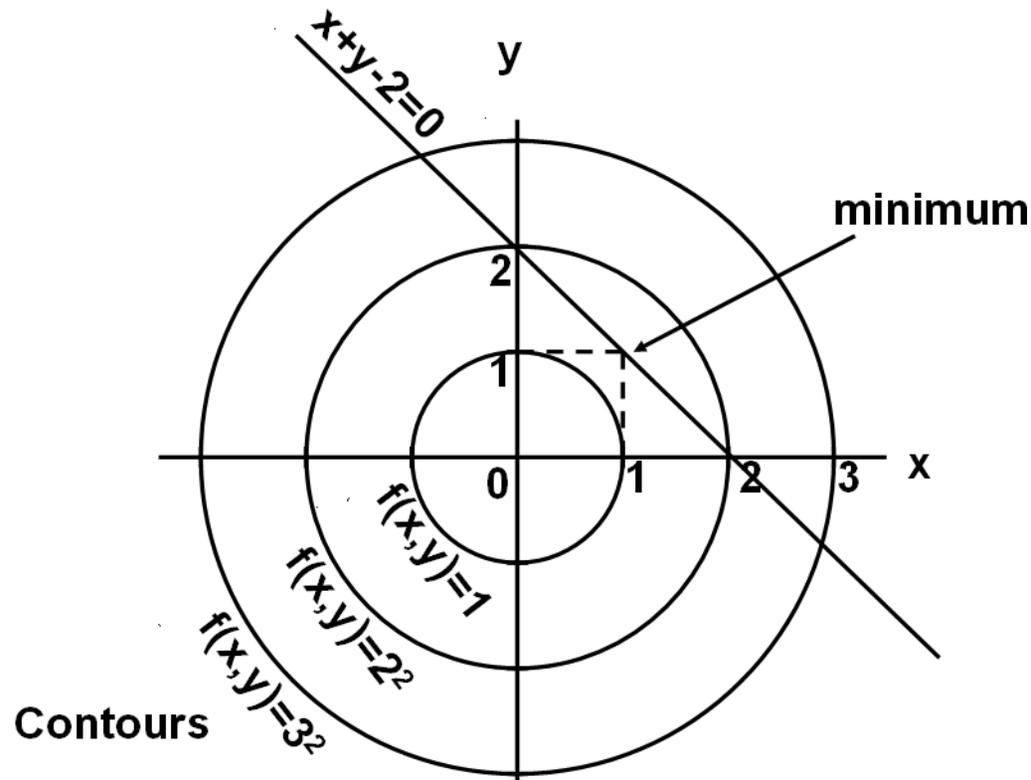
2.4 Exercises

Exercise 1

Minimise the function $f(x, y) = x^2 + y^2$, subject to the constraint $x + y - 2 = 0$.

(i) Do it mentally, or by inspection of the graphs.

(ii) Do it using Lagrange multiplier.

Do the results agree?

1. The contours of $f(x,y)$ are just circles, e.g. $x^2 + y^2 = 1$, $x^2 + y^2 = 2$, ... The circles get larger as the value increases.

2. The constraint $x + y - 2 = 0$ is a straight line with intercepts $x = 2$ or $y = 2$.

1. By symmetry, $f(x, y)$ is highest at the midpoint between the intercepts, where $x = y = 1$.

2. Therefore, $f(x, y) = 1^2 + 1^2 = 2$.

1. Let $g(x, y) = x + y - 2$. The constraint is then $g(x, y) = 0$.

2. The Lagrange function is

$$f(x, y) + \lambda g(x, y) = x^2 + y^2 + \lambda(x + y - 2) \qquad (5)$$

3. The gradient gives:

   1. Differentiate wrt x: $2x + \lambda = 0$.

   2. Differentiate wrt y: $2y + \lambda = 0$.

4. Solving with the constraint equation gives $\lambda = -2$ and $x = y = 1$, as before.

Exercise 2

Use your calculator to work out $\ln 10!$. Compare your answer with the simple version of Stirling's theorem ($N \ln N - N$). How big must N be for the simple version of Stirling's theorem to be correct to within (ii) 5% (ii) 1% ?

Answer

$\ln(10!) = 15.11$ whereas $10\ln(10)\text{-}10 = 13.03$. There is less than 5% difference for N = 24 and less than 1% for B = 91. Stirling's approximation is quite accurate even for relatively small N.

Exercise 3

Consider a 10000 distinguishable particles at room temperature, 298 K. Suppose that each particle has 2 energy levels, 0.01 eV and 0.02 eV. Find the number of the particles in each energy level. (Boltzmann's constant is 1.3807×10^{-23} J K^{-1}.)

Answer

Since the number is quite large, we assume that the probability at each energy level is given by Boltzmann's distribution $A \exp(-\varepsilon/k_B T)$.

At 0.01 eV, $A \exp(-\varepsilon/k_B T) = 0.6778A$.
At 0.21 eV, $A \exp(-\varepsilon/k_B T) = 0.4594A$.
The total is $0.6778A + 0.4594A = 10000$. So A $= 8794$.

Therefore the numbers are:

at 0.01eV, $0.6778 \times 8794 = 5961$;
at 0.02eV, $0.4594 \times 8794 = 4040$.

Exercise 4

Calculate the quantity $k_B T$ at room temperature, 298 K. Give the answer in eV. (Boltzmann's constant is 1.3807×10^{-23} J K^{-1}. Electron charge is 1.6×10^{-19} C.)

Answer

In Joules, $k_B T = 1.3807 \times 10^{-23} \times 298 = 4.114 \times 10^{-21}$ J.

In eV, $k_B T/e = 4.114 \times 10^{-21}/1.6 \times 10^{-19} = 0.026$ eV.

Note: Since $1/40 = 0.025$ is quite close to this answer, $k_B T$ at room temperature is often quoted as 1/40 eV.

Exercise 5

Consider a large number of distinguishable particles, at temperature T.. Each particle has 4 energy levels 0, $k_B T$, $2k_B T$ and $3k_B T$. Calculate the fraction of particles in each energy level.

Answer

Since the number is quite large, we assume that the probability at each energy level is given by Boltzmann's distribution $A \exp(-\varepsilon/k_B T)$.

First, calculate the following:

at energy 0, $\exp(-\varepsilon/k_BT) = \exp(0) = 1$.
at energy k_BT, $\exp(-\varepsilon/k_BT) = \exp(-1) = 0.3679$.
at energy $2k_BT$, $\exp(-\varepsilon/k_BT) = \exp(-2) = 0.1353$.
at energy $3k_BT$, $\exp(-\varepsilon/k_BT) = \exp(-3) = 0.0498$.

The sum is 1.553. The fractions are, therefore:

at energy 0, $1/1.553 = 0.6439$.
at energy k_BT, $0.3679/1.553 = 0.2369$.
at energy $2k_BT$, $0.1353/1.553 = 0.0871$.
at energy $3k_BT$, $0.0498/1.553 = 0.0321$.

Notice that fraction drops to nearly 1/10 after just $2k_BT$.

In statistical mechanics, we often want to know if an energy level is likely to be populated at some temperature. If the level is much higher than k_BT, then it is unlikely to be occupied.