

# 2018 Explorer Competition Part II

November 14, 2018

## Guidelines

Student teams will have a total of **two weeks** to work on each section of the 2018 Explorer Competition. It consists of two separate sections: one section on **quantum mechanics** and another on **statistical mechanics**. Teams may complete both sections or choose to complete only one, as is specified in the grading section below. For successful completion of both sections, we recommend that teams set aside at least 20 hours of time. Please refer to the submission explanation below for details on both formatting and the submission process.

## Scoring

Students are encouraged to work on as much of both sections of the exam as possible. However, teams **may choose to submit solutions for only one of the two sections** if they desire. The two **sections will be graded separately** and may not necessarily be worth the same amount of points. The award structure will be as follows:

1. Awards will be given to the four teams with the **highest score in each section**. There will be an award for first place, second place, and third place. One team can win an award for both sections, such as second place in quantum mechanics and third place in statistical mechanics. Teams are therefore encouraged to attempt solutions for both sections of the competition.
2. We will additionally award one **overall award to the highest scoring team** on the entire competition. A team which wins this overall award can still receive one of the top three awards for each individual section. The team that wins this overall award will most likely have completed both sections of the exam. It will be at the judges<sup>TM</sup> discretion to choose the overall award for the best submission.

## Collaboration Policy and External Resources

Students participating in the competition **may only correspond with members of their team**. Absolutely and unequivocally, **no other form of human correspondence is allowed**.

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This includes any form of correspondence with mentors, teachers, professors, and other students. Participating students are barred from posting content or asking questions related to the exam on the internet (except where specified below), and moreover, they are unequivocally barred from seeking the solution to any of the exams' parts from the internet or another resource. Students are allowed, however, to use the following resources for purposes of reference and computation:

- **Internet:** Teams may use the internet for purposes of reference with appropriate citation. Again, teams are in no way allowed to seek the solution to any of the exams' parts from the internet. For information about appropriate citation, see below.
- **Books and Other Literature:** Teams may use books or other literature, in print or online, for purposes of reference with appropriate citation. As with the use of the internet, teams are in no way allowed to seek the solution to any of the exams' parts from books or other literature.
- **Computational Software:** Teams may use computational software, e.g. Mathematica, Matlab, Python, whenever they deem it appropriate. Of course, teams must clearly indicate that they have used such software. Additionally, the judges reserve the right to deduct points for the use of computational software where the solution may be obtained simply otherwise.
- **Piazza:** We have created a Piazza page for competitors to ask any clarifying questions about the exam as they work through it. Questions will be answered by the person who wrote the exam. Competitors should again not interact with each other. The sign up link is [piazza.com/princeton\\_university\\_physics\\_competition/fall2018/phy101](https://piazza.com/princeton_university_physics_competition/fall2018/phy101). If, for some reason, it does not work, please just copy the link and paste it in a new tab. You will then need to enter the access code putigers.

## Citation

All student submissions that include outside material must include numbered citations. We do not prefer any style of citation in particular.

## Submission

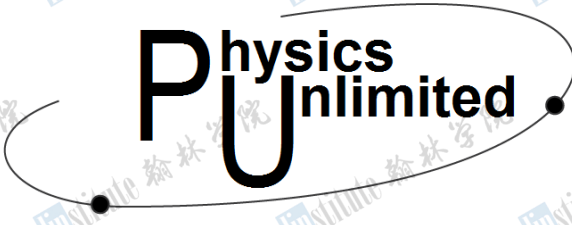
All submissions, regardless of formatting, **should include a cover page listing the title of the work, the date, and signatures of all team participants**. The work must be submitted as a single **PDF document** with the “.pdf.” extension. All other formatting decisions are delegated to the teams themselves. No one style is favored over another. That being said, we recommend that teams use a typesetting language (e.g. L<sup>A</sup>T<sub>E</sub>X) or a word-processing program (e.g. Microsoft Word, Pages). **Handwritten solutions are allowed**, but we reserve the right **to refuse grading of any portion of a team submission in the case that the writing or solution is illegible**.



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Teams must submit their solutions to the quantum mechanics portion of the Explorer Competition by **e-mailing [directors@physicsu.org](mailto:directors@physicsu.org) by 11:59 am (noon) Eastern Time (UTC-5) on Sunday, November 25, 2018**. Teams will not be able to submit their solutions to this section of the Explorer Competition at any later time. Any team member may send the submission. **The title of the submission e-mail should be formatted as “SUBMISSION - Team Name”**. All teams may make multiple submissions. However, we will **only grade the most recent submission submitted before the deadline**. Teams will receive confirmation once their submission has been received within at most two days. **In the case of extraordinary circumstances, please contact us as soon as possible.**

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## Statistical Mechanics

**Thermal physics** deals with collections of large numbers of particles, in the range of  $10^{23}$  or so. Every element in Nature that we can appreciably observe with our eyes, has already enough particles in it to qualify as subject for thermal physics. Many properties of the bulk matter (e.g. temperature, mean pressure, volume etc..) do not depend on the microscopic details of atomic physics and their study constitute the subject of **thermodynamics**. However, it is clear that to ensure a complete description of nature we need a combined study of also the microscopic properties of the constituents of a system.

We actually have no problem formulating their governing equations. Indeed the motions of atoms and molecules are described exactly by the laws of quantum mechanics. So, in principle, we could write down the exact laws of motion for a thermodynamic system and solve for the Schrodinger equation of the wave function representing the entire system. **Good luck with that!** The problem indeed is that in one mole of a substance there are in the order of  $N_A = 6 \cdot 10^{23}$  particles or molecules. This is a huge number and to solve the system exactly, we would need about  $10^{23}$  coupled equations with as many initial conditions. Quite a painful and useless task.

Indeed we are not at all interested in knowing the position and velocity of every particle in the system as a function of time. What we are interested in are quantities like the volume of the system, its pressure, heat capacity, etc. We can then notice that the amount of information we are interested in is actually absolutely minuscule compare to the number of degrees of freedom of the system. Thus a statistical approach is more than justified. As a matter of fact, those macroscopic quantities we are trying to quantify do not depend on the single motion of particles but on the average motions of all the particles in the system.

The goal here is to develop the basic principles of **statistical mechanics** starting from some fundamental assumptions and building up from them. As a first step we will refresh some elementary statistical concepts which will be crucial in order to fully understand the topics we will discuss later.

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# 1 Probability Theory and Statistics

## 1.1 Basic probability facts

When discussing probabilities it is always necessary to consider an “ensemble” consisting of a very large number  $\zeta$  of similarly prepared systems. For instance, by considering in throwing a die, one can give a statistical description by considering a very large number  $\zeta$  of similar dice thrown under the same circumstances (in principle  $\zeta \rightarrow \infty$ ). The probability of the outcome  $A$  is then defined as the ratio of the number of systems in the ensemble which exhibit this outcome to the total number of systems. We can write this symbolically as:

$$P(A) = \frac{\Omega(A)}{\Omega(\zeta)} \quad (1)$$

The set of all possible outcomes is called the universal set  $\Omega$ .<sup>1</sup> Every event  $A$  is a subset of  $\Omega$ .

Generally a Probability  $P$  is an assignment of numbers to each event  $A \subset \Omega$  which satisfies the following properties:

- $P(\Omega) = 1$
- $P(A) \geq 0 \quad \forall A \subset \Omega$
- if  $A \cap B = \emptyset$ , then  $P(A \cup B) = P(A) + P(B)$

If the outcome of an event  $B$  does not effect the probability of event  $A$  to occur, we say that  $A$  and  $B$  are *independent*. Indeed, this means that the realization of event  $B$  does not provide any information nor effect the outcome of event  $A$ . In this scenario, it becomes therefore clear that the probability that both event occur can be simply viewed as the product of the probabilities of the single events. In short when  $A$  and  $B$  are independent:

$$P(A \cap B) = P(A)P(B) \quad (2)$$

$$P(A \cup B) = P(A) + P(B) = P(A)P(B) \quad (3)$$

A *Random variable*  $X$  is an assignment of numbers to each element of the outcome space, that is a random variable is a function,  $X : \Omega \rightarrow \mathbb{R}$ . The most common description of a random variable is given by the notion of probability distribution which is a function  $p : \mathbb{R} \rightarrow [0,1]$  such that  $\sum_x p(x) = 1$  for  $x \in X$ . In short, a probability distribution is simply a function that provides the probabilities of occurrence of all possible outcomes in the outcome space  $\Omega$ .

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<sup>1</sup>here I used the standard notation but in relation to the notation used in eq.22, the universal set is defined as  $\Omega = \lim_{\zeta \rightarrow \infty} \Omega(\zeta)$

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## 1.2 Combinatorics

Looking at eq.22 immediately gives us a very important insight about computation of probabilities: we need to have a good method to **count** systems. Here I will list some basic facts about *combinatorial analysis* which is the branch of mathematics that studies the number of different ways of arranging things. Make sure you have a good understanding of these concepts before moving on to the next section. In fact, they will constitute a crucial skill for the study of statistical mechanics, where the first step in the resolution of every problem is to count the number of *states* of a certain system.

Let's consider a system A made of  $n$  distinct elements. An ordered arrangement of these  $n$  items is a **permutation** and the total number of permutations of such elements  $P_n$  is defined as:

$$P_n = n! \quad (4)$$

Now if I only look at  $p$  items among the  $n$  elements for  $p \leq n$ , the total number of arrangements is denoted as  $P_n^p$  and is equal to

$$P_n^p = \frac{n!}{(n-p)!} \quad (5)$$

Notice that for  $p = n$ ,  $P_n^p = P_n$  as we would expect.

So far we have only considered a system made of  $n$  distinct elements. However generally this is not always the case. I might have, for instance, systems which contain classes of indistinguishable elements. In this scenario, if I have a system of  $n$  elements composed of  $k$  distinct classes of  $a_k$  indistinguishable objects. The number of permutations  $P_{na_k}$  is equal to:

$$P_{na_k} = \frac{n!}{\prod_{k=1}^k a_k!} \quad (6)$$

Coming back to the system A of  $n$  distinct elements, we realize that by computing permutations we are inherently assuming that every time an element comes out, we can only pick elements from the  $n - 1$  left. If instead, we allow repetitions, the number of ordered arrangements is:

$$D_n^p = n^p \quad (7)$$

where  $p$  is defined as the number of times we can pick an element from a system containing  $n$  objects. In other words, we can view  $D_n^p$  as the number of possible arrangements of one event with  $n$  outcomes repeated  $p$  times.

That said, often we are not interested in the order of the elements but we want to determine the total number of different groups (sets) of  $p$  objects that could be formed from a total of  $n$  objects. An unordered collection of  $p$  items among the  $n$  elements is a **combination** and the total number of combinations  $C_n^p$  is defined as:

$$C_n^p = \binom{n}{p} = \frac{n!}{p!(n-p)!} \quad (8)$$



### 1.2.1 Exercise 1

In five card draw poker, a royal flush consists of the five highest ranking cards (ace, king, queen, jack, ten) in any one suit. On the first deal from a deck of 52, what is the probability of getting a royal flush?

*Hint:* what are the number of ways that a royal flush can occur compared to the total number of possible arrangements of 5 cards out of a deck of 52?

### 1.2.2 Exercise 2

Prove that  $\forall x, y \in \mathbb{R}$  and  $n \in \mathbb{N}$

$$(x + y)^n = \sum_{k=0}^n \binom{n}{k} x^k y^{n-k} \quad (9)$$

*Hint:* This is the **Binomial theorem**, a good way to prove it is by *induction* which means: prove the relation holds for  $n = 1$  element, then assume it's true for  $n$  elements and prove that the relation still holds for  $n+1$ .

## 1.3 Mean values, Dispersion and Probability distributions

What is meant by the mean or average of a quantity? Well, to better understand its meaning let's start with an example. Suppose we want to compute the average height of the people in our class. In this scenario we would write something like:

$$\text{Average height} = \bar{h} = \frac{N_{h_1} h_1 + N_{h_2} h_2 + N_{h_3} h_3 + \dots}{N_{h_1} + N_{h_2} + N_{h_3} + \dots}, \quad (10)$$

Where  $N_{h_i}$  is the number of students with height  $h_i$ . Now, as it follows from our discussion above, the probability to pick randomly a student with height  $h_i$  is simply  $P(h_i) = \frac{N_{h_i}}{N_{\text{tot}}}$ . We can therefore rewrite eq.10 in the form

$$\bar{h} = P(h_1)h_1 + P(h_2)h_2 + P(h_3)h_3 + \dots = \sum_{i=1}^N P(h_i)h_i \quad (11)$$

where  $N$  is the total number of different heights.

This is a general result of probability theory. So, for a general variable  $x$  which can take on any one of  $N$  possible values  $x_i$  with corresponding probability  $P_{x_i}$ , the mean value  $\bar{x}$ , denoted as  $\bar{x}$  is defined as:

$$\bar{x} = \sum_{i=1}^N P(x_i)x_i \quad (12)$$

Suppose that  $f(x)$  is some function of  $x$ . Then, for each of the  $N$  possible values of  $x$ , there is a corresponding value of  $f(x)$  which occurs with the same. It follows from our previous definition that the mean value of  $f(x)$  is given by:

$$\overline{f(x)} = \sum_{i=1}^N P(x_i)f(x_i) \quad (13)$$

Another important concept in probability theory is the *dispersion* of  $x$  which gives us a way to characterize the scatter around the mean value of the variable. The dispersion is defined as:

$$\overline{(\Delta x)^2} = \sum_{i=1}^N P(x_i)(x_i - \bar{x})^2 \quad (14)$$

Its value is clearly a positive number and it is equal to zero only if  $x_i = \bar{x} \forall x_i$ . The larger the spread of the values  $x_i$  around the mean, the larger the dispersion. This quantity thus measures the amount of scatter of values of the variable about its mean value. In other words, the dispersion essentially represents the width of the range over which  $x$  is distributed around its mean value  $\bar{x}$ .

Thus far we have implicitly been focusing on discrete state spaces and discrete random variables. That is, we have implicitly assumed that  $\Omega$  is a finite set. However, the rules of probability we have just discussed are still valid for non finite sets, we simply need to be more careful when calculating mean values. In particular we need to substitute the summations with an integral, and redefine the probability of  $x$  such that  $P(x) = \rho(x)dx$  where  $\rho(x)$  is the probability *density* of the random variable  $X$ . Then it follows:

$$\bar{x} = \int_{-\infty}^{+\infty} \rho(x)x dx \quad \overline{f(x)} = \int_{-\infty}^{+\infty} \rho(x)f(x)dx \quad (15)$$

$$\overline{(\Delta x)^2} = \int_{-\infty}^{+\infty} \rho(x)(x - \bar{x})^2 dx \quad (16)$$

Here I list some of the most known probability distributions which you might need during the course of this exam:

$$\text{Binomial Distribution} := P(n) = \frac{N!}{n!(N-n)!} p^n (1-p)^{N-n} \quad (17)$$

$$\text{Poisson Distribution} := P(n) = \frac{\lambda^n}{n!} e^{-\lambda} \quad (18)$$

$$\text{Gaussian Distribution} := P(u) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(u-\bar{u})^2}{2\sigma^2}} \quad (19)$$

Eq.17 describes the probability of an event, characterized with probability  $p$ , to occur  $n$  times in  $N$  trials. Eq.18 describes the probability of observing  $n$  events in a interval where  $\lambda$  is the average number of events per interval. Eq.19 is very useful to describe physical events when the number of events is very large. The Gaussian distribution is a continuous function which approximates the exact binomial distribution.

When dealing with large numbers, the calculation of  $n!$  becomes very laborious, you may find useful to remember the result of **Stirling's formula** which is a very good approximation for  $n \gg 1$ :

$$\ln n! \approx n(\ln n - 1) \quad \ln(1-n) \approx -n \quad (20)$$

### 1.3.1 Exercise

Prove that for  $N \gg n$  the Binomial distribution in eq.17 approximates to the Poisson distribution in eq.18.

*Hint:* While you can take  $\frac{n}{N} \ll 1$  or  $\frac{n^2}{N} \ll 1$  you cannot assume  $n \ll 1$ .

### 1.3.2 Exercise

A drunk guy starts out from a lamppost located on a street. Each time he takes a step, the probability of its begin to the right is  $p = \frac{1}{2}$  and is equal to the probability of its being to the left is  $q = 1 - p = \frac{1}{2}$ .

What is the probability that the man will be again at the lamppost after taking  $N$  steps

- a) if  $N$  is even?
- b) if  $N$  is odd?

### 1.3.3 Exercise

Consider the random walk problem in one dimension, the probability of a displacement between  $s$  and  $s + ds$  is given by the Gaussian distribution:

$$w(s)ds = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(s-l)^2}{2\sigma^2}} \quad (21)$$

After  $N$  steps,

- a) What is the mean displacement  $\bar{x}$  from the origin?
- b) What is the dispersion  $\overline{(\Delta x)^2}$ ?

*Hint:* In this case  $\bar{x} = N\bar{s}$  and  $\overline{(\Delta x)^2} = N\overline{(\Delta s)^2}$ . However this is not a general result thus, to get full credit, you will need to prove the above statements

## 2 Counting States

As we have seen in the multiple examples proposed in section 1, when computing probabilities it is always important to count the number of states of a system. Thus, the first step in solving any problem in statistical mechanics will be indeed to elucidate and count the states of a system in terms of its total energy  $E$ . To do so, we'll work out several examples to get a sense of how to approach generally these kinds of problems.

### 2.1 A Spin Chain

Let's consider a chain of  $N$  spins immersed in a magnetic field in 1-D<sup>2</sup>  $\mathbf{B} = H\hat{\mathbf{z}}$ . We will consider  $N$  fixed throughout the all discussion. Now, each of the spin is characterized by two states: it can either be spin up  $S_{\uparrow}$  or spin down  $S_{\downarrow}$  with equal probability  $P = \frac{1}{2}$ . The magnetic moment  $\vec{\mu}$  of the particles with spin up is positive on the  $z$  direction, meanwhile the one for spin down particles is negative. They both have the same magnitude  $|\vec{\mu}| = a$ . Thus, since the energy for 1 spin is given by  $E = -\vec{\mu} \cdot \mathbf{B}$ , we can write:

$$E_{\uparrow} = -aH \quad (22)$$

$$E_{\downarrow} = aH \quad (23)$$

Let's define then  $N_{\uparrow}$  to be the number of spin ups and  $N_{\downarrow}$  to be the number of spin pointing down. The total number of spins  $N$  is therefore simply given by  $N = N_{\uparrow} + N_{\downarrow}$ . The total energy, according to equations 22 and 23 is given by:

$$E = E_{\uparrow} + E_{\downarrow} = (N_{\downarrow} - N_{\uparrow})aH \quad (24)$$

#### 2.1.1 Exercise

Given the Spin chain described above

- a) Calculate the number of states at a given energy  $\Omega(E)$ .

*Hint:* In how many ways can the spins be distributed such that the total energy is  $E$ ?

- b) Compute  $\ln \Omega(E)$  for  $N \gg 1$ .

*Hint:* You may find useful to use **Stirling's formula** in its simplest form such that  $N! = \sqrt{2\pi N} e^{-N} N^N$

- c) Assume that the energy  $E$  is in a region where  $\omega(E)$  is appreciable, that it is not close to the extreme values  $\pm NaH$ . In this case apply a Gaussian approximation to part a) to obtain a simple expression for  $\Omega(E)$  as a function of  $E$ .

*Hint:* The total number of states will be maximal when  $E = 0$ , you may expand part a) around  $E = 0$  recalling that  $\ln \frac{(1+x)}{2} \approx \ln \frac{1}{2} + x - \frac{x^2}{2}$  for  $x \ll 1$

<sup>2</sup>1-D stands for 1 dimension



## 2.2 The Einstein Model of a Solid

Now let's move on to a system that's a bit more complicated, but also more representative of the systems typically encountered in physics. Consider a collection of microscopic systems that can each store any number of energy "units", all of the same size. Equal-size energy units are found in any quantum mechanical harmonic oscillators where the size of the energy units is equal to  $\hbar\omega$  where  $\hbar$  is the reduced Planck's constant and  $\omega$  is the angular frequency of the oscillator. We can model a solid as a collection of identical oscillators with quantized energy units. This model was first proposed by Albert Einstein in 1907, so we will refer to the system as an Einstein Solid.

Oscillator:	#1	#2	#3	Oscillator:	#1	#2	#3
Energy:	0	0	0	Energy:	3	0	0
	1	0	0		0	3	0
	0	1	0		0	0	3
	0	0	1		2	1	0
	2	0	0		2	0	1
	0	2	0		1	2	0
	0	0	2		0	2	1
	1	1	0		1	0	2
	1	0	1		0	1	2
	0	1	1		1	1	1

**Figure 1:** Microstates of a small Einstein solid consisting of only three oscillators, containing a total of zero, one, two or three units of energy

Let's start with a very small Einstein solid, composed of only 3 oscillators. fig.1 lists the various microstates that the system could have and the corresponding possible macrostates. There is just one macrostate with total energy 0, while there are three microstates with one unit of energy, six with two units and then with three units.

That is,

$$\Omega(0) = 1, \quad \Omega(1) = 3, \quad \Omega(2) = 6, \quad \Omega(3) = 10 \quad (25)$$

### 2.2.1 Exercise

Consider now an Einstein solid with  $N$  oscillators and  $q$  energy units.

- find the general formula for the number of states. Be aware, you will not get full credit without furnishing a somewhat rigorous proof for the formula you obtain.
- Using Stirling approximation as defined in eq.20, your result in part a) and that  $q \gg N$  prove that  $\Omega(E) \approx \left(\frac{e q}{N}\right)^N$

## 2.3 A Monoatomic Ideal Gas (IMG) of $n$ particles

Let's consider an ideal gas in a volume  $V$  made up of spinless mono-atomic particles. This is a particularly simple example, because for such a gas the particles possess translational but

no internal (e.g., vibrational, rotational, or spin) degrees of freedom. By definition of an ideal gas, inter-atomic forces thus the total energy of the gas is simply given by the total translational kinetic energy of its constituent particles.

$$E = \frac{1}{2m} \sum_{i=1}^N \mathbf{p}_i^2 \quad (26)$$

where  $m$  is the particle mass,  $N$  the total number of particles, and  $\mathbf{p}_i$  the vector momentum of the  $i^{th}$  particle. This situation can be achieved physically in the limit where the concentration  $\frac{N}{V}$  of the molecules is made sufficiently small, for the mean separation between molecules becomes so large that their mutual interaction becomes negligibly small.

Now each particle of this system can be fully described in terms of its position coordinates  $\mathbf{q}_i$  and its corresponding momentum  $\mathbf{p}_i$ . Let's assume for now that the each particle only moves in 1 dimension. In this case to describe the motion of each of them we can simply look at their two-dimensional phase space. As the coordinate and momentum of the particle change in time, the representative point  $(q_i; p_i)$  moves through this phase space.

In order to describe the situation in terms of where the possible states of the particle are countable, it is convenient to subdivide the ranges of the variables  $q$  and  $p$  into arbitrarily small discrete intervals. For example, we will divide our phase space in small cells of equal size  $\delta p \delta x = h_0$  such that only 1 state can be contained in the two-dimensional volume (area)  $h_0$ . It becomes clear than that to specify the number of possible states in such system we simply need to take the ratio of the area occupied in phase space by the particle over  $h_0$ .

The generalization of the above remarks to our ideal gas made of  $N$  particles in a volume  $V$  is immediate. In such a system each of the  $N$  particles is characterized by 3 position coordinates and  $3N$  degrees of freedom. The volume occupied by 1 state is then simply equal to:

$$V_{ps}^0 = \delta q_1 \delta p_1 \delta q_2 \delta p_2 \dots \delta q_{3N} \delta p_{3N} = h_0^{3N} \quad (27)$$

The number of states  $\Omega(E)$  lying between the energies  $E$  and  $E + \delta E$  is then equal to the ratio between the total Volume in the  $3N$  phase space occupied by the system and  $V_{ps}^0$ . In symbols:

$$\Omega(E) = \frac{1}{h_0^{3N}} \int_E^{E+\delta E} d^3 \mathbf{q}_1 \dots d^3 \mathbf{q}_N d^3 \mathbf{p}_1 \dots d^3 \mathbf{p}_N \quad (28)$$

Now since we assumed there is no potential energy whatsoever, the energy  $E$ , given by eq.26 is independent of the center of mass positions  $\mathbf{q}_i$  of the molecules. Hence eq.28 becomes:

$$\Omega(E) = \frac{V^N}{h_0^{3N}} \int_E^{E+\delta E} d^3 \mathbf{p}_1 \dots d^3 \mathbf{p}_N \quad (29)$$

where  $V$  is simply the volume of the container.

### 2.3.1 Exercise

By computing the integral in eq.29 prove that

$$\Omega(E) = BV^N E^{\frac{3N}{2}} \quad (30)$$

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where  $B$  is a constant of proportionality.

Also notice you can rewrite  $\Omega(E)$  in the simple form:

$$\Omega(E) = \frac{V^N}{h_0^{3N}} \chi(E) \quad (31)$$

where  $\chi(E) = \int_E^{E+\delta E} d^3\mathbf{p}_1 \dots d^3\mathbf{p}_N$ .

*Hint:* You may find useful to rewrite eq.26 in the form  $2mE = \sum_{i=1}^N \sum_{\alpha=1}^3 p_{i\alpha}^2$  and notice that it describes a sphere in the 3N-dimensional space of the momentum components with radius  $R(E) = (2mE)^{\frac{1}{2}}$ . Finally notice that to prove eq.30 you only need to find what  $\Omega(E)$  is proportional to.

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### 3 Interaction between systems: Conditions for Equilibrium

In the discussion of the previous section we have considered only *isolated* systems, thus systems that cannot exchange energy with its surroundings and are therefore characterized by a constant energy  $E$ . We also implicitly made a very important assumption, known as the *fundamental postulate* of thermodynamics. This postulate constitutes the base of our theory of statistical mechanics and is therefore important to elucidate it clearly:

An isolated system in *equilibrium* is equally likely to be in any of its accessible states

That is, if phase space is subdivided into small cells of equal size, then an isolated in equilibrium is equally likely to be in any of its accessible states<sup>3</sup>

Let's consider now a situation where it is known that an isolated system is *not equally* likely to be found in any of the states accessible to it. Our fundamental postulate asserts that this situation cannot be one where equilibrium prevails.

Generally speaking, suppose that the system at some initial time  $t$  is known to be in some *subset* of the states actually accessible to it. There are no restrictions which would prevent the system from being found in any of its accessible states at some later time since all the states *satisfy* the conservation of energy. It is therefore extremely unlikely that the system remains indefinitely in this restricted subset of states. Instead, the system will in the course of time always make transitions between all its various accessible states as a result of small interactions between its constituent particles.

The question stands up clearly: What will it happen to the system at some later time  $t^*$ . To answer such a question we may simply consider a statistical ensemble of such systems. The systems in the ensemble will constantly continue making transitions between the various accessible states through practically all the states in which it can possibly be found. One expects that the net effect of these constant transitions will be analogous to the effect of repeated shufflings of a deck of cards. In this scenario, if one keeps on shuffling long enough, eventually the cards get so mixed up that each one is *equally likely* to occupy any position in the deck, *irrespective* of how the deck was arranged initially. Similarly, in the case of the ensemble of systems, one

expects that the systems ultimately will be *uniformly* distributed over all accessible states. In other words, one expects that, no matter what the initial conditions are, an isolated system will ultimately reach its final equilibrium situation where it is equally likely to be found in any of its accessible states.

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<sup>3</sup> doesn't this remind you of the method we used in the previous section to calculate the number of states for an IMG?



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### 3.1 Thermal Interaction

A *thermal* interaction between two systems  $A$  and  $A'$  is defined as interaction where these two systems can exchange energy.

There are all sorts of mechanisms by which energy can be exchanged. However, in thermodynamics, we usually classify these mechanisms under two categories: **heat** and **work**.

**Heat** is defined as any spontaneous flow of energy from one object to another caused by a difference in temperature between the objects.<sup>4</sup>

**Work** is defined as any other transfer of energy into or taken out from the system. You do work on a system whenever you push on a piston, run current through a resistor. In each case we are increasing the total energy of the system through the help of some “agent” that is actively pumping energy into the system.<sup>5</sup>

Now, coming back to our composite system of  $A$  and  $A'$ , let's also assume that the combined system  $A_0 = A + A'$  is isolated so that its total energy  $E_0 = E + E'$  is conserved. Suppose that the systems  $A$  and  $A'$  are in equilibrium with each other. Notice that since  $E_0$  is constant, given energy  $E$  of the system  $A$ , we can view the energy of  $A'$  simply as  $E' = E_0 - E$ . Hence the number of accessible states for the entire system  $A_0$  can be regarded as a function of the single parameter  $E$ , the energy of system  $A$ . Our fundamental postulate asserts that in equilibrium  $A_0$  is equally likely to be in any of its states. From this it follows that, under these circumstances, the probability  $P(E)$  that the combined system  $A_0$  is in a configuration in which  $A$  has energy between  $E$  and  $E + \delta E$  is simply proportional to the total number of states of  $A_0$ :

$$\Omega_0(E) = \Omega(E)\Omega'(E_0 - E) \quad (32)$$

In symbols,  $P(E)$  is simply:

$$P(E) = C\Omega_0(E) = \frac{\Omega_0(E)}{\Omega_0^{tot}} \quad (33)$$

Let us now try to investigate the dependence of  $P(E)$  on the energy  $E$ . In view of eq.32, we notice that  $P(E)$  is proportional to the product of the multiplicities of the single systems. Moreover, as a function of increasing  $E$ ,  $\Omega(E)$  increases extremely rapidly while  $\Omega'(E_0 - E)$  decreases extremely rapidly.<sup>6</sup> The result is that the product of the two, which as just mentioned is proportional to  $P(E)$ , exhibits a very sharp maximum for some particular value  $\tilde{E}$  of the energy  $E$ .

To find the position of the maximum of  $P(E)$  or equivalently of the maximum of its loga-

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<sup>4</sup>I still haven't defined clearly what temperature is but I ask you to just hold on with me for another section or so and everything will become crystal clear.

<sup>5</sup>Notice the main difference with heat is characterized by the active nature of work compared to the automatic, passive process of heat transfer

<sup>6</sup>by working out the problems in section 2 you will find that  $\Omega(E)$  for the systems under consideration increases sharply by increasing  $E$

algorithm,<sup>7</sup> we need to find the value  $E = \tilde{E}$  such that:

$$\frac{d \ln P}{dE} = \frac{1}{P} \frac{dP}{dE} = 0 \quad (34)$$

Combining eq.32 and eq.33 we get:

$$\ln P(E) = \ln C + \ln \Omega(E) + \ln \Omega'(E') \quad (35)$$

Hence eq.34 becomes

$$\frac{\partial \ln \Omega(E)}{\partial E} + (-1) \frac{\partial \ln \Omega'(E')}{\partial E'} = 0 \quad (36)$$

or

$$\beta(\tilde{E}) = \beta'(\tilde{E}') \quad (37)$$

where  $\tilde{E}$  and  $\tilde{E}'$  correspond to the energies of  $A$  and  $A'$  at the maximum probability  $P(E)$ , and where we introduced the definition of a new quantity  $\beta$  with dimensions of a reciprocal energy:

$$\beta(E) = \frac{\partial \ln \Omega}{\partial E} \quad (38)$$

It is convenient to introduce a new *dimensionless* parameter  $T$ , known as the temperature of the system and defined as:

$$T = \frac{1}{k\beta} \quad (39)$$

$$\frac{1}{T} = \frac{\partial S}{\partial E} \quad (40)$$

where  $k$  is some the well known Boltzmann's constant having the dimensions of energy and we introduce another new quantity  $S$  known as the **entropy** of the system which is equal to  $S = k \ln \Omega$ .

We pointed out already that the maximum exhibited by  $P(E)$  at the energy  $\tilde{E}$  is very sharp, therefore there is a overwhelmingly large probability that at thermal equilibrium, the final energy of system  $A$  will be very closed to  $\tilde{E}$  and that of system  $A'$  will be very closed to  $\tilde{E}'$ . We can conclude then that at thermal equilibrium two conditions must be satisfied:

a)  $S_0 = S + S' = \text{maximum}$

b)  $T = T'$

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<sup>7</sup>we can make this assertion since changing from  $P(E)$  to  $\ln P(E)$  is a one to one mapping of a strictly increasing function which therefore does not change the location of the maximum

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### 3.2 Temperature & Entropy

We have now seen that particles and energy tend to rearrange themselves until the multiplicity  $\Omega$  is at (or very near) its maximum value. Notice that this condition is true, provided that we have enough particles and units of energy for the statistics of very large numbers to apply. That said, we have just stumbled upon a new law of physics, also known as the **second law of thermodynamics**:

The *spontaneous* flow of energy stops when a system is at, or very near, its *most likely* macrostate, that is, the macrostate with *greatest* multiplicity

Or more simply:

Multiplicity tends to increase

Now the intuition behind the definition of this new quantity, the **entropy**, is very simple. Since multiplicities tend to be very large numbers, which are very nasty to work with, it was found more convenient to work with the logarithm of the multiplicity instead of the multiplicity itself. For historical reasons it was also multiplied by the Boltzmann constant such that:

$$S = k \ln \Omega \quad (41)$$

In short, the entropy is just the logarithm of the number of ways of arranging the system (times the Boltzmann constant). Since the natural logarithm is a monotonically increasing function, a macrostate with higher multiplicity will also have higher entropy. We can thus restate the **second law of thermodynamics** in what is known as its most famous form:

Entropy tends to increase

The second condition for equilibrium, in subsection 3.1, is given in terms of the this new parameter  $T$ . If two systems, separately in equilibrium, are characterized by the same value of this parameter, then the systems will remain in equilibrium when brought into thermal contact with each other. From this definition it follows what is known as the **the zeroth law of Thermodynamics**:

If two systems are in thermal equilibrium with a third system, then they must be in thermal equilibrium with each other

On the other hand, if the two systems are characterized by different values of this parameter, they will *not* remain in equilibrium when brought in thermal contact. However, if these two systems are left in thermal contact long enough, eventually they will reach the equilibrium and will present a new and equal value of the parameter.

$T$  is known as the **temperature** of the system and, according to the discussion above, is, in a somewhat naive way, the “thing” that’s the same for two objects, after they have been in contact long enough.

To better understand the nature of this new thermodynamical concept we need to explore how it changes to bring the composite system to its most probable state. We know, according to the second law of thermodynamics, that in the process entropy needs to increase. We can then write this condition in the following form:

$$\Delta S + \Delta S' \geq 0 \quad (42)$$

$$\frac{\partial S(E_i)}{\partial E} \Delta E + \frac{\partial S(E'_i)}{\partial E} \Delta E' \geq 0 \quad (43)$$

Where  $\Delta E' = \Delta E$  since the composite system is isolated and thus the total energy transferred to one system has to be the same as the one given up by the other.

Now, without loss of generality, we can assume that in this process the energy transfer happens only *spontaneously* through heat  $Q$ . Thus, we can then rewrite eq.43 in the more compact form:

$$\left( \frac{1}{T_i} - \frac{1}{T'_i} \right) Q \geq 0 \quad (44)$$

Where we substitute  $\frac{1}{T} = \frac{\partial S}{\partial E}$ .

From this equation, it is clear that if  $Q \geq 0$  then  $T_i \leq T'_i$ . Hence, positive heat is always absorbed by the system at lower temperature and given off by the system at higher temperature. More generally if two objects are in thermal contact, the one that tends to *spontaneously* lose energy is that at the *higher* temperature. With this convention in mind let’s now restate the theoretical definition of temperature:

**Temperature** is the measure of the tendency of an object to spontaneously give up energy to its surroundings.

### 3.2.1 Limiting behaviour

The next question becomes what happens to the entropy and the temperature in the limiting case of very large and very small  $E$ .

As one goes to lower energy, every system described by quantum mechanics approaches the lowest possible energy  $E_0$  of its ground state. Corresponding to this energy there exists usually only one possible state, or there may be a relatively small number of degenerate states at energy  $E_0$ . Since  $S = k \ln \Omega$ , one can assert to excellent approximation that the entropy becomes vanishingly small as the system approaches its ground state energy.<sup>8</sup> In symbols:

$$\text{as } E \rightarrow E_0; \quad \Omega \rightarrow 1; \quad S \rightarrow 0 \quad (45)$$

<sup>8</sup>in the case of degenerate ground state, we can assert that as  $E \rightarrow E_0$   $S \rightarrow S_0$



This limiting behaviour of  $S$  can also be expressed in terms of the temperature of the system. From eq.44 we can show that  $\frac{\partial T}{\partial E} > 0$  which tells us that the temperature of a system has to increase with its energy.<sup>9</sup>

Hence it follows that as the energy decreases towards  $E_0$ ,  $T$  decreases and becomes very small. In the limiting case,  $T \rightarrow 0$ ,  $E$  must increasingly approach  $E_0$  and by virtue of eq.45, the entropy must then become negligibly small. Thus:

$$\text{as } T \rightarrow 0; \quad S \rightarrow 0 \quad (46)$$

This can also be seen as a particular instance of the **third law of thermodynamics**, in the case of no degeneracy at the ground state. More generally, the third law states that, given  $\Omega_0$  states at the lowest energy  $E_0$ , The entropy  $S$  of a system has the limiting property that:

$$\text{as } T \rightarrow 0_+; \quad S \rightarrow S_0 \quad (47)$$

where  $S_0$  is a constant independent of all parameters of the particular system.

### 3.3 More exam problems

#### 3.3.1 Exercise

Consider 2 Einstein solids:  $A$  (with  $N_A$  and  $q_A$ ) and  $B$  (with  $N_B$  and  $q_B$ ), together in an isolated system and let them exchange energy.

- If  $q_A + q_B = 100$  units,  $N_A = 300$ , and  $N_B = 100$ , how many units of energy are left in  $A$  at equilibrium?
- What is the maximum of the multiplicity of the combined system?
- What are the slopes  $\frac{\partial \ln \Omega_A}{\partial q_A}$  and  $\frac{\partial \ln \Omega_B}{\partial q_B}$  and how are they related to the maximum of  $\ln(\Omega_{\text{tot}})$ ?
- We now want to investigate the shape of the multiplicity near its peak. For simplicity, take the limit of  $q_A = q_B = \frac{q}{2}$ ,  $N_A = N_B = N$  with  $q_A \gg N_A$ . Expand around the maximum of the total multiplicity and give an expression for the dispersion in terms of  $q$  and  $N$ .

*Hint:* for part d) recollect the result found in exercise 2.2.1 for one solid.

#### 3.3.2 Exercise

Prove that  $\frac{\partial T}{\partial E} \geq 0$ .

*Hint:* it might be easier to start by showing  $\frac{\partial \beta}{\partial E} \leq 0$ . Think about what kind of shape should the probability distribution have and therefore what constraints need to be put for on the values of these partial derivatives.

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<sup>9</sup>if it's not completely clear why this is true, do not worry for now, you will prove it in one of the exercises at the end of the section!

### 3.3.3 Exercise

Given that  $\bar{p} = \frac{1}{\beta} \frac{\partial \ln \Omega}{\partial V}$ , prove the equation of state of a monoatomic ideal gas:

$$\bar{p}V = NkT \quad (48)$$

where  $N$  is the total number of molecules.

### 3.3.4 Exercise

Consider two spin systems  $A$  and  $A'$  placed in an external field  $H$ . System  $A$  and  $A'$  consist respectively of  $N$  and  $N'$  weakly interacting particles of spin  $\frac{1}{2}$  and magnetic moment  $\mu$  and  $\mu'$ . The two systems are initially isolated with respective total energies  $bN\mu H$  and  $b'N'\mu H'$ . They are then placed in thermal contact. Assume that  $|b| \ll 1$  and  $|b'| \ll 1$  so that you can apply the result found in part c) of exercise 2.1.1.

- In the most probable situation, how is the energy  $\tilde{E}$  of system  $A$  related to the energy  $\tilde{E}'$  of system  $A'$ ?
- What is the value of  $\tilde{E}$  of system  $A$ ?
- What is the probability  $P(E)dE$  that  $A$  has its final energy in the range between  $E$  and  $E + \delta E$ ?
- What is the dispersion  $\overline{(\Delta E)^2}$  in the final equilibrium situation?
- What is the value of the relative energy spread  $\frac{\overline{(\Delta E)^2}}{\tilde{E}}$  in the case when  $N' \gg N$ ?

### 3.3.5 Exercise

Show that the entropy of a spin chain is given by  $S = Nk[\ln(2 \cosh x) - x \tanh x]$  with  $x = \frac{\mu H}{kT}$ . What is  $S$  as  $T \rightarrow 0$  and  $T \rightarrow \infty$ ?

### 3.3.6 Exercise

A system consists of  $N_1$  molecules of type 1 and  $N_2$  molecules of type 2 confined within a box of volume  $V$ . The molecules are weakly interactive and constitute an ideal gas mixture.

- How does the total number of states  $\Omega(E)$  depends on the volume  $V$  of the system?

### 3.3.7 Exercise

A box is separated by a partition which divides its volume in the ratio 3 : 1. The larger portion contains 1000 molecules of  $Ne$  gas; the smaller contains 100 molecules of  $He$  gas. A small hole is punctured in the partition, and one waits until equilibrium is reached

- Find the mean number of molecules per type on both sides of the partition

- b) What is the probability of finding all 1000 molecules of  $Ne$  gas still in the larger portion and all 100 molecules of  $He$  gas in the smaller portion?

### 3.3.8 Exercise

Let's consider the thermal interaction between two systems where one is very much larger than the other. If the system  $A'$  is so large that its temperature parameter remains essentially unchanged, irrespective of any amount  $\Delta Q'$  which it may absorb, is then said to act as a **heat reservoir**, with respect to the small system  $A$ . In symbols this condition says that  $A'$  is such that:

$$\frac{\partial \beta'}{\partial E'} Q' \ll \beta' \quad (49)$$

Prove that  $\Delta S' = \frac{Q'}{T}$

### 3.3.9 Exercise

Recall the result you found in exercise 2.2.1 for the multiplicity an Einstein solid with  $N$  harmonic oscillators and  $q$  units of energy.

- a) Compute the Entropy of the system.
- b) We know that the mean energy of the system is  $\bar{E} = q\hbar\omega$ . Now let's define the heat capacity as  $C = \frac{\partial \bar{E}}{\partial T}$ . Prove that by expanding to second order in the energy level spacing,  $\frac{\hbar\omega}{kT}$ , that the heat capacity is given by:

$$C = Nk[1 - \frac{1}{12}(\frac{\hbar\omega}{kT})^2]. \quad (50)$$

- c) What happens at very low temperatures? Does it follow the 3rd law of Thermodynamics?