Density of states

In most of statistical mechanics that we learn we will be studying systems that are made up of point particles. Systems like ideal Maxwell gas, ideal Fermi gas and ideal Bose gas have particles as their constituents. This is so because particle picture always provides a good approximation for microscopic constituents of matter such as molecules or atoms.[1] Therefore we can say what the microstate of a gas is, if we know the microstate of each particle in it. The microstate of a particle, often referred to simply as the state of the particle, should give us every possible information relevant to describe its change with time. First we will learn how to specify the state of a particle that obeys Newton's law, usually called a *classical particle*. Later on we will take up the case of a *quantum particle* which obeys the more general laws of quantum mechanics.

States of a classical particle

As mentioned already, motion of a *classical particle* is governed by Newton's law.

$$\frac{d\mathbf{p}}{dt} = \mathbf{F} \tag{1}$$

where $\mathbf{p}$ is the linear momentum. For a particle of mass m the linear momentum is, of course, $\mathbf{p} = m\mathbf{v}$ in terms of the velocity $\mathbf{v}$ of the particle.

We will convince ourselves of this by considering a particle that moves in one-dimension, along just the X-axis, under various types of forces. (We will not need the vector notation for momentum in this case, as the momentum will only have one component).

- Free particle :

  When the particle feels no force, the Newton's law become simple

  $$\frac{dp_x}{dt} = 0 \tag{2}$$

  Clearly the velocity v and linear momentum $p = mv$ of this particle will remain constant. Its position $x(t)$ and velocity $p(t)$ at an instant of time t will be

  $$\begin{aligned} x(t) &= x(0) + vt = x(0) + \frac{p_x}{m} \\ v(t) &= v(0) = v = \frac{p_x}{m} \end{aligned} \tag{3}$$

  where $x(0)$ and $p(0)$ are its position and momentum at time $t = 0$.

[1] A point particle is one that has zero length when measured in any direction and thus occupy zero volume.

- Particle under a constant force:

  When the particle experience a constant force F, Newton's law looks

$$\frac{dp_x}{dt} = F \tag{4}$$

  The particle will have an acceleration $a = \frac{F}{m}$ and its position and velocity at a time t will be

$$\begin{aligned} x(t) &= x(0) + v(0)t + \frac{1}{2}at^2 = x(0) + \frac{p(0)}{m}t + \frac{1}{2}at^2 \\ v(t) &= \frac{p(0)}{m} + at \end{aligned} \tag{5}$$

- Particle under a simple harmonic force:

  When the particle experiences a simple harmonic force we have

$$\frac{dp_x}{dt} = -kx \tag{6}$$

  In this case the acceleration will vary with time. The position and velocity will be

$$\begin{aligned} x(t) &= x(0)\cos\omega t + \frac{p(0)}{m\omega}\sin\omega t \\ v(t) &= -x(0)\omega\ \sin\omega t + \frac{p(0)}{m}\cos\omega t \end{aligned} \tag{7}$$

  where the frequency of oscillation of the particle $\omega = \sqrt{\frac{k}{m}}$.

In all of the above examples one may notice that given the position and velocity of the particle at some initial time $t = 0$ that at any arbitrary instant t can be determined from the solutions in equations (3,5,7). We can say the pair of numbers that are the position and momentum of the particle specifies its state at any instant [2]. The solutions above implies that the state of a particle can be predicted at an instant t if it is known at some initial instant $t = 0$.

Phase space description

In a *phase space representation of the state* of a particle in one-dimension, one says the position and momentum (x, p_x) of the particle. If we choose x along the Cartesian X-axis and p_x along the Y-axis the resultant description of the state of the particle is called the *phase space*. Clearly, for a particle that could move in one space dimension, the phase space is two-dimensional.

If the particle is one that moves in all of the three space dimensions, its state will be represented by giving its position vector and momentum vector $(\mathbf{x}, \mathbf{p})$. In Cartesian coordinates, position is represented by three coordinates (x, y, z) and three momentum components

[2] Mathematically, this is a consequence of the fact that Newton's law, when stated in terms of position vector, is a second order differential equation.

(p_x, p_y, p_z). The phase space for this particle would be *six dimensional* - two for each space dimension. In below we consider the two examples to explain the phase space description of the dynamics of a classical particle.

(i) Free particle in one dimension

A particle that moves freely on a line of length L, bound by two elastic walls at $x = -\frac{L}{2}$ and $x = \frac{L}{2}$ will certainly have constant energy. The particle experience no force other than a contact force at the boundaries. Thus its energy must always be equal to its kinetic energy. In terms of the momentum p_x of the particle, the energy can be expressed as

$$E = \frac{p_x^2}{2m} \tag{8}$$

Since energy is a constant, the square of the momentum and absolute value of momentum will be a constant. However the momentum itself could change its sign when the particle gets reflected at the boundaries. The phase space description of the particle can be given by choosing its coordinate along the X-axis and the momentum along the Y-axis as shown in figure (1). [3]

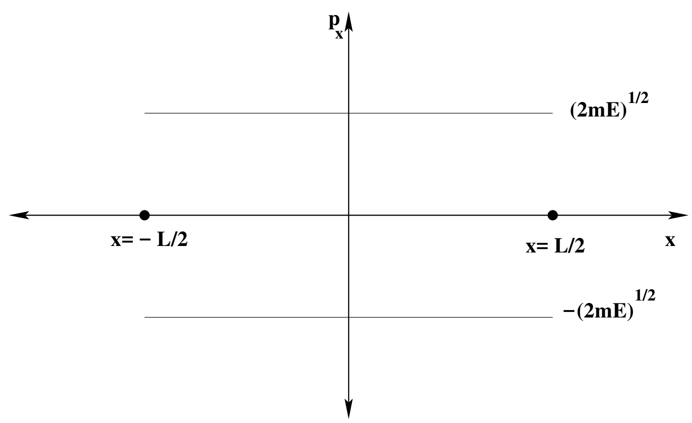

Figure 1: Phase space trajectory of free particle with energy E

All points along the phase space curve are all allowed states for the particle. Notice that if the walls were not there, the momentum of the particle (not just the magnitude of the momentum) would have been conserved too. Then the phase space description would consist of just a line parallel to the X-axis through $p = +\sqrt{2mE}$ if the particle is moving rightwards.

Suppose that we are not sure about the value of energy of the particle, except that it is between E and $E + dE$. What would the phase space trajectory that we could draw for this particle? Clearly the particle should be allowed all values of energy that lies in the interval $(E, E + dE)$ and nothing outside. The allowed states for this particle are those points with $\sqrt{2mE} \leq |p| \leq \sqrt{2m(E + dE)}$ and $-\frac{L}{2} \leq x \leq \frac{L}{3}$. The shaded area in the figure (2) represents all those states.

[3]Figures by Sreelakshmi M. Nair, MSc (Physics), U.C College

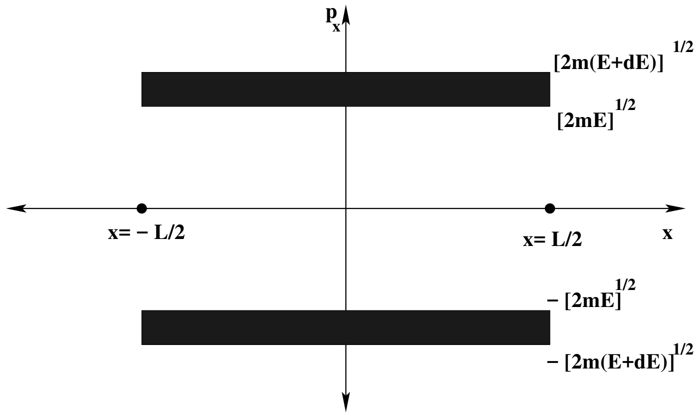

Figure 2: Phase space of free particle in one dimension with energy in the interval $(E, E+dE)$

(ii) Simple harmonic oscillator in one-dimension

For a simple harmonic oscillator of mass m with a fixed energy E we can always write

$$E = KE + PE = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 \tag{9}$$

Here p is its momentum and ω its frequency. In terms of its frequency, the force constant k can be expressed as $k = m\omega^2$.

It is straightforward to draw the phase space trajectory of the oscillator. The expression in equation (9) represents an ellipse in the p-x plane as in figure (3). Lengths of the semi-major axis and the semi-minor axis are $a = \sqrt{\frac{2E}{m\omega^2}}$ and $b = \sqrt{2mE}$ respectively. All points on the ellipse are allowed states for the particle. Again, for an oscillator

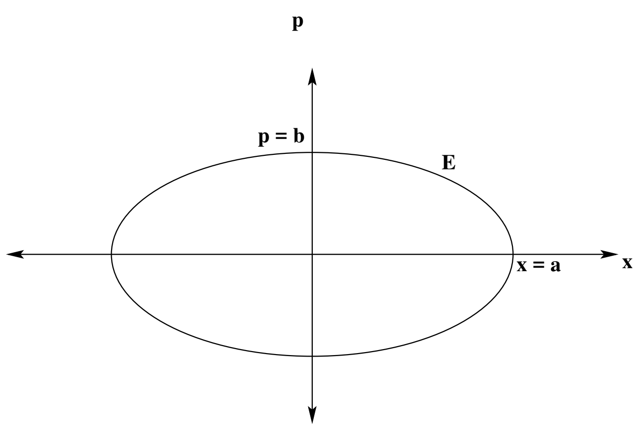

Figure 3: Phase space trajectory of a harmonic oscillator with energy E

with energy between E and $E + dE$ the phase space plot will be as in figure (4).

(iii) Free particle in a box

Now let us consider a more realistic system - a particle bound to move inside a cubical box of volume V, but otherwise free. The particle can move in three perpendicular

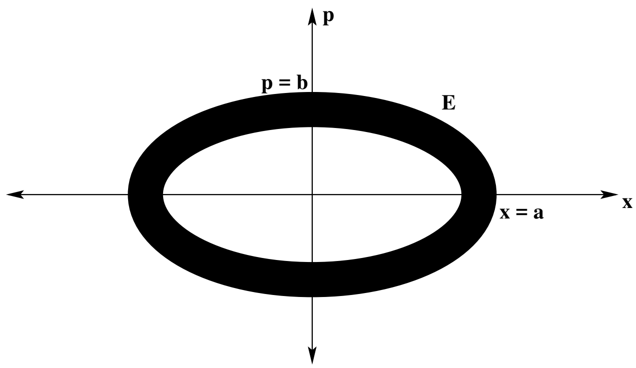

Figure 4: Phase space of a harmonic oscillator with energy between $(E, E + dE)$

directions and thus need three coordinates (x, y, z) to specify its position inside the box. Likewise its momentum will have three components (p_x, p_y, p_z). These position and momentum coordinates together specify its state at any instant of time. Being a free particle, its energy E is completely kinetic in nature. Thus

$$E = \frac{p_x^2 + p_y^2 + p_z^2}{2m} \tag{10}$$

To draw the phase space of this particle one needs a six mutually perpendicular axes. With every increasing dimension, the phase space adds two extra axes. Since the phase space is six dimensional, it is just not possible for us to represent this phase space in figures completely. For the free particle however there is a satisfactory way out. We note that the energy in equation (12) depends only on momentum components (p_x, p_y, p_z) for all values of position coordinates (x, y, z). Thus we could choose to represent only the momentum part of the phase space for any given value of energy. The expression in equation (12) represents the surface of a sphere of radius $\sqrt{E}$ in a space with (p_x, p_y, p_z) taken along three cartesian axis. The figure (5)

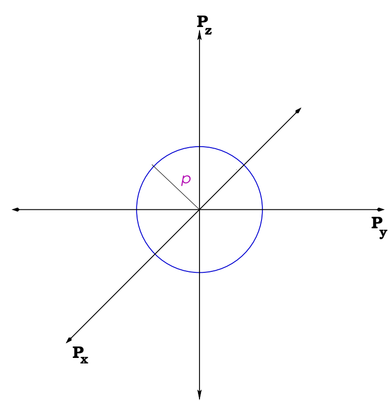

Figure 5: Phase space trajectory of free particle with energy E

This spherical surface is the momentum trajectory of the free particle in three dimensions. There is one such sphere for every position inside the box.

If we just know that the energy of the particle is between E and $E + dE$, the allowed phase space for the particle will be represented by all points between the spheres representing energy E and $E + dE$. Thus it will have the form of a spherical shell of inner radius $\sqrt{E}$ and outer radius $\sqrt{E + dE}$ as shown in figure (6).

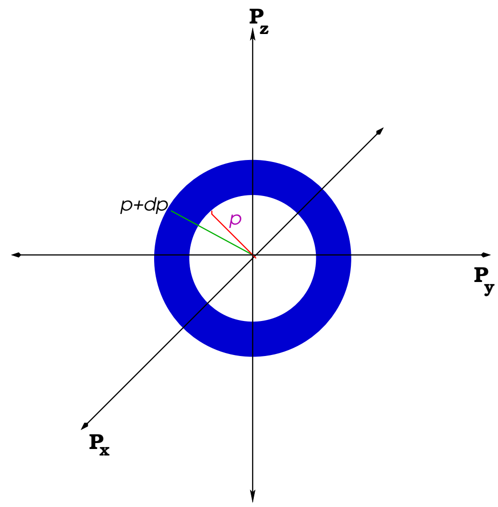

Figure 6: Phase space trajectory of free particle in 3D with energy between $(E, E + dE)$

Counting of microstates : Classical particle

(i) Free particle in one-dimension

Consider the free particle in one dimension, moving along X-axis between two perfectly elastic hard walls at $x = -\frac{L}{2}$ and $x = \frac{L}{2}$ having an energy between $(E, E + dE)$. Its phase space trajectory is as given in figure (2) above. As mentioned above, the allowed states of this particle are represented by points in the shaded region in figure (2). These states form the 'microstates' of this particle. Counting those microstates means counting the number of points in this region. How many point are these in the shaded region? An infinite number of them! In fact uncountably infinite. Then how do we count? Here we consider an analogy. Imagine that sand is spread in the shaded region with every grain of sand stuck to the paper leaving no gap between nearby ones. Now we can count the number of grains of sand in the shaded region. Assume that the grains of sand are all identical. Now if we know the area occupied by each grain of sand we can find their number by dividing the area of the shaded region with the area of each grain of sand. Thus if each state in the region were not points with zero area, but grains with finite area h we could count them. For simplicity let us assume that each grain of sand is a rectangle with sides parallel to X-axis and Y axis. If Δx and Δp_x respectively are the lengths of these sides then its area is

$$\Delta x \Delta p_x = h \tag{11}$$

We must divide the total area of the shaded region with h to find the number of states (grains) in there. In practice, what we have done is to assume that states are represented, not by points, but surfaces that have an area. This assumption is a trick that enabled counting of those states. In the end, classical states must be represented by points and thus the area of the phase space element h should be set to zero and it should not affect

The total area of the shaded rectangular region is

$$2L\ dp_x \tag{12}$$

where the the allowed momenta lies between p_x and $p_x + dp_x$.

From equation (8) we see that

$$dE = \frac{2p_x\ dp_x}{2m} \quad \Rightarrow \quad dp_x = \frac{mdE}{\sqrt{2mE}} = \sqrt{\frac{m}{2}}\frac{dE}{\sqrt{E}} \tag{13}$$

Substituting this into equation (12), we get the total area of the shaded region to be

$$2L\sqrt{\frac{m}{2}}\frac{dE}{\sqrt{E}} \tag{14}$$

Then the number of states in the shaded region is

$$\frac{L}{h}\sqrt{\frac{2m}{E}}dE \tag{15}$$

The factor $\frac{L}{h}\sqrt{\frac{2m}{E}}$ giving the number of states in unit energy interval at the energy value E is the *density of states* $\rho(E)$ for this particle. as shown in

(ii) Free particle in three dimensions

A free particle in a box of volume V having energy between $(E, E+dE)$, can be found in the states in the region shown in the figure XX above. To count the number of states we must again fix what is the "size" of one state. We will accept the value of phase space area element to be h as earlier. This means the following : for coordinate x and corresponding momentum p_x the smallest element in (x, p_x) plane has an area $\Delta x \Delta p_x$ of h. We have two more planes perpendicular to (x, p_x) : the (y, p_y) plane and (z, p_z) plane. Assume that the smallest elements in each of those planes also to have area h. We can imagine a box in our phase space made up of sheets that are parallel to the above planes. It will have a volume

$$(\Delta x \Delta p_x)(\Delta y \Delta p_y)(\Delta z \Delta p_z) = h^3 \tag{16}$$

This box is the smallest element of the six simensional phase space. It represents a "grain of sand" in the six dimensional phase space. This box represents a state in this phase space, just like the element $(\Delta x \Delta p_x)$ did for the two dimensional phase space.

Using this smallest element we can now count the number of states for our particle with energy between $(E, E + dE)$. The phase space description of this particle is the spherical shell described in figure (6) above. The number of states there can be determined by counting the number of "grains of sand" of volume h^3 each exist in that spherical shell in figure (6). Number of grains must be given by dividing the volume of the phase space $dV^{(D=6)}$ with the volume h^3 of each grain. The volume of the phase space consists a product of the volume of the box and the volume of the momentum space available for the particle with energy between E and $E + dE$.

$$dV^{(D=6)} = (dp_x dp_y dp_z)_{dE} \iiint_V dxdydz = V\,(dp_x dp_y dp_z)_{dE} \tag{17}$$

In the above, the integral over $dxdydz$ gave us the volume V of the box. We will now write volume of the momentum shell $(dp_x dp_y dp_z)_{dE}$ in terms of magnitude $p = |\mathbf{p}| = \sqrt{p_x^2 + p_y^2 + p_z^2}$ of the momentum vector as

$$(dp_x dp_y dp_z)_{dE} = 4\pi p^2 dp \tag{18}$$

Thus the volume of the phase of the the particle becomes

$$dV^{(D=6)} = V\left(4\pi p^2 dp\right) \tag{19}$$

Dividing the above answer with the volume h^3 of the smallest part of the phase space we get the number of states in the spherical shell as

$$\frac{V}{h^3} 4\pi p^2 dp \tag{20}$$

We could also write the number of states in terms of energy E. Noting that $p^2 = p_x^2 + p_y^2 + p_z^2 = 2mE$ according to equation (9). This gives us the momentum interval dp in terms of energy interval dE as follows

$$\begin{aligned} 2pdp &= 2mdE \\ \Rightarrow\ dp = \frac{2mdE}{2p} &= \sqrt{\frac{m}{2E}}dE \end{aligned} \tag{21}$$

Substituting this along with equation (9) into equation (20) we get

$$\frac{4\pi V}{h^3}\sqrt{2m^3E}dE = \rho(E)dE \tag{22}$$

as the number of states of a free particle in three dimensions having energy between $(E, E+dE)$. The factor $\rho(E)$ gives the number of microstates in a unit energy interval around energy value E. It is often called the *density of states*. As we can see the density of states for a free particle in three dimensions is proportional to $\sqrt{E}$.

(iii) N free particles in three dimensions

Finally we take up a system that we study in thermodynamics - N *identical* free particles in a box of volume V. When N is of the order of Avogadro's number, we call this an *ideal gas*. The state of such a system is specified provided we give state of each of the N particles as $(x^{(1)}, y^{(1)}, z^{(1)}, p_x^{(1)}, p_y^{(1)}, p^{(1)_z})$, $(x^{(2)}, y^{(2)}, z^{(2)}, p_x^{(2)}, p_y^{(2)}, p^{(2)_z})$, ..., $(x^{(N)}, y^{(N)}, z^{(N)}, p_x^{(N)}, p_y^{(N)}, p^{(N)_z})$. As we can see, there are of $6N$ quantities. Thus the phase space of N particles is $6N$ dimensional. We can generalize a lot of what we learned in the case of one free particle inside the box to this case. If these N particles cannot exchange energy with anything outside the box, their total energy E will be conserved. Moreover since they are all free we can write their energy as the sum of their kinetic energies as

$$\sum_{i=1}^{N} \frac{(p_x^{(i)})^2 + (p_y^{(i)})^2 + (p_z^{(i)})^2}{2m} = \frac{p^2}{2m} = E \tag{23}$$

in terms of the momentum components of each of the N particles. Analogous to the previous case, this equation represents a sphere of radius $\sqrt{2mE}$ in $3N$ dimensional momentum space.

If the N particles are allowed energy values between $(E, E + dE)$ the allowed configurations would lie in a spherical shell again in the $3N$ dimensional momentum space mentioned above. Volume of the smallest phase space element (grain of sand) in $6N$ dimensional phase space is easily seen to be

$$\begin{aligned}&\left(\Delta x^{(1)} \Delta p_x^{(1)}\right) \cdot \left(\Delta y^{(1)} \Delta p_y^{(1)}\right) \cdot \left(\Delta z^{(1)} \Delta p_z^{(1)}\right) \\ &\qquad \left(\Delta x^{(2)} \Delta p_x^{(2)}\right) \cdot \left(\Delta y^{(2)} \Delta p_y^{(2)}\right) \ldots \qquad \left(\Delta z^{(N)} \Delta p_z^{(N)}\right) = (h^3)^N = h^{3N}\end{aligned} \tag{24}$$

The above expression generalizes the expression 11 for 2 dimensional phase space and 16 for 6 dimensional phase space to the case of $6N$ dimensional phase space.

The number of states here could be counted by first finding the volume $dV^{(D=6N)}$ of that phase space. This can be found by multiplying the volume of allowed states in the momentum space for the N particles with the volume allowed for each of the N particles, ie., V^N. Explicitly,

$$\begin{aligned} dV^{(D=6N)} &= V^N \times \text{ Volume of the } 3N\text{-dimensional momentum shell} \\ &= V^N \frac{2\pi^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}\right)} p^{3N-1} dp \end{aligned} \tag{25}$$

Here p is the magnitude of the $3N$ dimensional "momentum vector" in equation (23). The function $\Gamma(\alpha)$ is called the Gamma function. It obeys the recursion relation

$$\Gamma(\alpha) = (\alpha - 1)\Gamma(\alpha - 1) \tag{26}$$

For integer α, $\Gamma(\alpha) = (\alpha - 1)!$
Also one can evaluate $\Gamma(\frac{1}{2}) = \sqrt{\pi}$.

From the above, the number of microstates corresponding to the above phase space region turns out to be

$$\frac{1}{h^{3N}} V^N \frac{2\pi^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}\right)} p^{3N-1} dp \tag{27}$$

Expressed as a function of energy using equation (23), we get the number of microstates between energy values $(E, E + dE)$ to be

$$\frac{1}{h^{3N}} dV^{(D=6N)} = \left(\frac{4\pi m}{h^2}\right)^{\frac{3N}{2}} \frac{V^N}{2\Gamma\left(\frac{3N}{2}\right)} E^{\frac{3N}{2}-1} dE = \rho(E)\, dE \tag{28}$$

We can identify the density of microstates for N particles in a box of volume V to be

$$\rho(E) = \left(\frac{4\pi m}{h^2}\right)^{\frac{3N}{2}} \frac{V^N}{2\Gamma\left(\frac{3N}{2}\right)} E^{\frac{3N}{2}-1} \tag{29}$$

Note that if we put $N = 1$ in equations (27) and (28), we get back the number of states for one particle in a three dimensional box that we found already in equations (20) and (22) respectively. This is a cross check for the expression for density of states that we derived.