

## CHAPTER I

# The Classical Framework

[Particles and Waves]

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*“Every description of natural processes must be based on ideas which have been introduced and defined by the classical theory”.* (Niels Bohr)

Beginning with the base created by Galileo Galilei (1564-1642) and Isaac Newton (1642-1727) and developed by the great savants of the eighteenth and nineteenth centuries [such as Lagrange (1736-1813), Euler (1707-1783), Laplace (1749-1837), d’Alembert (1717-1783), Poisson (1781-1840), Gauss (1777-1855), Hamilton (1805-1865), Michael Faraday (1791-1867) and James Clerk Maxwell (1831-1879)] one had at the eve of the twentieth century a beautiful and consistent framework that seemed to explain satisfactorily all observed physical phenomena that mankind was conscious of till that time. This structure was the Classical Mechanics of Particles, Rigid Bodies, Continuous Media and Fields.

- The cornerstone of this edifice was the **Newton’s Equation of Motion** :

$$\frac{d}{dt}\vec{P}_i = \vec{F}_i$$

The time rate of change of the momentum ( $\vec{P}_i = m_i \frac{d}{dt}\vec{r}_i$ ) of the  $i$ -th particle in a system of particles ( $m_i$  being its mass and  $\vec{r}_i$  its position vector specifying its location) is equal to the net force  $\vec{F}_i$  acting on it. Here by a particle is meant a point entity which possesses, however, a mass. A tangible body could be modelled as a composite of such point particles. The equation of motion holds in an inertial frame of reference which is one wherein a particle with no ascribable forces acting on it would continue to be in the state of rest or in a state of uniform rectilinear motion. Such a frame of reference could be imagined to be one far far away from all matter (and hence with no ascribable forces therein) or one in uniform rectilinear motion with respect to that.

- Equivalently one may describe the dynamics of a system of  $N$  particles (say) moving in three dimensions [ $3N$  co-ordinates  $\vec{r}_i = (x_i, y_i, z_i)$  with  $i = 1, 2 \dots N$ ] subject to some constraints (say  $c$  in number) through  $f = 3N - c$  **independent generalized co-ordinates**  $q_k$  ( $k = 1, \dots f$ ) ( $f$  = number of degrees of freedom) and corresponding generalized velocities  $\dot{q}_k = \frac{d}{dt}q_k$ . The **d’Alembert Principle of Virtual Work** enables one to introduce the notion of the generalized force  $F_k$  and for a conservative system these forces are derivable as the negative gradient of the potential  $V$  viz.  $F_k = -\frac{\partial}{\partial q_k}V$ . The state of the system at a given time  $t$  is described by specifying the generalized co-ordinates and velocities  $\{q_k, \dot{q}_k\}$ , and the time evolution of the state is most elegantly expressed in terms of the Lagrangian  $L$  defined through

$$L(\{q_k, \dot{q}_k\}, t) = T - V$$

where  $T$  and  $V$  are the kinetic and potential energies respectively. The Newton's Equation of Motion may be re-expressed in the form of the **Lagrange Equations of Motion**

$$\frac{\partial L}{\partial q_k} = \frac{d}{dt} \frac{\partial L}{\partial \dot{q}_k}$$

• The Lagrange equations of motion can be recast as a variational principle. The **Hamilton's Principle of Least Action** states that a system with co-ordinates  $\{q_k(t_i)\}$  at some initial time  $t_i$  and landing up with co-ordinates  $\{q_k(t_f)\}$  at some later time  $t_f$  shall follow such a path in the space of the co-ordinates so as to extremize the integral

$$S = \int_{t_i}^{t_f} dt L(\{q_k, \dot{q}_k\}, t)$$

viz.

$$\delta S = 0$$

Here  $S$ , known as the action, has the dimensions of energy times time or  $ML^2T^{-1}$ .

To extremize the functional  $S$  (a functional is a function of a function) with respect to the functions  $q_k(t)$  viz. the variation of the path, we use the Calculus of Variations. Consider arbitrary variations  $\delta q_k(t)$  in the paths joining the given initial and final positions viz. with end points  $q_k(t_i)$  and  $q_k(t_f)$  fixed, that is  $\delta q_k(t_i) = 0 = \delta q_k(t_f)$ . Note that  $\delta \dot{q}_k(t) = \frac{d}{dt} \delta q_k(t)$  as once a variation in path is considered the change in the slopes are simply the derivatives of this variation. Thus extremization of  $S$  with respect to variations in path implies

$$\begin{aligned} \delta S = 0 &\Rightarrow 0 = \delta \int_{t_i}^{t_f} dt L(\{q_k, \dot{q}_k\}, t) \\ &= \int_{t_i}^{t_f} dt \sum_k \left\{ \frac{\partial L}{\partial q_k} \delta q_k + \frac{\partial L}{\partial \dot{q}_k} \delta \dot{q}_k \right\} = \int_{t_i}^{t_f} dt \sum_k \left\{ \frac{\partial L}{\partial q_k} \delta q_k + \frac{\partial L}{\partial \dot{q}_k} \frac{d}{dt} \delta q_k \right\} \end{aligned}$$

Integrating the second term in the integrand (last step above) by parts

$$\int_{t_i}^{t_f} dt \frac{\partial L}{\partial \dot{q}_k} \frac{d}{dt} \delta q_k = \left[ \frac{\partial L}{\partial \dot{q}_k} \delta q_k \right]_{t_i}^{t_f} - \int_{t_i}^{t_f} dt \frac{d}{dt} \frac{\partial L}{\partial \dot{q}_k} \delta q_k = - \int_{t_i}^{t_f} dt \frac{d}{dt} \frac{\partial L}{\partial \dot{q}_k} \delta q_k$$

as  $\delta q_k = 0$  at the end-points  $t_i$  and  $t_f$ . Thus we arrive at

$$0 = \int_{t_i}^{t_f} dt \sum_k \left\{ \frac{\partial L}{\partial q_k} - \frac{d}{dt} \frac{\partial L}{\partial \dot{q}_k} \right\} \delta q_k$$

Since the integral must vanish for arbitrary  $\delta q_k$  the only way this can happen is for the expression in curly brackets to be equal to zero. Thus the Hamilton's Principle of Least Action gives us the Lagrange Equations of Motion which in turn follow from the Newton's Equation of Motion.

• Another reformulation of Classical Mechanics was again effected by William Rowan Hamilton. Introducing momenta  $p_k$  (termed as) canonically conjugate to the co-ordinate  $q_k$  via  $p_k = \frac{\partial L}{\partial \dot{q}_k}$ , the independent variables  $q_k$  and  $\dot{q}_k$  of the Lagrangian approach are traded for the independent variables  $q_k$  and  $p_k$  through the introduction of the Hamiltonian

$$H = -L + \sum_k p_k \dot{q}_k$$

which is then re-expressed in terms of  $q_k$  and  $p_k$ . The second-order Lagrange equations of motion are then translated into pairs of the **Hamilton's Equations of Motion**.

$$\dot{q}_k = \frac{\partial H}{\partial p_k}$$

$$\dot{p}_k = -\frac{\partial H}{\partial q_k}$$

• The Hamilton's Equation of Motion may be elegantly restated through the introduction of what are known as **Poisson brackets** which for any two dynamical variables  $A(\{q_k, p_k\})$  and  $B(\{q_k, p_k\})$  is defined through

$$[A, B]_{PB} = \sum_k \left( \frac{\partial A}{\partial q_k} \frac{\partial B}{\partial p_k} - \frac{\partial A}{\partial p_k} \frac{\partial B}{\partial q_k} \right)$$

Note that the Poisson bracket of a co-ordinate and its canonically conjugate momentum is unity.

$$[q_k, p_l]_{PB} = \delta_{kl}$$

where  $\delta_{kl}$  is the Kronecker delta which is unity if  $k = l$  & zero otherwise. The equations of motion in this formalism become

$$\dot{q}_k = [q_k, H]_{PB}$$

$$\dot{p}_k = [p_k, H]_{PB}$$

as can easily be checked to be nothing but the Hamilton's equations of motion using the definition of the Poisson bracket.

• Alternative ways of re-expressing mechanics is through a change from one set of canonically conjugate co-ordinates and momentum ( $\{q_k, p_k\} : [q_k, p_j]_{PB} = \delta_{ij}$ ) to another ( $\{Q_k, P_k\} : [Q_k, P_j]_{PB} = \delta_{ij}$ ) vide what is known as a **Canonical Transformation**. One such Canonical Transformation leads to the **Hamilton-Jacobi Formulation of Classical Mechanics**.

• From the mechanics of particles Leonard Euler and others developed the dynamics of rigid bodies (modelled as a system of particles constrained to move with the relative distance between each pair of constituent particles fixed). Similarly the mechanics of continuous fluids was also described by taking the distance between constituent particles (freely moving) to go to zero and at the same breath taking their masses to go to zero such that the mass per unit volume goes to a finite limit, the density of the fluid (taking the so-called hydrodynamical limit). One thus has the **Mechanics of Continuous Media** and also the **Theory of Fields**. Here in particular the physics of Electricity and Magnetism was captured through the work of Coulomb, Ampere, Gauss, Michael Faraday and others culminating in the **Maxwell's Equations for the Electromagnetic Field**,

• Another important area of advance was in the physics of matter in bulk described through **Thermal Physics**, whereby such a system, rather than being described through the detailed motion of its constituent 'particles', was characterised by gross variables such as its volume ( $V$ ), pressure ( $P$ ), temperature ( $T$ ), etc. Heat was recognized as a form of energy residing in the chaotic motion of the atoms and molecules of the system. The **Laws of Thermodynamics** were formulated. The first law was simply an expression of the conservation of energy stating that the heat ( $\Delta Q$ ) added to a system equals the sum of the change in its internal energy ( $\Delta U$ ) and the work ( $\Delta W$ ) done by the system ( $\Delta Q = \Delta U + \Delta W$ ), and the second law which is best formulated through the notion of entropy ( $S$ ) or degree of disorder in the system, a non-decreasing quantity in any change. These developments are associated with the names of Clausius, Kelvin and others. Maxwell

and Boltzmann and later Gibbs among others developed **Statistical Mechanics** which aims at providing a probabilistic interpretation of thermodynamics linking it to discussions of the most probable states of molecules obeying at its basis, however, the detailed mechanics of particles. Thus the relative probability that a system in equilibrium at a temperature  $T$  shall have an energy  $E$  is given by  $e^{-\frac{E}{k_B T}}$  where  $k_B$  is the Boltzmann constant.

While in the above discussion (on what we have called the Classical Framework) we have emphasised the conceptual aspects, one should also recognise that this development went hand in hand with diligent and imaginative experimentation and did also involve speculations and delving into the very nature of matter. It is therefore appropriate to add a few words on the classical view on the level of the nature of substance. Thus Newton with his Laws of Motion and his Universal Theory of Gravitation was able to explain the motion of the earth, of the moon and the planets, as also the tides in the oceans and the law of falling bodies on earth. Yet he went on to speculate on the nature of light (he adopted the corpuscular theory of light in that he conjectured that light rays consist of particles). Having observed the phenomenon of refraction of light he put forward the hypothesis that different colours corresponded to corpuscles of different sizes which while moving with the same speed in vacuum travel\* with different speeds in matter and hence one has refraction. This view was contested by Huyghens and also by Young who through his observations on interference phenomena (particularly the double slit experiment) argued cogently that this could be accounted for if light consisted of waves. Newton with his predilection for particles was also a staunch atomist and was sharply critical of those who believed in a continuum theory of matter. Indeed it is instructive to quote from his Optiks (Book 3, Part I):

*‘Quest 31. Have not the small Particles of Bodies certain Powers, Virtues or Forces, by which they act at a distance, not only upon the Rays of Light for reflecting, refracting and inflecting them, but also upon one another for producing a great Part of the Phenomena of Nature? For it is well known that Bodies act upon one another by the Attractions of Gravity, Magnetism and Electricity, and these Instances show the Tenor and Course of Nature, and make it not improbable that there be more attractive Powers than these ... The Attraction of Gravity, Magnetism and Electricity, reach to very sensible distances, and so have been observed by vulgar eyes, and there may be others which reach to so small distances as hitherto escape Observations ...’*

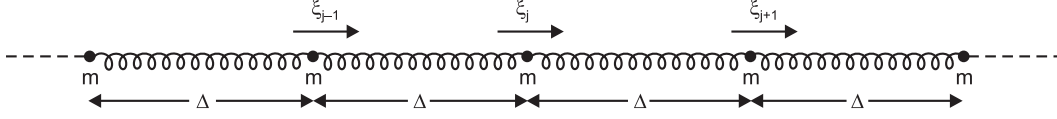
Most of the development in the understanding of the existence and the nature of atoms before Rutherford and Bohr was derived from the study of chemical reactions. A short note on the underlying history is given at the end of this Chapter.

## Appendix IA

As a prototype of continuum mechanics we discuss the longitudinal vibrations of a continuous elastic string, starting with a necklace of point particles (beads) of mass  $m$  connected to each other by massless springs of length  $\Delta$  which on elongation gives rise to restoring forces proportional to the extension (with Hooke’s constant  $\kappa$  say), and then going to the continuum limit. Consider each bead displaced from its equilibrium position by an amount  $\xi_j$  (in the case of the  $j$ th bead say). As far as the  $j$ th bead is concerned it experiences a force  $-\kappa(\xi_j - \xi_{j+1})$  due to the spring connected to its neighbour on the right and  $-\kappa(\xi_j - \xi_{j-1})$  due to that on the left.

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\*Interestingly this he based on his observations on the eclipses of the moons of Jupiter looking for possible colour by colour re-appearance of light after the eclipse which would have been the case had different colours moved with different velocities in vacuum. That such would not be easily detected, even if it were the case, was not clear at that time



**Fig.1.** Dynamics of a Necklace of Beads joined by Massless Springs

Consequently the Newton's Equation of Motion for the  $j$ th bead is

$$m \frac{d^2 \xi_j}{dt^2} = \kappa \{ (\xi_{j+1} - \xi_j) - (\xi_j - \xi_{j-1}) \}$$

Now we want to make this necklace of beads (say  $N$  beads in all and  $N - 1$  springs) to approach a continuous string of length  $L$ . In order to do that we need to take  $N \rightarrow \infty$ ,  $\Delta \rightarrow 0$  such that  $(N - 1)\Delta \rightarrow L$  and also  $m \rightarrow 0$  with  $m/\Delta \rightarrow \rho$  the mass per unit length of the string and moreover  $\kappa\Delta \rightarrow T$  the tension on the string. We then have a continuous string of length  $L$  with mass per unit length  $= \rho$ . Accordingly, the ordinal number of the beads ( $j$ ) must be replaced by (or promoted to) the continuous variable  $x$  measured along the string and thus  $\xi_j \rightarrow \xi(x)$ , the displacement at the point  $x$  along the string. Thus,

$$\xi_j \rightarrow \xi(x, t)$$

$$\xi_{j+1} \rightarrow \xi(x + \Delta, t) = \xi(x, t) + \Delta \frac{\partial}{\partial x} \xi(x, t) + \frac{\Delta^2}{2} \frac{\partial^2}{\partial x^2} \xi(x, t) + \dots$$

$$\xi_{j-1} \rightarrow \xi(x - \Delta, t) = \xi(x, t) - \Delta \frac{\partial}{\partial x} \xi(x, t) + \frac{\Delta^2}{2} \frac{\partial^2}{\partial x^2} \xi(x, t) + \dots$$

where appropriate Taylor's expansions have been instituted. These expressions when inserted into Newton's equation for the discrete system and the limit  $\Delta \rightarrow 0$  (with  $\frac{m}{\Delta} \rightarrow \rho$ ) taken, results in the partial differential equation

$$\rho \frac{\partial^2}{\partial t^2} \xi(x, t) = T \frac{\partial^2}{\partial x^2} \xi(x, t)$$

which is nothing but an equation for longitudinal waves along a continuous string. These waves would have a velocity  $v = \sqrt{\frac{T}{\rho}}$ .

Note that this system now has infinite degrees of freedom (as we have taken  $N \rightarrow \infty$ ) and thus, as a result, in order to specify the state of the string at any given time  $t$  we have to provide the values of  $\xi$  and  $\dot{\xi} = \frac{\partial \xi}{\partial t}$  at that instant at every point  $x$  along the string.

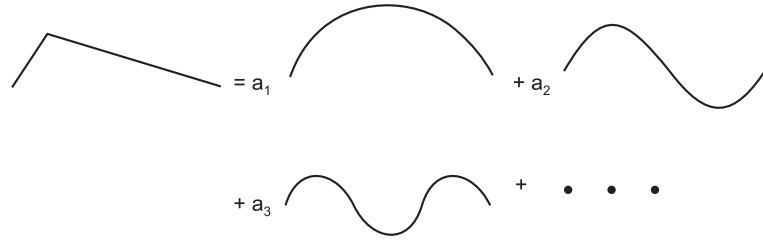
The same type of equation is also obtained for transverse vibrations of a string provided the displacements are not too large. Thus for a sonometer or a stringed musical instrument (such as a sitar) we may introduce modes of vibration of the string (viz. the fundamental and its harmonics or overtones) which are a basic set of solutions. In the case when the two ends of the string are fixed these may be taken to be standing waves of the form

$$\xi_n(x, t) = \sin\left(\frac{n\pi x}{L}\right) \cos(\omega_n t)$$

where  $n$  is an integer which guarantees the satisfaction of the boundary condition that  $\xi_n(x = 0, t) = 0 = \xi_n(x = L, t)$ ; and in order for it to be a solution of the wave equation we must have  $\rho\omega_n^2 = T\frac{n^2\pi^2}{L^2}$  or  $\omega_n = vk_n$  where  $\nu_n = \frac{\omega_n}{2\pi}$  is the frequency and  $k_n = \frac{2\pi}{\lambda_n}$  is the wave number, and of course  $\nu_n\lambda_n = v$  is the velocity of the wave. Any initial configuration of the plucked string

$\xi(x, t = 0)$  (as shown in the figure above) can be expanded via the Fourier Series into the normal modes:

The plucked string at a later time  $t$  shall evolve into  $\xi(x, t) = \sum_{n=0}^{\infty} a_n \sin(\frac{n\pi x}{L}) \cos(\omega_n t)$ .



**Fig.2.**  $\xi(x, t = 0) = \sum_{n=0}^{\infty} a_n \xi_n(x, t = 0) = \sum_{n=0}^{\infty} a_n \sin(\frac{n\pi x}{L})$

Often we are not interested in end effects and we want a string which is infinite or a string without ends. This is easily achieved by just identifying (joining) the two ends of the string of length  $L$  via periodic boundary conditions.

$$\xi(x = 0, t) = \xi(x = L, t)$$

We may look for travelling wave harmonic solutions  $\xi_{k,\omega}(x, t) = a_k e^{i(kx - \omega t)}$ . Here  $k$  is the wave-number viz.  $\lambda = \frac{2\pi}{k}$  is the wavelength (the distance marking the periodicity of  $\xi$  in  $x$ ). Also  $\nu = \frac{\omega}{2\pi}$  is the frequency,  $\frac{2\pi}{\omega}$  is the period in time after which at any given  $x$  the wave returns to its previous value. Of course  $e^{i(kx - \omega t)}$  is a solution of the wave equation provided  $\nu\lambda = \frac{\omega}{k} = v = \sqrt{\frac{T}{\rho}}$  (the wave velocity). Since  $\omega$  versus  $k$  is a straight line ( $\omega = v k$ ) we have what is called a linear dispersion curve which is to say that the wave-velocity ( $\frac{\omega}{k}$ ) is independent of the wave-length. Enforcing the periodic boundary condition  $\xi_{k,\omega}(x = 0, t) = \xi_{k,\omega}(x = L, t)$ , we see that we must have  $e^{ikL} = 1$  or  $kL = 2n\pi$ , where  $n$  is an integer. Thus we find that between the fundamental with wave-number  $2\pi/L$  and some wave-number  $k$  there are  $n = \frac{kL}{2\pi}$  modes. Therefore the number of modes (with periodic boundary conditions imposed) with wave-numbers between  $k$  and  $k + dk$  are

$$dn = \frac{L}{2\pi} dk$$

At any given time  $t$  the configuration of the string  $\xi(x, t)$  may be expanded into the modal functions

$$\xi(x, t) = \sum_{n=-\infty}^{n=+\infty} \xi_n(t) e^{ik_n x}$$

where  $k_n = n \cdot (\frac{2\pi}{L})$  are the wave-numbers of the modes. Also note that as  $\xi$  must be real  $\xi_n^* = \xi_{-n}$ . Instead of describing the system by  $\xi(x, t)$  we may equally well regard the Fourier components  $\xi_n(t)$  as the dynamical variables of the system. Substitution of the Fourier expansion of  $\xi$  into the wave-equation yields

$$\frac{d^2}{dt^2} \xi_n = -\omega_n^2 \xi_n$$

as the different modes are independent (here  $\omega_n^2 = v^2 k_n^2$ ). Note that the displacements  $\xi_n(t)$  corresponding to each mode behaves simply like a simple harmonic oscillator with its characteristic angular frequency  $\omega_n$ .

We thus have the equations of motion of a bunch of oscillators. Continuous systems such as strings and fields satisfying such wave-equations can thus alternatively be looked upon as a collection of an infinite number of oscillators corresponding to the different modes.

## Exercises

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*A pre-requisite of any course on Quantum Mechanics is familiarity with Classical Mechanics which you already have. Chapter I has been included just to remind you of what you have studied earlier and we are providing the following sample problems as exercises*

1. Consider a particle of mass  $m$  moving in one dimension under the action of a force proportional to the its displacement  $x$  from the origin and directed towards the origin (viz.  $F = -\kappa x$ ).
  - (a) Set up Newton's Equation of Motion for this system and solve it to obtain the solution  $x = A\cos(\omega t + \theta)$  where  $A$  and  $\theta$  are constants of integration and  $\omega = \sqrt{\frac{\kappa}{m}}$  is the so called classical frequency. What is the kinetic energy of the particle? What is its potential energy? What is its total energy? What is the average kinetic energy over a cycle?
  - (b) What is the Lagrangian for this system and what is the Lagrange's Equation of Motion?
  - (c) What is the momentum canonically conjugate to the coordinate  $x$ ? What is the Hamiltonian and what are the Hamilton's equations of motion for this system?
  
2. Consider a particle of mass  $m$  constrained to move along a circular hoop of radius  $a$  kept fixed in a vertical plane, at the surface of the earth (with a gravitational force  $\vec{F} = -mg\hat{k}$ , where  $\hat{k}$  is the unit vector upwards and  $g$  is the acceleration due to gravity). What is the total number of constraints? What is a convenient choice of generalized coordinate(s)? Set up the Lagrangian of the system. What is the canonically conjugate momentum? What is the Hamiltonian of the system? Write down the equation of motion.
  
3. Consider two particles of masses  $m_1$  and  $m_2$  moving in three dimensions [coordinates  $\vec{r}_1$  and  $\vec{r}_2$ ] interacting with each other via a potential  $V(\vec{r}_1, \vec{r}_2)$ . Show that if the system is to be displacement invariant (viz. independent of the choice of origin of coordinates) then the potential must be a function of  $\vec{r} = \vec{r}_1 - \vec{r}_2$ . Furthermore, if one has to have isotropy (independence with respect to the orientation of the coordinate axes) and there are no other intrinsic vectors of the particles<sup>†</sup>, show that the potential must be a function of  $r = |\vec{r}|$  viz. the force is what is known as 'central'. Set up the Lagrangian for such a system of two particles interacting through a central force. Make a transformation from  $\vec{r}_1, \vec{r}_2$  to  $\vec{r} = \vec{r}_1 - \vec{r}_2$ ,  $\vec{R} = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1 + m_2}$  in the Lagrangian. Find the momenta  $\vec{p}$  and  $\vec{P}$  canonically conjugate to  $\vec{r}$  and  $\vec{R}$ . This 'canonical transformation' is known as the laboratory to centre-of-mass transformation. Introduce the notation  $m = \frac{m_1 m_2}{m_1 + m_2}$  called the reduced mass.

<sup>†</sup> *Foot-note to this question:* Suppose the two particles had magnetic moments  $\vec{\mu}_1$  and  $\vec{\mu}_2$  what would be the force due to the magnetic interaction between the two, and what is the corresponding potential? This is to make you appreciate the fact that there could be non-central interactions too consistent with over all isotropy. Explain why this is consistent with over all isotropy.

4. Show that for the Kepler Problem [viz. potential  $V(r) = -\frac{\kappa}{r}$  following the notation of the previous exercise] apart from the orbital angular momentum  $\vec{\mathcal{L}} = \vec{r} \times \vec{p}$ , the vector  $\vec{A} = \frac{\vec{p} \times \vec{\mathcal{L}}}{m} - \kappa \frac{\vec{r}}{r}$  is also a constant of the motion. Show that  $\vec{A}^2 = \frac{2E\mathcal{L}^2}{m} + \kappa^2$  (here  $E$  is the energy). Calculate  $\vec{A} \cdot \vec{r}$  and

hence obtain the polar form of the elliptic orbit (for  $E < 0$ ) and demonstrate that  $\vec{A}$ , the so-called Runge-Lenz vector, is a constant vector pointing along the major axis of the elliptic orbit.

5. Consider the necklace of beads each of mass  $m$  jointed to each other by weightless string segments of length  $\Delta$  (providing tension  $T$ ) as discussed in the Appendix. Set up the Lagrangian of the system. Go to the limit  $\Delta \rightarrow 0$  and  $m \rightarrow 0$ :  $m/\Delta \rightarrow \rho$  and introduce the notion of a Lagrangian density. Obtain the Euler-Lagrange equation that minimizes the Action here to arrive at the wave equation for a substantive string. Introduce the momentum variable conjugate to  $\xi$  (in the notation of Appendix IA) and hence obtain the Hamiltonian density of the string and go on to write out the Hamilton's equations of motion for the string.

6. Suppose a system of free particles in one dimension are somehow kept at thermal equilibrium at some temperature  $T$ . Use the Maxwell-Boltzmann factor  $e^{-E/k_B T}$  (with  $k_B$ =Boltzmann constant) for the relative probability for the particle's energy to be  $E$  in order to find the average energy per particle.

Repeat the same for a system of simple harmonic oscillators. Also find the average values of the displacement  $x$  as also the mean-square displacement. What is the average energy per oscillator when the system is at a temperature  $T$ .

## BIOGRAPHICAL AND HISTORICAL NOTES

**Galileo Galilei (1564-1642)** : *studied medicine to please his father but was intensely interested in mathematics, physics and astronomy. He was an ill-paid professor of mathematics at Pisa in 1589, moved to Padua in 1591 and later to Florence in 1610 where he observed through his telescope (with a convex-objective and a concave-eyepiece) for the first time the mountains on the Moon, and the four satellites of Jupiter and several faint stars invisible to the naked eye. He described his observations in a book Sidereal Messenger. He lent support to the Copernican heliocentric cosmology through his famous work Dialogue on the Two Chief World Systems, Ptolemaic and Copernican in 1632.*

*This book is in the form of discussions, narrated day by day, between Salviatus (presenting the author's point of view), Simplicius (a 'simpleton' who blindly follows Aristotle's views on mechanics) and Segredus (an intelligent layman without any hang-ups).*

*The Catholic Church prohibited the reprinting of this work and Galileo was made to face trial before the Holy Office of the Inquisition for heresy and was found guilty.*

*In this context it is interesting to note some words he wrote to a friend: "Why is it that, in order to understand the world, we must begin with the investigation of the Words of God, rather than his Works? Is then the Work less venerable than the Word?"*

*He observed the isochronicity of a pendulum and through experiments with balls rolling down inclined planes demonstrated the time taken by bodies to fall through a given height was independent of their mass. His work on mechanics was completed while he was under house arrest and his work 'Discourses Concerning Two New Sciences' (1638) was smuggled out of Italy and published in Protestant Holland. He is often described as the Father of Modern Physics as he combined observation, controlled experiments, theory and mathematics!*

**Isaac Newton (1642-1727)** : *Newton was born in England in the year Galileo died in Italy. After grammar school he went to Trinity College, Cambridge in 1661, where he remained for nearly forty years. In 1665 because of the Great Plague he went back to his isolated home at Woolsthorpe*



and the next two years were ‘miraculous years’ when he invented and discovered the binomial theorem, the method of tangents, the differential calculus, dispersion of light, integral calculus, and he began to think about gravity and the orbit of the moon. When he returned to Trinity College in 1667 he was elected a Fellow and in 1669 became Lucasian Professor. In 1679 he was able to show from his mechanics that planets have elliptical orbits. Halley visited Newton in 1684 and urged him to write a work on dynamics which he did in eighteen months with his *Philosophiae Naturalis Principia Mathematica* - ‘The Mathematical Principles of Natural Philosophy’ the greatest book ever written, perhaps! Indeed Pierre-Simon Laplace wrote: ‘The Principia is pre-eminent above any other production of the human genius’. In 1704 he published another great work *Optiks*. Einstein wrote of him: “Nature was to him an open book”. The poet Wordsworth recorded his thoughts looking at the statue of the great thinker:

“..... looking forth by light  
Of moon or favouring stars, I could behold  
The antechapel where his statue stood  
Of Newton with his prism and silent face  
The marble index of a mind for ever  
Voyaging through strange Seas of Thought, alone”

**Leonhard Euler (1707-83)** : Swiss mathematician who studied at the University of Basle and became close friend with Daniel Bernoulli who persuaded him to join him at St. Petersburg in 1727 where he became professor of physics in 1730. He lost the sight of his right eye perhaps because of looking at the Sun during his astronomical studies. In 1741 joined Frederick the Great’s Berlin Academy of Science. In 1766 Euler accepted Catherine the Great’s offer of Directorship of St. Petersburg Academy where he became totally blind but continued his work. Euler was the most prolific mathematician in history - he systematized analysis, put calculus and trigonometry into its modern form, discovered the Euler’s number  $e = 2.71828\dots$ , developed series solutions, solved linear differential equations, developed partial differential calculus, developed mechanics, solved approximately the three body Earth, Sun and Moon problem, developed classical perturbation theory, worked on fluid flow, geometry and acoustics. He is well known for the Euler’s rule: A polyhedron with  $V$  vertices,  $F$  faces and  $E$  edges satisfies  $V+F-E=2$ , which should be known to every school-boy.

**d’Alembert (1717-83)** : French mathematician who discovered d’Alembert’s principle of mechanics. Clarified the concept of limit in calculus. In 1743 he published his *Traité de Dynamique* (Treatise on Dynamics) which include his principle of virtual work. He developed the theory of partial differential equations and solved such problems as that of the vibrating string and wave equation. He joined Euler, Clairault, Lagrange and Laplace in applying calculus to many problems in celestial mechanics.

**Lagrange(1736-1813)** : born in Turin of a French father and Italian mother he took to mathematics. In 1766 he moved to succeed Euler as Director of the Berlin Academy of Sciences. In 1797 he went to Paris as Professor of Mathematics at the *École Polytechnique*. He is famous for his great book *Analytical Mechanics* which he started writing when he was 19 and published only when he was 52. It developed mechanics using a combination of calculus and calculus of variations. Unlike Galileo and Newton he used no geometric methods (there were no diagrams!). Napoleon is said to have remarked to Lagrange on his book: “This work has no mention of God”, to which Lagrange supposedly replied: “Sire, I had no need of that hypothesis”.

**Laplace (1749-1827)** : French mathematician, astronomer and physicist who developed ce-

lestial mechanics and suggested (independently of Emanuel Kant) that the sun and the planets are formed from a rotating disc of gas. In 1773 he showed that the gravitational perturbations of one planet on another would not lead to instabilities in their orbits (Newton believed that such instabilities could lead to the end of the world without divine intervention). Between 1799 and 1825 he published his five volume work *Mecanique Celeste* which incorporated developments in mechanics since Newton. The book frequently uses the phrase it is obvious even though sometimes it is not so. Laplace also put a firm foundation on probability theory (binomial distribution). He also developed the concept of the potential. It is interesting to note that in his early years he collaborated with the great chemist Lavoisier. Laplace also worked in the planning of the Ecole Polytechnique with Napoleon. It was Laplace who suggested that the basic unit of length be taken as the metre and rationalized the metric system. It may also be noted that he died almost exactly a century after the death of Newton.

**Thomas Young (1773-1829)** : English physicist, physician and Egyptologist who while still a student discovered the role of the ciliary muscles on the accommodation of the eye through changes in the focal length of the optic lens, a finding that led to his election to the Royal Society in 1794. In 1801 he could describe and measure astigmatism. He suggested that the perception of colour is in the response to the primary colours: red, green and violet light, a theory later developed by Helmholtz and of use to colour photography and colour television. He showed how every colour could be represented by a point inside an equilateral triangle where the perpendicular distances to the three sides represent the proportion of the three primary colours. Here a theorem of geometry that the sum of these three perpendiculars is a constant equal to the height of the triangle was used. Young was able to assert that light consisted of waves on the basis of the observed interference phenomena. But the long shadow of the great Isaac Newton which dominated over England presented a great difficulty for the acceptance of his ideas by his contemporaries. He was quite taken aback by this resistance and turned his powers to decipher Egyptian picture writing from the signs on the Rosetta Stone, a problem that he solved (also worked out by the Frenchman, Champillion).

**Poisson (1781-1840)** : French mathematician and physicist who contributed to mechanics, electrostatics, elasticity, probability theory and complex analysis (he introduced the idea of contour integration). He was training to be a surgeon but Lagrange recognized his talent at the *École Polytechnique*.

**William Rowan Hamilton (1805-1865)** : Irish mathematician, born in Dublin, mastered 13 languages by the age of 13. At 10 developed interest in the mathematics of Newton and Laplace and later went to Trinity College, Dublin. His work on caustics in optics led him to the Principle of Least Action. Hamilton was appointed professor of astronomy at Dublin in 1827 and was made Astronomer Royal of Ireland. Though immortalized by his formulation of mechanics, he was strongly attracted by his study of quaternions (a noncommutative algebra). Hamilton was also poetically inclined and wrote reams of verse some of which he sent to the great poet Wordsworth who advised Hamilton to devote himself to physics, perhaps a great gain to both physics and literature.

**Charles Coulomb (1736-1806)** : French physicist who discovered the inverse square law of electric interactions by using a torsion balance he had invented capable of detecting forces equivalent to  $10^{-5}$  g.

**Karl Friedrich Gauss (1777-1855)** : A German and one of the world's greatest mathematicians. His father was a gardener and a merchant's assistant; Gauss when he was three years old

found an error in his father's arithmetic; told in school, when he was 10, to add all the numbers from zero to 100 wrote down the answer (5050) right away having discovered arithmetic progressions by himself. The Duke of Brunswick impressed by him paid for his education.

At the age of eighteen Gauss showed how to construct, using straight-edge and compass only, a regular heptadecagon (an equilateral 17 sided figure) thereby making an advance in plane geometry, after  $\sim 20$  centuries since Euclid (classical wisdom had it that such constructions were shown possible for regular polygons of sides numbering 3, 4, 5 and these multiplied by any power of two). This result was considered by Gauss himself as his greatest work and wrote to a friend that such a polygon be inscribed on his tomb after his death.

Gauss discovered the method of least square fitting. While studying he prepared his book *Disquisitiones Arithmeticae* laying the foundations of number theory and arithmetic. He proved the fundamental theorem of arithmetic that every natural number can be expressed as a product of prime numbers in just one way. Anticipated non-Euclidean Geometry as a boy. He discovered the Fundamental Theorem of Complex Analysis 14 years before Cauchy. He explored Conformal Mapping, Theory of Surfaces and Electromagnetism. With Weber he invented the electromagnetic telegraph. His contributions to topology and geometry are epoch-making. The Gaussian Error Curve is named after him. He transformed almost all branches of mathematics. It is appropriate perhaps to remember him through a quotation: Gauss in a letter to the geometrician Bolyai wrote: "It is not knowledge but the act of knowing that attracts me... when I have clarified a subject I turn away from it in order to go into darkness again".

**Oersted (1777-1851)** was a Danish physicist who discovered that an electric current produces a magnetic field. believing that there existed some relationship between electricity and magnetism he had an inspiration during a public lecture and demonstration one evening in 1820, when at the end of his lecture, said, "let me place the magnetic needle parallel to the wire carrying a current". He was surprised to see the small magnetic needle suffer a deflection. He devoted three months to further experimentation and published his results on the discovery of the magnetic effect of electric currents.

**Ampere (1775-1836)** : French physicist who while attending a meeting of the French Academy of Science and listening to a report by Arago on the work of Oersted on magnetic effect of electric currents, realised the importance of these results and repeated the experiments and found a relation between the direction of the current and the direction of the deflection of the magnetic needle which he summarised in the famous "right hand rule". He went on to making quantitative studies of the force between two parallel current carrying wires and found that it is inversely proportional to the square of the distance between them. Then Ampere made the mathematical formulation of the magnetic effect of currents which we now call Ampere's Law. He also proposed the hypothesis that the magnetism of a substance was due to molecular or atomic currents.

**Michael Faraday (1791-1867)** : British chemist and physicist. First to synthesize chlorocarbons ( $C_2Cl_6$  and  $C_2Cl_4$ ). Discovered benzene, and was the first to liquefy chlorine. Did mostly chemistry till 1830. 1830 onwards he studied electricity, discovered the laws of electrolysis, electromagnetic induction etc. Faraday, building on the developments made by Oersted and by Ampere, put forward the belief that since electricity could generate magnetism the reverse could very well be true (this he noted in his diary in 1822). After numerous experiments carried out over over the next ten years Faraday in 1831 announced his discovery of Electromagnetic Induction (also independently found by **Joseph Henry**). Faraday worked on the idea that forces of electricity and magnetism were also related to light. (Polarized light passing through a medium is affected by a magnetic field).

*During his studies on Electricity and Magnetism he formed the concept of field and lines of force. A supreme experimentalist and one with deep insight and intuition. What Galileo was to Newton, Faraday was to Maxwell. Faraday's father was an ailing blacksmith and the boy became a bookseller's errand boy at the age of 13. Here he read an article on electricity in an encyclopaedia he had to rebind and a book called Conversations in Chemistry which shaped his thoughts. He got tickets to attend Davy's last course of lectures at the Royal Institution and wrote down the notes elegantly, bound them and sent it to Davy who took him on as an assistant. His main weakness was a lack of mathematics training but despite that handicap with his deep intuition and relentless hard work he made huge, gigantic and pioneering strides.*

**Joseph Henry (1797-1878)** : *After Franklin he was the first American to devote himself to the study of electromagnetic phenomena on which he worked till he was 80 years old. He began as an apprentice to a watch-maker but the business failed. He began to write plays and acting for a living. By chance he came across a book on science and began to attend the Albany Academy. He obtained a position at the College of New Jersey (later my alma mater Princeton University) in 1832. He built electromagnets and studied them. He discovered electromagnetic induction independently. The unit of self inductance is named after Henry [a coil has a self-inducance of one henry (H) if the back emf in it is 1 volt when a current change of one ampere per second is made in it]. Henry was a Calvinist and refused increase of his salary for thirty years.*

**James Clerk Maxwell (1831-79)** *the great Scottish physicist who produced the unified theory of Electro-Magnetism and the Kinetic Theory of Gases. At school his country-accent and home-designed clothes gained him the name of 'Dafty' caused him to be shy. He was happier at the Edinburgh University. As early as 1849 he showed that all colours could be derived from the primary colours of red, green and blue. He suggested the idea of colour photography. Later (1850) he entered Trinity College, Cambridge. He secured a Professorship at Aberdeen and later moved to King's College, London. After the demise of his father (1865) he resigned his position at King's and went back to his family home in Scotland (but still doing research). He developed the kinetic theory of gases. He was not only a theorist but also an experimentalist. He showed in 1865 that the viscosity of gases is independent of pressure and is roughly proportional to temperature. In 1874 he was persuaded to become the first Cavendish Professor of Experimental Physics at Cambridge. He perfected with surpassing beauty the work of Faraday on Electromagnetism and introduced the notion of the Displacement Current. He developed the Field Concept and went on to anticipate electromagnetic waves. He contracted cancer and died in 1879 aged 48.*

**Sadi Carnot (1796-1832)** : *French physicist and one of the founders of thermodynamics through his idea of the idealised reversible heat engine. His father had been Napoleon's Minister of War, but left politics for science. Sadi was educated by his father and later at the Ecole Polytechnique and was an engineer in the army. He died young of cholera. His paper on the "Reflections on the Motive Power of Fire" (1824) was crucial for the development of thermodynamics though his arguments were based on caloric fluid theory of heat where heat was considered to be a fluid which flows from a higher level (temperature of the source) to a lower level (temperature of the sink) with the heat engine doing work in the process. It was only later that Carnot's work was truly appreciated by Kelvin and by Clausius.*

**Rudolf Clausius (1822-1888)** [*pronounced Klowzeeus*]: *A German theoretical physicist who was one of the founders of thermodynamics. His teachers included Ohm and Dedekind. The First Law of Thermodynamics was essentially due to Joule. The Second Law was due to Clausius who*

introduced the idea of Entropy. The Second Law generated great controversy but Clausius, Maxwell and W. Thomson (later Lord Kelvin) vigorously defended the ideas. Clausius did important work on the kinetic theory of gases and was the first to introduce the idea of mean free path and effective molecular radius.

**James Joule (pronounced jowl) (1818-1889)** was a British physicist. He established the mechanical theory of heat, and measured the mechanical equivalent of heat. His tutor was Dalton. He was encouraged in his work by W. Thomson (Kelvin). Studied heat generated by a current through a resistor. With Thomson he discovered the Joule-Thomson Effect.

**Hermann Helmholtz (1821-94):** German physicist and physiologist who discovered the Law of Conservation of Energy, made deep investigations on Electricity and Magnetism and delved into the physiology of vision and hearing. His student was Hertz whom he encouraged to work on Maxwell's idea of electromagnetic radiation. He was so illustrious even to the man in the street that people said of him: "He is only next to Bismarck!". Of course as far as we are concerned he was far far greater than Bismarck!

**William Thomson (Kelvin) (1824-1907)** was the son of a farm labourer. From Glasgow he went to Cambridge from where he went to Paris to work on heat with Regnault and returned to Glasgow where he worked for 53 years. As a young man he discovered Green's work and helped to publicise it. He did much to develop thermodynamics (he heard of Carnot's work when in Paris). It was he who proposed the absolute scale of temperature known to us as the Kelvin scale. Independent of Clausius he proposed the Second Law of Thermodynamics. He worked with Joule on the relationship of heat to work. He directed work on the first transatlantic cables. His home in Glasgow was the first to be lit by electricity. He was honoured with the title of Lord Kelvin.

**Ludwig Eduard Boltzmann (1844-1906)** was an Austrian. He established Statistical Mechanics and related kinetic theory of gases to thermodynamics. He extended the kinetic theory of gases introduced by Maxwell and developed ideas such as equipartition of average energy of a particle  $\frac{1}{2}k_B T$  per degree of freedom, as also the idea of the relative probability for a particle to have an energy  $E$  in a system at temperature  $T$  namely  $e^{-E/k_B T}$ , the so-called Maxwell-Boltzmann factor. He related the mechanics of a large number of particles in their most probable state to ideas of heat and entropy (or measure of disorder  $S$ ) and is immortalized by his famous  $S = k_B \ln W$ . He derived Stefan's Law of Black Body Radiation from basic thermodynamics. Depressed by the lack of appreciation of his work Boltzmann is said to have committed suicide while on holiday on the Adriatic Coast.

**Josiah Willard Gibbs (1839-94)** was the founder of Chemical Thermodynamics. One of the few US scientists of the nineteenth century. His was the second Ph.D. awarded in USA, a degree he won from Yale where he remained during his life. Chemists had difficulty in appreciating his ideas. But then later he was discovered by Planck, Einstein and others. Among his works the Phase Rule, Gibbs's Chemical Potential, Gibbsian Ensemble etc are outstanding. He is perhaps one of the greatest theoretical physicist born in USA.

## SOME NOTES ON THE CLASSICAL HISTORY OF THE CONCEPT OF ATOMS

*Thoughts on the possibility of the atomistic nature of matter go back to antiquity. Indeed Leucippus of Miletus, Democritus of Abdera and Kannad of India (who was known as the ‘atom eater’) speculated that matter consisted of indivisible atoms, which of course also implied that there was also a ‘vacuum’ (or empty space in between). This was considered logically necessary because once you invoke the existence of atoms you must inherit with it the space between atoms which is bereft of matter. Indeed the people who opposed this view held that vacuum is not possible and hence they argued that matter must be continually divisible. If we call this the prehistory of Atomism then the capstone of this period is marked by the great work of Lucretius (an Epicurean philosopher living in Rome of the first century B.C.) who wrote the book ‘De Rerum Natura’ (translated to ‘On the Nature of Things’) in the form of an epic philosophical poem (in hexameter).*

*However, the classical concept of the atom was developed scientifically using the tools of chemistry and physics mainly in the eighteenth and the nineteenth century. This development is sketchily discussed below through short notes on the main actors in this story.*

**Antoine Laurent Lavoisier (1743-1794):** *The French scientist known as the Father of Modern Chemistry. He clarified the composition of water and thereby began the subject of quantitative analysis. He overthrew the phlogiston doctrine by showing that phosphorus (and sulphur too) **increased** in weight when burnt and hence **gained** some material from the air (oxygen) rather than **lost** something (phlogiston) as believed earlier. Indeed after Robert Boyle demonstrated that metals become heavier on combustion it was decided that phlogiston had negative weight. The nature of Combustion was correctly explained by Lavoisier. Incidentally Laplace had worked with Lavoisier on the physiology of respiration and the composition of air. They were one of the earliest to have used Guinea Pigs for laboratory studies. His ‘Elementary Treatise on Chemistry’ is considered to be the first modern chemistry textbook. He worked for a private company known as the Farmer’s General which collected taxes for the Government. He designed plans for lighting a town at night, he ran a model farm, he developed the idea of savings banks and insurance societies and helped standardize weights and measures in France. He was also a liberal and greatly influenced by the progressive thoughts of the contemporary philosophers. However, unfortunately, after the French Revolution when Marat came to power he was guillotined for being a member of the Farmer’s General.*

**Henry Cavendish (1731-1810) :** *English chemist and physicist who came from a rich family of dukes etc. In 1749 he entered Cambridge and left in 1753 without a degree as he was scared of examinations. Cavendish avoided human contact as far as possible and communicated with his servants through written notes. Cavendish experimented with electricity in the 1770’s and made several important discoveries. He discovered hydrogen in 1766, as also made a systematic study of the nature of carbon dioxide. He also showed (as Lavoisier also did) that water results from the union of hydrogen and oxygen. He made the famous Cavendish experiment which enabled him to measure the universal gravitational constant  $G$ . Thus he was the very first person to measure the mass of the earth ! He was also the first person to measure the weights of gases and hence their densities. The Cavendish Physical Laboratory at Cambridge was named after him. Incidentally Cavendish published little and it was James Clerk Maxwell who was entrusted with the task of studying Cavendish’s notebooks and found out about the many discoveries and results obtained by this strange man.*

**John Dalton (1766-1844)** *was an English chemist and physicist who is best known for proposing the first quantitative atomic theory. He was the son of a poor weaver. From his school years and throughout his life he was interested in meteorology and kept daily records of weather conditions. At*

the age of twelve he began teaching at the local Quaker school. In 1793 he was appointed teacher of mathematics and natural philosophy at the New College in Manchester where he worked for the remainder of his life. From his interest in meteorology and the atmosphere he began investigating gases in general and in 1801 presented his law of partial pressures for mixtures of different gases. In 1823 he discovered the law of multiple proportions for chemical combination of elements in forming compounds and presented the first table of relative atomic weights. Between 1808 and 1827 he published in three parts his 'New System of Chemical Philosophy'.

**Joseph Louis Gay-Lussac (1778-1850)** lived in the time of the two 'revolutions': the French Revolution and the Revolution in Chemistry began by Lavoisier. When he was a child during the French Revolution his father was arrested and his tutor escaped from France. This was a blessing in disguise for he was admitted to the *École Polytechnique* which was a creation of the Revolution for the training of scientists and technologists. There he had teachers like Laplace and Berthollet (he imbibed the ideas of the great Lavoisier). He was later selected as a faculty member at that very institution. He made many studies on gases. He even ascended to 7000 ft above sea-level in a hydrogen balloon and had an adventurous spirit. He discovered that equal volumes of different gases suffer the same expansion when raised through the same range of temperature when the pressure is held fixed (that is what we call the Charles Law). Though Charles had found this earlier he had not published it. But Gay-Lussac is best known for his Law of Combining Volumes which he discovered in 1808 which states that when two gases react the volumes of the reactants and the products if gaseous are in the ratio of whole numbers (or integers).

**Amadeo Avogadro (1776-1856)** was born in Turin, Italy (though at that time Italy was not unified but consisted of different Provinces and Principalities) and took his law degree at an early age of sixteen and was a lawyer turned physicist and chemist. In 1811 he proposed the law that goes under his name that, equal volumes of all gases (at equal temperature and pressure) consist of the same number of molecules. What we now call the Avogadro number ( $N$ ) is the number of molecules in one mole (molecular weight in grams of a material) of any substance. He was the first to distinguish between atoms and molecules, though he did not use the word atom. He used the word *molécule intégrante* for molecules of a compound, *molécule constituante* for molecules of an element and *molécule élémentaire* for what we would now call atoms. In 1820 Avogadro was appointed professor of mathematics at Turin University. He was not recognised during his lifetime, perhaps because he travelled but little and Piedmont was far from the centres of scientific activities in Europe. Also perhaps because the very idea of molecule associated with an element was not acceptable by many because most chemists at that time thought that molecules can only form between different kinds of atoms through electric attraction or mutual affinity as it was called. Indeed soon after the experiments of Galvani and of Volta on electricity it was the predominant view that the electrical nature of the basic constituents was responsible for the formation of compounds. The Swedish chemist Berzelius called this approach that of 'dualism'. It was not until after his death that the great chemist Cannizzaro developed and propagated Avogadro's ideas. Indeed this happened (in 1860) almost half a century after Avogadro's proposal. Of course the actual value of the Avogadro number was only found later. Also the nature of the bonding of two hydrogen atoms into the molecule was only clarified after the birth of Quantum Mechanics.

**Dmitri Ivanovich Mendeleev (1834-1907)** : The great nineteenth Russian chemist who tabulated according to their atomic weights all chemical elements then known. This Periodic Table of Elements unified a vast body of information and was a crucial advance. Born in Tobolsk, Siberia the son of a local high school principal, he took a teacher's training degree at St. Petersburg and

graduated in chemistry in 1856. He then studied in France and Germany (where he studied with Bunsen) and became a Professor of Chemistry at the Technological Institute in St. Petersburg and a professor at the university of the same city in 1866. He resigned from there because of a dispute with the authorities there in 1890 and became the Director of the Bureau of Weights and Measures. He wrote his great textbook 'The Principles of Chemistry' between 1868 and 1870 where he classified the 63 elements then known. He found that if the elements are arranged in order of their atomic weights chemically related elements appear at regular intervals. Here however he had to use empirical knowledge in a very intuitive manner because many of the atomic weights were not known and actually as it was to be made clear much later the important quantity was not the atomic weight but the atomic number. Legally Mendeleev was a bigamist as he had not regularised his divorce from his first wife. It is said that he loved playing patience with cards and that he made cards for each element in which he wrote down their major chemical properties and would often spend hours arranging these 'chemical' rather than playing cards. The element  $Z=101$  discovered in 1955 was named Mendeleevium in his honour.

### **Electrochemistry & the Idea of the Atom:**

Ever since the experiments of Galvani and particularly Volta's clarification on the observations of his predecessor the electrical nature of matter became an important issue. Humphrey Davy made several important contributions such as the separation of alkali metal elements using electrolysis and indeed also discovered the element chlorine through the electrolysis of muriatic (which we now call hydrochloric) acid. It was, however, Michael Faraday who made a detailed and quantitative study of electrolysis through his discovery and enunciation of the underlying laws (around the year 1840) :

- The mass of a substance liberated or deposited at an electrode in the process of electrolysis is proportional to the quantity of electricity (current multiplied by the time) passed.
- The masses of elements liberated through the passage of the same quantity of electricity are proportional to their chemical equivalents.

While both Faraday and Maxwell believed that charge like mass could be indefinitely divisible, it is noteworthy to remark that Helmholtz in his Faraday Memorial Lecture in 1881 made the assertion: 'If we accept the hypothesis that elementary substances are composed of atoms, we cannot well avoid concluding that electricity itself is divided into elementary portions which behave like atoms of electricity'.

Of course the matter was elucidated when J.J. Thomson discovered the electron and then it was clear that the amount of electricity needed to deposit one gram mole of a univalent material should be  $eN$  where  $e$  was the charge of the electron and  $N$  the Avogadro number. The charge of the electron was measured by Millikan through his famous oil-drop experiment. One of the earliest attempts to estimate the Avogadro number was made by Loschmidt in 1865 using estimates of the molecular diameters and mean free paths (from the kinetic theory of gases) but that was rather rough. Later Perrin in 1908 used Brownian motion measurements and Einstein's 1905 paper on this question made a more accurate determination. Bragg in 1913 measured unit cell lengths using X-ray diffraction in crystals and from that tried to find  $N$ . With all these cross checks the picture hangs together very well indeed.