

Chapter 1. The Birth of Modern Physics

Notes:

- *Most of the material in this chapter is taken from Thornton and Rex, Chapter 1, “Thermodynamics” by E. Fermi (1936, Dover), Chapters 1 to 3, and “The Principles of Statistical Mechanics” by R. C. Tolman (1979, Dover).*

1.1 The State of Physics at the End of the 19th Century

By the end of the nineteenth century, already a large amount was known concerning the behaviour of objects subjected to forces of different kinds. But it had been a long and arduous road on the acquisition of this knowledge, with contributions from several great scientists. For example, the laws of mechanics began to really take shape with the work of **Galileo Galilei** (1564-1642), who performed several experiments that served as inspirations for generations of scientists that followed. He was the first, for example, to use the telescope to systematically study the skies and reveal the motions of planets and their satellites. These observations are closely related to the work of **Johannes Kepler** (1571-1630) who derived the so-called *Kepler’s Laws* to describe the motions of planets within our solar system. It is not a coincidence nor a surprise that these empirical laws were later explained by **Isaac Newton** (1642-1727), as he is perhaps the greatest physicist of all time (not to neglect his fundamental contributions to several fields of mathematics).

But the state of knowledge at the end of the nineteenth century was not simply limited to the laws of mechanics or their application to astronomy, for example. There was tremendous progress that followed with the development of two important theories whose formulation culminated in the latter half of the 1800s: electromagnetism and thermodynamics. We now very briefly summarize these theories (including mechanics) as they were understood at that time.

1.1.1 Mechanics - Newton’s Laws

It was Isaac Newton who first introduced the concepts of **mass** and **force**, to a large extent make sense of the experimental results obtained by previous scientists. Using these concepts, or principles, he was able to put forth three fundamental laws of motions (i.e., **Newton’s Laws of Motion**) upon which much of *classical physics*¹ rests:

- I. *A body remains at rest or in uniform motion unless acted upon by a net force.*
- II. *A body acted upon by a net force moves in such a manner that the time rate of change of the momentum equals the force.*

¹ We define as *classical* the physics theories that specifically arose approximately before the twentieth century, i.e., those exact theories we are discussing in this chapter. Conversely, *modern physics* is generally understood as consisting of the theories that followed, e.g., the theories of special and general relativity and quantum mechanics.

III. *If two bodies exert forces on each other, these forces are equal in magnitude and opposite in direction.*

The First Law would be meaningless without the concept of force, but it conveys a precise meaning for the concept of a “zero net force”. This tendency for a body to remain in its initial state of motion (or at rest) is called **inertia**. One should note that according to the first law, the only thing that matters is the resultant force. It is irrelevant whether two or three forces (or any number for that matter) are applied simultaneously, if they cancel each other out, then their effect (or lack thereof) is the same as that of having no force at all applied to the body. We then say that the body is in **equilibrium**.

The Second Law is very explicit: Force is the time rate of change of the **momentum**

$$\mathbf{p} \equiv m\mathbf{v}, \quad (1.1)$$

with m the mass, and \mathbf{v} the velocity of the body. We therefore rewrite the Second Law as

$$\begin{aligned} \mathbf{F}_{\text{net}} &= \frac{d\mathbf{p}}{dt} \\ &= \frac{d}{dt}(m\mathbf{v}), \end{aligned} \quad (1.2)$$

Although we still do not have a definition for the concept of mass, we can further transform equation (1.2), if we assume that it is a constant, to yield

$$\begin{aligned} \mathbf{F}_{\text{net}} &= m \frac{d\mathbf{v}}{dt} \\ &= m\mathbf{a}, \end{aligned} \quad (1.3)$$

with $\mathbf{a} \equiv d\mathbf{v}/dt$ the acceleration resulting from the action of the net force on the body.

The concept of mass is made clear with the Third Law. If we have two isolated bodies, 1 and 2, then the Third Law states that

$$\mathbf{F}_1 = -\mathbf{F}_2, \quad (1.4)$$

and from the Second Law we have

$$\frac{d\mathbf{p}_1}{dt} = -\frac{d\mathbf{p}_2}{dt}, \quad (1.5)$$

or using the acceleration \mathbf{a}

$$m_1 \mathbf{a}_1 = -m_2 \mathbf{a}_2$$

$$\frac{m_1}{m_2} = \frac{a_2}{a_1}, \quad (1.6)$$

with $a_i = |\mathbf{a}_i|$. If one chooses m_1 as the reference or unit mass, m_2 , or the mass of any other object, can be measured by comparison (if it is allowed to interact with m_1) of their measured accelerations. Incidentally, we can use equation (1.5) to provide a different interpretation of Newton's Second Law

$$\frac{d}{dt}(\mathbf{p}_1 + \mathbf{p}_2) = 0 \quad (1.7)$$

or

$$\mathbf{p}_1 + \mathbf{p}_2 = \text{constant}. \quad (1.8)$$

The momentum is conserved in the interaction of two isolated particles. This is a special case of the **conservation of linear momentum**. Also resulting from Newton's Laws are the **conservation of angular momentum** and the **conservation of energy**. These are important concepts that carry over to all other theories, classical or modern. As far as classical mechanics is concerned, the **conservation of mass** can also play a fundamental role in understanding the physical world.

Example – Kepler's Second Law from Newton's Laws and the conservation of angular momentum

Newton's accomplishments are numerous and far-reaching. The aforementioned three laws are far from the only things he is known for. The derivation or explanation of Kepler's Laws of Planetary Motion from the combination of Newton's Laws and his universal theory of gravitation is certainly a salient result of classical physics.

For Kepler's Second Law² in particular, we can start by considering the torque acting on a planet orbiting the Sun

$$\boldsymbol{\tau} = \mathbf{r} \times \mathbf{F}_{\text{grav}}, \quad (1.9)$$

where $\boldsymbol{\tau} = d\mathbf{L}/dt$ with \mathbf{L} the angular momentum. However, since the vector \mathbf{r} defining the position of the planet in relation to the Sun and the gravitational pull of the sun on the planet \mathbf{F}_{grav} are collinear, the torque on the planet is zero. It follows that the angular momentum of the planet is conserved.

² Kepler's Second Law states that "The area per unit time swept out by a radius from the Sun to a planet is constant."

Considering the definition for the angular momentum

$$\begin{aligned} \mathbf{L} &= \mathbf{r} \times \mathbf{p} \\ &= mrv \sin(\phi) \mathbf{e}_{\perp} \\ &= \text{constant}, \end{aligned} \tag{1.10}$$

where \mathbf{e}_{\perp} is the unit vector perpendicular to the orbital plane, m is the planet's mass, and ϕ is the angle between planet's linear momentum vector \mathbf{p} and \mathbf{r} (see Figure 1). Since the orbital motion takes place in a plane, we can use

$$\begin{aligned} v_{\perp} &\equiv v \sin(\phi) \\ &= \omega r, \end{aligned} \tag{1.11}$$

to transform equation (1.10) to

$$\begin{aligned} \frac{L}{m} &= r^2 \omega \\ &= r^2 \frac{d\theta}{dt}, \end{aligned} \tag{1.12}$$

since $\omega = d\theta/dt$. However, from Figure 1, the triangular area dA swept as the planet travels an infinitesimal angle $d\theta$ is one-half the product of the radius r and the arc $r d\theta$

$$dA = \frac{1}{2} r^2 d\theta. \tag{1.13}$$

Equation (1.12) then becomes

$$\frac{L}{2m} = \frac{dA}{dt}, \tag{1.14}$$

but since the angular momentum is conserved *the area swept per unit time* is found to agree with Kepler's Second Law, i.e.,

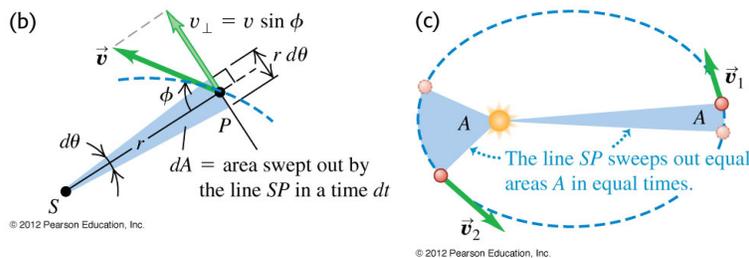


Figure 1 - The area swept by a planet orbiting the sun in a given time interval.

$$\frac{dA}{dt} = \text{constant}. \quad (1.15)$$

It also follows that the total area A swept over a finite interval $T_2 - T_1$ is constant since

$$\begin{aligned} A &= \int_{T_1}^{T_2} dA \\ &= \frac{L}{2m} \int_{T_1}^{T_2} dt \\ &= \frac{L}{2m} (T_2 - T_1). \end{aligned} \quad (1.16)$$

It therefore does not matter what part of the orbit the planet travels during the interval, the total area swept is the same (see Figure 1).

1.1.2 Electromagnetism

Another spectacular success of classical physics is the discovery of the laws that regulate the behaviour of charged particles and currents, and their associated electric and magnetic fields. This was accomplished starting in the eighteenth century by several scientists (too numerous to name here) and culminated with the seminal work of **James Clerk Maxwell** (1831-1879). The laws that define electromagnetism can be succinctly summarized with the so-called *Maxwell's Equations*³ (using MKS units)

$$\begin{aligned} \nabla \cdot \mathbf{D} &= \rho \\ \nabla \cdot \mathbf{B} &= 0 \\ \nabla \times \mathbf{H} &= \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t} \\ \nabla \times \mathbf{E} &= -\frac{\partial \mathbf{B}}{\partial t}, \end{aligned} \quad (1.17)$$

where the *electric displacement field* \mathbf{D} is related to the *electric field* \mathbf{E} through $\mathbf{D} = \epsilon \mathbf{E}$, with ϵ the electric permittivity, and the *magnetic induction field* \mathbf{B} to the *magnetic field* $\mathbf{H} = \mu \mathbf{H}$, with μ the permeability. The quantity \mathbf{J} in equations (1.17) is the *current density*. These equations must be supplemented with the *Lorentz Force* (**Hendrik Antoon Lorentz** 1853-1928) that describes the dynamics of a particle of charge q interacting with the electromagnetic field

$$\mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B}). \quad (1.18)$$

³ It is rarely acknowledged that the common differential form of Maxwell's Equations given here is due, not to Maxwell himself, but to the brilliant British mathematical physicist and electrical engineer **Oliver Heaviside** (1850-1925).

These equations can be used to explain a whole set of phenomena, from the basic dynamical behaviour of, and the radiation from, an electron, for example, to the working of an electrical motor. These equations were also used by Maxwell to predict the propagation of electromagnetic waves and show that light is a special case of this phenomenon.

Example – The propagation of electromagnetic waves in free space

We can study the behaviour of the electric field in free space, i.e., at a location away from any charge or current such that $\rho = \mathbf{J} = 0$, and where $\epsilon = \epsilon_0$ and $\mu = \mu_0$ are the constant permittivity and permeability of vacuum. We proceed by taking the curl of the fourth of equations (1.17)

$$\begin{aligned}\nabla \times (\nabla \times \mathbf{E}) + \frac{\partial}{\partial t} (\nabla \times \mathbf{B}) &= \nabla (\nabla \cdot \mathbf{E}) - \nabla^2 \mathbf{E} + \frac{\partial}{\partial t} \left(\mu_0 \epsilon_0 \frac{\partial \mathbf{E}}{\partial t} \right) \\ &= -\nabla^2 \mathbf{E} + \frac{1}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} \\ &= 0,\end{aligned}\tag{1.19}$$

where we have used the first and third of equations (1.17), the vector identity

$$\nabla \times (\nabla \times \mathbf{E}) = \nabla (\nabla \cdot \mathbf{E}) - \nabla^2 \mathbf{E},\tag{1.20}$$

and defined a new constant

$$c \equiv \frac{1}{\sqrt{\mu_0 \epsilon_0}}.\tag{1.21}$$

The gradient operator is defined such that for a function f we have when using Cartesian coordinates

$$\nabla f = \frac{\partial f}{\partial x} \mathbf{e}_x + \frac{\partial f}{\partial y} \mathbf{e}_y + \frac{\partial f}{\partial z} \mathbf{e}_z,\tag{1.22}$$

where \mathbf{e}_x , \mathbf{e}_y , and \mathbf{e}_z are unit vectors in the corresponding directions. It also follows from this that for an arbitrary vector \mathbf{a} the *divergence*, *curl*, and *Laplacian* are given by

$$\begin{aligned}
\nabla \cdot \mathbf{a} &= \frac{\partial a_x}{\partial x} + \frac{\partial a_y}{\partial y} + \frac{\partial a_z}{\partial z} \\
\nabla \times \mathbf{a} &= \left(\frac{\partial a_z}{\partial y} - \frac{\partial a_y}{\partial z} \right) \mathbf{e}_x + \left(\frac{\partial a_x}{\partial z} - \frac{\partial a_z}{\partial x} \right) \mathbf{e}_y + \left(\frac{\partial a_y}{\partial x} - \frac{\partial a_x}{\partial y} \right) \mathbf{e}_z \\
\nabla^2 f &= \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2}.
\end{aligned} \tag{1.23}$$

If we simplify equation (1.19) by considering the one-dimensional case where the electric field polarized in z is a function of, say, only the x direction, then we can write

$$\frac{\partial^2 E_z}{\partial x^2} - \frac{1}{c^2} \frac{\partial^2 E_z}{\partial t^2} = 0, \tag{1.24}$$

for which it can be verified that the general solution is

$$E_z = E_z(x \pm ct). \tag{1.25}$$

That is, the electric field is a function of the quantity $x \pm ct$ such that

$$\begin{aligned}
\frac{\partial^2 E_z}{\partial x^2} &= A E_z \\
\frac{\partial^2 E_z}{\partial t^2} &= c^2 A E_z,
\end{aligned} \tag{1.26}$$

with A some constant. Since the function

$$X \equiv x \pm ct \tag{1.27}$$

can be interpreted as the position at time t for some physical quantity initially located at x when $t = 0$, It therefore follows that equation (1.25) corresponds to an electric field that travels either to the right ('-' sign) or to the left ('+' sign) at the speed c . This can be made more apparent if we consider the particular solution

$$E_z = E_0 \cos[k(x - ct)], \tag{1.28}$$

where we can readily see that a fixed phase

$$\varphi = k(x - ct) \tag{1.29}$$

cannot and will not remain stationary at a location x for all times. For example, the case of $\varphi = 0$ will propagate (to the right) to successive positions $x = ct$.

1.1.3 Thermodynamics

Thermodynamics was established mainly as an empirical science that dealt with specific quantities pertaining to a given system. These quantities, which are used to specify the system's (physical or thermodynamic) state, can be mechanical in nature (e.g., pressure, volume, and work) while others are more subtle and needed the contributions of several scientists before a good understanding was attained (e.g., temperature, heat, and entropy).

The main results stemming from thermodynamics can be summarized by two fundamental laws:

The First Law of Thermodynamics: It generalizes the usual statement of conservation of mechanical energy encountered in Newtonian mechanics by also considering heat. It can be stated as follows: *The change in internal energy U of a system equals to the heat Q added to it plus the work W done on the system.* Mathematically this can be written as

$$\Delta U = Q + W. \quad (1.30)$$

The heat can thus be interpreted as the amount of energy received by the system in forms other than work.

The Second Law of Thermodynamics: Although the first law is essential in stating the conservation of energy (i.e., energy cannot be created out of nothing), it places no constraint on how energy can be transformed from one form into another. For example, although it is clear that an amount of work can be transformed into heat, can this heat be afterwards transform back into work? This question is addressed with the Second Law, which can be stated as follows (there are many different versions of this law): *It is not possible to convert heat completely into work without some other change in the system taking place.*

Example – The Specific Heat of an Ideal Gas

Thermodynamics was very useful in establishing important results that could be tested experimentally. For example, the independent work from early scientists (**Robert Boyle** 1627-1691, **Jacques Charles** 1746-1823, **Joseph Louis Gay-Lussac** 1778-1850, and **Amedeo Avogadro** 1776-1856) could be combined to establish the *equation of state* for the a so-called *ideal* or *perfect gas*

$$PV = nRT, \quad (1.31)$$

where P and V are the pressure and volume, n is the number of moles contained in the gas (one mole contains $N_A = 6.022 \times 10^{23}$ particles, with N_A the *Avogadro Number*, and $R = 8.31 \text{ J/mol} \cdot \text{K}$ is the *ideal gas constant*). This relation can in turn be combined with equation (1.30) to calculate the *heat capacity* at constant pressure C_p or constant volume C_v , respectively. To do so, we first consider infinitesimal changes in our system such that equation (1.30) becomes

$$dU = dQ + dW. \quad (1.32)$$

But the infinitesimal work done on the system can be written (since the pressure can be thought as energy per unit volume (as well as the force per unit area))

$$dW = -PdV, \quad (1.33)$$

and thus

$$dU + PdV = dQ. \quad (1.34)$$

For a given system containing n moles of gas, equation (1.31) makes it clear that the quantities P , V , and T cannot all be varied independently. For example, one could change the volume and the temperature, and the pressure would adjust itself to the new conditions. Alternatively, one could choose to vary the pressure and the temperature instead, while letting the volume expand or contract as needed, or vary the volume and the pressure with a resulting heating or cooling of the gas. In any case, one is left with a choice of two *independent variables* upon which to act. With T and V independent we can write the infinitesimal change in internal energy as

$$dU = \left(\frac{\partial U}{\partial V} \right)_T dV + \left(\frac{\partial U}{\partial T} \right)_V dT, \quad (1.35)$$

and equation (1.34) becomes

$$\left(\frac{\partial U}{\partial T} \right)_V dT + \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] dV = dQ. \quad (1.36)$$

In equations (1.35) and (1.36) the subscripts at the bottom of the parentheses indicate that the corresponding variable is to be held constant while the derivative is effected relative to the other independent variable.

Similarly, we can calculate a corresponding relation for dU when T and P are chosen as independent, but we must also ensure to express the other differential in equation (1.34) as

$$dV = \left(\frac{\partial V}{\partial T} \right)_P dT + \left(\frac{\partial V}{\partial P} \right)_T dP, \quad (1.37)$$

and therefore

$$\left[\left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P \right] dT + \left[\left(\frac{\partial U}{\partial P} \right)_T + P \left(\frac{\partial V}{\partial P} \right)_T \right] dP = dQ. \quad (1.38)$$

Finally, taking V and P as independent variables we have

$$\left(\frac{\partial U}{\partial P}\right)_V dP + \left[\left(\frac{\partial U}{\partial V}\right)_P + P\right] dV = dQ. \quad (1.39)$$

We can now use equations (1.36) and (1.38) to find expressions for the heat capacities

$$\begin{aligned} C_V &\equiv \left(\frac{\partial Q}{\partial T}\right)_V \\ &= \left(\frac{\partial U}{\partial T}\right)_V \\ C_P &\equiv \left(\frac{\partial Q}{\partial T}\right)_P \\ &= \left(\frac{\partial U}{\partial T}\right)_P + P \left(\frac{\partial V}{\partial T}\right)_P. \end{aligned} \quad (1.40)$$

For the case of an ideal gas it was shown experimentally by **James Joule** (1818-1889) that the internal energy of the gas is completely independent of the volume⁴. It therefore follows that

$$C_V = \frac{dU}{dT}, \quad (1.41)$$

and, from equation (1.34),

$$C_V dT + PdV = dQ. \quad (1.42)$$

Then using equation (1.31) for one mole of an ideal gas (i.e., $n=1$; the heat capacities are then called *molar heat capacities*) at constant pressure, the last of equations (1.40) becomes

$$C_P = C_V + R. \quad (1.43)$$

These relations could be verified experimentally and were found to work well for approximately ideal gases. But with the acceptance of the *Atomic Theory of Matter* it became possible to derive such equations (and much of thermodynamics, for that matter) through *Statistical Mechanics* and the *Kinetic Theory of Gases*. In fact, discrepancies between predicted and experimental values for the molecular heats were one clue that all was not perfect with classical physics at the end of the nineteenth century.

⁴ It can also be shown using the Second Law of Thermodynamics that the internal energy of any system that obeys equation (1.31) will be independent of the volume.

1.1.4 Statistical Mechanics

The statistical interpretation of thermodynamics, through *Statistical Mechanics* (or *Statistical Physics*), was established in the second half of the nineteenth century by Maxwell, **Ludwig Eduard Boltzmann** (1844-1906), and the American physicist **J. Willard Gibbs** (1839-1903). This theory brings us closer to the world of Modern Physics to come at the turn of the twentieth century in that it is based on the atomic theory of matter. Although atoms and molecules were still not well understood at the time (that would have to await the advent of *Quantum Mechanics*), the statistical interpretation of these constituents of matter would allow the calculation of important physical quantities and relations.

Example – The Maxwell-Boltzmann Distribution Law and the Equipartition of Energy

In his study of statistical mechanics Maxwell considered the constituent of matter (i.e., atoms and molecules) as billiard balls interacting with each other and their environment through collisions. It was he, and with a later contribution from Boltzmann, who derived the velocity distribution for an ensemble of N identical particles (i.e., atoms or molecules) composing a gas for which the total energy is fixed. This is the *Maxwell-Boltzmann Distribution Law*

$$f(\mathbf{v}) = N \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-m(v_x^2 + v_y^2 + v_z^2)/2kT}, \quad (1.44)$$

where m is the mass of a particle (the same mass for all), T the temperature of the gas, and $k \equiv R/N_A = 1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$ is the *Boltzmann Constant*. Alternatively, this distribution can be expressed using the speed $v = (v_x^2 + v_y^2 + v_z^2)^{1/2}$ distribution with

$$f(v) = 4\pi N \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-mv^2/2kT}, \quad (1.45)$$

which is shown in Figure 2. The distributions are normalized such that

$$\begin{aligned} N &= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(\mathbf{v}) dv_x dv_y dv_z \\ &= \int_0^{\infty} f(v) dv. \end{aligned} \quad (1.46)$$

It is then possible to use these equations to calculate mean values for different quantities pertaining to the gas. For example, the mean kinetic energy of a particle due to its velocity in, say, the x -direction will be given by

$$\begin{aligned}
\overline{K_x} &= \frac{1}{N} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{1}{2} m v_x^2 f(\mathbf{v}) dv_x dv_y dv_z \\
&= \frac{m}{2} \left(\frac{m}{2\pi kT} \right)^{3/2} \left(\int_{-\infty}^{\infty} v_x^2 e^{-mv_x^2/2kT} dv_x \right) \left(\int_{-\infty}^{\infty} e^{-mv_y^2/2kT} dv_y \right) \left(\int_{-\infty}^{\infty} e^{-mv_z^2/2kT} dv_z \right) \\
&= \frac{m}{2} \left(\frac{m}{2\pi kT} \right)^{3/2} \left(\int_{-\infty}^{\infty} v_x^2 e^{-mv_x^2/2kT} dv_x \right) \left(\int_{-\infty}^{\infty} e^{-mw^2/2kT} dw \right)^2 \\
&= \frac{m}{2} \left(\frac{m}{2\pi kT} \right)^{3/2} \left[\frac{1}{2\pi} \left(\frac{2\pi kT}{m} \right)^{3/2} \right] \left[\left(\frac{2\pi kT}{m} \right)^{1/2} \right]^2 \\
&= \frac{1}{2} kT,
\end{aligned} \tag{1.47}$$

where the first integral on the second line was integrated by parts and we used equations (1.44) and (1.46) for the second. Performing a similar calculations for the y and z directions we find that the total mean kinetic energy for one particle is

$$\overline{K} = \frac{3}{2} kT. \tag{1.48}$$

We can extend this result to a gas containing n moles for the total (internal) energy

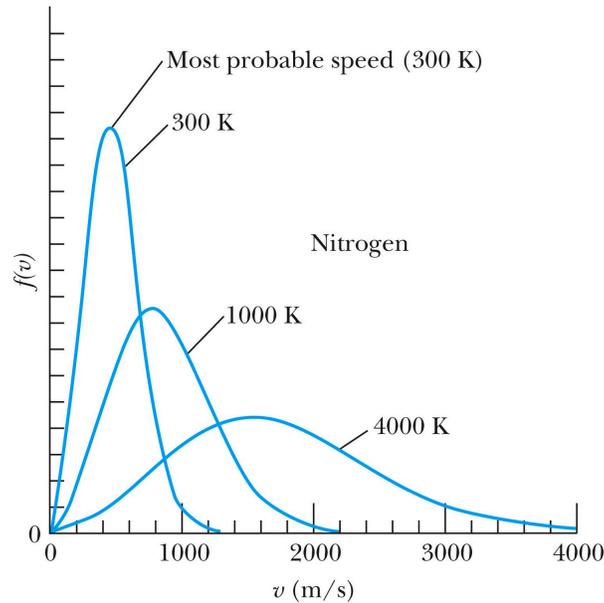


Figure 2 – The Maxwell-Boltzmann distribution, i.e., equation (1.45), for the nitrogen molecule at different temperatures.

$$U = \frac{3}{2}nN_A kT, \quad (1.49)$$

since $N = nN_A$, and find from equation (1.41) that the molar heat capacity (i.e., when $n = 1$) at constant volume

$$\begin{aligned} C_V &= \frac{3}{2}N_A k \\ &= \frac{3}{2}R. \end{aligned} \quad (1.50)$$

We then find that Statistical Mechanics provides us with a prediction for a fundamental quantity that arose within the context of thermodynamics.

But it is important to note that the result obtained with equation (1.47) for motion in one direction is a special case of the more general *Equipartition Theorem* of energy, which states that *each degree of freedom of a particle has an average energy of $kT/2$ associated to it*. The *degrees of freedom of a system are defined as all the independent ways that energy can be stored in a system*. For example, in the present case of a gas composed of colliding molecules considered here the only degrees of freedom arise from translational motions in three independent directions. That is, there are three such degrees.

On the other hand, a H_2 molecule made of two hydrogen atoms will have two more degrees of freedom associated to rotation about axes perpendicular to the axis joining the two nuclei, and another pair due to the possible vibration of the molecule from the stretching and compression of the bond joining the nuclei (for vibration there is one degree of freedom for the kinetic energy and another for the potential energy). We would then expect that a hydrogen molecule would have a heat capacity

$$\begin{aligned} C_V(H_2) &= (3+2+2) \cdot \frac{1}{2}N_A k \\ &= \frac{7}{2}N_A k. \end{aligned} \quad (1.51)$$

However, it is a characteristic of Quantum Mechanics that some degrees of freedom will only come into play when the energy of the system is high enough to excite them. For example, more energy is needed for the molecules in a hydrogen gas for rotational than translational motions, and even more for vibrations to take place. The resulting functional form of C_V/R as a function of the total energy of the gas (or the temperature) will then look like the curve shown in Figure 3. This “step-wise” behaviour of the molar heat capacity cannot be determined with classical mechanics, which would predict it to be a constant. It was **Albert Einstein** (1879-1955) who in 1907 first used the early ideas on energy quantization to improve on the results of classical physics and get accurate values

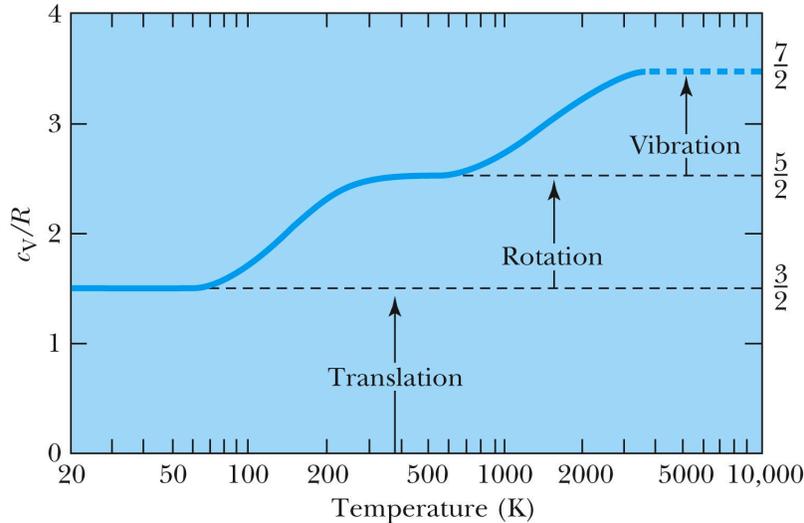


Figure 3 – The molar heat capacity for a diatomic molecule, such as the molecular hydrogen, that exhibits translational, rotational, and vibrational degrees of freedom.

for the heat capacity at high temperature. The Austrian physicist and chemist **Peter Debye** (1884-1966) eventually formulated a theory that correctly accounted for the observed behaviour at low temperature (as well as at high temperature) in 1912 (the so-called *Debye Model*).

1.2 Problems with Physics at the End of the 19th Century

We already saw in the previous section that thermodynamics and classical statistical mechanics (there is also a quantum mechanical version of statistical physics) could not adequately account for experimental measurements of heat capacities. This is one example of the limitations of classical mechanics, and it was eventually resolved by adopting the “new” ideas on the quantization of energy. But this was not the only problem facing classical physics at the end of the nineteenth century, indeed there were a few much more serious crises.

1.2.1 The Ether, or the Electromagnetic Medium

As was discussed in Section 1.1.2, Maxwell was able to show using the newly established theory of electromagnetism that electromagnetic waves could propagate in space. Although not exactly the same, electromagnetic waves have much in common with acoustic or sound waves. In fact, our simple derivation of the wave equation (see equation (1.24)) seems to imply that electromagnetic waves should propagate in vacuum. This, of course, went completely against anything physicists of that period could imagine. After all, acoustic waves on a pond need the water to propagate, just like sound waves need the air in order to be heard. How could electromagnetic waves propagate on nothing?

To avoid this apparent inconsistency, physicists then postulated that an electromagnetic medium must exist on which waves can propagate. This medium, which was assumed to

permeate all of space, was named the *ether*. But nature does not have to yield to human beliefs, and even the most sensitive experiments (most notably that of **Albert Michelson** (1852-1931) and **Edward Morley** (1838-1923) in 1887) could not detect the presence of the ether. The postulated electromagnetic medium did not exist.

The ether problem was solve by Einstein in 1905 when he published his *Theory of Special Relativity*, which is partly based on the postulate (and evidence from the Michelson-Morley experiment) that the speed of light is independent of the speed of the source from which it emanates. The notion of an electromagnetic medium was then shown to superfluous and not needed.

1.2.2 The Inertial Frames of Electromagnetism

Newtonian mechanics was in part build on the notion that there exit *inertial frames of reference* on which the laws of physics are the same. More precisely, an inertial frame is one that is in a uniform and non-accelerating state of motion. In fact, Newton's Laws are only applicable to such frame of references and his First Law can be used to define what an inertial frame is. It is often stated that Newton's Laws are *invariant* when moving from one inertial frame to another. This can be better understood mathematically.

If a particle of mass m has a velocity \mathbf{u}' relative to an observer who is at rest in an inertial frame K' , while this frame is moving with a constant velocity \mathbf{v} as seen by another observer at rest in another inertial frame K (note the necessity of having a constant relative velocity \mathbf{v}), then we would expect that the velocity \mathbf{u} of the particle as measured in K to be

$$\mathbf{u} = \mathbf{u}' + \mathbf{v}. \quad (1.52)$$

That is, it would seem reasonable to expect that velocities should be added together when transforming from one inertial frame to another⁵; such a transformation is called a *Galilean transformation*. If we write the mathematical form of the Second Law in frame K we have

$$\begin{aligned} \mathbf{F} &= m \frac{d\mathbf{u}}{dt} \\ &= m \frac{d(\mathbf{u}' + \mathbf{v})}{dt}, \end{aligned} \quad (1.53)$$

but since \mathbf{v} is constant

$$\mathbf{F} = m \frac{d\mathbf{u}'}{dt} = \mathbf{F}'. \quad (1.54)$$

⁵ The development of special relativity has showed that this law for the composition of velocities is approximate and only valid when these are small compared to the speed of light.

The result expressed through equation (1.54) is a statement of the invariance (or covariance) of Newton's Second Law. More precisely, the Second Law retains the same mathematical form no matter which inertial frame is used to express it, as long as velocities transform according to the simple addition rule stated in equation (1.52).

Another apparent problem with the theory of electromagnetism is that Maxwell's equations (see equations (1.17)) are *not* invariant to a Galilean transformation. That is, these equations change mathematical form when going from one Newtonian inertial frame to another, such as when using equation (1.52). It was natural for physicists of the nineteenth century to assume that Newton was right and Maxwell wrong. But electromagnetism seemed to be a very successful theory that agreed with experiments.

This problem was also eventually solved by Einstein's Theory of Special Relativity of 1905, where he showed that it was the other way around: Maxwell was right and Newton wrong. As it turns, Galilean transformations do not define inertial frames. Instead, the so-called *Lorentz Transformation*, previously and independently derived by Lorentz and the Irish physicist **George FitzGerald** (1851-1901), is the fundamental transformation that plays such a role (this transformation was also re-derived from scratch by Einstein in 1905). It followed that electromagnetism was found to be a theory perfectly consistent with special relativity. Newtonian mechanics, on the other hand, has shortcomings that are overcome by special relativity.

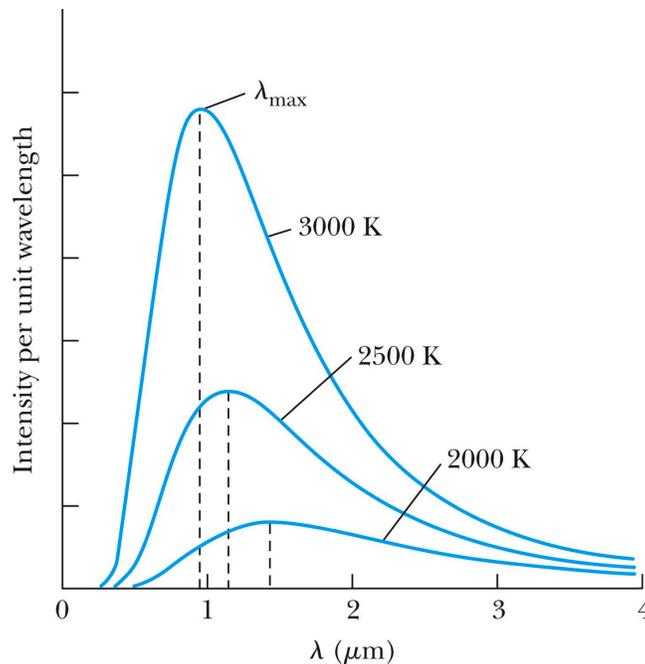


Figure 4 - The blackbody spectrum as a function of wavelength for three different temperature.

1.2.3 Blackbody Radiation

A *blackbody* is an object that absorbs all incident radiation and emits a continuous spectrum of radiation whose distribution and intensity depend only on its temperature (e.g., it does not depend on the nature of the body itself). Classical physics was unable to explain this spectrum. Although it was possible to explain the blackbody spectrum at low and high frequencies, no single theory could account for the shape of the whole spectrum (see Figure 4).

This all changed in 1900 when **Max Planck** (1858-1947) introduced the notion of quantization for the first time. Not only was he able to solve the blackbody problem, his idea was revolutionary and served as the foundation for the development of *Quantum Mechanics* in the decades to follow.