

# Rayleigh Scattering as the Origin of Molecular Randomness

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## Abstract

It is suggested that Rayleigh Scattering by thermal photons is the dominant process which causes molecular chaos in gases at moderate temperatures. A formula is derived for the frequency of such scattering events and the assertion that it is the origin of molecular randomness is justified by referencing the change in momentum imparted to the molecule during the event.

## Introduction

Rayleigh scattering is the process whereby light of all wavelengths is scattered by particles whose dimensions are much smaller than the wavelength of the light. From the point of view of classical electromagnetism, the incident light causes the electrons in the particle to vibrate in sympathy which then re-radiate the electromagnetic wave in all directions. In 1899 Lord Rayleigh published a paper <sup>[1]</sup> explaining why the sky is blue. Using Maxwell's electromagnetic theory of light he showed that the intensity of the scattered radiation was inversely proportional to the fourth power of the wavelength. This meant that blue light was scattered much more strongly than red light, hence the colour of the sky.

A modern formula <sup>[2]</sup> for the cross section for this process is

$$\sigma_s = \frac{2\pi^5}{3} \left( \frac{n^2-1}{n^2+2} \right)^2 \frac{d^6}{\lambda^4} \quad (1)$$

where  $n$  is the refractive index of the particle,  $d$  is its diameter and  $\lambda$  is the wavelength of light.

Putting  $n = 1.33$  this reduces to

$$\sigma_s \approx 10 \frac{d^6}{\lambda^4} \quad (2)$$

In spite of the fact that a single molecule does not have a refractive index, it turns out that this formula is remarkably accurate, even when applied to single molecules, and since I shall only need my calculations to be accurate to within an order of magnitude, I shall continue to use it.

Another point to make is that the whole basis on which Rayleigh's formula was deduced is flawed because the process of the scattering from a single molecule is actually a quantum phenomenon. This was pointed out by Einstein as early as 1916 <sup>[3]</sup> who realised at the time that the process of absorption and emission of a photon by a molecule was essentially stochastic.

The photons which comprise visible and infra red light do not have enough energy to excite even the rotational and vibrational modes of oxygen and nitrogen molecules, let alone cause excitation or ionization. There is no mechanism, therefore, by which such photons can be absorbed by or even donate significant energy to the molecule. We have to regard the photon as being temporarily bound to the molecule and almost immediately re-emitted in a random direction. Since the interaction does not involve the absorption of any energy, it is perfectly elastic; but, unlike collisions between the molecules themselves, it is not reversible. Prior information about the velocities of the two particles is erased and new subsequent information is created. Given the relevant data about the photon and the molecule before the event, it is impossible to predict the

direction in which the photon will be scattered; likewise, given the relevant data after the event, it is equally impossible to reconstruct the details of the situation before the event.

Rayleigh scattering has been suggested as the dominant process which causes decoherence in a quantum state by H. Uys et al <sup>[4]</sup>. Robert O. Doyle has suggested <sup>[5]</sup> that it is Raman scattering (i.e. inelastic scattering) which is the origin of irreversibility in gases. Probably the most popular current explanation of micro-irreversibility is that described by T. Matolesi <sup>[6]</sup> who concludes, rather naively, that “Irreversibility is a fundamental law of Nature. Reversible laws of some physical theories, such as mechanics, are only idealizations.” As far as I know, no one has yet put forward the remarkably simple suggestion that it is Rayleigh scattering which is the origin of the randomness which is necessary to explain why gas molecules can be considered to move chaotically and which is the justification for Boltzmann's H-theorem and ultimately for the validity of the Second Law of Thermodynamics.

But before we can jump to this important conclusion we must calculate how frequently Rayleigh scattering events occur in a gas at STP and, if they do occur sufficiently frequently, whether or not the effect on the motion of the molecules is big enough to trigger molecular chaos.

## The frequency of scattering events

Consider a light-tight box of side  $x$  containing  $N$  nitrogen molecules at STP. The walls of the box will be radiating thermal photons of typical energy  $E = kT$  and wavelength

$$\lambda = hc/kT \quad (3)$$

By Stefan's law, the total energy radiated from the walls of the box whose total area is  $6x^2$  will be

$$E_{total} = 6x^2\sigma T^4 \quad (4)$$

and the total number of photons radiated into the box every second will be

$$N_{photons/sec} = \frac{6x^2\sigma T^4}{kT} = \frac{6x^2\sigma T^3}{k} \quad (5)$$

Assuming that each of these photons only exist as long as it takes to cross the box, the actual number of photons present in the box at any one time is

$$N_{photons} = \frac{6x^2\sigma T^3}{k} \times \frac{x}{c} = \frac{6x^3\sigma T^3}{ck} \quad (6)$$

In a time  $t$  a photon will sweep out a volume of  $\sigma_s ct$  and the chances are that it will be scattered by a molecule if this volume is equal to the volume occupied by one molecule. We therefore have

$$\begin{aligned} \sigma_s ct &= x^3/N \\ t &= \frac{x^3}{\sigma_s cN} \end{aligned} \quad (7)$$

The overall frequency of scattering event in the box will therefore be

$$\frac{N_{photons}}{t} = \frac{6x^3\sigma T^3}{ck} \times \frac{\sigma_s cN}{x^3} = \frac{6\sigma\sigma_s N T^3}{k} \quad (8)$$

Using our heuristic formula for  $\sigma_s$

$$\sigma_s \approx 10 \frac{d^6}{\lambda^4} = 10 d^6 \left( \frac{kT}{hc} \right)^4 \quad (9)$$

hence

$$f \approx \frac{6\sigma N T^3}{k} \times 10d^6 \left(\frac{kT}{hc}\right)^4 \quad (10)$$

$$\approx \frac{60d^6\sigma N k^3 T^7}{h^4 c^4}$$

Using  $d = 4 \times 10^{-10}\text{m}$  and  $T = 300\text{ K}$ , the number of Rayleigh scattering events occurring in a litre of nitrogen gas at STP ( $N = N_A/22.4 = 2.7 \times 10^{22}$ ) is over 100 million every second.

The high values of both exponents of  $d$  and  $T$  mean that the frequency of scattering events drops very sharply with small molecules at low temperatures. For example, in a litre of Helium ( $d = 1 \times 10^{-10}\text{m}$ ) at 10 K we can expect a scattering event to occur only once in 7 days. (Note that this does not mean that a small sample of helium released into an evacuated chamber will take 7 days before it starts to obey the gas laws. It only means that we have 7 days in which to reverse the directions of all the molecules if we want to put them all back in the bottle from which they came!)

## The effects of a scattering event

It is often said that Rayleigh scattering is isotropic and that the frequency of the scattered light is identical to the frequency of the incident light. Neither of these statements are strictly true. If the scattered photon travels in a different direction to the incident photon, there must be a change in the photon's momentum. This implies that there will be a change in the molecule's momentum and that a small amount of energy must be transferred from one particle to the other. Notwithstanding the difficulty of explaining the precise dependence of the scattering angle from the basic principles of quantum electrodynamics, we can still estimate what happens in a typical scenario using just the law of conservation of momentum.

In any collision between a moving particle (the photon) and a relatively stationary one (the molecule), the maximum quantity of momentum which it is possible to transfer from the former to the latter is equal to two times the momentum of the former. On average we might expect the molecule to gain momentum approximately equal to that of the photon i.e.  $p_p = \frac{h}{\lambda} = \frac{kT}{c}$

The average momentum of a nitrogen molecule of mass  $m$  at a temperature  $T$  is

$$p_m = \sqrt{3mkT}$$

If the photon is scattered through a right angle, the molecule will be deviated by an angle equal to the ratio of these quantities i.e.

$$\alpha = \frac{p_p}{p_m} = \frac{kT}{c\sqrt{3mkT}} = \sqrt{\frac{kT}{3mc^2}} \quad (11)$$

For a nitrogen molecule at 300 K this works out to be  $5.7 \times 10^{-7}$  radians.

The question is – is this enough to trigger chaos in the gas and render the assumption of molecular randomness valid?

Suppose that in our sample of nitrogen gas at STP only one scattering event occurs. We shall assume, along with the standard assumptions of the kinetic theory of gases, that all subsequent collisions between molecules are perfectly elastic and that the molecules are spheres of radius  $a$ . Suppose also that the mean free path between collision is  $l$  and that the molecule that was nudged away from its original path was going to collide head on with another molecule. See *Fig. 1*.

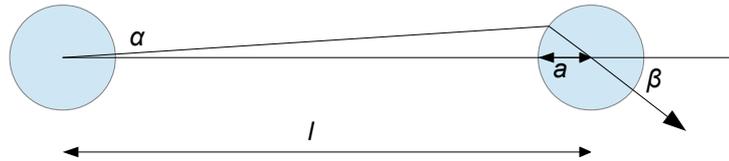


Fig 1

It is easy to see that the second molecule is going to move off in a direction which makes an angle  $\beta = \alpha \times l/a$  with the original line. Now the mean free path of nitrogen at STP is of the order of  $10^{-7}$  m so the ratio  $l/a$  is of the order of 500. It will only take 3 successive collisions for the molecule to completely miss the molecule which it would have hit had there been no scattering. The disturbance will now spread exponentially through the entire sample of gas like a nuclear explosion.

The upshot of this is that, gases are so sensitive to their initial conditions that the slightest disturbance caused by Rayleigh scattering by thermal photons is going to result in molecular chaos within a few nanoseconds.

## Conclusion

Boltzmann and Einstein recognized a long time ago that the motions of gas molecules were fundamentally random. It is, therefore, a great mystery to me why it is currently fashionable to deny this essential randomness and look for explanations of the second law in terms of Hamiltonian mechanics and/or chaos theory. Once you accept that Rayleigh scattering is a stochastic process which is happening all the time, the reason why reversing all the velocities of the molecules in a sample of gas will not result in their retracing their steps for more than a couple of collisions (Loschmidt's paradox) is obvious. Also, the fact that there is a finite chance of a gas returning to a low entropy state at some stage in the very very very distant future (Zermelo's recurrence theorem) cannot be used as a counter example to the general principle that entropy (almost) always increases.

Eddington famously said: "If someone points out to you that your pet theory of the universe is in disagreement with Maxwell's equations—then so much the worse for Maxwell's equations. If it is found to be contradicted by observation—well, these experimentalists do bungle things sometimes. But if your theory is found to be against the second law of thermodynamics I can give you no hope; there is nothing for it but to collapse in deepest humiliation." Once we accept the inherent randomness of molecular motions caused by Rayleigh scattering, the reason for Eddington's confidence becomes clear. The second law of thermodynamics is not a law at all; it is a tautology. What it says is simply this: In any universe which is not pre-destined, things that are likely to happen are more likely to happen than things which are not likely to happen. You can't disagree with that.

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