Diffusion, the ultimate step in a good mixture

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Chemical species such as carbon dioxide (CO₂) in the air, or sugar in coffee, end up, after a while, being intimately mixed with the surrounding fluid, even if it is at rest. The same mechanism transports heat through the stationary bodies until their temperature is uniform. Similarly, in a fluid layer subjected to friction, the force exerted on the surface is transmitted in its full thickness. In fluid environments, turbulence disperses the constituents, but does not reach molecular scales; it is the disordered agitation of molecules that completes this transport process called diffusion. We will see that it alone would be extremely slow but that turbulence helps it effectively.

The word diffusion is used with relatively varied meanings. What is common to all situations is the fact that a certain quantity is transported through a medium dispersed by the agitation of the elementary particles that constitute it. In physics, we distinguish two families of diffusion phenomena:

A transport phenomenon based on the properties of the medium under consideration, consisting of atoms or molecules in disordered agitation. It is characterized by the fact that the distribution of the transported quantity tends to become uniform; this quantity may be the concentration of a particular chemical species, heat or the amount of movement. The uniform end state is the thermodynamic equilibrium of the environment.

The phenomenon of diffraction of waves in a non-homogeneous environment, whether these waves are electromagnetic like light or acoustic like sound. These phenomena are described in other articles in this encyclopedia: The Colours of the Sky, Emission, Propagation and Perception of Sound. In the English language, this phenomenon of wave diffraction is referred to as scattering, which distinguishes it from diffusion itself.

In everyday language, the same word, diffusion, is used with even different meanings. Thus, it can refer to the transfer of
knowledge to a large number of people; it can also refer to the transmission of various types of information by radio (called radio broadcasting) or television (called television broadcasting).

1. The air at rest: an agitated set of molecules

In the article The Earth’s Atmosphere and Gaseous Envelope, the main components of dry air are mentioned: nitrogen (71%), oxygen (28%), argon (less than 1%), as well as some other gases in much smaller proportions. This set is made up of molecules, which occupy all the available space, a specific property of gases, which distinguishes them from the condensed states of matter (liquid or solid). These have their own volume, the solids also having their own shape.

Let’s start by sketching the main parameters of this molecular world which constitutes the relatively diluted gaseous media like air. The characteristic scales of molecular agitation (nanometric [1]) are completely beyond our senses. A few hypotheses, due to Boltzmann [2], make it possible to identify quite simply the orders of magnitude typical of this environment. Following Boltzmann, let us assume that the molecules are all spheres of the same diameter, which we will note $\sigma$, and of the same mass as we will note $m$. This already indicates the level of simplification proposed, since in reality the nitrogen (N2) and oxygen (O2) molecules are diatomic and look more like dumbbells than spheres. Let’s simplify even further by assuming that all these spheres have the same speed $c$. In fact, between collisions suffered by a molecule, its speed cannot be constant. Nevertheless, we will see that this scheme can lead to a suitable representation of the molecular world and its effects at macroscopic scales, with fairly accurate orders of magnitude.

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**Figure 1.** Typical pace of a molecule's broken line trajectory (black circle) and the volume it can sweep. Each collision with another molecule (grey circles) causes a reorientation of its trajectory. [Source: © René Moreau]

**Figure 2.** For a unit of time a mobile molecule. A sweeps a cylinder of diameter $\sigma$ and meets those which, like B, have their centre inside the cylinder of diameter $2\sigma$ and volume $\pi\sigma^2$, but not those which, like C, have their centre outside this cylinder. [Source: © René Moreau]
Let us also note \( n \) the number of molecules contained in a unit of volume and isolate one of them by thought. For one time unit (1 s), it travels the distance \( c \) along its trajectory in a broken line (Figure 1). Since we limit ourselves to orders of magnitude, let’s assume that all the other molecules with which it will have a collision are stationary. The molecules it will encounter are those whose centre is located in a cylinder whose diameter is twice that of the particle, \( 2\sigma \). The volume of this cylinder is equal to the area of its base (a disc of diameter \( \sigma \)) multiplied by the distance \( c \), i.e. \( \pi\sigma^2 \), and the number of molecules present in this cylinder is therefore \( \pi\sigma^2 \) (Figure 2). The average distance between two collisions is usually referred to as the \textbf{average free run} and denoted \( \lambda \); it is necessarily \( \lambda = 1/n\pi\sigma^2 \). The \textit{average} adjective implies that the real free paths between collisions of a molecule, visible in Figure 1, vary around \( \lambda \).

2. \textbf{Molecular parameters with macroscopic properties of a gas, or the reverse}

It is quite simple to link these parameters of the molecular world to some macroscopic quantities, measurable and accessible to our senses. These quantities - analyzed in the article \textit{Pressure, Temperature and Heat} - are pressure \( p \), temperature \( T \), mass of the volume unit (or density) \( \rho \) and viscosity \([3]\) \( \mu \). For this purpose, we have an almost obvious \textbf{first relationship} between molecular and macroscopic scales: mass \( m \) is the quotient \( m = M/NA \) between the molecular weight \( M \) and the Avogadro number (number of molecules per mole) \( NA = 6.022\times10^{23} \) mol\(^{-1}\). In addition, the density \( \rho \) must be equal to the product of the number \( n \) of molecules present in the volume unit multiplied by the mass of each molecule. We therefore have a \textbf{second relationship} between the parameters of the two worlds: \( \rho = nm \).

To connect the pressure \( p \) at a point in the gaseous medium to its molecular parameters, let us imagine that a flat solid surface of unit area \( (S = 1) \), whatever the chosen system of units, is placed somewhere in this gaseous medium. Each of the two sides of the surface will receive and accumulate the impulses of all the molecules that will hit it during the unit of time, coming from all directions, losing and regaining their kinetic energy, in the order of \( mc^2/2 \) for each of them. On average, the force exerted on the unit surface and equal to \( p \) must therefore be of the order of \( nmc^2 \). A rigorous calculation, taking into account the real velocities of the molecules encountered \([4]\), would lead to the expression \( p = nmc^2/3 \). In passing, we obtain an evaluation of the error due to the simplifying assumptions of the model adopted: the coefficient \( 1/3 \). The important thing here is that we have obtained a \textbf{third relationship} between the molecular parameters \( (n, m, c) \) and a macroscopic property, the pressure \( p \).

Since pressure and density are related to molecular parameters, it is sufficient - to express temperature - to identify the pressure \( p \) expressed above with the one that verifies the state equation of perfect gases: \( p\rho = RT/M \), where \( R = 8.314 \text{ m}^3\text{ Pa}\text{ mol}^{-1}\text{ K}^{-1} \) denotes the universal constant of perfect gases and \( M \) the average molar mass of the gas mixture. We obtain the \textbf{fourth relationship} \([5]\) \( T = Mc^2/3R \) which highlights the proportionality between the temperature \( T \) and the square of the velocity of the molecules \( c^2 \) (Read \textit{Pressure, Temperature and Heat}).

To these four relationships should be added the one that expresses the dynamic viscosity of the gas, which is established later in Section 5; \( \mu = nmc^2/3 \). So, with the following values, common for \textbf{sea-level air}

\[
p = 1.013 \times 10^5 \text{ Pa}, \ T = 288 \text{ K}, \ \rho = 1.22 \text{ kg.m}^{-3}, \ \nu = 10^{-5} \text{ m}^2\text{s}^{-1},
\]

the five relationships mentioned above lead to:

\[
n = 2.5 \times 10^{25} \text{ m}^{-3}, \ m = 4.8 \times 10^{-26} \text{ kg}, \ c = 497 \text{ m.s}^{-1},
\]

\[
d = 3.4 \times 10^{-9} \text{ m}, \ \sigma = 0.46 \times 10^{-9} \text{ m}, \ \lambda = 6 \times 10^{-8} \text{ m}.
\]

To get a fairly accurate idea of the scales of the molecular world, we can see that the number of molecules contained in a small cube of one micron on each side is about 25 million. We will deduce that the typical distance between two neighbouring molecules \( (d) \) is about 7 times their diameter \( (\sigma) \), that their average free path \( (\lambda) \) is about 60 nanometers, or about 130 times their diameter, and that the average speed of the molecules is slightly higher than the sound velocity (340 m.s\(^{-1}\)).

3. \textbf{The mechanism of diffusion in gases}
If we imagine a flat section somewhere in the middle of the gas domain at rest (Figure 3), we can say that so many molecules cross this section in both directions during the same unit of time; this is precisely what characterizes rest at macroscopic scales.

Let us suppose that a certain quantity $G$, such as the temperature or concentration of a given chemical species, has a non-uniform distribution in the vicinity of this flat section, larger on the $x>0$ side, smaller on the $x<0$ side ($x$ denotes the distance to this flat section counted on its normal). Under these conditions, the gas is no longer in thermodynamic equilibrium. Since molecules from $x>0$ carry more $G$ than those from $x<0$, this molecular agitation generates a net flow of $G$ through the plane $x = 0$, from the richest side ($x>0$) to the poorest side ($x<0$). It tends to standardize the distribution of $G$. It is this ability to transport any non-uniformly distributed quantity that is called diffusion; it is this ability that tends to establish the thermodynamic equilibrium of the gas.

However, the time required to establish this balance is much longer (hours or more) than the time between two molecular collisions (in the order of $\lambda/c \approx 1.4\times10^{-10}$ s). Under these conditions, collisions are so frequent around a given point that it can be assumed that molecules that leave the vicinity of that point after a collision all carry the same value of $G$, i.e. $G/n$ since $G$ refers to the value per unit volume. It is then said that this gas is in a state of local equilibrium.

Let’s imagine the experiment schematized in Figure 4. In its initial state, two gases are separated by a partition. Immediately
after the removal of the partition, the distribution of molecules in the cavity is not uniform. Gradually, as shown in Figure 4(2), the diffusion leads to the mixing of the two gases. The grey molecules, initially concentrated in the left part of the enclosure, reach the right part, and black molecules, initially concentrated in the right part, reach the left. This distribution continues until the distribution is uniform.

Molecules that pass through a flat surface unit perpendicular to the \(x\) direction (back to Figure 3) have, on average, the size \(G/n\). The distance from where they come is in the order of an average free journey \(\lambda\). The smallness of this length \(\lambda\) compared to the macroscopic dimensions justifies assuming linear, with a slope \(\Gamma_0\), the distribution \(G(x)\) in the vicinity of the cut located at \(x = 0\). This leads to the simple distribution: \(G = G_0 + \Gamma_0 x\). Let's even assume that the molecules that come from the \(x>0\) side all carry \(G^+ = G_0 + \Gamma_0 \lambda\), and that those that come from the \(x<0\) side carry \(G^- = G_0 - \Gamma_0 \lambda\).

![Figure 5. Volume located on either side of the surface unit, making it possible to estimate at \(n\lambda\) the number of molecules it contains and at \(nc/3\) the number of molecules that, having had their last collision in this volume, will cross the surface unit. [Source: © René Moreau](image)

To estimate the net flow of \(G\) through the unit area of the section, multiply the difference \(\gamma_0 \lambda\) by the number of molecules that cross this area per unit time from one side or the other. Note that, in the volume above the unit of area (see Figure 5), there are \(n\lambda\) molecules, and that each undergoes \(c/\lambda\) collisions per unit of time. As a result, the number of collisions, i.e. departures, is necessarily in the order of \(nc\). But only departures oriented towards the unit of surface must be taken into account. The calculation leads to the number \(nc/3\) (again a coefficient \(1/3\)).

Finally, the flow rate \(\phi\) of \(G\) through each unit of surface of the plane \(x = 0\) can be estimated by the relationship \(\phi = (c_\lambda/3) dG/dx\). The conclusion of this estimate is as follows: if a quantity \(G\) is distributed non-uniformly, the net flow of \(G\) transported by molecular agitation is proportional to the local gradient \(dG/dx\) and is expressed by a relationship of the form \(\phi = -D dG/dx\), where, by convention, the sign is placed - so that the flow is positive when \(dG/dx\) is negative (heat goes from the warm side to the cold side). The coefficient \(D\) appearing in this relationship is \(D = c_\lambda/3\). It is called the diffusivity of this gas; it is a purely kinematic quantity measured in \(m^2/s\). It is remarkable that it was possible to assess the diffusivity of the gas without specifying the nature of the size transported.

The numerical values given in section 2 are used to estimate air diffusivity. With \(c = 497\ m/s-1\) and \(\lambda = 6 \times 10^{-8}\ m\), we obtain: \(D \approx 10^{-5}\ m^2/s-1\). To give this value a practical meaning, let us return to the experience in Figure 4: If we note \(L\) the length of the enclosure, since diffusivity has the dimension of a square length divided by time \((L^2/T)\), the typical duration to reach the final state in equilibrium is necessarily in the order of \(L^2/D\). If \(L \approx 10\ cm\), this duration is about one hour. For this duration to be in the order of a second, the enclosure in Figure 4 would have to be about a millimeter long, as would be the case with a small bubble.

4. The turbulent diffusion

In most of the fluid environments in our environment, including air and water, turbulence is almost omnipresent. It is a phenomenon of agitation totally unrelated to the movement of molecules. Within a flow such as the wind, or as a marine current, it manifests itself in the presence of large scale, fairly large and easily measurable speed fluctuations. Even without imposed flow, in the presence of hydrodynamic instability \([6]\), turbulence is present as a set of vortices of all sizes entangled in each other. We can see a certain analogy with the molecular agitation described in the previous sections, but at the vortex scales, much
larger than the average free path of the molecules. This analogy led Prandtl [7] to suppose that it was possible to define a mixing length [8], similar to the average free path of the molecules of a gas.

Experimentally, various techniques have been used to evaluate this length of mixture, which represents the typical size of eddies. The smoke volutes in Figure 6, such as those rising above chimneys or volcanoes, give an idea of this and show that this size always adapts to the overall size of the flow. Note the difference between the lower (laminar) part of cigarette smoke, which widens slightly under the effect of molecular diffusion, and the upper (turbulent) part, whose much faster widening highlights the transport of various constituents of this smoke by the random eddies generated by the instability of the smoke plume.

The concept of mixing length, size noted below, is rather vague but it has the merit of allowing satisfactory orders of magnitude to be established. The situation where it is best justified is that of a boundary layer (see Figure 7). The expression suggested by Prandtl in such a boundary layer and generally adopted is \( l = \kappa y \), where \( y \) is the distance to the wall and \( \kappa \) a numerical constant determined by experience. With this expression of the length \( l \), the order of magnitude of the velocity fluctuations at the distance \( y \) from the wall can be estimated by \( u' \approx l \frac{dU}{dy} \). The analogy with gas agitation suggests reusing the expression of molecular diffusivity \( D = c \lambda / 3 \) by replacing \( c \) by \( u' \) and \( \lambda \) by \( l = \kappa y \). The turbulent diffusivity \( D_t \) within a boundary layer then becomes:

\[
D_t \approx u'l \approx \kappa^2 y^2 \frac{dU}{dy}
\]

For example, let us place ourselves within the atmospheric boundary layer, whose thickness is about a few hundred meters, at a distance from the ground \( y \approx 10 \text{ m} \) where the average speed is about 10 m.s\(^{-1}\) and where \( \frac{dU}{dy} \approx 1 \text{ s}^{-1}\). By adopting the value 0.1 for the constant \( \kappa \), derived from experiments, these estimates lead to a turbulent diffusivity \( D_t \approx 10 \text{ m}^2 \text{ s}^{-1} \), i.e. one million times higher than the molecular diffusivity. This value reduces the time required to achieve the turbulent mixture to about one-tenth of a second: \( t \approx \frac{l^2}{D_t} \approx 0.1 \text{ s} \). But this mixing is not complete because the components are only dispersed to the scale of the smallest vortices, which depends on the viscosity of the fluid. In the case of the atmospheric boundary layer, it is about one millimeter. It is the molecular agitation that completes the mixture to the molecular dimensions, and we know that this requires an \( L^2/D \) duration. In reality, molecular scattering begins within millimetre eddies where it coexists with turbulent dispersion. To simplify, let us assume that molecular scattering acts alone below the millimeter. With \( L \approx 10^{-3} \text{ m} \) and \( D \approx 10^{-5} \text{ m}^2 \cdot \text{s}^{-1} \), we still obtain a duration of about one tenth of a second.

From these estimates, it can be concluded that:

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Figure 6. Warmer and lighter than the ambient air, the smoke rises. Its charge in various combustion products makes it visible. In the lower part, we notice a first length without turbulence. Then, about 10 to 15 cm above the cigarette, hydrodynamic instability causes turbulence, causes eddies to appear and greatly widens the smoke plume. This enlargement is a manifestation of the difference between turbulent diffusion and molecular diffusion alone present in laminar regime. [Source: © Krunoslav Knezevic]
the turbulent diffusion only disperses the constituents to the scale of small eddies,
molecular diffusion completes this mixture,
the durations of the two mechanisms can have orders of magnitude in the order of one tenth of a second,
without turbulence, the time required to make a good mixture could reach several hours.

5. Mass and thermal diffusion

It is by the expression mass diffusivity that we usually refer to the diffusivity of a chemical species contained in the fluid medium. Suppose, therefore, that some of the molecules of the fluid considered, gas or liquid, are different from the others. Let’s take the example of water molecules (H2O) in the form of steam, in absolutely calm air over a large liquid area, such as a peaceful lake. And let us now note C the volumetric concentration of water in the air at any altitude z, a quantity initially noted as G before its nature was specified. To evaluate the net flow of water vapour to high altitudes, the law seen above leads to the expression $\dot{q} = -D \frac{dC}{dz}$. It’s Fick’s law. It is essential to be able to calculate the quantity of water extracted by diffusion from low altitudes, but it must be supplemented by a mass balance and by initial and boundary conditions.

Thermal diffusivity expression is reserved for heat transport by molecular agitation. Let us now assume that quantity G is the internal energy $E$ per unit volume of the gas, any infinitesimal variation of which is manifested by a temperature variation $dT$, according to the law $dE = \rho C_v dT$, where $C_v$ denotes the constant volume calorific capacity of the gas. Then the diffusion transport of this internal energy, i.e. heat, becomes $\dot{q} = -D C_v \frac{dT}{dz}$. It is common to write this expression called Fourier’s Law in one of the following two forms: $\dot{q} = -k \frac{dT}{dz}$, where $k = \rho C_v D$ is called the thermal conductivity of gas, or $\dot{q} = -\alpha \rho C_p \frac{dT}{dz}$, where $\alpha = \frac{k}{\rho C_p}$ is the thermal diffusivity of gas. The quantity $C_p$ then refers to the heating capacity at constant gas pressure.

The physical properties of the gases, especially air, introduced above ($D$, $k$, $\alpha$, $\mu$, $\nu$) are related to the molecular parameters $n$, $m$, $c$ and $\lambda$. Among them, for a given density gas, only the velocity of molecules $c$ is likely to vary with temperature $T$. And we saw that this dependence could be written: $T = \frac{Mc^2}{3R} = \frac{mc^2}{3kB}$. It can be deduced that the diffusivities of a gas ($D$, $k$, $\alpha$, $\mu$, $\nu$) vary like the square root of its temperature.

6. Diffusion of movement: viscosity

Let us now assume that the above notions remain valid in a fluid set in motion at macroscopic scales by moving a wall in its own plane. This hypothesis is very well justified as long as the typical durations of macroscopic motion (seconds or minutes, in general) are considerably longer than the time between two collisions of a molecule (about 10-11 s).

Figure 7. A boundary layer is always present on either side of a wing. Here the top surface layer (above the wing) lifts off the wall shortly after the leading edge and becomes turbulent, while the bottom surface layer (below the wing) remains laminar and very thin. In this wind tunnel experiment, the wing is fixed and the surrounding fluid flows to the right. [Source : ONERA, The French Aerospace Lab.]
The diffusion of a particular species within a mixture, like the diffusion of heat and the diffusion of the amount of movement, results from the agitation of elementary particles, molecules or atoms. It is a very slow transport mechanism, but without a competitor on microscopic scales.

In fluids such as air and water, which are not very viscous, turbulence disperses pollutants, heat and the amount of movement. But this mechanism cannot reach scales lower than those of the smallest vortices, controlled by viscosity, generally greater than one micron. Molecular diffusion relays it to complete the mixture.

The laws of diffusion were first discovered empirically before being the subject of theoretical models. Relatively simple in the case of diluted gases such as air, it could be sketched in this article. Its equivalent in the case of liquids is much more complex and still under investigation.

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References and notes

Cover image. Before sunrise, in the countryside, in the still motionless air, it is by diffusion that contaminants released by vegetation are transported into the air. [Source: pixabay, royalty-free].

[1] A nanometre is one billionth of a metre ($10^{-9}$ m), a micrometre, or micron, is one millionth of a metre (1 μm = 10$^{-6}$ m).

[2] Ludwig Boltzmann (1844-1906), an Austrian physicist and philosopher, introduced this molecular model called “hard spheres” that leads to a famous equation bearing his name.

[3] It is often substituted by the kinematic viscosity $\nu$, which is the quotient between the viscosity $\mu$ and the density $\rho$, i.e. $\nu = \frac{\mu}{\rho}$.

[4] All these velocities, with their respective orientations and values, can be represented using Maxwell's distribution function. Taking them into account would lead to lengthy calculations beyond the scope of this article.

[5] This expression is better known as $kBT = mc^2/3$, by introducing the Boltzmann constant $kB$, related to $R$ and the Avogadro number $NA = 6.0248 \times 10^{23}$, per $kB = R/NA= 1.380 \times 10^{-23}$ J/K (joule by Kelvin).

[6] For example, at dawn, as soon as the sun begins to warm the ground, by diffusion it heats the lowest layers of air, which become lighter than those above them. This situation where the heavy fluid is located above the light fluid is unstable.

[7] Ludwig Prandtl (1875-1953) was a German physicist, professor at the University of Munich, who made important contributions to fluid mechanics. He is credited with the founding ideas of boundary layer theory, the concept of mixture length and a simple theory for calculating the lift of a finite wing span.


[9] The property that $\varphi = -\tau$ can be established by writing the global equilibrium of a small gas domain located on the $z>0$ side of the wall that exerts the tangential force on the fluid $-\tau$. The expression of this global equilibrium is often referred to as the quantity of movement theorem.

[10] The establishment of this expression is actually due to Navier, Fourier's congener (see the focus on the Fathers of the diffusion concept).