On the barometric formula

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The barometric formula, relating the pressure $p(z)$ of an isothermal, ideal gas of molecular mass m at some height z to its pressure $p(0)$ at height $z=0$, is discussed. After a brief historical review, several derivations are given. Generalizations of the barometric formula for a nonuniform gravitational field and for a vertical temperature gradient are also presented. *© 1997 American Association of Physics Teachers.*

I. INTRODUCTION

The barometric formula

$$p(z)=p(0)\exp\left(-\frac{mgz}{kT}\right) \tag{1}$$

relates the pressure $p(z)$ of an isothermal, ideal gas of molecular mass m at some height z to its pressure $p(0)$ at height $z=0$, where g is the acceleration of gravity, k the Boltzmann constant, and T the temperature. In spite of its simplicity, namely the assumption of constant temperature, it applies reasonably well to the lower troposphere (for altitudes up to 6 km, the error is less than 5%[1]), and also to the stratosphere, up to 20 km (with $T=217$ K, that is, -57 °C).[1,2] The historical aspects linked to the barometric formula are fascinating. In Europe, by the end of the XVIth century, the accepted descriptions and explanations of natural phenomena were those of the Greek philosopher Aristotle (384–322 B.C.), whose influence over learned Christendom had been dominant since St. Thomas Aquinas (1226–1274). Nevertheless, Aristotle's treatises concerning the natural world were by then known to contain important mistakes, either as a result of the European voyages of discovery of the XVth and XVIth centuries (e.g., the possibility of life near the equator, or the existence of a new continent, America) or of other experimental observations (e.g., the structure of the human heart). In 1592, the Portuguese Jesuits began the publication of the last coherent corpus of Aristotelian philosophy. This work was organized, as usual, in the form of a series of commented Latin translations of Aristotle's works (*Commentarii Colegii Conimbricensis Societatis Iesu in Libros Aristotelis Stagiritae*).[3,4] Comments regarding the above-mentioned new discoveries (and others) are found at relevant points of the books concerning natural philosophy. Aristotle's authority, though acknowledged, was not blindly accepted by scholars,[5] and the importance of the ''experience [i.e., *empirical knowledge*], the mother of philosophy'' (in fact, in the best Aristotelian spirit) was stressed in the *Comments*.

Within a few decades, the accumulated knowledge obtained from both observation and active experimentation was going to make most of Aristotle's natural philosophy untenable. But at the time, the accepted general explanation for various phenomena associated with air pressure, like the working of water pumps, was still ''nature's abhorrence of a vacuum'' (an expression that is, however, posterior to Aristotle). This ''law'' is adhered to in the cited *Commentarii Physicorum* (Fig. 1).

Limited experimental evidence against an almighty *horror vacui* existed, however, as results from a passage of Galileo Galilei's (1564–1642) *Dialogues concerning two new sciences* (1638).[6] A pump had been built for raising water from a rainwater underground reservoir. When the reservoir level was high, the pump worked well. But when the level was low, the pump did not work. Having noticed this, Galileo (Sagredo in the *Dialogues*) asked the engineer in charge to repair the pump. To Galileo's surprise, he replied that it was working perfectly, it being well known that water could not rise more than about 10 m in a suction pump. The empirical knowledge therefore existed, probably for a long time (pumps based on air pressure were in use since Antiquity).[7]

However, no one had put forward a theory or suggested that an essentially empty space (neglecting vapor pressure) had to exist above the water surface in the case of pump ''malfunction.'' Galileo supposed that bulk water was glued on top of the pump by the vacuum (the Italian words used are *glutine*, *colla*, and *visco*), but that this glue had a limited resistance, breaking at a certain maximum weight.[6] Because of this explanation, he rightly conjectured (on false grounds) that the ''breaking'' height for other materials should be inversely proportional to their density.[6] Therefore, Galileo departed from the Aristotelian doctrine: After all, Nature manifested only a limited *horror vacui*, and a vacuum could be produced and maintained.

It appears that the correct explanation (atmospheric pressure) is due to Giambattista Baliani, a Genoese, that first suggested it to Galileo in a letter,[8] in 1630. However, as described, Galileo did not agree with such an explanation, not even mentioning it in his 1638 book.[6] The question remained however unsettled.[8] After his master's death, Galileo's disciple Evangelista Torricelli (1608–1647) devised a decisive experiment with the help of an *ad hoc* setup consisting of two long glass tubes (ca. 1.2 m) sealed at one end, and a bowl of mercury[9] (Fig. 2). This celebrated mercury column experiment, carried out in collaboration with another disciple of Galileo, the young Vincenzo Viviani (1622–1703), took place in 1643 or 1644. The purposes of the experiment were:[8,9] (i) to confirm the existence of a vacuum (following Galileo); (ii) to show that air pressure is the true explanation (against Galileo); and (iii) to display the varia-

COMMENTARII
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IESV,
In octo libros Phyſicorum Ariſtotelis Stagiritæ.

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Typis et expenſis Antonij à Mariz Vniuerſitatis Typographi.
Anno Domini, M.D.LXXXXII.
CVM PRIVILEGIO REGIS.

Fig. 1. Frontispiece of the book *Commentarii Physicorum* (printed in Coimbra in 1592), first volume of the series *Commentarii Colegii Conimbricensis Societatis Iesu in Libros Aristotelis Stagiritae*. Source: *Biblioteca Nacional de Lisboa*.

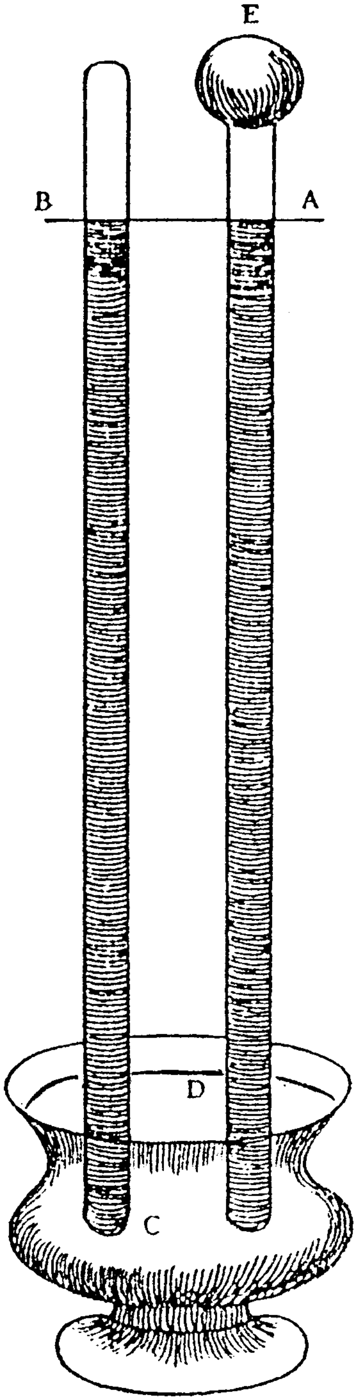
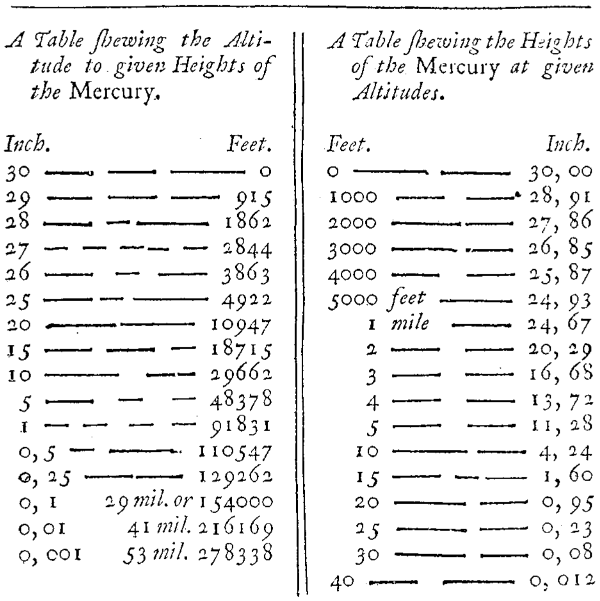


Fig. 2. A drawing of Torricelli's experimental setup.[9] The mercury column attained the same height in tubes A and B. The bowl contained mercury (C) and, above it and up to D, water. Upon raising tube A, as to place its lower end slightly above the mercury–water interface, the mercury column collapsed, and water rushed into the tube, filling it completely (up to E). According to Torricelli, this was the proof of the existence of a vacuum in the space above the mercury column.

tions of pressure with weather. Air pressure as the true cause was established by showing that the mercury height was the same in both tubes, in spite of the very different volumes of vacuum produced (Fig. 2). (The proof seemed, however, not totally convincing for other natural philosophers, as we shall see.) Torricelli was well aware of the great importance of his experiment, though he did not publicize it outside a small circle of friends and colleagues. But thanks to the exchange of scientific letters and to scientific travelers such as the French monk Marin Mersenne, it became rapidly known throughout Europe as the *Experiment from Italy*, although the name of its author appears to have been concealed.[8,10,11]

Variants of Torricelli's key experiment, and new ones, devised by the French polymath Blaise Pascal (1623–1662),[10,11] and by others, further strengthened Torricelli's theory beyond doubt. Of all experiments, the one that Pascal considered decisive was the record of the height of a column of mercury as a function of altitude: ''If air weight and pressure is the true cause, the height should decrease with an increase in altitude, as less air exerts weight on top of a mountain than at its base; on the other hand nature's abhorrence of a vacuum must be the same at both places.'' It may be remarked that the variation of air density with altitude had already been explicitly mentioned by Torricelli in a letter to Ricci:[9] ''(...) *the authors that have written about the twilight, say that the visible air, full of vapours, extends above us up to about 50 or 54 miles; this I believe is exaggerated, because I will show that if such were the case the vacuum resistance should be much stronger than what it actually is. But they have a way out, because they can say*



A Table ſhewing the Altitude to given Heights of the Mercury.

Inch.		*Feet.*
30		0
29		915
28		1862
27		2844
26		3863
25		4922
20		10947
15		18715
10		29662
5		48378
1		91831
0, 5		110547
0, 25		129262
0, 1	29 *mil. or*	154000
0, 01	41 *mil.*	216169
0, 001	53 *mil.*	278338

A Table ſhewing the Heights of the Mercury *at given Altitudes.*

Feet.	*Inch.*
0	30, 00
1000	28, 91
2000	27, 86
3000	26, 85
4000	25, 87
5000 *feet*	24, 93
1 *mile*	24, 67
2	20, 29
3	16, 68
4	13, 72
5	11, 28
10	4, 24
15	1, 60
20	0, 95
25	0, 23
30	0, 08
40	0, 012

Fig. 3. Calculations of $p(z)$ and $z(p)$, by E. Halley,[12] for $p(0)=30$-in. Hg (762-mm Hg), and a density of air ($z=0$) to mercury of 1 to 10 800.

that the air whose weight [density] is given by Galileo [1/400th of the density of water] belongs to the lowest region, where men and animals live, but that on top of the high mountains the air begins to be very pure and weights much less than 1/400th of the weight of water.'' The experiment devised by Pascal was carried out by his brother-in-law, Florin Périer, in 1648, at the Puy-de-Dôme, a lofty mountain in Auvergne. The results conformed to Pascal's expectation, the altitude variation of ca. 1 km entraining a decrease in the height of the column of mercury of ca.[10] 85 mm. Périer also repeated the experiment at the highest tower of the cathedral of Clermont-Ferrand (ca. 39 m height),[10,11] and observed a smaller but distinct variation of the height of the column of ca.[10] 5 mm. Encouraged by the results, Pascal himself repeated the experiment in Paris, at the St. Jacques tower (ca. 52 m height), having obtained similar results (the tower still exists, and has at its foot a statue of Pascal with a barometer).

A quantitative relation (barometric formula) was nonetheless not given by Pascal. The exponential dependence of pressure on height could only be obtained after the discovery of Boyle's law (Oxford, 1662), and was first recognized by the English physicist and astronomer Edmund Halley (1656–1742), also from Oxford University, in 1686.[12] He also gave, as an example, $p(z)$ and $z(p)$ in tabular form (Fig. 3), for the case of a ground ($z=0$) atmospheric pressure equal to 30 in. Hg (762-mm Hg) and a density of ground air to mercury of 1 to 10 800, this last value being obtained from a density of air to water of 1 to 800 and of a density of water to mercury of 1 to 13.5. Much later, the great French mathematician Pierre-Simon de Laplace (1749–1827) finally explicitly obtained the barometric formula (and extensions of it) in his *Traité de Mécanique Céleste*.[13] For this reason, the barometric formula is sometimes called Laplace's formula.

The barometer (name coined by Boyle) was very soon used for the measurement of altitude, although the results were subject to some error, owing to local pressure changes and temperature and composition variations (the real atmosphere not being in strict thermodynamic equilibrium). In 1801, the Colombian astronomer Caldas discovered that a thermometer could be used for the same purpose,[14] by measuring the boiling point of water, which depends on pressure through the Clapeyron equation.

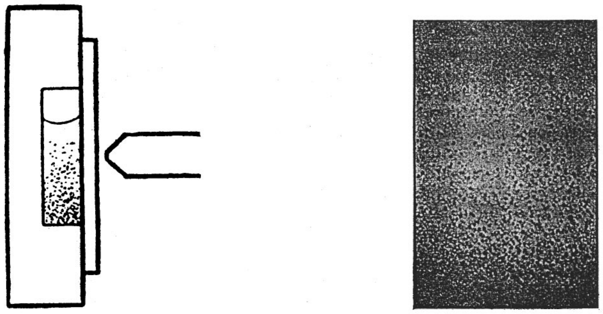


Fig. 4. Schematic representation of the microscope setup (left) used to take a photograph (right) showing the exponential distribution of the particles. From *Les Atomes*.[15]

In 1909, the French physicist Jean Perrin showed[15] that a suspension in water of tiny spherical particles (radii between 0.2 and 0.5 μm) obtained from tree resins obeys the barometric formula,[16] behaving as a miniature atmosphere, one whose ''molecules'' are visible with an optical microscope (Fig. 4).

II. DERIVATIONS OF THE BAROMETRIC FORMULA

We now discuss some ways of arriving at the barometric formula. Some are well known, others not so. Each one gives different insights on the problem.

A. Hydrostatic derivation

Consider a still gas contained in a vessel of height H. In equilibrium, the pressure at a given height z is

$$p(z)=p(H)+M(z)g, \tag{2}$$

where $M(z)$ is the mass of the gas in a column of unit area that extends from z to H,

$$M(z)=\int_z^H \rho_m(u)du, \tag{3}$$

where ρ_m is the mass density. From the perfect gas equation $pV=NkT$, where N is the number of molecules contained in the volume V, one obtains

$$\rho_m(z)=\frac{Nm}{V}=\frac{mp(z)}{kT}, \tag{4}$$

and the following integral equation is obtained:

$$p(z)=p(H)+\frac{m}{k}\int_z^H \frac{gp(u)}{T}\,du, \tag{5}$$

whose solution is Eq. (1) if it is assumed that g and T do not depend on height. A differential balance of forces can also be written from the start, as is common practice in textbooks and was originally done by Laplace:[13] In mechanical equilibrium, the opposite forces acting in a column of air of unit area between z and $z+dz$ must be equal:

$$p(z+dz)+\rho_m(z)gdz=p(z). \tag{6}$$

Combining Eqs. (4) and (6), one obtains the differential form of Eq. (5),

$$\frac{dp}{dz}=-\frac{mg}{kT}\,p. \tag{7}$$

The above derivations show that the view of atmospheric pressure as originating from the weight (per unit area) of all the air above the surface of the earth is essentially valid because $H\to\infty$ and thus $p(H)\to 0$.

Taking $p(0)=1.0$ atm and $g=9.8\ \mathrm{ms}^{-2}$, we get for the air mass per unit area $M(0)=p(0)/g=1.0\ \mathrm{kg\ cm}^{-2}$. This mass is exponentially distributed in height, according to Eq. (1). Were air an incompressible fluid (as mercury approximately is), its density would not vary with height. Assuming that in such a case the density was that for zero height, the total height of the air column, H_s, would be

$$H_s=\frac{M(0)}{\rho_m(0)}=\frac{kT}{mg}. \tag{8}$$

For our atmosphere and taking $T=290$ K, this height (the so-called scale height) is 8.5 km. Such a value was already correctly estimated by Halley,[12] simply by using the ratio of mercury to air densities mentioned above, as $H_s=762\ \mathrm{mm}\times 10800=8.3$ km. It is interesting to note that H_s is also the *average* height of an air molecule. Indeed, the probability of finding a certain molecule at a given height z obeys a distribution (density) function $w(z)$ that is proportional to the pressure, and it follows from Eq. (1) and from the normalization requirement that

$$w(z)=\frac{mg}{kT}\exp\left(-\frac{mgz}{kT}\right). \tag{9}$$

The mean of this probability density function is precisely Eq. (8).

B. Kinetic derivations

A consideration of the matter from the molecular-kinetic point of view is also interesting, and provides a clearer view of the way the exponential distribution is brought about.

1. Noninteracting molecules

Consider the following conceptual experiment: A large number of noninteracting molecules, initially at rest on a horizontal plane ($z=0$), are set into upward vertical motion at $t=0$, according to a given distribution of initial velocities, $f(v_0)$. If these molecules are under the influence of a constant gravitational field counteracting their ascent, they rise only up to a certain maximum height $z_m=v_0^2/2g$, falling back afterward. Assuming that collisions with the plane are elastic, each trajectory repeats an infinite number of times, i.e., the motion becomes periodic. For a given initial velocity v_0, the dependence of height on time is

$$z(t|v_0)=v_0t-\frac{1}{2}gt^2 \quad \text{if } t\in\left[0,\frac{2v_0}{g}\right]. \tag{10}$$

This dependence of height on time can also be expressed by a probability density function $w(z',t|v_0)$,

$$w(z',t|v_0)=\delta[z'-z(t|v_0)]. \tag{11}$$

For a given distribution of initial velocities $f(v_0)$, the overall height density function, $w(z',t)$, is

$$w(z',t)=\int_0^\infty f(v_0)\,\delta[z'-z(t|v_0)]\,dv_0. \tag{12}$$

It is expected that for long times Eq. (12) converges to a time-independent density function $w(z')$. This can indeed be shown (Appendix A). The limiting function $w(z')$ is

$$w(z')=\int_0^\infty f(v_0)w(z'|v_0)\,dv_0, \tag{13}$$

where

$$w(z'|v_0)=\begin{cases}\dfrac{g}{v_0\sqrt{v_0^2-2gz'}} & \text{if } z'\leqslant\dfrac{v_0^2}{2g}\\[2ex] 0 \quad \text{if } z'>\dfrac{v_0^2}{2g}\end{cases}, \tag{14}$$

and therefore

$$w(z')=\int_{\sqrt{2gz'}}^\infty f(v_0)\,\frac{g}{v_0\sqrt{v_0^2-2gz'}}\,dv_0. \tag{15}$$

What then is the distribution function $f(v_0)$ that leads to the exponential density, Eq. (9)? Substitution of Eq. (9) into Eq. (15) gives an integral equation whose solution is the sought-for function. However, it is Eq. (9) we want to obtain, and $f(v_0)$ must therefore be derived in another way. This can be done as follows: Because at $t=0$ (nonequilibrium) all molecules are present at $z=0$, and starting to move upward, it is clear that their initial velocity distribution *cannot* be the steady-state one, $f_s(v|z)$. The two are related by (Appendix C)

$$f_s(v|z)=\frac{\dfrac{f(\sqrt{v^2+2gz})}{v^2+2gz}}{\displaystyle\int_{-\infty}^{\infty}\frac{f(\sqrt{v^2+2gz})}{v^2+2gz}\,dv},\quad v\in\,]-\infty,+\infty[, \tag{16}$$

and by

$$f(v_0)=\frac{v_0^2f_s(v_0|0)}{\int_0^\infty v_0^2f_s(v_0|0)\,dv_0},\quad v_0\in[0,+\infty[. \tag{17}$$

Now, in order to emulate thermodynamic equilibrium, the *steady-state* velocity distribution function must be the unidimensional Maxwell–Boltzmann distribution; in particular, that should be true for $z=0$:

$$f_s(v|0)=\left(\frac{m}{2\pi kT}\right)^{1/2}\exp\left(-\frac{mv^2}{2kT}\right). \tag{18}$$

Inserting this distribution into Eq. (17), the initial distribution of velocities turns out to be

$$f(v_0)=4\pi v_0^2\left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left(-\frac{mv_0^2}{2kT}\right), \tag{19}$$

and substitution of this distribution into Eq. (15) finally yields the exponential density of heights, Eq. (9).

It is interesting to note that the initial distribution of velocities, Eq. (19), is identical to the Maxwell distribution of speeds [not to be confused with the Maxwell–Boltzmann distribution of velocities, Eq. (18)] for three-dimensional motion, which immediately shows that the initial average kinetic energy of the molecules along the z axis is $\frac{3}{2}kT$, and

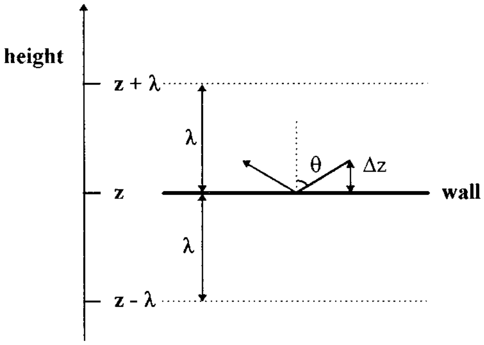


Fig. 5. The molecule starts at $z+\Delta z$ and at an angle θ with the normal.

not $\frac{1}{2}kT$, as happens in the steady state [Eq. (19)]. The reason for this difference is that 2/3 of the initial kinetic energy is taken up by the gravitational field, so that in the steady state the average molecular kinetic energy is indeed $\frac{1}{2}kT$, and the average molecular potential energy is kT, a result that also follows from the virial theorem.[17] Substitution of Eq. (19) into Eq. (16) confirms that, once the steady state is attained, a Maxwell–Boltzmann distribution of velocities [Eq. (18)] is obeyed at all heights, that is, the system is indeed isothermal.[18]

Of course, this mechanical model does not correspond to true thermodynamic equilibrium (it is nonergodic). It just behaves as if it were, because a Maxwell–Boltzmann-like distribution of velocities was imposed. Any distribution of initial velocities leads to a steady state, but only Eq. (19) is compatible with an exponential distribution of heights.

The above model shows that an exponential distribution of heights may still be observed in a very rarefied atmosphere where intermolecular collisions are infrequent. The model may appear to be of little practical significance, but, in fact, it may serve as a simple picture of the situation prevalent in the very high layers of the Earth's atmosphere.

2. Interacting molecules

A kinetic model incorporating collisions is more difficult to handle, because of the density dependence on height, and we only give a semiquantitative derivation based on the mean-free path, λ. Within a time interval equal to the mean time between collisions τ, only molecules initially located between z and $z+\lambda$ contribute to the pressure exerted on the upper surface of the wall (Fig. 5). Consider now a molecule starting at $z+\Delta z$, with velocity v, and hitting the surface at an angle with the normal θ. For simplicity, a linear trajectory is assumed, because the velocity change originated by the gravitational field is supposed to be small compared to the thermal velocity v. The time spent in such a free path is therefore approximately $\tau(\Delta z,\theta)=\Delta z/(v\cos\theta)$. In this way, the vertical component of the impact velocity is

$$v_z(\Delta z,\theta)=v\cos\theta+g\tau(\Delta z,\theta)=v\cos\theta+\frac{g\Delta z}{v\cos\theta}. \tag{20}$$

Hence, the momentum imparted to the wall is

$$2mv_z(\Delta z,\theta)=2m\left(v\cos\theta+\frac{g\Delta z}{v\cos\theta}\right).$$

The upper pressure on the wall is, therefore,

$$p_u\tau=\int_0^\lambda\int_0^{\theta_{\max}(\Delta z)}2m\left(v\cos\theta+g\frac{\Delta z}{v\cos\theta}\right)\times\tfrac{1}{2}\sin\theta\,d\theta n(z+\Delta z)d\Delta z, \tag{21}$$

where

$$\theta_{\max}(\Delta z)=\arccos\left(\frac{\Delta z}{\lambda}\right). \tag{22}$$

Similarly, the lower pressure on the wall is

$$\begin{aligned}p_l\tau&=\int_{-\lambda}^0\int_0^{\theta_{\max}(\Delta z)}2m\left(v\cos\theta+g\frac{\Delta z}{v\cos\theta}\right)\times\tfrac{1}{2}\sin\theta\,d\theta\,n(z+\Delta z)d\Delta z\\&=\int_0^\lambda\int_0^{\theta_{\max}(\Delta z)}2m\left(v\cos\theta-g\frac{\Delta z}{v\cos\theta}\right)\times\tfrac{1}{2}\sin\theta\,d\theta\,n(z-\Delta z)d\Delta z.\end{aligned} \tag{23}$$

Writing $n(z+\Delta z)$ as a truncated power series,

$$n(z\pm\Delta z)\cong n(z)\pm\left.\frac{dn}{dz}\right|_z\Delta z, \tag{24}$$

and equating the upper and lower pressures, one obtains, after some calculations,

$$n(z)=n(0)\exp\left(-\frac{4gz}{\overline{v^2}}\right), \tag{25}$$

and, with $\overline{v}=(8kT/\pi m)^{1/2}$, the exponential distribution is recovered, but the argument of the exponential is incorrect by a factor of $\pi/2$. It should be remarked at this point that the concepts of mean-free path and mean collision time are ill-defined, in the sense that they vary with height.[19] The above derivation shows however that a steady concentration and a linear momentum balance at a given height are achieved by compensating the higher velocity of descending molecules with a larger number of ascending ones.

C. Stochastic derivation

A dilute suspension of tiny particles in a liquid also obeys the barometric formula. However, the kinetic derivations outlined above apply to a perfect gas only. This is so, because, while both kinds of trajectories are similar if observed at low resolution, they cease to be self-similar at different magnifications: For the dilute gas, they are seen to be composed of long (as measured in terms of molecular diameters) straight-free paths with random orientations, while for the particles suspended in the liquid (or molecules of the liquid itself) the erratic pattern persists down to molecular dimensions. Changes of direction and velocity occur much more frequently in the last case, and a microscopic description based on the mean-free path concept is not appropriate. This kind of motion (Brownian motion) is approximately described by the diffusion (or Fokker–Planck) equation, for timescales larger than the decay time of the particle's velocity autocorrelation.[20–23] Therefore, such an equation applies also to the dilute gas, but on a much coarser (though in most cases still microscopic) scale.

With the above restrictions, the probability density function $w(z,t)$ of a diffusing particle under the action of a constant gravitational field directed along the negative z direction obeys a special kind of Fokker–Planck equation, called the Smoluchowski equation[21–22]

$$\frac{\partial w}{\partial t}=D\,\frac{\partial^2 w}{\partial z^2}+c\,\frac{\partial w}{\partial z}, \tag{26}$$

where D is the diffusion coefficient, $D=kT/f$, f being the drag coefficient (equal to $6\pi\eta r$ for a macroscopic sphere of radius r in a fluid of viscosity η) and $c=m'g/f$, m' being the apparent mass of the particle.[16]

The time evolution of $w(z,t)$, subject to the initial condition,

$$w(z,0)=\delta(z-z_0), \tag{27}$$

and to the boundary condition,

$$D\,\frac{\partial w}{\partial z}+cw=0 \quad \text{at} \quad z=0 \quad \text{for all} \quad t\geqslant 0, \tag{28}$$

which means that the particle starts its motion at $z=z_0$ [Eq. (27)] and cannot cross the plane $z=0$ [bottom of the vessel; Eq. (28)], is[21]

$$\begin{aligned} w(z,t)=&\frac{1}{2\sqrt{\pi D t}}\left\{\exp\left[-\frac{(z-z_0)^2}{4Dt}\right]+\exp\left[-\frac{(z+z_0)^2}{4Dt}\right]\right\}\\ &\times\exp\left[-\frac{c}{2D}\,(z-z_0)-\frac{c^2}{4D}\,t\right]\\ &+\frac{c}{D\sqrt{\pi}}\,e^{-cz/D}\int_{(z+z_0-ct)/2\sqrt{Dt}}^{\infty}\exp(-x^2)\,dx. \end{aligned} \tag{29}$$

At short times, a Gaussian-like curve is obtained, as for free diffusion; however, an asymmetry soon develops, owing to gravity. Finally, for $t\to\infty$, only the last term survives, yielding the exponential density. This density is more easily obtained by setting $\partial w/\partial t=0$ in Eq. (26) and solving the resulting ordinary differential equation.

For the case of particles suspended in a liquid, the exponential function can be used to explain sedimentation: While small particles may be approximately homogeneously distributed in a liquid, the aggregates formed when they coalesce, will have masses high enough to compress, so to speak, the exponential function, yielding a thin layer at the bottom. On the other hand, for a fixed particle mass, sedimentation can still be made to occur by increasing the acceleration g, as is done in centrifuges.

D. Statistical derivation

The most straightforward derivation of the barometric formula is perhaps from Boltzmann's distribution[24]

$$P(\mathbf{r},\mathbf{v})=\frac{\exp\left(-\dfrac{E(\mathbf{r},\mathbf{v})}{kT}\right)}{\displaystyle\int_V \exp\left(-\frac{E(\mathbf{r},\mathbf{v})}{kT}\right)d\mathbf{r}\,d\mathbf{v}}, \tag{30}$$

where V is the phase-space volume, and $P(\mathbf{r},\mathbf{v})$ the joint equilibrium distribution function for position and velocity. For three-dimensional motion in a constant gravitational field,

$$E(\mathbf{r},\mathbf{v})=\tfrac{1}{2}mv^2+mgz, \tag{31}$$

where $v=|\mathbf{v}|$. Hence, one obtains from Eq. (30)

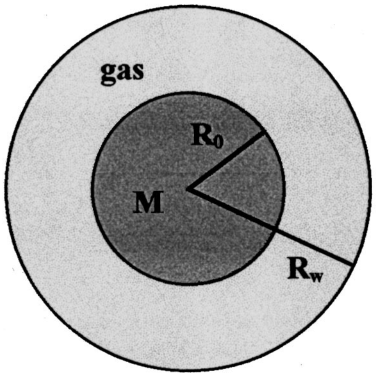


Fig. 6. A spherical solid body of mass M and radius R_0, surrounded by a gas of molecular mass m, externally contained by a massless spherical wall of radius R_w.

$$\begin{aligned} P(\mathbf{r},\mathbf{v})=&\frac{1}{L^2}\left(\frac{m}{2\pi kT}\right)^{3/2}\left(\frac{mg}{kT}\right)\exp\left(-\frac{mv^2}{2kT}\right)\\ &\times\exp\left(-\frac{mgz}{kT}\right), \end{aligned} \tag{32}$$

where L is the (very large) linear dimension of the container and $w(z)=\int\int\int P(\mathbf{r},\mathbf{v})d\mathbf{v}\,dx\,dy$ is again the exponential density.

III. TWO SIMPLE GENERALIZATIONS OF THE BAROMETRIC FORMULA

A. Nonuniform gravitational field

Boltzmann's equation [or Eqs. (5) or (7)] can be used to extend the previous results to the case where the gravitational field is not constant. Consider a spherical solid body of mass M and radius R_0 surrounded by a gas, externally contained by a massless spherical wall of radius R_W (Fig. 6). One obtains for the gas in thermodynamic equilibrium,

$$P(r)=\frac{r^2\,\exp\left(\dfrac{GmM/r}{kT}\right)}{\displaystyle\int_{R_0}^{R_W} r^2\,\exp\left(\frac{GmM/r}{kT}\right)dr}\quad r\in[R_0,R_W], \tag{33}$$

where $P(r)$ is the radial density function, such that $\int_{R_0}^{R_W}P(r)dr\;=\;1$, and G is the gravitational constant. The pressure at a given radius is obtained from the perfect gas law, rewritten as

$$p(r)=\rho_n kT, \tag{34}$$

where ρ_n, the number density, is

$$\rho_n=\frac{NP(r)dr}{4\pi r^2 dr}, \tag{35}$$

where N is the total number of molecules. Hence,

$$p(r)=\frac{P(r)N}{4\pi r^2}\,kT. \tag{36}$$

Using Eq. (33) and putting $z=r-R_0$, Eq. (36) can finally be rewritten as

$$p(z)=p(0)\exp\left(-\frac{mg_0R_0}{kT}\frac{z}{(z+R_0)}\right), \tag{37}$$

where g_0 is the acceleration of gravity for $z=0$, and $p(0)$ is given by

$$p(0)=\frac{\exp\left(\frac{mg_0R_0}{kT}\right)}{\int_{R_0}^{R_w}4\pi r^2\exp\left(\frac{GmM/r}{kT}\right)dr}NkT. \tag{38}$$

Equation (37) shows that the pressure approaches a constant, nonzero value for high z. If R_w is very large, almost all the gas exists far away from the solid body, whose gaseous skin becomes negligible. This means, as is well known, that for $R_w\rightarrow\infty$ no equilibrium distribution is possible. Therefore, if a gas is initially concentrated near the body's surface, forming an atmosphere, that atmosphere is only temporary, being bound to disappear completely (this result applies only to not too massive a body, otherwise relativistic effects must be taken into account). In the absence of more complex escape mechanisms (e.g., dissociative collisional processes), the time needed for depletion is a function of the fraction of molecules in the Maxwellian distribution with velocities higher than the escape velocity.[25]

The helium and argon existent in our planet are radioactive decay products. Their main source is natural gas, where they occur in almost the same volume fractions. If not separated and stored, they are lost forever into the atmosphere when the gaseous hydrocarbons are burned or simply liberated. One could thus expect to find helium and argon in roughly the same amounts in the atmosphere. However, argon is 1000 times more abundant than helium.[25] This happens because most of the helium released to the atmosphere throughout the ages has escaped to interplanetary space, on account of its lower mass.[25]

Because the Earth atmosphere contains several gases, and no significant convective and turbulent mixing occurs in the higher layers (above 100 km), these layers are richer in the lighter gases, such as hydrogen and helium,[25] as follows from the application of Eq. (1) to each gas separately.

B. Vertical temperature gradient

Consider now again the case of a uniform gravitational field but with a vertical temperature gradient. Assuming a linear variation of temperature with height, which is a good approximation for the troposphere,[1,2]

$$T(z)=T_0-\beta z, \tag{39}$$

where β is a positive constant, Eqs. (5) or (7) yield

$$p(z)=p(0)\left(1-\frac{\beta z}{T_0}\right)^{mg/k\beta}. \tag{40}$$

This equation represents well the pressure dependence on altitude for the whole troposphere (up to 11 km), with[1] T_0=288 K (15 °C) and β=6.5 K km^{-1}.

The fall of temperature with altitude in the troposphere is due to the fact that air is warmed mainly from the surface of the planet. This fall is, however, smaller than could be expected, because convection occurs (up to the tropopause).[25] On the other hand, there is a temperature rise in the stratosphere ($\beta=-1.0$ K km^{-1} from[2] 20 km to 32 km). This increase is associated with ozone, which concentrates in a layer about 20 km thick, and centered on an altitude of about 30 km. It strongly absorbs ultraviolet light from the Sun, and subsequently releases the corresponding energy as heat.[25] A flat temperature minimum at -57 °C is observed between 11 and 20 km,[1,2] corresponding to a compromise between the cooling and heating profiles.

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APPENDIX A

For a given initial velocity v_0', and after a great number of cycles, a plot of $z(v_0|t)$ in the vicinity of v_0' is a rapidly oscillating function. This occurs because the heights of two molecules simultaneously starting from $z=0$, but slightly differing in their respective initial velocities, first slowly diverge with time, and then, after many cycles, differ by an amount between 0 and $z_m(v_0)=v_0^2/2g$, that is critically dependent on $\Delta v = v_0 - v_0'$ (and on time). In this way, when t is large, and even for a very small Δv, all values between 0 and $z_m(v_0')$ occur many times in a plot of $z(v_0|t)$ in the vicinity of v_0'. It is therefore legitimate to replace the rapidly varying delta function by its average value,

$$\langle\delta(z'-z)(t|v_0')\rangle=\int_0^{z_m(v_0')}w(z|v_0')\delta(z'-z)dz$$
$$=w(z'|v_0'). \tag{A1}$$

The density function $w(z|v_0')$ is such that $w(z|v_0')\,dz$ is the fraction of time spent by a molecule between z and $z+dz$, given that its initial velocity was v_0' (Appendix B). One thus concludes that for a given z' the delta function of the integrand in Eq. (12) can be replaced by $w(z'|v_0)$, and the long time molecular height density function, $w(z')$, is given by Eq. (15).

APPENDIX B

The fraction of time spent between z and $z+dz$ by a molecule with initial velocity v_0, and after many cycles, $w(z|v_0)dz$, can be computed as the probability of finding the same molecule between z and $z+dz$, if the time of observation is a random variable with uniform distribution (the effect of the initial position is negligible after many cycles). This probability is obtained from the random variable transformation theorem.[26] Taking, for convenience, $t\in[0,v_0/g]$, one gets, from Eq. (10),

$$w(z|v_0)=\int_0^{v_0/g}\delta\left[z-\left(v_0t-\frac{1}{2}gt^2\right)\right]\frac{g}{v_0}dt \tag{B1}$$

performing the change of variable $x=v_0t-\frac{1}{2}gt^2$, Eq. (B1) becomes

$$w(z|v_0)=\int_0^{v_0^2/2g}\delta(z-x)\frac{g}{v_0\sqrt{v_0^2-2gx}}dx \tag{B2}$$

and Eq. (14) follows.

APPENDIX C

1. Steady-state distribution of velocities from the initial distribution of velocities

We first obtain the probability of finding at height z a molecule with initial velocity v_0, given that a molecule was found. The probability of finding between z and $z+dz$ a molecule with initial velocity v_0 is, as shown above, $w(z|v_0)dz$; on the other hand, the probability of finding at z a molecule, irrespective of its initial velocity, is $[\int_{\sqrt{2gz}}^{\infty}[w(z|v_0)dz]f(v_0)dv_0]$. In this way, the probability that, at height z, the observed molecule had initial velocity v_0 is

$$\alpha(v_0|z)=\frac{w(z|v_0)f(v_0)}{\int_{\sqrt{2gz}}^{\infty}w(z|v_0)f(v_0)dv_0}. \tag{C1}$$

Because v is related to v_0 by

$$v=\pm\sqrt{v_0^2-2gz}, \tag{C2}$$

one obtains, again by application of the random variable transformation theorem,[26] that the density function for the local velocity v is

$$f_s(v|z)=\frac{\dfrac{f(\sqrt{v^2+2gz})}{v^2+2gz}}{\displaystyle\int_{-\infty}^{\infty}\frac{f(\sqrt{v^2+2gz})}{v^2+2gz}\,dv}, \tag{C3}$$

which is the desired relation.

2. Initial distribution of velocities from the steady-state distribution of velocities

For $z=0$, Eq. (C3) reduces to

$$f_s(v|0)=\frac{\dfrac{f(|v|)}{v^2}}{\displaystyle\int_{-\infty}^{\infty}\frac{f(|v|)}{v^2}\,dv}, \tag{C4}$$

which can be rewritten as

$$f(v_0)=Nv_0^2f_s(v_0|0), \quad v_0\in[0,+\infty[, \tag{C5}$$

where N is a normalization constant. From this requirement, one finally obtains

$$f(v_0)=\frac{v_0^2f_s(v_0|0)}{\int_0^{\infty}v_0^2f_s(v_0|0)dv_0}, \quad v_0\in[0,+\infty[. \tag{C6}$$

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[1] J. V. Iribarne and W. L. Godson, *Atmospheric Thermodynamics* (Reidel, Dordrecht, The Netherlands, 1981), 2nd ed., Chap. 8.

[2] J. A. Dutton, *Dynamics of Atmospheric Motion* (Dover, New York, 1986), Chap. 4.

[3] The *Comments* were widely used by the Order in the colleges it held in Europe, America, Asia, and Africa. Their impact can be judged from the number of different European editions they enjoyed:[4] 112. René Descartes (1596–1650) read them, probably while as student of the Jesuit college of Paris (incidentally, he also denied the possibility of a vacuum). The existence of a (lost ?) translation into Chinese in ten volumes (first half of the XVIIth century) is also reported.[4] A modern English translation of Aristotle's works is *The Complete Works of Aristotle, The Revised Oxford Translation*, edited by J. Barnes (Princeton U.P., Princeton, 1984). A new English translation of Aristotle's *Physics* (where vacuum is discussed in Book IV) is available from Oxford U.P. (1996).

[4] Pinharanda Gomes, *Os Conimbricenses* (ICALP, Lisbon, 1992), and references therein.

[5] The same point, but regarding medieval commentators and other matters, is made by R. A. Uritam, ''Medieval science, the Copernican revolution, and physics teaching,'' Am. J. Phys. **42** (10), 809–819 (1974). Aristotelian and medieval physics are also discussed by A. Franklin, ''Principle of inertia in the Middle Ages,'' Am. J. Phys. **44**(6), 529–545 (1976). The importance of the role played by the *Societatis Iesu* in the early part of the *Scientific Revolution* was recently stressed by some science historians, to the point of being considered as ''the first true scientific society''; see e.g., *Les jésuites à la Renaissance*, edited by L. Giard (PUF, Paris, 1995).

[6] Galileo Galilei, *Discorsi e dimostrazioni matematiche, intorno à due nuove scienze attinenti alla mecanica & i movimenti locali* (Elzevier, Leyden, 1638), reprinted in *Galileo Galilei*, Nuova Ristampa della Edizione Nazionale, Vol. VIII, Giornata Prima, edited by G. Barbèra (Firenze, 1968), pp. 49–128; English translation, *Dialogues Concerning Two New Sciences* (Dover, New York, 1952).

[7] See, e.g., C. Singer, ''Science under the Roman Empire,'' in *From Magic to Science* (Dover, New York, 1958).

[8] M. Segre, *In the Wake of Galileo* (Rutgers U.P., New Jersey, 1991), Chaps. 4 and 5. The vacuum problematic is addressed at length in E. Grant, *Much Ado About Nothing, Theories of Space and Vacuum from the Middle Ages to the Scientific Revolution* (Cambridge U.P., Cambridge, 1981). It may be noted here that the term ''vacuum'' now applies to any situation of subatmospheric pressure. See, e.g., J. P. Hobson, ''The future of vacuum technology,'' J. Vac. Sci. Technol. A **2**(2), 144–149 (1984), the ''philosophical vacuum'' being called a ''perfect vacuum,'' whose ''absolute emptiness'' is in fact denied by modern Physics.

[9] T. Bonaventura, *Lezioni accademiche di Evangelista Torricelli*, edited by G. Guiducci and S. Franchi (Firenze, 1715), Letter to Ricci of 11th June, 1644, from E. Torricelli, *Opere*, edited by Loria and Vassura (Faenza, 1919), pp. 186–188.

[10] C. Licoppe, ''Le mercure, le vide et la clarté du monde,'' in *Blaise Pascal* (Les cahiers de Science & Vie, Paris, 1995).

[11] C. Thurot, ''Les expériences de Pascal sur le vide et la pesanteur de l'air,'' J. Phys. (Paris) **1**, 267–271 (1872).

[12] E. Halley, ''A Discourse of the Rule of the Decrease of the Height of the Mercury in the Barometer, according as Places are elevated above the Surface of the Earth, with an Attempt to discover the true Reason of the Rising and Falling of the Mercury, upon change of Weather,'' Philos. Trans. R. Soc. **16**, 104–116 (1686–1692). Note that Eq. (1) can be rewritten as

$$p(z)=p(0)\exp\left(-\frac{w_0z}{p(0)}\right),$$

where w_0 is the specific weight of air (for $z=0$), $w_0=\rho_m g$, and the mass density ρ_m is given by Eq. (4). By making $p(z)=w_m h(z)$, where w_m is the specific weight of mercury, and $h(z)$ the height of the column of mercury at altitude z, one finally obtains

$$h(z)=h(0)\exp\left[-\left(\frac{w_0}{w_m}\right)\left(\frac{z}{h(0)}\right)\right]$$

or

$$z=\left(\frac{w_m}{w_0}\right)\ln\left(\frac{h(0)}{h(z)}\right)h(0).$$

These were the dependencies arrived at by Halley.

[13] P. S. de La Place, *Traité de Mécanique Céleste*, Bk. 10, Chap. 4 (Paris, 1798–1825); English translation, *Mécanique Céleste* (Hilliard, Gray, Little and Wilkins, Boston, 1829–1839).

[14] (a) J. P. Negret, ''Boiling Water and the Height of Mountains,'' Phys. Teach. **24**, 290–292 (1986); (b) R. Ferreira, ''Resumo da Memória ''Sobre un nuevo metodo de medir la altura de las montanas por medio del termometro y el agua herviendo,'' por Don Francisco José de Caldas, datada de Quito, Abril de 1802,'' Quím. Nova **14**(2), 125–132 (1991).

[15] J. Perrin, ''Mouvement brownien et réalité moléculaire,'' Ann. Chim. Phys. **18**, 1–114 (1909). A more detailed discussion is given in Jean Perrin's classic *Les Atomes* (F. Alcan, Paris, 1913); English translation, *Atoms* (Ox Bow, Woodbridge, CT, 1990).

[16] Owing to the buoyancy of the liquid, the apparent mass m' is $m(1-\rho_L/\rho_P)$, where m is the true mass of the particle, and ρ_L and ρ_P are, respectively, the liquid's density and the particle's density ($\rho_P>\rho_L$ in

water; in glycerol, also studied by Perrin and co-workers,[15] $\rho_P < \rho_L$, the apparent mass was negative and the exponential distribution was inverted, with an accumulation at the upper surface). In the systems studied by Perrin the apparent ''molecular'' mass was ca. 10^9 higher than true molecular values, and therefore the variation with height was much more pronounced than in air, the average height of the particles being of only a few μm.

[17] In this treatment, we have implicitly assumed that the gas is contained in a vessel of infinite height. If an upper limit H is considered, the average molecular potential energy will be smaller than kT [see, P. T. Landsberg, J. Dunning-Davies, and D. Pollard, ''Entropy of a column of gas under gravity,'' Am. J. Phys. **62**(8), 712–717 (1994)], and the distribution of initial velocities will be different.

[18] See about this point: C. A. Coombes and H. Laue, ''A paradox concerning the temperature distribution of a gas in a gravitational field,'' Am. J. Phys. **53**(3), 272–273 (1985).

[19] A unidimensional derivation based on the mean free path was given before, G. W. Parker, ''An elementary kinetic derivation of the gravitational distribution,'' Am. J. Phys. **45**(5), 489 (1977); the exact formula obtained results, however, from a cancellation of errors in the approximations made.

[20] D. T. Gillespie, ''The mathematics of Brownian motion and Johnson noise,'' Am. J. Phys. **64**(3), 225–240 (1996).

[21] S. Chandrasekhar, ''Stochastic Problems in Physics and Astronomy,'' Rev. Mod. Phys. **15**(1), 1–91 (1943).

[22] N. G. van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1981), pp. 218–219.

[23] C. W. Gardiner, *Handbook of Stochastic Methods* (Springer-Verlag, Berlin, 1985), 2nd ed., pp. 195–210.

[24] F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill, New York, 1965).

[25] R. P. Wayne, *Chemistry of Atmospheres* (Clarendon, Oxford, 1991), 2nd ed., Chap. 2.

[26] N. G. van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1981), p. 19. See also B. Roy Frieden and D. T. Gillespie, ''Another proof of the random variable transformation theorem,'' Am. J. Phys. **54**(12), 1149–1150 (1986), and references therein.