# 6

*Thermal physics of ideal & real*

# GASES

**Introduction.** It was upon a gaseous anvil that thermodynamics and statistical mechanics were forged—this for the simple reason that gases are, in almost all relevant respects, much easier to describe than liquids or solids. Gases are (almost literally) to thermodynamics as free particles are to dynamics. In liquids and solids the physics of interparticle interaction is predominant, while in gases it can be treated as a perturbation . . . and we will be concerned here with (among other things) reviewing how that is accomplished.

Gases—classical and quantum, bosonic and fermionic—have already been called upon many times to illustrate points of principle and technique as they emerged from the preceding discussion. There exists, however, a parallel body of principle and technique that is *special* to gases. That material presents much that is of intrinsic interest, and acquires practical importance when one seeks to relate theory to the observed properties of *real* gases.

The physics of gases is one of those subjects that "goes on forever," and it should be recognized that the *thermal physics of gases* (which itself "goes on forever") falls as a sub-head within that larger discipline. My objective will be to review some of the major topics that fall under that sub-head: excluded will be everything having to do with non-thermalized gases, everything having to do with the *macro*scopic dynamics of gases (formation of shock waves, *etc*.).

**1. Thermodynamics of ideal gases.** To get this discussion under way I propose to look again to the elementary thermodynamics of *ideal* gases, but from a somewhat novel point of view. We start from the assumption that we are concerned with a simply bulk system

$$U(S,V,N) = \lambda U\big(\frac{S}{\lambda}, \frac{V}{\lambda}, \frac{N}{\lambda}\big)$$

It proves useful to notice that we can, if we wish (set $\lambda = N$) write

$$= Nu(s,v)$$

where

$u \equiv U/N \equiv$ **specific internal energy**
$s \equiv S/N \equiv$ **specific entropy**
$v \equiv V/N \equiv$ **specific volume**

and where the "specific meaning" of $u/s/v$ hinges on the meaning specifically assigned to the variable $N$, which refers to the sample size: $N$ might refer to the *mass* of the sample, or to the *mole number*, but will be taken to have the meaning

$N \equiv$ **number of molecules**

We accept as given the following statements of idealized fact:

> LAW OF BOYLE/MARIOTTE: If $T$ is held constant then (for every given/fixed gas sample) $pV$ is constant.
>
> LAW OF CHARLES/GAY-LUSSAC: If $V$ is held constant then (for every given/fixed gas sample) $p/T$ is constant.

These laws assert (respectively) the existence of presently unknown functions $f(T,N)$ and $g(V,N)$ such that

$$\left.\begin{aligned} pV &= f(T,N) \\ p/T &= g(V,N) \end{aligned}\right\} \tag{305}$$

Immediately $p = \dfrac{f(T,N)}{V} = Tg(V,N)$ from which we conclude that

$$\frac{f(T,N)}{T} = Vg(V,N) = \text{some mutual function } \mathcal{K}(N) \text{ of } N \text{ alone}$$

and that equations (305)

$$pV = T\cdot\mathcal{K}(N)$$

This equation will (as required) be <u>invariant under scale-up</u> $(V,N) \mapsto (\lambda V, \lambda N)$ if and only if $\mathcal{K}(\lambda N) = \lambda\mathcal{K}(N)$; *i.e.*, if and only if $\mathcal{K}(N)$ is homogeneous of degree one: $\mathcal{K}(N) = kN$. So we have

$$pV = NkT \tag{306}$$

We have, at this point, no reason to suppose that the constant $k$ is not (like so many other phenomenological constants) specific to each gas species, so the discovery that

$k$ is a species-independent **universal constant**

was an unexpected surprise, a mystery that remained opaque until clarified first by kinetic theory, then (and more generally) by statistical mechanics.[185]

Equation (306)—which can also be written

$$pv = kT \tag{307}$$

—places a fairly rigorous constraint on the functional structure of $u(s, v)$, for by

$$T = \Big(\frac{\partial U}{\partial S}\Big)_V = \Big(\frac{\partial u}{\partial s}\Big)_v \qquad \text{and} \qquad -p = \Big(\frac{\partial U}{\partial V}\Big)_S = \Big(\frac{\partial u}{\partial v}\Big)_s$$

we have

$$k\frac{\partial u}{\partial s} + v\frac{\partial u}{\partial v} = 0 \tag{308}$$

This is a linear partial differential equation that yields to analysis by separation of variables: writing $u(s, v) = F(s) \cdot G(v)$ we have

$$k\frac{d}{ds}\log F(s) + v\frac{d}{dv}\log G(v) = 0$$

giving

$$\left.\begin{aligned} k\frac{d}{ds}\log F(s) &= +a \\ v\frac{d}{dv}\log G(v) &= -a \end{aligned}\right\} \ : \ a \text{ is some mutual constant}$$

Immediately $F(s) = F(s_0)\exp\Big\{a\,\dfrac{s - s_0}{k}\Big\}$ and $G(v) = G(v_0)\Big(\dfrac{v_0}{v}\Big)^a$ so[186]

$$u(s, v) = u_0\Big(\frac{v_0}{v}\Big)^a \exp\Big\{a\,\frac{s - s_0}{k}\Big\} \tag{309}$$

This is (for each $a$) a *particular* solution of (308). More generally—by the linearity of (308)—we have

$$u(s, v) = \int A(a)\Big(\frac{v_0}{v}\Big)^a \exp\Big\{a\,\frac{s - s_0}{k}\Big\}\,da \tag{310}$$

where $A(a)$ can be specified *arbitrarily*. To make the same point another way:

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[185] In the latter connection it became clear that Boltzmann's constant $k$—the "gas constant per molecule"—is (like the $c$ in relativistic physics) by nature a *conversion factor*, a factor that describes the relation between *two different ways of measuring the same thing*.

[186] Compare (30) on page 43.

it follows from (310) that

$$T(s,v) = k^{-1}\int aA(a)\Big(\frac{v_0}{v}\Big)^a \exp\Big\{a\,\frac{s-s_0}{k}\Big\}\,da \tag{311.1}$$

$$p(s,v) = v^{-1}\int aA(a)\Big(\frac{v_0}{v}\Big)^a \exp\Big\{a\,\frac{s-s_0}{k}\Big\}\,da \tag{311.2}$$

so obviously we are in compliance with (307) *whatever* the structure we assign to $A(a)$. But—one of the lessons of this tale—there is more to thermodynamics than equations of state, and, as I will now argue, the structure of $A(a)$ is in fact severely constrained.

The principles of thermodynamics supply a general identity

$$\Big(\frac{\partial u}{\partial v}\Big)_T = T\Big(\frac{\partial p}{\partial T}\Big)_v - p$$

of which we have several times made use, and which at (86) we called the "thermodynamic equation of state." From $p(T,v) = kT/v$ it follows in the case at hand that

$$\Big(\frac{\partial u}{\partial v}\Big)_T = 0 \quad : \quad \left\{\begin{array}{l}u\text{, when expressed as a function of}\\ \text{the non-standard variables } T \text{ and } v,\\ \text{must in fact be } \underline{v\text{-independent}}\end{array}\right. \tag{312}$$

but to draw any direct conclusions we would have to construct $u(s(T,v),v)$ and that is not feasible, for (311.1) is too complicated to permit the functional inversion $T(s,v) \mapsto s(T,v)$ to be carried out in explicit detail. We have, therefore, to proceed by indirection: we observe that the isovolumetric specific heat

$$c_V \equiv C_V/N = \Big(\frac{\partial u}{\partial T}\Big)_v \text{ must be } v\text{-independent}$$

and then use Tobolsky's method to describe $c_V$ as a function of $s$ and $v$. As it happens, that labor lies already behind us, for at (85.1) we achieved a result that can be written

$$c_V = T\Big/\Big(\frac{\partial T}{\partial s}\Big)_v$$

and in the present context becomes

$$c_V = \frac{k^{-1}\displaystyle\int a^1 A(a)\Big(\frac{v_0}{v}\Big)^a \exp\Big\{a\,\frac{s-s_0}{k}\Big\}\,da}{k^{-2}\displaystyle\int a^2 A(a)\Big(\frac{v_0}{v}\Big)^a \exp\Big\{a\,\frac{s-s_0}{k}\Big\}\,da}$$

We readily convince ourselves that the $v$-dependence will disappear from the right side of the preceding equation if and only if $A(a)$ possesses the specialized structure

$$A(a) = u_0\delta(a-\hat{a}) \tag{313}$$

where $u_0$ and $\hat{a}$ are constants. The upshot of the preceding argument is that, while all of the $u$-functions (310) comply with the equation of state (307), only those of the restricted design (309) conform to the joint requirements of the 1st and 2nd laws of thermodynamics . . . and that (see again page 43) "ideal gas" refers to what is actually a one-parameter *family* of systems.

> HISTORICAL NOTE: Equation (312) draws attention to a property of ideal gases that is implicit in the laws of thermodynamics, but that was recognized *before those laws had been formulated*... for by about 1852 James Prescott Joule (1818–1889) had been led by a series of difficult experiments to the conclusion (see again Figure 4) that
>
> **the adiabatic free expansion of a dilute gas is isothermal**
>
> Joule had put his finger on a physical fact for which the kinetic theory of gases soon provided a ready explanation: when "ideal gas molecules" spill into an expanded volume they are required to "stretch no intermolecular springs;" energy conservation therefore means conservation of net *kinetic* energy, which is experienced as a constancy of the *temperature* (*i.e.*, of the mean kinetic energy of the individual molecules).

It now follows that

$$c_{\scriptscriptstyle V} = \frac{k^{-1}\hat{a}^1 u_0\Big(\dfrac{v_0}{v}\Big)^{\hat{a}}\exp\Big\{\hat{a}\,\dfrac{s-s_0}{k}\Big\}}{k^{-2}\hat{a}^2 u_0\Big(\dfrac{v_0}{v}\Big)^{\hat{a}}\exp\Big\{\hat{a}\,\dfrac{s-s_0}{k}\Big\}} = k/\hat{a}$$

We were prepared (by Joule) to find that $c_{\scriptscriptstyle V}$, though independent of $V$, depends semi-arbitrarily upon $T$, but discover that it has been forced by the laws of thermodynamics to be a *constant*. And from this it follows that $u(T,v)$ is of necessity a *linear* function of $T$:

$$u(T,v) = c_{\scriptscriptstyle V} T + \text{constant}$$

By natural convention we abandon the constant, which is to say: we adjust the energy reference level so as to conform to the stipulation that $u(0,v) = 0$.

One lucky benefit of the simplifications latent in (313) is that certain functional inversions that were formerly not feasible have become suddenly elementary. It follows, for example, from (309) that

$$s(u,v) = c_{\scriptscriptstyle V}\log\frac{u}{u_0} + k\log\frac{v}{v_0} + s_0 \tag{314.1}$$

which by $u = c_{\scriptscriptstyle V} T$ becomes

$$s(T,v) = c_{\scriptscriptstyle V}\log\frac{T}{T_0} + k\log\frac{v}{v_0} + s_0 \tag{314.2}$$

and by $pv = kT$ becomes

$$s(T,p) = \big\{c_{\scriptscriptstyle V} + k\big\}\log\frac{T}{T_0} - k\log\frac{p}{p_0} + s_0 \tag{314.3}$$

Bringing the last of those equations to (88.1) we find

$$c_p = T\Big(\frac{\partial s}{\partial T}\Big)_p = c_{\scriptscriptstyle V} + k \tag{315.1}$$

of which (compare (91.2) on page 80)

$$c_p > c_{\scriptscriptstyle V} \tag{315.2}$$

is a corollary.

Appealing once again to the equation of state we find

$$s(p, v) = c_{\scriptscriptstyle V} \log \frac{p}{p_0} + c_p \log \frac{v}{v_0} + s_0 \tag{314.4}$$

from which it follows that when an ideal gas sample is **isentropically expanded/compressed** one has

$$pV^\gamma = \text{constant} \tag{316.1}$$

where

$$\gamma \equiv c_p/c_{\scriptscriptstyle V} > 1 \tag{317}$$

is sometimes called the "isentropic exponent." Obvious variants of (316.1) are

$$\begin{aligned} Tv^{\gamma-1} &= \text{constant} \\ Tp^{(1-\gamma)/\gamma} &= \text{constant} \end{aligned}$$

One must look beyond thermodynamics itself to an underlying statistical model to gain theoretical insight into the *numerical value* assumed by $c_{\scriptscriptstyle V}$ in any particular case. For monatomic gases (dilute noble gases) one obtains[187]

$$c_{\scriptscriptstyle V} = \tfrac{3}{2}k \quad \text{whence} \quad c_p = \tfrac{5}{2}k \quad \text{and} \quad \gamma = \tfrac{5}{3}$$

Later we will want to give careful attention to the distinction between "reversible" and "irreversible" processes, but an anticipatory word may reduce the risk of confusion. As they apply to quasi-static processes the adjectives "adiabatic" and "isentropic" are synonyms:

$$đQ = TdS = 0 \quad \Longrightarrow \quad dS = 0$$

But Joule's "free expansion," which proceeds (Figure 4) irreversiblibly by the relaxation of a gross constraint (which is to say: *non*-quasi-statically), is adiabatic but *not* isentropic; indeed, it follows directly from (314.2) that

$$\Delta s_{\text{Joule}} \equiv s_{\text{after}} - s_{\text{before}} = k \log \frac{v + \Delta v}{v} > 0$$

as we had occasion to observe already on page 174 in connection with a discussion of Gibbs' paradox.

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[187] See again page 149 and Figure 54 on page 162.

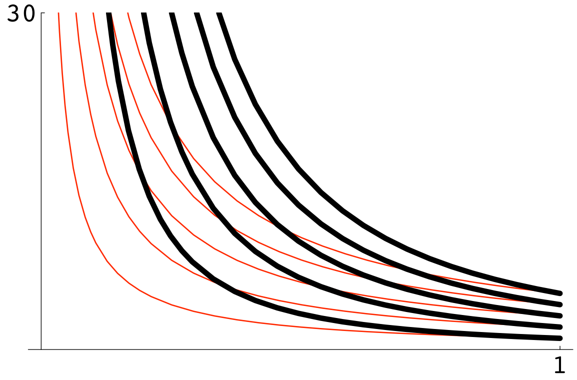

FIGURE 77: *Adiabats*

$$pv^\gamma = \text{constant} \;\; : \;\; \gamma = \tfrac{5}{3} \;\; : \;\; \text{constant} = 1, 2, 3, 4, 5$$

*of an ideal gas, inscribed on the* $pv$*-plane (*$v$ *runs* →, $p$ *runs* ↑*). For comparison the isotherms*

$$pv = \text{constant}$$

*are shown in red.*

**2. Distribution of molecular speeds at thermal equilibrium.** The notion that the properties of bulk matter are to be attributed to the properties of "atoms" can be traced back through Lucretius (*c* 97–54BC) and Epicurus (*c* 342–270BC) to Democritus (*c* 460–370BC) and was, of course, fundamental to Newton's view of the world. Newton himself attributed the gas laws (not very specifically) to repulsive forces that *static* atoms were imagined to expert upon one another. The idea that the properties of gases are to be attributed to *kinetic* activity of the atoms was developed in some quantitative detail by Daniel Bernoulli (1700–1782) in a paper—actually a chapter in a larger work (1738) devoted to hydrodynamics—that is generally considered to mark the beginning of the kinetic theory of gases, but which attracted little attention. John Harapath (1790–1868) independently reproduced and extended many of Bernoulli's results in a paper (1820) which the Royal Society declined to publish, and John Waterston (1811–1883) fared no better with the paper he submitted in 1845.[188] Several circumstances contributed to the disinterest-bordering-on-contempt

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[188] Waterston's paper remained unknown until 1891, when it was discovered in the Society's archives and published by Rayleigh. Waterston had better luck, however, with some of his other work. There is evidence that a 1851 publication (abstract of the kinetic theory paper) influenced Krönig (1856), which in turn influenced Clausius.

with which the work of the early kinetic theorists was received:

- the force of Newton's (in this instance misguided) influence;
- the prevalence of mistaken notions concerning the nature of temperature and heat;
- the widely-shared view that work based upon the "atomic hypothesis" was was necessarily too speculative to merit publication.

Each of those circumstances—except, perhaps, the last—had recently left the stage by the time Clausius (1822–1888) stepped upon it with his "Ueber die Art der Bewegung, welche wir Wärme nennen"[189] (1857) and became, in Maxwell's generous estimation, the founding father of kinetic theory. Clausius's early work—he remained intermittently active in the field until about 1870—contributed to Maxwell's decision in 1859 to turn his own attention to the kinetic theory. He wrote six major papers on the subject between 1860 (when he was twenty-nine) and the year of his death, in 1879, and it is the first of those papers that brings me to the point of the preceding remarks:

Bernoulli had been content to assume that all the molecules in an equilibrated gas *have the same speed* and, moreover, that one third of them move parallel to each of the three space axes. The assumption that molecules contrive to move with identical speeds is basic to the work also of Harapath, Waterston and other early kinetic theorists. Even Clausius, though not the first to abandon the second and most blatently artificial of Bernoulli's assumptions (Clausius assumed directional isotropy), found it natural to assume—at least tentatively —that all molecules in any given gas sample zip about with the same speed. But it was immediately evident to Maxwell that the molecules will move with a statistically-determined *variety* of speeds, and that the shape of that distribution is fundamental to the entire subject: with Maxwell the kinetic theory of gases abruptly became—as it has remained—a *statistical* theory, a kind of "statistical mechanics."[190]

The fundamental object in kinetic-theory-according-to-Maxwell is a function—I will call it $n(\boldsymbol{x}, \boldsymbol{v}, t)$—that, in a necessarily "course-grained" sense

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[189] This, of course, is the source of the title that Stephen Brush gave to his elaborate history of the kinetic theory of gases, and it is to that monograph[113] that I refer readers for details relating to the developments that I must be content here merely to encapsulate.

[190] Brush,[113] in his §5.1, asks how it happened that Maxwell was led so promptly to his "statistical approach," and concludes that he worked under the influence of a lengthy review of the probabilistic work of Quintelet that Sir John Herschel had published in 1850. C. W. F. Everitt, in Chapter 9 of his *James Clerk Maxwell: Physicist & Natural Philosopher* (1975), suggests that Maxwell may also have been predisposed to such an approach by his work on the "Saturn's ring problem" that—together with the first phase of his electrodynamical work—had engaged his concentrated attention (1855–1859) right up until the time he discovered Clausius' work and turned to kinetic theory.

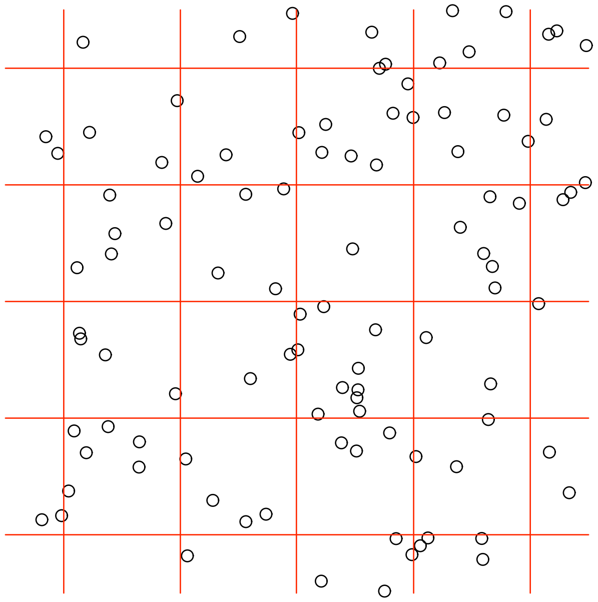

FIGURE 78: *"Course graining" presumes cells $d^3xd^3v$ large enough that the physical discreteness of the gas remains invisible—large enough that the cell statistic is well-defined and appears to change smoothly/infinitesimally from cell to neighboring cell, yet not so large that relevant detail is lost. It is a concept that seems transparent on its face, but is difficult to define with precision: it represents an attempt to adapt the methods of field theory to systems that in some essential respects (collisional dynamics, applications of the "mean free path" concept introduced by Clausius in 1858) must retain their discreteness. The cells and randomly positioned "molecules" in the figure clearly do not conform to the course graining principle, and suggest that any precise definition must take into account the* fluctational *statistics.*

(see the figure), describes the number of particles that at time $t$ occupy the neighborhood $d^3x$ of $\boldsymbol{x}$ and have velocities in the neighborhood $d^3v$ of $\boldsymbol{v}$. In all cases we have

$$\iiiint\!\!\!\iint n(\boldsymbol{x},\boldsymbol{v},t)\,d^3x\,d^3v = N$$

At thermal equilibrium we expect the particle density function to become $t$-independent (or "steady"), and in the absence of impressed forces (like gravity) we expect the $\boldsymbol{x}$-dependence to drop away (*i.e.*, we expect the gas to become spatially homogeneous), leaving

$$n(\boldsymbol{x},\boldsymbol{v},t) = \frac{N}{V}\cdot F(\boldsymbol{v}) \quad \text{with} \quad \iiint F(\boldsymbol{v})\,d^3v = 1$$

Evidently

$$F(\boldsymbol{v}) = \begin{cases} \text{fraction of the molecules that have} \\ \text{velocities in the neighborhood } d^3v \text{ of } \boldsymbol{v} \end{cases}$$

and is, in effect, a probability distribution function. We are brought thus to the starting point of Maxwell's ingenous argument:

Maxwell assumes that the velocity distribution is <u>isotropic in velocity space</u>; *i.e.*, that $F(\boldsymbol{v})$ depends upon the components $v_i$ of $\boldsymbol{v}$ only through the rotational invariant

$$v^2 \equiv \boldsymbol{v}\cdot\boldsymbol{v} = v_1^2 + v_2^2 + v_3^2$$

This is, in effect, to assume that $F(\boldsymbol{v})$ is of the form

$$F(\boldsymbol{v}) = \psi(v^2)$$

Maxwell assumes additionally that the $v_i$ are <u>independent random variables</u> (which, by isotropy, must be identically distributed), and is led thus to write

$$F(\boldsymbol{v}) = \phi(v_1)\phi(v_2)\phi(v_3) = \psi(v^2) \tag{318}$$

This is the famous **functional equation** that lies at the base of Maxwell's theory. We turn now to the matter of its solution.[191]

Differentiating with respect to $v_1$ and dividing by $F(\boldsymbol{v})$ we have

$$\frac{\phi'(v_1)}{\phi(v_1)} = \frac{\psi'(v^2)}{\psi(v^2)} \cdot 2v_1$$

giving

$$\frac{\phi'(v_1)}{v_1\phi(v_1)} = 2\frac{\psi'(v^2)}{\psi(v^2)}$$

Similarly

$$\begin{aligned} \frac{\phi'(v_2)}{v_2\phi(v_2)} &= 2\frac{\psi'(v^2)}{\psi(v^2)} \\ \frac{\phi'(v_3)}{v_3\phi(v_3)} &= 2\frac{\psi'(v^2)}{\psi(v^2)} \end{aligned}$$

The expression on the left side of the first equation is a function only of $v_1$, of the second . . . only of $v_2$, of the third . . . only of $v_3$. The same properties must, of necessity, attach also to the expressions on the right sides of those equations. But the latter expressions are *identical*. Consistency requires that the expression in question be some ($v_1$, $v_2$ and $v_3$-independent) *constant*.

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[191] For alternative discussions of the same problem see, for example, L. B. Loeb, *Kinetic Theory of Gases* (1927), page 75 or M. Born, *Natural Philosophy of Cause & Chance* (1949), Appendix 13. Maxwell himself considered the problem too elementary to merit discussion, and simply wrote down the solution.

Agreeing for the moment to call the constant $-\lambda$, we infer that $\phi(v)$ is a solution of

$$\phi'(v) = -\lambda v\phi(v)$$

Immediately

$$\phi(v) = Ae^{-\frac{1}{2}\lambda v^2}$$

which gives

$$F(\boldsymbol{v}) = A^3 e^{-\frac{1}{2}\lambda(v_1^2 + v_2^2 + v_3^2)}$$

Normalizability requires $\lambda > 0$: to render that condition automatic (and to obtain formulæ that look like Maxwell's) we write $1/\alpha^2$ in place of $\frac{1}{2}\lambda$ and obtain

$$\begin{aligned} F(\boldsymbol{v}) &= \Big(\frac{1}{\alpha\sqrt{\pi}}\Big)^3 e^{-(v_1^2 + v_2^2 + v_3^2)/\alpha^2} \quad : \quad \text{normalized} \qquad (319) \\ &= \begin{cases} \text{normal distribution centered at the} \\ \text{origin in 3-dimensional velocity space} \end{cases} \end{aligned}$$

In many contexts the directional information implicit in $\boldsymbol{v}$ is irrelevant: what one really wants to know about is the equilibrium distribution $f(v)$ in 1-dimensional "speed space." Immediately

$$f(v)\,dv = \Big(\frac{1}{\alpha\sqrt{\pi}}\Big)^3 e^{-v^2/\alpha^2} 4\pi v^2\,dv \tag{320}$$

From $\frac{d}{dv}f(v) \sim v\big(1-\frac{v^2}{\alpha^2}\big)e^{-(v^2/\alpha^2)}$ we see that $f'(v)$ vanishes at $v = 0$, at $v = \alpha$ and at $v = \infty$. This is evident already in Figure 73, which displays $f(v)$ in the case $\alpha = 1$, and supplies information

$$v_{\text{modal}} = \alpha \tag{321.1}$$

in which we can read a tentative (but as yet unphysical) interpretation of the parameter $\alpha$.[192] With the assistance of *Mathematica* we compute

$$v_{\text{mean}} = \langle v\rangle = \int_0^\infty vf(v)\,dv = \frac{2}{\sqrt{\pi}}\alpha = 1.12838\,\alpha \tag{321.2}$$

$$v_{\text{rms}} = \sqrt{\langle v^2\rangle} = \Big[\int_0^\infty v^2 f(v)\,dv\Big]^{\frac{1}{2}} = \sqrt{\tfrac{3}{2}}\,\alpha = 1.22474\,\alpha \tag{321.3}$$

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[192] It is evident in (319) that

$$\boldsymbol{v}_{\text{modal}} = \boldsymbol{0}$$

That the maximum of $f(v)$ is shifted away from the origin can be understood as a result of competition between the decreasing value of $F(\boldsymbol{v})$ and the increasing volume $4\pi v^2\,dv$ of spherical shells as one moves away from the origin in $\boldsymbol{v}$-space.

and find additionally that $v_{\text{median}}$—defined

$$\int_0^{\text{median}} f(v)\,dv = \int_{\text{median}}^{\infty} f(v)\,dv$$

—is located at a position

$$v_{\text{median}} = 1.08765\,\alpha \tag{321.4}$$

that conforms nicely to the rule of thumb[193]

$$v_{\text{median}} = \frac{2v_{\text{mean}} + v_{\text{modal}}}{3} = 1.08559\,\alpha$$

We note in passing that $v_{\text{modal}} < v_{\text{median}} < v_{\text{mean}} < v_{\text{rms}}$.

A physical interpretation of $\alpha$ emerges when we assign to the molecules a mass $m$ and look to the **expected kinetic energy/molecule**:

$$\varepsilon \equiv \langle \tfrac{1}{2}mv^2 \rangle = \tfrac{1}{2}m(v_{\text{rms}})^2 = \tfrac{3}{4}m\alpha^2$$

For then $U = N\varepsilon = N\frac{3}{4}m\alpha^2$ and, if we allow ourselves to borrow $U = N\frac{3}{2}kT$ from the *thermodynamics* of monatomic gases, we have

$$\alpha = \sqrt{2kT/m} \tag{322}$$

The Maxwellian distribution (320) becomes

$$f(v) = \Big(\frac{m}{2\pi kT}\Big)^{\frac{3}{2}} 4\pi v^2 e^{-\frac{1}{2}mv^2/kT} \tag{323}$$

and from (321.3) we obtain a statement

$$v_{\text{rms}} = \sqrt{3kT/m}$$

that speaks informatively about the thermal physics of a gas, but in a way that lies quite beyond the reach of thermodynamics.[194]

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[193] A. T. Doodson, "Relation of mode, median and mean in frequency curves," Biometrika **11**, 425 (1917).

[194] We compute, for example, that

$$v_{\text{rms}} = \begin{cases} 431 \text{ meter/second for argon at 300K} \\ 1.07\times10^{-4} \text{ meter/second for rubidium at} \\ \text{the } 39.5\times10^{-12}\text{K mentioned on page 210} \end{cases}$$

**3. Kinetic derivation of the perfect gas law: pressure.** A “kinetic theory of gases” must—minimally—produce $pV = NkT$ (which Bernoulli was the first to do, with a theory that can be criticized on the ground that it did not accomplish much else), and to achieve that objective we must first come to an understanding concerning the kinetic meaning of “pressure.” The essential idea is indicated by the following figure:

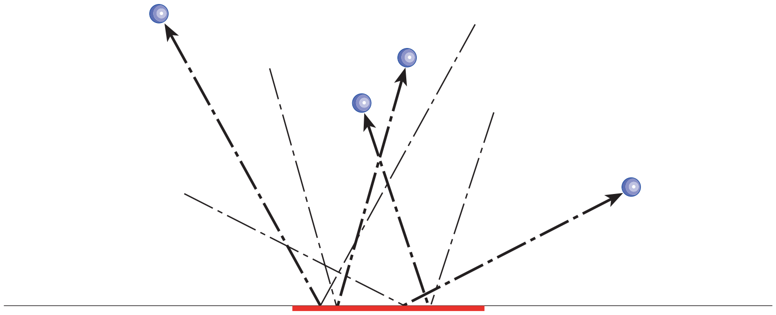

Figure 79: *In elementary kinetic theory one construes “pressure” to be a measure of the* <u>*time-averaged impulse per unit area*</u> *that the walls exert in order to elastically reflect*

$$\boldsymbol{p}_{\text{incident}} \equiv \boldsymbol{p}_{\parallel} + \boldsymbol{p}_{\perp} \quad\longmapsto\quad \boldsymbol{p}_{\text{reflected}} \equiv \boldsymbol{p}_{\parallel} - \boldsymbol{p}_{\perp}$$

*the incident hailstorm of molecules. It should be borne in mind that that imagery is specific to the kinetic theory of gases: it does not pertain usefully to “pressure” as the concept is encountered in the physics of solids, liquids, thermalized radiation...*

To develop the Maxwellian details we look to Figure 80. The cylinder has volume $dA \cdot vdt \cdot \cos\theta$ and contains (on average) a number of molecules given by

$$\frac{N}{V} f(v) \frac{\sin\theta\, d\varphi \cdot d\theta}{4\pi} dv \cdot dA \cdot vdt \cdot \cos\theta$$

To each such molecule the wall imparts an impulse given by $2mv\cos\theta$. The time-averaged impulse per unit area imparted to that $\{v, \theta, \varphi\}$-parameterized population is given therefore by

$$\text{partial pressure} = 2m\frac{N}{V} f(v)\, v^2 \frac{\sin\theta\, d\varphi \cdot d\theta}{4\pi} \cos^2\theta\, dv$$

and upon summing over all such populations[195] we obtain

$$p = 2m\frac{N}{V}\tfrac{3}{2}\alpha^2\frac{\tfrac{2}{3}\pi}{4\pi} = \frac{NkT}{V} \quad : \quad \text{PERFECT GAS LAW}$$

---

[195] Use $\displaystyle\int_0^{2\pi} d\varphi \cdot \int_0^{\frac{1}{2}\pi} \cos^2\theta \sin\theta\, d\theta = \tfrac{2}{3}\pi$ and recall that, by (321.3) and (322), $\displaystyle\int_0^{\infty} v^2 f(v)\, dv = \tfrac{3}{2}\alpha^2$ with $\alpha^2 = 2kT/m$.

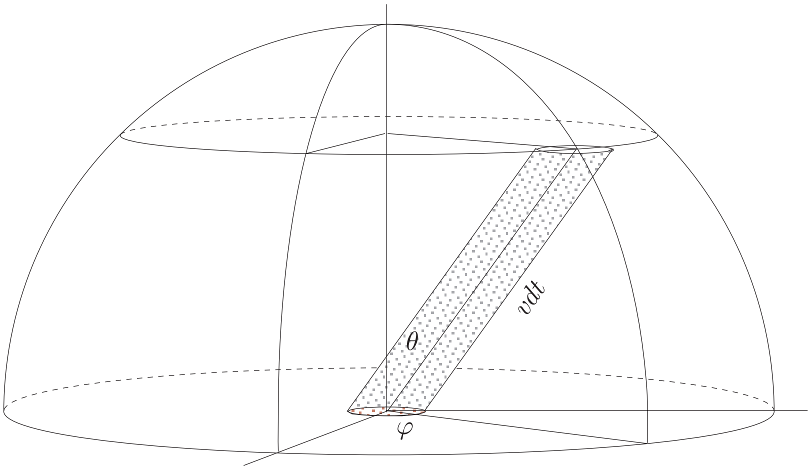

Figure 80: *Representation of the molecules that—approaching with speeds in the neighborhood dv of v from spherical addresses in the neighborhood* $\{d\theta, d\varphi\}$ *of* $\{\theta, \varphi\}$*—bounce in time dt off the wall element dA and rebound elastically toward spherical addresses in the neighborhood of* $\{\theta, \varphi+\pi\}$.

While ascribing "pressure" to "molecular mechanics at the wall" might be justified operationally (in the sense that it provides a fair representation of the action of most simple pressure gauges), the fact of the matter is that we find it useful to assign pressure also to *interior* points. We are led thus to a slight variant (Figure 81) of the preceding argument, the details of which are most conveniently developed (not in spherical coordiates, as above, but) in reference to a Cartesian coordinate system. We will find it instructive to allow $n(\boldsymbol{x}, \boldsymbol{v}, t)$ to be—at least initially—non-Maxwellian/arbitrary. We proceed from the observation that the total linear momentum $\boldsymbol{P}_{+}(\boldsymbol{x}, t; \hat{\boldsymbol{a}})\, dAdt$ of the molecules that in time $dt$ pass in the positive direction through the oriented surface-differential-at-$\boldsymbol{x}$ can be described

$$\begin{aligned}\boldsymbol{P}_{+}(\boldsymbol{x}, t; \hat{\boldsymbol{a}}) \cdot dAdt &= \int_{+} (m\boldsymbol{v})(v\cos\theta\, dAdt) n(\boldsymbol{x}, \boldsymbol{v}, t)\, d\boldsymbol{v} \\ &= +\int_{+} (m\boldsymbol{v})(\boldsymbol{v}\boldsymbol{\cdot}\hat{\boldsymbol{a}})\, n(\boldsymbol{x}, \boldsymbol{v}, t)\, d\boldsymbol{v} \cdot dAdt\end{aligned}$$

where $\displaystyle\int_{+}$ signifies integration over that half of velocity space in which $\boldsymbol{v}\boldsymbol{\cdot}\hat{\boldsymbol{a}} \geqslant 0$. The total momentum of the molecules that pass through in the negative direction (which is to say: positively with respect to $-\hat{\boldsymbol{a}}$) can by the same argument be described

$$\boldsymbol{P}_{-}(\boldsymbol{x}, t; \hat{\boldsymbol{a}}) \cdot dAdt = -\int_{-} (m\boldsymbol{v})(\boldsymbol{v}\boldsymbol{\cdot}\hat{\boldsymbol{a}})\, n(\boldsymbol{x}, \boldsymbol{v}, t)\, d\boldsymbol{v} \cdot dAdt$$

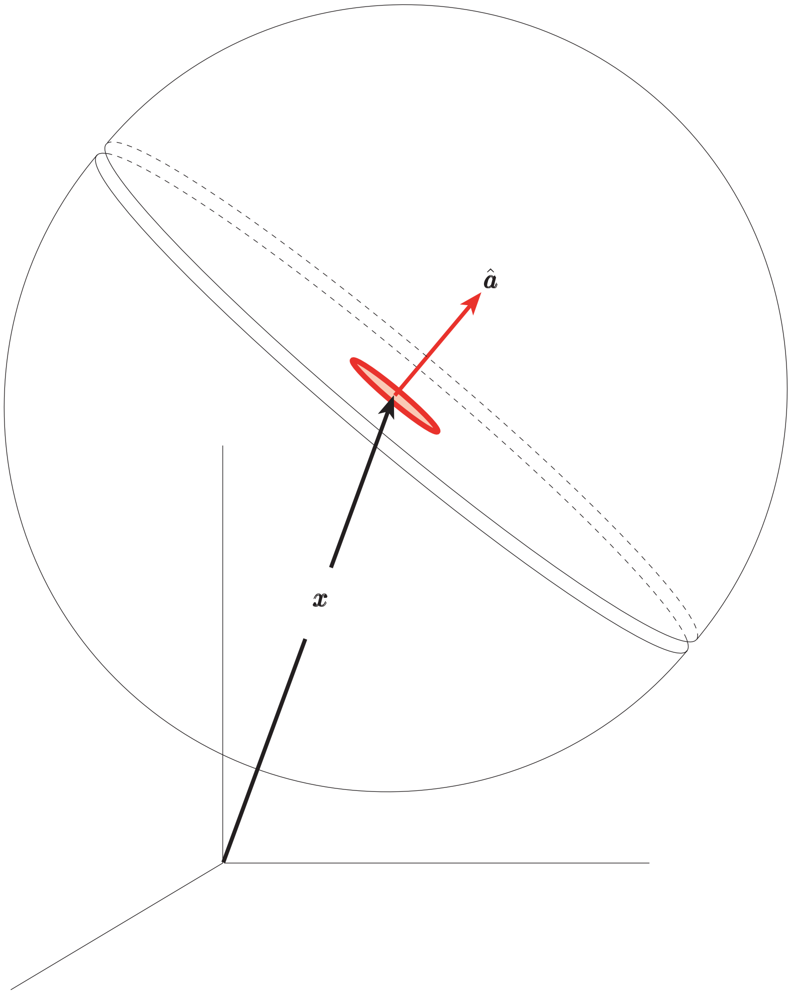

FIGURE 81: *If we look to the* <u>*signed momentum flux through an oriented ring*</u> *we are led to a conception of "pressure" that is meaningful at interior points. The unit vector* $\hat{\boldsymbol{a}}$ *describes the orientation of the ring-at-*$\boldsymbol{x}$*, which has differential area* $dA$*. Molecules that pass through the ring will be said to be* positive *or* negative *according as* $\hat{\boldsymbol{a}}\cdot\boldsymbol{v} \gtrless 0$.

To capture the essence of the physical idea presented in Figure 79 we introduce

$$\boldsymbol{P}(\boldsymbol{x},t;\hat{\boldsymbol{a}}) \equiv \boldsymbol{P}_{+}(\boldsymbol{x},t;\hat{\boldsymbol{a}}) - \boldsymbol{P}_{-}(\boldsymbol{x},t;\hat{\boldsymbol{a}}) = \int (m\boldsymbol{v})(\boldsymbol{v}\cdot\hat{\boldsymbol{a}})\, n(\boldsymbol{x},\boldsymbol{v},t)\, d\boldsymbol{v}$$

which, we note, can be written

$$\boldsymbol{P}(\boldsymbol{x},t;\hat{\boldsymbol{a}}) = \mathbb{P}(\boldsymbol{x},t)\,\hat{\boldsymbol{a}}$$

with

$$\mathbb{P}(\boldsymbol{x},t) \equiv \|P_{ij}(\boldsymbol{x},t)\|$$

and

$$P_{ij}(\boldsymbol{x},t) \equiv m\int v_i v_j\, n(\boldsymbol{x},\boldsymbol{v},t)\,d\boldsymbol{v} \tag{324}$$

From $\big[n(\boldsymbol{x},\boldsymbol{v},t)\,d\boldsymbol{v}\big] = \frac{1}{\text{volume}}$ it follows that[196]

$$\big[P_{ij}\big] = \frac{\text{energy}}{\text{volume}} = \frac{\text{force}}{\text{area}} = \text{pressure}$$

If, in particular, the number-density function $n(\boldsymbol{x},\boldsymbol{v},t)$ refers to a molecular distribution that is **homogeneous**, **isotropic** and **steady** it becomes natural to write

$$n(\boldsymbol{x},\boldsymbol{v},t)\cdot dv_1 dv_2 dv_3 = \frac{N}{V}\,\mathtt{n}(v)\cdot v^2\sin\theta\,d\varphi\,d\theta dv$$

with

$$\begin{aligned} v_1 &= v\,\sin\theta\cos\varphi \\ v_2 &= v\,\sin\theta\,\sin\varphi \\ v_3 &= v\cos\theta \end{aligned}$$

and where it is required of $\mathtt{n}(v)$ only that $\displaystyle\int_0^\infty \mathtt{n}(v)\,4\pi v^2 dv = 1$. It then follows (according to *Mathematica*) from (324) that

$$P_{ij} = \tfrac{1}{3}m\frac{N}{V}\int_0^\infty \mathtt{n}(v)\,4\pi v^4\,dv\cdot\delta_{ij}$$

and if we assign to $\mathtt{n}(v)\,4\pi v^2$ its *Maxwellian* value (323) we obtain

$$P_{ij} = \tfrac{1}{3}m\frac{N}{V}\int_0^\infty f(v)\,v^2\,dv\cdot\delta_{ij} = \frac{N}{V}kT\cdot\delta_{ij}$$

It is, by this line of argument, a property of Maxwellian gas that at all times $t$ and at all interior points $\boldsymbol{x}$ the signed momentum flux in the direction $\hat{\boldsymbol{a}}$ can be described

$$\boldsymbol{P}(\boldsymbol{x},t;\hat{\boldsymbol{a}}) = \frac{N}{V}kT\cdot\hat{\boldsymbol{a}}$$

In the argument that proceeded from Figure 80 we in effect placed $\boldsymbol{x}$ on the

---

[196] We note in passing that—no accident!—the construction (324) bears a marked resemblance to the construction that at (320) on page 223 in Chapter 3 of CLASSICAL ELECTRODYNAMICS (2001/2002) describes the stress-energy tensor $\sigma^{\mu\nu}$ of (relativistic) "dust."

wall, placed $\hat{\boldsymbol{a}}$ normal to the wall, and identified the resulting "signed momentum flux" with "pressure at the wall." By the more recent argument we have managed to carry the "pressure" concept into the interior of the gas: for Maxwellian gases we have—constantly, at all interior points—

$$\mathbb{P} = \begin{pmatrix} p & 0 & 0 \\ 0 & p & 0 \\ 0 & 0 & p \end{pmatrix} \quad \text{with} \quad p = \tfrac{1}{3}\operatorname{tr}\mathbb{P} = \frac{N}{V}kT$$

We have, with Maxwellian assumptions, recovered the perfect gas law . . . but we have, for our effort, been rewarded with something more:

Looking back again to (324), we are led to write

$$p(\boldsymbol{x},t) = \tfrac{1}{3}\operatorname{tr}\mathbb{P}(\boldsymbol{x},t) = \tfrac{1}{3}m\int(v_1^2 + v_2^2 + v_3^2)\,n(\boldsymbol{x},\boldsymbol{v},t)\,dv_1 dv_2 dv_3 \tag{325}$$

to assign plausible meaning to the **instantaneous local pressure** in the general (non-equilibrated non-Maxwellian) case. By this conception

$$\begin{aligned} \text{local pressure} &= \text{trace of a local symmetric matrix} \\ &= \text{local rotationally invariant scalar} \end{aligned}$$

and captures only *some* of the information written into the structure of the local **pressure tensor**.[197]

**4. Alternative derivations of the Maxwellian distribution.** The argument that led Maxwell (1860) to the Maxwellian distribution is subject to the criticism that it achieves its elegant efficiency by dint of a statistical assumption—namely,[198] that the components $v_i$ of $\boldsymbol{v}$ are independent random variables—the physical basis of which is by no means obvious. In 1866 Maxwell—granting that his former assumption "may appear precarious"—constructed an alternative derivation that went some distance toward recognizing that it is not by the laws of statistics but by the laws of *mechanics* that molecules move. He looked to binary collisions (Figure 82), and argued that at thermal equilibrium one should expect "detailed balance" in the sense that each scattering process (left) should occur with the same frequency as its time-reversed mate (right). Assuming (not the individual components $v_i$ of a single particle but) the $\boldsymbol{v}$ and $\boldsymbol{v}'$ of each colliding pair to be <u>statistically independent and identically distributed</u>, he was led to write

$$F(\boldsymbol{v})F(\boldsymbol{v}') = F(\boldsymbol{u})F(\boldsymbol{u}')$$

which in combination with the energy conservation condition

$$v^2 + v'^2 = u^2 + u'^2$$

---

[197] For more detailed discussion of this subject—and, indeed, of virtually *all* aspects of the kinetic theory of gases—see S. Chapman & T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (1960), which bears the subtitle "An account of the kinetic theory of viscosity, thermal conduction, and diffusion in gases."

[198] See again page 250.

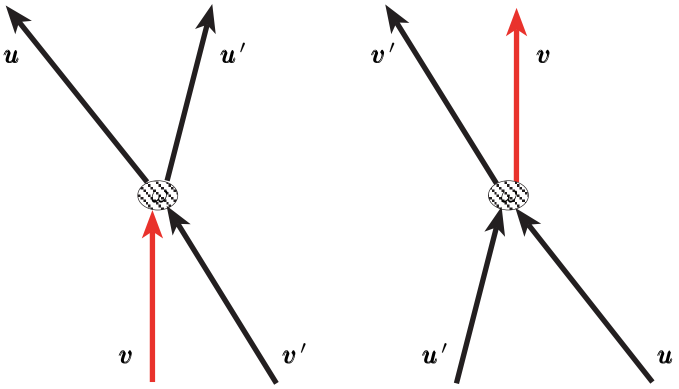

FIGURE 82: *At left*: *binary collision from which particles with initial velocities* $\boldsymbol{v}$ *and* $\boldsymbol{v}'$ *depart with velocities* $\boldsymbol{u}$ *and* $\boldsymbol{u}'$. *At right*: *the time-reversed process. The shaded blobs allude to the package of "impact parameters" that (except in the one-dimensional case) must be specified before the out-velocities become well-defined functions of the in-velocities*: *these enter into Boltzmann's line of argument, but not into Maxwell's.*

leads back again to (319). But here again, the argument hinges on a statistical assumption (if, arguably, a softer one), not upon a secure mechanical theorem.

Maxwell's revised argument was published in 1867, the same year that Boltzmann completed his doctorate and began the kinetic theoretic research that was to occupy him for nearly forty years, the initial objective of which was "to establish a direct connection between the $2^{\text{nd}}$ law of thermodynamics and the mechanical principle of least action."[199] Already in 1868 Boltzmann noticed that in the presence of a potential one has this generalization

$$n(\boldsymbol{x},\boldsymbol{v}) = N\cdot\frac{1}{Z}\,e^{-\frac{1}{kT}\left\{\frac{1}{2}mv^2+U(\boldsymbol{x})\right\}}$$

of Maxwell's result. Thus did gas theory give rise to the "Boltzmann factors"[200] destined to become fundamental to the statistical mechanics of *all* equilibrated systems, whether gaseous or not.

In that same early paper Boltzmann presented a **combinatorial derivation** of the Maxwellian distribution (now, by many authors, called the "Maxwell-Boltzmann distribution") of which I provide here a simplified account. Suppose $N$ identical molecules, each of mass $m$, are confined to a spatial volume $V$, within which they move freely (*i.e.*, in the absence of an impressed potential)

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[199] I quote Brush,[113] page 232. It was, by the way, already clear to Maxwell that the $2^{\text{nd}}$ law springs from statistics, *not* from mechanics.

[200] See again page 122.

with total energy $E$. Note that 3-dimensional velocity space, though generally unbounded, is for purposes of the present discussion bounded: it is spherical, with volume $\Omega = \frac{4}{3}\pi(2mE)^{\frac{3}{2}}$. Resolve the interior of that velocity-sphere into ennumerated "cells," and let $\omega_i$ denote the volume of the $i^{\text{th}}$ cell.[201] The probability that a molecule, if dropped randomly into 6-dimensional state space, will land in the $i^{\text{th}}$ cell is, we will assume, given by

$$p_i = \frac{\omega_i}{\Omega}$$

If we drop $N$ molecules into state space the likelihood that we will find $n_1$ molecules in cell #1, $n_2$ molecules in cell #2, *etc.* is given by

$$P = \frac{N!}{n_1!n_2!\cdots} p_1^{n_1} p_2^{n_2} \cdots$$

Boltzmann would have us maximize $P$—equivalently (but more conveniently): maximize

$$\log P = \log N! + \sum_i \big\{ n_i \log p_i - \log n_i! \big\}$$

—subject to the constraints

$$\sum_i n_i = N$$

$$\sum_i n_i \, \varepsilon_i = E$$

where $\varepsilon_i \equiv \frac{1}{2}mv_i^2$ and $v_i$ marks the location of the $i^{\text{th}}$ cell.

In leading Stirling approximation (page 106) we have

$$\log P = \big\{ N \log N - N \big\} + \sum_i n_i \big\{ \log p_i - \log n_i \big\} + N$$

and confront a *constrained maximization* problem, for which Lagrange devised the method of choice, the so-called "method of undetermined multipliers."[202] To

$$\delta \log P = \sum_i \big\{ \log p_i - \log n_i - 1 \big\} \delta n_i = 0$$

we add

$$(\alpha + 1) \sum_i \delta n_i = 0 \qquad \text{and} \qquad -\beta \sum_i \varepsilon_i \delta n_i = 0$$

---

[201] The artificial "discretization" of intrinsically continuous variables was, for Boltzmann, more than a trick: it was a point of methodological philosophy, and lent his work a "quantum mechanical" cast more than thirty years before the invention of quantum mechanics. See Brush,[113] page 235.

[202] See R. Courant & D. Hilbert, *Methods of Mathematical Physics* (1953), page 165 or D. ter Haar, *Elements of Statistical Mechanics* (1954), page 444.

and obtain $\log p_i - \log n_i + \alpha - \beta\varepsilon_i = 0$ or

$$n_i = p_i\, e^{\alpha - \beta\varepsilon_i}$$

Passing now to the continuous limit, we have

$$F(\boldsymbol{v}) = A^3\, e^{-\beta\frac{1}{2}mv^2}$$

From the simultaneous requirements that

$$\iiint F(\boldsymbol{v})\, d\boldsymbol{v} = \int_0^\infty A^3\, e^{-\beta\frac{1}{2}mv^2} 4\pi v^2\, dv = 1$$

and

$$\int_0^\infty \tfrac{1}{2}mv^2 \cdot A^3\, e^{-\beta\frac{1}{2}mv^2} 4\pi v^2\, dv = \tfrac{3}{2}kT$$

we are led back again to precisely Maxwell's result.[203]

The 24-year-old Boltzmann had every reason to be proud of himself (though his biographers suggest that was not his nature), for he had extracted Maxwell's result from a statistical assumption that has about it the "look of generality". . . by an argument that depends only incidentally/inessentially on the physics of gases (and not at all on the details of collisional mechanics). He had, in short, planted the seed of a *statistical theory of thermalized-systems-in-general*—a fact to which Maxwell himself drew attention in a long paper "On Boltzmann's theorem on the average distribution of energy in a system of material points" published shortly before his death in 1879. In retrospect, Maxwell's original argument is seen to be valuable as much for its shortcomings as for its striking success, for it was the two together that provided Boltzmann's motivation.

In setting up the identification

$$\text{Maxwellian distribution} \quad\Longleftrightarrow\quad \text{most probable distribution}$$

Boltzmann raised this subordinate question: *How* probable is "most probable"? That question was explored already in §6 of Chapter 3, in a discussion which led (as $N$ becomes large) to this one-word response: *Overwhelmingly*!

---

[203] Introduce (322) into (319). It is, by the way, a lesson of experience that Lagrange multipliers, when they arise from physical argument, usually have important physical significance. Certainly that is the case in the present instance, where we encounter

$$\text{Lagrange multiplier } \beta = \frac{1}{kT}$$

Boltzmann (1871), and also Maxwell (1879, in the paper mentioned above), were led therefore to remark—**ergodic hypothesis**[204]—that if $n(\boldsymbol{x},\boldsymbol{v},t)$ serially visited all values consistent with the imposed constraints... then it might plausibly be expected (on conjectured mechanical grounds) to spend nearly all of the time at or in the immediate vicinity of its Maxwellian most-probable value. Both recognized that while "ergodic theory" might be easiest to develop in relation to gases or other idealized simple systems it should—in principle—pertain to *all* thermalized systems.[205]

**5. Boltzmann equation & the H-theorem.** Retreating now from systems-in-general to gases in particular ... Boltzmann—like Maxwell before him—recognized it to be a fact of experience that an initially disequilibrated gas will spontaneously equilibrate

$$n(\boldsymbol{x},\boldsymbol{v},t) \xrightarrow{\qquad\qquad} n_{\text{Maxwellian}}(\boldsymbol{x},\boldsymbol{v}) \tag{326}$$

and drew from this fact some tentative conclusions relating to the *mechanical stability* of the Maxwellian distribution. Thus in 1872 was Boltzmann motivated to develop a **dynamical theory of disequilibrated gases** from which (326) might be recovered as a special consequence—a theory which I must on the present occasion be content merely to sketch.[206]

Represent the initial state of the gas by sprinkling points $\{\boldsymbol{x}_i,\boldsymbol{p}_i\}$ onto 6-dimensional phase space ... or which is (by $\boldsymbol{p} = m\boldsymbol{v}$) the same but more convenient: by sprinkling points $\{\boldsymbol{x}_i,\boldsymbol{v}_i\}$ onto 6-dimensional state space, and let $n(\boldsymbol{x},\boldsymbol{v},0)$ serve to describe (in the course-grained sense of Figure 78) the initial density of those points. Setting aside for the moment the effect of binary collisions, we assume that the particles move non-interactively, as described by the shared Lagrangian

$$L = \tfrac{1}{2}mv^2 - \underbrace{U(\boldsymbol{x})}_{\text{describes such EXTERNAL FORCES as may act upon the molecules}}$$

and will write

$$\begin{aligned}\boldsymbol{x} &\mapsto \boldsymbol{x}(t) = \boldsymbol{X}(\boldsymbol{x},\boldsymbol{v},t)\\ \boldsymbol{v} &\mapsto \boldsymbol{v}(t) = \boldsymbol{V}(\boldsymbol{x},\boldsymbol{v},t)\end{aligned}$$

to describe that motion.

From **Liouville's theorem** (*i.e.*, from the "incompressibility of phase flow") it follows now that

$$n\big(\boldsymbol{x}(t),\boldsymbol{v}(t),t\big) = n\big(\boldsymbol{x},\boldsymbol{v},0\big)$$

---

[204] See §10.10 "The ergodic hypothesis of Boltzmann and Maxwell" in Brush.[113] According to Brush the term "ergodic" was introduced by Boltzmann, but originally had a meaning rather different from the meaning it has acquired.

[205] For a more detailed account of the **method of the most probable distribution** see (for example) §4.3 in K. Huang's *Statistical Mechanics* (2nd edition 1987).

[206] For many of the missing details and basic references see STATISTICAL PHYSICS (1969), Chapter 2, pages 21–40.

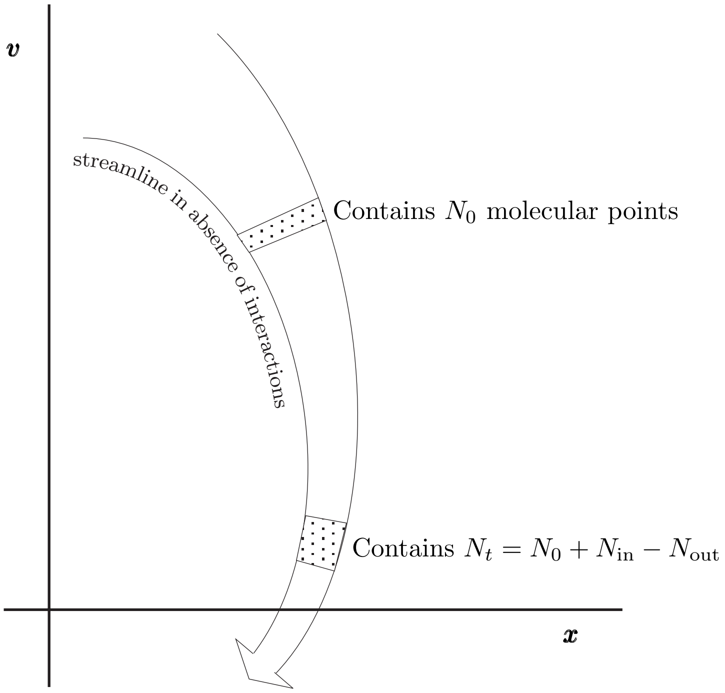

Figure 83: *Schematic representation of Boltzmann's collisional modification of Liouville's representation of the phase flow of a population of noninteractive molecules.*

which upon differentiation with respect to $t$ becomes

$$\Big\{\frac{\partial}{\partial t} + \boldsymbol{v}\boldsymbol{\cdot}\boldsymbol{\nabla}_x + \boldsymbol{a}\boldsymbol{\cdot}\boldsymbol{\nabla}_v\Big\}n(\boldsymbol{x},\boldsymbol{v},t) = 0 \;\;:\;\; \text{collisional interactions turned off}$$

where $\boldsymbol{a} \equiv \dot{\boldsymbol{v}} = \frac{1}{m}\boldsymbol{F} = -\frac{1}{m}\boldsymbol{\nabla}_x U$.

To take intermolecular collisions into account Boltzmann writes

$$\Big\{\frac{\partial}{\partial t} + \boldsymbol{v}\boldsymbol{\cdot}\boldsymbol{\nabla}_x + \boldsymbol{a}\boldsymbol{\cdot}\boldsymbol{\nabla}_v\Big\}n(\boldsymbol{x},\boldsymbol{v},t) = \text{In}[n] - \text{Out}[n]$$

where In$[n]$ and Out$[n]$ are functionals of $n(\boldsymbol{x},\boldsymbol{v},t)$ that describe respectively the rate at which collisions (see again Figure 82) are

- delivering molecules into and
- removing them from

the neighborhood of $\{\boldsymbol{x},\boldsymbol{v}\}$. Our immediate assignment is to construct workable descriptions of In$[n]$ and Out$[n]$.

We restrict our attention to *binary* collisions (predominant in dilute gases) and not that for two particles to collide they must be at the same point $\boldsymbol{x}$.

Energy and momentum conservation

$$u^2 + u'^2 = v^2 + v'^2 \qquad \text{and} \qquad \boldsymbol{u} + \boldsymbol{u}' = \boldsymbol{v} + \boldsymbol{v}'$$

impose only 4 constraints on the 6 components of the collision products $\boldsymbol{u}$ and $\boldsymbol{u}'$ so the collisional details are necessarily contingent upon specification of certain side conditions (the values of such generalized "impact parameters" as are relevant to the physics of the collisional processes in question: those will collectively be denoted $\omega$). That understood, we have

$$\begin{aligned} \boldsymbol{u} \ &= \boldsymbol{u}\ (\boldsymbol{v}, \boldsymbol{v}', \omega) \\ \boldsymbol{u}' &= \boldsymbol{u}'(\boldsymbol{v}, \boldsymbol{v}', \omega) \end{aligned}$$

Pretty clearly

$$\text{Out}[n]\, d\boldsymbol{v} = n(\boldsymbol{x}, \boldsymbol{v}, t)\, d\boldsymbol{v} \cdot \int n(\boldsymbol{x}, \boldsymbol{v}', t)\, d\boldsymbol{v}' \cdot \int A(\omega)\, d\omega$$

where $A(\omega)$ assigns statistical weight to the various $\omega$-values. Similarly but more awkwardly

$$\text{In}[n]\, d\boldsymbol{v} = \iiint_{[\boldsymbol{v}]} n(\boldsymbol{x}, \boldsymbol{u}, t)\, n(\boldsymbol{x}, \boldsymbol{u}', t) A(\omega')\, d\boldsymbol{u}\, d\boldsymbol{u}' d\omega'$$

where the $\iiint$ ranges over those coordinated values of $\boldsymbol{u}$, $\boldsymbol{u}'$ and $\omega'$ which (see again the right side of Figure 82) produce post-collisional velocities that lie in the neighborhood $d\boldsymbol{v}$ of $\boldsymbol{v}$. A change of variables (intended to reduce the awkwardness) gives

$$= d\boldsymbol{v} \iint n\big(\boldsymbol{x}, \boldsymbol{u}(\boldsymbol{v}, \boldsymbol{v}', \omega), t\big) n\big(\boldsymbol{x}, \boldsymbol{u}'(\boldsymbol{v}, \boldsymbol{v}', \omega), t\big) A(\omega) J\, d\boldsymbol{v}' d\omega$$

where, by the time-reversal invariance of the collision process, the Jacobian

$$J \equiv \left| \frac{\partial(\boldsymbol{u}, \boldsymbol{u}', \omega')}{\partial(\boldsymbol{v}, \boldsymbol{v}', \omega\ )} \right| = 1$$

Putting the pieces together we obtain the celebrated **Boltzmann equation**

$$\left\{ \frac{\partial}{\partial t} + \boldsymbol{v} \cdot \boldsymbol{\nabla}_x + \boldsymbol{a} \cdot \boldsymbol{\nabla}_v \right\} n = \iint (\bar{n}\, \bar{n}' - n\, n') A\, d\boldsymbol{v}' d\omega \tag{327}$$

where

$$\begin{aligned} n &\equiv n(\boldsymbol{x}, \boldsymbol{v}, t) \\ n' &\equiv n(\boldsymbol{x}, \boldsymbol{v}', t) \\ \bar{n} &\equiv \bar{n}(\boldsymbol{x}, \boldsymbol{v}, \boldsymbol{v}', t) \equiv n\big(\boldsymbol{x}, \boldsymbol{u}(\boldsymbol{v}, \boldsymbol{v}', \omega), t\big) \\ \bar{n}' &\equiv \bar{n}(\boldsymbol{x}, \boldsymbol{v}, \boldsymbol{v}', t) \equiv n\big(\boldsymbol{x}, \boldsymbol{u}'(\boldsymbol{v}, \boldsymbol{v}', \omega), t\big) \end{aligned}$$

The Boltzmann equation is a beast, a non-linear integro-differential equation that yields to exact analytical treatment only in a few artificial cases. It is, however, fundamental to a lot of physics, the equation one must solve—approximately (see Chapman & Cowling[197]), numerically—to address questions relating to the transport of mass/energy/momentum in dilute disequilibrated gases. Happily, we have no call to venture down that tangled trail: we are concerned with the thermal physics of *equilibrated* gases . . . and, at the moment, with the light Boltzmann was able to shed on the *approach* to equilibrium.

Let us, for simplicity, assume that our gas is subject to no externally impressed force ($U(\boldsymbol{x}) = 0 \Rightarrow \boldsymbol{a} = \boldsymbol{0}$) and—which is a bit more problematic—that spatial uniformity has been established ($\boldsymbol{\nabla}_x n = \boldsymbol{0}$):

$$n(\boldsymbol{x},\boldsymbol{v},t) \longmapsto \frac{N}{V}F(\boldsymbol{v},t) \quad \text{as on page 249}$$

The Boltzmann equation then becomes

$$\frac{\partial}{\partial t}F = \iint (\bar{F}\,\bar{F}{\,}' - F\,F{\,}')A\,d\boldsymbol{v}'d\omega \tag{328}$$

Thus prepared, Boltzmann (with the variational principles of mechanics on his mind?) had the genius to introduce

$$H \equiv \langle \log F\,\rangle = \int F\log F\,d\boldsymbol{v} \tag{329}$$

↑ upper case $\eta$, intended to suggest "entropy"

and to study $dH/dt$. Immediately

$$\frac{dH}{dt} = \int (1+\log F\,)\frac{\partial F}{\partial t}\,d\boldsymbol{v}$$

which by appeal to the simplified Boltzmann equation (328) becomes

$$\frac{dH}{dt} = \iiint (1+\log F\quad)(\bar{F}\,\bar{F}{\,}' - F\,F{\,}')A\,d\boldsymbol{v}\,d\boldsymbol{v}'d\omega$$

Under the $\iiint$ we can with impunity interchange $\boldsymbol{v}$ and $\boldsymbol{v}'$ (struck molecules with those doing the striking) so

$$= \iiint (1+\log F{\,}')(\bar{F}{\,}'\,\bar{F} - F{\,}'\,F)A\,d\boldsymbol{v}\,d\boldsymbol{v}'d\omega$$

And by time-reversal invariance (*i.e.*, by the familiar change of variables) the preceding equations become

$$= \iiint (1+\log \bar{F}\quad)(F\,F{\,}' - \bar{F}\,\bar{F}{\,}')A\,d\boldsymbol{v}\,d\boldsymbol{v}'d\omega$$

$$= \iiint (1+\log \bar{F}{\,}')(F{\,}'\,F - \bar{F}{\,}'\,\bar{F})A\,d\boldsymbol{v}\,d\boldsymbol{v}'d\omega$$

Adding these four (equivalent) expressions together and dividing by 4, we find

$$\frac{dH}{dt} = \tfrac{1}{4}\iiint \Big\{(\bar{F}\,\bar{F}{\,}' - F\,F{\,}')\log\frac{FF{\,}'}{\bar{F}\bar{F}{\,}'}\Big\}A\,d\boldsymbol{v}\,d\boldsymbol{v}'d\omega \tag{330}$$

Now $A(\omega)$ is, as a probability density, necessarily non-negative. Moreover,

$$\log\frac{FF'}{\bar F\bar F'}\ \text{ is }\begin{cases}\text{positive or negative according as } FF' \gtrless \bar F\bar F' \\ 0 \qquad\qquad\qquad \text{if and only if } FF' = \bar F\bar F'\end{cases}$$

It follows therefore from (330) that

$$\frac{dH}{dt} \leqslant 0, \quad \text{with equality if and only if } FF' \equiv \bar F\bar F' \tag{331.1}$$

which is **Boltzmann's H-theorem**: as the system relaxes (evolves) the value of $H$ necessarily decreases (see the figure), until at equilibrium we have[207]

$$H(t) \downarrow H(\infty) = H_{\text{min}} \qquad \text{and} \qquad FF' \equiv \bar F\bar F' \tag{331.2}$$

—the latter (I have used $\equiv$ to signal that $FF' = \bar F\bar F'$ holds for *all* values of $\boldsymbol{v}$ and $\boldsymbol{v}'$) being the statement of **detailed balancing**.[208]

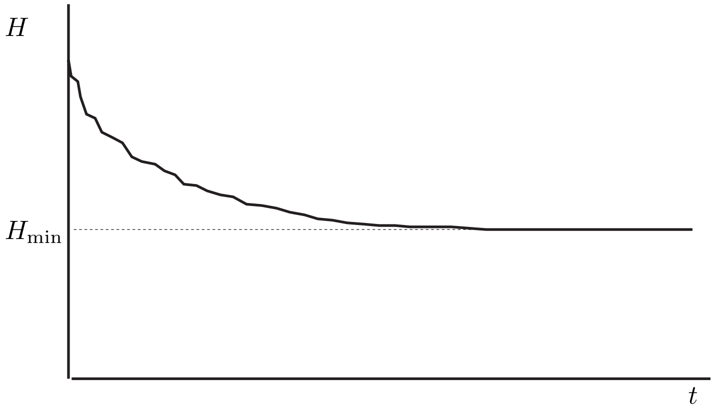

FIGURE 84: *Schematic representation of the temporal trend of* $H(t)$*, according to* (331)*. It is remarkable that Boltzmann was able to say sharp things about the trend while leaving us almost powerless to compute the details, or even to estimate the characteristic relaxation time.*

The equilibration of a gas, microscopically regarded, is a many-variable process that terminates non-uniquely. Kinetic theory presents a much-simplified account

$$n(\boldsymbol{x},\boldsymbol{v},t) \xrightarrow{\qquad\qquad} n(\boldsymbol{x},\boldsymbol{v},\infty) = n_{\text{Maxwellian}}(\boldsymbol{v})$$

of that process, of which (331.2) provides a pallid projection, a single-parameter representation. Remarkably, it is—by the following line of argument—possible

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[207] Implicit here is the assumption that $H$ is <u>bounded below</u>. For the proof see the footnote on page 70 of Chapman & Cowling.[197]

[208] See again page 257 and R. C. Tolman, *Principles of Statistical Mechanics* (1938), page 165.

to "de-project," to extract from (331.2) the specific design of the Maxwellian distribution. To that end we undertake to

$$\text{minimize } H \equiv \int F \log F \, d\boldsymbol{v}$$

subject to the requirements that

- the particle number $N$
- the total linear momentum $\boldsymbol{P}$ and
- the total energy $E$

have prescribed constant values. Those five constraints are readily brought to the form

$$\left.\begin{aligned} \int F(\boldsymbol{v})\, d\boldsymbol{v} &= 1 \\ \int m\boldsymbol{v} \cdot F(\boldsymbol{v})\, d\boldsymbol{v} &= \boldsymbol{P}/N \\ \int \tfrac{1}{2}mv^2 \cdot F(\boldsymbol{v})\, d\boldsymbol{v} &= E/N \end{aligned}\right\} \tag{332}$$

Immediately

$$\delta H = \int (1 + \log F)\delta F \, d\boldsymbol{v}$$

so if we again employ the Lagrange's method of undetermined multipliers (page 259) to implement the constraints we obtain

$$\int \Big\{(1 + \log F) + \alpha \tfrac{1}{2}mv^2 + \boldsymbol{\beta}\boldsymbol{\cdot} m\boldsymbol{v} + \gamma\Big\}\delta F \, d\boldsymbol{v} = 0$$

giving

$$F(\boldsymbol{v}) = e^{-(1+\gamma) - \alpha\frac{1}{2}mv^2 - \boldsymbol{\beta}\boldsymbol{\cdot} m\boldsymbol{v}} \equiv e^{-(av^2 + 2\boldsymbol{b}\boldsymbol{\cdot}\boldsymbol{v} + c)}$$

Returning with this information to (332) we (with *Mathematica*'s assistance) compute

$$\begin{aligned} e^{-c}(\pi/a)^{\frac{3}{2}} e^{b^2/a} &= 1 \\ -m(\boldsymbol{b}/a)\cdot e^{-c}(\pi/a)^{\frac{3}{2}} e^{b^2/a} &= \boldsymbol{P}/N \\ \tfrac{1}{2}m\frac{3a + 2b^2}{2a^2}\cdot e^{-c}(\pi/a)^{\frac{3}{2}} e^{b^2/a} &= E/N \end{aligned}$$

with $b^2 \equiv \boldsymbol{b}\boldsymbol{\cdot}\boldsymbol{b}$. For gases at rest $\boldsymbol{P} = \boldsymbol{0} \Rightarrow \boldsymbol{b} = \boldsymbol{0}$ and the preceding equations simplify:

$$\begin{aligned} e^{-c}(\pi/a)^{\frac{3}{2}} &= 1 \\ \tfrac{3}{4}(m/a)\cdot e^{-c}(\pi/a)^{\frac{3}{2}} &= E/N \end{aligned}$$

whence

$$a = \tfrac{3}{4}m/\varepsilon \quad : \quad \varepsilon \equiv E/N \equiv \text{average kinetic energy per molecule}$$

$$e^{-c} = (a/\pi)^{\frac{3}{2}} = \Big(\frac{3m}{4\pi\varepsilon}\Big)^{\frac{3}{2}}$$

It has been established that $\varepsilon = \frac{3}{2}kT$, so in the rest frame of a thermalized gas we have

$$F(\boldsymbol{v}) = \Big(\frac{m}{2\pi kT}\Big)^{\frac{3}{2}} e^{-\frac{1}{2}mv^2/kT}$$

which exactly the Maxwellian result, encountered first on page 251 and most recently on page 260.[209]

But the final movement of this sonata has yet to be performed. Noting that

$$F(\boldsymbol{v}) \mapsto \mathcal{F}(\boldsymbol{v}) \equiv \frac{N}{V}F(\boldsymbol{v}) \quad \text{sends} \quad H \mapsto \mathcal{H} \equiv \int \mathcal{F}\log\mathcal{F}\,d\boldsymbol{v}$$

we ask: What is the *value* of $\mathcal{H}_{\min}$? By computation

$$\begin{aligned} \mathcal{H}_{\min} &= \int_0^\infty \frac{N}{V}\Big(\frac{m}{2\pi kT}\Big)^{\frac{3}{2}} e^{-\frac{1}{2}mv^2/kT}\Big\{\log\Big[\frac{N}{V}\Big(\frac{m}{2\pi kT}\Big)^{\frac{3}{2}}\Big] - \frac{mv^2}{2kT}\Big\}4\pi v^2\,dv \\ &= \frac{N}{V}\Big\{\log\Big[\frac{N}{V}\Big(\frac{m}{2\pi kT}\Big)^{\frac{3}{2}}\Big] - \tfrac{3}{2}\Big\} \\ &= -\frac{Nk\big\{\log V + \frac{3}{2}\log T - \log N + \frac{3}{2}(1-\log[m/2\pi k])\big\}}{kV} \end{aligned} \tag{333}$$

Now, we've known for a long time[210] that the *entropy of an ideal monomolecular gas* can be described

$$S = Nk\big\{\log V + \tfrac{3}{2}\log T\big\} + \text{constant}$$

and[211] that the adjustment

$$\begin{gathered} \qquad\qquad\qquad\qquad\downarrow \\ S_{\text{indistinguishable}} = Nk\big\{\log V + \tfrac{3}{2}\log T - \log N\big\} + \text{constant} \end{gathered}$$

provides an avenue of escape from Gibbs' paradox. Evidently

$$S_{\text{indistinguishable}} = -kV\mathcal{H}_{\min}$$

and Boltzmann's $dH/dt \leqslant 0$ can be read as a statement—specific to the theory of gases—of the measured <u>entropy increase $dS/dt \geqslant 0$ that attends the thermalization process</u> . . . in gases, but presumably in *all* systems.

This, of course, presumes that we have means to step outside of the theory of thermalized systems (thermodynamics, statistical mechanics) and assign

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[209] We have argued here from $\delta H = 0$. Alternatively but equivalently, one could argue from the detailed balance condition $FF' \equiv \bar{F}\bar{F}'$: this is done by Chapman & Cowling,[197] pages 25–28.

[210] See (28) on page 42; also (23) on page 33, (188.2) on page 149.

[211] See again page 176.

entropy values to the *non-thermalized* states of many-body systems. And this, in the

$$S = k \log W$$

inscribed on Boltzmann's tombstone,[212] we *do* have.

The developments described above—which were worked out and published by Boltzmann during the 1870's, while Maxwell still lived—clarified some standing questions and at the same time posed some disturbing new questions. Both aspects of the work contributed vitally to the further development of thermal physics:

- Though rooted in the collisional physics of gases (rooted, that is to say, in kinetic theory—this though the influential Ernst Mach, beginning in 1872 and continuing up until his death in 1916, argued vigorously that "atoms do not exist"[213]), the abstracted essentials of Boltzmann's results suggested the possibility and rough outline of a statistical mechanics of (non-gaseous) systems-in-general.
- The drift of the $H$-theorem suggested that thermo*statics*—proper name of what we inappropriately call "thermodynamics"—might be embedded within a thermo*dynamics* that has things to say not only about equilibrated states but also about the irreversible *approach* to equilibrium, a theory into which $t$ enters as a variable.
- It was remarked by Kelvin (1874) that it is mysterious how classical mechanics—the time-reversal invariance of which was explicitly invoked at several points[214] by Boltzmann—can give rise to a result (the $H$-theorem) that does not share that invariance . . . and that it is not obvious where, in the chain of argument, the symmetry in question is broken. The problem is a deep one: it was addressed by Boltzmann himself but continued to fester, was vigorously debated by Loschmidt, Poincaré, Zermelo and others in the 1890's, and its quantum mechanical descendent is still kicking. To pursue the topic is to confront a fascinating nest of deep questions which, unfortunately, do not admit of brief discussion: I must, therefore, refer my reader to the vast literature.[215]

I conclude this discussion with a speculative remark: The $H$-theorem, as it issued Boltzmann's inquiry into the kinetic theory of gases, can be formulated

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[212] See again pages 34, 126 and 132. I remark again that the inscribed equation is due actually to Planck: see page 81 in E. Broda, *Ludwig Boltzmann*: *Man, Physicist, Philosopher* (1983). A photo of the tombstone faces the title page.

[213] See Chapter 8 in Brush[113] for a balanced discussion of Mach's position.

[214] See, for example, page 263.

[215] Places to start: §§6.3 & 14.7 in Brush;[113] Chapters 1 & 2 in Ehrenfest (cited on page 171); §4.4 in Huang;[205] pages 349–354 in ter Haar;[202] pages 58–64 in Born.[191]

$$\frac{dS}{dt} = \begin{cases} \text{non-negative expression that} \\ \text{issues from the averaged details of collisional dynamics and} \\ \text{vanishes when } S \text{ assumes the maximal value} \\ \text{consistent with all imposed constraints} \end{cases}$$

It seems plausible that to obtain a statement appropriate to systems-in-general we have only to abandon the second gas-specific line on the right, inserting in its place something like "issues from mechanical details of the relaxation process and." What *specifically* to insert on the right is case-dependent, and remains obscure in all cases (even the case addressed by Boltzmann!), but the "logistic equation"

$$\frac{dS}{dt} = r(S_{\max} - S)S \quad : \quad S_0 \equiv S_{\text{initial}} \leqslant S_{\max} \equiv S_m \tag{334.1}$$

(here $r$ is a constant with enforced physical dimensions) would appear to model the typical situation. The general solution can be described

$$S(t) = S_m\Big[1 + \frac{S_m - S_0}{S_0}\,e^{-rS_m t}\Big]^{-1} \tag{334.2}$$

and for $t$ so large that $\frac{S_m - S_0}{S_0}\,e^{-rS_m t} \ll 1$ one has

$$S(t) \sim S_m\Big[1 - \frac{S_m - S_0}{S_0}\,e^{-rS_m t} + \cdots\Big]$$

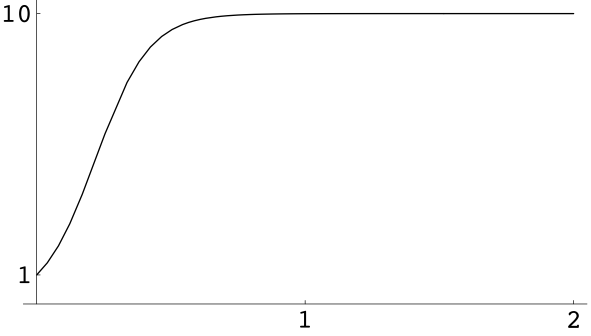

FIGURE 85: *Graph of the growth of* $S(t)$*, computed from* (334.2) *with* $r = 1$*,* $S_0 = 1$ *and* $S_m = 10$*.*

From $[r] = \frac{1}{[k]\cdot\text{time}}$ I infer that one would (at the very least) have to extract a "characteristic time" from the microphysics in order to make such a theory work. Note that (334.1) does mimic the nonlinearity of Boltzmann's equations.

**6. van der Waals gases.** We have been concerned thus far with the theory of *ideal* or *perfect* gases, which we have approached from several angles. That theory serves remarkably well to describe the properties of real gases that are sufficiently rare, sufficiently hot (yet not "relativistically hot:" $kT \approx mc^2$). And it describes the noble gases (weakly interactive molecules) under more moderate conditions. But physicists and engineers have been aware for centuries that the theory of ideal gases pertains only as a rough approximation to the physics of (for example) steam, and it is obvious that the theory fails totally to account for the **phase changes**

$$\text{gas} \xrightarrow[\text{condensation}]{\hspace{3em}} \text{liquid} \xrightarrow[\text{solidification}]{\hspace{3em}} \text{solid}$$

that gases were found in the early $19^{\text{th}}$ Century to undergo at low temperatures/ high pressures (and that are, of course, written onto the face of the physics of water vapor).

The **theory of real gases** begins, in effect, with the doctoral dissertation "On the continuity of the liquid and gaseous states" that Johannes Diderik van der Waals (1837–1923) submitted to Leiden University in 1873, and that the enthusiastic review published by Maxwell in 1874 brought to the attention of the world.[216]

One might suppose that van der Waals—if his objective was to modify the established theory of ideal gases—would proceed by modification of the statement

$$U(S,V,N) = NcT_0\Big(\frac{V_0}{V}\Big)^{k/c}\exp\Big\{\frac{S}{Nc}\Big\}$$

from which the entire theory (actually a $c$-parameterized *class* of theories) is known[217] to proceed. But in point of fact he elected to work closer to the

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[216] van der Waals came from a Leiden family of such modest means that his educational opportunities were limited. He was approaching 30 when he managed to obtain teaching certificates from Leiden University and to find employment as a secondary school teacher. Further study of mathematics and physics at the University was—because he had no command of Latin and Greek—not an option, so he worked independently until (owing to a lucky change in the law) it became possible to obtain an exemption from the classical language requirement. In 1876—at the age of nearly 40—van der Waals became the first (and was for 20 years the only!) professor of physics at the new University of Amsterdam. van der Waals' ideas quickly gained wide acceptance (Maxwell remarks of the thesis that it "has certainly directed the attention of more than one inquirer [himself] to the study of the Low-Dutch in which it is written") and one can look to his influence for the source of the traditional Dutch strength in experimental/theoretical many-body physics (recall that it was in Holland that helium was first liquified, and that both superconductivity and superfluidity were discovered). It is a tradition that continues undiminished: see recent volumes of Physica.

[217] See again page 63.

phenomenological surface of the theory, by modification of the equation of state

$$pV = NkT$$

—this even though the equation of state serves by itself to support only a fragment (the $c$-independent fragment) of the full theory. Though he sought to construct not a kinetic theory, certainly not a statistical mechanics, but only a *thermodynamics* of real gases, it was from the essential imagery of the kinetic theory that he took his point of departure. van der Waals conjectured that molecules experience

- strongly repulsive forces when sufficiently close together;
- weakly attractive forces ("van der Waals forces") when relatively far apart.

The "short-range strong repulsion" is consistent with the "billiard ball model" that had been employed already by others, and suggested to van der Waals (as it had suggested to others) that the volume available for exploration by a molecule should be described

$$\text{volume of box} - \underbrace{\text{net volume of other molecules}}_{=\,(N-1)\cdot(\text{volume } b \text{ of individual molecule})}$$

And from the conjectured "weak long-range attraction" he inferred that the walls, which exert pressure $p$ in their effort to reflect the incident molecular hailstorm (see again Figure 79), are assisted by the attractive action of molecules situated in the deeper interior of the box, who contribute a term proportional to

$$\frac{1}{\ell^{\text{some power, call it } n}} \quad : \quad \ell \equiv (V/N)^{\frac{1}{3}} \approx \text{mean intermolecular distance}$$

that describes what is, in effect, a "surface tension." One might expect on such grounds to have something like

$$\big[p + a(N/V)^{\frac{1}{3}n}\big]\big[V - Nb\big] = NkT$$

or (dividing by $N$)

$$\big(p + av^{-\frac{1}{3}n}\big)\big(v - b\big) = kT \quad : \quad v \equiv V/N \equiv \text{volume per molecule}$$

For whatever inspired reasons,[218] van der Waals set $n = 6$ to obtain finally

$$\big(p + av^{-2}\big)\big(v - b\big) = kT \tag{335}$$

**van der Waals' equation of state** (335) is actually an $(a, b)$-parameterized *class* of equations into which $a$ and $b$ enter as dimensioned constants

$$[p] = \text{pressure} \cdot \text{volume} \quad : \quad [b] = \text{volume}$$

and that refer to a similarly parameterized *population* of "van der Waals gases."

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[218] See Appendix 5 (especially §1) in ter Haar[202] for helpful discussion.

Division by $b$ gives

$$\big(p + (a/b^2)\mathcal{V}^{-2}\big)\big(\mathcal{V} - 1\big) = (k/b)T \tag{336}$$

where

$$\mathcal{V} \equiv v/b = \frac{\text{volume per molecule}}{\text{volume of molecule}}$$

provides a "dimensionless volume variable."[219] Subsequent division by $a/b^2$ gives

$$(\mathcal{P} + \mathcal{V}^{-2})(\mathcal{V} - 1) = \mathcal{T} \tag{337}$$

where

$$\mathcal{P} \equiv (b^2/a)p \qquad \text{and} \qquad \mathcal{T} \equiv (bk/a)T$$

provide dimensionless measures of pressure and temperature. The theory of ideal gases is so primitive that it does not permit the introduction of dimensionless variables. Their occurance is, on the other hand, a characteristic feature of van der Waals' theory, in which they provide an important resource. Immediately one has a

> RULE OF CORRESPONDING STATES: Let $\{p', v', T'\}$ refer to a state of a van der Waals gas $\mathfrak{G}_{a',b'}$ and let $\{p'', v'', T''\}$ refer to a state of $\mathfrak{G}_{a'',b''}$. The states in question "correspond"
>
> $$\{p', v', T'\} \longleftrightarrow \{p'', v'', T''\}$$
>
> if and only if they give rise to identical $\{\mathcal{P}, \mathcal{V}, \mathcal{T}\}$-values.

that acquires physical importance the moment one has established the true relevance of van der Waals' theory to the physics of diverse real gases. And (337) permits one to describe the analytic properties of *all van der Waals gases at the same time*. For graphical purposes, however, it proves more useful (more vividly informative) to work from (336), which I will notate

$$\big(p + \alpha\mathcal{V}^{-2}\big)\big(\mathcal{V} - 1\big) = \theta \tag{338}$$

and it is therefore upon (338) that I base my analytical remarks.

Immediately

$$p = \frac{\theta}{\mathcal{V} - 1} - \alpha\,\frac{1}{\mathcal{V}^2} \tag{339}$$

which is the **equation of the $\theta$-isotherm**. At high temperatures and low density ($\mathcal{V} \gg 1$) this gives back

$$\overset{\downarrow}{=} \frac{\theta}{\mathcal{V}}$$

the isotherms of an ideal gas: it is only at low temperatures and high density that van der Waals gases display their most distinctive features, and those (see

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[219] Only the values $\mathcal{V} > 1$ will be considered to be physical, since $\mathcal{V} < 1$ would make the box smaller than the net volume of the molecules it contains!

the figure) can be attributed to the circumstance that (339)—rewritten

$$p(\mathcal{V},\theta;\alpha)=\frac{\theta\mathcal{V}^2-\alpha(\mathcal{V}-1)}{\mathcal{V}^2(\mathcal{V}-1)}\tag{340}$$

or again

$$p\mathcal{V}^3-(p+\theta)\mathcal{V}^2+\alpha(\mathcal{V}-1)=0$$

—is cubic in $\mathcal{V}$. From (340) it is obvious that

- $p\uparrow\infty$ as $\mathcal{V}\downarrow 1$ with $\theta>0$ held constant
- $p\downarrow 0$ as (again isothermally) $\mathcal{V}\uparrow\infty$

and that $p$ vanishes also at a pair of points

$$\mathcal{V}=\frac{\alpha\pm\sqrt{\alpha^2-4\theta\alpha}}{2\theta}$$

that are

$$\left.\begin{matrix}\text{real}\\ \text{coindicent}\\ \text{imaginary}\end{matrix}\right\}\text{according as}\left\{\begin{matrix}\theta<\frac{1}{4}\alpha\\ \theta=\frac{1}{4}\alpha\\ \theta>\frac{1}{4}\alpha\end{matrix}\right.\tag{341}$$

The figure inspires interest also in the local extrema of the isothermal curves. To locate those we compute

$$\Big(\frac{\partial p}{\partial\mathcal{V}}\Big)_\theta=\frac{2\alpha(\mathcal{V}-1)^2-\theta\mathcal{V}^3}{\mathcal{V}^3(\mathcal{V}-1)^2}$$

and confront once again a cubic. To circumvent that awkwardness we use (338) to eliminate $\theta$ from the numerator and obtain

$$p(\mathcal{V};\alpha)=\alpha\frac{\mathcal{V}-2}{\mathcal{V}^3}\tag{342}$$

as a description of the curve that passes through *all* the extrema—what I will call the **equation of the extremal locus**. One looks now (see Figure 87) to the solutions of

$$p(\mathcal{V};\alpha)=p(\mathcal{V},\theta;\alpha)$$

to discover the points—call them $\mathcal{V}_1$, $\mathcal{V}_2$ and $\mathcal{V}_3=\infty$—at which the given isotherm is (respectively) locally minimal, locally maximal, or asymptotically minimal. From

$$\frac{\partial}{\partial\mathcal{V}}p(\mathcal{V};\alpha)=2\alpha\frac{\mathcal{V}-3}{\mathcal{V}^4}$$

we see that the extremal locus is itself maximal at $\mathcal{V}=3$. Where, according to (342), $p=\frac{1}{27}\alpha$. The isotherm through that point, according to (338), has $\theta=2\alpha\big(\frac{1}{27}+\frac{1}{9}\big)=\frac{8}{27}\alpha$. For that particular isotherm the extremal points $\mathcal{V}_1$ and $\mathcal{V}_2$ have *coalesced* at an *inflection point*, and isotherms with $\theta>\frac{8}{27}\alpha$ have *no* local minima/maxima.

The upshot: latent in the design of var der Waals' equation of state (335) is a distinguished **critical point** —located (in dimensionless coordinates) at

$$\mathcal{P}_{\mathsf{c}} = \tfrac{1}{27},\ \mathcal{V}_{\mathsf{c}} = 3,\ \mathcal{T}_{\mathsf{c}} = \tfrac{8}{27},$$

—the existence of which is at the same time

- a symptom of the literal failure of (335) and
- a key to the success of van der Waals' theory, taken as a whole.

Looking first to the "failure:"

From (342) we have $p = 0$