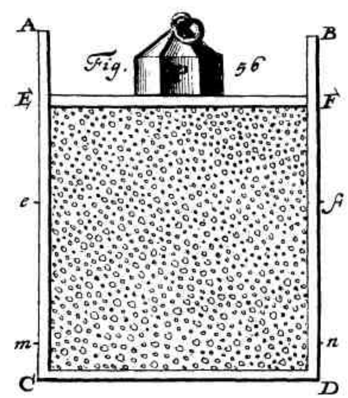
# 12. The Kinetic Theory, Part 1.



## 1. Early Kinetic Theory

- 18th-19th Century Caloric theories of heat:
  - *Pressure of a gas due to repulsive force of caloric particles.*
  - *Temperature is a measure of amount of caloric present.*
- 1830s-50s. Wave theory of heat:
  - *Heat is a vibrational motion of the ether.*
- 1840s:
  - *Joule's mechanical equivalent of heat and advocacy of the dynamical theory.*
- Early dynamical ("kinetic") theories of heat.
  - *A gas is made up of many particles.*
  - *Motion of particles is responsible for pressure and heat.*




Bernoulli (1738): $[\textit{pressure}] \propto [\textit{velocity}]^2$

Herepath (1820): $[\textit{temperature}] \propto [\textit{velocity}]$

Waterston (1843): $[\textit{temperture}] \propto [\textit{velocity}]^2$

*<u>Common assumption</u>: All particles move at same velocity.*

## 2. Maxwell's Velocity Distribution

*First Derivation (1860).* "Illustrations of the dynamical theory of gases"

- *Velocites of gas particles should vary due to collisions.*

"To find the average number of particles whose velocities lie between given limits, after a great number of collisions among a great number of equal particles."

- *Let*: $N$ = total # of particles.

  $Nf(\mathbf{v})\,d\mathbf{v}$ = *average* # of particles with velocity between $\mathbf{v}$ and $\mathbf{v} + d\mathbf{v}$.

- *Two Assumptions*:

  (i) Velocities are distributed identically in $x$-, $y$-, and $z$-directions.

  *So*: $f(\mathbf{v}) = g(v_x)g(v_y)g(v_z)$, for some function $g$.

  (ii) All directions of impact are equally likely.

  *So*: $f(\mathbf{v})$ depends only on $v = |\mathbf{v}|$.

*$Ng(v_x)\,dv_x$ = ave # particles with velocity between $v_x$ and $v_x + dv_x$*

- *This entails*:

$$f(\mathbf{v}) = \frac{1}{\alpha^3\pi^{3/2}} e^{-(v^2/\alpha^2)} = \text{ probability for velocity to be } \mathbf{v}.$$

• Uffink, J. (2007) "Compendium of the Foundations of Classical Statistical Physics", in J. Butterfield & J. Earman (eds.) *Philosophy of Physics*, Elsevier, pp. 923-1074.

*Aside: Proof.*

Assumptions (i) and (ii) entail $g(v_x) = Ce^{-(v_x^2/\alpha^2)}$ for constants $C$, $\alpha$.

*And*: $N = \int_{-\infty}^{\infty} Ng(v_x)\,dv_x = \int_{-\infty}^{\infty} NCe^{-(v_x{}^2/\alpha^2)}\,dv_x = NC\alpha\sqrt{\pi}$. *So* $C = \dfrac{1}{\alpha\sqrt{\pi}}$.

*So*: $f(\mathbf{v}) = \left(\dfrac{1}{\alpha\sqrt{\pi}} e^{-(v_x{}^2/\alpha^2)}\right)\left(\dfrac{1}{\alpha\sqrt{\pi}} e^{-(v_y{}^2/\alpha^2)}\right)\left(\dfrac{1}{\alpha\sqrt{\pi}} e^{-(v_z{}^2/\alpha^2)}\right) = \dfrac{1}{\alpha^3\pi^{3/2}} e^{-(v^2/\alpha^2)}$

- *Key concept*: $f(\mathbf{v})\,d\mathbf{v}$ is the *probability* for velocity to lie in range $(\mathbf{v}, \mathbf{v}+d\mathbf{v})$.

- *Recall*: Assumption (i): Velocities are distributed identically in $x$-, $y$-, and $z$-directions; so $f(\mathbf{v})$ takes general form $f(\mathbf{v}) = g(v_x)g(v_y)g(v_z)$.

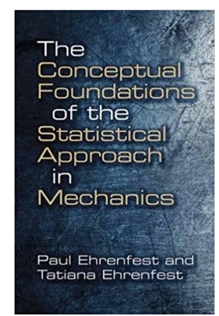
"As this assumption may appear precarious, I shall now determine the form of the function in a different manner." (1866)

- New derivation will appeal to *collisions* between gas particles.
  - Instead of assuming components of a single gas particle are independent, now just assume *initial velocities of colliding gas particles are independent ("Stoßzahlansatz")*.

*"Collision number assumption": Term coined later by Ehrenfest & Ehrenfest (1912).*

*Paul Ehrenfest*
(1880-1933)

*Tatiana Ehrenfest*
(1876-1964)



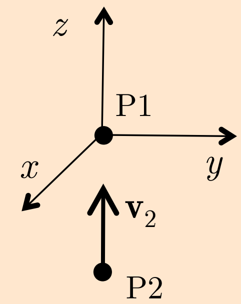
# *Second Derivation (1866).* "On the Dynamical Theory of Gases"

- *Consider*: Collisions with initial velocities $\mathbf{v}_1$, $\mathbf{v}_2$ and final velocities $\mathbf{v}_1'$, $\mathbf{v}_2'$.
- Let P1 be at rest ($r = 0$, $\theta = 0$, $z = 0$), and P2 traveling in $z$-direction towards P1 ($r = const.$, $\theta = const.$, $z(t) = z_0 + |\mathbf{v}_2 - \mathbf{v}_1|t$).

*Assumption (Stoßzahlansatz): Initial velocities are independent*

$$N(\mathbf{v}_1, \mathbf{v}_2) = \#\ \textit{of collisions during } dt \textit{ in which } (\mathbf{v}_1, \mathbf{v}_2) \rightarrow (\mathbf{v}_1', \mathbf{v}_2')$$
$$= N^2 f(\mathbf{v}_1) f(\mathbf{v}_2)\, d\mathbf{v}_1 d\mathbf{v}_2\, dV$$

- $Nf(\mathbf{v}_1)\, d\mathbf{v}_1 = \#$ *particles with initial velocity in* $(\mathbf{v}_1, \mathbf{v}_1 + d\mathbf{v}_1)$
- $Nf(\mathbf{v}_2)\, d\mathbf{v}_2 = \#$ *particles with initial velocity in* $(\mathbf{v}_2, \mathbf{v}_2 + d\mathbf{v}_2)$
- $dV = r dr d\theta dz = |\mathbf{v}_2 - \mathbf{v}_1| r dr d\theta dt$ = volume swept out by P2.




- *So*:

$$N(\mathbf{v}_1, \mathbf{v}_2) = N^2 f(\mathbf{v}_1) f(\mathbf{v}_2) |\mathbf{v}_2 - \mathbf{v}_1|\, d\mathbf{v}_1 d\mathbf{v}_2\, r dr d\theta\, dt$$
$$N(\mathbf{v}_1', \mathbf{v}_2') = N^2 f(\mathbf{v}_1') f(\mathbf{v}_2') |\mathbf{v}_2 - \mathbf{v}_1|\, d\mathbf{v}_1 d\mathbf{v}_2\, r dr d\theta\, dt$$

*Time-reversal invariance where* $|\mathbf{v}_2' - \mathbf{v}_1'| = |\mathbf{v}_2 - \mathbf{v}_1|$ *and* $d\mathbf{v}_1' d\mathbf{v}_2' = d\mathbf{v}_1 d\mathbf{v}_2$.

- *Now*: $f(\mathbf{v})$ is stationary *iff* $N(\mathbf{v}_1, \mathbf{v}_2) = N(\mathbf{v}_1', \mathbf{v}_2')$ *iff* $f(\mathbf{v}_1) f(\mathbf{v}_2) = f(\mathbf{v}_1') f(\mathbf{v}_2')$.
- *And*: This entails $f(\mathbf{v}) = Ce^{-(v^2/\alpha^2)}$ (1860 result).


- Uffink, J. (2007) "Compendium of the Foundations of Classical Statistical Physics", in J. Butterfield & J. Earman (eds.) *Philosophy of Physics*, Elsevier, pp. 923-1074.

*Aside: Maxwell's Uniqueness Argument*

- $f(\mathbf{v}_1)f(\mathbf{v}_2) = f(\mathbf{v}_1')f(\mathbf{v}_2')$ means that the initial-final transition $(\mathbf{v}_1, \mathbf{v}_2) \rightarrow (\mathbf{v}_1', \mathbf{v}_2')$ is equally probable as the final-initial transition $(\mathbf{v}_1', \mathbf{v}_2') \rightarrow (\mathbf{v}_1, \mathbf{v}_2)$.
- *Suppose not*: Suppose $(\mathbf{v}_1, \mathbf{v}_2) \rightarrow (\mathbf{v}'_1, \mathbf{v}_2')$ is more probable than $(\mathbf{v}_1', \mathbf{v}_2') \rightarrow (\mathbf{v}_1, \mathbf{v}_2)$.
- To remain stationary, there would have to be a closed transition cycle:

$$(\mathbf{v}_1, \mathbf{v}_2) \rightarrow (\mathbf{v}_1', \mathbf{v}_2') \rightarrow (\mathbf{v}_1'', \mathbf{v}_2'') \rightarrow ... \rightarrow (\mathbf{v}_1, \mathbf{v}_2).$$

- *But*:

> "...it is impossible to assign a reason why the successive velocities of a molecule should be arranged in this cycle rather than in the reverse order."

- *So*: $(\mathbf{v}_1, \mathbf{v}_2) \rightarrow (\mathbf{v}_1', \mathbf{v}_2') \rightarrow (\mathbf{v}_1'', \mathbf{v}_2'') \rightarrow ... \rightarrow (\mathbf{v}_1, \mathbf{v}_2).$

  must be equally probable as

  $(\mathbf{v}_1, \mathbf{v}_2) \leftarrow (\mathbf{v}_1', \mathbf{v}_2') \leftarrow (\mathbf{v}_1'', \mathbf{v}_2'') \leftarrow ... \leftarrow (\mathbf{v}_1, \mathbf{v}_2).$

- *But*: This just means that $(\mathbf{v}_1, \mathbf{v}_2) \rightarrow (\mathbf{v}_1', \mathbf{v}_2')$ is equally probable as $(\mathbf{v}_1', \mathbf{v}_2') \rightarrow (\mathbf{v}_1, \mathbf{v}_2)$.

# 3. Boltzmann's (1872) *H*-Theorem

"Further Studies on the Thermal Equilibrium of Gas Molecules"

*Ludwig Boltzmann*
(1844-1906)

"If one wants... to build up an exact theory... it is before all necessary to determine the probabilities of the various states that one and the same molecule assumes in the course of a very long time, and that occur simultaneously for different molecules. That is, one must calculate how the number of those molecules whose states lie between certain limits relates to the total number of molecules." .

- Let: $f(\mathbf{v}_1, t)\,d\mathbf{v}_1 = \#$ *particles with velocities in* $(\mathbf{v}_1,\ \mathbf{v}_1 + d\mathbf{v}_1)$ *at time* $t$
- Task: Determine how $f(\mathbf{v}_1, t)$ changes between $t$ and $t + dt$.
- Note: $f(\mathbf{v}_1, t+dt)\,d\mathbf{v}_1 = \#$ *particles with velocities in* $(\mathbf{v}_1,\ \mathbf{v}_1 + d\mathbf{v}_1)$ *at time* $t + dt$

$$= f(\mathbf{v}_1, t)\,d\mathbf{v}_1 + [\mathit{changes}]$$

$$= f(\mathbf{v}_1, t)\,d\mathbf{v}_1 + \frac{\partial f(\mathbf{v}_1, t)}{\partial t}\,dt\,d\mathbf{v}_1 + \ldots$$

*Taylor expansion of* $f(\mathbf{v}_1,\ t + dt)\,d\mathbf{v}_1$.

- So: $\dfrac{\partial f(\mathbf{v}_1, t)}{\partial t} = \dfrac{[\mathit{changes}]}{dt\,d\mathbf{v}_1}$


- Uffink, J. (2007) "Compendium of the Foundations of Classical Statistical Physics", in J. Butterfield & J. Earman (eds.) *Philosophy of Physics*, Elsevier, pp. 923-1074.
- Janssen, M. (preprint) "Dogs, Fleas, and Tree Trunks: The Ehrenfests Marking the Territory of Boltzmann's *H*-Theorem".

*Two types of [changes]*:

(i) Collisions during $dt$ in which particles with initial velocities in $(\mathbf{v}_1, \mathbf{v}_1 + d\mathbf{v}_1)$ end up with velocities outside $(\mathbf{v}_1, \mathbf{v}_1 + d\mathbf{v}_1)$. *Subtract* from $f(\mathbf{v}_1, t)\, d\mathbf{v}_1$.

(ii) Collisions during $dt$ in which particles with initial velocities outside $(\mathbf{v}_1, \mathbf{v}_1 + d\mathbf{v}_1)$ end up with velocities inside $(\mathbf{v}_1, \mathbf{v}_1 + d\mathbf{v}_1)$. *Add* to $f(\mathbf{v}_1, t)\, d\mathbf{v}_1$.

*Assumption (Stoßzahlansatz)*:

(a) $[\textit{type (i)}] = N^2 d\mathbf{v}_1 dt \int r\, dr \int d\theta \int d\mathbf{v}_2 f(\mathbf{v}_1, t) f(\mathbf{v}_2, t)\, |\, \mathbf{v}_2 - \mathbf{v}_1|$

(b) $[\textit{type (ii)}] = [\textit{time-reverse of (i)}] = N^2 d\mathbf{v}_1 dt \int r\, dr \int d\theta \int d\mathbf{v}_2 f(\mathbf{v}'_1, t) f(\mathbf{v}'_2, t)\, |\, \mathbf{v}_2 - \mathbf{v}_1|$

- *So*: $[\textit{changes}] = N^2 d\mathbf{v}_1 dt \int r\, dr \int d\theta \int d\mathbf{v}_2 \big(f(\mathbf{v}_1', t) f(\mathbf{v}_2', t) - f(\mathbf{v}_1, t) f(\mathbf{v}_2, t)\big)\, |\, \mathbf{v}_2 - \mathbf{v}_1|$

- *Thus (Boltzmann Equation)*:

$$\frac{\partial f(\mathbf{v}_1, t)}{\partial t} = N^2 \int r\, dr \int d\theta \int d\mathbf{v}_2 \Big(f(\mathbf{v}_1', t) f(\mathbf{v}_2', t) - f(\mathbf{v}_1, t) f(\mathbf{v}_2, t)\Big)\, |\, \mathbf{v}_2 - \mathbf{v}_1|$$

- *Now*: $\partial f(\mathbf{v}_1, t)/\partial t$ has a minimum when $f(\mathbf{v}_1', t)\, f(\mathbf{v}_2', t) = f(\mathbf{v}_1, t)\, f(\mathbf{v}_2, t)$.

- *And*: This entails $f(\mathbf{v}) = Ce^{-(v^2/\alpha^2)}$ (Maxwell's result).

*Boltzmann's Uniqueness Argument:*

- *Define "H-function"*: $H[f(\mathbf{v},t)] = \int d\mathbf{v} f(\mathbf{v},t) \ln f(\mathbf{v},t)$
- *Then*:

$$\frac{dH}{dt} = \int d\mathbf{v}_1\, d\mathbf{v}_1 ... \Big( f(\mathbf{v}_1', t) f(\mathbf{v}_2', t) - f(\mathbf{v}_1, t) f(\mathbf{v}_2, t) \Big) \ln \frac{f(\mathbf{v}_1, t) f(\mathbf{v}_2, t)}{f(\mathbf{v}_1', t) f(\mathbf{v}_2', t)}$$

- *Note*: Integrand has form $(x - y) \ln[y/x]$.
- *And*: This is always less than or equal to zero!

$x > y \;\Rightarrow\; (x-y)$ is pos, $\ln[y/x]$ is neg.

$x < y \;\Rightarrow\; (x-y)$ is neg, $\ln[y/x]$ is pos.

$x = y \;\Rightarrow\; (x-y) = \ln[y/x] = 0$.

- *So*: $\dfrac{dH}{dt} \leq 0$.
- *And*: The Maxwell distribution is the *unique* distribution for which $dH/dt = 0$.
- *Now*: What is $H$?

"It has thus been rigorously proved that whatever may have been the initial distribution of kinetic energy, in the course of time it must necessarily approach the form found by Maxwell... This [proof] actually gains much in significance because of its applicability to the theory of multi-atomic gas molecules. There too, one can prove for a certain quantity [$H$] that, because of the molecular motion, this quantity can only decrease or in the limiting case remain constant. Thus, one may prove that because of the atomic movement in systems consisting of arbitrarily many material points, there always exists a quantity which, due to these atomic movements, cannot increase, and this quantity agrees, up to a constant factor, exactly with the value that I found [in an earlier paper] for the well-known integral $\int dQ/T$."

"This provides an analytical proof of the Second Law in a way completely different from those attempted so far. Up till now, one has attempted to proof that $\int dQ/T = 0$ for a reversible cyclic process, which however does not prove that for an irreversible cyclic process, which is the only one that occurs in nature, it is always negative; the reversible process being merely an idealization, which can be approached more or less but never perfectly. Here, however, we immediately reach the result that $\int dQ/T$ is in general negative and zero only in a limit case..."

- $H$ is proportional to $-S$, where $S$ is the thermodynamic entropy!

*Does the H-Theorem prove the 2nd Law?*

- *In particular*: Has Boltzmann demonstrated irreversibility *purely* on the basis of Newtonian mechanics?
- *Problem (Burbury 1894; Bryan 1894)*: The *Stoßzahlansatz* is implicitly a time-asymmetric assumption!
  - *Stoßzahlansatz sez*: The number of collisions of the kind $(\mathbf{v}_1, \mathbf{v}_2) \to (\mathbf{v}_1', \mathbf{v}_2')$ is proportional to the product $f(\mathbf{v}_1)f(\mathbf{v}_2)$ of two functions of *initial velocities*.
  - *And*: From this (and other assumptions), Boltzmann derives $dH/dt \leq 0$.
  - *Suppose*: We replace the *Stoßzahlansatz* with the assumption that the number of collisions of the kind $(\mathbf{v}_1, \mathbf{v}_2) \to (\mathbf{v}_1', \mathbf{v}_2')$ is proportional to the product $f(\mathbf{v}_1')f(\mathbf{v}_2')$, of two functions of *final velocities*.
  - *Then*: Can derive $dH/dt \geq 0$!