
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.

- 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): \[ \text{pressure} \propto \text{velocity}^2 \]
  Herepath (1820): \[ \text{temperature} \propto \text{velocity} \]
  Waterston (1843): \[ \text{temperature} \propto \text{velocity}^2 \]

Common assumption: 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.

\[
N f(v) \, dv = \text{average # of particles with velocity between } v \text{ and } v + dv.
\]

- **Two Assumptions**:
  (i) Velocities are distributed identically in \( x-, y-, \) and \( z- \)directions.

  \[ f(v) = g(v_x)g(v_y)g(v_z), \text{ for some function } g. \]

  \( Ng(v_x) \, dv_x = \text{ave # particles with velocity between } v_x \text{ and } v_x + dv_x \)

  (ii) All directions of impact are equally likely.

  \[ f(v) \text{ depends only on } v = |v|. \]

- **This entails**:

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

Aside: Proof.
Assumptions (i) and (ii) entail \( g(v_x) = Ce^{-\frac{v_x^2}{\alpha^2}} \) for constants \( C, \alpha \).

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

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

- **Key concept:** \( f(v) \, dv \) is the probability for velocity to lie in range \((v, v + dv)\).

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

"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).
Consider: Collisions with initial velocities \( v_1, v_2 \) and final velocities \( v_1', v_2' \).

Let P1 be at rest \((r = 0, \theta = 0, z = 0)\), and P2 traveling in \(z\)-direction towards P1 \((r = \text{const.}, \theta = \text{const.}, z(t) = z_0 + |v_2 - v_1|t)\).

**Assumption (Stoßzahlansatz): Initial velocities are independent**

\[
N(v_1, v_2) = \# \text{ of collisions during } dt \text{ in which } (v_1, v_2) \rightarrow (v_1', v_2')
= N^2 f(v_1) f(v_2) dV
\]

- \( Nf(v_1) dv_1 \) = \# particles with initial velocity in \((v_1, v_1 + dv_1)\)
- \( Nf(v_2) dv_2 \) = \# particles with initial velocity in \((v_2, v_2 + dv_2)\)
- \( dV = rdrd\theta dz = |v_2 - v_1| rdrd\theta dt \) = volume swept out by P2.

**So:**

\[
N(v_1, v_2) = N^2 f(v_1) f(v_2) |v_2 - v_1| dv_1 dv_2 r dr d\theta dt
N(v_1', v_2') = N^2 f(v_1') f(v_2') |v_2 - v_1| dv_1 dv_2 r dr d\theta dt
\]

**Now:** \( f(v) \) is stationary \(\text{ iff } N(v_1, v_2) = N(v_1', v_2') \text{ iff } f(v_1) f(v_2) = f(v_1') f(v_2')\).

**And:** This entails \( f(v) = Ce^{-(v^2/\alpha^2)} \) \((1860 \text{ result})\).

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Aside: Maxwell's Uniqueness Argument

• \( f(v_1)f(v_2) = f(v_1')f(v_2') \) means that the initial-final transition \((v_1, v_2) \rightarrow (v_1', v_2')\) is equally probable as the final-initial transition \((v_1', v_2') \rightarrow (v_1, v_2)\).

• **Suppose not:** Suppose \((v_1, v_2) \rightarrow (v_1', v_2')\) is more probable than \((v_1', v_2') \rightarrow (v_1, v_2)\).

• To remain stationary, there would have to be a closed transition cycle:

\[
(v_1, v_2) \rightarrow (v_1', v_2') \rightarrow (v_1'', v_2'') \rightarrow ... \rightarrow (v_1, v_2).
\]

• **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:** \((v_1, v_2) \rightarrow (v_1', v_2') \rightarrow (v_1'', v_2'') \rightarrow ... \rightarrow (v_1, v_2)\).

must be equally probable as

\[
(v_1, v_2) \leftarrow (v_1', v_2') \leftarrow (v_1'', v_2'') \leftarrow ... \leftarrow (v_1, v_2).
\]

• **But:** This just means that \((v_1, v_2) \rightarrow (v_1', v_2')\) is equally probable as \((v_1', v_2') \rightarrow (v_1, v_2)\).
3. Boltzmann's (1872) $H$-Theorem

"Further Studies on the Thermal Equilibrium of Gas Molecules"

"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: $f(v_1, t) dv_1 = \#$ particles with velocities in $(v_1, v_1+dv_1)$ at time $t$

**Task:** Determine how $f(v_1, t)$ changes between $t$ and $t+dt$.

**Note:**

\[
\begin{align*}
\int f(v_1, t+dt) dv_1 &= \# \text{ particles with velocities in } (v_1, v_1+dv_1) \text{ at time } t+dt \\
&= f(v_1, t) dv_1 + \text{[changes]} \\
&= f(v_1, t) dv_1 + \frac{\partial f(v_1, t)}{\partial t} dt dv_1 + \ldots
\end{align*}
\]

Taylor expansion of $f(v_1, t+dt) dv_1$.

So:

\[
\frac{\partial f(v_1, t)}{\partial t} = \frac{[\text{changes}]}{dt dv_1}
\]

- 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 \((v_1, v_1 + dv_1)\) end up with velocities outside \((v_1, v_1 + dv_1)\). Subtract from \(f(v_1, t)\ dv_1\).

(ii) Collisions during \(dt\) in which particles with initial velocities outside \((v_1, v_1 + dv_1)\) end up with velocities inside \((v_1, v_1 + dv_1)\). Add to \(f(v_1, t)\ dv_1\).

Assumption (Stoßzahlansatz):

(a) \([\text{type (i)}] = N^2 dv_1 dt \int r dr \int d\theta \int dv_2 f(v_1, t) f(v_2, t) | v_2 - v_1|\)

(b) \([\text{type (ii)}] = \text{time-reverse of (i)} = N^2 dv_1 dt \int r dr \int d\theta \int dv_2 f(v_1', t) f(v_2', t) | v_2 - v_1|\)

So: \([\text{changes}] = N^2 dv_1 dt \int r dr \int d\theta \int dv_2 (f(v_1', t) f(v_2', t) - f(v_1, t) f(v_2, t)) | v_2 - v_1|\)

Thus (Boltzmann Equation):

\[
\frac{\partial f(v_1, t)}{\partial t} = N^2 \int r dr \int d\theta \int dv_2 (f(v_1', t) f(v_2', t) - f(v_1, t) f(v_2, t)) | v_2 - v_1|\]

Now: \(\frac{\partial f(v_1, t)}{\partial t}\) has a minimum when \(f(v_1', t) f(v_2', t) = f(v_1, t) f(v_2, t)\).

And: This entails \(f(v) = Ce^{-(v^2/\alpha^2)}\) (Maxwell's result).
Boltzmann's Uniqueness Argument:

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

- **Then:**
  \[
  \frac{dH}{dt} = \int d\mathbf{v}_1 d\mathbf{v}_1' \cdots (f(\mathbf{v}_1', t)f(\mathbf{v}_2', t) - f(\mathbf{v}_1, t)f(\mathbf{v}_2, t)) \ln \frac{f(\mathbf{v}_1, t)f(\mathbf{v}_2, t)}{f(\mathbf{v}_1', t)f(\mathbf{v}_2', t)}
  \]

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

  \[
  \begin{align*}
  x > y & \Rightarrow (x - y) \text{ is pos, } \ln[y/x] \text{ is neg.} \\
  x < y & \Rightarrow (x - y) \text{ is neg, } \ln[y/x] \text{ is pos.} \\
  x = y & \Rightarrow (x - y) = \ln[y/x] = 0.
  \end{align*}
  \]

- **So:** \( \frac{dH}{dt} \leq 0 \).
- **And:** The Maxwell distribution is the *unique* distribution for which \( \frac{dH}{dt} = 0 \).
- **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 $(\mathbf{v}_1, \mathbf{v}_2) \rightarrow (\mathbf{v}_1', \mathbf{v}_2')$ 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 $\frac{dH}{dt} \leq 0$.
  - **Suppose**: We replace the Stoßzahlansatz with the assumption that the number of collisions of the kind $(\mathbf{v}_1, \mathbf{v}_2) \rightarrow (\mathbf{v}_1', \mathbf{v}_2')$ is proportional to the product $f(\mathbf{v}_1')f(\mathbf{v}_2')$, of two functions of *final velocities*.
  - **Then**: Can derive $\frac{dH}{dt} \geq 0$!