Boltzmannian Statistical Mechanical Foundations of Irreversibility

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2\textsuperscript{nd} Law of Thermodynamics implies: 

\[ S = nc_v \ln \frac{T}{T_0} + nR \ln \frac{V}{V_0} \]

\[ \Delta S = S_f - S_i = nR \ln \frac{V_f}{V_i} > 0 \]

S will increase for every irreversible process occurring between two equilibrium states of a closed system. \( \rightarrow \) “Thermodynamic Arrow of Time”
Classical Dynamics

Dynamical State:

\[(q, p) \equiv \{q_1, \ldots, q_i \ldots ; p_1, \ldots p_i, \ldots \} \in \Gamma \quad , i = 1, \ldots, rN\]

Hamiltonian:

\[
H(q, p) = \sum_{i=1}^{rN} \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i=1}^{rN} \sum_{j=1}^{rN} \sum_{i \neq j} 4\varepsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right]
\]
e.g.

Eqn’s of motion:

\[
\begin{aligned}
\frac{dq_i}{dt} &= \frac{\partial H(q_1, \ldots q_i, \ldots ; p_1, \ldots p_i, \ldots)}{\partial p_i} \\
\frac{dp_i}{dt} &= -\frac{\partial H(q_1, \ldots q_i, \ldots ; p_1, \ldots p_i, \ldots)}{\partial q_i}
\end{aligned}
\]

\[\rightarrow [q_i(t), p_i(t)]\]
G-path in $\Gamma$ (Phase Space)
Two solutions to dynamical equations due to “time symmetry”

\[ [r_j(t), p_j(t)] \quad \text{and} \quad [\tilde{r}_j(t), \tilde{p}_j(t)] = r_j(-t), -p_j(-t) \]
Statistical Mechanics

\((q, p) \rightarrow 6 \times 10^{23} \text{ variables!} \)

\(\rightarrow F(r, v, t) \text{ Reduced Dynamical Description} \)

\[ F(r, v, t) \delta r \delta v = \# \text{ of .’s with } \sim r \text{ and } v \]

\[ F_{eq}(r, v) = F_{MB}(v) \equiv N \sqrt{\frac{2}{\pi}} \left( \frac{m}{kT} \right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2kT}} \]
Boltzmann’s Transport Equation:

\[
\frac{\partial F(r, v, t)}{\partial t} = -v \cdot \nabla_r F(r, v, t) + \iiint d\nu_1 b \, db \, d\epsilon |v_1 - v|[F'F'_1 - F_1F] + \Gamma_w,
\]

Boltzmann’s $H$-theorem:

If $F$ satisfies the BE, the functional

\[
H[F] \equiv \int dr \int d\nu F(r, v, t) \log F(r, v, t) = H(t)
\]

never decreases, i.e.

\[
\frac{dH(t)}{dt} \leq 0
\]
Boltzmann further showed:

\[ \frac{dH(t)}{dt} = 0 \]  only when  \[ F = F_{MB}(\nu) \]

And for an ideal gas  \[ \Delta S = -k\Delta H! \]

Implies  \[ S(F(q,p)) \]

and  \[ S(t) \]
Loschmidt’s Paradox:

How can we derive irreversible behavior from time-reversible dynamics?

Specifically, for every G-path which increases $S$, there is one that decreases it!

Indicated original BE derivation (using Stosszahlansatz) was not strictly mechanical
Loschmidt’s Paradox Resolution

1. # of microstates for $F_{MB} >$ than all others combined

2. Ergodic Hypothesis $\implies$ a time spent by a microstate in a region is proportional to its volume

$\implies$ Equilibrium is “the rule”

Deviations are the exceptions

• H:
The graphs show the relationship between time (s) and a variable labeled $H$ for different values of $10^{-17}$, $10^{-5}$, and $10^{-3}$. The graphs exhibit peaks and valleys over time, suggesting a dynamic process or measurement. The red and blue lines represent different conditions or data sets within each graph. The $x$-axis represents time in seconds, while the $y$-axis represents the variable $H$. The graphs appear to illustrate a comparison or study across these conditions.
Conclusions

1. Anti-kinetic evolutions exist, as indicated by Loschmidt.
2. These evolutions are unstable to small perturbations.
3. Statistical Interpretation:
   1. At each later time $t$, the value of $H$ for nearly every element is equal to each other, or very near each other. This $H$ value at each time corresponds to a point on a curve which is claimed to monotonically decrease until it reaches its minimum value, from which it never departs, just as observed for entropy (with a sign change) for a single system in reality.
   2. This “concentration curve” exactly corresponds to the BE $H$ curve.

While neither claim 1 or 2 have been proven, they could in principle, using only mechanical means, thus giving the Boltzmann Equation and $H$ a rigorous mechanical—albeit statistical—foundation.
Thank you for your time.

Questions?
Potential

- **Intermolecular, Lennard Jones**

- **Wall:**

  \[
  U_{x_i}^{\text{wall}} = C \left( \frac{1}{x_i^\alpha} + \frac{1}{(a - x_i)^\alpha} \right), \quad i = 1, 2
  \]
To restate the above, let us consider (as the Ehrenfests do) three values of $H$ much above $H_{eq} \equiv H_0$ such that $H_a < H_b < H_c$. If we consider a very long segment of the $H(t)$ curve (a.k.a. “$H$-curve”) and look at all intersections it has with the $H = H_b$ line, Loschmidt demands that we should observe the time sequence

$$H_c \quad \text{as often as} \quad H_c$$

$$H_b$$

$$H_a$$

where our implied axes are $+t$ pointing right, and $+H$ pointing up. However, the sequence

$$H_b$$

$$H_a \quad H_a$$

$H_a$ can still be expected to occur much more often since for any $H > H_0$ one expects $H$ to decrease due to the very large $[Z_{eq}]$ and indecomposability. Finally, the smallest fraction of $H_b$ instances should occur like

$$H_c \quad H_c$$

$$H_b$$