

Entropy production in the Boltzmann equation

Before we discuss entropy production in the Boltzmann equation, we briefly remind ourselves of the concepts of entropy in classical and quantum statistical mechanics

Statistical entropy

Generally entropy characterizes the information content of a statistical distribution

eg. thermal equilibrium

only minimal amount of information available in the form of $\{X_i\} = \{U, V, N\}$

Existence and maximality of entropy function $S(U, V, N)$ guaranteed by postulates of thermodynamics

Now to describe generic systems, need to generalize the concept to entropy functionals which describe the information content of

classical: statistical phase space distributions

quantum: statistical density operators

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General concept of entropy is adapted from information theory

Consider a measurement with $m=1, \dots, N$ possible outcomes, with probabilities $p_m \geq 0$ and $\sum_m p_m = 1$

Shannon entropy:
$$S_{\text{Shannon}} = -K \sum_{m=1}^N p_m \log(p_m)$$

constant

$$S_{\text{Shannon}} \geq 0 \quad (\text{since } \log(p_m) \leq 0, p_m \geq 0)$$

with $S_{\text{Shannon}} = 0$ if and only if $p_m = \delta_{m, m_0}$
i.e. outcome is determined exactly

Now in quantum systems with a finite dimensional Hilbert space, we have an analogous situation where the density matrix

$$\hat{\rho} = \sum_i p_i |\psi_i\rangle \langle \psi_i| \quad p_i \geq 0 \quad \langle \psi_i | \psi_j \rangle = \delta_{ij}$$

describes the probability to find the system in a given quantum state $|\psi_i\rangle$

von Neumann entropy:
$$S_vN = -k_B \text{Tr}(\hat{\rho} \log(\hat{\rho}))$$

which evaluated in the eigenbasis of the density operator $\hat{\rho}$ reduces to the Shannon entropy

$$S_q = -k_B \sum_i p_i \log(p_i)$$

// with $S_q \geq 0$ and $S_q = 0$ for pure quantum states

Now for classical systems the N -body phase space distribution f_N plays an analogous role to the density matrix and we define an analogy

classical entropy:

$$S_{ce} = -k_B \int d^{6N}V f_N(t, \{\vec{r}_i\}, \{\vec{p}_i\}) \log(f_N(t, \{\vec{r}_i\}, \{\vec{p}_i\}))$$

Since f_N is a probability density and not a probability $f_N > 1$ is allowed and one can find distributions with $S_{ce} < 0$, in fact $S_{ce} \rightarrow -\infty$ in the limit where all coordinates and momenta are known exactly

Despite this difference the entropy S_q, S_{cl} is exactly conserved under the microscopic Hamiltonian dynamics

Quantum system:

$$\begin{aligned} S_q(t) &= -k_B \text{Tr} [\hat{\rho}(t) \log(\hat{\rho}(t))] \\ &= -k_B \text{Tr} [U(t) \hat{\rho}(0) U^\dagger(t) \log(U(t) \hat{\rho}(0) U^\dagger(t))] \\ &\stackrel{UU^\dagger=1}{=} -k_B \text{Tr} [\hat{\rho}(0) \log(\hat{\rho}(0))] = S_q(t=0) \end{aligned}$$

$$\Rightarrow \frac{dS_q}{dt} = 0$$

Classical system: c.f. exercises $\frac{dS_{cl}}{dt} = 0$

Statistical entropy of microscopic N -body system is conserved as long as full N -body dynamics is considered

\Rightarrow microscopic dynamics preserves information content
no information is lost and the dynamics is reversible

Entropy in kinetic theory

Now if we want to make use of entropy considerations in the context of the Boltzmann equation, we face the challenge that we typically do not have the full N -body distribution but only the single particle distribution f .

However in the spirit of information theory we can define a single particle entropy based on $f_1(t, \vec{r}, \vec{p})$

Boltzmann entropy:

$$S_B(t) = -k_B \int \frac{d^3r d^3p}{(2\pi\hbar)^3} f_1(t, \vec{r}, \vec{p}) \log(f_1(t, \vec{r}, \vec{p}))$$

and we will now study the evolution of $S_B(t)$ in the Boltzmann equation

Boltzmann H-theorem

Boltzmann originally derived this theorem for the dimensionless quantity

$$H(t) = \int \frac{d^3r d^3p}{(2\pi\hbar)^3} f(t, \vec{r}, \vec{p}) \log(f(t, \vec{r}, \vec{p}))$$

such that $S_B(t) = -k_B H(t)$

Now if we consider the time derivative of $H(t)$

$$\begin{aligned} \frac{d}{dt} H(t) &= \int \frac{d^3r d^3p}{(2\pi\hbar)^3} \frac{d}{dt} \left[f(t, \vec{r}, \vec{p}) \log(f(t, \vec{r}, \vec{p})) \right] \\ &= \int \frac{d^3r d^3p}{(2\pi\hbar)^3} \frac{d}{dt} f(t, \vec{r}, \vec{p}) \left(\log(f(t, \vec{r}, \vec{p})) + 1 \right) \end{aligned}$$

Now from the Boltzmann equation, we have

$$\frac{d}{dt} f = - \frac{\vec{p}}{m} \vec{\nabla}_r f - \vec{\nabla}_p \cdot \vec{F} f + C[f]$$

So if we consider the terms individually we have

$$\int \frac{d^3r d^3p}{(2\pi\hbar)^3} \left(-\frac{\vec{p}}{m}\right) \left(\vec{\nabla}_r f(t, \vec{r}, \vec{p})\right) \left(\log(f(t, \vec{r}, \vec{p})) + 1\right)$$

$$= - \int \frac{d^3r d^3p}{(2\pi\hbar)^3} \vec{\nabla}_r \left[\left(\frac{\vec{p}}{m} f(t, \vec{r}, \vec{p})\right) \log(f(t, \vec{r}, \vec{p})) \right]$$

$$= 0$$

and similarly for the term $-\vec{F}(\vec{r}) \vec{\nabla}_p$,
 such that only collisions contribute to
 changes of $H(t)$ or $S_B(t)$

So we are left with evaluating

$$\frac{d}{dt} H(t) = \int \frac{d^3r d^3p}{(2\pi\hbar)^3} C[\Gamma](t, \vec{r}, \vec{p}) \left(\log(f(t, \vec{r}, \vec{p})) + 1\right)$$

where the collision integral is given by

$$C[\Gamma](t, \vec{r}, \vec{p}) = \int_{p_2, p_3, p_4} \mathcal{I}(p_1, p_2, p_3, p_4) = \int_{p_2, p_3, p_4} \tilde{w}(p_1, p_2 \rightarrow p_3, p_4) (f_3 f_4 - f_1 f_2)$$

Since the term $\propto 1$ is related to
 a collisional invariant $\chi(\vec{p})=1$ the

integral

$$\int \frac{d^3 r_i d^3 p_i}{(2\pi\hbar)^3} C(\mathcal{J})(\mathbf{h}_i, \mathbf{r}_i, \mathbf{p}_i) = 0$$

as per our discussion in the context of balance equations, so we find

$$\frac{d}{dt} H(t) = \int d^3 r_i \int_{p_1, p_2, p_3, p_4} \mathcal{I}(p_1, p_2, p_3, p_4) \log(f_i)$$

By using the symmetries of $\mathcal{I}(p_1, p_2, p_3, p_4)$ as in our derivation of balance equations, we can symmetrize this expression

$$= \frac{1}{4} \int d^3 r_i \int_{p_1, p_2, p_3, p_4} \mathcal{I}(p_1, p_2, p_3, p_4) \left[\log(f_1) + \log(f_2) - \log(f_3) - \log(f_4) \right]$$

$$= \frac{1}{4} \int d^3 r_i \int_{p_1, p_2, p_3, p_4} \tilde{w}(p_1, p_2 \rightarrow p_3, p_4) (f_3 f_4 - f_1 f_2) \log\left(\frac{f_1 f_2}{f_3 f_4}\right)$$

$$= \frac{1}{4} \int d^3 r_i \int_{p_1, p_2, p_3, p_4} \tilde{w}(p_1, p_2 \rightarrow p_3, p_4) \frac{f_3 f_4}{f_1 f_2} \left(1 - \frac{f_1 f_2}{f_3 f_4}\right) \log\left(\frac{f_1 f_2}{f_3 f_4}\right)$$

Now regarding the individual terms, we find

$$\underline{\tilde{w}} \geq 0, \quad \underline{f_3 f_4} \geq 0$$

$$\underline{\left(1 - \frac{f_1 f_2}{f_3 f_4}\right) \log\left(\frac{f_1 f_2}{f_3 f_4}\right)} = (1-x) \log(x)$$

for $x \leq 1$ we have $(1-x) \geq 0$ $\log(x) \leq 0$

for $x > 1$ we have $(1-x) \leq 0$ $\log(x) \geq 0$

$$\text{so } \underline{(1-x) \log(x) \leq 0} \quad \forall x \geq 0$$

Since the integrand is always ≤ 0
we conclude that

$$\boxed{\frac{d}{dt} H(t) \leq 0} \quad \Rightarrow \quad \boxed{\frac{d}{dt} S_B(t) \geq 0}$$

with $\frac{d}{dt} S_B(t) = 0$ if and only if

$$\tilde{w}(p_1, p_2 \rightarrow p_3, p_4) = 0 \quad \text{or} \quad f_1 f_2 = f_3 f_4 \quad \forall \vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{r}_4$$

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Calculates molecules that collisions lead to an increase of the entropy in the Boltzmann equation

Loschmidt paradox: What causes this increase of entropy / information loss, as Boltzmann equation was derived from the reversible microscopic dynamics?

Molecular chaos singles out a preferred time direction, neglecting correlations introduced in collision events

Beyond the Boltzmann equation information is shuffled into higher order n -body correlation functions, whose information is needed to reverse the dynamics

Even though reversibility is restored in the full microscopic theory, the Boltzmann entropy (considering only f_1) can still increase

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Solutions of the Boltzmann equation

Generally solutions to non-linear integro-differential equations are hard to find, even proofs of existence & uniqueness have only been achieved in recent years for phenomenologically relevant interactions

We will discuss two special kinds of solutions

- (near) equilibrium solutions
- (quasi) stationary non-equilibrium solutions

Equilibrium solutions:

Some important information about the existence of possible solutions is provided by the H-theorem

$\frac{dS}{dt} \geq 0$ implies that for stationary solutions where $S(t) = \text{const}$, the entropy has to be maximal

Generally distinguishes two types of solutions

global equilibrium (f_{eq}) $\boxed{\frac{\delta f_{eq}}{\delta t} = 0}$

i.e. all other terms on the LHS and RHS of the Boltzmann equation cancel each other out and the whole system is in equilibrium

local equilibrium ($f^{(0)}$) $\boxed{C[f^{(0)}] = 0} \quad \forall \mathbf{r}, \mathbf{p}$

i.e. the collision term vanishes, but $f^{(0)}$ is not necessarily a true independent solution of the Boltzmann equation due to gradients and external forces

Global equilibrium solutions

Expect that in the absence of external forces the system is homogeneous and can be described in terms of thermodynamic variables T, μ, \vec{v} related to the conserved quantities

We consider $f(t, \vec{r}, \vec{p}) = f(t, \vec{p})$, such that in the absence of forces

$$\frac{d}{dt} f(t, \vec{p}) = C[f](t, \vec{p}) = \int_{p_2, p_3, p_4} \underbrace{\tilde{w}(p_1, p_2 \rightarrow p_3, p_4)}_{\equiv \tilde{I}(p_1, p_2, p_3, p_4)} [f_1 f_2 - f_3 f_4] = 0$$

Stationary solutions ($\frac{df}{dt} = 0$) are obtained by zeros of the collision integral.

We can distinguish two different situations

balance: $\int_{p_2, p_3, p_4} \tilde{I}(p_1, p_2, p_3, p_4) = 0$

ie the net effect of all possible interactions

cancel each others

detailed balance:

$$I(p_1, i_2 | p_3, i_4) = 0$$

i.e. the net effect of each process is cancelled by its reverse process

Global & local equilibrium solutions satisfy the detailed balance criterion

$$I(p_1, i_2 | p_3, i_4) = \tilde{W}(i_1, i_2 \rightarrow i_3, i_4) [t_{3i_4} - t_{1i_2}] = 0$$

$$\Rightarrow \boxed{t_{3i_4} = t_{1i_2}}$$

for all possible combinations of i_1, i_2, i_3, i_4 allowed by the microscopic interaction process

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Now to construct these solutions, we take the logarithm of this equation

$$\log(f_1) + \log(f_2) = \log(f_3) + \log(f_4)$$

which shows that in order to satisfy detailed balance

$\log(f)$ is a collisional invariant

Since we already know the collisional invariants

particle number: $\chi(\vec{p}) = 1$

momentum: $\chi(\vec{p}) = \vec{p}$

energy: $\chi(\vec{p}) = \frac{\vec{p}^2}{2m}$

we can express $\log(f)$ as linear combination of the invariants

$$\log(f) = \lambda_0 + \vec{\lambda}_p \vec{p} + \lambda_e \frac{\vec{p}^2}{2m}$$

Such that

$$f_{eq}(\vec{p}) = e^{\lambda_0} e^{\lambda_1 \vec{p}} e^{\lambda_2 \frac{\vec{p}^2}{2m}}$$

where normalizability requires $\lambda_2 < 0$

Now in order to give the coefficients $\lambda_0, \lambda_1, \lambda_2$ a more intuitive meaning we can match the moments of the equilibrium distribution f_{eq} to the equilibrium state of an ideal gas

$$n = \int \frac{d^3p}{(2\pi\hbar)^3} f_{eq}(\vec{p})$$

$$\vec{P} = m n \langle \vec{v} \rangle = \int \frac{d^3p}{(2\pi\hbar)^3} \vec{p} f_{eq}(\vec{p})$$

$$e_{int} = \frac{3}{2} n k_B T = \int \frac{d^3p}{(2\pi\hbar)^3} \frac{\vec{p}^2}{2m} f_{eq}(\vec{p})$$

we find n, \vec{P}, T as a function of $\lambda_0, \lambda_1, \lambda_2$ such that f_{eq} can be expressed as

$$f_{\text{eq}}(\vec{p}) = n \left(\frac{2\pi\hbar^2}{mk_B T} \right)^{3/2} \exp\left(-\frac{(\vec{p} - m\vec{v}_0)^2}{2mk_B T} \right)$$

Maxwell-Boltzmann distribution