Theories of Everything:
Thermodynamics
Statistical Physics
Quantum Mechanics

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The Second Law *versus* *Classical Mechanics*

Why, for example, should a group of simple, stable compounds of carbon, hydrogen, oxygen and nitrogen struggle for billions of years to organize themselves into a professor of chemistry? [....] If we leave a chemistry professor out on a rock in the sun long enough the forces of nature will convert him into simple compounds of carbon, oxygen, hydrogen and nitrogen, calcium, phosphorus and small amounts of other minerals ...

Robert Pirsig, *Lila*

Thermodynamics is a powerful indicator for the direction of spontaneous chemical change.

Formation of water from hydrogen and oxygen:

$$\mathrm{H_2} + \frac{1}{2}\mathrm{O_2} \longrightarrow \mathrm{H_2O} \tag{1}$$

Entropy change of the water:

$$\begin{aligned}\Delta_r S^{\ominus} &= S_m^{\ominus}(\mathrm{H_2O}) - \frac{1}{2}S_m^{\ominus}(\mathrm{O_2}) - S_m^{\ominus}(\mathrm{H_2}) \\ &= 69.91 - \frac{1}{2} \times 205.138 - 130.684 = -163.343\,\mathrm{J/K}\end{aligned} \tag{2}$$

Heat of the reaction:

$$\Delta_r H^{\ominus} = -285.83\,\mathrm{kJ} \tag{3}$$

Entropy change of the environment:

$$\Delta_{\mathrm{omg}} S = -\frac{\Delta_r H^{\ominus}}{T} = 959.16\,\mathrm{J/K} \tag{4}$$

Entropy change of the universe:

$$\Delta_{\mathrm{tot}} S = \Delta_r S^{\ominus} + \Delta_{\mathrm{omg}} S = 795.82\,\mathrm{J/K} \tag{5}$$

As long as the total entropy increases, the entropy of the system can both increase and decrease.

Dissolving ammonium chloride:

$$\mathrm{NH_4Cl\,(s)} \longrightarrow \mathrm{NH_4^+\,(aq)} + \mathrm{Cl^-\,(aq)} \tag{6}$$

Entropy change of the system:

$$\begin{aligned}\Delta_r S^\ominus &= S_m^\ominus(\mathrm{NH_4^+\,(aq)}) + S_m^\ominus(\mathrm{Cl^-\,(aq)}) - S_m^\ominus(\mathrm{NH_4Cl\,(s)}) \\ &= 186.91 + 111.3 - 94.6 = 203.61\,\mathrm{J/K}\end{aligned} \tag{7}$$

A considerable increase in entropy (to be expected). But, dissolving this salt makes the solution cold.

Chemical Thermodynamics IV

$$\Delta_r H^\ominus = \Delta_f H^\ominus(\mathrm{NH_4^+}) + \Delta_f H^\ominus(\mathrm{Cl^-}) - \Delta_f H^\ominus(\mathrm{NH_4Cl})$$
$$= -167.16 - 132.51 + 314.43 = 14.76\,\mathrm{kJ} \quad (8)$$

An amount of 14.76 kJ heat is coming from the environment, which gives an entropy change:

$$\Delta_{\mathrm{omg}} S = \frac{-147600}{298.15} = -49.51\,\mathrm{J/K} \quad (9)$$

The entropy of the universe still increases:

$$\Delta_{\mathrm{tot}} S = \Delta_r S^\ominus + \Delta_{\mathrm{omg}} S = -49.51 + 203.61 = 164.10\,\mathrm{J/K} \quad (10)$$

A Major (Unsolved?) Problem

For all (known) processes in the universe the entropy increases.

Let a drop of wine fall into a glass of water; whatever be the law that governs the internal movement of the liquid, we will soon see it tint itself uniformly pink and from that moment on, however we may agitate the vessel, it appears that the wine and water can separate no more. All this, Maxwell and Boltzmann have explained, but the one who saw it in the cleanest way, in a book that is too little read because it is difficult to read, is Gibbs, in his *Principles of Statistical Mechanics*.

Henri Poincaré

Classical Mechanics

- Classical Hamiltonian $=$ Kinetic energy $+$ Potential Energy:

$$\mathcal{H} = \frac{p^2}{2m} + V(\vec{r}) \tag{11}$$

- Hamilton equations:

$$\frac{d\vec{r}}{dt} = \frac{\partial \mathcal{H}}{\partial \vec{p}}, \quad \frac{d\vec{p}}{dt} = -\frac{\partial \mathcal{H}}{\partial \vec{r}}, \quad \text{and} \quad \vec{p} = m\frac{d\vec{r}}{dt} \tag{12}$$

- Equivalence to Newton's equation:

$$m\vec{a} = \frac{d\vec{p}}{dt} = -\frac{\partial \mathcal{H}}{\partial \vec{r}} = -\frac{\partial V}{\partial \vec{r}} = \vec{F} \tag{13}$$

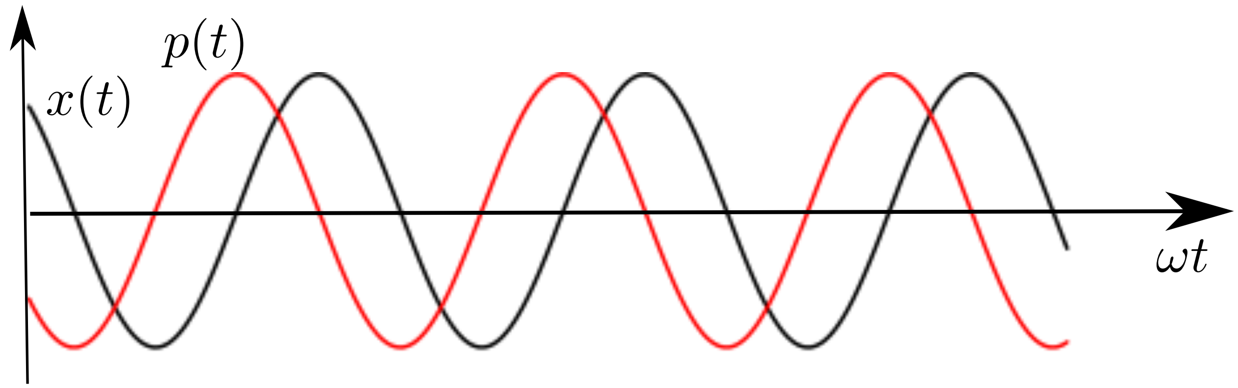
One–dimensional Harmonic Oscillator

- Hamiltonian:

$$\mathcal{H} = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 = E \tag{14}$$

- Hamilton's equations:

$$\frac{dx}{dt} = \frac{p}{m}, \qquad \frac{dp}{dt} = -m\omega^2 x \tag{15}$$



$$x(t) = \sqrt{\frac{2E}{m\omega^2}}\cos(\omega t + \phi) \qquad p(t) = -\sqrt{2mE}\sin(\omega t + \phi)$$

- *Time reversal invariance*: If $t \to -t$ then $\vec{p} \to -\vec{p}$ and the Hamilton equations remain the same.

The classical equations of motion are invariant with respect to time reversal. There is no direction of time: take a solution, replace t by $-t$ and you have an equally good solution.

Microscopic Reversibility

$\Downarrow$?

Macroscopic Irreversibility

Ludwig Boltzmann

Classical Statistical Mechanics

Phase Space

For N–particles with masses m_i we have:

- A Hamiltonian:

$$\mathcal{H} = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + V(\{r^N\}) \tag{16}$$

where V is a potential and $\{r^N\}$ the set of all particle positions.

- Trajectories: Solutions of the Hamilton Equations:

$$\frac{d\vec{r}_i}{dt} = \frac{\partial \mathcal{H}}{\partial \vec{p}_i} \quad \text{and} \quad \frac{d\vec{p}_i}{dt} = -\frac{\partial \mathcal{H}}{\partial \vec{r}_i} \tag{17}$$

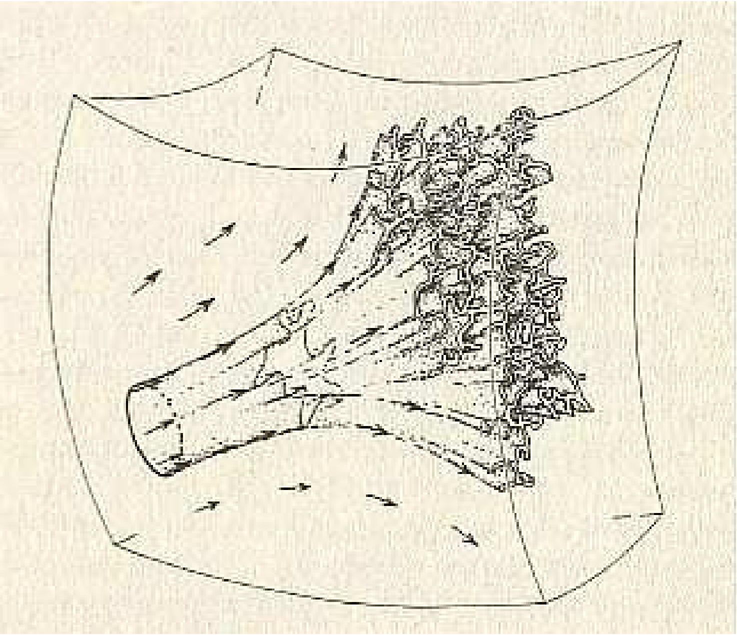
Phase Space II

- Phase Space: a $6N$ dimensional space in which each point respresents a microscopic state of the system.
- An Ensemble is a collection of trajectories with some common restraint, for instance the same total energy, or given temperature.
- Macrostate: state characterized by macroscopic parameters, for instance N, V, T.
- Microstate: state where all positions and all momenta of the particles are given: $\{\vec{r}^N, \vec{p}^N\}$.
- A trajectory is a line in Phase Space: $\{\vec{r}^N(t), \vec{p}^N(t)\}$, $t_0 < t < t_1$.

Phase Space Density

Probability of finding particle i with position between $\vec{r}_i$ and $\vec{r}_i + d\vec{r}_i$ and momentum between $\vec{p}_i$ and $\vec{p}_i + d\vec{p}_i$:

$$\rho(\{\vec{r}^N(t), \vec{p}^N(t)\}, t) d\vec{r}^N d\vec{p}^N \qquad (18)$$



- Liouville Theorem:

$$\frac{d\rho}{dt} = 0 \qquad (19)$$

The phase space fluid behaves like an incompressible liquid. Phase space volume is conserved.

- Trajectories cannot cross; trajectories starting close can diverge: almost all systems are chaotic.

R. Penrose, The Emperor's New Mind, Oxford University Press, 1989.

Liouville Equation

$$\frac{\partial \rho}{\partial t} = -\{\rho, \mathcal{H}\} = -\sum_i \left(\frac{\partial \rho}{\partial q_i}\frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial \mathcal{H}}{\partial q_i}\frac{\partial \rho}{\partial p_i} \right) \tag{20}$$

$\{A, B\}$ is called the Poisson Bracket

- Although the Liouville equation allows for a much broader class of densities, it is also valid for Newtonian dynamics.

Example: One particle in an external field.

$$\mathcal{H} = \frac{p_1^2}{2m} + V(\vec{r}_1) \tag{21}$$

$$\rho(\vec{r}, \vec{p}, t) = \delta(\vec{r} - \vec{r}_1(t))\delta(\vec{p} - \vec{p}_1(t)) \tag{22}$$

R.C. Tolman: The Principles of Statistical Mechanics, Dover, 1979.

Particle in External Field

- Average position:

$$\langle \vec{r} \rangle = \int d\vec{r} d\vec{p}\, \vec{r} \rho = \vec{r}_1(t) \tag{23}$$

- Equation of motion for $\vec{r}_1(t)$:

$$\begin{aligned} \frac{d\vec{r}_1}{dt} &= \frac{d}{dt} \int d\vec{r} d\vec{p}\, r \rho = \int d\vec{r} d\vec{p}\, \vec{r} \frac{\partial \rho}{\partial t} = - \int d\vec{r} d\vec{p}\, \vec{r} \{\rho, \mathcal{H}\} \\ &= \int d\vec{r} d\vec{p}\, \{\vec{r}, \mathcal{H}\} \rho = \int d\vec{r} d\vec{p}\, \frac{\vec{p}}{m} \rho = \frac{\vec{p}_1}{m} \end{aligned} \tag{24}$$

- Equation of motion for $\vec{p}_1(t)$:

$$\frac{d\vec{p}_1}{dt} = \vec{F}(\vec{r}_1) = - \frac{dV(\vec{r}_1)}{d\vec{r}_1} \tag{25}$$

Gibbs Entropy I.

Gibbs Entropy:

$$S_{\mathrm{G}} = -\sum_i p_i \ln p_i = -\int d\Gamma\, \rho \ln \rho \tag{26}$$

- This form of Gibbs' entropy does not change in time:

$$\frac{d}{dt} S_{\mathrm{G}} = -\int d\Gamma\, \frac{\partial}{\partial t} \rho \ln \rho = \int d\Gamma \{\rho \ln \rho, \mathcal{H}\} = 0 \tag{27}$$

- The equations of motion are microscopically reversible.

Equilibrium Distribution

- Maxwell–Boltzmann:

$$\rho_{\mathrm{eq}} = \frac{e^{-\beta\mathcal{H}}}{\int d\Gamma\, e^{-\beta\mathcal{H}}} \to \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} \tag{28}$$

- Normalization

$$Q = \int d\Gamma\, e^{-\beta\mathcal{H}} \tag{29}$$

- Equilibrium entropy:

$$S_{\mathrm{G}}^{\mathrm{eq}} = -\int d\Gamma\, \frac{e^{-\beta\mathcal{H}}}{Q}\left[-\beta\mathcal{H} - \ln Q\right] = \beta\left\langle E\right\rangle + \ln Q \tag{30}$$

- Therefore:

$$\boxed{A = -k_B T \ln Q} \tag{31}$$

Summary

- The Liouville equation provides a unified description of mechanical and statistical dynamics.
- However: no decay to equibrium and no increase of entropy.
- For later reference: the properties of the Poisson bracket are similar to those of the commutator in quantum mechanics.

Next: Coarse graining.

One–Particle Distribution Function

Rather than looking at all the particles, we concentrate on just one:

$$f(\vec{r}, \vec{v}, t) = \int d\Gamma_{n-1}\, \rho(\vec{r}, \vec{r}_2 \cdots \vec{r}_N, \vec{p}, \vec{p}_2 \cdots \vec{p}_N) \qquad (32)$$

The probability of finding <u>a</u> particle at position $\vec{r}$ with velocity $\vec{v}$ at time t.

The <u>Boltzmann equation</u> is an equation for the time dependence of this function:

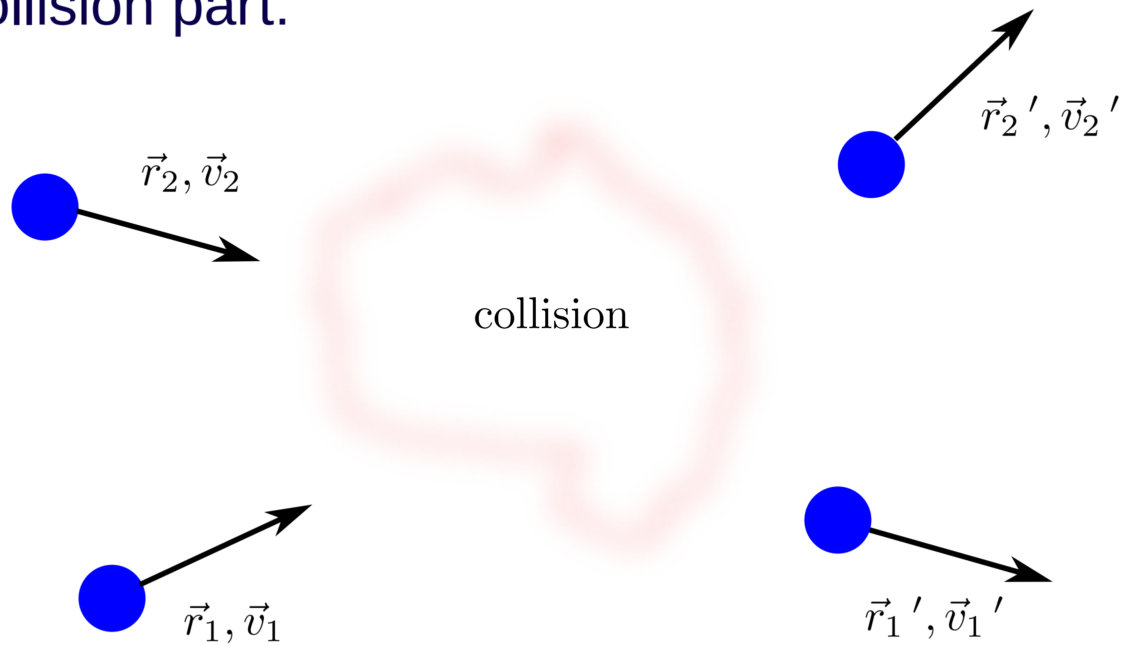
$$\frac{\partial f}{\partial t} = \left(\frac{\partial f}{\partial t}\right)_{\text{flow}} + \left(\frac{\partial f}{\partial t}\right)_{\text{collision}} \qquad (33)$$

Boltzmann Equation

- The flow part:

$$\left(\frac{\partial f}{\partial t}\right)_{\mathrm{flow}} = -\vec{v}\cdot\frac{\partial f}{\partial \vec{r}} + \frac{\vec{F}}{m}\cdot\frac{\partial f}{\partial \vec{v}} \tag{34}$$

- The collision part:



The Collision Term

- Dilute Gas, only two particle collisions

$$\left(\frac{\partial f}{\partial t}\right)_{\text{collision}} = - \int d\vec{r}_1 \cdots d\vec{v}_1{}' \, P(\vec{r},\vec{v},\vec{r}_1,\vec{v}_1,t) W(\vec{r},\vec{v},\vec{r}_1,\vec{v}_1|\vec{r}\,',\vec{v}\,',\vec{r}_1{}',\vec{v}_1{}') + \int d\vec{r}_1 \cdots d\vec{v}_1{}' \, P(\vec{r}\,',\vec{v}\,',\vec{r}_1{}',\vec{v}_1{}',t) W(\vec{r}\,',\vec{v}\,',\vec{r}_1{}',\vec{v}_1{}'|\vec{r},\vec{v},\vec{r}_1,\vec{v}_1) \tag{35}$$

- $W(\vec{r},\vec{v},\vec{r}_1,\vec{v}_1|\vec{r}\,',\vec{v}\,',\vec{r}_1{}',\vec{v}_1{}')$: collision cross section. Follows from interparticle potential.

- $P(\vec{r},\vec{v},\vec{r}_1,\vec{v}_1,t)$: two–particle distribution function.

Stosszahlansatz

- No correlation between the particles before the collision:

$$P(\vec{r}, \vec{v}, \vec{r}_1, \vec{v}_1, t) = f(\vec{r}, \vec{v}, t) f(\vec{r}_1, \vec{v}_1, t) \equiv f f_1 \qquad (36)$$

- Use symmetries of W (after a considerable amount of algebra):

The Boltzmann Equation:

$$\frac{\partial f}{\partial t} + \vec{v} \cdot \frac{\partial f}{\partial \vec{r}} + \frac{\vec{F}}{m} \cdot \frac{\partial f}{\partial \vec{v}} = - \int d\vec{v}_1 d\vec{v}\,' d\vec{v}_1\,' \left[f f_1 - f' f_1' \right] W(\vec{v}, \vec{v}_1 | \vec{v}\,', \vec{v}_1\,') \qquad (37)$$

Recap and Some Remarks

- Only binary collisions play a role.
- *Molecular Chaos*: no correlation between between positions and velocities of particles
- $f(\vec{r}, \vec{v}, t)$ varies slowly as function of position.
- *No correlations before the collision*
- Irreversibility is introduced by the previous assumption.
- The Boltzmann equation is the basis of quite an industry.

Boltzmann thought he solved the irreversibility problem, but of course he did not. He introduced it by his assumptions.

H–theorem

- Definition of $H(t)$:

$$H(t) = \int d\vec{r}d\vec{v}\, f(\vec{r},\vec{v},t)\ln f(\vec{r},\vec{v},t) \tag{38}$$

- Boltzmann was able to derive that:

$$\frac{dH}{dt} = \frac{1}{4}\int d\vec{r}\cdots d\vec{v}\,'\ (f'f_1' - f f')\ln\left(\frac{f f_1}{f' f_1'}\right) W(\vec{v},\vec{v}_1|\vec{v}\,',\vec{v}_1\,') \tag{39}$$

- It is easy to show that:

$$(f'f_1' - f f')\ln\left(\frac{f f_1}{f' f_1'}\right) \leq 0 \tag{40}$$

- Hence:

$$\boxed{\frac{dH}{dt} \leq 0}$$

Zermolo and Poincaré

- Umkehreinwand: Turn all velocities around and the system has to return to its initial state (Zermolo).

  Boltzmann's response: do it!

- Wiederkehreinwand: Every point in phase space is approached arbitrarily close in the course of time (Poincaré). So after some time the system has to return to its initial state.

  Boltzmann's response: You should wait so long.

Equilibrium State

In equilibrium the $=$ sign in Eq. (41) holds:

$$\left(f' f_1' - f f'\right) \ln \left(\frac{f f_1}{f' f_1'} \right) = 0 \tag{41}$$

This means that $\ln f$ is invariant under collisions:

$$\ln f + \ln f_1 = \ln f + \ln f_1' \tag{42}$$

There are three invariants: mass, momentum, and energy. So $\ln f$ must be a combination of those. This leads to

The Maxwell–Boltmann distribution

$$f_{\text{eq}}(\vec{r}, \vec{v}) = C(\vec{r}) e^{-\frac{1}{2}\beta m(\vec{v}-\vec{u})^2} \tag{43}$$

Exercises and Problems

Exercises and Problems

1. Without worrying about phase transitions and temperature dependence of entropy and enthalpy, at which temperature becomes the reverse reaction of (1) favorable?
2. Write down the Hamiltonian for the harmonic oscillator and the Hamilton equations that follow from it.
3. Write down the Hamiltonian for three interacting particles, and find the corresponding Newton equations of motion.
4. Derive, from the law of conservation of mass, the continuity equation of a fluid:
$$\frac{\partial \rho}{\partial t} = -\vec{\nabla} \cdot (\rho \vec{v}) \tag{44}$$
where ρ is the density of the fluid, and v the velocity.
5. Prove that for an incompressible fluid $\vec{\nabla} \cdot \vec{v} = 0$
6. Prove the Liouville theorem, and derive the Liouville equation, Eq. (19).
7. Prove the following properties of the Poisson bracket: $\{A, B\} = -\{B, A\}$ and the Jacobi Identity: $\{\{A, B\}, C\} + \{\{B, C\}, A\} + \{\{C, A\}, B\} = 0$

Exercises and Problems

8. Make sure you understand all the steps in Eq. (24), and derive the equation for the change of momentum, Eq. (25).
9. Use the Boltmann equation to derive the continuity equation. Hint: derive an equation for

$$n(\vec{r}, t) = \int d\vec{v}\, f(\vec{r}, \vec{v}, t) \tag{45}$$

10. Use the symmetries of W to derive Eq. 39. Actually this is quite a bit of work, but you may give it a try.
11. Prove Eq. (41). (This is not very hard.)
12. Derive Eq. (43).

Literature

1. R.C. Jennings, E. Engelmann, F. Garlaschi, A.P. Casazza, and G. Zucchelli, Photosynthesis and Negative Entropy production, *Biochim. Biophys. Acta*, **1709**, (2005), 251–255.
2. G.M. Wang, E.M. Sevick, E. Mittag, D.J. Searles, and D.J. Evans, Experimental Demonstration of Violations of the Second Law of Thermodynamics for Small Systems and Short Time Scales, *Phys. Rev. Lett.*, **89**, (2002), 050601.
3. J. Caro and L.L. Salcedo, Impediments to Mixing Classical and Quantum Dynamics, *Phys. Rev. A*, **60**, (1999), 842–852.
4. S. Mukamel, Comment on “Coherence and Uncertainty in Nanostructured Organic Photovoltaics”, *J. Phys. Chem. A*, **117**, (2013), 10563–10564.
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