Boltzmann's and Planck's Approach to Irreversibility

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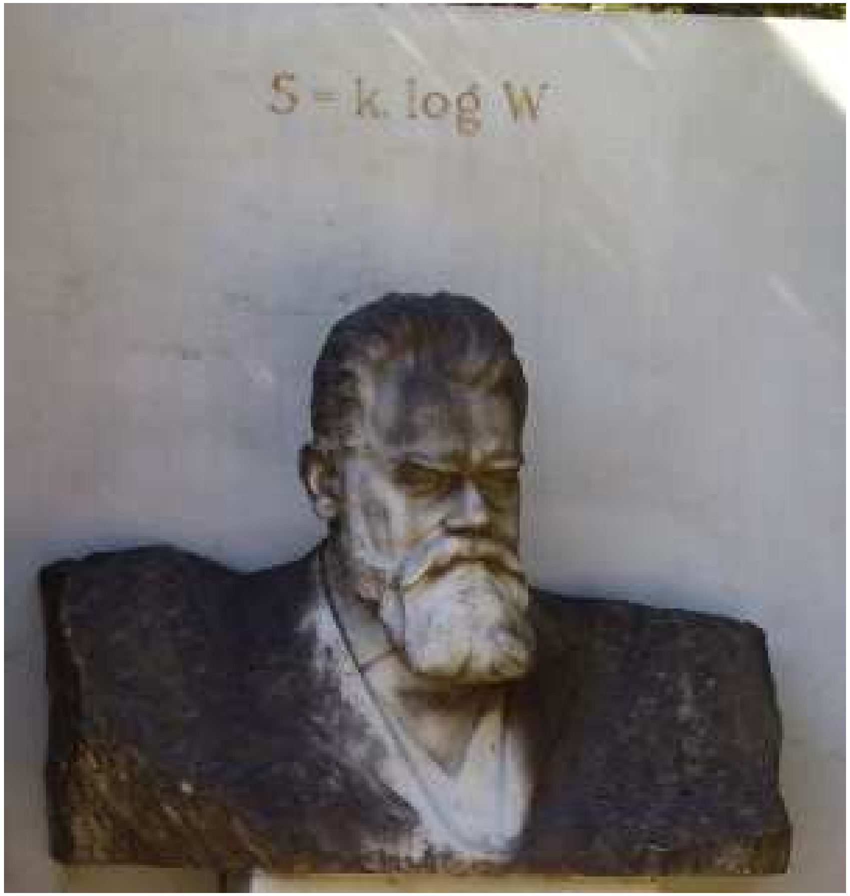
December 9, 2016



Ludwig Boltzmann, who spent much of his life studying statistical mechanics, died in 1906, by his own hand. Paul Ehrenfest, carrying on the same work, died similarly in 1933. Now it is our turn to study statistical mechanics.

Perhaps it will be wise to approach the subject cautiously.

David Goodstein, *States of Matter*.

Finally!

> "Finally, we can understand why a cup of coffee equilibrates in a room," said Tony Short, a quantum physicist at Bristol. "Entanglement builds up between the state of the coffee cup and the state of the room."

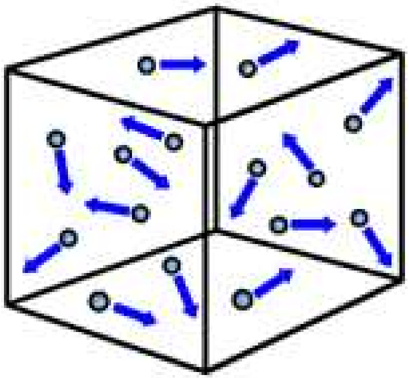
https://www.wired.com/2014/04/quantum-theory-flow-time/

> We prove, with virtually full generality, that reaching equilibrium is a universal property of quantum systems: almost any subsystem in interaction with a large enough bath will reach an equilibrium state and remain close to it for almost all times.

Linden *et al.*,Phys. Rev. E **79**, 061103 (2009)

Phase Space and the Liouville Equation

Hamiltonian and Hamilton Equations



Hamiltonian:

$$\mathcal{H} = T + V = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + \sum_{i \neq j} V(\vec{r}_i, \vec{r}_j) \tag{1}$$

Hamilton equations:

$$\frac{d\vec{r}_i}{dt} = \frac{\partial \mathcal{H}}{\partial \vec{p}_i} = \frac{\vec{p}_i}{m_i}, \qquad \frac{d\vec{p}_i}{dt} = -\frac{\partial \mathcal{H}}{\partial \vec{r}_i} = \vec{F}_i \tag{2}$$

Example: the Harmonic Oscilator (HO)

$$\mathcal{H} = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2 \tag{3}$$

$$\frac{d^2x}{dt^2} = -\omega^2 x \tag{4}$$

Phase Space Γ and Phase Space Density

Phase space (Γ) is the $6N$–dimensional space of all positions $\vec{r}^N = \{\vec{r}_i\}$ and all momenta $\vec{p}^N = \{\vec{p}_i\}$.

A point in phase space gives the state of the system.

Let $\rho(\vec{r}^N, \vec{p}^N, t)$ be a density distribution on phase space, that is:

$$\rho(\vec{r}^N, \vec{p}^N, t) d\vec{r}_1 d\vec{r}_2 \cdots d\vec{p}_N \equiv \rho(\vec{r}^N, \vec{p}^N, t) d\Gamma \tag{5}$$

is the 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 $\vec{p}_i + d\vec{p}_i$ at time t

For every dynamical variable $A(\vec{r}^N, \vec{p}^N)$ the average ("expectation value") is then given by

$$\langle A \rangle = \int d\Gamma \, A\rho \tag{6}$$

Liouville Equation

An equation of motion for ρ:

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum_{i=1}^{N} \left[\frac{\partial \rho}{\partial \vec{r}_i} \frac{d\vec{r}_i}{dt} + \frac{\partial \rho}{\partial \vec{p}_i} \frac{d\vec{p}_i}{dt} \right] \quad (7)$$

Liouville's theorem: (conservation of probability)

$$\frac{d\rho}{dt} = 0 \quad (8)$$

Phase space density behaves like an incompressible fluid.

Liouville Equation II

Use Liouville's theorem and the Hamilton equations to get

$$\frac{\partial \rho}{\partial t} = -\sum_{i=1}^{N}\left[\frac{\partial \rho}{\partial \vec{r}_i}\frac{\partial \mathcal{H}}{\partial \vec{p}_i} - [\frac{\partial \rho}{\partial \vec{p}_i}\frac{\partial \mathcal{H}}{\partial \vec{r}_i}\right] = \{\mathcal{H}, \rho\} \qquad (9)$$

Let A and B be dynamical variables. Then the Poisson Bracket $\{A, B\}$ is defined as

$$\{A, B\} = \sum_{i=1}^{N}\left[\frac{\partial A}{\partial \vec{r}_i}\frac{\partial B}{\partial \vec{p}_i} - \frac{\partial A}{\partial \vec{p}_i}\frac{\partial B}{\partial \vec{r}_i}\right] \qquad (10)$$

Note that

$$\frac{dA}{dt} = -\{\mathcal{H}, A\} \qquad (11)$$

Poisson Brackets

Antisymmetry: $\{B, A\} = -\{A, B\}$

Distributivity: $\{A, B + C\} = \{A, B\} + \{A, C\}$

Product rule: $\{AB, C\} = A\{B, C\} + \{A, C\}B$

Jacobi Identity: $\{A, \{B, C\}\} + \{B, \{C, A\}\} + \{C, \{A, B\}\} = 0$

The Jacobi identity implies that

$$\frac{d}{dt}\{A, B\} = \{\frac{dA}{dt}, B\} + \{A, \frac{dB}{dt}\} \tag{12}$$

Liouvillian (operator):

$$\hat{\mathcal{L}} \cdot = i\{\mathcal{H}, \cdot\} \tag{13}$$

so that

$$\frac{\partial \rho}{\partial t} = -i\mathcal{L}\rho \tag{14}$$

Equilibrium Distribution

From equilibrium statistical mechanics we know that the (canonical) equilibrium distribution is given by

$$\rho^{\mathrm{eq}} = \frac{e^{-\beta\mathcal{H}}}{\int d\Gamma\, e^{-\beta\mathcal{H}}} \qquad (15)$$

for a system in equilibrium at temperature $T = (k_B\beta)^{-1}$

Fundamental Problem (1) Show that (almost?) all initial distributions go to the equilibrium distribution.

Fundamental Problem (2) The Hamilton equations are invariant for time reversal. Decay to equilibrium clearly is not. How is that possible?

What can a Poor Boy do?

> The founding fathers of statistical mechanics, Boltzmann, Maxwell, Gibbs, and Einstein, invented the concept of ensembles to describe equilibrium and nonequilibrium macroscopic systems. In trying to justify the use of ensembles, and to determine whether the ensembles evolved as expected from nonequilibrium to equilibrium, they introduced further concepts such as "ergodicity" and "coarse graining." The use of these concepts raised mathematical problems that they could not solve, but like the good physicists they were they assumed that everything was or could be made all right mathematically and went on with the physics.

J.L. Lebowitz and O. Penrose, *Physics Today*, **26**, (1973), 155.

Don't you just want to be a good physicist (of the: 'Shut up, and calculate!' variety)?

Boltzmann's Equation and the H–Theorem.

μ–space: A lower (6) dimensional phase space, in which every point gives the position $\vec{r}$ and velocity $\vec{v}$ of a particle. A gas is a cloud of particles in this space.

One–particle density $f(\vec{r}, \vec{v}, t) d\vec{r} d\vec{v}$ is the number of particles with position in a volume $d\vec{r}$ at position $\vec{r}$ and velocity in a volume $d\vec{v}$ at velocity $\vec{v}$ at time t.

$$\int d\vec{v}\, f(\vec{r}, \vec{v}, t) = n(\vec{r}, t) : \quad \text{particle density} \tag{16}$$

$$\int d\vec{r} d\vec{v}\, f(\vec{r}, \vec{v}, t) = N : \quad \text{number of particles} \tag{17}$$

Boltzmann: Derive an equation for f.

Outline of the Derivation

f changes because of flow:

$$\left(\frac{\partial f}{\partial t}\right)_{\text{flow}} = -\vec{v}\cdot\frac{\partial f}{\partial \vec{r}} - \frac{\vec{F}}{m}\cdot\frac{\partial f}{\partial \vec{p}} \tag{18}$$

(compare Liouville equation) and because of collisions:

$$\left(\frac{\partial f(\vec{r},\vec{v},t)}{\partial t}\right)_{\text{coll}} = \int d\vec{r}_1 d\vec{v}_1 d\vec{r}\,' d\vec{v}\,' d\vec{r}\,'_1 d\vec{v}\,'_1 P_2(\vec{r}\,'\vec{v}\,', \vec{r}\,'_1\vec{v}\,'_1, t) W(\vec{r}\,'\vec{v}\,', \vec{r}\,'_1\vec{v}\,'_1 | \vec{r}\vec{v}, \vec{r}_1\vec{v}_1) - \int d\vec{r}_1 d\vec{v}_1 d\vec{r}\,' d\vec{v}\,' d\vec{r}\,'_1 d\vec{v}\,'_1 P_2(\vec{r}\vec{v}, \vec{r}_1\vec{v}_1, t) W(\vec{r}\vec{v}, \vec{r}_1\vec{v}_1 | \vec{r}\,'\vec{v}\,', \vec{r}\,'_1\vec{v}\,'_1) \tag{19}$$

Gain: particles with $\vec{r}\,'\vec{v}\,', \vec{r}\,'_1\vec{v}\,'$ collide and produce particles with $\vec{r}\vec{v}$ (first term) and $\vec{r}_1\vec{v}_1$.

Loss: Particles with the correct position and momentum are lost in a collision (second term).

Boltzmann Equation

$W(\vec{r}\,'\vec{v}\,', \vec{r}\,'_1\vec{v}\,'_1|\vec{r}\vec{v}, \vec{r}_1\vec{v}_1)$: transition function, can be calculated from interparticle potential.

$P_2(\vec{r}\vec{v}, \vec{r}_1\vec{v}_1, t)$: two particle distribution function.

Assumptions

1. Dilute gas, range of potential $\ll$ distance between particles.
2. Only binary collisions between spherical particles)
3. Spatial variation ignored within a volume element.
4. W has all the symmetries of the Hamiltonian (translation, time (velocity) reversal)
5. **Molecular Chaos**: $P_2(\vec{r}\vec{v}, \vec{r}_1\vec{v}_1, t) = f(\vec{r}\vec{v}, t)f(\vec{r}_1\vec{v}_1, t)$. Also known as *Stosszahlansatz*.

Boltzmann Equation II

A considerable amount of straightforward algebra later we get

The Boltzmann transport equation

$$\frac{\partial f}{\partial t} = -\vec{v} \cdot \frac{\partial f}{\partial \vec{r}} - \frac{\vec{F}}{m} \cdot \frac{\partial f}{\partial \vec{v}} + \int d\vec{v}_1 d\vec{v}' d\vec{v}'_1 \left(f' f'_1 - f f_1\right) C(\vec{v}, \vec{v}_1 | \vec{v}', \vec{v}'_1) \qquad (20)$$

with indices of f indicating the argument:

$$f \equiv f(\vec{r}, \vec{v}, t) \quad f_1 \equiv f(\vec{r}, \vec{v}_1, t) \quad \text{etc} \qquad (21)$$

This equation is the basis of a vast amount of literature and applications (according to WoS 12000 papers in the last ten years), as well as formal properties.

H–theorem

Here I am interested in only one thing: The H–theorem (300 papers between 2006–1016).

$$H = \int d\mu\, f(\vec{r}, \vec{v}, t) \ln f(\vec{r}, \vec{v}, t) \tag{22}$$

so that

$$\frac{dH}{dt} = \int d\mu\, (\ln f + 1) \frac{\partial f}{\partial t} = \int d\mu\, (\ln f + 1) \left(\frac{\partial f}{\partial t}\right)_{\text{coll}} \tag{23}$$

Insert the collision integral, and after similar algebraic manipulation leading to the Boltzmann equation, the result is

$$\frac{dH}{dt} = \int d\vec{r} d\vec{v} d\vec{v}' d\vec{v}_1 d\vec{v}_1' (f' f_1' - f f_1) \ln \frac{f f_1}{f' f_1'} C(\vec{v}\vec{v}_1 | \vec{v}'\vec{v}_1') \tag{24}$$

H–Theorem II

The integrand of Eq. (24) is always smaller than zero (see exercise 13). Therefore

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

That is: the function H can only decrease, which is irreversible behavior from reversible equations. *Is it really?*

If $f f_1 = f' f_1'$ H remains at its minimum value. In that case $\ln f$ is a *collision invariant*, of which there are three.

$$\ln f + \ln f_1 = \ln f' + \ln f_1' \tag{25}$$

Conservation laws in collisions:

$$m + m_1 = m' + m_1' \tag{26}$$

$$m\vec{v} + m_1\vec{v}_1 = m'\vec{v}\,' + m_1'\vec{v}_1\,' \tag{27}$$

$$\frac{1}{2}mv^2 + \frac{1}{2}m_1{v_1}^2 = \frac{1}{2}m'v'^2 + \frac{1}{2}m_1'{v_1'}^2 \tag{28}$$

Therefore

$$f^{\mathrm{eq}}(\vec{r},\vec{v}) = g(\vec{r})e^{am+m\vec{v}\cdot\vec{b}+c\frac{1}{2}mv^2} \tag{29}$$

Again some algebraic manipulation to get

$$f^{\mathrm{eq}}(\vec{r},\vec{v}) = g(\vec{r})e^{-\frac{1}{2}\beta m(\vec{v}-\vec{u})^2} \tag{30}$$

which gives the Maxwell–Boltmann distribution if we identify $\beta = 1/k_BT$. $\vec{u}$ is the average velocity at $\vec{r}$.

Loschmidt's Objection

According to the laws of mechanics, for each trajectory in phase space for which H decreases, there is another trajectory for which H increases, which is obtained from the former by reversing, at a particular instant, the signs of the velocities of all the molecules in the gas.

Poincaré–Zermolo Objection

Poincaré showed that for any starting point in phase space (except possibly for a set of measure zero) dynamical motion (which is volume preserving) will eventually lead the path arbitrarily close to the starting point. This is known as the *Recurrence Theorem*

On the basis of this Zermelo argued that if at any point in time H is not at its minimum value, the system will eventually visit this value again.

Remarks and Conclusions

- The existence of an equilibrium solution to the Boltzmann equation does not prove that all distributions converge to that solution. $e^{-\beta\mathcal{H}}$ is also a solution to the stationary Liouville equation, and not a single density matrix converges to that solution.
- The H–theorem does not prove that H always decreases. Only if the gas is in a state of molecular chaos this happens. But after a collision velocities are correlated, and molecular chaos is violated.
- There has been a lot of discussion about the precise meaning of the *Stosszahlansatz* and/or *Molecular Chaos*. See the literature section for some recent papers.

Ehrenfest Dog–Flea Model

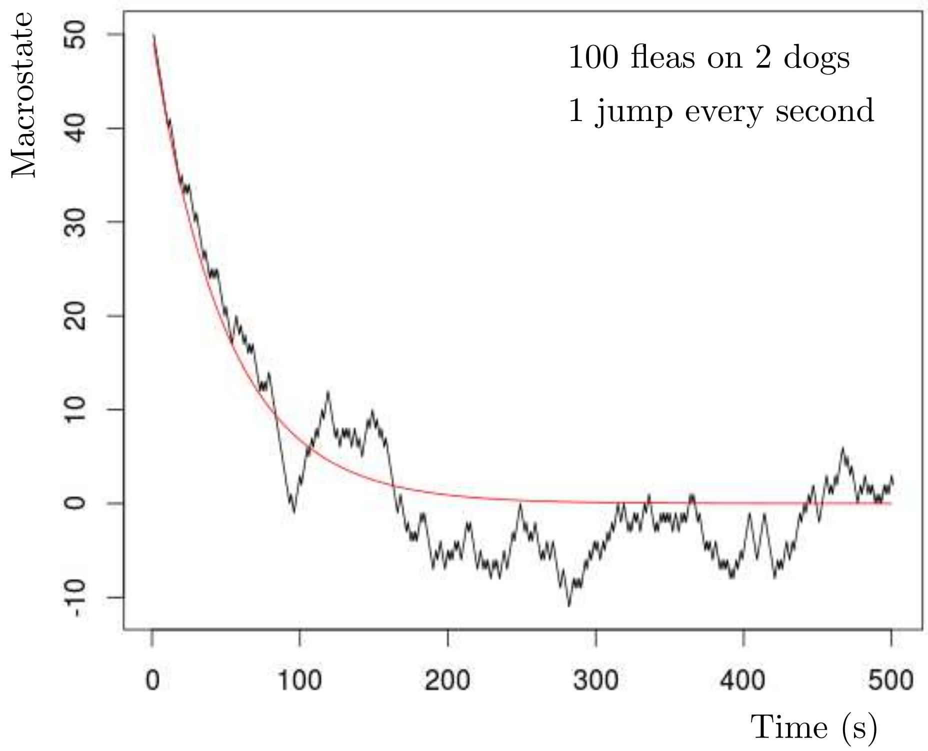
The Ehrenfest Urn Model

- Dog 1 (on the left) has $2N$ numbered fleas, dog 2 (on the right) is initially flea free.
- Every second we pick a random number between 1 and $2N$, look up the corresponding flea, and put it on the other dog.

Microstates and Macrostates

- A microstate is a complete specification of the positions of all fleas: fleas $n_1, n_2, n_3 \cdots n_{N+n}$ on dog 1, and fleas $n_{N+n+1}, \cdots n_{2N}$ on dog 2.
- A macrostate n is the number of fleas on each dog: $N+n$ on dog 1, and $N-n$ on dog 2.
- With macrostate n correspond $N_n = \frac{(2N)!}{(N+n)!(N-n)!}$ microstates.
- For 100 fleas there are in total $2^{100} \approx 1.3 \times 10^{30}$ microstates.
- Every jump brings you to another microstate. In the course of time all microstates are visited.
- The lifetime of the universe is $\sim 10^{18}$ s.

Simulations



- Black line: one realization.
- Red line: expectation for the average.

Master Equation and Some Elementary Results

$P(n|m;s)$: Probability of finding macrostate m after s steps if we start in macrostate n at time 0.

Master equation:

$$P(n|m,s{+}1) = \frac{R+m+1}{2R} P(n|m{+}1,s) + \frac{R-m+1}{2R} P(n|m{-}1,s) \tag{31}$$

Can be solved analytically (Kac*), The first moment can be derived directly from the equation

$$\langle m \rangle (s) = n\left(1 - \frac{1}{R}\right)^s \approx n e^{-s/R} \tag{32}$$

shown as the red line in the figure.

* In Wax's book.

Boltzmann and Gibbs Entropy

Boltzmann: The entropy is proportional to the number of microstates compatible with a given macrostate

$$S_{\mathrm{B}} = k_B \ln N_n = k_B \ln \frac{(2N)!}{(N+n)!(N-n)!}$$
$$\approx k_B \left[2N \ln 2N - (N+n)\ln(N+n) - (N-n)\ln(N-n)\right] \quad (33)$$

- S_{B} is a fluctuating quantity that can occasionally decrease.
- The equilibrium state is the one with maximum entropy: $n = 0$, for which

$$S_{\mathrm{B}}^{\mathrm{eq}} = 2Nk_B \ln 2 + \mathcal{O}(\ln N) \quad (34)$$

Boltzmann and Gibbs Entropy II

Gibbs: Entropy is an ensemble property.

- $S_\mathrm{G} = -k_B \sum_i p_i \ln p_i$
  $p_i =$ probability for a microstate.
- $S_\mathrm{G}^\mathrm{cg} = -k_B \sum_m P_m \ln \frac{P_m}{N_m}$
  $P_m =$ probability for a macrostate.

For the dog–flea model:

- $p_i = \frac{1}{2^{2N}}$: all microstates are equal.
- $P_m = \frac{1}{2^{2N}}\binom{2N}{N+n}$: some macrostates are more equal.

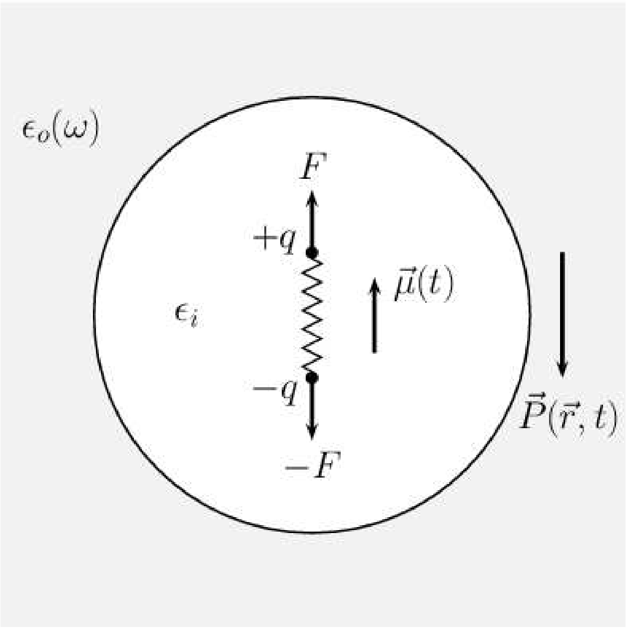
The Gibbs entropy does not fluctuate, and only increases in time.

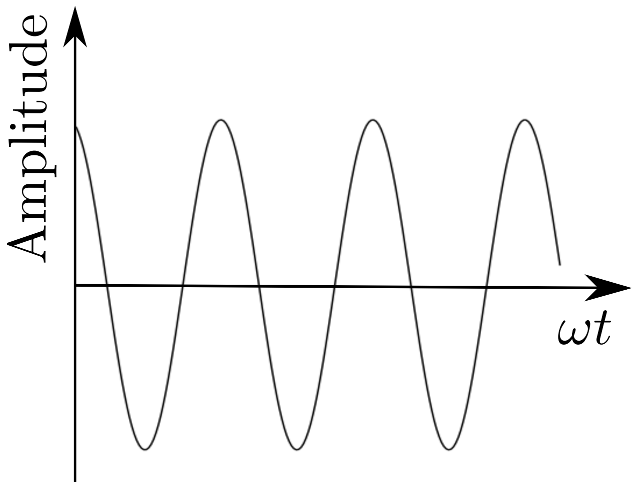
Some Further Results

1. P_m is a stationary, or equilibrium distribution.
2. Detailed Balance:
   $P_m P(m|m+1,1) = P_{m+1} P(m+1|m;1)$.
3. Decay to the stationary state.
4. Continuum limit: Smoluchowski equation for an elastically bound Brownian particle
5. The model is microscopically reversible and macroscopically irreversible.
6. Return to the initial state takes a long time.
7. How long does it take for 100 fleas?

Harmonic Oscillators

The Harmonic Oscillator





- Hamiltonian of the unperturbed oscillator:

$$\mathcal{H} = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 x^2 \qquad (35)$$

- Equation of Motion:

$$m\frac{d^2x}{dt^2} = -m\omega_0^2 x \qquad (36)$$

- Solution:

$$x(t) = A\cos(\omega_0 t + \phi) \qquad (37)$$

Solution Methods

- Trial and error (mostly taught in elementary courses): try an exponential $e^{\alpha t}$. This gives $\alpha^2 = -\omega_0^2$, or $\alpha = \pm i\omega_0$. General solution is then

$$A_1 e^{i\omega_0 t} + A_2 e^{-i\omega_0 t} \tag{38}$$

A_1 and A_2 follow from initial conditions.

- For linear initial value problems: use Laplace Transform.

$$\hat{f}(s) = \int_0^\infty dt\, e^{-st} f(t) \tag{39}$$

with inverse:

$$f(t) = \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} ds\, e^{st} \hat{f}(s) \tag{40}$$

The Damped Oscillator

- Equation of Motion:

$$m\frac{d^2x}{dt^2} = -m\omega_0^2 x - \zeta\frac{dx}{dt} \tag{41}$$

- Laplace Transform:

$$\left(s^2 + s\frac{\zeta}{m} + \omega_0^2\right) = \dot{x}_0 + s x_0 + \frac{\zeta}{m}x_0 \tag{42}$$

- Solution:

$$x(t) = \frac{1}{2\pi i}\int_{-i\infty}^{i\infty} ds\, \frac{\dot{x}_0 + (s+\zeta/m)x_0}{s^2 + s\zeta/m + \omega_0^2} e^{st} \tag{43}$$

The Damped Oscillator 2

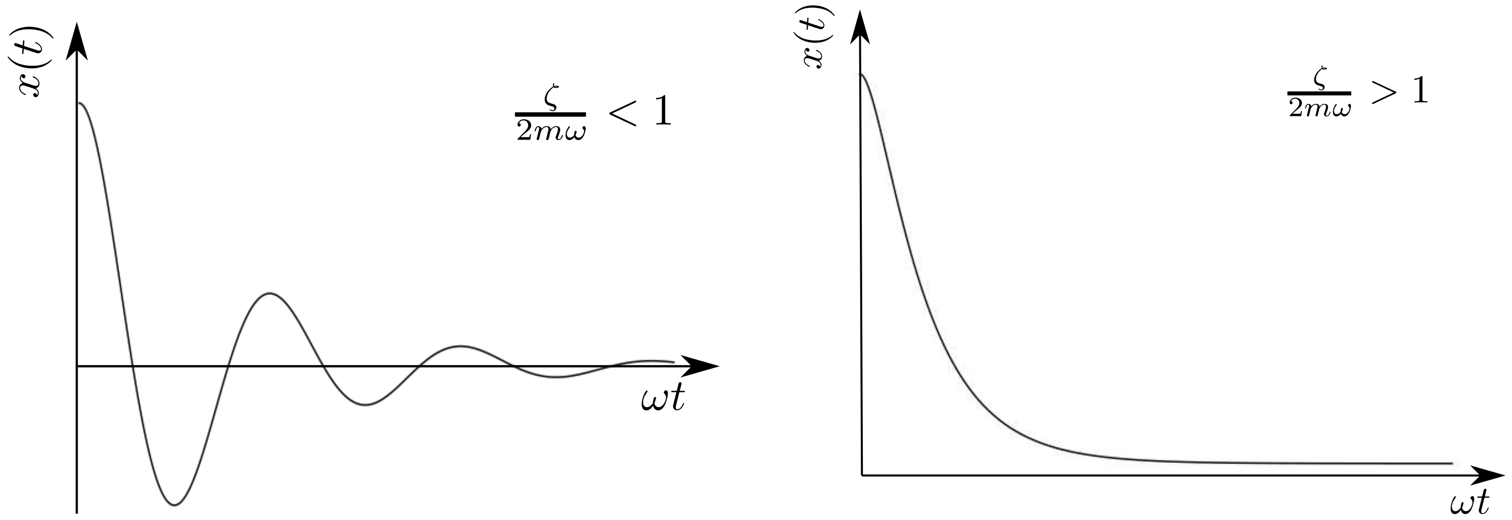
- Solution for $t \geq 0$:

$$x(t) = \frac{(\dot{x}_0 + (s_1 + \zeta/m)x_0)\, e^{s_1 t} - (\dot{x}_0 + (s_2 + \zeta/m)x_0)\, e^{s_2 t}}{s_1 - s_2} \qquad (44)$$

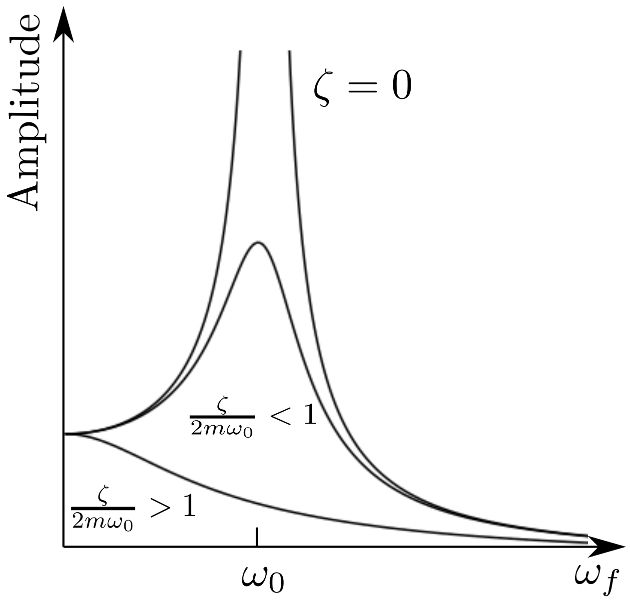
with

$$s_{1,2} = \omega_0 \left[-\frac{\zeta}{2m\omega_0} \pm \sqrt{\left(\frac{\zeta}{2m\omega_0}\right)^2 - 1} \right] \qquad (45)$$

- Graphs for underdamped and overdamped motion; *cf* Eq. (44).



Adding an External Force



- Equation of Motion:

$$m\frac{d^2x}{dt^2} = -m\omega_0^2 x - \zeta\frac{dx}{dt} + F_0\cos\omega_f t \tag{46}$$

- On the left: amplitude for the undamped, underdamped, and overdamped oscillator for an oscillating force.

- Solution (for times $t \gg (\zeta/2m)^{-1}$):

$$x(t) = \frac{F_0/m}{(\omega_0^2 - \omega_f^2)^2 + 4\omega_0^2\omega_f^2(\zeta/2m\omega_0)^2}\cos(\omega_f t + \phi) \tag{47}$$

with

$$\tan\phi = \frac{\zeta/2m\omega_0}{\omega_0^2 - \omega_f^2} \tag{48}$$

Role in Planck's Thinking

- Equation of Motion (Planck):

$$m\frac{d^2x}{dt^2} + \frac{2e^2\omega_0^2}{3mc^3}\frac{dx}{dt} + m\omega_0^2 x = \frac{e}{m}E(t) \tag{49}$$

- Friction term is due to 'radiation damping' and the external force is the electric field in the cavity.

> The study of conservative damping appears to me to be of fundamental importance due to the fact that through it one's view is opened towards the possibility of a general explanation of irreversible processes with the help of conservative forces.

M. Planck, 1896.

Boltzmann disagreed and pointed out that Planck's system was also microscopically reversible. Eventually Planck abandoned this idea.

The Langevin Equation

The oscillator is constantly buffeted by molecules in the environment. This leads to friction *and* random forces. External Force is a random force due to fluctuations in the medium (Brownian Motion).

- Equation of motion:

$$m\frac{d^2x}{dt^2} + \zeta\frac{dx}{dt} + m\omega_0^2 x = F_R(t) \tag{50}$$

- Random Force:

$$\langle F_R(t)\rangle = 0 \quad \text{and} \quad \Big\langle F_R(t)F_R(t')\Big\rangle = C\delta(t-t') \tag{51}$$

The average of the force is zero and is uncorrelated for different times.

Fluctuation–Dissipation Theorem

For long times the system should go to equilibrium:

$$\langle x^2 \rangle = \frac{k_B T}{m\omega_0^2} \quad \text{and} \quad \langle v^2 \rangle = \frac{k_B T}{m} \tag{52}$$

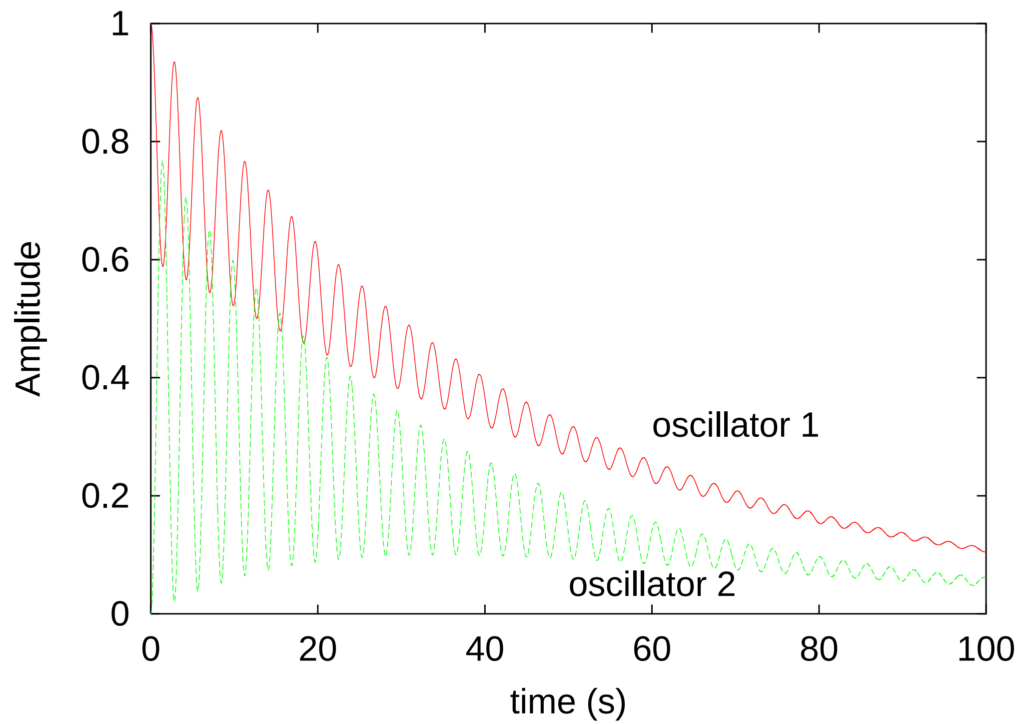
- Formal Solution (ignore initial conditions which decay rapidly anyway):

$$x(t) = \frac{1}{2\pi i} \int_{-i\infty}^{\infty} ds \, \frac{\hat{F}_R(s)/m}{(s - s_1)(s - s_2)} \tag{53}$$

- Consequence: strength of the random force is correlated with the friction

$$\lim_{t\to\infty} \langle x(t)^2 \rangle = \frac{k_B T}{m\omega_0^2} \quad \Longrightarrow \quad C = 2k_B T\zeta \tag{54}$$

Coupled Oscillators



m_1	1
m_2	1
ω_1	1
ω_2	2
γ	0.2
ζ	0.1

Equations of motion:

$$m_1 \frac{d^2 x_1}{dt^2} = -\omega_1^2 x_1 + \gamma x_2$$

$$m_2 \frac{d^2 x_2}{dt^2} = -\omega_2^2 x_2 - \zeta \frac{dx_2}{dt} + \gamma x_1$$

Langevin Equations, Non–Markovian Behavior

- Coupled equations

$$m_1 \frac{d^2 x_1}{dt^2} = -m_1 \omega_1^2 x + \gamma x_2$$
$$m_2 \frac{d^2 x_2}{dt^2} = -m_2 \omega_2^2 x - \zeta \frac{dx_2}{dt} + \gamma x_1 + F_R(t) \qquad (55)$$

lead to non–Markovian behavior of oscillator 1.

- Formally solve the second equation (use Fourier transforms):

$$x_2(\omega) = \frac{\gamma x_1(\omega) + F_R(\omega)}{m_2(\omega_2^2 - \omega^2) - i\omega\zeta} \qquad (56)$$

- And substitute in the first:

$$m_1(\omega_1^2 - \omega^2)x_1(\omega) - \frac{\gamma^2 x_1(\omega)}{m_2(\omega_2^2 - \omega^2) - i\omega\zeta} = \frac{\gamma F_R(\omega)}{m_2(\omega_2^2 - \omega^2) - i\omega\zeta} \qquad (57)$$

Langevin Equations, Non–Markovian Behavior

- Some minor rearrangement:

$$m_1(\omega_{\rm pmf}^2 - \omega^2)x_1(\omega) - i\omega\zeta_1(\omega)x_1(\omega) = \overline{F}_R(\omega) \tag{58}$$

- Potential of Mean Force ("Equilibrium Solvation"):

$$\omega_{\rm pmf}^2 = \omega_1^2\left(1 - \frac{\gamma^2}{\omega_1^2\omega_2^2}\right) \tag{59}$$

- Frequency dependent friction:

$$\zeta_1(\omega) = \frac{\gamma^2}{\omega_2^2}\frac{-i\omega + \zeta/m_2}{m_2(\omega_2^2 - \omega^2) - i\omega\zeta} \tag{60}$$

- Fluctuation–Dissipation Theorem:

$$\langle \overline{F}_R(\omega)\overline{F}_R(\omega')\rangle = 2k_BT\zeta_1(\omega)2\pi\delta(\omega - \omega') \tag{61}$$

Planck's Natural Radiation

> If you want consistency with thermodynamics, and with experience, this is only possible on the basis of a new hypothesis which is independent of the Maxwell equations. Such an hypothesis is contained in the later (section 9) introduced concept of "Natural Radiation". If an electromagnetic beam has the properties of natural radiation, this means succintly: the energy of the radiation is divided over the modes comprising the beam in a completely random way

M. Planck, 1899.

A Remark and A Question

The Remark

> In effect Planck is defining natural radiation as any actual field which permits the use of eqs. (13) with $\epsilon = \eta = 0$. That device is precisely the one Boltzmann had employed in defining molecular disorder, as any distribution that satisfied equation (II-1)

T.S. Kuhn, 1978.

The Question

Now read the Linden paper, and see if they make an assumption similar to molecular chaos, or natural radiation. Do you indeed feel that we “finally understand why a cup of coffee equilibrates”?

Tatiana Speaks

> But we should rather choose an example more closely related to physical theories; the present state of the world as it appears from the point of view of any statistical theory, kinetic theory, or quantum theory. These all affirm the world (or that part of it that is accessible to our investigation) tends to the most probable state and it is assumed that this tendency lasted a very long time before the appearance of organic life on earth and will last a very long time after this moment. But that implies that all this time the state of the world is far from being the most probable! So we seem to accept at the same time the most probable changes of the word state and a quite not probable state of the world itself.

T. Ehrenfest–Afanassjewa, 1958.

Exercises and Problems

Feynman's problem solving algorithm according to Murray Gell–Mann:

1. write down the problem;
2. think very hard;
3. write down the answer.

Exercises and Problems

1. Derive Eq. (4) from the Hamilton equations.
2. Show that the path of the HO in phase space is an ellips.
3. Prove Liouville's theorem, Eq. (8).
4. Calculate $\{\vec{r}_j, \vec{p}_k\}$.
5. Solve the Liouville equation for the HO with initial condition $\rho(x, p, 0) = \delta(x - x_0)\delta(p - p_0)$.
6. Prove Eq. (12).
7. Show that the Hamilton equations are invariant for time reversal.
8. What is the relation between $\rho(\vec{r}^N, \vec{p}^N, t)$ and $f(\vec{r}, \vec{v}, t)$?
9. Fill in the details in the derivation of the Boltzmann equation to get to (20).
10. Use the BBKGY hierarchy starting from the Liouville equation (see for instance ref.3) to give an alternative derivation of the Boltzmann equation.
11. Show that the flow term does not contribute to eq. (23).
12. Derive Eq. (24), using the symmetries of the function C, and permuting integration variables.
13. Show that $(x - y)\ln(y/x) \leq 0$.
14. Prove all the statements in the Dog–Flea model section.

Exercises and Problems

15. Use Laplace transform to derive Eq. (42).
16. Derive Eq. (44) from Eq. (43). You need complex integration for this, and use Cauchy's theorem. Prove first that the poles $s_{1,2}$ are in the negative half of the complex plane.
17. Use the Laplace transform to derive the solution of the forced oscillator Eq. (47). Ignore all terms related to the initial conditions or turning on the force.
18. Prove the fluctuation dissipation theorem, Eq. (54). Actually this involves quite a bit of work, and you may want to consult literature. Also about the relevance of this type of theorems.

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