

Kinetic Theory I [tsc7]

Physical kinetics covers a lot of ground. It is well developed and wide ranging. Here we explore some of its aspects as a bridge between equilibrium thermodynamics and equilibrium statistical mechanics.

Statistical concept of uncertainty:

Rolling dice has uncertain outcomes. Loaded dice reduce uncertainty.

The probabilities P_1, P_2, \dots, P_6 to show a 1, 2, \dots , 6, respectively, have been determined empirically for dice I, II, \dots , VI:

	1	2	3	4	5	6
I	$\frac{1}{6}$	$\frac{1}{6}$	$\frac{1}{6}$	$\frac{1}{6}$	$\frac{1}{6}$	$\frac{1}{6}$
II	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{3}{8}$
III	$\frac{1}{10}$	$\frac{1}{10}$	$\frac{1}{10}$	$\frac{1}{10}$	$\frac{1}{10}$	$\frac{1}{2}$
IV	0	0	0	0	0	1
V	$\frac{1}{16}$	$\frac{1}{16}$	$\frac{1}{16}$	$\frac{1}{16}$	$\frac{3}{8}$	$\frac{3}{8}$
VI	$\frac{3}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$

Intuitive assessment of the outcome uncertainty:

- The uncertainty is highest for die I and lowest for die IV.
- Dice II and VI have outcomes of equal uncertainty, higher than that of die I and lower than that of die I.
- The outcome of die III is less uncertain than that of dice II and III, but higher than that of die IV.
- The uncertainty for die V is harder to assess. It can be estimated to be closest to that for die III.

For an experiment that has n possible outcomes with probabilities P_1, \dots, P_n , any quantitative measure of *uncertainty* must satisfy the following criteria:

1. The uncertainty is a function $\Sigma = \Sigma(P_1, P_2, \dots, P_n)$.
2. The uncertainty is symmetric under permutations of the P_i .
3. The uncertainty is highest if all P_i are equal.
4. The uncertainty is zero if one outcome has probability $P_i = 1$.
5. The combined uncertainty for two independent experiments is the sum of their uncertainties: $P_{ij} = P_i^a P_j^b \Rightarrow \Sigma(\{P_{ij}\}) = \Sigma_a(\{P_i^a\}) + \Sigma_b(\{P_j^b\})$.

The following function is shown in [tex47] to satisfy all five criteria;

$$\Sigma(P_1, P_2, \dots, P_n) = - \sum_{i=1}^n P_i \ln P_i = -\langle \ln P \rangle. \quad (1)$$

If the outcomes of an experiment are characterized by a (normalized) probability distribution $p(x) \geq 0$, then the uncertainty is generalized into the functional,

$$\Sigma[p(x)] = - \int dx p(x) \ln (p(x)) = -\langle \ln p \rangle.$$

Statistical concept of information:

Information in the restricted sense employed here is carried by messages. Likely messages contain less information than unlikely messages.

The information content $I(M)$ of a message M is tied to the probability $P(M)$ that the message is being received.

Applicable criteria:

- If $P(A) < P(B)$ then $I(A) > I(B)$.
- If $P(A) = 1$ then $I(A) = 0$.
- If $P(A \cap B) = P(A)P(B)$ then $I(A \cap B) = I(A) + I(B)$.

The last criterion is about the information content of independent messages.

The information content (in the statistical sense) of a message is equal to the change in statistical uncertainty at the receiver:

$$P_1, P_2, \dots, P_n \xrightarrow{A} \bar{P}_1, \bar{P}_2, \dots, \bar{P}_n$$

$$\Rightarrow I(A) = \Sigma(P_1, P_2, \dots, P_n) - \Sigma(\bar{P}_1, \bar{P}_2, \dots, \bar{P}_n).$$

Applications:

- ▷ Statistical uncertainty: verification of criteria [tex47]
- ▷ Information regarding a census of birds [tex48]
- ▷ Information of sequenced messages [tex61]

Statistical uncertainty and entropy:

Looking ahead to statistical mechanics, we employ density operators,

$$\rho = \sum_n P_n |n\rangle\langle n|, \quad \sum_n P_n = 1, \quad (2)$$

as a bridge between the descriptions of microstates and macrostates.

Determining the microstate of a macroscopic system is almost always impossible in practice. It encodes the maximum information (in the statistical sense) we could have about it – the least uncertainty about it.

Thermodynamic information about a macroscopic system, which is readily attainable, can be extracted from the P_n of the density operator (2).

The function (1) with the P_n from (2) is a measure for the uncertainty about the microstate of the system.

Different ways of preparing a macroscopic system amount to different density operators (2) and, therefore, different uncertainties (1) about the microstate.

A macroscopic system settles down (at equilibrium) in a state of maximum entropy. While it approaches equilibrium, the entropy increases as does our uncertainty about the microstate.

It makes sense to (epistemologically) associate entropy with uncertainty about the microstate of a macroscopic system:

$$S = -k_B \langle \ln P \rangle = -k_B \sum_n P_n \ln P_n.$$

From this perspective, thermodynamic equilibrium is the macrostate that makes it hardest to predict the actual microstate.

Situations that make it difficult to find things are called disorderly. It is for this reason that entropy is associated with disorder in a macroscopic system.

Thermodynamic equilibrium is thus commonly identified as the state of maximum disorder under specific constraints.

Kinetics of classical ideal gas:

Our goal here is to gain a better understanding of thermodynamic equilibrium from the perspective of probability distributions for the state of individual particles that are constituents of a macroscopic system.

We use the classical ideal gas for this demonstration.

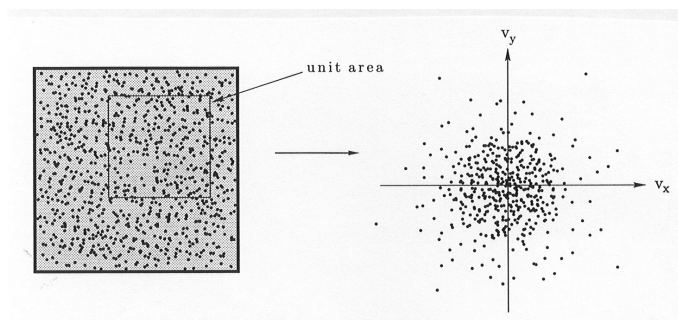
- The gas consists of N of point-like particles in a box of volume V .
- The motion of each particle is rectilinear with constant speed v .
- Interactions are limited to collisions with walls or between particles.
- The velocities and positions are randomized by collisions.
- Thermal equilibrium is characterized by a uniform position distribution $\rho(\mathbf{r}) = \text{const}$ and by a nonuniform velocity distribution $f(\mathbf{v})$.

Properties of the velocity distribution $f(\mathbf{v})$:

- ▷ $\int d^3v f(\mathbf{v}) = 1$ (normalization),
- ▷ $\int d^3v f(\mathbf{v}) \mathbf{v} = 0$ (symmetry),
- ▷ $\int d^3v f(\mathbf{v}) \left(\frac{1}{2} m v^2 \right) = \frac{1}{2} m \langle v^2 \rangle = \frac{U}{N} = \frac{3}{2} k_B T$ (internal energy),
- ▷ $p = \frac{1}{3} \frac{N}{V} m \langle v^2 \rangle = \frac{1}{3} \frac{N}{V} 3 k_B T \Rightarrow pV = N k_B T$ (equation of state),¹
- ▷ $S = -N k_B \int d^3v f(\mathbf{v}) \ln(f(\mathbf{v}))$ (entropy).

A variety of derivations of $\rho(\mathbf{r})$ and $f(\mathbf{v})$ will be discussed below.

Graphical representations of $\rho(\mathbf{r})$ and $f(\mathbf{v})$ in two dimensions.



¹The derivation of pressure from $f(\mathbf{v})$ is worked out in [tex49].

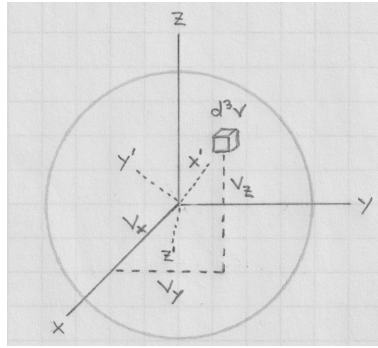
Maxwell velocity distribution:

Criteria used by Maxwell in his derivation [tex50]:

- statistical independence: $f(v_x, v_y, v_z) = f_1(v_x)f_1(v_y)f_1(v_z)$.
- spherical symmetry:

$$f_1(v_x)f_1(v_y)f_1(v_z) = f_1\left(\sqrt{v_x^2 + v_y^2 + v_z^2}\right) f_1(0)f_1(0).$$

- equipartition: $\frac{1}{2}m\langle v_\alpha^2 \rangle = \frac{1}{2}k_B T$, $\alpha = x, y, z$.



Maxwell velocity distribution:

$$\Rightarrow f(v_x, v_y, v_z) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{m(v_x^2 + v_y^2 + v_z^2)}{2k_B T}\right).$$

Speed distribution:

Integrate $f(v_x, v_y, v_z)$ over shell $v < \sqrt{v_x^2 + v_y^2 + v_z^2} < v + dv$.

$$\Rightarrow f_s(v) = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-mv^2/2k_B T}.$$

Energy distribution:

$$\text{Use } E = \frac{1}{2}mv^2, \quad v^2 dv = \frac{1}{2} \left(\frac{2}{m}\right)^{3/2} E^{1/2} dE.$$

$$\Rightarrow f_E(E) = \frac{2}{\sqrt{\pi}} (k_B T)^{-3/2} \sqrt{E} e^{-E/k_B T}.$$

Root-mean-square speed:

$$\langle v^2 \rangle = \int_0^\infty dv v^2 f_s(v) \Rightarrow \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3k_B T}{m}}.$$

Mean speed:

$$\langle v \rangle = \int_0^\infty dv v f_s(v) \Rightarrow \langle v \rangle = \sqrt{\frac{8k_B T}{\pi m}}.$$

Most frequent speed:

$$\left. \frac{df_s}{dv} \right|_{v_0} = 0 \Rightarrow v_0 = \sqrt{\frac{2k_B T}{m}} \Rightarrow f_s(v_0) = \sqrt{\frac{8m}{\pi k_B T}} e^{-1}.$$

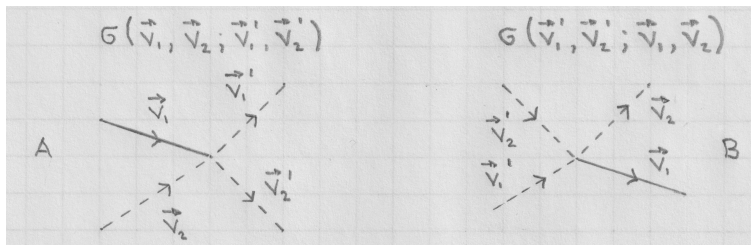
Applications:

- ▷ Maxwell velocity distribution in D dimensions [tex56]
- ▷ Energy distribution of N ideal gas atoms [tex57]
- ▷ Boltzmann's derivation of Maxwell velocity distribution [tex58]

Boltzmann equation:

Consider a dilute gas in a box with a uniform distribution of positions, $\rho(\mathbf{r}) = \text{const}$, and a nonequilibrium distribution $f(\mathbf{v}, t)$ of velocities. How does the latter approach equilibrium?

Boltzmann proposes a *kinetic equation*, which takes into account elastic pair collisions, characterized by a scattering cross section $\sigma(\mathbf{v}_1, \mathbf{v}_2; \mathbf{v}'_1, \mathbf{v}'_2)$, where the first (last) two variables are the velocities before (after) the collision.



During the (infinitesimal) time interval dt , the number of particles with velocities $\mathbf{v}_1 d^3v_1$ changes due to contributions A and B from two kinds of processes:

$$[f(\mathbf{v}_1, t + dt) - f(\mathbf{v}_1, t)] d^3v_1 = B - A$$

The number of collisions away from $\mathbf{v}_1 d^3 v_1$ is

$$A = dt d^3 v_1 \int d^3 v_2 \int d^3 v'_1 \int d^3 v'_2 \sigma(\mathbf{v}_1, \mathbf{v}_2; \mathbf{v}'_1, \mathbf{v}'_2) f(\mathbf{v}_1, t) f(\mathbf{v}_2, t).$$

The number of collisions into $\mathbf{v}_1 d^3 v_1$ is

$$B = dt d^3 v_1 \int d^3 v_2 \int d^3 v'_1 \int d^3 v'_2 \sigma(\mathbf{v}'_1, \mathbf{v}'_2; \mathbf{v}_1, \mathbf{v}_2) f(\mathbf{v}'_1, t) f(\mathbf{v}'_2, t).$$

In both terms, the first assumption is implied, whereas the second assumption is used in the construction of the Boltzmann equation:

- Assumption of molecular chaos, which neglects correlations produced by the collisions. The pair distribution thus factorizes:

$$f^{(2)}(\mathbf{v}_1, \mathbf{v}_2, t) = f(\mathbf{v}_1, t) f(\mathbf{v}_2, t).$$

- Symmetry assumptions of scattering cross section:

$$\sigma(\mathbf{v}_1, \mathbf{v}_2; \mathbf{v}'_1, \mathbf{v}'_2) = \sigma(\mathbf{v}_2, \mathbf{v}_1; \mathbf{v}'_2, \mathbf{v}'_1) = \sigma(\mathbf{v}'_1, \mathbf{v}'_2; \mathbf{v}_1, \mathbf{v}_2).$$

Boltzmann's kinetic equation:

$$\begin{aligned} \Rightarrow \frac{\partial}{\partial t} f(\mathbf{v}_1, t) = & - \int d^3 v_2 \int d^3 v'_1 \int d^3 v'_2 \sigma(\mathbf{v}_1, \mathbf{v}_2; \mathbf{v}'_1, \mathbf{v}'_2) \\ & \times \left[f(\mathbf{v}_1, t) f(\mathbf{v}_2, t) - f(\mathbf{v}'_1, t) f(\mathbf{v}'_2, t) \right]. \end{aligned}$$

This rendition of the Boltzmann equation applies only to the special case of spatially uniform velocity distributions. The most general rendition has a rich field of applications (topic for a different course).

***H*-function:**

Boltzmann's *H*-function,

$$H(t) \doteq \int d^3 v f(\mathbf{v}, t) \ln f(\mathbf{v}, t),$$

is related to the uncertainty in our knowledge of the particle velocities as contained in the distribution $f(\mathbf{v}, t)$: $H(t) = -\Sigma[f(\mathbf{v}, t)]$. The opposite sign is of no importance – an accidental choice.

Boltzmann's point was to show that if $f(\mathbf{v}, t)$ is a solution of the above kinetic equation, then $H(t)$ decreases monotonically in time and approaches a stationary value $H(\infty)$.

H-theorem:

We single out (as in the kinetic equation) a particle that has velocity \mathbf{v}_1 with probability $f(\mathbf{v}_1, t)$ at time t between collisions. The instantaneous H -function is

$$H(t) \doteq \int d^3v_1 f(\mathbf{v}_1, t) \ln f(\mathbf{v}_1, t).$$

and its derivative becomes

$$\frac{dH}{dt} = \int d^3v_1 \left[\frac{\partial f(\mathbf{v}_1, t)}{\partial t} \ln f(\mathbf{v}_1, t) + \frac{\partial f(\mathbf{v}_1, t)}{\partial t} \right].$$

The second term vanishes upon integration:

$$\int d^3v_1 \frac{\partial f(\mathbf{v}_1, t)}{\partial t} = \frac{d}{dt} \int d^3v_1 f(\mathbf{v}_1, t) = 0.$$

For the derivative in the first term, we substitute the kinetic equation:

$$\begin{aligned} \Rightarrow \frac{dH}{dt} = & - \int d^3v_1 \int d^3v_2 \int d^3v'_1 \int d^3v'_2 \sigma(\mathbf{v}_1, \mathbf{v}_2; \mathbf{v}'_1, \mathbf{v}'_2) \\ & \times \ln f(\mathbf{v}_1, t) \left[f(\mathbf{v}_1, t) f(\mathbf{v}_2, t) - f(\mathbf{v}'_1, t) f(\mathbf{v}'_2, t) \right]. \end{aligned}$$

Notice that all four velocities are integrated over. Next we use the symmetry properties of σ noted above and rewrite this expression with three velocity permutations implemented as follows:

$$\begin{aligned} dH/dt &= \cdots \{ \mathbf{v}_1 \leftrightarrow \mathbf{v}_2 \}, \{ \mathbf{v}'_1 \leftrightarrow \mathbf{v}'_2 \}, \\ dH/dt &= \cdots \{ \mathbf{v}_1 \leftrightarrow \mathbf{v}'_1 \}, \{ \mathbf{v}_2 \leftrightarrow \mathbf{v}'_2 \}, \\ dH/dt &= \cdots \{ \mathbf{v}_1 \leftrightarrow \mathbf{v}'_2 \}, \{ \mathbf{v}_2 \leftrightarrow \mathbf{v}'_1 \}. \end{aligned}$$

The addition of the four versions of dH/dt yields the following expression:

$$\begin{aligned} \Rightarrow 4 \frac{dH}{dt} = & - \int d^3v_1 \int d^3v_2 \int d^3v'_1 \int d^3v'_2 \sigma(\mathbf{v}_1, \mathbf{v}_2; \mathbf{v}'_1, \mathbf{v}'_2) \\ & \times \left[f(\mathbf{v}_1, t) f(\mathbf{v}_2, t) - f(\mathbf{v}'_1, t) f(\mathbf{v}'_2, t) \right] \\ & \times \left[\ln \left(f(\mathbf{v}_1, t) f(\mathbf{v}_2, t) \right) - \ln \left(f(\mathbf{v}'_1, t) f(\mathbf{v}'_2, t) \right) \right]. \end{aligned}$$

The function $h(x, y) \equiv (x - y)(\ln x - \ln y)$ is non-negative for $x, y > 0$ and is equal to zero if $x = y$. The scattering cross section σ is non-negative.

Consequence:

- General situations: $\frac{dH}{dt} \leq 0$,
- Stationary situations: $\frac{dH}{dt} = 0$ if $f(\mathbf{v}_1, t)f(\mathbf{v}_2, t) = f(\mathbf{v}'_1, t)f(\mathbf{v}'_2, t)$.

The (stationary) velocity distribution which makes H stationary is the Maxwell distribution (Boltzmann's derivation [tex58]).

The stationary H -function is related to the entropy of an ideal gas at equilibrium [tex59]:

$$S = -Nk_B H(\infty).$$

Here the uncertainty in our knowledge of particle velocities is a maximum.

H -theorem and irreversibility:

Q: How does the preferred time direction, selected by the monotonic time-dependence of $H(t)$, follow from the underlying microscopic dynamics, which is invariant under time reversal?

A: The solution $f(\mathbf{v}, t)$ of the Boltzmann equation is to be interpreted as representing the properties of an ensemble of systems, i.e. the average behavior of systems that are prepared equally (on a macroscopic level).

Consider the function,

$$\tilde{H}(t) = \int d^3v \tilde{f}(\mathbf{v}, t) \ln \tilde{f}(\mathbf{v}, t),$$

calculated via computer simulation, where $\tilde{f}(\vec{v}, t)$ now represents the velocity distribution of a single system.

Simulation data (shown below) show that $\tilde{H}(t)$ tends to decrease and approach an asymptotic value just as the function $H(t)$ does.

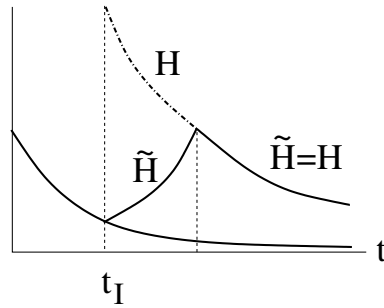
Effect of a velocity inversion (in simulation) at time t_I : $\tilde{H}(t)$ increases at $t > t_I$ for some time. Then $\tilde{H}(t)$ decreases again and approaches the same asymptotic value as $H(t)$ does.

We can interpret $-\tilde{H}(t)$ before the velocity inversion as our (growing) uncertainty about the particle velocities in the system.

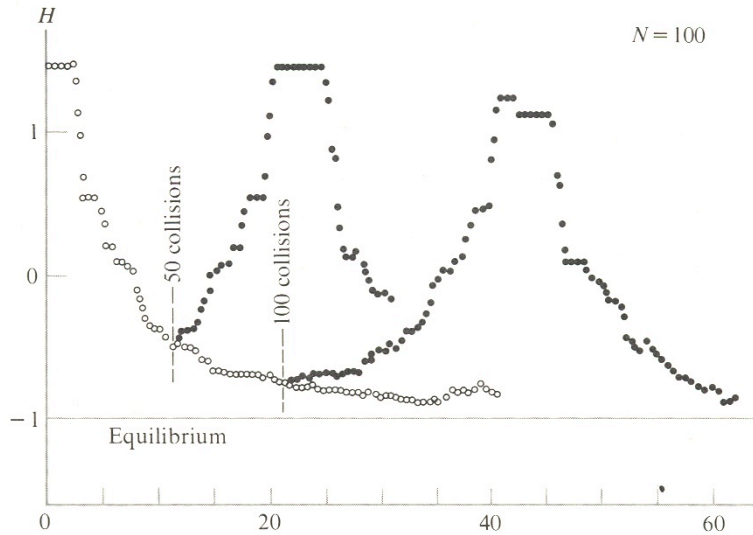
The information contained in $\tilde{f}(\mathbf{v}, t)$ over and above the three general properties from which the Maxwell distribution was derived is $\tilde{H}(t) - \tilde{H}(\infty)$. This information is insufficient to carry out the velocity inversion.

Performing the velocity inversion requires an influx of information beyond what is contained in $\tilde{f}(\mathbf{v}, t)$, which causes a discontinuous drop in uncertainty of our knowledge about the particle velocities.

At $t = t_I$, where the velocity inversion occurs, the function $H(t)$ jumps to a higher value and then decreases gradually as the information injected gets lost gradually due to collisions.



Data from computer simulation of 100 hard disks moving in a 2D box and undergoing elastic collisions. Initial state: disks positioned on a regular lattice with random velocities. Open circles: $\tilde{H}(t)$. Full circles: $\tilde{H}(t)$ when velocities are inverted after 50 or 100 collisions. [image from Prigogine 1980]



Boltzmann's H -theorem does not resolve the paradox between time-reversible dynamics and manifestations of irreversibility, it merely illuminates it.

There is growing consensus that the arrow of time is intimately related to the expansion of the universe.