

IRREVERSIBLE PROCESSES: PHENOMENOLOGICAL AND STATISTICAL APPROACH

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Keywords: Kinetic theory, thermodynamics, Boltzmann equation, Macroscopic theory

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Summary

The theory of irreversible phenomena is first discussed from the viewpoint of kinetic theory, via the Boltzmann equation, with a particular attention to the computation of transport coefficients for both simple gases and mixtures. Then the macroscopic theory of Onsager of irreversible thermodynamic phenomena is discussed.

1. Introduction

The Second Law of thermodynamics (see *Thermodynamic Systems and State Functions*) indicates that not all the processes compatible with the First Law can actually occur. Whereas one can easily perform work to heat up the system, it is not always enough to supply heat to increase the mechanical energy. At least two heat sources at different temperatures are needed as shown by Carnot's argument (sometimes one of the sources may be naturally supplied by the environment). Essentially the Second Law states that heat can never pass from a colder to a warmer body without some other related change occurring at the same time. The modern statement of this Principle of Dissipation is based upon the notion of entropy, introduced by Clausius in 1865. Clausius showed that for every thermodynamic system there exists a function of the state of the system, its entropy, denoted by S . The latter is defined by a differential relationship for the increase dS of the entropy of the system in an infinitesimally short time interval, during which a time reversible process occurs:

$$dS = \frac{d^*Q}{T} \quad (1)$$

Where d^*Q is the heat supplied to the system and T is the absolute temperature. (The notation d^*Q emphasizes that Q is not a state function and hence, in mathematical language, d^*Q is not an exact differential). For processes that are irreversible, one can only state that the increase of entropy in a process leading from an equilibrium state to another is larger than the increase that would occur a reversible process between the same two states:

$$dS \geq \frac{d^*Q}{T} \quad (2)$$

In order to transform this simple statement into a useful tool, it is necessary to build some structure for the evolution of the thermodynamic state of a system.

2. The Boltzmann Equation

The next step was provided by Boltzmann, who studied perfect gases with the tools of kinetic theory (see *Statistical Approach to Thermodynamics*). To explain the mechanical origin of irreversibility, Boltzmann considered what happens to the probability distribution of velocities of gas molecules when collisions occur. This led him to formulate a kinetic equation, subsequently called the Boltzmann equation, in which two-body collisions (like those between two billiard balls) play a leading role. Certain collisions (called direct collisions) cause decrease in the number of molecules with a certain velocity, while other collisions (called restoring collisions) increase that number. The occurrence of both direct and restoring collisions corresponds to the inherent reversibility of molecular events. Not only Boltzmann showed that the equation bearing his name admits Maxwell's distribution as an equilibrium solution, but he also gave a heuristic proof that it is the only possible one. To this end he introduced a quantity, which he denoted by E and was later (as here) denoted by H , defined in terms of the molecular velocity distribution. He then demonstrated that as a consequence of his equation, this function must always decrease in an isolated system or, at most, remain constant, the latter case occurring only if a state of statistical equilibrium prevails. Thus the Boltzmann equation is not time reversible. Boltzmann's result is usually quoted as the " H -theorem" and indicates that H must be proportional to (negative) entropy. H has an interesting interpretation as a measure of order in the molecular distribution; as a consequence S is a measure of randomness or chaos.

Despite its successes, the Boltzmann equation involves conceptual difficulties. Because it is time-irreversible, it violates the recurrence theorem of mechanics. This theorem states that the molecules composing a system of finite energy and size will return at some future time to very nearly their initial condition. Boltzmann proposed the correct way out of this paradox: his equation should be interpreted as describing what happens to most, not all, of the initial data. To illustrate this, two former students of Boltzmann, Paul and Tatyana Ehrenfest, introduced a picturesque model, colloquially referred to as the dog-flea model. Think of two dogs lying next to one another, with a total of N fleas shared between them. If the fleas jump only from one dog to the next, then after a time the number on each dog will have changed while the total number of fleas will be the

same. If the dogs are identical, after a long period of time we expect that each dog will have on the average $N/2$ fleas. This will be true even if all the fleas originally resided on only one dog. However, if one waits a much longer time, all the fleas will be back on the original dog. Something similar holds for the molecular dynamics; the recurrence time is, however, so long (extremely longer than the estimated age of the universe) that we never witness phenomena of this kind, which would violate the Second Law. The advantage of the Boltzmann equation is that its rigorous derivation can only be obtained by a limiting procedure, according to which these paradoxical events disappear because that occur at a time \bar{t} such that $\bar{t} \rightarrow \infty$, when the Boltzmann equation holds.

Moreover, it is possible to derive the laws of fluid flow, including the linear phenomenological equations, from the Boltzmann equation and to obtain explicit expressions for the heat conductivity and the viscosity of gases that agree with experimental measurements.

H was essentially defined by Boltzmann as the integral of $f \log f$ with respect to the molecular velocity, where \log denotes the natural logarithm and f is the one-particle distribution function. The latter, in the case of a monatomic gas, is a function of time t , position \mathbf{x} and molecular velocity \mathbf{v} and gives the expected number density of molecules in the six-dimensional phase space described by position \mathbf{x} and velocity \mathbf{v} . f satisfies the Boltzmann equation that can be written in the following form:

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \frac{\partial f}{\partial \mathbf{x}} = \int_{\mathbb{R}^3} \int_{\mathbb{S}} [f(\mathbf{x}, \mathbf{v}', t) f(\mathbf{x}, \mathbf{v}_*, t) - f(\mathbf{x}, \mathbf{v}, t) f(\mathbf{x}, \mathbf{v}_*, t)] |\mathbf{V}| \sigma_d (|\mathbf{V}|, \mathbf{V} \cdot \mathbf{n}) d\mathbf{v}_* d\mathbf{n} \quad (3)$$

where $\mathbf{V} = \mathbf{v}_* - \mathbf{v}$ is the relative velocity and σ_d the differential cross section. The velocities before a collision, \mathbf{v}' and \mathbf{v}_* are related to those after the same collision, \mathbf{v} and \mathbf{v}_* by

$$\begin{aligned} \mathbf{v}' &= \frac{1}{2}(\mathbf{v} + \mathbf{v}_* + |\mathbf{V}| \mathbf{n}), \\ \mathbf{v}_*' &= \frac{1}{2}(\mathbf{v} + \mathbf{v}_* - |\mathbf{V}| \mathbf{n}), \end{aligned} \quad (4)$$

Where \mathbf{n} is a unit vector, directed as the relative velocity after the collision. We denote three- and two-dimensional integrals by just one symbol \int , the dimensionality being clear from $d\mathbf{v}_*$ and $d\mathbf{n}$.

For polyatomic gases f depends on further variables describing the internal degrees of freedom of the molecule and the Boltzmann equation becomes more complicated.

By a detailed consideration of the properties of his equation, Boltzmann showed that the time derivative of H is never positive and vanishes if and only if the velocity distribution is a Maxwellian, provided the system cannot exchange heat with the

surroundings. The proof of this result requires that the space derivatives give zero contribution (such is the case for a gas in a spatially homogeneous state or inside a box with specularly reflecting walls). It is clear that H corresponds to the entropy except for a negative constant factor. The extension of this result to non-isolated systems was only provided in the second half of the 20th century and permits to deal with heat sources.

The molecular description is complicated since it must cover situations varying from ordinary temperature and pressures to nearly vacuum conditions. The case when the conditions occur was studied already by Maxwell and Boltzmann and was systematized by Chapman and Enskog in this century. The final result is better stated if one refers to the entropy per unit volume s .

$$\frac{\partial s}{\partial t} = \sigma = \sigma^{(r)} + \sigma^{(i)} \quad (5)$$

where σ is the entropy source per unit volume, decomposed into a reversible part

$$\sigma^{(r)} = -\nabla \cdot \left(s\mathbf{u} + \frac{\mathbf{q}}{T} \right) \quad (6)$$

and an irreversible one $\sigma^{(i)}$. Here \mathbf{q} is the heat flow vector and \mathbf{u} the (bulk) velocity vector; $\sigma^{(i)}$ in turn must be decomposed into two parts, the entropy transfer associated with the irreversible processes and a volume source that is non-negative. This decomposition will be discussed below.

According to the Chapman-Enskog solution of the Boltzmann equation for a simple gas (as opposed to a mixture) and in agreement with continuum mechanics, σ can be expressed as a sum of two terms, which can be written as a linear combination of $\sum_{ij} q_{ij} \eta_{ij}$ and $\sum_i q_i g_i$; here q_{ij}, η_{ij}, q_i , and g_i denote the components of the stress deviator, the rate of strain tensor, the heat flow vector, and the temperature gradient respectively. The same theory shows that in each of the above pairs of tensors and vectors, the first element depends linearly on the second with coefficients which may only depend on temperature and number density. This result must be postulated in continuum mechanics. The extensions of the theory to mixtures (see next section for details) shows that the pattern repeats itself: there are more gradients (the concentration densities also occur) and more quantities (such as the diffusion velocity) may depend on these quantities, but the entropy source is always a linear combination of terms which are products of two factors, a gradient and another factor describing a phenomenon typically associated with that gradient. New phenomena, such as thermal diffusion, were discovered by this kinetic theory approach that has, however, the serious limitation of being essentially restricted to rarefied gases. During World War II, thermal diffusion, an example of a so called cross-coupling in which a temperature gradient causes a diffusion flux, was used to separate fissionable isotopes of uranium.

Electric Phenomena can also be studied by means of a Boltzmann equation describing the statistical behavior of electrons. Results qualitatively similar to those found for a gas

can be proved in this case as well. In the next two sections we develop the Chapman-Enskog theory for the general case of a mixture.

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Biographical Sketch

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