

IV.3 Balance equations derived from the Boltzmann equation

We now investigate various balance equations that hold in a system obeying the Boltzmann equation, beginning with conservation laws, then going on with the celebrated H -theorem. Motivated by this theorem, we then define various equilibrium distributions.

IV.3.1 Conservation laws

IV.3.1 a Properties of the collision integral

Let $\mathcal{I}_{\text{coll.}}(1, 2, 3, 4)$ denote the integrand of the collision integral on the right-hand side of the Boltzmann equation (IV.15):

$$\left(\frac{\partial \bar{f}(1)}{\partial t} \right)_{\text{coll.}} = \int_{\vec{p}_2} \int_{\vec{p}_3} \int_{\vec{p}_4} \mathcal{I}_{\text{coll.}}(1, 2, 3, 4) \quad (\text{IV.18a})$$

with

$$\mathcal{I}_{\text{coll.}}(1, 2, 3, 4) \equiv \left[\bar{f}(3)\bar{f}(4) - \bar{f}(1)\bar{f}(2) \right] \tilde{w}(\vec{p}_1, \vec{p}_2 \rightarrow \vec{p}_3, \vec{p}_4) \quad (\text{IV.18b})$$

in the case of “classical” particles—the expression in the case of fermions resp. bosons can be read at once off Eq. (IV.16) resp. (IV.17).

This integrand obeys various properties that appear when the role of the particles are exchanged, irrespective of whether they are indistinguishable or not.

- (⊗) The integrand in the collision term of the Boltzmann equation is symmetric under the exchanges $\vec{p}_1 \leftrightarrow \vec{p}_2$ and $\vec{p}_3 \leftrightarrow \vec{p}_4$.

This symmetry is trivial.

- (⌘) The integrand in the collision term of the Boltzmann equation is antisymmetric under the simultaneous exchanges of $\vec{p}_1, \vec{p}_2$ with $\vec{p}_3, \vec{p}_4$.

This property is straightforward when one considers on the one hand the (mathematical) change of labels $1 \leftrightarrow 3, 2 \leftrightarrow 4$, which gives a minus sign, and on the other hand the physical microreversibility property encoded in Eq. (IV.5c).

Let $\chi(t, \vec{r}, \vec{p})$ denote a *collisional invariant*, i.e. a microscopic quantity which is conserved in every binary collision. Examples are particle number, linear momentum, or kinetic energy since the collisions are elastic: the quantity can thus be scalar or vectorial. One then has the general identity

$$\int \chi(t, \vec{r}, \vec{p}) \left(\frac{\partial \bar{f}}{\partial t} \right)_{\text{coll.}}(t, \vec{r}, \vec{p}) \frac{d^3 \vec{p}}{(2\pi\hbar)^3} = 0. \quad (\text{IV.19})$$

Let us use the notations $\bar{f}(1), \bar{f}(2), \dots$ as in Eq. (IV.15c), and accordingly $\chi(1) \equiv \chi(t, \vec{r}, \vec{p}_1)$, $\chi(2) \equiv \chi(t, \vec{r}, \vec{p}_2)$, and so on. Using Eq. (IV.18a) then gives

$$\int_{\vec{p}_1} \chi(1) \left(\frac{\partial \bar{f}(1)}{\partial t} \right)_{\text{coll.}} = \int_{\vec{p}_1} \int_{\vec{p}_2} \int_{\vec{p}_3} \int_{\vec{p}_4} \chi(1) \mathcal{I}_{\text{coll.}}(1, 2, 3, 4).$$

Exchanging first the dummy labels 1 and 2 of the integration variables, and invoking then the symmetry property (⊗) of the integrand of the collision term, one finds

$$\int_{\vec{p}_1} \chi(1) \left(\frac{\partial \bar{f}(1)}{\partial t} \right)_{\text{coll.}} = \int_{\vec{p}_2} \chi(2) \int_{\vec{p}_1} \int_{\vec{p}_3} \int_{\vec{p}_4} \mathcal{I}_{\text{coll.}}(2, 1, 3, 4) = \int_{\vec{p}_1} \int_{\vec{p}_2} \int_{\vec{p}_3} \int_{\vec{p}_4} \chi(2) \mathcal{I}_{\text{coll.}}(1, 2, 3, 4).$$

Combining the previous two equations, we may thus write

$$\int_{\vec{p}_1} \chi(1) \left(\frac{\partial \bar{f}(1)}{\partial t} \right)_{\text{coll.}} = \frac{1}{2} \int_{\vec{p}_1} \int_{\vec{p}_2} \int_{\vec{p}_3} \int_{\vec{p}_4} [\chi(1) + \chi(2)] \mathcal{I}_{\text{coll.}}(1, 2, 3, 4).$$

Invoking now the antisymmetry (⌘) after exchanging the dummy indices $1 \leftrightarrow 3$ and $2 \leftrightarrow 4$, one obtains

$$\int_{\vec{p}_1} \chi(1) \left(\frac{\partial \bar{f}(1)}{\partial t} \right)_{\text{coll.}} = \int_{\vec{p}_3} \chi(3) \int_{\vec{p}_1} \int_{\vec{p}_2} \int_{\vec{p}_4} \mathcal{I}_{\text{coll.}}(3, 4, 1, 2) = - \int_{\vec{p}_1} \int_{\vec{p}_2} \int_{\vec{p}_3} \int_{\vec{p}_4} \chi(3) \mathcal{I}_{\text{coll.}}(1, 2, 3, 4).$$

Similarly the exchange $1 \leftrightarrow 4$ and $2 \leftrightarrow 3$ yields:

$$\int_{\vec{p}_1} \chi(1) \left(\frac{\partial \bar{f}(1)}{\partial t} \right)_{\text{coll.}} = \int_{\vec{p}_4} \chi(4) \int_{\vec{p}_1} \int_{\vec{p}_2} \int_{\vec{p}_3} \mathcal{I}_{\text{coll.}}(4, 3, 2, 1) = - \int_{\vec{p}_1} \int_{\vec{p}_2} \int_{\vec{p}_3} \int_{\vec{p}_4} \chi(4) \mathcal{I}_{\text{coll.}}(1, 2, 3, 4).$$

Both previous lines lead to

$$\int_{\vec{p}_1} \chi(1) \left(\frac{\partial \bar{f}(1)}{\partial t} \right)_{\text{coll.}} = -\frac{1}{2} \int_{\vec{p}_1} \int_{\vec{p}_2} \int_{\vec{p}_3} \int_{\vec{p}_4} [\chi(3) + \chi(4)] \mathcal{I}_{\text{coll.}}(1, 2, 3, 4).$$

Gathering all intermediate results, there eventually comes

$$\int_{\vec{p}_1} \chi(1) \left(\frac{\partial \bar{f}(1)}{\partial t} \right)_{\text{coll.}} = \frac{1}{4} \int_{\vec{p}_1} \int_{\vec{p}_2} \int_{\vec{p}_3} \int_{\vec{p}_4} [\chi(1) + \chi(2) - \chi(3) - \chi(4)] \mathcal{I}_{\text{coll.}}(1, 2, 3, 4) = 0,$$

where the last identity comes from the local conservation property $\chi(1) + \chi(2) = \chi(3) + \chi(4)$ expressing the invariance of χ under binary collisions. $\square$

We can now replace χ by various conserved quantities.

IV.3.1 b Particle number conservation

As already mentioned, the (local) particle number density is the integral over momenta of the phase space distribution

$$n(t, \vec{r}) \equiv \int_{\vec{p}} \bar{f}(t, \vec{r}, \vec{p}). \quad (\text{IV.20a})$$

On the other hand, the particle-number flux density is naturally given by

$$\vec{J}_N(t, \vec{r}) \equiv \int_{\vec{p}} \bar{f}(t, \vec{r}, \vec{p}) \vec{v}, \quad (\text{IV.20b})$$

where each “phase-space cell” contributes with its velocity $\vec{v}$, weighted with the corresponding distribution.

Integrating now the Boltzmann equation (IV.8) over $\vec{p}$, and exchanging the order of the derivatives with respect to time or space and of the integral over velocities, the first term in the left-hand side gives $\partial n / \partial t$, the second term equals $\vec{\nabla}_{\vec{r}} \cdot \vec{J}_N$, while the third gives a vanishing contribution since $\bar{f}$ vanishes at the boundaries of velocity space, to ensure the convergence of the integral in the normalization condition (III.2a). In turn, considering identity (IV.19) with the collisional invariant $\chi = 1$, the integral over $\vec{p}$ of the collision term vanishes. All in all, one obtains the local conservation law

$$\frac{\partial n(t, \vec{r})}{\partial t} + \vec{\nabla} \cdot \vec{J}_N(t, \vec{r}) = 0, \quad (\text{IV.20c})$$

where we have dropped the now unnecessary subscript $\vec{r}$ on the gradient. This relation, known as *continuity equation*, is obviously of the general type (I.18). The immense progress is that n and $\vec{J}_N$ can now be computed starting from a microscopic theory—if $\bar{f}$ is known!—, instead of being postulated at the macroscopic level.

IV.3.1 c Energy conservation

As a second application, we can consider the collisional invariant $\chi(t, \vec{r}, \vec{p}) = \vec{p}^2 / 2m$, i.e. the kinetic energy.⁽⁴²⁾ We introduce the local kinetic-energy density

$$e_{\text{kin.}}(t, \vec{r}) = \int_{\vec{p}} \bar{f}(t, \vec{r}, \vec{p}) \frac{\vec{p}^2}{2m} \quad (\text{IV.21a})$$

and the local kinetic-energy flux density

$$\vec{J}_{E_{\text{kin.}}}(t, \vec{r}) = \int_{\vec{p}} \bar{f}(t, \vec{r}, \vec{p}) \frac{\vec{p}^2}{2m} \vec{v}. \quad (\text{IV.21b})$$

We first assume for simplicity that there is no external force acting on the particles.

Multiplying each term of the Boltzmann equation by $\vec{p}^2 / 2m$ and integrating over velocity, one finds the local conservation law

$$\frac{\partial e_{\text{kin.}}(t, \vec{r})}{\partial t} + \vec{\nabla} \cdot \vec{J}_{E_{\text{kin.}}}(t, \vec{r}) = 0, \quad (\text{IV.21c})$$

where identity (IV.19) has again been used.

⁽⁴²⁾... in the case of neutral particles.

In the presence of an external force $\vec{F}$ independent from the particle momentum, a straightforward integration by parts shows that there comes an extra term—the integral over velocity of $\vec{F} \cdot \vec{v}$ multiplied by $\bar{f}(t, \vec{r}, \vec{p})$ —, with a + sign if it is written as right-hand side of Eq. (IV.21c). This trivially corresponds to the work exerted by the external force per unit time.

Remarks:

* Alternatively, one can take for χ the sum of the kinetic energy $\vec{p}^2/2m$ and the potential energy due to the external force. The resulting balance equation is then the local conservation of total energy, of the type (IV.21c) with different energy density and flux density, even in the presence of the external force.

* As already noted in Sec. IV.1.2, the conservation of kinetic energy alone is conserved is related to the assumption of a weakly-interacting system, in which the relative amount of potential energy is small.

IV.3.1 d Momentum balance

Eventually, let χ be the i -th component p_i of linear momentum. Let

$$\vec{v}(t, \vec{r}) \equiv \frac{1}{n(t, \vec{r})} \vec{J}_N(t, \vec{r}) = \frac{1}{mn(t, \vec{r})} \int_{\vec{p}} \bar{f}(t, \vec{r}, \vec{p}) \vec{p} \quad (\text{IV.22a})$$

be the local *flow velocity* and

$$(\mathcal{J}_{\vec{p}})^{ij}(t, \vec{r}) = \frac{1}{n(t, \vec{r})} \int_{\vec{p}} \bar{f}(t, \vec{r}, \vec{p}) p^i v^j \quad (\text{IV.22b})$$

the j -th component of the local flux density of the i -th component of linear momentum.

By integrating the Boltzmann equation multiplied by p^i over momentum, one easily finds

$$\frac{\partial [mn(t, \vec{r}) v^i(t, \vec{r})]}{\partial t} + \sum_{j=1}^3 \frac{\partial}{\partial x^j} [n(t, \vec{r}) (\mathcal{J}_{\vec{p}})^{ij}(t, \vec{r})] = n(t, \vec{r}) F^i, \quad (\text{IV.22c})$$

which describes the rate of change of linear momentum under the influence of a force.

The property (IV.19) and the balance equations (IV.20)–(IV.22) will be recast in a different form in Sec. IV.5.1 below.

Remark: Inspecting Eqs. (IV.20b) and (IV.22a), one recognizes that the „local flow velocity“ is actually the average local velocity of particles, i.e. it is related to particle flow. In a relativistic theory, where particle number is not conserved—the corresponding scalar conserved quantity is rather a quantum number, like e.g. electric charge or baryon number—one may rather choose (after Landau) to define the flow velocity as the velocity derived from the flux of energy.

IV.3.2 H-theorem

A further consequence of the properties of the collision integral is the so-called H -theorem, which dates back to Boltzmann himself.

Given a solution $\bar{f}(t, \vec{r}, \vec{p})$ of the Boltzmann equation, a macroscopic quantity $H(t)$ is defined by⁽⁴³⁾

$$H(t) \equiv \int \bar{f}(t, \vec{r}, \vec{p}) \ln \bar{f}(t, \vec{r}, \vec{p}) d^6 \mathcal{V}, \quad (\text{IV.23})$$

with $d^6 \mathcal{V} \equiv d^3 \vec{r} d^3 \vec{p} / (2\pi\hbar)^3$ the measure on the (coarse-grained) single-particle phase space, as defined in Eq. (II.4b).

⁽⁴³⁾ $H(t)$ is not to be confused with the Hamilton function of the system. . .

One also defines a related quantity, which we shall for the time being without further justification call *Boltzmann entropy*, as

$$S_B(t) \equiv k_B \int \bar{f}(t, \vec{r}, \vec{p}) [1 - \ln \bar{f}(t, \vec{r}, \vec{p})] d^6\mathcal{V}, \quad (\text{IV.24})$$

with k_B the Boltzmann constant.

We can check at once the simple relation

$$S_B(t) = -k_B H(t) + \text{constant}, \quad (\text{IV.25})$$

where the unspecified constant is actually simply related to the total number of particles.

Remark: When adopting the generalizations (IV.16)–(IV.17) of the collision integral to fermions or bosons, one should accordingly modify the expressions of $H(t)$ and $S_B(t)$. For instance, one should consider

$$H(t) \equiv \int \left\{ \bar{f}(t, \vec{r}, \vec{p}) \ln \bar{f}(t, \vec{r}, \vec{p}) \pm [1 \mp \bar{f}(t, \vec{r}, \vec{p})] \ln [1 \mp \bar{f}(t, \vec{r}, \vec{p})] \right\} d^6\mathcal{V}, \quad (\text{IV.26})$$

where the upper (resp. lower) sign holds for fermions resp. bosons.

We can now turn to the *H-theorem*, which states that if just before a given time t_0 the system under study obeys the Boltzmann equation—and in particular fulfills the molecular chaos assumption—, then $H(t)$ decreases at time t_0

$$\frac{dH(t)}{dt} \leq 0. \quad (\text{IV.27})$$

There ensues at once that the Boltzmann entropy is increasing

$$\frac{dS_B(t)}{dt} \geq 0. \quad (\text{IV.28})$$

The proof of the *H-theorem* relies again on the properties of the collision integral. First, a straightforward differentiation yields, after exchanging the order of time derivative and integration over position and velocity,

$$\frac{dH(t)}{dt} = \int \frac{\partial}{\partial t} [\bar{f}(t, \vec{r}, \vec{p}) \ln \bar{f}(t, \vec{r}, \vec{p})] d^6\mathcal{V} = \int \frac{\partial \bar{f}(t, \vec{r}, \vec{p})}{\partial t} [1 + \ln \bar{f}(t, \vec{r}, \vec{p})] d^6\mathcal{V}.$$

Since $\bar{f}$ is a solution to the Boltzmann equation, the partial derivative $\partial \bar{f} / \partial t$ can then be rewritten with the help of Eq. (IV.8). The integral over $\vec{r}$ of the term $\vec{v} \cdot \vec{\nabla}_{\vec{r}} \bar{f}$ yields the difference of the values of $\bar{f}$ at the boundaries of position space, where f vanishes, so that the corresponding contribution is zero. The same reasoning and result hold for the integral over $\vec{p}$ of the term proportional to $\vec{\nabla}_{\vec{p}} \bar{f}$ —this is trivial if the force is velocity independent, and still holds when $\vec{F}$ depends on $\vec{v}$. All in all, one thus quickly finds

$$\frac{dH(t)}{dt} = \int \left(\frac{\partial \bar{f}}{\partial t} \right)_{\text{coll.}}(t, \vec{r}, \vec{p}) [1 + \ln \bar{f}(t, \vec{r}, \vec{p})] d^6\mathcal{V}. \quad (\text{IV.29})$$

This shows that $H(t)$ does not evolve in the absence of collision: the decrease in $H(t)$ is entirely due to the scattering processes.

To deal with the remaining integral in Eq. (IV.29), one can first use property (IV.19) with $\chi = 1$, to get rid of the constant 1 in the angular brackets of the integrand. We are then left with

$$\frac{dH(t)}{dt} = \int \left(\frac{\partial \bar{f}}{\partial t} \right)_{\text{coll.}}(t, \vec{r}, \vec{p}) \ln \bar{f}(t, \vec{r}, \vec{p}) d^6\mathcal{V} = \int \left[\int_{\vec{p}_1} \left(\frac{\partial \bar{f}(1)}{\partial t} \right)_{\text{coll.}} \ln \bar{f}(1) \right] d^3\vec{r},$$

where the second identity follows from renaming the integration variable $\vec{p}$ as $\vec{p}_1$ and using the shorthand notations already introduced in the previous section.

As in the proof of relation (IV.19) one can find by writing explicitly the collision integral in terms of its integrand and using the symmetry properties of the latter and the change of labels $1 \leftrightarrow 2$ the identities

$$\begin{aligned} \int_{\vec{p}_1} \left(\frac{\partial \bar{f}(1)}{\partial t} \right)_{\text{coll.}} \ln \bar{f}(1) &= \int_{\vec{p}_1} \int_{\vec{p}_2} \int_{\vec{p}_3} \int_{\vec{p}_4} \mathcal{I}_{\text{coll.}}(1, 2, 3, 4) \ln \bar{f}(1) = \int_{\vec{p}_2} \int_{\vec{p}_1} \int_{\vec{p}_3} \int_{\vec{p}_4} \mathcal{I}_{\text{coll.}}(2, 1, 3, 4) \ln \bar{f}(2) \\ &= \int_{\vec{p}_1} \int_{\vec{p}_2} \int_{\vec{p}_3} \int_{\vec{p}_4} \mathcal{I}_{\text{coll.}}(1, 2, 3, 4) \ln \bar{f}(2) \\ &= \frac{1}{2} \int_{\vec{p}_1} \int_{\vec{p}_2} \int_{\vec{p}_3} \int_{\vec{p}_4} \mathcal{I}_{\text{coll.}}(1, 2, 3, 4) [\ln \bar{f}(1) + \ln \bar{f}(2)]. \end{aligned}$$

Similarly one finds

$$\begin{aligned} \int_{\vec{p}_1} \left(\frac{\partial \bar{f}(1)}{\partial t} \right)_{\text{coll.}} \ln \bar{f}(1) &= - \int_{\vec{p}_1} \int_{\vec{p}_2} \int_{\vec{p}_3} \int_{\vec{p}_4} \mathcal{I}_{\text{coll.}}(1, 2, 3, 4) \ln \bar{f}(3) = - \int_{\vec{p}_2} \int_{\vec{p}_1} \int_{\vec{p}_3} \int_{\vec{p}_4} \mathcal{I}_{\text{coll.}}(1, 2, 3, 4) \ln \bar{f}(4) \\ &= - \frac{1}{2} \int_{\vec{p}_1} \int_{\vec{p}_2} \int_{\vec{p}_3} \int_{\vec{p}_4} \mathcal{I}_{\text{coll.}}(1, 2, 3, 4) [\ln \bar{f}(3) + \ln \bar{f}(4)]. \end{aligned}$$

This eventually gives

$$\frac{dH(t)}{dt} = \frac{1}{4} \int \left\{ \int_{\vec{p}_1} \int_{\vec{p}_2} \int_{\vec{p}_3} \int_{\vec{p}_4} \mathcal{I}_{\text{coll.}}(1, 2, 3, 4) [\ln \bar{f}(1) + \ln \bar{f}(2) - \ln \bar{f}(3) - \ln \bar{f}(4)] \right\} d^3 \vec{r}.$$

Replacing the integrand of the collision integral by its expression (IV.18b) and performing some straightforward algebra, one obtains

$$\begin{aligned} \frac{dH(t)}{dt} &= \frac{1}{4} \int \left\{ \int_{\vec{p}_1} \int_{\vec{p}_2} \int_{\vec{p}_3} \int_{\vec{p}_4} [\bar{f}(3)\bar{f}(4) - \bar{f}(1)\bar{f}(2)] \tilde{w}(\vec{p}_1, \vec{p}_2 \rightarrow \vec{p}_3, \vec{p}_4) \ln \frac{\bar{f}(1)\bar{f}(2)}{\bar{f}(3)\bar{f}(4)} \right\} d^3 \vec{r} \\ &= \frac{1}{4} \int \left\{ \int_{\vec{p}_1} \int_{\vec{p}_2} \int_{\vec{p}_3} \int_{\vec{p}_4} \bar{f}(3)\bar{f}(4) \left[1 - \frac{\bar{f}(1)\bar{f}(2)}{\bar{f}(3)\bar{f}(4)} \right] \ln \frac{\bar{f}(1)\bar{f}(2)}{\bar{f}(3)\bar{f}(4)} \tilde{w}(\vec{p}_1, \vec{p}_2 \rightarrow \vec{p}_3, \vec{p}_4) \right\} d^3 \vec{r}. \quad (\text{IV.30}) \end{aligned}$$

Now, the integrand is always negative—since $(1 - x) \ln x \leq 0$ for all x , while all other factors are positive—, which proves the H -theorem. $\square$

Remarks:

* Boltzmann's contemporaries strongly objected to his ideas, and in particular to the H theorem, due to their incomplete understanding of its content. One of the objections was that the assumed invariance of interactions under time reversal, combined with the invariance of the equations of motion (for instance the Hamilton equations) under time reversal, should lead to the equivalence of both time directions, while the H -theorem selects a time direction.

The answer to this apparent paradox is that $H(t)$ is not decreasing at any time, but only when the system satisfies the assumption of molecular chaos. Actually, the existence of a preferred time direction was somehow postulated from the beginning by Boltzmann, when he made the difference between the state of the system before a collision (molecular chaos, the particles are uncorrelated) and after (the particles are then correlated). There is thus no inconsistency if $H(t)$ distinguishes between both time directions.

* Defining the quantities

$$h(t, \vec{r}) \equiv \int_{\vec{p}} \bar{f}(t, \vec{r}, \vec{p}) \ln \bar{f}(t, \vec{r}, \vec{p}), \quad (\text{IV.31a})$$

$$\vec{\mathcal{J}}_H(t, \vec{r}) \equiv \int_{\vec{p}} \vec{v} \bar{f}(t, \vec{r}, \vec{p}) \ln \bar{f}(t, \vec{r}, \vec{p}), \quad (\text{IV.31b})$$

and

$$\sigma_H(t, \vec{r}) \equiv \int_{\vec{p}} \left(\frac{\partial \bar{\mathbf{f}}}{\partial t} \right)_{\text{coll.}}(t, \vec{r}, \vec{p}) [1 + \ln \bar{\mathbf{f}}(t, \vec{r}, \vec{p})] = \int_{\vec{p}} \left(\frac{\partial \bar{\mathbf{f}}}{\partial t} \right)_{\text{coll.}}(t, \vec{r}, \vec{p}) \ln \bar{\mathbf{f}}(t, \vec{r}, \vec{p}), \quad (\text{IV.31c})$$

one easily finds that they obey the local balance equation

$$\frac{\partial h(t, \vec{r})}{\partial t} + \vec{\nabla} \cdot \vec{\mathcal{J}}_H(t, \vec{r}) = \sigma_H(t, \vec{r}), \quad (\text{IV.31d})$$

which suggests the interpretation of h , $\mathcal{J}_H$ and σ_H as density, flux density and source density⁽⁴⁴⁾ of the H -quantity, respectively.

⁽⁴⁴⁾In this case it might be more appropriate to call it sink density, since $H(t)$ is decreasing.