IV.3.3 Equilibrium distributions

According to the H-theorem, $H(t)$ is a decreasing function of time—at least when the assumption of molecular chaos holds. Besides, the defining formula (IV.23) shows that $H(t)$ is bounded from below when the spatial volume $\mathcal{V}$ occupied by the system, and accordingly its total energy, is finite.

This follows from the finiteness of the available phase space—the finite energy of the system translates into an upper bound on momenta—and the fact that the product $x \ln x$ is always larger than $-1/\mathrm{e}$.

As a consequence, $H(t)$ converges in the limit $t \to \infty$, i.e. its derivative vanishes:

$$\frac{\mathrm{d}H(t)}{\mathrm{d}t} = 0 \tag{IV.32}$$

or equivalently $\mathrm{d}S_B(t)/\mathrm{d}t = 0$. In this section, we define and discuss two types of distributions that fulfill this condition:

- the *global equilibrium distribution* $\bar{\mathsf{f}}_{\text{eq.}}(\vec{r},\vec{p})$ is defined as a stationary solution of the Boltzmann equation
$$\frac{\partial \bar{\mathsf{f}}_{\text{eq.}}}{\partial t} = 0 \tag{IV.33}$$
obeying Eq. (IV.32). In that case, the system has reached global thermodynamic equilibrium, with uniform values of the temperature T and of the average velocity $\vec{\mathsf{v}}$ of particles, as well as of their number density n (or equivalently the chemical potential μ) when there is no external force. In particular, $\bar{\mathsf{f}}_{\text{eq.}}$ cancels the collision integral (IV.15c).

- *local equilibrium distributions*, hereafter denoted as $\bar{\mathsf{f}}^{(0)}(t,\vec{r},\vec{p})$, cancel the collision term of the Boltzmann equation—and thereby obey condition (IV.32)—, yet are in general not solutions to the whole equation itself.

In practice, an out-of-equilibrium system first tends, under the influence of collisions alone, towards a state of local equilibrium. In a second step, the interplay of collisions and the drift terms drives the system towards global equilibrium.

Remarks:

$*$ If the spatial volume occupied by the system is unbounded, then H resp. S_B is not necessarily bounded from below resp. above, and thus a state of global equilibrium may never be reached. This is for instance the case for a collection of particles expanding initially confined into a small region of space left free to expand into the vacuum.

$*$ Even if the system is confined in a finite volume, it may still be "stuck" in a persistent non-equilibrium setup. An example is that of a gas performing undamped "monopole" oscillations in a spherically symmetric harmonic trap, as studied theoretically e.g. in Ref. [34] and realized experimentally (to a good approximation) with cold ^{87}Rb atoms [35].

IV.3.3 a Global equilibrium

For simplicity, we begin with the case when the system is homogeneous and there is no external force. Consistency then implies that the distribution function $\bar{\mathsf{f}}$ is independent of $\vec{r}$. This in particular holds for the equilibrium distribution, $\bar{\mathsf{f}}_{\text{eq.}}(\vec{p})$, and the corresponding particle density n.

Inspecting the derivative (IV.30), one sees that the equilibrium condition $\mathrm{d}H(t)/\mathrm{d}t = 0$ can only be fulfilled if the always-negative integrand is actually vanishing itself, which implies the identity

$$\bar{\mathsf{f}}_{\text{eq.}}(\vec{p}_1)\bar{\mathsf{f}}_{\text{eq.}}(\vec{p}_2) = \bar{\mathsf{f}}_{\text{eq.}}(\vec{p}_3)\bar{\mathsf{f}}_{\text{eq.}}(\vec{p}_4),$$

for every quadruplet $(\vec{p}_1, \vec{p}_2, \vec{p}_3, \vec{p}_4)$ satisfying the kinetic-energy- and momentum-conservation relationships (IV.3) and allowed by the requirements on the system, in case the latter has a finite energy. From now on we assume that $\bar{\mathsf{f}}_{\text{eq.}}$ is everywhere non-zero.[46] Taking the logarithm of the above relation gives

$$\ln \bar{\mathsf{f}}_{\text{eq.}}(\vec{p}_1) + \ln \bar{\mathsf{f}}_{\text{eq.}}(\vec{p}_2) = \ln \bar{\mathsf{f}}_{\text{eq.}}(\vec{p}_3) + \ln \bar{\mathsf{f}}_{\text{eq.}}(\vec{p}_4),$$

which expresses that $\ln \bar{\mathsf{f}}_{\text{eq.}}(\vec{p})$ is a quantity conserved in any elastic two-to-two collision, and is thus a linear combination of additive collision invariants $\chi(\vec{p})$. Assuming that particle number—amounting to $\chi(\vec{p}) = 1$—, momentum $[\chi(\vec{p}) = \vec{p}]$ and kinetic energy $[\chi(\vec{p}) = \vec{p}^{\,2}/2m]$ form a basis of the latter,[47] one can write $\ln \bar{\mathsf{f}}_{\text{eq.}}(\vec{p}) = A' + \vec{B}\,' \cdot \vec{p} + C'\vec{p}^{\,2}$, with constant A', $\vec{B}\,'$, C'. Equivalently, one has (with new, related constants A, C and $\vec{p}_0$)

$$\bar{\mathsf{f}}_{\text{eq.}}(\vec{p}) = C\,\mathrm{e}^{-A(\vec{p}-\vec{p}_0)^2}. \tag{IV.34}$$

Following relation (IV.2), the momentum-space integral of $\bar{\mathsf{f}}_{\text{eq.}}(\vec{p})$ should yield the particle number density n, which necessitates $C = (4\pi\hbar^2 A)^{3/2} n$. The integral of the product $\bar{\mathsf{f}}_{\text{eq.}}(\vec{p})\,\vec{p}$ with $\bar{\mathsf{f}}_{\text{eq.}}$ of the form (IV.34) over the whole phase space then gives $\vec{p}_0$, which should equal the total momentum of the particles; the latter vanishes if the particles are studied in their global rest frame, yielding $\vec{p}_0 = \vec{0}$. Eventually, the momentum-space integral of $\bar{\mathsf{f}}_{\text{eq.}}(\vec{p})\,\vec{p}^{\,2}/2m$ should give n times the average kinetic energy per particle, while Eq. (IV.34), together with the relation between C and A found above, leads to $3n/4mA$. Denoting the average kinetic energy per particle by $\frac{3}{2}k_BT$, one thus finds $A = 1/2mk_BT$. All in all, one obtains

$$\boxed{\bar{\mathsf{f}}_{\text{eq.}}(\vec{p}) = n\left(\frac{2\pi\hbar^2}{mk_BT}\right)^{3/2} \mathrm{e}^{-\vec{p}^{\,2}/2mk_BT},} \tag{IV.35}$$

which is the Maxwell[an]–Boltzmann distribution.[48]

One easily checks that the latter actually also cancels the left-hand side of the Boltzmann equation in the absence of external force, i.e. it represents the global equilibrium distribution.

Remark: The Maxwell–Boltzmann distribution (IV.35) was probably known to the reader as the single-particle phase-space distribution of a classical ideal monoatomic gas at thermodynamic equilibrium studied in the canonical ensemble. Here it emerges as the (almost) universal long-time limit of the out-of-equilibrium evolution of a Boltzmann gas, in which the average energy per particle was "arbitrarily" denoted by $\frac{3}{2}k_BT$, where T has no other interpretation. This constitutes a totally different vision, yet the fact that both approaches yield the same distribution hints at the consistency of their results.

In case the system is subject to an external force deriving from a time-independent scalar potential, $\vec{F} = -\vec{\nabla}V(\vec{r})$, the stationary equilibrium solution of the Boltzmann equation is no longer spatially homogeneous, but becomes

$$\bar{\mathsf{f}}_{\text{eq.}}(\vec{r},\vec{p}) = n(\vec{r})\left(\frac{2\pi\hbar^2}{mk_BT}\right)^{3/2} \mathrm{e}^{-\vec{p}^{\,2}/2mk_BT} \quad \text{with} \quad n(\vec{r}) \equiv \frac{N\,\mathrm{e}^{-V(\vec{r})/k_BT}}{\displaystyle\int \mathrm{e}^{-V(\vec{r})/k_BT}\,\mathrm{d}^3\vec{r}}. \tag{IV.36}$$

[46] The identically vanishing distribution $\bar{\mathsf{f}} \equiv 0$ is clearly stationary and does fulfill condition (IV.32), yet it of course leads to a vanishing particle number, i.e. it represents a very boring system!

[47] A proof was given by Grad [36], which is partly reproduced by Sommerfeld [37, § 42]. An alternative argument is that if there were yet another kinematic collisional invariant in two-to-two scatterings, it would yield a fifth condition on the outgoing momenta—the requirement of having two particles in the final state leaves the constraints from energy and momentum conservation—, and thus restrict their angles, which is not the case.

[48] possibly up to the normalization factor, since in these lecture notes $\bar{\mathsf{f}}$ is dimensionless and normalized to the total number of particles, while the "usual" Maxwell–Boltzmann distribution is rather a probability distribution.

[an] J. C. Maxwell, 1831–1879

Boltzmann entropy of the global equilibrium distribution

Inserting the equilibrium distribution (IV.36) into the Boltzmann entropy (IV.24), one finds with the help of Eq. (A.1c)

$$S_B = Nk_B \ln\left[\frac{\mathcal{V}}{N}\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2}\right] + \frac{5}{2}Nk_B, \tag{IV.37}$$

where $\mathcal{V}$ is the volume occupied by the particles. This result coincides with the *Sackur*[ao]*–Tetrode*[ap] *formula* [38, 39] for the thermodynamic entropy of a classical ideal gas under the same conditions. This shows that at equilibrium the Boltzmann entropy, which is also defined out of equilibrium, coincides with the thermodynamic entropy.

IV.3.3 b Local equilibrium

A non-equilibrated macroscopic system of weakly-interacting classical particles will not reach the global equilibrium distribution (IV.35) at once, the approach to equilibrium can be decomposed in "successive" (not in a strict chronological sense, but rather logically) steps involving various time scales [cf. Eqs. (III.16), (III.17)]:

i. Over the shortest time scale $\tau_{\rm c}$, neighbouring particles scatter on each other. These collisions—which strictly speaking are *not* described by the Boltzmann equation—lead to the emergence of molecular chaos.

ii. Once molecular chaos holds, scatterings tend to drive the system to a state of local equilibrium, described by local thermodynamic variables as defined in chapter I: particle number density $n(t,\vec{r})$, temperature $T(t,\vec{r})$ and average particle velocity $\vec{\mathsf{v}}(t,\vec{r})$. That is, the single-particle distribution $\bar{\mathsf{f}}$ relaxes to a *local equilibrium distribution*, of the form

$$\boxed{\bar{\mathsf{f}}^{(0)}(t,\vec{r},\vec{p}) = n(t,\vec{r})\left[\frac{2\pi\hbar^2}{mk_BT(t,\vec{r})}\right]^{3/2}\exp\left\{-\frac{\left[\vec{p}-m\vec{\mathsf{v}}(t,\vec{r})\right]^2}{2mk_BT(t,\vec{r})}\right\},} \tag{IV.38}$$

which cancels the collision integral on the right-hand side of the Boltzmann equation. This relaxation takes place over a time scale $\tau_{\rm r}$, which physically should be (much) larger than $\tau_{\rm c}$ since it involves "many" local scatterings.

iii. Eventually, the state of local equilibrium relaxes to that of global equilibrium over the time scales $\tau_{\rm s}$, $\tau_{\rm e}$ defined in Eq. (III.16). This step in the evolution of the single-particle distribution $\bar{\mathsf{f}}$, which is now rather driven by the slow drift terms on the left-hand side of the Boltzmann equation, is more conveniently described in terms of the evolution of local thermodynamic quantities obeying macroscopic equations, in particular those of hydrodynamics, as will be described in Sec. IV.5.

Remark: In general, the distribution (IV.38) does not cancel the left-hand side of the Boltzmann equation and is thus not a solution of the equation. This is however not a problem, since the single-particle distribution $\bar{\mathsf{f}}$ never really equals a given $\bar{\mathsf{f}}^{(0)}$, it only tends momentarily towards it: the three steps which above have been described as successive actually take place simultaneously.

IV.3.3 c Equilibrium distributions of the Boltzmann equation for bosons and fermions

The kinetic equations with a collision integral which simulates either the Pauli[aq] principle of particles with half-integer spin [Eq. (IV.16)] or the "gregariousness" of particles with integer spin [Eq. (IV.17)] also obey an H-theorem, and thus tend at large time to respective stationary equilibrium distributions $\bar{\mathsf{f}}^{\rm F}_{\rm eq.}$ and $\bar{\mathsf{f}}^{\rm B}_{\rm eq.}$.

[ao] H. M. Sackur, 1895–1931 [ap] O. Tetrode, 1880–1914 [aq] W. Pauli, 1900–1958

Repeating a reasoning analogous to that in paragraph IV.3.3 a, with $\bar{\mathsf{f}}_{\rm eq.}$ replaced by $\bar{\mathsf{f}}^{\rm F}_{\rm eq.}/(1-\bar{\mathsf{f}}^{\rm F}_{\rm eq.})$ or $\bar{\mathsf{f}}^{\rm B}_{\rm eq.}/(1+\bar{\mathsf{f}}^{\rm B}_{\rm eq.})$, one finds after some straightforward algebra

$$\boxed{\bar{\mathsf{f}}^{\rm F}_{\rm eq.}(\vec{p}) = \frac{1}{C^{\rm F}\exp(\vec{p}^{\,2}/2mk_BT)+1}} \tag{IV.39a}$$

and

$$\boxed{\bar{\mathsf{f}}^{\rm B}_{\rm eq.}(\vec{p}) = \frac{1}{C^{\rm B}\exp(\vec{p}^{\,2}/2mk_BT)-1},} \tag{IV.39b}$$

with $C^{\rm F}$, $C^{\rm B}$ two constants ensuring the proper normalization of the distributions. These are respectively the Fermi–Dirac and Bose–Einstein distributions as found within equilibrium statistical mechanics for ideal quantum gases.