8.2: Boltzmann Transport Theory

Derivation of the Boltzmann equation

For simplicity of presentation, we assume point particles. Recall that

$$f(\mathbf{r},\mathbf{p},t)\,d^3\!r\,d^3\!p \equiv \begin{cases} \text{\rm\# of particles with positions within } d^3\!r \text{ of} \\ \mathbf{r} \text{ and momenta within } d^3\!p \text{ of } \mathbf{p} \text{ at time } t. \end{cases} \tag{8.2.1}$$

We now ask how the distribution functions $f(\mathbf{r},\mathbf{p},t)$ evolves in time. It is clear that in the absence of collisions, the distribution function must satisfy the continuity equation,

$$\frac{\partial f}{\partial t}+\boldsymbol{\nabla}\!\cdot\!(\mathbf{u}f)=0\ . \tag{8.2.2}$$

This is just the condition of number conservation for particles. Take care to note that $\boldsymbol{\nabla}$ and $\mathbf{u}$ are *six*-dimensional *phase space* vectors:

$$\begin{aligned} \mathbf{u} &= (\,\dot{x}\,,\,\dot{y}\,,\,\dot{z}\,,\,\dot{p}_x\,,\,\dot{p}_y\,,\,\dot{p}_z\,) \\ \boldsymbol{\nabla} &= \left(\frac{\partial}{\partial x},\frac{\partial}{\partial y},\frac{\partial}{\partial z},\frac{\partial}{\partial p_x},\frac{\partial}{\partial p_y},\frac{\partial}{\partial p_z}\right)\ . \end{aligned}$$

The continuity equation describes a distribution in which each constituent particle evolves according to a prescribed dynamics, which for a mechanical system is specified by

$$\frac{d\mathbf{r}}{dt}=\frac{\partial H}{\partial \mathbf{p}}=\mathbf{v}(\mathbf{p}) \qquad , \qquad \frac{d\mathbf{p}}{dt}=-\frac{\partial H}{\partial \mathbf{r}}=\mathbf{F}_{ext}\ , \tag{8.2.3}$$

where $\mathbf{F}$ is an external applied force. Here,

$$H(\mathbf{p},\mathbf{r})=\varepsilon(\mathbf{p})+U_{ext}(\mathbf{r})\ . \tag{8.2.4}$$

For example, if the particles are under the influence of gravity, then $U_{ext}(\mathbf{r})=m\mathbf{g}\cdot\mathbf{r}$ and $\mathbf{F}=-\boldsymbol{\nabla}U_{ext}=-m\mathbf{g}$.

Note that as a consequence of the dynamics, we have $\boldsymbol{\nabla}\!\cdot\!\mathbf{u}=0$, phase space flow is *incompressible*, provided that $\varepsilon(\mathbf{p})$ is a function of $\mathbf{p}$ alone, and not of $\mathbf{r}$. Thus, in the absence of collisions, we have

$$\frac{\partial f}{\partial t}+\mathbf{u}\cdot\boldsymbol{\nabla}f=0\ . \tag{8.2.5}$$

The differential operator $D_t\equiv\partial_t+\mathbf{u}\cdot\boldsymbol{\nabla}$ is sometimes called the 'convective derivative', because $D_t f$ is the time derivative of f in a comoving frame of reference.

Next we must consider the effect of collisions, which are not accounted for by the semiclassical dynamics. In a collision process, a particle with momentum $\mathbf{p}$ and one with momentum $\tilde{\mathbf{p}}$ can instantaneously convert into a pair with momenta $\mathbf{p}'$ and $\tilde{\mathbf{p}}'$, provided total momentum is conserved: $\mathbf{p}+\tilde{\mathbf{p}}=\mathbf{p}'+\tilde{\mathbf{p}}'$. This means that $D_t f\neq 0$. Rather, we should write

$$\frac{\partial f}{\partial t}+\dot{\mathbf{r}}\cdot\frac{\partial f}{\partial \mathbf{r}}+\dot{\mathbf{p}}\cdot\frac{\partial f}{\partial \mathbf{p}}=\left(\frac{\partial f}{\partial t}\right)_{coll} \tag{8.2.6}$$

where the right side is known as the *collision integral*. The collision integral is in general a *function* of $\mathbf{r}$, $\mathbf{p}$, and t and a *functional* of the distribution f.

After a trivial rearrangement of terms, we can write the Boltzmann equation as

$$\frac{\partial f}{\partial t}=\left(\frac{\partial f}{\partial t}\right)_{str}+\left(\frac{\partial f}{\partial t}\right)_{coll}, \tag{8.2.7}$$

where

$$\left(\frac{\partial f}{\partial t}\right)_{str}\equiv-\dot{\mathbf{r}}\cdot\frac{\partial f}{\partial \mathbf{r}}-\dot{\mathbf{p}}\cdot\frac{\partial f}{\partial \mathbf{p}} \tag{8.2.8}$$

is known as the *streaming term*. Thus, there are two contributions to $\partial f/\partial t$: streaming and collisions.

Collisionless Boltzmann equation

In the absence of collisions, the Boltzmann equation is given by

$$\frac{\partial f}{\partial t}+\frac{\partial \varepsilon}{\partial \mathbf{p}}\cdot\frac{\partial f}{\partial \mathbf{r}}-\boldsymbol{\nabla}U_{ext}\cdot\frac{\partial f}{\partial \mathbf{p}}=0\ . \tag{8.2.9}$$

In order to gain some intuition about how the streaming term affects the evolution of the distribution $f(\mathbf{r},\mathbf{p},t)$, consider a case where $\mathbf{F}_{ext}=0$. We then have

$$\frac{\partial f}{\partial t}+\frac{\mathbf{p}}{m}\cdot\frac{\partial f}{\partial \mathbf{r}}=0\ . \tag{8.2.10}$$

Clearly, then, *any* function of the form

$$f(\mathbf{r},\mathbf{p},t)=\varphi\big(\mathbf{r}-\mathbf{v}(\mathbf{p})\,t\,,\,\mathbf{p}\big) \tag{8.2.11}$$

will be a solution to the collisionless Boltzmann equation, where $\mathbf{v}(\mathbf{p})=\frac{\partial\varepsilon}{\partial\mathbf{p}}$. One possible solution would be the Boltzmann distribution,

$$f(\mathbf{r},\mathbf{p},t)=e^{\mu/k_BT}e^{-\mathbf{p}^2/2mk_BT}\ , \tag{8.2.12}$$

which is time-independent[1]. Here we have assumed a ballistic dispersion, $\varepsilon(\mathbf{p})=\mathbf{p}^2/2m$.

For a slightly less trivial example, let the initial distribution be $\varphi(\mathbf{r},\mathbf{p})=A\,e^{-\mathbf{r}^2/2\sigma^2}e^{-\mathbf{p}^2/2\kappa^2}$, so that

$$f(\mathbf{r},\mathbf{p},t)=A\,e^{-\left(\mathbf{r}-\frac{\mathbf{p}t}{m}\right)^2/2\sigma^2}\,e^{-\mathbf{p}^2/2\kappa^2}\ . \tag{8.2.13}$$

Consider the one-dimensional version, and rescale position, momentum, and time so that

$$f(x,p,t)=A\,e^{-\frac{1}{2}(\bar{x}-\bar{p}\,\bar{t})^2}\,e^{-\frac{1}{2}\bar{p}^2}\ . \tag{8.2.14}$$

Consider the level sets of f, where $f(x,p,t)=A\,e^{-\frac{1}{2}\alpha^2}$. The equation for these sets is

$$\bar{x}=\bar{p}\,\bar{t}\pm\sqrt{\alpha^2-\bar{p}^2}\ . \tag{8.2.15}$$

For fixed $\bar{t}$, these level sets describe the loci in phase space of equal probability densities, with the probability density decreasing exponentially in the parameter α^2. For $\bar{t}=0$, the initial distribution describes a Gaussian cloud of particles with a Gaussian momentum distribution. As $\bar{t}$ increases, the distribution widens in $\bar{x}$ but not in $\bar{p}$ – each particle moves with a constant momentum, so the set of momentum values never changes. However, the level sets in the $(\bar{x}\,,\,\bar{p})$ plane become elliptical, with a semimajor axis oriented at an angle $\theta = ctn^{-1}(t)$ with respect to the $\bar{x}$ axis. For $\bar{t} > 0$, he particles at the outer edges of the cloud are more likely to be moving away from the center. See the sketches in Figure [Fstreaming]

Suppose we add in a constant external force $\mathbf{F}_{ext}$. Then it is easy to show (and left as an exercise to the reader to prove) that any function of the form

$$f(\mathbf{r},\mathbf{p},t) = A\,\varphi\bigg(\mathbf{r} - \frac{\mathbf{p}\,t}{m} + \frac{\mathbf{F}_{ext}\,t^2}{2m}\,,\,\mathbf{p} - \frac{\mathbf{F}_{ext}\,t}{m}\bigg) \tag{8.2.16}$$

satisfies the collisionless Boltzmann equation (ballistic dispersion assumed).

[Fstreaming] Level sets for a sample $f(\bar{x},\bar{p},\bar{t}) = A\,e^{-\frac{1}{2}(\bar{x}-\bar{p}\bar{t})^2} e^{-\frac{1}{2}\bar{p}^2}$, for values $f = A\,e^{-\frac{1}{2}\alpha^2}$ with α in equally spaced intervals from $\alpha = 0.2$ (red) to $\alpha = 1.2$ (blue). The time variable $\bar{t}$ is taken to be $\bar{t} = 0.0$ (upper left), 0.2 (upper right), 0.8 (lower right), and 1.3 (lower left).

Collisional invariants

Consider a function $A(\mathbf{r},\mathbf{p})$ of position and momentum. Its average value at time t is

$$A(t) = \int\! d^3\!r\, d^3\!p\; A(\mathbf{r},\mathbf{p})\, f(\mathbf{r},\mathbf{p},t)\ . \tag{8.2.17}$$

Taking the time derivative,

$$\begin{aligned}
\frac{dA}{dt} &= \int\! d^3\!r\, d^3\!p\; A(\mathbf{r},\mathbf{p})\,\frac{\partial f}{\partial t} \\
&= \int\! d^3\!r\, d^3\!p\; A(\mathbf{r},\mathbf{p})\,\bigg\{ -\frac{\partial}{\partial\mathbf{r}}\cdot(\dot{\mathbf{r}} f) - \frac{\partial}{\partial\mathbf{p}}\cdot(\dot{\mathbf{p}} f) + \bigg(\frac{\partial f}{\partial t}\bigg)_{coll}\bigg\} \\
&= \int\! d^3\!r\, d^3\!p\; \bigg\{ \bigg(\frac{\partial A}{\partial\mathbf{r}}\cdot\frac{d\mathbf{r}}{dt} + \frac{\partial A}{\partial\mathbf{p}}\cdot\frac{d\mathbf{p}}{dt}\bigg) f + A(\mathbf{r},\mathbf{p})\,\bigg(\frac{\partial f}{\partial t}\bigg)_{coll}\bigg\}\ .
\end{aligned}$$

Hence, if A is preserved by the dynamics between collisions, then[2]

$$\frac{dA}{dt} = \frac{\partial A}{\partial\mathbf{r}}\cdot\frac{d\mathbf{r}}{dt} + \frac{\partial A}{\partial\mathbf{p}}\cdot\frac{d\mathbf{p}}{dt} = 0\ . \tag{8.2.18}$$

We therefore have that the rate of change of A is determined wholly by the collision integral

$$\frac{dA}{dt} = \int\! d^3\!r\, d^3\!p\; A(\mathbf{r},\mathbf{p})\,\bigg(\frac{\partial f}{\partial t}\bigg)_{coll}\ . \tag{8.2.19}$$

Quantities which are then conserved in the collisions satisfy $\dot{A} = 0$. Such quantities are called *collisional invariants*. Examples of collisional invariants include the particle number $(A = 1)$, the components of the total momentum $(A = p_\mu)$ (in the absence of broken translational invariance, due to the presence of walls), and the total energy $(A = \varepsilon(\mathbf{p}))$.

Scattering processes

What sort of processes contribute to the collision integral? There are two broad classes to consider. The first involves potential scattering, where a particle in state $|\Gamma\rangle$ scatters, in the presence of an external potential, to a state $|\Gamma'\rangle$. Recall that Γ is an abbreviation for the set of kinematic variables, $\Gamma = (\mathbf{p},\mathbf{L})$ in the case of a diatomic molecule. For point particles, $\Gamma = (p_x, p_y, p_z)$ and $d\Gamma = d^3\!p$.

We now define the function $w\big(\Gamma'|\Gamma\big)$ such that

$$w\big(\Gamma'|\Gamma\big)\, f(\mathbf{r},\Gamma;t)\, d\Gamma\, d\Gamma' = \begin{cases} \text{rate at which a particle within } d\Gamma \text{ of } (\mathbf{r},\Gamma) \\ \text{scatters to within } d\Gamma' \text{ of } (\mathbf{r},\Gamma') \text{ at time } t. \end{cases} \tag{8.2.20}$$

The units of $w\,d\Gamma$ are therefore $1/T$. The differential scattering cross section for particle scattering is then

$$d\sigma = \frac{w\big(\Gamma'|\Gamma\big)}{n\,|\mathbf{v}|}\, d\Gamma'\ , \tag{8.2.21}$$

where $\mathbf{v} = \mathbf{p}/m$ is the particle's velocity and n the density.

The second class is that of two-particle scattering processes, $|\Gamma\Gamma_1\rangle \to |\Gamma'\Gamma'_1\rangle$. We define the scattering function $w\big(\Gamma'\Gamma'_1\,|\,\Gamma\Gamma_1\big)$ by

$$w\big(\Gamma'\Gamma'_1\,|\,\Gamma\Gamma_1\big)\, f_2(\mathbf{r},\Gamma;\mathbf{r},\Gamma_1\,;\,t)\, d\Gamma\, d\Gamma_1\, d\Gamma'\, d\Gamma'_1 = \begin{cases} \text{rate at which two particles within } d\Gamma \text{ of } (\mathbf{r},\Gamma) \\ \text{and within } d\Gamma_1 \text{ of } (\mathbf{r},\Gamma_1) \text{ scatter into states within} \\ d\Gamma' \text{ of } (\mathbf{r},\Gamma') \text{ and } d\Gamma'_1 \text{ of } (\mathbf{r},\Gamma'_1) \text{ at time } t\backslash,, \end{cases} \tag{8.2.22}$$

where

$$f_2(\mathbf{r},\mathbf{p}\,;\,\mathbf{r}',\mathbf{p}'\,;\,t) = \Big\langle \sum_{i,j} \delta\big(\mathbf{x}_i(t) - \mathbf{r}\big)\,\delta\big(\mathbf{p}_i(t) - \mathbf{p}\big)\,\delta\big(\mathbf{x}_j(t) - \mathbf{r}'\big)\,\delta\big(\mathbf{p}_j(t) - \mathbf{p}'\big)\Big\rangle \tag{8.2.23}$$

is the nonequilibrium two-particle distribution for point particles. The differential scattering cross section is

$$d\sigma = \frac{w\big(\Gamma'\Gamma'_1\,|\,\Gamma\Gamma_1\big)}{|\mathbf{v} - \mathbf{v}_1|}\, d\Gamma'\, d\Gamma'_1\ . \tag{8.2.24}$$

We assume, in both cases, that any scattering occurs *locally*, the particles attain their asymptotic kinematic states on distance scales small compared to the mean interparticle separation. In this case we can treat each scattering process independently. This assumption is particular to rarefied systems, gases, and is not appropriate for dense liquids. The two types of scattering processes are depicted in Figure [FCIscatt].

[FCIscatt] Left: single particle scattering process $|\Gamma\rangle \to |\Gamma'\rangle$. Right: two-particle scattering process $|\Gamma\Gamma_1\rangle \to |\Gamma'\Gamma'_1\rangle$.

In computing the collision integral for the state $|\mathbf{r},\Gamma\rangle$, we must take care to sum over contributions from transitions *out of* this state, $|\Gamma\rangle \to |\Gamma'\rangle$, which reduce $f(\mathbf{r},\Gamma)$, and transitions *into* this state, $|\Gamma'\rangle \to |\Gamma\rangle$, which increase $f(\mathbf{r},\Gamma)$. Thus, for one-body scattering, we have

$$\frac{D}{Dt}\,f(\mathbf{r},\Gamma;t)=\left(\frac{\partial f}{\partial t}\right)_{coll}=\int\!d\Gamma'\,\Big\{w(\Gamma\,|\,\Gamma')\,f(\mathbf{r},\Gamma';t)-w(\Gamma'\,|\,\Gamma)\,f(\mathbf{r},\Gamma;t)\Big\}\ . \tag{8.2.25}$$

For two-body scattering, we have

$$\begin{aligned}\frac{D}{Dt}\,f(\mathbf{r},\Gamma;t)&=\left(\frac{\partial f}{\partial t}\right)_{coll}\\ &=\int\!d\Gamma_1\!\int\!d\Gamma'\!\int\!d\Gamma'_1\,\Big\{w\big(\Gamma\Gamma_1\,|\,\Gamma'\Gamma'_1\big)\,f_2(\mathbf{r},\Gamma';\mathbf{r},\Gamma'_1;t)\\ &\qquad\qquad -w\big(\Gamma'\Gamma'_1\,|\,\Gamma\Gamma_1\big)\,f_2(\mathbf{r},\Gamma;\mathbf{r},\Gamma_1;t)\Big\}\ .\end{aligned}$$

Unlike the one-body scattering case, the kinetic equation for two-body scattering does not close, since the LHS involves the one-body distribution $f\equiv f_1$ and the RHS involves the two-body distribution f_2. To close the equations, we make the *approximation*

$$f_2(\mathbf{r},\Gamma';\tilde{\mathbf{r}},\tilde{\Gamma};t)\approx f(\mathbf{r},\Gamma;t)\,f(\tilde{\mathbf{r}},\tilde{\Gamma};t)\ . \tag{8.2.26}$$

We then have

$$\begin{aligned}\frac{D}{Dt}\,f(\mathbf{r},\Gamma;t)\,&=\int\!d\Gamma_1\!\int\!d\Gamma'\!\int\!d\Gamma'_1\,\Big\{w\big(\Gamma\Gamma_1\,|\,\Gamma'\Gamma'_1\big)\,f(\mathbf{r},\Gamma';t)\,f(\mathbf{r},\Gamma'_1;t)\\ &\qquad\qquad -w\big(\Gamma'\Gamma'_1\,|\,\Gamma\Gamma_1\big)\,f(\mathbf{r},\Gamma;t)\,f(\mathbf{r},\Gamma_1;t)\Big\}\ .\end{aligned}$$

Detailed balance

Classical mechanics places some restrictions on the form of the kernel $w\big(\Gamma\Gamma_1\,|\,\Gamma'\Gamma'_1\big)$. In particular, if \Gamma^\sss{T}=(-\Bp,-\BL) denotes the kinematic variables under time reversal, then

w\big(\Gamma'\Gamma'_1 \, | \, \Gamma\Gamma_1\big)= w\big(\Gamma^\sss{T}\Gamma^\sss{T}_1 \, | \,\Gamma'{}^\sss{T}\Gamma'_1{}^\sss{T}\big)\ . \label{TRw}

This is because the time reverse of the process $|\Gamma\Gamma_1\rangle \to |\Gamma'\Gamma'_1\rangle$ is \tket{\Gamma'{}^\ssr{T}\Gamma'_1{}^\ssr{T}}\to\tket{\Gamma^\ssr{T}\Gamma^\ssr{T}_1}.

In equilibrium, we must have

w\big(\Gamma'\Gamma'_1 \, | \, \Gamma\Gamma_1\big)\,\,f^0(\Gamma)\,f^0(\Gamma\ns_1) \,d^4\!\Gamma= w\big(\Gamma^\sss{T}\Gamma^\sss{T}_1 \, | \,\Gamma'{}^\sss{T}\Gamma'_1{}^\sss{T}\big)\,f^0(\Gamma'{

where

d^4\!\Gamma\equiv d\Gamma\,d\Gamma\ns_1\,d\Gamma' d\Gamma'_1\qquad,\qquad d^4\!\Gamma^\sss{T}\equiv d\Gamma^\sss{T}\,d\Gamma_1^\sss{T}\,d\Gamma'{}^\sss{T} d\Gamma'_1{}^\sss{T}\ .

Since d\Gamma=d\Gamma^\sss{T} , we may cancel the differentials above, and after invoking Equation [TRw] and suppressing the common $\mathbf{r}$ label, we find

f^0(\Gamma)\,f^0(\Gamma\ns_1)=f^0(\Gamma'{}^\sss{T})\,f^0(\Gamma'_1{}^\sss{T})\ .

This is the condition of *detailed balance*. For the Boltzmann distribution, we have

$$f^0(\Gamma)=A\,e^{-\varepsilon/k_BT}\ , \tag{8.2.27}$$

where A is a constant and where $\varepsilon=\varepsilon(\Gamma)$ is the kinetic energy, $\varepsilon(\Gamma)=\mathbf{p}^2/2m$ in the case of point particles. Note that \ve({\Gamma^\sss{T}})=\ve(\Gamma). Detailed balance is satisfied because the kinematics of the collision requires energy conservation:

$$\varepsilon+\varepsilon_1=\varepsilon'+\varepsilon'_1\ . \tag{8.2.28}$$

Since momentum is also kinematically conserved,

$$\mathbf{p}+\mathbf{p}_1=\mathbf{p}'+\mathbf{p}'_1\ , \tag{8.2.29}$$

any distribution of the form

$$f^0(\Gamma)=A\,e^{-(\varepsilon-\mathbf{p}\cdot\mathbf{V})/k_BT} \tag{8.2.30}$$

also satisfies detailed balance, for any velocity parameter $\mathbf{V}$. This distribution is appropriate for gases which are flowing with average particle $\mathbf{V}$.

In addition to time-reversal, parity is also a symmetry of the microscopic mechanical laws. Under the parity operation P, we have $\mathbf{r}\to-\mathbf{r}$ and $\mathbf{p}\to-\mathbf{p}$. Note that a pseudovector such as $\mathbf{L}=\mathbf{r}\times\mathbf{p}$ is unchanged under P. Thus, \Gamma^\sss{P}=(-\Bp,\BL). Under the combined operation of $C=PT$, we have \Gamma^\sss{C}=(\Bp,-\BL). If the microscopic Hamiltonian is invariant under C, then we must have

w\big(\Gamma'\Gamma'_1 \, | \, \Gamma\Gamma\ns_1\big)=w\big(\Gamma^\sss{C}\Gamma_1^\sss{C} \, | \, \Gamma'{}^\sss{C}\Gamma'_1{}^\sss{C}\big)\ .

For point particles, invariance under T and P then means

$$w(\mathbf{p}',\mathbf{p}'_1\,|\,\mathbf{p},\mathbf{p}_1)=w(\mathbf{p},\mathbf{p}_1\,|\,\mathbf{p}',\mathbf{p}'_1)\ , \tag{8.2.31}$$

and therefore the collision integral takes the simplified form,

$$\begin{aligned}\frac{Df(\mathbf{p})}{Dt}&=\left(\frac{\partial f}{\partial t}\right)_{coll}\\ &=\int\!d^3\!p_1\!\int\!d^3\!p'\!\int\!d^3\!p'_1\,w(\mathbf{p}',\mathbf{p}'_1\,|\,\mathbf{p},\mathbf{p}_1)\,\Big\{f(\mathbf{p}')\,f(\mathbf{p}'_1)-f(\mathbf{p})\,f(\mathbf{p}_1)\Big\}\ ,\end{aligned}$$

where we have suppressed both $\mathbf{r}$ and t variables.

The most general statement of detailed balance is

$$\frac{f^0(\Gamma')\,f^0(\Gamma_1')}{f^0(\Gamma)\,f^0(\Gamma_1)}=\frac{w\big(\Gamma'\Gamma_1'\,|\,\Gamma\Gamma_1\big)}{w\big(\Gamma\Gamma_1\,|\,\Gamma'\Gamma_1'\big)}\ . \tag{8.2.32}$$

Under this condition, the collision term vanishes for $f=f^0$, which is the equilibrium distribution.

Kinematics and cross section

We can rewrite Equation [BEwp] in the form

$$\frac{Df(\mathbf{p})}{Dt}=\int\! d^3\!p_1\!\int\! d\Omega\,|\mathbf{v}-\mathbf{v}_1|\,\frac{\partial\sigma}{\partial\Omega}\,\Big\{f(\mathbf{p}')\,f(\mathbf{p}_1')-f(\mathbf{p})\,f(\mathbf{p}_1)\Big\}\ , \tag{8.2.33}$$

where $\frac{\partial\sigma}{\partial\Omega}$ is the *differential scattering cross section*. If we recast the scattering problem in terms of center-of-mass and relative coordinates, we conclude that the total momentum is conserved by the collision, and furthermore that the energy in the CM frame is conserved, which means that the magnitude of the *relative* momentum is conserved. Thus, we may write $\mathbf{p}'-\mathbf{p}_1'=|\mathbf{p}-\mathbf{p}_1|\,\hat{\mathbf{\Omega}}$, where $\hat{\mathbf{\Omega}}$ is a unit vector. Then $\mathbf{p}'$ and $\mathbf{p}_1'$ are determined to be

$$\begin{aligned}\mathbf{p}'&=\frac{1}{2}\big(\mathbf{p}+\mathbf{p}_1+|\mathbf{p}-\mathbf{p}_1|\,\hat{\mathbf{\Omega}}\big)\\ \mathbf{p}_1'&=\frac{1}{2}\big(\mathbf{p}+\mathbf{p}_1-|\mathbf{p}-\mathbf{p}_1|\,\hat{\mathbf{\Omega}}\big)\ .\end{aligned}$$

H-theorem

Let's consider the Boltzmann equation with two particle collisions. We define the local ($\mathbf{r}$-dependent) quantity

$$\rho_\varphi(\mathbf{r},t)\equiv\int\! d\Gamma\;\varphi(\Gamma,f)\,f(\Gamma,\mathbf{r},t)\ . \tag{8.2.34}$$

At this point, $\varphi(\Gamma,f)$ is arbitrary. Note that the $\varphi(\Gamma,f)$ factor has $\mathbf{r}$ and t dependence through its dependence on f, which itself is a function of $\mathbf{r}$, Γ, and t. We now compute

$$\begin{aligned}\frac{\partial\rho_\varphi}{\partial t}=\int\! d\Gamma\;\frac{\partial(\varphi f)}{\partial t}&=\int\! d\Gamma\;\frac{\partial(\varphi f)}{\partial f}\,\frac{\partial f}{\partial t}\\ &=-\int\! d\Gamma\;\mathbf{u}\cdot\boldsymbol{\nabla}(\varphi f)-\int\! d\Gamma\;\frac{\partial(\varphi f)}{\partial f}\,\bigg(\frac{\partial f}{\partial t}\bigg)_{coll}\\ &=-\oint\! d\Sigma\;\hat{\mathbf{n}}\cdot(\mathbf{u}\,\varphi f)-\int\! d\Gamma\;\frac{\partial(\varphi f)}{\partial f}\,\bigg(\frac{\partial f}{\partial t}\bigg)_{coll}\ .\end{aligned}$$

The first term on the last line follows from the divergence theorem, and vanishes if we assume $f=0$ for infinite values of the kinematic variables, which is the only physical possibility. Thus, the rate of change of ρ_φ is entirely due to the collision term. Thus,

$$\begin{aligned}\frac{\partial\rho_\varphi}{\partial t}&=\int\! d\Gamma\!\int\! d\Gamma_1\!\int\! d\Gamma'\!\int\! d\Gamma_1'\,\Big\{w\big(\Gamma'\Gamma_1'\,|\,\Gamma\Gamma_1\big)\,ff_1\,\chi-w\big(\Gamma\Gamma_1\,|\,\Gamma'\Gamma_1'\big)\,f'f_1'\,\chi\Big\}\\ &=\int\! d\Gamma\!\int\! d\Gamma_1\!\int\! d\Gamma'\!\int\! d\Gamma_1'\;w\big(\Gamma'\Gamma_1'\,|\,\Gamma\Gamma_1\big)\,ff_1\,(\chi-\chi')\ ,\end{aligned}$$

where $f\equiv f(\Gamma)$, $f'\equiv f(\Gamma')$, $f_1\equiv f(\Gamma_1)$, $f_1'\equiv f(\Gamma_1')$, $\chi=\chi(\Gamma)$, with

$$\chi=\frac{\partial(\varphi f)}{\partial f}=\varphi+f\,\frac{\partial\varphi}{\partial f}\ . \tag{8.2.35}$$

We now invoke the symmetry

$$w\big(\Gamma'\Gamma_1'\,|\,\Gamma\Gamma_1\big)=w\big(\Gamma_1'\,\Gamma'\,|\,\Gamma_1\,\Gamma\big)\ , \tag{8.2.36}$$

which allows us to write

$$\frac{\partial\rho_\varphi}{\partial t}=\frac{1}{2}\int\! d\Gamma\!\int\! d\Gamma_1\!\int\! d\Gamma'\!\int\! d\Gamma_1'\;w\big(\Gamma'\Gamma_1'\,|\,\Gamma\Gamma_1\big)\,ff_1\,(\chi+\chi_1-\chi'-\chi_1')\ . \tag{8.2.37}$$

This shows that ρ_φ is preserved by the collision term if $\chi(\Gamma)$ is a collisional invariant.

Now let us consider $\varphi(f)=\ln f$. We define $\mathsf{h}\equiv\rho\big|_{\varphi=\ln f}$. We then have

$$\frac{\partial\mathsf{h}}{\partial t}=-\frac{1}{2}\int\! d\Gamma\!\int\! d\Gamma_1\!\int\! d\Gamma'\!\int\! d\Gamma_1'\;w\,f'f_1'\cdot x\ln x\ , \tag{8.2.38}$$

where $w\equiv w\big(\Gamma'\Gamma_1'\,|\,\Gamma\Gamma_1\big)$ and $x\equiv ff_1/f'f_1'$. We next invoke the result

$$\int\! d\Gamma'\!\int\! d\Gamma_1'\;w\big(\Gamma'\Gamma_1'\,|\,\Gamma\Gamma_1\big)=\int\! d\Gamma'\!\int\! d\Gamma_1'\;w\big(\Gamma\Gamma_1\,|\,\Gamma'\Gamma_1'\big) \tag{8.2.39}$$

which is a statement of unitarity of the scattering matrix[3]. Multiplying both sides by $f(\Gamma)\,f(\Gamma_1)$, then integrating over Γ and Γ_1, and finally changing variables $(\Gamma,\Gamma_1)\leftrightarrow(\Gamma',\Gamma_1')$, we find

$$0=\int\! d\Gamma\!\int\! d\Gamma_1\!\int\! d\Gamma'\!\int\! d\Gamma_1'\;w\,\big(ff_1-f'f_1'\big)=\int\! d\Gamma\!\int\! d\Gamma_1\!\int\! d\Gamma'\!\int\! d\Gamma_1'\;w\,f'f_1'\,(x-1)\ . \tag{8.2.40}$$

Multiplying this result by $\frac{1}{2}$ and adding it to the previous equation for $\dot{\mathsf{h}}$, we arrive at our final result,

$$\frac{\partial\mathsf{h}}{\partial t}=-\frac{1}{2}\int\! d\Gamma\!\int\! d\Gamma_1\!\int\! d\Gamma'\!\int\! d\Gamma_1'\;w\,f'f_1'\,(x\ln x-x+1)\ . \tag{8.2.41}$$

Note that w, f', and f_1' are all nonnegative. It is then easy to prove that the function $g(x)=x\ln x-x+1$ is nonnegative for all positive x values[4], which therefore entails the important result

$$\frac{\partial\mathsf{h}(\mathbf{r},t)}{\partial t}\le 0\ . \tag{8.2.42}$$

Boltzmann's H function is the space integral of the h density: $\mathsf{H}=\int\! d^3\!r\;\mathsf{h}$.

Thus, everywhere in space, the function $\mathsf{h}(\mathbf{r},t)$ is monotonically decreasing or constant, due to collisions. In equilibrium, $\dot{\mathsf{h}}=0$ everywhere, which requires $x=1$,

$$f^0(\Gamma)\,f^0(\Gamma_1)=f^0(\Gamma')\,f^0(\Gamma_1')\ , \tag{8.2.43}$$

or, taking the logarithm,

$$\ln f^0(\Gamma)+\ln f^0(\Gamma_1)=\ln f^0(\Gamma')+\ln f^0(\Gamma_1')\ . \tag{8.2.44}$$

But this means that $\ln f^0$ is itself a collisional invariant, and if 1, $\mathbf{p}$, and ε are the only collisional invariants, then $\ln f^0$ must be expressible in terms of them. Thus,

$$\ln f^0 = \frac{\mu}{k_B T} + \frac{\mathbf{V}\cdot\mathbf{p}}{k_B T} - \frac{\varepsilon}{k_B T} \ , \tag{8.2.45}$$

where μ, $\mathbf{V}$, and T are constants which parameterize the equilibrium distribution $f^0(\mathbf{p})$, corresponding to the chemical potential, flow velocity, and temperature, respectively.