III.C The Bogoliubov-Born-Green-Kirkwood-Yvon Hierarchy

The full phase space density contains much more information than necessary for description of equilibrium properties. For example, knowledge of the one particle distribution is sufficient for computing the pressure of a gas. A one particle density refers to the expectation value of finding *any* of the N particles at location $\vec{q}$, with momentum $\vec{p}$, at time t, which is computed from the full density ρ as

$$
\begin{aligned}
f_1(\vec{p}, \vec{q}, t) &= \left\langle \sum_{i=1}^{N} \delta^3(\vec{p} - \vec{p}_i)\delta^3(\vec{q} - \vec{q}_i) \right\rangle \\
&= N \int \prod_{i=2}^{N} d^3\vec{p}_i d^3\vec{q}_i \rho(\vec{p}_1 = \vec{p}, \vec{q}_1 = \vec{q}, \vec{p}_2, \vec{q}_2, \cdots, \vec{p}_N, \vec{q}_N, t).
\end{aligned}
\tag{III.15}
$$

To obtain the second identity above, we used the delta functions to perform one set of integrals, and assumed that the density is symmetric with respect to permuting the particles. Similarly, a two body density can be computed from

$$
f_2(\vec{p}_1, \vec{q}_1, \vec{p}_2, \vec{q}_2, t) = N(N-1) \int \prod_{i=3}^{N} dV_i \; \rho(\vec{p}_1, \vec{q}_1, \vec{p}_2, \vec{q}_2, \cdots, \vec{p}_N, \vec{q}_N, t),
\tag{III.16}
$$

where $dV_i = d^3\vec{p}_i d^3\vec{q}_i$ is the contribution of particle i to phase space volume. The general s-particle density is defined by

$$
f_s(\vec{p}_1, \cdots, \vec{q}_s, t) = \frac{N!}{(N-s)!} \int \prod_{i=s+1}^{N} dV_i \; \rho(\mathbf{p}, \mathbf{q}, t) = \frac{N!}{(N-s)!}\rho_s(\vec{p}_1, \cdots, \vec{q}_s, t),
\tag{III.17}
$$

where ρ_s is a standard *unconditional PDF* for the coordinates of s particles, and $\rho_N \equiv \rho$. While ρ_s is properly normalized to unity when integrated over all its variable, the s-particle density has a normalization of $N!/(N-s)!$. We shall use the two quantities interchangably.

The evolution of the few-body densities is governed by the BBGKY hierarchy of equations attributed to Bogoliubov, Born, Green, Kirkwood, and Yvon. The simplest non-trivial Hamiltonian that can be studied in kinetic theory is

$$
\mathcal{H}(\mathbf{p}, \mathbf{q}) = \sum_{i=1}^{N} \left[\frac{\vec{p}_i{}^2}{2m} + U(\vec{q}_i) \right] + \frac{1}{2} \sum_{(i,j)=1}^{N} \mathcal{V}(\vec{q}_i - \vec{q}_j).
\tag{III.18}
$$

This Hamiltonian provides an adequate description of a weakly interacting gas. In addition to the classical kinetic energy of particles of mass m, it contains an *external potential*

U, and a *two-body interaction* $\mathcal{V}$, between the particles. In principle, three and higher body interactions should also be included for a realistic description, but they are not very important in the dilute gas (nearly ideal) limit.

For evaluating the time evolution of f_s, it is convenient to divide the Hamiltonian into

$$\mathcal{H} = \mathcal{H}_s + \mathcal{H}_{N-s} + \mathcal{H}', \tag{III.19}$$

where $\mathcal{H}_s$ and $\mathcal{H}_{N-s}$ include only interactions among each group of particles,

$$
\begin{aligned}
\mathcal{H}_s &= \sum_{n=1}^{s} \left[\frac{\vec{p}_n^{\,2}}{2m} + U(\vec{q}_n) \right] + \frac{1}{2} \sum_{(n,m)=1}^{s} \mathcal{V}(\vec{q}_n - \vec{q}_m), \\
\mathcal{H}_{N-s} &= \sum_{i=s+1}^{N} \left[\frac{\vec{p}_i^{\,2}}{2m} + U(\vec{q}_i) \right] + \frac{1}{2} \sum_{(i,j)=s+1}^{N} \mathcal{V}(\vec{q}_i - \vec{q}_j),
\end{aligned}
\tag{III.20}
$$

while the interparticle interactions are contained in

$$\mathcal{H}' = \sum_{n=1}^{s} \sum_{i=s+1}^{N} \mathcal{V}(\vec{q}_n - \vec{q}_i). \tag{III.21}$$

From eq.(III.17), the time evolution of f_s (or ρ_s) is obtained as

$$\frac{\partial \rho_s}{\partial t} = \int \prod_{i=s+1}^{N} dV_i \, \frac{\partial \rho}{\partial t} = \int \prod_{i=s+1}^{N} dV_i \, \{\rho, \mathcal{H}_s + \mathcal{H}_{N-s} + \mathcal{H}'\}, \tag{III.22}$$

where eq.(III.9) is used for the evolution of ρ. The three Poisson brackets in eq.(III.22) will now be evaluated in turn. Since the first s coordinates are not integrated, the order of integrations and differentiations for the Poisson bracket may be reversed, and

$$\int \prod_{i=s+1}^{N} dV_i \, \{\rho, \mathcal{H}_s\} = \left\{ \left(\int \prod_{i=s+1}^{N} dV_i \, \rho \right), \mathcal{H}_s \right\} = \{\rho_s, \mathcal{H}_s\}. \tag{III.23}$$

Writing the Poisson brackets explicitly, the second term of eq.(III.22) takes the form

$$\int \prod_{i=s+1}^{N} dV_i \, \{\rho, \mathcal{H}_{N-s}\} = \int \prod_{i=s+1}^{N} dV_i \sum_{j=1}^{N} \left[\frac{\partial \rho}{\partial \vec{p}_j} \cdot \frac{\partial \mathcal{H}_{N-s}}{\partial \vec{q}_j} - \frac{\partial \rho}{\partial \vec{q}_j} \cdot \frac{\partial \mathcal{H}_{N-s}}{\partial \vec{p}_j} \right]$$

(using eq.(III.20))

$$= \int \prod_{i=s+1}^{N} dV_i \sum_{j=s+1}^{N} \left[\frac{\partial \rho}{\partial \vec{p}_j} \cdot \left(\frac{\partial U}{\partial \vec{q}_j} + \frac{1}{2} \sum_{k=s+1}^{N} \frac{\partial \mathcal{V}(\vec{q}_j - \vec{q}_k)}{\partial \vec{q}_j} \right) - \frac{\partial \rho}{\partial \vec{q}_j} \cdot \frac{\vec{p}_j}{m} \right] = 0. \tag{III.24}$$

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The last equality is obtained after performing the integrations by part: The term multiplying $\partial\rho/\partial\vec{p}_j$ has no dependence on $\vec{p}_j$, while $\vec{p}_j/m$ does not depend on $\vec{q}_j$. The final term in eq.(III.22), involving the Poisson bracket with $\mathcal{H}'$, is

$$\int \prod_{i=s+1}^{N} dV_i \sum_{j=1}^{N} \left[\frac{\partial\rho}{\partial\vec{p}_j} \cdot \frac{\partial\mathcal{H}'}{\partial\vec{q}_j} - \frac{\partial\rho}{\partial\vec{q}_j} \cdot \frac{\partial\mathcal{H}'}{\partial\vec{p}_j} \right]$$

$$= \int \prod_{i=s+1}^{N} dV_i \left[\sum_{n=1}^{s} \frac{\partial\rho}{\partial\vec{p}_n} \cdot \sum_{j=s+1}^{N} \frac{\partial\mathcal{V}(\vec{q}_n - \vec{q}_j)}{\partial\vec{q}_n} + \sum_{j=s+1}^{N} \frac{\partial\rho}{\partial\vec{p}_j} \cdot \sum_{n=1}^{s} \frac{\partial\mathcal{V}(\vec{q}_j - \vec{q}_n)}{\partial\vec{q}_j} \right],$$

where the sum over all particles has been subdivided into the two groups. (Note that $\mathcal{H}'$ in eq.(III.21) has no dependence on the momenta.) Integration by parts shows that the second term in the above expression is zero. The first term involves the sum of $(N-s)$ expressions that are equal by symmetry and simplifies to

$$(N-s) \int \prod_{i=s+1}^{N} dV_i \sum_{n=1}^{s} \frac{\partial\mathcal{V}(\vec{q}_n - \vec{q}_{s+1})}{\partial\vec{q}_n} \cdot \frac{\partial\rho}{\partial\vec{p}_n}$$

$$= (N-s) \sum_{n=1}^{s} \int dV_{s+1} \frac{\partial\mathcal{V}(\vec{q}_n - \vec{q}_{s+1})}{\partial\vec{q}_n} \cdot \frac{\partial}{\partial\vec{p}_n} \left[\int \prod_{i=s+2}^{N} dV_i \, \rho \right]. \tag{III.25}$$

Note that the quantity in the above square brackets is ρ_{s+1}. Thus, adding up eqs.(III.23), (III.24), and (III.25),

$$\frac{\partial\rho_s}{\partial t} + \{\mathcal{H}_s, \rho_s\} = (N-s) \sum_{n=1}^{s} \int dV_{s+1} \frac{\partial\mathcal{V}(\vec{q}_n - \vec{q}_{s+1})}{\partial\vec{q}_n} \cdot \frac{\partial\rho_{s+1}}{\partial\vec{p}_n}, \tag{III.26}$$

or in terms of the densities f_s,

$$\frac{\partial f_s}{\partial t} + \{\mathcal{H}_s, f_s\} = \sum_{n=1}^{s} \int dV_{s+1} \frac{\partial\mathcal{V}(\vec{q}_n - \vec{q}_{s+1})}{\partial\vec{q}_n} \cdot \frac{\partial f_{s+1}}{\partial\vec{p}_n}. \tag{III.27}$$

In the absence of interactions with other particles, the density ρ_s for a group of s particles, evolves as the density of an incompressible fluid (as required by Liouville's theorem), and is described by the *streaming terms* on the left hand side of eq.(III.26). However, because of interactions with the remaining $N-s$ particles, the flow is modified by the *collision terms* on the right hand side. The collision integral is the sum of the terms corresponding to a potential collision of any of the particles in the group of s, with any of the remaining $N-s$ particles. To describe the probability of finding the additional particle that collides with a member of this group, the result must depend on the joint PDF of $s+1$ particles described by ρ_{s+1}. This results in a hierarchy of equations with $\dot{\rho}_1$ depends on ρ_2, $\dot{\rho}_2$ depends on ρ_3, etc., which is at least as complicated as the original equation for the full phase space density. To proceed further, a reasonable approximation for terminating the hierarchy is needed.

III.D The Boltzmann Equation

To estimate the relative importance of the different terms appearing in eqs.(III.27), let us examine the first two equations in the hierarchy,

$$\left[\frac{\partial}{\partial t} - \frac{\partial U}{\partial \vec{q}_1} \cdot \frac{\partial}{\partial \vec{p}_1} + \frac{\vec{p}_1}{m} \cdot \frac{\partial}{\partial \vec{q}_1}\right] f_1 = \int dV_2 \, \frac{\partial \mathcal{V}(\vec{q}_1 - \vec{q}_2)}{\partial \vec{q}_1} \cdot \frac{\partial f_2}{\partial \vec{p}_1}, \qquad \text{(III.28)}$$

and

$$\left[\frac{\partial}{\partial t} - \frac{\partial U}{\partial \vec{q}_1} \cdot \frac{\partial}{\partial \vec{p}_1} - \frac{\partial U}{\partial \vec{q}_2} \cdot \frac{\partial}{\partial \vec{p}_2} + \frac{\vec{p}_1}{m} \cdot \frac{\partial}{\partial \vec{q}_1} + \frac{\vec{p}_2}{m} \cdot \frac{\partial}{\partial \vec{q}_2} - \frac{\partial \mathcal{V}(\vec{q}_1 - \vec{q}_2)}{\partial \vec{q}_1} \cdot \left(\frac{\partial}{\partial \vec{p}_1} - \frac{\partial}{\partial \vec{p}_2}\right)\right] f_2 = $$
$$\int dV_3 \, \left[\frac{\partial \mathcal{V}(\vec{q}_1 - \vec{q}_3)}{\partial \vec{q}_1} \cdot \frac{\partial}{\partial \vec{p}_1} + \frac{\partial \mathcal{V}(\vec{q}_2 - \vec{q}_3)}{\partial \vec{q}_2} \cdot \frac{\partial}{\partial \vec{p}_2}\right] f_3 \quad .$$
$$\text{(III.29)}$$

Note that two of the streaming terms in eq.(III.29) have been combined by using $\partial \mathcal{V}(\vec{q}_1 - \vec{q}_2)/\partial \vec{q}_1 = -\partial \mathcal{V}(\vec{q}_2 - \vec{q}_1)/\partial \vec{q}_2$, which is valid for a *symmetric* potential such that $\mathcal{V}(\vec{q}_1 - \vec{q}_2) = \mathcal{V}(\vec{q}_2 - \vec{q}_1)$.

• *Time scales:* All terms within square brackets in the above equations have dimensions of inverse time, and we estimate their relative magnitudes by dimensional analysis, using typical velocities and length scales. The typical speed of a gas particle at room temperature is $v \approx 10^2 ms^{-1}$. For terms involving the external potential U, or the inter-atomic potential potential $\mathcal{V}$, an appropriate length scale can be extracted from the range of variations of the potential.

(a) The terms proportional to

$$\frac{1}{\tau_U} \sim \frac{\partial U}{\partial \vec{q}} \cdot \frac{\partial}{\partial \vec{p}} \, ,$$

involve spatial variations of the external potential $U(\vec{q})$, which take place over macroscopic distances L. We shall refer to the associated time τ_U, as an *extrinsic* time scale, as it can be made arbitrarily long by increasing system size. For a typical value of $L \approx 10^{-3} m$, we get $\tau_U \approx L/v \approx 10^{-5} s$.

(b) From the terms involving the inter-atomic potential $\mathcal{V}$, we can extract two additional time scales, which are *intrinsic* to the gas under study. In particular, the *collision duration*

$$\frac{1}{\tau_c} \sim \frac{\partial \mathcal{V}}{\partial \vec{q}} \cdot \frac{\partial}{\partial \vec{p}} \, ,$$

is the typical time over which two particles are within the effective range d, of their interaction. For *short range* interactions (including van der Waals and Lenard–Jones, despite their power law decaying tails), $d \approx 10^{-10} m$ is of the order of a typical atomic

size, resulting in $\tau_c \approx 10^{-12}s$. This is usually the shortest time scale in the problem. The situation is somewhat more complicated for *long range* interactions, such as the Coulomb gas in a plasma. For a neutral plasma, the Debye screening length λ replaces d in the above equation, as discussed in problems.

(c) There are also collision terms on the right hand side of eqs.(III.27), which depend on f_{s+1}, and lead to an inverse time scale

$$\frac{1}{\tau_\times} \sim \int dV \, \frac{\partial \mathcal{V}}{\partial \vec{q}} \cdot \frac{\partial}{\partial \vec{p}} \, \frac{f_{s+1}}{f_s} \sim \int dV \, \frac{\partial \mathcal{V}}{\partial \vec{q}} \cdot \frac{\partial}{\partial \vec{p}} \, N \frac{\rho_{s+1}}{\rho_s}.$$

The integrals are only non-zero over the volume of the inter-particle potential d^3. The term f_{s+1}/f_s is related to the probability of finding another particle per unit volume, which is roughly the particle density $n = N/V \approx 10^{26} m^{-3}$. We thus obtain the *mean free time*

$$\tau_\times \approx \frac{\tau_c}{nd^3} \approx \frac{1}{nvd^2}, \tag{III.30}$$

which is the typical distance a particle travels between collisions. For short range interactions, $\tau_\times \approx 10^{-8}s$ is much longer than τ_c, and the collision terms on the right hand side of eqs.(III.27) are smaller by a factor of $nd^3 \approx (10^{26}m^{-3})(10^{-10}m)^3 \approx 10^{-4}$.

The *Boltzmann equation* is obtained for short range interactions in the dilute regime by exploiting $\tau_c/\tau_\times \approx nd^3 \ll 1$. (By contrast, for long range interactions such that $nd^3 \gg 1$, the *Vlasov equation* is obtained by dropping the collision terms on the left hand side, as discussed in problems.) From the above discussion, it is apparent that eq.(III.28) is different from the rest of the hierarchy: It is the only one in which the collision terms are absent from the left hand side. For all other equations, the right hand side is smaller by a factor of nd^3, while in eq.(III.28) it may indeed dominate the left hand side. Thus a possible approximation scheme is to truncate the equations after the first two, by setting the right hand side of eq.(III.29) to zero.

The left hand side of the equation for f_2 includes terms proportional to both τ_U^{-1} and τ_c^{-1}. We shall argue that the two sets of terms can be treated independently, the former acting on center of mass, and the latter acting on relative coordinates. But f_2 is proportional to the joint PDF ρ_2 for finding one particle at $(\vec{p}_1, \vec{q}_1)$, and another at $(\vec{p}_2, \vec{q}_2)$, at the same time t. It is reasonable to expect that at distances much larger than the range of the potential $\mathcal{V}$, the particles are independent, i.e.

$$\begin{cases} \rho_2(\vec{p}_1, \vec{q}_1, \vec{p}_2, \vec{q}_2, t) \longrightarrow \rho_1(\vec{p}_1, \vec{q}_1, t)\rho_1(\vec{p}_2, \vec{q}_2, t), & \text{or} \\ f_2(\vec{p}_1, \vec{q}_1, \vec{p}_2, \vec{q}_2, t) \longrightarrow f_1(\vec{p}_1, \vec{q}_1, t)f_1(\vec{p}_2, \vec{q}_2, t), & \text{for} \quad |\vec{q}_2 - \vec{q}_1| \gg d, \end{cases} \tag{III.31}$$

For example, imagine that the gas particles are suddenly allowed to invade an empty volume after the removal of a barrier. The density f_1 will undergo a complicated evolution, and its relaxation time will be at least comparable to τ_U. The two body density f_2, will also reach its final value at a comparable time interval. However, it is expected to relax to a form similar to eq.(III.31) over a much shorter time of the order of τ_c. At separations comparable to d, the behavior of f_2 is governed by two particle collisions. At time intervals longer than τ_c (but possibly shorter than τ_U), the 'steady state' behavior of f_2 at small relative distances is thus obtained by equating the largest terms in eq.(III.29), i.e.

$$\left[\frac{\vec{p}_1}{m} \cdot \frac{\partial}{\partial \vec{q}_1} + \frac{\vec{p}_2}{m} \cdot \frac{\partial}{\partial \vec{q}_2} - \frac{\partial \mathcal{V}(\vec{q}_1 - \vec{q}_2)}{\partial \vec{q}_1} \cdot \left(\frac{\partial}{\partial \vec{p}_1} - \frac{\partial}{\partial \vec{p}_2} \right) \right] f_2 = 0. \qquad \text{(III.32)}$$

We expect $f_2(\vec{q}_1, \vec{q}_2)$ to have slow variations over the center of mass coordinate $\vec{Q} = (\vec{q}_1 + \vec{q}_2)/2$, and large variations over the relative coordinate $\vec{q} = \vec{q}_2 - \vec{q}_1$. Therefore, $\partial f_2 / \partial \vec{q} \gg \partial f_2 / \partial \vec{Q}$, and $\partial f_2 / \vec{q}_2 \approx -\partial f_2 / \partial \vec{q}_1 \approx \partial f_2 / \partial \vec{q}$, leading to

$$\frac{\partial \mathcal{V}(\vec{q}_1 - \vec{q}_2)}{\partial \vec{q}_1} \cdot \left(\frac{\partial}{\partial \vec{p}_1} - \frac{\partial}{\partial \vec{p}_2} \right) f_2 = - \left(\frac{\vec{p}_1 - \vec{p}_2}{m} \right) \cdot \frac{\partial}{\partial \vec{q}_2} f_2 \quad . \qquad \text{(III.33)}$$

The above equation (along with the boundary conditions imposed by eq.(III.31)) describes a steady state situation established by collisions in the center of mass frame of two particles.

The relaxation of f_1 to equilibrium is controlled by the collision terms on the right hand side of eq.(III.28), which can be written as

$$\left. \frac{df_1}{dt} \right|_{\text{coll.}} = \int d^3\vec{p}_2 d^3\vec{q}_2 \, \frac{\partial \mathcal{V}(\vec{q}_1 - \vec{q}_2)}{\partial \vec{q}_1} \cdot \left(\frac{\partial}{\partial \vec{p}_1} - \frac{\partial}{\partial \vec{p}_2} \right) f_2 \approx$$

$$\int d^3\vec{p}_2 d^3\vec{q}_2 \, \left(\frac{\vec{p}_1 - \vec{p}_2}{m} \right) \cdot \frac{\partial}{\partial \vec{q}_2} f_2 \quad . \qquad \text{(III.34)}$$

The first identity if obtained from eq.(III.28) by noting that the added term proportional to $\partial f_2 / \partial \vec{p}_2$ is a complete derivative and integrates to zero, while the second equality follows from eq.(III.33). (Since it relies on establishing the 'steady state' in the relative coordinates, this approximation is valid as long as we examine events in time with a resolution longer than τ_c.)

• *Scattering theory:* The integrand in eq.(III.34) is a derivative of f_2 with respect to $\vec{q}$ along the direction of relative motion $\vec{p} = \vec{p}_2 - \vec{p}_1$, of the colliding particles. As such, it can be integrated to $f_2(\vec{p}_1{}', \vec{Q}, \vec{p}_2{}', \vec{Q}, t) - f_2(\vec{p}_1, \vec{Q}, \vec{p}_2, \vec{Q}, t)$, where $\vec{p}_1{}'$, and $\vec{p}_2{}'$ are the

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momenta of the two particles immediately after the collision. (As we are only concerned with variations of f_1 at length scales larger than d, we shall ignore the small differences in positions before and after each collision.) More precisely, this is achieved by a change of variables from the three components of $\vec{q}_2$ to a one-dimensional variable a along the trajectory of motion, and a two component vector $\vec{b}$ perpendicular to it. The complicated curvilinear nature of this transformation need not bother us, as after the partial integration over a, we only need to specify the coordinates before the collision. It is customary to set $\vec{b} = \vec{0}$ for a head–on collision ($[\vec{p}_1 - \vec{p}_2] \parallel [\vec{q}_1 - \vec{q}_2]$). With this choice, $\vec{b}$ is known as the *impact* vector, and

$$\left.\frac{df_1}{dt}\right|_{\text{coll.}} = \int d^3\vec{p}_2 d^2\vec{b}\, |\vec{v}_1 - \vec{v}_2|\, [f_2(\vec{p}_1{}', \vec{q}_1, \vec{p}_2{}', \vec{q}_1, t) - f_2(\vec{p}_1, \vec{q}_1, \vec{p}_2, \vec{q}_1, t)]\,, \qquad \text{(III.35)}$$

where $|\vec{v}_1 - \vec{v}_2| = |\vec{p}_1 - \vec{p}_2|/m$ is the relative speed of the two particles.

It is more convenient to describe the scattering of two particles in terms of the relative momenta $\vec{P} = \vec{p}_1 - \vec{p}_2$ and $\vec{P}' = \vec{p}_1{}' - \vec{p}_2{}'$, before and after the collision. Note that $d^2\vec{b}\,|\vec{v}_1 - \vec{v}_2|$ is just the flux of particles impinging on the element of area $d^2\vec{b}$. For a given $\vec{b}$, the initial momentum $\vec{P}$ is deterministically transformed to the final momentum $\vec{P}'$. To find the functional form $\vec{P}'(|\vec{P}|, \vec{b})$, one must integrate the equations of motion. In elastic collisions, the magnitude of $\vec{P}$ is preserved, and it merely rotates to a final direction indicated by the angles $(\theta, \phi) \equiv \Omega(\vec{b})$ in spherical coordinates. Since there is a one to one correspondence between the impact vector $\vec{b}$, and the *solid angle* Ω, we make a change of variables between the two resulting in

$$\left.\frac{df_1}{dt}\right|_{\text{coll.}} = \int d^3\vec{p}_2 d\Omega\, \frac{d\sigma}{d\Omega} |\vec{v}_1 - \vec{v}_2|\, [f_2(\vec{p}_1{}', \vec{q}_1, \vec{p}_2{}', \vec{q}_1, t) - f_2(\vec{p}_1, \vec{q}_1, \vec{p}_2, \vec{q}_1, t)]\,. \qquad \text{(III.36)}$$

The Jacobian of this transformation $d\sigma/d\Omega$ has dimensions of area, and is known as the *differential cross-section*. It is equal to the area presented to an incoming beam which scatters into the solid angle Ω. In eq.(III.36), the out-going momenta $\vec{p}_1{}'$ and $\vec{p}_2'$ are functions of $\vec{p}_1$, $\vec{p}_2$, and Ω, obtained from the two conditions $\vec{p}_1{}' + \vec{p}_2' = \vec{p}_1 + \vec{p}_2$ (conservation of momentum), and $\vec{p}_1{}' - \vec{p}_2' = |\vec{p}_1 - \vec{p}_2|\hat{\Omega}$ (conservation of energy), as

$$\begin{cases} \vec{p}_1{}' = \left(\vec{p}_1 + \vec{p}_2 + |\vec{p}_1 - \vec{p}_2|\hat{\Omega}\right)/2, \\[2mm] \vec{p}_2{}' = \left(\vec{p}_1 + \vec{p}_2 - |\vec{p}_1 - \vec{p}_2|\hat{\Omega}\right)/2. \end{cases} \qquad \text{(III.37)}$$

For the scattering of two *hard spheres* of diameter d, it is easily to show that the scattering angle is related to the impact parameter b by $\sin(\theta/2) = b/d$ for all ϕ. The differential cross-section is then obtained from

$$d\sigma = b\, db\, d\phi = d\sin\left(\frac{\theta}{2}\right) d\cos\left(\frac{\theta}{2}\right)\frac{d\theta}{2}\, d\phi = \frac{d^2}{4}\sin\theta d\theta\, d\phi = \frac{d^2}{4}\, d\Omega.$$

(Note that the solid angle in three dimensions is given by $d\Omega = \sin\theta d\theta\, d\phi$.) Integrating over all angles leads to the total cross–section of $\sigma = \pi d^2$, which is evidently correct. The differential cross-section for hard spheres is *independent* of both θ and $|\vec{P}|$. This is not the case for soft potentials. For example, the Coulomb potential $\mathcal{V} = e^2/|\vec{Q}|$ leads to

$$\frac{d\sigma}{d\Omega} = \left(\frac{me^2}{2|\vec{P}|^2\sin^2(\theta/2)}\right)^2.$$

(The dependence on $|\vec{P}|$ can be obtained by obtaining a distance of closest approach from $|\vec{P}|^2/m + e^2/b \approx 0$.)

• The *Boltzmann* transport equation is obtained from eq.(III.36) after one further approximation known as the *assumption of molecular chaos*. The approximation consists of replacing f_2 by using eq.(III.31), leading to

$$\left[\frac{\partial}{\partial t} - \frac{\partial U}{\partial \vec{q}_1}\cdot\frac{\partial}{\partial \vec{p}_1} + \frac{\vec{p}_1}{m}\cdot\frac{\partial}{\partial \vec{q}_1}\right]f_1 =$$
$$-\int d^3\vec{p}_2 d\Omega\,\frac{d\sigma}{d\Omega}|\vec{v}_1 - \vec{v}_2|\left[f_1(\vec{p}_1,\vec{q}_1,t)f_1(\vec{p}_2,\vec{q}_1,t) - f_1(\vec{p}_1{}',\vec{q}_1,t)f_1(\vec{p}_2{}',\vec{q}_1,t)\right].$$

(III.38)

While the approximation $f_2(\vec{q}_1,\vec{q}_2) \to f_1(\vec{q}_1)f_1(\vec{q}_2)$, is certainly justified for separations much larger than d, in eq.(III.38) it has been applied to short distances describing collisions. The simplification results in a closed form equation for f_1 whose consequences we shall explore in the next section.

The streaming terms on the left hand side of the Boltzmann equation describe the motion of a single particle in the external potential U. The collision terms on the right hand side have a simple physical interpretation: The probability of finding a particle of momentum $\vec{p}_1$ at $\vec{q}_1$ is suddenly altered if it undergoes a collision with another particle of momentum $\vec{p}_2$. The probability of such a collision is the product of kinematic factors described by the differential cross-section $d\sigma/d\Omega$, the 'flux' of incident particles proportional to $|\vec{v}_2 - \vec{v}_1|$, and the joint probability of finding the two particles, approximated by $f_1(\vec{p}_1)f_1(\vec{p}_2)$. The first term on the right hand side of eq.(III.38) subtracts this probability

and integrates over all possible momenta and solid angles describing the collision. The second term, describes an *addition* to the probability which results from the inverse process: A particle can suddenly appear at $(\vec{p}_1, \vec{q}_1)$ as a result of a collision between two particles initially with momenta $\vec{p}_1\,'$ and $\vec{p}_2\,'$. The cross-section, and the momenta $(\vec{p}_1\,', \vec{p}_2\,')$ may have a complicated dependence on $(\vec{p}_1, \vec{p}_2)$ and Ω, determined by the specific form of the potential $\mathcal{V}$. Remarkably, various equilibrium properties of the gas are quite independent of this potential.