CHAPTER 4

DERIVATION AND PROPERTIES OF THE BOLTZMANN EQUATION

Neutral gases are usually characterized by short range interaction forces between the molecules and small or moderate densities. In this situation the well–known Boltzmann equation takes a key position.

4.1.   THE SMALL PARAMETER OF THE BOLTZMANN GAS

We consider the hierarchy (3.5.10) without external forces, i.e. $F_\alpha = 0$. We write the equations in a dimensionless form. To this end we use the range r_f of the interaction forces, the thermal velocity v_T and the characteristic strength ϕ_0 of the interaction potential. Denoting the dimensionless variables with asterisks we define:

$$r = r_f r^*, \ v = v_T v^*, \ \phi = \phi_0 \phi^*, \ t = (r_f/v_t)t^*, \ F_s = v_T^{-3s} F_s^*.$$

$$(4.1.1)$$

The hierarchy (3.5.10) then takes the form:

$$\partial F_s^* /\partial t^* + \sum_{i=1}^{s} v_i^* \cdot \partial F_s^* /\partial r_i^* - \phi_0/(mv_T^2) \sum_{i=1}^{s} \sum_{j=1}^{s}{}' \partial \phi^* (r_i^* - r_j^*)/\partial r_i^* \cdot$$

$$\partial F_s^* /\partial v_i^* = n_0 r_f^3 \ \phi_0/(mv_T^2) \sum_{i=1}^{s} \int \partial \phi^* (r_i^* - r_{s+1}^*)/\partial r_i^* \cdot$$

$$\partial F_{s+1}^* /\partial v_i^* \ d^3 r_{s+1}^* d^3 v_{s+1}. \qquad\qquad (4.1.2)$$

A Boltzmann gas is characterized by the conditions (2.2.46), i.e. the density of the gas should be low enough to allow for the small parameter

$$\epsilon_B = n_0 r_f^3 << 1. \qquad\qquad (4.1.3)$$

In the right hand side of (4.1.2) this parameter then appears in front of the summation sign. We might take (4.1.2) as a starting point for the derivation of a kinetic equation. It is more convenient, however, to write down the first two hierarchy equations in their dimensional form *and* an extra factor ϵ_B in the right hand side. In the eventual results, derived on basis of an expansion in powers of ϵ_B,

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this parameter is put equal to unity. This procedure is completely equivalent to an expansion based on the dimensionless equations. Therefore:

$$(\partial/\partial t + \boldsymbol{v} \cdot \partial/\partial \boldsymbol{r})F_1(\xi,t) = \epsilon_B \, n_0/m \int \partial\phi(\mathbf{r}-\mathbf{r}')/\partial \boldsymbol{r} \cdot$$

$$\partial \mathbf{F}_2(\xi,\xi',t)/\partial \boldsymbol{v} \, d\xi', \tag{4.1.4}$$

$$\left\{\partial/\partial t + \boldsymbol{v} \cdot \partial/\partial \boldsymbol{r} + \boldsymbol{v}' \cdot \partial/\partial \boldsymbol{r}' - \partial\phi(\mathbf{r}-\mathbf{r}')/\partial \boldsymbol{r} \cdot (\partial/\partial \boldsymbol{v} - \partial/\partial \boldsymbol{v}')\right\}$$

$$F_2(\xi,\xi',t) = \epsilon_B \, n_0/m \int \left\{\partial\phi(\mathbf{r}-\mathbf{r}'')/\partial \boldsymbol{r} \cdot \partial/\partial \boldsymbol{v}\right.$$

$$\left. + \, \partial\phi(\mathbf{r}'-\mathbf{r}'')/\partial \boldsymbol{r}' \cdot \partial/\partial \boldsymbol{v}'\right\} F_3(\xi,\xi',\xi'',t)d\xi''. \tag{4.1.5}$$

The presence of the parameter ϵ_B seduces us to try an expansion in powers of ϵ_B:

$$F_s = F_s^{(0)} + \epsilon_B F_s^{(1)} + ..., \, s = 1,2,... \tag{4.1.6}$$

In lowest order we obtain for F_1:

$$\partial F_1^{(0)}/\partial t + \mathbf{v} \cdot \partial F_1^{(0)}/\partial \boldsymbol{r} = 0, \tag{4.1.7}$$

and this is known to be the kinetic equation for a Knudsen gas, where the influence of intermolecular interactions on the one particle distribution function is completely neglected. It is, however, clear that such an approximation can only be expected to hold for dimensionless intervals of time and space satisfying

$$\Delta t^*, \Delta r^* << \epsilon_B^{-1}. \tag{4.1.8}$$

For the dimensional interval this implies:

$$\Delta r << r_f/\epsilon_B = (n_0 r_f^2)^{-1} = \text{mean free path},$$

$$\Delta t << r_f/(v_T \epsilon_B) = \text{collision time}[1]. \tag{4.1.9}$$

Mathematically the situation is similar to the following (trivial) example. If one wants to solve the differential equation

$$df/dt + \epsilon f = 0 \tag{4.1.10}$$

by means of an expansion in powers of the small parameter ϵ, i.e.

$$f = f_0 + \epsilon f_1 + \epsilon^2 f_2 + ..., \tag{4.1.11}$$

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[1]defined as the average time between two successive collisions of one molecule.

then, with the initial conditions $f_0 = 1$, $f_1 = f_2 = ... = 0$ at time t = 0, one finds that

$$df_0/dt = 0, \qquad f_0 = 1 \tag{4.1.12}$$

$$df_1/dt + f_0 = 0, \qquad f_1 = -t \tag{4.1.13}$$

$$df_2/dt + f_1 = 0, \qquad f_2 = \tfrac{1}{2}t^2, \tag{4.1.14}$$

etc. Of course we realize that (4.1.11) is simply the Taylor series of $f = \exp(-\epsilon t)$. As a power series in ϵ this series is non–uniformly convergent with respect to both ϵ and t. [2] The series is also asymptotic, but again non–uniformly with respect to ϵ and t. It is clear that the terms f_0, f_1, f_2, etc. possess decreasing orders of magnitude, only if $t << \epsilon^{-1}$. The phenomenon that the ratio f_{n+1}/f_n of two successive terms of a power series in ϵ increases indefinitely as a function of some other parameter (e.g. time), is called *secularity*. In the next section the multiple–time–scales formalism is presented. This formalism is a powerful tool that enables us to avoid secularities of purely mathematical origin (SAN1963, SAN1967,DAV1972).

4.2.   MULTIPLE–TIME–SCALES FORMALISM

This formalism is also called "extension method". A system of functions $f_i(t,\epsilon)$ is "extended" to a system of functions of more variables $\bar{f}_i\ (\tau_0,\tau_1,\tau_2,...,\epsilon)$. The functions f_i satisfy a number of differential equations. The system of equations for $\bar{f}_i$ is then obtained by replacing the $\partial/\partial t$–operator in the original system by

$$h_0(\tau_0,\tau_1,...)\ \partial/\partial\tau_0 + \epsilon h_1(\tau_0,\tau_1,...)\ \partial/\partial\tau_1$$

$$+ \epsilon^2 h_2(\tau_0,\tau_1,...)\ \partial/\partial\tau_2 + \ ... \tag{4.2.1}$$

The space of solutions is also extended, of course. The initial condition for $f_i(t=0,\epsilon)$ is transformed into a condition for $\bar{f}_i(\tau_0 = 0,\ \tau_1 = 0,\ \tau_2 = 0,\ ...,\ \epsilon)$ in the extended problem. The large space of solutions and, possibly, the choice of the functions $h_k(\tau_0,\tau_1,...)$ are used to present $\bar{f}_i$ as a power series in ϵ, which is uniformly convergent or asymptotic with respect to the variables $\tau_0,\ \tau_1,\ \tau_2$, etc. The functions $f_i(t,\epsilon)$ of the original problem are eventually obtained by the identification

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[2] $f(\epsilon,t)$ is approximated by a partial sum $S_N = \sum\limits_{n=0}^{N} a_n(t)\epsilon^n$. If $|f(\epsilon,t) - S_N| < \delta$ for $N > N_0(\delta,\epsilon,t)$, then the series is convergent and in fact uniformly convergent with respect to ϵ and t, if N_0 is independent of ϵ and t respectively. The series is asymptotic, if $|\epsilon|^{-N}|f(\epsilon,t) - S_N| < \delta$ for $|\epsilon| < \epsilon_0(\delta,N,t)$ and uniformly asymptotic, if ϵ_0 does not depend on t.

$$f_i(t,\epsilon) = \bar{f}_i \left[\tau_0 = \tau_0(\epsilon,t), \ \tau_1 = \tau_1(\epsilon,t),...,\epsilon \right], \tag{4.2.2}$$

where the functions $\tau_k(\epsilon,t)$ are the solutions of

$$\partial \tau_k/\partial t = \epsilon^k h_k(\tau_0,\tau_1, ...), \quad \tau_k(0) = 0 \tag{4.2.3}$$

with $k = 0,1,2,...$
     This formalism is now elucidated by means of two examples. Both in these examples and in our later applications in kinetic theory we have $h_k (\tau_0,\tau_1,...) = 1$, so that the solutions of (4.2.3) are given by

$$\tau_k = \epsilon^k t. \tag{4.2.4}$$

The first example concerns the trivial problem (4.1.10) with the initial condition $f(t=0,\epsilon) = 1$. It is sufficient to introduce two new independent variables: τ_0 and τ_1. The extended equation is:

$$\partial \bar{f} /\partial \tau_0 + \epsilon \ \partial \bar{f} /\partial \tau_0 + \epsilon \bar{f} = 0. \tag{4.2.5}$$

We substitute the expansion

$$\bar{f} (\tau_0,\tau_1,\epsilon) = \bar{f}_0(\tau_0,\tau_1) + \epsilon \bar{f}_1(\tau_0,\tau_1) + ... \tag{4.2.6}$$

into (4.2.5) and into the initial condition. We then find in successive orders:

$$(\epsilon^0) \ \partial \bar{f}_0/\partial \tau_0 = 0, \quad \bar{f}_0(\tau_0 = 0, \ \tau_1 = 0) = 1 \tag{4.2.7}$$

$$(\epsilon^1) \ \partial \bar{f}_1/\partial \tau_0 \ + \partial \bar{f}_0/\partial \tau_1 + \bar{f}_0 = 0, \quad \bar{f}_1(\tau_0 = 0, \ \tau_1 = 0) = 0 \tag{4.2.8}$$

$$(\epsilon^n) \ \partial \bar{f}_n/\partial \tau_0 + \partial \bar{f}_{n-1}/\partial \tau_1 + \bar{f}_{n-1} = 0, \quad \bar{f}_n(\tau_0 = 0, \ \tau_1 = 0) = 0 \tag{4.2.9}$$

From (4.2.7) we conclude:

$$\bar{f}_0 = A_0(\tau_1), \quad A_0(0) = 1. \tag{4.2.10}$$

Integration of (4.2.8) leads to

$$\bar{f}_1 = - \tau_0 \ (\partial A_0/\partial \tau_1 + A_0) + A_1(\tau_1). \tag{4.2.11}$$

The first term of the right hand side is a *secularity*. The purpose of the method is to avoid secularities. We therefore demand

$$\partial A_0/\partial \tau_1 + A_0 = 0. \tag{4.2.12}$$

Together with the initial condition of (4.2.10) this leads to

$$\bar{f}_0(\tau_0,\tau_1) = A_0(\tau_1) = \exp(-\tau_1), \tag{4.2.13}$$

which is, in essence, the solution of the problem. We also consider, however, the remaining equations. From (4.2.11,12) and the initial condition of (4.2.8) it follows that

$$\bar{f}_1(\tau_0,\tau_1) = A_1(\tau_1), \; A_1(0) = 0 \tag{4.2.14}$$

The equation (4.2.9) for $n = 2$ can now be integrated with the result:

$$\bar{f}_2 = -(\partial A_1/\partial \tau_1 + A_1)\tau_0 + A_2(\tau_1), \; A_2(0) = 0.$$

Removal of the secularity and (4.2.14) imply:

$$\bar{f}_1(\tau_0,\tau_1) = A_2(\tau_1) = 0 \; . \tag{4.2.15}$$

In a completely similar way it also follows that

$$\bar{f}_n(\tau_0,\tau_1) = 0, \, n \geq 2. \tag{4.2.16}$$

The solution of the "extended" problem (4.2.5) is therefore given by (4.2.13), i.e.

$$\bar{f}(\tau_0,\tau_1) = \exp(-\tau_1). \tag{4.2.17}$$

The corresponding solution of the original problem follows from (4.2.4):

$$f(t,\epsilon) = \exp(-\epsilon t) \; . \tag{4.2.18}$$

In this simple example it is possible to find the exact solution of the problem by means of multiple time scales.

4.2.1.   The Van de Pol Oscillator.

A less trivial example is the treatment of the Van de Pol equation, originally proposed for the description of a transmitter consisting of a triod and an oscillation circuit. The equation can be reduced to the dimensionless form

$$d^2x/d\tau^2 - \epsilon(1-x^2) \; dx/d\tau + x = 0. \tag{4.2.19}$$

If the oscillations are small, i.e. $|x| << 1$, linearization is appropriate:

$$d^2x/d\tau^2 - \epsilon \; dx/d\tau + x = 0, \tag{4.2.20}$$

and the solution

$$x = A \exp(\tfrac{1}{2}\epsilon\tau)\cos\{\tau(1-\epsilon^2/4)^{1/2}+\phi\} \qquad (4.2.21)$$

is immediately obtained. For $|\epsilon| << 1$ we may write

$$x = A \exp(\tfrac{1}{2}\epsilon\tau)\cos(\tau+\phi). \qquad (4.2.22)$$

If $\epsilon > 0$, then (4.2.21,22) describe a growing oscillation. After enough time has elapsed, the condition $|x| << 1$, necessary for linearization, will no longer be satisfied. Qualitatively we see from (4.2.19) that saturation of the instability may occur, when $|x|$ becomes larger than unity. In the case that $0 < \epsilon << 1$ we may try to describe the entire process of instability and saturation by solving (4.2.19) by means of a perturbation expansion in powers of ϵ. A pure power series,

$$x = x_0 + \epsilon x_1 + \epsilon^2 x_2 + ..., \qquad (4.2.23)$$

leads to

$$d^2x_0/d\tau^2 + x_0 = 0 \qquad (4.2.24)$$

and

$$d^2x_1/d\tau^2 + x_1 = (1-x_0{}^2)\, dx_0/d\tau \qquad (4.2.25)$$

in zeroth and first order respectively.
The solution of (4.2.24) is:

$$x_0 = A \cos\psi, \quad \psi = \tau + \phi. \qquad (4.2.26)$$

If we substitute this into (4.2.25), the solution in first order can be written as

$$x_1 = A_1\cos(\tau+\phi_1) - A^3/32 \sin(3\psi) + A/2(1- A^2/4)\tau \cos\psi. \quad (4.2.27)$$

The first term of the right hand side is the general solution of the homogeneous part of (4.2.25), the second term is a higher harmonic and the last term is secular. The difficulty is that in order to find the slow growth of (4.2.22) and the subsequent saturation, we would need al powers of ϵ in the present procedure. Therefore we now introduce the multiple–time–scales formalism. In fact we use two time variables and write instead of (4.2.23):

$$\bar{x}(\tau_0,\tau_1) = \bar{x}_0(\tau_0,\tau_1) + \epsilon\bar{x}_1(\tau_0,\tau_1) + ... \qquad (4.2.28)$$

The operator $\partial/\partial t$ is replaced by $\partial/\partial\tau_0 + \epsilon\partial/\partial\tau_1$, so that

$$\partial^2/\partial\tau^2 \rightarrow \partial^2/\partial\tau_0^2 + 2\epsilon\, \partial^2/\partial\tau_0\partial\tau_1 + \epsilon^2\, \partial^2/\partial\tau_1^2. \qquad (4.2.29)$$

In zeroth order we have:

$$\partial^2\bar{x}_0/\partial\tau_0^2 + \bar{x}_0 = 0 \qquad (4.2.30)$$

with the solution

$$\bar{x}_0 = A(\tau_1)\cos\bar{\psi}, \quad \bar{\psi} = \tau_0 + \phi(\tau_1).$$
(4.2.31)

In first order we find:

$$\partial^2\bar{x}_1/\partial\tau_0^2 + \bar{x}_1 = -2\,\partial^2\bar{x}_0/\partial\tau_0\partial\tau_1 - (1 - \bar{x}_0{}^2)\,\partial\bar{x}_0/\partial\tau_0,$$
(4.2.32)

or, with (4.2.31):

$$\partial^2\bar{x}_1/\partial\tau_0^2 + \bar{x}_1 = 2\,\partial A/\partial\tau_1 \sin\bar{\psi} + 2\,\partial\phi/\partial\tau_1 \cos\bar{\psi}$$

$$- A(1 - \tfrac{1}{4}A^2)\sin\bar{\psi} + \tfrac{1}{4}A^3\sin(3\bar{\psi}).$$
(4.2.33)

The solution is analogous to (4.2.27):

$$\bar{x}_1 = A_1(\tau_1)\cos\{\tau_0 + \phi_1(\tau_1\} - A^3/32\,\sin(3\bar{\psi})$$

$$+ \{\tfrac{1}{2}A(1 - \tfrac{1}{4}A^2) - \partial A/\partial\tau_1\}\tau_0\cos\bar{\psi} + \partial\phi/\partial\tau_1\,\tau_0\sin\bar{\psi}.$$
(4.2.34)

But now we are able to remove secularities:

$$\partial\phi/\partial\tau_1 = 0,$$
(4.2.35)

$$\partial A/\partial\tau_1 = \tfrac{1}{2}A(1 - \tfrac{1}{4}A^2).$$
(4.2.36)

This equation is solved by a simple quadrature:

$$A^2(\tau_1) = 4\left[1 + (4A_0{}^{-2} - 1)\exp(-\tau_1)\right]^{-1},$$
(4.2.37)

where A_0 is the initial condition

$$A_0 = A(\tau_1 = 0).$$
(4.2.38)

Equation (4.2.37) describes the growth (if $A_0 < 2$) of the amplitude $A(\tau_1)$ from the initial value A_0 to the final value $A_\infty = 2$.

Returning to the original variables x and τ by means of $x(t) = \bar{x}(\tau_0 = \tau, t_1 = \epsilon\tau)$ we conclude from (4.2.23,31,34,35,37) that

$$x(\tau) = 2\left[1 + (4A_0{}^{-2} - 1)\exp(-\epsilon\tau)\right]^{-1/2}\cos(\tau + \phi) - \tfrac{1}{4}\epsilon\left[1 + \right.$$

$$\left. + (4A_0{}^{-2} - 1)\exp(-\epsilon\tau)\right]^{-3/2}\sin(3\tau + 3\phi) + \epsilon A_1(\epsilon\tau)\cos\{\tau + $$

$$+ \phi_1(\epsilon\tau)\}, \tag{4.2.39}$$

where $A_1(\epsilon\tau)$ and $\phi_1(\epsilon\tau)$ are not yet known. Information about these functions may be obtained from the next order calculation. The last term of (4.2.39) is, however, not very interesting, because it is of the same form as the first term and only a small correction to it.
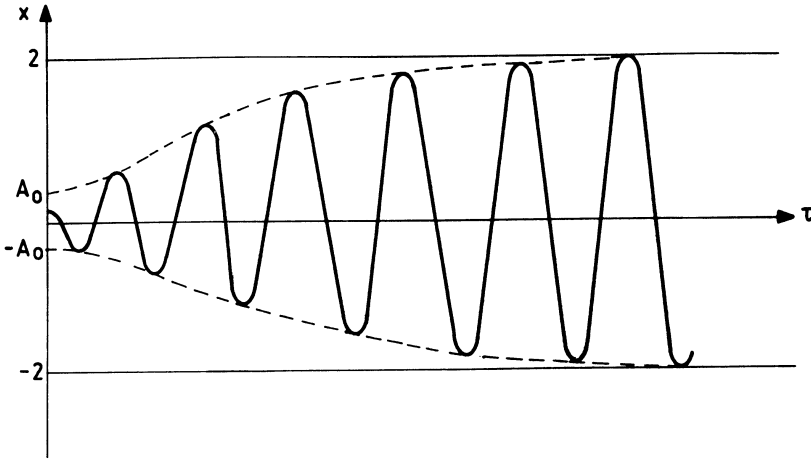

Figure 4. Solution (4.2.39) of the Van der Pol Equation.

The results obtained can also be derived by means of an averaging method, introduced by Bogoliubov, Krylov and Metropolski, see [KRY1947].

4.3.　DERIVATION OF THE BOLTZMANN EQUATION

We want to treat the equations (4.1.4,5) with the expansion (4.1.6) and the multiple–time–scales formalism. In order to do this we introduce the assumption that the non–uniformity of the system does not appear on distances of the order r_f, but is characterized by a length L which is not smaller than the mean free path $\lambda = n_0^{-1} r_f^{-2} = \epsilon_B^{-1} r_f$. Formally we write

$$F_1(r,v,t) = F(a,v,t) \tag{4.3.1}$$

with

$$a = \epsilon_B r, \tag{4.3.2}$$

so that

$$\partial F_1 / \partial r = \epsilon_B \, \partial F / \partial a \tag{4.3.3}$$

with the understanding that $\partial F / \partial a$ is of order unity. Similarly we introduce the function G by

$$F_2(r,v,r',v',t) = G(a,s,v,v',t) \tag{4.3.4}$$

with

$$s = r - r', \tag{4.3.5}$$

so that

$$\partial / \partial r = \epsilon_B \, \partial / \partial a + \partial / \partial s \, , \, \partial / \partial r' = - \partial / \partial s. \tag{4.3.6}$$

Using (4.3.3,6) we find in *zeroth order* from (4.1.4,5):

$$\partial F^{(0)} / \partial \tau_0 = 0 \tag{4.3.7}$$

and

$$\partial G^{(0)} / \partial \tau_0 + (v - v') \cdot \partial G^{(0)} / \partial s - m^{-1} \, \partial \phi / \partial s \cdot$$

$$(\partial / \partial v - \partial / \partial v') G^{(0)} = 0. \tag{4.3.8}$$

The time scale τ_0 describes changes which take place in time intervals of the order of the collision duration, i.e. $r_f v_T^{-1}$.

4.3.1. First Order Theory and Bogoliubov Boundary Condition.

From (4.1.4) and (4.3.3) we obtain in first order:

$$\partial F^{(1)} / \partial \tau_0 + \partial F^{(0)} / \partial \tau_1 + v \cdot \partial F^{(0)} / \partial a = n_0 / m \int \partial \phi / \partial s \cdot$$

$$\partial G^{(0)} / \partial v \, d^3 s d^3 v', \tag{4.3.9}$$

where the integration variable r' has been replaced by s in the right hand side. We do not write the first order equation for the pair distribution function, because it will not be used in the sequel. We assume that $G^{(0)}$ remains finite and independent of τ_0 for $\tau_0 \to \infty$. We then write:

$$G^{(0)} = G_A^{(0)} + G_T^{(0)} \tag{4.3.10}$$

with

$$G_A^{(0)} = \lim_{\tau_0 \to \infty} G^{(0)}, \quad \lim_{\tau_0 \to \infty} G_T^{(0)} = 0. \tag{4.3.11}$$

It is now possible to integrate (4.3.9) with respect to τ_0:

$$F^{(1)} = \tau_0 \left(- \partial F^{(0)} / \partial \tau_1 - \boldsymbol{v} \cdot \partial F^{(0)} / \partial \boldsymbol{a} + L_1 G_A^{(0)} \right)$$

$$+ \int_0^{\tau_0} L_1 G_T^{(0)}(\tau_0') d\tau_0' + F^{(1)^*}(\boldsymbol{a}, \boldsymbol{v}, \tau_1), \tag{4.3.12}$$

where L_1 is an abbreviation for the operator in the right hand side of (4.3.9):

$$L_1 = n_0/m \int d^3s d^3v' \, \partial \phi / \partial \boldsymbol{s} \cdot \partial / \partial \boldsymbol{v} \tag{4.3.13}$$

The first term in the right hand side of (4.3.12) is secular: for large τ_0 $\epsilon_B F^{(1)}$ is in danger of becoming larger than $F^{(0)}$. The secularity is removed by requiring

$$\partial F^{(0)} / \partial \tau_1 + \boldsymbol{v} \cdot \partial F^{(0)} / \partial \boldsymbol{a} = L_1 G_A^{(0)}. \tag{4.3.14}$$

This also means that (4.3.9) reduces to

$$\partial F^{(1)} / \partial \tau_0 = L_1 G_T^{(0)}. \tag{4.3.15}$$

Equation (4.3.14) is the basis for the lowest order kinetic equation. In order to construct it we have to express the right hand side as a functional of $F^{(0)}$. We write (4.3.8) in the abbreviated form

$$\partial G^{(0)} / \partial \tau_0 + H_2^{(0)} \, G^{(0)} = 0, \tag{4.3.16}$$

where $H_2^{(0)}$ is the zeroth order Hamilton operator for two interacting particles. The solution can formally be written as

$$G^{(0)}(\boldsymbol{a}, \boldsymbol{s}, \boldsymbol{v}, \boldsymbol{v}', \tau_0, \tau_1) = \exp(-\tau_0 H_2^{(0)}) G^{(0)}(\boldsymbol{a}, \boldsymbol{s}, \boldsymbol{v}, \boldsymbol{v}', 0, \tau_1). \tag{4.3.17}$$

We define the Bogoliubov streaming operator by [BOG1962]

$$S_{-\tau_0}^{(0)} = \exp(-\tau_0 H_2^{(0)}). \tag{4.3.18}$$

Operating on a function of $\boldsymbol{s}, \boldsymbol{v}$ and $\boldsymbol{v}'$ the operator shifts these arguments to values they had a time τ_0 earlier on trajectories determined by the Hamilton operator $H_2^{(0)}$. Therefore:

$$S_{-\tau_0}^{(2)} G^{(0)}(a,s,v,v',0,\tau_1) = G^{(0)}(a,S_{-\tau_0}^{(2)}s,$$

$$S_{-\tau_0}^{(2)}v, S_{-\tau_0}^{(2)}v',0,\tau_1). \tag{4.3.19}$$

We introduce at this point the pair correlation function. Its zeroth order part is defined by

$$G^{(0)}(a,s,v,v',\tau_0,\tau_1) = F^{(0)}(a,v,\tau_1)F^{(0)}(a,v',\tau_1)$$

$$+ g_2^{(0)}(a,s,v,v',\tau_0,\tau_1). \tag{4.3.20}$$

It then follows from (4.3.17,18,11) that

$$G_\Lambda^{(0)}(a,s,v,v',\tau_1) = F^{(0)}\{a,v_\infty(s,v,v'),\tau_1\}F^{(0)}\{a,$$

$$v_\infty'(s,v,v'),\tau_1\} + \lim_{\tau_0 \to \infty} S_{-\tau_0}^{(2)}g_2^{(0)}(a,s,v,v',0,\tau_1) \tag{4.3.21}$$

with

$$v_\infty(s,v,v') = \lim_{\tau_0 \to \infty} S_{-\tau_0}^{(2)}v \tag{4.3.22}$$

and a similar expression for $v_\infty'(s,v,v')$. We need $G_\Lambda^{(0)}$ in the prelude (4.3.14,13) to the kinetic equation. The integral over s involved is effectively restricted to a region with linear dimensions of the order r_f, the range of the intermolecular interaction potential. Therefore we need $G_\Lambda^{(0)}$ for finite s (of the order r_f), i.e. the pair distribution function of (strongly) interacting particles. This also means that the flowed back value of s in the last term of (4.3.21) is infinitely large. We now make the fundamental assumption that correlations in the past disappear at large particle distances. This assumption is known as the Bogoliubov boundary condition [BOG1962]. Therefore:

$$\lim_{\tau_0 \to \infty} S_{-\tau_0}^{(2)} g_2^{(0)}(a,s,v,v',0,\tau_1) = 0 \tag{4.3.23}$$

for $s \simeq r_f$.

It is this assumption that transform (4.3.14) into a genuine kinetic equation:

$$\partial F^{(0)}/\partial \tau_1 + v \cdot \partial F^{(0)} \, \partial a = L_1 F^{(0)}\{a,v_\infty(s,v,v'),\tau_1\}$$

$$F^{(0)}\{a,v_\infty'(s,v,v'),\tau_1\} \tag{4.3.24}$$

This is the precursor of the Boltzmann equation.

4.3.2. *Discussion of the Kinetic Equation. Limitations of Bogoliubov's Approach.*

The Bogoliubov boundary condition (4.3.23) may be verified on basis of the first order equation for the pair correlation function. The removal of secularities leads to a theory about the behaviour of $g_2^{(0)}$ as a function of τ_1. This problem has been dealt with extensively by Frieman and Goldman, [FRI1966]. Equation (4.3.23) appears to be correct, if the initial situation is a situation of molecular chaos, i.e.

$$g_2^{(0)}(a,s,v,v',0,0) = 0. \tag{4.3.25}$$

This is a sufficient, but not a necessary condition. It may be expected that "most" initial correlation functions lead to the Bogoliubov boundary condition. It is, however, difficult to establish the necessary condition. Attempts in this direction have been made by Sandri [SAN1963] and Schram [SCH1964] for the case of weak interaction. We will not pursue this topic here.

It should be checked, whether the term $\int_0^{\tau_0} L_1 G_T^{(0)}(\tau_0')d\tau_0'$ in (4.3.12) might

give rise to secular behaviour. We therefore study (4.3.15) and write it as

$$\partial F^{(1)}/\partial\tau_0 = n_0/m \int \partial\phi/\partial s \cdot \partial/\partial v \left\{ S_{-\tau_0}^{(2)} - S_{-\infty}^{(2)} \right\}$$

$$G^{(0)}(a,s,v,v',0,\tau_1)\ d^3v'd^3s. \tag{4.3.26}$$

We need only consider a sphere with a radius of order r_f in s–space. Therefore $\{S_{-\tau_0}^{(0)} - S_{-\infty}^{(2)}\}G^{(0)}$ disappears for $\tau_0 \gg |v{-}v'|^{-1}r_f$. If we now shift the integration variable v' to the relative velocity g,

$$g = v - v', \tag{4.3.27}$$

then the integration in g–space is restricted to a volume of the order $r_f^3\tau_0^{-3}$. We conclude that $\partial F^{(1)}/\partial\tau_0$ is proportional to τ_0^{-3}, so that the boundedness of $F^{(1)}$ is guaranteed.

The following comments should be made about the derivation of (4.3.24):
—   Although repulsive interaction between the molecules has been assumed, the derivation remains valid for many cases where also attraction plays a role, e.g. for the Lennard–Jones interaction:

$$\phi(s) = 4\epsilon\left[(s/\sigma)^{12} - (s/\sigma)^{6}\right]. \tag{4.3.28}$$

Molecular bonds cannot be formed by binary collisions, because the total energy in the conservation law

$$\tfrac{1}{2}\mu_r g^2 + \phi(s) = \tfrac{1}{2}\mu_r g_\infty^2, \tag{4.3.29}$$

is positive and $\phi(s) \to 0$ for large s. In (4.3.29), which is valid in the center of

mass system, g and g_∞ are relative speeds, respectively during and before (also after) the interaction, and μ_r is the reduced mass ($\mu_r = \frac{1}{2}m$ for identical particles).
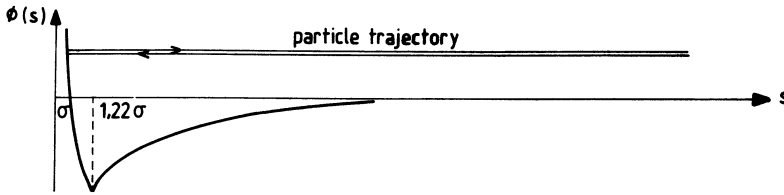

Figure 5 Lennard–Jones Potential.

Bonds can, however, be formed by ternary collisions. But these are very rare, if the Boltzmann parameter ϵ_B is small.

— In the Bogoliubov theory the concept of "synchronization" takes a central position. It implies the relaxation of multiple distribution functions to functionals of the one–particle distribution function within a few collision durations. In our derivation this is seen to happen with $G^{(0)}$, the lowest order approximation to the pair distribution function, cf. (4.3.21,23).
It is a consequence of the Bogoliubov boundary condition, which, as we have seen, was verified in first order on basis of initial molecular chaos by Frieman and Goldman, [FRI1966]. They also found the first correction to the Boltzmann equation, which was derived earlier by Choh and Uhlenbeck, [CHO1958]. From the work of Frieman and Goldman it also appears, however, that in the next order *not* all secularities can be removed. Sengers, [SEN1966], showed that in a two–dimensional gas the divergencies already occur in second order, so that the Choh–Uhlenbeck terms falls victim to them. The conclusion of this situation must be that the Bogoliubov synchronization is not valid in higher orders. These difficulties originate from the circumstance that every order of ϵ_B corresponds to a dynamical system of an isolated group of particles. The associated contribution to the collision integral diverges in time (if the group, in three dimensions, consists of four or more particles) as the result of the existence of (infinitely) long free trajectories between successive collisions. In physical reality, however, the average length of such free trajectories cannot be much larger than the mean free path. This argument breaks through the isolation of particle groups. It leads to the expectation that a rough approximation to a higher order contribution may be obtained by replacing time in divergent expressions by the mean collision time, i.e. by $\epsilon_B r_f v_T^{-1} = \lambda v_T^{-1}$. The contribution of order ϵ_B^2 diverges logarithmically in time. The first correction following the Choh–Uhlenbeck collision term is therefore expected to be of order $\epsilon_B^2 \ln \epsilon_B$. This also means that the theory

given in section 4.3.1 retains its validity as the theory of lowest significant order.

— The assumption contained in (4.3.1,2,3) is very mild. Inhomogeneities on the scale of the mean free path are allowed. When we, in Chapter 5, construct the asymptotic solution to the Boltzmann equation, which is shown to result into hydrodynamics, we have to introduce the more stringent assumption that the characteristic length of the inhomogeneities is much larger than the mean free path. Assumptions of the kind (4.3.1,2,3) are nevertheless absent in the theory of Bogoliubov. As a consequence in his theory a correction to the Boltzmann equation is found, describing a mixing of collisional and flow phenomena.

4.3.3. *Bogoliubov's Cylindrical Integration.*

We return to (4.3.24) in order to derive the Boltzmann equation in a more usual form. The right hand side can be written in a different way. From (4.3.8) with (4.3.11,27) we have:

$$\left\{ g \cdot \partial/\partial s - m^{-1} \, \partial\phi/\partial s \cdot (\partial/\partial v - \partial/\partial v') \right\} G_A^{(0)} = 0.$$

Integration with respect to s and v' leads to

$$m^{-1} \int \partial\phi/\partial s \cdot \partial G_A^{(0)}/\partial v \; d^3s d^3v' = m^{-1} \int \partial\phi/\partial s \cdot \partial G_A^{(0)}/\partial v' \; d^3s d^3v'$$

$$+ \int g \cdot \partial G_A^{(0)}/\partial s \; d^3s d^3v'. \tag{4.3.30}$$

The first term of the right hand side is of the form

$$\int \partial/\partial v' \cdot K d^3v' \text{ with } K = m^{-1} \int G_A^{(0)} \, \partial\phi/\partial s \; d^3s.$$

It disappears because of the Gauss' theorem and the postulate that distribution functions go to zero sufficiently fast, when one of the velocity arguments goes to infinity. The left hand side of (4.3.30) is (apart from a factor n_0) the same as the right hand side of (4.3.24). Therefore:

$$\partial F^{(0)}/\partial\tau_1 + v \cdot \partial F^{(0)}/\partial a \; = n_0 \int g \cdot \partial/\partial s \left[F^{(0)}\{a,v_\infty(s,v,v'),\tau_1\} \right.$$

$$\left. F^{(0)}\{a,v_\infty{}'(s,v,v'),\tau_1\} \right] d^3s d^3g. \tag{4.3.31}$$

Following [BOG1962] we now introduce cylindrical coordinates in s–space and choose the axis in the direction of g, i.e.

$$s = (b,\phi,z) \text{ and } g \cdot \partial/\partial s = g \, \partial/\partial z. \tag{4.3.32}$$

The point is that then the integration over z can be performed immediately with the result

$$\partial F^{(0)}/\partial \tau_0 + \boldsymbol{v} \cdot \partial F^{(0)}/\partial \boldsymbol{a} = n_0 \int d^3g \int_0^\infty db \int_0^{2\pi} d\phi bg \Big[\{ F^{(0)} F^{(0)} \}_{z \to +\infty}$$

$$- \{ F^{(0)} F^{(0)} \}_{z \to -\infty} \Big], \tag{4.3.33}$$

where the arguments of $F^{(0)}$ have been omitted for the sake of clarity.

When $z > 0$, the distance decreases at first when the streaming–back operation of Bogoliubov is applied. The possibility of interaction arises, after which (or rather *before* which in time τ_0) the distance increases again, see fig. 6. In this case we have:

$$\boldsymbol{v}_\infty(z \to +\infty, \ b,\phi,\boldsymbol{v},\boldsymbol{v}') = \hat{\boldsymbol{v}} \, (b,\phi,\boldsymbol{v},\boldsymbol{v}'),$$

$$\boldsymbol{v}_\infty{}'(z \to +\infty, \ b,\phi,\boldsymbol{v},\boldsymbol{v}') = \hat{\boldsymbol{v}}'(b,\phi,\boldsymbol{v},\boldsymbol{v}'), \tag{4.3.34}$$

where $\hat{\boldsymbol{v}}$ and $\hat{\boldsymbol{v}}'$ are the velocities *before* a collision, if the velocities *after* the collision are $\boldsymbol{v}$ and $\boldsymbol{v}'$ respectively.

When $z < 0$, the distance always increases under the streaming–back operation. Then no interaction has taken place in the (τ_0-) past. Therefore:

$$\boldsymbol{v}_\infty(z \to -\infty, \ b,\phi,\boldsymbol{v},\boldsymbol{v}') = \boldsymbol{v},$$

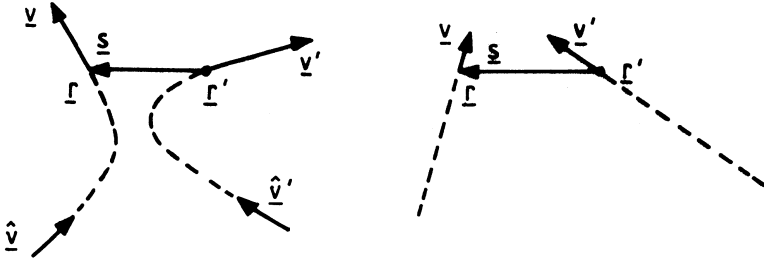$$\boldsymbol{v}_\infty{}'(z \to -\infty, \ b,\phi,\boldsymbol{v},\boldsymbol{v}') = \boldsymbol{v}'. \tag{4.3.35}$$

Figure 6. Two Cases of Streaming Back to the Past.

We may also call v, v' the velocities *before* and $\hat{v}, \hat{v}'$ the velocities *after* the (inverse) collision, since the collision proces is reversible. Using relative velocities according to

$$v' = v - g, \quad \hat{v}' = \hat{v} - \hat{g}, \tag{4.3.36}$$

the average zeroth order density in μ–space,

$$f(r,v,t) = n_0 F^{(0)}(r,v,t), \tag{4.3.37}$$

returning to the original variables with $\tau_1 = \epsilon_B t$, $a = \epsilon_B r$ and taking $\epsilon_B = 1$ eventually, we obtain the Boltzmann equation in the form:

$$\partial f / \partial t + v \cdot \nabla f = \int d^3 g \int_0^\infty db \int_0^{2\pi} d\phi\, bg \left\{ f(r,\hat{v},t) f(r, \hat{v} - \hat{g}, t) \right.$$

$$\left. - f(r,v,t) f(r, v - g, t) \right\}. \tag{4.3.38}$$

The interpretation is simple. Suppose that we multiply (4.3.38) with the volume $d^3 r d^3 v$ of a cell in μ–space around the position (r,v). The left hand side then represents the change of the number of molecules in that cell, when we follow it in its uniform motion. The righthand side describes the causes of this change. The second part of it represents collisions which remove particles from the cell, whereas the first one describes *inverse* collisions throwing molecules *into* the cell. This simple picture is in fact the basis of the intuitive derivation by Boltzmann himself, [BOL1872]. The collision integral has been obtained in lowest significant (in fact first) order of ϵ_B and therefore represents binary colllisions only. The Choh–Uhlenbeck term takes into account ternary interactions. This correction is given in Chapter 11, (11.3.12).

4.4.   DYNAMICS OF BINARY COLLISIONS.

Conservation of momentum and energy in a binary collision can be expressed by

$$2\hat{v} - \hat{g} = 2v - g = 2V_{12} \tag{4.4.1}$$

(V_{12} is the velocity of the center of mass of particles 1 and 2) and

$$\hat{v}^2 + |\hat{v} - \hat{g}|^2 = v^2 + |v - g|^2. \tag{4.4.2}$$

It is useful to introduce the vector ℓ as the change of v due to the collision:

$$\hat{v} = v + \ell. \tag{4.4.3}$$

It follows from (4.4.1) that

$$\hat{g} = g + 2l, \tag{4.4.4}$$

so that the expression between curly brackets in (4.3.38) may be transformed into

$$f(r,v+l,t)f(r,v-g-l,t) - f(r,v,t)f(r,v-g,t). \tag{4.4.5}$$

The conservation of energy (4.4.2) now reduces to

$$l^2 + g \cdot l = 0. \tag{4.4.6}$$

From (4.4.4) and (4.4.6) it also follows that the magnitude of the relative velocity does not change by a collision:

$$\hat{g} = g. \tag{4.4.7}$$

If the interaction potential depends on the distance between two molecules only, then the interaction force is central, cf. (2.2.19). The equations of motion describing the collision process of particles 1 and 2 are:

$$m\dot{v}_1 = -\partial\phi_{12}/\partial r_1 = -\partial\phi(s)/\partial s, \qquad \dot{r}_1 = v_1,$$
$$m\dot{v}_2 = -\partial\phi_{21}/\partial r_1 = +\partial\phi(s)/\partial s, \qquad \dot{r}_2 = v_2. \tag{4.4.8}$$

In the center of mass system moving with the velocity V_{12} with respect to the laboratory system, we have:

$$(v_1)_{\text{mmp}} = \tfrac{1}{2}g_{12},$$
$$(v_2)_{\text{mmp}} = -\tfrac{1}{2}g_{12}, \tag{4.4.9}$$

with $g_{12} = g$ before, and $g_{12} = g+2l$ after the collision. Subtracting the second line of (4.4.8) from the first we obtain:

$$\mu_r\dot{g}_{12} = -\partial\phi(s)/\partial s = -s/s \ \partial\phi(s)/\partial s, \quad s = g_{12}, \tag{4.4.10}$$

where $\mu_r = \tfrac{1}{2}m$ is the reduced mass.

From (4.4.10) conservation of angular momentum follows:

$$\dot{L} = d/dt(s \times \mu_r g_{12}) = \dot{s} \times \mu_r g_{12} + s \times \mu_r \dot{g}_{12} = 0,$$

so that the direction of $s \times g_{12}$ must be constant. Therefore the motion in the center of mass system takes place in a plane, see fig. 7.
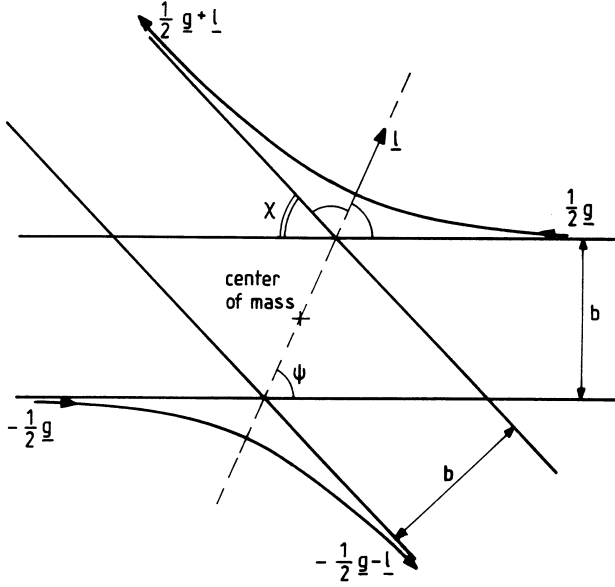
Figure 7. Binary Collision in the Center of Mass System.

As is shown in fig.7 the vector l is along the bisectrix of the angle between $\frac{1}{2}g$ and $\frac{1}{2}g + l$. This fact follows from (4.4.6):

$$\left(\tfrac{1}{2}g + l\right) \cdot l = \left(g \cdot l + l^2\right) - l \cdot \tfrac{1}{2}g = -l \cdot \tfrac{1}{2}g.$$

We also note that (4.4.6) can be rewritten as

$$l = g \cos\psi. \tag{4.4.11}$$

It is clear from the geometry that a simple relation exists between ψ and the deflection angle χ:

$$\chi + 2\psi = \pi. \tag{4.4.12}$$

Every interaction potential defines a relation

$$b = b(\chi, g). \tag{4.4.13}$$

This enables us to replace the integration over b in (4.3.38) by an integration over χ. The volume element is rewritten as

$$b\,db\,d\phi = b\,\partial b/\partial\chi\;d\chi\,d\phi = -I'(g,\chi)\sin\chi\,d\chi\,d\phi \qquad (4.4.14)$$

with the differential cross–section

$$I'(g,\chi) = b/\sin\chi\,|\,\partial b/\partial\chi\,|. \qquad (4.4.15)$$

Note that for a repulsive intermolecular force $\partial b/\partial\chi < 0$. If the intermolecular force is partly repulsive and partly attractive, then b is a multivalued function of χ. In the intervals of χ where this is the case, $|\,\partial b/\partial\chi\,|$ in (4.4.15) should be replaced by $\sum_i |\,\partial b_i/\partial\chi\,|$, where the subscript i distinguishes the different branches of $b(\chi)$. According to (4.4.11,12) the differential cross–section can be expressed as a function of l instead of χ:

$$I'(g,\chi) = I(g,l). \qquad (4.4.16)$$

It should be noted that $b \to \infty$ corresponds to $\chi \to 0$, $l \to 0$ and $b = 0$ (head–on collision) to $\chi = \pi$, $l = g$.

4.4.1. *An Explicit Form of the Boltzmann Equation.*

The collision integral of (4.3.38) is denoted by $(df/dt)_{\text{col}}$ and will be transformed into an integral over the entire l-space. As a first step we use (4.4.14,15):

$$(df/dt)_{\text{col}} = \int_0^\pi d\chi \int_0^{2\pi} d\psi \; g \, \sin\chi \, I'(g,\chi)\{...\},$$

where between the curly brackets the bilinear combination of distribution functions appearing in (4.3.38) is presumed to be present. From (4.4.11,12) we have:

$$d\chi = -2d\psi, \quad \sin\chi = 2\sin\psi \, \cos\psi = 2l/g \, \sin\psi,$$

so that

$$(df/dt)_{\text{col}} = 4\int_0^{\pi/2} d\psi \int_0^{2\pi} d\phi \; l \, \sin\psi \; I(g,l)\{...\}. \qquad (4.4.17)$$

Next we add a factor $\delta(l-g\cos\psi)$ and integrate over l from zero to infinity. This is justified by (4.4.11). After that we can extend the integral with respect to ψ from 0 to π, since $\delta(l-g\cos\psi) = 0$ for $\cos\psi < 0$. Noting that $d^3l = l^2\sin\psi \, dl\,d\psi\,d\phi$ and, because of property (1.3.6) of delta–functions, $\delta(l-g\cos\psi) = l\delta(l^2+g\cdot l)$, we can now write the Boltzmann equation (4.3.38) as

$$\partial f/\partial t + \boldsymbol{v}\cdot\nabla f = 4\int d^3g\int d^3l\,\delta(l^2+\boldsymbol{g}\cdot\boldsymbol{l})\,I(g,l)\{f(\boldsymbol{r},\boldsymbol{v}+\boldsymbol{l},t)$$

$$f(\boldsymbol{r},\boldsymbol{v}-\boldsymbol{g}-\boldsymbol{l},t) - f(\boldsymbol{r},\boldsymbol{v},t)f(\boldsymbol{r},\boldsymbol{v}-\boldsymbol{g},t)\}. \qquad (4.4.18)$$

This form has the advantage that all integrations are indicated explicitly. The differential scattering cross–section $I(g,l)$ is determined by the intermolecular interaction potential. The relation follows from (4.4.11,12,15,16) and an expression well known from classical mechanics, cf. e.g. [LAN1960]:

$$\psi = \int_{r_{\min}}^{\infty} \frac{b\,dr}{r^2\{1-b^2/r^2-2\phi(r)/(\mu_r g^2)\}^{\frac{1}{2}}}, \qquad (4.4.19)$$

where $r_{\min}$ is the distance of closest approach, implicitly given by

$$1 - b^2/r_{\min}^2 - 2\phi(r_{\min})/(\mu_r g^2) = 0. \qquad (4.4.20)$$

4.4.2 Cross–sections

We consider two examples:
— Coulomb interaction between two particles (electrons) with electric charge –e.
   Then $\phi(r) = \hat{e}^2/r$ with $\hat{e}^2 = e^2/(4\pi\epsilon_0)$. The procedure described above lead to
   the well–known Rutherford cross–section, cf. [LAN1960]:

$$I'(g,\chi) = \hat{e}^4/[4\,\mu_r^2 g^4\sin^4(\tfrac{1}{2}\chi)] \ ,$$

or, because of (4.4.11,12), to

$$I(g,l) = \hat{e}^4/(4\,\mu_r^2 l^4) \ . \qquad (4.4.21)$$

The last expression is seen to be independent of g.

— Hard spheres with diameter a. The corresponding potential is given by

$$\phi(r) = \begin{cases} \infty, \ r < a \\ 0 \ , \ r > a. \end{cases} \qquad (4.4.22)$$

For $b > a$ the solution of (4.4.20) is $r_{\min} = b$. Then (4.4.19) leads to

$$\psi = \int_{a}^{\infty} \frac{b\,dr}{r^2(1-b^2/r^2)^{\frac{1}{2}}} = \int_{0}^{1} \frac{d\xi}{(1-\xi^2)^{\frac{1}{2}}} = \frac{\pi}{2},$$

or $\chi = 0$, as should have been expected.
For $b < a$ we must obviously have $r_{\min} = a$. This is consistent with (4.4.20),

since $\phi(a)$ is not fixed. We now see from (4.4.19) that

$$\psi = \int_a^\infty \frac{b\,dr}{r^2(1-b^2/r^2)^{\frac{1}{2}}} = \int_0^{b/a} \frac{d\xi}{(1-\xi^2)^{\frac{1}{2}}} = \frac{\pi}{2}\arcsin(b/a),$$

or, with (4.4.12), $b/a = \cos(\chi/2)$. We then obtain from (4.4.15,16):

$$I(g,\ell) = I'(g,\chi) = \tfrac{1}{4}a^2. \tag{4.4.23}$$

The total cross section is πa^2. This result is self–explanatory.

4.5.   BOLTZMANN EQUATION AND MARKOV PROCESSES.

In this section we want to show a relation between the Boltzmann equation and the description of a class of stochastic processes, the so–called Markov processes. Therefore we consider a stochastic process $a(t)$. At any time t the quantity a may take all values, possibly within a restricted interval. The value of a can only be discussed in terms of probability densities.

We consider $a(t)$ at discrete points in time $l\Delta t$, $l = 0,1,2,...$, and introduce the combined probability density for values of a at $q+1$ successive instants of time: $p(a_0,a_1,a_2,a_3, ..., a_q)$. We also introduce *conditional* probability densities $p(a_1|a_0)$, $p(a_2|a_1,a_0)$, etc; $p(a|a_0)$ is the probability density for finding a_1 at time Δy, *given* the fact that $a = a_0$ at $t = 0$, $p(a_2|a_1,a_0)$ is the probability density for finding a_2 at time $2\Delta t$, given the fact that $a = a_1$ at $t = \Delta t$ and $a = a_0$ at $t = 0$, etc. The following formula is now obvious:

$$p(a_0,a_1,a_2,...,a_q) = p(a_0)p(a_1|a_0)p(a_2|a_1,a_0)...p(a_q|a_{q-1},...,a_0). \tag{4.5.1}$$

Here $p(a_0)$ is the (unconditional) probability density for the value a_0 at the initial time $t = 0$. We divide by $p(a_0)$ and write:

$$p(a_1,a_2,...,a_q|a_0) = p(a_1|a_0)p(a_2|a_1,a_0)...p(a_q|a_{q-1},...,a_0), \tag{4.5.2}$$

where the meaning of the combined conditional probability density $p(a_1,a_2,...,a_q|a_0)$ is obvious. Equally obvious is the relation

$$p(a_{q-1},a_q|a_0) = p(a_{q-1}|a_0)p(a_q|a_{q-1},a_0) \tag{4.5.3}$$

where three points in time $(0,(q-1)\Delta t,q\Delta t)$ are involved.
Markov–processes are defined by the property

$$p(a_q|a_{q-1},...,a_0) = p(a_q|a_{q-1}), \; q \geq 2. \tag{4.5.4}$$

The values $a_{q-2},...,a_0$ have been "forgotten". Very often it is possible to recognize a

"remembrance time" τ_R. The stochastic process $a(t)$ can then be treated as a Markov process, if

$$\Delta t \gg \tau_R. \tag{4.5.5}$$

In the case of Markov processes (4.5.2) reduces to

$$p(a_1, a_2, ..., a_q \mid a_0) = p(a_1 \mid a_0) p(a_2 \mid a_1,) ... p(a_q \mid a_{q-1}), \tag{4.5.6}$$

The statistical treatment of such processes is completely concentrated in two functions: $p(a_r)$ and $p(a_{r+1} \mid a_r)$, $r = 0,1...$

Applying the Markov property to (4.5.3) and integrating over a_{q-1} we obtain the Chapman–Kolmogorov equation, see [VKA1981]:

$$p(a_q \mid a_0) = \int p(a_q \mid a_{q-1}) \, p(a_{q-1} \mid a_0) da_{q-1} \tag{4.5.7}$$

We now change the notation and write $p_0(a, t+\Delta t)$ instead of $p(a_q \mid a_0)$ and $\psi(a' \rightarrow a, t, \Delta t)$ instead of $p(a_q \mid a_{q-1})$. The Chapman–Kolmogorov equation takes the form

$$p_0(a, t+\Delta t) = \int p_0(a', t) \psi(a' \rightarrow a, t, \Delta t) da'. \tag{4.5.8}$$

The interpretation is easy: $p_0(a,t)$ is the probability density for finding a at time t, given a_0 at $t = 0$, and $\psi(a' \rightarrow a, t, \Delta t)$ is the probability density for a transition from a' to a at time t during Δt.

For small Δt there exists a finite probability that no transition takes place at all and a probability proportional to Δt that one does occur, so that $\psi(a' \rightarrow a, t, \Delta t)$ becomes:

$$\psi(a' \rightarrow a, t, \Delta t) = \{1 - A(t)\Delta t\}\delta(a-a') + W_t(a' \rightarrow a)\Delta t + 0\{\Delta t\}^2\}, \tag{4.5.9}$$

where $W_t(a' \rightarrow a)$ is now a transition *rate*. The function $A(t)$ is related to W_t as a consequence of the normalization

$$\int \psi(a' \rightarrow a, t, \Delta t) da = 1, \tag{4.5.10}$$

which implies:

$$A(t) = \int W_t(a' \rightarrow a) da. \tag{4.5.11}$$

Substituting (4.5.9,10,11) into (4.5.8) we arrive at

$$p_0(a, t+\Delta t) = p_0(a,t) + \Delta t \int da' \left[p_0(a', t) W_t(a' \rightarrow a) \right.$$

$$-p_0(a,t)\, W_t(a \to a')\Big] + O\{(\Delta t)^2\},$$

where (4.5.11) has been used after interchange of a and a'. Dividing by Δt and taking the limit $\Delta t \to 0$ we obtain the *Pauli–master equation*, see [VKA81]:

$$\partial p_0(a,t)/\partial t = \int da' \Big[p_0(a',t)\, W_t(a' \to a) - p_0(a,t)\, W_t(a \to a') \Big]. \quad (4.5.12)$$

It should be observed, that the procedure of taking the limit $\Delta t \to 0$ might be inconsistent with (4.5.5). Actually (4.5.12) follows as a good approximation, if $\Delta t << \tau_p$, where τ_p is the characteristic time in which the functions $p_0(a,t)$ and $\psi(a' \to a, t, \Delta t)$ may change considerably. Therefore we must require:

$$\tau_R << \Delta t << \tau_p. \quad (4.5.13)$$

Instead of starting with a fixed value $a = a_0$ we may consider an initial probability density $p(a_0)$. Multiplication of (4.5.12) with $p(a_0)$ and integration over a_0 leads to the same equation for $P(a,t)$ given by

$$P(a,t) = \int p_0(a,t) p(a_0)\, da_0. \quad (4.5.14)$$

Of course we have:

$$p_0(a,o) = \delta(a-a_0), \quad P(a,o) = p(a). \quad (4.5.15)$$

The Pauli–master equation is a linear equation for $p_0(a,t)$ or $P(a,t)$. This should be kept in mind when we next observe that the Boltzmann equation, which in general is non–linear, may be written as a Pauli–master equation. Instead of the stochastic variable a we have the vector $\boldsymbol{v}$ and in the left hand side we replace the partial time derivative by a combination describing the change of the distribution function experienced by particles moving with velocity $\boldsymbol{v}$, i.e.

$$\partial f/\partial t + \boldsymbol{v} \cdot \nabla f = \int d^3 v' \Big[f(\boldsymbol{r},\boldsymbol{v}',t)\, W_t(\boldsymbol{v}' \to \boldsymbol{v},\boldsymbol{r})$$

$$- f(\boldsymbol{r},\boldsymbol{v},t)\, W_t(\boldsymbol{v} \to \boldsymbol{v}',\boldsymbol{r}) \Big]. \quad (4.5.16)$$

Multiplying with an infinitesimal element $d^3 v$ around the point $\boldsymbol{v}$ of velocity space we may interpret $d^3 v'\, d^3 v\, W_t(\boldsymbol{v}' \to \boldsymbol{v},\boldsymbol{r})$ as the number of transitions per unit of time from the element $d^3 v'$ around $\boldsymbol{v}'$ to the element $d^3 v$ around $\boldsymbol{v}$. A similar interpretation holds, of course, for $d^3 v\, d^3 v'\, W_t(\boldsymbol{v} \to \boldsymbol{v}',\boldsymbol{r})$. The transitions are caused by collisions. We can therefore write:

$$W_t(\boldsymbol{v}' \to \boldsymbol{v},\boldsymbol{r}) = \int W(\boldsymbol{v}',\boldsymbol{v}_1' \to \boldsymbol{v},\boldsymbol{v}_1) f(\boldsymbol{r},\boldsymbol{v}_1',t)\, d^3 v_1\, d^3 v_1'. \quad (4.5.17)$$

and, interchanging v and v', v_1 and v_1', a similar expression for $W_t(v \to v',r)$. Here $W(v',v_1' \to v,v_1)$ is a transition rate for the velocities of particle pairs.
The Boltzmann equation (4.4.18) is now obtained with

$$W(v',v_1' \to v,v_1) = W(v,v_1 \to v',v_1') = 8I(|v_1 - v|,|v' - v|)$$

$$\delta(v' + v_1' - v - v_1)\delta(v'^2 + v_1'^2 - v^2 - v_1^2), \qquad (4.5.18)$$

the transformations $v - v_1 = g$, $v' - v = l$ and the implementation of the v_1'-integration. The first equality in (4.5.18) is an example of "detailed balance", following directly from the reversibility of collisions. The Dirac-delta-functions express the conservation of momentum and kinetic energy in collisions.
The evolution of a gas with a small Boltzmann parameter may apparently be considered as a non-linear counterpart of a Markov process. It is not difficult to identify the times τ_R and τ_p of (4.5.13). The remembrance time is the time needed by the multiple distribution functions to "synchronize" (Bogoliubov) with the one particle distribution function, i.e. the collision duration:

$$\tau_R = r_f v_T^{-1}. \qquad (4.5.19)$$

The characteristic time τ_p, in which the one particle distribution function changes considerably, is the collision time (mean free flight time):

$$\tau_p = \epsilon_B^{-1} \tau_R = \lambda v_T^{-1}, \qquad (4.5.20)$$

where λ is the mean free path. Because $\epsilon_B \ll 1$, we can choose Δt in such a way that (4.5.13) is satisfied.

4.6.   PROPERTIES OF THE BOLTZMANN EQUATION

It is impossible to provide general solutions of the Boltzmann equation. Procedures leading to approximate solutions are described in Chapter 5. Here we will discuss some general properties, of which irreversibility is the most important one.

4.6.1 Positivity of the Distribution Function and Invariance under Time Reversal.

Only positive functions $f(r,v,t)$ can be considered for the interpretation of mean densities in μ-space. The following theorem is therefore important:

If $f(r,v,t=0) > 0$ in the entire μ-space, then $f(r,v,t) > 0$ for $t > 0$.

This can be easily proven, if f is everywhere continuous and differentiable. Suppose that the theorem does not hold. Then there exists at least one point in μ-space where f becomes zero at some time t_0 whereas f is still positive in its surroundings. We denote such a point by r_α, v_α and observe that we must have:

$$f(r_\alpha,v_\alpha,t_0) = 0, \quad \{\nabla_v f(r_\alpha,v,t_0)\}_{v=v_\alpha} = 0,$$

$$\{\nabla(r,v_\alpha,t_0)\}_{r=r_\alpha} = 0. \qquad (4.6.1)$$

From (4.4.18) we then conclude:

$$\left\{ \partial f(r_\alpha, v_\alpha, t)/\partial t \right\}_{t=t_0} = 4 \int d^3g \int d^3l \delta(l^2 + g \cdot l) I(g,l)$$

$$f(r_\alpha, v_\alpha + l) f(r_\alpha, v_\alpha - g - l, t_0) > 0 \qquad (4.6.2)$$

so that $f(r_\alpha, v_\alpha)$ becomes positive again.

A very important property which is not necessary (like positivity) because of the definition of f, is its *lack of invariance under time reversal*. Transforming according to

$$t' = -t, \; v' = -v, \; \hat{f}(r, v', t') = f(r, v, t) , \qquad (4.6.3)$$

changing integration variables in the right hand side of (4.4.18) through $g' = -g$, $l' = -l$ and omitting these primes again, we obtain:

$$-\partial \hat{f}/\partial t' - v' \cdot \nabla \hat{f} = 4 \int d^3g \int d^3l \; \delta(l^2 + g \cdot l) I(g,l) \Big\{ \hat{f}(r, v' + l, t')$$

$$\hat{f}\; r, v' - g - l, t') - \hat{f}(r, v', t') \hat{f}(r, v' - g, t') \Big\}, \qquad (4.6.4)$$

i.e. the left hand side of (4.4.18) reverses sign, the right hand side does not. This shows the irreversible character of (4.4.18). A reversible equation, e.g. the Klimontovich equation (3.2.6), is clearly invariant under the transformation (4.6.3). The Boltzmann equation discriminates between past and future, time has an "arrow". This phenomenon is more explicit in the so-called H-theorem of Boltzmann.

4.6.2 H-theorem for a uniform gas.

For the sake of simplicity we start with the relatively simple case where $f(r, v, t)$ is uniform: $\nabla f = 0$. We define a quantity $H(t)$ by

$$H(t) = \int f \ln f d^3 v. \qquad (4.6.5)$$

After multiplication of (4.4.18) with some function $\phi(r, v, t)$ and integration over v-space, it is possible to symmetrize the nine-fold integral in the right hand side. We will choose $\phi = 1 + \ln f$, so that the left hand side becomes equal to dH/dt. About the right hand side we will prove that it can never be positive. The conclusion is

$$dH/dt \leq 0. \qquad (4.6.6)$$

We will see in detail that this implies an irreversible relaxation towards thermal equilibrium.

The symmetrization announced above concerns

$$4 \int d^3g \int d^3l \int d^3v \phi(v) \delta(l^{\,2} + g \cdot l) I(g,l) \{ f(v+l)$$

$$f(v-g-l) - f(v)f(v-g)\}, \tag{4.6.7}$$

where the arguments r and t have been omitted. Two steps are involved:
- interchange of two particles amounting to the successive transformations
  $l \rightarrow -l,\ g \rightarrow -g,\ v \rightarrow v - g$ at fixed (v,g), (l,v), (l,g) respectively.
- interchange of direct and inverse collisions corresponding to the successive transformations $v \rightarrow v-l,\ g \rightarrow g-2l,\ l \rightarrow -l.$

In both operations $I(g,l)$ and $\delta(l^{\,2} + g \cdot l)$ are invariant. In the first one the arguments of the distribution functions within the two terms of (4.6.7) seperately are interchanged. These terms are therefore invariant, so that

$$\int d^3g \int d^3l \int d^3v [\phi(v) - \phi(v-g)] \delta(l^2 + g \cdot l) I(g,l)$$

$$\{f(v+l)\ f(v-g-l) - f(v)f(v-g)\} = 0. \tag{4.6.8}$$

In the second operation the arguments are interchanged *between* the two terms. so that the sign of the expression between curly brackets is reversed. Therefore:

$$\int d^3g \int d^3l \int d^3v [\phi(v) + \phi(v+l)] \delta(l^{\,2} + g \cdot l) I(g,l)$$

$$\{f(v+l)\ f(v-g-l) - f(v)f(v-g)\} = 0. \tag{4.6.9}$$

Implementation of *both* operations leads to an equation like (4.6.9) with $\phi(v-g-l)$ instead of $\phi(v + l)$. All this means that the expression (4.6.7) may be replaced by

$$\int d^3g \int d^3l \int d^3v [\phi(v) + \phi(v-g) - \phi(v+l) - \phi(v-g-l)]$$

$$\{f(v+l)\ f(v-g-l) - f(v)f(v-g)\}\ \delta(\ell^{\,2} + g \cdot l) I(g,l). \tag{4.6.10}$$

Multiplying (4.4.18) with $\phi(v,t) = 1 + \ln f(v,t)$ and integrating we arrive at

$$dH/dt = \int d^3v \int d^3g \int d^3l\ \delta(\ell^2 + g \cdot l) I(g,l) b(1-x) \ln x \tag{4.6.11}$$

with

$$x = a/b,\ a = f(v+l,t)f(v-g-l,t),\ b = f(v,t)f(v-g,t).$$

$$\tag{4.6.12}$$

Since $\delta(\ell^{\,2} + g \cdot l) I(g,l) b \geq 0$ and $(1-x)\ln x \leq 0$, (4.6.6) follows immediately. The function $H(t)$ decreases monotonously. Eventually a minimum value is reached, unless $H(t)$ decreases indefinitely. It can be proven, however, that H is bounded from below. This follows from the fact that the density $n = \int f d^3v$ and the kinetic

energy density, which is proportional to $\int v^2 f d^3 v$, must be finite. We write $\boldsymbol{v} = v\boldsymbol{\Omega}$ and $d^3 v = v^2 dv d^2\Omega$, where $\boldsymbol{\Omega}$ is the unit vector in the direction of $\boldsymbol{v}$ and $d^2\Omega$ is an infinitesimal solid angle. The point $\boldsymbol{v} = 0$ is representative for any point with finite v. The finiteness of n requires that $f < A(\Omega)v^{\delta-3}$ with $\delta > 0$ for $v \to 0$. We then easily find, that

$$\int_0^\Delta dv \int d^2\Omega v^2 f \ln f \le \Delta^\delta (c_1 \ln\Delta + c_2) \qquad (4.6.13)$$

with finite coefficients $c_{1,2}$. The contribution to H from the neighbourhood of $\boldsymbol{v} = 0$ (or any finite $\boldsymbol{v}$) is therefore finite. Comparing H with the kinetic energy density we see that the integral defining H can only diverge at infinity, if $\ln f$ decreases faster than $-v^2$ for $v \to \infty$. In that case $f < c_3 \exp(-c_4 v^2)$ with finite constants $c_{3,4}$. The integral would then, however, certainly converge.

Therefore, $H(t)$ relaxes to a minimum. When this has been reached, $dH/dt = 0$ and (4.6.11,12) imply:

$$\ln f_e(\boldsymbol{v} + \boldsymbol{l}) + \ln f_e(\boldsymbol{v}-\boldsymbol{g}-\boldsymbol{l}) - \ln f_e(\boldsymbol{v}) - \ln f_e(\boldsymbol{v}-\boldsymbol{g}) = 0 \qquad (4.6.14)$$

for

$$l^2 + \boldsymbol{g}\cdot\boldsymbol{l} = 0. \qquad (4.6.15)$$

The subscript e of f_e refers to the fact that the minimum of H corresponds to equilibrium. The solution to (4.6.14,15) at the same time causes the collision integral of (4.4.18) to disappear. A linear combination of the *collisional invariants* 1, $\boldsymbol{v}$ and v^2 is therefore such a solution:

$$\ln f_e(\boldsymbol{v}) = \gamma + \boldsymbol{\beta}\cdot\boldsymbol{v} - \alpha v^2. \qquad (4.6.16)$$

This is also the most general solution. The proof of this statement is not given here, but can be found in, e.g., [BAL1975]. We rewrite (4.6.16) as

$$f_e(\boldsymbol{v}) = A \exp\{-\alpha|\boldsymbol{v}-\boldsymbol{v}_0|^2\} \qquad (4.6.17)$$

with

$$A = \exp(\gamma + \beta^2/4\alpha), \; \boldsymbol{v}_0 = \boldsymbol{\beta}/(2\alpha). \qquad (4.6.18)$$

The constant velocity $\boldsymbol{v}_0$ is not interesting and is removed by a Galilei transformation. The constants A and γ are expressed in terms of the density n_0 and the absolute temperature T. For the density we have:

$$n_0 = \int f_e d^3 v = (\pi/\alpha)^{3/2} A, \qquad (4.6.19)$$

whereas the temperature is *defined* through the density of kinetic energy:

$$3/2 \ n_0 k_B T = \int 1/2 \ m v^2 f_e d^3 v = 3/4 \ m n_0 / \alpha. \qquad (4.6.20)$$

To obtain the last equality (4.6.19) was used. We arrive at the *Maxwellian distribution* in its usual form:

$$f_e(v) = n_0 \left[m/2\pi k_B T \right]^{3/2} \exp\left[-m v^2 / 2 k_B T \right]. \qquad (4.6.21)$$

A uniform gas obeying the Boltzmann equation and the *H*–theorem derived from it, must relax to thermal equilibrium and its distribution function must relax to (4.6.21).

4.6.3 H–theorem for a non–uniform gas.

We now consider the general case where the distribution function depends on position. We suppose that the gas is enclosed by a vessel. Moreover we admit an external force field and write the Boltzmann equation in the form

$$\partial f/\partial t + v \cdot \nabla f + m^{-1} f_{ext} \cdot \nabla_v f = J(f,f), \qquad (4.6.22)$$

where $J(f,f)$ is the (bilinear) collision integral. We multiply (4.6.22) with $1 + \ln f$ and integrate over the entire μ–space. If

$$\nabla_v \cdot f_{ext}(r,v) = 0, \qquad (4.6.23)$$

the last term of the left hand side is transformed into

$$\int d^3 v \nabla_v \cdot [f_{ext} f \ln f]$$

and disappears because of Gauss' theorem, provided that f approaches zero sufficiently fast as $v \to \infty$.
We now define

$$H_0(t) = \int_V H(t) d^3 r = \int_V d^3 r \int d^3 v \ f \ln f, \qquad (4.6.24)$$

and find:

$$dH_0/dt + I_w = \int_V d^3 r \int d^3 v \int d^3 g \int d^3 l \ \delta(\ell^2 + g \cdot l) I(g,l) b (1-x) \ln x, \qquad (4.6.25)$$

in analogy with (4.6.11). There is, however, an extra term:

$$I_{\mathrm{w}} = \int d^3r \int d^3v \; v \cdot \nabla(f \ln f) = \int d^2r \; n \cdot \int d^3v \; vf \ln f. \qquad (4.6.26)$$
$$\phantom{I_{\mathrm{w}} = \int d^3r}_{V} _{S}$$

The second equality has been obtained on basis of Gauss' theorem, S being the surface of the walls of the vessel and n the unit normal vector pointing into the wall. In the same way as in the preceding subsection we conclude that

$$dH_0/dt + I_{\mathrm{w}} \le 0. \qquad (4.6.27)$$

In order to investigate the influence of I_{w} it is necessary to specify the *gas–wall interaction*. One might assume that the walls are perfect mirrors. This is the simplest, but also a very unrealistic assumption. In this case we have the boundary condition

$$f(r_{\mathrm{w}}, \, v_{\mathrm{n}}, \, v_{\mathrm{t}}, t) = f(r_{\mathrm{w}}, \, -v_{\mathrm{n}}, v_{\mathrm{t}}, t), \qquad (4.6.28)$$

where r_{w} denotes positions at the walls, and

$$v_{\mathrm{n}} = n \cdot v, \quad v_{\mathrm{t}} = v - v_{\mathrm{n}}n = n \times(v \times n). \qquad (4.6.29)$$

As a consequence the integrand $v_{\mathrm{n}} f \ln f$ in (4.6.26) is an odd function of v_{n}, so that $I_{\mathrm{w}} = 0$ and

$$dH_0/dt \le 0. \qquad (4.6.30)$$

A similar, but modified, conclusion may be reached in the case of *diffuse reflection*. In this case molecules colliding with a wall get into equilibrium with the wall and return instantaneously into the gas with a Maxwellian distribution coresponding to the temperature T_{w} of the wall. Therefore (See fig.8):

$$f(r_{\mathrm{w}}, v, t) = (\alpha_{\mathrm{w}}/\pi)^{3/2} \exp(-\alpha_{\mathrm{w}} v^2), \text{ for } v_{\mathrm{n}} < 0 \qquad (4.6.31)$$

with

$$\alpha_{\mathrm{w}} = m/(2 k_{\mathrm{B}} T_{\mathrm{w}}). \qquad (4.6.32)$$

A good approximation to reality is often realized by a combination of mirroring and diffuse reflection:

$$f(r_{\mathrm{w}}, v_{\mathrm{n}}, v_{\mathrm{t}}, t) = A \, (\alpha_{\mathrm{w}}/\pi)^{3/2} \exp(-\alpha_{\mathrm{w}} v^2) + (1{-}A) f(r_{\mathrm{w}}, -v_{\mathrm{n}}, v_{\mathrm{t}}, t)$$

$$(4.6.33)$$

for $v_{\mathrm{n}} < 0$. The parameter A is called accommodation coefficient. The mirroring part of (4.6.33) does not contribute to I_{w}. In the following we therefore restrict ourselves to diffuse reflection, i.e boundary condition (4.6.28). We distinguish positive and negative v_{n} and write (4.6.26) as
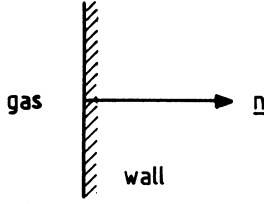
Figure 8. Gas–wall Configuration

$$I_w = \int d^2r \left\{ - \int\limits_{v_n < 0} |v_n| f_w \ln f_w d^3f + \int\limits_{v_n > 0} v_n f \ln f \, d^3v \right\}, \qquad (4.6.34)$$

where f_w is the distribution (4.6.31). Since f_w is an even function of v_n we can equally well write:

$$I_w = \int\limits_S d^2r \int\limits_{v_n > 0} v_n (f \ln f - f_w \ln f_w) d^3v . \qquad (4.6.35)$$

In the following discussion we will use the property

$$\int\limits_{v_n > 0} v_n f d^3v = \int\limits_{v_n < 0} |v_n| f_w d^3v = \int\limits_{v_n > 0} v_n f_w \, d^3v, \qquad (4.6.36)$$

where the first equality follows from the impenetrability of the walls and the second from the fact that f_w is an even function of v_n.

Moreover we will use a *lemma* valid for all positive x and y:

$$x \left(\ln x - \ln y \right) - x + y \geq 0. \qquad (4.6.37)$$

Proof. Define the function $\psi(x) = x \left(\ln x - \ln y \right) - x + y$, which also depends on the parameter y. The first derivative is $\psi'(x) = \ln x - \ln y$ and the second is $\psi''(x) = x^{-1} > 0$. Therefore $\psi(x)$ has an absolute mimimum at $x = y$. Since $\psi(x=y) = 0$, the lemma has been proved.

We now take $x = f$ and $y = f_w$ and find:

$$f \ln f \geq f \ln f_w + f - f_w. \qquad (4.6.38)$$

Substituting this into (4.6.35) and using (4.6.36) we obtain:

$$I_w \geq \int\limits_S d^2r \int\limits_{v_n > 0} v_n (f - f_w) \ln f_w \, d^3v. \qquad (4.6.39)$$

The definition (4.6.31) implies $\ln f_w = \text{const.} - \alpha_w v^2$. The constant does not contribute to (4.6.39), so that

$$I_w \geq - \int_S d^2r \int_{v_n > 0} \alpha_w v^2 v_n (f-f_w) d^3v. \tag{4.6.40}$$

We decompose v according to (2.2.6) into the hydrodynamic flow velocity $w(r,t)$ and the peculiar velocity c. The impenetrability of the walls implies $w_n(r_w,t) = 0$ and via (4.6.36):

$$\int_{c_n > 0} c_n (f-f_w) d^3c = 0. \tag{4.6.41}$$

Using this and the fact that the restriction $c_n > 0$ is superfluous, because $f = f_w$ for $c_n < 0$, we rewrite (4.6.40) as

$$I_w \geq - \alpha_w \int_S d^2r \int (2w \cdot c + c^2) c_n (f-f_w) d^3c. \tag{4.6.42}$$

Next we observe, that the contribution of f_w to the right hand side disappears, because the corresponding part of the integrand is an odd function of c_n, since $w \cdot c$ does not contain c_n. With the definitions of the kinetic pressure tensor and heat flux vector, given in (2.2.9) and exercise 3 of Chapter 2 respectively, we transform (4.6.42) into

$$I_w \geq - (k_B T_w)^{-1} \int_S d^2r \, n \cdot (P_k \cdot w_{slip} + q_k), \tag{4.6.43}$$

where also (4.6.32) has been used. We have provided the flow velocity w with the subscript "slip" to emphasize that a tangential flow at the walls is involved here. The integral in (4.6.43) has a simple physical meaning: both terms are energy transfers from the walls to the gas per unit time, $- \int_S d^2r \, n \cdot q_k$ is the heat transferred by molecules and $- \int_S n \cdot P_k \cdot w_{slip} d^2r$ is the work performed on the gas by shear stresses. The latter is negative in general: the walls are slightly heated by the gas slipping along them. From (2.3.27) and $w_n = 0$ it is immediately seen that the integral of (4.6.43), provided with the minus sign, represents the entire energy flow per unit time from the walls to the gas. That might have been concluded from (4.6.40) already, but the interesting decomposition in (4.6.43) would then have escaped notice.

From (4.6.27) and (4.6.43) we obtain

$$dH_0/dt \leq - (k_B T_w)^{-1} \, dQ/dt, \tag{4.6.44}$$

where dQ/dt is the heat delivered from the walls to the gas per unit time. If there is no heat exchange with the surroundings, or if heat is injected into the gas

$(dQ/dt > 0)$, the H–theorem (4.6.30) is valid.

As we will see in the next sub–section, H_0 is directly related to the entropy, S, of the gas:

$$S = -k_B H_0,$$ (4.6.45)

so that (4.6.44) can be written as

$$T_w dS \geq dQ.$$ (4.6.46)

The equality sign applies when instantaneous equilibrium between the gas and the walls prevails. The inequality is caused by irreversible processes in the gas.

We now investigate the consequences of (4.6.30) in analogy with the preceding subsection: H_0 decreases monotonously until a minimum value has been reached (asymptotically). In this equilibrium (4.6.14,15) must be valid again, so that f_e is a Maxwellian of the form (4.6.21), except that we might have position dependent density, flow velocity and temperature.
Therefore:

$$f_e = n(r) \left\{ m/(2\pi k_B T(r)) \right\}^{3/2} \exp\left[-m| v-w(r)|^2/(2k_B T(r)) \right].$$

(4.6.47)

However, because of (4.6.14,15) the collision integral of the Boltzmann equation (4.6.22) must vanish, so that f_e should satisfy

$$v \cdot \nabla f_e + m^{-1} F_{ext} \cdot \nabla_v f_e = 0$$ (4.6.48)

identically in the molecular velocity v. Dividing by f_e and performing the (logarithmic) differentiation we have:

$$v \cdot \nabla \ln(n T^{-3/2}) + m/(k_B T)(v-w) \cdot (v \cdot \nabla)w$$

$$+ m/(2k_B T^2)|v-w|^2 v \cdot \nabla T - 1/(k_B T) F_{ext} \cdot (v-w) = 0. \quad (4.6.49)$$

The coefficient of each occurring power of v is required to vanish. The highest one is $v^2 v$. Therefore:

$$\nabla T = 0,$$ (4.6.50)

i.e. the temperature must be uniform in equilibrium. The second term of (4.6.49) contains quadratic terms:

$$vv : \nabla w = 0.$$ (4.6.51)

We decompose ∇w into a symmetric and an antisymmetric part:

$$\nabla w = D + \Omega$$ (4.6.52)

with

$$D_{ik} = \tfrac{1}{2}\left[\partial w_k/\partial x_i + \partial w_i/\partial x_k\right], \quad \Omega_{ik} = \tfrac{1}{2}\left[\partial w_k/\partial x_i - \partial w_i/\partial x_k\right]$$

$$(4.6.53)$$

Now $vv : \Omega = 0$ because of symmetry reasons, so that (4.6.51) leads to the condition:

$$D = 0, \qquad\qquad\qquad (4.6.54)$$

i.e. the *deformation tensor* of hydrodynamics must disappear. The general solution to (4.6.54) is provided by a combination of uniform translation and rigid body rotation:

$$w(r) = w_0 + \omega \times r. \qquad\qquad\qquad (4.6.55)$$

The translation w_0 is uninteresting and may be eliminated by means of a Galilei transformation. The rigid body rotation can only take place, if the boundary conditions allow for it, which means, in general, that the vessel containing the gas will have to rotate itself.

The terms of (4.6.49) linear in v are:

$$v \cdot \nabla \ln(n T^{-3/2}) - m/(k_B T)\, w \cdot (v \cdot \nabla)w - 1/(k_B T)\, F_{ext} \cdot v = 0. (4.6.56)$$

We assume that the external force may be derived from a potential:

$$F_{ext} = -\nabla U. \qquad\qquad\qquad (4.6.57)$$

Furthermore we observe that $w \cdot (v \cdot \nabla)w = v \cdot \nabla(\tfrac{1}{2}w^2)$, so that (4.6.56) can be written as

$$v \cdot \nabla\left[\ln n - \{\tfrac{1}{2}m|\omega \times r|^2 - U\}/(k_B T)\right] = 0,$$

where also (4.6.50) and (4.6.55) with $w_0 = 0$ have been used. Therefore:

$$n(r) = \text{const.} \exp\left[-\{\tfrac{1}{2}m|\omega \times r|^2 - U\}/(k_B T)\right], \qquad (4.6.58)$$

i.e. the density is given by a Boltzmann factor with the potential U of the external force field and the potential $-\tfrac{1}{2}m|\omega \times r|^2$ of the centrifugal force.

Finally we have one term left in (4.6.49), which is independent of v. It leads to

$$\omega \times r \cdot \nabla U = 0. \qquad\qquad\qquad (4.6.59)$$

If both $\omega \neq 0$ and $U \neq 0$, then the rotational velocity $\omega \times r$ should lie in the equipotential surfaces of the external force.

4.6.4. The H–function and Entropy.

It is not difficult to calculate the equilibrium value of H_0. We substitute (4.6.21) into (4.6.24). Using

$$\int \exp(-\alpha v^2)d^3v = (\pi/\alpha)^{3/2}, \int v^2\exp(-\alpha v^2)d^3v = 3/2\pi^{3/2}\alpha^{-5/2}$$

we find

$$H_0 = N\left[\ln n_0 + 3/2 \ln \{m/(2\pi k_B T)\} - 3/2\right], \qquad (4.6.60)$$

where N is the total number of molecules.
     Next we consider the entropy of an ideal gas. The thermodynamic identity per unit of mass is expressed by

$$Tds = c_v dT + p\ d(1/\rho), \qquad (4.6.61)$$

where ρ is the mass density,

$$\rho = m\ n_0, \qquad (4.6.62)$$

c_v the specific heat at constant volume and p the pressure. The energy per unit of mass follows from (4.6.20):

$$e = 3k_B T/(2m), \qquad (4.6.63)$$

so that

$$c_v = \partial e/\partial t = 3k_B/m \ . \qquad (4.6.64)$$

The pressure follows from (2.2.9), if (4.6.21) is substituted for $n_0 F_1$:

$$P_k = pI, \ p = n_0 k_B T, \qquad (4.6.65)$$

where I is the unit tensor. Of course (4.6.65) is the equation of state of the ideal gas. The thermodynamic identity (4.6.61) is valid when the system behaves quasi–statically, i.e. the gas passes through a series of equilibrium states with possibly varying temperatures and mass densities. The distribution function retains the Maxwellian form (4.6.21) during such processes. Also in irreversible thermodynamics this point of view and (4.6.61) are supposed to hold. The difference with reversible thermodynamics is expressed by $TdS > dQ$ instead of $TdS = dQ$, cf. (4.6.46). Multiplying (4.6.61) with mN/T and using (4.6.62,64,65) we obtain:

$$dS = Nk_B\left[3dT/(2T) - dn_0/n_0\right], \qquad (4.6.66)$$

or, after integration:

$$S = Nk_B(3/2\ln T - \ln n_0) + C. \tag{4.6.67}$$

Choosing

$$C = 3/2N\left[k_B - \ln\{m/(2\pi k_B T)\}\right] \tag{4.6.68}$$

we see that (4.6.67) and (4.6.60) imply (4.6.45). It is only natural to postulate the relation $S = -k_B H_0$ also outside equilibrium. The H–theorem is then equivalent to the law stating that entropy can never decrease.

4.6.5 The Pair Distribution Function in Equilibrium.

In section 4.4 we have seen how the asymptotic (with respect to the fast time scale τ_0) binary distribution function in lowest order of the Boltzmann parameter can be written as

$$F_2(r,s,v,v',t) = F_1(r,v_\infty,t)F_1(r,v_\infty',t), \tag{4.6.69}$$

where v_∞ and v_∞' are defined by (4.3.22). In equilibrium $F_{1e} = n_0^{-1} f_e$ is a Maxwellian distribution given by (4.6.21). In the right hand side of (4.6.69) the factor $\exp[-m/(2k_B T)\,(v_\infty^2 + v_\infty'^2)]$ then appears. Because of energy conservation in binary collisions we have:

$$1/2m(v_\infty^2 + v_\infty'^2) = 1/2m(v^2 + v'^2) + \phi(s), \tag{4.6.70}$$

where $\phi(s)$ is the intermolecular interaction potential. In equilibrium (4.6.69) therefore leads to

$$F_{2e}(s,v,v') = F_{1e}(v)F_{1e}(v')\exp[-\phi(s)/(k_B T)]. \tag{4.6.71}$$

The radial distribution function $\mu(s)$, defined in (2.2.23) as F_2 integrated over all velocities, is then precisely the Boltzmann–factor appearing in (4.6.71). This enables us to calculate the first approximation for the interaction pressure, i.e. the first virial coefficient in the series

$$p/(nk_B T) = 1 + B(T)\,n_0/N_A + C(T)\,(n_0/n_A)^2 + .., \tag{4.6.72}$$

where N_A is the number of Avogadro and $n_0/N_A = V_m^{-1}$, i.e. the inverse of the volume per mole. If $\phi(s)$ depends on the distance only, (2.2.27b) and (2.2.19) lead to

$$P_{\rm int} = p_{\rm int}\,I, \quad p_{\rm int} = -2\pi n_0^2/3\int_0^\infty s^3\,d\phi/ds\,\exp\left[-\phi(s)/(k_B T)\right]ds. \tag{4.6.73}$$

For explicit examples we refer to the exercises.

4.7. DISCUSSION OF IRREVERSIBILITY

The irreversible behaviour of a gas reveals itself in transport processes such as heat conduction. Heat is conducted from warm to cold regions and not in the reversed direction. This is indeed also true for liquids and solids. As we will see in Chapter 5 the heat conduction equation

$$\rho c \ \partial T / \partial t = \nabla \cdot (\lambda \nabla T) \qquad (4.7.1)$$

can in the case of a Boltzmann gas be derived from an asymptotic solution to the Boltzmann equation. In (4.7.1) we have omitted some terms (convection, viscous dissipation) which are unimportant for the present discussion. The irreversible character of (4.7.1) can be shown explicitly through a separate H–theorem. We consider a closed system surrounded by heat isolating walls. We multiply (4.7.1) with T and integrate over the volume of the system. Using a well known vector identity we obtain:

$$\frac{d}{dt} \int_V \rho c T^2 d^3 r = 2 \int_V \{ \nabla \cdot (\lambda \, T \nabla T) - \lambda \, | \nabla T |^2 \} d^3 r. \qquad (4.7.2)$$

Gauss' theorem, Fourier's law for the heat flux q and the assumed isolation show that

$$\int_V \nabla \cdot (\lambda \nabla T) d^3 r = \int_F \lambda \, T n \cdot \nabla T d^2 r = - \int_F T n \cdot q d^2 r = 0. \qquad (4.7.3)$$

Therefore, since $\lambda > 0$,

$$d / dt \int_V \rho c T^2 d^3 r \leq 0, \qquad (4.7.4)$$

i.e. the "H–function" $\int_V \rho c T^2 d^3 r$ decreases monotonously until (asymptotically) a minimum value is reached. In that equilibrium also the right hand side of (4.7.2) must vanish. This is only possible, if

$$\nabla T = 0 \qquad (4.7.5)$$

everywhere within the isolated system. In other words: the heat conduction equation is responsible for a complete smoothing out of arbitrary distributions of initial temperatures. Something quite similar is true for the diffusion equation which has the same form as (4.7.1). Concentration gradients in a mixture eventually disappear as consequence of diffusion.

Although irreversibility on a macroscopic scale clearly manifests itself in nature, as illustrated by the above examples, serious conceptual difficulties are connected with it. How should the irreversibility of macroscopic

(phenomenological) physics be reconciled with the reversible nature of molecular dynamics? Already in Boltzmann's time this question was posed in a penetrating way. Two arguments were adduced to show the paradoxal charactor of the H-theorem.

I." Unkehreinwand" (reverse–objection) of Loschmidt.

According to the H–theorem H decreases steadily from some initial value at, say, $t = 0$. If one would reverse the velocities of all molecules at some time $t = t_0$ the system would have to return on its steps: H must increase and will reach its initial value at $t = 2t_0$, see fig.9. The answer to this objection should be sought in the
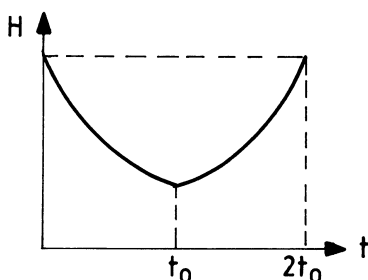

Figure 9. Violation of H–theorem.

derivation of the Boltzmann equation. The basis assumption is the Bogoliubov boundary condition, which is a generalization of the "Stosszahlansatz" (molecular chaos hypothesis) used by Boltzmann. Particles ready to collide, are uncorrelated. The collision then creates a statistical correlation. If the velocities of all molecules are reversed at $t = t_0$, then also the "Stosszahlansatz" is reversed: molecules ready to collide should possess exactly the right correlation in order to be uncorrelated after the collision. The situation at $t = 2t_0$ is statistically very different from the initial situation in spite of the fact that $H(2t_0) = H(0)$. Distant molecules are correlated in specific ways. The conclusion must be that an increase of H cannot be totally excluded, but is very improbable, because a prepared initial situation is required, which leads to the annihilation of correlations by collisions.

II. "Wiederkehreinwand" (return–objection) of Zermelo.

The objection of Zermelo was based on a theorem of Poincaré, which we state here without proof: Each dynamical system with a finite volume will after a fixed time τ_p (Poincaré cycle) return to a state in phase space close to its initial state within arbitrary prescribed margins. Of course, τ_p depends on the prescribed margins. A gas is a dynamical system of molecules and the theorem of Poincaré therefore implies that after a sufficiently long time H must have returned to a value arbitrarily close to its initial value.

     Formally speaking we have to acknowledge the correctness of Zermelo's objection. From a practical point of view, however, it is meaningless, because the

Poincaré cycles last much longer than any experiment. Boltzmann estimated that 10^{19} atoms in a volume of 1 cm^3 and with a thermal velocity of $5 \cdot 10^4$cm/s will reproduce all their coordinates within a margin of 10^{-7} cm and all their velocity components within a margin of 10^2cm/s, after a time $\tau_p = 10^{10^{19}}$ years! This example shows the abyss which may exist between conceptually correct statements and the behaviour of realistic physical systems. On the other hand, the example is not quite what is needed in the discussion of $H(t)$. A complete return of the system to its initial position in Γ–space is not required for the return of H to its initial value. The Boltzmann equation describes the *average* density in μ–space. Fluctuations around the average occur and it is conceivable, that extremely large fluctuations restore the initial state of the system. In this connection a calculation in "Theory of Heat" by R. Becker, [BEC1967], is very illuminating. Becker considers the Poincaré cycle for deviations from the average density in configuration space, i.e. the molecular distribution function integrated over velocity space. He finds the following curious table for a gas in a volume of 1 cm^3 at room temperature and atmospheric pressure:

Relative deviation $(n-n_0)/n_0$	Poincaré time τ_p
$2 \cdot 10^{-10}$	$4 \cdot 10^{-3}$ seconds
$3 \cdot 10^{-10}$	1 second
$4 \cdot 10^{-10}$	21 minutes
$5 \cdot 10^{-10}$	5 months
$6 \cdot 10^{-10}$	$3 \cdot 10^4$ years
$7 \cdot 10^{-10}$	$2 \cdot 10^{10}$ years

Table I. Poincaré cycles of density fluctuations.

Although this table is more realistic than the Poincaré cycle of Boltzmann, it is shown that the extremely small relative density deviation of 7.10^{-10} does not occur twice within the lifetime of the universe! We may conclude that the objection of Zermelo is devoid of significant implications for real physical systems.

4.8 EXERCISES

1.   Very often damping is related to loss of information. Consider a Knudsen gas of infinite extent. The initial distribution function is given by

$$f(r,v,t=0) = (\alpha/\pi)^{1/2}\exp(-\alpha v^2)[1+A\cos(kx)].$$

Determine the density $n(x,t)$

Solution

From (4.1.7), with $f = n_0 F_1^{(0)}$, we obtain:

$$f(r,v,t) = f(r-vt,v,t=0) = n_0(\alpha/\pi)^{3/2} \exp(-\alpha v^2)[1 + A \cos\{k(x-v_x t)\}].$$

Integration over velocity space leads to

$$n(x,t)/n_0 \quad = 1 + A(\alpha/\pi)^{1/2} \int\limits_{\infty}^{+\infty} \exp(-\alpha v_x^2)\cos(kv_x t)dv_x\cos(kx)$$

$$= 1 + A\,\cos(kx)\,\exp\left[-\,k^2 t^2/(4\alpha)\right]$$

2.. Derive the Rutherford cross–section (4.4.21)

Solution
With $r = b/\sigma$ and $\alpha = 2\hat{e}^2/(\mu_r g^2 b)$ (4.4.19) can be written as

$$\psi = \int\limits_0^{\sigma_{max}} (1 - \sigma^2 - \alpha\sigma)^{1/2}d\sigma \text{ with } \sigma_{max} = -\alpha/2 + (1 + \alpha^2/4)^{1/2}.$$

Introducing $\eta = (\sigma + \alpha/2)(1 + \alpha^2/4)^{-1/2}$ we find:

$$\psi = \int\limits_{\eta_{min}}^1 (1 - \eta^2)^{-1/2}d\eta = \pi/2 - \arcsin(\eta_{min}), \; \eta_{min} = \alpha/2(1 + \alpha^2/4)^{-1/2}.$$

Using (4.4.12) we obtain $\alpha = 2\tan(\chi/2)$. Then (4.4.15) leads to

$$I'(g,\chi) = (\sin\chi)^{-1}\left[2\hat{e}^2/(\mu_r g^2)\right]^2 1/(\alpha^3\cos^2(\chi/2)) = \hat{e}^4/(4\mu_r^2\,g^4\sin^4(\chi/2))$$

and to (4.4.21).

3.   Apply the Bogoliubov boundary condition in order to express the binary distribution function $G_A^{(0)}$ in terms of the molecular distribution $F^{(0)}$ in the case of Coulomb interaction.

Solution
According to (4.3.21,22,23) we can write:

$$G_A^{(0)}(a,s,v,v',\tau_1) = F^{(0)}(a, V + \tfrac{1}{2}g_\infty e, \tau_1)F^{(0)}(a, V - \tfrac{1}{2}g_\infty e, \tau_1), \qquad (4.8.1)$$

where $V = \tfrac{1}{2}(v + v')$ and because of (4.3.29),

$$g_\infty^2 = g^2 + 2\hat{e}^2/(\mu_r s) \qquad\qquad (4.8.2)$$

(energy conservation) and $\hat{e}^2 = e^2/(4\pi\epsilon_0)$, e being the electric charge of a particle and ϵ_0 the dielectric permittivity of the vacuum. The remaining task is the calculation of the unit vector e. This is most easily done on basis of the integral of the motion which is particular to fields proportional to s^{-1}, namely [LAN1960] $C = g \times L + \hat{e}^2 e_s$ with the (conserved) angular momentum $L = \mu_r$ $s \times g$ and $e_s = s/s$. After the collision $(\tau_0 \to \infty)$ $g_\infty = g_\infty e$ and $e_{s\infty} = e$. Therefore:

$$g_\infty e \times L + \hat{e}^2 e = C. \qquad (4.8.3)$$

Note that C is perpendicular to L. Taking the vectorial product with L we obtain:

$$g_\infty L^2 e + \hat{e}^2 L \times e = L \times C \qquad (4.8.4)$$

Elimination of $e \times L$ from (4.8.3,4) leads to

$$e = \frac{g_\infty L \times C + \hat{e}^2 C}{\hat{e}^4 + L^2 g_\infty^2} = C^{-2}\left[\left[g^2 + 2\hat{e}^2/(\mu_r s)\right]^{1/2} L \times C + \hat{e}^2 C\right], \qquad (4.8.5)$$

where for the last equality (4.8.2) has been used.

4. Calculate the difference $\Delta = I_w - 1/(k_B T_w)dQ/dt$, which according to (4.6.43) should be positive, for the case that f is a Maxwellian distribution with different temperatures for velocities parallel and perpendicular to the wall.

Solution
We have $f_w = (\alpha/\pi)^{3/2}\exp(-\alpha v^2)$ with $\alpha = m/(2k_B T_w)$ and $f = \alpha_t \alpha_n^{1/2}\pi^{-3/2}$ $\exp(-\alpha_t v_t^2 - \alpha_n v_n^2)$. Because of (4.6.41) we must have $\alpha_n = \alpha$. Substituting these expressions into (4.6.35) we obtain $I_w = 1/2F(\pi\alpha)^{-1/2}\ln(\alpha_t/\alpha)$. On the other hand $w_{slip} = 0$ and therefore $dQ/dt = -Fq_n$ with

$q_n = \frac{1}{2}m \int_0^\infty dv_n \int d^2 v_t v_n v^2(f-f_w)$. Calculation of the integrals yields

$q_n = m/4(\pi\alpha)^{-1/2}(\alpha_t^{-1} - \alpha^{-1})$, so that $\Delta = \frac{1}{2}F(\pi\alpha)^{-1/2}\left[\alpha/\alpha_t - 1 - \ln(\alpha/\alpha_t)\right]$, which is indeed always positive.

5. Calculate the virial coefficient $B(T)$ in equilibrium for the case of hard sphere interaction.

Solution
In order to avoid problems with singular integrals we define the hard sphere interaction potential as

$$\phi(s) = \begin{bmatrix} 0 & , \ s > a \\ \lambda(a-s), & s < a \end{bmatrix} \tag{4.8.6}$$

where a is the diameter of the spheres, and take the limit $\lambda \to \infty$ afterwards. Substituting (4.8.6) into (4.6.73) we find:

$$p_{\text{int}} \ = 2\pi n_0^2/3 \ \lim_{\lambda \to \infty} \exp\left[-\lambda_a/(k_B T)\right] (k_B T)^4/\lambda^3 \int_0^{\lambda_a/(k_B T)} \xi^3 \exp(\xi) d\xi$$

$$= (2\pi/3) \ n_0{}^2 a^3 k_B T = (2\pi/3) \ \epsilon_B n_0 k_B T, \tag{4.8.7}$$

where the Boltzmann parameter is defined by $\epsilon_B = n_0 a^3$. The virial coefficient is defined by (4.6.72) and therefore given by

$$B(T) = (2\pi/3) \ N_A a^3 = 4 V_0, \tag{4.8.8}$$

where V_0 is the volume per mole occupied by the molecules.