Chapter 2
Boltzmann Equation: A Gas of Grains

Abstract A simple but realistic and rich model for fluidized granular media is the gas of inelastic hard spheres. In this chapter its statistical description is reviewed. A key role is played by the assumption of Molecular-Chaos and by the Boltzmann equation. A comparison with the case of elastic hard spheres is made, pointing out the analogies and the differences. The chapter is concluded with the discussion of the protocols used for energy injection.

2.1 Collisions

Let us consider two point-like particles with masses m_1 and m_2, coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$ and velocities $\mathbf{v}_1$ and $\mathbf{v}_2$. One can introduce the center of mass vector $\mathbf{r}_c$:

$$\mathbf{r}_c = \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_1 + m_2} \tag{2.1}$$

and the relative position vector:

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2. \tag{2.2}$$

Their time derivatives are the velocity of the center of mass

$$\mathbf{v}_c = \frac{m_1\mathbf{v}_1 + m_2\mathbf{v}_2}{m_1 + m_2} \tag{2.3}$$

and the relative velocity

$$\mathbf{V}_{12} = \mathbf{v}_1 - \mathbf{v}_2. \tag{2.4}$$

The forces between these two particles depends only on their relative position and are of equal magnitude and pointing in opposite directions:

$$\mathbf{F}_{12}(\mathbf{r}) = -\mathbf{F}_{21}(\mathbf{r}). \tag{2.5}$$

This is equivalent to say that the center of mass does not accelerate, i.e.:

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$$\frac{d^2\mathbf{r}_c}{dt^2} = 0 \tag{2.6}$$

while the relative position obeys to the following equation of motion:

$$m^* \frac{d^2\mathbf{r}}{dt^2} = \mathbf{F}_{12}(\mathbf{r}) \tag{2.7}$$

where

$$m^* = \left(\frac{1}{m_1} + \frac{1}{m_2}\right)^{-1} \tag{2.8}$$

is the reduced mass of the system of two particles. If the "collision" is elastic an interaction potential can be introduced so that:

$$\mathbf{F}_{12} = -\frac{dU(r)}{dr}\hat{\mathbf{r}} \tag{2.9}$$

where $\hat{\mathbf{r}}$ is the unit vector along the direction of the relative position of the two particles. The force vector lies in the same plane where the relative position vector and relative velocity vector lie. The evolution of the relative position r is the evolution of the position of a particle of mass m^* in a central potential $U(r)$. The angular momentum of the relative motion $\mathbf{L} = \mathbf{r} \times m^*\mathbf{V}_{12}$ is conserved. This means that the particle trajectory, during the collision, will be confined to this plane. Figure 2.1 sketches the typical binary scattering event when the interacting force is repulsive (monotonically decreasing potential), in the center of mass frame.

In the center of mass frame the elastic scattering has a very simple picture: the velocities of the particles are $\mathbf{v}_{1c} = \mathbf{V}_{12}m^*/m_1$ and $\mathbf{v}_{2c} = -\mathbf{V}_{12}m^*/m_2$. The elastic collision conserves the modulus of the relative velocity V_{12} and therefore also the moduli of the velocities of the particles in the center of mass frame. If one consider the collision event as a black box and observes the velocities of the particles "before" and "after" the interaction (i.e. asymptotically, when the interaction is negligible), then the velocity vectors are simply rotated of an angle χ called *angle of deflection*, which also represents the angle between asymptotic initial and final directions of the relative velocity. During the collision the total momentum is conserved (this holds for both elastic and inelastic collisions) but is redistributed between the two particles, i.e. the variation of the momentum of the particle 1 is $\delta(m_1\mathbf{v}_1) = m^*(\mathbf{V}'_{12} - \mathbf{V}_{12})$ where the prime indicates the post-collisional relative velocity. Obviously $\delta(m_1\mathbf{v}_1) = -\delta(m_2\mathbf{v}_2)$. Finally, one can calculate the components of the momentum transfer parallel and perpendicular to the relative velocity:

$$\delta(m_1\mathbf{v}_1)_\parallel = -m^*V_{12}(1 - \cos\chi) \tag{2.10a}$$

$$\delta(m_1\mathbf{v}_1)_\perp = m^*V_{12}\sin\chi\,. \tag{2.10b}$$

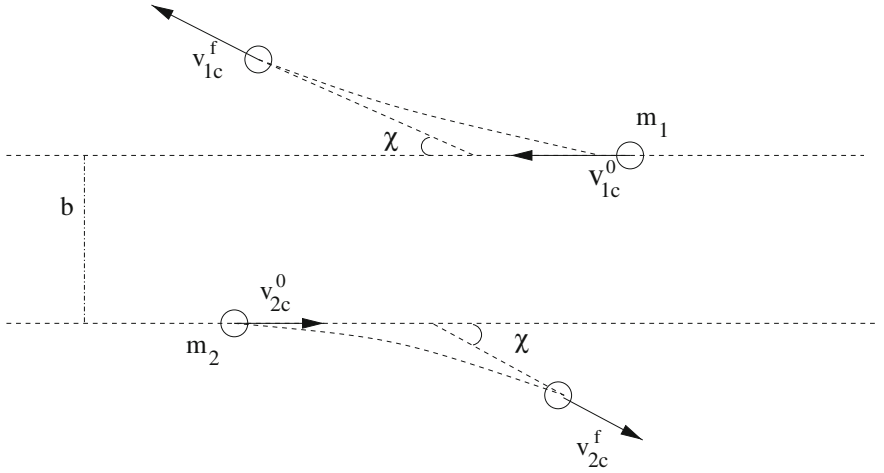

Fig. 2.1 The binary elastic scattering event in the center of mass frame, with a repulsive potential of interaction. The superscripts 0 and f denote initial and final velocities

To calculate the angle of deflection χ one needs the exact form of the interaction potential, the asymptotic initial relative velocity V_{12}^0 and the *impact parameter* b that is the minimal distance between the trajectories of the particles if there were no interaction between them:

$$\chi = \pi - 2\int_{r_m}^{\infty} dr \frac{b}{r}\left[r^2 - b^2 - \frac{2r^2 U(r)}{m^*(V_{12}^0)^2}\right]^{-1/2} \tag{2.11}$$

where r_m is the closest distance effectively reached by the two particles. From Eq. (2.11) it is evident that the angle of deflection decreases as the initial relative velocity increases.

2.1.1 Elastic Smooth Hard Spheres

Two hard spheres in 3D (hard disks in 2D, hard rods in 1D) of diameters σ_1 and σ_2 interact by means of a discontinuous potential $U(r)$ of the form:

$$U(r) = 0 \quad (r > \sigma_{12}) \tag{2.12a}$$

$$U(r) = \infty \quad (r < \sigma_{12}) \tag{2.12b}$$

where $\sigma_{12} = (\sigma_1 + \sigma_2)/2 = r_m$ is the distance of the centers of the spheres at contact. The potential in Eqs. (2.12a, 2.12b) can be taken as a definition of hard spheres systems. In this case the deflection angle is given by

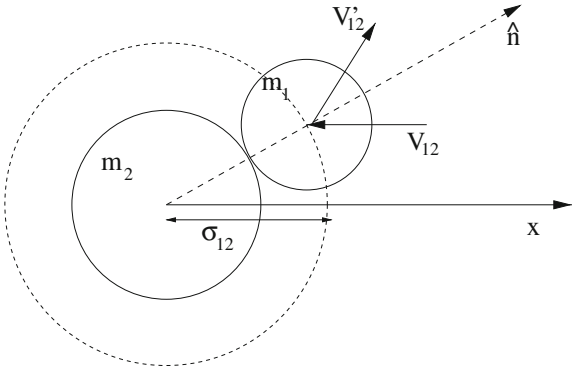

Fig. 2.2 The collision between two elastic smooth hard spheres

$$\chi = 2 \arccos\left(\frac{b}{\sigma_{12}}\right) \tag{2.13}$$

and the dependence from the initial relative velocity disappears: only geometry determines the deflection angle.

In the study of *smooth* hard spheres (i.e. such that particles' rotation is not relevant), a complete description of the dynamics requires only the positions of the centers $\mathbf{r}$ and their velocities $\mathbf{v}$. In particular the collision is an instantaneous transformation of the velocities of two particles i and j at contact which are "reflected" with the following rule (see Fig. 2.2):

$$\mathbf{v}_i' = \mathbf{v}_i - \frac{2m_2}{m_1 + m_2}\hat{\mathbf{n}}[\hat{\mathbf{n}} \cdot (\mathbf{v}_i - \mathbf{v}_j)] \tag{2.14}$$

$$\mathbf{v}_j' = \mathbf{v}_j + \frac{2m_1}{m_1 + m_2}\hat{\mathbf{n}}[\hat{\mathbf{n}} \cdot (\mathbf{v}_i - \mathbf{v}_j)] \tag{2.15}$$

where $\hat{\mathbf{n}} = (\mathbf{r}_i - \mathbf{r}_j)/|\mathbf{r}_i - \mathbf{r}_j|$ and the primes denote the velocities after the collision. This collision rule conserves momentum and kinetic energy. It only changes the direction of the component of the relative velocity of the particles in the direction of $\hat{\mathbf{n}}$ (normal component), leaving unchanged the tangential component.

2.1.2 Statistics of Hard Spheres Collisions

The concept of *mean free path* was introduced in 1858 by Rudolf Clausius [17] and paved the road to the kinetic theory of gases. For the sake of simplicity, here I consider a single species gas composed of elastic smoth hard spheres, all having the same diameter σ and mass m (see [16]).

The *mean free time* is the average time between two successive collisions of a single particle. I define $\omega_c dt$ the probability that a given particle suffers a collision

between time t and $t + dt$ (ω_c is called collision frequency) and assume that ω_c is independent of the past collisional history of the particle. The probability $f_{time}dt$ of having a free time between two successive collisions larger than t and shorter than $t + dt$ is equal to the product of the probability that no collision occurs in the time interval $[0, t]$ and the probability that a collision occurs in the interval $[t, t + dt]$:

$$f_{time}(t)dt = P_{time}(t)\omega_c dt, \tag{2.16}$$

where $P_{time}(t)$ is the survival probability, that is the probability that no collisions happen between 0 and t, and can be calculated observing that $P_{time}(t + dt) = P_{time}(t)P_{time}(dt) = P_{time}(t)(1 - \omega_c dt)$ so that $dP_{time}/dt = -\omega_c P_{time}$, i.e. $P_{time}(t) = e^{-\omega_c t}$.

Finally one can calculate the average of the free time using the probability density $f_{time}(t)$:

$$\tau_c = \int_0^\infty dt t f_{time}(t) = \int_0^\infty dt t \omega_c e^{-\omega_c t} = \frac{1}{\omega_c}. \tag{2.17}$$

With the same sort of calculations an expression for the mean free path, that is the average distance traveled by a particle between two successive collisions, can be calculated. One again assumes that there is a well defined quantity (independent of the collisional history of the particle) αdl which is the probability of a collision during the travel between distances l and $l + dl$. The survival probability in terms of space traveled is $P_{path}(l) = e^{-\alpha l}$ and the probability density of having a free distance l is $f_{path}(l) = e^{-\alpha l}\alpha$ so that the mean free path is given by:

$$\lambda = \frac{1}{\alpha} \tag{2.18}$$

Above, for simplicity, I have considered a homogeneous probability for collisions. A more precise treatment requires to consider the hard core collision process as a non-homogeneous stochastic Poisonnian process: indeed the transition rates for the particle's change of velocity depend on the relative velocity between the colliding particles [50]. This is discussed in details in Chap. 4.

The other important statistical quantity in the study of binary collisions is the so-called *differential scattering cross section s*. In a unit time a particle suffers a number of collisions which can be seen as the incidence of fluxes of particles coming with different approaching velocities $\mathbf{V}_{12}$ and scattered to new different departure velocities $\mathbf{V}'_{12}$. Given a certain approaching velocity $\mathbf{V}_{12}$ the incident particles arrive with slightly different impact parameters (due to the extension of the particles) and therefore are scattered in a solid angle $d\Omega'$. If I_0 denotes the intensity of the beam of particles that come with an average approaching speed $\mathbf{V}_{12}$, which is the number of particles intersecting in unit time a unit area perpendicular to the beam ($I_0 = nV_{12}$ with n the number density of the particles), then the rate of scattering dR into the

small solid angle element $d\Omega'$ is given by

$$\frac{dR}{d\Omega'} = I_0 s(\mathbf{V}_{12}, \mathbf{V}'_{12}) \tag{2.19}$$

where s is a factor of proportionality with the dimensions of an area (in $3D$) which is called differential cross section and depends on the relative velocity vectors before and after the collisions. The total rate of particles scattered in all directions, R is the integral of the last equation:

$$R = I_0 \int\int_{4\pi} d\Omega' s(\mathbf{V}_{12}, \mathbf{V}'_{12}) = S I_0 \tag{2.20}$$

and defines the total scattering cross section S.

In the case of a spherically symmetric central field of force, the differential cross section is a function only of the modulus of the initial relative velocity V_{12}, the angle of deflection χ, and the impact parameter b which in turn, once fixed the potential $U(r)$, is a function only of χ and V_{12}, that is $s = s(V_{12}, \chi)$. In particular it is easily seen that

$$s(V_{12}, \chi) = -\frac{b(V_{12}, \chi)}{\sin \chi} \frac{db}{d\chi}. \tag{2.21}$$

The differential scattering cross section for hard spheres is calculated from Eq. (2.21) obtaining a very simple formula: $s(V_{12}, \chi) = \sigma^2/4$ which can be integrated over the entire solid angle space giving an expression for the total cross section $S = \pi\sigma^2$. This result is consistent with the physical intuition of the cross section: it is the average of the areas of influence of the scatterer in the planes perpendicular to the approaching velocities of the incident particles.

To conclude this paragraph I recall that the collision frequency in a homogeneous stationary gas is related to the total scattering cross section by the relation

$$\omega_c = nS\langle V_{12} \rangle \tag{2.22}$$

where n is the uniform density of the gas and $\langle V_{12} \rangle$ is an average of the relative velocities. Assuming that velocities in the gas are independent and their distribution is the Maxwell-Boltzmann distribution:

$$P(\mathbf{v}) = \frac{m^{3/2}}{(2\pi k_B T)^{3/2}} e^{-\frac{mv^2}{2k_B T}} \tag{2.23}$$

the collision frequency can be calculated obtaining the formula:

$$\omega_c = \frac{2\sqrt{2}}{\sqrt{\pi}} n S v_T \tag{2.24}$$

where v_T is defined as

$$v_T = \sqrt{\frac{2k_B T}{m}}. \tag{2.25}$$

In the same way the mean free path is given by

$$\lambda = \frac{1}{\sqrt{2} n S}. \tag{2.26}$$

2.1.3 Inelasticity

Granular particles collide dissipating the kinetic energy of their relative motion [11]. This is due to the macroscopic nature of the grains: during the interaction, irreversible processes happen inside the grain and energy is dissipated in form of heat. In a collision between two free particles, these processes conserve momentum so that the velocity of the center of mass of the two grains is not modified.

Many models of the binary inelastic collision have been proposed (soft spheres [13, 25, 35, 51, 52] as well as hard spheres models [12, 21, 27, 41]): this is usually a relatively difficult problem. Simplification often pays more, as very idealized models lead to physically meaningful results. The most used model in granular gas literature is also the simplest: the gas of inelastic smooth hard spheres, with *fixed restitution coefficient*. It is given by the following prescriptions:

$$m_1 \mathbf{v}_1' + m_2 \mathbf{v}_2' = m_1 \mathbf{v}_1 + m_2 \mathbf{v}_2 \tag{2.27a}$$

$$(\mathbf{v}_1' - \mathbf{v}_2') \cdot \hat{\mathbf{n}} = -r(\mathbf{v}_1 - \mathbf{v}_2) \cdot \hat{\mathbf{n}} \tag{2.27b}$$

where, as usual, the primes denote the postcollisional velocities, $\hat{\mathbf{n}}$ is the unit vector in the direction joining the centers of the grains, and $0 \leq r \leq 1$. In this model the collisions happen at contact and are instantaneous. When $r = 1$ the gas is elastic and the rule coincides with the collision description for hard spheres given in the Sect. 2.1.1. When $r = 0$ the gas is perfectly inelastic, that is the particles exit from the collision with no relative velocity in the $\hat{\mathbf{n}}$ direction.

As a matter of fact, the transformation that gives the (primed) postcollisional velocities from the precollisional velocities of the two colliding particles is

$$\mathbf{v}_1' = \mathbf{v}_1 - (1 + r)\frac{m_2}{m_1 + m_2}((\mathbf{v}_1 - \mathbf{v}_2) \cdot \hat{\mathbf{n}})\hat{\mathbf{n}} \tag{2.28a}$$

$$\mathbf{v}_2' = \mathbf{v}_2 + (1 + r)\frac{m_1}{m_1 + m_2}((\mathbf{v}_1 - \mathbf{v}_2) \cdot \hat{\mathbf{n}})\hat{\mathbf{n}} \tag{2.28b}$$

Sometimes it may be useful to have the reverse transformation that give precollisional velocities from postcollisional ones, with the primes exchanged:

$$\mathbf{v}_1' = \mathbf{v}_1 - \left(1 + \frac{1}{r}\right) \frac{m_2}{m_1 + m_2} ((\mathbf{v}_1 - \mathbf{v}_2) \cdot \hat{\mathbf{n}}) \hat{\mathbf{n}} \tag{2.29a}$$

$$\mathbf{v}_2' = \mathbf{v}_2 + \left(1 + \frac{1}{r}\right) \frac{m_1}{m_1 + m_2} ((\mathbf{v}_1 - \mathbf{v}_2) \cdot \hat{\mathbf{n}}) \hat{\mathbf{n}} \tag{2.29b}$$

As it can be seen, the inverse transformation is equivalent to a change of the restitution coefficient $r \to 1/r$. Obviously, in the case of a perfectly inelastic gas ($r = 0$) there is no inverse transformation. I also note that in 1D and when $m_1 = m_2$ Eqs. (2.28a, 2.28b) become:

$$v_1' = \frac{1 - r}{2} v_1 + \frac{1 + r}{2} v_2 \tag{2.30a}$$

$$v_2' = \frac{1 + r}{2} v_1 + \frac{1 - r}{2} v_2 \tag{2.30b}$$

which correspond to an exact exchange of velocities in the elastic ($r = 1$) case, and in a sticky collision in the perfectly inelastic ($r = 0$) case. In dimensions higher than *one* the $r = 0$ case is very different from the so-called *sticky gas*, which is defined as a gas of hard spheres that in a collision become stuck together. In one dimension, instead, the $r = 0$ case may be considered equivalent to a sticky gas but a further prescription of "stickiness" must be given in order to consider collisions among more than two particles.

Variants of this models have been largely used in the literature. The importance of tangential frictional forces acting on the grains at contact may be studied taking into account the rotational degree of freedom of the particles, i.e. adding a variable $\boldsymbol{\omega}_i$ to each grain. The simplest model which takes into account the rotational degree of freedom of particles is the rough hard spheres gas [22, 28, 31, 36–38, 42]. In this model the postcollisional translational and angular velocities are given by the following equations (where the bottom signs in $\pm$ or $\mp$ are to be considered for particle 2):

$$\mathbf{v}_{1,2}' = \mathbf{v}_{1,2} \mp \frac{1 + r}{2} \mathbf{v}_n \mp \frac{q(1 + \beta)}{2q + 2} (\mathbf{v}_t + \mathbf{v}_r) \tag{2.31a}$$

$$\boldsymbol{\omega}_{1,2}' = \boldsymbol{\omega}_{1,2} + \frac{1 + \beta}{\sigma(1 + q)} [\hat{\mathbf{n}} \times (\mathbf{v}_t + \mathbf{v}_r)] \tag{2.31b}$$

where q is the dimensionless moment of inertia defined by $I = qm(\sigma/2)^2$ (with I the moment of inertia of the hard object), e.g. $q = 1/2$ for disks and $q = 2/5$ for spheres; $\mathbf{v}_n = ((\mathbf{v}_1 - \mathbf{v}_2) \cdot \hat{\mathbf{n}}) \hat{\mathbf{n}}$ is the normal relative velocity component, $\mathbf{v}_t = \mathbf{v}_1 - \mathbf{v}_2 - \mathbf{v}_n$ is the tangential velocity component due to translational motion, while $\mathbf{v}_r = -\sigma(\boldsymbol{\omega}_1 - \boldsymbol{\omega}_2)$ is the tangential velocity component due to particle rotation. In Eqs. (2.31a, 2.31b) the tangential restitution coefficient β appears: it may take any value between -1 and $+1$. When $\beta = -1$ tangential effects disappear, i.e. rotation is not affected by collision (rough spheres become smooth spheres). When

$\beta = +1$ the particles are said to have perfectly rough surface. It can be easily seen that (when $r = 1$) energy is conserved for $\beta = \pm 1$.

Other models for collisions have been introduced, justified by a deeper analysis of the collision process. In these models the restitution coefficient r (or the coefficients r and β in the more detailed description given above) depends on the relative velocity of the colliding particles. In particular it has been seen that the collision tends to become more and more elastic as the relative velocity tends to zero. This refined description, referred to as 'viscoelastic' model [10, 26], has relevance in different issues of the statistical mechanics of granular gases. An important kinetic instability of the cooling (and sometimes driven) granular gases is the so-called *inelastic collapse* [40, 41], i.e. a divergence of the local collision rate due to the presence of a few particles trapped very close to each other: simulations of the gas with the viscoelastic model have shown that this instability is removed, suggesting that it is an artifact of the fixed restitution coefficient idealization.

Here, I give an expression of the leading term for the velocity dependence of the normal restitution coefficient r in the viscoelastic model (the viscoelastic theory may be applied to give also a velocity dependent expressions for the tangential restitution coefficient):

$$r = 1 - C_1 |(\mathbf{v}_1 - \mathbf{v}_2) \cdot \hat{\mathbf{n}}|^{1/5} + \cdots \tag{2.32a}$$

where C_1 depends on the physical properties of the spheres (mass, density, radius, Young modulus, viscosity).

2.1.4 Inelastic Collapse

In the 1990s, several numerical studies have unveiled a problem in the model of inelastic collisions with a fixed restitution coefficient. Such a problem went under the name of "inelastic collapse". The simplest example involves just three particles on a line, as shown in Fig. 2.3 [5, 40]. The two outer particles move monotonically toward each other and the one in the middle bounces between them. One can easily show that, after the two collisions shown in the figure, the relation between the final and initial velocities is $\mathbf{u}' = \mathscr{M}\,\mathbf{u}$ where $\mathbf{u} = (\mathbf{v_1}, \mathbf{v_2}, \mathbf{v_3})^{\mathbf{T}}$ and $\mathscr{M}$ is a 3x3 matrix whose entries are quadratic polynomials in r. If this matrix has one real eigenvalue in the interval (0, 1), the cycle shown in Figure endlessly repeats with geometrically smaller space and time scales at each successive cycle. This requires $r = r_c < 7 - 4\sqrt{3} \approx 0.0718$ to happen. In this case an infinite number of collision happens in a finite time. When $r > r_c$, inelastic collapse can still occur but with the collective participation of more than three particles or with the presence of an inelastic wall (because of symmetry, this is equivalent to an interaction between four inelastic particles), as displayed in the Figure. As the coefficient of restitution r increases toward 1, the number of particles required for collapse increases. For instance, with $r = 0.8$, it is required that $N = 16$

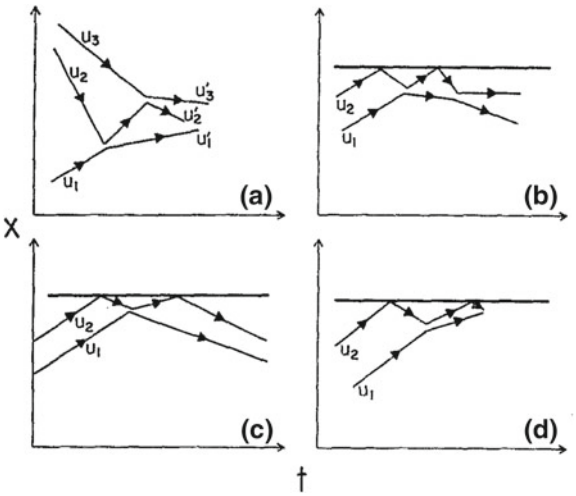

Fig. 2.3 Examples of particles' trajectories with or without a wall: **a** three particles collapse ($r < 7 - 4\sqrt{3} \approx 0.0718$); **b** two particles bouncing off an inelastic wall: when $r > 0.346015$ they finally leaves the wall and never come back; **c** critical value $r = 0.346015$, the inner ball remains stationary after two collisions with the other particle; **d** when $r < 3 - 2\sqrt{2} \approx 0.17157$ there is inelastic collapse. Reproduced with permission from McNamara and Young [40]. Copyright 1992, AIP Publishing LLC

particles bounce off an inelastic wall. Rough estimates suggest (in agreement with numerical calculations) that $N_{\min}(r) \approx ln(4/(1-r))/(1-r)$ as $r \to 1$.

In more than 1 dimension, the trapping necessary to have collapse can be realized in a large cluster, as shown in Fig. 2.4.

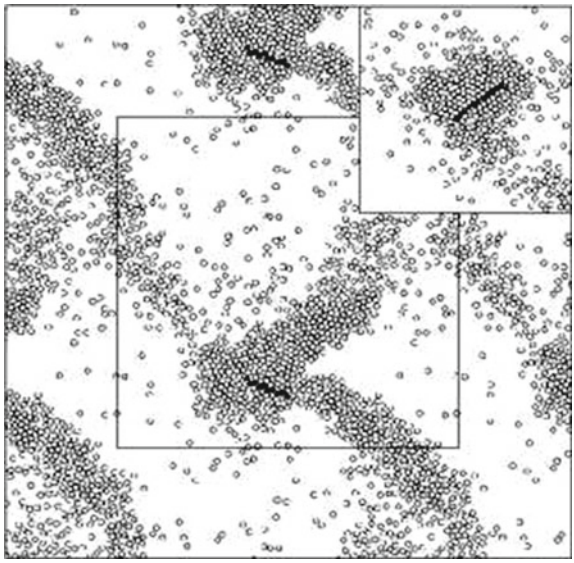

Fig. 2.4 A snapshot from a MD simulation of cooling inelastic *hard spheres*. The particles in *black* are those that have participated in the last collisions, just before a collapse. Reprinted with permission from Schorghofer and Zhou [48]. Copyright 1996 by the American Physical Society

2.2 The Boltzmann Equation

The Boltzmann equation for a gas of elastic or inelastic hard spheres can be derived in several ways [15]. Here, I review the typical reduction scheme which starts from the Liouville equation and goes through the BBGKY hierarchy.

2.2.1 Liouville and Pseudo-Liouville Equations

In order to discuss the behavior of a system of N identical hard spheres (of diameter σ and mass m) it is natural to introduce the phase space, i.e., a $6N$—dimensional space where the coordinates are the $3N$ components of the N position vectors of the sphere centers $\mathbf{r}_i$ and the $3N$ components of the N velocities $\mathbf{v}_i$. The state of the system is represented by a point in this space. I call $\mathbf{z}$ the $6N$-dimensional position vector of this point. If the positions $\mathbf{r}_i$ of the spheres are restricted in a space region Ω, then the full phase space $\mathbf{D}$ is given by the product $\Omega^N \times \Re^{3N}$

If the state is not known with absolute accuracy, one must introduce a probability density $P(z, t)$ which is defined by

$$Prob(z \in \mathbf{D} \quad \text{at time } t) = \int_{\mathbf{D}} P(\mathbf{z}, t) d\mathbf{z} \tag{2.33}$$

where $d\mathbf{z}$ is the Lebesgue measure in phase space. One implicitly assumes that the probability is a measure absolutely continuous with respect to the Lebesgue measure. The mean value of a dynamical observable $A(\mathbf{z})$ can be calculated from either the following expressions:

$$\int_{\infty} d\mathbf{z} P(\mathbf{z}, 0) A(\mathbf{z}(t)) = \int_{\infty} d\mathbf{z} P(\mathbf{z}, t) A(\mathbf{z}) \tag{2.34}$$

which are respectively the Lagrangian and Eulerian averages (analogous to the Heisenberg and Schroedinger averages in quantum mechanics). In Eq. (2.34) the time dependence of the observable A and of the distribution P is due to the time evolution operator S_t, also called *streaming operator*, that is $A(\mathbf{z}(t)) \equiv S_t(\mathbf{z}) A(\mathbf{z})$. Considering the equivalence in Eq. (2.34) as an inner product implies that

$$P(\mathbf{z}, t) = S_t^{\dagger} P(\mathbf{z}, 0) \tag{2.35}$$

where $S_t^{\dagger}$ is the adjoint of S_t.

In a general system (not necessarily made of hard spheres) with conservative and additive interactions, the force between the particle pair (ij) is $\mathbf{F}_{ij} = -\partial U(r_{ij})/\partial \mathbf{r}_{ij}$ so that the time evolution operator is given by:

$$S_t(\mathbf{z}) = \exp[tL(\mathbf{z})] = \exp\left[t\sum_i L_i^0 - t\sum_{i<j}\Theta(ij)\right] \tag{2.36}$$

where the *Liouville operator* $L(\mathbf{z})\ldots \equiv \{H(\mathbf{z}),\ldots\}$ is the Poisson bracket with the Hamiltonian, so that

$$L_i^0 = \mathbf{v}_i \cdot \frac{\partial}{\partial \mathbf{r}_i} \tag{2.37a}$$

$$\Theta(ij) = \frac{1}{m}\frac{\partial U(r_{ij})}{\partial \mathbf{r}_{ij}} \cdot \left(\frac{\partial}{\partial \mathbf{v}_i} - \frac{\partial}{\partial \mathbf{v}_j}\right) \tag{2.37b}$$

and $S_t(\mathbf{z})$ is a unitary operator, $S_t^\dagger = S_{-t}$, while $L^\dagger = -L$. In Eq. (2.36) the evolution operator S_t has been divided into a free streaming operator $S_t^0 = \exp[t\sum_i L_i^0]$ which generates the free particle trajectories, plus a term containing the binary interactions among the particles.

Finally the Liouville equation is obtained writing explicitly Eq. (2.35):

$$\frac{\partial}{\partial t}P(\mathbf{z},t) = \left(-\sum_i L_i^0 + \sum_{i<j}\Theta(ij)\right)P(\mathbf{z},t) \tag{2.38}$$

which is an expression of the incompressibility of the flow in phase space.

In the specific case of identical hard spheres, the interaction among particles is defined by Eqs. (2.12a, 2.12b). It can be shown that this kind of interaction carries no contraction of phase space at collision, i.e.

$$P(\mathbf{z}',t) = P(\mathbf{z},t) \tag{2.39}$$

where $\mathbf{z}'$ and $\mathbf{z}$ are the phase space points before and after a collision. This can be considered a form of detailed balance law. It is important to stress that $\mathbf{z}' \neq \mathbf{z}$: a collision represents a time discontinuity in the velocity section of phase space. In particular I use the elastic collision model defined in this list of prescriptions [it coincides with the collision rule for smooth hard spheres, see Eq. (2.14)]:

$$|\mathbf{r}_i - \mathbf{r}_j| = \sigma \tag{2.40a}$$

$$\hat{\mathbf{n}}_{ij} = (\mathbf{r}_i - \mathbf{r}_j)/\sigma \tag{2.40b}$$

$$\mathbf{V}_{ij} = \mathbf{v}_i - \mathbf{v}_j \tag{2.40c}$$

$$\mathbf{V}_{ij}\cdot\hat{\mathbf{n}}_{ij} < 0 \tag{2.40d}$$

$$\mathbf{z} \equiv (\mathbf{r}_1,\mathbf{v}_1,\mathbf{r}_2,\mathbf{v}_2,\ldots,\mathbf{r}_i,\mathbf{v}_i,\ldots,\mathbf{r}_j,\mathbf{v}_j,\ldots,\mathbf{r}_N,\mathbf{v}_N) \tag{2.40e}$$

$$\mathbf{z}' \equiv (\mathbf{r}_1,\mathbf{v}_1,\mathbf{r}_2,\mathbf{v}_2,\ldots,\mathbf{r}_i',\mathbf{v}_i',\ldots,\mathbf{r}_j',\mathbf{v}_j',\ldots,\mathbf{r}_N,\mathbf{v}_N) \tag{2.40f}$$

$$\mathbf{r}_i' = \mathbf{r}_i \tag{2.40g}$$

$$\mathbf{r}_j' = \mathbf{r}_j \tag{2.40h}$$

$$\mathbf{v}_i' = \mathbf{v}_i - \hat{\mathbf{n}}_{ij}(\hat{\mathbf{n}}_{ij} \cdot \mathbf{V}_{ij}) \tag{2.40i}$$

$$\mathbf{v}_j' = \mathbf{v}_j + \hat{\mathbf{n}}_{ij}(\hat{\mathbf{n}}_{ij} \cdot \mathbf{V}_{ij}) \tag{2.40j}$$

these relations conserve the total momentum and the total energy of the system.

In order to derive the Boltzmann equation, the collisions events $\mathbf{z} \to \mathbf{z}'$ are considered as boundary conditions and the Liouville Equation (2.38) is restricted to the interior of the phase space region $\Lambda \equiv \Omega^N \times \Re^{3N} - \Lambda_{ov}$ where

$$\Lambda_{ov} = \left\{ \mathbf{z} \in \Omega^N \times \Re^{3N} \mid \exists i, j \in \{1, 2, \ldots, N\} \, (i \neq j) \, : \, |\mathbf{r}_i - \mathbf{r}_j| < \sigma \right\} \tag{2.41}$$

is the set of phase space points such that one or more pairs of spheres are overlapping. With this conditions, the Liouville equation reads:

$$\frac{\partial}{\partial t} P(\mathbf{z}, t) = \left(- \sum_i \mathbf{v}_i \cdot \frac{\partial}{\partial \mathbf{r}_i} \right) P(\mathbf{z}, t) \quad (\mathbf{z} \in \Lambda) \tag{2.42a}$$

$$P(\mathbf{z}, t) = P(\mathbf{z}', t) \quad (\mathbf{z} \in \partial \Lambda). \tag{2.42b}$$

This version of the Liouville equation is time-discontinuous: this means that formal perturbation expansions used in usual many-body theory methods cannot be applied.

An alternative master equation for the probability density function in the phase space can be derived [18]. The streaming operator S_t for hard spheres is not defined for any point of the phase space $\mathbf{z} \in \Lambda_{ov}$. In the calculation of the average (2.34) of physical observables, this is not a problem, as the streaming operators appears multiplied by $P(\mathbf{z}, 0)$ which is proportional to the characteristic function $X(\mathbf{z})$ of the set Λ (the characteristic function is 1 for points belonging to the set and 0 for points outside of it). In perturbation expansions it is safer to have a streaming operator defined for every point of the configurational space. A standard representation, defined for all points in the phase space, has been developed for elastic hard spheres and is based on the binary collision expansion of $S_t(\mathbf{z})$ in terms of binary collision operators. The binary collision operator is defined in terms of two-body dynamics through the following representation of the streaming operator for the evolution of two particles:

$$S_t(1, 2) = S_t^0(1, 2) + \int_0^t d\tau \, S_\tau^0(1, 2) T_+(1, 2) S_{t-\tau}^0(1, 2), \tag{2.43}$$

with $S_t^0 = \exp(t L_0)$ the free flow operator and a collision operator

$$T_+(1, 2) = \sigma^2 \int_{\mathbf{V}_{12} \cdot \hat{\mathbf{n}} < 0} d\hat{\mathbf{n}} |\mathbf{V}_{12} \cdot \hat{\mathbf{n}}| \delta(\sigma \hat{\mathbf{n}} - (\mathbf{r}_1 - \mathbf{r}_2))(b_c - 1), \tag{2.44}$$

where b_c is a substitution operator that replaces $\mathbf{v}_1, \mathbf{v}_2$ with $\mathbf{v}_1', \mathbf{v}_2'$ (see Eqs. (2.40a)).

The Eq. (2.43) is a representation of the evolution of two particles as a convolution of free flow and collisional events. Noting that $T_+(1,2)S_\tau^0(1,2)T_+(1,2) = 0$ for $\tau > 0$ (two hard spheres cannot collide more than once), Eq. (2.43) can be put in the form

$$S_t(1,2) = \exp\{t[L_0(1,2) + T_+(1,2)]\}, \tag{2.45}$$

that can be generalized to the N-particle streaming operator (here considered for the case of an infinite volume):

$$S_{\pm t}(\mathbf{z}) = \exp\left\{\pm t\left[L_0(\mathbf{z}) \pm \sum_{i<j} T_\pm(i,j)\right]\right\} \tag{2.46}$$

where

$$T_-(1,2) = \sigma^2 \int\limits_{\mathbf{V}_{12}\cdot\hat{\mathbf{n}}>0} d\hat{\mathbf{n}}|\mathbf{V}_{12}\cdot\hat{\mathbf{n}}|\delta(\mathbf{r}_1 - \mathbf{r}_2 - \sigma\hat{\mathbf{n}})(b_c - 1). \tag{2.47}$$

Equation (2.46) defines the so-called *pseudo-streaming operator*. In order to write an analogue of the Liouville Equation (2.38), the adjoint of $S_{\pm t}$ is needed; its definition is identical to that in Eq. (2.46) but for the binary collision operators which must be replaced by their adjoints:

$$\overline{T}_\pm(1,2) = \sigma^2 \int\limits_{\mathbf{V}_{12}\cdot\hat{\mathbf{n}}\lessgtr 0} d\hat{\mathbf{n}}|\mathbf{V}_{12}\cdot\hat{\mathbf{n}}|[\delta(\mathbf{r}_1 - \mathbf{r}_2 - \sigma\hat{\mathbf{n}})b_c - \delta(\mathbf{r}_1 - \mathbf{r}_2 + \sigma\hat{\mathbf{n}})]. \tag{2.48}$$

Finally the pseudo-Liouville equation can be written:

$$\frac{\partial}{\partial t}P(\mathbf{z},t) = \left(-\sum_i L_i^0 + \sum_{i<j}\overline{T}_-(ij)\right)P(\mathbf{z},t). \tag{2.49}$$

This equation is the analogue of Eq. (2.38) for the case of hard core potential (hard spheres). In this sense it replaces Eqs. (2.42a, 2.42b) and its modification for inelastic collisions will be discussed in Sect. 2.3.

2.2.2 The BBGKY Hierarchy

Reduced (marginal) probability densities P_s are defined as

$$P_s(\mathbf{r}_1, \mathbf{v}_1, \mathbf{r}_2, \mathbf{v}_2, \ldots, \mathbf{r}_s, \mathbf{v}_s, t) = \int\limits_{\Omega^{N-s} \times \Re^{3(N-s)}} P(\mathbf{r}_1, \mathbf{v}_1, \mathbf{r}_2, \mathbf{v}_2, \ldots, \mathbf{r}_N, \mathbf{v}_N, t) \prod_{j=s+1}^{N} d\mathbf{r}_j d\mathbf{v}_j. \tag{2.50}$$

In order to derive an evolution equation for P_s the first step is to integrate Eqs. (2.42a, 2.42b) with respect to the variables $\mathbf{r}_j$ and $\mathbf{v}_j$ $(s+1 \leq j \leq N)$ over $\Omega^{N-s} \times \Re^{3(N-s)}$, obtaining:

$$\frac{\partial P_s}{\partial t} + \sum_{i=1}^{s} \int\limits_{\Lambda_s} \mathbf{v}_i \cdot \frac{\partial P}{\partial \mathbf{r}_i} \prod_{j=s+1}^{N} d\mathbf{r}_j d\mathbf{v}_j + \sum_{k=s+1}^{N} \int\limits_{\Lambda_s} \mathbf{v}_k \cdot \frac{\partial P}{\partial \mathbf{r}_k} \prod_{j=s+1}^{N} d\mathbf{r}_j d\mathbf{v}_j = 0, \tag{2.51}$$

where the integration space Λ_s extends to the entire $\Re^{3(N-s)}$ for the velocity variables, while it extends to Ω^{N-s} deprived of the spheres $|\mathbf{r}_i - \mathbf{r}_j| < \sigma$ $(i = 1, \ldots, N, i \neq j)$ with respect to the position variables.

The typical term in the first sum contains the integral of a derivative with respect to a variable $\mathbf{r}_i$ over which one does not integrate, but in the exchange of order between integration and derivation one must take into account the domain boundaries which depend on $\mathbf{r}_i$, writing:

$$\int\limits_{\Lambda_s} \mathbf{v}_i \cdot \frac{\partial P}{\partial \mathbf{r}_i} \prod_{j=s+1}^{N} d\mathbf{r}_j d\mathbf{v}_j = \mathbf{v}_i \cdot \frac{\partial P_s}{\partial \mathbf{r}_i} - \sum_{k=s+1}^{N} \int\limits_{\Lambda_s} P_{s+1} \mathbf{v}_i \cdot \hat{\mathbf{n}}_{ik} d\sigma_{ik} d\mathbf{v}_k \tag{2.52}$$

where $\hat{\mathbf{n}}_{ik}$ is the outer normal to the sphere $|\mathbf{r}_i - \mathbf{r}_k| = \sigma$, $d\sigma_{ik}$ is the surface element on the same sphere and P_{s+1} has k as its $(s+1) - th$ index.

The typical term in the second sum in Eq. (2.51) can be immediately integrated by means of the Gauss theorem, since it involves the integration of a derivative taken with respect to one of the integration variables (and assuming that the boundary of Ω is a specular reflecting wall or a periodical boundary condition):

$$\int\limits_{\Lambda_s} \mathbf{v}_k \cdot \frac{\partial P}{\partial \mathbf{r}_k} \prod_{j=s+1}^{N} d\mathbf{r}_j d\mathbf{v}_j = \sum_{i=1}^{s} \int P_{s+1} \mathbf{v}_k \cdot \hat{\mathbf{n}}_{ik} d\sigma_{ik} d\mathbf{v}_k + \sum_{i=s+1, i \neq k}^{N} \int P_{s+2} \mathbf{v}_k \cdot \hat{\mathbf{n}}_{ik} d\sigma_{ik} d\mathbf{v}_k d\mathbf{r}_i d\mathbf{v}_i. \tag{2.53}$$

The last term in the above equation, when summed over $s + 1 \leq k \leq N$ vanishes: this fact directly stems from the equivalence Eq. (2.42b). Moreover, in both above equations the integral containing the term P_{s+1} is the same no matter what the value of the dummy index k is, so that I can drop the index and write $\mathbf{r}_*, \mathbf{v}_*$ instead of $\mathbf{r}_k, \mathbf{v}_k$.

As a matter of fact, Eq. (2.51) finally reads:

$$\frac{\partial P_s}{\partial t} + \sum_{i=1}^{s} \mathbf{v}_i \cdot \frac{\partial P_s}{\partial \mathbf{r}_i} = (N-s) \sum_{i=1}^{s} \int P_{s+1} \mathbf{V}_i \cdot \hat{\mathbf{n}}_i d\sigma_i d\mathbf{v}_* \tag{2.54}$$

where $\mathbf{V}_i = \mathbf{v}_i - \mathbf{v}_*$, $\hat{\mathbf{n}}_i = (\mathbf{r}_i - \mathbf{r}_*)/\sigma$ and the arguments of P_{s+1} are $(\mathbf{r}_1, \mathbf{v}_1, \mathbf{r}_2, \mathbf{v}_2, \ldots, \mathbf{r}_s, \mathbf{v}_s, \mathbf{r}_*, \mathbf{v}_*, t)$. Integrations in Eq. (2.54) are performed over the 1-particle velocity space $\Re^3$ and over the sphere S^i (given by the condition $|\mathbf{r}_i - \mathbf{r}_*| = \sigma$) with surface elements $d\sigma_i$. Eq. (2.54) is complemented by reflecting boundary conditions (of the same kind of (2.40a)) on the reduced boundary surface Λ_s.

Equation (2.54) states that the evolution of the reduced probability density P_s is governed by the free evolution operator of the s-particles dynamics, which appears in the left hand side, with corrections due to the effect of the interaction with the remaining $(N-s)$ particle. The effect of this interaction is described by the right-hand side of this equation.

Usually Eq. (2.54) is written in a different form, obtained using some symmetries of the problem. In particular one can separate the sphere S^i of integration in the right-hand side, in the two hemispheres S^i_+ and S^i_- defined respectively by $\mathbf{V_i} \cdot \hat{\mathbf{n}}_i > 0$ and $\mathbf{V_i} \cdot \hat{\mathbf{n}}_i < 0$ (considering also that $d\sigma_i = \sigma^2 d\hat{\mathbf{n}}_i$):

$$\int P_{s+1} \mathbf{V}_i \cdot \hat{\mathbf{n}}_i d\sigma_i d\mathbf{v}_* = \sigma^2 \int_{\Re^3} \int_{S^i_+} P_{s+1} |\mathbf{V}_i \cdot \hat{\mathbf{n}}_i| d\hat{\mathbf{n}}_i d\mathbf{v}_* - \sigma^2 \int_{\Re^3} \int_{S^i_-} P_{s+1} |\mathbf{V}_i \cdot \hat{\mathbf{n}}_i| d\hat{\mathbf{n}}_i d\mathbf{v}_*, \tag{2.55}$$

and observe that in the S^i_+ integration are included all phase space points such that particle i and particle $*$ (the $(s+1)-th$ generic particle) are coming out from a collision: this means that on the sphere S^i_+ I can write the substitution

$$\begin{aligned} &P_{s+1}(\mathbf{r}_1, \mathbf{v}_1, \ldots, \mathbf{r}_i, \mathbf{v}_i, \ldots \mathbf{r}_s, \mathbf{v}_s, \mathbf{r}_i - \sigma \hat{\mathbf{n}}_i, \mathbf{v}_*) \\ &\quad \to P_{s+1}(\mathbf{r}_1, \mathbf{v}_1, \ldots, \mathbf{r}_i, \mathbf{v}_i - \hat{\mathbf{n}}_i(\hat{\mathbf{n}}_i \cdot \mathbf{V}_i), \ldots \mathbf{r}_s, \mathbf{v}_s, \mathbf{r}_i - \sigma \hat{\mathbf{n}}_i, \mathbf{v}_* + \hat{\mathbf{n}}_i(\hat{\mathbf{n}}_i \cdot \mathbf{V}_i)). \end{aligned} \tag{2.56}$$

Moreover one can make the change of variable in the second integral (that on the sphere S^i_-) $\hat{\mathbf{n}}_i \to -\hat{\mathbf{n}}_i$ which only changes the integration range $S^i_- \to S^i_+$. Finally, replacing $\hat{\mathbf{n}}_i$ with simply $\hat{\mathbf{n}}$ (and therefore $S^i_+ \to S_+$) one has:

$$\frac{\partial P_s}{\partial t} + \sum_{i=1}^{s} \mathbf{v}_i \cdot \frac{\partial P_s}{\partial \mathbf{r}_i} = (N-s)\sigma^2 \sum_{i=1}^{s} \int_{\Re^3} \int_{S_+} (P'_{s+1} - P_{s+1}) |\mathbf{V}_i \cdot \hat{\mathbf{n}}| d\hat{\mathbf{n}} d\mathbf{v}_*, \tag{2.57}$$

where I have defined

$$P'_{s+1} = P_{s+1}(\mathbf{r}_1, \mathbf{v}_1, \ldots, \mathbf{r}_i, \mathbf{v}_i - \hat{\mathbf{n}}_i(\hat{\mathbf{n}}_i \cdot \mathbf{V}_i), \ldots \mathbf{r}_s, \mathbf{v}_s, \mathbf{r}_i - \sigma \hat{\mathbf{n}}_i, \mathbf{v}_* + \hat{\mathbf{n}}_i(\hat{\mathbf{n}}_i \cdot \mathbf{V}_i)). \tag{2.58}$$

The system of Eqs. (2.57) is usually called the BBGKY hierarchy for the hard sphere gas (from Bogoliubov, Born, Green, Kirkwood and Yvon, sometimes called simply Bogoliubov hierarchy).

2.2.3 The Boltzmann Hierarchy and the Boltzmann Equation

In a rarefied gas, N is a very large number and σ is very small; let us say, to fix ideas, that we have a box whose volume is $1\,\mathrm{cm}^3$ at room temperature and atmospheric pressure. Then $N \simeq 10^{20}$ and $\sigma \simeq 10^{-8}$cm and [from Eq. (2.57)] for small s we have $(N-s)\sigma^2 \simeq N\sigma^2 \simeq 1\,\mathrm{m}^2$; at the same time, the difference between $\mathbf{r}_i$ and $\mathbf{r}_i + \sigma\hat{\mathbf{n}}$ can be neglected and the volume occupied by the particles ($N\sigma^3 \simeq 10^{-4}\mathrm{cm}^3$) is very small so that the collision between two selected particles is a rather rare event. In this spirit, the Boltzmann-Grad limit has been suggested as a procedure to obtain a closure for Eq. (2.57): $N \to \infty$ and $\sigma \to 0$ in such a way that $N\sigma^2$ remains finite. I stress the fact that (as seen in Sect. 2.1.2) the total number of collisions in the unit of time (for volume and typical velocities both of order 1) is proportional to the total scattering cross section multiplied by N, which for a system of hard spheres gives $N\pi\sigma^2$. The Boltzmann-Grad limit, therefore, states that the single particle collision probability must vanish, but the total number of collisions remains of order 1. Within this limit, the BBGKY hierarchy reads:

$$\frac{\partial P_s}{\partial t} + \sum_{i=1}^{s} \mathbf{v}_i \cdot \frac{\partial P_s}{\partial \mathbf{r}_i} = N\sigma^2 \sum_{i=1}^{s} \int_{\Re^3} \int_{S_+} (P'_{s+1} - P_{s+1}) |\mathbf{V}_i \cdot \hat{\mathbf{n}}| d\hat{\mathbf{n}} d\mathbf{v}_* \tag{2.59}$$

where the arguments of P'_{s+1} and of P_{s+1} are the same as above, except that the position of the $(s+1)-th$ particle ($\mathbf{r}'_*$ and $\mathbf{r}_*$) is equal to $\mathbf{r}_i$ (as $\sigma \to 0$). Equation (2.59) gives a complete description of the time evolution of a Boltzmann gas (i.e. the ideal gas obtained in the Boltzmann-Grad limit), usually called *the Boltzmann hierarchy*.

Finally, the Boltzmann equation is obtained if the *molecular chaos assumption* is taken into account

$$P_2(\mathbf{r}_1, \mathbf{v}_1, \mathbf{r}_2, \mathbf{v}_2, t) = P_1(\mathbf{r}_1, \mathbf{v}_1, t) P_1(\mathbf{r}_2, \mathbf{v}_2, t) \tag{2.60}$$

for particles that are about to collide (that is when $\mathbf{r}_2 = \mathbf{r}_1 - \sigma\hat{\mathbf{n}}$ and $\mathbf{V}_{12} \cdot \hat{\mathbf{n}} < 0$). This assumption naturally stems from the Boltzmann-Grad limit, as it is reasonable that, in the limit of vanishing single-particle collision rate, two colliding particles are uncorrelated. The lack of correlation of colliding particles is the essence of the molecular chaos assumption. I underline that nothing is said about correlation of particles that have just collided.

With the assumption (2.60) one can rewrite the first equation of the hierarchy (2.59), omitting the 1 subscript (and obvious time dependence) for simplicity:

$$\frac{\partial P(\mathbf{r}, \mathbf{v})}{\partial t} + \mathbf{v} \cdot \frac{\partial P(\mathbf{r}, \mathbf{v})}{\partial \mathbf{r}} = N\sigma^2 \int_{\Re^3} \int_{S_+} (P(\mathbf{r}, \mathbf{v}') P(\mathbf{r}, \mathbf{v}'_*) - P(\mathbf{r}, \mathbf{v}) P(\mathbf{r}, \mathbf{v}_*)) |\mathbf{V} \cdot \hat{\mathbf{n}}| d\mathbf{v}_* d\hat{\mathbf{n}} \tag{2.61}$$

with $\mathbf{v}' = \mathbf{v} - \hat{\mathbf{n}}(\mathbf{V}\cdot\hat{\mathbf{n}})$, $\mathbf{v}'_* = \mathbf{v}_* + \hat{\mathbf{n}}(\mathbf{V}\cdot\hat{\mathbf{n}})$, $\mathbf{V} = \mathbf{v} - \mathbf{v}_*$. This represents the Boltzmann equation for hard spheres. I also observe that the integral in Eq. (2.61) is extended to the hemisphere S_+ but could be equivalently extended to the entire sphere S^2 provided a factor $1/2$ is inserted in front of the integral itself, as changing $\hat{\mathbf{n}} \to -\hat{\mathbf{n}}$ does not change the integrand.

From a rigorous point of view, the molecular chaos has to be assumed and cannot be proved. However, it has been demonstrated that if the Boltzmann hierarchy has a unique solution for data that satisfy for $t = 0$ a generalized form of chaos assumption:

$$P_s(\mathbf{r}_1, \mathbf{v}_1, \ldots, \mathbf{r}_s, \mathbf{v}_s, t) = \prod_{j=1}^{s} P_1(\mathbf{r}_j, \mathbf{v}_j, t) \tag{2.62}$$

then Eq. (2.62) holds at any time and therefore the Boltzmann equation is fully justified. Otherwise it has also been proved that if Eq. (2.62) is satisfied at $t = 0$ and the Boltzmann equation (2.61) admits a solution for the given initial data, then the Boltzmann hierarchy (2.59) has at least a solution which satisfy (2.62) at any time t [34, 49].

2.2.4 Collision Invariants and H-theorem

The integral appearing in the right-hand side of Eq. (2.61) is usually called collision integral:

$$Q(P, P) = \int_{\Re^3}\int_{S_+} (P'P'_* - PP_*)|\mathbf{V}\cdot\hat{\mathbf{n}}|d\mathbf{v}_* d\hat{\mathbf{n}} \tag{2.63}$$

where I have used an intuitive contracted notation (the prime or $*$ must be considered applied to the velocity vector in the argument of the function P). In the collision integral, the position $\mathbf{r}$ is the same wherever the function P appears, and therefore it can be considered a parameter of $Q(P, P)$.

Let us have a look to the integral, for a generic function $\Phi(\mathbf{v})$,

$$\int_{\Re^3} Q(P, P)\Phi(\mathbf{v})d\mathbf{v} = \int_{\Re^3}\int_{\Re^3}\int_{S_+} (P'P'_* - PP_*)\Phi(\mathbf{v})|\mathbf{V}\cdot\hat{\mathbf{n}}|d\mathbf{v}_* d\hat{\mathbf{n}} d\mathbf{v} \tag{2.64}$$

which can be transformed in many alternative forms, using its symmetries. In particular one can exchange primed and unprimed quantities, as well as starred and unstarred quantities. With manipulations of this sort, it is immediate to get the following alternative form of Eq. (2.64):

$$\int_{\Re^3} Q(P,P)\Phi(\mathbf{v})d\mathbf{v} = \frac{1}{8}\int_{\Re^3}\int_{\Re^3}\int_{S_+}(P'P'_* - PP_*)(\Phi+\Phi_*-\Phi'-\Phi'_*)|\mathbf{V}\cdot\hat{\mathbf{n}}|d\mathbf{v}_* d\hat{\mathbf{n}}\Phi(\mathbf{v})d\mathbf{v} \tag{2.65}$$

From this equation it comes that if

$$\Phi+\Phi_* = \Phi'+\Phi'_* \tag{2.66}$$

almost everywhere in velocity space, then the integral of Eq. (2.65) is zero independent of the particular function P. Many authors have proved under different assumptions that the most general solution of Eq. (2.66) is given by

$$\Phi(\mathbf{v}) = C_1 + \mathbf{C}_2\cdot\mathbf{v} + C_3|\mathbf{v}|^2 \tag{2.67}$$

Furtherly, if $\Phi = \log P$, from Eq. (2.65) it follows that

$$\int_{\Re^3} Q(P,P)\Phi(\mathbf{v})d\mathbf{v} = \frac{1}{8}\int_{\Re^3}\int_{\Re^3}\int_{S_+}(P'P'_* - PP_*)\log(PP_*/P'P'_*)|\mathbf{V}\cdot\hat{\mathbf{n}}|d\mathbf{v}_* d\hat{\mathbf{n}}\Phi(\mathbf{v})d\mathbf{v} \le 0 \tag{2.68}$$

which follows from the elementary inequality $(z-y)\log(y/z) \le 0$ if $y, z \in \Re^+$. This becomes an equality if and only if $y = z$, therefore the equality sign holds in Eq. (2.68) if and only if

$$P'P'_* = PP_*. \tag{2.69}$$

This is equivalent to two important facts. First, $\Phi+\Phi_* = \Phi'+\Phi'_*$ [taking the logarithms of both sides of Eq. (2.69)], so that one can use the result (2.67) obtaining $P = \exp(C_1 + C_2\cdot\mathbf{v} + C_3|\mathbf{v}|^2) = C_0\exp(-\beta|\mathbf{v}-\mathbf{v}_0|^2)$ where I have defined $C_0 = \exp(C_1)$, $\beta = -C_3$ and $\mathbf{v}_0 = \mathbf{C}_2/2\beta$; this function is called Maxwell-Boltzmann distribution or simply Maxwellian. Second, $Q(P,P) \equiv 0$, i.e. the collision integral identically vanishes for the Maxwellian.

Equation (2.68) is a fundamental result of the Boltzmann theory (it is often called Boltzmann Inequality) and can be fully appreciated with the following discussion. I rewrite the Boltzmann Equation (2.61) with a simplified notation:

$$\frac{\partial P}{\partial t} + \mathbf{v}\cdot\frac{\partial P}{\partial \mathbf{r}} = N\sigma^2 Q(P,P). \tag{2.70}$$

I multiply both sides by $\Phi = \log P$ and integrate with respect to $\mathbf{v}$, obtaining a transport equation for the quantity Φ:

$$\frac{\partial H}{\partial t} + \frac{\partial}{\partial \mathbf{r}}\cdot\mathbf{j}_H = S_H \tag{2.71a}$$

$$H = \int_{\Re^3} P \log P d\mathbf{v} \tag{2.71b}$$

$$\mathbf{j}_H = \int_{\Re^3} \mathbf{v} P \log P d\mathbf{v} \tag{2.71c}$$

$$S_H = N\sigma^2 \int_{\Re^3} \log P\, Q(P, P) d\mathbf{v}. \tag{2.71d}$$

Then Eq. (2.68) states that $S_H \leq 0$ and $S_H = 0$ if and only if P is a Maxwellian. For example, if one looks for a space homogeneous solution of the Boltzmann equation, it happens that

$$\frac{\partial H}{\partial t} = S_H \leq 0 \tag{2.72}$$

that is the famous H-Theorem. It simply states that there exists a macroscopic quantity (H in this case) that decreases as the gas evolves in time and eventually goes to zero when (if and only if) the distribution P becomes a Maxwellian. When the homogeneity is not achievable (due to non-homogeneous boundary conditions) rigorous results are more complicated, but one is still tempted to say that the Maxwellian represents the local asymptotic equilibrium, with the spatial dependence carried by the parameters of this distribution function. For a discussion of the meaning of the H-theorem and the long debate about irreversibility and its many paradoxes, see [20].

2.2.5 The Maxwell Molecules

The collisional integral of Boltzmann equation for hard spheres, Eq. (2.63), contains a term $g = |\mathbf{V} \cdot \hat{\mathbf{n}}|$ which multiplies the probabilities of particles entering or coming out from a collision. In general, the collisional integral must contain the differential collision rate $dR/d\Omega$ for particle coming at a certain relative velocity (in modulus g and direction $\hat{\mathbf{n}}$, or equivalently scattering angle χ centered in the solid angle $d\Omega$), which may be expressed in terms of the scattering cross section s [see for example Eq. (2.19)]:

$$\frac{dR}{d\Omega} = g s(g, \chi) P_2(\mathbf{r}, \mathbf{r} + \sigma\hat{\mathbf{n}}, \mathbf{v}_1, \mathbf{v}_2, t) d\mathbf{v}_2. \tag{2.73}$$

I discussed in Sect. 2.1.2 the fact that the scattering cross section depends strongly on the kind of interaction between the molecules of the gas. For power law repulsive interaction potential $U(r) \sim r^{-(a-1)}$, the scattering angle χ depends on the relative energy $g^2/2$ and on the impact parameter b only through the combination $(g^2 b^{a-1})$. This means that there exists a function $\gamma(\chi)$ such that:

$$b = g^{-2/(a-1)} \gamma(\chi) \tag{2.74}$$

and this means that from relation (2.21) one obtains:

$$gs(g,\chi) \sim g^{1-4/(a-1)} \frac{\gamma(\chi)}{\sin\chi} \frac{d\gamma}{d\chi} \tag{2.75}$$

which holds in $d = 3$. The extension to generic dimension of the last equation is:

$$gs(g,\chi) \sim g^{1-2(d-1)/(a-1)} \frac{\gamma^{d-2}}{(\sin\chi)^{d-2}} \frac{d\gamma}{d\chi} \sim g^{1-2(d-1)/(a-1)} \alpha(\cos\chi). \tag{2.76}$$

Therefore, when $a = 1 + 2(d-1)$ (i.e. $a = 5$ for $d = 3$ and $a = 3$ for $d = 2$) the collision rate $gs(g,\chi)$ *does not depend upon* g. This property defines the so-called Maxwell molecules [19]. Interaction with $a < 1 + 2(d-1)$ are called soft interactions (e.g. the electrostatic or gravitational interaction). Interactions with $a > 1 + 2(d-1)$ are called hard interactions. Hard spheres ($a \to \infty$) belongs to this set of interactions, with $gs(g,\chi) \sim g$. It has been also studied the Very Hard Particles model, which is characterized by $gs(g,\chi) \sim g^2$, which is not attainable with an inverse power potential, as it requires an interaction harder than the hard sphere interaction.

The advantage of Maxwell molecules is that the Boltzmann equation is greatly simplified, as g does not appear in the collision integral. A further simplification of the Boltzmann equation came from Krook and Wu [32], who studied the Boltzmann equation of Maxwell molecules with an isotropic scattering cross-section, i.e $\alpha = const$, often called Krook and Wu model. A very large literature exists for linear and non-linear model-Boltzmann equations [for a review see [19]]. The importance of the Maxwell molecules model is the possibility of obtaining solutions for it: the general method (extended to other model-Boltzmann equations) is to obtain an expansion in orthogonal polynomial where the expansion coefficients are polynomial moments of the solution distribution function. For Maxwell molecules the moments satisfy a recursive system of differential equations that can be solved sequentially. Given an initial distribution, one can solve the problem if the series expansion converges. Bobylev [8] has shown that if one searches for *similarity* solutions [i.e. solutions with scaling form $P(\mathbf{v},t) \equiv e^{-\alpha t} F(e^{-\alpha t}\mathbf{v})$], then the solution can be found solving a recursive system of algebraic equation. The Maxwell molecules model has been subject of study also in the framework of the kinetic theory of granular gases [2, 4, 9].

2.2.6 The Enskog Correction

The Boltzmann-Grad limit (see Sect. 2.2.3) restricts the validity of the Boltzmann equation to rarefied gases. This conditions is necessary to consider valid the *Molecular Chaos* which states the independence of colliding particles. In principle, in fact, two colliding particles can be correlated due to an intersection of their collisional histories: one simple possibility is that they may have collided some time before

or, alternatively, they may have collided with particles that have collided before. Moreover, the spatial extension of particles (i.e. the fact that they are not really pointlike) restricts the possibilities of motion and as a consequence the degree of independence (this is the so called *excluded volume effect*). All these kinds of correlations become relevant when the gas is not in the situation considered by the Boltzmann-Grad limit, that is when the gas is not rarefied but (either moderately or highly) dense.

The first approach to the problem of not rarefied gases was introduced by Enskog [16]: he did not consider the effects of velocity correlations due to common collisional histories, but simply added to the Boltzmann equation an heuristic correction to take into account short range correlations on positions only. In general the two-body probability distribution function can be written in terms of the one-body functions:

$$P_2(\mathbf{r}_1, \mathbf{v}_1, \mathbf{r}_2, \mathbf{v}_2, t) = g_2(\mathbf{r}_1, \mathbf{v}_1, \mathbf{r}_2, \mathbf{v}_2) P_1(\mathbf{r}_1, \mathbf{v}_1) P_1(\mathbf{r}_2, \mathbf{v}_2) \tag{2.77}$$

where g_2 is the pair correlation function. The Molecular Chaos assumption states that before collisions $g_2(\mathbf{r}_1, \mathbf{r}_1 + \sigma\hat{\mathbf{n}}, \mathbf{v}_1, \mathbf{v}_2) \equiv 1$. In the Enskog theory the Molecular Chaos assumption is modified in the following way:

$$P_2(\mathbf{r}_1, \mathbf{v}_1, \mathbf{r}_1 + \sigma\hat{\mathbf{n}}, \mathbf{v}_2, t) = \Xi(\sigma, n(\mathbf{r}_1)) P_1(\mathbf{r}_1, \mathbf{v}_1) P_1(\mathbf{r}_1 + \sigma\hat{\mathbf{n}}, \mathbf{v}_2) \tag{2.78}$$

i.e. g_2 at contact is a function $\Xi(\sigma, n)$ of σ and local density $n(\mathbf{r}_1)$ only, for particles entering or coming out from a collision. The term $\Xi(\sigma, n)$ becomes a multiplicative constant in front of the collisional integral $Q(P, P)$, giving place to the so-called Boltzmann-Enskog equation. Of course, in a general non-homogeneous situation, the density is a spatially and temporally non-uniform quantity which can be described by a macroscopic field: one may assume (as it is in kinetic theory) that this field changes slowly in space-time, so that the Boltzmann-Enskog equation can be locally solved with constant n as it was a Boltzmann equation with an effective total scattering cross section $\Xi(\sigma, n) N\sigma^2$. For elastic hard disks or hard spheres, spatial correlations may be described by the formulas of Carnahan and Starling [14]:

$$\Xi(\sigma, n) = \frac{1 - 7\phi/16}{(1-\phi)^2} \quad (d = 2) \tag{2.79a}$$

$$\Xi(\sigma, n) = \frac{1 - \phi/2}{(1-\phi)^3} \quad (d = 3) \tag{2.79b}$$

where ϕ is the solid fraction ($\phi = n\pi\sigma^2/4$ in $d = 2$, $\phi = n\pi\sigma^3/6$ in $d = 3$). This formula is expected to work well with solid fractions below ϕ_c, where a phase transition takes place [1]. The Enskog correction produces, for example, important corrections to the transport coefficients and to the pressure terms in transport equations.

2.3 The Boltzmann Equation for Granular Gases

The binary collision operator $\overline{T}_-(1,2)$, for inelastic particles, must be changed [44] according to the inelastic collision rules, Eqs. (2.28a, 2.28b) and (2.29a, 2.29b). It must be noted that when $r = 1$ (elastic collisions), the two set of equations coincide, i.e. the direct or inverse collision are identical transformations. This is not true if $r < 1$. Therefore, in the definition of the inverse binary collision operators at the end of Sect. 2.2.1, that is $T_-(1,2)$ and $\overline{T}_-(1,2)$, I have put the same operator b_c that appears in the direct binary collision operators $T_+(1,2)$ and $\overline{T}_+(1,2)$, while in general it must be used the operator b_c' that replaces velocities with precollisional velocities [using the transformation given in Eqs. (2.29a, 2.29b)]. The adjoint of inverse binary inelastic collision operator (the only one needed in the following) therefore reads:

$$\overline{T}_-(1,2) = \sigma^2 \int\limits_{\mathbf{V}_{12}\cdot\hat{\mathbf{n}}>0} d\hat{\mathbf{n}}|\mathbf{V}_{12}\cdot\hat{\mathbf{n}}|\left[\frac{1}{r^2}\delta(\mathbf{r}_1-\mathbf{r}_2-\sigma\hat{\mathbf{n}})b_c' - \delta(\mathbf{r}_1-\mathbf{r}_2+\sigma\hat{\mathbf{n}})\right] \tag{2.80}$$

Deriving from this the BBGKY hierarchy and putting in the first equation of it the Molecular Chaos assumption, the Boltzmann Equation for granular gases is obtained [30, 44]:

$$\left(\frac{\partial}{\partial t} + L_1^0\right) P(\mathbf{r}_1,\mathbf{v}_1,t) = N\sigma^2 Q(P,P) \tag{2.81}$$

$$Q(P,P) = \int d\mathbf{v}_2 \int\limits_{\mathbf{V}_{12}\cdot\hat{\mathbf{n}}>0} d\hat{\mathbf{n}}|\mathbf{V}_{12}\cdot\hat{\mathbf{n}}|\left[\frac{1}{r^2}P(\mathbf{r}_1,\mathbf{v}_1',t)P(\mathbf{r}_1,\mathbf{v}_2',t) - P(\mathbf{r}_1,\mathbf{v}_1,t)P(\mathbf{r}_1,\mathbf{v}_2,t)\right] \tag{2.82}$$

where the primed velocities are defined in Eqs. (2.29a, 2.29b). A major difference with respect to the elastic case is the presence of the factor $1/r^2$ in front of the gain collisional term. This term is the main source of unbalance between gain and loss, and is at the basis of the violation of time reversal symmetry and of the H-theorem (see discussion in Sect. 2.3.6).

This equation has been first studied in the spatially homogeneous case (no spatial gradients, $L_1^0 = 0$), with the Enskog correction (i.e. a multiplying factor $\Xi(\sigma,n)$ in front of the collision integral) by Goldshtein and Shapiro [22] and by Ernst and van Noije [43]. The equation in this case reads

$$\frac{\partial}{\partial t}P(\mathbf{v}_1,t) = \Xi(\sigma,n)n\sigma^2 Q(P,P). \tag{2.83}$$

2.3.1 Average Energy Loss

It is useful to define a rescaled distribution, under the assumption of *spatial homogeneity*:

$$N P(\mathbf{r}, \mathbf{v}, t) = \frac{n}{v_T^3} \tilde{f}(\mathbf{v}/v_T) \tag{2.84}$$

with (assuming $k_B = 1$) $T(t) = m\langle \mathbf{v}^2 \rangle/3 = \frac{1}{2} m v_T^2(t)$ e $\mathbf{c} = \mathbf{v}/v_T$ and n the average number density. One sees that $N^2 Q \to n^2 v_T^{-2} \tilde{Q}$ where

$$\tilde{Q} = \int d\mathbf{c}_2 \int_+ d\hat{n} |\mathbf{c}_{12} \cdot \hat{n}| \left[\frac{1}{r^2} \tilde{f}(\mathbf{c}_1', t) \tilde{f}(\mathbf{c}_2', t) - \tilde{f}(\mathbf{c}_1) \tilde{f}(\mathbf{c}_2) \right]. \tag{2.85}$$

The main contribution to the time derivative of temperature is given by the effect of inelastic collisions: in homogeneous situations, where collisions reduce the kinetic energy by a quantity proportional to the kinetic energy itself, one expects to find $\dot{T} \propto T$. The rigorous calculations reads

$$\begin{aligned} \frac{d}{dt} \left(\frac{3}{2} n T \right) \Big|_{coll} &= \int d\mathbf{v} \frac{m v^2}{2} \sigma^2 N^2 Q(P, P) \\ &= \sigma^2 n^2 v_T \frac{m v_T^2}{2} \int d\mathbf{c}_1 c_1^2 \tilde{Q} = -\sigma^2 n^2 v_T T \mu_2 \end{aligned} \tag{2.86}$$

with

$$\mu_p = -\int d\mathbf{c}_1 c_1^p \tilde{Q} \tag{2.87}$$

so that

$$\frac{dT}{dt}|_{coll} = -\zeta(t) T \tag{2.88}$$

where

$$\zeta(t) = \frac{2\sqrt{2}}{3} n \sigma^2 \mu_2 \sqrt{\frac{T}{m}}. \tag{2.89}$$

Computation of μ_2, and therefore of ζ, requires the knowledge of $\tilde{f}(c, t)$.

2.3.2 Sonine Polynomials

It is useful to introduce a polynomial expansion which reveals useful in standard kinetic theory as well as in granular kinetic theory: in fact it serves the purpose of describing small corrections to the Maxwellian. Such small corrections appear in homogeneous granular gases, as well as in all (granular or elastic) dilute gases in spatially non-homogeneous situations. The expansion reads:

$$\tilde{f}(\mathbf{c}) = f_{MB}(\mathbf{c}) \left[1 + \sum_{p=1}^{\infty} a_p S_p(c^2) \right] \tag{2.90}$$

with the basic Maxwellian given by

$$f_{MB}(c) = \pi^{-3/2} exp(-c^2). \tag{2.91}$$

The polynomials S_p are said "Sonine" polynomials (they are in fact associated Laguerre polynomials $S_p^{(m)}$ with $m = d/2 - 1$) and constitute a complete set of orthogonal functions:

$$\int d\mathbf{c} f_{MB}(c) S_p(c^2) S_{p'}(c^2) = \frac{2(p+1/2)!}{\sqrt{\pi}\, p!} \delta_{pp'} = \mathscr{N}_p \delta_{pp'} \tag{2.92}$$

In granular homogeneous situations one finds good fit by using expression (2.90) stopping the expansion at $p = 2$. In dimension $d = 3$ the first polynomials read

$$S_0(x) = 1 \tag{2.93}$$

$$S_1(x) = -x + 3/2 \tag{2.94}$$

$$S_2(x) = \frac{x^2}{2} - \frac{5x}{2} + \frac{15}{8} \tag{2.95}$$

It is easy to verify that

$$\langle c^2 \rangle = \frac{3}{2}(1 - a_1) \tag{2.96}$$

and

$$\langle c^4 \rangle = \frac{15}{4}(1 + a_2). \tag{2.97}$$

Note also that

$$N \int d\mathbf{v} \frac{mv^2}{2} P(r, v, t) = \frac{mv_T^2}{2} n \int d\mathbf{c} c^2 \tilde{f}(\mathbf{c}) = \langle c^2 \rangle \frac{mv_T^2}{2} n \tag{2.98}$$

and

$$N \int d\mathbf{v} \frac{mv^2}{2} P(r, v, t) = n \frac{m\langle v^2 \rangle}{2} = \frac{3}{2} nT = \frac{3}{2} n \frac{mv_T^2}{2} \tag{2.99}$$

so that $\langle c^2 \rangle = 3/2$ and therefore $a_1 = 0$: the first non trivial coefficient is a_2.

Equations for a_2 are found once a model (boundary conditions) is specified.
The explicit expression for μ_2 reads

$$\mu_2 = -\int d\mathbf{c}_1 c_1^2 \int d\mathbf{c}_2 \int_+ d\hat{n} |\mathbf{c}_{12} \cdot \hat{n}| \left[\frac{1}{r^2} \tilde{f}(\mathbf{c}_1', t) \tilde{f}(\mathbf{c}_2', t) - f(\mathbf{c}_1) f(\mathbf{c}_2) \right] \tag{2.100}$$

By using the Sonine expansion truncated at $p = 2$, it is finally obtained

$$\mu_2 = \sqrt{2\pi}(1 - r^2) \left(1 + \frac{3}{16} a_2 + O(a_2^2) \right). \tag{2.101}$$

2.3.3 The Homogeneous Cooling State

This is the simplest granular regime: it is assumed spatial homogeneity and absence of any energy injection. The system is initialized with some initial non-trivial velocity distribution.

The rescaled distribution implies the appearance of additional contribution to the time-derivative:

$$\frac{\partial NP}{\partial t} = \frac{n}{v_T^3} \frac{\partial \tilde{f}}{\partial t} + \left(-\frac{3n}{v_T^4} \tilde{f} + \frac{n}{v_T^3} \frac{\partial \tilde{f}}{\partial c_1} \frac{\partial c_1}{\partial v_T} \right) \frac{dv_T}{dt}. \tag{2.102}$$

The following time evolution equation is obtained:

$$\frac{1}{v_T} \frac{\partial \tilde{f}}{\partial t} - \frac{1}{v_T^2} \frac{\partial (\mathbf{c}_1 \tilde{f})}{\partial \mathbf{c}_1} \frac{dv_T}{dt} = \sigma^2 n \tilde{Q}. \tag{2.103}$$

Recalling the expression for $\dot{T}(t) = -\zeta(t) T(t)$ as well as for $\zeta(t)$, one can see that

$$\frac{1}{v_T^2} \frac{dv_T}{dt}|_{coll} = \frac{1}{2 v_T T} \frac{dT}{dt} = -\frac{1}{3} \sigma^2 n \mu_2 \tag{2.104}$$

is time-independent.

It is usually assumed that a scaling function exists $\tilde{f} \to \tilde{f}_{HC}$ with $\frac{\partial \tilde{f}_{HC}}{\partial t} = 0$. If it exists, it must satisfy

$$\frac{\mu_2}{3} \frac{\partial (\mathbf{c}_1 \tilde{f}_{HC})}{\partial \mathbf{c}_1} = \tilde{Q}. \tag{2.105}$$

This is the kinetic definition of Homogeneous Cooling State.

The solution of the temperature equation reads:

$$T(t) = \frac{T(0)}{(1 + \frac{\zeta(0)t}{2})^2} \tag{2.106}$$

Eq. (2.106) is known as Haff's law [24].

Using the Sonine approximation truncated at the second polynomial one has

$$\zeta(t) = \frac{4\sqrt{\pi}}{3} n\sigma^2 \sqrt{\frac{T(t)}{m}} (1 - r^2) \left(1 + \frac{3}{16} a_2 + O(a_2^2)\right) = \frac{1 - r^2}{3} \omega_c(t) \tag{2.107}$$

with

$$\omega_c = 4\sqrt{\pi} n\sigma^2 \sqrt{\frac{T(t)}{m}} \left(1 + \frac{3}{16} a_2 + O(a_2^2)\right) \tag{2.108}$$

the collision frequency.

After the Haff's law, it is immediate to realize that

$$\omega_c \sim \frac{1}{1 + \zeta(0)t/2} \tag{2.109}$$

which means that the *cumulated number of collisions* goes as $\sim \ln(1 + \zeta(0)t/2)$. This observation suggests to introduce a new time-scale

$$\tau(t) = \tau_0 \ln(1 + \zeta(0)t/2) \tag{2.110}$$

with arbitrary τ_0, getting

$$\frac{\partial}{\partial t} = \frac{\tau_0 \zeta(0)/2}{1 + \zeta(0)t/2} \frac{\partial}{\partial \tau}. \tag{2.111}$$

This is interesting, since it shows that

$$\frac{1}{v_T(t)} \frac{\partial}{\partial t} = \frac{\tau_0 \zeta(0)/2}{v_t(0)} \frac{\partial}{\partial \tau}. \tag{2.112}$$

Finally, with the new time-scale, one has

$$\frac{\partial \tilde{f}}{\partial \tau} + \frac{n\sigma^2 \mu_2}{3} \frac{\partial (\mathbf{c}_1 \tilde{f})}{\partial \mathbf{c}_1} = \sigma^2 n \tilde{Q} \tag{2.113}$$

equivalent to the Boltzmann equation for particles under the effect of a force

$$F = \frac{n\sigma^2 \mu_2 \mathbf{c}}{3} \tag{2.114}$$

which is equivalent to a *positive* viscosity!

All this equivalence makes sense until the state remains homogeneous. I will show in Chap. 3 that the homogeneous cooling state is unstable for large wavelength perturbations.

Ernst and van Noije [43] have given estimates for the tails of the velocity distribution, using an asymptotic method employed by Krook and Wu [32]. This method assumes that for a fast particle the dominant contributions to the collision integral come from collisions with thermal (bulk) particles and that the gain term of the integral can be neglected with respect to the loss term.

The loss term in the Boltzmann equation reads

$$-\int dc_2 \int_{+} d\hat{n}|c_{12}\dot{\hat{n}}|\tilde{f}(c_1)\tilde{f}(c_2) \approx -\pi c_1 \tilde{f}(c_1). \tag{2.115}$$

If $\tilde{f}$ is isotropic, then $\mathbf{c}\frac{d}{d\mathbf{c}}\tilde{f} = c\frac{d}{dc}\tilde{f}$. Then it remains

$$\mu_2 \tilde{f} + \frac{1}{3}\mu_2 c \frac{d}{dc}\tilde{f} = -\pi c \tilde{f} \tag{2.116}$$

and for large c one finds

$$\tilde{f} \sim \exp\left(-\frac{3\pi}{\mu_2}c\right). \tag{2.117}$$

It must be recalled that $\mu_2 \sim (1-r^2)$, which means that this estimate is valid when $c > 1/(1-r^2)$.

2.3.4 Inelastic Maxwell Molecules

The inelastic version in one dimension of the Boltzmann equation for Maxwell molecules, discussed in Sect. 2.2.5, reads

$$\partial_\tau P(v,\tau) + P(v,\tau) = \beta \int du\, P(u,\tau) P\left(\beta v + (1-\beta)u, \tau\right) \tag{2.118}$$

where $\beta = 2/(1+r)$ and the τ counts the number of collisions per particle. It is interesting to remark that Eq. (2.118) is the master equation of the inelastic version of a process introduced by Ulam [6]: at each step an arbitrary pair is selected and the scalar velocities are transformed according to the rule of Eqs. (2.28a, 2.28b). This model has been considered for the first time by Ben-Naim and Krapivsky [4]. They obtained the evolution of the moments of the velocity distributions. Since at large times, $\langle v^n \rangle \sim \exp(-\tau q_n)$, and the decay rates $q_n \neq nq_2/2$ (they depend

non-linearly on n), they argued that such a multiscaling behavior prevents the existence of a rescaled asymptotic distribution f such that $P(v,\tau) \to f(v/v_0(\tau))/v_0(\tau)$, for large τ, where $v_0^2(\tau) = \int v^2 P(v,\tau)dv = E(\tau)$. On the contrary, the "multiscaling" behavior only indicates the fact that the moments of the rescaled distribution $\int x^n f(x)dx = \langle v^n\rangle/v_0^n$ diverge asymptotically for $n \geq 3$, and does not rule out the possibility of the existence of an asymptotic distribution with power law tails. In fact, the Fourier transform of Eq. (2.118)

$$\partial_\tau \hat{P}(k,\tau) + \hat{P}(k,\tau) = \hat{P}[k/(1-\beta),\tau]\hat{P}[k/\beta,\tau] \tag{2.119}$$

possesses several self-similar solutions of the kind $\hat{P}(k,\tau) = \hat{f}(kv_0(\tau))$, which correspond to the asymptotic rescaled distribution $P(v,\tau) = f(v/v_0(\tau))/v_0(\tau)$. Many of them do not correspond to physically acceptable velocity distributions [4]. The divergence of the higher moments implies a non analytic structure of $\hat{f}$ in $k = 0$, since $\langle v^n\rangle/v_0^n = (-i)^n \frac{d^n}{dk^n}\hat{f}(k)|_{k=0}$, and represents a guide in the selection of the physical solution, which is

$$f(v/v_0(\tau)) = \frac{2}{\pi\left[1+(v/v_0(\tau))^2\right]^2} \tag{2.120}$$

corresponding to the self-similar solution $\hat{f}(k) = (1+|k|)\exp(-|k|)$. Notice that (2.120) is a solution of Eq.(2.119) for every $r < 1$, i.e. the asymptotic velocity distribution does not depend on the value of $r < 1$. The discovery of this exact scaling solution [2] paved the way to a long list of papers by different groups, where the problem in more dimensions was tackled and rigorous results for convergence, uniqueness, etc. were obtained [7].

2.3.5 Bulk Driving

The randomly driven granular gas [introduced in [45, 46]] consists of an assembly of N identical hard objects (spheres, disks or rods) of mass m and diameter σ. I put, for simplicity, $k_B = 1$ (the Boltzmann constant). The grains move in a box of volume $V = L^d$ (L is the length of the sides of the box), with periodic boundary conditions, i.e. opposite borders of the box are identified. The mean free path (calculated exactly in Eq. (2.26) for the case of an homogeneous gas of 3D hard spheres with a Maxwellian distribution of velocities) can be roughly estimated as

$$\lambda = \frac{1}{nS} \tag{2.121}$$

where $n = N/V$ is the mean number density and S is the total scattering cross section. I stress the fact that S has the dimensions of a surface in $d = 3$ ($S \sim \sigma^2$), of a line in $d = 2$ ($S \sim \sigma$) and no dimensions in $d = 1$ (this is consistent with the fact that the diameter, in $d = 1$ is irrelevant).

The dynamics of the gas is obtained as the byproduct of two physical phenomena: continuous interaction with the surroundings and inelastic collisions among the grains. The first ingredient is modeled in the shape of a Langevin equation with exact fulfillment of the Einstein relation [see for example [33]], for the evolution of the velocities of the grains in the free time between collisions. The inelastic collisions follow the usual inelastic rule. The equations of motion for a particle i that is not colliding with any other particle, are:

$$m\frac{d}{dt}\mathbf{v}_i(t) = -\gamma_b \mathbf{v}_i(t) + \sqrt{2\gamma_b T_b}\boldsymbol{\eta}_i(t) \tag{2.122a}$$

$$\frac{d}{dt}\mathbf{x}_i(t) = \mathbf{v}_i(t). \tag{2.122b}$$

I call the parameters $\tau_b = m/\gamma_b$ and T_b *characteristic time of the bath* and *temperature of the bath*, respectively. The function $\boldsymbol{\eta}_i(t)$ is a stochastic process with average $\langle \boldsymbol{\eta}_i(t)\rangle = 0$ and correlations $\langle \eta_i^\alpha(t)\eta_j^\beta(t')\rangle = \delta(t-t')\delta_{ij}\delta_{\alpha\beta}$ (α and β being component indexes) i.e. a standard white noise.

In the dynamics of the N particles, as defined in Eqs. (2.122a, 2.122b) and by the inelastic hard core collision rules, the most important parameters are:

- the coefficient of normal restitution r, which determines the degree of inelasticity;
- the ratio $\rho = \tau_b/\tau_c$ between the characteristic time of the bath and the "global" mean free time between collisions.

On the basis of these two parameters, one can define three fundamental limits of the dynamics of our model:

- the elastic limit: $r \to 1^-$;
- the collisionless limit: $\rho \to 0$ ($\tau_c \gg \tau_b$);
- the cooling limit: $\rho \to \infty$ ($\tau_c \ll \tau_b$).

The *elastic limit* is smooth in dimensions $d > 1$, so that one can consider it equivalent to put $r = 1$. In this case the collisions mix up the components leaving constant the energy (in the center of mass frame as well in the absolute frame). One can assume that, in this limit, the effect of the collisions is that of homogenizing the positions of the particles and making their velocity distribution relax toward the Maxwellian with temperature $T = \langle v^2\rangle/d = \langle v_x^2\rangle$ [this temperature is equal to the starting kinetic energy, but is modified by the relaxation toward T_b due to the Langevin Eqs. (2.122a, 2.122b)]. In one dimension this mixing effect (toward a Maxwellian) is no more at work, as the elastic collisions exactly conserve the starting velocity distribution (the collisions can be viewed as exchanges of labels and the particles as non-interacting walkers).

In the *collisionless limit* we have $\tau_c \gg \tau_b$ and, therefore, the collisions are very rare events with respect to the characteristic time of the bath. In this case we can consider the model as an ensemble of non-interacting Brownian walkers, each following the Eqs. (2.122a, 2.122b). Therefore, whatever r is and in any dimension, the distribution

of velocities relaxes in a time τ_b toward a Maxwellian with temperature $T = \langle v^2 \rangle / d = T_b$ with a homogeneous density.

Finally, in the *cooling limit*, the collisions are almost the only events that act on the distribution of velocities, while between collisions the particles move almost ballistically. In this limit (if $r < 1$), the gas can be considered stationary only on observation times very long with respect to the time of the bath τ_b, where the effect of the external driving (the Langevin equation) emerges. For observation times larger than the mean free time τ_c but shorter than τ_b, the gas appears as a *cooling granular gas*.

To conclude this brief discussion on the expected behavior of the randomly driven granular gas model, I sketch a scenario with the presence of two fundamental stationary regimes:

- the "collisionless" stationary regime: when $\rho \ll 1$, i.e. approaching the *collisionless* limit; in this regime one expects, after a transient time of the order of τ_b, the stationary statistics of an ensemble of non-interacting Brownian particles (homogeneous density and Maxwell distribution of velocities, absence of correlations);
- the "colliding" stationary regime: when $\rho \gg 1$, i.e. approaching the *cooling* limit, but observing the system on times larger than τ_b; here, we expect to see anomalous statistical properties.

For this model, the Boltzmann equation includes two additional contributions which are equivalent to the "Fokker-Planck" operators which evolve the velocity distribution in a Langevin equation. The equation therefore reads:

$$\frac{\partial P}{\partial t} = n\sigma^2 Q(P, P) + \frac{\gamma_b}{m} \frac{\partial \mathbf{v} P}{\partial \mathbf{v}} + \frac{\gamma_b}{m} \frac{T_b}{m} \nabla_v P, \tag{2.123}$$

with $Q(P, P)$ defined in Eq. (2.81). Using the definition of rescaled distribution (2.84), and obviously $\dot{v}_T = 0$ (we are in a statistically stationary state), one gets

$$\frac{\partial \tilde{f}}{\partial t} = v_T n\sigma^2 \tilde{Q} + \frac{\gamma_b}{m} \frac{\partial \mathbf{c} \tilde{f}}{\partial \mathbf{c}} + \frac{\gamma_b}{2m} \frac{T_b}{T} \nabla_c \tilde{f}. \tag{2.124}$$

From the definition, it follows that

$$T = \frac{m}{d} \langle v^2 \rangle \tag{2.125}$$

and therefore

$$\langle v \dot{v} \rangle = \frac{\dot{T}}{2m} = -\frac{\gamma_b}{m} \langle v^2 \rangle + \frac{\gamma_b}{m} \frac{T_b}{m} - \zeta \frac{T}{2m}. \tag{2.126}$$

Imposing $\dot{T} = 0$, in the stationary state, we get

$$T - T_b = \zeta \tau_b T \tag{2.127}$$

which can be (numerically) solved to obtain T (I remind that $\zeta \propto (1 - r^2)T^{1/2}$). It is worth noting that r e τ_b appear through a factor $(1 - r^2)\tau_b$.

Assuming that at large velocities $\tilde{Q} \sim -\pi c \tilde{f}$, one finds

$$-\pi v_T n \sigma^2 c \tilde{f} + \frac{\gamma_b}{2m} \frac{T_b}{T} \left(\frac{d^2}{dc^2} + \frac{2}{c} \frac{d}{dc} \right) \tilde{f} + \frac{\gamma_b}{m} \left(3 + c \frac{d}{dc} \right) \tilde{f} = 0. \tag{2.128}$$

This has two different "solutions"

- in the limit $\gamma \to 0$ (with $T_b \to \infty$ with finite γT_b), one has $\tilde{f} \sim \exp(-c^{3/2})$ [43]
- when $\gamma > 0$ one apparently finds $\tilde{f} \sim \exp(-c^2)$ but in this case the approximations (in particular having neglected the gain term in the collisional integral) are not guaranteed.

I conclude this description of the bulk-driving model, by mentioning that recent experiments have demonstrated the relevance of this model for real fluidized granular systems [23, 47].

2.3.6 *Looking for a "Granular" H-theorem*

The H functional, see Eqs. (2.71a–2.71d), is monotonously non-increasing for an evolution dictated by the homogeneous *elastic* Boltzmann equation. When collisions are inelastic, however, monotonicity of H can no more be proven, and indeed numerical simulations demonstrate that it is no more true [3]. It is worth to mention a recent observation [39] which suggests a possible replacement of the Boltzmann H functional in the case of so-called Boltzmann-Fokker-Planck model (BFP). This model is basically the one discussed in Sect. 2.3.5, precisely it is represented by Eq. (2.123). Variants have also been considered, where the velocities are discretized and the Fokker-Planck operator is replaced by a stochatic jump operator with transition rates that satisfy detailed balance with respect to an equilibrium steady distribution.

The candidate Lyapunov functional is the following

$$H_C(t) = \int d\mathbf{v} P(\mathbf{v}, t) \log \frac{P(\mathbf{v}, t)}{\Pi(\mathbf{v})}, \tag{2.129}$$

where $\Pi(\mathbf{v})$ is the stationary velocity distribution reached asymptotically. Numerical observations and some analytical arguments indicate that for the BFP model the following relation holds

$$\frac{dH_C(t)}{dt} \leq 0. \tag{2.130}$$

In particular, in the *elastic* version of the BFP model, the result (2.130) can be demonstrated. Note that the elastic BFP model has a trivial steady state, but a non-trivial dynamics.

The origin of the apparently exact result (2.130) is still unknown and a general demonstration is awaited.

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