FROM MOLECULAR CHAOS TO DYNAMICAL CHAOS
An Introduction to Chaos Theory as it Relates to Nonequilibrium Statistical Mechanics
Lectures at the Institute for Theoretical Physics
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Chapter 1

Preface

"v'Ha-aretz hayta tohu va'vohu...v'ruaḣ Elokim meraḣefet al pnai ha-mayim."- Genesis, 1.2.

These notes are based on a series of lectures given to fourth year students at the Institute for Theoretical Physics at the University of Utrecht during the spring semester of 1994. The course of lectures was entitled *From Molecular Chaos to Dynamical Chaos.* Two students in the class, Lucas Neevens van Baal, and Iris Lafaille, took notes, edited them, and prepared a Latex manuscript that formed the basis for these notes. It is due to their hard work and desire to make the notes as clear as possible that the notes have reached this stage.

I apologize for not providing as complete a list of references as I would do for a more formal presentation. Each chapter begins with some key references, but they are by no means exhaustive. Other references are provided in the text, where appropriate. There are a few sources which I found very useful and I list them here:

1) E. Ott *Chaos in Dynamical Systems,* Cambridge University Press, Cambridge (1992).

2) *Microscopic Simulations of Complex Hydrodynamical Phenomena,* edited by M. Maréschal and B. Holian, Plenum Press, New York, (1992).

3) D. Ruelle and J.-P. Eckmann, "Ergodic Theory of Chaos and Strange Attractors", Rev. Mod. Phys. **57**, 617, (1985).

4) J. L. Lebowitz and O. Penrose, "Modern Ergodic Theory", in PHYSICS TODAY, February, 1973, pp.23-29.

5) A. Lasota and M. C. Mackey, *Chaos, Fractals, and Noise*, second ed., Springer-Verlag, New York, (1994).

I would like to thank the students who attended the course and participated in the class discussions as well as a number of colleagues who attended the lectures for helping me clarify many of the points presented here. Of course it is essential to acknowledge the assistance of Mr. van Baal, and Ms. Lafaille. I would like to thank my colleagues of the Institute for Theoretical Physics for their warm hospitality, their generous help, and their creatively critical attitude which was always refreshing. It is a pleasure to thank two colleagues in particular, Matthieu Ernst and Henk van Beijeren, for all of their help, support, and advice, and for many fruitful scientific collaborations which have continued for over thirty years, which have now evolved to collaborations on topics related to those covered in these lectures. Any clarity these notes may have is due in large part to many discussions, especially with Profs. Ernst and van Beijeren, but also with Drs. Donald Jacobs and Harmen Bussemaker. It is a pleasure to thank Prof. Nico van Kampen for interesting discussions on quantum chaos and on linear response theory. I would also like to express my gratitude to Ms. Leonie Silkens for her help on many matters during my stay in Utrecht. Thanks are also due to the Institute for Physical Science and Technology, The Department of Physics, the Office of the Dean of the College of Computer, Mathematical and Physical Sciences, and the Office of the Vice-President for Academic Affairs at the University of Maryland at College Park. In addition, Masao Yoshimura, Arnulf Latz, and Rainer Klages helped me enormously with the Latex file. Prof. John Weeks kindly provided Figure 3.1. I wish to thank Masao Yoshimura, Ernest Barreto, and Kenneth Snyder for careful readings of earlier versions of these notes which led to a large number of corrections, incorporated in the present edition.

There are two individuals at other universities to whom I also owe a debt of gratitude. Prof. Pierre Gaspard of the Université Libre de Bruxelles has aided me enormously in my understanding of the connections between non-equilibrium statistical mechanics and dynamical systems theory both through his writings and through our collaboration on a number of interesting topics. I also wish to thank Prof. E.G.D. Cohen of the Rockefeller University who through many years of close and fruitful collaboration, has helped shape my understanding of irreversible processes.

Finally I would like to acknowledge support from the National Science Foundation under Grants No. PHY-93-21312 and PHY-96-00428.

Chapter 2

Introduction

The purpose of this course is to present, in as coherent a form as I can, a survey of recent work on the statistical mechanics of irreversible processes in fluids that explores the foundations of the theory. This work appears, in a sense, as a corollary of the work on dynamical systems carried out by mathematicians and physicists over the last thirty years or so. Advances in the understanding of ergodic - and stronger- properties of dynamical systems of interest to physics provided by the deep and pioneering work of Sinai, Bunimovich, Chernov, and others on billiard systems, by the work of Sinai, Bowen and Ruelle on the fundamental theory of hyperbolic dynamical systems and by many other workers in this active field of research are beginning to have a profound influence on the foundations of statistical mechanics. The past few years have seen a much deeper understanding of transport theory, especially, beginning to take shape.

These lectures are designed to provide the background necessary for an understanding of these new developments in statistical mechanics. They begin with a traditional discussion of the Boltzmann transport equation, which still today is the centerpiece of our understanding of the hydrodynamic properties of fluids. After the Boltzmann equation and the assumptions made in its derivation are discussed, more general approaches to transport theory such as the Green-Kubo time correlation method are considered. Armed then with the basic tools of non-equilibrium statistical mechanics, the student is introduced to the fundamentals of chaos theory. The baker's transformation is used as the basic paradigm for understanding many aspects of the foundations of transport theory. This transformation is simple enough that it can be readily understood, but complex enough that many features of the theory of irreversible processes can be illustrated with its aid. The last section of the notes discuss recent developments in this area and are intended to form an introduction to the current research literature. We present two approaches to transport theory which have developed over the past few years, and which are based on the notions of chaos theory: (1) The escape-rate or chaotic scattering theory formalism for computing transport coefficients developed by P. Gaspard, Nicolis, Baras, and co-workers, and (2) The Gaussian thermostat method for computing transport coefficients developed by Nosé, Hoover, Evans, Morriss, Posch, Cohen, and co-workers. These two topics are, in my opinion, the first glimmers of what can be expected to be a new line of research in transport theory relating macroscopic properties of large systems to the properties of the underlying microscopic dynamics. Then we discuss a simple example of fractal forms that appear in the Green-Kubo formulation of transport phenomena. These forms are amusing and interesting in themselves, but should also be seen as a precursor to a more sophisticated approach to transport theory involving so-called Ruelle-Policott resonances. These latter are not discussed in these notes, but we hope that the reader will not be surprised by what she or he finds in the literature, after reading this chapter. Finally, the Boltzmann equation returns at the end in a new guise - as a basic method for computing the quantities, such as Lyapunov exponents, that arise naturally in a dynamical systems approach to random systems. The notes conclude with a brief guide to the literature and problem sets for the Course at the University of Utrecht, with solutions to many of the problems included.

It is my hope that these notes will serve to introduce students to this new area of research, to show that there are many deep, unsolved problems waiting for clever people to formulate them precisely and to solve them, and finally, perhaps, to show that the basic ideas provided by the founders of this subject-Maxwell, Boltzmann, and Gibbs- are beginning to be understood and verified by the mathematical and physical researches of the present day - one hundred years after these ideas were first developed.

Chapter 3

The Boltzmann Equation

3.1 Heuristic Derivation

[Reference: J.R. Dorfman and H. van Beijeren, "The Kinetic Theory of Gases" in *Statistical Mechanics,Part B*, B. Berne ed., Plenum Press, New York (1976)]

In 1872 Boltzmann introduced the basic equation of transport theory for dilute gases. His equation determines the time dependent position and velocity distribution function for the molecules in a dilute gas. We begin by presenting Boltzmann's derivation of this equation in order to illustrate both the equation as well as some of the problems that arise in the course of its derivation.

Consider a large vessel of volume V, containing N molecules which interact with central, pair-wise additive, repulsive forces. The latter requirement allows us to avoid the complications of long-lived "bound" states of two molecules which though interesting, are not central to our discussion here. We suppose that the pair potential has a strong repulsive core and a finite range a. A typical pair potential is illustrated in Fig. 3.1. The gas is taken to be dilute, meaning that the volume per particle is much greater than the size of a particle,$V/N \gg a^3$, or, equivalently, $na^3 \ll 1$, where $n = N/V$ is the number density of the particles.

Now we define a distribution function, $F(\vec{r}, \vec{v}, t)$, for the gas over a 6-dimensional position and velocity-space, $\vec{r}, \vec{v}$, such that

$$F(\vec{r}, \vec{v}, t)\delta\vec{r}\delta\vec{v} \equiv \text{ the number of particles in } \delta\vec{r}\delta\vec{v} \text{ around } \vec{r} \text{ and } \vec{v} \text{ at time } t.$$

$F(\vec{r}, \vec{v}, t)$ is the particle density in a 6-dimensional, one-particle phase space, often referred to as μ-space. To get an equation for $F(\vec{r}, \vec{v}, t)$, we take a region

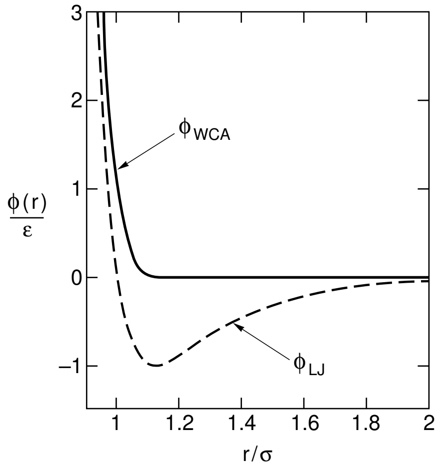

Figure 3.1: Typical pair potentials. Illustrated here are the Lennard-Jones pair potential, ϕ_{LJ}, and the associated Weeks-Chandler-Anderson potential, ϕ_{WCA}, which gives the same repulsive force as the Lennard- Jones potential. The relative separation coordinate is scaled by the distance σ, the point at which ϕ_{LJ} first passes through zero, and the energy axis is scaled by the well depth, ϵ.

$\vec{\delta r}\delta\vec{v}$ about a point $\vec{r}, \vec{v}$ in this space, that is large enough to contain a lot of particles, but small compared to the range of variation of F.

There are four mechanisms that change the number of particles in this region :

1) flow in or out of $\delta\vec{r}$, (the *free-streaming* term)

2) leave the $\delta\vec{v}$ region as a result of a (direct) collision , (the *loss* term)

3) enter the $\delta\vec{v}$ region after a (restituting) collision , (the *gain* term)

4) collide with the wall of the container, (if the region contains part of the walls), (the *wall* term) .

Assume there is a time scale δt which is sufficiently long that a great number of collisions can take place in each cell $\delta\vec{r}\delta\vec{v}$ in time δt, but which is too short for particles to cross a cell of size $\delta\vec{r}$. Then the change in the number of particles in $\delta\vec{r}\delta\vec{v}$ in time δt can be written as

$$[F(\vec{r}, \vec{v}, t + \delta t) - F(\vec{r}, \vec{v}, t)]\, \delta\vec{r}\delta\vec{v} = \Gamma_F - \Gamma_- + \Gamma_+ + \Gamma_W \tag{3.1}$$

where $\Gamma_F, \Gamma_-, \Gamma_+$,and Γ_W represent the changes in F due to the four mechanisms listed above, respectively. We suppose that each particle in the small region suffers at most one collision during the time interval δt, and calculate the change in F.

The computation of Γ_F is relatively straight forward. We simply consider the free flow of particles into and out of the region in time δt. An expression for this flow in the x-direction, for example, can be obtained by considering two thin layers of size $v_x\,\delta t\,\delta r_y\,\delta r_z$ that contain particles that move into or out of, a cell with its center at (x, y, z) in time δt (see Fig. 3.2).

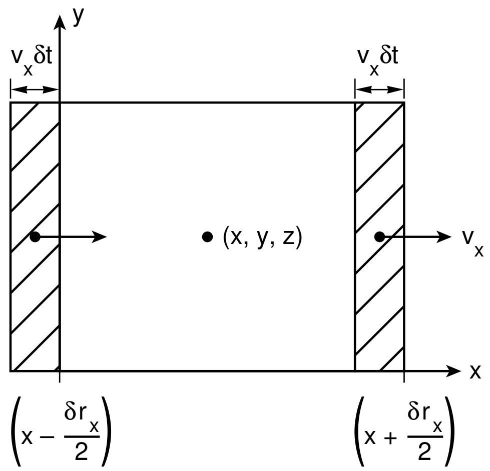

Figure 3.2: A schematic illustration of flow into and out of a small region. The hatched areas represent regions where particles enter and leave $\delta\vec{r}\delta\vec{v}$ in time δt.

The flow-term can be written as the difference between the number of particles entering and leaving the small region in time δt. Consider, for example, a cubical cell and look at the faces perpendicular to the x-axis. The flow of particles across the faces at $x - \frac{1}{2}\,\delta r_x$ and at $x + \frac{1}{2}\delta r_x$ is

$$\Gamma_F^{(x)} = v_x\,\delta t\,\delta r_y\,\delta r_z\,\delta\vec{v}\left[F(x - \frac{1}{2}\delta r_x, y, z, \vec{v}, t) - F(x + \frac{1}{2}\delta r_x, y, z, \vec{v}, t)\right]$$

and similar expressions for the y- and z-directions. F is supposed to be sufficiently smooth that it can be expanded in a Taylor series around (x, y, z) . The zeroth order terms between the brackets cancel and the first order terms add up. Neglecting terms of order δ^2 and summing over all directions then

$$\Gamma_F = -\delta\vec{v}\delta t\delta\vec{r}(\vec{v}\cdot\vec{\nabla})F(\vec{r}, \vec{v}, t) \tag{3.2}$$

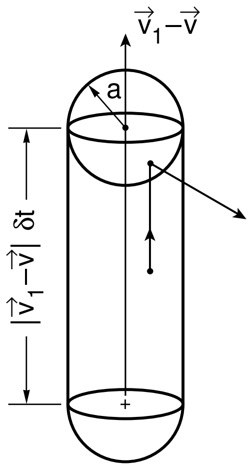

Figure 3.3: The $(\vec{v}_1, \vec{v})$ Collision Cylinder.

Next we consider the computation of the loss term, Γ_-. We need to calculate the number of collisions suffered by particles with velocity $\vec{v}$ in the region $\delta\vec{r}\delta\vec{v}$ in time δt assuming that each such collision results in a change of the velocity of the particle. We carry out the calculation in several steps. First, we focus our attention on a particular particle with velocity $\vec{v}$, and suppose that it is going to collide sometime during the interval t to $t + \delta t$ with a particle with velocity $\vec{v}_1$. Now set up a coordinate system with origin at the center of the particle with velocity $\vec{v}$, and with z-axis directed along the vector $\vec{g} = \vec{v}_1 - \vec{v}$. By examining Fig. 3.3 , one can easily see that if the particle with velocity $\vec{v}_1$ is somewhere at time t within the *collision cylinder* illustrated there, with volume $|\vec{v}_1 - \vec{v}|\, \pi a^2 \delta t$, this particle will collide sometime during the interval t to $t + \delta t$ with the particle with velocity $\vec{v}$, if no other particles interfere, which we assume to be the case. These collision cylinders will be referred to as $(\vec{v}_1, \vec{v})$-collision cylinders. We also ignore the possibility that the particle with velocity $\vec{v}_1$ might be at time t somewhere within the action sphere of radius a about the center of the velocity $\vec{v}$ particle since such events lead to terms that are of higher order in the density than those we are considering here, and such terms do not even exist if the duration of a binary collision is strictly zero, as would be the case for hard spheres, for example.

We now compute Γ_- by noting the following:

(a) The number of $(\vec{v}_1, \vec{v})$-collision cylinders in the region $\delta\vec{r}\delta\vec{v}$ is equal to the number of particles with velocity $\vec{v}$ in this region, $F(\vec{r},\vec{v},t)\delta\vec{r}\delta\vec{v}$.

(b) Each $(\vec{v}_1,\vec{v})$-collision cylinder has the volume given above, and the total volume of these cylinders is equal to the product of the volume of each such cylinder with the number of these cylinders, that is $F(\vec{r},\vec{v},t)\,|\vec{v}_1-\vec{v}|\,\pi a^2\,\delta\vec{r}\,\delta\vec{v}\,\delta t$.

(c) If we wish to know the number of $(\vec{v}_1,\vec{v})$ collisions that actually take place in this small time interval, we need to know exactly where each particle is located and then follow the motion of *all* the particles from time t to time $t+\delta t$. In fact this is what is done in computer simulated molecular dynamics. We wish to avoid this exact specification of the particle trajectories, and instead carry out a plausible argument for the computation of Γ_-. To do this Boltzmann made the following assumption, called the *Stosszahlansatz* :

The total number of $(\vec{v}_1,\vec{v})$ collisions taking place in δt equals the total volume of the $(\vec{v}_1,\vec{v})$-collision-cylinders times the number of particles with velocity $\vec{v}_1$ per unit volume.

After integration over $\vec{v}_1$, we obtain:

$$\Gamma_- = \delta\vec{r}\delta\vec{v}F(\vec{r},\vec{v},t)\int d\vec{v_1}\delta t\,\pi a^2|\vec{v_1}-\vec{v}|F(\vec{r},\vec{v_1},t) \tag{3.3}$$

The gas has to be dilute because the collision-cylinders are assumed not to overlap and also because collisions between more than two particles are neglected. Also it is assumed that F hardly changes over $\vec{\delta r}$ so that the distribution functions for both colliding particles can be taken at the same position $\vec{r}$.

The collection of assumptions that go into the calculation of Γ_- are collectively referred to as the assumption of *molecular chaos.* In this context, this assumption says that the probability that a pair of particles with given velocities will collide can be calculated by considering each particle separately and ignoring any correlation between the probability for finding one particle with velocity $\vec{v}$ and the probability for finding another with velocity $\vec{v}_1$ in the region $\delta\vec{r}$.

For the construction of Γ_+, we need to how two particles can collide in such a way that one of them has velocity $\vec{v}$ after the collision. The answer to this question can be found by a more careful examination of the "direct" collisions which we just discussed. To proceed with this examination we note that the factor πa^2 appearing in Eq. 3.3 can also be written as an integral over the impact parameters and azimuthal angles of the $(\vec{v}_1,\vec{v})$ collisions. That is, $\pi a^2 = \int b\,db\int d\epsilon$, where b, the impact-parameter, is the initial distance between the center of the incoming $\vec{v}_1$-particle and the axis of the collision-cylinder (z-axis), and ϵ is the angle between the x-axis and the position of particle (2) in the $x-y$-plane. Here $0 \leq b \leq a$, and $0 \leq \epsilon \leq 2\pi$. The laws of conservation of linear momentum, angular momentum, and energy require that both the impact parameter b, and $|\vec{g}| = |\vec{v}_1 - \vec{v}|$, the magnitude of the relative velocity, be the same before and after the collision. To see what this means let's follow the two particles through and beyond a direct collision. We denote all quantities after the collision by primes. The conservation of momentum

$$\vec{v}_1 + \vec{v} = \vec{v_1}' + \vec{v'}$$

implies, after squaring and using conservation of energy,

$$v_1^2 + v^2 = {v'_1}^2 + v^2,$$

that

$$\vec{v_1} \cdot \vec{v} = \vec{v_1}' \cdot \vec{v'}.$$

By multiplying this result by a factor of (-2), and adding the result to the conservation of energy equation, one easily finds $g = g' = \left|\vec{v_1'} - \vec{v'}\right|$ .This result, taken together with conservation of angular momentum, $\mu g b = \mu g' b'$, where $\mu = \frac{1}{2}m$ is the reduced mass of the two-particle system, shows that b is also conserved $b = b'$. This is illustrated in Fig. 3.4.

Next we denote the line between the centers of the two particles at the point of closest approach by the unit vector $\hat{k}$. In Fig. 3.4, it can also be seen that the vectors $-\vec{g}$ and $\vec{g'}$ are each other's mirror images in the direction of $\hat{k}$ in the plane of the trajectory of particles:

$$\vec{g'} = \vec{g} - 2(\vec{g} \cdot \hat{k})\hat{k}$$

and thus $(\vec{g} \cdot \hat{k}) = -(\vec{g'} \cdot \hat{k})$. Together with conservation of momentum this gives

$$\begin{aligned} \vec{v_1}' &= \vec{v_1} - (\vec{g} \cdot \hat{k})\hat{k} \qquad (3.4) \\ \vec{v'} &= \vec{v} + (\vec{g} \cdot \hat{k})\hat{k} \end{aligned}$$

The main point of this argument is to show that if particles with velocities $\vec{v'}$ and $\vec{v_1'}$ collide in the right geometric configuration with impact parameter b, such a collision will result in one of the particles having the velocity of interest $\vec{v}$ after the collision. These kinds of collisions which produce particles with

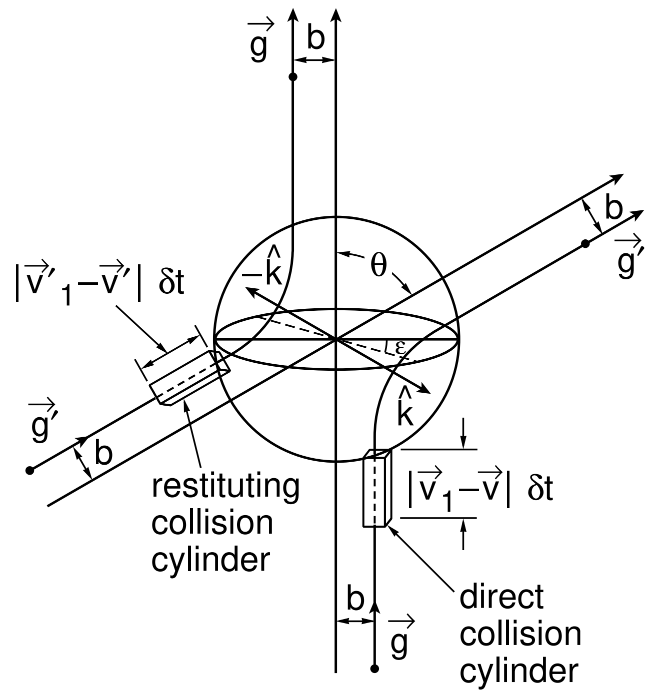

Figure 3.4: Direct and Restituting Collisions in the Relative Coordinate Frame. The collision cylinders as well as the appropriate scattering and azimuthal angles are illustrated.

velocity $\vec{v}$, contribute to Γ_+, and are referred to as "restituting" collisions. This is illustrated in Fig. 3.5 where particles having velocities $\vec{v'}$ and $\vec{v_1'}$ are arranged to collide in such a way that the unit-vector of closest approach, $\hat{k}$, is replaced by $-\hat{k}$. Consider, then, a collision with initial velocities $\vec{v_1}'$ and $\vec{v'}$ and the same impact-parameter as in the direct collision, but with $\hat{k}$ replaced by $-\hat{k}$. The final velocities are now $\vec{v_1}''$ and $\vec{v''}$, which are equal to $\vec{v_1}$ and $\vec{v}$, respectively, because

$$\vec{v_1}'' = \vec{v_1}' - (\vec{g'} \cdot \hat{k})\hat{k} = \vec{v_1}' + (\vec{g} \cdot \hat{k})\hat{k} = \vec{v_1} \tag{3.5}$$

Also

$$\vec{v''} = \vec{v'} - (\vec{g} \cdot \hat{k})\hat{k} = \vec{v}$$

Thus the increase of particles in our region due to restituting collisions with an impact parameter between b and $b + db$ and azimuthal angle between ϵ

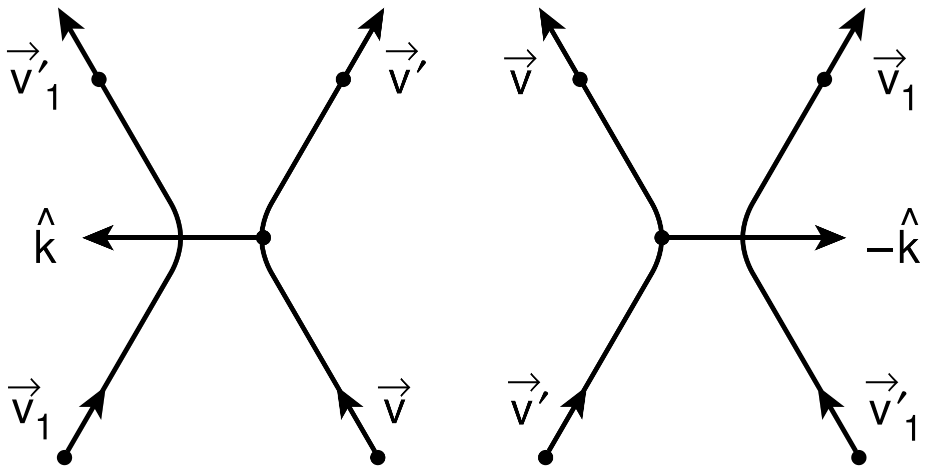

Figure 3.5: Schematic Illustration of the Direct and Restituting Collisions.

and $\epsilon + d\epsilon$ (see Fig. 3.4) can be obtained by adjusting the expression for the *decrease* of particles due to a 'small ' collision cylinder:

Loss : $\delta t b db d\epsilon |\vec{g}| F(\vec{r}, \vec{v}, t) F(\vec{r}, \vec{v_1}, t) \delta\vec{v} \delta\vec{v}_1 \delta\vec{r}$

Gain : $\delta t b db d\epsilon |\vec{g'}| F(\vec{r}, \vec{v'}, t) F(\vec{r}, \vec{v'_1}, t) \delta\vec{v'_1} \delta\vec{v'} \delta\vec{r}$

where b has to be integrated from 0 to a, and ϵ from 0 to 2π. Also by considering the Jacobian for the transformation to relative and center of mass velocities one easily finds that $d\vec{v_1} d\vec{v} = d\vec{V} d\vec{g}$, where $\vec{V}$ is the velocity of the center of mass of the two colliding particles with respect to the container. After a collision $\vec{g}$ is rotated in the center of mass frame, so the Jacobian of the transformation $(V, g) \to (V', g')$ is 1 and $d\vec{V} d\vec{g} = d\vec{V'} d\vec{g'}$. So

$$d\vec{v_1} d\vec{v} = d\vec{V} d\vec{g} = d\vec{V'} d\vec{g'} = d\vec{v'_1} d\vec{v'} \tag{3.6}$$

Now we are in the correct position to compute Γ_+, using exactly the same kinds of arguments as in the computation of Γ_-, namely the construction of collision cylinders, computing the total volume of the relevant cylinders and again making the *Stosszahlansatz.* Thus we find that

$$\Gamma_+ = \int d\vec{v'_1} \int b\, db \int d\epsilon \left|\vec{v'_1} - \vec{v'}\right| F\left(\vec{r}, \vec{v'}, t\right) F(\vec{r}, \vec{v'_1}, t) \delta\vec{r}\, \delta\vec{v'}\, \delta t.$$

For every value of the velocity $\vec{v}$ the velocity ranges $d\vec{v'_1} \delta\vec{v'}$ in the above expression are only over that range of velocities $\vec{v'}$, $\vec{v'_1}$ such that particles with velocity in the range $\delta\vec{v}$ about $\vec{v}$ are produced in the $\left(\vec{v'}, \vec{v_1'}\right)$ collisions. If we now use the equalities Eq. 3.6 as well as the fact that $|\vec{g}| = \left|\vec{g'}\right|$ we can write

$$\Gamma_+ = \int d\vec{v}_1 \int b\,db \int d\epsilon\, |\vec{v}_1 - \vec{v}|\, F(\vec{r}, \vec{v'}, t) F(\vec{r}, \vec{v_1}', t) \delta\vec{r}\delta\vec{v}\delta t \tag{3.7}$$

The term describing the interaction with the walls is discussed in the paper by Dorfman and van Beijeren mentioned at the beginning of this Chapter. Here we will not go into the detailed properties of this term, but will quote results as needed.

Finally all of the Γ-terms can be inserted in Eq. 3.1, and dividing by $\delta t\, \delta\vec{r}\, \delta\vec{v}$ gives the Boltzmann Transport Equation :

$$\frac{\partial F(\vec{r}, \vec{v}, t)}{\partial t} + (\vec{v} \cdot \vec{\nabla}_r F(\vec{r}, \vec{v}, t)) = J(F, F) + T_w \tag{3.8}$$

where $J(F, F) = \int d\vec{v_1} \int bdb \int d\epsilon |\vec{v}_1 - \vec{v}|\, [F' F_1' - F_1 F]$

The primes and subscripts on the F's refer to their velocity arguments, and the primed velocities in the gain term should be regarded as functions of the unprimed quantities according to Eq. 3.4 .

It is often convenient to rewrite the integral over the impact-parameter and the azimuthal angle as an integral over the unit-vector $\hat{k}$:

$$gb\,db\,d\epsilon = B(\vec{g}, \hat{k}) d\hat{k},$$

$$d\hat{k} = \sin(\pi - \psi) d(\pi - \psi) d\epsilon$$

where ψ is the angle between $\vec{g}$ and $\hat{k}$. Or $d\hat{k} = |\sin(\psi) d\psi d\epsilon|$ so

$$B(\vec{g}, \hat{k}) = |\vec{v_1} - \vec{v}| \left|\frac{b}{\sin(\psi)}\right| \left|\frac{db}{d\psi}\right|$$

with the restriction for purely repulsive potentials that $\vec{g} \cdot \hat{k} < 0$. As can be seen in Fig. 3.4

$$B(\vec{g'}, \hat{k}) = B(\vec{g}, -\hat{k}).$$

Let's apply this to the situation where the molecules are hard spheres of *diameter* a. We have $\frac{db}{d\psi} = \frac{da\sin(\psi)}{d\psi} = a\cos(\psi)$ (see Fig. 3.6) and $B(\vec{g}, \hat{k}) = ga^2 \cos(\psi) = a^2 |(\vec{g} \cdot \hat{k})|$ The Boltzmann equation for hard spheres is given then as

$$\frac{\partial F}{\partial t} + (\vec{v} \cdot \vec{\nabla}_r F) = a^2 \int d\vec{v_1} \int_{\vec{g}\cdot\hat{k}<0} d\hat{k} |\vec{g} \cdot \hat{k}|\, [F_1' F' - F_1 F] \tag{3.9}$$

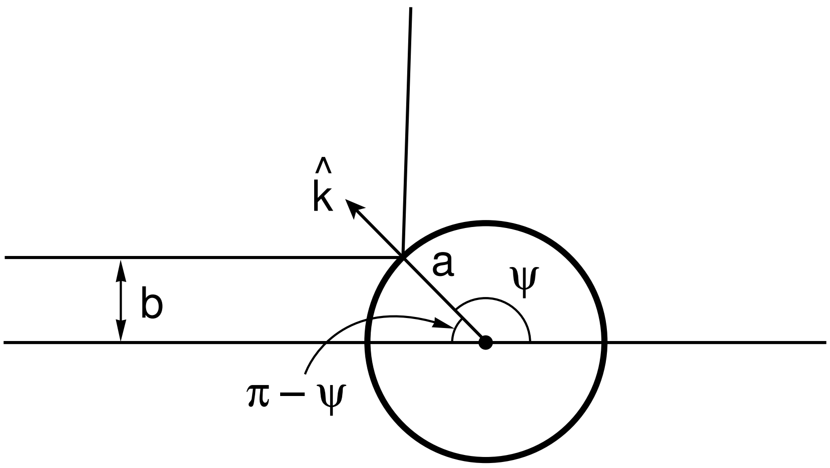

Figure 3.6: Hard-Sphere Collision Geometry in the Plane of the Collision.

This completes the heuristic derivation of the Boltzmann transport equation. Now we turn to Boltzmann's argument that his equation implies the Clausius form of the Second Law of Thermodynamics - namely, that the entropy of an isolated system will increase as the result of any irreversible process taking place in the system. This result is referred to as *Boltzmann's H-Theorem.*

3.2 Boltzmann's H-Theorem.

Boltzmann showed that under very general circumstances, there exists a time-dependent quantity, $H(t)$, that never increases in the course of time. This quantity is given by

$$H(t) \equiv \int d\vec{r_1} \int d\vec{v_1} F(\vec{r_1}, \vec{v_1}, t) \left[\ln(F(\vec{r_1}, \vec{v_1}, t) - 1\right] \tag{3.10}$$

Here the spatial integral is to be carried out over the entire volume of the vessel containing the gas, and for convenience we have changed the notation slightly. Now we differentiate H with time,

$$\frac{dH(t)}{dt} = \int d\vec{r_1} \int d\vec{v_1} \frac{\partial F_1}{\partial t} \ln(F_1) \tag{3.11}$$

and use the Boltzmann equation to find that

$$\frac{dH}{dt} = \int d\vec{r_1} \int d\vec{v_1} \left[-(\vec{v_1} \cdot \nabla F_1) + J(F_1, F_1) + T_w \right] \ln(F_1) \tag{3.12}$$

We are going to carry out some spatial integrations here. We suppose that the distribution function vanishes at the surface of the container and that there is no flow of energy or momentum into or out of the container. (We mention in passing that it is possible to relax this latter condition and thereby obtain a more general form of the Second Law than we discuss here. This requires a careful analysis of the wall-collision term T_w. The interested reader is referred to the article by Dorfman and van Beijeren. Here we will drop the wall operator since for the purposes of this discussion it merely ensures that the distribution function vanishes at the surface of the container). The first term can be written as

$$-\int d\vec{r_1} \int d\vec{v_1}\, \vec{v_1} \cdot \nabla \left[F_1(\ln(F_1) - 1) \right]$$

This can be evaluated easily in terms of the distribution function at the walls of the closed container and therefore it is zero. The second term of Eq. 3.12 is based on the *Stosszahlansatz*, and is

$$\frac{dH(t)}{dt} = \int d\vec{r_1} \int d\vec{v_1} \int d\vec{v_2} \int d\hat{k} B(\vec{g}, \hat{k}) \Psi(v_1)(F_1' F_2' - F_1 F_2) \tag{3.13}$$

with $\Psi(v_1) = \ln(F_1)$. The integrand may be symmetrized in $\vec{v_1}$ and $\vec{v_2}$:

$$\frac{dH(t)}{dt} = \frac{1}{2} \int d\vec{r_1} \int d\vec{v_1} \int d\vec{v_2} \int d\hat{k} B(\vec{g}, \hat{k}) \left[\Psi(v_1) + \Psi(v_2) \right] (F_1' F_2' - F_1 F_2)$$

For each collision there's an inverse one, so we also integrate over the inverse collisions :

$$\begin{aligned} \frac{dH(t)}{dt} &= \frac{1}{2} \int d\vec{r_1} \int d\vec{v_1'} \int d\vec{v_2'} \int d\hat{k} B(\vec{g}', -\hat{k}) \left[\Psi(v_1') + \Psi(v_2') \right] (F_1 F_2 - F_1' F_2') \\ &= -\frac{1}{2} \int d\vec{r_1} \int d\vec{v_1} \int d\vec{v_2} \int d\hat{k} B(\vec{g}, \hat{k}) \left[\Psi(v_1') + \Psi(v_2') \right] (F_1' F_2' - F_1 F_2) \end{aligned}$$

Add these expression and divide by 2 :

$$\frac{dH(t)}{dt} = \frac{1}{4} \int d\vec{r_1} \int d\vec{v_1} \int d\vec{v_2} \int d\hat{k} B(\vec{g}, \hat{k}) \ \left[\Psi_1 + \Psi_2 - \Psi_1' - \Psi_2' \right] (F_1' F_2' - F_1 F_2). \tag{3.14}$$

Or

$$\frac{dH}{dt} = \frac{1}{4}\int d\vec{r_1}\int d\vec{v_1}\int d\vec{v_2}\int d\hat{k} B(\vec{g},\hat{k}) \ln\left(\frac{F_1F_2}{F_1'F_2'}\right)(F_1'F_2' - F_1F_2). \quad (3.15)$$

If $F_1F_2 \neq F_1'F_2'$ then the integrand is negative, namely, if $F_1F_2 < F_1'F_2'$ then the second factor is positive and the first is negative. If $F_1F_2 > F_1'F_2'$ then the second is negative and the first is positive .

Both cases give a decreasing $H(t)$. That is

$$\frac{dH(t)}{dt} \leq 0 \quad (3.16)$$

The integral is zero only if for all $\vec{v}_1$ and $\vec{v}_2$:

$$F_1F_2 = F_1'F_2' \quad (3.17)$$

This is Boltzmann's H-theorem.

We now show that when H is constant in time, the gas is in equilibrium. The existence of an equilibrium state requires the rates of the restituting and direct collisions to be equal, that is, that there is a detailed balance of gain and loss processes taking place in the gas.

Taking the logarithm of Eq. 3.17 shows that $\ln(F_1)+\ln(F_2)$ has to be conserved for an equilibrium solution of the Boltzmann equation . Therefore $\ln F_1$ can generally be expressed as a linear combination, with constant coefficients of the $(d+2)$ quantities conserved by binary collisions, i.e. the number of particles, the d components of the linear momentum, where d is the number of dimensions, and the kinetic energy : $\ln(F_1) = A + \vec{B}\cdot\vec{v}_1 + Cv_1^2$. (Adding an angular momentum-term to $\ln(F_1F_2)$ is not independent of conservation of momentum, because the positions of the particles are the same.) The 'molecules' are assumed to have no internal degrees of freedom.

Then $F_1 \propto e^{\vec{B}\cdot\vec{v}_1 + C\vec{v}_1^2} = Ae^{-\frac{1}{2}\beta m\ (\vec{v}_1-\vec{u})^2}$. When H has reached its minimum value this is the well known Maxwell-Boltzmann distribution for a gas in thermal equilibrium with a uniform motion $\vec{u}$. So, argues Boltzmann, solutions of his equation for an isolated system approach an equilibrium state, just as real gases seem to do.

Up to a negative factor ($-k_B$, in fact) differences in H are the same as differences in the thermodynamic entropy, between initial and final equilibrium states. Boltzmann thought that his H-theorem gave a foundation of the second law of thermodynamics. The increase in entropy is a result of the collision-integral, whose derivation was based on the *Stosszahlansatz* .

This result raises quite a large number of questions, particularly the central one: Can a gas that is exactly described by the reversible laws of mechanics be characterized by a quantity that always decreases? Perhaps a *non-mechanical* assumption was introduced here. If so, this would suggest, although not imply, that Boltzmann's equation might not be a useful description of nature. In fact, though, this equation is so useful and accurate a predictor of the properties of dilute gases, that it is now often used as a test of intermolecular potential models.

Our next step is to see if we can understand the role of the *Stosszahlansatz* in Boltzmann's derivation and to see if we can understand on an intuitive level how to reconcile irreversible behavior with mechanical reversibility of the underlying dynamics. Also we need to understand, if possible, why the Boltzmann equation works so well. Although the answers to these questions will occupy not only this series of lectures, but also much future work, we first turn to a simple model introduced by Mark Kac which sheds some light on these questions.

3.3 Kac's Ring Model.

[References: M. Kac *Probability and Related Topics in Physical Science,* reprinted by the American Mathematical Society, Providence (1976), and G. Wannier, *Statistical Mechanics,* reprinted by Dover Publ. Co, New York (1987).]

The Kac ring model doesn't look much like the system of particles colliding with each other considered by Boltzmann. However like many clever models developed to help understand complex phenomena, this model is of great didactic value, and clarifies many issues. It does have a kind of "collision" and the *Stosszahlansatz* can be studied in detail from a more microscopic point of view. We proceed.

N lattice points are placed uniformly around a circle so that it is subdivided into N segments . Each segment contains one ball that can either be black or white. The motion is discretized into a sequence of time steps. At each time-step all of the balls shift one place clockwise (see Fig. 3.7). On *some* of the lattice sites there is a fixed marker whose job is to change the color of every ball that passes it. We wish to obtain an equation for the number of balls of each color after every time step.

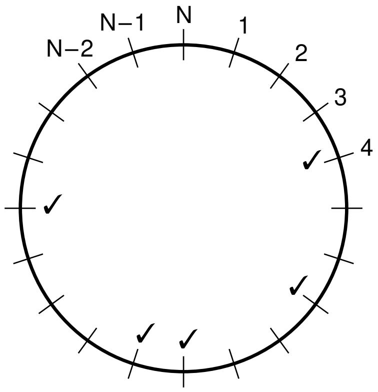

Figure 3.7: The Kac Ring Model.

Define

$B(t) =$ the number of black balls at time t.

$W(t) =$ the number of white balls at time t.

$b(t) =$ the number of black balls that are in front of a marker at time t

$w(t) =$ the number of white balls in front of a marker at time t

So

$$
\begin{aligned}
B(t+1) &= B(t) + w(t) - b(t) \\
W(t+1) &= W(t) + b(t) - w(t)
\end{aligned}
\tag{3.18}
$$

The difference between the number of black and white balls, $\Delta(t)$, satisfies the equation

$$
\Delta(t+1) = B(t+1) - W(t+1) = \Delta(t) - 2(b(t) - w(t)). \tag{3.19}
$$

This equation is exact, so far. However, there is little we can do with it. In order to calculate $\Delta\,(t)$, we can make an assumption similar to the *Stosszahlansatz*: we suppose that the fraction of white or black balls that change color at a given time step is equal to the probability μ that a lattice site has a marker on it, where μ is equal to the number of markers divided by the number of sites, N. That is,

$$\frac{b(t)}{B(t)} = \frac{w(t)}{W(t)} = \mu \tag{3.20}$$

Now we can solve Eq. 3.19 because it becomes :

$$\Delta(t+1) = \Delta(t) - 2(\mu B(t) - \mu W(t)) = (1-2\mu)\Delta(t) \tag{3.21}$$

This can be iterated to get for the first t timesteps

$$\Delta(t) = \Delta(0)(1-2\mu)^t. \tag{3.22}$$

Since $\mu \leq 1$, Eq. 3.22 predicts a strictly monotonic decay for $|\Delta(t)| \to 0$, in the limit that $t \to \infty$. This solution cannot be a very good description of the system for all times, because it is not consistent with many things that we know must be true:

(1) Eq. 3.22 is not time reversible while the elementary dynamics of this model is reversible. A change of sign of t simply changes a monotonically decreasing function into a monotonically increasing one. By looking at some simple examples, one can easily convince oneself that this equation cannot always be correct.

(2) There is always a number of steps, $t = 2N$, when the initial state of the system must be recovered. This is clear because after this number of time steps, each ball will have passed each marker twice, so each ball must be at its initial location with its initial color. (This is a trivial example of the Poincaré Recurrence Theorem, to be discussed later). This feature is not present in Eq. 3.22.

To resolve the contradiction between the reversible microscopic dynamics and the irreversible Eq. 3.22, we need to follow the suggestion of Boltzmann and adopt the point of view that Eq. 3.22 refers to the *average behavior of an ensemble of systems* rather than to the actual behavior of any member of the ensemble. One of the virtues of the Kac ring model is that we can easily see how this suggestion can be implemented.

In this case the ensemble is a large collection of Kac's rings, that initially have the same distribution of black and white balls, but with different distributions of markers. For each i independently, a fraction μ of the i^{th} site of all members of the ensemble has a marker. The following variables are used to describe the 'microscopic' state of a ring : For each site i, we define:

$$\eta_i(t) = 1, \text{if there is a black ball in front of site i at time t}$$

$$\eta_i(t) = -1, \;\; \text{if there is a white ball in front of site i at time t}$$

$$\epsilon_i = 1 \;\;\; \text{if there is no marker at i}$$

$$\epsilon_i = -1 \;\; \text{if there is a marker at i.}$$

Then $\Delta(t) = \sum_i \eta_i(t)$ and $\eta_{i+1}(t+1) = \epsilon_i \eta_i(t)$. Using this $t+1$ times to relate the left hand-side to the initial state of the systems, we obtain

$$\eta_{i+1}(t+1) = \epsilon_i \epsilon_{i-1} \dots \epsilon_{i-t} \eta_{i-t}(0)$$

So $\Delta(t+1) = \sum_i \epsilon_i \epsilon_{i-1} \dots \epsilon_{i-t} \eta_{i-t}(0)$.This is consistent with the recurrence time, since after $2N$ steps each ϵ appears twice and $\Delta(2N) = \Delta(0)$.

The ensemble average is given by
$\langle \Delta(t) \rangle_{ensemble} = \sum_i < \epsilon_{i-1}\epsilon_{i-2} \dots \epsilon_{i-t} > \eta_{i-t}(0)$,
where the average on the right hand-side denotes the average of t successive ϵ's. The indices can also be taken from 1 to t, since the distribution of markers is uniform over a ring. This means that this average can be taken outside the summation : $< \Delta(t) > = < \epsilon_1 \dots \epsilon_t > \Delta(0)$

Two cases need to be distinguished : The number of time-steps is less than N or it is larger than N. In the first case we don't need to worry about the periodicity of the system. The probability that a ball passes j markers in t steps is $\mu^j(1-\mu)^{t-j}$ multiplied by the number of possible ways to distribute them over t places, which is $\frac{t!}{j!(t-j)!}$. In the case of j markers , $\epsilon_1 \dots \epsilon_t = (-1)^j$. So for $0 < t < N$:

$$\langle \epsilon_1 \dots \epsilon_t \rangle = \sum_j^t \frac{t!}{j!(t-j)!}(-1)^j \mu^j (1-\mu)^{t-j} = (1-2\mu)^t$$

This leads to a result identical to Eq. 3.22, on the basis of the *Stosszahlansatz*!

$$< \Delta(t) > = < \epsilon_1 \dots \epsilon_t > \Delta(0) = (1-2\mu)^t \Delta(0) \qquad 0 \leq t \leq N \tag{3.23}$$

Now we need to consider the case where $2N \geq t > N$: Then we can write $t = N + s$, and $\Delta(t) = < \epsilon_1 \dots \epsilon_{N+s} >$ can be written as

$$\begin{aligned} < \epsilon_1 \dots \epsilon_{N+s} > &= < \epsilon_1 \epsilon_2 \dots \epsilon_N \epsilon_1 \epsilon_2 \dots \epsilon_{N+s} > = < \epsilon_{N+s+1} \dots \epsilon_{2N} > \\ &= < \epsilon_{s+1} \dots \epsilon_N > = < \epsilon_1 \dots \epsilon_{N-s} > = < \epsilon_1 \dots \epsilon_{2N-t} >, \end{aligned}$$

because the markers are distributed uniformly. The expression for Δ is the same as for $t < N$, but with t replaced by $2N - t$:

$$< \Delta(t) >_{ens}= (1 - 2\mu)^{2N-t} \Delta(0) \ , \quad N < t \leq 2N \tag{3.24}$$

For $t \to 2N$ the average of this ensemble attains its initial value again . Now we have seen how everything can be resolved in a simple case: Boltzmann's equation, Eq. 3.22, is *not* correct for any particular member of an ensemble of similar systems, but it may, over some range of time, characterize the average behavior of the ensemble. However, this range of times must be short compared to the microscopic recurrence times of the system. Note also that as the number of sites gets larger, the time interval over which the Boltzmann equation - for this model- gets larger, too. However, as the time approaches the recurrence time, the Boltzmann equation is not valid, even for the ensemble average, and it must be replaced by an "anti-Boltzmann"equation. This is an example of anti-thermodynamic behavior; it is strictly not possible to define a quantity that, like H, never increases for *all* times. We also note that the choice of the ensemble, with the random distribution of markers, is an essential feature of the model and this assists, so to speak, the Boltzmann-like evolution of the quantity $< \Delta >$. When we consider more realistic dynamical systems in later chapters, we will look for signs that the microscopic dynamics itself, while mechanically reversible, nevertheless provides a stochastic-like element that is responsible for the approach to equilibrium.

3.4 Tagged Particle Diffusion.

[Reference: S. Chapman and T.G. Cowling, *The Mathematical Theory of Non-Uniform Gases*, 3rd. edition, Cambridge U. Press, Cambridge (1970).]

It is one thing to derive the Boltzmann equation and to discuss the fundamental assumptions in the derivation. It is quite another thing to solve this equation. This is an entire subject in its own right. Here we illustrate the standard Chapman-Enskog method of solution for a simple non-equilibrium process in a fluid, namely, tagged particle diffusion. We imagine that a particle is immersed in a dilute gas that is in equilibrium. The immersed particle is mechanically identical to all of the other particles in the fluid, but it is tagged in some way that does not disturb its mechanical properties. On a computer this is easily accomplished, but in a real system one would have to use small isotopic differences as a tag on the particle. Our object is to determine the distribution function for the tagged particle. To simplify matters still further we will consider a hypothetical two-dimensional system. This only avoids some minor technicalities with three-dimensional vectors, which are not interesting here.

We suppose that the tagged particle collides with gas particles whose distribution function is an equilibrium, Maxwell-Boltzmann function $F_B(\vec{v}) = n\phi_0(\vec{v})$, where the subscript B denotes the bath particles, $\phi_0(\vec{v}) = (\frac{\beta m}{2\pi})^{\frac{1}{2}d} e^{-\frac{1}{2}\beta m v^2}$, n is the number-density of the bath-particles and d is the number of space dimensions. The Boltzmann equation for the tagged particle is

$$\frac{\partial F_T(\vec{r},\vec{v},t)}{\partial t} + \vec{v}\cdot\vec{\nabla}_r F_T(\vec{r},\vec{v},t) = \int d\vec{v_1} \int d\hat{k} B(\vec{g},\hat{k})\,[F'_B F'_T - F_B F_T] \quad (3.25)$$

In Eq. 3.25, $F_B = n\phi_0(\vec{v}_1)$, and $F_T = F_T(\vec{r},\vec{v},t)$.

The probability of finding the tagged particle at point $\vec{r}$ at time t regardless of its velocity is given by $P(\vec{r},t)$ where

$$P(\vec{r},t) = \int d\vec{v}\, F_T(\vec{r},\vec{v},t) \quad (3.26)$$

We expect this probability to satisfy a diffusion equation of the form

$$\frac{\partial P(\vec{r},t)}{\partial t} = D\nabla^2 P(\vec{r},t) \quad (3.27)$$

where D, the diffusion coefficient, is to be determined.

We begin our derivation of this diffusion equation, and the determination of the diffusion coefficient, by integrating the Boltzmann equation, Eq. 3.25 over the velocity of the tagged particle to obtain

$$\begin{aligned} \frac{\partial P(\vec{r},t)}{\partial t} + \int d\vec{v}(\vec{v}\cdot\vec{\nabla}F_T(\vec{r},\vec{v},t)) &= \\ = \int d\vec{v}\int d\vec{v}_1 \int d\hat{k} B(\vec{g},\hat{k})[F'_T F'_B - F_T F_B] \end{aligned}$$

The right hand side of this equation is zero because the the primed and unprimed variables can be interchanged as in the derivation of the H-theorem, since $d\vec{v}_1 d\vec{v} = d\vec{v'_1} d\vec{v'}$, and $B(\vec{g},\hat{k}) = B(\vec{g'},-\hat{k})$. This yields a conservation equation for the probability density for the tagged particle

$$\frac{\partial P(\vec{r},t)}{\partial t} + \vec{\nabla}\cdot\vec{J}_T = 0 \quad (3.28)$$

where the probability current for the tagged particle, $\vec{J}_T$, is

$$\vec{J}_T(\vec{r},t) = \int d\vec{v}\,\vec{v}\,F_T(\vec{r},\vec{v},t). \tag{3.29}$$

The essence of the Chapman-Enskog method for the solution of Eq. 3.25 is to note that if F_T were to have the form of a Maxwell-Boltzmann velocity distribution, then the collision integral on the right hand side of Eq. 3.25 would vanish, and F_T would only change in time due to the free streaming of the tagged paricle in the gas. This suggests the following picture for the change in F_T: The tagged particle is injected in the gas at some initial time. There is a "kinetic" stage where the distribution function for the tagged particle changes rapidly in time due to collisions. The kinetic stage lasts for a few mean free times or so. After this period, the tagged particle is nearly equilibrated to the rest of the gas as far as its velocity distribution is concerned, and from then on, the velocity distribution slowly reaches equilibrium, and the spatial probability distribution for the tagged particle slowly becomes uniform throughout the container, as the tagged particle diffuses. This last stage is a "hydrodynamic"stage, largely governed by diffusion of the particle in the gas.

This picture can be expressed mathematically by supposing that in the hydrodynamic stage F_T may be expanded about its "local"equilibrium form as

$$F_T(\vec{r},\vec{v},t) = P(\vec{r},t)\phi_0(\vec{v})\left[1 + \Phi_1(\vec{r},\vec{v},t) + \Phi_2(\vec{r},\vec{v},t) + \cdots\right] \tag{3.30}$$

where the functions $\Phi_1, \Phi_2, ...$ are to be determined. It is assumed that the Φ_i are proportional to the $i-th$ gradient of $P(\vec{r},t)$ so that Eq. 3.30 may be considered to be a systematic expansion of F_T in powers of the gradients. There is a consistency condition that the Φ_i must satisfy coming from eqs. 3.26 and 3.30, namely that

$$\int d\vec{v}\phi_0\left(\vec{v}\right)\Phi_i\left(\vec{r},\vec{v},t\right) = 0 \tag{3.31}$$

When this expansion is inserted in the conservation-law Eq. 3.28, one obtains

$$\frac{\partial P(\vec{r},t)}{\partial t} = -\vec{\nabla}\cdot\int d\vec{v}\,\vec{v}P(\vec{r},t)\phi_0(\vec{v})\left[1 + \Phi_1 + \Phi_2 + \cdots\right] \tag{3.32}$$

The first term on the right-hand side is odd in $\vec{v}$, so it is zero. The other terms are at least of second order in the gradients. So the expansion is consistent with the conservation-law if $\frac{\partial P}{\partial t}$ and $\nabla^2 P$ are of equal order. To first order the tagged particle probability-current,

$$\vec{J}_T = \int d\vec{v}\vec{v}P(\vec{r},t)\phi_0(\vec{v})\Phi_1(\vec{r}.\vec{v},t) + \cdots, \tag{3.33}$$

is proportional to $\vec{\nabla}P$ because that is the only available vector in the integrand. This proportionality-constant,D,is the diffusion-coefficient that appears in the diffusion equation $\frac{\partial P}{\partial t} = \vec{\nabla} \cdot (D\vec{\nabla}P(\vec{r},t))$. The expansion is now inserted in the Boltzmann equation :

$$\begin{aligned} & (\frac{\partial}{\partial t} + \vec{v} \cdot \vec{\nabla})(P(\vec{r},t)\phi_0(\vec{v})(1 + \Phi_1 + \cdots)) \qquad (3.34) \\ = \; & n \int d\vec{v_1} \int_{\vec{g}\cdot\hat{k}<0} d\hat{k}B(\vec{g},\hat{k}) \left[P(\vec{r},t)\phi_0(\vec{v})\phi_0(\vec{v}_1)(\Phi_1(\vec{v'}) - \Phi_1(\vec{v}))\right] \\ & + \cdots . \end{aligned}$$

Collecting all terms of first order, we obtain

$$\begin{aligned} & \phi_0(v)\vec{v} \cdot \vec{\nabla}P(\vec{r},t) = \qquad (3.35) \\ = \; & nP(\vec{r},t) \int d\vec{v_1} \int_{\vec{g}\cdot\hat{k}<0} d\hat{k}B(\vec{g},\hat{k})[\Phi_1(\vec{v'}) - \Phi_1(\vec{v})]\phi_0(\vec{v_1})\phi_0(\vec{v}) \end{aligned}$$

This is a linear, inhomogeneous equation in Φ_1 of the general form of a linear operator L acting on the function Φ_1, $L\Phi_1 = \alpha(v)$, with an inhomogeneous term, that can be solved :

$$\Phi_1 = L^{-1}\alpha(v) + \Phi_1^0,$$

where Φ_1^0 is a general solution of the homogeneous equation, $L\Phi_1^0 = 0$, provided the inhomogeneous term, $\alpha(v)$, is orthogonal to Φ_1^0. It is clear from Eq. 3.35 that Φ_1^0 must be proportional to $\phi_0\,(\vec{v})$ and that the inhomogeneous term, the left hand side of Eq. 3.35 is in fact orthogonal to it. Moreover, using Eq. 3.31, we can see that Φ_1^0 must be set equal to zero.

We expand $\Phi_1(\vec{v})$ in a complete set of orthogonal polynomials, the Sonine polynomials, and for the purpose of illustration, keep only the first term, $\Phi_1(\vec{v}) = \vec{a} \cdot \vec{v}$, where we must determine the vector $\vec{a}$ .If we insert this in Eq. 3.35, multiply by $\vec{v}$ and integrate over $\vec{v}$ then we find

$$\begin{aligned} & \int d\vec{v}\phi_0(\vec{v})\vec{v}(\vec{v} \cdot \vec{\nabla}P) = \qquad (3.36) \\ = \; & nP \int d\vec{v}_1 \int d\vec{v} \int d\hat{k}B(\vec{g},\hat{k})\phi_0(\vec{v})\phi_0(\vec{v}_1)\vec{v}(\vec{a} \cdot \vec{v'} - \vec{a} \cdot \vec{v}) \end{aligned}$$

By considering only the x-component, we find that the left hand side of Eq. 3.36 becomes :

$$LHS = \int d\vec{v}\phi_0(\vec{v})v_x(\vec{v}\cdot\vec{\nabla}P) = \frac{\partial P}{\partial x}\int d\vec{v}\phi_0(v)v_x^2 = \frac{1}{\beta m}\frac{\partial P}{\partial x},$$

because the integrand is odd in v_y. The particles are assumed to be hard 2-dimensional discs, with diameter σ. Then, $B(\vec{g},\hat{k}) = \sigma|\vec{g}\cdot\hat{k}|$ (see Fig. 3.6), so the right hand side of the x-component of Eq. 3.36 becomes :

$$RHS = nP\sigma\int d\vec{v}\int d\vec{v_1}\int_{\vec{g}\cdot\hat{k}<0} d\psi|\vec{g}||\cos(\psi)|\phi_0(\vec{v})\phi_0(\vec{v_1})v_x(\vec{a}\cdot\hat{k})(\vec{g}\cdot\hat{k}).$$

Here $\vec{v'} - \vec{v} = (\vec{g}\cdot\hat{k})\hat{k}$ is used.

We use a simple decomposition of the vector $\hat{k}$: $\hat{k} = \frac{1}{|\vec{g}|}\left[(\vec{g}\cdot\hat{k})\hat{g} + (\vec{g}_\perp\cdot\hat{k})\hat{g}_\perp\right]$ where the unit vectors $\hat{g}$, $\hat{g}_\perp$ are parallel or perpendicular, respectively, to $\vec{g}$. Then the integral over ψ (see Fig. 3.8) becomes

$$\begin{aligned}
&\int_{\frac{1}{2}\pi}^{\frac{3}{2}\pi} d\psi|\cos(\psi)|\left[(\hat{g}\cdot\hat{k})(\vec{a}\cdot\hat{g}) + (\hat{g}_\perp\cdot\hat{k})(\vec{a}\cdot\hat{g}_\perp)\right](\hat{g}\cdot\hat{k})\\
&= \int_{\frac{1}{2}\pi}^{\frac{3}{2}\pi} d\psi|\cos(\psi)|\left[(\vec{a}\cdot\hat{g})\cos(\psi) + (\vec{a}\cdot\hat{g}_\perp)\sin(\psi)\right]\cos(\psi)\\
&= \frac{4}{3}(\vec{a}\cdot\hat{g})
\end{aligned} \tag{3.37}$$

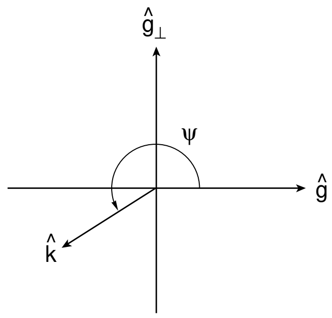

Figure 3.8: The Geometry for the $\vec{k}$ Integration.

Now we have

$$RHS = nP\sigma\frac{4}{3}\int d\vec{v}\int d\vec{v}_1|\vec{g}|v_x(\vec{a}\cdot\vec{g})\phi_0(\vec{v})\phi_0(\vec{v}_1).$$

To do the integral over $\vec{v}$ and $\vec{v_1}$ we convert to center of mass and relative velocities: $\vec{V} = \frac{1}{2}(\vec{v} + \vec{v_1})$ and $\vec{g} = \vec{v_1} - \vec{v}$. Using $d\vec{v_1}d\vec{v} = d\vec{V}d\vec{g}$ and $v_1^2 + v_2^2 = 2V^2 + \frac{1}{2}g^2$, the integral RHS becomes:

$$RHS = \frac{4}{3}nP\sigma\left(\frac{\beta m}{2\pi}\right)^2 \int d\vec{V} \int d\vec{g}e^{-\frac{1}{2}\beta m(2V^2+\frac{1}{2}g^2)}|\vec{g}|(\vec{a}\cdot\vec{g})\left[V_x - \frac{1}{2}g_x\right].$$

The first term is odd in V_x . In the inner-product, the terms that contain g_y terms are also odd :

$$\begin{aligned} RHS &= -\frac{2}{6}nP\sigma\frac{\beta m}{2\pi}\int d\vec{g}e^{-\frac{1}{4}\beta mg^2}|\vec{g}|a_x g_x^2 \\ &= -\frac{a_x nP\sigma\beta m}{6\pi}\int_0^\infty gdgd\phi e^{-\frac{1}{4}\beta mg^2}g(g^2\cos^2(\phi)) \\ &= -\frac{a_x nP\sigma\beta m}{12\pi}\frac{2\pi}{2}\frac{\partial^2}{\partial\beta^2}\frac{16}{m^2}(\frac{4\pi}{\beta m})^{\frac{1}{2}} \\ &= -\frac{2nP\sigma\beta a_x(\pi)^{\frac{1}{2}}}{(m)^{\frac{3}{2}}}(\beta)^{-\frac{5}{2}} \end{aligned}$$

Setting this equal to the left hand side of Eq. 3.36, we obtain for a_x

$$a_x = -\frac{1}{2Pn\sigma}\frac{\partial P}{\partial x}\left(\frac{\beta m}{\pi}\right)^{\frac{1}{2}} \tag{3.38}$$

Then similar arguments can be made for the other component of $\vec{a}$, and we have to first order in the gradient of P

$$F_T = P(\vec{r},t)\phi_0(v)(1 + (\vec{a}\cdot\vec{v})) = P\phi_0 - \phi_0\frac{1}{2n\sigma}(\frac{\beta m}{\pi})^{\frac{1}{2}}(\vec{v}\cdot\frac{\partial P}{\partial\vec{r}}) \tag{3.39}$$

Substituting this in Eq. 3.33, we find that $\vec{J_T}$ is

$$\begin{aligned} J_T(\vec{r},t) &= \int d\vec{v}\vec{v}\left[P(\vec{r},t)\phi_0(v) - \phi_0(v)\frac{1}{2n\sigma}(\frac{\beta m}{\pi})^{\frac{1}{2}}(\vec{v}\cdot\frac{\partial P}{\partial\vec{r}})\right] \\ &= -D\vec{\nabla}P(\vec{r},t) \end{aligned} \tag{3.40}$$

since the first term under the integral is odd in $\vec{v}$. The conservation law now is

$$\frac{\partial P(\vec{r},t)}{\partial t} = -\vec{\nabla}\cdot\vec{J_T}(\vec{r},t) = \vec{\nabla}\cdot(D\vec{\nabla}P(\vec{r},t)) \tag{3.41}$$

where the diffusion coefficient is given by

$$D = \frac{1}{2n\sigma(\pi\beta m)^{\frac{1}{2}}}.$$

This is diffusion equation for an isotropic system:

$$\frac{\partial P(\vec{r},t)}{\partial t} = D\vec{\nabla}^2 P(\vec{r},t) \tag{3.42}$$

It is interesting to conclude this section with a brief discussion of some of the properties of the solution of the diffusion equation. We will need these properties later on. Thus we consider a solution of a diffusion equation with the initial condition:

$$P(\vec{r}, t=0) = \delta(\vec{r} - \vec{r_0}).$$

If we express $P(\vec{r},t)$ as a Fourier transform,

$$P(\vec{r},t) = \int \frac{d\vec{k}}{(2\pi)^d} e^{i\vec{k}\cdot\vec{r}} P_k(t). \tag{3.43}$$

and for the δ-function use

$$P(\vec{r},0) = \delta(\vec{r} - \vec{r_0}) = \int \frac{d\vec{k}}{(2\pi)^d} e^{i\vec{k}\cdot(\vec{r}-\vec{r_0})} = \int \frac{d\vec{k}}{(2\pi)^d} P_k(0) e^{i\vec{k}\cdot\vec{r}},$$

so $P_k(t=0) = e^{-i\vec{k}\cdot\vec{r_0}}$, and we consider the diffusion equation in an arbitrary number of dimensions, d. The diffusion equation for the Fourier transform is

$$\int \frac{d\vec{k}}{(2\pi)^d} \left[\frac{\partial P_k(t)}{\partial t} - Dk^2 P_k(t)\right] e^{i\vec{k}\cdot\vec{r}} = 0 \tag{3.44}$$

This can be solved :

$$P_k(t) = e^{-Dk^2 t} P_k(0) = e^{-Dk^2 t} e^{-i\vec{k}\cdot\vec{r_0}} \tag{3.45}$$

Inserting this in Eq. 3.43, we obtain

$$P(\vec{r},t) = \int \frac{d\vec{k}}{(2\pi)^d} e^{-Dk^2 t + i\vec{k}\cdot(\vec{r}-\vec{r_0})} = (\frac{1}{4\pi Dt})^{\frac{1}{2}d} e^{-\frac{(\vec{r}-\vec{r_0})^2}{4Dt}}.$$

One of the most important quantities is the mean square displacement of the diffusing particle, which is given as

$$< (\vec{r} - \vec{r_0})^2 >_t = \int d\vec{r} P(\vec{r}, t)(\vec{r} - \vec{r_0})^2 = 2tDd \tag{3.46}$$

This linear growth of the mean*square* displacement with time is typical for diffusive motion . It is in contrast to free motion, where $(\vec{r} - \vec{r_0})^2 \propto t^2$. Finally, we note the Einstein relation between the mean square displacement and the diffusion coefficient given by

$$D = \frac{< (\vec{r} - \vec{r_0})^2 >}{2td}. \tag{3.47}$$

This completes our discussion of the Boltzmann equation and various issues related to it. Now we can begin to consider the theory of irreversible processes in fluids from a more fundamental point of view in order to bring out the features of chaotic dynamics which are central to these lectures. The background just presented is essential for an understanding of the point of our further discussions.