Is the Boltzmann equation reversible? A large deviation perspective on the irreversibility paradox

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Abstract We consider the kinetic theory of dilute gases in the Boltzmann–Grad limit. We propose a new perspective based on a large deviation estimate for the probability of the empirical distribution dynamics. Assuming Boltzmann molecular chaos hypothesis (Stosszahlansatz), we derive a large deviation rate function, or action, that describes the stochastic process for the empirical distribution. The quasipotential for this action is the negative of the entropy, as should be expected. While the Boltzmann equation appears as the most probable evolution, corresponding to a law of large numbers, the action describes a genuine reversible stochastic process for the empirical distribution, in agreement with the microscopic reversibility. As a consequence, this large deviation perspective gives the expected meaning to the Boltzmann equation and explains its irreversibility as the natural consequence of limiting the physical description to the most probable evolution. More interestingly, it also quantifies the probability of any dynamical evolution departing from solutions of the Boltzmann equation. This picture is fully compatible with the heuristic classical view of irreversibility, but makes it much more precise in various ways. We also explain that this large deviation action provides a natural gradient structure for the Boltzmann equation.

Keywords Boltzmann equation · Kinetic theory · Large deviation theory · Macroscopic fluctuation theory · Dilute gases · Gradient flows

1 Introduction

The Boltzmann equation [7] (see [8,9] for an english translation) is a cornerstone of statistical physics. It describes dilute gas dynamics at a macroscopic level, and has been the starting point for the kinetic theory of many other physical phenomena:

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the derivation of hydrodynamic equations [11,36], the kinetic theory of self gravitating systems [2], the relativistic Boltzmann equation, lattice Boltzmann algorithms for fluid mechanics [20], nuclear physics, and so on. While the underlying microscopic Hamiltonian dynamics is time reversible, Boltzmann's equation increases the entropy, as proven by Boltzmann's H-theorem. This irreversibility paradox has played a crucial role in the early development of statistical physics and led to long controversies, for instance between Boltzmann and Zermelo, that involved many of the leading physicists and mathematicians of the late nineteen century (see [8,9] for a collection of basic papers from the second half of the nineteenth century on the subject). This apparent paradox and the fact that the irreversible evolution of macroscopic laws is a natural consequence of the reversible microscopic dynamics was already well understood by Thomson [38], Maxwell and Boltzmann [6]. "Boltzmann's thoughts on this question have withstood the test of time", as stated by Lebowitz in a very nice discussion [28] (see also [29,24] for a pedagogical discussion of the irreversibility paradox and the meaning of entropy in relation with the Boltzmann equation). Boltzmann's explanation of the irreversibility paradox can be read in classical physics books [17] or more specialized mathematical physics books [10,37].

In a nutshell, Boltzmann's explanation is that the Boltzmann equation describes at a macroscopic level not all but most of the microscopic evolutions. If we consider a set of microscopic initial conditions compatible with a macroscopic distribution $f_0(\mathbf{r},\mathbf{v})$, then most of these initial conditions will have a dynamics compatible with the solution of the Boltzmann equation $f(\mathbf{r},\mathbf{v},t)$ with initial conditions $f(\mathbf{r},\mathbf{v},t) = f_0(\mathbf{r},\mathbf{v})$. More precisely, if we denote ε the inverse of the number of particles which are contained in a volume equal to the cube of the mean free path l ($\varepsilon = 1/\rho l^3$where ρ is the gas density), then the number of microscopic initial conditions which are compatible with $f_0(\mathbf{r},\mathbf{v})$ and that will actually follow the solution of the Boltzmann equation increases exponentially with $1/\varepsilon$. The evolution of the actual microscopic dilute gas should thus be observed with a dynamics that follows the solution of the Boltzmann equation with an overwhelming probability. Three ingredients are key in this explanation [28]: a) the great disparity between microscopic and macroscopic scales, measured by the smallness of the parameter ε, b) the fact that events are, as put by Boltzmann, determined not only by differential equations but also by initial conditions, and c) the use of probabilistic reasoning: it is not every microscopic state of a macroscopic system that will evolve in accordance with the second law, but only the 'majority" of states a majority which however becomes so overwhelming when the number of atoms in the system becomes very large that irreversible behavior becomes a near certainty.

While this heuristic understanding of the irreversibility paradox makes consensus, the actual proof of a theorem or even a precise theoretical characterization and quantification of this statement, are still lacking. This issue led to a very difficult mathematical challenge: proving the validity of the Boltzmann equation from the microscopic Hamiltonian dynamics. A first step has been achieved by Lanford's proof in the 70' [27], valid for times shorter than the mean collision time. While several impressive improvements have been achieved recently, for instance proofs for other potentials than hard sphere interactions [21,34], the time interval for which those theorem have

been proven remains quite small.

In this article, we will convey the idea that, although fascinating and very interesting, Lanford's proof and successive mathematical developments should be complemented by a conceptually different approach. We propose a perspective based on a large deviation theory for the estimate for the probability of the empirical distribution dynamics. Making assumptions akin to Boltzmann ones (mainly Boltzmann molecular chaos hypothesis), we derive a large deviation rate function, or action, that describes asymptotically for small ε (or equivalently the Boltzmann–Grad limit), the stochastic process for the empirical distribution. We consider the dynamics of the empirical distribution $f_\varepsilon(\mathbf{r},\mathbf{v},t) \equiv \varepsilon \sum_{n=1}^{N} \delta(\mathbf{v}-\mathbf{v}_n(t))\,\delta(\mathbf{r}-\mathbf{r}_n(t))$. Our main result is that the probability that $\{f_\varepsilon(t)\}_{0\le t\le T}$ remains in a neighborhood of a prescribed path $\{f(t)\}_{0\le t\le T}$ verifies

$$\mathbb{P}\left[\{f_\varepsilon(t)\}_{0\le t<T} = \{f(t)\}_{0\le t<T}\right] \underset{\varepsilon\downarrow 0}{\asymp} \exp\left(-\frac{\int_0^T \mathrm{d}t\, L\left[f,\dot{f}\right]}{\varepsilon}\right), \tag{1}$$

where $\underset{\varepsilon\downarrow 0}{\asymp}$ mean a log-equivalence when ε goes to zero, and where the large deviation Lagrangian L can be computed through a Legendre–Fenchel transform from the Hamiltonian H given by $H[f,p] = H_R[f,p] + H_C[f,p]$ with

$$H_R[f,p] = \frac{1}{2}\int \mathrm{d}\mathbf{v}_1\mathrm{d}\mathbf{v}_2\mathrm{d}\mathbf{v}_1'\mathrm{d}\mathbf{v}_2'\mathrm{d}\mathbf{r}\, w(\mathbf{v}_1',\mathbf{v}_2';\mathbf{v}_1,\mathbf{v}_2) \times f(\mathbf{r},\mathbf{v_1})f(\mathbf{r},\mathbf{v}_2)\left\{\mathrm{e}^{\left[-p(\mathbf{r},\mathbf{v}_1)-p(\mathbf{r},\mathbf{v}_2)+p\left(\mathbf{r},\mathbf{v}_1'\right)+p\left(\mathbf{r},\mathbf{v}_2'\right)\right]}-1\right\} \tag{2}$$

and

$$H_C[f,p] = -\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{v}\, p(\mathbf{r},\mathbf{v})\mathbf{v}.\frac{\partial f}{\partial \mathbf{r}}(\mathbf{r},\mathbf{v}). \tag{3}$$

Please note that the large deviation Hamiltonian H is a probabilistic concept and is not the Hamiltonian of the microscopic dynamics, in the analytical mechanics theory. We note that the result (1) is much in the spirit of large deviation results for the macroscopic description of paths for Markov processes [13] or of macroscopic fluctuation theory [1], in other contexts.

We prove that this action $\int_0^T \mathrm{d}t\, L\left[f,\dot{f}\right]$ is such that the Boltzmann equation appears as the most probable evolution. As a consequence, this gives the expected meaning to the Boltzmann equation as being the most probable evolution and a law of large numbers in the limit $\varepsilon \to 0$. However, beyond this law of large numbers, the probability of any macroscopic paths $\{f(t)\}_{0\le t\le T}$ departing from the solutions of the Boltzmann equation is fully quantified by (1). The concentration of the path measure is clearly quantified by ε. We prove that the entropy $S[f] = -\int \mathrm{d}\mathbf{v}\mathrm{d}\mathbf{r}\, f\log(f)$ is the negative of the quasi-potential of the stochastic process for the empirical density, for any f with the proper mass, energy and momentum, as should be expected.

In order to discuss the irreversibility/reversibility paradox it is useful to use two distinct and related notions of time reversibility. Time reversibility for a dynamical system, applied to the mechanical system of particles, states that under change of the

sign of time and velocity reversal, one obtains again a solution of the dynamical system equations. Time reversibility for a stochastic process, states that backward and forward histories of the stochastic process, also up to velocity reversal, have the same probabilities. The definition of the time reversibility of a stochastic process and its relation with detailed balanced are precisely discussed in section 3.3 point 9 (without velocity inversion) and point 10 (with velocity inversion). The key point we want to stress is that the time reversibility of the microscopic dynamics and the consideration of the microcanonical measure at a fixed energy, necessarily imply the time reversibility of the stochastic process of the empirical density. As explained in section 3.3 point 9 (without velocity inversion) and point 10, the time reversibility of the stochastic process for the empirical density has to translate into a time-reversal symmetry for the action. In section 4.2, we check this property as a time-reversal symmetry property of both the Lagrangian L and the Hamiltonian H. The main conclusion is that the action $\int_0^T L \, \mathrm{d}t$ is time reversible, and quantifies at a large deviation level the probabilities of the macroscopic evolution. Macroscopic dynamics is itself a time reversible stochastic process as one should expect. Moreover, this gives its full dynamical meaning to the entropy, in relation with recent fluctuation theorems. Those results are thus fully compatible with the classical picture of the irreversibility paradox but extend it and clarify it in several ways. Moreover from the action (1), the probability for the evolution of any macroscopic variable can be computed.

One clarification is worth stressing. For instance, we obtain the large deviation result (1) as a consequence of the molecular chaos hypothesis (Stosszahlansatz), and the action is actually time reversible. As a consequence we conclude that the irreversibility is not a consequence of the molecular chaos hypothesis (Stosszahlansatz); but it is rather a consequence of describing only the most probable evolution of the empirical density, or equivalently the evolution of the averaged evolution of the empirical density (law of large numbers).

This paper is not a mathematical one. We will actually not be able to derive the action that describes the large deviations of the empirical distribution dynamics from the microscopic Hamiltonian dynamics. We will achieve a much less ambitious goal. Starting from the classical Boltzmann's molecular chaos hypothesis (Stosszahlansatz), not approximating the evolution of the empirical density by the evolution of its average (law of large numbers) but looking at the stochastic process of all possible effects of molecule collisions, we will derive the action that describes the large deviations of the empirical distribution dynamics. With the same spirit and hypothesis as Boltzmann's one, we will extend his results from the law of large number level (the Boltzmann equation), to the large deviations level. Although the writing of the paper is at the level of rigor found in any theoretical physics textbook, the fact that the large deviation action is a consequence of Boltzmann's molecular chaos hypothesis should be considered as clear and rigorous. This argument is worth as much as Boltzmann's molecular chaos hypothesis is believed to be natural. However it is also clear that this is not a derivation from Newton's law, and such a derivation would require to prove the validity of Boltzmann's molecular chaos hypothesis, or an actual proof along other routes.

Proving either the Boltzmann equation and/or the validity of this natural large deviation action remains an open challenge for the future. We note however that Rezakhanlou has proven [35] a large deviation result for 1D stochastic dynamics mimicking the hard sphere dynamics. Rezakhanlou action is actually the same as the one we deduce from Boltzmann's molecular chaos hypothesis. This rigorous result, and the fact that Boltzmann's molecular chaos is an extremely natural hypothesis are clear hints that the formula (1-3) actually describes the large deviations of any generic dilute gas dynamics. Moreover, after the first writing of this article, for hard spheres and in the Boltzmann-Grad limit, Bodineau, Gallagher, Saint-Raymond and Simonella [4] have derived large deviation asymptotics that give an information equivalent to the large deviation formula (1-3), and valid for times of order of one collision time. Those impressive results extend for large deviations, Lanford's type theorems for the law of large number.

We also prove in this paper that this large deviation action provides a natural gradient structure for the Boltzmann equation. The Boltzmann collision operator is the gradient of the entropy in a generalized sense, where the measure of the distance to define the gradient is related to the large deviation action. The transport term of the Boltzmann equation is transverse to the gradient. This gradient structure has a very natural physical interpretation and might have very interesting mathematical consequences.

The original contributions of this work are: a) the derivation of the Boltzmann large deviation action from the molecular chaos hypothesis, giving an easy derivation of the large deviation Hamiltonian, and suggesting that this action should be valid way beyond the toy models considered by Rezakhanlou, b) the verification of the time-reversibility of the action and that the entropy is the quasipotential, c) the explanation of the interest of path large deviation to discuss the irreversibility paradox, d) stressing that a proper probabilistic interpretation of the molecular chaos hypothesis does not break time-reversal symmetry, e) the gradient structure of the Boltzmann equation, f) a unified view of known definitions and results about path large deviation theory: its relation with the structure of kinetic theories, entropy increase and decrease along relaxation and fluctuation paths, time-reversal symmetry of the action, relation with gradient structures, derivation of the action from the infinitesimal generator; which are essential to connect kinetic theories, large deviation theory, irreversibility and gradient flow structures.

Section 2 introduces the notations and is an introduction to the Boltzmann equation. Section 3 is an introduction to the theory of path large deviations and the related concepts: the quasipotential, the time reversibility of path actions, the Hamilton-Jacobi equation, the monotonicity of quasipotential evolutions, and so on. Section 4 derives the large deviation action for dilute gazes and studies its main properties. Section 5 discusses the gradient structure of the Boltzmann equation.

2 Introduction to the Boltzmann equation

This section introduces the notions of a dilute gas, collision rates, diffusion cross section, the Boltzmann-Grad limit, which are key one's in order to derive the Boltzmann equation. We give a heuristic derivation of the Boltzmann equation in the spirit of Boltzmann's discussion. Finally we present some of the key properties of the Boltzmann equation.

2.1 Dilute gases

2.1.1 Orders of magnitudes and dimensionless numbers

We consider the dynamics of a gas composed of atoms or molecules, in the simplest possible framework. We neglect any internal degrees of freedom. We assume that the dynamics is confined into a box of volume V. We assume that the N particles evolve through a Hamiltonian dynamics with short range two body interactions, for instance hard sphere collisions.

Several length scales are important to describe the gas: a typical atom size a, that we will defined more precisely below in relation with the diffusion cross section, a typical interparticle distance $1/\rho^{1/3}$ where ρ is the average gas density, the mean free path l which is the average length a particle travels between two collisions, and a typical box size $V^{1/3}$. The gas is said dilute if we have the following relation between those scales

$$a \ll \frac{1}{\rho^{1/3}} \ll l.$$

We also assume that the box size is either of the order of the mean free path $V^{1/3} \simeq l$ or much larger than the mean free path $l \ll V^{1/3}$.

We note that those four length scales are not independent from each other. If we consider particles in a box in the dilute gas limit, we have four dimensional independent parameters: the volume V, the particle number N or equivalently the average density $\rho = N/V$, the energy E or equivalently the inverse temperature $\beta = 1/k_B T$ where k_B is Boltzmann's constant ($E = 3N/2\beta$), and the typical value of the cross section a^2. A typical velocity is $v_T = \sqrt{1/m\beta}$, where m is the particle mass. The mean free path l can be determined from these quantities. Its order of magnitude is obtained by considering that the volume spanned be a particle between two collisions, $a^2 l$, should be equal to the typical volume occupied by each particle $1/\rho$. The mean free path is thus $l = c/a^2\rho$, where c is a non-dimensional number that depends on the collision kernel, for instance $c = \sqrt{2}/8$ for hard sphere collisions. In the following, for simplicity we call $l = 1/a^2\rho$ the mean free path. We will also use a typical collision time defined as $\tau_c = l/v_T = l\sqrt{m\beta} = \sqrt{m\beta}/a^2\rho$. The typical values, for instance for hydrogen at the room temperature and pressure are: $a \simeq 1.4\,10^{-10}$m, $\rho \simeq 2.\,10^{25}\,\mathrm{m}^{-3}$ ($1/\rho^{1/3} = 3.7\,10^{-9}$), leading to $l = 2.5\,10^{-6}$m and volume $V = 1\,\mathrm{m}^3$. The typical particle velocity is $v_T = 1.6\,10^3\,\mathrm{m.s}^{-1}$, which gives a collision time of order of $\tau_c = 6.7\,10^{-11}$s.

We have four independent dimensional numbers with two sets of units. There are thus two independent non dimensional numbers. We choose N as the first one. For the second one, we choose $\varepsilon = 1/l^3\rho = a^2/l^2 = a^6\rho^2$ which is the order of magnitude of the inverse of the particle number in a volume of size l^3. The limit $\varepsilon \to 0$ corresponds to the condition $a \ll \frac{1}{\rho^{1/3}} \ll l$. We note that the $N\varepsilon = V/l^3 = \alpha^{-3}$, where α is called the Knudsen number. We consider α fixed. Hence the constraint $V/l^3 \simeq 1$ (resp. $V/l^3 \gg 1$) is equivalent to $N\varepsilon \simeq 1$ or (resp. $N\varepsilon \gg 1$). We call a limit as $\varepsilon \to 0$ and $N \to \infty$ with either $N\varepsilon = \alpha^{-3}$ fixed or $N\varepsilon \gg 1$ a Boltzmann–Grad limit.

We note that in dimension d, the mean free path would be given by $a^{d-1}l\rho = 1$, and that the inverse of the number of particle in a volume of linear size the mean free path would be $\varepsilon = \left(\rho l^d\right)^{-1} = (a/l)^{d-1} = a^{d(d-1)}\rho^{d-1}$. The Boltzmann-Grad limit would still be defined as $\varepsilon \to 0$ with $\varepsilon N = \alpha^{-d}$ where α is a fixed constant, or $\varepsilon N \gg 1$, in dimension d. We also note that it is customary, in many mathematical papers and books, to define the Boltzmann-Grad denoting $a = \varepsilon' a_0$. In that case we would have $N\varepsilon = N\varepsilon'^{d-1}a_0^{d-1}/l^{d-1}$ and thus the Boltzmann-Grad limit is the limit $\varepsilon' \to 0$, with $N\varepsilon'^{d-1} = \alpha$ or $N\varepsilon'^{d-1} \gg 1$. For simplicity, we do not follow those classical mathematics notations, because as will be clear in the sequel, the large deviation rate will be of order $1/\varepsilon$ and the Gaussian fluctuations will be of order $\varepsilon^{1/2}$, whatever the dimension.

2.1.2 Collision rate

We consider a thread of particles with velocities $\mathbf{v}_1$ that meets a thread of particles with velocities $\mathbf{v}_2$. We assume that particles of each velocity type are distributed according to a homogeneous point Poisson process with densities $\rho(\mathbf{v}_1)$ and $\rho(\mathbf{v}_2)$ respectively. These particle distributions will give rise to collisions where $(\mathbf{v}_1, \mathbf{v}_2)$ particle pairs undergo a random change towards pairs of the type $(\mathbf{v}_1', \mathbf{v}_2')$, up to $(\mathrm{d}\mathbf{v}_1', \mathrm{d}\mathbf{v}_2')$. This occurs at a rate per unit of time and unit of volume (in units $\mathrm{m}^{-3}\mathrm{s}^{-1}$) which is proportional to the $\mathbf{v}_1$ incident particle density $\rho(\mathbf{v}_1)$, the $\mathbf{v}_2$ incident particle density $\rho(\mathbf{v}_2)$, $\mathrm{d}\mathbf{v}_1'$, and $\mathrm{d}\mathbf{v}_2'$. The proportionality coefficient is called the collision kernel and is denoted

$$w_0\left(\mathbf{v}_1', \mathbf{v}_2'; \mathbf{v}_1, \mathbf{v}_2\right)/2. \tag{4}$$

As $w_0\left(\mathbf{v}_1', \mathbf{v}_2'; \mathbf{v}_1, \mathbf{v}_2\right)\mathrm{d}\mathbf{v}_2'\mathrm{d}\mathbf{v}_1'\rho(\mathbf{v}_1)\rho(\mathbf{v}_2)$ is in units $\mathrm{m}^{-3}\mathrm{s}^{-1}$, w_0 is in units $\mathrm{m}^{-3}\mathrm{s}^5$.

The symmetry between particles 1 and 2 impose that

$$w_0(\mathbf{v}_1', \mathbf{v}_2'; \mathbf{v}_1, \mathbf{v}_2) = w_0(\mathbf{v}_1', \mathbf{v}_2'; \mathbf{v}_2, \mathbf{v}_1) = w_0(\mathbf{v}_2', \mathbf{v}_1'; \mathbf{v}_1, \mathbf{v}_2).$$

The time reversal symmetry of the microscopic Hamiltonian dynamics imposes that

$$w_0(\mathbf{v}_1', \mathbf{v}_2'; \mathbf{v}_1, \mathbf{v}_2) = w_0(-\mathbf{v}_1, -\mathbf{v}_2; -\mathbf{v}_1', -\mathbf{v}_2').$$

The space rotation symmetry imposes that for any rotation $\mathbf{R}$ that belongs to the orthogonal group $SO(3)$

$$w_0(\mathbf{v}_1', \mathbf{v}_2'; \mathbf{v}_1, \mathbf{v}_2) = w_0(\mathbf{R}\mathbf{v}_1, \mathbf{R}\mathbf{v}_2; \mathbf{R}\mathbf{v}_1', \mathbf{R}\mathbf{v}_2').$$

The combination of the time reversal symmetry and of the space rotation symmetry for $\mathbf{R} = -\mathbf{I}$, where $\mathbf{I}$ is the identity operator, implies the inversion symmetry

$$w_0(\mathbf{v}_1', \mathbf{v}_2'; \mathbf{v}_1, \mathbf{v}_2) = w_0(\mathbf{v}_1, \mathbf{v}_2; \mathbf{v}_1', \mathbf{v}_2'). \tag{5}$$

The local conservation of momentum and energy implies that

$$w_0(\mathbf{v}_1', \mathbf{v}_2'; \mathbf{v}_1, \mathbf{v}_2) = \sigma(\mathbf{v}_1', \mathbf{v}_2'; \mathbf{v}_1, \mathbf{v}_2) \delta\left(\mathbf{v}_1 + \mathbf{v}_2 - \mathbf{v}_1' - \mathbf{v}_2'\right) \delta\left(\mathbf{v}_1^2 + \mathbf{v}_2^2 - \mathbf{v}_1'^2 - \mathbf{v}_2'^2\right), \tag{6}$$

where σ is the diffusion cross section. σ is of the order of a^2 where a is a typical atom size. Integrating this expression over $\mathbf{v}_1'$ and $\mathbf{v}_2'$, using that σ is of the order of a^2, we see that the average number of collisions that a single particle pair with velocity $(\mathbf{v}_1, \mathbf{v}_2)$ undergoes per unit of time is of order $a^2 \|\mathbf{v}_1 - \mathbf{v}_2\| / V$.

2.2 Distribution functions

We consider N particles. Each particle $1 \leq n \leq N$ has a position $\mathbf{r}_n(t)$ and a velocity $\mathbf{v}_n(t)$, with initial conditions $\mathbf{r}_n(0)$ and $\mathbf{v}_n(0)$. We define the empirical distribution as

$$f_e(\mathbf{r}, \mathbf{v}, t) \equiv \sum_{n=1}^{N} \delta\left(\mathbf{v} - \mathbf{v}_n(t)\right) \delta\left(\mathbf{r} - \mathbf{r}_n(t)\right). \tag{7}$$

The normalization is such that $\int \mathrm{d}\mathbf{v}\mathrm{d}\mathbf{r}\, f_e(\mathbf{v}) = N$. The number of particles with position $\mathbf{r}_1$ up to $\mathrm{d}\mathbf{r}_1$ and velocity $\mathbf{v}_1$ up to $\mathrm{d}\mathbf{v}_1$ is $f_e\left(\mathbf{r}_1, \mathbf{v}_1\right) \mathrm{d}\mathbf{v}_1 \mathrm{d}\mathbf{r}_1$.

We assume that the particles evolve according to their own velocity and their mutual collision only. The evolution of the empirical density is given by

$$\frac{\partial f_e}{\partial t} + \mathbf{v}.\frac{\partial f_e}{\partial \mathbf{r}} = \mathscr{C}$$

where $\mathscr{C}$ accounts for the collision effects.

We consider an ensemble of initial conditions $(\mathbf{r}_n(0), \mathbf{v}_n(0))_{1 \leq n \leq N}$, distributed according to a measure
$f_N\left(\mathbf{r}_1, \mathbf{v}_1, ..., \mathbf{r}_N, \mathbf{v}_N, t = 0\right) \prod_n \mathrm{d}\mathbf{r}_n \mathrm{d}\mathbf{v}_n$. We assume that with respect to this measure, the probability to have the empirical distribution equal to a distribution $f(\mathbf{r}, \mathbf{v})$ concentrates close $f_0(\mathbf{r}_0, \mathbf{v}_0)$. We do not give a precise definition of this concentration property here, however one can think of a large deviation principle similar to the one that will be used latter on in section 4. We denote this concentration property $f_e \succ f_0$. $f_0(\mathbf{r}, \mathbf{v})$ can be alternatively understood as the average of f_e when averaging over the initial conditions described by the density f_N: $f_0 = \mathbb{E}_i(f_e)$.

It is natural to expect this concentration property to hold for later times $t > 0$, if t is not too large, in the Boltzmann-Grad limit. We then expect $f_e(t) \succ f(t)$, or alternatively $f(t) = \mathbb{E}_i(f_e(t))$. The aim of Boltzmann equation is to describe the temporal evolution of f in the Boltzmann-Grad limit.

2.3 Boltzmann's equation

2.3.1 Main assumptions and heuristic derivation

We recall that we consider an ensemble of initial conditions such that the empirical distribution concentrates for time $t = 0$: $f_e(t = 0) \succ f_0$. We are looking for the equation of the distribution function f such that $f_e(t) \succ f(t)$.

In order to derive Boltzmann's equation, we will make the following four assumptions, which are a reformulation of Boltzmann's initial hypotheses.

i) The collision duration can be neglected compared to the average collision time. The geometry of the collisions is also neglected (point particle assumption).

ii) The probability of three particle encounters is extremely low and will be neglected.

iii) ***Molecular chaos hypothesis:*** In classical physics textbooks in kinetic theory, the Boltzmann equation is often obtained formally through the BBGKY hierarchy. Then the molecular chaos hypothesis is usually stated as the property that the two point correlation function f_2 can be approximated by the product of two one point correlations functions f. This amounts to a property about the statistical independence of the colliding particles. This assumption allows one to close the BBGKY hierarchy and to obtain the Boltzmann equation. Mathematical proofs of the validity of the Boltzmann equation seeks to justify this assumption. For the sake of the following discussion, we will not go through the BBGKY hierarchy; we then define the molecular chaos hypothesis directly as a property of the statistics of the particle collisions. We will use the following assumption, that we still call ***the molecular chaos hypothesis***: at any time, for an overwhelming number of initial conditions, the effect of the collisions of type $(\mathbf{v}_1, \mathbf{v}_2) \to (\mathbf{v}'_1, \mathbf{v}'_2)$ on the distribution f_e can be quantified as if, locally in position space, the particles with velocity $\mathbf{v}_1$ up to $\mathrm{d}\mathbf{v}_1$ and $\mathbf{v}_2$ up to $\mathrm{d}\mathbf{v}_2$ would be statistically mutually independent and each distributed according to a local Poisson point process in position space with density $\rho(\mathbf{v}_1) = f(\mathbf{r}, \mathbf{v}_1, t)\mathrm{d}\mathbf{v}_1$ and $\rho(\mathbf{v}_2) = f(\mathbf{r}, \mathbf{v}_2, t)\mathrm{d}\mathbf{v}_2$ respectively. Then the definition of the collision kernel is relevant and the collision rate w is the only relevant physical quantity. This hypothesis iii) is the counterpart of the molecular chaos hypothesis (stosszahlansatz) used by Boltzmann. It is a very natural hypothesis that the local Poisson statistics should be created dynamically by streaming through particle velocity. This should also be the case for a collisionless ideal gas, as first suggested by Bogolyubov [5]. A dynamical foundation for collision less ideal gases has been given by Eyink and Spohn [15].

iv) **Law of large numbers:** In this section, following Boltzmann, we compute only the average number of collisions and we do not consider the possible fluctuations of the collision number around this average number.

With these hypothesis, we can write the effect of collisions. The distribution function $f(\mathbf{r}, \mathbf{v}, t)$ changes both because particles of velocity $\mathbf{v}$ are created or disappear through collisions. Using also the inversion symmetry (5), we readily obtain the Boltzmann equation

$$\frac{\partial f}{\partial t} + \mathbf{v}.\frac{\partial f}{\partial \mathbf{r}} = \int \mathrm{d}\mathbf{v}_2 \mathrm{d}\mathbf{v}'_1 \mathrm{d}\mathbf{v}'_2 \, w_0(\mathbf{v}'_1, \mathbf{v}'_2; \mathbf{v}, \mathbf{v}_2) \left[f\left(\mathbf{v}'_1, \mathbf{r}\right) f\left(\mathbf{v}'_2, \mathbf{r}\right) - f\left(\mathbf{v}, \mathbf{r}\right) f\left(\mathbf{v}_2, \mathbf{r}\right) \right].$$

The key hypothesis in this heuristic derivation of Boltzmann's equation are the molecular chaos hypothesis iii) and law of large numbers iv). While Boltzmann's molecular chaos hypothesis is usually the subject of much attention, hypothesis iv), is usually not commented upon. **Following assumption iv), only the average effect of collisions is taken into account in the evolution of the empirical distribution function. This is a natural hypothesis as in the Boltzmann-Grad limit the number of collisions that occur on a mesoscopic volume with a mean free path size is extremely large. Hypothesis iv) can thus be interpreted as a law of large numbers. While natural, this law of large numbers assumption necessarily implies that Boltzmann's equation can describe at best only the average or typical evolution of the empirical distribution.**

As discussed in section 4, hypothesis iv) can be relaxed, in order to analyze the stochastic process of the evolution of the distribution f that results from the hypothesis i), ii) and iii) only.

2.3.2 Main properties of the Boltzmann equation

We list the main properties of the Boltzmann equation

i) The total mass $\int \mathrm{d}\mathbf{v}\mathrm{d}\mathbf{r}\, f$ is conserved. As a consequence of the local conservation laws encoded in Eq. (6), the total momentum $\mathbf{P} = \int \mathrm{d}\mathbf{v}\mathrm{d}\mathbf{r}\,\mathbf{v} f$ and the total kinetic energy $E = \int \mathrm{d}\mathbf{v}\mathrm{d}\mathbf{r}\, f\mathbf{v}^2/2$ are locally conserved.

ii) The entropy

$$S[f] = -\int \mathrm{d}\mathbf{v}\mathrm{d}\mathbf{r}\, f\log(f)$$

increases: $\frac{\mathrm{d}S}{\mathrm{d}t} \geq 0$.

iv) Maxwell-Boltzmann distributions $f_{MB}(\mathbf{r},\mathbf{v}) = A\exp\left[-\beta\frac{(\mathbf{v}-\mathbf{U})^2}{2}\right]$ are stationary solutions of the Boltzmann equation.

iii) With some more assumptions on the collision kernel, one can prove that the entropy is strictly increasing except for Maxwell-Boltzmann distributions. In those cases, the Boltzmann equation then converges towards the Maxwell-Boltzmann distribution for which the mass, energy, and momentum are equal to the initial ones.

For completeness, we should discuss boundary conditions. In the following we will discuss the cases either of an infinite box, finite box with elastic collisions of the particles at the box wall, or particles on a three dimensional torus (periodic boundary conditions). Then, while the mass and the energy will be globally conserved, the momentum may or may not be globally conserved, depending on the boundary conditions. We do not discuss further the boundary conditions in the following.

3 Large deviations produced by a large number of small amplitude independent moves

When the evolution of a stochastic process is the consequence of the effect of a large number of small amplitude statistically independent moves, in the limit of a large

number of moves, a law of large numbers naturally follows. It is often very important to understand the large deviations with respect to this law of large number. For continuous time Markov processes, for instance diffusions with small noises, or more generally locally infinitely divisible processes, a general framework can be developed in order to estimate the probability of large deviations. In this section, we present this framework briefly, mainly the hypothesis on the generator that leads to large deviations and the formula for the large deviation action that quantifies the probability of those large deviations. We then define and recall the main properties of action minima, relaxation and fluctuation paths, quasipotentials, relation between action symmetry and detailed balance, and conservation laws, which are crucial for the analysis of large deviation properties. While the simple and synthetic presentation of this section, containing the key ideas without the mathematical discussion is original, most of the material in this section is classical. Our main reference is Freidlin–Wentzell textbook [19]. The point of view we proposed based on the Hamiltonian (8) has been much developed by [16]. Many aspects, like the relation between the action symmetry and detailed balance, are not treated in [19] or [16]. Those aspects are most probably classical too, some but not all of them are discussed in [1], section II.C. The following discussion is kept at a formal level, avoiding any mathematical technicalities that may hide the most important ideas.

3.1 Large deviation rate functions from the infinitesimal generator of a continuous time Markov process

We consider $\{X_\varepsilon(t)\}_{0\le t\le T}$, a family of continuous time Markov processes parametrized by a real number ε. For instance $X_\varepsilon(t)\in\mathbb{R}^n$. $\mathbb{E}_x$ denotes the conditional average over the Markov process given that $X_\varepsilon(0)=x$. We denote G_ε the infinitesimal generator of the process (the definition of the infinitesimal generator of a continuous time Markov process is given in section 7.1.1). We assume that for all $p\in\mathbb{R}^n$ the limit

$$H(x,p)=\lim_{\varepsilon\downarrow 0}\varepsilon G_\varepsilon\left[\mathrm{e}^{\frac{p.x}{\varepsilon}}\right]\mathrm{e}^{-\frac{p.x}{\varepsilon}} \tag{8}$$

exists. Then the family X_ε verifies a large deviation principle with rate ε and rate function

$$L(x,\dot{x})=\sup_p\left\{p\dot{x}-H(x,p)\right\}. \tag{9}$$

This means that the probability that the path $\{X_\varepsilon(t)\}_{0\le t<T}$ is in a neighborhood of $\{X(t)\}_{0\le t<T}$ verifies

$$P\left[\{X_\varepsilon(t)\}_{0\le t<T}=\{X(t)\}_{0\le t<T}\right]\underset{\varepsilon\downarrow 0}{\asymp}\exp\left(-\frac{\int_0^T \mathrm{d}t\,L\left(X,\dot{X}\right)}{\varepsilon}\right), \tag{10}$$

where the symbol $\underset{\varepsilon\downarrow 0}{\asymp}$ is a logarithm equivalence ($f_\varepsilon\underset{\varepsilon\downarrow 0}{\asymp}\exp(g/\varepsilon)\iff\lim_{\varepsilon\downarrow 0}\varepsilon\log f_\varepsilon=g$).

This result is proven for specific cases (diffusions, locally infinitely divisible processes) in the Theorem 2.1, page 127, of the third edition of Freidlin-Wentzell textbook [19]. A heuristic derivation is given in section 7.1, page 30, of this paper. The examples of a diffusion and of a Poisson process are discussed in section 7.1.3. We apply this framework to the fluctuations of the empirical distribution of a dilute gas in section 4.

In formula (8) the infinitesimal generator is tested through the function $e^{\frac{p.x}{\varepsilon}}$. In the small ε limit, this tests those changes of the observable which are of order of ε. The ε prefactor in the right hand side of equation (8) means that the overall effect of these small changes of order ε is expected to be of order $1/\varepsilon$. H in formula (8) thus accounts for the effects of a large number (of order $1/\varepsilon$) of small amplitude statistically independent moves (each one of order ε).

3.2 An example: large deviation for radioactive decay

We now consider the example of the large deviations of the radioactive decay of an ensemble of N independent particles. This example will be very useful in the following because of its analogy with collisions in dilute gas, to be studied in section 4.

3.2.1 Definition of a radioactive decay

We consider a radioactive decay from a state $x = 1$ to a state $x = 0$ at rate λ. By radioactive decay, we mean a pure death-process, where the event $1 \to 0$ occurs at a rate λ. Given that $x(t = 0) = 1$, the distribution of times at which the particle will decay is $\lambda \exp(-\lambda\tau)$. Let us assume that we have N particles x_n, with $1 \leq n \leq N$, each of which undergoes independently a radioactive decay at rate λ. We consider the ratio of particles that have not yet decayed at time t,

$$X_N(t) = \frac{1}{N}\sum_{n=1}^{N} x_n(t). \tag{11}$$

By the law of large numbers, we immediately know that $X_N(t)$ converge for large N to the average $\bar{X}(t)$ that satisfies

$$\frac{\mathrm{d}\bar{X}}{\mathrm{d}t} = -\lambda\bar{X} \tag{12}$$

and, using $\bar{X}(0) = 1$, we obtain $\bar{X}(t) = \exp(-\lambda t)$.

What is the probability to observe a path for X_N that is different from $\bar{X}$? We see that any particle decay changes the value of X_N by a factor $1/N$. A change of order 1 of the variable X_N is thus the result of N independent events, each one of amplitude $1/N$. It is thus natural to expect a large deviation estimate that states that

$$P\left[\{X_N(t)\}_{0\leq t\leq T} = \{X(t)\}\right] \underset{N\uparrow\infty}{\asymp} \exp\left(-NI(X)\right).$$

How to compute $I(X)$? For this problem, because the N particles are statistically independent, the answer can be obtained directly in many different ways. In the next section, we use the framework of section 3.1 in order to compute I.

3.2.2 Large deviation action for the radioactive decay of N particles

As the N particles are independent, the variable X_N (11) defines a continuous time Markov process. From the definition of the radioactive decay, and the definition of the infinitesimal generator of a Markov process (see section 7.1.1), we can compute straightforwardly (see section 7.1.1) the infinitesimal generator for the evolution of the variable X_N:

$$G_N[\phi](x) = N\lambda x\left[\phi\left(x-\frac{1}{N}\right)-\phi(x)\right],$$

where $x = n/N$ with n any integer number with $1 \leq n \leq N$, and ϕ is a real valued function on $[0,1]$. We also have $G_N[\phi](0) = 0$.

We get

$$\lim_{N\to\infty}\frac{1}{N}G_N\left[\mathrm{e}^{Npx}\right]\mathrm{e}^{-Npx} = H(x,p) \equiv \lambda x\left(\mathrm{e}^{-p}-1\right).$$

From the general discussion of section 3.1, we thus conclude that $I[X] = \int_0^T \mathrm{d}t\, L\left(X,\dot{X}\right)$, where L is the Legendre–Fenchel transform of H. We obtain

$$L(x,\dot{x}) = \dot{x}+\lambda x-\dot{x}\log\left(-\frac{\dot{x}}{\lambda x}\right) \text{ if } \dot{x}<0 \text{ and } -\infty \text{ otherwise.}$$

We note that the large deviation rate function has the property that X_N is necessarily decreasing, as imposed by its definition (11).

As explained in the following sections, the most probable evolution (the law or large numbers) verifies the relaxation path equation

$$\dot{x} = R(x) = \frac{\partial H}{\partial p}(x,0) = -\lambda x,$$

which is actually the same as (12), as expected.

3.3 Quasipotential, Hamilton Jacobi equation, time reversal symmetry, relaxation and fluctuation paths

We consider the properties of a stochastic process for which rare fluctuations are described, at the level of large deviations, by the action

$$\mathscr{A}[X] = \int_0^T \mathrm{d}t\, L\left(X,\dot{X}\right) = \sup_P \int_0^T \mathrm{d}t\, \left[P\dot{X}-H(X,P)\right]. \tag{13}$$

The most probable evolution corresponding to the action (13), and with initial condition $X_r(t=0) = x$ is called a ***relaxation path issued from*** x. It solves $\dot{X}_r = R(X_r)$, with initial condition $X_r(0,x) = x$, where $R(x) = \arg\inf_{\dot{x}} L(x,\dot{x})$.

We assume that the stochastic process X_ε has a stationary distribution $P_{s,\varepsilon}$ which dynamics follows the large deviation principle

$$P_{s,\varepsilon}(x) \equiv \mathbb{E}\left[\delta\left(X_\varepsilon - x\right)\right] \underset{\varepsilon\downarrow 0}{\asymp} \exp\left(-\frac{U(x)}{\varepsilon}\right), \tag{14}$$

where U is called the ***quasipotential***. In order to simplify the following discussion, we also assume that the relaxation equation has a single fixed point x_0 and that any solution to the relaxation equation converges to x_0. This assumption can be easily relaxed as done for instance in [19]. However this assumption is actually true for the dilute gas dynamics and simplifies much of the discussion. Then the quasipotential verifies

$$U(x) = \inf_{\left\{\{X(t)\}_{-\infty\leq t\leq 0} \middle| X(-\infty)=x_0 \text{ and } X(0)=x\right\}} \int_{-\infty}^{0} \mathrm{d}t\, L\left(X,\dot{X}\right).$$

The minimizer of this variational problem, that is the most probable path starting from x_0 and ending at x, is denoted $X_f(t,x)$ and is called the ***fluctuation path ending at x.***

We have the following properties which are direct consequences of the definitions of H and L, and whose proofs are given in sections 7.2 to 7.4:

1. H is a convex function of the variable p and $H(x,0)=0$, see sec. 7.2.1.
2. $L \geq 0$, see sec. 7.2.1.
3. For any x, $\dot{x}$ and p
$$p\dot{x} \leq L(x,\dot{x}) + H(x,p), \tag{15}$$
see sec. 7.2.1.
4. The relaxation paths solve the equation $\dot{x} = R(x)$ with $\inf_{\dot{x}} L(x,\dot{x}) = 0 = L\left(x,R(x)\right)$, and $R(x) = \frac{\partial H}{\partial p}(x,0)$, see sec. 7.2.2.
5. The quasipotential solves the stationary **Hamilton–Jacobi equation**
$$H(x,\nabla U) = 0, \tag{16}$$
see sec. 7.2.3.
6. **The fluctuation paths** solve the first order equation
$$\dot{X}_f = F(X_f) \equiv \frac{\partial H}{\partial p}\left(X_f, \nabla U(X_f)\right),$$
see sec. 7.2.4.
7. As H is convex, the quasipotential decreases along the relaxation paths
$$\frac{\mathrm{d}U}{\mathrm{d}t}(X_r) = H(X_r,0) - H(X_r,\nabla U(X_r)) + \frac{\partial H}{\partial p}(X_r,0).\nabla U(X_r) \leq 0,$$
see sec. 7.2.5.
8. As H is convex, the quasipotential increases along the fluctuation paths
$$\frac{\mathrm{d}U}{\mathrm{d}t}(X_f) = H(X_f,0) - H(X_f,\nabla U(X_f)) + \frac{\partial H}{\partial p}\left(X_f,\nabla U(X_f)\right).\nabla U(X_f) \geq 0,$$
see sec. 7.2.5.

9. ***Time reversal symmetry and detailed balance*** (see sec. 7.3.1). A stationary continuous time Markov process is said to be time reversible if its backward and forward histories have the same probabilities. This property is equivalent to the detailed balance condition (see sec. 7.3.1), or to the fact that the infinitesimal generator of the time reversed process is identical to the infinitesimal generator of the initial process. In sec. 7.3.1, we prove that at the level of large deviations, the time reversal symmetry (or detailed balance condition) reads either

$$\text{for any } x \text{ and } \dot{x},\ L(x,\dot{x}) - L(x,-\dot{x}) = \dot{x}.\nabla U,$$

or equivalently

$$\text{for any } x \text{ and p},\ H(x,-p) = H(x,p+\nabla U). \tag{17}$$

10. ***Generalized detailed balance*** (see sec. 7.3.2). For most physical systems the notion of time reversibility has to be extended, for instance in order to take into account that the velocity sign has to be changed in systems with inertia, or other fields have to be modified in the time-reversal symmetry. This is true for the time-reversal symmetry of dynamical systems, for instance of mechanical systems described by Hamiltonian equations, but also for the time-reversal symmetry of Markov processes. Such a generalized definition of time reversal symmetry is classical both in the physics and the mathematics literature, see for instance [22]. Let I be the involution that characterizes the time-reversal symmetry (for instance the map that correspond to velocity or momentum inversion in many systems). We assume that I is self adjoint for the scalar product, that is $I(x).p = I(p).x$. A continuous time Markov process is said to be time-reversal symmetric in the generalized sense if its backward histories with the application of I and its forward histories have the same probabilities. This definition is equivalent to either a generalized detailed balance condition that involves I (see sec. 7.3.2) or to the fact that the infinitesimal generator of the time reversed process is identical to the generator of the initial process up to application of the involution I. As explained in sec. 7.3.2, the detailed balance conditions for the quasipotential U combined with the involution I are $U(x) = U(I[x])$ on one hand and

$$L(x,\dot{x}) - L(x,-I[\dot{x}]) = I[\dot{x}].\nabla U$$

or equivalently

$$H(I[x],-I[p]) = H(x,p+\nabla U),$$

on the other hand.

11. As can be easily checked, if either the detailed balance or the generalized detailed balance conditions are verified, then U satisfies the stationary Hamilton-Jacobi equation (16).
12. If the detailed balance condition is verified, and if U is the quasipotential, then for a path $\{X(t)\}_{0\le t\le T}$ and its time reversed one $\{I[X(T-t)]\}_{0\le t\le T}$ we have the symmetry for the path probability

$$P\left[X_\varepsilon(t) = \{X(t)\}_{0\le t\le T}\right] \mathrm{e}^{-\frac{U(X(0))}{\varepsilon}} = P\left[X_\varepsilon(t) = \{I[X(T-t)]\}_{0\le t\le T}\right] \mathrm{e}^{-\frac{U(I[X(T)])}{\varepsilon}},$$

see sec. 7.3.

13. ***Conserved quantities*** (see sec. 7.2.6*)*. At the level of the large deviations, the condition for $C(x)$ to be a conserved quantity is either

$$\text{for any } x \text{ and } p,\ L(x,\dot{x}) = +\infty \text{ if } \dot{x}.\nabla C(x) \neq 0,$$

or

$$\text{for any } x \text{ and } p,\ \frac{\partial H}{\partial p}(x,p).\nabla C = 0. \tag{18}$$

14. ***A sufficient condition for U to be the quasipotential*** (see sec. 7.4). If U solves the Hamilton–Jacobi equation, if U has a single minimum x_0 with $U(x_0) = 0$, and if for any x the solution of the reverse fluctuation path dynamics $\dot{X} = -F(X) = -\frac{\partial H}{\partial p}(X, \nabla U(X))$ with $X(0) = x$ converges to x_0 for large times, then U is the quasipotential.

4 Large deviations for dilute gas dynamics and the Boltzmann equation

In section 2 we gave a heuristic derivation of the Boltzmann equation, following the hypotheses described in section 2.3.1, page 9. For this derivation, the key hypotheses are: the molecular chaos hypothesis iii), and the law of large numbers iv) assumptions (please see section section 2.3.1, page 9). In this section we relax the law of large number assumption iv), but still assume the molecular chaos hypothesis. This allows us to compute the action that describes the large deviations of the empirical distribution, under the molecular chaos hypothesis assumption.

We also discuss the properties of the large deviation action, prove its time-reversal symmetry, explain why the entropy is the negative of the quasipotential, and discuss the physical consequences in relation with the irreversibility paradox.

4.1 Derivation of the action for dilute gas dynamics

In the following we work with non dimensional variables and functions. A natural time scale for the dynamics is the typical collision time τ_c, while a natural spatial scale is the mean free path l ; we thus take as a time unit τ_c and space unit l such that with these units a typical velocity is of order one. As in section 2, we consider N particles in a volume V. Each particle $1 \leq n \leq N$ has a position $\mathbf{r}_n(t)$ and a velocity $\mathbf{v}_n(t)$. We assume that these N particles have a total mass M_0, momentum $\mathbf{P}_0$ and kinetic energy E_0 ; those values are conserved by the dynamics.

In order to clearly identify the large deviation rate, we want to make sure that all quantities remain of order 1 in the Boltzmann–Grad limit $\varepsilon \to 0$ and $N \to \infty$ with $\varepsilon N = \alpha^{-3}$ (or $\varepsilon N \gg 1$). As $\rho l^3 = 1/\varepsilon$, typical densities are of order $1/\varepsilon$, and typical velocities are of order one for our choice of units. If we would define the empirical distribution as in equation (7) it would be of order $1/\varepsilon$. We thus define a rescaled non dimensional empirical distribution as

$$f_\varepsilon(\mathbf{r},\mathbf{v},t) \equiv \varepsilon \sum_{n=1}^{N} \delta(\mathbf{v} - \mathbf{v}_n(t))\, \delta(\mathbf{r} - \mathbf{r}_n(t)). \tag{19}$$

The normalization is now such that $\int \mathrm{d}\mathbf{v}\mathrm{d}\mathbf{r} f_\varepsilon(\mathbf{v}) = N\varepsilon = V/l^3$, such that f_ε remains finite in the limit $\varepsilon \to 0$. Similarly, as the cross section is of order a^2, as velocities are of order one, the collision kernel is order $a^2/l^2 = \varepsilon$. We thus work with a rescaled collision kernel w defined such that a couple of particles with velocities $(\mathbf{v}_1, \mathbf{v}_2)$ in a volume element $\mathrm{d}\mathbf{r}$ has a microscopic collision of the type $(\mathbf{v}_1, \mathbf{v}_2) \to (\mathbf{v}'_1, \mathbf{v}'_2)$ that occurs with a rate per unit of volume equal to

$$\varepsilon w\left(\mathbf{v}'_1, \mathbf{v}'_2; \mathbf{v}_1, \mathbf{v}_2\right) \mathrm{d}\mathbf{v}'_1 \mathrm{d}\mathbf{v}'_2. \tag{20}$$

This new definition has to be compared with equation (4) ($w_0 = \varepsilon w$). As $f_\varepsilon = \varepsilon f_e$, and $w = w_0/\varepsilon$ where f_e and w_0 are the section 2 distribution function and collision kernel respectively, we note that Boltzmann's equation is unchanged by this rescaling.

This natural rescaling makes clear that the large deviation rate will be ε. Indeed, equations (19) and (20) readily show that individual collisions for each particle occur at a small rate of order ε and produce a small effect on the distribution function f of order of ε. As a consequence, on a time scale of order 1, $1/\varepsilon$ collisions occur each producing a change of order ε of the empirical distribution function, and thus producing an overall change of the distribution function f_ε of order 1. This clearly corresponds to a large deviation scaling with rate ε.

We now proceed with the derivation of the action. We compute, at a large deviation level, the probability that the empirical density f_ε remains close to a distribution function f. According to the molecular chaos hypothesis iii) (please see section 2.3.1, page 9), in order to evaluate the collision rates, we identify f_ε with f and make the hypothesis of a local point Poisson process. The number of particles with position $\mathbf{r}_1$ up to $\mathrm{d}\mathbf{r}_1$ and velocity $\mathbf{v}_1$ up to $\mathrm{d}\mathbf{v}_1$ is $f(\mathbf{r}_1, \mathbf{v}_1)\mathrm{d}\mathbf{v}_1\mathrm{d}\mathbf{r}_1/\varepsilon$. The number of particle couples, per unit volume, with the two particles with position $\mathbf{r}$ up to $\mathrm{d}\mathbf{r}$, and with the first particle with velocity $\mathbf{v}_1$ up to $\mathrm{d}\mathbf{v}_1$ and the second particle with velocity $\mathbf{v}_2$ up to $\mathrm{d}\mathbf{v}_2$ is $f(\mathbf{r}, \mathbf{v_1}) f(\mathbf{r}, \mathbf{v}_2)\mathrm{d}\mathbf{v}_1\mathrm{d}\mathbf{v}_2\mathrm{d}\mathbf{r}/2\varepsilon^2$. Combining this with (20) we obtain that the collision rate of the type $(\mathbf{v}_1, \mathbf{v}_2) \to (\mathbf{v}'_1, \mathbf{v}'_2)$ in the volume element $\mathrm{d}\mathbf{r}$ centered at a point $\mathbf{r}$ is

$$\frac{w(\mathbf{v}'_1, \mathbf{v}'_2; \mathbf{v}_1, \mathbf{v}_2)}{2\varepsilon} f(\mathbf{r}, \mathbf{v_1}) f(\mathbf{r}, \mathbf{v}_2)\,\mathrm{d}\mathbf{v}_1\mathrm{d}\mathbf{v}_2\mathrm{d}\mathbf{v}'_1\mathrm{d}\mathbf{v}'_2\mathrm{d}\mathbf{r}.$$

Each individual collision $(\mathbf{v}_1, \mathbf{v}_2) \to (\mathbf{v}'_1, \mathbf{v}'_2)$ in the volume element $\mathrm{d}\mathbf{r}$ centered at a point $\mathbf{r}$ changes the empirical velocity distribution (19) from $f(.,.)$ to

$$f(.,.) - \varepsilon\left[\delta(.-\mathbf{v}_1)\,\delta(.-\mathbf{r}) - \delta(.-\mathbf{v}_2)\,\delta(.-\mathbf{r})\right.$$

$$\left. + \delta\left(.-\mathbf{v}'_2\right)\delta(.-\mathbf{r}) + \delta\left(.-\mathbf{v}'_1\right)\delta(.-\mathbf{r})\right].$$

The infinitesimal generator of the empirical distribution is thus

$$G[\phi][f] = G_R[\phi][f] + G_C[\phi][f]$$

with

$$G_R[\phi][f] = \frac{1}{2\varepsilon}\int \mathrm{d}\mathbf{v}_1\mathrm{d}\mathbf{v}_2\mathrm{d}\mathbf{v}'_1\mathrm{d}\mathbf{v}'_2\mathrm{d}\mathbf{r}\, w(\mathbf{v}'_1,\mathbf{v}'_2;\mathbf{v}_1,\mathbf{v}_2) f(\mathbf{r},\mathbf{v_1}) f(\mathbf{r},\mathbf{v}_2) \\ \times\{\phi[f(.)+\varepsilon[-\delta(.-\mathbf{v}_1)\delta(.-\mathbf{r})-\delta(.-\mathbf{v}_2)\delta(.-\mathbf{r}) \\ +\delta(.-\mathbf{v}'_2)\delta(.-\mathbf{r})+\delta(.-\mathbf{v}'_1)\delta(.-\mathbf{r})]]-\phi[f]\}, \quad (21)$$

and

$$G_C[\phi][f] = -\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{v}\,\mathbf{v}.\frac{\partial f}{\partial \mathbf{r}}(\mathbf{r},\mathbf{v})\frac{\delta\phi}{\delta f(\mathbf{r},\mathbf{v})}, \quad (22)$$

where G_R is the collision contribution to the generator, and G_C accounts for the transport by the ballistic motion of the particles and the associated free transport of the distribution. Section 7.5 justifies that G_C takes this form for a deterministic free transport.

In view of the derivation of the large deviation action from the infinitesimal generator, discussed in section 3.1, more precisely equation (8), we define

$$H[f,p] \equiv \varepsilon G\left[\mathrm{e}^{\frac{1}{\varepsilon}\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{v} p(\mathbf{r},\mathbf{v}) f(\mathbf{r},\mathbf{v})}\right]\mathrm{e}^{-\frac{1}{\varepsilon}\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{v} p(\mathbf{r},\mathbf{v}) f(\mathbf{r},\mathbf{v})}, \quad (23)$$

where p is the momentum conjugated to f. Hence

$$H[f,p] = H_C[f,p] + H_R[f,p] \quad (24)$$

with

$$H_R[f,p] = \frac{1}{2}\int \mathrm{d}\mathbf{v}_1\mathrm{d}\mathbf{v}_2\mathrm{d}\mathbf{v}'_1\mathrm{d}\mathbf{v}'_2\mathrm{d}\mathbf{r}\, w(\mathbf{v}'_1,\mathbf{v}'_2;\mathbf{v}_1,\mathbf{v}_2) \\ \times f(\mathbf{r},\mathbf{v_1}) f(\mathbf{r},\mathbf{v}_2)\left\{\mathrm{e}^{\left[-p(\mathbf{r},\mathbf{v}_1)-p(\mathbf{r},\mathbf{v}_2)+p\left(\mathbf{r},\mathbf{v}'_1\right)+p\left(\mathbf{r},\mathbf{v}'_2\right)\right]}-1\right\} \quad (25)$$

and

$$H_C[f,p] = -\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{v}\, p(\mathbf{r},\mathbf{v})\mathbf{v}.\frac{\partial f}{\partial \mathbf{r}}(\mathbf{r},\mathbf{v}), \quad (26)$$

where the subscript R in H_R means reversible and the subscript C in H_C means conservative (see below).

From the discussion of section 3.1, we thus conclude that we have a large deviation principle with rate ε and action

$$\mathscr{A}[f] = \int_0^T \mathrm{d}t\, L\left[f,\dot{f}\right] = \int_0^T \mathrm{d}t \sup_p \left[\int p(\mathbf{r},\mathbf{v})\,\dot{f}(\mathbf{r},\mathbf{v})\,\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{v} - H[f,p]\right]. \quad (27)$$

We have thus computed the action for the evolution of the empirical distribution of a dilute gas, assuming the molecular chaos hypothesis.

4.2 Time reversal symmetry, quasipotential, fluctuation and relaxation paths

Let us discuss this action properties. First, the corresponding most probable evolution is given by $\frac{\partial f}{\partial t} = \frac{\delta H}{\delta p}[f,0]$ (see point 4 in section 3.3, or section 7.2.2). It is easily checked that this most probable evolution is Boltzmann's equation

$$\frac{\partial f}{\partial t} + \mathbf{v}.\frac{\partial f}{\partial \mathbf{r}} = \int \mathrm{d}\mathbf{v}_2 \mathrm{d}\mathbf{v}'_1 \mathrm{d}\mathbf{v}'_2 \, w(\mathbf{v}'_1, \mathbf{v}'_2; \mathbf{v}, \mathbf{v}_2) \left[f\left(\mathbf{v}'_1, \mathbf{r}\right) f\left(\mathbf{v}'_2, \mathbf{r}\right) - f\left(\mathbf{v}, \mathbf{r}\right) f\left(\mathbf{v}_2, \mathbf{r}\right) \right],$$

as expected.

We define the specific entropy in the dilute gas limit as

$$S[f\,|f_0\,] = -\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{v}\, f \log\left(\frac{f}{f_0}\right), \tag{28}$$

where $f_0 = f_{M_0,\mathbf{P}_0,E_0}$ is the Maxwell-Boltzmann distribution with mass M_0, momentum $\mathbf{P}_0$ and kinetic energy E_0. S is a relative entropy of f with respect to f_0. It is also the Boltzmann H function up to an additive constant.

We now discuss the time reversal symmetry. We define the time reversal involution (the velocity inversion involution) I by $I[f](\mathbf{r},\mathbf{v}) = f(\mathbf{r},-\mathbf{v})$. Then clearly $I^2 = Id$ and I is self adjoint for the L_2 scalar product. It is easily checked that $H_R(I[f],-I[p]) = H_R(f,-p) = H_R\left(f, p - \frac{\delta S}{\delta f}\right)$, and that $H_C(I[f],-I[p]) = H_C\left(f, p - \frac{\delta S}{\delta f}\right)$, where the last equality is a consequence of the conservation of the entropy by the free transport operator. As a consequence

$$H(I[f],-I[p]) = H\left(f, p - \frac{\delta S}{\delta f}\right), \tag{29}$$

which is the detailed balance condition with $-S$ as the quasipotential (see points 9) and 10) in section 3.3). We have thus checked that the large-deviation action is time-reversal symmetric. We note that the collision term and the transport term act differently with respect to the time reversal symmetry. The collision term is both time reversal symmetric and time reversal symmetric with respect to the involution I, while the transport term is time reversal symmetric only with respect to the involution I.

Using point 11) of section 3.3, we thus conclude that $-S$ solves the Hamilton–Jacobi equation.

We now discuss conserved quantities. From point 13) of section 3.3, a functional $C[f]$ is conserved for the large deviation action (27) if and only if $\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{v}\, \frac{\delta H}{\delta p}\frac{\delta C}{\delta f} = 0$. This is easily checked for the conservation laws for the mass

$$M = \int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{v}\, f,$$

the momentum

$$\mathbf{P} = \int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{v}\, \mathbf{v} f,$$

and the kinetic energy

$$E = \frac{1}{2}\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{v}\, \mathbf{v}^2 f,$$

as consequences of the microscopic conservation laws encoded in (6). We denote M_0, $\mathbf{P}_0$, and E_0 the initial values of the mass, momentum, and kinetic energy respectively (we note that depending on the boundary conditions, $\mathbf{P}$ may not be a conserved quantity, we let the reader adapt the discussion to this case).

Given that $-S$ solves Hamilton–Jacobi's equation and given the conservation laws, it is natural to assume that

$$U[f] = \begin{cases} -S[f|f_0] \text{ if } M[f] = M_0,\ \mathbf{P}[f] = \mathbf{P}_0, \text{ and } E[f] = E_0 \\ -\infty \text{ otherwise.} \end{cases}$$

is the quasipotential. This is also what should be expected from equilibrium statistical mechanics, in the microcanonical ensemble. We note that due to the convexity of U, we are in the case when U has a single minimum. This minimum of U is $f_0 = f_{M_0,\mathbf{P}_0,E_0}$, the Maxwell-Boltzmann distribution with mass M_0, momentum $\mathbf{P}_0$ and kinetic energy E_0.

We want to use point 14) of section 3.3 to establish that U is indeed the quasipotential. We note that due to the generalized time reversal symmetry of the action with respect to the entropy (29), in order to verify the hypothesis of point 14), it is sufficient to verify that the solution to the Boltzmann equation starting from any distribution function f with mass mass M_0, momentum $\mathbf{P}_0$ and kinetic energy E_0 converges for large time to the Maxwell-Boltzmann distribution $f_{M_0,\mathbf{P}_0,E_0}$. This property is actually true for generic non-degenerate kernels w. For a more precise discussion and hypothesis and the discussion of the rate of relaxation to equilibrium, please see [14] and [30], and references therein.

We thus conclude that in generic cases, as soon as the solution to Boltzmann's equation starting from any distribution function f with mass mass M_0, momentum $\mathbf{P}_0$ and kinetic energy E_0 converges for large time to the Maxwell-Boltzmann distribution $f_{M_0,\mathbf{P}_0,E_0}$, U is the quasipotential.

Finally, from the general discussion of section 3.3, points 7), 8) and 12), we deduce that the entropy increases along the relaxation paths (solution of Boltzmann's equation), that the fluctuation paths are the time reversed relaxation paths using the involution I, and thus that the entropy decreases along the fluctuation paths.

4.3 Physical discussion

4.3.1 The irreversibility paradox

Our main result is that the probability that $\{f_\varepsilon(t)\}_{0\le t\le T}$ remains in a neighborhood of a prescribed path $\{f(t)\}_{0\le t\le T}$ verifies

$$\mathbb{P}\left[\{f_\varepsilon(t)\}_{0\le t<T} = \{f(t)\}_{0\le t<T}\right] \underset{\varepsilon\downarrow 0}{\asymp} \exp\left(-\frac{\int_0^T \mathrm{d}t\, L\left[f,\dot{f}\right]}{\varepsilon}\right), \tag{30}$$

where the large deviation Lagrangian L is the Legendre-Fenchel transform of the Hamiltonian H, and H is defined through (24-27). This defines a statistical field theory whose large deviations are given through H.

We have proven in the previous section that:

i) The stochastic process with action (30) is time reversible. This is a consequence of the time reversal symmetry of L or H. Any path $\{f_\varepsilon(t)\}_{0\leq t<T}$ is possible with a probability given by (30).

ii) The most probable evolution from any state f_0 (a relaxation path) is the solution of the Boltzmann equation with initial condition f_0.

iii) The entropy $S[f] = -\int \mathrm{d}\mathbf{v}\mathrm{d}\mathbf{r}\, f\log(f)$ is the negative of the quasipotential for the statistical field theory. As a consequence it increases monotonically along any relaxation path, and thus along the evolution through the Boltzmann equation.

We believe that those properties clarify in a definitive way the seemingly paradox of irreversibility. It is fully compatible with the classical understanding following Boltzmann original ideas. We can summarize this result by the following sentences. The macrostates evolve according to a completely reversible stochastic process. Then the irreversibility is not a consequence of looking at the system at a macroscopic scale. However the change of scale for the description of the physical phenomena, produces entropic factors such that some evolutions of the macroscopic variables appear as much more probable than others. The irreversibility is thus a consequence of two combined effect: looking at macroscopic scale only and looking at only the most probable evolution. It is not a consequence of the change of scale for the description of the physical phenomena by itself.

We stress also that the molecular chaos hypothesis used to derive the large deviation action (30) does not break the time reversal symmetry.

4.3.2 The relation with fluctuating hydrodynamics and macroscopic fluctuation theory

Our work has been initially inspired by the works of Derrida and Lebowitz on the large deviation for stochastic particle dynamics, for instance for the Asymmetric Exclusion Process [13], and the works of the Rome group on macroscopic fluctuation theory [1]. One can consider the result (30) and (24-27) as a macroscopic fluctuation theory for the dynamics of dilute gases. Our is a macroscopic fluctuation theory which is relevant for a large class of physical systems which are dilute in the sense that the physical constituents interact in a way a dilute gas does.

The large deviation principle (30) can also be considered as a starting point for deriving large deviation results at a different scale. For instance can we deduce Landau's fluctuating hydrodynamics [26] and the related large deviations through a coarse-graining of the action (30)? Can we deduce the large deviation for a piston separating two boxes with dilutes gazes through a coarse-graining of (30)? Those are natural questions that will be addressed in future works.

4.3.3 Validity of the molecular chaos hypothesis

The main assumption to derive the large deviation action for dilute gas is the molecular chaos hypothesis. It is obviously outside of the scope of this paper to justify it. Let us however give few arguments to support it.

1) **The molecular chaos hypothesis is the most natural one.** First it has to be stressed that the molecular chaos hypothesis is the most natural order zero assumption for dilute gas dynamics, for both the law of large numbers and large deviation estimates. Most of the time, particles that undergo collisions come from spatial region very far apart and will rarely collide again. The correlation are therefore expected to be extremely weak in the dilute gas limit. We have to notice however, that making the molecular chaos hypothesis in order to study large deviations is a stronger assumption than making the assumption for the law of large number only. We believe that in the same way Boltzmann's equation is believed to actually describe most physical situations for dilute gas, the large deviation action (24-27) should describe large deviations in most physical situations. We discuss few possible exceptions like for instance shocks in the following.

Up to now, it has proven extremely difficult to quantify the effects of weak correlations and some possible corrections to Boltzmann's equation. It will probably be at least as difficult to discuss the related questions for the large deviation rate function.

2) **Perfect gas entropy, quasipotential and the Boltzmann-Grad limit.** Independently of the dynamics, the specific entropy for a perfect gas (28) is the leading order Boltzmann entropy of the macrostate f for the microcanonical measure, in the Boltzmann-Grad limit $\varepsilon \downarrow 0$ with $\varepsilon N \sim 1$ or $\varepsilon N \gg 1$. This was probably first noticed by Boltzmann himself, and this fact is usually explained in basic statistical mechanics lecture following the counting arguments of Boltzmann. For this reason, it was natural to expect this expression for the entropy to be the negative of the quasipotential for the large deviation rate function, up to conservation laws. The fact that the large deviation action (24-27) has the perfect gas entropy (28) as a quasipotential stress consistency of the large deviation rate function with its expected properties.

3) **Smoothness of f and the molecular chaos hypothesis.** The molecular chaos hypothesis iii), in section 2.3 on page 9, assumes that the effect of collisions can be well approximated as if the distribution of particles with velocity $\mathbf{v}$ would be locally the one of a Poisson point process with density derived from f. For the Boltzmann equation, this hypothesis would most probably not remain consistent if f would not be smooth. Similarly, for the large deviation action where f is now prescribed a-priori, this hypothesis requires to consider classes of smooth enough functions f for consistency. Given the dynamical mechanisms at hand (free transport and collisions), it seems natural to assume that f has variations that do not extend below the mean free path scale, this assumption being consistent with the molecular chaos hypothesis. We are unfortunately not able to be more precise on that point.

4.3.4 Gaussian fluctuations

The Gaussian fluctuations around the solution of the Boltzmann equation have been studied by a number of authors. For instance close to equilibrium they are described in Spohn's book [37] or have been studied mathematically [3]. Far for equilibrium macrostates f, the stochastic process of Gaussian fluctuations close to solutions of the Boltzmann equation has been described by physicists, please see for instance [23] and references therein. For instance equation (61) in section 4 of [23] gives a

formula for the two point correlation function of the Gaussian noise needed to obtain the fluctuating Boltzmann equation that describe those Gaussian fluctuations.

An important remark is that our large deviation principle (30) is fully compatible with the previous description of those Gaussian fluctuations, as far as small deviation are concerned. What is meant here is that by linearization of the Hamiltonian (24-27), one recovers exactly the two point correlations described by equation (61) of [23]. I do not reproduce the related easy computations here.

4.3.5 Large deviation principle for the Kac's model

Kac's model [25,32] is a continuous time Markov chain that mimics the homogeneous Boltzmann's equation, where only the velocity variable are represented. We consider N particles with velocities $(\mathbf{v}_1,...,\mathbf{v}_N) \in \mathbb{R}^{dN}$. The dynamics of the Kac's model is defined by the infinitesimal generator

$$G_N[\phi_N](\mathbf{v}_1,...,\mathbf{v}_N) = \frac{1}{2N}\sum_{n,m=1,n\neq m}^{N}\int \mathrm{d}\mathbf{v}'_1\mathrm{d}\mathbf{v}'_2\, w(\mathbf{v}'_1,\mathbf{v}'_2;\mathbf{v}_n,\mathbf{v}_m) \times\left\{\phi_N\left[C_{nm,\mathbf{v}'_1\mathbf{v}'_2}(\mathbf{v}_1,...,\mathbf{v}_N)\right]-\phi_N(\mathbf{v}_1,...,\mathbf{v}_N)\right\},$$

where $\phi_N : \mathbb{R}^{dN} \to \mathbb{R}$ is a test function in the N velocity space, and $C_{nm,\mathbf{v}'_1\mathbf{v}'_2}$ is the operator that replace the velocities $\mathbf{v}_n$ and $\mathbf{v}_m$ by $\mathbf{v}'_1$ and $\mathbf{v}'_2$ respectively (C_{nm} is defined for $n \neq m$; if $n < m$, $C_{nm,\mathbf{v}'_1\mathbf{v}'_2}(\mathbf{v}_1,...,\mathbf{v}_N) = (\mathbf{v}_1,...,\mathbf{v}_{n-1},\mathbf{v}'_1,\mathbf{v}_{n+1},...,\mathbf{v}_{m-1},\mathbf{v}'_2,\mathbf{v}_{m+1},...,\mathbf{v}_N)$). This is the generator of a dynamics for which a collision of the type $(\mathbf{v}_1,\mathbf{v}_2) \to (\mathbf{v}'_1,\mathbf{v}'_2)$ occurs with rate $w(\mathbf{v}'_1,\mathbf{v}'_2;\mathbf{v}_n,\mathbf{v}_m)/2N$.

By an easy computation analogous to the one discussed in section 4, one easily justify formally that the empirical density $f_e(\mathbf{v},t) \equiv \frac{1}{N}\sum_{n=1}^{N}\delta(\mathbf{v}-\mathbf{v}_n(t))$ verifies a large deviation principle

$$\mathbb{P}\left[\{f_\varepsilon(t)\}_{0\leq t<T} = \{f(t)\}_{0\leq t<T}\right] \underset{\varepsilon\downarrow 0}{\asymp} \exp\left(-\frac{\int_0^T \mathrm{d}t\, L\left[f,\dot{f}\right]}{\varepsilon}\right), \tag{31}$$

where the large deviation Lagrangian L is the Legendre-Fenchel transform of the Hamiltonian H, and H is defined by

$$H[f,p] = \frac{1}{2}\int \mathrm{d}\mathbf{v}_1\mathrm{d}\mathbf{v}_2\mathrm{d}\mathbf{v}'_1\mathrm{d}\mathbf{v}'_2 w(\mathbf{v}'_1,\mathbf{v}'_2,\mathbf{v}_1,\mathbf{v}_2) \times f(\mathbf{v}_1)f(\mathbf{v}_2)\left[\mathrm{e}^{p(v'_1)+p(v'_2)-p(v_1)-p(v_2)}-1\right].$$

This Hamiltonian is also, obviously, the one obtained from the Hamiltonian of the dilute gas large deviations (24-27), when restricting evolutions to spatially homogeneous solutions.

5 Gradient structure for the Boltzmann equation

There exists a close relation between the gradient structure of a many classical PDEs and the large deviations for the empirical density of related N particle dynamics. These PDE are obtained as laws of large number for the particle dynamics. When one describes the fluctuations of the empirical density at the level of large deviations, one obtain a large deviation rate function. The PDE appears as the most probable evolution, the action minimum. The large deviation rate function that measures the probability to depart from the most probable evolution also provides a natural metric structure for the PDE. When the large deviation action is time reversible, one can prove that the PDE solution is a gradient flow, with an energy (energy from the point of view of gradient flows) which is the quasipotential, and with a norm (in the quadratic case), or a metric structure (in the general case), that derives from the large deviation rate functions. These provide systematic connections between the limit of particle systems to PDE, large deviation theory, and gradient structure.

The gradient structure of an equation may be extremely useful both physically and mathematically: the energy (or quasipotential) landscape gives a first qualitative idea of the dynamics, the gradient structure explains convergence properties and sometimes convergence speeds. At a mathematical level, the gradient structure may be used to prove existence results in a very natural way.

Such gradient flow structures had been observed independently of large deviation theory, for instance by Otto [33]. For instance the heat equation, appears as a gradient structure with the entropy as a quasipotential and the Wasserstein distance as the metric structure, or the Vlasov–Mac-Kean equation has a gradient structure with the free energy as the quasipotential and the Wasserstein distance for the metric structure (see for instance [39]). Other examples include the Allen–Cahn equation, equations for porous media, and so on.

All those structures can be obtained (and thus explained) from the large deviation principle for the evolution of the empirical density. Some aspects of this connection were first understood for the case of Vlasov–Mac-Kean equation (Brownian particles with mean field interactions) in works by Dawson and Gärtner [12]. The connection between large deviations and gradient flows has been explained very clearly, with mathematical rigor in some specific cases, by Mielke, Peletier and Renger [31]. We give the definition of gradient flows in section 5.1 and briefly explain the relation between time reversible large deviation principles for paths and gradient flows in section 5.2.

As a consequence of the general relation between large deviation for paths and gradient structures, using the large deviation principle for the empirical density for dilute gazes, we can infer that a gradient structure exists for the Boltzmann equation. The Boltzmann equation is not time reversible, and the corresponding large deviation principle verifies a generalized detailed balance. As a consequence, the Boltzmann equation is not strictly speaking a gradient flow, but the collision operator of the Boltzmann equation has a gradient structure: the collision part is a gradient of the entropy with respect to a metric structure. As explained in section 5.4, this metric structure is not simple however. Moreover, the homogeneous Boltzmann equation is a gradient flow. This is explained in section 5.4.

5.1 Gradient flows

In this section we define gradient flows. We consider ψ^* a function of two variables x and p, and assume that ψ^* is a convex function with respect to the second variable. We call ψ the convex conjugated of ψ^* with respect to the second variable

$$\psi(x,v) = \sup_p \{vp - \psi^*(x,p)\}. \tag{32}$$

ψ^* is called the dissipation function. ψ^* is assumed to be non negative and such that $\psi^*(x,0) = 0$. $\psi^*(x,0) = 0$ implies that ψ is also non negative, and $\psi^* \geq 0$ implies that $\psi(x,0) = 0$.

A gradient flow with energy E and dissipation function ψ^* is defined as a solution $\{x(t)\}_{0\leq t\leq T}$ to the equation

$$E(x(T)) - E(x(0)) + \int_0^T \mathrm{dt}\,[\psi(x,\dot{x}) + \psi^*(x,-\nabla E)] = 0, \tag{33}$$

where $\dot{x}$ is the time derivative of x and ∇ the gradient for the canonical norm. The non negativity of ψ and ψ^* insures that the energy decreases with time.

When time derivation of (33) can be justified, we obtain

$$\dot{x}.\nabla E + \psi(x,\dot{x}) + \psi^*(x,-\nabla E) = 0.$$

Using Fenchel's inequality, we obtain that

$$\dot{x}.\nabla E + \psi(x,\dot{x}) + \psi^*(x,-\nabla E) \geq 0$$

is always verified. When ψ is differentiable, the equality is verified whenever

$$\dot{x} = \frac{\partial \psi^*}{\partial p}(x,-\nabla E).$$

This is the gradient flow differential equation and (33) is a weak form of this differential equation.

A special case of interest is when ψ^* is quadratic in the second variable, for instance $\psi^*(x,p) = pAp$ where A is a linear operator acting on the p space. Then we obtain the classical gradient flow

$$\dot{x} = -2A\nabla E,$$

with respect to the norm given by $\psi^*(x,p) = pAp$.

5.2 Gradient flows for time reversible path large deviations

Let assume a large deviation rate function for path $\{X_\varepsilon(t)\}$, with Hamiltonian $H(x,p)$, and its associated Lagrangian $L(x,\dot{x})$ obtained by Legendre–Fenchel transform:

$$P\left[\{X_\varepsilon(t)\}_{0\leq t<T} = \{X(t)\}_{0\leq t<T}\right] \underset{\varepsilon\downarrow 0}{\asymp} \exp\left(-\frac{\int_0^T \mathrm{d}t\, L\left(X,\dot{X}\right)}{\varepsilon}\right), \tag{34}$$

with $L(x,\dot{x}) = \sup_p \{p\dot{x} - H(x,p)\}$, and with quasipotential U such that $H(x,\nabla U) = 0$. We assume the time reversal symmetry with respect to the quasipotential U (see Eq. (17) page 15): for any p, $H(x,p+\nabla U) = H(x,-p)$. Equivalently H is a symmetric function of the second variable with respect to $\nabla U/2$: for any p, $H(x,\nabla U/2+p) = H(x,\nabla U/2-p)$. Using that $H(x,0) = 0$ (point 1 of page 13), we note that U solves the stationary Hamilton–Jacobi equation $H(x,\nabla U) = 0$.

In this section we justify that the relaxation paths for those dynamical large deviations are gradient flows for the dissipation function ψ^* given by (26) and the energy $E = U/2$.

We define the dissipation function ψ^* by

$$\psi^*(x,p) = H\left(x,\frac{\nabla U}{2}+p\right) - H\left(x,\frac{\nabla U}{2}\right) \tag{35}$$

The convexity of ψ^* follows from the convexity of H. We have $\psi^*(x,0) = 0$. Using the convexity of H, we have that $H(x,\nabla U/2) \leq \frac{1}{2}\left[H(x,\nabla U/2+p) + H(x,\nabla U/2-p)\right] = H(x,\nabla U/2+p)$ where the last equality is a consequence of the symmetry of H. This insures that ψ^* is non negative. Hence ψ^* has all the property of a dissipation function. We note moreover that ψ^* is even.

From the definition of ψ as the Legendre-Fenchel transform of ψ^*, L as the Legendre Fenchel transform of H, from (35), we get $\psi(x,\dot{x}) = L(x,\dot{x}) - \dot{x}.\nabla U/2 + H(x,\nabla U/2)$. Using $H(x,0) = 0$, we note that $H(x,\nabla U/2) = -\psi^*(x,-\nabla U/2)$, and thus

$$L(x,\dot{x}) = \psi(x,\dot{x}) + \psi^*\left(x,-\frac{\nabla U}{2}\right) + \dot{x}.\frac{\nabla U}{2}. \tag{36}$$

We recall that L is non negative and that the most probable evolution (the relaxation paths) are the paths $x(t)$ such that

$$\int_0^T \mathrm{d}t L(x,\dot{x}) = 0, \tag{37}$$

Comparing (37) and (33), and using (36) we immediately conclude that the relaxation paths coincide with gradient flows with respect to the energy $E = U/2$ and dissipation function ψ^*.

For a path large deviation principle given by the Hamiltonian H and the quasipotential U, we have thus proven that the relaxation paths are gradient flows for the dissipation function ψ^* given by (26) and the energy $E = U/2$.

Let us consider first the example of gradient diffusions

$$\mathrm{d}X_\varepsilon = -A\nabla U\mathrm{d}t + \sqrt{2\varepsilon}\sigma\mathrm{d}W_t$$

with $A \equiv \sigma\sigma^T$. One can compute the large deviation principle with rate ε (see page 32). The Hamiltonian is

$$H(x,p) = p.Ap - p.A\nabla U.$$

It it easily checked that U solves the stationary Hamilton-Jacobi equation $H(x,\nabla U) = 0$. With generic hypotheses, for instance the hypotheses used in section 7.4, U will be the quasipotential. It is easily checked that this dynamics is time-reversible. From (35), we compute the associated dissipation function, and we find $\psi^*(x,p) = pAp$, with the relaxation paths $\dot{X} = -A\nabla U$, as expected.

5.3 Dynamics with gradient-conservative structure and their relation with path large deviations

Let us now define a time reversible-conservative structure for a path large deviation. This definition is original. We consider a path large deviation principle

$$P\left[\{X_\varepsilon(t)\}_{0\le t<T} = \{X(t)\}_{0\le t<T}\right] \underset{\varepsilon\downarrow 0}{\asymp} \exp\left(-\frac{\int_0^T \mathrm{d}t\, L\left(X,\dot{X}\right)}{\varepsilon}\right), \tag{38}$$

with $L(x,\dot{x}) = \sup_p\{p\dot{x} - H(x,p)\}$, and with quasipotential U such that $H(x,\nabla U) = 0$. We assume that $H = H_R + H_C$ where H_R the time reversible part of the Hamiltonian which verifies the time reversal symmetry with respect to the quasipotential U: for any p, $H_R(x,p+\nabla U) = H_R(x,-p)$, and where H_C is the conservative part of the Hamiltonian such that for any x

$$\nabla U(x).\frac{\partial H_C}{\partial p}(x,0) = 0. \tag{39}$$

The relaxation path equation is

$$\dot{x} = \frac{\partial H_C}{\partial p}(x,0) + \frac{\partial H_R}{\partial p}(x,0). \tag{40}$$

We say that the vector field for the relaxation paths, $\frac{\partial H_C}{\partial p}(x,0) + \frac{\partial H_R}{\partial p}(x,0)$, has a gradient/conservative decomposition, where $\frac{\partial H_R}{\partial p}(x,0)$ is the gradient part (the gradient of the quasipotential with respect to a dissipative function) and $\frac{\partial H_C}{\partial p}(x,0)$ the conservative part (it conserves the quasipotential). Let me explain a bit more.

Following the discussion of section 5.2, thanks to time reversal symmetry for H_R, we know that the dynamics $\dot{x} = \frac{\partial H_R}{\partial p}(x,0)$ is a gradient flow with dissipation function

$$\psi^*(x,p) = H_R\left(x, \frac{\nabla U}{2} + p\right) - H_R\left(x, \frac{\nabla U}{2}\right)$$

and gradient flow energy $E = U/2$. Moreover equation $\dot{x} = \frac{\partial H_C}{\partial p}(x,0)$ conserves the value of the quasipotential thanks to the conservation equation (39). As a consequence the relaxation path equation systematically decreases the quasipotential, through the gradient of the quasipotential with respect to the dissipative function ψ^* and the further mixing due the conservative part.

Let us consider the example of diffusions with transverse decomposition:

$$\mathrm{d}X_\varepsilon = -A\left(X_\varepsilon\right)\nabla U\left(X_\varepsilon\right)\mathrm{d}t + G\left(X_\varepsilon\right)\mathrm{d}t + \sqrt{2\varepsilon}\sigma\left(X_\varepsilon\right)\mathrm{d}W_t$$

with $A \equiv \sigma\sigma^T$ and with the assumption that for any X, $G(X).\nabla U(X) = 0$ (transversality assumption). One can compute the large deviation principle with rate ε (see page 32). The Hamiltonian is

$$H(x,p) = p.Ap - p.A\nabla U + p.G.$$

It it easily checked that U solves the stationary Hamilton-Jacobi equation $H(x,\nabla U) = 0$, thanks to the transversality assumption. With generic hypotheses, for instance the hypotheses used in section 7.4, U will be the quasipotential. When $G \neq 0$, in general this dynamics is **not** time-reversible. As a consequence we do not expect this dynamics to be a gradient flow. However it clearly has a time reversible-conservative structure, with the definition given above. $H_R(x,p) = p.Ap - p.A\nabla U$ is the reversible part of the Hamiltonian while $H_C(x,p)$ is the conservative part. The transverse condition $G(X).\nabla U(X) = 0$ is indeed a conservation condition. As a consequence the relaxation path equation $\dot{X} = -A\nabla U + G$ has a gradient-conservative decomposition (in this case this is obvious).

We note that most equilibrium statistical mechanics stochastic processes with Gaussian noises, described by stochastic differential equations, for instance Hamiltonian dynamics in contact with a thermal bath, have a gradient-conservative structure, where G is the Hamiltonian vector-field and $-A\nabla U$ the deterministic part of the interaction with the thermal bath. Such a gradient-conservation structure is not limited to equilibrium stochastic differential equations with Gaussian noises. In the following section we discuss the gradient-conservation structure of the Boltzmann equation.

5.4 Gradient structure for the Boltzmann equation

In section 4 we have justified the large deviation structure associated to the Boltzmann equation. The large deviation principle (30) is an example of a large deviation principle (34) discussed in section 5.3. The Hamiltonian for the large deviations of the large deviations associated to the Boltzmann equation is given by $H = H_R + H_C$ with H_R given by (2) and H_C given by (3). We have justified in section 4 that H_R has the time-reversal symmetry and that H_C conserves the entropy. As a consequence $H = H_R + H_C$ is a reversible-conservative decomposition and the Boltzmann equation has a gradient-conservative structure. The transport term of the Boltzmann equation

is the conservative one, while the collision term is the gradient of half the entropy as a potential and a dissipation functional ψ^* given by

$$\psi^*[f,p] = H_R\left(f, -\frac{1}{2}\frac{\delta S}{\delta f} + p\right) - H_R\left(f, -\frac{1}{2}\frac{\delta S}{\delta f}\right).$$

This remark is very important from a physical point of view. This gradient-conservative decomposition insures all the expected properties of the entropy. Moreover the dissipation functional is the proper local measure of the metric related to entropy changes. This remark might also be of interest mathematically, as gradient-conservative decomposition should prove extremely useful to define the proper functional spaces and build the mathematical theory of the Boltzmann equation.

We conclude this section with a few simple remarks:

1. While we have an explicit formula for the Hamiltonian for the Boltzmann equation, there is probably no explicit formula for the Lagrangian. There is thus no explicit formula for neither ψ the Legendre-Fenchel conjugate of the dissipation function.
2. Some properties of L can be found in the paper [35].
3. It is easy to compute the dissipation function along a solution of the Boltzmann equation that verifies $L\left[f,\dot{f}\right] = 0$, however this is just a subensemble of the space $\left[f,\dot{f}\right]$.
4. For the linearized Boltzmann equation close to the equilibrium, H will be quadratic in p, and the expression for L might be explicit and the gradient structure might be explicit.

6 Conclusions and perspectives

In this paper, we have justified a large deviation principle for a dilute gas in the Boltzmann-Grad limit. This large deviation principle describes the probability of observing any evolution for the empirical distribution in the position-velocity space. The solution of this fundamental problem gives a specially clear perspective on the classical irreversibility paradox. We have explained how the large deviation action, Lagrangian and Hamiltonian, are natural consequences of the Boltzmann molecular chaos hypothesis. Using this hypothesis, rather than computing only the average evolution of the distribution function, as Boltzmann did, we have computed its full distribution and obtained the path large deviations.

We guess that this large deviation functional will have profound implications. First, the exercise described in this paper will probably be a classical textbook one, because of its conceptual importance. Then it opens the door to many questions. Can fluctuating hydrodynamics be obtained from this large deviation action for the empirical distribution through a hydrodynamic limit? Using this large deviation action, can we compute the large deviations for the dynamics of macroscopic variables, for instance for the evolution of a piston between two boxes? Can we compute large deviation rate functions for current of particle, for dilute gases flowing in between two

boundaries in contact with thermal baths? Could this large deviation principle be useful to study the property and dynamics of non-smooth solutions to the Boltzmann and or Navier–Stokes equations? Are there physical applications of this large deviation rate function? Could such an approach be generalized to other kinetic equations?

Although the justification we gave, based on the chaotic hypothesis, is extremely natural, a more precise justification would be welcomed. Could one justify the same action from a hierarchy, for instance a generalization of the BBGKY hierarchy? Would it be possible to give a full mathematical proof of the validity of this large deviation principle for short times?

Finally we have also explained that this large deviation principle implies a gradient-conservative structure for the Boltzmann equation. We believe that this will have deep consequences in the future in the mathematical study of the Boltzmann equation.

7 Appendices

7.1 Large deviation rate functions from the infinitesimal generator of a continuous time Markov process

7.1.1 Infinitesimal generator of a continuous time Markov process

We recall the notion of the infinitesimal generator of a continuous time Markov process. We consider the continuous time Markov processes $\{X(t)\}_{0\leq t\leq T}$, for instance $X(t)\in\mathbb{R}^n$. The infinitesimal generator acts on the test function $\phi:\mathbb{R}^n\to\mathbb{R}$ and is defined by

$$G[\phi](x)=\lim_{t\downarrow 0}\frac{\mathbb{E}_x[\phi(X(t))]-\phi(x)}{t}. \tag{41}$$

For example, for a diffusion $\mathrm{d}x=R(x)\mathrm{d}t+\sqrt{2}\mathrm{d}W_t$, the infinitesimal generator is $G[\phi](x)=R(x)\nabla\phi+\Delta\phi$, the adjoint of the Fokker–Planck equation.

As an example, let us compute the infinitesimal generator for the radioactive decay of a single particle, defined in section 3.2. If $X=1$ at time $t=0$, the probability that $X=1$ at time t, for small t, is $1-\lambda t$ up to terms of order two in t. The probability that $X=0$ at time t, for small t, is λt, up to terms of order two in t. If $X=0$ at time $t=0$, it remains zero for all time. Then

$$G[\phi](1)=\lambda\left[\phi(0)-\phi(1)\right].$$

and

$$G[\phi](0)=0.$$

We can write

$$G[\phi](x)=\lambda x(\phi(0)-\phi(1)).$$

The generator is $(\phi(0)-\phi(1))$ the value of the function after the jump minus its value before the jump multiplied by the jump rate λ.

In the example of the radioactive decay, $X_N(t)$ (11) is also a continuous time Markov process. We can compute directly its infinitesimal generator by studying all possible changes of the variable X_N. We then obtain

$$G_N[\phi](x) = N\lambda x\left[\phi\left(x-\frac{1}{N}\right)-\phi(x)\right],$$

where $x = n/N$ with n any integer number with $1 \leq n \leq N$, and ϕ is a real valued function on $[0,1]$. We also have $G_N[\phi](0) = 0$. The generator has on contribution per jump: $(\phi(x-1/N)-\phi(x))$ the value of the function after the jump minus its value before the jump multiplied by the jump rate $N\lambda x$. The jump rate in this case is a single particle jump rate λ multiplied by the density x multiplied by the total particle number N.

7.1.2 Heuristic derivation of the large deviation rate functions from the infinitesimal generator of a continuous time Markov process

We give in this section a heuristic derivation of the relation between (8), (9), and (10).

Let us consider trajectories $\{X_\varepsilon(t)\}_{0\leq t<\infty}$ starting at x. We denote $P_t(x,\dot{x})$ the probability that the Newton difference quotient $\frac{X(t)-x}{t}$ be equal to $\dot{x}$ after a time t:

$$P_{t,\varepsilon}(x,\dot{x}) \equiv \mathbb{E}_x\left[\delta\left(\frac{X_\varepsilon(t)-x}{t}-\dot{x}\right)\right]. \tag{42}$$

Let us first assume that for small time t, $P_{t,\varepsilon}$ verifies the large deviation estimate

$$P_{t,\varepsilon}(x,\dot{x}) \underset{\varepsilon\downarrow 0}{\asymp} \exp\left(-\frac{tL(x,\dot{x})}{\varepsilon}\right) \tag{43}$$

(more precisely, we take first the limit $\varepsilon\downarrow 0$: $L(x,\dot{x}) = -\lim_{t\downarrow 0}\lim_{\varepsilon\downarrow 0}\varepsilon\log P_{t,\varepsilon}(x,\dot{x})/t$). Then decomposing the path $X(t)$ in small subpaths, and using the Markov property, we can construct a path integral and the large deviation (10) holds. It is thus sufficient to prove the large deviation result (43) holds in order to conclude that (10) is true.

In order to assess the large deviation result (43), we can study the cumulant generating function of $P_{t,\varepsilon}$. A sufficient condition for (43) to hold is then given by Gärtner–Ellis theorem. If for all p, the limit

$$\begin{aligned} H(x,p) &= \lim_{t\downarrow 0}\lim_{\varepsilon\downarrow 0}\frac{\varepsilon}{t}\log\mathbb{E}_x\left[\exp\left(\frac{t}{\varepsilon}\frac{p.(X_\varepsilon(t)-x)}{t}\right)\right] \\ &= \lim_{t\downarrow 0}\lim_{\varepsilon\downarrow 0}\frac{\varepsilon}{t}\log\left\{\mathbb{E}_x\left[\exp\left(\frac{p.X_\varepsilon(t)}{\varepsilon}\right)\right]\exp\left(-\frac{p.x}{\varepsilon}\right)\right\} \end{aligned} \tag{44}$$

exists and H is everywhere differentiable then (10) will hold with L given by (9). Now, using the definition of the infinitesimal generator (41) we have

$$\frac{1}{t}\log\left\{\mathbb{E}_x\left[\exp\left(\frac{p.X_\varepsilon(t)}{\varepsilon}\right)\right]\exp\left(-\frac{px}{\varepsilon}\right)\right\}$$
$$= \frac{1}{t}\log\left\{1+tG_\varepsilon\left[\exp\left(\frac{px}{\varepsilon}\right)\right]\exp\left(-\frac{px}{\varepsilon}\right)+o(t)\right\}$$
$$= G_\varepsilon\left[\exp\left(\frac{px}{\varepsilon}\right)\right]\exp\left(-\frac{px}{\varepsilon}\right)+o(1).$$

Hence if the limit (8) exists then the large deviation estimate (10) holds.

7.1.3 Examples

The example of locally finitely indivisible processes is discussed in Freidlin-Wentzell textbook. This includes the diffusion and Poisson process cases discussed below.

Diffusion with small noise. We consider the diffusion

$$\mathrm{d}X_\varepsilon = R(X_\varepsilon)\mathrm{d}t + \sqrt{2\varepsilon}\sigma(X_\varepsilon)\mathrm{d}W_t$$

where $X_\varepsilon \in \mathbb{R}^n$, $R(.)$ is a vector field, σ a $n\times n$ matrix. We denote $a(x)\equiv\sigma(x)\sigma(x)^T$, where T stands for the transposition. The infinitesimal generator is

$$G_\varepsilon[\phi] = R.\nabla\phi + \varepsilon a : \nabla\nabla\phi,$$

where : is the symbol for the contraction of two second order tensors. Then it is easily checked that, from the definitions (8) and (9),

$$H(x,p) = p.ap + p.R.$$

Then, whenever a is invertible,

$$L(x,\dot{x}) = \frac{1}{4}(\dot{x}-R).a^{-1}(\dot{x}-R).$$

H and L are the classical Hamiltonian and Lagrangian for a diffusion with small noise.

Poisson process The case of a Poisson process is discussed in the book of Freidlin–Wentzell. This textbook considers a single Poisson process, rescaled in order to have an infinitesimal generator that fits with the asymptotics leading to a large deviation estimate, as in equation (8). We rather consider N independent Poisson processes $\{x_n(t)\}_{1\le n\le N}$ for which we will look at the large deviations for their empirical average. This case is more in line with what will be needed in this paper. The value x_n of each of these Poisson processes is increased by 1 at a rate 1 (the probability of x_n to increase by a jump equal to one during an infinitesimal time interval dt is dt).

We consider the average

$$X_N(t) = \frac{1}{N}\sum_{n=1}^{N} x_n(t).$$

During an infinitesimal interval dt, the probability for $X_N(t)$ to increases by an amount $1/N$ is Ndt. The infinitesimal generator is thus

$$G_N[\phi](x) = N\left[\phi\left(x+\frac{1}{N}\right)-\phi(x)\right].$$

Using (8) with $\varepsilon = 1/N$, we deduce that the process $\{X_N(t)\}$ verifies a large deviation principle with an action characterized by the Hamiltonian

$$H(x,p) = \exp(p) - 1.$$

7.2 Quasipotential, relaxation paths, fluctuation paths, and conservation laws

7.2.1 Some properties of the Lagrangian and of the Hamiltonian

L is a large deviation rate function for the variable $\dot{x}$. By definition, a large deviation rate function has zero as its minimum value. We thus have

$$\inf_{\dot{x}} L(x,\dot{x}) = 0 = L(x,R(x)), \tag{45}$$

where for the second equality we assume that the infimum is achieved at $\dot{x} = R(x)$. We also have

$$L(x,\dot{x}) \geq 0. \tag{46}$$

From the definition of the Hamiltonian H as a rescaled cumulant generating function (44), we can conclude that for any x, H is a convex function of the variable p and that

$$H(x,0) = 0. \tag{47}$$

The Legendre–Fenchel relation between L and H (9) implies that for any x and p

$$p\dot{x} \leq L(x,\dot{x}) + H(x,p) \tag{48}$$

from which, using (47) we verify again (46).

7.2.2 Relaxation paths

The relaxation paths $X_r(t,x)$ are the most probable paths of the dynamics described by the action (13), starting from a state x at time $t = 0$. They thus minimize the action. From the definition of R (45), as $L \geq 0$ and $L(x,R(x)) = 0$, relaxation paths thus solve

$$\dot{X}_r = R(X_r), \tag{49}$$

with the initial condition $X_r(0,x) = x$.

Moreover looking at the condition for the stationarity of the variational problem $0 = L(X,R(X)) = \sup_p [p.R(X) - H(X,p)]$, we conclude that the optimal is achieved for $p = 0$ and that

$$R(X_r) = \frac{\partial H}{\partial p}(X_r,0). \tag{50}$$

In the following, in order to keep the discussion simple, we assume that the relaxation dynamics has a single global point attractor x_0, with $R(x_0) = 0$. The generalization to multiple attractors or to other types of attractors could be considered following the classical discussion (see for instance [18]). As we will see, this hypothesis will be verified for the Boltzmann equation.

7.2.3 Quasipotential

We consider now the stationary distribution P_s of the processes X_ε which dynamics follows the large deviation principle (10). We assume that the stationary distribution also follows a large deviation principle:

$$P_s(x) \equiv \mathbb{E}\left[\delta\left(X_\varepsilon - x\right)\right] \underset{\varepsilon\downarrow 0}{\asymp} \exp\left(-\frac{U(x)}{\varepsilon}\right), \tag{51}$$

where U is called the quasipotential. In the case when the relaxation dynamics has a single global attractor x_0, the quasipotential is characterized by the variational problem

$$\begin{aligned} U(x) &= \inf_{\left\{X(t)\middle| X(-\infty)=x_0 \text{ and } X(0)=x\right\}} \int_{-\infty}^{0} \mathrm{d}t\, L(X,\dot{X}) \\ &= \inf_{\left\{X(t),P(t)\middle| X(-\infty)=x_0 \text{ and } X(0)=x\right\}} \int_{-\infty}^{0} \mathrm{d}t\, \left[P\dot{X} - H(X,P)\right]. \end{aligned} \tag{52}$$

It is a classical result, that can be found for instance in any textbook of classical mechanics, that the minimum of a variational problem with a Lagrangian solves a Hamilton–Jacobi equation. Then the quasipotential U solves the stationary Hamilton–Jacobi equation

$$H(x, \nabla U) = 0. \tag{53}$$

7.2.4 Fluctuation paths

The fluctuation paths are the minimizers of the quasipotential variational problem (52). They are very important as they describe the most probable path starting from the attractor x_0 and leading to a fluctuation x.

The fluctuation paths define a flow parametrized by x, that we denote $X_f(t,x)$ (the path evolution) and $P_f(t,x)$ (the conjugated momentum evolution). They verify the Euler-Lagrange equations

$$\begin{cases} \dot{X}_f = \ \frac{\partial H}{\partial p}\left(X_f, P_f\right) \\ \dot{P}_f = -\frac{\partial H}{\partial x}\left(X_f, P_f\right), \end{cases} \tag{54}$$

with the boundary conditions $X_f(-\infty,x) = x_0$ and $X_f(0,x) = x$. As any fluctuation path converges to x_0 as $t \downarrow -\infty$, we have $R(x_0) = \frac{\partial H}{\partial p}(x_0,0) = 0$. As H is a convex function of the variable p, the equation $\frac{\partial H}{\partial P}(x_0,p) = 0$ can have at most one root, from

which we deduce that $\lim_{t\downarrow-\infty} P_f(t,x) = 0$. Moreover, Hamilton's equations (54) conserve the Hamiltonian H along their dynamics. From the value of H for $t \downarrow -\infty$, we deduce that along the fluctuation paths $H(X_f, P_f) = 0$. From the variational characterization of the quasipotential (52), we then deduce that $U(x) = \int_{-\infty}^{0} \mathrm{d}t\, P_f(t,x)\dot{X}_f(t,x)$. It then follows that $\nabla U(x) = P_f(0,x)$. Using the flow property, it is clear that this relation is valid all along the fluctuation paths. Then for any x and t

$$\nabla U(X_f(t,x)) = P_f(t,x).$$

Using this result and (54), we deduce that the fluctuation paths solve the first order equation

$$\dot{X}_f = F(X_f) \equiv \frac{\partial H}{\partial p}\left(X_f, \nabla U(X_f)\right), \tag{55}$$

where the second equality defines the fluctuation path vector field F.

7.2.5 Decay (resp. increase) of the quasi potential along the relaxation(resp. fluctuation) paths

We now prove that the value of U characterizes the relaxation towards the attractor x_0: any relaxation path decreases U monotonously. Indeed, from (49) and (50), we have

$$\begin{aligned}\frac{\mathrm{d}U}{\mathrm{d}t}(X_r) &= \frac{\partial H}{\partial p}(X_r,0).\nabla U(X_r)\\ &= H(X_r,0) - H(X_r,\nabla U(X_r)) + \frac{\partial H}{\partial p}(X_r,0).\nabla U(X_r) \le 0\end{aligned}$$

where we have used (47) and the Hamilton–Jacobi equation (53) to write the second equality. The inequality is a consequence of the convexity of H with respect to its second variable. In case of strict convexity, which will be often the case, the equality holds if and only if $\nabla U(X_r) = 0$.

Moreover, the condition: for any $\alpha \in [0,1]$

$$(\nabla U)^T \frac{\partial^2 H}{\partial p^2}(X_r, \alpha\nabla U)\nabla U \ge CU \tag{56}$$

implies a convergence to equilibrium faster than e^{-Ct}. The condition that the quasipotential is uniformly convex in the norm of the second variation of H: for any p

$$p^T \frac{\partial^2 H}{\partial p^2}(x, \alpha\nabla U)\,\mathrm{Hess}U(x)p \ge Cp^T p \tag{57}$$

implies (56). In the case of the sum of N independent particles, where each follows a diffusion, the second variations of H are the Wasserstein distance and the condition (57) is a log-Sobolev inequality.

We now prove similarly that U increases monotonously along the fluctuation paths. Using (55), we have

$$\begin{aligned}\frac{\mathrm{d}U}{\mathrm{d}t}(X_f) &= \frac{\partial H}{\partial P}\left(X_f, \nabla U(X_f)\right).\nabla U(X_f) \\ &= H(X_f,0) - H(X_f,\nabla U(X_f)) + \frac{\partial H}{\partial P}\left(X_f,\nabla U(X_f)\right).\nabla U(X_f) \geq 0,\end{aligned}$$

where the second equality is a consequence of the Hamilton–Jacobi equation (53) and of (47), and the inequality is again a consequence of the convexity of H with respect to its second argument. Again if H is strictly convex the inequality is strict whenever $\nabla U(X_r) \neq 0$.

7.2.6 Conservation laws

It may happen that the stochastic process has a conservation law C: for any ε and t, $C(X_\varepsilon(t)) = C_0$. Then, $\dot{X}_\varepsilon(t).\frac{\partial C}{\partial x}(X_\varepsilon(t)) = 0$. As a consequence, from the definition of the Lagrangian (43), we deduce that

$$L(x,\dot{x}) = +\infty \text{ if } \dot{x}.\frac{\partial C}{\partial x}(x) \neq 0.$$

At the level of the Hamiltonian, using the Legendre–Fenchel transform (9), we conclude that the conservation law translates to the continuous symmetry property

$$\text{for any } x, p \text{ and } \alpha,\ H\left(x, p + \alpha\frac{\partial C}{\partial x}\right) = H(x,p) \tag{58}$$

or equivalently

$$\text{for any } x \text{ and } p,\ \frac{\partial H}{\partial p}(x,p).\frac{\partial C}{\partial x}(x) = 0. \tag{59}$$

Then as a function of its second variable, $H(x,.)$ is flat in the direction $\frac{\partial C}{\partial x}$.

As far as the Hamilton–Jacobi equation is concerned, this means that only the projection of the gradient of U on the orthogonal of ∇C matters.

7.3 Time reversal symmetry and detailed balance

7.3.1 Detailed balance

If the Markov process is time reversible, or equivalently if it verifies a detailed balance condition, this implies a time reversal symmetry for the path large deviation estimate (10), or equivalently the action (13). We explain this point in this section.

A stationary continuous time Markov process is said to be time reversible if its backward and forward histories have the same probabilities. We consider the transition probability P_T for the Markov process ($P_T(y;x)$ is the transition probability from the state x towards the state y). If for any states x and y,

$$P_T(y;x)P_S(x) = P_T(x;y)P_S(y), \tag{60}$$

we say that the process verifies a detailed balance property with respect to the distribution P_s. It is then very easily checked that P_S is a stationary distribution of the Markov process. The detailed balance condition is a necessary and sufficient condition for the Markov process to be time reversible. Another characterization of the time-reversibility of the process is that the infinitesimal generator of the time reversed process is identical to the infinitesimal generator of the initial process.

If for any ε the process $\{X_\varepsilon\}$ verifies a detailed balance property, then the large deviation dynamics will inherit this symmetry property. However, the converse is not necessarily true, the detailed balance property can hold at the level of the large deviations dynamics without holding at the level of the process $\{X_\varepsilon\}$.

For the process we are interested in, the condition for detailed balance can be written

$$P_{\Delta t,\varepsilon}(x,\dot{x})\,P_S(x) \underset{\Delta t\to 0}{\sim} P_{\Delta t,\varepsilon}(x+\Delta t\dot{x},-\dot{x})\,P_S(x+\Delta t\dot{x}),$$

where $P_{\Delta t,\varepsilon}$ is defined by (42). Using the large deviation estimates (43) and (51) evaluated for small Δt, the detailed balance condition writes: for any x and $\dot{x}$

$$L(x,\dot{x}) - L(x,-\dot{x}) = \dot{x}.\nabla U. \tag{61}$$

Using the Legendre–Fenchel relations between H and L (9), this detailed balance condition writes: for any x and p

$$H(x,-p) = H(x,p+\nabla U). \tag{62}$$

If H and U verify the detailed balance condition (62), using $H(x,0)=0$ (eq. (47)), we easily deduce that $H(x,\nabla U)=0$ which is the Hamilton-Jacobi equation. With some further conditions on U, see for instance section 7.4, we may conclude that U is the quasipotential.

Moreover, if detailed balance is verified, then one expects to observe the time reversal symmetry at the level of the relaxation and fluctuation paths. Indeed from (62), we easily derive $R(x) = \frac{\partial H}{\partial x}(x,0) = -\frac{\partial H}{\partial x}(x,\nabla U) = -F(x)$. We thus conclude that for Hamiltonians with detailed balance relation, the fluctuation paths are the time reversed of the relaxation paths.

7.3.2 Generalized detailed balance

For most physical systems the notion of time reversibility has to be extended, for instance in order to take into account that the velocity sign has to be changed in systems with inertia, or other fields have to be modified in the time-reversal symmetry. This is true for the time-reversal symmetry of dynamical systems, for instance of mechanical systems described by Hamiltonian equations, but also for the time-reversal symmetry of Markov processes. Such a generalized definition of time reversal symmetry is classical both in the physics and the mathematics literature, see for instance [22].

We consider a map I from the state space to itself. We assume that I is an involution ($I^2 = Id$) and that I is self adjoint for the canonical scalar product: for any x and y, $I(x).y = x.I(y)$. A continuous time Markov process is said to be time-reversal symmetric in the generalized sense if its backward histories with the application of I and

its forward histories have the same probabilities. If the distribution P_S is I-symmetric (for any x $P_S(I(x)) = P_S(x)$) and if for any states x and y,

$$P_T(y;x)P_S(x) = P_T(I(x);I(y))\,P_S(I(y))\,, \tag{63}$$

we say that the process verifies a generalized detailed balance property with respect to the distribution P_s and the symmetry I. It is then very easily checked that P_S is a stationary distribution of the Markov process. The generalized detailed balance condition is a necessary and sufficient condition for the Markov process to be time reversible in the generalized sense. Another characterization of the time-reversibility of the process in the generalized sense is that the infinitesimal generator of the time reversed process is identical to the generator of the initial process up to application of the involution I.

Then, the discussion of section 7.3.1 easily generalizes. The conditions of generalized detailed balance at the level of large deviation read $U(I(x)) = U(x)$ and

$$L(x,\dot{x}) - L(x,-I[\dot{x}]) = I[\dot{x}].\nabla U$$

or equivalently

$$H(I[x],-I[p]) = H(x,p+\nabla U)\,.$$

If a generalized detailed balance is verified, then the quasipotential solves the Hamilton–Jacobi equation and the fluctuation paths are the time reversed of the fluctuation paths composed with the symmetry I: $F(x) = -R(I(x))$.

7.4 A sufficient condition for U to be the quasipotential

We know that if U is the quasipotential then it solves the Hamilton–Jacobi equation $H(x,\nabla U) = 0$. The converse is not necessarily true. For instance $U = 0$ solves the Hamilton–Jacobi equation but is not the quasipotential.

We give a sufficient condition for U to be the quasipotential, in the simple case when U has a unique global minimum x_0.

If V solves the Hamilton–Jacobi equation and V has a single minimum x_0 with $V(x_0) = 0$, if moreover for any x the solution of the reverse fluctuation path dynamics $\dot{X} = -F(X) = -\frac{\partial H}{\partial p}(X,\nabla V(X))$, with $X(t=0) = x$, converges to x_0 for large times, then V is the quasipotential. We give now a simple proof.

From the definition of L (9), we have for any X and $\dot{X}$, $L\left(X,\dot{X}\right) \geq \dot{X}\nabla V(X) - H(X,\nabla V(X))$. Hence using that V solves the Hamilton, Jacobi equation ($H(x,\nabla V) = 0$), we obtain that for any X such that $X(0) = x$ and $X(-\infty) = x_0$

$$\int_{-\infty}^{0} \mathrm{d}t\, L\left(X,\dot{X}\right) \geq \int_{-\infty}^{0} \mathrm{d}t\, \dot{X}\nabla V(X) = V(x).$$

Hence, using the characterization of the quasipotential (52), we get $U(x) \geq V(x)$.

Moreover, from the definition of L (9), for any x and p we have

$$L\left(x, \frac{\partial H}{\partial p}(x,p)\right) = p\frac{\partial H}{\partial p}(x,p) - H(x,p).$$

If we apply this formula to the fluctuation path that verifies $\dot{X}_f = \frac{\partial H}{\partial p}\left(X_f, \nabla V(X_f)\right)$, with $p = \nabla U$, using moreover $H(x, \nabla V(x)) = 0$, we get

$$\int_{-\infty}^{0} \mathrm{d}t\, L\left(X_f, \dot{X}_f\right) = \int_{-\infty}^{0} \mathrm{d}t\, \dot{X}_f \nabla V(X_f) = V(x).$$

Hence $U(x) \leq V(x)$. We thus conclude that V is the quasipotential.

7.5 The infinitesimal generator for the free transport.

We consider N particles that undergo free transport. Each particle $1 \leq n \leq N$ has a position $\mathbf{r}_n(t)$ and a velocity $\mathbf{v}_n(t)$. Then the empirical distribution f verifies the equation

$$\frac{\partial f}{\partial t} = -\mathbf{v}.\frac{\partial f}{\partial \mathbf{r}}$$

Let us consider a ϕ functional of f. Then ϕ evolves according to

$$\frac{\mathrm{d}\phi}{\mathrm{d}t} = \int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{v}\, \frac{\partial f}{\partial t}(\mathbf{r}, \mathbf{v}) \frac{\delta \phi}{\delta f(\mathbf{r}, \mathbf{v})} = -\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{v}\, \mathbf{v}.\frac{\partial f}{\partial \mathbf{r}}(\mathbf{r}, \mathbf{v}) \frac{\delta \phi}{\delta f(\mathbf{r}, \mathbf{v})}.$$

Then the infinitesimal generator of the free transport is

$$G[\phi] = -\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{v}\, \mathbf{v}.\frac{\partial f}{\partial \mathbf{r}}(\mathbf{r}, \mathbf{v}) \frac{\delta \phi}{\delta f(\mathbf{r}, \mathbf{v})}.$$

If $\phi = \mathrm{e}^{\frac{\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{v}\, pf}{\varepsilon}}$, then

$$\frac{\delta \phi}{\delta f(\mathbf{r}, \mathbf{v})} = \frac{p(\mathbf{r}, \mathbf{v})}{\varepsilon} \mathrm{e}^{\frac{\int d\mathbf{r}_1 d\mathbf{v}_1\, pf}{\varepsilon}}$$

and

$$\varepsilon G\left[\mathrm{e}^{\frac{\int d\mathbf{r}d\mathbf{v}\, pf}{\varepsilon}}\right] \mathrm{e}^{-\frac{\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{v}\, pf}{\varepsilon}} = -\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{v}\, p(\mathbf{r}, \mathbf{v})\mathbf{v}.\frac{\partial f}{\partial \mathbf{r}}(\mathbf{r}, \mathbf{v}).$$

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References

1. Bertini, L., De Sole, A., Gabrielli, D., Jona-Lasinio, G., Landim, C.: Macroscopic fluctuation theory. Reviews of Modern Physics **87**(2), 593 (2015)
2. Binney, J., Tremaine, S.: Galactic dynamics. Princeton, NJ, Princeton University Press, 1987, 747 p. (1987)
3. Bodineau, T., Gallagher, I., Saint-Raymond, L.: From hard sphere dynamics to the stokes–fourier equations: An analysis of the boltzmann–grad limit. Annals of PDE **3**(1), 2 (2017)
4. Bodineau, T., Gallagher, I., Saint-Raymond, L., Simonella, S.: Fluctuation theory in the boltzmann–grad limit. Journal of Statistical Physics pp. 1–23 (2020)
5. Bogoliubov, N.: Problems of a dynamical theory in statistical physics. gostekhisdat, moscow (1946)(in russian). english translation in de boer, j., uhlenbeck, ge (eds.) studies in statistical mechanics, vol. 1 (1962)
6. Boltzmann, L.: Entgegnung auf die wärmetheoretischen betrachtungen des hrn. e. zermelo. Annalen der physik **293**(4), 773–784 (1896)
7. Boltzmann, L.: Vorlesungen über gastheorie, 2 vols. Barth, Leipzig **1898** (1896)
8. Brush, S.G.: Kinetic theory: The nature of gases and of heat, vol. 1. Elsevier (2013)
9. Brush, S.G.: Kinetic theory: Irreversible processes. Elsevier (2016)
10. Cercignani, C.: The boltzmann equation. In: The Boltzmann equation and its applications, pp. 40–103. Springer (1988)
11. Chapman, S., Cowling, T.G., Burnett, D.: The mathematical theory of non-uniform gases: an account of the kinetic theory of viscosity, thermal conduction and diffusion in gases. Cambridge university press (1990)
12. Dawson, D.A., Gartner, J.: Large deviations from the mckean-vlasov limit for weakly interacting diffusions. Stochastics (1987)
13. Derrida, B., Lebowitz, J.L.: Exact Large Deviation Function in the Asymmetric Exclusion Process. Physical Review Letters **80**, 209–213 (1998). DOI 10.1103/PhysRevLett.80.209
14. Desvillettes, L., Villani, C.: On the trend to global equilibrium for spatially inhomogeneous kinetic systems: the boltzmann equation. Inventiones mathematicae **159**(2), 245–316 (2005)
15. Eyink, G.L., Spohn, H.: Space-time invariant states of the ideal gas with finite number, energy, and entropy density. Translations of the American Mathematical Society-Series 2 **198**, 71–90 (2000)
16. Feng, J., Kurtz, T.G.: Large deviations for stochastic processes. 131. American Mathematical Soc. (2006)
17. Feynman, R.: The character of physical law. 1965. Cox and Wyman Ltd., London (1967)
18. Freidlin, M.I., Wentzell, A.D.: Random perturbations of dynamical systems. Springer - New York, Berlin (1984)
19. Freidlin, M.I., Wentzell, A.D.: Random Perturbations of Dynamical Systems. Springer-Verlag, 3dr ed. New York (2012)
20. Frisch, U., Hasslacher, B., Pomeau, Y.: Lattice-gas automata for the navier-stokes equation. Physical review letters **56**(14), 1505 (1986)
21. Gallagher, I., Saint Raymond, L., Texier, B.: From newton to boltzmann: the case of hard-spheres and short-range potentials. European Mathematical Society p. 150 (2014)
22. Gardiner, C.W.: Handbook of stochastic methods for physics, chemistry and the natural sciences. Springer Series in Synergetics, Berlin: Springer, —c1994, 2nd ed. 1985. Corr. 3rd printing 1994 (1994)
23. Gaspard, P.: Time-reversal symmetry relation for nonequilibrium flows ruled by the fluctuating boltzmann equation. Physica A: Statistical Mechanics and its Applications **392**(4), 639–655 (2013)
24. Goldstein, S., Lebowitz, J.L.: On the (Boltzmann) entropy of non-equilibrium systems. Physica D **193**, 53 (2004). DOI 10.1016/j.physd.2004.01.008
25. Kac, M.: Foundations of kinetic theory. In: Proceedings of The third Berkeley symposium on mathematical statistics and probability, vol. 3, pp. 171–197. University of California Press Berkeley and Los Angeles, California (1956)
26. Landau, L.D., Lifshitz, E.M.: Statistical Physics. Vol. 5 of the Course of Theoretical Physics. Pergamon Press (1980)
27. Lanford, O.E.: Time evolution of large classical systems. In: Dynamical systems, theory and applications, pp. 1–111. Springer (1975)
28. Lebowitz, J.L.: Boltzmann's entropy and time's arrow. Physics today **46**, 32–32 (1993)
29. Lebowitz, J.L.: Time's arrow and boltzmann's entropy. Scholarpedia **3**(4), 3448 (2008)

30. Lu, X., Mouhot, C.: On measure solutions of the boltzmann equation, part ii: Rate of convergence to equilibrium. Journal of Differential Equations **258**(11), 3742–3810 (2015)
31. Mielke, A., Peletier, M.A., Renger, D.M.: On the relation between gradient flows and the large-deviation principle, with applications to markov chains and diffusion. Potential Analysis **41**(4), 1293–1327 (2014)
32. Mischler, S., Mouhot, C.: Kac's program in kinetic theory. Inventiones mathematicae **193**(1), 1–147 (2013)
33. Otto, F.: The geometry of dissipative evolution equations: the porous medium equation (2001)
34. Pulvirenti, M., Saffirio, C., Simonella, S.: On the validity of the boltzmann equation for short range potentials. Reviews in Mathematical Physics **26**(02), 1450001 (2014)
35. Rezakhanlou, F.: Large deviations from a kinetic limit. The Annals of Probability **26**(3), 1259–1340 (1998)
36. Saint Raymond, L.: Hydrodynamic limits of the Boltzmann equation. 1971. Springer Science & Business Media (2009)
37. Spohn, H.: Large Scale Dynamics of Interacting Particles. Springer, New-York (2002)
38. Thomson, W.: The kinetic theory of the dissipation of energy. Proceedings of the Royal Society of Edinburgh **8**, 325–334 (1875)
39. Villani, C.: Optimal transport: old and new, vol. 338. Springer Science & Business Media (2008)