Physica A 392 (2013) 639–655

Contents lists available at SciVerse ScienceDirect

Physica A

journal homepage: www.elsevier.com/locate/physa

Time-reversal symmetry relation for nonequilibrium flows ruled by the fluctuating Boltzmann equation

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ARTICLE INFO

Article history:
Received 4 June 2012
Received in revised form 29 September 2012
Available online 24 October 2012

Keywords:
Dilute gas
Rarefied gas
Nonequilibrium steady state
Affinity
Stochastic process
Master equation

ABSTRACT

A time-reversal symmetry relation is established for out-of-equilibrium dilute or rarefied gases described by the fluctuating Boltzmann equation. The relation is obtained from the associated coarse-grained master equation ruling the random numbers of particles in cells of given position and velocity in the one-particle phase space. The symmetry relation concerns the fluctuating particle and energy currents of the gas flowing between reservoirs or thermalizing surfaces at given particle densities or temperatures.

1. Introduction

Since 1872, Boltzmann's equation has provided the main paradigm of our understanding of irreversible phenomena [1]. In isolated systems such as a dilute gas in a container, the H-theorem established by Boltzmann with his equation shows that any velocity distribution for the particles irreversibly converges at long time towards the Maxwell velocity distribution characterizing the thermodynamic equilibrium [2]. This relaxation towards equilibrium is generated by successive binary collisions between the particles composing the gas. They are described as in chemical kinetics by the mass action law, requiring that the rate of binary collisions be proportional to the concentrations of particles of the corresponding velocities in every volume element where the collisions happen. For this reason, Boltzmann's equation is nonlinear as it is the case for the mean-field kinetic equations describing macroscopic chemical reactions, except that the particle velocities are not macroscopic observables [3]. Nevertheless, finer observables closer to the microscopic level of description and, especially, fluctuations remain outside the framework of Boltzmann's theory [1,2].

Since the forties, a fluctuating Boltzmann equation has been proposed which rules the local velocity distribution function as a random variable, much in analogy with Langevin's stochastic equation [4–13]. This formulation provides a description closer to the microscopic level and, thus, is more suitable to understand the properties of the fluctuations. Although they are known to be time-reversal symmetric at equilibrium because of the principle of detailed balancing, few results are available about fluctuations in nonequilibrium steady states.

The purpose of the present paper is to establish a time-reversal symmetry relation valid out of equilibrium for the fluctuating Boltzmann equation. Such relations are the subject of the so-called fluctuation theorems, which have been obtained in particular for stochastic processes, e.g., diffusion processes ruled by Langevin's equations and their associate Fokker–Planck equation or continuous-time Markovian jump processes [14–18]. In general, a fluctuation theorem holds for

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0378-4371/$ – see front matter
doi:10.1016/j.physa.2012.10.006

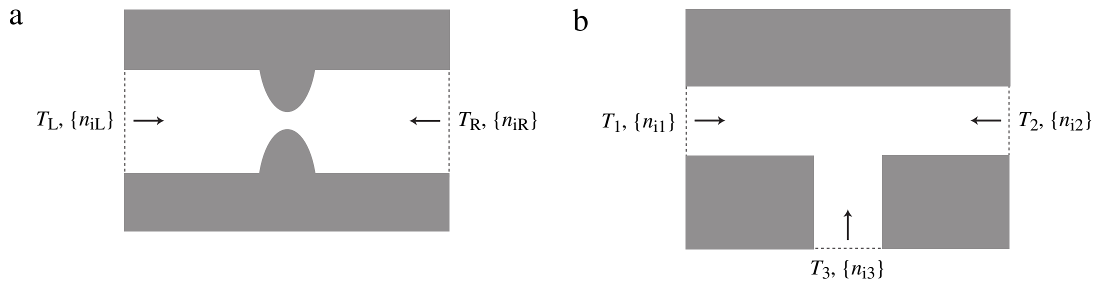

Fig. 1. Schematic representation of dilute or rarefied gases flowing through pores or pipes between reservoirs at given temperatures and particle densities. In gas mixtures, there are several particle species i and so many particle densities.

all the currents flowing across an open system in nonequilibrium steady states [19,20]. Such a theorem implies the second law of thermodynamics and it allows us to deduce generalizations of the Green–Kubo formulae and Onsager reciprocity relations for the nonlinear response properties [21,22]. Our aim is here to extend these fundamental results to the dilute and rarefied gases ruled by Boltzmann's equation [23–25]. We consider such gases flowing under nonequilibrium conditions in pores, pipes, or other ducts between several reservoirs, as illustrated in Fig. 1.

The paper is organized as follows. In Section 2, Boltzmann's equation is introduced as a mean-field equation in open geometries with gas–surface interactions. The symmetries of the collision kernel and, in particular, its time-reversal symmetry are discussed. In Section 3, the one-particle phase space is partitioned into cells and the coarse-grained master equation is obtained for the probability that the cells contain certain particle numbers. In Section 4, the diffusive approximation of the coarse-grained master equation is shown to lead to the fluctuating Boltzmann equation including the terms due to the contacts with the reservoirs. The time-reversal symmetry relation is proved in Section 5 where the corresponding fluctuation theorem is established. Conclusions are drawn in Section 6.

2. Boltzmann's equation as a mean-field kinetic equation

At the microscopic level of description, the motion of the particles composing the gas is ruled by Newton's equations for their positions and velocities $\{\mathbf{r}_n(t), \mathbf{v}_n(t)\}$. The one-particle distribution function is defined as the density to find one particle with the position $\mathbf{r}$ and the velocity $\mathbf{v}$ at the current time t:

$$f(\mathbf{r}, \mathbf{v}, t) \equiv \sum_n \delta\left[\mathbf{r} - \mathbf{r}_n(t)\right]\, \delta\left[\mathbf{v} - \mathbf{v}_n(t)\right] \tag{1}$$

for monoatomic particles without internal rotation or vibration. Given that the initial conditions of the particles are distributed according to some probability distribution for the whole system including the reservoirs, the one-particle distribution function (1) is a random variable, which may fluctuate. We may also consider its average value over the given probability distribution:

$$\langle f(\mathbf{r}, \mathbf{v}, t)\rangle \equiv \sum_n \langle \delta\left[\mathbf{r} - \mathbf{r}_n(t)\right]\, \delta\left[\mathbf{v} - \mathbf{v}_n(t)\right]\rangle, \tag{2}$$

which is expected to vary smoothly in space and time.

2.1. In the bulk of the flow

For a general classical system, the time evolution of the one-particle average distribution function (2) is ruled by the first equation of the Bogoliubov–Born–Green–Kirkwood–Yvon hierarchy [26–29]. The other equations of this hierarchy are ruling the many-particle average distribution functions. In the dilute-gas limit, the many-particle distribution functions factorize in terms of the one-particle function. The time evolution of the one-particle function is determined by the binary collisions and their differential cross section, which is obtained using classical scattering theory. Supposing that the particles are incoming every binary collision without statistical correlation as stated in the famous "Stosszahlansatz", Boltzmann's equation is deduced, which is a closed equation for the one-particle average distribution function (2) of the following form:

$$\frac{\partial\langle f\rangle}{\partial t} + \mathbf{v}\cdot\frac{\partial\langle f\rangle}{\partial \mathbf{r}} + \frac{\mathbf{F}}{m}\cdot\frac{\partial\langle f\rangle}{\partial \mathbf{v}} = \int d\mathbf{v}_2\, d\mathbf{v}_1'\, d\mathbf{v}_2'\; w\left(\mathbf{v}_1, \mathbf{v}_2|\mathbf{v}_1', \mathbf{v}_2'\right)\; \left(\langle f_1'\rangle\,\langle f_2'\rangle - \langle f_1\rangle\,\langle f_2\rangle\right) \tag{3}$$

where $\langle f\rangle = \langle f_1\rangle$ is the average distribution function at the position $\mathbf{r} = \mathbf{r}_1$ and the velocity $\mathbf{v} = \mathbf{v}_1$ of the first particle involved in the binary collision [26–29]. $\mathbf{F} = \mathbf{F}(\mathbf{r})$ is an external force field, which includes the repulsive forces of the walls of the duct. In general, the transition rate coefficients have the following symmetries:

$$\text{time-reversal symmetry: } w\left(\mathbf{v}_1, \mathbf{v}_2|\mathbf{v}_1', \mathbf{v}_2'\right) = w\left(-\mathbf{v}_1', -\mathbf{v}_2'| - \mathbf{v}_1, -\mathbf{v}_2\right), \tag{4}$$

$$\text{space-orthogonal symmetry: } w\left(\mathbf{v}_1, \mathbf{v}_2|\mathbf{v}_1', \mathbf{v}_2'\right) = w\left(\mathsf{R}\cdot\mathbf{v}_1,\ \mathsf{R}\cdot\mathbf{v}_2\middle|\,\mathsf{R}\cdot\mathbf{v}_1',\ \mathsf{R}\cdot\mathbf{v}_2'\right) \tag{5}$$