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

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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.

Keywords: Dilute gas, rarefied gas, nonequilibrium steady state, affinity, stochastic process, master equation.

I. 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, 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 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 II, 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 III, 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 IV, 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 V where the corresponding fluctuation theorem is established. Conclusions are drawn in section VI.
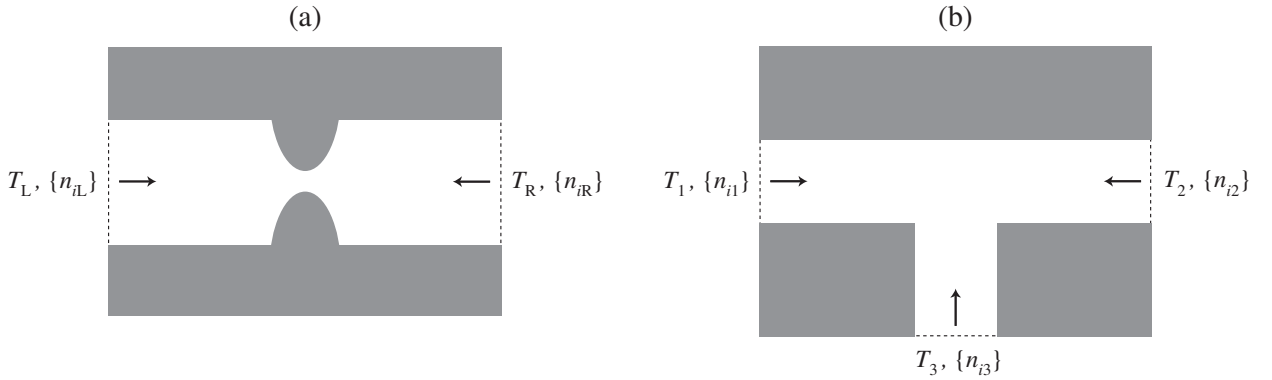
FIG. 1: Schematic representation of dilute or rarefied gases flowing through pores or pipes between reservoirs at given temperatures and particle densities. In gas mixtures, there are several particle species i and so many particle densities.

II. 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.

A. 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:

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

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

where R is a matrix belonging to the orthogonal group O(3) including spatial rotations and reflections [28, 29]. We also have the

$$\text{inversion symmetry:} \qquad w\left(\mathbf{v}_1, \mathbf{v}_2 | \mathbf{v}_1', \mathbf{v}_2'\right) = w\left(\mathbf{v}_1', \mathbf{v}_2' | \mathbf{v}_1, \mathbf{v}_2\right), \tag{6}$$

which is the symmetry under the time-reversal transformation combined with the spatial inversion of orthogonal matrix $\mathsf{R} = -\mathsf{I}$ where I is the identity matrix.

The transition rate coefficients are related to the differential cross section σ_{diff} of the binary collisions as

$$w\left(\mathbf{v}_1, \mathbf{v}_2 | \mathbf{v}_1', \mathbf{v}_2'\right) = \sigma_{\text{diff}}\ \delta\left(\mathbf{v}_1 + \mathbf{v}_2 - \mathbf{v}_1' - \mathbf{v}_2'\right)\ \delta\left(\mathbf{v}_1^2 + \mathbf{v}_2^2 - \mathbf{v}_1'^2 - \mathbf{v}_2'^2\right) \tag{7}$$

where the delta's express the conservation of linear momentum and kinetic energy in every binary collision. Setting $\mathbf{V}' = (\mathbf{v}_1' + \mathbf{v}_2')/2$ and $\mathbf{u}' = \mathbf{v}_1' - \mathbf{v}_2'$ and integrating over the velocities $d\mathbf{v}_1' d\mathbf{v}_2' = d\mathbf{V}' d\mathbf{u}' = d\mathbf{V}' u'^2 du' d\Omega$, Boltzmann's equation (3) takes its more usual form:

$$\frac{\partial \langle f \rangle}{\partial t} + \mathbf{v} \cdot \frac{\partial \langle f \rangle}{\partial \mathbf{r}} + \frac{\mathbf{F}}{m} \cdot \frac{\partial \langle f \rangle}{\partial \mathbf{v}} = \int d\mathbf{v}_2\ d\Omega\ \sigma_{\text{diff}}\ \|\mathbf{v}_1 - \mathbf{v}_2\|\ \left(\langle f_1' \rangle \langle f_2' \rangle - \langle f_1 \rangle \langle f_2 \rangle\right) \tag{8}$$

in terms of the differential cross section and the solid angle element $d\Omega$. For a gas of hard spheres of radius a, this cross section is given by $\sigma_{\text{diff}} = a^2$. Boltzmann's equation (8) conserves the total energy and the total number of particles.

In the absence of force field $\mathbf{F} = 0$, Boltzmann's equation is known to admit stationary solutions given by the overall equilibrium Maxwell-Boltzmann distributions:

$$f_{\text{eq}}(\mathbf{v}) = \left(\frac{m\beta}{2\pi}\right)^{3/2} n\ \exp(-\beta\epsilon) \qquad \text{with} \qquad \epsilon = \frac{1}{2} m \mathbf{v}^2 \tag{9}$$

for particles of mass m at the uniform temperature $T = (k_{\text{B}}\beta)^{-1}$ and density n. Together with the conservations of linear momentum and kinetic energy in the binary collisions, the time-reversal symmetry (4) implies the property of reciprocity:

$$w\left(\mathbf{v}_1, \mathbf{v}_2 | \mathbf{v}_1', \mathbf{v}_2'\right) f_{\text{eq}}(\mathbf{v}_1') f_{\text{eq}}(\mathbf{v}_2') = w\left(-\mathbf{v}_1', -\mathbf{v}_2' | -\mathbf{v}_1, -\mathbf{v}_2\right) f_{\text{eq}}(\mathbf{v}_1) f_{\text{eq}}(\mathbf{v}_2). \tag{10}$$

We notice that the same property still holds in an inertial frame moving at the velocity $\mathbf{V}_0$ where the equilibrium distribution is given by Eq. (9) with $\mathbf{v}$ replaced by $\mathbf{v} - \mathbf{V}_0$. Moreover, the property of reciprocity as well as the stationarity of Boltzmann's equation for the Maxwell-Boltzmann distribution hold locally at every space point in the system. These two features constitute the basis of what is called the local thermodynamic equilibrium in this system [26].

The main characteristic spatial scale of Boltzmann's theory is the *mean free path*:

$$\ell = \frac{1}{\sqrt{2}\,\sigma_{\text{tot}} n} \tag{11}$$

where $\sigma_{\text{tot}} = \int \sigma_{\text{diff}}\, d\Omega$ is the total cross section and n the particle density. The mean free path compares with two other spatial scales, namely, the interaction range which is of the order of the particle radius a, and the characteristic size L of the pipes, through which the gas is flowing. The description in terms of Boltzmann's equation is valid as long as the interaction range a remains significantly smaller than the other spatial scales:

$$a \ll \ell, L\,. \tag{12}$$

The condition $a \ll \ell$ requires that the gas is dilute because the total cross section goes as $\sigma_{\text{tot}} \sim a^2$ so that the particle density should be much smaller than its limit fixed by the particle volume: $n \ll a^{-3}$. Such gases may exist in two different regimes [23–25]: (1) If $a \ll \ell \ll L$, the dilute gas is well described by macroscopic hydrodynamics and Navier-Stokes equations, which can be deduced from Boltzmann's equation. (2) If $a \ll L \ll \ell$, the gas is said to be rarefied or in Knudsen regime, in which case Boltzmann's equation provides a unique reduced description of gas dynamics.

B.   At the boundaries

Several types of boundaries should be taken into account in open systems such as those depicted in Fig. 1.

1. At the reservoirs

First, there are the inlets from the reservoirs, by which gas is also evacuated in the opposite directions. The contacts with the reservoirs contribute to Eq. (3) by terms of the form:

$$\frac{\partial \langle f \rangle}{\partial t}\bigg|^{\mathrm{R}} = \sum_s \int_s d^2 S \, \delta(\mathbf{r} - \mathbf{r}_s) \, (\mathbf{n} \cdot \mathbf{v}) \, \theta(\mathbf{n} \cdot \mathbf{v}) \, [f_s(\mathbf{v}) - \langle f(\mathbf{r}, \mathbf{v}; t) \rangle] \tag{13}$$

where $\theta(x)$ is Heaviside's function, $\mathbf{r}_s$ is the position of a point on the surface s separating the system from the corresponding reservoir, $\mathbf{n}$ is a unit vector normal to the surface s and directed inside the system and

$$f_s(\mathbf{v}) = \left(\frac{m\beta_s}{2\pi}\right)^{3/2} n_s \, \exp(-\beta_s \, \epsilon) \qquad \text{with} \qquad \epsilon = \frac{1}{2} m \mathbf{v}^2 \tag{14}$$

is the Maxwell-Boltzmann distribution function of the gas incoming through the surface s from the reservoir at the temperature $T_s = (k_\mathrm{B} \beta_s)^{-1}$ and the particle density n_s. The contacts with the reservoirs are carried out at surfaces which are assumed to be far enough in the pipes for the flow profile to be independent of the details of the boundary conditions. We notice that the total energy and the total number of particles are no longer conserved inside open systems.

The inlets drive the system out of equilibrium if the reservoirs are at different temperatures or particle densities. For instance, in the case of the system of Fig. 1a with two reservoirs $s = \mathrm{L}, \mathrm{R}$ and one species of particles, the flow is characterized by four control parameters: the two temperatures and the two particle densities, $\{T_s, n_s\}_{s=\mathrm{L},\mathrm{R}}$. By convention, one of both reservoirs may be used as the reference reservoir with respect to which nonequilibrium conditions would be established. This role can be played by the right-hand reservoir that fixes the reference temperature T_R and the reference particle density n_R (or the corresponding chemical potential μ_R). The nonequilibrium constraints are thus determined by the two remaining control parameters, which define the thermodynamic forces also called the affinities:

$$\text{thermal affinity:} \qquad A_E = \beta_\mathrm{R} - \beta_\mathrm{L} \,, \tag{15}$$

$$\text{chemical affinity:} \qquad A_N = \beta_\mathrm{L}\mu_\mathrm{L} - \beta_\mathrm{R}\mu_\mathrm{R} = \ln \frac{n_\mathrm{L}\beta_\mathrm{L}^{3/2}}{n_\mathrm{R}\beta_\mathrm{R}^{3/2}} \tag{16}$$

where $\mu_{\mathrm{L},\mathrm{R}}$ are the chemical potentials of the monoatomic gas in the left- and right-hand reservoirs.

We notice that more than two affinities are defined for an open system in contact with more than two reservoirs at different temperatures or particle densities, as illustrated in Fig. 1b. In general, if the system is composed of r reservoirs and contains c particle species, there are $r(c + 1)$ control parameters $\{T_s, n_{is}\}$ with $s = 1, 2, ..., r$ and $i = 1, 2, ..., c$. If all the reservoirs communicate with each other through the open system, one of the r reservoirs can be taken as the reference reservoir so that the nonequilibrium conditions would be fixed by $(r-1)(c+1)$ different affinities. If some affinities are non vanishing, the system may reach a nonequilibrium steady state in the long-time limit. If all the affinities are vanishing, the system relaxes towards the thermodynamic equilibrium state and Boltzmann's equation admits the corresponding Maxwell-Boltzmann distribution as stationary solution.

2. At the surfaces

Now, we consider the interaction of the gas with solid surfaces, on which the particles are scattered.

In the simplest model, the gas particles undergo elastic collisions on the surface, so that the outgoing velocity is given by

$$\mathbf{v}' = \mathbf{v} - 2(\mathbf{n} \cdot \mathbf{v}) \, \mathbf{n} \tag{17}$$

where $\mathbf{n}$ is a unit vector normal to the surface at the point of collision. Accordingly, the velocity component perpendicular to the surface changes its sign: $\mathbf{n} \cdot \mathbf{v}' = -\mathbf{n} \cdot \mathbf{v}$. Moreover, the kinetic energy is conserved because $\mathbf{v}'^2 = \mathbf{v}^2$ at every collision. Therefore, the contact of the gas with the surface does not change its temperature or density, as if the gas was in a force field $\mathbf{F}(\mathbf{r})$ that is very steep at the surface. In this case, the contribution of the surface to Eq. (3) would be of the form

$$\frac{\partial \langle f \rangle}{\partial t}\bigg|^{\mathrm{S}} = \int_s d^2 S \, \delta(\mathbf{r} - \mathbf{r}_s) \, (\mathbf{n} \cdot \mathbf{v}) \, \theta(\mathbf{n} \cdot \mathbf{v}) \, \{\langle f[\mathbf{r}, \mathbf{v} - 2(\mathbf{n} \cdot \mathbf{v}) \, \mathbf{n}; t] \rangle - \langle f(\mathbf{r}, \mathbf{v}; t) \rangle\} \,, \tag{18}$$

which conserves the total energy and the total number of particles inside the system.

In general, the interaction of the gas with the surface of a solid depends on many different aspects. The scattering of particles with surfaces has been much studied and many processes are known besides elastic collisions: adsorption, desorption, transport on the surface, transport into or from the bulk of the solid, or possible reactions [30]. The solid surface is typically at some temperature that may differ from the temperature of the gas and a transfer of energy can go through the surface inside the solid. Here, the solid forming the container is supposed to have a high enough thermal conductivity so that its temperature is uniform. Under certain thermodynamic conditions of pressure and temperature, gas particles may diffuse into the solid and form a stable thermodynamic phase such as solid hydrides, oxides, or nanoporous composites. Under nonequilibrium conditions, the solid could thus become a sink or a source of gas particles, in which case the difference of chemical potentials of the particles between the gas and the solid would add an extra affinity. For simplicity, this situation is not considered here and only thermal exchanges between the gas and the solid are envisaged. Surface adsorption and desorption may also occur under the assumption that the surface is in local thermodynamic equilibrium with the gas so that the thermodynamic state of the surface (in particular, the particle coverages) is stationary. Under such circumstances, the contribution of the surface to Eq. (3) would be of the form

$$\frac{\partial \langle f \rangle}{\partial t}\bigg|^{\mathrm{S}} = \int_s d^2S \, \delta(\mathbf{r} - \mathbf{r}_s) \left[\int_{\mathbf{n} \cdot \mathbf{v}' < 0} d\mathbf{v}' |\mathbf{n} \cdot \mathbf{v}'| \, p_{\mathbf{r}}(\mathbf{v}|\mathbf{v}') \, \langle f(\mathbf{r}, \mathbf{v}'; t) \rangle - (\mathbf{n} \cdot \mathbf{v}) \, \theta(\mathbf{n} \cdot \mathbf{v}) \, \langle f(\mathbf{r}, \mathbf{v}; t) \rangle \right] \qquad (19)$$

where $p_{\mathbf{r}}(\mathbf{v}|\mathbf{v}')$ is the probability density that a particle impinging the surface at the position $\mathbf{r}$ with the velocity $\mathbf{v}'$ and $\mathbf{n} \cdot \mathbf{v}' < 0$ will be scattered to the velocity $\mathbf{v}$ such that $\mathbf{n} \cdot \mathbf{v} > 0$ [25]. We notice that the probability density does not depend on the position $\mathbf{r}$ if the surface is homogeneous and the scattering process is the same everywhere. In general, this function is normalized according to

$$\int_{\mathbf{n} \cdot \mathbf{v} > 0} p_{\mathbf{r}}(\mathbf{v}|\mathbf{v}') \, d\mathbf{v} = 1 \qquad \text{if} \qquad \mathbf{n} \cdot \mathbf{v}' < 0 \qquad (20)$$

and it satisfies the following two properties. The first one guarantees the preservation of equilibrium at the temperature T_s of the surface:

$$|\mathbf{n} \cdot \mathbf{v}| \, f_s(\mathbf{v}) = \int_{\mathbf{n} \cdot \mathbf{v}' < 0} p_{\mathbf{r}}(\mathbf{v}|\mathbf{v}') \, |\mathbf{n} \cdot \mathbf{v}'| \, f_s(\mathbf{v}') \, d\mathbf{v}' \qquad (21)$$

where $f_s(\mathbf{v})$ is the Maxwell-Boltzmann equilibrium distribution (14) at the temperature of the wall. The second is the property of reciprocity:

$$|\mathbf{n} \cdot \mathbf{v}'| \, f_s(\mathbf{v}') \, p_{\mathbf{r}}(\mathbf{v}|\mathbf{v}') = |\mathbf{n} \cdot \mathbf{v}| \, f_s(\mathbf{v}) \, p_{\mathbf{r}}(-\mathbf{v}'| - \mathbf{v}) , \qquad (22)$$

which is implied by the time-reversal symmetry of the underlying microscopic dynamics and the condition of local thermodynamic equilibrium of the surface at the temperature T_s of the Maxwell-Boltzmann equilibrium distribution $f_s(\mathbf{v})$ [25]. The contribution (19) conserves the total number of particles, but the total energy is not conserved during typical gas-surface interactions.

The special case (18) of elastic collision is recovered for

$$p_{\mathbf{r}}(\mathbf{v}|\mathbf{v}') = \delta \left[\mathbf{v}' - \mathbf{v} + 2(\mathbf{n} \cdot \mathbf{v}) \, \mathbf{n} \right] \qquad (23)$$

uniformly on the whole surface, which satisfies all the aforementioned properties. However, energy exchange typically happens during the lapse of time between the adsorption of the gas particles and their desorption. If a local thermodynamic equilibrium at the temperature of the solid is assumed, the particles are expected to be desorbed with the corresponding Maxwell-Boltzmann distribution. A very simple model achieving this condition is provided by the kernel

$$p_{\mathbf{r}}(\mathbf{v}|\mathbf{v}') = |\mathbf{n} \cdot \mathbf{v}| \, \frac{(m\beta_s)^2}{2\pi} \, \exp(-\beta_s \epsilon) \qquad \text{with} \qquad \epsilon = \frac{1}{2} m\mathbf{v}^2 , \qquad (24)$$

which is independent of the other velocity $\mathbf{v}'$ and which also satisfies the required properties. More realistic gas-surface kernels have been considered and discussed in the literature [25]. In principle, the form of the probability density should be determined by studying the quantum scattering of the particles with the surface on the basis of their atomic structure [30].

A gas of one species flowing in an open system connected to r reservoirs and containing w walls at so many different temperatures is characterized by $2r + w$ control parameters, namely, the $r + w$ temperatures of the reservoirs and

the walls and the r particle densities of the reservoirs. If one of the r reservoirs plays the role of reference, the nonequilibrium conditions are thus determined by $r + w - 1$ thermal affinities and $r - 1$ chemical affinities.

Remark. There exist further possible situations if surfaces are in relative motion with respect to one another, as in Couette-Taylor flows [25]. In such cases, the relative velocities of the surfaces are extra parameters controlling the nonequilibrium driving of the flow. In some other circumstances, the linear momentum of the flow can be conserved, e.g., if the gas moves freely or between parallel flat surfaces on which the particles undergo elastic collisions. In this case, the velocity distributions of the gas incoming from different reservoirs could have non-zero average velocities and an extra affinity is associated with the difference between the average velocities [31]. However, linear momentum is not conserved for typical geometries of the surfaces and gas-surface interactions, in which cases the thermal and chemical affinities are sufficient to characterize the nonequilibrium constraints on particle transport.

III. THE COARSE-GRAINED MASTER EQUATION

A. Generalities

At the mesoscopic level of description, the quantities of interest are typically fluctuating. This is for instance the case for transport processes or chemical reactions described at the mesoscale by stochastic equations of Langevin type and their associated Fokker-Planck equation, instead of macroscopic kinetic equations [3, 12, 13, 32–35].

Similar considerations have been applied to the Boltzmann equation and related kinetic equations [3–13]. The idea consists in supposing that the fluctuating distribution function (1) is ruled by a stochastic process. In order to obtain the master equation of this process, the one-particle phase space of the position and velocity variables $(\mathbf{r}, \mathbf{v})$ can be partitioned into fictitious cells centered around the phase-space points $(\mathbf{r}_\alpha, \mathbf{v}_\alpha)$. These cells are of volume $\Delta r^3 \Delta v^3$. The number of particles in the cell α at the current time t is defined by

$$N_\alpha(t) \equiv \int_\alpha f(\mathbf{r}, \mathbf{v}, t)\, d\mathbf{r}\, d\mathbf{v} \simeq f(\mathbf{r}_\alpha, \mathbf{v}_\alpha, t)\, \Delta r^3 \Delta v^3 \,. \tag{25}$$

Since the distribution function f is fluctuating, these particle numbers are random variables undergoing jumps every time a particle exits or enters the corresponding cell.

The probability to find $\{N_\alpha\}$ particles in the cells $\{\alpha\}$ at the current time t is denoted as

$$P = P(\mathbf{N}) = P\left(\{N_\alpha\}\right) \,. \tag{26}$$

When transitions happen, particles are exchanged between the cells so that it is useful to introduce the rising and lowering operators

$$\hat{E}_\alpha^{\pm 1} \Phi(..., N_\alpha, ...) = \Phi(..., N_\alpha \pm 1, ...) \tag{27}$$

acting on any function $\Phi(\mathbf{N}) = \Phi(\{N_\alpha\})$ by adding or removing one particle in the cell α [7, 12]. These operators can be written as

$$\hat{E}_\alpha^{\pm 1} = \exp\left(\pm \frac{\partial}{\partial N_\alpha}\right) \,, \tag{28}$$

which implies that they are adjoint to each other:

$$\left(\hat{E}_\alpha^{\pm 1}\right)^\dagger = \hat{E}_\alpha^{\mp 1} \,. \tag{29}$$

The master equation ruling the probability distribution (26) has the general form

$$\frac{dP}{dt} = \hat{L}\, P \qquad \text{with} \qquad \hat{L} = \hat{L}^{\mathrm{C}} + \hat{L}^{\mathrm{F}} + \hat{L}^{\mathrm{S}} + \hat{L}^{\mathrm{R}} \tag{30}$$

where the different linear operators describe the following contributions [7, 11, 12]:

$$\text{binary collisions:} \qquad \hat{L}^{\mathrm{C}} P = \sum_{\lambda\mu\rho\sigma} W^{\mathrm{C}}_{\lambda\mu\rho\sigma} \left(\hat{E}^{-1}_\lambda \hat{E}^{-1}_\mu \hat{E}^{+1}_\rho \hat{E}^{+1}_\sigma - 1 \right) N_\rho N_\sigma P \, ; \tag{31}$$

$$\text{free flights:} \qquad \hat{L}^{\mathrm{F}} P = \sum_{\lambda\rho} W^{\mathrm{F}}_{\lambda\rho} \left(\hat{E}^{-1}_\lambda \hat{E}^{+1}_\rho - 1 \right) N_\rho P \, ; \tag{32}$$

$$\text{surface collisions:} \qquad \hat{L}^{\mathrm{S}} P = \sum_{\lambda\rho} W^{\mathrm{S}}_{\lambda\rho} \left(\hat{E}^{-1}_\lambda \hat{E}^{+1}_\rho - 1 \right) N_\rho P \, ; \tag{33}$$

$$\text{exchanges with reservoirs:} \qquad \hat{L}^{\mathrm{R}} P = \sum_{\lambda} W^{\mathrm{R,in}}_{\lambda} \left(\hat{E}^{-1}_\lambda - 1 \right) P + \sum_{\lambda} W^{\mathrm{R,out}}_{\lambda} \left(\hat{E}^{+1}_\lambda - 1 \right) N_\lambda P \, . \tag{34}$$

The contribution (31) involves two lowering and two rising operators because two particles are incoming and outgoing every binary collision. The contribution (32) involves only one lowering and one rising operator because the free flight of a particle between two next-neighboring cells causes the particle number in one cell to decrease by a unit while the particle number increases by this unit in the other cell. The same concerns the contribution (33) of surface collisions whether they are elastic or inelastic. Finally, the contributions (34) due to the in- and out-flows of particles with the reservoirs only involve a single lowering or rising operator because they describe particles appearing in or disappearing from the system itself. Accordingly, the contributions (31)-(33) conserve the total number of particles inside the system, although the contributions (34) do not. Furthermore, each process removing particles from a cell should have a vanishing transition rate if no particle is present in the cell. Accordingly, the transition rate of this process should be proportional to the numbers of required particles in the corresponding cell. This explains that the transition rate of the binary collision $\rho\sigma \to \lambda\mu$ contains the two factors $N_\rho N_\sigma$ in Eq. (31). For the same reason, one such factor N_ρ is contained in the transition rates (32) and (33) of the free flights and surface collisions $\rho \to \lambda$, as well as in the transition rate of the exit $\lambda \to s$ of a particle to some reservoir s in the last terms of Eq. (34). The rate coefficients W's of the different contributions will be specified here below.

The time evolution of the average particle numbers

$$\langle N_\alpha \rangle \equiv \sum_{\mathbf{N}} N_\alpha \, P(\mathbf{N}) \tag{35}$$

and their higher statistical moments is ruled by a hierarchy of equations that can be deduced from the master equation (30) [12]. For dilute gases, the second moments can be supposed to be factorized in terms of the averages themselves [11–13], whereupon these latter quantities obey closed mean-field equations:

$$\frac{d}{dt}\langle N_\alpha \rangle = \frac{d}{dt}\langle N_\alpha \rangle \Big|^{\mathrm{C}} + \frac{d}{dt}\langle N_\alpha \rangle \Big|^{\mathrm{F}} + \frac{d}{dt}\langle N_\alpha \rangle \Big|^{\mathrm{S}} + \frac{d}{dt}\langle N_\alpha \rangle \Big|^{\mathrm{R}} \tag{36}$$

with the following contributions:

$$\text{binary collisions:} \qquad \frac{d}{dt}\langle N_\alpha \rangle \Big|^{\mathrm{C}} = 2 \sum_{\mu\rho\sigma} W^{\mathrm{C}}_{\alpha\mu\rho\sigma} \langle N_\rho \rangle \langle N_\sigma \rangle - 2 \sum_{\lambda\mu\sigma} W^{\mathrm{C}}_{\lambda\mu\alpha\sigma} \langle N_\alpha \rangle \langle N_\sigma \rangle \, ; \tag{37}$$

$$\text{free flights:} \qquad \frac{d}{dt}\langle N_\alpha \rangle \Big|^{\mathrm{F}} = \sum_{\rho} W^{\mathrm{F}}_{\alpha\rho} \langle N_\rho \rangle - \sum_{\lambda} W^{\mathrm{F}}_{\lambda\alpha} \langle N_\alpha \rangle \, ; \tag{38}$$

$$\text{surface collisions:} \qquad \frac{d}{dt}\langle N_\alpha \rangle \Big|^{\mathrm{S}} = \sum_{\rho} W^{\mathrm{S}}_{\alpha\rho} \langle N_\rho \rangle - \sum_{\lambda} W^{\mathrm{S}}_{\lambda\alpha} \langle N_\alpha \rangle \, ; \tag{39}$$

$$\text{exchanges with reservoirs:} \qquad \frac{d}{dt}\langle N_\alpha \rangle \Big|^{\mathrm{R}} = W^{\mathrm{R,in}}_{\alpha} - W^{\mathrm{R,out}}_{\alpha} \langle N_\alpha \rangle \, . \tag{40}$$

We notice that the master equation (30) is linear, although the mean-field kinetic equations (36) are nonlinear because of the terms (37) due to the binary collisions [3].

At equilibrium, the stationary solutions of the coarse-grained master equation (30) are given by multiple Poisson distributions of the following form:

$$P_{\mathrm{eq}}(\mathbf{N}) = \prod_{\alpha} \mathrm{e}^{-\langle N_\alpha \rangle} \frac{\langle N_\alpha \rangle^{N_\alpha}}{N_\alpha !} \qquad \text{with} \qquad \langle N_\alpha \rangle = f_{\mathrm{eq}}(\mathbf{v}_\alpha) \, \Delta r^3 \, \Delta v^3 \tag{41}$$

being the average values of the particle numbers in every cell α given in terms of the overall equilibrium Maxwell-Boltzmann distribution (9) at the uniform temperature $T = (k_{\mathrm{B}}\beta)^{-1}$ and density n. This multiple Poisson distribution represents the equilibrium state because it corresponds to the Maxwell-Boltzmann distribution (9) that is the equilibrium stationary solution of Boltzmann's equation (3).

B. In the bulk of the flow

1. Binary collisions

The rate coefficient of the transition $\rho\sigma \to \lambda\mu$ due to some binary collision is given by [11, 12]

$$W^{\mathrm{C}}_{\lambda\mu\rho\sigma} = \frac{1}{2\Delta r^3 \Delta v^6} \int_\lambda d\mathbf{v}_1 \int_\mu d\mathbf{v}_2 \int_\rho d\mathbf{v}'_1 \int_\sigma d\mathbf{v}'_2 \, w\left(\mathbf{v}_1, \mathbf{v}_2 | \mathbf{v}'_1, \mathbf{v}'_2\right) \delta_{\mathbf{r}_\mu, \mathbf{r}_\lambda} \delta_{\mathbf{r}_\rho, \mathbf{r}_\lambda} \delta_{\mathbf{r}_\sigma, \mathbf{r}_\lambda} \,. \tag{42}$$

These transitions do not change the positions but modify the velocities according to the collision rule. We notice that the symmetries (4)-(6) of the transition rate coefficients of Boltzmann's equation imply similar symmetries for the rate coefficients (42):

$$\text{time-reversal symmetry:} \qquad W^{\mathrm{C}}_{\lambda\mu\rho\sigma} = W^{\mathrm{C}}_{\rho^{\mathrm{T}}\sigma^{\mathrm{T}}\lambda^{\mathrm{T}}\mu^{\mathrm{T}}} \,, \tag{43}$$

$$\text{inversion symmetry:} \qquad W^{\mathrm{C}}_{\lambda\mu\rho\sigma} = W^{\mathrm{C}}_{\rho\sigma\lambda\mu} \,, \tag{44}$$

where $\alpha^{\mathrm{T}} = (\mathbf{r}_\alpha, \mathbf{v}_\alpha)^{\mathrm{T}} = (\mathbf{r}_\alpha, -\mathbf{v}_\alpha)$ is the time-reversed cell corresponding to the cell α. Moreover, since the binary-collision terms (31) of the master equation are summed over the four indices, the following symmetries also hold [8]

$$W^{\mathrm{C}}_{\lambda\mu\rho\sigma} = W^{\mathrm{C}}_{\mu\lambda\rho\sigma} = W^{\mathrm{C}}_{\lambda\mu\sigma\rho} = W^{\mathrm{C}}_{\mu\lambda\sigma\rho} \,. \tag{45}$$

The rate coefficients (42) also satisfy the property of reciprocity:

$$W^{\mathrm{C}}_{\lambda\mu\rho\sigma} \langle N_\rho \rangle_{\mathrm{eq}} \langle N_\sigma \rangle_{\mathrm{eq}} = W^{\mathrm{C}}_{\rho^{\mathrm{T}}\sigma^{\mathrm{T}}\lambda^{\mathrm{T}}\mu^{\mathrm{T}}} \langle N_\lambda \rangle_{\mathrm{eq}} \langle N_\mu \rangle_{\mathrm{eq}} \,, \tag{46}$$

so that the coarse-grained master equation (30) preserves the local thermodynamic equilibrium. The multiple Poisson distribution (41) is symmetric under time reversal because the Maxwell-Boltzmann distribution is invariant under velocity reversal $\mathbf{v} \to -\mathbf{v}$ so that $\langle N_\alpha \rangle = \langle N_{\alpha^{\mathrm{T}}} \rangle$ at equilibrium. Therefore, the transitions due to binary collisions obey the principle of detailed balancing, according to which the probabilities of every transition are equal to those of the opposite transition at the thermodynamic equilibrium [12, 13, 36].

2. Free flights

The rate coefficient of the events during which one particle is moving in free flight $\rho \to \lambda$ from the cell ρ to the cell λ is given by

$$W^{\mathrm{F}}_{\lambda\rho} = \frac{1}{\Delta r} \left(\mathbf{n}_{\lambda\rho} \cdot \mathbf{v}\right) \theta(\mathbf{n}_{\lambda\rho} \cdot \mathbf{v}) \, \delta_{\mathbf{r}_\lambda, \mathbf{r}_\rho + \Delta r \, \mathbf{n}_{\lambda\rho}} \delta_{\mathbf{v}_\lambda, \mathbf{v}_\rho} \tag{47}$$

where $\mathbf{n}_{\lambda\rho}$ is a unit vector directed from the center $\mathbf{r}_\rho$ of the cell ρ to the center $\mathbf{r}_\lambda$ of the cell λ [11, 13]. The Kronecker delta $\delta_{\mathbf{r}_\lambda, \mathbf{r}_\rho + \Delta r \, \mathbf{n}_{\lambda\rho}}$ expresses the fact that the transition occurs between nearest-neighboring cells such that $\mathbf{r}_\lambda = \mathbf{r}_\rho + \Delta r \, \mathbf{n}_{\lambda\rho}$. The other Kronecker delta $\delta_{\mathbf{v}_\lambda, \mathbf{v}_\rho}$ means that the velocity remains constant during the free flight. In the case where the particle undergoes an acceleration, $\delta_{\mathbf{v}_\lambda, \mathbf{v}_\rho}$ should be replaced by the appropriate expression taking into account the force field $\mathbf{F}(\mathbf{r})$ acting on the particle. Since the one-particle motion is time-reversal symmetric, the corresponding rate coefficients have the symmetry:

$$\text{time-reversal symmetry:} \qquad W^{\mathrm{F}}_{\lambda\rho} = W^{\mathrm{F}}_{\rho^{\mathrm{T}}\lambda^{\mathrm{T}}} \,. \tag{48}$$

The symmetry (48) holds because $\mathbf{n}_{\lambda\rho} = -\mathbf{n}_{\rho\lambda}$. Moreover, the rate coefficients (47) satisfy the property of reciprocity:

$$W^{\mathrm{F}}_{\lambda\rho} \langle N_\rho \rangle_{\mathrm{eq}} = W^{\mathrm{F}}_{\rho^{\mathrm{T}}\lambda^{\mathrm{T}}} \langle N_\lambda \rangle_{\mathrm{eq}} \tag{49}$$

where $\langle N_\alpha \rangle_{\mathrm{eq}}$ denotes the average number of particles in the cell α at the equilibrium state (41). Accordingly, the transitions due to free flights also obey the principle of detailed balancing at equilibrium.

In the dilute-gas limit [11–13], we recover Boltzmann's equation (3) in the bulk of the flow from Eqs. (36)-(38) with the rate coefficients (42) and (47).

C. At the boundaries

1. At the reservoirs

For open systems, the partition into cells $\{\alpha\}$ should be carried out in a finite volume between the reservoirs. The particles are entering and leaving the system from and to the reservoirs. These specific motions are ruled by the flow operator $\hat{L}^{\mathrm{FR}} = \hat{L}^{\mathrm{F}} + \hat{L}^{\mathrm{R}}$, including the contributions of the free flights (32) and the exchanges with the reservoirs (34). The key point is that this operator depends on the boundary conditions imposed on the system by the temperatures and particle densities of the flows incoming from the reservoirs. We first consider the simplest case of free flight between two reservoirs, as schematically depicted in Fig. 2.
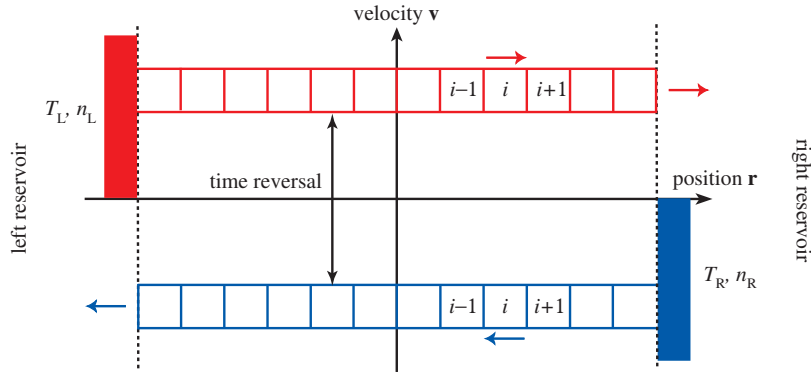

FIG. 2: Schematic phase portrait of free flights between two reservoirs from which the particles are incoming with different temperatures and densities.

The time-reversal transformation $(\mathbf{r}, \mathbf{v}) \to (\mathbf{r}, -\mathbf{v})$ maps the trajectories with positive velocity coming from the left-hand reservoir onto those with negative velocity coming from the right-hand reservoir. The phase space between both reservoirs is partitioned into cells. The cells at the boundaries exchange particles with the reservoirs. The particles move to the corresponding reservoir when they exit the open system. However, they enter into the system with a Maxwell-Boltzmann distribution at the temperature and density of the reservoir from which they come. Accordingly, the rate of the transition $N_\alpha \to N_\alpha + 1$ due to the entrance of one particle into a cell α in contact with one of both reservoirs depends on the temperature and density of this reservoir, as it is the case in the master-equation formulation of diffusion [34]. In the simple geometry of Fig. 2, the flow operator for particles in free flights at the velocities $\pm v$ acts on functions $\Phi(\{N_{i,\pm}\}_{i=1}^I)$ where $N_{i,\pm}$ is the number of particles in the cell at the position i and velocity $\pm v$. The free flight from one reservoir to the other is partitioned into I cells of size Δr so that the cell index i runs from $i = 1$ to $i = I$. For the particles of velocity $\pm v$, the flow operator with the inlets from the reservoirs would be:

$$\hat{L}^{\mathrm{FR}}\Phi = \frac{v}{\Delta r}\left[(\hat{E}_{1,+}^{-1} - 1)\langle N_+\rangle_{\mathrm{L}}\Phi + \sum_{i=1}^{I-1}(\hat{E}_{i,+}^{+1}\hat{E}_{i+1,+}^{-1} - 1)N_{i,+}\Phi + (\hat{E}_{I,+}^{+1} - 1)N_{I,+}\Phi \right.$$

$$\left. + (\hat{E}_{1,-}^{+1} - 1)N_{1,-}\Phi + \sum_{i=1}^{I-1}(\hat{E}_{i+1,-}^{+1}\hat{E}_{i,-}^{-1} - 1)N_{i+1,-}\Phi + (\hat{E}_{I,-}^{-1} - 1)\langle N_-\rangle_{\mathrm{R}}\Phi \right] \quad (50)$$

In the first term of this expression, $\langle N_+\rangle_{\mathrm{L}} = f_{\mathrm{L}}\Delta r^3\Delta v^3$ denotes the average number of particles incoming the cell $(1, +)$ with the velocity $+v$ from the left-hand reservoir at the temperature T_{L} and density n_{L}. In the last term, $\langle N_-\rangle_{\mathrm{R}} = f_{\mathrm{R}}\Delta r^3\Delta v^3$ is the average number of particles incoming the cell $(I, -)$ with the velocity $-v$ from the right-hand reservoir at the temperature T_{R} and density n_{R}. These average numbers can thus be expressed in terms of the equilibrium Maxwell-Boltzmann distribution function (14) in the corresponding reservoir $s = \mathrm{L}$ or R. For simplicity, only the particles moving at the kinetic energy $\epsilon = mv^2/2$ in one direction are here considered. We point out that the flow operator (50) does not conserve the total number of particles and the total energy.

The average particle numbers at the reservoirs are related to the thermal and chemical affinities (15) and (16) according to

$$A = \epsilon A_E + A_N = \ln\frac{\langle N_+\rangle_{\mathrm{L}}}{\langle N_-\rangle_{\mathrm{R}}} = \ln\frac{f_{\mathrm{L}}}{f_{\mathrm{R}}}. \quad (51)$$

The stationary solution of the master equation (30) for non-vanishing values of the affinities gives the invariant probability distribution of the corresponding nonequilibrium steady state. At equilibrium, the stationary solution of the master equation (30) is the multiple Poisson distribution (41) so that the temperatures and chemical potentials are equal and all the affinities are vanishing.

2. At the surfaces

In the case of elastic collisions on a surface, the particle follows a deterministic orbit which is piecewise straight. Let us consider an orbit coming from the right-hand reservoir, colliding on the surface and going back to the same reservoir. The speed $\|\mathbf{v}\|$ is conserved during the whole flight although the velocity direction undergoes the specular reflection given by Eq. (17). This is the case for every orbit of this kind. Accordingly, the motion along such orbits can be described as before by a partition into I cells of size Δr so that the cell index i runs from $i = 1$ to $i = I$. For an orbit interrupted by a specular reflection, the flow operator would be:

$$\hat{L}^{\mathrm{FS}}\Phi = \frac{v}{\Delta r}\left[(\hat{E}_{1,-}^{+1}\hat{E}_{1,+}^{-1} - 1)N_{1,-}\Phi + \sum_{i=1}^{I-1}(\hat{E}_{i,+}^{+1}\hat{E}_{i+1,+}^{-1} - 1)N_{i,+}\Phi + (\hat{E}_{I,+}^{+1} - 1)N_{I,+}\Phi \right.$$
$$\left. + \sum_{i=1}^{I-1}(\hat{E}_{i+1,-}^{+1}\hat{E}_{i,-}^{-1} - 1)N_{i+1,-}\Phi + (\hat{E}_{I,-}^{-1} - 1)\langle N_{-}\rangle_{\mathrm{R}}\Phi \right]. \tag{52}$$

Comparing with Eq. (50), we see that all the terms are now of propagative type except the terms at the right-hand reservoirs, which are the same as before. This means that the operator is of the same type as for a free flight from the right-hand reservoir back to itself and no difference in temperature or particle density manifests itself in this case.

The situation is different in the case where gas-surface interactions induce energy exchange described for instance by Eq. (19) with the simple thermal kernel (24). To fix the ideas, the surface is taken as $z = 0$ so that the normal unit vector is $\mathbf{n} = (0, 0, 1)$. If we discretize position and velocity, the corresponding operator in the coarse-grained master equation is given by

$$\hat{L}^{\mathrm{S}}\Phi = \sum_{\mathbf{r}}\delta_{z,0}\sum_{\substack{\mathbf{v}\\v_z>0}}\sum_{\substack{\mathbf{v}'\\v_z'<0}}\Delta v^3\,\frac{|v_z'|}{\Delta r}\,p(\mathbf{v}|\mathbf{v}')\left(\hat{E}_{\mathbf{rv}'}^{+1}\hat{E}_{\mathbf{rv}}^{-1} - 1\right)N_{\mathbf{rv}}\,\Phi \tag{53}$$

expressing the adsorption of a particle of velocity $\mathbf{v}'$ with $v_z' < 0$ and its desorption at the velocity $\mathbf{v}$ with $v_z > 0$ distributed according to a kernel satisfying the three properties (20), (21), and (22) inducing a thermalization at the temperature T_s of the surface. Accordingly, the total number of particles is conserved by this operator, although the total energy is not conserved if the collisions are inelastic at the surface. We notice that the operator (53) should be added to the free-flight operator $\hat{L}^{\mathrm{F}}$ to get the corresponding flow operator $\hat{L}^{\mathrm{FS}}$.

IV. THE FLUCTUATING BOLTZMANN EQUATION

In the diffusive limit, a functional master equation of Fokker-Planck type is deduced from the coarse-grained master equation (30) [11–13]. The diffusive limit is reached by considering cells containing sufficiently large numbers of particles that they can be described by Gaussian distributions while taking small enough cells to reach the continuum limit. The resulting functional equation of Fokker-Planck type rules the time evolution of the probability density functional, $\mathcal{P}[f] = \mathcal{P}[f(\mathbf{r}, \mathbf{v})]$, that the random distribution function (1) should take the given form $f(\mathbf{r}, \mathbf{v})$ at the current time t. In the basic situation without contact with reservoirs or thermalizing surfaces, the functional master equation writes:

$$\frac{\partial}{\partial t}\mathcal{P}[f] = -\int d\mathbf{r}\,d\mathbf{v}\,\frac{\delta}{\delta f(\mathbf{r},\mathbf{v})}\,\mathcal{A}[f]\,\mathcal{P}[f] + \frac{1}{2}\int d\mathbf{r}\,d\mathbf{v}\,d\mathbf{r}'\,d\mathbf{v}'\,\frac{\delta^2}{\delta f(\mathbf{r},\mathbf{v})\,\delta f(\mathbf{r}',\mathbf{v}')}\,\mathcal{B}[f]\,\mathcal{P}[f] \tag{54}$$

where the deterministic kinetic rate is given by

$$\mathcal{A}[f] = -\mathbf{v}\cdot\frac{\partial f}{\partial \mathbf{r}} - \frac{\mathbf{F}}{m}\cdot\frac{\partial f}{\partial \mathbf{v}} + \int d\mathbf{v}_2\,d\mathbf{v}_1'\,d\mathbf{v}_2'\,w\left(\mathbf{v}_1,\mathbf{v}_2|\mathbf{v}_1',\mathbf{v}_2'\right)\left(f_1'f_2' - f_1 f_2\right), \tag{55}$$

the diffusivity coefficient by

$$\mathcal{B}[f] = \delta(\mathbf{r} - \mathbf{r}') \int d\mathbf{v}_2 \, d\mathbf{v}_3 \, d\mathbf{v}_4 \, w \left(\mathbf{v}_1, \mathbf{v}_2 | \mathbf{v}_3, \mathbf{v}_4 \right) \left(f_1 \, f_2 + f_3 \, f_4 \right)$$
$$\times \left[\delta(\mathbf{v}_1 - \mathbf{v}') + \delta(\mathbf{v}_2 - \mathbf{v}') - \delta(\mathbf{v}_3 - \mathbf{v}') - \delta(\mathbf{v}_4 - \mathbf{v}') \right] , \tag{56}$$

and $\delta/\delta f$ denotes a functional derivative [11–13]. We notice that this functional master equation is of diffusion type as for the usual Fokker-Planck equations associated with Langevin stochastic differential equations. The average distribution function (2) obeys an equation at the top of a hierarchy of moment equations. If the noise amplitude is low enough, this hierarchy may be truncated and Boltzmann's equation (3) is thus recovered. To go beyond this mean-field approximation and consider the effects of the fluctuations, the functional master equation (54) should be used.

If the system is open, the exchanges of particles with the reservoirs are described at the mean-field level by the term (13) in the Boltzmann equation (3). For the coarse-grained master equation (30), this is taken into account by the boundary terms in the flow operator (50). In the diffusive limit, the following extra terms must be added to the deterministic kinetic rate (55) and the diffusivity coefficient (56):

$$\mathcal{A}^{\mathrm{R}}[f] = \sum_s \int_s d^2 S \, \delta(\mathbf{r} - \mathbf{r}_s) \, (\mathbf{n} \cdot \mathbf{v}) \, \theta(\mathbf{n} \cdot \mathbf{v}) \, \left[f_s(\mathbf{v}) - f(\mathbf{r}, \mathbf{v}) \right] , \tag{57}$$

$$\mathcal{B}^{\mathrm{R}}[f] = \delta(\mathbf{r} - \mathbf{r}') \, \delta(\mathbf{v} - \mathbf{v}') \sum_s \int_s d^2 S \, \delta(\mathbf{r} - \mathbf{r}_s) \, (\mathbf{n} \cdot \mathbf{v}) \, \theta(\mathbf{n} \cdot \mathbf{v}) \, \left[f_s(\mathbf{v}) + f(\mathbf{r}, \mathbf{v}) \right] . \tag{58}$$

Similarly, the presence of a thermalizing surface also contributes by corresponding terms $\mathcal{A}^{\mathrm{S}}[f]$ and $\mathcal{B}^{\mathrm{S}}[f]$.

The analogue of the Langevin equation associated with the functional Fokker-Planck equation (54) is the following stochastic integro-differential equation of Itô type for the random distribution function (1):

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \frac{\partial f}{\partial \mathbf{r}} + \frac{\mathbf{F}}{m} \cdot \frac{\partial f}{\partial \mathbf{v}} = \int d\mathbf{v}_2 \, d\mathbf{v}_1' \, d\mathbf{v}_2' \, w \left(\mathbf{v}_1, \mathbf{v}_2 | \mathbf{v}_1', \mathbf{v}_2' \right) \left(f_1' \, f_2' - f_1 \, f_2 \right) + g(\mathbf{r}, \mathbf{v}, t) \tag{59}$$

where $g(\mathbf{r}, \mathbf{v}, t)$ is a Gaussian white noise satisfying:

$$\langle g(\mathbf{r}, \mathbf{v}, t) \rangle = 0 , \tag{60}$$

$$\langle g(\mathbf{r}, \mathbf{v}, t) \, g(\mathbf{r}', \mathbf{v}', t') \rangle = \delta(t - t') \, \delta(\mathbf{r} - \mathbf{r}') \int d\mathbf{v}_2 \, d\mathbf{v}_3 \, d\mathbf{v}_4 \, w \left(\mathbf{v}_1, \mathbf{v}_2 | \mathbf{v}_3, \mathbf{v}_4 \right) \left(f_1 \, f_2 + f_3 \, f_4 \right)$$
$$\times \left[\delta(\mathbf{v}_1 - \mathbf{v}') + \delta(\mathbf{v}_2 - \mathbf{v}') - \delta(\mathbf{v}_3 - \mathbf{v}') - \delta(\mathbf{v}_4 - \mathbf{v}') \right] , \tag{61}$$

as shown explicitly in Ref. [11]. In an open system, the contacts with the reservoirs and thermalizing surfaces add the contributions

$$\langle g(\mathbf{r}, \mathbf{v}, t) \, g(\mathbf{r}', \mathbf{v}', t') \rangle^{\mathrm{R,S}} = \delta(t - t') \, \mathcal{B}^{\mathrm{R,S}}[f] \tag{62}$$

to the variance (61) of the noise.

Since the functional master equation (54) can be viewed as the continuum limit of the coarse-grained master equation (30), we shall use this latter which is more convenient to handle mathematically.

V. THE TIME-REVERSAL SYMMETRY RELATION AND ITS CONSEQUENCES

A. Counting statistics in steady states

We are interested in a symmetry relation concerning the counting statistics of fluctuating currents flowing across open systems in steady states. The counting statistics is established thanks to the probability distribution of the transfers of particles and energy between the reservoirs during some time interval [19].

To fix the setting, we consider the open system with two reservoirs sketched in Fig. 1a in a steady state corresponding to the affinities $\mathbf{A} = \{A_E, A_N\}$ defined by Eqs. (15) and (16) with respect to the temperature and particle density of the reference reservoir taken as the left-hand reservoir. This steady state is described by the stationary solution $P_{\mathrm{st}}(\mathbf{N}) = P_{\mathbf{A}}(\mathbf{N})$ of the master equation (30):

$$\frac{dP_{\mathbf{A}}}{dt} = \hat{L} \, P_{\mathbf{A}} = 0 . \tag{63}$$

This stationary probability distribution is used to calculate the statistical averages

$$\langle \cdot \rangle_{\mathbf{A}} = \sum_{\mathbf{N}} P_{\mathbf{A}}(\mathbf{N}) (\cdot) \tag{64}$$

of various observable quantities in the steady state characterized by the affinities $\mathbf{A}$, the reference temperature T_{R}, and the reference particle density n_{R}.

The particles randomly enter or exit the open system from and to each reservoir according to the stochastic process ruled by the master equation (30). This is the case in particular at the left-hand reservoir of Fig. 1a. The counting statistics of the energy and particle exchanges with the left-hand reservoir is carried out from the sequence of random events formed by the successive particle crossings of the fictitious surface $s = \mathrm{L}$ between the open system and the left-hand reservoir. This surface is depicted by the vertical dashed line on the left-hand side of Fig. 1a. The particles cross this fictitious surface in the incoming or outgoing direction, carrying with them their kinetic energy determined by their velocity.

Let us denote by $\{t_k\}_{k=-\infty}^{+\infty}$ the sequence of random times when a particle enters or exits the open system at the left-hand reservoir. The associated sequence $\{\sigma_k\}_{k=-\infty}^{+\infty}$ gives the random directions $\sigma_k = \pm 1$ of the particles crossing the fictitious surface: $\sigma_k = +1$ if the particle enters the system and $\sigma_k = -1$ if the particle exits. Moreover, we also need the corresponding sequence of random kinetic energies $\{\epsilon_k = m\mathbf{v}_k^2/2\}_{k=-\infty}^{+\infty}$ of the particles when they cross the surface with their velocity $\mathbf{v}_k$.

In the case of the simple stochastic process ruled by the flow operator (50) for the particles of velocity $\pm v$, we should take $\sigma_k = +1$ for the transition $N_{1,+} \to N_{1,+} + 1$, $\sigma_k = -1$ for the transition $N_{1,-} \to N_{1,-} - 1$, and $\sigma_k = 0$ for any other transition occurring at the time t_k, while $\epsilon_k = mv^2/2$. The transitions with $\sigma_k \neq 0$ thus happen in the only two cells $(1, \pm)$ that are in contact with the left-hand reservoir.

More generally, if particles are exchanged between a reservoir and a cell $\alpha = \mathbf{rv}$ in direct contact with the reservoir, we should take $\sigma_k = \pm 1$ for the transition $N_{\mathbf{rv}} \to N_{\mathbf{rv}} \pm 1$ occurring at the time t_k and $\epsilon_k = m\mathbf{v}^2/2$. By construction, the velocity $\mathbf{v}$ is compatible with the particle exchange between this cell and the reservoir.

In this setting, the instantaneous currents of energy and particles are defined by

$$j_E(t) = \sum_{k=-\infty}^{+\infty} \sigma_k \, \epsilon_k \, \delta(t - t_k) \,, \tag{65}$$

$$j_N(t) = \sum_{k=-\infty}^{+\infty} \sigma_k \, \delta(t - t_k) \,, \tag{66}$$

where the Dirac delta distributions $\delta(t - t_k)$ express the instantaneity of the random events of particles crossing the fictitious surface $s = \mathrm{L}$, because $\delta(t - t_k) = 0$ for $t \neq t_k$ and $\int_{-\infty}^{+\infty} f(t) \, \delta(t - t_k) \, dt = f(t_k)$ for any smooth enough function $f(t)$.

For counting statistics in *steady states*, the instantaneous currents at the reference reservoir play redundant roles. This follows from the fact that there should be as many independent currents as there are affinities for the thermodynamic description of nonequilibrium steady states [19, 20]. In the system of Fig. 1a, the nonequilibrium constraints are determined by the two affinities (15) and (16) so that there are only two currents that are independent. Here, they are taken as the energy current (65) and the particle current (66) at the left-hand reservoir.

In association with the instantaneous currents $\mathbf{j}(t) = \{j_E(t), j_N(t)\}$, we may also consider their integrals over some time interval $[0, t]$

$$\mathbf{G}(t) \equiv \int_0^t \mathbf{j}(\tau) \, d\tau \,, \tag{67}$$

such that their time derivative is equal to the instantaneous current $\mathbf{j} = d\mathbf{G}/dt$. The quantity $G_N(t)$ gives the net number of particles that have entered the system from the left-hand reservoir during the time interval $[0, t]$ and $G_E(t)$ the corresponding net income of energy from that reservoir. These observables are called Helfand moments in transport theory [37].

The full counting statistics is established by introducing the probability density

$$p_{\mathbf{A}}(\mathbf{J}, t) \equiv \langle \delta \left[\mathbf{J} - \mathbf{G}(t)/t \right] \rangle_{\mathbf{A}} \tag{68}$$

that the instantaneous currents averaged over a time interval t would take the values $\mathbf{J} = (1/t) \int_0^t \mathbf{j}(\tau) d\tau = \mathbf{G}(t)/t$. This probability density is defined by taking the statistical average (64) over the stationary probability distribution (63)

of the steady state corresponding to the affinities $\mathbf{A}$. The generating function of the statistical cumulants of the fluctuating currents is thus defined in the long-time limit by

$$Q_{\mathbf{A}}(\boldsymbol{\lambda}) \equiv \lim_{t \to \infty} -\frac{1}{t} \ln \int p_{\mathbf{A}}(\mathbf{J}, t) \exp(-\boldsymbol{\lambda} \cdot \mathbf{J}\, t)\, d\mathbf{J} \tag{69}$$

in terms of the counting parameters $\boldsymbol{\lambda} = \{\lambda_E, \lambda_N\}$ and the probability density (68) characterizing the steady state of affinities $\mathbf{A}$. The statistical cumulants are obtained by taking derivatives of the cumulant generating function with respect to the counting parameters and setting them equal to zero. For instance, the average values of the currents in the steady state (63) are given by the first derivatives:

$$\langle j_E \rangle_{\mathbf{A}} = \frac{\partial Q_{\mathbf{A}}}{\partial \lambda_E}(\mathbf{0})\,, \qquad\qquad \langle j_N \rangle_{\mathbf{A}} = \frac{\partial Q_{\mathbf{A}}}{\partial \lambda_N}(\mathbf{0})\,, \tag{70}$$

the diffusivities by the second derivatives, and the higher cumulants by further derivatives [20–22]. Using the definition (68), the cumulant generating function of the fluctuating currents can be written equivalently as

$$Q_{\mathbf{A}}(\boldsymbol{\lambda}) = \lim_{t \to \infty} -\frac{1}{t} \ln \left\langle \exp\left[-\boldsymbol{\lambda} \cdot \int_0^t \mathbf{j}(\tau)\, d\tau\right]\right\rangle_{\mathbf{A}} \tag{71}$$

in terms of the statistical average (64) in the steady state (63) [19, 20].

B.   The modified evolution operator

Now, our aim is to calculate the cumulant generating function (71) for the process ruled by the master equation (30). We follow the methods developed for general jump processes in Refs. [17, 20]. Using Eq. (64) and the definition (67), the cumulant generating function (71) can be expressed as

$$Q_{\mathbf{A}}(\boldsymbol{\lambda}) = \lim_{t \to \infty} -\frac{1}{t} \ln \sum_{\mathbf{N}} P_{\mathbf{A}}(\mathbf{N}) \left\langle e^{-\boldsymbol{\lambda} \cdot \mathbf{G}(t)}\right\rangle_{\mathbf{N}} \tag{72}$$

where appears the quantity

$$F(\mathbf{N}, t; \boldsymbol{\lambda}) \equiv \left\langle e^{-\boldsymbol{\lambda} \cdot \mathbf{G}(t)}\right\rangle_{\mathbf{N}} \tag{73}$$

that is the expectation value of the random variable, $\exp\left[-\boldsymbol{\lambda} \cdot \mathbf{G}(t)\right]$, conditioned on the system being in the state $\mathbf{N}$ at the time $t = 0$. This quantity is ruled by an evolution equation to be deduced from the master equation (30), as explained for related problems in Refs. [17, 20].

Indeed, the master equation (30) gives the probability to be in the state $\mathbf{N}$ at the time $t + dt$ in terms of the probability the system was in the states $\mathbf{N}'$ at the time t as

$$P(\mathbf{N}, t + dt) = P(\mathbf{N}, t) + dt \sum_{\mathbf{N}'(\neq \mathbf{N})} \left[(\hat{L})_{\mathbf{N}\mathbf{N}'}\, P(\mathbf{N}', t) - (\hat{L})_{\mathbf{N}'\mathbf{N}}\, P(\mathbf{N}, t)\right] + O(dt^2) \tag{74}$$

where the matrix element $(\hat{L})_{\mathbf{N}\mathbf{N}'}$ is the rate of the transition $\mathbf{N}' \to \mathbf{N}$, and $(\hat{L})_{\mathbf{N}'\mathbf{N}}$ the rate of the opposite transition $\mathbf{N} \to \mathbf{N}'$. If some transition corresponds to a particle entering or outgoing the system through the cell $\alpha = \mathbf{r}\mathbf{v}$ in contact with the left-hand reservoir, the integrated currents (67) multiplied by the counting parameters should jump by the value:

$$\boldsymbol{\lambda} \cdot \Delta \mathbf{G}_{\mathbf{N} \to \mathbf{N}'} = (\epsilon_{\mathbf{v}} \lambda_E + \lambda_N)\, \Delta N_{\mathbf{r}\mathbf{v}} \qquad \text{with} \qquad \Delta N_{\mathbf{r}\mathbf{v}} = N'_{\mathbf{r}\mathbf{v}} - N_{\mathbf{r}\mathbf{v}} = \pm 1 \tag{75}$$

where $\epsilon_{\mathbf{v}} = m\mathbf{v}^2/2$ is the kinetic energy of the particle. In the notations of Eqs. (65) and (66), we would have $\epsilon_k = \epsilon_{\mathbf{v}}$ and $\sigma_k = \Delta N_{\mathbf{r}\mathbf{v}} = \pm 1$ for the random event occurring at the time t_k.

Now, the quantity $F(\mathbf{N}, t + dt; \boldsymbol{\lambda})$ at the next time step dt can be calculated in terms of its previous values $F(\mathbf{N}', t; \boldsymbol{\lambda})$ by considering all the possible transitions $\mathbf{N}' \to \mathbf{N}$ happening in the time interval $[t, t + dt]$:

$$F(\mathbf{N}, t + dt; \boldsymbol{\lambda}) = F(\mathbf{N}, t; \boldsymbol{\lambda}) + dt \sum_{\mathbf{N}'(\neq \mathbf{N})} \left[(\hat{L})_{\mathbf{N}'\mathbf{N}}\, e^{-\boldsymbol{\lambda} \cdot \Delta \mathbf{G}_{\mathbf{N} \to \mathbf{N}'}}\, F(\mathbf{N}', t; \boldsymbol{\lambda}) - (\hat{L})_{\mathbf{N}'\mathbf{N}}\, F(\mathbf{N}, t; \boldsymbol{\lambda})\right] + O(dt^2)\,. \tag{76}$$

Taking the limit $dt \to 0$, we infer that the quantities (73) evolve in time according to

$$\frac{dF}{dt} = \hat{L}_{\boldsymbol{\lambda}}^{\dagger} F \tag{77}$$

under the modified operator defined by

$$\left(\hat{L}_{\boldsymbol{\lambda}}^{\dagger}\right)_{\mathbf{NN'}} = \left(\hat{L}_{\boldsymbol{\lambda}}\right)_{\mathbf{N'N}} = \left(\hat{L}\right)_{\mathbf{N'N}} \mathrm{e}^{-\boldsymbol{\lambda}\cdot\Delta\mathbf{G}_{\mathbf{N}\to\mathbf{N'}}} \qquad \text{for} \qquad \mathbf{N'} \neq \mathbf{N} \tag{78}$$

and

$$\left(\hat{L}_{\boldsymbol{\lambda}}^{\dagger}\right)_{\mathbf{NN}} = \left(\hat{L}_{\boldsymbol{\lambda}}\right)_{\mathbf{NN}} = -\sum_{\mathbf{N'}(\neq\mathbf{N})} \left(\hat{L}\right)_{\mathbf{N'N}} \tag{79}$$

in terms of the operator $\hat{L} = \hat{L}_{\mathbf{0}}$ of the master equation (30) [20]. The initial condition should be taken as $F(\mathbf{N}, 0; \boldsymbol{\lambda}) = 1$ to comply with the definition (73) and the fact that $\mathbf{G}(0) = 0$.

After a long enough time interval, the quantities (73) are expected to behave exponentially in time at a rate given by the leading eigenvalue of the modified operator (78). This leading eigenvalue is nothing other than the cumulant generating function (72) since this latter is obtained in the long-time limit so that

$$F(\mathbf{N}, t; \boldsymbol{\lambda}) \sim_{t \to +\infty} \mathrm{e}^{-Q_{\mathbf{A}}(\boldsymbol{\lambda})\,t} . \tag{80}$$

Inserting in Eq. (77), we conclude that the leading eigenvalue of the modified operator gives the cumulant generating function according to

$$\hat{L}_{\boldsymbol{\lambda}} \Psi = -Q_{\mathbf{A}}(\boldsymbol{\lambda})\,\Psi . \tag{81}$$

C. The theorem

The central result is that the modified operator has a remarkable symmetry under time reversal, as expressed by the

Theorem. *The modified operator (78)-(79) corresponding to the master equation (30) obeys the symmetry relation:*

$$\eta^{-1}\Theta\,\hat{L}_{\boldsymbol{\lambda}}\,(\Theta\,\eta\,\Phi) = \hat{L}_{\mathbf{A}-\boldsymbol{\lambda}}^{\dagger}\Phi \tag{82}$$

where $\Phi(\mathbf{N})$ denotes some arbitrary function, Θ is the involution performing the time-reversal transformation:

$$\Theta\,\Phi(\{N_{\alpha}\}) = \Phi(\{N_{\alpha^{\mathrm{T}}}\}) \qquad \text{so that} \qquad \Theta^2 = 1 \tag{83}$$

and $\eta(\mathbf{N})$ is the multiple Poisson distribution:

$$\eta(\mathbf{N}) = \prod_{\alpha} \mathrm{e}^{-\langle N_{\alpha}\rangle} \frac{\langle N_{\alpha}\rangle^{N_{\alpha}}}{N_{\alpha}!} \qquad \text{with} \qquad \langle N_{\alpha}\rangle = f_{\mathrm{R}}(\mathbf{v}_{\alpha})\,\Delta r^3\,\Delta v^3 \tag{84}$$

given in terms of the Maxwell-Boltzmann distribution $f_{\mathrm{R}}(\mathbf{v})$ of some reference reservoir, for instance the right-hand reservoir at the temperature T_{R} and density n_{R}.

This theorem is established as follows.

1. Proof for an open system in contact with two reservoirs

The first step is to notice that only the flow part of the master-equation operator is modified in Eq. (78):

$$\hat{L}_{\lambda_E,\lambda_N} = \hat{L}^{\mathrm{C}} + \hat{L}_{\lambda_E,\lambda_N}^{\mathrm{FR}} . \tag{85}$$

Indeed, the operator $\hat{L}^{\mathrm{C}}$ due to the binary collisions acts locally exchanging particles among all the cells corresponding to the *same* position. Since the quantity (75) is non zero only for particle exchanges at the boundary with the left-hand reservoir, there is no modification of the binary-collision operator.

Now, the binary-collision operator always obeys the symmetry relation:

$$\eta^{-1}\Theta\,\hat{L}^{\mathrm{C}}\,(\Theta\,\eta\,\Phi) = \hat{L}^{\mathrm{C}\dagger}\Phi\,, \tag{86}$$

as shown in Appendix A by using the property that the lowering and rising operators (27) act as follows on the product of the multiple Poisson distribution (84) with an arbitrary function Φ:

$$\hat{E}_{\alpha}^{-1}\,\eta\,\Phi = \frac{N_{\alpha}}{\langle N_{\alpha}\rangle}\,\eta\,\hat{E}_{\alpha}^{-1}\,\Phi\,, \tag{87}$$

$$\hat{E}_{\alpha}^{+1}\,\eta\,\Phi = \frac{\langle N_{\alpha}\rangle}{N_{\alpha}+1}\,\eta\,\hat{E}_{\alpha}^{+1}\,\Phi\,. \tag{88}$$

On the other hand, the flow operator (50) is modified according to Eq. (78) because it contributes to the exchange of particles with the left-hand reservoir where the quantity (75) is non zero, as explained here above. For particles at the energy $\epsilon = mv^2/2$, the flow operator (50) is thus modified by inserting a factor $\exp(\pm\lambda)$ with the counting parameter $\lambda = \epsilon\lambda_E + \lambda_N$ in the terms responsible for the incoming or outgoing of a particle from or to the left-hand reservoir. Hence, we get

$$\hat{L}_{\lambda_E,\lambda_N}^{\mathrm{FR}}\Phi = \frac{v}{\Delta r}\left[(\mathrm{e}^{-\lambda}\,\hat{E}_{1,+}^{-1}-1)\langle N_+\rangle_{\mathrm{L}}\Phi + \sum_{i=1}^{I-1}(\hat{E}_{i,+}^{+1}\hat{E}_{i+1,+}^{-1}-1)N_{i,+}\Phi + (\hat{E}_{I,+}^{+1}-1)N_{I,+}\Phi\right.$$
$$\left. + (\mathrm{e}^{+\lambda}\,\hat{E}_{1,-}^{+1}-1)N_{1,-}\Phi + \sum_{i=1}^{I-1}(\hat{E}_{i+1,-}^{+1}\hat{E}_{i,-}^{-1}-1)N_{i+1,-}\Phi + (\hat{E}_{I,-}^{-1}-1)\langle N_-\rangle_{\mathrm{R}}\Phi\right]. \tag{89}$$

As aforementioned, the multiple Poisson distribution (84) is symmetric under time reversal, $\Theta\eta = \eta$, where the time-reversal transformation acts as $\Theta N_{i,\pm} = N_{i,\mp}$, reversing the velocities $\pm v$ at every position $i = 1,2,...,I$. Moreover, we have the properties (29), (87), and (88) for the lowering and rising operators. Therefore, the transformation in the left-hand side of Eq. (82) has the effect of attributing the terms of positive velocity to those of negative velocity and vice versa. Furthermore, the boundary term with $\mathrm{e}^{-\lambda}\langle N_+\rangle_{\mathrm{L}}$ is transformed into $\mathrm{e}^{-\lambda}\langle N_+\rangle_{\mathrm{L}}/\langle N_{1,-}\rangle_{\mathrm{R}}$ and the boundary term with $\mathrm{e}^{+\lambda}$ into $\mathrm{e}^{+\lambda}\langle N_{1,+}\rangle_{\mathrm{R}}$. Now, the left-hand reservoir is at the temperature T_{L} and density n_{L} while the right-hand reservoir is used as reference so that $\langle N_{i,\pm}\rangle_{\mathrm{R}} = f_{\mathrm{R}}\Delta r^3\Delta v^3$ for all $i = 1,2,...,I$ according to Eq. (84), whereupon we have the equalities:

$$\mathrm{e}^{-\lambda}\,\frac{\langle N_+\rangle_{\mathrm{L}}}{\langle N_{1,-}\rangle_{\mathrm{R}}} = \mathrm{e}^{A-\lambda}\,, \tag{90}$$

$$\mathrm{e}^{+\lambda}\langle N_{1,+}\rangle_{\mathrm{R}} = \mathrm{e}^{-(A-\lambda)}\,\langle N_+\rangle_{\mathrm{L}} \tag{91}$$

with the affinity A defined by Eq. (51). Consequently, the two boundary terms with the counting parameter λ may exchange their role if we carry out the transformation $\lambda \to A - \lambda$. We thus obtain the symmetry relation of the flow operator:

$$\eta^{-1}\Theta\,\hat{L}_{\lambda_E,\lambda_N}^{\mathrm{FR}}\,(\Theta\,\eta\,\Phi) = \hat{L}_{A_E-\lambda_E,A_N-\lambda_N}^{\mathrm{FR}\dagger}\,\Phi\,. \tag{92}$$

Combining the results (86) and (92), the symmetry relation (82) is finally proved.

2. Proof for an open system also in contact with a thermalizing surface

Here, we consider the case where the system is open and includes a thermalizing surface described by the operator (53). Since energy exchange may occur at the surface, we have to introduce an extra counting parameter λ_E^{S} corresponding to an instantaneous current similar to Eq. (65) but defined at the surface. Accordingly, the operator (53) is modified to

$$\hat{L}_{\lambda_E^{\mathrm{S}}}^{\mathrm{S}}\Phi = \sum_{\mathbf{r}}\delta_{z,0}\sum_{\substack{\mathbf{v}\\v_z>0}}\sum_{\substack{\mathbf{v}'\\v_z'<0}}\Delta v^3\,\frac{|v_z'|}{\Delta r}\,p(\mathbf{v}|\mathbf{v}')\left[\mathrm{e}^{\lambda_E^{\mathrm{S}}(\epsilon'-\epsilon)}\hat{E}_{\mathbf{rv}'}^{+1}\hat{E}_{\mathbf{rv}}^{-1}-1\right]N_{\mathbf{rv}}\Phi \tag{93}$$

where $\epsilon = m\mathbf{v}^2/2$ and $\epsilon' = m\mathbf{v}'^2/2$. The identity

$$\eta^{-1}\Theta\,\hat{L}^{\mathrm{S}}_{\lambda^{\mathrm{S}}_E}\,(\Theta\,\eta\,\Phi) = \hat{L}^{\mathrm{S}\dagger}_{A^{\mathrm{S}}_E - \lambda^{\mathrm{S}}_E}\,\Phi \tag{94}$$

is obtained provided that the gas-surface interaction kernel satisfies:

$$\frac{|v'_z|\,p(\mathbf{v}|\mathbf{v}')}{|v_z|\,p(-\mathbf{v}'|-\mathbf{v})} = \mathrm{e}^{(A^{\mathrm{S}}_E - \beta_{\mathrm{R}})(\epsilon - \epsilon')}\,. \tag{95}$$

This is always guaranteed thanks to the property of reciprocity (22) if the affinity associated with the thermalizing surface is defined by

$$A^{\mathrm{S}}_E = \beta_{\mathrm{R}} - \beta_s \tag{96}$$

where $\beta_s = (k_{\mathrm{B}}T_s)^{-1}$ characterizes the Maxwell-Boltzmann distribution (14) at the surface temperature T_s. This expression agrees with the form (15) expected for a thermal affinity.

For an open system in contact with two reservoirs and a thermalizing surface, we have thus proved the symmetry relation (82) with the counting parameters $\boldsymbol{\lambda} = \{\lambda_E, \lambda_N, \lambda^{\mathrm{S}}_E\}$ and the affinities $\mathbf{A} = \{A_E, A_N, A^{\mathrm{S}}_E\}$ given by Eqs. (15), (16), and (96).

Such symmetry relations extend from the coarse-grained master equation to the fluctuating Boltzmann equation as long as this latter is the diffusive limit of the former together with their respective modified evolution operators.

D. The symmetry relation and the second law of thermodynamics

The consequence of Eq. (82) of the theorem is that the eigenvalue equation (81) can be transformed into

$$\hat{L}^{\dagger}_{\boldsymbol{\lambda}}\,\tilde{\Psi} = -Q_{\mathbf{A}}(\mathbf{A} - \boldsymbol{\lambda})\,\tilde{\Psi} \qquad \text{with} \qquad \tilde{\Psi} = \eta^{-1}\Theta\Psi\,, \tag{97}$$

showing that the adjoint of the modified operator $\hat{L}_{\boldsymbol{\lambda}}$ admits the eigenvector $\tilde{\Psi}$ associated with the leading eigenvalue $-Q_{\mathbf{A}}(\mathbf{A} - \boldsymbol{\lambda})$. According to the Perron-Frobenius theorem [38], $\hat{L}_{\boldsymbol{\lambda}}$ and $\hat{L}^{\dagger}_{\boldsymbol{\lambda}}$ have the same unique leading eigenvalue [17], whereupon we find the time-reversal symmetry relation for the cumulant generating function:

$$Q_{\mathbf{A}}(\boldsymbol{\lambda}) = Q_{\mathbf{A}}(\mathbf{A} - \boldsymbol{\lambda})\,. \tag{98}$$

The long-time behavior of the probability density (68) can be expressed in terms of the rate function $H_{\mathbf{A}}(\mathbf{J})$ as

$$p_{\mathbf{A}}(\mathbf{J}, t) \sim_{t\to\infty} \exp\left[-H_{\mathbf{A}}(\mathbf{J})\,t\right] \tag{99}$$

up to a subexponential prefactor. Using large-deviation theory [39], the rate function $H_{\mathbf{A}}(\mathbf{J})$ is obtained as the Legendre-Fenchel transform of the cumulant generating function [19, 20]

$$H_{\mathbf{A}}(\mathbf{J}) = \mathrm{Max}_{\boldsymbol{\lambda}}\left[Q_{\mathbf{A}}(\boldsymbol{\lambda}) - \boldsymbol{\lambda}\cdot\mathbf{J}\right]\,. \tag{100}$$

Now, the symmetry relation (98) of the cumulant generating function yields an equivalent symmetry relation for its Legendre-Fenchel transform [19, 20]

$$H_{\mathbf{A}}(-\mathbf{J}) - H_{\mathbf{A}}(\mathbf{J}) = \mathbf{A}\cdot\mathbf{J}\,. \tag{101}$$

As a consequence, we get the *current fluctuation theorem*:

$$\frac{p_{\mathbf{A}}(\mathbf{J}, t)}{p_{\mathbf{A}}(-\mathbf{J}, t)} \simeq_{t\to\infty} \exp\left(\mathbf{A}\cdot\mathbf{J}\,t\right) \tag{102}$$

for a flow ruled by the fluctuating Boltzmann equation. The flow is in a steady state characterized by the affinities $\mathbf{A}$ as well as the temperature and particle densities of the reference reservoir.

The symmetry relation (98) also implies that the generalizations of Green-Kubo formulae and Onsager reciprocity relations obtained in Ref. [21] for the nonlinear response coefficients extend to the nonequilibrium flows of dilute and rarefied gases ruled by the fluctuating Boltzmann equation.

A further remarkable consequence of the current fluctuation theorem is that the thermodynamic entropy production given by the sum of the affinities multiplied by the average values $\langle \mathbf{J} \rangle_{\mathbf{A}}$ of the currents flowing across the open system is always non-negative:

$$\frac{1}{k_{\mathrm{B}}} \frac{d_{\mathrm{i}} S}{dt} = \mathbf{A} \cdot \langle \mathbf{J} \rangle_{\mathbf{A}} \geq 0 \tag{103}$$

in the steady state of affinities $\mathbf{A}$ [40, 41]. This result is proved thanks to Jensen's inequality $\langle f(X) \rangle \geq f(\langle X \rangle)$ [42] holding for the convex function $f(X) = \exp(-X)$ with $X = \mathbf{A} \cdot \mathbf{J}\, t$ and the statistical average $\langle \cdot \rangle_{\mathbf{A}}$ over the steady state of affinities $\mathbf{A}$:

$$\left\langle \mathrm{e}^{-\mathbf{A} \cdot \mathbf{J}\, t} \right\rangle_{\mathbf{A}} \geq \mathrm{e}^{-\mathbf{A} \cdot \langle \mathbf{J} \rangle_{\mathbf{A}} t} . \tag{104}$$

According to the current fluctuation theorem (102), the left-hand side of this inequality is given by

$$\left\langle \mathrm{e}^{-\mathbf{A} \cdot \mathbf{J}\, t} \right\rangle_{\mathbf{A}} = \int p_{\mathbf{A}}(\mathbf{J}, t)\, \mathrm{e}^{-\mathbf{A} \cdot \mathbf{J}\, t}\, d\mathbf{J} \simeq \int p_{\mathbf{A}}(-\mathbf{J}, t)\, d\mathbf{J} \tag{105}$$

Since the last integral extends over all the real values of the currents $\mathbf{J}$, the change of variables $\mathbf{J} \to -\mathbf{J}$ shows that the integral is equal to unity by the normalization of the probability density of the fluctuating currents:

$$\int p_{\mathbf{A}}(-\mathbf{J}, t)\, d\mathbf{J} = 1 . \tag{106}$$

Therefore, the exponential decay rate of the left-hand side of Eq. (104) is vanishing

$$\lim_{t \to \infty} -\frac{1}{t} \ln \left\langle \mathrm{e}^{-\mathbf{A} \cdot \mathbf{J}\, t} \right\rangle_{\mathbf{A}} = 0 \tag{107}$$

so that its right-hand side is either constant or exponentially decaying, which proves the non-negativity of the entropy production (103) and the agreement of the theory with the second law of thermodynamics. Accordingly, the current fluctuation theorem (102) confirms Boltzmann's H-theorem at the level of the global currents flowing across the open systems of Fig. 1. Beyond, the current fluctuation theorem (102) allows us to understand how the current fluctuations behave if the steady state is displaced from the equilibrium state at $\mathbf{A} = 0$ where detailed balancing holds, towards the nonequilibrium states where irreversibility manifests itself.

VI. CONCLUSIONS

In this paper, a time-reversal symmetry relation has been established for all the random particle and energy currents of dilute or rarefied gases flowing in open systems ruled by the fluctuating Boltzmann equation. For this purpose, the fluctuating Boltzmann equation is obtained as the Langevin equation corresponding to a coarse-grained master equation for the random numbers of particles in fictitious cells partitioning the one-particle phase space [11–13]. The coarse-grained master equation rules the time evolution not only in the bulk of the fluid but also at its boundaries where the nonequilibrium constraints are imposed. These constraints are characterized in terms of the thermodynamic forces or affinities defined from the differences of temperatures or particle densities between gas reservoirs and, possibly, thermalizing surfaces.

The time-evolution operator of the coarse-grained master equation is composed of several terms corresponding to the different processes taking place in the bulk and at the boundaries. This linear operator is modified by introducing parameters counting the transfers of particles and energy at the boundaries. The cumulant generating function of the fluctuating currents is given as the leading eigenvalue of this modified operator. The central result is obtained by showing that the modified operator obeys the symmetry relation (82) involving the counting parameters and the affinities. As a consequence, the cumulant generating function has the symmetry (98) and the fluctuation theorem (102) is thus established for all the currents. These relations find their origin in the time-reversal symmetry of the underlying microscopic dynamics.

The fluctuation relation (102) implies the non-negativity of the entropy production (103) in agreement with the second law of thermodynamics. Furthermore, the fluctuation relation also implies the Green-Kubo formulae and Onsager reciprocity relations as well as their generalizations beyond linear response theory [21], which thus hold for dilute or rarefied gases ruled by the fluctuating Boltzmann equation, as the consequence of the symmetry relations here established.

These results concern in particular the numerical simulation of dilute or rarefied gases by methods such as the Direct Simulation Monte Carlo algorithm if the enunciated assumptions and, especially, the properties of reciprocity (10) and (22) are satisfied [25].

At equilibrium where the affinities vanish, the fluctuation relation (102) reduces to the expression of the principle of detailed balancing, according to which the probabilities of opposite fluctuations are equal. Out of equilibrium, a bias appears between these probabilities. Since the ratio of the probabilities of opposite fluctuations goes exponentially with time and the affinities, one of both probabilities may soon become so tiny that it would appear negligible, as nonequilibrium constraints increase. This is the case in regimes very far from equilibrium where the fluxes tend to become unidirectional. In extreme regimes for instance with shock waves, the fluctuation relation thus expresses the quasi full irreversibility of the flow due to the extreme rarity of fluctuations opposite to the average fluxes. It is only relatively close to equilibrium that the opposite fluctuations are not negligible.

In the present paper, the results have been obtained for gases composed of a single atomic species. However, the results extend to polyatomic molecular species, gas mixtures, as well as reacting dilute or rarefied gases, as long as the property of microreversibility may be assumed [43, 44]. The scope opened by these results is very broad since we may also envisage their extension to gases ruled by the relativistic Boltzmann equation or to gases of bosons or fermions ruled by the quantum Boltzmann equations [8, 45, 46].

APPENDIX A: TIME-RESERVAL SYMMETRY OF THE BINARY-COLLISION OPERATOR

In this appendix, the time-reversal symmetry relation (86) is proved for the binary-collision operator

$$\hat{L}^{\text{C}}\Phi = \sum_{\lambda\mu\rho\sigma} W^{\text{C}}_{\lambda\mu\rho\sigma} \left(\hat{E}^{-1}_\lambda \hat{E}^{-1}_\mu \hat{E}^{+1}_\rho \hat{E}^{+1}_\sigma - 1 \right) N_\rho \, N_\sigma \, \Phi \,. \tag{A1}$$

Using Eq. (29), its adjoint is given by

$$\hat{L}^{\text{C}\dagger}\Phi = \sum_{\lambda\mu\rho\sigma} W^{\text{C}}_{\lambda\mu\rho\sigma} \, N_\rho \, N_\sigma \left(\hat{E}^{-1}_\rho \hat{E}^{-1}_\sigma \hat{E}^{+1}_\lambda \hat{E}^{+1}_\mu - 1 \right) \Phi \,. \tag{A2}$$

Using the time-reversal operator (83) and Eqs. (87)-(88), the expression in the left-hand side of Eq. (86) is transformed as follows:

$$\eta^{-1}\Theta\,\hat{L}^{\text{C}}\,(\Theta\,\eta\,\Phi) \;=\; \eta^{-1} \sum_{\lambda\mu\rho\sigma} W^{\text{C}}_{\lambda\mu\rho\sigma} \, \hat{E}^{-1}_{\lambda^{\text{T}}} \hat{E}^{-1}_{\mu^{\text{T}}} \hat{E}^{+1}_{\rho^{\text{T}}} \hat{E}^{+1}_{\sigma^{\text{T}}} \, N_{\rho^{\text{T}}} \, N_{\sigma^{\text{T}}} \, \eta \, \Phi - \sum_{\lambda\mu\rho\sigma} W^{\text{C}}_{\lambda\mu\rho\sigma} \, N_{\rho^{\text{T}}} \, N_{\sigma^{\text{T}}} \, \Phi$$

$$= \sum_{\lambda\mu\rho\sigma} W^{\text{C}}_{\lambda\mu\rho\sigma} \frac{\langle N_{\rho^{\text{T}}}\rangle_{\text{R}} \langle N_{\sigma^{\text{T}}}\rangle_{\text{R}}}{\langle N_{\lambda^{\text{T}}}\rangle_{\text{R}} \langle N_{\mu^{\text{T}}}\rangle_{\text{R}}} \, N_{\lambda^{\text{T}}} \, N_{\mu^{\text{T}}} \, \hat{E}^{-1}_{\lambda^{\text{T}}} \hat{E}^{-1}_{\mu^{\text{T}}} \hat{E}^{+1}_{\rho^{\text{T}}} \hat{E}^{+1}_{\sigma^{\text{T}}} \, \Phi - \sum_{\lambda\mu\rho\sigma} W^{\text{C}}_{\lambda\mu\rho\sigma} \, N_{\rho^{\text{T}}} \, N_{\sigma^{\text{T}}} \, \Phi \,. \tag{A3}$$

Now, summing over all the cells α gives the same result as summing over the time-reversed cells α'^{T}, so that we find

$$\eta^{-1}\Theta\,\hat{L}^{\text{C}}\,(\Theta\,\eta\,\Phi) = \sum_{\lambda\mu\rho\sigma} W^{\text{C}}_{\rho^{\text{T}}\sigma^{\text{T}}\lambda^{\text{T}}\mu^{\text{T}}} \frac{\langle N_\lambda\rangle_{\text{R}} \langle N_\mu\rangle_{\text{R}}}{\langle N_\rho\rangle_{\text{R}} \langle N_\sigma\rangle_{\text{R}}} \, N_\rho \, N_\sigma \, \hat{E}^{-1}_\rho \hat{E}^{-1}_\sigma \hat{E}^{+1}_\lambda \hat{E}^{+1}_\mu \, \Phi - \sum_{\lambda\mu\rho\sigma} W^{\text{C}}_{\rho^{\text{T}}\sigma^{\text{T}}\lambda^{\text{T}}\mu^{\text{T}}} \, N_\lambda \, N_\mu \, \Phi \,. \tag{A4}$$

By using the property of reciprocity (46) with respect to the equilibrium state of the right-hand reservoir, the first term is transformed to get

$$\eta^{-1}\Theta\,\hat{L}^{\text{C}}\,(\Theta\,\eta\,\Phi) = \sum_{\lambda\mu\rho\sigma} W^{\text{C}}_{\lambda\mu\rho\sigma} \, N_\rho \, N_\sigma \, \hat{E}^{-1}_\rho \hat{E}^{-1}_\sigma \hat{E}^{+1}_\lambda \hat{E}^{+1}_\mu \, \Phi - \sum_{\lambda\mu\rho\sigma} W^{\text{C}}_{\rho^{\text{T}}\sigma^{\text{T}}\lambda^{\text{T}}\mu^{\text{T}}} \, N_\lambda \, N_\mu \, \Phi \,. \tag{A5}$$

By using Eqs. (43)-(44) to transform the second term, we finally obtain

$$\eta^{-1}\Theta\,\hat{L}^{\text{C}}\,(\Theta\,\eta\,\Phi) = \sum_{\lambda\mu\rho\sigma} W^{\text{C}}_{\lambda\mu\rho\sigma} \, N_\rho \, N_\sigma \left(\hat{E}^{-1}_\rho \hat{E}^{-1}_\sigma \hat{E}^{+1}_\lambda \hat{E}^{+1}_\mu - 1 \right) \Phi \,, \tag{A6}$$

which is identical to the adjoint operator (A2). Q. E. D.

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