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TIME-REVERSAL SYMMETRY RELATIONS FOR FLUCTUATING CURRENTS IN NONEQUILIBRIUM SYSTEMS*

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Fluctuation relations for currents are established in several classes of systems. For the effusion of noninteracting particles through a small hole in a thin wall, a fluctuation relation for the particle current is directly proved from the Hamiltonian microdynamics by constructing the exact invariant probability measure, which is shown to break time-reversal symmetry under nonequilibrium conditions. Current fluctuation relations are also obtained for the stochastic processes ruled by the Smoluchowski and Fokker–Planck master equations by modifying the master operator with the current counting parameters. Finally, the same method is applied to the coarse-grained master equation of the fluctuating Boltzmann equation to establish the fluctuation relation for the currents in dilute or rarefied gases.

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1. Introduction

The dichotomy between microreversibility and irreversibility at the macroscale is a puzzling aspect of natural phenomena. Recently, great advances have been carried out in the understanding of this fundamental question with the advent of time-reversal symmetry relations valid from close to far from equilibrium. These symmetry relations include the fluctuation relations for random quantities giving the entropy production after statistical averaging [1–6], for the random nonequilibrium work performed on time-dependent systems [7–10], as well as for the fluctuating currents of particles and energy flowing across a nonequilibrium system [11–14]. These latter

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relations are particularly useful to study the coupling between several currents in electronic devices and energy transduction in molecular machines [15–17]. On the one hand, the fluctuation relations find their origin in the microreversibility of the underlying Hamiltonian dynamics of the particles composing the systems. On the other hand, they characterize the breaking of time-reversal symmetry in the probability distributions of nonequilibrium steady states and the directionality induced by the nonequilibrium constraints [18].

The purpose of the present paper is to establish fluctuation relations for currents in several classes of systems and to show that these relations can explain the dichotomy between the time-reversal symmetry at the microscopic level of description and its breaking under nonequilibrium conditions at the statistical level of description.

In Section 2, the fluctuation relations for currents are presented as well as their implications for the second law of thermodynamics and response theory in nonequilibrium systems. Moreover, methods to establish these relations are outlined. In Section 3, we consider the effusion of noninteracting particles through a small hole in a thin wall separating space in two reservoirs. The stationary probability distribution is exactly constructed in this system, allowing us to illustrate the phenomenon of time-reversal symmetry breaking under nonequilibrium conditions while the underlying Hamiltonian dynamics keeps its microreversibility. Moreover, the stationary probability distribution is used to rigorously derive the current fluctuation relation from the Hamiltonian microdynamics, along lines previously followed for the multibaker map [19].

Beyond, systems of interacting particles are also considered. In Sections 4 and 5, current fluctuation relations are obtained for a Brownian particle driven out of equilibrium by an external force, as described by the Smoluchowski equation in the overdamped regime and the Fokker–Planck equation in the presence of inertial effects. Here, the method used to derive these results is based on the master equation of the stochastic process. The linear operator of the master equation is modified to depend on counting parameters for the currents flowing across the system and to give the cumulant generating function of the currents as the leading eigenvalue of the so-modified operator [3, 4, 20]. The modified operator is shown to obey a symmetry relation involving the affinities or thermodynamic forces driving the system out of equilibrium. The symmetry of the modified operator implies the symmetry of the cumulant generating function, hence the current fluctuation relation.

In Section 6, the same method is extended to derive a current fluctuation relation for dilute and rarefied gases ruled by the fluctuating Boltzmann equation. Gas-surface interactions are also taken into account. The method is applied to the coarse-grained master equation that has a form similar to the chemical master equation [21], for which the current fluctuation theorem has been previously established [11–13]. In this way, it is shown that the generalizations of Onsager reciprocity relations to the nonlinear response properties obtained in Refs. [11, 14] also apply to the gas flows ruled by the fluctuating Boltzmann equation. Conclusions and perspectives are drawn in Section 7.

2. Time-reversal symmetry relations and their implications

2.1. The microscopic and statistical levels of description

The underlying Hamiltonian microdynamics is known to be time-reversal symmetric in many systems. In the presence of an external magnetic field, the symmetry is extended by reversing also the magnetic field. On large scales, phenomena are observed and the measured properties are quantities that are combinations of the microscopic degrees of freedom. Examples of such observable quantities are the particle numbers and energies in the different parts of a system and the associated currents flowing between these parts. These quantities can be defined at the mechanical level of description in terms of the microscopic degrees of freedom of the underlying Hamiltonian dynamics.

This latter determines the time evolution of the observable quantities along the trajectories followed by the system. These trajectories are given by the solutions of the Hamiltonian equations of motion and they depend on the initial conditions of the total system. *A priori*, these initial conditions are free to take any value in the state space of the system, would it be the phase space of positions and momenta of the particles in classical mechanics or the Hilbert space of wavefunctions in quantum mechanics. However, the initial conditions are distributed in a way that is specific to the phenomenon under observation. The distribution of initial conditions usually defines a probability measure and an associated statistics. In this way, a statistical description is introduced in the framework of the microdynamics. Moreover, it is often the case that the distribution of initial conditions evolves after some transient behavior towards a stationary distribution depending on external parameters controlling the phenomenon under observation. These external parameters are the external force or magnetic fields, as well as the temperatures and chemical potentials of the reservoirs in contact with the parts of the system where the phenomenon of interest is observed. If the total system is composed of a domain in contact with one or several reservoirs and if the phenomenon of interest is described at the macroscale in terms of partial differential equations, the boundary conditions depend on these external parameters. In this way, natural systems can have different levels of description: at the microscale in terms of the Hamiltonian dynamics ruling the trajectories of particles in phase space, on mesoscopic scales in terms of a statistical description based on probability distributions and, finally, on the largest scale in terms of ordinary or partial differential equations for the macrovariables.

If the temperature and the chemical potentials are uniform, the system is in equilibrium and the statistical description is based on the Gibbsian probability distributions. If the uniformity conditions are not satisfied, the system is out of equilibrium and energy should be supplied from outside to maintain the directionality of the currents flowing across the system. The currents and their fluctuations are described in terms of nonequilibrium probability distributions that deviate from the equilibrium ones. The nonequilibrium probability distributions are the solutions of Liouville's equation of statistical mechanics or the solutions of the master equation of one of the reduced stochastic descriptions. The master equation rules the time evolution of the probability $P(\omega, t)$ that the system is in some coarse-grained state ω relevant to the phenomenon of interest at the time t

$$\partial_t P = \hat{L} P \,, \tag{1}$$

where $\hat{L}$ is a linear operator. The linearity guarantees the conservation of the total probability $\sum_\omega P(\omega, t) = 1$. A stationary solution defines an equilibrium or nonequilibrium stationary probability distribution. If the Gibbsian stationary probability distributions are symmetric under time reversal, this is not necessarily the case for the nonequilibrium distributions, which may break this symmetry. There is no contradiction with the time-reversal symmetry of Liouville's equation induced by the symmetry of the underlying Hamiltonian dynamics because the solution of an equation may have a lower symmetry than the equation itself, which is well known in condensed matter physics for the phenomena of spontaneous symmetry breaking.

2.2. Fluctuation relations for currents

In spite of the time-reversal symmetry breaking of nonequilibrium distributions, the underlying symmetry continues to prevail in the form of symmetry relations such as Onsager's reciprocity relations valid in the regime of linear response close to equilibrium or the so-called fluctuation relations also valid far from equilibrium in the regimes of nonlinear response. Several types of fluctuation relations have been proved in systems under transient, stationary, or time-dependent conditions and for different kinds of quantities [1–17]. Many effort has been devoted to fluctuating quantities that would correspond to the entropy production after statistical averaging [1–6]. However, the fluctuations are the feature of the ceaseless collisions among the molecules composing matter, as the Brownian motion reveals. The fluctuations are observed for the position and velocity of the Brownian particles, as well as for the particle numbers and the currents in phenomena such as critical opalescence and electrical noises [22, 23]. In this regard, the fluctuations have a mechanical origin. A remarkable result is that time-reversal symmetry relations have also been obtained for the fluctuating currents flowing across a system that may be driven out of equilibrium [11–17]. The external parameters that control a nonequilibrium stationary distribution are the so-called affinities $\boldsymbol{A}$ including

$$\text{the thermal affinities:} \qquad \frac{1}{k_{\rm B}T_j} - \frac{1}{k_{\rm B}T_i}\,, \tag{2}$$

$$\text{the chemical affinities:} \qquad \frac{\mu_{ip}}{k_{\rm B}T_i} - \frac{\mu_{jp}}{k_{\rm B}T_j}\,, \tag{3}$$

between the reservoirs $i, j = 1, 2, \ldots, r$ at the temperatures $\{T_i\}$ and the chemical potentials $\{\mu_{ip}\}$ for the different particle species $p = 1, 2, \ldots, s$ and where $k_{\rm B}$ is Boltzmann's constant [24–26]. One of the reservoirs is taken as a reference of temperature and chemical potentials. The system is driven out of equilibrium if other reservoirs have different temperatures or chemical potentials. The nonequilibrium conditions are thus fixed by $(r-1)(s+1)$ different affinities. All these affinities are vanishing at equilibrium. The affinities also include those due to the external forces $\boldsymbol{F}_{\rm ext}$ performing some work on the system.

The random variables of interest are the quantities of matter and energy $\Delta\boldsymbol{Q} = \{\Delta Q_\alpha\}$ that are transferred between the reservoirs during a time interval $[0, t]$. There are as many such quantities as there are affinities. The fluctuating currents are thus defined as $\boldsymbol{J} = \Delta\boldsymbol{Q}/t$. Alternatively, these fluctuating currents can be defined as $\boldsymbol{J} = \int_0^t \boldsymbol{j}(t')\,dt'$ using the instantaneous fluctuating currents $\boldsymbol{j}(t)$ expressed in terms of the degrees of freedom of the Hamiltonian microdynamics. If $P_{\boldsymbol{A}}$ denotes the probability distribution under stationary conditions specified by the affinities $\boldsymbol{A}$, the fluctuation relation for the currents reads

$$\frac{P_{\boldsymbol{A}}(\boldsymbol{J})}{P_{\boldsymbol{A}}(-\boldsymbol{J})} \simeq_{t\to\infty} e^{\boldsymbol{A}\cdot\boldsymbol{J}\,t}\,. \tag{4}$$

This relation compares the opposite fluctuations of the currents. At equilibrium where $\boldsymbol{A} = 0$, the principle of detailed balancing is recovered according to which opposite fluctuations are equiprobable. Out of equilibrium, the fluctuation relation expresses the directionality induced by nonvanishing affinities. Since the probabilities of opposite fluctuations have a ratio increasing or decreasing with time, one of both fluctuations will soon dominate over the opposite and a directionality thus appears under nonequilibrium conditions. The fluctuation relation (4) finds its origin in the time-reversal symmetry of the underlying Hamiltonian dynamics and it is compatible with the second law of thermodynamics. Indeed, Jensen's inequality $\langle e^x \rangle \geq e^{\langle x \rangle}$ with $x = -\boldsymbol{A}\cdot\boldsymbol{J}\, t$ and the statistical average $\langle\cdot\rangle_{\boldsymbol{A}}$ over the probability distribution $P_{\boldsymbol{A}}$ implies the nonnegativity of the entropy production given by the sum of the affinities multiplied by the statistical averages of the fluctuating currents

$$\frac{1}{k_{\rm B}}\frac{d_{\rm i}S}{dt} = \boldsymbol{A}\cdot\langle\boldsymbol{J}\rangle_{\boldsymbol{A}} \geq 0\,. \tag{5}$$

The symmetry relation (4) can be alternatively expressed in terms of the generating function of the statistical cumulants defined as

$$Q_{\boldsymbol{A}}(\boldsymbol{\lambda}) \equiv \lim_{t\to\infty} -\frac{1}{t}\ln\int P_{\boldsymbol{A}}(\boldsymbol{J})\, e^{-\boldsymbol{\lambda}\cdot\boldsymbol{J}\, t}\, d\boldsymbol{J}\,. \tag{6}$$

Inserting the symmetry relation (4) in this definition, we find the more compact expression

$$Q_{\boldsymbol{A}}(\boldsymbol{\lambda}) = Q_{\boldsymbol{A}}(\boldsymbol{A}-\boldsymbol{\lambda})\,. \tag{7}$$

Reciprocally, the fluctuation relation (4) can be inferred from the relation (7) under specific conditions using the theory of large deviation [27].

The fundamental result is that symmetry relations between the statistical cumulants of the currents and their coefficients of response to nonequilibrium perturbations can be deduced from the symmetry relation (7). The Onsager reciprocity relations are recovered in this way for the linear response coefficients [28]. Most remarkably, their generalization to the nonlinear response coefficients can also be obtained, which extends response theory to far-from-equilibrium regimes [11, 14]. These relations are essential for the understanding of the coupling between different transport processes, *e.g.*, for energy transduction in molecular motors, electron counting statistics in quantum dots and quantum transport, thermoelectric effects, or mass separation by effusion [15–17, 29, 30]. The current fluctuation relation (4) has thus fundamental implications for nonequilibrium phenomena down to the nanoscale.

2.3. Symmetry of the modified operator

Several methods exist to establish a current fluctuation relation in a specific system. In systems of noninteracting particles, the current fluctuation relation can be deduced from the Hamiltonian dynamics as shown in Section 3 for effusion. In systems of interacting particles, where particular degrees of freedom obey a stochastic process in some scaling limit, the master equation ruling the stochastic process can be used to deduce the current fluctuation relation. Schnakenberg's graph theory allows us to decompose the stochastic process into cycles and to identify the affinities [13, 31]. The linear operator $\hat{L}$ of the master equation (1) is modified to let it depend on the counting parameters $\boldsymbol{\lambda}$ of the cumulant generating function (6). The adjoint of the modified operator should be ruling the conditional expected values

$$F(\omega, t; \boldsymbol{\lambda}) \equiv \left\langle e^{-\boldsymbol{\lambda}\cdot\boldsymbol{J}\,t} \right\rangle_{\boldsymbol{A},\omega}\,, \tag{8}$$

given that the system is in the state ω at the initial time $t = 0$ for the process characterized by the affinities $\boldsymbol{A}$

$$\partial_t\, F = \hat{L}^{\dagger}_{\boldsymbol{\lambda}}\, F\,. \tag{9}$$

In the long-time limit, the conditional expected values (8) are decaying exponentially at a rate given by the cumulant generating function (6) so that this latter can be calculated as the leading eigenvalue of the modified operator or its adjoint

$$\hat{L}_{\boldsymbol{\lambda}}\, \Psi = -Q_{\boldsymbol{A}}(\boldsymbol{\lambda})\, \Psi\,. \tag{10}$$

If the modified operator obeys the symmetry relation

$$\eta^{-1}\, \Theta\, \hat{L}_{\boldsymbol{\lambda}}\, (\Theta\, \eta\, \Phi) = \hat{L}^{\dagger}_{\boldsymbol{A}-\boldsymbol{\lambda}}\, \Phi\,, \tag{11}$$

where Φ is an arbitrary function, Θ is the time-reversal transformation acting on the coarse-grained states $\{\omega\}$, and η is the equilibrium stationary distribution at the temperature and chemical potentials of the reference reservoir, its leading eigenvalue satisfies the symmetry relation (7) as a consequence [3, 4, 20]. Therefore, the symmetry of the modified operator implies the symmetry of the cumulant generating function. This method to establish the current fluctuation theorem is particularly convenient in stochastic processes with a known master equation and it will be used for systems ruled by the Smoluchowski equation in Section 4, the Fokker–Planck equation Section 5, and the fluctuating Boltzmann equation Section 6.

3. Symmetry relation for effusion in Hamiltonian dynamics

3.1. The invariant probability measure for a gas of noninteracting particles

In order to show that the fluctuation relation (4) can be deduced directly from the underlying Hamiltonian microdynamics without using the theory of stochastic processes and its master equation, let us consider the effusion of an ideal gas through a small hole in a thin wall separating the gas between two reservoirs at different temperatures and densities (see Fig. 1). The ideal gas is composed of monoatomic particles of mass m moving in free flight and undergoing elastic collision on the thin wall W. The free flights are the solutions of Hamilton's equations for the single-particle position $\boldsymbol{r} \in \mathbb{R}^3$ and momentum $\boldsymbol{p} \in \mathbb{R}^3$ with the Hamiltonian function given by

$$H = \frac{\boldsymbol{p}^2}{2m} \,. \tag{12}$$

Moreover, the free flights are eventually interrupted by elastic collisions on the thin wall W reflecting the z-component of the momentum according to the collision rule $\boldsymbol{p}' = \boldsymbol{p} - 2\,(\boldsymbol{p} \cdot \boldsymbol{u}_z)\,\boldsymbol{u}_z$, where $\boldsymbol{u}_z$ is the unit vector in the z-direction perpendicular to the thin wall W. The motion of every particle is thus ruled by a Hamiltonian flow Φ^t in the single-particle phase space $\mathcal{M} = \{(\boldsymbol{r}, \boldsymbol{p}) \in (\mathbb{R}^3 \setminus W) \otimes \mathbb{R}^3\}$. This single-particle Hamiltonian flow is symplectic, obeys Liouville's theorem, and is symmetric under the time-reversal transformation $\Theta(\boldsymbol{r}, \boldsymbol{p}) = (\boldsymbol{r}, -\boldsymbol{p})$: $\Theta \circ \Phi^t \circ \Theta = \Phi^{-t}$. This microreversibility is illustrated in Fig. 1 (a).

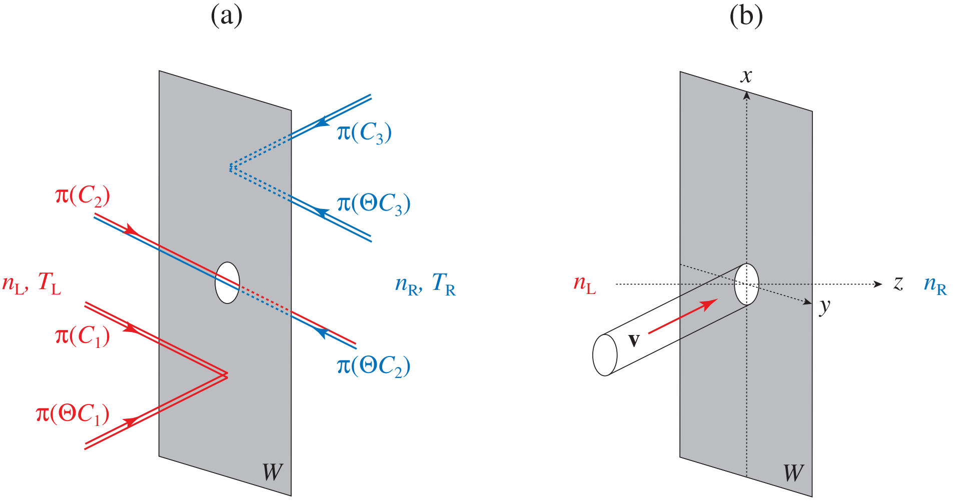

Fig. 1. (a) Schematic representation of an effusion process in the physical position space $\boldsymbol{r} = (x, y, z) \in (\mathbb{R}^3 \setminus W)$, where the wall W separates the position space between the two reservoirs, where the gas of noninteracting particles has different temperatures and densities. The wall W has a hole of area σ. The figure depicts the projection $\pi(\boldsymbol{r}, \boldsymbol{p}) = \boldsymbol{r}$ of three types of phase-space orbits C_i and their time reversal ΘC_i (with $i = 1, 2, 3$). (b) Representation of the cylindrical volume containing the particles with the velocity $\boldsymbol{v} = \boldsymbol{p}/m$ crossing the boundary between both reservoirs through the hole during some time interval $[0, t]$.

In the left-hand reservoir, the particles arrive from $z = -\infty$ with velocities distributed according to a Maxwell–Boltzmann distribution at the temperature $T_{\rm L}$ and the density $n_{\rm L}$. In the right-hand reservoir, the particles arrive from $z = +\infty$ with velocities distributed according to a Maxwell–Boltzmann distribution at the temperature $T_{\rm R}$ and the density $n_{\rm R}$. The single-particle distribution function has thus the Maxwell–Boltzmann form

$$f(\boldsymbol{r},\boldsymbol{p}) = \frac{n_C}{(2\pi m k_{\rm B} T_C)^{3/2}} \exp\left(-\frac{\boldsymbol{p}^2}{2mk_{\rm B}T_C}\right) , \tag{13}$$

where the particle density n_C and the temperature T_C take the values associated with the orbit C to which the phase-space point $(\boldsymbol{r},\boldsymbol{p})$ belongs and corresponding to the domain from which the orbit is coming. For the three types of possible orbits depicted in Fig. 1 (a), these values are the following

$$n_C = n_{\rm L}\,, \quad T_C = T_{\rm L} \qquad \text{for} \qquad (\boldsymbol{r},\boldsymbol{p}) \in C_1\,,\ \varTheta C_1\,,\ C_2\,; \tag{14}$$

$$n_C = n_{\rm R}\,, \quad T_C = T_{\rm R} \qquad \text{for} \qquad (\boldsymbol{r},\boldsymbol{p}) \in C_3\,,\ \varTheta C_3\,,\ \varTheta C_2\,. \tag{15}$$

The distribution function is invariant under the Hamiltonian flow, $f[\varPhi^t(\boldsymbol{r},\boldsymbol{p})] = f(\boldsymbol{r},\boldsymbol{p})$. Nevertheless, it is not symmetric under time reversal, $f[\varTheta(\boldsymbol{r},\boldsymbol{p})] \neq f(\boldsymbol{r},\boldsymbol{p})$, for nonequilibrium constraints such that $n_{\rm L} \neq n_{\rm R}$ or $T_{\rm L} \neq T_{\rm R}$.

The single-particle distribution function gives the density of particles in an element of volume $d\boldsymbol{r}\, d\boldsymbol{p}$ at some point $(\boldsymbol{r},\boldsymbol{p})$ in the single-particle phase space $\mathcal{M}$. Because of the infinite spatial extension of the reservoirs, the ideal gas contains an infinite number of particles and its microstate is given by the point

$$\boldsymbol{\varGamma} = (\boldsymbol{r}_1,\boldsymbol{p}_1,\boldsymbol{r}_2,\boldsymbol{p}_2,\ldots,\boldsymbol{r}_N,\boldsymbol{p}_N,\ldots) \in \boldsymbol{\mathcal{M}} = \mathcal{M}^\infty\,. \tag{16}$$

In this infinite-particle system, the Hamiltonian flow $\boldsymbol{\varGamma}_t = \boldsymbol{\varPhi}^t(\boldsymbol{\varGamma}_0)$ is also time-reversal symmetric

$$\boldsymbol{\varTheta} \circ \boldsymbol{\varPhi}^t \circ \boldsymbol{\varTheta} = \boldsymbol{\varPhi}^{-t}\,, \tag{17}$$

where $\boldsymbol{\varTheta}$ is the time-reversal transformation acting on the microstate (16) by reversing all the momenta: $\boldsymbol{p}_a \to -\boldsymbol{p}_a$, $\forall\, a \in \mathbb{N}_0$.

For the infinite-particle system, an invariant probability measure μ can be constructed as a Poisson suspension on the basis of the invariant distribution function (13) [32]. For any six-dimensional domain $\mathcal{D} \subset \mathcal{M}$ of the single-particle phase space $\mathcal{M}$, we consider the random events

$$\mathcal{A}_{\mathcal{D},N} = \{\boldsymbol{\varGamma} \in \boldsymbol{\mathcal{M}} :\ \mathrm{card}(\boldsymbol{\varGamma} \cap \mathcal{D}) = N\}\ , \tag{18}$$

for which there are N particles in the domain $\mathcal{D}$. The average number of particles in the phase-space domain $\mathcal{D}$ is given by

$$\nu(\mathcal{D}) = \int_{\mathcal{D}} f(\boldsymbol{r},\boldsymbol{p})\, d\boldsymbol{r}\, d\boldsymbol{p} \tag{19}$$

in terms of the single-particle distribution function (13).

We notice that the trajectories bouncing between the sharp edges of the hole at $z = 0$ play no role in this system because they form a set of zero Lebesgue measure and they are fully unstable with an infinite positive Lyapunov exponent. If the wall W was not thin and had a nonvanishing width, there might exist trajectories trapped forever in the hole with finite positive or zero Lyapunov exponents. If they existed, such trapped trajectories would control part of the dynamics and should be taken into account, but this is not the case here since the wall is assumed to be thin with a vanishing width.

For a system of noninteracting particles, the number N of particles in the domain $\mathcal{D}$ is a random variable of the Poisson distribution

$$\mu\left(\mathcal{A}_{\mathcal{D},N}\right) = \frac{\nu(\mathcal{D})^N}{N!}\, e^{-\nu(\mathcal{D})}\,. \tag{20}$$

Moreover, random events in which disjoint domains have given particle numbers are statistically independent so that

$$\mu\left(\mathcal{A}_{\mathcal{D}_1,N_1} \cap \mathcal{A}_{\mathcal{D}_2,N_2}\right) = \mu\left(\mathcal{A}_{\mathcal{D}_1,N_1}\right)\, \mu\left(\mathcal{A}_{\mathcal{D}_2,N_2}\right) \qquad \text{if} \qquad \mathcal{D}_1 \cap \mathcal{D}_2 = \emptyset\,. \tag{21}$$

Both Eqs. (20) and (21) define the probability distribution of the so-called Poisson suspension [32]. We have the

Lemma. The probability to find N particles in a domain $\mathcal{D} = \mathcal{D}_1 \cup \mathcal{D}_2$ composed of two disjoint domains $\mathcal{D}_1 \cap \mathcal{D}_2 = \emptyset$ is again a Poisson distribution with an average equal to $\nu(\mathcal{D}) = \nu(\mathcal{D}_1) + \nu(\mathcal{D}_2)$.

Indeed, since the domains $\mathcal{D}_1$ and $\mathcal{D}_2$ are disjoint, the number of particles in the domain $\mathcal{D} = \mathcal{D}_1 \cup \mathcal{D}_2$ is equal to $N = N_1 + N_2$, where N_1 is the number of particles in the domain $\mathcal{D}_1$ and N_2 the number in $\mathcal{D}_2$. Both N_1 and N_2 are distributed according to the Poisson distributions of averages $\nu(\mathcal{D}_1)$ and $\nu(\mathcal{D}_2)$ and the statistical independence (21) implies that

$$\begin{aligned} \mu\left(\mathcal{A}_{\mathcal{D},N}\right) &= \sum_{N_1=0}^{N} \mu\left(\mathcal{A}_{\mathcal{D}_1,N_1} \cap \mathcal{A}_{\mathcal{D}_2,N-N_1}\right) \\ &= \sum_{N_1=0}^{N} \mu\left(\mathcal{A}_{\mathcal{D}_1,N_1}\right)\, \mu\left(\mathcal{A}_{\mathcal{D}_2,N-N_1}\right) = \frac{\nu(\mathcal{D})^N}{N!}\, e^{-\nu(\mathcal{D})} \end{aligned} \tag{22}$$

with $\nu(\mathcal{D}) = \nu(\mathcal{D}_1) + \nu(\mathcal{D}_2)$. Q.E.D.

As a consequence, the measure μ is normalized to unity and, therefore, defines a probability measure. This probability measure is invariant under the time evolution of the Hamiltonian flow $\boldsymbol{\Phi}^t$

$$\mu\left(\boldsymbol{\Phi}^t\mathcal{A}\right) = \mu\left(\mathcal{A}\right) \tag{23}$$

for any random event $\mathcal{A}$. This is the consequence of the stationarity of the single-particle distribution function (13), $f[\Phi^t(\boldsymbol{r},\boldsymbol{p})] = f(\boldsymbol{r},\boldsymbol{p})$, which implies the invariance $\nu\left(\Phi^t\mathcal{D}\right) = \nu\left(\mathcal{D}\right)$ of the measure (19). The flow $\boldsymbol{\Phi}^t$ in the infinite phase space $\boldsymbol{\mathcal{M}}$ and the invariant probability measure of the Poisson suspension defines the infinite-particle dynamical system $(\boldsymbol{\Phi}^t, \boldsymbol{\mathcal{M}}, \mu)$. This dynamical system is known to have the ergodic, mixing, and the Bernoulli properties [32]. Although the flow $\boldsymbol{\Phi}^t$ has the microreversibility (17), the dynamical system is not symmetric under time reversal because

$$\mu\left(\boldsymbol{\Theta}\mathcal{A}\right) \neq \mu\left(\mathcal{A}\right) \qquad \text{unless} \qquad n_{\rm L} = n_{\rm R} \quad \text{and} \quad T_{\rm L} = T_{\rm R}\,, \tag{24}$$

as already pointed out in Ref. [33]. The time-reversal symmetry is thus broken at the statistical level of description for the stationary probability distribution μ under nonequilibrium conditions $n_{\rm L} \neq n_{\rm R}$ or $T_{\rm L} \neq T_{\rm R}$.

3.2. Exact current fluctuation relation for effusion

In this framework, the counting statistics of the particle and energy currents can be fully characterized. Here, we only consider the particle current under the condition that the temperature is uniform $T_{\rm L} = T_{\rm R} \equiv T$ so that the momentum Maxwell–Boltzmann distribution is everywhere given by

$$\varphi(\boldsymbol{p}) = \frac{1}{(2\pi m k_{\rm B}T)^{3/2}} \exp\left(-\frac{\boldsymbol{p}^2}{2mk_{\rm B}T}\right)\,. \tag{25}$$

The net current flowing between the left-hand and the right-hand reservoirs during the time interval $[0,t]$ is given by $J = \Delta N/t$ in terms of the difference $\Delta N = N_+ - N_-$ between the number $N_\pm$ of particles crossing the hole with a positive (respectively, negative) z-component of their velocity coming from the left-hand (respectively right-hand) reservoir. All the particles contributing to the number N_+ are contained in a phase-space domain $\mathcal{D}_+$ incident on the hole of area σ during the time interval $[0,t]$ with $p_z > 0$ and $z < 0$. The particles of a given momentum $\boldsymbol{p} = m\boldsymbol{v}$ satisfying this condition are contained in a cylinder of basis given by the hole and of height equal to $v_z t$. All the particles in this cylinder are flowing through the hole during the time interval $[0,t]$ (see Fig. 1 (b)). In position space, the volume of this cylinder is equal to $\sigma v_z t$. Therefore, the average number of particles in the domain $\mathcal{D}_+$ is given by

$$\nu_+ = \nu(\mathcal{D}_+) = \int_{\mathcal{D}_+} f(\boldsymbol{r},\boldsymbol{p})\, d\boldsymbol{r}\, d\boldsymbol{p} = t\,\sigma\, n_{\rm L} \int_{p_z>0} \frac{p_z}{m}\, \varphi(\boldsymbol{p})\, d\boldsymbol{p} = t\,\sigma\, n_{\rm L} \sqrt{\frac{k_{\rm B}T}{2\pi m}}\,, \tag{26}$$

where we used Eq. (13) for an orbit $C = L$ on which the condition (14) holds. Similarly, the average number of particles flowing from the right-hand to the left-hand reservoir during the time interval $[0,t]$ is given by

$$\nu_- = \nu(\mathcal{D}_-) = \int_{\mathcal{D}_-} f(\boldsymbol{r},\boldsymbol{p})\, d\boldsymbol{r}\, d\boldsymbol{p} = t\,\sigma\, n_{\rm R} \int_{p_z<0} \frac{p_z}{m}\, \varphi(\boldsymbol{p})\, d\boldsymbol{p} = t\,\sigma\, n_{\rm R} \sqrt{\frac{k_{\rm B}T}{2\pi m}}\,, \tag{27}$$

where $\mathcal{D}_-$ is the phase-space domain containing the orbits with $p_z < 0$ and $z > 0$ going through the hole during this time interval.

Now, the probability that the number of particles crossing the hole during the time interval $[0,t]$ is equal to $n = \Delta N \in \mathbb{Z}$ is given by

$$P(n,t) = e^{-(\nu_+ + \nu_-)} \left(\frac{\nu_+}{\nu_-}\right)^{n/2} I_n\left(2\sqrt{\nu_+\nu_-}\right) \tag{28}$$

in terms of the modified Bessel function defined by [34]

$$I_n(z) = I_{-n}(z) = \left(\frac{z}{2}\right)^n \sum_{k=0}^{\infty} \frac{(z^2/4)^k}{k!\,(k+n)!} \tag{29}$$

and the average particle numbers (26) and (27). Indeed, $n = \Delta N = N_+ - N_-$ is the difference between two Poissonian random variables. For $n \geq 0$, we have that

$$\begin{aligned} P(n,t) &= \sum_{k=0}^{\infty} \mu(\mathcal{A}_{\mathcal{D}_+,n+k})\, \mu(\mathcal{A}_{\mathcal{D}_-,k}) \\ &= \sum_{k=0}^{\infty} e^{-\nu_+} \frac{\nu_+^{n+k}}{(n+k)!}\, e^{-\nu_-} \frac{\nu_-^k}{k!} \\ &= e^{-(\nu_+ + \nu_-)} \left(\frac{\nu_+}{\nu_-}\right)^{n/2} I_n\left(2\sqrt{\nu_+\nu_-}\right) \end{aligned} \tag{30}$$

with the modified Bessel function (29) for $z = 2\sqrt{\nu_+\nu_-}$. A similar calculation holds for $n < 0$.

If we compare opposite fluctuations of the current, we find the following:

Current fluctuation theorem: *The probability distribution of the net random number ΔN of particles flowing from the left-hand to the right-hand reservoir during the time interval $[0,t]$ obeys the symmetry relation*

$$\frac{P(\Delta N,t)}{P(-\Delta N,t)} = e^{A\,\Delta N}\,, \qquad \textit{where} \qquad A = \ln\frac{\nu_+}{\nu_-} = \ln\frac{n_{\rm L}}{n_{\rm R}} \tag{31}$$

is the affinity driving the particle current out of equilibrium.

This result follows from the symmetry $I_n(z) = I_{-n}(z)$ of the modified Bessel function and the fact that the quantity $\ln(\nu_+/\nu_-)$ is equal to the chemical affinity (3) between two reservoirs at different particle densities but the same temperature

$$A = \frac{1}{k_{\rm B}T}\,(\mu_{\rm L} - \mu_{\rm R}) = \ln\frac{n_{\rm L}}{n_{\rm R}}\,, \tag{32}$$

since the chemical potential of an ideal gas of monoatomic particles is given by $\mu = k_{\rm B}T\ln\left(c\,n\,T^{-3/2}\right)$ with a constant c, hence the need of temperature uniformity $T_{\rm L} = T_{\rm R} = T$. If the temperature is not uniform, an extended fluctuation theorem holds by considering the particle and energy currents together [29, 30].

Here, the main point is that the current fluctuation theorem is directly established on the basis of the Hamiltonian dynamics and ergodic theory, showing that there is, in principle, no need to use the stronger assumptions of the theory of stochastic processes. Of course, the time derivative of the probability (30) gives us the master equation of the stochastic process ruling the particle transport

$$\frac{d}{dt}P(n,t) = w_+\,P(n-1,t) + w_-\,P(n+1,t) - (w_+ + w_-)\,P(n,t) \tag{33}$$

with the transition rates $w_\pm = d\nu_\pm/dt$. This is a further consequence of the fact that the infinite-particle dynamical system is a Bernoulli flow, as established in ergodic theory [32], but this does not preclude the conclusion that the fluctuation theorem can be directly established from the underlying Hamiltonian dynamics. The crucial ingredient is the rigorous construction of the invariant probability measure under equilibrium and nonequilibrium conditions. In this construction, the breaking of the time-reversal symmetry is manifest under nonequilibrium conditions for the infinite-particle dynamical system $(\boldsymbol{\Phi}^t, \boldsymbol{\mathcal{M}}, \mu)$ of the statistical description, although the Hamiltonian flow $\boldsymbol{\Phi}^t$ ruling the time evolution of the individual trajectories keeps the underlying microreversibility.

4. Symmetry relation for the Smoluchowski equation

The current fluctuation theorem can also be established for the Brownian motion in a uniform external force $\boldsymbol{F}_{\rm ext}$ in systems of infinite spatial extension. The microscopic theory of the Brownian motion has been established in the sixties under the condition that the mass m of the Brownian particle is much larger than the mass of the molecules of the surrounding fluid [35–37]. The microscopic theory proceeds by deducing the master equation for the Brownian particle from the Liouville equation of the total system composed of the Brownian particle and the molecules.

In the overdamped regime, the ratio between the relaxation time associated with the friction coefficient ζ and the square of the inertial time due to the mass m of the colloidal particle

$$\frac{t_{\rm relax}}{t^2_{\rm inertial}} \simeq \frac{\zeta}{m} \tag{34}$$

is large enough, so that the effects of friction overwhelm the inertial effects. In this regime, the master equation for the probability density $p(\boldsymbol{r},t)$ that the colloidal particle is found in the position $\boldsymbol{r}\in\mathbb{R}^3$ at the time t is given by the *Smoluchowski equation*

$$\partial_t\, p = -\boldsymbol{\nabla}\cdot(\beta\, D\, \boldsymbol{F}\, p) + D\,\nabla^2 p\,, \qquad \text{where} \qquad \boldsymbol{F} = -\boldsymbol{\nabla}U + \boldsymbol{F}_{\rm ext} \tag{35}$$

is the force field to which the particle is subjected, $D = k_{\rm B}T/\zeta$ is the diffusion coefficient, and $\beta = (k_{\rm B}T)^{-1}$ is the inverse of the thermal energy $k_{\rm B}T$ at the fluid temperature T [22, 23]. The force field $\boldsymbol{F}$ is supposed to result from a uniform external force $\boldsymbol{F}_{\rm ext}$ superposed to an energy potential $U(\boldsymbol{r})$ that extends periodically in space.

Smoluchowski's equation can be written in the form $\partial_t\, p = \hat{L}\, p$ in terms of the linear operator $\hat{L}$ given by the right-hand member of Eq. (35). Here, the fluctuating current of interest is the drift motion of the colloidal particle. The conditional expected value $\langle e^{-\boldsymbol{\lambda}\cdot\boldsymbol{r}_t}\rangle_{\boldsymbol{r}_0}$ that the colloidal particle is found at the time t in the position $\boldsymbol{r}_t$, given that it was initially in the position $\boldsymbol{r}_0$ is ruled by the adjoint of the modified operator

$$\hat{L}_{\boldsymbol{\lambda}} = e^{-\boldsymbol{\lambda}\cdot\boldsymbol{r}}\,\hat{L}\,e^{\boldsymbol{\lambda}\cdot\boldsymbol{r}}\,. \tag{36}$$

For Smoluchowski's equation (35), this modified operator takes the form

$$\hat{L}_{\boldsymbol{\lambda}} = \hat{L} + 2\,D\,\boldsymbol{\lambda}\cdot\boldsymbol{\nabla} - \beta\,D\,\boldsymbol{\lambda}\cdot\boldsymbol{F} + D\,\boldsymbol{\lambda}^2\,, \tag{37}$$

where $\hat{L} = \hat{L}_{\boldsymbol{0}}$ is the unmodified linear operator.

Now, the modified operator obeys the symmetry relation

$$\eta^{-1}\,\hat{L}_{\boldsymbol{\lambda}}\,(\eta\,\phi) = \hat{L}^{\dagger}_{\boldsymbol{A}-\boldsymbol{\lambda}}\,\phi \qquad \text{for any function } \phi(\boldsymbol{r}) \tag{38}$$

with the Boltzmann factor $\eta = \exp\left[-\beta U(\boldsymbol{r})\right]$ and the affinity

$$\boldsymbol{A} = \frac{\boldsymbol{F}_{\rm ext}}{k_{\rm B}T} \tag{39}$$

due to the external force driving the Brownian particle out of equilibrium. The energy potential $U(\boldsymbol{r})$ is internal to the system and does not contribute to the nonequilibrium drift of the Brownian particle. Without the external force $\boldsymbol{F}_{\rm ext}$, the Brownian particle would undergo an unbiased random walk characteristic of thermodynamic equilibrium.

The symmetry relation (38) is the analogue of Eq. (11) since the Smoluchowski equation only concerns the probability distribution in a position that remains unchanged under the time-reversal transformation $\Theta(\boldsymbol{r},\boldsymbol{p}) = (\boldsymbol{r},-\boldsymbol{p})$. As explained in Section 2, the consequence of the symmetry (38) is the current fluctuation relation

$$\frac{P_{\boldsymbol{A}}(\Delta\boldsymbol{r}_t)}{P_{\boldsymbol{A}}(-\Delta\boldsymbol{r}_t)} \simeq_{t\to\infty} e^{\boldsymbol{A}\cdot\Delta\boldsymbol{r}_t} \tag{40}$$

for the probability that the colloidal particle has the displacement $\Delta\boldsymbol{r}_t = \boldsymbol{r}_t - \boldsymbol{r}_0$ during the time interval $[0,t]$ under the effect of the affinity (39). Therefore, the cumulant generating function (6) of the random displacement $\Delta\boldsymbol{r}_t$ obeys the symmetry relation (7). In particular, the average drift velocity is given by

$$\boldsymbol{V} = \lim_{t\to\infty}\frac{1}{t}\,\langle\Delta\boldsymbol{r}_t\rangle_{\boldsymbol{A}} = \frac{\partial Q_{\boldsymbol{A}}}{\partial\boldsymbol{\lambda}}(\boldsymbol{0}) \tag{41}$$

and the higher cumulants by further derivatives with respect to the parameters $\boldsymbol{\lambda}$. The average drift velocity vanishes with the affinity. The response coefficients are given by expanding $\boldsymbol{V}(\boldsymbol{A})$ in powers of the components of the affinity $\boldsymbol{A} = \{A_\alpha\}_{\alpha=x,y,z}$. As the consequence of the current fluctuation relation (40), the Onsager reciprocity relations can be generalized from the linear to the nonlinear response coefficients, as shown elsewhere [11, 14].

For example, the current fluctuation relation concerns the Brownian motion in an optical lattice and driven in nonequilibrium steady states by a uniform external force such as the force due to the acceleration g of gravity: $\boldsymbol{F}_{\rm ext} = -mg\boldsymbol{u}_z$.

5. Symmetry relation for the Fokker–Planck equation

The current fluctuation relation (40) can also be established for the Brownian motion, where the inertial effects are not negligible because the ratio

(34) takes a finite value. For this purpose, we may consider the master equation for the time evolution of the probability density $\mathcal{P}(\boldsymbol{r},\boldsymbol{p},t)$ that the colloidal particle is found in the position $\boldsymbol{r}\in\mathbb{R}^3$ with the momentum $\boldsymbol{p}\in\mathbb{R}^3$ at the time t, which is given by the Fokker–Planck equation

$$\frac{\partial\mathcal{P}}{\partial t} = -\frac{\boldsymbol{p}}{m}\cdot\frac{\partial\mathcal{P}}{\partial\boldsymbol{r}} - \boldsymbol{F}\cdot\frac{\partial\mathcal{P}}{\partial\boldsymbol{p}} + \frac{\partial}{\partial\boldsymbol{p}}\cdot\left(\zeta\,\frac{\boldsymbol{p}}{m}\,\mathcal{P}\right) + \zeta\,k_{\mathrm{B}}T\,\frac{\partial^2\mathcal{P}}{\partial\boldsymbol{p}^2}\,, \tag{42}$$

where

$$\boldsymbol{F} = -\boldsymbol{\nabla}U + \boldsymbol{F}_{\mathrm{ext}}$$

if the colloidal particle moves in an energy potential $U(\boldsymbol{r})$ that extends periodically in space under the effect of the uniform external force $\boldsymbol{F}_{\mathrm{ext}}$. The Fokker–Planck equation can also be written in the form $\partial_t\mathcal{P} = \hat{L}\,\mathcal{P}$ where the linear operator $\hat{L}$ is given by the right-hand member of Eq. (43).

The modified operator giving the cumulant generating function of the random displacements of the colloidal particle as its leading eigenvalue by Eq. (10) is again defined by Eq. (36). The so-modified Fokker–Planck operator takes the form

$$\hat{L}_{\boldsymbol{\lambda}} = \hat{L} - \boldsymbol{\lambda}\cdot\frac{\boldsymbol{p}}{m} \tag{43}$$

in terms of the unmodified linear operator $\hat{L} = \hat{L}_{\mathbf{0}}$. This modified operator obeys the symmetry relation (11) with the time-reversal transformation $\Theta(\boldsymbol{r},\boldsymbol{p}) = (\boldsymbol{r},-\boldsymbol{p})$, the Boltzmann factor

$$\eta = \exp\left\{-\beta\left[\frac{\boldsymbol{p}^2}{2m} + U(\boldsymbol{r})\right]\right\} \tag{44}$$

for equilibrium in the internal potential $U(\boldsymbol{r})$, and the affinity (39) driving the Brownian particle out of equilibrium. Consequently, the current fluctuation relation (40) is here also obtained for the random displacements $\Delta\boldsymbol{r}_t = \boldsymbol{r}_t - \boldsymbol{r}_0$ of the Brownian particle during the time interval $[0,t]$, whereupon the symmetry relations for the cumulants and the response coefficients also hold for the stochastic process ruled by the Fokker–Planck equation [14].

6. Symmetry relation for the fluctuating Boltzmann equation

6.1. *Interacting particles in dilute or rarefied gases*

For interacting particles in dilute or rarefied gases, the current fluctuation relation (4) can be established by using the fluctuating Boltzmann equation, which has been proposed since the late forties [38–47]. The conceptual advantage over the Boltzmann's equation itself is that this latter is a nonlinear kinetic equation that cannot be considered as the master equation of a stochastic process. For this purpose, the master equation should indeed be linear. Nonlinear kinetic equations are familiar in macroscopic chemical kinetics for the time evolution of the concentrations of the different chemical species taking part in reactions [21]. At the mesoscopic level of description, these concentrations are fluctuating because they represent particle densities known to fluctuate since the pioneering work of Smoluchowski [22, 23]. The densities and concentrations are fluctuating fields extending in space and ruled by stochastic partial differential equations as in fluctuating hydrodynamics [48]. The situation is analogue to the case of a single particle although a whole field is fluctuating. Therefore, time-reversal symmetry relations can also be envisaged for these spatially extended systems under out-of-equilibrium conditions where fluctuating currents are induced by external driving. In this way, a current fluctuation relation has been obtained for processes ruled by the fluctuating diffusion equation in Ref. [12]. Drawing on the analogy between a fluctuating particle density $n(\boldsymbol{r},t)$ and a fluctuating single-particle distribution function $f(\boldsymbol{r},\boldsymbol{v},t)$, the scheme can be generalized to the fluctuating Boltzmann equation under nonequilibrium conditions [49].

As an example, we may consider a dilute or rarefied gas flowing through a nanopore in a wall separating two reservoirs at different temperatures and particle densities (see Fig. 2). The difference with respect to the situation treated in Section 3 is that the particles are no longer independent because they interact and exchange energy and momentum during binary collisions. Moreover, the particles may also exchange energy by scattering on surfaces at given temperatures, inducing gas–surface interactions [50].

Fig. 2. Schematic representation of a dilute or rarefied gas flowing through a nanopore between two reservoirs at given temperatures and particle densities.

6.2. The fluctuating Boltzmann equation

The fluctuating Boltzmann equation is a stochastic differential equation for the single-particle distribution function $f(\boldsymbol{r},\boldsymbol{v},t)$ of the form

$$\frac{\partial f}{\partial t} = \mathcal{A}^{\rm F}[f] + \mathcal{A}^{\rm C}[f] + \mathcal{A}^{\rm R}[f] + \mathcal{A}^{\rm S}[f] + g(\boldsymbol{r},\boldsymbol{v},t)\,, \tag{45}$$

where $\mathcal{A}^{\rm F,C,R,S}[f]$ are the deterministic rates due to the single-particle Hamiltonian flow, the binary collisions, the particle exchanges with the reservoirs, and the gas–surface interactions, while $g(\boldsymbol{r},\boldsymbol{v},t)$ is a Gaussian white noise satisfying

$$\langle g(\boldsymbol{r},\boldsymbol{v},t)\rangle \;=\; 0\,, \tag{46}$$

$$\left\langle g(\boldsymbol{r},\boldsymbol{v},t)\, g\left(\boldsymbol{r}',\boldsymbol{v}',t'\right)\right\rangle \;=\; \delta\left(t-t'\right)\,\Big(\mathcal{B}^{\rm F}[f] + \mathcal{B}^{\rm C}[f] + \mathcal{B}^{\rm R}[f] + \mathcal{B}^{\rm S}[f]\Big)\,, \tag{47}$$

where the diffusivities $\mathcal{B}^{\rm F,C,R,S}[f]$ depend on $f(\boldsymbol{r},\boldsymbol{v},t)$ itself [38–47].

The single-particle Hamiltonian flow is described by

$$\mathcal{A}^{\rm F}[f] = -\boldsymbol{v}\cdot\frac{\partial f}{\partial \boldsymbol{r}} - \frac{\boldsymbol{F}}{m}\cdot\frac{\partial f}{\partial \boldsymbol{v}} \tag{48}$$

and $\mathcal{B}^{\rm F}[f]=0$ because it is noiseless.

The binary collisions contribute by the Boltzmannian collision term

$$\mathcal{A}^{\rm C}[f] = \int d\boldsymbol{v}_2\, d\boldsymbol{v}_1'\, d\boldsymbol{v}_2'\, w\left(\boldsymbol{v}_1,\boldsymbol{v}_2|\boldsymbol{v}_1',\boldsymbol{v}_2'\right)\,\left(f_1'\, f_2' - f_1\, f_2\right)\,, \tag{49}$$

where $f=f_1$ is the distribution function at the position $\boldsymbol{r}=\boldsymbol{r}_1$ and the velocity $\boldsymbol{v}=\boldsymbol{v}_1$ of the first particle before the binary collision, f_1' the distribution function of the first particle after the binary collision, while f_2 and f_2' the distribution functions of the second particle before and after the collision. The corresponding diffusivity is given by

$$\begin{aligned}\mathcal{B}^{\rm C}[f] \;=\; & \delta(\boldsymbol{r}-\boldsymbol{r}')\int d\boldsymbol{v}_2\, d\boldsymbol{v}_3\, d\boldsymbol{v}_4\, w\left(\boldsymbol{v}_1,\boldsymbol{v}_2|\boldsymbol{v}_3,\boldsymbol{v}_4\right)\,\left(f_1\, f_2 + f_3\, f_4\right) \\ & \times\left[\delta\left(\boldsymbol{v}_1-\boldsymbol{v}'\right) + \delta\left(\boldsymbol{v}_2-\boldsymbol{v}'\right) - \delta\left(\boldsymbol{v}_3-\boldsymbol{v}'\right) - \delta\left(\boldsymbol{v}_4-\boldsymbol{v}'\right)\right]\,,\end{aligned} \tag{50}$$

where $f_a = f(\boldsymbol{r},\boldsymbol{v}_a)$ for $a=1,2,3,4$ [45–47]. The transition rate coefficients are related to the differential cross section $\sigma_{\rm diff}$ of the binary collisions by

$$w\left(\boldsymbol{v}_1,\boldsymbol{v}_2|\boldsymbol{v}_1',\boldsymbol{v}_2'\right) = \sigma_{\rm diff}\,\delta\left(\boldsymbol{v}_1+\boldsymbol{v}_2-\boldsymbol{v}_1'-\boldsymbol{v}_2'\right)\,\delta\left(\boldsymbol{v}_1^2+\boldsymbol{v}_2^2-\boldsymbol{v}_1'^2-\boldsymbol{v}_2'^2\right)\,, \tag{51}$$

where the delta's express the conservation of linear momentum and kinetic energy in every binary collision. In general, the transition rate coefficients have the following symmetries

$$\text{time-reversal symmetry:} \quad w\left(\boldsymbol{v}_1, \boldsymbol{v}_2 | \boldsymbol{v}_1', \boldsymbol{v}_2'\right) = w\left(-\boldsymbol{v}_1', -\boldsymbol{v}_2' | -\boldsymbol{v}_1, -\boldsymbol{v}_2\right) , \tag{52}$$

$$\text{space-orthogonal symmetry:} \quad w\left(\boldsymbol{v}_1, \boldsymbol{v}_2 | \boldsymbol{v}_1', \boldsymbol{v}_2'\right) = w\left(\mathsf{R}\cdot\boldsymbol{v}_1, \mathsf{R}\cdot\boldsymbol{v}_2 \big| \mathsf{R}\cdot\boldsymbol{v}_1', \mathsf{R}\cdot\boldsymbol{v}_2'\right) , \tag{53}$$

where R is a matrix belonging to the orthogonal group O(3) including spatial rotations and reflections [51].

The inflow and outflow from and to the reservoirs are described by

$$\begin{aligned} \mathcal{A}^{\mathrm{R}}[f] &= \sum_{i=1}^{r} \int_{S_i} d^2S\, \delta(\boldsymbol{r}-\boldsymbol{r}_i)\, (\boldsymbol{n}\cdot\boldsymbol{v})\, \theta(\boldsymbol{n}\cdot\boldsymbol{v})\, \left[f_i(\boldsymbol{v}) - f(\boldsymbol{r},\boldsymbol{v})\right] , & (54) \\ \mathcal{B}^{\mathrm{R}}[f] &= \delta(\boldsymbol{r}-\boldsymbol{r}')\, \delta(\boldsymbol{v}-\boldsymbol{v}') \sum_{i=1}^{r} \int_{S_i} d^2S\, \delta(\boldsymbol{r}-\boldsymbol{r}_i)\, (\boldsymbol{n}\cdot\boldsymbol{v})\, \theta(\boldsymbol{n}\cdot\boldsymbol{v}) \\ &\quad \times \left[f_i(\boldsymbol{v}) + f(\boldsymbol{r},\boldsymbol{v})\right] , & (55) \end{aligned}$$

where $S_i = \{\boldsymbol{r}_i \in \mathbb{R}^3\}$ is the boundary with the i^{th} reservoir, $\boldsymbol{n}$ is a unit vector normal to the boundary, the Heaviside function $\theta(\boldsymbol{n}\cdot\boldsymbol{v})$ selects the incoming velocities, and

$$f_i(\boldsymbol{v}) = \left(\frac{m\beta_i}{2\pi}\right)^{3/2} n_i\, \exp(-\beta_i\, \epsilon) \qquad \text{with} \qquad \epsilon = \tfrac{1}{2} m \boldsymbol{v}^2 \tag{56}$$

is the Maxwell–Boltzmann distribution function of the gas coming from the reservoir at the temperature $T_i = (k_{\mathrm{B}}\beta_i)^{-1}$ and the particle density n_i $(i = 1, 2, \ldots, r)$.

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 [52]. The solid surface is typically at some temperature that may differ from the temperature of the gas so that energy transfer to the solid can take place at the surface. Here, the solid forming the surface is supposed to have a high enough thermal conductivity so that its temperature is uniform. Under such circumstances, the contribution of the surface S_l to Eq. (45) is of the form

$$\mathcal{A}^{\rm S}[f] = \int_{S_l} d^2S\;\delta(\boldsymbol{r}-\boldsymbol{r}_l) \times \left[\;\int_{\boldsymbol{n}\cdot\boldsymbol{v}'<0} d\boldsymbol{v}'|\boldsymbol{n}\cdot\boldsymbol{v}'|\;p_{\boldsymbol{r}}(\boldsymbol{v}|\boldsymbol{v}')\;f(\boldsymbol{r},\boldsymbol{v}') - (\boldsymbol{n}\cdot\boldsymbol{v})\;\theta(\boldsymbol{n}\cdot\boldsymbol{v})\;f(\boldsymbol{r},\boldsymbol{v})\right], \quad (57)$$

where $p_{\boldsymbol{r}}(\boldsymbol{v}|\boldsymbol{v}')$ is the probability density that a particle impinging the surface at the position $\boldsymbol{r}$ with the velocity $\boldsymbol{v}'$ and $\boldsymbol{n}\cdot\boldsymbol{v}'<0$ will be scattered to the velocity $\boldsymbol{v}$ such that $\boldsymbol{n}\cdot\boldsymbol{v}>0$ [50]. In general, this function is normalized according to

$$\int_{\boldsymbol{n}\cdot\boldsymbol{v}>0} p_{\boldsymbol{r}}(\boldsymbol{v}|\boldsymbol{v}')\;d\boldsymbol{v} = 1 \qquad \text{if} \qquad \boldsymbol{n}\cdot\boldsymbol{v}'<0\,, \quad (58)$$

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

$$|\boldsymbol{n}\cdot\boldsymbol{v}|\;f_l(\boldsymbol{v}) = \int_{\boldsymbol{n}\cdot\boldsymbol{v}'<0} p_{\boldsymbol{r}}(\boldsymbol{v}|\boldsymbol{v}')\;|\boldsymbol{n}\cdot\boldsymbol{v}'|\;f_l(\boldsymbol{v}')\;d\boldsymbol{v}'\,, \quad (59)$$

where $f_l(\boldsymbol{v})$ is the corresponding equilibrium Maxwell–Boltzmann distribution (56). The second is the property of reciprocity

$$|\boldsymbol{n}\cdot\boldsymbol{v}'|\;f_l(\boldsymbol{v}')\;p_{\boldsymbol{r}}(\boldsymbol{v}|\boldsymbol{v}') = |\boldsymbol{n}\cdot\boldsymbol{v}|\;f_l(\boldsymbol{v})\;p_{\boldsymbol{r}}(-\boldsymbol{v}'|-\boldsymbol{v})\,, \quad (60)$$

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_l of the Maxwell–Boltzmann equilibrium distribution $f_l(\boldsymbol{v})$ [50]. In the special case of elastic collision, the function is given by

$$p_{\boldsymbol{r}}(\boldsymbol{v}|\boldsymbol{v}') = \delta\left[\boldsymbol{v}'-\boldsymbol{v}+2(\boldsymbol{n}\cdot\boldsymbol{v})\,\boldsymbol{n}\right] \quad (61)$$

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. In the case where the particles are adsorbed on the surface and soon desorbed with the Maxwell–Boltzmann distribution of the surface temperature $T_l = (k_{\rm B}\beta_l)^{-1}$, the function can be taken as

$$p_{\boldsymbol{r}}(\boldsymbol{v}|\boldsymbol{v}') = |\boldsymbol{n}\cdot\boldsymbol{v}|\;\frac{(m\beta_l)^2}{2\pi}\;\exp(-\beta_l\epsilon) \qquad \text{with} \qquad \epsilon = \tfrac{1}{2}m\boldsymbol{v}^2\,, \quad (62)$$

which also satisfies the required properties. More realistic gas–surface interactions have been considered and discussed in the literature [50]. The contribution (57) conserves the total number of particles, but the total energy is not conserved during typical gas–surface interactions. The corresponding diffusivity $\mathcal{B}^{\rm S}[f]$ can be obtained as well.

In general, the gas is composed of several particle species $p = 1, 2, ..., s$, it is flowing between r reservoirs at the temperatures and particles densities $\{T_i, n_{ip}\}$ with $i = 1, 2, ..., r$, and it is in contact with the surfaces of w walls at the temperatures $\{T_l\}$ with $l = 1, 2, ..., w$. Consequently, the steady state of the system is controlled by $r+w$ temperatures and rs particle densities. If one of the reservoirs is taken to fix the reference equilibrium temperature and chemical potentials, there should be $(r-1)(s+1)+w$ affinities controlling the nonequilibrium conditions: $r-1+w$ thermal affinities (2) and $s(r-1)$ chemical affinities (3).

6.3. The coarse-grained master equation

The master equation of the Fokker–Planck type associated with the fluctuating Boltzmann equation is a functional master equation ruling the time evolution of the probability density functional, $\mathcal{P}[f] = \mathcal{P}[f(\boldsymbol{r}, \boldsymbol{v})]$, that the random single-particle distribution function would be given by the function $f(\boldsymbol{r}, \boldsymbol{v})$ at the current time t [45]. A method to deal with this formidable master equation is to coarse grain the system into fictitious cells of volume $\Delta r^3 \Delta v^3$ centered around the phase-space points $(\boldsymbol{r}_\alpha, \boldsymbol{v}_\alpha)$. The random number of particles in the cell α at the current time t is thus given by

$$N_\alpha(t) \equiv \int\limits_\alpha f(\boldsymbol{r}, \boldsymbol{v}, t)\, d\boldsymbol{r}\, d\boldsymbol{v} \simeq f(\boldsymbol{r}_\alpha, \boldsymbol{v}_\alpha, t)\, \Delta r^3 \Delta v^3 \,. \tag{63}$$

The probability $P(\boldsymbol{N}, t)$ to find $\boldsymbol{N} = \{N_\alpha\}$ particles in the cells $\{\alpha\}$ at the current time t is ruled by the master equation

$$\frac{dP}{dt} = \hat{L}\, P \,, \qquad \text{where} \qquad \hat{L} = \hat{L}^{\rm F} + \hat{L}^{\rm C} + \hat{L}^{\rm R} + \hat{L}^{\rm S} \tag{64}$$

are the following contributions from:

$$\text{free flights:}\ \ \hat{L}^{\rm F} P = \sum_{\lambda\rho} W^{\rm F}_{\lambda\rho} \left(\hat{E}_\lambda^{-1} \hat{E}_\rho^{+1} - 1 \right) N_\rho P \,; \tag{65}$$

$$\text{binary collisions:}\ \ \hat{L}^{\rm C} P = \sum_{\lambda\mu\rho\sigma} W^{\rm C}_{\lambda\mu\rho\sigma} \left(\hat{E}_\lambda^{-1} \hat{E}_\mu^{-1} \hat{E}_\rho^{+1} \hat{E}_\sigma^{+1} - 1 \right) \times N_\rho N_\sigma P \,; \tag{66}$$

$$\text{exchanges with reservoirs:}\quad \hat{L}^{\mathrm{R}}P = \sum_{\lambda} W_{\lambda}^{\mathrm{R,in}}\left(\hat{E}_{\lambda}^{-1}-1\right)P + \sum_{\lambda} W_{\lambda}^{\mathrm{R,out}}\left(\hat{E}_{\lambda}^{+1}-1\right)N_{\lambda}P\,; \tag{67}$$

$$\text{surface collisions:}\quad \hat{L}^{\mathrm{S}}P = \sum_{\lambda\rho} W_{\lambda\rho}^{\mathrm{S}}\left(\hat{E}_{\lambda}^{-1}\hat{E}_{\rho}^{+1}-1\right)N_{\rho}P\,. \tag{68}$$

These operators are expressed in terms of the rising and lowering operators

$$\hat{E}_{\alpha}^{\pm 1}P(\ldots,N_{\alpha},\ldots) = P(\ldots,N_{\alpha}\pm 1,\ldots) \tag{69}$$

adding or removing one particle in the cell α [41, 46].

At equilibrium where the affinities are vanishing so that the temperatures and chemical potentials are equal, the stationary solution of the master equation (64) is the multiple Poisson distribution

$$P_{\mathrm{eq}}(\boldsymbol{N}) = \prod_{\alpha} e^{-\langle N_{\alpha}\rangle}\frac{\langle N_{\alpha}\rangle^{N_{\alpha}}}{N_{\alpha}!} \qquad \text{with} \qquad \langle N_{\alpha}\rangle = f_{\mathrm{eq}}(\boldsymbol{v}_{\alpha})\,\Delta r^{3}\,\Delta v^{3}\,. \tag{70}$$

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

$$W_{\lambda\rho}^{\mathrm{F}} = \frac{1}{\Delta r}\,(\boldsymbol{n}_{\lambda\rho}\cdot\boldsymbol{v})\,\theta(\boldsymbol{n}_{\lambda\rho}\cdot\boldsymbol{v})\,\delta_{\boldsymbol{r}_{\lambda},\boldsymbol{r}_{\rho}+\Delta r\,\boldsymbol{n}_{\lambda\rho}}\,\delta_{\boldsymbol{v}_{\lambda},\boldsymbol{v}_{\rho}}\,, \tag{71}$$

where $\boldsymbol{n}_{\lambda\rho}$ is a unit vector directed from the center $\boldsymbol{r}_{\rho}$ of the cell ρ to the center $\boldsymbol{r}_{\lambda}$ of the cell λ [45, 47].

The rate coefficient of the transition $\rho\sigma\to\lambda\mu$ due to some binary collision is given by [45, 46]

$$W_{\lambda\mu\rho\sigma}^{\mathrm{C}} = \frac{1}{2\Delta r^{3}\Delta v^{6}}\int_{\lambda}d\boldsymbol{v}_{1}\int_{\mu}d\boldsymbol{v}_{2}\int_{\rho}d\boldsymbol{v}_{1}'\int_{\sigma}d\boldsymbol{v}_{2}'\,w\left(\boldsymbol{v}_{1},\boldsymbol{v}_{2}|\boldsymbol{v}_{1}',\boldsymbol{v}_{2}'\right) \times\delta_{\boldsymbol{r}_{\mu},\boldsymbol{r}_{\lambda}}\,\delta_{\boldsymbol{r}_{\rho},\boldsymbol{r}_{\lambda}}\,\delta_{\boldsymbol{r}_{\sigma},\boldsymbol{r}_{\lambda}}\,. \tag{72}$$

These transitions do not change the positions but modify the velocities according to the collision rule.

Similar expression can be obtained for the rate coefficients $W_{\lambda}^{\mathrm{R,in}}$, $W_{\lambda}^{\mathrm{R,out}}$, and $W_{\lambda\rho}^{\mathrm{S}}$ from the deterministic kinetic rates (54) and (57) for exchanges with the reservoirs and gas–surface interactions.

The exchange of particles between two reservoirs is schematically depicted in Fig. 3 for particles of velocity $\pm v$ jumping between the cells $\alpha = (i,\pm)$ with $i = 1, 2, ..., I$ extending from the left-hand to the right-hand reservoirs. The time-reversal transformation maps every cell with a given velocity $\pm v$ onto the cell with the opposite velocity $\mp v$: $\Theta(i,\pm) = (i,\mp)$. Restricting ourselves for simplicity to the particles of velocities $\pm v$, the flow operator $\hat{L}^{\rm FR} = \hat{L}^{\rm F} + \hat{L}^{\rm R}$, including the contributions of the free flights (65) and the exchanges with the reservoirs (67) reads

$$\begin{aligned}
\hat{L}^{\rm FR} P \;=\; & \frac{v}{\Delta r}\Bigg[\left(\hat{E}^{-1}_{1,+} - 1\right)\langle N_+\rangle_{\rm L}\, P + \sum_{i=1}^{I-1}\left(\hat{E}^{+1}_{i,+}\hat{E}^{-1}_{i+1,+} - 1\right) N_{i,+}\, P \\
& + \left(\hat{E}^{+1}_{I,+} - 1\right) N_{I,+}\, P + \left(\hat{E}^{+1}_{1,-} - 1\right) N_{1,-}\, P \\
& + \sum_{i=1}^{I-1}\left(\hat{E}^{+1}_{i+1,-}\hat{E}^{-1}_{i,-} - 1\right) N_{i+1,-} P + \left(\hat{E}^{-1}_{I,-} - 1\right)\langle N_-\rangle_{\rm R} P\Bigg] . \qquad (73)
\end{aligned}$$

In the first term of this expression, $\langle N_+\rangle_{\rm L} = f_{\rm L}\Delta r^3 \Delta v^3$ denotes the average number of particles coming into the cell $(1,+)$ with the velocity $+v$ from the left-hand reservoir at the temperature $T_{\rm L}$ and density $n_{\rm L}$. In the last term, $\langle N_-\rangle_{\rm R} = f_{\rm R}\Delta r^3 \Delta v^3$ is the average number of particles coming into the cell $(I,-)$ with the velocity $-v$ from the right-hand reservoir. These average numbers are expressed in terms of the equilibrium Maxwell–Boltzmann distribution function (56) in the corresponding reservoir. These average particle numbers at the reservoirs are related to the thermal and chemical

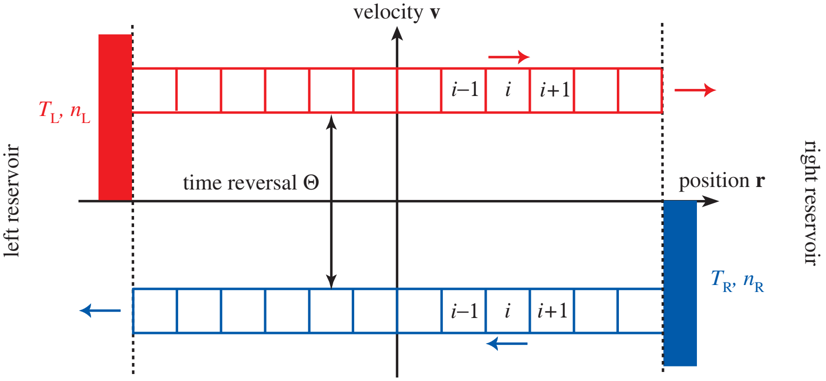

Fig. 3. Schematic phase portrait of the free motion between two reservoirs from which the particles are incoming with different temperatures and densities.

affinities

$$A_E = \beta_{\mathrm{R}} - \beta_{\mathrm{L}}\,, \tag{74}$$

$$A_N = \beta_{\mathrm{L}}\mu_{\mathrm{L}} - \beta_{\mathrm{R}}\mu_{\mathrm{R}} = \ln \frac{n_{\mathrm{L}}\beta_{\mathrm{L}}^{3/2}}{n_{\mathrm{R}}\beta_{\mathrm{R}}^{3/2}}\,, \tag{75}$$

where $\mu_{\mathrm{L,R}}$ are the chemical potentials of the monoatomic gas in the left- and right-hand reservoirs and $\beta_{\mathrm{L,R}}$ the corresponding inverse temperatures. Indeed, the logarithm of the ratio of the aforementioned average particle numbers is given by

$$\ln \frac{\langle N_+\rangle_{\mathrm{L}}}{\langle N_-\rangle_{\mathrm{R}}} = \ln \frac{f_{\mathrm{L}}}{f_{\mathrm{R}}} = A_N + \epsilon\, A_E \equiv A\,, \tag{76}$$

where $\epsilon = mv^2/2$ is the kinetic energy of the particles. The stationary solution of the master equation (1) for nonvanishing values of the affinities gives the invariant probability distribution of the corresponding nonequilibrium steady state.

The interaction of the gas with a surface is schematically represented in Fig. 4, in a similar diagram as in Fig. 3. To fix the ideas, the surface is taken as $z = 0$ so that the normal unit vector is $\boldsymbol{n} = (0, 0, 1)$. If we discretize position and velocity, the term (57) describing gas–surface interaction in the

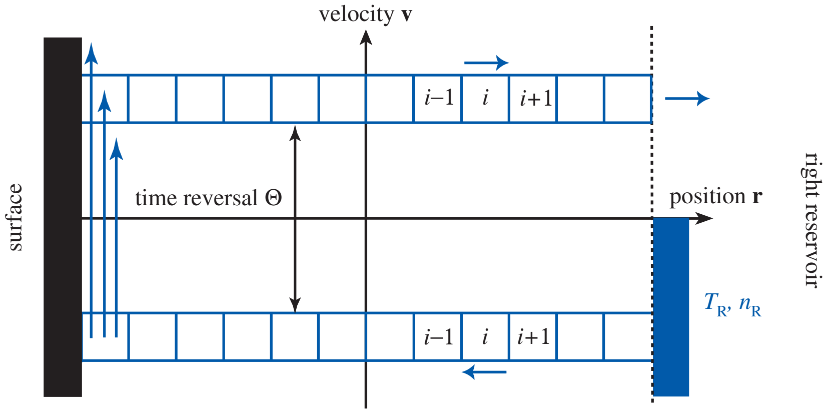

Fig. 4. Schematic phase portrait of free motion from the right reservoir, elastic or inelastic collisions with a surface, and the motion back to the right reservoir. At the surface, the different vertical arrows depict the different possible transitions due to elastic or inelastic collisions. Elastic collisions induce transitions at constant kinetic energy $\epsilon = mv^2/2$, which is not the case for inelastic collisions.

coarse-grained master equation is given by

$$\hat{L}^{\mathrm{S}} P = \sum_{\boldsymbol{r}} \delta_{z,0} \sum_{\substack{\boldsymbol{v}\\ v_z>0}} \sum_{\substack{\boldsymbol{v}'\\ v_z'<0}} \Delta v^3 \, \frac{|v_z'|}{\Delta r} \, p(\boldsymbol{v}|\boldsymbol{v}') \left(\hat{E}^{+1}_{\boldsymbol{rv}'} \, \hat{E}^{-1}_{\boldsymbol{rv}} - 1\right) N_{\boldsymbol{rv}} \, P \tag{77}$$

expressing the adsorption of a particle of velocity $\boldsymbol{v}'$ with $v_z' < 0$ and its desorption at the velocity $\boldsymbol{v}$ with $v_z > 0$ distributed according to a function $p(\boldsymbol{v}|\boldsymbol{v}')$ satisfying the three properties (58), (59), and (60) inducing a thermalization at the temperature T_l 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.

6.4. The modified operator

Now, the linear operator (65)–(68) of the master equation (64) can be modified in order to perform the counting of the particles and the energy exchanged with the reservoirs and the surfaces. In the case of an open system in contact with two reservoirs, the counting parameters are $\boldsymbol{\lambda} = (\lambda_N, \lambda_E)$. The off-diagonal elements of the modified operator are given in terms of the operator $\hat{L} = \hat{L}_{\boldsymbol{0}}$ of the master equation (64) by

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

where

$$\boldsymbol{\lambda}\cdot\Delta\boldsymbol{G}_{\boldsymbol{N}\to\boldsymbol{N}'} = (\lambda_N + \epsilon_{\boldsymbol{v}} \, \lambda_E) \, \Delta N_{\boldsymbol{rv}} \qquad \text{with} \qquad \Delta N_{\boldsymbol{rv}} = N'_{\boldsymbol{rv}} - N_{\boldsymbol{rv}} = \pm 1 \tag{79}$$

for a transition in which a particle of kinetic energy $\epsilon_{\boldsymbol{v}} = m\boldsymbol{v}^2/2$ enters or exits the system through the cell $\alpha = \boldsymbol{rv}$ in contact with the left-hand reservoir. The diagonal elements are not modified

$$\left(\hat{L}_{\boldsymbol{\lambda}}\right)_{\boldsymbol{N}\boldsymbol{N}} = - \sum_{\boldsymbol{N}'(\neq\boldsymbol{N})} \left(\hat{L}\right)_{\boldsymbol{N}'\boldsymbol{N}} \, . \tag{80}$$

In particular, the operator (73) ruling the inflow, outflow and free flights of particles between two reservoirs and acting on functions $\varPhi(\boldsymbol{N})$ is modified into

$$\begin{aligned} \hat{L}^{\mathrm{FR}}_{\lambda_N,\lambda_E}\varPhi \; = \; \frac{v}{\Delta r} \Bigg[& \left(e^{-\lambda} \, \hat{E}^{-1}_{1,+} - 1\right) \langle N_+\rangle_{\mathrm{L}} \, \varPhi + \sum_{i=1}^{I-1} \left(\hat{E}^{+1}_{i,+}\hat{E}^{-1}_{i+1,+} - 1\right) N_{i,+} \, \varPhi \\ & + \left(\hat{E}^{+1}_{I,+} - 1\right) N_{I,+} \, \varPhi + \left(e^{+\lambda} \, \hat{E}^{+1}_{1,-} - 1\right) N_{1,-} \, \varPhi \\ & + \sum_{i=1}^{I-1} \left(\hat{E}^{+1}_{i+1,-}\hat{E}^{-1}_{i,-} - 1\right) N_{i+1,-} \, \varPhi + \left(\hat{E}^{-1}_{I,-} - 1\right) \langle N_-\rangle_{\mathrm{R}} \, \varPhi \Bigg] \end{aligned} \tag{81}$$

with the counting parameter $\lambda = \lambda_N + \epsilon\lambda_E$ appearing in the only terms contributing to the exchange of particles with the left-hand reservoir, where the quantity (79) is non-zero. For particles at the energy $\epsilon = mv^2/2$, the flow operator (73) is thus modified by inserting a factor $\exp(\pm\lambda)$ in the terms responsible for incoming or outgoing particles from or to the left-hand reservoir.

Similarly, the operator (77) describing gas–surface interaction is modified by introducing an extra counting parameter $\lambda_E^{\rm S}$ for the energy exchanged during inelastic collisions with the surface to get

$$\hat{L}^{\rm S}_{\lambda_E^{\rm S}}\varPhi = \sum_{\boldsymbol{r}} \delta_{z,0} \sum_{\substack{\boldsymbol{v}\\ v_z>0}} \sum_{\substack{\boldsymbol{v}'\\ v'_z<0}} \Delta v^3 \, \frac{|v'_z|}{\Delta r}\, p(\boldsymbol{v}|\boldsymbol{v}')\, \left[e^{\lambda_E^{\rm S}(\epsilon'-\epsilon)} \hat{E}^{+1}_{\boldsymbol{r}\boldsymbol{v}'}\, \hat{E}^{-1}_{\boldsymbol{r}\boldsymbol{v}} - 1\right] N_{\boldsymbol{r}\boldsymbol{v}}\, \varPhi\,, \tag{82}$$

where $\epsilon = m\boldsymbol{v}^2/2$ and $\epsilon' = m\boldsymbol{v}'^2/2$.

In contrast, the collision operator (66) is not modified because the binary collisions locally exchange particles among all the cells corresponding to the *same* position in the bulk of the system so that the quantity (79) remains equal to zero for these transitions.

Therefore, the operator is modified into

$$\hat{L}_{\lambda_N,\lambda_E,\lambda_E^{\rm S}} = \hat{L}^{\rm C} + \hat{L}^{\rm FR}_{\lambda_N,\lambda_E} + \hat{L}^{\rm S}_{\lambda_E^{\rm S}}\,. \tag{83}$$

We notice the additive structure due to the statistical independence between the different types of transitions. Accordingly, every operator can be treated separately.

6.5. The symmetry of the modified operator

The symmetry relation (11) can be established for each one of them by taking $\eta(\boldsymbol{N})$ as the multiple Poisson distribution (70) at the temperature $T_{\rm R}$ and density $n_{\rm R}$ of the right-hand reference reservoir and the time-reversal transformation as

$$\varTheta\,\varPhi(\{N_{\boldsymbol{r},\boldsymbol{v}}\}) = \varPhi(\{N_{\boldsymbol{r},-\boldsymbol{v}}\})\,. \tag{84}$$

We find that

$$\eta^{-1}\varTheta\,\hat{L}^{\rm C}\,(\varTheta\,\eta\,\varPhi) = \hat{L}^{\rm C\dagger}\varPhi\,, \tag{85}$$

$$\eta^{-1}\varTheta\,\hat{L}^{\rm FR}_{\lambda_N,\lambda_E}\,(\varTheta\,\eta\,\varPhi) = \hat{L}^{\rm FR\dagger}_{A_N-\lambda_N,A_E-\lambda_E}\varPhi\,, \tag{86}$$

$$\eta^{-1}\varTheta\,\hat{L}^{\rm S}_{\lambda_E^{\rm S}}\,(\varTheta\,\eta\,\varPhi) = \hat{L}^{\rm S\dagger}_{A_E^{\rm S}-\lambda_E^{\rm S}}\varPhi\,, \tag{87}$$

in terms of the thermal and chemical affinities (74)–(75) controlling the energy and particle currents from the left-hand reservoir to the right-hand reference reservoir, and the thermal affinity controlling the energy current from the surface to the same right-hand reference reservoir

$$A_E^{\rm S} = \beta_{\rm R} - \beta_{\rm S}\,, \tag{88}$$

where $\beta_{\rm S} = (k_{\rm B}T_{\rm S})^{-1}$ characterizes the Maxwell–Boltzmann distribution (56) at the surface temperature $T_{\rm S}$ [49].

The symmetry (85) results from the time-reversal symmetry (52) of the transition rate coefficients of Boltzmann's equation itself, which thus also concerns the rate coefficients (72).

The symmetry (86) of the modified operator (81) is obtained by using the properties

$$\left(\hat{E}_\alpha^{\pm 1}\right)^\dagger = \hat{E}_\alpha^{\mp 1}\,, \tag{89}$$

$$\hat{E}_\alpha^{-1}\,\eta\,\varPhi = \frac{N_\alpha}{\langle N_\alpha\rangle}\,\eta\,\hat{E}_\alpha^{-1}\,\varPhi\,, \tag{90}$$

$$\hat{E}_\alpha^{+1}\,\eta\,\varPhi = \frac{\langle N_\alpha\rangle}{N_\alpha+1}\,\eta\,\hat{E}_\alpha^{+1}\,\varPhi \tag{91}$$

of the lowering and rising operators (69), where $\varPhi(\boldsymbol{N})$ is an arbitrary function and $\eta(\boldsymbol{N})$ is given by the multiple Poisson distribution (70). This distribution has the symmetry $\varTheta\eta = \eta$ under the time-reversal transformation $\varTheta N_{i,\pm} = N_{i,\mp}$ reversing the velocities $\pm v$ at every position $i = 1, 2, \ldots, I$. Therefore, the transformation in the left-hand side of Eq. (86) has the effect of permuting the terms of positive velocity with those of negative velocity. Furthermore, the boundary term with $e^{-\lambda}\langle N_+\rangle_{\rm L}$ is transformed into $e^{-\lambda}\langle N_+\rangle_{\rm L}/\langle N_{1,-}\rangle_{\rm R}$ and the boundary term with $e^{+\lambda}$ into $e^{+\lambda}\langle N_{1,+}\rangle_{\rm R}$. Now, the left-hand reservoir is at the temperature $T_{\rm L}$ and density $n_{\rm L}$ while the right-hand reservoir is used as reference so that $\langle N_{i,\pm}\rangle_{\rm R} = f_{\rm R}\Delta r^3\Delta v^3$ for all $i = 1, 2, ..., I$, whereupon we find the required consistency between the two equalities

$$e^{-\lambda}\,\frac{\langle N_+\rangle_{\rm L}}{\langle N_{1,-}\rangle_{\rm R}} \;=\; e^{A-\lambda}\,, \tag{92}$$

$$e^{+\lambda}\langle N_{1,+}\rangle_{\rm R} \;=\; e^{-(A-\lambda)}\,\langle N_+\rangle_{\rm L} \tag{93}$$

with the affinity A defined by Eq. (76). 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 (86).

The symmetry (87) of the modified operator (82) holds because the function $p(\boldsymbol{v}|\boldsymbol{v}')$ satisfies the property of reciprocity (60) that finds its origin in the microreversibility of the gas–surface interactions.

For an open system in contact with two reservoirs and a thermalizing surface, the symmetry relation (11) can thus be proved with the counting parameters $\boldsymbol{\lambda} = \{\lambda_N, \lambda_E, \lambda_E^{\rm S}\}$ and the affinities $\boldsymbol{A} = \{A_N, A_E, A_E^{\rm S}\}$ given by Eqs. (74), (75), and (88) [49]. As a consequence, the cumulant generating function (6) of the corresponding fluctuating currents obeys the symmetry relation (7). As explained in Section 2, this establishes the current fluctuation relation (4) for dilute or rarefied gases ruled by the fluctuating Boltzmann equation.

7. Conclusions and perspectives

The time-reversal symmetry relations obtained in the present paper characterize the fluctuations of the particle and energy currents flowing across systems subjected to nonequilibrium constraints. They find their origin in the microreversibility of the underlying Hamiltonian dynamics. Yet, they arise because the stationary probability distribution breaks the time-reversal symmetry at the statistical level of description, as shown for the case of effusion in noninteracting gases.

The generality of the relationship between fluctuation relations and symmetry breaking phenomena is suggested by recent work showing that fluctuation relations also hold for equilibrium probability distributions where the spin-reversal symmetry is broken by an external magnetic field, as in the Ising model [53, 54]. The mathematical scheme is similar with the external magnetic field playing the role of the affinities and the fluctuating magnetization the role of the fluctuating currents. This connection also supports the result that the thermodynamic entropy production can be interpreted as a quantity characterizing the time-reversal symmetry breaking, as shown elsewhere [55].

Beyond the case of effusion in noninteracting gases, a fluctuation relation for currents is here established for Smoluchowski's master equation describing a Brownian particle driven out of equilibrium by an external force. This result is valid not only close to equilibrium, but also far from equilibrium in regimes where nonlinear response can become important. If the inertial effects cannot be neglected, the driven Brownian motion is described by the Fokker–Planck equation, for which the current fluctuation relation is also deduced. The method used to obtain these relations consists in modifying the linear operator of the master equation with parameters counting the transfers of particles and energy. The cumulant generating function of the fluctuating currents is thus obtained from the leading eigenvalue of the modified operator. Remarkably, the modified operator of the Smoluchowski and Fokker–Planck master equations present the special symmetry (11) under time reversal. This symmetry is expressed in terms of the affinities or thermodynamic forces driving the system out of equilibrium with respect to some reference equilibrium state. Since the symmetry holds for the operator, it implies the symmetry relation of the cumulant generating function and, therefore, the fluctuation relation for the currents.

This method turns out to be very powerful and allows us to extend these results to stochastic processes taking place in dilute or rarefied gases ruled by the fluctuating Boltzmann equation. In order to derive the symmetry relation, the system is coarse grained into cells between which the particles are randomly jumping. The symmetry relation can then be established for the modified operator of the coarse-grained master equation. Several types of processes take place in the gas: free flights, binary collisions, elastic or inelastic collisions with surfaces, and the exchange of particles and kinetic energy with the reservoirs. These different processes are ruled by different operators as long as they are statistically independent. The time-reversal symmetry of the collisions and the corresponding property of reciprocity satisfied by the transition rates imply the symmetry of the modified operators, allowing us to establish the fluctuation relation for the currents in dilute and rarefied gases. As a corollary, the generalizations of the Green–Kubo formulae and the Onsager reciprocity relations obtained in Refs. [11, 14] for the nonlinear response coefficients are extended to these gases. The present results are complementary to those obtained elsewhere for open quantum systems [56, 57].

These fundamental results open important perspectives, on the one hand, to understand in a fundamental way the origins of thermodynamic irreversibility and, on the other hand, to investigate the properties of nonequilibrium stochastic processes down to the nanoscale. These symmetry relations can be experimentally tested for the Brownian motion in optical lattices and driven out of equilibrium by an external force. An experimental challenge is to measure the fluctuations of the currents in gas flow such as effusion. Ultrathin membranes such as graphene with a small hole could be envisaged for the effusion of fluorescent molecules in order to perform their counting in slow enough flows. Full counting statistics is already possible for electrons in quantum dots [58], but the analogue with atoms or molecules has not yet been carried out.

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