Fluctuation theorem for entropy production during effusion of an ideal gas with momentum transfer

Kevin Wood,[1,2] C. Van den Broeck,[3] R. Kawai,[4] and Katja Lindenberg[1]
[1]*Department of Chemistry and Biochemistry and Institute for Nonlinear Science, University of California San Diego, 9500 Gilman Drive, La Jolla, California 92093-0340, USA*
[2]*Department of Physics, University of California San Diego, 9500 Gilman Drive, La Jolla, California 92093-0340, USA*
[3]*Hasselt University, Diepenbeek, B-3590 Belgium*
[4]*Department of Physics, University of Alabama at Birmingham, Birmingham, Alabama 35294, USA*
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We derive an exact expression for entropy production during effusion of an ideal gas driven by momentum transfer in addition to energy and particle flux. Following the treatment in Cleuren *et al.* [Phys. Rev. E **74**, 021117 (2006)], we construct a master equation formulation of the process and explicitly verify the thermodynamic fluctuation theorem, thereby directly exhibiting its extended applicability to particle flows and hence to hydrodynamic systems.

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I. INTRODUCTION

Since the pioneering work of Onsager [1] on the relation between linear response and equilibrium fluctuations, his insights have been further formalized in, for example, the theory of linear irreversible processes [2] and the fluctuation-dissipation theorem [3]. Over the past decade some new surprising results have been discovered that suggest relations valid far away from equilibrium, notably the fluctuation [4,5] and work [6] theorems. The fluctuation theorem, originally demonstrated for nonequilibrium steady states in thermostated systems, has been proven in a number of different settings. Basically, it states that during an experiment of duration t, it is exponentially more likely to observe a positive entropy production ΔS rather than an equally large negative one

$$\frac{P_t(\Delta S)}{P_t(-\Delta S)} = e^{\Delta S/k}. \tag{1}$$

In the application to nonequilibrium steady states, the above result is typically only valid in the asymptotic limit $t \to \infty$ and expresses a symmetry property of large deviations.

We address another scenario in which the system is perturbed out of a state which is initially at equilibrium. The so-called transient fluctuation theorem is then valid for all times t. We consider the problem of a Knudsen flow between ideal gases that have overall nonzero momentum. In this case, the stationary state is reached instantaneously, so that there is no distinction between the transient and steady state versions of the theorem. We show that the system obeys a detailed fluctuation theorem which includes Eq. (1) as a special case. Our calculation is an extension of the one given in Ref. [7] to include momentum transfer. The interest of this extension is manifold. First, the derivation of the fluctuation theorem is somewhat more complicated since the momentum is a quantity which is odd under velocity inversion. Second, momentum, together with particle number and energy, are the conserved quantities whose transport forms the basis of hydrodynamics. Our derivation therefore puts the fluctuation theorem fully in this context (see also Ref. [8]). Finally, as a by-product, we calculate the Onsager matrix for the Knudsen flow problem including momentum transport.

In Sec. II we formulate the fluctuation theorem for effusion with momentum transfer for an ideal gas. Section III generalizes the derivation of the master equation and cumulant generating function in Ref. [7] to the case with momentum transfer. Verification of the fluctuation theorem is detailed in Sec. IV, and the lowest order cumulants are exhibited in Sec. V. We use these results to verify the Onsager relations for this nonequilibrium system in Sec. VI. We end with a brief conclusion in Sec. VII. Some details of the calculations are presented in appendices.

II. FLUCTUATION THEOREM FOR EFFUSION WITH MOMENTUM TRANSFER

We begin by considering two (infinitely) large neighboring reservoirs A and B each of which contains an ideal gas of uniform density n_i in equilibrium at temperature T_i, $i \in A,B$. In addition, the particles of gas i have an overall center of mass velocity V_i in the $\mathbf{e}_x$ direction (Fig. 1). That is, the velocity distributions of the gas particles take the Maxwellian form

$$\phi_i = \left(\frac{m}{2\pi k T_i}\right)^{3/2} \exp\left(-\frac{m(\mathbf{v} - V_i \mathbf{e}_x)^2}{2kT_i}\right). \tag{2}$$

The two reservoirs are separated by a common adiabatic wall parallel to the $\mathbf{e}_x$ direction, with a hole of surface area σ whose linear dimensions are small compared with the mean free path of the particles. As a result, the local equilibrium in each reservoir is not disturbed by the exchange of mass, heat, and momentum during a finite time interval t in which the hole is open. Upon a transfer of total energy ΔU, particles ΔN, and momentum Δp_x during this time interval, the overall change in entropy for the system is given by

$$\begin{aligned}\Delta S &= \Delta S_A + \Delta S_B \\ &= -\frac{1}{T_A}\Delta U + \left(\frac{\mu_A}{T_A} - \frac{mV_A^2}{2T_A}\right)\Delta N + \frac{V_A}{T_A}\Delta p_x + \frac{1}{T_B}\Delta U \\ &\quad - \left(\frac{\mu_B}{T_B} - \frac{mV_B^2}{2T_B}\right)\Delta N - \frac{V_B}{T_B}\Delta p_x\end{aligned}$$

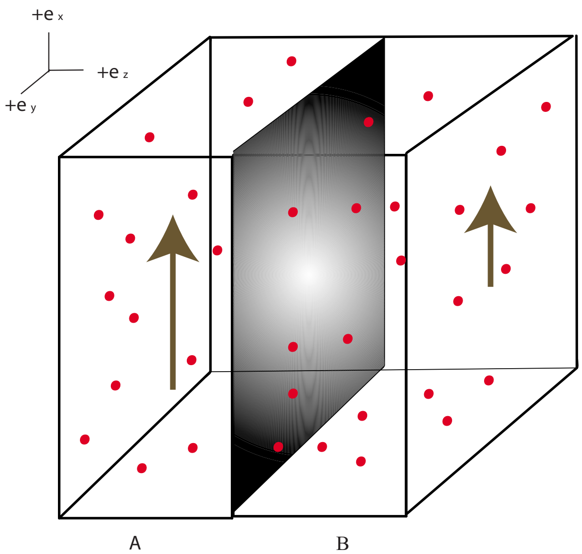

FIG. 1. (Color online) The ideal gas in compartment A is characterized by temperature T_A, number density n_A, and flow velocity V_A. Similarly, the ideal gas in compartment B is characterized by temperature T_B, number density n_B, and flow velocity V_B. Velocities V_A and V_B are represented by the vertical arrows within each compartment and are taken to be parallel to the adiabatic wall separating the two gases.

$$= \mathcal{A}_U \Delta U + \mathcal{A}_N \Delta N + \mathcal{A}_{p_x} \Delta p_x, \tag{3}$$

where we have introduced the thermodynamic forces for energy, particle, and momentum transfer [9]

$$\mathcal{A}_U = \frac{1}{T_B} - \frac{1}{T_A},$$

$$\mathcal{A}_N = \frac{\mu_A}{T_A} - \frac{mV_A^2}{2T_A} - \left(\frac{\mu_B}{T_B} - \frac{mV_B^2}{2T_B}\right) = k \ln\left[\frac{n_A}{n_B}\left(\frac{T_B}{T_A}\right)^{3/2}\right] + \left(\frac{mV_B^2}{2T_B} - \frac{mV_A^2}{2T_A}\right),$$

$$\mathcal{A}_{p_x} = \frac{V_A}{T_A} - \frac{V_B}{T_B}. \tag{4}$$

In the equation for $\mathcal{A}_N$, we have used the expression for the chemical potential μ of an ideal gas at rest. Since the explicit expression for the thermodynamic forces in systems with momentum is not readily available, we provide a brief derivation in Appendix A.

The variables ΔU, ΔN, and Δp_x all correspond to fluctuating quantities influenced by single particle crossings on each side of the adiabatic wall. As a result, the total entropy production ΔS, which will be observed during the time duration t, is likewise a fluctuating quantity. The fluctuation theorem provides a relation between the probability of observing entropy production equal to $+\Delta S$ and the probability of observing entropy production equal to $-\Delta S$, as expressed in Eq. (1). Due to the absence of memory effects, ΔS is in fact a stochastic process with independent increments: contributions to ΔS from any two equal, nonoverlapping time intervals are independent identically distributed random variables. It is therefore convenient to introduce the cumulant generating function, which takes the form

$$\langle e^{-\lambda \Delta S} \rangle \equiv e^{-tg(\lambda)}. \tag{5}$$

The fluctuation theorem, Eq. (1), is then equivalent to the following symmetry property [5]:

$$g(\lambda) = g(k^{-1} - \lambda). \tag{6}$$

As the derivation in Appendix B points out, one can augment the observation of the entropy production with additional variables, while retaining the form of the fluctuation theorem. Hence the following more detailed fluctuation theorem, which is expressed in terms of the joint probability density involving all three conserved quantities, particle number, momentum, and energy, is obtained:

$$\frac{P_t(\Delta U, \Delta N, \Delta p_x)}{P_t(-\Delta U, -\Delta N, -\Delta p_x)} = e^{\Delta S/k}. \tag{7}$$

Since the increments of ΔU, ΔN, and Δp_x are also independent, we can write the corresponding cumulant generating function as

$$\langle e^{-(\lambda_U \Delta U + \lambda_N \Delta N + \lambda_{p_x} \Delta p_x)} \rangle = e^{-tg(\lambda_U, \lambda_N, \lambda_{p_x})}. \tag{8}$$

The detailed fluctuation theorem is equivalent to the following symmetry relation, cf. Eq. (6):

$$g(\lambda_U, \lambda_N, \lambda_{p_x}) = g(\mathcal{A}_U k^{-1} - \lambda_U, \mathcal{A}_N k^{-1} - \lambda_N, \mathcal{A}_{p_x} k^{-1} - \lambda_{p_x}). \tag{9}$$

Note that Eq. (7), apart from implying the normal fluctuation theorem Eq. (1), also implies fluctuation theorems for particle, energy, and momentum transfer individually when the complementary thermodynamic forces are zero:

$$\frac{\mathcal{P}_t(\Delta U)}{\mathcal{P}_t(-\Delta U)} = e^{\Delta S/k}; \quad \mathcal{A}_N = \mathcal{A}_{p_x} = 0,$$

$$\frac{\mathcal{P}_t(\Delta N)}{\mathcal{P}_t(-\Delta N)} = e^{\Delta S/k}; \quad \mathcal{A}_U = \mathcal{A}_{p_x} = 0,$$

$$\frac{\mathcal{P}_t(\Delta p_x)}{\mathcal{P}_t(-\Delta p_x)} = e^{\Delta S/k}; \quad \mathcal{A}_U = \mathcal{A}_N = 0. \tag{10}$$

We now proceed with an explicit evaluation of the probability density $P_t(\Delta U, \Delta N, \Delta p_x)$. This result allows an explicit verification of the fluctuation theorem. It also contains additional information including the Onsager regression matrix, as well as higher order response coefficients.

III. MASTER EQUATION AND CUMULANT GENERATING FUNCTION

If we choose a sufficiently small time interval dt, the contributions to the quantities ΔU, ΔN, and Δp_x arise from individual particles crossing the hole. The kinetic theory of gases allows us to calculate the probability per unit time,

$T_{i\to j}(E,p_x)$, to observe a particle with kinetic energy $E=\frac{1}{2}mv^2$ and momentum $p_x=mv_x$ crossing the hole from reservoir i to reservoir j. Specifically, the transition rate in question is given by (see Appendix C)

$$T_{i\to j}(E,p_x)=\frac{\sigma n_i}{m(k\pi T_i)^{3/2}}\left(E-\frac{p_x^2}{2m}\right)^{1/2}\times\exp\left[-\frac{m}{2kT_i}\left(\frac{2\left(E-\frac{p_x^2}{2m}\right)}{m}+\left(\frac{p_x}{m}+V_i\right)^2\right)\right], \tag{11}$$

with $(i,j)=(A,B)$ or $(i,j)=(B,A)$. Hence, the probability density $P_t(\Delta U,\Delta N,\Delta p_x)$ obeys the master equation

$$\begin{aligned}\partial_t P_t(\Delta U,\Delta N,\Delta p_x)=&\int_{-\infty}^{\infty}dp_x\int_{p_x^2/2m}^{\infty}dE\,T_{A\to B}\\&\times P_t(\Delta U-E,\Delta N-1,\Delta p_x-p_x)\\&+\int_{-\infty}^{\infty}dp_x\int_{p_x^2/2m}^{\infty}dE\,T_{B\to A}\\&\times P_t(\Delta U+E,\Delta N+1,\Delta p_x+p_x)\\&-P_t(\Delta U,\Delta N,\Delta p_x)\int_{-\infty}^{\infty}dp_x\int_{p_x^2/2m}^{\infty}dE\\&\times(T_{A\to B}+T_{B\to A}).\end{aligned} \tag{12}$$

We have written $T_{i\to j}(E,p_x)$ without the arguments for economy of notation. We can arrive at the cumulant generating function by first multiplying both sides of the equation by $\exp[-(\lambda_U\Delta U+\lambda_N\Delta N+\lambda_{p_x}\Delta p_x)]$ and subsequently integrating ΔU, Δp_x over all space and summing ΔN over all integers. We thus have the expression

$$\partial_t\tilde{P}(\lambda_U,\lambda_N,\lambda_{p_x})=\tilde{P}(\lambda_U,\lambda_N,\lambda_{p_x})I_1+\tilde{P}(\lambda_U,\lambda_N,\lambda_{p_x})I_2-\tilde{P}(\lambda_U,\lambda_N,\lambda_{p_x})I_3, \tag{13}$$

where

$$I_1\equiv e^{-\lambda_N}\int_{-\infty}^{\infty}dp_x\int_{p_x^2/2m}^{\infty}dE\,T_{A\to B}e^{-(\lambda_U E+\lambda_{p_x}p_x)},$$

$$I_2\equiv e^{\lambda_N}\int_{-\infty}^{\infty}dp_x\int_{p_x^2/2m}^{\infty}dE\,T_{B\to A}e^{(\lambda_U E+\lambda_{p_x}p_x)},$$

$$I_3\equiv\int_{-\infty}^{\infty}dp_x\int_{p_x^2/2m}^{\infty}dE\,(T_{A\to B}+T_{B\to A}),$$

$$\tilde{P}(\lambda_U,\lambda_N,\lambda_{p_x})\equiv\int_{-\infty}^{\infty}d\Delta U\int_{-\infty}^{\infty}d\Delta p_x\sum_{\Delta N=-\infty}^{\infty}\exp(-\lambda_U\Delta U-\lambda_N\Delta N-\lambda_{p_x}\Delta p_x)P_t(\Delta U,\Delta N,\Delta p_x). \tag{14}$$

From this expression we can write $g(\lambda_U,\lambda_N,\lambda_{p_x})$, defined in Eq. (8), as

$$g(\lambda_U,\lambda_N,\lambda_{p_x})=I_3-(I_1+I_2). \tag{15}$$

The I integrals in Eq. (14) can easily be performed by switching to the variable $z=E-p_x^2/2m$ and integrating z from zero to infinity and p_x over all space, as before. We thereby arrive at our final expression for $g(\lambda_U,\lambda_N,\lambda_{p_x})$:

$$g(\lambda_U,\lambda_N,\lambda_{p_x})=\sigma\left(\frac{k}{2\pi m}\right)^{1/2}\left[n_AT_A^{1/2}\left(1-\frac{G_A}{(1+kT_A\lambda_U)^2}\right)+n_BT_B^{1/2}\left(1-\frac{G_B}{(1-kT_B\lambda_U)^2}\right)\right], \tag{16}$$

where

$$G_A\equiv\exp\left(-\lambda_N-\frac{mV_A^2\lambda_U-kmT_A\lambda_{p_x}^2+2mV_A\lambda_{p_x}}{2(1+kT_A\lambda_U)}\right),$$

$$G_B\equiv\exp\left(\lambda_N+\frac{mV_B^2\lambda_U+kmT_B\lambda_{p_x}^2+2mV_B\lambda_{p_x}}{2(1-kT_B\lambda_U)}\right). \tag{17}$$

Notice that $g(\lambda_U,\lambda_N,\lambda_{p_x})$ can be written as a sum of two contributions

$$g(\lambda_U,\lambda_N,\lambda_{p_x})=g_A(\lambda_U,\lambda_N,\lambda_{p_x})+g_B(\lambda_U,\lambda_N,\lambda_{p_x}), \tag{18}$$

with

$$g_A(\lambda_U,\lambda_N,\lambda_{p_x})=\sigma\left(\frac{k}{2\pi m}\right)^{1/2}\times n_AT_A^{1/2}\left(1-\frac{G_A}{(1+kT_A\lambda_U)^2}\right),$$

$$g_B(\lambda_U,\lambda_N,\lambda_{p_x})=\sigma\left(\frac{k}{2\pi m}\right)^{1/2}\times n_BT_B^{1/2}\left(1-\frac{G_B}{(1-kT_B\lambda_U)^2}\right). \tag{19}$$

This additivity property arises from the statistical independence of the fluxes from $A\to B$ and $B\to A$.

IV. FLUCTUATION SYMMETRY

The explicit verification of the symmetry relation (9), and hence of the fluctuation theorem, simply involves the realization that under the symmetry operation $\mathcal{T}$—that is, under the transformation given by the right-hand side of Eq. (9)—the term containing the exponential in g_A (which we call $g_{A,1}$) becomes the corresponding term from g_B (which we call $g_{B,1}$) and similarly, the original $g_{B,1}$ term becomes $g_{A,1}$, thereby preserving the overall structure of g. Mathematically, we can express this as

$$\mathcal{T}[g_{A,1}]=g_{B,1},\qquad \mathcal{T}[g_{B,1}]=g_{A,1}, \tag{20}$$

where

$$g_{A,1} = \sigma\left(\frac{k}{2\pi m}\right)^{1/2} n_A T_A^{1/2}(1 + kT_A\lambda_U)^{-2}G_A, \tag{21}$$

and

$$g_{B,1} = \sigma\left(\frac{k}{2\pi m}\right)^{1/2} n_B T_B^{1/2}(1 - kT_B\lambda_U)^{-2}G_B. \tag{22}$$

The steps are purely algebraic and straightforward, involving the intermediate steps (which we exhibit to provide some intermediate guide)

$$\mathcal{T}[g_{A,1}] = \sigma\left(\frac{k}{2\pi m}\right)^{1/2} n_A T_A^{1/2}(1 + kT_A\Lambda_U)^{-2}\exp\left\{-\ln\left[\frac{n_A}{n_B}\left(\frac{T_B}{T_A}\right)^{3/2}\right] - \Lambda_N\right\}\exp\left[\frac{-mV_A^2\Lambda_U + kmT_A\Lambda_{p_x}^2}{2(1 + kT_A\Lambda_U)}\right]$$
$$\times\exp\left(\frac{-2mV_A\Lambda_{p_x}}{2(1 + kT_A\Lambda_U)}\right)$$
$$= \sigma\left(\frac{k}{2\pi m}\right)^{1/2} n_A T_A^{1/2}\Lambda^{-2}\left[\frac{n_B}{n_A}\left(\frac{T_A}{T_B}\right)^{3/2}\right]\exp\left[\lambda_N + \frac{2\Lambda\left(\frac{mV_A^2}{2kT_A} - \frac{mV_B^2}{2kT_B}\right) - mV_A^2\Lambda_U}{2\Lambda}\right]\exp\left(\frac{kmT_A\Lambda_{p_x}^2 - 2mV_A\Lambda_{p_x}}{2\Lambda}\right), \tag{23}$$

where

$$\Lambda_U \equiv \frac{1}{kT_B} - \frac{1}{kT_A} - \lambda_U,$$

$$\Lambda_{p_x} \equiv \frac{V_A}{kT_A} - \frac{V_B}{kT_B} - \lambda_{p_x},$$

$$\Lambda_N \equiv \frac{V_B^2 m}{2kT_B} - \frac{V_A^2 m}{2kT_A} - \lambda_N,$$

$$\Lambda \equiv \frac{T_A}{T_B}(1 - kT_B\lambda_U). \tag{24}$$

Following straightforward (albeit tedious) simplification, this reduces to $g_{B,1}$. A similar result holds for $\mathcal{T}[g_{B,1}]$, and therefore the fluctuation theorem symmetry is satisfied.

V. CUMULANTS

The joint cumulant κ_{ijk} of power i in energy flux, j in particle flux, and k in momentum flux appears as a coefficient in the Taylor expansion of the cumulant generating function, namely,

$$g_A(\lambda_U,\lambda_N,\lambda_{p_x}) = -\frac{1}{t}\sum_{i,j,k=0}^{\infty}\frac{(-1)^{i+j+k}\lambda_U^i\lambda_N^j\lambda_{p_x}^k}{i\,!\,j\,!\,k!}\kappa_{ijk}. \tag{25}$$

While our expression for $g_A(\lambda_U,\lambda_N,\lambda_{p_x})$ allows us to calculate joint cumulants of any order, we here mention only the first and second order results. The former are relevant for verifying the Onsager relations in the subsequent section and are given by

$$\kappa_{100} = \langle\Delta U\rangle$$
$$= t\sigma\left(\frac{k}{2\pi m}\right)^{1/2}\left[n_A T_A^{1/2}\left(2kT_A + \frac{mV_A^2}{2}\right) - n_B T_B^{1/2}\left(2kT_B + \frac{mV_B^2}{2}\right)\right],$$

$$\kappa_{010} = \langle\Delta N\rangle = t\sigma\left(\frac{k}{2\pi m}\right)^{1/2}(n_A T_A^{1/2} - n_B T_B^{1/2}),$$

$$\kappa_{001} = \langle\Delta p_x\rangle = t\sigma\left(\frac{km}{2\pi}\right)^{1/2}(n_A V_A T_A^{1/2} - n_B V_B T_B^{1/2}). \tag{26}$$

Note that the cumulant associated with energy $\langle\Delta U\rangle$ contains terms corresponding to both particle transport and momentum transport. Furthermore, we can calculate the second cumulants, which include the energy-momentum covariance:

$$\kappa_{200} = \langle\delta\Delta U^2\rangle = t\sigma\left(\frac{k}{32\pi m}\right)^{1/2}(\kappa_{200,A} + \kappa_{200,B}),$$

$$\kappa_{020} = \langle\delta\Delta N^2\rangle = t\sigma\left(\frac{k}{2\pi m}\right)^{1/2}(T_A^{1/2}n_A + T_B^{1/2}n_B),$$

$$\kappa_{002} = \langle\delta\Delta p_x^2\rangle = t\sigma\left(\frac{km}{2\pi}\right)^{1/2}(\kappa_{002,A} + \kappa_{002,B}),$$

$$\kappa_{110} = \langle\delta\Delta U\,\delta\Delta N\rangle = t\sigma\left(\frac{k}{8\pi m}\right)^{1/2}(\kappa_{110,A} + \kappa_{110,B}),$$

$$\kappa_{101} = \langle\delta\Delta U\,\delta\Delta p_x\rangle = t\sigma\left(\frac{km}{8\pi}\right)^{1/2}(\kappa_{101,A} + \kappa_{101,B}),$$

$$\kappa_{011} = \langle \delta\Delta N \delta\Delta p_x \rangle = t\sigma\left(\frac{km}{2\pi}\right)^{1/2}(n_A V_A T_A^{1/2} + n_B V_B T_B^{1/2}), \tag{27}$$

where

$$\kappa_{200,i} = n_i T_i^{1/2}[24k^2T_i^2 + 12kmV_i^2T_i + (mV_i^2)^2],$$

$$\kappa_{002,i} = n_i T_i^{1/2}(kT_i + mV_i^2),$$

$$\kappa_{110,i} = n_i T_i^{1/2}(4kT_i + mV_i^2),$$

$$\kappa_{101,i} = n_i V_i T_i^{1/2}(6kT_i + mV_i^2) \tag{28}$$

for $i \in A, B$.

VI. ONSAGER RELATIONS

Averaging Eq. (3) and taking the time derivative leads us to an equation for the average entropy production

$$\frac{d}{dt}\langle \Delta S\rangle = \mathcal{J}_U\mathcal{A}_U + \mathcal{J}_N\mathcal{A}_N + \mathcal{J}_{p_x}\mathcal{A}_{p_x}, \tag{29}$$

with the macroscopic fluxes $\mathcal{J}_X$ defined as

$$\mathcal{J}_U = \frac{d}{dt}\langle \Delta U\rangle = \sigma\left(\frac{k}{2\pi m}\right)^{1/2}\left[n_A T_A^{1/2}\left(2kT_A + \frac{mV_A^2}{2}\right) - n_B T_B^{1/2}\left(2kT_B + \frac{mV_B^2}{2}\right)\right],$$

$$\mathcal{J}_N = \frac{d}{dt}\langle \Delta N\rangle = \sigma\left(\frac{k}{2\pi m}\right)^{1/2}(n_A T_A^{1/2} - n_B T_B^{1/2}),$$

$$\mathcal{J}_{p_x} = \frac{d}{dt}\langle \Delta p_x\rangle = \sigma\left(\frac{km}{2\pi}\right)^{1/2}(n_A V_A T_A^{1/2} - n_B V_B T_B^{1/2}). \tag{30}$$

While these fluxes are in general complicated nonlinear functions of the affinities $(\mathcal{A}_U, \mathcal{A}_N, \mathcal{A}_{p_x})$, near equilibrium we can write

$$T_A = T - \frac{\Delta T}{2}, \quad T_B = T + \frac{\Delta T}{2},$$

$$n_A = n - \frac{\Delta n}{2}, \quad n_B = n + \frac{\Delta n}{2},$$

$$V_A = V - \frac{\Delta V}{2}, \quad V_B = V + \frac{\Delta V}{2}, \tag{31}$$

and expand the forces and fluxes to first order in the small deviations ΔT, Δn, and ΔV. To linear order, the thermodynamic forces become

$$\mathcal{A}_U = -\frac{\Delta T}{T^2},$$

$$\mathcal{A}_N = \frac{mV}{T}\Delta V + \left(\frac{3k}{2T} - \frac{mV^2}{2T^2}\right)\Delta T - \frac{k}{n}\Delta n,$$

$$\mathcal{A}_{p_x} = -\frac{\Delta V}{T} + \frac{V}{T^2}\Delta T. \tag{32}$$

Taylor expansions of the fluxes $\mathcal{J}_U$, $\mathcal{J}_N$, and $\mathcal{J}_{p_x}$ [Eq. (30)] allow us to write

$$\bar{J} = \boldsymbol{L}\bar{A}, \tag{33}$$

where $\bar{J} = (\mathcal{J}_U, \mathcal{J}_N, \mathcal{J}_{p_x})^T$ and $\bar{A} = (\mathcal{A}_U, \mathcal{A}_N, \mathcal{A}_{p_x})^T$. The Onsager matrix $\boldsymbol{L}$ is given by

$$\boldsymbol{L} = \sigma\left(\frac{k}{2\pi m}\right)^{1/2} nT^{3/2}\begin{pmatrix} 6kT + 3mV^2 + \frac{(mV^2)^2}{4kT} & 2 + \frac{mV^2}{2kT} & \frac{1}{2}mV\left(6 + \frac{mV^2}{kT}\right) \\ 2 + \frac{mV^2}{2kT} & \frac{1}{kT} & \frac{mV}{kT} \\ \frac{1}{2}mV\left(6 + \frac{mV^2}{kT}\right) & \frac{mV}{kT} & m + \frac{(mV)^2}{kT} \end{pmatrix}, \tag{34}$$

which clearly has the required symmetry $L_{ij} = L_{ji}$. The Onsager relations (33) fully detail the complex coupling between energy, particle, and momentum transport in the linear regime. We note in passing that

$$\det \boldsymbol{L} = \sigma\left(\frac{2mk}{\pi}\right)^{1/2} nT^{3/2}, \tag{35}$$

which vanishes only for massless particles. Hence the system under consideration does not possess the tight coupling property, and Carnot and Curzon Ahlborn efficiencies cannot be attained [10].

Note that in the case of moving gases, $V \neq 0$, the presence of a temperature gradient alone $(\Delta n = \Delta V = 0)$ is sufficient to produce a nonzero net flux of momentum. Note also that when there is only a momentum gradient, $\Delta T = \Delta n = 0$, the heat, particle, and momentum fluxes reduce to

$$\mathcal{J}_U = -\sigma n\left(\frac{kT}{2\pi m}\right)^{1/2} mV\Delta V,$$

$$\mathcal{J}_N = 0,$$

$$\mathcal{J}_p = -\sigma n\left(\frac{kT}{2\pi m}\right)^{1/2} m\Delta V. \tag{36}$$

Therefore, when we choose the velocities to be equal but opposite so that $V=0$, the only nonzero flux is due to momentum transport. In other words, momentum exchange takes place without a net exchange of particles or energy.

VII. CONCLUSION

The work and fluctuation theorems are quite remarkable. They are basically one further step in Onsager's program to take into account the time-reversal symmetry of the microscopic dynamics. This results in a stringent constraint on the probability density of the entropy production. The implications of this result are still being explored. In this paper we have shown by an explicit microscopically exact calculation that the fluctuation theorem applies for the effusion between ideal gases with nonzero overall momentum. This sets the stage for the application of the formalism in fluctuating hydrodynamics. In particular, we have demonstrated via a simple, analytically tractable model that momentum transfer can be seamlessly incorporated with mass and heat exchange in applications of the fluctuation theorem, thereby explicitly demonstrating its utility for the study of all traditionally relevant quantities in hydrodynamics.

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APPENDIX A

We can derive the thermodynamic forces for an ideal gas of N particles in volume $\mathcal{V}$ with nonzero momentum by considering the entropy $S(U,N,\mathcal{V})$ of a gas at rest as a function of U, the total energy, N, and $\mathcal{V}$. Because adding an overall velocity to the gas does not change its volume in phase space and hence its entropy, we can write the entropy $S(U,N,\mathcal{V},p)$ of a flowing gas which depends on the total momentum p in terms of the entropy $S_0(U,N,\mathcal{V})$ of a gas at rest. We note that $p \equiv NmV$, where V is the overall center of mass velocity of the gas, and we choose lowercase p to avoid confusion with pressure. Now we can write

$$S(U,N,\mathcal{V},p) = S_0\left(\left(U - \frac{p^2}{2Nm}\right),N,\mathcal{V}\right) = S_0(\epsilon,N,\mathcal{V}), \tag{A1}$$

where $\epsilon \equiv U - p^2/2Nm$ represents the internal energy of the gas. The Sackur-Tetrode formula [11] provides the explicit expression for $S(\epsilon,N,\mathcal{V})$ which, with Eq. (A1) leads to

$$S = kN \ln\left[\frac{\mathcal{V}}{N}\left(\frac{U - \frac{p^2}{2mN}}{N}\right)^{3/2}\right] + \frac{3}{2}kNK. \tag{A2}$$

Here h is Planck's constant, m is the mass of a single gas particle, and $K \equiv \left[\frac{5}{3} + \ln\left(\frac{4\pi m}{3h^2}\right)\right]$ is a mass-dependent constant. We can write the total entropy change of the effusion process considered here as

$$\begin{aligned} dS &= \frac{\partial S_A}{\partial U_A}dU_A + \frac{\partial S_A}{\partial N_A}dN_A + \frac{\partial S_A}{\partial p_A}dp_A + \frac{\partial S_B}{\partial U_B}dU_B + \frac{\partial S_B}{\partial N_B}dN_B \\ &\quad + \frac{\partial S_B}{\partial p_B}dp_B \\ &= dU\left(\frac{\partial S_B}{\partial U_B} - \frac{\partial S_A}{\partial U_A}\right) + dN\left(\frac{\partial S_B}{\partial N_B} - \frac{\partial S_A}{\partial N_A}\right) \\ &\quad + dp\left(\frac{\partial S_B}{\partial p_B} - \frac{\partial S_A}{\partial p_A}\right), \end{aligned} \tag{A3}$$

where S_i corresponds to Eq. (A2) with $U \to U_i$, $N \to N_i$, and $p \to p_i$, $i \in A,B$, and we have used momentum, energy, and particle conservation to write $dU = -dU_A = dU_B$, $dN = -dN_A = dN_B$, and $dp = -dp_A = dp_B$. Performing the above calculations and considering that the total energy U of an ideal gas with overall momentum p at temperature T is given by

$$U = \frac{3NkT}{2} + \frac{p^2}{2mN}, \tag{A4}$$

we arrive after simplification at the expressions given in Eq. (4).

APPENDIX B

We give a derivation of the fluctuation theorem, Eq. (7), by adapting to the present case the procedure introduced in Ref. [12]. We consider the Hamiltonian evolution of a system, consisting of two disjoint subsystems A and B initially at equilibrium characterized by microcanonical distributions with total particle number, momentum, energy and volume equal to N_i, p_i, U_i and $\mathcal{V}_i$, $i = A,B$, respectively. At the initial time, the constraint separating both systems is broken. It is assumed that this can be achieved without any external work, momentum exchange or other perturbation of the subsystems. This is clearly the case for the opening of a hole in the adiabatic wall separating ideal gases, as considered here. After a time interval of duration t, the constraint is again introduced at no cost of energy or momentum. One records the new values of the parameters N_i', p_i', and U_i'. The amounts $(\Delta N, \Delta p, \Delta U)$ that are transported from system A to system B will depend on the specific run, i.e., on the starting configuration at $t=0$. Let the volume in phase space corresponding to the initial states that lead to the transport of these amounts be denoted by $\Omega_{(N_i,p_i,U_i)}(\Delta N, \Delta p, \Delta U)$. The probability to observe such a realization is then given by

$$P_{(N_i,p_i,U_i)}(\Delta N,\Delta p,\Delta U)=\frac{\Omega_{(N_i,p_i,U_i)}(\Delta N,\Delta p,\Delta U)}{\Omega_{(N_i,p_i,U_i)}},\quad \text{(B1)}$$

where $\Omega_{(N_i,p_i,U_i)}$ is the total phase space volume. We now apply this very same result for parameter values N_i', $-p_i'$ and U_i', $i=A,B$, and consider the probability of transporting the amounts $(-\Delta N,\Delta p,-\Delta U)$. Apart from velocity inversion, the final values in this procedure are then the initial ones of the first scenario, i.e., $(N_i,-p_i,U_i)$. The corresponding probability reads

$$P_{(N_i',-p_i',U_i')}(-\Delta N,\Delta p,-\Delta U)=\frac{\Omega_{(N_i',-p_i',U_i')}(-\Delta N,\Delta p,-\Delta U)}{\Omega_{(N_i',-p_i',U_i')}}.\quad \text{(B2)}$$

By microreversibility, there is a one-to-one correspondence between each trajectory in the first situation with the time reversed trajectory in the second situation. Furthermore, since Hamiltonian dynamics preserves phase volume, the numerators in the right-hand side of Eqs. (B1) and (B2) are identical. We conclude that

$$\frac{P_{(N_i,p_i,U_i)}(\Delta N,\Delta p,\Delta U)}{P_{(N_i',-p_i',U_i')}(-\Delta N,\Delta p,-\Delta U)}=\frac{\Omega_{(N_i',-p_i',U_i')}}{\Omega_{(N_i,p_i,U_i)}}=\exp\left(\frac{\Delta S}{k_B}\right),\quad \text{(B3)}$$

where we used the fact that the entropy of a state is Boltzmann's constant times the logarithm of the phase space volume Ω of that state. ΔS is thus the entropy difference between states with and without the primes. We now note that inverting the momenta of the gases does not change the statistics of particle and energy transport, but will obviously change the sign of the momentum transfer $P_{(N_i',-p_i',U_i')}(-\Delta N,\Delta p,-\Delta U)=P_{(N_i',p_i',U_i')}(-\Delta N,-\Delta p,-\Delta U)$. Hence we can rewrite Eq. (B3) as follows:

$$\frac{P_{(N_i,p_i,U_i)}(\Delta N,\Delta p,\Delta U)}{P_{(N_i',p_i',U_i')}(-\Delta N,-\Delta p,-\Delta U)}=\exp\left(\frac{\Delta S}{k}\right).\quad \text{(B4)}$$

Finally, we consider the thermodynamic limit of infinitely large systems with finite particle density $n_i=N_i/\mathcal{V}_i$, momentum density $mV_i=p_i/N_i$, and energy density $u_i=U_i/\mathcal{V}_i$. We furthermore assume that the effects of the removal of the constraint do not scale with the volume, so that during the finite time t it results in nonextensive changes in the parameter values. Hence we can drop the subindices of P on the left-hand side of Eq. (B4). Adding the subindex t to emphasize the duration of the exchange, one can thus rewrite Eq. (B4) as Eq. (7) of the main text.

APPENDIX C

Here we briefly derive the formula for the transition rate $T_{A\to B}(E,p_x)$ using the kinetic theory of gases. We consider the $\hat{z}$ direction to point from reservoir A to reservoir B. We require $T_{A\to B}(E,p_x)dEdp_xdt$, the probability to observe a particle with kinetic energy in the range $(E,E+dE)$ and momentum in the range (p_x,p_x+dp_x), to cross the hole from A to B in a time interval dt. The z component of the position of a particle with velocity $\boldsymbol{v}$ must be located within a cylinder of base area σ (the area of the hole) and height v_zdt measured from the wall. Furthermore, the particle must be traveling towards the hole in a direction which we define as the $+\boldsymbol{e}_z$ direction (see Fig. 1). That is, the component of the particle's velocity in the direction normal to the surface area of the hole must be positive so that it is traveling from reservoir A to reservoir B. The appropriate expression is

$$T_{A\to B}(E,p_x)=\int_{-\infty}^{\infty}dv_x\int_{-\infty}^{\infty}dv_y\int_0^{\infty}dv_z\sigma v_z n_A\phi_A(\boldsymbol{v},V_A)\times\delta\left(\frac{mv^2}{2}-E\right)\delta(mv_x-p_x),\quad \text{(C1)}$$

where $\phi_A(\boldsymbol{v},V_A)$ is the Maxwellian given by Eq. (2), and we have explicitly noted its dependence on $\boldsymbol{v}$ and V_A. A similar equation holds for $T_{B\to A}$. The v_x integral is trivial because of the second delta function, and the remaining integrals can be easily performed by changing to polar coordinates (R,θ), given by

$$R^2=v_y^2+v_z^2,\quad \tan\theta=\frac{v_y}{v_z}.\quad \text{(C2)}$$

This yields the expressions given in Eq. (11).

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