A local fluctuation theorem for large systems

Guillaume Michel\textsuperscript{1,}\textsuperscript{*} and Debra J. Searles\textsuperscript{2,}\textdagger

\textsuperscript{1}D\textsuperscript{é}partement de Physique, École Normale Sup\textsuperscript{é}rieure, 24 Rue Lhomond, 75 005 Paris, France
\textsuperscript{2}Queensland Micro- and Nanotechnology Centre, Griffith University, Brisbane Qld 4111, Australia
\textsuperscript{3}Australian Institute of Bioengineering and Nanotechnology and School of Chemistry and Molecular Biosciences, The University of Queensland, Brisbane Qld 4072, Australia

(Dated: August 21, 2012)

The fluctuation theorem characterizes the distribution of the dissipation in nonequilibrium systems and proves that the average dissipation will be positive. For a large system with no external source of fluctuation, fluctuations in properties will become unobservable and details of the fluctuation theorem are unable to be explored. In this letter, we consider such a situation and show how a fluctuation theorem can be obtained for a small open subsystem within the large system. We find that a correction term has to be added to the large system fluctuation theorem due to correlation of the subsystem with the surroundings. Its analytic expression can be derived provided some general assumptions are fulfilled, and its relevance it checked using numerical simulations.

PACS numbers: 02.50.Ey, 05.20.-y, 05.40.Ca, 05.70.Ln

INTRODUCTION

In classical thermodynamics, nonequilibrium systems are irreversible. That is, the second law of thermodynamics stipulates that a macroscopic system evolves in one direction and fluxes have a definite sign. However, the second law is strictly applicable only to large systems or where properties are measured over long time scales. As the size of the system decreases, unusual events caused by thermal fluctuations become more frequent, and average values of the flux with the opposite sign to that predicted for a thermodynamic system are observable over finite periods. These effects are quantified by the Fluctuation Theorem (FT), which states that for a system initially at equilibrium and driven out of equilibrium,

\[ \ln \left( \frac{p(\Omega_t = A)}{p(\Omega_t = -A)} \right) = A \]  \hspace{1cm} (1)

where \( \Omega_t \) is an extensive function, the dissipation function measured over a period of \( t \) \textsuperscript{1}. which describes how irreversible a process is. In this equation, \( p(\Omega_t = A) \) refers to the probability that \( A \) takes on a value \( A \pm dA \). Eq. (1) is also asymptotically valid for steady-states. Initially based on a heuristic derivation and numerical evidence \textsuperscript{2}, fluctuation relations have been derived for closed systems in many different frameworks (see \textsuperscript{1,}3–\textsuperscript{5} for early results). Recently the fluctuation theorem has been used to measure physical quantities in experiments, for instance the torque of a molecular motor \textsuperscript{6}. In general, the use of the FT is relevant when the work done by the external forces is similar to the thermal energy \( k_B T \) (or its equivalent if another kind of thermal equilibrium is reached, \textit{e.g.} \textsuperscript{3}). Otherwise, it reduces to stating irreversibility, because the probability of observing a negative dissipation is so small that it can be considered impossible. Therefore, in large systems, \textsuperscript{1} can not be properly tested or applied. To deal with such a situation, one can record the dissipation over a small open subsystem where thermal fluctuations are sizeable. The dissipation in the subsystem will not satisfy equation (1) in general, and in this manuscript we consider if an analytical expression for a Local Fluctuation Theorem (LFT) can be obtained.

Some experimental and theoretical work has been carried out on local fluctuation theorems since 1998. Measurements of local properties for steady states have been shown to satisfy fluctuation relations \textsuperscript{2,}9–\textsuperscript{10}. However, these studies employ an effective temperature, which can be considered to provide an \textit{ad hoc} correction coefficient to the fluctuation relations. Gallavotti showed why the fluctuation theorem is expected to be valid at long times for the local entropy creation rate for weakly coupled systems \textsuperscript{11}. Ayton et al. \textsuperscript{12} considered the local fluctuation theorem for the dissipation function (1), and provided numerical results. In the present paper, we show that in a highly correlated system, the local dissipation obeys a LFT which is (1) with a linear correction term. The result explains the previous effective temperatures, the correction term can be analytically described in some cases, and it vanishes in the low correlation limit.

In the next section we derive a LFT, then we numerically investigate the relevance of our assumptions in a realistic system.

A LOCAL FLUCTUATION THEOREM

Consider a large system that fulfils the assumptions of the FT, \textit{i.e.} the invariance of the initial distribution function under time-reversal mapping, ergodic consistency and time-reversibility of the equations of motion \textsuperscript{1}. The FT can then be derived for an arbitrary phase
function $\Phi(\Gamma)$ odd under time-reversal, 
\[
\ln \left( \frac{p(\Phi_t = A)}{p(\Phi_t = -A)} \right) = -\ln \left( \langle e^{-\Omega_t} \rangle_{\Phi_t=A} \right)
\]
If $\Phi$ is chosen to be the dissipation function, (2) becomes the usual FT. Here, we split $\Omega$ into two contributions $\Omega_\ell$ and $\Omega_\ell^*$, where $\Omega_\ell$ is the dissipation function measured over an arbitrary volume of length $\ell$, and choose $\Phi = \Omega_\ell^*$. In this case, (2) becomes a local fluctuation theorem 
\[
\ln \left( \frac{p(\Omega_{\ell,t} = A)}{p(\Omega_{\ell,t} = -A)} \right) = A - \ln \left( \langle e^{-\Omega_\ell^{*}} \rangle_{\Omega_\ell=A} \right)
\]
This equation provides an exact expression for the correction term. If there is no correlation between the two local dissipations, this term vanishes and $\Omega_\ell$ obeys a bare FT (1). Otherwise, some assumptions have to be made to obtain an effective description of this term. We will make two main assumptions. The first one is that one can consider the local dissipation as a random variable instead of a phase function so that, 
\[
\Omega_{\ell,t} = \alpha \Omega_{\ell,t} + \xi
\]
where $\alpha$ is a coefficient that depends on the shape and size of the subvolume, and $\xi$ a random variable that is not correlated with $\Omega_{\ell,t}$. Physically, the first term describes the very strong correlations that exist near the boundaries between the two domains, and $\xi$ stands for the dissipation far away from the volume of interest, which does not depend on $\Omega_{\ell,t}$. Quadratic and higher order terms are neglected in (4), but do not seem relevant. This relation between the two local dissipations leads to an exact expression for the LFT,
\[
\ln \left( \frac{p(\Omega_{\ell,t} = A)}{p(\Omega_{\ell,t} = -A)} \right) = (1 + \alpha)A
\]
This model explains why the left hand side of (5), called the asymmetry function, has been experimentally found to be a linear function of $A$ with a slope that is not unity. Given our assumption of non-correlation between $\xi$ and $\Omega_{\ell,t}$, the coefficient $\alpha$ is 
\[
\alpha = \frac{\langle \Omega_{\ell,t}^2 \rangle_{\Omega_{\ell,t}} - \langle \Omega_{\ell,t}^2 \rangle_{\Omega_{\ell,t}=A}}{\langle \Omega_{\ell,t}^2 \rangle - \langle \Omega_{\ell,t}^2 \rangle_{\Omega_{\ell,t}=A}}
\]
In solid states, typical lengths of correlation in the dissipation are typically much smaller than that of the subvolume that has to be considered, and this correction term can be neglected. Significant exceptions are systems close to a phase-transition, in which case an analytic expression for $\alpha$ can often be derived (e.g. for the Ising model). On the other hand, in liquid and gas, correlation lengths are larger as particles can travel thought several subvolumes, and we shall see that they can be related to diffusion lengths. We focus on such systems, consisting a fluid driven out of equilibrium by an external field that produces a dissipative flux. This is very general and includes the studies on fluidized granular medium, and Rayleigh-Bénard convection, but can also model Poiseuille or Couette flows, diffusion processes, and so on. To simplify the notation we consider the case where the field, $F_e$ and dissipative flux $J$ are in the same direction and then the dissipation function reads 
\[
\Omega_\ell = \beta F_e J_t
\]
where $\beta$ is the inverse temperature to which the system would relax in the absence of the field, and we adopt the notation that the average value of $J$ is positive in a dissipative system. Then $\alpha$ refers to the spatial correlations of the integrated flux $J_t$ : 
\[
\alpha = \frac{\langle J_{\ell,t}^2 \rangle_{\Omega_{\ell,t}} - \langle J_{\ell,t} \rangle_{\Omega_{\ell,t}}^2}{\langle J_{\ell,t}^2 \rangle - \langle J_{\ell,t} \rangle^2}
\]
Another expression for this coefficient can be derived after defining details about the subvolume. We consider a rectangular unit cell of length $L$ and with field applied in the $x$-direction. The subvolumes are obtained by dividing the cell into slices orthogonal to the direction of the field with width $\ell$ (see figure 1, but note that the following computations can be adapted to other situations. In this case, the relevant correlations are fully described by the function $C(x)$ defined by 
\[
C(x) = \frac{\langle j_t(0) j_t(x) \rangle - \langle j_t(0) \rangle \langle j_t(x) \rangle}{\langle j_t(0) \rangle^2 - \langle j_t(0) \rangle^2}
\]
where for $J_{\ell,t}$ centred on $x$, $j_t(x) = \lim_{t \to 0} J_{\ell,t}(x)/\ell$ is the flux density at $x$. This function describes the decay of spatial correlations: if there is no correlation between the flux in these two sections, as when $x$ goes to infinity, this term is equal to zero. On the other hand, $C(0) = 1$ due to the normalisation. A typical correlation length in the fluid can then be defined by
\[
\ell_0 = \int_0^\infty C(x)dx
\]
This length is to be compared to the subvolume's to know whether a bare fluctuation theorem (1) is expected to be valid ($\ell \gg \ell_0$) or if a LFT is required. 
We then make a second general assumption : noting that the function $C$ satisfies $C(0) = 1$, $C(\infty) = 0$ and has a typical decay length of $\ell_0$, we assume it is modelled by an exponential decay $C(x) = e^{-x/\ell_0}$. Considering this implies that $\langle j_t(0) j_t(x) \rangle - \langle j_t(0) \rangle \langle j_t(x) \rangle = Ae^{-x/\ell_0}$. $\alpha$ is then explicitly computable and assuming $L$ is large, (5) becomes
\[
\ln \left( \frac{p(\Omega_{\ell,t} = A)}{p(\Omega_{\ell,t} = -A)} \right) = (1 + \frac{1}{\ell_0 (1 - e^{-x/\ell_0})})A
\]
This LFT provides an analytic expression for the correlation term, which vanishes in the low correlation limit ($\ell \gg \ell_0$) and can be used instead of an effective temperature. In derivation of (11), we consider the large system length $L \gg \ell_0$.

We now consider a particular case and show that it is possible to derive an expression for the correlation length under some conditions. Our system consists of $N$ particles of charge $c_i$ subject to a field in the $x$ direction, and the dissipative flux becomes $J_i = \int_0^L \sum_{i=1}^N c_i v_{x,i} \, ds$ where $v_{x,i}$ is the $x$ component of the velocity for particle $i$. For a system close to equilibrium, the correlation length, $\ell_0$ takes its origin in the Brownian motion of the particles, and for large $L$ the following equalities hold:

\[
\int_0^L \langle j_i(0) j_i(x) \rangle \, dx = \frac{\langle (\Delta x)^2 \rangle}{2 \ell_0} \quad \text{(12)}
\]

\[
\langle j_i(0) j_i(0) \rangle = \frac{\langle |\Delta x| \rangle}{L} \quad \sum_{i=1}^N c_i^2 \quad \text{(13)}
\]

where $\Delta x = x(t) - x(0)$ is the $x$-displacement for one particle and $L$ the length of the system, which does not appear in the final equilibrium expression for $\ell_0$,

\[
\ell_0 = \frac{\langle (\Delta x)^2 \rangle}{2 \langle |\Delta x| \rangle} = \frac{\pi \langle (\Delta x)^2 \rangle}{8} \quad \text{(14)}
\]

The last equality comes from the assumption of a Gaussian distribution for $\Delta x$. If the external field is not too high, $\ell_0$ is close to its equilibrium value and (14) provides a much more convenient way to measure it (directly or via the Einstein relation).

Therefore, we have seen that for a fluid (or gas) driven out of equilibrium by an external field, the local dissipation recorded in a section of length $\ell$ fulfills (11) with $\ell_0$ given by (14) provided: the system is large, the field not too large (so that $\ell_0$ is close to its equilibrium value) and the decay of correlations is reasonably described by an exponential function.

**NUMERICAL STUDY**

To present an application of this LFT and check the relevance of our assumptions, a system of color-charged particles between atomic walls was numerically studied. Color charges are similar to electric charges in that the particles feel a force proportional to their charge from the field, but there are no Coulomb interactions between the particles. The system is a high density gas in a long channel surrounded by thermostated walls. The dynamics are,

\[
\dot{q}_i = \frac{p_i}{m} \quad \text{(15a)}
\]

\[
\dot{p}_i = F_i(q) + c_i F_e e_x - S_i (\alpha p_i + k(q - q_{eq})) \quad \text{(15b)}
\]

where $q_i$, $p_i$ and $c_i = (-1)^i$ are the coordinates, momenta and colour of the $i$th particle ($c_i = 0$ for wall particles) and $S_i$ is a switch equal to 1 for the wall particles and zero otherwise. $F_e$ is the interparticle force on a particle, derived from a Weeks-Chandler-Anderson short-ranged repulsive pair potential $[14]$, $k$ the strength of the traps that fix the positions of wall particles, and $F_e$ the external field which induces a flux $J = \sum_{i=1}^N c_i v_{x,i}$. Finally, $\alpha$ is a Gaussian thermostat that fixes the kinetic energy of the walls: the fluid particles are not thermostated and obey their natural dynamics. The simulation used 320 particles in a two-dimensional space with periodic boundary conditions. The wall temperature was set at 1, the wall density at 0.8, the fluid’s at 0.4, the field at $F_e = 0.08$, the length of system at $L = 50.6$ and the integration time at $t = 80$. All trajectories started from the equilibrium distribution. The volume was divided into subvolumes as described above. This system is showed fig.1

The mean value of the total dissipation is $\langle \Omega \rangle \approx 36$ and in 500 000 samples no negative value was observed. On the other hand, the local dissipation recorded in the volume of length $\ell$ showed in fig.1 was 14.4 times smaller than the total volume. It consequently produced a number of negative values of $\Omega$ and its asymmetry function can be computed. As expected, it is a linear function with a slope larger than one, see fig.2.

The correlation length $\ell_0$ was measured out of equilibrium by fitting $C(x) = e^{-x/\ell_0}$ to the simulated values of $C(x)$ and was found to be very close to its equilibrium value, related to a diffusion process and given by (14), cf. fig3. This tends to show that $\ell_0$ would often be experimentally equal to its equilibrium value, as external fields used in molecular dynamics simulations are very large (in this simulation, the mean velocity eventually reaches a few percent of the thermal one). The main assumption of the derivation was that an exponential decay $e^{-x/\ell_0}$ would fit the function $C(x)$, which is not exact, cf. fig4.

Using the calculated value of $\ell_0 = 4.56$ at $t = 80$, and $\ell = 3.52$, the slope predicted by (11) is 3.30 which is in good agreement with the numerically determined

![FIG. 1. A schematic diagram of the system studied. Wall particles are thermostated and represented in black ($c_i = 0$), whereas fluid particles can be blue ($c_i = 1$) or red ($c_i = -1$).](image)
Asymmetry function ρ\(\ell\)(A) = \ln(p(Ω_{\ell,t} = A)/p(Ω_{\ell,t} = -A)), is found to be a straight line of slope 3.147 ± 0.001.

FIG. 3. Evolution of the correlation length \(\ell_0\) determined out of equilibrium using a fit of \(C(x) = e^{-x/\ell_0}\) to the simulated data at various times. The dashed line is its theoretical equilibrium value determined using (14) and the Einstein relation.

slope of 3.146 ± 0.001 determined from the data shown in fig. 2. In fig. 3 the predicted and actual slopes are compared for a range of \(l\), and are shown to be in very good agreement. Therefore, even if the correlation decay is not exactly exponential, which could happen as this function is system-dependant, the predictions of this LFT remain robust.

FIG. 4. The decay of spatial correlations in the integrated flux calculated with (\(\bigtriangleup\)) (crosses) and is exponential model \(e^{-x/\ell_0}\), where \(\ell_0\) is the equilibrium correlation length estimated assuming a diffusive process (solid line).

FIG. 5. Slope of the asymmetry function (left hand side of (11)) versus the length of the subsystem. The dashed line is the theoretical result derived in section 2 with the coefficient \(\ell_0\) estimated at equilibrium via a diffusive process.

CONCLUSION

In this letter, we considered a class of large systems (liquid or gas driven out of equilibrium by an external field). A local fluctuation theorem is derived for the dissipation measured in a section orthogonal to the field and provides an explicit expression for the slope of its asymmetry function. The proof can be adapted to describe other shapes of subvolumes. Therefore, arbitrary effective temperatures no longer have to be used. This result holds provided some assumptions are fulfilled, mainly a low external field and an exponential decay of correlations in the flux. According to the numerical study, this last condition is not restrictive, and a reasonable accor-
dance is enough for this LFT to be verified. Finally, we pointed out that the need to resort to a LFT depends on the ratio $\ell/\ell_0$, where $\ell$ is the length of the subvolume over which the local dissipation is measured and $\ell_0$ is related to an equilibrium diffusion process and can be easily measured via the Einstein relation. As discussed in [13], this FT is also asymptotically valid for steady states with an additional assumption of a form of decay of correlations in the dissipation with time.

We would like to thank the Australian Research Council for the support of this project.

[1] D. J. Evans and D. J. Searles, Adv. in Phys. 51, 1529 (2002)
[2] D. J. Evans, E. G. D. Cohen, and G. P. Morriss, Phys. Rev. Lett. 71, 2401 (1993)
[3] D. J. Evans and D. J. Searles, Phys. Rev. E 50, 1645 (1994)
[4] G. Gallavotti and E. G. D. Cohen, Phys. Rev. Lett. 74, 2694 (1995)
[5] J. L. Lebowitz and H. Spohn, J. Stat. Phys. 95, 333 (1999)
[6] K. Hayashi, H. Ueno, R. Iino, and H. Noji, Phys. Rev. Lett. 104, 218103 (2010)
[7] K. Feitosa and N. Menon, Phys. Rev. Lett. 92, 164301 (2004)
[8] S. Ciliberto and C. Laroche, J. Phys. IV (France) 8, 215 (1998)
[9] S. Ciliberto, N. Garnier, S. Hernandez, C. Lacpatia, J. F. Pinton, and G. R. Chavarria, Physica A 340, 240 (2004)
[10] X.-D. Shang, P. Tong, and K.-Q. Xia, Phys. Rev. E 72, 015301 (2005)
[11] G. Gallavotti, Physica A 263, 39 (1999)
[12] G. Ayton, D. Evans, and D. Searles, J. Chem. Phys. 115, 2033 (2001)
[13] D. J. Searles, L. Rondoni, and D. J. Evans, J. Stat. Phys. 128, 1337 (2007)
[14] J. D. Weeks, D. Chandler, and H. C. Andersen, J. Chem. Phys. 54, 5237 (1971)