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A unified description of two theorems in non-equilibrium statistical mechanics: The fluctuation theorem and the work relation

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Abstract. – The fluctuation theorem (FT) and the work relation (WR) are two relations that extend our understanding of thermodynamics to non-equilibrium systems. While often treated as distinct relations, they are in fact closely related. In this letter we generalise these relations, showing that they are fundamental relations of statistical systems, and use these generalised forms to connect the FT and WR through a new set of relations, the conjugate work relations. We then take these general forms of the FT and WR, and show that they reduce to original forms under deterministic dynamics, before finally exploring their application to an experimental system.

The understanding of thermodynamics is largely confined to equilibrium states. The field of "nonequilibrium thermodynamics" represents an extension of the 19th century concepts of equilibrium thermodynamics to systems that are *close to*, or *near* equilibrium. Moreover, these traditional concepts are limited in application to large systems, referred to as the "thermodynamic limit". However, in the last decade, two new theorems have been introduced: these theorems firstly, lift the restriction of the thermodynamic limit, allowing thermodynamic concepts to be applied to small systems, and secondly, apply to systems that may be far-from-equilibrium. The first of these theorems, the fluctuation theorem (FT) [1–7], generalises the second law of thermodynamics so that it applies to small systems, including those far from equilibrium. The second, the work relation (WR) [8–12] (also known as the Jarzynski equality or the Non-equilibrium free energy theorem), provides a method of predicting equilibrium free energy differences from experimental trajectories along far-from-equilibrium paths. Both of these theorems are at odds with a traditional understanding of the 19th century thermodynamics where equilibrium is central and the second law inviolate. However these theorems are critical to the application of thermodynamic concepts to systems of interest to scientists and engineers in the 21st century.

Most recently, the FT and WR have been experimentally demonstrated. Each of these demonstrations consisted of sampling the response of a system to an imposed external field

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and measuring the energy or work along non-equilibrium paths. Liphardt *et al* [13] measured the force required to pull the ends of a single RNA chain beyond the chain's contour length and used the WR to infer the free energy change associated with a tension-induced unfolding transition of the molecule. More recently, Douarche *et al.* [14] demonstrated the WR for a mechanical torsional pendulum. The FT was first demonstrated experimentally by Wang *et al.* [15, 16]: they measured the work required to translate a particle-filled optical trap. Carberry *et al.* [17] further demonstrated the FT using a colloidal bead localised in a stationary optical trap with a time-dependent trapping constant. Each of these experimental demonstrations considered either the WR or FT for specific systems and independently of the other theorem. However, as we demonstrate in this letter, the FT and WR are closely connected when treated as general relations of thermodynamic systems, despite their differences in specific applications.

In this letter we provide a unified description of these fluctuation relations, as well as examples of the theorems applied in statistical ensembles and experiment. First, we present standard definitions of the two most often used theorems, the FT and WR, using consistent notation. The arguments of these theorems characterise the energy of the system along non-equilibrium trajectories. Through this generalised notation, we show first, that the arguments of these theorems are related and second, that there exist a set of theorems that characterise the fluctuations of the arguments. This unified description emphasises the similarity of the theorems while preserving their differences. The importance of these theorems is in their application to real systems and we demonstrate the theorems' differences by recasting the general formalism for specific systems: i) for arbitrary systems under deterministic dynamics, described under three different statistical ensembles, and ii) for the specific experimental system of a colloidal particle in an optical trap of time-varying strength.

The fluctuation theorem (FT) of Evans *et al.* [1, 2] describes how a system's irreversibility develops in time from a completely time-reversible system at short observation times, to a thermodynamically irreversible one at infinitely long times. Let ξ_τ be the vector of co-ordinates that describe the system at some time $t = \tau$, and $\lambda(t)$ represent an external field that is, in general, time-dependent. The response of the system to an external field is detailed in the evolution of the co-ordinates: let $\{\xi_0, \xi_\tau\}$ represent the complete set of system trajectories that evolve from an initial co-ordinate, ξ_0, to a final co-ordinate, ξ_τ.The size of the set will vary with the dynamics; for example, under deterministic dynamics, there exists a unique trajectory initialised at ξ_0 or that terminates at ξ_τ, while under stochastic dynamics there may exist an infinite number of trajectories in the set $\{\xi_0, \xi_\tau\}$. For any set $\{\xi_0, \xi_\tau\}$, there exists a conjugate set of "anti-trajectories" denoted by $\{\xi^*_\tau, \xi^*_0\}$. Here, the superscript $*$ represents a time reversal map of the co-ordinates, *i.e.*, a reversal of the time parity of the co-ordinates; for example, for trajectories in deterministic phase space, $\xi_\tau = (\boldsymbol{q}_\tau, \boldsymbol{p}_\tau)$ and $\xi^*_\tau = (\boldsymbol{q}_\tau, -\boldsymbol{p}_\tau)$ where $\boldsymbol{q}$ and $\boldsymbol{p}$ are the co-ordinates and momenta of the constituents of the system. While a particular trajectory and its conjugate antitrajectory may both be solutions of the equations of motion, the observed evolution of a large macroscopic system proceeds preferentially in one "time-forward" or irreversible direction. However, for smaller systems, the probability of observing anti-trajectories can be significant and the FT quantitatively details this transition from perfectly reversible trajectories to irreversible ones as system size and/or trajectory duration increases.

The FT relates the relative probabilities of observing trajectories of duration τ that are characterised by the dissipation function, Ω_τ, taking on arbitrary values, $a \pm \mathrm{d}a$, and $-a \mp \mathrm{d}a$ respectively:

$$\frac{P_F(\Omega_\tau = a)}{P_F(\Omega_\tau = -a)} = \exp{[a]}. \tag{1}$$

These probabilities are measured over the "forward" ensemble F, that represents the ensemble of trajectories generated for a system that starts in a time invariant distribution of co-ordinates $f_e(\xi, \lambda(0))$ under a constant external field $\lambda(0)$, and evolves under a time-dependent external field $\lambda(t)$ for $0 \le t \le \tau$ to a new distribution $f(\xi, \lambda(\tau), \tau)$. Initially, the system need only be in a time-invariant state, either an equilibrium state, or a non-equilibrium steady state. However, for simplicity, we will restrict our discussion to an initial equilibrium state. The FT can also be used to derive an ensemble average, known as the Kawasaki Identity (KI) [7,18]:

$$\langle \exp[-\Omega_\tau] \rangle_F = 1, \tag{2}$$

where the brackets indicate an ensemble average.

The argument of the FT and KI, the dissipation function, Ω_τ, is a measure of the system's reversibility under an external field and is related to the ratio of probabilities of observing sets of trajectories and their time-reverse or anti-trajectories. It is a quantity that is similar to entropy production in that it obeys a second law-like relation: $\langle \Omega_\tau \rangle \ge 0$. Let $P_F(\{\xi_0, \xi_\tau\})$ represent the probability distribution over the ensemble of trajectories F. Furthermore, let $\mathrm{d}v(\{\xi_0, \xi_\tau\})$ represent the infinitesimal volume in trajectory space around $\{\xi_0, \xi_\tau\}$. The dissipation function can be expressed as the ratio of probability densities for an arbitrary trajectory set and its conjugate:

$$\exp\left[\Omega_\tau(\{\xi_0, \xi_\tau\})\right] \equiv \frac{P_F(\{\xi_0, \xi_\tau\})}{P_F(\{\xi_\tau^*, \xi_0^*\})} \frac{\mathrm{d}v(\{\xi_0, \xi_\tau\})}{\mathrm{d}v(\{\xi_\tau^*, \xi_0^*\})}. \tag{3}$$

Equation (3) is a general definition that reduces to the definition of Ω_τ given for deterministic systems in [1], and the definition of Ω_τ given for stochastic systems in [4]. This definition is valid only if, for every set of trajectories $\{\xi_0, \xi_\tau\}$, there exists a conjugate trajectory set $\{\xi_\tau^*, \xi_0^*\}$ of non-zero probability. It is worth noting that for many systems, the inclusion of the volume elements for the trajectory space is irrelevant as they will be equal in size; however, there are some systems, notably thermostatted deterministic systems, where probability volumes change with the evolution of the system, and these volumes may differ in size.

The Work Relation (WR) predicts that the Helmholtz free energy difference, ΔA, between two equilibrium states in the canonical ensemble, can be determined from a specifically defined work function, ΔW, measured over trajectories of the system:

$$\langle \exp\left[-\beta \Delta W\right] \rangle_F = \exp\left[-\beta \Delta A\right]. \tag{4}$$

Here $\beta \equiv (k_\mathrm{B}T)^{-1}$, where T is the thermostat temperature. These trajectories can be sampled over arbitrary time, τ, and over arbitrary rates of change of the external field, $\dot{\lambda}$. As $\dot{\lambda}$ approaches zero, the distribution of measured ΔW narrows towards the quasi-static result of $\Delta W = \Delta A$, and $\langle \Omega_\tau \rangle = 0$, but measurements are not limited to this case.

In the same way that the Kawasaki Identity, eq. (2), relates to the fluctuation theorem, eq. (1), the WR is related to a fluctuation-like relation called the Crooks equality [11]:

$$\frac{P_F(\Delta W = a)}{P_R(\Delta W = -a)} = \exp[-\beta \Delta A] \exp[a]. \tag{5}$$

As with the FT, the subscripts on the probability distributions of the LHS specify the ensemble of non-equilibrium trajectories. However, unlike the FT, the numerator and denominator are evaluated over different ensembles of trajectories. We can express the ensemble of trajectories for the denominator similarly to the ensemble described by F. If we let $\lambda^*(t)$ denote the time-reversed external field such that $\lambda^*(t) = \lambda(\tau - t)$, then R represents the ensemble of trajectories which starts with a time-invariant distribution $f_e(\xi, \lambda(\tau))$ and evolves under $\lambda^*(t)$ for $0 \leq t \leq \tau$ to distribution $f(\xi, \lambda^*(\tau), \tau)$. That is the LHS of eq. (5) is a ratio of probabilities that the work function takes on equal magnitudes, but opposite sign, when there is time-reverse application of the external field.

In the original papers [8,9], the work function ΔW was defined specifically for the canonical ensemble. Before we present a more general, dynamics-independent definition of ΔW, it is useful to first introduce a similar dimensionless function, the distributed work function ΔW_d:

$$\exp\left[\Delta W_d(\{\xi_0, \xi_\tau\})\right] \equiv \frac{P_F(\{\xi_0, \xi_\tau\})}{P_R(\{\xi_\tau^*, \xi_0^*\})} \frac{\mathrm{d}v(\{\xi_0, \xi_\tau\})}{\mathrm{d}v(\{\xi_\tau^*, \xi_0^*\})}. \tag{6}$$

Note that the denominator of this definition differs from that of Ω_τ, eq. (3), in that it considers a distribution with a time-reverse application of the external field, λ. Like the definition of Ω_τ, the definition of ΔW_d requires that the probability distribution in the denominator is non-zero. From the definitions of ΔW_d, an ensemble average, and normalised probability distributions, we can immediately express an equality similar to the WR and KI,

$$\langle \exp\left[-\Delta W_d\right]\rangle_F = 1, \tag{7}$$

as well as a Crooks equality-like expression,

$$\frac{P_F(\Delta W_d = a)}{P_R(\Delta W_d = -a)} = \exp\left[a\right]. \tag{8}$$

This distributed work function reduces in the canonical ensemble to the dissipative work of Crooks [11], and shares the same form for its fluctuation relations as the Hatano-Sasa function [19,20], though it is a distinct function.

Now let us return to the original argument of the WR: the work function ΔW. To define this function, we need to define a partition function for two time-invariant or equilibrium states, characterised by $\lambda(0)$ and $\lambda(\tau)$. Let $z_{\lambda(0)}$ and $z_{\lambda(\tau)}$ represent the partition functions of the equilibrium states associated with external fields $\lambda(0)$ and $\lambda(\tau)$, so that the definition of ΔW is

$$\exp\left[\Delta W(\{\xi_0, \xi_\tau\})\right] \equiv \frac{P_F(\{\xi_0, \xi_\tau\})}{P_R(\{\xi_\tau^*, \xi_0^*\})} \frac{\mathrm{d}v(\{\xi_0, \xi_\tau\})}{\mathrm{d}v(\{\xi_\tau^*, \xi_0^*\})} \frac{z_{\lambda(0)}}{z_{\lambda(\tau)}}. \tag{9}$$

In the same way that eqs. (7) and (8) follow from the definition of ΔW_d, the definition of ΔW yields

$$\langle \exp\left[-\Delta W(\{\xi_0, \xi_\tau\})\right]\rangle = \frac{z_{\lambda(\tau)}}{z_{\lambda(0)}}. \tag{10}$$

and

$$\frac{P_F(\Delta W = a)}{P_R(\Delta W = -a)} = \exp[a]\frac{z_{\lambda(\tau)}}{z_{\lambda(0)}}. \tag{11}$$

From statistical mechanics, the ratio of the partition functions is equal to the exponential change in the free energy function. For example, in the canonical ensemble, the appropriate free energy is the Helmholtz free energy, and the last two equations are equivalent to the original WR and the Crooks equality, with β absorbed into the work and free energy terms.

From the definitions of Ω_τ, ΔW_d, and ΔW, it is straightforward to show that these functions are related according to

$$\begin{aligned} \Omega_\tau(\{\xi_0, \xi_\tau\}) &= \Delta W_d(\{\xi_0, \xi_\tau\}) - \omega_d(\{\xi_\tau^*, \xi_0^*\}), \\ \Omega_\tau(\{\xi_0, \xi_\tau\}) &= \Delta W(\{\xi_0, \xi_\tau\}) - \omega(\{\xi_\tau^*, \xi_0^*\}), \end{aligned} \tag{12}$$

where we introduce ω_d and ω as the normalised conjugate work function and conjugate work function, respectively:

$$\exp\left[\omega_d(\{\xi_\tau^*,\xi_0^*\})\right] \equiv \frac{P_F(\{\xi_\tau^*,\xi_0^*\})}{P_R(\{\xi_\tau^*,\xi_0^*\})}\frac{\mathrm{d}v(\{\xi_\tau^*,\xi_0^*\})}{\mathrm{d}v(\{\xi_\tau^*,\xi_0^*\})}, \tag{13}$$

$$\exp\left[\omega(\{\xi_\tau^*,\xi_0^*\})\right] \equiv \frac{P_F(\{\xi_\tau^*,\xi_0^*\})}{P_R(\{\xi_\tau^*,\xi_0^*\})}\frac{\mathrm{d}v(\{\xi_\tau^*,\xi_0^*\})}{\mathrm{d}v(\{\xi_\tau^*,\xi_0^*\})}.\frac{z_{\lambda(0)}}{z_{\lambda(\tau)}}. \tag{14}$$

Equations (12) show the connection between the arguments of the FT and Crook equality.

When the time-invariant distributions $f_e(\xi,\lambda(0))$ and $f_e(\xi,\lambda(\tau))$ are identical, these conjugate work functions vanish and $\Omega_\tau = \Delta W_d = \Delta W$. An example of such as system is that used by Wang *et al.* to first demonstrate the FT experimentally: a colloidal particle weakly held in an optical trap that is translated. Initially, the particle is equilibrated in a stationary trap that is translated over the time-period $0 \le t \le \tau$. For $t \ge \tau$, the particle relaxes to an equilibrated state with a stationary trap. Wang *et al.* constructed distributions of Ω_τ for $0 \le t \le \tau$ for the trajectories of the colloidal particle and were able to demonstrate that these distributions followed eq. (1). However, according to eqs. (12), their distributions of Ω_τ are equivalent to distributions of ΔW or ΔW_d. Consequently, their experimental demonstration was also a demonstration of the WR and the Crooks Equality in the specific case of $\Delta A = 0$ [21]. Furthermore, in the same way that Ω_τ obeys the FT and KI, ΔW obeys the Crooks equality and WR, and ΔW_d follows eqs. (7) and (8), both conjugate work functions, ω_d, and ω also obey similar relations. For ω_d,

$$\frac{P_F(\omega_d(\{\xi_\tau^*,\xi_0^*\})=a)}{P_R(\omega_d(\{\xi_\tau^*,\xi_0^*\})=a)} = \exp[a], \tag{15}$$

$$\langle\exp[-\omega_d]\rangle = 1, \tag{16}$$

and for ω, these are

$$\frac{P_F(\omega(\{\xi_\tau^*,\xi_0^*\})=a)}{P_R(\omega(\{\xi_\tau^*,\xi_0^*\})=a)} = \frac{z_{\lambda(\tau)}}{z_{\lambda(0)}}\exp[a], \tag{17}$$

$$\langle\exp[-\omega(\{\xi_\tau^*,\xi_0^*\})]\rangle = \frac{z_{\lambda(\tau)}}{z_{\lambda(0)}}. \tag{18}$$

We refer to these above relations as "conjugate work relations" or cWRs, in accord with the analogous expressions cast for ΔW. The conjugate work, ω, relates the arguments of the FT (Ω_d) and WR (ΔW) in eqs. (12) and the cWRs relate how fluctuations Ω_d and ΔW differ.

Up to this point, all of the expressions have been cast in terms of generalised trajectories, $\{\xi_0,\xi_\tau\}$, that are not specific to the type of dynamics, deterministic or stochastic. In table I we present expressions for each of these functions, Ω_τ, ΔW_d, ω_d, ΔW, and ω that result under deterministic dynamics, where the generalised trajectory $\{\xi_0,\xi_\tau\}$ has been mapped to the phase-space trajectory, $\mathbf{\Gamma}(t)$ $0 \le t \le \tau$. These expressions are given for three different statistical ensembles (micro-canonical, canonical, and isothermal-isobaric ensembles), governed by a general Hamiltonian, $\mathcal{H}$, with an additional ergostat, thermostat, and barostat [22]. The removal of heat by these thermostats gives rise to a phase-space compression factor Λ [23]. It is important to note that the temperature in these expressions corresponds to the temperature of the thermostat, or equivalently the equilibrium temperature of the two time-invariant states, if they exist. While the system is in a non-equilibrium state, the temperature is ill-defined; however, this is irrelevant to the derivation. In deterministic dynamics, the requirement for the existence of conjugate trajectories to define Ω_τ, ω_d and ω limit the application of the

TABLE I – *Table of arguments to the FT, WR, and conjugate WR for three ensembles of deterministic dynamics. In this table, $\mathcal{H}$ is the Hamiltonian for the system, $\beta = 1/k_BT$ where T is the temperature, $\Delta\mathcal{H}_1(\mathbf{\Gamma}(t)) = \mathcal{H}_1(\mathbf{\Gamma}(t)) - \mathcal{H}_1(\mathbf{\Gamma}(0))$, $\Delta\mathcal{H}(\mathbf{\Gamma}(t)) = \mathcal{H}_2(\mathbf{\Gamma}(t)) - \mathcal{H}_1(\mathbf{\Gamma}(0))$, $\delta\mathcal{H}(\mathbf{\Gamma}(t)) = \mathcal{H}_2(\mathbf{\Gamma}(t)) - \mathcal{H}_1(\mathbf{\Gamma}(t))$, p is the pressure, V is the volume, ΔS is the dimensionless entropy change $(S_2 - S_1)/k_B$, ΔA is the change in Helmholtz free energy $A_2 - A_1$, ΔG is the change in Gibbs free energy $G_2 - G_1$. Λ is the phase space compression which is related to the heat flow of the system; for thermostated systems, Λ will be cancelled with an equivalent term in the Hamiltonian as shown in a review by Evans & Searles* [7]. *The subscript "1" represents the initial state, and the subscript "2" represents the final state.*

	Micro-canonical	Canonical	Isothermal-Isobaric
P_F	$\frac{\mathrm{d}v(\mathbf{\Gamma})}{\int \mathrm{d}v(\mathbf{\Gamma})}$	$\frac{\exp[-\beta\mathcal{H}(\mathbf{\Gamma})]\mathrm{d}v(\mathbf{\Gamma})}{\int \mathrm{d}v(\mathbf{\Gamma})\exp[-\beta\mathcal{H}(\mathbf{\Gamma})]}$	$\frac{\exp[-\beta[\mathcal{H}(\mathbf{\Gamma})+pV]]\mathrm{d}v(\mathbf{\Gamma})}{\int \mathrm{d}v(\mathbf{\Gamma})\exp[-\beta[\mathcal{H}(\mathbf{\Gamma})+pV]]}$
Ω_τ	$-\int_0^t \Lambda(\mathbf{\Gamma}(s))\mathrm{d}s$	$\beta[\Delta\mathcal{H}_1(\mathbf{\Gamma}(t))] - \int_0^t \Lambda(\mathbf{\Gamma}(s))\mathrm{d}s$	$\beta[\Delta\mathcal{H}_1(\mathbf{\Gamma}(t)) - p\Delta V] - \int_0^t \Lambda(\mathbf{\Gamma}(s))\mathrm{d}s$
ΔW_d	$\Delta S - \int_0^t \Lambda(\mathbf{\Gamma}(s))\mathrm{d}s$	$\beta[\Delta\mathcal{H}(\mathbf{\Gamma}(t))] - \int_0^t \Lambda(\mathbf{\Gamma}(s))\mathrm{d}s - \beta\Delta A$	$\beta[\Delta\mathcal{H}(\mathbf{\Gamma}(t)) - p\Delta V - \Delta G] - \int_0^t \Lambda(\mathbf{\Gamma}(s))\mathrm{d}s$
ω_d	ΔS	$\beta[\delta\mathcal{H}(\mathbf{\Gamma}(t)) - \Delta A]$	$\beta[\delta H(\mathbf{\Gamma}(t)) - p\Delta V - \Delta G]$
ΔW	$-\int_0^t \Lambda(\mathbf{\Gamma}(s))\mathrm{d}s$	$\beta[\Delta\mathcal{H}(\mathbf{\Gamma}(t))] - \int_0^t \Lambda(\mathbf{\Gamma}(s))\mathrm{d}s$	$\beta[\Delta\mathcal{H}(\mathbf{\Gamma}(t)) - p\Delta V] - \int_0^t \Lambda(\mathbf{\Gamma}(s))\mathrm{d}s$
ω	0	$\beta[\delta\mathcal{H}(\mathbf{\Gamma}(t))]$	$\beta[\delta\mathcal{H}(\mathbf{\Gamma}(t)) - p\Delta V]$

FT and work relations such that the FT and WR never apply simultaneously, except in the particular case where the conjugate work functions vanish and $\Omega_\tau = \Delta W_d = \Delta W$, *i.e.*, when the free energy change is zero.

An example of the application of the theorems to experiment involves a colloidal particle held in an optical trap. This experiment was first used by Wang *et al.* to demonstrate the FT [15], showing that fluctuations accumulated along the particle's trajectories can be in contradiction to what one would expect from the second law of thermodynamics. An optical trap is formed when a transparent micron-sized particle, whose index of refraction is greater than that of the surrounding medium is located within a focused laser beam. The refracted rays differ in intensity over the volume of the sphere and exert a small force on the particle, drawing it towards the focal point or trap centre. This force is proportional to the displacement of the particle from the focal point and the proportionality constant, k, can be increased by adjusting the laser power. Values of k can be of the order of pN/μm and particle displacements can be resolved down to tens of nanometers, meaning that fluctuations of order a few percent of k_BT can be measured along a particle's trajectory. A "ramp" experiment corresponds to recording the trajectories of such an optically trapped particle, initially at equilibrium in an optical trap of strength k_1 and perturbed from equilibrium as the trap strength is increased linearly to k_2, and "ramped" down continuously back to k_1 over a time 2τ. The external field is only symmetric in time at $t = 0$ and $t = 2\tau$, and therefore for any time $0 < t < 2\tau$, the ensemble of trajectories in the forward direction will not contain a complete set of conjugate trajectories. This means that the definitions of the dissipation function and conjugate work function are valid only at $t = 0$ and $t = 2\tau$, and invalid over $0 < t < 2\tau$: consequently, the FT and cWR will not apply except at $t = 0$ and $t = 2\tau$. However, at all times along this trajectory, a complete set of conjugate trajectories will exist in the reverse ensemble to those trajectories in the forward ensemble, and consequently, the Crooks equality and the WR will hold. Thus, despite the unified description that we present here, these theorems do not always apply simultaneously, as evidenced by this example.

In this letter we have developed a new definition for these fluctuation relations that show they are general relations of statistical physics, but can also be used to apply these relations to experimental systems. These definitions also supply the conditions necessary to apply these relations, and show that while these relations are intimately connected at the theoretical level, it may be necessary to apply them separately at the practical level.

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