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Jarzynski's Identity

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Abstract

Jarzynski's identity relates the equilibrium free energy difference ΔF to the work W carried out on a system during a non-equilibrium transformation. In physics literature, the identity is usually written in the form: $\langle e^{-\beta W} \rangle = e^{-\beta \Delta F}$, where the average is said to be taken over all trajectories in the phase space. The identity in this form has been derived in different ways and published by many authors (see references). Since the identity involves taking an "average over trajectories", it is natural to interpret this average as the expectation relative to a probability measure on trajectories, while assuming that the system evolves stochastically. In the present work, Jarzynski's identity is formulated and proved mathematically rigorously. It is written in the form $\mathbb{E}[e^{-\beta W}] = e^{-\beta \Delta F}$, where $\mathbb{E}$ is the expectation relative to a probability measure on phase space paths. For this probability measure, some analytical assumptions under which Jarzynki's identity holds are found.

Keywords: Jarzynski's identity, probability measures on phase space paths, integration over phase space paths, non-equilibrium statistical mechanics.

1 Notation and assumptions

Let us assume that evolution of our system is described by a stochastic process $\Gamma_t(\omega) = \omega(t)$, $\omega \in \mathrm{C}([0,T], X)$, where $X = \mathbb{R}^{2d}$ is a phase space, $[0,T]$ is a time interval. Let $\mathcal{H} : X \times \Lambda \to \mathbb{R}$ be a Hamiltonian, $\Lambda \subset \mathbb{R}^l$ be an open set of values of an external parameter $\overline{\lambda} = (\lambda^1, \lambda^2, \dots, \lambda^l)$. Consider

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the situation when the control parameter is a function of time $\lambda : [0,T] \to \Lambda$. Thus, we consider actually a time dependent Hamiltonian $\mathcal{H}(x, \lambda(t))$. We assume that at time $t = 0$ the distribution on the phase space X is given by the following density function:

$$q_{\lambda(0)}(x) = \frac{e^{-\beta\mathcal{H}(x,\lambda(0))}}{\int_X e^{-\beta\mathcal{H}(x',\lambda(0))}\,dx'} = \frac{1}{Z_{\lambda(0)}}\, e^{-\beta\mathcal{H}(x,\lambda(0))},$$

where $\beta = 1/(k_B T)$, k_B is the Boltzmann constant, T is the temperature of the system, $Z_{\overline{\lambda}} = \int_X e^{-\beta\mathcal{H}(x,\overline{\lambda})}\,dx$ is the partition function. We assume that Γ_t is a Markov process, and consider a family of transition density functions for the process Γ_t:

$$\mathfrak{P} = \{p_\lambda(s,x,t,y) : [0,T] \times X \times [0,T] \times X \to \mathbb{R},\ \lambda \in V[0,T]\}\ ,$$

where $V[0,T]$ is the space of left continuous functions of bounded variation $[0,T] \to \Lambda$. We define the distribution $\mathbb{L}_\lambda$ of Γ_t. The finite dimensional distributions of Γ_t are given by

$$\int_{\mathrm{C}([0,T],X)} f(\omega(t_0), \omega(t_1), \ldots, \omega(t_n))\, \mathbb{L}_\lambda(d\omega) = \int_X dx_0\, q_{\lambda(t_0)}(x_0)$$
$$\int_X dx_1\, p_\lambda(t_0, x_0, t_1, x_1)) \cdots \int_X dx_n\, p_\lambda(t_{n-1}, x_{n-1}, t_n, x_n)\, f(x_0, x_1, \ldots, x_n)$$

where $\mathcal{P} = \{0 = t_0 < \cdots < t_n = T\}$ is a partition of the interval $[0,T]$, $f : X^{n+1} \to \mathbb{R}$ is a bounded continuous function. The measure $\mathbb{L}_\lambda$ is defined on all Borel subsets of $\mathrm{C}([0,T],X)$ by the Kolmogorov extension theorem. Consider the family of probability measures on $\mathrm{C}([0,T],X)$:

$$\mathfrak{L} = \{\mathbb{L}_\lambda,\ \lambda \in V[0,T]\}\ .$$

If evolution of the system is controlled by some $\lambda \in V[0,T]$, then the distribution of Γ_t is the measure $\mathbb{L}_\lambda$.

We also assume, that if the control parameter λ is a constant on a time interval $(\xi, \tau) \subset [0,T]$, and is equal to some value $\overline{\lambda}$, then for all $s, t \in (\xi, \tau)$

$$p_\lambda(s,x,t,y) = p(x,y,\overline{\lambda})\ , \tag{1}$$

where $p(\,\cdot\,,\,\cdot\,,\,\cdot\,) :\ X \times X \times \Lambda \to \mathbb{R}$ is a probability density function satisfying the conditions:

$$\int_X q_{\overline{\lambda}}(x)\, p(x,y,\overline{\lambda})\, dx = q_{\overline{\lambda}}(y)\ , \tag{2}$$

$$\int_X p(x,z,\overline{\lambda})\, p(z,y,\overline{\lambda})\, dz = p(x,y,\overline{\lambda})\ . \tag{3}$$

Lemma 1. *Let for each $x \in X$, $p(x,\cdot,\overline{\lambda})$ be a probability density function satisfying* (2) *and* (3). *Let $\mathcal{P} = \{0 = t_0 < t_1 < \cdots < t_n = T\}$ be a partition of $[0,T]$, and let*

$$\lambda(\,\cdot\,) = \lambda(t_0) + \sum_{i=1}^{n} \lambda(t_i)\, \mathbb{I}_{(t_{i-1},t_i]}(\,\cdot\,). \tag{4}$$

Then,

$$\begin{aligned}\tilde{p}_\lambda(s,x,t,y) = \int_X dx_1\, p(x,x_1,\lambda(\tau_1)) \int_X dx_2\, p(x_1,x_2,\lambda(\tau_2)) \ldots \\ \int_X dx_{k-1}\, p(x_{k-2},x_{k-1},\lambda(\tau_{k-1})) \int_X dx_k\, p(x_{k-1},x_k,\lambda(\tau_k))\, p(x_k,y,\lambda(t))\end{aligned} \tag{5}$$

is a transition density function for all $0 \leqslant s \leqslant t \leqslant T$, $x,y \in X$, and $\{\tau_1 < \ldots < \tau_k < t\} = (\mathcal{P} \cup \{t\}) \cap [s,t]$, i.e. $\int_X \tilde{p}_\lambda(s,x,t,y)\, dy = 1$, and $\tilde{p}_\lambda$ satisfies the Chapman-Kolmogorov equation.

Proof. We verify the Chapman-Kolmogorov equation for function $\tilde{p}_\lambda(s,x,t,y)$ defined by (5). Let $r \in [s,t]$, $\mathcal{P}_1 = \{\tau_1 < \tau_2 < \cdots < \tau_k < r\} = (\mathcal{P} \cup \{r\}) \cap [s,r]$, and let $\mathcal{P}_2 = \{\xi_1 < \xi_2 < \cdots < \xi_m < t\} = (\mathcal{P} \cup \{t\}) \cap [r,t]$. This construction implies that $(\mathcal{P}_1 \cup \mathcal{P}_2 \cup \{t\}) = (\mathcal{P} \cup \{t\}) \cap [s,t]$, and that $r \in (\tau_k, \xi_1]$ where $(\tau_k, \xi_1]$ is an interval of the partition $\mathcal{P}$. We have:

$$\begin{aligned}\int_X dy\, \tilde{p}_\lambda(s,x,r,y)\, \tilde{p}_\lambda(r,y,t,z) = & \int_X dx_1\, p(x,x_1,\lambda(\tau_1)) \int_X dx_2\, p(x_1,x_2,\lambda(\tau_2)) \ldots \\ & \int_X dx_k\, p(x_{k-1},x_k,\lambda(\tau_k)) \int_X dy\, p(x_k,y,\lambda(r)) \\ & \int_X dz_1\, p(y,z_1,\lambda(\xi_1)) \int_X dz_2\, p(z_1,z_2,\lambda(\xi_2)) \ldots \\ & \int_X dz_m\, p(z_{m-1},z_m,\lambda(\xi_m))\, p(z_m,z,\lambda(t))\ .\end{aligned} \tag{6}$$

Note that $\lambda(r) = \lambda(\xi_1)$, and hence, by (3),

$$\int_X dy\, p(x_k,y,\lambda(r)) p(y,z_1,\lambda(\xi_1)) = p(x_k,z_1,\lambda(\xi_1))\ .$$

Replacing in (6) $\int_X dy\, p(x_k,y,\lambda(r)) p(y,z_1,\lambda(\xi_1))$ with $p(x_k,z_1,\lambda(\xi_1))$, we obtain that the right hand side of (6) equals $\tilde{p}_\lambda(s,x,t,z)$ by definition. ☐

Introduce the notation:

$$\mathcal{L}_{step} = \{\lambda(\,\cdot\,) = \lambda(t_0) + \sum_{i=1}^{n} \lambda(t_i)\, \mathbb{I}_{(t_{i-1},t_i]}(\,\cdot\,)\}$$

the space of all step functions of the form (4) corresponding to different partitions $\mathcal{P} = \{0 = t_0 < \cdots < t_n = T\}$.

Lemma 2. *Let $\lambda \in \mathcal{L}_{step}$, and let the transition density function is given by (5). Then, finite dimensional distributions of the measure $\mathbb{L}_\lambda$ are given by*

$$\int_\Omega f(\omega(t_{i_1}), \ldots, \omega(t_{i_k})))\, \mathbb{L}_\lambda(d\omega) = \int_X dx\, q_{\lambda(t_0)}(x) \int_X dx_1\, p(x, x_1, \lambda(t_1)) \ldots \int_X dx_n\, p(x_{n-1}, x_n, \lambda(t_n))\, f(x_{i_1}, \cdots, x_{i_k})$$

where $f : X^k \to \mathbb{R}$ is Lebesgue-measurable.

Proof. The proof follows immediately from the definition of the measure $\mathbb{L}_\lambda$, and from Lemma 1. □

2 Jarzynski's identity

We define the work W_λ performed on the system by

$$W_\lambda : \mathrm{C}([0,T], X) \to \mathbb{R}, \quad W_\lambda(\omega) = \int_0^T \Big\langle \frac{\partial \mathcal{H}(\Gamma_t(\omega), \lambda(t))}{\partial \overline{\lambda}}\,,\, d\lambda(t) \Big\rangle \tag{7}$$

where $\langle\ ,\ \rangle$ is the scalar product in $\mathbb{R}^l \supset \Lambda$, and the integral at the right hand side is the Lebesgue-Stieltjes integral, i.e. the sum of the Lebesgue-Stieltjes integrals (here $(\lambda^1(t), \ldots, \lambda^l(t)) = \lambda(t)$):

$$\sum_{i=1}^{l} \int_0^T \frac{\partial \mathcal{H}(\Gamma_t(\omega), \lambda(t))}{\partial \lambda^i}\, d\lambda^i(t)\ .$$

In the following, we skip the sign of the scalar product in (7), and simply write

$$W_\lambda(\omega) = \int_0^T \frac{\partial \mathcal{H}(\Gamma_t(\omega), \lambda(t))}{\partial \overline{\lambda}}\, d\lambda(t)\ .$$

Let $F_\lambda = -\frac{1}{\beta} \ln Z_\lambda$ (free energy of the system), and let $\Delta F = F_{\lambda(T)} - F_{\lambda(0)}$ be the free energy difference. Let $\mathbb{E}_{\mathbb{L}_\lambda}$ denote the expectation relative to the measure $\mathbb{L}_\lambda$.

Theorem 1 (Jarzynski). *Let the family of distributions* $\mathfrak{L} = \{\mathbb{L}_\lambda, \lambda \in V[0,T]\}$ *with transition density functions* $p_\lambda \in \mathfrak{P}$ *satisfy the following assumptions:*

1. *If* $\lambda \in V[0,T]$ *is constant on* $(\xi,\tau) \subset [0,T]$ *and equals* $\overline{\lambda}$*, then, on* (ξ,τ)*,* p_λ *is given by* (1) *where* $p(\,\cdot\,,\,\cdot\,,\,\cdot\,)$ *satisfies* (2) *and* (3)*;*
2. *If* $\lambda \in \mathcal{L}_{step}$*, then* p_λ *is given by* (5)*;*
3. *If* $\lambda_n \to \lambda$ *uniformly on* $[0,T]$*, then* $\mathbb{L}_{\lambda_n} \to \mathbb{L}_\lambda$ *weakly;*
4. *The partial derivative* $\frac{\partial \mathcal{H}}{\partial \overline{\lambda}}(x,\overline{\lambda})$ *is continuous in* $(x,\overline{\lambda})$*, and there exists a continuous function* $\psi : \Lambda \to \mathbb{R}$ *such that*

$$\min_i \inf_{x\in X} \frac{\partial \mathcal{H}(x,\overline{\lambda})}{\partial \lambda^i} > \psi(\overline{\lambda}). \tag{8}$$

Then, $e^{-\beta W_\lambda}$ *is* $\mathbb{L}_\lambda$*-integrable, and for all* $\lambda \in V[0,T]$

$$\mathbb{E}_{\mathbb{L}_\lambda}[e^{-\beta W_\lambda}] = e^{-\beta \Delta F}.$$

Lemma 3. *Let* $\lambda(t) \in V[0,T]$ *be a jump function, i.e. a function of the form*

$$\lambda(t) = \sum_{t_n < t} h_n$$

where $h_n = \lambda(t_n + 0) - \lambda(t_n)$ *are jumps at the points* $t_0, t_1, \ldots, t_n, \ldots,$ *and* $\sum_n |h_n| < \infty$*. Further, let us assume that the partial derivative* $\frac{\partial \mathcal{H}}{\partial \overline{\lambda}}(x,\overline{\lambda})$ *is a continuous function* $X \times \Lambda \to \mathbb{R}^l$*. Then,*

$$W_\lambda(\omega) = \sum_n \big(\mathcal{H}(\omega(t_n), \lambda(t_n+0)) - \mathcal{H}(\omega(t_n), \lambda(t_n))\big)\ . \tag{9}$$

If, moreover, the set of jump points $\{0 = t_0 < t_1 < \cdots < t_n = T\}$ *is finite, then*

$$W_\lambda(\omega) = \sum_{i=0}^{n-1} \big(\mathcal{H}(\omega(t_i), \lambda(t_{i+1})) - \mathcal{H}(\omega(t_i), \lambda(t_i))\big)\ .$$

Proof. We have

$$\int_0^T \frac{\partial \mathcal{H}(\omega(t),\lambda(t))}{\partial \overline{\lambda}}\, d\lambda(t) = \sum_i \int_{\{t_i\}} \frac{\partial \mathcal{H}(\omega(t),\lambda(t))}{\partial \overline{\lambda}}\, d\lambda(t)\ . \tag{10}$$

Further,

$$\int\limits_{\{t_i\}} \frac{\partial \mathcal{H}(\omega(t),\lambda(t))}{\partial \overline{\lambda}}\, d\lambda(t) = \lim_{\varepsilon\to 0}\int_{t_i}^{t_i+\varepsilon} \frac{\partial \mathcal{H}(\omega(t),\lambda(t))}{\partial \overline{\lambda}}\, d\lambda(t)$$
$$= \lim_{\varepsilon\to 0}\Big(\int_{t_i}^{t_i+\varepsilon} \frac{\partial \mathcal{H}(\omega(t_i),\lambda(t))}{\partial \overline{\lambda}}\, d\lambda(t) + R(\omega,t_i,\varepsilon)\Big) \tag{11}$$

where

$$R(\omega,t_i,\varepsilon) = \int_{t_i}^{t_i+\varepsilon}\Big(\frac{\partial \mathcal{H}(\omega(t),\lambda(t))}{\partial \overline{\lambda}} - \frac{\partial \mathcal{H}(\omega(t_i),\lambda(t))}{\partial \overline{\lambda}}\Big)\, d\lambda(t) \to 0 \quad \text{as } \varepsilon\to 0, \tag{12}$$

where the convergence holds by continuity of ω on $[0,T]$, and by uniform continuity of $\frac{\partial\mathcal{H}}{\partial\overline{\lambda}}(x,\overline{\lambda})$ on the compact $\omega[0,T]\times\overline{\lambda[0,T]}$ (the bar over $\lambda[0,T]$ denotes its closure). Further, taking into account that $\mathcal{H}(\omega(t_i),\lambda(t))$ is a function of bounded variation in t, we obtain

$$\int_{t_i}^{t_i+\varepsilon} \frac{\partial \mathcal{H}(\omega(t_i),\lambda(t))}{\partial \overline{\lambda}}\, d\lambda(t) = \int_{t_i}^{t_i+\varepsilon} d\mathcal{H}(\omega(t_i),\lambda(t))$$
$$= \mathcal{H}(\omega(t_i),\lambda(t_i+\varepsilon)) - \mathcal{H}(\omega(t_i),\lambda(t_i))\ .$$

Passing in this equality to the limit as $\varepsilon\to 0$, and taking into consideration (11) and (12), we obtain

$$\int\limits_{\{t_i\}} \frac{\partial \mathcal{H}(\omega(t),\lambda(t))}{\partial \overline{\lambda}}\, d\lambda(t) = \mathcal{H}(\omega(t_i),\lambda(t_i+0)) - \mathcal{H}(\omega(t_i),\lambda(t_i))\ .$$

This together with identity (10) completes the proof of the lemma. □

Proof of Theorem 1. First we consider the case when $\lambda\in\mathcal{L}_{step}$. By Lemma 3,

$$W_\lambda(\omega) = \sum_{i=0}^{n-1}\Big(\mathcal{H}(\omega(t_i),\lambda(t_{i+1})) - \mathcal{H}(\omega(t_i),\lambda(t_i))\Big).$$

Without loss of generality, we can consider $t_0 = 0$, $t_n = T$, adding these points with zero jumps if necessary. Thus, $W_\lambda(\omega)$ is a cylinder function, i.e.

a function that depends on ω only at a finite number of points. By Lemma 2, we obtain:

$$\begin{aligned}
\mathbb{E}_{\mathbb{L}_\lambda}[e^{-\beta W_\lambda}] &= \int_{C([0,T],X)} e^{-\beta \sum_{i=0}^{n-1} (\mathcal{H}(\omega(t_i),\lambda(t_{i+1}))-\mathcal{H}(\omega(t_i),\lambda(t_i)))}\, \mathbb{L}_\lambda(d\omega) \\
&= \int_X dx_0\, q_{\lambda(t_0)}(x_0) \int_X dx_1\, p(x_0, x_1, \lambda(t_1)) \cdots \\
&\quad \int_X dx_{n-1} p(x_{n-2}, x_{n-1}, \lambda(t_{n-1})) \frac{e^{-\beta\mathcal{H}(x_{n-1},\lambda(t_n))}}{e^{-\beta\mathcal{H}(x_0,\lambda(t_0))}} \prod_{i=0}^{n-1} \frac{e^{-\beta\mathcal{H}(x_{i-1},\lambda(t_i))}}{e^{-\beta\mathcal{H}(x_i,\lambda(t_i))}} \ .
\end{aligned} \tag{13}$$

Note that (2) implies

$$\int_X \frac{e^{-\beta\mathcal{H}(x,\overline{\lambda})}}{e^{-\beta\mathcal{H}(y,\overline{\lambda})}}\, p(x, y, \overline{\lambda})\, dx = 1 \ . \tag{14}$$

Changing the order of integration in (13) gives:

$$\begin{aligned}
\mathbb{E}_{\mathbb{L}_\lambda}[e^{-\beta W_\lambda}] = &\int_X e^{-\beta\mathcal{H}(x_{n-1},\lambda(t_n))}\, dx_{n-1} \\
&\int_X \frac{e^{-\beta\mathcal{H}(x_{n-2},\lambda(t_{n-1}))}}{e^{-\beta\mathcal{H}(x_{n-1},\lambda(t_{n-1}))}}\, p(x_{n-2}, x_{n-1}, \lambda(t_{n-1}))\, dx_{n-2} \\
&\cdots \\
&\int_X \frac{e^{-\beta\mathcal{H}(x_1,\lambda(t_2))}}{e^{-\beta\mathcal{H}(x_2,\lambda(t_2))}}\, p(x_1, x_2, \lambda(t_2))\, dx_1 \\
&\int_X \frac{e^{-\beta\mathcal{H}(x_0,\lambda(t_1))}}{e^{-\beta\mathcal{H}(x_1,\lambda(t_1))}}\, p(x_0, x_1, \lambda(t_1))\, dx_0\, \frac{1}{Z_{\lambda(t_0)}} \ .
\end{aligned} \tag{15}$$

Thus, (14) implies:

$$\mathbb{E}_{\mathbb{L}_\lambda}[e^{-\beta W_\lambda}] = \frac{Z_{\lambda(T)}}{Z_{\lambda(0)}} \ ,$$

and we have proved the theorem for $\lambda \in \mathcal{L}_{step}$.

Now let $\lambda \in V[0,T]$ be arbitrary. We can construct a sequence of step functions $\lambda_n \in \mathcal{L}_{step}$ converging uniformly to λ on $[0,T]$, and such that $V_0^T[\lambda_n] < V_0^T[\lambda_C] + V_0^T[\lambda_J]$, where $\lambda(t) = \lambda_C(t) + \lambda_J(t)$ is the Lebesgue decomposition of $\lambda(t)$ into the sum of a continuous function $\lambda_C(t)$ and a jump function $\lambda_J(t) = \sum_{t_k<t} h_k$ with $\sum_k |h_k| < \infty$, and V_0^T denotes variation on $[0,T]$. Obviously, both functions λ_C and λ_J can be uniformly approximated by step functions $(\lambda_C)_n \in \mathcal{L}_{step}$ and $(\lambda_J)_n \in \mathcal{L}_{step}$ so that $V_0^T[(\lambda_C)_n] < V_0^T[\lambda_C]$ and $V_0^T[(\lambda_J)_n] < V_0^T[\lambda_J]$.

Consider functions

$$\varphi_n(\omega) = e^{-\beta \int_0^T \frac{\partial \mathcal{H}(\omega(t),\lambda_n(t))}{\partial \overline{\lambda}}\, d\lambda_n(t)}.$$

Since $\lambda_n(t)$ are step functions, then, by what was proved,

$$\int_\Omega \varphi_n(\omega)\, \mathbb{L}_{\lambda_n}(d\omega) = \frac{Z_{\lambda(T)}}{Z_{\lambda(0)}} \quad \text{for all } n. \tag{16}$$

We show existence of the following limit for each fixed $\omega \in \Omega$:

$$\lim_{n\to\infty} \varphi_n(\omega) = e^{-\beta \int_0^T \frac{\partial \mathcal{H}(\omega(t),\lambda(t))}{\partial \overline{\lambda}}\, d\lambda(t)} = e^{-\beta W_\lambda(\omega)}. \tag{17}$$

We have

$$\begin{aligned}\int_0^T \frac{\partial \mathcal{H}(\omega(t),\lambda_n(t))}{\partial \overline{\lambda}}\, d\lambda_n(t) = {}& \int_0^T \frac{\partial \mathcal{H}(\omega(t),\lambda(t))}{\partial \overline{\lambda}}\, d\lambda(t) \\ &+ \int_0^T \frac{\partial \mathcal{H}(\omega(t),\lambda(t))}{\partial \overline{\lambda}}\, d\big(\lambda_n(t) - \lambda(t)\big) \\ &+ \int_0^T \Big(\frac{\partial \mathcal{H}(\omega(t),\lambda_n(t))}{\partial \overline{\lambda}} - \frac{\partial \mathcal{H}(\omega(t),\lambda(t))}{\partial \overline{\lambda}}\Big)\, d\lambda_n(t).\end{aligned} \tag{18}$$

Note that, since $\lambda(t)$ is of bounded variation, the set $\lambda[0,T] \subset \mathbb{R}^l$ is bounded. Due to continuity of $\frac{\partial \mathcal{H}}{\partial \overline{\lambda}}(x,\overline{\lambda})$ in $(x,\overline{\lambda})$, $\frac{\partial \mathcal{H}}{\partial \overline{\lambda}}(x,\overline{\lambda})$ is bounded and uniformly continuous on $\omega[0,T] \times \overline{\lambda[0,T]}$. Hence, for an arbitrary $\varepsilon > 0$, and for sufficiently large n,

$$\Big|\frac{\partial \mathcal{H}(\omega(t),\lambda_n(t))}{\partial \overline{\lambda}} - \frac{\partial \mathcal{H}(\omega(t),\lambda(t))}{\partial \overline{\lambda}}\Big| < \varepsilon$$

for all $t \in [0,T]$, and subsequently, for the third term on the right hand side of (18) the following estimate holds:

$$\Big|\int_0^T \Big(\frac{\partial \mathcal{H}(\omega(t),\lambda_n(t))}{\partial \overline{\lambda}} - \frac{\partial \mathcal{H}(\omega(t),\lambda(t))}{\partial \overline{\lambda}}\Big)\, d\lambda_n(t)\Big| < \varepsilon \left(V_0^T[\lambda_C] + V_0^T[\lambda_J]\right).$$

Since by assumption, $\frac{\partial\mathcal{H}}{\partial\overline{\lambda}}(x,\lambda)$ is continuous in (x,λ), one can find a uniform approximation of the function $\frac{\partial\mathcal{H}}{\partial\overline{\lambda}}(\omega(\,\cdot\,),\lambda(\,\cdot\,)) : [0,T] \to \mathbb{R}^l$ by step functions.[1] Thus, we can apply Helly's first theorem to the second term on the right hand side of (18), and conclude that it converges to zero as $n \to \infty$. Finally, we obtain that for each fixed $\omega \in \Omega$,

$$\int_0^T \frac{\partial\mathcal{H}(\omega(t),\lambda_n(t))}{\partial\overline{\lambda}}\, d\lambda_n(t) \to \int_0^T \frac{\partial\mathcal{H}(\omega(t),\lambda(t))}{\partial\overline{\lambda}}\, d\lambda(t) \quad \text{as} \quad n \to \infty\,. \tag{19}$$

Obviously, (19) implies (17). By Assumption 4 of the theorem, there exists a constant $M > 0$ such that

$$\min_i \frac{\partial\mathcal{H}(x,\lambda_n(t))}{\partial\lambda^i} > -M \quad \text{and} \quad \min_i \frac{\partial\mathcal{H}(x,\lambda(t))}{\partial\lambda^i} > -M$$

for all $x \in X$, for all $t \in [0,T]$, for all n. This implies

$$e^{-\beta\int_0^T \frac{\partial\mathcal{H}(\omega(t),\lambda(t))}{\partial\overline{\lambda}}\, d\lambda(t)} < e^{\beta\, M\, V_0^T[\lambda]},\ e^{-\beta\int_0^T \frac{\partial\mathcal{H}(\omega(t),\lambda_n(t))}{\partial\overline{\lambda}}\, d\lambda_n(t)} < e^{\beta\, M\, (V_0^T[\lambda_C]+V_0^T[\lambda_J])}. \tag{20}$$

The weak convergence $\mathbb{L}_{\lambda_n} \Rightarrow \mathbb{L}_\lambda$ implies tightness of the system $\{\mathbb{L}_{\lambda_n},\mathbb{L}_\lambda\}$ by Prokhorov's theorem. Uniform boundedness of the system of functions $\{\varphi_n, e^{-\beta W_\lambda}\}$ provided by inequalities (20), implies tightness of $\{\varphi_n\,\mathbb{L}_{\lambda_n}, e^{-\beta W_\lambda}\mathbb{L}_\lambda\}$. We show weak convergence $\varphi_n\,\mathbb{L}_{\lambda_n} \Rightarrow e^{-\beta W_\lambda}\mathbb{L}_\lambda$. Fix an arbitrary small $\sigma > 0$ and find a compact $K_\sigma \subset \Omega$ such that

$$\int_{K_\sigma} e^{-\beta\, W_\lambda(\omega)}\mathbb{L}_\lambda(d\omega) > 1-\sigma \quad \text{and} \quad \int_{K_\sigma} \varphi_n(\omega)\,\mathbb{L}_{\lambda_n}(d\omega) > 1-\sigma \quad \text{for all } n. \tag{21}$$

We show that the pointwise convergence (17) is uniform on K_σ. Since convergence (17) holds for all points of an arbitrary small finite δ-net of K_σ, it suffices to prove that the family $\{\varphi_n(\omega), e^{-\beta\, W_\lambda(\omega)}\}$ is equicontinuous on K_σ, i.e. that for an $\varepsilon > 0$, there exists a $\delta > 0$ such that $|\varphi_n(\omega_1) - \varphi_n(\omega_2)| < \varepsilon$ for all n and $|e^{-\beta\, W_\lambda(\omega_1)} - e^{-\beta\, W_\lambda(\omega_2)}| < \varepsilon$ whenever $\|\omega_1 - \omega_2\| < \delta$. By Arzelá-Ascoli's theorem, functions $\omega \in K_\sigma$ are uniformly bounded. This implies that $\cup_{t\in[0,T]}\pi_t(K_\sigma) \subset X$ is bounded. Here $\pi_t : \mathrm{C}([0,T],X) \to X, \omega \mapsto \omega(t)$ is the

[1] The function $\frac{\partial\mathcal{H}}{\partial\overline{\lambda}}(\omega(\,\cdot\,),\lambda(\,\cdot\,)) : [0,T] \to \mathbb{R}^l$ is not necessarily continuous since we do not assume that $\lambda : [0,T] \to \mathbb{R}^l$ is continuous. However, we can find a uniform approximation of $\lambda : [0,T] \to \mathbb{R}^l$ by step functions, and hence, we can find a uniform approximation of $\frac{\partial\mathcal{H}}{\partial\overline{\lambda}}(\omega(\,\cdot\,),\lambda(\,\cdot\,)) : [0,T] \to \mathbb{R}^l$ by step functions. Helly's first theorem applied below, holds for any measurable function that can be uniformly approximated by step functions.

evaluation mapping. By uniform convergence $\lambda_n \rightrightarrows \lambda$, one can find a compact $K \subset \Lambda$ such that $\lambda_n[0,T] \subset K$ for all n, and $\lambda[0,T] \subset K$. $\frac{\partial \mathcal{H}}{\partial \overline{\lambda}}(\,\cdot\,,\,\cdot\,)$ is uniformly continuous on $\cup_{t\in[0,T]}\pi_t(K_\sigma) \times K$. We have:

$$\int_0^T \Big(\frac{\partial \mathcal{H}(\omega_1(t), \lambda_n(t))}{\partial \overline{\lambda}} - \frac{\partial \mathcal{H}(\omega_2(t), \lambda_n(t))}{\partial \overline{\lambda}} \Big)\, d\lambda_n(t)$$
$$< \sup_{\substack{t\in[0,T],\\ \overline{\lambda}\in K}} \Big| \frac{\partial \mathcal{H}(\omega_1(t), \overline{\lambda})}{\partial \overline{\lambda}} - \frac{\partial \mathcal{H}(\omega_2(t), \overline{\lambda})}{\partial \overline{\lambda}} \Big| \, (V_0^T[\lambda_C] + V_0^T[\lambda_J])\ .$$

Thus, uniform continuity of $\frac{\partial \mathcal{H}}{\partial \overline{\lambda}}(\,\cdot\,,\,\cdot\,)$ on $\cup_{t\in[0,T]}\pi_t(K_\sigma) \times K$ implies equicontinuity of $\varphi_n(\omega)$ on K_σ. Continuity (and hence unform continuity) of $e^{-\beta\, W_\lambda}$ on K_σ follows immediately using the same argument. Thus, we have shown that convergence (17) is uniform on K_σ. Finally, we obtain the weak convergence $\varphi_n\, \mathbb{L}_{\lambda_n} \Rightarrow e^{-\beta\, W_\lambda}\, \mathbb{L}_\lambda$:

$$\int_\Omega f(\omega)\, \varphi_n(\omega)\, \mathbb{L}_{\lambda_n}(d\omega) - \int_\Omega f(\omega)\, e^{-\beta\, W_\lambda(\omega)}\, \mathbb{L}_\lambda(d\omega)$$
$$= \int_{K_\sigma} f(\omega)(\varphi_n(\omega) - e^{-\beta\, W_\lambda(\omega)})\, \mathbb{L}_\lambda(d\omega) \tag{22}$$
$$+ \Big(\int_{K_\sigma} f(\omega)\, e^{-\beta W_\lambda(\omega)}\, \mathbb{L}_{\lambda_n}(d\omega) - \int_{K_\sigma} f(\omega)\, e^{-\beta W_\lambda(\omega)}\, \mathbb{L}_\lambda(d\omega) \Big) \tag{23}$$
$$+ \int_{\Omega\setminus K_\sigma} f(\omega)\, \varphi_n(\omega)\, \mathbb{L}_{\lambda_n}(d\omega) + \int_{\Omega\setminus K_\sigma} f(\omega)\, e^{-\beta W_\lambda(\omega)}\, \mathbb{L}_\lambda(d\omega)\ , \tag{24}$$

where $f : \Omega \to \mathbb{R}$ is bounded and continuous. Since φ_n converges to $e^{-\beta W_\lambda}$ uniformly on K_σ, the term (22) converges to zero. By assumption on weak convergence $\mathbb{L}_{\lambda_n} \Rightarrow \mathbb{L}_\lambda$, the term (23) also converges to zero. The rest two terms in (24) are small by (21). Hence, the relation

$$\mathbb{E}_{\mathbb{L}_\lambda}[e^{-\beta W_\lambda}] = \frac{Z_{\lambda(T)}}{Z_{\lambda(0)}} = e^{-\beta \Delta F}$$

holds for the measure $\mathbb{L}_\lambda$ and for the work W_λ with an arbitrary function $\lambda \in V[0,T]$. The theorem is proved. □

Corollary 1. *Let assumptions 1–4 of Theorem 1 be fulfilled, and let* $f:\ X \to \mathbb{R}$ *be bounded and continuous. Then,*

$$\mathbb{E}_{\mathbb{L}_\lambda}[(f \circ \pi_T)\, e^{-\beta\, W_\lambda}] = \mathbb{E}_T[f]\; \mathbb{E}_{\mathbb{L}_\lambda}[e^{-\beta\, W_\lambda}] \tag{25}$$

where $\pi_t : \mathrm{C}([0,T], X) \to X, \pi_t(\omega) = \omega(t)$ *is the evaluation mapping,* $\mathbb{E}_T$ *is the expectation relative to the measure* $\frac{1}{Z_{\lambda(T)}}\, e^{-\beta\, \mathcal{H}(x,\lambda(T))} dx$.

Proof. We just have to prove (25) for $\lambda \in \mathcal{L}_{step}$. If we assume that (25) holds for each step function $\lambda_n \in \mathcal{L}_{step}$, where $\lambda_n \rightrightarrows \lambda$ on $[0,T]$, then the weak convergence $\varphi_n \mathbb{L}_{\lambda_n} \Rightarrow e^{-\beta W_\lambda} \mathbb{L}_\lambda$ and Theorem 1 imply (25) for all $\lambda \in V[0,T]$.

Assuming that $\lambda \in \mathcal{L}_{step}$, we repeat the argument of (13) and (15), while using relation (14). Specifically, we obtain:

$$
\begin{aligned}
&\mathbb{E}_{\mathbb{L}_\lambda}[(f \circ \pi_T)\, e^{-\beta W_\lambda}] \\
&= \int\limits_X \frac{e^{-\beta \mathcal{H}(x_n,\lambda(t_n))}}{Z_{\lambda(t_n)}} f(x_n)\, dx_n \int\limits_X \frac{e^{-\beta \mathcal{H}(x_{n-1},\lambda(t_n))}}{e^{-\beta \mathcal{H}(x_n,\lambda(t_n))}}\, p(x_{n-1}, x_n, \lambda(t_n))\, dx_{n-1} \\
&\quad \dots \\
&\quad \int\limits_X \frac{e^{-\beta \mathcal{H}(x_0,\lambda(t_1))}}{e^{-\beta \mathcal{H}(x_1,\lambda(t_1))}}\, p(x_0, x_1, \lambda(t_1))\, dx_0\, \frac{Z_{\lambda(t_n)}}{Z_{\lambda(t_0)}} = \mathbb{E}_T[f]\, \frac{Z_{\lambda(t_n)}}{Z_{\lambda(t_0)}} \\
&= \mathbb{E}_T[f]\, \mathbb{E}_{\mathbb{L}_\lambda}[e^{-\beta W_\lambda}]\ .
\end{aligned}
$$

□

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References

[1] *C. Jarzynski*, Nonequilibrium equality for free energy differences, Phys Rev Lett (78): 2690, 1997.

[2] *C. Jarzynski*, Equilibrium free-energy differences from nonequilibrium measurements: A master-equation approach, Physical Review E 56, pp. 5018-5035, 1997.

[3] *C. Jarzynski*, Targeted free energy perturbation, Physical Review E, 2002

[4] *G. E. Crooks*, Path-ensemble averages in systems driven far from equilibrium, Physical review E 61, pp 2361-2366, 2000

[5] *G. E. Crooks*, Nonequilibrium Measurements of Free Energy. Differences for Microscopically Reversible Markovian Systems. Journal of Statistical Physics, Vol. 90, Nos 5/6, 1998.

[6] *G. E. Crooks*, Entropy production fluctuation theorem and the nonequilibrium work relation for free energy differences, Physical Review E, 60, pp. 2721-2726, 1999.

[7] *E. Schöll-Paschinger, C. Dellago*, A proof of Jarzynski's non-equilibrium work theorem for dynamical systems that conserve the canonical distribution, J. Chem. Phys. 125, 2006.

[8] *W. Lechner, H. Oberhofer, C. Dellago, and P. L. Geissler*, Equilibrium free energies from fast-switching simulations with larg time steps, Journal of Chemical Physics 124, 044113 (2006)

[9] *Hummer G, Szabo A.*, Free energy surfaces from single-molecule force spectroscopy. Acc Chem Res (38): 504-13, 2005.

[10] *M.A. Cuendet*, Statistical Mechanical Derivation of Jarzynski's Identity for Thermostated Non-Hamiltonian Dynamics, Physical review letters 96, 120602-4, 2006

[11] *M.A. Cuendet*, The Jarzynski identity derived from general Hamiltonian or non-Hamiltonian dynamics reproducing NVT or NPT ensembles, Journal Of Chemical Physics 125, 144109, 2006