Entropy Production in Small Systems

A study of the Jarzynski equality

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Outline

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1. The Jarzynski Equality
2. Systems with Feedback Control
3. Non-isothermal Systems
4. Summary

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The Jarzynski Equality

- $\phi(x, \lambda(t))$ - conservative potential, x - position, $\lambda(t)$ - time dependent protocol. Work done from $t = 0$ to $t = \tau$:

$$\Delta W = \int_0^\tau \frac{\partial \phi(x, \lambda(t))}{\partial \lambda} \frac{d\lambda(t)}{dt} dt \tag{1}$$

- $\beta = 1/k_B T$, k_B - Boltzmann's constant, T - constant environment temperature, ΔF - change in Helmholtz free energy. Jarzynski equality:

$$\left\langle e^{-\beta \Delta W} \right\rangle = e^{-\beta \Delta F} \tag{2}$$

- From Jensen's inequality $\langle \exp(z) \rangle \geq \exp \langle z \rangle$:

$$\langle \Delta W \rangle \geq \Delta F \tag{3}$$

c.f. $\Delta W \geq \Delta F$.

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The System of Interest

- $\phi(x, \lambda(t)) = \phi(x, \kappa(t)) = \frac{1}{2}\kappa(t)x^2$. Overdamped Langevin equation:

$$\dot{x} = \frac{\kappa(t)}{m\gamma}x + \left(\frac{2k_B T}{m\gamma}\right)^{1/2}\xi(t) \tag{4}$$

  $\kappa(t)$ - spring constant, γ - friction coefficient, m - particle mass, $\xi(t)$ - gaussian white noise: $\langle\xi(t)\rangle = 0$ and $\langle\xi(t)\xi(t')\rangle = \delta(t - t')$.

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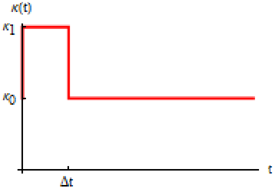

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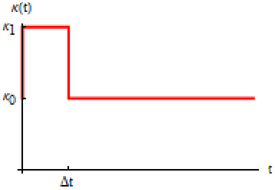

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Modelling the System

- Dimensionless variables:

$$t' = \gamma t \qquad x' = \left(\frac{\kappa_0}{k_B T}\right)^{1/2} x \qquad \xi'(t) = \gamma^{-1/2}\xi(t) \tag{5}$$

- $x_{n+1} = x(t + \Delta t)$, $x_n = x(t)$, small timestep Δt. Finite difference update:

$$x_{n+1} = (1 - \alpha(t)\,\Delta t)\,x_n + \sqrt{2\alpha_0\,\Delta t}\,N_t^{t+\Delta t}(0,1) \tag{6}$$

where $\alpha_i = \kappa_i / m\gamma^2$, $N_t^{t+\Delta t}(0,1)$ - unit normal random variable.

- Perform step-up/step-down process for N cycles. Measure dimensionless work values $\Delta W_i' = \Delta W_i / k_B T$ for each cycle $i = 1, \ldots, N$. Find average:

$$\left\langle e^{-\Delta W'} \right\rangle = \frac{1}{N}\sum_{i=1}^{N} e^{-\Delta W_i'} \tag{7}$$

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Measurement and Feedback

- Maxwell's demon - takes measurement, applies feedback to system based on measurement so as to reduce entropy.
- Systems with feedback control - converts information into energy.
- Applied to our system:
- Landauer's principle - entropy increase associated with information erasure.

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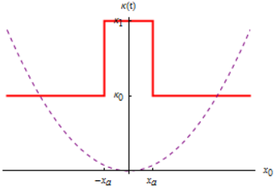

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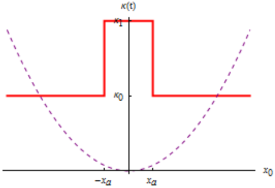

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Generalization of the Jarzynski Equality

- Jarzynski-Sagawa-Ueda equality:

$$\left\langle e^{-\beta(\Delta W+\Delta F)} \right\rangle = \gamma_E \quad (8)$$

- Efficacy parameter, zero error in measurement:

$$\gamma_E = \operatorname{erf}\left(\sqrt{\frac{\kappa_1}{2k_BT}}x_a\right) - \operatorname{erf}\left(\sqrt{\frac{\kappa_0}{2k_BT}}x_a\right) + 1 \quad (9)$$

- Optimal range, zero error in measurement:

$$x_a^2 = \frac{k_BT}{\kappa_1 - \kappa_0}\ln\left(\frac{\kappa_1}{\kappa_0}\right) \quad (10)$$

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Results

α_1	Average	γ_E
1.01	1.0017 ± 0.0001	1.0018
1.05	1.0086 ± 0.0008	1.0087
1.10	1.0169 ± 0.0015	1.0171
1.20	1.0336 ± 0.0036	1.0332
1.40	1.0614 ± 0.0077	1.0630
1.75	1.1096 ± 0.0160	1.1087
2.00	1.1410 ± 0.0270	1.1376
4.00	1.2639 ± 0.0878	1.2998
6.00	1.2937 ± 0.0870	1.3964

Table : Results for numerical test of the Jarzynski-Sagawa-Ueda equality, with $\alpha_0 = 1.0$, $\Delta t = 10^{-5}$, and $N = 10^3$.

Optimal Change in Spring Constant

- For maximising γ_E, optimal protocol - step change to κ_1. Optimal value of κ_1 to change to?
- For position x_0 at start of cycle, optimal change: $\kappa_1(x_0) \propto 1/x_0^2$. Problems - divergent.
- Use features of optimal solution:
- For zero error in measurement:

$$\gamma_E = \text{erf}\left(\sqrt{\frac{\kappa_u}{2k_BT}}x_a\right) - \text{erf}\left(\sqrt{\frac{\kappa_0}{2k_BT}}x_a\right) + \text{erf}\left(\sqrt{\frac{\kappa_0}{2k_BT}}x_b\right) - \text{erf}\left(\sqrt{\frac{\kappa_l}{2k_BT}}x_b\right) + 1 \quad (11)$$

- Optimal ranges, zero error in measurement:

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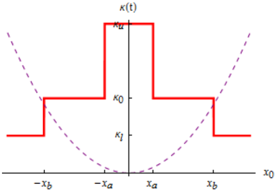

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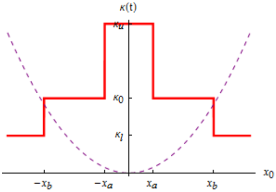

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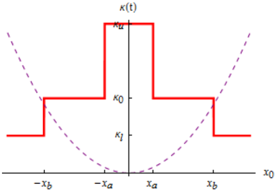

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Results

α_u	Average	γ_E
1.01	1.047 ± 0.007	1.056
1.05	1.054 ± 0.003	1.066
1.10	1.065 ± 0.005	1.077
1.20	1.084 ± 0.006	1.098
1.40	1.117 ± 0.010	1.135
1.75	1.174 ± 0.023	1.188
2.00	1.198 ± 0.033	1.220
4.00	1.362 ± 0.221	1.377
6.00	1.388 ± 0.275	1.461

Table : Results for numerical test of the optical protocol of the Jarzynski-Sagawa-Ueda equality, with $\alpha_0 = 1.0$, $\alpha_I = 0.8$, $\Delta t = 10^{-5}$, and $N = 10^3$.

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Generalization of the Jarzynski Equality

- $$\dot{x} = -\frac{\kappa(t)}{m\gamma}x + \left(\frac{2k_B T(x)}{m\gamma}\right)^{1/2}\xi(t) \tag{13}$$
  where $T(x) = T_0\left(1 + \left(\kappa_T x^2/2k_B T_0\right)\right)$.
- The Jarzynski-Tsallis equality for cyclic step-up/step-down non-isothermal processes:
  $$\left\langle \exp_{q_+}\left(-\Delta W_{0\to 1}/k_B T_0\right)\exp_{q_-}\left(-\Delta W_{1\to 0}/k_B T_0\right)\right\rangle = 1 \tag{14}$$
  where $\Delta W_{0\to 1} = \frac{1}{2}\left(\kappa_1 - \kappa_0\right)x_0^2$, $\Delta W_{1\to 0} = \frac{1}{2}\left(\kappa_0 - \kappa_1\right)x_1^2$, and
  $$\exp_q(z) = \left(1 + (1-q)\,z\right)^{\frac{1}{1-q}} \tag{15}$$
  with $q_\pm = 1 \pm \kappa_T/\left(\kappa_1 - \kappa_0\right)$.
- Non-isothermal finite difference update with dimensionless variables:
  $$x_{n+1} = \left(1 - \alpha(t)\,\Delta t\right)x_n + \left[\left(2\alpha_0 + \alpha_T x_n^2\right)\Delta t\right]^{1/2} N_t^{t+\Delta t}(0,1) \tag{16}$$
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  where $\alpha_i = \kappa_i/m\gamma^2$.

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α_1	α_T	Average
1.01	1.005	1.0000 ± 0.0001
1.05	1.025	1.000 ± 0.0011
1.10	1.050	1.000 ± 0.0017
1.20	1.100	0.9996 ± 0.0021
1.40	1.200	1.0008 ± 0.0072
1.75	1.375	0.9963 ± 0.0122
2.00	1.000	1.0016 ± 0.0245
4.00	2.500	1.0019 ± 0.0852
6.00	3.500	1.0157 ± 0.1150

Table : Results for numerical test of the Jarzynski-Tsallis equality, with $\alpha_0 = 1.0$, $\Delta t = 10^{-5}$, and $N = 10^3$.

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- Jarzynski-Sagawa-Ueda equality.
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Outlook

- Optimal protocol - experimental work in department.
- Errors in measurement.
- Jarzynski-Tsallis equality - further confirmation.
- *Ponmurugan, M. Tsallis statistics generalization of non-equilibrium work relations. arXiv preprint arXiv:1110.5153 (2011).*
- Non-isothermal case - Tsallis statistics.
- More general non-isothermal processes.

Outlook

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