Fluctuating observation time ensembles and an analogous Jarzynski equality in the thermodynamics of trajectories

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Overview

- Thermodynamics of trajectories
  - *s*-ensemble
- Fluctuating observation time
  - *x*-ensemble
  - Relation to *s*-ensemble
- Transition path sampling
  - Efficiency of the *x*-ensemble
- Analogous Jarzynski equality

s-ensemble

- Considering stochastic processes described by master equations : $\partial_t \rho(t) = W[\rho(t)]$
  - Classical - $W \equiv \sum_{C' \neq C} A(C \to C')|C'\rangle\langle C| - \sum_C R(C)|C\rangle\langle C|$
  - Quantum - $W \equiv -i[H,\rho] + \sum_{i=1}^{N_L} L_i \rho L_i^\dagger - \frac{1}{2}\sum_{i=1}^{N_L}\{L_i^\dagger L_i, \rho\}$
- Observe time record of some event – eg photon emission from an atomic source
- Probability of observing K events has a large-deviation (LD) form in the long time limit :

$$P_\tau(K) \approx e^{-t\varphi(K/\tau)}$$

- Can obtain moment generating function :

$$Z_\tau(s) \equiv \sum_{K=0}^{\infty} P_\tau(K)\, e^{-sK} \approx e^{\tau\theta(s)}$$

- θ and φ related by a Legendre transform :

$$\theta(s) = -min_{K/\tau}[\varphi(K/\tau) + sK/\tau]$$

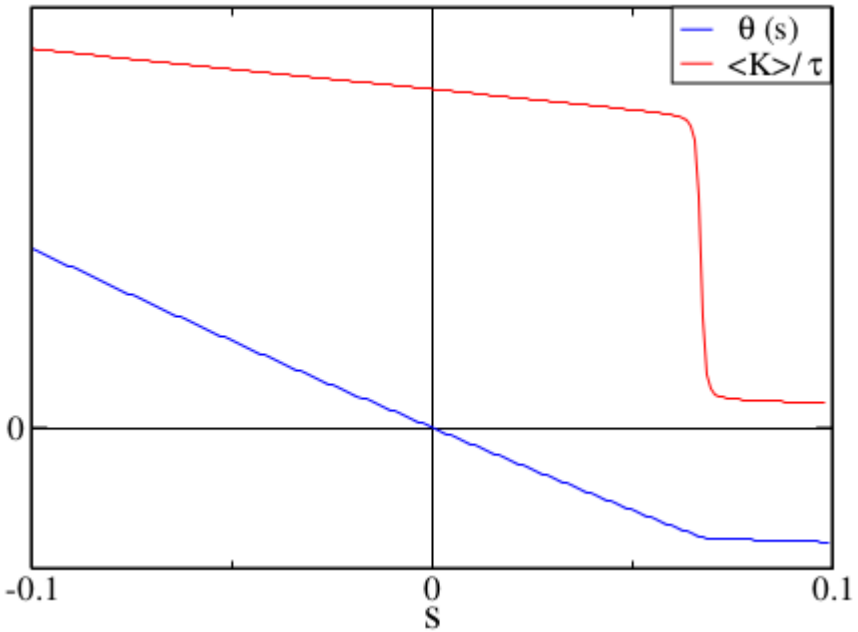
s-ensemble

- Can extract θ(*s*) directly from the largest eigenvalue of the *deformed* master operator, $\boldsymbol{W}_s$

$$W_s(\rho_s) = -i[H,\rho] + e^{-s} L_1 \rho L_1^\dagger + \sum_{i=2}^{N_L} L_i \rho L_i^\dagger - \frac{1}{2}\sum_{i=1}^{N_L} \{L_i^\dagger L_i, \rho\}$$

- *n*-th cumulant of the activity obtained from θ(*s*)

$$\frac{\langle\langle K^n \rangle\rangle}{\tau} = (-)^n \frac{\partial^n}{\partial s^n} \theta(s)\Big|_{s=0}$$



s defines an *ensemble of trajectories* with probability

$$P_s(\boldsymbol{X}_\tau) = \frac{e^{-sK} P(\boldsymbol{X}_\tau)}{Z_\tau(s)}$$

s-ensemble

- s-ensemble: Fixed time, fluctuating event numbers
  - “Grand Canonical Ensemble”
  - Time ~ “Volume”
  - K ~ “Particle Numbers”
  - $\varphi(K/\tau)$ ~ “Entropy density”
  - $\theta(s)$ ~ ”Free Energy”
  - s ~ “Chemical Potential”

x-ensemble

- As with thermodynamic ensembles, free to choose which quantities are fixed and which vary
- *x*-ensemble: fix event numbers, K, allow time to fluctuate
  - Probability that observing K events takes a time t:

$$P_K(t) \approx e^{-K\psi(\tau/K)}$$

  - Moment Generating Function

$$Z_t(s) \equiv \int_0^\infty d\tau P_K(t) e^{-x\tau} \approx e^{Kg(x)}$$

  - Again, ψ and g are related by a Legendre transformation:

$$g(x) = -min_{\tau/K}[\psi(\tau/K) + x\tau/K]$$

  - Can define a transfer matrix

$$\boldsymbol{T}_x \equiv \sum_{C' \neq C} \frac{A_s(C \to C')}{x + R(C)} |C'\rangle\langle C|$$

$$\boldsymbol{T}_x \equiv \sum_{i=1}^{N_L} L_i[(x + \boldsymbol{R})^{-1}(\rho)] L_i^\dagger \quad ; \quad \boldsymbol{R} \equiv iH_{eff}\rho - i\rho H_{eff}$$

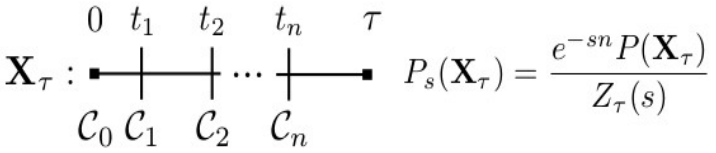
  - By relating $\mathbf{W}_s$ and $\mathbf{T}_x$, can show

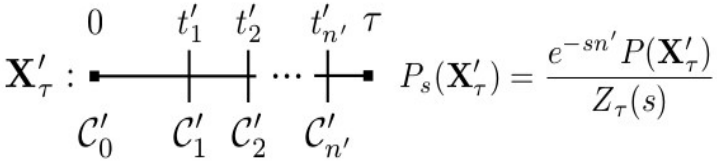
$$g(x) = \theta^{-1}(x) \qquad \theta(s) = g^{-1}(s)$$

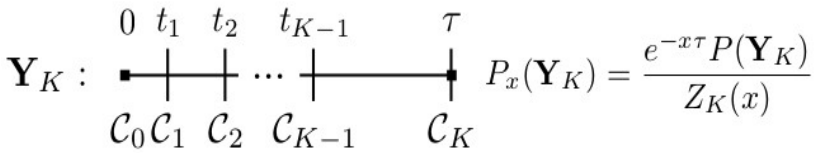
Generalised ensembles

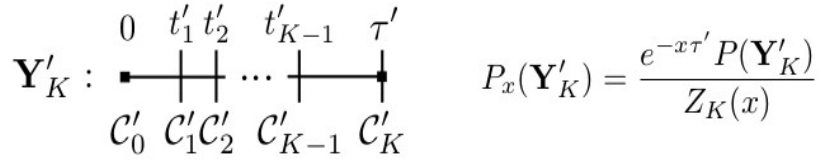
- s-ensemble: Fixed time, fluctuating event numbers
  - “Grand Canonical Ensemble”
  - Time ~ “Volume”
    - fixed
  - K ~ “Particle Numbers”
    - fluctuates
  - φ(K/τ) ~ “Entropy density”
  - θ(s) ~ ”Free Energy”
  - s ~ “Chemical Potential”

- *x*-ensemble: Fixed event numbers, fluctuating time
  - “Isobaric-isothermal Ensemble”
  - Time
    - fluctuates
  - K
    - fixed
  - Ψ(τ/K)
  - g*(x)* - “Grand Potential”
  - *x* ~ “Pressure”









Transition path sampling (TPS)

- Motivation :
  - Efficiently generate 'rare' events
  - Well suited to the *s*/*x*-ensemble description
- TPS is a Metropolis-Hastings algorithm applied to trajectories rather than static configurations
- Method :
  - Simulate systems using continuous-time Monte Carlo
  - Random walk through the space of trajectories
  - Bias the random walk towards the ensemble of trajectories defined by

$$P_s(\boldsymbol{X}_\tau) = \frac{e^{-sK} P(\boldsymbol{X}_\tau)}{Z_\tau(s)} \quad ; \quad P_x(\boldsymbol{Y}_K) = \frac{e^{-x\tau} P(\boldsymbol{Y}_K)}{Z_K(x)}$$

Dellago, C., Bolhuis, P. G. and Geissler, P. L. (2003) Transition Path Sampling, in Advances in Chemical Physics, Volume 123 (eds I. Prigogine and S. A. Rice), John Wiley & Sons, Inc., Hoboken, NJ, USA.

Transition path sampling (TPS)

- Algorithm :
  1. Generate a trajectory, Y, and calculate observables of interest τ, **M**...
  2. Propose a new trajectory, Y'(τ', **M')**
  3. Calculate the change in the observables of interest, Δτ =τ'-τ, etc...
  4. Accept or reject the proposed trajectory with probability

$$P_{accept} = min\left\{1, e^{-x\Delta\tau - s\Delta K}\right\}$$

  5. Repeat steps 2-4 until the trajectory has “equilibrated” to the desired values of *x*,**s**

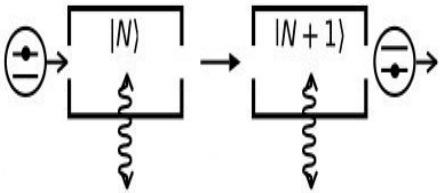
x-ensemble TPS scheme

- Typically with fixed observation time, use “forwards-backwards shooting/shifting”
  - On average, half of an old trajectory is replaced
- With fixed total event numbers, K, a trajectory is fully described by K sets of random numbers
  - Modifying one (or more) of the sets of random numbers produces a legitimate trajectory
  - Method of Crooks/Chandler
- Furthermore, it is possible to reconstruct the *s*-ensemble from *x*-ensemble numerics

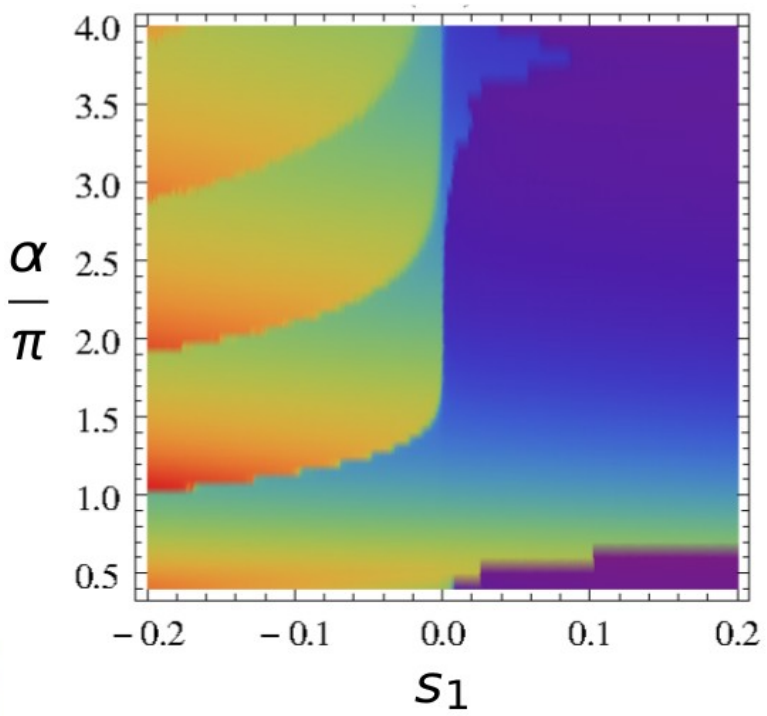
G.E Crooks and D. Chandler, Phys. Rev. E. **64** 026109 (2001)

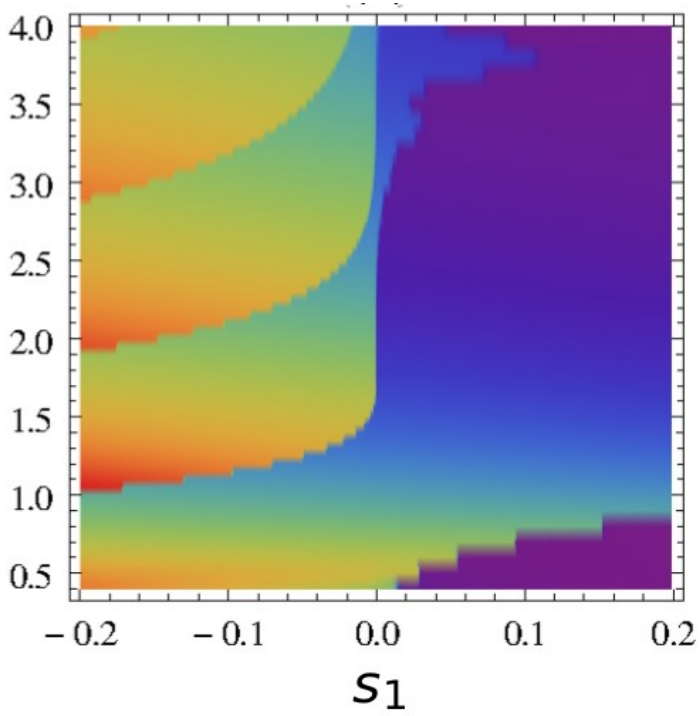
Results : Micromaser

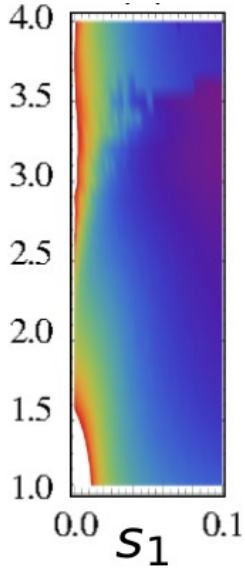
$$L_1 = \sqrt{r}\sin\frac{\left(\varphi\sqrt{aa^\dagger}\right)}{\sqrt{aa^\dagger}}a \qquad L_2 = \sqrt{r}\cos\left(\varphi\sqrt{aa^\dagger}\right)$$



$$L_3 = \sqrt{\kappa}\,a \qquad L_4 = \sqrt{\gamma}\,a^\dagger$$







$$\alpha \equiv \varphi\sqrt{r/(\kappa-\gamma)}$$

Analogous Jarzynski equality

- Other properties of thermodynamic ensembles should be preserved in the *thermodynamics of trajectories*
- Of particular interest, Jarzynski equality allows for calculation of free-energy differences between two equilibrium states, using non-equilibirum (fast) processes

$$\left\langle e^{-W/kT} \right\rangle = e^{-\Delta F/kT}$$

- Important to remember there are two layers to the dynamics: the non-equilibrium trajectory taken by a system, and the *meta-dynamics* of a the trajectory being "equilibrated" to a trajectory typical of the ensemble defined by *x*, through TPS
- Free-energy difference between two states becomes the difference in the LD function g(*x*) between two trajectories from ensembles defined by values x_i, x_f

$$\Delta F = g(x_f) - g(x_i)$$

- Need to identify a candidate for "work"

Analogous Jarzynski equality - Method

- Meta-dynamics of trajectories: Move in a series of N TPS steps from some x_i to some x_f
- Identify “meta-work” done in taking the system from x_i to x_f as

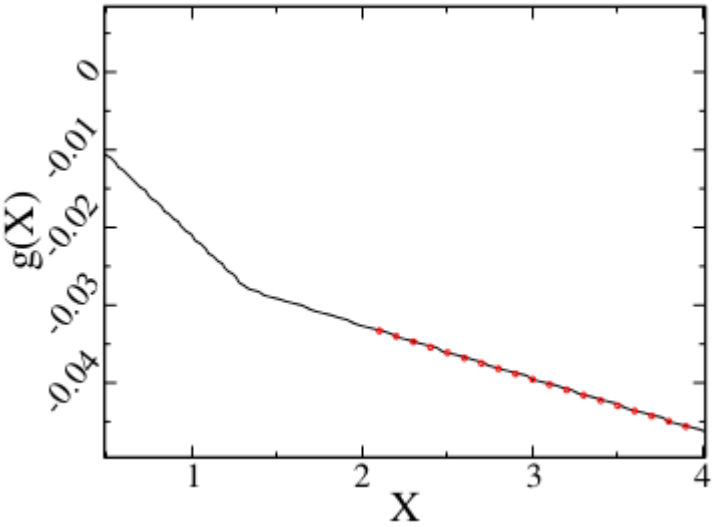
$$W = \sum_{i=1}^{i=N-1} \left(x_{i+1} - x_i\right) \tau_i$$

- “Equilibrate” the trajectory to x_f
- Reverse process: move from x_f to x_i
- Repeat the process J times to build a distribution of meta-work done for each of the forward and reverse processes respectively
- x can change quickly - “out of meta-equilibrium” but needs to be some overlap in the work distributions for the forward and reverse processes
- Meta-free-energy difference calculated the iterative Bennets Acceptance Ratio (BAR) method

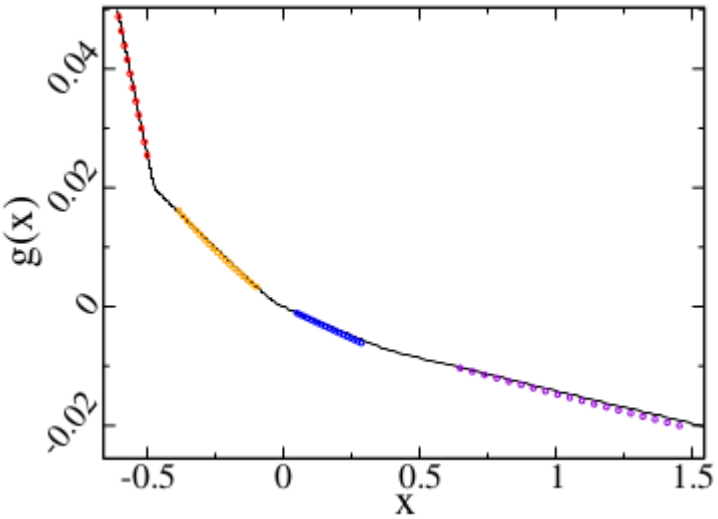
$$\Delta g^{(n+1)} = -\ln \frac{\sum_{j=1}^{J} \left[1 + e^{W_{forward,j} - \Delta g^{(n)}}\right]^{(-1)}}{\sum_{j=1}^{J} \left[1 + e^{W_{reverse,j} - e^{\Delta g^{(n)}}}\right]^{(-1)}}$$

Analogous Jarzynski equality

$\alpha = 1.2\,\pi$

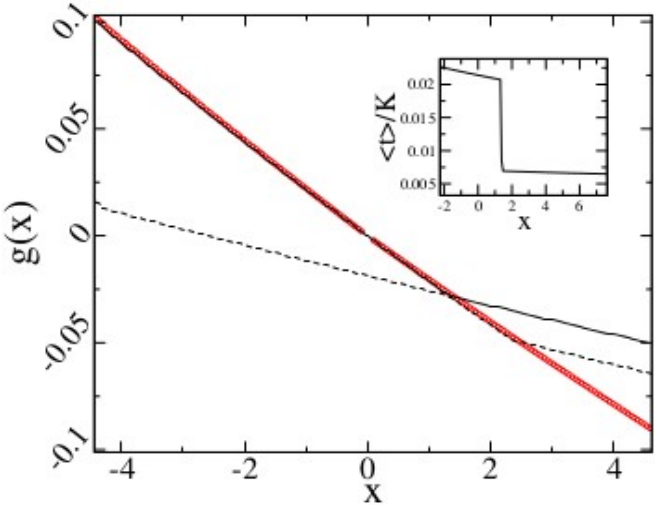


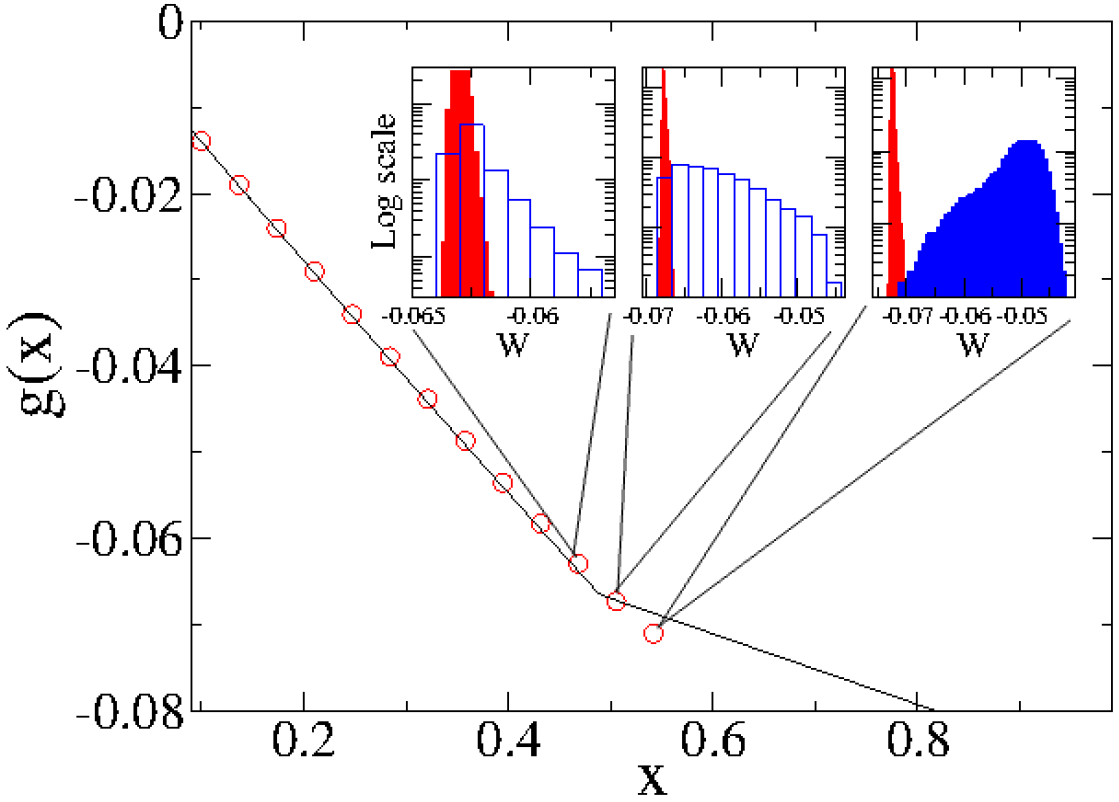
$\alpha = 4\,\pi$



Analogous Jarzynski equality

$\alpha = 1.2\,\pi$





Conclusions

- Flexible language – pick the ensemble most suited to the problem
  - Can convert between ensembles at a later stage
- Fluctuating time ensembles can potentially (depending on the system) provide orders of magnitude greater efficiency in the simulation of atypical trajectories
  - Applicable in any case trajectories can be fully described by a sequence of sets of random numbers
  - Can predict sources of efficiency gain for a system
  - Worst case scenario *s*-ensemble and *x*-ensemble TPS schemes are roughly equivalent in performance
- Analogous Jarzynski equality provides a direct method of calculating meta-free-energy differences in the thermodynamics of trajectories
- Potential scope to explore useful properties and relations of other thermodynamic ensembles