Statistical Mechanics
E0415

Fall 2023, lecture 9
Fluctuation relations

… previous take home…

QA:

“I chose the article https://www.nature.com/articles/s41598-019-49172-3 due to the interesting applications in combinatorial problems. It is also related to scheduling which is interesting. In the article the scheduling problem was presented with an ising spin hamiltonian. The problem was solved with quantum annealing. The results were promising with a fixed sample size and fixed annealing duration.

The probability of success can be improved with reverse annealing although not uniformly. The quantum annealing approach may not work for larger problems but it is possible to decompose the problem into smaller parts where the method described could work. Additionally, there have not been performance comparisons to conventional methods used to solve the same problem. In the article a specific schedule was studied while different schedule parameters can impact the obtained results. In further research, the effect of quantum tunneling on the hard constraints and the noise of the processor impacting the results require more analysis. “

… summaries…

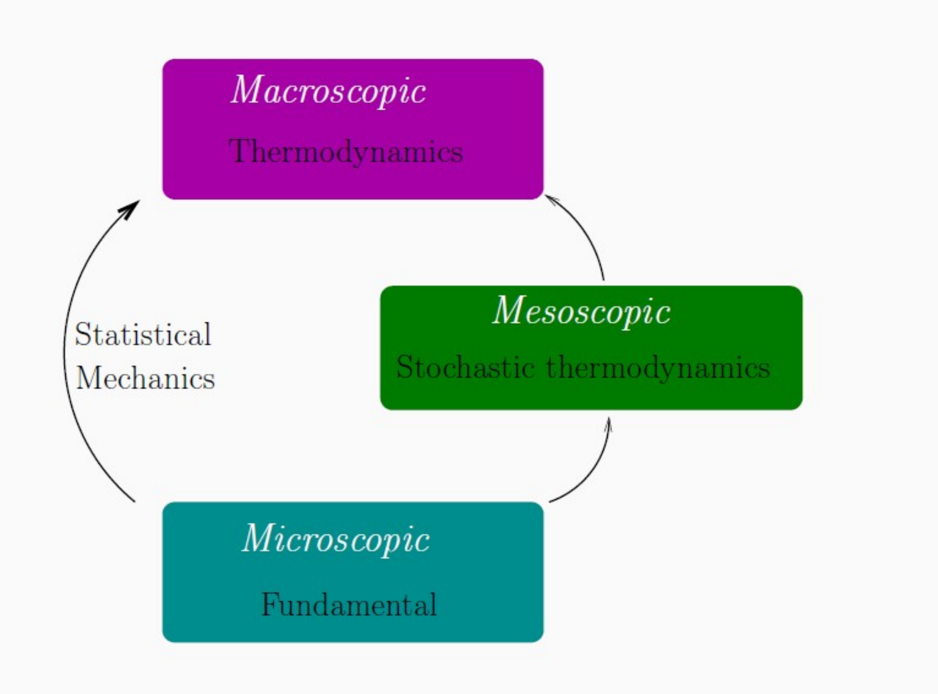
"I picked the article about QKZM because I felt like the concept was interesting and relevant for many applications, but I didn't yet get a great handle on it during the last lecture or the presentations before that. The defect density and varying the annealing rate were clear, but what I was missing is the interpretation and the context in which this relates to the nature of the phase transition more generally.

The article describes both an experimental and numerical study of several quantum phase transitions in a 1D chain of atoms. The system is composed of Rb atoms, that can either be in the electronic ground state, or the excited Rydberg state. By varying the terms of the many body hamiltonian, different quantum phases can be studied. Specifically, the QKZM is realised by sweeping the detuning frequency in the hamiltonian with varying rates. First, an Ising universality class system is examined numerically and with the experimental setup, and agreement between the behavior is found for the critical exponents. The phase transitions here are between an unordered phase, where most atoms up to quantum fluctuations are in the ground state, and one of several ordered states with periodicity of 2, 3 or 4, where a pattern of excited and ground state atoms alternates, the symmetry broken by occasional defects that are used to study the properties of the phase transition.In the period 2 (Ising class) case, the shape of the universally scaling distance correlation function is also discussed, and corrections to the QKZM predicted simple correlation are observed. The more complex period 3 and 4 phase transitions experimentally agree with the universality classes of the 3- and 4-state chiral clock systems respectively. The experimental method presented could be useful further in exploration of quantum optimization problems and lattice gauge theories, both of which do sound useful and I would like to know something about if I find the time :) “.

Fluctuation relations

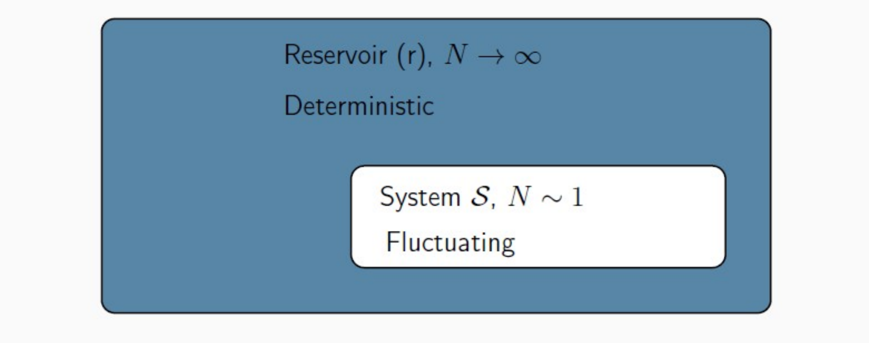
What happens in small systems so that large numbers do not rule?

Systems, where fluctuations and the thermodynamics of information are important.



[thanks to Luca Peliti, Napoli]

We forget about quantum statistical mechanics.



Prerequisite: relative entropy

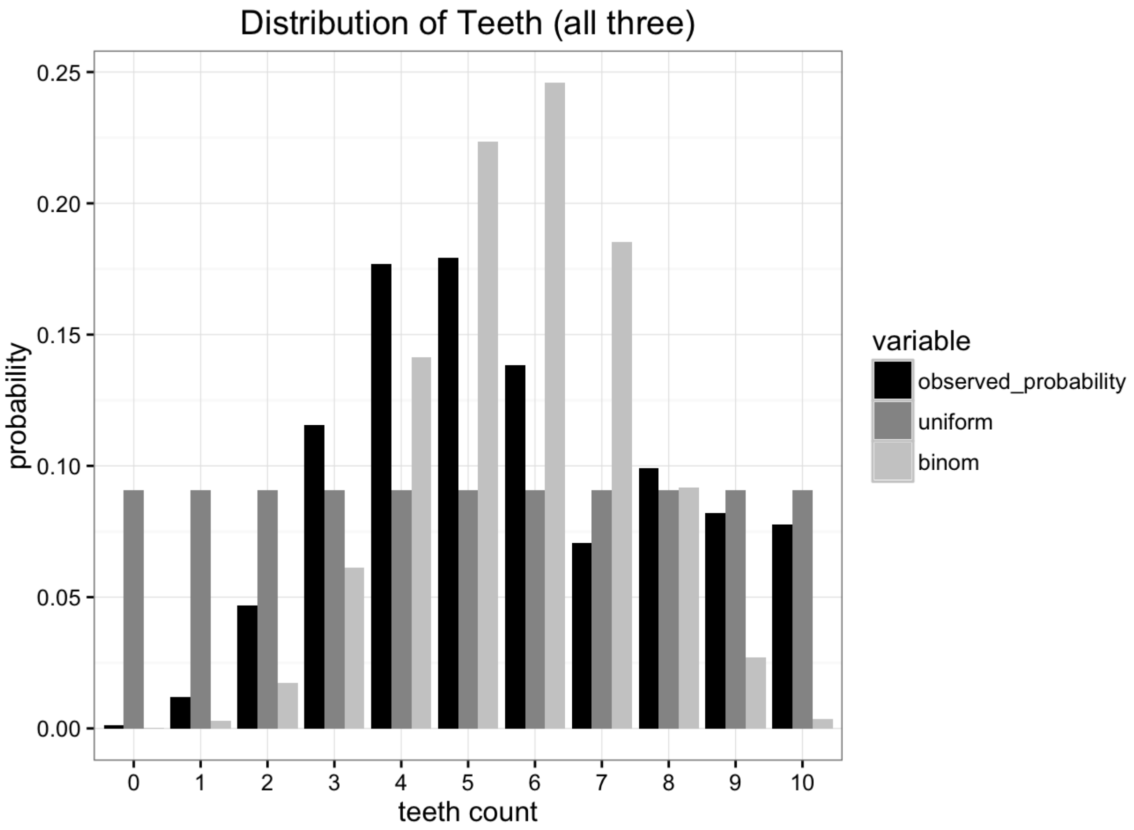
The **relative entropy** (or **Kullback-Leibler divergence**) of two pdf's p and q is a measure of their difference

$$D_{\mathrm{KL}}(p\|q) = \sum_x p_x \log \frac{p_x}{q_x}$$

Properties:

- $D_{\mathrm{KL}}(p\|q) \geq 0$
- $D_{\mathrm{KL}}(p\|q) \neq D_{\mathrm{KL}}(q\|p)$
- $D_{\mathrm{KL}}(p\|q) = 0 \Leftrightarrow p_x = q_x, \forall x$

KL explained



Observations: which distribution fits best (entropy loss)?

Binomial or uniform?

KL entropy/divergence 0.477 vs. 0.388.

(0.30 vs. 0.477)

[Thanks to Will Kurt]

Recall that the fluctuation theorem, Eq. (2), compares the entropy production probability distribution of a process with the entropy production distribution of the corresponding time-reversed process. For example, with the confined gas we compare the entropy production when the gas is compressed to the entropy production when the gas is expanded. To allow this comparison of forward and reverse processes, we will require that the entropy production is odd under a time reversal, i.e., $\omega_F = -\omega_R$, for the process under consideration. This condition is equivalent to requiring that the final distribution of the forward process, $\rho_F(x_{+\tau})$, is the same (after a time reversal) as the initial phase-space distribution of the reverse process, $\rho_R(\bar{x}_{+\tau})$, and vice versa, i.e., $\rho_F(x_{+\tau}) = \rho_R(\bar{x}_{+\tau})$ and $\rho_R(x_{-\tau}) = \rho_F(\bar{x}_{-\tau})$. In the next section, we will discuss two broad types of work process that fulfill this condition. Either the system begins and ends in equilibrium or the system begins and ends in the same time symmetric nonequilibrium steady state.

This time-reversal symmetry of the entropy production allows the comparison of the probability of a particular path, $x(t)$, starting from some specific point in the initial distribution, with the corresponding time-reversed path,

$$\frac{\rho_F(x_{-\tau})\mathcal{P}[x(+t)|\lambda(+t)]}{\rho_R(\bar{x}_{+\tau})\mathcal{P}[\bar{x}(-t)|\bar{\lambda}(-t)]} = e^{+\omega_F}. \qquad (7)$$

This follows from the the conditions that the system is microscopically reversible, Eq. (5), and that the entropy production is odd under a time reversal.

Now consider the probability, $P_F(\omega)$, of observing a particular value of this entropy production. It can be written as a δ function averaged over the ensemble of forward paths,

$$P_F(\omega) = \langle \delta(\omega - \omega_F) \rangle_F$$
$$= \int\int\int_{x_{-\tau}}^{x_{+\tau}} \rho_F(x_{-\tau})\mathcal{P}[x(+t)|\lambda(+t)]$$
$$\times \delta(\omega - \omega_F)\mathcal{D}[x(t)]dx_{-\tau}\, dx_{+\tau}.$$

Here $\int\int\int_{x_{-\tau}}^{x_{+\tau}} \cdots \mathcal{D}[x(t)]dx_{-\tau}\, dx_{+\tau}$ indicates a sum or suitable normalized integral over all paths through phase-space, and all initial and final phase-space points, over the appropriate time interval. We can now use Eq. (7) to convert this average over forward paths into an average over reverse paths,

$$P_F(\omega) = \int\int\int_{x_{-\tau}}^{x_{+\tau}} \rho_R(\bar{x}_{+\tau})\mathcal{P}[\bar{x}(-t)|\bar{\lambda}(-t)]$$
$$\times \delta(\omega - \omega_F)e^{+\omega_F}\mathcal{D}[x(t)]dx_{-\tau}\, dx_{+\tau}$$
$$= e^{+\omega}\int\int\int_{x_{-\tau}}^{x_{+\tau}} \rho_R(\bar{x}_{+\tau})\mathcal{P}[\bar{x}(-t)|\bar{\lambda}(-t)]$$
$$\times \delta(\omega + \omega_R)\mathcal{D}[x(t)]dx_{-\tau}\, dx_{+\tau}$$
$$= e^{+\omega}\langle \delta(\omega + \omega_R)\rangle_R = e^{+\omega}P_R(-\omega).$$

The δ function allows the $e^{+\omega}$ term to be moved outside the integral in the second line above. The remaining average is over reverse paths as the system is driven in reverse. The final result is the entropy production fluctuation theorem, Eq. (2).

The theorem readily generalizes to other ensembles. As an example, consider an isothermal-isobaric system. In addition to the heat bath, the system is coupled to a volume bath, characterized by βp, where p is the pressure. Then the microscopically reversible condition, Eq. (5), becomes

$$\frac{\mathcal{P}[x(+t)|\lambda(+t)]}{\mathcal{P}[\bar{x}(-t)|\bar{\lambda}(-t)]} = \exp\{-\beta Q[x(t),\lambda(t)]$$
$$- \beta p \Delta V[x(t),\lambda(t)]\}.$$

Both baths are considered to be large, equilibrium, thermodynamic systems. Therefore, the change in entropy of the heat bath is $-\beta Q$ and the change in entropy of the volume bath is $-\beta p \Delta V$, where ΔV is the change in volume of the system. The entropy production should then be defined as

$$\omega = \ln \rho(x_{-\tau}) - \ln \rho(x_{+\tau}) - \beta Q - \beta p \Delta V. \qquad (8)$$

The fluctuation theorem, Eq. (2), follows as before. It is possible to extend the fluctuation theorem to any standard set of baths, so long as the definitions of microscopic reversibility and the entropy production are consistent. In the rest of this paper we shall only explicitly deal with systems coupled to a single heat bath, but the results generalize directly.

III. TWO GROUPS OF APPLICABLE SYSTEMS

In this section we will discuss two groups of systems for which the entropy fluctuation theorem, Eq. (2), is valid. These systems must satisfy the condition that the entropy production, Eq. (6), is odd under a time reversal, and therefore that $\rho_F(x_{+\tau}) = \rho_R(\bar{x}_{+\tau})$.

First consider a system that is in equilibrium from time $t = -\infty$ to $t = -\tau$. It is then driven from equilibrium by a change in the controlled parameter, λ. The system is actively perturbed up to a time $t = +\tau$, and is then allowed to relax, so that it once again reaches equilibrium at $t = +\infty$. For the forward process the system starts in the equilibrium ensemble specified by $\lambda(-\infty)$, and ends in the ensemble specified by $\lambda(+\infty)$. In the reverse process, the initial and final ensembles are exchanged, and the entropy production is odd under this time reversal. The gas confined in the diathermal cylinder satisfies these conditions if the piston moves only for a finite amount of time.

At first it may appear disadvantageous that the entropy production has been defined between equilibrium ensembles separated by an infinite amount of time. However, for these systems the entropy production has a simple and direct interpretation. The probability distributions of the initial and final ensembles are known from equilibrium statistical mechanics:

$$\rho_{eq}(x|\lambda) = \frac{e^{-\beta E(x,\lambda)}}{\sum_x e^{-\beta E(x,\lambda)}} = \exp\{\beta F(\beta,\lambda) - \beta E(x,\lambda)\}. \qquad (9)$$

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Entropy production fluctuation theorem and the nonequilibrium work relation for free energy differences

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$$\langle e^{-\beta W} \rangle = e^{-\beta \Delta F}.$$

Jarzynski… Crooks

$$\frac{P_F(+\omega)}{P_R(-\omega)} = e^{+\omega}.$$

Jarzynski' equality

$E_x = E_x(\lambda)$, $\lambda = \lambda(t)$ ("protocol")

Idea: measure free energy difference by a loop, and using probabilities for a path given a particular control λ.

Assumes detailed balance along the trajectory/path (loop).

- Start from equilibrium: $p_x(t_0) = p_x^{\mathrm{eq}}(\lambda_0)$, $p_{\hat{x}}(t_0) = p_{x_\mathrm{f}}^{\mathrm{eq}}(\lambda_\mathrm{f})$:

$$\frac{\mathcal{P}_{\boldsymbol{\lambda}}(\boldsymbol{x})}{\mathcal{P}_{\hat{\boldsymbol{\lambda}}}(\hat{\boldsymbol{x}})} = \mathrm{e}^{-(\mathcal{Q}(\boldsymbol{x})+F_\mathrm{f}-E_{x_\mathrm{f}}-(F_0-E_{x_0}))/k_\mathrm{B}T}$$

$$= \mathrm{e}^{-(\mathcal{Q}(\boldsymbol{x})-\Delta E)/k_\mathrm{B}T}\,\mathrm{e}^{-\Delta F/k_\mathrm{B}T} = \mathrm{e}^{\mathcal{W}(\boldsymbol{x})/k_\mathrm{B}T}\,\mathrm{e}^{-\Delta F/k_\mathrm{B}T}$$

- *Jarzynski's equality*:

$$\underbrace{\left\langle \mathrm{e}^{-\mathcal{W}/k_\mathrm{B}T} \right\rangle}_{\text{non-eq.}} = \underbrace{\mathrm{e}^{-\Delta F/k_\mathrm{B}T}}_{\text{eq}}$$

- Examples:
  - Quasi-static transformation: $p_x(t) = p_x^{\mathrm{eq}}(\lambda(t))$:

$$\left\langle \mathrm{e}^{-\mathcal{W}/k_\mathrm{B}T} \right\rangle \simeq \exp\left[-\frac{1}{k_\mathrm{B}T}\int \mathrm{d}t\ \dot{\lambda}(t)\ \langle \partial_\lambda E\rangle_{p^{\mathrm{eq}}(\lambda(t))}\right] = \mathrm{e}^{-\Delta F/k_\mathrm{B}T}$$

  - Sudden transformation $E_x(\lambda_\mathrm{i}) \longrightarrow E_x(\lambda_\mathrm{f})$:

$$\left\langle \mathrm{e}^{-\mathcal{W}/k_\mathrm{B}T} \right\rangle = \int \mathrm{d}x\ \mathrm{e}^{-(E_{\lambda_F}(x)-E_{\lambda_\mathrm{i}}(x))/k_\mathrm{B}T}\,\mathrm{e}^{(F_{\lambda_\mathrm{i}}-E_{\lambda_\mathrm{i}}(x))/k_\mathrm{B}T}$$

$$= \mathrm{e}^{-(F_{\lambda_\mathrm{f}}-F_{\lambda_\mathrm{i}})/k_\mathrm{B}T}$$

Relation to 2nd law of thermodynamics

Take a reversible process, so that the free energy change is zero.

Thus, the expectation value of the exponential is zero.

But, this implies there are paths with W smaller than zero!

Dissipated work and KL entropy

- Probability distribution of $\mathcal{W}$:

$$P_{\boldsymbol{\lambda}}(W) = \int \mathcal{D}\boldsymbol{x}\, \mathcal{P}_{\boldsymbol{\lambda}}(\boldsymbol{x})\, \delta(\mathcal{W}(\boldsymbol{x}) - W)$$

- Relative entropy of $\mathcal{P}_{\boldsymbol{\lambda}}(\boldsymbol{x})$ and $\mathcal{P}_{\hat{\boldsymbol{\lambda}}}(\hat{\boldsymbol{x}})$:

$$\begin{aligned} D_{\mathrm{KL}}(\mathcal{P}_{\boldsymbol{\lambda}} \| \mathcal{P}_{\hat{\boldsymbol{\lambda}}}) &= \int \mathcal{D}\boldsymbol{x}\, \mathcal{P}_{\boldsymbol{\lambda}}(\boldsymbol{x}) \log \frac{\mathcal{P}_{\boldsymbol{\lambda}}(\boldsymbol{x})}{\mathcal{P}_{\hat{\boldsymbol{\lambda}}}(\hat{\boldsymbol{x}})} = \int \mathcal{D}\boldsymbol{x}\, \mathcal{P}_{\boldsymbol{\lambda}}(\boldsymbol{x})\, \frac{\mathcal{W}(\boldsymbol{x}) - \Delta F}{k_{\mathrm{B}}T} \\ &= \int \mathrm{d}W\ P_{\boldsymbol{\lambda}}(W)\, \frac{W - \Delta F}{k_{\mathrm{B}}T} = \int \mathrm{d}W\ P_{\boldsymbol{\lambda}}(W) \log \frac{P_{\boldsymbol{\lambda}}(W)}{P_{\hat{\boldsymbol{\lambda}}}(-W)} \\ &= \frac{1}{k_{\mathrm{B}}T} \left\langle \mathcal{W}^{\mathrm{diss}} \right\rangle \end{aligned}$$

- Let $P_{\boldsymbol{\lambda}}(W)$ be close to a Gaussian:

$$P_{\boldsymbol{\lambda}}(W) \propto \exp\left[-\frac{(W - \langle \mathcal{W} \rangle)^2}{2\sigma_W^2} \right]$$

then

$$\left\langle \mathcal{W}^{\mathrm{diss}} \right\rangle = \langle \mathcal{W} \rangle - \Delta F = \frac{\sigma_W^2}{2k_{\mathrm{B}}T}$$

Other similar relations

- Crooks, Seifert…
- Non-Equilibrium Steady-States (“NES”), large deviation theories

Callavotti-Cohen

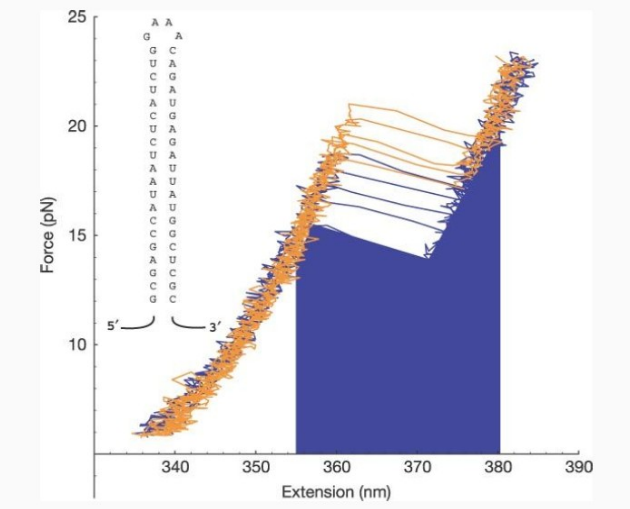
$$\frac{\mathcal{P}_{\boldsymbol{\lambda}}(\boldsymbol{x}|x_0)}{\mathcal{P}_{\hat{\boldsymbol{\lambda}}}(\hat{\boldsymbol{x}}|\hat{x}_0 = x_{\mathrm{f}})} = \exp\left(-\frac{1}{k_{\mathrm{B}}T}\sum_{k=1}^{n} \mathcal{Q}_{x_{k+1}x_k}\right) = \mathrm{e}^{\Delta S^{(\mathrm{r})}(\boldsymbol{x})/k_{\mathrm{B}}}$$

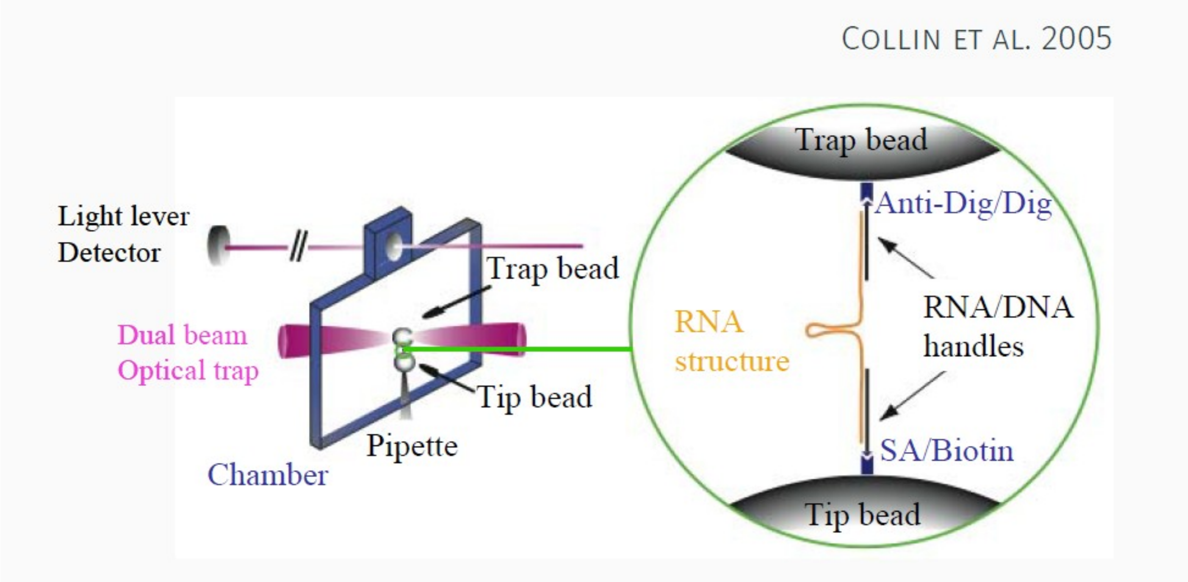
Applications to “small-N” systems

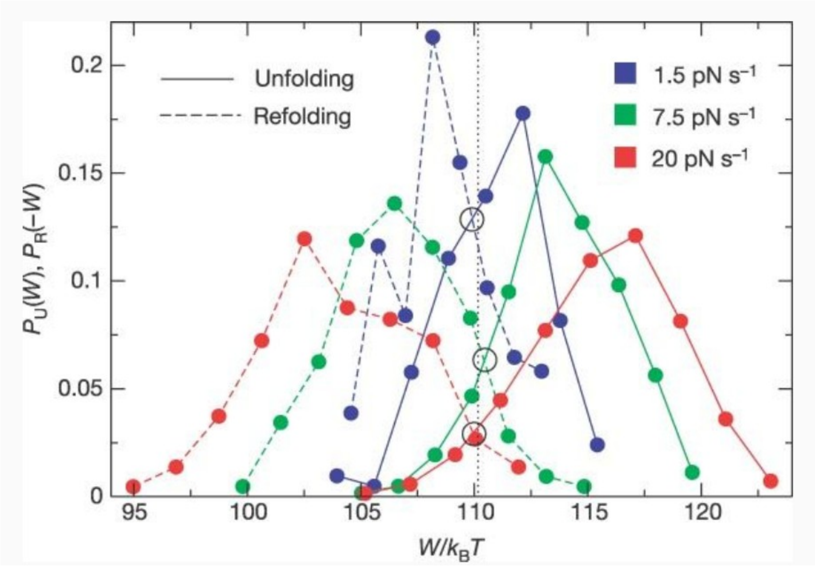
and thermodynamics: biology!

Fluctuations of stochastic reaction processes, entropy, information.

RNA hairpin







First real application “experimentally”.

Next take home

This time we study some basics of non-equilibrium thermodynamics. This field is effectively 15 years old (in terms of getting serious attention and applications). One very important issue is what to do in the quantum realm (how to define work is key question) but here we keep it simple. The Sethna book is even though the most modern not on par with current understanding. There is a bunch of lecture notes of varying sophistication (you may find those by Udo Seifert for instance) but we instead refer to the seminar notes of Jarzynski found at https://math.ucr.edu/home/baez/thermo/Jarzynski_SFI_Tutorial_Nonequilibrium_Statistical_Mechanics.pdf. .

The key points are: what does the Jarzynski equality mean, why is it important?

We have again then a pick of two recent with lo and behold, both having Chris Jarzynski as one of the authors.

You may have a look at his own review of the state of this field
https://www.sciencedirect.com/science/article/pii/S0378437119312075

or check an application to biological systems
https://journals.aps.org/prl/abstract/10.1103/PhysRevLett.124.228101

And your task is like the previous time "2+8" sentences on the selection and main points.