Statistical Mechanics E0415

Fall 2022, lecture 9
Fluctuation relations

… previous take home…

QA:

"I chose the paper about Quantum Annealing to Nurse Scheduling Problem, because previously I’ve worked with D-wave’s Ocean platform on new quantum annealing algorithms for solving the Vehicle Routing Problem (VRP) and I wanted to expand my understanding on it. Additionally, for our presentation I got very familiar with KZM and needed a break from it. In the paper, nurse scheduling problem (NSP), a NP-hard problem, is studied as a quantum unconstrained binary optimization (QUBO) problem using Quantum Annealing (QA). They use commercial quantum annealer available from D-Wave Systems to implement several hard constraints. The QUBO problem is directly mapped into the Ising model using a simple change of variable and solved by QA which is used as a method to find the minimum energy configuration of the Hamiltonian of NSP. The constraints include upper and lower limit of the number of breaks, the number of nurses in duty for each shift slot, upper and lower limit of time interval between two days of duty. The researchers concluded that the current technology of quantum annealers are insufficient to work with realistic sizes of number of nurses and working days. The result can be improved in some cases with reverse annealing. They commented that their study is a good sign for the potential usage of quantum annealers for real life problems.

… summaries…

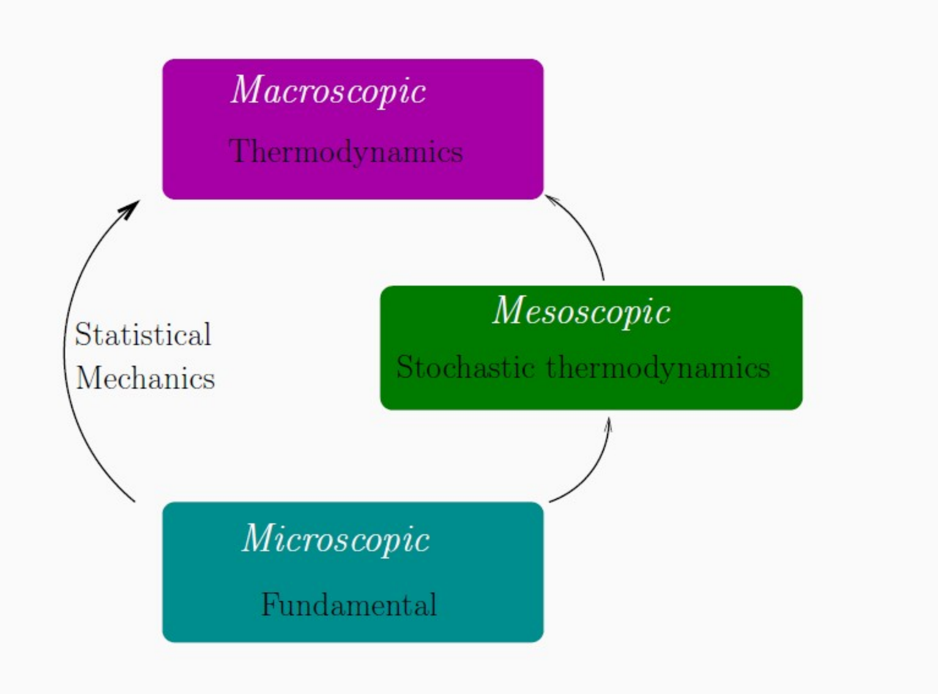
KZ

"From the two articles, I chose the latter one, about quantum Kibble-Zurek mechanism, since its topic seemed more interesting and it was shorter. In the article, an experimental setup consisting of an 1D-array of Rb atoms with tunable interactions was used to study the quantum Kibble-Zurek mechanism describing a specific type of second-order phase transitions. By changing the detuning of the coupling between a ground state and excited Rydberg state, the system went through different quantum phase transitions into symmetry-broken states. Importantly, the sweeping speed of the control parameter affected the domain size of the new phase after QPT, with slower sweeping leading to larger domains. The study also showed that the QPT to Z2-ordered phase is included in the Ising universality class but its critical exponents defy the predictions of the mean-field approximation. Furthermore, the authors studied the phase transitions into Z3- and Z4-ordered phases and found that these phases can be described with symmetry breaking within the universality class of chiral clock models

Fluctuation relations

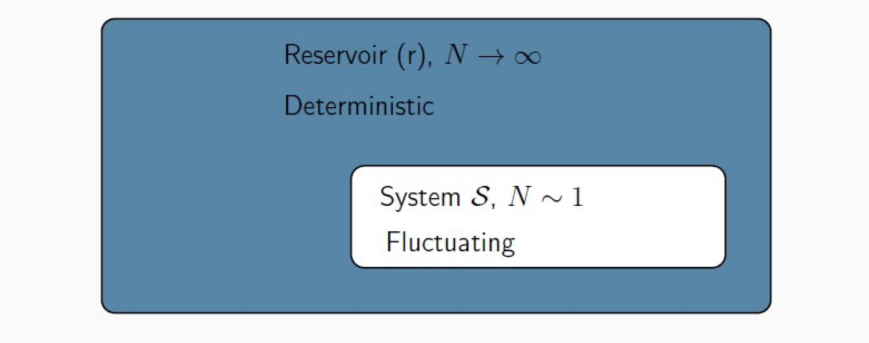
What happens in small systems so that large numbers do not rule?

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



[thanks to Luca Peliti, Napoli]

We forget about quantum statistical mechanics.



Prerequisite: relative entropy

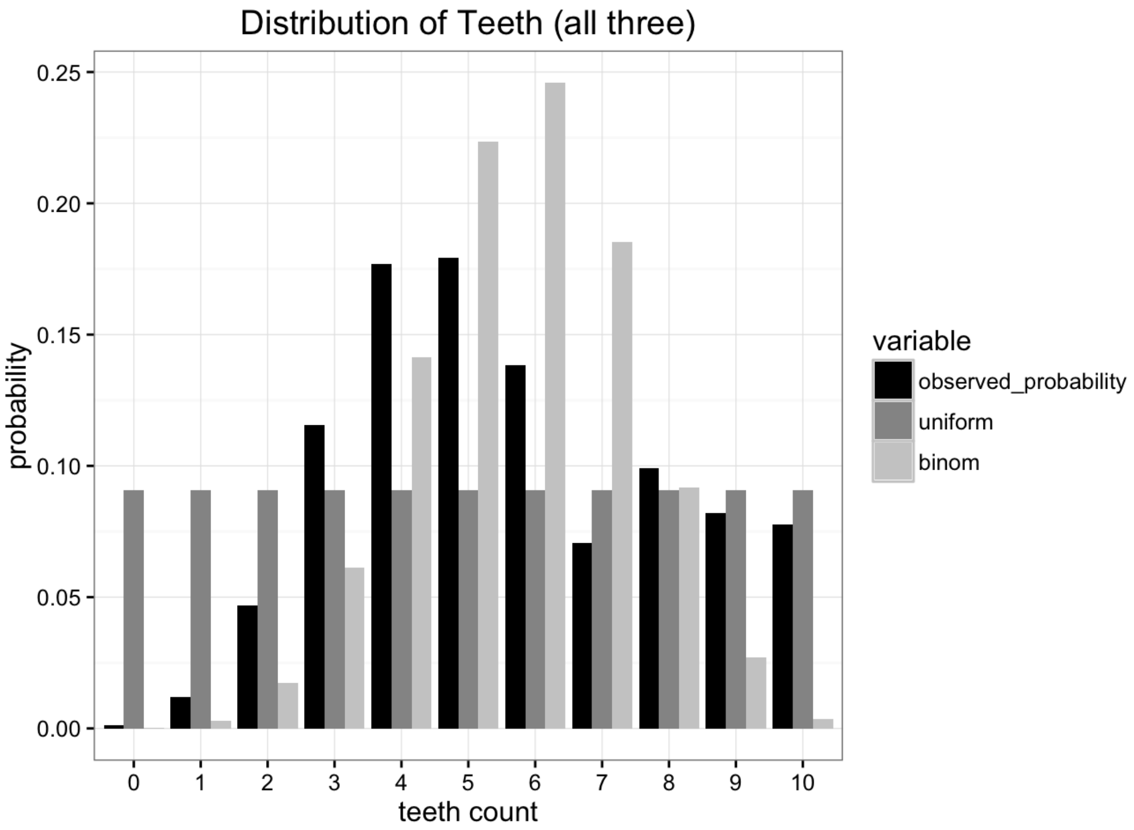
The **relative entropy** (or **Kullback-Leibler divergence**) of two pdf's p and q is a measure of their difference

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

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]

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.

Thus, the expectation value of

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 $\mathcal{P}_{\hat{\boldsymbol{\lambda}}}(\hat{\boldsymbol{x}})$:

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

- 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

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

Other similar relations

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

Callavotti-Cohen

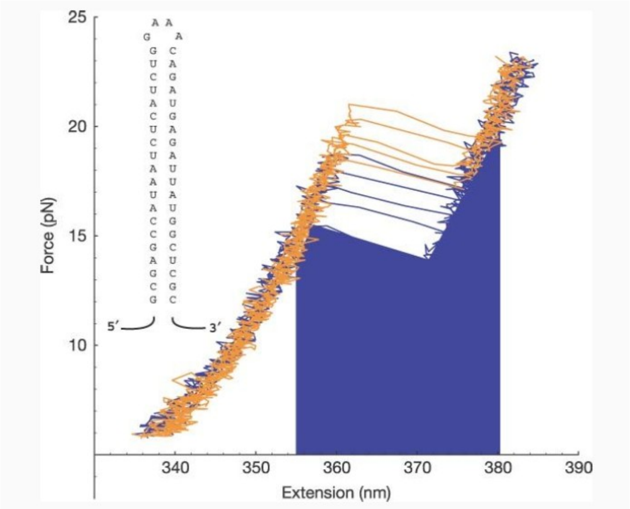
$$\frac{\mathcal{P}_{\boldsymbol{\lambda}}(\boldsymbol{x}|x_0)}{\mathcal{P}_{\hat{\boldsymbol{\lambda}}}(\hat{\boldsymbol{x}}|\hat{x}_0{=}x_{\mathrm{f}})} = \exp\left(-\frac{1}{k_{\mathrm{B}}T}\sum_{k=1}^{n} Q_{x_{k+1}x_k}\right) = \mathrm{e}^{\Delta S^{(\mathrm{r})}(\boldsymbol{x})/k_{\mathrm{B}}}$$

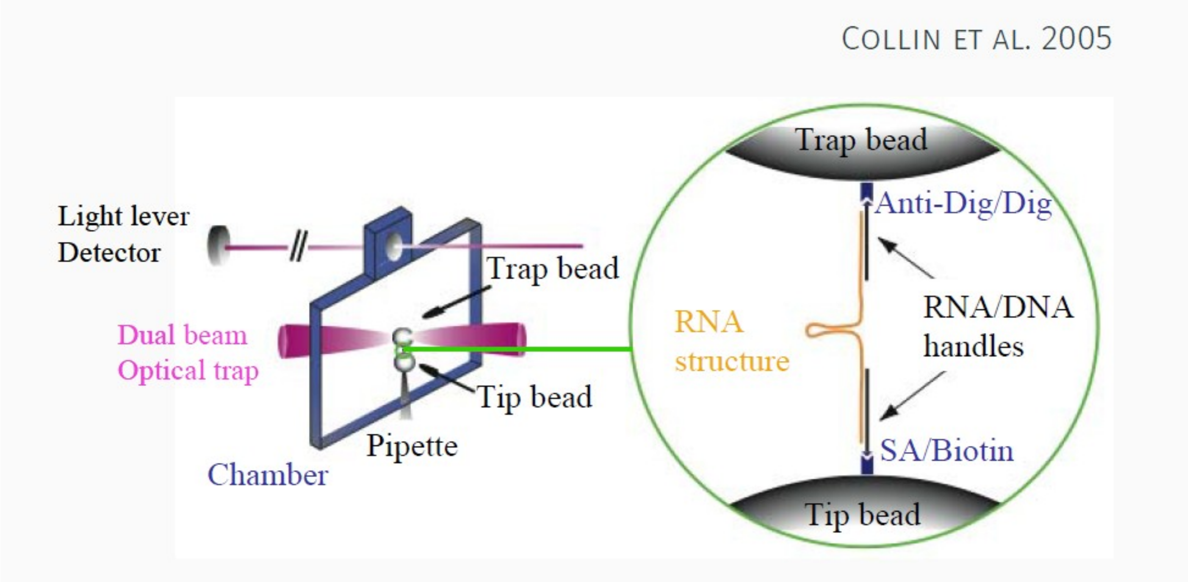
Applications to “small-N” systems

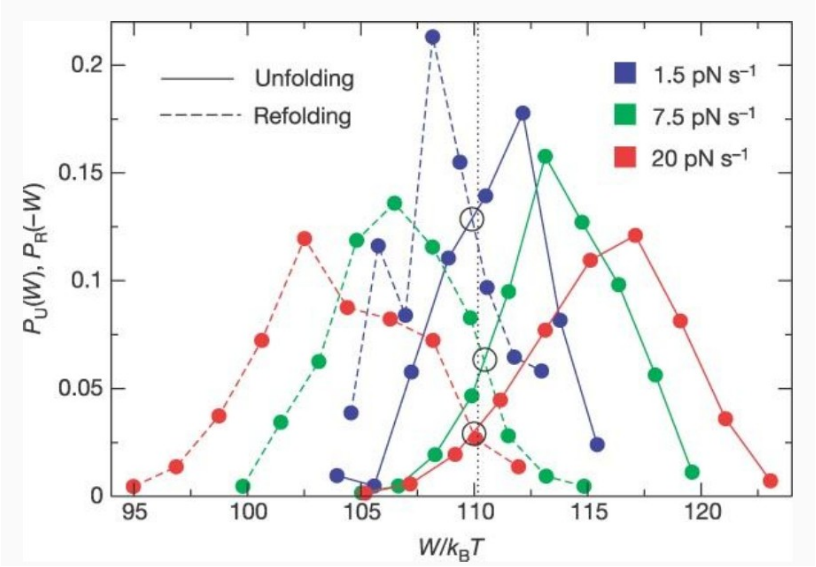
and thermodynamics: biology!

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.