Statistical Mechanics
E0415

Fall 2020, lecture 9
Fluctuation relations

… previous take home…

"This week I chose the paper with an application outside of physics for a change. Also, as I have done some previous studies on cryptography, where we discussed NP-hard problems a lot, I was interested to see how a quantum computing approach could possibly deal with them.“

"I chose the article “Application of Quantum Annealing to nurse Scheduling problem” as I got quickly interested about it because of the quantum computing. Quantum annealing is a branch that I have little prior knowledge about, which made it even more interesting. D-Wave has surprisingly nice videos on their YouTube page, as a side note. "

"I chose the 'Application of Quantum Annealing to Nurse Scheduling Problem'-article because I wanted to see how the concepts of quantum physics could be applied to systems, that on surface have nothing in common with quantum mechanics.“

"I chose to read about the Kibble-Zurek mechanism, since I had not heard about it before and it seemed intriguing. Another reason was that I picked up some very familiar methods (DMRG) and concepts such as different Zn-ordered phases and clock models that I have worked with before, so I wanted to understand how they were used in this research. "

… summaries…

"In the paper, the authors pose the NSP as a quantum unconstrained binary optimizaiton (QUBO) problem. The QUBO problem is trivially **mapped into the ising model** that is then solved using quantum annealing (QA). Quantum annealing is a heuristic method to find a minumum of an objective function, in this case the Hamiltonian of the NSP. The built Hamiltonian is basically a combination of quadratic terms corresponding to the constraints of the problem. The constraints of the NSP here are that the shift's nurses must be able to do the required work, the nurses must have a sensible schedule and that the nurses must not work on consecutive days.

The authors utilize a commercially available quantum annealer. They find that, with current technology, the minimum of the Hamiltonian can be found with nonzero probability via QA for small, non-practical, numbers of nurses and working days. The obtained results can, in some cases, be improved by reverse annealing."

"The paper uses a Rydberg atom quantum simulator to study the growth of spatial correlations while crossing the QPT. This study allows the experimental verification of the quantum Kibble-Zurek mechanism for an Ising-type QPT. Specific to this study, the QKZM postulates that when the time scale over which H changes becomes faster than the response time, non-adiabatic excitations prevent the continued growth of correlated regions.

With a many-body Hamiltonian in one dimension, the study examines different QPTs into states with varying broken symmetries. For example, their results show that the QPT into the Z2-ordered space is in the Ising universality class with certain critical exponents, consistent with quantitative predictions.

Their detailed inspection of the correlation functions give results that imply complex dynamics in the formation and spreading of defects. In the more complex Z3-ordered phase, the most-likely defect shifts from Z2-like for weaker interactions to Z4-like as the interaction strength increases, and the Z3-symmetry breaking is suggested to be in the universality class of the chiral clock model.

Overall, the observations of the study provide new insights into the physics of exotic quantum phase transitions."

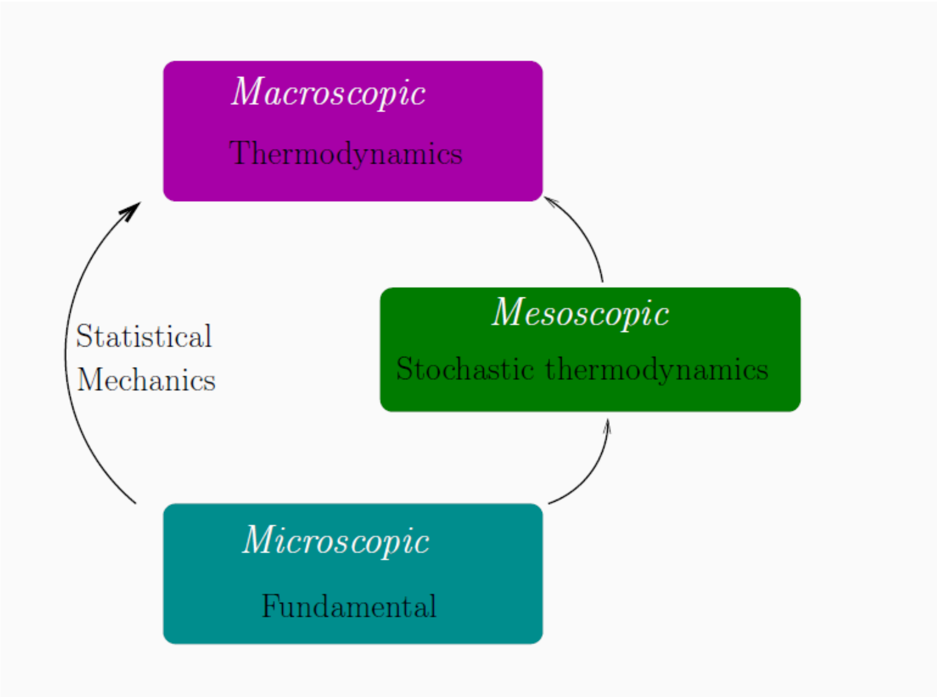
Fluctuation relations

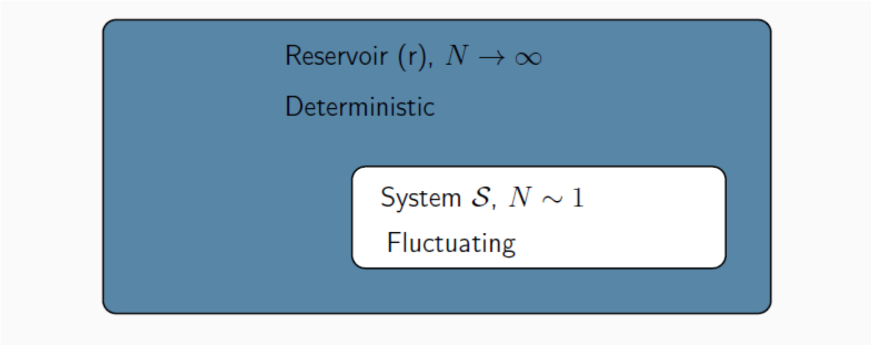
What happens in small systems so that large numbers do not rule?

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

[thanks to Luca Peliti, Napoli]

We forget about quantum statistical mechanics.





Prerequisite: relative entropy

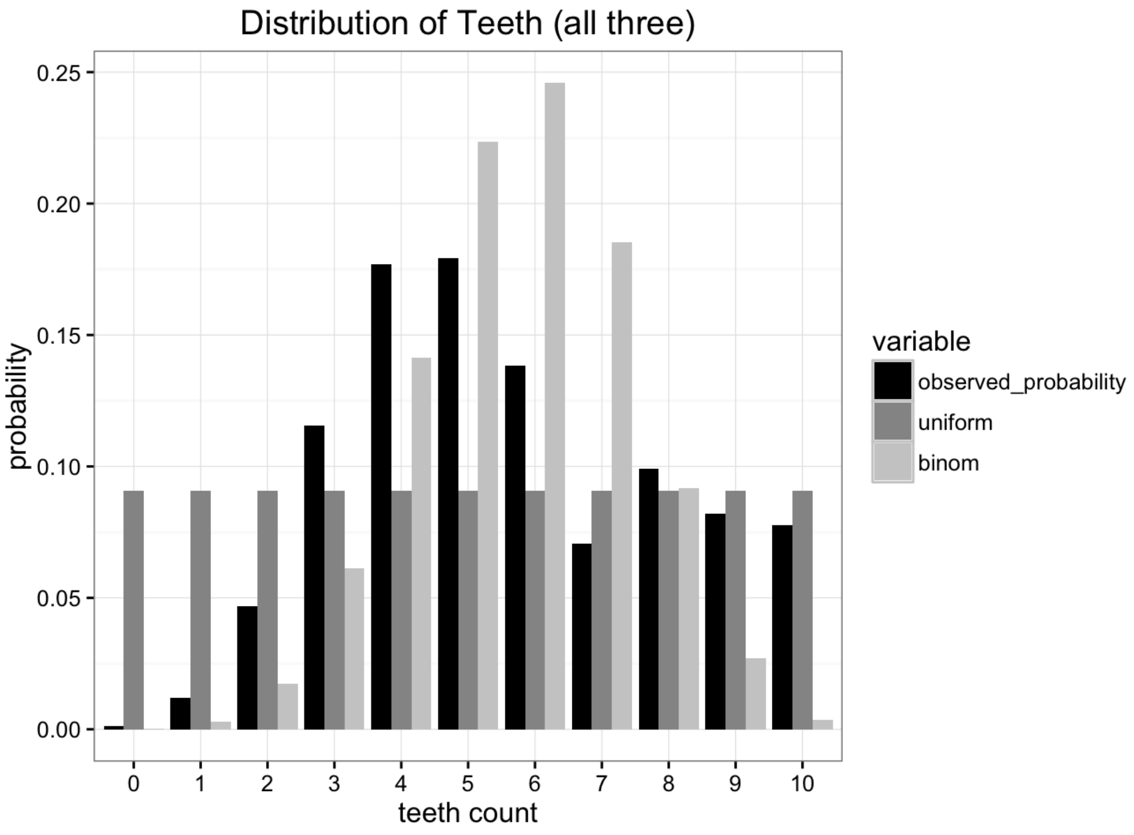
The **relative entropy** (or **Kullback-Leibler divergence**) of two pdf's p and q is a measure of their difference

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

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



Observatíons: 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 $\langle W \rangle \geq 0$.

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

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

Other similar relations

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

Callavotti-Cohen

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

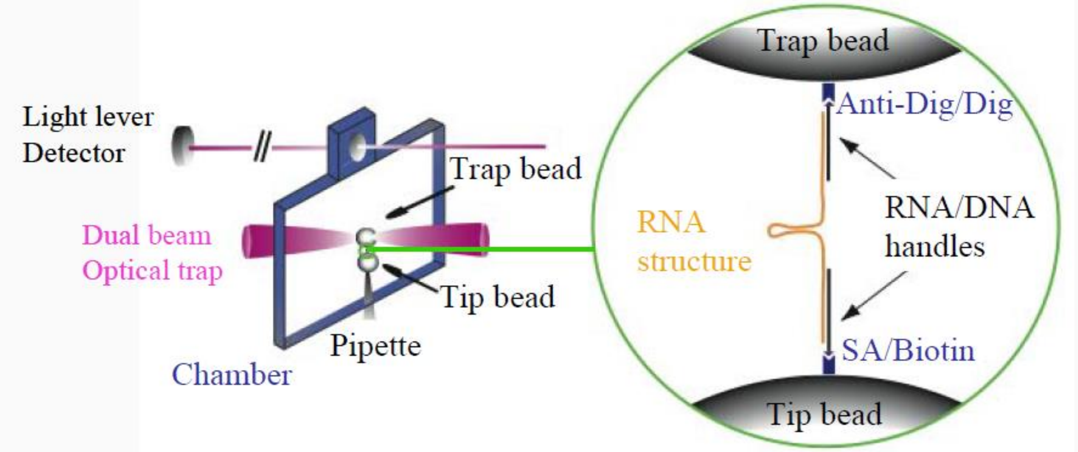
Applications to “small-N” systems

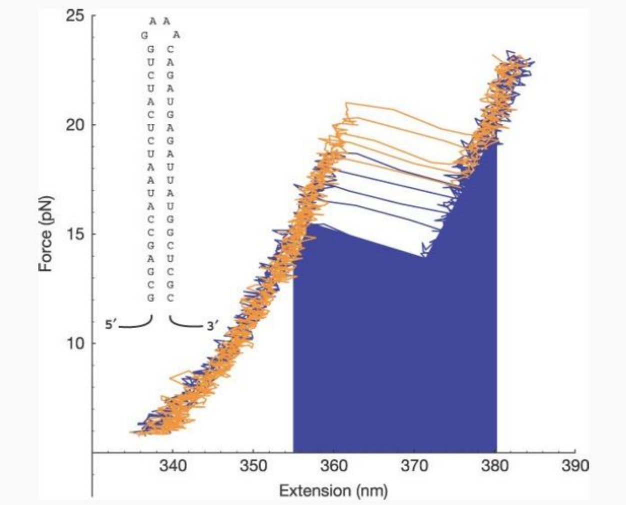
and thermodynamics: biology!

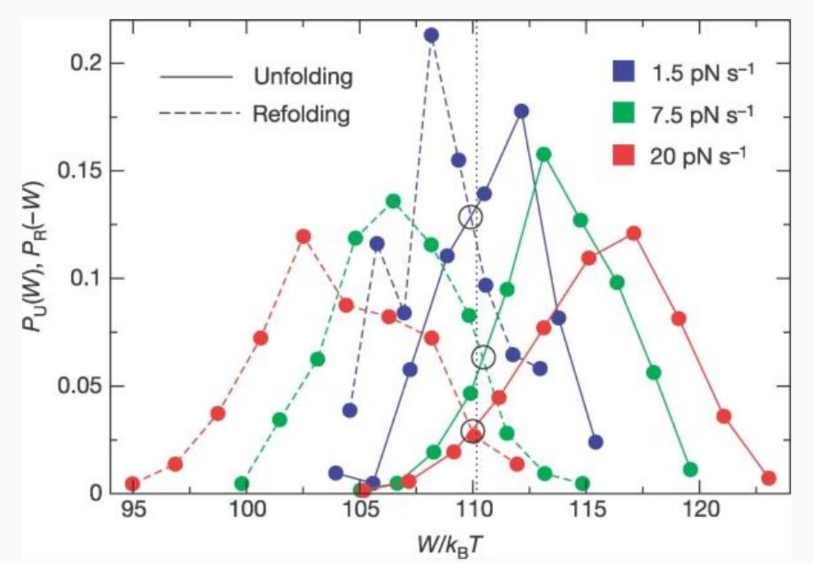
Fluctuations of stochastic reaction processes, entropy, information.

RNA hairpin

COLLIN ET AL. 2005







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 lecture notes by Fourcade (https://www-liphy.univ-grenoble-alpes.fr/IMG/pdf/poly.pdf) and you should read that to back up the lecture summary Ch. 7.

The key points are: what does the Jarzynski equality mean, what happens in its derivation (the details are not required as in "exam") and the Szilard example.

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.