Notes on the Dynamics of Disorder

Quaestiones quaedam philosophicae

(Certain philosophical Problems)

(Open problems regarding the dynamics of disorder

Gavin E. Crooks

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On the Nature of Research

If we knew what we were doing, it would not be called research – Albert Einstein

Below are several introductory problems in non-equilibrium thermodynamics. These are open, research grade problems. This means that I don't know the answers. In fact the questions may not even be well formed, tractable, or interesting. Nor do I know that the problem hasn't already been resolved. The correct solution may involve an hour ~~in the library~~ on Google tracking down the right citation. Or the solution might require 5 years and a thesis. *caveat emptor.*

1 The fluctuations of dissipation

1.1 Hummer-Szabo iso-tension extension

In single molecule pulling experiments, the experimentalist directly controls the distance between a fixed bead and the centre of the optical trap. Therefore, they are directly measuring the free energy as a function of extension (and including a contribution form the free energy of the tap itself.) Hummer and Szabo showed how to remove the free energy of the harmonic trap [2, 3], so that you can obtain the free energy of the molecule as a function of molecular extension.

Problem: Can adapt the Hummer-Szabo trick so as to transform from a constant length ensemble to a constant tension ensemble? The advantage of constant tension is that if the energy is additive $E(x) = E^1(x^1) + E^2(x^2) \ldots$ (say the energy of the DNA handles, plus the energy of a RNA hairpin, plus the energy of the harmonic trap) then the free energy also splits into independent components. Does the math work out? Are the necessary observables actually observable in a real experiment? Bonus: Demonstrate with a computer simulation (Suggestion: Hummer-Szabo have some simple, one-dimensional models of molecular pulling experiments.) Double Bonus: Talk an experimentalist into actually doing the experiment.

1.2 Jarzynski negative dissipation inequality

Chris Jarzynski showed that [1]

$$P(D \leqslant d) \leqslant e^{-d}$$

where D is the dissipation. Prove or disprove that this is a a tight bound. Can one always find a distribution that meets the bound for a particular d? If not, is there a tighter bound?

It might be worth investigating a simple binary distribution for starters. Or it may be possible to always saturate the bound with an appropriate choice of Gaussian distribution. There may also be connections to large deviation statistics.

Bonus: Is it possible to have a system where the entropy goes down more often than not, but the average is still positive? Abstractly the answer is yes, but can we devise a physically reasonable model system that exhibits this behavior.

1.3 From Jarzynski to the the CFT

The Conjugate Fluctuation Theorem immediately implies the Jarzynski equality. But the Jarzynski equality does not appear to directly imply the CFT.

Problem: Can the CFT be derived starting from the Jarzynski equality? Is so, what's the core of the argument? If not, what additional principle has to be adjoined to Jarzynski to recover CFT?

1.4 Fluctuation theorems for Langevin dynamics

Directly proving microscopic irreversibility for particular models of reality is often tricky. Langevin dynamics is particularly tricky. One would like a compact expression for the action (The logarithm of the probability) of a Langevin trajectory, and then show that the action obeys the expected symetry under time reversal. But the math is hard, and the literature is rife with errors.

Several generalized cases of Langevin dynamics do not appear to have been adequately solved. (The approaches I've seen for the cases below are either incomplete, or so obscure that I can't tell if the solution is correct. Or both.)

1) What is the action for a Langevin trajectory with position dependent friction? (For instance, a colloidal particle will have a different friction coefficient near a wall due to hydrodynamic effects.) Provide a transparent derivation.

2) Bonus: What's the action for *overdampled* Langevin dynamics with position dependent friction? It turns out that the overdamped limit is really hard to get right. The mathematics is tough.

3) Prove the work fluctuation theorem for *generalized* Langevin dynamics. There are at least two papers that purport to do this, written almost simultaneously. (Find them, I've mislaid the references.) But they both assume that initially the system and environment are decoupled, so that initially there are are no correlations between the environment and system. This seems like a copout, since it is those bath-system correlations that make generalized Langevin dynamics interesting. Remove the copout. (This may require careful consideration of the flow of energy and information between the system and environment. And instead of an initial state, the initial condition will have to be an entire trajectory segment.)

References

[1] C. Jarzynski. Microscopic analysis of Clausius-Duhem processes. *J. Stat. Phys.*, 96(1-2):415–427, 1999. doi:10.1023/A:1004541004050. (page 1).

[2] G. Hummer and A. Szabo. Free energy reconstruction from nonequilibrium single-molecule pulling experiments. *Proc. Natl. Acad. Sci. U.S.A.*, 98(7):3658–3661, 2001. doi:10.1073/pnas.071034098. (page 1).

[3] G. Hummer and A. Szabo. Free energy surfaces from single-molecule force spectroscopy. *Acc. Chem. Res.*, 38(7):504–513, 2005. doi:10.1021/ar040148d. (page 1).