Langevin equation and Thermodynamics

Relating Stochastic dynamics with Thermodynamic Laws

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MOTIVATION

- There are at least three levels of description of classical dynamics: **thermodynamic**, **stochastic** and **microscopic**
- Thermodynamics and microscopic Hamiltonian dynamics are connected by Boltzmann formalism. Similarly, how do we relate thermodynamics to stochastic dynamics?
- More specifically, can the laws of thermodynamics be applied to stochastic, non equilibrium systems?

- We begin from Langevin and Fokker-Planck equation
- Langevin equation:

$$\dot{x} = \mu F(x, \lambda) + \zeta \tag{1}$$

  where the force $F(x, \lambda) = -\partial_x V(x, \lambda) + f(x, \lambda)$
- λ is an external control parameter of the force
- The noise characterized by $\langle \zeta(\tau) \rangle = 0$ and $\langle \zeta(\tau)\zeta(\tau') \rangle = 2D\delta(\tau - \tau')$ with $D = \mu T$ (Einstein relation)

Fokker-Planck equation

- Fokker Planck equation:

$$
\begin{aligned}
\partial_\tau p(x,\tau) &= -\partial_x j(x,\tau) \\
&= -\partial_x(\mu F(x,\lambda)p(x,\tau) - D\partial_x p(x,\tau))
\end{aligned} \tag{2}
$$

- The Langevin equation describes the evolution of an individual trajectory, while the Fokker-Planck describes the evolution of the ensemble.

LANGEVIN AND FOKKER-PLANCK EQUATION

- Path integral representation to Langevin dynamics:

$$p[x(\tau)|x_0] \equiv exp\Big[-\int_0^t d\tau \Big(\frac{(\dot{x}-\mu F)^2}{4D} + \frac{\mu \partial_x F}{2}\Big)\Big] \qquad (3)$$
$$\equiv exp[-\mathcal{A}[x(\tau)]]$$

- Here the action $\mathcal{A} = \frac{1}{D}\int L d\tau$ with the Lagrangian $L = \frac{(\dot{x}-\mu F)^2}{4} + \frac{\mu D \partial_x F}{2}$

LANGEVIN DYNAMICS

PATH INTEGRAL FORMALISM

- We have the Langevin equation $\dot{x} = \mu F(x, \lambda) + \zeta$
- We discretize time ($t \equiv i\epsilon$, $i = 0, \cdots, N$) and rewrite discrete Langevin equation (Stratonovich discretization).

$$\frac{x_i - x_{i-1}}{\epsilon} = \frac{\mu}{2}[F_i(x_i) + F_{i-1}(x_{i-1})] + \zeta_i \tag{4}$$

- The probability distribution of the x_i is related to the Gaussian noise distribution with a transformation Jacobian.

$$p(\{x_i\}|x_0) = det(\frac{\partial \zeta_j}{\partial x_i})p(\{\zeta_j\}) \tag{5}$$

PATH INTEGRAL FORMALISM

- The noise distribution is Gaussian $p(\zeta_j) \sim exp(-\frac{\epsilon}{4D}\zeta_j^2)$ and the first two moments are characterized by $\langle \zeta_j \rangle = 0$ and $\langle \zeta_i \zeta_j \rangle = \frac{2D}{\epsilon}\delta_{ij}$
- The Gaussian noise translates into the Gaussian part of the action, the determinant yields the non-Gaussian force derivative contribution.
- In discrete form the equation becomes:

$$p(\{x_i\}|x_0) \equiv exp\Big[- \frac{1}{4D\epsilon}\Big[\sum_{i=1}^{N}(x_i - x_{i-1} - \epsilon\mu F_i(x_i))^2\Big] - \frac{\epsilon\mu}{2}\sum_{i=1}^{N}\partial_{x_i}F_i(x_i)\Big] \tag{6}$$

- $\epsilon \to 0$ yields the continuous limit.

- Here we identify heat dissipated by the system as q (contrary to our usual thermodynamic convention). So $dq = -dQ$
- Potential has two contributions: $dV = \frac{\partial V}{\partial \lambda} d\lambda + \frac{\partial V}{\partial x} dx$
- external work done: $dw = \frac{\partial V}{\partial \lambda} d\lambda + f dx$
- From energy conservation then, heat dissipated is

$$\begin{aligned} dq &= dw - dV \\ &= F dx \end{aligned} \tag{7}$$

- For an individual trajectory then, $w[x(\tau)] - q[x(\tau)] = \int_0^t d\tau [\frac{\partial V}{\partial \lambda} \dot{\lambda} + \frac{\partial V}{\partial x} \dot{x}] = V(x_t, \lambda_t) - V(x_0, \lambda_0)$

- Total entropy of the given system:

$$S(\tau) = -\int dx p(x,\tau) \ln p(x,\tau) \tag{8}$$

- This can be rewritten as $S(\tau) = \langle - \ln p(x,\tau) \rangle_{neq}$
- We identify the **stochastic entropy** as $s(\tau) = - \ln p(x,\tau)$ so that system entropy $S(\tau) = \langle s(\tau) \rangle_{neq}$.
- Stochastic entropy change is then $\Delta s = - \ln \frac{p(x_t,\lambda_t)}{p(x_0,\lambda_0)}$

Second Law

Integral Fluctuation Theorem

- Total entropy change along a trajectory $\Delta S_{tot} \equiv \Delta S_m + \Delta s$
- Our claim is that using $p[x(\tau)|x_0] \equiv exp[-\mathcal{A}[x(\tau)]]$ and the concept of time reversed paths, we will present a stronger form of the second law of Thermodynamics.
- This is the Integral Fluctuation Theorem (IFT) that states that ΔS_{tot} follows the equality $\langle exp(-\Delta S_{tot}) \rangle = 1$

Second Law

Time forward and time reversed

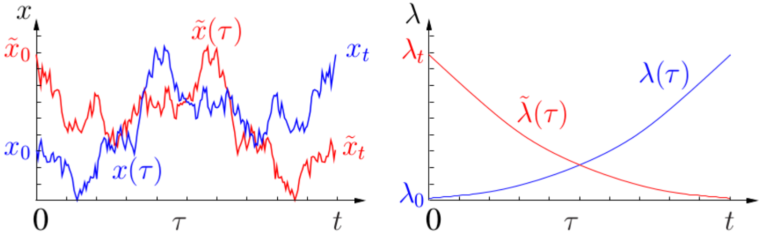

Figure: Time forward(blue) and time reversed(red) trajectories of position and external parameter λ [4]. Mathematically, $\tilde{\lambda}(\tau) \equiv \lambda(t-\tau)$, $\tilde{x}(\tau) \equiv x(t-\tau)$. So, $\tilde{x}_t = x_0$ and $\tilde{x}_0 = x_t$.

Second law

proof of IFT

- We begin with $p[x(\tau)|x_0] \equiv exp[-\mathcal{A}[x(\tau)]]$
- For time reversed path: $p[\tilde{x}(\tau)|\tilde{x}_0] \equiv exp[-\tilde{\mathcal{A}}[\tilde{x}(\tau)]]$
- Since $A[x(\tau)] = \int_0^t d\tau \left(\frac{(\dot{x}-\mu F)^2}{4D} + \frac{\mu \partial_x F}{2} \right)$, $\tilde{A}[\tilde{x}(\tau)]$ is given by $\int_0^t d\tau \left(\frac{(\dot{\tilde{x}}-\mu F)^2}{4D} + \frac{\mu \partial_{\tilde{x}} F}{2} \right)$
- Because only $\dot{x}$ is odd under time reversal, in the ratio of probabilities only the cross term remains

$$
\begin{aligned}
\frac{p[x(\tau)|x_0]}{p[\tilde{x}(\tau)|\tilde{x}_0]} &= exp\Big[\frac{\mu}{D}\int_0^t d\tau \dot{x}(\tau) F(x(\tau), \lambda(\tau))\Big] \\
&= exp[q[x(\tau)]/T] \\
&= exp[\Delta S_m]
\end{aligned} \tag{9}
$$

Proof of IFT

Normalization

- If we sum over all possible paths originating in x_0, then it will sum up to one. $1 = \int_{x_0} d[x(\tau)]p[x(\tau)|x_0]$

$$\begin{aligned} 1 &= \int p_0(x_0)dx_0 \int_{x_0} d[x(\tau)]p[x(\tau)|x_0] \\ &= \int d[x(\tau)]p[x(\tau)|x_0]p_0(x_0) \end{aligned} \tag{10}$$

- Similarly for the time reversed path:

$$1 = \int d[\tilde{x}(\tau)]p[\tilde{x}(\tau)|\tilde{x}_0]p_1(\tilde{x}_0) \tag{11}$$

- We rewrite eq. 11 as:

$$1 = \int d[\tilde{x}(\tau)]p[x(\tau)|x_0]p_0(x_0)\frac{p[\tilde{x}(\tau)|\tilde{x}_0]p_1(\tilde{x}_0)}{p[x(\tau)|x_0]p_0(x_0)} \qquad (12)$$

- Sum over backward paths is equivalent to sum over forward paths.

$$1 = \int d[x(\tau)]p[x(\tau)|x_0]p_0(x_0)exp[-\Delta S_m]\frac{p_1(x_t)}{p_0(x_0)} \qquad (13)$$

- So $\langle exp[-\Delta S_m]\frac{p_1(x_t)}{p_0(x_0)}\rangle = 1$

Second law

Proof of IFT

- By definition of Stochastic entropy, $\Delta s = -\ln \frac{p(x_t,\lambda_t)}{p(x_0,\lambda_0)}$
- $p_1(x_t)$ was the initial distribution of the time reversed path, or in other words the final distribution of the time forward path.
- So we gain $\langle exp(-\Delta S_m - \Delta s)\rangle = \langle exp(-\Delta S_{tot})\rangle = 1$
- This is the formulation of Integral Fluctuation Theorem (IFT). Using Jensen's inequality ($\langle e^x \rangle \geqslant e^{\langle x \rangle}$) one gets back $\langle \Delta S_{tot} \rangle \geqslant 0$.

JARZYNSKI RELATION

- In our expression $\langle exp[-\Delta S_m]\frac{p_1(x_t)}{p_0(x_0)}\rangle = 1$, if we consider initial and final states to be equilibrium states, then:

$$p_0(x) = \frac{1}{\mathcal{Z}} e^{-\frac{V(x,\lambda_0)}{T}} = e^{-\frac{V(x,\lambda_0)-\mathcal{F}(\lambda_0)}{T}}$$

- Similarly $p_1(x) = e^{-\frac{V(x,\lambda_t)-\mathcal{F}(\lambda_t)}{T}}$
- Putting in the values:

$$\left\langle exp\left[-\frac{q}{T}\right] exp\left[-\frac{\Delta V - \Delta\mathcal{F}}{T}\right]\right\rangle = 1$$

- Using $q = w - \Delta V$, we find that:

$$\langle exp[-w/T]\rangle = exp[-\Delta F/T] \tag{14}$$

- This is the **Jarzynski relation** which relates equilibrium free energy difference with non equilibrium work.

CONCLUSION

- Our aim was to demonstrate how one can relate laws of Thermodynamics to stochastic non equilibrium systems.
- We find that the first law can be applied on the level of individual trajectories.
- Using the concept of time forward and time reversed paths, we derived a stronger statement of the second law of thermodynamics valid for an ensemble.
- From IFT, one can derive the Jarzynski relation that relates the free energy difference of states with non equilibrium work.

References

[1] Seifert U., *Stochastic thermodynamics, fluctuation theorems, and molecular machines*, 2012

[2] Sekimoto K., *Langevin Equation and Thermodynamics*, 1998

[3] Crooks G., *Entropy production fluctuation theorem and the nonequilibrium work relation for free energy differences*, 2008

[4] Seifert U., *Stochastic thermodynamics: lecture notes, Research centre Jülich*, 2008

THANK YOU

- A convex function is a continuous function whose value at the midpoint of every interval in its domain does not exceed the arithmetic mean of its values at the ends of the interval.

$$\lambda f(x_1) + (1-\lambda) f(x_2) \geqslant f(\lambda x_1 + (1-\lambda) x_2)$$

- This generalizes to:

$$\sum_{i=1}^{N} a_i f(x_i) \geqslant f(\sum_{i=1}^{N} a_i x_i)$$

with $\sum_{i=1}^{N} a_i = 1$

- We take $a_i = 1/N$ and identify $f(x) = e^x$ as a convex function.
- We get $\langle e^x \rangle \geqslant e^{\langle x \rangle}$