Fluctuation theorem and entropy production in statistical mechanics and turbulence

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Non-equilibrium Stat Mech & Turbulence, Warwick, July 2006

Outline

1. Fluctuation Theorems & Work Relations
   - Equilibrium vs Non-Equilibrium
   - Langevin Model
   - Path Integral & Configurational entropy
   - Derivations & Applications
2. Statistics of Entropy Production
   - Large Deviation Functional and Fluctuation Theorem
   - Polymer in a (gradient) flow, regular and chaotic
3. Entropy/Work Production in Turbulence: Speculations
   - Work & Kolmogorov flux

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- Equilibrium = Detailed Balance + No External Fields
  FLUCTUATION DISSIPATION THEOREM
  e.g. molecule/polymer in a thermal bath
- Non-Equilibrium #1
  Under Detailed Balance but in Time-Dependent External Field
  WORK (JARZYNSKI) RELATION
  e.g. manipulations with bio-molecules
- Non-Equilibrium #2
  Statistical Steady State with Broken Detailed Balance
  FLUCTUATION THEOREM
  e.g. polymer in a steady flow; statistically steady turbulence
- Generic Non-Equilibrium
  Temporarily Driven with Broken Detailed Balance
  FLUCTUATION THEOREM
  e.g. Rayleigh-Taylor Turbulence

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Fluctuation Theorem

Non-Conservative Forces but Autonomous Dynamics (Non-Equilibrium #2)

$$\frac{p(+\Sigma)}{p(-\Sigma)} = e^{\Sigma},$$

$p(\Sigma)$ is the distribution of observed values of a quantity Σ representing dissipation or entropy production.

Bibliography:

Evans, Cohen, Morris (1993)
Evans, Searles (1994)
Gallavotti, Cohen (1995)
Kurchan (1998)
Lebowitz, Spohn (1999)

Work (Entropy Production) Relation

Non-Autonomous Dynamics (Non-Equilibrium #1): for any fixed value of an externally controlled, λ, system is in a Gibbs' state, characterized by the free energy, $\mathcal{F}(\lambda)$. Executing a fixed time-dependent protocol, $\lambda(t)$, $-\tau < t < \tau$, repeatedly one gets the following relation for average

Jarzynski equality:

$$\langle e^{-\Sigma} \rangle = \exp\left(\mathcal{F}_{\lambda(-\tau)} - \mathcal{F}_{\lambda(+\tau)}\right)$$

Bibliography:

Bochkov, Kuzovlev (1977)
Jarzynski (1997)
Crooks (1998,1999,2000)
Hatano (1999)
Hummer, Szabo (2001)
Hatano, Sasa (2001)

Unified Framework: Generalized Fluctuation Theorems and Work Relations

Fluctuation Theorem:

$$\frac{p(+\Sigma')}{p(-\Sigma')} = e^{\Sigma'},$$

Jarzynski Equality:

$$\langle e^{-\Sigma'} \rangle = 1$$

Recent Progress:

Maes, Poincaré (2003)
Maes, Netocny (2003)
Chernyak, Chertkov, Jarzynski (2005,2006)
Seifert (2005)
Kurchan (2005)
Reid, Sevick, Evans (2005)
Speck, Seifert (2005)
Imparato, Peliti (2006)

Outline

Langevin Model

- Over-damped classical system *(e.g. polymer in a solution)*

$$\frac{d}{dt}x_i = F_i(\mathbf{x};\lambda) + \xi_i(t;\mathbf{x};\lambda), \quad i = 1,\cdots,N$$

$$\langle \xi_i \rangle = 0, \quad \left\langle \xi_i(t)\,\xi_j(t') \right\rangle = G_{ij}\,\delta(t-t')$$

- Fokker-Planck

$$\frac{\partial p}{\partial t} = -\partial^i(F_i p) + \frac{1}{2}\partial^i\left(G_{ij}(\partial^j p)\right) \equiv \mathcal{L}_\lambda p = -\partial^i J_i$$

$$\mathbf{J}(\mathbf{x},t) \equiv (1/2)\mathbf{G}(\mathbf{v}-\nabla)p, \quad p^S(\mathbf{x};\lambda) = \exp\left(-\varphi(\mathbf{x};\lambda)\right)$$

$$v^i \equiv 2\Gamma^{ij}F_j, \quad A^i \equiv v^i + \partial^i\varphi, \quad \Gamma^{ij}G_{jk} = \delta^i_k$$

- Detailed Balance?

SATISFIED

$$\mathbf{v}(\mathbf{x};\lambda) = -\nabla U(\mathbf{x};\lambda)$$

$$p_{\mathrm{stat}}(x) \propto e^{-U(\mathbf{x};\lambda)}$$

BROKEN

$$\mathbf{v}(\mathbf{x};\lambda) \neq -\nabla U(\mathbf{x};\lambda)$$

$$\mathbf{A}, \mathbf{J}_{\mathrm{stat}} \neq \mathbf{0}$$

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Outline

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Path Integral

- Forward/Reversed Protocol: $\lambda^{\rm F}_t$: $[A,B]$; $\lambda^{\rm R}_t=\lambda^{\rm F}_{-t}$.

$$\mathcal{P}^{\rm F/R}[X|\mathbf{x}_{-\tau}] = \mathcal{N}\exp\left(-\int_{-\tau}^{+\tau}dt\,\mathcal{S}_+(\mathbf{x}_t,\dot{\mathbf{x}}_t;\lambda^{\rm F/R}_t)\right),$$
$$\mathcal{P}^{\rm F/R}[X] = p^S_A(\mathbf{x}_{-\tau})\,\mathcal{P}^{\rm F/R}[X|\mathbf{x}_{-\tau}]$$
$$\mathcal{S}_+(\mathbf{x},\dot{\mathbf{x}};\lambda) = \frac{1}{2}(\dot{x}_i-F_i)\Gamma^{ij}(\dot{x}_i-F_i)+\frac{1}{2}\partial^i F_i.$$

- "Conjugated twin" of the trajectory: $X^\dagger\equiv\{\mathbf{x}^\dagger_t\}^{+\tau}_{-\tau}$, $\mathbf{x}^\dagger_t=\mathbf{x}_{-t}$

$$\mathcal{P}^{\rm R}\left[X^\dagger|\mathbf{x}^\dagger_{-\tau}\right]=\mathcal{N}\exp\left[-\int_{-\tau}^{+\tau}dt\,\mathcal{S}_+(\mathbf{x}^\dagger_t,\dot{\mathbf{x}}^\dagger_t;\lambda^{\rm R}_t)\right]$$
$$=\mathcal{N}\exp\left[-\int_{-\tau}^{+\tau}dt\,\mathcal{S}_-(\mathbf{x}_t,\dot{\mathbf{x}}_t;\lambda^{\rm F}_t)\right],\quad \mathcal{S}_-(\mathbf{x},\dot{\mathbf{x}};\lambda)\equiv\mathcal{S}_+(\mathbf{x},-\dot{\mathbf{x}};\lambda)$$

Path Integral

- Forward/Reversed Protocol: λ_t^{F}: $[A,B]$; $\lambda_t^{\mathrm{R}} = \lambda_{-t}^{\mathrm{F}}$.

$$\mathcal{P}^{\mathrm{F/R}}[X|\mathbf{x}_{-\tau}] = \mathcal{N}\exp\left(-\int_{-\tau}^{+\tau} dt\, \mathcal{S}_+(\mathbf{x}_t,\dot{\mathbf{x}}_t;\lambda_t^{\mathrm{F/R}})\right),$$
$$\mathcal{P}^{\mathrm{F/R}}[X] = p_A^S(\mathbf{x}_{-\tau})\,\mathcal{P}^{\mathrm{F/R}}[X|\mathbf{x}_{-\tau}]$$
$$\mathcal{S}_+(\mathbf{x},\dot{\mathbf{x}};\lambda) = \frac{1}{2}(\dot{x}_i - F_i)\Gamma^{ij}(\dot{x}_i - F_i) + \frac{1}{2}\partial^i F_i.$$

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$$= \mathcal{N}\exp\left[-\int_{-\tau}^{+\tau} dt\,\mathcal{S}_-(\mathbf{x}_t,\dot{\mathbf{x}}_t;\lambda_t^{\mathrm{F}})\right], \quad \mathcal{S}_-(\mathbf{x},\dot{\mathbf{x}};\lambda) \equiv \mathcal{S}_+(\mathbf{x},-\dot{\mathbf{x}};\lambda)$$

Configurational Entropy

- Reversed Protocol, Forward Dynamics

$$\frac{\mathcal{P}^{\mathrm{F}}[X]}{\mathcal{P}^{\mathrm{R}}[X^{\dagger}]} = \frac{p_A^S(\mathbf{x}_{-\tau})\mathcal{P}^{\mathrm{F}}[X|\mathbf{x}_{-\tau}]}{p_B^S(\mathbf{x}^{\dagger}_{-\tau})\mathcal{P}^{\mathrm{R}}[X^{\dagger}|\mathbf{x}^{\dagger}_{-\tau}]} = \exp(R^{\mathrm{F}}[X])$$

Entropy/Work

$$R^{\mathrm{F}}[X] = \int^{\mathrm{F}} dt\, \dot{\lambda}_t^{\mathrm{F}} \frac{\partial\varphi}{\partial\lambda} + \int^{\mathrm{F}} d\mathbf{x}\cdot\mathbf{A}$$

$$= \int^{\mathrm{F}} dt\, \left(\dot{\lambda}_t^{\mathrm{F}} \frac{\partial\varphi}{\partial\lambda} + 2\dot{x}_j\Gamma^{ij}F^j + \dot{x}_j\,\partial^j\varphi\right)$$

- There exist other formulations,
  e.g. for Reversed Protocol and Reversed Dynamics

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$$\frac{\mathcal{P}^{\rm F}[X]}{\mathcal{P}^{\rm R}[X^\dagger]} = \frac{p_A^S(\mathbf{x}_{-\tau})\mathcal{P}^{\rm F}[X|\mathbf{x}_{-\tau}]}{p_B^S(\mathbf{x}^\dagger_{-\tau})\mathcal{P}^{\rm R}[X^\dagger|\mathbf{x}^\dagger_{-\tau}]} = \exp(R^{\rm F}[X])$$

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Outline

Fluctuation Theorem

$$\begin{aligned}
\rho^{\mathrm{F}}(R) &\equiv \int \mathcal{D}X\, \mathcal{P}^{\mathrm{F}}[X]\, \delta\left(R - R^{\mathrm{F}}[X]\right) \\
&= \int \mathcal{D}X\, \mathcal{P}^{\mathrm{R}}[X^\dagger]\, \exp\left(R^{\mathrm{F}}[X]\right)\, \delta\left(R - R^{\mathrm{F}}[X]\right) \\
&= \exp(R) \int \mathcal{D}X^\dagger\, \mathcal{P}^{\mathrm{R}}[X^\dagger]\, \delta\left(R + R^{\mathrm{R}}[X^\dagger]\right) \\
&= \exp(R)\rho^{\mathrm{F}}(-R)
\end{aligned}$$

Work (Jarzynski) Relation

$$\Rightarrow \langle \exp(-R) \rangle = \int dR\, \exp(-R)\rho^{\mathrm{F}}(R) = \int dR \rho^{\mathrm{F}}(-R) = 1$$

Application in chem/bio physics

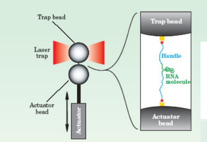

Figure 4. Testing the Jarzynski equality. A molecule of RNA is attached to two beads and subjected to reversible and irreversible cycles of folding and unfolding. A piezoelectric actuator controls the position of the bottom bead, which, when moved, stretches the RNA. An optical trap formed by two opposing lasers captures the top bead, and the change in momentum of light that exits the two-beam trap determines the force exerted on the molecule connecting the two beads. The difference in positions of the bottom and top beads gives the end-to-end length of the molecule. The blowup shows how the RNA molecule (green) is coupled with the two beads via molecular handles (blue). The handles end in chemical groups (red) that can be stuck to complementary groups (yellow) on the bead. The blowup is not to scale: The diameter of the beads is around 3000 nm, much greater than the 20-nm length of the RNA.

Equilibrium Information from Nonequilibrium Measurements in an Experimental Test of Jarzynski's Equality

Jan Liphardt,[1,4] Sophie Dumont,[2] Steven B. Smith,[3] Ignacio Tinoco Jr.,[1,4] Carlos Bustamante[1,2,3,4]*

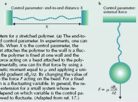

Figure 3. Control parameters for a stretched polymer. (a) The end-to-end distance X is the fixed control parameter. In experiments, one can vary X by moving the walls. When X is the control parameter, the force acting on a bead that attaches the polymer to the wall is a fluctuating variable. (b) Here the polymer is fixed at one wall and the control parameter is the force acting on a bead attached to the polymer at its free end. Experimentally, one can fix that force by using a magnetic bead with magnetic moment equal to μ and applying a uniform external magnetic field gradient $\partial B_z/\partial z$. By changing the value of the gradient, one controls the force F acting on the bead. For a fixed F, the polymer's extension is a fluctuating variable. In general, the relation between force and extension for a small system whose response is not linear will depend on which variable is the control parameter and which is allowed to fluctuate. (Adapted from ref. 17.)

Jarzynski equality:

$$\langle e^{-\Sigma} \rangle = \exp\left(\mathcal{F}_{\lambda(-\tau)} - \mathcal{F}_{\lambda(+\tau)}\right)$$

Gain

Fast exploration of the phase space

But ...

The number of *necessary* observations grows as what is typical in equilibrium is atypical (rare) for a fast protocol, and vise versa.

Current Focus of Research

Design of efficient protocols for the free energy exploration

Outline

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Σ is the generalized work produced by an external field in time, or the energy (heat) dissipated by the system in time t, or the entropy generated in time t

Large Deviation Functional

$$\mathcal{P}(\Sigma;t) \propto \exp\left(-tQ(\Sigma/t)\right)$$

Fluctuation Theorem

$$Q(\omega) - Q(\omega) = \omega$$

disclaimer

"complex" averaging (noise+disorder) may brake FT *(see below)*

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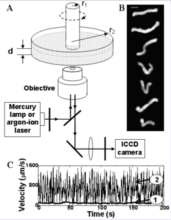
Model

$$\dot{x}_i = \sigma_{ij} x_j - \partial_{x_i} U(\mathbf{x}) + \xi_i$$

$\sigma_{ij}(t) x_j$ is force exerted by flow on polymer

$$\langle \xi_i(t) \xi_j(t') \rangle = 2T\delta(t-t')\delta_{ij}$$



Steinberg et al.(2004)

$$\Sigma \equiv \int_0^t dt' \dot{x}^\alpha(t') \sigma^{\alpha\beta} x^\beta(t')$$

$$\mathcal{P}_\pm \sim \int_{\rho(0)=\mathbf{x}_0}^{\rho(t)=\mathbf{x}_t} \mathcal{D}\rho \exp[-\mathcal{S}_\pm]$$

$$\mathcal{S} = \mathcal{S}_+ - \mathcal{S}_- = \frac{-\Sigma + U(\mathbf{x}(0)) - U(\mathbf{x}(t))}{T}$$

Model

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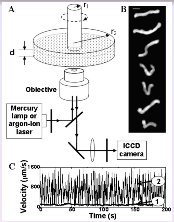

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Generating functional

$$\Psi_s \equiv \exp\left(-\frac{s\Sigma}{T}\right), \quad \partial_t \Psi_s = \hat{L}_s \Psi_s$$

$$\hat{L}_s = -\nabla^\alpha \left(\sigma^{\alpha\beta} x^\beta - \partial_{x^\alpha} U(\mathbf{x})\right) + T\nabla^\alpha \nabla^\alpha$$

$$\nabla^\alpha = \partial^\alpha + \frac{s}{T}\hat{\sigma}^{\alpha\beta} x^\beta$$

Linear elasticity, $U(\mathbf{x}) = \mathbf{x}^2/(2\tau)$ & $\hat{\sigma} = \text{const}$

$t \to \infty$: looking for the "ground" state in a Gaussian form

$$\Psi_s = \exp(-\lambda_s t) \exp\left(-x_i B_s^{ij} x_j\right)$$

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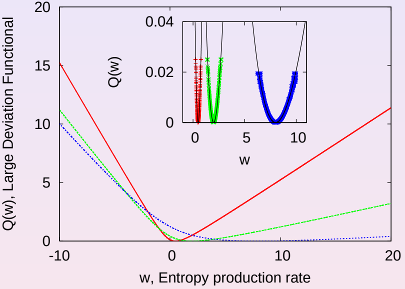
Linear Elasticity, Constant Flow

- $d = 2$
- $\hat{\sigma} = \begin{pmatrix} a & b + c/2 \\ b - c/2 & -a \end{pmatrix}$

Answer

$$\mathcal{P}(\Sigma) \sim \exp\left(-tQ(\Sigma/(Tt))\right)$$

$$Q(w) = \frac{\sqrt{(4+c^2\tau^2)(w^2+c^2\tau^2)}}{2c\tau} - 1 - \frac{w}{2}$$



To notice

- $Q(w)$ depends only on rotation, c
- FT is satisfied: $Q(w) - Q(-w) = w$
- Linear asymptotics for large deviations, $|\omega| \gg 1$

Chaotic flow case

Annealed vs Quenched

- $\mathcal{F}_\sigma \equiv \langle \mathcal{P}_\sigma(\Omega) \rangle_\xi$

  $\log\langle\mathcal{F}_\sigma\rangle_\sigma \quad \text{vs} \quad \langle\log\mathcal{F}_\sigma\rangle_\sigma$

- Standard FT for annealed: $Q(w) - Q(-w) = w$

- Modified FT for quenched: $\langle[\mathcal{F}_\sigma]^n\rangle \sim \exp\left(-tQ_n(\Omega/Tt)\right)$

  $Q_n(w) - Q_n(-w) = nw$

Lack of FT for the Largish Deviations: $w \gg \langle w \rangle$

Gaussian $\hat{\sigma}$: $-\log\langle\mathcal{F}_\sigma\rangle \propto \sqrt{w}$

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$$\partial_t \mathbf{u} + (\mathbf{u}\nabla)\mathbf{u} + \nabla p = \nu \Delta \mathbf{u} + \mathbf{f}$$

Work produced in time t

$\Sigma_1 = 1/2 \int_0^t dt' \int d\mathbf{r}(\mathbf{uf})$

Energy dissipated in time t

$\Sigma_2 = \nu/2 \int_0^t dt' \int d\mathbf{r}(\nabla u)^2$

Suggestions:

- Test Large Deviations: at $t \gg \tau_L$, $\mathcal{P}(\Sigma) \sim \exp\left(-tQ(\Sigma/t)\right)$ In case it works, $Q(w)$ may serve gives an ultimate measure of possible "universality" classes in turbulence
- Check if Fluctuation Theorem applies: $Q(w) - Q(-w) = w$
- Verify if $Q_1 = Q_2 = \cdots$
- Work Relations and Protocol Optimization may find practical applications in Non-Stationary Turbulence

$$\partial_t \mathbf{u} + (\mathbf{u}\nabla)\mathbf{u} + \nabla p = \nu \Delta \mathbf{u} + \mathbf{f}$$

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$\Sigma_2 = \nu/2 \int_0^t dt' \int d\mathbf{r}(\nabla u)^2$

Suggestions:

- Test Large Deviations: at $t \gg \tau_L$, $\mathcal{P}(\Sigma) \sim \exp\left(-tQ(\Sigma/t)\right)$ In case it works, $Q(w)$ may serve gives an ultimate measure of possible "universality" classes in turbulence
- Check if Fluctuation Theorem applies: $Q(w) - Q(-w) = w$
- Verify if $Q_1 = Q_2 = \cdots$
- Work Relations and Protocol Optimization may find practical applications in Non-Stationary Turbulence

Summary

- Production of entropy/work (in finite time) is a universal characteristic explaining breakdown of the detailed balance
- Generalized Fluctuation Theorem gives a useful and nontrivial relation
- Large Deviation Functional is an ultimate and rich tester of a non-equilibrium stat mech system (e.g. turbulence)