Onsager-Machlup Theory for Nonequilibrium Steady States and Fluctuation Theorems

Tooru Taniguchi and E. G. D. Cohen

The Rockefeller University, New York

1. Introduction

1.1. Past : Fluctuation Theories in Nonequilibrium Physics

- **Fluctuation-Dissipation Theorem**

  (*Near equilibrium:* Transport coefficients and fluctuation correlations)

- **Onsager-Machlup Fluctuation Theory**

  (*Near equilibrium:* Relaxation process → average decay of a fluctuation away from equilibrium follows linear macroscopic law; Onsager's principle of minimum energy dissipation; the most probable path)

- **Fluctuation Theorems**

  ("*Far" from equilibrium:* Asymmetric property of probability distribution functions of fluctuations)

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1.2. New : Contents of This Talk

1. **Generalization of Onsager-Machlup Fluctuation Theory to Nonequilibrium Steady States**

Onsager-Machlup Lagrangian → Transition probability

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Entropy production → Second law of thermodynamics *(for average)*

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Heat
Work, Internal energy → Energy conservation law *(for any fluctuation)*

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2. **Fluctuation Theorems by a Functional Integral Approach**

- Nonequilibrium detailed balance relations
- Fluctuation theorems for work and friction
- Extended fluctuation theorem for heat

1.3. Model: Dragged Brownian Particle

(for a nonequilibrium steady state)

- **Langevin Equation**

Friction force

$$m\frac{d^2x_t}{dt^2} = -\alpha\frac{dx_t}{dt} - \kappa\,(x_t - vt) + \zeta_t$$

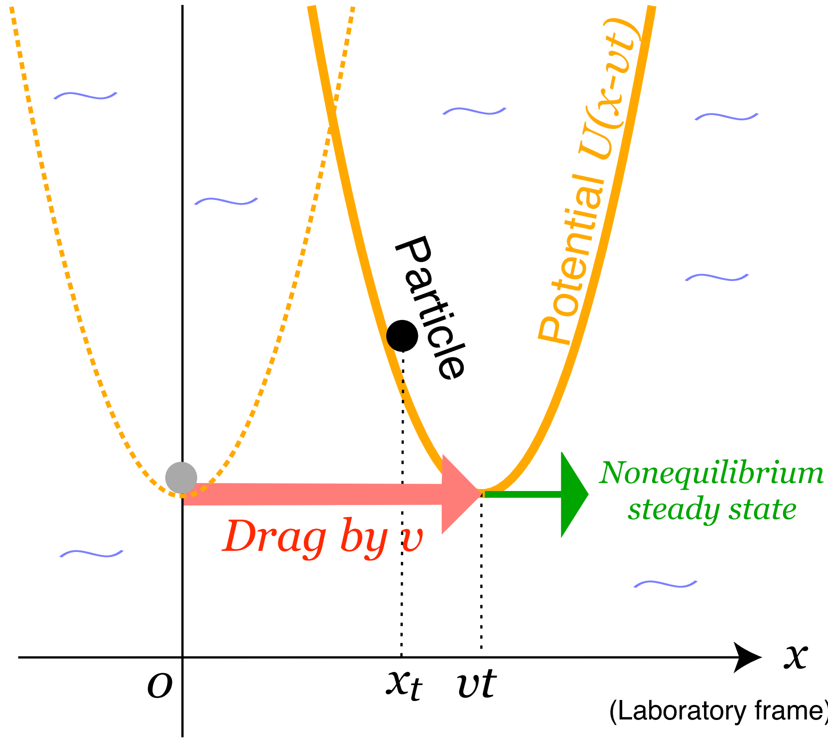
Harmonic force

$$U(x) = \frac{1}{2}\kappa x^2$$

Gaussian-white noise

$$\langle \zeta_t \rangle = 0,$$

$$\langle \zeta_{t_1}\zeta_{t_2} \rangle = \frac{2\alpha}{\beta}\delta(t_1 - t_2)$$



- **Over-Damped Assumption**

Neglect inertial effect: $m\, d^2x_t/dt^2 \approx 0$ (or simply $m \approx 0$)

$$\frac{dx_t}{dt} = -\frac{1}{\tau_r}(x_t - vt) + \frac{1}{\alpha}\zeta_t \quad , \qquad \tau_r \equiv \frac{\alpha}{\kappa}$$

- **Comoving Frame y : Frame Moving with Velocity v**

$$y_t \equiv x_t - vt$$

$$\frac{dy_t}{dt} = -\frac{1}{\tau_r}y_t - v + \frac{1}{\alpha}\zeta_t$$

Nonequilibrium effect

Laboratory experiments (e.g. a Brownian particle captured in an optical trap, or an electric circuit consisting of a resister and capacitor, etc.)

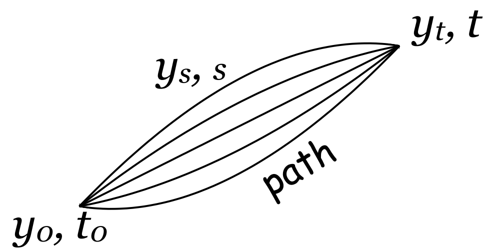
2. Onsager-Machlup Theory for Nonequilibrium Steady States

- **Transition Probability of Particle Position in Time**

$$F\begin{pmatrix} y_t & y_0 \\ t & t_0 \end{pmatrix} = \int_{y_0}^{y_t} \mathcal{D}y_s \, \exp\left[\int_{t_0}^{t} ds \, L^{(v)}(\dot{y}_s, y_s)\right]$$

Functional integral

Probability functional for a path $\{y_s\}$



- **Onsager-Machlup Lagrangian function**

$D \equiv \frac{k_B T}{\alpha}$ Einstein relation

$$L^{(v)}(\dot{y}_s, y_s) \equiv -\frac{1}{4D}\left(\dot{y}_s + v + \frac{y_s}{\tau_r}\right)^2$$

$$= -\frac{1}{2k_B}\left[\frac{\alpha}{2T}(\dot{y}_s + v)^2 + \frac{\alpha}{2T}\left(\frac{y_s}{\tau_r}\right)^2 - \dot{\mathcal{S}}^{(v)}(\dot{y}_s, y_s)\right]$$

- **Connection with Thermodynamics**

$$\dot{\mathcal{S}}^{(v)}(\dot{y}_s, y_s) \equiv -\frac{1}{T}\kappa y_s(\dot{y}_s + v)$$ Entropy production rate, because:

[i] Second Law of Thermodynamics *(holds for average)*

$$\dot{S}^{(v)}(\langle \dot{y}_t \rangle, \langle y_t \rangle) \geq 0$$

[ii] Energy Conservation Law *(holds for any fluctuation)*

$$\mathcal{Q}_t(\{y_s\}) = \mathcal{W}_t^{(v)}(\{y_s\}) - \Delta\mathcal{U}(y_t, y_0)$$

Nonequilibrium effect
(zero in equilibrium: v=0)

Heat

$$\mathcal{Q}_t(\{y_s\}) \equiv T \int_{t_0}^{t} ds\, \dot{S}^{(v)}(\dot{y}_s, y_s)$$

Entropy production rate

Functional

Work

$$\mathcal{W}_t^{(v)}(\{y_s\}) \equiv \int_{t_0}^{t} ds\, (-\kappa y_s) v$$

Harmonic Force

Internal Energy Difference

$$\Delta\mathcal{U}(y_t, y_0) \equiv U(y_t) - U(y_0)$$

Potential $U(y) = \frac{1}{2}\kappa y^2$

3. Fluctuation Theorems

- **Nonequilibrium Detailed Balance (I)**

  [Due to non-zero υ: nonequilibrium effect]

Probability for a forward path

Boltzmann factor for work done

$$f_{eq}(y_0)\, e^{\int_{t_0}^{t} ds\, L^{(\upsilon)}(\dot{y}_s, y_s)}\, e^{-\beta \mathcal{W}_t^{(\upsilon)}(\{y_s\})}$$

$$= f_{eq}(y_t)\, e^{\int_{t_0}^{t} ds\, L^{(-\upsilon)}(-\dot{y}_s, y_s)}$$

Probability for a backward path

Equilibrium detailed balance for υ=0

$$f_{eq}(y_0)\, F\left(\begin{array}{c|c} y_t & y_0 \\ t & t_0 \end{array}\right)\Bigg|_{\upsilon=0} = f_{eq}(y_t)\, F\left(\begin{array}{c|c} y_0 & y_t \\ t & t_0 \end{array}\right)\Bigg|_{\upsilon=0}$$

Equilibrium distribution

$$f_{eq}(y) = \sqrt{\frac{\kappa\beta}{2\pi}} \exp\left[-\beta U(y)\right]$$

3.1. Fluctuation Theorem for Work

- Distribution function of (dimensionless) work

$$P_w(W,t) = \left\langle\!\left\langle \delta\left(W - \beta \mathcal{W}_t^{(v)}(\{y_s\})\right)\right\rangle\!\right\rangle_t$$

Functional average

$$\langle\!\langle X(\{y_s\})\rangle\!\rangle_t \equiv \int dy_t \int_{y_0}^{y_t} \mathcal{D}y_s \int dy_0 \; e^{\int_{t_0}^{t} ds\, L^{(v)}(\dot{y}_s, y_s)} f(y_0,t_0)\, X(\{y_s\})$$

Distribution of y_o at t_o

- Work fluctuation theorem

Nonequilibrium detailed balance

$$\lim_{t\to+\infty} \frac{P_w(W,t)}{P_w(-W,t)} = \exp(W)$$

for any $f(y_0,t_0)$

3.2. Fluctuation Theorem for Friction

- Energy loss by friction

$$\mathcal{R}_t^{(v)}(y_t, y_0) = \int_{t_0}^{t} ds\ (-\alpha \dot{y}_s)\, v$$

Friction force

Boltzmann factor for energy loss by friction

- Nonequilibrium detailed balance (II)

No change of the sign of v

$$f_{eq}(y_0) e^{\int_{t_0}^{t} ds\ L^{(v)}(\dot{y}_s, y_s)} e^{-\beta \mathcal{R}_t^{(v)}(y_t, y_0)} = f_{eq}(y_t)\, e^{\int_{t_0}^{t} ds\ L^{(v)}(-\dot{y}_s, y_s)}$$

- Distribution function of (dimensionless) friction

$$P_r(R,t) = \left\langle\!\!\left\langle\ \delta\left(R - \beta \mathcal{R}_t^{(v)}(y_t, y_0)\right)\ \right\rangle\!\!\right\rangle_t$$

- Friction fluctuation theorem

$$\frac{P_r(R,t)}{P_r(-R,t)} = \exp(R) \qquad \text{for} \qquad f(y_0, t_0) = f_{eq}(y_0)$$

(The friction FT is not correct for the steady state initial condition even for $t \to \infty$.)

3.3. Extended Fluctuation Theorem for Heat
(in the long time limit)

- Heat distribution function

Work distribution (Gaussian)

Energy-difference distribution (Exponential)

$$P_q(Q,t) \overset{t\to+\infty}{\sim} \int dW \int d\Delta\mathcal{U}\, P_w(W,t)\, P_{\Delta e}(\Delta\mathcal{U},t)\, \delta(Q-W+\Delta\mathcal{U})$$

$$= \left[e^{-Q+2\overline{W}_t} \mathrm{erfc}\left(-\frac{Q-3\overline{W}_t}{2\sqrt{\overline{W}_t}}\right) + e^{Q} \mathrm{erfc}\left(\frac{Q+\overline{W}_t}{2\sqrt{\overline{W}_t}}\right)\right]$$

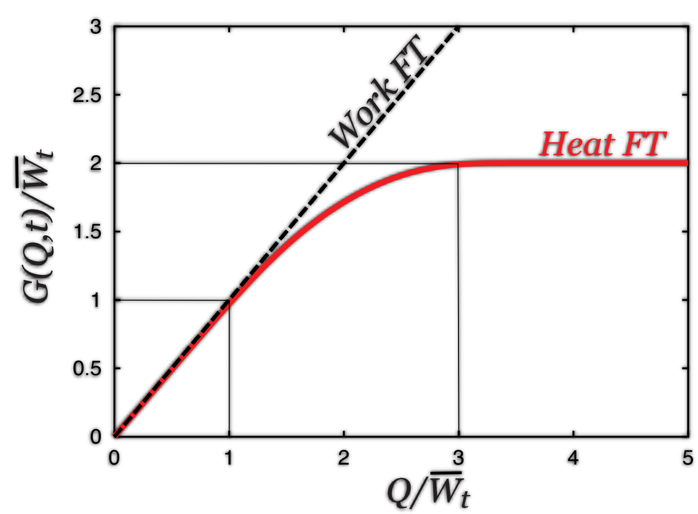
Energy conservation

Exponential tail

$$\overline{W}_t \overset{t\to+\infty}{\sim} \alpha\beta v^2 t\ , \quad \mathrm{erfc}(x) \equiv (2/\sqrt{\pi}) \int_x^{+\infty} dz\ \exp(-z^2)$$

- Heat fluctuation theorem (scaled)

$$G(Q,t) \equiv \ln \frac{P_q(Q,t)}{P_q(-Q,t)}$$



Experimental check of the heat FT using an electric circuit (Garnier and Ciliberto, 2005)

4. Conclusion

- **Generalization of Onsager-Machlup Theory to Nonequilibrium Steady States**
  - Thermodynamics and fluctuations from the Onsager-Machlup Lagrangian function (the second law of thermodynamics, the energy conservation law, etc.)

Onsager-Machlup Lagrangian function

- **Fluctuation Theorems using a Functional Integral Approach**
  - Usage of nonequilibrium detailed balance relations for derivation of fluctuation theorems for work and friction
  - Simple argument for the extended fluctuation theorem for heat

Reference: T. Taniguchi and E. G. D. Cohen, e-print cond-mat/0605548

Appendix: Notations in This Talk

- **m**: mass
- **α**: friction coefficient
- **κ**: spring constant
- **T**: temperature
- **k_B**: Boltzmann constant
- **$\beta=1/(k_B T)$**: inverse temperature
- **v**: velocity to drag the particle
- **$\tau_r= \alpha/\kappa$**: relaxation time
- **ζ_t**: Gaussian white random force
- **$\langle \ldots \rangle$**: ensemble average
- **$D=1/(\alpha\beta)$**: diffusion constant
- **$U(y)$**: harmonic potential
- **$L^{(v)}(\dot{y},y)$**: Lagrangian function
- **$\dot{S}^{(v)}(\dot{y},y)$**: entropy production rate
- **Q**: heat
- **W**: work
- **ΔU**: internal energy difference
- **$f_{eq}(y)$**: equilibrium distribution function
- **$f(y,t)$**: distribution of position y at time t
- **$P_w(W,t)$**: work distribution
- **$P_r(R,t)$**: friction distribution
- **$P_q(Q,t)$**: heat distribution
- **$\langle\langle \ldots \rangle\rangle_t$**: functional average