Quasi-Static Hydrodynamic Limits and their Large Deviations

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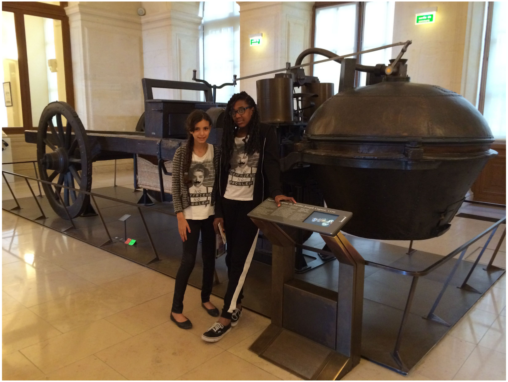
The problem with thermodynamics

> *Every mathematician knows that it is impossible to understand any elementary course in thermodynamics.*

V.I. Arnold, Contact Geometry: the Geometrical Method of Gibbs's Thermodynamics. (1989)

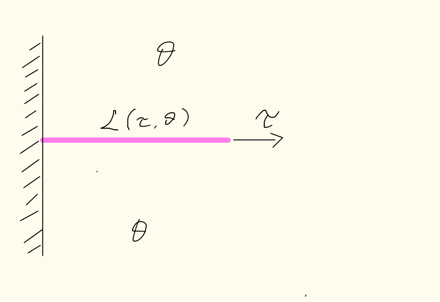
Thermodynamics concerns **Macroscopic Objets** at **Macroscopic Time Scale**

Vapor machine of Joseph Cugnot (1770)



A simple thermodynamic system

A one dimensional system (rubber under tension):



Mechanical Equilibrium:

$$\mathcal{L} = \mathcal{L}(\tau), \qquad \tau = \text{tension}$$

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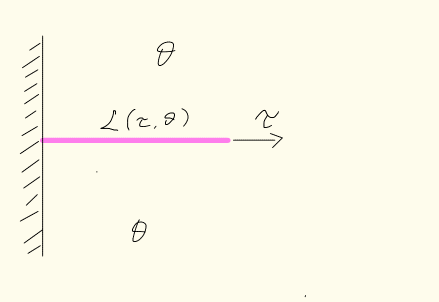

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Thermodynamic Equilibrium

$$\mathcal{L} = \mathcal{L}(\tau, \theta)$$

θ is the **temperature**

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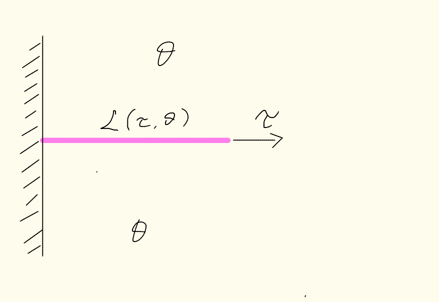

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Thermodynamic Equilibrium

$$\mathcal{L} = \mathcal{L}(\tau, \theta)$$

θ is the **temperature**
Empirical definition of temperature.

- There exists a family of thermodynamic equilibrium states, parametrized by certain extensive or intensive variables. – lenght (volume) L and energy U (extensive)
- In a thermodynamics transformation,

$$\Delta U = W + Q$$

W : mechanical work done by the force $\bar{\tau}$,
Q : energy exchanged with the heat bath (*Heat*).

Quasi-Static Transformations

Existence of thermodynamic processes where the system is always at some equilibrium. These processes are described by continuous curves on the space of parameters. This way we can define *isothermal* lines and *adiabatic* lines etc.

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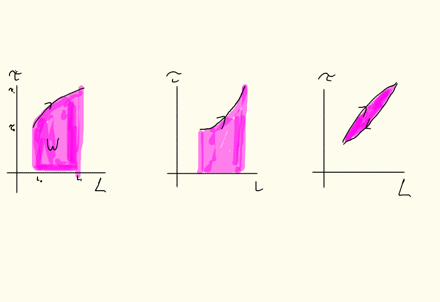
We can consider this as a *hidden principle* of thermodynamics. But, quoting Zemanski,

> *Every infinitesimal in thermodynamics must satisfy the requirement that it represents a change in a quantity which is small with respect to the quantity itself and large in comparison with the effect produced by the behavior of few molecules.*

Thermodynamic transformations and Cycles

- reversible or quasi-static tranformations:

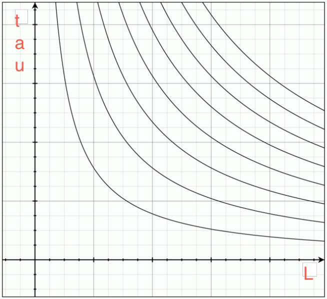


$$W = \oint \tau dL = -Q$$

Special quasi-static transformations

- **Isothermal:** System in contact with a *thermostat* while the external force τ is doing work:

$$\text{đ}W = \tau d\mathcal{L} = \tau \left(\frac{\partial \mathcal{L}}{\partial \tau}\right)_\theta d\tau = -\text{đ}Q + dU$$



Special quasi–static Transformations

- **Adiabatic:** $đQ = 0$.

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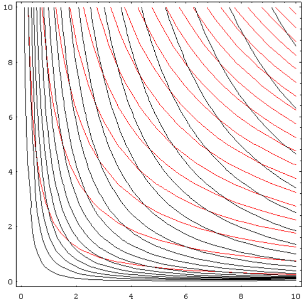
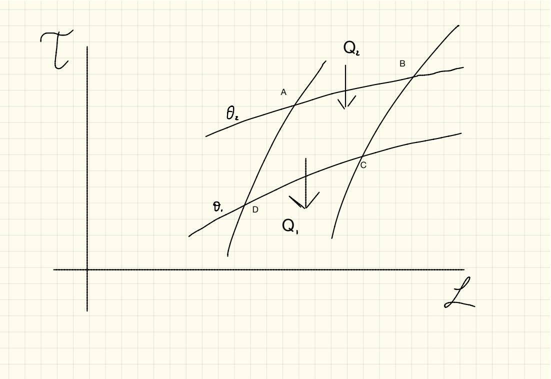
$$\frac{d\tau}{d\mathcal{L}} = -\frac{\partial_{\mathcal{L}} U}{\partial_{\tau} U}$$



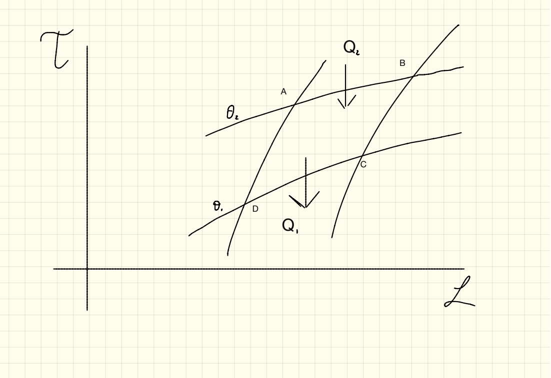
Carnot Cycles



$A \to B$, $C \to D$ isothermal
$B \to C$, $D \to A$ adiabatic

$$W = \oint \tau d\mathcal{L} = Q_h - Q_c = -\oint đQ$$

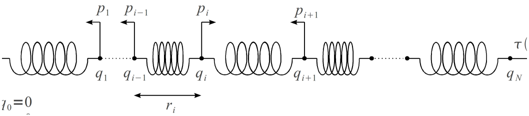
2nd Principle and Entropy



$$0 = \frac{Q_h}{T_h} - \frac{Q_c}{T_c}$$

$$\oint \frac{\text{đ}Q}{T} = 0, \qquad dS = \frac{\text{đ}Q}{T}.$$

Quasi-Static Isothermal Hydrodynamic Limit



Slowly changing tension:

$$\mathcal{H}_N(t) = \sum_{i=1}^{N} \left(\frac{p_i^2}{2} + V(r_i) \right) + \bar{\tau}(t) q_N$$

plus random collisions with particles of the *heat bath*: at independent random times

$$p_i(t) \longrightarrow \tilde{p}_j \sim \mathcal{N}(0, T)$$

Isothermal Dynamics

$$\begin{cases} dr_i(t) = & n^{2+\alpha}(p_i(t) - p_{i-1}(t))dt \\ dp_i(t) = & n^{2+\alpha}\left(V'(r_{i+1}(t)) - V'(r_i(t))\right) dt \\ & -n^{2+\alpha}\gamma p_i(t)dt + n^{1+\alpha/2}\sqrt{2\gamma\beta^{-1}}dw_i(t), \quad i = 1, .., N-1 \\ dp_n(t) = & n^{2+\alpha}\left(\bar{\tau}(t) - V'(r_n(t))\right) dt \\ & -n^{2+\alpha}\gamma p_n(t)\, dt + n^{1+\alpha/2}\sqrt{2\gamma\beta^{-1}}dw_n(t). \end{cases}$$

$\{w_i(t)\}_i$: n-independent Wiener processes,
$\alpha > 0$ for quasistatic driving from $\bar{\tau}(t)$.

Isothermal Dynamics

The generator of the process is given by

$$\mathcal{L}_n^{\bar{\tau}(t)} := n^{2+\alpha}\left(\mathcal{A}_n^{\bar{\tau}(t)} + \gamma \mathcal{S}_n\right), \tag{1}$$

where $\mathcal{A}_n^{\bar{\tau}}$ is the Liouville generator

$$A_n^{\bar{\tau}} = \sum_{i=1}^{n} (p_i - p_{i-1}) \partial_{r_i} + \sum_{i=1}^{n-1} (V'(r_{i+1}) - V'(r_i)) \partial_{p_i} + (\bar{\tau} - V'(r_n)) \partial_{p_n} \tag{2}$$

while $\mathcal{S}_n$ is the operator

$$\mathcal{S}_n = \sum_{i=1}^{n} \left(\beta^{-1} \partial_{p_i}^2 - p_i \partial_{p_i}\right) \tag{3}$$

Canonical Gibbs measures

$$\mathcal{G}(\tau, \beta) = \log\left[\sqrt{2\pi\beta^{-1}} \int e^{-\beta(V(r)-\tau r)} dr\right].$$

The stationary measure is given by

$$d\mu_{\tau,\beta} = \prod_{j=1}^{n} e^{-\beta(\mathcal{E}_j - \tau r_j) - \mathcal{G}(\tau,\beta)} dr_j dp_j = g_{\tau,\beta}^{(n)} \prod_{j=1}^{n} dr_j dp_j$$

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$$\mathfrak{r}(\tau,\beta) = \beta^{-1}\partial_\tau\mathcal{G}(\tau,\beta) = \int r_j\, d\mu_{\tau,\beta}$$

$$U(\tau,\beta) = -\partial_\beta\mathcal{G}(\tau,\beta) = \int V(r_j)d\mu_{\tau,\beta} + \frac{1}{2\beta} = \int \mathcal{E}_j\, d\mu_{\tau,\beta}$$

$$S(U,r) = \inf_{\tau,\beta>0}\{-\beta\tau r + \beta U + \mathcal{G}(\tau,\beta)\} \quad \text{Entropy}$$

$$F(r,\beta) = \sup_{\tau}\{\tau r - \beta^{-1}\mathcal{G}(\tau,\beta)\} \quad \text{Free Energy}$$

$$\tau(r,\beta) = \partial_r F(r,\beta).$$

Irreversible Isothermal Transformations

$\alpha = 0$: diffusive space-time scale,

$$\frac{1}{N}\sum_i G(i/N) r_i(t) \underset{N\to\infty}{\longrightarrow} \int_0^1 G(y) r(y,t) dy$$

$$\partial_t r(t,y) = \partial_{yy}\tau(r(t,y),\beta),$$
$$\partial_y r(t,y)|_{y=0} = 0, \quad \tau(r(1,t),\beta) = \bar{\tau}(t).$$

In the diffusive time scale, there is a need of infinite time to converge to the new thermodynamic equilibrium, and this is an irreversible *non-quasistatic* trasformation.

Quasi-Static Isothermal Hydrodynamic Limit

(Letizia-Olla, AOP 2018, De Masi-Olla JSP 2015)

For $\alpha > 0$, for all $t > 0$

$$\frac{1}{n}\sum_{i=1}^{n} G(i/n) r_i(t) \underset{n\to\infty}{\longrightarrow} \bar{r}(t) \int_0^1 G(x)\, dx$$

where we denote $\bar{r}(t) = \mathfrak{r}(\beta, \bar{\tau}(t)) = \beta^{-1}(\partial_\tau \mathcal{G})(\beta, \bar{\tau}(t))$ is the equilibrium volume at temperature β^{-1} and tension $\bar{\tau}(t)$.

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Similar result with macroscopic profile of temperatures $\beta(y)$

$$\frac{1}{n}\sum_{i=1}^{n} G(i/n) r_i(t) \underset{n\to\infty}{\longrightarrow} \int_0^1 G(x)\bar{r}(t,y)\, dx$$

with $\bar{r}(t,y) = \mathfrak{r}(\beta(y), \bar{\tau}(t))$: *quasistatic non-equilibrium transformations*.

Proof of isothermal QS limit

$f_t^n(r_1, p_1, \dots, r_n, p_n)$ the density of the distribution at time t with respect to $\mu_{\bar\tau(t),\beta}$:

$$\partial_t \left(f_t^n g^n_{\bar\tau(t),\beta} \right) = \left(\mathcal{L}_n^{\bar\tau(t)*} f_t^n \right) g^n_{\bar\tau(t),\beta}$$

$$H_n(t) = \int f_t^n \log f_t^n \, d\mu_{\bar\tau(t),\beta}, \quad H_n(0) = 0$$

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$$\frac{d}{dt} H_n(t) = -n^{2+\alpha} \gamma \beta^{-1} \int \sum_{i=1}^{n} \frac{(\partial_{p_i} f_t^n)^2}{f_t^n} \; d\mu^{c,n}_{\bar\tau(t),\beta}$$
$$-\beta \bar\tau'(t) \int \sum_{i=1}^{n} (r_i - \bar r(t)) \, f_t^n \; d\mu^{c,n}_{\bar\tau(t),\beta}.$$

proof of isothermal QS limit

By entropy inequality, for any $\lambda > 0$ small enough

$$
\begin{aligned}
&\beta\bar\tau'(t) \int \sum_{i=1}^{n} (r_i - \bar r(t))\, f_t^n \; d\mu^{c,n}_{\bar\tau(t),\beta} \\
&\le \lambda^{-1} \log \int e^{\lambda\beta\bar\tau'(t)\sum_{i=1}^n (r_i - \bar r(t))} \; d\mu^{c,n}_{\bar\tau(t),\beta} + \lambda^{-1} H_n(t) \\
&\le \lambda C n + \lambda^{-1} H_n(t),
\end{aligned}
$$

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$$\frac{d}{dt} H_n(t) \leq \lambda^{-1} H_n(t) + \lambda C n,$$

and since $H_n(0) = 0$, it follows that $H_n(t) \leq e^{t/\lambda} \lambda C t\, n$. This is not yet what we want to prove but it implies that

$$\int_0^T \int \sum_{i=1}^{n} \frac{(\partial_{p_i} f_t^n)^2}{f_t^n} \; d\mu^{c,n}_{\bar{\tau}(t),\beta} \; dt \leq \frac{C}{n^{1+\alpha}}.$$

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This gives only information on the distribution of the velocities. Uning *entropic hypocoercive bounds* we have the same for

$$\int_0^T \int \sum_{i=1}^n \frac{(\partial_{q_i} f_t^n)^2}{f_t^n} \; d\mu^{c,n}_{\bar\tau(t),\beta} \; dt \le \frac{C}{n^{1+\alpha}}.$$

where $\partial_{q_i} = \partial_{r_i} - \partial_{r_{i+1}}$. and this is enough to prove that

$$\int \frac{1}{n} \sum_{i=1}^n (r_i - \bar r(t)) \, f_t^n \; d\mu^{c,n}_{\bar\tau(t),\beta} \longrightarrow 0,$$

i.e.

$$\frac{H_n(t)}{n} \longrightarrow 0.$$

Isothermal limit: Work, Heat and Free Energy

Energy:

$$U_n := \frac{1}{n}\sum_{i=1}^{n}\left(\frac{p_i^2}{2} + V(r_i)\right)$$

$$U_n(t) - U_n(0) = \mathcal{W}_n(t) + Q_n(t) \tag{4}$$

$$\mathcal{W}_n(t) = n^{1+\alpha}\int_0^t \bar{\tau}(s)p_n(s)ds = \int_0^t \bar{\tau}(s)\frac{dq_n(s)}{n}$$

$$\longrightarrow \int_0^t \bar{\tau}(s)d\bar{r}(s) := \mathcal{W}(t)$$

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$$Q_n(t) = \gamma\, n^{1+\alpha}\sum_{j=1}^{n}\int_0^t ds\left(p_j^2(s) - \beta^{-1}\right)$$

$$+\, n^{\alpha/2}\sum_{j=1}^{n}\sqrt{2\gamma\beta^{-1}}\int_0^t p_j(s)dw_i(s).$$

it may look horribly divergent but...

Isothermal limit: Work, Heat and Free Energy

$$\lim_{n\to\infty} (U_n(t) - U_n(0)) = u(\bar{\tau}(t), \beta) - u(\bar{\tau}(0), \beta) \tag{5}$$

where $u(\tau, \beta) = -\partial_\beta \mathcal{G}(\tau, \beta)$ is the average energy for $\mu_{\beta,\tau}$.

$$Q_n(t) \underset{n\to\infty}{\longrightarrow} Q(t) = u(\bar{\tau}(t), \beta) - u(\bar{\tau}(0), \beta) - \mathcal{W}(t). \tag{6}$$

which is the first principle of thermodynamics for quasistatic isothermal transformations.

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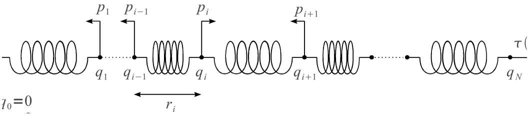
For the Free Energy:

$$\mathcal{F}(\bar{r}(t), \beta) - \mathcal{F}(\bar{r}(0), \beta) = \int_0^t \bar{\tau}(s) d\bar{r}(s) = \mathcal{W}(t)$$

i.e. Clausius equality.
Equivalently, by $\mathcal{F} = u - \beta^{-1} S$,

$$\beta^{-1} \left(S(\bar{r}(t), u(t)) - S(\bar{r}(0), u(0)) \right) = Q(t) \tag{7}$$

Adiabatic Quasi-Static Limit



$$
\begin{aligned}
dr_i &= n^{1+\alpha}(p_i - p_{i-1})\, dt \\
dp_i &= n^{1+\alpha}(V'(r_{i+1}) - V'(r_i))\, dt, \qquad i = 1, \ldots, n-1, \\
dp_n &= n^{1+\alpha}(\bar{\tau}(t) - V'(r_n))\, dt
\end{aligned}
\tag{8}
$$

Adiabatic thermodynamic transformation

We start at $t = 0$ with the equilibrium $\mu^{c,n}_{\bar{\tau}(0),\beta(0)}$. Correspondingly there is an average energy $e(0)$ give by

$$\bar{u}(0) = u(\beta(0), \tau(0)) = -\partial_\beta \mathcal{G}(\beta(0), \tau(0))$$

The macroscopic work

$$W(t) = \int_0^t \bar{\tau}(s) d\bar{r}(s),$$

$$\bar{r}(t) = \mathbf{r}(\beta(t), \bar{\tau}(t)) = \beta(t)^{-1} (\partial_\tau \mathcal{G})(\beta(t), \bar{\tau}(t))$$

Then the energy at time t, by the first law, is given by

$$\bar{u}(t) = \bar{u}(0) + W(t)$$

that gives the temperature at time t as

$$\beta(t) = (\partial_e S)(\bar{u}(t), \bar{r}(t)).$$

Adiabatic = isoentropic:

$$S(\bar{u}(t), \bar{r}(t)) - S(\bar{u}(0), \bar{r}(0)) = \int_0^t \left(\beta(s)\bar{u}'(s) - \beta(s)\bar{\tau}(s)\bar{u}'(s)\right) ds = 0.$$

For $\alpha >?$ (2 or 4/3...), for all $t > 0$

$$\frac{1}{n}\sum_{x=1}^{n} G(x/n) r_x(t) \underset{n\to\infty}{\longrightarrow} \bar{r}(t) \int_0^1 G(y)\, dy$$
$$\frac{1}{n}\sum_{x=1}^{n} G(x/n) \mathcal{E}_x(t) \underset{n\to\infty}{\longrightarrow} \bar{u}(t) \int_0^1 G(y)\, dy$$

No results yet for deterministic dynamics.
Some preliminary results with some stochastic perturbations that conserve energy and volume.

Where is the difficulty?

$$\frac{d}{dt}H_n(t) = -\int f_t^n \partial_t g^n_{\beta(t),\bar\tau(t)} \prod_{j=1}^n dr_j dp_j$$

$$= \int \sum_{j=1}^n \left[-\beta'(t)\left(\mathcal{E}_j - e(t)\right) + (\beta(t)\bar\tau(t))'\left(r_j - r(t)\right)\right] f_t^n d\mu_{\beta(t),\bar\tau(t)}.$$

Then all one has to prove is

$$\lim_{n\to\infty}\int_0^T dt\left[\int \frac{1}{n}\sum_{j=1}^n \mathcal{E}_j f_t^n d\mu^{c,n}_{\bar\tau(t),\beta(t)} - e(t)\right] = 0$$

$$\lim_{n\to\infty}\int_0^T dt\left[\frac{1}{n}\int q_n f_t^n d\mu^{c,n}_{\bar\tau(t),\beta(t)} - r(t)\right] = 0 \tag{9}$$

Remarke on the thermodynamic entropy

This would be equivalent as proving that (in probability wrt the initial configuration distributed by $\mu_{\beta(0),\tau(0)}$)

$$S\left(\frac{1}{n}\sum_{j=1}^{n}\mathcal{E}_j(t), \frac{q_n(t)}{n}\right) - S\left(\frac{1}{n}\sum_{j=1}^{n}\mathcal{E}_j(0), \frac{q_n(0)}{n}\right) \xrightarrow[n\to\infty]{} 0$$

Adiabatic QS transformation are isoentropic!

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Adiabatic QS transformation are isoentropic!

No need to prove increase of thermodynamic entropy, this will come naturally from the isothermal QS transformations.

Large Deviations from the QS limit

De Masi-Olla 2018

Symmetric Simple Exclusion in $\{-N, \dots, N\}$ with boundary reservoirs at density $\rho_-(t)$ and $\rho_+(t)$:

$\eta(x) \in \{0, 1\}$, $\alpha > 0$

$$L_{N,t} = N^{2+\alpha}[L_{\text{exc}} + L_{b,t}], \qquad t \geq 0, \quad \alpha > 0$$

$$L_{\text{exc}} f(\eta) = \gamma \sum_{x=-N}^{N-1} \Big(f(\eta^{(x,x+1)}) - f(\eta) \Big) \tag{10}$$

$$L_{b,t} f(\eta) = \sum_{\mathrm{J}=\pm} \rho_{\mathrm{J}}(t)^{1-\eta(\mathrm{J}N)} (1 - \rho_{\mathrm{J}}(t))^{\eta(\mathrm{J}N)} [f(\eta^{\mathrm{J}N}) - f(\eta)]$$

QS limit for SSE

$$\lim_{N\to\infty} \pi_N(t,y) := \sum_x 1_{[Ny,Ny+1]}(x)\eta_t(x) \longrightarrow \bar{\rho}(y,t)$$

$$\bar{\rho}(y,t) = \frac{1}{2}[\rho_+(t) - \rho_-(t)]r + \frac{1}{2}\left[\rho_+(t) + \rho_-(t)\right], \qquad y \in [-1,1]$$

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$$\begin{aligned} h(t,x) = &\{\text{number of jumps } x \to x+1 \text{ up to time } t\} \\ &- \{\text{number of jumps } x+1 \to x \text{ up to time } t\}, \end{aligned}$$

Define

$$h_N(t,y) = \frac{1}{N^{1+\alpha}} h(t,[Ny]).$$

$$\lim_{N\to\infty} \mathbb{E}_{\eta_0}\Big(h_N(t,y)\Big) = \bar{J}(t) := -\frac{\gamma}{2}\int_0^t [\rho_+(s) - \rho_-(s)]ds.$$

Large Deviations

For $J(t)$ and $\rho(t,y)$ such that $\rho(t,\pm 1) = \rho_\pm(t)$,

$$\mathbb{P}_{\eta_0}\left(h_n \sim J, \pi_N \sim \rho\right) \ \sim \ e^{-N^{1+\alpha} I(J,\rho)}$$

$$I(J,\rho) = \frac{1}{4}\int_0^T \int_{-1}^1 \frac{\left(J'(t) + \partial_y \rho(t,y)\right)^2}{\rho(t,y)(1-\rho(t,y))} dy\, dt.$$

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Gallavotti-Cohen Fluctuation Relation

$$I(-J,\rho) = I(J,\rho) - \int_0^T J'(t) \log \frac{\rho_+(t)(1-\rho_-(t))}{\rho_-(t)(1-\rho_+(t))} dt, \tag{11}$$