A thermodynamical theory for nonequilibrium systems

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Nonequilibrium stationary states

- Nonequilibrium statistical mechanics poorly understood
- Stationary states are the simplest generalization of equilibrium states
- Local equilibrium

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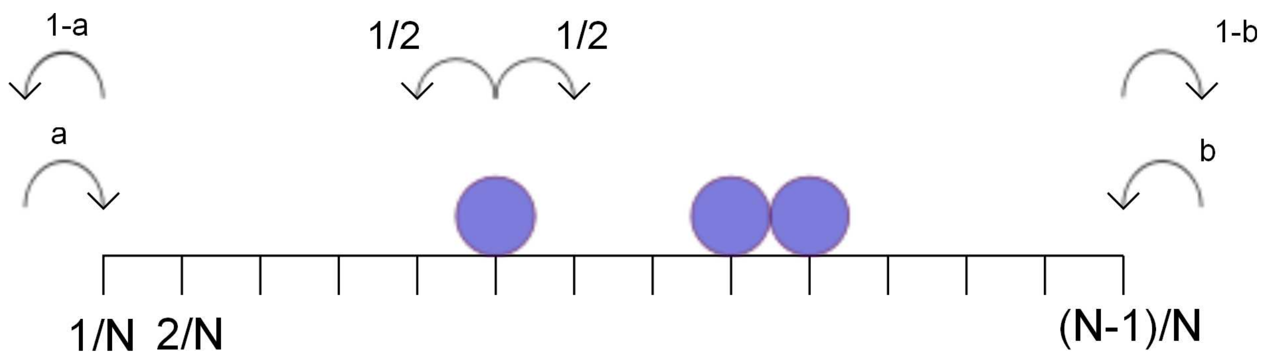
- Nonequilibrium statistical mechanics poorly understood
- Stationary states are the simplest generalization of equilibrium states
- Local equilibrium
- Long range correlations
- Non local thermodynamic variables
- Dynamics play a role



EP@

- $\Lambda \subset \mathbb{R}^d \quad N \geq 1 \quad \{x/N \in \Lambda : x \in \mathbb{Z}^d\}$
- $\lambda : \partial\Lambda \to \mathbb{R}$ chemical potential
- Creation: $\dfrac{e^{\lambda(x/N)}}{1+e^{\lambda(x/N)}}$ annihilation $\dfrac{1}{1+e^{\lambda(x/N)}}$
- $\eta_t = \{\eta_t(x/N) : x/N \in \Lambda\}$
- ν_λ^N stationary state

Diffusion coefficient $D(\rho)$

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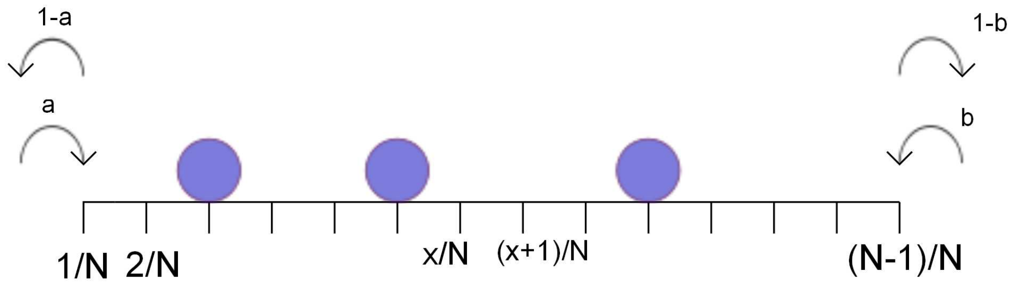

- Fix $\alpha < \beta$
- $J_{x,x+1}(t)$ net flow through $\{x/N, (x+1)/N\}$ in $[0, t]$
- Expect $J_{x,x+1}(t) \; \approx \; tN^{-1}(\beta - \alpha)$

$$D(\alpha) \;=\; \lim_{\beta \downarrow \alpha} \lim_{N \to \infty} \lim_{t \to \infty} \frac{N}{t(\beta - \alpha)} \mathbb{E}\big[J_{x,x+1}(t)\big]$$

- $D(\rho) = (1/2)I$

Mobility $\chi(\rho)$

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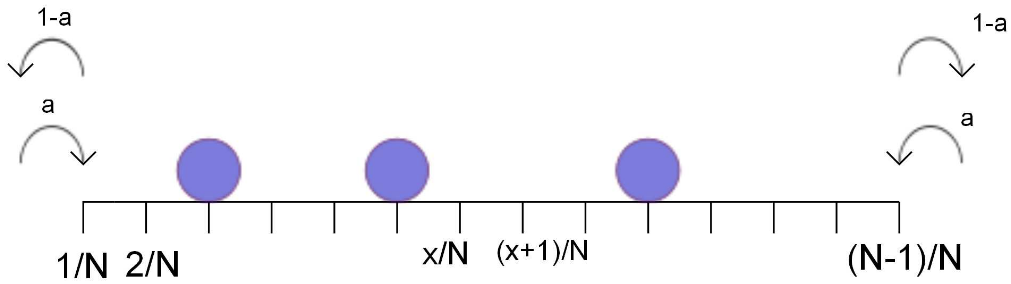

- Fix α
- $J_{x,x+1}(t)$ net flow through $\{x/N, (x+1)/N\}$ in $[0,t]$
- Expect $J_{x,x+1}(t)^2 \approx t$

$$\chi(\alpha) = \lim_{N\to\infty} \lim_{t\to\infty} \frac{1}{t}\mathbb{E}\left[J_{x,x+1}(t)^2\right] ,$$

- $\chi(\alpha) = \alpha(1-\alpha)\, I$

Stationary density profile

- $\pi^N = \frac{1}{N^d} \sum_{x/N \in \Lambda} \eta(x/N)\delta_{x/N}$
- $\nu_\lambda^N\{\pi^N \approx \bar{\rho}\} \sim 1$

$$\begin{cases} \nabla \cdot D(\rho)\nabla\rho = 0 \\ f'(\rho(x)) = \lambda(x) \quad x \in \partial\Lambda \end{cases}$$

- $D(\rho)$ diffusion coefficient $D(\rho) = (1/2)I$
- f equilibrium specific free energy $\quad f(a) = a \log a + (1-a)\log(1-a)$
- Einstein relation $\quad D(\rho) = \chi(\rho)\, f''(\rho)$

Nonequilibrium free energy

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- $D(\rho)$ diffusion coefficient $D(\rho) = (1/2)I$
- f equilibrium specific free energy $\quad f(a) = a\log a + (1-a)\log(1-a)$
- $\gamma \neq \bar\rho$
- $\nu_\lambda^N\{\pi^N \approx \gamma\} \sim e^{-N^d S_\lambda(\gamma)}$
- $S_\lambda(\cdot)$ nonequilibrium free energy

Equilibrium × Nonequilibrium

- λ constant $\quad \nu_\lambda^N$ no correlations

$$S_\lambda(\gamma) \;=\; \int_\Lambda \left\{\gamma \log \frac{\gamma}{\bar{\rho}} + [1-\gamma] \log \frac{1-\gamma}{1-\bar{\rho}}\right\} dx$$

Equilibrium $\times$ Nonequilibrium

- λ constant $\quad \nu_\lambda^N$ no correlations

$$S_\lambda(\gamma) \;=\; \int_\Lambda \Big\{ \gamma \log \frac{\gamma}{\bar\rho} + [1-\gamma] \log \frac{1-\gamma}{1-\bar\rho} \Big\} \, dx$$

- $d=1 \quad \Lambda=(0,1) \quad \lambda(0) \neq \lambda(1) \quad \nu_\lambda^N[\eta(x/N);\eta(y/N)] = O(N^{-1})$
- Derrida, Lebowtiz, Speer (2002) Bertini, De Sole, Gabrielli, Jona-Lasinio, L. (2002)

$$S_\lambda(\gamma) = \int_0^1 \Big\{ \gamma \log \frac{\gamma}{F} + [1-\gamma] \log \frac{1-\gamma}{1-F} + \log \frac{F_x}{\beta-\alpha} \Big\} \, dx$$

$$\begin{cases} \dfrac{F_{xx}}{(F_x)^2} \;=\; \dfrac{\gamma - F}{F(1-F)} \,, \\ F(x) = e^{\lambda(x)}/[1+e^{\lambda(x)}] \,, \quad x \in \partial\Lambda \end{cases}$$

(DLS)

Hydrodynamic limit

- $\pi_t^N = \frac{1}{N^d} \sum_{x/N \in \Lambda} \eta_{tN^2}(x/N) \delta_{x/N}$
- $\pi_0^N \to \gamma(x)\, dx$
- De Masi, Presutti et al. 80's Guo, Papanicolaou, Varadhan 86
- $\mathbb{P}_\gamma \big[\pi^N \approx w\,,\ [0,T] \big] \sim 1$

$$\begin{cases} \partial_t w = \nabla \cdot D(w) \nabla w \\ f'(w(t,x)) = \lambda(x) \quad x \in \partial\Lambda \\ w(0,\cdot) = \gamma(\cdot) \end{cases}$$

- Stationary solution $\bar{\rho}$ globally attractive

Action Functional

- Kipnis, Olla, Varadhan (1989), Donsker, Varadhan (1989), Quastel, Rezakhanlou, Varadhan (1999), Bertini, L., Mourragui (2010)
- $u(t,\cdot) \qquad t \in [-T,0]$
- $\mathbb{P}_{u(-T)}\big[\,\pi^N \approx u\,,\,[-T,0]\,\big] \sim e^{-N^d I_{[-T,0]}(u)}$
- $K(\rho)H = -\nabla\cdot\big(\chi(\rho)\nabla H\big) \qquad H(x)=0 \qquad x\in\partial\Lambda$
- mobility: $\chi(a) = a(1-a)I$

$$I_{[-T,0]}(u) := \int_{-T}^{0} dt \int_\Lambda dx\,\big[\partial_t u - \nabla\cdot D(u)\nabla u\big]\,K(u)^{-1}\,\big[\partial_t u - \nabla\cdot D(u)\nabla u\big]$$

Quasi-potential

- $I_{[-T,0]}(u)$

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- Bodineau and Giacomin (2004), Farfan (2010)
- V_λ is the nonequilibrium free energy:
- $\nu_\lambda^N\{\pi^N \approx \gamma\} \sim e^{-N V_\lambda(\gamma)}$
- Holds for large class of systems in any dimension

Two problems

Optimal trajectory:

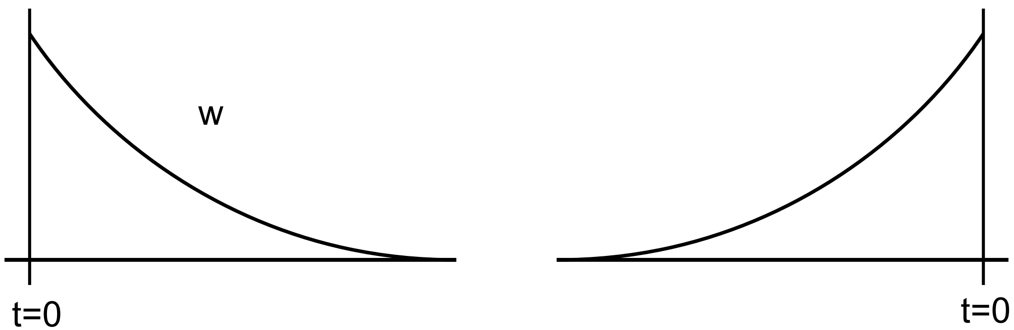
- $V_\lambda(\gamma) = \inf_{T>0} \inf_{\substack{u(-T)=\bar\rho \\ u(0)=\gamma}} I_{[-T,0]}(u)$
- $V_\lambda(\gamma) = \inf \{ I(u) : u(-\infty) = \bar\rho \,,\, u(0) = \gamma \}$

Static variational problem for the quasi-potential

- DLS, BDGJL $\quad d = 1$, few models, explicit formula for $V_\lambda(\gamma)$

Optimal trajectory: reversible case

- $\inf \{ I(u) : u(-\infty) = \bar{\rho} \,,\, u(0) = \gamma \}$
- Onsager, Machlup (1953)   Reversible case (λ constant)
- Relaxation path:
  - $\partial_t w = \nabla \cdot D(w) \nabla w \quad w(0) = \gamma \quad w(t,x) = f'(\lambda(x)) \quad x \in \partial\Lambda$
- Fluctuation path:
  - $v(t) = w(-t) \quad v$ optimal



- Luchinsky, McKlintock (1996)   Analogue electrical circuits

Optimal trajectory: non-reversible case

- Time reversed dynamics has hydrodynamic description
- $\bar{\rho}$ global attractor
- $w(t,\cdot) \quad -\infty < t \leq 0 \quad w(-\infty) = \bar{\rho} \quad w(0) = \gamma$
- $(\theta w)(t) = w(-t)$
- $T > 0 \quad [-T, 0] \quad \nu_\lambda^N(w_{-T})\,\mathbb{P}_{w_{-T}}(w) = \nu_\lambda^N(w_0)\,\mathbb{P}^*{}_{w_0}(\theta w)$
- $S_\lambda(w_{-T}) + I_{[-T,0]}(w) = S_\lambda(u_0) + I^*_{[0,T]}(\theta w)$
- $S_\lambda(\bar{\rho}) + I(w) = S_\lambda(\gamma) + I^*_{[0,\infty)}(\theta w)$
- w^* relaxation path adjoint dynamics $w^*(0) = \gamma$
- $v(t) = w^*(-t) \quad v$ optimal $\quad V_\lambda(\gamma) = S_\lambda(\gamma) - S_\lambda(\bar{\rho})$

Hamiltonian-Jacobi equation

- Action: $K(\rho)H = -\nabla \cdot \big(\chi(\rho)\nabla H\big) \qquad H(x) = 0 \qquad x \in \partial\Lambda$
- $I_{[-T,0]}(u) := \int_{-T}^{0} dt \int_{\Lambda} dx \, [\partial_t u - \nabla \cdot D(u)\nabla u] \, K(u)^{-1} \, [\partial_t u - \nabla \cdot D(u)\nabla u]$
- Lagrangian:

$$\mathbb{L}(u, u_t) \; = \; \int_{\Lambda} dx \, \big[\partial_t u - \nabla \cdot D(u)\nabla u\big] K(u)^{-1} \big[\partial_t u - \nabla \cdot D(u)\nabla u\big]$$

- Hamiltonian:

$$\begin{aligned}\mathbb{H}(\gamma, h) \; &= \; \sup_g \big\{ \langle g, h \rangle - \mathbb{L}(\gamma, g) \big\} \\ &= \; \langle \nabla h \cdot \chi(\gamma) \nabla h \rangle \; + \; \langle \nabla \cdot D(\gamma) \nabla \gamma, h \rangle\end{aligned}$$

- Hamilton-Jacobi equation: $\mathbb{H}\Big(\gamma, \dfrac{\delta V_\lambda}{\delta \gamma}\Big) = 0$

1. Transformations

Basic assumptions

1. Local density $u(t,x)$ and current $j = j(t,x)$

$$\partial_t u + \nabla \cdot j = 0$$

2. Constitutive equation $j = J(t, u(t))$:

$$J(t,\rho) = -D(\rho)\nabla\rho + \chi(\rho)\, E(t) \ ,$$

- $D(\rho)$ diffusion coefficient $\chi(\rho)$ mobility

3. Boundary condition

$$f'\big(u(t,x)\big) = \lambda(t,x) \ , \qquad x \in \partial\Lambda \ .$$

- f is the equilibrium specific free energy

4. Einstein relation $D(\rho) = \chi(\rho)\, f''(\rho)$

Energy balance

$$W_{[0,T]} = \int_0^T dt \left\{ - \int_{\partial\Lambda} d\sigma(x)\, \lambda(t,x)\, j(t,x) \cdot \hat{n}(x) + \int_\Lambda dx\, j(t,x) \cdot E(t,x) \right\} ,$$

- Second law of thermodynamics (Clausius inequality)

$$W_{[0,T]}[\lambda, E, \rho] \geq F(u(T)) - F(\rho) ,$$

- F equilibrium free energy:

$$F(\rho) = \int_\Lambda dx\, f(\rho(x))$$

Energy balance

$$W_{[0,T]} = \int_0^T dt \Big\{ - \int_{\partial\Lambda} d\sigma(x)\, \lambda(t,x)\, j(t,x) \cdot \hat{n}(x) + \int_\Lambda dx\, j(t,x) \cdot E(t,x) \Big\} \ ,$$

- $\lambda = f'(u(t)) \qquad D(\rho) = \chi(\rho)\, f''(\rho) \qquad J(t,\rho) = -D(\rho)\nabla\rho + \chi(\rho)\, E(t)$

$$W_{[0,T]} = \int_0^T dt \Big\{ - \int_{\partial\Lambda} d\sigma\, f'(u(t))\, j(t) \cdot \hat{n} + \int_\Lambda dx\, j(t) \cdot E(t) \Big\} \ ,$$

$$= \int_0^T dt \int_\Lambda dx \big\{ - \nabla \cdot \big[f'(u(t))\, j(t) \big] + j(t) \cdot E(t) \big\}$$

$$= \int_0^T dt \int_\Lambda dx \big[- f'(u(t)) \nabla \cdot j(t) - f''(u(t)) \nabla u(t) \cdot j(t) + j(t) \cdot E(t) \big]$$

$$= \int_0^T dt\, \frac{d}{dt} \int_\Lambda dx\, f(u(t)) \ + \int_0^T dt \int_\Lambda dx\ j(t) \cdot \chi(u(t))^{-1} j(t) \ ,$$

2. Equilibrium states: $J(u) = 0$

Reversible and quasi static transformations

- $E = 0$
- Spatially homogenous equilibrium $\lambda =$ cte
- $\bar{\rho}_\lambda =$ cte $f'(\bar{\rho}_\lambda) = \lambda$

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- Spatially homogenous equilibrium $\lambda =$ cte
- $\bar{\rho}_\lambda =$ cte $\quad f'(\bar{\rho}_\lambda) = \lambda$
- $\lambda_0 \quad \lambda_1$
- $\bar{\rho}_0 = \bar{\rho}_{\lambda_0} \longrightarrow \bar{\rho}_1 = \bar{\rho}_{\lambda_1}$
- $\lambda(t) = \lambda_0$, $t \leq 0 \quad \lambda(t) = \lambda_1$, $t \geq T$

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- $\lambda(t) = \lambda_0$, $t \leq 0 \quad \lambda(t) = \lambda_1$, $t \geq T$
- *reversible transformation*: energy exchanged is minimal
- *quasi static transformation*: variation of the chemical potential is very slow

Reversible and quasi static transformations

$$
\begin{aligned}
W &= \int_0^\infty dt \, \frac{d}{dt} \int_\Lambda dx \, f(u(t)) \; + \int_0^\infty dt \int_\Lambda dx \; j(t) \cdot \chi(u(t))^{-1} j(t) \\
&= F(\bar\rho_1) - F(\bar\rho_0) + \int_0^\infty dt \int_\Lambda dx \; j(t) \cdot \chi(u(t))^{-1} j(t)
\end{aligned}
$$

- No regularity assumption of the chemical potential in time

Reversible and quasi static transformations

$$W = \int_0^\infty dt \, \frac{d}{dt} \int_\Lambda dx \, f(u(t)) \; + \int_0^\infty dt \int_\Lambda dx \; j(t) \cdot \chi(u(t))^{-1} j(t)$$

$$= F(\bar\rho_1) - F(\bar\rho_0) + \int_0^\infty dt \int_\Lambda dx \; j(t) \cdot \chi(u(t))^{-1} j(t)$$

- No regularity assumption of the chemical potential in time
- Smooth $\lambda(t)$ $\quad \lambda_\delta(t) = \lambda(\delta t) \quad u_\delta(t)$
- $J(t,\rho) = J(\rho) = -D(\rho)\nabla\rho \quad D(\rho) = \chi(\rho) \, f''(\rho)$

$$W = F(\bar\rho_1) - F(\bar\rho_0) + \int_0^\infty dt \int_\Lambda dx \, \nabla f'(u_\delta(t)) \cdot \chi(u_\delta(t)) \nabla f'(u_\delta(t)) \; ,$$

Reversible and quasi static transformations

$$W = F(\bar\rho_1) - F(\bar\rho_0) + \int_0^\infty dt \int_\Lambda dx \, \nabla f'(u_\delta(t)) \cdot \chi(u_\delta(t)) \nabla f'(u_\delta(t))$$

- $\bar\rho_{\lambda_\delta(t)} \qquad \lambda_\delta(t)$
- $\nabla f'(\bar\rho_{\lambda_\delta(t)}) = 0$

$$\int_0^\infty dt \int_\Lambda dx \, \nabla\big[f'(u_\delta(t)) - f'(\bar\rho_{\lambda_\delta(t)})\big] \cdot \chi(u_\delta(t)) \nabla\big[f'(u_\delta(t)) - f'(\bar\rho_{\lambda_\delta(t)})\big]$$

- $u_\delta(t) - \bar\rho_{\lambda_\delta(t)} = O(\delta)$

Reversible and quasi static transformations

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- $\bar{\rho}_{\lambda_\delta(t)} \qquad \lambda_\delta(t)$
- $\nabla f'(\bar{\rho}_{\lambda_\delta(t)}) = 0$

$$\int_0^\infty dt \int_\Lambda dx\, \nabla \left[f'(u_\delta(t)) - f'(\bar{\rho}_{\lambda_\delta(t)}) \right] \cdot \chi(u_\delta(t)) \nabla \left[f'(u_\delta(t)) - f'(\bar{\rho}_{\lambda_\delta(t)}) \right]$$

- $u_\delta(t) - \bar{\rho}_{\lambda_\delta(t)} = O(\delta)$
- Reversible transformation $\quad W = \Delta F$
- No special property of $\lambda(t)$

Excess work

- $\lambda(0) = \lambda_0 \qquad \bar{\rho}_0$
- Transformation $\lambda(t) \qquad \lambda(t) \longrightarrow \lambda_1 \qquad \bar{\rho}_1$
- *excess work*:

$$W_{\mathrm{ex}} \;=\; W[\lambda, E, \rho] - \min W \;=\; \int_0^\infty dt \int_\Lambda dx\, j(t) \cdot \chi(u(t))^{-1} j(t)$$

- $j(t) = J(u(t)) = -D(u)\nabla u \qquad D(\rho) = \chi(\rho)\, f''(\rho)$

$$W_{\mathrm{ex}} \;=\; -\int_0^\infty dt \int_\Lambda dx\, \nabla f'(u(t)) \cdot J(u(t))$$

Excess work and quasi-potential

- Relaxation path: $(\lambda_0, \bar{\rho}_0)$ λ_1 for $t > 0$ $u(t) \longrightarrow \bar{\rho}_1$

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- $\nabla f'(\bar\rho_1) = 0$

$$\begin{aligned} W_{\rm ex}[\lambda_1, \bar\rho_0] &= \int_0^\infty dt \int_\Lambda dx\, \big[f'(u(t)) - f'(\bar\rho_1)\big] \nabla \cdot J(u(t)) \\ &= -\int_0^\infty dt \int_\Lambda dx\, \big[f'(u(t)) - f'(\bar\rho_1)\big]\, \partial_t u(t) \\ &= \int_\Lambda dx\, \big[f(\bar\rho_0) - f(\bar\rho_1) - f'(\bar\rho_1)\big(\bar\rho_0 - \bar\rho_1\big)\big] = V_{\lambda_1}(\bar\rho_0) \end{aligned}$$

- $W_{\rm ex}$ is not the difference of a thermodynamic potential

3. Nonequilibrium states

Adjoint hydrodynamics

- $\partial_t u + \nabla \cdot J(u(t)) = 0$
- Adjoint hydrodynamics   chemical potential λ fixed
- $\partial_t u + \nabla \cdot J^*(u(t)) = 0$
- $\frac{1}{2}\{J(\rho) + J^*(\rho)\} = -\chi(\rho)\,\nabla\frac{\delta V_\lambda(\rho)}{\delta\rho}$

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- $J_{\mathrm{S}}^{\lambda}(\rho) = \frac{1}{2}\{J(\rho) + J^*(\rho)\} = -\chi(\rho)\,\nabla \frac{\delta V_\lambda(\rho)}{\delta \rho}$
- $J_{\mathrm{A}}^{\lambda}(\rho) = \frac{1}{2}\{J(\rho) - J^*(\rho)\} = J(\rho) - J_{\mathrm{S}}^{\lambda}(\rho)$

Hamilton-Jacobi equation

- $J_{\mathrm{S}}^{\lambda}(\rho) = \dfrac{1}{2}\{J(\rho) + J^*(\rho)\} = -\chi(\rho)\,\nabla \dfrac{\delta V_\lambda(\rho)}{\delta \rho}$
- $J_{\mathrm{A}}^{\lambda}(\rho) = \dfrac{1}{2}\{J(\rho) - J^*(\rho)\} = J(\rho) - J_{\mathrm{S}}^{\lambda}(\rho)$
- Hamilton-Jacobi equation: $\mathbb{H}\left(\gamma, \dfrac{\delta V_\lambda}{\delta \gamma}\right) = 0$
- $\mathbb{H}(\gamma, h) \;=\; \langle \nabla h \cdot \chi(\gamma) \nabla h \rangle \;+\; \langle \nabla \cdot D(\gamma) \nabla \gamma, h \rangle$

$$\left\langle \nabla \frac{\delta V_\lambda}{\delta \gamma} \cdot \chi(\gamma) \nabla \frac{\delta V_\lambda}{\delta \gamma} \right\rangle \;-\; \left\langle D(\gamma) \nabla \gamma \,\cdot\, \nabla \frac{\delta V_\lambda}{\delta \gamma} \right\rangle = 0$$

Hamilton-Jacobi equation

- $J_{\mathrm{S}}^{\lambda}(\rho) = \frac{1}{2}\{J(\rho) + J^{*}(\rho)\} = -\chi(\rho)\,\nabla\frac{\delta V_{\lambda}(\rho)}{\delta\rho}$
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$$\Big\langle\nabla\frac{\delta V_{\lambda}}{\delta\gamma}\cdot\chi(\gamma)\nabla\frac{\delta V_{\lambda}}{\delta\gamma}\Big\rangle \;-\; \Big\langle D(\gamma)\nabla\gamma \,\cdot\, \nabla\frac{\delta V_{\lambda}}{\delta\gamma}\Big\rangle = 0$$

- $J(\rho) \;=\; -D(\rho)\nabla\rho$
- $\int_{\Lambda} dx\, J_{\mathrm{S}}^{\lambda}(\rho)\cdot\chi(\rho)^{-1}J_{\mathrm{A}}^{\lambda}(\rho) = 0$

Work to maintain stationary state

- $\lambda \quad u(t) = \bar{\rho}_\lambda \quad 0 \le t \le T$

$$W_{[0,T]} = \int_0^T dt \, \frac{d}{dt} \int_\Lambda dx \, f(u(t)) \; + \; \int_0^T dt \int_\Lambda dx \; j(t) \cdot \chi(u(t))^{-1} j(t)$$

$$= \int_0^T dt \int_\Lambda dx \; J(u(t)) \cdot \chi(u(t))^{-1} J(u(t))$$

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- $J(\rho) = J_{\mathrm{S}}^{\lambda}(\rho) + J_{\mathrm{A}}^{\lambda}(\rho)$
- $J_{\mathrm{S}}^{\lambda}(\rho) = -\chi(\rho) \, \nabla \dfrac{\delta V_\lambda(\rho)}{\delta \rho}$
- $\dfrac{\delta V_\lambda(\bar{\rho}_\lambda)}{\delta \rho} = 0 \qquad J_{\mathrm{S}}^{\lambda}(\bar{\rho}_\lambda) = 0$

Work to maintain stationary state

- $\lambda \qquad u(t) = \bar{\rho}_\lambda \qquad 0 \le t \le T$

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- $J(\rho) = J_{\mathrm{S}}^\lambda(\rho) + J_{\mathrm{A}}^\lambda(\rho)$
- $J_{\mathrm{S}}^\lambda(\rho) = -\chi(\rho) \, \nabla \dfrac{\delta V_\lambda(\rho)}{\delta \rho}$
- $\dfrac{\delta V_\lambda(\bar{\rho}_\lambda)}{\delta \rho} = 0 \qquad J_{\mathrm{S}}^\lambda(\bar{\rho}_\lambda) = 0$

$$W_{[0,T]} = T \int_\Lambda dx \; J_A^\lambda(\bar{\rho}_\lambda) \cdot \chi(\bar{\rho}_\lambda)^{-1} J_A^\lambda(\bar{\rho}_\lambda)$$

Renormalized work

- Fix $T > 0$ profile ρ ch. pot. $\lambda(t)$
- $u(t)$ $j(t)$ $t \geq 0$

$$W^{\text{ren}}_{[0,T]}[\lambda,\rho] = W_{[0,T]}[\lambda,\rho] - \int_0^T dt \int_\Lambda dx\, J_{\text{A}}^{\lambda(t)}(u(t)) \cdot \chi(u(t))^{-1} J_{\text{A}}^{\lambda(t)}(u(t))$$

Renormalized work

- Fix $T > 0$ profile ρ ch. pot. $\lambda(t)$
- $u(t)$ $j(t)$ $t \geq 0$

$$W^{\text{ren}}_{[0,T]}[\lambda, \rho] = W_{[0,T]}[\lambda, \rho] - \int_0^T dt \int_\Lambda dx\, J_{\mathrm{A}}^{\lambda(t)}(u(t)) \cdot \chi(u(t))^{-1} J_{\mathrm{A}}^{\lambda(t)}(u(t))$$

- Orthogonality $J_{\mathrm{S}}^{\lambda(t)}(u(t))$, $J_{\mathrm{A}}^{\lambda(t)}(u(t))$

$$W^{\text{ren}}_{[0,T]}[\lambda, \rho] = F(u(T)) - F(\rho) + \int_0^T dt \int_\Lambda dx\, J_{\mathrm{S}}^{\lambda(t)}(u(t)) \cdot \chi(u(t))^{-1} J_{\mathrm{S}}^{\lambda(t)}(u(t))$$

Clausius inequality

$$W^{\text{ren}}_{[0,T]}[\lambda,\rho] = F(u(T)) - F(\rho) + \int_0^T dt \int_\Lambda dx \, J_{\mathrm{S}}^{\lambda(t)}(u(t)) \cdot \chi(u(t))^{-1} J_{\mathrm{S}}^{\lambda(t)}(u(t))$$

- $\lambda(t) \to \lambda_1$
- $J_{\mathrm{S}}^{\lambda(t)}(u(t)) \to J_{\mathrm{S}}^{\lambda_1}(\bar{\rho}_1) = 0$

$$W^{\text{ren}}[\lambda,\rho] = F(\rho_1) - F(\rho) + \int_0^\infty dt \int_\Lambda dx \, J_{\mathrm{S}}^{\lambda(t)}(u(t)) \cdot \chi(u(t))^{-1} J_{\mathrm{S}}^{\lambda(t)}(u(t))$$

Clausius inequality

$$W^{\text{ren}}_{[0,T]}[\lambda,\rho] = F(u(T)) - F(\rho) + \int_0^T dt \int_\Lambda dx\, J_{\mathrm{S}}^{\lambda(t)}(u(t)) \cdot \chi(u(t))^{-1} J_{\mathrm{S}}^{\lambda(t)}(u(t))$$

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$$W^{\text{ren}}[\lambda,\rho] \geq F(\rho_1) - F(\rho)$$

$$W[\lambda,\rho] \geq W^{\text{ren}}[\lambda,\rho] \geq F(\rho_1) - F(\rho)$$

Quasi static transformations

- $\lambda(0) = \lambda_0 \qquad \rho(0) = \bar{\rho}_{\lambda_0}$
- $\lambda(t) = \lambda_1 \qquad t \geq T$
- $\delta > 0 \qquad \lambda_\delta(t) = \lambda(\delta t) \qquad (u_\delta(t), j_\delta(t))$

$$\int_0^\infty dt \int_\Lambda dx\, J_{\mathrm{S}}^{\lambda_\delta(t)}(u_\delta(t)) \cdot \chi(u_\delta(t))^{-1} J_{\mathrm{S}}^{\lambda_\delta(t)}(u_\delta(t))$$

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- $\bar{\rho}_\delta(t) = \bar{\rho}_{\lambda_\delta(t)}$
- $J_{\mathrm{S}}^{\lambda_\delta(t)}(\bar{\rho}_\delta(t)) = 0$

$$\int_0^\infty dt \int_\Lambda dx \, \big[J_{\mathrm{S}}^{\lambda_\delta(t)}(u_\delta(t)) - J_{\mathrm{S}}^{\lambda_\delta(t)}(\bar{\rho}_\delta(t))\big] \cdot \chi(u_\delta(t))^{-1} \big[J_{\mathrm{S}}^{\lambda_\delta(t)}(u_\delta(t)) - J_{\mathrm{S}}^{\lambda_\delta(t)}(\bar{\rho}_\delta(t$$

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$$W^{\text{ren}} = \Delta F = F(\bar{\rho}_1) - F(\bar{\rho}_0)$$

Excess work

- $\lambda(t) \longrightarrow \lambda_1$
- initial density profile ρ.

$$W_{\rm ex}[\lambda, \rho] = W^{\textsf{ren}}[\lambda, \rho] - \min W^{\textsf{ren}}[\lambda', \rho]$$

$$= \int_0^\infty dt \int_\Lambda dx \, J_{\rm S}^{\lambda(t)}(u(t)) \, \cdot \chi(u(t))^{-1} J_{\rm S}^{\lambda(t)}(u(t))$$

Relaxation path: excess work and quasi potential

- $(\lambda_0, \bar{\rho}_0) \qquad \lambda_1 \qquad t \geq 0$
- $u(t) \longrightarrow \bar{\rho}_1$

$$\begin{aligned} W_{\text{ex}}[\lambda_1, \bar{\rho}_0] &= \int_0^\infty dt \int_\Lambda dx\, J_{\text{S}}^{\lambda_1}(u(t)) \cdot \chi(u(t))^{-1} J_{\text{S}}^{\lambda_1}(u(t)) \\ &= \int_0^\infty dt \int_\Lambda dx\, J^{\lambda_1}(u(t)) \cdot \chi(u(t))^{-1} J_{\text{S}}^{\lambda_1}(u(t)) \end{aligned}$$

Relaxation path: excess work and quasi potential

- $(\lambda_0, \bar{\rho}_0) \qquad \lambda_1 \qquad t \geq 0$
- $u(t) \longrightarrow \bar{\rho}_1$

$$W_{\rm ex}[\lambda_1, \bar{\rho}_0] = \int_0^\infty dt \int_\Lambda dx\, J_{\rm S}^{\lambda_1}(u(t)) \cdot \chi(u(t))^{-1} J_{\rm S}^{\lambda_1}(u(t))$$
$$= \int_0^\infty dt \int_\Lambda dx\, J^{\lambda_1}(u(t)) \cdot \chi(u(t))^{-1} J_{\rm S}^{\lambda_1}(u(t))$$

$$\int_0^\infty dt \int_\Lambda dx\, \nabla \cdot J^{\lambda_1}(u(t))\, \frac{\delta V_{\lambda_1}(u(t))}{\delta \rho} = -\int_0^\infty dt \int_\Lambda dx\, \partial_t u(t)\, \frac{\delta V_{\lambda_1}(u(t))}{\delta \rho}$$

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$$\int_0^\infty dt \int_\Lambda dx\, \nabla \cdot J^{\lambda_1}(u(t)) \, \frac{\delta V_{\lambda_1}(u(t))}{\delta \rho} \; = \; - \int_0^\infty dt \int_\Lambda dx\, \partial_t u(t) \, \frac{\delta V_{\lambda_1}(u(t))}{\delta \rho}$$

$$W_{\mathrm{ex}}[\lambda_1, \bar{\rho}_0] = V_{\lambda_1}(\bar{\rho}_0) - V_{\lambda_1}(\bar{\rho}_1) \; = \; V_{\lambda_1}(\bar{\rho}_0)$$