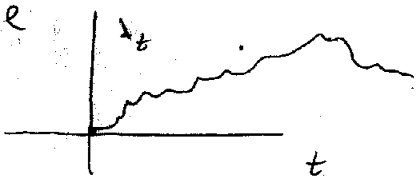
Classical fluctuation relations:

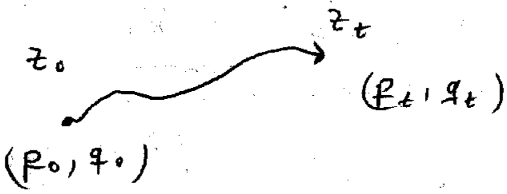
$z = (p, q)$ $\quad \lambda_t$ parameter $\quad t \in [0, \tau]$

→ force protocol



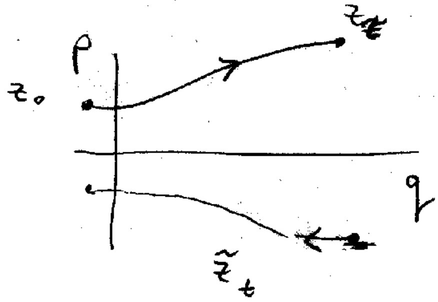
$$\boxed{H(z,t) = H_0(z) - \lambda_t\, Q(z)}$$

$$\dot{p} = -\frac{\partial H}{\partial q} \; ; \qquad \dot{q} = \frac{\partial H}{\partial p}$$



$$\boxed{z_t = \varphi_{t,0}[z_0; \lambda]}$$

time reversal:



$\epsilon(z)$: $z \to z'$

$(p, q) \to (-p, q)$

- assume $H_0(z) = H_0(\epsilon(z))$

  (α parameters $\quad H_0(z, \alpha) = H_0(\epsilon z, \epsilon \alpha)$)

- $Q(\epsilon(z)) = \epsilon_Q \cdot Q(z)$

$$\tilde{\lambda}_t \equiv \lambda_{\tau - t} \; ; \qquad \tilde{z}_t = z_{\tau - t}$$

$$\boxed{\varphi_{t,0}[z_0; \lambda] = \epsilon\, \varphi_{\tau - t, 0}[\epsilon z_\tau; \epsilon_Q \lambda_{\tau - t}]}$$

Fluctuation relations:

$$Z_0 \equiv \int dz_0 \; e^{-\beta H_0(z_0)} \; ; \quad \text{assume} \quad \rho_0(z_0) = \frac{e^{-\beta H_0(z_0)}}{Z_0}$$

random initial cond.

equilibrium! ergodic!

$$\Rightarrow \quad \frac{dH}{dt} = \underbrace{\dot{p} \cdot \frac{\partial H}{\partial p} + \dot{q}\frac{\partial H}{\partial q}}_{\overset{\shortparallel}{\emptyset}} + \frac{\partial H}{\partial t} = -\dot{\lambda}_t\, Q(z_t)$$

Jarzynski

$$\Rightarrow \quad \boxed{W_\ast[z_0;\lambda] = -\int_0^\tau dt\ \dot\lambda_t\, Q_t} \quad Q_t = Q(z_t)$$

"inclusive" work

$$W_\ast(z_0;\lambda) = H(z_\tau,\lambda_\tau) - H(z_0,\lambda_0) = H_0(z_\tau,\lambda_\tau) - H_0(z_0,\lambda_0) - \lambda_\tau Q_\tau$$

exclusive work:

$$\frac{dH_0}{dt} = \dot p \frac{\partial H_0}{\partial p} + \dot q \frac{\partial H_0}{\partial q} = \dot p \frac{\partial H}{\partial p} + \dot q \frac{\partial H}{\partial q} + \lambda_t \underbrace{\left(\dot p \frac{\partial Q}{\partial p} + \dot q \frac{\partial Q}{\partial q}\right)}_{\frac{dQ}{dt} = \dot Q_t}$$

$$\Rightarrow \quad \boxed{W_0[z_0;\lambda] = \int_0^\tau dt\ \lambda_t\, \dot Q_t = H_0(z_\tau) - H_0(z_0)}$$

$$z_\tau = \varphi_{\tau,0}(z_0,\lambda)$$

Statement: $\quad u_t$ arbitrary function
B_t arbitrary observable
λ any protocol

$$\boxed{\left\langle e^{\int_0^\tau dt\ u_t B_t}\, e^{-\beta W_0} \right\rangle_\lambda = \left\langle e^{\int_0^\tau dt\ \tilde u_t\, \epsilon_B B_t} \right\rangle_{\epsilon_Q \tilde\lambda}}$$

generating functional

Proof:

$$\frac{1}{Z_0}\int dz_0\ \cancel{e^{-\beta H_0(z_0)}}\ e^{-\beta H_0(z_\tau)}\ \cancel{e^{\beta H_0(z_0)}}\ e^{\int_0^\tau dt\ u_t B(z_t)}$$

$$\int_0^\tau dt\ u_t B(z_t) = \int_0^\tau dt\ B(z_{\tau-t})\cdot \underbrace{u_{\tau-t}}$$

φ_t volume conserving $\longrightarrow \int dz_0 \ldots = \int dz_\tau \ldots$

$$B(z_{\tau-t}) = B\left(\epsilon\, \varphi_t[\epsilon z_\tau, \tilde\lambda_t\cdot\epsilon_Q]\right) = \epsilon_B\, B\left(\varphi_t[\epsilon z_\tau; \tilde\lambda_t\cdot\epsilon_Q]\right)$$

$$\text{l.h.s} = \frac{1}{Z_0}\int d(\epsilon z_\tau)\ e^{-\beta H_0(\epsilon z_\tau)}\ e^{\int_0^\tau dt\ \tilde u_t\, \epsilon_B B_t}\ \Bigg|_{\tilde\lambda_t\cdot\epsilon_Q}$$

$\epsilon z_\tau \to z_0$ change of var.

$$= \left\langle e^{\int_0^\tau dt\ \tilde u_t\, \epsilon_B B_t} \right\rangle_{\epsilon_Q \tilde\lambda_t} \qquad \square$$

Consequences :

- Bochkov – Kuzovlev equality ('77 ?)

$$U_t = \emptyset \Rightarrow \boxed{\langle e^{-\beta W_0} \rangle_\lambda = 1}$$

- $e^{-\beta W_0} \geq 1 - \beta W_0 \quad \Rightarrow \quad \langle W_0 \rangle \geq 0 \quad !$
- $P(W_0 < 0) \neq \emptyset \,!$

- Onsager relations $\Leftrightarrow \frac{\delta}{\delta U_t} \frac{\delta}{\delta \lambda_{t'}}$??

- rather $\quad U_t B_t \Rightarrow \sum_\mu U_t^\mu B_t^\mu$

$$\frac{\delta}{\delta U_t^\mu} \frac{\delta}{\delta U_{t'}^\nu} \underset{\lambda = \emptyset}{\Rightarrow} \quad \langle B_t^\mu B_{t'}^\nu \rangle_0 = \epsilon_\mu \epsilon_\nu \langle B_{\tau - t}^\mu B_{\tau - t'}^\nu \rangle_0$$

$$\Rightarrow \boxed{\langle B_t^\mu B_0^\nu \rangle = \epsilon_\mu \epsilon_\nu \langle B_t^\nu B_0^\mu \rangle_0}$$

Work statistics :

$$\boxed{p_0[w;\lambda] \equiv \langle \delta(w - W_0) \rangle_\lambda} = \int dz_0\, \rho_0(z_0)\, \delta(w - H_0(z_\tau) + H_0(z_0))$$

its generating function

$$G_0(u) \equiv \int dw\, e^{iu \cdot w} p_0(w) = \langle e^{iu \cdot W_0} \rangle_\lambda$$

statement :

$$\boxed{\frac{p_0[w;\lambda]}{p_0[-w; \epsilon_Q \tilde{\lambda}]} = e^{\beta w}}$$

~ ~~detailed~~ balance (Kurchan, Jarzynski, 2007)

proof :

$$\int dz_0 \frac{1}{Z_0} e^{-\beta H_0(z_0)} \delta(w - H_0(\underbrace{z_\tau}_{\varphi_\tau[z_0,\lambda]}) + H_0(z_0)) =$$

$$e^{-\beta H_0(z_\tau)} e^{\beta w} = e^{-\beta H_0(\epsilon z_\tau)} e^{\beta w}$$

$$= \int d(\epsilon z_\tau) \frac{1}{Z_0} e^{-\beta H_0(\epsilon z_\tau)} e^{\beta w} \delta(-w - H_0(\underbrace{\epsilon z_0}_{\varphi_\tau[\epsilon z_\tau, \epsilon_Q \tilde{\lambda}]}) + H_0(\epsilon z_\tau))$$

$$\epsilon z_\tau \Rightarrow \tilde{z}_0$$

$$= e^{\beta w} p_0[-w, \epsilon_Q \tilde{\lambda}] \qquad \square$$

meaning: one does not get back work, even if one reverses the path!

Generalizations for inclusive work:

$$W = -\int_0^\tau \dot{\lambda}_t Q_t\, dt = \int_0^\tau \lambda_t \dot{Q}_t\, dt - \lambda_t Q_t \Big|_0^\tau = W_0 - \lambda_t Q_t \Big|_0^\tau$$

$= H_\tau - H_{t=0}$

assume that H was in equilibrium!

$$\rho(z, \lambda_t) = e^{-\beta H(z,t)} / Z(\lambda_t) \; ; \qquad Z(\lambda_t) = \int dz\, e^{-\beta H(z, \lambda_t)} = e^{-\beta F_t}$$

$$\Rightarrow \quad \boxed{\left\langle e^{\int_0^\tau v_t B_t\, dt} e^{-\beta W} \right\rangle_\lambda = e^{-\beta \Delta F} \left\langle e^{\int_0^\tau \tilde{v}_t B_t\, dt\, \epsilon_B} \right\rangle_{\epsilon_Q \tilde{\lambda}}}$$

$$\Rightarrow \quad \boxed{\left\langle e^{-\beta W} \right\rangle_\lambda = e^{-\beta \Delta F}}$$

1997, Jarzynski
"Jarzynski equality"

$\rightarrow \langle W \rangle \geq \Delta F.$

$$\boxed{p(w) \equiv \left\langle \delta(w - W) \right\rangle_\lambda} \quad \Rightarrow \quad G(u) = \left\langle e^{iu\cdot W} \right\rangle_\lambda$$

$$\boxed{\frac{p(w; \lambda)}{p(-w; \epsilon_Q \tilde{\lambda})} = e^{\beta(W - \Delta F)}}$$

Crooks, 1999
"Crooks fluctuation theorem"

notice: for cyclic protocols $\Delta F = 0$; ~~$W = W_0$~~