

Outline.

- 1) Review of entropy / second law in thermodynamics.
- 2) Fluctuation theorems
 - Transient (Jarzynski, Crooks, Seifert)
 - SSFT (Gallavotti - Cohen, Kurchan, Spohn - Lebowitz)
- 3) Derivation for systems with Markovian dynamics.

Lecture 1 (Transient)

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FLUCTUATION THEOREMS IN NONEQUILIBRIUM PHYSICS.

Brief review of thermodynamics, notion of entropy, ~~and~~ equilibrium statistical physics, Linear response theory.

First law of thermodynamics. - Conservation of energy.

$$dU = \delta Q + \delta W$$

heat flow into system work done on system

Second law of thermodynamics:

Clausius: Impossible for a refrigerator, working in a cycle, to transfer heat from cold to hot reservoir with (no other changes).

- Leads to concept of absolute temperature.
- For a reversible process $\frac{\delta Q}{T} = dS$ is a perfect differential.

Hence entropy S is a function of the state variables.

Fundamental equation $S = S(U, V, N)$

Statistical mechanics.

$$S = k \ln \Omega(U, V, N)$$

Phase space volume
in energy shell around
 U

No. of states.

Relation between Thermodynamics and Mechanics.

$$\Omega = \frac{1}{h^{3N}} \int d^3q d^3p \delta(H(q, p) - U)$$

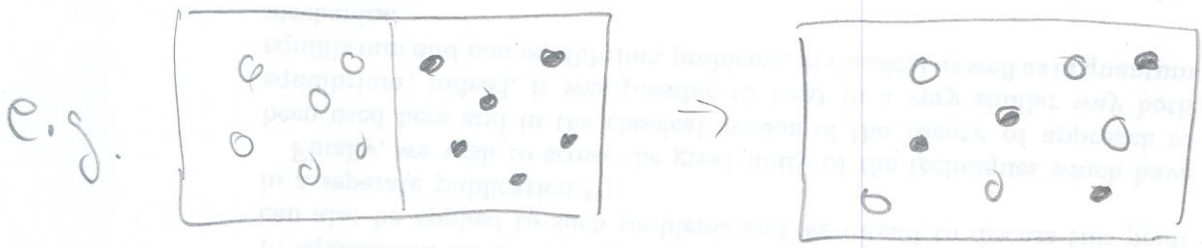
Note: S is a function of the thermodynamic state and not a function of phase space variables (q, p) .

In stat mech, it is a property of an ensemble or a probability distribution in phase space.

$$S = -k \sum_i p_i \ln p_i$$

p_i = Probability of being in
ith microscopic

The second law also tells us that for an irreversible process the total entropy of the universe increases.



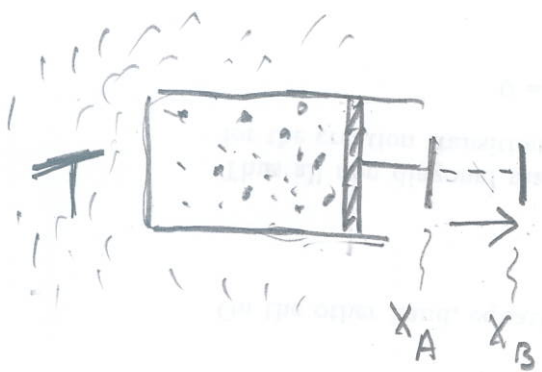
* Entropy is defined only for equilibrium states. IF A system goes from one equilibrium state A to another equilibrium state B then

the $S_B - S_A \geq 0$.

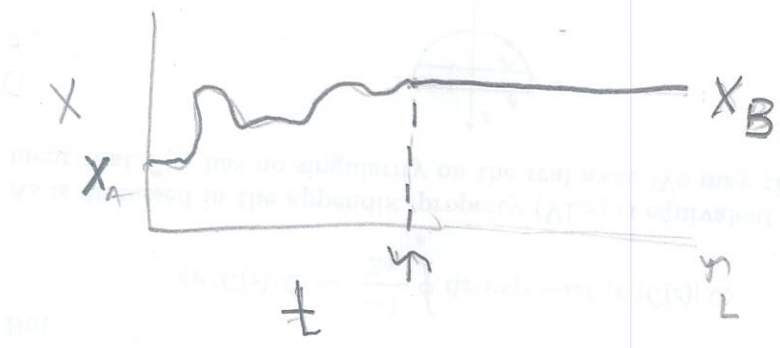
for an isolated system
 otherwise total entropy change ≥ 0 .

For systems that are not isolated but in contact with either heat baths or particle reservoir it is useful to construct other "thermodynamic free energies".

Consider system in contact with heat bath at temperature T



Imagine moving a piston from position x_A to x_B in a finite time τ . At the end of τ we wait for a long time and allow the system to equilibrate to temperature T .



Let Q = heat absorbed by system in time τ_L

W = Work done on system

$$\Delta S = S(x_B) - S(x_A)$$

Then 2nd Law $\frac{-Q}{T} + \Delta S \geq 0$

1st Law $Q = \Delta U - W$

Hence $\frac{1}{T} [T \Delta S - \Delta U + W] \geq 0$

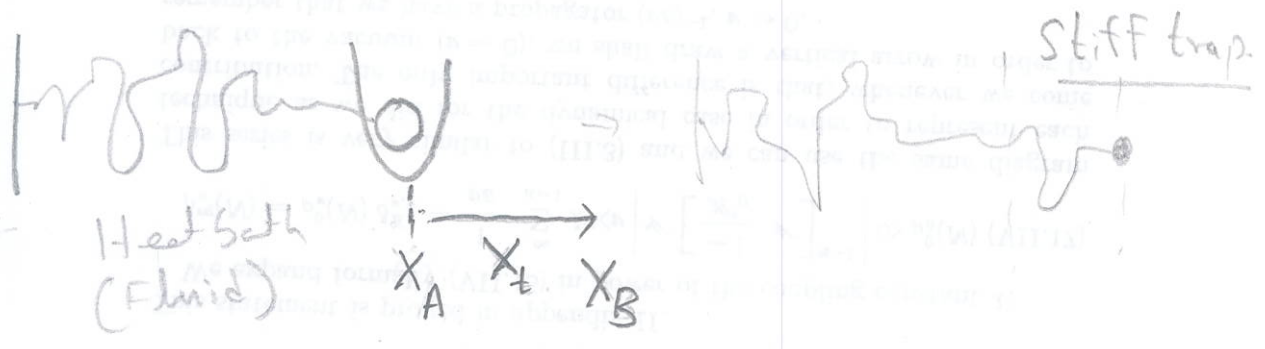
For an isothermal process $F = U - TS$
 $\Delta F = \Delta U - T \Delta S$

∴ We have change in entropy

$$\Delta S_{tot} = \frac{1}{T} (W - \Delta F) \geq 0$$

$$\frac{\Delta S_{tot}}{k_B} = \beta (W - \Delta F) \geq 0$$

Now imagine doing an experiment on a small system such as a RNA molecule.



Free energy is a function of T, X, N

$F = F(T, N, X)$ We do an experiment where $X = X_t$ is the time dependent parameter

which changes from value X_A to $X_B \rightarrow$ Specifies the driving protocol.

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• At time $t=0$ the polymer is in thermal equilibrium at temperature T and end-to-end distance fixed to x_A .

• We stretch the polymer from x_A to x_B ^{in time} τ following the protocol x_t

• The polymer has a Hamiltonian H which depends on the parameter x_t , $H = (q_1, q_2, \dots, q_n, p_1, \dots, p_n; x_t)$

The work done
$$W_J = \int_0^\tau dt \frac{\partial H}{\partial x_t} = \int_0^\tau dt \frac{\partial H}{\partial x_t} \dot{x}_t$$

Can be measured.

* Unlike the thermodynamic work W , W_J in a small system, \uparrow the work W_J is ^{now} a fluctuating variable.

If we repeat our experiment with the same protocol we will measure different values of W_J because:

W_J is a function of the path in phase space along which the system evolves. This fluctuates because

- (1) initial conditions fluctuate
- (2) path fluctuates because of interactions with heat bath.

For a particular realization it is possible that $W_J - \Delta F < 0$.

"Transient violation of the second law" - discussed by Perrin.

Can show $\langle W_J \rangle - \Delta F > 0$.

Define: $S = \beta(W_J - \Delta F)$, entropy generated on a particular realization of the stretching experiment. Fluctuating variable with a distribution $P(S)$.

Fluctuation theorems: General results on these entropy production fluctuations.

Jarzynski's Equality

$\langle e^{-S} \rangle = 1 \Rightarrow \langle e^{-\beta W_J} \rangle = e^{-\beta \Delta F}$] EXACT EQUALITY.

Jensen's inequality $e^{-\langle X \rangle} \leq \langle e^{-X} \rangle$

$\Rightarrow e^{-\beta \langle W_J \rangle} \leq e^{-\beta \Delta F}$

$\Rightarrow \langle W_J \rangle \geq \Delta F$

$\langle e^{-\beta W_J} \rangle = \int_{-\infty}^{\infty} e^{-\beta W_J} P(W_J) dW_J$

Not the characteristic function.

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Proof: $H = H(\bar{q}, \bar{p}; \lambda_t)$ $\lambda_0 = \lambda_A, \lambda_T = \lambda_B$

Simplest Version:

• At $t=0$ system is in contact with a heat bath and so in thermal equilibrium at temperature T .

• The free energy of the system is

$$F(T, \lambda_A) = -k_B T \ln Z(\lambda_A)$$

$$Z(\lambda_A) = \int e^{-\beta H(\lambda_A)} d\bar{q} d\bar{p}$$

• The contact with heat bath is then removed and the work protocol λ_t is started.

Between times $0 - \tau$ system evolves through Hamiltonian dynamics

$$\dot{q}_i = \frac{\partial H(\lambda_t)}{\partial p_i} \quad \dot{p}_i = -\frac{\partial H(\lambda_t)}{\partial q_i}$$

• Measure work done in time τ

$$W_J = \int_0^\tau dt \frac{\partial H}{\partial t}$$

Note

$$\frac{dH}{dt} = \underbrace{\frac{\partial H}{\partial q_i} \dot{q}_i + \frac{\partial H}{\partial p_i} \dot{p}_i}_{=0} + \frac{\partial H}{\partial t}$$

Hence
$$W_J = H(\bar{q}(r), \bar{p}(r), \lambda_r) - H(\bar{q}(0), \bar{p}(0), \lambda_0)$$

$$= H_B - H_A$$

$\therefore \langle e^{-\beta W_J} \rangle$ \rightarrow average over initial configurations

$$= \int e^{-\beta(H_B - H_A)} \underbrace{d\bar{q}_0 d\bar{p}_0 \frac{e^{-\beta H_A}}{Z_A}}_{\text{Prob. of initial state}}$$

$$= \int d\bar{q}_0 d\bar{p}_0 \frac{e^{-\beta H_B}}{Z_A}$$

Liouville's theorem $d\bar{q}_0 d\bar{p}_0 = d\bar{q}_r d\bar{p}_r$

Using $\int d\bar{q}_r d\bar{p}_r e^{-\beta H_B} = Z_B$, we get

$$\boxed{\langle e^{-\beta W_J} \rangle = \frac{Z_B}{Z_A} = e^{-\beta(F_B - F_A)}} \rightarrow \text{QED.}$$

Quantum systems (Kurchan, Tasaki)

Work has to be defined in terms of measurements.

• At $t=0$ system in equilibrium \rightarrow measure it's energy. System evolves unitarily over time $\tau \rightarrow$ measure energy again. $W_S = E_\tau - E_0$.

• At $t=0$ don't we find the system in an energy eigenstate $E_\alpha(0)$ with probability $\frac{e^{-\beta E_\alpha(0)}}{Z_A}$.

• The eigenstate $|\Psi_\alpha(0)\rangle$ evolves to $U_\tau |\Psi_\alpha(0)\rangle$

where $U_\tau = \mathbb{T} \left[e^{-\frac{i}{\hbar} \int_0^\tau dt \hat{H}(\lambda_t)} \right]$

• At $t=\tau$ we will find the system in an energy eigenstate $E_\beta(\tau)$ with probability

$$|\langle \Psi_\beta(\tau) | U_\tau | \Psi_\alpha(0) \rangle|^2$$

• Work done is $W_S = E_\beta(\tau) - E_\alpha(0)$

$$E_\alpha(t) \text{ satisfies } H(\lambda t) |\Psi_\alpha(t)\rangle = E_\alpha(t) |\Psi_\alpha(t)\rangle \quad (11)$$

instantaneous eigenstates.

$$\therefore \langle e^{-\beta W_J} \rangle$$

$$= \sum_{\alpha, \beta} e^{-\beta(E_B(\tau) - E_\alpha(0))} \frac{e^{-\beta E_\alpha(0)}}{Z_A} \langle \Psi_\beta(\tau) | U_\tau | \Psi_\alpha(0) \rangle \langle \Psi_\alpha(0) | U_\tau^\dagger | \Psi_\beta(\tau) \rangle$$

$$= \frac{\sum_{\beta} e^{-\beta E_B(\tau)}}{Z_A} = \frac{Z_B}{Z_A} = e^{-\beta \Delta F} \quad [\text{OED}]$$

J.E is an example of an "integrated F.T."

We now give an example of a "detailed

F.T." — Crook's identity.

Again a classical system isolated from heat bath at $t=0$.

$$P(W_J) = \int d\bar{q}_0 d\bar{p}_0 \delta(W_J - (H_B - H_A)) \frac{e^{-\beta H_A}}{Z_A}$$

\downarrow
 $H_A = H_B - W_J$

$$= \int d\bar{q}_r d\bar{p}_r \delta(-W_J - (H_A - H_B)) \frac{e^{-\beta H_B}}{Z_B} \left(e^{\beta W_J} \frac{Z_B}{Z_A} \right)$$

Now if we consider the transformation (time reversal)

$$q'_i = q_i, \quad p'_i = -p_i, \quad t' = \tau - t \quad \text{we see that}$$

q'_i, p'_i satisfy the equations of motion with

the time-reversed protocol $\bar{\lambda}_t = \lambda_{\tau-t}$.

Hence under this protocol the system will

evolve from $(\bar{q}_r, -\bar{p}_r)$ at time $t=0$ to

$(\bar{q}_0, -\bar{p}_0)$ at time $t=\tau$.

Work done is $H_A - H_B = -(H_B - H_A)$

work done in forward protocol.

$$\therefore \int d\bar{q}_r d\bar{b}_r \delta(-w_j - (H_A - H_R)) \frac{e^{-\beta H_B}}{Z_B}$$

$$= P_R(-w_j)$$

$P_R(w_j) \equiv$ Distribution of work under the protocol $\bar{\lambda}_t$.

Hence $\mathcal{P}(w_j) = P_R(-w_j) e^{\beta(w_j - \Delta F)}$

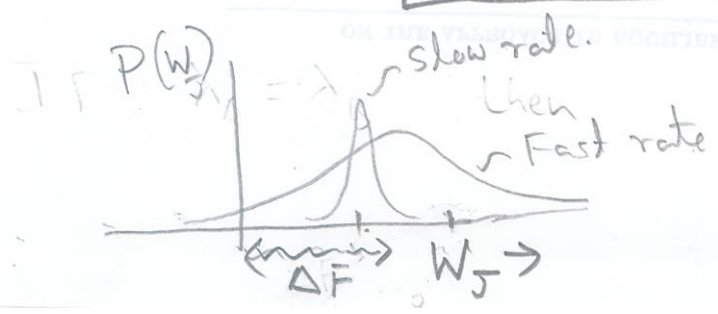
OR for $\mathcal{S} = \beta(w_j - \Delta F)$

$$\boxed{\frac{P(\mathcal{S})}{P_R(-\mathcal{S})} = e^{\mathcal{S}}} \quad \text{Crook's Identity}$$

J.E follows from C.E.

$$\int dw_j P(w_j) e^{-\beta(w_j - \Delta F)} = \int_{-\infty}^{\infty} P_R(-w_j) dw_j = 1$$

$$\Rightarrow \boxed{\langle e^{-\beta w_j} \rangle = e^{-\beta \Delta F}}$$



Transient Fluctuation Theorems are (4)
Interesting because:

- General results valid far from equilibrium.
Tells us about how improbable rare fluctuations are.
- Possible method for estimating equilibrium free energy profile from non-equilibrium measurements. (experiments and simulations)
- Verified in experiments on RNA stretching and trapped colloidal particles.