A deterministic approach to the foundations of statistical thermodynamics

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What would we like to know about a (equilibrium/nonequilibrium) thermodynamic system?

- What is the equilibrium distribution function?
- How do properties evolve out of equilibrium?
- Can we derive the 2^{nd} Law?
- Relaxation to equilibrium?
- Relaxation to a steady state?
- Is there only one steady state?

…

Plan

1. Thermostatted nonequilibrium dynamical systems
2. Transient fluctuation theorem

   2nd Law
3. Thermodynamic interpretation of the dissipation function
4. The dissipation theorem Response theory
5. T-mixing
6. Extensions
   - Relaxation to equilibrium & equilibrium distribution functions
   - Steady state fluctuation theorem

1. Thermostatted nonequilibrium dynamical systems

- Nonequilibrium molecular dynamics algorithms
  - Deterministic equations of motion modified to model effects of thermodynamic gradients of mechanical forces.
  - Homogeneous/inhomogeneous:

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m} + \mathbf{C}_i(\Gamma) \bullet \mathbf{F_e}$$

$$\dot{\mathbf{p}}_i = F_i(\mathbf{q}) + \mathbf{D}_i(\Gamma) \bullet \mathbf{F_e}$$

$\Gamma = (\mathbf{q}, \mathbf{p})$
$\mathbf{q}_i$: particle position
$\mathbf{p}_i$: particle momentum
$\mathbf{C}_i$ and $\mathbf{D}_i$: couple particles to field, $\mathbf{F_e}$

    - We select **C** and **D** so that equations of motion are reversible

  - Boundary driven
    - Wall particles treated different to produce the required flow/transport

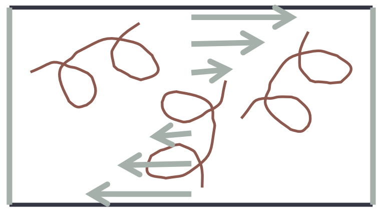
1. Thermostatted nonequilibrium dynamical systems

Examples:

- Homogeneous Couette flow with strain rate $\dot{\gamma}$

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m} + \mathbf{i}\dot{\gamma}y_i$$

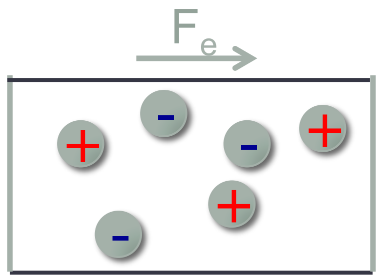
$$\dot{\mathbf{p}}_i = \mathrm{F}_i - \mathbf{i}\dot{\gamma}p_{yi}$$



- Particles with charge, c_i in a field, $\mathbf{F}_e$

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m}$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i + c_i\mathbf{F}_e$$



- Boundary driven Couette flow

Fluid

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m}$$

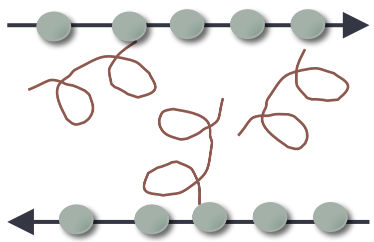
$$\dot{\mathbf{p}}_i = \mathbf{F}_i$$

Wall

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m}$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - k(q_{xi} - q_{xi}^0)\mathbf{i}$$

$$\dot{q}_{xi}^0 = \pm \tfrac{1}{2}\dot{\gamma}L_y$$



1. Thermostatted nonequilibrium dynamical systems

- Thermostat / ergostat
  - Various mechanisms – remove heat generated by field

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m} + \mathbf{C}_i(\Gamma) \bullet \mathbf{F}_e$$
$$\dot{\mathbf{p}}_i = \mathbf{F}_i(\mathbf{q}) + \mathbf{D}_i(\Gamma) \bullet \mathbf{F}_e - S_i \alpha(\Gamma) \mathbf{p}_i,$$

  - S_i is a switch that determines if all particles, or some (e.g. wall particles) are thermostatted or ergostatted
  - A can take on a range of forms: fix kinetic energy (Gauss's principle of least constraint), generate a canonical ensemble…
  - Can be made arbitrarily far from the system so details of thermostatting mechanism do not affect physics of the system

1. Thermostatted nonequilibrium dynamical systems

$$\nabla_{\Gamma} \bullet \dot{\Gamma} = \Lambda (= -3N_t \alpha)$$

$$S^t d\Gamma = d\Gamma e^{\int_0^t \Lambda(S^s \Gamma) ds} (= d\Gamma e^{-3N_t \int_0^t \alpha(S^s \Gamma) ds})$$

$$f_t(S^t \Gamma) = f_0(\Gamma) e^{-\int_0^t \Lambda(S^s \Gamma) ds} (= f_0(\Gamma) e^{3N_t \int_0^t \alpha(S^s \Gamma) ds})$$

2. The transient fluctuation theorem

- General form of fluctuation relations:

$$\frac{\Pr(X_t = A)}{\Pr(X_t = -A)} = \ldots$$

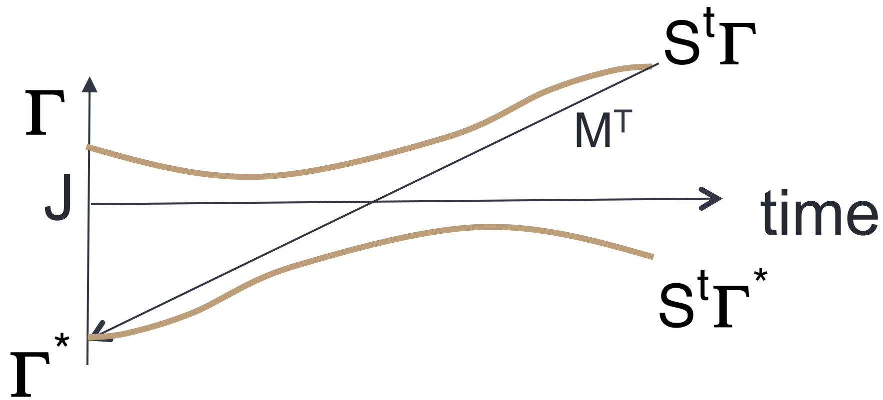
$$X_t = \int_0^t X(S^s\Gamma)\,ds; \quad \overline{X}_t = \frac{1}{t}\int_0^t X(S^s\Gamma)\,ds$$

$\Pr(X_t = A)$ is the probability that X_t takes on a value A±dA

- Wide variety
  - Transient/ steady state; different properties in the argument; deterministic, stochastic, limiting expression of valid under all conditions
- Transient fluctuation theorem for dissipation function of a deterministic system:

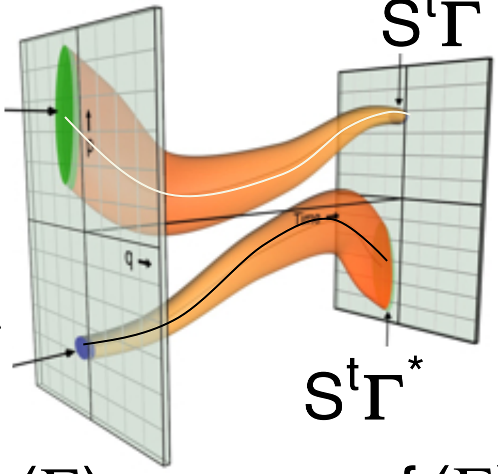
$$\frac{\Pr(\Omega_t = A)}{\Pr(\Omega_t = -A)} = e^A$$

- Derivation



2. The Transient Fluctuation Theorem

Consider two trajectories related by time reversal symmetry..



$$\frac{\Pr(d\Gamma)}{\Pr(d\Gamma^*)} = \frac{f_0(\Gamma)d\Gamma}{f_0\left(\Gamma^*\right)d\Gamma^*}$$

$$= \frac{f_0(\Gamma)}{f_0\left(S^t\Gamma\right)} e^{-\Lambda_t(\Gamma)}$$

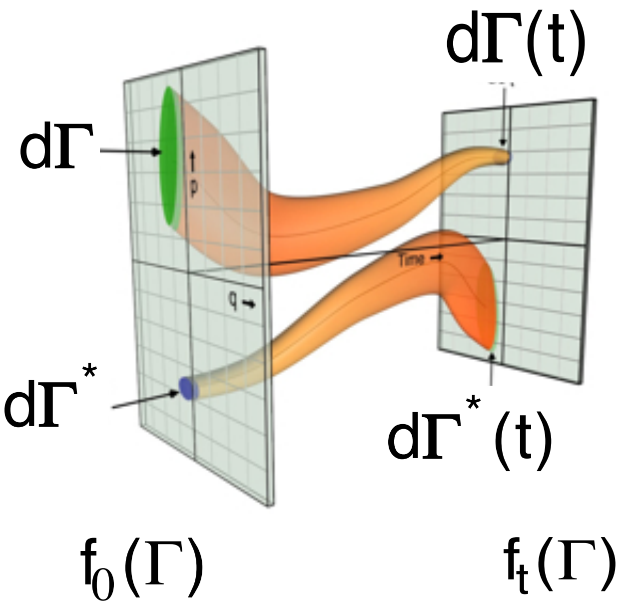
$$\equiv e^{\Omega_t(\Gamma)}$$

$$\Omega_t(\Gamma) = \ln \frac{f_0(\Gamma)}{f_0\left(S^t\Gamma\right)} - \Lambda_t$$

$$\frac{\Pr(\Omega_t = A)}{\Pr(\Omega_t = -A)} \equiv e^A$$

2. The Transient Fluctuation Theorem

Now consider the relative probability of observing the phase volumes $d\Gamma$ and $d\Gamma^*$



$$\frac{\Pr(d\Gamma)}{\Pr(d\Gamma^*)} = \frac{f_0(\Gamma)d\Gamma}{f_0\left(\Gamma^*\right)d\Gamma^*}$$

$$= \frac{f_0(\Gamma)}{f_0\left(S^t\Gamma\right)} e^{-\Lambda_t(\Gamma)}$$

$$\equiv e^{\Omega_t(\Gamma)}$$

Define:

$$\Omega_t(\Gamma) = \ln \frac{f_0(\Gamma)}{f_0(\Gamma(t))} - \Lambda_t$$

Sum over all $d\Gamma$ for which : $\Omega_t = A$

$$\frac{\Pr(\Omega_t = A)}{\Pr(\Omega_t = -A)} \equiv e^A$$

3. Thermodynamic interpretation

What is the dissipation function in some cases of interest?

- NVT – field driven nonequilibrium state

$$\Omega_t = \frac{J_t}{k_B T} F_e V$$

- System subject to a change in temperature

$$\Omega_t = \left(\frac{1}{k_B T_1} - \frac{1}{k_B T_2} \right) \left(H_0(t) - H_0(0) \right)$$

$$\Omega = \Sigma + O(F_e^2) = \int_V dV \frac{\sigma(\mathbf{r})}{k_B} + O(F_e^2)$$

Evans & Searles, Ad. Phys. **51**, 1529-1585 (2002)
Sevick, Prabhakar, Williams & Searles, Ann. Rev. Phys. Chem. **59**, 603-633 (2008)

3. Thermodynamic interpretation of the dissipation function

From the FR, can derive:

$$\langle \Omega_t \rangle \geq 0$$

equality implies equilibrium.

The time integrated dissipation function can also be interpreted as the relative entropy production.

3. Thermodynamic interpretation of the dissipation function

$$\Omega_t = \frac{J_t}{k_B T} F_e V$$

The fluctuation relation can be written:

$$\frac{\Pr(\overline{J}_t = A)}{\Pr(\overline{J}_t = -A)} \equiv e^{AV\beta F_e t}$$

- as volume, time or field increase the probability of observing negative currents decreases exponentially.
- in the thermodynamic limit, current is always positive – for small systems it is not

Evans & Searles, Ad. Phys. **51**, 1529-1585 (2002)
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3. Thermodynamic interpretation of the dissipation function

- The fluctuation theorem: $$\frac{p(\Omega_t = A)}{p(\Omega_t = -A)} = e^A$$

- The second law inequality: $$\langle \Omega_t \rangle \geq 0$$

$$\Omega(t) = -\frac{J(t)}{k_B T(t)} F_e V = -\Lambda(t) = \frac{\dot{Q}(t)}{k_B T(t)}$$ For NVE only!

- Ω is related to the rate of extensive entropy production in linear irreversible thermodynamics and relative entropy:

$$-\frac{J}{k_B T} F_e V = \Sigma = \int_V dV \frac{\sigma(\mathbf{r})}{k_B}$$

$$\frac{p(\Sigma_t = A)}{p(\Sigma_t = -A)} = e^A$$

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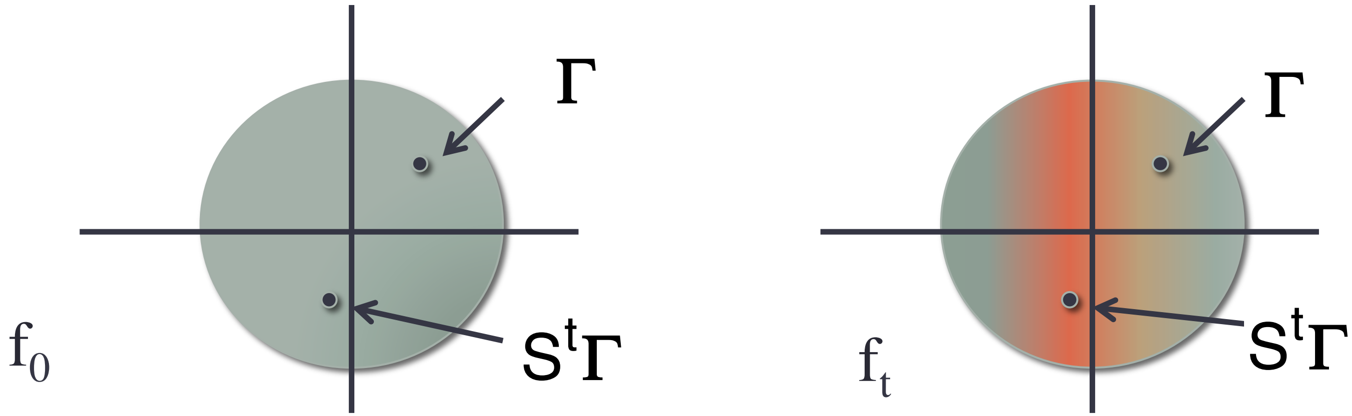
4. The dissipation theorem

- How do the distribution function and properties evolve with time?

$$\langle B(t) \rangle = \int B(\Gamma) f_t(\Gamma) d\Gamma$$



4. The dissipation theorem

- The Lagrangian form of the Liouville equation gives:

$$f_t(S^t\Gamma) = e^{-\Lambda_t(\Gamma)} f_0(\Gamma)$$

- The time integral of the dissipation function is defined via:

$$\frac{f_0(\Gamma)}{f_0\left(S^t\Gamma\right)} e^{-\Lambda_t(\Gamma)} \equiv e^{\Omega_t(\Gamma)}$$

- Substitute for $f_0(\Gamma)$

$$f_t(S^t\Gamma) = e^{\Omega_t(\Gamma)} f_0(S^t\Gamma)$$

- This is true for any Γ, so transform $S^t\Gamma \to \Gamma$

$$f_t(\Gamma) = e^{\Omega_t(S^{-t}\Gamma)} f_0(\Gamma) = e^{\int_{-t}^{0} \Omega(S^s\Gamma)ds} f_0(\Gamma)$$

4. The dissipation theorem

$$f_t(\Gamma) = e^{\Omega_t(S^{-t}\Gamma)} f_0(\Gamma) = e^{\int_{-t}^{0} \Omega(S^s\Gamma)ds} f_0(\Gamma)$$

- Now consider phase variables:
- We can use the distribution function to evaluate

$$\langle B(t) \rangle = \int B(\Gamma) f_t(\Gamma) d\Gamma = \int B(\Gamma) e^{\int_{-t}^{0} \Omega(S^s\Gamma)ds} f_0(\Gamma) d\Gamma$$

- By differentiation and integration (for autonomous systems)

$$\langle B(t) \rangle = \langle B(0) \rangle + \int_0^t \langle B(s)\Omega(0) \rangle ds$$

- Note that the ensemble averages are wrt to the initial distribution.

Comparison with past work..

$$f(\Gamma(0),t) = e^{\int_{-t}^{0}\Omega(\Gamma(s))ds} f(\Gamma(0),0)$$

- Kawasaki - adiabatic (unthermostatted)
- Evans and Morriss - homogeneously thermostatted nonequilibrium dynamics (Gaussian isokinetic) (TTCF)
- In linear response regime, gives Green-Kubo, fluctuation-dissipation expressions
- This is more general – arbitrary dynamics, relaxation
- Like TTCF is an efficient way of determining phase variables at low fields

What can we do with this?

- Relaxation to equilibrium (ergodic theory for Hamiltonian systems, but open question in others)
- Derive relationships for equilibrium ensemble
- Steady state fluctuation theorem
- Relaxation to steady states

5. T-mixing

- Decay of correlations
- Differs from mixing of ergodic theory - it applies to transients
- "Infinite time integrals of transient time correlation functions of zero mean variables converge"

$$\left| \int_0^\infty ds \, \langle A(0)B(s) \rangle_0 \right| < \infty$$

- A special case of T-mixing is $\Omega \; T-\text{mixing}$ for which .

$$\left| \int_0^\infty ds \, \langle \Omega(0)B(s) \rangle_0 \right| < \infty$$

6. Implications – relaxation to equilibrium

- What is equilibrium?

$$f_t(\Gamma) = e^{\int_{-t}^{0} \Omega(S^s\Gamma)ds} f_0(\Gamma)$$

Iff

$$\Omega(\Gamma, t) = 0 \qquad \forall \quad \Gamma, t$$

then the initial distribution is the equilibrium distribution.

6. Implications - Relaxation to equilibrium

- Assume a known initial distribution, that is not necessarily an equilibrium distribution

$$f_0(\Gamma) = \frac{e^{-\beta H(\Gamma)+g(\Gamma)}}{\int d\Gamma\, e^{-\beta H(\Gamma)+g(\Gamma)}}$$

For thermostatted dynamics, can show that $\Omega = \dot{g}$

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m}$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i(\mathbf{q}) - \alpha(\Gamma)\mathbf{p}_i$$

$$\langle \Omega_t \rangle = \langle g(t) \rangle - \langle g(0) \rangle = \int_0^t \langle g(s)\dot{g}(0) \rangle ds$$

If t-mixing (transient correlations decay), then eventually $t>t_c$ the system reaches equilibrium (non-dissipative) state.

$$\langle g(t) \rangle = \langle g(0) \rangle + \int_0^{t_c} \langle g(s)\dot{g}(0) \rangle ds + \int_{t_c}^{t} \langle g(s) \rangle \langle \dot{g}(0) \rangle ds$$

6. Implications - Relaxation to equilibrium

$$\langle g(t)\rangle = \langle g(0)\rangle + \int_0^{t_c} \langle g(s)\dot{g}(0)\rangle ds + \int_{t_c}^{t} \langle g(s)\rangle\langle \dot{g}(0)\rangle ds$$

$$= \langle g(0)\rangle + \int_0^{t_c} \langle g(s)\dot{g}(0)\rangle ds$$

Since

$$\langle g(t)\rangle\langle \dot{g}(0)\rangle = 0$$

So at long times, there is no dissipation and the system must be at equilibrium

$$\langle g(t)\rangle = \langle g(0)\rangle + \int_0^{t_c} \langle g(s)\dot{g}(0)\rangle ds$$

6. Implications - Relaxation to equilibrium

- Assume unknown distribution – system at equilibrium

$$f_0(\Gamma) = \frac{e^{-\beta H(\Gamma)+g(\Gamma)}\delta(K-K_0)\delta(p-p_0)}{\int d\Gamma\, e^{-\beta H(\Gamma)+g(\Gamma)}\delta(K-K_0)\delta(p-p_0)}$$

For thermostatted dynamics, can show that $\Omega = \dot{g}$

and at equilibrium, $\Omega = 0$ for all Γ and t. Therefore g is constant,

$$f_0(\Gamma) = \frac{e^{-\beta H(\Gamma)}\delta(K-K_0)\delta(p-p_0)}{\int d\Gamma\, e^{-\beta H(\Gamma)}\delta(K-K_0)\delta(p-p_0)}$$

6. Implications – steady state fluctuation theorem

$$\Omega_t(\Gamma) = \ln \frac{f_0(\Gamma)}{f_0\left(S^t\Gamma\right)} - \Lambda_t$$

$$\frac{\Pr(\Omega_t = A)}{\Pr(\Omega_t = -A)} \equiv e^A$$

$$\frac{\Pr(B_t = A)}{\Pr(B_t = -A)} = \frac{\int f_0(\Gamma)\delta(B_t(\Gamma) - A)\,d\Gamma}{\int f_0(\Gamma^*)\delta(B_t(\Gamma^*) + A)\,d\Gamma^*}$$

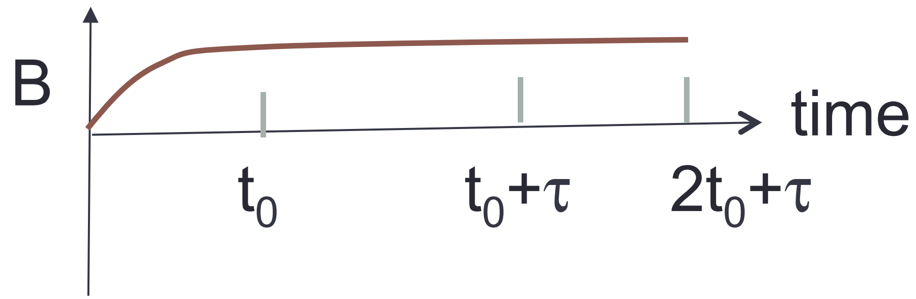
$$= \frac{\int f_0(\Gamma)\delta(B_t(\Gamma) - A)\,d\Gamma}{\int f_0(S^t\Gamma)\delta(B_t(\Gamma) - A)e^{\Lambda_t}\,d\Gamma}$$

$$= \frac{\int f_0(\Gamma)\delta(B_t(\Gamma) - A)\,d\Gamma}{\int e^{-\Omega_t}\delta(B_t(\Gamma) - A)\,d\Gamma}$$

$$= \left\langle e^{-\Omega_t} \right\rangle_{B_t = A}^{-1}$$

6. Implications – steady state fluctuation theorem

$$\frac{\Pr(B_t = A)}{\Pr(B_t = -A)} = \left\langle e^{-\Omega_t} \right\rangle^{-1}_{B_t=A}$$



$$\frac{\Pr(\bar{\Omega}^{ss}_\tau = A)}{\Pr(\bar{\Omega}^{ss}_\tau = -A)} = \left\langle e^{-\Omega_t} \right\rangle^{-1}_{\bar{\Omega}^{ss}_\tau=A} = e^A \left\langle e^{-\int_0^{t_0}\Omega(S^s\Gamma)ds - \int_\tau^{\tau+2t_0}\Omega(S^s\Gamma)ds} \right\rangle^{-1}_{\bar{\Omega}^{ss}_\tau=A}$$

$$\lim_{\tau\to\infty}\frac{1}{\tau}\ln\frac{\Pr(\bar{\Omega}^{ss}_\tau = A)}{\Pr(\bar{\Omega}^{ss}_\tau = -A)} = A + \frac{1}{\tau}\ln\left\langle e^{-\int_0^{t_0}\Omega(S^s\Gamma)ds - \int_\tau^{\tau+2t_0}\Omega(S^s\Gamma)ds} \right\rangle^{-1}_{\bar{\Omega}^{ss}_\tau=A}$$

D. J. Searles, L. Rondoni and D. J. Evans, J. Stat. Phys., **128**, 1337 (2007)

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- Relaxation to a steady state?
- Is there only one steady state? – what happens if multiple steady states and/or quasi-equilibrium states?

…

7. Summary

- Dissipation function
  - Central importance in nonequilibrium statistical mechanics - appears in the **fluctuation theorem**, **second law inequality**, **dissipation theorem** and **relaxation theorem**
- Dissipation theorem
  - Nonlinear response of phase functions
  - Shows how a distribution function changes due to application/ change/removal of a field
- Relaxation theorem
  - Shows how system relaxes to equilibrium – can be non-monotonic
  - Derive equilibrium distribution functions

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