

The Foundations of Classical Statistical Thermodynamics

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1

Outline

- Dynamical systems (v brief)
- Thermostats (v brief)
- Phase space and ensembles
- Liouville Equation
- Fluctuation Theorem and corollaries
- Dissipation Theorem
- Linear and nonlinear response theory, Green-Kubo relations
- Relaxation Theorem
- Derivation of the canonical (Maxwell-Boltzmann) equilibrium distribution function
- Connection with equilibrium Thermodynamics
- Nonequilibrium Free Energy Relations

Maxwell on the Second Law

Hence the Second Law of thermodynamics is continually being violated and that to a considerable extent in any sufficiently small group of molecules belonging to any real body. As *the number of molecules in the group is increased*, the deviations from the mean of the whole become smaller and less frequent; and when the number is increased till the group includes a sensible portion of the body, the probability of a measurable variation from the mean occurring *in a finite number of years* becomes so small that it may be regarded as practically an impossibility.

J.C. Maxwell, Nature, **17**, 278(1878)

Thermostatted Dynamical Systems (Evans & Hoover et. al 1980's)

Typically we deal with adiabatic Hamiltonian N-particle systems ($i=1,N$) - W.R. Hamilton 1805-1865)

$$\dot{\mathbf{q}}_i = \frac{\partial H(\mathbf{q}, \mathbf{p})}{\partial \mathbf{p}_i}$$

$$\dot{\mathbf{p}}_i = -\frac{\partial H(\mathbf{q}, \mathbf{p})}{\partial \mathbf{q}_i}$$

and often $H(\Gamma) \equiv H(\mathbf{q}, \mathbf{p}) \equiv H(\mathbf{q}_1, \dots, \mathbf{q}_N, \mathbf{p}_1, \dots, \mathbf{p}_N) = K(\mathbf{p}) + \Phi(\mathbf{q})$. Whereupon

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

$$\dot{\mathbf{p}}_i = -\frac{\partial \Phi}{\partial \mathbf{q}_i} \equiv \mathbf{F}_i$$

We observe that

$$\Lambda^{\text{ad}} \equiv \frac{\partial}{\partial \Gamma} \cdot \dot{\Gamma} = 0$$

Example: Thermostatted SLLOD equations for planar Couette flow

(Evans and Morriss (1984))

Consider a system described by the time reversible thermostatted equations of motion (Hoover et al):

$$\dot{\mathbf{q}}_i = \mathbf{p}_i / m + \mathbf{C}_i \cdot \mathbf{F}_e$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i + \mathbf{D}_i \cdot \mathbf{F}_e - \alpha S_i \mathbf{p}_i : \quad S_i = 0, 1; \quad \sum_i S_i = N_{\text{res}}$$

Example:

Slod NonEquilibrium Molecular Dynamics algorithm for shear viscosity - is **exact** for adiabatic flows.

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

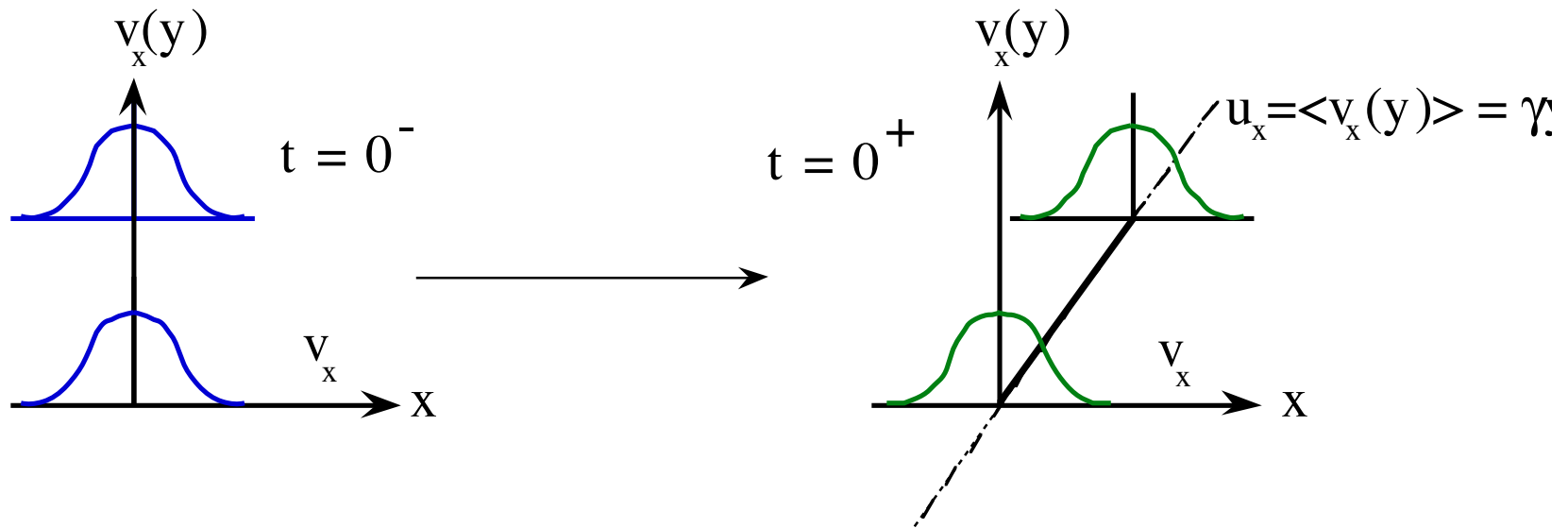
$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{i}\gamma\Theta(t)p_{yi} - \alpha\mathbf{p}_i$$

which is equivalent to:

$$\ddot{\mathbf{q}}_i = \frac{\mathbf{F}_i}{m} + \mathbf{i}\gamma\delta(t)y_i - \alpha(\dot{\mathbf{q}}_i - \mathbf{i}\gamma y_i)$$

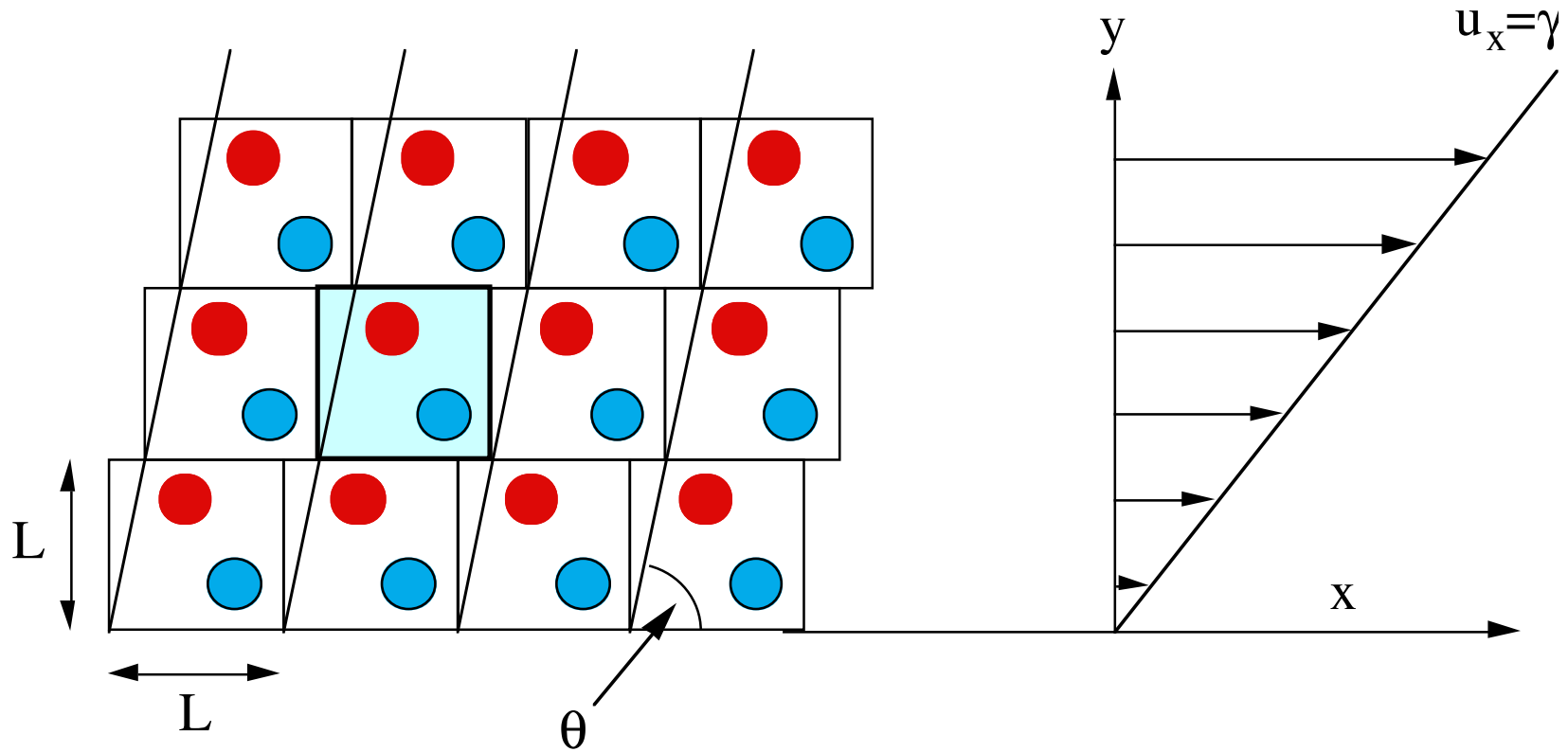
There is no Hamiltonian function that generates adiabatic SLLOD .

The Sllod equations of motion are equivalent to Newton's equations for $t > 0+$, with a linear shift applied to the initial x -velocities of the particles.



Therefore adiabatic Sllod is exact arbitrarily far from equilibrium.

Lees-Edwards (1972) periodic boundary conditions for shear flow



How does the internal energy $H_0 \equiv K + \Phi$ change under SLLOD?

$$\begin{aligned}\dot{H}_0^{\text{ad}} &= \sum \dot{\mathbf{p}}_i \cdot \frac{\partial K}{\partial \mathbf{p}_i} + \dot{\mathbf{q}}_i \cdot \frac{\partial \Phi}{\partial \mathbf{q}_i} \\ &= \sum -\dot{\gamma} p_{yi} \cdot \frac{\mathbf{p}_i}{m} - \dot{\gamma} y_i \cdot \mathbf{F}_i \\ &= -\dot{\gamma} \sum \frac{p_{yi} p_{xi}}{m} + y_i F_{xi} \equiv -\dot{\gamma} P_{xy} V\end{aligned}$$

where P_{xy} is the xy -element of the pressure tensor. At low strain rates we expect Newton's Law (1687) of viscosity to hold namely,

$$\lim_{\dot{\gamma} \rightarrow 0} P_{xy}(\dot{\gamma}) = -\eta \dot{\gamma}$$

where η is the so-called shear viscosity.

If we add in the thermostating terms then

$$\dot{H}_0 = -\gamma P_{xy} V - 2K\alpha$$

If we then choose the thermostat multiplier as

$$\alpha = -\gamma P_{xy} V / 2K$$

and the internal energy will be a constant of the motion. This is called a Gaussian ergostat. (Evans and Hoover 1982). These equations of motion can be derived from Gauss' Principle of Least Constraint (Gauss 1829). Possible assessment topic. This multiplier could also be chosen to fix the kinetic energy of the system - Gaussian isokinetic thermostat. On average the thermostat multiplier will be positive since viscous work is done on the system which is then converted into heat and removed by the thermostat.

In a nonequilibrium steady state time averages satisfy the equation:

$$\overline{\dot{H}_0} = -\gamma \overline{P_{xy}} V - 2K \overline{\alpha} = 0$$

$$= \overline{W} + \overline{Q} = \text{work} + \text{heat}$$

All equations of motion are time reversal symmetric - but more on this later!

The concept of *ensembles* in statistical mechanics (Boltzmann 1871, Maxwell 1879)

In a macroscopic thermal system we only control a few *state* variables: temperature or total energy, pressure or total volume, total mass or number of molecules. To specify the microstate of a system Γ we need $O(N_A)$ variables! Yet experience tells us that a specification of the few state variables is all we need to correctly predict macroscopic properties: specific heats viscosity etc.

“I have found it convenient, instead of considering one system of material particles, to consider a large number of systems similar to each other in all respects, except the initial circumstances of the motion, which are supposed to vary from system to system, the total energy being the same in all.” (Maxwell 1879)

Liouville's Theorem (1838)

- Let $M(t)$ be the total number of ensemble members inside an arbitrary phase space volume V_{Γ}

$$M(t) = \int_{V_{\Gamma}} d\Gamma f(\Gamma, t) \quad \text{and} \quad \frac{dM}{dt} = \int_{V_{\Gamma}} d\Gamma \frac{\partial f(\Gamma, t)}{\partial t}$$

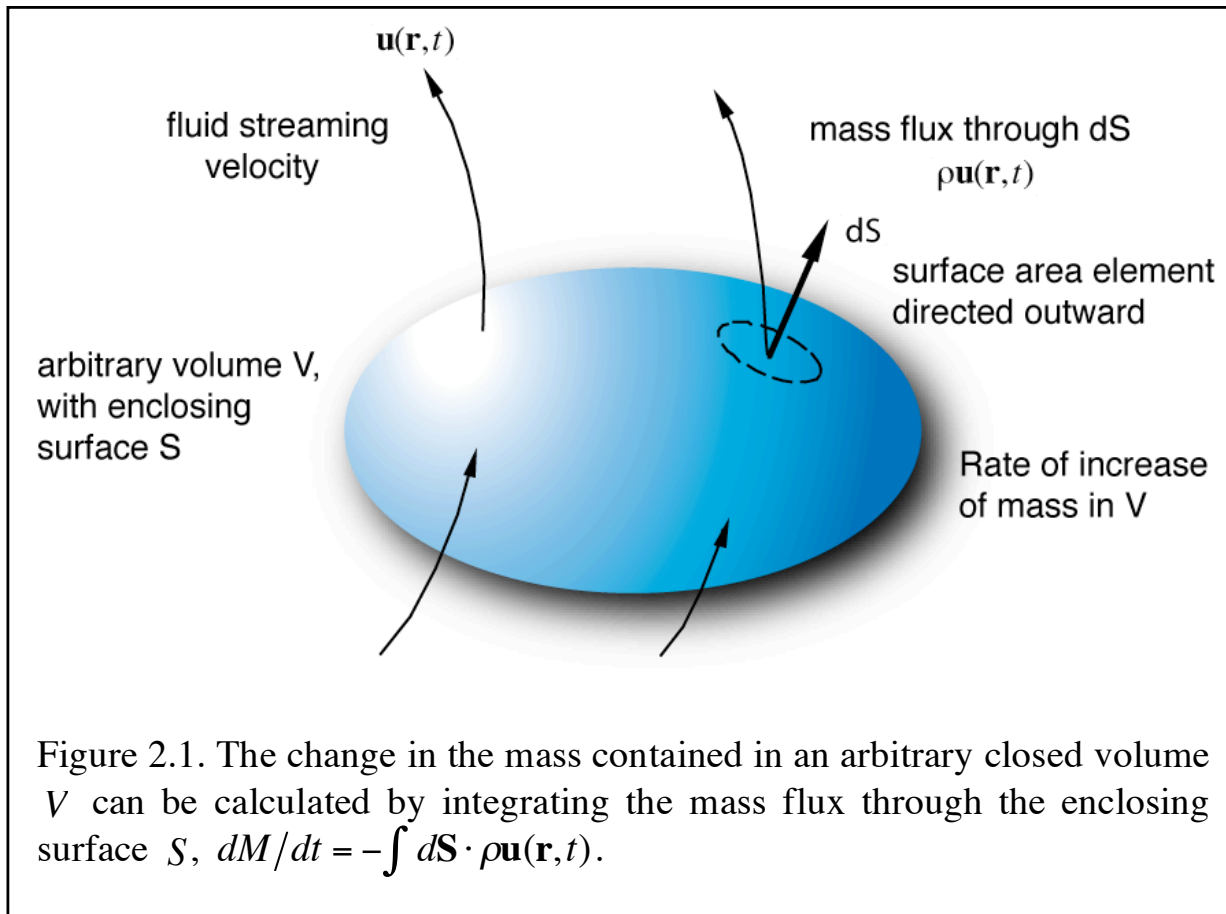
the $f(\Gamma, t)$ is the phase space density at position Γ and time t . Since mass is conserved, the only way that the mass in the volume V_{Γ} can change is by flowing through the enclosing surface, S_{Γ} (see Figure below).

$$\frac{dM(t)}{dt} = - \int_{S_{\Gamma}} dS_{\Gamma} f(\Gamma, t) \dot{\Gamma}(\Gamma, t) = \int_{V_{\Gamma}} d\Gamma \frac{\partial}{\partial \Gamma} \cdot [\dot{\Gamma} f(\Gamma, t)]$$

Since the volume is arbitrary,

$$\frac{\partial f(\Gamma, t)}{\partial t} = - \frac{\partial}{\partial \Gamma} \cdot [\dot{\Gamma} f(\Gamma, t)]$$

This is Liouville's Theorem (1838)



This diagram is for the analogous mass continuity equation.

Liouville's Theorem (contd)

The chain rule gives:

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \dot{\Gamma} \cdot \frac{\partial f}{\partial \Gamma} = -f \frac{\partial}{\partial \Gamma} \cdot \dot{\Gamma}$$

For adiabatic Hamiltonian systems

$$\frac{df}{dt} = 0$$

while for thermostatted Hamiltonian systems (AI Γ e.g. thermostatted SLLOD)

$$\frac{df}{dt} = -f\Lambda = +3N_{\text{res}}\alpha(t)f(\Gamma, t)$$

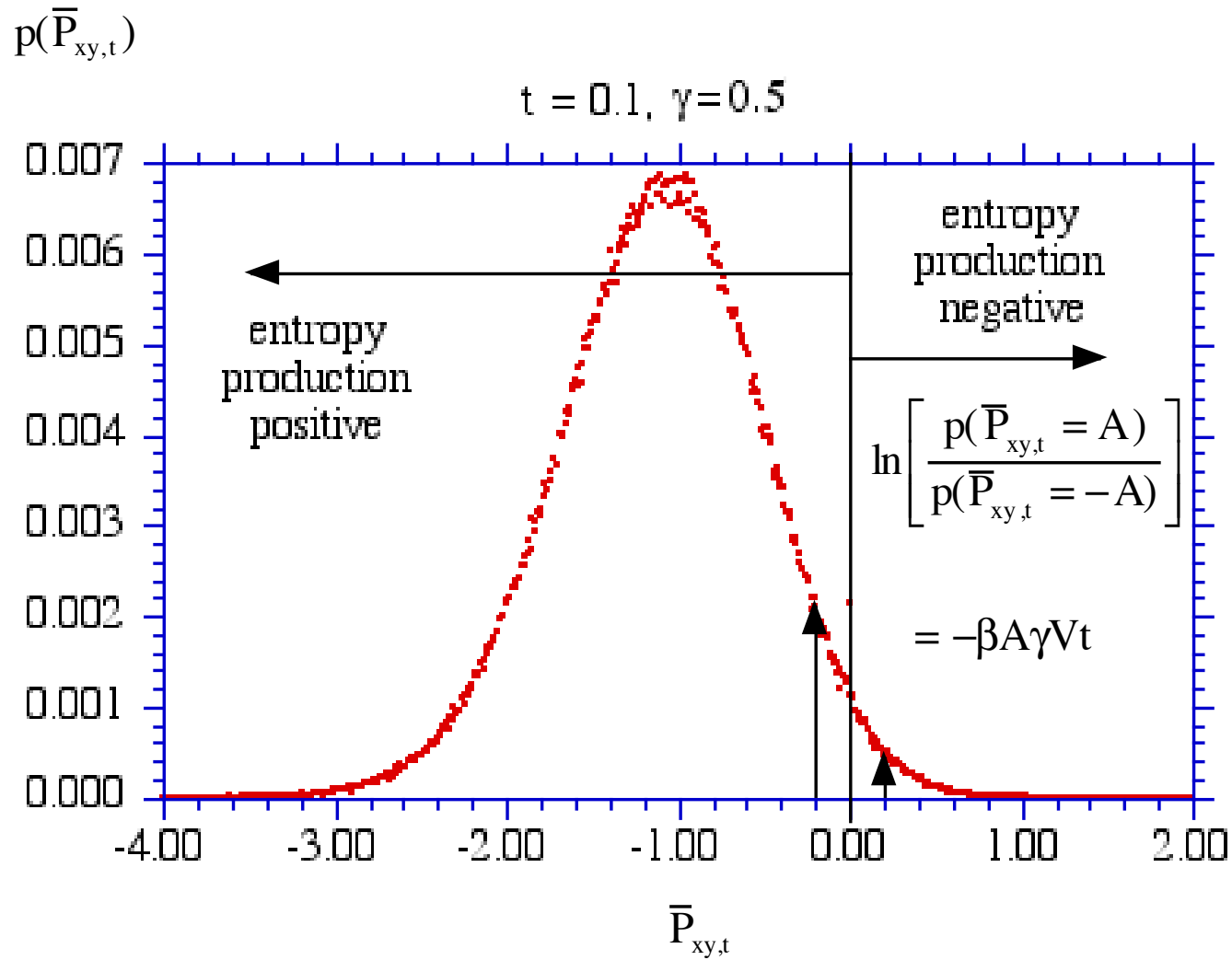
Fluctuation Theorem (Roughly).

The first statement of a Fluctuation Theorem was given by Evans, Cohen & Morriss, 1993. This statement was for isoenergetic nonequilibrium steady states.

If $\Sigma = -\beta J F_e V = \int_V dV \sigma(\mathbf{r}) / k_B$ is total (extensive) irreversible entropy production rate/ k_B and its time average is: $\bar{\Sigma}_t \equiv (1/t) \int_0^t ds \Sigma(s)$, then

$$\frac{p(\bar{\Sigma}_t = A)}{p(\bar{\Sigma}_t = -A)} = \exp[At]$$

Formula is exact if time averages (0,t) begin from the initial phase $\Gamma(0)$, sampled from a given initial distribution $f(\Gamma(0),0)$. It is true asymptotically $t \rightarrow \infty$, if the time averages are taken over steady state trajectory segments. The formula is valid for **arbitrary** external fields, F_e .



Evans, Cohen & Morriss, PRL, **71**, 2401(1993).

Why are the Fluctuation Theorems important?

- Show how irreversible macroscopic behaviour arises from time reversible dynamics.
- Generalize the Second Law of Thermodynamics so that it applies to small systems observed for short times.
- Imply the Second Law InEquality $\langle \Omega_t \rangle \geq 0, \forall t, N$
- Are valid arbitrarily far from equilibrium regime
- In the linear regime FTs imply both Green-Kubo relations and the Fluctuation dissipation Theorem.
- Are valid for stochastic systems (Lebowitz & Spohn, Evans & Searles, Crooks).
- New FT's can be derived from the Langevin eqn (Reid et al, 2004).
- A quantum version has been derived (Mukamel, Monnai & Tasaki), .
- Apply **exactly** to transient trajectory segments (Evans & Searles 1994) and asymptotically for steady states (Evans et al 1993)..
- Apply to all types of nonequilibrium system: adiabatic and driven nonequilibrium systems and relaxation to equilibrium (Evans, Searles & Mittag).
- Can be used to derive *nonequilibrium* expressions for *equilibrium* free energy differences (Jarzynski 1997, Crooks).
- Place (thermodynamic) constraints on the operation of nanomachines.

The Liouville equation is analogous to the mass continuity equation in fluid mechanics.

$$\frac{\partial f(\Gamma, t)}{\partial t} = - \frac{\partial}{\partial \Gamma} \cdot [\dot{\Gamma} f(\Gamma, t)] \equiv -iL f(\Gamma, t)$$

or for thermostatted systems, as a function of time, along a streamline in phase space:

$$\frac{df(\Gamma, t)}{dt} = \left[\frac{\partial}{\partial t} + \dot{\Gamma}(\Gamma) \cdot \frac{\partial}{\partial \Gamma} \right] f(\Gamma, t) = -f(\Gamma, t) \Lambda(\Gamma), \quad \forall \Gamma, t$$

Λ is called the *phase space compression factor* and for a system in 3 Cartesian dimensions

$$\Lambda(\Gamma) = -3N_{\text{res}} \alpha(\Gamma)$$

The formal solution is:

$$f(\Gamma(t), t) = \exp\left[-\int_0^t ds \Lambda(\Gamma(s))\right] f(\Gamma(0), 0)$$

More on Thermostats

Deterministic, time reversible, homogeneous thermostats were simultaneously but independently proposed by Hoover and Evans in 1982. Later we realised that the equations of motion could be derived from Gauss' Principle of Least Constraint (Evans, Hoover, Failor, Moran & Ladd (1983)).

The form of the equations of motion is

$$\begin{aligned}\dot{\mathbf{q}}_i &= \mathbf{p}_i / m + \mathbf{C}_i(\Gamma) \cdot \mathbf{F}_e \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i(\mathbf{q}) + \mathbf{D}_i(\Gamma) \cdot \mathbf{F}_e - S_i \alpha(\Gamma) \mathbf{p}_i\end{aligned}$$

α can be chosen such that the energy is constant or such that the kinetic energy is constant. In the latter case the equilibrium, field free distribution function can be proved to be the isokinetic distribution,

$$f(\Gamma) \sim \delta\left(\sum_{\text{wall}} p_i^2 / 2m - 3Nk_B T / 2\right) \exp[-\Phi(\mathbf{q}) / k_B T]$$

In 1984 Nosé showed that if α is determined as the time dependent solution of the equation

$$\frac{d\alpha}{dt} = \left[\left(\sum_{\text{wall}} p_i^2 / 2m \right) / (3N_{\text{wall}} k_B T / 2) - 1 \right] / \tau^2$$

then the equilibrium canonical distribution

$$f(\Gamma) \sim \exp[-H_0(\Gamma) / k_B T]$$

is preserved by the equations of motion.

Aside: - Thermostats and Equilibrium

Consider “ μ ” thermostats described by the equations of motion:

$$\dot{q}_{i\delta} = \frac{p_{i\delta}}{m} + C_{i\delta\gamma} F_{e\gamma}$$

$$\dot{p}_{i\delta} = F_{i\delta} + D_{i\delta\gamma} F_{e\gamma} - \alpha |p_{i\delta}|^{\mu-1} p_{i\delta}$$

where Einstein notation is used, $\delta, \gamma = x, y, z$, $q_{i\delta}$ is the position of the i -th particle in the δ -direction, $p_{i\delta}$ is the momentum of the i -th particle in the δ -direction, $C_{i\delta\gamma}(\Gamma)$ and $D_{i\delta\gamma}(\Gamma)$ couple the system with the external field, $F_{e\gamma}$

At $F_{e\gamma} = 0$:

- all μ -thermostats that violate Gauss Principle do not generate an equilibrium state and,
- among μ -thermostats that satisfy Gauss's Principle to fix the $\mu+1$ moment of the velocity distribution, only the conventional Gaussian isokinetic thermostat ($\mu=1$) possesses an equilibrium state.

Time reversibility

Consider an arbitrary phase function B .

$$dB(\Gamma) / dt = \dot{\Gamma} \cdot \partial B / \partial \Gamma \equiv iL(\Gamma)B(\Gamma)$$

The formal solution via infinite order Taylor series is,

$$B(\Gamma(t)) = \exp[+iL(\Gamma(0))t]B(\Gamma(0))$$

(Prove by differentiation.) Now consider a time reversal mapping

$$M^T[B(\Gamma)] = M^T[B(\mathbf{q}, \mathbf{p})] \equiv B(\mathbf{q}, -\mathbf{p})$$

The phase variable B at time t can be retraced back to time zero by applying the inverse propagator (ie reversing the direction of time).

$$\exp[-iLt]B(t) = \exp[-iLt]\exp[iLt]B(0) = B(0)$$

Since $M^T iL(\Gamma) = -iL(\Gamma)M^T$ we can also return to the origin by applying the time reversal mapping but always going forward in time.

$$M^T e^{iLt} M^T e^{iLt} \Gamma(0) = M^T e^{iLt} M^T \Gamma(t) = e^{-iLt} \Gamma(t) = \Gamma(0)$$

Such dynamics is called time reversal symmetric dynamics.

Thomson on reversibility

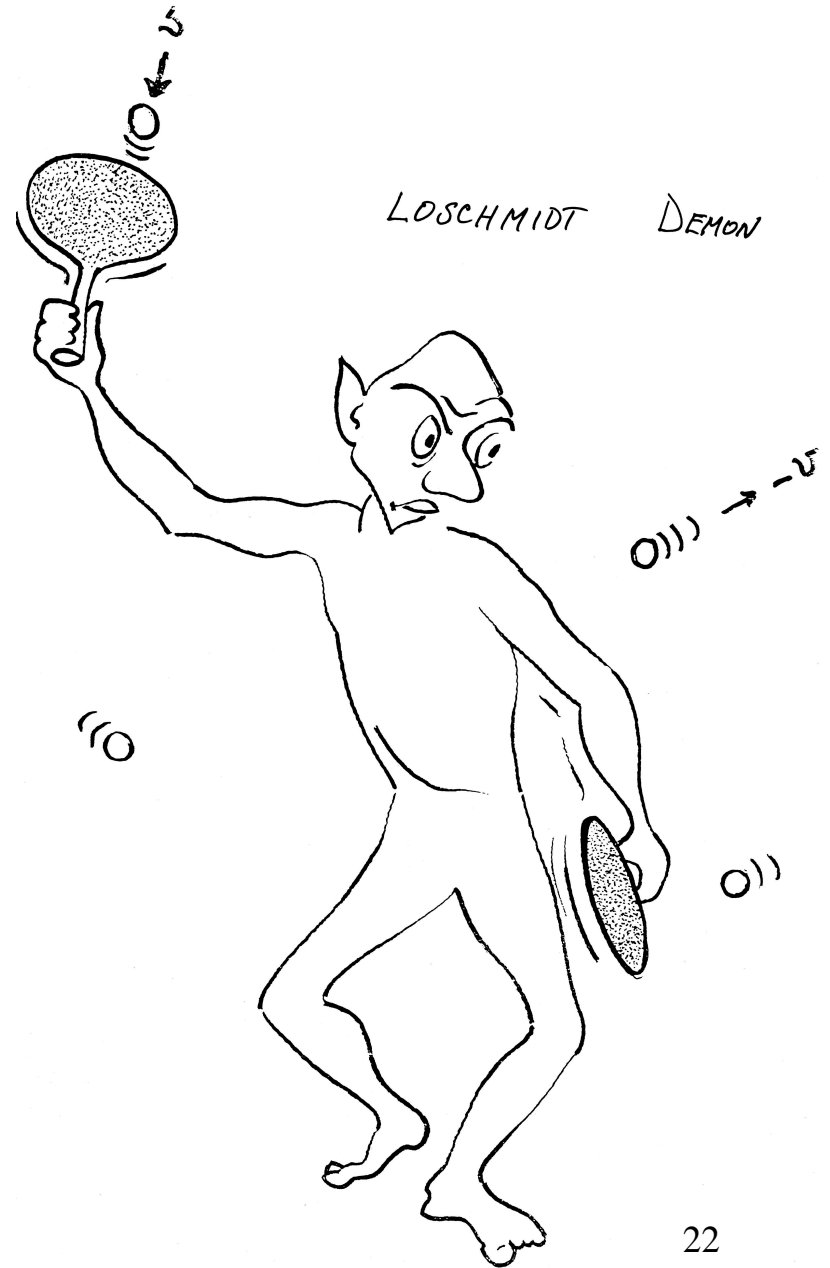
The instantaneous reversal of the motion of every moving particle of a system causes the system to move backwards each particle along its path and at the same speed as before...

W. Thomson (Lord Kelvin) 1874
(cp J. Loschmidt 1878)

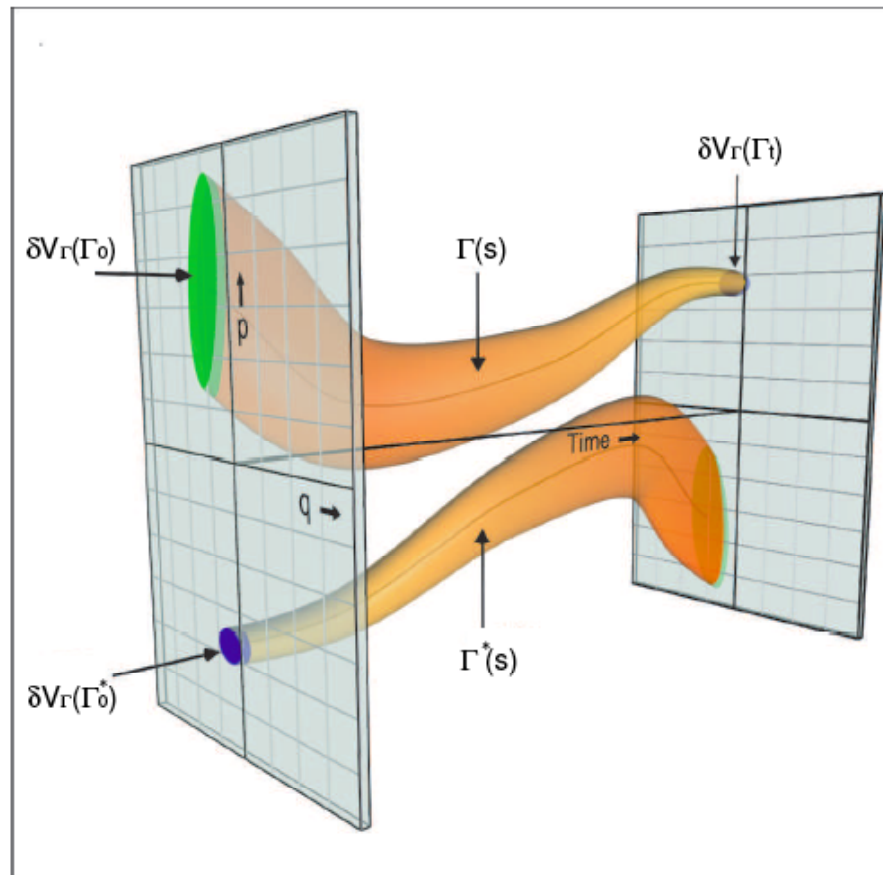
Loschmidt Demon

The Loschmidt Demon applies
a time reversal mapping:

$$\Gamma = (\mathbf{q}, \mathbf{p}) \rightarrow \Gamma^* = (\mathbf{q}, -\mathbf{p})$$



Phase Space and reversibility



The Dissipation function is defined as: (Searles & Evans 2000)

$$\int_0^t ds \, \Omega(\Gamma(s)) \equiv \ln \left(\frac{f(\Gamma(0), 0)}{f(\Gamma(t), 0)} \right) - \int_0^t \Lambda(\Gamma(s)) ds$$

$$= \bar{\Omega}_t \equiv \Omega_t$$

We know that

$$\frac{p(\delta V_{\Gamma}(\Gamma(0), 0))}{p(\delta V_{\Gamma}(\Gamma^*(0), 0))} = \frac{f(\Gamma(0), 0) \delta V_{\Gamma}(\Gamma(0), 0)}{f(\Gamma^*(0), 0) \delta V_{\Gamma}(\Gamma^*(0), 0)}$$

$$= \frac{f(\Gamma(0), 0)}{f(\Gamma(t), 0)} \exp \left[- \int_0^t \Lambda(\Gamma(s)) ds \right]$$

$$= \exp[\Omega_t(\Gamma(0))]$$

Assumptions :

- If $f(\Gamma(0), 0) \neq 0$ then $f(\Gamma(t), 0) \neq 0$.
- Also $f(\Gamma, 0) = f(M^T(\Gamma), 0)$

Evans Searles TRANSIENT FLUCTUATION THEOREM

Choose $\delta V_{\Gamma}(\Gamma(0), 0; \bar{\Omega}_t(\Gamma(0))) = A \pm \delta A$

$$\begin{aligned} \frac{p(\delta V_{\Gamma}(\Gamma(0), 0; \bar{\Omega}_t(\Gamma(0))) = A)}{p(\delta V_{\Gamma}(\Gamma^*(0), 0))} &= \frac{f(\Gamma(0), 0) \delta V_{\Gamma}(\Gamma(0))}{f(\Gamma^*(0), 0) \delta V_{\Gamma}(\Gamma^*(0))} \\ &= \frac{f(\Gamma(0), 0)}{f(\Gamma(t), 0)} \exp \left[- \int_0^t \Lambda(\Gamma(s)) ds \right] \\ &= \exp[\Omega_t(\Gamma(0))] = \exp[At] \end{aligned}$$

So we have the **Transient Fluctuation Theorem** (Evans and Searles 1994)

The derivation is complete.

$$\ln \frac{p(\bar{\Omega}_t = A)}{p(\bar{\Omega}_t = -A)} = At$$

FT for different ergodically consistent bulk ensembles driven by a dissipative field, F_e with conjugate flux J .

In each of these cases $\Omega_t = \Sigma_t = -\beta J_t V F_e$

Isokinetic or Nose-Hoover dynamics/isokinetic or canonical ensemble

$$\ln \frac{p(\bar{J}_t = A)}{p(\bar{J}_t = -A)} = -At F_e \beta V \quad -J F_e V \equiv \frac{dH_0^{\text{ad}}}{dt}$$

Isoenergetic dynamics/microcanonical ensemble

$$\ln \frac{p(\bar{J}\bar{\beta}_t = A)}{p(\bar{J}\bar{\beta}_t = -A)} = -At F_e V \quad \text{or} \quad \ln \frac{p(\bar{\Lambda}_t = A)}{p(\bar{\Lambda}_t = -A)} = -At \quad -J F_e V \equiv \frac{dH_0^{\text{ad}}}{dt}$$

(Note: This second equation is for steady states, the Gallavotti-Cohen form for the FT (1995).)

Isobaric-isothermal dynamics and ensemble.

$$\ln \frac{p(\bar{J}_t = A)}{p(\bar{J}_t = -A)} = -At F_e \beta V \quad -J F_e V \equiv \frac{dI_0^{\text{ad}}}{dt}$$

(Searles & Evans, *J. Chem. Phys.*, **113**, 3503–2609 (2000))

Dissipation function for shear flow in the canonical ensemble

If the equations of motion are isokinetic Slod

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

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

and the initial ensemble is canonical (We will have more to say about the canonical distribution later.)

$$f(\mathbf{\Gamma}, 0) = \frac{\delta[K(\mathbf{p}) - 3N\beta^{-1}/2] \exp[-\beta H_0(\mathbf{\Gamma})]}{\int d\mathbf{\Gamma} \delta[K(\mathbf{p}) - 3N\beta^{-1}/2] \exp[-\beta H_0(\mathbf{\Gamma})]}$$

you can prove that the dissipation function is (to leading order in N) - Assignment 2.

$$\Omega_t(\mathbf{\Gamma}) = -\beta \int_0^t ds P_{xy}(\mathbf{\Gamma}(s)) \gamma V$$

Note: $\mathbf{\Gamma} \equiv \mathbf{\Gamma}(0)$

Consequences of the FT

Connection with Linear irreversible thermodynamics

In thermostatted canonical systems where dissipative field is constant,

$$\begin{aligned}\Sigma &= -\langle J \rangle F_e V / T_{\text{soi}} \\ &= -\langle J \rangle F_e V / T_{\text{res}} + O(F_e^4) \\ &= \langle \Omega \rangle + O(F_e^4)\end{aligned}$$

So in the weak field limit (for canonical systems) the average dissipation function is equal to the “rate of spontaneous entropy production” - as appears in linear irreversible thermodynamics. Of course the TFT applies to the nonlinear regime where linear irreversible thermodynamics does not apply.

The Integrated Fluctuation Theorem (Ayton, Evans & Searles, 2001).

If $\langle \dots \rangle_{\bar{\Omega}_t > 0}$ denotes an average over all fluctuations in which the time integrated entropy production is positive, then,

$$\left[\frac{p(\bar{\Omega}_t > 0)}{p(\bar{\Omega}_t < 0)} \right] = \left\langle e^{-\bar{\Omega}_t t} \right\rangle_{\bar{\Omega}_t > 0}^{-1} = \left\langle e^{-\bar{\Omega}_t t} \right\rangle_{\bar{\Omega}_t < 0} > 1$$

gives the ratio of probabilities that the Second Law will be satisfied rather than violated. The ratio becomes exponentially large with increased time of violation, t , and with system size (since Ω is extensive).

The Second Law Inequality

(Searles & Evans 2004).

If $\langle \dots \rangle_{\bar{\Omega}_t > 0}$ denotes an average over all fluctuations in which the time integrated entropy production is positive, then,

$$\begin{aligned}
 \langle \bar{\Omega}_t \rangle &= \int_{-\infty}^{\infty} \left(A p(\bar{\Omega}_t = A) \right) dA \\
 &= \int_0^{\infty} \left(A p(\bar{\Omega}_t = A) - A p(\bar{\Omega}_t = -A) \right) dA \\
 &= \int_0^{\infty} \left(A p(\bar{\Omega}_t = A) (1 - e^{-At}) \right) dA \\
 &= \left\langle \bar{\Omega}_t (1 - e^{-\bar{\Omega}_t t}) \right\rangle_{\bar{\Omega}_t > 0} \geq 0, \quad \forall t > 0
 \end{aligned}$$

If the pathway is quasi-static (i.e. the system is always in equilibrium): $\Omega(t) = 0, \forall t$

The instantaneous dissipation function *may* be negative. However its time average cannot be negative. Note we can also derive the SLI from the Crooks Equality - later.

The NonEquilibrium Partition Identity (Carberry et al 2004).

$$\langle \exp(-\bar{\Omega}_t t) \rangle = 1$$

For thermostatted systems the NonEquilibrium Partition Identity (NPI) was first proved for thermostatted dissipative systems by Evans & Morriss (1984). It is derived trivially from the TFT.

$$\begin{aligned} \langle \exp(-\bar{\Omega}_t t) \rangle &= \int_{-\infty}^{+\infty} dA \, p(\bar{\Omega}_t = A) \exp(-At) \\ &= \int_{-\infty}^{+\infty} dA \, p(\bar{\Omega}_t = -A) \\ &= \int_{-\infty}^{+\infty} dA \, p(\bar{\Omega}_t = A) = 1 \end{aligned}$$

NPI is a necessary but not sufficient condition for the TFT.

Steady State ESFT

$$\lim_{t \rightarrow \infty} \frac{\Pr(\bar{\Omega}_t^{ss} = A)}{\Pr(\bar{\Omega}_t^{ss} = -A)} = \exp[At + O(1)]$$

$$= \exp[At], \text{ since } At = O(t^{1/2})$$

We expect that *if* the statistical properties of steady state trajectory segments are independent of the particular equilibrium phase from which they started (the steady state is ergodic over the initial equilibrium states), we can replace the ensemble of steady state trajectories by trajectory segments taken from a single (extremely long) steady state trajectory.

This gives the Evans-Searles Steady State Fluctuation Theorem

$$\lim_{t \rightarrow \infty} \frac{\Pr(\bar{\Omega}_t^{ss} = A)}{\Pr(\bar{\Omega}_t^{ss} = -A)} = \exp[At]$$

The Dissipation Theorem (Evans et.al. 2008)

From the streaming version of the Liouville equation

$$f(\Gamma(t), t) = e^{-\int_0^t ds \Lambda(\Gamma(s))} f(\Gamma(0), 0)$$

Then from the definition of the dissipation function

$$f(\Gamma(0), 0) = f(\Gamma(t), 0) e^{\int_0^t ds [\Omega(s) + \Lambda(s)]}$$

Substituting gives

$$f(\Gamma(t), t) = e^{\int_0^t ds \Omega(\Gamma(s))} f(\Gamma(t), 0), \forall \Gamma(t)$$

Realising that $\Gamma(t)$, is just a dummy variable

$$\begin{aligned} f(\Gamma(0), t) &= e^{\int_0^t ds \Omega(\Gamma(s-t))} f(\Gamma(0), 0) \\ &= e^{-\int_0^t d\tau \Omega(\Gamma(\tau))} f(\Gamma(0), 0) \end{aligned}$$

An aside on normalisation

From the nonequilibrium partition identity:

$$\langle \exp(-\bar{\Omega}_t) \rangle = \int d\Gamma \exp[-\int_0^t ds \Omega(\Gamma(s))] f(\Gamma, 0) = 1, \quad \forall t$$

$$\int d\Gamma \exp[-\int_0^{-t} ds \Omega(\Gamma(s))] f(\Gamma, 0) = \int d\Gamma f(\Gamma, t) = 1, \quad \forall t$$

The distribution function is normalized. This is in spite of the fact that from the Second Law Inequality:

$$\int d\Gamma \int_0^t ds \Omega(\Gamma(s)) f(\Gamma, 0) = \langle \Omega_t \rangle \geq 1, \quad \forall t$$

In nonequilibrium steady states the distribution collapses towards a strange attractor that covers almost all of phase space.

The Dissipation Theorem - cont.

$$\langle B(t) \rangle = \int d\Gamma(0) B(\Gamma(0)) e^{-\int_0^{-t} d\tau \Omega(\Gamma(\tau))} f(\Gamma(0), 0)$$

$$\begin{aligned} d\langle B(t) \rangle / dt &= \int d\Gamma(0) B(\Gamma(0)) \Omega(\Gamma(-t)) f(\Gamma(0), t) \\ &= \int d\Gamma(0) B(\Gamma(t)) \Omega(\Gamma(0)) f(\Gamma(0), 0) \end{aligned}$$

$$\langle B(t) \rangle = \langle B(0) \rangle_{f(\Gamma, 0)} + \int_0^t ds \langle \Omega(0) B(s) \rangle_{F_e, f(\Gamma, 0)}$$

This is an exceedingly general form of the **Transient Time Correlation Function** expression for the nonlinear response (Evans & Morriss 1984). If the initial distribution is preserved by the field free dynamics,

$$\langle B(t) \rangle = \langle B(0) \rangle - \beta V F_e \int_0^t ds \langle J(0) B(s) \rangle_{F_e}$$

that can be linearized to give the **Green-Kubo** (1957) expression for the limiting linear response,

$$\lim_{F_e \rightarrow 0} \langle B(t) \rangle = \langle B(0) \rangle - \beta V F_e \int_0^t ds \langle J(0) B(s) \rangle_{F_e=0}$$

The Relaxation Theorem (Evans et.al. 2009)

Consider a field free dynamics with a subset of thermostatted particles

$$\begin{aligned} \dot{\mathbf{q}}_i &= \mathbf{p}_i / m_i \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i(\mathbf{q}) - S_i(\alpha \mathbf{p}_i + \boldsymbol{\gamma}_{\text{th}}) \end{aligned} \quad \text{with} \quad K_{\text{th}} \equiv \sum_{i=1}^N S_i \frac{p_i^2}{2m_i} = \text{cons}$$

and the momentum of the thermostatted particles sums to zero. This dynamics implies that when $K_{\text{th}} = (3N_{\text{th}} - 4)\beta_{\text{th}}^{-1} \equiv K_0$

$$f(\Gamma, 0) \equiv f_c(\Gamma, 0) = \frac{\delta(K_{\text{th}} - K_0) \delta(\mathbf{p}_{\text{th}}) \exp[-\beta_{\text{th}} H_0(\Gamma)]}{\iint d\Gamma \delta(K_{\text{th}} - K_0) \delta(\mathbf{p}_{\text{th}}) \exp[-\beta_{\text{th}} H_0(\Gamma)]}$$

There is no dissipation: $\Omega_c(\Gamma) = 0, \quad \forall \Gamma$

And from the dissipation theorem this distribution is preserved by the dynamics.

The Relaxation Theorem - cont.

From the definition of dissipation integral,

$$\Omega_t(\Gamma(0)) = \beta_{\text{th}}[H_0(\Gamma(t)) - H_0(\Gamma(0))] + \int_0^t ds (3N_{\text{th}} - 4)\alpha(s)$$

From the dynamics

$$\beta_{\text{th}}[H_0(\Gamma(t)) - H_0(\Gamma(0))] = -2K_{\text{th}}\beta_{\text{th}} \int_0^t ds \alpha(s)$$

So if (this is called an **equipartition relation**)

$$K_{\text{th}} = \frac{(3N_{\text{th}} - 4)\beta_{\text{th}}^{-1}}{2} \equiv \frac{(3N_{\text{th}} - 4)k_B T_{\text{th}}}{2}$$

there is no dissipation anywhere in phase space

$$\Omega_t(\Gamma(0)) = 0, \forall \Gamma(0), t.$$

Consider a deviation from the canonical distribution

$$f(\Gamma, 0) \equiv \frac{\delta(K_{\text{th}} - K_0) \delta(\mathbf{p}_{\text{th}}) \exp[-\beta_{\text{th}} H_0(\Gamma) - \gamma g(\Gamma)]}{\int d\Gamma \delta(K_{\text{th}} - K_0) \delta(\mathbf{p}_{\text{th}}) \exp[-\beta_{\text{th}} H_0(\Gamma) - \gamma g(\Gamma)]}$$

For this distribution the dissipation function is

$$\bar{\Omega}_t(\Gamma(0))t = \gamma[g(\Gamma(t)) - g(\Gamma(0))] \equiv \gamma \Delta g(\Gamma(0), t)$$

Unless g is a constant of the motion, the dissipation theorem implies this distribution function is not preserved.

$$f(\Gamma, t) = \exp[-\gamma \Delta g(\Gamma, -t)] f(\Gamma, 0)$$

For ergodic systems a time independent, dissipationless distribution is unique and is called an *equilibrium* canonical distribution function.

Further, the dissipation function satisfies the Second Law Inequality ,

$$\gamma \langle \Delta g(\Gamma, t) \rangle_{f(\Gamma, 0)} = \int_0^\infty A(1 - e^{-A}) p(\gamma \Delta g(\Gamma, t) = A) dA$$

$$\geq 0, \quad \forall t, f(\Gamma, 0)$$

This inequality is somewhat analogous to the Boltzmann H-theorem.

Thus if the initial distribution differs from the canonical distribution there will *always* be dissipation and on *average* this dissipation is *positive*. This remarkable result is true for arbitrary g - provided it is an even function of the momenta.

Using the Dissipation Theorem and the Second Law Inequality we see that:

$$\langle g(t) \rangle_{f(\Gamma, 0)} - \langle g(0) \rangle_{f(\Gamma, 0)} = \gamma \int_0^t ds \langle \dot{g}(0) g(s) \rangle_{f(\Gamma, 0)} \geq 0, \quad \forall t$$

We assume that at sufficiently long time there is a decay of correlations

$$\begin{aligned}
 \langle g(t) \rangle_{f(\Gamma,0)} &= \langle g(0) \rangle_{f(\Gamma,0)} + \gamma \int_0^{t_c} ds \langle \dot{g}(0) g(s) \rangle_{f(\Gamma,0)} + \gamma \int_{t_c}^t ds \langle \dot{g}(0) \rangle_{f(\Gamma,0)} \langle g(s) \rangle_{f(\Gamma,0)} \\
 &= \langle g(0) \rangle_{f(\Gamma,0)} + \gamma \int_0^{t_c} ds \langle \dot{g}(0) g(s) \rangle_{f(\Gamma,0)} \\
 &= \langle g(t_c) \rangle_{f(\Gamma,0)}
 \end{aligned}$$

where we have used the fact that g is an even function of the momenta and hence $\langle \dot{g}(0) \rangle_{f(\Gamma,0)} = 0$ showing that the last term on the first line is zero.

$$\lim_{t \rightarrow \infty} \frac{d}{dt} \langle g(t) \rangle_{f(\Gamma,0)} = 0$$

So for sufficiently long times there is no dissipation and the system must be in its unique equilibrium state.

This completes the proof of the Relaxation Theorem.

Connection with thermodynamics

We *postulate* that

$$A(T = T_{\text{th}}, N, V) = Q(T_{\text{th}}, N, V) \\ \equiv -k_B T_{\text{th}} \ln \left[\iint d\Gamma \delta(K_{\text{th}} - K_0) \delta(\mathbf{p}_{\text{th}}) \exp[-\beta_{\text{th}} H_0(\Gamma)] \right]$$

From classical thermodynamics $U = A - T \frac{\partial A}{\partial T}$

Whereas if we differentiate Q with respect to T_{th} , $\langle H_0 \rangle = Q - T_{\text{th}} \frac{\partial Q}{\partial T_{\text{th}}}$

Noting that when $T = T_{\text{th}} = 0$, that $A(0) = U(0) = \langle H_0(0) \rangle = Q(0)$, we observe that A and Q satisfy the same differential equation with the same initial condition, and hence our postulate is proven.

NonEquilibrium Free Energy Relations

Jarzynski Equality (1997).

Equilibrium Helmholtz free energy differences can be computed **nonequilibrium** thermodynamic path integrals. For nonequilibrium isothermal pathways between two equilibrium states

$$f(\Gamma, 0) \sim \exp[-\beta H_1(\Gamma)] \rightarrow f(\Gamma, t) \sim \exp[-\beta H_2(\Gamma)]$$

$$\beta \Delta W(t) \equiv \beta[H_2(t) - H_1(0)] - \int_0^t ds \Lambda(s)$$

implies,

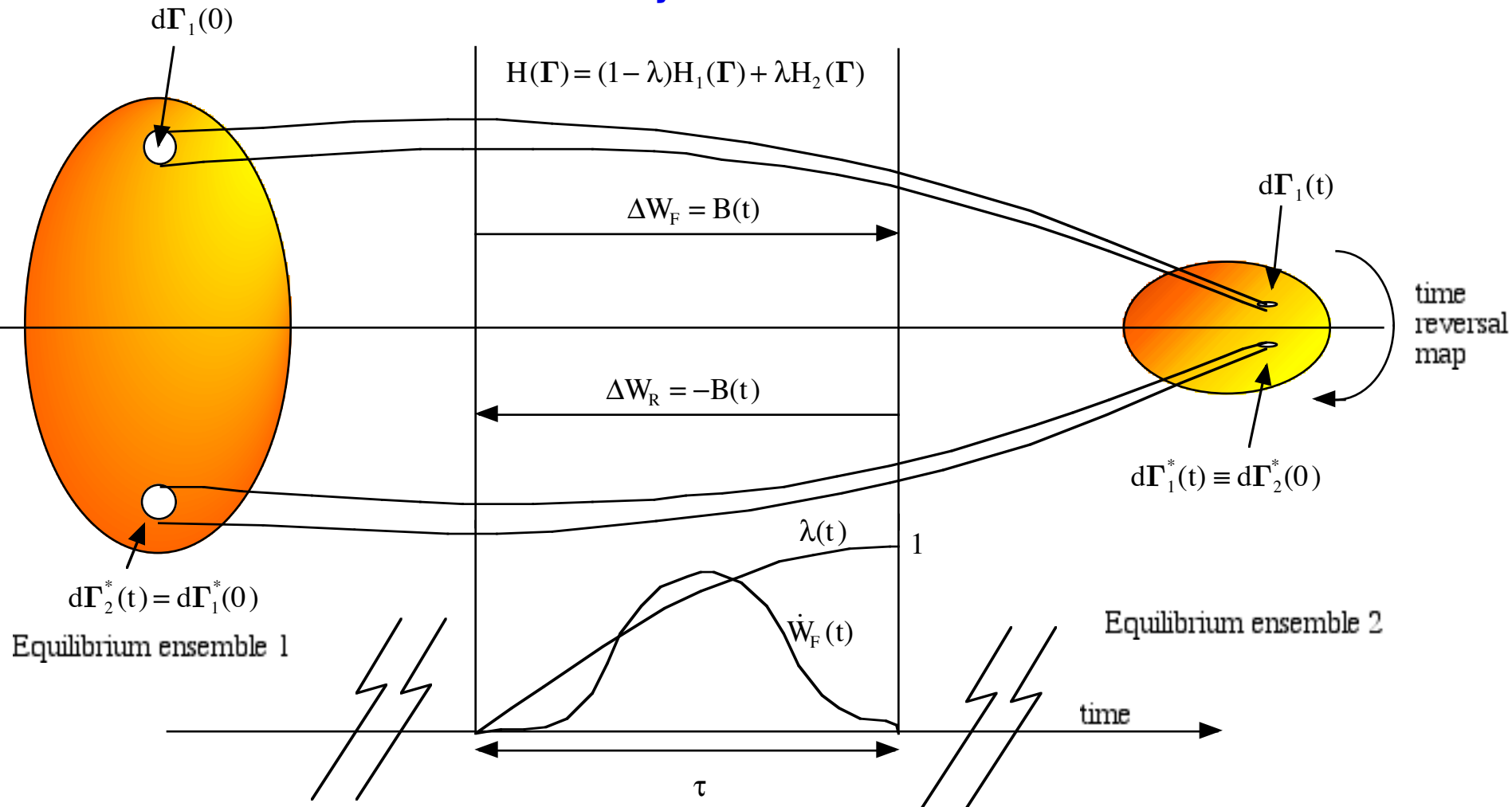
$$\langle \exp[-\beta \Delta W] \rangle_F = \exp[-\beta \Delta A_F]$$

NB $\Delta A = A_2 - A_1$ is the difference in Helmholtz free energies, and if $\Delta A = 0$ then JE = KI

Crooks Equality (1999).

$$\frac{p_F(\Delta W = B)}{p_R(\Delta W = -B)} = \exp[-\beta(\Delta A - B)]$$

Crooks-Jarzynski Schematic



$$\frac{P_{1 \rightarrow 2}(\Delta W(\Gamma_1) = B)}{P_{2 \rightarrow 1}(\Delta W(\Gamma_2^*) = -B)} = \exp[-\beta((A_2 - A_1) - B)] \Rightarrow \langle \exp[-\beta \Delta W] \rangle_F = \exp[-\beta \Delta A] \quad \text{Evans, Mol. Phys., 20, 1551(2003)}$$

Jarzynski Equality proof:

systems are deterministic and canonical

$$\begin{aligned}
 \langle \exp[-\beta \Delta W(\Gamma_1(0))] \rangle_{1 \rightarrow 2} &= \int d\Gamma_1(0) f_1(\Gamma_1(0), 0) \exp[-\beta [H_2(\Gamma_1(t)) - H_1(\Gamma_1(0))] + \int_0^t ds \Lambda(\Gamma(s))] \\
 &= \int d\Gamma_1(0) f_1(\Gamma_1(0), 0) \frac{f_2(\Gamma_2(0), 0) d\Gamma_2(0) z_2}{f_1(\Gamma_1(0), 0) d\Gamma_1(0) z_1}, \quad \text{NB } \Gamma_2(0) \equiv \Gamma_1(t) \\
 &= \frac{z_2}{z_1} \int d\Gamma_2(0) f_2(\Gamma_2(0), 0) = \exp[-\beta (A_2 - A_1)]
 \end{aligned}$$

Crooks proof:

$$\begin{aligned}
 \frac{P_{1 \rightarrow 2}(\Delta W(\Gamma_1) = B)}{P_{2 \rightarrow 1}(\Delta W(\Gamma_2^*) = -B)} &= \frac{f_{\text{eq},1}(\Gamma_1, 0) d\Gamma_1}{f_{\text{eq},2}(\Gamma_2^*, 0) d\Gamma_2^*} \\
 &= \exp[\beta \Delta W_F(\Gamma_1)] \frac{z_2}{z_1} = \exp[\beta (B - (A_2 - A_1))]
 \end{aligned}$$

Proof of generalized Jarzynski Equality.

For any ensemble we define a generalized “work” function as:

$$\begin{aligned}\exp[\Delta X_\tau(\Gamma)] &\equiv \frac{\text{Pr}_{1,\text{eq}}(\Gamma_0, \delta\Gamma_0) Z(\lambda_1)}{\text{Pr}_{2,\text{eq}}(\Gamma_\tau, \delta\Gamma_\tau) Z(\lambda_2)} \\ &= \frac{f_{1,\text{eq}}(\Gamma_0) \delta\Gamma_0 Z(\lambda_1)}{f_{2,\text{eq}}(\Gamma_\tau) \delta\Gamma_\tau Z(\lambda_2)}\end{aligned}$$

We observe that the modulus of the Jacobian gives the volume ratio:

$$\left\| \frac{\partial \Gamma_\tau}{\partial \Gamma_0} \right\| = \frac{\delta\Gamma_\tau}{\delta\Gamma_0} = \frac{f_1(\Gamma_0, 0)}{f_1(\Gamma_\tau, \tau)}$$

We now compute the expectation value of the generalized work.

$$\begin{aligned}\langle \exp[-\Delta X_\tau(\Gamma)] \rangle &= \int d\Gamma_0 f_1(\Gamma_0) \frac{f_2(\Gamma_\tau) \delta\Gamma_\tau Z(\lambda_2)}{f_1(\Gamma_0) \delta\Gamma_0 Z(\lambda_1)} \\ &= \frac{Z(\lambda_2)}{Z(\lambda_1)} \int d\Gamma_\tau f_2(\Gamma_\tau) = \frac{Z(\lambda_2)}{Z(\lambda_1)}\end{aligned}$$

If the ensembles are canonical and if the systems are in contact with heat reservoirs at the same temperature

$$\begin{aligned}\langle \exp[-\Delta X_\tau(\Gamma)] \rangle_{1,\text{eq}} &= \int d\Gamma_0 f_{1,\text{eq}}(\Gamma_0) \frac{f_{2,\text{eq}}(\Gamma_\tau) \delta\Gamma_\tau Z(\lambda_2)}{f_{1,\text{eq}}(\Gamma_0) \delta\Gamma_0 Z(\lambda_1)} \\ &= \frac{Z(\lambda_2)}{Z(\lambda_1)} \int d\Gamma_\tau f_{2,\text{eq}}(\Gamma_\tau) = \frac{Z(\lambda_2)}{Z(\lambda_1)}\end{aligned}$$

$$\Rightarrow \Delta X_\tau(\Gamma) = \beta(H_2(\Gamma_\tau) - H_1(\Gamma_0)) - \beta\Delta Q_\tau(\Gamma_0)$$

$$= \beta\Delta W_\tau(\Gamma_0) \quad \text{QED}$$

Further comments on thermostats

T_{th} is the so-called kinetic temperature of the thermostat. If the thermostat has a comparable number of degrees of freedom to the system of interest, the thermostat like the system of interest, may be far from equilibrium. Thus the thermodynamic temperature would be undefined. However the Fluctuation and Dissipation Theorems remain valid!

In a thought experiment we can move the thermostat arbitrarily far from the system of interest and simultaneously greatly increase the number of degrees of freedom in the thermostat. In the limit, the thermostat can be viewed as being in thermodynamic equilibrium. In this case the details of the thermostat are unimportant and the kinetic temperature of the thermostat becomes the true thermodynamic temperature of the thermostat.

The dissipation function thus becomes nonlocal: the quotient of the work done on the system of interest and the equilibrium thermodynamic temperature of the remote thermostat.