Dissipation and the Foundations of Classical Statistical Thermodynamics

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(July, 2011, Max Planck Inst. fur Complex Systems, Dresden)
Outline

- Dynamical systems (v brief)
- Thermostats (v brief)
- Phase space and ensembles
- Phase Continuity 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)
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):

\[ \dot{q}_i = p_i / m + C_i \cdot F_e \]

\[ \dot{p}_i = F_i + D_i \cdot F_e - \alpha S_i p_i : \quad S_i = 0, 1; \quad \sum_i S_i = N_{res} \]

Example:

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

\[ \dot{q}_i = \frac{p_i}{m} + i\gamma y_i \]

\[ \dot{p}_i = F_i - i\gamma p_y - \alpha p_i \]

which is equivalent to:

\[ \ddot{q}_i = \frac{F_i}{m} + i\gamma \delta(t)y_i - \alpha (\dot{q}_i - i\gamma y_i) \]

There is no Hamiltonian function that generates adiabatic SLLOD.
If we add in the thermostatting terms assuming $A \Gamma$ then

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

If we then choose the thermostat multiplier as

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

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:

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

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

All equations of motion are time reversal symmetric - but more on this later!
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 $\Sigma = -\beta J_{Fe} V = \int_V dV \sigma(r) / k_B$ 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 $t \to \infty$, if the time averages are taken over steady state trajectory segments. The formula is valid for arbitrary external fields, $F_e$. 
\[ p(\overline{P}_{xy,t}) \]

\[ t = 0.1, \gamma = 0.5 \]

\[ \ln \left( \frac{p(\overline{P}_{xy,t} = A)}{p(\overline{P}_{xy,t} = -A)} \right) = -\beta A\gamma Vt \]

The phase continuity equation (Gibbs, 1902) is analogous to the mass continuity equation in fluid mechanics.

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

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

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

\(\Lambda\) is called the phase space expansion factor and for a system in 3 Cartesian dimensions

\[
\Lambda(\Gamma) = -3N_{th} \alpha(\Gamma)
\]

The formal solution is:

\[
f(\Gamma(t), t) = \exp\left[-\int_0^t ds \ \Lambda(\Gamma(s))\right] f(\Gamma(0), 0)
\]
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)
The Loschmidt Demon applies a time reversal mapping:

$$\Gamma = (q,p) \rightarrow \Gamma^* = (q,-p)$$
Phase Space and reversibility
The Dissipation function is defined as: (Searles & Evans. 2000 - implicit earlier)

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

\[ = \bar{\Omega}_t t \equiv \Omega_t \]

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

We know that

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

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

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

The dissipation function is in fact a generalised irreversible entropy production - see below.
Evans Searles TRANSIENT FLUCTUATION THEOREM

Choose

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

\[
\frac{p(\delta V_\Gamma (\Gamma(0), 0; \bar{\Omega}_t(\Gamma(0))) = A))}{p(\delta V_\Gamma (\Gamma^*(0), 0))} = \frac{f(\Gamma(0), 0)\delta V_\Gamma (\Gamma(0), 0)}{f(\Gamma^*(0), 0)\delta V_\Gamma (\Gamma^*(0), 0)}
\]

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

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

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

The derivation is complete.

\[
\ln \frac{p(\bar{\Omega}_t = A)}{p(\bar{\Omega}_t = -A)} = At
\]
Dissipation function for shear flow in the canonical ensemble

If the equations of motion are isokinetic Sllofd

\[ \dot{q}_i = \frac{p_i}{m} + i\gamma y_i \]
\[ \dot{p}_i = F_i - i\gamma p_i - \alpha p_i \]

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

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

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

\[
\Omega_t(\Gamma) = -\beta \int_0^t ds \ P_{xy}(\Gamma(s)) \gamma N
\]

Note: \( \Gamma \equiv \Gamma(0) \)
Consequences of the FT

Connection with Linear irreversible thermodynamics

In driven thermostatted canonical systems satisfying AIΓ where dissipative field is constant,

\[ \Sigma = - \left\langle J \right\rangle F_e V / T_{soi} \]

\[ = - \left\langle J \right\rangle F_e V / T_{res} + O(F_e^4) \]

\[ = \left\langle \Omega \right\rangle + O(F_e^4) \]

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 Second Law Inequality

(Searles & Evans 2004).

If \( \langle \ldots \rangle_{t>0} \) denotes an average over all fluctuations in which the time integrated entropy production is positive, then,

\[
\langle \overline{\Omega}_t \rangle = \int_{-\infty}^{\infty} (A p(\overline{\Omega}_t = A)) dA \\
= \int_0^{\infty} \left( A p(\overline{\Omega}_t = A) - A p(\overline{\Omega}_t = -A) \right) dA \\
= \int_0^{\infty} \left( A p(\overline{\Omega}_t = A)(1 - e^{-At}) \right) dA \\
= \langle \overline{\Omega}_t (1 - e^{-\overline{\Omega}_t t}) \rangle_{\overline{\Omega}_t > 0} \geq 0, \quad \forall \ t > 0
\]

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).

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.

\[
\langle \exp(-\Omega_t t) \rangle = 1
\]

\[
\langle \exp(-\Omega_t t) \rangle = \int_{-\infty}^{+\infty} dA \, p(\Omega_t = A) \exp(-At)
\]

\[
= \int_{-\infty}^{+\infty} dA \, p(\Omega_t = -A)
\]

\[
= \int_{-\infty}^{+\infty} dA \, p(\Omega_t = A) = 1
\]

NPI is a necessary but not sufficient condition for the TFT.
The Dissipation Theorem (Evans et.al. 2008)

From the streaming version of the phase continuity 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

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

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

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

\[ = e^{-\int_0^{-t} d\tau \Omega(\Gamma(\tau))} f(\Gamma(0), 0) \]
The Dissipation Theorem - cont.

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

\[ \frac{d\langle B(t) \rangle}{dt} = \int d\Gamma(0) B(\Gamma(0)) \Omega(\Gamma(-t)) f(\Gamma(0),t) \]

\[ = \int d\Gamma(0) B(\Gamma(t)) \Omega(\Gamma(0)) f(\Gamma(0),0) \]

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

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

\[ \dot{q}_i = \frac{p_i}{m_i} \]

\[ \dot{p}_i = F_i(q) - S_i(\alpha p_i + \gamma_{th}) \]

and the momentum of the thermostatted particles sums to zero. This dynamics implies that when \( K_{th} = (3N_{th} - 4)\beta_0^{-1} \equiv K_0 \)

\[ f(\Gamma,0) \equiv f_C(\Gamma,0) = \frac{\delta(K_{th} - K_0)\delta(p_{th})\exp[-\beta_0 H_0(\Gamma)]}{\int d\Gamma \delta(K_{th} - K_0) \delta(p_{th})\exp[-\beta_0 H_0(\Gamma)]} \]

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

And from the dissipation theorem this distribution is preserved by the dynamics. An \textit{equilibrium system} is simply a system where the dissipation is zero everywhere in the allowed phase space.
The Relaxation Theorem - cont.

From the definition of dissipation integral,

\[ \Omega_t(\Gamma(0)) = \beta_0 [H_0(\Gamma(t)) - H_0(\Gamma(0))] + \int_0^t ds (3N_{th} - 4)\alpha(s) \]

From the dynamics

\[ \beta_0 [H_0(\Gamma(t)) - H_0(\Gamma(0))] = -2K_0\beta_0 \int_0^t ds \alpha(s) \]

So if (this is called an equipartition relation)

\[ 2K_0\beta_0 = (3N_{th} - 4) \quad \text{or} \quad K_0 = (3N_{th} - 4)\beta_0^{-1} / 2 \]

there is no dissipation anywhere in phase space:

\[ \Omega_t(\Gamma(0)) = 0, \forall \Gamma(0), t. \]
Consider a deviation from the canonical distribution

\[
f(\Gamma,0) = \frac{\delta(K_{th} - K_0)\delta(p_{th})\exp[-\beta_0 H_0(\Gamma) - \gamma g(\Gamma)]}{\int d\Gamma \delta(K_{th} - K_0)\delta(p_{th})\exp[-\beta_0 H_0(\Gamma) - \gamma g(\Gamma)]}
\]

For this distribution the dissipation function is

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

Since the system is \textit{t-mixing} the are no constants of the motion other than \( p_{th}, K_{th} \). Hence \( g \) is not constant of the motion & there is dissipation. Further the dissipation theorem implies this distribution function is not preserved.

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

For t-mixing systems the time independent, dissipationless distribution is \textit{unique} (\textit{i.e.} ergodic) and it is called an \textit{equilibrium} canonical distribution function.

Wednesday, 6 July 2011
Further, the dissipation function satisfies the Second Law Inequality,

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

\[ > 0, \quad \forall t, f(\Gamma, 0) \]

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 in fact *positive* (there can be no cancellation). This remarkable result is true for arbitrary real \( g \) - provided it is an even function of the momenta.

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

\[ \langle g(t) \rangle_{f(\Gamma, 0)} - \langle g(0) \rangle_{f(\Gamma, 0)} = \gamma \int_0^t ds \langle \dot{g}(0) g(s) \rangle_{f(\Gamma, 0)} > 0, \quad \forall t \]
We assume that at sufficiently long time there is a decay of correlations (T-mixing
N.B. T-mixing is not the mathematicians mixing condition!)

\[ \langle g(t) \rangle_{f(\Gamma,0)} = \langle g(0) \rangle_{f(\Gamma,0)} + \gamma \int_0^{t_c} ds \langle \dot{g}(0) g(s) \rangle_{f(\Gamma,0)} + \gamma \int_{t_c}^t ds \langle \dot{g}(0) g(s) \rangle_{f(\Gamma,0)} \]

\[ = \langle g(0) \rangle_{f(\Gamma,0)} + \gamma \int_0^{t_c} ds \langle \dot{g}(0) g(s) \rangle_{f(\Gamma,0)} \]

\[ = \langle g(t_c) \rangle_{f(\Gamma,0)} \]

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.

\[ \lim_{t \to \infty} \frac{d}{dt} \langle g(t) \rangle_{f(\Gamma,0)} = 0 \]

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

• Comment on covariant definition of dissipation. • cp entropy production!

This completes the proof of the Relaxation Theorem.
Connection with thermodynamics

We postulate that: \( A(T = T_0, N, V) = Q(T_0, N, V) \)

\[
\equiv -k_B T_0 \ln \left[ \iiint d\Gamma \delta(K_{th} - K_0)\delta(p_{th}) \exp[-\beta_0 H_0(\Gamma)] \right]
\]

where as before, \( k_B T_0 \equiv \beta_0^{-1} \equiv 2K_0 / (3N_{th} - 4) \)

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

Whereas if we differentiate \( Q \) with respect to \( T_0 \), \( \langle H_0 \rangle = Q - T_0 \frac{\partial Q}{\partial T_0} \)

Noting that when \( T = T_0 = 0 \), that \( A(0) = U(0) = \langle H_0(0) \rangle = Q(0) \), we observe that \( A \) and \( Q \) satisfy the same differential equation:

\[
x \frac{\partial Y(x)}{\partial x} - Y(x) + U(x) = 0 \text{ with the same initial condition, } U(0) = Y(0) \text{ and}
\]

hence our postulate is proven.