Thermodynamics of diffusion processes

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Text-book wisdom

"**Isolated** systems evolve to the state of equilibrium in which
the entropy reaches its **maximal** value"
"The **entropy** is a measure of the degree of randomness"
"The heat bath drives an **open** system to its equilibrium state
at the bath temperature"

Associations

non-equilibrium random dynamics → asymptotic equilibrium
(un)certainty, information, entropy functionals, **entropy** and **time**

Entropic mess

(Partially random order:) Boltzmann, Gibbs, **Shannon**, relative, conditional, **Kullback-Leibler**, Renyi, Tsallis, Wehrl, ..., information entropy, differential entropy, Kolmogorov-Sinai entropy...von Neumann

Problem addressed

time evolution of a continuous probability density → **dynamics** of its entropy

$$\rho(x) \to \rho(x,t) \Longrightarrow \mathcal{S}(\rho) \to \mathcal{S}(\rho)(t)$$

$$\Downarrow$$

entropy methods in **random** motion

$$\Downarrow$$

Laws of thermodynamics and Helmholtz-type extremum principles in **diffusion** processes

"Everything of importance has been said before
by someone who did not discover it"

$\Downarrow$

"Nothing is ever discovered for the first time"
(*laws of discovery, after M. V. Berry and A.Whitehead*)

"Nobody knows what entropy is in reality, that is why
in the debate you will always have an advantage" (*J. von Neumann, 1948*)

"In the physical sciences, the **entropy**
is a measure of the degree of randomness
and the **tendency** of physical systems
to become less and less organized"

"The usefulness of the concept of entropy (and the Second Law) depends on our ability to define entropy of a physical system in a calculable way."

Text-book wisdom:

"All **isolated** systems evolve to the state of equilibrium
in which the entropy reaches its maximal value"

"The heat bath drives an **open** system to its equilibrium state at the bath temperature"

Adopted hierarchy of thermodynamical systems:

isolated
closed
open

(borrowed from the Glansdorf - Prigogine theory of non-equilibrium phenomena)

Entropy methods in random motion:

(e.g. the *large time asymptotic of the* **heat** *and* **Fokker-Planck** *equations*)

(i) Consider $\partial_t u = \Delta u$, with $x \in R^n$, $t \in R^+$ and $u(.,t=0) = u_0(.) \geq 0$ and $\int u_0(x)dx = 1$. As $t \to \infty$, we have $u(x,t) \simeq \rho(x,t) = (4\pi t)^{-n/2} \exp[-x^2/4t]$.

Analyze the $t \to \infty$ rate of convergence of

$$\|u - \rho\|_{L^1}(t) \doteq \int |u(x,t) - \rho(x,t)| dx$$

Note that for two density functions f and g we have the **Csiszár-Kullback inequality**:

$$\mathcal{K}(f,g) = \int f \ln(f/g) dx \geq (1/2)\|f - g\|_{L^1}^2$$

Outcome (i): If ρ_t is a solution of the heat equation with the initial data ρ_0 and one takes $\rho_\alpha(x) = (1/\sqrt{2\alpha\pi}) \exp[-x^2/2\alpha]$, then we have an asymptotic $1/t$ decay of the initially prescribed Kullback-Leibler "distance"

$$\mathcal{K}(\rho_t, \rho_{\alpha+kt}) \leq \mathcal{K}(\rho_0, \rho_\alpha)[\alpha/(\alpha + kt)]\,.$$

(ii) Consider $\partial_t f = \Delta f + \nabla \cdot (bf)$, where $f(.,t) = f_0 \geq 0$, $\int f_0(x)dx = 1$. We assume that the forward drift $b = b(x)$ has a gradient form.

Analyze: Let f_* be the stationary solution of the F-P equation, what is the $t \to \infty$ rate of convergence of $\|f - f_*\|_{L^1}(t) \doteq \int |f(x,t) - f_*(x)| dx$ towards the value 0 ?

Outcome (ii): The outcome, albeit not completely general, is that $f_t \doteq f(x,t)$, $t \geq 0$ decays *in relative entropy* to a Gaussian, the speed of such decay being exponential

$$\mathcal{H}_c(t) \simeq \exp(-\alpha t)\mathcal{H}_c(0)\,,$$

where $\mathcal{H}_c(t) \doteq \mathcal{H}_c(f_t, f_*) \doteq -\mathcal{K}(f_t, f_*)$, with $\alpha > 0$ and $t > 0$.

Quantum "detour" - thermodynamics of open systems

(after R. Alicki, (2000))

(i) take for granted that **the bath drives the system to an equilibrium state**

ρ_t stands for the (reduced) density matrix of a quantum system in a combined weak coupling and adiabatic approximation of the general system-reservoir dynamic problem, $t \geq 0$:

$$\frac{d}{dt}\rho_t = -i[H_{sys}(t), \rho_t] + L_{diss}(t)\rho_t \doteq L(t)\rho_t$$

An **internal energy** of the system:

$$E(t) = Tr(\rho_t H_{sys}(t))$$

The **work** performed on the system by external forces:

$$W(t) = \int_0^t Tr[\rho_s(\frac{d}{ds}H_{sys}(s))]ds$$

The **heat** supplied to the system by the reservoir:

$$Q(t) = \int_0^t Tr[(\frac{d}{ds}\rho_s)H_{sys}(s)]ds$$

(ii) The first law of thermodynamics:

$$\frac{d}{dt}E(t) = \frac{d}{dt}W(t) + \frac{d}{dt}Q(t)$$

(iii) The second law of thermodynamics:

- use the **relative entropy** $S(\rho|\sigma) = Tr(\rho \ln \rho - \rho \ln \sigma)$ and a **stationary state** input: $L(t)\rho_{eq} = 0$, with $\rho_{eq} = Z^{-1}\exp[-\beta H_{sys}(t)]$. Then:

$$\frac{d}{dt}S(\rho_t|\rho_{eq}) = \sigma(\rho_t) + \frac{1}{T}\frac{dQ}{dt}$$

where $\sigma(\rho_t) \geq 0$ stands for the **entropy production, while $\dot{Q}/T$ refers to the entropy/heat exchange with the bath**. So, $TdS \geq dQ$.

Thermodynamics of closed but non-isolated systems - A resumé

(Back to the classical Glansdorf-Prigogine lore)

Ist law:

$$dU = dQ + dW$$

IInd law:

$$dS = d_{int}S + d_{ext}S$$

$$d_{int}S \geq 0$$

$$d_{ext}S = \frac{dQ}{T}$$

(For a reversible process we have $d_{int}S = 0$)

Large time behavior - Extremum principles for irreversible processes

(1) U and V (volume) constant → **maximum of entropy** is preferred:

$$d_{int}S = TdS - dQ \geq 0$$

together with **a minimum for the entropy production**:

$$\frac{d}{dt}\left(\frac{d_{int}S}{dt}\right) < 0$$

(2) S and V constant → **minimum internal energy** is preferred:

$$dU = -Td_{int}S \leq 0$$

(3) T and V constant → **minimum of $F = U - TS$ (Helmholtz free energy)** is preferred:

$$dF = -Td_{int}S \leq 0$$

(4) further principles refer to the minimum of the Gibbs free energy and this of enthalpy (we skip them)

(*according to Kondepudi and Prigogine, 1998)*

Helmholtz free energy - complements

Consider an **equilibrium** state in statistical mechanics, with β as an inverse temperature.

i-th microstate: energy (level) E_i, $i \in I$, with statistical weight $\exp(-\beta E_i)$

macrostate: choose a sample $E \doteq \{E_{i_1}, E_{i_2}, ..., E_{i_n}, ...\}$

$$\Downarrow$$

free anergy F

$$F(\beta) = -\frac{1}{\beta} \ln Z(\beta)$$

statistical sum (partition function) Z

$$Z(\beta) = \sum_E \exp(-\beta E_i)$$

internal energy notion U

$$U = -\frac{\partial}{\partial \beta} \ln Z(\beta) = \langle E \rangle \doteq \sum_i E_i \exp(-\beta E_i)$$

entropy notion S, $(T = 1/\beta)$

$$U - F \doteq TS$$

"**maximum** entropy principle"

$$\Downarrow$$

"principle of **minimum** free energy"

Let p_i be a probability of occurence of a microstate E_i in the macrostate configuration E, $\sum p_i = 1$.
A **minimum** of

$$F = U - \beta^{-1} S = F[p] = \sum_i (p_i E_i + \frac{1}{\beta} p_i \ln p_i)$$

is achieved for a canonical distribution:

$$p_i = \frac{1}{Z} \exp(-\beta E_i)$$

Define $S[p] = -\sum p_i \ln p_i$ and $U = \sum E_i p_i$.

In order to get an equilibrium distribution associated with the **Shannon** (Boltzman-Gibbs) entropy S, we need to **extremize** the functional:

$$\Phi[p] = -\sum p_i \ln p_i - \alpha \sum p_i - \beta \sum E_i p_i$$

where α and β are the Lagrange multipliers

We have (p_i^* denotes an equilibrium probability, e.g. an ultimate solution)

$$\delta\Phi[p] = 0 = [-\ln p_i^* - 1 - \alpha - \beta E_i]\delta p_i$$

(with arbitrary variations δp_i). Multiply the result by p_i, sum up, use the constraints (normalization and the fixed internal energy value) →

$$\alpha + 1 = S_* - \beta U_*$$

$$\Downarrow$$

$$p_i^* = \exp[-S_* + \beta U_*] \exp(-\beta E_i) = \exp\beta(F_* - E_i) \doteq \frac{1}{Z}\exp(-\beta E_i)$$

Notice that we deal here with a discrete probability measure, i.e. the set of p_i^*'s such that $\sum p_i^* = 1$.

S_* is the Shannon entropy of this discrete measure. In view of $F = U - \beta^{-1}S$, the Shannon entropy has been **maximized** under the normalization (probability measure) and fixed internal energy constraints.

To be sure that the above F^* is indeed a minimum, let us consider the **relative Kullback-Leibler** entropy:

$$K(p, q) \doteq \sum p_i \ln(\frac{p_i}{q_i})$$

and use the measure $p_* \equiv \{p_i^*\}$ as the reference one (e g. q):

We have (K is a convex function with a minimum at 0):

$$K(p, p_*) = -S - \sum p_i[-S_* + \beta U_* - \beta E_i] = \beta(F - F_*) \geq 0$$

Thermodynamics of random motion

$$m\ddot{x} + m\gamma\dot{x} = -\nabla V(x,t) + \xi(t)$$
$$\langle f\xi(t)\rangle = 0$$
$$\langle \xi(t)\xi(t')\rangle = \sqrt{2m\gamma k_B T}\,\delta(t-t')$$
$$\Downarrow$$
$$\frac{\partial}{\partial t}f(x,u,t) = \left[-\frac{\partial}{\partial x}u + \frac{\partial}{\partial u}\left(\gamma u + (1/m)\nabla V(x,t)\right) + \frac{\gamma k_B T}{m}\frac{\partial^2}{\partial u^2}\right] f(x,u,t)$$

Define (we leave aside an issue of dimensional adjustments):

$$\mathcal{S}(t) = -\int dx\, du f \ln f = -\langle \ln f\rangle$$

$$E(x,u,t) = \frac{mu^2}{2} + V(x,t) \to U = \langle E\rangle$$

The **Ist law** $dU = dQ + dW$ takes the form

$$\dot{\mathcal{Q}} + \dot{W} = \dot{U}$$

where $\dot{W} = \langle \partial_t V\rangle$ stands for the **work externally performed upon the system**.

With assumptions concerning the proper behavior of $f(x,u,t)$ at x,u integration boundaries (sufficiently rapid decay at infinities) we have:

$$\dot{\mathcal{Q}} = \gamma(k_B T - \langle mu^2\rangle)$$

$$\dot{\mathcal{S}} = \gamma\left[\frac{k_B T}{m}\langle\left(\frac{\partial \ln f}{\partial u}\right)^2\rangle - 1\right]$$

and hence, in view of $(1/T)dQ = d_{ext}S$ the **IInd law** follows:

$$\dot{\mathcal{Q}} - k_B T\dot{\mathcal{S}} = -\frac{\gamma}{m}\langle\left(k_B T\frac{\partial \ln f}{\partial u} + mu\right)^2\rangle = -T\dot{S}_{int} \leq 0$$

We denote $S \doteq k_B\mathcal{S}$ and so arrive at $\dot{Q} \leq T\dot{S}$ i.e. $dQ \leq TdS$.

An obvious analog of the **Helmholtz free energy** reads:

$$F \doteq \langle E + k_B T \ln f \rangle = U - TS$$

$$\Downarrow$$

$$\dot{F} - \dot{W} = \dot{Q} - T\dot{S} = -T\dot{S}_{int} \leq 0$$

A byproduct of our discussion is: $dF \leq dW$ (!)
For time-independent $V = V(x)$ we have the standard **Helmholtz extremum principle**, i.e. the F-theorem:

$$\dot{F} = \dot{Q} - T\dot{S} \doteq -T\dot{S}_{int} \leq 0$$

$$\Downarrow$$

$$dF = -TdS_{int} \leq 0$$

setting a minimum of F at F_*. That is determined in terms of a unique stationary state $f_*(x,u) = \frac{1}{Z}\exp\left[-\frac{E(x,u)}{k_B T}\right]$, towards which any initially given f asymptotically relaxes.

Thermodynamics of spatial random motion

$$\dot{x} = b(x,t) + A(t)$$

$$\langle A(s) \rangle = 0\,,\ \langle A(s)A(s') \rangle = \sqrt{2D}\delta(s-s')$$

$$\Downarrow$$

$$\partial_t \rho = D\triangle\rho - \nabla\cdot(b\rho)$$

We assume the gradient form for $b = b(x,t)$, D is a diffusion constant with dimensions of $\hbar/2m$ or $k_B T/m\beta$. By introducing $u(x,t) = D\nabla \ln\rho(x,t)$ we deduce $v(x,t) = b(x,t) - u(x,t) \Rightarrow \partial_t\rho = -\nabla(v\rho)$.

The **Shannon entropy**, typically is **not** a conserved quantity.

$$\mathcal{S}(t) = -\int \rho(x,t)\,\ln\rho(x,t)\,dx = \langle \ln\rho \rangle$$

$$\Downarrow$$

(with boundary restrictions that $\rho, v\rho, b\rho$ vanish at spatial infinities or finite interval borders, remembering that $v = b + u$ and $u = D\nabla \ln \rho$)

$$\frac{d\mathcal{S}}{dt} = \int [\rho\, (\nabla \cdot b) + D \cdot \frac{(\nabla\, \rho)^2}{\rho}]\, dx$$

$$\Updownarrow$$

$$D\dot{\mathcal{S}} \doteq D\, \langle \nabla \cdot b \rangle + \left\langle u^2 \right\rangle = - \langle v \cdot u \rangle\ = \left\langle v^2 \right\rangle - \langle b \cdot v \rangle$$

$$\Updownarrow$$

$$\dot{\mathcal{S}} = \dot{\mathcal{S}}_{int} + \dot{\mathcal{S}}_{ext}$$

where:

$$k_B T \dot{\mathcal{S}}_{int} \doteq m\beta \left\langle v^2 \right\rangle \geq 0$$

stands for the **information entropy production**.

Upon setting $b = \frac{F}{m\beta}$ and $D = k_B T/m\beta$ we have

$$k_B T \dot{\mathcal{S}}_{ext} \doteq \dot{\mathcal{Q}} \doteq - \int F \cdot j\, dx = -m\beta \, \langle b \cdot v \rangle$$

which (as long as negative !!!) may be interpreted as the **heat dissipation rate**.

In view of: $\dot{\mathcal{Q}} = -\int F \cdot j\, dx$, there is definitely some form of power release involved.

Note: with $T\dot{S} \doteq k_B T \dot{\mathcal{S}}$, we do have the **IInd law**:

$$T\dot{S}_{int} = T\dot{S} - \dot{Q} \geq 0 \Rightarrow T\dot{S} \geq \dot{Q}$$

We assume that $V = V(x)$ does not depend on time and therefore:

$$j = \rho v = \frac{\rho}{m\beta}[F - k_B T \nabla \ln \rho] \doteq -\frac{\rho}{m\beta} \nabla \Psi$$

i.e. $v = -(1/m\beta)\nabla\Psi$. Since $F = -\nabla V$, we can define:

$$\Psi = V + k_B T \ln \rho$$

$$\Downarrow$$

$$\langle \Psi \rangle = \langle V \rangle - TS$$

where $S \doteq k_B \mathcal{S}$.

We recognize the familiar formula

$$F = U - TS$$

(1) $F \doteq < \Psi >$ stands for the**Helmholtz free energy**
(2) $U \doteq < V >$ stands for the (mean) **internal energy**

$$\Downarrow$$

($\rho V v$ needs to vanish at the integration volume boundaries)

$$\dot{F} = \dot{Q} - T\dot{S} = -(m\beta)\left\langle v^2 \right\rangle = -k_B T \dot{\mathcal{S}}_{int} \leq 0$$

As long as there is an information entropy production, the "Helmholtz free energy" decreases as a function of time towards its minimum. If there is none, the "Helmholtz free energy" remains constant.

For the special case of the free Brownian motion we have $V = 0 = b$, while $v = -D\nabla \ln \rho = -u$, and so (recognize the **Fisher information** functional):

$$\dot{Q} = 0 \Rightarrow \dot{F} = -T\dot{S} = -m\beta D^2 \int [\frac{(\nabla \rho)^2}{\rho}]\, dx \leq 0$$

In the present case $S(t)$ grows monotonically with time.

Quantum mechanical INTERLUDE

- Coherent state

$$\rho(x) = \tfrac{1}{[2\pi\sigma^2]^{1/2}} \exp\big[- \tfrac{(x-x_0)^2}{2\sigma^2} \big]$$
$$\Downarrow$$
$$\mathcal{S}(\rho) = \tfrac{1}{2}\ln(2\pi e\sigma^2)$$

- Coherent state for the harmonic oscillator; $D = \hbar/2m$ and
$q(t) = q_0 \cos(\omega t) + (p_0/m\omega)\sin(\omega t)$,
$p(t) = p_0 \cos(\omega t) - m\omega q_0 \sin(\omega t)$.

$$\rho(x,t) = \left(\frac{2\pi D}{\omega}\right)^{-1/2} \exp\left[-\frac{\omega}{2D}\,\left(x - q(t)\right)^2\right]$$
$$\Downarrow$$
$$\sigma^2 = \frac{D}{\omega} \to \frac{d\mathcal{S}}{dt} = 0$$

- Free quantum dynamics for a Gaussian wave-packet

$$\rho(x,t) = \frac{\alpha}{[\pi(\alpha^4 + 4D^2t^2)]^{1/2}} \exp\left(-\frac{x^2\alpha^2}{\alpha^4 + 4D^2t^2}\right) .$$

$$\Downarrow$$
$$\sigma^2 \to \sigma^2(t) = \frac{\alpha^4 + 4D^2t^2}{2\alpha^2} \to \frac{d\mathcal{S}}{dt} = \frac{4D^2t}{\alpha^4 + 4D^2t^2}$$

- Squeezed state of the oscillator (atomic units)

$$\sigma^2 \to \sigma^2(t) = \frac{1}{2}\left(\frac{1}{s^2}\sin^2 t + s^2\cos^2 t\right)$$

- Non-quantum example: free Brownian motion; $D = k_BT/m\beta$

$$\sigma^2 \to \sigma^2(t) = 2Dt$$

Side **comment (i):**

For general probability distributions $p(x)$ with a **fixed** variance σ we have $S(p) \leq \frac{1}{2}\ln(2\pi e\sigma^2)$. $S(p)$ would become maximized if and only if p is a Gaussian: $p \rightarrow \rho$.

Side **comment (ii)**:

We address a general **time-dependent setting**. Before, by admitting $\sigma = \sigma(t)$, we gave a number of examples for time-dependent information entropy $S(\rho_t)$ (c.f. free quantum evolution, in the non-quantum context a good example is the free Brownian motion).

Side **comment (iii):**

Recall the Fourier transform for normalized Schrödinger wave functions, together with the notions of **position and momentum representation** wave packets.

Given an eigenfunction $\psi(x)$ of the energy operator, we denote $(\mathcal{F}\psi)(p)$ its Fourier transform. The corresponding probability densities follow:

$$\rho(x) = |\psi(x)|^2 \quad \text{and} \quad \tilde{\rho}(p) = |(\mathcal{F}\psi)(p)|^2.$$

Denote:

$$S_q = -\int \rho(x)\ln\rho(x)dx \qquad \text{and} \qquad S_p = -\int \tilde{\rho}(p)\ln\tilde{\rho}(p)dp$$

There holds the **entropic uncertainty relation** (Białynicki-Birula/Mycielski) between two forms (position and momentum respectively) of the information entropy:

$$S_q + S_p \geq (1 + \ln\pi)$$

In case of more than one space dimension, an extra factor d (dimensionality) should precede $(1 + \ln\pi)$.

Measures of localization, ENTROPIC INEQUALITIES

For an ρ with finite mean and variance fixed at σ^2, we have:

$$\mathcal{S}(\rho) \le \frac{1}{2}\ln\left(2\pi e\sigma^2\right)$$

$$\Downarrow$$

$$\frac{1}{\sqrt{2\pi e}}\exp[\mathcal{S}(\rho)] \le \sigma$$

We consider $\rho_\alpha \doteq \rho(x-\alpha)$ and fix at σ^2 the value $\langle (x-\alpha)^2\rangle = \langle x^2\rangle - \alpha^2$ of the variance. Let us define the Fisher information (localization measure) of ρ_α:

$$\mathcal{F}_\alpha \doteq \int \frac{1}{\rho_\alpha}\left(\frac{\partial \rho_\alpha}{\partial \alpha}\right)^2 dx \ge \frac{1}{\sigma^2}$$

INEQUALITIES OF VARIOUS SORTS FOLLOW

$$\frac{1}{\sigma^2} \le (2\pi e)\,\exp[-2\mathcal{S}(\rho)] \le \mathcal{F}_\alpha$$

Under an additional decomposition/factorization ansatz (of the quantum mechanical $L^2(R^n)$ provenance) that $\rho(x) \doteq |\psi|^2(x)$, where a real or complex function $\psi = \sqrt{\rho}\exp(i\phi)$ is a normalized element of $L^2(R)$,we have:

$$\mathcal{F}_\alpha = 4\int \left(\frac{\partial\sqrt{\rho}}{\partial x}\right)^2 dx \le 16\pi^2\tilde{\sigma}^2$$

$$\frac{1}{\sigma^2} \le \mathcal{F}_\alpha \le 16\pi^2\tilde{\sigma}^2$$

$$\frac{1}{4\pi\tilde{\sigma}} \le \frac{1}{\sqrt{2\pi e}}\exp[\mathcal{S}(\rho)] \le \sigma$$

Outcome: the differential entropy $\mathcal{S}(\rho)$ typically may be expected to be a well behaved quantity: with finite both lower and upper bounds.

Thermodynamics of the Schrödinger picture evolution

$\big($*A disreputed (?) hint: "la thermodynamique cachée" after L. de Broglie*$\big)$

$$i\partial_t\psi = -D\Delta\psi + \frac{\mathcal{V}}{2mD}\psi\,.$$

$\mathcal{V} = \mathcal{V}(\overrightarrow{x}, t)$, continuous (it is useful, if bounded from below) function with dimensions of energy, $D = \hbar/2m$

$\big($*After L. de Broglie, we can set* $k_B T_0 \doteq \hbar\omega_0 \doteq mc^2$ *which yields* $D = \hbar/2m \equiv k_B T_0/m(2\omega_0)$ *i.e.* $\beta \equiv 2\omega_0\big)$

Admit the Madelung decomposition: $\psi = \rho^{1/2}\exp(is/2D)$ with the phase function $s = s(x,t)$ defining $v = \nabla s$

$$\Downarrow$$

$$\partial_t\rho = -\nabla(v\rho)$$

$$\partial_t s + \frac{1}{2}(\nabla s)^2 + (\Omega - Q) = 0$$

$$\Omega \doteq \mathcal{V}/m$$

$$Q = 2D^2\frac{\Delta\rho^{1/2}}{\rho^{1/2}} = \frac{1}{2}u^2 + D\nabla\cdot u$$

The probability density $|\psi|^2 = \rho$ is propagated by a Fokker-Planck equation with the drift $b = v - u = \nabla(s - D\ln\rho)$ where $u = D\nabla\ln\rho$.

$$\partial_t\rho = D\triangle\rho - \nabla\cdot(b\rho)$$

$$\mathcal{S}(t) = -\int \rho(x,t)\,\ln\rho(x,t)\,dx$$

$$\Downarrow$$

$$D\dot{\mathcal{S}} = \left\langle v^2\right\rangle - \langle b\cdot v\rangle \doteq D(\dot{\mathcal{S}}_{int} + \dot{\mathcal{S}}_{ext})$$

which is a direct analog of the **IInd law**:

$$\dot{\mathcal{S}}_{int} = \dot{\mathcal{S}} - \dot{\mathcal{S}}_{ext} = (1/D)\left\langle v^2\right\rangle \geq 0 \Rightarrow \dot{\mathcal{S}} \geq \dot{\mathcal{S}}_{ext}$$

To arrive at an analog of the **Ist law**, we need to translate to the present setting the previous thermodynamic notions U and $F = U - TS$. Define:

$$v = \nabla s = \nabla(s + D \ln \rho) - D\nabla \ln \rho \doteq$$

$$-\frac{1}{m\beta}\nabla(V + k_B T_0 \ln \rho) \doteq -\frac{1}{m\beta}\nabla\Psi$$

so we have

$$-m\beta\langle s\rangle \equiv \langle\Psi\rangle = \langle V\rangle - T_0 S \Longrightarrow F = U - T_0 S\,.$$

With $b(x,t) = -(1/m\beta)\nabla V$, we finally recover the I^{st} **law**:

$$\dot{U} = \langle\partial_t V\rangle - m\beta\langle bv\rangle = \dot{W} + \dot{\mathcal{Q}}$$

with the **externally performed work entry** $\dot{W} = \langle\partial_t V\rangle$ and $k_B T_0 \dot{\mathcal{S}}_{ext} = \dot{Q} = -m\beta\langle bv\rangle$.

The unitary **quantum dynamics** warrants the existence of an obvious constant (!) of motion, the mean value of an energy operator (Hamiltonian of the system $\langle\psi|\hat{H}|\psi\rangle \doteq m\,\mathcal{H}$:

$$\mathcal{H} = (1/2)[\left\langle v^2\right\rangle + \left\langle u^2\right\rangle] + \langle\Omega\rangle = -\left\langle\partial_t s\right\rangle \doteq \mathcal{E} = const\,.$$

Therefore the **Helmholtz-type extremum principle** for the quantum motion reads:

$$\dot{F} - \dot{W} = -m\beta_0 \frac{d}{dt}(\langle s\rangle + \mathcal{E}t) = -T\dot{S}_{int} \leq 0\,.$$

and we note that the property $\dot{F} \leq \dot{W}$ is common to all hitherto considered dissipative and non-dissipative cases.

Thermodynamic discrimination between random and quantum motions

$$\textbf{Quantum}: \; \dot{F} - \dot{W} = -m\beta_0 \frac{d}{dt}(\langle s\rangle + \mathcal{E}t) = -T_0 \dot{S}_{int} \leq 0\,.$$

$$\textbf{Random}: \; \dot{F} - \dot{W} = \dot{F} - \langle \partial_t V\rangle = -T\dot{S}_{int} \leq 0\,,$$

Note 1: For Smoluchowski processes $\dot{W} = 0$ and thus $\dot{F} = -\dot{S}_{int} \leq 0$.

Note 2: For phase space diffusion processes we have $\dot{W} = \langle \partial_t V\rangle \geq 0$ for the "work performed **upon** the system" and $\dot{W} = \langle \partial_t V\rangle < 0$ for the "work performed **by** the system". In the latter case $\dot{F} \leq 0$, otherwise $\dot{F}$ may be positive or have undefined sign.

Note 3: Let us invoke the **minimum entropy production principle**:

$$\frac{d}{dt}\dot{S}_{int} < 0$$

typically expected to hold for dissipative motions. Then $d\dot{F}/dt > 0$ for a negative-definite function $\dot{F}$, or $d(\dot{F} - \dot{W})/dt > 0$ for a negative definite $\dot{F} - \dot{W}$.

Note 4: In the quantum motion the sign of $d\dot{S}_{int}/dt$ is undefined in:

$$\frac{d}{dt}\dot{F} = -T_0 \frac{d}{dt}\dot{S}_{int}$$

Remembering that $T_0\dot{S}_{int} = m\beta_0\langle v^2\rangle$ and recalling the respective forms of $\mathcal{H}_{quantum}$ and $\mathcal{H}_{diffusion}$, we have:

quantum case

$$\frac{d}{dt}\dot{F} = +\,\beta_0 \frac{d}{dt}(m\langle u^2\rangle + 2\langle \mathcal{V}\rangle)$$

diffusion

$$\frac{d}{dt}\dot{F} = -\,\beta_0 \frac{d}{dt}(m\langle u^2\rangle + 2\langle \mathcal{V}\rangle$$

Case 1: *Free evolution*

$$\rho(x,t) = \frac{\alpha}{[\pi(\alpha^4+4D^2t^2)]^{1/2}} \exp\left(-\frac{x^2\alpha^2}{\alpha^4+4D^2t^2}\right)$$

$$s(x,t) = \frac{2D^2x^2t}{\alpha^4+4D^2t^2} - D^2 \arctan\left(-\frac{2Dt}{\alpha^2}\right)$$

$$D(\dot{\mathcal{S}})_{int} = \langle v^2 \rangle = \frac{8D^4t^2}{\alpha^2(\alpha^4+4D^2t^2)}$$

$$\mathcal{E} = \frac{1}{2}(\langle v^2\rangle + \langle u^2\rangle) = \frac{D^2}{\alpha^2}\,,$$

The entropy production attains its maximum and $\dot{F}$ decreases towards its minimal value $\dot{F}^{min} = m\beta_0\mathcal{E} - T_0\dot{S}_{int}^{max}$.

Case 2: *Steady state in a harmonic potential* $\mathcal{V} = \frac{1}{2}\omega^2 x$

$$\rho(x,t) = \left(\frac{\omega}{2\pi D}\right)^{1/2} \exp\left[-\frac{\omega}{2D}\,(x-q(t))^2\right]$$

$$s(x,t) = (1/m)\,[xp(t) - (1/2)p(t)q(t) - mD\omega t]\,,$$

$q(t) = q_0\cos(\omega t) + (p_0/m\omega)\sin(\omega t)$ and $p(t) = p_0\cos(\omega t) - m\omega q_0\sin(\omega t)$. $v = \nabla s = p(t)/m$

$$D(\dot{\mathcal{S}})_{in} = \frac{p^2(t)}{m^2}$$

so that in view of $E/m = \mathcal{E} = p_0^2/2m^2 + \omega x_0^2/2 + D\omega$ and $D = k_BT/m\beta_0 = \hbar/2m$, we get

$$\dot{F} = \omega k_BT_0 + m\beta_0[\frac{p_0^2}{2m^2} + \omega\frac{x_0^2}{2} - \frac{p^2(t)}{m^2}] = \omega k_BT_0 + \beta_0[m\omega\frac{x^2(t)}{2} - \frac{p^2(t)}{2m}]\,.$$

Case 3: *Stationary state*

We take a harmonic oscillator ground state as a reference. The entropy production vanishes, since $v = 0$. Then, we have $\dot{F} = m\beta_0\mathcal{E}_0 = \beta_0E_0$, where $E_0 = \hbar\omega/2 = mD\omega$. Therefore

$$F(t) = (k_BT_0)\omega t + const$$

Because of $-m\beta_0\langle s\rangle = F$ and $\langle s\rangle = s$, we have

$$s(t) = -D\omega t + const\,,$$

as should be the case in the exponent of the stationary wave function $\psi = \rho^{1/2}\exp(is/2D)$. Indeed, $-E_0t/2D = -\omega t/2 = s(t)/2D - const$.

OUTLOOK

(i) The major observation of the paper is that the **Helmholtz F-theorem**, while enhanced by the external work term, appears to be more universal than expected. **An unambiguous meaning can be given to the two laws of thermodynamics** far beyond their (equilibrium thermodynamics) domain of origin.

(ii) What seems to be worth further investigation is a physically deeper insight into the functioning of the **work term** $\dot{W}$, here identified with the time rate of **"work performed** *upon* the system", or alternatively - if negative - that of **"work performed** *by* the system".

(iii) The notion of the **physically active "environment"** or "surrounding" seems to be not implicit, but necessary for a consistency of the formalism.

Notice that there is a profound difference between the dissipative and quantum motion scenarios which can be seen in the asymptotic behavior of principal quantities. The F-theorem for standard diffusion processes gives account of the possible convergence of a probability density to the stationary (equilibrium) one. In the quantum setting it is the temporal behavior of the mean value of the quantum phase that carries a signature of (whatever) "quantum equilibrium". This equilibrium notion has no affinity with the quantum probability density asymptotic.

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