ENTROPY AND TIME: THERMODYNAMICS OF DIFFUSION PROCESSES*

Piotr Garbaczewski

Institute of Physics, University of Opole
Oleska 48, 45-052 Opole, Poland
`pgar@uni.opole.pl`

We give meaning to the first and second laws of thermodynamics in case of mesoscopic out-of-equilibrium systems which are driven by diffusion-type, specifically Smoluchowski, processes. The notion of entropy production is analyzed. The role of the Helmholtz extremum principle is contrasted to that of the more familiar entropy extremum principles.

PACS numbers: 02.50.Ey, 05.20.–y, 05.40.Jc

1. Introduction

We aim at a consistent thermodynamic description of diffusion-type processes which model the dynamics of non-equilibrium systems at the mesoscopic scale, [1–5]. It is known that given the equilibrium properties of a mesoscopic (molecular) system, it is possible to deduce a stochastic nonequilibrium, albeit near-equilibrium, dynamics in terms of Fokker–Planck equations and their probability density solutions, [1].

We basically go in reverse and abandon any prescribed concept of local or global equilibrium and ask for these thermodynamic properties that give account of a convergence (if any, this property is not automatically granted) towards an equilibrium state, even if initially a system is arbitrarily far from equilibrium, [11–13]. Our focus is on a quantitative description of energy (heat, work, entropy and entropy production) transfer time rates in the mean, between a particle and its thermal environment.

We explore the extremum principles which are responsible for the large time asymptotic of the process, [6]. Thermodynamic function(al)s, like *e.g.* an internal energy, Helmholtz free energy and Gibbs–Shannon entropy are

---

inferred, through suitable averaging, from the time-dependent continuous probability densities, [1, 8–10] and [11–14]. Assuming appropriate (natural) boundary data we demonstrate that generically the corresponding extremum principle amounts to minimizing the Helmholtz free energy of random motion, see also [3].

The following hierarchy of thermodynamical systems is adopted: *isolated* with no energy and matter exchange with the environment, *closed* with the energy but *no* matter exchange and *open* where energy-matter exchange is unrestricted. With the standard text-book wisdom in mind that all isolated systems evolve to the state of equilibrium in which the entropy reaches its maximal value, we focus our further attention on *closed* random systems and their somewhat different asymptotic features.

A concise resume of a non-equilibrium thermodynamics of *closed* systems comprises the basic conservation laws for the time rates of internal energy, heat, work and entropy exchange. The energy conservation implies the I$^{\text{st}}$ law of thermodynamics: an internal energy U changes by dU in time dt, according to

$$dU = \delta Q + \delta W \,, \tag{1}$$

where we distinguish the imperfect differentials by δ. Normally (which will *not* necessarily be the case in our further discussion) one interprets dU as an increase in internal energy of the system due to absorbed heat $\delta Q > 0$ and work $\delta W < 0$ performed by the system upon its environment.

The II$^{\text{nd}}$ law correlates the time rates of entropy, entropy production and heat exchange between the system and its environment:

$$\dot{S} = (\dot{S})_{\text{int}} + (\dot{S})_{\text{ext}} \,. \tag{2}$$

The entropy time rate of change is here manifestly decomposed into two contributions: $(\dot{S})_{\text{int}}$ is induced by irreversible processes that are intrinsic to the system, while $(\dot{S})_{\text{ext}}$ refers to an energy exchange between the system and its environment.

Since $(\dot{S})_{\text{int}} \geq 0$, this *entropy production* term is interpreted as the major signature of the II$^{\text{nd}}$ law, quite apart form its specific verbal formulation. The remaining $(\dot{S})_{\text{ext}}$ term is related to the heat exchange via $(\dot{S})_{\text{ext}} dt = \delta Q/T$, where T is the temperature, [6, 7].

We emphasize that neither heat nor work can be interpreted as legitimate thermodynamic functions. Moreover, the very notion of entropy, sometimes viewed as a fundamental thermodynamic quantity, appears to be a secondary — derived notion. In the forthcoming statistical description, this issue will become straightforward, once we shall relate probabilities and statistics of random events to the (information) entropy notion.

At this point there is no mention of stationary or steady states, nor any restriction upon the speed of involved, basically irreversible dynamical

process. For the record, we indicate that in case of a reversible process we would have $(\dot{S})_\text{int} = 0$ so that an overall entropy change would arise solely due to the flow of heat.

Thermodynamical extremum principles are usually invoked in connection with the large time behavior of irreversible processes. One looks for direct realizations of the entropy growth paradigm, undoubtedly valid for isolated systems, [14], compare *e.g.* also a collection of various entropy optimization strategies in Ref. [17].

Among a number of admissible thermodynamic extremum principles, just for reference in the present context, we single out a specific one. If the temperature T and the available volume V are kept constant, then the minimum of the Helmholtz free energy $F = U - TS$ is preferred in the course of the system evolution in time, and there holds $\dot{F} = -T(\dot{S})_\text{int} \leq 0$.

2. Randomness *vs* uncertainty: Boltzmann and Gibbs–Shannon entropies

We know that a result of an observation of any random phenomenon cannot be predicted a priori (*i.e.* before an observation), hence it is natural to quantify an uncertainty of this phenomenon. Let us consider $\mu = (\mu_1, \ldots, \mu_N)$ as a probability measure on N distinct (discrete) events $A_j, 1 \leq j \leq N$ pertaining to a model system. Assume that $\sum_{j=1}^{N} \mu_j = 1$ and $\mu_j = \text{prob}(A_j)$ stands for a probability for an event A_j to occur in the game of chance with N possible outcomes.

The expression, whose functional (logarithmic term) provenance may be traced back to the thermodynamical notion of Gibbs entropy,

$$S(\mu) = -\sum_{j=1}^{N} \mu_j \ln \mu_j \qquad (3)$$

stands for the measure of the *mean uncertainty* of the possible outcome of the game of chance and at the same time quantifies the *mean information* which is accessible from an experiment (*i.e.* actually playing the game).

If we identify random event values $A_1, \ldots, A_N$ with labels for particular discrete "states" of the system, we may interpret Eq. (3) as a measure of uncertainty of the "state" of the system, *before* this particular "state" it is chosen out of the set of all admissible ones. This well conforms with the standard meaning attributed to the Shannon information entropy: it is a measure of the degree of ignorance concerning which possibility (event A_j) may hold true in the set $\{A_1, A_2, \ldots, A_N\}$ with a given a priori probability distribution $\{\mu_1, \ldots, \mu_N\}$.

Notice that:

$$0 \leq \mathcal{S}(\mu) \leq \ln N \qquad (4)$$

ranges from certainty (one entry whose probability equals 1 and thus no information is missing) to maximum uncertainty when a uniform distribution $\mu_j = 1/N$ for all $1 \leq j \leq N$ occurs. In the latter situation, all events (or measurement outcomes) are equiprobable and $\log N$ sets maximum for a measure of the "missing information".

By looking at all intermediate levels of randomness allowed by the inequalities Eq. (3) we realize that the lower is the Shannon entropy the less information about "states" of the system we are missing, *i.e.* we have more information about the system. If the Shannon entropy increases, we actually loose an information available about the system. Consequently, the difference between two uncertainty measures can be interpreted as an information gain or loss.

Anticipating various thermodynamic connotations (*cf.* Boltzmann and Gibbs entropy notions) we must be careful while introducing (potentially obvious) notions of events, states, microstates and macrostates of a physical (or biological) system, *cf.* [13]. The celebrated Boltzmann formula

$$\mathcal{S} = k_{\mathrm{B}} \ln W \doteq -k_{\mathrm{B}} \ln P \qquad (5)$$

sets a link of entropy of the (thermodynamical) system with the probability $P = 1/W$ that an appropriate "statistical microstate" can occur. Here, W stands for a number of all possible (equiprobable) microstates that imply the prescribed macroscopic (*e.g.* thermodynamical) behavior corresponding to a *fixed* value of $\mathcal{S}$.

It is instructive to recall that if P is a probability of an event *i.e.* of a particular microstate, then $-\ln P$ (actually, with $\log_2$ instead of $\ln$) may be interpreted as "a measure of information produced when one message is chosen from the set, all choices being equally likely" ("message" to be identified with a "microstate"). Another interpretation of $-\ln P$ is that of a degree of uncertainty in the trial experiment.

Remark 1: As a pedestrian illustration let us invoke a classic example of a molecular gas in a box which is divided into two halves denoted "1" and "2". We allow the molecules to be in one of two elementary *states: A_1* if a molecule can be found in "1" half-box and A_2 if it placed in another half "2". Let us consider a particular n-th *macrostate* of a molecular gas comprising a total of G molecules in a box, with n molecules in the state A_1 and $G - n$ molecules in the state A_2. The total number of ways in which G molecules can be distributed between two halves of the box in this prescribed macrostate, *i.e.* the number $W = W(n)$ of distinct equiprobable *microstates,* clearly is $W(n) = G!/[n!(G - n)!]$. Here, $P(n) = 1/W(n)$ is a

probability with which any of microstates may occur in a system bound to "live" in a given macrostate. The maximum of $W(n)$ and thus of $k_B \ln W(n)$ corresponds to $N_1 = N_2 = n$, see *e.g.* at the "dog-flea" model discussion [16].

To get a better insight into the information-uncertainty intertwine, let us consider an ensemble of finite systems which are allowed to appear in any of $N > 0$ distinct elementary states. The meaning of "state" is left unspecified, although an "alphabet" letter may be invoked for convenience.

Let us pick up randomly a large sample composed of $G \gg 1$ single systems, each one in a certain (randomly assigned) state. We record frequencies $n_1/G \doteq p_1, \ldots, n_N/G \doteq p_N$ with which the elementary states of the type $1, \ldots, N$ do actually occur. This sample is a substitute for a "message" or a "statistical microstate" in the previous discussion.

Next, we identify the number of *all* possible samples of that fixed size G which would show up the very same statistics $p_1, \ldots, p_N$ of elementary states. We interpret those samples to display the same "macroscopic behavior".

It was the major discovery due to Shannon that the number W of relevant "microscopic states" can be approximately read out from each single sample and is directly related to the introduced a priori probability measure $\mu_1, \ldots, \mu_N$, with an identification $p_i \doteq \mu_i$ for all $1 \leq i \leq N$, by the Shannon formula:

$$\ln W \simeq -G \sum_{i=1}^{N} p_i \ln p_i \doteq -G \, \mathcal{S}(\mu) \,. \tag{6}$$

On the basis of this formula, we can consistently introduce $\mathcal{S}(\mu)$ as the *mean information* per each (i-th) elementary state of the N-state system, as encoded in a given sample whose size $G \gg 1$ is sufficiently large.

By pursuing the Shannon's communication theory track, [13], we can identify states of the model system with "messages" (strings) of an arbitrary length $G > 0$ which are entirely composed by means of the prescribed N "alphabet" entries (*e.g.* events or alphabet letters A_j with the previous probability measure μ). Then, Eq. (6) may be interpreted as a measure of *information* per alphabet letter, obtained *after* a particular message (string $\equiv$ state of the model system) has been received or measured, *cf.* our discussion preceding Eq. (6).

In this case, the Gibbs–Shannon entropy (by historical reasons we rename Shannon's $\mathcal{S}(\mu)$ the Gibbs–Shannon) interpolates between a maximal information (one certain event) and a minimal information (uniform distribution), *cf.* Eq. (4). The above discussion may serve as a useful introduction to an issue of the Shannon information workings in genomes and DNA sequences, [18].

Till now, we have considered discrete probability distributions and their uncertainty/delocalization measures (Gibbs–Shannon entropy). The main objective of the present paper is a discussion of the temporal behavior of Gibbs–Shannon entropy of a continuous probability distribution.

We shall focus on continuous probability distributions on R. The corresponding Gibbs–Shannon entropy is introduced as follows:

$$\int \rho(s)\, ds = 1 \rightarrow \mathcal{S}(\rho) = -\int \rho(s) \ln \rho(s) ds\,. \tag{7}$$

At this point it is instructive to mention that in the realistic (data analysis) framework, one encounters discrete probability data that are inferred from frequency statistics, encoded in various histograms. Definitely, there are *no* continuous probability densities at work. They typically appear as computationally useful continuous approximations of discrete probability measures.

The situation becomes involved in the case of the corresponding Gibbs–Shannon entropies, where the approximation issue is delicate. Even if one follows a pedestrian reasoning, we can firmly justify and keep under control the limiting behavior, [11, 19]:

$$\sum_1^N \mu_j = 1 \rightarrow \int \rho ds = 1\,. \tag{8}$$

An immediate question is: what can be said about the mutual relationship of $S(\mu) = -\sum_1^N \mu_j \ln \mu_j$ and $S(\rho) = -\int \rho(s) \ln \rho(s) ds$?

We first observe that $0 \leq -\sum_1^N \mu_j \ln \mu_j \leq \ln N$ and consider an interval of length L on a line with the a priori chosen partition unit $\Delta s = L/N$. Next, we define: $\mu_j \doteq p_j \Delta s$ and notice that (formally, we bypass an issue of dimensional quantities)

$$S(\mu) = -\sum_j (\Delta s) p_j \ln p_j - \ln(\Delta s)\,. \tag{9}$$

Let us fix L and allow N to grow, so that Δs decreases and the partition becomes finer. Then

$$\ln(\Delta s) \; \leq \; -\sum_j (\Delta s) p_j \ln p_j \; \leq \; \ln L\,, \tag{10}$$

where

$$S(\mu) + \ln(\Delta s) = -\sum_j (\Delta s) p_j \ln p_j \Rightarrow S(\rho) = -\int \rho(s) \ln \rho(s) ds\,. \tag{11}$$

$S(\rho)$ is the Shannon information entropy for the probability measure on the interval L. In the infinite volume $L \to \infty$ and infinitesimal grating $\Delta s \to 0$ limits, the density functional $S(\rho)$ may be unbounded both from below and above, even non-existent, and seems to have lost any computationally useful link with its coarse-grained version $S(\mu)$.

However, the situation is not that bad, if we invoke standard methods [11, 19] to overcome a dimensional difficulty, inherent in the very definition of $S(\rho)$, while admitting dimensional units. Namely, we can from the start take a (sufficiently small) partition unit Δs to have dimensions of length. We allow s to carry length dimension as well. Then, the dimensionless expression for the Shannon entropy of a continuous probability distribution reads:

$$S_\Delta(\rho) = - \int \rho(s) \ln[\Delta s \, \rho(s)] ds \tag{12}$$

and all of a sudden, a comparison of $S(\rho)$ and its coarse-grained version $S(\mu))$ appears to make sense. We can legitimately set estimates for $|S(\mu) - S_\Delta(\rho)|$ and directly verify the approximation validity of $S(\mu)$ for a discrete probability distribution, in terms of the entropy $S_\Delta(\rho)$ for a Δs-rescaled continuous probability distribution, when the partition becomes finer.

Remark 2: The value of $\mathcal{S}(\rho_\alpha)$ is α-independent if we consider $\rho_\alpha(x) = \rho(x - \alpha)$. This reflects the translational invariance of the Shannon information measure. Let us furthermore investigate an effect of the scaling transformation. We denote $\rho_{\alpha,\beta} = \beta \, \rho[\beta(x - \alpha)]$, where $\alpha > 0, \beta > 0$. The respective Shannon entropy reads: $\mathcal{S}(\rho_{\alpha,\beta}) = \mathcal{S}(\rho) - \ln\beta$. An adjustment $\beta \equiv \Delta s$ sets an obvious link with our previous discussion.

Remark 3: In the present paper we are interested in properties of various continuous probability distributions, and *not* their coarse-grained versions. Therefore our further discussion will be devoid of any dimensional or partition unit connotations. Since negative values of the Shannon entropy are now admitted, instead of calling it an information measure, we prefer to tell about a "probability localization measure", "measure of surprise" or "measure of information deficit".

3. Helmholtz free energy and its extremum

Consider an equilibrium state in statistical mechanics, with β as an inverse temperature. As the i-th microstate we take an energy (level) E_i, $i \in I$, with a statistical (Boltzmann) weight $\exp(-\beta E_i)$. The macrostate is introduced as follows: choose a sample $E \doteq \{E_{i_1}, E_{i_2}, \ldots, E_{i_n}, \ldots\}$ and define the associated

$$F(\beta) = -\frac{1}{\beta} \ln Z(\beta) \tag{13}$$

with a statistical sum (partition function) Z

$$Z(\beta) = \sum_E \exp(-\beta E_i)\,. \tag{14}$$

An internal energy reads

$$U = -\frac{\partial}{\partial \beta} \ln Z(\beta) = \langle E \rangle \doteq \sum_i E_i \exp(-\beta E_i) \tag{15}$$

while an entropy notion S with $T = 1/\beta$ appears through

$$U - F \doteq TS\,. \tag{16}$$

The "maximum entropy principle" may be replaced by (or at least — rewritten as) the "principle of minimum free energy". Indeed, let p_i be a probability of occurrence of a microstate E_i in the macrostate configuration E, $\sum p_i = 1$. A minimum of

$$F = U - \beta^{-1}S = F[p] = \sum_i \left(p_i E_i + \frac{1}{\beta} p_i \ln p_i \right) \tag{17}$$

is achieved for a canonical distribution:

$$p_i = \frac{1}{Z} \exp(-\beta E_i)\,. \tag{18}$$

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:

$$\Phi[p] = -\sum p_i \ln p_i - \alpha \sum p_i - \beta \sum E_i p_i\,, \tag{19}$$

where α and β are the Lagrange multipliers. We have (p_i^* denotes an equilibrium probability, *e.g.* an ultimate solution)

$$\delta \Phi[p] = 0 = [-\ln p_i^* - 1 - \alpha - \beta E_i]\delta p_i \tag{20}$$

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

$$\alpha + 1 = S_* - \beta U_* \tag{21}$$

$$\Downarrow$$

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

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

S_* is the Shannon entropy of this discrete probability measure. In view of $F = U - \beta^{-1}S$, the Shannon entropy actually 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:

$$K(p, q) \doteq \sum p_i \ln\left(\frac{p_i}{q_i}\right) \tag{22}$$

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):

$$K(p, p_*) = -S - \sum p_i[-S_* + \beta U_* - \beta E_i] = \beta(F - F_*) \geq 0 \tag{23}$$

as anticipated before.

In the case of discrete probability distributions, in view of Eq. (16), a minimum of F is achieved in conjunction with a maximum for S. Below, we shall demonstrate that such property is not a generic feature when continuous probability distributions come into consideration.

4. Thermodynamics of random phase-space motion

Now we pass to a detailed investigation of time-dependent continuous probability distributions and the large time behavior of their entropies. Let us begin from a concise resumé of the (non-equilibrium) thermodynamics of *closed* but non-isolated systems. The laws of thermodynamics may be reproduced in the form [7]: $dU = \delta Q + \delta W$ and $dS = d_{\text{int}}S + d_{\text{ext}}S$, where $d_{\text{int}}S \geq 0$ and $d_{\text{ext}}S = \delta Q/T$.

With respect to the large time behavior, the following extremum principles for irreversible processes are typically invoked:

1. U and V (volume) constant $\rightarrow$ maximum of entropy is preferred: $d_{\text{int}}S = TdS - \delta Q \geq 0$, together with a minimum for the entropy production: $\frac{d}{dt}\left(\frac{d_{\text{int}}S}{dt}\right) < 0$,

2. S and V constant $\to$ minimum internal energy is preferred: $dU = -Td_{\mathrm{int}}S \leq 0$,

3. T and V constant $\to$ minimum of $F = U - TS$ (Helmholtz free energy) is preferred: $dF = -Td_{\mathrm{int}}S \leq 0$.

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

The Helmholtz extremum principle will be of utmost importance in our further discussion, as opposed to more traditional min/max entropy principles.

We are interested not only in the existence of an extremal probability density, but also at an approach of $\rho(x,t)$ towards such a stationary density in the course of time. Then the varied time dependent properties of the Helmholtz free energy, Gibbs–Shannon and Kullback–Leibler entropies will be of interest.

Let us consider a phase-space diffusion process governed by the Langevin equation:

$$m\ddot{x} + m\gamma\dot{x} = -\nabla V(x,t) + \xi(t) \tag{24}$$

with standard assumptions about properties of the white noise: $\langle \xi(t) \rangle = 0$, $\langle \xi(t)\xi(t') \rangle = \sqrt{2m\gamma k_{\mathrm{B}}T}\,\delta(t - t')$. Accordingly, the pertinent phase-space density $f = f(x, u, t)$ is a solution of the Fokker–Planck–Kramers equation with suitable initial data:

$$\frac{\partial}{\partial t}f(x,u,t) = \left[-\frac{\partial}{\partial x}u + \frac{\partial}{\partial u}\left(\gamma u + \frac{1}{m}\nabla V(x,t) \right) + \frac{\gamma k_{\mathrm{B}}T}{m}\frac{\partial^2}{\partial u^2} \right]f. \tag{25}$$

Let us define the Gibbs–Shannon entropy $\mathcal{S} = \mathcal{S}(t)$ of a continuous probability distribution :

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

(By dimensional reasons we should insert a factor h with physical dimensions of the action under the logarithm, *i.e.* use $\ln(hf)$ instead of $\ln f$, but since we shall ultimately work with time derivatives, this step may be safely skipped.)

An internal energy U of the stochastic process reads

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

and the I$^{\mathrm{st}}$ law takes the form

$$T(\dot{\mathcal{S}})_{\mathrm{ext}} + \langle \partial_t V \rangle = \dot{U}\,, \tag{26}$$

where $\langle \partial_t V \rangle$, if positive, is interpreted as the time rate of work externally performed *upon* the system. If negative, then we would deal with work performed *by* the system.

Furthermore, let us introduce an obvious analog of the Helmholtz free energy:

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

so that

$$\dot{F} - \langle \partial_t V \rangle = T(\dot{S})_{\text{ext}} - T\dot{S} = -T(\dot{S})_{\text{int}} \leq 0 \,. \tag{27}$$

The above result is a direct consequence of the Kramers equation. Under suitable assumptions concerning the proper behavior of $f(x, u, t)$ at x, u integration boundaries (sufficiently rapid decay at infinities) we have [4]

$$T(\dot{S})_{\text{ext}} = \gamma \left(k_B T - \langle mu^2 \rangle \right) \,,$$

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

and thence, the IInd law

$$-\frac{\gamma}{m} \left\langle \left(k_B T \frac{\partial \ln f}{\partial u} + mu \right)^2 \right\rangle = -T(\dot{S})_{\text{int}} \leq 0 \,. \tag{28}$$

As a byproduct of the discussion we have $\dot{F} \leq \langle \partial_t V \rangle$. For time-independent $V = V(x)$ we deal with the standard F-theorem (the extremum principle pertains to the Helmholtz free energy F which is minimized in the course of random motion).

The above discussion encompasses both the forced and unforced (free) Brownian motion. When $V(x) \equiv 0$, then no asymptotic state of equilibrium (represented by a probability density) is accessible, the motion is sweeping. In the forced case, we assume a priori an existence of a unique stationary state, *cf.* [14, 15], for the above phase-space random dynamics:

$$f_*(x, u) = \frac{1}{Z} \exp \left[-\frac{E(x, u)}{k_B T} \right] \,.$$

In this case, the time rate of the conditional Kullback–Leibler entropy:

$$\mathcal{H}_c(f_t | f_*) = -\int f \ln \frac{f}{f_*} dx du$$

$$= \mathcal{S}(t) - \ln Z - \frac{\langle E(x, u) \rangle}{k_B T} \tag{29}$$

directly appears in the F-theorem:

$$k_{\mathrm{B}}T\dot{\mathcal{H}}_c = -\dot{F} = +T(\dot{S})_{\mathrm{int}} \geq 0\,. \tag{30}$$

The (negative definite) conditional entropy grows monotonically towards its maximum at 0. Notice that $(\dot{S})_{\mathrm{int}} \geq 0$, but neither $\langle\partial_t V\rangle$ nor $\dot{S}$ need to be positive and may show quite complicated patterns of temporal behavior, [14,15] and [11,12]. (Both f_* and $\mathcal{H}_c$ are non-existent in case of free Brownian motion.)

Let us point out that the above discussion is sufficiently general to include a number of currently fashionable problems, like *e.g.* that of molecular motors. To see an obvious link it suffices to mention a typical "Brownian motor input" *i.e.* an explicit functional form of the time-dependent driving component of the exerted force and its conservative term in Eq. (24), *cf.* [20]. As an example we may consider:

$$m\ddot{x} + m\gamma\dot{x} = -\nabla V(x,t) + a\cos(\Omega t) + F + \xi(t)\,, \tag{31}$$

where F is a constant external force, and the spatially periodic rachet (broken reflection symmetry) potential $V(x)$ is adopted. An example of the ratchet potential is: $V(x) = V_0[\sin(2\pi x) + c_1\sin(4\pi x) + c_2\sin(6\pi x)]$.

5. Thermodynamics of the Smoluchowski process

Analogous thermodynamical features are encountered in spatial random motions, like *e.g.* standard Smoluchowski processes and their generalizations. Let us consider

$$\dot{x} = b(x,t) + A(t) \tag{32}$$

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

Given an initial probability density $\rho_0(x)$. We know that the diffusion process drives this density in accordance with the Fokker–Planck equation

$$\partial_t\rho = D\triangle\rho - \nabla(b\rho)\,. \tag{33}$$

We introduce $u = D\ln\rho$ and $v = b - u$ which obeys $\partial_t\rho = -\nabla(\rho v)$.
The Gibbs–Shannon entropy of ρ

$$\mathcal{S}(t) = -\langle\ln\rho\rangle \tag{34}$$

typically is not a conserved quantity. We impose boundary restrictions that $\rho, v\rho, b\rho$ vanish at spatial infinities or other integration interval borders. We consider:

$$D\dot{\mathcal{S}} = \langle v^2\rangle - \langle b\,v\rangle\,. \tag{35}$$

We may pass to time-independent drift fields and set $b = \frac{f}{m\gamma}$, $j \doteq v\rho$, $f = -\nabla V$ plus $D = k_{\mathrm{B}}T/m\gamma$. Then:

$$\dot{\mathcal{S}} = (\dot{\mathcal{S}})_{\mathrm{int}} + (\dot{\mathcal{S}})_{\mathrm{ext}}\,, \tag{36}$$

where

$$k_{\mathrm{B}}T(\dot{\mathcal{S}})_{\mathrm{int}} \doteq m\gamma \left\langle v^2 \right\rangle \geq 0 \tag{37}$$

stands for the entropy production rate, while

$$k_{\mathrm{B}}T(\dot{\mathcal{S}})_{\mathrm{ext}} = -\int f\, j\, dx = -m\gamma \left\langle b\, v \right\rangle \tag{38}$$

(as long as negative which is not a must) may be interpreted as the heat dissipation rate:$-\int f\, j\, dx$.

In view of $j = \rho v = \frac{\rho}{m\gamma}[f - k_{\mathrm{B}}T\nabla \ln \rho] \doteq -\frac{\rho}{m\gamma}\nabla \Psi$ *i.e.* $v = -(1/m\gamma)\nabla \Psi$ and $f = -\nabla V$, we can introduce

$$\Psi = V + k_{\mathrm{B}}T \ln \rho \tag{39}$$

whose mean value stands for the Helmholtz free energy of the random motion

$$F \doteq \left\langle \Psi \right\rangle = U - TS\,. \tag{40}$$

Here $S \doteq k_{\mathrm{B}}\mathcal{S}$ and an internal energy is $U = \left\langle V \right\rangle$. Since we assume ρ and $\rho V v$ to vanish at the integration volume boundaries, we get

$$\dot{F} = -(m\gamma)\left\langle v^2 \right\rangle = -k_{\mathrm{B}}T(\dot{\mathcal{S}})_{\mathrm{int}} \leq 0\,. \tag{41}$$

Clearly, F decreases as a function of time towards its minimum, or remains constant.

Let us consider the stationary regime $\dot{\mathcal{S}} = 0$ associated with an (a priori assumed to exist, [14]) invariant density ρ_*. Then,

$$b = u = D\nabla \ln \rho_*$$

and

$$-\left(\frac{1}{k_{\mathrm{B}}T}\right)\nabla V = \nabla \ln \rho_* \implies \rho_* = \frac{1}{Z}\exp\left[-\frac{V}{k_{\mathrm{B}}T}\right]\,. \tag{42}$$

Hence

$$\Psi_* = V + k_{\mathrm{B}}T \ln \rho_* \implies \left\langle \Psi_* \right\rangle = -k_{\mathrm{B}}T \ln Z \doteq F_* \tag{43}$$

with $Z = \int \exp(-V/k_{\mathrm{B}}T)dx$. F_* stands for a minimum of the time-dependent Helmholtz free energy F. Because of

$$Z = \exp\left(-\frac{F_*}{k_{\mathrm{B}}T}\right) \tag{44}$$

we have

$$\rho_* = \exp\left[\frac{(F_* - V)}{k_{\mathrm B}T}\right] . \tag{45}$$

Therefore, the conditional Kullback–Leibler entropy, of the density ρ relative to an equilibrium density ρ_* acquires the form

$$k_{\mathrm B}T\mathcal{H}_c \doteq -k_{\mathrm B}T \int \rho \ln\left(\frac{\rho}{\rho_*}\right) dx = F_* - F . \tag{46}$$

In view of the concavity property of the function $f(w) = -w \ln w$, $\mathcal{H}_c$ takes only negative values, with a maximum at 0. We have $F_* \leq F$ and $k_{\mathrm B}T\dot{\mathcal{H}}_c = -\dot{F} \geq 0$. $\mathcal{H}_c$ is bound to grow monotonically towards 0, while F drops down to its minimum F_* which is reached for ρ_*. The Helmholtz free energy minimum, in the present context (and in contrast to the previously described case of discrete probability measures), remains divorced from any extremal property of the Gibbs–Shannon entropy. Only the Kullback–Leibler entropy shows up an expected asymptotic behavior. See *e.g.* also [14, 15].

6. Outlook

Standard (thermodynamical) notions of entropy are basically introduced under equilibrium conditions and are not considered in the time domain. Our discussion was tailored specifically to non-equilibrium systems and processes. Any conceivable idea of approaching the state of equilibrium, or passing from one such state to another (steady) state, always involves the time dependence and the related, often rapid, non-equilibrium dynamical process.

The major tool invoked in connection with both equilibrium and non-equilibrium phenomena is that of Gibbs–Shannon entropy whose definition directly involves time-dependent probability distributions. However, let us recall that except for the thermodynamical Clausius case, the very notion of entropy is non-universal and purpose-dependent, [12]. Our entropy choice has served a concrete purpose: encompassing a temporal behavior of specific probability distributions associated with diffusion-type processes.

The sole entropy methods are neither exclusive nor sufficient to give full account of the asymptotic properties of diffusion processes. Additional inputs pertaining the regularity properties of solutions of Fokker–Planck equations are necessary to guarantee an existence of a stationary solution and to demonstrate that any other solution of the pertinent equation must finally decay to the stationary one in the large time asymptotic.

For standard diffusion-type processes, we have discussed, the standard min/max entropy principles do not literally work, [17]. It is the Helmholtz free energy which shares proper extremal behavior. On the other hand it is

the conditional Kullback–Leibler entropy which (together with its time rate) stays in close affinity with the Helmholtz free energy of the diffusion process and with the involved entropy production.

The advantage of our methodology is an explicit insight into the temporal behavior of various thermodynamics functionals whose definition is normally restricted to equilibrium(or near-equilibrium) phenomena. The conceptual meaning of the Helmholtz free energy, or Gibbs–Shannon entropy is consistently elevated to the time-domain, for far from equilibrium systems. The auxiliary notions of work and heat transfer rates have received a transparent interpretation as well.

REFERENCES

[1] D. Reguera, J.M. Rubi, J.M.G. Vilar, *J. Phys. Chem.* **B109**, 21502 (2005).

[2] J.M.G. Vilar, J.M. Rubi, *Proc. Nat. Acad. Sci. (NY)*, **98**, 11081 (2001).

[3] H. Hasegawa, *Progr. Theor. Phys.* **57**, 1523 (1977).

[4] K. Shizume, *Phys. Rev.* **E52**, 3495 (1995).

[5] T. Munakata, A. Igarashi, T. Shiotani, *Phys. Rev.* **E57**, 1403 (1998).

[6] P. Glansdorf, I. Prigogine, *Thermodynamic Theory of Structure, Stability and Fluctuations*, Wiley, NY 1971.

[7] D. Kondepudi, I. Prigogine, *Modern Thermodynamics*, Wiley, NY 1998.

[8] H. Qian, *Phys. Rev.* **E65**, 016102 (2002).

[9] T. Hatano, S.I. Sasa, *Phys. Rev. Lett.* **86**, 3463 (2001).

[10] U. Seifert, *Phys. Rev. Lett.* **95**, 040602 (2005).

[11] P. Garbaczewski, *Phys. Lett.* **A 341**, 33 (2005).

[12] P. Garbaczewski, *J. Stat. Phys.* **123**, 315 (2006).

[13] P. Garbaczewski, *Entropy* **7**, 253 (2005).

[14] M.C. Mackey, M. Tyran-Kamińska, *Physica A* **365**, 360 (2006).

[15] M.C. Mackey, M. Tyran-Kamińska, *J. Stat. Phys.* **124**, 1443 (2006).

[16] V. Ambegaokar, A.A. Clerk, *Am. J. Phys.* **67**, 1068 (1999).

[17] J.N. Kapur, H.K. Kesavan, *Entropy Optimization Principles with Applications*, Academic Press, Boston 1992.

[18] H.D. Chen *et al.*, *Phys. Rev. Lett.* **94**, 178103 (2005).

[19] T.M. Cover, J.A. Thomas, *Elements of Information Theory*, Wiley, NY 1991.

[20] L. Machura *et al.*, *Phys. Rev. Lett.* **98**, 040601 (2007).