Free energy for non-equilibrium quasi-stationary states

A. E. Allahverdyan and N. H. Martirosyan

Yerevan Physics Institute - Alikhanian Brothers Street 2, Yerevan 375036, Armenia

received 10 November 2016; accepted in final form 7 April 2017
published online 3 May 2017

PACS 05.70.Ln -- Nonequilibrium and irreversible thermodynamics
PACS 05.10.Gg -- Stochastic analysis models (Fokker-Planck, Langevin, etc.)
PACS 05.20.-y -- Classical statistical mechanics

Abstract -- We study a class of non-equilibrium quasi-stationary states for a Markov system interacting with two different thermal baths. We show that the work done under a slow, external change of parameters admits a potential, i.e., the free energy. Three conditions are needed for the existence of free energy in this non-equilibrium system: time-scale separation between variables of the system, partial controllability (external fields couple only with the slow variable), and an effective detailed balance. These conditions are facilitated in the continuous limit for the slow variable. In contrast to its equilibrium counterpart, the non-equilibrium free energy can increase with temperature. One example of this is that entropy reduction by means of external fields (cooling) can be easier (in the sense of the work cost) if it starts from a higher temperature.

Introduction. -- One reason for the effectiveness of thermodynamics is that its concepts and ideas apply beyond the domain of equilibrium states, e.g., in real life thermodynamics is applied to systems having different temperatures, even though such states do not belong to equilibrium. There are specific mechanisms for this applicability, e.g., thermodynamics applies to systems that are perturbatively close to equilibrium [1–4]. Another general mechanism is the time-scale separation. In fact, this mechanism is inherent in the structure of thermodynamics, which is built up via the notion of a quasi-static process [3]. It is also important in statistical physics of open systems, where even low-dimensional systems can play the role of a thermal bath, provided that they are fast [5,6]. A related point is seen in stochastic thermodynamics, where the notion of white (i.e., fast) noise is relevant [7].

There is already a body of work concerning thermodynamic aspects of systems with time-scale separation [8–26]. In particular, much attention was devoted to the effective temperature of glassy systems, where the time-scale separation emerges from the many-body physics [8,10–12]. Recent works studied time-scale separation in stochastic thermodynamics focusing on dissipative features such as entropy production [13–18].

Time-scale separation is a much wider notion, and it is frequent also in biology and society, where it allows to reduce the complexity of emergent structures [27,28]. Indeed, components of such systems enjoy a certain autonomy (though in different ways): fast variables “live” under fixed values of the slow ones, while the slow variables “see” stationary distributions of the fast ones.

We aim to look at a class of stationary, non-equilibrium states for a Markov stochastic system that is out of equilibrium due to interaction with two different thermal baths; see [29] for an introduction to such systems. We impose three conditions:

-- Time-scale separation: the system under consideration consists of two variables, fast and slow.
-- Partial controllability: external fields act on the slow variable only. This assumption can be validated from operational reasons: it is normally difficult to have a precise control on variables that move fast.

Both conditions need not hold for the equilibrium situation (equal temperatures of the thermal baths), where thermodynamics applies under any type of controllability and the ratio of characteristic times.

-- Transition rates of the slow variable hold certain constraints—they are given by activation rates, or the slow variable lives in a tree-like structure— that amount to an effective detailed balance that holds after averaging (tracing out) over the fast variable.

Under these conditions the slow (isothermal) work done on this system admits a potential, i.e., there exists the free energy. This definition is unambiguous, because the work is defined for an arbitrary non-equilibrium state [4]; see the discussion after (15) for details of this point. Hence the free energy need not have further equilibrium
exact average energy in the stationary state, $\epsilon_N^i$ the following master equation for two discrete variables

\[
\dot{p}_{ij} = \sum_{\alpha} \{ \rho_{ij|\alpha} p_{j\alpha} - \rho_{ji|\alpha} p_{i\alpha} \} + \epsilon \sum_{\gamma} [\omega_{\alpha\gamma|i} p_{i\gamma} - \omega_{\gamma\alpha|i} p_{i\alpha}],
\]

where $p_{i\alpha}$ is the joint probability of $i$ and $\alpha$, $\rho_{ij|\alpha}$ and $\omega_{\alpha\gamma|i}$ are the transition probabilities for $i \rightarrow j$ (for a fixed $\alpha$) and $\alpha \rightarrow \gamma$ (for a fixed $i$), respectively. In (1), $\epsilon$ is a small parameter that makes $\{\alpha\}$ slower than $\{1\}$. We assume that all sums over Latin (Greek) indices run from 1 to $n$ (from 1 to $N$).

The transitions are controlled by different thermal baths at temperatures $T_1 = 1/\beta_1 > 0$ and $T_s = 1/\beta_s > 0$, respectively. Hence the transition probabilities $\rho_{ij|\alpha}$ and $\omega_{\alpha\gamma|i}$ hold the detailed balance conditions (see, e.g., [2,7]):

\[
\rho_{ij|\alpha} e^{-\beta E_{i\alpha}} = \rho_{ji|\alpha} e^{-\beta E_{j\alpha}},
\]

\[
\omega_{\alpha\gamma|i} e^{-\beta E_{i\alpha}} = \omega_{\gamma\alpha|i} e^{-\beta E_{i\alpha}}.
\]

Without loss of generality we parametrize (3) as

\[\omega_{\alpha\gamma|i} = e^{B_{\alpha\gamma|i}} + \frac{2}{\beta_s (E_{i\gamma} - E_{i\alpha})}, \quad B_{\alpha\gamma|i} = B_{\gamma\alpha|i},\]

where $B_{\alpha\gamma|i}$ accounts for the symmetric part of $\alpha \leftrightarrow \gamma$.

**Time-scale separation.** Holds when $\epsilon$ in (1) is sufficiently small; see fig. 1. This is a reliable approximation, since its predictions are close to the exact stationary probability even for moderately small $\epsilon$; see the left panel of fig. 1.

We now work out the stationary state ($\dot{p}_{i\alpha} = 0$) of (1) for a small $\epsilon$ following the standard perturbation theory approach; see [30] for a rigorous presentation and [31] for a physical discussion. One puts into (1)

\[p_{i\alpha} = B_{i\alpha}^{[0]} + \sum_{\alpha \geq 1} e^\alpha B_{i\alpha}^{[\alpha]},\]

and obtains for successive terms which are of order $O(1)$ and $O(\epsilon^a)$, respectively,

\[\sum_{\alpha} \rho_{ij|\alpha} B_{j\alpha}^{[0]} - \rho_{ji|\alpha} B_{i\alpha}^{[0]} = 0,\]

\[\sum_{\alpha} \rho_{ij|\alpha} B_{j\alpha}^{[\alpha]} - \rho_{ji|\alpha} B_{i\alpha}^{[\alpha]} + \sum_{\gamma} \omega_{\alpha\gamma|i} B_{j\alpha}^{[\alpha-1]} - \omega_{\gamma\alpha|i} B_{i\alpha}^{[\alpha-1]} = 0, \quad a \geq 1.\]

Note that there are solvability conditions found from summing (7) over $i$:

\[\sum_{\gamma} \omega_{\alpha\gamma|i} B_{j\alpha}^{[\alpha-1]} - \omega_{\gamma\alpha|i} B_{j\alpha}^{[\alpha-1]} = 0, \quad a \geq 1.\]

Now (6) and (8) with $a = 1$ are solved as

\[B_{i\alpha}^{[0]} = \rho_{i\alpha} p_{\alpha},\]

where we used (2), the stationary conditional probability $\bar{p}_{i\alpha}$ of the fast variable has the equilibrium form

\[\bar{p}_{i\alpha} = e^{-\beta E_{i\alpha}} / Z_{\alpha}[\beta], \quad Z_{\alpha}[\beta] = \sum_k e^{-\beta E_{i\alpha}},\]

and where the probability $\bar{p}_\alpha$ of the slow variable is found from (8) with $a = 1$.

\[\sum_{\gamma} \Omega_{\alpha\gamma} p_{\gamma} - \Omega_{\gamma\alpha} p_{\alpha} = 0, \quad \Omega_{\alpha\gamma} = \sum_{i} \omega_{\alpha\gamma|i} \bar{p}_{i\gamma}.\]

The meaning of (9) is that the fast variable relaxes to the conditional equilibrium, which determines via (11) and the effective rates $\Omega_{\alpha\gamma}$ the probability $p_{\alpha}$ of the slow variable.

Due to $\sum_{\alpha} p_{\alpha} = 1$ $\sum_{\alpha} \rho_{i\alpha} p_{\alpha} = 1$, eq. (9) implies the normalization condition: $\sum_{\alpha} B_{i\alpha}^{[0]} = 0$ for $a \geq 1$. Thus, $B_{i\alpha}^{[1]}$ is found from this condition, from (7) with $a = 1$,
and from (8) with \( a = 2 \). Expectedly, for a small \( \epsilon \) we get \( B^{(l)}_{\alpha \gamma} = \mathcal{O}(\epsilon) \). Now the right panel of fig. 1 confirms this fact with numeric results, but it also shows that the difference between (9) and \( p_{\alpha} \) is a sublinear function of \( \epsilon \) for a larger values of \( \epsilon \). This is favorable for the approximation

\[
p_{\alpha} = \bar{p}_{\alpha} p_{\alpha}^*,
\]

that we adopt from now on for the stationary probability \( p_{\alpha} \) of (1).

**External fields.** are introduced via time-dependent parameters \( a(t) = (a_1(t), \ldots, a_A(t)) \) in the energy \( E_{\alpha}(a) \) of the system. We assume that

\[
E_{\alpha}(a) = E_{\alpha}(a) + \tilde{E}_{\alpha}(a),
\]

where \( \tilde{E}_{\alpha} \) does not depend on \( a \). Equation (13) means that external fields couple only with the slow variable, e.g., because it is difficult to control fast objects. The stationary probabilities (12) depend on parameters \( a \) (through (13).

Now \( a(t) \) is slow as compared to the relaxation of both fast and slow variables. The temperatures \( T \) and \( T_s \) are constant. Hence the (quasi-stationary) probabilities of the system are found from (12), where \( a \) is replaced by \( a(t) \). The differential thermodynamic work \( w \) is [2] (see (13))

\[
w = \sum_{\alpha} \bar{p}_{\alpha} \partial_{\alpha} E_{\alpha} = \sum_{\alpha} \bar{p}_{\alpha} \partial_{\alpha} E_{\alpha},
\]

where \( \partial_{\alpha} \) is the gradient in the \( \alpha \)-space. Note that relations between thermodynamic and mechanic work have to be specified in the context of concrete applications [32]. This has to do with the following freedom in the definition (14): \( \partial_{\alpha} E_{\alpha} \) (and hence \( w \)) will change upon adding to \( E_{\alpha} \) a factor \( \varphi(a) \) that does not depend on \( a \), but depends on \( a \) (this is akin to the gauge-freedom of the potential energy in mechanics).

Hence the energies \( E_{\alpha} \) need to be specified, before defining the work \( w \) [32].

Each component of \( w = (w_1, \ldots, w_A) \) can have a separate physical meaning, since components of \( a \) may be driven by different sources.

The integral work is a line integral in the \( \alpha \)-space:

\[
W = \int_{t_{in}}^{t_{f}} \frac{dt}{d\alpha} \left( \int_{a_{in}}^{a_{f}} da \right) w(t) = \int_{a_{in}}^{a_{f}} da \left( \int_{t_{in}}^{t_{f}} dt \right) w(t),
\]

where \( a_{in} = a(t_{in}) \) and \( a_{f} = a(t_{f}) \) are the initial and final values of \( a(t) \) reached at times \( t_{in} \) and \( t_{f} \), respectively. We stress that (15) refers to slow changes of parameters \( a(t) \), but if we change \( \bar{p}_{\alpha} \) in (14) to the time-dependent probability \( \bar{p}_{\alpha} \) found from (1), then the same expression for work applies for arbitrary processes [4].

The work admits a potential \( (i.e., \text{free energy } \mathcal{F}) \) if

\[
w = \partial_{\alpha} \mathcal{F}, \quad \mathcal{F} = \mathcal{F}(a) - \mathcal{F}(a_{in}).
\]

If (16) does not hold, the work extraction \( (i.e., W < 0) \) by means of a slow, cyclic \( (a_{in} = a_t) \) variation of \( a \) is possible. Indeed, if \( W \neq 0 \), then \( W \) changes its sign when the cycle is passed in the opposite direction. The extracted work is determined by the closed-contour integral.

Below we give pertinent examples of \( W \neq 0 \) for cyclic processes; see (39). Now we turn to studying cases, in which (16) does hold despite the fact that \( T_s \neq T \).

**Non-equilibrium free energy for the activation rate.** An example of slow dynamics is given by the activation energy rate in (4) [7]

\[
\omega_{\alpha \gamma} = e^{\beta E_{\gamma}} , \quad B_{\alpha \gamma} = b_{\alpha \gamma}(E_{\gamma} + E_{\alpha})/2.
\]

One interpretation of (17) is that there is a barrier with energy \( E^* \) that is larger than all other energies. Choosing \( E^* = 0 \), we see that \( \omega_{\alpha \gamma} \) in (17) assumes the standard Arrhenius form.

Now \( \Omega_{\alpha \gamma} \) in (11) depends only on \( \gamma \): \( \Omega_{\alpha \gamma} = \Omega_\gamma \). The probability \( \bar{p}_{\alpha} \) in (11) is found via the detailed balance condition \( \Omega_{\alpha \gamma} \bar{p}_{\gamma} = \Omega_{\gamma \alpha} \bar{p}_{\alpha} \). This leads to \( \bar{p}_{\gamma} \propto 1/\Omega_\gamma \).

Thus, we get from (10), (11), (13), (17)

\[
\bar{p}_{\alpha} = \mu_{\alpha} e^{-\beta E_{\alpha}} / \sum_{\gamma} \mu_{\gamma} e^{-\beta E_{\gamma}} ,
\]

where \( \mu_{\alpha} \) corresponds to the weight of the energy \( E_{\alpha} \) and is expressed via the statistical sum of the fast variable:

\[
\mu_{\alpha} = \bar{Z}_\alpha[\beta] / \bar{Z}_\gamma[\beta - \beta_s], \quad \bar{Z}_\alpha[\beta] \equiv \sum_{k} e^{-\beta E_{\alpha}} .
\]

Note that \( \mu_{\alpha} \) does not depend on \( a \) due to (20) and (13). Equations (13), (16), (18) imply the existence of a free energy:

\[
\mathcal{F} = -T_s \ln \left[ \sum_{\alpha} \mu_{\alpha} e^{-\beta E_{\alpha}} \right] .
\]

Recall that \( \mathcal{F} \) is defined up to a constant,

\[
\mathcal{F} \rightarrow \mathcal{F} + \mathcal{C},
\]

that can depend on anything besides \( a \) [32]. Equation (21) is obtained under a specific choice of \( \mathcal{C} \) that proves useful below when calculating derivatives of (21).

**Temperature-dependence of \( \mathcal{F} \) and entropy reduction (cooling) via external fields.** The free energy \( F_{\mathrm{eq}}(a) = -T \ln \sum_{k} e^{-\beta E_{\alpha}} \) of an equilibrium system is a decreasing function of the temperature:

\[
\partial_T F_{\mathrm{eq}}(a) = -S_{\mathrm{eq}}(a) \leq 0,
\]

where \( S_{\mathrm{eq}}(a) \) is the entropy. Since \( F_{\mathrm{eq}}(a) \) is defined under a specific choice of an additive and temperature-dependent constant (cf. (22)), (23) changes for a different choice of the constant. Hence (23) cannot be interpreted directly. But it can be related to the work cost of a cooling process via externally driven parameters \( a(t) \) [33].

Normally, cooling means temperature reduction of a macroscopic system that has a single and well-defined temperature. But the needs of NMR physics [34], atomic and molecular physics [35,36], quantum computation [37] etc. led to generalizing this definition [33,38,39]. In these fields
one needs to reduce the entropy of a system that is coupled to a fixed-temperature thermal bath. Reducing the bath temperature is not feasible. But it can be feasible to reduce the entropy via external fields. For instance, in NMR spin systems, entropy decrease for a spin means its polarization increase, which is necessary for the NMR spectroscopy [34].

Thus, our definition of cooling amounts to an isothermal process, where \( a(t) \) slowly changes from \( a_{in} \) to \( a_t \) and achieves a lower final entropy. For the equilibrium situation this means \( S_{eq}(a_t) < S_{eq}(a_{in}) \) (dynamic aspects of this problem are analyzed in [33]). Now

\[

\partial_T[F_{eq}(a_t) - F_{eq}(a_{in})] = S_{eq}(a_{in}) - S_{eq}(a_t) \geq 0 \tag{24}
\]

compares two setups at different temperatures, but at the same values \( a_{in} \rightarrow a_t \) of the external fields. Equation (24) means that the work cost \( F_{eq}(a_t) - F_{eq}(a_{in}) \) of cooling increases with the temperature \( T \), i.e., cooling from a higher temperature is harder, as expected.

Turning to the non-equilibrium free energy \( F \), we characterize its temperature dependence via \( \partial_T F|_T \) and \( \partial_T F|_{T_s} \), since \( T \) and \( T_s \) are independent parameters. We deduce for the activation energy rate (17), (19)

\[

\partial_T F|_T = -S_s - \sum_{\alpha} \hat{p}_\alpha \left[ \beta \hat{E}_\alpha(\beta - \beta_s) + \ln \mu_\alpha \right] = -S_s - \sum_{\alpha} \hat{p}_\alpha \int_0^{\beta_s} d\beta \left[ \hat{E}_\alpha(\beta - \beta_s) - \hat{E}_\alpha(\beta - y) \right], \tag{25}
\]

\[

\partial_T F|_{T_s} = \frac{\beta_s^2}{\beta_s} \sum_{\alpha} \hat{p}_\alpha \left[ \hat{E}_\alpha(\beta - \beta_s) - \hat{E}_\alpha(\beta) \right], \tag{26}
\]

where

\[

S_s = - \sum_{\alpha} \hat{p}_\alpha \ln \hat{p}_\alpha, \tag{27}
\]

is the entropy of the slow variable (cf. (23)), and

\[

\hat{E}_\alpha = \frac{1}{Z(\beta)} \sum_k \hat{E}_{k\alpha} e^{-\beta \hat{E}_{k\alpha}} \tag{28}
\]

is the conditionedly averaged energy of the fast variable; cf. (10). \( \hat{E}_\alpha(\beta) \) monotonously decays from \( \max_k |\hat{E}_{k\alpha}| \) to \( \min_k |\hat{E}_{k\alpha}| \) as \( \beta \) increases from \( -\infty \) to \( \infty \). Hence we get in (25), (26)

\[

\partial_T F|_T \leq 0, \quad \partial_T F|_{T_s} \geq 0. \tag{29}
\]

Now we explore implications of \( \partial_T F|_{T_s} \geq 0 \) for a cooling process. Let us denote by

\[

\hat{S}_s(\beta) = - \sum_i \hat{p}_{i|\alpha} \ln \hat{p}_{i|\alpha} = \beta \hat{E}_\alpha + \ln \hat{Z}_\alpha, \tag{30}
\]

the entropy of the fast variable conditioned by a fixed value \( \alpha \) of the slow variable, cf. (10). Recall that \( S_s + \sum_\alpha \hat{p}_\alpha \hat{S}_s(\beta) \) amounts to the full entropy \(-\sum_\alpha \hat{p}_\alpha \ln \hat{p}_\alpha\).

We denote \( \hat{S}_1 = \min_\alpha [\hat{S}_s(\alpha)] \). Then we can define a cooling process, where all energies \( E_{i\neq 1} \) in (13) slowly increase leading to \( \hat{p}_1 \rightarrow 1 \), see (18). Though the process is realized by external fields holding the partial controllability restriction (13), we still get a cooling of the whole (slow plus fast) system. Indeed, not only the entropy \( S_s \) of the slow variable decreases to zero, but also the conditional entropy of the fast variable decreases from its initial value \( \sum_\alpha \hat{p}_\alpha S_s(\beta) \) to a smaller value \( \hat{S}_1(\beta) \).

We note that the considered cooling process can also decrease the internal energy of the system. Recall that the internal energy is defined as (cf. (12), (13))

\[

\sum_{\alpha} E_{\alpha i} \hat{p}_{i|\alpha} \hat{p}_\alpha = \sum_{\alpha} E_{\alpha} \hat{p}_\alpha + \sum_{\alpha} \hat{E}_\alpha \hat{p}_\alpha, \tag{31}
\]

where \( \hat{E}_\alpha \) is given by (28). Since \( \hat{S}_1 \) and \( \hat{E}_\alpha \) are equilibrium quantities (see (27), (28)), \( \hat{S}_1 \) is an increasing function of \( \hat{E}_\alpha \). Hence it can be possible to choose \( \hat{E}_1 = \min_\alpha [\hat{E}_\alpha] \) in addition to \( \hat{S}_1 = \min_\alpha [\hat{S}_s(\alpha)] \). We can also choose \( \hat{E}_1 = \min_\alpha [\hat{E}_\alpha] \). Then \( \hat{p}_1 \rightarrow 1 \) means that the internal energy (31) decreases during the cooling.

The cooling process incurs a work cost (cf. (21))

\[

\Delta F = -T_s \ln [e^{-\beta \hat{E}_1} - F] \geq 0, \tag{32}
\]

where \( F \) is the initial free energy. Now \( \Delta F > 0 \) means that the work is taken from the external source, hence this is indeed a work cost.

The change of \( \Delta F \) with the temperature \( T \) of the fast variable reads from (26)

\[

\partial_T \Delta F|_{T_s} = -\frac{\beta_s^2}{\beta_s} \sum_{\alpha} \hat{p}_\alpha \left[ \hat{E}_\alpha(\beta - \beta_s) - \hat{E}_\alpha(\beta) \right] - \hat{E}_1(\beta - \beta_s) + \hat{E}_1(\beta)] \tag{33}
\]

Let us now indicate several scenarios for \( \partial_T \Delta F|_{T_s} \leq 0 \) in (33), and show that they are consistent with condition \( \hat{S}_1 = \min_\alpha [\hat{S}_s(\alpha)] \) that defines the cooling process. For example, in (33) one can take \( \hat{E}_1(\beta - \beta_s) \simeq \hat{E}_1(\beta) \), but \( \hat{E}_\alpha \neq \hat{E}_\alpha(\beta - \beta_s) \neq \hat{E}_\alpha(\beta) \). Another example is to make \( \beta_s \) small. Then \( \hat{E}_\alpha(\beta - \beta_s) - \hat{E}_\alpha(\beta) \propto C_0 \), \( C_0 \) amounts to the heat capacity \( C_0 \geq 0 \), and then \( \partial_T \Delta F|_{T_s} < 0 \) can be implied by \( C_0 > C_1 \), which is consistent with \( \hat{S}_1 = \min_\alpha [\hat{S}_s(\alpha)] \).

We conclude from \( \partial_T \Delta F|_{T_s} < 0 \) that it can be easier (in terms of the work cost) to cool from higher temperatures than from the lower ones. Note that the result survives also in the near-equilibrium limit \( \beta \approx \beta_s \).

The above effect relates to change the temperature \( T \) of the fast variable. The first formula in (29) suggests that such an effect will not be seen, if one varies \( T_s \). Indeed, (25) shows that one normally has \( \partial_T \Delta F|_T \geq 0 \), which is an effective equilibrium situation, where cooling from a higher temperature will incur a larger work cost, cf. (24). The full equilibrium formula is established as

\[

[\partial_T \Delta F|_T + \partial_T \Delta F|_{T_s}] \geq 0.
\]

**Tree-like topology of the slow variable.** - Free energy (21) exists for general rates (4), if the topology of connections between the states \( \alpha, \gamma, \ldots \) in (11) is that of a tree (a network without loops or closed cycles): for a fixed
We get for the rotor of the work \( \omega \) (cf. (14) and (20))
\[
\partial_{a_2} w_{a_1} - \partial_{a_1} w_{a_2} = \langle (\partial_{a_2} E) \partial_{a_1} [\ln (1 + T \beta_1 \ln Z)] - (\partial_{a_1} E) \partial_{a_2} [\ln (1 - T \beta_1 \ln Z)] \rangle,
\]
where \( \langle X \rangle \equiv \sum_a \bar{p}_a X_a \). Equation (39) shows how far the work is from having a gradient when the partial controllability (13) does not hold. It also determines the amount of work extracted from a cycle in the \((a_1, a_2)\)-space. Now since (39) is a correlation, the existence of a gradient for \( w_p \) can be recovered if fluctuations are negligible.

**Quasi-continuous limit for the slow variable.** – Recall that the index \( \gamma = 1, \ldots, N \) numbers the states of the slow variable. We now consider the case in which these states are arranged over a segment of a line (1D situation), so that only transitions from one neighbor state to another are allowed. This is an example of birth-death processes that have many applications [41]. If the segment is finite and the states are homogeneously and densely located in it, then one can pass to the continuous limit, where instead of a discrete index \( \gamma \) we shall have a continuous variable \( x \) [42,43]. The continuous limit is achieved by
\[
E_i \gamma \rightarrow E_i(x), \quad E_{i+1} \gamma \rightarrow E_i(x) + \epsilon E_i'(x),
\]
where \( x \) is a continuous parameter, \( \epsilon \) is a small parameter (the distance between the states \( \gamma \) and \( \gamma + 1 \) on the segment), and where \( A'(x) \equiv \partial A(x)/dx \). We now expand in (4) over a small \( \epsilon \)
\[
\omega_{\gamma+1} | i = \exp \left[ B_{\gamma+1} | i \right] \left( 1 + \beta_\gamma (E_i \gamma - E_i \gamma + 1)/2 \right),
\]
and get in (1) (see [42,43] for similar derivations)
\[
\sum_\gamma \left[ \omega_{\gamma} | i \right] p_{\gamma} - \omega_{\gamma} | a \left[ p_{\gamma} \right] = \beta_\gamma [\xi_{\gamma+1} - \xi_{\gamma}]
\]
\[
+ \xi_{\gamma+1} - \xi_{\gamma} + \epsilon \sum_i (E_i \gamma - E_{i+1} \gamma) (p_{\gamma+1} | i - p_{\gamma} | i),
\]
and
\[
\xi_{\gamma+1} = \epsilon \sum_i (E_i \gamma + 1 - E_i \gamma) (p_{\gamma+1} | i + p_{\gamma} | i)/2.
\]

Taking in (43) the continuum limit, we get from (1)
\[
p_i(x, t) = \sum_j [p_{ij} | x \left] p_j(x) - p_{ji} | x \left[ p_i(x, t) + \epsilon^2 \partial_x J_i(x, t),
\]
where \( p_i(x) \) is the joint probability of \( i \) and \( x \):
\[
\sum_j \int dx p_i(x, t) = 1, \quad p_i(x, t) \quad \text{is the probability current related to the slow variable}.
\]
Equation (44) shows that as compared to (1) the slow-fast limit is facilitated due to the additional small factor \( \epsilon^2 \).

This is confirmed by fig. 1 which shows that the slow-fast limit improves when the number \( N \) of states of the slow variable is large. Thus, the above continuous limit is a way to get the time-scale separation naturally.

We treat (44) with the same time-scale separation argument (5)–(11) with minor modifications for the continuous
The stationary conditional probability is still \( \tilde{p}_{|i|} \propto e^{-\beta E_i(x)} \). For the stationary probability density \( \bar{p}(x) \) \— which holds the zero-current condition \( \sum_i J_i(x) = 0 \) \— we obtain from (44), (45)

\[
\bar{p}(x) \propto e^{-\beta E_i(x)} \mu(x), \quad \mu(x) = e^{b(x)} \sum_i e^{-\beta \dot{E}_i(x)},
\]

\[
h'(x) = (\beta - \beta_i) \frac{\sum_i \dot{E}_i(x)e^{\dot{B}_i(x) - \beta \dot{E}_i(x)}}{\sum_i e^{\dot{B}_i(x) - \beta \dot{E}_i(x)}}, \quad (46)
\]

where, by analogy with (13), (35), \( E_i(x; \alpha) = E(x; \alpha) + \dot{E}_i(x) \), \( B_i(x; \alpha) = B(x; \alpha) + \dot{B}_i(x) \). The free energy is given as in (21) by \( \mathcal{F} = -T_s \ln \int dx \mu(x)e^{-\beta E(x)} \). Note that it goes to the equilibrium expression for \( T_s = T \).

Non-equilibrium free-energy with equilibrium features. \— A particular case of (46) is when \( \dot{B}_i(x) \) does not depend on \( i \), i.e., \( \dot{B}_i(x) = 0 \). Now the non-equilibrium free energy reads [20]:

\[
\mathcal{F} = -T_s \ln \left[ \int dx \left( \sum_i e^{-\beta E_i(x)} \right)^{\beta_s/\beta} \right]. \quad (47)
\]

The following features of \( \mathcal{F} \) are deduced directly from (47) [20]. They all are very similar to those of the equilibrium free energy.

- \( \mathcal{F} \) is the potential for the work \( \text{without} \) restriction (13), i.e., now \( \alpha \) can also enter \( \dot{E}_i(x) \):

\[
E_i(x; \alpha) = E(x; \alpha) + \dot{E}_i(x).
\]

- For temperature derivatives we get

\[
\partial_T \mathcal{F}^0 = -S, \quad \partial_T \mathcal{F}^0 = -S_s.
\]

Where \( S \equiv -\int dx \sum_i \tilde{p}_i(x) \ln \tilde{p}_i(x) \) and \( S_s \equiv -\int dx \tilde{p}(x) \ln \tilde{p}(x) \), respectively, the conditional entropy of the fast variable, and the marginal entropy of the slow variable (cf. (27)). Hence the anti-thermodynamic cooling effect noted in (33) is impossible here.

Note the analogy between (49) and the equilibrium formula \( \partial_T \mathcal{F}_\text{eq} = -S_\text{eq} \). It leads us to \( \mathcal{F}_\infty = U - T_s S_s - T S \), where \( U = \int dx \sum \mu_k(x) E_k(x) \) is the average (overall) energy. This expression for \( \mathcal{F}_\infty \) already appeared in the physics of Brownian motion [19,20] and glasses [12].

Equation (47) has an intuitively appealing meaning [19–26], since it implies that the free energy \( -T \sum_i e^{-\beta E_i(x)} \) of the fast variable (evaluated at a fixed value of the slow variable) serves as an effective potential \( U_{\text{eff}}(x) \) for the (Gibbs) distribution of the slow variable: \( \tilde{p}(x) \propto e^{-\beta \mu(x)} \). And then \( \mathcal{F}_\infty \) is the free energy related to that effective Gibbs distribution: \( \mathcal{F}_\infty = -T_s \ln \int dx e^{-\beta \mu(x)} \). While this heuristic explanation is frequently applied in statistical physics, we should keep in mind from the above derivation that \( \mathcal{F}_\infty \) exists \( \text{due} \) to the continuous limit, e.g., assuming \( \dot{B}_{mg} = 0 \) in the discrete case does not recover the above equilibrium features (for \( T \neq T_s \)).

Summary. \— We studied a class of non-equilibrium stationary states generated by two thermal baths at different temperatures. Three conditions were assumed:

i) There are fast and slow variables (time-scale separation).

ii) External fields act only on the slow variable.

iii) The transition rates of the slow variable hold an effective detailed balance. Examples of the effective detailed balance are the activation transition rate for an arbitrary topology of connections, and arbitrary rates for a tree-like topology.

Conditions iii) are similar to those governing the non-pumping theorem [44–48]. It considers a stochastic system coupled to a single thermal bath \( \text{—} \) but driven by an oscillating external field \( \text{—} \) and studies conditions under which the time-averaged probability currents vanish. The non-pumping theorem has extensions beyond the activation rates and loop-less networks [49].

Under conditions i)–iii) there exists a non-equilibrium free energy. It describes quasi-stationary isothermal processes, and is defined via the potential of the work done via a slow variation of the external parameters. As compared to its equilibrium counterpart, the non-equilibrium free energy can be an increasing function of the bath temperature. As a physical demonstration of this feature we studied the free-energy cost of isothermal cooling (i.e., entropy reduction via slow external fields): this cost can decrease if the cooling starts from a higher temperature. It is interesting to compare this finding with the Mpemba phenomenon [50,51]: given two samples of water that are identical except for their initial temperature, the initially hotter sample cools (and freezes) quicker than the colder one. This can have relatively straightforward physical explanations, e.g., some part of the hotter water can evaporate thus decreasing its amount and making its cooling easier. The Mpemba phenomenon disappears once such scenarios are ruled out [51]. To compare our finding with the Mpemba effect, we first of all note that our cooling is not spontaneous. We focus on an (isothermal) entropy reduction of the system by means of external fields. (Still our cooling process is slow and it leaves the system in its locally stationary state.) Hence we study not the speed of cooling, but its work cost, as determined by the free energy. The effect we found is impossible in equilibrium, because the equilibrium free energy is a decreasing function of the temperature. However, we show that this effect survives close to equilibrium. Thus, the second difference with the Mpemba phenomenon is that our effect is out of equilibrium, as it relates to two different temperatures.

The existence of the free energy is facilitated in the (one-dimensional) continuous limit of the slow variable. Now time-scale separation comes out naturally, and there is a situation where a non-equilibrium free energy exists for all driven parameters, i.e., assumption ii) can be relaxed.

The free energy allows to involve ideas of equilibrium thermal physics for understanding non-equilibrium stationary states; other approaches that aim at a
thermodynamical description of such states are studied in [52–59].

***

This work is partially supported by COST MP1209 and by the ICTP through the OEA-AC-100.

REFERENCES

[1] Zubarev D. N., Morozov V. and Ropke G., Statistical Mechanics of Nonequilibrium Processes (John Wiley & Sons, New York) 1996.
[2] Stratonovich R. L., Nonlinear Nonequilibrium Thermodynamics I (Springer-Verlag, Berlin) 1992.
[3] Meikner J., in A Critical Review of Thermodynamics, edited by Stuart E. B., Gal-On B. and Brainard A. J. (Mono Book Corporation, Baltimore, MD) 1970, p. 40.
[4] Ballan R., From Microphysics to Macrophysics, Vol. I (Springer) 1992.
[5] Jarzynski C., Phys. Rev. Lett., 74 (1995) 2937.
[6] Rieger J., Baba N., Gelfert K., Just W. and Kantz H., Phys. Rev. Lett., 94 (2005) 054103.
[7] Sekimoto K., Stochastic Energetics (Springer, Berlin) 2010.
[8] Cugliandolo L. F., Kurchan J. and Peliti L., Phys. Rev. E, 55 (1997) 3898.
[9] Casas-Vázquez J. and Jou D., Rep. Prog. Phys., 66 (2003) 1937.
[10] Cugliandolo L. F., J. Phys. A, 44 (2011) 483001.
[11] Bertin E., Martens K., Dauchot O. and Droz M., Phys. Rev. E, 75 (2007) 031120.
[12] Nieuwenhuizen T. M., Phys. Rev. E, 61 (2000) 267; J. Chem. Phys., 115 (2001) 8083.
[13] Celani A., Bo S., Eichhorn R. and Aurell E., Phys. Rev. Lett., 109 (2012) 260603.
[14] Esposito M., Phys. Rev. E, 85 (2012) 041125.
[15] Puglisi A., Pigolotti S., Rondoni L. and Vulpiani A., J. Stat. Mech. (2010) P06015.
[16] Gomez-Marin A., Parrondo J. M. R. and van den Broeck C., Phys. Rev. E, 78 (2008) 011107.
[17] Tom T. and de Oliveira M. J., Phys. Rev. E, 91 (2015) 042140.
[18] Ziener R., Maritan A. and Hinrichsen H., J. Stat. Mech. (2014) P08014.
[19] Landauer R. and Woo J., Phys. Rev. A, 6 (1972) 2205.
[20] Allahverdyan A. E. and Nieuwenhuizen Th. M., Phys. Rev. E, 62 (2000) 845.
[21] Coolen A. C. C., Penney R. W. and Sherrington D., J. Phys. A, 26 (1993) 3681.
[22] Penney R. and Sherrington D., J. Phys. A, 27 (1994) 4027.
[23] Dotsenko V., Franz S. and Mezard M., J. Phys. A, 27 (1994) 2351.
[24] Allahverdyan A. E. and Petrosyan K. G., Phys. Rev. Lett., 96 (2006) 065701.
[25] Ritter O. M., D’Alessio P. C. T. and Figueiredo W., Phys. Rev. E, 69 (2004) 016119.
[26] Ilg P. and Barat J.-L., J. Phys.: Conf. Ser., 40 (2006) 76.
[27] Roijdestvenski I. et al., BioSystems, 50 (1999) 71.
[28] Gunawardena J., PLoS ONE, 7 (2012) e36321.
[29] Zia R. K. P., Shaw L. B., Schmitmann B. and Astalos R. J., Comput. Phys. Commun., 127 (2000) 23.
[30] Pavliotis G. A. and Stuart A. M., Multiscale Methods: Averaging and Homogenization (Springer-Verlag, Berlin) 2008.
[31] van Kampen N. G., Phys. Rep., 124 (1985) 69.
[32] Vilar J. M. G. and Rubi J. M., J. Non-Equilib. Thermodyn., 36 (2011) 123.
[33] Allahverdyan A. E., Hovhannisyan K., Janzing D. and Mahler G., Phys. Rev. E, 84 (2010) 041109.
[34] Abragam A. and Goldman M., Rep. Prog. Phys., 41 (1978) 395; Sorensen O. W., Prog. Nucl. Magn. Reson. Spectrosc., 21 (1989) 503.
[35] Ketterle W. and Pritchard D. E., Phys. Rev. A, 46 (1992) 40514054.
[36] Bartana A., Kosloff R. and Tannor D. J., J. Chem. Phys., 106 (1997) 1435.
[37] Fernandez J. M., Lloyd S., Mor T. and Roychowdhury V., Int. J. Quantum Inf., 2 (2004) 461.
[38] Wu L.-A., Segal D. and Brumer P., Sci. Rep., 3 (2013) 1824.
[39] Briegel H. J. and Popescu S., Proc. R. Soc. London, Ser. A, 469 (2013) 20110290.
[40] Zia R. K. P. and Schnittmann B., J. Stat. Mech. (2007) P07012.
[41] van Kampen N. G., Stochastic Processes in Physics and Chemistry (Elsevier, Amsterdam) 2007.
[42] Agmon N. and Hofffield J. J., J. Chem. Phys., 78 (1983) 6947.
[43] Risken H., The Fokker-Planck Equation (Springer-Verlag, Berlin) 1984.
[44] Rahav S., Horowitz J. and Jarzynski C., Phys. Rev. Lett., 101 (2008) 140602.
[45] Chernyak Y. V. and Sintysyn N. A., Phys. Rev. Lett., 101 (2008) 160601.
[46] Mandal D. and Jarzynski C., J. Stat. Mech. (2011) P10006.
[47] Mandal D., EPL, 108 (2014) 50001.
[48] Asban S. and Rahav S., Phys. Rev. Lett., 112 (2014) 050601.
[49] Martirosyan N. H., Chin. J. Phys., 55 (2017) 500.
[50] Mpeeva E. B. and Osborne D. G., Phys. Education, 4 (1969) 172; Kell G. S., Am. J. Phys., 37 (1969) 564; Auerbach D., Am. J. Phys., 63 (1995) 882; Jeng M., Am. J. Phys., 74 (2006) 514.
[51] Burridge H. C. and Linden P. F., Sci. Rep., 6 (2016) 37665.
[52] Keizer J., J. Chem. Phys., 69 (1978) 2609; 82 (1985) 2751.
[53] Ben-Amotz D. and Honig J. M., Phys. Rev. Lett., 96 (2006) 020602.
[54] Blythe R. A., Phys. Rev. Lett., 100 (2008) 030601.
[55] Paquette G. C., Thermodynamics of non-equilibrium steady states, arXiv:0905.3565.
[56] Robinson J. M., Equality statements for entropy change in open systems, arXiv:0711.4957.
[57] Komatsuz T. S. and Nakagawa N., Phys. Rev. Lett., 100 (2008) 030601.
[58] Ge H. and Qian H., Phys. Rev. E, 81 (2010) 051133.
[59] Bouchet F., Gawedzki K. and Nardini C. J., J. Stat. Phys., 163 (2016) 1157.