Work extraction from microcanonical bath

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Abstract – We determine the maximal work extractable via a cyclic Hamiltonian process from a positive-temperature ($T>0$) microcanonical state of a $N \gg 1$ spin bath. The work is much smaller than the total energy of the bath, but can be still much larger than the energy of a single bath spin, e.g. it can scale as $\mathcal{O}(\sqrt{N \ln N})$. Qualitatively the same results are obtained for those cases, where the canonical state is unstable (e.g., due to a negative specific heat) and the microcanonical state is the only description of equilibrium. For a system coupled to a microcanonical bath the concept of free energy does not generally apply, since such a system — starting from the canonical equilibrium density matrix $\rho_T$ at the bath temperature $T$ — can enhance the work extracted from the microcanonical bath without changing its state $\rho_T$. This is impossible for any system coupled to a canonical thermal bath due to the relation between the maximal work and free energy. But the concept of free energy still applies for a sufficiently large $T$. Here we find a compact expression for the microcanonical free-energy and show that in contrast to the canonical case it contains a linear entropy instead of the von Neumann entropy.

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How much work can be extracted from a state of a physical system via cyclic processes? This question governs our understanding of energy conversion and storage, and hence is central for thermodynamics \cite{1–8}. The basic answer, known as the Thomson’s formulation of the second law, is that an equilibrium state cannot yield work. This formulation is an axiom in thermodynamics, but its first-principle derivations were given in the literature for a canonical (Gibbsian) equilibrium state \cite{2}. The main consequence of Thomson’s formulation is that only non-equilibrium states can be sources of work. The maximal work extractable from such states via a cyclic process was studied both for macroscopic \cite{1} and finite systems \cite{4–6}.

One instance of the maximal work is especially well-known, because it provides the physical meaning of free energy \cite{1}. Consider a quantum system with Hamiltonian $H$ and initial density matrix $\rho$. This system is in contact with a canonical thermal bath at temperature $T$. External fields act cyclically on the system + bath. Assuming no system-bath coupling both initially and finally, the maximal work extracted by the fields reads \cite{1}:

$$W_{\text{max}} = F[\rho] - F[\rho_{\text{eq}}], \quad F[\rho] = \text{tr}(\rho H) + T \text{tr}(\rho \ln \rho),$$

where $F[\rho]$ is the free energy and $\rho_{\text{eq}} = e^{-H/T}/\text{tr}[e^{-H/T}]$ is the canonical equilibrium state of the system, which is its final state after work extraction \cite{1}. The maximal work is determined by the deviation of $\rho$ from its canonical equilibrium value $\rho_{\text{eq}}$ as quantified by the free energy \eqref{eq:1}.

One notes however that all the above results refer to a specific notion of equilibrium, viz. the canonical state. Another concept of equilibrium is given by the microcanonical state, which describes an isolated system equilibrated due to its internal mechanism \cite{11}, or an open system coupled weakly to its environment (so weak that no energy is exchanged) \cite{8,12}. This is a more fundamental notion of equilibrium: i) under certain conditions the canonical state can be derived from it for a weakly

\textsuperscript{1}The maximization of work is carried out over all cyclic and time-dependent (in the sense of \eqref{eq:9}) Hamiltonians acting on the system + bath \cite{1}; for more details see, e.g., Appendix E of \cite{9}. One can show that the work \eqref{eq:1} can be achieved for a Hamiltonian, where external fields act only on the system and on its coupling to the bath \cite{9,10}. This set-up is local (advantage), but it has to be slow (drawback).
coupled subsystem [1]. ii) In contrast to the canonical state, whose preparation refers to an external thermal bath, the microcanonical state can be applied to a closed few-body system provided that it satisfies certain chaoticity features [13,14]. iii) Since local stability conditions of the canonical state are more demanding—a fact closely related to the no work extraction feature[1]—there are situations, where the equilibrium can be described by the microcanonical state only, since the canonical state for them is unstable [15]. For such systems, frequently realized via long-range interactions, the entropy is a non-concave function of energy, and hence the notorious macroscopic equivalence between canonical and microcanonical state is broken [15]. Even if this macroscopic equivalence holds, it is by no means obvious that in the argument around (1) one can substitute the canonical state of the thermal bath by the microcanonical state (with the same temperature), because in general the work (1) is not a macroscopic quantity, i.e. it does not scale with the number of bath particles. This is however widely done in literature, e.g., when introducing the free energy as in (1) one basically never specifies the equilibrium state of the bath; see, e.g., [1,7].

We revisit the maximal work extraction problem for a thermal bath in a quantum microcanonical state. It was noted already some work can be extracted via a cyclic Hamiltonian process from a few-particle microcanonical system [3]. Recent papers studied to which extent the extraction of work from a one-particle classical microcanonical state can be carried out by physically realistic Hamiltonians [16,17]. Our purposes here are different:

- We focus on finding the maximal amount of work extractable from a macroscopic microcanonical state of $(N \gg 1)$-particle thermal bath.

- We also determine the work extracted via a system coupled to a microcanonical thermal bath, and check whether the reasoning (1) generalizes at least qualitatively, i.e. whether the concept of free energy applies to the microcanonical situation.

The subject of work extraction via a system coupled to a thermal bath is an active research topic. References [17–21] discuss various set-ups for this problem: quantum, classical, with or without state-dependent feedback etc. Recall that (1) is at the core of relations between statistical thermodynamics and information theory [7]. The term $\text{tr}[(\rho - \rho_{eq})H]$ on the right-hand side of (1) is the energy extracted from the system, while the remaining (entropic) part comes from the bath. If $\text{tr}[(\rho - \rho_{eq})H]$ is negligible (e.g., because $H$ contains only few almost degenerate energy levels), the work is extracted from the bath due to the difference between the initial entropy and its canonical equilibrium value. This relation between the entropy and work is the essential part of information-driven engines (e.g., Szilard’s engine) [7]. In contrast, various forms of fuel operate due to the initial non-equilibrium energy, i.e. the term $\text{tr}[(\rho - \rho_{eq})H]$ in (1).

**Microcanonical thermal bath.** The microcanonical state is characterized by two parameters: energy $E$ and width $\sigma$ [1]. The corresponding density matrix is diagonal in the energy representation, all energies within the interval $[E-\sigma, E+\sigma]$ have equal probabilities, all other energies have probability zero. For a $(N \gg 1)$-particle system the number $d(E,\sigma)$ of energy levels within the interval $[E-\sigma, E+\sigma]$ defines the microcanonical entropy [1]:

$$S(E) = \ln d(E, \sigma) = \mathcal{O}(N),$$

where the choice of $\sigma$ should not influence the leading $\mathcal{O}(N)$ behavior of $S(E)$. Equation (2) is the von Neumann entropy for the microcanonical density matrix (6); see also footnote 2. For clarity we want to work with a specific model of a macroscopic microcanonical system (bath).

This is the basic model of the field: $N \gg 1$ uncoupled two-level spins; each spin has energies $0$ and $\delta > 0$ [8]. Some of our results extend to more general bath models, as seen below.

The bath Hamiltonian reads (diag[…] means diagonal matrix in the energy representation)

$$H = \text{diag}[0, \delta, 2\delta, \ldots, \delta N],$$

where each element $\delta k$ is repeated $d_k$ times,

$$d_k \equiv \frac{N!}{k!(N-k)!}.$$  

(4)

Hence every energy shell $\delta k$ is $d_k$-degenerate. Denote

$$e_k = (1, \ldots, 1), \quad 0_k = (0, \ldots, 0), \quad D_k \equiv \sum_{m=0}^{k} d_m,$n

(5)

where $e_k (0_k)$ is the vector of $k$ 1’s (0’s).

For the present model of bath the microcanonical state is easy to define: all energies $\delta M$ have equal probability $\frac{1}{\delta M}$; all other energies have zero probability. Thus we put $\sigma \to 0$, the minimal thermodynamically consistent width for this model. Note that the degeneracy of the energy levels is convenient, since it allows to set $\sigma \to 0$. It is however not essential; an effective degeneracy will be anyhow regained for a small but finite $\sigma > 0$, since the energy levels of a macroscopic system are located very densely [1]. The bath initial state reads in representation (3)

$$\Omega_i = \frac{1}{d_M} \text{diag}[0_{D_{M-1}}, e_{D_M}, 0_{D_N-D_M}].$$

(6)

For $N \gg 1$ this microcanonical state does have desired features expected from thermodynamics, e.g. macroscopic equivalence with the canonical state, equilibration of a small subsystem, third law [8]. The density matrix of a single bath spin is Gibbsian $\propto \text{diag}[1, e^{-\delta k/T}]$ with [8]

$$e^{-\delta k/T} = m/(1 - m), \quad m = M/N.$$

(7)

2Equation (2) is one of two standard definitions of the microcanonical entropy [1]. Another definition is $\ln \text{tr}[P_{E,E_0}]$, where $E_0$ is the lowest energy and $P_{E,E_0}$ is the projector on the subspace $[E,E_0]$. For macroscopic systems both definitions typically agree with each other within the order $\mathcal{O}(N)$, where $N \gg 1$ is the number of particles. For finite systems the second definition is preferable [13,18].
The same $T$ is recovered as microcanonical temperature \cite{1}
\[ 1/T = \partial S(E)/\partial E, \quad E = \delta M, \quad S(E) = \ln d_M, \]  
where $S(E)$ is the microcanonical entropy (2). This equivalence can be shown via formula (17) that is proven below.

Note that although the spins are uncoupled, the microcanonical state does not reduce to the tensor product of the separate spin states (otherwise it would amount to the canonical state). It contains inter-spin correlations. Ultimately, this is the reason why, as seen below, a microcanonical bath can yield work in a cyclic process.

We restrict ourselves with $M/N \leq 1/2$, i.e. positive temperatures. The case with $M/N > 1/2$ is definitely less interesting, because now each spin of the bath is in a state with a negative temperature. Such states are trivially active, i.e. they yield work in a cyclic process.

**Work extraction.** – At some initial time $t = 0$ the bath Hamiltonian $H(t)$ becomes time-dependent due to interaction with sources of work. Consider a cyclic process
\[ H(0) = H(\tau) = H, \]  
where $\tau$ is the final time. The work extracted in this thermally isolated cyclic Hamiltonian process is
\[ W = \text{tr}(H[\Omega_f - \Omega_t]) = \delta M - \text{tr}(iH\Omega_t), \quad \Omega_t = U\Omega U^\dagger, \]  
where $\Omega_t$ is the final state of the bath, and $U = T e^{-iH/\hbar} \int ds H(s)$; $T$ means chronologization. Conversely, for a given unitary $U$ one can construct a class of Hamiltonians that generate $U$ and satisfies (9) \cite{5}.

Condition (9) is necessary for the system to be an autonomous carrier of energy that should deliver work to another system (e.g. to a work-source) via an interaction which switches on and off at well-defined times. Hence this is a cyclic Hamiltonian process.

We now maximize the total work $W$ —or minimize the final energy $tr(H\Omega_f)/$— over all cyclic Hamiltonians, i.e. over unitary operators $U$. Note from (10) that
\[ \text{tr}(H\Omega_t) = \sum_{a,b=1}^{2^N} E_{ab} C_{ab} \langle b|\Omega_t|b\rangle, \quad C_{ab} \equiv \langle b|U|a\rangle^2, \]  
where $\{E_{ab}\}_{a,b=1}^{2^N}$ are, respectively, the eigenvalues and eigenvectors of $H$ (see (3)), and the elements $\langle b|\Omega_t|b\rangle$ are defined in (6). Three conditions in (12) mean that the matrix $C_{ab}$ is double-stochastic \cite{22}. Conversely, every such matrix can be represented as $C_{2} \equiv \langle b|U|a\rangle^2$ for some unitary $U$ \cite{22}. Every double-stochastic matrix equals a convex sum of permutation matrices $\Pi^{[a]}$ (Birkhoff’s theorem \cite{22}): \[ C = \sum \lambda_a \Pi^{[a]}, \quad \sum \lambda_a = 1, \]  
where each matrix $\Pi^{[a]}$ acting on a column-vector $x$ amounts to permuting (in a certain way) the elements of $x$. Equation (11) shows that $tr(H\Omega_t)$ is a linear function of the matrix $C = \{C_{ab}\}$. Hence its minimum over the unitary operators $U$, that is its minimum over double-stochastic matrices $C_{ab}$, is reached for $C_{ab}$ equal to some permutation matrix $\tilde{\Pi}$. It is clear from (11) that $\tilde{\Pi}$, when acting on the vector $\langle b|\Omega_t|b\rangle$ permutes its elements such that all its non-zero (equal to each other) elements concentrate at lowest energies $\{E_{ab}\}_{a=1}^{2^N}$ \cite{5}. For the final state we have $\langle a|\Omega_t|a\rangle = \sum_i \Pi_{ab} \langle b|\Omega_t|b\rangle$. Hence the lowest-energy final state compatible with $\Omega_t$ reads
\[ \Omega_t = \frac{1}{d_M} \text{diag} \{d_{m}, 0_{N - d_{m}} \}. \]  

Once $\tilde{\Pi}$ is found we can employ the standard procedure of constructing the corresponding unitary operator $U$ and the cyclic Hamiltonian \cite{5}. Note that $\tilde{\Pi}$ does depend on the energy of the initial state $\Omega_t$: $\tilde{\Pi}$ applied on a microcanonical state with a different energy will not lead to the maximal work extraction. This does not differ from (say) the ordinary Carnot cycle, whose implementation also demands knowing the initial state of the working body.

The maximal work $W_{\text{max}}$ reads from (13), (10): \[ W_{\text{max}} = \delta M - \frac{k}{d_M} \sum_{k=0}^{M - \ell} k d_k + (M - \ell + 1)(d_M - \sum_{k=0}^{M - \ell} d_k). \]

After summation by parts,
\[ W_{\text{max}} = \delta \left[ \ell - 1 + \frac{1}{d_M} \sum_{k=0}^{M - \ell} D_k \right], \]  
where $D_k$ is defined in (5), and where integer $\ell = \ell(M)$ is found from \[ \sum_{k=0}^{M - \ell - 1} d_k > d_M \geq \sum_{k=0}^{M - \ell} d_k. \]  

Equation (14), (15) hold for any microcanonical state (3), (6); the specific form (4) is not necessary.

We shall now calculate $W_{\text{max}}$ for two limits: $T \to \infty$ and a finite $N$, and then $N \to \infty$ and a finite $T$.

**Doubly maximized work.** – We set the number of spins $N$ to a large, but a finite number, and maximize $W_{\text{max}}(T)$ over all positive temperatures of the $N$-spin bath. The maximum is reached for $T = \infty$ (or $M = N/2$ as (7) shows) and provides an upper bound for the work extractable from the positive temperature bath. We now calculate $W_{\text{max}}(\infty)$. Consider the sum $\sum_{k=0}^{N/2} d_k = \sum_{m=0}^{N/2} d_{N/2 - m}$ in (15). The dominant summation region is $m \sim \ell$. We shall see below that $\ell \ll N$. Hence for (4) we use the Gaussian approximation $d_{N/2 - m} = 2\sqrt{\pi} e^{-m^2/N}$ (see footnote \footnote{It is derived from (4) via Stirling’s formula $N! \simeq (N/e)^N$ and expanding over $m$.}). Change the sum to integral, and find $\ell$ from
\[ 1 = \int_{\ell}^\infty dx e^{-x^2/2N^2}; \quad \ell = \sqrt{N \left( \frac{\ln \frac{N}{4\text{Im}(N/4)}}{\ln\left(\frac{N}{4\text{Im}(N/4)}\right)} + \frac{\text{Im}(N/4)}{\frac{N}{4\text{Im}(N/4)}} \right)}. \]  

The second term under square root is negligible if $N$ is large. Equation (14) then implies (for $N \gg 1$):
\[ W_{\text{max}} = \delta \int_{\ell}^\infty dx x e^{-x^2/2N^2} = \delta \ell \approx \frac{\delta}{2} \sqrt{N \ln N}. \]  

This is a reachable upper bound for the work extractable from the $N$-spin microcanonical bath.
Finite temperatures and thermodynamic limit. – We employ (4) and assume the standard thermodynamic limit: \( m = M/N < 1/2 \) (and hence \( T > 0 \)) in (7) is a fixed finite number for \( M, N \to \infty \). We note from (4) and (7) that for any fixed finite numbers \( m, \ell \) and \( N \to \infty \),
\[
\frac{d_{N,\ell} - \ell}{d_{N,\ell}} = e^{-\ell\delta/T} \left[ 1 + O \left( \frac{1}{N} \right) \right]. \tag{17}
\]
Since the sums in (14), (15) are dominated by their largest terms, using (17) (with \( m < 1 \) and integer \( \ell \)) amounts to calculating these sums via geometrical progression, e.g.,
\[
\frac{1}{d_{M}} \sum_{k=0}^{M-\ell-1} d_k = \sum_{k=0}^{\infty} k = e^{-\ell\delta/T}. \tag{18}
\]
We get for \( \ell \) and \( W_{\max} \)
\[
W_{\max}(T) = \delta \left[ \ell - 1 + v^\ell (1-v)^{-2} \right],
\]
where \( [x] \) is the ceiling (upper) integer part of \( x \), e.g., \([0.99] = 1\), \([-0.99] = 0\). According to (19), \( \ell \) grows to infinity with \( T \); \( \ell = 1 \) for \( e^{-\ell\delta/T} \leq \frac{1}{2} \), \( \ell = 2 \) for \( \frac{2}{1+\sqrt{5}} \leq e^{-\ell\delta/T} \leq \frac{1}{2} \), \( \ell = 3 \) for \( 0.6823 \leq e^{-\ell\delta/T} \leq \frac{1}{2+2\sqrt{5}} \) etc.

\( W_{\max}(T) \) is a continuous function of \( T \), but \( W_{\max}(T) \) has jumps at the temperatures, where \( \ell \) changes, and one energy shell in the final density matrix (13) is completely filled; see (15) and fig. 1. Hence
\[
W_{\max}(T) = O(\delta) \text{ for } N \gg 1 \text{ and } T = O(\delta). \tag{20}
\]

The situation is symmetric with respect to different spins of the bath. Hence after the work extraction the initial energy of each bath spin changes negligibly \( = O(1/\delta) \). The final state of each spin is diagonal in the energy representation and thus after work extraction it has a well defined temperature that differs from the initial temperature by \( O(1/\delta) \). Recall that the Gibbsian state as such cannot yield work in a cyclic process [9] [2]. Hence the work is extracted due to inter-spin correlations present initially in the microcanonical state.

Equation (18) shows that \( W_{\max}(T) \) increases faster than \( T \):
\[
W_{\max}(T) = T \left[ \ln \left( \frac{T}{\delta} \right) + 1 \right] \text{ for } T \gg \delta, \tag{21}
\]
where we used \( \ln(1-v)/\ln v \approx \ln(1-v)/v \). Equation (21) is practically good already for \( T > 1.5 \delta \). Now \( W_{\max} \) can be much larger than the energy of a single bath spin. In the limit \( T \gg \delta \) this energy is equal to \( \delta/2 \); see (7).

Microcanonical states not equivalent to the canonical one. – Equation (20) does not depend on the concrete form (4) of \( d_k \). What is needed for (20) is that the sum \( \sum d_k \) is dominated by its last term \( d_M \). Then (15) implies \( \ell = O(1) \), and (14) leads to (20). Hence (20) generalizes Thomson’s formulation of the second law to the microcanonical situation. In particular, (20) holds for those \( d_k \), where the macroscopic equivalence between microcanonical and canonical states is violated. As an example consider (3), (6) with \( d_M = e^{N(M/N)^2} \). This spectrum satisfies all above conditions and leads to (20).

Now the entropy \( \ln d_M \) is a convex function of energy \( \delta M \). Hence the specific heat \( C = [\frac{d^2 S(E)}{dE^2}]^{-1} \) calculated from (8) is negative, and the macroscopic equivalence between canonical and microcanonical states is clearly violated, because \( C > 0 \) is an automatic consequence of the canonical state [1]. Such convex-entropy spectra are realized in macroscopic long-range interacting systems [15].

Another example of convex entropy and canonical-microcanonical non-equivalence, where still (20) holds, is the first-order microcanonical phase transition [11,15], where in the vicinity of some critical energy \( E_c \), \( \frac{dS(E)}{dE} \) has a jump:
\[
\frac{dS(E)}{dE} \bigg|_{E \to E_+} = \frac{1}{\sqrt{5}}, \quad \frac{dS(E)}{dE} \bigg|_{E \to E_-} = \frac{1}{\sqrt{5}}. \tag{22}
\]
This describes coexistence of two phases with different temperatures. Since a more stable phase should have a larger entropy, we get \( T_b < T_c \) [1]. The above non-equivalence is seen here, because at a canonical first-order phase transition different phases have the same temperature [1]. Even though two phases at different temperatures do co-exist, the extracted work has the same order of magnitude (20) as for a homogeneous-temperature microcanonical state.

System coupled to the bath. – An important instance of the maximal work problem is the amount of work extractable from a thermal bath in the presence of a smaller system coupled to it; see (1). How much work can be extracted from a combined state of a two level system with energies \( 0 \) and \( \epsilon > 0 \) and the microcanonical thermal bath? Answering this question will allow us to understand to which extent the concept of the free energy applies to the microcanonical situation. Before starting the analysis we should like to stress again that so far the statistical physics literature has not distinguished between canonical and microcanonical situations when introducing and applying the free-energy concept; see, e.g., [1].

Let the initial density matrix of the two-level system be \( \rho_i \); its eigenvalues are \( \pi_0 > \pi_1 \). The spectrum of the overall initial state \( \rho_i \equiv \rho_i \otimes \Omega \) reads (see (6), (5))
\[
\operatorname{Spec}[\rho_i] = \frac{1}{d_M} \begin{bmatrix} \pi_0 e_{d_M}, \pi_1 e_{d_M}, 0 & 2D_N - 2d_M \end{bmatrix}, \quad \pi_0 > \pi_1.
\tag{22}
\]
Both initially and finally the two-level system and bath do not interact. Hence the overall Hamiltonian $\mathcal{H}$ reads
\[
\mathcal{H} = \mathcal{H}(\tau) = H_S \otimes 1 + 1 \otimes H
\]
where $H$ is given by (3), and $H_S$ is the two-level Hamiltonian with energies 0 and $\epsilon$. We recall that each symbol $k\delta$ (or $\epsilon + k\delta$) in (24) is repeated $d_k$ times. Once we consider unitary work extraction processes, the final state of the overall system will have the same eigenvalues (22). Recalling our discussion between (11) and (13) it should be clear that the minimal final energy for the overall system is achieved for the unitary operator that forces $R_\rho$ to have the same eigenvectors as $\mathcal{H}$ and permutes the eigenvalues (22) such that the largest eigenvalue is matched with the smallest energy, next to the largest eigenvalue with the next to the smallest energy and so on. Note that Spec$[R_\rho]$ is already ordered in a non-increasing way. It remains to order (24) in a non-decreasing way and write the lowest final average energy as a scalar product of two vectors
\[
\text{tr}(\mathcal{H}[R_\rho - R_{\rho - 1}]) = W_{\text{max}} + W_{\text{sur}} + \text{tr}(H_S[\rho_{1} - \rho_{1}]),
\]
where $W_{\text{max}}$ + $W_{\text{sur}}$ is the work coming from the bath. Here $W_{\text{max}}$ is given by (14) (the maximal work extracted from the bath alone) and we defined the surplus work $W_{\text{sur}}$ (work extracted from the bath, but due to the system).

Obviously, $W_{\text{sur}} + \text{tr}(H_S[\rho_{1} - \rho_{1}]) \geq 0$, since $\text{tr}(\mathcal{H}[R_{\rho} - R_{\rho - 1}])$ results from optimizing over a larger set of parameters than $W_{\text{max}}$. Note that $\text{tr}(H_S[\rho_{1} - \rho_{1}])$ appears also on the right-hand side of (1), and there is some analogy between $W_{\text{sur}}$ and the entropy difference $T(\text{tr}[-\rho_{\text{eq}} \ln \rho_{\text{eq}} + \rho \ln \rho])$ in (1), which is the work extracted from the canonical bath. There the work $W_{\text{max}}$ extracted from the canonical equilibrium bath alone (without the system) is zero.

The scalar product (25) is calculated straightforwardly; for clarity we focus on the thermodynamic limit regime (17):
\[
W_{\text{max}} + W_{\text{sur}} = \delta(\pi_{1}F_{2} + (\pi_{0} - \pi_{1})F_{1}),
\]
where $W_{\text{max}}$ is given by (18) and we defined, for $k = 1, 2$,
\[
F_k \equiv k(\ell_{1k} - 1) + v^{\ell_{1k}} \frac{1 + v^{\alpha}}{1 - v} \left[ \frac{1 - v^{\alpha}}{1 - v} + \frac{\alpha v^{\alpha}}{1 + v^{\alpha}} \right] \]
\[
+ \alpha \text{sign}(\ell_{1k} - \ell_{2k}) \left[ k - v^{\ell_{2k}} \frac{(1 + v^{1+\alpha})}{1 - v} \right],
\]
\[
P_k \equiv \frac{v^{\ell_{1k}+\alpha}}{1 - v} + \text{sign}(\ell_{1k} - \ell_{2k}) \left[ k - v^{\ell_{2k}} \frac{(1 + v^{1+\alpha})}{1 - v} \right] \]
Recall that $\text{sign}(0) = 0$, $\alpha = [\frac{x}{\delta}]$, and that $[x]$ and $\delta$ are defined after (25) and (18), respectively.

The final state $\rho_{T}$ of the two-level system is diagonal in its energy representation. The eigenvalues of $\rho_{T}$ are read off from (28). The excited state of $\rho_{T}$ is less populated than the ground state; otherwise it can still provide work via a cyclic process. In this specific sense the two-level system partially equilibrates; recall that $\rho_{T}$ is arbitrary.

Figure 1 displays $W_{\text{max}}(T)$ and $W_{\text{sur}}(T)$ for a representative range of parameters. It is seen that for $\alpha = 0$, $W_{\text{max}} \geq 0$ and both $W_{\text{max}}$ and $W_{\text{sur}}$ monotonically increase with $T$. For $\alpha > 0$ the positivity of $W_{\text{sur}}$ is recovered only for a sufficiently high $T$ provided that $\pi_{0} \neq \pi_{1}$; see fig. 1. For $\pi_{0} = \pi_{1}$, we always get $W_{\text{sur}} < 0$.

Consider now $\epsilon < \delta$ (i.e. $\alpha = 0$ in (25)) and assume $\epsilon \equiv e^{-\delta/T} \leq 1/3$ for simplicity. Equations (27)–(30) produce
\[
W_{\text{sur}} = v\delta(2\pi_{0} - 1)(1 - v)^{-2},
\]
\[
\text{tr}(H_S[\rho_{1}]) = e^{\frac{1}{v} (v \pi_{0} + (1 - 3v)\pi_{1})} (1 - v)^{-1}.
\]
Equation (31) shows that, in addition to $W_{\text{sur}} + \text{tr}(H_S[\rho_{1}]) \geq 0$, the work extracted from the bath is enhanced, $W_{\text{sur}} > 0$, for any state of the two-level system besides the completely mixed one, where $\pi_{0} = \pi_{1} = \frac{1}{2}$.

The energy difference $\text{tr}(H_S[\rho_{1} - \rho_{1}])$ can be positive or negative. Hence parameters can be tuned such that it is zero, e.g., from (32) and for $\epsilon = T \ln 2 < T \ln 3 < \delta$ we get that initially canonical equilibrium two-level system, $\pi_{0} = 1 - \pi_{1} = (1 + e^{-\epsilon/T})^{-1} = \frac{1}{2}$, enhances the work extracted from the bath without changing its marginal state: $\rho_{1} = \rho_{T}$. Hence for enhancing the work extracted from the microcanonical bath one needs that the system is ordered: its state should not be completely mixed, while the maximal enhancing is achieved for a pure state. But the state of the system need not change.

A non-equilibrium system coupled to canonical equilibrium bath can enhance the work extracted from the bath only at the cost of changing (towards equilibrium) its initially non-equilibrium state; see (1). The free energy measures this change. For the microcanonical bath, the work can be enhanced already by an equilibrium two-state system without changing its marginal state. We conclude that the concept of the free energy does not generally apply to a system coupled to a microcanonical bath.

But this concept applies in the high-temperature limit. For $T \gg \epsilon$, we get from (27)–(30) and from (21):
\[
W_{\text{sur}} = (1 - 2\pi_{1})T \ln 2,
\]
\[
\text{tr}(H_S[\rho_{1}]) = e^{1/2}.
\]
Equation (34) means that the final state of the two-level system is completely mixed, which for the present high-temperature case coincides with the canonical equilibrium
state. Equation (33) predicts work enhancement only if initially the two-level system was out of equilibrium (recall that $\frac{1}{\mu} \geq \pi_1$). Hence for $T > \delta$, we recover the logics of the canonical-bath situation, but not its letter, because for a canonical bath $W_{\text{surf}}$ reduces to the difference between two von Neumann entropies that are logarithmic functions of the initial eigenvalues $\pi_0$ and $\pi_1$; cf. our remark after (26).

We shall show elsewhere that a for a $\mu$-level system in a state (density matrix) $\rho$ ordered as $\pi_0 \geq \pi_1 \geq \ldots \geq \pi_{\mu-1}$, we can define the linear entropy as

$$L[\rho] = \sum_{k=1}^{\mu-1} \pi_k [(k+1) \ln (k+1) - k \ln k].$$

Generalizing (33), the surplus work $W_{\text{surf}}$ extracted from a high-temperature microcanonical bath in contact with this system is then

$$W_{\text{surf}} = T (\ln \mu - L[\rho]) = T(\frac{1}{\mu} - L[\rho]),$$

where $\frac{1}{\mu}$ is the maximally mixed state of the $\mu$-level system.

For a system that is out of equilibrium the von Neumann entropy $-\text{tr}(\rho \ln \rho)$ instead of $L[\rho]$. Note that $\ln \mu \geq L[\rho] \geq 0$: the upper (lower) limit is reached for the maximally mixed (pure) $\rho$.

Hence for a system in initial state $\rho$ and Hamiltonian $H_{S}$ coupled to the high-temperature microcanonical bath one can define the microcanonical free energy $F[\rho] = \text{tr}(H_S \rho) - T L[\rho]$, whose difference $F[\rho] - F[\rho_0]$ (after adding to $W_{\text{max}}$ extracted from the bath alone) defines the maximal work extracted from the system + bath.

**Summary.** — We reformulated Thomson’s formulation of the second law for a ($N > 1$)-particle equilibrium bath in a microcanonical state: if the bath temperature $T$ is finite, the maximal work extractable from the bath via a cyclic Hamiltonian process is $\geq \delta$, where $\delta$ is the energy of a single bath particle. The maximal work tends to $\delta \sqrt{N \ln N}$ if $N$ is large but fixed and $T \to \infty$. The reformulation applies equally well to both ordinary microcanonical states, which are macroscopically equivalent to canonical states, and convex-entropy microcanonical states for which no canonical state can be defined, e.g., because of a negative specific heat [15].

The existence of such states demonstrates that a viewpoint on a microcanonical state as emerging from measuring the energy of the canonical state is not generally valid. Thermodynamics of such systems can have peculiarities [23], but we saw that they satisfy the same generalized Thomson’s formulation much in the same way as ordinary microcanonical states. The work extraction is possible, since the microcanonical state of the bath is not Gibbsian, though each of its constituent can be in a Gibbsian state.

It is widely known that only a non-equilibrium system can lead—at the expense of changing its state towards equilibrium—to work extraction from a canonical bath [1]. This work is given by the free-energy difference (1). In contrast, a canonical equilibrium system (having the same temperature as the bath) can enhance the work extracted from the microcanonical bath without changing its marginal state. Hence the concept of free energy, in the sense of the maximal work, does not generally apply to the microcanonical situation. The application of the concept is recovered for $T \gg \delta$, but the canonical expression of the free energy is not restored, instead it should be formulated via the linear entropy (35).

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