Fundamental limitations for quantum and nano thermodynamics

Michał Horodecki[1] & Jonathan Oppenheim[2,31]

[1] *IFTIA, University of Gdańsk, 80-952 Gdańsk, Poland*
DAMTP, University of Cambridge, CB3 0WA, Cambridge, UK
University College of London, Department of Physics & Astronomy, London, WC1E 6BT and London Interdisciplinary Network for Quantum Science

The relationship between thermodynamics and statistical physics is valid in the *thermodynamic limit* – when the number of particles involved becomes very large. Here we study thermodynamics in the opposite regime – at both the nano scale, and when quantum effects become important. Applying results from quantum information theory we construct a theory of thermodynamics in these extreme limits. In the quantum regime, we find that the standard free energy no longer determines the amount of work which can be extracted from a resource, nor which state transitions can occur spontaneously. We derive a criteria for thermodynamical state transitions, and find two free energies: one which determines the amount of work which can be extracted from a small system in contact with a heat bath, and the other which quantifies the reverse process. They imply that generically, there are additional constraints which govern spontaneous thermodynamical processes. We find that there are fundamental limitations on work extraction from nonequilibrium states, due to both finite size effects which are present at the nano scale, as well as quantum coherences. This implies that thermodynamical transitions are generically irreversible at this scale, and we quantify the degree to which this is so, and the condition for reversibility to hold. There are particular equilibrium processes which approach the ideal efficiency, provided that certain special conditions are met.

One of the most basic quantities in thermodynamics is the Helmholtz free energy

$$F(\rho) = \langle E(\rho) \rangle - TS(\rho) \tag{1}$$

with T the temperature of the ambient heat bath that surrounds the system, $S(\rho)$ the entropy of the system, and $\langle E \rangle$ its average energy. It tells us whether a system at constant volume and in contact with a heat bath can make a spontaneous thermodynamical transition from one state to another. A transition can only happen if the free energy of the final state is lower than that of the initial state. The difference in free energy between the initial and final state is also the amount of work which can be extracted from a system in a thermal bath. It is also gives the amount of work required to perform the reverse process, since thermodynamics at the macroscopic scale is reversible.

However, the free energy is only valid in the thermodynamical limit – when ρ is composed of many particles and is classical, in the sense that it is in a state which is a probabilistic mixture of different energies. But thermodynamical effects are not only important in the macroscopic regime – they are becoming increasingly important as we probe and manipulate small systems from the micro up to the mesoscopic scale. Already, molecular motors and micro-machines[1–6] have been constructed in the lab[7–10] and thermodynamical effects are increasingly important in quantum devices and in the construction of quantum computers and memory[11, 12]. Likewise, quantum effects have implications for thermodynamics [13–15]. Here, we derive two free energies which are valid even when the thermodynamical limit is not taken, and even when the system is quantum. We also derive a criteria for state to state transitions, and a criteria for when transitions between two classical states can be made reversible in the micro-regime.

We will first consider a quantum system

$$\rho = \sum \sigma(E, E', g, g') |E, g\rangle\langle E', g'| \tag{2}$$

with a fixed Hamiltonian H and eigenstates of energy E given by $|E, g\rangle$, in contact with a heat bath. We are interested in the types of state transitions which are allowed, and in particular, our ability to use the system as a resource to extract work. We will then consider the case where the Hamiltonian of the initial and final state is not the same, so that the system undergoes a non-cyclic evolution.

Instead of considering macroscopic work (the pushing out of a piston, or the raising of a weight), we consider microscopic work – for example, the exciting of an atom from its ground state to an excited state (Figure 1). We can thus use a two level system to store work. Because the amount of extractable work can be small, we require precise accounting of all sources of energy. We thus consider a paradigm where extraction of work, and other operations must be done using energy conserving operations[16], so that any energy which is transferred to or from the resource system and heat bath, is transferred from or to the system which stores work. This casts thermodynamics as a *resource theory*[16–21], which allows us to exploit some mathematical machinery from information theory. Thermodynamics is then viewed as a theory involving state transformations in the presence of a thermal bath. The extraction or

FIG. 1: A macroscopic heat engine which performs work by lifting a heavy object a certain height (left). In the quantum or micro-regime, we can think of work as the ability to excite a two-level system from one energy state to a higher one (right). Having many of these atoms would allow us to perform macroscopic work – for example, we could use the atoms in a laser. An amount of work W can be used to produce a transition from the state $|0\rangle\langle 0|$, to the state $|1\rangle\langle 1|$, with Hamiltonian $\hat{W} = W|1\rangle\langle 1|$ (we call such a two-level system, the *work qubit*, or *wit*). We can use such a system as a basic work storage unit, since our results will not depend on what physical system is used.

expenditure of work can be included in such a paradigm, because it is equivalent to a state transformation – the state of the work qubit is raised or lowered from one energy eigenstate to another. We call the class of operations that are allowed *Thermal Operations* – a fuller discussion of which is contained in Section A of the Appendix.

Having precisely accounted for all sources of energy, we can show in Section D of the Appendix, that the quantity which replaces the Helmholtz Free Energy for calculating the extractable work in the quantum regime is

$$F_\epsilon^{min}(\rho) = -kT \inf_{\omega_\epsilon} \ln \sum h(\omega_\epsilon, g, E_i) e^{-\beta E_i} \tag{3}$$

where $\omega = \sum_E P_E \rho_\epsilon P_E$ with $P_E = |E\rangle\langle E|$ is the state ρ decohered in the energy eigenbasis (i.e. off-diagonal terms are set to zero), ω_ϵ is any state such that $||\omega_\epsilon - \omega||_1 \leq \epsilon$ and $h(\omega_\epsilon, g, E_i)$ is 1 if energy level $|g, E_i\rangle$ is populated and 0 otherwise. β is the inverse temperature, and k is Boltzmann's constant. The significance of ϵ is that it takes into account the situation where we allow a tiny probability ϵ of failing to draw work[22]. In terms of information theoretic quantities, we can write

$$F_\epsilon^{min}(\rho) - F_\epsilon^{min}(\tau) = T D_{min}^\epsilon(\rho||\tau) \tag{4}$$

, where $D_{min}^\epsilon(\omega||\tau) := -\inf_{\omega_\epsilon} \ln \mathsf{tr}\, \Pi_{\omega_\epsilon} \tau$ is the min-relative entropy[23] with Π_{ω_ϵ} the projector onto the support of ω_ϵ and τ is the Gibbs state $\tau = Z^{-1} \sum_{E,g} e^{-\beta E} |E, g\rangle\langle E, g|$ with partition function Z. The min-relative entropy and single-shot free energy has been independently introduced to quantify work extraction from classical states using a model of a series of independent interactions with a heat bath[24]

In the thermodynamical limit $D_{min}(\rho||\tau)$ becomes[25] $S(\rho||\tau)$ the relative entropy $S(\rho||\tau) := -\mathsf{tr}\, \rho \log \tau + \mathsf{tr}\, \rho \log \rho$. Thus, while the maximum amount of work W which can be extracted when a macroscopic system is in contact with a heat bath, is $W(\rho) = F(\rho) - F(\tau)$, more generally it is $W = F_\epsilon^{min}(\rho) - F_\epsilon^{min}(\tau)$ and only in the thermodynamical limit do we recover the traditional result.

Although the quantity of Equation (3) looks very different to the Helmholtz Free Energy, it can be compared to it easily in the situation where the system's energy fluctuations δE are small compared with the average energy $\langle E \rangle$ as is the case with macroscopic thermodynamical systems. We then find by Taylor expanding Equation (3) and taking the zeroeth order approximation that

$$F_\epsilon^{min}(\rho) \approx \sup_{\omega_\epsilon} [\langle E \rangle - kT \ln \mathrm{rank}(\omega_\epsilon)] \tag{5}$$

In the case where the system is diagonal in the energy eigenbasis i.e.

$$\rho = \sum_{E,g,g'} \sigma_{E,g,g'} |E, g\rangle\langle E, g'| \quad , \tag{6}$$

we have that $\rho = \omega$. Then, for extensive systems and the case of many particles n, the quantity $\ln \mathrm{rank}(\omega_\epsilon) = \ln \mathrm{rank}(\rho_\epsilon) \approx S(\rho)$ [25] with ϵ going to zero exponentially fast in n. We then have that Equation (5) approaches the Helmholtz Free Energy.

In general however, $\inf_{\rho_\epsilon} \mathrm{rank}(\rho_\epsilon)$ is larger than the entropy $S(\rho)$, especially in the case where we just have a single system in the micro-regime, meaning that F_ϵ^{min} is smaller than the free energy. The finite size of the system means that less work can be extracted.

There is a second reason why a limitation exists on the amount of extractable work. A quantum system ρ needn't be in the form of Equation (6) and in particular can have off-diagonal terms connecting different energy eigenstates. However, it is not ρ which enters into Equation (3), but rather the state ρ decohered in the energy eigenbasis, namely ω. Thus, to zeroeth order, rather than the rank of ρ_ϵ replacing the entropy, it is the rank of ρ_ϵ dephased in the energy eigenbasis that replaces the entropy. This quantity is generally larger than the rank of ρ_ϵ which is why for systems with quantum coherences of energy, there is a further limitation on how much work can be extracted. As an example, consider the pure quantum state

$$|\psi\rangle = \sum_{E,g} \sqrt{\frac{e^{-\beta E}}{Z}} |E, g\rangle \quad . \tag{7}$$

It has entropy and rank equal to zero. However, when dephased in the energy eigenbasis to produce ω, it becomes the Gibbs state, and has free energy $-kT \ln Z$; no work can be extracted from it, despite it having zero entropy. However, as we approach the thermodynamic limit, the coherences matter less and less, and the free energy in the quantum case approaches the free energy for classical states[21], and again, F_{min} approaches the Helmholtz Free Energy.

The fact that at the quantum or nanoscale one can't extract the work as given by the free energy, implies that there is an inherent irreversibility in thermodynamic transformations. This can also be seen as follows – the maximum amount of work which can be extracted from a system ρ in contact with a heat bath is given by $F_{min}(\rho) - F_{min}(\tau)$. In the process, the system is transformed from state ρ to the Gibbs state τ. But if we wish to use work to perform the reverse process, namely transform Gibbs states into ρ using work, then we show in D of the Appendix that the amount of work which is required is $F_\epsilon^{max}(\rho) - F_\epsilon^{max}(\tau)$ with

$$F_\epsilon^{max}(\rho) = kT \inf_{\rho_\epsilon} \log \min\{\lambda : \rho \leq \lambda\tau\} - kT \ln Z \tag{8}$$

in the case where ρ is diagonal in the energy eigenbasis. In general, $F_\epsilon^{min} \leq F_\epsilon^{max}$, so that at the nanoscale we can generally extract less work from a resource than is required to create the resource, leading to a fundamental irreversibility in thermodynamical processes. In terms of information theoretic quantities, $F_\epsilon^{max}(\rho) - F_\epsilon^{max}(\tau) = TD_{max}(\rho||\tau)$, where $D_{max}(\rho||\tau) := \log \min\{\lambda : \rho \leq \lambda\tau\}$ is the max-relative entropy[23]. As we approach the thermodynamic limit $F_\epsilon^{min} \approx F_\epsilon^{max}$, and reversibility is restored[25].

More generally, we would like criteria which tells us whether one state can be transformed into another under some thermodynamical process. As we have seen, because of finite size or quantum effects, the decreasing of the free energy is not a valid criteria which determines whether a thermodynamic transition can occur. For transitions between a system ρ and a system σ, both diagonal in the energy eigenbasis, we can derive such criteria, which we call thermo-majorization. It is based on the majorization condition for state transformations which is a necessary and sufficient condition for state transformations under permutation maps. It's construction is given in Section C of the Appendix, and we state the result in Box 2.

In the case where ρ is not diagonal in the energy eigenbasis, but the final state σ is diagonal, then transformations are possible if and only if transformations are possible from ω to σ. The reason is simple – dephasing in the energy eigenbasis commutes with Thermal Operations[21] since the latter must conserve energy. Since we can dephase the final state without changing it (as it is already diagonal in the energy basis) we can use the fact that dephasing commutes with our operations to instead dephase the initial state without changing whether the transformation is possible.

In the case where the final state is also non-diagonal in the energy basis, the criteria for which transformations are possible depends on the coupling one has with the system, and especially, the degree of control one has of the system. Thus far, our results have not depended on having fine-grained control of the system and heat bath – the interaction depends on macroscopic variables such as total energy E, but the mapping between microstates g does not matter[21]. This is not necessarily the case during the formation process of states with off-diagonal terms. Thus, while Equation (3) for the extractable work holds in general, the same is not true of Equation (8) for the formation process. This is because for the formation process of transforming Gibb's states into a state ρ which is not diagonal in the energy eigenbasis, it is generally not possible to make such a transformation using Thermal Operations without additional resources. In the case of formation of many copies n of ρ, the additional resource can be two level pure states in a superposition of energy levels[21], and the number of them required is sublinear in n and hence vanishes as a fraction of n.

So far we have considered transitions between the states of a system with fixed Hamiltonian. This might suggest that our approach does not cover the microscopic analogue of thermodynamical processes between equilibrium states with different initial and final Hamiltonians[3], such as isothermal expansions of a gas in a container. Yet, fundamentally, a time dependent Hamiltonian is only an effective picture of a fixed Hamiltonian of a larger system, and we shall show below how to describe such transitions in the microscopic regime.

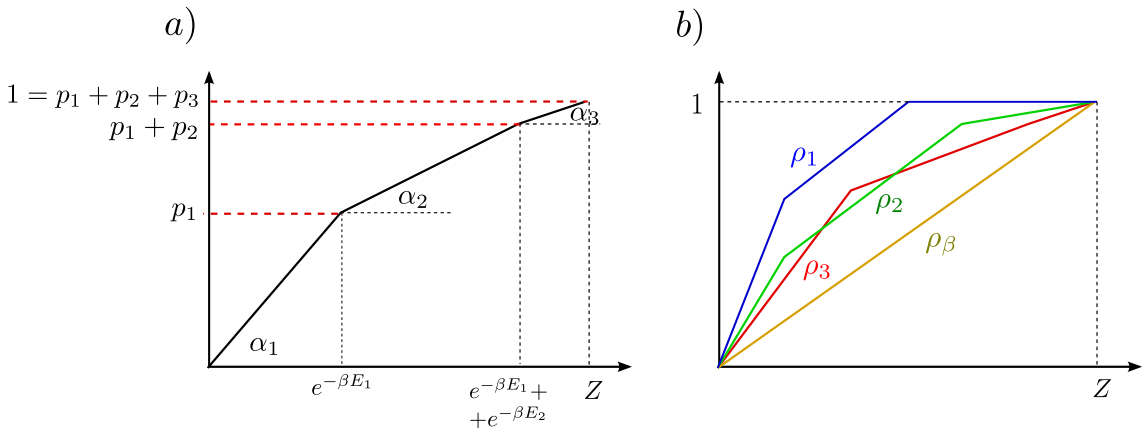

FIG. 2: Consider probabilities $p(E, g)$ of the initial system ρ to be in the g'th state of energy E. Now let us put $p(E, g)\mathrm{e}^{-\beta E}$ in decreasing order $p(E_1, g_1)\mathrm{e}^{-\beta E_1} \geq p(E_2, g_2)\mathrm{e}^{-\beta E_2} \geq p(E_3, g_3)\mathrm{e}^{-\beta E_3}$... – we say that the eigenvalues are β-ordered. We can do the same for system σ i.e. $\mathrm{e}^{-\beta E_1} q(E_1, g_1) \geq \mathrm{e}^{-\beta E_2} q(E_2, g_2) \geq \mathrm{e}^{-\beta E_3} q(E_3, g_3)$.... Then the condition which determines whether we can transform ρ into σ is depicted in the above figure. Namely, for any state, we construct a curve with points k given by $\{\sum e^{-\beta E_i}/Z, \sum_i^k p_i\}$. Then a thermodynamical transition from ρ to σ is possible if and only if, the curve of ρ lies above the curve of σ.

Namely we introduce a qubit on system C which we can act on to switch the Hamiltonian from H to H' (we call this the *switching qubit*). We can for example take the total Hamiltonian to be

$$H_{tot} = |0\rangle\langle 0|_C \otimes H + |1\rangle\langle 1|_C \otimes H' + W|1\rangle\langle 1| \tag{9}$$

and take the initial state of the work qubit, switching qubit and system to be $|00\rangle\langle 00|_{CW} \otimes \rho$ and final state to be $|11\rangle\langle 11|_{CW} \otimes \sigma$, so that we are effectively changing the Hamiltonian acting on ρ, and gaining or losing work in the work qubit when we make the transition to σ. We now consider a transitions between ρ and τ', and want to know what value (positive or negative) for W allows us to make this transition.

The results, obtained by means of thermo-majorization are depicted in Figure 3. One finds

$$W = F_\epsilon^{min}(\omega) - F_\epsilon^{min}(\tau') \tag{10}$$

for extracting work, and for the amount of work required to form ρ (provided it is diagonal in energy eigenbasis) from the thermal state, we obtain

$$W = F_\epsilon^{max}(\rho) - F_\epsilon^{max}(\tau') \tag{11}$$

This result does not depend on the form of the Hamiltonian of Equation (9) – we only require that at late times, there is no interaction between the work qubit and the other systems (since we need to be able to separate out the work qubit to use in some future process).

To derive Equations (10)-(11), we β-order the p_i and q_i corresponding to $\rho \otimes |00\rangle\langle 00|$, and $\sigma \otimes |11\rangle\langle 11|$ respectively. Then the thermo-majorization coordinates k of $\rho \otimes |00\rangle\langle 00|$ are given by $\{\sum_1^k e^{-\beta E_i}, \sum_1^k p_i, \}$, and those of $\sigma \otimes |11\rangle\langle 11|$ are $\{\sum_1^k e^{-\beta(E_i'+W)}, \sum_1^k q_i, \}$. The thermo-majorization condition for a transition is that for all k, the points associated with ρ are above that of σ and they take a particularly simple form when either ρ or σ is the thermal state. These two cases are shown in Figure 3. The case where the final state is thermal for Hamiltonian H', $\sigma = \tau'$, and the work qubit is excited corresponds to distillation, since no further work can be drawn for fixed H' once the state is thermal, and a transition to another state can always be followed by a transition to the thermal state. Therefore drawing work by relaxing the state to a thermal state is completely general, and gives us Equation (10). If ρ has off-diagonal terms, then the distillable work is given by the decohered version ω in Equation (10), due to the same reasoning as we used earlier – the final state is simply the work qubit, since everything else can be thrown away, and therefore is diagonal in the energy eigenbasis. Since decohering the final state doesn't change the final state, and decohering with respect

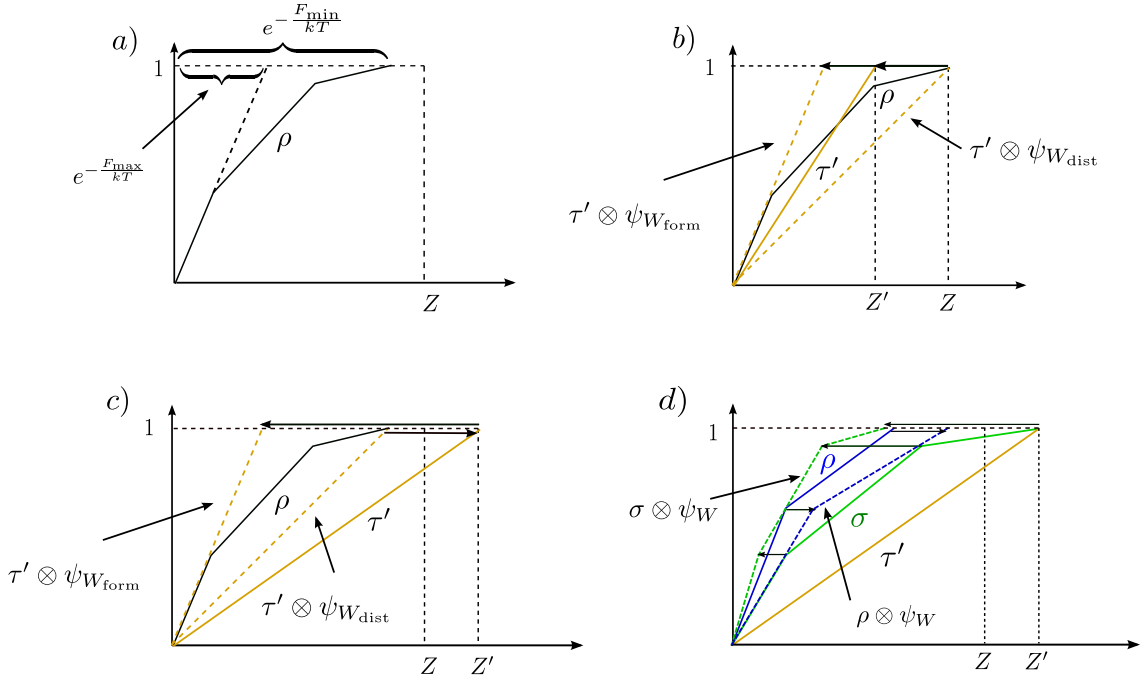

FIG. 3: **Distillable work and work of formation.** (a) Graphical representation of two free energies. For Gibbs state they coincide. (b),(c): The scenario of changing Hamiltonian we can mimic by adding to the system S ancilla C switching between initial H and final Hamiltonian H', with partition functions Z, Z', respectively. We consider transition $\rho \to \tau'$ and $\tau' \to \rho$, and obtainable works denote by W_{dist} and W_{dist} respectively. The works can be of either signs. Adding/Subtracting work to a Gibbs state is graphically represented as changing the its slope. Formation is depicted by arrow going from ρ to τ', distillation by arrow going from τ' to ρ. The directions of arrow to the right/left means that the work is positive/negative in given transition. Positive work, means that we obtain work during the process. We depict two out of possible four cases of work signs: (b) both works are negative (c) work of formation is negative while work of distillation is positive. (d) The interconversion of two arbitrary states is depicted.

to the total Hamiltonian commutes with thermal operations, we can do it to the initial state without affecting the amount of work extractable.

The case where we adjust W so that $\rho \otimes |00\rangle\langle 00|_{CW}$ is thermo-majorized by $\sigma \otimes |11\rangle\langle 11|_{CW}$ gives us the formation process, and free energy of Equation (10). The case where both initial and final states ρ,σ are thermal is also depicted in Figure 3, and leads to the ideal classical result, namely that a transition is possible if and only if

$$W = -T \ln Z/Z' \tag{12}$$

i.e. the work is given by the difference of standard free energies (1). This is a very different result to Equation (3), where the work qubit and system have no interaction term as in Equation (9). It shows that for thermal equilibrium states there can be reversibility in some thermodynamical processes, provided they are between two thermal equilibrium states and the Hamiltonian changes. In the picture of a fixed Hamiltonian, this required at least one additional system (the switching qubit), which is effectively not in contact with the heat bath, and we do not draw the maximal amount of extractable work from the total working body, given by $F_\epsilon^{min}(\rho_S \otimes |0\rangle\langle 0|_C)$. The final state is thermal only on a subsystem S and therefore the amount of drawn work is not optimal.

In general, we only get reversibility if there exists a W, such that the thermo-majorization plot of the initial state $\{\sum e^{-\beta E_i}/Z, \sum_i^k p_i\}$, can get mapped onto the plot of the final state $\{\sum e^{-\beta(E_i'+W}/Z', \sum_i^k q_i\}$. Thus reversibility requires a very special condition. It is this lack of reversibility which requires two free energies. There is a connection here with other resource theories. Consider the set of states which are preserved under the class of operations – in entanglement theory, these are separable states, and for Thermal Operations, we show in Section E of the Appendix that it is the Gibbs state. Now, if the theory is reversible, then under certain conditions, the relative entropy distance

to the preserved set is the unique measure which governs state transformations[20, 26]. For Thermal Operations, the relative entropy distance to the Gibbs state is precisely the free energy difference[27]. Here, in the case of finite sized systems, we see that although we don't have reversibility, the relative entropy distance to the preserved set again enters the picture, but it is the min and max relative entropy. These quantities are monotonically decreasing under the class of Thermal Operations, and provide two measures for state transitions.

[1] Scovil, H. E. D. & Schulz-DuBois, E. O. Three-level masers as heat engines. *Phys. Rev. Lett.* **2**, 262–263 (1959). URL `http://link.aps.org/doi/10.1103/PhysRevLett.2.262`.

[2] Geusic, J. E., Schulz-DuBios, E. O. & Scovil, H. E. D. Quantum equivalent of the carnot cycle. *Phys. Rev.* **156**, 343–351 (1967). URL `http://link.aps.org/doi/10.1103/PhysRev.156.343`.

[3] Alicki, R. The quantum open system as a model of the heat engine. *J. Phys. A: Math. Gen.* **12**, L103–L107 (1979).

[4] Howard, J. Molecular motors: structural adaptations to cellular functions. *Nature* **389**, 561–567 (1997).

[5] Geva, E. & Kosloff, R. On the classical limit of quantum thermodynamics in finite time. *The Journal of chemical physics* **97**, 4398 (1992).

[6] Linden, N., Popescu, S. & Skrzypczyk, P. How small can thermal machines be? the smallest possible refrigerator. *Physical review letters* **105**, 130401 (2010).

[7] Scovil, H. E. D. & Schulz-DuBois, E. O. Three-level masers as heat engines. *Phys. Rev. Lett.* **2**, 262–263 (1959). URL `http://link.aps.org/doi/10.1103/PhysRevLett.2.262`.

[8] Scully, M. O. Quantum afterburner: Improving the efficiency of an ideal heat engine. *Phys. Rev. Lett.* **88**, 050602 (2002). URL `http://link.aps.org/doi/10.1103/PhysRevLett.88.050602`.

[9] Rousselet, J., Salome, L., Ajdari, A. & Prost, J. Directional motion of brownian particles induced by a periodic asymmetric potential. *Nature* **370**, 446–447 (1994).

[10] Faucheux, L. P., Bourdieu, L. S., Kaplan, P. D. & Libchaber, A. J. Optical thermal ratchet. *Phys. Rev. Lett.* **74**, 1504–1507 (1995). URL `http://link.aps.org/doi/10.1103/PhysRevLett.74.1504`.

[11] Landauer, R. *IBM J. Res. Develop.* **5**, 183 (1961).

[12] Bennett, C. H. The thermodynamics of computation-a review. *Int. J. Theor. Phys.* **21**, 905–940 (1982).

[13] Gemmer, J., Michel, M., Michel, M. & Mahler, G. *Quantum thermodynamics: Emergence of thermodynamic behavior within composite quantum systems* (Springer Verlag, 2009).

[14] Popescu, S., Short, A. & Winter, A. Entanglement and the foundations of statistical mechanics. *Nature Physics* **2**, 754–758 (2006).

[15] Del Rio, L., Åberg, J., Renner, R., Dahlsten, O. & Vedral, V. The thermodynamic meaning of negative entropy. *Nature* **474**, 61–63 (2011).

[16] Janzing, D., Wocjan, P., Zeier, R., Geiss, R. & Beth, T. Thermodynamic cost of reliability and low temperatures: Tightening Landauer's principle and the second law. *Int. J. Theor. Phys.* **39**, 2717–2753 (2000). quant-ph/0002048.

[17] Werner, R. F. Quantum states with einstein-podolsky-rosen correlations admitting a hidden-variable model. *Phys. Rev. A* **40**, 4277–4281 (1989).

[18] Bennett, C. H., DiVincenzo, D. P., Smolin, J. A. & Wootters, W. K. Mixed-state entanglement and quantum error correction. *Phys. Rev. A* **54**, 3824–3851 (1996). quant-ph/9604024.

[19] Horodecki, M., Horodecki, P. & Oppenheim, J. Reversible transformations from pure to mixed states and the unique measure of information. *Phys. Rev. A* **67**, 062104 (2003). quant-ph/0212019.

[20] Horodecki, M., Oppenheim, J. & Horodecki, R. Are the laws of entanglement theory thermodynamical? *Phys. Rev. Lett.* **89**, 240403 (2002). quant-ph/0207177.

[21] F.G.S.L. Brandao, M. Horodecki, J. Oppenheim, J. Rennes and R.W. Spekkens, "The Resource Theory of Quantum States Out of Thermal Equilibrium" in preparation.

[22] Dahlsten, O., Renner, R., Rieper, E. & Vedral, V. Inadequacy of von neumann entropy for characterizing extractable work. *New Journal of Physics* **13**, 053015 (2011).

[23] Datta, N. Min-and max-relative entropies and a new entanglement monotone. *Information Theory, IEEE Transactions on* **55**, 2816–2826 (2009).

[24] J. Ahlberg, to appear.

[25] For extensive, isotropic systems, correlations don't play a role in thermodynamical quantities, and we may thus take the system to be composed of many systems in state $\rho^{\otimes n}$. We then obtain the classical results[21], and the smoothed min and max entropies approach the von-Neumann entropy[28].

[26] Brandao, F. G. & Plenio, M. B. A reversible theory of entanglement and its relation to the second law. *Nat. Phys.* **4**, 873 (2008). arXiv:0710.5827.

[27] Donald, M. J. Free energy and the relative entropy. *Journal of Statistical Physics* **49**, 81–87 (1987).

[28] Renner, R. Ph.D. thesis, ETH, Zurich (2005).

[29] Bennett, C. H., Bernstein, H. J., Popescu, S. & Schumacher, B. Concentrating partial entanglement by local operations. *Phys. Rev. A* **53**, 2046–2052 (1996). quant-ph/9511030.

[30] Janzing, D. & Beth, T. Quasi-order of clocks and their synchronism and quantum bounds for copying timing information. *IEEE Trans. Inf. Theory* **49**, 230–240 (2003).

[31] Gour, G. & Spekkens, R. W. The resource theory of quantum reference frames: manipulations and monotones. *New J. Phys.* **10**, 033023 (2008).
[32] Marvian, I. & Spekkens, R. W. Pure state asymmetry. *arXiv:1105.1816 [quant-ph]* (2011).
[33] Uhlmann, A. *Wiss Z. Karl-Marx-Univ. Leipzig* **20**, 633 (1971).
[34] Alicki, R. & Lendi, L. *Quantum dynamical semigroups and applications* (Springer, 1993).

Acknowledgements We thank Robert Alicki, Fernando Brandao, Sandu Popescu and Charles Bennett for discussions. We thank Lidia del Rio for Figure 1, and comments on our draft. JO is supported by the Royal Society. MH is supported by Polish Ministry of Science and Higher Education grant N N202 231937 and by EC IP QESSENCE. MH acknowledge the hospitality the of Quantum Computation group at DAMTP, and JO thanks the National Quantum Information Centre of Gdansk and the Dale Farm Residents Association for their hospitality while the manuscript was being completed.

Appendix A: Thermodynamics as a resource theory

In the micro-regime, when the amount of work which can be extracted might be of the order of kT, we need to very precisely define what we mean by work, and what processes are allowed during the extraction of work from a system. For our purposes, obtaining work ΔW means to obtain an eigenstate of the Hamiltonian with energy W_{out} starting from an eigenstate of energy W_{in}, where $W_{in} - W_{out} = \Delta W$. In our approach it will turn out, that the amount of work we can extract from a given system does not depend on the Hamiltonian of the system which stores the work, and the particular levels we choose. We can thus consider a system of the smallest dimension, which carries work W. This is a two level system with Hamiltonian $\hat{W} = W|1\rangle\langle 1|$. We shall call this a *work qubit* (in short, a *wit)*, and let $|\psi_W\rangle$ denote the excited state $|1\rangle$ with energy W. This is the most economical way of storing work.

Since drawing or adding work can be represented as a state transformation, it is natural to consider thermodynamics as a resource theory. Namely, one considers some class of operations, and then asks how much of some resource can be obtained. Recent examples of such theories include entanglement theory[20, 29], thermodynamics with no Hamiltonian[19], thermodynamics of erasure[30] and operations which respect a symmetry[31, 32]. Here, we use the class of operations which corresponds to thermodynamics[21, 30], and then ask by how much we can excite a system initially in a pure ground state. It can be shown that there are a number of equivalent ways of describing this class of operations[21].

Since we are interested in extracting work in the presence of a heat bath, one starts by allowing a free resource of a heat bath, with Hilbert space $\mathcal{H}_R$. The heat bath is in a Gibbs state τ, with arbitrary Hamiltonian and we further allow the addition of any auxiliary system S' with Hamiltonian $H_{S'}$ in a Gibbs state. Without loss of generality, we can take the initial Hamiltonian to be non-interacting at very early times between the reservoir R and the system of interest S, as well as any ancillas. We also want that initially (and finally), the work qubit is not interacting with the rest of the system, since we want to be able to store the work, and use it in some other process. We thus have initially $H_{tot} = H_R + H_S + H_{S'} + \hat{W}$.

We now require that all manipulations conserve energy. This ensures that all sources of work are properly accounted for, and that external systems are not adding or taking away work. The dynamics can be implemented by an interaction Hamiltonian, however, if we wish to maintain a precise accounting of all energy, then the interaction term needs to vanish at the beginning and end of the protocol, otherwise it allows us to pump work into the system at no cost. Essentially we need to ensure conservation of total energy. This also means that if we wish to model a time-dependent Hamiltonian, we should do so by means of a time-independent Hamiltonian with a clock included in the system. It is not difficult to show [21], that all of these paradigms which conserve energy, are equivalent to unitary transformation commuting with the total Hamiltonian. Essentially, since accounting for all sources of energy requires that the initial and final Hamiltonian are the same, the dynamics must map eigenstates of the Hamiltonian to eigenstates with the same energy. This is equivalent to considering a fixed Hamiltonian, and allowing operations which commute with the Hamiltonian. We also allow discarding subsystems (partial trace). We call this class - *Thermal Operations*.

Note that this paradigm allows one to include time independent Hamiltonians as in the example discussed in the Main Section

$$H_{tot} = |0\rangle\langle 0|_C \otimes H + |1\rangle\langle 1|_C \otimes H' + W|1\rangle\langle 1| \tag{A1}$$

Via a similar mechanism, one can include interacting terms which vanish at early and late times.

Generally, we are interested in transitions between (ρ_S, H_S) and $(\sigma_{S'}$ and $H_{S'})$ (extracting work will be a special case of such a transition). Since in the described approach, the Hamiltonian is fixed, such a transition means actually $(\rho_S \otimes \tau_{S'}, H_S + H_{S'}) \to (\tau_S \otimes \sigma_{S'}, H_S + H_{S'})$. where we have the same initial and final Hamiltonian.

1. Assumptions on heat bath, and its relation to the system

We also assume that Hamiltonians of all systems of concern (i.e. heat bath Hamiltonian, auxiliary systems, the resource system itself) have minimal energy zero. Let E_R be energies of reservoir, and E_S be energies of the system. Let $E_R^{\max}$, and $E_S^{\max}$ be the largest energy of the heat bath and system, respectively (of course a typical heat bath will have $E_R^{\max} = \infty$).

Our heat bath will be large, while our resource states will be small. This means that the system Hilbert space will be fixed, while the energy of the heat bath (and other relevant quantities such as size of degeneracies) will tend to infinity.

We now make some assumptions concerning the state and Hamiltonian of the heat bath. The heat bath is in a Gibbs state with inverse temperature β. Moreover there exists set of energies $\mathcal{E}_R$ such that the state of the heat bath occupies energies from $\mathcal{E}_R$ with high probability, i.e. for the projector $P_{\mathcal{E}_R}$ onto the states with energies $\mathcal{E}_R$ we have

$$\mathsf{tr}\, P_{\mathcal{E}_R}\rho_R \geq 1-\delta \tag{A2}$$

and it has the following properties:

(i) The energies E in $\mathcal{E}_R$ are peaked around some mean value, i.e. they satisfy $E \in \{\langle E\rangle - O(\sqrt{\langle E\rangle}), \ldots \langle E\rangle + O(\sqrt{\langle E\rangle})\}$

(ii) For $E \in \mathcal{E}_R$ the degeneracies $g_R(E)$ scale exponentially with E, i.e.

$$g_R(E) \geq e^{cE} \tag{A3}$$

where c is a constant.

(iii) For any three energies E_R, E_S and E'_s such that $E_R \in \mathcal{E}_R$ and E_S, E'_S are arbitrary energies of the system, there exist $E'_R \in \mathcal{E}_R$ such that $E_R + E_S = E'_R + E'_S$.

(iv) For $E \in \mathcal{E}_R$ the degeneracies $g_R(E)$ satisfy $g_R(E-E_S) \approx g_R(E)e^{-\beta E_S}$, or more precisely:

$$\left|\frac{g_R(E)e^{-\beta E'_S}}{g_R(E-E_S)} - 1\right| \leq \delta \tag{A4}$$

for all energies E_S of the system S.

Discussion of assumptions:

Ad. (i) This is a standard property of a heat bath.

Ad. (ii) Follows from the condition (i) of small fluctuations combined with extensivity of energy.

Ad. (iii) Follows from continuity of the spectrum of the heat bath, which is usually the case.

Ad. (iv) Follows from

$$\begin{aligned} g(E+\Delta E) &= e^{S(E+\Delta E)} \\ &\approx e^{S(E)+\Delta E\frac{\partial S(E)}{\partial E}} \\ &= g(E)e^{\beta\Delta E} \end{aligned} \tag{A5}$$

with $S(E) := \ln g(E)$. and $\beta := \frac{\partial S(E)}{\partial E}$.

It is also easy to see that a product $\tau^{\otimes n}$ of many copies of independent Gibbs states satisfies the above assumptions.

Appendix B: Notation and preliminary facts.

We shall now need a bit of notation. Let us define η_E^X as a state of a system X proportional to the projection on to a subspace of energy E (according to the Hamiltonian H_X on this system). In particular, η_{E-E_S} is given by

$$\eta_{E-E_S} = g(E-E_S)^{-1}\sum_g |E-E_S, g\rangle_R\langle E-E_S, g| \tag{B1}$$

where $g = 1, .., g(E - E_S)$, i.e. η_{E-E_S} is the maximally mixed state of the reservoir with support on the subspace of energy $E_R = E - E_S$. We shall also use notation $\eta_K = \mathbb{I}/K$ where the identity acts on a K dimensional space.

Let us note that the total space $\mathcal{H}_R \otimes \mathcal{H}_S$ can be decomposed as follows

$$\mathcal{H}_R \otimes \mathcal{H}_S = \bigoplus_E \left(\bigoplus_{E_S} \mathcal{H}^R_{E-E_S} \otimes \mathcal{H}^S_{E_S} \right) \tag{B2}$$

(here for $E \leq E_S$ and $E \geq E_R^{\max} + E_S^{\max}$ the summation over E_S is suitably constrained, however we are interested only in energies E_R from $\mathcal{E}_R$, hence these cases will not occur).

Consider an arbitrary state ρ_{RS} which has support within $E_S^{\max} \leq E \leq E_R^{\max}$. We can rewrite it as follows

$$\rho_{RS} = \sum_E \sum_\Delta P_E \rho_{RS} P_{E+\Delta} \tag{B3}$$

Here $\Delta = -E_S^{\max}, \ldots, E_S^{\max}$. The blocks $P_E \rho_{RS} P_{E+\Delta}$ we can further divide into sub-blocks

$$P_E \rho_{RS} P_{E+\Delta} = \sum_{E_S \in I_\Delta} \mathbb{I}_R \otimes P_{E_S} P_E \rho_{RS} P_{E+\Delta} \mathbb{I}_R \otimes P_{E_S+\Delta} \tag{B4}$$

where $I_\Delta = \{0, \ldots, E_S^{\max} - \Delta\}$ for $\Delta \geq 0$ and $I_\Delta = \{-\Delta, \ldots, E_S^{\max}\}$ for $\Delta \leq 0$. The sub-blocks map the Hilbert space $\mathcal{H}^R_{E-E_S} \otimes (\mathcal{H}^S_{E_S+\Delta}$ onto $\mathcal{H}^R_{E-E_S} \otimes \mathcal{H}^S_{E_S})$

We can then extract the state ρ_S

$$\rho_S = \sum_{E_S, E'_S} P_{E_S} \rho_S P_{E'_S} \tag{B5}$$

as follows:

$$P_{E_S} \rho_S P_{E'_S} = \sum_E \mathsf{tr}_{\mathcal{H}^R_{E-E_S}} (P^R_{E-E_S} \otimes P_{E_S} P_E \rho_{RS} P_{E+E'_S-E_S} P^R_{E-E_S} \otimes P_{E'_S}) \tag{B6}$$

We then have the following technical result that will be a basis for most of our derivations:

Theorem 1. *We consider set of energies*

$$\mathcal{E} = \{E : E - E_S \in \mathcal{E}_R\} \tag{B7}$$

where $\mathcal{E}_R$ satisfies assumptions (i), (ii) *and* (iii) *listed above. Then*

$$\forall E \in \mathcal{E} \quad ||\frac{1}{p_E} P_E \rho_R \otimes \rho_S P_{E+\Delta} - \oplus_{E_S} \eta_{E-E_S} \otimes P_{E_S} \rho_S P_{E_S}|| \leq 2\delta \tag{B8}$$

and

$$\sum_{E \in \mathcal{E}} p_E \geq 1 - 2\delta \tag{B9}$$

where $p_E = \mathsf{tr}(P_E \rho_R \otimes \rho_S)$.

Proof. Here we sketch the proof for $\Delta = 0$. For $\Delta \neq 0$ the proof is similar. Let us fix an energy block E. Let $E_R = E - E_S$. The state $\tau_R \otimes \rho_S$ restricted to the energy E block is given by

$$P_E \tau_R \otimes \rho_S P_E = \frac{1}{Z_R} \sum_{E_S} e^- \beta E - E_S g_R(E - E_S) \mathbb{I}_R^{E-E_S} \otimes P_{E_S} \rho_S P_{E_S} \tag{B10}$$

where Z is partition function for system R, and $\mathbb{I}_R^{E-E_S}$ is identity on the subspace $\mathcal{H}_R^{E-E_S}$, see (B2). Using (iv) we have $g_R(E - E_S) = g_R(E) e^{-\beta E_S}$ we get

$$P_E \tau_R \otimes \rho_S P_E \approx \frac{1}{Z_R} e^{-\beta E} g_R(E) \sum_{E_S} \frac{\mathbb{I}_R^{E-E_S}}{g_R(E) e^- \beta E_S} \otimes P_{E_S} \rho_S P_{E_S} \tag{B11}$$

Since $\frac{\mathbb{I}_R^{E-E_S}}{g_R(E) e^- \beta E_S} = \eta_{E-E_S}$. Moreover, if we drop the prefactor, the state is normalised, hence we obtain the claim.

Appendix C: Transformations of classical states: condition in terms of majorization

Here we will provide a necessary and sufficient condition for transforming the diagonal part of a density matrix of one state into the diagonal part of another state acting on the same system. The condition will be in terms of the so called *majorization* condition, and it will be necessary and sufficient for state transformations of classical states (i.e. diagonal in the energy eigenbasis). The result is contained in the theorem 2.

From the expression (B8) it follows that a block of fixed energy E contains only the diagonal part of ρ_S:

$$P_E \rho_R \otimes \rho_S P_E \approx \oplus_{E_S} \eta_{E-E_S} \otimes P_{E_S} \rho_S P_{E_S} \tag{C1}$$

Note that we can tensor out a maximally mixed state of size independent of both E_S and E, and apply unitaries conditioned on the maximally mixed state. We do that by writing

$$\eta_{E-E_S} = \frac{\mathbb{I}_K}{K} \otimes \frac{\mathbb{I}_{K'_{E_S}}}{K'_{E_S}} \tag{C2}$$

where $K'_{E_S} = g(E - E_S)/K$. Due to our assumptions about the heat bath, the degeneracy of each energy state is exponentially large in energy, so we can take such K that both K and K' are exponentially large in energy. Thus a given fixed energy block E can be represented as a tensor product of two systems R_1^E and $R_2^E S^E$ in a state

$$\frac{1}{p_E} P_E \rho_R \otimes \rho_S P_E \approx \frac{\mathbb{I}_K}{K} \oplus_{E_S} \frac{\mathbb{I}_{K'_{E_S}}}{K'_{E_S}} \otimes P_{E_S} \rho_S P_{E_S} \tag{C3}$$

We know [19] that then any mixture of unitary transformations can be performed on the system $R_2^E S^E$, provided K is large with respect to K'_E, and we shall choose K, and the size of the total system, in such a way, that this is so, and at the same time K'_E can be large too, which we will need further. We shall below use notation η'_{E-E_S} to denote the maximally mixed state acting on system R_2^E.

Twirling The following operation being a mixture of unitaries will prove useful. For each fixed E_S we apply a random unitary to R_2^E, and identity to the part S^E. This operation does not change the final state of the system, but greatly simplifies the form of the total state: namely for any initial state on $R_2^E S^E$, the final state is of the form

$$\oplus_{E_S} \eta'_{E-E_S} \otimes \sigma_{E_S} \tag{C4}$$

Finally let us note that we cannot perform any other operation, on the state than a mixture of unitaries, because, for the total state of fixed energy block (C1) we can only apply some fixed unitary. since in the process of tracing our over the reservoir, we will sum over blocks, which effectively performs some mixture of unitaries. However, the state with $\frac{\mathbb{I}}{K}$ tensored out does not actually differ much from the state (C1), as we anyway will take the system R_2^E to be large. Thus the output state coming from a mixture of unitaries performed on the state with and without $\frac{\mathbb{I}}{K}$ being tensored out have the same effect on the final form of the state of the system S. We should now now recall, that the possibility of transforming one state into another by a convex combinations of unitary transformations is simply given by the majorization conditions[33].

The majorization condition reads as follows: we have two sets of eigenvalues put in decreasing order $\{\lambda_i\}$ and $\{\lambda'_i\}$, and we say that $\{\lambda_i\}$ majorizes $\{\lambda'_i\}$ when

$$\sum_{i=1}^{l} \lambda_i \geq \sum_{i=1}^{l} \lambda'_i \tag{C5}$$

for all l. We say that ρ majorizes σ if the eigenvalues of ρ majorize the eigenvalues of σ.

In this way obtain the following theorem which will be the basis for our further results.

Theorem 2. *Consider two states ρ_S and σ_S diagonal in energy eigenbasis, on a system with Hamiltonian H_S. The transition $(\rho_S, H_S) \otimes (\sigma_S, H_S)$ by means of thermal operations is possible if and only if the state*

$$\oplus_{E_S} \eta_{E-E_S} \otimes P_{E_S} \rho_S P_{E_S} \tag{C6}$$

majorizes

$$\oplus_{E_S} \eta_{E-E_S} \otimes \sigma_{E_S} \tag{C7}$$

for E large enough. Moreover, if the above majorization relation holds for two states ρ_S and σ_S not necessarily diagonal in energy eigenbasis, then there exists σ'_S such that for all E_S $P_{E_S} \sigma_S P_{E_S} = P_{E_S} \sigma'_S P_{E_S}$, and the transition $(\rho_S, H_S) \to (\sigma'_S, H_S)$ is possible.

Note that in the proof we have used the assumptions (i-iii) about the heat bath but not (iv). The latter will be used when we will need to get rid of the heat bath in the majorization expressions.

Finally, it is intuitively obvious, that if we add to a heat bath a small system in a Gibbs state, this is again a larger heat bath, i.e. it still satisfies our assumptions. Indeed, consider a heat bath R which satisfies assumptions (i-iv), and another system S', and consider the total Hamiltonian being a sum of Hamiltonians $H_R + H_{S'}$. The tensor product of two Gibbs states is a Gibbs state of a total system. Since the original heat bath is large, and our system is small, then the conditions i, ii and iii are obviously satisfied. Then, writing

$$g^{RS'}(E) = \sum_{E_{S'}} g^R(E - E_{S'}) g^{S'}(E_{S'}) \tag{C8}$$

and using the property iv of g^R one gets

$$g^{RS'}(E) \approx g^R(E) Z_{S'} \tag{C9}$$

where $Z_{S'}$ is the partition function for S'. This implies, in particular, that $g^{RS'}$ also satisfies the condition iv.

This proves the following intuitively obvious lemma:

Lemma 3. *Transition between $\rho_S \otimes \tau_{S'} \to \sigma_S \otimes \tau_{S'}$ is possible if and only if transition $\rho_S \to \sigma_S$ is possible.*

Thus adding a system in a Gibbs state makes sense only, if we consider transition between systems with different Hamiltonian. Then we bring in a system in a Gibbs state, only in order to have that Hamiltonian in future processes e.g. we might then transform the Gibbs state into another state which needed to have that Hamiltonian.

The conditions given thus far for state transformations are all that is needed to draw the full amount of work from a state, or to form a state from a heat bath. This is done in sections D and E. For the remainder of this section, we continue with more general state transformations.

1. Thermo-majorization

We shall now provide an efficient method of finding, whether a transition $(\rho, H) \to (\sigma, H)$ is possible, for states which commute with Hamiltonian H. The condition of transformations of the diagonal part of a density matrix given by theorem 2 in terms of majorization involves not only the state, but also the heat bath, hence it is not always directly useful. We shall now express the condition given by majorization in terms of the states of system S themselves which will result in an efficient algorithm to decide whether a transition between two diagonal states is possible or not. Essentially, we need to write the eigenvalues of the state and heat bath, in terms of eigenvalues of only the state. We shall assume that our input state and output states are diagonal in their energy bases, however, even if they are not, the condition we derive determines possible transformations of the diagonal part of the density matrix, thus the condition becomes necessary, but ceases to be sufficient.

Let $p_{E_S,g}$ be eigenvalues of ρ and $q_{E_S,g}$ be eigenvalues of σ. Then, due to proposition 2 and the condition (iv), the state $P_E \rho_R \otimes \rho_S P_E$ after normalisation is close to the state having the following eigenvalues:

$$e^{\beta E_S} \frac{p(E_S, g)}{g_R(E)} \tag{C10}$$

with multiplicity $g_R(E) e^{-\beta E_S}$, where E_S runs over all energies of the system, and g runs over degeneracies. Similarly, $P_E \rho_R \otimes \sigma_S P_E$ has eigenvalues $e^{-\beta E_S} \frac{q(E_S,g)}{g_R(E)}$ with the same multiplicity.

The eigenvalues are very small, and they are collected in groups, where they are the same, hence the majorization amounts to comparing integrals. If one puts eigenvalues into decreasing order, one obtains a stair-case like function, and majorization in the limit will be to compare the integrated functions (which are then piece-wise linear functions).

To see how it works, we need to put the eigenvalues in nonincreasing order. The ordering is determined by the ordering of the quantities $e^{\beta E_S} p_{E_S,g}$. This determines the order of $p(E_S, g)$ (which in general will not be decreasing order anymore). We shall denote such ordered probabilities as p_i, and the associated energy of the eigenstate as E_i. E.g. p_1 is equal to the $p(E_S, g)$ such that $e^{\beta E_S} p(E_S, g)$ is the largest. Note that for fixed E_S the order is the same as order of $P_{E_S,g}$, while for different E_S it is altered by the Gibbs factor. We do the same for σ, which results in q_i.

The eigenvalues are thus ordered by taking into account Gibbs weights:

$$\underbrace{\frac{p_1 e^{\beta E_1}}{d_E}}_{\substack{\text{multiplicity} \\ \approx d_E e^{\beta E_1}}} \geq \underbrace{\frac{p_2 e^{\beta E_2}}{d_E}}_{\substack{\text{multiplicity} \\ \approx d_E e^{\beta E_2}}} \geq \dots \tag{C11}$$

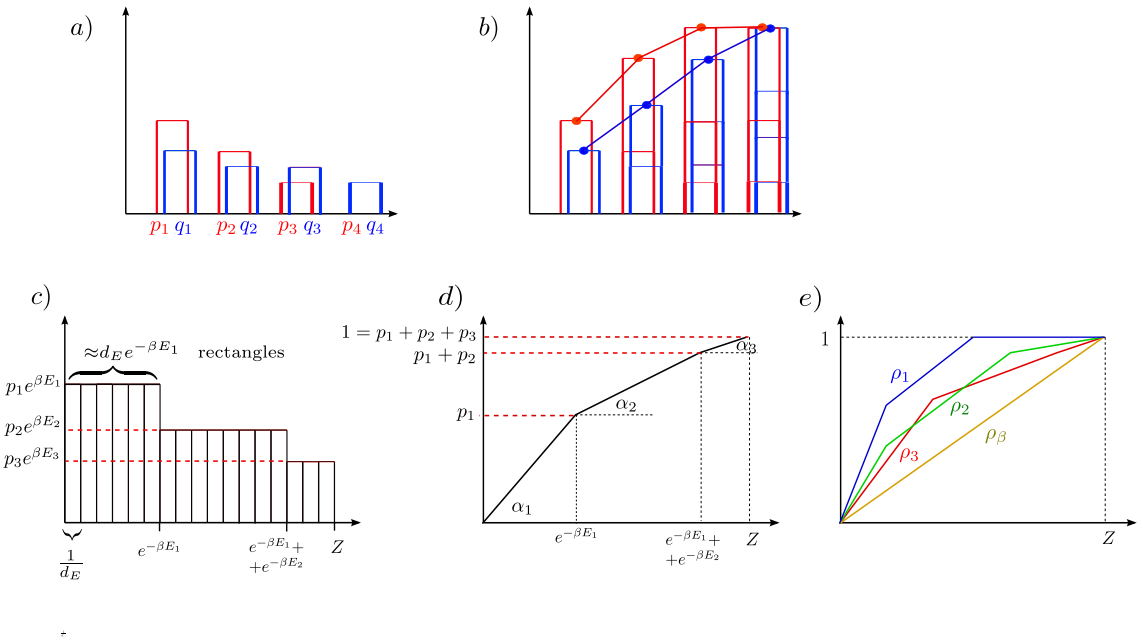

FIG. 4: **Thermo-majorization**. I. Standard majorization: (a) the histograms of probability distributions $\{p_i\}$ and $\{q_i\}$. (b) The distribution $\{p_i\}$ majorizes distribution $\{q_i\}$ if for all l $\sum_{i=1}^{l} p_i \geq \sum_{i=1}^{l} q_l$. Graphically,this means that the entire plot corresponding to $\{p_i\}$ is above the plot corresponding to $\{q_i\}$. II. Thermo-majorization. (c) Here the histograms consist of groups of numerous columns of the same height. We set their base to $1/d_E$ where $d_E = g_R(E)$, which defines a stair-way looking function defined on interval $[1, Z]$, where Z is partition function. As a result, the plot analogous to that of (b), in the limit of large E (which implies $d_E \to \infty$) becomes integral of that function presented on panel (d). The angles are given by $\tan(\alpha_i) = p_i e^{\beta E_i}$ hence they are decreasing. (e) checking thermo-majorization conditions amounts to comparing the plots which are piecewise linear functions. The state ρ_1 thermo-majorizes each other state, while the thermal τ is thermo-majorized by all other states. Thus we can transform ρ_1 into ρ_2, ρ_3 and τ and all states can be transformed into τ. On the other hand, ρ_2 and ρ_3 are incomparable, hence neither can be transformed into one another by Thermal Operations.

where d_E is a shorthand for $g_R(E)$. We shall now ascribe to vector $\{p_i\}$ a function mapping interval $[0, Z]$ into itself. On the y axis, we put subsequent sums $\sum_{i=1}^{l} p_i$, $l = 1, \ldots, d$ where d is the number of all probabilities, and on the x axis, we put sums $\sum_{i=1}^{l} e^{-\beta E_i}$, with the final point being at $x = Z$. This gives $d+1$ pairs: $(0,0), (p_1, e^{-\beta E_1}), (p_1 + p_2, e^{-\beta E_1} + e^{-\beta E_2}), \ldots, (Z, 1)$. We join the points, and it will gives us a graph of a function, $f_p(x)$. It is easy to see, that in the limit of large $g_R(E)$, the eigenvalues of ρ majorize eigenvalues of σ if and only if $f_p(x) \geq f_q(x)$ for all $x \in [0, Z]$. The described scheme is presented on figure C 1.

Note that the Gibbs state in this picture is represented by a trivial function $f_\beta(x) = Zx$ hence any state can be transformed into a Gibbs state. Note that one can generalise our new type of majorization, by replacing Gibbs state with an arbitrary state, obtaining an interesting mathematical generalisation of standard majorization. Likewise, although here the relevant conserved quantity is energy, one can generalise to operations which commute with any conserved quantity.

Appendix D: Transitions involving pure excited states

In preparation for deriving the expression for extracting work from a resource, or forming a state from the thermal state by adding work, we will derive the condition for transitions involving a pure energy eigenstate. In particular, we will derive the expression for extracting a pure excited state, and the expression for forming a state from a pure excited state. Then in Section E, we will use the results in this section to derive our two free energies.

1. Distillation: extracting a pure excited state

In this section we derive the condition for when a given mixed state ρ_S with Hamiltonian H_S can be transformed into a pure excited state ψ_W - an eigenstate of the Hamiltonian $H_{S'}$ with eigenvalue W. Let us first consider the case

where we wish to extract ψ_W with no probability of failure, from a state diagonal in the energy basis. We will then extend our result to arbitrary states.

According to Lemma 3 we need to take an initial state $\rho_S \otimes \tau_{S'}$ and the final state is an arbitrary state of the system SS' of the form $\sigma_S \otimes |\psi^W\rangle\langle\psi^W|_{S'}$. Due to Theorem 2, and Eq. (C9) a transition is possible when the state

$$\bigoplus_{E_S} \eta^{RS'}_{E-E_S} \otimes P_{E_S}\rho_S P_{E_S} \tag{D1}$$

majorizes

$$\bigoplus_{E_S} \eta^{R}_{E-E_S-W} \otimes P_{E_S}\sigma P_{E_S} \otimes |\psi_W\rangle_{S'}\langle\psi_W| \tag{D2}$$

However, since σ is arbitrary, and the target state of S' is pure, this is equivalent to the condition

$$\text{rank}_{in} \geq \text{rank}_{out}. \tag{D3}$$

where rank_{in} and rank_{out} are ranks of the state (D1) and (D2), respectively.

The rank of the initial state is equal to

$$\text{rank}_{in} = \sum_{E_S} g_{RS'}(E - E_S)\text{rank}_{E_S}(\rho_S) \tag{D4}$$

where $\text{rank}_{E_S}(\rho)$ is the rank of $P_{E_S}\rho_S P_{E_S}$, and as in Eq. C9

$$g_{RS'}(E - E_S) = g_R(E - E_S)Z_{S'}. \tag{D5}$$

The maximal rank of the target state is given by

$$\text{rank}_{out} = \sum_{E_S} g_R(E - E_S - W)g_S(E_S) \tag{D6}$$

Now, using (D5) and $g_R(E + \Delta E) \approx g_R(E)e^{\beta\Delta E}$ we obtain that eq. D3 implies

$$\sum_{E_S} \frac{e^{-\beta(E_S)}}{Z}\text{rank}_{E_S}(\rho_S) \leq \sum_{E_{S'}} \frac{e^{-\beta(E_{S'})}}{Z'}\text{rank}_{E_{S'}}(\psi_W) \tag{D7}$$

which can be written as

$$D_{\min}(\rho_S||\tau_S) \geq D_{\min}(\psi^W_{S'}||\tau_{S'}) \tag{D8}$$

with $D_{\min}(\rho_S||\tau_S) := -\ln \text{tr}\,\Pi_\rho \tau$. In general this quantity is the min-relative entropy[23].

We can now ask about the case when ρ is not diagonal in the energy eigenbasis. In such a case, we simply replace ρ with $\omega = \sum_{Eg,g'} |E,g\rangle\langle E,g|\rho_\epsilon|E,g'\rangle\langle E,g'|$ in Equation (D8). The reason, is that Theorem 2 states necessary and sufficient conditions for transforming the diagonal entries of one density matrix into the diagonal entries of another. In the case of an initial state with off-diagonal entries, it gives necessary conditions. However the diagonal entries of a pure excited energy eigenstate determines uniquely that state itself, thus the condition must also be sufficient. An alternative argument in terms of commuting of the dephasing operation and thermal operations is given in the Main Section.

Note that the operation which gets implemented to map one state to another is simply a mapping from eigenstates of the initial state within each energy block E, to mappings of eigenstates of the final state within the same energy block. However, any such mapping will do, and there are a huge number of them. Thus the experimenter does not need to know which unitary she is implementing, provided that it conserves energy. She thus needs very little control over her systems – she simply chooses any unitary which maps the macroscopic variables of one state (in this case, total energies (E_R, E_S), to macroscopic variables of the final state (in this case, a pure energy eigenstate with no degeneracy on some system, and total energy on another $(E_R + E_S - W)$. The same is true of the formation process described in the next section.

2. Formation of a resource state from a thermal bath and pure excited state

Just as one can draw work from a state which is out of equilibrium from the rest of the thermal bath, it is also possible to perform the reverse process – create a state from the thermal bath by adding work. Here we provide conditions for transition from a pure excited state to a given target diagonal state. We will then use it in Section E to derive the amount of work which is required to create a state.

We thus take the initial state to be of the form

$$\rho^{in} = \psi_S^W \otimes \tau_{S'} \tag{D9}$$

and the output state

$$\rho^{out} = \rho_{SS'} \tag{D10}$$

We shall now use Theorem 2. To this end we have to check the majorization condition between the following states:

$$\eta_{E-W}^{RS'} \otimes |\psi^W\rangle_S\langle\psi^W| \tag{D11}$$

and

$$\oplus_{E_{S'}} \eta_{E-E_{S'}}^{RS} \otimes p_{E_{S'}} \rho_{S'}^{E_{S'}} \tag{D12}$$

where in (D11) we have used Eq. (C9).

However, the former state has only one eigenvalue $1/g_{RS'}(E-W)$ with multiplicity $g_{RS'}(E-W)$. Therefore, the majorization condition is that all eigenvalues of the latter state are no greater than this eigenvalue. I.e. we need that

$$g_{RS'}(E-W)^{-1} \geq g_{RS}(E-E_{S'})^{-1} \lambda_{E_{S'}}^{\max} \tag{D13}$$

holds for all $E_{S'}$, where $\lambda_{E_{S'}}^{\max}$ is the maximal eigenvalue of $P_{E_{S'}} \rho_{S'} P_{E_{S'}}$ i.e. it is the maximal eigenvalue of $\rho_{S'}$ in the subspace of energy $E_{S'}$. Since the Hamiltonian for RSS' is the sum of H_R, H_S and $H_{S'}$, we obtain that

$$g_{RS'}(E-W) = \sum_{E_{S'}} g_R(E-W-E_{S'}) g'_S(E_{S'})$$
$$g_{RS}(E-E_{S'}) = \sum_{E_S} g_R(E-E_{S'}-E_S) g_S(E_S)$$

Now we use the fact that R is a heat bath, and we apply our assumption (A4) which says that

$$g_R(E-W-E_{S'}) \approx g_R(E) e^{-\beta(W+E_{S'})} \tag{D14}$$

and

$$g_R(E-E_{S'}-E_S) \simeq g_R(E) e^{-\beta(E_S+E_{S'})} \tag{D15}$$

we can thus rewrite the majorization condition (D13) as follows

$$\frac{1}{Z_{S'}} e^{-\beta E_{S'}} \geq \frac{1}{Z_S} e^{-\beta W} \lambda_{E_{S'}}^{\max} \tag{D16}$$

for all $E_{S'}$. On the other hand, one can compute that

$$D_{\max}(\psi_S^W || \tau_S) = Z_S e^{\beta W}, \quad D_{\max}(\rho_{S'} || \tau_{S'}) = \max_{E_{S'}} Z_{S'} e^{\beta E_{S'}} \lambda_{E_{S'}}^{\max} \tag{D17}$$

where $D_{\max}(\rho||\tau) := \log \min\{\lambda : \rho \leq \lambda\tau\}$ is the max-relative entropy[23]. Thus, the transition $(\psi_S^W, H_S) \to (\rho_{S'}, H_{S'})$ is possible if and only if

$$D_{\max}(\psi_S^W || \tau_S) \geq D_{\max}(\rho_{S'} | \tau_{S'}). \tag{D18}$$

Appendix E: Extractable work, and work of formation

We now use the results of Secs. D 2 and D 1 to discuss the amount of work that can be drawn from a system in contact with a heat bath of temperature T, and the amount of work that is needed to create one. In thermodynamics, both quantities are equal and are given by free energy. In our case we obtain two free energies, F_{min} governing extracting work, and the other, F_{max}, governing creation of the system. In this section, we derive the expression for F_{min} and F_{max} in the case where we wish to extract the full amount of work available, or create a total state out of thermal states. This corresponds to Equations (3) and (8). The more general result of Equations (10) and (11) following from thermo-majorization is contained in the Main Section.

We propose to define the process of drawing or spending work as raising or lowering the energy level of an eigenstate of a Hamiltonian $\hat{W}$ of a system. This system is used to store the energy provided by drawing work. Thus we draw work ΔW if we transform a state $|E\rangle$ into $|E'\rangle$ such that $E' - E = W$ $H_W|E\rangle = E$ and $H|E\rangle = E$. Expending work, would mean the reverse process. Since our results don't depend on the system used to store work, we take the most elementary system than can be used, namely a two level system with energy gap W.

Thus consider a system S in state ρ_S. We add a work system with Hamiltonian $\hat{W}$ in a state $|E\rangle$. Our initial state is thus $\rho_S \otimes |E\rangle\langle E|$ and the final state $|E'\rangle\langle E'|$. Using the results of section D 1 we obtain, that $\rho_S \otimes |E\rangle\langle E|$ can be transformed into $|E'\rangle\langle E'|$ if and only if

$$D_{\min}(\rho_S \otimes |E\rangle\langle E|) \geq D_{\min}(|E'\rangle\langle E'|), \tag{E1}$$

where we use the shorthand notation $D_{\min}(\rho) \equiv D_{\min}(\rho|\tau)$. Since $D_{\min}$ is additive, and for energy eigenstates $|E\rangle$ we have

$$D_{\min}(|E\rangle) = \beta E - \ln Z_W \tag{E2}$$

where Z is the partition function of the work system, we can rewrite (E1) as

$$kTD_{\min}(\rho_S) \geq W \tag{E3}$$

This allows us to define the free energy F_{min} as follows:

$$F_{min} = F_\beta + kTD_{min} \tag{E4}$$

where F_β is the standard free energy of the equilibrium state (we have anyway that for thermal states $F_{min} = F_\beta$). The work that can be drawn from a non-equilibrium state is thus equal to the the free energy difference ΔF_{min}:

$$W_{dist}(\rho) = F_{min}(rho) - F_{min}(tau) \tag{E5}$$

We now wish to allow some probability of failure[22] – namely, we might not produce $\psi_{S'}^W$ exactly, but rather a state ψ_ϵ^W ϵ-close to ψ^W i.e. such that

$$||\psi_\epsilon^W - \psi^W|| \leq \epsilon. \tag{E6}$$

Since thermal operations are completely positive trace preserving maps, then if we imagine the same operations were performed on some initial state $||\rho_\epsilon - \rho|| \leq \epsilon$ then the final state will also satisfy Equation (E6). We can thus replace $D_{min}(\rho||\tau)$ with $D^\epsilon_{min}(\rho||\tau) := -\sup_{\rho_\epsilon} - \ln \mathsf{tr}\,\Pi_\rho \tau$. This is known as the smooth-min entropy[23].

Analogously we define work which is needed to create a system, i.e. we consider a transition $|E\rangle\langle E| \to |E'\rangle\langle E'| \otimes \rho_S$, and in an analogous way obtain that the minimal work $W = E' - E$ to ensure this transition is given by

$$W_{form}(\rho) = F_{max}(\rho) - F_{max}(\tau) \tag{E7}$$

where F_{max} is a max-free energy given by

$$F_{max} = F_\beta + kTD_{max}. \tag{E8}$$

This comes from simply solving Equation (D18) for the value of W required for the transition, to obtain

$$W = kT \inf_{\rho_\epsilon} \log \min\{\lambda : \rho \leq \lambda\tau\} \tag{E9}$$

As in the distillation process, we can consider ϵ-close formation processes, since we will generally want to tolerate some small error in the creation of a resource, particularly if it can save us needing a large amount of work. We thus obtain the expression for F_ϵ^{max} in the Main Section.

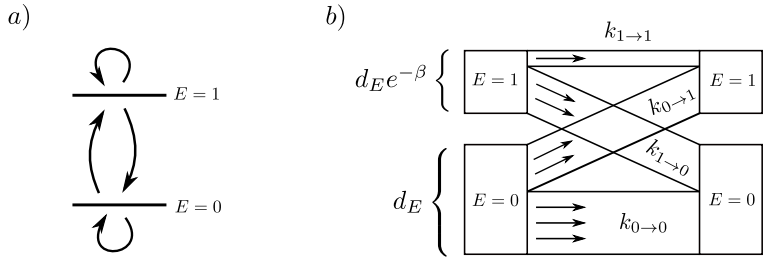

FIG. 5: Transitions for two level system with energy levels $E = 0$ and $E = 1$. a) There are four possible transitions b) the number of states of bath corresponding to each level is proportional to the Boltzmann factor.

Appendix F: Characterisation of Thermal Operations

We have provided an algorithm for deciding whether a state can be transformed into another state, given by thermo-majorization. However the algorithm does not tell us what kind of operations (completely positive maps) we can perform by means of Thermal Operations. Below we shall show, that all possible processes are precisely those that preserve the Gibbs state. This implies that if we have reversibility of state transformations (as is the case when we have many copies of a state[21]), then the unique measure which determines whether a transformation is possible, is given by the relative entropy distance to the Gibbs state[20]. This quantity is the difference between free energy of a state of interest and that of Gibbs state [27]. However, here, we do not have reversibility, thus there are at least two inequivalent functions which are non increasing under thermal operations (F_{min} and F_{max}).

We start with a state $\tau_R \otimes \rho_S$ and write

$$\tau_R \otimes \rho_S \approx \sum_{E\in\mathcal{E}} p_E \rho_{RS}^E \tag{F1}$$

with

$$\rho_{RS}^E = \frac{1}{P_E} P_E \tau_R \otimes \rho_S P_E \tag{F2}$$

where $\mathcal{E}$ consists of very large energies in comparison with system energies, and $p_E = \mathsf{tr}(\tau_R \otimes \rho_S P_E)$. We shall now fix one energy block, and show, that even when restricting just to permutations of basis vectors within the block (being products of eigenstates of τ_R to eigenvalues E_R and eigenstates of ρ_S to eigenvalues E_S, such that $E_R + E_S = E$) we can perform arbitrary operation on system S which preserve the Gibbs state. Then, we will argue that the operation on the system S can be made the same for each energy block (for $E \in \mathcal{E}$).

To prove the first claim, for simplicity, let us assume that the Hamiltonian H_S is nondegenerate (extension to the degenerate case is immediate). As follows from Theorem 2, in such a fixed subspace, the eigenvalues of our state form groups labelled by energy E_S. Within each group, we have $g_R(E)e^{-\beta E_S}$ eigenvalues all equal to $\frac{p(E_S)}{g_R(E)e^{-\beta E_S}}$. Permutations of basis vectors result in transferring some subsets of a given group to other groups. Let us then use indices i in place of E_S, so that $p_{E_S} \to p_i$ and $g_R(E)e^{-\beta E_S} \to d_i$. We shall denote by $k_{i\to j}$ the "transition current" i.e. the number of eigenstates that have been moved from the i-th group to the $j-th$ group. Clearly $k_{i\to j}$ satisfy

$$\begin{aligned} \sum_j k_{i\to j} &= d_i \\ \sum_i k_{i\to j} &= d_j \end{aligned} \tag{F3}$$

The transition "currents" are illustrated on Fig. 5. After an operation given by some fixed set of $k_{i\to j}$ satisfying the above transitions, we obtain a new state, whose probabilities q_i are given by

$$q_j = \sum_i k_{i\to j} \frac{p_i}{d_i} \tag{F4}$$

Thus, we can define transition probabilities $p_{i\to j}$ as

$$p_{i\to j} = \frac{k_{i\to j}}{d_i} \tag{F5}$$

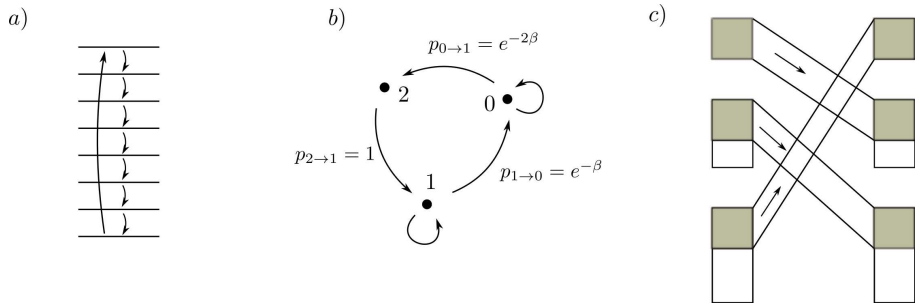

FIG. 6: Quasi-cycles. a) In quasi cycle for each level there is only one transition to a different level b) quasi-cycle for three level system. The points represent levels with energies $0, 1$ and 2; probability $p_{2\to2}$ of staying in level 2 vanishes. c) Currents for three-level quasi-cycle: the shaded microstates are subjected to a cycle, while the ones not shaded are left untouched.

Then the condition (F3) means that the $p_{i\to j}$ ensure normalisation, so that the only constraint on possible process is (F3). However, since $\frac{d_i}{d_j} = \frac{e^{\beta E_j}}{e^{\beta E_j}}$, the latter condition means simply that the Gibbs state is preserved. This ends the proof, that for fixed E we can perform all Gibbs preserving operations. Finally, given arbitrary Gibbs preserving transformation on S we perform for every total energy block permutation that results in this transformation. In this way the needed transformation is performed on the initial state of system S. Of course, Thermal Operations obviously do preserve Gibbs state, hence we obtain, that Thermal Operations are arbitrary operations that preserve Gibbs state.

Let us discuss this result in the context of the detailed balance condition. The latter is the property that $\frac{p_{i\to j}}{p_{j\to i}} = e^{-\beta(E_j - E_i)}$. As we will see, Thermal Operations need not satisfy detailed balance; they should merely preserve the Gibbs state as a whole. To provide an example, let us distinguish a class of Gibbs-preserving processes called quasi-cycles: we put the energy levels on a circle, and from one level, one can go only to the next neighbouring level, as in Figure 6

The simplest description of a quasi-cycle is in terms of quantities $k_{i\to j}$. Namely, we choose an order of levels, put them on a circle, fix a direction, and the process is to take all states from the group of states with the largest energy E_S, and shift them to the states with the energy level in the chosen direction. I.e. the process is determined by $p_{i\to i+1} = e^{-\beta(E_{\max} - E_i)}$, where $E_{\max}$ is the maximal energy, and E_i is the energy of $i-th$ level.

For two level systems, the class of Gibbs preserving operations is the same as the class of operations satisfying the detailed balance condition, and all possible processes are parametrised by a single number $r \in [0, 1]$, which is the probability of mixing two basic processes: the identity operation, and the two-level quasi-cycle. For three level systems, there are processes that preserve the Gibbs state, but do not satisfy detailed balance, an example being the three-level quasicycle. It turns out that the class of Gibbs preserving maps is strictly more powerful that the class of detailed-balance maps. An example is the transition between $(0, \frac{1}{2}, frac12)$ and $(\frac{1}{2}e^{-2\beta}, \frac{1}{2}(1 - e^{-}\beta), \frac{1}{2}(e^{-\beta} - e^{-2\beta} + 1)$ with the energy levels given by $(0, 1, 2)$. It turns out that the only Gibbs preserving operation that can transform the first state into the second one is the quasi-cycle $0 \to 1 \to 2$. This means that such a transition is impossible by means of weak coupling with the heat-bath [34], as at weak coupling the detailed balance condition is satisfied.