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GIAN PAOLO BERETTA

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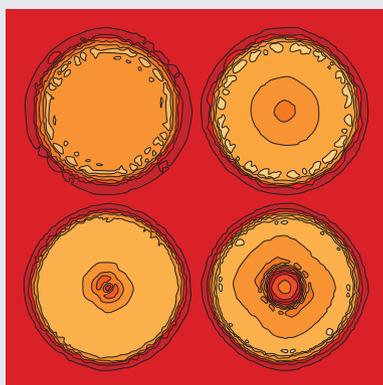
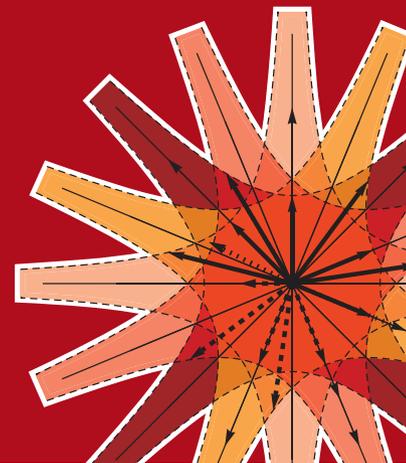
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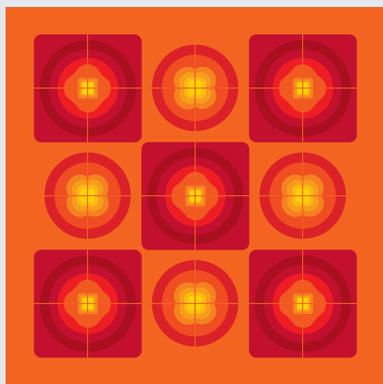
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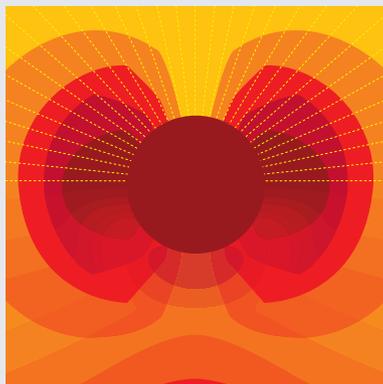
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# Quantum thermodynamic Carnot and Otto-like cycles for a two-level system

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**Abstract** – Within the recent revival of interest in quantum heat engines between two thermal reservoirs whereby the working substance is a two-level system, it has been suggested that the celebrated Carnot heat-to-work conversion efficiency  $1 - (T_{\text{low}}/T_{\text{high}})$  cannot be reached. Contrary to this suggestion, we show that reaching the Carnot bound not only is not impossible and does not require an infinite number of heat baths and infinitesimal processes, but it is also within reach of the current experimental techniques. It is sufficient to cycle smoothly (slowly) over at least three (in general four) values of the tunable energy level gap  $\Delta$  of the system, by varying  $\Delta$  not only along the isoentropics, but also along the isotherms. This is possible by means of the recently suggested maser-laser tandem technique. We base our proof on the general thermodynamic equilibrium properties of a two-level system together with a careful distinction between the Gibbs relation  $dE = T dS + (E/\Delta) d\Delta$  and the energy balance equation  $dE = \delta Q^+ - \delta W^-$ . We derive bounds to the net-work to high-temperature-heat ratio (energy efficiency) for a Carnot cycle and for the “inscribed” Otto-like cycle. By representing these cycles on useful thermodynamic diagrams, we infer and confirm important aspects of the second law of thermodynamics.

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**Introduction.** – Recent studies [1–7] of Maxwell demons, quantum heat engines (often called Carnot engines even if the cycle is not a Carnot cycle), and quantum heat pump, refrigeration and cryogenic cycles operating between two heat sources at  $T_{\text{high}}$  and  $T_{\text{low}}$  find maximal efficiencies lower than the celebrated Carnot net-work to high-temperature-heat ratio,  $1 - (T_{\text{low}}/T_{\text{high}})$ . In particular, ref. [4], in studying a specific two-iso-energy-gap/two-isoentropic-processes Otto-type cycle for a spin-1/2 system, seems to hint that the quantum nature of the working substance implies a fundamental bound to the thermodynamic efficiency of heat-to-work conversion, lower than the celebrated Carnot bound.

Pioneering studies [8] of quantum equivalents of the Carnot cycle for multilevel atomic and spin systems appeared soon after the association of negative temperatures with inverted population equilibrium states of pairs of energy levels [9,10] and the experimental proof of the maser principle [11].

In tune with these early studies, here we show [12] that a Carnot cycle for a two-level system is possible, at least in

principle, but requires cycling over a range of values of the energy level gap  $\Delta$ . A critical and characteristic feature of this cycle is that along the isotherms the value of  $\Delta$  must vary continuously and hence the two-level system must experience simultaneously a work and a heat interaction. Usually, the different typical time scales underlying mechanical and thermal interactions imply fundamental technological difficulties that are among the main reasons why the Carnot cycle has hardly ever been engineered with normal substances. In the framework of quantum thermodynamics the understanding and modeling of mechanical and thermal interactions is a current research topic, having to do with entanglement, decoherence [13], relaxation [14], adiabatic (unitary) accessibility [15], but a recent suggestion by Scully [1] indicates that the use of a “maser-laser tandem” may provide an effective experimental means to implement the simultaneous heat and work interaction by smooth (slow<sup>1</sup>) continuous change of the

<sup>1</sup>The energy level gap  $\Delta$  must be tuned slowly so as to maintain the system along a sequence of thermodynamic-equilibrium states, thereby avoiding irreversible relaxation effects that would obtain if fast tuning of  $\Delta$  drives the system off equilibrium. Such kind of inefficiencies are discussed in refs. [5,6].

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magnetic field necessary to realize the isotherms of our Carnot cycle: the maser serves as the incoherent (heat) energy and entropy exchange mechanism, the laser as the coherent (work) energy exchange.

Consider a two-level system with a one-parameter Hamiltonian  $H(\Delta)$  such that the energy levels are  $\varepsilon_1 = -\Delta/2$  and  $\varepsilon_2 = \Delta/2$ , for example a spin-1/2 system, in a magnetic field of intensity  $B$ , with  $\Delta = 2\mu_B B$  and  $\mu_B = e\hbar/2m_e = 9.274 \times 10^{-24} J/T$  Bohr's magneton.

For our purposes here it suffices to consider the canonical Gibbs states (the stable equilibrium states of quantum thermodynamics), *i.e.*, the two-parameter family of density operators  $\rho(T, \Delta)$  with eigenvalues  $p$  and  $1-p$ , mean value of the energy  $E$ , and entropy  $S$  given by the relations

$$\rho(T, \Delta) = \frac{\exp[-H(\Delta)/k_B T]}{\text{Tr} \exp[-H(\Delta)/k_B T]}, \quad (1)$$

$$p = \frac{1}{1 + \exp(\Delta/k_B T)} = \frac{1}{2} + \frac{E}{\Delta}, \quad (2)$$

$$E = \text{Tr} \rho(T, \Delta) H(\Delta) = \frac{\Delta}{2} \tanh \left[ -\frac{\Delta/2}{k_B T} \right], \quad (3)$$

$$S = -k_B \text{Tr} \rho \ln \rho = -k_B [p \ln p + (1-p) \ln(1-p)] \\ = -k_B \left[ \left( \frac{1}{2} + \frac{E}{\Delta} \right) \ln \left( \frac{1}{2} + \frac{E}{\Delta} \right) + \left( \frac{1}{2} - \frac{E}{\Delta} \right) \ln \left( \frac{1}{2} - \frac{E}{\Delta} \right) \right]. \quad (4)$$

We note that the thermodynamic-equilibrium "fundamental relation"  $S = S(E, \Delta)$  for this simplest system takes the explicit form  $S = S(E/\Delta)$  given by the last of eqs. (4). As is well known, all equilibrium properties can be derived from the fundamental relation. We also note the following dependences on the two parameters (temperature  $T$  and energy level gap  $\Delta$ ): eq. (3) implies that the ratio  $E/\Delta$  depends only on the ratio  $\Delta/T$ , therefore, eqs. (2) and (4) imply that also  $p$  and  $S$  are functions of the ratio  $\Delta/T$  only.

It is clear from (3) and (4) that for an isoentropic process,

$$S = \text{const} \Leftrightarrow \frac{E}{\Delta} = \text{const} \Leftrightarrow \frac{\Delta}{T} = \text{const} \Leftrightarrow \frac{E}{T} = \text{const} \quad (5)$$

and, hence, also the Massieu characteristic function  $M = S - (E/T)$  is constant. More generally, by differentiating the second of eqs. (4) and using eqs. (2), (3) and the identity  $\ln[(1 + \tanh x)/(1 - \tanh x)] = 2x$  with  $x = -\Delta/2k_B T$ , we find

$$dS = -k_B \ln \frac{p}{1-p} dp = -k_B \ln \frac{1+2E/\Delta}{1-2E/\Delta} d\frac{E}{\Delta} \\ = \frac{\Delta}{T} d\frac{E}{\Delta} = \frac{1}{T} dE - \frac{E}{T\Delta} d\Delta, \quad (6)$$

therefore, the following Gibbs relation holds for all processes in which the initial and final states of the two-level system are neighboring thermodynamic-equilibrium states:

$$dE = T dS + (E/\Delta) d\Delta. \quad (7)$$

Next we write the energy balance equation assuming that the system experiences both net heat and work interactions [16] with other systems in its environment (typically a heat bath or thermal reservoir at some temperature  $T_Q$ , and a work sink or source, respectively),

$$dE = \delta Q^{\leftarrow} - \delta W^{\rightarrow}, \quad (8)$$

where we adopt the standard notation by which a left (right) arrow on symbol  $\delta Q$  ( $\delta W$ ) means heat (work) received by (extracted from) the system, when  $\delta Q^{\leftarrow}$  ( $\delta W^{\rightarrow}$ ) is positive (negative).

Comparing the right-hand sides of eqs. (7) and (8), the following identification of addenda,  $\delta Q^{\leftarrow} = T dS$  and  $\delta W^{\rightarrow} = (-E/\Delta) d\Delta$  is tempting, but not valid in general unless we make further important assumptions. To prove and clarify this last assertion, we consider two counterexamples, in both of which the system changes between neighboring thermodynamic-equilibrium states so that both eqs. (7) and (8) hold.

As a first counterexample, consider a system which experiences a work interaction with no heat interaction ( $\delta Q^{\leftarrow} = 0$ ). The energy change  $dE$  is provided by the work interaction only, while the entropy change  $dS$ , required to maintain the system at thermodynamic equilibrium, is generated within the system by irreversible relaxation and decoherence. In this case, the entropy balance equation is  $dS = \delta S_{\text{gen}}$ , where  $\delta S_{\text{gen}}$  denotes the entropy generated by irreversibility. The work is

$$\delta W^{\rightarrow} = -\frac{E}{\Delta} d\Delta - T \delta S_{\text{gen}} \quad \left[ \leq -\frac{E}{\Delta} d\Delta \text{ if } T > 0 \right], \quad (9)$$

and, of course, the process is possible only if  $dS \geq 0$ .

As a second counterexample, consider a system which experiences no (net) work interaction and a heat interaction with a source at temperature  $T_Q$  so that the entropy exchanged with the heat source is  $\delta S^{\leftarrow} = \delta Q^{\leftarrow}/T_Q$ . In this case, the energy change  $dE$  is provided by the heat interaction only, while the entropy change  $dS$  required to maintain the system at thermodynamic equilibrium is partly provided by the heat source and partly generated within the system by irreversibility ( $dS = \delta Q^{\leftarrow}/T_Q + \delta S_{\text{gen}}$ ). The heat is

$$\delta Q^{\leftarrow} = T dS + \frac{E}{\Delta} d\Delta \quad [\neq T dS \text{ if } d\Delta \neq 0], \quad (10)$$

and the process is possible, for  $T > 0$ , only if

$$\frac{E}{\Delta} d\Delta \leq \left( 1 - \frac{T}{T_Q} \right) dE. \quad (11)$$

The two examples show clearly that the correct association between the work and heat exchanged, and the energy and entropy changes, cannot be made by just comparing eqs. (7) and (8) without considering also the entropy balance equation

$$dS = \frac{\delta Q^{\leftarrow}}{T_Q} + \delta S_{\text{gen}}, \quad \text{with } \delta S_{\text{gen}} \geq 0, \quad (12)$$

written here assuming the system experiences heat interaction(s) with a single heat source, bath or thermal reservoir at temperature  $T_Q$ . This balance equation specifies unambiguously what part of the entropy change is due to exchange via heat interaction(s) and what part is generated spontaneously within the system due to its internal dynamics (relaxation, decoherence). Eliminating  $dE$  and  $dS$  from eqs. (7), (8) and (12), we find

$$\delta W^{\rightarrow} = -\frac{E}{\Delta} d\Delta + \left(1 - \frac{T}{T_Q}\right) \delta Q^{\leftarrow} - T \delta S_{\text{gen}}. \quad (13)$$

This reduces to  $\delta W^{\rightarrow} = (-E/\Delta) d\Delta$  if and only if

$$\delta S_{\text{gen}} = \frac{\delta Q^{\leftarrow}}{T} - \frac{\delta Q^{\leftarrow}}{T_Q}, \quad (14)$$

*i.e.*, only when entropy generation is due exclusively to the heat interaction across the finite temperature difference between system and heat source, and not to other irreversible spontaneous processes induced in the system by other interactions that tend to pull the system off thermodynamic equilibrium (see footnote <sup>1</sup>).

Equation (14) and the condition  $\delta S_{\text{gen}} \geq 0$  imply that the system can receive heat only if  $-1/T_Q \geq -1/T$ , which for positive temperatures implies  $T_Q \geq T$ . As evidenced by Ramsey [10],  $-1/T$  measures the thermodynamic equilibrium escaping tendency of energy by heat interaction, and is a better indicator of “hotness” than the temperature  $T$  because it validly extends to negative-temperature states. Figure 1 shows graphs of energy  $E$ , entropy  $S$ , and Massieu function plotted as functions of  $-1/k_B T$  and  $\Delta$ , as well as graphs of  $E$ ,  $S$  and  $\Delta$  *vs.*  $S$ .

Each graph in fig. 1 shows a Carnot cycle, *i.e.*, a sequence of an isothermal process 1-2 at a high temperature  $T_{\text{high}}$ , an isentropic 2-3, another isothermal process at a temperature  $T_{\text{low}} < T_{\text{high}}$ , and another isentropic 4-1. Because  $S = S(\Delta/T)$  ( $S$  decreasing with  $\Delta/T$  for  $T > 0$ ), it is clear that the isentropic changes between  $T_{\text{low}}$  and  $T_{\text{high}}$  and the isothermal changes between  $S_1 = S_4$  and  $S_2 = S_3$  are possible only by changing the energy level gap  $\Delta$ . Therefore, to have  $S_2 > S_1$ , we need  $\Delta_2/T_{\text{high}} = \Delta_3/T_{\text{low}} < \Delta_4/T_{\text{low}} = \Delta_1/T_{\text{high}}$ , *i.e.*,

$$\frac{\Delta_{\text{high}}}{\Delta_{\text{low}}} \left[ \frac{T_{\text{low}}}{T_{\text{high}}} \right]^2 = \frac{\Delta_4}{\Delta_2} > \frac{\Delta_4}{\Delta_1} = \frac{T_{\text{low}}}{T_{\text{high}}} = \frac{\Delta_3}{\Delta_2} > \frac{\Delta_{\text{low}}}{\Delta_{\text{high}}}, \quad (15)$$

where, noting that  $\Delta_3 < \Delta_2 < \Delta_1$  and  $\Delta_3 < \Delta_4 < \Delta_1$ , we set  $\Delta_{\text{low}} = \Delta_3$  and  $\Delta_{\text{high}} = \Delta_1$ . Relations (15) imply (see also figure legend) general bounds on the net-work to high-temperature-heat ratio (Carnot coefficient),

$$1 - \frac{\Delta_{\text{high}}}{\Delta_{\text{low}}} \left[ \frac{T_{\text{low}}}{T_{\text{high}}} \right]^2 < \frac{W_{\text{net},1234}^{\rightarrow}}{Q_{12}^{\leftarrow}} = 1 - \frac{T_{\text{low}}}{T_{\text{high}}} < 1 - \frac{\Delta_{\text{low}}}{\Delta_{\text{high}}}. \quad (16)$$

Notice that  $\Delta_2 \geq \Delta_4$  depending on whether  $\Delta_{\text{low}}/\Delta_{\text{high}} \geq (T_{\text{low}}/T_{\text{high}})^2$ . Indeed, we may choose arbitrarily  $T_{\text{high}}$ ,  $T_{\text{low}} < T_{\text{high}}$ ,  $\Delta_{\text{high}} = \Delta_1$ , and

$\Delta_{\text{low}} = \Delta_3 < \Delta_{\text{high}} T_{\text{low}}/T_{\text{high}}$ . Then, we must set  $\Delta_2 = \Delta_{\text{low}} T_{\text{high}}/T_{\text{low}}$  and  $\Delta_4 = \Delta_{\text{high}} T_{\text{low}}/T_{\text{high}}$ . To obtain a Carnot cycle between only three values of  $\Delta$ , we may set  $\Delta_{\text{low}} = \Delta_{\text{high}} (T_{\text{low}}/T_{\text{high}})^2$  so that  $\Delta_2 = \Delta_4$ .

Of course, if the cycle is reversed, we obtain, instead of a heat-engine effect, a refrigeration or heat-pump effect.

Each graph in fig. 1 shows also an Otto-type cycle [4,6] bound by the same  $T_{\text{high}}$  and  $T_{\text{low}}$ , *i.e.*, a sequence of an iso-energy-gap process 1'-2' at  $\Delta'_{\text{high}}$ , an isentropic 2'-3', another iso-energy-gap process 3'-4' at  $\Delta'_{\text{low}}$ , and another isentropic 4'-1'. Here, the fact that  $S = S(\Delta/T)$  is a decreasing function of  $\Delta/T$  for  $T > 0$ , implies that to have  $S_{2'} > S_{1'}$ , we need  $\Delta'_{\text{high}}/T_{\text{high}} = \Delta'_{\text{low}}/T_{3'} < \Delta'_{\text{high}}/T_{1'} = \Delta'_{\text{low}}/T_{\text{low}}$ , *i.e.*,

$$\frac{T_{\text{high}}}{T_{\text{low}}} \left[ \frac{\Delta'_{\text{low}}}{\Delta'_{\text{high}}} \right]^2 = \frac{T_{3'}}{T_{1'}} > \frac{T_{3'}}{T_{\text{high}}} = \frac{\Delta'_{\text{low}}}{\Delta'_{\text{high}}} = \frac{T_{\text{low}}}{T_{1'}} > \frac{T_{\text{low}}}{T_{\text{high}}}. \quad (17)$$

Relations (17) imply (see also figure legend) general bounds on the net-work to high-temperature-heat ratio,

$$1 - \frac{T_{\text{high}}}{T_{\text{low}}} \left[ \frac{\Delta'_{\text{low}}}{\Delta'_{\text{high}}} \right]^2 < \frac{W_{\text{net},1'2'3'4'}^{\rightarrow}}{Q_{1'2'}^{\leftarrow}} = 1 - \frac{\Delta'_{\text{low}}}{\Delta'_{\text{high}}} < 1 - \frac{T_{\text{low}}}{T_{\text{high}}}. \quad (18)$$

Notice that  $T_{3'} \geq T_{1'}$  depending on whether  $(\Delta'_{\text{low}}/\Delta'_{\text{high}})^2 \geq T_{\text{low}}/T_{\text{high}}$ . Thus, to obtain a special Otto-like cycle with  $T_{3'} = T_{1'}$  and efficiency  $1 - (T_{\text{low}}/T_{\text{high}})^{1/2}$ , we may set  $(\Delta'_{\text{low}}/\Delta'_{\text{high}})^2 = T_{\text{low}}/T_{\text{high}}$  so that  $\Delta_2 = \Delta_4$ . Notice also that in terms of the iso-energy-level gaps of the Carnot cycle in which the Otto cycle is inscribed, the case  $T_{3'} > T_{1'}$  obtains for  $(T_{\text{low}}/T_{\text{high}})^{5/2} < \Delta_{\text{low}}/\Delta_{\text{high}} < (T_{\text{low}}/T_{\text{high}})^{3/2}$ . In this range, the Otto cycle cannot be run in reverse (refrigeration or heat-pump) mode between two heat baths, for in such mode the hot bath temperature must be at most  $T_{1'}$  and the cold bath at least  $T_{3'}$ .

Because the iso-energy-gap processes (iso-magnetic field for spin-1/2 system) which characterize the Otto-type cycle are not isotherms, if they are obtained [4] by contacts with heat baths at  $T_{\text{high}}$  and  $T_{\text{low}}$ , respectively, they involve entropy generation due to irreversibility resulting from the heat exchange (see eq. (14)) across a large temperature difference (decreasing as  $T_{1'} \rightarrow T_{\text{high}}$  and  $T_{3'} \rightarrow T_{\text{low}}$ ). These and other realistic irreversibilities are modeled in ref. [6] with a Kossakowski-Lindblad-type linear dissipative term in the quantum dynamical law, as a means to describe relaxation to equilibrium and decoherence, required for example to decouple the system from the heat source, *i.e.*, to model dynamically the heat interactions. The only way to avoid these inefficiencies is the impractical sequence of infinitesimal contacts with an infinite collection of hot heat baths covering the temperature range between  $T_{1'}$  and  $T_{\text{high}}$  and an infinite collection of cold heat baths covering the temperature range between  $T_{3'}$  and  $T_{\text{low}}$ .

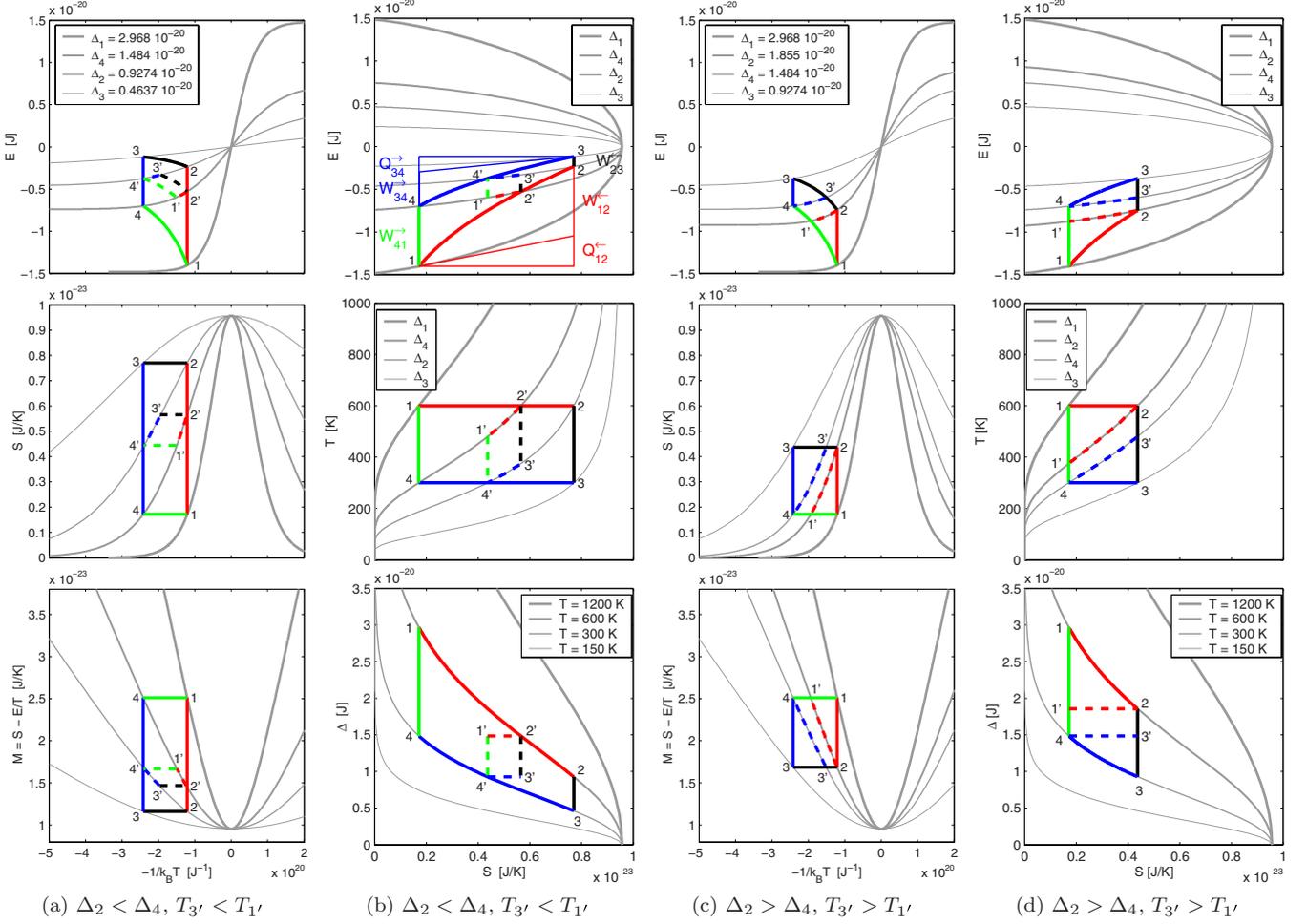


Fig. 1: (Color online) Graphs of thermodynamic equilibrium properties of a spin-1/2 system. Panels (a) and (c): graphs of energy  $E$ , entropy  $S$ , Massieu function  $M = S - (E/T)$  vs.  $-1/k_B T$  at four values of the energy level gap  $\Delta$ . Panels (b) and (d): graphs of energy  $E$  and temperature  $T$  vs. entropy  $S$  at four values of  $\Delta$ , and of the energy level gap  $\Delta$  vs.  $S$  at four values of temperature. The four values of  $\Delta$  in (a) and (b) correspond to magnetic-field intensities of 1600, 500, 250, and 800 T, respectively; in (b) and (d) of 1600, 1000, 500, and 800 T (these extremely large values are chosen for ease of visualization at ordinary temperatures and intermediate entropies). On each graph, the 1-2-3-4 paths represents a Carnot cycle: isotherm 1-2 at  $T_{\text{high}} = 600$  K, isentropic 2-3, isotherm 3-4 at  $T_{\text{low}} = 300$  K, isentropic 4-1. For these cycles,  $Q_{12}^{\leftarrow} = T_{\text{high}}(S_2 - S_1)$ ,  $W_{12}^{\leftarrow} = E_2 - E_1 - Q_{12}^{\leftarrow}$ ,  $W_{23}^{\leftarrow} = E_3 - E_2$ ,  $Q_{34}^{\leftarrow} = T_{\text{low}}(S_2 - S_1)$ ,  $W_{34}^{\leftarrow} = E_3 - E_4 - Q_{34}^{\leftarrow}$ ,  $W_{41}^{\leftarrow} = E_4 - E_1$  and, therefore,  $W_{\text{net},1234}^{\leftarrow} = W_{34}^{\leftarrow} + W_{41}^{\leftarrow} - W_{12}^{\leftarrow} - W_{23}^{\leftarrow} = (T_{\text{high}} - T_{\text{low}})(S_2 - S_1) = Q_{12}^{\leftarrow}[1 - (T_{\text{low}}/T_{\text{high}})]$ . The 1'-2'-3'-4' paths ( $2' = 2$  and  $4' = 4$  in (c) and (d)) represent instead an Otto-type cycle of the kind considered in refs. [4,6]: iso-energy-gap process 1'-2' with  $T \leq T_{\text{high}} = 600$  K, isentropic 2'-3', iso-energy-gap 3'-4' with  $T \geq T_{\text{low}} = 300$  K, isentropic 4'-1'. For these Otto-type cycles,  $\Delta_{1'} = \Delta_{2'} = \Delta'_{\text{high}} = \max(\Delta_2, \Delta_4)$ ,  $\Delta_{3'} = \Delta_{4'} = \Delta'_{\text{low}} = \min(\Delta_2, \Delta_4)$ ,  $Q_{1'2'}^{\leftarrow} = E_{2'} - E_{1'}$ ,  $W_{4'1'}^{\leftarrow} = E_{4'} - E_{1'} = E_{1'}[(\Delta'_{\text{low}}/\Delta'_{\text{high}}) - 1]$ ,  $W_{2'3'}^{\leftarrow} = E_{3'} - E_{2'} = E_{2'}[(\Delta'_{\text{low}}/\Delta'_{\text{high}}) - 1]$  and, therefore,  $W_{\text{net},1'2'3'4'}^{\leftarrow} = W_{4'1'}^{\leftarrow} - W_{2'3'}^{\leftarrow} = Q_{1'2'}^{\leftarrow}[1 - (\Delta'_{\text{low}}/\Delta'_{\text{high}})]$ .

In this paper, instead, by showing the feasibility of a Carnot cycle for a two-level system, with no need of sequences of infinitesimal heat exchanges with an infinite number of heat baths, we show that the quantum nature of the working substance does not impose any fundamental bound, other than the celebrated Carnot bound, to the thermodynamic efficiency of heat-to-work conversion when two different temperature thermal reservoirs are available. The possibility of engineering simultaneously heat and work interactions as needed for the isotherms of the

Carnot cycle seems within the reach of the current experiments, *e.g.*, via a maser-laser tandem technique [1]. The Carnot cycle “efficiency” is higher, as it should, than that of the “inscribed” Otto-like cycle at the center of recent studies [1–6].

Only twenty years ago quantum thermodynamics and pioneering proposals to incorporate the second law of thermodynamics into the quantum level of description were considered “adventurous” schemes [17,18]. Discussions in quantum terms of old thermodynamic problems

such as that of “unitary accessibility” [15] or of defining entropy for non-equilibrium states, were perceived as almost irrelevant speculations. Today’s experimental techniques bring thermodynamics questions back to the forefront of quantum theory. Remarkably, the rigorous application of energy and entropy balances, provides ideas and guidance, and the second law remains a perpetual source of inspiration towards the discovery of new physics.

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