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Bath-generated work extraction and inversion-free gain in two-level systems

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Abstract

The spin–boson model, often used in NMR and ESR physics, quantum optics and spintronics, is considered in a solvable limit to model a spin one-half particle interacting with a bosonic thermal bath. By applying external pulses to a non-equilibrium initial state of the spin, work can be extracted from the thermalized bath. It occurs on the timescale $\mathcal{T}_2$ inherent to quantum coherence. The work (partly) arises from heat given off by the surrounding bath, while the spin entropy remains constant during a pulse. This presents a new mechanism and time and temperature regimes for limiting the validity of the Clausius inequality and Thomson's formulation of the second law (cycles cost work). Apart from this, starting from a fully disordered state, coherence can be induced by employing the bath. A gain from a positive-temperature (inversion-free) two-level system is shown to be possible.

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1. Introduction

The consensus between thermodynamics and quantum mechanics lies at the heart of modern physics. The viewpoint expressed in textbooks [1], namely that thermodynamical laws and relations are extendible to the quantum situation, was recently strengthened by consideration of microscopic analogues of the Carnot engine [2], quantum Szilard machines [3] and the Jaynes principle [4]. Some of the basic thermodynamical processes were recently proposed to be realizable in quantum-optical setups [5].

We have recently discussed [6, 7] situations—displayed via the exactly solvable model of a harmonic Brownian oscillator coupled to its thermal bath—where several formulations of the second law are not valid in the quantum situation: the Clausius inequality $đQ \leqslant T\,\mathrm{d}S$ can be broken, the rates of energy dispersion and entropy production can be negative, and several cycles are possible where heat extracted from a bath is fully converted into work.

The cause of the breakdown of the universal thermodynamic picture was the entanglement between the Brownian particle and its bath, which can be visualized as the occurrence of a cloud of interaction modes (photons or phonons) around the central system. The cloud is not present at high temperatures, but, due to the non-vanishing coupling to the bath, it builds up at low T, inducing non-thermodynamic physics. Nevertheless, these findings support the Thomson formulation of the second law (cycles cost work) applied to an equilibrium initial distribution, for which an exact proof exists [8].

Here we present a complementary mechanism, based on the quantum coherence, which provides another scenario for limiting the validity of the second law. It is realized in two-level systems coupled to a thermal bath and subject to external forces. A similar system already refreshed our understanding of thermodynamics, because after Hahn discovered the spin–echo in NMR physics [9], this phenomenon was discussed in a thermodynamical context [10], and it was even suspected to endanger the second law [11].

We consider the 'spin–boson model' for a spin-$\frac{1}{2}$ (an electron, a two-state atom in a field or a two-level Josephson junction) interacting with a bath of harmonic oscillators [12, 13]. The Hamiltonian reads

$$\begin{aligned} &\mathcal{H} = \mathcal{H}(\Delta) = \mathcal{H}_S + \mathcal{H}_B + \mathcal{H}_I && \mathcal{H}_S = \frac{\varepsilon}{2}\hat{\sigma}_z + \frac{\Delta}{2}\hat{\sigma}_x \\ &\mathcal{H}_B = \textstyle\sum_k \hbar\omega_k \hat{a}_k^\dagger \hat{a}_k && \mathcal{H}_I = \frac{1}{2}\sum_k g_k\big(\hat{a}_k^\dagger + \hat{a}_k\big)\hat{\sigma}_z. \end{aligned} \tag{1}$$

$\mathcal{H}_S, \mathcal{H}_B$ and $\mathcal{H}_I$ stand for the Hamiltonians of the spin, the bath and their interaction, respectively. $\hat{\sigma}_x$, $\hat{\sigma}_y$ and $\hat{\sigma}_z = -\mathrm{i}\hat{\sigma}_x\hat{\sigma}_y$ are the Pauli matrices, and $\hat{a}_k^\dagger$ and $\hat{a}_k$ are the creation and annihilation operators of the bath oscillator with the index k, while the g_k are the coupling constants. For an electron in a magnetic field B, $\varepsilon = \bar{g}\mu_B B$ is the energy, with $\bar{g}$ the gyromagnetic factor and μ_B the Bohr magneton. In ESR physics [14] the model represents an electron spin interacting with a bath of phonons, for NMR it can represent a nuclear spin interacting with a spin bath, since in certain natural limits the latter can be mapped to the oscillator bath [15]. In quantum optics it is suitable for describing a two-level atom interacting with a photonic bath [15, 16].

Starting from general physical arguments [12], one typically takes the quasi-Ohmic spectral density of the bath

$$J(\omega) = \sum_k \frac{g_k^2}{\hbar\omega_k}\delta(\omega_k - \omega) = \frac{g\hbar}{\pi}\,\mathrm{e}^{-\omega/\Gamma} \tag{2}$$

where $g \ll 1$ is a dimensionless damping constant and the exponential cuts off the coupling at $\omega \gg \Gamma$, the maximal frequency of the bath. The thermodynamic limit for the bath has been taken here which allows a thermodynamic analysis of a small system (the spin) coupled to a large bath.

First, we consider the model with $\Delta = 0$, which is a prototype of a variety of physical systems [12], and known to be exactly solvable [12, 13], since the z-component of the spin is conserved, and with it the spin energy. Physically it means that we restrict ourselves to times much less than the relaxation time $\mathcal{T}_1$ of the longitudinal component $\langle\hat{\sigma}_z\rangle$. The von Neumann evolution equation for $\hat{a}_k(t)$ (Heisenberg representation) has the exact solution

$$\sum_k g_k\big[\hat{a}_k^\dagger(t) + \hat{a}_k(t)\big] = \hat{\eta}(t) - \hat{\sigma}_z G(t) \tag{3}$$

where we denoted the quantum noise operator

$$\hat{\eta}(t) = \sum_k g_k\big[\hat{a}_k^\dagger(0)\,\mathrm{e}^{\mathrm{i}\omega_k t} + \hat{a}_k(0)\,\mathrm{e}^{-\mathrm{i}\omega_k t}\big] \tag{4}$$

which will act as a random force on the spin, and where

$$G(t) = \sum_k \frac{g_k^2}{\hbar\omega_k}(1 - \cos\omega_k t) = \frac{g\hbar\Gamma}{\pi}\frac{\Gamma^2 t^2}{1 + \Gamma^2 t^2}. \tag{5}$$

Thus $1/\Gamma$ is the relaxation time of the bath, and for $t \gg 1/\Gamma$ the system is in the thermodynamical regime [1, 10].

1.1. Separated initial state

Because our purpose is to discuss thermodynamical relations in experimentally realizable non-equilibrium situations, we consider two types of initial setup: separated initial states and preparation via an excitation in the equilibrium state. To describe situations where the spin was suddenly brought into contact with the bath, e.g. an electron injected into a semiconductor, an atom injected into a cavity or an exciton created by external radiation, we make the assumption that initially, at $t = 0$, the spin and the bath are in a separated state, the latter being Gibbsian at temperature $T = 1/\beta$: $\rho(0) = \rho_S(0) \otimes \exp(-\beta\mathcal{H}_B)/Z_B$, where $\rho_S(0)$ is the initial density matrix of the spin. Here the quantum noise is stationary and Gaussian with average zero and time-ordered autocorrelation function: $K_{\mathcal{T}}(t - t') = \langle \mathcal{T}\hat{\eta}(t)\hat{\eta}(t')\rangle$, where $\mathcal{T}$ stands for the time-ordering operator and the brackets for the trace over the initial state. For $t > 0$ it holds that

$$K_{\mathcal{T}}(t) = \hbar^2[\ddot{\xi}(t) - \mathrm{i}\ddot{G}_1(t)] \tag{6}$$

where an explicit calculation yields

$$\xi(t) = \frac{g}{\pi}\ln\frac{\Gamma^2\left(1 + \frac{T}{\hbar\Gamma}\right)\sqrt{1 + \Gamma^2 t^2}}{\Gamma\left(1 + \frac{T}{\hbar\Gamma} - \mathrm{i}\frac{Tt}{\hbar}\right)\Gamma\left(1 + \frac{T}{\hbar\Gamma} + \mathrm{i}\frac{Tt}{\hbar}\right)} \tag{7}$$

$$G_1(t) = \frac{g}{\pi}\Gamma t - \gamma(t) \qquad \gamma(t) = \frac{g}{\pi}\arctan\Gamma t. \tag{8}$$

The Heisenberg equations for the spin operators $\hat{\sigma}_\pm = \hat{\sigma}_x \pm \mathrm{i}\hat{\sigma}_y$ have, with $\omega_0 = \varepsilon/\hbar$, the solution

$$\hat{\sigma}_\pm(t) = \exp(\pm\mathrm{i}\omega_0 t)\,\hat{\Pi}_\pm(t,0)\hat{\sigma}_\pm(0) \qquad \hat{\Pi}_\pm(t_1,t_0) \equiv \mathrm{e}^{-\mathrm{i}G_1(t_1-t_0)}\mathcal{T}\exp\pm\frac{\mathrm{i}}{\hbar}\int_{t_0}^{t_1}\mathrm{d}s\,\hat{\eta}(s) \tag{9}$$

$\eta(t)$, depending only on $\hat{a}_k(0)$ and $\hat{a}_k^\dagger(0)$, commutes with $\hat{\sigma}_{x,y,z}(0)$. Thus one gets by evaluating the time-ordered product with the help of Wick's theorem

$$\langle\hat{\sigma}_\pm(t)\rangle = \mathrm{e}^{\pm\mathrm{i}\omega_0 t - \xi(t)}\langle\hat{\sigma}_\pm(0)\rangle. \tag{10}$$

For $t \gg 1/\Gamma$ equation (7) brings $\xi(t) \approx t/\mathcal{T}_2$, $\mathcal{T}_2 = \hbar/(gT)$. Thus $\mathcal{T}_2$ can be identified with the transversal decay time.

The density matrix of the spin reads

$$\rho_S = \tfrac{1}{2}[1 + \langle\hat{\sigma}_x(t)\rangle\hat{\sigma}_x + \langle\hat{\sigma}_y(t)\rangle\hat{\sigma}_y + \langle\hat{\sigma}_z(t)\rangle\hat{\sigma}_z]. \tag{11}$$

Its von Neumann entropy equals $S_{\mathrm{vN}} = -\mathrm{tr}\,\rho_S\ln\rho_S = -p_1\ln p_1 - p_2\ln p_2$, where $p_{1,2} = \frac{1}{2} \pm \frac{1}{2}|\langle\vec{\sigma}\rangle|$. In the course of time $|\langle\vec{\sigma}(t)\rangle|$ decays to $|\langle\hat{\sigma}_z(0)\rangle|$, which makes the von Neumann entropy increase. Since there is no heat flow—the energy is conserved—this is a particular case of the H-theorem, which is one of the formulations of the second law; see [17] for a recent discussion.

1.2. A sudden pulse

So far we considered the Hamiltonian (1) with $\Delta = 0$. A fast rotation around the x-axis is described by taking a large Δ during a short time δ_1, so that within δ_1 the influence of the rest of the Hamiltonian can be neglected (fast pulse [14]). The evolution operator describing the pulse becomes $U_1 = \exp(-\mathrm{i}\delta_1 \mathcal{H}(\Delta)/\hbar) \approx \exp\left(\frac{1}{2}\mathrm{i}\theta_1\hat{\sigma}_x\right)$, with $\theta_1 = -\delta_1\Delta/\hbar$ the rotation angle,

$$U_1^{-1}\begin{pmatrix}\hat{\sigma}_y\\ \hat{\sigma}_z\end{pmatrix}U_1 = \begin{pmatrix}\hat{\sigma}_y\cos\theta_1 + \hat{\sigma}_z\sin\theta_1\\ \hat{\sigma}_z\cos\theta_1 - \hat{\sigma}_y\sin\theta_1\end{pmatrix}. \tag{12}$$

During the sudden switchings of $\Delta(t)$ from 0 to Δ and from Δ to 0, the state of the system does not change, so $\rho(t+\delta_1) = U_1\rho(t)U_1^{-1}$. The work done by the source is the change of the total energy (since the overall energy is conserved, this is the amount of energy which flowed to the source inducing the external field [1, 10]):

$$W_1(t) = \mathrm{tr}\,\rho(t)\big(U_1^{-1}\mathcal{H}U_1 - \mathcal{H}\big). \tag{13}$$

In the present case it becomes

$$W_1 = -\frac{\varepsilon}{2}(1-\cos\theta_1)\langle\hat{\sigma}_z(0)\rangle - \frac{\varepsilon}{2}\sin\theta_1\langle\hat{\sigma}_y(t)\rangle + \frac{1}{2}(1-\cos\theta_1)G(t) - \frac{\hbar\dot{\xi}(t)}{2}\sin\theta_1\langle\hat{\sigma}_x(t)\rangle. \tag{14}$$

Our main interest is work extraction from the bath. We therefore first consider the limit $\varepsilon \to 0$, where the spin has no energy. For small g and for $t \gg 1/\Gamma$

$$W_1 = (1-\cos\theta_1)\frac{g\hbar\Gamma}{2\pi} - \sin\theta_1\frac{gT}{2}\langle\hat{\sigma}_x(0)\rangle\,\mathrm{e}^{-t/\mathcal{T}_2}. \tag{15}$$

If for a fixed t, temperature is neither too large nor too small, $T\mathrm{e}^{-t/\mathcal{T}_2} > (\hbar\Gamma/\pi)\tan\frac{1}{2}\theta_1$, work can be extracted ($W_1 < 0$), provided the spin started in a coherent state $\langle\hat{\sigma}_x(0)\rangle = 1$. This possibility *to extract work from the bath* disappears on the timescale $\mathcal{T}_2$, because then the coherence is lost, $\langle\hat{\sigma}_{x,y}(t)\rangle \to 0$. The existence of work extraction by means of a cycle (pulse) goes against the non-equilibrium Thomson formulation of the second law.

Now note that heat $\Delta\mathcal{Q}$ received by the spin is standardly defined [1, 10] as $\Delta\mathcal{Q} = \Delta\mathcal{U} - W$, where W is the work, and $\Delta\mathcal{U} = \varepsilon\Delta(\langle\hat{\sigma}_z\rangle)/2$ is the change of the spin's energy during the action of the extremal field. Under a rotation the length $|\langle\vec{\sigma}\rangle|$, and with it the von Neumann entropy, is left invariant, so one has a process with $\Delta\mathcal{Q} = -W_1 > 0$, $\Delta S_{\mathrm{vN}} = 0$, violating the Clausius inequality $\Delta\mathcal{Q} \leqslant T\Delta S_{\mathrm{vN}}$. This inequality is one of the non-equilibrium formulations of the second law [1, 10]; it connects thermal disorder (heat) with the configurational disorder (entropy). The appearance of the von Neumann entropy in this inequality and further details on it are discussed in [17].

A pulse with $\theta_1 = \pi$ is called 'classical', since it does not generate coherent terms $\langle\hat{\sigma}_{x,y}\rangle$. According to equation (15) it costs energy. Combinations of π pulses can extract work from a non-thermalized bath, i.e. for times $\sim 1/\Gamma$.

1.3. Initial preparation via a rotation

Let us now consider another realistic non-equilibrium initial state: a Gibbsian of the total system, $\rho_G = \exp(-\beta\mathcal{H})/Z$, in which at $t = 0$ the spin is rotated ('zeroth pulse') over an angle $\theta_0 = \frac{1}{2}\pi$ around the y-axis, thus mapping $\hat{\sigma}_z \to \hat{\sigma}_x$, $\hat{\sigma}_x \to -\hat{\sigma}_z$. Such a state models the optical excitation of the spin, as is done in NMR and spintronics. (A rotation around the x-axis would yield closely related results, e.g. in equations (16), (17) and (20) time-dependent sines and cosines would be interchanged.) Though $\rho(0)$ does not have a product form, the problem remains exactly solvable. For the pulse described by (12) and (13) one now gets for $t \gg 1/\Gamma$ the decomposition $W_1 = \Delta\mathcal{U}_1 - \Delta\mathcal{Q}_1$ with the change in energy of the spin

$$\Delta\mathcal{U}_1 = -\frac{\varepsilon}{2}\sin\theta_1 \sin\,\omega_0 t \tanh\frac{\beta\varepsilon}{2}\,\mathrm{e}^{-t/\mathcal{T}_2} \tag{16}$$

and the heat absorbed from the bath

$$\Delta\mathcal{Q}_1 = -(1-\cos\theta_1)\frac{g\hbar\Gamma}{2\pi} + \frac{gT}{2}\sin\theta_1\cos\omega_0 t\tanh\frac{\beta\varepsilon}{2}\,\mathrm{e}^{-t/\mathcal{T}_2}. \tag{17}$$

An interesting case is where work is performed by the total system ($W_1 < 0$) solely due to heat taken from the bath ($\Delta\mathcal{Q} > 0$, $\Delta\mathcal{U} = 0$). This process, possible by choosing $t = 2\pi n/\omega_0$ with integer n, is forbidden by folklore-minded formulations of the second law. Note that the Clausius inequality is violated since $\Delta S_{\mathrm{vN}} = 0$.

The work needed at time zero to rotate the spin is $W_0 = (\varepsilon/2)\tanh(\beta\varepsilon/2) + g\hbar\Gamma/(2\pi)$ representing the work done on the spin and on the bath, respectively. It can be verified that the total work $W_0 + W_1$ is always positive, so Thomson's formulation for a cyclic change [8] (here: the combination of the pulses at time $t = 0$ and t) starting from equilibrium is obeyed.

1.4. Two pulses in a rotated initial Gibbsian state

Typical measurements in NMR physics are carried out on disordered ensembles of many independent spins [14]. If each spin is in a slightly different external field, the frequency $\omega_0 = \varepsilon/\hbar$ can be viewed as a random quantity (inhomogeneous broadening) for which we assume the distribution

$$p(\omega_0) = \frac{1}{\pi}\frac{[\mathcal{T}_2^*]^{-1}}{(\omega_0-\bar{\omega}_0)^2 + [\mathcal{T}_2^*]^{-2}} \tag{18}$$

having average $\bar{\omega}_0$ and inverse width $\mathcal{T}_2^*$, typically much smaller than $\mathcal{T}_2$. Here $\mathcal{T}_2^*$ defines a new relaxation time for the average (collective) transversal components. In this case the gain for a single pulse is washed out, leaving only a loss, the first term of equation (17). Nevertheless, as in spin–echo experiments, the effect survives when two pulses are considered. We consider again the initial Gibbsian state rotated over $\frac{1}{2}\pi$ around the y-axis, and perform a first π pulse around the x-axis at time t_1 and a second $\frac{1}{2}\pi$ pulse at time $t_2 = t_1 + \tau$. In the regime of small g and large $t_1 \sim \mathcal{T}_2$ the work in the second pulse is

$$W_2 = \frac{g\hbar\Gamma}{2\pi} - \frac{1}{2}\mathrm{e}^{-t_1/\mathcal{T}_2}\varepsilon\sin\omega_0\tau\tanh\frac{\beta\varepsilon}{2} - \tfrac{1}{2}\mathrm{e}^{-t_2/\mathcal{T}_2}\tanh\frac{\beta\varepsilon}{2}\cos\omega_0 t_1(\varepsilon\sin\omega_0\tau + gT\cos\omega_0\tau). \tag{19}$$

At moderate times only slowly oscillating terms survive. They are the ones that involve $\Delta t = t_2 - 2t_1$. For the average of the total work $W_1 + W_2$ this brings

$$W = \frac{3g\hbar\Gamma}{2\pi} - \frac{\hbar}{2}\mathrm{e}^{-t_2/\mathcal{T}_2 - |\Delta t|/\mathcal{T}_2^*}\tanh\frac{\beta\hbar\bar{\omega}_0}{2}\left\{\bar{\omega}_0\sin\bar{\omega}_0\Delta t + \left[\frac{1}{\mathcal{T}_2} - \frac{\mathrm{sg}(\Delta t)}{\mathcal{T}_2^*}\left(1 + \frac{\beta\hbar\bar{\omega}_0}{\sinh\beta\hbar\bar{\omega}_0}\right)\right]\cos\bar{\omega}_0\Delta t\right\}. \tag{20}$$

For a Δt near $2\pi n/\bar{\omega}_0$ the odd terms cancel, and W again exhibits work extracted solely from the bath. At $\Delta t = 0$ one gets, using $\mathrm{sg}(0) = 0$, a result close to equation (15).

1.5. Bath-induced gain without inversion

It is common knowledge that a two-level system with population inversion, i.e. with a negative temperature, is capable of amplifying light and represents the basic working mechanism of lasers and masers. In this context a bath is typically considered as a source of undesirable noises and relaxation towards equilibrium, supposed drawbacks for amplification [16]. Here we show that the bath can nevertheless play a totally different role, namely in *assisting* work extraction (gain) by means of a *positive* temperature state in the two-level system. In the absence of coupling to the bath such an effect is strictly prohibited by the second law applied to a positive temperature spin state [8].

We consider separated initial conditions with $\langle\hat{\sigma}_x(t)\rangle = \langle\hat{\sigma}_y(t)\rangle = 0$, and apply a $-\frac{1}{2}\pi$ pulse around the x-axis at time $t_0 = 0^+$, and a $\frac{1}{2}\pi$ pulse at t. For $t \gg 1/\Gamma$ the work $W = \Delta\mathcal{U} - \Delta\mathcal{Q}$ is set by:

$$\begin{aligned} \Delta\mathcal{U} &= -\frac{\varepsilon}{2}[1 - \mathrm{e}^{-\xi(t)}\cos\omega_0 t]\langle\hat{\sigma}_z\rangle + \frac{g\varepsilon}{4}\,\mathrm{e}^{-\xi(t)}\sin\omega_0 t \\ \Delta\mathcal{Q} &= -\frac{g\hbar\Gamma}{\pi} + \frac{1}{2}gT\,\mathrm{e}^{-\xi(t)}\sin\omega_0 t\,\langle\hat{\sigma}_z\rangle \end{aligned} \tag{21}$$

where ξ was defined in (7). In the inversion-free case, the initial state of the spin is a Gibbsian connected to a positive temperature $T_0 = 1/\beta_0$, for which $\langle\hat{\sigma}_z\rangle = -\tanh\frac{1}{2}\beta_0\varepsilon \leqslant 0$. Let us first investigate the case $T_0 = \infty$ (completely random state, $\langle\hat{\sigma}_{x,y,z}\rangle = 0$). The work W can be negative (gain) provided $\varepsilon > 4\hbar\Gamma/\pi$. This situation can be met in quantum optical two-level systems [16, 22] and in NMR [18]. This mechanism concerns work extraction *with the help of the bath* (it disappears for $g \to 0$), but *not from the bath*, since now $\Delta\mathcal{Q} < 0$. The origin of the effect is that although the state of the spin was completely disordered initially, the first pulse does generate some coherence. Due to back reaction of the bath one has after the pulses $\langle\hat{\sigma}_y(t)\rangle = \sin\gamma(t)\exp(-\xi(t))\sin\omega_0 t$, where $\gamma(t)$ of equation (8) goes from 0 to $\frac{1}{2}g$ on the timescale $1/\Gamma$, the reaction time of the bath. At finite T_0 the term $\Delta\mathcal{U}$ can still be negative when $T_0 \gtrsim \varepsilon/g$, which can be met for not-too-small g, a condition anyhow needed for having a sizeable effect. From a thermodynamic point of view the gain can just be seen as a flow of energy from a high temperature (of the spin) to a lower one (of the bath), and the outside world (gain). Note that there exist other mechanisms for inversionless gain [16]. The crucial difference as compared to the present proposal is that they operate with (at least) three-level systems (atoms), and—most importantly—there the effect appears due to special, non-thermal states of the atom itself. Frequently these states can be disclosed as containing a hidden inversion [16].

1.6. Feasibility

Let us mention a few aspects favouring the feasibility of the reported scheme. (1) Work and heat were measured in NMR experiments more than 35 years ago [19]; (2) our main effects do survive the averaging over disordered ensembles of spins. (3) There are experimentally realized examples of two-level systems, which have sufficiently long $\mathcal{T}_2$ times, and admit external variations on times smaller than $\mathcal{T}_2$: (i) for atoms in optical traps $\mathcal{T}_2 \sim 1$ s, $1/\Gamma \sim 10^{-8}$ s, and there are efficient methods for creating non-equilibrium initial states and manipulating atoms by external laser pulses [22]; (ii) for an electronic spin injected or optically excited in a semiconductor $\mathcal{T}_2 \sim 1\,\mu$s [20]; (iii) for an exciton created in a quantum dot $\mathcal{T}_2 \sim 10^{-9}$ s [21] (in cases (ii) and (iii) $1/\Gamma \sim 10^{-13}$ s and femtosecond (10^{-15} s) laser pulses are available); (iv) in NMR physics $\mathcal{T}_2 \sim 10^{-6} - 1$ s and the duration of pulses can be comparable with $1/\Gamma \sim 1\,\mu$s.

2. Conclusion

We report a new mechanism, displayed via the spin–boson model, which limits the validity of the Clausius inequality and Thomson's formulation of the second law. In particular, work can be extracted from the equilibrated bath by means of external pulses (cycles). The cause of the effect lies in quantum coherence of the spin (transversal components), in the presence of coupling to the bath. The effect does not exist for classical pulses, as they do not excite coherence. Otherwise, characteristic times and temperature can be large $\mathcal{T}_2 \lesssim 10\,\mathrm{s}$, $T \geqslant 100\,\mathrm{K}$.

It is instructive to compare with quantum limits to the second law presented in [6, 7]. There the main issue lies in entanglement between the Brownian particle and its bath, reflected in the non-Gibbsian stationary state of the particle. Characteristic times are in the nanosecond regime and temperatures in the (sub-)Kelvin regime.

For the current model the presence of entanglement remains to be demonstrated. As seen from (1) the Gibbs state of the total system will imply for the state of the spin the same Gibbs distribution with the Hamiltonian $\mathcal{H}_S$. In this context let us stress the general reasons for viewing the spin and the bath as two *different* subsystems: (i) observational accessibility: the bath is not observed in experiments, while the spin is; (ii) timescale separation: the bath relaxation time is much smaller than that of the spin; (iii) no backreaction: the spin does not perturb the collective variables of the bath due to its macroscopic character.

We finally show that gain is possible from a positive temperature (inversion-free) initial state, due to the non-intuitive phenomenon of bath-induced coherence, a new principle for bath generated lasing and masing.

All these effects are in perfect agreement with the *equilibrium* Thomson formulation of the second law [8].

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