QUANTUM REFRIGERATORS AND THE III-LAW OF THERMODYNAMICS

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ABSTRACT

Quantum thermodynamics addresses the emergence of thermodynamical laws from quantum mechanics. The III-law of thermodynamics has been mostly ignored. There are seemingly two independent formulation of the third law of thermodynamics, both originally stated by Nernst. The first is known as Nernst heat theorem, which is purely static, and implies that the entropy flow from any substance at the absolute zero is zero. And the second formulation known as the unattainability principle practically state that no refrigerator can cool a system to absolute zero at finite time. We explore the dynamic version which is the vanishing of rate of temperature decrease of a cooled quantum bath when $T \to 0$. The III-law is then quantified dynamically by evaluating the characteristic exponent ξ of the cooling process:

$$\frac{dT(t)}{dt} \propto -T^{\xi}$$

when approaching absolute zero, $T \to 0$. A generic continuous model of a quantum refrigerator is presented. The refrigerator is a nonlinear device merging three currents from three heat baths: a cold bath to be cooled, a hot bath as an entropy sink, and a driving bath which is the source of cooling power. A heat-driven refrigerator (absorption refrigerator) is compared to a power-driven refrigerator. Similar results are obtained from reciprocating Otto refrigerators. When optimized, all cases lead to the same exponent ξ, showing a lack of dependence on the form of the working medium and the characteristics of the drivers. The characteristic exponent is therefore determined by the properties of the cold reservoir and its interaction with the system. Two generic heat bath models are considered: a bath composed of harmonic oscillators and a bath composed of ideal Bose/Fermi gas. The restrictions on the interaction Hamiltonian imposed by the third law which are discussed.

INTRODUCTION

Quantum thermodynamics is the study of thermodynamical processes within the context of quantum dynamics. Thermodynamics preceded quantum mechanics, consistence with thermodynamics led to Planck's law, the dawn of quantum theory. Incorporating the ideas of Planck on black body radiation, Einstein (1905), quantised the electromagnetic field [1]. *Quantum thermodynamics* is devoted to unraveling the intimate connection between the laws of thermodynamics and their quantum origin requiring consistency. For many decades the two theories developed separately. Scovil [2; 3; 4] pioneered the study of quantum engines and quantum ref refrigerators showing the equivalence of the Carnot engine [5] with the three level Maser.

With the establishment of quantum theory the emergence of thermodynamics from quantum mechanics becomes a key issue. The two theories address the same subject from different viewpoints. This requires a consistent view of the state and dynamics of matter. Despite its name, dynamics is absent from most thermodynamic descriptions. The standard theory concentrates on systems close to equilibrium. We advocate a dynamical perspective on quantum thermodynamics [6] and in particular its implication on the III-law of thermodynamics. I will emphasis *learning by example* analyzing quantum refrigerators to unravel the III-law.

Quantum mechanics has been used to reintroduce dynamical processes into thermodynamics. In particular, the theory of quantum open systems supplies the framework to separate the system from its environment. The Markovian master equation pioneered by Lindblad and Gorini-Kossakowski-Sudarshan (LGKS generator) [7; 8] is one of the key elements of the theory of quantum thermodynamics [9; 10]. The dynamical framework allows to reinterpret and justify the theory of finite time thermodynamics [11; 12; 13] which addresses thermodynamical processes taking place in finite time.

Two major classes of refrigerators will serve to illustrate the III-law, continuous and reciprocating. These classes can be examined up to the level of a single quantum device. The prime example of a continuous quantum refrigerator is laser cooling. In this case light is used to power the refrigerator. The device can be understood as reversing the operation of a 3-level laser [4; 14; 15; 16; 17; 18; 19; 20; 21; 22; 23; 24; 25; 26; 27]. An important addition is a quantum absorption refrigerator which is a refrigerator with heat as its power source [28; 29; 19; 30]. An example could be a refrigerator driven by sunlight [31]. Amazingly, in all these examples a thermodynamical description is appropriate up to the level of a single open quantum system [10; 32; 33; 34].

The minimum requirement for constructing a continuous refrigerator is a system connected simultaneously to three reservoirs [12]. These baths are termed hot, cold and work reservoir as described in Fig. 1.

This framework has to be translated to a quantum description of its components which include the Hamiltonian of the system $\hat{H}_s$ and the implicit description of the reservoirs. Different designs of refrigerators are reflected in the Hamiltonian of the working medium.

Reciprocating refrigerators operate by a working medium shuttling heat from the cold to the hot reservoir. The task is carried out by a controlled dynamical system. A change in the

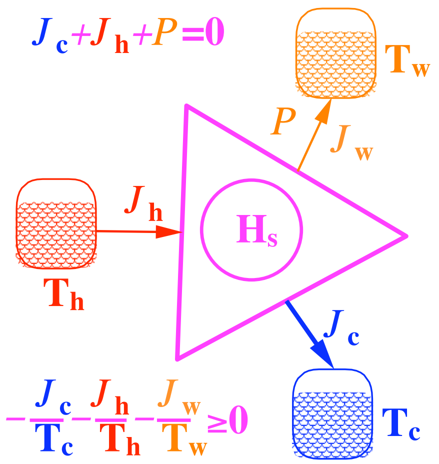

Figure 1. A quantum heat pump designated by the Hamiltonian $\hat{H}_s$ coupled to a work reservoir with temperature T_w, a hot reservoir with temperature T_h and a cold reservoir with temperature T_c. The heat and work currents are indicated. In steady state $\mathcal{J}_h + \mathcal{J}_c + \mathcal{P} = 0$ and the entropy production $\frac{\mathcal{J}_h}{T_h} + \frac{\mathcal{J}_c}{T_c} + \frac{\mathcal{J}_w}{T_w} \geq 0$.

Hamiltonian of the system is accompanied by a change in the internal temperature. Upon contact with the cold side the temperature of the working medium is forced to be lower than T_c-the cold bath temperature. In a quantum reciprocating refrigerator the control of temperature is governed by manipulating the energy levels of the system through external perturbation [35; 36; 37].

The adiabatic condition is an important idealisation in thermodynamics. In quantum thermodynamics their is a close connection to the quantum adiabatic condition. When the adiabatic conditions are not fulfilled, additional work is required to reach the final control value. For an isolated system this work is recoverable since the dynamics are unitary and can be reversed. The coherences stored in the off-diagonal elements of the density operator carry the required information to recover the extra energy cost and reverse the dynamics. Typically, this energy is not recoverable due to interaction with a bath that causes energy dephasing. This lost energy is the quantum version of friction [38; 39; 40].

There are several strategies to minimise the effect of quantum friction. One possibility, termed *quantum lubrication*, is to force the state of the system to commute with the instantaneous Hamiltonian $[\hat{\rho}(t), \hat{H}(t)] = 0$. This can be achieved by adding an external source of phase noise [41]. In the case of quantum refrigerators this noise was always harmful leading to a minimum temperature the refrigerator can reach [37; 42].

Is it possible to find non-adiabatic control solutions with an initial and final state diagonal in the energy representation $[\hat{\rho}_i, \hat{H}(0)] = 0$, $[\hat{\rho}_f, \hat{H}(t_f)] = 0$? This possibility, which relies on special dynamical symmetries, has been termed *shortcut to adiabaticity* [43; 44; 45; 46; 36; 47; 48]. The idea is to optimise the scheduling function $f(t)$ of the control $\hat{H}_C(t) = \hat{V}_C f(t)$ in such a way that in the shortest time the frictionless transformation from an initial value of the control function to a final value is achieved. Refrigerators which are able to approach $T_c \to 0$ are frictionless.

Eventually all refrigerators converge to a universal behaviour where the heat conductivity with the cold bath and the heat capacity of the cold bath determine the III-law characteristics.

THE QUANTUM TRICYCLE

A quantum description enables to incorporate dynamics into thermodynamics. The tricycle model is the template for almost all continuous engines and refrigerators. The tricycle engine has a generic structure displayed in Fig. 1.

The basic model consists of three thermal baths: a hot bath with temperature T_h, a cold bath with temperature T_c and a work bath with temperature T_w.
Each bath is connected to the engine via a frequency filter which we will model by three oscillators:

$$\hat{H}_F = \hbar\omega_h \hat{a}^\dagger \hat{a} + \hbar\omega_c \hat{b}^\dagger \hat{b} + \hbar\omega_w \hat{c}^\dagger \hat{c} \ , \tag{1}$$

where ω_h, ω_c and ω_w are the filter frequencies on resonance $\omega_w = \omega_h - \omega_c$.
The device operates as an engine by removing an excitation from the hot bath and generating excitations on the cold and work reservoirs. In second quantization the hamiltonian describing such an interaction becomes:

$$\hat{H}_I = \varepsilon \left(\hat{a}\hat{b}^\dagger \hat{c}^\dagger + \hat{a}^\dagger \hat{b}\hat{c} \right) \ , \tag{2}$$

where ε is the coupling strength.
The device operates as a refrigerator by removing an excitation from the cold bath and from the work bath and generating an excitation in the hot bath. The r.h.s of the Hamiltonian of Eq. (2) describes this action.

The frequency filters select from the continuous spectrum of the bath the working component to be employed in the tricycle. These frequency filters can be constructed also from two-level-systems (TLS) or formulated as qubits [32]. Finally, the interaction term is strictly non-linear incorporating three heat currents simultaneously. This crucial fact has important consequences. A linear device cannot operate as a heat engine or refrigerator [49].

The I-law of thermodynamics is the energy balance of heat currents originating from the three baths and collimating on the system [50; 9],:

$$\frac{dE_s}{dt} = \mathcal{J}_h + \mathcal{J}_c + \mathcal{J}_w \ . \tag{3}$$

At steady state no heat is accumulated in the tricycle thus $\frac{dE_s}{dt} = 0$. In addition entropy is only generated in the baths leading to the II-law of thermodynamics:

$$\frac{d}{dt}\Delta S_u = \frac{\mathcal{J}_h}{T_h} + \frac{\mathcal{J}_c}{T_c} + \frac{\mathcal{J}_w}{T_w} \geq 0 \ . \tag{4}$$

When the temperature $T_w \to \infty$ no entropy is generated in the power bath. An energy current with no accompanying entropy production is equivalent to producing pure power: $\mathcal{P} = \mathcal{J}_w$ where $\mathcal{P}$ is the output power.

A reduced description for the dynamical equations of motion of tricycle are set within the formalism of quantum open system:

$$\frac{d}{dt}\hat{\rho}_s = \mathcal{L}\hat{\rho}_s \tag{5}$$

where $\hat{\rho}_s$ is the density operator of the tricycle $\mathcal{L}$ is the Liouville superoperaor. Under Markovian conditions $\mathcal{L}$ takes the form of the Gorini-Kossakowski-Sudarshan-Lindlad (GKS-L) generator [7; 8]. We chose to present the generator in Heisenberg form for the system operator $\hat{O}$

$$\frac{d}{dt}\hat{O} = \mathcal{L}^*(\hat{O}) \;=\; \frac{i}{\hbar}[\hat{H}_s,\hat{O}] + \sum_k \hat{V}_k\hat{O}\hat{V}_k^\dagger - \frac{1}{2}\{\hat{V}_k\hat{V}_k^\dagger,\hat{O}\} \quad (6)$$

Where the operators $\hat{V}_k$ are system operators still to be determined. The task of evaluating the modified system Hamiltonian $\hat{H}_s$ and the operators $\hat{V}_k$ is made extremely difficult due to the nonlinear interaction in Eq. (2). Any progress from this point requires a specific description of the heat baths and approximations to deal with the nonlinear terms.

The noise driven absorption refrigerator

The absorption refrigerator is the most simple example of a device able to cool up to the absolute zero. Other devices such as power driven refrigerators lead to very similar results. In the absorption refrigerator the noise is the source of power driving the refrigerator replacing Eq. (2) with:

$$\hat{H}_I = f(t)\left(\hat{a}^\dagger\hat{b} + \hat{a}\hat{b}^\dagger\right) = f(t)\hat{X}\,, \quad (7)$$

where $f(t)$ is the noise field. $\hat{X} = (\hat{a}^\dagger\hat{b} + \hat{a}\hat{b}^\dagger)$ is the generator of a swap operation between the two oscillators. In addition $\hat{X}$ is part of a closed set of $SU(2)$ operators , $\hat{Y} = i(\hat{a}^\dagger\hat{b} - \hat{a}\hat{b}^\dagger)$, $\hat{Z} = \left(\hat{a}^\dagger\hat{a} - \hat{b}^\dagger\hat{b}\right)$ and the Casimir $\hat{N} = \left(\hat{a}^\dagger\hat{a} + \hat{b}^\dagger\hat{b}\right)$.

The Heisenberg equation for tricycle operators $\hat{O}$ reduced to:

$$\frac{d}{dt}\hat{O} \;=\; i[\hat{H}_s,\hat{O}] + \mathcal{L}_n(\hat{O}) + \mathcal{L}_h(\hat{O}) + \mathcal{L}_c(\hat{O})\,, \quad (8)$$

where $\hat{H}_s = \hbar\omega_h\hat{a}^\dagger\hat{a} + \hbar\omega_c\hat{b}^\dagger\hat{b}$. For a Gaussian source of white noise characterised by zero mean $\langle f(t)\rangle = 0$ and delta time correlation $\langle f(t)f(t')\rangle = 2\eta\delta(t-t')$. The noise dissipator becomes $\mathcal{L}_n(\hat{O}) = -\eta[\hat{X},[\hat{X},\hat{O}]]$ [51].

The generators $\mathcal{L}_h$ and $\mathcal{L}_c$ become the standard energy relaxation terms driving oscillator $\omega_h\hat{a}^\dagger\hat{a}$ to thermal equilibrium with temperature T_h and $\mathcal{L}_c$ drives oscillator $\hbar\omega_b\hat{b}^\dagger\hat{b}$ to equilibrium T_c [52].

$$\begin{aligned}
\mathcal{L}_h(\hat{O}) \;&=\; \Gamma_h(N_h+1)\left(\hat{a}^\dagger\hat{O}\hat{a} - \tfrac{1}{2}\left\{\hat{a}^\dagger\hat{a},\hat{O}\right\}\right) \\
&\quad + \Gamma_h N_h\left(\hat{a}\hat{O}\hat{a}^\dagger - \tfrac{1}{2}\left\{\hat{a}\hat{a}^\dagger,\hat{O}\right\}\right) \\
\mathcal{L}_c(\hat{O}) \;&=\; \Gamma_c(N_c+1)\left(\hat{b}^\dagger\hat{O}\hat{b} - \tfrac{1}{2}\left\{\hat{b}^\dagger\hat{b},\hat{O}\right\}\right) \\
&\quad + \Gamma_c N_c\left(\hat{b}\hat{O}\hat{b}^\dagger - \tfrac{1}{2}\left\{\hat{b}\hat{b}^\dagger,\hat{O}\right\}\right)
\end{aligned} \;. \quad (9)$$

In the absence of the stochastic driving field these equations drive oscillator a and b separately to thermal equilibrium provided that $N_h = (\exp(\frac{\hbar\omega_h}{kT_h}) - 1)^{-1}$ and $N_c = (\exp(\frac{\hbar\omega_c}{kT_c}) - 1)^{-1}$. The kinetic coefficients $\Gamma_{h/c}$ are determined from the system bath coupling and the spectral function [14].

The absorption refrigerator can also be powered by a high temperature source. At the high temperature limit of the work bath $T_w \to \infty$ the nonlinearity of Eq. (2) can be simplified. The generator of dissipation of the work bath becomes:

$$\begin{aligned}
\mathcal{L}_w(\hat{O}) \;&=\; \Gamma_w(N_w+1)\left(\hat{a}^\dagger\hat{b}\hat{O}\hat{b}^\dagger\hat{a} - \tfrac{1}{2}\left\{\hat{a}^\dagger\hat{a}\hat{b}\hat{b}^\dagger,\hat{O}\right\}\right) \\
&\quad + \Gamma_w N_w\left(\hat{a}\hat{b}^\dagger\hat{O}\hat{a}^\dagger\hat{b} - \tfrac{1}{2}\left\{\hat{a}\hat{a}^\dagger\hat{b}^\dagger\hat{b},\hat{O}\right\}\right)
\end{aligned}\,. \quad (10)$$

where $N_w = (\exp(\frac{\hbar\omega_w}{kT_h}) - 1)^{-1}$. At finite temperature $\mathcal{L}_w(\hat{O})$ does not lead to a close set of equations. But in the limit of $T_w \to \infty$ it becomes equivalent to the Gaussian noise generator: $\mathcal{L}_w(\hat{O}) = -\eta/2\left([\hat{X},[\hat{X},\hat{O}]] + [\hat{Y},[\hat{Y},\hat{O}]]\right)$, where $\eta = \Gamma_w N_w$.

The equations of motion in both case are closed to the $SU(2)$ set of operators. The cooling current $\mathcal{J}_c = \langle\mathcal{L}_c(\hbar\omega_c\hat{b}^\dagger\hat{b})\rangle$, is solved for stationary conditions for $\hat{N}$ and $\hat{Z}$.

Optimal cooling power is obtained for balanced heat conductivity $\Gamma_h = \Gamma_c \equiv \Gamma$, then:

$$\mathcal{J}_c \;=\; \hbar\omega_c\frac{2\eta\Gamma(N_c - N_h)}{\Gamma + 4\eta}\;. \quad (11)$$

Cooling occurs for $N_c > N_h \Rightarrow \frac{\omega_h}{T_h} > \frac{\omega_c}{T_c}$ which is the Carnot condition. The coefficient of performance (COP) for the absorption chiller is defined by the relation $COP = \frac{\mathcal{J}_c}{\mathcal{J}_n}$, with the help of Eq. (11) we obtain the Otto cycle COP [53]:

$$COP \;=\; \frac{\omega_c}{\omega_h - \omega_c} \;\leq\; \frac{T_c}{T_h - T_c}\;. \quad (12)$$

Optimizing the cooling current $\mathcal{J}_c$ Eq. (11) first with respect to the gain $G = N_h - N_c$ leads to $\omega_c \propto T_c$. Then optimizing the power input leads to $\mathcal{J}_c \propto \hbar\omega_c\Gamma$. This means that the cooling rate as $T_c \to 0$ depends on the characteristics of the heat conductivity as the filter frequency $\omega_c \to 0$. Other continuous driven refrigerators show the same phenomena [20].

RECIPROCATING REFRIGERATORS

The quantum reciprocating refrigerator employes a working medium to shuttly heat from the cold to the hot reservoir. This requires a Hamiltonian that can be controlled externally changing the energy level structure. Typically the external control influences only part of the Hamiltonian operator::

$$\hat{H} \;=\; \hat{H}_{int} + \hat{H}_{ext}(\omega) \quad (13)$$

where $\omega = \omega(t)$ is the time dependent external control field. Generically, the internal and external parts do not commute $[\hat{H}_{int},\hat{H}_{ext}] \neq 0$. This has a profound effect on the adiabatic segments of the refrigerator since then $[\hat{H}(t),\hat{H}(t')] \neq 0$. A state which was initially prepared to be diagonal in the temporary energy eigenstates, cannot follow adiabatically the changes in energy levels induced by the control. The result is an additional power required to execute the adiabatic segment termed quantum friction [38]. This friction has been found to limit the performance of the heat engines [39; 54; 41; 40]. In quantum refrigerators the frictional heating in the expansion-demagnetization segment limits the minimal temperature of the working medium. This in turn puts a restriction on the minimum temperature that can be achieved. This means that a refrigerator that can reach the absolute zero has to be frictionless.

One obvious solution to a frictionless operation is perfect adiabatic following i.e. at each time the system is diagonal in the temporary energy eigenstates. The drawback of such an approach is that it requires ever increasing time to execute this move when the temperature approaches $T_c = 0$. The question then arises what is the minimum time required to execute an adiabatic move.

Demanding that only at the initial and final time the system is diagonal in the energy representation leads to additional opportunities for frictionless solutions. For a working medium consisting of harmonic oscillators such solutions have been found [46; 36; 48] which are characterized by a fast finite expansion time. If negative frequencies are permissible this time can be reduced further [43]. For these models where the energy gap can be controlled to follow the cold bath temperature T_c, the absolute zero seems attainable.

THE QUANTUM OTTO HEAT PUMP

The Otto model is a solvable example of a reciprocating refrigerator. The objective is to optimize the cooling rate in the limit when the temperature T_c of the cold bath approaches absolute zero. A necessary condition for operation is that upon contact with the cold bath the temperature of the working medium be lower than the bath temperature $T_{int} \leq T_c$ [55]. The opposite condition exists on the hot bath. To fulfil these requirements the external controls modify the internal temperature by changing the energy level spacings of the working fluid. The control field varies between two extreme values ω_c and ω_h, where ω is a working medium frequency induced by the external field. The working medium consists of an ensemble of non interacting particles in a harmonic potential. The Hamiltonian of this system, $\hat{\mathrm{H}} = \frac{1}{2m}\hat{\mathrm{P}}^2 + \frac{K(t)}{2}\hat{\mathrm{Q}}^2$, is controlled by changing the curvature $K = m\omega^2$ of the confining potential.

The cooling cycle consists of two heat exchange branches alternating with two adiabatic branches. The heat exchange branches (the *isochores*) take place with ω =constant, while the adiabatic branches take place with the working medium decoupled from the baths. This is reminiscent of the Otto cycle in which heat is transferd to the working medium from the hot and cold baths under constant volume conditions.

The heat carrying capacity of the working medium limits the amount of heat Q_c which can be extracted from the cold bath. Under the quantum adiabatic condition. This means also $n_D \geq n_h^{eq}$, leading to $\mathcal{Q}_c \;\leq\; \hbar\omega_c\left(n_c^{eq} \;-\; n_h^{eq}\right)$. Maximum $\mathcal{Q}_c$ is obtained for high frequency $\hbar\omega_h \gg k_B T_h$, leading to $n_h^{eq} = 0$ and $E_A = \frac{1}{2}\hbar\omega_h$ being the ground state energy. Then for $T_c \to 0$:

$$\mathcal{Q}_c^* \;=\; \hbar\omega_c n_c^{eq} \;=\; \hbar\omega_c e^{-\frac{\hbar\omega_c}{k_B T_c}} \;\leq\; k_B T_c \tag{14}$$

where we have substituted the value of n_c^{eq} obtained from the partition function and the last inequality is obtained by optimizing with respect to ω_c leading to $\hbar\omega_c^* = k_B T_c$. The general result is that as $T_c \to 0$, $\mathcal{Q}_c^*$ and ω_c^* become linear in T_c.

Only a finite cycle period τ leads to a non vanishing cooling power $\mathcal{R}_c = \mathcal{Q}_c/\tau$. This cycle time $\tau = \tau_{hc} + \tau_c + \tau_{ch} + \tau_h$ is the sum of the times allocated to each branch. An upper bound on the cooling rate $\mathcal{R}_c$ is required to limit the exponent as $T_c \to 0$. The optimal cooling rate $\mathcal{R}_c^{opt}$ depends on the time allocation on the different branches.

Optimization of the cooling rate

For sufficiently low T_c, the rate limiting branch of the cycle is cooling the working medium to a temperature below T_c along the expansion *adiabat*). As $T_c \to 0$, the total cycle time τ is of the order of the time of this cooling adiabat, τ_{hc}, which tends to infinity.

Quantum friction is completely eliminated if the *adiabat* proceeds quasistatically with $\mu \ll 1$. This leads to a scaling law $\mathcal{R}_c \propto T^{\delta}$ with $\delta \geq 3$. It turns out however that it is not the only frictionless way to reach the final state at energy $E_D = (\omega_c/\omega_h)E_A$. Other possibilities which require less time and result in improved scaling, $\delta = 2$ and $\delta = 3/2$ $\delta \sim 1$ have been worked out.

All frictionless solutions lead to an upper bound on the optimal cooling rate of the form:

$$\mathcal{R}_c \leq A\omega^{\nu} n_c^{eq} \tag{15}$$

where A is a constant and the exponent ν is either $\nu = 2$ for the $\mu = const$ solution or $\nu = \frac{3}{2}$ for the three-jump solution of attractive potentials [36] and $\nu \sim 1$ for repulsive potentials [47]. Optimizing $\mathcal{R}_c$ with respect to ω_c leads to a linear relation between ω_c and T_c,

At high compression ratio $\omega_h \gg \omega_c$ and if in addition $\omega_c \ll \Gamma$ we obtain:

$$\mathcal{R}_c^* \;\approx\; \hbar\omega_c^2 n_c^{eq} \tag{16}$$

for the $\mu = const$ frictionless solution. For the three-jump frictionless solution if one restricts to attractive traps:

$$\mathcal{R}_c^* \;\approx\; \frac{1}{2}\hbar\omega_c^{\frac{3}{2}}\sqrt{\omega_h}n_c^{eq} \;\;, \tag{17}$$

and for repulsive traps [47]:

$$\mathcal{R}_c^* \;\approx\; \frac{1}{2}\hbar\omega_c \log\omega_c\sqrt{\omega_h}n_c^{eq} \;\;, \tag{18}$$

Due to the linear relation between ω_c and T_c, Eq. (16) and (17) the exponent δ where $\delta = 3$ for the quasistatic scheduling, $\delta = 2$ for the constant μ frictionless scheduling and $\delta = \frac{3}{2}$, $\delta \sim 1$ for the three-jump frictionless scheduling.

Once optimising the time allocated for the adiabatic expansion it becomes clear that the heat transport branch will become eventually the time limiting step. This means that as $T_c \to 0$ the reciprocating and the continuous refrigerator will both be limited by the heat transport rate Γ_c.

THE III-LAW

The third law of thermodynamics was initiated by Nernst [56; 57; 58]. Nernst formulated two independent statements. The first is a purely static (equilibrium) one, also known as the "Nernst heat theorem": phrased:

> The entropy of any pure substance in thermodynamic equilibrium approaches zero as the temperature approaches zero.

The second formulation is dynamical, known as the unattainability principle:

> It is impossible by any procedure, no matter how idealised, to reduce any assembly to absolute zero temperature in a finite number of operations [59; 58].

There is an ongoing debate on the relations between the two formulations and their relation to the II-law regarding which and if at all, one of these formulations implies the other [60; 61; 62; 63]. Quantum considerations can illuminate these issues.

At steady state the second law implies that the total entropy production is non-negative, cf. Eq. (4). When the cold bath approaches the absolute zero temperature, it is necessary to eliminate the entropy production divergence at the cold side. When $T_c \to 0$ the entropy production scales as

$$\dot{S}_c \sim -T_c^{\alpha} \quad , \quad \alpha \geq 0 \ . \tag{19}$$

For the case when $\alpha = 0$ the fulfilment of the second law depends on the entropy production of the other baths, which should compensate for the negative entropy production of the cold bath. The first formulation of the III-law modifies this restriction. Instead of $\alpha \geq 0$ the III-law imposes $\alpha > 0$ guaranteeing that at absolute zero the entropy production at the cold bath is zero: $\dot{S}_c = 0$. This requirement leads to the scaling condition of the heat current $\mathcal{J}_c \sim T_c^{\alpha+1}$.

The second formulation is a dynamical one, known as the unattainability principle; *No refrigerator can cool a system to absolute zero temperature at finite time*. This formulation is more restrictive, imposing limitations on the system bath interaction and the cold bath properties when $T_c \to 0$ [20]. The rate of temperature decrease of the cooling process should vanish according to the characteristic exponent ζ:

$$\frac{dT_c(t)}{dt} \sim -T_c^{\zeta}, \quad T_c \to 0 \ . \tag{20}$$

Solving Eq. (20), leads to;

$$T_c(t)^{1-\zeta} = T_c(0)^{1-\zeta} - ct \quad , for\ \zeta < 1 \ , \tag{21}$$

where c is a positive constant. From Eq. (21) the cold bath is cooled to zero temperature at finite time for $\zeta < 1$. The III-law requires therefore $\zeta \geq 1$. In order to evaluate Eq.(20) the heat current can be related to the temperature change:

$$\mathcal{J}_c(T_c(t)) = -c_V(T_c(t))\frac{dT_c(t)}{dt} \ . \tag{22}$$

This formulation takes into account the heat capacity $c_V(T_c)$ of the cold bath. $c_V(T_c)$ is determined by the behaviour of the degrees of freedom of the cold bath at low temperature. Therefore the scaling exponents can be related $\zeta = 1 + \alpha - \eta$ where $c_V \sim T_c^{\eta}$ when $T_c \to 0$.

To get additional insight specific cases are examined. The quantum refrigerator models differ in their operational mode being either continuous or reciprocating. When $T_c \to 0$ the refrigerators have to be optimised adjusting to the decreasing temperature. The receiving mode of the refrigerator has to become occupied to transfer energy. The rate of this process is proportional to a Boltzmann term $\omega_c^{\gamma}\exp[-\frac{\hbar\omega_c}{k_BT_c}]$. When optimised for maximum cooling rate the energy difference of the receiving mode should scale linearly with temperature $\omega_c \sim T_c$ [15; 28; 36; 19; 20]. Once optimised the cooling power of all refrigerators studied have the same dependence on the coupling to the cold bath. This means that the III-law depends on the scaling properties of the heat conductivity $\gamma_c(T_c)$ and the heat capacity $c_V(T_c)$ as $T_c \to 0$.

Harmonic oscillator cold heat bath

The harmonic heat bath is a generic type of a quantum bath. It includes the electromagnetic field: A photon bath, or a macroscopic piece of solid; a phonon bath, or Bogliyubov excitations in a Bose-Einstein condensate. The model assumes linear coupling of the refrigerator to the bath. The standard form of the bath's Hamiltonian is:

$$\hat{H}_{int} = (\hat{b} + \hat{b}^{\dagger})\left(\sum_k (g(k)\hat{a}(k) + \bar{g}(k)\hat{a}^{\dagger}(k))\right) \ ,$$

$$\hat{H}_B = \sum_k \omega(k)\hat{a}^{\dagger}(k)\hat{a}(k) \ , \tag{23}$$

where $\hat{a}(k), \hat{a}^{\dagger}(k)$ are annihilation and creation operators for a mode k. For this model the weak coupling limit procedure leads to the LGKS generator with the cold bath relaxation rate given by [20]

$$\gamma_c \equiv \gamma_c(\omega_c) = \pi(\sum_k |g(k)|^2\delta(\omega(k) - \omega_c)\left[1 - e^{-\frac{\hbar\omega(k)}{k_BT_c}}\right]^{-1} \ . \tag{24}$$

For the Bosonic field in d-dimensional space, and with the linear low-frequency dispersion law ($\omega(k) \sim |k|$) the following scaling properties for the cooling rate at low frequencies are obtained

$$\gamma_c \sim \omega_c^{\kappa}\omega_c^{d-1}\left[1 - e^{-\hbar\omega_c/k_BT_c}\right]^{-1} \tag{25}$$

where ω_c^{κ} represents the scaling of the coupling strength $|g(\omega)|^2$ and ω_c^{d-1} the scaling of the density of modes. It implies the following scaling relation for the cold current

$$\mathcal{J}_c \sim T_c^{d+\kappa}\left[\frac{\omega_c}{T_c}\right]^{d+\kappa}\frac{1}{e^{\hbar\omega_c/k_BT_c} - 1} \tag{26}$$

Optimization of Eq. (26) with respect to ω_c leads to the frequency tuning $\omega_c \sim T_c$ and the final current scaling

$$\mathcal{J}_c^{opt} \sim T_c^{d+\kappa}. \tag{27}$$

Taking into account that for low temperatures the heat capacity of the bosonic systems scales like

$$c_V(T_c) \sim T_c^d \tag{28}$$

which produces the scaling of the dynamical equation, Eq. (20):

$$\frac{dT_c(t)}{dt} \sim -(T_c)^{\kappa}. \tag{29}$$

Similarly, the same scaling Eq. (29) is achieved for the periodically driven refrigerator, with the optimization tuning $\omega_c, \lambda \propto T_c$.
The III-law implies a constraint on the form of interaction with a bosonic bath

$$\kappa \geq 1. \tag{30}$$

For standard systems like electromagnetic fields or acoustic phonons with linear dispersion law $\omega(k) = v|k|$ and the form-factor $g(k) \sim |k|/\sqrt{\omega(k)}$ the parameter $\kappa = 1$ as for low ω, $|g(\omega)|^2 \sim |k|$. However, the condition (30) excludes exotic dispersion laws $\omega(k) \sim |k|^{\alpha}$ with $\alpha < 1$ which anyway produce the infinite group velocity forbidden by the relativity theory. Moreover, the popular choice of Ohmic coupling is excluded for systems in dimension $d > 1$. The condition (30) can be also compared with the condition

$$\kappa > 2 - d \quad , \tag{31}$$

which is necessary to assure the existence of the ground state for the bosonic field interacting by means of the Hamiltonian (23). The third law loses its validity if the cold bath does not have a ground state. For a harmonic bath this could happen if even one of the effective oscillators has an inverted potential.

The existence of a ground state

A natural physical stability condition which should be satisfied by any model of an open quantum system is that its total Hamiltonian should be bounded from below and should possess a ground state. In the quantum degenerate regime even a mixture of isotopes will segregate and lead to a unique ground state. In the case of systems coupled linearly to bosonic heat baths it implies the existence of the ground state for the following bosonic Hamiltonian (compare with (23)):

$$H_{bos} = \sum_k \left\{ \omega(k) a^{\dagger}(k) a(k) + (g(k) a(k) + \bar{g}(k) a^{\dagger}(k)) \right\} \quad . \tag{32}$$

Introducing a formal transformation to a new set of bosonic operators

$$a(k) \mapsto b(k) = a(k) + \frac{\bar{g}(k)}{\omega(k)} \; . \tag{33}$$

we can write

$$H_{bos} = \sum_k \omega(k) b^{\dagger}(k) b(k) - E_0, \; E_0 = \sum_k \frac{|g(k)|^2}{\omega(k)} \tag{34}$$

with the formal ground state $|0\rangle$ satisfying

$$b(k)|0\rangle = 0, \text{ for all } k. \tag{35}$$

For the interesting case of an infinite set of modes $\{k\}$, labeled by the d-dimensional wave vectors, two problems can appear:

1) The ground state energy E_0 can be infinite, i.e. does not satisfy

$$\sum_k \frac{|g(k)|^2}{\omega(k)} < \infty. \tag{36}$$

2) The transformation (33) can be implemented by a unitary one, i.e. $b(k) = U a(k) U^{\dagger}$ if and only if

$$\sum_k \frac{|g(k)|^2}{\omega(k)^2} < \infty. \tag{37}$$

Non-existence of such a unitary implies non-existence of the ground state (35) (in the Fock space of the bosonic field) and is called *van Hove phenomenon* [64].

While the divergence of the sums (36), (37) (or integrals for infinite volume case) for large $|k|$ can be avoided by putting an *ultra-violet cutoff*, the stronger condition (37) imposes restrictions on the form of $g(k)$ at low frequencies. Assuming, that $\omega(k) = v|k|$ and $g(k) \equiv g(\omega)$ the condition Eq. (37) is satisfied for the following low-frequency scaling in the d-dimensional case

$$|g(\omega)|^2 \sim \omega^{\kappa}, \; \kappa > 2 - d. \tag{38}$$

These conditions on the dispersion relation of the cold bath required for a ground state are identical to the conditions for the III-law Eq. (31). The consistency with the III-law ensures the existence of the ground state.

Ideal Bose/Fermi gas cold heat bath

An important generic cold bath consists of a degenerate quantum gas composed of ideal Bose or Fermi gas. The model refrigerator consists of the working medium of (infinitely) heavy particles with the internal structure approximated (at least at low temperatures) by a two-level-system (TLS) immersed in the low density gas at the temperature T_c. Insight into the III-law comes from realising that the degenerate gas is in equilibrium with a normal part. The external refrigerator only couples to the normal part. Once the temperature approaches zero the fraction of the normal part decreases, eventually nulling the cooling current. Another source of excitations are collective excitations of Bogoliubov type [65]. The low energy tail can be described as a phonon bath with linear dispersion thus the previous section covered the III-law for these excitations.

The Markovian dynamics of such systems was derived by Dumcke [66] in the low density limit and N-level internal structure. For the case of the TLS there is one receiving Bohr frequency ω_c. Cooling occurs due to the non-elastic scattering leading to energy exchange with this frequency [20]:

$$\gamma_c = 2\pi \mathbf{n} \int d^3\vec{p} \int d^3\vec{p}' \delta(E(\vec{p}') - E(\vec{p}) - \hbar\omega_c) f_{T_c}(\vec{p}_g) |T(\vec{p}', \vec{p})|^2 \tag{39}$$

with $\mathbf{n}$ the particles density, $f_{T_c}(\vec{p}_g)$ the probability distribution of the gas momentum strictly given by Maxwell's distribution, $\vec{p}$ and $\vec{p}'$ are the incoming and outgoing gas particle momentum.

$E(\vec{p}) = p^2/2m$ denotes the kinetic energy of gas particle.
At low-energies (low-temperature), scattering of neutral gas at 3-d can be characterized by s-wave scattering length a_s, having a constant transition matrix, $|T|^2 = (\frac{4\pi a_s}{m})^2$. For this model the integral (39) is calculated

$$\gamma_c = (4\pi)^4 (2\pi m T_c)^{-\frac{1}{2}} a_s^2 \mathbf{n} \omega_c \mathcal{K}_1 \left(\frac{\hbar\omega_c}{2k_B T_c}\right) e^{\frac{\hbar\omega_c}{2k_B T_c}} \;, \qquad (40)$$

where $\mathcal{K}_p(x)$ is the modified Bessel function of the second kind. Notice that formula (40) is also valid for an harmonic oscillator instead of TLS, assuming only linear terms in the interaction and using the Born approximation for the scattering matrix.

Optimizing formula (22) with respect to ω_c leads to $\omega_c \sim T_c$. Then the scaling of the heat current becomes:

$$\mathcal{J}_c^{opt} \sim \mathbf{n} (T_c)^{\frac{3}{2}} \;\; . \qquad (41)$$

When the Bose gas is above the critical temperature for the Bose-Einstein condensation the heat capacity c_V and the density $\mathbf{n}$ are constants. Below the critical temperature the density $\mathbf{n}$ in formula (39) should be replaced with the density $\mathbf{n}_{ex}$ of the exited states, having both $c_V, \mathbf{n}_{ex}$ scale as $\sim (T_c)^{\frac{3}{2}}$ which finally implies

$$\frac{dT_c(t)}{dt} \sim -(T_c)^{\frac{3}{2}} \;\; . \qquad (42)$$

In the case of Fermi gas at low temperatures only the small fraction $\mathbf{n} \sim T_c$ of fermions participate in the scattering process and contribute to the heat capacity, the rest is "frozen" in the "Dirac sea" below the Fermi surface. Again, this effect modifies in the same way both sides of (20) and therefore (42) is consistent with the III-law. Similarly, a possible formation of Cooper pairs below the critical temperature does not influence the scaling (42).

Figure 2 demonstrates the III-law showing the vanishing of the cooling current $\mathcal{J}_c$ and the temperature decrease rate $\frac{dT_c}{dt}$ as a function of T_c for the cases of the harmonic bath and Bose gas bath.

The dynamical version of the III-law is up for critical analysis [20]. The examples of quantum refrigerators show that the cooling exponents are independent of the type of refrigerator model used. The III-law exponents depend on the cold bath characteristics, the ratio between the heat conductivity and the heat capacity for a specific bath. This ratio should scale as $\sim T_c^{\zeta}$, $\zeta > 1$ for the III-law to hold cf, Eq. (20). There has been a recent challenge to the III-law claiming that zero temperature can be reached [30; 67]. In our view this discrepancy is caused by an uncontrolled approximation leading to the particular dispersion used.

CONCLUSIONS

Quantum thermodynamics is applicable up to the level of a single particle [6]. Very simple models have the same thermodynamical characteristics of macroscopic devices. For example efficiency at maximum power related to finite-time-thermodynamics. Also the quantum and thermodynamical adiabatic behaviour are closely linked. Deviations lead to friction resulting in reduced efficiency.

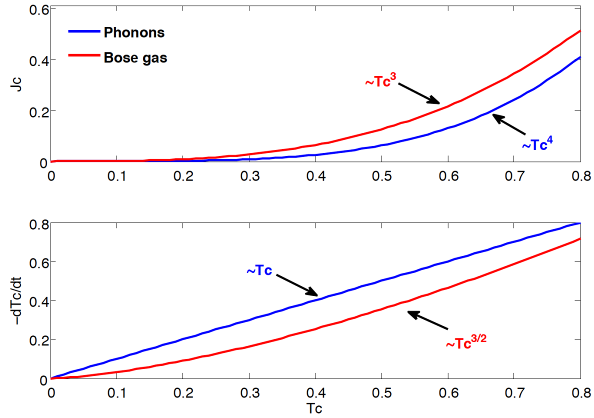

Figure 2. A demonstration of the III-law. The vanishing of the cooling current and the rate of temperature decrease as $T_c \to 0$. The harmonic bath in 3-d indicated in blue and Bose gas in three dimensions indicated in red. The Bose gas cools faster when $T_c \to 0$ but its rate of temperature decrease is slower than the harmonic bath.

After analysing many types of continuous and reciprocating refrigerators universal conclusions can be drawn. When $T_c \to 0$ the colling current is the product of three terms:

$$\mathcal{J}_c \sim -\hbar\omega_c \Gamma_c G$$

where $\hbar\omega_c$ is the energy quantum to be extracted from the cold bath. Γ_c is the rate of extraction or the heat conductivity. $G = N_h - N_c$ is the gain, the population difference between the hot and cold side. Optimizing the gain leads to $\omega_c \sim T_c$. This means that fulfilment of the III-law requires the ratio Γ_c/c_V to vanish as $T_c \to 0$, otherwise the cold bath can be cooled to its ground state in finite time.

The III-law can be thought of as an attempt to isolate completely a subsystem. Once a system is cooled to the absolute zero temperature it reaches a pure ground state and therefore becomes disentangled from the rest of the universe. The III-law is a statement that obtaining an isolated pure state is an idealisation impossible at finite time.

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