The maser as a reversible heat engine

Tomáš Opatrný(a)
Department of Physics, Texas A&M University, College Station, Texas 77843
and Department of Theoretical Physics, Palacký University, 17. listopadu 50, 77200 Olomouc,
Czech Republic

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In a maser, a state selector sends excited molecules or atoms to a resonant cavity, while ground-level particles are not allowed to enter the resonator. The excited particles radiate their energy in the form of coherent electromagnetic oscillation. In this way the thermal energy of the atoms is transformed into useful work. Is this transformation equivalent to the Maxwell demon violating the second law? We explain the thermodynamics of an idealized maser system which works as a reversible heat engine and show how the second law reveals its validity during the conversion of heat into coherent radiation and mechanical work. We discuss different working regimes of the system. In particular, the ideal engine can either work with two heat reservoirs and convert heat into maser radiation with the Carnot efficiency, or, if working with a single heat reservoir, the engine can convert mechanical work entirely into maser radiation. © 2005 American Association of Physics Teachers.

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I. INTRODUCTION

An essential characteristic of a maser, a quantum generator of microwave radiation, is a state selector in which a beam of atoms or molecules passes through an inhomogeneous electric or magnetic field. The trajectories of the particles depend on their internal states, so that only excited particles are allowed to enter the maser resonator, where their energy is transformed into coherent radiation. Feynman specifically considered the ammonia maser to illustrate some of the basic principles of quantum mechanics.1 (For more interesting details on masers, including their fascinating history, see Refs. 2 and 3.)

At first glance the state selection process seems to be inconsistent with the laws of thermodynamics,4 because it behaves just like the proverbial Maxwell demon that violates the second law of thermodynamics by sorting out hot molecules from cold molecules. We can imagine the excited atoms, after depositing their energy in the maser cavity, being sent along with the unexcited atoms to a hot reservoir to go through the excitation process all over again. In this way the atoms cyclically absorb heat energy from the reservoir and release it in the maser as useful coherent work. The reservoir cools and the maser works—apparently an example of perpetual motion of the second kind.

The crucial point is that the state selector in a maser works with atomic or molecular beams, that is, highly nonequilibrium entities. The Maxwell demon, on the other hand, sorts out hot and cold molecules in systems at thermal equilibrium. The situation has been analyzed recently using a model where a single atom, in the form of an “atomic pulse,” takes energy from a single thermal reservoir, radiates the energy in the maser, and then cycles back to the reservoir.5 It was found that the spatial volume occupied by the atom doubles after each cycle. Thus the empty space serves as a second reservoir, or “source of negentropy.” 6 Clearly this method can work only if sufficient space is available, or if the volume occupied by the atom is compressed back to its initial value.

The model in Ref. 5 assumes irreversible processes, which means that the conversion of heat into work is not optimum. In this article we present a model of a single atom maser that works in closed cycles like a heat engine, that is, a device that converts heat energy into work. In our model, heat is exchanged with thermal reservoirs during each cycle and mechanical and maser work is generated (or spent). All the processes considered are reversible, so that optimum conversion of heat into work is achieved. It is shown that the engine can serve as a “Carnot maser” when converting heat into maser radiation, with its efficiency being that of a Carnot cycle. The engine also can work in a different regime when converting mechanical work into maser radiation and vice versa: the efficiency of this conversion is shown to reach unity.

II. MASER CYCLES WITH A SINGLE ATOM

A schematic of the engine is depicted in Fig. 1. The working fluid is thermal radiation in a cylinder with perfectly reflecting walls, and a single two-level particle. We will assume the particle is an atom, without any loss of generality. The thermodynamics of thermal radiation (or photon gas) has been discussed.7–9 We use the property that radiation pressure can produce work when increasing the cylinder volume, and that the radiation can exchange heat reversibly with a reservoir, a black body of the same temperature and infinite heat capacity. In our model, the radiation is brought into contact with a thermal reservoir at temperature $T_1$, while the atomic center-of-mass motion has temperature $T_2$. 10 The internal state of the atom is assumed to be completely decoupled from the center-of-mass degrees of freedom.

At the beginning of the cycle, the atom is in its ground internal state, and its center-of-mass motion is characterized by the volume constraint $V_0$ and a thermal distribution of velocity corresponding to the temperature $T_2$, which is superimposed on a much larger average velocity $v$.

The atomic center-of-mass distribution behaves like a “pulse” with its volume corresponding to the uncertainty of the atomic position. The average pulse velocity $v$ should be sufficiently large so that the volume changes due to the thermal velocity distribution can be neglected during the cycle (or repairable by a proper atom-focusing device). In contact with the thermal radiation, the atomic internal state is heated to temperature $T_1$. The atom is then sent to the state selector...
Fig. 1. Scheme of the cycle. A two-level atom in the ground state is brought into contact with blackbody radiation and its internal state is heated to temperature $T_1$. The heating is done reversibly so that useful work $W_{\text{rad}}$ can be extracted. The atom then passes through a state selector (SS) that channels it into different paths depending on whether it is in the ground or excited state. The excited atom deposits its energy in a resonant maser cavity doing thus work $W_{\text{m}}$. The alternate paths are then reunited and the volume occupied by the atom is compressed to the initial value. The compression is done isothermally by spending work $W_{\text{comp}}$ with temperature $T_2$.

(a strongly inhomogeneous electric or magnetic field). The trajectory of an excited atom goes through the maser cavity resonant with the atomic transition, while the trajectory of a ground-state atom does not. The velocity of the atomic pulse and the strong coherent field in the cavity are arranged such that the time spent in the cavity corresponds to one half of the Rabi oscillation period. Thus, an excited atom deposits its energy in the form of a maser field.

Because the atomic pulse has two possible trajectories to follow, it now occupies twice the initial volume. To bring the atom back to the initial state, the volume is compressed isothermally by contact with a reservoir at temperature $T_2$. The atom then occupies the initial volume $V_0$ and returns to its ground-internal state so that it is ready to repeat the cycle. During the cycle some mechanical work was performed by expanding and compressing the thermal radiation, and by compressing the atomic center of mass. Useful maser work was done in the cavity and some heat was exchanged with the reservoirs. We will analyze the cycle under the condition that each process is done reversibly.

III. WORK FROM REVERSIBLE HEATING OF THE ATOM

The lower energy atomic internal state and the hot reservoir form a nonequilibrium system from which useful work can be extracted. The general theory that determines the maximum work that can be extracted from such systems is discussed in Ref. 11, and some specific examples are discussed in Refs. 12 and 13. We review some general results in Appendix A.

A two-level atom with energy level difference $\epsilon$ is heated by thermal radiation. To make this process reversible, we have to bring the atom in contact with radiation at the same temperature. To do so, we follow the cycle shown in Fig. 2. The radiation, initially at temperature $T_1$ and confined to volume $V_1$ (state 1), is subjected to adiabatic expansion. Because the radiation pressure $\propto T^4$, useful work can be generated when increasing the volume by moving the piston. The adiabatic condition requires perfectly reflecting walls; when the volume enclosed by such walls increases, each mode of the radiation increases its wavelength accordingly. The energy of the photons decreases with increasing wavelength so that the radiation temperature drops. The expansion is continued until the system is in state 2 in Fig. 2, which is at temperature $T_0$ equal to the two-level atom temperature. (See Appendix B for the basic relations of thermodynamic processes involving thermal radiation; for more details see Refs. 7–9.) The temperature $T_0$ (ideally absolute zero) is the lowest achievable temperature during the adiabatic expansion. The resulting volume is $V_2 = V_1(T_1/T_0)^3$ (see Eq. (B6)).

In the next step, the atom is brought into contact with the radiation, and the composite system (the radiation and the internal atomic state) is adiabatically compressed until the temperature becomes $T_1$. Because the atom now contributes to the heat capacity of the system, compression is easier than with radiation alone. More precisely, when adiabatically compressing the radiation, the pressure increases slower in the presence of the atom than without it. This behavior can be seen from the following calculations and also can be understood intuitively. We can imagine the radiation pressure arising from photons scattering off the perfectly reflecting walls. An atom in the system could absorb one of the photons which will then not contribute to the pressure. When the system reaches temperature $T_1$, its volume is less than $V_1$ (state 3 in Fig. 2).

In the final step, the system undergoes isothermal expansion to the initial volume $V_1$ due to contact with the heat reservoir at temperature $T_1$, and once again useful work is done. During the cycle, the net work $W_{\text{rad}}$ extracted corresponds to the area within the cycle in the $PV$ diagram. When only the radiation goes through the cycle, the temperature and pressure changes are governed by Eqs. (B6) and (B7). The presence of the atom changes the thermodynamic properties of the system (see Appendix C for the thermodynamic features of the atom). The internal energy of the combined system is

$$E = E^{(\text{rad})} + E^{(\text{at})},$$

where the radiation energy $E^{(\text{rad})}$ and the atomic energy $E^{(\text{at})}$ are given in Eqs. (B1) and (C2). If we differentiate the internal energy and use the thermodynamic relation,

$$dE = T dS - p dV,$$

along with $dS = 0$, we obtain the relation

$$dE = T dS - p dV,$$
\[
\frac{dV}{dT} = - \frac{3V}{T} + \frac{3}{4b} \frac{C^{(a)}(T)}{T^4},
\]
where the atomic heat capacity \(C^{(a)}(T)\) is defined in Eq. (C3).

The differential equation (3) can be solved using an integrating factor (see, for example, Ref. 14)
\[
V(T) = V_0 \left( \frac{T_0}{T} \right)^3 - \frac{3}{4bT_0^4} \int_{T_0}^{T} \frac{C^{(a)}(T')}{T'^4} dT',
\]
with the boundary condition \(V(T_0) = V_0\). Equation (4) can be rewritten in the pressure-dependent form
\[
V(P) = V_0 \left( \frac{P_0}{P} \right)^{3/4} - \Delta V(P),
\]
where
\[
\Delta V(P) = \frac{3}{4bT_0^3} \int_{P_0}^{P} \left( \frac{P_0}{P} \right)^{3/4} \frac{C^{(a)}(T)}{T} dP.
\]
is the difference of the volumes occupied by the radiation with and without the atom. (It is interesting that the maximum achievable volume difference depends only on the wavelength of the resonant radiation: \(\Delta V_{\text{max}} \approx 0.82(\lambda/2\pi)^3\), where \(\lambda = 2\pi c/\epsilon\).) The extracted work, corresponding to the area of the cycle in the \(PV\) diagram, can be calculated from Eq. (6) as
\[
W_{\text{rad}} = \int_{P_0}^{P_1} \Delta V(P) dP,
\]
and becomes
\[
W_{\text{rad}} = \frac{3P_0^{3/4}}{4bT_0^3} \int_{P_0}^{P_1} dP \int_{T_0}^{T_1} \frac{C^{(a)}(T)}{T} dT.
\]
If we change the order of integration, we obtain
\[
W_{\text{rad}} = \frac{3P_0^{3/4}}{4bT_0^3} \int_{T_0}^{T_1} \frac{C^{(a)}(T)}{T} dT \int_{T_0}^{T_1} \frac{dP}{P_0(P_0/P)^{1/4}},
\]
which yields
\[
W_{\text{rad}} = T_1 \int_{T_0}^{T_1} \frac{C^{(a)}(T)}{T} dT - \int_{T_0}^{T_1} C^{(a)}(T) dT.
\]

Equation (10) corresponds exactly to the general results shown in Eqs. (A2) and (A3) of Appendix A. In the limit of \(T_0 \to 0\) (assuming a perfect state selector), we obtain the simple result
\[
W_{\text{rad}} = T_1 S^{(a)}(T_1) - E^{(a)}(T_1) = kT_1 \ln [1 + \exp(-\epsilon/kT_1)],
\]
where the atomic entropy \(S^{(a)}(T)\) is given by Eq. (C4). Note that although during the process a relatively low temperature \(T_0\) has been reached, we do not assume any external reservoir with this temperature and \(T_0\) does not influence the efficiency.

**IV. MASER WORK**

After passing through the state selector, an excited atom deposits its energy in the maser cavity. Because ideally the maser radiation is in a pure quantum state, its entropy is zero and all the radiation energy can be considered to be work done by the system. The average work per cycle done by the maser is
\[
W_{\text{maser}} = p_e E^{(a)}(T_1) / kT_1 = (1.278) kT_1,
\]
where the excited-state probability \(p_e\) is given by Eq. (C1a). If the temperature \(T_1\) is given, we can find the value of \(\epsilon\) that maximizes the average work produced through the maser. From \((\partial W_{\text{maser}}/\partial \epsilon)T_1 = 0\), we find that the optimal \(\epsilon\) satisfies
\[
\epsilon / kT_1 = x_0,
\]
where \(x_0\) is the solution of the equation
\[
1 + e^{-x_0} - x_0 e^{-x_0} = 0.
\]
The numerical solution of Eq. (14) yields \(x_0 \approx 1.278\). The maximum work per cycle done by the maser is thus
\[
W_{\text{maser}} = kT_1 \frac{x_0}{e^{x_0} + 1} \approx 0.278 kT_1.
\]

**V. REVERSIBLE COMPRESSION OF THE VOLUME**

After passing through the state selector, the atomic pulse occupies twice the initial volume: it has a probability \(p_e\) of being in one space of volume \(V_0\), and a probability \(p_g\) of being in another space of same volume \(V_0\). To bring the total volume back to the initial value, we can use a “flying compressor” which is at rest relative to the atomic pulses. To make the compression reversible, we proceed as follows. Let us isothermally compress the volume occupied by the initially excited atom from \(V_0\) to \(V_e\), and the volume occupied by the ground-state atom from \(V_0\) to \(V_g\), where the values of \(V_e\) and \(V_g\) satisfy
\[
V_e + V_g = V_0, \quad V_e/V_g = p_e/p_g.
\]
Isothermal compression means that the atom is contained by walls at constant temperature \(T_2\) to which it can deposit any excess kinetic energy that would otherwise increase when narrowing the position spread. The two volumes are then combined into a single volume \(V_0\) occupied by the atom. We stress that this operation is reversible: we always can proceed backward to divide a volume occupied by one particle into two parts occupied with probabilities proportional to the partial volumes. Let the temperature of the reservoir that cools the atomic center of mass during the isothermal compression be \(T_2\). Thus, with probability \(p_e\) we have to do work
\[
W_e = kT_2 \ln \frac{V_0}{V_e} = -kT_2 \ln p_e,
\]
and with probability \(p_g\) the work
\[
W_g = kT_2 \ln \frac{V_0}{V_g} = -kT_2 \ln p_g.
\]
The average work spent during the compression is then
\[
W_{\text{comp}} = p_e W_e + p_g W_g = -kT_2 (p_e \ln p_e + p_g \ln p_g) = T_2 S^{(a)}(T_1).
\]
If \(p_e \neq p_g\) (which is always the case for finite \(T_1\)), this spent work is smaller than \(kT_2 \ln 2\) which would correspond to a direct compression of \(2V_0\) to \(V_0\).
VI. ENERGY BALANCE AND THE EFFICIENCY OF THE CYCLE

In our model, energy is exchanged in the form of heat, maser work, and mechanical work. We now consider different aspects of the energy transfer.

A. Conversion of heat into useful work

The net useful work \( W_{\text{net}} \) obtained in one cycle is the sum of the net mechanical work

\[
W_{\text{mech}} = W_{\text{rad}} - W_{\text{comp}},
\]

and the maser output \( W_{\text{maser}} \) is

\[
W_{\text{net}} = W_{\text{rad}} + W_{\text{maser}} - W_{\text{comp}}.
\]

If we use the results of Eqs. (11), (12), and (19), we find

\[
W_{\text{net}} = (T_1 - T_2) S^\text{(at)}(T_1).
\]

The heat input is equal to the sum of the atomic energy and the extracted work during the cycle,

\[
Q_{\text{in}} = W_{\text{rad}} + W_{\text{maser}} = T_1 S^\text{(at)}(T_1).
\]

The efficiency of conversion of heat into useful work is

\[
\eta = W_{\text{net}} / Q_{\text{in}},
\]

\[
\eta = 1 - \frac{W_{\text{comp}}}{W_{\text{rad}} + W_{\text{maser}}} = 1 - \frac{T_2}{T_1},
\]

that is, the efficiency is equal to that of a Carnot machine. We would expect this result because the engine only comes into contact with reservoirs at temperatures \( T_1 \) and \( T_2 \) and all the steps in the cycle are reversible.

B. Conversion of mechanical work into maser work

If \( T_1 = T_2 \), we find \( W_{\text{maser}} = -W_{\text{mech}} \). We also can see that \( Q_{\text{in}} = 0 \), so that the device serves as an engine converting mechanical work entirely into maser work (or vice versa, if run in reverse) without any net production or consumption of heat.

C. Conversion of heat into maser work

Depending on the values of \( T_1 \) and \( T_2 \), the fraction of input heat converted into maser and mechanical work varies. We now determine the specific values for which no net mechanical work is created or spent, and the device works like a “Carnot maser” converting heat energy purely into maser work with the efficiency limited only by the second law. We set \( W_{\text{mech}} = 0 \) and use Eqs. (20), (11), and (19) to find that for fixed \( T_1 \) and \( \epsilon \), the value of \( T_2 \) is

\[
T_2 = T_1 \left[ 1 + \frac{x}{(e^\epsilon + 1) \ln(1 + e^{-\epsilon})} \right]^{-1},
\]

where \( x = e^\epsilon T_1 \). In particular, if \( \epsilon \) is chosen to produce maximum maser output, \( x = x_0 \) (see Eqs. (13) and (14)), we find that \( T_2 \approx 0.469 T_1 \). Generally, if the temperature \( T_2 \) is lower than the value given by Eq. (25), both maser work and useful mechanical work are produced. Otherwise, some mechanical work must be spent to obtain maser output.

D. Cycle with irreversible steps

Finally, we compare our results to the case where the heating of the atom in thermal radiation is irreversible (as in Ref. 5), and the center of mass is brought to the initial state through a straightforward isothermal compression of the volume \( 2V_0 \) to \( V_0 \). Then \( W_{\text{mech}} = -W_{\text{comp}} = -kT_2 \ln 2 \), the heat input is \( Q_{\text{in}} = E^\text{(at)}(T_1) \), the maser work is \( W_{\text{maser}} = E^\text{(at)}(T_1) \), so that \( W_{\text{net}} = E^\text{(at)}(T_1) - kT_2 \ln 2 \). We can see that positive net work can be obtained only if the temperatures \( T_1 \) and \( T_2 \) are sufficiently different from each other. If we choose to work with a single thermal reservoir, that is, \( T_1 = T_2 \), then the device converts mechanical work into maser radiation with efficiency \( W_{\text{maser}} / |W_{\text{mech}}| = E^\text{(at)}(T_1) / (kT_1 \ln 2) \). In the regime of maximum maser output with \( e^\epsilon T_1 = x_0 \) (see Sec. IV), the efficiency is \( \approx 0.40 \), that is, substantially less than the unit efficiency of the reversible cycle.

VII. CONCLUDING REMARKS

There are many simplifications assumed in our model, and it is useful to discuss their consequences. Probably the crudest idealization is the description of an atom as a two-level system. This assumption is well justified if the atom interacts with a strong (quasi)monochromatic field resonant with one of the atomic transitions, but it is not if the atom interacts with blackbody radiation. In principle, we could avoid this assumption by considering a multistate selector that sends a multilevel atom to one of many different maser cavities according to the state in which the atom is found. This approach would be more rigorous, but we would gain little in physical insight beyond that provided by our simple model. In our calculations, we have assumed that the atom is in the ground state after being sorted in the state selector or after depositing its energy in the maser cavity. By ground state we mean zero temperature, which contradicts the third law of thermodynamics. However, we should realize that a zero-temperature cooling would be possible only if the center-of-mass motion were already in a zero-temperature state. Otherwise, it is always possible that the atom accidentally goes the wrong way in the state selector, or that it spends the wrong amount of time in the maser cavity, leaving it in the excited state. These effects would, of course, lead to a decrease of the engine efficiency. However, they are negligible if the actual atomic temperature \( T_0 \) satisfies \( kT_0 \ll \epsilon \).

The inhomogeneous field of the state selector affects the shape of the atomic pulse: even though the volume of the pulse is conserved, it can be strongly deformed. We have assumed that the volume occupied by the atom fits the compressor cylinder. To make this situation possible, we have to assume an atom-optics device that returns the pulse to its original form. This device would be an atom-optical counterpart of devices that correct optical aberrations.

We have assumed that (outside the state selector) the internal states are completely decoupled from the center-of-mass motion. This assumption requires that the recoil of the atom due to the emission or absorption of radiation must be negligible relative to its thermal motion. We can check that this requirement leads to the condition \( \epsilon^2 \ll me^2 kT_2 \), where \( m \) is the atomic mass.

Besides these simplifications, we made several other idealized assumptions, such as the existence of perfectly reflecting cylinder walls to ensure adiabatic work with the blackbody radiation. Such ideal conditions may not be possible, but we can regard even the building of the first masers and lasers as a difficult and costly leap from mundane conditions.
The entropy change associated with the process of relaxation: \( \Delta S_{\text{relax}} \) can be written as
\[
\Delta S_{\text{relax}} = S^{(\text{at})}(T_1) - S^{(\text{at})}(T_0) \quad \text{or} \quad \frac{E^{(\text{at})}(T_1) - E^{(\text{at})}(T_0)}{T_1}.
\]
(A3)

APPENDIX A: MAXIMUM WORK FROM A NONEQUILIBRIUM SYSTEM

We can bring a system from a nonequilibrium state to equilibrium in different ways (see Fig. 3). Let us assume that the external parameters of the system (for example, volume) are the same at the beginning and at the end of the process. The easiest way is to leave the system alone, isolated from the external world. The energy of the system does not change, and during relaxation to the equilibrium state, entropy \( \Delta S_{\text{relax}} \) is produced. Nothing useful is gained this way. A better way is to engineer a reversible process during which the system entropy remains constant, but its energy decreases. Because no heat is exchanged with the external world, the energy removed from the system is equal to the extracted work \( W \).

The value of \( W \) can be found from very general considerations. In the triangle in Fig. 3 we can see the relation between the maximum extracted work \( W \) and the change of entropy during relaxation \( \Delta S_{\text{relax}} \),
\[
\Delta S_{\text{relax}} = \left( \frac{\partial S}{\partial E} \right)_V W.
\]
(A1)

From Eq. (2), we can see that \( (\partial E/\partial S)_V = T \), so that Eq. (A1) can be written as
\[
W = T \Delta S_{\text{relax}},
\]
(A2)

where \( T \) is the final temperature of the system.

To calculate the maximum work that can be extracted from a system composed of a two-level atom at temperature \( T_0 \) and a thermal reservoir at temperature \( T_1 \), we first find the entropy change associated with the process of relaxation:
\[
\Delta S_{\text{relax}} = S^{(\text{at})}(T_1) - S^{(\text{at})}(T_0) \quad \text{or} \quad \frac{E^{(\text{at})}(T_1) - E^{(\text{at})}(T_0)}{T_1}.
\]
(A3)

The first two terms on the right-hand side represent the entropy increase of the atom when heated from \( T_0 \) to \( T_1 \), and the last term is the entropy decrease of the reservoir with temperature \( T_1 \) when transferring heat \( \delta Q = E^{(\text{at})}(T_1) - E^{(\text{at})}(T_0) \) to the atom.

APPENDIX B: THERMODYNAMICS OF BLACKBODY RADIATION

The internal energy of blackbody radiation is given by
\[
E^{(\text{rad})} = bVT^4,
\]
(B1)

where
\[
b = \frac{4\pi^2k^4}{15\hbar^3c^3},
\]
(B2)

\( \sigma = 5.67 \times 10^{-8} \text{Wm}^{-2} \text{K}^{-4} \) is the Stefan-Boltzmann constant, \( k \) is the Boltzmann constant, \( \hbar \) is the Planck constant, and \( c \) is the vacuum speed of light. If we use the relation
\[
P = \frac{E^{(\text{rad})}}{3V},
\]
(B3)

the equation of state for radiation is found to be
\[
P = \frac{1}{3} bT^4.
\]
(B4)

(Equation (B3) can be obtained either from electrodynamic considerations, or, as discussed in Ref. 7, the thermodynamics of blackbody radiation including Eqs. (B1) and (B4) can be obtained from the expression for the free energy \( F = -(1/3)bVT^4 \).) The behavior during adiabatic changes of the volume can be found setting \( dS = 0 \) in Eq. (2), and then using Eq. (B4) and the differential of Eq. (B1):
\[
\frac{dT}{T} = \frac{dV}{3V}.
\]
(B5)

Equation (B5) can be solved for the change of volume from \( V_1 \) to \( V_2 \) to give
\[
\frac{T_2}{T_1} = \left( \frac{V_1}{V_2} \right)^{1/3}.
\]
(B6)

The pressure is given by
\[
\frac{P_2}{P_1} = \left( \frac{V_1}{V_2} \right)^{4/3},
\]
(B7)

which means that the thermal radiation under adiabatic volume changes behaves as an ideal gas with the constant \( \gamma = 4/3 \).

APPENDIX C: THERMODYNAMICS OF A TWO-LEVEL ATOM

We consider a two-level atom with an excited state \( e \) and a ground state \( g \), their energy difference being \( \epsilon \). In thermal equilibrium at temperature \( T \) the probabilities of these states are
\[
p_e(T) = \frac{e^{-\epsilon}}{1 + e^{-\epsilon}}.
\]
(C1a)
where \( x = e/kT \). If we choose the energy of the ground state to be zero, the mean energy is

$$ E^{(at)}(T) = p_g(T)\epsilon = \epsilon \frac{e^{-x}}{1 + e^{-x}}. \quad (C2) $$

The atomic heat capacity is

$$ C^{(at)}(T) = \frac{\partial E^{(at)}}{\partial T} = kx^2 \frac{e^{-x}}{(1 + e^{-x})^2}, \quad (C3) $$

and the entropy is

$$ S^{(at)}(T) = -k(p_e \ln p_e + p_g \ln p_g) $$

$$ = k \ln(1 + e^{-x}) + \frac{E^{(at)}}{T}. \quad (C4) $$

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4Present address: Department of Theoretical Physics, Palacký University, 17. listopadu 50, 77200 Olomouc, Czech Republic.


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