# Thermodynamics of simple quantum systems 

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#### Abstract

A set of examples is presented to illustrate the principles of quantum thermophysics, a theory in which systematic quantum mechanical calculations are used to derive thermodynamic relations.


Do not follow in the steps of the ancients, but look for what they had been seeking. Matsuo Basho †

## 1. Introduction

There are two traditional chapters of natural science where a real understanding of the inner workings would have been impossible without the concepts of contemporary quantum theory. One of these is much older than the other chemistry. The other is thermodynamics. Both are based on the peculiar laws of motion of particles in the microscopic world that have been adequately described only in the 20th century - and they still often defy the grasp of conventional common sense.

Centuries of empirical studies of chemical transformations gave rise to wonderful technologies, laid the foundations of ore processing and modern metallurgy. There were epoch-making theoretical milestones on this way: Lavoisier's law, Mendeleev's periodic table, formulas of spectral line series. However, only the construction of a consistent quantum theory of the simplest chemical element - an atom of hydrogen - helped to produce a crystal clear picture of the chemical world. Only then it was possible to identify the

[^0]number of element in the periodic table with the wholenumbered charge of its nucleus, and to explain the physical nature of the chemical bond.

The history of thermodynamics is much shorter. The stumbling block in the way of its validation was the second law of thermodynamics enunciated by the German mathematical physicist Rudolf Julius Emanuel Clausius, which states that heat cannot pass from a colder body to a warmer body without external force. Ingenious and ever more sophisticated attempts to harmonize this postulate with the principles of classical dynamics invariably failed, shattering the belief that it is at all possible. As a matter of fact, the futility of such attempts follows from simple considerations of dimensionality. Among other things, the classical laws of motion imply self-similarity of things on any scale - from the music of the spheres in celestial mechanics to the laws of motion of microscopic particles. Accordingly, from this standpoint the direction of energy transfer is completely determined by the microphysical initial conditions not subject to any additional constraints not known in the macroscopic mechanics.

The discovery in theoretical physics of a new dimensional world constant - Planck's constant - completely revolutionized the situation and called for radical revision of the laws of motion as applied to the microscopic world. In the end, it was for this reason that the mathematical methods of quantum theory were capable of proving the unfortunate second law. The physical assumptions of this proof are already contained in the logical structure of the famous Einstein-Podolsky-Rosen paradox, which has boggled many minds for decades.

It has long been noted that confidence in formal constructions and proofs is much reinforced by the availability of illustrative examples - exactly solvable models of the theory. In classical mechanics such simple models are well known: the elastic collision of massive spheres, motion in a homogeneous field of gravity, Kepler's problem. In quantum theory such examples used for the purposes of verification and validation are the hydrogen atom, the quantum harmonic oscillator, and the rigid rotator.

In this paper we attempt to construct a 'survival kit' of exactly solvable models for quantum thermophysics, which
allow the expression of thermodynamic relations by the consistent quantum calculation techniques.

The mathematical basis for this approach was laid before World War II in the works of Otto Klein [1] and Walter Elsasser [2]. Very useful philosophical considerations on this matter can be found in the collection of papers by Werner Heisenberg [3] published towards the end of his life. Theoretical developments of the problem of quantum stochasticity were necessary for the formulation of the quantum theory of open systems [4], the physical theory of information [5], and the quantum theory of relaxation [6]. Further treatment of various aspects of quantum thermodynamics and kinetics can be found in Refs [7-9].

## 2. Quantum heat exchange

We start by discussing the general principles of thermophysics, which will then be illustrated with concrete models. By H we denote the Hamilton operator of an isolated physical system with a discrete energy spectrum. The eigenvectors $|n\rangle$ and eigenvalues $E_{n}$ of this operator are defined in the usual way:

$$
\begin{equation*}
\mathbf{H}|n\rangle=E_{n}|n\rangle, \tag{1}
\end{equation*}
$$

where $n$ numbers the steady states (not the energy levels). By using such numeration we eliminate the necessity of additional indices in the case of degeneracy of energy levels.

By $\langle n| \rho|m\rangle$ we denote the time-independent density matrix of the state of the system in the Heisenberg energy representation. For the equilibrium (Gibbsian) state we must take

$$
\begin{equation*}
\langle n| \rho|m\rangle=\rho_{n} \delta_{n m}=Z^{-1} \exp \left(-\frac{E_{n}}{T}\right) \delta_{n m} \tag{2}
\end{equation*}
$$

where $T$ is the energy temperature, and the sum-over-states $Z$ is found from the normalization condition

$$
\begin{equation*}
\operatorname{Sp} \rho=\sum_{n} \rho_{n}=1 . \tag{3}
\end{equation*}
$$

We denote by $S$ the quantum entropy of state (see Ref. [5])

$$
\begin{equation*}
S=-\operatorname{Sp} \rho \ln \rho=-\sum_{n, m}\langle n| \rho|m\rangle\langle m| \ln \rho|n\rangle, \tag{4}
\end{equation*}
$$

without limiting a priori the validity of this formula to the state of thermal equilibrium (2). The mean energy of the system in an arbitrary state is found by plain averaging

$$
\begin{equation*}
\langle E\rangle=\operatorname{Sp} \rho \mathrm{H}=\sum_{n} E_{n}\langle n| \rho|n\rangle . \tag{5}
\end{equation*}
$$

The equilibrium state (2) corresponds to the maximum entropy for a fixed mean energy [2] and is the ultimate type of mixed state that arises upon collision of initially independent quantum systems [8].

Now let us describe the interaction of the system with its physical environment. In this section we only consider such impacts on the system that do not change its energy spectrum $\left\{E_{n}\right\}$ and the set of eigenvectors $\{|n\rangle\}$. As will be shown below, this is equivalent to the convention of taking into account only the energy processes of heat exchange type. As far as adiabatic macroprocesses are concerned, their quantum description involves deformations of the energy spectrum, and they will be discussed in Section 3.

Assume that the interaction of the system with the environment gives small increments $d \rho_{n}$ to the eigenvalues $\rho_{n}$ of the equilibrium density matrix (2). Taking into account the necessary condition of normalization

$$
\begin{equation*}
\sum_{n} \mathrm{~d} \rho_{n}=0, \tag{6}
\end{equation*}
$$

after substitution into Eqn (4) and (5) we get the known Clausius relation

$$
\begin{equation*}
\mathrm{d} S=\frac{\mathrm{d}\langle E\rangle}{T} \tag{7}
\end{equation*}
$$

that links the change in entropy to the amount of energy transferred through heat exchange.

Now consider the collision of two quantum subsystems (for example, two molecules, not necessarily identical). The Hamiltonians of the discrete parts of the energy spectra of these subsystems, interaction not included, we denote by $\mathbf{H}_{\mathrm{I}}$, $\mathbf{H}_{\text {II }}$. The initial mixed states of subsystems we select to be at equilibrium at temperatures $T_{\mathrm{I}}$ and $T_{\mathrm{II}}$ and statistically independent from each other. We assume that the interaction $\mathbf{H}_{\text {int }}$ conserves the total energy $\left[\mathbf{H}_{\text {int }}, \mathbf{H}_{\mathrm{I}}+\mathbf{H}_{\mathrm{II}}\right]=0$, and only exists within the time interval $t_{c}$, constant throughout the interval.

Observe that there is also a more consistent approach to 'switch-on' and 'switch-off' of the interaction. These events may be due, for example, to the quasiclassical free motion of subsystems coming close to each other and retreating, which is not included in the Hamiltonians with a discrete spectra of eigenvalues. If desired, such an analysis could be performed without much effort, but this would have encumbered our treatment with unnecessary details.

By $\langle n| \rho_{0}|m\rangle$ and $\langle v| \sigma_{0}|\mu\rangle$ we denote the density matrices of the initial thermal states of the form (2) of the first and second subsystems at temperatures $T_{\mathrm{I}}$ and $T_{\mathrm{II}}$. The initial state of the total system that includes both subsystems is described by the matrix product

$$
\begin{equation*}
\langle n, v| R_{0}|m, \mu\rangle=\langle n| \rho_{0}|m\rangle\langle v| \sigma_{0}|\mu\rangle . \tag{8}
\end{equation*}
$$

Here and further we shall mark the base vectors of the first system with Roman characters, and those of the second with Greek. By $S_{0 I}$ and $S_{0 I I}$ we denote the initial entropies of subsystems calculated according to Eqn (4). The entropy $S$ of the total system in state (8) is the sum of these:

$$
\begin{equation*}
S=S_{0 \mathrm{I}}+S_{0 \mathrm{II}} \tag{9}
\end{equation*}
$$

In the interaction representation we write the resulting density matrix of the total system after collision of the subsystems as

$$
\begin{equation*}
\langle n, v| R|m, \mu\rangle=\langle n, v| \mathrm{U}^{+} \rho_{0} \sigma_{0} \mathrm{U}|m, \mu\rangle, \tag{10}
\end{equation*}
$$

where

$$
\begin{equation*}
\mathbf{U}=\exp \left(\mathbf{i} \mathbf{H}_{\mathrm{int}} t_{\mathrm{c}}\right) \tag{11}
\end{equation*}
$$

(we use the system of units in which $\hbar=1$ ). After the interaction, the subsystems will generally no longer be statistically independent, and their individual (local) states will correspond to the density matrices [6]

$$
\begin{align*}
& \langle n| \rho|m\rangle=\sum_{v}\langle n, v| R|m, v\rangle  \tag{12}\\
& \langle v| \sigma|\mu\rangle=\sum_{n}\langle n, v| R|n, \mu\rangle \tag{13}
\end{align*}
$$

Under our condition $\left[\mathbf{H}_{\mathrm{int}}, \mathbf{H}_{\mathrm{I}}+\mathbf{H}_{\mathrm{II}}\right]=0$, these matrices are again diagonal in the energy representation that diagonalizes the Hamiltonian matrices $\langle n| \mathrm{H}_{\mathrm{I}}|m\rangle$ and $\langle v| \mathrm{H}_{\mathrm{II}}|\mu\rangle$.

We denote by $S_{\mathrm{I}}$ and $S_{\mathrm{II}}$ the entropies of states (12) and (13) respectively, and find the change in the total entropy resulting from the collision:

$$
\begin{equation*}
\Delta S=S_{\mathrm{I}}+S_{\mathrm{II}}-S \tag{14}
\end{equation*}
$$

The following inequality is essential for the quantum theoretical validation of thermodynamics (see Ref. [5])
$\Delta S \geqslant 0$,
which is worth discussing in greater detail.
First of all, inequality (15) holds for any initial states of subsystems, and its validity only depends on one sufficient condition: the initial statistical independence of the colliding subsystems. It was the immanently quantum nature of the occurrence of states of particles with indefinite energies upon collision that made Einstein doubt the logical completeness of quantum theory, and led to the formulation of the famous paradox.

On the other hand, a similar inequality exists in the classical theory of probabilities, where it ensures the nonnegativity of the correlation entropy of two statistically bound random variables. The corresponding theorem was proved by Claude Shannon [10] as part of the foundation of the mathematical theory of information. This result is ideologically closely related to the well-known Boltzmann's theorem concerned with the behavior of classical entropies of one-particle distribution functions in corpuscular kinetics. In both these cases, however, the probability distributions are 'superimposed' on the laws that govern the behavior of dynamic systems, whereas the genesis of primal stochasticity remains behind the scene.

The key role in contemporary quantum thermodynamics belongs to Klein's entropy lemma [1], which only attracted the serious attention of physicists in the post-war years [11, 12]. It allows the direct extension of Shannon's theorem to quantum entropies of the form (4), which proves inequality (15). It is this inequality that provides for the theoretical validation of the second law.

We assume that the change of the states of subsystems caused by the interaction between them is small, and express the asymptotic relation that links the magnitude of the quasiequilibrium energy transfer to the small increment of total entropy $\mathrm{d} S$. First we calculate the change of the mean energy of the first subsystem $\mathrm{d}\left\langle E_{I}\right\rangle$. Given that the resulting density matrix $\langle n| \rho|m\rangle$ remains diagonal in the energy representation as long as the total energy is conserved, we write

$$
\begin{equation*}
\mathrm{d}\left\langle E_{\mathrm{I}}\right\rangle=\sum_{n} E_{n}^{(\mathrm{I})}\left(\rho_{n}-\rho_{0 n}\right)=\sum_{n} E_{n}^{(\mathrm{I})} \mathrm{d} \rho_{n}, \tag{16}
\end{equation*}
$$

where $\rho_{0 n}$ are the equilibrium values at temperature $T_{\mathrm{I}}, \rho_{n}$ are the eigenvalues of matrix (12), and $E_{n}^{(\mathrm{I})}$ are the eigenvalues of operator $\mathbf{H}_{\mathrm{I}}$. The change of the mean energy of the second subsystem is $\mathrm{d}\left\langle E_{\text {II }}\right\rangle=-\mathrm{d}\left\langle E_{\mathrm{I}}\right\rangle$, by virtue of the same condition $\left[\mathbf{H}_{\text {int }}, \mathbf{H}_{\mathrm{I}}+\mathbf{H}_{\mathrm{II}}\right]=0$.

In a similar way we write the change of entropies of subsystems and the magnitude of the small total increment $\mathrm{d} S$ from (14). Using (2) and (2), in the linear approximation with respect to $\mathrm{d} \rho_{n}, \mathrm{~d} \sigma_{v}$ we get

$$
\begin{equation*}
\mathrm{d} S=\mathrm{d}\left\langle E_{\mathrm{I}}\right\rangle\left(\frac{1}{T_{\mathrm{I}}}-\frac{1}{T_{\mathrm{II}}}\right) . \tag{17}
\end{equation*}
$$

This expression is not exact - it only holds asymptotically on condition that the perturbation introduced into the initial equilibrium states of subsystems I and II at the time of collision is small enough. According to inequality (15), the quantity $\mathrm{d} S$ is always non-negative, which, together with expression (17), gives a mathematical proof of the Clausius postulate as applied to the physical conditions described above.

Let us now consider concrete examples.

### 2.1 Spin-spin collision

Let us analyze the spontaneous heat transfer on the interaction of two electron spins that occur in homogeneous permanent magnetic field of strength $\mathcal{H}$. In this model, each partner of the collision is described by a Hamiltonian of the form (see Ref. [13])

$$
\begin{equation*}
\mathbf{H}_{\mathrm{I}, \mathrm{II}}=-\frac{e \mathcal{H}}{m_{0} c} \mathbf{s}_{z}^{(\mathrm{I}, \mathrm{II})} \tag{18}
\end{equation*}
$$

where $e$ and $m_{0}$ are the charge and mass of electron at rest, $c$ is the velocity of light, and the $z$ axis coincides with the direction of the field. The symbol $\mathbf{s}_{z}^{(1, I I)}$ denotes the conventional operators of the spin $z$-components which act on the spinor variables of the first and the second electrons respectively. The energy spectra of these subsystems each contain just two nondegenerate levels

$$
\begin{equation*}
E_{1,2}=\mp \frac{e \mathcal{H}}{2 m_{0} c} \tag{19}
\end{equation*}
$$

(numbered in the order of increasing energy). The nondisturbed Hamiltonian of the total system $\mathbf{H}_{\mathrm{I}}+\mathbf{H}_{\mathrm{II}}$ is characterized by three levels $2 E_{1}, E_{1}+E_{2}, 2 E_{2}$, of which the second is doubly degenerate.

The Hamiltonian of interaction we express in antisymmetrical form

$$
\begin{equation*}
\mathbf{H}_{\mathrm{int}}=\gamma\left(\mathbf{s}_{x}^{(\mathrm{II})} \mathbf{s}_{y}^{\mathrm{II})}-\mathbf{s}_{y}^{(\mathrm{II})} \mathbf{s}_{x}^{\mathrm{II})}\right), \tag{20}
\end{equation*}
$$

which ensures compliance with the condition $\left[\mathbf{H}_{\text {int }}, \mathbf{H}_{\mathrm{I}}+\mathbf{H}_{\text {II }}\right]=0$, and the real-valued matrix elements of transform (11). Over the time of collision $t_{\mathrm{c}}$, the unitary evolution operator $\mathbf{U}$ accomplishes a simple rotation in the two-dimensional subspace of states $|1,2\rangle(n=1, v=2)$, and $|2,1\rangle$ with equal energies [9]:

$$
\left(\begin{array}{ll}
\langle 1,2| \mathrm{U}|1,2\rangle & \langle 1,2| \mathrm{U}|2,1\rangle  \tag{21}\\
\langle 2,1| \mathrm{U}|1,2\rangle & \langle 2,1| \mathrm{U}|2,1\rangle
\end{array}\right)=\left(\begin{array}{cc}
\cos \varphi & -\sin \varphi \\
\sin \varphi & \cos \varphi
\end{array}\right),
$$

where $\varphi=\gamma t_{\mathrm{c}} / 2$. The nondegenerate symmetrical states $|1,1\rangle$ and $|2,2\rangle$ do not change.

The initial equilibrium eigenvalues of the density matrix of the first subsystem $\rho_{01}$ and $\rho_{02}$ are expressed in the compact form

$$
\begin{equation*}
\rho_{01,2}=\left[2 \cosh \left(\frac{\omega}{2 T_{\mathrm{I}}}\right)\right]^{-1} \exp \left( \pm \frac{\omega}{2 T_{\mathrm{I}}}\right) \tag{22}
\end{equation*}
$$

where $\omega=e \mathcal{H} / m_{0} c$ is the resonance frequency of the paramagnetic quantum transition between levels 2 and 1. The initial eigenvalues of the density matrix of the second subsystem $\sigma_{01}$ and $\sigma_{02}$ are expressed by a similar formula, where $T_{\mathrm{I}}$ is replaced by $T_{\mathrm{II}}$.

Unfolding transform (10) with the aid of matrix (21), we calculate the trace of the matrix and use expression (12) to find the resulting eigenvalue

$$
\begin{equation*}
\rho_{1}=\rho_{01}+2 \sin ^{2} \varphi \frac{\sinh X}{Z_{\mathrm{I}} Z_{\mathrm{II}}} \tag{23}
\end{equation*}
$$

where

$$
\begin{align*}
& X=\frac{\omega}{2} \frac{T_{\mathrm{I}}-T_{\mathrm{II}}}{T_{\mathrm{I}} T_{\mathrm{II}}}  \tag{24}\\
& Z_{\mathrm{I}, \mathrm{II}}=2 \cosh \left(\frac{\omega}{2 T_{\mathrm{I}, \mathrm{II}}}\right) \tag{25}
\end{align*}
$$

Assuming that the collision parameter $\gamma t_{\mathrm{c}} \ll 1$ is small, we get

$$
\begin{equation*}
\mathrm{d} \rho_{1}=\frac{1}{2}\left(\gamma t_{\mathrm{c}}\right)^{2} \frac{\sinh X}{Z_{\mathrm{I}} Z_{\mathrm{II}}} \tag{26}
\end{equation*}
$$

According to condition (6), we have, which allows us to immediately calculate the change of energy of the first subsystem:

$$
\begin{equation*}
\mathrm{d}\left\langle E_{1}\right\rangle=-\frac{1}{2}\left(\gamma t_{\mathrm{c}}\right)^{2} \omega \frac{\sinh X}{Z_{\mathrm{I}} Z_{\mathrm{II}}} . \tag{27}
\end{equation*}
$$

It is easy to see that this energy transfer is only positive when $T_{\text {II }}>T_{\mathrm{I}}$, and vice versa.

The change of total entropy $\mathrm{d} S$ (14) in the same approximation is

$$
\begin{equation*}
\mathrm{d} S=\left(\gamma t_{\mathrm{c}}\right)^{2} X \frac{\sinh X}{Z_{\mathrm{I}} Z_{\mathrm{II}}} \tag{28}
\end{equation*}
$$

Thus, $\mathrm{d} S$ is positive for all $X \neq 0$. Comparison of formulas (28) and (27) reveals that the asymptotic relation (17) holds.

Observe that when further terms of expansion in powers of $\gamma t_{\mathrm{c}}$ are taken into account in the formulas for energy transfer and increase of total entropy, expression (17) is not necessarily satisfied. The appropriate correction to the formula for $\mathrm{d} S$ lacks universality, and depends on the particular properties of the model in question (see Ref. [7]).

### 2.2 Dipole transitions in an atom

Let us describe the elementary heat exchange processes of emission and absorption of light quanta when the atom (subsystem I) is engaged in the interaction with quantum oscillator of electromagnetic field (subsystem II). Consider two nondegenerate atomic levels with energies $E_{1}$ and $E_{2}$, and assume that the atom is at the crest of the electric field of one of the modes of the optical resonator with the frequency

$$
\begin{equation*}
\omega=E_{2}-E_{1} . \tag{29}
\end{equation*}
$$

The operator of the field energy of this mode (quantum oscillator), its eigenvectors and eigenvalues are represented in the conventional manner [14]

$$
\begin{equation*}
\mathbf{H}_{\text {II }}|v\rangle=\omega\left(\mathbf{a}^{+} \mathbf{a}+\frac{1}{2}\right)|v\rangle=\omega\left(v+\frac{1}{2}\right)|v\rangle, \tag{30}
\end{equation*}
$$

where $\mathbf{a}$ is the photon annihilation operator, and $v=0,1, \ldots$.

The Hamiltonian of the electrodipole interaction between the atom and the field oscillator is

$$
\begin{equation*}
\mathbf{H}_{\mathrm{int}}=\hat{\mathcal{D}} \hat{\mathcal{E}} \tag{31}
\end{equation*}
$$

where $\hat{\mathcal{D}}$ is the operator of projection of the dipole moment onto the direction of the electric field (for the sake of simplicity and definiteness we assume plane polarization), and $\hat{\mathcal{E}}$ is the operator of field strength in the appropriate region of space. The nondiagonal matrix element of the dipole moment we consider as a numerical constant for the quantum transition in question. Since the steady states of optical electron $|1\rangle$ and $|2\rangle$ in the atom display a definite (positive or negative) parity, the diagonal matrix elements of the dipole $\langle 1| \mathcal{D}|1\rangle$ and $\langle 2| \mathcal{D}|2\rangle$ are zero.

Expressing operator $\hat{\mathcal{E}}$ in the standard way in terms of the canonical variables of the field oscillator [14], we write down the nonzero matrix elements of perturbation in the energy representation

$$
\begin{align*}
\langle 1, v| \mathrm{H}_{\mathrm{int}}|2, v-1\rangle & =\gamma \sqrt{v} \\
\langle 2, v| \mathrm{H}_{\mathrm{int}}|1, v+1\rangle & =\gamma \sqrt{v+1} \tag{32}
\end{align*}
$$

where $\gamma$ is the constant of interaction (assumed to be realvalued), proportional to $\langle 1| \mathcal{D}|2\rangle$. The duration of interaction $t_{\mathrm{c}}$ in this case ought to be interpreted as the characteristic lifetime of a photon in the resonator, which depends on the quality of the latter.

Now we again consider the initial thermal states of the subsystems. Without violating the generality, we assume that the lower energy level is $E_{1}=0$, and the energy of oscillator is $\omega / 2$. Then the equilibrium eigenvalues of the density matrices are

$$
\begin{align*}
& \rho_{01,2}=\left(1+\mathrm{e}^{-\omega / T_{\mathrm{I}}}\right)^{-1} \exp \left(-\frac{E_{1,2}}{T_{\mathrm{I}}}\right),  \tag{33}\\
& \sigma_{0 v}=\left(1-\mathrm{e}^{-\omega / T_{\mathrm{II}}}\right) \exp \left(-\frac{\omega v}{T_{\mathrm{II}}}\right) . \tag{34}
\end{align*}
$$

The exact solution describing the evolution of such an initial state of the complete system under the action of perturbation (32) can be found in Ref. [9]. Currently we are only interested in the solution for small values of the parameter $\gamma t_{\mathrm{c}}$, and so we use the perturbation theory which adds clarity to our reasoning.

Observe that for finding the magnitude of energy transfer $\mathrm{d}\left\langle E_{\mathrm{I}}\right\rangle$ we now only need to calculate the value of $\mathrm{d} \rho_{2}$. In the first order of perturbation theory we use expressions (10) and (12) to write

$$
\begin{equation*}
\mathrm{d} \rho_{2}=\left(\gamma t_{\mathrm{c}}\right)^{2}\left[\rho_{01} \bar{v}-\rho_{02}(\bar{v}+1)\right] \tag{35}
\end{equation*}
$$

where

$$
\begin{equation*}
\bar{v}=\sum_{v} v \sigma_{0 v}=\left[\exp \left(\frac{\omega}{T_{\mathrm{II}}}\right)-1\right]^{-1} . \tag{36}
\end{equation*}
$$

After some straightforward algebra we find

$$
\begin{equation*}
\mathrm{d}\left\langle E_{\mathrm{I}}\right\rangle=-\frac{1}{2}\left(\gamma t_{\mathrm{c}}\right)^{2} \omega \frac{\sinh X}{\cosh \left(\omega / 2 T_{\mathrm{I}}\right) \sinh \left(\omega / 2 T_{\mathrm{II}}\right)} \tag{37}
\end{equation*}
$$

We see that the direction of spontaneous transfer of energy once again satisfies the postulate of Clausius. Calculating the
increase of total entropy $\mathrm{d} S$, we come to the asymptotic expression (17), as in our previous physical example.

### 2.3 Heat exchange between light beams

Let us consider the heat exchange associated with the linear redistribution of energy between two monochromatic light beams of thermal origin. Different possible forms of a such process are discussed in book [5]: partial reflection of two mutually perpendicular beams from a semitransparent skew mirror, spontaneous pumping of optical energy caused by scattering by a small inhomogeneity, etc. Here we shall consider a somewhat refined but physically quite sound simple model from this range.

Assume that two statistically independent light beams (two running wave oscillators) travel in one and the same direction, but have mutually perpendicular directions of plane polarization. We shall be concerned with the statistical properties of beams which are also polarized in two perpendicular planes, but directed at some angle to the original beams. It is known (see Ref. [5]) that the transition to the new (rotated) polarizations is mathematically equivalent to the transform of states of two-dimensional isotropic oscillator with a unitary operator

$$
\begin{equation*}
\mathbf{U}=\exp \left[\frac{\alpha}{2}\left(\mathbf{a}^{+} \mathbf{b}-\mathbf{b}^{+} \mathbf{a}\right)\right], \tag{38}
\end{equation*}
$$

where $\mathbf{a}$ and $\mathbf{b}$ are the operators of annihilation of quanta of the first and the second oscillators (polarizations). The matrix elements of such a transform in the energy representation $\langle n, v| \mathrm{U}|m, \mu\rangle$ for very profound reasons coincide with the coefficients of the irreducible matrix representations of unitary group $\mathrm{SU}(2)$, which were known to mathematicians long before the advent of specifically quantum problems. In the contemporary language of mathematical physics they can be readily expressed in terms of spinor algebra [15].

For our purposes, however, it will again suffice to analyze the asymptotic solution at small $\alpha$. Observe that angle $\alpha$ in this model plays the same role as the collision parameter $\gamma t_{\mathrm{c}}$ in previous examples. Expanding the exponential (38) and using a linear approximation for the nondiagonal elements and a second-order approximation for the diagonal elements based on the standard matrix elements of operators $\mathbf{a}$ and $\mathbf{a}^{+}, \mathbf{b}$ and $\mathbf{b}^{+}$[14], we write out the nonzero terms:

$$
\begin{align*}
& \langle n, v| \mathrm{U}|n, v\rangle=1-\frac{\alpha^{2}}{8}(2 n v+n+v), \\
& \langle n, v| \mathrm{U}|n-1, v+1\rangle=\frac{\alpha}{2} \sqrt{n(v+1)}  \tag{39}\\
& \langle n, v| \mathrm{U}|n+1, v-1\rangle=-\frac{\alpha}{2} \sqrt{(n+1) v} .
\end{align*}
$$

As before, we consider the initial equilibrium states of subsystems at temperatures $T_{\mathrm{I}}$ and $T_{\mathrm{II}}$. Their oscillator Hamiltonians $\mathbf{H}_{\mathrm{I}}, \mathbf{H}_{\mathrm{II}}$, eigenvectors $|n\rangle,|v\rangle$, and eigenvalues are given by the usual expressions of the form (30) in terms of operators $\mathbf{a}$ and $\mathbf{b}$ respectively. The initial eigenvalues of the density matrix of the first subsystem are expressed by the familiar formula

$$
\begin{equation*}
\rho_{0 n}=\left(1-\mathrm{e}^{-\omega / T_{\mathrm{I}}}\right) \exp \left(-\frac{\omega n}{T_{\mathrm{I}}}\right), \tag{40}
\end{equation*}
$$

and $\sigma_{0 v}$ of the second subsystem are expressed in exactly the same way in terms of $T_{\text {II }}$ (34).

Now let us look more closely at the structure of the density matrix of the complete system $\langle n, \nu| R|m, \mu\rangle$ after transform (10), performed with the approximately unitary matrix (39). We calculate the diagonal elements up to the terms $\alpha^{2}$ :

$$
\begin{aligned}
& \left.\langle n, v| R|n, v\rangle=\sum_{m, \mu} \rho_{0 m} \sigma_{0 \mu}|\langle m, \mu| \mathrm{U}| n, v\right\rangle\left.\right|^{2} \\
& =\rho_{0 n} \sigma_{0 v}\left\{1+\frac{\alpha^{2}}{2} \sinh X\left[v(n+1) \mathrm{e}^{X}-n(v+1) \mathrm{e}^{-X}\right]\right\}(41)
\end{aligned}
$$

where the variable $X$ is once again given by Eqn (24). We see that the resulting light beams are no longer statistically independent. By simple summation of the last expression with respect to $n$ and $v$, we can prove that the matrix is normalized.

In addition to the diagonal elements, matrix (10) also contains elements of the type

$$
\begin{equation*}
\langle n, v| R|n-1, v+1\rangle, \quad\langle n, v| R|n+1, v-1\rangle \tag{42}
\end{equation*}
$$

which are nondiagonal with respect to both pairs of indices at once. We are not going to write them out explicitly.

It is important that, according to Eqn (12) and (13), elements of this type do not participate in the shaping of the 'local' matrices $\langle n| \rho|m\rangle$ and $\langle v| \sigma|\mu\rangle$, and therefore do not affect any observable properties of the resulting beams. Moreover, any direct physical measurement performed on either of the beams will irreversibly destroy these elements. In spite of this, it is the presence of these elements that ensures general reversibility of the situation: using the inverse transform to go back to the initial polarizations (on condition that no measurements have been made in the meantime), we arrive at two independent thermal beams. In other words, we encounter a physical reality that is not observable in principle in 'local' experiments on both resulting beams but is nevertheless real. As a matter of fact, the wave function itself displays such peculiar properties.

It is sometimes said that matrix elements of type (42) contain information on the mutual coherence of the beams, although such a statement can hardly add anything to our understanding. It is likely that this situation currently just cannot be interpreted in any language except the language of mathematics.

Unfortunately, such delicate circumstances are not always fully realized by many physicists. The analysis often reduces to a purely verbose interpretation of the results of quantum mechanics. In his late publications W Heisenberg repeatedly warned that verbal images of not only the lay language but also of traditional science refer to a view of the world entirely different from the concepts of quantum theory.

In fact, the foundations of quantum theory are selfconsistent and self-sufficient. Its results do not contradict the experiments, and do not lead to formal inconsistencies as long as there is no attempt to interpret quantum mechanics in the language of classical physics, which is definitely not suited for the purpose.

Now let us finish our calculations. From the structure of expression (41) we see that the calculation of $\rho_{n}$ from Eqn (12) in this case simply implies replacing the quantum number $v$ with its mean value $\bar{v}$, which in turn is expressed in terms of $T_{\text {II }}$ by the conventional Planck formula (36). Discarding the unperturbed component $\rho_{0 n}$, we write

$$
\begin{equation*}
\mathrm{d} \rho_{n}=\frac{\alpha^{2}}{2} \sinh X\left[\bar{v}(n+1) \mathrm{e}^{X}-n(\bar{v}+1) \mathrm{e}^{-X}\right] \rho_{0 n} \tag{43}
\end{equation*}
$$

Calculation of the energy transfer $\mathrm{d}\left\langle E_{\mathrm{I}}\right\rangle$ reduces to multiplying $\mathrm{d} \rho_{n}$ by $\omega n$ with subsequent summation. Given that the mean squared number of quanta $\overline{n^{2}}$ is given by the known formula for Bose distribution

$$
\begin{equation*}
\overline{n^{2}}=\sum_{n} n^{2} \rho_{0 n}=\bar{n}+2 \bar{n}^{2}, \tag{44}
\end{equation*}
$$

after some algebra we get

$$
\begin{equation*}
\mathrm{d}\left\langle E_{\mathrm{I}}\right\rangle=-\frac{\alpha^{2} \omega}{8} \frac{\sinh X}{\sinh \left(\omega / 2 T_{\mathrm{I}}\right) \sinh \left(\omega / 2 T_{\mathrm{II}}\right)} . \tag{45}
\end{equation*}
$$

Finally, calculating the increment of entropy

$$
\begin{equation*}
\mathrm{d} S=-\sum_{n} \ln \rho_{0 n} \mathrm{~d} \rho_{n}-\sum_{v} \ln \sigma_{0 v} \mathrm{~d} \sigma_{v} \tag{46}
\end{equation*}
$$

with due account for Eqn (6) and a similar condition for $\mathrm{d} \sigma_{v}$, we prove that this quantity is positive for all $X \neq 0$, which for the third time confirms the validity of asymptotic relation (17).

Now let us briefly summarize the general features of quantum heat transfer illustrated by the examples above.
(1) In all three examples the direction of spontaneous energy transfer complies with Clausius' postulate.
(2) The change of total entropy $\mathrm{d} S$ is non-negative.

## 3. Adiabatic processes

Let us now discuss another type of energy action on physical systems. Here we are dealing with such processes that do not involve transitions from one level to another. This time we are concerned with the changes in thermal states associated with the deformation of the discrete spectrum itself - a certain regular change in the distances between its energy levels.

Observe that the examples discussed in this section are well known and have been published more than once in textbooks on statistical thermodynamics. Nevertheless, we believe that these examples ought to be discussed at least in brief in the general context of the consistently quantum approach to the problems of thermodynamics.

### 3.1 Cooling by demagnetization

Consider again the thermal distribution (22) of 'relative populations' of two energy levels of electron spin in a permanent magnetic field. If we vary the field strength $\mathcal{H}$ slowly enough without changing the eigenvalues of the density matrix $\rho_{01}$ and $\rho_{02}$ (which implies the absence of quantum transitions), then the temperature of the system will vary according to the adiabatic law

$$
\begin{equation*}
\frac{\mathcal{H}}{T}=\text { const } . \tag{47}
\end{equation*}
$$

Quantum entropy $S$ remains unchanged in the course of this process, because the values of $\rho_{01}$ and $\rho_{02}$ remain the same.

This simple example clearly illustrates the cause underlying the well-known effect of deep cooling resulting from adiabatic demagnetization of a paramagnetic specimen initially placed in a thermostat in a strong magnetic field.

### 3.2 Planck's adiabat

Consider the oscillator of a standing light wave of wavelength $\lambda$ in a one-dimensional optical resonator (a pair of facing
parallel mirrors) of length $L$. The frequency of the oscillator is linked to its mode number $j$ by the simple formula

$$
\begin{equation*}
\omega_{j}=\frac{\pi c}{L} j \tag{48}
\end{equation*}
$$

where $j=2 L / \lambda$ is the whole number of half-waves fitting into the length of the resonator.

We set the initial thermal distribution $\rho_{0 n}$ in the form (40) at temperature $T$. If we now slowly change the length of the resonator (the quality of the resonator is assumed infinite), the frequency of the selected $j$ th mode will change according to Eqn (48). The separation between the energy levels of oscillator will change accordingly, and, given that the values of $\rho_{0 n}$ remain the same, the temperature will vary according to the adiabatic law

$$
\begin{equation*}
L T=\text { const } \tag{49}
\end{equation*}
$$

If we consider the initial thermal states of all modes of the resonator (field oscillators) at the same temperature, then the distribution of the mean number of quanta $\bar{n}_{j}$ is given by Planck's formula (36). A sufficiently slow change of the length of resonator $L(t)$ ensures the equilibrium nature of this distribution, which is easily checked with the same formulas.

Such a transformation can be interpreted as the Doppler shift of the frequency of each photon repeatedly bouncing off the moving mirror. Naturally, the total number of light quanta in a given mode is conserved.

It is also quite easy to construct the three-dimensional extension of this example, defining the spectral modes in a cubic resonator of volume $V=L^{3}$. The same train of arguments will bring us to the known equation of adiabat for thermal radiation

$$
\begin{equation*}
V T^{3}=\text { const } \tag{50}
\end{equation*}
$$

### 3.3 Thermal particle in a potential well

For our third example we take the textbook problem of energy levels of a nonrelativistic particle in infinitely deep potential well of length $L$. The energy spectrum of the system in this case is nondegenerate and is described by the known formula

$$
\begin{equation*}
E_{n}=\frac{\pi^{2}}{8 m_{0} L^{2}} n^{2} \tag{51}
\end{equation*}
$$

where $n=1,2, \ldots$. The canonical distribution of eigenvalues $\rho_{n}$ at temperature $T$ is still given by Eqn (2), so their constancy, as $L$ is varied, is ensured by the conservation of the product $T L^{2}$. In the form more traditional for thermodynamics, we get the adiabat of a classical one-dimensional gas:

$$
\begin{equation*}
L T^{1 / 2}=\text { const } \tag{52}
\end{equation*}
$$

The almost obvious three-dimensional extension of this result gives the conventional adiabat of Boltzmann's ideal gas

$$
\begin{equation*}
V T^{3 / 2}=\mathrm{const} \tag{53}
\end{equation*}
$$

It is surprising how closely related are this simple quantum problem and the piston of a steam engine!

## 4. Conclusion

Ascertaining the fundamentally quantum origins of the second law, we cannot bypass the sacramental issue of the source of irreversibility - on which, according to Max Planck, 'the entire thermodynamics stands and falls' (see Ref. [16]).

The initial increase of the sum of two entropies from zero is already encountered in the problem of collision of two particles. The wave function of the two-particle system as a whole still exists, but becomes less and less local as the collision partners recede. This unusual situation was actually predetermined by the very acceptance of the main postulate of quantum mechanics - the principle of superposition of physical states. Formulated this century, this principle will apparently become the cornerstone of physical reasoning for future generations of scientists.

It is more or less natural that the specific features of quantum collisions will still remain when we take into consideration the subsequent interactions of particles with an increasing number of external objects. There is no such thing as a resonator of infinite quality, and it is not possible to achieve complete thermal insulation of a gas volume. To say nothing of the showers of cosmic particles that pass through any man-made device and take part in the physical processes.

Because of this, it would be a mistake to try to take into account all possible components of the open system in the nonlocal quantum state - the more so since all our physical measurements are essentially local. We should rather admit that the model an isolated dynamic system created for the sake of convenience is now taking revenge on its creators, making them seek a way out of the 'crazy infinity' like fractals or dynamic chaos.

Of course, many physical and philosophical questions remain, but the mathematical scheme of emergence of empirical irreversibility through quantum nonlocality is gradually becoming clear.

Another important problem is the necessity of using the classical continuous time $t$ in the description of quantum processes. This situation gives rise to a number of fundamental inconsistencies, noted by Erwin Schrödinger [17]. In the problems discussed above this comes up in the description of switching of the interaction on and off. Even when this description is done with great care, it is still necessary to use a quasi-classical approximation of, for example, free motion of molecules that brings them close and drives the apart. Such an approach is even aesthetically alien to the pure logic of quantum theory, but so far it is not possible to do without it.

In any case, the obstinate mechanistic mentality is gradually losing ground. A new physical vision of the Universe has to mature, but this will take Time, of this concept whereof we might have.

## References

1. Klein O Z. Phys. 72767 (1931)
2. Elsasser W M Phys. Rev. 52987 (1937)
3. Heisenberg W Across the frontiers. Translated from the German by Peter Heath (New York: Harper \& Row, 1974)
4. Davies E B Quantum Theory of Open Systems (London: Academic Press, 1976)
5. Mityugov V V Fizicheskie Osnovy Teorii Informatsii (Physical Foundations of Information Theory) (Moscow: Sovetskoe Radio, 1976)
6. Blum K Density Matrix Theory and Applications (New York: Plenum Press, 1981) [Translated into Russian (Moscow: Mir, 1983)]
7. Mityugov V V Izv. Vuzov. Ser. Radiofizika 32 (4) 436 (1989) [Radiophys. Quantum Electron. 32328 (1989)]
8. Mityugov V V Usp. Fiz. Nauk 163 (8) 103 (1993) [Phys. Usp. 36744 (1993)]
9. Braĭlovskiĭ A B, Vaks V L, Mityugov V V Usp. Fiz. Nauk 166795 (1996) [Phys. Usp. 29745 (1996)]
10. Shannon C PIRE 37 (1) 10 (1949) [Translated into Russian: Shannon C Raboty po Teorii Informatsii i Kibernetike (Works on Information Theory and Cybernetics) (Moscow: IL, 1963) p. 433]
11. Stratonovich R L Izv. Vuzov. Ser. Radiofizika 8 (1) 115 (1965)
12. Gel'fer Ya M, Lyuboshits V L, Podgoretskiĭ M I Paradoks Gibbsa i Tozhdestvennost' Chastits v Kvantovol̆ Mekhanike (Gibbs' Paradox and Identity of Particles in Quantum Mechanics) (Moscow: Nauka, 1975)
13. Landau L D, Lifshits E M Kvantovaya Mekhanika (Quantum Mechanics) (Moscow: GIFML, 1963) [Translated into English (Oxford: Pergamon Press, 1965)]
14. Heitler W The Quantum Theory of Radiation (Oxford: Clarendon Press, 1954) [Translated into Russian (Moscow: IL, 1956)]
15. Bashkanskiĭ E G, Mityugov V V Teor. Mat. Fiz. 7 (3) 348 (1971)
16. Gel'fer Ya M Istoriya i Metodologiya Termodinamiki i Statisticheskol̆ Fiziki (History and Methodology of Thermodynamics and Statistical Physics) (Moscow: Vysshaya Shkola, 1969)
17. Schrödinger E Sitzungsber. Preuss. Akad. Wiss., Phys.-Math. Kl. 12238 (1931) [Translated into Russian: in Eĭnshteĭnovskiŭ Sbornik 1982-1983 (Moscow: Nauka, 1986) p. 259]

[^0]:    Basho Matsuo (1644-1694) - Japanese poet known for his composition of haiku infused with the spirit of Zen Buddhism.

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