The second law of thermodynamics is riddled with (in percentage terms extremely rare) exceptions

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(Dated: February 16, 2016)

Abstract

Statistical mechanics descriptions of the second law of thermodynamics generally imply point-like particles driven by a dissipative overall mechanism for their simultaneous time-evolution. As the number of involved particles grows larger, it becomes more and more unlikely that they by itself adopt an off-equilibrium state with lower entropy. We present a macroscopic counterexample of the second law that repeatedly and spontaneously produces an entropy sink, thus recurrently enables us to harvest energy that sidesteps all the compensation interactions with the surroundings. Hence, this mechanism extracts energy from a single reservoir. This proves true in an experiment and is explained as a consequence of size effects, among them nonzero particle extent that marginally amend crucial peculiarities of thermodynamic equilibrium dynamics.

Keywords: Second law violation; Entropy; Constrained Brownian motion; Micro- and nanostructures; Dissipation

PACS numbers: 05.40.-a; 05.70.-a; 47.56.+r; 61.46.-w
I. INTRODUCTION

Most of the insights in an entropy context have been gained comparatively late in science history, at least in the version of today’s textbooks. In part, this is because the second law in some respects is counterintuitive if we disregard the internal microstructure (atoms, molecules) of matter. Only the statistical nature of thermal energy gives rise to another quantity, namely entropy that is not a conserved one in the spirit of Noether’s theorem but, e.g., quantifies the number of possibilities the microscopic constituents of gases and liquids may be arranged. Interestingly, also entropy contains “certain aspects” of a conserved quantity: generalized entropies such as the Kolmogorov entropy are dynamical invariants in systems $\dot{x}(t) = F(x(t))$ with irregular time-evolution $x(t)$.

We start our actual discussion with Ref. [1] that provides a helpful view of Loschmidt’s paradox. These authors infer that non-equilibrium situations which evolve the same way as time reversal would exhibit, although physically possible, can be observed with zero probability. We fully agree but supplement a major issue. Second law violations in a sense resemble embedding of the rational numbers in the reals. The probability to “accidentally meet” a rational one is precisely zero. Nevertheless, since we know how to set up rational numbers, it is well possible to list examples. Below we present an intentional construction of such a rare situation, namely a second law violation among the infinitely more frequent cases where the second law holds true.

Often the potential occurrence of second law violations is mapped to the question whether a so-called Maxwell’s demon can exist. Such an agent is thought to inspect the constituents of, say, a liquid on a microscopic level and to separate the fast particles from the slow ones. This type of considerations has a long, doleful history, sometimes due to an unclear situation whether or not the demon is part of the system under investigation. In our approach we pursue quite another course, namely we organize a situation where a spontaneous departure from thermodynamic equilibrium takes place. We achieve a quasi-equilibrium between Brownian particles and those of their host medium, and so this marginal deviation from equilibrium is attended with thermal processes of minor efficiency. Qualitatively, however, we face a second law exception with all its imperative consequences such as energy extraction out of a single reservoir.
II. EXPERIMENTAL SETUP

Now we outline the essentials of our experimentally realized device. One of its major features is a porous medium that acts as a moderate obstacle to Brownian motion in a liquid. Some of the Brownian particles by chance enter the region of the obstacle. Then, motion and accessible positions of the particles within the porous vicinity are subject to geometrical restrictions, leading to constrained or "frustrated" Brownian motion. We anticipate that this constitutes an entropy sink where the overall entropy, i.e., not just the one of the captured particles with respect to their prior state, gets reduced if the obstacle (or trap) is suitably tailored. This arrangement entails a slight departure from thermodynamic equilibrium of all the liquid (particles of the host medium plus Brownian ones). The larger Brownian particles transfer a small fraction of their kinetic equilibrium energy to their immediate neighborhood that this way marginally warms up. We harvest this "extra energy" beyond equilibrium, and we postpone a description how to organize this in a recurrent manner. The physical background on Brownian fluctuations as well as thermodynamics in general may be found in textbooks [2, 3]. For entropic consequences if particles enter a porous medium, see [4]. Further, Brownian particles in confined cavities are an ongoing research subject, Ref. [5] presents a recent approach. But, to our knowledge, related possible limits of the second law’s validity have never been tackled, or at most in a rather indirect manner.

Figure 1 provides a schematic view of the setup that, at first glance, appears rather simple. A plug of glass fibers, as they commonly get used for filtering purposes in chemistry, is sandwiched between two so-called thermoelectric generators (TEGs). On the two narrow sides of this device (front, rear in figure), we place glass plates (not shown) that limit the plug laterally. The TEGs are squares of 30 mm side length and contain 127 semiconductor thermocouples connected in series, each. Thus, the Seebeck effect produces a voltage if the two faces of a TEG are at different temperatures. The thickness of the plug of glass wool (spacing of the TEGs) amounts to 7 mm and the TEGs are some 6 mm immersed into saturated solution of potassium permanganate in water at room temperature. The clearance of the TEGs down to the bottom of the shallow container with the liquid is around 2 mm (whereas the plug stands right on the bottom). These geometrical settings prove quite interdependent in their impact on our measured outcome, thus any change involves a new overall optimization.
FIG. 1: Left: View of the particle trap made of glass fibers, sandwiched between two thermoelectric generators (TEGs) with efficiency 0.058 V/K, each and immersed into KMnO₄ solution. Right: Circuit diagram with the TEGs represented as battery symbols, for polarities see text, as well as voltmeter and load resistor.

Expectedly, the geometrical conditions inside the plug are crucial to motion and density of Brownian particles therein, namely the two types of hydrated ions in the KMnO₄ solution. As far as this can be manufactured, the fibers are aligned vertically and at bottom and top of the plug they are cut off. Clearly, a too dense plug handicaps the particles (thus retards their diffusion) too strongly. As a rule of thumb, only around 5% of the entire plug consist of massive glass. Most conveniently, the plug is assembled by an array of small parallel bundles, since otherwise capillary forces tend to cluster the fibers into dense regions, while emptying the rest. Altogether, the initial state of the experiment is the plug of glass fibers (framed by the two TEGs) soaked by capillary forces with saturated KMnO₄ solution.

Further, Fig. 1 presents also the circuit diagram and, for the sake of readability, we use battery symbols for the TEGs. The series circuit of the two TEGs is performed such that both of them measure a temperature difference between inside the plug and the surrounding liquid with same polarity in their thermovoltages (not visible in the figure). Hence, the
voltmeter displays their sum $U$, and the sign is chosen to be positive if the plug is warmer than around it. The load resistor $R_L$ equals 6.8 $\Omega$ which is twice the internal resistance of a TEG, and so the device operates at maximum power consumption $U^2/R_L$.

III. MEASUREMENTS AND RESULTS

The actual experiment consists of recurrent flushing of the plug from above, and in the meantime diffusion (or Brownian motion) refills the plug to an amount that is just adequate. All the time we measure the temperature difference between plug and surrounding liquid in the container, that is essentially the thermal effects within the plug, see Fig. 2. First we outline the technical procedure, and afterwards we turn to the outcome. The very first flush at $t = 0$ in the top row panels is deficient due to the saturated solution initially present in the plug, which poorly matches the other system parameters. Amazingly, the amount of flushing water of 8 cm$^3$ is a comparatively uncritical setting. The one crucial point is to organize the totality of experimental parameters in a way that the particle density gradient between just flushed region (plug and favorably somewhat beyond) and adjacent saturated solution is sufficiently steep. This turns out to be quite an elaborate procedure of trial and error along gradients of improvement. A too blurred zone is inadmissible, but we get by with a slightly inhomogeneous plug that only in some areas by chance meets all the requirements. However, the allowable volume in parameter space is tiny. In our view, to further enhance reproducibility we should find appropriate “open” polymers whose chains replace the glass fibers, but this then would turn into a really costly enterprise.

To the left in all our curves we see the lowermost part of a peak that is by far the strongest thermal effect, namely warming due to flushing away the evaporatively cooled surface water from the (rough) top of the plug. The system parameters must be such that this peak is over rather quickly, since the subsequent structure on the right-hand side in the upper panels is now the effect we are after. As the Brownian particles enter the trap, they lose a small percentage of their (at least translatory) kinetic energy in favor of the host medium that warms up. The particles are now in a quasi-equilibrium with the water molecules, and so equipartition is ill-defined since there is no temperature that strictly applies to all of the liquid. This situation persists as the particles diffuse further into the trap, while new ones enter underneath. The spontaneous transition from equilibrium to a slight deviation thereof
FIG. 2: Top row: The rise at some 25 min after flushing issues from an energy loss of the Brownian particles in favor of the host medium, caused by spontaneous deviation from thermodynamic equilibrium of all the particles in the liquid. Only the bottom region of the trap (particle inlet) brings about heating, and so the plotted voltages by far underestimate the strength of this mechanism. Bottom panels: In plain water, the suggested effect has gone. Apart from that, the lasting descent within the plotted time windows is owing to different thermal conditions such as evaporation rate in the absence of dissolved particles. Regarding voltage measurement, the precision lies well within ±0.01 mV throughout the figure.

FIG. 3: As in the upper panels of Fig. 2 but this time the plug of glass fibers just slightly has missed the geometrical conditions for the desired diffusion profile as a function of time. Hence, the particle flow into the trap was insufficient, which was clearly visible to the unaided eye. The plots show little effect, if at all.

entails an entropy sink. Note that only the bottom region contributes to heating, which renders conversion of voltages into temperatures somewhat dangerous. Moreover, the high fluid level in the container (or deep immersion of the TEGs, see above) raises the stability and thus improves the signal to noise ratio.
For comparison, we may look at the four bottom panels in Fig. 2 where the effect in question has disappeared. There we used the very same plug after replacing the KMnO$_4$ solution by plain water. Just for readability we reset the time scale to zero (actually zero means 14 hours in the upper scale). Here there is no reason to omit the first run, and the intervals between consecutive plots are shorter since we do not need to wait until diffusion has refilled the plug. Further, in Fig. 3 we display the same situation as in the upper panels of Fig. 2 (thus with KMnO$_4$ solution) using another plug that almost looked alike. Nevertheless, it obviously has missed the requirements. We recognize similar plots as in the top row of Fig. 2 but simply without the increase that is the outcome of our endeavors. The desirable effect is absent, maybe up to an insignificant hint thereof.

IV. THEORY: THE CONCEPT AND MODELS

In order to substantiate our proposed mechanism of a marginal deviation from thermodynamic equilibrium between Brownian particles and host medium, we first recall some basics of Brownian motion and diffusion. Then we discuss the all-important differences thereof. We state the Langevin equation for a particle

$$m \ddot{x}(t) = -\beta \dot{x}(t) + F_c(t) + F_{ext}$$

that, besides friction term and possible external force, comprises the random driving force $F_c(t)$ due to collision. Frequently, external force means gravitation, but here this is negligible since the hydrated ions of KMnO$_4$ do not sediment to the ground. The collision force is thought to be a long-term function of time, i.e., an irregular sequence of many different collisions.

This may be newly considered as a sum over many particles, as soon as we accept that ergodicity applies in this case. Conveniently, isotropy removes the random term from this sum, and as a final prerequisite we make use of equipartition that introduces temperature. This way, after some steps of rearrangement we arrive at our preferred version of Eq. (1), namely an equation that also covers the few just above stated clear-cut assumptions. This reads

$$\frac{d^2}{dt^2} \langle x(t)^2 \rangle_x + \frac{\beta}{m} \frac{d}{dt} \langle x(t)^2 \rangle_x = \frac{2k_B T}{m},$$

where the spatial mean value of squared distances the particles have departed from their
starting point is our new variable. The stationary solution of Eq. (2) is a fairly known result, namely the linearly growing mean value
\[ \langle x(t)^2 \rangle_x = 2Dt, \quad D = \frac{k_B T}{\beta}. \] (3)

Here, \( D \) is the diffusion constant as it enters the two major statements for unconstrained diffusion
\[ j_n(x, t) = -D \nabla n(x, t), \quad \frac{\partial n(x, t)}{\partial t} = D \Delta n(x, t). \] (4)

The vector \( j_n(x, t) \) denotes the particle current density, and Eqs. (4) describe Brownian motion as an overall diffusion phenomenon of many particles with density \( n(x, t) \). We recognize that already unrestricted diffusion constitutes a quasi-equilibrium of Brownian particles with the host medium, since there exists a macroscopic time-evolution while the density gradients tend to even out. Admittedly the process is slow, and so the equipartition law stays almost unaffected.

However, we aim at a somewhat stronger deviation of the particles from equilibrium with the background medium, although in terms of equilibrium energy this always remains a minor percentage. Ref. [6] shows that the diffusion constant \( D \) strongly depends on limiting geometrical conditions, comparable to the cavities in our plug of glass wool. The particles used by these authors are somewhat larger but, since [6] provides an experiment, the findings there do not depend on the choice of theories we might consider to be appropriate. In Ref. [7] we performed a preliminary experiment, also based on dissolved KMnO\(_4\) and its diffusion within glass wool. There we report on benefits of this choice, among them the exceptionally strong color (of the MnO\(_4^-\) ions) that permits visual inspection of particle density and its propagation velocity inside the glass fiber environment. However, the setup in [7] suffers from an unrecoverable shortcoming, namely the single-step approach that cannot be upgraded to perpetual operation. Thus, the quasi-equilibrium between Brownian particles and host medium may always be taken as a transient regime prior to full equilibrium.

This problem is settled now. Our new device admits recurrent flushing that enables us to repeatedly harvest the energy attended with the rise in the upper curves of Fig. 2. Outside the trap, the equipartition energy of the Brownian particles gets restored. Hence, there is an ongoing heat transfer from the container into the trap. This transfer is not at all a consequence of thermal equilibration that is much slower, and we may well bias the thermovoltages such that the achieved increase starts at zero. We emphasize that this rise
is the issue where the second law gets violated, and so the various thermal interactions with environment are immaterial. They affect just the temperature level (ordinates in Fig. 2) where the warming happens, and we do not supply any thermal insulation.

The gained (or actually transferred) energy may be used now to organize flushing. But this poses merely an engineering task, and by no means a matter of principle. The flushing water may (optionally) be recycled by prior evaporation out of the container. Again, the associated thermal interactions with the environment just influence amount and temperature gradient of the heat backflow from there. Note that, within the realm of the second law, such a delayed return of energy borrowed from the surroundings is not admitted.

An engine designed as outlined above will indeed run perpetually. Its efficiency $\eta$ fulfills $\eta_C < \eta \ll 1$ where the Carnot efficiency $\eta_C$ is tiny since all occurring temperature differences (apart from the initial peaks in Fig. 2) are minor. Based on the efficiency 0.058 V/K of the used commercial TEGs and on geometry considerations, the relevant temperature increase due to our proposed mechanism is in the order of 0.1 K. Probably the limit of low efficiency has not so much been investigated, since generally we aim at engines as efficient as possible. However, we think it is not a surprise that close to this limit the crucial inequality $\eta > \eta_C$ more likely gets a chance for a practical implementation.

Entropic phenomena caused by particle size are not new, depletion forces are a long-known example, see Refs. [8, 9]. In order to model the energy transfer from the Brownian particles to the smaller ones of the background medium inside the porous vicinity, we suggest to rewrite the diffusion constant $D$ in Eqs. (3) as

$$\tilde{D} = \frac{k_B T}{\beta(d, r_p) + \tilde{\beta}(d, r_p, r_h)}$$

where we purposely modify the coefficient $\beta$ of the dissipative term in Eq. (1). The distance $d$ in (5) is the typical spacing between the glass fibers, and $r_p$ means particle radius (that optionally may be split up into two different ones according to the unequal types of hydrated ions). Then, $r_h$ denotes the typical radial extent of a host medium particle. The first term $\beta(d, r_p)$ in the denominator of Eq. (5) is inspired by Ref. [6], namely by the relative confinement of Brownian particles that strongly enters the diffusion constant. In addition, the term $\tilde{\beta}(d, r_p, r_h)$ accommodates also $r_h$. This ansatz may well prove adequate, since the measured energy transfer to the host medium is hard to imagine if we suppose all the particles to be indistinguishable. We rule out a host or background medium that behaves
just as a continuum, and its smaller constituents are less inhibited in motion by the cavity size. Moreover, an approach in the spirit of a generalized Fick-Jacobs equation \[4, 5\] would be rather inconvenient for our geometry of aligned glass fibers (see above). Thus we stick to Eqs. (4) and (5), although we are quite far from a suitable parametrization of (5). But, once this is accomplished, we think the observed heating effect is primarily a function of \(\tilde{\beta}(d, r_p, r_h)\).

Thermal fluctuations, above all Brownian ones are sometimes said to be crucial to generally explain the occurrence of irreversibility, not least because Eq. (1) is dissipative. We point to Jarzynski’s equality

\[
\langle e^{-W/k_B T} \rangle = e^{-\Delta F/k_B T}
\]

(6)

that relates the Helmholtz free energy difference \(\Delta F\) to the work \(W\) supplied to (or extracted from) a system, regardless whether or not we slowly pursue a reversible path of quasi-static states starting at equilibrium situation of reservoir temperature \(T\) \[10\]. Here, in \(F = U - TS\) with \(U\) being the internal energy, the dissipation-caused term \(TS\) of entropy \(S\) well may grow. The inequality (entropy remains or rises, or also \(\langle W \rangle \geq \Delta F\)) is removed, and this supports strict validity of the second law that this way might relate to other physical statements.

However, we focus on a somewhat different issue, namely thermodynamics of small systems, Refs. \[11–13\] meet our purposes. The cavities in our particle trap are such limited systems that just weakly couple to their environment, i.e., largely to adjacent hollows. Already the constrained Brownian fluctuations inherently comprise all the properties needed for the (marginal) second law violation in Fig. 2.

Likewise, we may look at Brownian fluctuations within the framework of linear response theory. Suppose \(x(t)\) is a (here scalar) unperturbed system’s signal. Instead, we state the progressing time-average of its response to a generalized scalar external force \(f(t)\) as

\[
\langle x_{\text{resp}}(t) \rangle_t = \int_{-\infty}^{\infty} \Theta(t - \tau) \chi(t - \tau) f(\tau) d\tau.
\]

(7)

Then, the Fourier transform \(\tilde{\chi}(\omega)\) of the linear response function or susceptibility \(\chi(t)\) enters

\[
\tilde{P}(\omega) = \frac{2k_B T}{\omega} \text{Im}\tilde{\chi}(\omega)
\]

(8)

that is the fluctuation-dissipation theorem, see \[2, 3\]. The Heaviside function \(\Theta(t - \tau)\) in Eq. (7) assures causality with respect to the effect of \(f(t)\), and \(\tilde{P}(\omega)\) in (8) means the Fourier transform of \(x(t)^2\) or power spectral density. In a second law context, causality is
of utmost importance since we deal with the physics of a spontaneous departure from strict
equilibrium, very much in contrast to fictitious time reversal in an irreversible process.

For a Brownian particle, theorem (8) states that the dissipation caused by \( f(t) \), thus
essentially \( \text{Im} \tilde{\chi}(\omega) \), has the same physical origin as the Brownian fluctuations (characterized
by the \( \tilde{P}(\omega) \) distribution) themselves. The cavity size or rather walls introduce now such an
\( f(t) \) that selectively acts on particle size. Again, this substantiates the marginal deviation
from the subtle properties of true equilibrium dynamics.

We complete our choice of theoretical fundamentals and models with a regard to quantum
Brownian motion \cite{14,15}. But, instead of replacing classical quantities by their quantum
mechanical analogues (such as momentum operators), we scrutinize those quantum trajec-
tories (for electrons) that exhibit physically correct velocities. These velocities, or at least
their magnitudes, are indispensable if we aim at plain assignment to "unambiguous" ther-
odynamics. The key point is consistency with wave mechanics, see \cite{16} for derivation and
numerical values of velocities, momenta, and energies in Sommerfeld’s theory of metals. In
Ref. \cite{17} we present actual trajectories (for one or more electrons in atoms) that, by virtue
of position vectors \( \mathbf{x}(t) \), even provide angular momenta. Up to some poorly surmountable
numerical hurdles, they agree with wave mechanics. On this footing, we think of an elec-
tron gas theory that more than so far will overcome the gap between classical and quantum
mechanical many-body theories. Again, this would greatly enlarge the reach of the second
law and of its exceptions.

V. CONCLUSIONS

In sum, we investigate the dependence of dynamics in a liquid on particle size in a
geometrically constrained environment. Brownian motion of larger particles immersed into
a background medium of smaller ones is an obvious candidate for this intention. This way,
the geometrical structure of a confinement matters, while for point-like particles any cavity is
of infinite relative extent. Then, we organize the overall conditions of a diffusion experiment
such that unequally sized particles no longer carry the same equipartition energy. By virtue
of differently strong inhibition, they spontaneously adopt marginally deviant kinetic energies,
which establishes a quasi-equilibrium. It is of utmost importance to recognize that even in
the long run this situation does not tend to the "usual" thermodynamic equilibrium. Hence,
there is no temperature that strictly holds for all of the particles. In terms of equilibrium energy, the deviations thereof are minor but, nevertheless, they constitute a second law exception.

We outline and, as far as possible with our present setup, quantitatively evaluate what this means in terms of efficiency. Undoubtedly it is much easier to design an arrangement that exceeds Carnot efficiency if we approach the limit of zero efficiency. In this contribution we shall not scrutinize what measures might improve the performance, and where this has fundamental limits. Admittedly, automatized recurrent flushing of the particle trap is still missing, since on an engineering level this cannot be carried out readily. But we strongly substantiate that this will never destroy our envisaged entropy (and energy) balance. Our work primarily covers entropic implications of size effects (cavities, particles), and there we present results and viewpoints that, to our knowledge, are new. In particular, we make use of these size effects in a pertinent way that unveils a second law violation. That is what we have introduced by means of a particular experiment and, in our view, explained in a retraceable manner. Thus we present here a proof of concept, but the general situation is far from being settled.

Acknowledgment

The author thanks R. Maier, L. Pauli, P. Robmann, and U. Straumann for constructive discussions.

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