

Does the second law of thermodynamics really hold good without exception?

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Abstract

A major part of the many thermally driven processes in our natural environment as well as in engineering solutions of Carnot-type machinery is based on the second law of thermodynamics (or principle of entropy increase). An interesting link between macroscopically observable quantities of an ensemble (state variables) and the thermal velocity of its individual constituents such as molecules in a liquid is provided by the Brownian motion of suspended larger particles. We postulate a "frustrated Brownian motion" that occurs if these particles get partially trapped in an environment of suitable geometrical conditions. This dissipates a small fraction of the kinetic energy attended with the Brownian motion and deposits it inside the trap, and so this constitutes a mechanism that by itself transfers thermal energy from cold to warm. We note that this is just a marginally admitted, slowly evolving effect driven by a thermodynamic quasi-equilibrium, thus being of limited efficiency in terms of energy density attainable per unit of time. However, a simple experiment suggests that this process indeed is allowed to take place, and the envisaged applications then are straightforward.

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I. INTRODUCTION

The question whether it is possible to satisfy our energy needs without to burn down some kind of fuel has attracted scientists over many centuries. Apart from the use of other natural resources (mainly sun, water power, and wind), the proposed ideas range from absolutely bizarre up to ingenious. While it appears not too hard to accept conservation of total energy including heat according to the first law of thermodynamics, the second law certainly deserves a closer look at its practical implications. We may ask where it poses an ultimate limit concerning energy exploration in a technical or economical sense. Why is it impossible to cross a lake with a boat just by cooling down the water in the lake? The second law states that we need two reservoirs of heat at different temperatures, and it has never been observed that we get by with just one of them, i.e., the lake in our example.

Our above example is almost archetypal for lots of practical and sometimes also theoretical questions that relate to the second law of thermodynamics. We face a situation where the energy under consideration is all present, but the second law prohibits access to it. In this contribution we claim that there is a way out of this difficulty, i.e., our approach spontaneously creates a temperature difference that may be used in a traditional way. However, we also anticipate that our experimental setup does not work too efficiently. Nevertheless, besides aspects of principle, a numerical estimation clearly offers a chance for an economically relevant implementation of a future power supply, e.g., of an entire power plant. Further, to gain energy from the environment undoubtedly would be beneficial to the climate. Including the exhaust heat of a Carnot-like thermal engine that makes use of the achieved temperature difference, we think of an energy economy that (theoretically) is just neutral with all respects.

Concerning entropy, we refer to some of the forthcoming sections below. We think it is hard to discuss this matter in full generality, while the restriction to our specific experimental arrangement renders the pertinent questions much easier. But we may already address the crucial issue, namely the meaning of a local entropy sink with regard to the situation in the environment.

The main goal of this work is to reconsider certain aspects of Brownian motion within the particular context of the second law of thermodynamics. On this score, we scrutinize some actually well-known peculiarities of the Brownian motion in a less common framework

of methods. The textbooks [1–3] provide general thermodynamics, where [3] also gives a little survey of technically relevant thermal engines. Concerning a more specific focus on Brownian motion, we recommend Refs. [4–6]. In a slightly enlarged context, we also may look at particle motion in a homogeneous liquid [7], i.e., in the absence of larger immersed Brownian particles. It is important to recognize that the Brownian particles contribute to a thermodynamic (nearby) equilibrium situation that comprises the host medium where they are accommodated. Thus, the Brownian motion should not be considered to be "externally" powered by the thermal energy of, say, a liquid water reservoir at some temperature. Instead, the driving force emerges from the local and momentaneous deviation from the statistical average of certain relevant properties the water molecules may adopt, their momenta being of particular importance. Brownian motion requires no external Newtonian driving force other than the one supplied by the randomly occurring asymmetry in the local neighborhood of a particle.

Then, by chance, such a particle on its path may enter a suitably prepared trap (see below). If many particles therein slow down, they accumulate thermal energy at this place, since a small fraction of their kinetic energy gets transferred to the local environment. Although the Brownian particles are in thermodynamic equilibrium (actually it is a quasi-equilibrium, see below) with the ones of the host medium, the trap may well react upon the different size of particles. Our experiments suggest that this causes the Brownian particles to slightly increase their tiny deviation from equilibrium.

Does this imply that we even might achieve a cyclically (perpetually) operating thermal engine? The indispensable prerequisite to such a machine is its ability to remove the particles from the trap in a way that consumes less energy than they previously have supplied. We postpone a further discussion of this matter until the experiment is described and the measurements are explained within the scope of our suggested mechanism. But we emphasize that already a partial realization, i.e., a partial compensation of the energy needed to empty the trap, may well be greatly relevant to technical applications. Admittedly, our performed experiment does not yet comprise removal and reinjection of the Brownian particles. At present, it covers only the single-step mode where the particles spontaneously transfer energy along a temperature gradient in the "uphill" direction.

In a way, this resembles an everyday situation all of us possibly have experienced now and then. The stormy weather in autumn whirls around the leaves from the trees, and

we consider the situation where a litter basket is present. Initially, the walls of the basket prevent the leaves from entering, and so the coverage (leaves per area) inside is lower than outside. But then, under suitable overall conditions, there is even a crossover where the density inside starts to exceed the one in the surroundings, since the walls now capture the leaves inside the basket. Thus, we face a situation that more or less pictures the one described above: within the basket (that serves as our trap) numerous leaves (Brownian particles) are present. We recognize that these leaves basically are at rest, since the litter basket limits their available volume. Moreover, to far extent the filled basket also keeps off the wind, i.e., there is almost no driving force anymore that might influence their state in the sense of position and momentum.

II. THEORY

A. Brownian motion and diffusion

Although Brownian motion is a well-investigated subject matter known for a long time, we shall briefly revisit some issues that will be important below. The situation where a Brownian particle undergoes a (single) collision with a neighboring molecule of the host medium may be described by the Langevin equation

$$m\ddot{\mathbf{x}}(t) = -\beta\dot{\mathbf{x}}(t) + \mathbf{F}_c(t) + \mathbf{F}_{ext}. \quad (1)$$

Here $-\beta\dot{\mathbf{x}}(t)$ denotes the usual friction term, $\mathbf{F}_c(t)$ is the random driving force due to the collision, and \mathbf{F}_{ext} means a possible external force such as gravitation. The latter is negligible in our situation of small particles (see below) that do not sediment to the ground.

We may now perform the sum over many of these collisions, i.e., we consider a longer period of the rapidly varying random force $\mathbf{F}_c(t)$ above. This can be shown to be equivalent to the more convenient sum over many (identical) particles. Further, we make use of isotropy that removes the random term from the achieved sum, and we assume also the equipartition theorem to hold true in this case. Then, after some steps of rearrangement we arrive at an equation for the spatial mean value of the squared distances the particles have departed from their starting point, namely

$$\frac{d^2}{dt^2}\langle \mathbf{x}(t)^2 \rangle_x + \frac{\beta}{m} \frac{d}{dt}\langle \mathbf{x}(t)^2 \rangle_x = \frac{2kT}{m}. \quad (2)$$

In our particular situation of Brownian motion, equipartition relates the mean kinetic energy of a particle to its thermal energy. With regard to the three translatory degrees of freedom, for N (in ideal circumstances spherical) particles this reads

$$\sum_{i=1}^N m \dot{\mathbf{x}}_i(t)^2 = 3NkT, \quad (3)$$

where k and T are the Boltzmann constant and temperature, respectively. Clearly, N in Eq. (3) must be large, such that the sum does not fluctuate anymore. For small N or even for a single particle, we have to replace $\dot{\mathbf{x}}(t)^2$ by its time average $\langle \dot{\mathbf{x}}(t)^2 \rangle_t$.

The stationary solution of Eq. (2) is recognized to grow linearly in time. In the most common notation it may be written as

$$\langle \mathbf{x}(t)^2 \rangle_x = 2Dt, \quad (4)$$

with the diffusion constant

$$D = \frac{kT}{\beta} = \frac{kT}{6\pi\eta r}, \quad (5)$$

where the second part of (5) applies to the important special case of spherical particles in a liquid. Moreover, the viscosity η exhibits quite a strong dependence on temperature, even in water.

We think it deserves attention that, even in our context of Brownian motion, the equipartition principle nicely stands an experimental confirmation of its validity. Generally it is the Avogadro number that gets determined in a rather indirect manner, and the result turns out to be correct within an almost amazing precision of roughly one percent. In our view this is not really evident. Over a large range of size and mass of the Brownian particles, they carry a mean translatory kinetic energy of $(3/2)kT$ each, just as the other particles (e.g., water molecules) of the host medium do.

Now we may focus on another important property of the Brownian motion, namely its fractal scaling behavior. This emerges from an inspection of the particle trajectories at different scales of length and time. Equation (4) suggests that, provided fractal behavior is present, to rescale spatial extents by some factor of A and the time by A^2 should preserve the global aspects of a Brownian trajectory (but not its local details). Figure 1 presents such trajectories, namely numerical solutions $\mathbf{x}(t)$ of Eq. (1), which already exhibits the major issues of this circumstance. We simulate the driving force $\mathbf{F}_c(t)$ in (1) by truly decorrelated

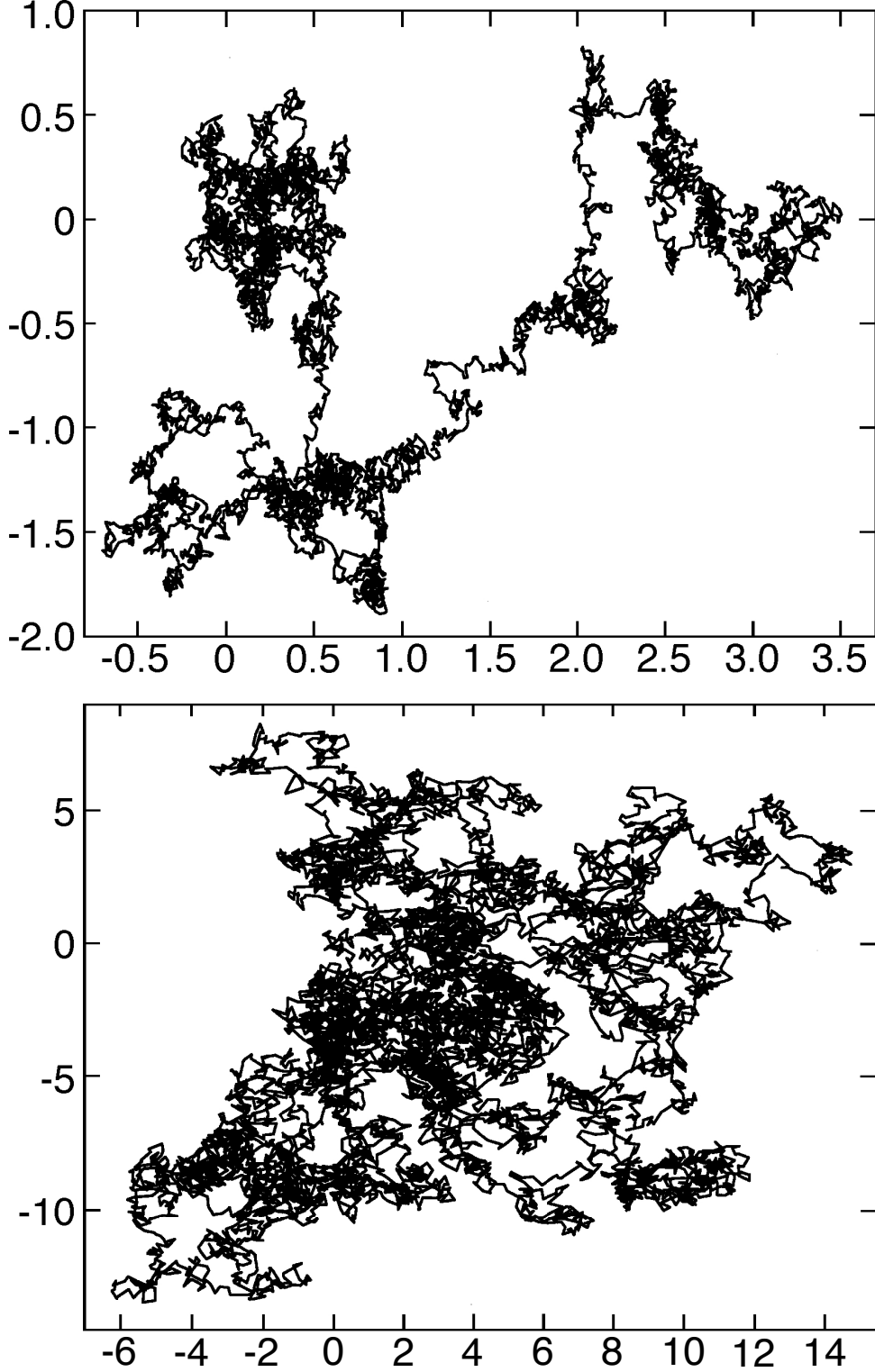


FIG. 1: Top: Two-dimensional Brownian motion based on 2×10^6 points of a trajectory $\mathbf{x}(t)$ that solves Eq. (1), 10^4 out of them being plotted. Bottom: This time we use 2×10^8 points, again 10^4 of them are displayed, and so the resolution is reduced by a factor of 100. If we compare the two panels, we note self-similar properties (see text) as well as spatial extents according to Eq. (4).

random numbers, and so we look at the special situation of a Wiener process. The bottom panel shows a two-dimensional Brownian motion based on 2×10^8 points or time-steps, where the resolution is such that 10^4 points are plotted. The upper part of the figure pictures the very same motion with only 2×10^6 points, and again 10^4 out of them being used to display the curve. In other words, the upper panel shows the first percent of the bottom trajectory, but the resolution above is 100 times better. We observe the roughly 10 times larger linear spatial extents in the bottom panel, while it covers a period of time that is as much as 100 times longer. This applies also to a situation in one or in three dimensions, since a move into, say, the direction perpendicular to Fig. 1 does not depend on the motion within the plotted two dimensions.

At first glance, the agreement appears to be rather poor: the upper motion exhibits noticeable excursions, whereas the bottom situation looks more compact. However, this impression is not really significant. The two trajectories start at $(0/0)$ in their plotted frames, and so we recognize that the upper curve initially represents quite a local blur. Moreover, due to the different scales of length such excursions seemingly are less pronounced in the bottom panel. Altogether, Fig. 1 is meant to simulate the quite well defined ordinary situation outside the particle trap, i.e., the reference case in the absence of an obstacle to the Brownian motion. We anticipate that, due to insurmountable computational hurdles, most of the differences occurring inside the trap must be quantified on an experimental basis.

Solution (4) tells us also that we deal with phenomena in a diffusion context. The peculiarities of Brownian motion theory appear just from a detailed inspection of a single particle motion, rather than of a particle density $n(\mathbf{x}, t)$. This way we also may recognize the Brownian particles to be in a quasi-equilibrium with the ones of the host medium. Diffusion processes are time-dependent evolutions but actually they are rather slow, and so this just insignificantly affects the equipartition energy value of $(3/2)kT$. Usually, diffusion processes are described by two major statements, namely

$$\mathbf{j}_n(\mathbf{x}, t) = -D\nabla n(\mathbf{x}, t) \quad (6)$$

and, assuming there is no particle source other than the initial one,

$$\frac{\partial n(\mathbf{x}, t)}{\partial t} = D\Delta n(\mathbf{x}, t). \quad (7)$$

The vector $\mathbf{j}_n(\mathbf{x}, t)$ in (6) is the particle current density, and $\Delta = \nabla^2$ denotes the Laplacian operator.

Sometimes Eq. (7) is generalized in the sense that all the processes that formally adopt this type of dependence on space and time are said to be "diffusion-like". Probably heat conduction is the most common example, but there is a variety of phenomena where a gradient in some quantity tends to even out in a diffusion manner.

Actually, the modified or retarded diffusion mechanism inside the particle trap (see experimental section below) may well be regarded as a further example of generalized diffusion. Concerning the trajectory $\mathbf{x}(t)$ of an individual particle, this is what we call "frustrated Brownian motion". The numerous interaction events of such a particle with the internal surfaces of the trap involve dissipative (inelastic) contributions, which is significantly beyond what we might tackle in terms of dynamical systems modeling. These interactions hardly may be incorporated into an equation of type (1), and so we cannot offer a modified plot in the spirit of Fig. 1. In all probability such an attempt would not be able to care for the exact geometrical situation of an individual interaction process, thus providing us just with a summary effect (based on assumptions) of the trap. We rather might try to generalize Eq. (7) up to the extent where it reproduces the measured overall effects (for all the Brownian particles). But this necessarily means that we parametrize our diffusion model, and particularly the appearance of a rather faint effect likely may emerge from a suitable parameter choice.

A possibility for such generalization steps may be the Fokker-Planck equation [5] that, in addition to Eq. (7), comprises a drift term. But this will by far not suffice to simulate the experimental situation inside the cavities of the trap, and so it definitely cannot bypass the need for free parameters. Therefore, we think an experiment should answer the open questions.

Nevertheless, our idea of dissipated translatory particle energy inside the trap is largely motivated by diffusion (or Brownian motion) theory itself. We face a particle density gradient that drives the diffusion mechanism and that inherently represents a quasi-equilibrium. The trap then may cause the Brownian particles to depart somewhat stronger from thermodynamic equilibrium energy (particles plus host medium), namely from the equipartition value of $(3/2)kT$ per particle. After all, we think this energy difference between quasi-equilibrium (usual diffusion process outside the trap) and actual situation based on a slightly more pronounced deviation from equilibrium (inside) produces our measured effect, i.e., the temperature gradient under consideration.

B. Fluctuations in general

Since in a diffusion context we deal with a quasi-equilibrium, we should be aware of an important link between equilibrium and non-equilibrium statistics, namely the celebrated fluctuation-dissipation theorem. Essentially it states a relation between thermal fluctuations and the response of a system to an external disturbance. For a Brownian particle the theorem says that the dissipative frictional drag the particle undergoes upon an externally powered dislocation has the same physical origin as the Brownian fluctuations themselves. This is also the basic assumption to (strictly) derive the first part of Eq. (5). A thorough discussion may be found in [2, 5], but here we merely state the particularly simple and experimentally well-investigated version

$$\tilde{P}(\omega) = \frac{2kT}{\omega} \text{Im}\tilde{\chi}(\omega). \quad (8)$$

$\tilde{P}(\omega)$ denotes the power spectral density, namely the Fourier transform of $x(t)^2$ that is a squared "system output" with almost no restriction to its physical meaning. Since the squares imply a nonzero time average, Eq. (8) requires the situation of a stationary random process: the Wiener-Khinchin theorem then permits the Fourier transform of $x(t)^2$ in terms of a transformed autocorrelation function. Further, $\tilde{\chi}(\omega)$ is the Fourier transformed susceptibility or linear response function $\chi(t)$. Including $\Theta(t - \tau)$ that is the Heaviside function, $\chi(t)$ most conveniently may be introduced by the statement

$$\langle x_{resp}(t) \rangle_t = \int_{-\infty}^{\infty} \Theta(t - \tau) \chi(t - \tau) f(\tau) d\tau. \quad (9)$$

Here $f(t)$ means a generalized scalar external force, and $\lambda H^1(x, t) = x_{resp}(t)f(t)$ denotes the corresponding time-dependent perturbation in the overall Hamiltonian function $H(x, y, \dots, t) = H^0(x, y, \dots) + \lambda H^1(x, t)$. Clearly, $f(t)$ must be organized in a way that $H^1(x, t)$ adopts the dimension of an energy. To first order in λ , we recover the response $x_{resp}(t)$ to $f(t)$ that is linear in f (just as, e.g., in a linear spring), in accordance with Eq. (9). The Heaviside function assures causality, i.e., the effect of the force $f(t)$ that acts at some point of time cannot appear prior to this very moment. Generally $x_{resp}(t)$ may depend on all the past values $f(t)$ for $t < t_0$ up to some time $t = t_0$ of interest, say, up to present. This yields a progressing time-average $\langle x_{resp}(t) \rangle_t$ that may strongly depend on t_0 and adds to the (time-independent) mean value $\langle x_0(t) \rangle_t$ of the unperturbed signal. Thus, we arrive at the observable "up to present average" $\langle x(t) \rangle_t$ of the total system's output. Then,

the imaginary part of $\tilde{\chi}(\omega)$ in statement (8) describes the dissipated energy caused by $f(t)$, while $\tilde{P}(\omega)$ characterizes and quantifies the fluctuations.

It has been known for a long time (actually since the pioneering investigations of L. Boltzmann) that on small scales in space and time the second law of thermodynamics fails. See Ref. [8] for a recent experiment where the deviations from equilibrium thermodynamics become quantified. In a way, such approaches always relate to the fluctuation-dissipation theorem (however, the authors in [8] prefer a version of their own that facilitates a comparison with experiment). For a theoretical discussion of finite size effects we recommend [9]. There, some pertinent quantities and processes that usually appear in a context of macroscopic equilibrium thermodynamics are reconsidered for ensembles with limited heat capacities, where the thermal fluctuations cause additional implications. In such cases, to achieve the correct limit for infinite size and/or time is of particular importance.

The short-term production or consumption of entropy prior to equilibrium necessarily involves a time-dependent entropy definition, we refer to an instructive treatise on this matter [10]. Most commonly, the time-dependence gets introduced by an intuitive generalization of the Gibbs entropy stated in terms of an evolving N -particle probability density W_N , namely

$$S(t) = -k \int W_N(\mathbf{r}_i, \mathbf{p}_i, t) \ln W_N(\mathbf{r}_i, \mathbf{p}_i, t) d^3 r_i d^3 p_i. \quad (10)$$

The index i in Eq. (10) is meant to denote the totality of particle labels, and we assume N to be the number of all the particles (Brownian ones plus host medium) within some experimentally relevant piece of volume. Further, definition (10) ignores degrees of freedom other than translatory ones and, hence, the integration is thought to cover a $6N$ -dimensional phase space. The time-dependence in $S(t)$ is not primarily supposed to characterize fluctuations in small systems: it rather applies to macroscopic ensembles that have not yet arrived at their thermodynamic equilibrium. Then, Ref. [10] exemplifies that a system's entropy in an off-equilibrium situation does not always grow monotonically, thus may exhibit temporary minima, and so we may ask whether our suggested violation of the second law is nothing but a momentaneous entropy loss that later on gets compensated.

However, we urge the reader to recognize the time-dependence in a diffusion experiment (see below) to be notoriously slow and, on top of that, we observe the outcome of a macroscopic thermal situation that largely is spatially averaged. In simple terms, the deviations from thermodynamic equilibrium are minute, and so they definitely cannot account for too

prominent time variations. Thus, a drop in the overall system's entropy surely cannot be attributed to a temporary event due to some kind of fluctuations. The concluding section below addresses entropy accounting in our specific experimental setup in terms of equilibrium thermodynamics. Admittedly, our proposed dissipation of kinetic energy within the trap implies that the Brownian particles leave the equilibrium with the liquid (although the experimental deviation is really a minor fraction of the equilibrium energy). But this is definitely not a fluctuation in the spirit of theorem (8), and in all probability it is not a temporary entropy minimum (in $S(t)$ above) on the way to a maximum that will persist. We cannot continuously take advantage of an entropy minimum appearing significantly out of an equilibrium situation. The experiment below in fact has the power to decide where the additional thermal energy in the particle trap originates from, namely from the surrounding liquid where the trap is located. Hence, at given particle density distribution the measurable temperature gradient lowers the total entropy content in the overall (closed) system, but this is just a scarcely admitted marginal deviation from equilibrium. Similarly, the second law in the version where it prohibits a perpetually operating machine is only marginally supported by statistical thermodynamics.

Clearly, the dissipation process comes to an end after some time, but this happens essentially because the filled trap cannot accept further particles anymore. Then, expectedly, the experiment exhibits a subsequent thermal compensation flow that equilibrates the achieved temperature gradient (and thus produces entropy). Therefore, this entropy contribution is just a feature of our present single-step experiment, and the costs to empty the trap in a continuous manner will be discussed later on in the experimental section. Very importantly, even during the crucial phase of the experiment where the particle trap accumulates heat at the cost of the surroundings, we deal with a diffusion-like process attended with a quasi-equilibrium.

We already stated some of the arising difficulties on the way to dynamical modeling of the measured temperature differences. Actually we lack both a microscopically sound description of the interaction events between Brownian particles and the trap, and also their summary effect in terms of temperature and entropy. We are aware of recent theoretical developments that trace back a macroscopic system's entropy to the behavior of its individual particles along their trajectories [11], which also extends to numerical examples [12]. These issues are intimately interwoven with the fluctuation-dissipation theorem (8) and its alternate versions,

consult also the pertinent references quoted in [11, 12]. Apparently the statistical limit for many-particle systems correctly yields the ensemble entropy $S(t)$ above, and so it seems to be adequate to define a trajectory-dependent entropy $s(t)$. Such a "single-particle entropy" is defined in quite an intuitive way as $s(t) = -k \ln p(\mathbf{x}(t), t)$. Here $p(\mathbf{x}(t), t)$ means the probability (per volume unit) to find the particle, e.g., at the moment t_0 near $\mathbf{x}(t_0)$.

With regard to modeling and numerical simulation, in fact this meets our key problem. We intend to understand a Brownian particle that (above all within the trap) is in an off-equilibrium situation, although being in contact with a heat reservoir. At present we recognize a growing literature on fluctuation theorems generalized to non-equilibrium situations, as an example see Ref. [13]. Here it is crucial to distinguish the global non-equilibrium in the host medium (heat reservoir) from the one that refers to a single particle with respect to its neighbors in an ensemble, both issues matter in our experiment. The time-evolution of the above $s(t)$ (and thus also of the envisaged $S(t)$ for an experimentally relevant ensemble) should consistently incorporate entropy consumption due to our measured energy transfer from outside into the trap. However, our present knowledge about "frustrated" Brownian trajectories inside the trap is clearly insufficient in order to turn this new type of information into a conclusive numerical simulation of our measurements. From a theoretical as well as numerical viewpoint, quasi-equilibria are inherently difficult to handle, since the macroscopic phenomena or quantities we are after always represent small disturbances on top of a strongly dominating background situation.

Besides diffusion, we would like to state an everyday example of a thermodynamic quasi-equilibrium, namely the macroscopic air flow in the atmosphere. Such weather events may well reach the strength of a hurricane, but actually this is just a minor deviation from thermodynamic equilibrium. Probably nobody is that small-minded to claim an undefined or ill-defined temperature due to non-equilibrium. But it is also true that the deviation from equilibrium rapidly increases with the strength of a storm, because of the velocity square in the kinetic energy of the air flow. We think it is illustrative to compare the numerical values of such kinetic energies to the thermal ones, also in a diffusion context. The atmosphere provides excellent opportunities to study self-ordering or pattern formation phenomena. There exist also many laboratory systems within this context and, as far as we can see it, all of them deal with a quasi-equilibrium as an indispensable prerequisite.

In a supplementary remark we point to the quantum mechanical analogue to diffusion

processes that is factual and certainly exceeds a merely formal correspondence to Eqs. (6) and (7). Apart from some restrictions that we shall specify below, the time-dependent Schrödinger equation

$$i\hbar\frac{\partial\psi(\mathbf{x},t)}{\partial t} = -\frac{\hbar^2}{2m}\Delta\psi(\mathbf{x},t) \quad (11)$$

may be recognized to be well within the scope of this matter. The right-hand side in (11) presents the free particle Hamiltonian that acts on the particle's wave function $\psi(\mathbf{x},t)$. Definitely $\psi(\mathbf{x},t)$ is not yet a density in the spirit of its modulus square, and there is also a complex prefactor in Eq. (11). Nevertheless, a decaying quantum mechanical wave packet has much in common with a diffusion process. In the end we experience the spreading of a particle density or, in the single particle case, of a probability density. It is essential that a considered particle is free: if we admit a Hamiltonian supplemented with a potential $V(\mathbf{x})$ that captures, say, an atomic electron within some local environment, the diffusion analogy breaks down and then we face entirely different quantum phenomena.

Actually there are various interesting links between Schrödinger wave mechanics, classical Newtonian dynamics, and also statistical thermodynamics, for a recent review see [14], and so in our view it should be possible to transfer some of the here presented issues into a quantum mechanical context. In many respects this also relates to the so-called quantum Brownian motion [15]. These viewpoints, however, are not really the subject matter of the present article, but we would like to address such questions on a more speculative basis.

III. EXPERIMENT

A. Intention and setup

The purpose of our performed experiment is twofold. First, we would like to confirm our claims and to prove the feasibility of our suggestion that a device based on the described physical effects really is able to operate. Secondly, modeling and simulation of the used type of trap for the Brownian particles (see below) in our view is close to impossible without introduction of free parameters. An experiment closes this gap and may guide us to firm conclusions.

Figure 2 presents the entire setup. We use a Petri dish of 10 cm diameter that is filled with 30 cm³ water. Within some reasonable limits such numerical values are not that critical

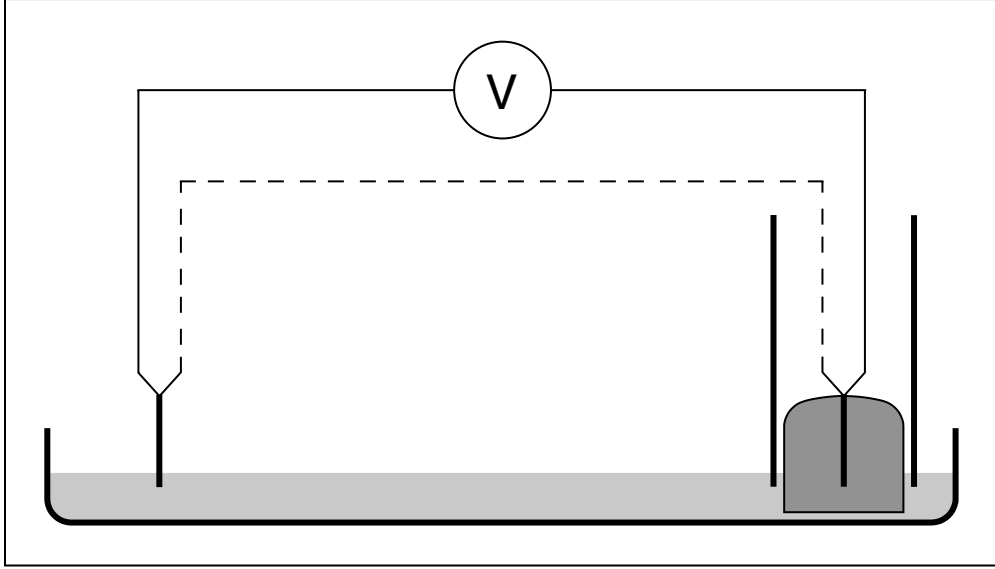


FIG. 2: Experimental setup located in a Petri dish. To the right there is our particle trap that merely features a plug of glass wool inside a glass tube. Further, we point to the two sensors of the thermocouple, where the one outside the trap serves as a reference to the expected temperature increase due to dissipated kinetic energy of the Brownian particles. The full and dashed wires connected to the sensors refer to either alloy of the thermocouple.

in the sense that they essentially affect the quantitative details of our plotted results. To the right we place a glass tube of 1.5 cm inside diameter, and therein we put a plug of glass wool as it frequently gets used for filtering purposes in chemistry. The plug of glass fibers serves as a particle trap, and so it certainly is one of our most important ingredients. Further, there are the two sensor electrodes of a chromel-alumel thermocouple that measure possibly occurring tiny temperature differences. These electrodes have a length of 1 cm each and are soldered to the contact points between the two different alloys of the thermocouple. The output voltage (due to the Seebeck effect) amounts to approximately $40 \mu\text{V/K}$ with quite a linear characteristic.

At some moment, roughly at the foremost point of the Petri dish as it is drawn in Fig. 2 (closest to the observer, i.e., at equal distance to the two sensors of the thermocouple), we supply a few tenths of a gram potassium permanganate crystallites. Once these tiny KMnO_4 crystals are dissolved in the host medium, they exhibit quite a strong color close to the one of raspberries, a circumstance that will prove extremely helpful (see below). The exact amount of supplied crystallites actually is of minor importance, since we are always

in a range where some surplus KMnO_4 is left over in solid form after the experimentally elapsed period of time. Then, the hydrated ions of the dissolved potassium permanganate are our Brownian particles.

Since these particles represent two sorts of ions that, besides their opposite charge, are unequally sized, we actually deal with a modified version of "true" Brownian motion based on, e.g., colloidal neutral objects with (preferably) a δ -shaped size and mass distribution. However, this circumstance will not affect the forthcoming considerations. The hydrated ions are also subject to equipartition and, on a large range of length scales, they diffuse in a very similar manner compared to neutral particles. Figure 1 illustrates how they by accident may end up in the particle trap. As indicated further above, the idea of the experiment is to measure the accumulation of thermal energy inside the trap, since therein we expect the Brownian particles to dissipate a small part of their kinetic energy.

The color of the KMnO_4 solution should be seen as an essential part of the experiment. It admits an observation of the two different time scales within and outside the trap, respectively. Inside we experience a propagation velocity in the order of 1 cm per hour, while elsewhere it rather amounts to 1 cm per second. These velocities refer to the outermost particle front that can be observed, and not to an average distance $\langle \mathbf{x}(t)^2 \rangle_x^{1/2}$ in the bearing of Eqs. (2) and (4). Probably most other imaginable particle types color too faintly in order to enable us to track how they creep into the glass wool. Since potassium permanganate quite strongly tends to oxidize combustible objects (and then the MnO_4 ions reduce to manganese dioxide), we should pay attention that only sufficiently inert materials (e.g., for the temperature sensors) get in touch with the liquid. For example, a particle trap made of cotton wool is inadequate.

Further, the particle size deserves some special comments. The theory section above explains that all the particles, regardless of their size, have an average kinetic energy of $(3/2)kT$. We might consider Indian ink with its size spectrum of the carbon particles between diameters of some $0.1 \mu\text{m}$ (microns) up to more than $100 \mu\text{m}$. In principle this works just as well, but since these particles are that big we cannot get sufficiently many of them into a given volume of water. This then limits the attainable energy density within the particle trap. On top of that, the Brownian motion becomes inconveniently slow. There is a wealth of other ink types that split up into greatly different raw materials, but generally their particles are also too large. Then, there are micelles with a typical diameter range of,

say, 10 nm (such as the ones in soapy water) up to 100 nm, and so again this is somewhat too much. We may try other ionic crystals but, apart from size effects, their thermal properties upon dissociation and dilution in a solvent vary dramatically. Finally, our choice of potassium permanganate proves alright, although there may be many other possibilities we have not yet investigated. The (hydrated) ionic particles are significantly larger than the water molecules of the host medium, which is a prerequisite to our simple type of particle trap. On the other hand, they are not too large, in order to gather them in an adequately high density. Thus we are left with a compromise that may well be further optimized.

From a technical viewpoint, shape, size, and density of the hand-made plug of glass wool is the most critical matter in the experiment. Concerning reproducibility, it must be clear that we cannot repeatedly manufacture such a plug with the very same properties. For example, if the glass wool is too tightly stuffed into the glass tube, the Brownian particles are too strongly hindered from entering the trap. (The water, however, immediately is there due to capillarity.) If the process of particle accumulation works too slowly, there is enough time to cool down and hence to destroy a measurable effect.

In fact it is the major problem in our experiment that the outcome quite sensitively depends on the details of the plug. This arises from the circumstance that we deal with several simultaneously occurring heating and cooling effects. There is the endothermic solution enthalpy (that comprises the exothermic hydration heat), the exothermic enthalpy of dilution as the particles move on, the thermal energy due to our expected effect inside the trap, and also thermal equilibration as time goes by. Note that many textbooks on physical chemistry incorporate the term "enthalpy of dilution" into a somewhat more general concept, namely enthalpy of mixing. The asymmetry due to the plug of glass wool in Fig. 2 provides an opportunity for all the occurring thermal effects to become manifest in the measured time-dependent temperature difference. At first glance, the experiment looks quite simple, but then we face a nontrivial balance between several thermal energies that strongly depends on various geometrical conditions, particularly the ones inside the trap.

Conversely, to perform the experiment is really cheap, and so we may repeat it many times. Reproducibility then refers just to the qualitative shape of the measured curves (see below). The details, however, depend on the particular properties of the plug used at a time. Although this circumstance poses an experimental difficulty it still can be handled, thus in our view it cannot depreciate or disqualify our statements concerning the second law

of thermodynamics. An obvious advantage of the glass wool is the possibility to immediately modify certain properties such as its density. In a future stage of the experiment, however, we think the plug of glass wool probably gets replaced by some well-defined type of micro- or nanostructures, and so the above mentioned problems hopefully will drop.

B. Measurements

At this point, we would like to present our results that are summarized in Fig. 3. All the curves are recorded in a way that the first 30 min show the stability before supply of the KMnO_4 crystallites at $t = 0$. We always plot the measured thermoelectric voltage U between the two sensors of the thermocouple versus time. The sign has been chosen such that an increase in this electric potential difference means the particle trap gets warmer with respect to the reference sensor.

Then, the conversion into a temperature difference is given by the further above stated value of $40 \mu\text{V}/\text{K}$ due to the type of thermocouple, or $1 \mu\text{V}$ on the ordinate axis means 0.025 K . Thus, our observed effects are in the order of 0.1 K that already poses certain stability problems with regard to temperature drifts as well as voltage measurement reliability. However, the difference measurement cancels some of these difficulties. The recorded points are spaced by mesh-intervals of 5 min and the resolution is $1 \mu\text{V}$, and so the points cover a range of $\pm 0.5 \mu\text{V}$ around their plotted values.

We might significantly improve the quality of the data by means of a much higher sampling rate. A subsequent convolution with an (e.g., Gaussian) window function of adequate width then would act as a low-pass filter, as we performed it for rather noisy input signals [16]. There we also performed a more advanced filtering procedure based on a nearest neighbors search. This time, however, we were not equipped on the same level of data acquisition. The fluctuations are recognized to be largely within $\pm 1 \mu\text{V}$ around the expectation values, which actually does not conflict with the size of the discussed structures. Once we have experienced the approximate width of the relevant features in the measured signal, we may also consider to cut off the low-frequency noise. In Fig. 3, however, we prefer to show the plain measurements, and we renounce a numerical procedure in order to prettify the plotted curves.

We also should be aware of a "pitfall" that arises from the difference measurement.

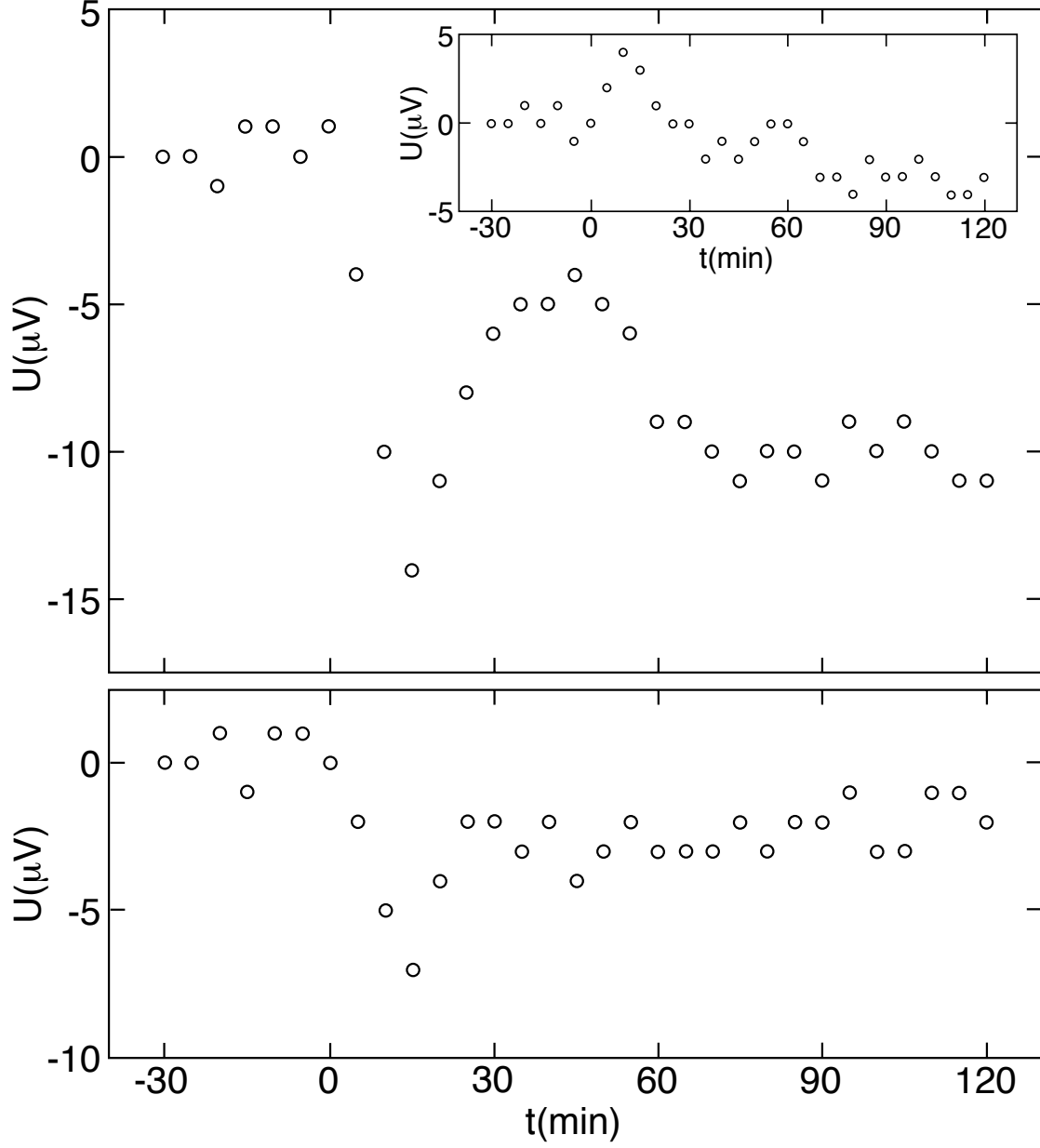


FIG. 3: Top: Temperature difference between the two sensors as a function of time, see text. The recorded thermovoltage amounts to some $40 \mu\text{V}/\text{K}$ and the KMnO_4 crystallites have been supplied at $t = 0$ on the abscissa. Besides the initial trough (mainly due to dilution heat) we observe quite a pronounced structure that quantifies the dissipated translatory energy of the Brownian particles. Bottom: Reference plot based on a slightly modified particle trap that avoids appearance of the effect. The inset offers another type of comparison where one of the sensors is kept at constant external reference temperature.

In plain terms, we cannot distinguish whether a sensor gets heated or the other one cools down. On the other hand, this works much more precisely than two independent temperature measurements, since the small temperature effect within the particle trap happens relatively to the environment elsewhere in the Petri dish. The upper panel in Fig. 3 exhibits the effect we are after, as we shall explain below in this section. The bottom curve is recorded under the same conditions, except that the particle trap is slightly modified in a way that the effect does not appear. Therefore, the bottom panel serves as a reference to the top one. Additionally, the inset in Fig. 3 presents a temperature measurement inside the trap relative to a constant external reference temperature.

In the upper panel we recognize quite a conspicuous trough around $t = 15$ min that mainly emerges from warming up the reference sensor electrode. Initially dilution heat seems to dominate other contributions, because many of the dissolved particles rapidly (within a few seconds) proceed to the reference sensor. To a smaller extent (and somewhat delayed) this affects also the other sensor hidden in the trap. Then, the structure at larger times contains our predicted effect among other heating and cooling contributions (see above). However, the strongly significant drop between some 50 through 70 min on the abscissa can certainly not be interpreted as a process that warms up the reference sensor. We suggest that this decrease quantifies the expected effect. Based on a fairly cautious interpretation of the measurement statistics we observe a thermovoltage difference around $\Delta U = 4.5 \mu\text{V}$. The accumulated thermal energy gradually decays by cooling down to the temperature of the liquid right underneath the particle trap. Note in Fig. 3 that all of our temperature variations really are minor, and so interactions with the environment (such as radiative heat loss or uptake) are insignificant contributions.

We cannot expect this type of recording (e.g., the plot in the upper panel) at the end to level off at the same value as in the beginning, since thermal conduction in water across the Petri dish happens rather slowly. Equilibration over larger distances is clearly beyond the plotted period of time. Solutions $T(\mathbf{x}, t)$ of the thermal conduction equation for simplified model geometries confirm that this is really so. On a significantly longer time scale (a few hours beyond the plotted data) there is equilibration, and expectedly we measure a curve that gradually approaches its initial level.

In addition, we observe the important fact that the time scale of the achieved effect, i.e., of the structure centered at $t \approx 45$ min, agrees well with the clearly visible penetration of

the Brownian particles into the trap. In view of the strongly retarded diffusion mechanism inside the trap it appears almost evident that such measurements quite sensitively depend on the geometrical details of the plug.

The bottom panel displays the very same type of measurement, except that the plug of glass wool is some 0.3 cm longer. In the top curve the lower end of the sensor coincides with the low end of the glass tube, and so the bottom situation refers to a sensor that is 0.3 cm higher up. Our suggested mechanism of heat accumulation due to frustrated Brownian motion does not even stand such a small alteration, since then it takes too much time for the particles to produce a measurable effect. Meanwhile cooling down has compensated the heat accumulation, and so the outcome shows no time-dependence beyond the initial trough. The relevant heating effect (that is absent now in the bottom plot) proves reproducible, but actually it appears only in a rather small volume of the parameter space that describes the totality of possible traps. Apart from length and density of the plug, we are unable to name all the parameters that matter, and different plugs with almost equal visible appearance may well cause remarkably different results.

By virtue of the strong color, also for some modified plugs in the spirit of the bottom example we aim at an observation of the progress in propagation as the particles creep into the trap. As far as possible, however, everything else (besides the plug length) is kept equal in the two presented panels. In sum, we conclude that our suggested process of heat transfer from outside into the trap works only marginally, thus raising some difficulties to specify the the relevant geometrical criteria.

Moreover, if we compare the two panels we note that the strength of the minimum at $t \approx 15$ min also quite sensitively depends on geometrical details. We think the trough in the bottom curve is somewhat meager, but we have chosen this plot because of its excellent long-term stability of the voltage measurement conditions, which is not always the case. Apart from the mentioned geometry aspects, we should also keep in mind that our plots in Fig. 3 represent (among other contributions) small differences between energy quantities of large magnitude. The ionic solution involves two very strong thermal effects, namely dissociation and hydration that together amount to quite a moderate solution heat.

Another purpose of the bottom panel is to guarantee that the relevant structure in the upper curve is not induced by, e.g., heat production due to oxidation of some contamination in the glass wool. Otherwise, the bottom curve would exhibit this feature as well. Similarly,

we can rule out the possibility that our observed thermal effect is caused by adsorption of Brownian particles at the glass fibers. In the upper panel, one might also consider a possible retarded heat flow out of the particle trap (that is now assumed to undergo insignificant heating effects) into the cooler surrounding liquid. But, again, the bottom panel does not support or admit this version to explain the upper measurement.

Furthermore, we think such plots as the bottom one strongly confirm our imagination that the relevant thermal feature in the upper panel really constitutes an entropy sink, and not just an entropy transfer within the Petri dish (or even into the environment). The thermal compensation flow at 50 through 70 min produces entropy and restores the "standard" situation, namely the one that throughout the recorded period of time has never been left in the bottom panel. Altogether, in our view it is justified to interpret the drop of some $4.5 \mu\text{V}$ in the upper curve to be a measure for our expected effect of dissipated kinetic particle energy.

As we have indicated above, the inset in Fig. 3 presents an "absolute" temperature measurement inside the particle trap. The reference sensor is now placed in a second Petri dish filled with water kept at constant (room) temperature throughout the measurement. Just as in the other two curves, initially dilution enthalpy predominates. But now this concerns only the sensor inside the trap, and so this causes a noticeable peak. This heating process, however, cannot last too long: the liquid underneath the trap is also subject to some retarded cooling due to consumption of solution heat (see above), which gradually becomes more important along the time axis. The subsequent feature (towards $t = 60$ min) again displays the effect under consideration. We definitely do not pretend the small increase of temperature there to be significant. However, our predicted mechanism of heat accumulation is an effect relative to the liquid in the Petri dish where the trap is located, and not primarily one with respect to an external reference. In short terms, the inset in Fig. 3 disregards all the temperature effects in the immediate neighborhood of the particle trap.

C. Quantitative and practical implications

Now we are ready to quantify how much the observed thermovoltage effect of roughly $4.5 \mu\text{V}$ means in terms of energy density. First, we calculate the number of molecules in 1 g water, namely 3.34×10^{22} of them. Suppose now, one out of 1000 water molecules

gets replaced by a Brownian particle that undergoes a "full stop" in the trap. This yields 3.34×10^{19} particles per gram that contribute a dissipated kinetic energy of $(3/2)kT$ each. At room temperature we end up with an appreciable energy density of 0.20 J/g. Since 4.186 J/g correspond to a temperature increase of 1 K in water, our 0.20 J/g are able to warm up the water by 0.048 K, which amounts to some $U = 1.9 \mu\text{V}$ based on our type of thermocouple. However, we measured more than twice as much, i.e., more than two Brownian particles within a 10 by 10 by 10 cube of water molecules have completely lost their translatory kinetic energy they previously possessed in a time average. Clearly, this example serves just as an illustration for the size of our measured effect, in fact there will be many particles that dissipate only a small fraction of their kinetic energy. Based on our careful above assumption "two out of 1000" we arrive at an energy density of 0.4 J/g if water is our host medium for the particles. However, diffusion-like processes always are inconveniently slow, see abscissae in Fig. 3. In terms of power, these 0.4 J/g are produced approximately within an hour. This is by far not sufficient to drive a car, but we think, e.g., of applications like hydrogen extraction from sea water in a huge power plant.

Up to now, we suppressed the inevitable step where we have to empty the trap and reinject the Brownian particles. This way, in a time average they again adopt a translatory energy of $(3/2)kT$ each, and again some percentage of the altogether present particles enter the trap and deposit part of their energy there, and so on. We shall not underestimate this type of engineering task, but we think in all probability this should be possible. A suitably shaped and dimensioned siphon tube might even be adequate, but in our present version of the experiment the water (plus particles) flow therein would be inadmissibly small. In this particular setup we also must organize a way to compensate for the loss of plain water in the trap, in order to keep upright the particle density gradient. Once this situation is established, the trap causes an oppositely directed temperature gradient that, within certain limits, does not keep off the particles. No matter how we get there, this "feedback mechanism" for the Brownian particles ideally may happen in a slow and reversible process, and so, in principle, there will be no extra supply of energy due.

One might be tempted to object that filling the trap happens spontaneously, thus augments the overall system's entropy, and so it requires external intervention to empty the trap in a continuous or cyclic manner. However, in the theory section we already substantiated that heat transfer into the trap is just a marginally permitted tiny deviation from thermo-

dynamic equilibrium. This resembles the diffusion process itself, since the particle density gradient actually drives the dynamics of dilution, although this just insignificantly affects the equipartition value of $(3/2)kT$. Thus we deal with two spontaneously running processes, namely (i) the one that irreversibly tends to even out the particle density gradients, and (ii) the creation of a temperature gradient that lowers the overall entropy. The limit of infinitely slow removal and reinjection of particles raises no energy costs at all, since then there is no density gradient equilibration anymore. In any case, a tiny fraction of $(3/2)kT$ per particle suffices to overcome a density gradient. Thus we may organize things in a way that the summary effect of (i) and (ii) above decreases the entropy.

The continuous equilibration of the achieved temperature difference goes along with reinjection of the Brownian particles, since this carries slightly more kinetic energy into the trap compared to what the captured particles keep in their nearby equilibrium state. No matter whether the thermal compensation flow happens in an irreversible conduction process (e.g., as in our presented single-step experiment) or whether we run a partly reversible thermal engine, the overall amount of entropy within the closed system will stay constant. Just the rate of particle feedback and the thermal energy flow in such a steady state will depend on many parameters, above all geometrical ones.

We also suppressed the actual physical mechanism under consideration, namely how the Brownian motion gets modified such that the particles dissipate part of their translatory energy. To consider Brownian particles confined within some limited cavity is not really new, we point to [17–19], but these authors largely focused on other aspects of this matter. The strongly different time scales within and outside the particle trap (see above) clearly indicate that the trap greatly influences a particle trajectory $\mathbf{x}(t)$. The geometrical constraints reduce the probability for a particle to enter the trap and to move on therein. At given particle density this corresponds to a lower entropy, compared to the same volume of liquid outside the trap. In a sense, this acts as a repelling hurdle, and sometimes this is said to be an entropic barrier the particles have to surmount [20].

The trap involves also a so-called depletion force [21], for a more recent approach consult Ref. [22]. This force again relates to entropy, since it emerges from a geometrical exclusion of host molecules (water) at certain locations. Depletion effects generally are discussed in a context of particles larger than our hydrated ions, but such phenomena definitely should be seen as part of the overall interaction with the trap. However, the dissipation process

inside the plug of glass wool remains to be an intuitive picture, since we cannot trace a single particle's path in its geometrical details. The trap seems to handicap the particles to an extent where they must slightly depart from the thermodynamic (quasi-) equilibrium with the host medium, but they hardly may aggregate to stable clusters.

A microscopically sound description of the interaction between a single particle (a hydrated ion) and the trap surely is beyond our present possibilities, since this then should be a precise *ab initio* calculation without parameters that optionally may account for the suggested effect. In the theory section we already addressed the problem, and the circumstance that our Brownian particles are hydrated ions renders the intended calculation particularly elaborate. Thus we cannot present a trustworthy result in a context similar to Fig. 1 for the frustrated Brownian motion inside the trap. This also prevents us from an approach in the spirit of [11], recall our pertinent discussion in the theory section. We would like to simulate the particle motion in small cavities of variable shape as well as in the trap as a whole, but it appears obvious that this cannot be carried out readily. Besides the observable (and partly known) changes in the diffusion properties, we also expect further important quantities to be modified. Such characteristic quantities ultimately relate to the particle dynamics, we think, e.g., of scaling properties and velocity distribution spectra. Some of these peculiarities certainly are crucial to type and relative incidence of interactions with the internal surfaces of the trap.

Conversely, on a merely qualitative basis it appears reasonable to assume inelastic contributions in such interactions. At least we expect these dissipative processes to happen among other, truly elastic scattering or reflection events. Altogether, we are positively convinced that our imagination of dissipated kinetic particle energy stands a closer inspection based on various analytical methods, theoretical as well as experimental ones, where the theoretical ones may well be large-scale enterprises. Most importantly, the temperature effect attended with the energy accumulation has been measured.

IV. CONCLUSIONS AND OUTLOOK

First, we would like to keep our above promise to discuss our specific experimental arrangement in a context of accounting and possible time-dependent displacements of entropy. In a closed system the entropy stays constant as long as only reversible processes (such as

the operation of a Carnot engine) are going on therein. Our mechanism of spontaneous heat transfer from outside to inside the particle trap, i.e., from cold to warm, may easiest be regarded as a time reversed movie of an irreversible process. Thus, it clearly represents a local decrease of entropy (although in terms of energy percentage this is just a marginal effect on top of a thermodynamic equilibrium situation). This, just by itself, is not unusual, e.g., isothermal compression as it may be part of a Carnot working cycle is an archetypal "specimen" of such processes. Whenever we force a system to adopt a state with lower probability, the important relation $S = S_0 + k \ln P$ tells us that we have lowered the system's entropy S . However, apart from small fluctuations around a mean value of S , such processes always are attended with an entropy increase elsewhere in the environment. But in our investigated process of warming up the particle trap this is definitely not the case, since we deal with an entirely internal affair that does not involve the environment. Apparently the Brownian particles manage to "tap" the energy content of the liquid outside the trap. Later on, when heat accumulation necessarily gets terminated in our single-step experiment, we observe a thermal compensation flow that reverses the previous energy transfer, see upper panel in Fig. 3.

In our view, this decrease in temperature of the (filled) particle trap is a conclusive argument for our suggested mechanism, and we do not see an alternate way to explain the experimental facts on plausible grounds. Therefore, we conceived the strong impression that this experiment indeed contradicts the second law of thermodynamics. Further, the system as Fig. 2 represents it should be considered as a closed one, i.e., there is no exchange of heat or of matter with the environment. We think this is quite well realized in our simple experiment: at our minute temperature changes there is little heat loss or uptake by virtue of radiative, conductive, or convective effects.

Once we have accepted the possibility of spontaneous heat accumulation at the cost of another (cooler) place inside a (still closed) considered system, we think of applications that are strictly prohibited within traditional thermodynamics. But, admittedly, our presented mechanism evolves rather slowly. Primarily we would like to "borrow" some accumulated energy from the total energy content of the system. We simply may "use it up" by means of all sorts of reversible and irreversible processes, since the achieved temperature difference permits us to run thermal engines. Finally, when all the borrowed energy, e.g., mechanical one, is dissipated again and exists now only in thermal form, we provide a feedback to the

place where we got it from. This way the initial state gets restored, and we are ready to enter the next cycle of energy acquisition and dissipation. In principle, i.e., in an unrealistically strict implementation, this type of energy economy is just self-sufficient.

A closed laboratory system, particularly a small one, may be advantageous to investigate the aspects of principle in a well-controlled manner. However, there is a considerable shortcoming that, in turn, is even beneficial to large-scale experiments (i.e., sufficiently large that the system may be regarded as an open one). Some of our energy demands are such that we cannot immediately dissipate and "recycle" them. An obvious example is to build a house. The bricks in the upper floors keep their potential energy almost forever, and so there is always an amount of energy that subtracts from the overall thermal situation. Within chemistry and particularly in biochemistry we certainly find more striking examples. In all probability man's evolution is not able to level off at a steady state, and so these considerations in fact matter. At present, however, to store energy in any manifestation other than thermal one may greatly help to unburden the earth climate.

Our setup sketched in Fig. 2 is completely left-right symmetric, except for the presence of the particle trap. Thus, without the trap all the temperature effects would just cancel. Apart from the inset, everything we observe in Fig. 3 is uniquely due to the particle trap. Now we attempt to settle the crucial question, namely: why does our specific experimental arrangement contradict the second law of thermodynamics while other observations apparently do not? We think the answer lies in a peculiarity of the Brownian motion that generally has been investigated in a somewhat one-sided manner. The driving force that ultimately lends the translatory energy to the Brownian particles (we do not consider internal energy contributions) and that finally moves them into the particle trap arises from "accidentally" occurring deviations from the time-averaged situation in the host medium. It is essential to recognize that the Brownian fluctuations inherently constitute also a systematic dislocation according to Eq. (4) in the theory section. This mechanism results in the macroscopically observable phenomenon of diffusion and, provided a density gradient, it continuously accumulates particles in the trap. Such a particle transfer into the trap operates at extremely low energy costs, since a particle's kinetic energy just marginally depends on the density of surrounding other Brownian particles. Thus, in our view, it appears feasible to organize compensation for these costs by means of the dissipated fraction of the initial kinetic particle energy.

By virtue of the equipartition value $(3/2)kT$, the amount of a particle's translatory energy of motion is equally important, but this is not primarily what we are after. Our experimental arrangement purposely detects an effect that is driven by statistically occurring off-equilibrium situations: we aim at Brownian particles inside the trap, although they have started (and have picked up a tiny share of their kinetic energy) elsewhere. The trap then must be able to distinguish between the different size of particles and thus provide an obstacle to the Brownian motion, but this is merely a geometrical affair. On an empirical basis, Fig. 3 exemplifies that a setup with the ingredients of Fig. 2 indeed has the power to serve as a touchstone for the rarely occurring possible second law violations.

Further, it may be noteworthy that our particle trap is not at all meant to be a so-called Maxwell's demon, since a momentaneous thermal fluctuation that kicks a Brownian particle into some direction happens by itself. Likewise, the dissipation of kinetic energy inside the trap occurs spontaneously as well. Actually it is the purpose of our approach to get by without an external agent that separates the fast particles of an ensemble from the slow ones. We already substantiated that our system is a closed one (i.e., there is some insignificantly small heat exchange with the environment), and therefore such a demon anyway would be part of the system under consideration. We measure a resulting effect that originates from the above discussed thermally induced short-term variations or asymmetries appearing in a particle's local environment. After all, they cause an ongoing supply of further (equally fast) particles to the trap.

The crucial prerequisite to accomplish a temperature difference is a spontaneous mechanism that transfers some particles other than the ones from the host medium from outside into the trap, and the Brownian motion gets that done. Once a particle is in, the trap must be able to cause a slight departure from equilibrium with the host medium, in order to receive a small fraction of the kinetic particle energy in thermal form. In a sense, the result of these two issues constitutes the "opposite" of an irreversible process such as the thermal energy flow that equilibrates different temperatures. Our approach ultimately acts as a "filter" that selects and stores momentaneous deviations from a thermodynamic equilibrium, although this appears to be only a marginally admitted effect among the overall phenomenology attended with Brownian dynamics. That is why we think the finally achieved spontaneous creation of a temperature gradient is not really that far from what we may expect to happen on well-established thermodynamical grounds. All in all, apart from

fundamental and theoretical aspects involved in this subject matter, we think the present contribution offers an entirely new look at our future possibilities to make use of energy resources.

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