Experimental exploration of the Arrow of Time

(and the emergence of the Second Law of Thermodynamics)

G.C. Spalding, Illinois Wesleyan University *1 November 2017*

A Brownian particle in a parabolic potential well should be considered a *canonical* example for teaching statistical physics, directly following the case of a flat-bottomed potential well (free diffusion). A microparticle in an optical trap behaves much like a classical mass on a spring, characterized by a spring stiffness, k, and so is described in terms of a parabolic potential.

In the case of a 2002 experiment by Genmiao M. Wang *et al.*, the trap stiffness $k \sim 0.1\text{pN}/\mu\text{m}$, meaning that the optical trap was quite <u>*weak*</u> so that the position of the microparticle within the trap was not very strictly constrained. Still, once the trap stiffness is known, one can use Hooke's law to calculate, from any observed **position** of the microparticle, the optical restoring force associated with the trap, $\boldsymbol{F}_{\text{opt}}$.

In this experiment the trapped particle resided within a closed sample cell filled with water, which acted as a large ***thermal reservoir*** at room temperature. The microparticle was small enough that thermal agitation of its position was easily detectable using standard microscopy methods for particle tracking. Over a span of two seconds, an ensemble of the particle's thermally agitated positions was recorded and then averaged to yield the equilibrium position, $\boldsymbol{x}_0$, of this Brownian particle within the optical potential well.

In the case of a flat-bottomed potential well, Brownian motion is ballistic on ultra-short time scales, but these time scales were simply ***too short to be observable*** in the work of Wang *et al.*, crossing over after a time determined by the rate of energy dissipation, $t_f = 1/(2\gamma) = m/6\pi\eta a$, to the familiar linear growth of the mean squared displacement: $\langle x^2 \rangle = 2Dt$, where D is the diffusivity of the bead, $D = k_{\text{B}}T/6\pi\eta a$, and the numerical prefactor is set by the dimensionality.

For a parabolic potential there is no range of travel over which the particle will not feel a restoring force. Nevertheless, because of observed phenomenology (specifically the power spectrum describing displacements from the equilibrium position), practitioners colloquially say that it is as if the particle takes time to "feel the walls," and that over short (but observable) time scales, there seems to be *free* diffusion within the trap. Of course such colloquial phrasing leaves something out, but it is appropriate to identify a crossover from this "short time" limit, set by the rate of energy dissipation as a fraction of the natural frequency, $\omega_0 = \sqrt{k/m}$, and characterized by $\tau_0 = 6\pi\eta a/k$. A formal derivation of the power spectrum including, at all times, the Hooke's law restoring force that is provided by the laser, yields a standard Lorentzian with a corner frequency set by $1/\tau_0$ and, equivalently, an autocorrelation function given by:

$$\langle x(t)x(t+\tau)\rangle = \frac{k_{\text{B}}T}{6\pi\eta a\tau_0} e^{-\tau/\tau_0}.$$

In the next step of the experiment of Wang *et al.* the piezoelectric stage upon which the sample cell is mounted begins moving at constant velocity $v_{\text{opt}} = -1.25\ \mu$m/s, so it would take approximately 5 seconds to traverse the 6.3-micron diameter of the trapped microparticle, were it to remain at a fixed position. In fact, the motion of the closed sample cell imposes a hydrodynamic drag. Because the ballistic limit is restricted to what Einstein described as *experimentally inaccessible* time scales, the time-average particle position will be located where the drag force is balanced by $\mathbf{F}_{\text{opt}}$. That is, the experiment <u>*done by Wang*</u> could only observe the particle once it had already reached terminal velocity, as hydrodynamics sweeps it to a new equilibrium position in the "downstream" direction relative to $\boldsymbol{x}_0$ (*i.e.*, this is the **most probable** direction of motion). Nevertheless, over short times, of course, Brownian dynamics ensures that the particle trajectories will contain *some* upstream excursions, which constitute a **calculable** fraction in any histogram of particle trajectory steps. Again, the characteristic time associated with the trap is $\tau_0 = 6\pi\eta a/k \approx 0.5$ sec for the parameters given. The aim of the experiment is to test whether or not the theoretical framework for calculating this fraction (published as a "Fluctuation Theorem" by Debra Searles and Denis Evans) is consistent with experimental observations.

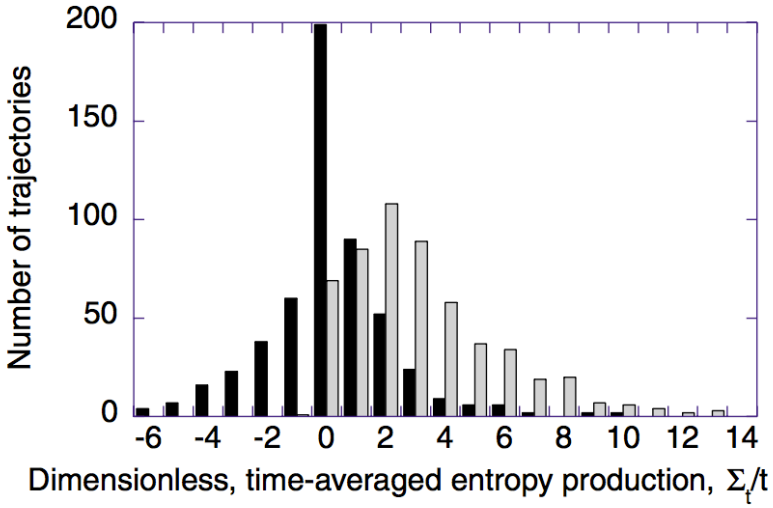
What Searles and Evans did was to construct a measure of any changes in *entropy*, which in this case can be associated with the trapped microparticle, which acts as a small sub-system connected to the larger thermal reservoir of the surrounding fluid. Because entropy is usually denoted by the letter *S*, Searles and Evans use the capital greek letter sigma to denote a related quantity, which they argue constitutes a (dimensionless) measure of **entropy production**:

$$\Sigma_t = \frac{\int_0^t \boldsymbol{F_{opt}}(\boldsymbol{s}) \cdot \boldsymbol{v_{opt}} dt}{k_B T}$$

In this ratio, the *net work done against the optical forces* is compared to $k_B T$, which roughly describes the scale of the available thermal fluctuations. This is akin to the classic formula from thermodynamics for changes in entropy:

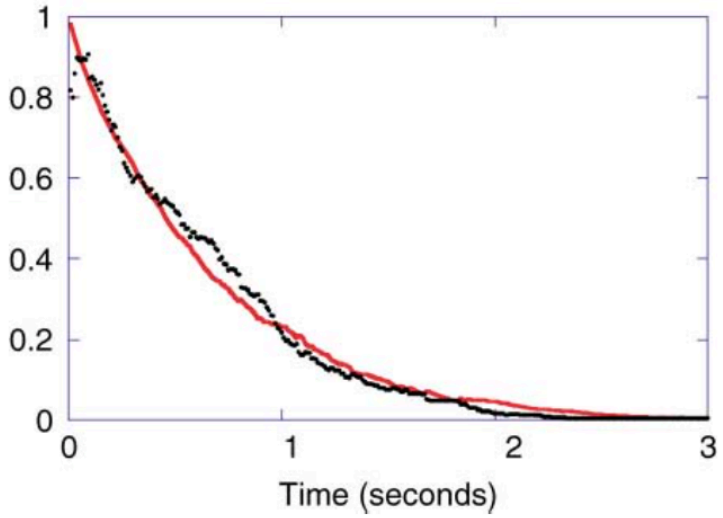
$$\Delta S = \frac{Q}{T}.$$

Because the reservoir is taken to maintain a fixed temperature, the internal energy is taken to be unchanged and so $Q = \Delta W$. Again, particle trajectories in the downstream direction are considered to be "moves toward the more probable" and so are associated with an increase in entropy, while trajectories in the opposite direction are said to be "entropy consuming."



In the experiment of Wang *et al.*, the onset of the motion of the stage is defined to be $t = 0$, and in their **Figure 1** (above), histograms of the time-averaged entropy production, Σ_t/t, corresponding to $t = 10^{-2}$ seconds ($\ll \tau_0$) and, separately, $t = 2$ seconds ($\sim 4\tau_0$) are plotted for 540 particle trajectories. At $t = 10^{-2}$ seconds, the trajectories are distributed evenly among entropy-consuming trajectories ($\Sigma_t < 0$) and entropy-producing trajectories ($\Sigma_t > 0$). At $t = 2$ seconds, the number of trajectories shifted to the positive side, with entropy-producing trajectories outnumbering entropy-consuming trajectories. In other words, time-reversal symmetry is, quite naturally, broken over long time scales. This is said to reflect the emergence of the so-called "**Arrow of Time**" or, equivalently, the Second Law of Thermodynamics, which is – and always was – a statement that systems tend to move toward the more probable *in the limit of sufficiently large samples*.

The Searles-Evans framework makes a *specific prediction* about how the Second Law emerges, which is reflected in **Figure 2** of Wang *et al.* (below), for which the number of entropy-consuming and entropy-producing trajectories is counted from $t = 0$ to 3 seconds, and the *ratio of the two* is plotted against time, as the discrete black data points shown in the plot.



In the limit of short times, the ratio approaches unity (reflecting time-reversal symmetry), but goes to zero over 2.5 seconds ($\sim 5\tau_0$) with the form of the evolution predicted by the Fluctuation Theorem (FT).

In particular, the Searles-Evans FT in "integrated form" *predicts* the relative probabilities of entropy-consuming and entropy-producing trajectories should be given by:

$$\frac{\Pr(\Sigma_t < 0)}{\Pr(\Sigma_t > 0)} = \langle \exp(-\Sigma_t) \rangle_{\Sigma_t > 0}$$

where the right-hand-side brackets are meant to indicate an average over all entropy-producing trajectories. Thus, the right-hand side of the equality is also determined experimentally, and is shown as the red line in the figure. To within experimental limits, the Searles-Evans equality is consistent with the dependences indicated by the observations. A computer simulation also reinforces the notion that the model is descriptive of this sort of experiment. Both the simulation and experimental data show the predicted exponential decrease in the number of entropy-consuming trajectories with time. So, our next step should be a discussion of the physical reasons *for* this equality.

Note that this is not (quite) a ratio of Boltzmann factors. In fact, that's the whole point!

Boltzmann's tormenter, Loschmidt, debated him, publically, over the issue of how microscopic equations of motion that exhibit *time-reversal symmetry* can lead to *irreversible* macroscopic behavior. In 2002, Evans and Searles wrote, "Unlike the Boltzmann equation, the FT is completely consistent with Loschmidt's observation that for time reversible dynamics, every dynamical phase space trajectory and its conjugate time reversed 'anti-trajectory', are both solutions of the underlying equations of motion." So, once again, the key lies in **illuminating** how time-reversal symmetry is destroyed.

Here's my take on it: ***dissipation*** of energy is always at the heart of the matter. As energy spreads out among many reservoir degrees of freedom, the chances of it taking a time-reversed path become more and more negligible. Considering the available "trajectories" for energy dispersal, it is as if I were in a maze of enormous complexity: over short times I might be able to retrace a few steps, but little chance of that persists over longer times, and so time-reversed paths become an *inaccessibly* small fraction.

If we construct an *ultra-fast* position detector, we can clearly go beyond the work of Wang, *et al*. To date, only Mark Raizen's group has been able to experimentally access the "ballistic" diffusion regime, and so this presents relatively unexplored terrain. In any case, I wish to publish, in the *American Journal of Physics*, an article that will be accessible to undergraduate physics majors, ideally with a more comprehensive (in once sense or another) set of data taken by IWU students. For the case at hand, it will take more *work* to establish a simple, intuitive relation between dissipation and the onset of irreversibility. – So it may also be useful to also discuss other kinds of situations. For the (quite distinct) case of simple wave propagation, the rate at which the

phase advances is determined by the energy, and so it is not surprising to find that phase *memory* is destroyed by inelastic scattering: that is (as with the case at hand), time-reversal symmetry is broken by energy dissipation. In another (quite distinct) context, there is considerable current interest in considering whether or not there can be a physical model of quantum wavefunction collapse. When we speak of, say, a single photon (or some other microscopic quantum-mechanical object), any detection event will, in the end, involve amplification from the microscopic to the macroscopic (classical) world of meters and observers. Such amplification is always irreversible, as with the avalanche that occurs in any Geiger-mode detector. Cal Tech physicist Sean Carroll, author of *The Big Picture*, has collaborated with the *Minute Physics* YouTube channel to produce a series of five very brief videos that serve as general-audience "micro-tutorials" on topics of relevance to our discussions. The first of these can be found at this link. There may be a number of *additional* cases where the relation between irreversibility and dissipation of energy is perhaps a bit more transparent. Your input is requested.

Evan and Searles claim that, more generally, "We now know that the Second Law of Thermodynamics can be derived assuming **ergodicity** at equilibrium, and causality. We take the assumption of causality to be axiomatic. It is causality which ultimately is responsible for breaking time reversal symmetry and which leads to the possibility of irreversible macroscopic behavior. …The Fluctuation Theorem does much more than merely prove that in large systems observed for long periods of time, the Second Law is overwhelmingly likely to be valid. The Fluctuation Theorem *quantifies* the probability of observing Second Law violations in small systems observed for a short time."

A more generalized discussion of the broader class of Fluctuation Theorems developed since the early 1990's can be found in a special "Perspective" included in this month's issue of *Nature Nanotechnology*. A related blurb about the author of that Perspective, Jeremy England, tries to suggest that this issue could, essentially, be the "**Secret of Life Itself**." Though, to me, Jeremy England's initial efforts seem to muddle cause and effect, I really do think that F.T. theorems have enormous potential for unlocking essential understanding of molecular biology, as has already been partly demonstrated by the work of Carlos Bustamante's group at Berkeley, which were the first to experimentally confirm that key, new fluctuation theorems allow for the recovery of RNA folding *free energies*, a key feat, given that biomolecular transitions of this sort occur under nonequilibrium conditions and involve significant hysteresis effects that had previously been taken to preclude any possibility of extracting such equilibrium information from experimental data. In fact, work *now being done* on fluctuation theorems (both theoretically and experimentally) is among the most significant in all of statistical physics within the past three decades. These theorems have great general importance, and include extension of the Second Law of Thermodynamics into the realm of biomolecules and nano-machines. Clearly such work opens up vast new intellectual opportunities. Yes, DNA folding and loop formation have been implicated as playing key roles in turning on and off gene expression, but the importance of these systems is central to *all* of the physical sciences. Polymer physics was highlighted for its theoretical significance when Pierre deGennes was awarded the Nobel Prize in Physics for discovering that "methods developed for studying order phenomena in simple systems can be generalized to more complex forms of matter, in particular to liquid crystals and polymers." Our attention to, say, the packing of DNA follows in this tradition: it would be a huge mistake to think of such biological work only within the context of its direct biological applications; this is a vibrant, open field of basic *physics*, where there remains a great deal of work left to do – and is of considerable technological interest (conjuring images of futuristic information storage systems having a capacity rivaling that of the human brain).

1. G.M. Wang, E. Sevick, E. Mittag, D.J. Searles, D.J. Evans, *Phys. Rev. Lett.*, **89,** 050601 (2002).

2. D.J. Evans, D.J. Searles, *Advances in Physics*, **51**, 1529 (2002).

3. Jeremy L. England, *Nature Nanotech.*, **10**, 919 (2015).