The Kawasaki identity and the Fluctuation Theorem

D. M. Carberry, S. R. Williams, G. M. Wang, E. M. Sevick, and Denis J. Evans
Research School of Chemistry, The Australian National University, Canberra ACT 0200, Australia

(Received 9 January 2004; accepted 9 August 2004)

In this paper we show that the Fluctuation Theorem of Evans and Searles [D. J. Evans, D. J. Searles, Phys. Rev. E **50**, 1645 (1994)] implies that the Kawasaki function $\langle \exp(-\Omega_t) \rangle$ is unity for all time t. We confirm this relationship using experimental data obtained using optical tweezers, and show that the Kawasaki function is a valuable diagnostic tool. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1802211]

In 1993 the first quantitative description of entropy production in finite systems was given by the Fluctuation Theorem (FT) of Evans *et al.*[1] In the decade since, a great deal of research has been carried out on various forms of the FT,[2–7] including two recent experiments.[8,9] Combined, this research demonstrates that the FT is correct and that it places thermodynamic constraints on the operation of nanomachines. In its most general form, the theorem provides an analytic expression for the probability that the dissipative flux flows in the direction opposite to that required by the second law of thermodynamics. The argument of the theorem is the dissipation function Ω_t. In the case of thermostated dissipative systems, the ensemble average of the dissipation function $\langle \Omega_t \rangle$ is the time integral of the irreversible entropy production rate. The FT relates the probability of observing a process of duration t with $\Omega_t = A \pm dA$, $P(\Omega_t = A)$, to that of a process with the same magnitude of dissipation change, but of opposite sign:

$$\frac{P(\Omega_t = -A)}{P(\Omega_t = A)} = \exp(-A). \tag{1}$$

The theory and experiments also compare an integrated form of the FT, the IFT. It predicts the frequency of "negative-Ω_t" trajectories (similar to "entropy-consuming" trajectories[8]) $\Omega_t < 0$ to "positive-Ω_t" trajectories (similar to "entropy-producing trajectories") $\Omega_t > 0$:

$$\frac{P(\Omega_t < 0)}{P(\Omega_t > 0)} = \langle \exp(-\Omega_t) \rangle_{\Omega_t > 0}, \tag{2}$$

where the brackets on the right-hand side (RHS) denote an average accumulated only over positive-Ω_t trajectories. Since the original FT publication, several other versions of the theorem have been shown to exist for various systems,[10] and are tabulated in a recent review.[11]

While much research has focused on the FT, the Kawasaki function[12] $\langle \exp(-\Omega_t) \rangle$, which is intimately related to the FT, has rarely been discussed. A proof by Evans and Searles[13] shows that the Kawasaki function obeys the identity

$$\langle \exp(-\Omega_t) \rangle \equiv 1. \tag{3}$$

We call this equation the Kawasaki Identity (KI). In this paper we show that the KI is a direct result of the FT and that the Kawasaki function is a useful diagnostic tool. The deviation of the Kawasaki function from unity provides an immediate indicator to the effectiveness of the phase-space sampling and to the quality of the results.

First we show that the KI follows directly from the FT, Eq. (1), and the definition of an ensemble average. The ensemble average of the Kawasaki function can be written as

$$\langle \exp(-\Omega_t) \rangle = \int_{-\infty}^{\infty} P(A) \exp(-A) dA, \tag{4}$$

where $P(A)$ is the normalized probability density of observing a trajectory of duration t with dissipation production $\Omega_t = A$. Substituting the FT, Eq. (1), for $P(A)\exp(-A)$ gives

$$\langle \exp(-\Omega_t) \rangle = \int_{-\infty}^{\infty} P(-A) dA. \tag{5}$$

A change of variable plus the normalization condition of $P(A)$ shows that

$$\langle \exp(-\Omega_t) \rangle = \int_{-\infty}^{\infty} P(-A) dA = \int_{-\infty}^{\infty} P(B) dB = 1. \tag{6}$$

This proves that if the FT holds, then the KI is satisfied. However, the KI is not a sufficient condition for the FT. To illustrate this we present a counter example which obeys the KI but does not satisfy the Fluctuation Theorem.[14] Consider a distribution function $P(A)$ that is the sum of two Gaussian distributions $G_1(A)$ and $G_2(A)$ which have the same mean but different variances. The normalized distribution function is

$$P(A) = \tfrac{1}{2} G_1(A) + \tfrac{1}{2} G_2(A),$$

$$P(A) = \frac{1}{\sqrt{2\pi}} \left[\frac{1}{2} \exp\left(-\frac{(A-\mu)^2}{2} \right) + \frac{1}{4} \exp\left(-\frac{(A-\mu)^2}{8} \right) \right], \tag{7}$$

where μ has been chosen to ensure that $\langle \exp(-A) \rangle = 1$. This occurs for $\mu = 1.508\,266$. However, notice that the distribution function $P(A)$ fails to satisfy the FT, Eq. (1). That is, $P(A) \neq P(-A)\exp(A)$, as shown in Fig. 1. As such we can say that the FT gives a more detailed description of the systems' properties than the KI. As the KI is a necessary, but not

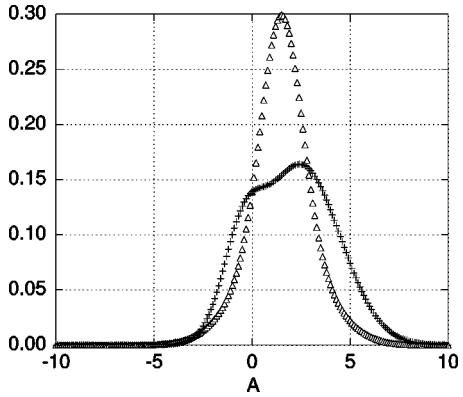

FIG. 1. From Eq. (7) the distribution functions $P(A)$ and $P(-A)\exp(A)$, (Δ) and ($\times$) respectively, are plotted vs A. The mean of $P(A)$ was chosen to be $\mu=1.508\,266$ so that the distribution is normalized and the Kawaskai Identity is satisfied. Notice that the distribution $P(-A)\exp(A)$ is different from $P(A)$. In order for the FT to be satisfied, these distributions must be equivalent, $P(A)=P(-A)\exp(A)$.

a sufficient, condition for the FT we may use the KI as a diagnostic aid when analyzing trajectories to test the FT.

As the derivation above shows, rare negative-Ω_t trajectories that are contrary to expectations of the Second Law are *necessary* for the KI to hold. Positive-Ω_t trajectories frequently contribute to the Kawasaki function, but each contribution is small in magnitude due to the negative sign in the exponential. As the dissipation produced along a trajectory increases (i.e., becomes more positive), its contribution to the Kawasaki function decreases exponentially. On the other hand, the infrequent negative-Ω_t trajectories contribute rarely to the average, but each contribution is exponentially significant. The exponential rarity of observing negative-Ω_t trajectories is *exactly* compensated by the negative exponential in the Kawasaki function. The result is that the Kawasaki function has a constant value of unity for all times t. Without the occurrence of negative-Ω_t trajectories, it is impossible for the KI to hold.

To demonstrate the KI in an experiment we consider the time-dependent relaxation of a colloidal particle in an optical trap. An optical trap is formed when a transparent, micron-sized particle, whose index of refraction is greater than that of the surrounding medium, is located within a focused laser beam. The refracted rays differ in intensity over the volume of the sphere and exert a sub-pico-Newton force ($1\,\mathrm{pN}=10^{-12}$ N) on the particle, drawing it towards the region of highest light intensity. The optical trap is harmonic near the focal point, meaning that its contribution to the system's potential energy is $\frac{1}{2}k(\mathbf{r}\cdot\mathbf{r})$, where $\mathbf{r}$ is the position of the particle relative to the center of the trap and k is the trapping constant or trap strength which can be tuned by adjusting the laser power. In the experiments reported here, the colloidal particle is initially localized in a trap of strength k_0 over a sufficiently long time so that its position is described by an equilibrium distribution. At $t=0$ the optical trap strength is increased discontinuously from k_0 to k_1 so that we more tightly confine or ''capture'' the particle.

The particle's position is recorded as it relaxes to its new equilibrium distribution and we evaluate the dissipation function of each trajectory as

$$\Omega_t=\frac{1}{2k_BT}(k_0-k_1)(\mathbf{r}_t^2-\mathbf{r}_0^2). \tag{8}$$

In this equation $\mathbf{r}_0$ is the initial position of the particle along a trajectory and $\mathbf{r}_t$ is the position of the particle along the same trajectory at time t after the trap strength has been changed. For a rigorous derivation of Eq. (8) from stochastic Langevin dynamics, we refer the reader to Reid *et al.*[15] It should be noted that $\langle\Omega_t\rangle$ is a positive definite quantity. This can be shown by considering Eq. (8). In the case of $(k_0-k_1)<0$ (i.e., a weak trap going to a strong trap) then $\langle\mathbf{r}_t^2-\mathbf{r}_0^2\rangle<0$ as the particle is likely to be confined closer to the center of the optical trap. In the reverse case if $(k_0-k_1)>0$ then we would expect $\langle\mathbf{r}_t^2-\mathbf{r}_0^2\rangle>0$ as the particle has enough energy to move further from the center of the trap. In either case the product yields a positive definite quantity. In fact, as a consequence of the FT, it is easy to prove $\langle\Omega_t\rangle>0$ for all t.[16] For a physical interpretation of Eq. (8), consider the dimensionless work done as a result of the change in the trap strength, which can be written as

$$\frac{1}{k_BT}\int_0^t ds\,\Delta\mathbf{f}\mathbf{v}\equiv\frac{1}{k_BT}\int_0^t ds[(\mathbf{f}\mathbf{v})-(\mathbf{f}_0\mathbf{v})], \tag{9}$$

where $\mathbf{f}$ is the optical force acting on the particle in the strong trap, $\mathbf{f}_0$ is the force in the weak trap, $\Delta\mathbf{f}$ is the difference in the forces and $\mathbf{v}\equiv d\mathbf{r}/dt$ is the velocity of the particle. The first term on the RHS is the work accumulated along the particle's path of duration t. The second term on the RHS is a hypothetical work: it is the work accumulated over the same path in the case where the trap strength is not increased. An analogy can be made with the extra work done by a mountain climber due to a snowstorm, i.e., the work done by the climber during his ascent up a snow-covered mountain minus the work that he would have done along the same path without snow. One can show that this extra work attributed to the increased trap strength, Eq. (9), reduces to the rigorously derived definition of Ω_t, Eq. (8).

The optical trap is formed using a 1 W infrared laser ($\lambda=980$ nm, Cell Robotics, USA) and a $100\times$(N.A.$=1.3$) oil-immersion objective lens. The position of a 6.3 μm diameter latex particle (Interfacial Dynamics Co., USA) located within the optical trap is determined, with a resolution of 15 nm, by projecting its image onto a quadrant photodiode (S4349 Hamamatsu, Japan). The optical trap strength is controlled by adjusting the laser intensity, which we achieve in a 2–3 ms timeframe. Electronic signals from the intensity photodiode are synchronized with that of the quadrant photodiode at 1 kHz, providing data with electronic markers which signal the change in the strength of the optical trap. The data collection is fully automated enabling thousands of trajectories to be collected without the presence of an operator.

Approximately 3000 particles were added locally into a 4.0 ml solution of 10 mM *Tris*-HCl + 1 mM EDTA, maintained at a *p*H of 7.5. One particle was optically trapped, isolated from the other particles, used to calibrate the quadrant photodiode position detector, and then used to record

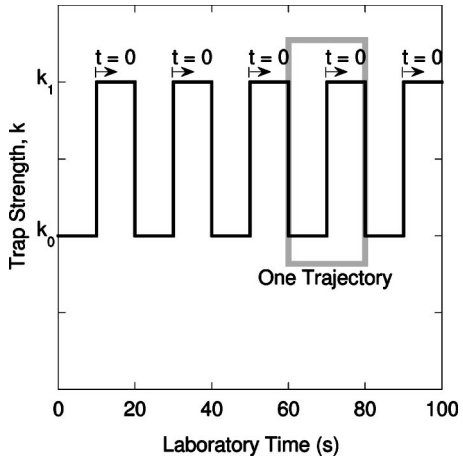

FIG. 2. Optical trap strength k vs. laboratory time, showing the discontinuous cycling between low trap strength k_0 and high trap strength k_1 with a period of 20 sec. A single ''trajectory'' (box) corresponds to the particle positions recorded over a single cycle, centered around $t=0$ when the trap strength is increased.

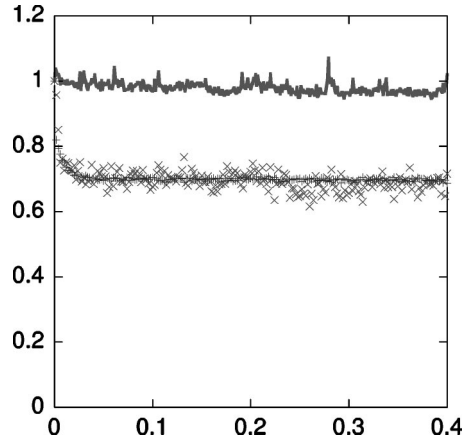

FIG. 3. An example of the IFT and Kawasaki function, constructed from a well sampled data set. The Kawasaki function is denoted as the (line), the LHS of the IFT as ($\times$), and the RHS of the IFT as ($+$). The Kawasaki function is ≈ 1, matching the expected Kawasaki Theorem result. The IFT results are also in good agreement. The optical trap constants were $[k_0^x,k_0^y]=[1.55,1.84]$ pN/μm and $[k_1^x,k_1^y]=[2.39,3.30]$ pN/μm. 2100 trajectories were collected.

trajectories as the particle relaxes to its new equilibrium distribution. Due to the possibility of anharmonicity in the optical trap we evaluated the trap constants k_0 and k_1 in both the x and y coordinates separately yielding trap constants $[k_0^x,k_0^y]$ and $[k_1^x,k_1^y]$. By doing so, Eq. (8) changes to become

$$\Omega_t=\frac{1}{2k_BT}(k_0^x-k_1^x)(x_t^2-x_0^2)+\frac{1}{2k_BT}(k_0^y-k_1^y)(y_t^2-y_0^2).$$

The optical trapping constants $[k_0^x,k_0^y]$ and $[k_1^x,k_1^y]$ were determined by sampling the particles position at the required laser powers for 120 sec at 200 Hz. The data was then analyzed with the equipartition theorem $k^x=k_BT/\langle x^2\rangle$ and $k^y=k_BT/\langle y^2\rangle$ to determine the trapping constants. We cycled the strength of the optical trap discontinuously between a weak trap strength $[k_0^x,k_0^y]$ and a strong trap strength $[k_1^x,k_1^y]$ with a period of 20 sec. An experimental ''trajectory'' corresponds to a trace of the particle's position over 10 sec in the weak trap ($-10<t<0$ sec) and a further 10 sec in the strong trap ($0\geqslant t>10$ sec) as indicated in Fig. 2. It is essential that all trajectories use the same particle as the calibration of the quadrant photodiode position detector is sensitive to slight differences in particle size and light transmission. Whenever an ensemble measure, such as the Kawasaki function, depends sensitively upon rare events, considerable care must be taken when rejecting data from that ensemble of experiments. If we eliminate one or more trajectories from our analysis because they are uncharacteristic, then we might well be eliminating the ''rare'' trajectory that contributes significantly to $\langle\exp(-\Omega_t)\rangle$. On the other hand, uncontrollable experimental errors do occur, such as sharp and large fluctuations in the mains voltage, or a rogue particle displacing the optically trapped particle, among many others that give erroneous trajectories. Thus, ''uncharacteristic'' trajectories should only be removed when a likely cause is identified. Further experimental details can be found in Carberry *et al.*[8] and Carberry.[17]

In the experiment detailed above and in our previous FT experiments,[8,9] we used the Kawasaki function as a quality control tool. The exponential nature of the Kawasaki function is capable of highlighting numerous errors including (but not limited to) particle exchange and interference, laser power fluctuations and miscalibration of the photodetector. However when the optical tweezers have been correctly calibrated, and the experimental conditions optimized, good results are obtained and the KI holds. Figure 3 shows a result

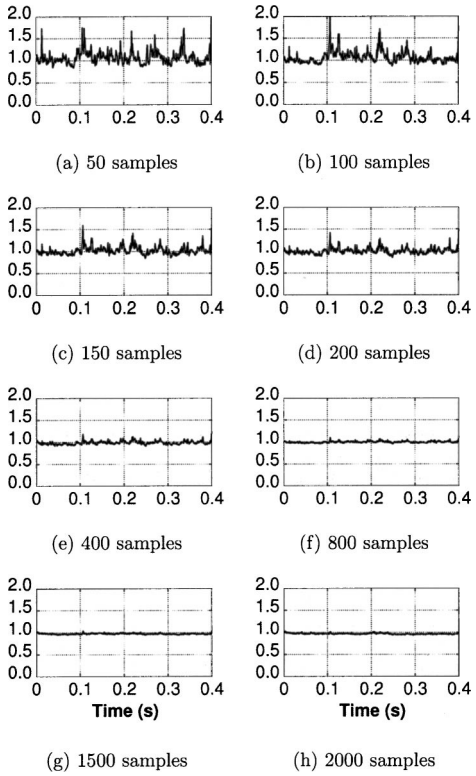

FIG. 4. The Kawasaki function is plotted with various numbers of experimental trajectories, as indicated.

where the Kawasaki Identity and the IFT are satisfied within experimental and statistical uncertainties.

Infrequent sampling of statistically rare events also has a major effect on the value of the Kawasaki function. This is particularly evident for the Wang experiment.[9] As the probability of observing rare, negative-Ω_t events decreases, more trajectories need to be sampled in order to ensure the Kawasaki Identity remains valid. In the long time limit, where the probability of observing these rare, negative-Ω_t trajectories approaches 0, the experimental estimates of the Kawasaki function deviate from 1.

The problem of infrequent sampling can also be illustrated using this ''capture'' experiment. In Fig. 4(a) through 4(h) we show how the experimental estimate of the Kawasaki function improves with increasing numbers of sampled trajectories. By watching the evolution of the Kawasaki function it becomes clear that as more trajectories are analyzed the Kawasaki function approaches its expected value of unity.

In conclusion, we have shown that the Kawasaki Identity is a necessary, but not sufficient, condition for the FT to hold. Additionally, we have shown that the Kawasaki function is useful when analyzing experimental data. It provides an excellent indicator to the quality of the results, shows times where the phase space sampling has been insufficient and also indicates where errors may have occurred.

[1] D. J. Evans, E. G. D. Cohen, and G. P. Morriss, Phys. Rev. Lett. **71**, 2401 (1993).
[2] G. Gallavotti and E. G. D. Cohen, Phys. Rev. Lett. **74**, 2694 (1995).
[3] J. Kurchan, J. Phys. A **31**, 3719 (1998).
[4] G. Gallavotti, Physica A **263**, 39 (1999).
[5] G. E. Crooks, Phys. Rev. E **60**, 2721 (1999).
[6] C. Jarzynski, J. Stat. Phys. **98**, 77 (2000).
[7] L. Rondoni, T. Tel, and J. Vollmer, Phys. Rev. E **61**, 4679 (2000).
[8] D. M. Carberry, J. C. Reid, G. M. Wang, E. M. Sevick, D. J. Searles, and D. J. Evans, Phys. Rev. Lett. **92**, 140601 (2004).
[9] G. M. Wang, E. M. Sevick, E. Mittag, D. J. Searles, and D. J. Evans, Phys. Rev. Lett. **89**, 050601 (2002).
[10] R. van Zon and E. G. D. Cohen, Phys. Rev. E **67**, 046102 (2003).
[11] D. J. Evans and D. J. Searles, Adv. Phys. **51**, 1529 (2002).
[12] T. Yamada and K. Kawasaki, Prog. Theor. Phys. **38**, 1031 (1967).
[13] D. J. Evans and D. J. Searles, Phys. Rev. E **52**, 5839 (1995).
[14] In the limiting case where there is only a weak change in the trap strength and the trajectory is observed over infinite time $t\rightarrow\infty$ the Kawasaki Identity and the FT are equivalent. That is, distributions $P(\Omega_t)$ that obey the Kawasaki Identity must also obey the FT and there is a direct mathematical equivalence between the Kawasaki Identity and FT. This is a result of the central limit theorem dictating that $\lim_{t\rightarrow\infty}^{\Delta k\rightarrow 0} P(\Omega_t)$ is a Gaussian distribution (see D. J. Evans, D. J. Searles, and L. Rondoni, *cond-mat/0312353*, for a discussion about this double limit). Note $P(\Omega_t)$ will always obey the Kawasaki Identity by virtue of the Liouville equation. However, in the more general case explored here, where the trajectory time is of finite duration and the change in trap strength is appreciable, the central limit theorem no longer applies and $P(\Omega_t)$ is not Gaussian. Consequently, a distribution $P(\Omega_t)$ may satisfy the Kawasaki Identity, but need not satisfy the FT, as shown by the example in the text. However, if $P(\Omega_t)$ satifies the FT, then the Kawasaki Identity must indeed hold.
[15] J. C. Reid, D. M. Carberry, G. M. Wang, E. M. Sevick, D. J. Searles, and D. J. Evans, Phys. Rev. E **70**, 016111 (2004).
[16] D. J. Searles, D. J. Evans, Aust. J. Chem (submitted).
[17] D. M. Carberry, Thesis dissertation.