Institute of Physics, Bhubaneshwar
27 May 2013

You can't vanguish Maxwell's demon

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May 27, 2013

An experimentalist and a theoretician

- When an experimentalist announces a result, every one believes it, except the experimentalist !
- When a theoretician announces a result, no one believes it, except the theoretician !
- I am going to tell you of a result
- **PRAMANA** did not believe it; the paper was rejected
- Fortunately Physical Review E accepted it; Physica A accepted it.

Work in a in a nutshell

- Let τ denote the time taken for a process in which a macroscopic property changes its value as per a pre-fixed experimental protocol; for example
  - the volume of a gas in a cylinder is changed from V_i to V_f, by moving a piston uniformly from time $t = 0$ to time $t = \tau$:

$$V(t) = V_i + (V_f - V_i)\ \frac{t}{\tau}$$

  - external field influencing an Ising spin system is changed from B_i to B_f uniformly from time $t = 0$ to time $t = \tau$.

$$B(t) = B_i + (B_f - B_i)\ \frac{t}{\tau}$$

- (quasi-static) reversible limit obtains when $\tau \to \infty$
- For τ finite, the process is irreversible
- In the limit $\tau \to \infty$ we call it a Thermodynamic process.

Work in a nutshell ... continued

- Let $p(\tau)$ denote the probability that the second law of thermodynamics is violated
- RESULT: $p(\tau)$ increases when τ increases and in the reversible limit, it tends to one-half !!!
- This result is definitely counter-intuitive and on the face of it, as an anonymous referee opined, is absurdly Wrong !
- But I shall convince you, it is right .... and the reason why it is right is rather trivial !
- Then, how do we comprehend it ?
- Let me begin from the beginning ....

Let me begin by saying thanks

Thanks to

Somen

for the invitation.

Thanks to :

- G. Anjan Prasad :

  Work fluctuations in model non-equilibrium systems, M. Tech. (CT) Thesis (2008),

- Madhumita Gopalan :

  Free energy differences in model systems, M. Tech. (CT) Thesis (2008),

  who started the work in the first place,

- N Suman Kalyan :

  A note on non-equilibrium work fluctuations and equilibrium free energies,

  Physica **A 390** 1240 (2011),

- Siva Nasarayya Chari, :

  Study of nonequilibrium work distributions from a fluctuating lattice Boltzmann model,

  Phys. Rev. **E 85**, 041117 (2012),

  who suffered in the process,

- Inguva Ramarao, V S S Sastry and N Satyavathi

  who partenered.

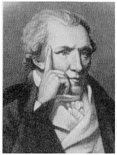
- A closed system in equilibrium at temperature T
- It draws $đQ$ of heat by a (quasi static) reversible process carried out at temperature T
- In general, $đQ$ can not be expressed as a differential of a function; it is not a perfect differential; hence we denote it as $đQ$ and not as dQ.
- However, $đQ/T$ is a perfect differential. Clausius [1] denoted it by dS and named S as entropy.

[1] R. Clausius (1865) , On different forms of the fundamental equations of mechanical theory of heat and their convenience of applications reprinted in J. Kestin (Ed.), The Second Law of Thermodynamics, Dowden, Hutchinson and Ross, Stroudsburg PA (1976)

- The entropy of the system increases[2] by an amount given by,

$$dS = \frac{đQ}{T}$$

- What is the work done during the process ?
- To answer this question consider the first law of thermodynamics stated as $W = dU - đQ$,



[2] the entropy of the surroundings decreases by precisely the same amount so that the total change in entropy is zero : the process is reversible (and hence, necessarily quasi static).

- First law is a statement of conservation of energy in terms of what happens in the interior of the system and on its boundaries.
- It is valid for all processes - quasi static, non-quasi static, reversible, irreversible or otherwise
- however if the process is (quasi-static) reversible then we can replace $đQ$ by TdS and write $W = dU - TdS$.

If the process is also isothermal then

$$W = d(U - TS) = dF$$

where F denotes Helmholtz free energy.
Thus the reversible work done, W_R, equals free energy change, dF. *i.e.* $W_R = dF$
in what follows we shall use dF and W_R interchangeably.

- What is the relation between free energy and work if the process is not quasi-static (and hence irreversible) ?
- To answer the question we start with the Second-Law-inequality, $dS > \frac{đQ}{T}$ for an irreversible process.
- From the above we get,

$$\begin{aligned} đQ &< TdS \\ W &> dU - TdS \\ &> d(U - TS) \\ &> dF \\ &> W_R \end{aligned}$$

- The work done on the system exceeds the free energy change.
- At best, the above is what all that thermodynamics can tell us....

- What is the meaning of the statement : $W > dF$?
- Consider an experiment that represents the process.
  - we call it a switching process since it can not be depicted as a path in a thermodynamic phase diagram
  - the initial equilibrium state will appear as a point in the phase diagram
  - at the end of the process, if we allow the system to equilibrate, it will appear as point at some other place in the phase diagram
  - hence the word "switching"
- Different switching experiments, all carried out with the same protocol, can in principle yield different values of W.
  - if the switching experiment is quasi static, all the experiments will yield the same work value.

- Thus we have to deal with an ensemble of values of W and not with just one value of W
- Let the ensemble of values of W be denoted by Ω.
- It is quite possible that several elements of Ω will be less than ΔF, thus 'violating ' the Second law.
- the fraction the ensemble with W less than W_R is usually referred to as the probability of violation of the second law
- However the ensemble average of work is always greater than or equal to the reversible work : $\langle W \rangle \ \geq \ W_R$.
- $\langle W \rangle - W_R$ is called dissipation.

- Let the probability distribution $\rho(W, \tau)$ describe the ensemble Ω.
- In the (quasi-static) reversible limit of $\tau \to \infty$ we shall have

$$\rho(W, \tau) = \delta(W - dF)$$

- If τ is finite then the probability of Second law 'violation' is given by,

$$p = \int_{-\infty}^{dF} dW \rho(W, \tau).$$

- If τ is large but not infinity, then we can expect $\rho(W, \tau)$ to be a Gaussian with cumulants,

$$\begin{aligned} \zeta_1 &= \langle W \rangle \\ \zeta_2 &= \sigma_W^2 = \langle W^2 \rangle - \langle W \rangle^2 \\ \zeta_n &= 0 \quad \forall \quad n \geq 3 \end{aligned}$$

Thus,

$$\rho(W; \text{large } \tau) = \frac{1}{\sqrt{2\pi\zeta_2}} \exp\left[\frac{(W - \zeta_1)^2}{2\zeta_2}\right]$$

- Fluctuation-dissipation theorem of Callen and Welton: (see Phys. Rev. 83, 34 (1951))
    - consider a process which is nearly quasi-static, obtained when τ is large but not infinity,
    - Then, dissipation, given by $\zeta_1 - W_R$, is proportional to fluctuation ζ_2.
    - the relation between fluctuations and dissipation is given by,

$$\zeta_1 - W_R = \frac{1}{2}\beta\zeta_2$$

$$\text{OR}$$

$$W_R = \zeta_1 - \frac{1}{2}\beta\zeta_2$$

- Measuring energies in units of $k_B T = 1/\beta$, the above can be expressed as

$$-\beta W_R = -\beta\zeta_1 + \frac{1}{2}(-\beta)^2\zeta_2$$

- Let $\phi(\beta)$ denote the moment generating function of W given by

$$
\begin{aligned}
\phi(\beta) &= \int_{-\infty}^{+\infty} dW \ \exp(-\beta W)\rho(W,\tau) = \langle \exp(-\beta W) \rangle \\
&= \sum_{k=0}^{\infty} \frac{(-\beta)^k}{k!} M_k
\end{aligned}
$$

where M_k is the $k-$th moment of W.

- Let

$$\psi(\beta) = \log \phi(\beta) = \sum_{k=1}^{\infty} \frac{(-\beta)^k}{k!} \zeta_k$$

denote the cumulant generating function of W.

- Let us look at the Callen-Welton fluctuation-dissipation relation:

$$-\beta dF = -\beta\zeta_1 + \frac{1}{2}(-\beta)^2\zeta_2$$

- We recognize the RHS as the cumulant generating function of a Gaussian random variable for which third and higher cumulants are identically zero.
- Consider a process with τ not large;
- the system would be thrown far from equilibrium during such a process.
- There is no reason to expect W to be Gaussian;
- the third and higher order cumulants of W shall be non-zero. Including them will lead to :

$$-\beta W_R = -\beta\zeta_1 + \frac{1}{2}(-\beta)^2\zeta_2 + \sum_{n=3}^{\infty}\frac{1}{n!}(-\beta)^n\zeta_n$$

- Taking exponential of both sides of the above equation, we get,

$$\begin{aligned}\exp(-\beta W_R) &= \exp\left[\sum_{n=1}^{\infty}\frac{1}{n!}(-\beta)^n\zeta_n\right] \\ &= \phi(\beta) \\ &= \langle\exp(-\beta W)\rangle\end{aligned}$$

which is called Jarzynski identity, see PRL, 78, 2690 (1997), relating non-equilibrium work fluctuations to equilibrium free energies. Note $W_R = dF$

W and Q are two modes of energy transfer

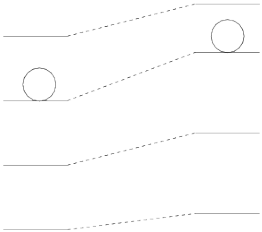
ϵ_j : energy of the microstate indexed by j

p_j : probability of the microstate indexed by j

$$
\begin{aligned}
U &= \sum_j p_j \epsilon_j \\
dU &= \sum_j \left[\epsilon_j \ dp_j + p_j \ d\epsilon_j \right] \\
&= \sum_j \epsilon_j dp_j + \sum_j p_j d\epsilon_j \\
&= \quad đq \quad + \quad đW
\end{aligned}
$$

- $\sum_j \epsilon_j dp_j$ refers to Heat;
  - This term refers to the energy absorbed by the system from the reservoir in the form of heat.
  - during this process, the energy (ϵ_j) of a micro state (j) does not change.
  - only the occupation probabilities $\{p_i\}$ change.
- $\sum_j p_j d\epsilon_j$ refers to Work done on the system.
  - during this process the occupation probabilities - $\{p_j\}$ do not change.
  - only the energy (ϵ_j) of the micro states (j) changes.
  - *e.g.* when we change volume (boundary conditions) the energy eigenvalues of the system change.

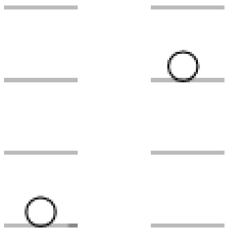
$$W = \sum_j p_j d\epsilon_j$$



- the system remains in the same micro state; only the energy of the microstate changes taking the system along with it.

Proof that $W = \sum_i p_j d\epsilon_j$

$$
\begin{aligned}
\sum_j p_j d\epsilon_j &= \sum_j p_j \left(\frac{\partial \epsilon_j}{\partial V}\right)_{\{p_j\}} dV \\
&= \left(\frac{\partial}{\partial V} \sum_j p_j \epsilon_j\right)_{\{p_j\}} dV \\
&= \left(\frac{\partial U}{\partial V}\right)_{S,N} dV \\
&= -P\ dV
\end{aligned}
$$



- The energies of the micro states do not change; the energy put in (or extracted out) **in the form of heat** induces the system to make a transition from one micro state to another of higher (or lower) energy; such a transition could occur even otherwise by a spontaneous fluctuation.

Proof that $Q = \sum_i \epsilon_j \ dp_j$

$$S = -k_B \sum_j p_j \log p_j ; \ dS = -k_B \sum_j [dp_j + dp_j \log p_j]$$

$$\left[\sum_j dp_j = 0 \right] ; \ dS = -k_B \sum_j dp_j \log p_j$$

$$\left[p_j = \exp[-\beta \epsilon_j]/Z \right] ; \qquad \log p_j = -\beta \epsilon_j - \log Z$$

$$dS = k_B \sum_j dp_j [\beta \epsilon_j + \log Z]$$

$$\left[\sum_j dp_j \log Z = 0 \right] \qquad dS = k_B \beta \sum_j dp_j \epsilon_j ;$$

$$T dS = \sum_j dp_j \epsilon_j = đ q_R$$

- Recall we wrote that for a general process $W_R \le \langle W \rangle$, and the equality obtains when we have a (quasi static) reversible process.
- $\langle W \rangle$ refers to the average work done on the system:
  - A switching experiment consists of a sequence of alternating heat and work steps;
  - carry out the switching experiment for a very large number of times with the same **protocol** and get $\{W_i \ : \ i = 1,\ 2,\ \cdots\}$.
  - calculate the arithmetic average,

$$\langle W \rangle = \lim_{N\to\infty} \overline{W}_N = \frac{1}{N}\sum_{i=1}^{N} W_i$$

- Why should the work done on the system differ from one switching experiment to another ? Ans: heat step is not reproducible and not reversible while the work step is reproducible and reversible.

$$H = -\sum_{\langle i,j\rangle} P_2(\cos\theta_{i,j}) - \frac{E^2}{2}\sum_i P_2(\cos\theta_i)$$

- In the above i and j are nearest neighbour sites and is denoted by $\langle i,j\rangle$. The first sum runs over all possible distinct nearest neighbour pairs of sites.
- each site carries a headless spin whose orientation is defined by three direction cosines in fixed laboratory co-ordinate system
- $\theta_{i,j}$ is the angle between the spins in the nearest neighbour site i and j
- E is the external electric field oriented along the Z axis; θ_i is the angle between the electric field and the spin at the site i.

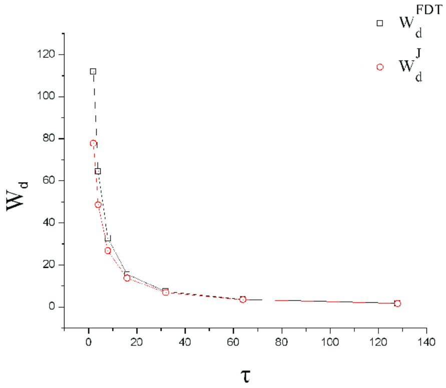
See Physica A (2011)

- start with an arbitrary initial spin configuration and employing Metropolis algorithm equilibrate the system at the desired value of β with external field E set to zero.
- consider a micro state from the equilibrium ensemble; calculate the energy;
- E is switched from zero to ΔE; calculate the energy of the micro state with the field switched on;
- Work is calculated from the energy change due to field change keeping the micro state the same; Call this a work step.
- then implement a heat step: Do not change the external field; change the orientation of a randomly chosen spin by a random amount and accept/reject *à la* Metropolis; carry out one Monte Carlo sweep

- The work and heat steps are repeated until the electric field attains a pre fixed value. In the simulation we switch electric field from 0 to 0.1. Let n be the number of work steps. Then $\Delta E = E/n$.
- In the limit $n \to \infty$ and hence $\Delta E \to 0$ we get a quasi-static process.
- for n sufficiently large we get close to a (quasi-static) reversible process where the fluctuation-dissipation relation of Callen and Welton can be employed.
- for small n the system is driven far from equilibrium; however we can calculate free energy from Jarzynski identity

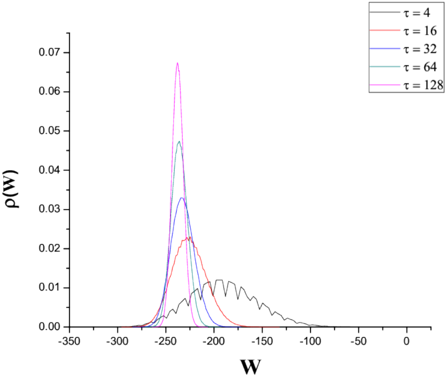
see Physica A (2011)

Figure: Dissipation as a function of switching time τ calculated from Fluctuation Dissipation Theorem and from Jarzynski identity. The dissipation decreases with increase of τ and in the (quasi-static) reversible limit of $\tau \to \infty$, it goes to zero

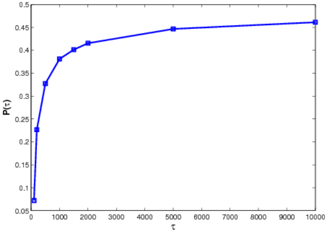


see Physica A (2011)

Figure: Distribution of work for various switching times. For small switching time the distribution is not Gaussian. When switching time increases the curve becomes Gaussian and in the quasi static limit it becomes sharply peaked



- Probability of violation of second law, $p(\tau)$ as a function of τ. We observe that $p(\tau) \to \frac{1}{2}$ in the reversible limit $(\tau \to \infty)$. !!
- Ideal gas in an external potential; lattice Boltzmann simulation; see PRE (2012)



Though the result seems to be counter intuitive, it could be explained through a simple argument

- Recall

$$p(\tau) = \int_{-\infty}^{W_R} \rho(W;\tau)dW$$

- Define a random variable

$$\hat{W} = W - W_R$$

- Then

$$p(\tau) = \int_{-\infty}^{0} \rho(\hat{W};\tau)d\hat{W}$$

- For large τ, the distribution of $\hat{W}$ is Gaussian with mean

$$W_d = \langle \hat{W} \rangle = \langle W \rangle - W_R$$

and variance σ^2.

- Note W_d is the dissipation and is proportional to fluctuations σ^2.
- When $\tau \to \infty$ dissipation tends to zero; σ^2 also tends to zero;
- But $\sigma = \sqrt{\hat{W}} \;>>\; \langle \hat{W} \rangle$ for $\langle \hat{W} \rangle \to 0$.
  - $x \;>\; 1 : \sqrt{x} \;<\; x$
  - $x \;=\; 1 : \sqrt{x} \;=\; x$
  - $x \;<\; 1 : \sqrt{x} \;>\; x$
- We have a Gaussian distribution whose mean goes to zero, fast, and whose standard deviation goes to zero, slow as $\tau \to \infty$;
- $p(\tau \to \infty)$ is the integral of the Gaussian from $-\infty$ to 0 which goes to one half.
- Q.E.D.

- What we say is in the same spirit as Maxwell's demon violating the second law
    - J C Maxwell, Nature (London) **17**, 257 (1878)
    - H S Leff and A F Rex, *Maxwell's Demon*, Adam Hilger (1990);
    - H S Leff and A F Rex, *Maxwell's Demon - 2* IoP (2003)
- Correspondence between statistical mechanics and thermodynamics is robust in the thermodynamic limit
- such a correspondence may not always exist for small systems :
    - Measured value would differ from one experiment to the other;
    - some of the measured values will not be consistent with what thermodynamics tells us

- for more quantitative and elaborate arguments see
  - N Suman Kalyan, Anjan Prasad, V S S Sastry, and K P N Murthy,

    A note on non-equilibrium work fluctuations and equilibrium free energies,

    Physica **A 390** 1240 (2011)

  - Siva Nasarayya Chari, Inguva Ramarao, and K P N Murthy,

    Study of nonequilibrium work distributions from a fluctuating lattice Boltzmann model,

    Phys. Rev. **E 85**, 041117 (2012)

$$p_- = p(w' \le 0) = \int_{-\infty}^{0} \rho(w',\tau)\ dw'\ ;\ [=\ p(\tau)]\ ,$$

$$p_+ = p(w' > 0) = \int_{0}^{\infty} \rho(w',\tau)\ dw'\ .$$

Assume $\rho(w',\tau)$ to be a Gaussian, in the near quasi-static regime,

$$\rho(w',\tau) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(w')^2/2\sigma^2}\ .$$

$$\left\langle e^{-\beta w'} \right\rangle_- = \frac{\int_{-\infty}^{0} e^{-\beta w'} \rho(w',\tau)\ dw'}{\int_{-\infty}^{0} \rho(w';\tau)\ dw'} = \left\{ 1 + \mathrm{erf}\left(\frac{\beta\sigma}{\sqrt{2}} \right) \right\} e^{\left(\frac{\beta\sigma}{\sqrt{2}}\right)^2}\ ,$$

$$\left\langle e^{-\beta w'} \right\rangle_+ = \frac{\int_{0}^{\infty} e^{-\beta w'} \rho(w',\tau)\ dw'}{\int_{0}^{\infty} \rho(w',\tau)\ dw'} = \left\{ 1 - \mathrm{erf}\left(\frac{\beta\sigma}{\sqrt{2}} \right) \right\} e^{\left(\frac{\beta\sigma}{\sqrt{2}}\right)^2}\ .$$

Very close to the quasi-static limit (τ is very large), variance of $\rho(w', \tau)$ is infinitesimally small. Hence we can write,

$$\sigma \approx \epsilon \ .$$

$$\begin{aligned} p_- &= \frac{1 - \left\langle e^{-\beta w'} \right\rangle_+}{\left\langle e^{-\beta w'} \right\rangle_- - \left\langle e^{-\beta w'} \right\rangle_+} \\ &\approx \frac{1 - [1 - \epsilon]}{[1 + \epsilon] - [1 - \epsilon]} \\ &\approx \frac{1}{2} \end{aligned}$$

So what ?

- Work fluctuations provide a powerful tool in the hands of the experimentalists:
  - they no longer need to ensure that their experimental protocol be quasi static
  - They can obtain equilibrium free energies from non-equilibrium measurements

and

THANKS