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FLUCTUATIONS IN DISSIPATIVE WORK IN A THERMOMECHANICALLY DRIVEN SIMPLE HARMONIC OSCILLATOR

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When a system undergoes a spontaneous thermodynamic process, we expect the entropy of the universe to increase. In elementary thermodynamics textbooks this is demonstrated by calculating the difference in thermodynamic properties of the initial and final equilibrium situations. For a system that is continuously driven by external thermal or mechanical forces, we also expect there to be entropy generation, though we now might want to define the entropy change without reference to equilibrium properties. It could be said that the term ‘entropy’ should only ever refer to an equilibrium property, so we need to tread carefully.

Nevertheless, recent developments in non-equilibrium statistical physics suggest how one can define a quantity that strongly resembles irreversible entropy change. These insights have also led to the Fluctuation Theorem(s) [1,2] and the Jarzynski equality [3]. We have studied a so-called dissipation functional for the simple case of a thermomechanically-driven harmonic oscillator, in order to demonstrate that it may be related to irreversible, or dissipative thermodynamic work. In the limit of an equilibrium to equilibrium process the mean of this quantity can be equated with entropy production. We can also characterise how it might vary with different realisations of the process. We find that there are periods of the process during which the mean of the irreversible work decreases. Our analysis quantifies this dissipation and occasional ‘antidissipation’, as well as providing an average rate of irreversible work that goes beyond the usual linear regime.

The dynamical model that we employ describes a particle in a harmonic potential with a time-dependent spring constant, subject to an additional white noise force parameterised by a time-dependent temperature. We consider the overdamped limit, for which the stochastic dynamics are represented by

$$dq = -\frac{\kappa(t)q}{\gamma m} dt + \left(\frac{2k_B T(t)}{\gamma m} \right)^{1/2} dw(t) \quad (1)$$

where q is the particle position, $\kappa(t)$ is the time-dependent spring constant, $T(t)$ is the time-dependent heat bath

temperature, m is the mass of the particle, γ is the friction coefficient, k_B is Boltzmann’s constant and $dw(t)$ is the increment at time t in a Wiener process.

This familiar model may be used to explore the properties of the following dissipation functional:

$$\Omega_{\kappa,T}[q] = \ln(p_{\kappa,T}[q]/p_{\bar{\kappa},\bar{T}}[\bar{q}]) \quad (2)$$

where $p_{\kappa,T}[q]$ is the probability density for the occurrence of a spatial path $q(t)$ under the thermomechanical process defined by $\kappa(t)$ and $T(t)$ over a chosen time interval starting at $t=0$, given an initial probability density for $q(0)$. Ω is a functional of the path $q(t)$ and its time-reversed counterpart $\bar{q}(t)$. An overbar is similarly used to denote the time-reversed driving functions. The initial system is taken to be in thermal equilibrium for both the process and its reversed counterpart. An ensemble of paths generated by the stochastic dynamics and the specified functions $\kappa(t)$ and $T(t)$, then gives rise to a distribution P of values of Ω which may be shown to satisfy a detailed fluctuation theorem, or more specifically a Crooks relation:

$$P_{\kappa,T}(\Omega) = \exp(\Omega) P_{\bar{\kappa},\bar{T}}(-\Omega) \quad (3)$$

which ensures that the mean value of Ω over the ensemble is positive. Nevertheless, substantial deviations from the mean are possible for a simple system, and paths with negative values of Ω might readily be generated.

The property $\langle \Omega \rangle \geq 0$ might therefore tempt one to identify the mean dissipation functional as a non-equilibrium version of irreversible entropy change. However, a careful analysis reveals that for an isothermal process Ω actually represents the quantity $W_d = W - \Delta F$, namely the excess of mechanical work performed on the system over the difference in Helmholtz free energies of systems at equilibrium under the initial and final Hamiltonians. Only for a process that ends in a long equilibration period does the mean of W_d correspond to an irreversible entropy change. Ω might be a process variable of an individual system with the property that its mean over all trajectories of the system is positive, and with a form reminiscent of definitions of irreversible entropy change in classical thermodynamics, but it differs from a change in equilibrium entropy. One

confounding feature is that its mean can decrease with time, as we now show.

For the simple model under consideration, it is possible to determine the behaviour of Ω through use of the stochastic solution to eq. (1) over time intervals of constant κ and T . The path probability $p_{\kappa,T}[q]$ may then be evaluated by representing a general thermomechanical process as a sequence of time periods with constant driving parameters, and multiplying together a set of transition probability densities to quantify the stochastic dynamics of the sequence. An explicit expression for $\Omega_{\kappa,T}[q]$ can then be obtained together with a value for its mean over the ensemble of paths, namely

$$\langle \Omega_{\kappa,T} \rangle = \int [dq] p_{\kappa,T}[q] \Omega_{\kappa,T}[q] \quad (4)$$

By evaluating this integral, we can show that

$$\begin{aligned} \langle \Omega \rangle &= \int_0^t dt' \left[\frac{\dot{K}(t')}{\xi} \int_0^{t'} dt'' T(t'') \exp \left(-\frac{2}{\xi} \int_{t''}^{t'} \kappa(\hat{t}) d\hat{t} \right) \right] \\ &\quad + \frac{T(0)}{2\kappa(0)} \int_0^t dt' \left[\dot{K}(t') \exp \left(-\frac{2}{\xi} \int_0^{t'} \kappa(\hat{t}) d\hat{t} \right) \right] - \Delta \left(\frac{F}{k_B T} \right) \end{aligned} \quad (5)$$

where $\xi = m\gamma$, $K(t) = \kappa(t)/T(t)$ and

$$\Delta \left(\frac{F}{k_B T} \right) = \frac{1}{k_B} \left(\frac{F_j}{T_j} - \frac{F_0}{T_0} \right) \quad (6)$$

where F_0 and F_j denote the Helmholtz free energies of the oscillator when in equilibrium at the initial and final values, respectively, of the spring constant κ and temperature T .

For a process with slowly varying $\kappa(t)$ and constant T , eq. (5) reduces to

$$\langle \Omega \rangle = \int_0^t dt' \left(\frac{\dot{\kappa}(t')}{2\kappa(t')} \right)^2 \frac{\xi}{\kappa(t')} \quad (7)$$

which takes a form for the entropy production expected according to linear non-equilibrium thermodynamics. The mean value is explicitly positive. In the quasistatic limit of vanishingly small $\dot{\kappa}$, the mean dissipation functional is zero. Both these features are necessary if $\langle \Omega \rangle$ is to play the role of an irreversible entropy change for a non-equilibrium process.

However, although the mean value of Ω over an ensemble of paths is positive, its time evolution is not necessarily monotonic. The general expression eq. (5) can evolve in a complex manner with time, depending on the parameters of the process. This is illustrated in Figure 1 for a particular process with sinusoidal evolution in κ and constant T . The conclusion is that if we were to misinterpret $\langle \Omega \rangle$ as irreversible entropy change during a non-equilibrium process, then we should expect to see temporary violations of the law of inexorable entropy increase. What we see in Figure 1 is, in fact, the quite acceptable temporary decrease in the mean accumulated dissipative work at various stages of the process.

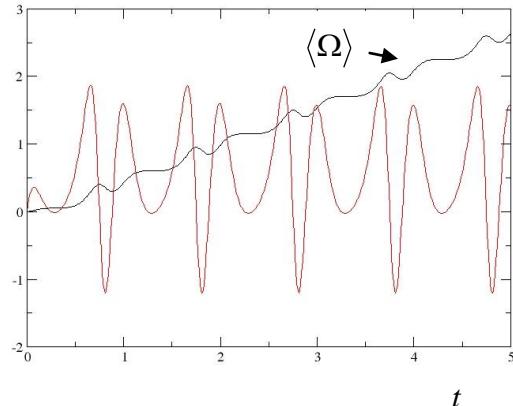


Figure 1. The behaviour of the mean value of the dissipation functional for an isothermal process with a sinusoidally varying spring constant. The horizontal axis is time, the curve indicated with an arrow is $\langle \Omega \rangle$ and the other curve is its gradient, indicating that the rate of change of mean dissipation functional can be negative. Notice, though that $\langle \Omega \rangle$ is always positive.

We have numerically determined the probability distribution of Ω at a selected times after the start of the process. The example distribution illustrated in Figure 2 has a substantial extension into the range of negative Ω . Such behaviour, if the system has ended the process in thermal equilibrium, would suggest that entropy might occasionally be destroyed during the process. It should be noted that this would become much less likely for a system with many more degrees of freedom. In the thermodynamic limit, entropy destruction becomes statistically improbable. In any case, the change in entropy is more accurately the mean of this distribution, which is positive. Clearly one has to tread extremely carefully when specifying exactly what is meant by entropy change.

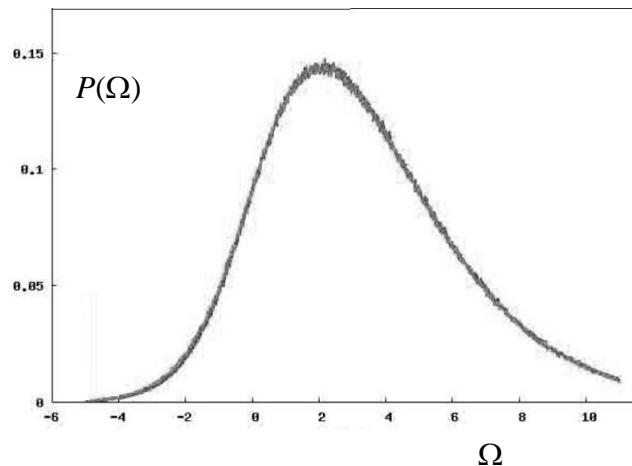


Figure 2. The distribution of values of dissipation functional Ω over an ensemble of paths for a harmonic oscillator undergoing a particular thermomechanical process.

References

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