Stochastic Thermodynamics*

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Standard thermodynamics pertains to a system in equilibrium. The meaning of equilibrium is that all fields such as temperature, pressure, magnetic, electric fields, etc., are held fixed, and the system is allowed sufficient time so that all dynamical variables, e.g., position, momentum, and their functions, remain constant in time, on the average. If any of the aforesaid fields is changed to another value, the system, in general, is expected to come to a new equilibrium after a time much longer than what is known as the ‘relaxation time’. Standard thermodynamics, however, does not touch upon the issue of the relaxation time or the time-evolution of the system. In recent years, there has been an upsurge of interest in nanoscience, especially in the context of biology and materials, wherein the systems of interest are so tiny that they are hardly ever in equilibrium. Therefore, there is a need to go beyond standard thermodynamics and treat fluctuating, time-dependent effects. Stochastic Thermodynamics is one such important development that is pedagogically reviewed in this article. Our treatment will be restricted to classical systems.

1. Introduction

Thermodynamics is often referred to as ‘The Mother of All Sciences’, embracing physics, chemistry, and biology. Interestingly, the subject evolved from man’s quest for deriving energy from heat sources in order to perform useful work. Thus were born engines—Carnot, Otto, Rankin, and Ericsson—which ushered in the first industrial revolution. It was evident from the beginning

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**Keywords**

Engine, thermodynamics, statistical mechanics, dissipation, Langenvin equation, stochastic thermodynamics.
that not all the heat can be converted to work, leading to the concept of efficiency—the ratio of the work to heat—that can never reach 100%. Indeed the Carnot cycle (1824) led Clausius (1854) to develop the concept of entropy and the formulation of the laws of thermodynamics [1].

The usual treatments of thermodynamics [2–6], based on potentials such as Helmholtz free energy, Gibbs free energy, enthalpy, etc., are restricted to systems in thermal equilibrium. However, if external conditions are altered, equilibrium is disturbed, and there arises a need to incorporate fluctuations and dissipative effects. Interestingly, this is true even for steady-state (i.e., time-independent) attributes, e.g., the electrical conductivity (discussed in Sec. 3), which is the response to an electric field. Therefore, this article aims to develop non-equilibrium effects a la what is currently phrased as stochastic thermodynamics. While macroscopic concepts of free energy, entropy, etc., are applicable to large systems, e.g., locomotive engines, condensed matter, etc., stochastic thermodynamics is highly relevant for nano entities, e.g., colloidal particles, biopolymers, molecular motors, etc., wherein fluctuations are ubiquitous.

In order to motivate the reader, we present a very brief overview of thermodynamics and statistical mechanics in Sec. 2. In Sec. 3, we remind the reader of how college and university students almost inadvertently bump into the concepts of dissipation, though the underlying profound ideas stay elusive. These concepts are further built up in Sec. 4, in terms of the Langevin equation that anchors the mathematical depiction of Brownian motion and diffusion. Some of the details are relegated to the Appendix (intended for the more advanced and curious reader). With this background material of Sec. 2–4, we get down to the main task of introducing stochastic thermodynamics, in Sec. 5. The formulation is illuminated in Sec. 6 with the aid of an illustrative example of a harmonic oscillator that allows for a tutorial exercise on—where we began—viz., the efficiency of engines. Our principal conclusions are summarized in Sec. 7.
2. Thermodynamics and Statistical Mechanics: Salient Features

The first two laws of thermodynamics can be summarized as [2–3],

\[ \Delta Q = dU + \Delta W, \]  \hspace{1cm} (1)

\[ \Delta Q = T \Delta S. \] \hspace{1cm} (2)

Here, \( Q \) stands for heat, \( U \) for energy (also called internal energy), \( W \) for work, \( S \) for entropy, and \( T \) for the temperature. The symbol \( \Delta \) prefixing \( Q \) and \( W \) underscores the fact that the corresponding quantities signify incremental heat and incremental work, respectively. On the other hand, the straight ‘d’ in front of \( U \) means that the latter is an exact differential, i.e., when integrated, yields only the end-point results. The first law of thermodynamics (1) suggests that not all of the heat \( Q \) supplied to a system can be converted to useful work \( W \)—a part of the heat goes to increase the internal energy \( U \). Therefore, the efficiency of an engine \( \eta = (W/Q) \) is always bounded by unity.

While heat can be physically perceived—we burn our finger if we accidentally touch fire—the second law, (2), contains two enigmatic entities: the temperature \( T \) and the entropy \( S \). What do they mean? The answer is satisfactorily obtained when the ‘macroscopic’ subject of thermodynamics is ensconced upon the base of ‘microscopic’ mechanics. Thus, \( T \) gets related to the average (denoted by \( < \ldots > \) below) of the kinetic energy (K.E.), of kinetic theory and \( S \) to the logarithm of the number of microstates \( \Omega \)—an idea shaped by statistical mechanics:

\[ < \text{K.E.} > \sim k_B T, \] \hspace{1cm} (3)

\[ S \sim k_B \log (\Omega). \] \hspace{1cm} (4)

Intriguingly, the prefactor in the right hand side of both (3) and (4) is the same constant \( k_B \) attributed to Boltzmann (1844–1906), a leading founding figure of both kinetic theory and statistical mechanics. It is the latter subject which provides a microscopic...
elucidation of thermodynamics through what is called the partition function $Z$, defined by [3–7].

$$Z = \text{Tr}\{\exp(-H/k_B T)\}, \quad (5)$$

where, $\text{Tr} [...]$ denotes a sum over all the microstates which in practical terms can be taken as the eigenstates of an underlying Hamiltonian $H$ (kinetic plus potential energy). While $H$ contains all the microscopic variables such as the position and momentum, the ‘tracing’ operation leads to the macroscopic attribute of $Z$. Indeed, the route to thermodynamics is paved by the formula:

$$Z = \exp(-F/k_B T), \quad (6)$$

where $F$ in thermodynamics is known as the Helmholtz free energy:

$$F = U - TS. \quad (7)$$

The further contact with thermodynamics is facilitated by the relation:

$$U = \langle H \rangle = k_B T^2 \langle \partial/\partial T \rangle \{ \log (Z) \}. \quad (8)$$

The meaning of the partial derivative with respect to temperature $T$ is that in the process, all other variables such as volume, pressure, etc., are kept constant.

It is then evident that $F$ and $U$ provide the complete (and essential) link via the partition function $Z$, between thermodynamics and statistical mechanics. This can be appreciated further by rewriting the laws of thermodynamics, (1), as

$$\Delta W = T dS - dU = -dF - S dT. \quad (9)$$

Clearly then, the work done in the context of an engine can be computed by simply integrating $U$ over an iso-entropic process or
integrating $F$ over an isothermal process. On the other hand, $U$ and $F$ can be independently calculated \textit{a la} Z. It should be added that $\Delta W$ itself is determined by $PdV$ (for mechanical work) or—$BdM$ (for magnetic work) or $Ed\Pi$ (for electrical work). (Here, $P$ is the pressure, $V$ is the volume, $B$ is the magnetic field, $M$ is the magnetization, $E$ is the electric field, and $\Pi$ is the polarization.)

3. Dissipative Effects

Given this background to thermodynamics and its foundational basis of statistical mechanics, it is important to reflect on the fact that both these subjects necessarily presume the system at hand to be in equilibrium. The meaning of ‘equilibrium’, as mentioned earlier, is that the average values of all dynamical variables are independent of time. This implies that the underlying theories are incapable of dealing with how the system under consideration evolves in time. For instance, if an external magnetic field is applied to disturb the magnetic equilibrium, one can only discuss what happens when the system eventually settles to a new equilibrium—the passage to the final state is beyond the realm of thermodynamics and statistical mechanics.

However, the fact that heat engines cannot reach the maximum efficiency of 100% tacitly indicates that there are dissipative forces at work; dissipation is a ubiquitous fact of nature. If there were no friction, we would not be able to walk; cars would not be able to run, etc. This should not come as a surprise to high school students because the underlying concepts already show up in the physics curriculum. We will take two examples, one from mechanics and the other from electricity, to illustrate where dissipation is encountered.

3.1 Ball Falling Through Oil

Consider the familiar instance of a spherical ball of radius $a$ and mass density $\rho_b$ being dropped in a tall jar containing a viscous medium of some oil of mass density $\rho_o$ [8]. But for friction/dissipation, the ball would have continued to accelerate downwards, instead, The fact that heat engines cannot reach the maximum efficiency of 100% tacitly indicates that there are dissipative forces at work; dissipation is a ubiquitous fact of nature.
it attains a steady velocity governed by the equation for the velocity $v$ (in the direction of gravity):

$$\frac{dv(t)}{dt} = g(1 - \rho_a/\rho_b) - \Upsilon v(t). \quad (10)$$

The first term on the right-hand side is the buoyancy-subtracted pull downward on account of the acceleration due to gravity $g$, whereas, the last second term on the right arises from the thrust upward as a result of friction characterized by the coefficient $\Upsilon$. The latter is related through the Stokes relation to the viscosity $\zeta$ by

$$\Upsilon = 6\pi a \zeta. \quad (11)$$

The discerning student would note the remarkable fact that (10) does not remain invariant if the time $t$ is switched to $-t$ that leads to $v(-t) = -v(t)$! Thus time-reversal invariance—sacrosanct for microscopic equations of motion is violated if there is dissipation! ‘Why’ and how (10) is to be understood only in an averaged ‘semi-macroscopic’ sense will be discussed below. Suffice it to say at this stage that in the steady-state the ‘terminal’ velocity is given by

$$v_{\text{st}} = g(1 - \rho_a/\rho_b)/\Upsilon, \quad (12)$$

which, in combination with (11), yields a laboratory measurement of $\zeta$.

### 3.2 Ohm–Drude Law

Consider the current through a metallic wire due to a battery creating an electric field $E$ through the wire. Again the equation of motion of the charge carrier—electron in the present instance—is identical in form to (10) above [9, 10]:

$$\frac{dv(t)}{dt} = -eE/m_e - v(t)/\tau. \quad (13)$$
The only small difference is that the gravity-term is replaced by the force due to the electric field \( E \) (\( -e \) being the charge and \( m_e \) the mass of the electron), and the friction coefficient \( \Upsilon \) is substituted as \( 1/\tau \). In the context of electrical conduction, \( \tau \) is variously called scattering time, collision time, or relaxation time.

The above equation can be recast in a more familiar structure of current \( I \) in a wire of length \( l \), area of cross-section \( A \), resistance \( R \) and inductance \( L \), driven by an electromotive force \( \varepsilon \) as

\[
\frac{dI(t)}{dt} = \varepsilon /\left[L - (R/L)I(t)\right], \quad (13')
\]

if we identify \( \tau \) as \( L/R \) (\( R = \rho l/A \), \( \rho \) being the specific resistance).

Further connection with the Ohm–Drude law is made by looking at the steady-state velocity, relating the latter to the current density, and using Ohm’s law:

\[
J = -nev_{st} = \sigma E. \quad (14)
\]

The electrical conductivity \( \sigma \) is then given by the Drude relation in terms of the number density \( n \):

\[
\sigma = ne^2 \tau/m. \quad (15)
\]

This relation is consistent with the expression of \( R \) in (13') if we remember that \( \sigma = 1/\rho \).

The remarkable aspect of Eqs. (12) and (15)—describing non-equilibrium evolution in two distinct physical contexts—is that they contain steady-state attributes which nonetheless depend on dissipative parameters \( \Upsilon \) and \( \tau \). Where do they originate? The answer is provided by Einstein’s analysis of the Brownian motion [11]. Whether it is a ball falling down a viscous substance or an electron moving through a resistive wire, the moving object suffers damping because of interaction with the surrounding composed of liquid molecules as in the example in Sec. 3.1, or defects/phonons/other electrons as in the example in Sec. 3.2 on the Ohm–Drude law. Is it then possible to dovetail such damp-
ing parameters to the laws of thermodynamics, especially to heat transfer $\Delta Q$, which inevitably must connote to dissipation.

Before answering this question, it is meaningful to seek a microscopic genesis of damping by explicitly bringing in the surrounding degrees of freedom. This leads to what is called the Langevin equation, which is discussed in Sec. 4 below and the Appendix.

4. Langevin Equation

Take for instance (10) which can be rewritten in a more general context of a conservative system in terms of the momentum $p$ and the potential energy $V(x)$, as

$$\frac{dp(t)}{dt} = -\frac{dV(x)}{dx} - \eta p(t). \tag{16}$$

Though (16) is in one dimension, generalization to three dimensions is straightforward. Now, having recognized that the friction $\eta$ originates, in the example of Sec. 3.1, from the cumulative effect of collisions with the surrounding oil molecules, we can model the random collisions in terms of a stochastic force $f(t)$. Thus (16) can be generalized to

$$\frac{dp(t)}{dt} = -\frac{dV(x)}{dx} - \eta p(t) + f(t). \tag{17}$$

By ‘stochastic’ we mean that the force $f(t)$ is not just a regular function of the time $t$ but keeps varying from sample to sample, i.e., $f(t)$ belongs to an ensemble of functions.

By ‘stochastic’ we mean that the force $f(t)$ is not just a regular function of the time $t$ but keeps varying from sample to sample, i.e., $f(t)$ belongs to an ensemble of functions. The only way (16) can emerge from (17) is by ensuring that the average of $f(t)$ is zero:

$$< f(t) >= 0. \tag{18}$$

Thus, (16) is to be interpreted as the ensemble-averaged version of the stochastic differential equation (17), known as the Langevin (1905) equation [12–15].

What is then the relation between the damping parameter $\eta$ and the ‘noisy’ force $f(t)$? The answer is obtained by considering the free-particle case (i.e., $V(x) = 0$) and explicitly solving (17) for
the momentum $p(t)$ as

$$p(t) = e^{-\Upsilon t} \left[ p(0) + \int_0^t dt' e^{\Upsilon t'} f(t') \right].$$  \hspace{1cm} (19)

Here $p(0)$ is the initial value of the momentum at time $t = 0$. Taking the ensemble-average of the square of (19), and employing (18) we obtain

$$< p^2(t) >= e^{-2\Upsilon t} \left[ p^2(0) + \int_0^t dt' \int_0^{t'} dt'' e^{\Upsilon (t+t'')} < f(t') f(t'') > \right].$$  \hspace{1cm} (20)

The interpretation of $< f(t') f(t'') >$ is that it measures the correlation of $f(t)$ with itself at two different times $t'$ and $t''$. Now, in the Langevin model, $f(t)$ is assumed to be purely random, i.e.,

$$< f(t') f(t'') > = 0, \text{ if } t' \neq t''$$

But, for $t' = t''$, $< f^2(t') >$ must be finite. Thus, we may write for the ‘correlation function’:

$$< f(t') f(t'') > = \Gamma \delta(t' - t''),$$  \hspace{1cm} (21)

where $\Gamma$ is a constant and $\delta(t)$ is a delta-function of $t$. Substituting (21) into (20) and carrying out the time integrals we derive

$$< p^2(t) >= e^{-2\Upsilon t} p^2(0) + \Gamma (1 - e^{-2\Upsilon t})/2\Upsilon.$$  \hspace{1cm} (22)

We now come to an important step that yields a relation between $\Gamma$—the pre-factor of the noise correlation (cf., (21))—and $\Upsilon$, the friction coefficient that appears in the ‘phenomenological’ Eqn. (16). Before we carry this out mathematically, it is instructive to ponder on the underlying idea. Imagine the example in Sec. 3.1 again, when the solid mass, as it falls under gravity, encounters random collisions from the surrounding oil molecules, which are much smaller in size. The oil is in thermal equilibrium at a fixed temperature $T$, say. Thus its molecules move with a mean kinetic energy proportional to $T$, in accordance with the equipartition theorem [3–7]. If the solid ball (of Sec. 3.1) were stationary, it would encounter collisions uniformly from all possible
directions. However, as it falls downward it meets with more oil molecules from the forward direction than from backward. The net result is an upward viscous force, which is modeled in (16–17) to be proportional to the instantaneous velocity of the ball, the proportionality constant being the friction coefficient \( \Gamma \). As the velocity increases by virtue of the acceleration due to gravity, so does the viscous force, which eventually cancels the downward gravitational force. When the net force is zero, the ball acquires a ‘terminal’ speed as it comes to equilibrium with the surrounding oil medium. At this stage, the kinetic energy of the ball must be governed by the equipartition theorem as well, concomitant with the same temperature \( T \). Mathematically then, the steady-state is implemented in (22) by setting \( t = \infty \) and simultaneously replacing the L.H.S. with \( k_B T \). Thus we arrive at the coveted relation:

\[
\Gamma = 2mTk_B T. \tag{23}
\]

Given that \( \Gamma \) measures the strength of correlation arising out of the fluctuations in the noise \( f(t) \) (cf., (21)), whereas \( \Gamma \) parameterizes dissipation (cf. (17)), (23) is the deep embodiment of the fluctuation-dissipation relation [4, 11, 12].

The underlying idea of approach-to-equilibrium of a physical system—the falling ball in Sec. 3.1, or a conducting electron driven through a resistive wire in Sec. 3.2—that it eventually reaches equilibrium with its surroundings, is a profound statement on the inner consistency of statistical mechanics. This observation, though typified here \textit{vis-á-vis} the Langevin equation, is the fundamental principle of nonequilibrium statistical mechanics. A system in interaction with the degrees of freedom of an external heat bath at a fixed temperature \( T \), if let go, would eventually attain equilibrium at the same temperature \( T \). This has prompted Kadanoff to dub the Langevin treatment of Brownian motion, sketched above, as ‘the Einstein approach to statistical mechanics’ [13]. Indeed, stochastic thermodynamics [14], discussed in the next section, is also built on the same idea. It is instructive then to indicate how the Langevin equation can be derived from the first principles,
employing a system-plus-bath approach [15]. That treatment is relegated to the Appendix.

5. Stochastic Thermodynamics

Following Sekimoto [14], we assume that the state of the system is altered by an amount \((-dx\)). Multiplying the forces in (17) by \((-dx\)) would then represent the energy balance:

\[-(dp/dr)dx = (dV(x)/dx)dx - [\mathcal{T}p(t) + f(i)]dx. \tag{24}\]

Here, the terms within the square brackets represent the forces due to the interaction between the system and the heat bath (with \(-\mathcal{T}p(t)\) being the systematic damping force, sometimes called the Stokes force and \(f(i)\) the rest of the fluctuating force).

We may now juggle the left hand side of (24) and rewrite it for incremental changes as

\[-\Delta p, \frac{\Delta x}{\Delta t} = -d(p^2/2m). \tag{25}\]

Imagine at this stage that the potential energy \(V(x)\) depends not just on the system’s coordinate \(x\) but also on another parameter \(a\) which can be independently varied. (An explicit example will be given in Sec. 6 below.) Thus we write

\[dV(x, a) = \left[ \frac{\partial V(x, a)}{\partial x} \right]_a dx + \left[ \frac{\partial V(x, a)}{\partial a} \right]_x da, \tag{26}\]

which implies that the first term on the right of (24) would have to be modified as

\[dV(x, a) - \left[ \frac{\partial V(x, a)}{\partial a} \right]_x da,\]

yielding from (24) and (25),

\[0 = d(H) - \left[ \frac{\partial V(x, a)}{\partial a} \right]_x da - [\mathcal{T}p(t) + f(t)]dx, \tag{27}\]

where

\[H = p^2/2m + V(x, a), \tag{28}\]
is the Hamiltonian of the system.

Given that the internal energy $U$, in statistical mechanics, is the average value of $H$, i.e., $< H >$ [cf., (8)], (27) has the nice interpretation *vis-à-vis* the law of thermodynamics, (1), if we recognize that $-\left[ \frac{\partial V(x,a)}{\partial a} \right]_x \, \delta a$ is the incremental work done by the system. Thus we reach the following identification as far as stochastic thermodynamics is concerned:

\[
\Delta W = \Delta Q - dU, \quad (29a)
\]
\[
\Delta U = p^2/2m + V(x,a), \quad (29b)
\]
\[
\Delta W = -\left[ \frac{\partial V(x,a)}{\partial a} \right]_x \, \delta a, \quad (29c)
\]
\[
\Delta Q = [-\tau p(t) + f(t)] \, dx. \quad (29d)
\]

The basic thermodynamic principle is encapsulated in (29). The useful work done by the system is the heat dumped into it by the external bath minus the increase in its internal energy. We must emphasize, however, that, unlike standard thermodynamics, all the quantities on the right side of (29 a–c) are fluctuating stochastic variables! The formulation is illustrated by the familiar example of a harmonic oscillator, in Sec. 6 below.

6. Harmonic Oscillator as Nano Engine

We assume that our system is a nanoparticle, the potential energy of which has the form

\[
V(x,a) = ax^2/2 = m\omega^2 x/2, \quad a = m\omega^2. \quad (30)
\]

That is, the particle is taken to be a harmonic oscillator of mass $m$ and frequency $\omega$ [16]. In order to put this system in the context of thermodynamics, the standard scenario is that the particle is in interaction with an infinitely large number of degrees of freedom that constitute a heat bath which is kept at a temperature $T$. We summarize now the well-known expressions of the thermodynamic potentials which can be derived from $Z$ of (5), wherein
the trace is replaced by a double integral over the position \( x \) and momentum \( p \), yielding

\[
U = k_B T, \quad (31a)
\]

\[
F = k_B T \log (\hbar \omega/k_B T), \quad (31b)
\]

\[
S = k_B [1 - \log (\hbar \omega/k_B T)]. \quad (31c)
\]

The expression for \( U \) is just the statement of the equipartition theorem. Here the Planck constant \( \hbar \), still appears in classical formulae, merely though as a normalization constant in the phase space integrals, as far as the partition function \( Z \) is concerned (cf., (5) and (A.9)) [4]. The underlying assumption is that the oscillator is in a box of fixed volume \( V \). It is evident that the entropy \( S \) depends only on the dimensionless ratio \( \omega (= \hbar \omega/k_B T) \), which must be kept fixed for an isentropic process. Further, in standard thermodynamics,

\[
dF = -SdT - PdV, \quad (32)
\]

which implies that \( F \) is regarded as a function of two variables \( T \) and \( V \). Here, however, as (31) shows, \( F \) is a function of \( T \) and \( \omega \). Thus, an isochoric process in the present instance can be viewed as one in which the frequency \( \omega \) is kept constant.

6.1 Efficiency from Standard Thermodynamics

The Carnot cycle is schematically shown in Figure 1. In so far as the heat transfer (from the hot source) is concerned, only the isothermal branch \( 1 \rightarrow 2 \) and the isentropic branch \( 4 \rightarrow 1 \) are relevant. The net work done is given by

\[
W = [W_{1\rightarrow 2} + W_{3\rightarrow 4}] + [W_{2\rightarrow 3} + W_{4\rightarrow 1}]. \quad (33)
\]

Separate square brackets are used here to distinguish between isothermal and isentropic processes. From the discussion below (9) it is evident then

\[
W = [(F_1 - F_2) + (F_3 - F_4)] + [(U_2 - U_3) + (U_4 - U_1)].
\]
From Figure 1, it is obvious that the terms within the second set of square brackets sum to zero, leaving behind

\[ W = k_B(T_h - T_c) \log(\omega_1/\omega_2). \]  

(34)

On the other hand, in computing the heat transfer from the hot source, we have to reckon with only the isothermal process at \( T_h \) because the isentropic process does not involve any heat transfer. Thus

\[ Q = Q_{1 \rightarrow 2} = U_{1 \rightarrow 2} + W_{1 \rightarrow 2} = W_{1 \rightarrow 2} = F_1 - F_2 = k_B T_h \log(\omega_1/\omega_2). \]  

(35)

Combining (34) and (35) we find for the efficiency of the Carnot cycle

\[ \eta = (1 - T_c/T_h), \]  

(36)

the familiar result.

**6.2 Efficiency from Stochastic Thermodynamics**

Stochastic thermodynamics allows an independent calculation of the efficiency from the equation of motion. From the detailed discussion in the text, it is expected that in the steady-state, when the engine is expected to reach thermal equilibrium, the answers in Sec. 6.1 and 6.2 should match. The incremental 'work operator' is now given by

\[ \Delta W = -m \omega^2 x^2 \, d\omega/\omega. \]  

(37)
From (33) then

\[ W = \left[ - \int_{\omega_1}^{\omega_2} d\omega \cdot <m\omega^2x^2 >_{T_h} /\omega \right. \]

\[ - \int_{\omega_3}^{\omega_4} d\omega \cdot <m\omega^2x^2 >_{T_c} /\omega \] + \]

\[ [- \int_{\omega_2}^{\omega_3} d\omega \cdot <m\omega^2x^2 >_{\alpha} /\omega \]

\[ - \int_{\omega_4}^{\omega_1} d\omega \cdot <m\omega^2x^2 >_{\alpha} /\omega \]. \]  \hspace{1cm} (38)

Here the angular brackets \(< ... >\) imply that the concerned quantities are to be evaluated in the steady-state, and the subscripts indicate either isothermal process (constant \(T\)) or isentropic process (constant \(\alpha\)). Using then the equipartition theorem for a system in thermal equilibrium,

\[ <m\omega^2x^2 >_{T_h} = 2k_BT_h, \]

\[ <m\omega^2x^2 >_{T_c} = 2k_BT_c. \]

\[ <m\omega^2x^2 >_{\alpha} = 2h\omega. \]  \hspace{1cm} (39)

The last two terms within the square parentheses in (38) then add up to zero, yielding

\[ W = k_B(T_h - T_c) \log (\omega_1/\omega_2), \] \hspace{1cm} (34')

which is identical to (34) above.

Next, the heat gained from the hot source, in the thermal equilibrium state, is

\[ Q = -\infty^{\omega_2} \omega_1 d\omega \cdot <m\omega^2x^2 >_{T} h/\omega \]

\[ = k_B T_h \cdot \log(\omega_1/\omega_2), \] \hspace{1cm} (35')

thus leading to the same result for the efficiency as in (36) above.
7. Conclusions

We have presented in this article an overview of a relatively new subject of stochastic thermodynamics that got developed over the last two decades. The presentation is carried out in a style that should be accessible to advanced high school and college students of physics and chemistry as we build up the story, step by step, from basic mechanics and thermodynamics.

The subject of stochastic thermodynamics takes us beyond the usual thermodynamics and, therefore, incorporates in a natural way dissipative parameters and *inter alia* provides a framework in which thermodynamic potentials like the internal energy and the free energy are given new interpretations in terms of dynamics. The appropriate dynamical equation is the Langevin equation, which is at the heart of Brownian motion and diffusion. A first-principles-derivation of the Langevin equation is given in the Appendix in order to put matters in perspective.

Though fluctuations in thermodynamic quantities are not explicitly treated here, there is enough indication for advanced readers to pursue such a course. We have illustrated all our derived results of stochastic thermodynamics towards computing the efficiency of a Carnot engine when the latter is viewed as a nanomotor in the form of a harmonic oscillator.

Even though our analyses are restricted to classical systems, they can be generalized to the quantum domain [16]. The necessary generalization of the model discussed here naturally involves quantum Langevin equations, in which the stochastic force $f(t)$ in (17) would be a quantum operator [17]. But because a time-varying quantum operator does not commute, even with itself, at different times, the correlation of $f(t)$ cannot be a delta function, unlike (21). What such non-Markovian-ness does to the efficiency of quantum engines, especially at low temperatures, is beyond the scope of the present article and is relegated to future work [18].
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Appendix

We now give a microscopic ‘derivation’ of the Langevin equation from a first-principles Hamiltonian, which is energy-conserving (sans dissipation), to start with. Consider then a particle of mass \( m \) in an arbitrary potential \( V(x) \), where \( x \) is the three-dimensional coordinate. The particle is in interaction with a bunch of harmonic oscillators, of mass \( m_j \) and frequency \( \omega_j \) (\( j = 1 \rightarrow N \)), through a linear coupling. The set of oscillators would eventually be viewed to constitute a heat bath. The Hamiltonian for the entire system can be written as

\[
H = \frac{p^2}{2m} + V(x) + \sum_j \left[ \frac{p_j^2}{2m_j} + m_j \omega_j^2 (x_j - C_j x/m_j \omega_j^2)^2 / 2 \right],
\]

(A.1)

where \( p(t) \) is the particle momentum, \( \{p_j, x_j\}_{j=1}^N \) are harmonic oscillator coordinates and \( C_j \)'s are coupling constants. The Newton's equations of motion can be written as

\[
\frac{dp_j}{dt} = -\frac{\partial V(x)}{\partial x} + \sum_j C_j (x_j - C_j x/m_j \omega_j^2),
\]

(A.2a)

\[
\frac{dp_j}{dt} = -m_j \omega_j^2 (x_j - C_j x/m_j \omega_j^2).
\]

(A.2b)

Combining the second equation with the definition of momentum leads to the second order differential equation:

\[
\frac{d^2 x_j}{dt^2} = -\omega_j^2 (x_j - C_j x/m_j \omega_j^2).
\]

(A.3)

This is nothing but the harmonic oscillator equation with an inhomogeneous term proportional to \( x(t) \). At this stage, it may be emphasized that all the equations of motion in (A.2–A.3) are time-reversal invariant. Toward the objective to make these equations ‘dissipative’, we carry out the first step, viz., integrate (A.3) in the forward direction of time (i.e., introduce ‘an arrow of time’):
Step 1

\[ x_j(t) = \cos(\omega_j t)x_j(0) + \sin(\omega_j t)p_j(0)/m_j\omega_j \]

\[ + (C_j/m_j\omega_j) \int_0^t dt'x(t')\sin[\omega_j(t - t')]. \quad (A.4) \]

Integrating by parts and using the definition of the momentum again, (A.4) can be re-expressed as

\[ x_j(t) - C_jx(t)/m_j\omega_j^2 = \]
\[ \cos(\omega_j t)[x_j(0) - C_jx(o)/m_j\omega_j^2] + \]
\[ \sin(\omega_j t)p_j(0)/m_j\omega_j \]
\[ + (C_j/m_j\omega_j^2) \int_0^t dt'\rho(t')\cos[\omega_j(t - t')]. \quad (A.5) \]

Substituting (A.5) into (A.2a) we arrive at

\[ \frac{dp}{dt} = -\partial V(x)/\partial x \]
\[ - \int_0^t dt'\zeta(t - t')p(t')/m + f(t), \quad (A.6) \]

where the ‘friction’ is given by

\[ \zeta(t) = \Sigma_j \cos(\omega_j t)C_j^2/m_j\omega_j^2, \quad (A.7) \]

and the ‘force’

\[ f(t) = \Sigma_j(C_j \cos(\omega_j t)[x(o)/m_j\omega_j^2] + C_j \sin(\omega_j t)p_j(0)/m_j\omega_j) \quad (A.8) \]

It is instructive to note that though (A.7) has the structure of a Langevin equation, the ‘friction’ term at time \( t \) depends on a preceding time \( t' \), thus inviting itself the epithet of a ‘memory function’. Further, both the friction and the ‘noisy’ force owe their origin to the surrounding harmonic oscillator system. In particular, \( f(t) \) is a noise in the sense of statistical ‘fluctuation’, the latter being governed by the initial values of the coordinates—of both the system and its surroundings—and the momenta. Because the friction has memory, (A.6) is referred to as a ‘generalized
Langevin equation’, which, still, however, respects time-reversal invariance!

In order to connect the noise to the systematic damping and be able to endow the surrounding system the attribute of a heat bath, we now carry out the next step in which the harmonic oscillators are taken to be in thermal equilibrium at a temperature $T$.

Step 2

We consider an initial ensemble of states in which $p(o)$ and $x(o)$ are held fixed, but the harmonic oscillator variables are drawn at random from a canonical distribution given by the Gibbs measure [4–7]

$$P(p_j(o), x_j(o)) = e^{-H/k_BT}/\Pi_j \int dp_j(o)dx_j(o)e^{-H/k_BT}. \quad (A.9)$$

It is then easy to check that

$$<f(t)> = 0, <f(t)f(t')> = k_BT\zeta(t-t'). \quad (A.10)$$

which is then the generalization of the fluctuation-dissipation relation quoted in (21) of the text.

Step 3

We now take the third step by taking the number of the number of harmonic oscillators to be infinitely large with a continuous distribution of frequencies so that

$$\Sigma_j \rightarrow N \int_{-\infty}^{\infty} d\omega g(\omega) \quad (A.11)$$

where $g(\omega)$ is the density of states. Further, we assume that all masses and coupling constants are the same:

$$m_j = m, C_j = C/\sqrt{N}. \quad (A.12)$$

From (A.7) then

$$\zeta(t) = C^2 \int_{-\infty}^{\infty} d\omega g(\omega) \cos(\omega t)/m\omega^2. \quad (A.13)$$
If \( g(\omega) \) is assumed to be quadratic in \( \omega \) with an upper cut-off \( \omega_c \), that is finally taken to be very large, then,

\[
g(\omega) = \frac{3\omega^2}{\omega_c^3}, \quad \omega < \omega_c,
\]

\[
= 0, \quad \omega > \omega_c. \quad (A.14)
\]

A physical motivation for the quadratic frequency dependence of \( g(\omega) \) and why the underlying assumption goes under the name of ‘Ohmic dissipation’, are given in the next paragraph. Using (A.14), we obtain

\[
\zeta(t) = \left( \frac{3C^2}{m\omega_c^2} \right) \sin(\omega_c t) / \omega_c t. \quad (A.15)
\]

In this regime the particle’s momentum \( p(t) \) may be assumed to vary slowly over time scales \( \omega_c^{-1} \) and the right hand side of (A.15) can be replaced by a delta function in \( t \):

\[
\zeta(t) = 2mT \delta(t).
\]

\[
T = \frac{3\pi C^2}{2m^2 \omega_c^3}. \quad (A.16)
\]

With these approximations, (A.6) reduces to the usual Langevin equation quoted in (17) of the text. The above three steps enumerated above then elucidate how irreversibility is arrived at from completely reversible equations of motion.

The assumption on the density of states \( g(\omega) \), as listed under (A.14), constitutes, what is called, the ‘Ohmic dissipation’. The name is derived from the fact that if the potential \( V(x) \) is that of a harmonic oscillator the corresponding Langevin (17) is one of a noise-driven electric charge in an LCR circuit, wherein the position \( x \) is the charge \( q \), the mass of the particle \( m \) is the inductance \( L \), \( 1/a \) (of (30)) is the capacitance \( C \) and \( 1/T \) is the resistance \( R \), as per Ohm’s law in its standard form [8].

The Carnot cycle consists of an isothermal process followed by an isentropic process, then another isothermal process culminated into an isentropic process. The nature of the latter demands that the frequencies are not independent but are governed by the relations \( \hbar \omega_3/k_B T_c = \hbar \omega_2/k_B T_h \) and \( \hbar \omega_4/k_B T_c = \hbar \omega_1/k_B T_h \).
Suggested Reading

[17] S Dattagupta and S Puri, in Ref. [15].
[18] S Dattagupta, Quantum mechanics of open systems and stochastic thermodynamics (to be submitted).