Finite time corrections to the efficiencies of heat engines based on quantum Brownian oscillator

S. Chaturvedi[1]

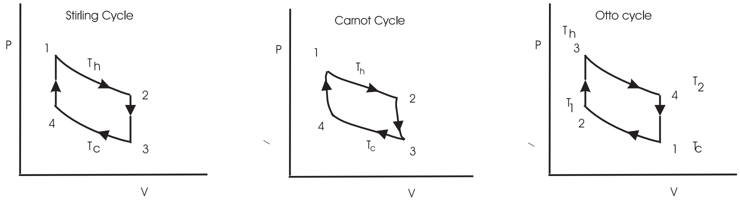
Department of Physics
IISER Bhopal
Bhopal

ISFNQC18, SNBNCBS, Kolkata

29 January 2018

[1] Based on a work in collaboration with G S Agarwal

Some important heat engines



- Stirling engine: Originally conceived in 1816 by Robert Stirling, a scottish inventor, as a rival to the steam engine.
- Carnot engine: A theoretical thermodynamic cycle proposed by Nicolas Léonard Sadi Carnot in 1823.
- Otto engine : The earliest prototype four stroke engine developed by Nikolaus August Otto in Cologne, Germany in 1876.

Microscopic realizations through a colloidal particle in a harmonic trap

Working substance : A single colloidal particle in a harmonic trap.

Externally controllable variables:

- spring constant (or equivalently the frequency ω of the trap. Can be viewed as inversely proportional to the 'volume' in the context of macroscopic heat engines.
- ambient temperature.

Stirling Engine

$$
\begin{array}{ccccccc}
\omega_1,\, T_c & & & \text{Isothermal} & & & \omega_2,\, T_c \\
 & & 3 & \longrightarrow & 4 & & \\
 & & & \tau_c & & & \\
\text{Isochoric} & & \uparrow & & \downarrow & & \text{Isochoric} \\
 & & & \tau_h & & & \\
 & & 2 & \longleftarrow & 1 & & \\
\omega_1,\, T_h & & & \text{Isothermal} & & & \omega_2,\, T_h
\end{array}
$$

$$\omega_2 > \omega_1, \;\; T_h > T_c \qquad ,$$

Realized experimentally by Blickle and Bechinger [Nature Physics **8** 143-146 (2012)].

Carnot Engine

$$\begin{array}{ccccccc}
\omega_1, T_h & & & \text{Isothermal} & & & \omega_2, T_h \\
& 1 & & \longrightarrow & & 2 & \\
& & & \tau_h & & & \\
\text{Isentropic} & \uparrow & & & & \downarrow & \text{Isentropic} \\
& & & \tau_c & & & \\
& 4 & & \longleftarrow & & 3 & \\
\omega_4, T_c & & & \text{Isothermal} & & & \omega_3, T_c
\end{array}$$

$$\omega_1 > \omega_4 > \omega_2 > \omega_3, \;\; T_h > T_c, \;\; \beta_h \omega_2 = \beta_c \omega_3, \beta_h \omega_1 = \beta_c \omega_4$$

$$\beta \equiv 1/K_B T$$

Otto Engine

$$
\begin{array}{ccccccc}
\omega_c,\, T_2 & & \text{Isentropic} & & \omega_h,\, T_h \\
& 4 & \longleftarrow & 3 & \\
& & \tau_1 & & \\
\text{Isochoric} & \downarrow & & \uparrow & \text{Isochoric} \\
& & \tau_2 & & \\
& 1 & \longrightarrow & 2 & \\
\omega_c,\, T_c & & \text{Isentropic} & & \omega_h,\, T_1
\end{array}
$$

$$\omega_h > \omega_c >, \;\; T_h > T_c, \;\; \beta_c\omega_c = \beta_1\omega_h, \;\; \beta_h\omega_h = \beta_2\omega_c, \qquad .$$

Efficiencies from Thermodynamics

The knowledge of the internal energy U and the Helmholtz free energy $F = U - TS$ for a quantum harmonic oscillator

$$U = \hbar\omega[n(\omega, T) + 1/2], \;\; n(\omega, T) \equiv \frac{1}{(e^{\beta\hbar\omega} - 1)},$$
$$F = \frac{1}{\beta}\ln(2\sinh(\beta\hbar\omega/2))$$

which in the classical limit $\beta\hbar\omega << 1$ read

$$U = 1/\beta$$
$$F(\omega, T) = \frac{1}{\beta}\ln(\beta\hbar\omega)$$

together with the the thermodynamic conservation law

$$\Delta U = \Delta Q - \Delta W;$$

enable one to compute the efficiency

$$\eta = \frac{\text{Work done by the system}}{\text{Heat flow into the system at } T_h}.$$

for the three engines:
While for the Carnot and the Otto engine the efficiency as defined turns out to be the same in both classical and quantum cases

Carnot

$$\eta_c^{\text{cl}} = \eta_c^{\text{q}} = \eta_c = \left(1 - \frac{T_c}{T_h}\right).$$

Otto

$$\eta_o^{\text{cl}} = \eta_o^{\text{q}} = 1 - \frac{U(4) - U(1)}{U(3) - U(2)} = \left(1 - \frac{\omega_c}{\omega_h}\right).$$

in the Stirling case the two differ

Stirling

$$\eta_s^{\mathrm{q}} = \frac{1 - Y/X}{1 + Z/X} \quad ,$$

$$X = \ln\left(\frac{\sinh(\beta_h \hbar\omega_2/2)}{\sinh(\beta_h \hbar\omega_1/2)}\right), \quad Y = \frac{\beta_h}{\beta_c} \ln\left(\frac{\sinh(\beta_c \hbar\omega_2/2)}{\sinh(\beta_c \hbar\omega_1/2)}\right) \quad ,$$

$$Z = \frac{\beta_h}{2}[\hbar\omega_1 \coth\left(\beta_h \hbar\omega_1/2\right) - \frac{\hbar\omega_2}{2}\{\coth\left(\beta_h \hbar\omega_2/2\right) + \coth\left(\beta_c \hbar\omega_2/2\right)\}].$$

In the classical limit

$$\eta_s^{\mathrm{cl}} = \frac{\eta_c}{1 + \eta_c / \ln(\frac{\omega_2^2}{\omega_1^2})}, \quad \eta_c = 1 - \frac{T_c}{T_h}.$$

We note that in deriving these results one has to bring in a factor of half before the second term in the denominator to make them coincide with those quoted by Blickle and Bechinger. The origin and dependence on dissipation of this factor are discussed in detail in

G S Agarwal, S. Chaturvedi Phys Rev E 88, 012130 (2013).

Need to go beyond standard thermodynamics

- To compute finite time corrections to the efficiencies of various heat engines both in the quantum and the classical cases.
- To understand the origin of the ad hoc factor of half in the context of the Stirling cycle

Beyond standard thermodynamics

To go beyond the standard thermodynamic assumptions we need a framework which treats the system modelling the engine as an open system and permitting proper inclusion of dissipative effects and the possibility of varying the sytstem potential and the ambient temperature. In the present context, such a framework is provided by the dynamics of a quantum Brownian oscillator of frequency ω in contact with a heat bath at temperature T is described by the master equation

$$\frac{\partial}{\partial t}\rho = -\frac{i}{\hbar}[\hat{p}^2/2m + \frac{1}{2}m\omega^2\hat{q}^2, \rho] \\ - \frac{2\kappa m\omega}{\hbar}(n(\omega, T) + 1/2)([\hat{q}, [\hat{q}, \rho]]) - \frac{i\kappa}{\hbar}([\hat{q}, \{\hat{p}, \rho\}]),$$

where $\hat{q}$ and $\hat{p}$ are denote the position and momentum operators obeying the commutation relations $[\hat{q}, \hat{p}] = i\hbar$.

Wigner phase space description

$$\widehat{\rho} \mapsto W_{\widehat{\rho}}(q,p) = \mathrm{Tr}\left\{\widehat{\rho}\,\widehat{W}(q,p)\right\} \;;$$

$$\widehat{W}(q,p) = \frac{1}{(2\pi\hbar)} \int_{-\infty}^{\infty} dq' \; |q + \frac{1}{2}q'\rangle\langle q - \frac{1}{2}q'| \; e^{i\,pq'/\hbar},$$

Use of the Wigner description turns the master equation into a Fokker-Planck equation for $W(q,p)$

$$\frac{\partial}{\partial t}W = [-\frac{\partial}{\partial q}\left(\frac{p}{m}\right) + \frac{\partial}{\partial p}\left(2\kappa p + \left(\frac{\partial V(q,a)}{\partial q}\right)\right) + D\frac{\partial^2}{\partial p^2}]W,$$

where

$$V(q,a) = \frac{1}{2}aq^2, \qquad a \equiv m\omega^2,$$

and

$$D = 2m\hbar\omega\kappa(n(\omega,T) + \frac{1}{2}), \quad n(\omega,T) = (e^{\beta\hbar\omega} - 1)^{-1}.$$

The parameter a, the ‘spring constant’, will be taken to be controlled externally.

The Langevin equations equivalent to the above FPE read:

$$\dot{q} = \frac{p}{m},$$
$$\dot{p} = -2\kappa p - \frac{\partial}{\partial q} V(q,a) + f(t),$$
$$< f(t) f(t') >= 2D\delta(t-t').$$

The LE's lend themselves to a nice thermodynamics intepretation :
Rewriting the second as

$$-(-2\kappa p + f(t)) + \dot{p} + \frac{\partial}{\partial q} V(q,a) = 0,$$

and multiplying it by dq and using

$$dV = \frac{\partial V(q,a)}{\partial q} dq + \frac{\partial V(q,a)}{\partial a} da,$$

one obtains

$$-(-2\kappa p + f(t))dq + d(p^2/2m + V(q,a)) - \frac{\partial V(q,a)}{\partial a}da = 0$$

The three terms in the above equation may now be identified in an intuitively plausible manner as:

$$d\mathcal{Q} = (-2\kappa p + f(t))dq,\ \ d\mathcal{U} = d(p^2/2m + V),$$
$$d\mathcal{W} = -\frac{\partial V(q,a)}{\partial a}da,$$

leading to the energy balance equation:

$$-d\mathcal{Q} + d\mathcal{U} + d\mathcal{W} = 0,$$

with $d\mathcal{Q}$ (-$d\mathcal{Q}$) understood as the heat flow into of (out) the system and $d\mathcal{W}$ (-$d\mathcal{W}$) as the work done by (on) the system.

The stochastic averages of these quantities denoted by dQ,dU and dW respectively relate directly to the corresponding thermodynamic quantities and capture the thermodynamic conservation laws.

The computation of the work done, heat absorbed can now be carried out from the knowledge of $\langle q^2\rangle, \langle p^2\rangle, \langle qp\rangle$
Thus, for instance, calculation of ΔW for the $1 \to 2$ step of the Carnot engine :

$$\Delta W_{1\to 2} = \int_1^2 d\mathcal{W} = -\int_{\omega_1}^{\omega_2} m\omega\langle q^2\rangle_{T=T_c} d\omega,$$

$$\Delta U_{1\to 2} = \int_1^2 dU$$

$$= \left(\frac{\langle p^2\rangle}{2m} + \frac{1}{2}m\omega^2\langle q^2\rangle\right)_2 - \left(\frac{\langle p^2\rangle}{2m} + \frac{1}{2}m\omega^2\langle q^2\rangle\right)_1$$

One recovers the results from thermodynamics when the relevant moments appearing in these expressions are replaced by their steady state values.

Finite time corrections: Complementarity relations

We next consider the situation when the system starts out at equilibrium with a bath at temperature T, and the frequency is changed from its initial value ω_0 to its final value ω_1 in a finite time either isothermally (T held fixed) or isentropically (ω/T held fixed) and focus on computing finite time corrections to the standard thermodynamic results.

The equations for the second moments that follow from the Langevin or the Fokker-Planck equation may be written as

$$\frac{d}{dt}X(t) = A(t)X(t) + Y(t),$$

where

$$X(t) = \begin{pmatrix} \langle q^2 \rangle \\ \langle qp \rangle \\ \langle p^2 \rangle \end{pmatrix}, A(t) = \begin{pmatrix} 0 & \frac{2}{m} & 0 \\ -m\omega^2(t) & -2\kappa & \frac{1}{m} \\ 0 & -2m\omega^2 & -4\kappa \end{pmatrix},$$

$$Y(t) = \begin{pmatrix} 0 \\ 0 \\ 2D(t) \end{pmatrix}.$$

(At this stage, as indicated, we allow the frequency and the diffusion coefficients to be independent functions of t, Later however, we would specialise to situations appropriate to isothermal or isentropic variation of the frequency.)

Putting $t = s\tau$ and expanding $X(t)$ as

$$X(t) = X^{(0)}(s) + \frac{1}{\tau}X^{(1)}(s) + \cdots ,$$

we obtain

$$A(s)X^{(0)}(s) + Y(s) = 0 \Rightarrow X^{(0)}(s) = -A^{-1}(s)Y(s),$$
$$X^{(1)}(s) = A^{-1}(s)\frac{d}{ds}X^{(0)}(s).$$

The first of these equations can be taken to describe the situation where the system is in the steady state corresponding to the instantaneous values of ω and D and the second as describing deviations from this steady state. These equations then give

$$\langle q^2(s)\rangle^{(0)} = \frac{D(s)}{2m^2\omega^2(s)\kappa}; \langle q(s)p(s)\rangle^{(0)} = 0;$$
$$\langle p^2(s)\rangle^{(0)} = \frac{D(s)}{2\kappa},$$

and

$$\langle q^2(s)\rangle^{(1)} = -[\frac{8\kappa^2 + 2\omega^2(s)}{8\kappa\omega^2(s)}\frac{d}{ds}\langle q^2(s)\rangle^{(0)}$$
$$+ \frac{1}{m\omega^2(s)}\frac{d}{ds}\langle q(s)p(s)\rangle^{(0)} + \frac{1}{4\kappa m^2\omega^2(s)}\frac{d}{ds}\langle p^2(s)\rangle^{(0)}],$$
$$\langle q(s)p(s)\rangle^{(1)} = \frac{m}{2}\frac{d}{ds}\langle q^2(s)\rangle^{(0)}$$
$$\langle p^2(s)\rangle^{(1)} = -[\frac{m^2\omega^2(s)}{4\kappa}\frac{d}{ds}\langle q^2(s)\rangle^{(0)} + \frac{1}{4\kappa}\frac{d}{ds}\langle p^2(s)\rangle^{(0)}].$$

These equations give finite time corrections to the variances. As the diffusion coefficient is a function of both ω and T we now specialize to the situations where

- (a) ω is time dependent, T is held fixed (Isothermal Case)
- (b) ω, T both are time dependent but ω/T is held fixed (Isentropic case).

Carnot engine

$$
\begin{array}{ccccc}
\omega_1,\ T_h & & \text{Isothermal} & & \omega_2,\ T_h \\
 & 1 & \longrightarrow & 2 & \\
 & & \tau & & \\
\text{Isentropic} & \uparrow & & \downarrow & \text{Isentropic} \\
 & & \tau & & \\
 & 4 & \longleftarrow & 3 & \\
\omega_4,\ T_c & & \text{Isothermal} & & \omega_3,\ T_c
\end{array}
$$

$$\omega_1 > \omega_4 > \omega_2 > \omega_3, \;\; T_h > T_c,$$
$$\beta_h\omega_2 = \beta_c\omega_3, \beta_h\omega_1 = \beta_c\omega_4,$$

Here we compute the finite time corrections to the Carnot efficiency

$$\eta = 1 - \frac{|Q_{3\to 4}|}{|Q_{1\to 2}|}$$

for the case when the two isothermal steps are carried out in a finite time τ with ω varied so as to minimize irreversible work. For simplicity we give the results in the classical case.

In the overdamped regime

$$\eta = 1 - \frac{\beta_h}{\beta_c} \frac{\left[1 + \frac{3\kappa}{\tau} \frac{1}{\ln\left(\frac{\omega_4}{\omega_3}\right)} \left(\frac{1}{\omega_3} - \frac{1}{\omega_4}\right)^2\right]}{\left[1 - \frac{3\kappa}{\ln\left(\frac{\omega_4}{\omega_3}\right)} \left(\frac{\beta_h}{\beta_c}\right)^2 \left(\frac{1}{\omega_3} - \frac{1}{\omega_4}\right)^2\right]}$$

$$\approx \eta_c - \frac{3\kappa}{\tau} \left(\frac{T_c}{T_h}\right) \left[1 + \left(\frac{T_c}{T_h}\right)^2\right] \frac{1}{\ln\left(\frac{\omega_4}{\omega_3}\right)} \left(\frac{1}{\omega_3} - \frac{1}{\omega_4}\right)^2$$

In the underdamped regime on the other hand one finds

$$\eta = \eta_c - \frac{1}{\kappa\tau}\left(\frac{T_c}{T_h}\right)\ln\left(\frac{\omega_4}{\omega_3}\right)$$

Complementarity relations
Efficiency at maximum power
Work fluctuations

....