A quasi-static process, despite being an idealized concept, is of great importance in equilibrium thermodynamics. Several textbook models of heat cycles such as Carnot cycle, Otto cycle and so on, are based on these processes which run infinitely slowly, but may or may not be reversible. Further, any framework for nonequilibrium processes involving rates and fluxes, quite understandably, must approach the limiting case of equilibrium theory when these fluxes become negligible in response to vanishing thermodynamic forces. In particular, in the linear response regime, the generalized fluxes are assumed to be linear functions of the forces. The resulting linear-irreversible framework is immensely successful in unifying diverse, coupled phenomena such as Seebeck, Peltier, Dufour effects and so on.

In this letter, we apply the linear-irreversible framework to a heat engine operating between two heat reservoirs. The restriction to near-equilibrium conditions demands that the temperature difference between the reservoirs is small and the duration of the heat cycle (τ) is sufficiently long. Further, the generalized fluxes are not defined as instantaneous quantities (time derivatives of macroscopic variables, as in Onsager formalism), but as time-averages over one cycle (X/τ). We determine the constraints on the Onsager coefficients in the flux-force relations, taking into account the ideal limits of quasi-static and reversible cycles. A connection will be established between the reciprocal property of Onsager coefficients and the equivalence of quasi-static and reversible cycles. It is shown that violation of this reciprocity implies that quasi-static and reversible cycles are not equivalent. Further, it is possible to construct a reversible cycle in a finite duration, or in other words, achieve a finite power output at Carnot efficiency.

Let Qh denote the heat absorbed in one cycle from the hot reservoir at temperature Th, and Qc be the amount of heat rejected to the cold reservoir at temperature Tc. The work performed by the engine is

\[ W = Q_h - Q_c > 0, \quad (1) \]

while the total change in the entropy of the reservoirs is

\[ \Delta S = \frac{Q_c}{T_c} - \frac{Q_h}{T_h}, \quad (2) \]

The working medium undergoes a cycle and so does not involve a net change in its entropy. Now, if Qc is treated as a floating variable, it may be eliminated from Eqs. (1) and (2), so that the second law inequality (ΔS ≥ 0) implies W ≤ QhηC, where ηC = 1 - Tc/Th is the Carnot efficiency. Thus, the second law sets an upper bound for work as Wrev = QhηC, obtained under a reversible operation (ΔS = 0). In general, we can write

\[ W = W_{\text{rev}} - T_c \Delta S, \quad (3) \]

The deficit, Wrev - W, is referred to as the lost work—the energy that is not available for work during the irreversible operation.

Now, let us consider the time-dependence of the energy-conversion process. The rate of total entropy production per cycle, \( \dot{S} = \Delta S/\tau \), can be written as:

\[ \dot{S} = \frac{1}{\tau} \left( \frac{W}{T_c} \right) + \dot{Q}_h \left( \frac{1}{T_c} - \frac{1}{T_h} \right), \quad (4) \]

where \( \dot{Q}_h = Q_h/\tau \). Following the flux-force framework of linear-irreversible thermodynamics, we identify two generalized fluxes (Ji) and the corresponding thermodynamic forces (Xi):

\[ J_1 = \frac{1}{\tau}, \quad X_1 = -\frac{W}{T_c}, \quad \text{and} \]
\[ J_2 = \dot{Q}_h, \quad X_2 = \frac{1}{T_c} - \frac{1}{T_h}, \quad (5) \]

which imply \( \dot{S} \equiv J_1 X_1 + J_2 X_2 \). J1 is the number of cycles executed per unit time, and so represents the rate at which the heat cycle proceeds. Since the forces and the fluxes are assumed to be small, we are dealing here with long cycle durations close to equilibrium. The process 2, satisfying \( J_2 X_2 > 0 \), denotes a spontaneous process leading to positive entropy production, while the process 1 with \( J_1 X_1 < 0 \) is the driven or non-spontaneous process which cannot proceed in the absence of process

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2. The linear regime implies that the flux-force relations are in the form: $J_i = \sum_{j=1}^{2} L_{ij} X_j$, where $i = 1, 2$. Here, the phenomenological coefficients $L_{ij}$ will be referred to as Onsager coefficients. They are assumed fixed within the regime of small forces. Then, $\dot{S}$ becomes a binary quadratic form in $X_1$ and $X_2$, and the inequality $\dot{S} \geq 0$ imposes the following conditions:

$$L_{11}, L_{22} \geq 0, \quad 4L_{11}L_{22} \geq (L_{12} + L_{21})^2.$$  \hspace{1cm} (7)

There seems no reason, per se, to assume the reciprocal relation ($L_{12} = L_{21}$) which was originally derived by Onsager from the principle of microscopic reversibility and the theory of equilibrium fluctuations \cite{2}.

Explicitly, the flux-force relations are given by:

$$\frac{1}{\tau} = -L_{11} \frac{W}{T_c} + L_{12} \frac{\eta_c}{T_c}, \hspace{1cm} (8)$$

$$\frac{Q_h}{\tau} = -L_{21} \frac{W}{T_c} + L_{22} \frac{\eta_c}{T_c}. \hspace{1cm} (9)$$

Assuming $L_{11} > 0$, we can eliminate $W$ from the above pair of equations, to write:

$$\frac{Q_h}{\tau} = \frac{L_{21}}{L_{11}} \frac{1}{\tau} + \left| L \right| \frac{\eta_c}{L_{11} T_c}. \hspace{1cm} (10)$$

where the determinant $|L| = L_{11}L_{22} - L_{12}L_{21}$ satisfies $|L| \geq 0$. Let us first assume, $|L| = 0$, which is also known as the tight-coupling condition \cite{8}. Under this condition, the fluxes $J_1$ and $J_2$ become proportional to each other. Therefore, Eq. (10) yields:

$$Q_h = \frac{L_{21}}{L_{11}} > 0, \hspace{1cm} (11)$$

which requires $L_{21} > 0$. Then, from the $|L| = 0$ condition, we have $L_{12} \geq 0$.

Now, consider the approach towards the quasi-static operation ($\tau \rightarrow \infty$) in Eq. (8). The work output in this limit is given by: $W_{qs} = (L_{12}/L_{21}) \eta_c$. Then, Eq. (8) may be rewritten in the form:

$$W = W_{qs} - \frac{T_c}{L_{11} \tau}. \hspace{1cm} (12)$$

Thus, the work output may be controlled by varying $\tau$, while the magnitude of $Q_h$ is kept fixed. So, as $\tau$ is decreased, the work output decreases and vanishes at the minimum duration: $\tau_{min} = T_c/L_{12} \eta_c$.

It is well known that a quasi-static operation may or may not imply a reversible operation \cite{11,9}. If it does, then as $\tau \rightarrow \infty$ for our cycle, we also have $\Delta S \rightarrow 0$. This equivalence has a number of interesting consequences. We can now write: $W_{qs} = W_{rev}$, which yields $Q_h = L_{12}/L_{11}$. Upon comparison with Eq. (10), we obtain:

$$L_{12} = L_{21}, \hspace{1cm} (13)$$

thus obtaining the reciprocal relation for Onsager coefficients. Conversely, from the general relations derived above, we can write: $W_{qs} = (L_{12}/L_{21})W_{rev}$. Thus, the validity of Onsager reciprocity for macroscopic linear-irreversible, cyclic engines implies that quasi-static and reversible operations of the engine are equivalent. This is the first main result of this letter.

Furthermore, under the condition $W_{qs} = W_{rev}$, the comparison of Eqs. (5) and (12) yields:

$$\Delta S = \frac{1}{L_{11}}. \hspace{1cm} (14)$$

Thus, the total entropy produced varies inversely with the cycle duration—consistent with the assumption that the quasi-static operation implies reversible operation.

On the other hand, a quasi-static process may not be reversible, and involve some entropy production $\Delta S_{qs} > 0$. A familiar situation is the presence of friction between different parts of the engine, which may not vanish even if the cycle is made infinitely slow. Then, from Eq. (3), we can write: $W_{qs} = W_{rev} - T_c \Delta S_{qs}$. So, in general, we have: $W_{qs} \leq W_{rev}$, which implies that $L_{12} \leq L_{21}$. Thus, the condition $L_{12} < L_{21}$ represents the fact that the quasi-static work is less than the reversible work—indicating the presence of friction or viscous forces. Related to this, we also have the result for quasi-static efficiency: $\eta_{qs} = W_{qs}/Q_h = (L_{12}/L_{21}) \eta_c \leq \eta_c$.

If $|L| > 0$, then from Eq. (10), $Q_h$ diverges in the quasi-static limit \cite{10}. Since $W_{qs}$ is finite, so the efficiency vanishes in the quasi-static limit. Clearly, the latter does not imply a reversible cycle in the $|L| > 0$ case. A natural and intriguing question here is whether it is possible to achieve reversible operation in a finite duration (since $Q_h$ is finite). In recent years, the possibility of achieving the Carnot efficiency in finite time, or in other words, a finite power output along with Carnot efficiency, has attracted attention \cite{11,10}. We now approach this issue for the case of cyclic, linear-irreversible engines.

Eliminating $\tau$ from Eqs. (8) and (9), and using the reversible work condition, $W = Q_h \eta_c$, we obtain the quadratic equation: $L_{11} Q_h^2 - (L_{12} + L_{21})Q_h + L_{22} = 0$, whose solutions are:

$$Q_h = \frac{L_{12} + L_{21} \pm \sqrt{(L_{12} + L_{21})^2 - 4L_{11}L_{22}}}{2L_{11}}. \hspace{1cm} (15)$$

The only real solution in the above is obtained when the the third condition in Eq. (7) reduces to an equality:

$$(L_{12} + L_{21})^2 = 4L_{11}L_{22}, \hspace{1cm} (16)$$

and therefore

$$Q_h = \frac{L_{12} + L_{21}}{2L_{11}} \geq 0. \hspace{1cm} (17)$$

The magnitude of the reversible work—performed in a finite duration—is then given by $W_{rev} = (L_{12} + L_{21}) \eta_c/2L_{11}$. Note that the above expression for $Q_h$ holds specifically for the reversible operation. Unlike the
The duration $\tau_{rev}$ of the reversible cycle can be calculated from Eqs. (8) and (17) as:

$$\frac{1}{\tau_{rev}} = (L_{12} - L_{21}) \frac{\eta_C}{2T_c},$$

which requires $L_{12} \geq L_{21}$. Using the positivity condition on the quasi-static work, $W_{qs} = (L_{12}/L_{11})\eta_C > 0$, we can set $L_{12} > 0$. Then, the inequality $L_{12} + L_{21} \geq 0$ in Eq. (17) implies that $L_{21} \geq -L_{12}$. These considerations constrain the possible values of $L_{21}$ as follows:

$$-L_{12} \leq L_{21} \leq L_{12}.$$  

Since, the minimum allowed value of $L_{21}$ is $-L_{12}$, so the minimum value of $\tau_{rev}$ is $T_c/L_{12}\eta_C \equiv \tau_{min}$ at which the work output vanishes. On the other hand, for $(L_{12} - L_{21}) \to 0^+$, we have $\tau_{rev} \to \infty$, implying that if Onsager reciprocity holds, then the reversible operation is obtained only in the quasi-static limit. In other words, Onsager reciprocity must be violated for the heat cycle undergoing reversible operation in a finite duration.

The power output at reversible operation, $P_{rev} = W^{rev}_{\tau}/\tau_{rev}$, is given by:

$$P_{rev} = \frac{L_{12}^2 - L_{21}^2}{4L_{11}} \frac{\eta_C^2}{T_c}.$$  

Thus, for a given value of $L_{12}$, the power output at reversible operation vanishes at both the extreme values of $L_{21}$ (Eq. (19)): at its minimum value, we have zero work output, whereas at the maximum value of $L_{21}$, the Onsager reciprocity holds, leading to a diverging duration of the reversible cycle.

Using the second inequality in Eq. (19), we can write $(L_{12}/L_{11})\eta_C \geq (L_{12} + L_{21})\eta_C/2L_{11}$, or $W_{qs} \geq W^{rev}_{\tau}$, where the equality is obtained when $\tau_{rev} \to \infty$ (see Eq. (18)). Thus, we have the interesting result that the finite-time reversible work is bounded from above by the quasi-static work. Based on the results obtained so far, we may order the different work outputs as follows:

$$W^{(\tau)}_{rev} \leq W_{qs} \leq W_{rev}.$$  

Fig. 2 clarifies the meaning of the above inequalities in terms of relative magnitudes of the Onsager coefficients.

Finally, we study the optimization of average power output, $\bar{W} = W/\tau$. Setting $dW/d\tau = 0$, the optimal duration of the cycle is: $\tau^* = 2\tau_{min}$. We note that the maximum power condition is not affected by whether $|L| > 0$ or $|L| = 0$. The work performed at maximum power is $W^* = W_{qs}/2$. So, the maximum power is $W^* = W^*/\tau^* = L_{12}^2\eta_C^2/4L_{11}T_c$, and the efficiency at maximum power (EMP), $\eta^* = W^*/Q_h$, is:

$$\eta^* = \frac{L_{12}^2}{2|L| + L_{12}L_{21}} \frac{\eta_C}{2}.$$  

The above expression was also derived as EMP for an autonomous engine based on a thermoelectric setup in the presence of external magnetic field. The asymmetry ratio $(x \equiv L_{12}/L_{21})$ and the generalized figure of merit $(y \equiv L_{12}L_{21}/|L|)$ for $L = 0$ or the tight-coupling condition, the above formula is simplified to $\eta^* = \eta_{qs}/2$. Since $L_{12} \leq L_{21}$ for the tightly coupled case, we conclude that $\eta^* \leq \eta_C/2$. The upper bound of half-Carnot value is obtained when quasi-static and reversible operations are equivalent and so the reciprocal relation holds. This result was known for autonomous, linear-irreversible engines obeying the tight-
have quasi-static and the reversible operations, simultaneously. We have $L_{12} < L_{21}$, when the quasi-static cycle is not reversible, whereas $L_{12} > L_{21}$ holds when the reversible cycle is not quasi-static, or in other words, achieved in a finite duration. The corresponding comparison between different magnitudes of work output per cycle, also illustrating the inequalities in Eq. (21).

Figure 2. a) A cyclic, linear-irreversible engine follows the Onsager reciprocal relation ($L_{12} = L_{21}$) if it approaches the quasi-static and the reversible operations, simultaneously. We have $L_{12} < L_{21}$, when the quasi-static cycle is not reversible, whereas $L_{12} > L_{21}$ holds when the reversible cycle is not quasi-static, or in other words, achieved in a finite duration. b) The coupling condition along with Onsager reciprocity \cite{8, 17}. It was further noted in Ref. \cite{17} that there are no thermodynamic constraints on the allowed values of the real parameter $x$. However, for the case of an $R(x)$ engine, there is a constraint on $x$ due to Eq. (19), so that we have $-1 \leq 1/x \leq +1$, or $|x| \geq 1$. Thus, for such engines, the EMP is simplified to the form:

\begin{equation}
\eta^* = \frac{\eta_C}{1 + (1/x)^2}.
\end{equation}

Notably, the half-Carnot value, established earlier as the upper bound for EMP, is breached here. Moreover, EMP is a function only of the parameter $x$, and as $|x| \rightarrow \infty$, the EMP can approach the Carnot bound.

Concluding, we have considered the performance of a cyclic heat engine within linear-irreversible framework. It is remarkable that the idealized processes of equilibrium thermodynamics have a bearing on the reciprocal properties of phenomenological coefficients describing the strength of couplings in the near-equilibrium regime. Our main general conclusions are: Onsager reciprocal relation implies that the reversible operation is obtained in infinite time or quasi-static limit. Since $W_{qs}$ is finite, so in order to obtain Carnot efficiency, $Q_h$ should also be finite in that limit. This necessarily implies $|L| = 0$. On the other hand, even for $|L| = 0$, we may have a quasi-static operation which is irreversible. This requires violation of Onsager reciprocity—indeed, particular, $L_{12} < L_{21}$. When $|L| > 0$, $Q_h$ diverges in the quasi-static limit and so the efficiency vanishes. Interestingly, there is possibility of reversible operation in a finite duration, for which $L_{12} > L_{21}$ must be obeyed apart from other conditions mentioned in the text. Thus, violation of the Onsager reciprocal relation implies that quasi-static and reversible operations are not equivalent (see also Fig. 2). It may be remarked that our treatment of Onsager reciprocity and its violation has been more at an abstract level, without going into the aspect of concrete, physical realizations. Even so, the consistency of some of the results with the steady-state thermoelectric setups \cite{11}, such as the constraints for reversible operation in finite duration, indicate a wider basis for these results.

The model considered here involves only two forces, which is the simplest example of an irreversible system exhibiting coupled processes. Several lines of inquiry may be visualized in this context. It would be interesting to highlight the parallels relating Onsager reciprocity with vanishing fluxes and reversible operations in the case of autonomous engines. A generalization incorporating more than two forces and/or larger number of heat reservoirs is important. Apart from power output, the study of other figures of merit including refrigerator models will be desirable. Finally, the study of implications for stochastic thermal machines would foster an interesting line of inquiry.

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