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Efficiencies in thermodynamics when temperature-dependent energy levels exist

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Based on a generalized form of the second law of thermodynamics, in which the temperature-dependent energy levels of a system are appropriately included in the entropy generation, we show that the effect reasonably appears in efficiencies of thermodynamic processes.

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I. INTRODUCTION

The equality expression of the Clausius inequality is referred to as the entropy balance equation and its use is nowadays common in chemical engineering and mechanical engineering [1–3]. The equality was originally articulated by Clausius [4, 5] and its importance was later recounted by Tolman and Fine [6]. Our present focus is on the entropy generation S_G associated with any irreversible processes when a system has temperature-dependent energy levels. Thus, the total entropy change dS is balanced by the entropy transferred with heat δQ through the boundary with temperature T plus the generated one; $dS = \delta Q/T + S_G$. The value of S_G depends on the operational path that the system experienced.

Electronic energy levels that determine electronic properties of solids depend on temperature (e.g. [7, 8]) and its statistical mechanics has been addressed [9]. It is well known that the bandgap in semiconductors depends on temperature [10] and the Varshni relation [11] provides the form (for a recent refined formulation, see [12] and references therein). Indeed, the experimental evidence of temperature-dependent energy levels in conductivity and mobility has been reported [13]. Also, its direct effect on the Peltier heat, has been discussed based on the Helmholtz free energy ([14–16] and references cited therein).

Thus, it is natural to expect that the temperature-dependent energy levels in materials should contribute to entropy generation in irreversible heat transfer and thermodynamic cycles. We aim at presenting the explicit formulation of the second law equality in such situations. The inclusion of the effect leads to the rectification of efficiencies in thermodynamic processes.

II. A GENERALIZED SECOND LAW

The generalized second law:

$$dS = \frac{dU}{T} - \frac{1}{T}\Big\langle \frac{dE_l}{dT} \Big\rangle dT, \tag{1}$$

emerges from the explicit inclusion of temperature-dependent energy levels $E_l(T)$ in the partition function $\sum_l \exp(-\frac{E_l(T)}{kT})$ in statistical mechanical ensemble theory [7, 8] and it is also derived in modeling communication channels as a thermal system [17, 18]. It provides a consistent temperature irrespective of the number of particles in the system [19]. The mean value denoted by brackets is understood by the statistical average with an equilibrium distribution. Since the internal energy is the ensemble average of the system microstates; $U = \langle E_l(T)\rangle$ thus $\langle dE_l/dT\rangle \neq d\langle E_l\rangle/dT = dU/dT$, the quantity $\langle dE_l/dT\rangle$ does not represent the heat capacity.

The above relation Eq. (1) holds regardless of whether or not a process is reversible. Therefore, in irreversible processes, the perfect differential dU must read as a sum of heat exchanged $(\delta Q)_{irr}$ and work exchanged $(\delta W)_{irr}$ so that we have

$$dS = \frac{(\delta Q)_{irr}}{T} + S_G, \quad S_G = \frac{(\delta W)_{irr}}{T} - \frac{1}{T}\Big\langle \frac{dE_l}{dT} \Big\rangle dT. \tag{2}$$

The entropy generated within the system must be positive $S_G > 0$; it means that the irreversibly exchanged work is larger than the quantity $\langle dE_l/dT\rangle dT$. The above relation implies also that a system has the entropy generation solely due to the temperature-dependent energy levels even when a process is reversibly done (i.e., under no exchanged work), or when a process proceeds at constant volume. That is, since entropy is neither produced nor extinguished at the boundary of the two contacted systems, the above relation tells us that the entropy change occurs also via the internal temperature dependency in addition to the transferred entropy associated with heat through the boundary.

In terms of the effective heat $\delta Q' = \delta Q - \langle dE_l/dT\rangle dT$ [20], we can rewrite the law as the usual form $dS = \delta Q'/T$ for reversible processes, where dU is regarded as $\delta Q = (\delta Q)_{rev}$ with no exchanged mechanical work.

III. APPLICATIONS

The discrimination between reversible and irreversible flow of heat into and out of a system is essential, i.e., $(\delta Q)_{rev} \neq (\delta Q)_{irr}$ as the dissipated work (or lost work, e.g. Ref. [22, 23]) is defined by $(\delta W)_{diss} = (\delta W)_{irr} - (\delta W)_{rev} = (\delta Q)_{rev} - (\delta Q)_{irr}$. The sign convention for

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the work here: positive when it is done on the system (negative when performed by the system). Therefore, it is also $(\delta W)_{diss} = (-(\delta W)_{rev}) - (-(\delta W)_{irr})$.

A. Heat transfer

Heat transfer occurring in a finite temperature difference is an irreversible process. We consider the entropy generation associated with it, say, along a conducting device. Therefore, the effective heat that the device receives at the boundary of a higher temperature source (T_h) is given as

$$(\delta Q'_h)_{irr} = (\delta Q_h)_{irr} - \left\langle \frac{dE_l}{dT} \right\rangle_{T_h} (dT)_h \tag{3}$$

where $(dT)_h$ is a temperature difference induced by heat transfer at the boundary of the higher temperature side. It is measurable if we measure the Seebeck elective motive force dV_h across the device boundary and use the Seebeck coefficient by the relation $S = dV_h/(dT)_h$. The effective heat $(\delta Q'_h)_{irr}$ simply moves to a lower temperature side (T_c) irreversibly. Thus, the energy balance reads;

$$(\delta Q'_h)_{irr} + (-\delta Q'_h)_{irr} = 0. \tag{4}$$

Because the heat passes through and reaches the lower temperature side with no entropy change, the entropy balance reads

$$0 = \frac{(\delta Q'_h)_{irr}}{T_h} - \frac{(\delta Q'_h)_{irr}}{T_c} + S_G. \tag{5}$$

From the above two balance equations, the entropy generation is provided as

$$\begin{aligned} S_G &= (\delta Q'_h)_{irr}\left(\frac{1}{T_c} - \frac{1}{T_h}\right) \\ &= \left[(\delta Q_h)_{irr} - \left\langle \frac{dE_l}{dT} \right\rangle_{T_h} (dT)_h\right] \frac{T_h - T_c}{T_h T_c}, \end{aligned} \tag{6}$$

where we have substituted Eq. (3). If no temperature dependence exists in energy levels, we recover the usual entropy generation $S_G = (T_h - T_c)(\delta Q_h)_{irr}/(T_h T_c)$ [1–3, 22, 24].

B. Heat engine

In a context of the thermoelectric power cycle, it can be regarded as a heat engine with electrons serving as the working fluid. The balance equations in terms of the effective heat for a cycle are

$$\left\{ \begin{array}{l} 0 = dU = (\delta Q'_h)_{irr} + (\delta W_h)_{irr} + (\delta Q'_c)_{irr} + (\delta W_c)_{irr} \\ 0 = dS = \frac{(\delta Q'_h)_{irr}}{T_h} - \frac{(\delta Q'_c)_{irr}}{T_c} + S_G. \end{array} \right. \tag{7}$$

where $(\delta W_h)_{irr}$ and $(\delta W_c)_{irr}$ are work done irreversibly from the higher and lower temperature sources, respectively. The total work that the system gives to the sources during the cycle $-(\delta W)_{irr}$ becomes $-(\delta W_h)_{irr} - (\delta W_c)_{irr}$ and it can be expressed by Eq. (7) as

$$-(\delta W)_{irr} = (\delta Q'_h)_{irr}\left(1 - \frac{T_c}{T_h}\right) - T_c S_G. \tag{8}$$

If the cycle is done reversibly, the generation of entropy is null $S_G = 0$ and replacing the suffixes by rev, we have the usual Carnot form $(\delta W)_{rev} = (\delta Q_h)_{rev}(1 - T_c/T_h)$ in which $(\delta Q_h)_{rev}$ is heat reversibly transferred out of the higher temperature source. We have therefore the thermal efficiency η for this engine defined as the ratio of the actual work and the invested effective heat:

$$\begin{aligned} \eta = \frac{-(\delta W)_{irr}}{(\delta Q'_h)_{irr}} &= 1 - \frac{T_c}{T_h} - \frac{T_c S_G}{(\delta Q'_h)_{irr}} \\ &= 1 - \frac{T_c}{T_h} - \frac{T_c S_G}{(\delta Q_h)_{irr} - \langle \frac{dE_l}{dT} \rangle_{T_h} (dT)_h} \end{aligned} \tag{9}$$

Since the Carnot cycle has maximum in the efficiency among all types, we find that this expression indicates that a relation $(\delta Q_h)_{irr}/(dT)_h > \langle \frac{dE_l}{dT} \rangle_{T_h}$ has to be satisfied.

We next consider the thermodynamic efficiency ϵ (e.g. [24]), which is different from the thermal efficiency η and is quantified by the ratio of the practical work $-(\delta W)_{irr}$ and its maximum that the system can give. The maximum value is equivalent to the reversible work $-(\delta W)_{rev}$:

$$\begin{aligned} \epsilon = \frac{-(\delta W)_{irr}}{-(\delta W)_{rev}} &= \frac{(\delta Q'_h)_{irr}\left(1 - \frac{T_c}{T_h}\right) - T_c S_G}{(\delta Q_h)_{rev}\left(1 - \frac{T_c}{T_h}\right)} \\ &= \frac{(\delta Q'_h)_{irr}}{(\delta Q_h)_{rev}} - \frac{T_c T_h S_G}{(T_h - T_c)(\delta Q_h)_{rev}} \end{aligned} \tag{10}$$

Note that the first term in the second line becomes $(\delta Q_h)_{irr}/(\delta Q_h)_{rev}$ if the energy levels of the system does not depend on temperature (i.e. the prime mark on δQ_h is dropped) and it reduces to unity as per the assumption in many textbooks.

In practice, measuring work in reversible processes needs infinite time and real processes involve irreversible work $(\delta W)_{irr}$ which can be measurable in finite time. A way out of inferring the amount of the reversible work from the irreversible counterpart is invoking a relation known as the Jarzynski equality [25] that holds as long as fluctuations are not large; $\langle e^{-(\delta W)_{irr}/kT} \rangle = e^{-\Delta F/kT}$, where ΔF is the Helmholtz free energy difference between initial and final states and k is the Boltzmann constant. The ΔF is equivalent to the reversible work $(\delta W)_{rev}$ done on the system during the process. The brackets denote taking the arithmetic mean over the number of trials after taking the statistical mean of the factor over possible states. This equality relation was employed to derive a rectification of the second law [26, 27]. Substituting Eq. (8) into the equality and rearranging it, the reversible work can be expressed as

$$\begin{aligned}-(\delta W)_{rev} &= kT_h \ln\left\langle e^{-\frac{(\delta W)_{irr}}{kT_h}}\right\rangle \\ &= kT_h \ln\langle \exp\left[(T_h - T_c)\frac{(\delta Q'_h)_{irr}}{T_h} - T_c S_G\right]\rangle.\end{aligned}$$

Hence, combining this with Eq. (3) we have

$$\epsilon = \frac{\eta_C(\delta Q'_h)_{irr} - T_c S_G}{kT_h \ln\langle \exp\left[\eta_C(\delta Q'_h)_{irr}\right]\rangle}. \qquad (11)$$

where η_C denotes the Carnot thermal efficiency $1 - T_c/T_h$.

C. Heat pump

Peltier devices function as a heat pump by the Peltier effect; electrons carry heat from cold to hot junctions (e.g. [28, 29]). In this section, we address a measure of performance for a heat pump device, which transfers heat from a lower temperature source to a higher one. The coefficient of performance (COP) is a quantity of a significant importance in a refrigerator. We find that the expression of the COP defined below is not affected by the existence of the temperature dependent energy levels. The system absorbs an effective heat $(\delta Q'_c)_{irr}$ irreversibly from a lower heat source with temperature T_c and receives the irreversible work $(\delta W)_{irr}$, then delivers an effective heat $(\delta Q'_h)_{irr}$ irreversibly to a higher temperature side with T_h. Accordingly, we have the balance equations for energy and entropy:

$$\begin{cases} 0 = dU = (\delta Q'_c)_{irr} + (\delta W)_{irr} + (-(\delta Q'_h)_{irr}) \\ 0 = dS = \frac{(\delta Q'_c)_{irr}}{T_c} + \frac{-(\delta Q'_h)_{irr}}{T_h} + S_G. \end{cases} \qquad (12)$$

Thus, the irreversibly received work $(\delta W)_{irr} = (\delta Q'_h)_{irr} - (\delta Q'_c)_{irr}$ is

$$(\delta W)_{irr} = -\left(1 - \frac{T_h}{T_c}\right)(\delta Q'_c)_{irr} + T_h S_G. \qquad (13)$$

Hence, the expression of the COP defined as the ratio of the absorbed heat and the received work [24] contains no explicit temperature-dependent energy levels:

$$COP = \frac{(\delta Q'_c)_{irr}}{(\delta W)_{irr}} = \frac{T_c}{T_h - T_c}\left(1 - \frac{T_h S_G}{(\delta W)_{irr}}\right). \qquad (14)$$

Of course, this implies that the maximum performance $T_c/(T_h - T_c)$ attains when the cycle is done reversibly $(S_G = 0)$.

IV. SUMMARY AND CONCLUSIONS

Temperature-dependent energy levels in materials affect transport properties such as the thermoelectric coefficients and this fact should be appropriately taken into account in a rigorous way for the irreversible processes that occur in the devices. A formulation of the second law which is suitably reflected by this effect in materials operated in a thermodynamic environment leads to a new direction. The efficiencies of thermodynamic processes are rectified accordingly. This study might offer a possible theoretical ground for evaluating entropy generation in nanoengines based on temperature-dependent energy levels.

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