Effect of temperature-dependent energy levels on exergy

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Keywords: energy, temperature-dependent energy levels, thermodynamics, exergy, second law, effective heat

Abstract
The performances of solar cells and thermoelectric materials are governed by thermodynamics. The material properties of these have temperature dependence due to thermal expansions of lattices and an effect of electron–phonon coupling etc. The temperature-dependent energy levels has been included in statistical mechanics, naturally requiring a rectification of the second law of thermodynamics with an effective heat. In such a framework, we show that exergy associated with internal energy of isolated systems can be increased in irreversible processes. We furthermore see how the effect of the temperature-dependent energy levels appears in the thermodynamic performance in terms of the second law efficiency.

1. Introduction
Exergy is an important quantity which quantifies a potential amount of work that any thermodynamic system possesses [1]. It is a relative measure requiring a reference environmental state at which the system comes to equilibrium. In any irreversible processes, exergy is consumed and when we apply this measure to analyze material resources it is highly affected by the ambient temperature at which a system is placed.

The material properties are temperature dependent [2], causing internal irreversibilities. These play an important role in the performance of electricity generations. Thermoelectric generators are typical materials, in which the Seebeck coefficient, thermal conductivity and electrical resistivity change according to temperature [3]. For example, the methylammonium lead iodide (MAPBI3) perovskite which performs as photovoltaic solar cells is known to exhibit significant temperature-dependent changes in its structure [4]. It is reported that the maximum of the valence band and the minimum of conduction band energy levels substantially shift depending on temperature [4]. The energy level alignment and open circuit voltage of the solar cells accordingly should be influenced by this energy shifts when operating at different temperatures.

To incorporate these highly indispensable effects in materials, we in general need to take into consideration the effects of a temperature-dependent electron–phonon coupling and of an exciton binding energy. The most relevant resource at present is semiconductor thermoelectric devices, whose energy gap varies according to temperature [5, 6]. They have been studied in terms of the theory of solid state physics [7–9]. At present, however, the balance equations in entropy and in exergy are devoid of explicit contributions from this important effect. The present author addressed the temperature-dependent energy levels in thermodynamic processes and has shown several combined forms in thermodynamic efficiencies [10, 11].

In this paper, we address how such a set of energy levels that depends on temperature influences the exergy formulas in a theoretical point of view. It would be of importance from the perspective of the design of energy storage system and from a precise evaluation of performance. The organization of the paper is as follows: we briefly expound our views on effective heat in the next section. Exergy of the effective heat and of internal energy are formulated in sections 3 and 4 respectively. We conclude our assertion and an implication to design of solar cells and thermoelectricity in the last section.
2. Effective heat and a generalized second law

Inclusion of dependency of energy levels on temperature as a material property has been considered in statistical mechanics [12–15]. However, the present standard formulation of equilibrium statistical mechanics is devoid of the explicit appearance of the temperature-dependent energy levels. Recently, how the existence of the temperature-dependent energy levels relates to the finiteness of small systems was investigated [16–18]. As it stands, however, the explicit effect on the thermodynamics in irreversible processes and thermodynamic efficiencies were neither considered nor formulated until recently [10, 11].

It is straightforward to see the associated rectification of the entropy change \( dS \) when energy levels of the system are temperature dependent. Let \( E(T) \) be the \( \ell \) th energy level determined according to temperature. Starting from the key relation that links thermodynamics and statistical mechanics, i.e., \( S = U/T + k \ln Z \) with the partition function \( Z = \sum \exp \left( -\frac{E(T)}{kT} \right) \), the entropy change is found to be

\[
dS = \frac{dU}{T} + k \ln Z,
\]

\[
= \frac{dU}{T} - \frac{1}{T} \left( \frac{dE}{dT} \right) dT.
\]

The change of the internal energy \( U \) of a system in the first term of the above consists of heat influx and work exchanged with surroundings, i.e., the first law of thermodynamics. But when a system has no moving parts such as thermoelectric elements we may ignore the mechanical work due to the fixed volume. As a result, only heat flux contributes to the internal change \( dU = \delta Q \). This case is derived as a generalization of the second law in the consideration of information processing where communication channels are influenced by environmental thermal noise [19, 20]. Note that the above expression holds irrespective of whether a process proceeds reversibly or irreversibly. By introducing the effective heat

\[
\delta Q_{\text{eff}} = \delta Q - \left( \frac{dE}{dT} \right) dT,
\]

we have substantively the same expression as the standard form of the entropy change \( dS = \delta Q_{\text{eff}} / T \). One may interpret this as follows: in the course of transporting heat from a higher temperature material, an amount of heat is necessary to keep the material structure on its surface. This quantity is on average proportional to \( (dE/dT) \). In order to have a consistent thermodynamics description, one must use the effective heat. In standard treatment, the heat \( \delta Q \) is assumed to be transferred from a system to external with no loss through the boundary that separates them. However, in terms of the effective heat, we describe that the heat is decreased by an amount \( (dE/dT) dT \) at the boundary of the system side and the heat moves to the external by the amount \( \delta Q_{\text{eff}} \).

An approximate value of the factor will be estimated at the end of section 4.

3. Exergy associated with effective heat

Having motivated by the effective heat stemming from the temperature-dependent energy levels, we have an interest in how this affects useful work we can utilize. Heat conveys exergy (e.g. [21–23]). Exergy or available energy of heat for a closed system is considered in this section. It follows from the standard derivation of exergy associated with heat flow. The exergy content of heat \( \delta Q_{\text{eff}} \) transferred isothermally at temperature \( T \) when the dead state environment is set \( (T_d, P_d) \) is shown to be expressed as

\[
\Phi = \left( 1 - \frac{T_d}{T} \right) \delta Q_{\text{eff}}.
\]

This implies that the heat transferred to the external is the effective heat, i.e., the original heat \( \delta Q \) subtracted by the temperature-dependent contribution in a medium. For the change in internal energy \( dU \), the first law of thermodynamics should read as

\[
dU = \delta Q_{\text{eff}} + \delta W.
\]

Therefore, when a system has a moving part that allows the volume change, the exergy content \( \Phi(dU) \) can be expressed as the sum of the two

\[
\Phi(dU) = \Phi(\delta Q_{\text{eff}}) + \Phi(\delta W),
\]

The first term means inflow of exergy due to the transferred effective heat and the second term outflow from the system by the performance of work that takes negative value. The exergy content of the work \( \delta W \) is the useful work denoted as \( \delta W_u \); \( \Phi(\delta W) = \delta W_u \). The work during the volume change is estimated as the useful work \( \delta W_u \) subtracted by work required against the dead state pressure \( P_d \), i.e., the relation \( \delta W = \delta W_u - P_d dV \) holds.
Furthermore, recalling that the exergy of the internal energy in standard engineering thermodynamics is expressed as
\[ F = \bar{U} - T_0 S_0 \]
the exergy content of the effective heat reduces to
\[ F = \bar{Q} - T_0 S_0 \]
where the first law equation \( (4) \) is used. By the relation \( dS = \delta Q / T \), we find the following expression for the exergy:
\[ F(\delta Q) = \left( 1 - \frac{T_0}{T} \right) \delta Q. \]

The amount of exergy brought from the effective heat \( \delta Q \) when a system starts with a specific state with temperature \( T_1 \) and moves to another state with \( T_2 \) is thus given by the integral of equation \( (7) \) over this temperature range:
\[ \Phi(Q) = \int_{T_1}^{T_2} \left( 1 - \frac{T_0}{T} \right) \delta Q. \]

This is the general expression of the exergy of effective heat. When a system experiences an isobaric process, the heat capacity of the material in general is dependent on temperature, i.e., \( c_p(T) \) and the heat change within the material that appears in the integrand should read as \( dQ = c_p(T) dT \).

Thermoelectric devices produce entropy during the irreversible processes. (For a recent review, see \[ (24) \] and references therein.) Now, we consider a situation in figure 1, where the change of variables in a heat transfer process through boundary is depicted. The system(s) represents a thermoelectric material and the suffix \( \text{out} \) denotes external. The net entropy generated at the boundary is denoted as \( S_{G,\text{net}} \) and it is expressed:
\[ S_{G,\text{net}} = \frac{\delta Q_{\text{eff}}}{T_{\text{out}}} - \frac{\delta Q}{T_s} \]
\[ = \left( \frac{1}{T_{\text{out}}} - \frac{1}{T_s} \right) \delta Q - \frac{1}{T_{\text{out}}} \left( \frac{dE_l}{dT} \right) dT. \]

We find that the net entropy generation is reduced by the amount of the factor that arises from the temperature-dependent energy levels. The relevant temperature of this effect is not the system’s \( T_s \) but the external one \( T_{\text{out}} \). On the other hand, the destroyed exergy \( E_{\text{d}} \), which is defined by the difference between input and output exergies associated with the heat, is:

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\[ \text{Figure 1.} \] The schematic of transports of heat, entropy, and exergy over finite temperature difference through a boundary. The heat \( \delta Q \) at the temperature \( T_s \) of a system is transferred across a boundary layer, where the entropy \( S_{G,\text{net}} \) is produced. The effective heat \( \delta Q_{\text{eff}} \) is released to an external system with temperature \( T_{\text{out}} \), during which the amount of exergy \( \Phi_d \) is destroyed.
\( \Phi_U = \Phi_{\text{in}} - \Phi_{\text{out}} = \left(1 - \frac{T_0}{T_i}\right) \delta Q - \left(1 - \frac{T_0}{T_{\text{out}}}\right) \delta Q_{\text{eff}} \)

\( = \left(\frac{1}{T_{\text{out}}} - \frac{1}{T_i}\right) T_0 \delta Q + \left(1 - \frac{T_0}{T_{\text{out}}}\right) \left(\frac{dE_i}{dT}\right) dT. \) \hspace{1cm} (10)

When the energy levels of the system do not depend on temperature, we recover the usual form of exergy destruction; that is, the first term only represents it.

4. Exergy associated with internal energy

The exergy of an internal energy \( \Phi_U \) is defined as the maximum useful work that a system can provide an environment by a reversible process based on the internal energy. From an arbitrary state \((U, V, S)\) to the dead state \((U_0, V_0, S_0)\), it is expressed as [23]:

\[ \Phi_U = U - U_0 + P_0(V - V_0) - T_0(S - S_0). \] \hspace{1cm} (11)

For devices that have no volume change we may omit the second term and the first term is simply replaced by \( c_v(T - T_0) \) with the constant volume heat capacity \( c_v(T) \). Considering an isobaric process where \( \delta Q = c_v(T) dT \) holds and using the entropy change \( S - S_0 = \delta Q_{\text{eff}} / T \), the exergy \( \Phi_U \) is expressed as:

\[ \Phi_U = c_v(T - T_0) - T_0 \int_{T_0}^T \frac{c_v(T)}{T} dT + T_0 \int_{T_0}^T \frac{1}{T} \left(\frac{dE_i}{dT}\right) dT. \] \hspace{1cm} (12)

In addition to the usual expression of exergy, the third term is required as a correction. In general, the average value of the differential of energy levels of thermoelectric materials with respect to temperature should be calculated from density of states of its associated semiconductor materials by statistical mechanics. The density of states is usually a function of energy only and has no temperature dependence [25], but when it comes to the energy levels that corresponds to the internal energy \( U \) of materials it does have the temperature dependence \( E(T) \) as denoted in the present consideration. According to the general treatment of temperature-dependent energy levels [15], the relation between the mean energy \( \bar{E} \) of \( E(T) \) averaged over ensemble and the mean energy \( U \) is given as:

\[ U = \bar{E} - T \left(\frac{dE_i}{dT}\right). \] \hspace{1cm} (13)

Recalling that the density of states of \( U \) for a semiconductor material is proportional to \( U^{1/2} \) [25] and hence the entropy reads \( S = k \ln U^{1/2} + \text{const.} \) By a standard relation between entropy and energy \( dS / dU = 1 / T \) with the fact that the mean energy \( \bar{E} \) can be regarded as the order of \( kT \), we find that the factor \( (dE_i / dT) \) is the order of the Boltzmann constant \( k \). From this estimation, we can simply rewrite the above correction for the exergy (i.e., the third term of equation (12)) as \( gkT_0 \ln(T / T_0) \), with \( g \) being the proportionality constant. This correction term contributes a small amount compared to the other two if \( g \) is small enough. Regarding this argument, it is worth mentioning that the estimate of \( (dE_i / dT) \sim k \) has recently shown to be valid also for some systems such as ideal gases and two-level systems when the particle number is large, and for single quantum systems as well [18].

5. Expression of second law efficiency

The second law efficiency \( \eta_2 \) defines the ratio of the input and output exergies and it is defined also as:

\[ \eta_2 := \frac{W_{\text{rev}}}{W_{\text{rev}} + T_0 S_{\text{G,net}}}. \] \hspace{1cm} (14)

Because the reversible work needs infinite time to measure, it is practically useful if we can estimate it from work value irreversibly obtained in a finite time. The Jarzynsky equality devised in nonequilibrium statistical mechanics [26] bridges between reversible and irreversible works and it serves a useful purpose for the present consideration. The equality states that the reversible work in a process can be deduced by repeating real observation of work \( W_{\text{irr}} \) and averaging them:

\[ \exp\left(-\frac{W_{\text{rev}}}{kT}\right) = \left\{ \exp\left(-\frac{W_{\text{irr}}}{kT}\right) \right\}. \] \hspace{1cm} (15)

This relation leads to an expression for the reversible work; \( W_{\text{rev}} = -kT \ln \left( \exp(-W_{\text{irr}} / kT) \right) \). Therefore, if we consider a solid state device that follows the nonequilibrium work relation, substituting this into the above definition of the second law efficiency, we can have an expression for the efficiency as...
\[ \eta_2 = \frac{1}{1 - \frac{1}{kT \ln \left\{ \exp \left( -\frac{W_{rev}}{kT} \right) \right\}}}. \]  

Note that the efficiency contains the temperature-dependent energy levels through the entropy generation \( S_{G, net} \) (equation (9)). Alternatively, we may also express the second law efficiency via the dissipated work and the Gouy–Stodola theorem \( W_d = T_0 S_{G, net} \) [27, 28]. The dissipated work \( W_d = W_{rev} - W_{irr} \) plays a central role in exergy analysis. It is referred to as different terms such as lost work and irreversibility in different fields. From equation (14), we have an expression:

\[ \eta_2 = \frac{W_{rev}}{W_{rev} - (kT \ln \left\{ \exp \left( -\frac{W_{irr}}{kT} \right) \right\}) + W_{irr}}. \]

Although thermoelectric devices do not have moving parts, the applications of the nonequilibrium work equality is valid through the net entropy generation (the Gouy–Stodola theorem). However, in general, the applicability of equation (15) should also be reminded when a system receives time dependent forces such as single-molecule pulling experiments, where the usual link between work and changes in Hamiltonian does not hold. This remark is pointed out in an exchange [29–31] and as a corollary the breakdown of the equality relation is argued.

6. Conclusions

Exergy as the quality of energy is based on the second law of thermodynamics. Because a generalized form of the second law that incorporates the temperature-dependent energy levels has been proposed in the literature, it is natural to take the effect into the exergy expression. Thermal expansion of lattice structures of materials by temperature increase impacts on the energy levels of semiconductor materials such as MAPbI\(_3\). As temperature increases the maximum of the valence band energy level shifts towards a lower side. This fact indicates that we should employ the notion of the effective heat in exergy evaluation of solid materials. Although the contribution from the temperature-dependent energy levels to the exergy might be tiny for each cell, it could be enormous and non-negligible as a whole and could have potential applications for electricity harvesting.

Acknowledgments

The author thanks Waseda University Library for necessary references for this work.

Funding

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

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