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Fluctuation theorem for entropy production at strong coupling*

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Fluctuation theorems have been applied successfully to any system away from thermal equilibrium, which are helpful for understanding the thermodynamic state evolution. We investigate fluctuation theorems for strong coupling between a system and its reservoir, by path-dependent definition of work and heat satisfying the first law of thermodynamics. We present the fluctuation theorems for two kinds of entropy productions. One is the informational entropy production, which is always non-negative and can be employed in either strong or weak coupling systems. The other is the thermodynamic entropy production, which differs from the informational entropy production at strong coupling by the effects regarding the reservoir. We find that, it is the negative work on the reservoir, rather than the nonequilibrium of the thermal reservoir, which invalidates the thermodynamic entropy production at strong coupling. Our results indicate that the effects from the reservoir are essential to understanding thermodynamic processes at strong coupling.

Keywords: fluctuation theorem, entropy production, strong coupling

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1. Introduction

Fluctuation theorems (FTs) are applied to explaining thermodynamic behaviors of microscopic or macroscopic dynamics in a system away from thermodynamic equilibrium.[1–4] In particular, since Jarzynski's proposal for an equality between the non-equilibrium work and the free energy difference,[5] there has been increasing attention on the fluctuations regarding different thermodynamic quantities.[6–8] One of the famous FTs was proposed by Crook to connect the probability of an entropy production (EP) along the forward trajectory with that along the reverse one.[9] Subsequent developments have extended the conditions in Ref. [9] to more general situation, such as the differential FT[10,11] for the joint probabilities of EP regarding arbitrary initial and final generalized coordinates. This generalized FT was also verified experimentally by an optically levitated nanosphere[12] and generalized again to the case with arbitrary measurements and feedback.[13] Recently, the EP was also extended to analyzing the elliptical thermal cloak.[14–16] Moreover, the FT itself was quantized,[17–19] although definitions of work and heat in quantum systems are still in debate.[20] Meanwhile, experimentally verifying the Jarzynski equality was also extended from the classical consideration[21–23] to the quantum counterpart by trapped ions.[24,25]

In this work, we consider a thermodynamic system interacting strongly with its reservoir, which is recently a hot topic[26–30] for both quantum and classical systems. The effects of strong coupling in equilibrium thermodynamics were first considered by the potential of mean force.[31] The associated problems include identification of work and heat in the strong coupling case[27–29] and estimate of the strong coupling effects on the energy transfer.[26,30] For example, the internal energy was defined by the potential of mean force, and work and heat were assumed to be associated with the change of the corresponding states of the system, from which FTs of the EP were obtained.[27,28] Such a definition of work and heat was also applied to another publication for the Jarzynski equality at strong coupling.[32]

This paper focuses on the FT of informational EP through microscopic reversibility. We also explore a generalized FT of thermodynamic EP in the case of a strong system–reservoir coupling based on a trajectory-dependent definition of work and heat. In this generalized FT, new terms originated from the effects of reservoir appear. Discussion is made for avoiding violation of the second law of thermodynamics at strong coupling by justifying the FT of the informational EP.

2. Redefinition of thermodynamic quantities

We consider an isolated composite system comprising a system and its reservoir, whose Hamiltonian is given by

$$H(z,\lambda) = H_{\rm s}(x,\lambda) + H_{\rm r}(y) + H_{\rm I}(x,y), \tag{1}$$

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where $H_{\rm s}$ is the Hamiltonian of the system driven by the control parameter λ, $H_{\rm r}$ is for the reservoir, and $H_{\rm I}$ is regarding the system–reservoir interaction. Here the strong coupling implies either a system–reservoir interaction comparable to other characteristic quantities in the Hamiltonian or non-Gibbs state in the system or reservoir. In fact, there exists correlation between the system and reservoir when the composite system reaches an equilibrium state. In our protocol, the control parameter is designed as $\lambda_0 \longrightarrow \lambda(t) \longrightarrow \lambda$ for the forward process. The interaction Hamiltonian is generally written as $H_{\rm I} = \sum_i \Theta_{\rm s}^i \Theta_{\rm r}^i$. For simplicity, here we reduce it to $H_{\rm I} = \Theta_{\rm s}\Theta_{\rm r}$. Moreover, $z = (x, y)$ means the point in the total phase space $\Gamma = \Gamma_{\rm s} \otimes \Gamma_{\rm r}$, with $\Gamma_{\rm s}$ and $\Gamma_{\rm r}$ being the phase spaces of the system and its reservoir, respectively.

As a comparison, we first check the definition in the weak coupling case. In terms of stochastic thermodynamics, the fluctuating internal energies (or called internal energies on the trajectory level) of the system and its reservoir are defined, respectively, as $e_{\rm s} = H_{\rm s}(x, \lambda)$ and $e_{\rm r} = H_{\rm r}(y)$,[34,35] in which the interaction energy is excluded from both the internal energies. We argue that such a definition can be reasonably extended to the case of strong coupling based on the fact that the interaction energy belongs neither to the system nor to the reservoir, but comes from the coupling in between.

Considering the difference from the weak coupling, we need to redefine work and heat on the trajectory level. To this end, we may first check the corresponding definitions on the ensemble level, which are given by the ensemble average for the fluctuating quantities, e.g., $U_{\rm s} = \langle H_{\rm s}(x)\rangle_{\rm s}$ ($U_{\rm r} = \langle H_{\rm r}(y)\rangle_{\rm r}$) as the internal energy of the system (reservoir), where the ensemble average means $\langle H_{\rm s}(x)\rangle_{\rm s} = \int p_{\rm s}(x) H_{\rm s}(x)\,{\rm d}x$ ($\langle H_{\rm r}(y)\rangle_{\rm r} = \int p_{\rm r}(y) H_{\rm r}(y)\,{\rm d}y$) with $p_x(x)$ ($p_{\rm r}(y)$) being the probability distribution function (PDF) of the system (reservoir). As the internal energies change due to the interaction, we may define the work and heat by the decrease of the interaction energy, i.e., ${\rm d}W_{\rm s} + {\rm d}W_{\rm r} + {\rm d}Q_{\rm s} + {\rm d}Q_{\rm r} = -{\rm d}\langle H_{\rm I}(z)\rangle$, where $\langle H_{\rm I}(z)\rangle = \int p(z) H_{\rm I}(z)\,{\rm d}z$ is the ensemble average of the interaction, with $p(z)$ being the PDF of the composite system. In quantum thermodynamics, the work is usually defined as an uncorrelated quantity,[36] i.e., ${\rm d}W_{\rm s} + {\rm d}W_{\rm r} = -{\rm d}\langle H_{\rm I}(z)\rangle_{\rm unc}$, with $\langle H_{\rm I}(z)\rangle_{\rm unc} = \langle\Theta_{\rm s}\rangle_{\rm s}\langle\Theta_{\rm r}\rangle_{\rm r}$. So, the work done on the system and the reservoir can be written, respectively, as

$$\begin{aligned} {\rm d}W_{\rm s} &= -\langle\Theta_{\rm s}\rangle_{\rm s}\,{\rm d}\langle\Theta_{\rm r}\rangle_{\rm r}, \\ {\rm d}W_{\rm r} &= -\langle\Theta_{\rm r}\rangle_{\rm r}\,{\rm d}\langle\Theta_{\rm s}\rangle_{\rm s}. \end{aligned} \tag{2}$$

Correspondingly, the heat is defined as a correlated quantity, i.e., ${\rm d}Q_{\rm s} + {\rm d}Q_{\rm r} = -[{\rm d}\langle H_{\rm I}(z)\rangle - {\rm d}\langle H_{\rm I}(z)\rangle_{\rm unc}]$, which, after some algebra, is rewritten as ${\rm d}Q_{\rm s} + {\rm d}Q_{\rm r} = {\rm d}\langle H_{\rm s}(x)\rangle + {\rm d}\langle H_{\rm r}(y)\rangle + {\rm d}\langle H_{\rm I}(z)\rangle_{\rm unc}$. As a result, the heat transferred to the system and to the reservoir can be defined, respectively, as

$$\begin{aligned} {\rm d}Q_{\rm s} &= {\rm d}\langle H_{\rm s}(x)\rangle + \langle\Theta_{\rm s}\rangle_{\rm s}\,{\rm d}\langle\Theta_{\rm r}\rangle_{\rm r}, \\ {\rm d}Q_{\rm r} &= {\rm d}\langle H_{\rm r}(y)\rangle + \langle\Theta_{\rm r}\rangle_{\rm r}\,{\rm d}\langle\Theta_{\rm s}\rangle_{\rm s}. \end{aligned} \tag{3}$$

For our purpose as clarified later, we rewrite the heat dissipated to the reservoir in a finite process as

$$Q_{\rm r} = \Delta\langle H_{\rm r}(y)\rangle + \delta Q_{\rm r}, \tag{4}$$

where $\delta Q_{\rm r} = \int \langle\Theta_{\rm r}\rangle_{\rm r}\,{\rm d}\langle\Theta_{\rm s}\rangle_{\rm s}$ is the correction of the heat at strong coupling with respect to the weak coupling case. This correction can be understood as a negative work done on the reservoir under the requirement of the first law of thermodynamics.

Based on the ensemble results as above, we can straightforwardly define work and heat on the trajectory level. The work done on the system and its reservoir are given, respectively, by

$$\begin{aligned} w_{\rm s} &= -\int \Theta_{\rm s}(x)\,{\rm d}\langle\Theta_{\rm r}\rangle_{\rm r}, \\ w_{\rm r} &= -\int \Theta_{\rm r}(y)\,{\rm d}\langle\Theta_{\rm s}\rangle_{\rm s}, \end{aligned} \tag{5}$$

and the heat transferred to the system and its reservoir are, respectively,

$$\begin{aligned} q_{\rm s} &= \Delta H_{\rm s} + \int \Theta_{\rm s}(x)\,{\rm d}\langle\Theta_{\rm r}\rangle_{\rm r}, \\ q_{\rm r} &= \Delta H_{\rm r} + \int \Theta_{\rm r}(y)\,{\rm d}\langle\Theta_{\rm s}\rangle_{\rm s}. \end{aligned} \tag{6}$$

Similar to the ensemble result, the heat transferred to the reservoir can be rewritten as

$$q_{\rm r} = \Delta H_{\rm r} + \delta q_{\rm r}, \tag{7}$$

where $\delta q_{\rm r} = \int \Theta_{\rm r}(y)\,{\rm d}\langle\Theta_{\rm s}\rangle_{\rm s}$ represents the heat correction at strong coupling with respect to the weak coupling case. Obviously, the first law of thermodynamics is also satisfied at trajectory level.

Now we discuss a property of the heat under the time reversal. In our case, the time reversal means that both the control parameter and time are all reversed. The time reversed control parameter $\bar{\lambda}(-t)$ means that $\lambda \longrightarrow \lambda(t) \longrightarrow \lambda_0$ in the reverse process. As the Liouville equation is invariant under the time reversal, the PDF keeps unchanged in both the forward and reverse processes, i.e., $p_{\rm s}(t) = \bar{p}_{\rm s}(-t)$ and $p_{\rm r}(t) = \bar{p}_{\rm r}(-t)$.[37] As a result, the heat is an odd function under the time reversal.

3. FT of informational EP

We consider the FT of informational EP from the microscopically reversible dynamics. As the composite system is isolated, the microscopical reversibility means

$$P_{\rm F}[z(t)\,|\lambda(t)] = P_{\rm R}[\bar{z}(-t)\,|\bar{\lambda}(-t)], \tag{8}$$

where $P_{\rm F}[z(t)\,|\lambda(t)]$ describes the PDF of the composite system evolving along a trajectory $z(t)$ when the control parameter $\lambda(t)$ is given by the forward protocol, while

$P_{\rm R}(\bar{z}(-t)\,|\bar{\lambda}(-t)]$ is the PDF of the corresponding time reverse trajectory, as presented in Appendix A.

Under the above reversible condition, we can obtain an FT of informational EP. In stochastic thermodynamics the stochastic entropy is defined as $s=-\ln p$, where p is the probability. Using this definition we can define the informational EP as

$$\Sigma_{\rm inf}=\ln p_{\rm s}^0-\ln p_{\rm s}+\ln p_{\rm r}^0-\ln p_{\rm r}, \tag{9}$$

where $p_{\rm s}^0$ ($p_{\rm r}^0$) and $p_{\rm s}$ ($p_{\rm r}$) are the initial and final PDFs of the system (the reservoir). This EP measures the entropy change of the total system, which, as clarified in the following, will be coincided with thermodynamic EP (defined later) if the coupling is weak and the reservoir remains in a Gibbs state. From the reversibility of the PDF, i.e., $p_{\rm s}(t)=\bar{p}_{\rm s}(-t)$ and $p_{\rm r}(t)=\bar{p}_{\rm r}(-t)$, we obtain that both the final PDFs of the forward process are the same as the initial ones of the reverse process, i.e., $p_{\rm s}=\bar{p}_{\rm s}^0$ and $p_{\rm r}=\bar{p}_{\rm r}^0$, and vice versa. Under this condition, the informational EP is obviously an odd function, i.e., $\Sigma_{\rm inf}^{\rm F}=-\Sigma_{\rm inf}^{\rm R}$, where $\Sigma_{\rm inf}^{\rm F}$ ($\Sigma_{\rm inf}^{\rm R}$) is the informational EP in a forward (reverse) process. As a result, we obtain

$$\frac{p_{\rm s}^0(x_0)p_{\rm r}^0(y_0)P_{\rm F}[z(t)\,|\lambda(t)]}{\bar{p}_{\rm s}^0(\bar{x}_0)\bar{p}_{\rm r}^0(\bar{y}_0)P_{\rm R}[\bar{z}(-t)\,|\bar{\lambda}(-t)]}=\mathrm{e}^{\Sigma_{\rm inf}^{\rm F}}, \tag{10}$$

$$P_{\rm F}(\Sigma_{\rm inf})=\mathrm{e}^{\Sigma_{\rm inf}}P_{\rm R}(-\Sigma_{\rm inf}), \tag{11}$$

where $P_{\rm F}(\Sigma_{\rm inf}^{\rm F})$ ($P_{\rm R}(\Sigma_{\rm inf}^{\rm R})$) is the probability of observing a particular value of the informational EP in a forward (reverse) process (see Appendix A for more details). Equation (11) is formally identical to a previously presented thermodynamic EP at weak coupling.[9] This implies that the informational EP could be employed for both weak coupling and strong coupling cases.

Using the above results, we obtain an integral FT, which is actually another form of the second law of thermodynamics from the viewpoint of information. If we denote the ensemble average by $\langle \mathrm{e}^{-\Sigma_{\rm inf}}\rangle=\int \mathrm{e}^{-\Sigma_{\rm inf}}P_{\rm F}(\Sigma_{\rm inf})\,\mathrm{d}\Sigma_{\rm inf}$, then from Eq. (11) we have

$$\langle \mathrm{e}^{-\Sigma_{\rm inf}}\rangle=\int P_{\rm R}(-\Sigma_{\rm inf})\,\mathrm{d}\Sigma_{\rm inf}=1, \tag{12}$$

which means that the averaged informational EP is never negative, i.e., $\langle\Sigma_{\rm inf}\rangle\geq 0$. This also implies that the informational EP can be used to indicate the direction of the thermodynamic evolution, even in the strong coupling case.

4. FT of thermodynamic EP

In stochastic thermodynamics, the thermodynamic EP is defined as[39]

$$\Sigma_{\rm therm}=\ln p_{\rm s}^0-\ln p_{\rm s}+\beta q_{\rm r}. \tag{13}$$

Assuming the reservoir initially in a Gibbs state, i.e., $p_{\rm r}^0=Z_{\rm r}^{-1}\exp[-\beta H_{\rm r}(y_0)]$, with $Z_{\rm r}=\int\exp[-\beta H_{\rm r}(y_0)]\,\mathrm{d}y_0$ being partition function, which has always been assumed in studying the second law of thermodynamics, we obtain the entropy change of the reservoir as

$$\ln p_{\rm r}^0-\ln p_{\rm r}=d(p_{\rm r}\,|p_{\rm r}^{\rm eq})+\beta(q_{\rm r}-\delta q_{\rm r}), \tag{14}$$

where $d(p_{\rm r}\,|p_{\rm r}^{\rm eq})=\ln p_{\rm r}^{\rm eq}-\ln p_{\rm r}$ is the entropy difference between the two distributions $p_{\rm r}$ and $p_{\rm r}^{\rm eq}$. This entropy difference $d(p_{\rm r}\,|p_{\rm r}^{\rm eq})$ describes the deviation from thermal equilibrium of the reservoir. Then Eq. (13) turns to be a relation between the two EPs,

$$\Sigma_{\rm inf}=\Sigma_{\rm therm}+d(p_{\rm r}\,|p_{\rm r}^{\rm eq})-\beta\delta q_{\rm r}, \tag{15}$$

where the last two terms on the right-hand side of the above equality appear due to the strong coupling. In weak coupling limit with the reservoir in a thermal equilibrium state, Eq. (15) is reduced to $\Sigma_{\rm inf}=\Sigma_{\rm therm}$ due to $d(p_{\rm r}\,|p_{\rm r}^{\rm eq})=0$ and $\delta q_{\rm r}=0$.

If the reservoir is driven out of the thermal equilibrium, i.e., in a non-Gibbs state, but $\delta q_{\rm r}$ is still zero, we obtain, from Eqs. (10) and (15), the FT of the thermodynamic EP as follows:

$$P_{\rm F}(\Sigma_{\rm therm})=\mathrm{e}^{\Sigma_{\rm therm}}P_{\rm R}^{\rm eq}(-\Sigma_{\rm therm}), \tag{16}$$

where $P_{\rm R}^{\rm eq}(\Sigma_{\rm therm})$ represents the probability of observing a particular value of the thermodynamic EP in a reverse process with the initial distribution being $p_{\rm r}^0=Z_{\rm r}^{-1}\exp[-\beta H_{\rm r}(\bar{y}_0)]$ (see Appendix B for details). From this result we reach an integral FT as

$$\langle \mathrm{e}^{-\Sigma_{\rm therm}}\rangle=1, \tag{17}$$

which indicates the same fluctuation for both the EPs. In other words, these two kinds of EPs are equivalent in measuring the irreversibility in this case, which also implies that the thermodynamic EP could be employed even in the case out of the thermal equilibrium of the reservoir.

However, the thermodynamic EP does not work in the strong coupling case. Different from Eq. (17), FT at strong coupling can be written as

$$\langle \mathrm{e}^{-\Sigma_{\rm therm}}\rangle=\gamma, \tag{18}$$

where the factor γ, different from unity, is given by

$$\gamma=\iiint \mathrm{e}^{-\beta\delta q}\bar{p}_{\rm s}^0(\bar{x}_0)\bar{p}_{\rm r}^{\rm eq}(\bar{y}_0)P_{\rm R}[\bar{z}(-t)\,|\bar{\lambda}(-t)]\times\delta(\Sigma_{\rm therm}+\Sigma_{\rm therm}^{\rm R})D[z(t)]\,\mathrm{d}\bar{z}_0\,\mathrm{d}\bar{z}\,\mathrm{d}\Sigma_{\rm therm}, \tag{19}$$

as derived in Appendix B. Moreover, equation (18) can be rewritten as a generalized FT, i.e.,

$$\langle \mathrm{e}^{-\Sigma_{\rm therm}-\kappa}\rangle=1, \tag{20}$$

where the new term $\kappa=\ln\gamma$ is due to the nonzero negative work done on the reservoir at strong coupling. This form is very similar to a previous result obtained in a nonequilibrium system subject to a feedback control, where the new term κ is replaced by the mutual information obtained by measurements.[38] In fact, measurements yield the same effects on the system as the reservoir, which implies that the term κ plays the same role as the feedback control.

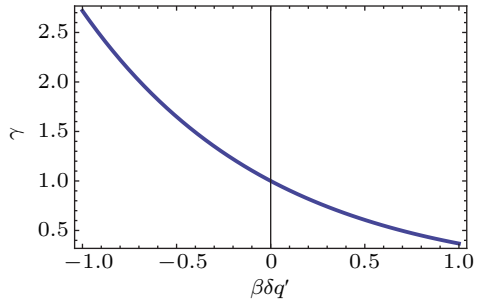


Fig. 1. The factor γ with respect to the heat correction $\delta q'$. In the interval $\delta q' \in (-\infty, 0]$, the case of $\gamma > 1$ implies the negative thermodynamic FT.

More importantly, appearance of the factor κ also implies that the second law of thermodynamics as expressed by the thermodynamic EP may be violated, i.e., $\langle \Sigma_{\rm therm} \rangle \leq 0$. To further clarify this point, we exemplify a special case that the heat correction in a system has a saddle point in the paths with all possible initial points in the total phase space. As a result, Eq. (18) can be approximated as[40]

$$\begin{aligned}\gamma =& \ \mathrm{e}^{-\beta\delta q'} \iiint \bar{p}_{\rm s}^{0}(\bar{x}_0)\bar{p}_{\rm r}^{\rm eq}(\bar{y}_0)P_{\rm R}[\bar{z}(-t)\,|\,\bar{\lambda}(-t)] \\ & \times \delta(\Sigma_{\rm therm}+\Sigma_{\rm therm}^{\rm R})D[z(t)]\,\mathrm{d}\bar{z}_0\,\mathrm{d}\bar{z}\,\mathrm{d}\Sigma_{\rm therm} \\ =& \ \mathrm{e}^{-\beta\delta q'}, \end{aligned} \tag{21}$$

where in the first line we have used the fact that the main contribution in the integral comes from the neighborhood of the saddle point, and in the second equality we have considered Eq. (B7) whose integral with respect to $\Sigma_{\rm therm}$ is equal to 1. Thus $\delta q'$ is the heat correction at the saddle point. In this context, we find that the ensemble average of the heat correction $\delta Q_{\rm r}$ is of the same order of magnitude as the heat correction $\delta q'$. To be more clarified, we plot Fig. 1 to show the possible region given by Eq. (21) for the negative thermodynamic EP, i.e., $\delta q' \in [-\infty, 0]$.

In fact, we can give a more exact condition under which the above-mentioned violation occurs. For this purpose, we consider a second-law lemma. By applying the Liouville equation of the composite system followed by partial integration, we find that the Shannon entropy of the composite system is a constant, i.e., $S_{\rm sr} = S_{\rm sr}^0$. If the PDFs of the system and reservoir are initially uncorrelated, the Shannon entropy is additive, i.e., $S_{\rm sr} = S_{\rm s}^0 + S_{\rm r}^0$. As a result, we obtain the following second-law lemma

$$\Delta S_{\rm s} + \Delta S_{\rm r} = I, \tag{22}$$

where $p^0(z) = p_{\rm s}^0(x)p_{\rm r}^0(y)$ is assumed. The term $I = S_{\rm s} + S_{\rm r} - S_{\rm sr}$ is the mutual information at the final time, where the entropy of the system (reservoir) $S_{\rm s} = -\sum p_{\rm s}(x)\ln p_{\rm s}(x)$ ($S_{\rm r} = -\sum p_{\rm r}(y)\ln p_{\rm r}(y)$) is the Shannon entropy of the system (reservoir) and also the ensemble average of the corresponding stochastic entropy. Similarly, $S_{\rm sr} = -\sum p(z)\ln p(z)$ is the Shannon entropy of the composite system. Under the condition that the reservoir is initially in a Gibbs state, i.e., $\Delta S_{\rm r} = -\sum p_{\rm r}(y)\ln p_{\rm r}(y) - \beta\langle H_{\rm r}(y_0)\rangle - \ln Z_{\rm r}$, we employ the ensemble average of the thermodynamic EP as

$$\langle \Sigma_{\rm therm} \rangle = \Delta S_{\rm s} + \beta Q_{\rm r}, \tag{23}$$

and we have

$$\beta\langle H_{\rm r}(y_0)\rangle = \Delta S_{\rm s} + \beta\langle H_{\rm r}(y)\rangle - \langle \Sigma_{\rm therm}\rangle + \beta\delta Q_{\rm r}. \tag{24}$$

Combining Eqs. (22), (23) with Eq. (24), we obtain

$$\langle \Sigma_{\rm therm} \rangle = I + D + \beta\delta Q_{\rm r}, \tag{25}$$

where the term

$$D = \sum_y p_{\rm r}(y)\,\mathrm{d}[p_{\rm r}(y)\,|\,p_{\rm r}^{\rm eq}(y)] = -\sum p_{\rm r}(y)\ln[p_{\rm r}(y)/p_{\rm r}^{\rm eq}(y)]$$

is a relative entropy. As a result, the sufficient condition of the violation is

$$\beta\delta Q_{\rm r} < -(I+D), \tag{26}$$

which may be satisfied at strong coupling. It implies that the thermodynamic EP is invalidated due to the heat correction, rather than the nonequilibrium effect from the thermal reservoir.

The above results indicate that the thermodynamic EP should be replaced by the informational EP in the strong coupling case in order to satisfy the second law of thermodynamics. We notice that information is introduced into the thermodynamics when we consider a thermodynamic process subject to quantum mechanics.[41] However, different from violation of thermodynamic laws due to quantum correlation involved,[42,43] the violation of the second law of thermodynamics in our case is due to the new definition of work and heat. More specifically, we are treating a purely classical situation, but in the strong coupling case effects regarding the reservoir should be seriously considered. The heat correction due to strong coupling, which is from the negative work on the reservoir, is more important than the nonequilibrium effect from the thermal reservoir in the difference between the thermodynamic EP and the informational EP.

5. Conclusions

In summary, we have explored the FT of entropy production in the case of the strong system–reservoir coupling by redefining heat and work to be trajectory-dependent. In comparison with previous definition regarding the changes of the corresponding state parameters, our definition is consistent with the concept of the thermodynamics. We have compared the informational EP with the thermodynamic EP, and presented a generalized FT of the thermodynamic EP. We have also found that, due to non-zero negative work on the reservoir in the strong coupling case, the thermodynamic EP should be replaced by the informational EP in order to keep the second law

of thermodynamics satisfied. These results would be helpful for understanding thermodynamic behavior in the strong coupling situation, particularly for example, for the effects from the reservoir on the observation.

Appendix A: Details of the FT of informational EP

To show the microscopic reversibility, we begin from the probability distribution of a trajectory $P_{\rm F}[z(t)\,|\lambda(t)] = \delta[z(t) - z(z_0,t)]$, where $z(t)$ represents any trajectory started from a phase point z_A chosen from the initial PDF, and $z(z_0,t)$ represents a special trajectory from the phase point z_0. From the microscopic reversibility, the time reverse trajectory of the special trajectory $\bar{z}(\bar{z}_0,-t)$ remains identical to the trajectory $z(z_0,t)$, i.e., $\bar{z}(\bar{z}_0,-t) = z(z_0,t)$. As a result, the probability distribution of a trajectory $z(t)$ is equal to that of its time reverse trajectory $z(z_0,t)$, i.e.,

$$P_{\rm R}[\bar{z}(t)\,|\bar{\lambda}(-t)] = P_{\rm F}[z(t)\,|\lambda(t)]. \tag{A1}$$

By a delta function, the probability $P_{\rm F}(\Sigma_{\rm inf}^{\rm F})$ of observing a particular value of the informational EP in a forward process can be obtained as the average over all forward trajectories and over all initial and final phase points, i.e.,

$$P_{\rm F}(\Sigma_{\rm inf}) = \iint p_{\rm s}^0(x_0)p_{\rm r}^0(y_0)P_{\rm F}[z(t)\,|\lambda(t)] \times \delta(\Sigma_{\rm inf} - \Sigma_{\rm inf}^{\rm F})D[z(t)]\,{\rm d}z_0\,{\rm d}z, \tag{A2}$$

where $\int\cdot D[z(t)]$ represents the sum over all paths in total phase space, and $\int\cdot\,{\rm d}z_0\,{\rm d}z$ the integral over all initial and final phase-space points. Using the result

$$\frac{p_{\rm s}^0(x_0)p_{\rm r}^0(y_0)P_{\rm F}[z(t)\,|\lambda(t)]}{\bar{p}_{\rm s}^0(\bar{x}_0)\bar{p}_{\rm r}^0(\bar{y}_0)P_{\rm R}[\bar{z}(-t)\,|\bar{\lambda}(-t)]} = {\rm e}^{\Sigma_{\rm inf}^{\rm F}}, \tag{A3}$$

the average over all forward trajectories can be converted to that over reverse trajectories

$$P_{\rm F}(\Sigma_{\rm inf}) = {\rm e}^{\Sigma_{\rm inf}} \iint \bar{p}_{\rm s}^0(\bar{x}_0)\bar{p}_{\rm r}^0(\bar{y}_0)P_{\rm R}[\bar{z}(-t)\,|\bar{\lambda}(-t)] \times \delta(\Sigma_{\rm inf} + \Sigma_{\rm inf}^{\rm R})D[z(t)]\,{\rm d}z_0\,{\rm d}z, \tag{A4}$$

where the term ${\rm e}^{\Sigma_{\rm inf}}$ is moved outside the integral due to the δ function, and $\Sigma_{\rm inf}^{\rm F} = -\Sigma_{\rm inf}^{\rm R}$ is used. Through the microscopic reversibility $\bar{z}(\bar{z}_0,-t) = z(z_0,t)$, we obtain $\int\cdot D[z(t)] = \int\cdot D[\bar{z}(-t)]$, and $\int\cdot\,{\rm d}z_0\,{\rm d}z = \int\cdot\,{\rm d}\bar{z}_0\,{\rm d}\bar{z}$. As a result, the probability in its time reverse process equals

$$P_{\rm R}(-\Sigma_{\rm inf}) = \iint \bar{p}_{\rm s}^0(\bar{x}_0)\bar{p}_{\rm r}^0(\bar{y}_0)P_{\rm R}[\bar{z}(-t)\,|\bar{\lambda}(-t)] \times \delta(\Sigma_{\rm inf} + \Sigma_{\rm inf}^{\rm R})D[z(t)]\,{\rm d}z_0\,{\rm d}z. \tag{A5}$$

Combining Eqs. (A4) and (A5), we obtain the the FT of the informational EP.

Appendix B: Details of the generalized FT of thermodynamic EP

For the initial probability distribution of the reservoir $p_{\rm r}^0 = Z_{\rm r}^{-1}\exp[-\beta H_{\rm r}(y_0)]$, we have $\ln p_{\rm r}^0 = -\ln Z_{\rm r} - \beta H_{\rm r}(y_0)$, which, by means of the definition of heat, implies $\ln p_{\rm r}^0 = -\ln Z_{\rm r} - \beta[H_{\rm r}(y) - q_{\rm r} + \delta q_{\rm r}]$, and can be rewritten as

$$\ln p_{\rm r}^0 = \ln p_{\rm r}^{\rm eq} + \beta(q_{\rm r} - \delta q_{\rm r}), \tag{B1}$$

where $p_{\rm r}^{\rm eq} = Z_{\rm r}^{-1}\exp[-\beta H_{\rm r}(y)]$ is a Gibbs distribution at final time. Unfortunately, the final distribution of the reservoir may not be this Gibbs distribution, since the equilibrium state at strong coupling is different from the Gibbs state. As a result, the entropy change of the reservoir is

$$\ln p_{\rm r}^0 - \ln p_{\rm r} = d(p_{\rm r}\,|p_{\rm r}^{\rm eq}) + \beta(q_{\rm r} - \delta q_{\rm r}), \tag{B2}$$

with $d(p_{\rm r}\,|p_{\rm r}^{\rm eq}) = \ln p_{\rm r}^{\rm eq} - \ln p_{\rm r}$ being the entropy difference. Substituting Eq. (B2) into Eq. (10) yields

$$\frac{p_{\rm s}^0(x_0)p_{\rm r}^0(y_0)P_{\rm F}[z(t)\,|\lambda(t)]}{\bar{p}_{\rm s}^0(\bar{x}_0)\bar{p}_{\rm r}^0(\bar{y}_0)P_{\rm R}[\bar{z}(-t)\,|\bar{\lambda}(-t)]} = {\rm e}^{\Sigma_{\rm therm} + d(p_{\rm r}|p_{\rm r}^{\rm eq}) - \beta\delta q_{\rm r}}. \tag{B3}$$

To obtain Eq. (15), we begin from the probability of observing a particular value of the thermodynamic EP in a forward process $P_{\rm F}(\Sigma_{\rm therm})$. Similar to $P_{\rm F}(\Sigma_{\rm inf})$, the probability $P_{\rm F}(\Sigma_{\rm therm})$ can be written as

$$P_{\rm F}(\Sigma_{\rm therm}) = \iint p_{\rm s}^0(x_0)p_{\rm r}^0(y_0)P_{\rm F}[z(t)\,|\lambda(t)] \times \delta(\Sigma_{\rm therm} - \Sigma_{\rm therm}^{\rm F})D[z(t)]\,{\rm d}z_0\,{\rm d}z. \tag{B4}$$

Substituting Eq. (B3) with $\delta q_{\rm r} = 0$ into Eq. (B4), we find

$$P_{\rm F}(\Sigma_{\rm therm}) = {\rm e}^{\Sigma_{\rm therm}} \iint {\rm e}^{d(p_{\rm r}|p_{\rm r}^{\rm eq})}\bar{p}_{\rm s}^0(\bar{x}_0)\bar{p}_{\rm r}^0(\bar{y}_0)P_{\rm R}[\bar{z}(-t)\,|\bar{\lambda}(-t)] \times \delta(\Sigma_{\rm therm} + \Sigma_{\rm therm}^{\rm R})D[z(t)]\,{\rm d}z_0\,{\rm d}z, \tag{B5}$$

where the condition that the thermodynamic EP is an odd function under the time reversal is used. Using the identity ${\rm e}^{d(p_{\rm r}|p_{\rm r}^{\rm eq})} = p_{\rm r}^{\rm eq}/p_{\rm r}$, we obtain

$$P_{\rm F}(\Sigma_{\rm therm}) = {\rm e}^{\Sigma_{\rm therm}} \iint \bar{p}_{\rm s}^0(\bar{x}_0)\bar{p}_{\rm r}^{\rm eq}(\bar{y}_0)P_{\rm R}(\bar{z}\,|\bar{z}_0) \times \delta(\Sigma_{\rm therm} + \Sigma_{\rm therm}^{\rm R})D[z(t)]\,{\rm d}z_0\,{\rm d}z. \tag{B6}$$

Using $\int\cdot D[z(t)] = \int\cdot D[\bar{z}(-t)]$ and $\int\cdot\,{\rm d}z_0\,{\rm d}z = \int\cdot\,{\rm d}\bar{z}_0\,{\rm d}\bar{z}$, we have

$$P_{\rm R}^{\rm eq}(-\Sigma_{\rm therm}) = \iint \bar{p}_{\rm s}^0(\bar{x}_0)\bar{p}_{\rm r}^{\rm eq}(\bar{y}_0)P_{\rm R}(\bar{z}\,|\bar{z}_0) \times \delta(\Sigma_{\rm therm} + \Sigma_{\rm therm}^{\rm R})D[z(t)]\,{\rm d}z_0\,{\rm d}z, \tag{B7}$$

where $P_{\rm R}^{\rm eq}(-\Sigma_{\rm therm})$ describes the probability of observing a particular value of the thermodynamic EP in a reverse process the reservoir stopped at a Gibbs state $\bar{p}_{\rm r}^{\rm eq}(\bar{y}_0)$. Combining Eqs. (B6) and (B7), we achieve Eq. (15).

Now we demonstrate the form of γ in Eq. (18). Combining Eqs. (B3) and (B4), we obtain $P_{\rm F}(\Sigma_{\rm therm})$ as

$$P_{\rm F}(\Sigma_{\rm therm}) = {\rm e}^{\Sigma_{\rm therm}} \iint {\rm e}^{-\beta\delta q}\bar{p}_{\rm s}^{0}(\bar{x}_0)\bar{p}_{\rm r}^{\rm eq}(\bar{y}_0)P_{\rm R}(\bar{z}\,|\bar{z}_0\,) \times \delta(\Sigma_{\rm therm}+\Sigma_{\rm therm}^{\rm R})D[z(t)]\,{\rm d}z_0\,{\rm d}z, \tag{B8}$$

whose integral FT is

$$\left\langle {\rm e}^{-\Sigma_{\rm therm}}\right\rangle = \iiint {\rm e}^{-\beta\delta q}\bar{p}_{\rm s}^{0}(\bar{x}_0)\bar{p}_{\rm r}^{\rm eq}(\bar{y}_0)P_{\rm R}(\bar{z}\,|\bar{z}_0\,) \times \delta(\Sigma_{\rm therm}+\Sigma_{\rm therm}^{\rm R})D[z(t)]\,{\rm d}z_0\,{\rm d}z\,{\rm d}\Sigma_{\rm therm}. \tag{B9}$$

Therefore, the factor γ is given by

$$\gamma = \iiint {\rm e}^{-\beta\delta q}\bar{p}_{\rm s}^{0}(\bar{x}_0)\bar{p}_{\rm r}^{\rm eq}(\bar{y}_0)P_{\rm R}(\bar{z}\,|\bar{z}_0\,) \times \delta(\Sigma_{\rm therm}+\Sigma_{\rm therm}^{\rm R})D[z(t)]\,{\rm d}z_0\,{\rm d}z\,{\rm d}\Sigma_{\rm therm}. \tag{B10}$$

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