Complementarity relation for irreversible process derived from stochastic energetics

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When the process of a system in contact with a heat bath is described by classical Langevin equation, the method of stochastic energetics [K. Sekimoto, J. Phys. Soc. Jpn. 66 (1997) 1234] enables to derive the form of Helmholtz free energy and the dissipation function of the system.

We prove that the irreversible heat $Q_{irr}$ and the time lapse $\Delta t$ of an isothermal process obey the complementarity relation, $Q_{irr} \Delta t \geq k_B T \Delta S_{min}$, where $\Delta S_{min}$ depends on the initial and the final values of the control parameters, but it does not depend on the pathway between these values.

KEYWORDS: irreversible thermodynamics, complementarity, energetics, Langevin

The relations of thermodynamics tell that, when we change quasi-statically the control parameters of a system in contact with a heat bath, the work $W$ needed for the change is equal to the change of Helmholtz free energy, $\Delta F$, which consists of the reversible heat released to the heat bath, $Q_{rev}$, and the change of internal energy, $\Delta U$, as $Q_{rev} + \Delta U = \Delta F$. When the change of the control parameter is not quasi-static, the needed work is more than the reversible one, i.e., $W + \Delta F \geq 0$, and the released heat $Q$, which obeys the energy conservation law $Q + \Delta U = W$, is larger than $Q_{rev}$ by the amount so-called irreversible heat $Q_{irr} \equiv Q - Q_{rev} = W - \Delta F$.

In order to assess the released heat $Q$ under a given protocol of control parameters, we need both a dynamical model of a system and a proper kinematical interpretation of the heat release from the system. One of the present authors have introduced a method to obtain $Q$ in the systems whose dynamics is described by Langevin equations. We will show below that, if applied to slow change of control parameters, this method, which we shall provisionally call stochastic energetics, enables to formulate reversible and irreversible thermodynamics of processes of the system in contact with a heat bath.

First we recapitulate the main idea of stochastic energetics in the case of a single heat bath. Let $x = \{x_1, \ldots, x_n\}$ represent the state of the fluctuating system and let $a = \{a_1, \ldots, a_r\}$ be the parameters which control the system through the potential $U(x; a)$. The Langevin equation is assumed to be as follows,

$$0 = -\Gamma \cdot \frac{dx}{dt} + \xi(t) - \frac{\partial U}{\partial x}(x; a),$$

where $\Gamma$ is a positive definite and symmetric friction matrix, which we assume to be constant, and $\xi(t)$ is white and Gaussian random forces characterized by $\langle \xi(t) \rangle = 0$ and $\langle \xi(t) \xi(t') \rangle = 2\Gamma k_B T \delta(t-t')$. As far as we can regard $\xi$ as a mechanical balance equation, the balance equation for energy is obtained by making the scalar products of each term with $dx(t) \equiv x(t + \frac{dt}{2}) - x(t - \frac{dt}{2})$ along the realized trajectory,

$$-(-\Gamma \cdot \frac{dx}{dt}(t) + \xi(t)) \cdot dx(t) = \frac{\partial U}{\partial a}(x(t); a(t)) \cdot da(t) - dU(x(t); a(t)),$$

where we have used the identity $dU = \frac{\partial U}{\partial x} \cdot dx + \frac{\partial U}{\partial a} \cdot da$, which is valid for stochastic variables as far as the multiplication is defined in the Stratonovich sense.

The left hand side is the heat released to the heat bath, $dQ$, since $-(-\Gamma \frac{dx}{dt}(t) + \xi(t))$ is the reaction force which the system exerts onto the heat bath. The energy conservation law implies that $dQ + dU$ should be equal to the work $dW$ done by the external agent to the system, hence

$$dW = \frac{\partial U}{\partial a}(x(t); a(t)) \cdot da(t).$$

Suppose that the control parameters $a$ is changed (by some external agent) from $a_i$ at $t = 0$ to $a_f$ at $t = \Delta t$. The total work $W$ done to the system in the course of a particular process $x(t)$ ($0 \leq t \leq \Delta t$) is then,

$$W = \int_0^{\Delta t} dt \frac{\partial U}{\partial a}(x(t); a(t)) \cdot \frac{da(t)}{dt}.$$

That the work $W$ is defined before we take ensemble average is both conceptual and practical advantage of stochastic energetics as compared with the master equation approach. The ensemble average of $W$ over possible realization of $\{\xi(t)\}_{0 \leq t \leq \Delta t}$ is expressed as

$$W \equiv \langle W \rangle = \int_0^{\Delta t} dt \left[ \int dx P(x, t) \frac{\partial U}{\partial a}(x; a(t)) \right] \cdot \frac{da(t)}{dt},$$

where $P$ is the probability distribution function of $x$. 

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which obeys the following Fokker-Planck equation:

\[
\frac{\partial P}{\partial t}(x, t) = -\mathcal{L}_{FP}(a(t))P(x, t) = \frac{\partial}{\partial x} \cdot \Gamma^{-1} \cdot \left( \frac{\partial U}{\partial x}(x; a(t)) + k_B T \frac{\partial}{\partial x} \right) P(x, t). \tag{6}
\]

Below we describe the main results, whose derivation will be given in the last part of the text. Let \( \hat{a}(s) \) be a given protocol of the control parameter \( a \) with a unit time lapse (\( \Delta t = 1 \)) satisfying \( \hat{a}(0) = a_i \) and \( \hat{a}(1) = a_f \). We assume, for convenience, the unit of time to be the characteristic time of equilibration of \( P(x, t) \) when \( a \) is fixed at a typical value of the protocol. Then for the stretched or slowed-down protocol \( a(t) = \hat{a}(s/\Delta t) \) with a large time lapse \( \Delta t \), the following asymptotic formula for \( W \) holds:

\[
W = \Delta F + \frac{k_B T}{\Delta t} \int_0^1 ds \left( \frac{d\hat{a}(s)}{ds} \right) \cdot \Lambda(\hat{a}(s)) \cdot \frac{d\hat{a}(s)}{ds} + O((\Delta t)^{-2}), \tag{7}
\]

where \( \Delta F \) is the difference of the Helmholtz free energy, \( \Delta F \equiv F(a_f) - F(a_i) \) with

\[
F(a) = -k_B T \log \left\{ \int dx \exp \left[ -\frac{U(x; a)}{k_B T} \right] \right\} \text{ const},
\]

and \( \Lambda(a) \) is a positive definite \( n \times n \) matrix defined by

\[
\Lambda(a) = -\int dx \int dx' \frac{\partial P_{eq}(x; a)g(x, x'; a)}{\partial a} \cdot \left( \frac{\partial P_{eq}(x'; a)}{\partial a} \right), \tag{9}
\]

where \( P_{eq}(x; a) \equiv e^{-U(x; a)/k_B T} / \int dx e^{-U(x; a)/k_B T} \) is the equilibrium distribution under a given parameter value, \( a \), and the kernel \( g(x, x'; a) \) is defined as the solution of the following equation

\[
-\mathcal{L}_{FP}(a)[P_{eq}(x; a)g(x, x'; a)] = \delta(x - x'). \tag{10}
\]

The result (7) tells firstly that, in the limit of slow and smooth change of external parameters \( (\Delta t \to \infty) \), the stochastic energetics reproduces correctly the thermodynamic relation of quasi-static isothermal processes, \( W = \Delta F \). Secondly, for large but finite time lapse \( \Delta t \), the irreversible heat \( Q_{irr} \) behaves asymptotically as \( \sim \frac{\Delta F}{\Delta t} \) with the proportionality constant depending on the scaled protocol \( \hat{a}(s/\Delta t) \). The integral on the right hand side of (7) is analogous to a classical action of free particle with a ‘mass’ \( 2\Lambda \) being dependent on the ‘position’ \( a \). The minimum value of this integral, which we denote by \( S_{min}(a_i, a_f) \), should be realized by a certain ‘classical’ path, or the optimal (scaled) protocol \( \hat{a}^*(s) \) \( (0 \leq s \leq 1) \). We then come to the following complementarity relation which is correct asymptotically for \( \Delta t \to \infty \),

\[
Q_{irr} \Delta t \geq k_B T S_{min}(a_i, a_f). \tag{11}
\]

The above relation implies a sort of uncertainty relation that the estimation of the Helmholtz free energy function by the measurement of mechanical work \( W \) inevitably includes a deviation \( Q_{irr} \) whose lower bound is controlled by the inverse of the measuring time \( \Delta t \), at least in moderately slow measurements.

**Remark 1.** The dissipation function \( \Phi \) of linear irreversible thermodynamics is usually defined as \( dQ_{irr} = 2\Phi(\frac{d\theta}{dt}) \). In our method \( \Phi \) is obtained if we neglect the \( O((\Delta t)^{-2}) \) terms in (7) and rewrite the integral there using \( a(t) \) instead of \( \hat{a}(s) \):

\[
\Phi(\frac{d\theta}{dt}) = k_B T \cdot \frac{d\theta}{dt} \cdot \Lambda(a(t)) \cdot \frac{d\theta}{dt}. \tag{12}
\]

**Remark 2.** In terms of the spectral representation of the Fokker-Planck operator,

\[
\mathcal{L}_{FP}(a) = \sum_{m=0}^{\infty} |m; a\rangle \lambda_m(a) \langle m; a|,
\]

with \( 0 = \lambda_0(a) < \lambda_1(a) \leq \lambda_2(a) \leq \ldots \) and \( \langle m; a|n; a\rangle = \delta_{mn} \), the kernel \( \Lambda(a) \) is formally expressed as

\[
\Lambda(a) = \frac{1}{(k_B T)^2} \times \sum_{m=1}^{\infty} \langle 0| a \rangle \cdot \left[ \frac{\partial U}{\partial a} \right] |m; a\rangle \cdot \frac{1}{\lambda_m(a)} \cdot \langle m; a| \frac{\partial U}{\partial a} |0; a\rangle. \tag{13}
\]

Here \( a \) appears merely as a parameter.

**Remark 3.** The function \( g(x, x'; a) \) is the Green’s function of a Hermitian operator;

\[
k_B T \cdot \frac{\partial}{\partial x} \cdot \Gamma^{-1} P_{eq}(x; a) \cdot \left( \frac{\partial}{\partial x} \right) g(x, x'; a) = \delta(x - x'). \tag{14}
\]

Especially when \( x \) is a single variable, \( x \), and \( \Gamma \), a constant \( \gamma \), the explicit form of \( g(x, x'; a) \) is

\[
g(x, x'; a) = \frac{\gamma}{2k_B T} \cdot \text{sgn}(x - x') \int_{x'}^{x} \frac{dz}{P_{eq}(z; a)}. \tag{15}
\]

**Remark 4.** If the control parameters \( a \) are constrained to change along a single trajectory, say \( \hat{a}(\theta) \), where \( 0 \leq \theta \leq 1 \) is the contour parameter with \( \hat{a}(0) = a_i \) and \( \hat{a}(1) = a_f \), then \( Q_{irr} \) depends yet on how \( \theta \) depends on the scaled time \( s \), as well as on the time lapse \( \Delta t \). The integral in (7) then becomes \( \int_0^1 \Lambda(\theta(s)) |\frac{d\theta(s)}{ds}|^2 ds \), where

\[
\Lambda(s) = \frac{\left( \frac{d\hat{a}(s)}{ds} \right) \cdot \Lambda(\hat{a}(s)) \cdot \frac{d\hat{a}(s)}{ds}}{4k_B T}. \tag{16}
\]

If we note that this integral becomes the simple action \( \int_0^1 |\frac{d\theta(s)}{ds}|^2 ds \) by the transformation \( du(s) \equiv \Lambda(\theta(s))^{1/2} \frac{d\theta(s)}{ds} \), the minimum of the integral is explicitly given as \( \left[ \frac{1}{0} \right]^1 \Lambda(\theta)^{1/2} \frac{d\theta}{dt} \right|^2 \). Although not apparent, this result is invariant under the relabeling of the contour parameter.

As an illustration, let us apply our formulae to the case of \( U(x; a) = \frac{1}{2} \cdot x^2 \) with the single variable \( x \) and the single control parameter \( a \), with \( \Gamma \) a constant \( \gamma \). In \( O((\Delta t)^0) \) order we recover the correct (configurational) free energy

\[
\Delta F = \frac{k_B T}{2} \text{ log } \frac{a_f}{a_i}. \tag{17}
\]

In this case \( F \) is purely of entropic origin since, from
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equipartition theorem, the internal energy is independent of the ‘width’ of the potential, $\sim 1/\sqrt{a}$.

In $O((\Delta t)^{-1})$ order, we obtain the irreversible heat

$$Q_{\text{irr}} = \frac{\gamma k_B T}{4 \Delta t} \int_0^1 ds \frac{1}{\tilde{a}(s)} \left[ \frac{d\tilde{a}(s)}{ds} \right]^2 + O((\Delta t)^{-2}).$$  \(18\)

The integral can be minimized by the following scaled protocol;

$$\tilde{a}(s)_{\text{optimum}} = \left[ \frac{s}{\sqrt{a_f}} + \frac{1-s}{\sqrt{a_i}} \right]^{-2},$$  \(19\)

and the asymptotic complementarity relation reads as follows,

$$Q_{\text{irr}} \Delta t \geq \frac{\gamma k_B T}{4} \left[ 1 - \frac{1}{\sqrt{a_i}} \right]^2.$$  \(20\)

Proof of (7) If we introduce the scaled time $s = t/\Delta t$ and the probability distribution with this argument, $\hat{P}(x, s; \Delta t) \equiv \hat{P}(x, s, \Delta t)$, the equations (5) and (6) becomes, respectively,

$$W = \int_0^1 ds \frac{d\tilde{a}(s)}{ds} \cdot \int dx \frac{\partial \overline{U}}{\partial a}(x; \tilde{a}(s)) \hat{P}(x, s; \Delta t) \hspace{1cm} 21$$

$$\frac{1}{\Delta t} \frac{1}{ds} \frac{\partial \hat{P}}{\partial s}(x, s; \Delta t) = -\mathcal{L}_{\text{FP}}(\tilde{a}(s)) \hat{P}(x, s; \Delta t).$$ \(22\)

For large $\Delta t$, we may solve \(22\) perturbatively in the form of

$$\hat{P}(x, s; \Delta t) = \hat{P}^{(0)}(x, s) + \frac{1}{\Delta t} \hat{P}^{(1)}(x, s) + \cdots$$ \(23\)

In the lowest order $\hat{P}^{(0)}$ obeys $\mathcal{L}_{\text{FP}}(\tilde{a}(s)) \hat{P}^{(0)}(x, s) = 0$, and the normalization condition $\int dx \hat{P}^{(0)}(x, s) = 1$. Then, $\hat{P}^{(0)}(x, s)$ is the equilibrium distribution for a given parameter $\tilde{a}(s)$, i.e.,

$$\hat{P}^{(0)}(x, s) = P_{\text{eq}}(x; \tilde{a}(s)).$$ \(24\)

From (5) and the identity $\int dx \frac{\partial \psi}{\partial a}(x; a) P_{\text{eq}}(x; a) = \frac{\partial P_{\text{eq}}}{\partial a}(a)$, the $O((\Delta t)^0)$ term of $W$ becomes $F(a_f) - F(a_i)$.

In the next order, \(22\) becomes, $-\mathcal{L}_{\text{FP}}(\tilde{a}(s)) \hat{P}^{(1)}(x, s) = \frac{\partial P_{\text{eq}}}{\partial a}(x; \tilde{a}(s))$. Using \(24\), the solution is given as

$$\hat{P}^{(1)}(x, s) = P_{\text{eq}}(x; \tilde{a}(s)) \times \left[ \int dx' g(x, x'; \tilde{a}(s)) \frac{\partial P_{\text{eq}}}{\partial s}(x'; \tilde{a}(s)) + \chi \right],$$ \(25\)

where $\chi$ is to be determined from the normalization condition, $\int dx \hat{P}^{(1)}(x, s) = 0$. After performing this, and noting the relation $\frac{\partial \tilde{a}(s)}{\partial s}(x; \tilde{a}(s)) = t\left( \frac{\partial P_{\text{eq}}}{\partial a}(x'; \tilde{a}(s)) \right)$.

$$\frac{d\tilde{a}(s)}{ds},$$ the kernel $\Lambda(\tilde{a}(s))$ in (7) becomes as follows,

$$\Lambda(a) = \frac{1}{k_B T} \int dx \int dx' t \left( \frac{\partial U}{\partial a}(x; a) \right) P_{\text{eq}}(x; a) \times P_{\text{eq}}(x; a) \psi(x) = \int dx [\delta(x - x) - P_{\text{eq}}(x; a)] \psi(x) \hspace{1cm} 27$$

for an arbitrary function of $\psi(x)$. Next the factors $t \left( \frac{\partial U}{\partial a}(x; a) \right) P_{\text{eq}}(x; a)$ in (26) can be rewritten as

$$t \left( \frac{\partial U}{\partial a}(x; a) \right) P_{\text{eq}}(x; a) = -k_B T \frac{\partial P_{\text{eq}}}{\partial a}(x; a) + P_{\text{eq}}(x; a) \int dx' t \left( \frac{\partial U}{\partial a}(x; a) \right) P_{\text{eq}}(x; a).$$ \(28\)

Here the second term on the right hand side $(\propto P_{\text{eq}}(x; a))$ does not contribute to the integral of (26) since the following identity holds for an arbitrary function, $\psi(x)$,

$$\int dx P_{\text{eq}}(x; a) \psi(x) = 0.$$ \(29\)

Now the integral in $\Lambda(a)$ is of the form of

$$\int dx \frac{\partial P_{\text{eq}}}{\partial a}(x; a) \psi(x),$$ and since the following identity

$$\int dx \frac{\partial P_{\text{eq}}}{\partial a}(x; a) \psi(x) \hspace{1cm} 30$$

holds for an arbitrary function $\psi(x)$, we come to the expression (9).

In this letter we have considered the irreversible process near equilibrium states. Although it may not have been explicitly stated, the complementarity relation itself is derivable from phenomenological dissipation function. The method of stochastic energetics not only gives a concrete form of the bound of the uncertainty between $Q_{\text{irr}}$ and $\Delta t$, but it is also applicable to not slow processes such as thermal ratchets or far from equilibrium non-steady states. How the irreversible heat does or does not depend on the models under the non-slow processes is a challenging problem in future.

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