

## Langevin Equation and Thermodynamics

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We introduce a framework of energetics into the stochastic dynamics described by Langevin equation in which fluctuation force obeys the Einstein relation. The energy conservation holds in the individual realization of stochastic process, while the second law and steady state thermodynamics of Oono and Paniconi [Y. Oono and M. Paniconi, this issue] are obtained as ensemble properties of the process.

### §1. Introduction

This symposium features the statistics, stochastics and phenomenological theories of diverse areas, and the present paper is also on these aspects, especially from the viewpoint of energy, which I tentatively call *stochastic energetics*. There are at least three levels of description of (classical) dynamical systems. One is a microscopic Hamiltonian dynamics including all degrees of freedom of the system concerned, whose evolution is deterministic. There is also a macroscopic thermodynamic formalism with thermodynamics variables. The thermodynamics formalism usually does not specify the dynamics of a system, but the system is supposed to be somehow controlled by external agents. The intermediate level between them would be the stochastic dynamics such as the Langevin equation. At this level, we define the dynamics but it is not deterministic, and we introduce external agents to control the system but they only partly control it.

We already know several relations between these three levels. For example, Zwanzig-Mori formalism relates the Hamilton dynamics and a generalized Langevin equation by using projection method. If we allow a Markovian approximation, we obtain the usual Langevin equation.<sup>1)</sup> Also the framework of statistical mechanics enables us to predict equilibrium thermodynamics if we are given the Hamiltonian. And the foundation of statistical mechanics, or ergodic theory, is still a research subject of fundamental physics.

As we have exemplified the relation between the micro level and the macro level, and also the one between the micro level and the stochastic level, the question then is 'how is stochastic dynamics related to thermodynamics?' There have been pioneering work,<sup>2)-6)</sup> which taught us about the condition needed for consistency of stochastic dynamics with thermodynamics. To describe it, let us take a simple Langevin equation,

$$\gamma \frac{dx}{dt} = -\frac{dU}{dx} + \xi(t). \quad (1.1)$$

Here  $x$  is the dynamical variable(s) of a system,  $\gamma$  the friction constant,  $U$  the

potential energy for  $x$ , and  $\xi(t)$  is the thermal noise from a heat bath, which we assume to obey Gaussian and white correlated stochastic process with the properties (hereafter we take the unit of  $k_B = 1$ ),

$$\langle \xi(t) \rangle = 0, \quad \langle \xi(t)\xi(t') \rangle = 2\gamma T \delta(t - t'). \quad (1.2)$$

The coefficient of  $\delta(t - t')$  in the last equation is from the Einstein relation by which  $x$  obeys the canonical distribution at the temperature  $T$  after a long time unless  $U$  depends explicitly on time.

Intensive study has also been done by Lebowitz and his colleagues since late 50s<sup>7)</sup> on the master equations consistent with either canonical or grand-canonical ensembles. After completion of our framework,<sup>8)</sup> we noticed their work and found that ours is along the line of their master equation approach, with more emphasis on the mechanical aspects of an individual realization of stochastic process. Recently, since the proposal of Ajdari and Prost,<sup>9)</sup> many models of thermal ratchet that rectifies thermal fluctuating force to yield a systematic work have been proposed and studied.<sup>14)</sup> Those works, which are based on the framework of Langevin equation, however, lacked the analysis of energetics, except for some attempts.<sup>10)</sup>

Our question is, then, how Langevin dynamics is related to the first and second law of equilibrium thermodynamics and also to non-equilibrium thermodynamics. There might be a skepticism that a Langevin equation, or especially  $\gamma \frac{dx}{dt}$  term, describes only irreversible processes. In fact, if we multiply  $\frac{dx}{dt}$  both sides of (1.1), we have

$$\frac{dU}{dt} = -\gamma \left| \frac{dx}{dt} \right|^2 - \xi(t) \frac{dx}{dt}, \quad (1.3)$$

which would tell us that the rate of the change of potential energy of the system is given by a definitely negative term together with the term which is apparently non-constructive. But this interpretation is, of course, misleading, since, if so, Langevin equations may not describe thermal activation processes as Kramers<sup>11)</sup> did successfully in 1940.

## §2. Framework of stochastic energetics

Thus we assert that Langevin equations can describe reversible thermodynamic processes. More concretely we start with the following assertion: If a Langevin equation represents the balance of forces on a system, then the Langevin dynamics conserves the energy of the system plus the surrounding heat bath. This is essentially the first law of thermodynamics applied to an individual realization of the stochastic process. Let us take a simple example (1.1) again. If we rearrange the terms in (1.1), we have the expression

$$0 = -\gamma \frac{dx}{dt} + \xi(t) - \frac{dU}{dx}. \quad (2.1)$$

The first two terms on the right-hand side (r.h.s.) are due to the interaction between the system and the heat bath;  $-\gamma \frac{dx}{dt}$  is the systematic force, and  $\xi(t)$  is the remaining fluctuating force. The last term is, on the other hand, the force due to the system's

potential. These forces on the system's degree of freedom  $x$  sum up to make zero, that is, the balance of forces is established at every moment of time (the framework is valid also if we incorporate the inertia term, see Ref. 8)).

Suppose that the state of the system has changed by  $dx$ . The multiplication of the forces in (2.1) by  $(-dx)$  should represent the energy balance,

$$0 = - \left( -\gamma \frac{dx}{dt} + \xi(t) \right) dx + \frac{dU}{dx} dx . \quad (2.2)$$

On the r.h.s. of (2.2),  $-\left(-\gamma \frac{dx}{dt} + \xi(t)\right)$  is the *reaction* force to the heat bath exerted by the system since it is the minus sign of the force exerted to the system by the heat bath, as mentioned above. The remaining term is the change of  $U$ . What is the work done by the reaction force? We may identify it as the discarded *heat* by the system into the heat bath, which we denote by  $dQ$ ,

$$dQ \equiv - \left( -\gamma \frac{dx}{dt} + \xi(t) \right) dx. \quad (2.3)$$

(The sign convention here is opposite to the usual macroscopic thermodynamics;  $Q = -Q$ .) The energy balance, therefore, is symbolically expressed as

$$0 = dQ + dU. \quad (2.4)$$

Let us consider a slight extension of the above example, which, in fact, is general enough to discuss thermodynamic processes. We assume that the potential energy  $U$  depends, not only on the system's variable  $x$ , but on the variable  $a$  which represents the effect of an external agent (or agents),

$$\gamma \frac{dx}{dt} = - \frac{\partial U(x, a)}{\partial x} + \xi(t). \quad (2.5)$$

The argument above applies again, and we obtain the energy balance equation,

$$0 = - \left( -\gamma \frac{dx}{dt} + \xi(t) \right) dx + \frac{\partial U(x, a)}{\partial x} dx. \quad (2.6)$$

Here the last term of (2.6) is no more the total differential of  $U$ . To complete the differential form, we must add to the both side the quantity,  $\frac{\partial U}{\partial a} da$ . We then have the general expression of the energy balance as

$$\frac{\partial U}{\partial a} da = dQ + dU. \quad (2.7)$$

Now, from the energy conservation law of *mechanics* the left-hand side (l.h.s.) of (2.7) must be the work done by the external system through the change of the variable  $a$ . We may summarize that, for the type of Langevin dynamics (2.5), the following law of energy balance is obtained,<sup>8)</sup>

$$dW = dQ + dU, \quad (2.8)$$

where the work by the external system,  $dW$ , has been defined as

$$dW \equiv \frac{\partial U}{\partial a} da. \quad (2.9)$$

We should note that, in the above expressions,  $dx$  and, consequently,  $dU$  are the actual changes obeying the Langevin dynamics (2.5) during the time interval  $dt$  when we specify a particular realization of both the fluctuation force  $\xi(t)$  and the protocol of the parameter  $a$ . Another remark is that all the multiplication of fluctuating quantities, e.g.  $\xi(t)dx$ , should be understood in the sense of Stratonovich calculus.<sup>12)</sup> What we have introduced above is not any new dynamics, but a framework of energetics for a stochastic dynamics. We have noticed that the heat bath receives the reaction force from the system although we assume, as usual, that the heat bath is not affected by the system.

### §3. Thermal energy transducer and converter

Before exploring more of the thermodynamics by the above framework, we describe some applications of it to show how it works. Suppose that there are two heat baths with the temperature  $T_1$  and  $T_2$ , respectively, and that, in each heat bath, a vane is immersed (Fig. 1). These vanes can undergo rotational Brownian motion characterized by the temperature of the heat bath and the friction constants,  $\gamma_1$  and  $\gamma_2$ , respectively, if these vanes are uncoupled. Now we introduce the coupling between the rotation angles,  $x_1$  and  $x_2$  of these two vanes through the potential energy  $U(x_1, x_2)$ . We expect there to occur a heat flow from the high temperature bath, say the  $T_1$  side, to the cooler side, say the  $T_2$  side. The corresponding Langevin equations are

$$\gamma_1 \frac{dx_1}{dt} = -\frac{\partial U(x_1, x_2)}{\partial x_1} + \xi_1(t), \quad (3.1)$$

$$\gamma_2 \frac{dx_2}{dt} = -\frac{\partial U(x_1, x_2)}{\partial x_2} + \xi_2(t), \quad (3.2)$$

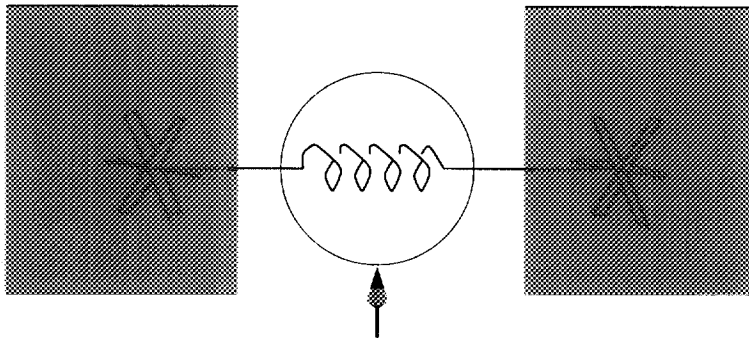


Fig. 1. Thermal energy transducer: In each heat bath (shaded), a vane is immersed. The two vanes are connected to a spring (center). An external agent (thick arrow) may change the potential energy of the spring (see § 5).

where the fluctuating force terms obey the Gaussian and white processes with  $\langle \xi_i(t) \rangle = 0$  and  $\langle \xi_i(t) \xi_i(t') \rangle = 2\gamma_i T_i \delta(t - t')$ , for  $i = 1$  or  $2$ , while we assume that the cross-correlation is zero,  $\langle \xi_1(t) \xi_2(t') \rangle = 0$ . Especially, if we assume the coupling by a harmonic spring having the elasticity against the twist, or the angle differences of the two vanes,  $U(x_1, x_2) = \frac{K}{2}(x_1 - x_2)^2$ , then the ensemble average of heat flow in the steady state is explicitly given by

$$\left\langle \frac{dQ_2}{dt} \right\rangle = \frac{K}{\gamma_1 + \gamma_2} (T_1 - T_2) = - \left\langle \frac{dQ_1}{dt} \right\rangle. \quad (3.3)$$

We can also show that if many heat baths are coupled by a quadratic potential like  $U(x_1, \dots, x_n) = \frac{1}{2} \sum_i \sum_j K_{ij} x_i x_j$  with  $\{K_{ij}\}$  a positive definite symmetric matrix, then the rate of the discarded heat to each bath is the linear combination of the temperatures of these heat baths.

A little but ingenious sophistication of the above setup is due to Feynman,<sup>13)</sup> which is now called the Feynman ratchet (Fig. 2). There, one vane is attached to a ratcheted wheel, and also to a loading system, while the other vane is replaced by a simple board and the latter is connected to the pawl which interacts with the ratchet wheel. If the board is in a cooler bath (i.e., if  $T_1 > T_2$  in Fig. 2), this pawl acts as a (physical) Maxwell's demon. Then the ratchet wheel undergoes a systematic rotation, and we can extract a net work of lifting up the load unless the latter is excessively heavy. In this system we can define the efficiency of energy conversion,  $\eta$ , as the fraction of energy used to lift up the load out of the total energy coming from the warmer heat bath. If the load under  $T_1 \neq T_2$  is just as heavy as to stall the rotation of the ratchet wheel on the average, the efficiency  $\eta$  is much smaller than  $(T_1 - T_2)/T_1$  (here  $T_1 > T_2$  is assumed), despite what would be anticipated from Carnot's heat engine operated through quasi-equilibrium processes.<sup>13)</sup> This is because the stalled state does not correspond to an equilibrium state as Feynman argued, but to the steady heat conduction state as described above in Fig. 1. The equilibrium state ( $T_1 = T_2$ ) has neither an analogy to Carnot cycle.<sup>14)</sup>

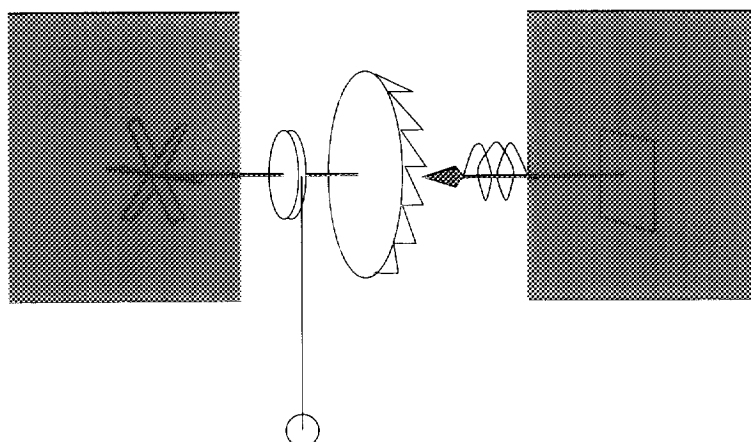


Fig. 2. Feynman's ratchet:<sup>13)</sup> A pawl (thick arrow) horizontally presses the ratchet wheel (center) with aid of a spring. See, for details, the text.

Before concluding this section, let us digress to the notion of entropy production which has been one of the central issues of irreversible thermodynamics people. As we shall show in the next section, stochastic energetics based on the Langevin dynamics involves the Helmholtz free energy as an isothermal reversible work, and we need not to introduce the entropy as a separate concept. We shall, however, write down the equation of entropy balance in the above two examples. Let  $P(x_1, x_2, t)$  be the probability distribution function of  $x_1$  and  $x_2$  of these examples with a given initial condition. The probability current along  $x_i$  direction is given by  $J_i \equiv \frac{T_i}{\gamma_i} \left( \frac{\partial P}{\partial x_i} + \frac{P}{T_i} \frac{\partial U}{\partial x_i} \right)$ , and  $P$  obeys the equation  $\frac{\partial P}{\partial t} = -\sum_{i=1}^2 \frac{\partial J_i}{\partial x_i}$ . If we introduce the entropy of the system,  $S$ , by  $S(t) \equiv -\int P \log P d\Gamma$  with  $d\Gamma \equiv dx_1 dx_2$ , then we have the following balance equation:<sup>7)</sup>

$$\frac{dS}{dt} + \sum_{i=1}^2 \frac{1}{T_i} \frac{dQ_i}{dt} = \sum_{i=1}^2 \frac{\gamma_i}{T_i} \int \frac{J_i^2}{P} d\Gamma. \quad (3.4)$$

The right-hand side is the so-called entropy production.

#### §4. Thermodynamics from stochastic energetics

When the parameter  $a$  is controlled by an external agent, the laws of thermodynamics are formulated by considering a thermodynamic system which consists of the ensemble of an extensive number of the independent stochastic systems working with the different realizations of the  $\xi(t)$ . Then the first law is immediately obtained from (2.7) as (hereafter we shall use the expressions of the thermodynamics quantities per an individual stochastic system),<sup>15)</sup>

$$\left\langle \frac{\partial U}{\partial a} \right\rangle da = \langle dQ \rangle + \langle dU \rangle. \quad (4.1)$$

The second law of thermodynamics is obtained by recalling the expression of the work done by an external agent (2.9). From (2.9), we shall show that the reversible isothermal work of the thermodynamic system at the temperature  $T$  is<sup>15)</sup>

$$\langle dW \rangle = dF(T, a), \quad (T = \text{fixed, quasi-equilibrium}) \quad (4.2)$$

where  $F(T, a)$  is the Helmholtz free energy defined, up to a constant, as

$$F(T, a) = -T \log \left[ \int e^{-\frac{U(x, a)}{T}} dx \right]. \quad (4.3)$$

To evaluate  $\langle dW \rangle$ , or  $\langle \frac{\partial U}{\partial a} \rangle$  in (2.9), we introduce the probability distribution function  $P(x, t)$  of the system's state variable,  $x$ . Corresponding to the Langevin equation (2.5),<sup>12)</sup>  $P(x, t)$  obeys the Fokker-Planck equation

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial x} \frac{1}{\gamma} \left( \frac{\partial U}{\partial x} + T \frac{\partial}{\partial x} \right) P. \quad (4.4)$$

Using  $P$ , we have

$$\left\langle \frac{\partial U}{\partial a} \right\rangle = \int \frac{\partial U(x, a)}{\partial a} P(x, t) dx. \quad (4.5)$$

For the quasi-equilibrium processes,  $P(x, t)$  may be replaced, in the lowest order approximation, by the equilibrium distribution function with the instantaneous value of the control parameter,  $a = a(t)$ ,

$$P(x, t) \simeq P_{\text{eq}}(x; a(t)) \equiv \frac{e^{-\frac{U(x, a)}{T}}}{\int dx' e^{-\frac{U(x', a)}{T}}}. \quad (4.6)$$

Then we may use the Ehrenfest type identity concerning the equilibrium ensemble average  $\langle \frac{\partial U}{\partial a} \rangle_{\text{eq}}$  which is easily verified from (4.3) and (4.6),

$$\left\langle \frac{\partial U}{\partial a} \right\rangle_{\text{eq}} = \frac{\partial F(T, a)}{\partial a}, \quad (4.7)$$

which leads to the expression (4.2). We have shown that the stochastic energetics relates Langevin dynamics and isothermal process in the limit of  $\frac{da}{dt} \rightarrow 0$ . Then, a question is how far we can explore non-equilibrium processes, i.e., the processes at finite rate of change of  $a(t)$ . Though we have no rigorous answers to it, a plausible domain of applicability is the process within the steady or non-steady processes near equilibrium so that the distortion of the velocity distribution function from the Maxwellian distribution be of higher order correction in  $\frac{da}{dt}$  than those explicitly appearing in the results.

Our framework may still deal with far from equilibrium processes since we do *not* assume the local equilibrium (Gibbs) distribution to hold at each moment of time. We can derive the linear nonequilibrium thermodynamics and especially the expression of kinetic coefficient, the latter of which cannot be obtained within the frameworks with local equilibrium assumption for the system. As the lowest order correction to the result (4.2), we have <sup>15)</sup>

$$\langle dW \rangle = dF + \left( \frac{da}{dt} \cdot \Lambda(a) \cdot \frac{da}{dt} \right) dt + \dots, \quad (4.8)$$

where the second and the further terms represent the irreversible work. The second term corresponds to the lowest order distortion,  $P_1(x, t)$ , of the probability function from the (instantaneous) equilibrium one,  $P_{\text{eq}}(x, a(t))$ ,

$$P(x, t) = P_{\text{eq}}(x; a(t)) + P_1(x, t) + \dots, \quad (4.9)$$

which can be obtained by the systematic expansion of the Fokker-Planck equation (4.4). As a result, the kinetic coefficient  $\Lambda(a)$  is given as a functional of the instantaneous value of  $a(t)$  (see, for details, Ref. 15)). The smallness parameter of the above expansion is the ratio of the time-scale of the change of  $a(t)$  to the equilibration time of the system. Under given initial and final values of the parameter  $a$ , the slowness of the whole process cannot be defined only by the time interval  $\Delta t$  of the process. The slowness of the process is unambiguously stated in the following way: Suppose we take a history, or a protocol, of the parameter  $a = \hat{a}(t)$  for the time interval  $0 \leq t \leq 1$ , and call it a scaled protocol. Now we uniformly stretch the scaled protocol along the time axis to have the time protocol between 0 and  $\Delta t$ ;  $a(t) = \hat{a}(\frac{t}{\Delta t})$ . With this

scaled protocol and (4.8), the total irreversible work,  $\langle \Delta W \rangle - \Delta F$ , which is defined as the integration of  $\langle dW \rangle - dF$  over the interval  $0 \leq t \leq \Delta t$ , is asymptotically given as

$$\langle \Delta W \rangle - \Delta F \sim \frac{1}{\Delta t} \left( \int_0^1 \frac{d\hat{a}}{dt} \cdot \Lambda(\hat{a}) \cdot \frac{d\hat{a}}{dt} dt \right), \quad \Delta t \rightarrow \infty. \quad (4.10)$$

This leads us to a kind of (asymptotic) complementarity relation for  $\Delta t \rightarrow \infty$ ,<sup>16)</sup>

$$[\langle \Delta W \rangle - \Delta F] \cdot \Delta t \geq \mathcal{S}_{\min}(a_i, a_f) > 0, \quad (4.11)$$

where  $\mathcal{S}_{\min}(a_i, a_f)$  is the minimum of the integral on the r.h.s. of (4.10) over all scaled protocols under the fixed initial and final values of  $a$ ,  $a_i = a(0)$  and  $a_f = a(\Delta t)$ . As  $\Lambda(a)$  is found to be a positive definite symmetric matrix, the minimum is positive unless  $a_i \neq a_f$ . (We will not go into the subtlety about the finite variation property of  $\hat{a}$ .) The above relation tells that the irreversible work for a given  $\Delta t$  cannot be smaller than a positive lower bound which is inversely proportional to  $\Delta t$ . The relation is also described in the way reminiscent of the uncertainty principle of quantum mechanics, that is, the precise determination of the Helmholtz free energy function through the observation of the work  $\langle \Delta W \rangle$  requires indefinitely large experimental time  $\Delta t$ .

In the context of linear nonequilibrium thermodynamics, the integrand of (4.10) is twice the dissipation function,  $\Psi$ . Usually the dissipation function has been employed to consider steady nonequilibrium states with  $\frac{da}{dt} = \text{const}$ . Here we have extended this usage to the non-steady processes with a finite time interval. As for the external system which controls the parameter  $a(t)$ , the external system receives the potential force  $-\frac{\partial F}{\partial a}$  and the ‘friction’ force  $-\Lambda(a) \cdot \frac{da}{dt}$ . For example, we can imagine to change the spring constant of a harmonic potential  $U(x, a) = \frac{a}{2}x^2$ , where the system’s degree of freedom,  $x$ , is coupled to the heat bath of the temperature  $T$ .

### §5. Model study of steady state thermodynamics<sup>17)</sup>

It is conceivable to extend our study of quasi-equilibrium processes to what we may call quasi-steady processes.<sup>18)</sup> For example, in Fig. 1 with the coupling potential  $U = \frac{a}{2}(x - x')^2$  (here we denote  $a$  for  $K$ ), we can ask the force to change the spring constant  $a$ . Here the heat flows between the two heat baths as an irreversible process even if the parameter  $a$  is kept constant. If we focus on the system of the spring with the vanes being attached to both ends, we may ask what potential (reversible) force and the frictional (irreversible) force are received by the external agent. In the present example, these force are found to be,  $-\frac{2T^*}{a}$  and  $-\frac{\gamma^* T^*}{2a^3} \cdot \frac{da}{dt}$ , respectively, where  $T^* \equiv \frac{\gamma' T + \gamma T'}{\gamma + \gamma'}$  and  $\gamma^* \equiv \frac{2\gamma\gamma'}{\gamma + \gamma'}$ .

In the thermodynamic formalism of steady states,<sup>18)</sup> we discuss the system’s thermodynamics such as quasi-steady processes or thermodynamic potential in terms of properly chosen external operations and the data obtained thereby. In general steady states, the external system controlling the system’s parameter and the driving system that keeps the system far from equilibrium may be identical. In such case we must be careful in extracting the reversible and irreversible works concerning the change the state of the system out of the total work done by the driving system.



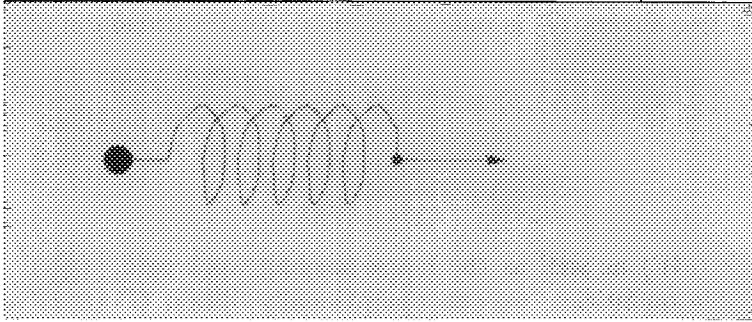


Fig. 3. Driven.

Let us consider a simple system that exhibits this aspect Ref. 17)(Fig. 3). A bead (the thick dot in Fig. 3), whose position is denoted by  $x$ , is subject to the influence of a heat bath (at rest) of the temperature  $T$ . The friction constant of the bead in the heat bath is  $\gamma$ . The bead is connected to an external agent via a spring. The potential energy of the spring is assumed to be  $U(x - a(t), b(t))$ , where  $a(t)$  and  $b(t)$  are controlled by the external agent. The parameter  $a(t)$  may be regarded, up to a constant difference, as the position of the opposite end of the spring (the thin dot in Fig. 3). We can specify the system's state by the variable  $X = x - a(t)$ . The difference from the previous example of two vanes is that we study the thermodynamics of the system under the change of the *drive*  $v(t) \equiv \frac{da(t)}{dt}$ , not that of  $a(t)$  itself. The pertinent Langevin equation is given as

$$\gamma \frac{dX}{dt} = - \frac{\partial}{\partial X} [U(X, b(t)) + \gamma v(t)X] + \xi(t). \quad (5.1)$$

The stochastic properties of  $\xi(t)$  is assumed as before (see the description below (1.1)). It is natural to define the (nonequilibrium) Helmholtz free energy  $F^*(T, \mathcal{V}, b)$  as

$$F^*(T, \mathcal{V}, b) \equiv -T \log \left[ \int e^{-\frac{[U(X, b) + \gamma \mathcal{V} X]}{T}} dx \right]. \quad (5.2)$$

If we can obtain  $F^*(T, \mathcal{V}, b)$  in an operational way similar to the one we demonstrated in the previous section (see (4.2)), we may describe the system's thermodynamics and study the potential function  $U(X, b)$ , etc. The point is that  $\langle dW \rangle$  is not zero even under a constant drive,  $v(t) = \text{const} (\neq 0)$ , when  $a(t)$  changes steadily. In order to extract the net work to change the system's thermodynamics state, we must carefully subtract the *house-keeping* work needed for a macroscopic ensemble of the stochastic system to keep its instantaneous state as a steady state. The latter work is  $\frac{1}{\gamma} \langle \frac{\partial U}{\partial X} \rangle^2 dt$  and we find, after a straightforward calculation, the second law of the quasi-steady isothermal processes, which corresponds to (4.2) for quasi-equilibrium processes,

$$\langle dW \rangle - \frac{1}{\gamma} \left\langle \frac{\partial U}{\partial X} \right\rangle^2 dt = dG^*(T, \langle X \rangle, b), \quad (T = \text{fixed, quasi-steady}) \quad (5.3)$$

where the new free energy  $G^*$  is related to the Legendre transform of  $F^*$  as

$$G^*(T, \langle X \rangle, b) \equiv F^*(T, \mathcal{V}, b) - \mathcal{V} \frac{\partial F^*(T, \mathcal{V}, b)}{\partial \mathcal{V}}, \quad (5.4)$$

$$\langle X \rangle = \frac{1}{\gamma} \frac{\partial F^*(T, \mathcal{V}, b)}{\partial \mathcal{V}}. \quad (5.5)$$

Since the work  $\langle dW \rangle$  as well as the house-keeping work rate  $\frac{1}{\gamma} \langle \frac{\partial U}{\partial X} \rangle^2$  are, in principle, measurable quantities, we can operationally obtain  $G^*$  or  $F^*$  and thus the potential  $U(X, b)$  through the quasi-steady processes. It is not yet clear whether a thermodynamic potential can always be obtained by a general recipe. A system of the Brownian particle confined in a three-dimensionally rotating potential may be a good test.

### §6. Concluding remarks

We have shown that the method of stochastic energetics provides a link between Langevin dynamics and thermodynamics. The energy conservation, which underlies the first law of thermodynamics, is realized for each realization of stochastic process. The present method may be useful where the fluctuations are important, such as metastable states including those in proteins, diffusion processes including ion transport across ion channels, as well as theoretical studies on the Maxwell demon,<sup>19)</sup> etc.

The relation between the phenomenological approach<sup>18)</sup> and the statistical approach<sup>20)</sup> is not yet established. We should explore also the possible extension of the method, such as to an discrete stochastic processes where the small scale stochastic fluctuation is further eliminated,<sup>21)</sup> the open systems with particle exchanges,<sup>22)</sup> non-Gaussian external noise<sup>23)</sup> and non-Gibbsian statistics.

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