

Chapter 4

Concept of Heat on Mesoscopic Scales

In this chapter we introduce the concept of heat in the physics of the Langevin equation, as well as its discrete version.

In the fluctuating world, some important aspects of the system cannot be described in terms of the ensemble average of physical observables. Einstein was among the first to study the connection between fluctuations and energy in the fluctuating world [1]. Then Kramers described this connection in the context of stochastic processes. In his seminal paper [2], he represented a chemical reaction as a process in which the state of molecule(s) undergoes fluctuations and eventually changes its state qualitatively. That is, the molecules' state (reaction coordinate) which was originally found near the bottom of a potential ($U(x)$) can overcome a potential barrier, see Fig. 4.1. Kramers analyzed this situation by constructing a Fokker–Planck equation, called the Kramers equation, and derived the reaction rate (or transition rate).

Now, our interest is how much energy is exchanged between the system and the thermal environment along an individual realization of such process. Does the energy exchanged vary from one realization to other, or not? Knowing the conservation law of energy, we may argue that the energy absorbed from the thermal environment equals to the height of the potential energy barrier. In order to *show* explicitly the transferred energy and answer to the above question, the Fokker–Planck (Kramers) equation is not appropriate, because this equation deals with an ensemble of stochastic processes, but not an individual one. Therefore, our study of energetics should be based on the Langevin equations¹:

$$\frac{dp}{dt} = -\frac{\partial U(x, a)}{\partial x} - \gamma \frac{p}{m} + \xi(t), \quad \frac{dx}{dt} = \frac{p}{m} \quad (\text{underdamped}) \quad (4.1)$$

or

$$0 = -\frac{\partial U(x, a)}{\partial x} - \gamma \frac{dx}{dt} + \xi(t) \quad (\text{overdamped}), \quad (4.2)$$

if the inertial term is negligible.

¹ In the following, we shall omit the symbol \hat{X} , etc., denoting a random variable or a stochastic process, unless some confusion is possible.

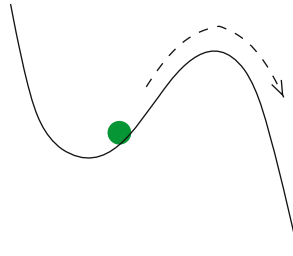


Fig. 4.1 Kramers' picture of chemical reaction: A new state is reached once a potential barrier is overcome (*dashed arrow*) with the help of the thermal fluctuations

The fluctuating world described by a Langevin equation supposes a minimal triad consisting of a system, a thermal environment, and an external system. Along a single realization of the stochastic process, energy is exchanged among these three components. Heat is defined as the energy exchanged between the system and the thermal environment. The law of energy balance is derived for each realization. Many theoretical models have been studied by this framework, and several experimental demonstrations of this law have been done. For numerical simulations, the framework of energetics turned out to require more precision than a simple convergence of the solution of the Langevin equation. The framework of energetics is also formulated for the discrete Langevin equation. In both continuous and discrete cases, the ensemble properties of energetics can be reduced once the energetics for an individual realization is formulated.

When a fluctuating system is in contact with two thermal environments, the energetics shows some aspects which are not found in the macroscopic case. Of special interest is the energetics of autonomous heat engines: (i) Feynman pawl and ratchet wheel and (ii) Büttiker–Landauer ratchet.

In this chapter we focus mainly on heat. The aspects related to work will be discussed in the next chapter.

4.1 Framework

*4.1.1 *The Similarity of Setup Between the Fluctuating World and the Thermodynamics Leads to a Natural Definition of Mesoscopic Heat*

4.1.1.1 Triad: System, Thermal Environment, and External System

The Langevin equations (4.1) or (4.2) involve three parts, i.e., system, thermal environment, and external system as mentioned in Chap. 1. The summary below emphasizes the parallelism with thermodynamics described in Chap. 2.

System: Of the whole world, a part which is properly cut out is called the system.

Its state is represented by x (and p) in (4.1) or (4.2). These equations describe the evolution of the state of the system. We consider that the potential energy and the kinetic energy belong to the system.²

Thermal environment: The background system to which the system is connected is called the thermal environment. This environment is characterized in itself by a single parameter, the temperature T . The conservation laws for the total energy, mass or volume, and momentum have no effect on the state of the thermal environment. The environment returns instantaneously to its equilibrium state and keeps no memories of the system's action in the past. The interaction between the system and the thermal environment is characterized by the friction coefficient γ as well as temperature. The strength of the thermal random force, $\xi(t)$, is specified by these two parameters.³

External system: It is an agent which is capable of controlling macroscopically the system through the parameter a of the potential energy $U(x, a)$. The term "external" indicates that the evolution of the parameter a is not determined by Eqs. (4.1) or (4.2). In the case of coupled Langevin equations, e.g., of the system described by the state variables (x_1, x_2) , the x_2 could take the position of a , that is, the external system with respect to the subsystem, x_1 . For the moment, however, we reserve the concept of the external system for the variables whose dynamics are not determined by stochastic equations.⁴

The above triad is our starting point. In terms of characteristic timescale, we normally suppose that they represent the intermediate (system), micro (thermal environment), and macro (external system) scales, respectively. Not all composite fluctuating systems may be decomposed into this type of triad. But we start from an elementary prototype.

4.1.1.2 Definition of Heat in the Fluctuating World

In the macroscopic world, we do not observe the vigorous molecular motions of a hot object. We can detect it by touch, by the melting of ice in contact, etc., through some amplifying mechanisms of microscopic thermal motions. In the microscopic world, on the contrary, we have no notion of "hotness," but everything is represented

² This point will be discussed later in more detail in Sect. 4.1.2.

³ Unlike the macroscopic thermodynamics, the definition of thermal environment does not exclude the interaction energy between the system and the thermal environment. This point has not been well discussed.

⁴ More discussion is given in Chap. 6.

We do not allow the external system to control the interaction between the system and the thermal environment. In other words, γ should not depend on a . The reason will be described later (Sect. 4.1.2.2).

as motion. The fluctuating world is between these two limits. Let us try to imagine the mechanical processes undergone by a Brownian particle.

The law of action and reaction: Depending on the velocity of a Brownian particle dx/dt , this particle should receive the unbalanced number of collisions with environment, e.g., solvent molecules, more from forward than from backward. The total transfer of momentum per unit time is the restoring force $-\gamma dx/dt$ and the random thermal force $\xi(t)$ with zero mean. We suppose that the *law of action and reaction* holds always between the Brownian particle and its environment: when the environment exerts a force $-\gamma dx/dt + \xi(t)$ on the particle, the particle exerts the reaction force, $-(-\gamma dx/dt + \xi(t))$, on the environment.

Concept of heat: Let us denote by $dx(t)$ the evolution of x over a time interval dt , according to the Langevin equation. It is determined for each realization. The work done by the particle on the environment upon this change $dx(t)$ is equal to the product of this variation and the above mentioned reaction force, that is, $-(-\gamma dx/dt + \xi(t)) \circ dx(t)$. We adopt the Stratonovich-type product \circ in the above. (Justification is given below.) This work can be either positive or negative. When positive, it represents energy lost by the system. From the standpoint of the environment, energy $(-\gamma dx/dt + \xi(t)) \circ dx(t)$ is lost as work to the Brownian particle. In any case, $(-\gamma dx/dt + \xi(t)) \circ dx(t)$ is the energy transferred from the environment to the system. We then define this energy transfer as heat [3]. Although the microscopic motions in the thermal environment are not explicitly represented in the Langevin equation, the law of action and reaction allows us to identify how much energy has been transferred.

Sign convention and the formula of heat: As in macroscopic thermodynamics (Chap. 2), we assign the positive sign for the energy received by the system. For instance, when a positive amount of work is done on the system by the thermal environment, we say that the system receives a positive amount of heat $d'Q > 0$. The equation defining $d'Q$ then reads

$$d'Q \equiv \left(-\gamma \frac{dx}{dt} + \xi(t) \right) \circ dx(t). \quad (4.3)$$

When inertia is taken into account, we replace dx/dt above by p/m . We shall use the same sign convention for the work done by the external system on the system (see below). In (4.3) and hereafter, we add “d dash (d')” to the heat Q or the work W when it concerns the process during an infinitesimal time, dt . We distinguish this from “ d ” and reserve the latter for the differential.⁵ In general $d'Q$ is not differentials.

⁵ That is, the differentials of a monovalent function, like $dx(t)$, or the total differentials of multi-valued function, like $dU(x, a)$.

4.1.2 *Energy Balance Along a Single Realization Follows from the Definition of Heat

4.1.2.1 The Law of Energy Balance

The definition of heat (4.3) and the Langevin equations (4.1) or (4.2) are sufficient to establish the relation of energy balance. See Fig. 4.2.

Energy balance with inertia: The reaction force by the thermal environment in (4.3) is rewritten using (4.1). Then $d'Q$ becomes $d'Q = (dp/dt + \partial U/\partial x) \circ dx(t)$. We then use the identities for the kinetic energy and the potential energy:

$$\frac{dp}{dt} \circ dx(t) = \frac{dp}{dt} \circ \frac{p}{m} dt = d\left(\frac{p^2}{2m}\right),$$

$$\frac{\partial U}{\partial x} \circ dx(t) = dU(x(t), a(t)) - \frac{\partial U}{\partial a} \circ da.$$

We recall that Stratonovich calculus allows us to use the usual rules of calculus about the differentials. After substituting these two expressions in the last expression of $d'Q$, we obtain

$$d\left(\frac{p^2}{2m} + U(x, a)\right) = d'Q + \frac{\partial U}{\partial a} \circ da. \tag{4.4}$$

Now we identify the total energy E of the system

$$E \equiv \frac{p^2}{2m} + U(x, a) \tag{4.5}$$

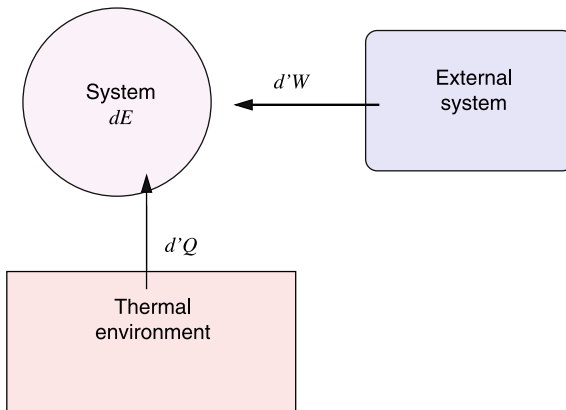


Fig. 4.2 Energy balance among dE , $d'Q$, and $d'W$

and the work done by the external system on the system

$$d'W \equiv \frac{\partial U}{\partial a} \circ da. \quad (4.6)$$

Then (4.4) is expressed in the form shown in Fig. 4.2:

$$dE = d'Q + d'W. \quad (4.7)$$

Equation (4.7) expresses the balance of energy concerning the system. It is analogous to the first law of thermodynamics; both are based on the principle of energy conservation in nonrelativistic system.⁶ We would stress that (4.7) holds for each realization of the stochastic process. A purely mechanical energy balance, $dE = d'W$, will hold in case that a can be changed “suddenly,” that is, very fast with respect to the characteristic relaxation time of x , but slow enough so as not to violate the time resolution of the Langevin model.

Energy balance without inertia: The definition of heat (4.3) and the Langevin equation (4.2) leads to the following result:

$$dU(x, a) = d'Q + \frac{\partial U}{\partial a} \circ da. \quad (4.8)$$

The calculation is very similar to and even simpler than the previous case. The energy balance relation is

$$dU = d'Q + d'W \quad (\text{when the inertia can be neglected}). \quad (4.9)$$

Compared to (4.7), the kinetic energy term is missing from the complete differential form. However, if the temperature T depends on the variable x , the evolution equation (1.94) in Sect. 1.3.2.1 leads to the general form of energy balance (4.7).

The above is the basis of stochastic energetics, i.e., the energetics of a single realization of stochastic process associated with the Langevin equation. The assignments of E , $d'Q$, and $d'W$ are all consistent with the law of mechanics and the usual definition of work. And the law of energy balance is not postulated but is derived from the Langevin equation.

The choice of Stratonovich-type calculus for $d'Q$ (4.3) was crucially important for the derivation of the law of energy balance. In the overdamped case, the temporal integration of (4.3) requires some care. The separate integral of $-\gamma dx/dt \circ dx(t)$ or of $\xi(t) \circ dx(t)$ does not assure finite results.

⁶ Can we conceive the similar problem about a relativistic system? We should remember that the thermal environment imposes a particular reference frame to define $dx/dt = 0$, i.e., the Langevin equation does not support the Galilean invariance.

4.1.2.2 Remarks

General

1. Energetics about a single realization is more detailed than energetics based on the Fokker–Planck equation. The latter describes an ensemble statistics at each instant of time. For the purpose of studying the energy exchange associated with a particular fluctuation event the latter method is not adequate. For example, an exceptionally large heat absorption should be associated to a rare event of climbing over an energy barrier. This characteristics will be masked if we used the ensemble statistics because such rare fluctuations in the ensemble are not synchronized in time (See also Sect. 4.2.2 below).

We know, however, that the Fokker–Planck equation contains the same information as the Langevin equation. There is no contradiction between this statement and the previous one. The above mentioned difference concerns their solutions, i.e., the difference between the instantaneous probability distributions and the single realization of stochastic process.⁷

2. In some literatures after [3] the heat for the overdamped system was defined using the following identity:

$$dU(x, a) = \frac{\partial U}{\partial x} dx + \frac{\partial U}{\partial a} da. \quad (4.10)$$

They argued that the term, $\frac{\partial U}{\partial x} dx$, must be the heat since it is the total change of energy dU less the work, $\frac{\partial U}{\partial a} da$. For the underdamped case, the corresponding identity for $E = p^2/(2m) + U$ reads

$$\begin{aligned} dE(p, x, a) &= \frac{p}{m} dp + \frac{\partial U}{\partial x} dx + \frac{\partial U}{\partial a} da \\ &= \left[\frac{dp}{dt} + \frac{\partial U}{\partial x} \right] dx + \frac{\partial U}{\partial a} da. \end{aligned} \quad (4.11)$$

The last expression gives the definition of heat such as $d'Q = \left[\frac{dp}{dt} + \frac{\partial U}{\partial x} \right] dx$, with the quantities in [] being the negative of inertial and potential forces. These are mathematically correct as an identity. Einstein treated heat in the above mentioned way when he formulated statistical mechanics.⁸ Also this way will be adopted for the energetics of the discrete Langevin equation (Sect. 4.1.2.6).

The definition of heat (4.3) is, however, more general for the system with inhomogeneous temperature $T(x)$ [4]: The overdamped Langevin equation, interpreted in the Stratonovich sense, is (see (1.94))

⁷ Roughly speaking, the correspondence between $(\partial P(x, t)/\partial t)dt$ and $\{\langle dE \rangle, \langle d'W \rangle, \langle d'Q \rangle\}$ is far from 1 to 1, while the mapping $\{dx(t), da(t)\} \mapsto \{dE, d'W, d'Q\}$ in the overdamped case is almost bijection.

⁸ Y. Oono pointed this out to the author.

$$\gamma \frac{dx}{dt} = -\frac{\partial}{\partial x} \left[U(x, a) + \frac{k_B T(x)}{2} \right] + \xi(t), \quad (4.12)$$

where the random thermal force, $\xi(t)$, is multiplicative. In this case, the definition of heat, (4.3), leads to energy balance (4.7), where the energy E is redefined as $E \equiv k_B T(x)/2 + U(x, a)$, not as (4.5). Also the definition based on the law of action reaction, (4.3), provides a clearer view of heat when stochastic energetics is generalized for the fluctuating hydrodynamics (Sect. A.4.7.1) and for the suspension of hard spheres (Sect. A.4.7.2).

About Heat

1. Long before the introduction of the concept of heat [3], an attempt to relate the Langevin equation to the thermal physics had been made [5]. They derived the following expression about the energy, $dE = d[p^2/2m + U(x, a)]$:

$$dE = -\frac{2\gamma}{m} \left(\frac{p^2}{2m} - \frac{k_B T}{2} \right) dt + d'W + \sqrt{2\gamma k_B T} \frac{p}{m} \cdot dB_t. \quad (4.13)$$

Here “ \cdot ” before dB_t denotes the product of Itô type. See Appendix A.4.1 for the derivation. Equation (4.13) is mathematically equivalent to (4.7), but the nonanticipating term ($\sim \cdot dB_t$) was explicitly sorted out. As mentioned above, Itô-type calculus is preadapted to the ensemble average, and the first term on the right-hand side has an allusion that the Langevin dynamics generates only the relaxation processes to equilibrium, like the equipartition. By contrast, (4.7) emphasizes balance of energy for individual processes.

2. Can heat defined in the above be derived by the projection method, the method which transformed the microscopic Hamiltonian dynamics to the Langevin equation (see Sect. 1.2.1.5)? There are simple cases where we can identify energies or heat on two levels: In the model from which Zwanzig demonstrated the nonlinear Langevin equation (Sect. 1.2.1.3), the potential energy $U_0(X)$ in the resulting Langevin equation (1.41) was nothing but the proper energy of X in the starting Hamiltonian dynamics, apart from an additive constant that reflects the eliminated microscopic degrees of freedom. A similar situation will be realized when a Brownian particle in a fluid moves under an optical trapping potential [6]. However, it is not the case in general. While the law of energy conservation holds in both levels of description, what are meant by energy and by heat differ generally from one level to the other.⁹ The full analysis of energy and heat at different levels of description will be done in Chap. 6 [7]. Here we note only two points:

- (1) The potential energy $U_{\text{eq}}(\mathbf{A})$ in the Langevin equation (1.42) obtained by projection method is in fact a (constrained) free energy (see (1.45)).

⁹ “Each level has its own thermodynamics.”

- (2) The heat [energy] of different levels of description can be related quantitatively.

We will, therefore, continue to use the definitions of the heat and energy in this section. Whenever necessary, we can translate those quantities to their counterpart on the microscale.¹⁰

About Work

1. In Sect. 4.1.1.1 we prohibited the external system to control the interaction between the system and the thermal environment. One reason is now clear from the above formalism: our definition of work is based on the potential force. Related but more fundamental reason is that the stochastic energetics is conscious about the scales of description: For example, let us consider the rotational Brownian motion of a vane in a fluid medium (cf. Fig. 4.6). The friction coefficient γ can be modified by changing the shape of the vanes.¹¹ In order to assess the work to change the friction coefficient γ for this motion, we need structural and mechanical information about the interface between the system and the thermal environment. Such a requirement conflicts with our assumption about the thermal environment: the latter should be memory-free, nonstructured, and uncorrelated. A solution for the above example would be to include some region of the thermal environment near the interface as a part of the extended system. See Sect. 7.1.1.5 for a concrete procedure of redefining the system.
2. The work $d'W$ has been defined such that it is 0 if the control parameter a is constant. For example, suppose that a represents a constant external force $g_0 > 0$ applied to a Brownian particle (position $x(t)$) in the direction of $x > 0$. According to our definition, the external system applying this force does not do work while the particle drifts toward $x(t) \rightarrow \infty$. We count $(-g_0 dx)$ as a part of the change of the internal energy of the *system*. Therefore, we regard that the particle dissipates its potential energy $-g_0 x$. In contrast, if an external system increases the force strength from $g = 0$ to g_0 , then $\int_0^{g_0} (-x(t)) \circ dg(t)$ should be counted as the work on the system, $d'W$.¹²

4.1.2.3 Examples

Deformation of an Ideal Chain

Let us consider an ideal chain consisting of many microscale rigid rods joined together by completely flexible joints (Fig. 4.3). The only interactions are steric repulsion among rods. Therefore, the system's potential energy, $U(\{\mathbf{x}_i\})$, is constant

¹⁰ The impatient reader could give a quick glance at Sect. 6.2 (especially the Eq. (6.23)) of Chap. 6, where \tilde{F} stands for $U(x, a)$ here.

¹¹ This example has been brought by T. S. Komatsu.

¹² Jarzynski discussed this issue [8] in the context of Jarzynski nonequilibrium work relation (Sect. 5.4.1).

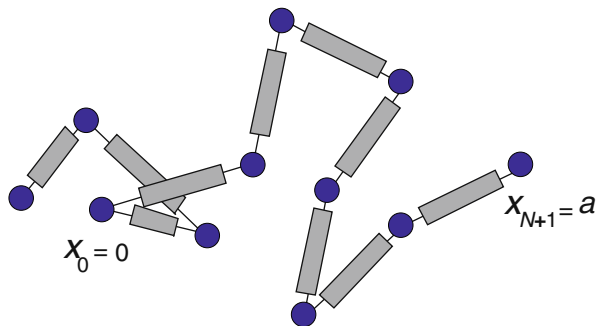


Fig. 4.3 Ideal chain consisting of rigid rods (*gray rectangles*) and free joints (*filled discs*) immersed in a thermal environment. One end, $x_{N+1} \equiv a$, can be externally controlled, while the other end, x_0 , is fixed at $x = 0$

as function of the positions of joints, $\{\mathbf{x}_i\}$ ($0 \leq i \leq N + 1$). Equilibrium statistical mechanics tells that this system shows (entropic) elasticity with respect to the end-to-end distance $|\mathbf{x}_{N+1} - \mathbf{x}_0|$, and the average elastic force for a given end-to-end distance is proportional to $k_B T$. Now we are interested in the energetics during the free shrinkage of this chain after the end point $\mathbf{x}_{N+1} \equiv a$ is released while the other end point \mathbf{x}_0 is fixed at $\mathbf{x} = 0$. Above all, no work is done by the external system; $d'W = 0$. If the overdamped Langevin equation describes well the conformational changes of this system, the balance of energy (4.7) tells immediately that $d'Q = dU = 0$. If the inertia of the rods and joints are not negligible, (4.9) tells that the heat should balance with the kinetic energy, through $d'Q = dE$. Using this framework of energetics, energy exchange can be studied for different initial conditions. One situation of special interest might be the relaxation of a stretched long chain, either with or without Brownian particle at the movable end, \mathbf{x}_{N+1} . This issue provokes many problems about the heat on mesoscopic scales. We will discuss this in depth in Chaps. 5 and 6.

“Jump-and-catch” mechanism of binding

In proteins, often a large conformational change is caused by the interaction between very localized and specific binding sites, see Fig. 4.4 (top). We might ask

- (i) How does a short-ranged bonding interaction (of some \AA range) cause a large-scale conformational change of proteins (of 10-nm range)?
- (ii) What supplies the energy for the proteins to deform prior to the release of the bonding energy?

There is no work in (4.7), $d'W = 0$. The balance of energy is then $dU = d'Q$. As for the potential energy U , Fig. 4.4 (bottom) gives the decomposition of the energy into the short-range binding interaction, U_{bond} , and the energy of protein's

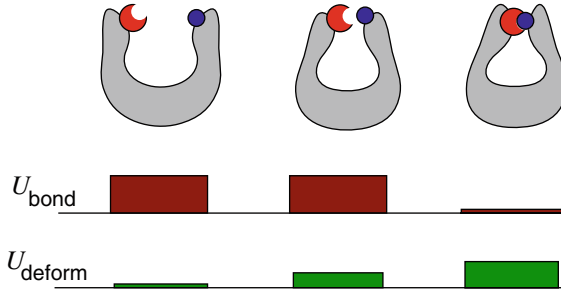


Fig. 4.4 Schematic presentation of the “jump-and-catch” transition (*top*) and its energetics (*bottom*). A protein (*shaded object*) has an intramolecular binding pair (*filled disc and filled crescent*). The height of rectangles shows the energies U_{bond} (upper law) and U_{deform} (lower law), respectively. The process of jump (from *left to right*) requires to borrow energy from the thermal environment

conformation change, U_{deform} . In order to achieve the transition from the “open” state (left) to the “closed” state (right), the thermal environment can transfer heat $d'Q$ to the protein.¹³ The supplied energy is stocked as the potential energy for deformation, $dU_{\text{deform}} = d'Q > 0$. If bond formation is unsuccessful, the protein conformation will return to the relaxed state, and the stocked energy is returned to the thermal environment as heat. If bond formation occurs, the binding energy of the bond $-dU_{\text{bond}} > 0$ is released to the thermal environment, while the deformation energy dU_{bond} is retained in the proteins. If the gain of the bond energy $|dU_{\text{bond}}|$ overcomes the energy cost of deformation, dU_{deform} , we have $(dU_{\text{deform}} + dU_{\text{bond}}) < 0$, and the transition is stabilized.

In the above, the thermal environment worked as a bank of (free) energy. It allowed the protein to explore large deformations and find a short-ranged binding pair which were originally far apart. While the average energy of fluctuations is $\sim k_B T \simeq 4\text{pN nm}$ per a degree of freedom, rare fluctuations may attain the heat transfer of more than $10k_B T$. If the protein waits long enough time, e.g., $\sim \text{ms}$, it can attain large conformational fluctuations.¹⁴

Borrowing energy from the thermal environment is a characteristic feature of the fluctuating world. This principle is fully used to extract work from the thermal or chemical energy. Energetics of mesoscopic thermal and chemical engines are discussed in Sects. 8.1.1 and 8.1.2. Stochastic energetics brings much more informations with respect to the ensemble theory of statistical mechanics.

¹³ Here we abuse the notations $d'Q$, etc., to represent finite variations.

¹⁴ A rough order estimation: if a binding pair diffuses with diffusion coefficient $D = 10^{-7}\text{cm}^2/\text{s}$ from the initial separation $\ell = 5\text{ nm}$, the pair can meet in $\simeq \ell^2/(2D) \simeq 10^{-6}\text{ s}$ times the Boltzmann factor $e^{\epsilon/k_B T}$, where ϵ is the barrier energy of protein deformation. Then the waiting for 1 ms may allow to cross a barrier ϵ of $\tau e^{\epsilon/k_B T} = 1\text{ ms}$, or $\epsilon \simeq 7k_B T$.

4.1.2.4 Experimental Demonstration of Energy Balance

What does the measurement of heat mean if heat is directly associated with the fluctuating motions? Is $d'Q$ neither readily observable in experiments nor calculated from observable quantities? The first question concerns the very question of the heat, and it is discussed in Chap. 6. For the second question, the brief answer is yes. Recent experimental technique [6, 9] enabled to measure both the energy change dU and the work $d'W$ at high accuracy.¹⁵ The heat $d'Q$ is, therefore, assessed using the balance of energy (4.7) i.e., $dU = d'Q + d'W$. They used either optically trapped bead [6] or brass wire-held pendulum [9]. See Fig. 4.5. They observed, on the one hand, the time series of the fluctuating variable $x(t)$, i.e., the position of the trapped bead or the tiny rotation angle of the pendulum, respectively, at a high temporal resolution (faster than ms). On the other hand, the potential function $U(x, a)$, and therefore the (reaction) force $\partial U/\partial x$, are identified through separate calibrating experiment. With these data of $x(t)$ together with the protocol of the external parameter, $a(t)$, the energy change $dU(x, a)$ and the work $d'W = \partial U/\partial x da(t)$ were deduced.

The heat $d'Q$ was not measured independently by these experiments, nor was the law of energy balance proven. However, these experiments also demonstrated the Jarzynski's nonequilibrium work theorem and the fluctuation theorem (see Sects. 5.4.1 and 5.4.2). The latter verification implies that the process $x(t)$ is a Markovian process. Therefore, the overdamped Langevin equation is a good model for these experiments.¹⁶

We should note that, in the experiments cited above, the potential energy is a true energy, i.e., without entropic part. Therefore, the molecular heating up of the local environment should be observed if a very sensitive thermometer is developed and if experiments are conducted at very low temperature. For the moment ultralow temperature experiments involving the energy balance have not been done. But there are already the measurements of thermal conduction by phonons [10] and that by photons [11].

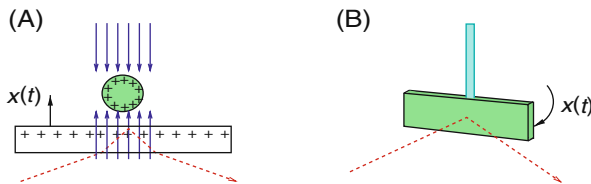


Fig. 4.5 Schematic setups for measuring dU and $d'W$. (a) Optically trapped bead [6] and (b) brass wire-held pendulum [9]. The dashed lines are light for detecting $x(t)$. The parallel *arrows* (a) and *rectangle* (b) denote the optical+electrostatic and mechanical mechanisms, respectively, for the restoring forces

¹⁵ For example, [6] had an error of only $\sim k_B T/4$ vs. about $10k_B T$ of total energy variations.

¹⁶ The effect of inertia is too short lived (~ 10 ns) to be captured.

4.1.2.5 Numerical Precision Required for the Energetics

Energetics of stochastic process brings a new notion in the numerical calculation of the Langevin equation or of the SDE. We have to distinguish between the convergence of solution and the convergence of the associated energetics. In fact the latter requires a higher precision of the solution than its mere convergence.

It concerns the “overdamped” case, where we neglect the inertia. Let us take a simple Langevin equation:

$$0 = -\frac{dU(x)}{dx} - \gamma \frac{dx}{dt} + \xi(t), \quad (4.14)$$

where $\langle \xi(t) \rangle = 0$ and $\langle \xi(t)\xi(t') \rangle = \sqrt{2\gamma k_B T} \delta(t - t')$. Our object is to solve this equation by using discretization in time with a finite time step, h . We fix the total time interval of integration. The total number of steps N is, therefore, $N \propto \frac{1}{h}$.

The discretized solution with an arbitrary $\xi(\cdot)$ is said to converge to the true solution of (4.14) with the same $\xi(\cdot)$ if the difference between the discretized (rectilinear) $x(t)$ approaches indefinitely to the true $x(t)$ in the limit of $h \rightarrow 0$. Let us take the simplest convergent scheme of discretization:

$$0 = -\frac{dU(\tilde{x}_t)}{dx} h - \gamma(x_{t+h} - x_t) + w_{t,t+h}, \quad (4.15)$$

where¹⁷ $w_{t,t+h} \equiv \sqrt{2\gamma k_B T} (B_{t+h} - B_t)$ with B_t being the Wiener process, and $\tilde{x}_t \equiv \theta x_t + (1 - \theta)x_{t+h}$ with θ being arbitrary for the moment except that it is normal to choose such that $0 \leq \theta \leq 1$. In fact (4.15) is an integral of (4.14) from t to $t+h$. There is, therefore, a value $\theta \in [0, 1]$ for which (4.15) is exact.¹⁸ We can show that, with any choice of θ , the error in $x(t)$ by this scheme is $\mathcal{O}(h^{\frac{1}{2}})$. (See Appendix A.4.2.) In other words, the difference between the approximate $x(t)$ of (4.14) and the true $x(t)$ of (4.15) decreases as $\mathcal{O}(N^{-\frac{1}{2}})$ for $N \rightarrow \infty$. The explicit and lowest order Euler scheme uses $\theta = 0$. Therefore, this scheme is convergent with the error in $x(t)$ being $\mathcal{O}(N^{-\frac{1}{2}})$.

In order to numerically assess heat, we need to integrate the heat $d'Q$ of (4.3). The unambiguous choice to discretize $d'Q$ in the lowest order is

$$\Delta Q \equiv \frac{1}{h} [-\gamma(x_{t+h} - x_t) + w_{t,t+h}](x_{t+h} - x_t). \quad (4.16)$$

Similarly, the change in the potential energy should be expressed as

$$\Delta U \equiv U(x_{t+h}) - U(x_t). \quad (4.17)$$

¹⁷ If we abuse the integral and derivative, $w_{t,t+h} = \int_t^{t+h} \xi(s) ds$ and $\xi(t) = dB_t/dt$.

¹⁸ But such θ depends on x , $\xi(\cdot)$, and t .

The convergence of energetics, therefore, requires the error of each step, $\Delta r \equiv \Delta U - \Delta Q$, to be less than $\sim h$ so that the cumulated error $\sim N \Delta r$ vanishes for $N \rightarrow \infty$. In Appendix A.4.2 we show that this condition requires taking $\theta = \frac{1}{2}$ in (4.15). With this choice, the error in the solution of $x(t)$ itself is better than otherwise, and the convergence in $x(t)$ is of $\mathcal{O}(N^{-\frac{3}{2}})$ instead of $\mathcal{O}(N^{-\frac{1}{2}})$.

What occurs if we took $\theta \neq \frac{1}{2}$ in (4.15)? Suppose, for example, the case of $U(x, a) = U(x)$ with a single minimum. Apparently the time-discretized $x(t)$ behaves normally, since this is a good approximate of the true solution. The residence time distribution of $x(t)$ will approach the canonical distribution. Therefore, the time average of $U(x_t)$ approaches its canonical average. At the same time, the energy balance of (4.9) should be $dU = d'Q$, because $d'W = 0$ here. Numerically, however, the simple scheme predicts $\Delta Q = \mathcal{O}(h)$ at each step, that is, heat is generated or absorbed steadily, in contradiction to the conservation of energy.

4.1.2.6 Energy Balance for Discrete States

For a particular realization of a discrete Markov process, the system undergoes a transition from the state $i_{\alpha-1}$ to the state i_α at time t_α with $1 \leq \alpha \leq n$ and $0 < t_1 < \dots < t_n < t$. The energy level of the system changes accordingly. We denote by $E_i(a)$ the energy of state i , which may depend on time through the external parameter a . In the context of master equation, the energy balance of this process has long been discussed: along the process between $t = 0 (\equiv t_0)$ and $t = t (\equiv t_{n+1})$ it is written as follows:

$$\Delta E = \Delta'W + \Delta'Q, \quad (4.18)$$

where the change of energy ΔE ,

$$\Delta E = E_{i_n}(a(t)) - E_{i_0}(a(0)), \quad (4.19)$$

is decomposed into work which is assigned as

$$\Delta'W \equiv \sum_{\alpha=0}^n [E_{i_\alpha}(a(t_{\alpha+1})) - E_{i_\alpha}(a(t_\alpha))] \quad (4.20)$$

and heat defined by

$$\Delta'Q \equiv \sum_{\alpha=1}^n [E_{i_\alpha}(a(t_\alpha)) - E_{i_{\alpha-1}}(a(t_\alpha))]. \quad (4.21)$$

In order to deal with individual processes, we have introduced the discrete ‘‘Langevin equation’’ (3.32), i.e.,

$$\frac{d}{dt} |\psi_i\rangle = \sum_j (|j\rangle - |\psi_i\rangle) \cdot \zeta_{\psi_i, j}(t).$$

Through a process, the energy of the system changes as $E_{\psi_t}(a(t))$. Using the discrete Langevin equation, the energetics defined above can be described simply.

We first express the energy $E_{\psi_t}(a(t))$ using an energy operator, $E(a)$, defined by

$$E(a) \equiv \sum_i E_i(a) |i\rangle \langle i|. \quad (4.22)$$

Then the energy for the state $|\psi_t\rangle$ is

$$E_{\psi_t}(a(t)) = \langle |E(a(t))| \psi_t \rangle, \quad (4.23)$$

where $\langle | \equiv \sum_j \langle j|$ [12]. With these notations, the energy balance, which corresponds to $dE = d'W + d'Q$ for the Langevin equation, is as follows:¹⁹

$$d[\langle |E(a(t))| \psi_t \rangle] = \langle |d[E(a(t))]| \psi_t \rangle + \langle |E(a(t))d[| \psi_t \rangle] \rangle. \quad (4.24)$$

4.1.3 The Ensemble Average Heat Flux has Several Different Expressions

In this section we will derive the formula for the average heat transferred per unit time to the system from thermal environments.

4.1.3.1 Case with Inertia

We consider the Langevin equation (4.1). We will derive a formula for the average of heat $d'Q$ over the stochastic processes between t and $t + dt$. For this purpose, the Itô-type representation of the energy balance (4.13), that is,

$$\begin{aligned} d'Q &= dE - d'W \\ &= -\frac{2\gamma}{m} \left(\frac{p^2}{2m} - \frac{k_B T}{2} \right) dt + \sqrt{2\gamma k_B T} \frac{p}{m} \cdot dB_t \end{aligned} \quad (4.25)$$

is the most convenient. The result is

$$\langle d'Q \rangle = -\frac{2\gamma}{m} \left[\left\langle \frac{p^2}{2m} \right\rangle - \frac{k_B T}{2} \right] dt. \quad (4.26)$$

The result indicates that, independent of the form of the potential function $U(x, a)$, the exchange of heat with the thermal environment proceeds through the kinetic energy of the system.²⁰

¹⁹ We remind that the vectors $|j\rangle$ or $\langle j|$ are nominative, and their time derivatives are always 0, even if the physical state “j” changes through the parameter $a(t)$.

²⁰ For the Langevin equation without inertia, the kinetic energies exchanged between the system and the thermal environment are hidden, but should exist. That $\langle d'Q \rangle$ is linear in the imbalance

This simple formula gives an illusion of stability, but may mask what occurs in the system. For example, suppose that the system starts from a metastable state of a potential $U(x)$ as in Fig. 4.1. Until the system escapes from the metastable valley, $\frac{p^2}{2m}$ remains $\simeq \frac{k_B T}{2}$, but the net release of the heat will occur from the escaping particle beyond the potential barrier.

4.1.3.2 Case Without Inertia

If the temporal resolution is not enough to observe, we assume that the kinetic energy $\frac{p^2}{2m}$ is mostly equal to $\frac{k_B T}{2}$. However, the substitution of this hypothesis into (4.26) leads to $\langle d'Q \rangle = 0$ for any process. This is apparently wrong. We must, therefore, reformulate the average heat for the case without inertia from the Langevin equation (4.2), and the definition of heat, $d'Q = (-\gamma dx/dt + \xi(t)) \circ dx$. The results is

$$\langle d'Q \rangle = -\frac{1}{\gamma} \left[\left\langle \left(\frac{\partial U}{\partial x} \right)^2 \right\rangle - k_B T \left\langle \frac{\partial^2 U}{\partial x^2} \right\rangle \right] dt. \quad (4.27)$$

The derivation is given in Appendix A.4.3.²¹

As example of (4.27), suppose that the potential energy is harmonic, $U(x) = \frac{K}{2}x^2$. The above formula then gives

$$\langle d'Q \rangle = -\frac{2K}{\gamma} \left[\frac{K}{2} \langle x^2 \rangle - \frac{k_B T}{2} \right] dt. \quad (4.28)$$

4.1.3.3 Expression of Average Heat Flow in Terms of the Probability Current

The above results can be cast into a common form, using the probability current of the Fokker–Planck equation. We calculate the average heat $\langle d'Q \rangle$ as $\langle d'E \rangle - \langle d'W \rangle$, where the energy function $E(X, P, a)$ is $P^2/(2m) + U(X, a)$ in the case with inertia (Sect. 4.1.3.1) and $E(X, a) = k_B T/2 + U(X, a)$ in the case without inertia (Sect. 4.1.3.2). Using the probability density \mathcal{P} obeying the Fokker–Planck equation, the above relation is

$$\begin{aligned} \frac{\langle d'Q \rangle}{dt} &= \frac{d}{dt} \int E \mathcal{P} d\Gamma - \frac{da}{dt} \int \frac{\partial E}{\partial a} \mathcal{P} d\Gamma \\ &= \int E \frac{\partial \mathcal{P}}{\partial t} d\Gamma, \end{aligned} \quad (4.29)$$

of the kinetic energy comes from the linearity of the Langevin equation in γ . The Navier–Stokes equation of hydrodynamics is also the linear theory from this point of view.

²¹ A byproduct of (4.27) is the equilibrium relationship, when the parameter a is fixed: $\left\langle \left(\frac{\partial U}{\partial x} \right)^2 \right\rangle_{\text{eq}} = k_B T \left\langle \frac{\partial^2 U}{\partial x^2} \right\rangle_{\text{eq}}$. This equality can also be obtained using the canonical equilibrium distribution $\propto e^{-U/k_B T}$.

where $d\Gamma \equiv dXdP$ (with inertia) and $d\Gamma \equiv dX$ (without inertia), respectively. We then substitute for $\frac{\partial P}{\partial t}$ the Fokker–Planck equation, $\frac{\partial P}{\partial t} = -\nabla \cdot \mathbf{J}$, see (1.76) and (1.78) in Sect. 1.2.3.2. with $\nabla \cdot \mathbf{J} = \partial J_x/\partial X + \partial J_p/\partial P$ (with inertia) and $\nabla \cdot \mathbf{J} = \partial J_x/\partial X$ (without inertia), respectively. The probability fluxes (J_x , J_p) in case with inertia and J_x in case without inertia are defined, respectively, by (1.79) and by (1.77). Performing the integral by parts, and assuming that the boundary terms vanish, we obtain the following formulas²²:

$$\begin{aligned} \frac{\langle d'Q \rangle}{dt} &= \int \left[\frac{\partial E}{\partial X} J_x + \frac{\partial E}{\partial P} J_p \right] dXdP && \text{(with inertia effect),} \\ \frac{\langle d'Q \rangle}{dt} &= \int \frac{\partial U}{\partial X} J_x dX && \text{(without inertia effect).} \end{aligned} \tag{4.30}$$

The expressions of the average heat (4.30) have long been found in the context of Fokker–Planck equation [13].

The first equation of (4.30) includes, as special case, the result for the purely mechanical system. In that case, $E = H$, $(J_x, J_p) = \left(\frac{dX}{dt} \mathcal{P}, \frac{dP}{dt} \mathcal{P} \right)$, and (X, P) obey the Hamiltonian equation, $\left(\frac{dX}{dt}, \frac{dP}{dt} \right) = (-\partial H/\partial P, \partial H/\partial X)$. We then have $\frac{\partial E}{\partial X} J_x + \frac{\partial E}{\partial P} J_p \equiv 0$, that is, the heat transfer in the first equation of (4.30) vanishes identically.

4.2 Generalization

4.2.1 Heat on the Mesoscopic Scale Can Be Generalized to the System in Contact with More Than One Thermal Environments

4.2.1.1 Formal Results

When more than one thermal environment interacts with a system, the analysis of average heat flux in the previous section can be generalized. In order to avoid direct interactions *among* the thermal environments, we assume that the thermal environments do not couple with the same degree(s) of freedom of the system. We assume a simple model energy of the system:

$$E(\{x_i, p_i\}, a) = \sum_i \frac{p_i^2}{2m_i} + U(\{x_i\}, a), \quad (i = 1, \dots, n), \tag{4.31}$$

²² An alternative proof of (4.30) will be given in the next section.

where m_i is the mass of the i th degrees of freedom, and a is external control parameter(s). The Langevin equation for the i th degree of freedom is

$$\begin{aligned}\frac{dx_i}{dt} &= \frac{p_i}{m_i} \\ \frac{dp_i}{dt} &= -\gamma_i \frac{p_i}{m_i} - \frac{\partial U}{\partial x_i} + \sqrt{2\gamma_i k_B T_i} \theta_i(t),\end{aligned}\quad (4.32)$$

where γ_i are the friction constants associated with the coupling between the system and the i th thermal environment of the temperature T_i .²³ $\theta_i(t)$ are white Gaussian random noises with zero mean and $\langle \theta_i(t)\theta_j(t') \rangle = \delta_{i,j}\delta(t-t')$.

The heat from the i th thermal environment to the system, $d'Q_i$ is defined as

$$d'Q_i = \left(-\gamma \frac{p_i}{m_i} + \xi_i(t) \right) \circ dx_i, \quad (4.33)$$

while the work $d'W$ is defined as before,

$$d'W = \frac{\partial U}{\partial a} \circ da. \quad (4.34)$$

It is easy then to verify that the balance of energy:

$$dE = d'W + \sum_i d'Q_i, \quad (4.35)$$

Following exactly the same procedure as we did in Sect. 4.1.3.1 for a single thermal environment, we can derive the following formula of the average heat flux from i th thermal environment to the system: (cf. (4.30))²⁴:

$$\begin{aligned}\frac{\langle d'Q_i \rangle}{dt} &= \int \left[\frac{\partial E}{\partial X_i} J_{i,x} + \frac{\partial E}{\partial P_i} J_{i,p} \right] dXdP \quad (\text{with inertia effect}), \\ \frac{\langle d'Q_i \rangle}{dt} &= \int \frac{\partial U}{\partial X_i} J_{i,x} dX \quad (\text{without inertia effect}),\end{aligned}\quad (4.36)$$

where $J_{i,x} \equiv \frac{P_i}{m_i} \mathcal{P}$ and $J_{i,p} \equiv -\left(\frac{\partial U}{\partial X_i} + \gamma_i \frac{P_i}{m_i} \right) \mathcal{P} - \gamma_i k_B T_i \frac{\partial}{\partial P_i} \mathcal{P}$ are the i th flux components of the Fokker–Planck equation associated with X_i and P_i , in the case with inertia, and also $J_{i,x} \equiv -\frac{1}{\gamma_i} \left[\frac{\partial U}{\partial X_i} \mathcal{P} + k_B T_i \frac{\partial}{\partial X_i} \mathcal{P} \right]$ is the i th probability flux associated with X_i in the case without inertia. The derivation is given in Appendix A.4.4.

The interpretation of terms like $\frac{\partial E}{\partial X_i} J_{i,x} + \frac{\partial E}{\partial P_i} J_{i,p}$ as an analog of $d'Q = (dp/dt + \partial U/\partial x) \circ dx(t)$ (see the paragraph above (4.4)) would be far fetched, because the derivation of (4.36) uses integral by parts. The former, therefore, is not adapted to a local interpretation.

²³ If some “internal” degrees of freedom do not directly interact with the thermal environments, we assign $\gamma_i = 0$ for those degrees of freedom.

²⁴ Here $dX \equiv \prod_i dX_i$ and $dP \equiv \prod_i dP_i$.

About the average heat fluxes, a type of “H-theorem” has been derived [13]. It concerns the Shannon entropy S of the system:

$$S \equiv - \int \mathcal{P} \log \mathcal{P} d\Gamma. \quad (4.37)$$

Direct reorganization of terms shows the following equalities:²⁵

$$\frac{dS}{dt} - \sum_i \frac{1}{k_B T_i} \frac{\langle d'Q_i \rangle}{dt} = \int \frac{1}{\mathcal{P}} \sum_i \frac{\gamma_i}{k_B T_i} \left[\frac{P_i}{m_i} \mathcal{P} + k_B T_i \frac{\partial \mathcal{P}}{\partial P_i} \right]^2 dX dP$$

(underdamped),

$$\frac{dS}{dt} - \sum_i \frac{1}{k_B T_i} \frac{\langle d'Q_i \rangle}{dt} = \int \frac{1}{\mathcal{P}} \sum_i \frac{\gamma_i (J_{i,x})^2}{k_B T_i} dX \quad (\text{overdamped}).$$

The right-hand sides of these identities are nonnegative. Therefore,

$$\frac{dS}{dt} - \sum_i \frac{1}{k_B T_i} \frac{\langle d'Q_i \rangle}{dt} \geq 0 \quad (4.38)$$

in both cases. This inequality is interpreted [13] as that the Shannon entropy of the whole system is nondecreasing, $-\frac{1}{k_B T_i} \frac{\langle d'Q_i \rangle}{dt}$ is regarded as the increment rate of the Shannon entropy of i th thermal environment. In the steady state, where $dS/dt = 0$, (4.38) implies the inequality:

$$\sum_i \frac{1}{k_B T_i} \frac{\langle d'Q_i \rangle}{dt} \leq 0 \quad (\text{stationary state}). \quad (4.39)$$

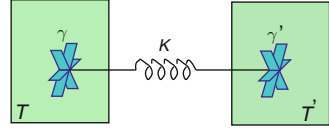
This relation imposes a constraint among the steady-state heat currents.

4.2.1.2 Conduction, Partition, and Diffusion of Heat Between Two Thermal Environments

Apart from the formal results, we will take below a simple model system that interacts with two thermal environments (Fig. 4.6). We will see several different aspects: heat conduction through mechanical motion of system, the partition of heat into two environments upon the external work on the system, and the diffusion of heat between two environments through the system.

²⁵ We use $\int (\partial \mathcal{P} / \partial t) \log \mathcal{P} d\Gamma = \int \sum_i \mathbf{J}_i \cdot \nabla_i \log \mathcal{P}$, where ∇_i denotes the derivatives with respect to i th degree of freedom. We use also $-\sum_i \int \left(\frac{P_i}{m_i} \frac{\partial}{\partial X_i} - \frac{\partial U}{\partial X_i} \frac{\partial}{\partial P_i} \right) \mathcal{P} d\Gamma = 0$, assuming that the surface integral vanishes.

Fig. 4.6 Two vanes immersed in their respective thermal environments. These vanes are mechanically connected by a spring. See the text



Model

In Fig. 4.6 two thermal environments are at the temperatures T and T' , respectively. In each of these a vane is immersed. The coupling of these vanes to their thermal environments is characterized by the friction coefficients γ and γ' , respectively. The two vanes are joined through a harmonic torsional spring with the elastic constant, K . We will neglect the inertia effect for a moment. Let us denote by x and x' the rotation angles of the vanes in the environment of temperature T and T' , respectively. The Langevin equations for the vanes are

$$0 = -\gamma\dot{x} + \xi(t) - K(x - x'), \quad 0 = -\gamma'\dot{x}' + \xi'(t) - K(x' - x), \quad (4.40)$$

where $\xi(t)$ and $\xi'(t)$ are two independent Gaussian white noises with zero mean and $\langle \xi(t_1)\xi(t_2) \rangle = 2\gamma k_B T \delta(t_1 - t_2)$ and $\langle \xi'(t_1)\xi'(t_2) \rangle = 2\gamma' k_B T' \delta(t_1 - t_2)$. We will use the “dot” (\dot{x} etc.) to mean the time derivative.

We define heat by $d'Q = (-\gamma\dot{x} + \xi) \circ d'x$ and $d'Q' = (-\gamma'\dot{x}' + \xi') \circ d'x'$. The balance of energy is in a time differential form,

$$\frac{d'Q}{dt} + \frac{d'Q'}{dt} = \frac{d}{dt} \left[\frac{K}{2}(x - x')^2 \right] - \frac{(x - x')^2}{2} \frac{dK}{dt}. \quad (4.41)$$

The first and second terms on the right-hand side of (4.41) shows dE/dt and $d'W/dt$, respectively.

We can also show the following relation:

$$\gamma \frac{d'Q}{dt} - \gamma' \frac{d'Q'}{dt} = K(x - x') \circ (\xi(t) + \xi'(t)). \quad (4.42)$$

Moreover, we can derive the Langevin equation for the relative rotation angle, $\mu \equiv x - x'$, from the original coupled Langevin equation:

$$\frac{d\mu}{dt} = -\left(\frac{1}{\gamma} + \frac{1}{\gamma'} \right) K \mu + \left(\frac{\xi(t)}{\gamma} - \frac{\xi'(t)}{\gamma'} \right). \quad (4.43)$$

These three equations give the heat currents $\frac{d'Q}{dt}$ and $\frac{d'Q'}{dt}$ for each realization of $(\xi(), \xi'())$. Since $Q(t) \equiv \int_0^t (d'Q/dt) dt$ and $Q'(t) \equiv \int_0^t (d'Q'/dt) dt$ are quadratic functionals in the Gaussian stochastic processes, ξ and ξ' , detailed statistics of $Q(t)$ and $Q'(t)$ are available through the generating function $\langle e^{-\lambda Q(t)} \rangle$, etc. Using this fact, for example, the theorem of heat fluctuation [14] has been tested [15]. This theorem

is a development of the so-called fluctuation theorem (FT) [16, 17]. See also [18] and a recent review to date [19]. We will not go into details of these statistics. Below we will discuss the average and variance of heat currents.

Note: The original coupled Langevin equation is decoupled by using the relative angle, μ , and the “center of diffusion” $X \equiv (\gamma x + \gamma' x')/(\gamma + \gamma')$. The latter obeys a free rotative Brownian motion, $(\gamma + \gamma')\dot{X} = \xi(t) + \xi'(t)$.²⁶ Therefore, the diffusion of X does not contribute to the heat currents.

Heat Conduction Between Two Thermal Environments

Using the solution of (4.43) for $\mu(t)$, the averages of (4.42) and (4.41)²⁷:

$$\frac{\langle d'Q \rangle}{dt} + \frac{\langle d'Q' \rangle}{dt} = \frac{K(t)}{2} \frac{d}{dt} \langle (x - x')^2 \rangle, \quad (4.44)$$

$$\gamma \frac{\langle d'Q \rangle}{dt} - \gamma' \frac{\langle d'Q' \rangle}{dt} = K(t)(k_B T - k_B T'). \quad (4.45)$$

In the steady state with K constant, the right-hand side of (4.44) vanishes. Then we have the average heat currents:

$$\frac{\langle d'Q \rangle}{dt} = -\frac{\langle d'Q' \rangle}{dt} = \frac{K}{\gamma + \gamma'} (k_B T - k_B T'). \quad (4.46)$$

The above result describes the heat conduction mediated by a mechanical spring. When $T = T'$ the average heat current vanishes. Also if γ or γ' goes to infinity, there is no conduction. The average heat current increases with K . It means that the stiffer spring can transmit energy more efficiently from one thermal environment to the other. According to (4.46) the heat current diverges in the limit $K \rightarrow \infty$. This apparently unphysical result is a sign of the abuse of the Langevin equation without inertia: In the limit of high stiffness of the spring, the timescale $\sim (\gamma + \gamma')/K$ characterizing the variation of $\mu = (x - x')$ is beyond the time resolution of the modeling by such Langevin equation. In order to avoid the spurious divergence, the model has to take into account the effects of inertia, for example, due to the moment of inertia of the vanes. In the limit of $K = \infty$, appropriate Langevin equations are as follows:

$$I\ddot{x} = -\gamma\dot{x} + \xi(t) + f(t), \quad I'\ddot{x}' = -\gamma'\dot{x}' + \xi'(t) - f(t), \quad (4.47)$$

where I and I' are the moments of inertia of the vanes, $\pm f(t)$ is the force of action/reaction through the rigid spring, determined so that $x(t) - x'(t) = 0$ at

²⁶ The “apparent temperature” for this diffusion is $(\gamma T + \gamma' T')/(\gamma + \gamma')$.

²⁷ Technical detail: We use a rule $\int_0^t \delta(s) ds = \frac{1}{2}$ to be consistent with the Stratonovich type calculus

any t .²⁸ A new energy balance relation is written as

$$\frac{d'Q}{dt} + \frac{d'Q'}{dt} = \frac{d}{dt} \left(I \frac{\dot{x}^2}{2} + I' \frac{\dot{x}'^2}{2} \right) \quad (4.48)$$

and the average heat current in the steady state is

$$\frac{\langle d'Q \rangle}{dt} = - \frac{\langle d'Q' \rangle}{dt} = \frac{\gamma\gamma'}{(\gamma + \gamma')(I + I')} (k_B T - k_B T'). \quad (4.49)$$

Nanomachine to Absorb the Heat vs. Maxwell's Demon

It will be instructive to look the above model from the standpoint of the hot reservoir. Let us suppose that $T > T'$. How do things look like if we observe the microscopic events around the vane in the high-temperature environment of temperature T ?

The rotational motion of the vane $x(t)$ is apparently random, and the thermal environment (T) is isolated except for the mechanical link through the vane immersed therein. However, this random motion of the vane results in extracting energy from this environment. Moreover, the ‘‘Feynman pawl and ratchet’’ (Sect. 1.3.4) replaces the spring by more intelligent attachments and enables work to be done using the energy extracted through this random motion.

If we compare the above situations with the experiment of agitating a ‘‘spoon’’ in water, often mentioned after J. P. Joule (around 1850), the spoon could only warm it up. Therefore, the random motion of the vane in the high-temperature environment T is essentially different from the agitation of the spoon. What is the difference? We note that the extraction of energy by the vane does not contradict the second law of thermodynamics. What the second law excludes is the extraction of energy from a system with a single thermal environment. Our system of vanes would indeed cease to extract the energy as soon as we remove the second thermal environment (temperature $T' (< T)$).

The key to the answer is related to the well-known ‘‘paradox of Maxwell's demon’’: The demon D sits by a gate between two containers of gas, which are initially at the same temperature. D and the two containers are isolated from the rest of the world. D can recognize the velocity of the gas particles coming toward the gate. Now D operates the gate so that only the hot particles go from the left container to the right one, and that only the cool particles go from the right container to the left one. Then D can create the temperature difference between the two containers. This contradicts with the zeroth and second laws of thermodynamics. The fault of logic in this paradox is that, in fact, D must keep contact with a low-temperature environment so that D can recognize the velocities of gas particles.

Coming back to our vane that absorbs heat, it recognizes the fluctuations in the hot environment T and moves so that it absorbs energy. For this action, contact with

²⁸ K can be neglected for $(\gamma^{-1} + \gamma'^{-1})^{-1}/(I + I') \gg (\gamma + \gamma')/K$. See (4.49) below.

the cool environment T' is indispensable. It is the hot environment that exerts the random force on the vane, but the motion of the vane is not incoherent like Joule's spoon. To see this point clearer, let us analyze the behavior of $x(t)$ of the system (4.40) putting $T' = 0$. Under this assumption we can solve the second equation of (4.40) for $x'(t)$:

$$x'(t) = \frac{K}{\gamma'} \int_0^{+\infty} e^{-\frac{K}{\gamma'}s} x(t-s) ds. \quad (4.50)$$

Substituting this result into the first equation of (4.40), we have the following equation for $x(t)$:

$$\gamma \dot{x}(t) = -K \left[x(t) - \frac{K}{\gamma'} \int_0^{+\infty} e^{-\frac{K}{\gamma'}s} x(t-s) ds \right] + \xi(t). \quad (4.51)$$

The integral on the right-hand side of (4.51), i.e., $x'(t)$ of (4.50), shows a feedback control in the restoring force. As x' follows adaptively to the motion of x in the past, the restoring force, $-K(x(t) - x'(t))$, is weakened as compared with a spring with fixed end ($x'(t) = \text{const.}$). As the result, the vane $x(t)$ returns less energy to the environment T than what was injected from this environment. A related model is found in [20].

Based on (4.51) we can design a cooling device in the fluctuating world: we somehow trap a Brownian particle (position $x(t)$) around the trapping center (the position $x'(t)$). If $x(t)$ can be observed and if the feedback circuit can change $x'(t)$ quickly enough to realize (4.50), then we can extract energy around the Brownian particle as if the particle is in contact with another environment with $T' = 0$.

Partition of Heat

Now we suppose that $T = T'$ for the two thermal environments while they have no direct contact with each other. The object is to find how much heat the spring absorbs from respective thermal environments when the spring constant $K(t)$ is slowly lowered. Analogous situation was mentioned in Sect. 2.2, see, Fig. 4.7. There, the volume of the cylinder $V(t)$ played a role of the inverse square root of the spring constant, $K(t)^{-1/2}$. If we pull up the piston quasistatically, what will be the partitioning of the heat supplied from these environments?

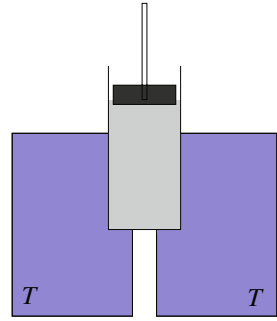
Conventional thermodynamics did not answer to this question.²⁹

The average heat currents are found from the relation (4.45) with $T = T'$ and (4.44). The result is

$$\gamma \frac{\langle d'Q \rangle}{dt} = \gamma' \frac{\langle d'Q' \rangle}{dt} = \frac{\gamma\gamma'}{\gamma + \gamma'} \frac{K(t)}{2} \frac{d}{dt} \langle (x - x')^2 \rangle. \quad (4.52)$$

²⁹ Linear nonequilibrium thermodynamics may devise a model with introducing phenomenological thermal resistances. In the present model, γ and γ' are sufficient.

Fig. 4.7 (The same figure as Fig. 2.4.) Partition of heat into two thermal environments of the same temperature T (left and right boxes) through the change of the volume of a gas (center)



This shows that whatever the change of $K(t)$ is, the heat currents are partitioned according to the inverse ratio of γ and γ' . More heat is exchanged with the environment of smaller value of γ . In particular, for the slow change of $K(t)$, we may have a concrete result: Using the equipartition law, $K(t)\langle(x - x')^2\rangle/2 = k_B T/2$, we integrate (4.52) to obtain the average cumulate heat from respective environments, $\langle\Delta Q\rangle$ and $\langle\Delta Q'\rangle$:³⁰

$$\gamma\langle\Delta Q\rangle = \gamma'\langle\Delta Q'\rangle = \frac{\gamma\gamma'}{\gamma + \gamma'}k_B T \ln \sqrt{\frac{K_{\text{init}}}{K_{\text{fin}}}} \quad (\text{quasistatic}), \quad (4.53)$$

where K_{init} and K_{fin} are the initial and final values of $K(t)$. If the spring is softened indefinitely ($K(t) \rightarrow +0$), the external system extract arbitrarily large amount of energy from the thermal environments, in the proportion of γ^{-1} vs. γ'^{-1} .³¹

Diffusion of Heat

Even in the case of $T = T'$ and $K = \text{const.}$, heat flows randomly between the two thermal environments. The cumulated heat undergoes a Brownian motion around the average steady change. For the case of $K = \text{const.}$, this fluctuation is characterized by the “thermal diffusion constant” \mathcal{D} through the following relation:

$$\left\langle \left[\int_0^t \frac{d'Q}{dt} dt - \int_0^t \frac{\langle d'Q \rangle}{dt} dt \right]^2 \right\rangle = 2\mathcal{D}t. \quad (4.54)$$

Some calculation shows³²

$$\mathcal{D} = \frac{K}{\gamma + \gamma'} \left(\frac{\gamma k_B T + \gamma' k_B T'}{\gamma + \gamma'} \right) \left(\frac{\gamma' k_B T + \gamma k_B T'}{\gamma + \gamma'} \right). \quad (4.55)$$

³⁰ We integrate $\frac{K(t)}{2} \frac{d}{dt} \frac{k_B T}{K(t)} = \frac{k_B T}{2} \frac{d}{dt} \ln \frac{1}{K(t)}$.

³¹ The energy in the spring is $\sim k_B T/2$, independent of the stiffness.

³² The expression of \mathcal{D} in the Japanese Version [21] should be corrected as that of (4.55).

See Appendix A.4.5 for the derivation. This formula is invariant under the exchange of T and T' . At high temperature and/or for very slow change of $K(t)$, the diffusion of heat may mask the prediction about the partition of heat, (4.53).

4.2.2 Energetics of Thermal Ratchet Motors

We revisit the thermal ratchet motors (Sect. 1.3.4) and discuss several aspects of energetics. Figure 4.8 recapitulates the Feynman pawl and ratchet and Büttiker and Landauer ratchet.

4.2.2.1 Heat Leak and Onsager Coefficient in the Feynman Pawl and Ratchet Wheel

Introduction

As mentioned in Sect. 1.3.4 the Feynman ratchet model played an important role in the construction of the stochastic energetics.

We recall below the Langevin equation of this model:

$$0 = -\gamma \frac{dx}{dt} - \frac{\partial U}{\partial x} + \sqrt{2\gamma k_B T} \theta(t), \quad 0 = -\gamma' \frac{dy}{dt} - \frac{\partial U}{\partial y} + \sqrt{2\gamma' k_B T'} \theta'(t), \quad (4.56)$$

where $U(x, y) = U_1(x - \phi(y)) + U_2(y) - fx$, and $\theta(t)$ and $\theta'(t)$ are mutually independent white Gaussian random noises with zero mean and $\langle \theta(t)\theta(t') \rangle = \langle \theta'(t)\theta'(t') \rangle = \delta(t - t')$. For $T \neq T'$ this model can rotate on average the ratchet wheel x in one direction. Here the load f is regarded as a part of the system, and its

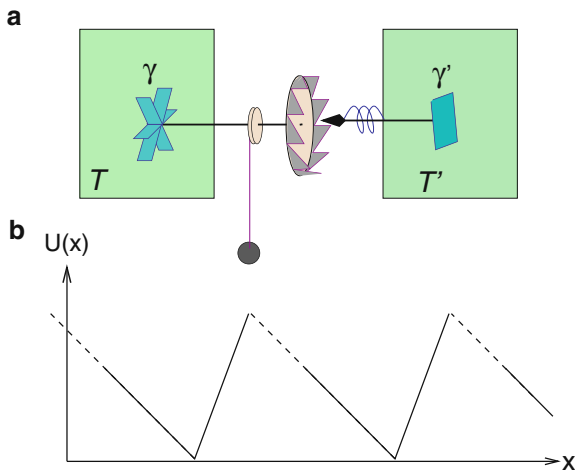


Fig. 4.8 (a) Feynman ratchet and pawl and (b) Büttiker and Landauer ratchet. (The same figures as Figs. 1.9 and 1.10. See those legends.)

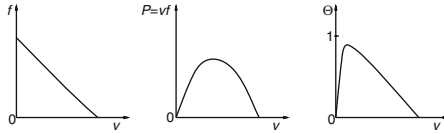


Fig. 4.9 Schematic presentation of the load f , power $P = vf$, and the energy efficiency Θ of motors as function of its velocity v . The force at $v = 0$ is the *stall force*

potential energy ($-fx$) is counted in the system's potential energy. This system is, therefore, autonomous with no external parameters.

After Feynman, there have been many variations of his model, and we will not go into details of those model. We only summarize in Fig. 4.9 general qualitative features of this model, in terms of the average working velocity $v = \langle \dot{x} \rangle$, load f , average power output $P = vf$, and the efficiency Θ , i.e., the ratio of P to input energy from high temperature bath (T) *normalized* by the Carnot maximum value, $|\Delta T|/T$ (see (2.24)).

We will discuss mainly two aspects of energetics: the stalled state where the load is just strong enough that the motor moves neither forward nor backward, and around the equilibrium state where the efficiency by linear nonequilibrium thermodynamics becomes undetermined (of $0/0$ type).

Stalled State and Efficiency

One of the main questions was if Feynman's model can attain $\Theta = 1$, i.e., the efficiency of the ideal Carnot engine.³³ Feynman himself argued affirmatively in the original textbook [22], since he focused on the critical and rare events when a pawl finds a new space between the ratchet tooth. Later his argument was represented more formally in terms of some stochastic boundary condition at the peaks of the ratchet profile [23].

While these critical events are essential for the function of this motor, the other "nonsuccessful" fluctuations are also important from the energetics point of view. Especially, at the stalled state Parrondo [24] and then the author [3] noticed that the efficiency should be $\Theta = 0$. While the pawl jiggles around a valley between neighboring ratchet tooth, the fluctuations of the ratchet wheel and those of the pawl are mechanically coupled. Heat conduction from the high-temperature environment to the low-temperature one then takes place, as we have analyzed a simple case in Sect. 4.2.1.2.

The same reasoning can also be described in terms of the probability flux of the Fokker–Planck equation at the stalled state. The stationary probability flux (J_x, J_y) exhibits vorticity in the phase space (xy -plane) [25, 26], which can then be related to the dissipation of heat without contributing to work.

³³ That is, the ratio η of the available work to the supplied heat from the high-temperature (T) thermal environment is $\eta_{\max} \equiv 1 - T'/T$.

In conclusion, there is a leakage of heat at the finite rate at the stalled state. The efficiency of energy conversion then vanishes at the stalled state. Experience shows that, if the parameters of the model are well tuned, efficiency can attain almost 1 (theoretical maximum) just off this stalled state while the efficiency *at* the stalled is 0. The efficiency has, therefore, a dip at this state. From practical viewpoint, if the size of the system is increased, the effect of jiggling may become negligible, and the dip in the efficiency may be too narrow to be observed. Discrete modeling may also suppress or lessen this jiggling.

Near Equilibrium State and Onsager Coefficients

Near the equilibrium, $T \simeq T'$, and weak load, $f \sim 0$, Onsager coefficients characterize the function of Feynman ratchet on macroscopic (ensemble average) level.

In this framework, the average velocity of wheel rotation $\mathcal{J}_p = \langle \frac{dx}{dt} \rangle$ (see (1.114)) and the heat flux \mathcal{J}_q from the hot thermal environment are linearly related to the thermodynamic force concerning the load, f/T , and the temperature gradient, $\Delta T/T^2$ ($\Delta T \equiv T' - T$) with the symmetric Onsager coefficients [27, 28]:

$$\begin{pmatrix} \mathcal{J}_p \\ \mathcal{J}_q \end{pmatrix} = \begin{pmatrix} \mu T & L_{pq} \\ L_{pq} & \lambda T^2 \end{pmatrix} \cdot \begin{pmatrix} f/T \\ \Delta T/T^2 \end{pmatrix}, \quad (4.57)$$

where $\mu = \mathcal{J}_p/f$ for $\Delta T = 0$ and $\lambda = \mathcal{J}_q/\Delta T$ for $f = 0$ are, respectively, the mobility coefficient and the heat conductivity coefficient. Onsager theory says that the off-diagonal coefficients L_{pq} are the same. This symmetry in the context of ratchet motors has been discussed in [29]. Exactly at equilibrium ($f = \Delta T = 0$), the above phenomenology is not valid. For example, the efficiencies of energy conversion become singular, simply because (4.57) yields 0/0, nondeterminate. In fact, in the very vicinity of equilibrium, the fluctuations in the fluxes dominate the average fluxes, and the fluctuations are not singular.

The modeling by the Langevin equation tells the underlying mechanism of the relation (4.56), especially, of the cross-coupling coefficient L_{pq} .

First, we notice that there is no *kinetic* cross-coupling in the Langevin equation (4.56), that is, no forces on x directly drives dy/dt , or vice versa. It is through the potential coupling $U(x, y)$ that the cross-coupling L_{pq} is realized. Through the nonlinearity of this potential coupling, the model also predicts the nonlinear force–flux relation. There are models of heat engine that assume the cross-coupling as a kinetic mechanism. (See below.)

Second, the modeling by the Langevin equation allows the analysis of energetics along an individual process. Even at equilibrium, a *cycle* of fluctuations in (x, y) -space can accompany the transfer of heat coupled with the space translocation (wheel rotation).³⁴ In fact this analysis gives the physical interpretation of the

³⁴ Because of detailed balance at equilibrium, forward cycles and backward cycles occur equally likely. Due to this cancellation this phenomena cannot be captured by macroscopic phenomenology.

cross-coupling constant L_{pq} almost quantitatively [30]. Below we summarize their analysis.

Using a slightly modified model of Feynman pawl and ratchet wheel, the “quantum” of the transferred heat, q_{step} , is measured upon a directed, e.g., forward, step of ratchet potential (in equilibrium). Assuming that this quantum step is not singular at $f = 0$, the relation between the \mathcal{J}_q and the (small) load f is written as $\mathcal{J}_q = q_{\text{step}}(\mu f)/\ell_{\text{step}}$, where ℓ_{step} is known step size of the ratchet potential. Comparing this relation with (4.57), the coefficient L_{pq} is $L_{pq} = q_{\text{step}}\mu T/\ell_{\text{step}}$. This result is valid also at $f = 0$. On the other hand the Einstein relation tells that μT is the diffusion coefficient, $\ell_{\text{step}}^2/\tau_{\text{step}}$, where τ_{step} is the characteristic time of spontaneous step in equilibrium. τ_{step} is also measurable from the model analysis. Combining the above results the cross-coupling coefficient is directly correlated with the energetics of a single-step event:

$$L_{pq} = q_{\text{step}} \left(\frac{\ell_{\text{step}}}{\tau_{\text{step}}} \right). \quad (4.58)$$

This argument is confirmed numerically and is also justified from the calculation of Green–Kubo formula [28].³⁵

4.2.2.2 Inertia as a Singular Perturbation: Case of Büttiker and Landauer Ratchet

Introduction

Stochastic energetics has been applied to the Büttiker and Landauer ratchet (see Fig. 4.8 (b) and Sect. 1.3.4.3).

For the model without inertia, (1.112), i.e.,

$$\gamma dx = \sqrt{2\gamma k_B T(x)} \circ dB_t - \frac{\partial}{\partial x} \left[U(x, a) + fx + \frac{k_B T(x)}{2} \right] dt, \quad (4.59)$$

the analysis showed the efficiency Θ of energy conversion up to ³⁶ [4, 31]. The maximum is attained in the stall state.

If the inertia is taken into account, the model is (1.111), i.e.,

$$\frac{dp}{dt} = -\frac{\partial U(x)}{\partial x} - f - \gamma \frac{p}{m} + \xi(t), \quad \frac{dx}{dt} = \frac{p}{m}, \quad (4.60)$$

³⁵ Note that the potential energy of the system $U(x, y)$ does not contribute to the “quantum” of the transferred heat, q_{step} , except for the load’s potential energy, $f\ell_{\text{step}}$. The remaining part of $U(x, y)$ returns to the original value, on the average, after a “quantum” cycle is completed.

³⁶ i.e., the Carnot efficiency η up to $\eta_{\text{max}} = 1 - T'/T$.

where $\xi(t)$ is the white Gaussian noise with $\langle \xi(t)\xi(t') \rangle = 2\gamma k_B T(x)\delta(t - t')$. The analysis of the latter model concluded that the efficiency should drop to 0 at the stalled state [32–34], in contradiction to the model without inertia.

This discrepancy implies that the limit of $m \rightarrow 0$ is not equivalent to the model with $m = 0$. If we put $m = 0$ in the Langevin equation, the equation changes the order of differential. Such a change may drastically affect the behavior of $x(t)$, and the energetics of Büttiker and Landauer ratchet is sensitive to this change.

Scale of Description

To better understand the cause of discrepancy and to know the true efficiency, we first remember that we should respect the time resolution of each Langevin equation (see, Sect. 1.3.2). In fact, both models abuse the Langevin equations beyond their validity range. When a particle moves across the discontinuity of the temperature, the environment for the particle changes within an infinitesimal time, shorter than any finite time resolution that is associated with a Langevin model.

Next we note the role of the velocity relaxation time. This time is finite for the model with inertia, $\tau_p \equiv m/\gamma$, while it is assumed to be infinitesimal for the model without inertia. We have a physical argument (see below) that, if we keep track of this timescale τ_p , the sudden jump of temperature is “buffered” and the model with inertia gives a meaningful result. We should not take the overdamped limit first.

Physical argument

When a particle switches its thermal environment, a thermalization of the kinetic energy of the particle occurs. On the average, the particle’s kinetic energy will relax toward its (new) equipartition value. Through this process, an irreversible heat exchange takes place with a new thermal environment [35, 32]. This is the cause of heat leakage.

To discuss more quantitatively, suppose that a particle moves from the temperature T to the temperature T' . When the particle cross the border, its motion is almost ballistic during the time $\sim \tau_p \equiv m/\gamma$. During this period, the particle keeps its original velocity $\sim v_{th} \equiv \sqrt{k_B T/m}$. Then thermalization occurs, and the particle exchanges energy, which is about the difference of the equipartition kinetic energy $|k_B T - k_B T'|/2$. This energy does not depend on m .

In summary, as far as the particle’s kinetic energy is concerned, the temperature border is smoothed. The effective “temperature gradient” is $\sim |T - T'|/(v_{th}\tau_p) \propto m^{-1/2}$. [36, 32]. The heat leakage through the thermalization of the kinetic energy occurs with this temperature gradient. At the stalled state this heat leakage continues at a finite rate. The efficiency is, therefore, 0 at the stalled state.

The conclusion is parallel to the Feynman pawl and ratchet wheel. But the mechanism of the leakage in the two models is very different. The maximum of the efficiency is realized near but off the stalled state, and less than the Carnot limit.

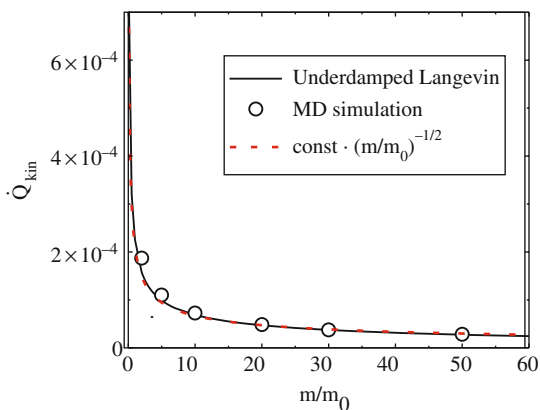
Kinetic Argument

Is there a remedy for the model without inertia to recover the above mentioned leakage [33, 34]? Below is the argument against this possibility: for a Wiener process, or a overdamped free Brownian motion ($0 = -\gamma dx/dt + \xi$), there is no characteristic timescale. The implication is that, once it visits a point, it revisits the same point indefinitely many times within a short period. Therefore, the to-and-fro of the particle at the temperature boundary can occur indefinitely many times, before the bias field drives the particle off the boundary. It is, therefore, impossible to incorporate the thermalization of kinetic energy in the overdamped model. If the space is discretized [37], this problem disappears apparently. But justification is needed for the discretization.

Proof by Numerics

The above physical argument supporting the Langevin model with inertia was finally verified by a careful molecular dynamic simulation [38]. Their analysis of energy transfer confirmed the divergence $\propto m^{-1/2}$ of the heat leakage (\dot{Q}_{kin}) due to the kinetic energy carried by the particle. See, Fig. 4.10. Their simulation used 2D hard-core gas as thermal environments of two different temperatures. The gas is dense enough that the Knudsen number (mean-free path/system size) is < 1 . The $\dot{Q}_{\text{kin}} \propto m^{-1/2}$ behavior holds well even for $\tau_p = m/\gamma$ as small as the microscopic time, i.e., the inverse collision frequency of gas particles against the Brownian particle.³⁷

Fig. 4.10 Kinetic energy contribution of heat transfer, \dot{Q}_{kin} . It diverges as $(m/m_0)^{-1/2}$, where m and m_0 are, respectively, the mass of the Brownian particle and the mass of the gas particle constituting the model thermal environment (Figure by the courtesy of R. Kawai)



³⁷ This result also justifies the Langevin equation with inertia down to the microscopic timescale. The validity of this equation at the intermediate scale, $\sim 10\text{--}10^2 \tau_p$, will be scrutinized in Sect. 6.3.1.

In conclusion, the study of Büttiker and Landau ratchet gives a lesson that an apparent reasonable result (Carnot’s limit) can be wrong, and apparently singular result can be true.

4.2.3 Fluctuating Open System Does Not Exchange Chemical Potential as Energy of Particle

4.2.3.1 * Definition of the System

On the level of description of the Langevin equation, we always identify the positions of particles. We, therefore, take into account explicitly the space coordinates. We define as the *open system* a spatial region Ω within an entire space which the particles can explore. For example, Ω can be a volume confined by a piston and a cylinder with a valve (cf. Fig. 7.18), or a focused region of laser light under optical tweezers. Or Ω can also represent binding potential wells on a membrane (cf. Fig. 8.3).

We call “particle environment” the complementary region, Ω^c . We assume that the entire system, $\Omega \cup \Omega^c$, is closed and immersed in a thermal environment of temperature T . In this chapter, the particle environment need not be very large. See Fig. 4.11 (*top*). The stochastic energetics described up to the previous sections applies to this entire system. For simplicity we will consider only one species of particles.

We suppose that each particle (position $x_j(t) \in \Omega \cup \Omega^c$) obeys the Langevin equation without inertia term:

$$0 = -\gamma \frac{dx_j}{dt} + \xi_j(t) - \frac{\partial E_{\text{tot}}}{\partial x_j} \quad (j = 1, \dots, N), \quad (4.61)$$

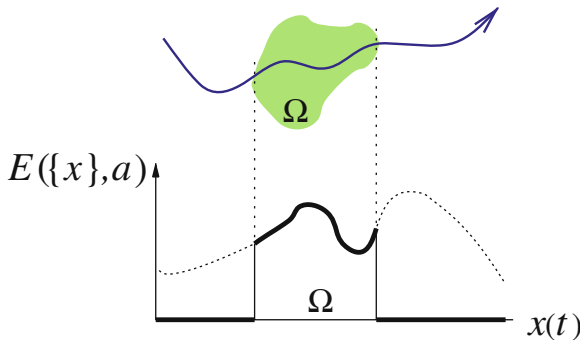


Fig. 4.11 *Top*: Open system Ω and its “particle environment” Ω^c , which is outside of Ω . Thick curve is a trajectory of the particle which passes through the system. *Bottom*: The energy of the system, $E_{(\{x\},a)}$ (thick curve and thick line segments). In the absence of particles, the energy of open system is zero, $E(\{\}, a) = 0$

with $\{\xi_j(t)\}$ being mutually independent white Gaussian random forces with zero mean and correlations $\langle \xi_j(t)\xi_k(t') \rangle = 2\gamma k_B T \delta_{j,k} \delta(t-t')$.³⁸

However, we explicitly describe only those particles in the system Ω . Once a particle exits from the system, we lose track of it, i.e., we lose its degree of freedom. In summary, the open system is a region, and the particles belong to this system while they are in this region.

4.2.3.2 * States of Open System

It is useless to distinguish *all* the particles in the entire system, first because any particular particle can spend most of the time in the environment, Ω^c , second because we need not to distinguish which particular particles are in the system, whether or not this particle is the one which has left the system before.

We, therefore, define the state of an open system as follows:

$$\begin{aligned}
 \{\} &: \text{“Null” state, where there is no particle in } \Omega. \\
 \{x_1\} &: \text{the state with one particle at } x_1. \\
 \{x_1, x_2\} &: \text{the state with two particles with their positions being } x_1 \text{ and } x_2. \\
 &\dots \\
 \{x_1, \dots, x_n\} &: \text{the state with } n \text{ particles with their positions being } x_1, \dots, x_n. \\
 &\dots
 \end{aligned} \tag{4.62}$$

Therefore, the number of particles in the system, $\hat{n}(t)$, is also a random variable.³⁹ If there are more than one species of particles, we will distinguish them and denote $x_1^{(\alpha)}$, etc.

4.2.3.3 Energy of Open System

As the energy of an open system, we count only the energies of those particles in the region Ω . Interactions among the particles require a refinement to this definition. This complication is unavoidable since energy of small system does not have the extensive character, in general.

One-Particle Energy of the Open System

For a moment we shall ignore all the interactions among the particles. Let us denote by $U_1(x, a)$ the energy of a particle at the position x . We assume that $U_1(x, a)$ is defined on the entire system, $x \in \Omega \cup \Omega^c$. As for the dependence on the external

³⁸ The generalization to the case with inertia is straightforward, but we will not discuss here.

³⁹ For those who know second quantization, this state space may be reminiscent of the Fock space. In the Fock space, however, the identity of individual particles is lost because of the symmetrization or antisymmetrization of the product states of single particle. In the present state space, the particle's identity is preserved while particle remains in the system.

parameter a , we require that $U_1(x, a)$ depends on a only for $x \in \Omega$.⁴⁰ The reason is that we have excluded the direct interactions between the external system and the system’s environment. The one-particle energy U_1 has an arbitrariness of an additive constant.

If only one particle passes through the system Ω , the system’s energy will change as shown in Fig. 4.11 (*bottom*). If there are N particles in the entire system, the energy of the system, E , is represented as (see (4.62))

$$E = \sum_{j=1}^N U_1(x_j, a) \theta_{\Omega}(x_j), \tag{4.63}$$

where we have introduced the (single-particle) characteristic function $\theta_{\Omega}(x)$ for the zone Ω :

$$\theta_{\Omega}(x) = \begin{cases} 1 & (x \in \Omega), \\ 0 & (x \notin \Omega). \end{cases} \tag{4.64}$$

Remark on the choice of Ω : Often Ω may be chosen as a region surrounded by potential barriers. So as to describe the external control of these barriers, it is practical to include the barrier region as a part of Ω and count the barrier potential in U_1 .⁴¹ If the system’s periphery is an electric double layer, then the potential energy $U_1(x, a)$ has a physical discontinuity across this layer. In this case it is practical to define Ω so that the double layer is found in the interior of Ω . The stochastic energetics of the transmembrane diffusion of ions may explain that, if diffusion is caused by the difference of ion concentrations, it will release no heat, while if it is due to the electrostatic double layer, it accompanies a heat release. The electrochemical potential alone does not distinguish these two cases.

Inclusion of the Interactions Among Particles

Things become suddenly complicated if the particles interact among themselves [39]. For example, let us consider the situation of Fig. 4.12; the two particles are

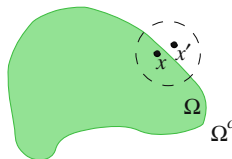


Fig. 4.12 The situation where a particle in the environment (x') is within the interaction distance (illustrated by the *dashed circle*) of another particle in the system (x) across the system boundary $\partial\Omega$. We will then count the interaction energy as a part of energy of the system, E (see the text)

⁴⁰ That is, $\partial U_1/\partial a = 0$ if $x \notin \Omega$.

⁴¹ Ω is considered to be a “closed set.”

close to each other across the boundary of Ω , and that interactions between them are not negligible. There is no a priori reason to include or ignore this interaction energy as a part of energy of the system, E . The same is true for the interaction energy involving more than two particles. For macroscopic thermodynamics, the premise of the extensive property of thermodynamic quantities justified to exclude such ambiguity.⁴² In the study of mesoscopic systems, however, we cannot avoid this boundary effect.

We will then take up the following definition for the energy of the system. If a cluster of particles are interacting with each other, and if at least one of those particles is in Ω , we count this interaction energy in the energy of the system, E .

Leaving the details of analysis in Appendix A.4.6, the result is

$$\begin{aligned}
 E = & \sum_{i=1}^N U_1(x_i, a) \theta_{\Omega}^{(1)}(x_i) + \sum_{j=1}^N \sum_{k=j+1}^N U_2(x_j, x_k) \theta_{\Omega}^{(2)}(x_j, x_k) \\
 & + \sum_{j=1}^N \sum_{k=j+1}^N \sum_{l=k+1}^N U_3(x_j, x_k, x_l) \theta_{\Omega}^{(3)}(x_j, x_k, x_l) + \dots, \quad (4.65)
 \end{aligned}$$

where $U_2(x_j, x_k)$ and $U_3(x_j, x_k, x_l)$ are properly defined two and three body interactions, etc., and $\theta_{\Omega}^{(2)}(x_j, x_k)$, $\theta_{\Omega}^{(3)}(x_j, x_k, x_l)$, \dots , takes the value 1 if at least one of their argument takes the value in Ω and 0 otherwise. Because of the sharp boundary of the system Ω , the energy of the system E can vary discontinuously.

The above definition of the system's energy is not the unique choice. Nor this choice is proven to be the best one. Apparently, this definition needs modifications when there are two open systems Ω_1 and Ω_2 which share a part of their boundaries.

For later use, we write down also the total energy E_{tot} of the entire system $\Omega \cup \Omega^c$:

$$\begin{aligned}
 E_{\text{tot}} = & \sum_{i=1}^N U_1(x_i, a) + \sum_{j=1}^N \sum_{k=j+1}^N U_2(x_j, x_k) + \sum_{j=1}^N \sum_{k=j+1}^N \sum_{l=k+1}^N U_3(x_j, x_k, x_l) + \dots \\
 & \quad (4.66)
 \end{aligned}$$

Remark : Necessity of steric repulsion for a single-particle binding site. On the level of description by the Langevin equations, the hard-core repulsive interaction between particles should be explicitly accounted for as a part of the term U_2 , even if the single-particle binding potential, $U_1(x, a)$, affords only room for single particle. Otherwise, more than one particles, e.g., $\{x_1, x_2\}$, can enter the same binding site at the same time. As is the case with usual hard-core repulsion, the last interaction has no direct contribution to the energy of the system: it only restricts the available phase space of x_1, x_2 , etc.

⁴² In all cases, we exclude the long-range interactions: we exclude unscreened electrostatic interaction and gravitational interaction.

4.2.3.4 Energy Balance of Open System

During dt all the particles in the entire system undergo small steps. For those particles which continue to belong to the system Ω , we will apply the previous definition of the heat. We call this heat internal heat and denote it by $d'Q^{(\text{in})}$. Using $\theta_\Omega(x)$, internal heat is

$$d'Q^{(\text{in})} \equiv \sum_j \theta_\Omega(x_j) \left(-\gamma \frac{dx_j}{dt} + \xi_j(t) \right) \circ dx_j. \quad (4.67)$$

The work $d'W$ is also defined as before:

$$d'W \equiv \sum_j \theta_\Omega(x_j) \frac{\partial U_1(x_j, a)}{\partial a} da(t). \quad (4.68)$$

We can rewrite this as follows:

$$d'W = \sum_{j=1}^N \frac{\partial[\theta_\Omega(x_j)U_1(x_j, a)]}{\partial a} da(t) = \frac{\partial E_{\text{tot}}}{\partial a} da(t). \quad (4.69)$$

Recall that E_{tot} depend on a only through $U_1(x, a)$ and the latter depends on a only when $x \in \Omega$.

Because the particles can migrate during the time dt , and because the energy E should be updated upon the migration of particles, we do not expect the relation $dE = d'Q^{(\text{in})} + d'W$ (wrong). In order to compare dE and $d'Q^{(\text{in})} + d'W$, we use, in addition to the Langevin equation (4.61), the following identity, valid for any functions $f(x, a)$ and $\theta(x)$:

$$d[f(x, a)\theta(x)] \equiv \left[\frac{\partial f(x, a)}{\partial a} da + \frac{\partial f(x, a)}{\partial x} dx \right] \theta(x) + f(x, a)d\theta(x). \quad (4.70)$$

We then find the law of energy balance for the open system [39]:

$$dE = d'W + d'Q^{(\text{in})} + d'Q^{(\text{mig})} + d'Q_{\partial\Omega}. \quad (4.71)$$

Below, we will briefly describe the additional terms, $d'Q^{(\text{mig})} + d'Q_{\partial\Omega}$.⁴³ We used the notation “ Q ” for these terms because these energies are not directly controlled by the external system.

$d'Q^{(\text{mig})}$: *Heat due to the migration of particles.* This term accounts for the energy caused by the migration of particles. In the identity (4.70), this energy comes from the last term on the right-hand side. This energy is as follows:

$$dQ^{(\text{mig})} \equiv \sum_{j=1}^N U_1(x_j, a)d\theta_\Omega^{(1)}(x_j) + \sum_{j=1}^N \sum_{k=j+1}^N U_2(x_j, x_k)d\theta_\Omega^{(2)}(x_j, x_k) + \dots \quad (4.72)$$

⁴³ For the details, see [39].

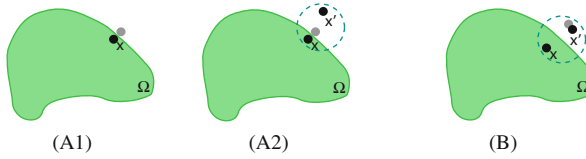


Fig. 4.13 The first (A1) and second (A2) terms on the *right-hand side* of (4.72) for $dQ_{\partial\Omega}^{(\text{mig})}$, and the term (4.73) for $dQ_{\partial\Omega}$ (B). These terms appear when a particle changes its position from the gray disc to its adjacent black disc in each figure

Figure 4.13 (A1) and (A2) illustrates the first and second terms, respectively. In (4.72), $d\theta_{\Omega}^{(p)}(x_{j_1}, \dots, x_{j_n})$ takes nonzero value when, during the infinitesimal time dt , a particular p -particle cluster comes to participate in the system ($d\theta_{\Omega}^{(p)} = 1$) or ceases to belong to the system ($d\theta_{\Omega}^{(p)} = -1$).

$d'Q_{\partial\Omega}$: Heat due to the interaction with the particles just outside the boundary. As illustrated in Fig. 4.13 (B), the system's energy changes also by the displacement of those particles which are outside Ω but interacts with a particle (or particles) inside Ω . For example, the terms in $dQ_{\partial\Omega}$ attributed to the two-particle interaction are

$$\sum_{j=1}^N \sum_{k=j+1}^N \theta_{\Omega}^{(2)} \left(\frac{\partial U_2}{\partial x_j} dx_j + \frac{\partial U_2}{\partial x_k} dx_k \right) - \sum_{j=1}^N \theta_{\Omega}^{(1)}(x_j) \sum_{k=1}^{N(k \neq j)} \theta_{\Omega}^{(2)} \frac{\partial U_2}{\partial x_j} dx_j, \quad (4.73)$$

where $U_2 \equiv U_2(x_j, x_k)$ and $\theta_{\Omega}^{(2)} \equiv \theta_{\Omega}^{(2)}(x_j, x_k)$. Only those terms with j and k such that $x_j \in \Omega$ and $x_k \notin \Omega$ [or $x_k \notin \Omega$ and $x_j \in \Omega$] contribute and leave the terms, $(\partial U_2(x_j, x_k)/\partial x_k) dx_k$ [or $(\partial U_2(x_j, x_k)/\partial x_j) dx_j$]. General expression is more complicated but the principle is the same [39].

It is important to notice that, in the present level of description of open system, the chemical potential μ appears nowhere in the energy balance equation.⁴⁴ See (2.9) for comparison. The chemical potential, which reflects the density of particles, appears when we move from the scales where we can in principle follow the individual particle to the scales where we view the system through the external system. This is the subject of Sect. 5.2.1.4.

4.3 Discussion

4.3.1 Applicability of Stochastic Energetics to Different Forms of Langevin Equations

The method of stochastic energetics can be applied to different forms of Langevin equations. We mention three examples below. These will show how the basic

⁴⁴ For example, we do not say unconditionally such as “an electron carries the Fermi energy, ε_F , (=chemical potential of electrons) when it moves across a junction.”

framework is applied, i.e., the assignment of system and its environment, definition of heat, and the relation of energy balance.

Hydrodynamic fluctuations have become more and more accessible through the Brownian particle in a real fluid [40] or through a molecular dynamic simulation of fluid jet [41]. The fluid dynamic equation with spontaneous thermal noise is described by a Langevin equation for field. This subject is called fluctuating hydrodynamics and is developed by Landau and Lifshitz [42]. The energetic aspects associated with these fluctuation phenomena can be formulated along the principle described in Sect. 4.1. In Appendix A.4.7.1 we derive the formula of energy balance for the fluctuation hydrodynamics, with several simplifying restrictions.

The stochastic motion of suspended hard spheres has been described by the Langevin equation. In this Langevin equation, there is cross-coupling between the force on a sphere and the velocities of the other spheres, due to hydrodynamic interactions. In Appendix A.4.7.2 we derive the formula of energy balance for the suspension of hard spheres, based on the recent model equation by [43, 44].

Stochastic motion expressed by curvilinear coordinates, or the stochastic motion on a curved manifolds (surface, curve, etc.) are described by Langevin equations with multiplicative noises. That is, the amplitudes of thermal random force depend on the variable of the equation. In Appendix A.4.7.3 we derive the formula of energy balance for the Langevin equation on the manifold.

4.3.2 Applicability to Nonequilibrium Processes and Limitations of the Langevin Description

The Langevin equation has the microscopic basis of the projection technique (Sect. 1.2). But in order that its derivation and the Markov approximation justify the Langevin equation, the eliminated degrees of freedom, i.e., the thermal environment, should behave not far from the equilibrium fluctuations.

A question is how far we can extend the use of the Langevin equation beyond the equilibrium fluctuations. Can we study the transient or steady nonequilibrium phenomena, especially their energetics?

There are many examples where stochastic energetics are applied to the nonequilibrium phenomena, and their studies brought, in most cases, physically sound and interesting insights about the nonequilibrium phenomena. Below is an incomplete list of those studies:

- Theoretical analysis of the energetics of the ratchet models. (There are many papers and we refer only two reviews, [45, 46].)
- Theoretical demonstration of the fluctuation theorem about the heat [47, 48]
- Definition of pathwise entropy [48].
- Numerical analysis of the Feynman pawl and ratchet [26, 49].
- Experimental assessment of the energy balance.

1. Using optically trapped bead [6].
 2. Using the brass wire-held pendulum [9]
- A formulation of steady–state thermodynamics. [50, 51].
 - The violated fluctuation–dissipation relation in nonequilibrium steady states.
 1. The short-time limit of the discrepancy in the fluctuation–dissipation (FD) relation for the velocity in nonequilibrium steady state can be expressed in terms of the average heat flow to the thermal environment [52, 53].⁴⁵
 2. [54] extended the relation of [53] to the Langevin equations with memory. An elementary derivation of [53] is also found therein.
 3. [55] checked [53] using an optically driven colloid and also demonstrated [54] using a Brownian particle in a viscoelastic fluid [56].
 - Fluctuation–dissipation-like relation in nonequilibrium steady states [57]. The authors demonstrated that, if the velocity \dot{x} is replaced by the relative velocity with respect to the “mean velocity,” $v_s(x) \equiv j_s/p_s(x)$, the ratio of the steady-state probability flux j_s to the steady-state probability, $p_s(x)$.⁴⁶

Still, we could mention the case where Langevin modeling is *invalid* under nonequilibrium setup. Suppose that we measure the random force on a Brownian particle while we apply a constant force onto it, e.g., in the positive x direction. In this steady non–equilibrium state, the spatial symmetry of $\pm x$ is apparently broken. We, therefore, expect a broken symmetry in the statistics of the random force (i.e., the “skewness” in the force distribution). However, the thermal random force of the Langevin equation, $\xi(t)$, is always symmetric, by definition.

Therefore, we should be conscious about what type of nonequilibrium settings we can study using the Langevin equation and its stochastic energetics. There is no unique criterion for this point, partly because it depends on our exigence, partly because our knowledge of nonequilibrium phenomena is incomplete. Still the reflection on the above successful examples and also on the cases of abuse suggests the following (evident) thing:

This method works if the non-equilibrium is in the system, but it does not work if the non-equilibrium is at the interface between the system and the environment.

In fact, the absence of skewness in the random force mentioned above is apparently the latter case.

⁴⁵ For the Langevin equation without inertia, both the velocity response and the velocity correlation diverge in the short-time limit, $|t - t'| \downarrow 0$. But the difference remains finite.

⁴⁶ A drawback to this beautiful formula is that $v_s(x)$ is not a local observable as function of x and t .

4.3.3 Comments

Can we associate entropy with each trajectory?

Entropy and its production along a stochastic trajectory has been proposed to derive the “integral fluctuation theorem” [48]. This somehow contradictory notion, entropy vs. individual sample, is in fact well defined in the context of the path ensemble average. In this book we limit to discuss those observables which are determined or measured for an isolated realization.

Is it only the degrees of freedom that vary in an open system?

Open systems concern the creation and annihilation of some object. The open system that we describe in this book is a special and simple case because we have fixed the kind of objects that are created. More generally, the state of the object (and its energy, etc.), as well as its position, may also vary. For example, actin gel is generated and degraded within a cell. There, the newly created gel can vary its elastic moduli as well as its state of deformation. In other words, it is the *functions* which are inserted to or deleted from an open system. We discuss this point in Appendix A.4.8.

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