

Chapter 5

Work on the Mesoscopic Systems

The balance of energy in Chap. 4 has been heuristically introduced by an analogy to mechanics. We have interpreted work to thermal environments as heat, and energy balance took the form of the first law of thermodynamics. However, it was not clear if the structure of energetics on the scale of fluctuations adapts truly to that of thermodynamics. In this chapter we will scrutinize the work done through the change of the external parameter a . The thermodynamic relationship between work and thermodynamic functions will be found. In other words, this chapter deals with the “second law” of thermodynamics. The quotation mark “” is used because we always assume the equilibrium thermodynamic character of the thermal environment.

Before the introduction of stochastic energetics, even the balance of energy on the level of Langevin equation has not been truly realized and used in the studies of fluctuation phenomena. But what is more surprising would be that the Langevin equation can realize the reversible, or quasistatic, processes. From the microscopic viewpoint, the Markov approximation breaks the time-reversal symmetry of (pure) mechanical systems. From the standpoint of the system, however, the thermal environment does not cause by itself irreversibility. The work done is equal to the change of the Helmholtz free energy of the system in the limit of slow variation of the control parameter. This convergence occurs for *each* realization of the stochastic process.

The difference with macroscopic thermodynamics is the absence of the fourth law. We do not use the extensive property with respect to the system size. For the fluctuating system we should think over what is the external system and what is the external parameters.

Once quasistatic process is understood, we should study the processes with finite but slow change of control parameters. Such processes have their own importance because (i) the irreversible work (dissipation) and the slowness of the control obeys a complementarity relation and (ii) the relation between the external system and the system exhibits a parallelism with the relation between the system and the thermal environment.

When the external parameter is changed at a finite rate, the irreversible work is a random variable, and its average is shown to be nonnegative. The demonstration uses the Jarzynski nonequilibrium work relation (for continuous case) or the fluctuation theorem (for discrete case).

5.1 * Work Done by External System

What does the parameter “a” stands for?

In case that the potential energy function, $U(x, a)$, represents a “rigid container” (that is, $U = 0$ for $|x| < a$ and $U = \infty$, otherwise), the parameter a is the one that controls the *position* of the hard wall. If, however, $U(x, a)$ takes the form of $U_0(x) - ax$, then a is the parameter to control the uniform external *force* field applied to the state point, x . Thus a can represent either the position or the force, depending on the case.¹ In both cases, a is regarded to be a slow variable to characterize the state of an external system: In case of the rigid container, a is related to the position of the wall as a whole. In the case of the uniform field, a is related to the position of the source of the field.

$U(x, a)$ includes all the interaction energy between the system and the external system. Therefore, $-\partial U(x, a)/\partial a$ is the force which the system exerts on the external system. By the same token as in Sect. 4.1.1.2, the external system exerts the reaction force, $\partial U(x, a)/\partial a$, onto the system. The expression (4.6), that is, $d'W \equiv \frac{\partial U}{\partial a} \circ da$ is the product of this force with the “displacement,” da . It is naturally understood to be the work to the system.

Where is the boundary between the system and the external system?

We do not describe the dynamics of the external system. It implies the hypothesis that the external system is not influenced by the system’s state and its dynamics.

In reality, however, it is very difficult to impose a fixed position of a rigid wall: first of all, there does not exist microscopically rigid container, and the container is also subject to thermal fluctuations. In order to take into account the fluctuation of the wall surface, one may regard the materials composing the wall surface as a part of a new enlarged system. Then the question is where we separate the system and the external system and how we define a (see Sects. 5.2.3.3 below). To the author’s knowledge, no systematic argument is developed about the condition of the external control parameter.

We deal with the cases where x represents a very few, typically a single degree of freedom. We assume that stable control parameter(s) a can be found. Such simplifications allow us to concentrate on the principal things. We must, however, remember all the above mentioned ambiguities when we consider a modeling of experimental setups.

What enables the comparison between different equilibrium states?

If the parameter a is fixed, the system visits its different states so that the cumulated residence time distribution approaches asymptotically the canonical equilibrium dis-

¹ Microscopically, the interaction with the rigid wall is also due to the force field by the wall onto the system’s variable.

tribution at a given temperature T and at the fixed value of a . For this system, those equilibrium states specified by other values of a have not particular meaning.² It is the external system and its controllability against the system that define the *process* from one equilibrium to the other one. It is the force $\partial U/\partial a$ that tells which equilibrium state is preferred by the system among the candidates parameterized by a .

Remarks

- (1) We have excluded direct interactions between the external system and the thermal environment.

Therefore, in $\partial U/\partial a$ the potential energy U can always be replaced by the total energy U^{tot} of the system *plus* environments. When we apply the framework to an experimental setup, the above point should be verified. For example, if we apply an electric field to a protein motor, the influence of the field on the surrounding water as thermal environment is not a priori counted in the original formalism of stochastic energetics.

- (2) Keeping the value of a constant is in general not equivalent to keeping constant the force on the system, $-\partial U(x, a)/\partial x$.

The only exception is if $U(x, a)$ can be written in the form of $U_0(x) - \phi(a) x$. Otherwise, keeping $\partial U(x, a)/\partial x$ constant needs the adaptation of $a(t)$. Such a feedback control from $\hat{x}(t)$ to $a(t)$ introduces a correlation between the protocol of $a(t)$ and the particular realization.³

- (3) Force, $\partial U(x, a)/\partial a$, depends on the resolution of a .

For example, if we added small “details” $u(a) = \epsilon \sin(\frac{a}{\epsilon})$ to $U(x, a)$, the resulting force would be changed by $\cos(\frac{a}{\epsilon})$.⁴

5.2 Work Under Infinitely Slow Variation of Parameters

5.2.1 The Quasistatic Work of a Single Trajectory Leads to a Pertinent Free Energy and Is, Therefore, Reversible

5.2.1.1 * Simple Example

Let us consider a Brownian particle trapped by a harmonic potential, $U(x, a) = a x^2/2$, see Fig. 5.1 (left). The external system controls the “spring” constant, a . For example, a laser tweezer can trap a Brownian particle, and its light intensity can be controlled, see Fig. 5.1 (right). Neglecting the inertia effect, the Langevin equation for the Brownian particle is written as follows:

² The system does not know what boundary conditions are variable and what others are not.

³ cf. the nanomachine to absorb the heat (Sects. 4.2.1.2).

⁴ cf. the coarse graining about x , Sects. 1.3.2.2.

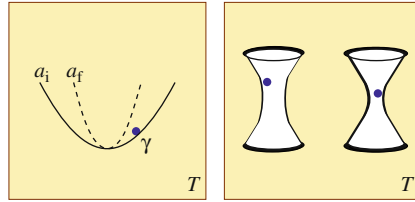


Fig. 5.1 (Left) Brownian particle (thick dot) in thermal environment (temperature T) is trapped in a harmonic potential (thick curves). The external system changes the profile of this potential. (Right) Trapping of Brownian particle under laser tweezer. The focusing controls the profile of trapping potential

$$-\frac{\partial U(x, a)}{\partial x} + \left[-\gamma \frac{dx}{dt} + \xi(t) \right] = 0, \quad (5.1)$$

where $\xi(t)$ is the Gaussian white random noise with zero mean and $\langle \xi(t)\xi(t') \rangle = 2\gamma k_B T \delta(t - t')$.

We will calculate the work done to change a from a_i to a_f taking very long operation time, τ_{op} . A similar model has been considered in Sects. 4.2.1.2. But here we do *without* the ensemble averages over realizations. The work W to change the parameter $a(t)$ from a_i to a_f is

$$W = \int_{a(0)=a_i}^{a(\tau_{\text{op}})=a_f} \frac{\partial U(x(t), a)}{\partial a} da(t) = \frac{1}{2} \int_{a(0)=a_i}^{a(\tau_{\text{op}})=a_f} x(t)^2 da(t). \quad (5.2)$$

In the above, the value of W is evaluated with a particular realization of $x(t)$ obeying the Langevin equation (5.1). Therefore, W is a random variable. We will see that, in the limit of $\tau_{\text{op}} \rightarrow \infty$, the random variable W converges to a single value which depends only on a_i and a_f , not the protocol of $a(t)$.

We formulate the limit of slow process as in Sects. 1.3.3.2. That is, first we define a protocol $\tilde{a}(s)$ that takes unit time, i.e., $\tilde{a}(0) = a_i$ and $\tilde{a}(1) = a_f$. And then we “expand” this protocol to the time τ_{op} by $a(t) \equiv \tilde{a}(\frac{t}{\tau_{\text{op}}})$.⁵ Using this representation of the protocol, the last integral of (5.2) is then written as

$$\begin{aligned} W &= \frac{1}{2} \int_0^1 x(\tau_{\text{op}} s)^2 \frac{d\tilde{a}(s)}{ds} ds \\ &= \int_{s=0}^{s=1} \frac{1}{\tilde{a}(s)} \frac{d\tilde{a}(s)}{ds} ds \times \frac{1}{\tau_{\text{op}} ds} \frac{\tilde{a}(s) x(\tau_{\text{op}} s)^2}{2} d(\tau_{\text{op}} s). \end{aligned} \quad (5.3)$$

We interpret the second line on the right-hand side as follows: if τ_{op} is large enough, we can imbed a very long history of $x(t)$ in the small element ds for which $\tilde{a}(s)$ scarcely changes. More precisely, we compare τ_{op} with the characteristic

⁵ $\tilde{a}(s)$ must be a continuous function of s .

timescale of (5.1), i.e., $\gamma/\min(a)$. If $\tau_{\text{op}}ds$ is much larger than this timescale, i.e., $\mathcal{N} \equiv \tau_{\text{op}}ds/(\gamma/\min(a)) \gg 1$, then $x(\tau_{\text{op}}s)$ in the integrand experiences large number ($\sim \mathcal{N}$) of uncorrelated, or i.i.d., fluctuations. Then the underlined part of the integral in (5.3) is the longtime average of $ax(t)^2/2$ with a being virtually fixed.⁶ By the footnote below (1.105), this temporal average converges to its canonical average, $k_B T/2$. Therefore, we have

$$W \rightarrow \frac{k_B T}{2} \int_{s=0}^{s=1} \frac{d\tilde{a}(s)}{\tilde{a}(s)} = k_B T \ln \sqrt{\frac{a_f}{a_i}} \quad (\tau_{\text{op}} \rightarrow \infty). \quad (5.4)$$

For finite \mathcal{N} , the typical error is estimated to be $\sim \mathcal{N}^{-1/2}$ by the central limit theorem (see Sects. 1.1.2.3).⁷ The result (5.4) is instructive for two reasons:

1. The result is definite. Although $x(t)$ varies temporally and differs from one realization to another, the work W takes asymptotically the same value.
2. The result corresponds to the statistical mechanical result. In the Gibbs' statistical mechanics, the Helmholtz free energy $F(a, \beta)$ ($\beta \equiv 1/k_B T$) of the present system is

$$F(a, \beta) = -k_B T \ln \frac{1}{\sqrt{a}} + (\text{terms independent of } a). \quad (5.5)$$

The work W obtained above is equal to the difference of this free energy, $F(a_f, \beta) - F(a_i, \beta)$. This correspondence is what we expect for any quasistatic thermodynamic process.

Gibbs statistical mechanics considers the ensemble of realizations. Any results from that framework is, therefore, the statistical average over the ensemble. The approach of the Fokker–Planck equation also yields results about the ensemble of realizations. The above analysis, however, dealt with only a single realization. For $\mathcal{N} \rightarrow \infty$ the convergence is of probability 1 due to the property of *self-averaging* for slow process. In this sense, the thermodynamic structure appeared due to the (strong) law of large numbers (of realizations).⁸

5.2.1.2 * General Theory

When a system is in contact with a single thermal environment of temperature T , the work W done by the external system on the system is given by

⁶ $(\tau_{\text{op}}ds)^{-1} A(s, \tau_{\text{op}}s) d(\tau_{\text{op}}s)$ is approximated by $(\tau_{\text{op}}ds)^{-1} \int_{\tau_{\text{op}}s}^{\tau_{\text{op}}s+\tau_{\text{op}}ds} A(s, T) dT$, and the last expression is then approximated by the “long” time average about T . This approach is called the *method of multiple scale*. See, for example, Chap. 6 of [1].

⁷ This argument owes to C. Jarzynski in the context of his analysis of ergodic adiabatic invariant [2, 3].

⁸ Y. Oono, private communication.

$$W = \int_{a(0)=a_i}^{a(\tau_{\text{op}})=a_f} \left. \frac{\partial U(x, a)}{\partial a} \right|_{(x,a)=(x(t),a(t))} da(t). \quad (5.6)$$

We will show that, in the limit of slow variation of the operation ($\tau_{\text{op}} \rightarrow \infty$), the work W converges to the difference of the Helmholtz free energy, ΔF , defined by

$$\Delta F \equiv F(a_f, \beta) - F(a_i, \beta), \quad e^{-\beta F(a, \beta)} \equiv \int e^{-\beta U(X, a)} dX. \quad (5.7)$$

Derivation : In Sects. 1.3.3.2 we have demonstrated that for the integral

$$\hat{\mathcal{I}} \equiv \int_{a(0)=a_i}^{a(\tau_{\text{op}})=a_f} \Phi(\hat{x}(t), a(t)) da(t) \quad (5.8)$$

converges to the following integral over the parameter a in the limit of slow variation of $a(t)$:

$$\hat{\mathcal{I}} \rightarrow \int_{a_i}^{a_f} \langle \Phi(\cdot, a) \rangle_{\text{eq}} da \quad (\tau_{\text{op}} \rightarrow \infty), \quad (5.9)$$

where $\langle \Phi(\cdot, a) \rangle_{\text{eq}}$ is defined in (1.109), that is, $\langle \Phi(\cdot, a) \rangle_{\text{eq}} \equiv \int \Phi(X, a) \mathcal{P}^{\text{eq}}(X, a; T) dX$, and $\mathcal{P}^{\text{eq}}(X, a; T)$ is the canonical probability distribution at $k_B T = \beta^{-1}$ with a given value of a

$$\mathcal{P}^{\text{eq}}(X, a; T) \equiv \frac{e^{-\beta U(X, a)}}{\int e^{-\beta U(X', a)} dX'}. \quad (5.10)$$

We show next that the limit in (5.9) is unique, independent of the protocol $\tilde{a}(s)$ between a_i and a_f . Applying the above general formula to $\Phi(X, a) = \partial U(x, a)/\partial a$, we have $\langle \partial U(x, a)/\partial a \rangle_{\text{eq}}$ in the integrand. This can be rewritten by using the so-called Ehrenfest formula:⁹

$$\left\langle \frac{\partial U(x, a)}{\partial a} \right\rangle_{\text{eq}} \equiv \int \frac{\partial U(x, a)}{\partial a} \mathcal{P}^{\text{eq}}(X, a; T) dX = \frac{\partial F(a, \beta)}{\partial a}. \quad (5.11)$$

By integrating the rightmost of (5.11) with respect to a , we have ΔF . (End.)

In summary, we have shown that the following relation is valid for any individual realization:

$$W \rightarrow \Delta F \quad (\tau_{\text{op}} \rightarrow \infty). \quad (5.12)$$

⁹ We can verify (5.11) by differentiating the normalization condition of the canonical distribution, $\int e^{\beta(F(a, \beta) - U(X, a))} dX = 1 \Rightarrow \int \frac{\partial}{\partial a} e^{\beta(F(a, \beta) - U(X, a))} dX = 0$.

5.2.1.3 Discrete Case

The work W due to the change of parameter $a(t)$ on this level of description has been given:¹⁰

$$W = \int_0^{\tau_{\text{op}}} \left\langle \left| \frac{dE(a(t))}{dt} \right| \psi_t \right\rangle dt = \int_{a(0)=a_i}^{a(\tau_{\text{op}})=a_f} \left\langle \left| \frac{dE(a(t))}{da} \right| \psi_t \right\rangle da(t). \quad (5.13)$$

In the limit of slow variation of $a(t)$, we can replace the integrand in the rightmost of (5.13) by the canonical average, $\langle dE(a)/da \rangle_{\text{eq}}$, thus

$$W \rightarrow \int_{a_i}^{a_f} \left\langle \frac{dE(a)}{da} \right\rangle_{\text{eq}} da \quad (\tau_{\text{op}} \rightarrow \infty). \quad (5.14)$$

For $\langle dE(a)/da \rangle_{\text{eq}}$ we use the Ehrenfest formula, $\langle dE(a)/da \rangle_{\text{eq}} = \partial F(a, \beta)/\partial a$.¹¹ In summary, we have the formula for any individual realization:

$$\begin{aligned} W - \Delta F &= \int_{a(0)=a_i}^{a(\tau_{\text{op}})=a_f} \left[\left\langle \left| \frac{dE(a(t))}{da} \right| \psi_t \right\rangle - \left\langle \frac{dE(a)}{da} \right\rangle_{\text{eq}} \Big|_{a=a(t)} \right] da(t) \\ &\rightarrow 0 \quad (\tau_{\text{op}} \rightarrow \infty). \end{aligned} \quad (5.15)$$

5.2.1.4 Quasistatic Process of Open System

We can immediately apply the result (5.12) to the entire system including the system and the “environment,” $\Omega \cup \Omega^c$. Using the expression of the work $d'W$, (4.69), we have

$$W \rightarrow \Delta F_{\text{tot}} \quad (\tau_{\text{op}} \rightarrow \infty), \quad (5.16)$$

where F_{tot} is the Helmholtz free energy of the entire system, defined by¹²

$$e^{-F_{\text{tot}}/k_{\text{B}}T} = \frac{1}{N_{\text{tot}}!} \int e^{-E_{\text{tot}}/k_{\text{B}}T} d^{N_{\text{tot}}}x, \quad (5.17)$$

where N_{tot} is the number of particles in the entire system, and the integral runs over the entire system for each particle.

¹⁰ See Sects. 3.3.1.3 and 4.1.2.6. We wrote W instead of $\Delta'W$ for the consistency of notations between (5.12) above and (5.15) below.

¹¹ We use $\sum_j e^{\beta(F(a, \beta) - E_j(a))} = 1 \Rightarrow \sum_j \frac{\partial}{\partial a} e^{\beta(F(a, \beta) - E_j(a))} = 0$.

¹² For the facility of calculation we put the factor $(N_{\text{tot}}!)^{-1}$ and render F_{tot} extensive. See below.

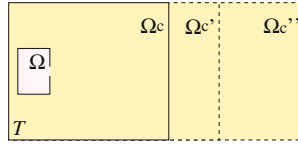


Fig. 5.2 An open system Ω and several “environments,” Ω^c , $\Omega^{c'}$, and $\Omega^{c''}$

We need to relate ΔF_{tot} to the thermodynamical quantity of open system. For this purpose we take the volume of the “environment,” $\|\Omega^c\|$, to infinity in F_{tot} , while keeping only the part which is relevant to the open system. See in Fig. 5.2. The result is

$$\lim_{\|\Omega^c\| \rightarrow \infty} \Delta F_{\text{tot}} = \Delta J. \quad (5.18)$$

Derivation: First we identify the volume specific free energy $f^c(T, \mu)$ by

$$f^c(T, \mu) = \lim_{\|\Omega^c\| \rightarrow \infty} \frac{F_{\text{tot}}}{\|\Omega^c\|}.$$

Then we define J by subtracting from F_{tot} the (asymptotic) free energy of the environment, $\|\Omega^c\| f^c(T, \mu)$:

$$J(a, t, \mu) \equiv \lim_{\|\Omega \cup \Omega^c\| \rightarrow \infty} [F_{\text{tot}} - \|\Omega^c\| f^c(T, \mu)]. \quad (5.19)$$

This $J(a, T, \mu)$ is the thermodynamic potential for the open system Ω (see Sect. 2.1.4). $J(a, T, \mu)$ represents the particle environment only through the temperature T and the chemical potential of the particle in the environment, μ (or the density of the particles in Ω^c). Since $f^c(T, \mu)$ characterizing the particle environment should not depend on the external parameter a , we arrive at the result (5.18). (*End.*)

In conclusion, the quasistatic work done on the open system for a particular realization of stochastic process is given by the change of the thermodynamic potential for the open system [4]:

$$W \rightarrow \Delta J \quad (\tau_{\text{op}} \rightarrow \infty). \quad (5.20)$$

In Appendix A.5.1 we recall a statistical mechanical derivation of J in (5.19) with simplifying assumptions. The result writes

$$e^{-J/k_B T} = \sum_{n=0}^{\infty} e^{-(F^{(n)} - \mu n)/k_B T}, \quad (5.21)$$

where $F^{(n)}$ is the Helmholtz free energy of the open system Ω when it contains n particles;

$$e^{-F^{(n)}/k_B T} \equiv \frac{1}{n!} \int_{(\Omega)} e^{-E_n/k_B T} d^n x. \quad (5.22)$$

The relations (5.16) and (5.18) are the key steps through which the chemical potential (in J) enters the energetics based on the Langevin equation.

5.2.1.5 Remark: Gibbs' Paradox and Extensivity

At the end of Sects. 3.3.2.4, we noticed that the combinatorial factor $N_A!$, etc., in the formula (3.53) appeared independently from the particle–wave duality of the quantum physics. This factor came simply from the fact that we do not distinguish any A molecule from other A molecules. In fact these combinatorial factors are independent of whether or not the molecules consist of isotope forms or have internal parameters of long memory *as far as* the molecular reaction $A + B \rightleftharpoons AB$ is not influenced by this variability. Also in (5.22) above, the factor $n!$ came out from purely combinatorial reason, not of quantum mechanics.

The so-called Gibbs' paradox is related to this combinatorial factor. This paradox says that

- (i) In order for the thermodynamic functions to be extensive, we need to divide the phase integrals like (5.22) by the combinatorial factor corresponding to the permutation of identical particles.
- (ii) Since this operation is not explained by classical mechanics, the factor is ascribed to the particle–wave duality of quantum mechanics.¹³

The resolution of the paradox is that

- (i) In the study of the thermodynamic *processes* in the classical regime, increasing *all* the materials by, for example, twice is not a thermodynamic process. It contradicts the conservation of mass–energy. Therefore, the *absolute* value of the thermodynamic functions are not observable, and its extensivity is merely a convenient choice. However, the extensivity is imposed on the differences of the thermodynamic observables.
- (ii) In quantum mechanics, the individuality of identical particles is lost upon collision due to the particle–wave duality. But also in classical mechanics, the individuality is lost when we describe the chemical reactions or the processes of open systems in terms of the number of each molecular species.

Thus the factor of $n!$ in (5.22) appeared without evoking quantum mechanics.

¹³ The duality asserts that the permutations among identical particles do not make new quantum states.

5.2.2 The Criterion of the Quasistatic Process Refers to the Force on the External System

We define quasistatic process by the limiting process that realizes the convergence of (5.12) or (5.15). In such processes, the work W does not depend on the protocol defined by $\tilde{a}(s)$ ($0 < s < 1$), whatever is the number of components of a .¹⁴

A quasistatic process is reversible or retractable in the sense that the process that retraces the same pathway in the parameter space costs no work. The work ΔF to go is exactly compensated by the work $(-\Delta F)$ to return.

If the control process makes a closed loop and returns to the initial point, i.e., those $\tilde{a}(s)$ satisfying $\tilde{a}(0) = \tilde{a}(1)$, the quasistatic work is 0.¹⁵ Whether or not such a process leaves any change after closure of the trajectory is a subtle question. We will discuss it later (5.2.3.4). That the Langevin equation derived by using the Markov approximation can realize the reversible process emphasizes the importance of being conscious about the scale of description.

In macroscopic thermodynamics, the quasistatic process is characterized such that “at each instant of time the system realizes the equilibrium state under a given constraints.” However, the equilibrium state is defined as “the state which is realized in the system after infinitely long time under a given constraints.” These two statements are incompatible unless we define the limiting procedures unambiguously. But macroscopic thermodynamics does not describe the temporal changes.

On the level of Langevin equation, one could consider the closeness to the quasistatic process by comparing the probability density $\mathcal{P}(X, a(t), t)$ obtained through the Fokker–Planck equation with the canonical equilibrium distribution, $\mathcal{P}^{\text{eq}}(X, a; T)$, by using a suitable measure such as the Kullback–Leibler distance, $D(\mathcal{P}||\mathcal{P}^{\text{eq}})$ (see (1.81)). However, the general theory in the previous section gives natural and operational criterion of the quasistatic process: We note that the difference $W - \Delta F$ in the continuous process is

$$W - \Delta F = \int_{a(0)=a_i}^{a(\tau_{\text{op}})=a_f} \left[\left. \frac{\partial U(x(t), a)}{\partial a} \right|_{a=a(t)} - \left\langle \frac{\partial U(x, a)}{\partial a} \right\rangle_{\text{eq}} \right] da(t). \quad (5.23)$$

Thus we measure the approach to the quasistatic process by the effect of the replacement of force by its instantaneous equilibrium expectation value *in the integral* (5.23). That is

$$\left. \frac{\partial U(x(t), a)}{\partial a} \right|_{a=a(t)} \simeq \left\langle \frac{\partial U(x, a)}{\partial a} \right\rangle_{\text{eq}} \Big|_{a=a(t)} \quad (5.24)$$

¹⁴ By “protocol” we distinguish, for example, $\tilde{a}(s)$ from $\tilde{a}(s^2)$.

¹⁵ Precisely speaking, F and the parameter space should be such that the closed loop can be continuously shrunk to a point passing only the quasistatic processes.

or

$$\left\langle \left| \frac{dE(a)}{da} \right| \psi_t \right\rangle \Big|_{a=a(t)} \simeq \left\langle \frac{dE(a)}{da} \right\rangle_{\text{eq}} \Big|_{a=a(t)}, \quad (5.25)$$

in the integral by $a(t)$. This is a much more specific criterion than the comparison of the probability densities. The quantity $\frac{\partial U(x(t), a)}{\partial a} \Big|_{a=a(t)} - \left\langle \frac{\partial U(x, a)}{\partial a} \right\rangle_{\text{eq}} \Big|_{a=a(t)}$ will appear again in the context of asymptotic estimation of the “error,” $W - \Delta F$ for the nonquasistatic process (Sects. 5.3.1).

5.2.3 Quasistatic Work Reflects Some Aspects of the System’s State, but Not All

5.2.3.1 Simple Case 1: Deformation of an Ideal Chain

In the aforementioned example (Sects. 4.1.2.3 esp. Fig. 4.3), we can calculate the quasistatic work to stretch the chain. The Helmholtz free energy of the ideal chain is $F(a, \beta) = -k_B T \log Z(a)$, where $Z(a)$ is proportional to the number of configurations of the chains having the end-to-end distance a . Therefore, the work to displace the end point a from a_i to a_f is

$$W = \Delta F = k_B T \log \frac{Z(a_i)}{Z(a_f)} \quad (\text{quasistatic}).$$

As $Z(a)$ is decreasing function of $|a|$ (i.e., the chain is less flexible for large $|a|$), the external system does a positive work W to stretch the chain. According to the law of energy balance, $dE = d'W + d'Q$, this work is immediately released to the thermal environment ($-d'Q = d'W$), because the energy of the ideal chain is constant.

5.2.3.2 Simple Case 2: Van der Waals Forces

When two molecules are placed at the distance r , the induced and/or permanent dipoles of these molecules undergo thermal and quantum fluctuations. Because of long-range electrostatic interactions the fluctuations of the two molecules are correlated and, therefore, depend on the distance r . Interaction is attractive and its free energy $F_{VdW}(r, \beta)$ ($\beta = 1/k_B T$) writes $F(r, \beta) \sim -c(T)r^{-6}$ at (moderately) large distance, where $c(T)$ is a function of temperature and other molecular parameters.

On the level of description of fluctuations, the interaction force between the molecules fluctuates in time. The free energy $F(r, \beta)$ is measured by the time-averaged force on the external system. If we change the distance r from r_i to r_f quasistatically in a particular realization, the work needed W is

$$W = c(T) \left[\frac{1}{r_i^6} - \frac{1}{r_f^6} \right] \quad (\text{quasistatic}).$$

5.2.3.3 Single Molecule Ideal Gas

We will consider a single (Newtonian) particle confined in a 1D cylinder and piston at temperature T . A naive question is whether the equation of state of the ideal gas, $PV = k_B T$, with $N = 1$ molecule between the pressure P and the 1D volume V holds. But the primary question is how we can set the problem up and how we can define the pressure and volume.

System: Let us consider a model schematized in Fig. 5.3. The molecule (filled disc) moves ballistically and collides elastically with the walls of the cylinder and piston (the T-shaped tip) and otherwise moves ballistically. The position x and the momentum p of the molecule obeys the following Newton equation:

$$\frac{dx}{dt} = \frac{p}{m}, \quad \frac{dp}{dt} = -\frac{\partial U_{\text{pis}}}{\partial x} - \frac{\partial U_{\text{T}}}{\partial x}, \quad (5.26)$$

where m is the mass of the molecule, and $U_{\text{pis}}(x, x_{\text{pis}})$ stands for the interaction energy between the molecule and the piston tip. x_{pis} is the position of the piston tip. We will define $U_{\text{T}}(x, x_{\text{T}})$ below.

System–thermal environment interface: We introduce a thermal wall (left vertical wall of the chamber). This is mechanically coupled to the thermal environment. We assume the overdamped Langevin equation for the position x_{T} of the thermal wall:

$$0 = -\gamma \frac{dx_{\text{T}}}{dt} + \xi_{\text{T}}(t) - \frac{\partial U_{\text{T}}}{\partial x_{\text{T}}}, \quad (5.27)$$

where $\xi_{\text{T}}(t)$ is the white Gaussian random noise with zero mean and $\langle \xi_{\text{T}}(t) \xi_{\text{T}}(t') \rangle = 2\gamma k_B T \delta(t - t')$. $U_{\text{T}} = U_{\text{T}}(x, x_{\text{T}})$ represents the interaction energy between the

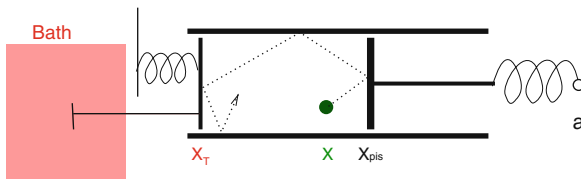


Fig. 5.3 Schematic setup of piston and cylinder system for a single particle. The particle (*thick dot*: position x) is confined within a volume (*central rectangle*) enclosed by (1) a thermal wall (*left vertical wall*: position x_{T}) which is linked to the thermal environment (*shaded rectangle* “bath”) and is supported by a fixed point (spring to the left of the thermal wall), (2) cylinder walls (*upper and lower horizontal walls*), and (3) “piston tip” (*right vertical wall*: position x_{pis}), which is connected to the controlled point (*open circle*: position a) through a coupling potential (*spring* between x_{pis} and a)

molecule and the thermal wall as well as the supporting potential energy of the thermal wall.

System–external system interface: We assume that the piston is just a microscopic tip. This tip is connected through a spring to the macroscopic apparatus (the right-most open circle at a). The position x_{pis} and momentum p_{pis} of the piston tip obey the Newton equation:

$$\frac{dx_{\text{pis}}}{dt} = \frac{p_{\text{pis}}}{m_{\text{pis}}}, \quad \frac{dp_{\text{pis}}}{dt} = -\frac{\partial U_{\text{pis}}}{\partial x_{\text{pis}}} - \frac{\partial U_{\text{el}}}{\partial x_{\text{pis}}}, \quad (5.28)$$

where m_{pis} is the mass of the piston tip. $U_{\text{el}} = U_{\text{el}}(x_{\text{pis}}, a)$ is the internal energy of the piston and depends only on $x_{\text{pis}} - a$. The energies, $U_{\text{T}}(x, x_{\text{T}})$ and $U_{\text{pis}}(x, x_{\text{pis}})$, are expected to behave like sharp repulsive walls, blowing up as $x - x_{\text{T}}$ or $x_{\text{pis}} - x$ decrease to 0, respectively.

Balance of energy and quasistatic work: The balance of energy is found to be

$$d\left(\frac{p^2}{2m} + \frac{p_{\text{pis}}^2}{2m_{\text{pis}}} + U_{\text{T}} + U_{\text{pis}} + U_{\text{el}}\right) = d'Q + d'W, \quad (5.29)$$

where

$$d'Q \equiv \left(-\gamma \frac{dx_{\text{T}}}{dt} + \xi_{\text{T}}(t)\right) \circ dx_{\text{T}}, \quad d'W \equiv \frac{\partial U_{\text{el}}}{\partial a} da. \quad (5.30)$$

According to the general theory of Sects. 5.2.1.2, the quasistatic work for the displacement of the macroscopic apparatus a is the change of the Helmholtz free energy, $F(a, \beta)$, where

$$e^{-\beta F(a, \beta)} = C(\beta) \int e^{-\beta[U_{\text{T}}(x, x_{\text{T}}) + U_{\text{pis}}(x, x_{\text{pis}}) + U_{\text{el}}(x_{\text{pis}}, a)]} dx dx_{\text{T}} dx_{\text{pis}}. \quad (5.31)$$

Here $C(\beta)$ is a factor independent of the external parameter, a .

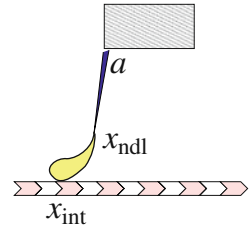
Thermodynamic pressure: On the other hand, we can define pressure by an analogy to macroscopic thermodynamics:

$$dW \equiv -P(a, \beta) da \quad (\text{quasistatic process}). \quad (5.32)$$

The pressure P thus defined is the time-averaged force that the macroscopic apparatus receives at a . Using the law $W = \Delta F$ for the quasistatic process, we can identify this pressure P with the thermodynamic pressure:

$$P = -\frac{\partial F(a, \beta)}{\partial a}. \quad (5.33)$$

Fig. 5.4 Force apparatus (position a) binds the protein motor head through a needle (position x_{ndl}). The motor interacts with filament (position x_{int})



Volume: It is not evident how a can be related to the “volume” of the chamber. Unless the repulsive walls in $U_T(x, x_T)$ and $U_{\text{pis}}(x, x_{\text{pis}})$ are infinitely steep (i.e., the rigid wall), the volume cannot be unambiguously defined. The ambiguity due to the finite gradient of the potential energies, $\partial U_T/\partial x$ and $\partial U_{\text{pis}}/\partial x$, is important when the system’s spatial extent, $x_{\text{pis}} - x_T$, is small. $a - \langle x_{\text{pis}} \rangle$ depends on a as well as temperature. Therefore, we cannot identify da with $d\langle x_{\text{pis}} \rangle$. That is, we cannot replace $dW = Pda$ by “ $dW = Pd\langle x_{\text{pis}} \rangle$.”

In summary, controlling displacement and controlling force for small systems are not equivalent. In statistical mechanics, the saddle-point method or Darwin–Fowler method assured that these two are equivalent. (See a related discussion in [5].)

Figure 5.3 was a toy model. But a somehow similar setup is used to measure the interaction between a single head of myosin (protein motor) and an actin filament, see Fig. 5.4. The motor–filament interaction occurs at x_{int} while the AFM apparatus controls the position a . The motor head is bound to the latter by a needle at x_{ndl} . If the position of x_{ndl} is optically measured, the result reflects both the motor–filament interaction and the thermal fluctuations of the motor and of the needle. An optical technique has been developed to suppress the thermal fluctuation of measuring devices (down to 5K!) [6]. The energetics of the feed-back-controlled system is discussed in [7].

5.2.3.4 Work-Free Transport of Heat and Particles

Suppose that the control parameter a has more than one component and that it is changed along a closed loop, $\hat{a}(0) = \hat{a}(1)$.¹⁶ If the process is quasistatic, the work is 0. But the system’s state can undergo a nontrivial change [8].

We consider the cyclic change of potential energy profile, $U(x, \hat{a})$, as shown in Fig. 5.5. We will regard the state point $x(t)$ as the position of a Brownian particle under the potential energy U . We impose a periodic boundary condition, i.e., the rightmost end (R) is continued to the leftmost end (L). Or, we assume that the system is open toward the reservoirs of particles in (L) and (R). In any case this quasistatic cycle transports particles from the left (L) to the right one (R) on the average. The calculus is given in Appendix A.5.2.

This transport without costing work indicates subtlety of the quasistatic process:

¹⁶ We use the scaled protocol $\tilde{a}(s)$ introduced in Sects. 5.2.2.

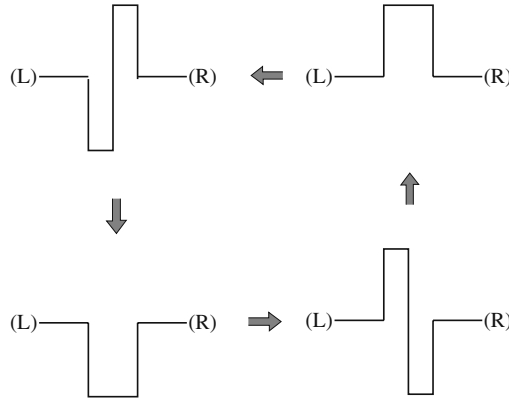


Fig. 5.5 Profile of potential $U(x, a)$ vs. x between the *left*-particle environment (L) to the *right* one (R). *Thick arrow* indicates the progress of the potential profile. (Figure adapted from Fig. 2 of [8])

- (i) Even in the quasistatic process, we cannot always approximate $P(x, t)$ of the Fokker–Planck equation by the equilibrium density, $P_{\text{eq}}(x, a; T)$. If we did it, the probability flux $J[P] \equiv -\frac{1}{\gamma} \left[\frac{\partial U}{\partial x} P + k_B T \frac{\partial P}{\partial x} \right]$ is always 0, and we would not have transport.¹⁷
- (ii) In the quasistatic limit, work has a potential function, i.e., the free energy $F(a, \beta)$. However, the probability flux J is not necessary the gradient of a potential function.

Remarks:

1. It is essential that the potential profile undergoes a cyclic change. If the profile change is a simple go-and-back along the same pathway, there is no net transport. The left–right asymmetry of the potential profile is a necessary but not sufficient condition.
2. Experimental demonstrations of such work-free transport must face the fluctuating part of the transport: in taking the quasistatic limit, the fluctuation in the number of transported particles per cycle will diverge as $\sqrt{t_{\text{cyc}}}$ with the time spent for a cycle, t_{cyc} . The prefactor of $\sqrt{t_{\text{cyc}}}$ can be decreased by raising the energy scales of the potential U . However, it then makes the condition for the quasistatic process more and more stringent, or it requires larger cycle time, t_{cyc} . More discussion will be given in Chap. 7.
3. The work-free quasistatic transport can be realized also in conventional thermodynamics by, for example, using the (macroscopic) Carnot cycle. In the formula of the reversible efficiency, $\eta_{\text{rev}} = (T_h - T_l)/T_h$ (see Sect. 2.3.3), the case $T_h = T_l$

¹⁷ This is general remark when we use linear nonequilibrium thermodynamics. The flux of energy or mass is caused by their small spatial gradients across the local regions in which the equilibrium is assumed.

assures the transport of heat between the two thermal environments of identical temperature without work $\eta_{\text{rev}} = 0$.

4. The work-free transport discussed above does not contradict the second law of thermodynamics: the heat or particles transported between the environments of the same temperature or chemical potential cannot be the source of later work.

5.3 Work Under Very Slow Variation of Parameters

We will analyze the processes taking a finite time τ_{op} from $a(0) = a_i$ to $a(\tau_{\text{op}}) = a_f$. The quantity of interest is the difference between the work W and the increment of the Helmholtz free energy, ΔF . We call this difference the *irreversible work*,

$$W_{\text{irr}} \equiv W - \Delta F. \quad (5.34)$$

See Fig. 5.6. For continuous process described by Langevin equation, it is written as (see (5.12))

$$W_{\text{irr}} = \int_{a_i}^{a_f} \left[\frac{\partial U(x(t), a(t))}{\partial a} - \left\langle \frac{\partial U(x, a(t))}{\partial a} \right\rangle_{\text{eq}} \right] da(t). \quad (5.35)$$

For finite τ_{op} , the irreversible work W_{irr} is a random variable, whose value varies from one realization to the other. In this section and next section we deal with the average of W_{irr} over the ensemble of paths, $\langle W_{\text{irr}} \rangle$.

5.3.1 The Average Irreversible Work and the Time Spent for the Work are Complementary

When the interval τ_{op} to change the parameter $a(t)$ is large, a general law of $\langle W_{\text{irr}} \rangle$ is [9]

- (1) The product, $\langle W_{\text{irr}} \rangle \tau_{\text{op}}$, is bounded below for $\tau_{\text{op}} \rightarrow \infty$.
- (2) This lower bound, which we denote by $S(a_i, a_f)$, is positive for $a_i \neq a_f$.

That is,

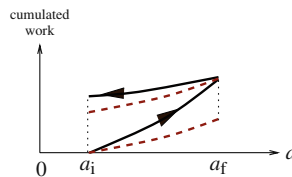


Fig. 5.6 Cumulated work (*solid curves*) along the change of parameter, $a_i \rightarrow a_f \rightarrow a_i$. The difference from the quasistatic work (*dashed curves*) gives the irreversible work, W_{irr}

$$\langle W_{\text{irr}} \rangle \tau_{\text{op}} \geq S(a_i, a_f) \quad (\tau_{\text{op}} \rightarrow \infty). \quad (5.36)$$

5.3.1.1 Origin of the Complementarity Relation

The above result comes out from the following expression of $\langle W_{\text{irr}} \rangle$. The details of calculation is given in Appendix. A.5.3.

$$\langle W_{\text{irr}} \rangle = \int_0^{\tau_{\text{op}}} \frac{da}{dt} \Lambda(a) \frac{da}{dt} dt + \mathcal{O}((\tau_{\text{op}})^{-2}). \quad (5.37)$$

Here the symmetric matrix¹⁸ $\Lambda(a)$ is defined by

$$\Lambda(a) \equiv \beta \left\langle \left\langle \left[\frac{\partial U}{\partial a} - \left\langle \frac{\partial U}{\partial a} \right\rangle_{\text{eq}} \right] \bullet (-g) \bullet \left[\frac{\partial U}{\partial a} - \left\langle \frac{\partial U}{\partial a} \right\rangle_{\text{eq}} \right] \right\rangle \right\rangle_{\text{eq}}, \quad (5.38)$$

with $\langle \langle A \bullet (-g) \bullet A \rangle \rangle_{\text{eq}}$, defined by¹⁹

$$\langle \langle A \bullet (-g) \bullet A \rangle \rangle_{\text{eq}} \equiv \iint P^{(\text{eq})}(x) A(x) (-g(x, x', a)) P^{(\text{eq})}(x') A(x') dx dx'. \quad (5.39)$$

The Green function $g(x, x'; a)$ is defined by

$$\frac{1}{\gamma} \frac{\partial}{\partial x} P^{(\text{eq})}(x) \frac{\partial}{\partial x} g(x, x'; a) = \delta(x - x'). \quad (5.40)$$

The integral on the right-hand side of (5.37) is always nonnegative.²⁰

To derive the complementarity relation (5.36) we will extract τ_{op} from (5.37): we represent $a(t)$ in (5.37) by the rescaled protocol, $\tilde{a}(s) \equiv a(s\tau_{\text{op}})$ with $0 \leq s \leq 1$ (see, Sects. 5.2.1.1). We then have the following asymptotic relation:

$$\langle W_{\text{irr}} \rangle \tau_{\text{op}} = \int_0^1 \frac{d\tilde{a}}{ds} \Lambda(a) \frac{d\tilde{a}}{ds} ds + \mathcal{O}((\tau_{\text{op}})^{-1}). \quad (5.41)$$

The first term on the right-hand side is positive and a functional of the rescaled protocol, $\tilde{a}(s)$. We can, therefore, define the lower bound of this integral as $S(a_i, a_f)$:

¹⁸ when a has more than one component.

¹⁹ $P^{(\text{eq})}(x) \equiv P^{(\text{eq})}(x, a; T)$ is the canonical equilibrium density for a given parameter a .

²⁰ The operator on the left-hand side of (5.40) is self-adjoint and, therefore, has real spectra. This operator is of the form of diffusion operator with an inhomogeneous diffusion constant, $D(x) = \frac{1}{\gamma} P^{(\text{eq})}(x, a)$. Since diffusion is a purely relaxing phenomena, the spectra of the above operator are all negative except of a single 0, corresponding to the constant eigenfunction. As the inverse operator of this diffusion operator, the Green function g , is a symmetric function with respect to x and x' . Moreover, the spectra of g are the inverse of the diffusion operator and, hence, all real and negative. From the last fact, $\Lambda(a)$ is positive definite.

$$S(a_i, a_f) \equiv \min_{\tilde{a}} \left[\int_0^1 \frac{d\tilde{a}}{ds} \Lambda(a) \frac{d\tilde{a}}{ds} ds \right], \quad (5.42)$$

where the minimum is sought for with all the continuous rescaled protocols $\tilde{a}(s)$ under the conditions, $\tilde{a}(0) = a_i$ and $\tilde{a}(1) = a_f$. Since $S(a_i, a_f)$ does not depend on the protocol between these end points, this is what we should have in (5.36).

5.3.1.2 Implication of the Complementarity Relation

1. An interpretation of the complementarity relation (5.36) is that the loss in the work becomes large if the operation is done in haste (i.e., with small τ_{op}). The *total* loss is proportional to the average rate of the change of the parameter.
2. Another interpretation is to regard $\langle W_{\text{irr}} \rangle \equiv \langle W \rangle - \Delta F$ as an error of the measurement of the thermodynamic information, ΔF .²¹ Then (5.36) is reminiscent of the complementarity relations of quantum mechanics between the energy and the time, $\Delta E \Delta t \geq \hbar/2$. Unlike the quantum mechanical principle of uncertainty, the ‘‘Planck constant’’ $S(a_i, a_f)$ depends on the system and the temperature. In particular, $S(a_i, a_f)$ depends linearly on γ through the Green function, g .
3. The formula (5.38) expresses $\Lambda(a)$ in terms of the correlation function of the ‘‘deviative force,’’ $\frac{\partial U}{\partial a} - \left\langle \frac{\partial U}{\partial a} \right\rangle_{\text{eq}}$. In the next section we will see that $\Lambda(a)$ plays the role of (linear) friction coefficient relating the rate of change of the parameter, da/dt , to its conjugate frictional force.
4. What type of the protocol $a(t)$ realizes the lower bound of the complementarity relation (5.36)? Given a total time τ_{op} , the expression (5.41) implies that we should avoid the route of a along which the friction coefficient $\Lambda(a)$ is large.²² If we cannot avoid such region, e.g., when a has only one component, we should spend more time in that region than elsewhere.

5.3.2 *For the External System the Weak Irreversible Work is Ascribed to a (Macro) Frictional Force

From the standpoint of the external system (‘‘Ext’’), the quasistatic work W is apparently stored in the system as the increment of the potential energy, ΔF (Sect. 2.2). There is a parallelism: the external system ‘‘Ext’’ does not see the degrees of freedom of the system on the one hand, and the system (‘‘Sys’’) does not see those degrees of freedom in the thermal environment on the other hand.²³

²¹ cf. The standard deviation of W_{irr} decreases with τ_{op} as $\mathcal{O}((\tau_{\text{op}})^{-1/2})$. See Sects. 5.2.1.1.

²² If $\Lambda(a)$ has anisotropy, the orientation of the route as well as its location should be optimized.

²³ Below is an example of how the world looks differently from different viewpoints: study of the fluctuations of cell motility is an ‘‘activity measurement’’ for biologists but ‘‘passive measure-

The study of the irreversible work W_{irr} now provides a further parallelism: $\Lambda(a)$ for the “Ext” corresponds to γ (friction coefficient) for “Sys.” In fact, if we combine the results of Sects. 5.2 and 5.3, the average work $\langle W \rangle$ done through a slow change of the parameter a is

$$\begin{aligned} \langle W \rangle &= \Delta F + \int_0^{\tau_{\text{op}}} \frac{da}{dt} \Lambda(a) \frac{da}{dt} dt \\ &= \int_{a_i}^{a_f} da(t) \left[\frac{\partial F}{\partial a} + \Lambda(a) \frac{da}{dt} \right], \end{aligned} \tag{5.43}$$

with an error of $\mathcal{O}((\tau_{\text{op}})^{-1})$. The second line of (5.43) allows the interpretation that “Ext” applies the force, $\frac{\partial F}{\partial a} + \Lambda(a) \frac{da}{dt}$, onto “Sys.” See Fig. 5.7. By the law of action–reaction, the external system receives the potential force, $-\frac{\partial F}{\partial a}$, and the friction force, $-\Lambda(a) \frac{da}{dt}$. Therefore, $\Lambda(a)$ is the friction constant for the parameter $a(t)$.

To take into account the deviation of W from $\langle W \rangle$, we introduce a noise term $\mathcal{E}(t)$ such that

$$W = \int_{a_i}^{a_f} da(t) \left[\frac{\partial F}{\partial a} + \Lambda(a) \frac{da}{dt} - \mathcal{E}(t) \right], \tag{5.44}$$

where the noise term behaves as²⁴ $\int_{a_i}^{a_f} \mathcal{E}(t) da(t) \sim \mathcal{O}((\tau_{\text{op}})^{-1/2})$. We can rewrite (5.44) as

$$\Delta F = \int_{a_i}^{a_f} \left[-\Lambda(a) \frac{da}{dt} + \mathcal{E}(t) \right] da(t) + W, \tag{5.45}$$

The last expression is similar to the law of energy balance for the Langevin equation, $dE = d'Q + d'W$. Schematically, the parallelism is

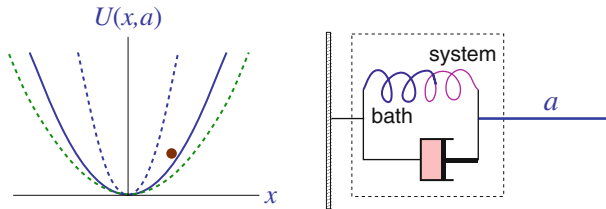


Fig. 5.7 (Left) A system and its control by an external parameter a . (Right) The system viewed from the external system as a black box

ment” for rheologists. Study of the response of cell against external perturbations is a “passive measurement” for biologists and “active measurement” for rheologists.

²⁴ cf. Footnote 21.

$$\begin{aligned}
\text{“Sys”} &\longleftrightarrow \text{“Ext”} \\
x &\longleftrightarrow a \\
U(x) &\longleftrightarrow F(a, \beta) + \text{“?”} \\
\gamma &\longleftrightarrow \Lambda(a) \\
\text{random thermal force: } \xi &\longleftrightarrow \text{system noise: } \mathcal{E} \\
\text{time resolution} &\longleftrightarrow \tau_{\text{op}}
\end{aligned}$$

In the above schema, we have not considered the dynamical evolution of the parameter $a(t)$. Therefore, “?” in the above is not specified. On the last row, the time resolution of the Langevin equation should be larger than the bath’s relaxation time on the one hand, and τ_{op} should be larger than the system’s relaxation time on the other hand. If the “time resolution” τ_{op} is too large, there is no noise \mathcal{E} . A question is whether there is a smooth limit from stochastic energetics to macroscopic thermodynamics when the size of the system goes to infinity. The parallelism across different scales can also be found between the system and its subsystem. This issue is addressed in the next chapter.

Note: Throughout this section we have assumed that the temperature is constant. The process including the time-dependent temperature, $T(t)$, has been studied in Matsuo (1999, unpublished paper). The author showed the Clausius’ inequality, $\oint d'Q/T \leq 0$, using stochastic energetics and statistical entropy.

5.4 Work Under the Change of Parameter at Arbitrary Rates

5.4.1 Jarzynski’s Nonequilibrium Work Relation Leads to the Nonnegativity of the Average Irreversible Work

The Jarzynski’s nonequilibrium work relation [10] is an important equation to assure the nonnegativity of the average irreversible work, $\langle W_{\text{irr}} \rangle$. If a Markov process with parameter(s) a has an equilibrium state for each value of a , and if the initial state obeys a canonical distribution, the irreversible work, W_{irr} , for the process between t_0 and t satisfies

$$1 = \langle e^{-\beta W_{\text{irr}}} \rangle_{\text{eq}}. \quad (5.46)$$

First it has been demonstrated for a thermally isolated system to which work is added mechanically. Later the relation turned out to be valid more generally. We show a brief demonstration using a form of the Feynman–Kac formula.²⁵ Those who are not interested in the mathematical details may skip to Sects. 5.4.1.2.

²⁵ The description of this section is based on [11] and the series of lectures by C. Jarzynski at Institut Henri Poincaré (Oct. 2007).

5.4.1.1 Jarzynski's Nonequilibrium Work Relation

Path Probability of Markov Process and Generating Operator

Suppose there is a Markov process, whose transition rate depends on a parameter $a_t \equiv a(t)$. We denote by $K(x, t|x_0, t_0)$ the conditional probability to find \hat{x}_t at x at the time t , given that it started from x_0 at the initial time, t_0 : $K(x, t_0|x_0, t_0) = \delta(x - x_0)$. Formally $K(x, t|x_0, t_0)$ can be written as

$$K(x, t|x_0, t_0) = \int_{(x_0, t_0)} P[X|x_0, t_0] \mathcal{D}X, \quad (5.47)$$

where $P[X|x_0, t_0]$ is the probability for the path X over the time interval $[t_0, t]$, and $\int_{(x_0, t_0)} \dots \mathcal{D}X$ denotes the path integral with the initial condition, (x_0, t_0) . We define the generating operator $\mathcal{L}(a_t)$ of $K(x, t|x_0, t_0)$ through

$$\frac{\partial K(x, t|x_0, t_0)}{\partial t} = \mathcal{L}(a_t)K(x, t|x_0, t_0). \quad (5.48)$$

Weighed Path Probability

Now we consider another Markov process whose transition probability, $G(x, t|x_0, t_0)$, is

$$G(x, t|x_0, t_0) = \int_{(x_0, t_0)} e^{\int_0^t w_t dt'} P[X|x_0, t_0] \mathcal{D}X, \quad (5.49)$$

where $P[X|x_0, t_0]$ is always the path probability for the path X governed by $\mathcal{L}(a_t)$. w_t can depend on x and on a . $G(x, t|x_0, t_0)$ satisfies $G(x, t_0|x_0, t_0) = \delta(x - x_0)$.

From (5.49) $G(x, t + dt|x', t)$ can be written as

$$\begin{aligned} G(x, t + dt|x', t) &\simeq (1 + w_t dt)K(x, t + dt|x', t) \\ &\simeq (1 + w_t dt)[1 + dt\mathcal{L}(a_t)]\delta(x - x'). \end{aligned} \quad (5.50)$$

To go to the second line (5.48) has been used. This formula will be used later.

Feynman–Kac Formula

A simple version of Feynman and Kac tells²⁶ that $G(x, t|x_0, t_0)$ obeys

$$\frac{\partial G}{\partial t} = (\mathcal{L}(a_t) + w_t)G. \quad (5.51)$$

That is, $G(x, t|x_0, t_0)$ is generated by $\mathcal{L}(a_t) + w_t$.

²⁶ In physicists' language, the general Feynman–Kac formula gives the (Feynman's) path integral representation of the solution of an SDE of Itô type. In the path integral, the "action" in the exponential is the sum of the kinetic part $\propto \gamma \dot{x}^2$ and the potential part $\propto U(x, a)$. To apply to the SDE of Stratonovich type, the action should be "corrected" by $\propto \partial^2 U / \partial x^2$.

The outline of the proof is as follows. As a Markov process $G(x, t + dt|x_0, 0)$ obeys the Chapman–Kolmogorov equation,²⁷ i.e.,

$$G(x, t + dt|x_0, 0) = \int G(x, t + dt|x', t)G(x', t|x_0, 0)dx'. \quad (5.52)$$

Substituting (5.50) into (5.52) and keeping up to the order of $\mathcal{O}(dt)$, we have $G(x, t + dt|x_0, t_0) \simeq (1 + w_t dt + dt\mathcal{L}(a_t))G(x, t|x_0, t_0)$. This means (5.51).²⁸ The $G(x, t|x_0, t_0)$ defined above is, therefore, the Green’s function of (5.51).

Evolution of $e^{-\beta\mathcal{H}_t}$

We apply the Feynman–Kac formula to the case where a “Hamiltonian” $\mathcal{H}_t \equiv \mathcal{H}(x, a_t)$ satisfies $\mathcal{L}(a_t)e^{-\beta\mathcal{H}_t} = 0$ for each t . We then define w_t by

$$w_t \equiv -\beta \frac{\partial \mathcal{H}(x, a_t)}{\partial a_t} \frac{da_t}{dt}. \quad (5.53)$$

From w_t , the work done to the system by an external system during the interval $[t_0, t]$ is given by

$$\beta W_{t,t_0} = - \int_{t_0}^t w_{t'} dt'. \quad (5.54)$$

Then $e^{-\beta\mathcal{H}_t}$ satisfies $\frac{\partial}{\partial t} e^{-\beta\mathcal{H}_t} = (\mathcal{L}(a_t) + w_t)e^{-\beta\mathcal{H}_t}$. In fact $\frac{\partial}{\partial t} e^{-\beta\mathcal{H}_t} = w_t e^{-\beta\mathcal{H}_t}$ is an identity, and we can add $0 = \mathcal{L}(a_t)e^{-\beta\mathcal{H}_t}$ to each side of this equation.

$e^{-\beta\mathcal{H}_t}$ as a solution of $\frac{\partial}{\partial t} e^{-\beta\mathcal{H}_t} = (\mathcal{L}(a_t) + w_t)e^{-\beta\mathcal{H}_t}$ can be expressed using the Green’s function $G(x, t|x_0, t_0)$:

$$e^{-\beta\mathcal{H}_t} = \int G(x, t|x_0, t_0)e^{-\beta\mathcal{H}_{t_0}} dx_0. \quad (5.55)$$

Jarzynski Nonequilibrium Work Relation

We divide both sides of (5.55) by $e^{-\beta F_0} \equiv \int e^{-\beta\mathcal{H}_{t_0}} dx_0$, and there substitute (5.49) and (5.54) for $G(x, t|x_0, t_0)$. The result is

²⁷ The Chapman–Kolmogorov equation means the following. The totality of the paths from (x_0, t_0) to (x, t) is given as the sum of those paths that pass through a “gate” at x_g at a fixed time t_g , then summed over all x_g . For the Markov process the probability weight for the paths from (x_0, t_0) to (x, t) via (x_g, t_g) can be factorized into those weights of each segments.

²⁸ If (5.51) is a Fokker–Planck equation, then (5.49) gives its formal explicit solution using $P[X|x_0, t_0]$. If (5.51) is a Schrödinger equation, (5.49) again gives its formal explicit solution in the same manner [12].

$$e^{\beta F_{t_0}} e^{-\beta \mathcal{H}_{t_0}} = \int \left[\int_{(x_0, t_0)} P[X|x_0, t_0] e^{-\beta W_{t, t_0}} \mathcal{D}X \right] e^{\beta(F_{t_0} - \mathcal{H}_{t_0})} dx_0. \quad (5.56)$$

Integration of (5.56) over x gives

$$e^{-\beta(F_t - F_{t_0})} = \langle e^{-\beta W_{t, t_0}} \rangle_{\text{eq}}, \quad (5.57)$$

where $e^{-\beta F_t} \equiv \int e^{-\beta \mathcal{H}_t} dx$, and $\langle \cdot \rangle_{\text{eq}}$ denotes the path average starting from the initial canonical probability density $e^{\beta(F_{t_0} - \mathcal{H}_{t_0})}$ at t_0 . Equation (5.57) is called Jarzynski nonequilibrium work relation. Note that $\mathcal{L}(a_t)$ can be either the Liouville operator²⁹ of conserved dynamical process or the Fokker–Planck operator of stochastic process.

The result (5.59) due to Jarzynski [10] is very general since it holds for any protocol of $a(t)$ with any finite time τ_{op} of the process. The Jarzynski nonequilibrium work relation can be used to measure ΔF from the protocol of $a(t)$ at finite rate of change:

$$\Delta F = -k_B T \ln \langle e^{-\beta W} \rangle_{\text{eq}}. \quad (5.58)$$

Here the average is taken over the paths starting from canonical equilibrium. This relation works very well for small systems [13, 14]. With increasing number of degrees of freedom, this method requires a lot of data for a good statistics. The reason is that very rare events for W is dominantly important in the average because of its exponential dependence, $\langle e^{-\beta W} \rangle$ [15].

The precision of “canonical” initial condition in the above is important: a counterexample has been demonstrated for the “microcanonical” initial condition [16]. We come back to the implication of this example later (see, the end of Sect. 7.1.3).

5.4.1.2 Nonnegativity of $\langle W_{\text{irr}} \rangle$

We will show the nonnegativity, $\langle W_{\text{irr}} \rangle \geq 0$, in condition that the process starts with the canonical equilibrium state with a given initial parameter, $a = a(t_0)$.

In (5.57), $F_t - F_{t_0}$ is ΔF and W_{t, t_0} is a work of a particular realization, W . We can, therefore, identify $W_{t, t_0} - (F_t - F_{t_0}) = W - \Delta F$ as the irreversible work, W_{irr} . Then (5.57) is

$$1 = \langle e^{-\beta W_{\text{irr}}} \rangle_{\text{eq}}. \quad (5.59)$$

We now apply Jensen’s inequality, $\langle e^{-z} \rangle \geq e^{-\langle z \rangle}$ to (5.59), where $\langle \cdot \rangle$ is average over any normalized probability density of z .³⁰ The result yields the inequality for $\langle W_{\text{irr}} \rangle_{\text{eq}}$:

²⁹ See the paragraph containing (A.10).

³⁰ Jensen’s inequality is the relation for any concaved function, $f(z)$, the function with $f''(z) \geq 0$. On the graph of $f(z)$ vs. z , the center of mass of the points $(z_1, f(z_1)), \dots, (z_n, f(z_n))$

$$\langle W_{\text{irr}} \rangle_{\text{eq}} \geq 0. \quad (5.60)$$

The inequality (5.60) includes the case of quasistatic process, where $\langle W_{\text{irr}} \rangle_{\text{eq}} = 0$. Recall that in Sects. 5.2.1.2 we obtained a stronger statement, $W_{\text{irr}} = 0$, for an *individual* quasistatic process.

Remark. There is a different definition of the average irreversible work, which is not directly related to the work measurement [17]. Using the probability density $P(x, t)$, we define the statistical entropy, $S \equiv - \int P \ln P dx$, and then the quasi-free energy, $\tilde{F} \equiv \langle U \rangle - TS$, where $\langle U \rangle = \int U P dx$. Then the following inequality is proven:

$$\frac{\langle d'W \rangle}{dt} - \frac{d\tilde{F}}{dt} = \int \gamma \frac{J[P]^2}{P} dx \geq 0, \quad (5.61)$$

where $J[P]$ is the probability current of the Fokker–Planck equation. The formula (5.61) has essentially the same content as the “H-theorem” (4.38) in Chap. 4.

5.4.2 The Fluctuation Theorem Leads to Jarzynski’s Nonequilibrium Work Relation for Discrete Process

We consider the stochastic processes characterized by the transition rates such as $w_{i \rightarrow j}(a)$ from a discrete state i to another state j , where a is an external control parameter (see Sects. 3.3.1.4 and 3.3.1.3). We assume that for each value of a , the transition probability admits the canonical equilibrium probability $P_i^{\text{eq}}(a)$ satisfying the detailed balance condition:

$$P_i^{\text{eq}}(a)w_{i \rightarrow j}(a) = P_j^{\text{eq}}(a)w_{j \rightarrow i}(a). \quad (5.62)$$

The so-called (a version of) fluctuation theorem (FT) or Crook’s relation for the irreversible work, W_{irr} , is [18, 19].

$$\frac{P_R(-W_{\text{irr}})}{P_R(W_{\text{irr}})} = e^{-\beta W_{\text{irr}}}, \quad (5.63)$$

where $P_R(W_{\text{irr}})$ is the probability density for W_{irr} . Integration of $e^{-W_{\text{irr}}} P_R(W_{\text{irr}})$ gives the average, $\langle e^{-W_{\text{irr}}} \rangle$, while the integration of $P_R(-W_{\text{irr}})$ gives unity. Therefore, the Jarzynski nonequilibrium work relation for the discrete process is derived:

$$\langle e^{-\beta W_{\text{irr}}} \rangle_{\text{eq}} = 1. \quad (5.64)$$

Finally the nonnegativity of the average irreversible work, $\langle W_{\text{irr}} \rangle_{\text{eq}} \geq 0$, is derived.

(some can be redundant) is always found above this graph. Especially this center of mass, $(\frac{1}{n} \sum_{i=1}^n z_i, \frac{1}{n} \sum_{i=1}^n f(z_i))$, is vertically above $(\frac{1}{n} \sum_{i=1}^n z_i, f(\frac{1}{n} \sum_{i=1}^n z_i))$.

In Appendix A.5.4 we sketch the derivation of the fluctuation theorem. Jarzynski nonequilibrium work relation and the fluctuation theorem have emerged in the same epoch as the emergence of stochastic energetics. In addition to those papers cited above, we refer to the other essential papers that initiated the approach described in this section [20–24, 18, 25]. There are preceding studies such as Bochkov and Kuzovlev [26–29] (see a commentary by [30]) and Kawasaki and Gunton [31]³¹ in the 1970’s. Comprehensive textbooks on these subjects are to be written by the original contributors. In this book we mentioned only briefly the outline of some demonstrations.

5.5 Discussion

5.5.1 How Fast Can the External Parameter Be Changed?

In Sect. 5.4, no constraints has been put on the maximum rate of the parameter change, $da(t)/dt$. There are situations where a very large value of $da(t)/dt$ is considered.

One case is the optimal control problem. The control protocol with the least cost can have discontinuities in $a(t)$ at the initial and final times.³² When the inertia is neglected, the effect of the discontinuity of $a(t)$ on the eliminated momentum should be carefully analyzed (cf. the Büttiker and Landauer ratchet Sects. 4.2.2.2).

The other case is the numerical discretization. When we simulate a Langevin equation with time-dependent parameter $a(t)$, we introduce discontinuity in $a(t)$ through the temporal discretization and the cutoff error of $a(t)$. The actual protocol $a(t)$ includes very small but very frequent jumps. If the result of stochastic energetics were to be sensitive to the limit of fine discretization, all the numerical calculations and the modeling of experiments for fluctuating phenomena would be dubious. Fortunately, in most cases the energetics is robust against this limit, though we cannot yet define rigorously the general condition of validity.

Let us take as example a Brownian particle (position: $x(t)$) moving in a harmonic potential. The center of the potential is $a(t)$ and the “spring” constant is K . The Langevin equation is

$$-\gamma \frac{dx}{dt} + \xi(t) - K[x - a(t)] = 0. \quad (5.65)$$

The general solution for $\langle x(t) \rangle$ of (5.65) is $\langle x(t) \rangle = a(t) + e^{-Kt/\gamma}(a_i - a(t)) + (K/\gamma) \int_0^t e^{-Ks/\gamma}(a(t-s) - a(t))ds$. We compare the two protocols: (i) a smooth linear protocol $a(t) = a_i + V_a t$ with V_a constant and (ii) stepwise protocol with the

³¹ S.I. Sasa brought me this link.

³² The discontinuity is related to the intrinsic nonlocal characteristic of the optimization problem. See [32, 33]. This discontinuity modifies the minimum of the average irreversibility $\langle W_{\text{irr}} \rangle$. But the effect on the complementarity relation (Sects. 5.3.1) is a higher order correction in $(\tau_{\text{op}})^{-1}$.

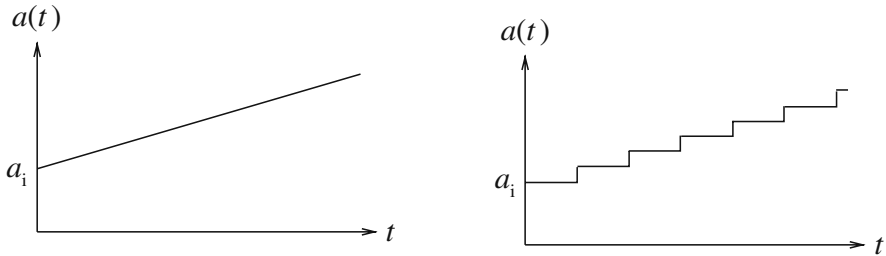


Fig. 5.8 (Left) Smooth linear protocol $a(t) = a_i + V_a t$ and (Right) stepwise protocol $a(t) = a_i + \delta a [V_a t / \delta a]$

same average rate, $a(t) = a_i + \delta a [V_a t / \delta a]$, where $[z]$ denotes the integer part of $z (\leq 0)$. See Fig. 5.8. Using the above solution, the average work per unit time is (i) γV_a^2 and (ii) $\bar{W} = V_a^2 (K \delta t / 2) \coth(\delta K t / (2\gamma))$ with $\delta t = \delta a / V_a$. The second \bar{W} converges smoothly to the first in the limit of the fine steps $\delta t \rightarrow 0$.

5.5.2 Can We Change a Parameter Slowly Enough for the Quasistatic Process?

The answer is no. We will show in Chap. 7 that (i) there are cases where the quasistatic process is intrinsically impossible and (ii) but such nonquasistatic processes do not necessarily cause large irreversible work. The more important consequence of these processes is that the external system loses information and controllability of the system's state.

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