Stochastic Energetics

K Sekimoto LNP 799 (Springer 2010)

Part I Basic
1. Langevin equations

7   Characteristic function

$$\Phi_y(\phi) = \int dy\, e^{i\phi y} p(y). \tag{0.0.1}$$

From this we get (if g is holomorphic along the real axis)

$$\langle g(y) \rangle = g(-id/d\phi)\Phi_y(\phi)|_{\phi=0} \tag{0.0.2}$$

because $\langle y^n \rangle = (-id/d\phi)^n \Phi_y(\phi)|_{\phi=0}$.

    If y belongs to $N(0,\sigma^2)$, we have Novikov's theorem

$$\langle y f(y) \rangle = \langle y^2 \rangle \langle f'(y) \rangle. \tag{0.0.3}$$

18   Langevin equation

$$\frac{dp}{dt} = -\gamma \frac{p}{m} + \xi(t) \tag{0.0.4}$$

with

$$\langle \xi(t)\xi(s) \rangle = 2b\delta(t-s). \tag{0.0.5}$$

19   Notice that the equation is not Galilean invariant: $p \to p - mV$, because the medium is not translated.

Einstein relation:

The average of the kinetic energy is

$$\overline{\frac{p^2}{2m}} = \lim_{t\to\infty} \frac{1}{t} \int_0^t dt\, \frac{p(t)^2}{2m} \equiv \langle p^2/2m \rangle_t \tag{0.0.6}$$

From (0.0.4)

$$p(t) = p_0 e^{-t(\gamma/m)} + \int_0^t ds\, e^{-(\gamma/m)(t-s)}\xi(s) = p_0 e^{-t(\gamma/m)} + \int_0^t ds\, e^{-(\gamma/m)s}\xi(t-s). \tag{0.0.7}$$

Therefore,

$$\frac{p(t)^2}{2m} = \frac{p_0^2 e^{-2t(\gamma/m)}}{2m} + \frac{1}{2m} \int_0^t ds \int_0^t ds'\, e^{-(\gamma/m)(s+s')}\xi(t-s)\xi(t-s') \tag{0.0.8}$$

Time averaging this, we get

$$\left\langle \frac{p(t)^2}{2m} \right\rangle_t = \lim_{t\to\infty} \int_0^t ds \int_0^t ds'\, e^{-(\gamma/m)(s+s')} \langle \xi(t-s)\xi(t-s') \rangle_t \tag{0.0.9}$$

20   Thanks to the law of large numbers, $\langle \xi(t-s)\xi(t-s') \rangle_t = \langle \xi(t-s)\xi(t-s') \rangle = 2b\,\delta(s-s')$, so

$$\left\langle \frac{p(t)^2}{2m} \right\rangle_t = \lim_{t\to\infty} \frac{1}{2m} \int_0^t ds \int_0^t ds' \, e^{-(\gamma/m)(s+s')} 2b\,\delta(s-s') = \frac{b}{m} \int_0^\infty ds\, e^{-(2\gamma/m)s} = \frac{b}{2\gamma} = \frac{1}{2}k_BT.$$
$$(0.0.10)$$

Therefore, $b = \gamma k_B T$ or
$$\langle \xi(t)\xi(t') \rangle = 2\gamma k_B T \delta(t-t'). \tag{0.0.11}$$

Remark: This implies that $|\xi|$ is not bounded; if bounded unbounded nature of δ would not show up.

Needless to say, ensemble average also gives the same result.

   If the time resolution is sufficiently coarser than m/γ, then the overdamped version is obtained.

《《**Systematic reduction**》》 To perform the reduction directly from the Langevin equation, we stretch the time as $\tau = \zeta t = t/\epsilon$; Let us write a small quantity $1/\zeta = \epsilon$. In terms of this new time the original Langevin equation reads
$$d\boldsymbol{r} = \epsilon(\boldsymbol{p}/m)d\tau, \tag{0.0.12}$$
$$d\boldsymbol{p} = (-\boldsymbol{p}/m + \boldsymbol{F}/\zeta)d\tau + \sqrt{2k_BT/\zeta}dB(\tau), \tag{0.0.13}$$

where the time-scaled Wiener process $dB(\tau)$ is defined as $\langle dB(\tau)dB(\tau) \rangle = d\tau$; since this is ζdt, the multiplicative factor is scaled with ζ. We expand the solution as $\boldsymbol{r} = \boldsymbol{r}_0 + \epsilon\boldsymbol{r}_1 + \cdots$, $\boldsymbol{p} = \boldsymbol{p}_0 + \epsilon\boldsymbol{p}_1 + \cdots$.

   To the zeroth order we have
$$d\boldsymbol{r}_0 = 0, \tag{0.0.14}$$
$$d\boldsymbol{p}_0 = -(\boldsymbol{p}_0/m)d\tau + \sqrt{2k_BT/\zeta}d\boldsymbol{B}(\tau). \tag{0.0.15}$$

Notice that the second equation is a closed equation for the momentum. In the $\zeta \to \infty$ limit, $\boldsymbol{p}_0$ relaxes to its equilibrium distribution extremely rapidly. This is what we can intuitively expect: the velocity field equilibrates very quickly around the Brownian particle.

   Simple order-by-order calculation to the second order gives
$$d\boldsymbol{r} = \epsilon(\boldsymbol{p}_0(t)/m)d\tau + \epsilon^2(1 - e^{-\tau/m})\boldsymbol{F}d\tau, \tag{0.0.16}$$
$$= (\boldsymbol{p}_0(t)/m)dt + (\boldsymbol{F}/\zeta)dt. \tag{0.0.17}$$

In the last line we have discarded the transcendentally small term $e^{-\zeta t/m}$. The first term is a noise: its correlation function reads (let us consider only its x-component) (assuming that $\zeta \gg 1$)
$$\left\langle \frac{p_0(t)}{m} \frac{p_0(s)}{m} \right\rangle = \frac{k_BT}{m} e^{-\zeta|t-s|/m}. \tag{0.0.18}$$

In the $\zeta \to \infty$ limit, this becomes proportional to the delta function, because $(1/2\tau)e^{-|t|/\tau}$ becomes very sharp in the $\tau \to 0$ limit, but its area below the graph is always unity. Thus, we know
$$\frac{k_BT}{m} e^{-\zeta|t-s|/m} \simeq \frac{2k_BT}{\zeta}\delta(t-s). \tag{0.0.19}$$

We have arrived at
$$d\boldsymbol{x} = \frac{\boldsymbol{F}}{\zeta} + \sqrt{\frac{2k_BT}{\zeta}}d\boldsymbol{B}(t). \tag{0.0.20}$$

   There is of course a way to derive the Smoluchowski equation from the Fokker-Planck equation. Along this route the best way is to use the renormalization group theoretical approach to singular perturbation theory.[1]

Notice that coarse-graining adds high frequency components. Sekimoto analogized this with $\sqrt{1+x^2} \sim |x|$ for $|x| \gg 1$. It is a good lesson to learn that coarse-graining can add high frequency components. However, this is actually trivial, because large salce become small scales after scaling alone (not high freq portion removed).
The short time components are not reliable.

22     $D = k_B T/\gamma$.

24   For a long distance diffusion $\propto \sqrt{t}$ (with $D \sim 10^{-13}$ m^2/s) is less efficient than systematic transport $\propto t$ (motor speed of $v_m \sim 10^{-6}$ m/s). The 'comparable length scale' can be obtained dimensional-analytically ($[D] = L^2/T$, $[v_m] = L/T$, so $[D/v_m] = L$) as $D/v_m \sim 10^{-7}$ m or 0.1 μm, the size of Bacteria.

     Anisotropic particle:

26   Notice the mirror asymmetry should not cause any translation.

Langevin equation may be obtained by the Markov approximation of microscopic mechanics. Zwanzig's solvable model: interactions are harmonic springs. The model is purely mechanical, time-reversal symmetry is preserved without any approximation.

31   When the medium particle distribution is assumed to be equilibrium, then the time reversal symmetry is lost.

39   Ito-Stratonovich correspondence (note $df = f' \circ dx$)

$$dx = adt + bdB = \left(a - \frac{\partial b^2/4}{\partial x} \right) dt + b \circ dB. \tag{0.0.21}$$

$\langle\!\langle$**Wong-Zakai's theorem**$\rangle\!\rangle$ The Langevin equations with physical noise as

$$dx = a(x,t)dt + \sigma(x,t) \circ dB, \tag{0.0.22}$$

where $\circ$ is used to denote clearly that the term is NOT interpreted in Itô's sense, but in the usual calculus sense. Since Itô's lemma tells us

$$d \int_0^{B(t)} \sigma(x)dx = \sigma(B(t))dB(t) + \frac{1}{2} \left. \frac{d\sigma}{dx} \right|_{x=B} dt, \tag{0.0.23}$$

and since the LHS can be calculated as the ordinary calculus formula, the $\circ$ product must be interpreted as

$$\sigma(B(t)) \circ dB = \sigma(B(t))dB(t) + \frac{1}{2}\sigma'(B(t))dt. \tag{0.0.24}$$

This implies that, if we wish to apply Itô calculus to (0.0.22), we must interpret ($\rightarrow$**??**)

$$\sigma(x,t) \circ dB = \sigma(x,t)dB + \frac{1}{2}\frac{\partial \sigma}{\partial x}dxdB = \sigma(x,t)dB + \frac{1}{2}\sigma\frac{\partial \sigma}{\partial x}dt. \tag{0.0.25}$$

Thus, the physical Langevin equation (0.0.22) with the noise term dependent on x must be mathematically interpreted as

$$dx = \left(a(x,t) + \frac{1}{2}\sigma\frac{\partial \sigma}{\partial x} \right) dt + \sigma(x,t)dB. \tag{0.0.26}$$

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[1] L. Y. Chen, N. D. Goldenfeld, and Y. Oono, "Renormalization group theory and variational calculations for propagating fronts," Phys. Rev. E **49**, 4502-4511 (1994); an introductory review is Y. Oono. "Renormalization and asymptotics," Intl. J. Mod. Phys. B **14**, 1327-1361 (2000).

The relation between (0.0.22) and (0.0.26) is called *Wong-Zakai's theorem.*

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Physical Langevin equation reads with $\circ$. As a good example $dz = i\omega(t)zdt$ with stochastic changes in ω.

41   Correlation between the potential force and random force for

$$0 = -\frac{\partial U}{\partial x} - \gamma\frac{dx}{dt} + \xi(t). \tag{0.0.27}$$

42   Using $U \circ dx = Udx + (1/2)U'dx^2 = Udx + (k_B T/\gamma)U'dt$

$$\int \frac{\partial U}{\partial x} \circ \sqrt{2\gamma k_B T}dB \;=\; \int \frac{\partial U}{\partial x}\sqrt{2\gamma k_B T}dB + \frac{1}{2}\int \frac{\partial^2 U}{\partial x^2}dx\sqrt{2\gamma k_B T}dB \quad (0.0.28)$$

$$=\; \int \frac{\partial U}{\partial x}\sqrt{2\gamma k_B T}dB + k_B T\int \frac{\partial^2 U}{\partial x^2}dt, \tag{0.0.29}$$

where we have used $dx = \sqrt{2\gamma k_B T}dB/\gamma$. This leads us to

$$\left\langle \frac{\partial U}{\partial x}\xi \right\rangle = \gamma k_B T\left\langle \frac{\partial^2 U}{\partial x^2}\right\rangle. \tag{0.0.30}$$

Notice that this quantity vanishes in the underdamped case.

43   Simple Euler scheme gives for $dx = adt + \sigma dB$

$$\Delta x = a\Delta t + \sigma\Delta B \tag{0.0.31}$$

Since the last term is of order $\sqrt{\Delta t}$, $a(x + \Delta x) = a(x) + a'(x)\Delta x$ is only accurate to order $\sqrt{\Delta t}$. Generally speaking, in stochastic equations, the convergence of the solution does not necessarily imply convergece to the right physics (e.g., energy conservation requires a higher precision. see p147).

48   FDT.

Thermodynamics

78   Free energy is an effective potential energy. Note that the fundamental relation without dissipation $\Delta A = W$ or $dA = d'W$ that is, A is a potential for force relevant to work.

82   When $\Delta A < W$, the difference is the unused work, which is dissipated as heat. HOWEVER, do not forget that there are reversible component of heat. Since $\Delta A = \Delta E - T\Delta S$ or $T\Delta S = \Delta E - \Delta A$, $\Delta E - \Delta A$ corresponds to the reversible portion of heat.

84   Coupling of two processes one is uphill and the other downhill of the free energy surface is the most important feature of thermodynamics (applications). This can be illustrated as an overall downhill process of the composite free energy surface.

87   The second law tells us that $\Theta = (-W)/(-\Delta A)$ cannot be larger than 1 (for any isothermal process).

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90   The first order phase transition accompanies the compensation between enthalpy and entropy. Or the first order phase transition is between low energy (ordered) state and high entropy (disordered) state. Increase in energy is compensated by increase in entropy.

Chemical Reactions

110   Poisson noise

$$\zeta(t) = \sum \delta(t - t_i), \tag{0.0.32}$$

where the random spike positions $\{t_i\}$ obeys

$$P\left(\int_t^{t+\Delta t} dt\, \zeta(t) = n \right) = \frac{(r\Delta t)^n}{n!} e^{-r\Delta t}, \tag{0.0.33}$$

where $r\ (>0)$ is the spiking rate and is given by $r = \langle \zeta(t) \rangle$, because

$$\left\langle \int_t^{t+\Delta t} dt\, \zeta(t) \right\rangle = \int_t^{t+\Delta t} dt\, \langle \zeta(t) \rangle = r\Delta t. \tag{0.0.34}$$

We could model chemical reactions through using Poisson process to describe the occurrence of a particular reaction, The reaction rate is given by r, so if we have numerous distinct reaction, we must introduce many rs corresponding to them.

112   Gillespie algorithm
However, uniform simulation along the time axis may not be wise, especially when reactions are rare. Thus, a event-driven scheme should be used.
Let v_i be the reaction rate for the ith reaction. We assume that the reaction events obey Poisson. Then, the probability that no reaction occurs for Δt is given by

$$P_0(\Delta t) = e^{-\sum v_i \Delta t}. \tag{0.0.35}$$

When a reaction occurs, what is the probability for the ith reaction to happen? This is given by $v_i / \sum v_i$. Using random numbers, we can perform these random choices.(see `https://cran.r-project.org/web/packages/GillespieSSA/GillespieSSA.pdf` for an elementary introduction and exercises).

Mesoscopic heat

137   The system consists of three parts: the system proper, thermal environment and external system.

138   The law of action and reaction holds between the Brownian particle and its environment: for

$$\frac{dp}{dt} = -\frac{\partial U(x,a)}{\partial x} - \gamma \frac{p}{m} + \xi(t), \quad \frac{dx}{dt} = \frac{p}{m}, \tag{0.0.36}$$

$-\gamma v + \xi(t)$ is the force acting on the Brownian particle. Thus

$$dQ = (-\gamma v + \xi(t)) \circ dx \tag{0.0.37}$$

is the work done to the system by the thermal environment. The first law (the energy balance) reads

$$dE = dQ + dW \tag{0.0.38}$$

with

$$
\begin{aligned}
dQ &= \frac{dp}{dt} \circ dx + \frac{\partial U(x,a)}{\partial x} \circ dx = \frac{dp}{dt} \circ \frac{p}{m} dt + \frac{\partial U(x,a)}{\partial x} \circ dx &(0.0.39)\\
&= d\left(\frac{p^2}{2m}\right) + \frac{\partial U(x,a)}{\partial x} \circ dx &(0.0.40)
\end{aligned}
$$

and $E = p^2/2m + U$. Therefore,

$$dE = d\left(\frac{p^2}{2m}\right) + \frac{\partial U(x,a)}{\partial x} \circ dx + \frac{\partial U(x,a)}{\partial a} \circ da = dQ + \frac{\partial U(x,a)}{\partial a} \circ da \tag{0.0.41}$$

140   This implies the following identification:

$$dW = \frac{\partial U(x,a)}{\partial x} \circ da. \tag{0.0.42}$$

141   Under overdamped conditions (0.0.37) implies that $dQ = (\partial U/\partial x) \circ dx$. However, even under this condition, if T is space-dependent we just use (0.0.37) directly. In this case

$$E = \frac{1}{2} k_B T(x) + U(x,a) \tag{0.0.43}$$

and the Langevin equation reads

$$\gamma \frac{dx}{dt} = -\frac{\partial}{\partial x}\left(\frac{1}{2} k_B T(x) + U(x,a)\right) + \xi(t). \tag{0.0.44}$$

142   If we use the Ito calculus

$$d(p^2/2m) = (p/m)dp + (1/2m)(dp)^2 = (p/m)dp + (\gamma k_B T/m)dt, \tag{0.0.45}$$

That is, if we ignore the correlation between p and dp, we must compensate this with the second term. If we do not (i.e., if we use the ordinary calculus and the limit), the second term is still in the first term. This is basically Wong-Zakai:

$$p \circ dx = p dx + (\gamma k_B T/m)dt \tag{0.0.46}$$

Therefore, dE reads

$$dE = -\frac{2\gamma}{m}\left(\frac{p^2}{2m} - \frac{k_B T}{2}\right)dt + d'W + \sqrt{2\gamma k_B T}\frac{p}{m}dB. \tag{0.0.47}$$

143   Up to this point the external agent is not allowed to modify the system-environment relation. For example by modifying the shape we could change γ, but this cannot be done with a memory-free medium, contradicting the Markov assumption.

149   The average heat is

$$d\langle Q \rangle = -\frac{2\gamma}{m}\left(\frac{p^2}{2m} - \frac{k_B T}{2}\right)dt \tag{0.0.48}$$

150   If overdamped, then $dQ = (-\gamma v + \xi) \circ dx = (\partial U/\partial x) \circ dx$, so using Wong-Zakai (note that $dx = -(\partial U/\partial x)dt/\gamma + \sqrt{2k_B T/\gamma}dB$)

$$\begin{aligned}
dQ &= \frac{\partial U}{\partial x}dx + \frac{1}{2}\frac{\partial^2 U}{\partial x^2}dx^2 = \frac{\partial U}{\partial x}dx + \frac{k_B T}{\gamma}\frac{\partial^2 U}{\partial x^2}dt \tag{0.0.49}\\
&= -\frac{1}{\gamma}\left(\frac{\partial U}{\partial x}\right)^2 dt + \frac{k_B T}{\gamma}\frac{\partial^2 U}{\partial x^2}dt + \sqrt{\frac{2k_B T}{\gamma}}\frac{\partial U}{\partial x}dB \tag{0.0.50}
\end{aligned}$$

Hence,

$$d\langle Q \rangle = -\frac{1}{\gamma}\left\langle \left(\frac{\partial U}{\partial x}\right)^2 \right\rangle dt + \frac{k_B T}{\gamma}\left\langle \frac{\partial^2 U}{\partial x^2} \right\rangle dt. \tag{0.0.51}$$

Contact with more than one heat baths: however, no system variable with two distinct heat baths to avoid direct interactions among heat baths.
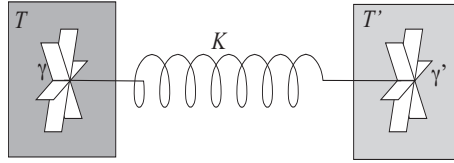

Figure 0.0.1:

Writing $dB = \omega dt$ formally

$$\begin{aligned}
0 &= -\gamma\frac{dx}{dt} + \sqrt{2\gamma k_B T}\omega(t) - K(x - x'), \tag{0.0.52}\\
0 &= -\gamma'\frac{dx'}{dt} + \sqrt{2\gamma' k_B T'}\omega(t) - K(x' - x), \tag{0.0.53}
\end{aligned}$$

Thus,

$$dQ = (-\gamma\dot{x} + \xi(t)) \circ dx = K(x - x') \circ dx, \quad dQ' = K(x' - x) \circ dx' \tag{0.0.54}$$

That is,

$$dQ + dQ' = K(x - x') \circ (dx - dx') = d[K(x - x')2/2] - ([x - x']^2/2)dK \tag{0.0.55}$$

If K is constant, in a steady state $dQ = dQ' = 0$. On the other hand, with the aid of Wong-Zakai ($d\omega = \xi dt$ etc., formally)

$$\begin{aligned}
\gamma dQ' - \gamma' dQ &= \gamma' K(x' - x) \circ dx' - \gamma K(x - x') \circ dx \tag{0.0.56}\\
&= \gamma' K(x' - x)\, dx' - \gamma K(x - x')dx + \frac{1}{2}K(dx' - dx)\gamma' dx' - \frac{1}{2}K(dx - dx')\gamma dx \tag{0.0.57}
\end{aligned}$$

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Notice that

$$\begin{aligned}
\gamma' K(x'-x)\,dx' - \gamma K(x-x')dx &= K(x'-x)[d\omega' - K(x'-x)] - K(x-x')[d\omega - K(x-x')] \\
&= K(x'-x)d\omega' - K(x-x')d\omega. \quad (0.0.58)
\end{aligned}$$

155   Therefore, this vanishes on the average. Notice that $dx\,dx' = 0$ and $dx^2 = 2k_B T\,dt/\gamma$, etc., so

$$\frac{1}{2}K(dx'-dx)\gamma' dx' - \frac{1}{2}K(dx-dx')\gamma dx = K(k_B T' - k_B T) \quad (0.0.59)$$

From the above calculations we obtain

$$\langle dQ \rangle = -\langle dQ' \rangle = \frac{k_B K\,dt}{\gamma + \gamma'}(T - T'). \quad (0.0.60)$$

156   This heat transport is due to mechanical coupling. The heat converted into work at the high temperature end is possible due to a feedback control that reduces the return of energy from the other side.

157   Partition of heat: In the situation of Fig. 0.0.1, a work is supplied to the spring. We can then ask how much heat goes to which bath. If $T = T'$, then

$$\gamma \frac{d}{dt}\langle Q \rangle = \gamma' \frac{d}{dt}\langle Q' \rangle = \frac{\gamma\gamma'}{\gamma + \gamma'}\frac{K(t)}{2}\frac{d}{dt}\langle (x-x')^2 \rangle. \quad (0.0.61)$$

or, if the process is slow enough, $K(t)(x-x')^2/2 = k_B T/2$ is allowed, and

$$d\langle Q \rangle = \frac{\gamma'}{\gamma + \gamma'}\frac{k_B T}{2}K(t)d\frac{1}{K(t)} = -\frac{\gamma'}{\gamma + \gamma'}\frac{k_B T}{2}d\log K(t). \quad (0.0.62)$$

Thus, for example,

$$\Delta\langle Q(t) \rangle = \frac{\gamma' k_B T}{\gamma + \gamma'}\log\sqrt{\frac{K_{init}}{K_{fin}}}. \quad (0.0.63)$$

Thus, the contact with smaller friction get more heat. Also if $K \to 0$, Q can be indefinitely large.

158   Even if $T = T'$ and not work is added, random fluctuation of heat (diffusion of heat) can occur.

159   Thermal ratchet.[2] Generally the equations are

$$\begin{aligned}
0 &= -\gamma\frac{dx}{dt} - \frac{\partial U}{\partial x} + \sqrt{2\gamma k_B T}\,\omega \quad (0.0.64) \\
0 &= -\gamma'\frac{dx}{dt} - \frac{\partial U}{\partial x} + \sqrt{2\gamma' k_B T}\,\omega' \quad (0.0.65)
\end{aligned}$$

with $U = U_1(x - \phi(y)) + U_2(y) - fx$. $v = \langle \dot{x} \rangle$ and the average power output is $P = vf$.

160   If the load is just strong to make $v = 0$. Under the stalled condition, what actually

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[2]Reviews: Parrondo & De Cisneros Appl Phys A 75 129 (2002); Reimann PR 361 57 (2002).

happens is the thermal connection through the device between the two heat baths without any work, so the efficiency is 0.

Near the equilibrium (linear regime) noneq thermodynamics argument is available.[3]

172   Strictly speaking Langevin systems should not be applicable to nonequilibrium situations, but at least qualitatively successful examples are many. Generally speaking,
This method works if the nonequilibrium in the system, but it does not work if the nonequilibrium is at the interface between the system and the environment.

Mesoscopic work

176   Let $U(x, a)$ be the potential energy including all the interaction energy between the system and the external system. Since a is the 'coordinates' of the external system $-\partial U \partial a$ is the force exerted by the system to the external system, so the work done to the system read

$$dW = \frac{\partial U}{\partial a} \circ da. \tag{0.0.66}$$

This depends on the resolution on a.

In the present approach it is assumed that the external system is not influenced by the system('s state and dynamics). However, in reality, this condition is hard to impose, so we must consider where the boundary is between the system and the rest. There seems no systematic argument.

178   A particle in a laser trap:

$$-\frac{\partial U(x, a)}{\partial a} + \left[-\gamma \frac{dx}{dt} + \xi(t) \right] = 0. \tag{0.0.67}$$

The work done to the system by changing the spring constant reads

$$W = \int_{a_i}^{a_f} \frac{\partial U}{\partial a} da = \frac{1}{2} \int_{a_i}^{a_f} x(t)^2 da(t) = \frac{1}{2} \int_{a_i}^{a_f} a(t) x(t)^2 d\log a(t) \tag{0.0.68}$$

for a given sample path $x(t)$. Now, let us introduce the time scale parameter τ and write $t = \tau s$, so that $s = 0$ corresponds to the intial time and $s = 1$ the final time. Write $\tilde{a}(s) = a(\tau s)$:

$$W = \frac{1}{2} \int_{t_i}^{t_f} a(t) x(t)^2 \frac{d\log a(t)}{dt} = \sum_k \int_{t_k}^{t_k + \tau ds} \frac{1}{2} a(t) x(t)^2 dt \frac{d\log a(t)}{dt}. \tag{0.0.69}$$

For very large τ (slow process), the law of large numbers tells us

$$\int_{t_k}^{t_k + \tau ds} \frac{1}{2} a(t) x(t)^2 dt = k_B T \tau ds \tag{0.0.70}$$

179   and the Riemann sum becomes

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[3]van den Broeck & Kawai PRL 96 210601 (2006); Komatsu & Nakagawa, EPJ B 38 457 (2006); Prost et al., RMP 69 1269 (1997).

$$W = \frac{1}{2} k_B T \int \tau ds \frac{d\log a(t)}{dt} = k_B T \log \sqrt{\frac{a_f}{a_i}} \tag{0.0.71}$$

This result correspnds to the thermodynamic result:

$$A(a, T) = -k_B T \log(1/\sqrt{a}). \tag{0.0.72}$$

This relation to equilibrium thermodynamics holds for general $U(x, a)$, because

$$\left\langle \frac{\partial U}{\partial a} \right\rangle = \frac{\partial}{\partial a} A(a, \beta). \tag{0.0.73}$$

182   Thus, as expected $W \to \Delta A$ in the slow limit. If the system is open, a similar formula holds with an appropriate thermodynamic potential.

184   The irreversible work is the difference $W - \Delta A$, so

$$W_{irr} = \int da \left[\frac{\partial U(x, a)}{\partial a} - \left\langle \frac{\partial U(x, a)}{\partial a} \right\rangle \right]. \tag{0.0.74}$$

186   One particle ideal gas with a heat bath (= thermally vibrating piston) is very similar.

188   Cyclic process. The work done is zero.

190   Work/time complementarity: $W_{irr}\tau \geq$ some positive constant. In the slow process limit, the irreversible portionn must not depend on the sign of da/dt, so we must be able to wrtie

$$\langle W_{irr} \rangle = \int dt \frac{da}{dt} \Lambda(a) \frac{da}{dt}. \tag{0.0.75}$$

192   Therefore,

$$\langle W \rangle = \Delta A + \int da \, \Lambda(a) \frac{da}{dt} = \int da \left[\frac{\partial A}{\partial a} + \Lambda(a) \frac{da}{dt} \right]. \tag{0.0.76}$$

Then, W must have the following form with a stochastic element Xi:

$$W = \int da \left[\frac{\partial A}{\partial a} + \Lambda(a) \frac{da}{dt} - \Xi(t) \right]. \tag{0.0.77}$$

or

$$\Delta A = \int da \left[-\Lambda(a) \frac{da}{dt} + \Xi(t) \right] + W. \tag{0.0.78}$$

Thus the dissipation may be ascribed to a macroscopic frictioin Λ.

195   Jarznski and work theorem
       For Mamrkovian case, the most efficient derivation of Jarzynsk's equality may be as follows.

Consider a Markov process whose transition rate depends on time (i.e., not a stationary process). Let us write the transition rate q_{ij} as $q_{ij}(t)$ (transitions are $i \leftarrow j$)). Let $p_s(i|k; t)$ be a distribution satisfying

$$\sum_j q_{ij}(t) p_s(j|k; t) = 0. \tag{0.0.79}$$

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That is, if the transition probability is fixed to be the one at time t, then $p_s(i|k;t)$ is the stationary state of this fictitious Markov process. Let us assume that we may write

$$p_s(i|k;t) = e^{-H(i|k;t)}. \tag{0.0.80}$$

Obviously,

$$\frac{d}{dt}p_s(i|k;t) = \sum_j q_{ij}(t)p_s(j|k;t) - \frac{\partial H(i|k;t)}{\partial t}p_s(i|k;t). \tag{0.0.81}$$

Its solution may be written in terms of the path integral as

$$p_s(i|k;t) = \left\langle \exp\left(-\int_0^t ds \frac{\partial H(x(s)|k;s)}{\partial s}\right)\right\rangle_{k\to i}, \tag{0.0.82}$$

where $\langle\ \rangle$ implies the average over all the paths connecting k and i in time t. If the initial condition is $p_s(i|k;0) = e^{-H_0(i|k)}$, then[4]

$$p_s(i|k;t) = \sum_{i_0} \left\langle \exp\left(-\int_0^t ds \frac{\partial H(x(s)|i_0;s)}{\partial s}\right)\right\rangle_{i_0\to i} e^{-H_0(i_0|k)}. \tag{0.0.83}$$

This is probably the most general version of Jarzynski's equality.[5] Let

$$p_s(x;t) = \frac{1}{Z_0}e^{-\beta H(t)}, \tag{0.0.84}$$

and $i\mathcal{L}_t = [\,\cdot\,,H(t)]_{PB}$. Then,

$$\mathcal{L}_t p_s(x;t) = 0. \tag{0.0.85}$$

Therefore, we have

$$\frac{\partial}{\partial t}p_s(x;t) = \mathcal{L}_t p_s(x;t) - \beta \frac{\partial H(t)}{\partial t}p_s(x;t). \tag{0.0.86}$$

This has exactly the same structure as (0.0.81), so (0.0.83) becomes Jarzynski's equality.

An elementary exposition follows:

Jarzynski's equality[6]

Suppose a thermostated system has a parameter $\lambda(t)$ that can be changed experimentally externally from $\lambda(0)$ to $\lambda(1)$. Let W be the work needed to perform this change. Then, the free energy change ΔA from the equilibrium state with $\lambda(0)$ and to that with $\lambda(1)$ may be obtained by

$$\langle e^{-\beta W}\rangle = e^{-\beta \Delta A}, \tag{0.0.87}$$

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[4]Here, $\partial H(x(s)|i_0;s)/\partial s$ may look like a matrix, so the time ordering operator T seems to be required, but actually T is not needed, because the second variable i_0 is fixed, so we are not treating this as a matrix.

[5]G E Crooks, "Path-ensemble averages in systems driven far from equilibrium," Phys. Rev. E **61**, 2361-2366 (2000). See also G Hummer and A Szabo, "Free energy reconstruction from nonequilibrium single-molecule pulling experiments," PNAS **98**, 3658-3661 (2001).

[6]C. Jarzynski, "Nonequilibrium equality for free energy differences", Phys. Rev. Lett. **78**, 2690-2693 (1997). The latest note dispelling misunderstanding is: C. Jarzynski, J. Stat. Mech. 2004, P09005, "Nonequilibrium work theorem for a system strongly coupled to a thermal environment." Chris Jarzynsky calls his equality, 'nonequilibrium work theorem.' In this latest paper, Jarzynski discusses how H may be interpreted as the effective Hamiltonian of the system when the system interacts strongly with the heat bath; this is directly relevant to 'single molecule physiology.' How did he arrive at this remarkable formula? He realized the relation when he was analyzing a numerical experimental result. That is, the relation was suggested first empirically.

where the average is over many experiments with the same protocol. This is called *Jarzynski's equality*.[7,8]

More precisely, suppose a system is described classically with the Hamiltonian $H(x, \lambda(t))$ with a time-dependent parameter $\lambda(t)$, which may be externally controlled. The initial state a is distributed canonically at the temperature $T = k_B/\beta$ and with the Hamiltonian $H(x, \lambda_0)$. Let state b be an equilibrium state with the Hamiltonian $H(x, \lambda_1)$ at the same temperature. We fix the protocol to change the system by fixing the function $\lambda(t)$ ($\lambda(0) = \lambda_0$ and $\lambda(t_f) = \lambda_1$, where t_f is the last time to modify the parameter). We embed this system in a large thermostat that can be described by a Hamiltonian H_0. Let us write the Hamiltonian of the whole system as $H_w(z, \lambda(t))$, where z denotes the phase variables of the whole system collectively. This Hamiltonian includes the interaction Hamiltonian between the system and the thermostat. We assume this effect may be ignored.

Now, W is the work done on the system during the change under the condition that the whole system is isolated.[9] Then, the above equality holds.

Warning. The final state actually reached by the protocol at time t_f is usually very different from the final equilibrium state we are interested in. ▢

Exercise 1. There is a macromolecule whose end-to-end distance can be controlled. We change its length from L_0 to L_1 in one second (linearly in time). The free energy difference of the equilibrium states with parameters $L_0 = 1$nm and $L_1 = 3$nm is given by $\Delta A = 40$pNnm (= pico newton $\times$ nanometer) (i.e., the stretching increases the free energy this much if one does this in a quasiequilibrium fashion). The experiments told us that the work done to the molecule W was distributed according to a Gaussian distribution, and the average work was $\langle W \rangle = 60$pNnm. Assuming that the temperature is 300K, find the variance of the work. (Check that $300k_B = 4$pNnm). ▢

Exercise 2. It is often hard to obtain equilibrium free energy change with actual experiments performed at finite speeds. Thus, sometimes Jarzynski's equality is practically meaningful. Read the paper: "Equilibrium information from nonequilibrium measurements in an experimental test of Jarzynski's equality" by Liphardt et al.[10] in Science **296**, 1832-1835 (2002), and summarize the content.[11] ▢

Discussion 1. There is a box separated into two compartments with a separating wall. One compartment is empty but the other is filled with gas. Now, the separating wall is removed by sliding quickly without any work. In this case, the free energy decreases because entropy increases. However, there is definitely no external work. Therefore, Jarzynski's equality cannot hold. ▢

Demonstration of Jarzynski's equality

The work done on the system is given by $W = H_w(z(t_f), \lambda_b) - H_w(z(0), \lambda_a)$, because it is as a whole isolated. Therefore,

$$\langle e^{-\beta W} \rangle = \frac{1}{Y_a} \int dz(0) e^{-\beta H(z(0), \lambda_a) - \beta W} \tag{0.0.88}$$

$$= \frac{1}{Y_a} \int dz(0) e^{-\beta H(z(t_f), \lambda_b)}. \tag{0.0.89}$$

Here, Y_a is the partition function for the system with the Hamiltonian $H(x, \lambda_a)$ + the thermo-

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[7]The equality holds if the system obeys a Markov process as seen above.

[8]For a cycle (i.e., $\Delta A = 0$), this was demonstrated by Bochkov and Kuzovlev in the 1980's (according to C. Jarzynski); G. N. Bochkov and Yu. E. Kuzovlev, Zh. Eksp. Teor. Fiz. **72**, 238 (1977) [Sov. Phys.-JETP **45**, 125 (1977)]; Physica **106A**, 443, 480 (1981).

[9]For the following equality to be correct, the temperature of the whole system must not change, but if the bath is large enough, this is not a constraint.

[10]by J. Liphardt, S. Dumont, S. B. Smith, I. Tinoco, Jr., and C. Bustamante.

[11]See also a recent paper by the same group: PNAS **99** 13544-13548 (2002), and Jensen et al. on GlpF PNAS **99** 6731 (2002).

stat. According to Liouville's theorem, this reads

$$\langle e^{-\beta W} \rangle = \frac{1}{Y_a} \int dz(t_f) e^{-\beta H(z(t_f), \lambda_b)} = \frac{Y_b}{Y_a}, \qquad (0.0.90)$$

where Y_b is the partition function for the system with the Hamiltonian $H(x, \lambda_b)$ + the thermostat. Since the Hamiltonian of the thermostat is intact, and we ignore the interaction Hamiltonian that may depend on the parameter λ, $Y_b/Y_a = Z_b/Z_a$, where Z_c is the canonical partition function for the system with the Hamiltonian $H(x, \lambda_c)$. Thus, we have demonstrated (0.0.87).[12]

Since e^{-x} is convex, (0.0.87) implies

$$\langle W \rangle \geq \Delta A. \qquad (0.0.91)$$

This is Thomson's principle.

Warning. Notice that the whole system is isolated, so if the total work done to the system is large, then the final temperature would be definitely higher than the initial one. *Still* (0.0.87) holds. However, ΔA compared there is *not* the free energy change between the initial and the actual final equilibrium states experiments realize.

Jarzynski's equality and rare fluctuations

We know that the difference $W - \Delta A$ can be made large without bound. Still, Jarzynski's equality (0.0.87) holds. What does this mean?

Let us consider the simplest case; we make a cycle, and the initial and the final equilibria are identical. $\Delta A = 0$, so

$$\langle e^{-\beta W} \rangle = 1. \qquad (0.0.92)$$

If we make a rapid change, very likely $W > 0$; maybe it is often very large. Still, the equality must hold, so we need fairly large negative W occasionally. That is, we must wait for a fairly large scale 'violation' of the second law (cf. **??**). This implies that we must wait for a very long time to use (0.0.87) for a macroscopic system or for a process with large dissipation, even if a system under study is not macroscopic.

Exercise 1. Imagine a cylinder with a piston containing an ideal gas. The whole system is in a thermostat. Let us pull out the piston extremely rapidly (ignore the mass of the piston), and then very slowly and gently we return the piston to the original position. [Do not believe that all the questions below can be answered with the conditions given here; Appropriate information must be added.]

(1) What is the total work needed on the average?

(2) What is the heat generated?

(3) What sort of fluctuations does one have to wait for (0.0.87) to hold?

(4) Estimate their probabilities.

(5) How long should we wait for such fluctuations? ☐

Probability of violation of the second law

We have seen that fluctuation can go to a considerable extent against the second law. After all, fluctuation decreases (local) entropy and without such fluctuations Jarzynski's equality cannot hold.

Let the classical system[13] under study be described by its canonical coordinates y and

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[12]This is the derivation given in the original paper, but it is hardly justifiable, because 'no change' in the heat bath does not imply the ratio of its partition functions before and after the change of the heat bath is unity (it is ∞/∞). If we can model the whole system as a Markov process, we can justify the formula as we will see in **??**.

[13]not necessarily a deterministic system, but must be Markovian.

externally controllable parameters λ. The system history may be expressed by $\{y(t), \lambda(t)\}$. We assume that the system satisfies the following *microscopic reversibility*:

$$P(\{x, \lambda\}_0^t | x(0)) / P(\{\overline{x}, \overline{\lambda}\}_t^0 | x(t)) \equiv P(\rightarrow) / P(\leftarrow) = e^{-\beta Q(\{x, \lambda\}_0^t)}, \qquad (0.0.93)$$

where $\{x, \lambda\}_0^t$ is the path = history with a given protocol $\lambda(t)$, and the overline indicates the time reversal operation.[14] Q is the energy absorbed by the system from the heat bath during the forward process. [**C**] Is this interpretation of Q consistent with the usual operational definition of heat?

If the initial and the final states are in equilibrium, the difference of the surprisal $-\log \rho$ is interpreted as the entropy change. Therefore, we may assume[15]

$$\Sigma = \log \rho(x(0)) / \rho(x(t)) - \beta Q, \qquad (0.0.94)$$

where Σ is the entropy production, $\rho(x(t))$ is the distribution of canonical coordinates at time t.[16] Notice that the probability of the entropy production to be Σ by the forward dynamics is given by

$$P_F(\Sigma) = \sum \rho(x(0)) P(\rightarrow), \qquad (0.0.95)$$

where the sum is over all the transitions compatible with the entropy production Σ. An analogous formula can be written for the backward dynamics P_R

$$P_R(-\Sigma) = \sum \rho(x(t)) P(\leftarrow). \qquad (0.0.96)$$

There is a one to one correspondence between the forward and reversed paths, so the sum above is over exactly the same paths (although reversed in time) in the sum for P_F. We wish to compute

$$\frac{P_F(+\Sigma)}{P_R(-\Sigma)} = \frac{\sum \rho(x(0)) P(\rightarrow)}{\sum \rho(x(t)) P(\leftarrow)}. \qquad (0.0.97)$$

Combining (0.0.93) and (0.0.94), we obtain for each path

$$\frac{\rho(x(0)) P(\rightarrow)}{\rho(x(t)) P(\leftarrow)} = e^{\Sigma} \qquad (0.0.98)$$

Now, take the following trivial identity:

$$\frac{a}{b} = \frac{c}{d} \quad \Rightarrow \quad \frac{a}{b} = \frac{c}{d} = \frac{a+c}{b+d}. \qquad (0.0.99)$$

Therefore, (0.0.97) implies

$$P_F(\Sigma) / P_R(-\Sigma) = e^{\Sigma}. \qquad (0.0.100)$$

This is called the *fluctuation theorem*. This type of theorems hold for sufficinetly chaotic dynamical systems.[17]

Exercise 1. The fluctuation theorem may be experimentally checked with a small system.

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[14]The conditional probability implies that we do not take the (equilibrium or stationary) distribution of the states into account.

[15][**C**] The original paper: G. E. Crooks, "Entropy production fluctuation theorem and the nonequilibrium work relations from free energy differences," Phys. Rev. E **60**, 2721 (1999) claims that the result is applicable far away from equilibrium, but it is questionable simply because we have no clear definition of entropy away from equilibrium.

[16]Precisely speaking, this ratio must be the reciprocal of the Radon-Nikodym derivative $d\rho(x(t))/d\rho(x(0))$.

[17]This type of relation was first found numerically by D. J. Evans, E. G. D. Cohen and G. P. Morriss, Phys. Rev. Lett. **71**, 2401 (1993), and later proved for Anosov dynamical systems by G. Gallavotti and E. G. D. Cohen, J. Stat. Mech. **80**, 931 (1995) (see **??**). The form given here is due to G. E. Crooks, Phys. Rev. E **60**, 2721 (1999).

Read Wang et al. Phys. Rev. Lett. **89**, 050601-1 (2002)[18] and summarize its content. □
Remark. There have been numerical and empirical attempts to check the fluctuation theorem: M. Dolowschi(a)k and Z. Kovács, "Fluctuation formula for nonreversible dynamics in the thermostated Lorentz gas," Phys. Rev. E **65** 066217-1-4 (2002). This is for a driven periodic Lorentz gas, and is consistent. □

Relation of fluctuation theorem to Jarzynski's equality
Let W_d be the dissipated part of the work done to the system. Then,

$$\Sigma = \beta W_d \tag{0.0.101}$$

Therefore, from (0.0.97) we have

$$\langle e^{-\beta W_d} \rangle_F = 1. \tag{0.0.102}$$

We know $W_d = W - \Delta F$, this is Jarzynski's equality.
Discussion 1.[19] We can also derive

$$\langle e^{\Sigma} \rangle_R = 1. \tag{0.0.103}$$

This is, so to speak, an anti-Jarzynski equality. Can we use it? □

199   Comparison of stepwise (simple fuction) and smooth changes. Do they agree? Yes, if δt is sufficiently small.

Heat
203   Each description scale has its own definition of heat.
What is explicitly observed and controlled?

204   Langevin equation (p52) with a small amplitude high-frequency periodic potential

$$\gamma \dot{x} = -U_M'(x) + a_0 - V'(x) + \sqrt{2\gamma k_B T} \xi(t), \tag{0.0.104}$$

where U_m is the periodic potential

208   System can have different levels of randdom variables. If a system has fast variables y and slow variables x, the Hamiltonian reads $H(x, y, a)$, where a is an extrenal macro-control parametrer.

$$Z(\beta, a) = Tr_{x,y} e^{-\beta H} = e^{-\beta F(\beta, a)}, \ \ Z(\beta, x, a) = Tr_y e^{-\beta H} = e^{-\beta \tilde{F}(\beta, x, a)}, \tag{0.0.105}$$

where $\tilde{F}(\beta, x, a)$ is the Landau free energy. Notice that $\tilde{F}$ is an effective Hamiltonian at the level of slow variables. Thus, this may be understood a the mesoscopic energy. On the pther hand, the average of the Hamiltonian (the calorimetric energy) is the internal energy at this level, so

$$\tilde{E} = \frac{\partial \beta \tilde{F}}{\partial \beta}. \tag{0.0.106}$$

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[18]by G. M. Wang, E. M. Sevick, E. Mittag, D. J. Searles and D. J. Evans, "Experimental demonstration of violations of the second law of thermodynamics for small systems and short time scales."

[19]from the question by Mr Y. Liu

$$\tilde{E} - \tilde{F} = -T\frac{\partial \tilde{F}}{\partial T} = Td\tilde{S} \tag{0.0.107}$$

The Langevin eqution for x reads

$$\gamma\frac{dx}{dt} + \xi(t) - \frac{\partial}{\partial x}\tilde{F}(\beta, x, a) = 0. \tag{0.0.108}$$

The stochastic energetic for this is the mesoscopic thermodynamics:

$$d\tilde{F} = d\tilde{Q} + d\tilde{W} = \frac{\partial \tilde{F}}{\partial x}dx + \frac{\partial \tilde{F}}{\partial a}da, \tag{0.0.109}$$

where

$$d\tilde{W} = \frac{\partial \tilde{F}}{\partial a}da \tag{0.0.110}$$

$$d\tilde{Q} = \left(-\gamma\frac{dx}{dt} + \xi\right) \circ dx = \frac{\partial \tilde{F}}{\partial x} \circ dx \tag{0.0.111}$$

If x is slow enough, from y, the motino of x is always quasistatic. Therefore, thermodynamics holds with x and a as external parameters. Then heat at this level is $Td\tilde{S}$, the mesoscopic entropy. Now, calorimetrically,

$$d\tilde{E} = d\tilde{W} + dQ_{cal} \tag{0.0.112}$$

where Q_{cal} is the calorimetric heat and

$$dQ_{cal} = d\tilde{Q} - T\frac{d\tilde{F}}{dT} = d\tilde{Q} + Td\tilde{S}. \tag{0.0.113}$$