Advanced Studies in Theoretical Physics
Vol. 12, 2018, no. 4, 189 - 195
HIKARI Ltd, www.m-hikari.com
https://doi.org/10.12988/astp.2018.8520

Free Energy Differences Determined from a Nonequilibrium Model

Paul Bracken

Department of Mathematics
University of Texas, Edinburg, TX, USA

Abstract

It has been shown recently that the Helmholtz free energy difference between two equilibrium states can be determined based on an ensemble of finite-time measurements of the work performed in changing an external parameter. This idea is extended by regarding the work as a random variable much as in a process like Brownian motion. A model is described where the free energy is calculated based on a probability distribution declared to satisfy detailed balance.

PACS: 42.60.Da

Keywords: heat bath, free energy, probability, detailed balance, ensemble, average

Equilibrium statistical mechanics is a well established field, however the study of nonequilibrium processes is still under development. This is especially the case for non-equilibrium processes in the realm of small systems. In this case, fluctuations become important and must therefore be included in the description. Such fluctuations seem to have a basis in experiment as first recorded by Evans, Cohen and Gallavotti in the $90s$ [**1,2**]. This development has led to the development that work performed during a nonequilibrium process can be interpreted as a random variable which obeys a set of exact relations that have an impact on the nature of irreversibilty and the second law.

In some sense, this supplements or generalizes the second law. In addition to thermal fluctuations some microscopic systems also receive a strong contribution from quantum fluctuations. In quantum systems, it can be said that both thermal and quantum fluctuations have to be considered [**3**].

A finite classical system can depend on some external parameter τ, where for example, the system consists of a box which encloses a gas and τ is a parameter specifying the volume. After the system equilibrates with a heat reservoir at temperature T, the external parameter τ may be switched infinitely slowly from an initial value $\tau = 0$ to a final value which will be taken to be $\tau = 1$.

The system remains in quasi-static equilibrium with the reservoir throughout the process. The total work performed on the system will equal the Helmholtz free energy difference between the initial and final states

$$W_{\infty} = \Delta F = F_1 - F_0. \tag{1}$$

In (1), the variable F_{τ} denotes the equilibrium free energy of the system at temperature T for a fixed τ, and this is valid for extremely slow changes of parameter [**4-5**].

After allowing the system and reservoir to equilibrate, τ is switched at a finite rate. The system will lag behind quasi-static equilibrium with the reservoir. The total work will depend on the microscopic initial conditions of both system and reservoir. An ensemble of such measurements, prepared by letting the system equilibrate with the reservoir will yield a distribution of values for the work. A stochastic process can be defined by a map such that $\rho(W,t)\,dW$ is the probability that the work performed by taking the parameter τ from 0 to 1 over a time t will fall between W and $W+dW$. In the limit $t \to \infty$, the case $W_{\infty} = \Delta F$ is regained and $\rho \to \delta(W - \Delta F)$ in this limit. Processes such as Brownian motion have also been looked at this way, and it might be useful to establish a link between this subject and what is discussed here. As in Brownian motion, the aspect of self-similarity with all paths starting from the same point with the same transition probabilities may play a role.

For finite t, the distribution ρ acquires a finite width, and this is a manifestation of the fluctuations in W from one change to the next. Effectively, the variable W is being considered as a random variable. Here we would like to formulate this process as a type of Wiener process where for some later time $t > 0$, the work is to be regarded as the random variable W_t. This is somewhat analogous to the situation with Brownian motion. The probability measure $A \to P(W_t \in A)$ that assigns numbers in the interval $[0,1]$ to suitably chosen subsets $A \subset \mathbb{R}$ is called the distribution of W_t, and any such map is called a stochastic process. The stochastic process X_s is said to be a Wiener process if the finite dimensional distributions are of the form

$$P(X_{s_1} \in A_1, \dots, X_{s_n} \in A_n)$$

$$= \int_{A_n} dx_n \cdots \int_{A_2} dx_2 \int_{A_1} dx_1\, K(x_n - x_{n-1}, s_n - s_{n-1}) \cdots K(x_2 - x_1, s_2 - s_1)\, K(x_1, s_1) \tag{2}$$

and if the initial distribution is $P(X_0 \in A_0) = 1 (= 0)$ if $A_0 \ni 0$ (otherwise). If the origin is the starting point, equivalently, one writes $X_0 = 0$. This product structure tells us that, given the present value of W_t, the distribution of $W_{t'}$ at some later time t' is completely determined and does not depend any further on the past history of the evolution. A stochastic process with this property is said to have no memory and is called a Markov process. Given initial data, by solving the equation of motion, the future state of the system can be obtained without knowing what happened in the past.

It is the intention here to present a development of a result due to Jarzynski [**6-7**] which is valid for any switching time t and can be expressed in the form

$$\langle e^{-\beta W} \rangle = \int dW\, \rho(W,t) e^{-\beta W} = e^{-\beta \Delta F}, \tag{3}$$

where $\beta^{-1} = k_B T$. This gives the value of an equilibrium quantity $\Delta\, F$ in terms of an ensemble of finite-time nonequilibrium meaqsurements.

Moreover, using Jensen's inequality which states that

$$\langle e^{-\beta W} \rangle \geq e^{-\beta \langle W \rangle} \tag{4}$$

applied to (3) yields,

$$e^{-\beta \Delta F} \geq e^{-\beta \langle W \rangle}. \tag{5}$$

Since the exponential function is a monotone function, (5) implies that [**7-9**]

$$\langle W \rangle \geq \Delta\, F. \tag{6}$$

Consider a system whose evolution in time is described by a trajectory $\mathbf{x}(t)$. The evolution of interest is not that of an isolated system, but rather that of a system in contact with a heat bath. Thus, the trajectory can be considered stochastic, to reflect the random influence of the heat bath. Suppose there exists a parameter-dependent Hamiltonian, $H_\tau(\mathbf{x})$, which for a fixed value of τ gives the total energy of the system in terms of its instantaneous state $\mathbf{x}$, τ and the external forces imposed on the system. If the system becomes isolated, H_τ generates a time evolution of the system [**10-12**].

Based on this $H_\tau(\mathbf{x})$, the partition function can be defined as

$$Z_\tau(\beta) = \int d\mathbf{x}\, \exp\big(-\beta H_\tau(\mathbf{x}) \big), \tag{7}$$

and then the free energy of the system,

$$F_\tau(\beta) = -\frac{1}{\beta} \log \big(Z_\tau(\beta) \big). \tag{8}$$

The free energy difference $\Delta F = F_1 - F_0$ is the main quantity of interest for a fixed β. The evolution will depend on the externally imposed time dependence of τ. This describes the external circumstances which the system faces.

Given a time-dependent parameter τ and an associated trajectory $\mathbf{x}(t)$ describing the system's evolution, the total work carried out on the system is given by the integral

$$W = \int_0^{t_s} \frac{d\tau}{dt} \frac{\partial H_\tau}{\partial t}(\mathbf{x}(t))\, dt. \tag{9}$$

In the event of isolated system evolution, the integral can be carried to the form,

$$W = H_1(\mathbf{x}(t_s)) - H_0(\mathbf{x}(0)). \tag{10}$$

The work performed on the system is the change in energy of the system.

Once the system is placed in direct contact with a heat bath, this no longer holds. There is a continual exchange of energy with the exterior bath. Let the parameter τ vary between 0 and 1, and select arbitrary partitions of both the trajectory and the parameter variable τ. These partitions may be written $P_\tau = \{\tau_0, \tau_1, \dots, \tau_N\}$ and $P_{\mathbf{x}} = \{\mathbf{x}_0, \mathbf{x}_1, \dots, \mathbf{x}_N\}$ hence $\tau_k = k/N$ in the regular case. The initial point in phase space $\mathbf{x}_0$ is taken from a canonical distribution with $\tau_0 = 0$ and an amount of work $\Delta\, W = H_{\tau_1}(\mathbf{x}_0) - H_{\tau_0}(\mathbf{x}_0)$. is performed on the system. The next point in P_τ is selected and associated to $\mathbf{x}_1$ and this process is continued until the entire trajectory is mapped out until the parameter has increased to the value $\tau = 1$.

The total work performed during this process is found by adding up all the individual works

$$W = \sum_{n=1}^{N} \Delta\, H_n = \sum_{n=1}^{N} [H_{\tau_n}(\mathbf{x}_{\tau_n}) - H_{\tau_{n-1}}(\mathbf{x}_{\tau_{n-1}})]. \tag{11}$$

The quasi-static limit is obtained by letting the number of steps becomes arbitrarily large and as far as integrability is concerned, the sums can be thought of as sums of step functions of small constant pieces, so the integrals should exist at least in the Lebesgue sense.

A complete trajectory $(\mathbf{x}_0, \dots, \mathbf{x}_N)$ can as noted be obtained by taking discrete changes in the value τ with random jumps in phase space as described by the partitions, so for example, an input $\mathbf{x}$ is taken and an output $\mathbf{x}'$ is associated to it. A probability distribution $P_\tau(\mathbf{x}|\mathbf{x}')$ can be given for generating this $\mathbf{x}'$ from the starting value $\mathbf{x}$ for a given value of τ. It is not necessary to know these distributions in explicit form. However it is required that detailed balance be satisfied for each τ in the following explicit form,

$$\int d\mathbf{x}\, e^{-\beta H_\tau(\mathbf{x})}\, P_\tau(\mathbf{x}|\mathbf{x}') = e^{-\beta H_\tau(\mathbf{x}')} \tag{12}$$

This is done in such a way that a canonical distribution of inputs $\mathbf{x}$ produces a canonical distribution of outputs.

The probability of obtaining a particular trajectory $(\mathbf{x}_0, \dots, \mathbf{x}_N)$ over the course of such a process is given by

$$P(\mathbf{x}_0, \dots, \mathbf{x}_N) = \frac{1}{Z_0} e^{-\beta H_0(\mathbf{x}_0)} P_{\tau_1}(\mathbf{x}_0|\mathbf{x}_1) \cdots P_{\tau_N}(\mathbf{x}_{N-1}|\mathbf{x}_N). \tag{13}$$

There is an alternation beteen discrete changes in parameter τ and discrete jumps in phase space until the entire trajectory has been generated and the parameter has reached the value one. Using (11) for the total work performed during this discrete switching process with (13), we have therefore,

$$\langle e^{-\beta W} \rangle =$$

$$\int d\mathbf{x}_0 d\mathbf{x}_1 \dots d\mathbf{x}_N \, \frac{1}{Z_0} \, e^{-\beta H_0(\mathbf{x}_0)} e^{-\beta \Delta H_1(\mathbf{x}_0)} P_{\tau_1}(\mathbf{x}_0|\mathbf{x}_1) \cdots e^{-\beta \Delta H_N(\mathbf{x}_{N-1})} P_{\tau_N}(\mathbf{x}_{N-1}|\mathbf{x}_N). \tag{14}$$

From the form of ΔH_1, it is clear that the term $\exp(-\beta H_0(\mathbf{x}_0))$ can be combined with the term $\exp(-\beta \Delta H_1(\mathbf{x}_0))$ to yield the term $\exp(-\beta H_{\tau_1}(\mathbf{x}_0))$. The only other factor in the integrand that is to be associated with this that depends on $\mathbf{x}_0$ is $P_{\tau_1}(\mathbf{x}_0|\mathbf{x}_1)$. The integral of this product over $\mathbf{x}_0$ can be performed by using (12) to give

$$\int d\mathbf{x}_0 \, P_{\tau_1}(\mathbf{x}_0|\mathbf{x}_1) \exp(-\beta H_{\tau_1}(\mathbf{x}_0)) = \exp(-\beta H_{\tau_1}(\mathbf{x}_1)). \tag{15}$$

This is the first of a sequence of $N + 1$ integrals in (14), and there remain N to complete. Next combine the term $\exp(-\beta H_{\tau_1}(\mathbf{x}_1))$ which was produced in writing (15) with the subsequent exponential factor in the integrand $\exp(-\beta H_{\tau_2}(\mathbf{x}))$, so there results the exponential term $\exp(-\beta H_{\tau_2}(\mathbf{x}_1))$.

Next integrate over the variable $\mathbf{x}_1$ using (12) again, and repeat this strategy until the finite number of integrations have been carried to completion. At the end of the process of combining the neighboring exponential terms in the integrand and then integrating over the corresponding $\mathbf{x}_k$ using (12), we are left with in the last step the integral

$$\langle e^{-\beta W} \rangle = \int d\mathbf{x}_N \, \frac{1}{Z_0} \exp(-\beta H_1(\mathbf{x}_N)) = \frac{Z_1}{Z_0} = e^{-\beta \, \Delta F}. \tag{16}$$

By setting up this type of procedure, the desired result (3) has been arrived at.

References

[1] D. J. Evans, E. G. D. Cohen and G. P. Morris, Probability of second law violations in shearing steady states, *Phys. Rev. Letts.*, **71** (1993), 2401-2404. https://doi.org/10.1103/physrevlett.71.2401

[2] G. Gallavotti and E. G. D. Cohen, Dynamical Ensembles in Nonequilibrium Statistical Mechanics, *Phys. Rev. Letts.*, **74** (1995), 2694-2697.

https://doi.org/10.1103/physrevlett.74.2694
[3] C. W. Gardiner, *Quantum Noise*, Springer-Verlag (Berlin), 1991. https://doi.org/10.1007/978-3-662-09642-0

[4] L. D. Landau and E. M. Lifshitz, *Statistical Physics*, Pergamon Press, Oxford, 1990.

[5] R. P. Feynman, *Statistical Mechanics, A Set of Lectures*, 2nd Ed, Westview Press, 1998.

[6] W. P. Reinhardt and J. E. Hunter III, Variational path optimization and upper and lower bounds to free energy changes via finite time minimization of external work, *J. Chem. Phys.*, **97** (1992), 1599-1601. https://doi.org/10.1063/1.463235

[7] C. Jarzynski, Nonequilibrium Equality for Free Energy Differences, *Phys. Rev. Letts.*, **78** (1997), 2690-2693. https://doi.org/10.1103/physrevlett.78.2690

[8] C. Jarzynski, Equilibrium free-energy differences from nonequilibrium measurements: A master-equation approach, *Phys. Rev. E*, **56** (1997), 5018-5035. https://doi.org/10.1103/physreve.56.5018

[9] G. Roepstorff, *Path Integral Approach to Quantum Physics*, Springer-Verlag, Berlin, 1994. https://doi.org/10.1007/978-3-642-57886-1

[10] G. E. Crooks, Nonequilibrium Measurements of Free Energy Differences for Microscopically Reversible Markovian Systems, *J. Stat. Phys.*, **90** (1998), 1481-1487. https://doi.org/10.1023/a:1023208217925

[11] G. E. Crooks, Path-ensemble averages in systems driven far from equilibrium, *Phys. Rev. E*, **61** (2000), 2361-2366. https://doi.org/10.1103/physreve.61.2361

[12] G. E. Crooks, On the Jarzynski relation for dissipative quantum dynamics, *J. Stat. Mech.: Theory and Experiment*, **2008** (2008), P10023. https://doi.org/10.1088/1742-5468/2008/10/p10023

Received: May 30, 2018; Published: June 26, 2018