# Free Energy Changes, Fluctuations, and Path Probabilities

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## Abstract

We illustrate some of the static and dynamic relations discovered by Cohen, Crooks, Evans, Jarzynski, Kirkwood, Morriss, Searles, and Zwanzig. These relations link nonequilibrium processes to equilibrium isothermal free energy changes and to dynamical path probabilities. We include ideas suggested by Dellago, Geissler, Oberhofer, and Schöll-Paschinger. Our treatment is intended to be pedagogical, for use in an updated version of our book on *Time Reversibility, Computer Simulation, and Chaos*. Comments are very welcome.

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## I. INTRODUCTION

The past 18 years have seen an explosion of activity linking *nonequilibrium* processes to entropy production, fluctuations, and free-energy changes. This work connects equilibrium statistical mechanics to far-from-equilibrium dynamics. Typically initial conditions are taken from Gibbs' equilibrium ensembles with the subsequent dynamics featuring explicitly time-dependent forces. In the end time averages with the time-dependent forces are related to equilibrium phase-space averages. This work makes contact with nonequilibrium steady state analysis as a longtime lowfield limiting case. Because it sets the stage for further theoretical advances and practical applications, these novel force-control activities deserve critical consideration. We consider two aspects of this recent research here: (1) calculating isothermal free energy differences in terms of far-from-equilibrium work; and (2) calculating the relative probabilities of *nonequilibrium* forward and reversed trajectories. We illustrate both these ideas here for a simple nonequilibrium oscillator problem.

In both cases we can make definite verifiable statements concerning *nonequilibrium* trajectories, by relating these trajectories to phase-space distributions taken from Gibbs' statistical mechanics. The new work goes well beyond Green and Kubo's linear-response theory in that it describes evolving systems far from equilibrium.

In Section II we describe Jarzynski's recent generalization of Kirkwood and Zwanzig's statistical mechanical perturbation theories. In Section III we illustrate these free-energy ideas for a toy-model oscillator, using both Hamiltonian and Nosé-Hoover dynamics. In Section IV we describe one of Crook's relations for the relative probabilities of forward and backward trajectories, and apply it to the same model oscillator system. Section V is a summary, putting this work in perspective with other contemporary efforts to enhance our understanding of nonequilibrium systems.

## II. FLUCTUATIONS IN NONEQUILIBRIUM STEADY STATES

Gibbs'[1] (and Boltzmann's) statistical mechanics is the well-established last word in relating equilibrium thermodynamic properties to microscopic phase-space states. *Nonequilibrium* properties and processes lack such a clear foundation. Their understanding is still in a state of flux. Close to equilibrium perturbation theory can be applied. Green and Kubo

used linear-response theory to treat the linear transport laws—Fick's diffusion, Newton's viscosity, Fourier's heat conduction. Green and Kubo expressed the transport coefficients in terms of equilibrium (Gibbsian) time correlation functions.

*Strongly* nonequilibrium situations are still hard to treat theoretically. These harder problems include not just the traditional "approach to equilibrium" based on Hamiltonian mechanics and Liouville's theorem, but include also analyses of nonequilibrium steady states based on deterministic, but mostly nonHamiltonian, thermostats. These thermostats can generate fractal steady-state phase-space distribution functions quite different to Gibbs' smooth canonical distributions[2].

Before computer simulation became commonplace perturbation theory was the most promising basis for a thermodynamic treatment of nonequilibrium situations. Kirkwood[3] and Zwanzig[4] computed isothermal free-energy differences directly from Gibbs' equilibrium phase-space distributions. Here we illustrate their work, as well as the recent improvements which have extended it.

Kirkwood introduced a "coupling parameter", $0 < \lambda < 1$, used to change the Hamiltonian by an amount $\Delta\mathcal{H}$:

$$\mathcal{H}(q,p,\lambda) = \mathcal{H}_0(q,p) + \lambda\Delta\mathcal{H}(q) \ .$$

Increasing the coupling parameter from 0 to 1 converts the "reference Hamiltonian" to a new one, $\mathcal{H}_1(q,p) = \mathcal{H}_0(q,p) + \Delta\mathcal{H}(q)$. The coupling parameter can be used to "turn on" an external field, like gravity, or to make a change in the interparticle forcelaw.

The corresponding $\lambda$-dependent canonical partition function, $Z$, and Helmholtz' free energy, $A$,

$$e^{-A(N,V,T,\lambda)/kT} = Z(N,V,T,\lambda) = \prod [\int\int dqdp/h] e^{-\mathcal{H}(q,p,\lambda)/kT} \ ,$$

vary smoothly with $\lambda$ from their reference values to the fully-perturbed ones:

$$A(N,V,T,1) - A(N,V,T,0) = kT \ln \frac{Z(N,V,T,0)}{Z(N,V,T,1)} \equiv \int_0^1 \langle \Delta H \rangle_\lambda d\lambda \ .$$

The overall response of the energy to the perturbation $\lambda\Delta\mathcal{H}$ made it possible to compute the corresponding (Helmholtz) free-energy change.

19 years later Zwanzig suggested making a "sudden", rather than continuous, change in $\lambda$, providing a simpler formulation of the same free-energy change:

$$A(N,V,T,1) - A(N,V,T,0) = kT \ln \frac{Z(N,V,T,0)}{Z(N,V,T,1)} = \langle \Delta\mathcal{H} \rangle_{\lambda=0} \ ,$$

with the average value of the perturbation computed using the phase-space distribution of the unperturbed Hamiltonian. If the perturbed and unperturbed phase-space distributions are not too different Zwanzig's approach is the simpler and cheaper of the two procedures.

Kirkwood and Zwanzig's procedures can equally-well be expressed in terms of the equilibrium phase-space distribution function $f(q, p, T, \lambda)$:

$$kT \ln[Z(0)/Z(1)]_{\rm Kirkwood} = \int_0^1 d\lambda \prod (\int \int dqdp) f(q, p, T, \lambda) \Delta\mathcal{H}(q) \ .$$

$$kT \ln[Z(0)/Z(1)]_{\rm Zwanzig} = \prod (\int \int dqdp) f(q, p, T, \lambda = 0) \Delta\mathcal{H}(q) \ .$$

Both these perturbation-theory approaches assume constant temperature throughout. Isothermal Monte Carlo simulations are well-suited to these equilibrium perturbation approaches[5].

*Dynamical* isothermal simulations became possible with the isokinetic approach to thermostating of the 1970s[6] and especially with the isothermal canonical thermostat introduced by Nosé in 1984[7, 8]. With these new temperature-control tools it became possible to generalize Kirkwood and Zwanzig's equilibrium phase-space ideas to far-from-equilibrium dynamical simulations[9–11].

In 1993 Evans, Cohen, and Morriss suggested a nonequilibrium phase-space measure applicable to deterministic thermostated steady-state simulations[9]. Evans and Searles clarified the applicability of this nonequilibrium measure (it becomes correct at long times) the following year[10].

Jarzynski's profound 1997 insight was that the phase-space distribution function $f(q, p, \lambda)$ need not be an equilibrium quasistatic one so long as the $\lambda$-dependent trajectory, with $\lambda = \lambda(t)$, follows Hamiltonian or Nosé-Hoover mechanics[11]. Then the mechanical description, through Liouville's Theorem, describes the nonequilibrium flow of phase-space probablity density.

Let us consider first the familiar Hamiltonian case. Then the probability density $f(q, p, \lambda(t), t)$ propagates unchanged, as does also the comoving phase volume $\otimes(q, p, t)$, even if the underlying Hamiltonian $\mathcal{H}(q, p, \lambda(t))$ is wildly time-dependent. This means that the initial equilibrium probability density at $(q_0, p_0)$: $f(q_0, p_0, \lambda = 0)$ is *identical to* the final one, at $(q_1, p_1)$: $f(q_1, p_1, \lambda = 1)$—provided that the intervening $(0 \to 1)$ dynamics is all Hamiltonian. *During* the process the "work" done by $\lambda$ along a particular phase-space trajectory is $W \equiv \int_0^1 \Delta\mathcal{H} d\lambda$. Consider then the phase-space average, over the unperturbed

distribution of trajectory starting points, of $e^{-\Delta\mathcal{H}/kT} = e^{-W/kT}$. Here the total work $W$ is evaluated *at* the time when $\lambda$, after its specified variation along the path, has reached its final value of unity:

$$\int\int f(q_0, p_0, \lambda = 0) e^{-\Delta\mathcal{H}(\lambda=1)/kT} dqdp \equiv \int\int f(q_1, p_1, \lambda = 1) dqdp \longrightarrow$$

$$Z(\lambda = 0)\langle e^{-\Delta H/kT}\rangle_0 = Z(\lambda = 1) \Longleftrightarrow e^{(A_0 - A_1)/kT} \equiv \langle e^{-W/kT}\rangle_0 \ .$$

This last equation, Jarzynski's remarkable free-energy identity (or "equality", or "relation", or "Theorem") gives the *equilibrium* free-energy difference in terms of arbitrarily *far-from-equilibrium* phase-space trajectories.

The dynamics need not be Hamiltonian. Jarzynski extended the free-energy relation to include thermostated Nosé-Hoover dynamics[11]. In that thermostated case the comoving phase volume changes with time:

$$\frac{\otimes(t)}{\otimes(0)} = \frac{f(0)}{f(t)} = \frac{(dqdpd\zeta)_t}{(dqdpd\zeta)_0} \equiv e^{-\int_0^t \zeta(t')dt} \ ,$$

where $\zeta(t')$ is the Nosé-Hoover thermostating friction coefficient. In the end the free-energy result is exactly the same, as we will detail and check numerically in the next Section, with a simple example problem.

Naturally enough, some doubted these surprising results. See, for instance, references [12] and [13]. After some prodding by naysayers, Jarzynski published more details and extensions of his proofs, valid for stochastic thermostats as well as for the Hamiltonian and Nosé-Hoover situations, and including *any* time-reversible equations of motion which maintain the canonical distribution[13]. Let us consider the Nosé-Hoover case in more detail.

For the Nosé-Hoover motion equations an "extended" (to include $\zeta$) canonical distribution is maintained by the equations of motion:

$$\{\ \dot{q} = p/m\ ;\ \dot{p} = F - \zeta p\ \}\ ;\ \dot{\zeta} = [(K/K_0) - 1]/\tau^2 \Longleftrightarrow f \propto e^{-\mathcal{H}/kT} e^{-\zeta^2\tau^2/2} \ .$$

Here $\zeta$ is a control variable, controlling the kinetic energy $K \propto p^2$. $K_0$ is the kinetic energy corresponding to the specified temperature $T$ and $\tau$ is the (arbitrary) relaxation time controlling the timescale of the resulting kinetic temperature fluctuations. This same derivation can be carried through with the generalized distribution [including the factor $e^{-(\zeta\tau)^2/2}$] at time 0. Multiplying that distribution by the exponential of $-W/kT$, gives again the generalized distribution when $\lambda$ reaches unity and establishes Jarzynski's free-energy

relation for Nosé-Hoover dynamics. The only new aspect is the need to take the changing phase-volume change into account, as is most clearly described by Schöll-Paschinger and Dellago[14]. Let us illustrate the Kirkwood-Zwanzig-Jarzynski ideas with a simple example, a harmonic oscillator whose force constant varies with time.

## III. THE FREE ENERGY THEOREMS ILLUSTRATED FOR AN OSCILLATOR

To illustrate first Kirkwood's coupling-parameter idea, as extended later by Zwanzig and Jarzynski, consider a thermostated (canonical distribution) one-dimensional harmonic oscillator with unit mass. We choose to increase the oscillator force constant $\kappa$ from unity to four as $\lambda(t)$ is slowly increased ("quasistatically"; "reversibly") from 0 to 1:

$$1 < [\kappa \equiv 1 + 3\lambda] < 4 \longrightarrow$$

$$Z(\lambda) = (1/h) \int_{-\infty}^{+\infty} e^{-p^2/2kT} dp \int_{-\infty}^{+\infty} e^{-(1+3\lambda)q^2/2kT} dq = kT/h\nu \ ; \ 2\pi\nu = \sqrt{1+3\lambda} \ .$$

$$\phi = (1/2)q^2[1+3\lambda] \rightarrow \ln \frac{Z(N,V,T,0)}{Z(N,V,T,1)} = \ln \left[ \frac{(kT/h\nu_0)}{(kT/h\nu_1)} \right] = \ln \left[ \frac{(kT/h\nu_0)}{(kT/2h\nu_0)} \right] = \ln 2 \ .$$

For simplicity we choose unit temperature, $kT = \langle p^2/m \rangle = 1$. The completed perturbation reduces the rms fluctuations in $\langle q^2 \rangle$ by a factor of two and increases the Helmholtz free energy by $kT \ln 2$. Kirkwood's quasistatic analysis calculates the partition-function ratio by integration of the work associated with the perturbation:

$$\ln \frac{Z(N,V,T,0)}{Z(N,V,T,1)} = -\int_0^1 (\partial \ln Z/\partial\lambda) d\lambda = \int_0^1 (3/2) d\lambda/(1+3\lambda) = (1/2)[\ln(4) - \ln(1)] = \ln 2 \ .$$

From this standpoint the free energy difference is simply the integrated work needed to make a very gradual, reversible change in the Hamiltonian.

Zwanzig's approach is standard perturbation theory. It corresponds physically to a *sudden* change in the Hamiltonian,

$$\mathcal{H} = (q^2 + p^2)/2 \stackrel{\text{sudden}}{\longrightarrow} (4q^2 + p^2)/2 \ .$$

The free energy change can then be written as the average value of the perturbation's effect on the unperturbed ($\lambda = 0$) canonical probability density:

$$A(N,V,T,0) - A(N,V,T,1) = kT \ln \langle e^{-(3/2)q^2/kT} \rangle_0 = kT \ln(kT/4)/(kT/2) = -kT \ln(2) \ .$$

Jarzynski's nonequilibrium generalizations of these Gibbsian ideas can be checked by using either Hamiltonian or Nosé-Hoover dynamics to implement the perturbation. This choice is not entirely coincidental. Dettmann showed that single-temperature Nosé-Hoover mechanics has its roots in an underlying Hamiltonian[15].

Using a relaxation time of unity, and unit temperature, the equations of motion for $(0 < t < 1)$ in the two cases are:

$$\dot{q} = p \ ; \ \dot{p} = -q(1+3t) \ ; \ \dot{I} = 3q^2/2 \ [\text{Hamiltonian}] \ ;$$

$$\dot{q} = p \ ; \ \dot{p} = -q(1+3t) - \zeta p \ ; \ \dot{\zeta} = p^2 - 1 \ ; \ \dot{I} = 3q^2/2 \ [\text{Nosé} - \text{Hoover}] \ .$$

For each trajectory we compute the exponential of the work integral

$$e^{-\int_0^1 W(t')dt/kT} = e^{-W/kT} = e^{I_0 - I_1} \ .$$

The complete trajectory integral, $I(1) - I(0)$ includes the work done on the oscillator by the perturbation, and includes also (in the Nosé-Hoover case) the changing phase volume.

$$\int_0^1 \dot{I} dt = W/kT \ [\text{Hamiltonian}] \ ; \ \int_0^1 \dot{I} dt = W/kT \ln[\otimes(0)/\otimes(1)] \ [\text{Nosé} - \text{Hoover}] \ .$$

In the Nosé-Hoover case this last result follows from the useful identity:

$$\dot{\mathcal{H}}_\lambda = (d/dt)[(q^2(1+3t) + p^2 + \zeta^2)/2] = (3q^2/2) - \zeta \Longrightarrow$$

$$\int\int\int (dqdpd\zeta/h)_0 e^{-\mathcal{H}_0/kT} e^{-W/kT} = \int\int\int (dqdpd\zeta/h)_1 e^{-[4q^2 + p^2 + \zeta^2)/2]} \equiv Z_1 \ .$$

The expression in square brackets is the "extended" Nosé-Hoover Hamiltonian $\mathcal{H}_\lambda$. In the Nosé-Hoover case the "extended" partition functions $Z_0$ and $Z_1$ include integrations over the thermostat variable $\zeta$.

For numerical Runge-Kutta integration of trajectories we chose the initial values of $(q, p)$ or $(q, p, \zeta)$ from equilibrium (Gaussian) distributions $\propto e^{(-q^2 - p^2)/2}$ or $e^{(-q^2 - p^2 - \zeta^2)/2}$. We verified Jarzynski's relations numerically by choosing and analyzing *millions* of trajectories. We computed average values of the left side, $\langle e^{-W} \rangle$, and the right side, $e^{\Delta A/kT}$, of the Jarzynski relations. For 100 million collisions, with either Hamiltonian or Nosé-Hoover mechanics, his predicted average value of the partition-function ratio, $I = (1/2)$, is nicely reproduced, with four- to five-figure accuracy, perfectly consistent with both versions of Jarzynski's 1997 theorem. Such Theorems are also valid for other deterministic and stochastic equations of motion as is detailed in References [16]-[19].

## IV. CROOK'S REVERSIBILITY RELATION

Crooks and Jarzynski used a variation of these ideas[16] to compute the relative probabilities of forward and reversed nonequilibrium trajectories. Their work makes contact with the seminal 1993 and 1994 papers of Evans, Cohen, Morriss, and Searles[9, 10]. Though Crooks and Jarzynski emphasize stochastic dynamics we illustrate one of their results here for time-reversible deterministic Hamiltonian dynamics. This version of their Theorem (or "result", or "relation", or "identity") can also be viewed as an illustration (or consequence) of "detailed balance" or "microscopic reversibility", the equal likelihood of forward and backward trajectories linking two microstates. For convenience we will choose those as states of the time-dependent oscillator at times 0 and 1.

In order to understand their formulation of the problem let us compare two probabilities: the "forward" orbit of a canonical oscillator going from the phase point $(q_0, p_0)$ at time 0 to $(q_1, p_1)$ at time 1; the "backward" orbit of the oscillator, equilibrated at $(q_1, -p_1)$ and going backward to $(q_0, -p_0)$. On the forward orbit the force constant increases from 1 to 4; on the backward orbit the force constant decreases, from 4 to 1. The probability for the forward and reversed trajectories are not equal because the initial energies and free energies differ. In the forward and backward directions the normalized rates are proportional to

$$e^{(A-H)_0/kT}(dqdp)_0 \ ; \ e^{(A-H)_1/kT}(dqdp)_1 \ ,$$

with

$$\Delta H = H_1 - H_0 = W = \int_0^1 (3/2) q^2 dt \ ; \ \Delta A = A_1 - A_0 = kT \ln 2 \ .$$

Evidently the ratio of the forward and backward rates is:

$$\frac{e^{(A-H)_0/kT}(dqdp)_0}{e^{(A-H)_1/kT}(dqdp)_1} = e^{(-\Delta A + W)/kT} \ .$$

The *dqdp* phase-volume elements cancel according to Liouville's Theorem. This is (one of) Crook's "Fluctuation Theorems", a simple consequence of the time reversibility of the Hamiltonian equations of motion. Like the free energy theorems, it can easily be checked by Runge-Kutta integration.

If we view the extra dissipated work as a time-integrated entropy production,

$$\Delta S = (W - \Delta A)/T \ ,$$

then this fluctuation theorem has the same form as the longtime steady-state relation[9]

$$\ln\left[\frac{prob(+\sigma)_\tau}{prob(-\sigma)_\tau}\right] = [\sigma\tau/k] \ ,$$

where the entropy production rates $\sigma$ are observed average values during an averaging "time window" of length $\tau$.

## V. PERSPECTIVES

Jarzynski's isothermal free-energy relations link equilibrium statistical mechanics to nonequilibrium dynamics. Though the Jarzynski work includes arbitrary time-dependent forces this approach requires equilibrium initial conditions and is limited to a single fixed temperature $T$. We still need theories for treating more general nonlinear problems, such as stationary shockwaves. Shockwaves link together equilibrium states with two different temperatures. Within the shockwave the temperature is a tensor, with $T_{xx} \neq T_{yy}$[18].

We still need good methods for understanding the fractal phase-space structures of systems with two or more temperatures, not just one. So far the only connection between the smooth Liouville-Theorem approach of the present work and truly nonlinear steady states is at the linear level of the Central Limit Theorem and Green-Kubo linear response.

The processes for which the recent theorems are relevant involve entropy changes of only a few $k$ and energy changes of only a few $kT$. Macroscopic consequences of the Fluctuation Theorems are simply unobservable. Even so, from the theoretical standpoint the new ideas are stimulating, relating "real" finite-rate processes to equilibrium thermodynamics. Unlike Kirkwood and Zwanzig's earlier efforts, the new approaches do have counterparts in micron-scale laboratory experiments in which long molecules or latex balls are manipulated with external forces. The back-and-forth fluctuations in these many-body systems can be approximated with theoretical results for thermostated models with a few degrees of freedom. See the reviews [19] and [20] for references. Evidently all three routes to understanding, theory, simulation, and experiment are linked together by these revolutionary ideas.

From the computational standpoint the new theorems are not particularly "useful" for free-energy work. A careful investigation showed that the original ideas of Kirkwood and Zwanzig are less costly than Jarzynski's in making numerical free-energy estimates[17].

The literature on this subject is particularly hard to follow. There is a tension between

derivations treating the most general case possible and special cases, which are easier to grasp. Fairly widespread confusion is evident from the several papers purporting to find flaws in the published proofs. There is an enduring need for more example problems to explore the useful ranges of the many theorems.

The derivations make use of the detailed reversibility of Hamiltonian or thermostated mechanics. Systems away from equilibrium for a few Lyapunov times cannot be reversed due to Lyapunov instability. Typically the phase volume shrinks, forward in time, so that the reversed trajectory, with growing phase volume, is dynamically unstable, and soon seeks out a phase-space attractor rather than following the repellor. Shockwaves illustrate another difficulty in reversing irreversible processes. From the macroscopic standpoint an attempt to reverse a strong shockwave would result instead in a nearly isentropic rarefaction fan. Whether or not this qualitative irreversibility will have a counterpart in the highly nonequilibrium systems which can be treated theoretically remains to be seen.

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