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Thermodynamics as a nonequilibrium path integral

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Abstract
Thermodynamics is a well-developed tool to study systems in equilibrium but no such general framework is available for nonequilibrium processes. The only hope for a quantitative description is to fall back upon the equilibrium language as often done in biology. This gap is bridged by the work theorem. By using this theorem, we show that the Barkhausen-type nonequilibrium noise in a process, repeated many times, can be combined to construct a special matrix $S$ whose principal eigenvector provides the equilibrium distribution. For an interacting system, $S$, the equilibrium distribution can be obtained from the free case without any requirement of equilibrium.

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(Some figures in this article are in colour only in the electronic version)

1. Introduction

A system in thermodynamic equilibrium has no memory of its past. Consequently, there is no leading role for time in the ensemble-based statistical mechanics except the subservient one to maintain equilibrium among the internal degrees of freedom and with external sources. This wisdom gets exploited in the dynamics-based algorithms such as Monte Carlo, molecular dynamics, stochastic quantization, to name a few, to attain equilibrium from any arbitrary state albeit in infinite time. Even a thermodynamic process involving changes in parameters is an infinite sequence of equilibrium states, and is therefore infinitely slow. A finite-duration process, not destined to equilibrate at every instant of time, maintains a memory of the initial conditions or a short time correlation of states. The biased sampling of the phase space keeps these processes outside the realm of statistical mechanics and thermodynamics. In this equilibrium–nonequilibrium dichotomy, a work theorem [1, 2, 4–6] attempts to bridge the gap by providing a scheme for obtaining the thermodynamic free energy difference from a properly weighted nonequilibrium path integral [4, 5].

We show in this paper that purely nonequilibrium measurements of work done give an operator $S$, defined on the phase or configuration space, whose normalized principal right
eigenvector is the equilibrium probability distribution. Our result is valid for any number of parameters including temperature and interaction. With this extension, we can obtain the equilibrium distribution by constructing a matrix $S$ connecting any two allowed states of the system without any reference to equilibrium anywhere, thereby completely blurring the boundary between equilibrium and nonequilibrium. This finds direct application in out-of-equilibrium phenomena such as hysteresis.

Barkhausen noise is an example of nonequilibrium response of a ferromagnet as the magnetic field is changed at a given rate [8, 9]. By measuring the voltage induced in a secondary coil as the current in the primary coil wound around a ferromagnet is changed, one obtains the time variation of the magnetization. The noisy signal one obtains is not unique but stochastic in nature, reflecting the fluctuating microscopic response to the external field. Such signals have been analyzed in the past to extract information such as avalanche statistics, material characteristics, etc. Our results find a different use of the Barkhausen noise to construct the $S$ matrix. Similar constructions for other cases such as protein or DNA dynamics in vivo, pulling of polymers in single-molecule experiments etc, call for a new class of experiments to monitor the noise signals during these events.

This paper is organized as follows. In section 2, we recapitulate the work theorem, introduce the paths and discuss the connection between the work theorem and the histogram transformation of equilibrium statistical mechanics. In section 3, we give a simple and general dynamics-independent proof of the relation between the equilibrium probability distribution and the work done in nonequilibrium paths. This relation in some form is already known [4, 5] but our derivation allows us in generalizing the result to other cases involving temperature, interactions, etc. Section 4 deals with the main result of this paper. There we prove the eigenvalue equation for $S$. A few examples are also given there. How to obtain the operator $S$ directly from the experimental measurements of Barkhausen noise is also discussed here. Numerical verifications of some of the results are presented in section 5 by taking the 2D Ising model as an example. We summarize in section 6.

2. Work theorem and path integral

2.1. Work theorem

Consider a classical system described by a Hamiltonian $H(\Lambda, x)$ where $\Lambda$ is an external field that couples to its conjugate, a microscopically defined quantity, $x$. The thermodynamic state is specified by temperature $T$ and field $\Lambda$. Let us start with the system at $\Lambda = 0$ in thermal equilibrium at temperature $T$. The external field $\Lambda$ is changed in some given way from 0 to a final value $\lambda$, in a finite time $\tau$ or in a finite number of steps $n$, letting the system evolve in contact with the heat reservoir. No attempt is made to ensure equilibrium during the process. The variation of $x$ along the nonequilibrium path ($x(t)$ versus $t$) and the instantaneous final (boundary of the path) value of $x$, $x_b$, when the field reaches $\lambda$, are noted. The work done along the nonequilibrium path by the external source (as in [2]) is

$$W = \int_0^\tau \frac{\partial H}{\partial \Lambda} \frac{d\Lambda}{dt} \, dt,$$

in time $\tau$, and it varies from path to path. The difference between the two definitions of work in the context of work theorem, one used in [1] and the other in [2], is discussed in [3]. For the sake of notational simplicity, we choose

$$H = H_0 + H_1(\Lambda, x) = H_0 - \Lambda \, x,$$

where $H_0$ is the energy for $\Lambda = 0$. There is not much loss of generality in choosing the form of equation (2) because $\Lambda$ and $x$ refer to any pair of conjugate variables so that $x$ itself need
not be a linear function of the internal coordinates. As an example, in an interacting spin problem in a magnetic field $h \equiv h/\Lambda_1$, \( H = H_0 - h \sum_k s_k \), where $s_k$ is the spin variable at a site denoted by $k$, with $x = \sum_k s_k$. Often $\Lambda$ can be taken as the switching parameter to turn on a perturbation or interaction in a Hamiltonian $H = H_0 - H'$ with $H_\Lambda = H_0 - \Lambda H'$.

The work theorem [1, 2] provides the equilibrium free energy difference $\Delta F$ between the two states with $\Lambda = 0$ and $\Lambda = \lambda$, both at inverse temperature $\beta = 1/k_BT$ ($k_B$ is the Boltzmann constant), from the nonequilibrium work done as

$$\Delta F = -\frac{1}{\beta} \ln(e^{-\beta W}),$$

(3)

where $\langle \ldots \rangle$ denotes the average over all possible paths.

2.2. Paths: equilibrium and nonequilibrium

We are using here a description of a state by the intensive parameters which actually characterize the surroundings. In equilibrium, any system is expected to have the values of the intensive parameters same as that of the environment. A change in any of the parameters, say $\Lambda$, from $\Lambda_0$ to $\Lambda$, would require heat and/or energy transfer. The work done on or by the system is determined by the change in the free energies, independent of the path of variation of the intensive parameters. This is expressed as

$$\Delta F = W_{eq} = -\int_{\Lambda_0}^{\Lambda} x_{eq}(\Lambda) d\Lambda,$$

(4)

where $\Delta F = F(\beta, \lambda) - F(\beta, \lambda_0)$. Here, $x_{eq}(\Lambda) = \int x P_\Lambda(x) dx$ is the equilibrium average at the instantaneous values of the intensive parameters, and $P_\Lambda(x)$ is the corresponding equilibrium probability distribution of $x$. This follows from the identification of the equilibrium value of $x$ as $x_{eq} = -\partial F/\partial \Lambda$, in contrast to the conjugate ensemble definition $\Lambda = \partial F/\partial x$ where $F(\beta, x)$ is the fixed-$x$ ensemble free energy.

For convenience, let us discretize the integrals. For example, for $\Lambda \in [\lambda_0, \lambda]$, we have a sequence $(\Lambda_0, \Lambda_1, \ldots, \Lambda_n = \lambda)$ and the continuum is recovered by taking the usual limit of $n \to \infty$ with $\max{\Delta \Lambda_i} = \Lambda_{i+1} - \Lambda_i \to 0$. The work done can be rewritten as

$$W_{eq} = -\sum_{i=0}^{n} \Delta \Lambda_i \left\{ \sum_x P_{\Lambda_i}(x) x \right\}.$$

(5)

By interchanging the sums over $x$ and $\Lambda$, we define (i) a sequence $\{x_i|i = 0, \ldots, n\}$ as instantaneous values, and (ii) a sequence-dependent work done as $W = \sum_i x_i \Delta \Lambda_i$, to reinterpret equation (5) as an average over these $x_i$’s. Therefore,

$$W_{eq} = -\sum_{\{x_i\}} P[x_i] \sum_i x_i \Delta \Lambda_i,$$

(6)

where $P[x_i] = \prod_i P_{\Lambda_i}(x_i)$ is the joint probability of obtaining the particular sequence $\{x_i\}$ because for a thermodynamic process, there is no memory. Going over to the continuum limit, the thermodynamic process of varying $\Lambda$ is now seen as equivalent to choosing a path in the configuration space and re-weight the paths according to the probability of its occurrence in the $\Lambda$-ensemble. The relation between the free energy change and work, equation (4), now has a path integral meaning where the process takes the system over the microstates and one averages the work over individual paths.

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This thermodynamic connection is valid only in equilibrium. The work theorem generalizes this idea by replacing \( P[\lambda] \) by the nonequilibrium probability of obtaining a path and asserting

\[
e^{-\beta \Delta F} \equiv \frac{Z_\lambda}{Z_0} = \int \mathcal{D}\lambda' e^{-\beta W},
\]

where \( \int \mathcal{D}\lambda' \) stands for the normalized sum over paths, i.e. sum over intermediate \( \lambda' \)'s with appropriate probabilities.

### 2.3. Histogram transformation and infinitely fast process

There is a fundamental transformation rule obeyed by the partition function, often used in numerical simulations as the histogram method [7]. This transformation connects the equilibrium probability distributions at two parameter values, \( \Lambda = \lambda_0 \) and \( \Lambda = \lambda \), as

\[
P_\lambda(x) = P_{\lambda_0}(x) e^{\beta(\lambda - \lambda_0)x} \sum_x P_{\lambda_0}(x) e^{\beta(\lambda - \lambda_0)x},
\]

where the sum in the denominator is over the allowed values of \( x \). The denominator on the right-hand side of equation (8) is \( Z_\lambda/Z_{\lambda_0} \) where \( Z_\lambda \) is the partition function at an inverse temperature \( \beta \),

\[
Z_\lambda = \sum_{\text{states}} e^{-\beta H_0} e^{\beta \Lambda x}.
\]

From equation (1), \( (\lambda - \lambda_0)x \) can be taken as the work done in an instantaneous process that changes \( \Lambda \) from \( \lambda_0 \) to \( \lambda \) without changing \( x \). The probability of obtaining \( x \) for equilibrium at \( \lambda_0 \) is \( P_{\lambda_0}(x) \), and therefore the sum in the denominator of equation (8) is the path integral of equation (7) because \( x \) does not change. This gives the work theorem.

### 3. Equilibrium probability distribution

In this section, we use the discrete version of the process to re-derive the equilibrium probability distribution from the work theorem in a general and dynamics-independent way. For the kind of nonequilibrium processes mentioned in section 2.2, the equilibrium probability distribution of \( x \) at a parameter value \( \lambda \) can be obtained from a weighted path integral [4, 5]

\[
P_\lambda(x) = \int \mathcal{D}\lambda' e^{-\beta W} \delta(x_b - x) \int \mathcal{D}\lambda' e^{-\beta W},
\]

where \( x_b \) is the instantaneous boundary value at the end of the path, and the denominator is the same as that of the rhs of equation (7). This is in the form of a path integral where the paths are weighted by a Boltzmann-like factor \( \exp(-\beta W) \). The same was established previously in specific cases, such as the Master equation approach [2], the Feynman–Kac formula [5] and Monte Carlo dynamics [4].

The equilibrium average \( x_{eq} \) is defined as

\[
x_{eq} = \frac{1}{\beta} \frac{\partial}{\partial \Lambda} \ln Z_\Lambda = \lim_{\delta \to 0} \left( \beta \frac{Z_\Lambda}{Z_0} \right)^{-1} \frac{1}{\delta} \left( \frac{Z_\Lambda}{Z_0} - \frac{Z_{\Lambda-\delta}}{Z_0} \right),
\]

where work theorem is to be used for the partition functions.

The system starts in equilibrium at temperature \( T \) and \( \Lambda = 0 \), and then \( \Lambda \) is built up at constant \( T \) as a sequence of infinitely fast jump of \( \Delta \lambda = \lambda/n \), each jump followed by a finite time evolution in contact with the heat bath. Consider now two \( n \)-step processes, one process
with a final field $\lambda$ and another one with $\lambda - \delta$ ($\delta \to 0$ at the end). In fact, the second process is just a copy (replica) of the first one in every respect except at the last stage (figure 1). For the last jump, the change in $\Lambda$ for replica 1 is $\Delta_1 \lambda$ while for replica 2 it is $\Delta_1 \lambda - \delta$.

A path is specified or defined by the sequence $\{x_i | i = 0, \ldots, n-1\}$. The changes in $x_i$ at any step is because of internal dynamics or exchange of heat with the external reservoirs. We do not need to let the system evolve once the field reaches the final desired value. Therefore, the sequence $\{x_i | i = 0, \ldots, n-1\}$ is the same for both the replicas. The work done $W_1, W_2$ along an $n$-step nonequilibrium path for replicas 1, 2 is related via

$$W_2 = W_1 + \delta x_{n-1},$$

(12)

where $W_1$ is of the form given above in equation (6). The work theorem of equation (7) when used in equation (11) yields

$$x_{eq} = \lim_{\delta \to 0} \frac{1}{\beta} \sum_{\text{paths}} e^{\beta \sum_{i=0}^{n-1} \Delta_i} (1 - e^{-\beta \delta x_{n-1}})$$

$$= \int \mathcal{D}x e^{-\beta W}$$

$$\int \mathcal{D}x e^{-\beta W} (x_b \equiv x_{n-1}).$$

(13)

This shows that the equilibrium average can be expressed in terms of the boundary value with proper weightage of the paths. The above proof can be generalized to any moments of $x$.

Now if $P(x)$ is the distribution of $x_b$ that gives the average in equation (13),

$$x_{eq} = \langle x \rangle = \int x P(x) \, dx,$$

(14)

then $P(x)$ can be written as

$$P(x) = \frac{\int \mathcal{D}x e^{-\beta W} \delta(x_b - x)}{\int \mathcal{D}x e^{-\beta W}}.$$

(15)

as quoted in equation (10). We now invoke the moment theorem [12] which, in our case, states that for a probability distribution without sufficiently long tails, the moments uniquely specify the distribution. Since these conditions are satisfied by the equilibrium probability distributions for any finite system, the moment theorem applies. Since the moments from the nonequilibrium path integral are the equilibrium moments, $P(x)$ is the equilibrium distribution: $P(x) = P_{eq}(x)$. This completes the proof.
3.1. Generalization

In general, for a Hamiltonian of the form $H = H(\{\Lambda_\alpha\}, \{X_\alpha\})$, the equilibrium distribution $P(E, x_1, x_2, \ldots)$, at some given parameter values $\{\lambda_\alpha\}$ and temperature $\beta^{-1}$, can be obtained in the same way provided the paths start from an equilibrium state for $H = H_0$, where $H_0$ gives the energy for all $\Lambda_\alpha = 0$ and $W$ is the total work done on the system along a nonequilibrium path by each of the externally controlled parameters. Here $E$ corresponds to the energy from $H_0$ only. Our starting $H_0$ may be a free Hamiltonian for a mechanical system and can as well be zero for interacting spin-like systems.

Consider the Hamiltonian $H = \gamma H_0$ for a spin-like system (i.e. without any kinetic energy). In this case, one of the $\{\Lambda_\alpha\}$ could be the strength of interaction. Let us start with $\gamma = 0$, i.e. the starting point is any random configuration of the free system or a non-interacting system, and then change $\gamma$ in some given way from $\gamma = 0$ to $\gamma = 1$. We thus generate the equilibrium distribution of $H_0$ at a particular $\beta$, by doing a similar nonequilibrium path averaging. Note that we need the product $\beta W$ everywhere. So we can discretize temperature instead of $\lambda_\alpha$, and the process can be reinterpreted as cooling down to a finite temperature from an initial infinite temperature. In the usual formulation of work theorem, $\Lambda$ refers to mechanical parameters such as the pulling force in AFM, which are under direct control of the experimentalists. In contrast, other intensive parameters such as temperature may not be controlled with this level of precision in experiments. But this finds various applications in numerical experiments. Such thermal quenches are quite common in numerical simulations and our results show how these can be harnessed to extract equilibrium information as well. The ensemble of states obtained in the above-discussed way at the end of the path is not a representative sample of the equilibrium ensemble at the concerned temperature and field. However, the history-averaged distribution is the equilibrium distribution. The boundary states would relax to reach equilibrium via energy transfer to the reservoirs but that part of the process is not required. This difference becomes important and visible in systems exhibiting hysteresis as e.g. for a ferromagnet.

3.2. Application to a ferromagnet to obtain an equilibrium magnetization curve

The above-mentioned scheme can be used to obtain the equilibrium probability distribution or thermodynamic quantity from a process which is arbitrarily away from equilibrium and at all temperatures including phase transition points. Now we apply our result to the case of hysteresis of a ferromagnet below the critical temperature ($T_C$). Consider a Hamiltonian: $H = H_0 - hM$. The external magnetic field is varied from $-h_0$ to $+h_0$ in a fixed manner and then reversed. $\langle M \rangle$ is calculated using equation (13). Below the critical temperature, the magnetization ($M$) versus magnetic field ($h$) curve shows a discontinuity at $h = 0$ for a system of infinite size. For a finite system, there is no discontinuity, the $M$–$h$ curve is continuous passing through the origin and the slope of the $M$–$h$ curve at $h = 0$ increases as the system size increases. But, in reality, when experiments or simulations are carried out, instead of single retraceable curve passing through the origin, we obtain a loop called hysteresis loop, no matter how slowly we vary the magnetic field. A common technique to obtain the equilibrium curve is to connect the vertices of the sub-loops [9]. Here, the weighted nonequilibrium path integral scheme is a way out to obtain the equilibrium magnetization curve. We verify this for the Ising ferromagnet and discuss the observations about it in section 5.
4. Equilibrium probability distribution from an eigenvalue equation: operator $S$

In this section, we derive the main result of this paper: equilibrium probability distribution as an eigenfunction of a nonequilibrium operator $S$.

Using the discrete notation, we can write equation (10) as

$$P_{\lambda}(x) = \frac{Z_{\lambda}}{Z_{\lambda_0}} \sum_{\text{paths}} e^{-\beta W} \delta_{\lambda_0, x},$$

by using the work theorem, equation (3), that

$$\sum_{\text{paths}} e^{-\beta W} = \frac{Z_{\lambda}}{Z_{\lambda_0}}.$$  \hspace{1cm} (17)

Again, writing \(\sum_{\text{paths}} = \sum_{x_i} P_{\lambda_0}(x_i) \sum'_{\text{paths}}\), where the primed summation denotes the sum for the fixed initial value of \(x = x_i\) with appropriate probability and \(P_{\lambda_0}(x_i)\) denotes the equilibrium distribution of \(x_i\) for \(\Lambda = \lambda_0\), we obtain

$$P_{\lambda}(x) = \frac{Z_{\lambda}}{Z_{\lambda_0}} \sum_{x_i} \sum_{\text{paths}}' P_{\lambda_0}(x_i) e^{-\beta W} \delta_{\lambda_0, x_i}. $$  \hspace{1cm} (18)

By using the transformation rule for the partition function (section 2.3),

$$\frac{Z_{\lambda}}{Z_{\lambda_0}} = \sum_x P_{\lambda_0}(x) e^{\beta(\lambda - \lambda_0)x}, $$  \hspace{1cm} (19)

to absorb \(Z_{\lambda_0}/Z_{\lambda}\) into the probability distribution. This transforms \(P_{\lambda_0}(x_i)\) into \(P_{\lambda}(x_i)\) in equation (18) as

$$P_{\lambda}(x) = \sum_{x_i} \sum_{\text{paths}}' e^{-\beta W - \beta(\lambda - \lambda_0)x_i} \delta_{\lambda_0, x_i} P_{\lambda}(x_i) $$

$$= \sum_{x_i} S_{x, x_i} P_{\lambda}(x_i), $$  \hspace{1cm} (21)

$$\Rightarrow S \mathbb{P}_{\lambda} = \mathbb{P}_{\lambda}, $$  \hspace{1cm} (22)

with \(\mathbb{P}_{\lambda}\) as a column vector of \(\{P_{\lambda}(x)\}\) and the matrix elements of \(S\) as

$$S_{x_i, x} = \sum_{\text{paths}}' e^{-\beta W - \beta(\lambda - \lambda_0)x_i}. $$  \hspace{1cm} (23)

The summation in equation (23) is over all paths that start from an equilibrium distribution of \(\Lambda = \lambda_0\) with the value of \(x\) as \(x_i\) and end in a state with \(\Lambda = \lambda\) and \(x = x_f\), with proper normalization (denoted by prime).

Although we use the simple Hamiltonian \(H = H_0 - \Lambda x\) in the construction, equation (23) can be generalized for a Hamiltonian \(H = H_0(L(x, x))\) because equation (19) has the general form

$$\frac{Z_{\lambda}}{Z_{\lambda_0}} = \sum_x P_{\lambda_0}(x) e^{-\beta[H(\Lambda, x) - H(\Lambda_0, x)]}. $$

Now we address the remaining problem—the normalization of the primed summation over paths in equation (23). This problem is inherited from equation (17). Note that the lhs of equation (17) is equal to 1 for \(\lambda = \lambda_0\) with \(W = 0\). So we choose the hidden factor \(a posteriori\) by demanding proper normalization of the final probability distribution. This condition can
be ensured in a process or in a system-independent way by choosing \( \sum x \in x_i = f(x_i) = 1 \) (equation (21)), i.e. by making the column sum of \( S \) independent of \( x_i \). By this normalization of the sum of each column to unity, it is also guaranteed that the principal eigenvalue is 1. The corresponding right principal eigenvector has all the elements real and non-negative—a necessary condition to be a probability distribution, and when normalized, such that the sum of all elements is unity, this eigenvector gives the equilibrium probability distribution.

The number of rows and columns in \( S \) is determined by the number of allowed values of \( x \). For continuum of states, the matrix equation is to be replaced by an integral eigenvalue equation.

Hence, in brief, the scheme to obtain the equilibrium distribution at some parameter value \( \lambda \) and temperature \( \beta \) is as follows: pre-fix some arbitrary or convenient-to-start-with initial parameter value \( \lambda_0 \) which will be the same for all paths/experiments. Choose a microstate from the equilibrium distribution at the field \( \lambda_0 \) and denote its value of \( x \) as \( x_i \). Change the parameter value from \( \lambda_0 \) to \( \lambda \) in some predetermined way and measure the work done by the external parameter on the system according to equation (1). Repeat the experiments several times and construct the matrix \( S \) using equation (23). Next, each column of the matrix is normalized to unity. The normalized principal eigenvector is the equilibrium probability distribution, \( P_{\lambda}(x) \), at the field \( \lambda \).

Equation (22) is the main result of this paper, and it is not restricted to only one external parameter and can be generalized to any parameter as mentioned above. The matrix \( S \) connects any two allowed states of the system without any reference to equilibrium anywhere, and yet its principal eigenvector determines the equilibrium distribution. Despite resemblance, there is no similarity either with the stochastic matrix of a Markov process or the adiabatic switching of interaction in a quantum system because \( S \) is constructed out of a finite process and needs global information about the work done.

Another issue that occurs in this approach via \( S \) is the question of ergodicity which connects the Gibbsian statistical mechanics with equilibrium thermodynamics. The nonequilibrium dynamics used to construct \( S \) may not respect ergodicity but the starting points for the paths in principle span the whole phase space, even in the case when one starts with a free non-interacting system. It seems that ergodicity of the free non-interacting system is sufficient to generate the equilibrium distribution.

### 4.1. Examples

#### 4.1.1. Example 1: extreme cases

Consider an extreme case: a complete equilibrium evolution of the system, where at each step the system reaches its equilibrium. Take a simple system: a single-spin problem in the magnetic field \( h \) and temperature \( \beta^{-1} \): \( \beta H = -Ks \), where \( s = \pm 1 \) and \( K = \beta h \). For an \( n \)-step process, \( K \) varies from 0 to \( nk \) in steps of \( k \), and the column-normalized \( S \) matrix can be calculated exactly, where at each step the spin reaches the corresponding equilibrium state, as

\[
S = \begin{pmatrix}
P_{nk}(+) & P_{nk}(+)
P_{nk}(-) & P_{nk}(-)
\end{pmatrix},
\tag{24}
\]

where \( P_{nk}(\pm) \) is the equilibrium probability of finding \( \pm 1 \) spin at the \( n \)th step. Thus, for a complete equilibrium evolution of the system, the elements of the matrix \( S \) are unique, and therefore \( S \) has only one and unique eigenvector. In that case, the principal eigenvalue is 1, and all other eigenvalues are 0. We may conclude that a complete reducibility of \( S \) is the signature of a thermodynamic process.
Equation (24) is to be compared with the extreme nonequilibrium process as embodied in equation (8). For this instantaneous change in \( \lambda \), \( S = I \), the identity matrix with no zero eigenvalues.

If at each of these \( n \) steps, the system evolves for a time \( \Delta t \) in contact with the bath, then \( S_n,\Delta t \to S_{eq} \) as \( \Delta t \to \infty \). The smallness of the rest of the eigenvalues would indicate how close to equilibrium the system is.

The dynamics of a many-body system might be compartmentalized into slow modes and fast modes, where the fast modes would equilibrate much more quickly than slow ones. How many such fast modes have actually equilibrated can be gauged by the number of zero eigenvalues. The \( S \) matrix is not necessarily symmetric, though real, and there is a possibility of pairs of complex conjugate eigenvalues, with their magnitudes going to zero as equilibrium is reached.

4.1.2. Example 2: Barkhausen noise and the matrix \( S \). We now show the practical feasibility of the operator method for a magnet by using the Barkhausen noise [8, 9] as recorded through the output voltage across a secondary coil wound around a ferromagnetic material. Though the Barkhausen noise has seen many applications, its use for equilibrium properties has not been anticipated.

Consider the Hamiltonian

\[
H = H_0 - h M. \tag{25}
\]

Here the magnetic field \( h \) and magnetization \( M \) correspond to \( \Lambda \) and \( x \) respectively. The field is varied from \( h_i \) to \( h_f \) in a time interval \( \tau \) at a constant rate \( \dot{h} \). The Barkhausen effect is a noisy signal proportional to the change in magnetization, \( \eta(t) = \frac{dM(t)}{dt} \). So by integrating the Barkhausen noise up to time \( t \), one obtains the nonequilibrium instantaneous magnetization of the material. Therefore, we can write the work-related exponent in equation (23) as

\[
W + [h(\tau) - h(0)] M_i = -\dot{h} \int_0^\tau dt \int_0^t \eta(t') dt', \tag{26}
\]

which, in a discretized form, looks like

\[
W + [h_f - h_i] M_i = -\Delta h \sum_{j=1}^{n-1} \sum_{k=1}^j \eta_k, \tag{27}
\]

where the Barkhausen noise at the \( k \)th step is \( \eta_k = M_k - M_{k-1} \). Hence, the matrix elements \( S_{M_i, M_j} \) take the form

\[
S_{M_i, M_j} = \sum_{\text{expts}} \exp \left[ \frac{\beta \Delta h}{n-1} \sum_{j=1}^{n-1} \sum_{k=1}^j \eta_k \right], \tag{28}
\]

expressed entirely in terms of the Barkhausen noise along the nonequilibrium paths. The primed summation over paths that start with \( M_i \) and end at \( M_f \) includes proper normalization as mentioned earlier.

For other cases, e.g. for the case of a polymer pulled at a constant rate of change of force, one needs to monitor the time variation of the pulled point displacement \( dx/dt \) versus \( t \). This information can then be used in equation (28) to obtain the corresponding \( S \).
5. Numerical verification of results

Our claims about the probability have been verified for the case of 2D Ising model on a square lattice, \( L \times L \), where \( L \) is the size of the lattice with periodic boundary condition. Consider the Hamiltonian

\[
H = -J \sum_{\langle k,l \rangle} s_k s_l - h \sum_k s_k,
\]

(29)

where \( J \) is the interaction strength, \( h \) is the external magnetic field and \( s_k = \pm 1 \) is the spin at the \( k \)th site of a square lattice. Here \( \sum_{\langle k,l \rangle} \) denotes the sum over nearest-neighbor spins. Here \( J \) and \( h \) play the roles of the external parameter (\( \Lambda_1 \)) and \( \sum_{\langle k,l \rangle} s_k s_l \) and \( \sum_k s_k \) are the internal variables (\( x \)).

We find equilibrium probability distribution for given \( J \) and \( h \) using a weighted nonequilibrium path integral, normalizing the eigenfunction of \( S \), and compare those with the equilibrium probability distribution obtained from a usual Monte Carlo procedure. The overlap of the two distributions is determined by the Bhattacharyya coefficient [10] defined as

\[
BC = \sum_{E,M} \sqrt{P_h(E, M)P_{eq}(E, M)} = 1 - \epsilon,
\]

(30)

with \( BC = 0 \) for no overlap and \( BC = 1 \) for complete overlap.

5.1. Numerical verification of the equilibrium probability distribution starting from a uniform distribution

Let us take an 8 \( \times \) 8 lattice and start from \( H = 0 \). Each time we start from a state chosen from a uniform distribution and reach the final state with \( J = 1 \) and \( h = 1 \) in \( n \) steps. At each \( i \)th step, \( J \) is switched from \( J_i \) to \( J_i+1 \) and the external magnetic field from \( h_i \) to \( h_{i+1} \),

\[
\Delta J = J_{i+1} - J_i = J/n \quad \text{and} \quad \Delta h_i = h_{i+1} - h_i = h/n,
\]

keeping the spin configuration unchanged, and the amount of work done on the system,

\[
W_i = -\Delta J_i E_i - \Delta h_i M_i,
\]

is calculated, where \( M_i \) is the magnetization and \( E_i \) is \( \sum s_k s_l \) at the \( i \)th step. Then we let the system relax at that field \( h_i, J_i \) and \( \beta \) for a while, but do not equilibrate. Thus, the work done along a path consisting of \( n \) steps is

\[
W = -\sum_{i=0}^{n-1} \Delta J_i E_i + \Delta h_i M_i,
\]

which is different for different paths. We find the weighted distribution

\[
P_{J,h}(E, M) = \int DX e^{-\beta W} \delta(E_b - E) \delta(M_b - M) / \int DX e^{-\beta W},
\]

(31)

and then

\[
P_{J,h}(M) = \sum_E P(E, M)
\]

and

\[
P_{J,h}(E) = \sum_M P(E, M).
\]

It is observed that these distributions merge well with the corresponding equilibrium distributions, and for \( P_{J,h}(E) \) (figure 2(a)) and \( P_{J,h}(M) \) (figure 2(b)), we obtain \( \epsilon \sim 10^{-3} \) (equation (30)).
5.2. Equilibrium magnetization curve using the nonequilibrium path integral

For this case, the lattice size is $8 \times 8$ and the interaction strength is kept fixed at $J = 1$. Each time we start from an equilibrium distribution of $h = -h_0$. The field is varied from $-h_0$ to $+h_0$ in $n$ steps. $W(n)$ versus $n$ data are recorded and $\langle M \rangle(h)$ is calculated using equation (13).

We plot the weight-averaged magnetization curve, $\langle M \rangle(h)$, along with the hysteresis loop, average magnetization over samples, against $h$ for $h_0 = 0.2$ in figure 3 and $h_0 = 2$ in figure 4.

A retraceable equilibrium curve is obtained as expected though the nominally averaged magnetization neither changes sign nor makes a complete loop (figure 3) [11]. This reflects the fact that though in majority the magnetization does not reach the correct value, there are a few rare samples for which the spins do flip, and these rare configurations, which are close to equilibrium, get more weight in the weighted path integral to give the correct equilibrium curve.

For the larger field, we obtain a curve which is much narrower than the hysteresis curve (figure 4). The equilibrium curve obtained this way is still not a single curve. The width of the loop might be connected to the droplet time scale, and signals the need for a more careful sum over paths to take care of droplet fluctuations.
Figure 4. Plot of the weighted average $M(h)$ versus $h$ (dashed lines) and hysteresis loop, simple averaged $M$ versus the magnetic field $h$ (solid line) for an $8 \times 8$ lattice. $h$ varies from $-2$ to $2$ in 100 steps.

Figure 5. Plot of the equilibrium distribution $P_{eq}(M)$ versus $M$ (boxes with dotted line) and normalized principal eigenvector $P_{h}(M)$ (dashed line with circles) with $J = 1$, $h = 1$, $\beta = 0.2$ and $n = 1000$ for (a) a $4 \times 4$ lattice and (b) an $8 \times 8$ lattice, showing that $P_{h}(M) = P_{eq}(M)$, i.e. eigenfunction is indeed an equilibrium distribution.

5.3. Numerical verification of the eigenvalue equation

We start from an equilibrium ensemble at an inverse temperature $\beta = 0.2$ (kept fixed throughout the experiment), $J = 1$ and $h = 0$. Each time we start from a state chosen from its equilibrium distribution and reach the final state with $J = 1$ and $h = 1$ in $n$ steps in the same way as described above and calculate the amount of work done on the system at the $i$th step: $W_i = -\Delta h_i M_i$. We find the matrix elements

$$S_{M_i, M_f} = \sum_{\text{paths}} e^{-\beta W - \beta (h - h_0) M_i} \delta_{M_i, M_f}. \quad (32)$$

After the matrix is constructed, we normalize the sum of each column to unity and find the normalized principal eigenvector corresponding to the principal eigenvalue 1, which is guaranteed. We compare the normalized eigenfunction with the actual equilibrium distribution for $L = 4$ and 8. We see that these distributions merge with the corresponding equilibrium distributions for $L = 4$ (figure 5(a)) and $L = 8$ (figure 5(b)) with $\epsilon \sim 10^{-4}$ (equation (30)).
6. Summary

In this paper, we show and verify numerically that the repeated nonequilibrium measurements of work done to connect any two microstates of a system can be used to construct a matrix $S$ whose principal eigenvector is the equilibrium distribution. The matrix elements of $S$ (equation (23)) for a Hamiltonian $H(\Lambda_1, x)$ with $(\Lambda_1, x)$ as a conjugate pair are

$$S_{i, f} = \sum_{\text{paths}} e^{-\beta W + \beta [H(\lambda, x_i) - H(\lambda_0, x_i)]},$$

where the summation is over all paths that start from an equilibrium distribution of externally controlled parameter $\Lambda = \lambda_0$ with the value of the conjugate variable $x$ as $x_i$ and end in a state with $\Lambda = \lambda$ and $x = x_f$, with proper normalization. The work done $W$ is defined in equation (1). The values of the elements of $S$ depend on the details of the process, and therefore there can be many different $S$, but all will have the same invariant principal eigenvector. In this way, the distribution of an interacting system can be obtained from a free, non-interacting one without any reference to equilibrium anywhere. In the process, we also provide a dynamics-independent proof of the result that the equilibrium probability distribution can be obtained using the nonequilibrium path integral. Besides giving a new perspective of thermodynamics and statistical mechanics, our result has direct implications for new ways in numerical simulations and experiments.

References