

Generalized black-box large deviation simulations: High-precision work distributions for extreme non-equilibrium processes in large systems

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The distributions of work for strongly non-equilibrium processes are studied using a very general form of a large-deviation approach, which allows one to study distributions of almost arbitrary quantities of interest for equilibrium, non-equilibrium stationary and even non-stationary processes. The method is applied to varying quickly the external field in a wide range $B = 3 \leftrightarrow 0$ for critical ($T = 2.269$) two-dimensional Ising system of size $L \times L = 128 \times 128$. To obtain free energy differences from the work distributions, they must be studied in ranges where the probabilities are as small as 10^{-240} , which is not possible using direct simulation approaches. By comparison with the exact free energies, which are available for this model for the zero-field case, one sees that the present approach allows one to obtain the free energy with a very high relative precision of 10^{-4} . This works well also for non-zero field, i.e., for a case where standard umbrella-sampling methods seem to be not so efficient to calculate free energies. Furthermore, for the present case it is verified that the resulting distributions of work for forward and backward process fulfill Crooks theorem with high precision. Finally, the free energy for the Ising magnet as a function of the field strength is obtained.

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Studying non-equilibrium work processes [1, 2] has become a useful tool to extract information about physical systems. Particular useful are the Jarzynski relation [3] and the related Crooks theorem [4], which allow one to extract equilibrium information from non-equilibrium systems. Here, a system in contact with a heat bath at temperature T is prepared initially in equilibrium, under the influence of some external parameter $B = B_1$. Next it is driven out of equilibrium via quickly [5] varying $B = B_1 \rightarrow B_2$, into another state, while performing some work W . The Jarzynski relation relates the free energy difference ΔF between the *equilibrium* states at $B = B_1$ and $B = B_2$ to the work W performed during the non-equilibrium process $B = B_1 \rightarrow B_2$:

$$\langle e^{-W/T} \rangle = e^{-\Delta F/T}, \quad (1)$$

where $\langle \dots \rangle$ denotes the combined average over the initial equilibrium distribution and all possible process paths. In a similar way, the theorem of Crooks relates the distributions of work $P(W)$ for the forward process and of the negated work $P_{\text{rev}}(-W)$ for the reverse process $B = B_2 \rightarrow B_1$ (where one starts in equilibrium at $B = B_2$) to the same ΔF via:

$$\frac{P(W)}{P_{\text{rev}}(-W)} = e^{(W-\Delta F)/T}. \quad (2)$$

Hence, $P(W)$ and $P_{\text{rev}}(-W)$ should intersect at $W^* = \Delta F$. Unfortunately, the average of (1) and the region where the two distributions intersect are *often* dominated by exponentially small probabilities, making finite-sampling errors particular strong [6]. Thus, the author of this work is only aware of applications which exhibit either a small number of degrees of freedom, or where the initial and final states $B = B_1, B_2$ are very similar to each other. E.g., for the Ising model in an external field B , work distributions have been obtained [7, 8]

for rather large systems exhibiting $N = 128^2$ spins, but successfully only in the paramagnetic and in the ferromagnetic phases, where the work distribution could be approximated very well by a Gaussian. At the critical point, it was only possible to sample the work distribution reliably for very slow and small changes of the field, making the direct application of the approach not successful.

As it is shown in this work, the work distributions can be obtained very reliably via large-deviation or importance-sampling techniques [9], which are able to address large-deviation regions [10] of interest using bias functions. Such techniques have been previously applied numerically to study work distributions for small systems [11, 12]. If one targets not obtaining the full work distribution but is interested just in free energy differences, it was suggested from results of simulations [13] and analytical studies [14] of small model systems, that applying work theorems cannot compete with direct umbrella-sampling techniques which explicitly obtain the distribution of the energy over large ranges of the support. Thus, these results were rather discouraging. Nevertheless, in the present work not only work distributions are obtained over a large range of the support, but it is also shown for a sample strongly non-equilibrium process in a large system with a non-Gaussian work distribution that a large-deviation non-equilibrium work-sampling approach turns out to give very accurate results.

The algorithm presented in this work is a very general “black-box” type approach which renders it applicable to study the distribution of almost any quantity of interest for equilibrium, non-equilibrium stationary and even non-stationary processes. The algorithm is here applied to work distributions of the Ising model in a non-zero field. In previous work the free energy could be obtained using umbrella-sampling approaches for only rather small systems [15]. This is in contrast to the zero-field case, where indeed umbrella sampling is most efficient. Here, the work distributions for

the non-zero-field case are directly obtained down to probabilities as small as 10^{-240} such that the Jarzynski relation (1) and Crooks theorem (2) can be directly evaluated. For this purpose, the explicit biased sampling not only over the paths but also over the initial equilibrium distribution is included and simulations are performed for a large range of freely adjustable bias weights, allowing to obtain the distributions over hundreds of decades in the probability. The simulations are performed for large systems and strongly non-equilibrium paths.

The ferromagnetic Ising model in a field $B \geq 0$ is studied here, given by a set of N Ising spins $s_i = \pm 1$ and described by the Hamiltonian $H = -J \sum_{\langle i,j \rangle} s_i s_j - B \sum_i s_i$. The first sum runs over all bonds connecting neighboring sites of a square lattice of size L , i.e., $N = L \times L$. Periodic boundary conditions are applied in both directions. The system is coupled to a heat bath at temperature $T = 2.269$, about the critical temperature for the ferromagnet-paramagnet phase transition.

Next, the numerical approaches are described. Processes were considered, where the system is started in equilibrium and within n_{iter} steps the field is changed. For the *forward* process it was increased from $B = 0$ to $B = B_{\text{max}}$, i.e., in each step by $\Delta B = B_{\text{max}}/n_{\text{iter}}$. Thus, during each step l the work $W_l = -\sum_i s_i \Delta B$ was performed, the total work is $W = \sum_l W_l$. After each field increment, one sweep of a Monte Carlo (MC) simulation [16] with single-spin flip Metropolis dynamics was performed. Hence, in each sweep, N times a spin was randomly chosen and a spin flip, exhibiting an energy change ΔH , was accepted with probability $\min\{1, \exp(-\Delta H/T)\}$. The initial equilibrium configuration was obtained by starting in a random configuration and performing 1000 steps of the Wolff cluster algorithm [17], which should ensure equilibration since the auto-correlation time for this algorithm is of the order of $\tau \approx 10$ at T_c [18]. Also for $B_{\text{max}} = 3$ the *reverse* process was considered where the system was started in equilibrium at $B = B_{\text{max}}$ and the process $B = B_{\text{max}} \rightarrow 0$ is performed in an analogous way as for the forward process. Since the equilibrium configuration for this case is almost fully magnetized at this large value of $B = B_{\text{max}}$ (typically $0.002N$ spins are flipped), the initial configurations were obtained by starting with all spins up and performing one sweep of the single-spin flip dynamics prior to the $B = B_{\text{max}} \rightarrow 0$ process.

For the case $N = 128^2$ and 10^6 independent simulations, the histograms $P(W)$ of work for the forward and $P_{\text{rev}}(-W)$ for the reverse process are shown in Fig. 1. According to the theorem of Crooks, the two histograms should intersect at $W^* = \Delta F$. This appears to be somewhere between $W = -50000$ and $W = -45000$, which on the first sight is only a small interval compared the support of the distribution $P(W)$ visible in Fig. 1. Nevertheless, the probabilities become so small, that it is impossible to see the intersection using any feasible number of standard simulations runs. Actually, as it is shown below, the crossing appears where $P(W) = P_{\text{rev}}(-W) \approx 10^{-57}$. Hence, numerical large deviations techniques have to be used, to address this region.

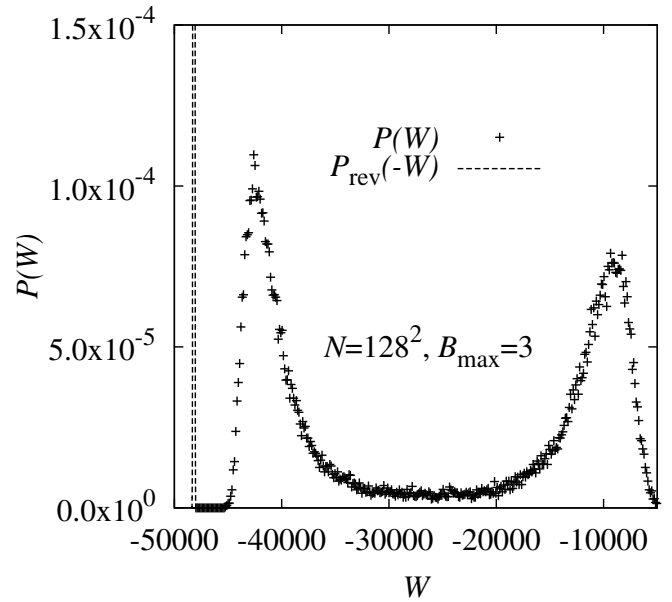


FIG. 1: Simple-sampling distribution $P(W)$ of work for an Ising system with $N = 128^2$ spins for the forward $B = 0 \rightarrow 3$ and the mirrored distribution $P_{\text{rev}}(-W)$ for the reverse process $B = 3 \rightarrow 0$.

The algorithm presented here is different compared to well-known algorithms as, e.g., the “cloning” approach [19–21], and consists of a second MC-simulation level. Each configuration is represented by a vector $\xi = (\xi_1, \xi_2, \dots, \xi_M)$ of suitable length M (see below). The basic idea is that the entries of ξ are random variables uniformly distributed in $[0, 1]$, which are used to feed the random process under investigation. Hence, e.g., when performing the work distributions, the random decisions are not based on numbers drawn from random number generators, but, in a defined manner, on the entries of ξ . Here, for the forward process, the first $n_{\text{Wolff}}(2N + 1)$ entries are used to feed $n_{\text{Wolff}} = 10$ iterations of the Wolff algorithm, starting from a precomputed (1000 Wolff iterations) equilibrium configuration $s^{(0)}$. This allows to sample the equilibrium distribution prior to the work process. Each Wolff iteration consist of choosing one seed spin (consuming one entry of ξ) plus a cluster growth, where possibly for each of the $2N$ bonds it has to be decided randomly whether it is “activated” or not, for details of the Wolff algorithm see Ref. [17]. Note that each bond is assigned a specific entry of ξ (for each Wolff iteration, respectively), independent of whether the bond is tried to be activated or not. Next, the n_{iter} work sweeps are performed, consisting of $n_{\text{iter}} - 1$ single-spin-flip MC sweeps (the last sweep after the final field increment can be omitted), where for each sweep $2N$ entries of ξ are consumed, one for randomly selecting a spin, and one for the Metropolis criterion (also if $\Delta H < 0$). Hence, for one full process $M = n_{\text{Wolff}}(2N + 1) + (n_{\text{iter}} - 1)2N$ entries, corresponding to random numbers, are used. For the reverse process, where no Wolff algo-

rithm is used, $M = 2N + (n_{\text{iter}} - 1)2N = n_{\text{iter}}2N$. Each process fed by ξ results in a work $W(\xi)$. Now, the second-level MC consist of changing a small number (here 400) of the entries of ξ , each drawn again uniformly from $[0, 1]$, leading to a “trial configuration” ξ' with corresponding work $W(\xi')$. The new configuration is accepted with the Metropolis probability $\min\{1, \exp(-(W(\xi') - W(\xi))/T_{\text{MC}})\}$, otherwise ξ is kept for the next second-level MC step. Thus, the observed distribution of work will exhibit a Boltzmann bias $P_{T_{\text{MC}}}(W) \sim P(W)e^{-W/T_{\text{MC}}}$. Note that T_{MC} is a freely adjustable parameter, different from the temperature T of the Ising system, which allows to center the observed distribution in different regions. Therefore, by performing the simulation for different values of T_{MC} such that the resulting distributions $P_{T_{\text{MC}}}(W)$ overlap, one can reconstruct the desired distribution $P(W)$ via reweighting and gluing the distributions together [22]. Note that instead of using a Boltzmann bias for the observed work, one could also use an umbrella sampling on the ξ vectors to obtain $P(W)$ directly. However, this was tried during the present work extensively, but the Boltzmann bias was more efficient.

Seen in an abstract manner, the approach is based on a configuration vector ξ , an evaluation function $\tilde{H}(\xi)$, a simple dynamics changing the configuration vector to create trial vectors ξ' and a Metropolis criterion (involving “temperature” T_{MC}), which accepts ξ based on $\tilde{H}(\xi)$ and $\tilde{H}(\xi')$. All problem-specific details are included in the function \tilde{H} . Hence, if \tilde{H} was the energy of a spin system, then the second-level MC would be a standard MC simulation. But \tilde{H} can represent almost any process, like for the present application where it states the work W arising from an equilibrium sampling followed by a strongly non-equilibrium work process. Using this general view on the large-deviation simulation, it is clear that the approach can be applied basically to any equilibrium, non-equilibrium stationary and even non-stationary process which transforms a vector of a random numbers into a measurable result, independent of how involved this transformation is. Hence, the approach should be applicable to *any* random process which can be simulated on a computer.

For the simulations, a number between 4 ($B_{\text{max}} = 0.25$) and 37 ($B_{\text{max}} = 3$) of temperatures $T_{\text{MC}} \in [1.5, 200]$ were considered. The spacing ΔT_{MC} between the MC temperatures ranged from 0.1 for low values of T_{MC} up to 100 for larges values. For each value of T_{MC} , 10^6 MC trials were performed, taking about 6 hours on a core of standard 2.66 GHz Intel Westmere processor, i.e., just $37 \times 6 = 222$ core hours for the strongest field $B_{\text{max}} = 3$.

Concerning the analysis of the simulation leading to the full work distribution, the intersection region of the distributions of work for the forward and reverse processes are shown in Fig. 2 for $B_{\text{max}} = 3$. The two distributions $P(W)$ and $P_{\text{rev}}(-W)$ intersect at $W^* \approx -47443$. For comparison, also the exact free energy difference was obtained. For the zero-field case, the exact free energy F_0 is known analytically [23] for finite-size systems. For the case $B > 0$, if B is large, the system is almost fully magnetized, except for a few single-

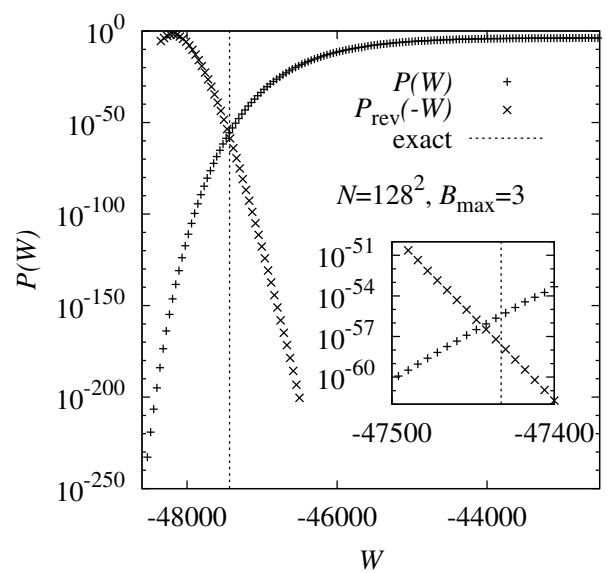


FIG. 2: Distribution of works for the forward and mirrored distribution for the reverse process for $B = 0 \leftrightarrow 3$, $L = 128$. According to the theorem of Crooks, these distributions are expected to intersect at $W^* = \Delta F$ signifying the free-energy difference ΔF . The exact free-energy difference is indicated by the vertical line. The inset shows a blow up of the intersection region.

spin excitations. Hence, the free energy is given via $F_B = -T \log \left(e^{(2+B)N/T} \left[1 + \sum_{k=1}^N \binom{N}{k} \exp^{-(8+2B)k/T} \right] \right)$, where only few terms of the sum around the typical number k of excited spins (about $0.002N$ for $B = 3$) contribute significantly. For $L = 128, B = 3.0$, this results in $\Delta F = F_B - F_0 \approx -47433$. Thus, the relative deviation of the estimated from the exact free energy difference is only $(\Delta F - W^*)/\Delta F = 0.0002$.

To verify whether the data fulfills Crooks theorem (2), the histogram for the reverse process was rescaled accordingly, see Fig. 3. This is confirmed by the data with high precision. Note that testing Crooks theorem may also conveniently serve as a check that the second-level MC simulations are equilibrated.

To obtain ΔF using the Jarzynski relation (1), the integral $\langle \exp(-W/T) \rangle = \int \exp(-W/T) P(W) dW$ has to be evaluated, resulting in $\Delta F \approx -47438$, which has a relative deviation 0.0001 from the exact result. The integrand is shown in Fig. 4. Note that only the region close to the peak around $W = -48100$ contributes significantly to the integral, which deviates much from the point where $P(W)$ and $P_{\text{rev}}(-W)$ intersect. Nevertheless, one has to obtain the full distribution in a region ranging from its peak value at $W = -42000$ down to $W = -48200$ to get $P(W)$ right. For the reverse process, the evaluation (see inset of Fig. 3) results in $-\Delta F = 47450$, which deviates by a factor of 0.0004 from the exact value. Note that one has to obtain $P_{\text{rev}}(W)$ over an even broader support, which is probably the reason for the somehow smaller

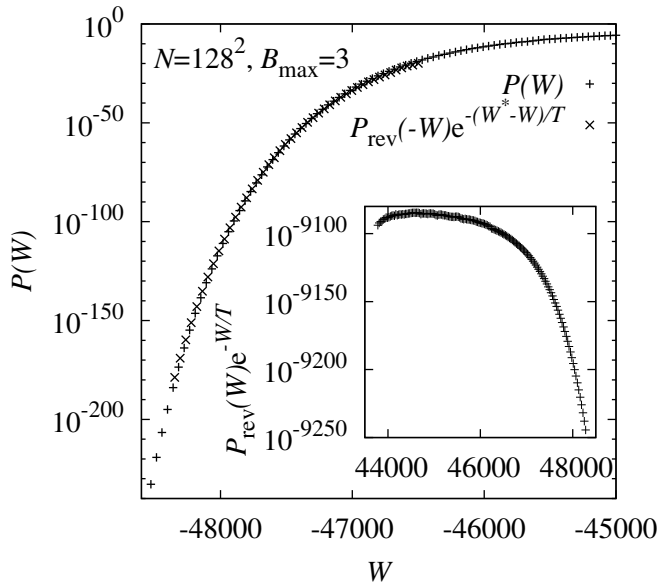


FIG. 3: Distribution of works for the forward and rescaled-mirrored distribution for the reverse process. The inset exhibits the integrand $P_{\text{rev}}(W) \exp(-W/T)$ used to obtain $\langle \exp(-W/T) \rangle$ from the reverse process $B = 3 \rightarrow 0$.

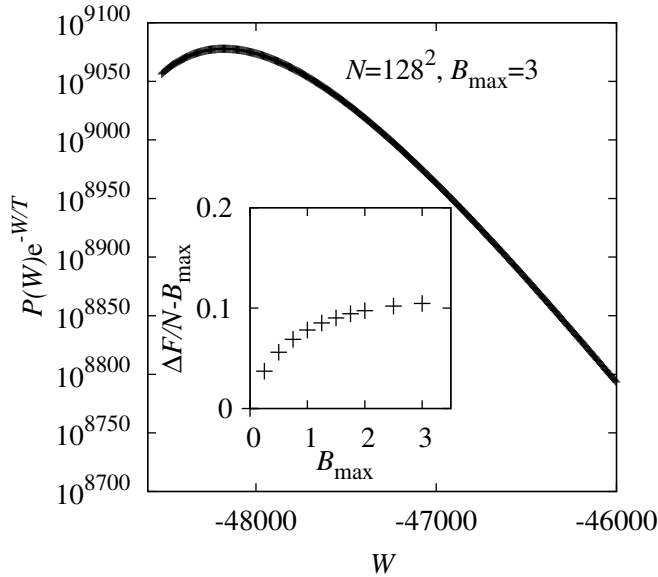


FIG. 4: Integrand $P(W) \exp(-W/T)$ used to obtain $\langle \exp(-W/T) \rangle$. Inset: Resulting free energy difference ΔF per spin N (minus B_{max}) as a function of the final magnetic field B_{max} for the forward process.

accuracy compared to the forward process.

The forward process was performed for different values of B_{max} , see inset of Fig. 4. The amount by which $\Delta F/N$ is larger than B_{max} describes the entropy loss due to the alignment of the spins to the field.

To summarize, a biased sampling approach is introduced,

which is based only on a Markov-chain evolution of a vector of entries from the interval $[0, 1]$, seen as an input vector of random numbers to an arbitrary stochastic process, which can be treated as a black box within the approach.

Here, high-precision determination of work distributions for Ising magnets in a field were performed, for large systems and strongly non-equilibrium processes, hence for cases where traditional direct approaches for measuring work distributions completely fail. In the past only close-to equilibrium processes could be studied with small accuracy [7, 8]. Still, the path sampling applied here is very general, since no details of the path construction have to be known to efficiently sample the corresponding work distribution down to probabilities as small as 10^{-240} . This contrasts the approach with previous problem-specific yet quite successful techniques, like the “shooting approach” [24] or “cloning” [19–21].

The work distributions are used to extract free energy differences for Ising systems in a field using the Jarzynski relation [3] and the theorem of Crooks [4]. Note that for determining the free energy of the Ising system *without a field*, very good other approaches exist. Using the convenient Wang-Landau umbrella sampling [25], the free energy was determined very accurately for systems of size $N = 256^2$. Based on measuring the large-deviation properties of the number of components for Fortuin-Kasteleyn clusters even systems of size $N = 1000^2$ could be treated [26]. Recently it was claimed [13] that in general umbrella-sampling approaches should be superior or at least equally efficient as applying large-deviation techniques to work distributions to measure free-energy differences. Nevertheless, for the present study of an Ising systems *in a field*, using umbrella-sampling only sizes of $N = 42^2$ could be studied so far [15], about ten times smaller than the sizes addressed in the present study. Hence, for certain systems, e.g., for an Ising magnet in a field, almost the full work distribution can be determined using the present approach. But even aiming only at determining free energy differences, the present very general approach might be superior to highly-evolved existing techniques. The observed failure of Refs. [13, 14] might be due to the fact that there only very small systems could be studied. Also it could be due to the specific “shooting” algorithm [24] which might not be most suitable for fully random processes. Finally, for some past studies also single [12] or very many [11] specific bias functions were used, while here a Boltzmann reweighting for few selected weights was performed, which allows to address different regions of interest independently.

Due to the black-box structure of the algorithm presented here, it allows to study equilibrium, non-equilibrium stationary and even non-stationary systems. Hence, for future work, many applications of this algorithm can be anticipated.

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